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Synthesis and characterization of Triphenylamine modified azobenzene dyes

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[†]Electronic Supplementary Information (ESI) available: Experimental; Synthesis of **4a-d**; ¹H NMR, HRMS. Additional figures of UV,CVand SCLC of **1a-d** measurement

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ABSTRACT: A series of triphenylamine modified azobenzenes were synthesized and studied theoretically and experimentally. D-A-D structures of these dyes were revealed with an intramolecular charge transfer (ICT) from both triphenylamine or indoline units (donor) to the central azobenzene unit (acceptor). Both computational and experimental results indicate that a stronger electron donating ability of the donor enhances the degree of ICT and improve their HOMO energies. The absorption spectra indicate an increased light absorption by enhanced ICT effect. The intermolecular interaction also affects their absorption ability. The strongest intermolecular interaction results in the best light absorption ability in films. An obviously increased hole mobility was also found as the ICT was enhanced. These dyes were used as hole transport materials (HTM) of perovskite solar cells to investigate their feasibility. It is revealed that the solubility and filming ability are significant for the photovoltaic performance of devices.

Keywords: Dyes, triphenylamine, intramolecular charge transfer, hole transport material, solar cells

1. Introduction

Triphenylamine derivatives are one kind of significant dyes and have been widely investigated because of their strong emissions and excellent hole transport mobility and therefore potential applications have been paid attention to the fields of organic light emitting diodes[1-5], sensors[6-8], solar cells[9-13], and photochromophore[14-16]. Specially the important dye-2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene(spiro-OMeTAD) has been widely used as hole transport material (HTM) in various solar cells and the power conversion efficiencies (PCE) exceeding 19 % based on organic-inorganic halide CH₃NH₃PbI₃ perovskites have been reported[17]. However, Spiro-OMeTAD requires multi-step synthesis and very expensive. Therefore high hole-transportation ability of cheaper dyes remain a challenge for highly efficient solar cells.

Numerous novel compounds have been developed by altering the electron donor modules and conjugation bridge of spiro-OMeTAD. As-constructed spiro-bridged[18-20], linear π -conjugated structured[21, 22] and sheet-shaped structured[23] compounds together with star- π -systems[24] have good film morphological stability and reduced molecule aggregation ability. High hole mobility can be achieved by doping metal complex[25-28] and then a relatively satisfactory performance (PCE of 11-17 %) was attained by employing these compounds as the HTMs of solar cells. However the PCE was not higher than that of spiro-OMeTAD. The synthesis is complicate yet. The hole mobility is only about 10^{-4} cm²·V⁻¹·S⁻¹ for spiro-OMeTAD in pristine form[29]. Additional dopants are required for applications. The dopants bring the device instability,which are unfavorable for practical applications[30]. Thus a novel structure is expected for high performance HTMs to overcome above disadvantages.

Conductive polymers such as poly(triarylamine) (PTAA) and P3HT are alternative HTMs because of their excellent filming ability and stability. Moreover, better hole mobility could be achieved by donor-acceptor (D-A) structure design, such as benzo[1,2,5]thiadiazole based polymer, of which higher hole mobility $(6.68 \times 10^{-4} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{S}^{-1})$ and deeper HOMO energy level (-5.24 eV) than those of P3HT (2.45×10^{-4} cm²·V⁻¹·S⁻¹ and -5.10 eV, respectively) result in a better performance in the application of perovskite solar cells (6.64 % vs 4.24 % of PCE)[31]. Kwon[32] reported a D-A polymer, Poly[2,5-bis(2-decyldodecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione-(E)-1,2-di(2,2'-bithiophen-5-yl)ethane with a hole mobility of 10^{-3} cm²·V⁻¹·S⁻¹. Therefore, a PCE of 9.2 % was achieved in the perovskite solar cell based on this polymer which was higher than that of the doped Spiro-OMeTAD (7.6 %). Recently a photoconversion efficiency of 12.32 % was reported with diketopyrrolopyrrole (DPP) based D-A polymer as the HTM in perovskite solar cells[33]. D-A structure has been revealed to be able to enhance the photoinduced intramolecular charge transfer, which facilitates the transfer of photogenerated cations, and thus attain long charge separated state lifetime and high hole mobility[34]. However, the polymeric HTMs have the disadvantages of poor reproducibility and complex synthesis process.

