

**UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE PATENT TRIAL AND APPEAL BOARD**

SAMSUNG DISPLAY CO., LTD.
Petitioner,
v.
PICTIVA DISPLAYS INTERNATIONAL LTD.
Patent Owner.

IPR2024-01094

October 24, 2025



pictivadisplays

The Werner Ground Fails for Multiple Reasons

1[b] wherein the *electron-conducting layer* is *obtained by joint vaporization* of a metal complex ... with an organic compound

9. The organic electronic component according to claim 1, which is *formed as an organic LED (OLED)* which additionally comprise an organic emitting layer.

- Not obvious to combine $W_2(hpp)_4$ and BPhen or TAZ as electron-conducting layer in OLEDs
 - Two out of billions of possibilities
 - Success unpredictable
 - Werner's later work confirmed unsuitability of $W_2(hpp)_4$ and BPhen as electron-conducting layer in OLEDs
- Not obvious to use "joint vaporization" to process $W_2(hpp)_4$ and BPhen or TAZ

2. The organic electronic component according to claim 1, wherein the organic compound *coordinates* to the metal complex due to the joint vaporization.

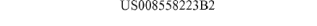
- Petitioner's expert provided no analysis under Samsung's proposed construction of the term "coordinate", as adopted by the district court
- The '223 patent cannot be used to provide a missing limitation

8. The organic electronic component according to claim 1, wherein at least parts of the organic compounds bridge two metal complexes together, so that *a chain-like structure of the metal complexes is formed* and/or at least parts of the organic compounds bridge more than two metal complexes together, so that *a network-like structure of the metal complexes is formed*.

- Structure shown on Pet. 37 not formed
- The '223 patent cannot be used to provide a missing limitation

Ma is Not Prior Art: Not Publicly Accessible Until Dec. 2008, After Priority Date

'223 Patent

													
US008558223B2													
(12) United States Patent Schmid et al.	(10) Patent No.: US 8,558,223 B2 (45) Date of Patent: Oct. 15, 2013												
(54) ORGANIC ELECTRONIC COMPONENT AND METHOD FOR THE PRODUCTION THEREOF	<i>1101.51/00</i> (2006.01) <i>1101.51/40</i> (2006.01)												
(75) Inventors: Günter Schmid , Hemhofen (DE); Ralf Krause , Erlangen (DE); Andreas Kantz , Höchststadt (DE); Jürgen Adler , Kleinsiebach (DE); Stefan Seidel , Nittendorf (DE); Arvid Hunze , Erlangen (DE)	(52) U.S. Cl. USPC 257/40 ; 257/E51.002; 438/99 (58) Field of Classification Search USPC 257/40; E51.002; 438/99 See application file for complete search history.												
(73) Assignee: OSRAM Opto Semiconductors GmbH , Regensburg (DE)	(56) References Cited U.S. PATENT DOCUMENTS												
(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(h) by 0 days.	<table border="0" style="width: 100%;"> <tr> <td style="width: 30%;">4,398,803 A *</td> <td style="width: 30%;">8/1983 Pohl et al.</td> <td style="width: 40%; text-align: right;">349/181</td> </tr> <tr> <td>5,471,111 A *</td> <td>9/1988 Ticks et al.</td> <td style="text-align: right;">525/182</td> </tr> <tr> <td>5,432,014 A *</td> <td>7/1995 Sano et al.</td> <td style="text-align: right;">428/690</td> </tr> <tr> <td>5,447,662 A *</td> <td>9/1995 Herr et al.</td> <td style="text-align: right;">252/582</td> </tr> </table>	4,398,803 A *	8/1983 Pohl et al.	349/181	5,471,111 A *	9/1988 Ticks et al.	525/182	5,432,014 A *	7/1995 Sano et al.	428/690	5,447,662 A *	9/1995 Herr et al.	252/582
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5,447,662 A *	9/1995 Herr et al.	252/582											
(Continued)													
FOREIGN PATENT DOCUMENTS													
(21) Appl. No.: 13/121,099	CN 1261760 8/2000												
(22) PCT Filed: Sep. 25, 2009	CN 1700829 11/2005												

(22) PCT Filed: **Sep. 25, 2009**

(65)	Prior Publication Data	Primary Examiner: Joshua Howard
	US 2011/0309340 A1 Dec. 22, 2011	(74) Attorney, Agent, or Firm — Cozen O'Connor
(30)	Foreign Application Priority Data	(57) ABSTRACT
Sep. 26, 2008 (DE)	10 2008 049 286	An organic electronic component, including a substrate, a first electrode, a second electrode, an electron-conducting layer which is arranged such that it is electrically conductively connected to at least one of the electrodes, wherein the
Nov. 7, 2008 (DE)	10 2008 056 391	

(30) **Foreign Application Priority Data**

Sep. 26, 2008	(DE)	10 2008 049 286
Nov. 7, 2008	(DE)	10 2008 056 391

1

Web-of-Science Database Record for Ma

Organic light-emitting diodes based on new n-doped electron transport layer

By [Ma, JW](#) (Ma, J. W.) ^[1]; [Xu, W](#) (Xu, Wei) ^[1]; [Jiang, XY](#) (Jiang, X. Y.) ^[1]; [Zhang, ZL](#) (Zhang, Z. L.) ^[1] , ^[2]

[Are you this author?](#)

Source

SYNTHETIC METALS ▾

Volume: 158 Issue: 21-24 Page: 810-814

DOI: [10.1016/j.synthmet.2008.05.009](#)

Published	DEC 2008
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Author Information	Keywords Plus: ELECTROLUMINESCENT DEVICES; HOLE-INJECTION; EFFICIENCY; VOLTAGE; PHthalocyanine Corresponding Address: Ma, J. W. (corresponding author) ▼ Shanghai Univ, Dept Mat Sci, Shanghai 201800, Peoples R China E-mail Addresses : majunwei250802944@163.com Addresses : ▼ ¹ Shanghai Univ, Dept Mat Sci, Shanghai 201800, Peoples R China ▼ ² Shanghai Univ, Minist Educ, Key Lab Adv Display & Syst Applicat, Shanghai 200072, Peoples R China E-mail Addresses : majunwei250802944@163.com
Categories/ Classification	Research Areas: Materials Science; Physics; Polymer Science Citation Topics: 2 Chemistry > 2.114 Organic Semiconductors > 2.114.321 OLEDs Sustainable Development Goals: 07 Affordable and Clean Energy

Undisputed: claims supported by foreign priority applications

The Ma Ground Fails for Multiple Reasons

1[b] wherein the electron-conducting layer is obtained by joint vaporization of a metal complex ... with an organic compound

2. The organic electronic component according to claim 1, wherein the organic compound **coordinates** to the metal complex due to the joint vaporization.

8. The organic electronic component according to claim 1, wherein at least parts of the organic compounds bridge two metal complexes together, so that **a chain-like structure of the metal complexes is formed** and/or at least parts of the organic compounds bridge more than two metal complexes together, so that **a network-like structure of the metal complexes is formed**.

- Samsung's technical expert in the district court admitted that Ma does not disclose "joint vaporization"

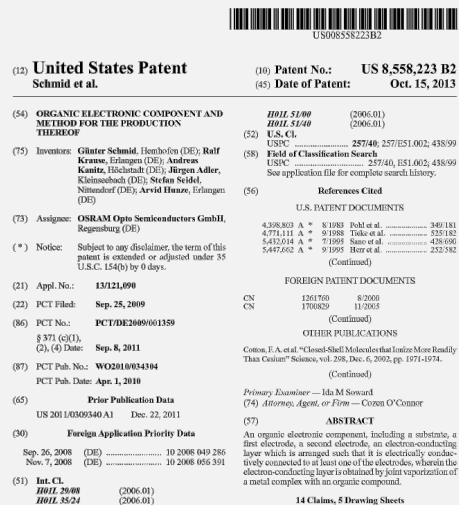
- Petitioner's expert provided no analysis under Samsung's proposed construction of the term "coordinate", as adopted by the district court
- Reliance on infringement assertions misplaced: no BPhen-like structure in accused products
- The '223 patent cannot be used to provide a missing limitation
- No demonstration of inherency

- Reliance on infringement assertions misplaced: BPhen-like structures not involved
- '223 patent cannot be used to provide a missing limitation
- No demonstration of inherency

The '223 Patent

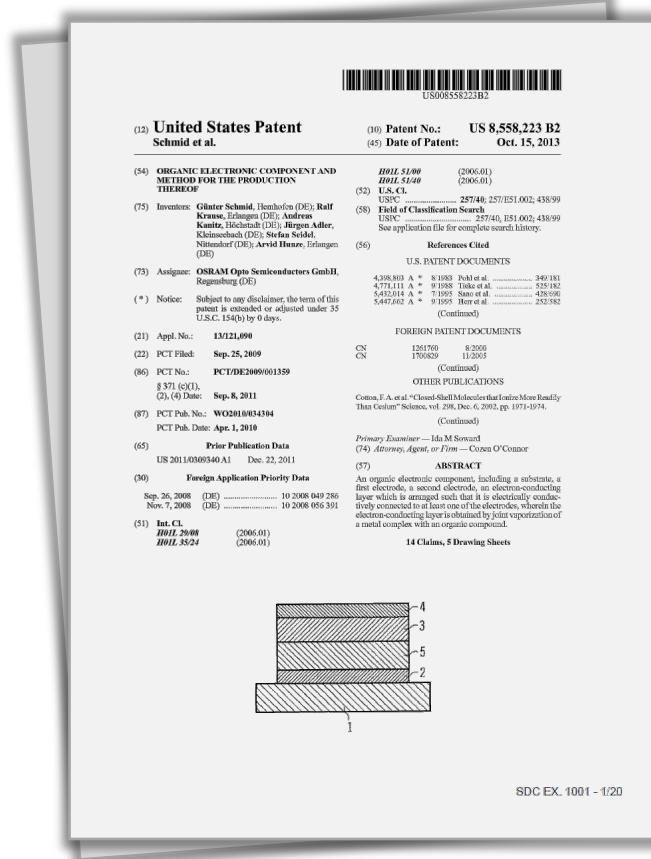
Problem to Be Solved by the '223 Patent: High Electron Conductivity without Crystallinity

A common problem in organic electronic components is to provide a layer which has a very high degree of electron conductivity. The electron conductivity in the component is often the decisive variable for the efficiency and serviceable life of the component. In the case of an organic LED (OLED), the recombination of electrons and holes serves to form excitons which can excite substances to emit radiation. In these components, the luminescence also depends directly upon the exciton density which in turn depends upon the recombination of electrons and holes. In some components, purely crystalline layers are used for transportation of electrons. These purely crystalline layers have the disadvantage that they comprise regions of different conductivity. As a consequence, the charge carriers always select the path of least resistance. Therefore, a non-uniform electron flow is obtained in this layer. At the locations where a considerably increased electron flow occurs, the layer can become overheated and thus damaged. In the case of electroluminescent components, this irregular electron flow also leads to inhomogeneous emission. In the regions where a higher electron flow occurs and more excitons are formed, the component emits more radiation and is thus brighter than in the regions where a lower electron flow is present.



SDC EX. 1001 - 1/20

'223 Solution Compensates Reduced Charge Carrier Mobility with Increased Number of Electron Carriers



inhomogeneous emission. The problem is mitigated by a macroscopically to nanoscopically amorphous electron-conducting layer. Such a layer can be obtained by the joint vaporization of the organic compound with a metal complex, whereupon the organic compound coordinates to the metal complex and thereby prevents crystallization. However, the metal complex must be used to ensure that the now macroscopically to nanoscopically amorphous structure still has effective electron-conducting properties. This can be effected, for example, by virtue of the fact that the additional compound provides additional charge carriers. An organic compound which coordinates to the metal complex and thus forms microcrystalline structures is able to accept additional charge carriers which are provided by the central atom. Therefore, the mobility of the charge carriers which is reduced in comparison with the crystalline layer is compensated by increasing the number of charge carriers. An organic electronic component, for example an OLED which comprises this type of layer, gives homogeneous light. At the grain boundaries of OLED devices, which comprise macrocrystalline layers, the conductivities change such that inhomogeneous light impressions are obtained or for example an LED is destroyed by over-current at certain locations.

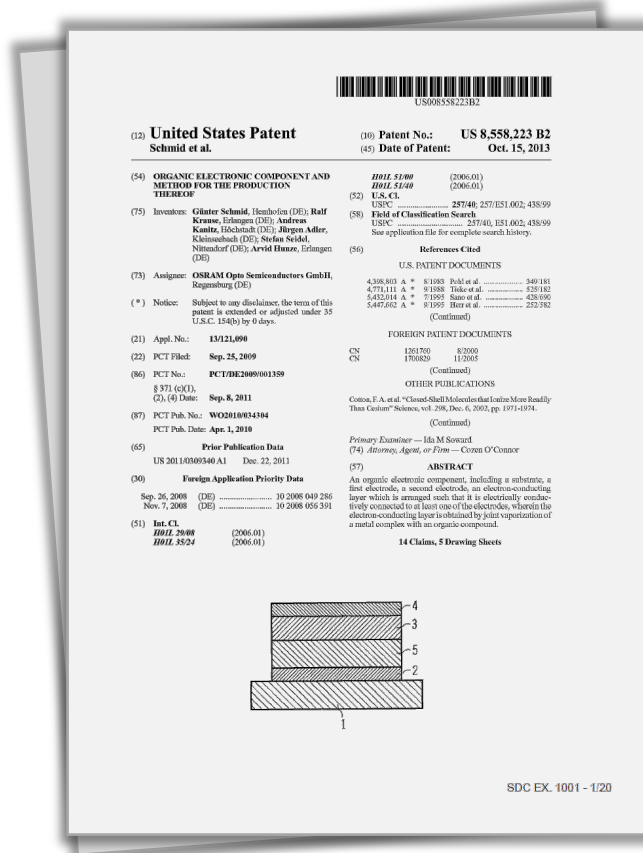
C-C Single Bonding in Organic Compound Reduces Steric Hindrance to Facilitate Coordination to Metal Center

1. An organic electronic component, comprising:
a substrate,
a first electrode,
a second electrode,
an electron-conducting layer which is arranged in such a way that it is electrically conductively connected to at least one of the electrodes,
wherein the electron-conducting layer is obtained by joint vaporization of a metal complex, which comprises a central metal atom, with an organic compound, wherein the organic compound comprises a heteroaromatic compound which is conjugated with an aromatic compound via a C—C bond.

In a further embodiment of the organic electronic component, the organic compound comprises a heteroaromatic compound which is conjugated with an aromatic compound via a C—C bond.

A C—C bond is understood to be a carbon-carbon single bond; the heteroaromatic compound and the aromatic aromatic compound are thus not condensed. In contrast to the condensed systems, a system of this type, in which the heteroaromatic compound is linked with further aromatic compounds via C—C single bonds, has the advantage that it is not so sterically demanding and voluminous, and therefore can coordinate more easily to a metal complex or can coordinate better to several metal complexes simultaneously. The heteroatom in the heteroaromatic compound is preferably N, O or S, wherein N is particularly preferred.

'223 Solution Compensates Reduced Charge Carrier Mobility with Increased Number of Electron Carriers



In a vacuum recipient, an electrically heatable silica or ceramic crucible is charged with 200 mg of $W_2(TBD-A)_4$. A further silica or ceramic crucible is charged with the organic compound of above-mentioned structure I. A glass plate 60 mm×60 mm having a structured ITO-electrode (indium tin oxide) is attached to a substrate holder approximately 25 cm away from the crucibles. The substrate mask is closed and the two sources are regulated to a deposition rate of 4.5 nm/s. The molar ratio of the metal complex to the organic compound during vaporization was 1 to 9. An electron-conducting layer having a layer thickness of 150 nm is deposited. The electron-conducting layer has a three-dimensional network of the metal complex $W_2(TBD-A)_4$ and the organic compound I. The organic electronic component is completed with a 150 nm thick aluminum electrode.

In a further method variant, the organic compound of the above-mentioned structure II is used instead of the organic compound of the above-mentioned structure I.

'223 Solution Reduces Driving Voltages and Increases Efficiency & Lifetime

FIG 6

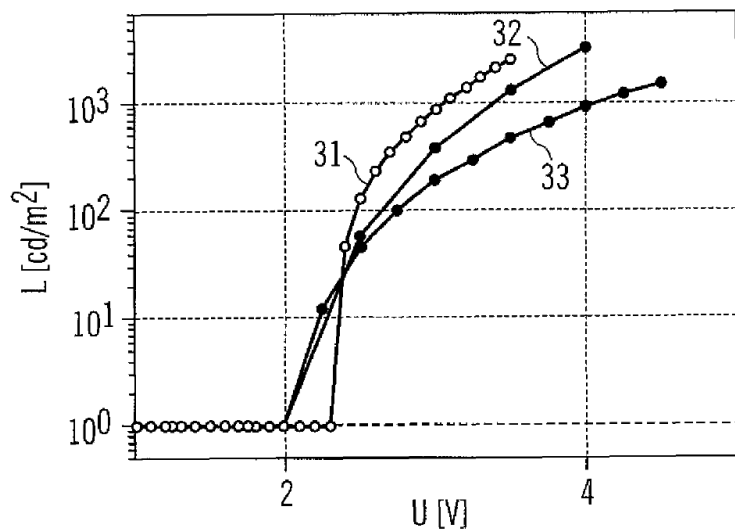


FIG 7

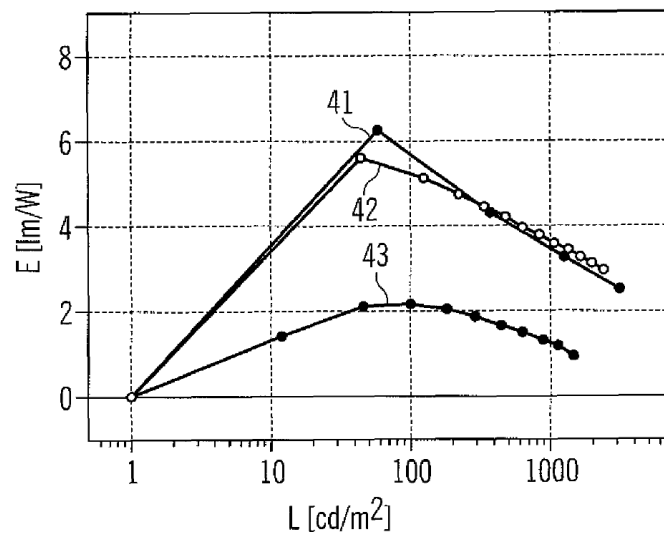


FIG 8

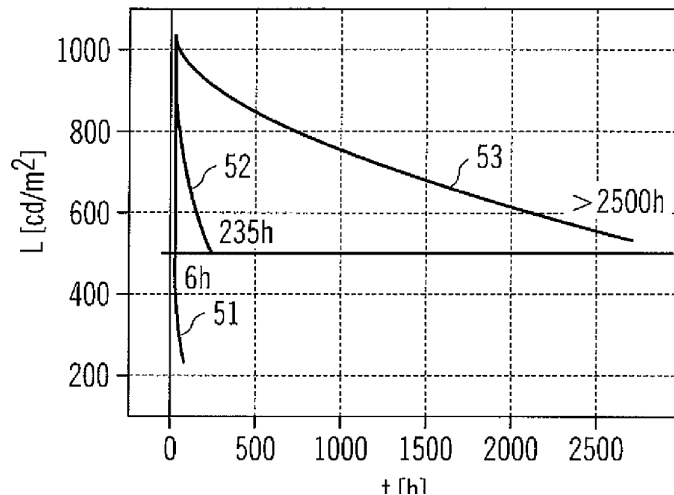
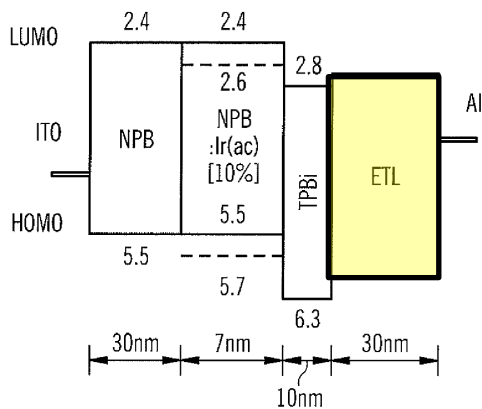
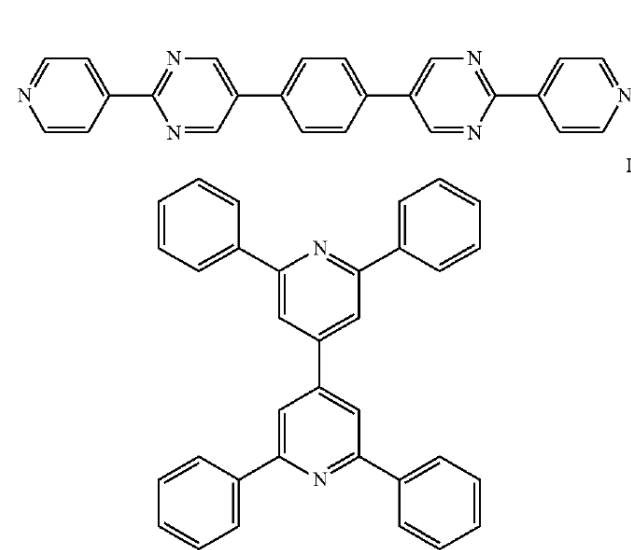


FIG 4



- 33, 43, 51: compound I + 0.7 nm LiF
- 32, 41, 52: compound I + 10 mol% $W_2(hpp)_4$
- 31, 42, 53: compound II + 10 mol% $W_2(hpp)_4$



Claim Construction Adopted by District Court

“metal complex” (’223 Patent, Claim 1, 2, 10, 11, 13, 14)	“a compound containing one or more metal elements that coordinate to one or more non-metal elements, fragments or ions, excluding metal oxides”
“wherein the organic compound coordinates to the metal complex due to the joint vaporization” (’223 Patent, Claim 2)	Plain and ordinary meaning
“coordinate[s]” (’223 Patent, Claim 2, 11, 14)	“form[s] a chemical bond between two atoms in which a shared pair has been supplied by one of the two atoms”
“chain-like structure” (’223 Patent, Claim 12)	“a structure in which at least parts of organic compounds bridge exactly two metal complexes together”
“network-like structure” (’223 Patent, Claim 12)	“a structure in which at least parts of organic compounds bridge more than two metal complexes together”
“degree of cross-linking of the electron-conducting layer” (’223 Patent, Claim 13)	“degree of linking between the metal complex and the organic compound in the electron-conducting layer”

Werner Does Not Render Obvious the Challenged Claims

- One of millions of unpredictable combinations
- $W_2(hpp)_4$ & BPhen/TAZ Not Expected to be Suitable as Electron-Conducting Layer
- No disclosure of joint vaporization of the combination

Dr. Rand's Reason to Combine Legally Inadequate

Barry Rand
Expert Witness

SAMSUNG

“So when I think about what a POSA would do, I think about whether one can expect a reasonable likelihood of success, and that depends upon the type of layer I want to make. If you are telling me from the layers made in Werner, then I would expect a reasonable likelihood of success for processing $W_2(hpp)_4$ and BPhen in a lower vacuum.”

EX2042, 207:6-13; POR 8

- Motivation to combine separate and independent from reasonable expectation of success
- Possibility of processing $W_2(hpp)_4$ and BPhen does not mean sufficiently “electron conducting” for OLEDs

Motivation to Combine Not Shown by the Fact that the Elements Were Known or Disclosed as Interchangeable



- “the Board erred as a matter of law with regard to the motivation to combine.”
- ***“It does not suffice to meet the motivation to combine requirement to recognize that two alternative arrangements ...were both known in the art” and allegedly “may be applied to any computer controlled aiming system”***
- Such disclosures “do not provide any reason why a skilled artisan would use [one alternative] instead of [the other]”

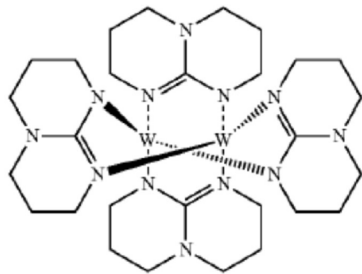
Virtek Vision Int’l ULC v. Assembly Guidance Sys., 97 F.4th 882, 886-87 (Fed. Cir. 2024)

Alleged Combinations

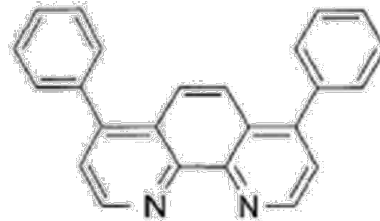
1. An organic electronic component, comprising:
a substrate,
a first electrode,
a second electrode,
an electron-conducting layer which is arranged in such a way that it is electrically conductively connected to at least one of the electrodes,
wherein the electron-conducting layer is obtained by joint vaporization of a metal complex, which comprises a central metal atom, with an organic compound, wherein the organic compound comprises a heteroaromatic compound which is conjugated with an aromatic compound via a C—C bond.

- Metal Complex: $W_2(hpp)_4$
- Organic Compound:
 - BPhen
 - TAZ (not for claims 2, 6, 8, 11-13)

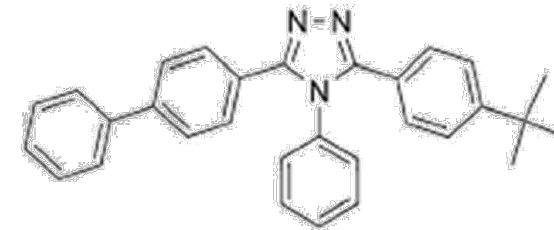
EX1001, 19:9-23



$W_2(hpp)_4$



BPhen = bathophenanthroline
(4,7-Diphenyl-1,10-phenanthroline)
C₂₄H₁₆N₂



TAZ
3-(4-Biphenyl)-4-phenyl-5-tert-butylphenyl-1,2,4-triazoles

Werner Does Not Suggest the Specific Combinations

Werner Discloses A Large Number of Organic Compounds (“Matrix Materials”)

Barry Rand
Expert Witness

SAMSUNG

Q. How many different types -- let me put it this way. **How many different matrix materials did Werner disclose?** Hundreds? Thousands? Hundreds of thousands?

A. Werner discloses a lot of matrix material.

Q. How many?

A. It's hard to count.

Q. Can you give me an order of magnitude?

A. I can't give you an order of magnitude estimate that's going to have any accuracy.

Q. Is it going to be more than a thousand?

A. **It will be more than one thousand.**

EX2042, 137:3-18; POR 7

At Least 1,000 Disclosed Organic Compounds

Dr. Rand Confirms that Werner Discloses Over 1,000 Organic Compounds

Barry Rand
Expert Witness

SAMSUNG

Q. Do you think that -- *you're not changing your testimony from April, are you?*

A. Why would I do that?

Q. Just making sure.

A. *The answer is no.*

EX2056, 149:1-4; Sur-Reply 3-4

**April 2025 Testimony Admitted that Werner Disclosed At
Least 1,000 Organic Compounds**

Werner Discloses A Large Number of Metal Complexes

Barry Rand
Expert Witness

SAMSUNG

Q. So just between the $M_2(\text{Carboxylate})$, $M_2(\text{AlkylCOO})_4$, we are talking about over 2,000 already; right? And we haven't really counted the CT [CP] complexes, the $M_2(\text{hpp})_4$ possibilities? Right? So fair to say there's going to be a few thousand possibilities? At least a few thousand possibilities in claim 22; right?

A. Fair to say that there is over a thousand.

Q. Over 2,000 actually?

A. **Over 2,000. Sure. I will agree with that.**

22. Use according to any of claims 1 to 21, characterized in that the complex is: $M_2\text{hpp}_4$ with M being Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W; $M_2(\text{AlkylCOO})_4$ with M being Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W and with each alkyl being identical or different, with C1 to C10; $M_2(\text{Guanidinate})_4$ with M being Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W; $M_2(\text{Formamidinate})_4$ with M being Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W; $M_2(\text{Carboxylate})_4$ with M being Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W; $M_2(\text{Halide})_4$ with M being Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W; $\text{Bis}(\eta^5\text{-cyclopentadienyl})M$ with M being Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W; $\text{Benzene-M}-(\eta^5\text{-cyclopentadienyl})$ with M being Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W, where one or more hydrogen atoms of the ligands can be replaced by other groups including alkyl groups.

