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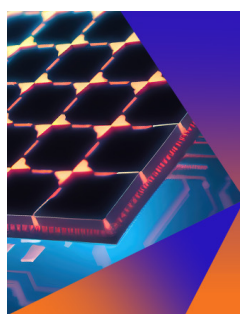


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Pyronin B as a donor for *n*-type doping of organic thin films

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We present an approach to stable *n*-type doping of organic matrices using organic dopands. To circumvent stability limitations inherent in strong organic donors, we produce the donor from a stable precursor compound *in situ*. As an example, pyronin B chloride is studied as a dopant in a 1,4,5,8-naphthalene tetracarboxylic dianhydride matrix. Conductivities up to 2×10^{-4} S/cm are obtained, which is two orders of magnitude higher than obtained previously using bis(ethylenedithio)-tetrathiafulvalene as a dopant [A. Nollau, M. Pfeiffer, T. Fritz, and K. Leo, *J. Appl. Phys.* **87**, 4340 (2000)]. Field-effect measurements are used to prove *n*-type conduction. Other matrices which can be doped are N,N'-dimethyl-perylene-3,4,9,10-tetracarboxylic diimide and fullerene C₆₀, frequently used in organic solar cells. Visible light and Fourier-transform infrared spectroscopy confirm the donor properties of pyronin B. © 2003 American Institute of Physics. [DOI: 10.1063/1.1583872]

In contrast to classical silicon technology, *n*- and *p*-type doping of organic semiconductors for device applications has rarely been studied. We have recently shown^{1,2} that two key effects of doping, the reduction of ohmic losses in transport layers and the creation of ohmic contacts by tunneling through thin space charge layers, can be achieved in organic semiconductors as well. Hole transport layers doped with tetrafluoro-tetracyanoquinodimethane (F₄-TCNQ), a strong acceptor molecule, and alkali-metal-doped electron transport layers incorporated in an optimized organic light-emitting diode (OLED) yield outstanding performance in terms of operation voltage and efficiency.^{3,4} Recently, we have also shown that doped transport layers allowed us to realize efficient inverted OLEDs, which are, for example, a key requirement for OLEDs with opaque substrates.^{5,6}

For *n*-type doping of electron transport layers in OLEDs, the use of alkali metals such as Li or Cs is currently the only available approach.^{3,4} However, it suffers from the high doping ratios on the order of 1:1 needed for high conductivity,⁷ thus completely changing the matrix properties as well. Furthermore, metal ions tend to diffuse in the device during growth and operation.⁸ Therefore, it is not possible to prepare well-defined doping profiles; rather thick undoped buffer layers are needed to protect the emission region from the dopants that act as quenching sites, and the device stability is compromised.

Unfortunately, an organic donor that can be used for typical electron transport materials is not yet available. These materials are only weakly electron accepting, imposing requirements on the position of the highest occupied molecular orbital (HOMO) of the donor which are difficult to meet. In fact, one of the strongest known organic donor, bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF) has been reported⁹ to form deep donor states already in 1,4,2,8-naphthalene tetracarboxylic dianhydride (NTCDA), which has a lowest unoccupied molecular orbital (LUMO) of about 1 eV deeper than for example,

tris (8-hydroxy-quinolinato)-aluminum.^{9,10} Stronger donors are not easily synthesized and handled due to their chemical instability. Hence, finding an organic donor material with the ability to dope electron transport layers of typical OLEDs is still a challenging task.

Here, we present an approach to circumvent the stability problems of strong donor molecules. In conventional doping, the neutral donor molecules are mixed into the matrix material by coevaporation. A charge transfer then occurs, leaving the donor positively charged. In our approach the volatile donor (or the corresponding cation itself) is created *in situ* from a stable precursor compound.¹¹ For example, one can form a radical that has to be stable enough to be incorporated on the layer. There, a charge transfer occurs, forming the donor cation. The latter, in fact, can be much more stable (e.g., in a salt), since the condition for successful doping now is that the LUMO of the donor cation is above the LUMO of the (neutral) matrix molecule. In this case, electrons will stay on the matrix molecules because these are the more strongly electron accepting species. There is no restriction for the HOMO energy of the donor cation.