Above discussions indicate that D-A conjugated organic molecules may be the most promising candidate for high performance HTMs. Sun licheng et al[35] designed a benzodithiophene based D-A molecule BDT-C1 with the high hole mobility $(3.18 \times 10^{-4} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{S}^{-1})$ and conductivity $(1.16 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1})$ in pristine form. The average PCE of 13.4 % for BDT-C1 was only slightly lower than the Spiro-OMeTAD (13.9 %). Yang yang reported two dopant-free D-A molecules, DERDTS–TBDT [36] and DOR3T-TBDT[37], of which the devices showed a PCE of 16.2 % and 14.9 %, respectively. They are comparable to or even better than that of the devices

using the doped Spiro-OMeTAD (14.0 %) as HTMs under equivalent conditions. Moreover, the D-A structure may also reduce the HOMO-LUMO gap, and thus enhance the light harvesting ability of HTMs in the long wavelength range, making it possible to participate as light absorbers together with perovskite in the low energy region[38]. Recently Michael Grätzel[39] developed A-D-A type molecular HTMs with which the devices achieved a PCE of 10.3-11.4 % without any dopant, though the hole mobilities are around 4×10^{-5} cm²·V⁻¹·S⁻¹. In this paper, we report a new kind of D-A-D type molecular dyes, triphenylamine-modified azobenzene (**1a-d**). The structures are shown in scheme 1. The synthesis was discussed. Then the computation and electrochemical results together with absorption spectra were investigated in detail and it was found that these novel dyes may be applied in organic solar cells. Finally we report their application in Perovskite Solar Cells.

2. Experimental section

2.1. Materials

Nitrobenzyl-triphenylphophonium-bromide(NTB), Benzyl triphenylphosphonium bromide (BTB),N,N'-di(4-octyloxyphenyl)aniline, 4-(p-tolyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole were prepared according to the literature[40-42]. Triphenylamine (AR, 98 %) and 4-formyl-4',4"-dimethyltriphenylamine (**2b**) (AR, 98 %) were obtained from TCI, PbI₂ was purchased from Aldrich. Hydroiodic acid (AR, 45 wt% in water) and methylamine (AR, 27 % in methanol) were bought from Sinopharm Chemical Reagent Co. Ltd. Other reagents were commercially available and used without further purification.

2.2. Instrumentation and measurement conditions

¹HNMR spectra were obtained on a Varian INOVA-500MHZ superconducting spectrometer. The ESI mass and HR-ESI mass spectra were obtained on a Thermo Fisher LCQ Deca XP MAX mass spectrometer. MALDI-TOF mass and HR-MALDI-TOF mass spectra were obtained on a microOTOF-Q II mass spectrometer respectively. Absorption spectra were taken on a Nicolet Evolution 300 UV-visible spectrometer. Electrochemical properties were measured using a BAS 100W electrochemical analyzer and performed in a three-electrode cell. A glassy carbon electrode was used as working electrode, Ag/AgNO₃ electrode as reference electrode and platinum as auxiliary electrode. Scan rates were 100 mV/s. The dichloromethane containing 0.05 mol/L tetrabutylammonium hexafluorophosphate (TBAPF₆) was employed as the medium for all the cyclic voltammetric experiments. All solutions were purged using nitrogen gas prior to the electrochemical measurement.

2.3. Computational details

Geometry optimizations of the molecules were carried out using the three-parameter exchange functional of Becke and correlation functional of Lee, Yang and Parr (B3LYP)[43-45]with the 6-31G(d) basis set in in a dichloromethane environment without any symmetry constraints. In order to confirm the optimized geometry as a global minimum, frequency calculations at the same level of theory were performed, All the calculations were performed using Gaussian09 package[46]. Detailed description of computational methods can also be found in our previous studies[47].