EX2042, 144:6-17; POR 7; EX1005, cl. 22

At Least 2,000 Disclosed Metal Complexes

At Least 2 Million Combinations

$$1,000 \times 2,000 = 2,000,000$$

No Reasonable Expectation of Success

Barry Rand
Expert Witness
SAMSUNG

- Q. How many of those millions of combinations would they [POSITAs] have a reason for expectation of success?
- A. Again I can't quantify like a percent value of that because it is *very much dependent upon so many factors that go into making an organic electronic device* and OLED is one of them, but there are numerous organic electronic devices, numerous criteria that one wants to consider for the processing of that material, for the device application, for the operating condition, that I can't give an exact figure on the percent of combinations that might reasonably lead to success because it will be *very much dependent on the constraints of the condition of a person of ordinary skill in the art.*

EX2042, 147:10-148:4; POR 7

Very Low Conductivity When Expressly Disclosed Matrix Materials Are Doped with W2(hpp)4

EX2044 (Werner et al.)

TABLE 1

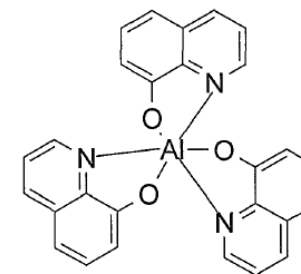
CV data, empirically determined LUMO energies and measured conductivities of various electron transport materials
(BAIq₂ = bis(2-methyl-8-quinolinato)-4-(phenylphenolato) aluminium (III), BPhen = bathophenanthroline, Alq₃ = tris (8-hydroxyquinoline) aluminium, Cl6-Alq = tris (5,7-dichloro-8-hydroxyquinoline) aluminium)

Matrix material	LUMO in eV (determined by CV with Fe/Fe ⁺ as internal standard)		σ (conductivity) in S/cm with a doping concentration of 5 mol %
		σ (conductivity) in S/cm undoped	
Alq ₃	2.4	<1E-10	9.2E-8
BPhen	2.42	<1E-10	4E-9
BAIq ₂	2.39	<1E-10	8e-8

As can be seen from Table 1, the conductivities achieved with the known matrix materials are still insufficient and very low.

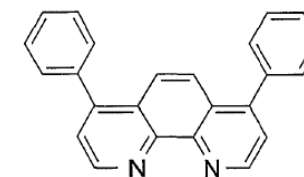
EX2044, Table 1; Sur-reply 4-5

EX1005 (Werner et al.)



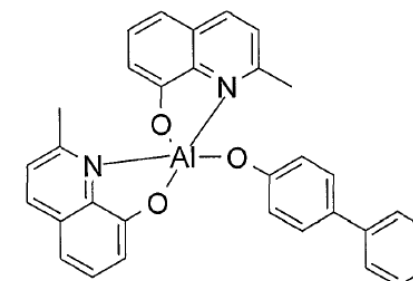
tris(8-hydroxyquinolinato)aluminum

Alq₃



BPhen = bathophenanthroline
(4,7-Diphenyl-1,10-phenanthroline)
C24H16N2

BPhen



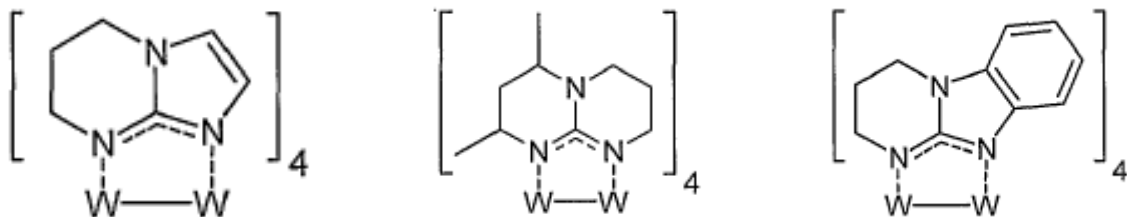
Bis(2-methyl-8-quinolinolato)-4-(phenylphenolato)-aluminum(III) BAIq₂

EX1005, 57/89 (original page 54); Pet. 24-25; Reply 1-2

Poor Conductivity for Combinations of “Expressly” Discloses Species

Dr. Rand Cannot Predict the Conductivity Resulting from Combining Expressly Disclosed Species

Rand Testimony



Discussing doping BPhen with the compounds above:

Q What would be the **conductivity compared to tungsten2(hpp)4 and BPhen?**

A: Also **challenging to know without conducting the experiment.**

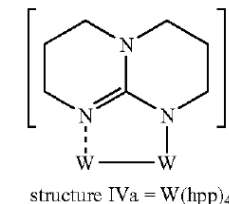
Q Do you expect it to be **higher or lower?**

A: **I really can't say.**

EX2056[Rand], 223:22-224:6 (objections omitted), see also 223:3-14; Sur-reply 4

EX2044: Patent by Werner

Doping BPhen with



Matrix material	LUMO in eV (determined by CV with Fe/Fe ⁺ as internal standard)	σ (conductivity) in S/cm undoped	σ (conductivity) in S/cm with a doping concentration of 5 mol %
Alq ₃	2.4	<1E-10	9.2E-8
BPhen	2.42	<1E-10	4E-9
BAlq ₂	2.39	<1E-10	8e-8

As can be seen from Table 1, the conductivities achieved with the known matrix materials are still **insufficient and very low.**

EX2044, Table 1; Sur-reply 4-5

Not Obvious if Having to Try Each of Numerous Possible Choices



“to have a reasonable expectation of success, one must be motivated to do more than merely to vary all parameters or try each of numerous possible choices until one possibly arrived at a successful result”

In re Stepan, 868 F.3d 1342, 1347 (Fed. Cir. 2017)

Werner Cites Journal Articles and Discloses Specific Examples of Metal Complexes

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization International Bureau

(43) International Publication Date September 15, 2005 (09/15/2005)

(10) International Publication Number WO 2005/086251 A2

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(25) Filing Language: German

(26) Publication Language: German

(30) Priority Data: 10 2004 010 954 0 March 3, 2004 (03/03/2004) DE

(71) Applicant (for all designated states except the US): NOVALED GMBH [DE/DE]; Tatzberg 49, 01307 Dresden (DE)

(72) Inventors; and (75) Inventors/Applicants (for the US only): WERNER, Angar [DE/DE]; Altenberger Strasse 20, 01277 Dresden (DE); KÜHL, Olaf [DE/DE]; Martelsstrasse 10, 04416 Meitzschberg (DE); GESSLER, Simon [DE/DE]; Hauptstrasse 79, 69117 Heidelberg (DE); HARADA, Ken-ichi [DE/DE]; Blumenstrasse 90, 01307 Dresden (DE); HARTMANN, Horst [DE/DE]; Wolkenstrasse 4, [Continued on the next page]

(84) Designated States (unless otherwise indicated, for every available national protection type): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GR, HT, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MY, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SI, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every available regional protection type): ARPO, BW, GH, GM, KE, LS, MW, MZ, NA, SD, SI, SZ, TZ, UG, ZM, ZW, Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, [Continued on the next page]

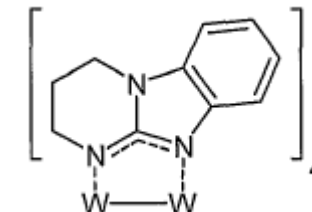
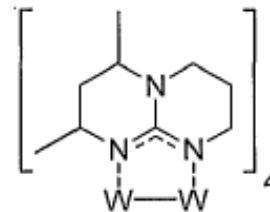
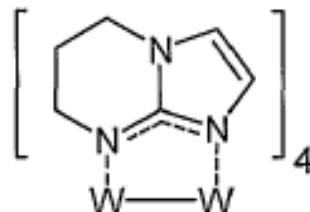
(54) Title: USE OF A METAL COMPLEX AS N-DOPANT FOR AN ORGANIC SEMICONDUCTING MATRIX MATERIAL, ORGANIC SEMICONDUCTOR MATERIAL, AND ELECTRONIC COMPONENT, AS WELL AS DOPANT AND LIGAND AND METHOD FOR PRODUCING THE SAME

(57) Abstract: The invention relates to the use of a metal complex as n-dopant for doping an organic semiconducting matrix material for modifying the electrical properties of the same, wherein the compound represents an n-dopant with regard to the matrix material. The aim of the invention is to provide n-doped organic semiconductors for matrix materials that have little reduction potential while achieving high conductivities. According to the invention, a neutral electron-rich metal complex having a central atom as the preferably neutral or charged transition metal atom having a valence electron number of at least 16 is used as the dopant compound. The complex can especially be multilaminar and comprises at least one metal-metal bond. At least one ligand can form a pi-complex with the central atom, or can be a bridging ligand, especially bipy, a borate, carbamate or transacyclonitrile or comprise at least one carbanion carbon atom or a boron atom selected from the group including C (carbene), Si (silylene), Ge (germylene), Sn, Pb. The invention also relates to novel n-dopants and methods for producing them.

WO 2005/086251 A2

SDC EX. 1005 - 2/89

EX1005 at 39-52 (original page numbers)



Carbenes

For the synthesis of N-heterocyclic carbenes (NHC), several standard procedures are known in the literature: the imidazole method, the thioketone method, and the silver oxide method (metal transfer method). See, for example: W. A. Herrmann, Angew. Chem., Int. Ed. Engl. 41 (2002) 1290-1309; W. A. Herrmann, C. Kocher, Angew. Chem., Int. Ed. Engl. 36 (1997) 2162-87; A. H. Cowley, J. Organomet. Chem. 617-8 (2001) 105-9; T. Westkamp, V. P. W. Böhm, W. A. Herrmann, J. Organomet. Chem. 600 (2000) 12-22.

Silylenes

The synthesis of N-heterocyclic silylenes is carried out analogously to the corresponding germylenes. However, silicon(IV) chloride is used, which must then be reduced (see, for example: M. Denk, R. Lennon, R. Hayshi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner, N. Metzler, J. Am. Chem. Soc. 116 (1994) 2691-2; B. Gehrhus, M. F. Lappert, J. Organomet. Chem. 617-8 (2001) 209-23).

Pi-perimeter

There are many compounds of pi-perimeter ligands and their metal complexes, leading to a variety of synthesis routes. Examples include:

Cyclopentadienyl: C. Janiak, H. Schumann, Adv. Organomet. Chem. 33 (1991) 331; J. Okuda, Top. Curr. Chem. 160 (1991) 99; N. J. Coville, K. E. du Plooy, W. Pickl, Coord. Chem. Rev. 116 (1992) 1; R. L. Halterman, Chem. Rev. 92 (1992) 965; M. L. Hays, T. P. Hanusa, Adv. Organomet. Chem. 40 (1996) 117; S. Brydges, L. E. Harrington, M. J. McGlinchey, Coord. Chem. Rev. 233-4 (2002) 75; T. Cuenca, P. Royo, Coord. Chem. Rev. 193-5 (1999) 447-98.

Arene: A. S. Abd-El-Aziz, Coord. Chem. Rev. 233-4 (2002) 177; A. S. Abd-El-Aziz, Coord. Chem. Rev. 203 (2000) 219; R. D. Pike, D. A. Sweigart, Coord. Chem. Rev. 187 (1999) 183.

Dozens of Articles Cited for other Preferred Metal Complexes

DEMONSTRATIVE EXHIBIT – NOT EVIDENCE

Pictiva slide, p. 25

Journal Articles Generally Discloses Specific Compounds

Barry Rand
Expert Witness
SAMSUNG

Q. When you publish with them [collaborator] --

A. Okay.

Q. -- do you discuss specific compounds?

A. When I publish with them, **we discuss and disclose specific compounds, yes.** That's the way that we know that we can enable a reader to reproduce our experiments.

Q. Do you know whether that's a typical way of publishing research results in peer-reviewed journals?

A. Again, I can't speak for others. But I would say, **in general, you'd want to use -- you know, provide sufficient information such that a reader can replicate your experiments.**

EX2056, 220:24-25, 221:11-222:1 (objections omitted); Sur-Reply 3

Other Specific Examples of Non-hpp Ligands

Barry Rand

Expert Witness

SAMSUNG

Q. So when you refer to **cyclopentadienyl**, that would be the 5-membered ring with hydrogens in all five positions, correct?

A. Correct.

...

Q. **Guanidine**. And that's a specific compound, correct?

A. Guanidine is a specific compound, yes.

...

Q. What's the structure of Terpy?

A. That's the **Terpyridine**; is that correct?

Q. Correct.

A. It's three pyridine rings where those are linked together by carbon-carbon single bonds.

Q. And is that a specific compound or class of compound?

A. It's a specific compound. If you're asking if there are maybe more than one isomer, there are.

POSITAs Would Recognize at Least 64 Species for Compounds 1-64

Barry Rand

Expert Witness

SAMSUNG

Q. Now, for the 64 compounds that we discussed earlier, of them, the lowest molecular weight species will be the ones where the R is hydrogen; is that correct?

A. The 64 classes of compound, assuming R is an option to be able to be used in all of the R positions, then **yes**, given that hydrogen is the lightest element on the periodic table, using all of -- ***filling all of those R positions with hydrogen would yield the lowest molecular weight compound of each of those classes.***

Q. ***Would those 64 specific compounds be known to a POSITA?***

A. Again, these are classes of compounds, not specific compounds. But it's -- ***as long as a POSITA had this document***, which I think we've made the assumption that that person does, ***then it would be known to them.***

EX2056, 224:21-225:17 (objections omitted); Sur-Reply 3

Still Tens of Thousands of Combinations

Guanidine,
cyclopentadienyl,
terpyridine

Specific
Examples

$$(64+3+6) \times 9 \times 1,000 = 657,000$$

Simplest
molecule of 64
classes of ligands

9 preferred
central metals

Disclosed
matrix
materials

The diagram illustrates the calculation of combinations for a complex system. The equation $(64+3+6) \times 9 \times 1,000 = 657,000$ is centered. Above it, 'Guanidine, cyclopentadienyl, terpyridine' and 'Specific Examples' have arrows pointing to the first part of the equation. Below it, 'Simplest molecule of 64 classes of ligands', '9 preferred central metals', and 'Disclosed matrix materials' have arrows pointing to the same part. A red box at the bottom states '~180 Years to Test the Combinations'.

~180 Years to Test the Combinations

Werner Does Not Render Obvious the Challenged Claims

- One of millions of unpredictable combinations
- $W_2(hpp)_4$ & BPhen/TAZ Not Expected to be Suitable as Electron-Conducting Layer
- No disclosure of joint vaporization of the combination

Werner Taught Energy Level Requirements for Electron Donor (Metal Complex) and Electron Acceptor (Organic Material)

(12) **United States Patent**
Hofmann et al.

(10) **Patent No.:** US 7,911,129 B2
(45) **Date of Patent:** Mar. 22, 2011

(54) **ARRANGEMENT FOR AN ORGANIC
PIN-TYPE LIGHT-EMITTING DIODE AND
METHOD FOR MANUFACTURING**

CA 2549309 9/2005
(Continued)

(75) **Inventors:** Michael Hofmann, Dresden (DE); Jan Birnstock, Dresden (DE); Jan Blochwitz-Nimoth, Dresden (DE); Ansgar Werner, Dresden (DE); Martin Pfeiffer, Dresden (DE); Kentaro Harada, Dresden (DE)

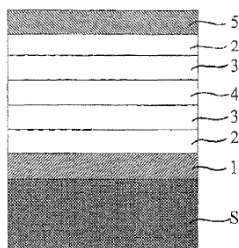
OTHER PUBLICATIONS
C.W. Tang et al. Organic Electroluminescent Diodes, Applied Physics Letters, vol. 51, No. 12 Sep. 21, 1987 pp. 913-991.
(Continued)

(75) **Inventors:** Michael Hofmann, Dresden (DE); Jan Birnstock, Dresden (DE); Jan Blochwitz-Nimoth, Dresden (DE); Ansgar Werner, Dresden (DE); Martin Pfeiffer, Dresden (DE); Kentaro Harada, Dresden (DE)

U.S. PATENT DOCUMENTS
4,356,429 A 10/1982 Tang
4,769,292 A 9/1988 Tang et al.
5,093,698 A 3/1992 Egusa
5,500,537 A 3/1996 Tsunuma et al.
(Continued)

namer, where then the emission layer and the doped charge carrier transport layer are formed from an organic matrix material. Furthermore, a method for manufacturing such arrangements is stated.

21 Claims, 7 Drawing Sheets



Pictiva EX2043
Samsung v Pictiva
IPR2024-01094

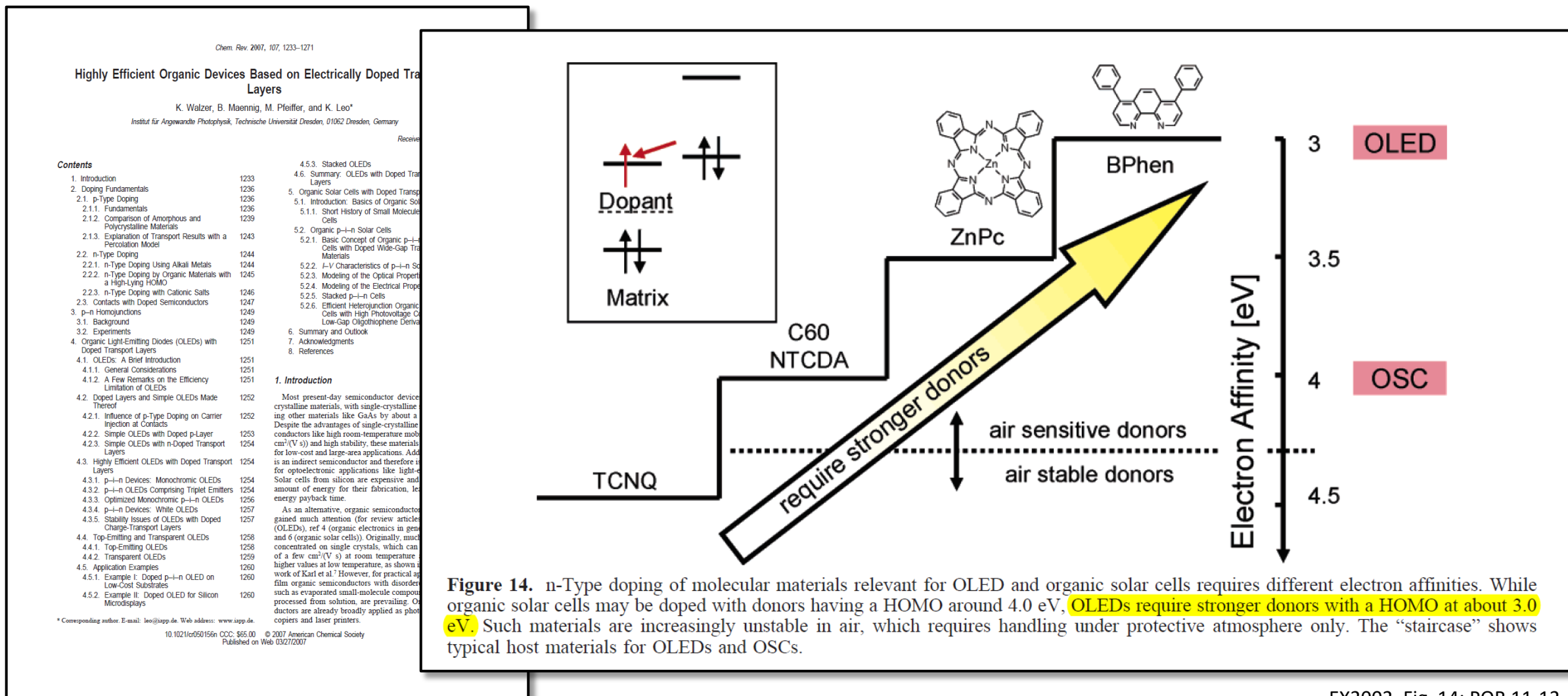
dope matrix materials with a far smaller electron affinity. The well known matrix material BPhen has, for example, an electron affinity between 3.0 eV (estimation from ionisation potential and optical band gap) and 2.4 eV (estimation from cyclovoltammetry). However, it can be expected that, for materials with an electron affinity smaller by 0.5 eV, a doping effect with caesium cannot be achieved. For a molecular n-dopant, and based on the details for p-dopants, in the result the electron affinity of the matrix EA(O2) shall not drop below the value, reduced by 0.5 eV, of the ionisation potential of the donor IP(D).

Consequently, the following relationships result from the requirement of the doping capability: $IP(O1) < EA(A) + 0.5 \text{ eV}$ and/or $EA(O2) > IP(D) - 0.5 \text{ eV}$. The following applies in the case of doping with caesium: $EA(O2) > 1.9 \text{ eV}$.

EX2043, 10:50-64; POR 3

EX2043

Others Recognize the Need for n-Dopants with High-Lying HOMOs



EX2002, Fig. 14; POR 11-12

EX2002 (2007 Chem. Rev.)

DEMONSTRATIVE EXHIBIT – NOT EVIDENCE

Pictiva slide, p. 32

Werner Discusses Gas-Phase, Not Solid-State, Ionization Potential

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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10 2004 010 954.0 March 3, 2004 (03/03/2004) DE

(71) Applicant (for all designated states except the US):
NOVALED GMBH [DE/DE]; Tatzberg 49, 01307
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(72) Inventors; and
(73) Inventors/Applicants (for the US only): WERNER,
Asgar [DE/DE]; Altenberger Strasse 20, 01277 Dresden
(DE). KÜHL, Olaf [DE/DE]; Mittelstrasse 10, 04416
Markkleeberg (DE). GESSLER, Simon [DE/DE];
Hauptstrasse 79, 69117 Heidelberg (DE). HARADA,
Kentaro [DE/DE]; Blumenstrasse 90, 01307 Dresden
(DE). HARTMANN, Horst [DE/DE]; Wollnerstrasse 4,

(74) Attorneys: SCHOLZ, Volker et al.; Boehmert &
Boehmert, Holleralle 32, 28209 Bremen (DE).

(81) Designated States (unless otherwise indicated, for every
available national protection type): AE, AG, AL, AM,
AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH,
CN, CO, CR, CU, CZ, DK, DM, DZ, EC, EE, EG, ES,
FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP,
KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV,
MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO,
NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK,
SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,
VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every
available regional protection type): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ,
TM), European (AT, BE, BG, CH, CY, CZ, DE, DK,

[Continued on the next page]

(54) Title: USE OF A METAL COMPLEX AS N-DOPANT FOR AN ORGANIC SEMICONDUCTING MATRIX
MATERIAL, ORGANIC SEMICONDUCTOR MATERIAL, AND ELECTRONIC COMPONENT, AS WELL AS DOPANT
AND LIGAND AND METHOD FOR PRODUCING THE SAME

(57) Abstract: The invention relates to the use of a metal complex as n-dopant for doping an organic semiconducting matrix
material for modifying the electrical properties of the same, wherein the compound represents an n-dopant with regard to the
matrix material. The aim of the invention is to provide n-doped organic semiconductors for matrix materials that have little
reduction potential while achieving high conductivities. According to the invention, a neutral electron-rich metal complex having
a central atom as the preferably neutral or charged transition metal atom having a valence electron number of at least 16 is used
as the dopant compound. The complex can especially be multinuclear and comprises at least one metal-metal bond. At least one
ligand can form a pi-complex with the central atom, or can be a bridging ligand, especially hpp, a borate, carbonate or
triazacyclohexane or comprise at least one carbonous carbon atom or a bivalent atom selected from the group including C
(carbene), Si (silylene), Ge (germylene), Sn, Pb. The invention also relates to novel n-dopants and methods for producing them.

WO 2005/086251 A2

SDC EX. 1005 - 2/89

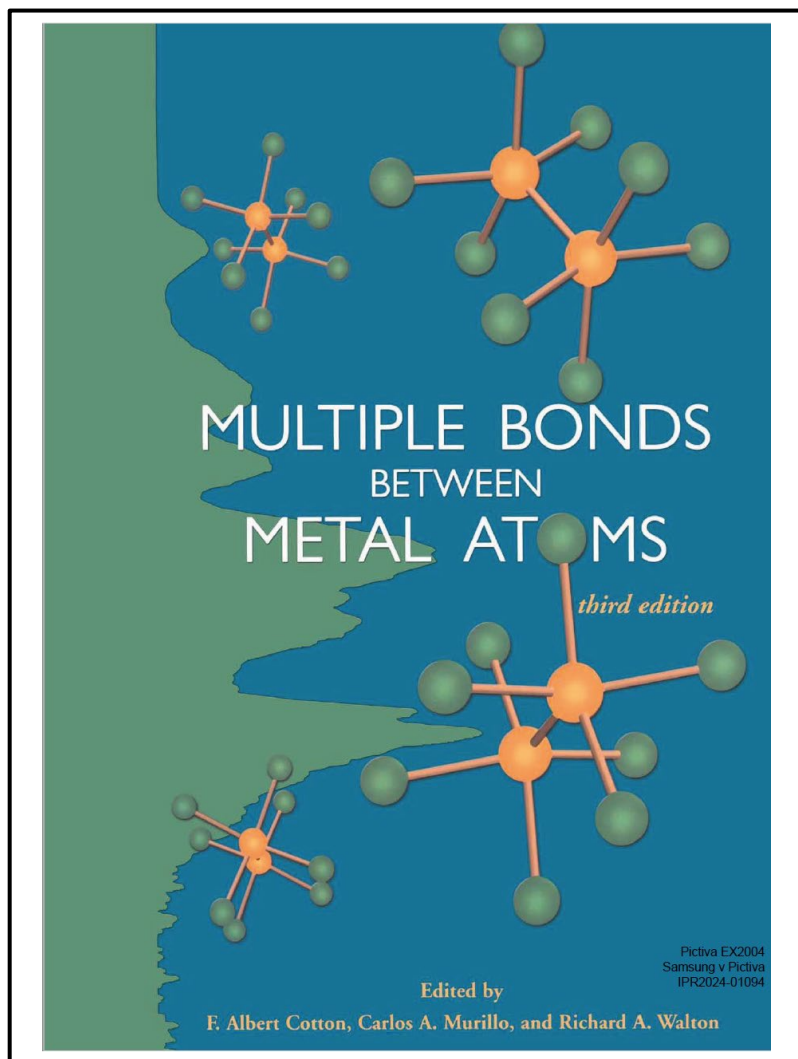
Ionization potential/oxidation potential

Preferably, the metal complex according to the invention has an ionization potential in the gas phase of ≤ 6.4 eV, preferably ≤ 6 eV, in particular ≤ 5.5 eV. In particular, the ionization potential of the complex in the gas phase can be ≤ 5.0 eV or ≤ 4.5 eV.

The gas phase ionization potential I_{pg} of the compounds usable according to the invention can, for example, be determined relative to tetrathiafulvalene (TTF), which is: $I_{pg} = 6.4$ eV (see R. Gleiter, E. Schmidt, D. O. Cowan, J P. Ferraris, J. Electr. Spec. Rel. Phenom. 2, 207 (1973)).

