Organic Semiconductors

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A Soluble Dynamic Complex Strategy for the Solution-Processed Fabrication of Organic Thin-Film Transistors of a Boron-Containing Polycyclic Aromatic Hydrocarbon

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Abstract: *The solution-processed fabrication of thin films of organic semiconductors enables the production of cost-effective, large-area organic electronic devices under mild conditions. The formation/dissociation of a dynamic B–N coordination bond can be used for the solution-processed fabrication of semiconducting films of polycyclic aromatic hydrocarbon (PAH) materials. The poor solubility of a boron-containing PAH in chloroform, toluene, and chlorobenzene was significantly improved by addition of minor amounts (1 wt% of solvent) of pyridine derivatives, as their coordination to the boron atom suppresses the inherent propensity of the PAHs to form π-stacks. Spin-coating solutions of the thus formed Lewis acid–base complexes resulted in the formation of amorphous thin films, which could be converted into polycrystalline films of the boron-containing PAH upon thermal annealing. Organic thin-film transistors prepared by this solution process displayed typical p-type characteristics.*

Solution-processable organic semiconductors are attractive materials for the preparation of flexible, cost-effective, large-area devices, for example, organic field-effect transistors (OFETs) and photovoltaics (OPVs), under mild conditions.[1] However, π-conjugated semiconducting materials generally suffer from poor solubility in common organic solvents, which hampers device fabrication from their solution. One way to circumvent this problem is the introduction of solubilizing substituents to the π-conjugated skeleton, for example, long or branched alkyl chains[2] or bulky trialkylsilyl groups.[3] Alternatively, the π-conjugated skeletons can be connected in a nonplanar fashion, which may also improve the solubility.[4] Another promising strategy is the use of soluble precursors for organic semiconductors that contain thermally or photochemically removable solubilizing groups.[5] Various types of soluble precursors have been reported not only for small molecules such as acenes,[6,7] benzoporphyrins,[8] and oligothiophenes,[9] but also for semiconducting polymers.[10,11] The conversion of these materials into the corresponding pristine semiconductors posterior to the formation of the thin films can be accomplished via several covalent bond-cleavage reactions, for example, retro-Diels–Alder reactions,[6,8,10d] the thermolysis of ester, amide, or carbamate groups,[9,10a–c] or the photo-elimination of α-diketones[7] (Figure 1). In this context, the gradual formation of the pristine semiconductors is beneficial to prepare highly crystalline thin films. Although this soluble precursor method is useful for the fabrication of solution-processed devices, it requires more reaction steps to synthesize the precursors than using the pristine π-conjugated materials directly.

As an alternative to the soluble precursor method, we herein disclose a concept for the device fabrication of insoluble organic semiconductors, namely a soluble dynamic

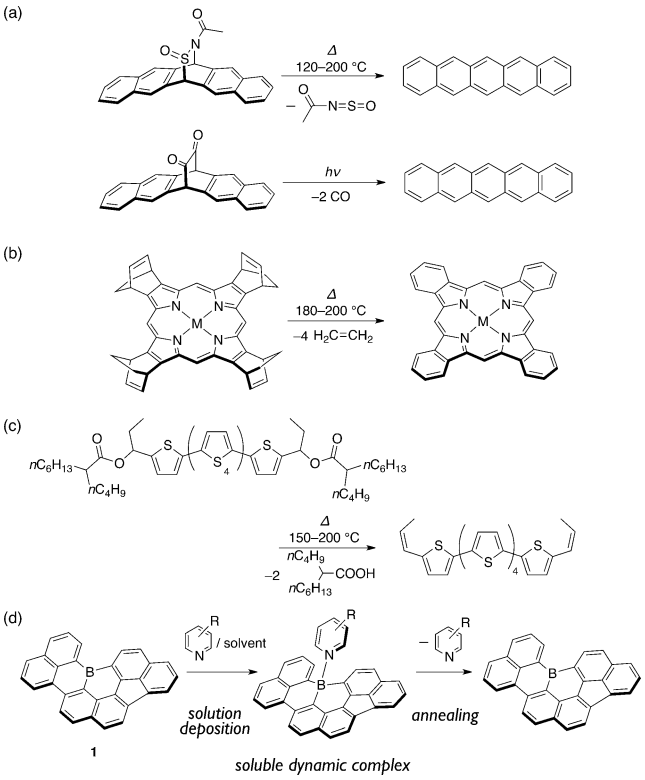

Figure 1. Soluble precursor methods for the preparation of thin films of semiconducting materials: a) pentacenes, b) benzoporphyrins, and c) an oligothiophene derivative, and d) a soluble dynamic complex strategy for the thin film preparation of boron-containing PAH **1**.

