## Novel Panchromatic Absorption Material, Isoindigo-based A- $\pi$ -A- $\pi$ -A Small Molecule

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One A– $\pi$ –A– $\pi$ –A small molecule [I(TPTA)<sub>2</sub>], containing two planar acceptor units, isoindigo, and 2,4,6-triphenyl-1,3,5triazine (TPTA) with thiophene as bridge, was synthesized by the Suzuki coupling reaction. The obtained molecule exhibits panchromatic absorption between 300 and 720 nm with a large half band width up to 350 nm in thin solid film. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of [I(TPTA)<sub>2</sub>] are -5.50 and -3.82 eV. Density functional theory (DFT) calculations indicated that the structure of [I(TPTA)<sub>2</sub>] is quite planar and that the electron density is mainly delocalized over the central isoindigo and thiophene units.

Compounds with acceptor-donor (A-D) architecture possess an intramolecular charge-transfer (CT) absorption band in the longer wavelength direction due to the introduction of an acceptor unit, so that the absorption of these compounds is broadened. Panchromatic absorption (PS) polymers can be achieved from a semirandom copolymer containing two different acceptors with a traditional donor bridge, mainly thiophene, and these PS polymers have made great contributions to the application in solar cells.<sup>1-4</sup> Besides these PS polymers, PS small molecules are also attracting increasing interest. Small molecules possess numerous advantages including relatively simple synthesis and purification, monodispersity and welldefined structure, no end group contaminants, high chargecarrier mobility, and better batch-to-batch reproducibility.<sup>5</sup> To broaden the absorption spectra of small molecules, lots of different types of molecules were synthesized, including D- $\pi$ -A,8 D-A-D and A-D-A,29 D-π-A-π-D,10,11 A-D,12 and so on (A: acceptor and D: donor). Take the D- $\pi$ -A<sup>8</sup> molecule as an example, it can achieve panchromatic absorption and shows potential applications in solar cells as a donor materials.

Recently, isoindigo has been frequently used in A–D type organic materials for its fused conjugated structure, high molar absorptivity, and electron-deficient nature, and these characteristics make isoindigo-based compounds show low band-gap, strong  $\pi$ - $\pi$  interactions, high crystallinity, and high charge-carrier mobility.<sup>12–17</sup>

In this paper, we report the synthesis of an A– $\pi$ –A– $\pi$ –A small molecule [I(TPTA)<sub>2</sub>], in which isoindigo and 2,4,6triphenyl-1,3,5-triazine (TPTA) were used as coelectron acceptor units (A) to broaden the absorption range, and 3-isooctylthiophene was used as the donor bridge ( $\pi$ ) to reduce the steric hindrance between the two acceptor units and guarantee the solubility. Meanwhile, TPTA was selected as the acceptor unit also because of its large nucleophilic susceptibility and high electron affinity.<sup>18,19</sup> The resultant small molecule exhibits a broad absorption gap from 300 to 720 nm with a large half band width of 350 nm. The chemical structure of this  $A-\pi-A-\pi-A$  small molecule is shown in Figure 1.

The synthetic details are shown in Scheme S1 in the Supporting Information. Compound 4 and tributyl[4-(2-ethyl-hexyl)thiophen-2-yl]stannane were coupled by the Stille reaction to yield compound 6 and then compound 7 was obtained easily by the bromination of 6 with NBS. The target product [I(TPTA)<sub>2</sub>] was prepared by the Suzuki coupling of compound 7 and compound 9. The chemical structure of the [I(TPTA)<sub>2</sub>] molecule was characterized by <sup>1</sup>H NMR (nuclear magnetic resonance), <sup>13</sup>C NMR, and HRMS (high-resolution mass spectrum).

Figure S1 shows the thermal gravimetric analysis (TGA) of [I(TPTA)<sub>2</sub>]. The TGA shows that the degradation temperature  $(T_d)$  of [I(TPTA)<sub>2</sub>] is around 407 °C (5% decomposition). The normalized ultraviolet-visible (UV-vis) absorption spectra of [I(TPTA)<sub>2</sub>] in chloroform (CF) solution and as thin solid film are shown in Figure 2, and the optical data are summarized in Table 1. [I(TPTA)<sub>2</sub>] shows a broad absorption band with three peaks around 365, 452, and 573 nm in dilute solution, while at ca. 410 nm, the film absorption appears stronger than the solution absorption, which leads to the phenomenon that in thin solid film, [I(TPTA)<sub>2</sub>] appears to have a very broad absorption band through the entire visible spectrum. We assign this phenomenon to the good planarity of [I(TPTA)<sub>2</sub>] in thin solid film. We can also observe a large half band width up to 350 nm in the entire normalized UV-vis absorption spectra. This performance of [I(TPTA)<sub>2</sub>] in the neat film state could be described as panchromatic absorption from 300 to 720 nm. On the other hand, [I(TPTA)<sub>2</sub>] shows a ca. 10 nm red shift on going from chloroform solution to thin solid film, indicating increased ordered structure in the solid state. The optical band gap  $(E_g^{opt})$ calculated from the absorption edge of the solid state film is 1.72 eV.

The electrochemical property of  $[I(TPTA)_2]$  was studied by the cyclic voltammetry method. Figure S2 shows the cyclic voltammogram of  $[I(TPTA)_2]$  film on a glassy carbon working electrode in 0.1 M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>)/CH<sub>3</sub>CN electrolyte at a scan rate of 100 mV s<sup>-1</sup> with saturated calomel reference electrode (SCE) as the



Figure 1. Chemical structure of synthesized small molecule.