For our study, we consider cationic dyes, because these molecules already consist of an organic cationic part. The intention is to separate the cationic structure from the compound and use it as the dopant.

After initial experiments with rhodamine B (RhB) chloride, we have investigated the closely related compound pyronin B (PyB) chloride [see inset of Fig. 1(c)] because its molecular structure is less complicated and thus facilitates conclusions concerning the doping mechanisms. NTCDA was chosen as a matrix material to compare with previous results.⁹

PyB chloride (Acros) and NTCDA (Aldrich) (see insets of Fig. 1) are available commercially. The dopant materials have been used as delivered, and NTCDA has been purified twice by gradient sublimation. Substrates have been cleaned by ultrasonic treatment in acetone and ethanol and rinsing in deionized water. Silver contacts (0.2 mm spacing) have been evaporated on fused silica substrates. For field-effect mea-

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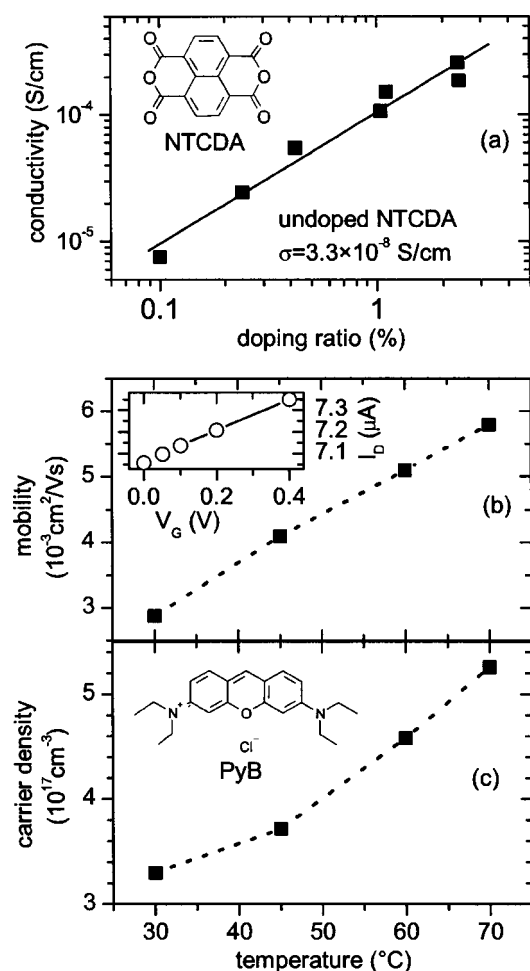


FIG. 1. Electrical properties of doped NTCDA thin films. (a) Conductivity of doped NTCDA layers vs doping concentration. (b) Field-effect mobility of a 1:91 doped NTCDA layer. Inset: Typical field effect signal. (c) Electron density derived from field-effect measurement.

measurements, a silicon substrate with interdigitated gold contacts having spacings of 0.01 mm, and 90 nm SiO₂ as gate insulation has been employed. Sample preparation has been carried out in a high vacuum chamber ($p < 4 \times 10^{-4}$ Pa). After heating the substrates at 130 °C, layers of 30 nm thickness with different doping ratios have been deposited by coevaporation.¹² The evaporation rate has been 2 Å/s for NTCDA. The electrical measurements have been carried out after stabilization of the sample, achieved by heating to 70 °C. Occasionally, an increase in conductivity after preparation over several hours has been observed; however, the samples always reached a steady state.

