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Green Synthesis of Polycyclic Benzimidazole Derivatives and Organic Semiconductors

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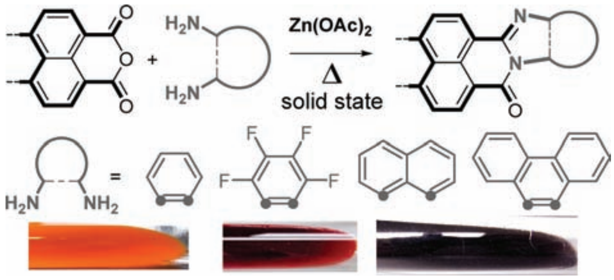
ABSTRACT



Polycyclic benzimidazole derivatives, an important class of compounds in organic electronics and photovoltaics, were prepared using a solvent-free "green" process based on heating carboxylic acid anhydrides and arylene diamines in the presence of zinc acetate in the solid state. Products were isolated and purified directly by train sublimation of the crude reaction mixtures. The reaction conditions were optimized using various carboxylic acid anhydrides. Optical and electrochemical properties of these materials are also described.

Because of their stability and high light absorptivity, the benzimidazole derivatives of naphthalene, perylene, and phenylene carboxylic acids are compounds of importance in pigment and dye chemistry[1] and organic electronics.[2] Notable examples are naphthalene tetracarboxylic acid bisbenzimidazole (NTCBI) and perylene tetracarboxylic acid bisbenzimidazole (PTCBI), which are also important n-type semiconductors in organic thin-film transistors (OTFTs) and organic photovoltaics (OPVs).[2] The successful application of these materials is predicated on their availability in high purity at low cost.

Typical conditions used for the condensation reaction of diamines with carboxylic acid anhydrides involve heating under reflux in AcOH.[1,3] For PTCBI, harsh conditions and use of high boiling and/or toxic solvents capable of maintaining reactivity and overcoming the poor solubility of intermediates are required[4] and are the limiting factor. For example, the NTCBI and PTCBI derivatives require trifluoroacetic acid as a solvent for chromatography.[4c,5] This is hazardous to health and a cause for environmental concern, and as a result, environmentally benign "green" synthetic routes have received increasing attention.[6]

Although solvent-free reactions are among the key issues in green chemistry, relatively few instances of solvent-free synthesis and purification are known. Here, sublimation is

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an inherently solvent-free technique which is relatively easy to do. It is scalable and most importantly affords highly pure materials, a potential boon for organic electronics. In fact, due to high purity requirements, organic electronic materials are usually purified by sublimation before fabricating thin films by thermal evaporation. Thus, we decided to investigate solid state condensation and direct sublimation (SSC-DS), synthesis of polycyclic benzimidazoles, which requires short reaction time, simpler workup, and high yields of pure products. Here, an efficient "green" synthesis of NTCBI, PTCBI, and similar benzimidazoles focused on limiting byproducts and waste, and minimal organic solvent use is presented. Also, the opto-electronic properties of polycyclic benzimidazoles are described.

