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Wide Band-Gap Bismuth-based p-Dopants for Opto-Electronic Applications

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Abstract: *Ten new efficient p-dopants for conductivity doping of organic semiconductors for OLEDs are identified. The key advantage of the electrophilic tris(carboxylato) bismuth(III) compounds is the unique low absorption of the resulting doped layers which promotes the efficiency of OLED devices. The combination of these features with their low fabrication cost, volatility, and stability, make these materials very attractive as dopants in organic electronics.*

The use of molecules as semiconductors is of high current interest for building innovative opto-electronic devices.[1–3] The nature of these soft materials enables new features, such as transparency or flexibility[4,5] and some devices such as organic light-emitting diodes (OLEDs) are already on the market.[6] However, in particular for OLED lighting, it is necessary to further increase the efficiency and the lifetime of the devices while reducing their cost. One of the key strategies to promote the organic semiconductor (OSC) device performance is doping.[7] Doping improves the device efficiency by reducing the device resistance, thereby its power consumption. However, the main drawback of p- and n-doping for optical applications, such as OLEDs, is the creation of open-shell radicals or charge-transfer complexes that may absorb the light emitted by the device.[8–10] To reduce this drawback, what is required are: 1) efficient and processable dopants with a 2) high optical band-gap (above 3.1 eV) and 3) which do not form visible-light absorbing species upon doping.

Since the p-side of an OLED is often thicker than the n-side,[11,12] the demand for doped OSCs with a low absorption is higher for p- than n-doping. Several solutions already exist for p-doping of OSCs. Organic electron acceptors, such as F_4TCNQ represent a powerful and efficient way to increase the conductivity of hole-transport materials (HTMs) for OLEDs.[7,13,14] However, F_4TCNQ is rather expensive, has a strong intrinsic absorption in the visible spectrum (optical band-gap around 2.5 eV)[10] and doped HTM thin-films appear colored due to absorption in the green to red spectral range (from 2.0 eV to 1.1 eV).[10] Some cheaper alternatives, such as transition metal oxides (TMOs), are also widely used.[15–17] TMOs are efficient for p-doping of OLED HTMs and usually have a wide intrinsic band-gap (around 3 eV).[18] Nevertheless, the doped HTMs usually strongly absorb in the visible range.[8,9] Furthermore, TMOs are challenging to process by vacuum deposition due to their usually high sublimation temperatures.[19]

Selected metal-containing Lewis acids are electron acceptors combining the volatility of organic electron acceptors and the affordability of TMOs and are thus candidates for p-dopants. The potential of inorganic Lewis acids, such as $FeCl_3$, $SbCl_5$, and BiF_3, was already demonstrated in OLEDs,[21,22] but the small size of these molecules promotes their diffusion overtime in the device. Lewis acidic metal complexes, such as fluorinated benzoato copper(I) have also been recently investigated for p-doping.[20]

The introduction of Lewis acids in a HTM may favor the formation of Lewis acid-base adducts, since most of the HTMs used for OLEDs are arylamines,[23,24] that is, susceptible Lewis bases with lone-pairs and π–π delocalized electron-pair donors. The formation of Lewis acid–base adducts has already been explained by perturbation molecular orbital theory and corresponds to the formation of hybrid-charge-transfer complexes, theoretically and experimentally investigated.[10,25] Such adducts have their own band-gap (Figure 1), and the presence of this band-gap can diminish the OLED efficiency.

Herein, tris(carboxylato)bismuth(III) compounds are reported as p-dopants for HTMs used in OLEDs. HTMs doped with these Lewis acids exhibit enhanced conductivities, comparable to the state-of-the-art doped OSC systems. Moreover, the doped HTMs show a high transparency, since the dopants' intrinsic band-gap is in the UV region and the band-gap of the resulting adducts in the IR one. These complexes were investigated since bismuth is a non-hazardous element and Bi^{III} compounds have a large coordination

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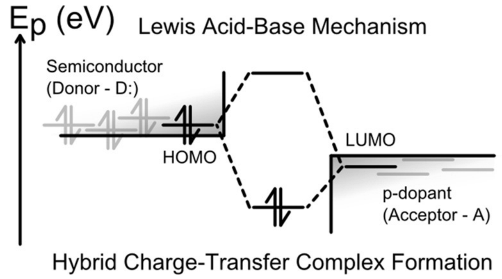

