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# One-Pot Domino Carbonylation Protocol for Aromatic Diimides toward n-type Organic Semiconductors

#### Xiaolong Fu, Yonggang Zhen\*, Zhenjie Ni, Yang Li, Huanli Dong, Jay S. Siegel and Wenping Hu

Abstract: Aromatic diimides are one of the most important chromophores in the construction of n-type organic semiconductors, which lag far behind p-type counterpart but is necessary for the ambipolar transistors, p-n junctions and organic complementary circuits. Herein, we establish a facile one-pot domino synthetic protocol for aromatic diimides via palladium-catalyzed carbonylation of tetrabromo aromatic precursors. Taking tetrabromocorannulene (TBrCor) and tetrabromo-2,7-di-tert-butylpyrene (TBrPy) as the typical examples, we achieved diimide derivatives in yields about 50%, one order of magnitude higher than that of the traditional multistep diimidization. As demonstrated in the case of corannulene diimide, the efficient diimidization not only allows the LUMO levels to be lowered significantly but also provides an ordered and closer packing structures, opening up possibilities to the development of ntype semiconducting materials based on a variety of aromatic systems.

The last two decades has witnessed tremendous progress in organic semiconductors with widespread applications in organic field effect transistors  $(OFETs)^{[1]}$ , organic solar cells  $(OPVs)^{[2]}$ , and organic light-emitting diodes  $(OLED)^{[3]}$ . However, n-type organic semiconductors lag far behind p-type counterpart in terms of molecular diversity, carrier mobility as well as air stability, preventing the development in the ambipolar transistors, p–n junctions and organic complementary circuits.<sup>[4]</sup> Diimidization of aromatic systems can enhance electron affinity values significantly, thus opening up the possibility to achieve promising n-type materials including pyromellitic diimides (PMDI),<sup>[5]</sup> naphthalene diimides (NDI),<sup>[6]</sup> anthracene diimides

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- [c] Supporting information for this article is given via a link at the end of the document.

(ADI),<sup>[7]</sup> pyrene diimides (PyDI),<sup>[8]</sup> perylene diimides (PDI)<sup>[6a, 6d, 9]</sup> as well as biazulene diimides (BAzDI)<sup>[10]</sup>. Previously we reported single crystals of tetrachlorinated diperylene diimide with an electron mobility as high as 4.65 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>.<sup>[9b]</sup> The electron mobilities from NDI- and PDI-based small molecules have reached up to 8.6 and 6.0 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively.<sup>[6d, 11]</sup> PyDI derivatives exhibit efficient electron transport properties with electron mobility up to 3.08 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>.<sup>[8c]</sup> However, a long-standing issue hindering the development of novel aromatic diimides is the inefficient and tedious multistep syntheses requiring cyanation, hydrolysis, dehydration and imidization (**Figure 1**).



Figure 1. Representative aromatic diimides and the usual multi-step synthetic route from tetrabromo-precusors.

Although aromatic imides can be judiciously prepared through Friedel–Crafts reaction between aromatic carbonyl chlorides and isocyanates in the presence of aluminum chloride,<sup>[12]</sup> Heck-style palladium-catalyzed carbonylation to form amides<sup>[13]</sup> rarely has been used to achieve diimide derivatives mainly because of the low-yield domino carbonylation reactions.<sup>[14]</sup> Herein, we report a facile one-pot palladium-catalyzed carbonylation diimidization of tetrabrominated aromatic rings, and optimize the reaction parameters of CO source, catalyst ligand field, Brønsted base and solvent. Taking tetrabromocorannulene (TBrCor) and tetrabromo-2,7-di-tert-butylpyrene (TBrPy) as lead examples, we

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achieved diimide derivatives in yields about 50%, one order of magnitude higher than traditional methods.<sup>[8c, 15]</sup> The electron affinity values increase by more than 1 eV relative to the parent compounds. Notably, corannulene diimide (CorDI) assembles into one dimensional microribbons with close face-to-face  $\pi$ - $\pi$  stacking, thus facilitating electron carrier transport with carrier mobility up to 0.05 cm $^2$  V $^1$ s $^{-1}$ – one of the highest mobilities for corannulene derivatives.<sup>[16]</sup>