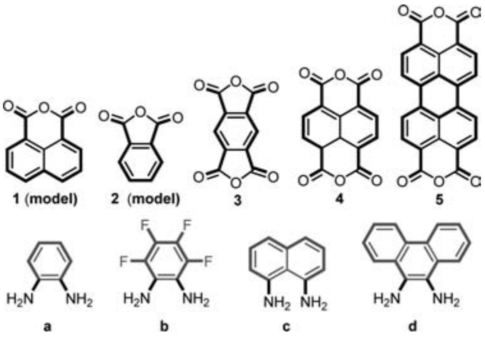
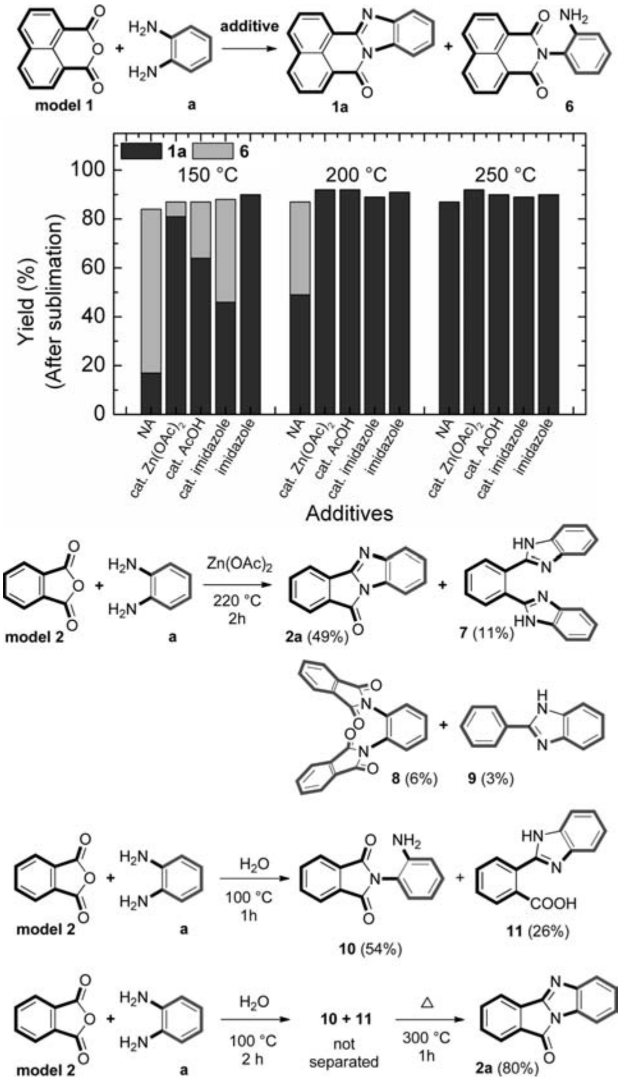


Figure 1. Starting materials used in this study: carboxylic acid anhydrides and diamines.

Various combinations of carboxylic acid anhydrides and diamines were examined (Figure 1). The SSC-DS method was studied first on two model systems: 1,8-naphthalic anhydride **1** and 1,2-diaminobenzene **a**, and phthalic anhydride **2** with diaminobenzene **a**. First, we screened the conditions using catalysts and promoters described in the literature syntheses of **1a**[3−5,7] in the solid state reaction (Scheme 1, top). At lower than 150 °C, **6** was obtained as the major product. The yields of **1a** increased in the presence of imidazole (melt, 1 h, 46−90%, depending on the imidazole amount), acetic acid (melt, 1 h, 64%), and zinc acetate (melt, 1 h, 81%). At 200 °C, in a sealed tube followed by sublimation (10^{-6}−10^{-7} Torr) of the crude, all of the typical catalysts such as imidazole, acetic acid, and zinc acetate furnished high yields (ca. 90+% after sublimation; see Scheme 1, center). However, the products obtained using imidazole or acetic acid were darker and contained an impurity, which was difficult to remove by sublimation and required chromatography to obtain pure **1a**, whereas a zinc acetate product was bright yellow after sublimation (see Supporting Information). Without a catalyst, the yield of **1a** was lower (Scheme 1, center). Thus, zinc acetate was selected for further optimization, not only because of high yield but also because of high purity of the product.

Scheme 1. Model Reactions for **1a** and **2a**



In contrast to model 1, the reaction of anhydride **2** with 1,2-diaminobenzene (model reaction 2, Scheme 1) is known to yield a number of products,[8] presumably due to the strain in the 5*H*-pyrrolo[1,2-*a*]imidazol-5-one structure of **2a**. When an excess amount of either starting material was used, the bisbenzimidazole **7** or bisphthalimide **8** was formed in high yields.[9] Also, **2a** reacts with 1,2-diaminobenzene to give bisbenzimidazole **7** even at 100 °C. Thus, even a strict 1:1 reagent proportion yields byproducts **7**−**9** in the SSC-DS.