EX1005, 36:19-37:3; Sur-Reply 8

$W_2(hpp)_4$ Ionizes at 3.76 eV



EX2004 (Cotton Textbook)

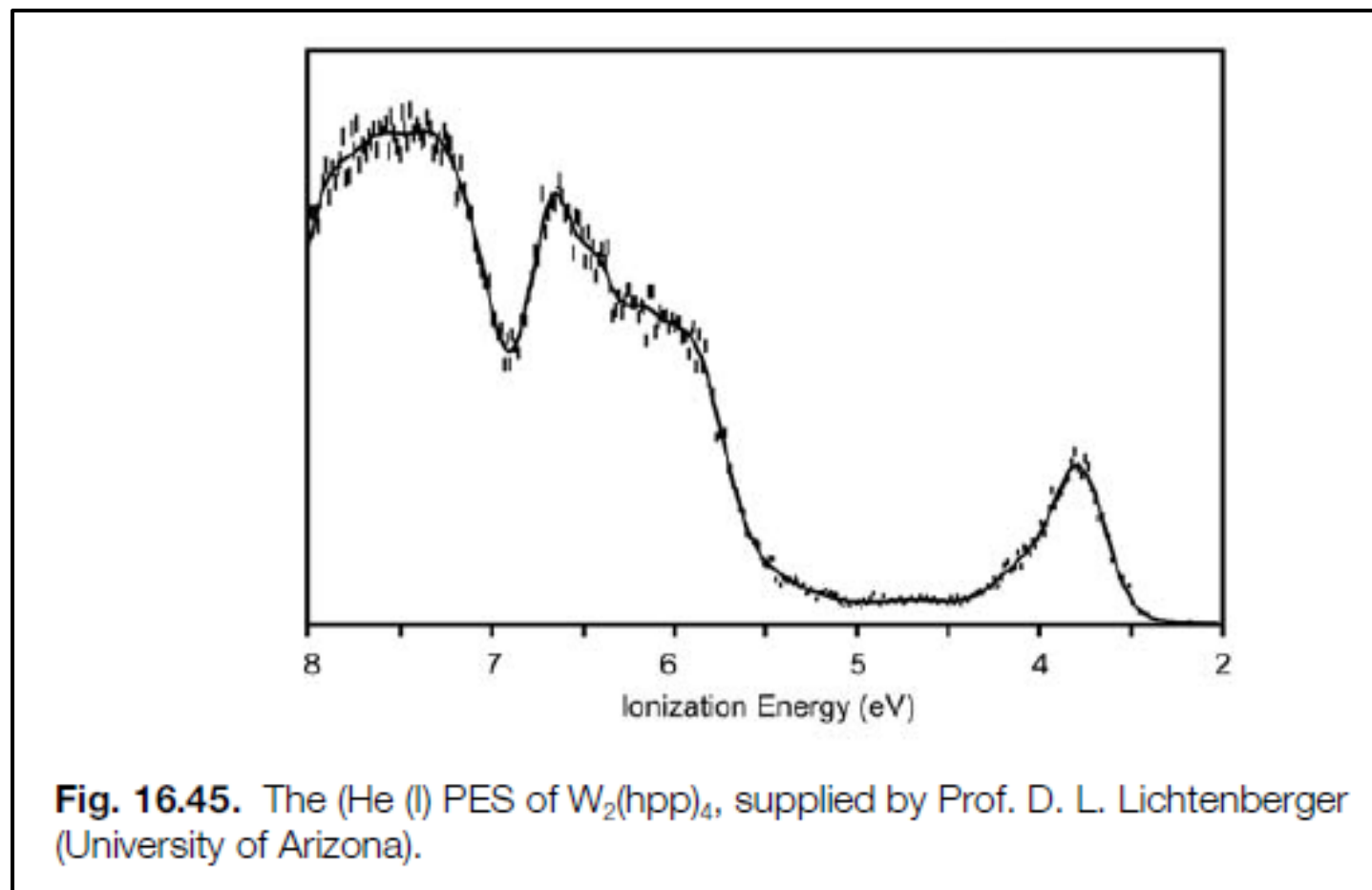
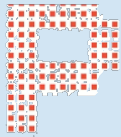


Fig. 16.45. The (He I) PES of $W_2(hpp)_4$, supplied by Prof. D. L. Lichtenberger (University of Arizona).

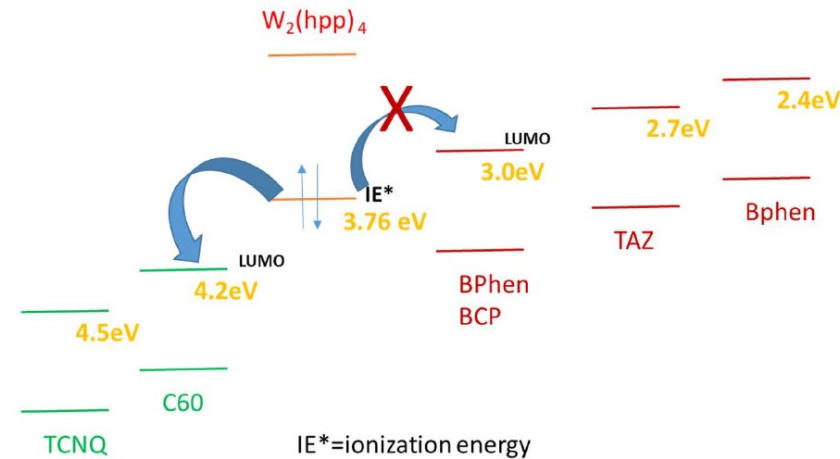
EX2004, p. 770, ; POR 11.

Gap between HOMO of $W_2(hpp)_4$ and LUMO of Bphen/TAZ > 0.5 eV

Professor Schanze
Expert Witness



pictiva displays



“70. Put another way, the 0.76-1.36 eV difference in the LUMO level of BPhen and the ionization level of $W_2(hpp)_4$ and the 1.06 eV difference in the LUMO level of TAZ and the ionization energy of $W_2(hpp)_4$ would **discourage rather than motivate a person of ordinary skill in the art to combine $W_2(hpp)_4$ with BPhen or TAZ to obtain an n-doped layer as Samsung suggests, especially in light of the experimental results that Werner later reported**. That is, a person of ordinary skill in the art would not consider $W_2(hpp)_4$ to be a suitable n-dopant for BPhen or TAZ for use in OLEDs.”

EX2041, para. 70; POR 12, 17

The Estimated 2.5 eV Solid-State Ionization Potential for $W_2(hpp)_4$ Unreliable

Professor Schanze
Expert Witness



pictiva displays

Q. And the 2.5 eV is in reference to the *Fu paper in JACS 2005, pages 7227 to 7234*. Is that correct?

A. Well, that's what the patent says. Yes.

...

Q. So I have posted the Fu paper as *Exhibit 2105* in the chat.

...

Q. Okay. And you have reviewed this paper before. Correct?

A. Yes, counsel. I have reviewed it.

Q. *Does this paper reference the tungsten HPP4* compound anywhere?

A. *No*. It does not.

Q. And does it discuss conversion of the solution phase results to solid phase IP potential, anywhere in the paper?

A. It does not.

Q. And the compounds that's referenced here are *pure organic compounds in the Fu paper*. Is that correct?

A. *Yes*. That is my understanding. It's a variety of different organic compounds, and organic ions, and free radicals.

Q. Would a person of ordinary skill in the art extrapolate the results in this paper to ditungsten HPP4 if they wanted to determine the ionization potential of the ditungsten HPP4?

A. No.

Q. *And do you have any idea how Werner derived the 2.5 eV number from this paper?*

A. *No. I do not.*

Q. *Would you consider that 2.5 eV number based on the side [cite] of the Fu paper, to be a reliable number?*

A. I have no basis that -- to expect it to be reliable. *So I would say it's not reliable.*

EX1021, 149:20-152:1 (objections omitted); Sur-Reply 8-9

Dr. Rand Did Not Bother to Review the Fu Paper

Barry Rand
Expert Witness

SAMSUNG

Q. And you didn't bother to take a look at *the underlying paper where the 2.5 eV came from*, correct?

A. I wouldn't use the word "bother," but *I didn't refer to it*. I used the '541 patent as the source of the 2.5 eV ionization potential.

EX2056, 65:8-13; Sur-Reply 9

Dr. Rand Cannot Testify to the Reliability of the 2.5eV Number

Dr. Rand Did Not Review Fu to Verify the Reliability of the 2.5eV Number

Barry Rand
Expert Witness

SAMSUNG

Q. *Don't you think that you should read Fu* to see whether the [2.5 eV] estimate is a reasonable one?

A. *I don't see why I would need to do that.*

Q. Does Fu even mention tungsten2(hpp)4?

A. Again, I'm not sure. *I didn't read Fu.*

EX2056, 67:25-68:5

Dr. Rand Cannot Testify to the Reliability of the 2.5eV Number

Werner Later Confirmed Unsuitability of $W_2(hpp)_4$ and BPhen


US007972541B2

(12) **United States Patent**
Werner et al.

(10) **Patent No.:** US 7,972,541 B2
(45) **Date of Patent:** Jul. 5, 2011

(54) **DOPED ORGANIC SEMICONDUCTOR MATERIAL**

(75) Inventors: **Ansgar Werner**, Dresden (DE); **Andrea Lux**, Dresden (DE); **Josef Salbeck**, Kaufungen (DE)

(73) Assignee: **Novaled AG**, Dresden (DE)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 357 days.

(56) **References Cited**
U.S. PATENT DOCUMENTS

2,566,208 A 8/1951 Jenkins
3,083,242 A 3/1963 Ramsden
3,282,450 A 12/1965 Blazynski
3,558,671 A 1/1971 Martin
3,563,751 A 2/1971 Cohen
4,003,943 A 1/1977 Fukunaga
4,066,569 A 1/1978 Lim
4,133,821 A 1/1979 West et al.
4,618,453 A 10/1986 Kim
4,669,016 A 10/1986 Reid et al.

(75) Inventors: **Ansgar Werner**, Dresden (DE); **Andrea Lux**, Dresden (DE); **Josef Salbeck**, Kaufungen (DE)

(50) **Foreign Application Priority Data**
Nov. 10, 2005 (EP) 05024515

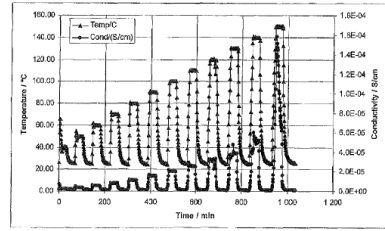
(51) Int. Cl.
H01L 29/08 (2006.01)
H01L 33/00 (2010.01)
H01B 1/12 (2006.01)
B32B 9/06 (2006.01)

(52) U.S. Cl. **252/519.2**; 428/690; 257/40; 257/102; 257/103

(58) **Field of Classification Search** 257/40; 257/102, 103; 252/519.2; 428/690
See application file for complete search history.

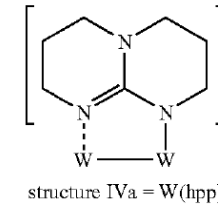
29 Claims, 2 Drawing Sheets

ABSTRACT
The present invention relates to a doped organic semiconductor material comprising at least one organic matrix material, which is doped with at least one dopant, the matrix material being selected from a group consisting of certain phenanthroline derivatives; and also an organic light-emitting diode which comprises such a semiconductor material.



Pictiva EX2044
Samsung v Pictiva
IPR2024-01094

Doping BPhen with



Matrix material	LUMO in eV (determined by CV with Fe/Fe ⁺ as internal standard)	σ (conductivity) in S/cm undoped	σ (conductivity) in S/cm with a doping concentration of 5 mol %
Alq ₃	2.4	<1E-10	9.2E-8
BPhen	2.42	<1E-10	4E-9
BAIq ₂	2.39	<1E-10	8e-8

As can be seen from Table 1, the conductivities achieved with the known matrix materials are still insufficient and very low. ...

EX2044, Table 1; Sur-reply 4-5

EX2044

Werner Later Confirmed Unsuitability of $W_2(hpp)_4$ and BPhen



US007972541B2

(12) **United States Patent**
Werner et al.

(10) **Patent No.:** US 7,972,541 B2
(45) **Date of Patent:** Jul. 5, 2011

(54) **DOPED ORGANIC SEMICONDUCTOR MATERIAL**

(56) **References Cited**

U.S. PATENT DOCUMENTS

(75) Inventors: **Ansgar Werner**, Dresden (DE); **Andrea Lux**, Dresden (DE); **Josef Salbeck**, Kaufungen (DE)

2,566,208 A 8/1951 Jenkins
3,083,242 A 3/1963 Ramsden
3,282,450 A 12/1965 Blazjak

(73) Assignee: **Novaled AG**, Dresden (DE)

3,558,671 A 1/1971 Martin
3,563,751 A 2/1971 Cohen
4,003,943 A 1/1977 Fukunaga

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) to 357 days.

4,066,569 A 1/1978 Lim
4,133,821 A 1/1979 West et al.
4,618,453 A 10/1986 Kim
1,066,016 A 10/1990 Boud et al.

(75) Inventors: **Ansgar Werner**, Dresden (DE); **Andrea Lux**, Dresden (DE); **Josef Salbeck**, Kaufungen (DE)

(50) **Foreign Application Priority Data**

Nov. 10, 2005 (EP) 05024515

Assistant Examiner — Jason P. Thomas

(74) **Attorney, Agent, or Firm** — Sutherland, Ashill & Brennan, LLP

(51) **Int. Cl.**

H01L 29/08 (2006.01)
H01L 33/00 (2010.01)
H01B 1/12 (2006.01)
B32B 9/06 (2006.01)

(57) **ABSTRACT**

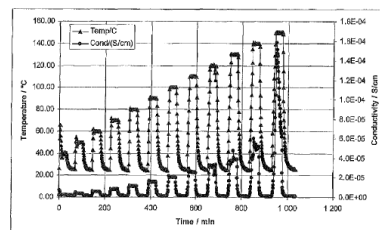
The present invention relates to a doped organic semiconductor material comprising at least one organic matrix material, which is doped with at least one dopant, the matrix material being selected from a group consisting of certain phenanthroline derivatives; and also an organic light-emitting diode which comprises such a semiconductor material.

(52) **U.S. Cl.** 252/519.2; 428/690; 257/40; 257/102; 257/103

(58) **Field of Classification Search** 257/40; 257/102, 103; 252/519.2; 428/690

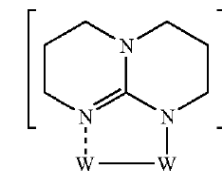
See application file for complete search history.

29 Claims, 2 Drawing Sheets



Pictiva EX2044
Samsung v Pictiva
IPR2024-01094

Film made with Bphen +



structure IVa = $W(hpp)_4$

COMPARATIVE EXAMPLE 2

Comparative Example 2 was carried out in a manner analogous to the procedure according to Example 2, but BPhen was used instead of the matrix material Ie. The resulting conductivity of the layer is 4×10^{-7} S/cm. As can be seen from FIG. 2, such a semiconductor material is stable only up to a temperature of 70° C.

By comparing FIGS. 1 and 2, it can be seen that the conductivity of a semiconductor material consisting of IVa:B-Phen is too low for use in organic light-emitting diodes. When using the matrix material Ie, the conductivity is increased by a factor of 5 and the temperature stability is 70° C. higher.

EX2044

EX2044, 10:9-19; Sur-reply 4-5

Werner Considers 10^{-7} S/cm Low Conductivity

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
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(71) Applicant (for all designated states except the US):
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(74) Attorneys: SCHOLZ, Volker et al.; Bochnert, Holleralle 32, 28209 Bremen (DE)

(81) Designated States (unless otherwise indicated, available national protection type): AE, AT, AU, AZ, BA, BB, BG, BR, BW, BY, CN, CO, CR, CU, CZ, DK, DM, DZ, EC, FI, GB, GD, GE, GH, GM, HR, HU, ID, KE, KG, KP, KR, KZ, LC, LK, LR, LS, MA, MD, MG, MK, MN, MW, MX, MZ, NL, OM, PG, PH, PL, PT, RO, RU, SC, SI, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, available regional protection type): AR, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, ZW, Eurasian (AM, AZ, BY, KG, KZ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LI, LU, LV, MC, MT, NL, NO, PL, PT, RO, RU, SE, SI, SK, SM, TR, UA, UK, US), International (WO).

(54) Title: USE OF A METAL COMPLEX AS N-DOPANT FOR AN ORGANIC SEMICONDUCTOR MATERIAL, ORGANIC SEMICONDUCTOR MATERIAL, AND ELECTRONIC COMPONENT, AS WELL AS LIGAND AND METHOD FOR PRODUCING THE SAME

(57) Abstract: The invention relates to the use of a metal complex as n-dopant for doping an organic semiconductor material for modifying the electrical properties of the same, wherein the compound represents an n-dopant with matrix material. The aim of the invention is to provide n-doped organic semiconductors for matrix materials, reduction potential while achieving high conductivities. According to the invention, a neutral electron-rich metal complex is used as the dopant compound. The complex can especially be multimeric and comprises at least one metal-metal bond. The complex can form a pi-complex with the central atom, or can be a bridging ligand, especially hpp, a borate, triazacyclohexane or comprise at least one carbonium carbon atom or a bivalent atom selected from the group (carbene), Si (silylene), Ge (germylene), Sn, Pb. The invention also relates to novel n-dopants and methods for producing them.

[Continued on another page]

Example 3:

A layer of fullerene C60 was doped with the metal complex cobaltocene. First, a pure layer of the fullerene was produced by sublimation in high vacuum. This layer had a low conductivity of 1×10^{-7} S/cm. The doped layer was then placed in a container containing an evaporator filled with cobaltocene. The container was filled with nitrogen. The cobaltocene was thermally sublimated in this container. The cobaltocene deposited on the surface of the fullerene layer formed a thin highly doped layer there. The transverse current measured in the layer increased by 3 orders of magnitude. The conductivity of the highly doped layer was thus at least 1×10^{-4} S/cm. The doped fullerene layer was subsequently

SDC EX. 1005 - 2/89

EX1005, 62:24-34; Sur-Reply 5

EX2044

DEMONSTRATIVE EXHIBIT – NOT EVIDENCE

Pictiva slide, p. 41

Werner Later Confirmed Unsuitability of $W_2(hpp)_4$ and BPhen

US007972541B2

(12) **United States Patent**
Werner et al.

(10) **Patent No.:** US 7,972,541 B2
(45) **Date of Patent:** Jul. 5, 2011

(54) **DOPED ORGANIC SEMICONDUCTOR MATERIAL**

(75) **Inventors:** Ansgar Werner, Dresden (DE); Andrea Lux, Dresden (DE); Josef Salbeck, Kaufungen (DE)

(73) **Assignee:** Novaled AG, Dresden (DE)

(*) **Notice:** Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 357 days.

(56) **References Cited**
U.S. PATENT DOCUMENTS

2,566,208 A	8/1951	Jenkins
3,083,242 A	3/1963	Ramsden
3,282,450 A	12/1965	Blazajak
3,558,671 A	1/1971	Martin
3,563,751 A	2/1971	Cohen
4,003,943 A	1/1977	Fukunaga
4,066,569 A	1/1978	Lim
4,133,821 A	1/1979	West et al.
4,618,453 A	10/1986	Kim
4,669,016 A	10/1986	Heid et al.

(75) **Inventors:** Ansgar Werner, Dresden (DE); Andrea Lux, Dresden (DE); Josef Salbeck, Kaufungen (DE)

(50) **Foreign Application Priority Data**

Nov. 10, 2005 (EP) 05024515

(51) **Int. Cl.**
H01L 29/08 (2006.01)
H01L 33/00 (2010.01)
H01B 1/12 (2006.01)
B32B 9/06 (2006.01)

(52) **U.S. Cl.** 252/519.2; 428/690; 257/40; 257/102; 257/103

(58) **Field of Classification Search** 257/40; 257/102, 103; 252/519.2; 428/690
See application file for complete search history.

(74) **Attorney, Agent, or Firm** — Sutherland, Ashill & Brennan, LLP

(57) **ABSTRACT**
The present invention relates to a doped organic semiconductor material comprising at least one organic matrix material, which is doped with at least one dopant, the matrix material being selected from a group consisting of certain phenanthroline derivatives; and also an organic light-emitting diode which comprises such a semiconductor material.

29 Claims, 2 Drawing Sheets

Temperature / °C
Conductivity / S/cm

Time / min

Pictiva EX2044
Samsung v Pictiva
IPR2024-01094

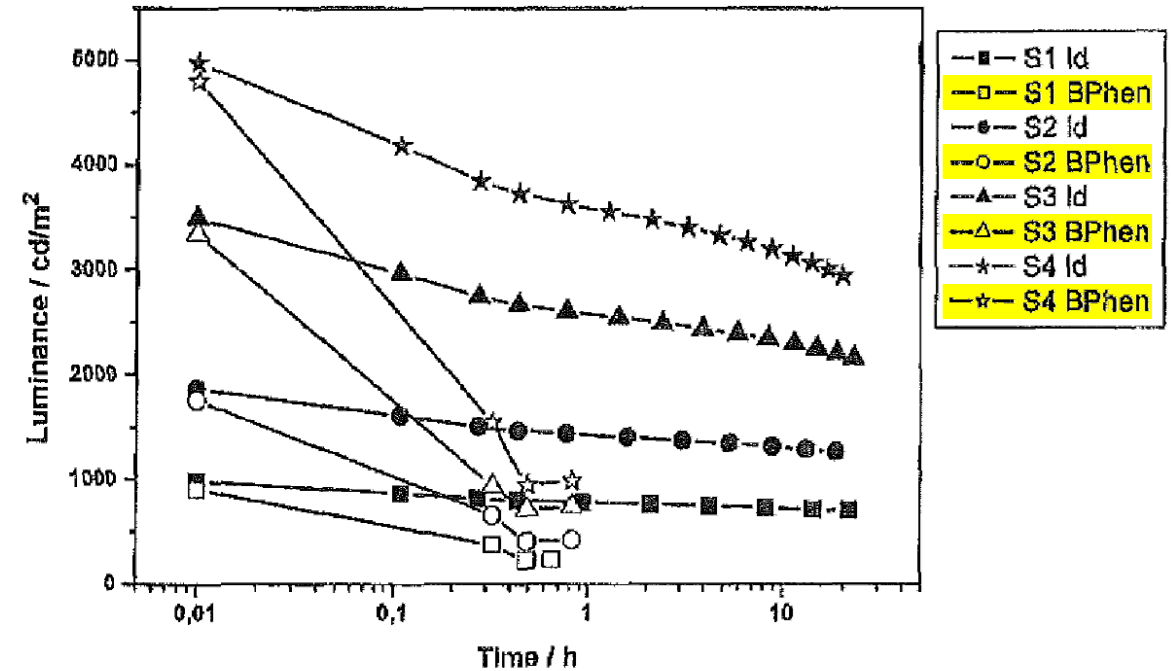


Fig. 3

T50: from “about five or six minutes” at 6000 cd/m² to “about 20 minutes” at 1,000 cd/m²

EX2044

Werner Confirms Unpredictability

EX2044 (Werner et al.)

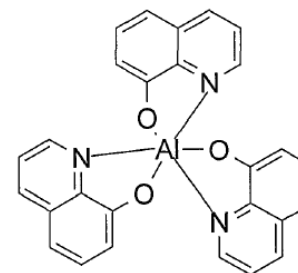
Matrix material	LUMO in eV (determined by CV with Fe/Fe ⁺ as internal standard)	σ (conductivity) in S/cm undoped	σ (conductivity) in S/cm with a doping concentration of 5 mol %
-----------------	---	--	---

Alq ₃	2.4	<1E-10	9.2E-8
BPhen	2.42	<1E-10	4E-9
BAIq ₂	2.39	<1E-10	8e-8

As can be seen from Table 1, the conductivities achieved with the known matrix materials are still **insufficient and very low.** ...

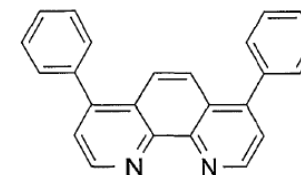
EX2044, Table 1; Sur-reply 4-5

EX1005 (Werner et al.)



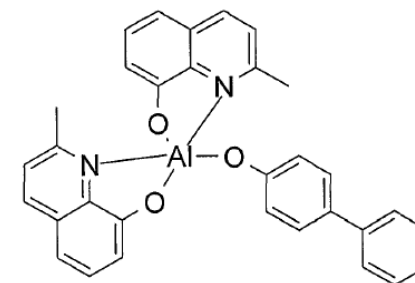
tris(8-hydroxyquinolino)aluminum

Alq₃



BPhen = bathophenanthroline
(4,7-Diphenyl-1,10-phenanthroline)
C₂₄H₁₆N₂

BPhen



Bis(2-methyl-8-quinolinolato)-4-(phenylphenolato)-aluminum(III)

BAIq

EX1005, p.54; Pet. 24-25; Reply 1-2

Poor Conductivity for Combinations of “Expressly” Discloses Species

Werner Confirms Unpredictability

EX2044, Table 1

Matrix material	LUMO in eV (determined by CV with Fe/Fe ⁺ as internal standard)	σ (conductivity) in S/cm undoped	σ (conductivity) in S/cm with a doping concentration of 5 mol %
Alq ₃	2.4	<1E-10	9.2E-8
BPhen	2.42	<1E-10	4E-9
BAlq ₂	2.39	<1E-10	8e-8

As can be seen from Table 1, the conductivities achieved with the known matrix materials are still insufficient and very low.

EX2044, Table 1; Sur-reply 4-5

EX2044, Table 2

It has surprisingly been found that certain phenanthroline derivatives can be used as matrix materials which can if necessary be doped with metal complex dopants. By incorporating suitable electron-attracting substituents at certain positions in the phenanthroline skeleton, electronic properties of the semiconductor material can be set in a targeted manner, so that the LUMO of the phenanthroline derivate falls within a range which means that it can be doped with metal complex dopants, in particular having the structure IV.

R	T _g (° C.)	T _s (° C.)	LUMO (eV)	Conductivity (S/cm)*
Ia R2, R4, R5, R7 = H R1, R3, R6, R8 = phenyl	106	260	2.47	3E-4
Ib R2, R4, R5, R7, R8 = H R3, R6 = phenyl R1 = 1-naphthyl	104	265	2.42	5E-6
Ic R2, R4, R5, R7 = H R3, R6 = phenyl R1, R8 = naphthyl	119	280	2.5	2E-6
Id R2, R4, R5, R7 = H R3, R6 = phenyl R1, R8 = 1-(4,4'-biphenyl)	140	317	2.53	6E-5
Ie R2, R4, R5, R7 = H R3, R6 = phenyl R1, R8 = 1-phenanthryl	165	317	2.51	2E-6

*Concentration IVa (W₂(hpp)₄): 5 mol %

EX2044, 8:44-53, Table 2; Sur-Reply 5 n.2, 7

Similar Measured LUMO Levels, but Orders of Magnitude Differences in Conductivity

Werner Confirms Unpredictability

EX2044, 5 mol % $W_2(hpp)_4$

Matrix material	LUMO in eV (determined by CV with Fe/Fe ⁺ as internal standard)	σ (conductivity) in S/cm undoped	σ (conductivity) in S/cm with a doping concentration of 5 mol %
Alq ₃	2.4	<1E-10	9.2E-8
BPhen	2.42	<1E-10	4E-9
BAIq ₂	2.39	<1E-10	8e-8

R	Tg (° C.)	Ts (° C.)	LUMO (eV)	Conductivity (S/cm)*
Ie R2, R4, R5, R7 = H R3, R6 = phenyl R1, R8 = 1-phenanthryl	165	317	2.51	2E-6

*Concentration IVa ($W_2(hpp)_4$): 5 mol %

EX2044, Tables 1-2; Sur-reply 4-5

EX2044, 4 mol % $W_2(hpp)_4$

COMPARATIVE EXAMPLE 2

Comparative Example 2 was carried out in a manner analogous to the procedure according to Example 2, but BPhen was used instead of the matrix material Ie. The resulting conductivity of the layer is 4×10^{-7} S/cm. As can be seen from FIG. 2, such a semiconductor material is stable only up to a temperature of 70° C.

By comparing FIGS. 1 and 2, it can be seen that the conductivity of a semiconductor material consisting of IVa:B-Phen is too low for use in organic light-emitting diodes. When using the matrix material Ie, the conductivity is increased by a factor of 5 and the temperature stability is 70° C. higher.