2.4. Synthesis

2.4.1. General synthetic step of the aldehyde derivatives

Aldehyde derivatives were synthesized by a revised method of the literature[48]. Phosphorous oxychloride (POCl₃) (10 mL, 107 mmoL, 1.0 equiv.) was added dropwise to DMF (8 mL, 107 mmoL, 1.0 equiv.) at 0 °C. The mixture was stirred at 25 °C for 1 h. Triphenylamine or its derivatives (**Ar**) (107 mmol, 1.0 equiv.) was added and the reaction mixture was stirred and heated at 90 °C for 3 h. After cooling down to room temperature, the mixture was poured into 50 mL cold distilled H₂O and extracted with dichloromethane (3×20 mL). The combined organic layer was dried with anhydrous Na₂SO₄ and then filtered. The filtrates were concentrated by rotary evaporation. The target compounds were purified by column chromatography on silica gel using petroleum:ethyl aceate (v:v = 4:1) as the eluent.

4-formyltriphenylamine(2a)

Yield 76% as orange solid, $R_f = 0.44$, m.p.=132 °C; ESI-MS: m/z =273.3(M)⁺. ¹H NMR (CDCl₃, 500 MHz) δ : 9.81 (s, 1H, -CHO), 7.68 (d, J = 8.8 Hz, 2H), 7.34 (t, J = 9.0 Hz, 4H), 7.17 (d, J = 9.0 Hz, 4H), 7.15 (d, J = 9.0 Hz, 2H), 7.12-6.98 (m, 2H), ¹³C NMR (CDCl₃, 500 MHz) δ : 190.29, 153.30, 146.10, 131.26, 129.68, 129.10, 126.27, 125.10, 119.32.

4-formyl-4',4"-dioctyloxyltriphenylamine (2c)

Yield 80 % as orange oil liquid, $R_f = 0.57$, HR-ESI-MS: m/z = 530.3630[M+H]⁺ (calcd for $C_{35}H_{48}NO_3^+$: m/z = 530.3629). ¹H NMR (CDCl₃, 500 MHz) δ : 9.75 (s, 1H, -CHO), 7.63 (d, J = 9.0 Hz, 2H), 7.12 (d, J = 9.0 Hz, 4H), 6.88 (d, J = 9.0 Hz, 4H), 6.85 (d, J = 9.0 Hz, 2H), 3.95 (t, J = 6.5 Hz, 4H), 1.82-1.76 (m, 4H), 1.50-1.44 (m, 4H), 1.38-1.26 (m, 16H), 0.90 (t, J = 6.5 Hz, 6H),

¹³C NMR (CDCl₃, 500 MHz) δ: 190.15, 157.09, 154.35, 138.84, 131.60, 128.20, 128.00, 116.92, 116.94, 68.40, 32.00, 29.60, 29.54, 29.47, 26.31, 22.90, 14.26.

4-(p-tolyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole-7-carbaldehyde (2d)

Yield 83% as orange solid, $R_f = 0.37$, m.p.= 79 °C, ESI-MS: m/z = 277.1(M)⁺, HR-ESI-MS: m/z = 278.1538[M+H]⁺ (calcd for $C_{19}H_{20}NO^+$: m/z = 278.1539).¹HNMR(CDCl₃, 500MHz) δ : 9.69 (s, 1H.-CHO), 7.63 (s, J = 8.5 Hz, 1H), 7.50 (d, J = 8.5 Hz, 1H), 7.16-7.23 (m, 4H), 6.71 (d, J = 8.8 Hz, 1H), 4.91 (m, 1H), 3.81 (m, 1H), 2.36 (s, 3H), 1.49-2.14 (m, 6H). ¹³C NMR (CDCl₃, 500 MHz) δ : 189.90, 154.42, 138.54, 135.70, 134.34, 133.89, 130.33, 127.99, 125.26, 122.68, 105.97, 70.32, 44.80, 35.62, 33.41, 24.42, 21.18.

2.4.2. General synthetic step of Nitro-derivatives

This compound was prepared by a revised method of the literature[49]. NaH (1.00 g, 4.0 mmoL) were added into an anhydrous tetrahydrofuran (100 mL) of NTB (4.20 g, 8.8 mmoL) and the reaction mixture was stirred at room temperature for 3 h. The colour of solution changed from white to deep red, Afterwards compound **2** (2.40 g, 8.0 mmoL) was added to the solution and refluxing at 80 °C. After the reaction was complete, the mixture was slowly poured into cold distilled H₂O (50 mL) and extracted with dichloromethane (3×20 mL). The combined organic layer was dried with anhydrous Na₂SO₄ and then filtered. The combined filtrates were concentrated by rotary evaporation. The products were purified by column chromatography on silica gel using cyclohexane:dichloromethane (v:v= 2:1) as the eluent.