Figure 1. Frontier molecular orbital diagram of a hybrid-charge-transfer complex of a donating organic semiconductor and an accepting p-dopant, or Lewis acid–base adduct of an electron-pair donor and electron-pair acceptor couple.

sphere to form stable charge-transfer complexes,[26] which is prerequisite for doping HTMs. In addition, the electrophilicity of the $\mathrm{Bi^{III}}$ core can be tuned by varying the carboxylato ligands to modulate the Lewis acidity of the complex.[27–30]

Using Lewis acids instead of oxidizing agents considerably reduces the density of visible-light absorbing $\mathrm{HTM^{\bullet+}}$ radical cations in the doped layers, owing to the partial charge-transfer nature of the doping mechanism. A set of carboxylato bismuth(III) compounds having different substitution patterns and fluorination degree has been synthesized (Figure 2 and the Supporting Information), except the commercially available tris(acetato)bismuth(III). After their purification by gradient temperature sublimation (ca. 230 °C at 10^{-6} mbar at least 2 times), the ten volatile carboxylato bismuth complexes were tested as p-dopants. They showed doping behavior that was depending on both the nature and the ratio of co-sublimed materials. The current–voltage characteristics of the doped HTMs are improved by orders of magnitude from the poorly fluorinated dopants to the fluorine-rich tris(carboxylato)bismuth(III) (see Supporting Information for the detailed device characteristics). The conductivity of the layers measured on interdigitated-electrode devices confirms the p-doping to be responsible for the current improvement of the diodes (Figure 3). The highest conductivity was achieved with one mole of $\mathrm{Bi(tfa)_3}$ in two mole of spiro-TTB reaching $2.3\times10^{-4}\,\mathrm{S\,cm^{-1}}$, which is an order of magnitude higher than if doped with $\mathrm{F_4TCNQ}$[34] and the same order of magnitude as if doped with a widely used commercial dopant.[34] In addition to its high conductivity, the materials show low absorption of visible light. UV/Vis-NIR absorption spectra of the pure dopants showed an optical band-gap (absorption onset) from 3.7 eV to 4.1 eV (Figure 4 for spectra). The spectra of the thin films also showed a negligible change when exposed to air for an hour, indicating a good stability of the pure dopants, even as thin films.

The high optical band-gap of the doped films implies that the "unreacted state" of the dopant would not reduce the device efficiency in an OLED by absorbing the generated light. In fact, HTMs doped with the tris(benzoato)bismuth(III) compounds exhibit only a very minor absorption of visible light in the spectrum due to doping (Figure 5). Co-evaporation with 1-TNata, α-NPB, and spiro-TTB in 200 nm thick layers at a dopant:HTM ratio 1:2 leads only to a slight increase of the absorption in the 3.1 eV to 1.55 eV range, with respect to the pristine HTM materials. Even in the most unfavorable case, the (1:2) $\mathrm{Bi(4\text{-}pftl)_3}$-doped spiro-TTB layer is only 1.65 time more absorbing at 2.40 eV (516 nm—green) than the pristine spiro-TTB reference. We note that for a ratio of one mole of $\mathrm{Bi(4\text{-}pftl)_3}$ to two moles of spiro-TTB, the volume share of the dopant in the semiconductor is about 15%. As shown in Figure 3, lower concentrations are sufficient to reach comparable conductivities, and result in high transparency.

The bismuth complexes used in this study are Lewis acidic as a result of the electrophilicity of the $\mathrm{Bi^{III}}$ centers induced by fluorinated carboxylato ligands and are thus expected to dope HTMs via the Lewis acid-based mechanism. These donor–acceptor couples are expected to be closed-shell complexes with a weak electron donation induced by a small resonance integral β.[10,25] The neutral off-state appearance of the doped thin films is in line with the idea of the doping mechanism to not promote the formation of stable and strongly visible-light absorbing $\mathrm{HTM^{\bullet+}}$ radical cations on a redox-driven mechanism. We note that radicals may still be statistically generated by thermal activation, but they are not expected to play a significant role in the absorption spectra.[10]

One of the bismuth p-dopants was also tested in the hole injection layer (HIL) in a white OLED device (WOLED) to assess the applicability of this family of p-dopants in a complete emitting device (see Table 1). The performance of the $\mathrm{Bi^{III}}$-doped device is compared to a reference device which has the same structure except from a hole injection layer being doped with a commercially available p-dopant widely used in the field of organic electronics. The p-dopant concentration was individually optimized for these two dopants.

