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Toward Electron-Deficient Pyrene Derivatives: Construction of Pyrene Tetracarboxylic Diimide Containing Five-Membered Imide Rings

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Electron-deficient pyrene-1,2,6,7-tetracarboxylic diimide (PyrDI) and its cyano derivative (PyrDI-CN) have been designed and synthesized as a new family of aromatic diimides. PyrDI has two unexpected five-membered imide rings and can form excimers facilely in solid state. These new pyrene derivatives are promising *n*-type semiconductors for organic electronics.

Aromatic diimides are among the most promising and versatile candidates for *n*-type organic semiconductors.¹⁻³ Many imide derivatives have been developed, which exhibit excellent optical and electrical properties.^{1,4-9} Naphthalene diimides (**NDI**)¹⁰⁻¹⁴ and perylene diimides (**PDI**)¹⁵ are the most widely studied aromatic imides due to their high stability, strong assembly tendency and unique opto-electronic properties.¹⁶ However, new aromatic diimides are still rare. Only few other types of acenes have been decorated with imide groups to construct new organic semiconductors recently, such as anthracene diimide (**ADI**)^{17,18}, tetracene bisimide (**TBI**), and pentacene bisimide (**PBI**)^{19,20}. The difficulty in synthesis as well as lack of structural diversity limit the rapid development of novel aromatic imides.

Many novel aromatics derived from pyrene have been developed and widely investigated in organic electronics due to their unique properties.²¹⁻²⁴ However, extending the π -conjugation plane of pyrene by fusing imide groups is unknown. Three isomers might be obtained if two imide groups are fused onto pyrene core centrosymmetrically (Fig. 1). One has five-membered imide rings fused at the non-*K*-region of pyrene. Another has five-membered imide rings fused at the *K*-region of pyrene. The third kind of isomer has two six-membered imide rings. These pyrene diimides will

diversify the structures of aromatic imides and further broaden the application of pyrene derivatives as *n*-type semiconductors, but none of them has been reported so far. Compared with those *K*-region fused pyrene derivatives, fusion at the non-*K*-region is an alternative strategy to extend π framework of pyrene and to obtain unique properties due to the different conjugation modes.^{21,22} However, previous works have shown that fusion at the non-*K*-region of pyrene is of challenge because of the low reactivity at C2 and C7 positions of pyrene.²⁵





Herein, we report the development of a new type of aromatic diimide, pyrene-1,2,6,7-tetracarboxylic diimide (**PyrDI**) and its cyano derivative, by a concise synthetic route. The synthetic route to **PyrDI** and **PyrDI-CN** is shown in Scheme 1. A lithium-halogen exchange of commercially available 1,6-

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dibromopyrene (1) with *n*-BuLi and subsequent quenching by carbon dioxide afforded pyrene-1,6-dicarboxylic acid (2) in 60% yield. Treated with oxalyl dichloride, dicarboxylic acid 2 was then converted to the corresponding acyl chloride 3 quantitatively, which was used in the following reaction without further purification. The cyclization reaction between 3 and isopropyl isocyanate was optimized by screening Lewis acids, solvents, temperature and reaction time.^{19,20} Finally, AICl₃ was employed as an efficient Lewis acid to give the target PyrDI in high yield. Interestingly, PyrDI has two five-membered imide rings on pyrene. However, its isomer 5 with sixmembered imide rings was not observed. The unique selectivity of the five-membered imide rings in PyrDI was investigated by density functional theory (DFT) calculations, which reveal that the cyclization at C2 and C7 positions of pyrene to form five-membered imide rings overcomes a lower energy barrier than the six-membered ones (Fig. S1).



To diversify the structure of pyrene-based diimides, further functionalization of **PyrDI** was explored. Catalyzed by Ircomplex in the presence of bis(pinacolato)diboron, **PyrDI** was directly borylated at the least sterically hindered C4 and C9 positions to give the diborylated compound **PyrDI-Bpin (6)** in high yield.²⁶ The boryl groups on **6** can be converted to a wide range of desirable synthons for particular applications.²⁷ Herein, to develop *n*-type semiconductors, the boryl groups were transformed into cyano groups to lower the energy levels, yielding **PyrDI-CN (7)** in 41% isolated yield.^{27,28} All the structures were fully characterized by ¹H and ¹³C NMR

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spectroscopy and high resolution mass spectrometry (see the Supporting Information).



Fig. 2 (a) Single crystal structure of **PyrDI** with thermal ellipsoids shown at the 50% probability. Hydrogen atoms are omitted for clarity. (b) The structure of the nearest two molecules, viewed along a axis. (c) The π -stacking structure of the nearest two molecules. (d) Crystal packing diagram of **PyrDI** viewed along b axis.

The single crystals of PyrDI were obtained as light yellow needles by slow evaporation of the mixed solution of 4 in chloroform and hexane. As shown in Fig. 2, the aromatic electrophilic substitution mediated by AICl₃ took place at the less active C2 and C7 positions of pyrene to form the fivemembered imide rings rather than the expected six-membered ones resulted from cyclization at the K-region.¹⁹ Both fivemembered imide rings are almost coplanar with the pyrene core. PyrDI belongs to the triclinic space group, in which two molecules alternately pack on the opposite face to generate a one dimensional columnar structure with an average π - π stacking distance of 3.40 Å. The two nearest pyrene cores in one column stack with only slight slipping, leading to a large overlap of the conjugated backbones as shown in Fig. 2b and 2c. The close π - π stacking and the large spatial overlap of the π -conjugated planes in columns indicate strong intermolecular interactions within PyrDI molecules in the solid state, which is beneficial to their controllable self-assembly and charge carrier transport.

