PUBLIC VERSION

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.

Case No. IPR2024-01094
Patent No. 8,558,223

DECLARATION OF PROFESSOR KIRK S. SCHANZE

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I, Kirk S. Schanze, declare as follows:

I. Introduction

1. I have been retained as an independent expert on behalf of Pictiva Displays International Ltd. ("Patent Owner") to provide certain technical background for the Werner and Ma references that form the basis for the Grounds of unpatentability in the Petition for IPR2024-01094.

2. For this service, I am compensated for my time at my normal consulting rate. My compensation does not depend on the outcome of any matter or on any of the opinions provided below. I have no financial interest in this matter.

3. My testimony herein is based on my technical background, my years of experience in the field of organic light emitting diodes ("OLED") and my review of the materials cited herein.

4. I provide my testimony from the perspective of a person of ordinary skill in the art at the time of the invention (further address below). I am familiar with the knowledge and skill level of these people based on my 25 years of experience in the OLED field and frequent interactions with such people. For example, at the time of the invention, I had many interactions with postdocs and researchers who had a comparable level of skills as a person of ordinary skill in the art as defined below, including those in my research group.

II. Qualification and Experience

5. I am currently the Robert A. Welch Distinguished University Chair in the Chemistry Department at the University of Texas, San Antonio. A copy of my CV is attached as Appendix A.

6. I earned by 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, Berkley from 1984-1986.

7. In 1986, I was appointed an Assistant Professor in the Department of Chemistry of the University of Florida. I became an Associate Professor at the University of 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 Robert A. Welch Distinguished Professor.

8. 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.

9. 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.

10. 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 were submitted annually for consideration to be published.

11. I currently serve as the Deputy Editor for the journal ACS Central Science. This is a premier journal published by ACS Publications in the broad field of Chemistry and allied fields in biology, physics and materials science.

12. My research primarily focuses on work in the fields of conjugated polymers, photochemistry, emission spectroscopy, and organic electronics, including materials and fabrication of organic light emitting diodes and organic solar cells. I am an expert in light applications, including lasers and light sources, spectral filtering, and optical measurements.

13. I have 25 years of experience in the field of organic light emitting diodes and materials, with more than 50 peer reviewed publications and 6 patents in the field. My laboratory is currently engaged in exploring the phenomenon of luminescence (light emission). For example, in our applied work, we are using the light emission process of molecules and materials to develop novel light emitting devices (such as polymer LEDs, a type of OLED), and novel fluorescent sensors. I have collaborated with other academic or industrial laboratories to fabricate OLED devices, and am currently collaborating with researchers at the North Carolina State University on deep blue electrophosphorescent OLED materials and devices. I therefore have familiarity with both the material aspects and the device structural aspects of OLED devices.

III. Skilled Artisan

14. I understand that Samsung defines a person of ordinary skill in the art at the time of the invention as someone with "a university degree in chemistry and additional expertise or a second university degree in the field of electrical engineering, particularly optoelectronics, or alternatively a university degree in electrical engineering and additional expertise or a second university degree in the field of chemistry." Pet. at 14.

15. I have reviewed Dr. Rand's curriculum vitae, and I don't see him having either a degree in the field of chemistry or additional expertise in the field

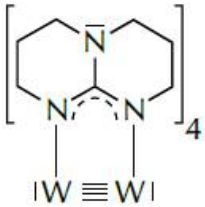
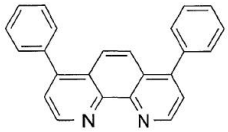
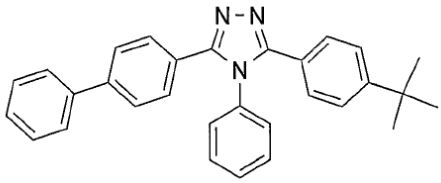
of chemistry, as commonly understood by a chemist. To the extent that his alleged expertise came from his work on OLEDs, then by virtue of my work in OLEDs and solar cells, I would have also had gained expertise in optoelectronics and electrical engineering.

16. This is particularly true in light of the subject matter of the ’223 patent. It is my opinion that the subject matter relates mostly to the chemistry and material properties of the electron-conducting layer, with only basic knowledge on the structure of the OLED devices required. I have that device-side knowledge through my years of work in OLEDs. For example, I had “spent several years studying the structure and function of organic optoelectronic components,” including OLEDs, and I have “detailed knowledge of the chemical structure of light-emitting organic layers and the transport of charge carriers to these layers.” Pet. 14. Thus, I qualify as a person “work[ing] at the interface between … (charge carrier transport and light emission processes in optoelectronic components) and chemistry, in particular organic chemistry (materials and layer stack combinations suitable)” for OLEDs. *Id.*

17. Thus, I was at least a person of ordinary skill in the art, if not one with above average skills, at the time of the invention.

IV. WO 2005/086251 (Werner)

18. I have reviewed the Werner reference. I have been asked to opine on the disclosures of Werner, including whether the litany of metal complexes and matrix materials listed by Werner would have motivated a person of ordinary skill in the art to jointly evaporate tetrakis(1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidinato)-ditungsten (II) ("$W_2(hpp)_4$") and bathophenanthroline ("BPhen") or 3-4(-biphenyl)-4-phenyl-5-*tert*-1,2,4-triazole) ("TAZ") as proposed. It is my opinion that it does not.

 $W_2(hpp)_4$	 BPhen = bathophenanthroline (4,7-Diphenyl-1,10-phenanthroline) C24H16N2	 TAZ

A. A Person of Ordinary Skill in the Art Would Not Have Combined $W_2(hpp)_4$ with BPhen or TAZ

19. Samsung does not explain why a person of ordinary skill in the art would have chosen $W_2(hpp)_4$ together with BPhen or TAZ out of the millions or even billions of possibilities. For at least the combination of $W_2(hpp)_4$ with BPhen, it appears that Samsung selected the pair because the ''223 patent

specifically mentioned $W_2(hpp)_4$ and BPhen. Petition at 18-19 ("Werner discloses that the materials for this layer may include (i) the metal complex $W_2(hpp)_4$, which has two central metal (W) atoms and is in fact the same metal complex that is used in each embodiment of the '223 patent; and an [sic] (ii) the organic compound BPhen, which comprises a heteroaromatic compound which is conjugated with an aromatic compound via a C—C bond, and which is accordingly identified in the '223 patent as Compound VI."). I understand that it is improper to use the inventors' insight as the roadmap to piece together the prior art.

20. It is my opinion that a person of ordinary skill in the art would not have combined $W_2(hpp)_4$ with BPhen or TAZ because of the misalignment of the ionization potential of $W_2(hpp)_4$ and the electron affinities of BPhen and TAZ. According to other patents by Novaled, the ionization potential of a molecular n-dopant like $W_2(hpp)_4$ should be no more than 0.5 eV below the electron affinity of the organic compound to be doped. For example, U.S. Patent No. 7,911,129 ("Novaled '129 patent"), which names some of the same inventors as Werner, discusses the energy level alignment for p-doping and n-doping. EX2043, 7:1-6 ("a stack of organic layers with a p-doped hole transport layer from the organic matrix material O1, an electron block layer from the organic matrix material[] O1, the emission layer 4, a hole block layer from the organic matrix material O2 and an

n-doped electron transport layer from the organic matrix material O2.”). The Novaled ’129 patent states:

> For a molecular n-dopant, … 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: …EA(O2)>IP(D)-0.5eV.

EX2043 [US7,911,129], 10:56-63.

21. Another Novaled patent, U.S. Patent No. 7,972,541 (“Novaled ’541 patent”), to which Werner is a first-named inventor, states

> In the case of n-doping, the dopant acts as electron donor and transfers electrons to a matrix which is characterized by a sufficiently high electron affinity. The matrix is therefore reduced. Due to the transfer of electrons from the n-dopant to the matrix, the charge carrier density of the layer is increased. The extent to which an n-dopant is able to donate electrons to a suitable matrix with electron affinity and thereby increase the charge carrier density and thus also the electrical conductivity depends in turn on the relative situation between the HOMO of the n-dopant and the LUMO of the matrix. If the HOMO of the n-dopant is above the LUMO of the matrix with electron affinity, electron transfer can take place. ***If the HOMO of the n-dopant is below the LUMO of the matrix with electron affinity, electron transfer can also take place, provided that the energy difference between the two orbitals is small enough to allow a certain thermal population of the higher energy***

> ***orbital.*** The smaller this energy difference, the higher the conductivity of the resulting layer should be. However, the highest conductivity is to be expected in the case where the HOMO level of the n-dopant is above the LUMO level of the matrix with electron affinity. The conductivity can in practice be measured and is an indication as to how well the electron transfer from the donor to the acceptor operates, provided that the charge carrier mobilities of different matrices are comparable.

EX2044 [US7,972,541], 3:5-30.

22. Novaled '541 patent too proposes that "the matrix material has an energy level for the lowest unoccupied molecular orbital (LUMO), which differs by 0-0.5 [e]V from the ionization potential (HOMO) of the dopant, preferably by 0-0.3 [e]V, particularly preferably by 0-0.15[e]V." *Id.*, 8:19-23. Of course, n-doping can also occur when "the matrix material has an electron affinity (LUMO energy level), which is lower than the ionization potential (HOMO) of the dopant." 8:24-26.[1] But suffice to say, at the time of the invention, the understanding was

[1] The Novaled '541 patent explains that "'lower' means that the LUMO energy level has a greater numerical value than the HOMO energy level. Since the two parameters are given negatively from the vacuum level, this means that the absolute HOMO energy value is greater than the absolute LUMO energy value." EX2044 [US7,972,541] at 8:26-31.

that in order to obtain effective n-doping from a molecular dopant such as $W_2(hpp)_4$, the ionization potential of the dopant should be no more than 0.5 eV lower than electron affinity of the organic material to be doped.

23. Thus, for example, if the electron affinity of BPhen was known as between 2.4-3.0 eV, (*see* US 7,911,129, 10:50-54), then the ionization potential (or HOMO) of the n-dopant should be no lower than 2.9-3.5 eV (that is, the numerical value of the ionization energy should be less than 2.9-3.5 eV).

24. The gas phase ionization potential of $W_2(hpp)_4$ is 3.76 eV (peak) with an onset at 3.51 eV. EX2004 [Cotton Textbook] at 770 ("the $W_2(hpp)_4$ molecule is the most easily oxidized molecule known: its δ ionization has an onset value of 3.51 eV and a peak (vertical) value of 3.76 eV.")[2]

[2] I use the gas phase ionization potential because the Petition focuses on the gas phase interaction of the metal complex and the organic compound, (*e.g.*, Petition at 39-46), so the gas phase ionization potential is more relevant than the solid state one.

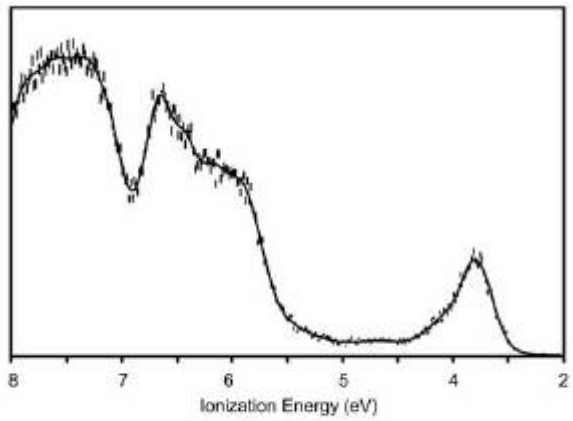


Fig. 16.45. The (He (I) PES of $W_2(hpp)_4$, supplied by Prof. D. L. Lichtenberger (University of Arizona).

(EX2004, p. 770, Fig. 16.45)

25. Hence, according to Novaled's and Werner co-inventors' teaching, a person of ordinary skill in the art would not have regarded $W_2(hpp)_4$ as a suitable n-dopant for BPhen.

26. TAZ, which has a LUMO that is comparable to or slightly higher than BPhen (see discussion below), would also not be understood as a suitable matrix to be n-doped by $W_2(hpp)_4$.

27. These and other reasons are explained further below.

1. Trillions of Possible Combinations

28. I understand that Dr. Rand was deposed in this proceeding. I understand that he agreed that Werner disclosed "more than one thousand" matrix materials" (137:3-18) and "[o]ver 2,000" metal complexes (144:6-17), resulting in over 2 million combinations:

> Q. Okay. 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 [Rand Tr.], 137:3-18.

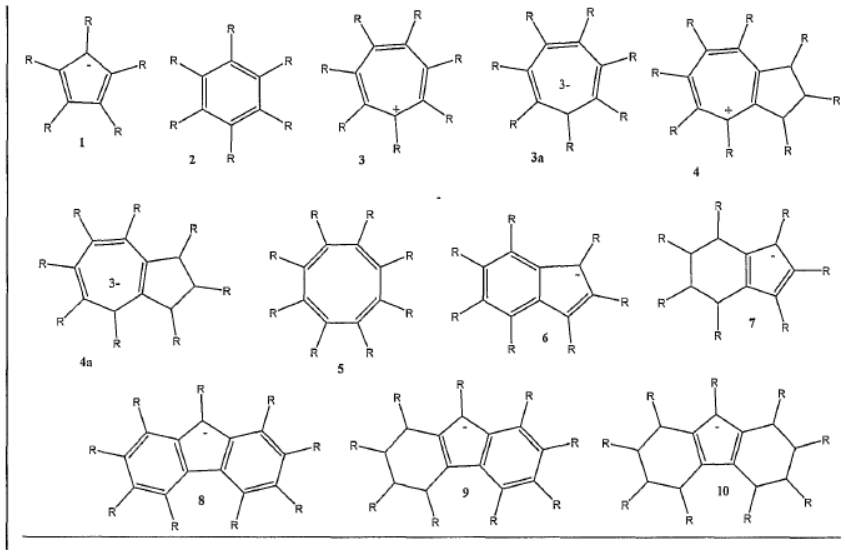
> Q. So ***just between the M2(Carboxylate), M2(AlkylCOO)4, we are talking about over 2,000 already; right***? And we haven't really counted the CT [*sic*, cp] complexes, the M2(hpp)4 possibilities? Right? So fair to say there's going to be a few thousand possibilities? At least a few thousand possibilities in [Werner] 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***.

EX2042 [Rand Tr.], 144:6-17.

29. But as I explain below, Werner's disclosures encompasses far more than 2,000 metal complexes and 1,000 organic matrix materials, rendering the possible combinations in the trillions.

(a) Millions of Metal Complexes Disclosed By Werner

30. Werner took a kitchen sink approach when listing the various "advantageous classes of compounds." *See* EX1005-10 to EX1005-55. He starts with "Pi-complexes," which appear to potentially cover any complexes with "a double bond or a triple bond" "wherein the multiple bond can represent, for example, a C-C, C-O, C-N, S-O, N-O bond, without being limited to these." EX1005-10. According to Werner, the pi-complex can be an alkene, an alkyne, an allyl complex, a diene complex (such as a butadiene or a cyclobutadiene), a cyclopentadienyl anion, a cycloheptatrienyl cation, a cycloheptatrienyl trianion, a cyclooctadienyl dianion, a carbonyl, a phosphine, aryl (*e.g.*, benzene rings), etc. *Id.*, EX1005-11. As particularly preferred examples, he listed compounds 1-10 with effectively open-ended substitutions at each carbon atom around the rings. EX1005-13.



31. For example, Werner states:[3]

> The residues R in the base compounds 1-10 can be the same or different, be open-chain or part of a ring or ring system, and are preferably selected from: alkyl, including cycloalkyl, aryl, the above heteroatoms. The alkyl or aryl groups can be fully or partially substituted with one or more, same or different heteroatoms from the above list. It should be understood that the above residues R can also generally be residues according to the invention with a +I effect and/or +M effect on an unsaturated or aromatic ring (or P instead of N). Generally, the residues R in the inventive compounds can also have unsaturated groups, e.g., with C=C, C=N bonds, or the like.

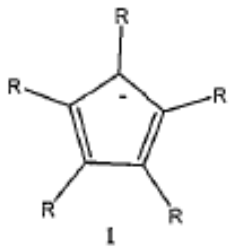
EX1005-13.

32. A person of ordinary skill in the art would recognize that with this broad language, each general structure can result in at least thousands of possible compounds.

---

[3] In the paragraph, the "above heteroatoms" and "heteroatoms from the above list" refer to the heteroatoms discussed on EX1005-12/89 (original page number 9) that lists the "following atoms [that] can be used as heteroatoms: B, Al, Ga, In, N, P, As, Sb, Si, Ge, Sn, Pb, O, S, Se, Te."

33. Take for example the cyclopentadienyl anion shown as Compound 1. This is the ligand used in cobaltocene, the metal complex used in example 3 on EX1005-65.



34. For this compound, even if we limit the residual R to the simplest unsubstituted alkyl (methyl, ethyl, propyl and isopropyl) or phenyl group, that would result in 237 possible combinations:

- 5 combinations of the same R's
- 5*4 for 4 positions with the same R and one different R'
- 60 combinations for 3 positions with the same R's (5 possibilities for the first R, two combinations for arranging the same 3 R's around the ring, and 6 ways of selecting two different R's from the remaining 4 R groups)
- 60 combinations for 2 positions with the same R's and then different R's in the three remaining positions (5 possibilities for the first R, two combinations for arranging the same 2R's around the ring (the two R's are attached to C1 and C2 of the ring or to C1 and C3 of the ring) and 6 ways where the remaining three positions all have different R's)

- 120 combinations for 2 positions with the same R's, 2 positions with the same R's (there are 10 possible pairs of R and R', each pair having four possible arrangements around the ring, with R, R, R' and R' attaching respectively to C1, C2, C3, C4; C1, C2, C3, C5; C1, C3, C2, C4; and C1, C3, C4, C5, and 3 possibilities for the remaining carbon on the ring);
- 12 combinations where each carbon has a different substituent.