The comparison shows that the $\mathrm{Bi^{III}}$-based dopant can be favorably used in a WOLED and the performance of the device with respect to efficiency, driving voltage, and steady-state lifetime, is comparable to state-of-the-art WOLEDs. In particular the higher EQE of the $\mathrm{Bi^{III}}$-doped device, even at a higher luminance, is of importance, which we attribute to the lower absorbance arising from both the high band-gap of the dopant (over 3.1 eV), and the low absorption of the charge-transfer complex. In the case of the reference device, the lower EQE could at least partly be due to the absorption of the

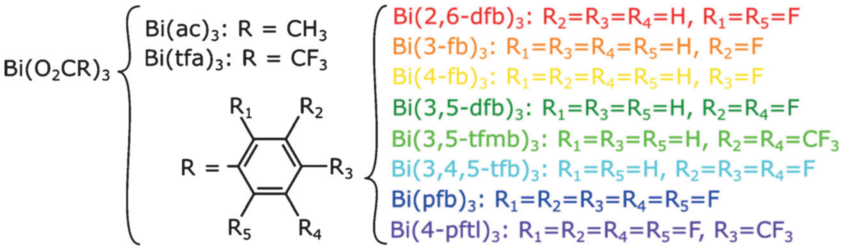

Figure 2. Chemical formula of the different tris(carboxylato)bismuth(III) which were used as p-dopants.