The absorption spectra of **PyrDI** and **PyrDI-CN** in chloroform are shown in Fig. 3. For **PyrDI**, there are three absorption bands in visible light region peaking at 445, 420 and 388 nm. Compared to the absorption maximum of pyrene peaked at 334 nm, the incorporation of two imide groups leads to a large red shift of 110 nm. This can be attributed to the extension of the π -conjugation plane and the intramolecular charge

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transfer after introduction of imide groups to pyrene core. When incorporation of another two cyano groups, the longwavelength absorption maximum significantly blue shifts to 431 nm. The band gaps (E_g) calculated from absorption onset are 2.73 eV for **PyrDI** and 2.83 eV for **PyrDI-CN**, respectively. The electrochemical properties of **PyrDI** and **PyrDI-CN** were investigated by cyclic voltammetry (Fig. S6). Two reversible reduction peaks were observed for **PyrDI** and **PyrDI-CN**. The LUMO levels of **PyrDI** and **PyrDI-CN** were calculated to be -3.44 and -3.84 eV respectively. The incorporation of cyano groups greatly decreases the LUMO level of **PyrDI-CN**, which is favourable to electron injection and transport in **PyrDI-CN**.



Fig. 3 Absorption spectra of PyrDI and PyrDI-CN in $CHCl_3$ solution (1.0 \times 10 5 M).

DFT calculations were performed to investigate the electronic structures of PyrDI and PyrDI-CN. As shown in Fig. 4, both **PyrDI** and **PyrDI-CN** show rigid and planar π -conjugated backbones. The HOMO/LUMO energy levels of PyrDI and PyrDI-CN were calculated to be -6.51/-3.28 eV and -7.20/-3.94 eV, respectively. The lowered energy levels as compared to those of pyrene are attributed to the strong electronwithdrawing ability of imide and cyano groups. PyrDI and PyrDI-CN show similar HOMOs distribution, which is mainly localized on the central pyrene core with a nodal plane passing through the long axis. However, the distribution of LUMOs for PyrDI and PyrDI-CN is a little different. For PyrDI, the LUMO is delocalized over the entire molecular backbone, involving both imide groups. While for PyrDI-CN, there is no LUMO distribution on the central two atoms in pyrene backbone. The incorporation of imide groups and cyano groups not only decreases the electron density of pyrene but also changes its orbital distribution.



Fig. 4 Calculated molecular orbitals of pyrene, **PyrDI** and **PyrDI**-**CN**. The calculation was performed at B3LYP/6-311+G(d,p) level.

Pyrene excimer is an important photophysical phenomena and shows promising application in optoelectronic devices and biosensors.²⁹⁻³² We are curious about whether **PyrDI** also exhibits similar properties. Therefore, the emission feature of PyrDI in the solid state was investigated. Polystyrene (PS) was chosen as a polymer matrix to tune the concentration of PyrDI. The fluorescence spectra of the casted films of PyrDI in PS were measured as a function of PyrDI concentration as shown in Fig. 5. At the low concentration of 0.25 wt% PyrDI, three structural fluorescence bands peaked at 446, 475, and 507 nm were observed, which was identical to those of dilute PyrDI solution. When the concentration was increased to 1.0 wt%, the intensity of the fluorescence peaks at 475 and 507 nm increased. Further increasing the concentration to 5 wt%, the fluorescence intensity of PyrDI gradually decreased, and a new broad fluorescence band appeared at around 517 nm. The unstructured intense long-wavelength emission peak at around 517 nm, accompanied with the disappearance of monomeric vibrational emission peaks, indicates the formation of **PyrDI** excimers.^{33,34} What's more, the eximer emission peaked at 517 nm red-shifted to 550 nm as the concentration is further increased to 100 wt % (neat film). The change of the fluorescence peaks from 517 nm to 550 nm was attributed to the different intermolecular packing, from partially overlapped excimer to fully overlapped one, which was also observed in perylene films.35



Fig. 5 PL spectra of **PyrDI** in PS films upon varying the concentrations from 0.25 wt % to neat film. The fluorescence spectra were normalized by the maximum intensity.

In conclusion, a new type of electron-deficient pyrene derivative, pyrene-1,2,6,7-tetracarboxylic diimide **PyrDI** with five-member imide rings and its cyano derivative **PyrDI-CN**, were developed through an efficient synthetic strategy. The incorporation of imide and cyano groups not only extends the π -conjugation plane of pyrene, but also decreases the electron density of pyrene core dramatically. The formation of excimers was observed in the solid state of **PyrDI**. The development of pyrene diimide expands the field of non-*K*-region functionalization of pyrene and provides new candidates for organic electronics and supramolecular chemistry. In addition, the low LUMO levels of **PyrDI** and **PyrDI-CN** make them promising building blocks for *n*-type semiconducting materials.

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