EXAMPLE 2

A glass substrate is provided with contacts made of indium tin oxide. A layer of Ie (Table 2) doped with a dopant of structure IVa is then produced on the substrate. The doping concentration of the dopant IVa is 4 mol %. The conductivity of the layer is 2×10^{-6} S/cm at room temperature. The sample

EX2044, 9:55-10:20; Sur-Reply 5 & n.2

Petitioner's Expert Unable to Explain the 100X Differences in Conductivity

Barry Rand

Expert Witness

SAMSUNG

“So yes, it's 5-mole percent instead of 4-mole percent, which indicates to me that these were two different experiments. Given that there are multiple inventors, they even could have been *conducted by two different people*, whether the measurement or the making or the fabrication or both. And, yeah, the dope -- the conductivity is 4 times 10 to the minus 9 siemens per centimeter here in Table 1, clearly a different experiment than the comparative Example 2 with 4-mole percent where it's 4 times 10 to the minus 7. *So there's a two orders of magnitude difference.*

Again, *the reasons are kind of unclear to me*. Either *they're just reporting an experiment that was not very reproducible or it's a typo*. I don't -- it's hard for me to say with certainty what the reason is for the differences in the reporting.”

EX2056, 52:19-53:10; Sur-Reply 5

Non-reproducible Results → No Reasonable Expectation of Success

Petitioner's Expert Unable to Explain the 100X Differences in Conductivity

Barry Rand

Expert Witness

SAMSUNG

Q. And you don't have an explanation for the two orders of magnitude difference? Right?

A. I -- like, as I -- as I've told you over the previous few answers and responses, there are various factors that could have contributed to it, *different people*, because there are numerous inventors; various *device-to-device variation that it might just be underlying in the system*, which I can't know about; *factors in their experiments*; or a simple *typo*. And it's hard to know. I can't assert one way or the other.

EX2056, 56:10-23 (objections omitted)

Non-reproducible Results → No Reasonable Expectation of Success

Reported Differences in BCP and BPhen Electrical Properties Further Demonstrates Unpredictability

Journal of Applied Physics

RESEARCH ARTICLE | NOVEMBER 09 2006

Efficient organic photovoltaic devices using a combination of exciton blocking layer and anodic buffer layer

M. Y. Chan; C. S. Lee; S. L. Lai; M. K. Fung; F. L. Wong; H. Y. Sun; K. M. Lau; S. T. Lee

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J. Appl. Phys. 100, 094506 (2006)
<https://doi.org/10.1063/1.2363649>

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Appl. Phys. Lett. (June 2012)

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Chin. J. Chem. Phys. (October 2012)

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SDC EX. 1034 - 1/5

TABLE II. Electronic properties of BPhen and BCP, and their electron mobilities at an electric field of 3.6×10^5 V/cm.

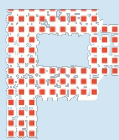
EBL	E_A (eV)	I_P (eV)	μ (cm ² /V s)	Ref.
BPhen ^a	2.9	6.4	5.0×10^{-4}	20
BCP ^a	2.9	6.4	5.0×10^{-6}	17

^aIt should be noted that mobility values of BPhen and BCP were measured using time-of-flight and transient electroluminescence techniques, respectively. The difference of the two orders of magnitude indicates that BPhen has a much better electron transporting ability as compared to BCP.

EX1034, Table 2; Sur-Reply 10

$W_2(hpp)_4$ + Bphen Is Not Electron Conducting

Professor Schanze
Expert Witness



pictiva displays

Q. So why don't we first look at [EX2044] table one?

A. Okay.

Q. The second entry in table one reports the conductivity of BPhen doped with five mol percent of ditungsten two -- ditungsten HPP4. Correct?

A. Yes. If you accept what's written here, yes. ***Conductivity is reported as four times 10 to minus nine siemens per centimeter.***

Q. Okay.

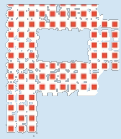
Would a person of ordinary skill in the art consider the resulting film to be electron – to be electron-conducting, given the report of conductivity?

A. **No.** It's very low conductivity.

EX1021, 152:16-153:4; Sur-Reply 5-6; POR 17-18

$W_2(hpp)_4$ + Bphen Not Suitable for OLEDs

Professor Schanze
Expert Witness



pictiva displays

Q. Werner considers that the conductivity of the resulting film is too low for use in organic light-emitting diodes.

Is that correct?

A. If I read the paragraph starting with line 15, from column 10, it says that:

"By comparing Figures 1 and 2, it can be seen that ***the conductivity of a semiconductor material consisting of [IV]A, which is the tungsten HPP complex, and BPhen, is too low for use in organic light-emitting diodes.***"

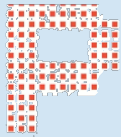
Q. Now, *given this disclosure, would a person of ordinary skill in the art be motivated to use BPhen doped with $W_2(hpp)_4$ as an electron-conducting layer for use in OLED?*

A. **No.**

EX1021, 153:19-154:14; Sur-Reply 5-6; POR 17-18

$W_2(hpp)_4$ + Bphen Has Too Poor a Lifetime to Be Suitable for OLEDs

Professor Schanze
Expert Witness



pictiva displays

Discussing comparative example 3:

Q. And what is the reported brightness over time?

A. So according to line 52, in one hour, the brightness decreased from 4,800 candelas per meter to lower than 1,000 candelas per meter.

...

Q. So would a POSITA consider the OLED device that's reported in comparative example number three to be a suitable device for use as an OLED?

A. No.

EX1021, 156:12-157:11 (objections omitted); Sur-Reply 11

Ma's Conductivity Measurement Does Not Inform the Electron Conductivity of $W_2(hpp)_4$ + Bphen

Rand Reply Declaration

³ Ma Figure 5 reports current density as a function of voltage. Current density (mA/cm²) and conductivity (σ) are directly related through a variation of Ohm's law where $J = \sigma E$ (where J is current density, σ is conductivity and E is the electric field). Accordingly, a two- to three-fold increase in current density would result in a two- to three-fold fold increase in conductivity, and thus it is acceptable to compare current density increases in Ma with conductivity increases in the '541 patent.

EX1020, p. 6 n.3

Rand Testimony

- Ma used a vertical stack for measurement
- There is resistivity through both the Bphen layer and other layers and interfaces
- Rand does not know the relative ratio of resistivity between Bphen and other layers
- "Ma's Figure 5 devices also include a BCP layer, and ***"Who knows what that's going to do"***"

EX2056, 25:1-28:19, 31:13-33:23, Sur-Reply 6

Ma's Conductivity Measurement Does Not Inform the Electron Conductivity of $W_2(hpp)_4$ + Bphen

EX2044

- Using a “lateral” structure
- Measuring conductivity of bulk film

EX2056, 19:24-21:10, Sur-Reply 6

Ma

- Using a “vertical” structure
- Measured conductivity varies greatly depending on resistivity of other layers in the vertical stack and at the interfaces
- ***“would be challenging to, ..., give an absolute value of conductivity in this [Ma] device”***
- Ma's Figure 5 devices also include a BCP layer, and ***“Who knows what that's going to do”***
- Orders of magnitude increase in bulk conductivity may result only in 2x fold increase in observed conductivity

EX2056, 25:1-28:19, 31:13-33:23, Sur-Reply 6

Samsung Expert Unable to Apportion Measured Resistivity to Different Parts of the Vertical Device

Barry Rand
Expert Witness

SAMSUNG

Q. And do you know what's **the relative value of the interfacial resistivity compared to the bulk resistivity** through the film in the vertical direction?

A. **I do not know that**, no.

Q. Do you have **a guess as to the relative magnitude**?

A. **I'm unable to offer that guess** with the information that I've, you know, taken from Ma, my many readings of it.

EX2056, 26:14-23; Sur-reply 6

In a Vertical Structure Like Ma, Observed Conductivity Does Not Scale Linearly with Bulk Conductivity of the Electron Conducting Layer

Barry Rand
Expert Witness

SAMSUNG

- Q. *So observed conductivity for the electron-only device goes up by a factor of 2 though the bulk conductivity for the BPhen film went up by 100, correct?*
- A. In the scenario that you are displaying where initially the BPhen layer and the rest of the system were approximately of equal resistivity and then you dropped by a factor of a lot, the resistivity of the BPhen layer, *yes*, in that scenario, which I'm unwilling to assert is the scenario in Ma, but in the scenario that you described hypothetically, *yes*, it would – the current at a specific voltage would go up by a factor of 2 -. -- despite 100 times change in conductivity of that one layer.

EX2056, 33:9-34:2 (objections omitted); Sur-reply 6

Werner Does Not Render Obvious the Challenged Claims

- One of millions of unpredictable combinations
- $W_2(hpp)_4$ & BPhen/TAZ Not Expected to be Suitable as Electron-Conducting Layer
- No disclosure of joint vaporization of the combination

Werner Discloses Multiple Process Methods

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
September 15, 2005 (09/15/2005)

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(71) Applicant (for all designated states except the US):
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(72) Inventors; and
(73) Inventors/Applicants (for the US only): WERNER, Aungar [DE/DE]; Altenberger Strasse 20, 01277 Dresden (DE); KÜHL, Olaf [DE/DE]; Mittelstrasse 10, 04416 Markkleeberg (DE); GESSLER, Simon [DE/DE]; Hauptstrasse 79, 69117 Heidelberg (DE); HARADA, Kentaro [DE/DE]; Blumenstrasse 90, 01307 Dresden (DE); HARTMANN, Horst [DE/DE]; Wollnerstrasse 4,

(74) Attorneys: SCHOLZ, Volker et al.; Boehmert & Boehmert, Hollerallee 32, 28209 Bremen (DE).

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[Continued on next page]

(54) Title: USE OF A METAL COMPLEX AS N-DOPANT FOR AN ORGANIC SEMICONDUCTING MATRIX MATERIAL, ORGANIC SEMICONDUCTOR MATERIAL, AND ELECTRONIC COMPONENT, AS WELL AS DOPANT AND LIGAND AND METHOD FOR PRODUCING THE SAME

(57) Abstract: The invention relates to the use of a metal complex as n-dopant for doping an organic semiconducting matrix material for modifying the electrical properties of the same, wherein the compound represents an n-dopant with regard to the matrix material. The aim of the invention is to provide n-doped organic semiconductors for matrix materials that have little reduction potential while achieving high conductivities. According to the invention, a neutral electron-rich metal complex having a central atom as the preferably neutral or charged transition metal atom having a valence electron number of at least 16 is used as the dopant compound. The complex can especially be multinuclear and comprises at least one metal-metal bond. At least one ligand can form a pi-complex with the central atom, or can be a bridging ligand, especially hpp, a borate, a carborane or triacyclicsilane or comprise at least one carbon-carbon bond or a bivalent atom selected from the group including C (carbene), Si (silylene), Ge (germylene), Sn, Pb. The invention also relates to novel n-dopants and methods for producing them.

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SDC EX. 1005 - 2/89

Implementation of doping

The doping of the respective matrix material with the n-dopants according to the invention can be carried out by one or a combination of the following methods:

- Co-evaporation in vacuum with a source for the matrix material and one for the dopant
- Sequential deposition of the matrix material and the n-dopant on a substrate with subsequent diffusion of the dopant, in particular through thermal treatment
- Doping a matrix layer by a solution of n-dopants followed by evaporation of the solvent, in particular through thermal treatment
- Surface doping of a matrix material layer by a surface-applied layer of dopants
- Preparation of a solution of matrix molecules and dopants and subsequent formation of a layer from this solution by conventional methods such as solvent evaporation or spin-coating

EX1005, 59:12-30; POR 15

Werner Does Not Suggest Simultaneous Evaporation is Suitable for All Metal Complex and any Matrix Materials

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(72) Inventors; and
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(81) Designated States (unless otherwise indicated, all designated states): AT, AU, AZ, BA, BB, BG, BR, BW, CA, CN, CO, CR, CU, CZ, DK, DM, DZ, FI, GB, GD, GE, GH, GM, HR, HU, KE, KG, KP, KR, KZ, LC, LK, LR, MA, MD, MG, MK, MN, MW, MX, NZ, OM, PG, PH, PL, PT, RO, RU, SA, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, all designated states): AM, AR, AT, AU, AZ, BA, BB, BG, BR, BW, CA, CN, CO, CR, CU, CZ, DK, DM, DZ, FI, GB, GD, GE, GH, GM, GR, GU, HK, HN, HU, IL, IN, JP, KE, KG, KP, KR, KZ, LC, LK, LR, MA, MD, MG, MK, MN, MW, MX, MY, NZ, OM, PG, PH, PL, PT, RO, RU, SA, SD, SI, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, VC, VN, YU, ZA, ZM, ZW.

(54) Title: USE OF A METAL COMPLEX AS N-DOPANT FOR AN ORGANIC SEMICONDUCTOR MATERIAL, ORGANIC SEMICONDUCTOR MATERIAL, AND ELECTRONIC COMPONENT, AS WELL AS METHOD FOR PRODUCING THE SAME

(57) Abstract: The invention relates to the use of a metal complex as n-dopant for doping an organic semiconductor material for modifying the electrical properties of the same, wherein the compound represents an n-dopant matrix material. The aim of the invention is to provide n-doped organic semiconductor for matrix material reduction potential while achieving high conductivities. According to the invention, a neutral electron-rich metal complex as the preferably neutral or charged transition metal atom having a valence electron number of 10 or more as the dopant compound. The complex can especially be multinuclear and comprises at least one metal-metal bond. The complex can form a pi-complex with the central atom, or can be a bridging ligand, especially bipyridine, a terpyridine, a phenanthroline, or a porphyrin, or a complex of at least one carbonium carbon atom or a bivalent atom selected from the group consisting of (carbene), Si (silylene), Ge (germylene), Sn, Pb. The invention also relates to novel n-dopants and methods for producing the same.

The provided metal complex is evaporated simultaneously with the matrix material. According to the example, the matrix material is phthalocyanine-zinc or fullerene C₆₀. The n-dopant and matrix material can be evaporated in such a way that the layer deposited on a substrate in a vacuum evaporation system has a doping ratio of n-dopant to matrix material of 1:10.

EX1005, 64:10-15; POR 15

SDC EX. 1005 - 2/89

No Evidence that a POSITA Would Evaporate a Polymeric Matrix Material

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(72) Inventors; and
(73) Inventors/Applicants (for the US only): WERNER, Aungar [DE/DE]; Altenberger Strasse 20, 01277 Dresden (DE). KÜHL, Olaf [DE/DE]; Mittelstrasse 10, 04416 Markkleeberg (DE). GESSLER, Simon [DE/DE]; Hauptstrasse 79, 09117 Heidelberg (DE). HARADA, Kentaro [DE/DE]; Blumenstrasse 90, 01307 Dresden (DE). HARTMANN, Horst [DE/DE]; Wollnerstrasse 4,

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(84) Designated States (unless otherwise indicated, for every available regional protection type): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, [Continued on the next page]

(54) Title: USE OF A METAL COMPLEX AS N-DOPANT FOR AN ORGANIC SEMICONDUCTING MATRIX MATERIAL, ORGANIC SEMICONDUCTOR MATERIAL, AND ELECTRONIC COMPONENT, AS WELL AS DOPANT AND LIGAND AND METHOD FOR PRODUCING THE SAME

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WO 2005/086251 A2

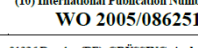
SDC EX. 1005 - 2/89

The matrix material can consist partially (> 10 or > 25 wt%) or essentially (> 50 wt% or > 75 wt%) or entirely of a metal phthalocyanine complex, a Buckminster fullerene, possibly also a porphyrin complex, in particular a metal porphyrin complex, an oligothiophene, oligophenyl, oligophenylene vinylene, or oligofluorene compound, with the oligomers preferably comprising 2-500 or more, preferably 2-100 or 2-50 or 2-10 monomeric units.

The oligomer can also comprise > 4, > 6, or > 10 or more monomeric units, in particular for the ranges indicated above, such as 4 or 6-10 monomeric units, 6 or 10-100 monomeric units, or 10-500 monomeric units. The monomers or oligomers can be substituted or unsubstituted, and block or mixed polymers of the mentioned oligomers can also be present. The matrix can also be a mixture of oligomers with different chain lengths, as is typical for conventional polymer layers.

EX1005, 56:5-19 (original page 53:5-19); Sur-Reply 11-12

Undisputed: Example # 3 Uses Sequential, Not Simultaneous, Evaporation

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(43) International Publication Date September 15, 2005 (09/15/2005)	PCT WO 2005/086251 A2
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(26) Publication Language: German	
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(72) Inventors; and Inventors/Applicants (for the US only): WERNER, August [DE/DE], Altenberger Strasse 20, 01277 Dresden (DE), KÜHL, Olaf [DE/DE], Mittelstraße 10, 04416 Mehlisberg (DE), GESSLER, Simon [DE/DE], Hauptstraße 79, 09117 Heideberg (DE) HARADA, Kentaro [DE/DE], Blumenthorstrasse 90, 01307 Dresden (DE), HARTMANN, Horst [DE/DE], Wollastrasse 4, 01307 Dresden (DE)	(54) Designated States (unless otherwise indicated, for every available regional protection type): ARIPO (BW, GE, GM, KE, LS, MW, MZ, NA, SD, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, NL, PL, PT, RO, RU, SE, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW).
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[Continued on the next page]

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Example 3:

A layer of fullerene C60 was doped with the metal complex cobaltocene. First, a pure layer of the fullerene was produced by sublimation in high vacuum. This layer had a low conductivity of $1 \cdot 10^{-7}$ S/cm. The doped layer was then placed in a container containing an evaporator filled with cobaltocene. The container was filled with nitrogen. The cobaltocene was thermally sublimated in this container. The cobaltocene deposited on the surface of the fullerene layer formed a thin highly doped layer there. The transverse current measured in the layer increased by 3 orders of magnitude. The conductivity of the highly doped layer was thus at least $1 \cdot 10^{-4}$ S/cm. The doped fullerene layer was subsequently

EX1005, 65:24-34 (original page 62:24-34); EX2042 Rand, 203:13-19; POR 15-16; Sur-Reply 11-12

Simultaneous Evaporation is Not Necessarily “Joint Vaporization”

EX1005

The provided metal complex is evaporated simultaneously with the matrix material. According to the example, the matrix material is phthalocyanine-zinc or fullerene C₆₀. The n-dopant and matrix material can be evaporated in such a way that the layer deposited on a substrate in a vacuum evaporation system has a doping ratio of n-dopant to matrix material of 1:10.

EX1005, 64:10-15; Pet. 26

Samsung Expert

Q. Is simultaneous vaporization the same as joint vaporization?

A. No. Not necessarily.

Q. What is broader?

A. Simultaneous vaporization would be broader.

EX2106, 103:12-16, discussed in EX2056, 153:24-155:16, Sur-Reply 11

**Dr. Rand Did Not Review Dr. Kymissis's
Deposition Transcript and Does Not
Disagree with Him**

Evidence in Record Only Disclosed Solution Reactions of W₂(hpp)₄ Before '223



Reaction between W₂(hpp)₄ and CH₂Cl₂. To 50 mg of 1, 15 ml of CH₂Cl₂ was added. This resulted in the immediate formation of a brown solution. After about 10 min, a dark brown precipitate formed. After filtration, the brown solution was layered with hexanes and dark brown crystals of W₂(hpp)₄Cl₂ · 4CH₂Cl₂ · 2 · 4CH₂Cl₂ grew within 2 days.

Reaction between W₂(hpp)₄ and C₆₀. C₆₀ (23.5 mg, 0.033 mmol) was dissolved with the aid of a sonicator in 40 ml toluene, giving a reddish purple solution. Separately, 1 (30 mg, 0.033 mmol) was dissolved in 20 ml toluene. The solution of 1 was transferred to the solution of C₆₀ via cannula, resulting in a dark purplish red precipitate within 5 min. The nearly colorless liquid phase was discarded. The solid was dried under vacuum. It was insoluble in THF, DMSO and other common organic solvents. The solid was air-sensitive and turned to dark brown when exposed to air. IR (cm⁻¹, KBr): 2937 (w), 2836 (w), 1735 (w), 1696 (m), 1681 (m), 1646 (s), 1540 (s), 1452 (m), 1379 (s), 1308 (m), 1256 (w), 1199 (m), 1137 (w), 1059 (m), 1029 (m), 803 (s), 735 (w), 672 (m), 571 (w), 517 (w), 467 (w).

Reaction between W₂(hpp)₄ and TCNQ. Solutions of 1 (30 mg, 0.033 mmol) in 25 ml THF, and TCNQ (6.7 mg, 0.033 mmol) in 15 ml THF were prepared. The THF solution of TCNQ was transferred to the solution of 1 by cannula. A transient green color was observed. Within 1 min, a cloudy off-white suspension formed. The colorless liquid was discarded, and the remaining solid was washed with 10 ml of dichloromethane, and then dried under vacuum. The solid was air-sensitive and turned pinkish brown when exposed to air. The yield was essentially quantitative. IR (cm⁻¹, KBr): 3422 (br, m), 2937 (w), 2858 (w), 2157 (s), 2097 (s), 1539 (m), 1496 (m), 1447 (w), 1379 (m), 1309 (s), 1215 (m), 1131 (w), 1031 (w), 823 (br, s), 750 (w).

It is clear, however, that 1 is a strong reducing agent with an enormous potential for use on organic substrates in organic solvents. This is an area of great current interest [30].

EX2008, 122, Experimental Section; *id.*, 124; POR 16.

EX2009 Does Not Disclose Joint Vaporization

Rand Reply Declaration

35. Further, Ex.2008, Cotton 2003 does not conclude that $W_2(hpp)_4$ *should* be used *only* in a solution. Rather, the authors recognized that using $W_2(hpp)_4$ in organic solvents has a “potential” and “is an area of great current interest,” which clearly indicates that the use of $W_2(hpp)_4$ in a solution was not established as of 2003. Ex.2008 at 124. In fact, Cotton et al. published an article in which a gas-phase reaction was performed with $W_2(hpp)_4$. Ex.2009, Ref. 16 (“Samples were handled and spectra were obtained using rigorous air-sensitive techniques . . . $W_2(hpp)_4$ sublimed at 250° to 280°C.”). And, Ex.2044 describes using $W_2(hpp)_4$ in particular with matrix materials having evaporation temperatures over 200 °C, (Ex.2044, 8:39-40) which suggests its use in the gas phase.

EX1020, para. 35; Sur-Reply 12

Rand Testimony

- Q. Does Footnote 16 describe a charge transfer reaction between the metal complex and an organic compound?
- A. No. Reference 17 [sic, 16] doesn't specifically describe any charge transfer reaction between a metal complex and an organic compound.

EX2056, 121:10-16 (objections omitted), see also 121:17-122:2 (clarifying Reference 17 in the answer was meant to be Reference 16), Sur-Reply 12

EX2009, n. 16 Discusses Measurement of Ionization Potential of Metal Complexes

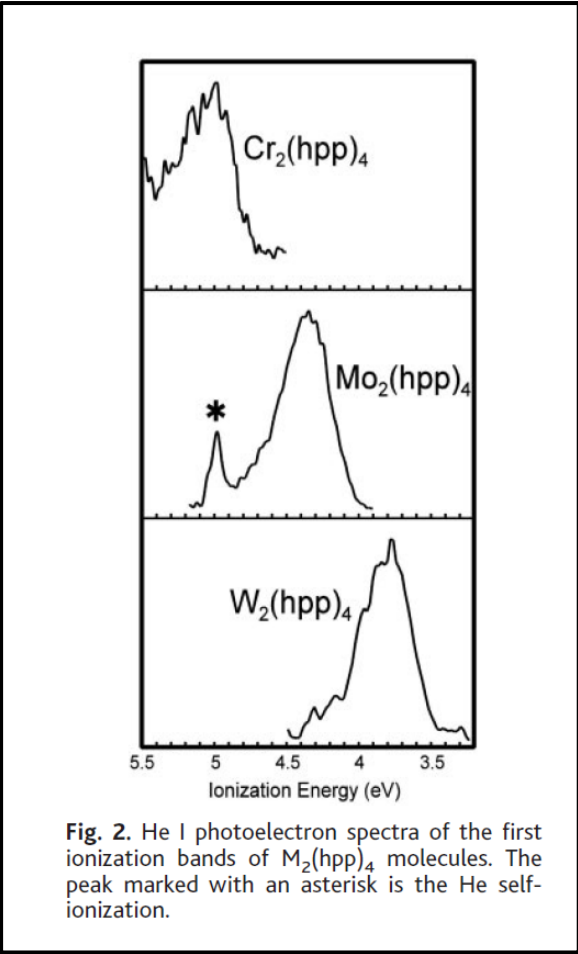


Fig. 2. He I photoelectron spectra of the first ionization bands of $M_2(hpp)_4$ molecules. The peak marked with an asterisk is the He self-ionization.

Closed-Shell Molecules That Ionize More Readily Than Cesium

F. Albert Cotton,^{1*} Nadine E. Grohn,² Jiajie Gu,^{3*} Fenglin Huang,⁴ Dennis L. Lichtenberger,^{5*} Carlos A. Murillo,^{6*} Laura Q. Van Dorp,⁷ Chad C. Wilhoit^{8*}

We report a class of molecules with extremely low ionization enthalpies, one member of which has been determined to have a gas-phase ionization energy (ionized, 3.5 eV) lower than that of the cesium atom (which has the lowest gas-phase ionization energy of the elements) or of any other known closed-shell molecule or neutral transient species reported. The molecules are dimetal complexes with the general formula $M_2(hpp)_4$, where M is Cr, Mo, or W, and hpp is the anion of 1,3,4,6,7,8-hexaphyridine-2(1H)-pyrimidin-2(1H)-pyrimidine, structurally characterized in the solid state, spectroscopically characterized in the gas phase, and modeled with their relativistic computations. The low-energy ionization of each molecule corresponds to the removal of an electron from the delta bonding orbital of the quadruple metal-metal bond, and a strong interaction of this orbital with a filled orbital on the top ligands largely accounts for the low ionization energies.

The phenomena of oxidation (electron loss) and reduction (electron gain) are fundamental to chemistry. From where these processes do not occur in such, more complex chemical processes and properties, such as toxic and corrosive metal complexes and metalloproteins, can be understood by analyzing them as a sum of ionization and reduction steps. Tables of ionization enthalpies, electron affinities, and electrode reduction potentials are essential to understanding and teaching chemistry.

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Fig. 1. A thermal ellipsoid drawing of the quadruply bonded $Mo_2(hpp)_4$ molecule (in $Mo_2(hpp)_4$) based on X-ray crystallography (P. E. Grohn, unpublished data). The temperature of the data collection was 100 K. The $Mo-Mo$ bond length is 2.101(1) Å, the $Mo-W$ bond length is 2.101(1) Å, and the $W-W$ bond length is 2.101(1) Å.

Mo (7), and W (12, 13), have been measured and are shown in Fig. 2. The He I gas-phase photoelectron spectra of the three $M_2(hpp)_4$ molecules were recorded by means of an instrument and experimental methods that have been described previously (15–18). The

16. Samples were handled and spectra were obtained using rigorous air-sensitive techniques (17), although the samples were not exceptionally air-sensitive, with half-lives of the solid powders in air (in Arizona) observed to be roughly on the order of a minute and longer. $Cr_2(hpp)_4$ sublimed at 200° to 230°C in the instrument ($\approx 10^{-4}$ Torr), $Mo_2(hpp)_4$ sublimed at 220° to 250°C, and $W_2(hpp)_4$ sublimed at 250° to 280°C. Temperatures were monitored using a “K” type thermocouple passed through a vacuum feedthrough and attached directly to the sample cell. Any free Hhpp in the samples was observed at temperatures from 100° to 200°C before observation of the dimetal complexes. All free Hhpp ionizations occur above 7 eV (18). During data collection, the instrument resolution (measured using full width at half maximum of the argon $^{2}P_{3/2}$ peak) was 0.020 to 0.035 eV. Satellite intensity in the He I spectra due to the He I β resonance line emission from the source was removed. This satellite intensity is about 3% of the intensity of the He I α line emission and at 1.869 eV higher photon energy. The spectrum of the $W_2(hpp)_4$ molecule was also obtained with the He II photon source, showing that the first ionization band is not produced indirectly by any absorptive or other resonance process dependent on the energy of the excitation source.

