Synthesis and Photophysical Properties of Aromatic Fused Ring Small Molecule Acceptor Materials Based on Two-dimensional indacenodithiazole for Organic Solar Cells

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Abstract. A new two-dimensional conjugated core unit 2DIDTz was synthesized based on indacenodithiazole with thiophene side chain. Then, a linear two-dimensional conjugated small molecule acceptor material, namely IDTzIID, based on 2DIDTz as core unit and (E)-1,1'-bis(2-ethylhexyl)-[3,3'-biindolinylidene]-2,2'-dione (IID) as end-groups was designed and synthesized through Still coupling reaction. There is a strong intermolecular charge transfer (ICT) between the IID and 2DIDTz. The structure and purity of the IDTzIID target compound was examined by 1H NMR. The IDTzIID showed good solvent properties in organic solvents. The IDTzIID showed wide and broad absorption with a band gap of 1.63 eV which can be matched with polymer donor materials for advanced organic solar cells.

1. Introduction
In recent years, organic photoelectric materials have attracted more and more attention as one of the hotspots of scientific frontier research, especially, non-fullerene small molecule acceptor materials [1]. Non-fullerene small molecule acceptor materials contain many types such as B-N units [2], perylene diimide (PDI) [3], diketopyrrolopyrrole (DPP) [4] and acceptor–donor–acceptor (A–D–A) backbone structure based small molecule acceptor materials [5]. A-D-A type small molecule acceptor materials have received widespread attention due to the advantages of low cost and larger material pool [6]. Now, efficient photovoltaic materials have made great progress through device optimization and structural design strategies. As a result, designing and synthesizing high-efficiency new organic small molecule aromatic fused ring compounds and improving photoelectric conversion efficiency (PCE) is one of the research hotspots at this stage [7]. Recently, the PCE of tandem organic solar cell devices based on organic polycyclic fused ring small molecule acceptors has successfully exceeded 17% [8], indicating that organic fused ring small molecule acceptor materials have great development value and commercial potential.

For the modification strategy, it can be divided into one-dimensional modification and two-dimensional modification. The two-dimensional modification is mainly concentrated on the two-dimensional conjugated benzodithiophene (BDT) fragment. The ultraviolet-visible spectrum of the two-dimensional conjugated structure molecule mainly contains two absorption peaks: a conjugate main chain absorption peak and a conjugate side chain absorption peak. Compared with the one-dimensional system, the two-dimensional conjugated structure has a larger conjugated system, and there is stronger intermolecular interaction between the side chains [9]. The introduction of a two-dimensional conjugated thiophene side chain on BDT fragment can reduce the energy level and
broaden the absorption. Consequently, we introduced a two-dimensional conjugate side chain on indacenodithiazole to adjust the solubility and ultraviolet absorption spectrum of the molecule. On the other hand, (E)-1,1'-bis(2-ethylhexyl)-[3,3'-biindolinylidene]-2,2'-dione (IID) has a strong electron-withdrawing effect and can form a strong intramolecular charge transfer (ICT) with indacenodithiazole with a broaden absorption spectrum. Figure 1 shows small molecule acceptor materials based on IID and indacenodithiazole [10].

Figure 1. small molecule acceptor materials based on IID and indacenodithiazole.

2. Synthesis

Compounds 1 and 2 were synthesized according to literature reports. The synthetic route of IDTzIID was depicted in Scheme 1. IDTzIID was synthesized through Still coupling reaction between compounds 1 and 2 with a yield of 54%. Compound 1 (0.15 g, 0.09 mmol) and compound 2 (0.15 g, 0.27 mmol) were placed in a 100 ml single-neck round bottom flask. Catalysts Pd(2dba)₃ (0.003 g, 0.004 mmol) and P(o-tol)₃ (0.003 g, 0.010 mmol) were added to a 50 ml Shrek tube. Compound 1 and compound 2 were dissolved in 15 ml and 20 ml toluene, respectively, and the mixture was added dropwise to a Shrek tube and the flask was evacuated and backfilled with N₂ three times. The mixture was refluxed for 25 h, under the N₂ atmosphere. After the mixture being cooled to room temperature, the solvents were removed under reduced pressure. The dark residue was purified by flash column chromatography (silica gel) with PE ether CH₂Cl₂ (2:1), give a dark solid (0.10 g, 54%).