Figure 1(a) shows the conductivity of NTCDA layers doped with PyB. With increasing dopant concentration, a systematic increase up to four orders of magnitude compared to undoped NTCDA ($\sigma = 3.3 \times 10^{-8}$ S/cm) is observed, accompanied by a drop in activation energy from 0.40 to 0.25 eV. The highest conductivity reached in the series is 2×10^{-4} S/cm at room temperature for the 1:42 doped sample. This is about two orders of magnitude higher than using BEDT-TTF as a dopant.⁹

The doped layers are stable up to 120 °C, where desorption of the NTCDA matrix occurs. In a PTCDA matrix, stability of the doping effect has been observed up to 160 °C. When the samples are exposed to air, the conductivity van-

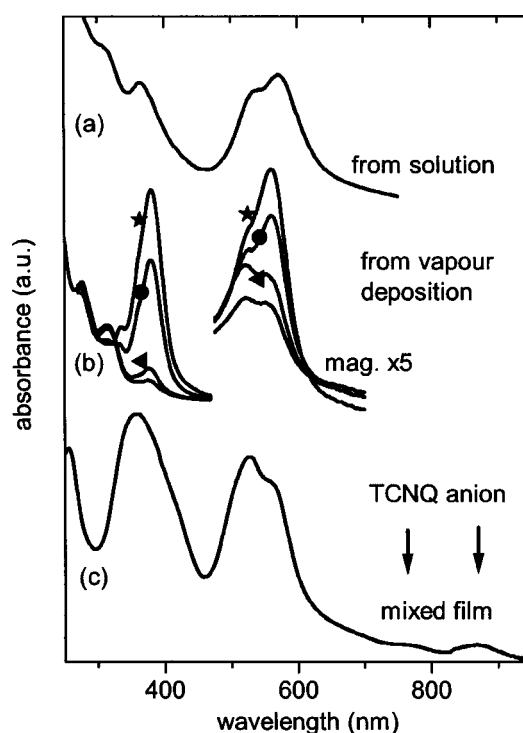


FIG. 2. VIS spectroscopy (a) PyB chloride thin film prepared from propanol solution, (b) PyB thin film prepared by vapor deposition [Time delay in (b): no sign—shortly after break of vacuum; triangle—35 min; circle—18 h, star—90 h], (c) mixed layer PyB: TCNQ 1:10. Spectra are offset for clarity.

ishes, indicating compensation by oxygen in a *n*-type semiconductor. The effect of air is reversible.

We have performed field-effect measurements to prove the conduction type and to measure the charge carrier density. Figures 1(b) and 1(c) show the results for a 1:91 doped sample. The inset of Fig. 1(b) gives a typical dependence of drain current I_D from gate voltage V_G . The positive sign of the field effect confirms *n*-type conduction. Figure 1(b) shows the field-effect mobilities calculated from a linear fit using formula¹³

$$I_d = \frac{Z}{L} \mu C_i \left(V_g - V_t - \frac{V_d}{2} \right) V_d, \quad (1)$$

where L and Z are the separation and the length of the contacts, respectively, μ is the (field-effect) mobility, C_i is the capacity per square of the insulating layer, and V_g , V_d , and V_t are gate, drain, and threshold voltages, respectively. The order of magnitude of the mobility is in good agreement with the findings of Laquindanum *et al.*¹⁴

We calculate the charge carrier densities [Fig. 1(c)] by combination with conductivity data. We find a thermally activated electron density with an activation energy of 115 meV. Hence, deep donor states are formed in NTCDA by doping. The electron concentration is 3.3×10^{17} cm⁻³ at room temperature, which is about two orders of magnitude lower than the nominal concentration of evaporated dopant molecules.