Compound **2a** is not the first product of the reaction. One possible pathway is through intermediates **10** and **11**

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observed in the previous report, where yields were 20−30%.[9,10] These two intermediates could be obtained in good yield (54% for **10** and 26% for **11**) when the reaction is carried out in boiling water (Scheme 1, bottom). Because **10** and **11** are almost insoluble in water while the starting materials are soluble, the precipitate of **10** and **11** can be easily collected and separated. Both **10** and **11** can be converted to **2a** during the sublimation and therefore do not have to be separated. This aqueous method yields **2a** in an 80% yield after heating at 250−300 °C and sublimation (Table 1). While the aqueous synthesis of **10** and **11** adds another synthetic step, it is still a nontoxic and inexpensive solvent. Pyromellitic dianhydride **3** also afforded **3a** in a 42% yield after sublimation (Table 1).

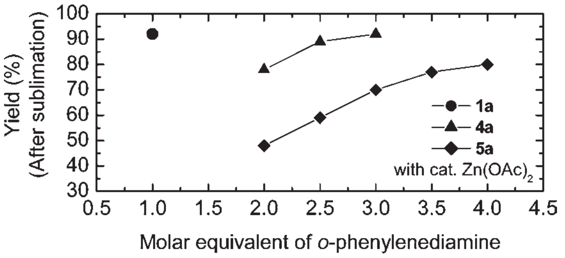
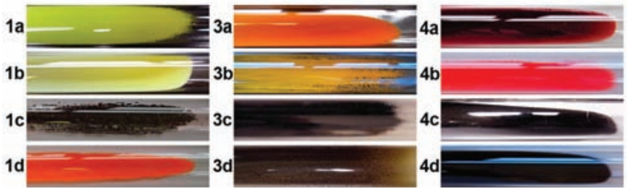


Figure 2. Effect of the amount of a diamine on product yield.

Table 1. Summary Yields of Condensation Products after Train Sublimation (Photographs below Show Sublimed Products). Conditions: Series **1** and **2**, Diamine Anhydride 1:1; Series **3**, 2 Equiv of Diamine; Series **4**, 3 Equiv of Diamine; Series **5**, 4 Equiv of Diamine

	1	**2**	**3**	**4**	**5**
a	$92\%^{a*}$	$49\%^{a}$, $77\%^{b}$	$42\%^{b}$	$92\%^{c}$	$80\%^{c}$
b	$80\%^{c}$	$52\%^{d}$	$33\%^{d}$	$81\%^{e}$	$11\%^{e}$
c	$77\%^{a}$	$80\%^{a}$, $35\%^{b}$	$53\%^{a}$	$77\%^{c}$	$36\%^{c}$
d	$86\%^{a}$	$66\%^{b}$	$20\%^{b}$	$87\%^{c}$	$5.5\%^{c,f}$



[a] At 220 °C, 2 h with catalytic amount of $Zn(OAc)_2$. [b] At 100 °C, 1 h in H_2O, then heated at 300 °C for 1 h. [c] At 250 °C, 3 h with catalytic amount of $Zn(OAc)_2$. [d] At 100 °C, 1 h in H_2O, then heated at 300 °C for 2 h. [e] At 300 °C, 3 h with catalytic amount of $Zn(OAc)_2$. [f] **5d** appears to be decomposing at 600 °C required for the sublimation.

From the perspective of potential applications, the NTCBI **4a** and PTCBI **5a** are the more important products and particular attention was devoted to their synthesis. As alluded to above, the diamine anhydride stoichiometry is a factor important for achieving not only a high product yield but also a high purity product in SSC-DS. Figure 2 shows **1a**, **4a**, and **5a** yields as a function of the 1,2-diaminobenzene proportion. In the case of the model reactions, excess diamine did not improve the product yields; however, in the case of **4a** and **5a**, improved yields were observed. The excess of a volatile diamine fraction is recovered during the sublimation. As a result, better yields and easy separation were achieved for NTCBI **4a** and PTCBI **5a**.

The yields of benzimidazole and bisbenzimidazole products obtained by SSC-DS and the aqueous condensation method are summarized in Table 1,[11] with photos of selected products "as sublimed". **3a**−**d**, **4a**−**d**, and **5a**−**d** are obtained as mixtures of isomers.