#### Table 1. Optimization of reaction conditions.



Entry	Catalyst/Ligand	CO	Solvent	Base	Yield <sup>a</sup>
	(3 mol %)	source			(%)
1	Pd(OAc) <sub>2</sub>	CO	Toluene	DBU	11
2	Pd(OAc) <sub>2</sub>	CO	Toluene	DABCO	trace
3	Pd(OAc) <sub>2</sub>	CO	Toluene	КОН	n.d. <sup>b</sup>
4	Pd(OAc) <sub>2</sub>	CHCl <sub>3</sub>	Toluene	CsOH	n.d. <sup>b</sup>
5	Pd(OAc) <sub>2</sub>	Mo(CO) <sub>6</sub>	Toluene	DBU	7
6	Pd(OAc) <sub>2</sub> /tBu <sub>3</sub> PHBF <sub>4</sub>	CO	Toluene	DBU	23
7	Pd(OAc) <sub>2</sub> /Xantphos	CO	Toluene	DBU	14
8	Pd(OAc) <sub>2</sub> /Ad <sub>2</sub> PnBu	CO	Toluene	DBU	52
9	Pd(OAc) <sub>2</sub> /Ad <sub>2</sub> PnBu	CO	Xylene	DBU	trace
10	Pd(OAc) <sub>2</sub> /Ad <sub>2</sub> PnBu	CO	DMAc	DBU	9
11	Pd(OAc) <sub>2</sub> /Ad <sub>2</sub> PnBu	Mo(CO) <sub>6</sub>	Toluene	DBU	41

a. Isolated yields. b. Not dected.

our initial investigation of the For intramolecular decarboxylative coupling, we chose the readily available TBrCor,<sup>[17]</sup> CO (1 atm), and butylamine as a test substrate (Table 1). Inspired by Alper's catalyst,<sup>[18]</sup> we first attempted a combination of Pd(OAc)<sub>2</sub> (3 mol %) as the catalyst and DBU as the base in toluene at 110 °C for 24 h. and found the yield of CorDI was only 11%. Studies on the Brønsted base revealed that DABCO and KOH were ineffective at promoting the desired transformation. Changing the CO source to chloroform with CsOH gave no detectable product; however, Mo(CO)<sub>6</sub> was a possible safer alternative albeit with slightly less efficiency. Screening the ligand series <sup>t</sup>Bu<sub>3</sub>PHBF<sub>4</sub>, Xantphos and Ad<sub>2</sub>PnBu (CataCXium A) produced CorDI in 23%, 14%, and 52% yields, respectively. Replacing toluene with another low-polarity solvent xylene or the polar solvent DMAc gave much lower yield. These optimization studies showed that the bulky and election-rich ligand Ad<sub>2</sub>PnBu enhanced the yield significantly, such that replacing CO with the safer reagent Mo(CO)<sub>6</sub> still afforded a 41% yield of CorDI in the optimized conditions (Pd(OAc)<sub>2</sub>/Ad<sub>2</sub>PnBu/DBU/Toluene).





Applying these optimized conditions on TBrPy and butylamine yields pyrene diimide (PyDI) in 54% yield (Scheme 1). Despite a slightly lower yield, use of Mo(CO)<sub>6</sub> is more convenient and less dangerous than CO gas. Mo(CO)<sub>6</sub> became the best practice CO source when demonstrating the substrate scope of the domino carbonylation protocol (Table S1). For aliphatic amines we observed higher yields with short-chain amines, which is similar to the case of phthalimides.<sup>[19]</sup> The carbonylation reaction of 1,8dibromobenzene proceeded smoothly even with unsubstituted aniline possessing relatively low nucleophilicity, which was not observed for 1,2-dibromobenzene.<sup>[19]</sup> Very interestingly, we found that the replacement of unsubstituted aniline by bulky 2,6di(isopropyl) substituted aniline led to the formation of isonaphthalimide due to the big steric hindrance. Thus we proposed two pathways for the carbonylation protocol in term of the steric effect (Scheme 2). Unsubstituted or dimethyl substituted tetrabromobenzene gave moderate yields while tetrachlorobenzene afforded no detectable product. The one-pot Pd-catalyzed carbonylative diimidization is relatively efficient (30-70 % yield) in contrast to the traditional multi-step diimidization (2-5% yield).[8c, 15]

Scheme 2. Two possible pathways for the carbonylation protocol.