(E)-4-(4-nitrostyryl)-N,N-diphenylaniline (**3a**)

Yield 75% as red solid, $R_f = 0.31$, m.p.= 149 °C, HR-ESI-MS: m/z = 415.1417[(M+Na)⁺] (calcd for $C_{26}H_{20}N_2O_2Na^+$: m/z = 415.1417). ¹H NMR (CDCl₃, 500 MHz) δ : 8.21 (d, J = 8.5 Hz, 2H), 7.60 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 7.30 (m, 4H), 7.23 (d, J = 16.5 Hz, 1H), 7.14 (d, J = 7.5 Hz, 4H), 7.10-7.06 (m, 4H), 7.02 (d, J = 16.5 Hz, 1H). ¹³C NMR (CDCl₃, 500 MHz) δ : 148.81, 147.46, 146.50, 144.55, 133.13, 130.03, 129.66, 128.25, 126.73, 125.22, 124.39, 123.84, 122.93.

(E)-4-(4-nitrostyryl)-N,N-di(4-(methyl)phenyl)aniline (**3b**)

Yield 75% as red solid, $R_f = 0.32$, m.p.= 162 °C, HR-ESI-MS: m/z = 421.1911[(M+H)⁺] (calcd for $C_{28}H_{25}N_2O_2^+$: m/z = 421.1911). ¹H NMR (CDCl₃, 500 MHz): δ 8.20 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 9.0 Hz, 2H), 7.38 (d, J = 8.5 Hz, 2H), 7.21 (d, J = 16.0 Hz, 1H), 7.11 (d, J = 8.5 Hz, 4H), 7.04 (d, J = 8.5 Hz, 4H), 7.00 (m, 3H), 2.35(s, 6H). ¹³C NMR (CDCl₃, 500 MHz) δ : 149.23, 146.56, 144.92, 144.63, 133.60, 133.30, 130.29, 129.06, 128.15, 126.62, 125.46, 124.37, 123.85, 121.65, 21.18.

(E)-4-(4-nitrostyryl)-N,N-di(4-(octyloxyl)phenyl)aniline (3c)

Yield 73% as orange oil liquid, $R_f = 0.31$, HR-ESI-MS: m/z = 648.3923 (M)⁺(calcd for $C_{42}H_{52}N_2O_4^+$: m/z = 648.3922). ¹H NMR (CDCl₃, 500 MHz) δ : 8.20 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 16.0 Hz, 1H), 7.08 (d, *J* = 8.5 Hz, 4H), 6.95 (d, *J* = 16.0 Hz, 1H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.85(d, *J* = 9.0 Hz, 4H), 3.94 (t, *J* = 6.5 Hz, 4H), 1.81-1.76 (m, 4H), 1.49-1.43 (m, 4H), 1.38-1.26 (m, 16H), 0.90 (t, *J* = 6.5 Hz, 6H). ¹³C NMR (CDCl₃, 500 MHz) δ : 155.94, 151.93, 149.04, 140.74, 140.57, 130.25, 129.18, 127.71, 127.03, 127.00, 125.12, 123.56, 120.26, 115.48, 68.52, 32.00, 29.98, 29.60, 29.48, 26.24, 22.89, 14.29. (E)-7-(4-nitrostyryl)-4-p-tolyl-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole (**3d**)

Yield 50 % as black solid, $R_f = 0.30$, m.p. = 157 °C, HR-ESI-MS: m/z = 419.1727[(M+Na)⁺] (calcd for $C_{26}H_{24}N_2O_2Na^+$: m/z = 419.1730). ¹H NMR (CDCl₃, 500 MHz) δ : 8.18 (d, J = 8.5 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.37 (s,1H), 7.15-7.25 (m, 6H), 6.93 (d, *J* = 16.5 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 4.85 (m, 1H), 3.84 (m, 1H), 2.36 (s, 3H), 1.65-2.13 (m, 6H). ¹³C NMR (CDCl₃, 500 MHz) δ: 149.35, 146.06, 145.31, 139.98, 135.98, 134.12, 132.36, 130.12, 128.43, 126.84, 126.24, 124.37, 123.06, 121.53, 120.83, 107.47, 69.62, 45.45, 35.43, 33.86, 24.67, 21.09.