35. Adding in the possible substitution with heteroatoms along the methyl, ethyl, propyl or isopropyl chain or phenyl ring, the number of possibilities would increase geometrically. For instance, if each of methyl, ethyl, propyl, isopropyl or phenyl is permitted one substitution with a heteroatom, that would create five more possible "R" groups. In that case, the number of possible combinations for Compound I increases to nearly 6,964:

- 10 combinations of the same R's
- 10*9 for 4 positions with the same R and one different R'
- 720 combinations for 3 positions with the same R's (10 possibilities for the first R, two combinations for arranging the same 3 R's around the ring, and 36 ways of selecting two different R's from the remaining 9 R groups)
- 1680 combinations for 2 positions with the same R's and then different R's in the three remaining positions (10 possibilities for the first R, two combinations for arranging the same 2R's around the ring (the two R's are

attached to C1 and C2 of the ring or to C1 and C3 of the ring) and 84 ways where the remaining three positions all have different R's)

- 1,440 combinations for 2 positions with the same R's, 2 positions with the same R's (there are 45 possible pairs of R and R', each pair having four possible arrangements around the ring, with R, R, R' and R' attaching respectively to C1, C2, C3, C4; C1, C2, C3, C5; C1, C3, C2, C4; and C1, C3, C4, C5, and 8 possibilities for the remaining carbon on the ring);
- 3024 combinations where each carbon has a different substituent (10*9*8*7*6/(5 fold symmetry*2 head-to-tail)).

36. Now if we further increase the degree of substitution (*e.g.*, permitting two substitutions per methyl, ethyl, propyl, isopropyl or phenyl group), then that would lead to 15 possible R groups, and the number of possible combinations for Compound I becomes 55,371:

- 15 combinations of the same R's
- 15*14 for 4 positions with the same R and one different R'
- 2730 combinations for 3 positions with the same R's (15 possibilities for the first R, two combinations for arranging the same 3 R's around the ring, and 91 ways of selecting two different R's from the remaining 14 R groups)
- 10,920 combinations for 2 positions with the same R's and then different R's in the three remaining positions (15 possibilities for the first R, two

combinations for arranging the same 2R's around the ring (the two R's are attached to C1 and C2 of the ring or to C1 and C3 of the ring) and 364 ways where the remaining three positions all have different R's selecting from 14 possible groups)

- 5,460 combinations for 2 positions with the same R's, 2 positions with the same R's (there are 105 possible pairs of R and R', each pair having four possible arrangements around the ring, with R, R, R' and R' attaching respectively to C1, C2, C3, C4; C1, C2, C3, C5; C1, C3, C2, C4; and C1, C3, C4, C5, and 13 possibilities for the remaining carbon on the ring);
- 36,036 combinations where each carbon has a different substituent (15*14*13*12*11/(5 fold symmetry*2 head-to-tail)).

37. There are, however, far more than 15 possible R groups. Werner did not limit the R group to methyl, ethyl, propyl, isopropyl or phenyl-based moieties, and it did not limit the degree of substitutions. Werner also did not limit the type of substitution. And even common substitutions would already include dozens of variations, such as hydroxyl, ether, amino, carbonyls (carboxylates, ketones, aldehydes, amides, ketamines …), pyridyl, immino, imido, phosphine, phosphide etc. As the degrees of substitution, the type of substitution, and/or the number of carbon atoms in the alkyl or aryl residue increase, there will be more possibilities of R and hence more possible Compound I variations (the number of possible

variations would be number of possible R to the fifth power). And this is for Compound I.

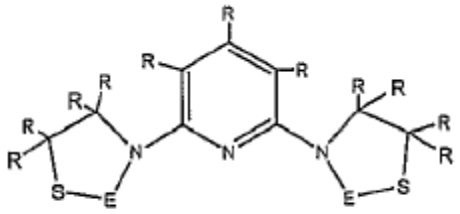
38. Other compounds, such as Compounds 2-10, with even more carbons, would have even more possibilities. For example, for the six-membered compound 2, 15 possible R's would lead to 15*14*13*12*11*10/(6*2) = 300,300 possibilities if all R's are different. These numbers add up quickly.

39. And that is just for ligands. Each ligand can also complex with different metal centers. For instance, Group III metal Sc, Group IV metals, Ti, Zr and Hf, Group V metal (V, Nb and Ta), Group VI metals (Cr, Mo), Group VII metals (*e.g.*, Mn, Re), Group VIII metals (Fe, Ru, Os), Group IX metals (Co, Rh and Ir), Group X metal (Ni) and lanthanide metals such as Y, La all had known complexation with cyclopentadienyl anion or its derivatives, and sometimes in different oxidation states. Hence, there could easily be millions of possible combinations.

40. Besides pi-complexes, Werner also lists (a) "[p]addlewheel complexes and multinuclear complexes in general," (b) complexes with ligands "selected from the group of borates, carboranes, triazacycloalkanes, triazacycloalkenes, pyrroles, thiophenes, pyrazoles, imidazoles, thiazoles, oxazoles, pyridines, pyridazines, pyrimidines [and] pyrazines," (c) complexes with "[t]ripod ligands," (d) complexes with fullerenes, (e) complexes with pincer ligands such as compounds 19-37, 38-

46 and 47-56, (f) complexes with carbene ligands; (g) complexes with silylene ligands; and (h) complexes with germylene ligands, among others. EX1005-10 to EX1005-55. Again, borates, carboranes etc. are each just a generic term that can encompass millions of possible compounds.

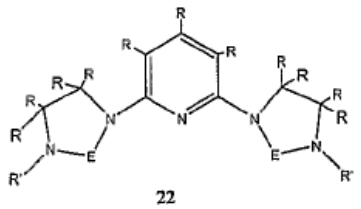
41. Even if one is to examine the list on EX1005-63 to 64 in "Application examples," there are still millions of possible metal complexes. For instance, one preferred example is Fe(Ligand)2, where the ligand is one of compounds 20 to 37 with E selected from C, Ge or Si, and with R being preferably hydrogen, methyl or ethyl. Werner also says that instead of Fe, the central metal could also be Cr, Mn, Co, Ni, Cu, Zn, Mo or W for a total of nine (9) possible metal centers. For compound 21, when the two E's are different (*e.g.*, C & Ge, C &Si, or Ge and Si), the compound does not have a symmetry, and the possible combination would be the multiple of (3^{11}, 3 possibilities per R and 11 R's), the three variations where E's are different, and 9 possible metal centers = 3^{11}*3*9 = 4,782,969.



21

42. If we are to limit ligand 21 to R being H or methyl and E being both C or both Ge, that would still result in 2^{11}*9 =18,432 possibilities. And applying

similar analysis to ligands 22-24 and limiting them to R being H or methyl and E being C and Ge result in 73,729 (2^{13}*9) for compound 22, 4608 (2^{9}*9) possibilities for compound 23, and 1152 (2^{7}*9) possibilities for compound 24.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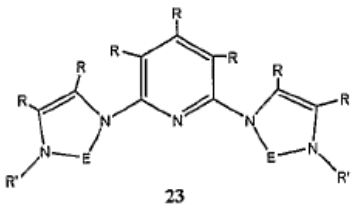
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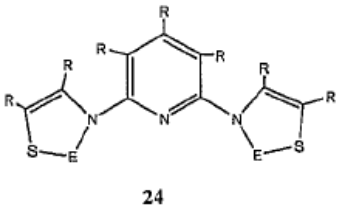

24

43. That is, for just $M(L_2)$ and the most preferred variations, one would still get about 100,000 variations. And Werner does not explain the advantages or disadvantages of these hundreds of thousands possibilities over other short-listed possibilities, including over $W_2(hpp)_4$.

44. Thus, it is my opinion that given Werner's disclosures, a POSITA would not have picked $W_2(hpp)_4$ from the hundreds of thousands or even millions of possibilities in even the most preferred examples on pages 60-61 of the reference (EX1005-63 to EX1005-64).

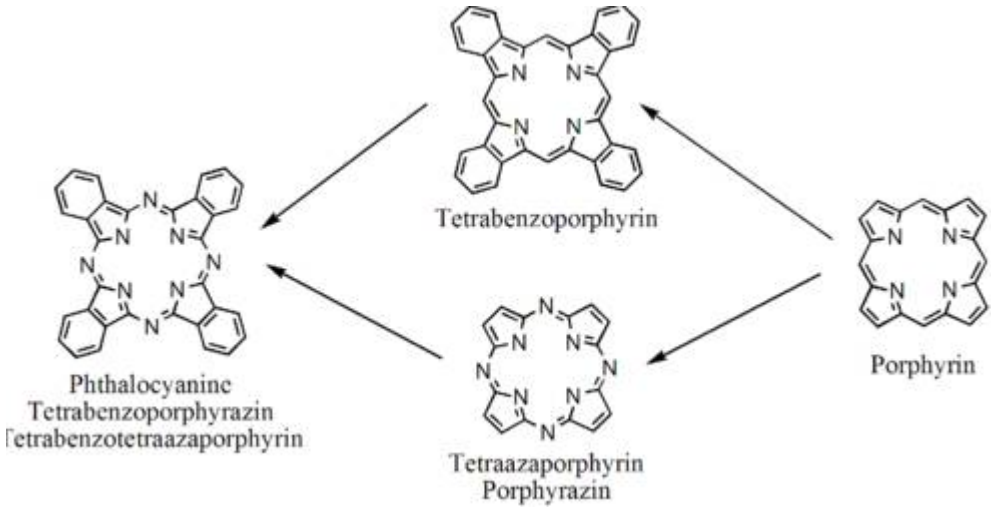
(b) Millions of Possible Matrix Materials Disclosed By Werner

45. Werner also lists a large number of possible matrix materials. Werner states:

> The matrix material can consist partially (> 10 or > 25 wt%) or 5 essentially (> 50 wt% or > 75 wt%) or entirely of <u>a metal phthalocyanine complex</u>, <u>a Buckminster fullerene</u>, 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.

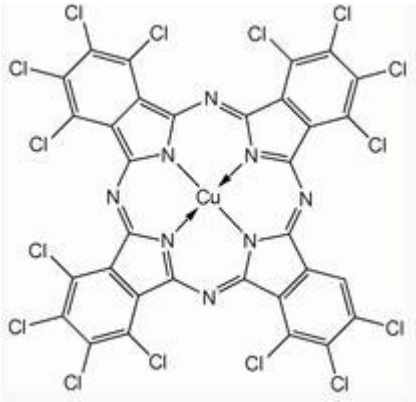


(https://en.wikipedia.org/wiki/Phthalocyanine#:~:text=Phthalocyanine%20(H%202Pc)%20is,Phthalocyanine).

46. Metal phthaolcyanine, fullerene, metal porphyrin, oligothiophene, oligophenyl, oligophenylene-vinylene, or oligofluorene are all classes of materials,

and can include not only different substitutions around the phthaolcyanine rings, porphyrin rings, fullerenes, but also, different coordination environment for the metal compounds. For example, Werner states that metal phthalocyanine complexes or porphyrin complexes can be "in the form of oxo (Me=O), dioxo (O=Me=O), imino, diimino, hydroxo, dihydroxo, amino, or diamino complexes, without being limited to these." EX1005-56:29-34. And "the phthalocyanine or porphyrine complex can be partially hydrogenated" without disturbing the mesomeric ring system. *Id.*, 56:34-36.

47. Phthalocyanines and porphyrins can have different substitutions. For example, the outer aryl rings of the phthalocyanine complex can be substituted with different amounts of halides (see below for an example of hexadecachlorophthalocyaninatocopper (Cl_{16}-CuPc).



48. Fluoride substituted phthalocyaninato complexes were also known, for example, hexadecafluorophthalocyaninatozinc (F_{16}-ZnPc) n-doped with TTN was known. *See* EX2003-2016ChemReview, 13720 (citing Reference No. 114

published in 2005). Substitution with these electron withdrawing groups tends to lower the LUMO level of the resulting metal complexes, making them easier to be n-doped. *Id.*, 13720 (noting that ZnPc without substitution "has a substantially higher LUMO than F16-ZnPc, making it even more difficult to dope").

49. Additionally, substitution with electron withdrawing carbonyls, imino, phenyl type of ligands could also lead to more pi-electron distribution, a property that Werner apparently finds desirable. EX1005-56:34-36 (emphasizing the preference for not disturbing the mesomeric ring scheme, which distributes pi-electrons over the ring system). Hence, given the number of possible positions for substitution and the known type of electron withdrawing groups, the possible number of metal phthalocyanines is large. For instance, if we just look to substituting the phthalocyanine ring with Cl or F, for each peripheral ring that would lead to 4 possibilities for 1 halide per peripheral ring, 8 possibilities for 2 halides per peripheral ring + 16 possibilities for 3 halides per peripheral ring and 10 possibilities for 4 halides, for a total of 38 possibilities per ring. There are four peripheral rings, yielding 73815 combinations if all rings are different and each combination can have 6 different arrangements around the metal center (e.g., clockwise, ABCD, ABDC, ACBD, ACDB, ADBC, ADCB), resulting in a total of 442,890 possibilities. This number does not include combinations where two or more of the ring are the same.

50. Furthermore, Werner states that the preferred metals for phthaolcyanine is Mg, Zn, Fe, Ni, Co, Cu, Mn or V. EX1005-56:36-57:2. This, coupled with the number of possible phthalocyanines, yields over 3.5 million possible combinations.

51. In addition to the above, Werner also states that matrix materials can be "a compound with triarylamine or a spirobifluorene compound," materials with "electron-donating substituents such as alkyl or alkoxy groups," "[q]uinolinato complexes," "[p]henanthrolines" and "[h]eteroaromatics, in particular, triazole." EX1005-56 to-58. Those can easily yield another millions of possibilities.

52. Furthermore, while Werner mentions that BPhen or TAZ "can be used as a matrix material," Werner also notes that the matrix material "preferably consists entirely of a metal phthalocyanine complex, in particular ZnPc, a porphyrin complex, or a Buckminster fullerene, in particular fullerene C60." EX1005-58. A person of ordinary skill in the art would view this statement as suggesting that BPhen and TAZ could be used, but the preferred ones would be metal pthalocyanine or porphyrin complex or a fullerene, in particular ZnPc or C_{60}.

53. This suggestion becomes even clearer when the examples are reviewed, which involved only ZnPc and C_{60}. *See* EX1005-64 to -65 (Examples 1-3). Werner did not demonstrate n-doping for BPhen or TAZ using any of his enumerated donor compounds.

2. No Suggestion of Forming an Electron Conducting Layer using $W_2(hpp)_4$ with BPhen or TAZ

54. Given the number of possible metal donor complexes and matrix materials, unless Werner or another reference gives specific suggestion of combining $W_2(hpp)_4$ with BPhen or TAZ, a person of ordinary skill in the art would not have examined the combination in particular.

55. I understand that Dr. Rand testified that he did not think a person of ordinary skill in the art would claim whether a particular combination would work or not:

> Q: So would a person of ordinary skill in the art walk away to say that any of the metal complex that Werner listed is going to work with any of the matrix materials?
> A. I don't think any person of ordinary skill in the art would claim that something will or will not work. But I think upon reading this, they would have a reasonable expectation of success for a great many combinations of dinuclear metal complexes and matrix material hosts.

EX2042 [Rand Tr.], 146:21-147:9.

56. I also understand that Dr. Rand testified that there are "so many factors" and "numerous criteria" that would decide whether a particular combination would have a reasonable expectation of success or not:

> Q. How many of those millions of combinations would they 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 [Rand Tr.], 147:10-148:4. But Dr. Rand does not disclose any of those factors or criteria to explain why a person of ordinary skill in the art would have chosen the particular combination he proposed. In fact, Dr. Rand acknowledges that his obviousness analysis concerned whether a person of ordinary skill in the art could expect a reasonable expectation of success, but I understand that reason to combine and reasonable expectation of success are two independent aspects of the obviousness analysis:

> 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 W2(hpp)4 and BPhen in a lower vacuum.

EX2042 [Rand Tr.] at 207:6-13.

57. I note that Werner itself never specifically points to $W_2(hpp)_4$ and BPhen or TAZ as possible combinations. Notably, although Werner mentions the synthesis of a ditungsten compound with a substituted hpp ligand, (see EX1005-47, Example 5), Werner does not use it in its three "Application examples." This would suggest to a person of ordinary skill in the art that the ditungsten complex is not an effective donor.

58. As I have explained above (*e.g.*, paragraphs 20-26), at the time of the invention, based especially on Werner and co-inventors' discussions in other patents, a person of ordinary skill in the art would understand that the HOMO or ionization potential of a molecular n-dopant, such as $W_2(hpp)_4$, should be no lower than the LUMO or electron affinity of the organic material to be doped minus 0.5 eV.

59. I understand that Dr. Rand implied that when $W_2(hpp)_4$ is combined with BPhen, there may only be partial charge transfer for improved conductivity. EX2042 [Rand Tr.], 248:3-250:16. But that does not mean the LUMO level of the organic compound and the HOMO level of $W_2(hpp)_4$ can be far apart. As Werner and co-inventors disclosed in Novaled '129 and '541 patents, the suitable HOMO level of $W_2(hpp)_4$ is higher than or no more than 0.5 eV lower than the LUMO level of the organic compound.

60. Dr. Rand also implied that because "there are substantial error in the determination of a LUMO energy" and because ZnPc (with a nominal electron affinity of 3.5 eV compared to BPhen's 3.0 eV) was shown to be successfully doped by $Cr_2(hpp)_4$, "a POSA would still be inclined to attempt to see if there is success in the combination of W2(hpp)4 with BPhen" and that "they would have a reasonable expectation of success to improve the conductivity of such a mixture." EX2042 [Rand Tr.], 247:19-248:9, 132:20-134:18.

61. The claims, however, are not directed to simply a mixture of a metal complex and an organic compound, but "an organic electronic component," which I understand Samsung maps to an OLED and claim 9 of the '223 patent specifically requires it be "formed as an organic LED (OLED) which additionally comprises an organic emitting layer." Petition at 19; '223 patent, claim 9. Thus, the salient question, given Samsung's theory is, whether a person of ordinary skill in the art would have combined BPhen or TAZ with $W_2(hpp)_4$ for use an electron-conducting layer in OLEDs. Based on the disclosures in Novaled '129 and '541, and given the differences in the LUMO level of BPhen and TAZ and the HOMO level of $W_2(hpp)_4$, it is my opinion that a person of ordinary skill in the art would not.