No Separate Organic Compounds in the Measurements

EX2044 Uses Evaporation Temperature as a Proxy for Thermal Stability of the Doped Films, Not as an Indication of Processing Conditions

Rand Reply Declaration

35. Further, Ex.2008, Cotton 2003 does not conclude that $W_2(hpp)_4$ *should* be used *only* in a solution. Rather, the authors recognized that using $W_2(hpp)_4$ in organic solvents has a “potential” and “is an area of great current interest,” which clearly indicates that the use of $W_2(hpp)_4$ in a solution was not established as of 2003. Ex.2008 at 124. In fact, Cotton et al. published an article in which a gas-phase reaction was performed with $W_2(hpp)_4$. Ex.2009, Ref. 16 (“Samples were handled and spectra were obtained using rigorous air-sensitive techniques . . . $W_2(hpp)_4$ sublimed at 250° to 280°C.”). And, Ex.2044 describes using $W_2(hpp)_4$ in particular with matrix materials having evaporation temperatures over 200 °C, (Ex.2044, 8:39-40) which suggests its use in the gas phase.

EX1020, para. 35; Sur-Reply 12

EX2044

Preferably, the matrix material has an evaporation temperature of at least 200° C.

The matrix materials used according to the invention for the semiconductor material moreover have an improved level of thermal stability compared to the prior art, which can be attributed in particular to increased sublimation and decomposition temperatures. The efficiency of an OLED according to the invention is also increased.

EX2044, 8:39-40, 8:62-67; Sur-Reply 12

Reference to Evaporation Temperature is for Films' Improved Thermal Stability, Not for Processing Conditions

Evaporative Temperature and Sublimation Temperatures Used Interchangeably

Barry Rand
Expert Witness

SAMSUNG

Q. So when the literature says the matrix has an evaporation temperature of 200 degrees, that could also refer to the sublimation temperature; is that correct?

A. ***"Evaporation" and "sublimation" are often used interchangeably.*** What I think is being expressed here is the temperature to reach some flux of material to a substrate.

EX2056, 203:19-202:1; Sur-Reply 12

EX2044 Does Not Disclose Joint Vaporization

US007972541B2

(12) **United States Patent**
Werner et al.

(10) **Patent No.:** US 7,972,541 B2
(45) **Date of Patent:** Jul. 5, 2011

(54) **DOPED ORGANIC SEMICONDUCTOR MATERIAL**

(75) **Inventors:** Ansgar Werner, Dresden (DE); Andrea Lux, Dresden (DE); Josef Salbeck, Kaufungen (DE)

(73) **Assignee:** Novalux AG, Dresden (DE)

(*) **Notice:** Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 357 days.

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H01L 33/00 (2010.01)
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B32B 9/06 (2006.01)

(52) **U.S. Cl.** 252/519.2; 428/690; 257/40; 257/102; 257/103

(58) **Field of Classification Search** 257/40; 257/102; 103; 252/519.2; 428/690
See application file for complete search history.

(56) **References Cited**

U.S. PATENT

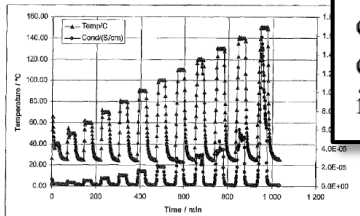
2,566,208 A 8/1951
3,083,242 A 3/1963
3,226,450 A 12/1965
3,558,671 A 1/1971
3,563,751 A 2/1971
4,003,943 A 1/1977
4,066,569 A 1/1978
4,133,821 A 1/1979
4,618,453 A 10/1986
4,960,916 A 10/1990
5,093,698 A 3/1992

FOREIGN PATEN
CA 2549399

OTHER PUB
Akiba, Kin-Ya et al., "Direct Syn-
dihydrobenzothiazoles from 3-me-
thione and some mechanistic as-
Society of Japan, vol. 52(1), pp. 1

(57) **ABST**
The present invention relates to
tor material comprising at least
which is doped with at least one
line derivatives; and also an
which comprises such a semic

29 Claims, 2 D



Pictiva EX2044
Samsung v Pictiva
IPR2024-01094

EXAMPLE 1

Selected phenanthroline derivatives, which are shown in Table 2 below, were used as matrix material for doping with $W_2(hpp)_4$ (structure IVa), and the conductivity was measured. The results are summarized in Table 2.

EXAMPLE 2

A glass substrate is provided with contacts made of indium tin oxide. A layer of Ie (Table 2) doped with a dopant of structure IVa is then produced on the substrate. The doping concentration of the dopant IVa is 4 mol %. The conductivity of the layer is $2 \cdot 10^{-6}$ S/cm at room temperature. The sample is then subjected to a temperature cycle. The temperature

EXAMPLE 3

A glass substrate is provided with contacts made of indium tin oxide. The layers spiro-TTB doped with p-dopant 2-(6-dicyanomethylene-1,3,4,5,7,8-hexafluoro -6H-naphthalen-2-ylidene)malononitrile (50 nm, 4 mol %), 2,2',7,7'-tetrakis (N,N'-diphenylamino)-9,9'-spirobifluorene, N,N'-di (naphthalen-2-yl)-N,N'-diphenylbenzidine doped with emitter dopant iridium(III)bis(2-methyldibenzo[f,h]quinoxaline)-(acetylacetonate) (20 nm, 10% by weight), Id (10 nm), Id doped with IVa (60 nm, 4 mol %)/Al (100 nm) are then deposited thereon one after the other. The organic light-emitting diode thus produced emits orange-red light.

EX2044, Examples 1-3; Sur-reply 12

Werner Does Not Disclose or Suggest Coordination

2. Dependent Claim 2: The organic electronic component according to claim 1, wherein the organic compound coordinates to the metal complex due to the joint vaporization.

Werner discloses the additional elements in claim 2. Ex.1003, ¶74.

First, Werner discloses a metal complex that can coordinate to an organic compound. Ex.1003, ¶75. For example, Werner discloses $W_2(hpp)_4$ as one of the examples of the “electron-rich neutral metal complex” for the n-doped organic semiconductor layer. Werner, 60:17–21 (“ M_2hpp_4 with M equals Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, or W”); *see also id.* 13:16–21 (“Preferably, at least one ligand, two, several, or all ligands are selected from the group of halides, carboxylates, formamidinates, pyrimido-pyrimidines including their anions, in particular substituted or unsubstituted pyrimido [1,2-a]pyrimidine or their anions, *in particular hpp* (*hpp: anion of 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine ...* .”) (emphasis added). $W_2(hpp)_4$ has two central metal atoms (tungsten), and the ability to coordinate with an organic compound. Ex.1003, ¶75. Indeed, the '223 patent confirms that “W is a preferred central metal atom” due to “the ability to coordinate with additional ligands [i.e., organic compounds]” and that “[i]t is particularly preferred if all of the central atoms in the metal complex are W.” '223 patent, 3:4–8.

Second, Werner discloses an organic compound that can coordinate to a metal complex. Ex.1003, ¶76. For example, Werner discloses that “[i]n particular, BPhen can be used as the matrix material.” Werner, 55:5–6. The '223 patent purports that BPhen (Compound VI) is one of the compounds that “are particularly well suited as an organic compound for the electron-conducting layer” because it “comprises several coordination sites for metal complexes.” '223 patent, 7:43–48; *see also id.* 7:47–63 (“These compounds I–XIII ... have large delocalized electron systems [which] ... enable the compounds to accept and transport further negative charges very effectively since this additional charge can be easily distributed onto several atoms in the molecule. Therefore, a coordinated metal complex can effectively transfer a negative charge to the organic compound coordinated thereto.”).

Third, Werner discloses that “the metal complex is evaporated simultaneously with the matrix material” to form an n-doped organic semiconductor layer. Werner, 61:10–11; Ex.1003, ¶77. The '223 patent discloses that “[b]y virtue of the joint vaporization of the metal complex with an organic compound, the two compounds interact with one another in the gas phase or when they meet one another on the substrate surface” '223 patent, 1:60–63. Because $W_2(hpp)_4$ and BPhen are the materials that can coordinate when jointly vaporized according to the '223 patent, Werner discloses that *the organic compound coordinates to the metal complex due to the joint vaporization*. Ex.1003, ¶77.

- '223 is not Werner and no evidence of comparable processes
- “can coordinate” does not show inherency

“metal complex” (’223 Patent, Claim 1, 2, 10, 11, 13, 14)	“a compound containing one or more metal elements that coordinate to one or more non-metal elements, fragments or ions, excluding metal oxides”
“wherein the organic compound coordinates to the metal complex due to the joint vaporization” (’223 Patent, Claim 2)	Plain and ordinary meaning
“coordinate[s]” (’223 Patent, Claim 2, 11, 14)	“form[s] a chemical bond between two atoms in which a shared pair has been supplied by one of the two atoms”
“chain-like structure” (’223 Patent, Claim 12)	“a structure in which at least parts of organic compounds bridge exactly two metal complexes together”
“network-like structure” (’223 Patent, Claim 12)	“a structure in which at least parts of organic compounds bridge more than two metal complexes together”
“degree of cross-linking of the electron-conducting layer” (’223 Patent, Claim 13)	“degree of linking between the metal complex and the organic compound in the electron-conducting layer”

MS. BAILY: And so the Plaintiffs' construction, which expands the meaning of 'coordinates' to any kind of bonding interaction is too broad. The claims do not use the word 'bonding'; they use the term 'coordinates' which specifies a particular kind of interaction, a particular kind of bonding.

Now, I know that this is extrinsic evidence, but I do

want to say that in chemistry there is a specific meaning to a coordinate bond that is well-understood, and so that is why we have cited to Your Honor many dictionary definitions that confirm that a coordinate bond is a specific kind of bond, number one; and it's one in which one atom provides both shared electrons. And so countless dictionaries include that definition because that is the plain and ordinary meaning of 'coordinate' or 'coordinate bond' in chemistry.

The dictionaries also indicate that a dative bond is a synonym. That's why we reverted to using those words. But perhaps, you know, the additional clarity for the jury where we're talking about the definition of a dative bond or a coordinate bond, which is where both electrons are shared from one atom to another, perhaps that would be helpful.

Werner Evaporation Conditions Does Not Necessarily Result in Coordination

Barry Rand
Expert Witness

SAMSUNG

- Q. What is the joint vaporization conditions he [Werner] used?
- A. That's described in more detail, but on page 56, line 17A, talks about co-evaporation in a vacuum with a source for the matrix material and one source for the dopant.
- Q. *Does that necessarily result in interaction between the two materials?* Any vaporization conditions are going to result in interactions between the BPhen and W2(hpp)4?
- A. **It depends.**

EX2042, 200:14-201:2; POR 19

Werner Evaporation Conditions Does Not Necessarily Result in Coordination

Barry Rand
Expert Witness

SAMSUNG

Q. Will the type of interactions, if any, depend, depend on the processing conditions?

A. Absolutely.

Q. So there may be no interaction and [sic, under] some process conditions and there may be [l]ot [of] interactions in some other, under some other process conditions; right?

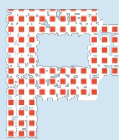
A. Yes.

EX2042, 199:20-200:6; POR 18-19

No Evidence that Werner and 223 Used the Same Processes or that a POSITA Knew 223's Processing Condition

Undisputed: Prior Art Does Not Suggest Coordination to $W_2(hpp)_4$

Professor Schanze
Expert Witness



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101. Samsung posits that a person of ordinary skill in the art would have understood that $W_2(hpp)_4$ could coordinate with additional ligands, such as BPhen or TAZ. But while some tungsten complexes could coordinate additional ligands, (see EX2004-Cotton-textbook, p.187 (noting that ditungsten carboxylates $W_2(O_2CR)_4$ has the ability to form axial adducts), the crystal structure of $W_2(hpp)_4$ did not show coordination of any solvent complexed to the axial positions of the tungsten centers (*see* EX2008, 123).

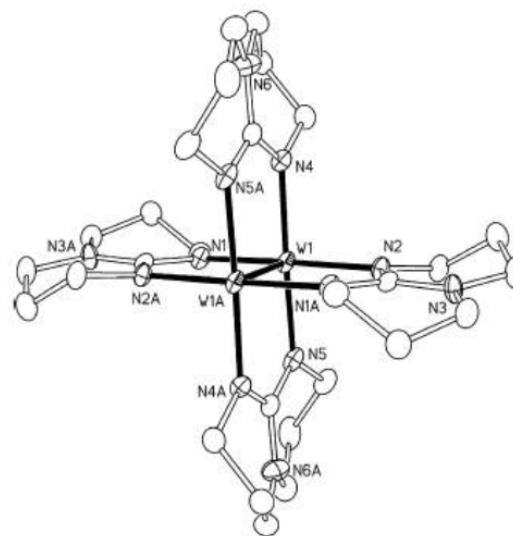
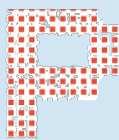


Fig. 1. An ellipsoid plot of $W_2(hpp)_4$, 1, with atoms drawn at the 30% probability level. All hydrogen atoms have been omitted for clarity.

EX2041, para. 101; POR 19-20

Undisputed: Prior Art Does Not Suggest Coordination to $W_2(hpp)_4$

Professor Schanze
Expert Witness



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102. And upon reacting with CH_2Cl_2 , $W_2(hpp)_4$ is oxidized to $W_2(hpp)_4Cl_2$. Even though an oxidized tungsten center should be less electron rich (because it has lost electrons) and therefore has more propensity to bind to ligands, the crystal structure still revealed a fairly long W-Cl bond, indicating that the chloride ions are fairly distant from the tungsten centers. EX2008 at 124. The “long W...Cl separations” “indicat[e] that there is no significant axial bonding.” *Id.*

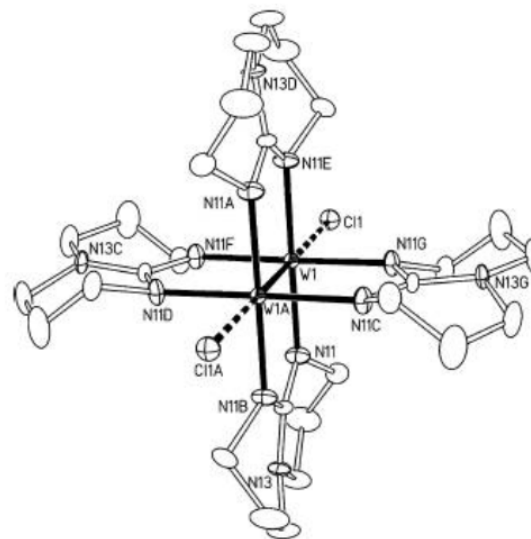
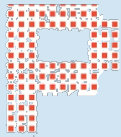


Fig. 2. Displacement ellipsoid plot of one orientation of the disordered $W_2(hpp)_4Cl_2$ molecule in $2 \cdot 4CH_2Cl_2$. Atoms are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

EX2041, para. 102; POR 20

Undisputed: Prior Art Does Not Suggest Coordination to W₂(hpp)₄

Professor Schanze
Expert Witness



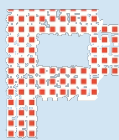
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103. A person of ordinary skill in the art would understand that there is effectively no coordination to the empty coordination site of the tungsten atom by the chloride ion. Hence, the crystal structures of W₂(hpp)₄ and W₂(hpp)₄Cl₂ do not suggest to a person of ordinary skill in the art that BPhen or TAZ would coordinate to the tungsten centers in the electron rich W₂(hpp)₄ or W₂(hpp)₄Cl₂. Instead, they would suggest no binding of these ligands to the tungsten center.

EX2041, para. 103; POR 21

Undisputed: Petitioner's Reliance on $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ Misplaced

Professor Schanze
Expert Witness



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108. Hence, given that $\text{W}_2(\text{hpp})_4$ is very electron rich compared to $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ or even $\text{W}_2(\text{O}_2\text{CCF}_3)_4$, a person of ordinary skill in the art would not expect $\text{W}_2(\text{hpp})_4$ to coordinate to aryl rings to accept electrons. That is because it is already electron rich and does not need to receive electrons from a weak-donor like aryl rings. Thus, a person of ordinary skill in the art would not expect the electron rich tungsten metal centers in $\text{W}_2(\text{hpp})_4$ to behave like the electrophilic $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ or to coordinate to pi-bonds to further increase its electron density.

109. Moreover, O_2CCF_3^- is a much smaller ligand than hpp, leaving the metal centers more exposed (less sterically encumbered) and allowing the aromatic ring to approach the metal center and coordinate to it via the π -bond. The electron rich $\text{W}_2(\text{hpp})_4$, on the other hand, has the four more bulky hpp ligands surrounding the metal center.

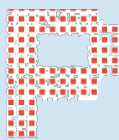
EX2041, para. 108-109; POR 21-22

DEMONSTRATIVE EXHIBIT – NOT EVIDENCE

Pictiva slide, p. 78

Petitioner's Own Depiction of Bonding Mode Demonstrates No Coordination

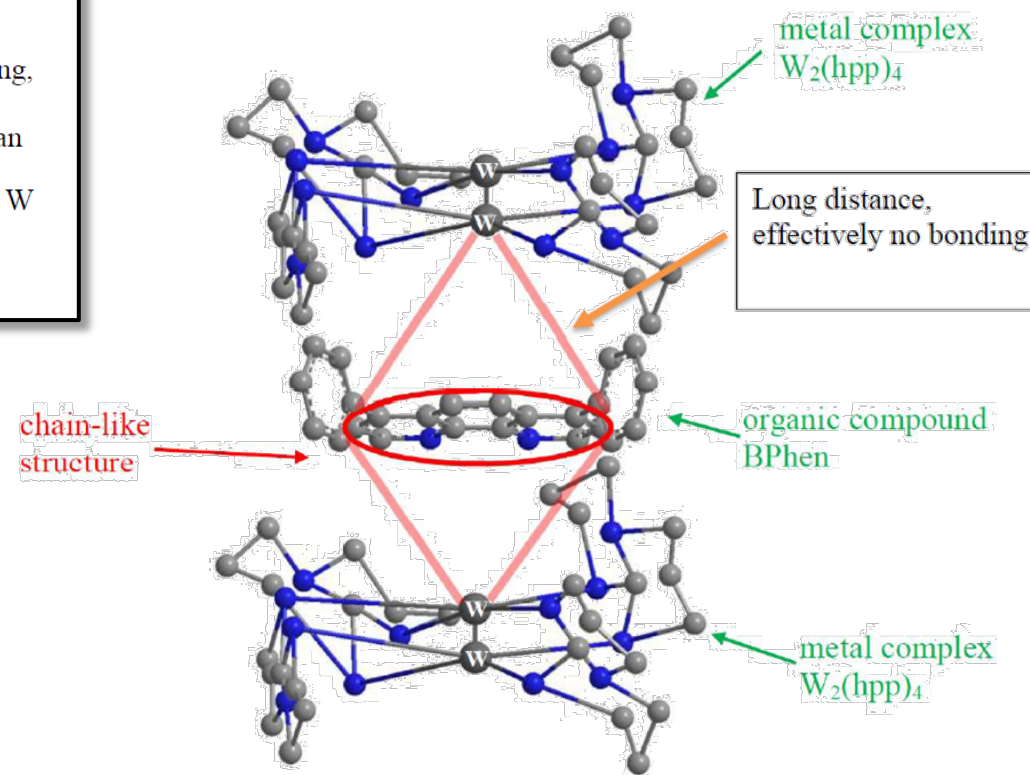
Professor Schanze
Expert Witness



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110. Thus, if Dr. Rand's depiction below was even a possibility, it would indicate to a person of ordinary skill in the art that the steric hindrance around the tungsten centers renders the coordination around tungsten unfavorable.

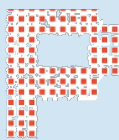
Specifically, the cyclohexyl rings of the hpp ligands would repel the phenyl ring, increasing the distance between tungsten and the phenyl ring. This would mean that there is effectively no coordination (electronic interaction) between the W metal center and the phenyl ring.



EX2041, para. 110; POR 22-23

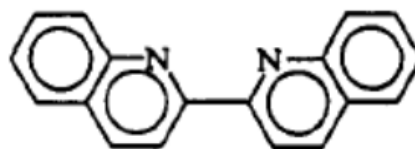
BPhen Cannot Coordinate to the Empty Axial Position of W2(hpp)4

Professor Schanze
Expert Witness

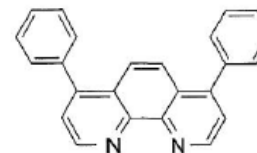


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125. Also notable is the authors' observation that no ligation occurred with bqn, a complex with more rigid ring system, to form a paddlewheel structure (the type of structure that Samsung suggests would form in the ditungsten complex). EX2017-1993Crawford, 3132-33. The authors surmised that there were steric repulsions between the fused rings of bqn and the existing ligands on the Rh centers that hinder bqn from approaching the axial position of the Rh centers. *Id.*



bqn

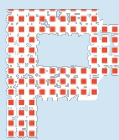


BPhen = bathophenanthroline
(4,7-Diphenyl-1,10-phenanthroline)
C₂₄H₁₆N₂

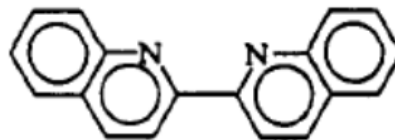
EX2041, para. 125; POR 23

BPhen Cannot Coordinate to the Empty Axial Position of $W_2(hpp)_4$

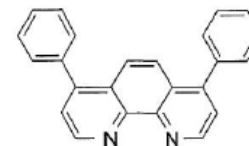
Professor Schanze
Expert Witness



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bqn



BPhen = bathophenanthroline
(4,7-Diphenyl-1,10-phenanthroline)
 $C_{24}H_{16}N_2$

126. bqn may be regarded as a good model compound to assess BPhen's ability to form paddlewheel complexes given the rigidity of its fused rings. The steric repulsions bqn experienced from the existing ligands of the Rh center provide a good indication of the steric repulsions that BPhen would experience when it approaches the W center in $W_2(hpp)_4$. That is, prior art would indicate to a person of ordinary skill in the art that a rigid compound like BPhen is unlikely to coordinate to a metal center with a paddlewheel structure.

EX2041, para. 125-126; POR 23

DEMONSTRATIVE EXHIBIT – NOT EVIDENCE

Pictiva slide, p. 81

Ma Is Not Prior Art

- Petitioner has not met its burden to establish that Ma was publicly available prior to December 2008—after the undisputed priority date.
 - Garland Declaration is insufficient and should be accorded no weight.
 - Belated Munford Declaration does not cure the deficiencies.
 - Dr. Rand's Declaration is irrelevant.

Ma Was Not Publicly Accessible Until Dec. 2008, After Priority Date

'223 Patent

 US008558223B2	
(12) United States Patent Schmid et al.	(10) Patent No.: US 8,558,223 B2 (45) Date of Patent: Oct. 15, 2013
(54) ORGANIC ELECTRONIC COMPONENT AND METHOD FOR THE PRODUCTION THEREOF	1101L 51/00 (2006.01) 1101L 51/40 (2006.01) (52) U.S. CL. 257/40; 257/E51.002; 438/99 USPC
(75) Inventors: Günter Schmid , Hemhofen (DE); Ralf Krause , Erlangen (DE); Andreas Kanitz , Höchststadt (DE); Jürgen Adler , Kleinsiebach (DE); Stefan Seidel , Nittendorf (DE); Arvid Hunze , Erlangen (DE)	(58) Field of Classification Search USPC 257/40; E51.002; 438/99 See application file for complete search history.
(73) Assignee: OSRAM Opto Semiconductors GmbH , Regensburg (DE)	(56) References Cited U.S. PATENT DOCUMENTS 4,398,803 A * 8/1983 Pohl et al. 349/181 4,771,111 A * 9/1988 Tiede et al. 525/182 5,432,014 A * 7/1995 Sano et al. 428/690 5,447,602 A * 9/1995 Herr et al. 252/582 (Continued)
(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.	FOREIGN PATENT DOCUMENTS CN 1261760 8/2000 CN 1700829 11/2005
(21) Appl. No.: 13/121,090	
(22) PCT Filed: Sep. 25, 2009	

(22) PCT Filed: **Sep. 25, 2009**

(65) **Prior Publication Data**
US 2011/0309340 A1 Dec. 22, 2011
(74) **Attorney, Agent, or Firm** — Cozen O'Connor
(30) **Foreign Application Priority Data**
Sep. 26, 2008 (DE) 10 2008 049 286
Nov. 7, 2008 (DE) 10 2008 056 391

(30) **Foreign Application Priority Data**
Sep. 26, 2008 (DE) 10 2008 049 286
Nov. 7, 2008 (DE) 10 2008 056 391

Web-of-Science Database Record for Ma

Organic light-emitting diodes based on new n-doped electron transport layer

By [Ma, JW \(Ma, J. W.\)](#) ^[1]; [Xu, W \(Xu, Wei\)](#) ^[1]; [Jiang, XY \(Jiang, X. Y.\)](#) ^[1]; [Zhang, ZL \(Zhang, Z. L.\)](#) ^[1], ^[2]

Are you this author?

Source

SYNTHETIC METALS

Volume: 158 Issue: 21-24 Page: 810-814

DOI: [10.1016/j.synthmet.2008.05.009](#)

Published DEC 2008

Indexed 2008-12-01

Published

DEC 2008

Indexed

2008-12-01

Keywords Plus: ELECTROLUMINESCENT DEVICES; HOLE-INJECTION; EFFICIENCY; VOLTAGE; PHTHALOCYANINE

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Categories/ Classification

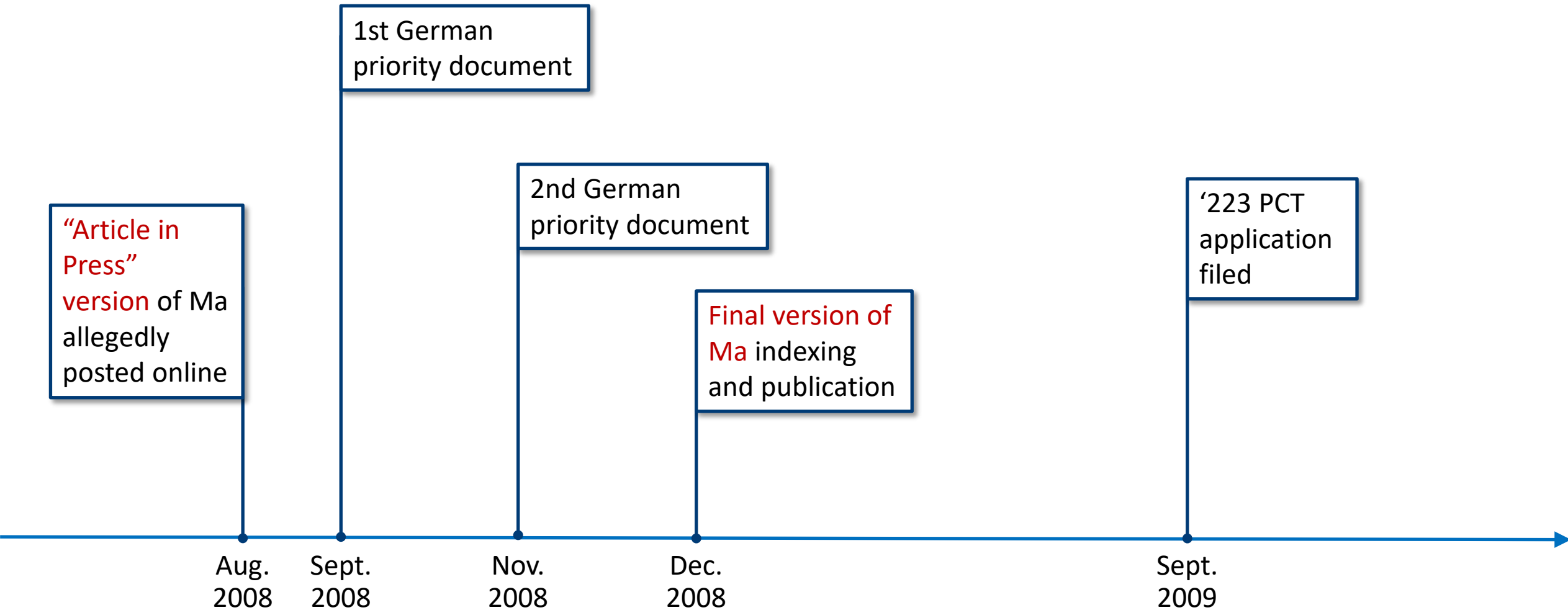
Research Areas: Materials Science; Physics; Polymer Science

Citation Topics: [2 Chemistry](#) > [2.114 Organic Semiconductors](#) > [2.114.321 OLEDs](#)

Sustainable Development Goals: [07 Affordable and Clean Energy](#)

Undisputed: claims supported by foreign priority applications

Relevant Time Line



Indexing by Subject Matter Is Critical

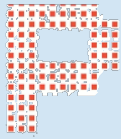


“Indexing only by title and author’s name did not amount to the references being either cataloged or indexed in a meaningful way. ***Indexing by subject offers meaningful assurance that an ordinarily skilled artisan, exercising reasonable diligence, will be able to locate a particular reference*** among the many volumes stored in a library. ... Indexing is no more or less important in evaluating the public accessibility of online references than for those fixed in more traditional, tangible media.”