2.4.3. General synthetic step of azobenzene derivtives

LiAlH₄ (1.90 g, 50 mmoL) was added to the anhydrous tetrahydrofuran (200 mL) of Compound **3** (13 mmoL) and the reaction mixture was stirred and refluxed for 2 h under N₂. After the reaction was complete. Then the solvent was removed, The residue was dispersed in CH₂Cl₂, filtered off the suspension and washed with distilled H₂O. The organic phase was concentrated by rotary evaporation. Then the products were obtained by column chromatography on silica eluting with petroleum : dichloromethane(v:v = 3:1) as the eluent.

(E)-4,4'-bis(4-N,N-diphenylaminostyryl)azobenzene (1a)

Yield 80% as red solid, $R_f = 0.25$, m.p. = 219 °C, MALDI-TOF: m/z= 720.210 (M⁺), HR-MALDI-MS: m/z = 721.3325 [(M+H)⁺] (calcd for $C_{52}H_{42}N_4^+$: m/z = 721.3326). ¹H NMR (CDCl₃, 500 MHz) δ :7.94-7.92 (d, *J* = 8.5 Hz, 4H), 7.64 (d, *J* = 8.5 Hz, 4H), 7.43 (d, *J* = 8.5 Hz, 4H), 7.30-7.27 (m, 8H), 7.19 (d, *J* =16.5 Hz, 2H), 7.14 (d, *J* = 7.5 Hz, 8H), 7.08-7.04 (m, 10H). ¹³C NMR (CDCl₃, 500 MHz) δ : 150.75, 149.08, 144.01, 140.50, 133.00, 130.10, 130.00, 129.95, 128.00, 126.75, 125.60, 125.00, 123.40, 122.00.

(E)-4,4'-bis(4-N,N-di(p-tolyl)aminostyryl)azobenzene (1b)

Yield 85% as red solid, $R_f = 0.26$, m.p. = 238 °C, MALDI-TOF: m/z = 776.261(M⁺), HR-MALDI-MS: m/z = 777.3952 [(M+H)⁺] (calcd for $C_{56}H_{49}N_4^+$: m/z = 777.3951).¹H NMR (CDCl₃, 500 MHz) δ : 7.92 (d, J = 8.5 Hz, 4H), 7.63-7.612 (d, J = 8.5 Hz, 4H), 7.38 (d, J = 8.5 Hz, 4H), 7.16 (d, J = 16.5 Hz, 2H), 7.09 (d, J = 8.0 Hz, 8H), 7.04-7.02 (m, 14H), 2.33(s, 12H). ¹³C NMR (CDCl₃, 500 MHz) δ : 151.80, 148.30, 145.00, 140.50, 133.00, 130.10, 130.00, 129.90, 127.50, 126.80, 125.60, 125.00, 123.40, 122.0, 20.80.

(E)-4,4'-bis(4-N,N-di(p-octyloxylphenyl)aminostyryl)azobenzene (1c)

Yield 87% as red oil liquid, $R_f = 0.24$, MALDI-TOF: m/z=1232.746 (M⁺), HR-MALDI-MS: m/z = 1232.8051 (M⁺) (calcd for C₈₄H₁₀₄N₄O₄: m/z = 1232.8052). ¹H NMR (CDCl₃, 500 MHz) δ : 7.92 (d, J = 8.5 Hz, 4H), 7.61 (d, J = 8.5 Hz, 4H), 7.35 (d, J = 8.5Hz, 4H), 7.17-6.95 (m, 12H), 6.92 (d, J = 16.5 Hz, 4H), 6.84 (d, J = 7.5 Hz, 8H), 3.94 (t, J = 5.5Hz, 8H), 1.82-1.76 (m, 8H), 1.51-1.23 (m, 40H), 0.95-0.84 (m, 12H). ¹³C NMR (CDCl₃, 500 MHz) δ : 148.11, 144.80, 144.04, 138.69, 134.71, 132.82, 131.14, 128.84, 127.13, 125.52, 124.98, 123.15, 121.75, 120.28, 119.59, 106.59, 68.34, 44.15, 34.14, 32.56, 28.68, 23.36, 19.80, 14.35.