62. In fact, when Novaled made a film of BPhen doped with 4-5 mol% $W_2(hpp)_4$, the resulting film's conductivity is "insufficient and very low" and "too

low for use in organic light-emitting diodes." EX2044 [US7,972,541], 4:44-45, 4:1-43, Table 1, 10:9-19. Moreover, the film was "stable only up to a temperature of 70° C," and a device with 4 mol% doped $W_2(hpp)_4$ in BPhen saw its brightness decreased from 4800 cd/m^2 to less than 1000 cd/m^2 (nearly 80% decrease) in less than one hour. *Id.*, 10:12-14, 10:48-52. A person of ordinary skill in the art would recognize that the combination is simply unsuitable for use in OLEDs.

63. The results were consistent with the understanding of a person of ordinary skill in the art at the time of the invention. As reflected in the 2007 Chemical Review by Walzer and co-authors, OLEDs were believed to "require … donors with a HOMO at about 3.0 eV." EX2002_2007WalzerChemReivew, 1244.[4]

[4] The values for the energy levels discussed here are absolute values, and the energy levels are negative.

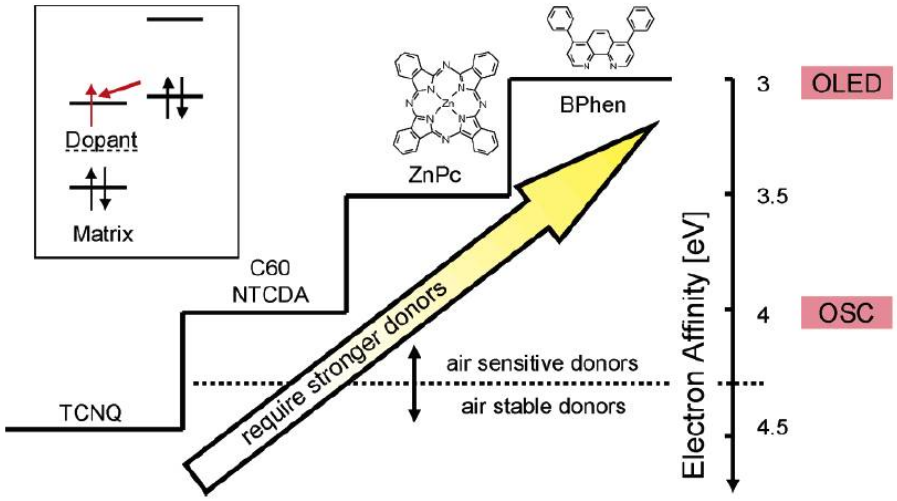


Figure 14. n-Type doping of molecular materials relevant for OLED and organic solar cells requires different electron affinities. While organic solar cells may be doped with donors having a HOMO around 4.0 eV, OLEDs require stronger donors with a HOMO at about 3.0 eV. Such materials are increasingly unstable in air, which requires handling under protective atmosphere only. The "staircase" shows typical host materials for OLEDs and OSCs.

(EX2002_2007WalzerChemReivew, 1244, Fig. 14).

64. Walzer et al. observed that "typical OLED electron-transporting materials … have a rather low electron affinity of around 3.0 eV." *Id.* This is reflected in the figure reproduced above, which shows that the LUMO of BPhen, is approximately 0.5 eV and 1.0 eV higher than those of ZnPc and C_{60}, respectively, such that donation of electrons from $W_2(hpp)_4$ to BPhen (and TAZ that has a LUMO level similar to or slightly higher than BPhen) are more difficult than for ZnPc and C_{60}.

65. As the authors of the 2007 Chemical Review article noted, for OLED materials with a LUMO of around 3.0 eV (or an electron affinity around 3.0 eV), the HOMO level of the electron donor should be about 3.0 eV. The HOMO level is the energy level of the highest occupied molecular orbital, and according to

Koopman's theorem, the first ionization energy of a molecule should theoretically be equal to the negative of the energy of the HOMO of the molecule (though they often differ in absolute values).

66. $W_2(hpp)_4$, was reported to have an onset of ionization in the gas phase at about 3.51eV and a peak gas phase ionization energy of about 3.76 eVs. *See* EX2004-Cotton-textbook, 770 ("the $W_2(hpp)_4$ molecule is the most easily oxidized molecule known: its δ ionization has an onset value of 3.51 eV and a peak (vertical) value of 3.76 eV").

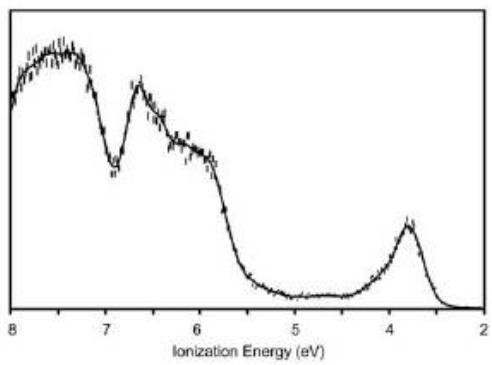
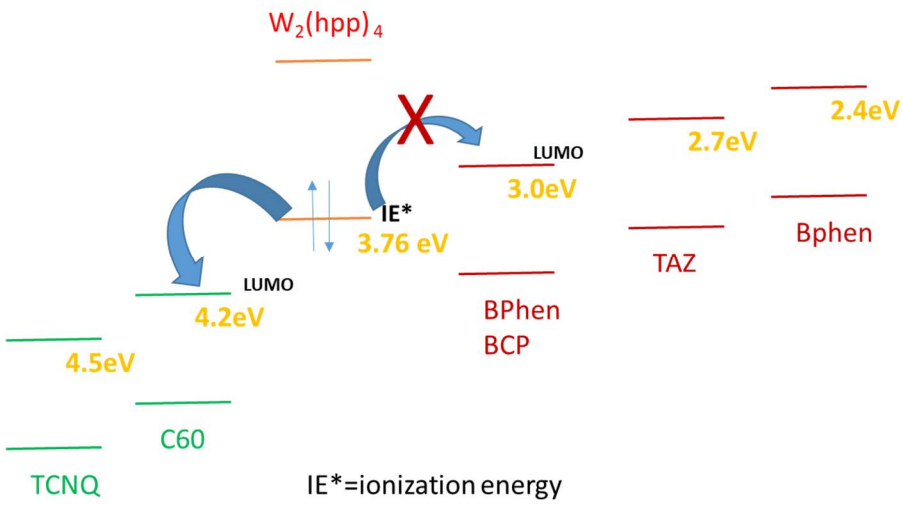


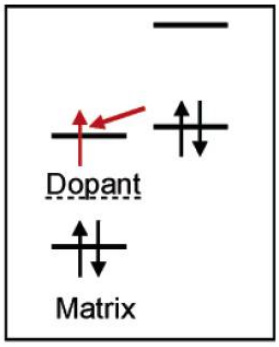
Fig. 16.45. The (He (I) PES of $W_2(hpp)_4$, supplied by Prof. D. L. Lichtenberger (University of Arizona).

67. Thus, its HOMO would be considered to have an energy level about 3.76 eV. That means, the electron transfer from $W_2(hpp)_4$ to BPhen (and TAZ), whether partial or complete, would be endothermic and unfavorable. In contrast, the electron transfer from $W_2(hpp)_4$ to C_{60} and TCNQ (two compounds that $W_2(hpp)_4$ was able to reduce) would be favorable. I also note that 3.76 eV is more than 0.5 eV lower than the LUMO of BPhen (2.4 eV to 3.0 eV).

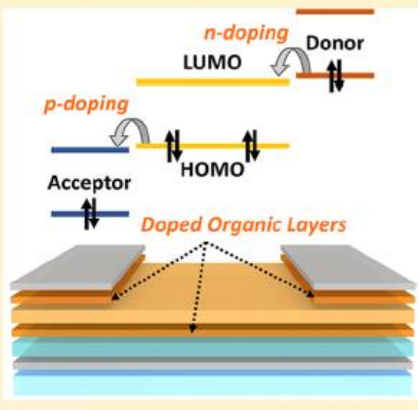


68. I also note that at the time of the invention, the literature discusses n-doping in terms of electron donation from an n-dopant's HOMO to a lower-lying LUMO of an organic material to be doped.[5] For instance, a person of ordinary skill in the art would understand that n-doping by $W_2(hpp)_4$ occurs by removing an electron from the donor (the energy for which is ionization energy) and injecting it into the LUMO of the matrix material, as illustrated below:

[5] And Werner's objective is to dope matrix materials with n-dopant. *See* EX1005-59.



(EX2002-2007-Chem-Review, 1244, Fig. 14 (noting "n-Type doping of molecular materials relevant for OLED and organic solar cells requires different electron affinities"[6] and "OLEDs require stronger donors with a HOMO at about 3.0 eV.")



(EX2003-Chem-Review, Abstract)

69. A person of ordinary skill in the art would therefore expect that electron donation from a donor to an acceptor would occur when the HOMO or

[6] Under the Hartree-Fock model, the LUMO orbital energy is a Koopman's approximation to minus the electron affinity (EA). *See* EX2013, introduction. For small molecules, the estimates are often inaccurate in terms of absolute values. *Id.*

ionization energy of the donor is higher than the LUMO energy level of the acceptor, such as when $W_2(hpp)_4$ is paired with C_{60} or TCQN. Alternatively, if the LUMO energy level of the electron acceptor is the same as or higher than the ionization energy of the donor, the difference in the energy levels should be relatively small, such as within 0.5 eV to make the electron injection not too energetically unfavorable. An energy difference of more than 0.5 eV as in the case of BPhen/TAZ and $W_2(hpp)_4$ would be viewed as too energetically unfavorable for electron transfer from $W_2(hpp)_4$ to BPhen/TAZ to occur. *See* EX2043 [US7,911,129], 10:56-60 ("For a molecular n-dopant, … 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)."), 10:61-63 ("the following relationships result from the requirement of the doping capability: … EA(O2)>IP(D)- 0.5 eV"); EX2044 [US 7,972,541] at 8:19-23 ("It is also proposed that the matrix material has an energy level for the lowest unoccupied molecular orbital (LUMO), which differs by 0-0.5 [e]V from the ionization potential (HOMO) of the dopant, preferably by 0-0.3 [e]V, particularly preferably by 0-0.15 [e]V.")

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.

71. I now provide references that indicate the LUMO levels of BPhen, TAZ, C_{60} and TCNQ.

72. The reported LUMO levels for BPhen differed quite significantly. For example, Novaled reported that the electron affinity for BPhen ranges "between 3.0 eV (estimation from ionisation potential and optical band gap) and 2.4 eV (estimation from cyclovoltammetry)." EX2043 [US7,911,129] at 10:50-54.

73. Li and co-authors reported 2.5eV as the LUMO level for BPhen. EX2005, Figure 4:

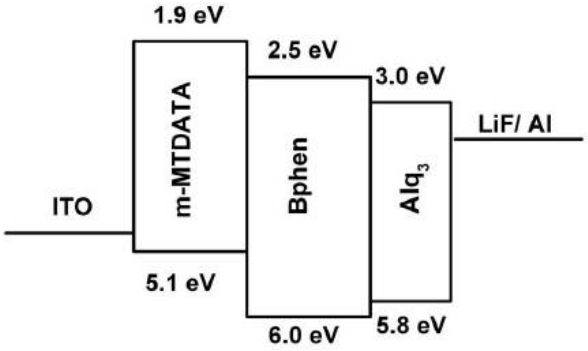


FIG. 4. Schematic LUMO and HOMO energy level diagram of three-layer OLED device.

74. Mr. Li obtained the 2.5eV value from a paper by Xin. EX2006, Fig. 7:

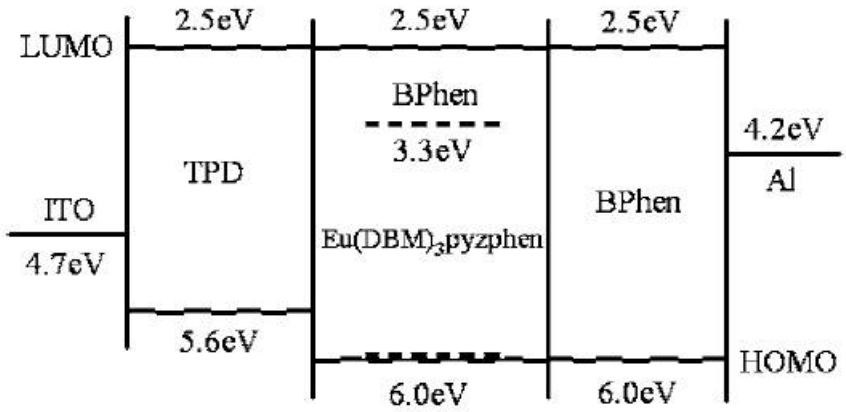


FIG. 7. Energy level diagram of the device used in this paper.

75. In contrast, Ma considered BPhen to have a LUMO of about 3.0 eV. EX1017, 813. Ma referenced a Naka paper for this value. I have reviewed the referenced paper, but could not find a value for the HOMO/LUMO levels of BPhen. EX2014. I also note that the 2007 Chemical Review paper by Walzer et al. regarded BPhen as having an electron affinity of about 3.0eV, though it is not clear what was the source of that value. EX2002-2007-Chem-Review, Fig. 14.

76. This variation in the exact LUMO level of BPhen, however, does not change my conclusion because even a 0.76 eV difference in the LUMO level of BPhen and the ionization energy of $W_2(hpp)_4$ would be considered too large and energetically unfavorable. My conclusion is consistent with Werner and co-inventor's recommendation that the electron affinity of the organic compound

should be greater than the ionization potential (HOMO) of the dopant minus 0.5 eV. EX2043 [US 7,911,129], 10:61-63. Because $W_2(hpp)_4$'s ionization potential is 3.76 eV, and BPhen's LUMO at 2.4–3.0 eV is less than 3.76-0.5=3.26 eV, a person of ordinary skill in the art would not combine $W_2(hpp)_4$ with BPhen. My conclusion is also consistent with Walzer's observation that donors with HOMO levels of 3.0 eV (and higher) are needed to n-dope materials such as BPhen suitable for OLED applications. And although a somewhat lower HOMO energy level[7] can result in some charge transfer, the energy difference between the HOMO of the donor and LUMO of the acceptor cannot be too large. That upper threshold on the HOMO-LUMO difference, according to Novaled '129 patent (which names Werner as a co-inventor), is 0.5 eV. EX2043 [US7,911,129], 10:56-64.

77. TAZ's LUMO was reported to be about 2.7eV. EX2007, Fig. 3.

[7] That is, the HOMO energy level of the dopant lies below the LUMO energy level of the matrix material to be n-doped.

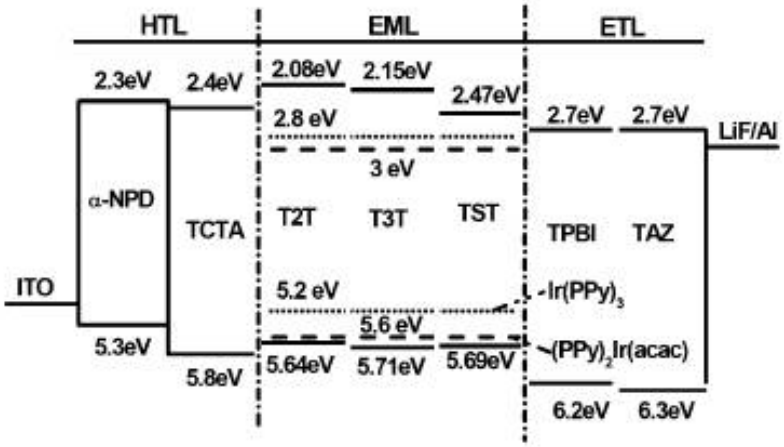


Fig. 3 Energy levels of the HTLs, EMLs, and ETLs used in this study.

78. There is thus again a large gap (>0.5 eV) in the LUMO energy level of TAZ and the ionization energy of $W_2(hpp)_4$. In light of the energy gap, a person of ordinary skill in the art would not have used $W_2(hpp)_4$ as a n-dopant for TAZ or expected that n-doping to be successful. I am not aware of any report of combining $W_2(hpp)_4$ with TAZ.

79. The estimated LUMO level of C_{60} was reported to be about 4.2 eV. *See* EX2011, Fig. 3 (see below). This value is consistent with that shown in Figure 14 of the 2007 Chemical Review Article by Walzer et al. EX2002-2007ChemReivew, Fig. 14.

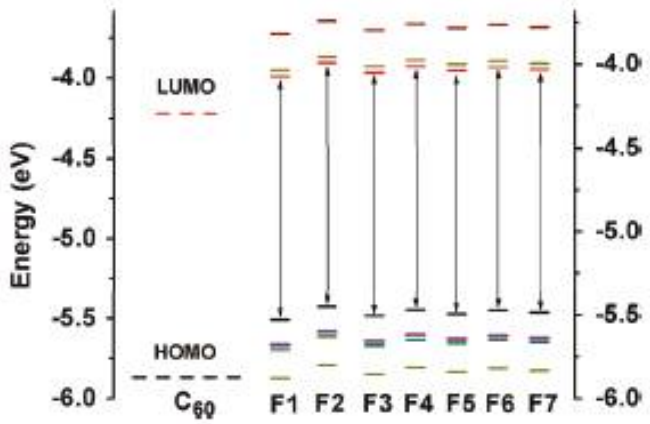


Figure 3. Energy levels of C_{60} and its derivatives calculated at the PBEPBE/6-311G(d,p) level. C_{60} has 5-fold degenerated HOMOs and 3-fold degenerated LUMOs, while the related energy levels for fullerene derivatives become nondegenerated. The HOMO and LUMO levels for the fullerene derivatives are denoted with arrow lines.

80. The LUMO level of TCNQ is about 4.5eV, as shown in Figure 14 of the 2007 Chemical Review article. EX2002-2007ChemReivew, Fig. 14.

81. That is, C_{60}'s and TCNQ's LUMO energy levels are below the ionization energy of $W_2(hpp)_4$, making the electron transfer from $W_2(hpp)_4$ to these compounds energetically favorable.

82. It was therefore not surprising that after Cotton, other research groups also studied doping of C_{60} with $W_2(hpp)_4$. *See* EX2003-2016-Chem-Rev at 13720 (citing references 121, 122 and 126 for using $W_2(hpp)_4$ as a dopant), 13746 (listing references 121, 122 and 126; the title for reference 122 indicates that it relates to doping of C_{60} and Reference 126 is the Cotton Science paper (EX2009); EX2016 (https://onlinelibrary.wiley.com/doi/10.1002/pssa.201330049) (abstract of Reference 121 indicates that authors studied C_{60} layer doped with $W_2(hpp)_4$).