The target compound IDTzIID was characterized by ¹H NMR. As shown in Figure 2, ¹H NMR (CDCl₃, 400 MHz, ppm): δ 9.14-9.20 (m, 4H, Ph-H), 7.77-7.78 (d, J = 4.0 Hz, 2H, Th-H), 7.47-7.49 (d, J = 4.0 Hz, 2H, Th-H), 7.31-7.35 (t, J = 8.0 Hz, 2H, Ph-H), 7.15-7.16 (d, J = 4.0 Hz, 2H, Th-H), 6.91-6.92 (d, J = 4.0 Hz, 2H, Ph-H), 6.87-6.88 (d, J = 4.0 Hz, 2H, Th-H), 6.76-6.78 (d, J = 8.0 Hz, 2H, Ph-H), 6.67 (s, 2H, Ph-H), 6.67 (s, 2H, Ph-H), 3.65-3.74 (m, 8H, CH₂), 2.90-2.98 (m, 4H, CH₂), 2.81-2.83 (m, 4H, CH₂), 1.86-1.96 (m, 4H, CH), 1.62-1.75 (m, 4H, CH), 1.31-1.42 (m, 66H, CH₂), 0.89-1.02 (m, 48H, CH₃).
3. Results and discussion.

IDTzIID has good solvent properties in conventional solvents such as dichloromethane, chloroform and tetrahydrofuran. The UV-visible absorption spectrum of IDTzIID in solution and film state is shown in the Figure 3, and corresponding data were listed in Table 1.

![Figure 3. The UV-visible absorption spectrum of IDTzIID in solution and film state.](image)

IDTzIID has a large conjugated rigid framework structure, showing strong and broad absorption peaks at 300-750 nm in solution and film state. The maximum absorption peak of the solution state is located at 398, 498 and 622 nm. The maximum absorption peak of the film state is located at 400, 460 and 608 nm. The optical band gap of IDTzIID was 1.63 eV. The apparent absorption peaks in the 300-450 nm range are due to the π-π* transition between the molecules. The molecules are all of the A-D-A configuration, and the push-pull electronic structure allows the molecules to have broad and
strong absorption peaks in the 450-750 nm range, which is caused by intramolecular charge transfer (ICT). In the state of the molecular solid film, the spectral absorption peak showed significantly red-shifted compared with the spectral absorption in the chloroform solution, which reflects the good planarity of the molecule, and stronger intermolecular interaction and better accumulation in the state of the solid film. The spacing of the molecules becomes smaller and the accumulation is more compact and orderly.

Table 1. The optical data IDTzIID.

| Compound | $\lambda_{\text{max sol.}}$ [nm] | $\lambda_{\text{max film.}}$ [nm] | $E_{\text{g opt}}$ [eV] |
|----------|-----------------|-----------------|-----------------|
| IDTzIID  | 398, 498, 622   | 400, 460,608    | 1.63            |

4. Conclusion
In conclusion, we designed and synthesized a new two-dimensional conjugated small molecule acceptor material, namely IDTzIID. There is a strong intermolecular charge transfer (ICT) between the IID and 2DIDTz. The structure and purity of the IDTzIID target compound was examined by 1H NMR. The IDTzIID showed good solvent properties in organic solvents. The IDTzIID showed wide and broad absorption with a band gap of 1.63 eV. In the state of the molecular solid film, the spectral absorption peak showed significantly red-shifted compared with the spectral absorption in the chloroform solution. Our results illustrated that two-dimensional conjugate strategy is an effective method for designing efficient organic solar cells acceptor materials.

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