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complex strategy, which relies on the dynamic formation/dissociation behavior of a Lewis acid–base complex (Figure 1 d). Polycyclic aromatic hydrocarbons (PAHs) that contain embedded Lewis acidic boron atoms represent ideally suited π-electron systems for this concept. These materials have recently attracted increasing attention as a new class of semiconductors, as well as a model for boron-doped graphene.[12] Although most of organoboron compounds are sensitive to oxygen and water unless having steric protection of the boron atoms, these boron-containing PAHs are substantially stable owing to the structural constraint of the tricoordinate boron centers in a planar fashion, even in the absence of any steric protection of the boron atoms. Based on these principles, we synthesized various types of planarized triarylboranes[13] and other expanded boron-containing PAHs.[14] Other research groups also reported partially or fully constrained triarylboranes,[15] some of which have helicene structures, giving rise to improved solubility and processability owing to the slight distortion of the molecular framework.[15a,b] Despite the structural constraint of the boron atoms in these π-skeletons, these compounds maintain Lewis acidity and spontaneously form Lewis acid–base complexes even with weakly basic pyridines. However, these B–N coordination bonds are labile and undergo dissociation in solution upon heating or photoirradiation, resulting in pronounced thermochromism[14a] and dual fluorescence.[14c] Based on this notion, we envisioned that the dynamic behavior of these Lewis acid–base complexes may be exploited to fabricate organic thin-film transistors of insoluble semiconducting PAH materials in the solution process. A similar approach has been reported for poorly soluble aromatic carboxylates of lanthanides in the context of fabricating organic light-emitting diodes.[16] Notably, this strategy does not require any elaborate synthesis of soluble precursors, while thermal annealing conditions to remove the Lewis bases can be modulated by selecting pyridine derivatives with varying Lewis basicity.

To test this concept, we chose trinaphthylborane **1** as a model compound. Despite its partially fused structure, **1** exhibits a completely planar geometry and is thus able to form π-stacked columnar structures in the crystalline state. In a preliminary study, we confirmed that vapor deposition of **1** allows the fabrication of OFETs, in which **1** acts as an active layer, although the hole mobility is low ($9.3\times10^{-6}\,cm^2V^{-1}s^{-1}$).[14c] The partially fused structure of **1** endows this compound with a relatively high Lewis acidity compared to the fully fused boron-containing PAHs synthesized so far.[14a,d] An association constant of $5.1\times10^3\,M^{-1}$ was observed for **1** and pyridine in toluene at 25 °C. Upon coordination of pyridine to **1**, its geometry changes from planar to bowl-shaped, and the thus formed tetracoordinate boron center prevents the formation of the π-stacked columnar structure.[14c] This structural modification significantly improves the solubility of **1** in various solvents (Table 1). At room temperature, tricoordinate **1** exhibits poor solubility ($<1.0\,g\,L^{-1}$) and low saturation concentrations (<0.1 wt%) in common organic solvents such as chloroform, toluene, or chlorobenzene. In sharp contrast, **1** shows a much higher solubility in pyridine, which is reflected in a saturation concentration that is more than an order of magnitude higher ($14.8\,g\,L^{-1}$; 1.5 wt%). It should be noted that ca. 1 wt% concentration of materials is normally required for the spin-coating fabrication of thin films.

Table 1: Solubility and saturation concentrations of **1** in some organic solvents.

Solvent	Solubility [$g\,L^{-1}$][a]	Saturation concentration [wt%]
$CHCl_3$	0.38	0.026
toluene	0.25	0.029
chlorobenzene	0.78	0.070
pyridine	14.8	1.5

[a] Measured at 25 °C.

Subsequently, a thermally induced dissociation could be observed for the resulting Lewis acid–base complex with pyridine, **1·Py**, even in the solid state. By the addition of hexane to a pyridine solution of **1**, an orange powdery sample of **1·Py** precipitated, which is distinct from the red powdery sample of **1**. The obtained orange powder of **1·Py** did not change color, even after drying in vacuo at room temperature for several hours. The thermal stability of the Lewis acid–base complex **1·Py** was examined in the solid state by thermogravimetric analysis (TGA; Figure 2). Upon increasing the temperature, a first weight loss (18%) was observed at

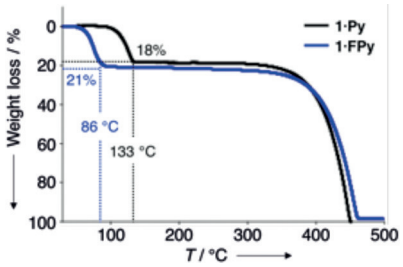

Figure 2. TGA profiles of Lewis acid–base complexes **1·Py** (black) and **1·FPy** (blue). The measurements were carried out under a nitrogen atmosphere using a heating rate of 5 °C min^{-1}.