Blue Calypso, LLC v. Groupon, Inc., 815 F.3d 1331, 1349 (Fed. Cir. 2016) (cleaned up)

Patent Owner Provided Evidence That Ma Was Not Indexed or Published Until December 2008

Professor Schanze
Expert Witness

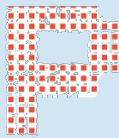


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116. Additionally, as I recall, in 2008-2009, Elsevier journals often did not promptly index new articles, especially online-only versions. Thus, it was my recollection that new articles often could not be located unless one knew the author's names or the title of the article. It is also my recollection that in 2008-2009, Elsevier's search tool⁵ had limited keyword search capability as it often failed to identify articles of interest. Additionally, during the relevant time period (2008-2009), indexing services, such as Clarivate Web of Science did not index online only articles, making them difficult or impossible to locate.

Patent Owner Provided Evidence That Ma Was Not Indexed or Published Until December 2008

Professor Schanze
Expert Witness



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150. For example, as shown by the screen shot below, the Ma article was not indexed by Web of Science until December 2008. I personally captured the screen shot from the Web of Science web site.

Organic light-emitting diodes based on new n-doped electron transport layer

By: Ma, JW (Ma, J. W.)^[1]; Xu, W (Xu, W.)^[2]

Source: SYNTHETIC METALS
Volume: 158 Issue: 21-24 Page: 2121-2124
DOI: 10.1016/j.synthmet.2008.05.009

Published	DEC 2008
Indexed	2008-12-01

Document Type: Article

Abstract: Organic light-emitting diodes with a new n-doped electron transport layer (ETL), a methyldiphenyl(phenylamino) triphenylamine (MDPPA) as the carrier transport layers with diode structure. Compared with the referenced device, the device with the new ETL device are enhanced by approximately 10% in the conductivity of the transport layer. The device with the new ETL device are enhanced by approximately 10% in the conductivity of the transport layer. The device with the new ETL device are enhanced by approximately 10% in the conductivity of the transport layer.

Keywords: Organic light-emitting diodes; n-doped electron transport layer; triphenylamine; methyldiphenyl(phenylamino) triphenylamine; diode structure.

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Categories/ Classification: Research Areas: Materials Science; Physics; Polymer Science
Citation Topics: 2 Chemistry > 2.114 Organic Semiconductors > 2.114.321 OLEDs
Sustainable Development Goals: 07 Affordable and Clean Energy

(EX204)

Published

DEC 2008

Indexed

2008-12-01

EX2041, para. 150; EX2024; POR 34

Ms. Garland's Ma-Specific Testimony Fails to Establish Ma's Public Accessibility

Ms. Garland
Unavailable Declarant

SAMSUNG

9. I obtained a copy of Exhibit A through ScienceDirect, where it is maintained in the ordinary course of Elsevier's business. Exhibit A is a true and correct copy of the Exhibit, as it existed on or about November 8, 2024.
10. The article and abstract from Science Direct shows the date of publication for the first online version. Science Direct populates this information using persistent publication metadata that is embedded in the articles metadata. Once this publication metadata has been first calculated it is not changed.
11. J. Ma, et. Al., "Organic light-emitting diodes based on new n-doped electron transport layer" was published in Synthetic Metals, Vol. 158, Issues 21-24 and was available online on August 29, 2008. The article is currently available for public download from the Elsevier digital library, Science Direct.

EX1018, paras. 9-11; POR 28-31

- **No Information Regarding the Version as Existed before Critical Date**
 - **Not averring that the "first online version" is identical to the final version**
- **No Information on Searchability of the "the first online version"**
- **No Information on When Abstracts Were Made Available or Searchable**
- **No Information on When the EX1007 version of Ma Was First Made Available for Public Download**

Petitioner Apparently Never Had Any Intent to Produce Ms. Garland for Deposition

Petitioner responds that Patent Owner's email is misleading and, in places, factually incorrect. Petitioner submitted a form declaration that the publisher Elsevier provides to explain the public availability of its publications. That declaration was signed by Dr. Garland of Elsevier, who resides in the United Kingdom. When Patent Owner requested to take a deposition of Dr. Garland, we inquired of Elsevier, but we understand that Dr. Garland is unwilling to testify. Petitioner does not think that cross-examination of Dr. Garland is necessary on this form declaration whose contents do not appear to be in any reasonable dispute, so Petitioner has not sought to compel her testimony. Without presenting argument, Petitioner respectfully directs the Board's attention to its decisions in *Mylan Pharms. Inc. v. Biogen MA Inc.*, IPR2018-01403, Paper 99 (Feb. 5, 2020); *Coastal Industries, Inc. v. Shower Enclosures Am., Inc.*, IPR2017-00573, Paper 27 (Feb. 20, 2018); and *Johns Manville Corp. v. Knauf Insulation, Inc.*, IPR2015-01453, Paper 16 (PTAB Mar. 14, 2016).

EX3102 at 2

No Weight Should Be Given to the Garland Testimony

Petitioner Could Have Submitted the Belated Munford Declaration Pre-Institution, at the Time of the Garland Declaration

Ms. Munford
Librarian

SAMSUNG

- Q. And in November of 2024 when you were first contacted, were you asked to draft a declaration in connection with this case?
- A. I don't recall if I was explicitly asked to write a declaration in November. We may have had some scheduling to figure out or some time to do some background research before we formalized the decision to make a declaration. ***But work included in this deposition was begun in November.***

...

- Q. And ***how much time did you spend preparing this declaration?***
- A. I'd estimate somewhere ***between six and seven hours.***
- Q. Is there a reason it took from November of 2024 to August of 2025 to prepare the declaration?
- A. ***I was following the schedule preferred by my clients. I don't recall any issues that would have delayed the creation of the declaration.***

EX2059, 6:17-25, 8:13-21; Sur-Reply 2

Petitioner Offers No Reason for Delaying the Declaration until Reply

Dr. Rand's Irrelevant Testimony Was Based on a *Post-Invention Article in a Different Journal*

Dr. Rand

SAMSUNG



- Rand has no personal knowledge of publication process for *Synthetic Metals*
- No evidence that his experience in publication with *Organic Electronics* can be extrapolated to *Synthetic Metals*

Sur-Reply 15-16

The 2009 article is in *Organic Electronics*, not *Synthetic Metals*

EX1020

DEMONSTRATIVE EXHIBIT – NOT EVIDENCE

Pictiva slide, p. 91

Dr. Rand Has No Relevant Experience in *Synthetic Metals* Publication Procedures

Rand Reply Declaration

39. I am familiar with the publication process of Elsevier journals because many of my research articles have been published in Elsevier journals over the course of my career, including in the 2008–2009 time period. For example, I am the first and corresponding author of an article titled “Organic solar cells with sensitized phosphorescent absorbing layers,” published in a journal called *Organic Electronics* published by Elsevier in 2009. Ex.1027. The cover of this article shows “Article history” under “Article Info,” as reproduced below.

EX1020, para. 39

Rand Testimony

- Q. Between 2008 and 2009, did you publish in "Synthetic Metals"?
- A. ***Between 2008 and 2009, I did not publish in the journal "Synthetic Metals" in that time period, no.***
- Q. Before 2009, did you ever publish in "Synthetic Metals"?
- A. ***Before 2009, I did not publish in "Synthetic Metals."***
- Q. Do you know the publication process for all Elsevier journals in the 2008 and 2009 time period?
- A. "Synthetic Metals" -- sorry. Elsevier is a large publishing house with many journals, so ***I can't assert that I understand the publishing process in all Elsevier journals either now or then.***

EX2056, 184:24-185:13; Sur-Reply 15-16

Ms. Munford's Belated Declaration Is Woefully Insufficient to Establish Public Accessibility of the Ma Article Prior to December 2008

Ms. Munford

SAMSUNG

- **No personal knowledge**, and provided **no direct evidence**.
- **Relied instead on:**
 - Unsubstantiated date on the face of the Ma article;
 - The deficient Garland Declaration;
 - Archived “Articles in Press” webpage from *December* 2008;
 - Notations on articles and webpages *after* the critical date;
 - A 2008 search page (but no search results, evidence of indexing, or evidence Internet-only article searchable); and
 - A Penn State University library page lacking any reference to Ma or the Synthetic Metals journal.

EX2059, 18:24-19:4, 20:11-22:24, 23:9-22, 28:5-31:17, 30:3-31:17, 35:1-21, 36:17-24, 47:19-48:2, 49:6-22, 49:24-50:10, 51:3-5, 60:14-61:22 61:23-62:1; Sur-Reply 16-19

Ms. Munford Provides No Evidence that Ma Was Listed as an “Article in Press” Before December 2, 2008 (After the Critical Date)

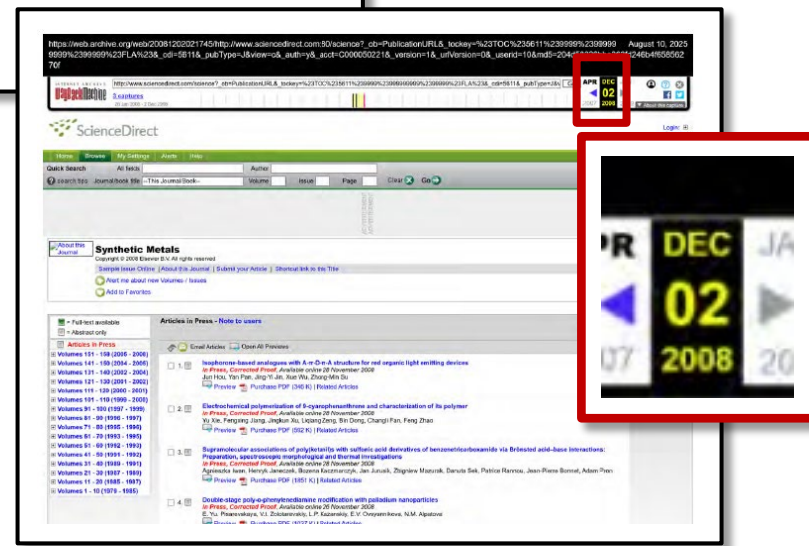
Ms. Munford

SAMSUNG

Before we move on, just to clarify, you don't have any evidence that the Ma article was in fact listed on this Articles In Press web page prior to December 2nd, 2008; correct?

MR. GARR: Objection.

THE WITNESS: Correct. The Articles In Press web capture I have is dated December, and I do not have any previous captures to rely on.



No Evidence of Relied-Upon Revision Notations Used Before November 2008

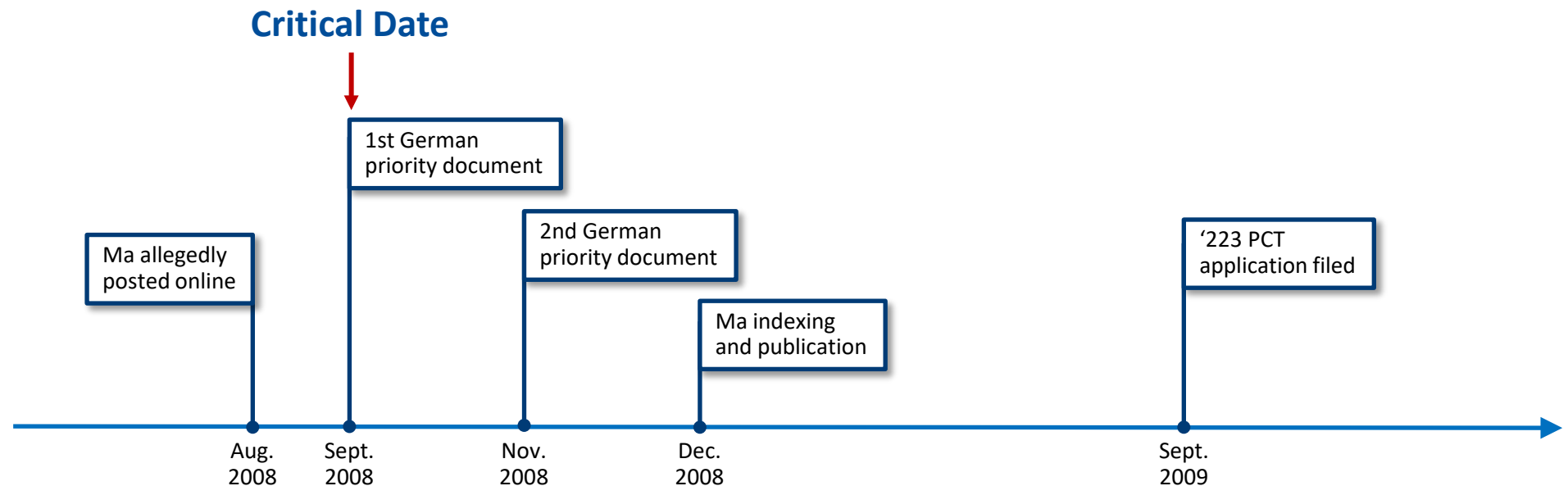
Ms. Munford

SAMSUNG

Q. Am I also correct that ***there is no evidence in your declaration that this revised form notation was used in Synthetic Metals' journal articles in August 2008?***

A. **Correct.** The only evidence provided is from **November 2008.**

EX2059, 23:9-14; Sur-Reply 17



DEMONSTRATIVE EXHIBIT – NOT EVIDENCE

No Evidence of Relied-Upon Corrected Proof Notation Used for Ma Before December 2008

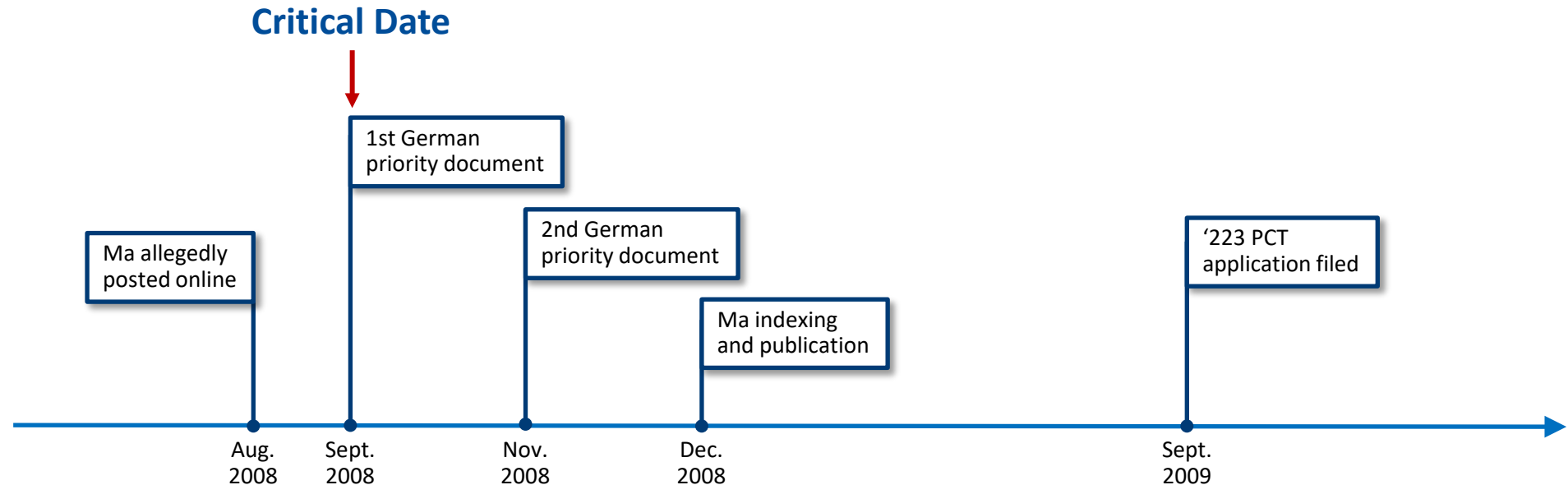
Ms. Munford

SAMSUNG

Q. Ms. Munford, do you have **any evidence** that this **In Press, Corrected Proof notation** was provided in connection with the Ma article **prior to December 2, 2008**?

A. **I do not.**

EX2059, 35:17-21; Sur-Reply 17



DEMONSTRATIVE EXHIBIT – NOT EVIDENCE

Ms. Munford Provides No Independent Evidence that Ma Was Available for Purchase Before December 2, 2008

Ms. Munford

SAMSUNG

Q. Again, I just want to be clear that you do not rely on any evidence, other than the date listed on the Ma article and the Garland declaration, that specifically purports to demonstrate that the Ma article was available to the public on August 29th of 2008?

A. I rely on the date on the paper itself. I rely on the Garland declaration. It feels relevant to note that Appendix 2 [captured on 12/2/2008] that we are reviewing right now also reflects that date.

But *I do not have any specific information on the Ma article's availability before this December capture*. Only discussions of the definition of Articles In Press and their availability via Elsevier.

EX2059, 31:4-17 (objections omitted); Sur-Reply 16

Ms. Munford Provides No Independent Evidence that the “Purchase PDF” Link Was Available Before December 2, 2008

Ms. Munford

SAMSUNG

- “The only indication that this Purchase PDF link would be available, prior to the date [12/2/2008] captured by the Internet Archive, would be in **the August 2008 date claimed by the paper itself** and by **the declaration from Elsevier.**”
- “**The only knowledge** I have related to the specific Purchase PDF link is related to **this December capture.**”
- “The only personal experience I would have would be reviewing and discussing the documents included within the declaration. I would not have personal experience for saying -- for example, accessing the Ma article at the time.”

EX2059, 27:11-20, 27:22-28:3, 30:3-12 (objections omitted); Sur-Reply 15-16

Ms. Munford Provides No Independent Evidence that the “Purchase PDF” Link Was Available Before December 2, 2008

Ms. Munford

SAMSUNG

- “The only indication that this Purchase PDF link would be available, prior to the date [12/2/2008] captured by the Internet Archive, would be in **the August 2008 date claimed by the paper itself** and by **the declaration from Elsevier.**”
- “**The only knowledge** I have related to the specific Purchase PDF link is related to **this December capture.**”
- “The only personal experience I would have would be reviewing and discussing the documents included within the declaration. I would not have personal experience for saying -- for example, accessing the Ma article at the time.”

EX2059, 27:11-20, 27:22-28:3, 30:3-12 (objections omitted); Sur-Reply 15-16

Ms. Munford Has No Personal Knowledge Regarding Purchasing Online-Only Elsevier Articles in Relevant Period

Ms. Munford

SAMSUNG

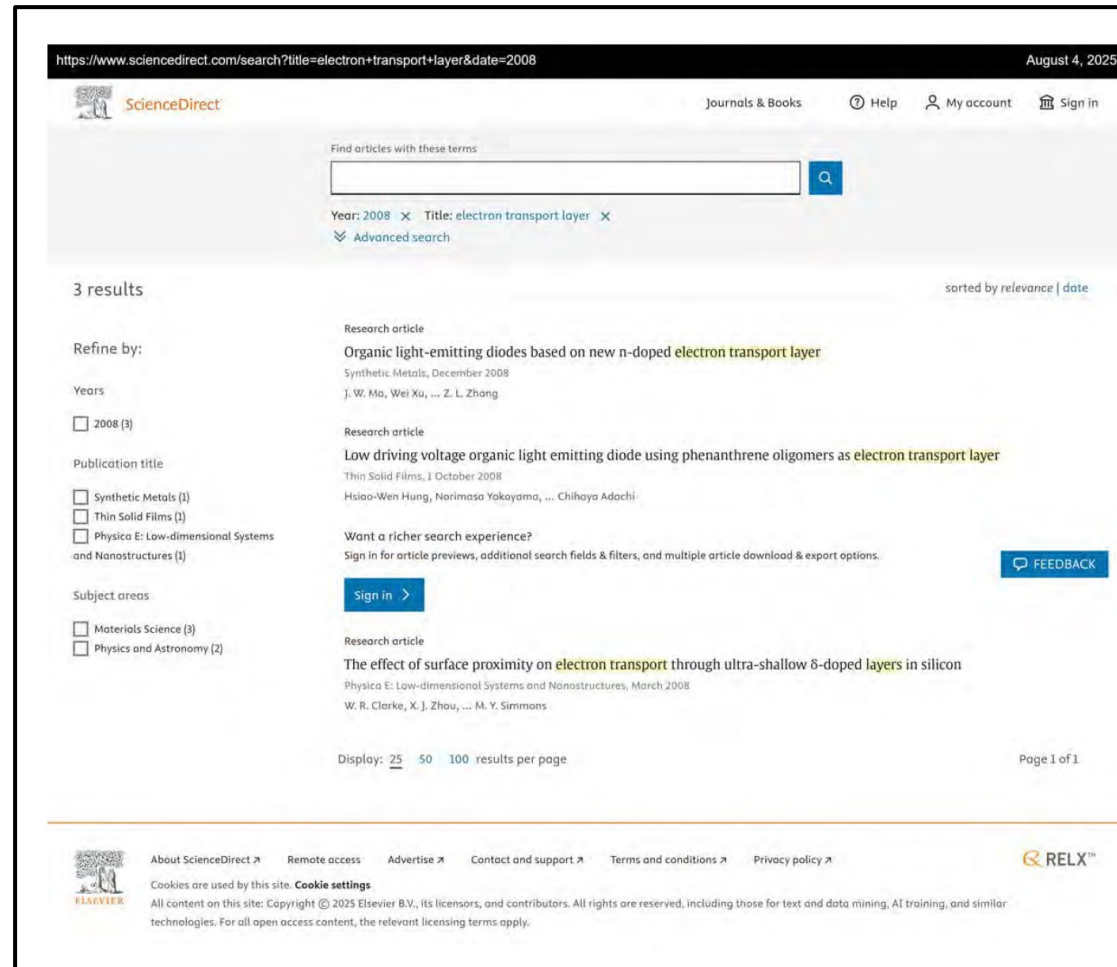
- Q. So you don't have any knowledge, for example, whether any member of the public could purchase a PDF of the Ma article using this link?
- A. **Using this link specifically, I do not have personal experience of that.**

EX2059, 33:15-19; Sur-Reply 16

Only Search Example Used 2025 Interface and Based on Title Search

Ms. Munford

SAMSUNG



EX1037, Appendix 11

No Knowledge of Title Unless Already Aware of the Article

Ms. Munford Provides No Competent Evidence of Search Capability in the Relevant Period

Ms. Munford

SAMSUNG

The screenshot shows the Elsevier Advanced Product Search interface. The URL bar indicates a Wayback Machine capture of the page from June 3, 2025. The page layout includes a left sidebar with navigation links, a main search area with various filters, and a right sidebar with a 'Search Through Articles' section. The search filters include 'Browse by subject' (Physical sciences, Health sciences, Social sciences, Life sciences), 'Browse by product type' (Books, Journals, Electronic products, Bibliographic databases, Newsletters and other product types, All product types), and 'Advanced product search'. The 'Advanced product search' section has fields for Keyword, Publication title, Author (books only) or editor, ISBN/ISSN, and Publication date (after and before). There are also checkboxes for 'Search publications within a subject area' and 'Search for the following publication type(s)'. The 'Search' button is visible at the bottom of the search area.

EX1037, Appendix 9

No Evidence that Ma Could Be Located Via Keyword or Even Title Search Before Critical Date

Ms. Munford Provides No Evidence Regarding When or Even If the Ma Article Was Indexed by Keywords

Ms. Munford

SAMSUNG

Q. And your declaration does not include any evidence that the Ma article was indexed by Elsevier according to keyword; correct?

A. Allow me to review real quick.

(Document reviewed by the witness.)

Declaration doesn't include information that the Ma article was indexed by keyword. Although, I believe the Synthetic Metals' journal was.

Q. Am I correct that your declaration doesn't include any specific evidence that the *Synthetic Metals' journal* was indexed according to keyword?

A. Allow me to review.

(Document reviewed by the witness.)

I don't believe that there is any evidence that this journal was indexed by Elsevier at the time.

EX2059, 49:6-22; Sur-Reply 17

Ms. Munford Provides No Evidence that “Articles in Press” Were Searchable in the Relevant Period

Ms. Munford

SAMSUNG

“I believe that the Articles In Press designation, included in the Articles In Press page, indicates that it was discoverable within the Elsevier database. *But I do not see any affirmative evidence that Articles In Press were included within those searches.* I also don't see any evidence that excludes Articles In Press.”

EX2059, 49:24-50:10 (objections omitted); Sur-Reply 17

The “Purchase PDF” Option Does Not Imply Searchability

Ms. Munford

SAMSUNG

- Q. And *you would have to agree with me that simply because a PDF of a journal article is available on a website, that does not indicate that searchable text of that same article is also available* on the website; correct?
- A. I would say that there is *no definitive correlation* between the two. You could have examples of material where full text be present and the PDF is not. *You could also have examples where the PDF is present and the full text is not.*

EX2059, 59:14-24 (objections omitted); Sur-Reply 17

Evidence Regarding Penn State University Is Irrelevant and Includes No Reference to the Ma Article or the Synthetic Metals Journal

Ms. Munford

SAMSUNG

Q. And if we look at that specific entry on Page 108 of Exhibit 1037, under Elsevier ScienceDirect, full text journal articles, the document states:

"The system provides access to the electronic versions of the Elsevier journals that we subscribe to"...

However, **there is no indication in Appendix 14 as to whether or not Penn State University subscribed to the Synthetic Metals' journal in particular**; correct?

A. **That's correct.**

Q. And your declaration includes ***no evidence that Penn State did in fact subscribe to the Synthetic Metals' journal***; correct?

A. ***That's correct.***

Q. The Elsevier ScienceDirect entry in Appendix 14 also states:

"Current issues and back files are included."

But ***it does not include any representation about Articles In Press***; correct?