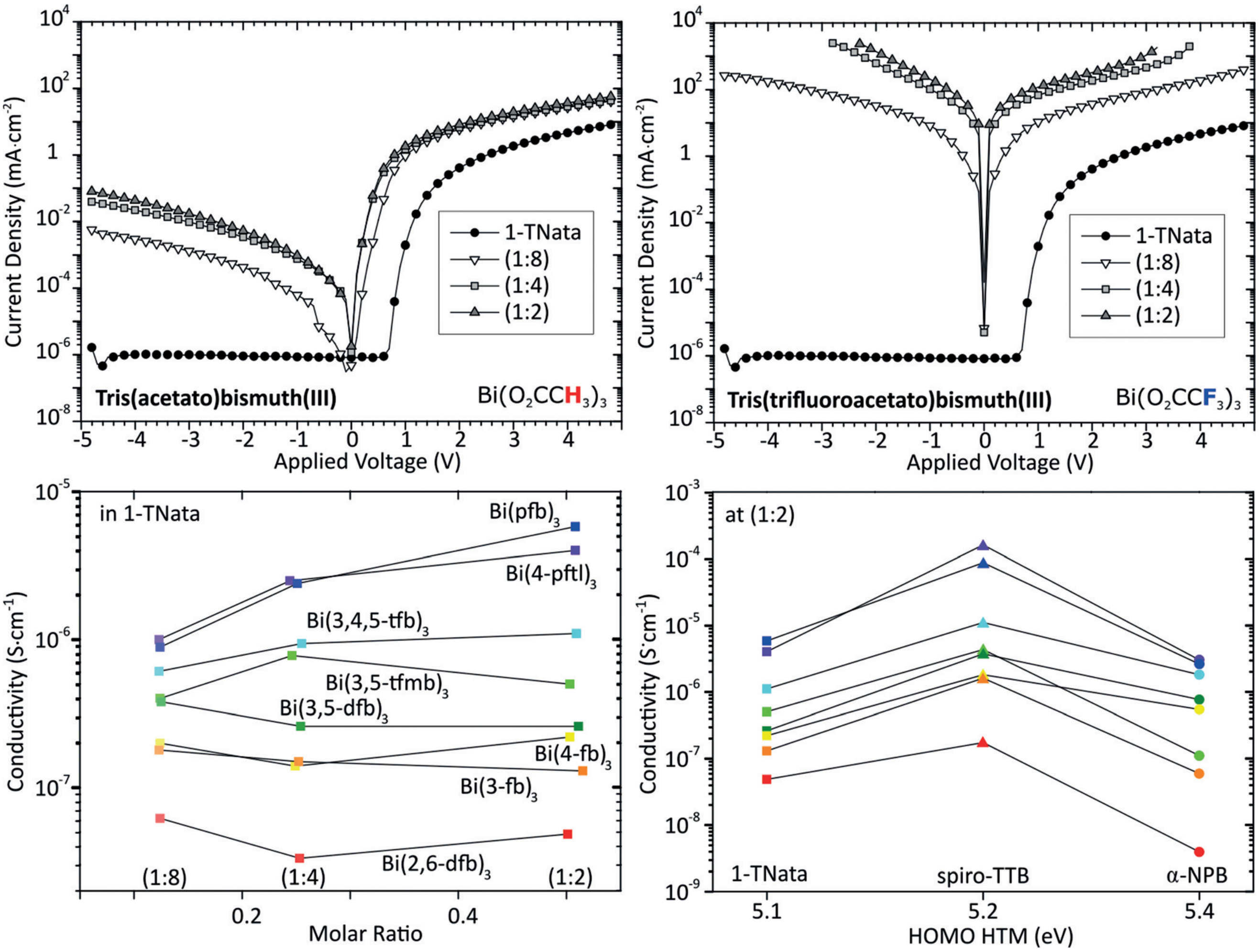

Figure 3. Current-density–voltage characteristics of 1-TNata (4,4′,4′′-tris(*N*-(1-naphtyl)-*N*-phenylamino)triphenylamine) stacked devices, doped with the non-fluorinated Bi(ac)$_3$ (top left) and the perfluorinated Bi(tfa)$_3$ (top right). Conductivities of 1-TNata layers doped with different concentrations of a series of fluorinated benzoato bismuth (bottom left) and conductivities of 1-TNata, spiro-TTB (2,2′,7,7′-tetra(*N*,*N*-ditolyl)amino-9,9-spiro-bifluorene), and α-NPB (*N*-*N*′-di(1-naphtyl)-*N*,*N*′-diphenyl benzidine) layers with the same series of dopants (bottom right). HOMO level energy values from the literature.[31–33]

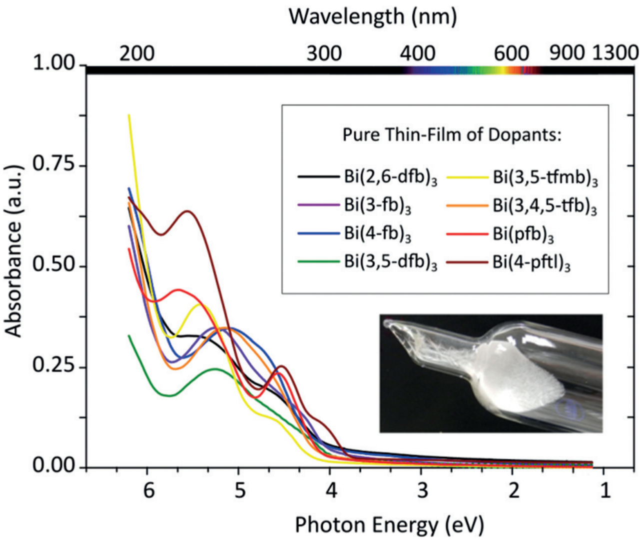

Figure 4. UV/Vis-NIR spectra of the pure p-dopant thin films (thickness of 50 ± 5 nm), displaying an optical band-gap around 4.0 eV.

dopant, as its optical band-gap is located at 2.3 eV.[32] We observe, that Bi^{III} dopants can in general replace common p-dopants using the same host materials and without any adjustments of the organic stack.

In addition, ampoule tests of this Bi^{III} compound demonstrate its stability up to at least 300 °C (ca. 70 °C above the sublimation temperature of the material) while the reference dopant shows decomposition at 289 °C under thermogravimetric analysis conditions.[35] Above 300 °C, the color of the Bi^{III} dopant slightly changes, but elemental analysis of the material treated at 315 °C did not show any change of chemical composition, suggesting an even higher thermal stability.