The electrochemical properties of CorDI and PyDI were investigated using cyclic voltammetry using Ag/AgCI as reference electrode, platinum as working electrode and ferrocene as internal standard. The cyclic voltammograms for CorDI and PyDI showed two reversible reduction waves in a negative potential range from -1.0 to -2.5 eV versus ferrocene (Fc/Fc<sup>+</sup>; **Figure 2a**). From the first half-wave reduction potentials, we estimated LUMO levels of -3.50 eV for CorDI and -3.26 eV for PyDI, which are 1.16 and 1.57 eV lower compared with unmodified corannulene<sup>[15]</sup> and 2,7-di-tert-butylpyrene<sup>[8c]</sup> respectively, demonstrating the strong electron-withdrawing ability of diimides group. CorDI's first reduction potential is remarkably similar to that found for azaindenocorannulene monoimde.<sup>[20]</sup>

CorDI or PyDI shows a maximum absorption peak at 392 or 426 nm in contrast to that of corannulene or pyrene with a maximum peak at 288 or 337 nm respectively (**Figure 2b**).<sup>[8c]</sup> After diimidization of corannulene and pyrene, the absorption spectra show a large bathochromic shift of 80~100 nm as a result of  $\pi$ -conjugated structure extension. The band gaps (E<sub>g</sub>) calculated from the absorption spectra were 2.87 eV for CorDI and 2.67 eV for PyDI respectively.

Density functional theory (DFT) calculations for highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of CorDI and PyDI relative to corannulene and pyrene were performed at Gaussian B3LYP/6-31+g(d,p) level (**Figure 2c**). The LUMO/HOMO levels of corannulene, CorDI, pyrene and PyDI were calculated to be –

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1.58/-5.96, -3.10/-6.59, -1.49/-5.35 and -3.12/-5.98 eV respectively, also suggesting the introduction of diimide group significantly lowers the LUMO levels. CorDI maintains the bowl-shaped structure similar to corannulene while PyDI molecule adopts a planar and rigid conjugated backbone like pyrene. The LUMO electron density of CorDI and PyDI delocalizes all over the entire molecular structure while the HOMO electron density localizes mainly on the parent aromatic cores.



**Figure 2.** (a) Cyclic voltammetry of CorDI and PyDI in CH<sub>2</sub>Cl<sub>2</sub> solution using Ag/AgCI as reference electrode and ferrocene as internal standard. (b) Normalized UV-Vis absorption spectra of Corannulene (magenta line), CorDI (red line), pyrene (navy line) and PyDI (blue line) in CH<sub>2</sub>Cl<sub>2</sub> solution. (c) Frontier molecular orbital diagrams of Corannulene, CorDI, pyrene and PyDI.

To elucidate the relationship between molecular structures and packing structures, crystals of CorDI and PyDI suitable for single-crystal X-ray structure analysis were obtained by slow evaporation of CHCI<sub>3</sub>/CH<sub>3</sub>OH and toluene solutions respectively at room temperature. It should be noted that the crystal of CorDI could only be resolved by the synchrotron radiation facility due to the very small size.<sup>[21]</sup> Although the resolution and completeness of single-crystal diffraction data is not high, the information about cell parameters and packing arrangement is reliable. CorDI single crystal belongs to the triclinic P-1 space group with lattice constants a = 7.19 Å, b = 16.35 Å, c = 20.88 Å,  $\alpha = 82.01^\circ$ ,  $\beta = 83.78^\circ$ ,  $\gamma = 88.86^\circ$ . In the structure of CorDI the bowl-shaped configuration of corannulene core is retained with a slight rim-to-hub bowl depth decrease from ~0.87 Å to ~0.82 Å after diimidization. The ear depth from hub carbon atoms to the plane defined by the four ear-like carbonyl carbon atoms is ~1.39 Å (Figure 3a). Whereas the parent corannulene shows a highly disordered packing structure dominated by C-H···π interactions, CorDI molecules adopt one-dimensional slipped stacking motif with very close bowl-in-bowl π-π contacts of 3.29-3.39 Å and a large  $\pi$ -orbital overlap along *a* axis (**Figure 3c.e**). Beside the intrastack interactions, there are very strong convexconvex  $\pi$ - $\pi$  interactions of 3.34–3.36 Å as well as C–H···O interactions of 2.45-2.69 Å between two adjacent columns (Figure 3e), which are stacked in an opposite direction to compensate the dipole moment induced from the bowl-in-bowl stacking. PyDI single crystal belongs to the monoclinic  $P_{2_1/C}$  space group crystal with lattice constants a = 6.16 Å, b = 10.28 Å, c = 24.14 Å,  $\alpha = \gamma = 90^{\circ}$ ,  $\beta = 96.35^{\circ}$ . As shown in **Figure 3b**, five-membered imide rings were coplanar with the pyrene core, thus extending the  $\pi$ -conjugated system. Due to the steric hindrance effects of tert-butyl group, PyDI molecules also adopt one-dimensional slipped stacking arrangement with an intermolecular  $\pi$ - $\pi$  distance of 3.39 Å but a small  $\pi$ -orbital overlap along *a* axis (**Figure 3d**,f). In *ab* plane, all the stacks orientate in the same direction while in *ac* plane the neighbouring stacks have a dihedral angle of 68.13° in term of the pyrene plane with very weak tert-butyl C-H···O intermolecular interactions (**Figure 3f**).