A. **That's correct.**

EX2059, 61:2-22; Sur-Reply 17-18

Ms. Munford Provides No Evidence that Ma Was Accessed in August 2008

Ms. Munford

SAMSUNG

Q. Is it also correct that your declaration includes ***no evidence of any individual accessing the Ma article in August of 2008?***

A. ***That's Correct.***

EX2059, 61:23-62:1; Sur-Reply 16

Ms. Munford's Testimony Fails to Establish "Printed Publication" Status of Ma

Ms. Munford

SAMSUNG

- Allegedly had experience accessing articles through databases
- But presented no evidence that she ever accessed or could have accessed an Elsevier Article in Press before the critical date
- Presented no evidence of ever being able to search for and locate an Article in Press before the critical date
- Presented no affirmative evidence that Articles in Press were included in any of the databases that she worked with before the critical date
- Provided no affirmative evidence of when Ma was included in any of the databases

EX2059, 33:11-14, Sur-Reply 17

Ma Does Not Render Obvious the Challenged Claims

- Ma does not disclose joint vaporization
- No analysis of “central metal atom” under Samsung’s claim interpretation
- Ma does not disclose coordination of Bphen to Liq

Dr. Kymissis Does Not Consider Ma as Describing Joint Vaporization

Dr. Kymissis
Expert Witness
SAMSUNG

CONFIDENTIAL – ATTORNEYS’ EYES ONLY

UNITED STATES DISTRICT COURT
EASTERN DISTRICT OF TEXAS
MARSHALL DIVISION

Pictiva DISPLAYS INTERNATIONAL LTD., et al., Plaintiffs, vs. Samsung ELECTRONICS CO., LTD., Samsung ELECTRONICS AMERICA, INC., Defendants.	Civil Action Nos. 2:23-cv-40945-JRG 2:24-cv-40532-JRG
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EXPERT REPORT OF IOANNIS KYMISSIS, PH.D.,
REGARDING THE VALIDITY OF U.S. PATENT NOS.
8,558,223 AND 8,723,164

Pictiva EX2051
Samsung v Pictiva
IPR2024-01094

452. *Joint vaporization:* Ma recounts that BPhen and Liq were co-deposited using evaporation to form an ETL.³³⁴ Like all the other layers in Ma’s device, the ETL was “fabricated by conventional thermal evaporation in a high vacuum chamber with a base pressure of 1×10^{-5} Torr. The deposition rate was

453. Under Pictiva’s view that the accused products contain an electron-conducting layer that is obtained by “joint vaporization” (which I disagree with), then Ma discloses this limitation. I do not agree that this process constitutes “joint vaporization.” I intend to offer more detailed opinions on this topic in my rebuttal report.

EX2051, para. 452-453, POR 56

Dr. Kymissis Does Not Consider Ma as Describing Joint Vaporization

Dr. Kymissis
Expert Witness

SAMSUNG

Exhibit 19 synthetic Metals, "Organic
light-emitting diodes based on
new n-doped electron transport
layer," J.W. Ma, Wei Xu,
X.Y. Jiang, Z.L. Zhang, five
pages

Q. ***Does Exhibit 19 disclose joint vaporization?***

A. So I'm not sure. And there is some discussion of the deposition, but it is not -- you know, it is a relatively short paper; so ***I can't say whether or not it represents joint vaporization.***

EX2106, 154:3-7; Sur-Reply 20

Dr. Kymissis Does Not Consider Ma as Describing Joint Vaporization

Dr. Kymissis
Expert Witness

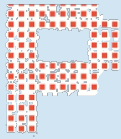
SAMSUNG

- Q. Does codeposition necessarily result in joint vaporization or does joint vaporization – *does this codeposition necessarily mean there was joint vaporization?*
- A. So, again, *not necessarily*. The -- *the question of joint vaporization depends on a number of factors*, including the presence of the materials together; also, their opportunity to interact; some energetic and kinetic factors. And so, again, *we need to know more details in order to reach any conclusion about joint vaporization in the system.*

EX2106, 154:8-20 (objections omitted); Sur-Reply 20

Dr. Schanze Agrees that Ma Does Not Provide Sufficient Detail to Determine Whether Joint Vaporization Occured

Professor Schanze
Expert Witness



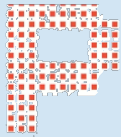
pictiva displays

154. In other words, he believes that Ma's ETL was formed by joint vaporization of Liq and BPhen because Ma discloses that BPhen:Liq was "co-deposited." *Id.* I disagree because Ma provides no information on its evaporator configuration, the position of the sources, or the degree of intersection, if any, of the plumes from the Liq-source and the BPhen-source.

EX2041, para. 154; POR 54-55

Dr. Schanze Agrees with Dr. Kymissis that Ma Does Not Provide Sufficient Details to Determine Whether Joint Vaporization Occured

Professor Schanze
Expert Witness



pictiva displays

Q. So let me ask you, what is a common and ordinary meaning of joint vaporization to Dr. Kymissis?

A. So the witness' response is:

"So again, in my -- I -- in my report, I describe if you go to paragraph 52 in my non-infringement report, I provide that, you know, at least a POSITA would understand that joint vaporization required that the metal compound and the organic compound could be co-evaporated so they are present together in the vapor phase. And so, again, it also depends on the pressure, because that determines how much interaction the two materials will have in the vapor phase. If the pressure is very low, then the mean free path is long. If the pressure is high, they have more opportunity to interact. But it also depends on the structure of the evaporation sources and whether the plumes are allowed to interact in a way that permits the reaction to occur in the vapor phase. So it is not a simple understanding but that is generally what a person of ordinary skill in the art would recognize as joint vaporization."

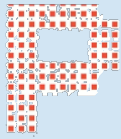
...

Q. *Does the Ma reference provide the details mentioned by Dr. Kymissis, that is needed to determine whether there is joint vaporization or not?*

A. *To my understanding, no, Ma does not provide sufficient information to define joint vaporization, as it's been described by Kymissis in his deposition.*

Dr. Schanze Agrees with Dr. Kymissis's Interpretation of Co-Deposition

Professor Schanze
Expert Witness



pictiva displays

Q. [EX2106] Eighty-one, line 22, through 82, lines three.

A. Okay.

A. So the transcript reads:

"If you evaporate something at the same time, is that -- will that result in joint vaporization."

And answer:

"Not necessarily."

And then follow-up answer:

"It really depends on the details of the deposition, the pressure, the reactivity of the two materials, the degree of intermixing."

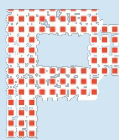
Q. ***Is that consistent with your understanding of whether co-deposition necessarily results in joint vaporization?***

A. ***Yes.***

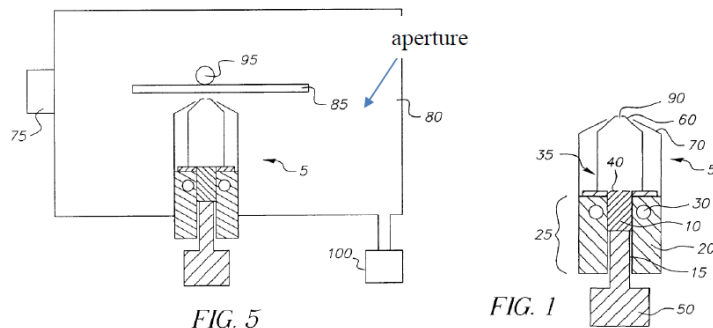
EX1021, 171:22-172:18 (objections omitted); Sur-Reply 19

Dr. Schanze Agrees that Co-Deposition Does Not Necessarily Mean Joint Vaporization

Professor Schanze
Expert Witness



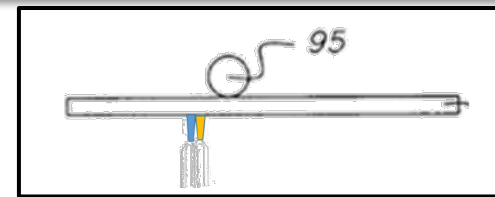
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156. In the above figure, 80 is the deposition chamber connected to a vacuum source 100 to keep the pressure at 1 torr or less. *Id.*, 8:1-3. Element 75 is a load lock “which can be used to load uncoated OLED substrate 85,” and unload coated OLED substrates. *Id.*, 8:3-5. “OLED substrate 85 can be moved by translational apparatus 95 to provide even coating of vaporized organic material 10 over the entire surface of OLED substrate 85.” *Id.*, 8:5-8. The vaporization apparatus 5 has one or more apertures 90 at the top. *Id.*, Fig. 1, 3:54-55. The plume from the vaporization apparatus 5 can deposit the organic material in a line-of-sight fashion. Thus, if the chamber includes a second apparatus 5 for a second material, the two materials can be heated simultaneously but at a given time, each source deposits the respective material at a different portion of the substrate and both materials are deposited at the same location on the substrate in a “sequential”

fashion as the substrate is moved back and forth between the sources (or as the substrate is rotated to ensure uniform coating).

157. Such a “sequential” deposition may be a form of co-deposition because different materials are deposited on the same substrate at the same time (albeit at different spots at a given time) and the end result is a mixed film with both materials in a macroscopically homogenous form,¹¹ but that is not the “joint vaporization” contemplated by the ’223 patent, which would involve depositing two materials to a same location on the substrate at the same time (*e.g.*, the two plumes intersect and intermix before hitting the same areas of the substrate). *E.g.*, ’223, 1:60-63 (“By virtue of the joint vaporization of the metal complex with an organic compound, these two compounds interact with one another in the gas phase or when they meet one another on the substrate surface.”).



¹¹ Dr. Kymissis refers to a process in which a host material and a dopant are co-evaporated from different sources in a same chamber as “sequential co-evaporation.” EX2052 [Kymissis Rebuttal], ¶243. This shows that “co-evaporation” or “co-deposition” does not necessarily mean joint vaporization.

Dr. Schanze's German Declaration Relates to Claims Excluding BPhen

Professor Schanze
Expert Witness



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- 21 The now-applicable main request specifies an additional important aspect for achieving good electronic properties – namely, the selection of a particularly advantageous organic compound for that purpose. Claim 1 of the main request can be structured as follows, with the features marked in green (cc) to ff)) being additions to granted claim 1:

1	Organic electronic component comprising
a)	a substrate,
b)	a first electrode,
c)	a second electrode,
d)	an electron-conducting layer,
aa)	which is arranged such that it is electrically conductively connected to at least one of the electrodes,
bb)	which is obtained by co-evaporation of a metal complex that includes a metal central atom, and an organic compound, whereby
(1)	through the co-evaporation the organic compound is coordinated to the metal complex.
cc)	wherein the organic compound comprises a system of aromatics and heteroaromatics that are each connected to one another by a carbon-carbon single bond,
dd)	wherein the system comprises more than one heteroaromatic,
ee))	wherein the organic compound comprises only heteroaromatics whose rings are formed of six atoms and contain nitrogen as the heteroatom, and
ff)	wherein the system comprises 5 to 8 aromatics and heteroaromatics, wherein the aromatics and heteroaromatics may each independently be substituted with methyl, phenyl, 2-pyridyl, 3-pyridyl, or 4-pyridyl.

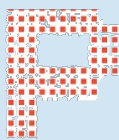
EX1032, para. 21; Sur-Reply 21

DEMONSTRATIVE EXHIBIT – NOT EVIDENCE

Pictiva slide, p. 117

Dr. Schanze's German Declaration Relates to Claims Excluding BPhen

Professor Schanze
Expert Witness



pictiva displays

26 If a carbon–carbon single bond connects two (hetero)aromatics, the two connected (hetero)aromatics are not fused (cf. para. [0020] of the patent-in-suit). This means that the two (hetero)aromatics are not fused into a single larger (hetero)aromatic but remain largely separate and are connected only via a carbon–carbon single bond. For better understanding, this is illustrated using the unclaimed compound BPhen, which is disclosed in most prior art documents in the nullity action. BPhen consists of a heteroaromatic that is connected via carbon–carbon single bonds to two further aromatics. The heteroaromatic consists of three aromatic six-membered rings that are fused together. The heteroaromatic contains two heteroatoms, specifically two nitrogens (element symbol N):

EX1032, para. 26; Sur-Reply 21

Ma's Deposition Rate Does Not Inform Whether Joint Vaporization Occurred

Rand Reply Declaration

45. Ma further discloses that that “[t]he deposition rate was *maintained* at 0.5 ± 0.2 Å/s for the organic materials” and that it used “two independent quartz sensors” to monitor the “deposition *rates* for the co-deposition layer.” Ex.1007, 811 (emphasis added). As I testified, this means, the rates of neither vapor streams dropped to zero, and thus were not, for example, sequentially deposited (i.e., not vaporized together). Ex.2042, 81:11–82:7 (“A. During the time of the deposit of the film formation that the rates . . . not going to zero.”). Thus, in my opinion, a POSA would understand Ma’s disclosure of a “BPhen:LiQ ETL [that] was *co-deposited*” to teach (or at a minimum strongly suggest) that the ETL was *obtained by joint vaporization* of Liq and BPhen.

EX1020, para.45

Rand Testimony

Q. In Ma, ***the stated 0.5 plus/minus 0.2 angstroms per second, that's the total deposition rate for all the organic materials?***

A. **Right.**

Q. And it's ***not the deposition rate for each of the organic materials?***

A. **That's right.**

EX2056, 181:4-10; Sur-Reply 21-22

Can't Tell from Total Deposition Rate the Deposition Rate for Each Component

Ma's Deposition Rate Does Not Inform Whether Joint Vaporization Occurred

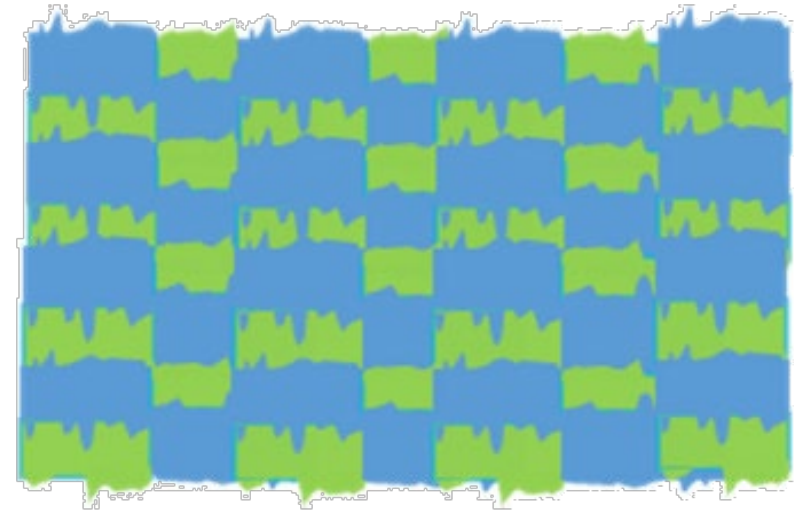
Rand Reply Declaration

44. In my opinion, Dr. Schanze's arguments in relation to a hypothetical deposition chamber for a "macroscopically homogenous" but potentially microscopically heterogeneous film is completely irrelevant to Ma. Ex.2041, ¶¶155–157. The purpose of Ma was to assess the current density using different percentages of Liq doping. The authors would have no reason to prepare a film that is only "macroscopically homogenous" but microscopically heterogeneous across the different locations of a test substrate because it would introduce excessive variability and render the data noncomparable and unreliable.

EX1020, para.44



Ma's Potential Structure



"[E]ach source deposits the respective material at a different portion of the substrate and both materials are deposited at the same location on the substrate in a "sequential" fashion as the substrate is moved back and forth between the sources (or as the substrate is rotated to ensure uniform coating)."

EX2041, para. 156; POR 54-55, Sur-Reply 22

Structure Described by Dr. Schanze Differs from Examples Provided by Rand

The Petition Does Not Seek to Modify Ma’s Process to Achieve Joint Vaporization

Petition

Third, Ma discloses that *the electron-conducting layer is obtained by joint vaporization of a metal complex with an organic compound* because the electron transport layer (ETL) was formed by joint vaporization of a metal complex (Liq) and an organic compound (BPhen). Ex.1003, ¶141; Ma, 811 (“a 50 nm-thick *BPhen:Liq ETL* was co-deposited on the EML. In the co-deposition process, organic sources were independently controlled. ... *All the layers (organic layers, and Al electrode) of the devices were fabricated by conventional thermal evaporation* in a high vacuum chamber with a base pressure of 1×10^{-5} Torr.”) (emphasis added).

Pet. 59

POR Notes the Theory in Petition

Although Petitioner characterizes Ground 2 as an obviousness ground, it does not assert that any limitation is missing for claim 1. Pet. 54-60. Instead, it proceeds under the obviousness ground only because it disagrees with Pictiva’s claim interpretation regarding the term “metal complex” and “central metal atom.” Pet. 58-59. But Petitioner does not set forth any modification. *Id.* Hence, the Petition effectively only presents an anticipation theory. To prevail under anticipation, Petitioner must show that Ma expressly or inherently discloses all elements arranged as in the claim. *Net MoneyIn, Inc. v. VeriSign, Inc.*, 545 F.3d 1359, 1369 (Fed. Cir. 2008). But even under obviousness, for a limitation that is not expressly disclosed, Petitioner must show that the missing element was the “natural result” of the combination of prior art elements. *PAR Pharm.*, 773 F.3d at 1195.

Here, Petitioner argues that Ma discloses joint vaporization of Liq and BPhen because Ma discloses that “BPhen:Liq ETL was co-deposited on the EML.” Pet. 59. There is no analysis, however, that Ma’s co-deposition process is one of joint vaporization of Liq and BPhen. *Id.*

Reply Improperly Injects New Theories

Petition

Third, Ma discloses that *the electron-conducting layer is obtained by joint vaporization of a metal complex with an organic compound* because the electron transport layer (ETL) was formed by joint vaporization of a metal complex (Liq) and an organic compound (BPhen). Ex.1003, ¶141; Ma, 811 (“a 50 nm-thick *BPhen:Liq ETL* was co-deposited on the EML. In the co-deposition process, organic sources were independently controlled. ... *All the layers (organic layers, and Al electrode) of the devices were fabricated by conventional thermal evaporation* in a high vacuum chamber with a base pressure of 1×10^{-5} Torr.”) (emphasis added).

Pet. 59

Reply

Under a preponderance standard, Ma’s disclosures are sufficient to render joint vaporization at least obvious. This is the most natural interpretation of “co-deposition” for forming a layer, particularly when there is nothing to indicate that materials were vaporized sequentially. Ex.1020, ¶¶46-51. Additionally, a POSA would recognize that vaporizing materials together would best achieve Ma’s objective of assessing the current density using different Liq doping percentages. Ex.1020, ¶51; Ma, 811.

Reply 22; Sur-Reply 1

Improper New Theory

Ma Does Not Render Obvious the Challenged Claims

- Ma does not disclose joint vaporization
- No analysis of “central metal atom” under Samsung’s claim interpretation
- Ma does not disclose coordination of Bphen to Liq

Samsung Takes Inconsistent Claim Construction Positions

Dr. Kymissis
Expert Witness

SAMSUNG

UNITED STATES DISTRICT COURT
EASTERN DISTRICT OF TEXAS
MARSHALL DIVISION

PICTIVA DISPLAYS INTERNATIONAL
LTD., *et al.*,

Plaintiffs,

vs.

SAMSUNG ELECTRONICS CO., LTD.,
SAMSUNG ELECTRONICS AMERICA,
INC.,

Defendants.

Civil Action No.
2:23-cv-00945-BEG
2:23-cv-00945-BEG

EXPERT REPORT OF IOANNIS KYMISSIS, Ph.D.,
REGARDING THE NON-INFRINGEMENT OF
U.S. PATENT NOS. 8,588,223 AND 8,723,164

Pictiva EX2052
Samsung v Pictiva
IPR2024-01094

2. Lithium Is Not Centrally Located in Liq

100. The lithium atom in Liq is not located at the center of the molecule, but rather on an arm on the side:⁷⁷

EX2052, 49; POR 56-58

Samsung Takes Inconsistent Claim Construction Positions

Dr. Kymissis
Expert Witness

SAMSUNG

UNITED STATES DISTRICT COURT
EASTERN DISTRICT OF TEXAS
MARSHALL DIVISION

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Pictiva EX2052
Samsung v Pictiva
IPR2024-01094

3. Lithium Does Not Enable Liq to Coordinate with Additional Ligands

106. The '223 patent specification describes the role of the central metal atom in providing “free coordination sites” for the metal complex: “During or after coordination of the organic compound, preferably none of the previously present ligands of the metal complex is separated, thus, no ligand exchange takes place. So, the metal complex is able to accept further additional ligands and thus *comprises at the central atom free coordination sites which can be occupied by further ligands.*”⁷⁹

107. However, directly to the contrary, the lithium atom in Liq does not perform this critical role for the “central metal atom,” which would indicate to a POSITA that it is not a “central metal atom” as described and claimed in the '223 patent.

EX2052, 52; POR 56-58

DEMONSTRATIVE EXHIBIT – NOT EVIDENCE

Pictiva slide, p. 125

Samsung Takes Inconsistent Claim Construction Positions

Dr. Kymissis
Expert Witness

SAMSUNG

UNITED STATES DISTRICT COURT
EASTERN DISTRICT OF TEXAS
MARSHALL DIVISION

PICTIVA DISPLAYS INTERNATIONAL
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EXPERT REPORT OF IOANNIS KYMISSIS, Ph.D.,
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U.S. PATENT NOS. 8,558,223 AND 8,723,164

Pictiva EX2052
Samsung v Pictiva
IPR2024-01094

4. Lithium Does Not Enable Liq to Have a High Disposition and Ability to Provide “Free” Electrons

113. The '223 patent specification directly links the claimed central metal atom to the ability of its containing metal complex to have a “high disposition and ability to provide ‘free’ electrons” for use in coordinate bonds;⁸¹

In this case, W is a preferred central metal atom. It is particularly preferred if all of the central atoms in the metal complex are W. The elements Cr, Mo and W prove to be particularly advantageous for two reasons. On the one hand, they have the ability to coordinate with additional ligands and on the other hand, with a suitable selection of the ligands, their metal complexes have a very low ionization enthalpy. *This means that these metal complexes have a high disposition and ability to provide “free” electrons.* These electrons can be transferred for example to the additionally bonded ligands.

114. However, directly to the contrary, the lithium atom in Liq does not perform this critical role for the “central metal atom,” which would indicate to a POSITA that it is not a “central metal atom” as described and claimed in the '223 patent.

EX2052, 55; POR 56-58

DEMONSTRATIVE EXHIBIT – NOT EVIDENCE

Pictiva slide, p. 126

Petitioner Is Required to Show that Different Positions Are Warranted

[[VIEW_THIS]]

Patent Trial and Appeal Board



PTAB designates as informative a decision addressing a petitioner's different claim construction positions in district court and at the PTAB

Cambridge Mobile Telematics, Inc. v. Sfara, Inc., IPR2024-00952, Paper 12 (PTAB Dec. 13, 2024) – informative as to majority opinion

In this decision denying institution, the Board addresses circumstances in which a petitioner argues in district court that a claim limitation should be construed as means-plus-function and argues in a petition for inter partes review that the PTAB should construe the same limitation using the plain and ordinary meaning. The majority opinion determines that the petition should, at a minimum, explain why the different positions are warranted or, alternatively, set forth a means-plus-function construction for the limitation.

[Learn more](#) about this precedential and informative decision.

Cambridge Mobile cited on POR 57

Petitioner's Approach Risks Inconsistent Outcomes

Ma Does Not Render Obvious the Challenged Claims

- Ma does not disclose joint vaporization
- No analysis of “central metal atom” under Samsung’s claim interpretation
- Ma does not disclose coordination of Bphen to Liq

“metal complex” (’223 Patent, Claim 1, 2, 10, 11, 13, 14)	“a compound containing one or more metal elements that coordinate to one or more non-metal elements, fragments or ions, excluding metal oxides”
“wherein the organic compound coordinates to the metal complex due to the joint vaporization” (’223 Patent, Claim 2)	Plain and ordinary meaning
“coordinate[s]” (’223 Patent, Claim 2, 11, 14)	“form[s] a chemical bond between two atoms in which a shared pair has been supplied by one of the two atoms”
“chain-like structure” (’223 Patent, Claim 12)	“a structure in which at least parts of organic compounds bridge exactly two metal complexes together”
“network-like structure” (’223 Patent, Claim 12)	“a structure in which at least parts of organic compounds bridge more than two metal complexes together”
“degree of cross-linking of the electron-conducting layer” (’223 Patent, Claim 13)	“degree of linking between the metal complex and the organic compound in the electron-conducting layer”

MS. BAILY: And so the Plaintiffs' construction, which expands the meaning of 'coordinates' to any kind of bonding interaction is too broad. The claims do not use the word 'bonding'; they use the term 'coordinates' which specifies a particular kind of interaction, a particular kind of bonding.

Now, I know that this is extrinsic evidence, but I do

want to say that in chemistry there is a specific meaning to a coordinate bond that is well-understood, and so that is why we have cited to Your Honor many dictionary definitions that confirm that a coordinate bond is a specific kind of bond, number one; and it's one in which one atom provides both shared electrons. And so countless dictionaries include that definition because that is the plain and ordinary meaning of 'coordinate' or 'coordinate bond' in chemistry.

The dictionaries also indicate that a dative bond is a synonym. That's why we reverted to using those words. But perhaps, you know, the additional clarity for the jury where we're talking about the definition of a dative bond or a coordinate bond, which is where both electrons are shared from one atom to another, perhaps that would be helpful.

Samsung Takes Inconsistent Positions in IPR and District Court Proceeding

Dr. Rand
Expert Witness
SAMSUNG

Q. And *you did not determine whether the coordination involved lithium nitrogen bonding; correct?*

A. *Correct*. We've already established this previously.

EX2042, 93:2-6, POR 5, 62

- No Evidence of “Coordinate” under Any Reasonable Claim Construction
- No Evidence of “Coordinate” under Samsung’s Proposed Construction Adopted by the District Court

Samsung Takes Inconsistent Positions in IPR and District Court Proceeding

Dr. Rand
Expert Witness

SAMSUNG

Q. And you don't know whether the coordination involved the lithium Pi bonding; correct? Or whether the Pi bonding is through the two ligands, through the ligands?