To conclude, several Lewis acidic tris(carboxylato)bismuth(III) complexes of varied electrophilicity have been synthesized. This set of materials features different conductivity enhancements of OSCs which are commonly used as HTM for OLED applications. Moreover, pure films as well as doped-HTM films show only a very weak absorption in the visible part of the spectrum. In addition to

Table 1: WOLED performances with a diffuse outcoupling foil containing 140 nm HIL doped with one of the Bi^{III} compounds compared to one doped with a commercially available pdopant. Measurements conducted in an Ulbricht sphere except LT70 determination. LT70 from accelerated testing at 25 °C, $J = 30$ mA cm^{-2}.

Device	L [cd m^{-2}]	P_{eff} [lum W^{-1}]	I_{eff} [cd A^{-}]	EQE [%]	Cx/Cy	U [V]	J [mA cm^{-2}]	CCT [K]	LT70 [h]
Bi^{III}-doped HIL	2700	37.6	71.7	31.6	0.420/0.400	6.0	3.8	3300	650
reference device	1900	37.6	72.9	25.1	0.371/0.455	6.1	2.6	4600	610

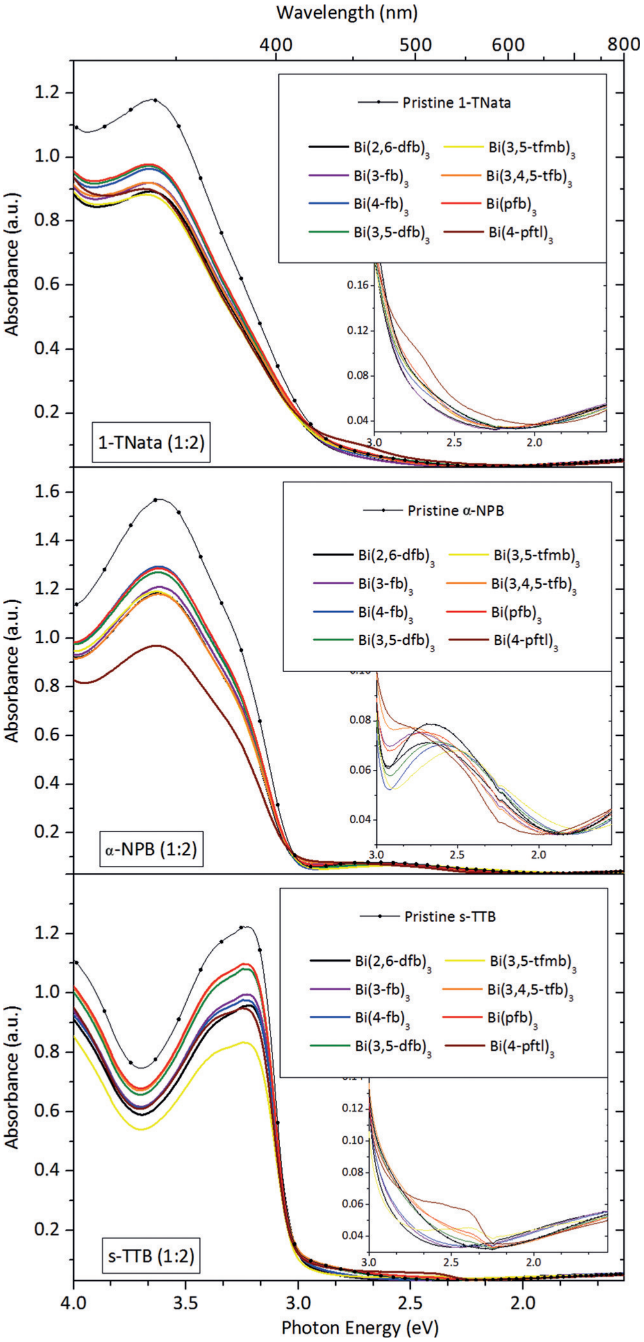

Figure 5. UV/Vis spectra of the 200-nm-thick (1:2)-doped OSCs films, co-evaporated with the different tris(benzoato)bismuth p-dopants, compared to the pristine references. As these spectra show, the off-state appearance after doping was neutral and the films did not exhibit any visible color change.

these ideal electrical and optical performance data, the compounds are easy to synthesize, comparable cheap, and have a good air and temperature stability and thus fulfil all requirements for opto-electronic applications. Finally, we demonstrated that the performance of white OLEDs with a HIL doped with one of the new dopants was at least as good as with a standard commercially available dopant widely used in OLEDs.

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Keywords: bismuth · donor–acceptor systems · doping · OLEDs · organic electronics

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