**Figure 3.** Single-crystal structures of CorDI (a,c,e) and PyDI (b,d,f). (a,b) Top views and side views of single molecular structures. (c,d) Packing structures wherein hydrogen atoms are omitted for clarity. (e,f) Intermolecular  $\pi$ - $\pi$  or C-H···O contacts between adjacent molecules.

In view of the large  $\pi$ -orbital overlap and closer packing structure of CorDI relative to PyDI, we focused on the investigation of charge transport behaviour of CorDI. Because single crystals have no grain boundaries as well as less charge carrier traps and defects, microcrystals of CorDI (**Figure 4a**) were grown by drop casting the toluene solution to reveal the intrinsic electrical characteristics. As shown in the transmission electron microscope (TEM) image (**Figure 4b**), highly regular microribbon-shaped crystals were observed. The corresponding selected area electron diffraction (SAED) patterns of this microribbon (**Figure 4c**) at different areas covering the whole length were identical, indicating that the whole microribbon was a single crystal. It can be concluded that the CorDI microribbon grows along the [100] direction, which coincides with the columnar  $\pi$ - $\pi$  stacking of bowl-shaped CorDI molecules.

OFET device Single crystal was fabricated on (OTS)-treated octadecyltrichlorosilane SiO<sub>2</sub>/Si substrates working as insulator/ gate electrode. Then, silver electrodes were thermally evaporated onto the substrate to complete the device using an organic ribbon as shadow mask (Figure 4d). Performance of the transistor is characterized by a Keithley 4200-SCS semiconductor parameter analyzer under inert conditions. Transfer and output characteristics of the transistors were shown in Figure 4e and 4f. Single crystal OFET device exhibited n-type transistor behavior with mobility of 0.05 cm<sup>2</sup> V<sup>-1</sup>  $s^{-1}$  and on/off ratio > 10<sup>6</sup>, which is among the highest values for n-type corannulene derivatives.9



**Figure 4.** (a) Optical image of CorDI microribbons. (b) TEM image of a representative CorDI microribbon. (c) Corresponding SAED pattern. (d) Schematic diagrams of single crystal OFET device structure. (e, f) Typical transfer and output characteristics of single crystal OFET based on one CorDI microribbon.

In conclusion, a series of aromatic diimides including CorDI and PyDI were synthesized facilely through one-pot carbonylation of tetrabrominated aromatic compounds, in yields one order of magnitude higher than previous multi-step syntheses. As demonstrated in the case of corannulene diimide, the efficient diimidization not only allows the LUMO levels to be lowered significantly but also provides an ordered and closer packing structures, opening up possibilities to the development of n-type semiconducting materials based on a variety of aromatic systems.

**Keywords:** organic semiconductor • domino synthesis • aromatic diimide

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### **Entry for the Table of Contents**

## COMMUNICATION

Aromatic diimides: A facile one-pot domino synthetic protocol for aromatic diimides via palladium-catalyzed carbonylation has been established. This methodology not only allows the LUMO levels to be lowered significantly but also provides an ordered and closer packing structures, opening up possibilities to the development of n-type semiconducting materials based on a variety of aromatic systems.



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