Likewise, the reported reaction between $W_2(hpp)_4$ and TCNQ can be explained by the fact that the LUMO energy level for TCNQ (about 4.5 eV, *see* EX2002-2007ChemReview, Fig. 14) is below the ionization potential of $W_2(hpp)_4$.

83. In summary, given that the LUMO energy levels of BPhen and TAZ lie much higher than the HOMO of $W_2(hpp)_4$ (as reflected by its ionization energy) and that $W_2(hpp)_4$ was believed to donate electrons to organic materials by removing electrons from its HOMO for transfer (whether partially or completely) into the LUMO of the organic compound, a person of ordinary skill in the art would not view n-doping of BPhen or TAZ as an energetically favorable process or had a reasonable expectation that n-doping would be successful for use in an OLED application.

84. I understand that the ’223 patent disclosed that doping BCP (Compound V) with $W_2(hpp)_4$ led to higher current densities. *See* ’223 patent, 16:61-17:21. I understand that Samsung argues that this is evidence that a person of ordinary skill in the art would have had a reasonable expectation of success of doping BPhen or TAZ with $W_2(hpp)_4$. I understand that it is not appropriate to argue obviousness based on what the inventors did or observed. As I have explained above, without the teaching from the inventors, a POSITA would not believe that $W_2(hpp)_4$ is a suitable n-dopant for BPhen or TAZ in OLED

applications. That the inventors demonstrated something unexpected is not evidence of obviousness without that foresight.

85. Moreover, the LUMO energy level of Compound V (or BCP) was reported to be 3.0- 3.1 eV. *See* EX2035, Fig. 10); EX2036 [164IPREX1016], Fig. 4.

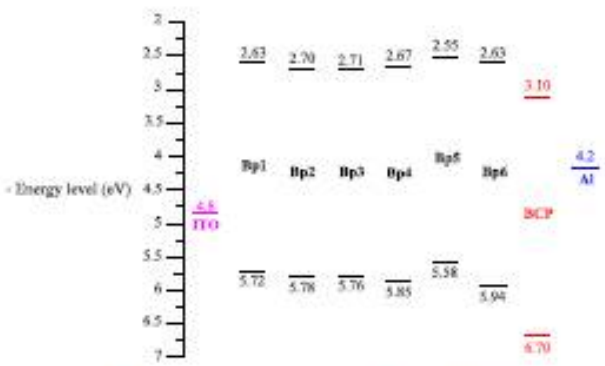


Figure 10. Comparison of the HOMO–LUMO energy levels of **P1–6** and those of BCP, indium tin oxide (ITO), and aluminum.

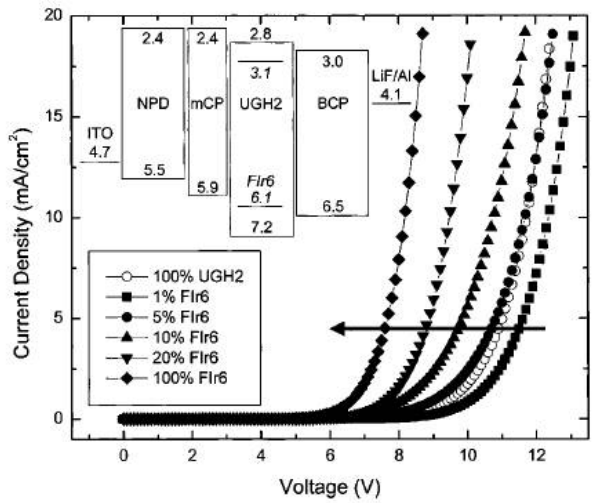


FIG. 4. $J-V$ characteristics for ITO/NPD (40 nm)/mCP (15 nm)/UGH2:x% FIr6 (25 nm)/BCP (40 nm)/LiF (0.5 nm)/Al (50 nm) OLEDs. The arrow points in the direction of increasing FIr6 concentration. **Inset**: Proposed energy level scheme for the device under zero applied bias.

86. If BPhen's LUMO level is 2.4 eV, then BPhen's and TAZ's LUMO levels are about 0.6-0.7 eV and 0.3-0.4 eV respectively above the LUMO level of BCP. If so, then the fact that the inventors succeeded in doping BCP with $W_2(hpp)_4$ also would not suggest to a person of ordinary skill in the art that they would have a reasonable likelihood to be able to dope BPhen or TAZ with $W_2(hpp)_4$, given the larger difference between the ionization energy of $W_2(hpp)_4$

and the LUMO energies of BPhen and TAZ, which makes n-doping energetically less favorable for BPhen and TAZ.

87. But even if the LUMO level of BCP is about the same as that of BPhen, the fact that the inventors succeeded in using $W_2(hpp)_4$ to dope BCP does not mean that a person of ordinary skill in the art, without the creativity and insight of the inventors, would have done the same. Nor does it mean that they would have had a reasonable expectation that the n-doping would result in something suitable for use in the OLED application, given the recommendations by Novaled ’129 and ’541 patents and the results reported by Novaled ’541 patent.

88. Samsung may argue that a person of ordinary skill in the art would have expected success because alkaline metals such as Li and Cs had been used to n-dope phenanthrolines and the known ionization energy of these metals are lower than $W_2(hpp)_4$. *See* EX2009_2002CottonScience, 1971 (“Lithium and sodium atoms have ionization enthalpies above 5 eV (5.39 and 5.14 eV, respectively), and only the heavier alkali metals have ionization enthalpies less than 5 eV, with the cesium atom having the lowest of all the elements at 3.89 eV[.]”).

89. But alkaline metals were thought to dope BPhen through a different mechanism, one via improving electron injection in OLED. *See* EX2002_2007ChemReview, § 2.2 (list “three different approaches to obtain efficient n-type doping,” first being “the use of alkali metals, which has [sic]

frequently been used to improve electron injection in OLEDs" and second being "the search for new molecular compounds that have extremely high-lying HOMOs"; use of $W_2(hpp)_4$ is an example of the second approach). The exact mechanism was not clear and could be complicated. *Id.*, 1244-45, § 2.2.1. In that regard, the Novaled researchers recognize the differences between doping by alkali metals and doping by molecular n-dopants. Thus, while, they recommend that for molecular n-dopant, the electron affinity of the organic material to be doped should not be more the 0.5 eV higher than the ionization potential of the dopant, they recognize that when Cs is used as the dopant, electron affinity of the organic material is only required to be greater than 1.9 eV:

> Consequently, the following relationships result from the requirement of the doping capability: IP(O**1**)<EA(A)+**0**.5 eV and/or EA(O**2**)>IP(D)**–0**.5 eV. The following applies in the case of doping with caesium: EA(O**2**)>1.9 eV.

(EX2043 [US7,911,129] at 10:61-64)

90. Furthermore, when metals of low work function improve electron injection into electron transporting layers, that was thought to be "due to the good match of their work functions with the lowest unoccupied molecular orbital level of the ETL." EX2010_2008JAppPhys, 104502-1. "The widely measured work function of lithium is about 2.95-3.1 eV," (*see* EX2037_2016_SEI_tunneling_JPS, 225), though some put it as low as 2.49 eV or so (*see* EX2038_1949PhyReview,

abstract). This energy range, from about 2.5 eV to about 3.1 eV, matches well with the reported BPhen LUMO energy level (2.4-3.0 eV). In other words, when BPhen is doped by an elemental metal such as Li, the relevant parameter is the work function of the metal, and not its ionization energy. Additionally, as even the brief summary in the 2007 Chemical Review article indicates, the exact doping pathway with alkali metal was unclear, and there could be other factors that make the doping energetically more favorable. EX2002, 1244-45. But none of those factors appear at issue for molecular n-dopants with high-lying HOMOs, such as $W_2(hpp)_4$. That is, the successful doping of an organic material with Li or Cs would not indicate to a person of ordinary skill in the art that the same would be expected with a molecular dopant $W_2(hpp)_4$.

91. $W_2(hpp)_4$ was also reported to destroy organic compounds. For instance, the Cotton group reported that when $W_2(hpp)_4$ reacted with methylene chloride, it formed $W_2(hpp)_4Cl_2$, indicating that the CH_2Cl_2 molecule was destroyed in the reaction. EX2008_Cotton_Inorganic_Chem_Comm, 123-124.

92. Werner, however, states that it has "the object of specifying metal complexes as n-dopants for doping an organic semiconducting matrix material, … without adverse effects on the matrix material, …." EX1005-5:21-28. A reagent that would potentially destroy a small molecule is not one that would be expected to lead to use "without adverse effects on the matrix material." Hence, given

Werner's stated object and $W_2(hpp)_4$'s known property, a person of ordinary skill in the art would be wary of combining $W_2(hpp)_4$ with small organic molecules such as BPhen and TAZ. Nor is there any evidence that they would reasonably expect to obtain an electron-conducting layer with sufficiently high conductivity suitable for OLED applications.

93. I also understand that Dr. Rand suggests that a person of ordinary skill in the art would "be open to attempting numerous combinations, stoichiometries, mixing ratios of the two compounds to explore that parameter space completely." EX2042 [Rand Tr.], 250:3-11. I understand that Dr. Rand has no knowledge of the loading level of W2(hpp)4 in BPhen before acceptable film was no longer possible, the amount of loading needed to obtain appreciable charge transfer, the film quality at that loading level, or the adhesion of the film to adjacent layers at that loading. *Id.*, 251:1-253:16.

94. I understand that 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. As such, Dr. Rand's suggestion that a person of ordinary skill in the art would simply try numerous variations to arrive at a successful result is evidence of non-obviousness, and not obviousness.

95. In summary, Samsung and Dr. Rand do not appear to have considered the specific electronic properties of the organic compounds and metal complexes, and used instead the 223 patent's disclosure as a roadmap to cherry-pick $W_2(hpp)_4$ and BPhen/TAZ. Without the inventors' teaching, however, it is my opinion that a person of ordinary skill in the art would not have chosen those specific combinations for *e.g.*, the OLED applications, especially in light of the differences in the organic complexes' LUMO energy levels and the ionization potential of $W_2(hpp)_4$, and the disclosures in Novaled '129 and '541 patents.

B. Co-Evaporation of $W_2(hpp)_4$ with BPhen or TAZ

96. Werner also does not suggest using joint evaporation to combine BPhen or TAZ with $W_2(hpp)_4$. In particular, in the section "Implementation of doping," Werner lists five doping methods, and only one of them is "[c]o-evaporation in vacuum with a source for the matrix material and one for the dopant." EX1005-59:13-30. In the "Application examples," when Werner states that "[t]he provided metal complex is evaporated simultaneously with the matrix material," he also states that "the matrix material is phthalocyanine-zinc or fullerene C_{60}" in those examples. EX1005-64 ("Application Examples"), EX1005-64:10-12 (describing methods for the application examples). Thus, reading Werner as a whole does not suggest to a person of ordinary skill in the art to jointly evaporate $W_2(hpp)_4$ with BPhen or TAZ.

97. Furthermore, even in those application examples, a person of ordinary skill in the art would recognize that the metal complex and the matrix material are not all evaporated simultaneously. In Example 3, for example, "a pure layer of the fullerene was produced by sublimation in high vacuum" at first. EX1005-65:25-26. It is clear from the context that fullerene was not doped until "cobaltocene was thermally sublimated" and "deposited on the surface of the fullerene layer [to] form[] a thin highly doped layer there." EX1005-65:24-31 ("A layer of fullerene C_{60} was doped with the metal complex cobaltocene. First, a pure layer of fullerene was produced by sublimation in high vacuum. … 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."). That is, fullerene and cobaltocene were deposited in sequence, not simultaneously, following method (b) for "Implementation of doping." EX1005-59:19-21 ("Sequential deposition of the matrix material and the n-dopant on a substrate with subsequent diffusion of the dopant, in particular through thermal treatment"). Dr. Rand agrees that sequential evaporation is used in this example. EX2042 [Rand Tr.], 203:13-19 ("Q: And the specific examples of processing conditions include sequential deposition; correct? A: On page 56 in the

B section, that includes sequential deposition and that is also one of the examples later on; example 3 on page 62, yes.”).

98. Hence, Werner as a whole suggests that the specific method of deposition would depend on matrix materials and metal complexes, and does not suggest that $W_2(hpp)_4$ should be jointly evaporated with BPhen or TAZ.

99. At the time of the invention, the only reported reaction conditions with $W_2(hpp)_4$ were carried out in solutions. For instance, the Cotton group explored the use of $W_2(hpp)_4$ as a strong reducing agent with methylene chloride (CH_2Cl_2), fullerene C_{60}, and TCQN. Reducing a material means electrons are donated from the reducing agent (e.g., $W_2(hpp)_4$) to the matrix materials, a process that can lead to doping of the matrix materials. But all the reactions took place in solutions. EX2008, 122 (see “Experimental” section: reaction between $W_2(hpp)_4$ and CH_2Cl_2 is carried out in CH_2Cl_2, a common solution; reaction with C_{60} was carried out in a toluene solution; and reaction with TCQN is in a THF solution).

100. The Cotton group concluded that $W_2(hpp)_4$ “is a strong reducing agent with an enormous potential for use on organic substrates ***in organic solvents***.” EX2008 at 124. And they recommended exploring using $W_2(hpp)_4$ in “chemistry in living organisms.” *Id.* at 125. Studies for living organisms are done in liquid phase, not gas phase. That is, at the time of the invention, the art does not disclose,

suggest or provide any motivation to react $W_2(hpp)_4$ with an organic compound in gas phase, let alone through joint vaporization.

C. Coordination of BPhen or TAZ to the Tungsten Metal Center in $W_2(hpp)_4$

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).

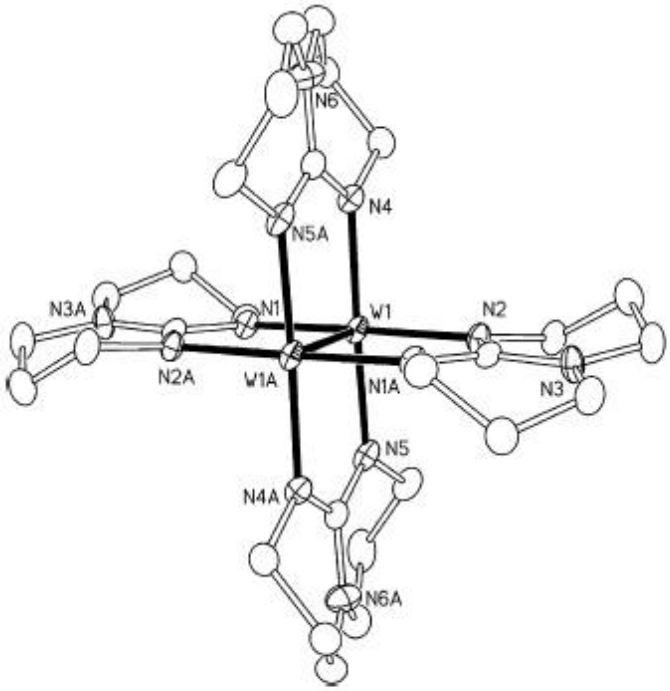


Fig. 1. An ellipsoid plot of $W_2(hpp)_4$, **1**, with atoms drawn at the 30% probability level. All hydrogen atoms have been omitted for clarity.

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*.

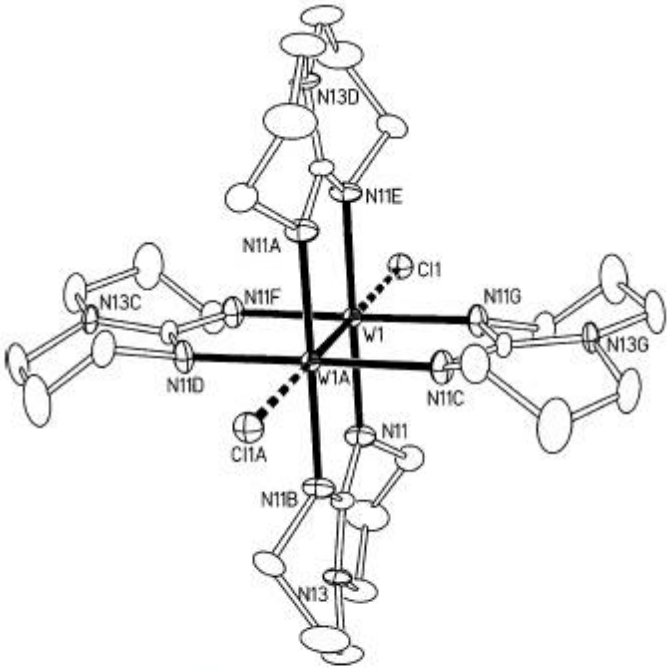


Fig. 2. Displacement ellipsoid plot of one orientation of the disordered $W_2(hpp)_4Cl_2$ molecule in **2** · $4CH_2Cl_2$. Atoms are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

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 $W_2(hpp)_4$ and $W_2(hpp)_4Cl_2$ 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 $W_2(hpp)_4$ or $W_2(hpp)_4Cl_2$. Instead, they would suggest no binding of these ligands to the tungsten center.

104. The coordination of electrophilic (electron poor) $Rh_2(O_2CCF_3)_4$ with hexamethylbenzene does not suggest that similar coordination would occur in the electron rich ditungsten compound. Rather, a person of ordinary skill in the art would understand that $Rh_2(O_2CCF_3)_4$ and $W_2(hpp)_4$ complex have completely different electronic and likely steric properties.

105. Unlike the electron rich $W_2(hpp)_4$, the metal centers in $Rh_2(O_2CCF_3)_4$ are electron deficient because the trifluoroacetate ligand is understood to be highly electron withdrawing. The rhodium center was therefore understood to be electrophilic and would more readily accept pi-electron donation from the aromatic rings.

106. When tungsten is coordinated to carboxylates with electron-withdrawing substituents, its axial positions can also coordinate to electron-donating solvent molecules, such as THF, though there is no report of arene-adducts with tungsten carboxylates. See EX2004_Cottonbook, 187-188.