133 °C, which should be attributed to the complete release of pyridine from **1·Py** (theoretical value: 17%). A second weight loss was observed at about 380 °C, which should most likely be ascribed to the decomposition of **1** (5% weight loss temperature: $T_{d5}=384$ °C).[14c] This result indicated that pyridine can be completely removed from Lewis complex **1·Py** without decomposition by simple heating in the solid state.

Lewis complexes of **1** with various other pyridine derivatives, including 4-methylpyridine (MePy), 3-chloropyridine (ClPy), and 3-fluoropyridine (FPy), were obtained in a similar manner to that using pyridine, and their thermal behavior was monitored by TGA (Figure 2; Supporting Information, Figure S1). The first-step weight losses of 23%, 25%, and 21% were observed for **1·MePy**, **1·ClPy**, and **1·FPy**, respectively, which are in good agreement with the theoretically expected values. The weight loss temperatures increased in the order **1·FPy** (86 °C) < **1·ClPy** (92 °C) < **1·MePy** (129 °C) < **1·Py** (133 °C). The weaker Lewis bases ClPy and FPy are more easily released than Py and MePy, even though the boiling

point of ClPy (155 °C) is higher than that of Py (115 °C). This result indicated that the weight loss temperature is correlated to the Lewis basicity rather than to the boiling point of the pyridine derivative. It is also noteworthy that the weight loss temperature of **1·FPy** (86 °C) is much lower than those of other soluble pentacene precursors that undergo retro-Diels–Alder reactions (120–200 °C).[5b]

Thin films of **1·Py** were deposited on Si/SiO_2 or glass substrates by spin-coating a chloroform solution of trinaphthylborane **1** that contained 1 wt % of pyridine against chloroform. The UV/Vis absorption spectrum of the spin-coated **1·Py** film on the glass substrate showed a strong absorption band at 360 nm and a weak absorption band at 450 nm, which is similar to the absorption of **1·Py** in toluene (Figure 3; Supporting Information, Figure S2). Upon annealing the film at 180 °C, the absorbance in the visible region increased and the absorption onset reached 615 nm. After 5 min of annealing, the absorption spectrum of the film was similar to that of a vapor-deposited film of **1** (Supporting Information, Figure S3), indicative of the successful thermal conversion of **1·Py** into **1** on a glass substrate.

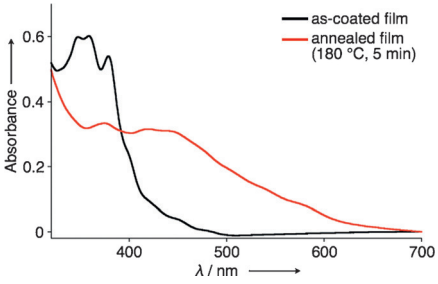

Figure 3. UV/Vis absorption spectra of a spin-coated film of **1·Py** on a glass substrate prior (black) and posterior (red) to annealing at 180 °C.

The optical band gap (E_g) of the prepared film of **1** was estimated to be 2.02 eV based on the absorption onset. For this thin film, an ionization potential (I_p) of 5.61 eV was determined by photoelectron spectroscopy in air (Supporting Information, Figure S5). The electron affinity (E_a) of 3.59 eV was estimated from these I_p and E_g values, which is comparable to that estimated from the reduction potential of **1** determined by cyclic voltammetry (3.62 eV; −1.48 V vs. Fc/Fc^+ in THF).[14c,17] This electronic structure, particularly the high I_p value, suggests potential applications for **1** in air-stable p-type OFET materials.

The surface morphology of the spin-coated film on the Si/SiO_2 substrate was studied by X-ray diffraction analysis (Figure 4a; Supporting Information, Figure S6). The as-coated film of **1·Py** did not show any diffraction peaks and was thus considered amorphous. Upon annealing at 180 °C, several diffraction peaks appeared, indicative of the formation of some ordered phase. However, the observed diffraction pattern was not identical to that of a crystalline powder sample of **1**, which was obtained from sublimation, indicating the formation of a different phase in the annealed thin film. Crystallization upon thermal annealing was confirmed by optical microscope images (Supporting Information, Figure S9). While a uniform and smooth surface was observed for the as-coated film of **1·Py**, the annealed film has small crystal domains. The polarized optical microscopy (POM) displayed these domains as a bright image when observed under the crossed Nicols. The roughness of the annealed film morphology was assessed by atomic force microscopy (AFM) (Figure 4b; Supporting Information, Figure S10), which revealed a polycrystalline rough surface with significant boundaries between rod-like crystallites. These randomly oriented crystallites showed a root mean square roughness of 15 nm. The formation of a crystalline thin film upon annealing a spin-coated film of **1·Py** stands in contrast to the fact that the direct vapor deposition of **1** afforded an amorphous film, which did not show any diffraction peaks (Supporting Information, Figure S7).