Because the bisbenzimidazole compounds such as PTCBI and NTCBI are n-type semiconductors (and electron transporting materials) with high potential impact in solar cells (OPVs) and OTFTs, we were quite interested in their octa-fluoro analogues obtained from the tetrafluoro-1,2-diaminobenzene **b**.[12] So far, fluorinated bisbenzimidazoles attracted little attention despite their potentially high electron affinity, which could make them valuable n-type semiconductors in organic electronic applications. **1b**−**5b** were successfully synthesized in good yield, although the reaction, due to lower amine nucleophilicity, required a higher temperature (300 °C). At temperatures < 300 °C, the reaction was incomplete, showing a mixture of imido compounds.

Reactions of 1,8-diaminonaphthalene **c** and naphthalene carboxylic anhydride derivatives **1**, **4**, and **5** gave yields similar to the model reactions with 1,2-diaminobenzene **a**. The reactions of anhydrides **2** and **3** differed from the model reaction that yielded **2a**. Here, the SSC-DS method with the zinc acetate catalyst gave yields superior to the aqueous conditions, which is attributed to less strained fused six- and five-membered rings in the 12*H*-isoindolo-[2,1-*a*]perimidin-12-one system.[8b]

With the products in hand, we investigated their photophysical and electrochemical properties. The results for the series **1a**−**d** and **4a**−**d** are summarized in Figure 3 and Table 2. For solubility reasons, some materials were investigated as thin films. The UV−vis spectra of compounds **1a**−**d** and **4a**−**d** are characterized by broad $\pi-\pi^*$ transition and extinction coefficients of 8000 M^{-1} cm^{-1}.[1b,4b] In compounds **4**, this band is broader, presumably due to the presence of aggregates in the solutions.[4d] Compounds **1a** and **1b** show the $\pi-\pi^*$ transition at 350−420 nm, while **1c** and **1d** show broad $\pi-\pi^*$ transition at 390−600 and 370−500 nm respectively; these broad and red-shifted bands attributed to a charge transfer character and the extended π conjugation in the naphthalene and phenanthrene moieties.[13,14] In the case of the series **1a**−**d** and between **4a** and **4b**, the emission

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(11) Known compounds: **1**−**5a** and **1**−**5c**. For the comparison of reaction yields and conditions, see the Supporting Information.

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energy correlates with the quantum efficiency (energy gap law).[15] This effect is apparent for **1a**,**b** and **4a**,**b**, compounds that differ only in the C−H and C−F bonds. The electron-withdrawing fluorine atoms induce a 33 nm blue shift in the emission maximum compared to **1a**. The effect of fluorine electronegativity on the emission of **4b** resulted in a 36 nm blue shift compared to **4a**. The quantum yields are higher for compounds **1b** and **4b** (82% vs 71% and 11% vs 2%), while the lifetimes are shorter (9.0 ns vs 11.1 and 4.0 ns vs 4.9 ns). The compounds **4c** and **4d** are insoluble.

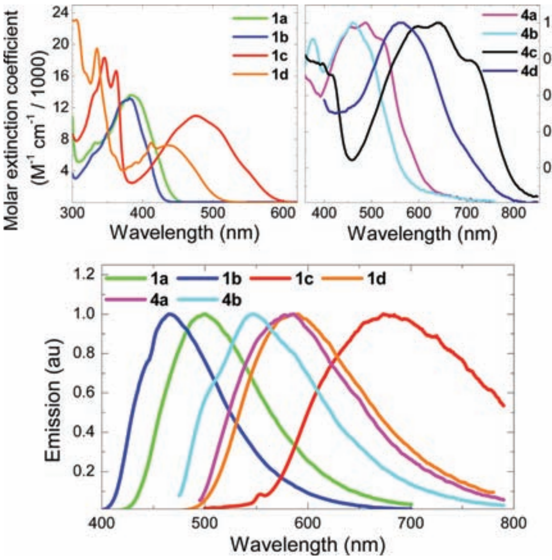

Figure 3. Absorption spectra of **1a**−**1d** (10^{-5} M in CH_2Cl_2) and normalized spectra of **4a**−**4d** (film), and normalized fluorescence spectra of **1a**−**1d** and **4a**−**4b** (in CH_2Cl_2).