107. The δ ionization of $W_2(O_2CCF_3)_4$ appears at 7.39 eV. In contrast, the gas phase ionization of $W_2(hpp)_4$ starts at 3.51eV. EX2004_Cotton_textbook, 186, 189. This demonstrates that the ligands have a profound effect on the electronic

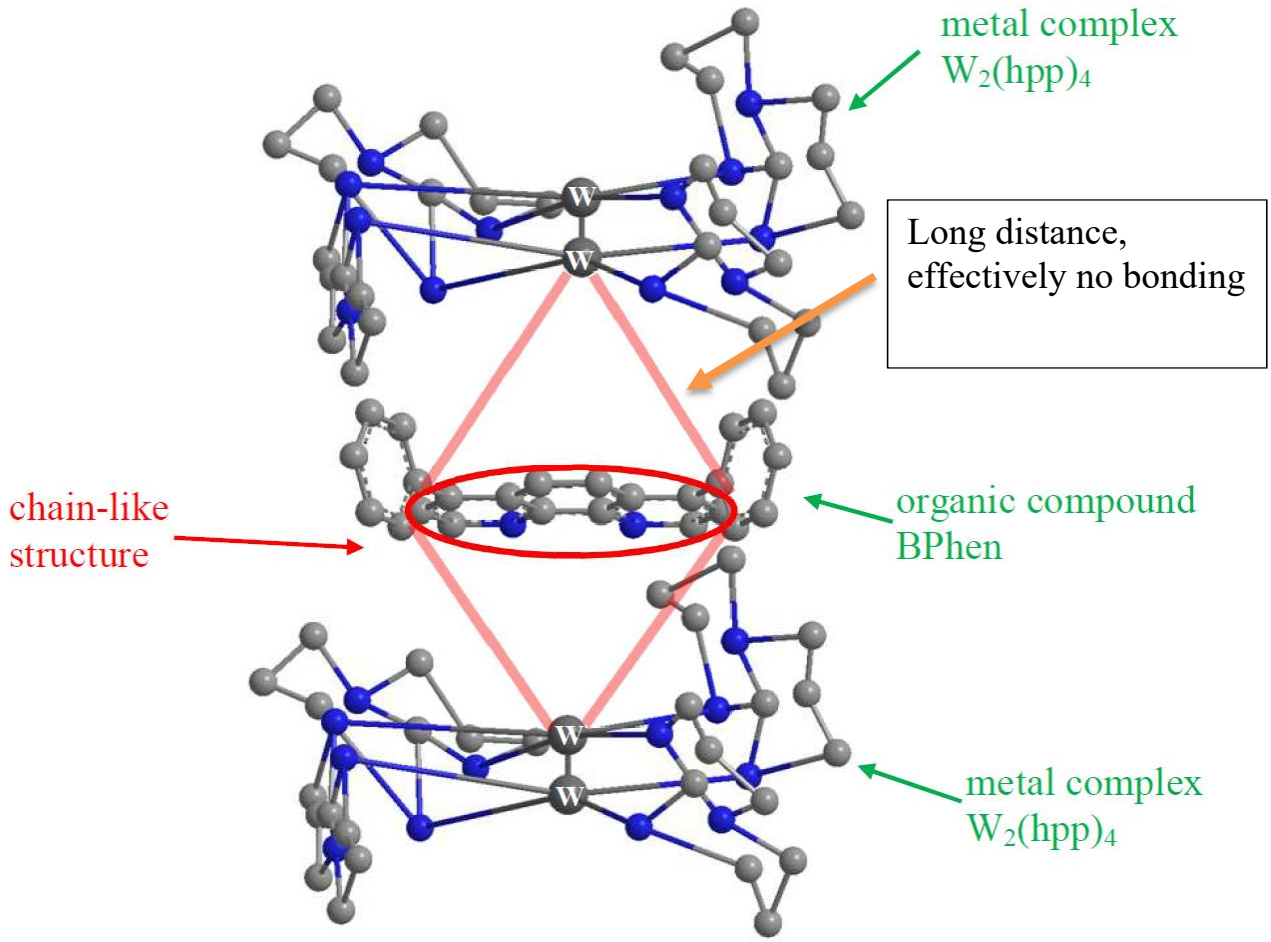
properties of the metals, making the metal center more electrophilic or more electron rich.

108. Hence, given that $W_2(hpp)_4$ is very electron rich compared to $Rh_2(O_2CCF_3)_4$ or even $W_2(O_2CCF_3)_4$, a person of ordinary skill in the art would not expect $W_2(hpp)_4$ 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 $W_2(hpp)_4$ to behave like the electrophilic $Rh_2(O_2CCF_3)_4$ 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 $W_2(hpp)_4$, on the other hand, has the four more bulky hpp ligands surrounding the metal center.

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.



111. The bonding strength between W's pi*-orbital and the aryl ring's pi-electrons drops off exponentially as the distance between the metal center and the aromatic ring increases. As such, a person of ordinary skill in the art would not view a configuration above, with the tungsten center and the aryl ring far apart, as involving coordination of BPhen to the tungsten center.

112. At deposition, Dr. Rand states that when he drew the analogy between the dirhodium complex and the ditungsten complex, he was trying to make the point that "these rhodium complexes with dinuclear cores, much like the dinuclear core of a ditungsten complex, can coordinate to a molecule such as hexamethyl benzene, then it would seem there is ***a chance of success*** that it would coordinate to a compound like BPhen, which not only possesses phenyl ring constituents, but also the phenanthroline unit." EX2042 [Rand Tr.], 193:13-194:1. But as I have explained above, a person of ordinary skill in the art would recognize the large differences in steric and electronic environment between Cotton's dirhodium compound and $W_2(hpp)_4$ as well as the difference between hexamethylbenzene and BPhen to reasonably expect any coordination between

113. Dr. Rand also has no evidence that the picture he drew on page 43 of his declaration would have existed in the mixture of BPhen and $W_2(hpp)_4$. EX2042 [Rand Tr.], 194:13-195:12. He did no experiments and performed no simulation or calculation. *Id.*, 199:14-19 ("Q: Did you conduct any calculation or experiment to determine the type of interaction between W2(hpp)4 and BPhen? A: I have not conducted any experiment to determine the nature of the interaction between BPhen and W2(hpp)4."); 199:9-13 ("Q: So you did a simulation? A: Characterization does not have to be a simulation.").

114. Thus, he tried to de-emphasize the only structure he drew for the alleged coordination, and claimed his "intention was to show an example of an interaction without being specific, without being limited to the option for others, nor limiting that it has to be a Pi-interaction." *Id.*, 196:3-9. But Dr. Rand offered no other forms of alleged coordination. *Id.*, 195:22-196:2 ("So when it comes to exactly the tungsten complex and BPhen, yes, this is the only illustration that's in the declaration."). And Dr. Rand is not willing and/or able to characterize the interaction. *Id.*, 197:22-198:15.

115. Dr. Rand concedes, however, that the type of interactions will depend on the processing condition:

> 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, a lot of] interactions in some other, under some other process conditions; right?
> A. Yes.

EX2042 [Rand Tr.], 199:20-200:6.

116. He also concedes that not all co-evaporation conditions will result in interactions between the BPhen and W2(hpp)4:

> Q. Okay. What is the joint vaporization conditions he 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 [Rand Tr.], 200:14-201:2.

117. But Dr. Rand has not provided any evidence on the exact process conditions that a person of ordinary skill in the art would have used in order to obtain the type of interaction he depicted on page 43 of his declaration. Nor has he shown what other interactions might exist between BPhen and $W_2(hpp)_4$. Thus, he cannot show that the claimed coordination necessarily flows from or is the natural result of co-evaporating BPhen and $W_2(hpp)_4$.

118. In that regard, I also want to comment on the meaning of the term "the organic compound coordinates to the metal complex …." As a preliminary matter, I disagree that the coordination has to be via a dative bond as Samsung argues in the district court. For example, the '223 patent teaches that "[t]he coordination of the organic compound to the central atom can be effected directly via a further atom or else also via an aromatic system." EX1001, 2:19-21. A person of ordinary skill in the art would understand that coordination of an organic

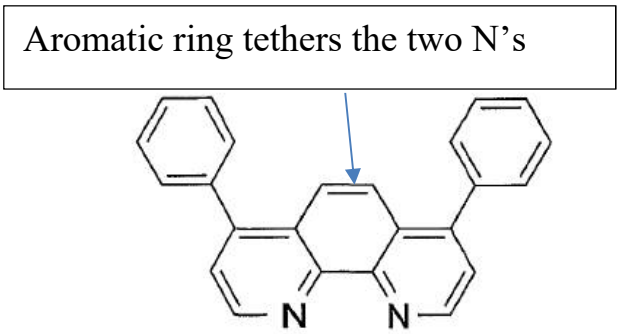
compound to a central atom (*i.e.*, metal center or metal atom) of a metal complex via an aromatic system could be via pi-bonding, ionic interactions, electrostatic interactions, or other non-dative bonding. As an example of coordination via a non-dative bond, the '223 patent specifically mentions a paper by Cotton, where the aromatic ring interacts with the rhodium metal center through pi-bonding. *Id.*, 2:28-38; Pet. 34 (annotated Cotton Figure 1 by Samsung). But I also disagree that a person of ordinary skill in the art would regard any interaction between the metal complex and the organic compound as satisfying this coordination requirement. Instead, the term "coordinates" connotes interactions between the metal center and the organic compounds, *e.g.*, interactions between filled and vacant orbitals of the metal center (*i.e.*, central metal atom) and the organic compound, and/or electrostatic or ionic interactions between positively charged metal center and negatively charged moieties in the organic compound. '223 patent, 2:17-18 ("the organic compound coordinates to the metal atom"), 2:19-21 ("coordination of the organic compound to the central atom …"); 2:45-47 ("each of the two central atoms has a coordination site ….").

119. In summary, given the state of art, a POSITA would not have viewed that BPhen or TAZ would coordinate to the ditungsten atoms, certainly not in the manner suggested by Samsung and Dr. Rand.

D. A Person of Ordinary Skill in the Art Would Not Expect BPhen or TAZ to Form Chain-Like or Network-Like Structure with $W_2(hpp)_4$

120. As explained above, at the time of the invention, a person of ordinary skill in the art would not have expected BPhen to coordinate to the $W_2(hpp)_4$ given the electron richness of the tungsten center. It certainly would not coordinate to BPhen in the manner suggested by Samsung to form chain-like or network-like structures.

121. A person of ordinary skill in the art would also have expected that if BPhen coordinates to a metal center, the two nitrogen atoms of BPhen would coordinate to the same metal center, instead of coordinating to two different metal centers. This is because the two nitrogen atoms are tethered together by a rigid, fused aromatic backbone and the two nitrogen atoms are therefore fixed in positions.



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

122. This geometry makes the two nitrogen atoms in BPhen more suitable to form a relatively stable five membered ring around a same metal center if the metal would coordinate to it in the first instance. For example, for instance, in a 2005 paper, researchers examined the coordination chemistry of a bis-phenanthroline compound 1 (biphen), among others, with copper(I). *See* EX2028 _Heterocycles 2005, abstract, 552.

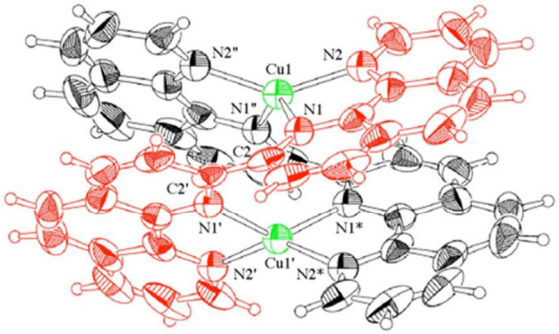


Figure 4. ORTEP drawing of $[Cu_2\mathbf{1}_2](PF_6)_2$. Counter anions are omitted for clarity. Four phen units are all related to symmetric operations.

123. The crystallography of the isolated products show the structure above. EX2028, 556. In the compound, the two nitrogen atoms on the same phenanthroline ring coordinate to the same copper center, and the two phenanthroline rings in the same molecule coordinate to different single-nuclear copper centers. The crystal structure also does not show any interactions between the copper metal center and the pi-bonds of the phenanthroline rings.

124. Paddlewheel structures formed by bipyridine ligands also strongly suggest that the two nitrogen atoms of BPhen would bind to a single metal center.

In bipyridine compounds, two bipyridyl rings are linked together through a C-C single bond, which actually affords it with more degrees of rotational freedom than the fused BPhen ring. Nevertheless, even with that degree of freedom, bipyridyl ligands bind to a single Rh center in Rh2 paddlewheel structures. *See* EX2018-Crawford-1997, Figs. 1-3; EX2017-Crawford1993, Figs. 2-4.

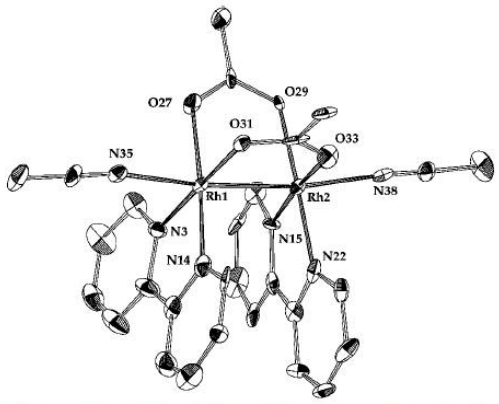


Figure 1. ORTEP representation of the cation of complex **6a** at the 50% probability level. Carbon atoms are numbered sequentially around from N and O atoms.

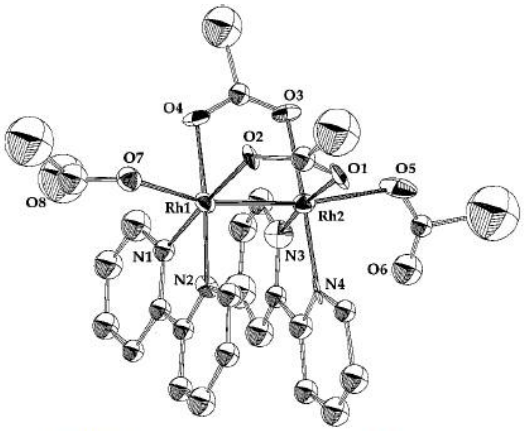


Figure 2. ORTEP representation of complex **9**; F atoms are omitted for clarity.

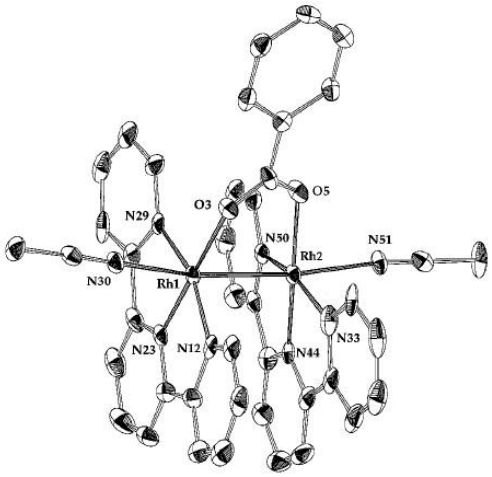


Figure 3. ORTEP representation of the cation of complex **16** at the 50% probability level. Carbon atoms are numbered sequentially around from N and O atoms, and hydrogen atoms have been omitted for clarity.

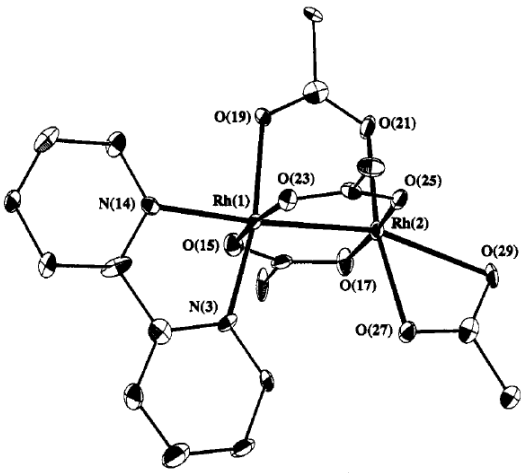


Figure 2. ORTEP representation of complex **3** at the 50% probability level. Carbon atoms are numbered sequentially clockwise from N(3) to N(14). Other carbon atoms are numbered sequentially from labeled atoms.

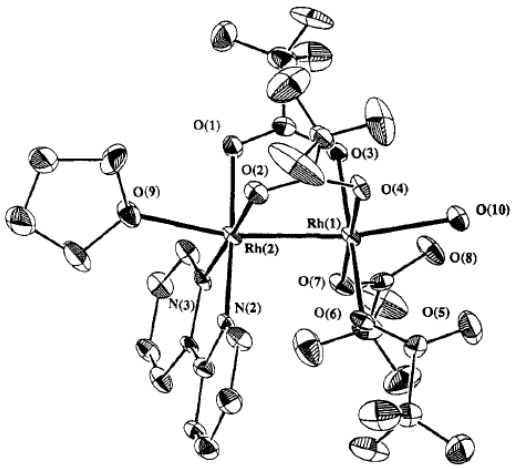


Figure 3. ORTEP representation of complex **5** at the 50% probability level. Carbon atoms C(8)–C(17) and C(19)–C(22) belong to bpy and THF rings; respectively. The other carbons are carboxylate atoms.

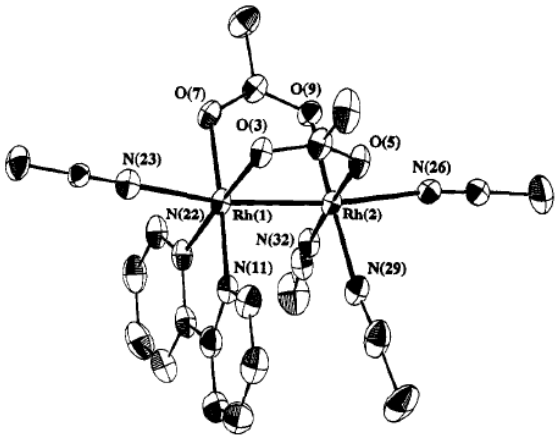
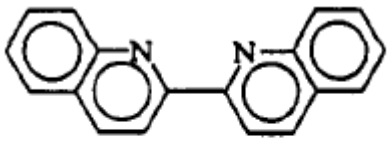
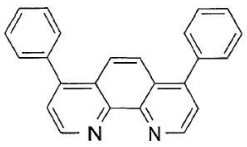


Figure 4. ORTEP representation of $[Rh_2(OAc)_2(bpy)(MeCN)_4]^{2+}$, the cation of complex **7**, at the 50% probability level. Carbon atoms are numbered sequentially clockwise from N(11) to N(22). Other carbon atoms are numbered sequentially from labeled atoms.