Figure 2. Normalized UV-vis absorption spectra of synthesized small molecule in solution and as thin film.

Table 1. Thermal, optical, and electrochemical properties of  $[I(TPTA)_2]$ 

$T_{\rm d}/^{\circ}{ m C}^{ m a}$	407
$\lambda/\mathrm{nm^b}$	573
$\lambda/\mathrm{nm^{c}}$	582
$\lambda/\mathrm{nm}^{\mathrm{d}}$	720
$E_{\rm g}/{\rm eV^e}$	1.72
$E_{\rm ox}/{ m V}^{ m f}$	1.08
$E_{\rm re}/{ m V}^{ m f}$	-0.60
HOMO/eV <sup>g</sup>	-5.50 (-5.28)
LUMO/eV <sup>h</sup>	-3.82 (-2.94)

<sup>a</sup>The decomposition temperature ( $T_d$ ) was taken as 5% weight loss under a nitrogen atmosphere. <sup>b</sup>The absorption peak measured in chloroform solution. <sup>c</sup>The absorption peak measured in thin solid film state. <sup>d</sup>The absorption onset measured in thin solid film state. <sup>e</sup>Calculated from the empirical equation:  $E_g = 1240/\lambda_{onset}$ . <sup>f</sup>Read from cyclic voltammograms. <sup>g</sup>Estimated from the onset of oxidation wave of CV (calculated by density functional theory). <sup>h</sup>Estimated from the onset of reduction wave of CV (calculated by density functional theory).

reference electrode. The electrochemical data are recorded in Table 1. The HOMO and LUMO levels are calculated according to the empirical formula  $E_{\text{HOMO}} = -e[E_{\text{ox}} - (-4.8) - 0.38] \text{ eV}$  and  $E_{\text{LUMO}} = -e[E_{\text{re}} - (-4.8) - 0.38] \text{ eV}$ , where -4.8 eV is the redox potential of ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) internal reference vs. vacuum and 0.38 eV is the redox potential of ferrocene/ferrocenium reference vs. SCE measured in the same conditions.

The energy band gap of  $[I(TPTA)_2]$  calculated from the HOMO and LUMO energy levels is 1.68 eV, which is consistent with the optical band gap estimated from absorption onset in solid thin film.

Density functional theory (DFT) calculations which were performed with the B3LYP/6-31G level using Gaussian 09 were employed to investigate the electronic structure and geometry of  $[I(TPTA)_2]$ , and the corresponding results are shown in Figure 3. To reduce the computation time and maintain the accuracy in estimation, methyl groups were used to replace the long alkyl chains for calculations.<sup>20</sup> The electron density of the HOMO was mainly delocalized over the central isoindigo, thiophene, and benzene, and the electron density of the LUMO was concen-



Figure 3. Optimized molecular geometries and frontier molecular orbits of  $[I(TPTA)_2]$  evaluated using DFT.

trated on the isoindigo group, demonstrating that the isoindigo unit has much stronger electron-withdrawing property than the 2,4,6-triphenyl-1,3,5-triazine block. From the side view of the molecular geometry, it was clearly observed that the backbone of [I(TPTA)<sub>2</sub>] was highly coplanar. The dihedral angle between thiophene and isoindigo is 25.1 and 36.8° between thiophene and TPTA. The high coplanarity of the backbone of [I(TPTA)<sub>2</sub>] is beneficial for  $\pi$ - $\pi$  stacking of its backbone in solid state, which is consistent with the broad UV-vis absorption spectra. To study the influence of the side chain on the planarity of the backbone, we also calculated the geometry (Figure S3) of this molecule without any side chain, which shows more planarity than the methyl-substituted model. The reason could be attributed to the steric hindrance caused by the methyl side chain on thiophene units as reported by Andersson et al.<sup>20</sup> From the DFT calculations, the HOMO and LUMO energy levels of  $[I(TPTA)_2]$  were found to be -5.28 and -2.94 eV, respectively.

The normalized photoluminescence (PL) spectra of the molecule in chloroform solution with a concentration of  $1 \times 10^{-3} \text{ mol L}^{-1}$ , excited at the absorption maximum wavelength (580 nm), is illustrated in Figure S4. The PL spectrum of [I(TPTA)<sub>2</sub>] has only one peak at about 705 nm, which is attributed to the isoindigo and thiophene segments.

In conclusion, one novel isoindigo and 2,4,6-triphenyl-1,3,5-triazine (TPTA) based A– $\pi$ –A– $\pi$ –A-type narrow band-gap molecule, [I(TPTA)<sub>2</sub>], was synthesized by the Suzuki coupling method. Our preliminary results exhibited that the isoindigo and 2,4,6-triphenyl-1,3,5-triazine (TPTA)-based A– $\pi$ –A– $\pi$ –Atype narrow band-gap molecular can achieve panchromatic absorption. Further work to exploit the application of this small molecule is underway.

The authors are deeply grateful to the NSFC (Nos. 21274134, 51173199, and 61405209), New Century Excellent Talents in University (No. NCET-11-0473), and Qingdao Municipal Science and Technology Program (Nos. 13-1-4-200-jch and 11-2-4-22-hz) for financial support.

Supporting Information is available electronically on J-STAGE.

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