(E)-4,4'-bis(4-p-tolyl-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indol-7-yl)vinyl)azobenzene (1d)

Yield 88 % as deep red solid, $R_f = 0.21$, m.p. = 226 °C, MALDI-TOF: m/z=728.843(M⁺), HR-MALDI-MS: m/z = 728.3873 (M⁺) (calcd for $C_{52}H_{48}N_4$: m/z = 728.3873). ¹H NMR (CDCl₃, 500 MHz) & 7.91 (d, J = 8.0 Hz 4H), 7.61 (d, J = 8.0 Hz, 4H), 7.38 (s, 2H), 7.21-7.16 (m, 12H), 6.98 (d, J = 16.5 Hz, 2H), 6.89 (d, J = 8.0 Hz, 2H), 4.83 (m, 2H), 3.85 (m, 2H), 2.35 (s,6H), 2.12-1.50 (m,12H). ¹³C NMR (CDCl₃, 500 MHz) & 151.56, 148.27, 140.77, 140.13, 137.28, 135.54, 133.36, 130.74, 129.80, 126.54, 126.14, 123.45, 122.39, 120.69, 107.38, 69.40, 45.24, 35.02, 33.70, 24.28, 20.94.

2.5. Solar cell fabrication

Methyl ammonium iodide (CH₃NH₃I) was prepared according to the reported procedure[50]. Substrates are fluorine-doped tin oxide conducting glass (FTO, Pilkington, thickness: 2.2 mm, sheet resistance 14 Ω /square). Patterned FTO glass was first cleaned with mild detergent, rinsed with distilled water for several times and subsequently with ethanol in an ultrasonic bath, finally dried under air stream.

For fabricating the device, 30 nm-thickness TiO_2 compact layer was spin-coated on the pre-cleaned FTO glass, then sintered at 500 °C. Subsequently, 200 nm-thickness mesoporous TiO_2 anatase compact layer (dyesol 18NR-T paste) were deposited according to the literature[51]. CH₃NH₃PbI₃ was deposited on the mesoporous TiO_2 film by using a sequential method as reported[52]. Azobenzene derivatives chlorobenzene solutions with a concentration of 5 mg mL⁻¹ were spin-coated on the mesoporous $TiO_2/CH_3NH_3PbI_3$ film at 3000 rpm for 20 s. Finally, 80 nm-thickness Au electrode was thermally evaporated under the vacuum of 10^{-7} Torr.

2.6. Device measurement

For J-V characteristics, the cells were illuminated under 100 mW cm⁻² (AM 1.5) by an Oriel solar simulator 91160A while the data were recorded on Keithley 2602. A mask with a window of 0.10 cm² was used to define the active area of the cell. The monochromatic incident photon-to-electron conversion efficiency (IPCE) spectrum was obtained on a lab-made IPCE testing system[53, 54].

2.7. Instrumentation and Mobility measurements

The hole-only devices were fabricated by spin-coating PEDOT:PSS (Baytron PVP Al4083) onto pre-cleaned, patterned indium tin oxide (ITO) substrates. Films of azobenzene derivatives were spin-coated on top from the chloroform solution with a concentration of 5 mg mL⁻¹. The film thickness was controlled at about 100 nm. As a counter electrode Al was deposited on top by vacuum evaporation. The current density–voltage curves of the devices were recorded with a

Keithley 2400 source. For the hole-only devices, space charge limitation of current (SCLC) is described as

$$J = \frac{9\epsilon\epsilon_0\mu_0 V^2}{8L^3} \qquad (1)$$

where ε is the dielectric constant of the transport material, ε_0 is the permittivity of the vacuum, μ_0 is the zero-field mobility, *J* is the current density, and *L* is the thickness of the film[55]. Then the square root of J was plotted against the voltage and the hole mobility can be calculated from the slope.