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 positon of the Rh centers. *Id.*



bqn



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

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.

127. This supports Pictiva's theory and the '223 patent's teaching that two heteroaromatic rings linked by C-C single bonds and spacer moieties can facilitate coordination to different metal centers. But this does not support Samsung's theory that a person of ordinary skill in the art would expect the two nitrogen atoms on the same phenanthroline ring to bridge two different metal centers, or in the case of a paddlewheel complex, any metal center.

128. Other studies also consistently showed that ***when and if*** BPhen coordinates to a metal complex, the two nitrogens in the phenanthroline ring would coordinate to the same metal center.

129. For example, in EX2029, it was shown that the two nitrogen atoms in the phenanthroline moiety coordinate to the same single-nuclear Mn(II) metal center. EX2029, abstract. Additional examples showing the same coordination chemistry can be seen from EX2030 Fig. 1 (each phenanthroline ring coordinates to the same Fe(II) metal center); EX2031 (each phenanthroline ring coordinates to

a Ni(II) or Fe(II) center); EX2032 (each phenanthroline ring coordinates to a Ru(II) center).

130. Thus, given the state of the art at the time of the invention and the knowledge of BPhen coordination to metal centers, when a person of ordinary skill in the art wanted to form a chain-like structure between a metal complex and an organic compound with the claimed structure, they would not have chosen BPhen because BPhen, if it coordinates to a metal center, it would coordinate to only a single metal center and not two metal centers. Additionally, as I noted above, BPhen is unlikely to form a paddlewheel structure given its structural rigidity and the consequent steric repulsions with the hpp ligands on the tungsten metal center.

131. A person of ordinary skill in the art also would not have performed the reaction with $W_2(hpp)_4$ in gas phase as opposed to in an inert solution, because at the time of the invention, only solution-based reactions had been reported for $W_2(hpp)_4$.

132. Samsung also argues that "a POSA would have been motivated to combine Method (a) [joint evaporation] and Method (e) [solution-based process] … to prepare a mixture of matrix material and dopant …." Pet. 41. Samsung argues that this "would allow for $W_2(hpp)_4$ and BPhen to be in close proximity in the gas phase, so as to allow for BPhen to bridge two (or more) $W_2(hpp)_4$ molecules …." *Id.* I do not understand the logic behind this conclusion.

133. By dissolving the metal complex and the BPhen in a solution and then vaporizing the resulting mixture, the possibility for a $W_2(hpp)_4$ molecule to collide with BPhen decreases significantly as $W_2(hpp)_4$ will more likely collide with a solvent molecule existing in much higher numbers than the solute BPhen. For example, Professor Cotton explained that $Rh_2(O_2CCF_3)_4$ were prepared using sublimation-deposition to avoid having solvent molecules compete with weak donor ligands for axial coordination. EX2004_Cottonbook, 467. This would suggest to a POSITA that solvents suppress rather than promote coordination of ligands to the metal center. That is, the use of solvents reduces, and not increases, the likelihood of $W_2(hpp)_4$ coordinating to BPhen due to joint vaporization.

134. Furthermore, to the extent that any "coordination" between BPhen and $W_2(hpp)_4$ occur in the solution phase, that coordination would not be "due to joint vaporization" as required by claim 2.

135. A person of ordinary skill in the art therefore would not have combined co-evaporation and solution based process, as Samsung suggests, because it would not lead to better ligand coordination due to joint vaporization. A person of ordinary skill in the art would also understand that, even though Werner claims that the different methods may be combined, these methods are not modular, and cannot be combined at will.

136. Samsung also argues that a POSITA would have evaporated $W_2(hpp)_4$ and BPhen from a single crucible as opposed to two crucibles. Pet. 41-44. Even if true, that does not change the fact that at the time of the invention, there was no suggestion of using evaporation to react or dope an organic compound with $W_2(hpp)_4$ or that such a process condition would necessarily lead to the claimed coordination.

137. Additionally, Samsung and its expert do not explain how a person of ordinary skill in the art could control the respective rates of deposition for $W_2(hpp)_4$ versus BPhen, given their disparate enthalpy of evaporation. When evaporating from two different sources, each source can be controlled independently with different temperatures, for example, to control the deposition rates.

138. The Werner II reference (EX1009, U.S. Publication No. 2007/0249148) does not support Samsung's conclusion that $W_2(hpp)_4$ and BPhen could be deposited from a single source. Specifically, Werner II targets co-deposition of materials whose "sublimation/vaporization temperatures … differ by less than approximately 50º C, preferably less than approximately 20º C." EX1009, [0021]; *see also* [0032] (mixture of tetracene and tetrafluoro-tetracyano-quniodimethane), [0034] (mixture of two organic compounds NTCDA and LCV). There is no evidence that $W_2(hpp)_4$ and BPhen (or TAZ) are such a pair.

139. Moreover, Werner II warns against mixing strong donor-acceptor charge-transfer pairs. For example, co-evaporation of premixed m-MTDATA and F4-TCNQ was either unsuccessful or no doping occurred. *Id*., [0039]-[0041], [0043]-[0044]. F4-TCNQ, a strong electron acceptor, was a known p-dopant for m-MTDATA. EX2019, abstract (describing an OLED device with an F4-TCNQ-doped m-MTDATA layer). Thus, if as Samsung argues, $W_2(hpp)_4$ and BPhen was expected to react, a person of ordinary skill in the art who had read Werner II as a whole would not have premixed them in light of Werner II's warning, contrary to Samsung's argument.

140. Samsung also argues that a POSITA would have modified deposition parameters to obtain "a more uniform layer of coordinated BPhen and $W_2(hpp)_4$" to "allow for the more efficient transfer of electrons through that layer." Pet. 44. That understanding, however, would have come from the inventors. EX1001, 1:60:2:16. For example, the inventors teach that "[t]he compounds are deposited in the coordinated state, so that a layer is formed, in which a short-range order is provided." *Id*., 1:64-66. The inventors then explain that "[b]y virtue of the coordination of the organic compound on the metal complexes, and the associated overlap of the orbitals, additional electrons can be transferred from the metal to the ligand via a metal complex-ligand-electron transfer[.]" *Id*., 2:6-10. "These electrons can be available for electron transportation in the organic electronic

component," and "[b]y increasing the 'free' electrons, the electron conductivity in the component is significantly improved." *Id*., 2:11-14. "This leads to an increase in efficiency and serviceable life of the organic electronic component." *Id*., 2:14-15. Thus, the stated reason for making the modification did not come from the prior art, but from the inventors' insight. Nor has Samsung or Dr. Rand provided any process condition under which the alleged uniformity would have obtained. Again, a process is not obvious if a person of ordinary skill in the art would have had to vary all parameters in order to arrive at the one successful combination.

141. Samsung also urges the use of low vacuum to evaporate $W_2(hpp)_4$ and BPhen, citing the Shtein paper. Pet. 44-45. The Shtein paper, however, describes depositing a single material, not a mixture of materials. EX1008, 4012 ("Experiment": depositing "thin films of Alq_3"). There is no evidence that the method would have worked with a mixture of materials with substantially different sublimation or vaporization temperatures.

142. Samsung argues that OVPD's higher vapor pressure could facilitate the coordination chemistry. A person of ordinary skill in the art would not have expected OVPD to facilitate coordination. In OVPD, "a hot, nonreactive carrier gas is used to transport an organic vapor toward a cooled substrate onto which the organic materials condense." EX1008, 4006. Under the OVPD condition, both the metal complex and the BPhen molecule would thus encounter inert gas molecules

existing in far larger numbers. The metal complex and BPhen would then collide more frequently with the inert gas molecules that are present in far large numbers, resulting in fewer, rather than more, productive collisions between BPhen and $W_2(hpp)_4$.

143. In summary, at the time of the invention, there was no evidence that a person of ordinary skill in the art would have expected BPhen to coordinate to more than one metal center if at all, or that they could have reacted BPhen with $W_2(hpp)_4$ through vaporization as opposed to a solution-based approach that was done for all the $W_2(hpp)_4$-based reactions up to that point.

E. Werner Does Not Disclose or Suggest Cross-Linking

144. Werner does not mention forming chain-like or network-like structures between its metal complexes and matrix materials. Werner also does not mention cross-linking. And neither Samsung nor its expert has pointed to anything in the prior art that taught "the degree of cross-linking is related to electron conductivity and that the ratio between the metal complex and the organic compound during vaporization affects the electron conductivity of the electron-conducting layer." Pet. 53.

145. It is my opinion that the above-stated knowledge came from the inventors. See Pet. 52-53 (citing the '223 patent's disclosure for the teaching that "[t]he formation of chain-like or network-like structures enable additional electrons

to be able to be transferred from the metal complexes to the organic compounds"). And because others did not have the inventors' insight, they would not have had any reason to modify reaction conditions to adjust the cross-linking density.

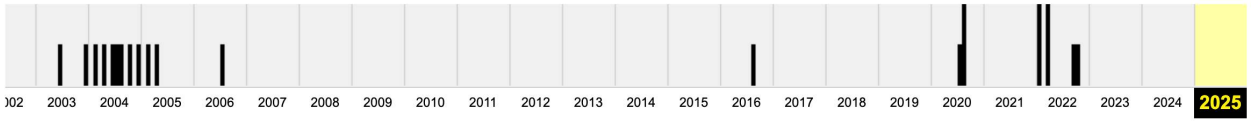
146. Moreover, as I explained above, BPhen is not even likely to bind to $W_2(hpp)_4$ that has a paddlewheel structure because the steric repulsion between the rigid fused ring system and the bulky hpp ligand would prevent BPhen from approaching the axial position to coordinate, similar to what is observed for a Rh2-complex. *See* EX2017-1993-Crawford, 3132-33.

V. The Ma Reference

A. *Synthetic Metals* Journal

147. I have been asked to provide some background information regarding *Synthetic Metals*, the journal in which the Ma reference was published.

148. *Synthetic Metals* is a journal published by for-profit publisher Elsevier. While popular in the 1980s and early 1990s, as more researches and resources were devoted to optoelectronics, many journals of higher calibers with an emphasis on optoelectronics-related research had been established. By 2008/2009, *Synthetic Metals* had long ceased to be a journal that researchers in optoelectronics would actively monitor for new articles. For example, the WayBack machine did not archive www.elsevier.com/locate/synmet between 2007 and 2015 and just once each in 2006 and 2016. *See* screen capture below:



EX2025 (screenshot of Internet Archive captures of www.elsevier.com/locate/synmet), available at <https://web.archive.org/web/20250000000000*/www.elsevier.com/locate/synmet> (last visited May 3, 2025).

149. 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 authors' names or the title of the article. It is also my recollection that in 2008-2009, Elsevier's search tool[8] 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.

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.

[8] It was my recollection that Elsevier used similar search tools for its various journals in 2008/2009.

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

By
Are you this author?

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Abstract

Organic light-emitting diodes with 8-hydroxy-quinolinato lithium doped 4'7-diphyenyl-1, 10-phenanthroline as electron transport layer (ETL), and etrafluro-tetracyano-quinodimethane doped 4,4',4 ''-tris(3-methylphenylphenylamono) triphenylamine 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. (C) 2008 Elsevier B.V. All rights reserved.

Keywords

Author Keywords: Organic light-emitting diodes; Doping concentration; Carrier transport; Conductivity
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

(EX2024)

151. I understand that Samsung's expert in two other IPR proceedings, Dr. Holmes, testified that he used Web of Science to locate articles of interest in the relevant period. But as can be seen above, Ma was not indexed until December

2008, which would indicate that it could not be located by Web of Science before then.

B. '223 Patent's Foreign Priority Supports the Claims

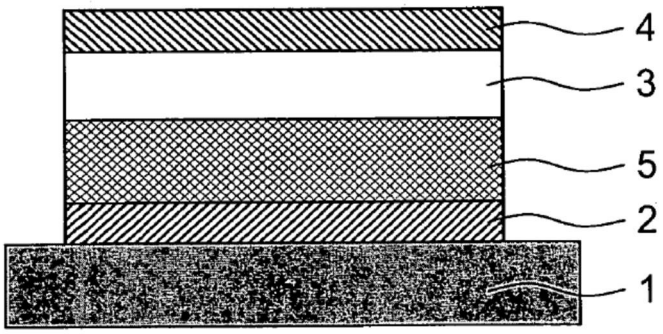
152. I have been asked to confirm that the foreign priority document DE10200849286 provides full support to the challenged claims. It does, as shown by the chart below.

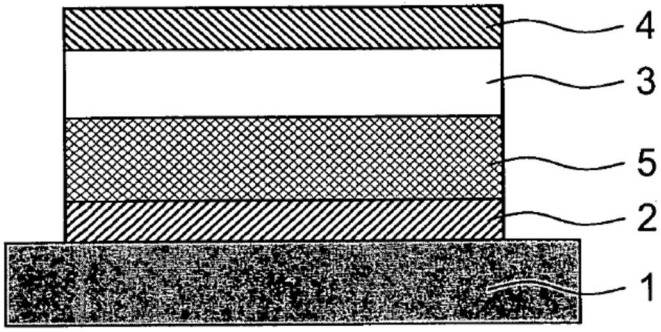
Claim Element[9]	**As-filed DE102008049286 (EX2026)**[10]
1[pre].	Claim 1: "Organic electronic component, comprising …." *See also, e.g.,* Title: "Organic electronic component and method for its manufacture" Abstract: "Organic electronic component, comprising …." 1:5: "An organic electronic component according to Claim 1 is specified." 2:13-26: "Through the joint evaporation of the metal complex with an organic compound, … [t]he compounds are deposited in the coordinated state, so that a layer is formed in which short-range order is provided. The term short-range order is understood to mean that not the entire layer per se is crystalline, but that the organic compounds are disposed around the metal complex in its immediate environment according to a specific pattern that depends on the selected metal complex and the organic compound. However, the entire

[9] Using the same numbering as Petitioner.

[10] Challenged claims only.

Claim Element[9]	**<u>As-filed DE102008049286 (EX2026)</u>**[10]
	layer itself is amorphous and thus does not have a long-range order. By coordinating the organic compound at the metal complexes and the associated overlap of the orbital, additional electrons can be transferred from the metal to the ligand by a metal-ligand charge-transfer complex. These electrons can be available for electron transportation in the organic electronic component. By increasing the 'free' electrons, the electron conductivity in the component is significantly improved. This leads to an increase in the efficiency and serviceable life of the organic electronic component."
[1a.1]. a substrate, a first electrode, a second electrode,	Claim 1: "Organic electronic component, comprising – a substrate (1), – a first electrode (2), – a second electrode (4), …." *See also*, *e.g.*, Abstract: "Organic electronic component, comprising a substrate, a first electrode, a second electrode, …" 2:8: "An embodiment of the organic electronic component comprises a substrate, a first electrode, a second electrode …." 22:4-8: "One variant of the method for manufacturing an organic electronic component comprises the method steps: providing a substrate as method step A), applying a first electrode in process step B), depositing an electron-conducting layer on the substrate as method step C), applying a second electrode in the process step D), wherein the electron-conducting layer is deposited by simultaneous vaporization of a metal complex and an organic compound." 27:7-8: "Figure 1 shows a layer sequence comprising a

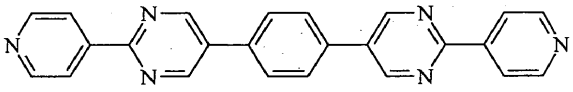
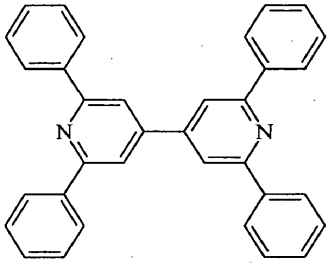
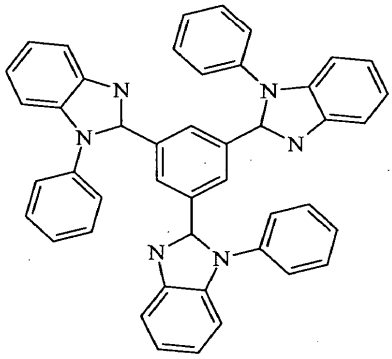
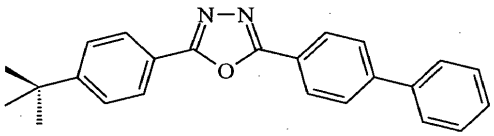
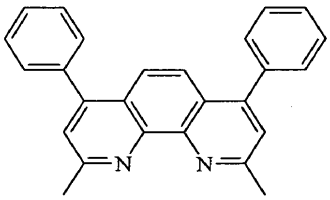
Claim Element[9]	**<u>As-filed DE102008049286 (EX2026)</u>**[10]
	substrate 1, a first electrode 2 and a second electrode 4 arranged thereon." Fig. 1 and associated text: Fig 1 
[1a.2]. an electron-conducting layer which is arranged in such a way that it is electrically conductively connected to at least one of the electrodes,	Claim 1: "Organic electronic component, comprising … – an electron-conducting layer (3) arranged such that it is electrically conductively connected to at least one of the electrodes, …." *See also*, *e.g.*, Abstract: "Organic electronic component, comprising a substrate, a first electrode, a second electrode, an electron-conducting layer arranged such that it is electrically conductively connected to at least one of the electrodes …." 2:8-10: "An embodiment of the organic electronic component comprises a substrate, a first electrode, a second electrode, and an electron-conducting layer arranged such that it is electrically conductively connected to at least one of the electrodes …."