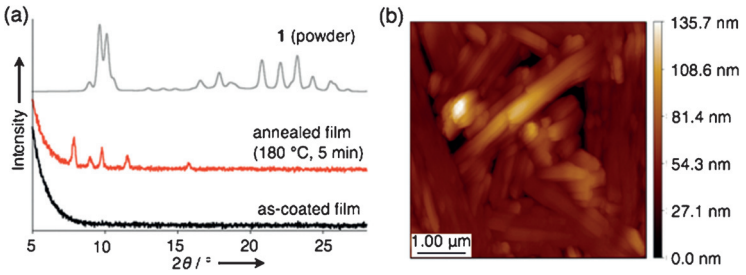

Figure 4. a) XRD spectra of a thin film of **1·Py** prior and posterior to annealing, as well as of a sublimated crystalline powder sample of **1**; b) AFM image of a thin film of **1·Py** on the Si/SiO_2 substrate posterior to thermal annealing (180 °C; 5 min). Spin-coated films of **1·Py** were prepared under conditions identical to those used for the fabrication of OFETs.

Bottom-gate top-contact OFET devices were fabricated using a heavily n-doped Si substrate with a thermally grown 100-nm thick SiO_2 film as the gate insulator, and the SiO_2 surface was treated with hexamethyldisilazane (HMDS). A chloroform solution of **1** (0.5 wt %) including 1 wt % of pyridine was spin-coated onto the substrate (30 s; 2000 rpm; in air). The spin-coated films thus obtained were annealed (180 °C; 5 min) in air to remove any pyridine derivative. Then, 50-nm thick gold electrodes were deposited as the source and drain on top of the organic thin films through a shadow mask under vacuum. FET properties were measured with a semiconducting parameter analyzer in air. The solution-processed OFETs of **1**, prepared via the **1·Py** precursor, exhibited typical p-type FET characteristics (Figure 5). The field-effect mobility (μ_{FET}) was calculated in the saturation regime. The highest μ_{FET} measured was $2.5\times10^{-4}\,cm^2\,V^{-1}\,s^{-1}$ (average μ_{FET}: $1.7\times10^{-4}\,cm^2\,V^{-1}\,s^{-1}$) with an on/off current ratio (I_{on}/I_{off}) of 9×10^3 and a threshold voltage (V_{th}) of −12.3 V. This hole mobility is superior to that of the previously reported vapor-deposited film ($9.3\times10^{-6}\,cm^2\,V^{-1}\,s^{-1}$ for the holes),[14c] which is probably due to the higher crystallinity that was observed by X-ray diffraction analysis. OFETs prepared using

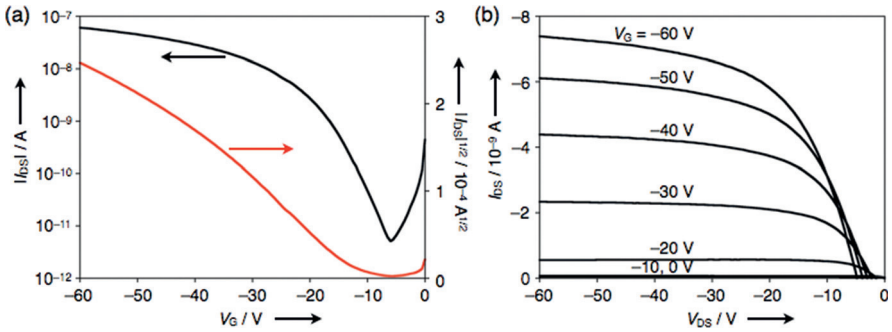

Figure 5. OFET characteristics of **1** prepared from **1·Py**: a) transfer characteristics in the saturation regime at the drain-source voltage (V_{DS}) of −60 V; b) output characteristics at different gate voltages (V_G).

1·MePy displayed similar characteristics (Supporting Information, Figures S4, S8, S9, S11, and S12).

In summary, we demonstrated a concept for the fabrication of OFETs in solution based on the dynamic complexation/dissociation behavior of the Lewis acid–base complex of a boron-containing PAH. The solubility of the planar π-electron system was drastically enhanced by addition of 1 wt% of Lewis basic pyridines. Spin-coating these soluble Lewis complexes resulted in the formation of amorphous thin films, which could be converted into polycrystalline films of the pristine boron-containing PAH by simple annealing. Top-contact FET devices using **1** as a semiconducting layer, fabricated by this method, displayed typical p-type characteristics with a better hole mobility (2.5×10^{-4} $cm^2 V^{-1} s^{-1}$) than that of the corresponding vapor-deposited FET. Although the device performance still requires further optimization, this proof-of-concept study clearly demonstrates the potential of such boron-doped PAHs for applications in organic electronics.[18]

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Keywords: boron · Lewis acid–base complexes · organic semiconductors · polycyclic aromatic hydrocarbons · solubility modulation

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