To study the origin of the doping effect, we have carried out visible light (VIS) spectroscopic investigations of pure and mixed thin films. In Fig. 2(b), the absorption of a thin film of 26 nm PyB made by vapor deposition is compared to the spectrum of a PyB coating made by evaporating the sol-

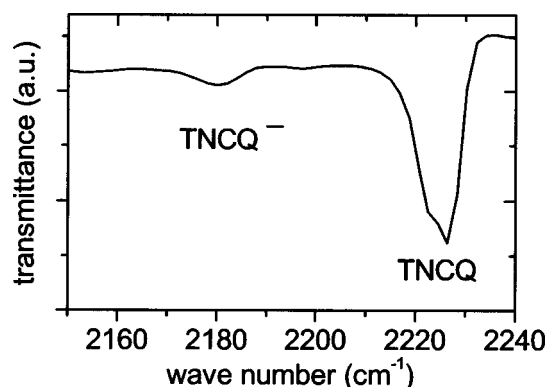


FIG. 3. FTIR spectrum of PyB:TCNQ 1:10. The two peaks correspond to neutral TCNQ and TCNQ anion, respectively.

vent of a propanol solution [Fig. 2(a)]. In contrast to the pristine material, vapor-deposited PyB is colorless. However, when exposed to air, the absorption in the spectral range of PyB is increased, as also shown in Fig. 2(b). We therefore assume that PyB is reduced before it goes into the vapor phase. In air, the molecule is oxidized again to give the colored cationic form.

When PyB is used as a dopant, it is oxidized by the matrix molecules in order to provide free electrons in the matrix. We therefore investigated mixed films of PyB and TCNQ, a strong organic acceptor, made by coevaporation (doping ratio 1:10). The result is shown in Fig. 2(c). The two absorption peaks at about 540 and 360 nm are clearly visible, confirming an immediate oxidation of the reduced form of PyB in the TCNQ matrix. In accordance with Ref. 15, the small peak at 869 nm is assigned to the TCNQ anion.

The oxidation state of TCNQ can also be determined clearly from Fourier-transform infrared (FTIR) measurements. Depending on the negative charge stored on the TCNQ molecules, the cyano group stretching modes exhibit a shift.¹⁶ In the 1:10 sample, we observe modes for the neutral TCNQ and its anion (see Fig. 3). The peak heights are as expected from the doping ratio. Thus, the reduced PyB, formed upon evaporation, reduces TCNQ to its anion. We have carried out similar experiment using NTCDA as a matrix. In this case, we did not observe the PyB cation. This is probably due to the low ionization degree in that matrix, where reduced PyB forms deep donor states.

In order to prove the doping effect to be independent of the chemical structure of the matrix, we performed comparative doping experiments with the fullerene C_{60} , perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) and N,N'-dimethyl-perylene-3,4,9,10-tetracarboxylic diimide (MePTCDI) as matrices. For these materials, we also find an enhanced conductivity for samples doped with RhB (see Table I). The results could be immediately used to improve the performance of organic solar cells employing these material as electron transport layers.^{17–19}

In summary, we have presented an approach to *n*-type doping of organic semiconductors. Cationic dyes are efficient

TABLE I. Conductivities of several matrices in the doped and undoped state.

Matrix	Dopant	Doping ratio	Conductivity	
			Undoped [S/cm]	Doped [S/cm]
NTCDA	PyB	1:42	3.3×10^{-8}	1.9×10^{-4}
C_{60}	RhB	1:15	1×10^{-6}	3.6×10^{-4}
PTCDA	RhB	1:50	3.5×10^{-6}	7×10^{-5}
Me-PTCDI	RhB	1:143	3×10^{-6}	6×10^{-5}

donors for *n*-type doping of organic evaporated matrixes. Studies of the doping effect in a NTCDA matrix proves pyronin B to be a better dopant than the strong organic donor BEDT-TTF. Spectroscopic investigations reveal that from the stable precursor compound PyB chloride, a reduced form of PyB, probably the neutral radical, is formed *in situ*. Electron transfer from the reduced Pyronin B to the matrix gives rise to *n*-type doping. The strong donor character of the reduced, colorless form of PyB is attributed to the energetic stabilization of its oxidized cationic form by a more favorable resonance structure that also leads to the deep color of the cationic form.

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