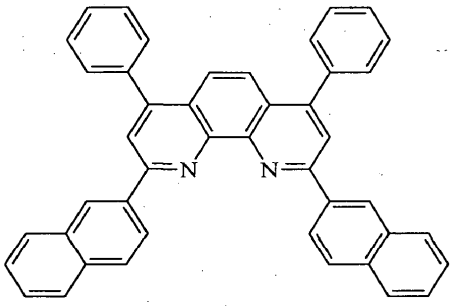
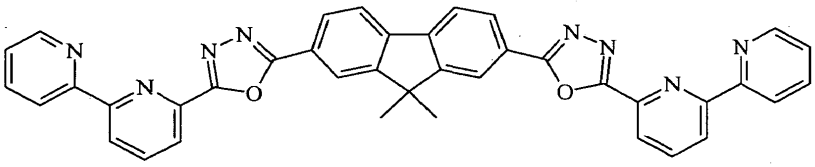
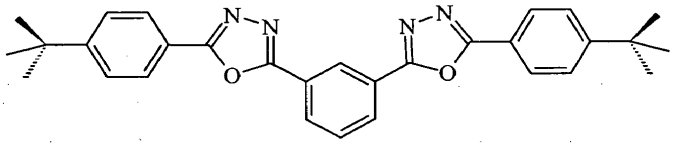
Claim Element[9]	**<u>As-filed DE102008049286 (EX2026)</u>**[10]
	See also Fig. 1 and associated text Fig 1 
[1b]-[1c].	Claim 1: "Organic electronic component, comprising … – an electron-conducting layer (3) …, wherein the electron-conducting layer (3) is obtained by joint vaporization of a metal complex with an organic compound, wherein the metal complex comprises a central metal atom." Claim 5: "Organic electronic component according to any of the above claims, wherein the organic compound comprises a heteroaromatic compound conjugated to an aromatic compound with a C-C bond." *See also*, *e.g.*, Abstract: "Organic electronic component, comprising a substrate, a first electrode, a second electrode, an electron-conducting layer arranged such 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 with an organic compound."

Claim Element[9]	**<u>As-filed DE102008049286 (EX2026)</u>**[10]
	2:8-11: "An embodiment of the organic electronic component comprises a substrate, a first electrode, a second electrode, and an electron-conducting layer arranged such 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 with an organic compound." 6:12-13 ("In a further embodiment of the organic electronic component, the organic compound comprises a heteroaromatic compound.") 6:17-7:1 ("Compared to an aromatic compound, a heteroaromatic compound has the advantage that it can coordinate to a metal complex not only via the aromatic system (π electrons), …, but that the coordination can also be achieved directly via the heteroatom."). 7:6-7 ("In a further embodiment of the organic electronic component, the organic compound comprises a heteroaromatic compound that is conjugated with an aromatic compound via a C-C bond."). 7:10-13 ("a system of this type, in which the heteroaromatic compound is linked with further aromatic compounds via single C-C bonds, has the advantage that it is not as sterically demanding and voluminous, and can thus coordinate more easily to a metal complex, or better coordinate to several metal complexes at the same time."). 30:11-12: "This electron-conducting layer can be obtained by joint vaporization of the metal complex with the organic compound."
Claim 2	Claim 2: "Organic electronic component according to Claim 1, wherein the organic compound coordinates to the metal complex due to the joint vaporization."

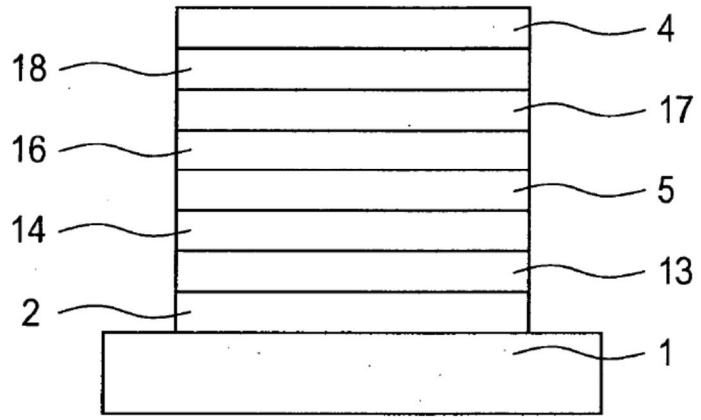
Claim Element[9]	**As-filed DE102008049286 (EX2026)**[10]
	See also, *e.g.*, 2:13-15 ("Through the joint evaporation of the metal complex with an organic compound, these two compounds interact with each other in the gas phase. This interaction causes the compounds to be mutually coordinated."); 17:6-10 ("By suitable selection of the metal complexes, …, and suitable selection of the organic compounds, … the joint vaporization of the metal complex with the organic compound in the gas phase results in interactions, so that the compounds coordinate together. Coordination is also retained when forming the electron-conducting layer."). 23:7-10 ("there is also the possibility that the metal complexes and the organic compound meet each other first on the surface to be coated or upon contact with the surface and the organic compound coordinates to the metal complex while forming the electron-conducting layer."). 19:3-9 ("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, wherein 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."). 22:18-19: "In a further method variant, the organic compound coordinates to the metal complex by means of joint vaporization." DE '391 [EX2027], 2:13-15 ("When the metal complex vaporizes together with an organic compound, these two

Claim Element[9]	**<u>As-filed DE102008049286 (EX2026)</u>**[10]
	compounds interact with each other in the gas phase or when they meet on the substrate surface.”).
Claim 3	Claim 3: “Organic electronic component according to any of the above claims, wherein the metal complex comprises more than one central metal atom.” *See also*, *e.g.*, 4:1-6 (“In a further embodiment of the organic electronic component, the metal complex comprises more than one central atom.” [¶] The presence of more than one central atom improves the possibility that several organic compounds will coordinate simultaneously to the metal complex. The metal complex preferably comprises two central metal atoms.”).
Claim 4	Claim 4: “Organic electronic component according to any of the above claims, wherein the central metal atom is, or the central metal atoms are, selected from Cr, Mo, or W.” *See also*, *e.g.*, 5:1-2: “In an embodiment of the organic electronic component, the central atom is, or the central atoms are, selected from: Cr, Mo or W.”
Claim 6	Claim 7: “Organic electronic component according to any of the above claims, wherein the organic compound is selected from: [same chemical formula]” *See also*, *e.g.*, 9:12-13 & 10-12: “In a further embodiment of the organic electronic component, the organic compound is selected from:

Claim Element[9]	**As-filed DE102008049286 (EX2026)[10]**
	 I  II  III  IV  V

Claim Element[9]	**<u>As-filed DE102008049286 (EX2026)</u>**[10]
	 XI  XII  XIII
Claim 8	Claim 9: "Organic electronic component according to any of the above claims, wherein at least parts of the organic compounds bridge two metal complexes with one another such 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 such that a network-like structure of the metal complexes is formed." *See also*, *e.g.*, 12:5-8: "These compounds I through XIII not only permit the formation of two-dimensional chains, but also the formation of three-dimensional networks by virtue of their plurality of coordination sites. In this case, an organic compound coordinates to more than two metal complexes." 16:6-9: "These compounds XIV through XXV not only permit the formation of two-dimensional chains, but also the

Claim Element[9]	**As-filed DE102008049286 (EX2026)**[10]
	formation of three-dimensional networks by virtue of their plurality of coordination sites. In this case, the organic compound coordinates to more than two metal complexes." 17:1-4: "In an embodiment of the organic electronic component, at least parts of the organic compounds bridge two metal complexes together, so that a chain-like structure is formed and/or at least parts of the organic compounds bridge together more than two metal complexes, so that a network-like structure is formed." 18:9-14: "This example clearly shows that it is possible to coordinate to several metal complexes simultaneously by means of a suitable choice of organic compound. By the corresponding selection of the metal complexes, more than one organic compound can also coordinate to said metal complexes, thus resulting in chain-like and/or network-like structures in the electron-conducting layer."
Claim 9	Claim 10: "Organic electronic component according to any of the above claims, formed as an organic LED (OLED) that additionally comprises an organic emitting layer (5)." *See also*, *e.g.*, 21:1-2 ("The organic electronic component is preferably formed as an organic LED (OLED), which comprises an electroluminescent layer."). 27:16-24: "Figure 2 shows an embodiment of the component formed as an OLED. The figure shows a schematic side view of a layer stack of nine layers. A first electrode 2, which is for example transparent and made of ITO (indium-tin oxide), is 30 arranged on a substrate 1, which is for example made of glass. A hole injection layer 13, on which in turn a hole transport layer 14 is arranged, is arranged on this electrode 2. An organic active layer - the organic emitting layer 5 - is located on the hole transport layer 14. A hole-blocking layer 16 is arranged on

Claim Element[9]	**<u>As-filed DE102008049286 (EX2026)</u>**[10]
	said organic emitting layer 5, followed by an electron transport layer 17, and on which an electron injection layer 18 is arranged. A second electrode 4, for example a metal electrode, is located on the electron injection layer 18." Figure 2 and associated text: Fig 2 
Claim 10	Claim 11: "Method for manufacturing an organic electronic component, comprising the method steps of: A) providing a substrate (1), B) applying a first electrode (2), C) depositing an electron-conducting layer (3) on the substrate (1), D) applying a second electrode (4), wherein the electron-conducting layer (3) is deposited by simultaneous vaporization of a metal complex and an organic compound." Claim 5: "Organic electronic component according to any of the above claims, wherein the organic compound comprises a

Claim Element[9]	**As-filed DE102008049286 (EX2026)**[10]
	heteroaromatic compound conjugated to an aromatic compound with a C-C bond." *See also*, *e.g.*, Citations for claim 1. 22:4-11: "One variant of the method for manufacturing an organic electronic component comprises the method steps: providing a substrate as method step A), applying a first electrode in process step B), depositing an electron-conducting layer on the substrate as method step C), applying a second electrode in the process step D), wherein the electron-conducting layer is deposited by simultaneous vaporization of a metal complex and an organic compound. [¶] Such a method can, for example, be used to produce an organic electronic component, as claimed in claim 1." 7:7-9: "In a further embodiment of the organic electronic component, the organic compound comprises a heteroaromatic compound that is conjugated with an aromatic compound via a C-C bond." *see also* 7:8-14.
Claim 11	Claim 12: "Method according to Claim 11, wherein, during the simultaneous vaporization, the organic compound coordinates in the gas phase to the metal complex." *See also*, *e.g.*, 2:13-15: "Through the joint evaporation of the metal complex with an organic compound, these two compounds interact with each other in the gas phase. This interaction causes the compounds to be mutually coordinated." 17:6-9: "By suitable selection of the metal complexes, …, and suitable selection of the organic compounds, …, the joint

Claim Element[9]	**<u>As-filed DE102008049286 (EX2026)</u>**[10]
	vaporization of the metal complex with the organic compound in the gas phase results in interactions, so that the compounds coordinate together." 23:1-3: "Due to the simultaneous vaporization of metal complexes and organic compounds, both compounds are simultaneously present next to each other in the gas phase. This enables the organic compound to coordinate to the metal complex in the gas phase."
Claim 12	Claim 13: "Method according to any of Claims 11 or 12, wherein the electron-conducting layer (3) is deposited as a chain-like or network-like structure." *See also*, *e.g.*, citations for claim 8. 17:11-8:1: "These chains or networks are deposited as such in the vaporization process and are also present as such in the electron-conducting layer in the organic electronic component. The formation of chain-like or network-like structures enables additional electrons to be transferred from the metal complexes to the organic compounds; said electrons are then available for charge transport in the electron-conducting layer." 18: 11-14: "By the corresponding selection of the metal complexes, more than one organic compound can also coordinate to said metal complexes, thus resulting in chain-like and/or network-like structures in the electron-conducting layer." 23:12-13: "In a further method variant, the electron-conducting layer is deposited as a chain-like or network-like structure." 23:15-18: "The coordination of the organic compound to the metal complex in the gas phase allows chain-like or network-like structures to form. These chain-like or network-like structures are then also deposited as such and are also present

Claim Element[9]	**<u>As-filed DE102008049286 (EX2026)</u>**[10]
	as such in the electron-conducting layer in the organic electronic component."
Claim 13.	Claim 14: "Method according to Claim 13, wherein the degree of cross-linking of the electron-conducting layer (3) is controlled by the ratio between the metal complex and the organic compound during vaporization." *See also*, *e.g.*, 24:1-3: "In one method variant, the degree of cross-linking of the electron-conducting layer is controlled by the ratio between the metal complex and the organic compound during vaporization." 24:5-7: "The degree of cross-linking and thus the formation of network-like or chain-like structures can be controlled by the ratio of metal complex to organic compound. Referring to the molar ratio, the organic compound is vaporized in excess compared to the metal complex."
Claim 14.	Claim 15: "Method according to any of Claims 11 through 14, wherein the organic compound does not coordinate to the metal complex prior to vaporization." *See also*, *e.g.*, 24:13-14: "In a further method variant, the organic compound does not coordinate to the metal complex prior to vaporization."

C. Ma Does Not Disclose its Co-Deposition Conditions

153. Dr. Rand asserts the following:

> 141. ***Third***, it is my opinion that 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). 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).

(EX1003, ¶ 141)

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.

155. For example, below is an illustration of an evaporation chamber with a single-source. EX2045 [US7,704,554].

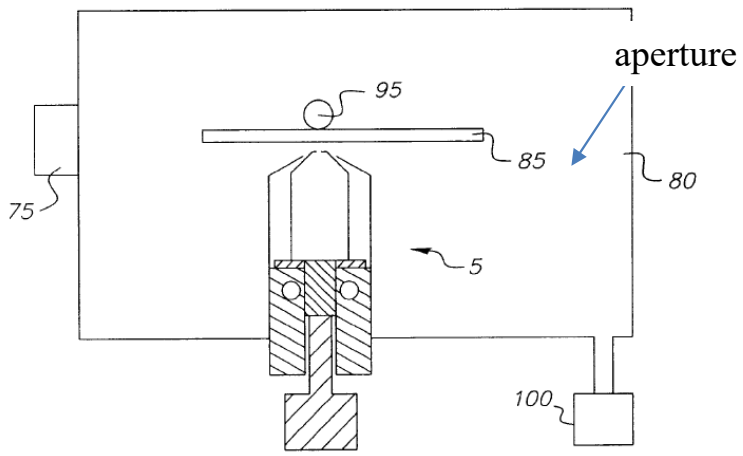


FIG. 5

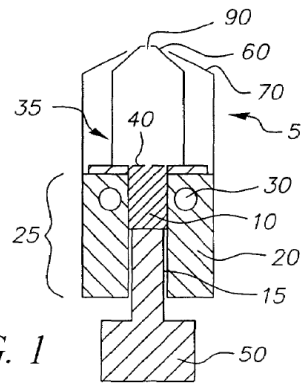


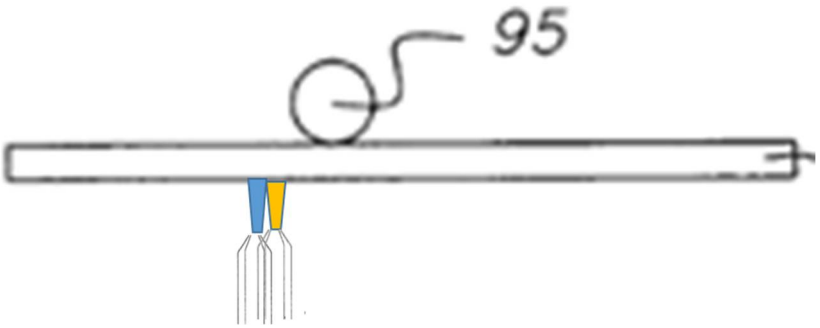
FIG. 1

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 OELD 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.").

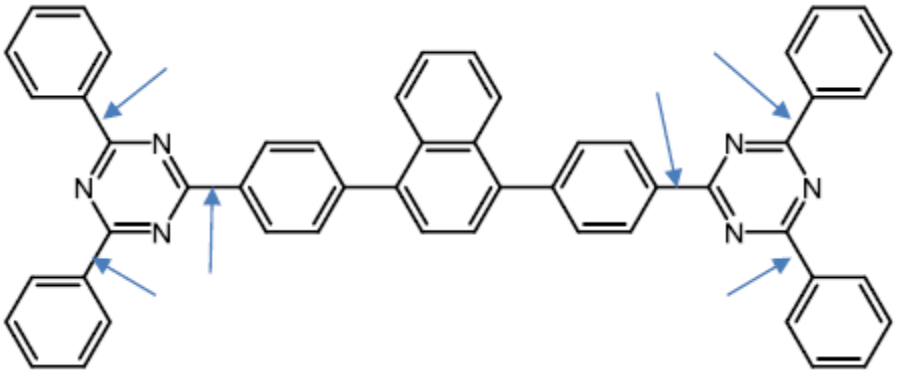
[11] Dr. Kymissis refers to a process in which [redacted] as "sequential co-evaporation." EX2052 [Kymissis Rebuttal], ¶243. This shows that "co-evaporation" or "co-deposition" does not necessarily mean joint vaporization.



158. I understand that for the joint vaporization limitation, Samsung and Dr. Rand only argues that Ma discloses this limitation, but not that it would be obvious to do so. As I explain above, Ma neither expressly nor inherently discloses that its co-deposition is the joint vaporization as claimed by the ’223 patent.

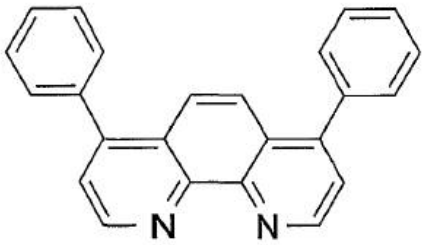
D. BPhen versus Bistriazine Compound Used in Samsung Products

159. I have been asked to comment on the chemical properties of BPhen and the bistriazine compound below.



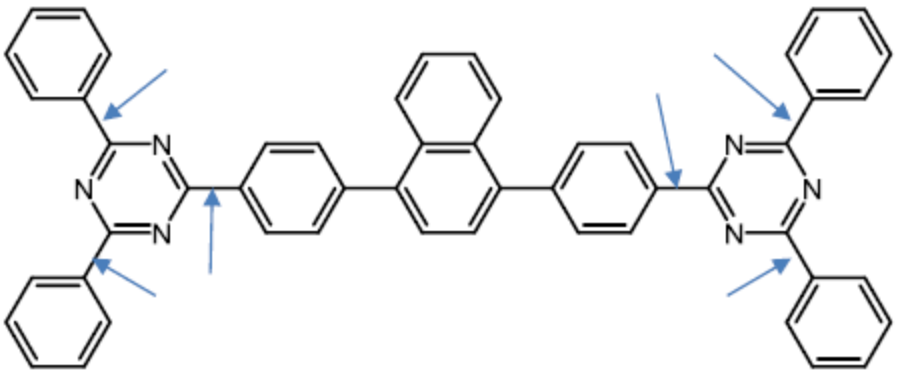
160. As I have noted above, in BPhen, the two nitrogen atoms in the phenanthroline ring are tethered by the rigid and fused aromatic backbone such

that they are relatively fixed in place and configured to form a stable five-membered ring around a single metal center, if the steric and electronic properties of the metal and ligand match (that is, if the metal center is not shielded by bulky ligands to hinder approach by the BPhen ligand and the metal center has the right energy level and orbital symmetry to interact with BPhen's HOMO or LUMO).