A. **I didn't limit myself to the requirement of a specific type of coordination between types of bonds or types of atoms.**

EX2042, 93:7-13

- **No Evidence of “Coordinate” under Either Party’s Claim Construction**

Dr. Rand Cannot Say Bonding Interactions Occurred at Li Atom Center

Dr. Rand
Expert Witness

SAMSUNG

Q. Do you [know] whether Pi complexes are formed at the center of the lithium atom?

A. I don't know that specifically.

EX2042, 94:10-12, POR 5, 62

- **No Evidence of “Coordinate” under Either Party’s Claim Construction**

Dr. Rand Cannot Determine the Type of Interactions

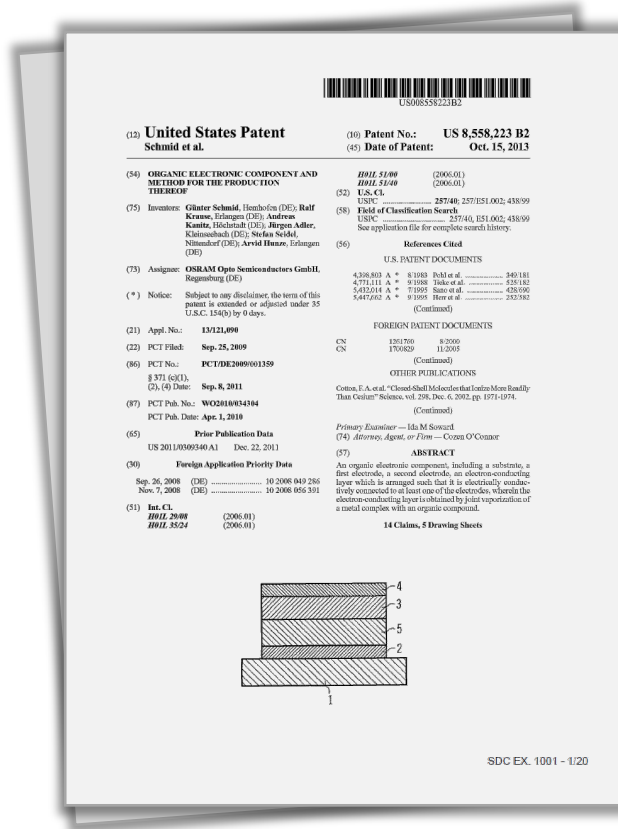
Dr. Rand
Expert Witness
SAMSUNG

- Q. Would there be chemical bonds formed between nitrogen and lithium necessarily?
- A. Again it's hard to specify the exact atoms within the compounds because these do contain delocalized orbitals, and **I'm only offering that the orbitals will interact. Specific atoms is hard to provide an opinion.**
- Q. And when you say the atoms, the atoms can be the ligand and the organic compound; correct?
- A. When I say atoms, I mean any of the atoms in either of the compounds. But ***I'm not comfortable being specific about the exact nature of the interaction in, between those two compounds.***

EX2042, 211:22-212:14, POR 5, 62

- **No Evidence of “Coordinate” under Either Party’s Claim Construction**

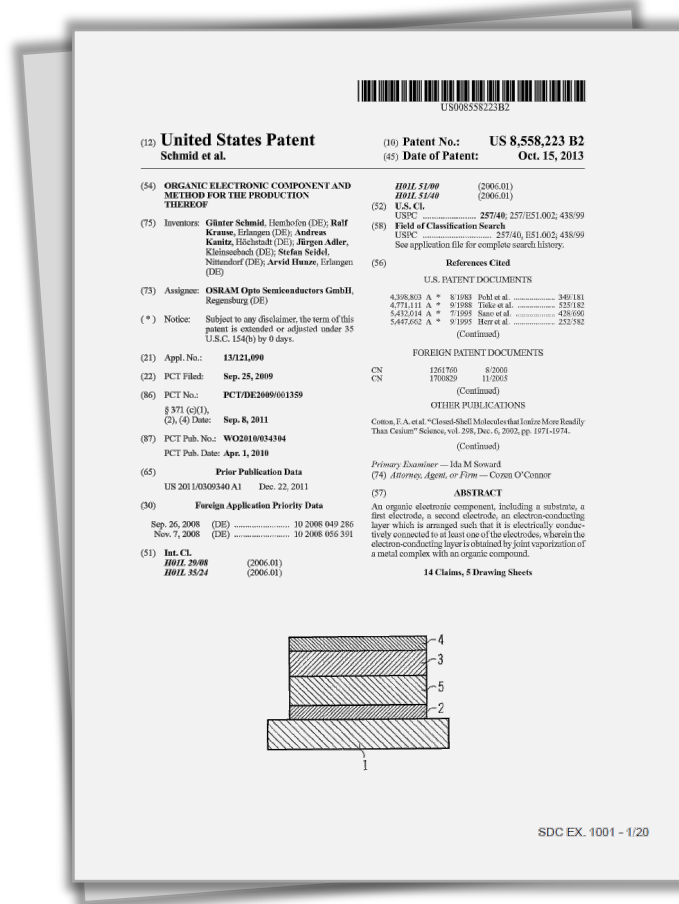
Coordination Does Not Necessarily Occur in All Systems



The coordination of the organic compound to the central atom **can be effected** directly via a further atom or else also via an aromatic system. During or after coordination of the organic compound, preferably none of the previously present ligands of the metal complex is separated, thus, no ligand exchange takes place. So, the metal complex is able to accept further additional ligands and thus comprises at the central atom free coordination sites which can be occupied by further ligands.

“Can” Coordinate ≠ “Coordinates”

Coordination Does Not Necessarily Occur in All Systems



The compounds illustrated in the structures I to XIII are particularly well suited as an organic compound for the electron-conducting layer. Each of these compounds comprises both an aromatic compound and also a nitrogen heterocycle. Each of these compounds thus comprises several coordination sites for metal complexes. These compounds I to XIII **allow not only for** the formation of two-dimensional chains, but, by virtue of their multiplicity of coordination sites, they also allow for the formation of three-dimensional networks. In this case, an organic compound coordinates to more than two metal complexes. Furthermore, these compounds have large delocalized electron systems, such as for example condensed aromatic compounds or aromatic compounds which are in electronic conjugation with each other. These delocalized electron systems enable the compounds to accept and transport further negative charges very effectively since this additional charge can be easily distributed onto several atoms in the molecule. Therefore, a coordinated metal complex can effectively transfer a negative charge to the organic compound coordinated thereto. Furthermore, electrons of the organic compounds I to XIII can also be transferred effectively amongst the organic compounds themselves. This is also crucial for good electron conductivity in the electron-conducting layer.

“allow... for”
coordination does
not mean
coordination occurs

Processing Conditions Affects Coordination

Barry Rand
Expert Witness

SAMSUNG

Q. Will the type of interactions, if any, depend, depend on the processing conditions?

A. Absolutely.

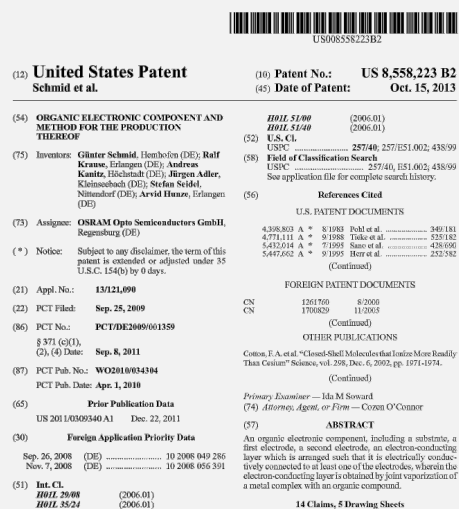
Q. So there may be no interaction and [sic, under] some process conditions and there may be not [sic, lots of] interactions in some other, under some other process conditions; right?

A. Yes.

EX2042, 199:20-200:6; POR 60

'223 Contemplates Non-Coordination Interactions

The compounds illustrated in the structures I to XIII are particularly well suited as an organic compound for the electron-conducting layer. Each of these compounds comprises both an aromatic compound and also a nitrogen heterocycle. Each of these compounds thus comprises several coordination sites for metal complexes. These compounds I to XIII allow not only for the formation of two-dimensional chains, but, by virtue of their multiplicity of coordination sites, they also allow for the formation of three-dimensional networks. In this case, an organic compound coordinates to more than two metal complexes. Furthermore, these compounds have large delocalized electron systems, such as for example condensed aromatic compounds or aromatic compounds which are in electronic conjugation with each other. These delocalized electron systems enable the compounds to accept and transport further negative charges very effectively since this additional charge can be easily distributed onto several atoms in the molecule. Therefore, a coordinated metal complex can effectively transfer a negative charge to the organic compound coordinated thereto. Furthermore, electrons of the organic compounds I to XIII can also be transferred effectively amongst the organic compounds themselves. This is also crucial for good electron conductivity in the electron-conducting layer.



SDC EX. 1001 - 1/20

Ma's Theory re Improved Conductivity Does Not Suggest Coordination

Synthetic Metals 158 (2008) 810–814

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Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet



Organic light-emitting diodes based on new n-doped electron transport layer

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ABSTRACT

Organic light-emitting diodes with 8-hydroxy-quinolino lithium doped 4,7-diphenyl-1, 10-phenanthroline as electron transport layer (ETL) and tetrafluoro-tetracyano-quinodimethane doped 4,4',4''-tris(3-methylphenyl)phenylamine as hole transport layer (HTL) are demonstrated. The conductivity of carrier transport layers with different doping concentration is examined by hole-only and electron-only devices. Compared with the referenced device (without doping), the current efficiency and power efficiency of the p-i-n device are enhanced by approximately 51% and 89%, respectively. This improvement is attributed to the improved conductivity of the transport layers and the efficient charge balance in the emission zone.

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1. Introduction

Since the discovery of organic light-emitting devices (OLEDs), there has been a considerable interest in developing OLEDs with high efficiency for display applications [1]. In order to lower driving voltage and enhance power efficiency, it is critical to enhance the carrier injection from the electrode to the transporting layer and to increase the transport conductivity [2,3]. The hole injection can be improved by increasing the work function of ITO with different surface treatments such as O₂ plasma or UV-ozone treatment of ITO surface [4]. It can also be enhanced by introducing hole injection layer (HIL), such as copper phthalocyanine (CuPc) [5], starburst polyamines [6], polymeric PEDT:PSS [7] and 4,4',4''-tris(N-(2-naphthyl)-N-phenylamino)triphenylamine (2-TNATA) between the ITO/hole transport layer (HTL) interface.

Recently, the p-doping of HTL has drawn a lot of attentions because of its ability to enhance hole injection and lower driving voltages in OLEDs. The p-doping HTL is typically made by co-evaporating the hole transporting materials with a strong electron acceptor like tetrafluoro-tetracyano-quinodimethane (F₄-TCNQ) [8], or oxidants like SbCl₅ [9], FeCl₃ [10] and iodine [11]. p-Doping can

also achieve ohmic conductivity to reduce driving voltage of device and the proper control of doping levels can also lead to efficient carrier injection by tunnelling [12].

However, organic molecules are known to be poor in electron injection and transport compared with that of hole. Many attempts have been made to improve the electron injection and transport, including using low work function metals [13–15] as cathode, or inserting a thin interlayer between cathode and electron transporting layer [16–20] to enhance electron injection. Great efforts have been made to enhance the electron conductivity [21–24]. Kido and Matsumoto [22] reported the improved electron transport by doping Li into tris(8-hydroxyquinoline) aluminum (Alq₃). Fong et al. [21] also demonstrated that the device performance was enhanced significantly by doping 4,7-diphenyl-1, 10-phenanthroline (Bphen) into Alq₃ as a cohost electron transport layer (c-ETL). However, few studies have been reported about using lithium quinolinato complex such as 8-hydroxy-quinolinato lithium (Liq) as an electron injection layer [25], and no work has yet been reported about using Liq-doped Bphen as electron transport layer (ETL).

In this paper, we have demonstrated a device with a new n-doping (33 wt.% Liq:Bphen) layer as ETL and p-type (m-MTDATA:x wt.% F₄-TCNQ) layer as HTL. Here, 33 wt.% Liq is chosen due to the fact that the device with the doping ratio of 33 wt.% Liq demonstrates the best current density vs voltage (J–V) curve among all the electron only devices. Using this method, we obtained a sig-

* Corresponding author. Tel.: +86 21 69980357.
E-mail address: majunwei250802944@163.com (J.W. Ma).

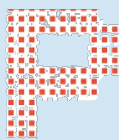
0379-6779/\$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.synmet.2008.05.009

SDC EX. 1007 - 1/5

These *J–V* characteristics of electron-only devices suggest that a certain doping ratio of Liq to Bphen can improve the electron transport ability of the co-deposited layer. The advantage of using Bphen:Liq as ETL can be explained by electron hopping exchange alongwith their LUMO. In a single host device, electrons hop along the LUMO in Bphen. Since the LUMO–LUMO difference between Bphen (3.0 eV) [29] and Liq (3.1 eV) [28] is neglectable, subject to their similar LUMO. Transport manifolds alongwith their LUMO are expected to exhibit a certain extent of overlap after a mixing ratio goes beyond 17 wt.%. Therefore, it's likely that a large energetic disorder between Bphen and Liq contributes to electron hopping, implying that electron hopping among Bphen and Liq sites is favorable [29]. Therefore, the high electron conductivity of Bphen:Liq may be originated from short hopping length for electron transport, compared to the pure Bphen HTL. However, the current conduction is reduced slightly as the doping ratio further increases to 50 wt.%. This result may be attributed to the effect of carrier quench and generation of defects. The detailed reasons are possibly the same as that of the heavy doping concentration of F₄-TCNQ into *m*-MTDATA in the hole-only devices

Ma's Improved Conductivity Need Not Result from Coordination

Professor Schanze
Expert Witness



pictivadisplays

182. In that regard, I disagree that the increase in electron conductivity of the mixed film indicates formation of a charge transfer complex and coordination of BPhen to Liq. Rather, as Ma theorizes, the increased conductivity is due to shorter hopping distances, which in turn is due to shorter molecular distances between two adjacent molecules:

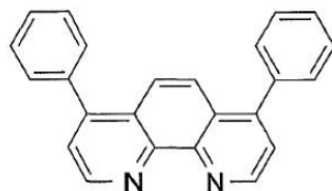
183. The reduction in neighboring molecular distances could be due to denser packing in a mixed film than in a neat BPhen film. For example, Liq or a dissociated lithium ion¹² might be able to intercalate between BPhen molecules to shorten the hopping distances. But that does not suggest any bonding interactions (*i.e.*, coordination) between BPhen and Liq.

Petitioner's Reliance on Pictiva's Infringement Theory Is Misplaced

Professor Schanze
Expert Witness

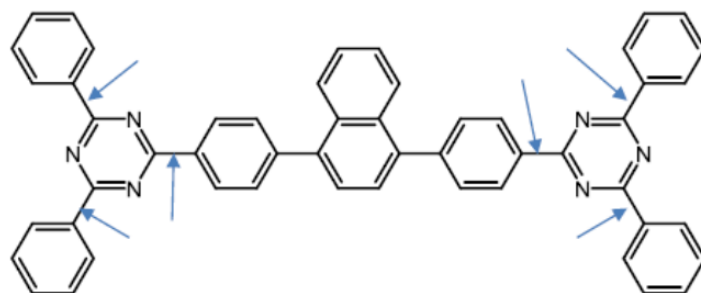


pictiva displays

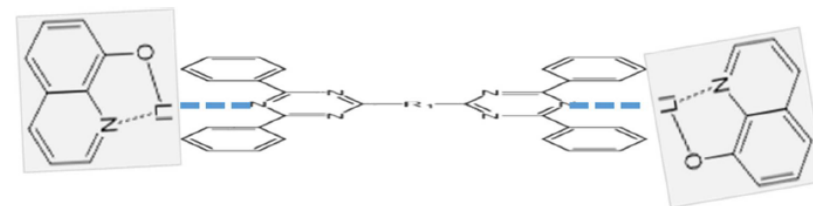


BPhen = bathophenanthroline
(4,7-Diphenyl-1,10-phenanthroline)
C₂₄H₁₆N₂

161. This differs from a ligand with two nitrogen-containing rings spaced apart by a chain of aromatics that can freely rotate around the C-C single bonds.



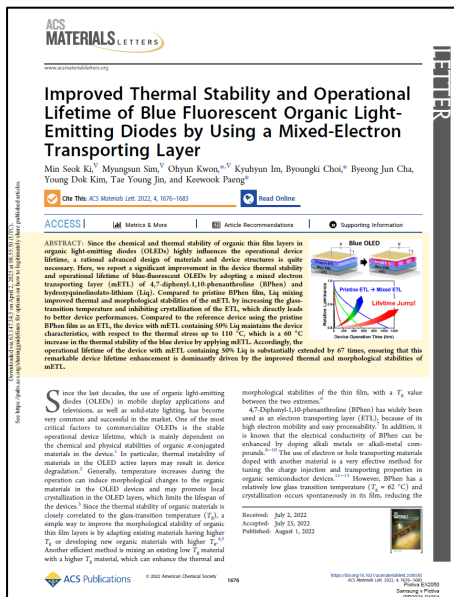
162. In the above ligand, each of the triazine rings can coordinate to at least one separate metal center, as illustrated below.



(Note, the Liq molecule likely approaches the ligand at an angle to the plane defined by the triazine ring for at least steric reasons and likely also to maximize molecular orbital overlap with the pair of electrons on nitrogen.)

EX2041, para. 161-162; POR 58

Ki Does Not Show Coordination between Liq and BPhen



When BPhen was mixed with Liq (17%–83%), the binding energy of N 1s peak increased to 398.6 eV, having similar peak position with the 100% Liq film. In the case of 100% Liq, a small shoulder also appeared on the higher binding energy region, compared to the mixture films, which can be attributed to the formation of various coordination complexes when Liq exists alone resulting in a complicated electronic state of nitrogen.^{31,38} Interestingly, the N 1s spectra of the mixture films cannot be fully deconvoluted with the N 1s spectra of pristine Liq and Bphen (see Figure S4 in the Supporting Information), implying that Liq and Bphen are not simply in their physical mixture, but their chemical interaction exists in the mixture.

- Meaning of “coordination” unclear
- “coordination” only w.r.t. “when Liq exists alone,” not between Liq and Bphen
- No evidence that “chemical interaction” means “coordination” as properly construed

EX2055 at 1678; Sur-Reply 24

Ki and Ma Used Different Processing Conditions: No Inherency

	Ki (EX1031)	Ma (EX1005)
Pressure (torr)	10^{-7}	10^{-5}
Sum of deposition rates (Å/s)	~2	0.5±0.2
Evaporator configuration	N/A	N/A
Degree of overlap of plumes	N/A	N/A

Additional Slides

Pictiva Asserts No Further Evidence Is Required To Demonstrate “Coordination” Beyond Materials And Processing Conditions

are structural features that enable coordination. Co-evaporation results in maximum proximity between the two molecules and allows orbital interaction, enabling the formation of coordinative bonds between the orbitals of the Liq complex and those of compound $^{742}\text{C}_{52}\text{H}_{34}\text{N}_6$. As shown in the examples of Patent-in-Suit 2 and described in para. [0034], no additional technical measure is needed beyond co-evaporation of the compounds – provided that the metal complex and the organic compound are suitable for forming coordination bonds. As shown above, this is true for lithium complexes. As also

Ex. 1025 Complaint in German Proceeding, ¶ 108

Pictiva Asserts No Further Evidence Is Required To Demonstrate “Coordination” Beyond Materials And Processing Conditions

are structural features that enable coordination. Co-evaporation results in maximum proximity between the two molecules and allows orbital interaction, enabling the formation of coordinative bonds between the orbitals of the Liq complex and those of compound ⁷⁴²C₅₂H₃₄N₆. As shown in the examples of Patent-in-Suit 2 and described in para. [0034], no additional technical measure is needed beyond co-evaporation of the compounds – provided that the metal complex and the organic compound are suitable for forming coordination bonds. As shown above, this is true for lithium complexes. As also

Not
BPhen

Ex. 1025 Complaint in German Proceeding, ¶ 108

Pictiva Asserts No Evidence Of Coordination Is Needed Beyond Materials And Processing Conditions

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PETERREINS SCHLEY
PATENT AND TRADEMARK ATTORNEYS

Regional Court of Munich I
– 21st Civil Chamber –
Lenbachplatz 7
80333 Munich

Via beA (special electronic mailbox for attorneys)
(beA correspondence requested to Attorney Dr. Thoma)

Contains color illustrations

The undersigned assumes
for court costs based on a preliminary estimate

21 O 13746/23
Hearing date: December 18, 2024

Munich, March 7, 2024
Our reference: 51112-0002LL1

Statement of Extension of Claim

by Pictiva Displays International Ltd., The Glasshouses GH2, 92
Georges Street Lower, Don Laoghaire, Dublin,
Ireland, A96 VR66, represented by the
Managing Director Angela Quinlan, same
address

– Plaintiff –

Legal counsel: The attorneys of Peterreins Schley Patent- und
Rechtsanwälte PartG mbB, lead counsel Dr.
Thomas Adam, with the involvement of the
patent attorneys of the firm, in particular Patent
Attorney Dipl.-Ing. Felix Glöckler and Patent
Attorney Dipl.-Chem. Markus Coelin,
Hermann-Sack-Str. 3, 80331 Munich

vs.

SDC EX. 1025 - 2/47

$^{742}\text{C}_{52}\text{H}_{34}\text{N}_6$. As shown in the examples of Patent-in-Suit 2 and described in para. [0034], no additional technical measure is needed beyond co-evaporation of the compounds – provided that the metal complex and the organic compound are suitable for forming coordination bonds. As shown above, this is true for lithium complexes. As also

Ex. 1025 Complaint in German Proceeding, ¶ 108

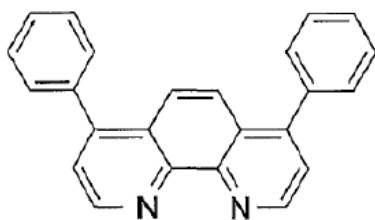
Ex. 1025

See Pet. Reply, 23-25

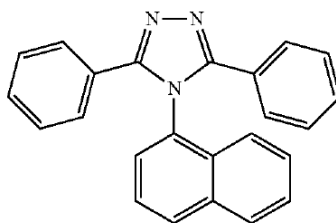
COVINGTON

Demonstrative Exhibit – Not Evidence 56

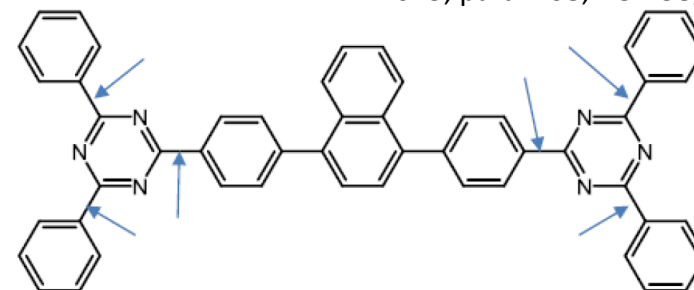
108 The presence of Li^+ in Liq and of nitrogen (N) sites in the organic compound $^{742}\text{C}_{52}\text{H}_{34}\text{N}_6$ are structural features that enable coordination. Co-evaporation results in maximum proximity between the two molecules and allows orbital interaction, enabling the formation of coordinative bonds between the orbitals of the Liq complex and those of compound $^{742}\text{C}_{52}\text{H}_{34}\text{N}_6$. As shown in the examples of Patent-in-Suit 2 and described in para. [0034], no additional technical measure is needed beyond co-evaporation of the compounds – provided that the metal complex and the organic compound are suitable for forming coordination bonds. As shown above, this is true for lithium complexes. As also demonstrated earlier, nitrogen-containing organic compounds – and in particular heterocyclic compounds with three nitrogen atoms, such as compound X of Patent-in-Suit 2 and compound $^{742}\text{C}_{52}\text{H}_{34}\text{N}_6$ in the contested embodiment – are suitable for forming coordination bonds with metal complexes. Accordingly, this feature is also fulfilled.



BPhen = bathophenanthroline
(4,7-Diphenyl-1,10-phenanthroline)
 $\text{C}_{24}\text{H}_{16}\text{N}_2$ EX1005, 57/89



X
EX1001, col. 7



Compound 742, POR 58

EX1025, para. 108; POR 58; Sur-Reply 21

Pictiva Argued BPhen Coordinates To Liq When Jointly Vaporized

CONFIDENTIAL – PROTECTIVE ORDER MATERIAL

Anlage PS 15
Pictiva Displays International LLC
Samsung Electronics GmbH v.
LG Electronics (Az. 21 O 2503)
Patentstreitigkeit
Replik v. 18.03.2024

Expert Opinion

Provided by Prof. Schanze

1. Qualifications and Professional Background

1. I am currently the Professor and Robert A. Welch Distinguished University Chair in Chemistry at the University of Texas at San Antonio and Deputy Editor of *ACS Central Science*.
2. I earned my B.S. in Chemistry from Florida State University in 1979 and my Ph.D. in Organic Chemistry from the University of North Carolina, Chapel Hill, in 1983. I was a Postdoctoral Research Associate in the Department of Chemistry at the University of North Carolina, Chapel Hill from 1983-1984. I was then a Miller Postdoctoral Fellow in the Chemistry Department of the University of California, Berkeley from 1984-1986. In 1986 I was appointed an Assistant Professor in the Department of Chemistry of the University of Florida. I became an Associate Professor at Florida in 1992 and was appointed full Professor in 1997. From 1997 to 2016 I held various Professorship chairs as outlined in my CV. In 2016 I moved to my current position at the University of Texas, San Antonio, where I serve as the Welch Distinguished Professor.
3. Throughout my career I have earned various honors and awards, including the Globalization Award from American Chemical Society (ACS) in 2018. I was made a Fellow of the ACS in 2011 and won the Florida Award from the Florida Section of ACS in 2009. I have also been awarded many Visiting Professor and Lecturer appointments at various universities throughout Asia. A full list of my Honors and Awards is provided in my CV.
4. I have also held many professional service positions, such as the Chair of the Editor Search Committee for the ACS in 2014 and 2015 and I was the Chair of the ACS Publications Editors Conference in San Diego in 2016. I was Associate Editor of the American Chemical Society (ACS) Journal *Langmuir* from 2000 – 2008. From 2008 - 2023 I served as founding Editor in Chief (EIC) of *ACS Applied Materials & Interfaces*. This is one of the largest technical journals in the field of materials chemistry and materials science. As EIC, I overviewed the review of more than 20,000 papers that are submitted annually for consideration to be published.

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SDC EX. 1026 - 1/18

39. Kang et al. report in exhibit 11 on page 140207, right col:

“the complexation of ETL (BPhen) and Liq was proved by analyses of the Gibbs – DiMarzio prediction and X-ray photoelectron spectroscopy[16].”

40. As a side remark, for the benefit of the Court, the reference to complexation in the above quote means the same as coordination in the sense of the patent-in-suit, i.e. reference is made to a coordination of LiQ with the pyridinic nitrogen atoms of BPhen. For further information, BPhen has the following structure:

Ex. 1026 Schanze Expert Opinion, ¶¶ 39-40

*Reference [16] is to Ki (Ex. 2050)

Ex. 1026

See Pet. Reply, 23-25

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Demonstrative Exhibit – Not Evidence 57

Pictiva Argued BPhen Coordinates To Liq When Jointly Vaporized

CONFIDENTIAL – PROTECTIVE ORDER MATERIAL

Anlage PS 15
Pictiva Displays International LLC
Samsung Electronics GmbH v.
LG Electronics Inc. (No. 21-0-2503)
Patent No. 10,000,000
Filed 10/15/2024

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- Ki, not Ma
- Pictiva’s definition of “coordination” here differs from the one adopted by the district court

Pictiva Presents Inconsistent Positions

42. Thus, there is direct experimental evidence of the pyridinic nitrogen atoms of BPhen coordinating to the LiQ metal complex.

Ex. 1026 Schanze Expert Opinion, ¶ 42

request), ¶26 (“unclaimed compound BPhen”). As such, Petitioner’s reliance on statements in the German proceeding is misplaced and those statements do not support Petitioner’s argument that in Ma, BPhen coordinates to Liq. EX1032, ¶¶26-

PO’s Sur-Reply, 23

41. In the above quote, Kang et al. reference lit. [16] which is attached to my opinion as exhibit 13. In exhibit 13, a film obtained by co-evaporation of LiQ with BPhen is analyzed by X-ray photoelectron spectroscopy (XPS). It is reported in the paragraph bridging the columns of page 1678 and the following paragraph that the XPS signals of the pyridinic nitrogen and of the lithium are synchronously shifted and that this implies a chemical interaction between LiQ and the pyridinic nitrogen atoms of BPhen and not just the mere co-existence “side-by side” as it is present in a purely physical mixture:

“X-ray photoelectron spectroscopy (XPS) was performed to investigate molecular interaction between BPhen and Liq. ... In case of BPhen, the N 1s peak of pristine BPhen sample was centered at 398.2 eV, which could be assigned to sp²-hybridized pyridinic nitrogen in the BPhen molecule. Interestingly, the N 1s spectra of the mixture films cannot be fully deconvoluted with the N 1s spectra of pristine Liq and BPhen (see Figure S4 in the Supporting Information), implying that Liq and BPhen are not simply in their physical mixture, but their chemical interaction exists in the mixture. In the Li 1s spectra, 100% Liq showed a peak at 55.6 eV. When 17% of Bphen was mixed to Liq, a red-shift of Li 1s peak to 55.1 eV was observed and no additional shifts were observed as the molar ratio of Bphen increased further. The synchronous peak shifts observed in N 1s and Li 1s spectra upon mixing Bphen and Liq, the binding energy increase in N 1s from pristine Bphen (~0.4 eV) and the binding energy decrease in Li 1s from 100% Liq (~0.5 eV), imply some chemical interaction between the N atoms (Bphen) and the Li atom (Liq).”

42. Thus, there is direct experimental evidence of the pyridinic nitrogen atoms of BPhen coordinating to the LiQ metal complex.

- Ref. 16 = Ki
- Reliance on Ki to prove coordination a new theory (See Pet. generally)
- Ki and Ma used different processing conditions (Sur-Reply 21, 24-25)
- Ki presented experimental results, Ma did not (Sur-Reply 24-25)
- Ma’s conductivity theory implies physical interaction, not chemical bonding (POR 63; EX2041, para. 182-183)
- Pictiva’s interpretation of the term “coordinate” is broader than that adopted by the district court, but much narrower than that by Dr. Rand (POR 62-63)

EX1026