Table 2. Photophysical and Electrochemical Properties of **1a**−**d** and **4a**−**d**

compd	λ_{abs} (nm)[a]	λ_{em} (nm)[b]	Φ_F[c]	τ (ns)	HOMO (eV)[d]	LUMO (eV)[e]
1a	384	499	0.71	11.1	−5.86	−3.06
1b	382	466	0.82	9.0	−6.06	−3.16
1c	475	682	NE	NE	−5.07	−2.96
1d	436	589	0.15	5.5	−5.51	−3.08
4a	484	585	0.02	4.9	−5.79[f]	−3.78[f]
4b	471	549	0.11	4.0	−6.01[f]	−3.92[f]
4c	609	NE	NE	NE	−5.17[f]	−3.63[f]
4d	562[f]	NE	NE	NE	−5.37[f]	−3.70[f]

[a] The lowest energy maxima. [b] Excited at the lowest energy maxima. [c] Absolute fluorescence quantum yield determined by a calibrated integrating sphere (errors < 10%). [d] Estimated from HOMO = LUMO − E_g, wherein E_g calculated from the optical absorption data (**1a**−**d**, solution; **4a**−**d**, film). [e] Estimated vs vacuum level from $E_{LUMO} = -4.80 - E_{1/2}^{red}$, where $E_{1/2}^{red}$ determined by cyclic voltammetry in 0.1 M solution of Bu_4NClO_4 in CH_2Cl_2 (**1a**−**d**) or film (**4a**−**d**) (vs Fc/Fc$^+$). [f] In film. NE = not estimated due to weak signal.

Cyclic voltammetry traces of compounds **1a**−**d** and **4a**−**d** revealed a clear first reduction peak (see Supporting Information). The calculated HOMO and LUMO levels are summarized in Table 2. The fluoro derivatives **1b** and **4b** showed higher electron affinity compared to other derivatives in the series **1** and **4**, respectively. Since the naphthalene and phenanthrene derivatives **1c** and **1d** exhibit a similar LUMO energy, the red shift in **1c** absorption is due to the low-lying HOMO level. The HOMO levels in series **4** correspond to the compounds of series **1**, whereas the HOMO of **1a** is similar to **4a**, **1b** to **4b**, etc. The series **4a**−**d** shows LUMO levels deeper for ca. 0.7 eV compared to the respective compounds in series **1**, an observation that explains the significantly lower HOMO−LUMO gap, as evidenced by the dark (almost black) color in series **4a**−**d**.

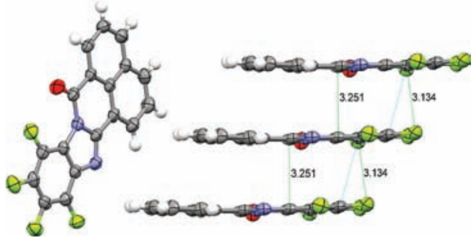

Figure 4. ORTEP of **1b** (thermal ellipsoids 50% probability).

X-ray single-crystal analysis of **1b** revealed C═O···H interactions, while the electron-deficient carbons bearing the fluoro substituents display strong interaction with the fluorine atoms of the adjacent molecule, displaying a short contact and a distance of 3.13 Å. The π−π stacking and intermolecular distance in a column was ∼3.30 Å, suggesting strong interactions (Figure 4).

In conclusion, a series of polycyclic benzimidazole derivatives were prepared using a solid state condensation in the presence of catalytic zinc acetate followed by direct sublimation. This solvent-free method gives yield superior or comparable to traditional solution-based procedures but is easy to do and, according to preliminary results, tolerates a wide range of substituents. The products are obtained by train sublimation, and their purity exceeds 99%. Valuable semiconductors such as NTCBI and PTCBI and their fluoro analogues that show higher fluorescence quantum yield, higher electron affinity, and strong intermolecular interactions were prepared. Their application in organic electronics, namely, OTFT, is currently underway.

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Supporting Information Available. Full experimental detail and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.