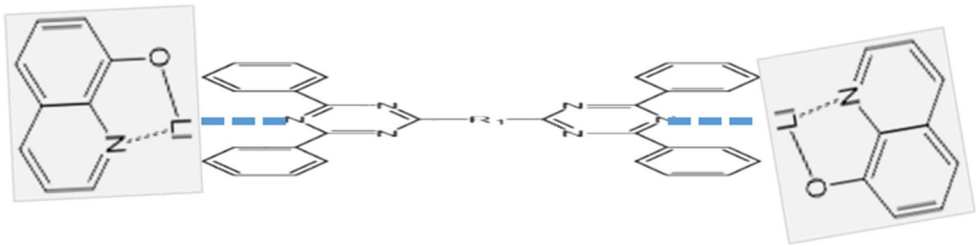


BPhen = bathophenanthroline
(4,7-Diphenyl-1,10-phenanthroline)
C24H16N2

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.)

163. Additionally, lithium cation supposedly can interact strongly with benzene rings, with a bond dissociation energy up to 161 kJ/mol (or about 38.5 kcal/mol). *See* EX2046 [2016 Chem. Review Rodgers], 5665, Table 20 (147 kJ/mol is at 373K or 100 ºC, and 150 kJ/mol is at 298K or about 25 ºC).

Table 20. Sequential Bond Dissociation Energies (kJ/mol) of $(C_6H_6)_{x-1}M^+-C_6H_6$[a]

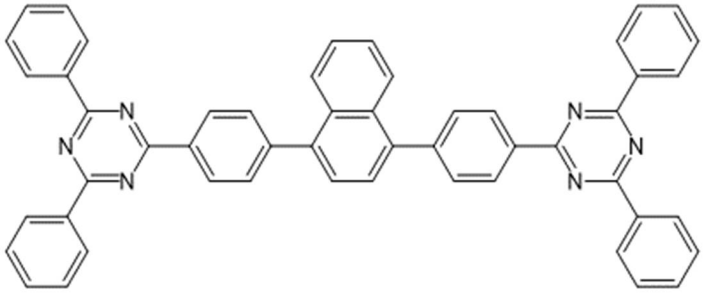
M^+	ref[b]	$x = 1$	$x = 2$
Li^+	C[278]	161 (14), 147 (10),[c] 150 (15)[d]	104 (7)

164. Lithium cation also supposedly can interact with naphthalene, with a bond dissociation energy of up to 187 kJ/mol (or about 44.7 kcal/mol). *See* EX2046 [2016 Chem Review Rodgers], 5666, Table 21.

165. The two nitrogen atoms in BPhen, on the other hand, if coordination occurs, would coordinate to the same metal center rather than different metal centers. This is because the rigid vinylene backbone anchors the two nitrogen atoms in a relatively fixed position such that the two nitrogen atoms can form a

relatively stable five-membered ring with a metal center, rather than each coordinating to a different metal (if the pyridyl nitrogen would coordinate to the metal center in the first instance), as explained in ¶¶ 121-130 above.

166. As such, I agree with Pictiva that its assertion that the bistriazine complex can form a chain structure with Liq does not mean BPhen can do the same.



167. This is because, in contrast to the structure above, where the two triazine rings are spaced apart by C-C single bonds and spacer aromatic rings, the geometry of the two nitrogen atoms in the rigid, fused heteroaromatic ring makes coordination of BPhen to a single metal center more favorable; and the close proximity of the two nitrogen atoms also makes it sterically difficult for the second nitrogen to coordinate to a different metal center.

168. The coordination sphere, such as steric effects of the heteroaromatics are therefore quite different between BPhen and the triazine compound use in the Accused Products.

E. No Evidence of BPhen Coordination to Liq

169. Samsung suggests that Liq would form an arene adduct like $Rh_2(O_2CF_3)_4$. As I have explained above, the trifluoroacetate ligand ($^-O_2CCF_3$) was known to be highly electron withdrawing, such that rhodium is highly electrophilic (that is, it tends to accept electrons from an electron donor). On the other hand, the six methyl groups in hexamethylbenzene (C_6Me_6) increases the electron density of the pi-system of the phenyl ring. This makes the sharing of the pi-electrons through the electron-deficient rhodium's pi*-orbital (formed from anti-bonding interactions of d_{xz}-d_{xz} and d_{yz}-d_{yz}) thermodynamically very favorable in $Rh_2(O_2CF_3)_4$.

170. Liq, on the other hand, is described as an n-dopant for BPhen. An n-dopant is generally understood to donate, instead of accepting, electrons (although it is unclear, in light of Ma at 813, whether Liq in Ma actually served as an electron donor).

171. Moreover, lithium atoms and cations do not have d-orbitals; and unlike the highly electron withdrawing trifluoroacetate moiety, the hydroxyquinolato anion is considered electron donating. Additionally, unlike hexamethylbenzene with six electron donating methyl groups that increase the electron density of the pi-system, BPhen's "planar central structure," or the phenanthroline ring, is substituted with phenyl rings which are considered to be

slightly electron withdrawing. As a result, the coordination environment for Liq and BPhen is completely different than that for $Rh_2(O_2CF_3)_4$ and hexamethylbenzene.

172. Furthermore, the reaction condition deployed by Cotton for forming the complex of the arene adducts of $Rh_2(O_2CF_3)_4$ differs greatly from that reported by Ma. According to Cotton, the arene adduct was formed over 2 weeks, indicating that the reaction is likely a slow one producing a thermodynamic mixture. (EX1012 (see synthesis of the dirhodium adduct)). In contrast, the thermal evaporation and deposition of Liq and BPhen in Ma took place on the order of 1,000 seconds (or about 17 minutes). Ma, 811 (deposition rate for organic materials is ~0.5 Å/s, thus it would take about 50 nm/0.5Å/s =1000 seconds to deposit a 50 nm layer Liq-doped ETL). A person of ordinary skill in the art would view the thermal evaporation process as likely yielding kinetic products because of the short reaction span.

173. Samsung then points to the ’223 patent’s teaching that BPhen “can … form chain-like structures when coordinated to certain metal complexes.” Pet. 66. But that statement does not say and a person of ordinary skill in the art would not interpret this statement as saying that BPhen would form a chain-like structure with every metal complex, including with the lithium center under Ma’s reaction conditions. Indeed, when BPhen coordinates to a metal center, BPhen coordinates

in a bidendate fashion to a single metal center given the rigid ring structure, as I have discussed above. While it is possible that a metal center may interact with the phenyl or phenanthroline's pi-electrons, Samsung has not presented any evidence that this mode of interaction exists between the lithium cation of Liq and BPhen.

174. The literature thus supports the '223 patent's teaching that two heteroaromatic rings in a single organic ligand facilitate coordination of the ligand to different metal centers to form a chain-like or network-like structure. *See* EX1001, 3:53-67 ("Preferably, the organic compound comprises more than one heteroaromatic compound. This enables the organic compound to coordinate to several metal complexes simultaneously. In contrast to an aromatic compound, a heteroaromatic compound has the advantage that it is not only able to coordinate to a metal complex via the aromatic system (π-electrons), as described in the publication by Cotton in Organometallics which is cited above, but furthermore the coordination can also be effected directly via the heteroatom. The greater the number of heteroaromatic compounds in the organic compound, the greater the number of possible coordination sites for a metal complex. Here, N is a preferred heteroatom. Due to the mostly free electron pair, N has very good coordination properties with respect to metal complexes.").

175. But the literature does not support Samsung's theory that the two nitrogen atoms on the same phenanthroline ring or a combination of a nitrogen

atom and an aromatic ring would be expected to bridge two different single-nuclear metal centers such as to the lithium centers of Liq. I am not aware of any such compounds had been reported by 2008/2009.

176. I also note that the ’223 patent does not teach that BPhen would always form a chain-like or network-like structure with any metal complex. Instead, the ’223 patent teaches the type of structures that may lead to the claimed structures; and a POSITA would understand the combination that would lead to the claimed structures. For instance, the ’223 patent teaches that “[t]he presence of more than one central atom improves the possibility that several organic compounds will coordinate simultaneously to the metal complex.” EX1001, 2:42-44; *see also* EX1001, 2:49-58 (discussing Cottons’ dirhodium complex and its adduct with an aromatic in the context of discussing why “[m]etal complexes having two central atoms are particularly well suited for the formation of chains”). In contrast, Samsung does not argue in this proceeding that Liq has more than one central atom. Thus, it has not explained why the state of the art would have suggested to a person of ordinary skill in the art that doping Liq in BPhen would form a chain-like or network-like structure given BPhen’s tendency to coordinate to a single metal center at a time (if coordinated at all).

177. I also understand that Dr. Rand is not offering any opinion on which atoms in BPhen would be interacting with which atoms in Liq. EX2042 [Rand Tr.], 211:22-222:14.

> 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.

178. In the ’223 patent, when coordination occurs, that is between the metal center and the organic compound, and not between any atom of the metal compound and the organic compound. ’223, 2:6-10 (referencing “metal-ligand—charge-transfer complex), 2:17-18 (“the organic compound coordinates to the metal atom”); 2:45-47 (“each of the two central atoms has a coordination site ….”), 3:14-17 (“By virtue of this coordination and the associated metal complex-ligand-electron transfer (charge-transfer complex), the electron-conducting layer can be provided with additional electrons for charge transport.”), 3:56-61 (“In contrast to an aromatic compound, a heteroaromatic compound has the advantage that it is not

only able to coordinate to a metal complex via the aromatic system (π-electrons), as described in the publication by Cotton in Organometallics which is cited above, but furthermore the coordination can also be effected directly via the heteroatom.”). The coordination in Cotton is between metal centers and organic moieties; and a person of ordinary skill in the art would understand the coordination of the heteroatoms to the complex is between the heteroatoms and the metal centers. Hence, I disagree with Dr. Rand that coordination is satisfied by any interaction between any atom of the organic compound with any atom of the metal complex. Coordination in the context of the ’223 patent is a bonding interaction between the metal center and the organic compound.

179. I understand that Dr. Rand claims that when he approached the ’223 patent, he “considered coordination in a very basic sense, in the broadest sense, that there are numerous ways that one could coordinate between molecules.” EX2042 [Rand Tr.], 72:21-73:2, 76:12-16, 259:13-14. I understand that in the IPR proceedings, the claims are to be construed under the *Philips* standard, and not the broadest reasonable interpretation standard, and I also understand that even under the broadest reasonable interpretation standard, the interpretation has to be reasonable in light of the specification. The specification makes clear that the coordination is in reference to coordination to metal center, and not any random atom-atom interactions.

180. Ultimately, Dr. Rand confirmed that he did not determine whether the alleged coordination involved lithium nitrogen bonding or whether pi-complexes are formed at the center of the lithium atom. *Id.*, 93:2-6, 94:10-12.

> Q: And you did not determine whether the coordination involved lithium nitrogen bonding; correct?
> A. Correct. We've already established this previously.
> ***
> Q: Do you [know] whether Pi complexes are formed at the center of the lithium atom?
> A. I don't know that specifically.

181. Without determining whether any bonds formed at the metal center, Dr. Rand has not shown that BPhen coordinates to Liq under Ma's processing condition.

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:

> 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.

Ma, 813.

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 ion[12] might be able to intercalate between BPhen molecules to

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[12] EX2100 at 677 ("Binding energy between Li and quinolate unit is weaker than that of LiF and it can give better performances as an electron injection layer than LiF."); EX2101 at 3018-3019 ("The concept of reduction of the interface material by the thermally activated aluminum leading to dopable metals such as Li

shorten the hopping distances. But that does not suggest any bonding interactions (*i.e.*, coordination) between BPhen and Liq.

184. I also note my agreement with Dr. Rand that processing conditions can alter intermolecular interactions within a film:

> 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 interactions in some other, under some other process conditions; right?
> A. Yes.

EX2042 [Rand Tr.] 199:21-200:6. Thus, the presence or absence of coordination in BPhen:Liq in one material set and/or process condition does not indicate that the same is true under another process condition or for another material set. Nor would the improvement in conductivity observed in Ma translates to similar improvement in other systems. *See*, *e.g.*, EX2047, 2201925-2 ("Although we fabricated a blue OLED [Device-5] with Liq used as the EIL and BPhen doped

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and Mg … explains satisfactorily the observed device improvements with LiF, MgO and lithium complexes."); Ma at 811 (Ma's device includes a LiF injection layer).

with Liq used as the ETL, its operating voltage was much higher than that of Device-3 (Figure S1, Supporting Information"), Fig. 1 (Device-3 has undoped BPhen layer); EX2048, Fig. S1 (Device-3 and Device-5 differs in that Device-3 has an undoped BPhen layer and Device-5 has mixed BPhen:Liq); EX2049_Angel, Fig. 2 (driving voltage and EQE decreased slightly upon doping of BPhen with Liq); EX2050_Ki, Figs. 4(a)-(b) (increased driving voltages, lower EQE and slightly lower luminance upon doping of ETL with Liq).

185. Samsung also argues that coordination, if any, was "due to joint vaporization" because "any coordination between Liq molecules and BPhen molecules could occur only after the separately-sourced Liq and BPhen are jointly vaporized and interact with each other." Pet. 64. In the district court, however, Samsung argues that "due to joint vaporization" requires the coordination to be directly attributable to joint vaporization. That coordination, if any, occurs after co-deposition occurs does not mean the coordination is necessarily directly attributable to joint vaporization. For example, an interaction between BPhen and Liq molecules (under Dr. Rand's broad view of coordination) could have been due to reorganization in response to any electrical stress applied to the electron transport layer during testing.

F. Ma in light of Shtein Does Not Disclose or Suggest Using OVPD to Obtain a More Uniform Film of Liq and BPhen

186. I understand that Samsung asserts that a person of ordinary skill in the art would have modified parameters of deposition to achieve coordination of BPhen and Liq in gas phase. Pet. 70. Samsung argues that "a deposited layer of coordinated BPhen and Liq will contain a more uniform distribution of BPhen and Liq, than if the BPhen and Liq are individually deposited …." *Id.* Samsung asserts that a person of ordinary skill in the art would be motivated to obtain a deposited layer with more uniform distribution of BPhen and Liq allegedly because "[a] POSA would have understood that a more uniform layer of coordinated BPhen and Liq would allow for the more efficient transfer of electrons through that layer." *Id.*

187. To the extent coordination of BPhen to Liq is possible and coordination increases the uniformity of the film and hence performance as Samsung states, that benefit can also be achieved if the coordination occurs when BPhen and Liq reacts on the deposition surface. See EX1001, 11:20-24 ("the joint vaporization of the metal complex with the organic compound in the gas phase ***or on the deposited surface results in interactions***, so that the compounds coordinate to each other"). Since the deposited films are built molecular layer by molecular layer, the coordination (if any) would not just occur at the top surface as Samsung

seems to assume, but would occur as each molecular layer as the molecules are deposited, therefore forming a uniform film. Samsung therefore has made a wrong assumption about what happens in thermal deposition.

188. Additionally, I have not seen any evidence in the record that a person of ordinary skill in the art would have known the conditions under which a substantial amount of BPhen would react with Liq in order to produce a more uniform distribution of BPhen and Liq. Pet. 70. A person of ordinary skill in the art would not have expected OVPD to achieve that goal or to promote coordination of BPhen to Liq.

189. This is because the Shtein paper does not demonstrate that the method could have worked with a mixture of compounds, especially if they had substantially different vaporization or sublimation temperatures/enthalpies. Instead, Shtein only performed the experiment with a single compound Alq3, instead of a mixture. EX1008 at Experiment.

190. Moreover, in OVPD, "a hot, nonreactive carrier gas is used to transport an organic vapor toward a cooled substrate onto which the organic materials condense." EX1008 at 4006. There is no evidence that OVPD could lead to a uniform film of Liq and BPhen or even that the condition would induce coordination of BPhen to Liq in the gas phase. For instance, there is no explanation why the presence of large amounts of inert gas molecules would not

interfere with the chance that a Liq moiety would collide with BPhen to form coordination. No analysis was done on what the net effect of the complicated and unpredictable thermodynamics and kinetics would be.

191. Indeed, given the complexity of thermodynamics and kinetics, a person of ordinary skill in the art would not have reasonably expected that OVPD would have promoted coordination of Liq with BPhen and resulted in a more uniform film of Liq and BPhen.

G. Ma Does Not Disclose or Suggest Cross-Linking

192. I have also been asked to comment on whether Ma's teaching of an optimal ratio of Liq and BPhen for best electron conductivity would have motivated a person of ordinary skill in the art to adjust the cross-linking density or that they would have understood that the degree of cross-linking density would affect electron conductivity.

193. It is my opinion that they would not.

194. First, there is no evidence that a person of ordinary skill in the art would have even viewed the mixture of Liq and BPhen as forming a cross-linked structure, let alone that they would be motivated to control the degree of cross-linking density. Nor is there any evidence that a person of ordinary skill in the art would have understood that the ratio of Liq and BPhen would have led to different degrees of cross-linking.

195. Second, the only teaching that Samsung cites to support its argument that the degree of cross-linking is related to the electron conductivity comes from the ’223 patent. Pet. 73-74. I understand that it is not proper to use the inventors’ own insight against them in arguing obviousness because an inventor’s path to invention is not evidence of obviousness.

I declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code.

Executed on May 5, 2025, in San Antonio, Texas.

K. S. Schanze

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