3. Results and discussion

3.1. Synthesis and characterization

The triphenylamine modified azobenzenes **1a-d** were synthesized from various donors, triphenylamine or indoline derivatives, by Vilsmer formylation reaction, Wittig and reduction reaction (Scheme 1). Aldehydes **2a**, **2c** and **2d** were first obtainedin good yields (76-83 %) via Vilsmer formylation reaction. The vilsmer reagent, which was prepared from the POCl₃ and DMF (molar ratio 1:1) at 0 °C under the N_2 , was the key to the yields. Low temperature may be benefit to the stability of vilsmer reagents. For triphenylamine, the same nucleophilic reactivity of three para-benzene positions may produce dialdehydes[56], leading to relatively low yield of **2a** (76%); while only one active-site in indoline and octyloxyl-triphenylamine together with their higher electron density in comparison to triphenylamine result in better yield of **2c** (80%) and **2d** (83%). Then Wittig reactions were performed by reacting **2a-d** with NTB Wittig reagent to yield compounds **3a-d**. The electron withdrawing ability of nitro group can stabilize the Wittig reagent anion, and benefit the Wittig reaction. Though a high temperature (80 °C) was required for the synthesis of **3a-d**, a relatively high yield was reached as about 70%.

Nitro groups may be reduced to amino or azo groups depending on the reducers. Previously we used SnCl₂ as reducing reagents and **3a**, **3b** and **3d** were converted into amine derivatives[57]. Herein LiAlH₄ was employed to reduce **3a-d** in tetrahydrofuran. The reduction reaction starts from the attack of hydrogen anion on nitrogen cation, resulting in an intermediate N-nitroso derivatives. N-nitroso derivatives may be further reduced to amine derivatives. Since N-aryl group can stabilize N-nitroso derivatives, a coupling reaction is allowed between N-nitroso and amine derivatives, which finally produces the azo derivatives **1a-d**. Moreover the electron-rich substituents(methyl, alkoxyl) and indoline-nitroaromatics benefit the stability of the intermediate N-nitroso derivatives, and thus boost their coupling reaction with amine derivatives, leading to a higher yield of **1b-d** (~90 %) than nonsubstituent-nitroarene substrate **1a** (80 %). The structure of all compounds was confirmed by ESI-MS, HR-ESI-MS, MALDI-TOF, HR-MALDI-TOF, ¹H NMR and ¹³C NMR. The single crystal of **1a** (Fig.1) further confirm its trans-structure.

3.2. Computational results

As the trans-structure of compounds **1a-d** was identified, we conducted density functional theory (DFT) computation to investigate their molecular orbitals. As shown in Fig.2, the electron distribution of the HOMO is homogeneously delocalized over the triphenylamine or indoline group (donor) and the styryl-linear conjugated part, and the electron distribution of the LUMO is confined to the styryl and the azobenzene unit (acceptor), which is similar to those of **4a-d**[58]. The intramolecular charge transfer (ICT) from both donor groups to the central acceptor is found based on the molecular orbitals of **1a-d**. The large differences in their Stokes shifts in polar and non-polar aprotic solvents (Table S1) confirm the presence of ICT. Therefore compounds **1a-d**

have a typical D-A-D structure. As we further study HOMO and LUMO energies of **1a-c**, it is discovered that both energies are improved as introducing electron donating groups such as methyl and alkoxyl onto the triphenylamine unit. This effect is more significant for HOMO, leading to a reduced Eg cal (calculated HOMO-LUMO energy gap) in **1b** and **1c**.

3.3. Electrochemical Properties

Fig.3 gives the electrochemical curves of **1a-d** in CH₂Cl₂ solutions at 298K. All compounds show one quasi-reversible oxidation wave, corresponding to the electron loss process of the triphenylamine or indoline modules. This is comparable with the oxidation wave of **4a-d** (See Fig S1). But the oxidation potentials are clearly improved in **1a-d** (0.83, 0.81, 0.37 and 0.48 V vs Ag/AgNO₃ in CH₂Cl₂, respectively) in comparison with those of **4a-d** (0.60, 0.58, 0.35 and 0.24 V vs Ag/AgNO₃ in CH₂Cl₂, respectively). Previous studies reveal a D-A stucture for compounds **4a-d** and the triphenylamine or indoline module plays as a donor[58]. Herein the azo group is electron withdrawing, and thus enhances the charge transfer degree from the triphenylamine or indoline module (donor) to the styryl module (acceptor), leading to an increase of stability for **1a-d** when compared to that of the reference compounds **4a-d**. Moreover, as we compare the oxidation potential of **1a-c**, it is found that the electron donating groups at the donor such as methyl in **1b** and octyloxyl in **1c** may reduce their stability. This result agrees with that of **4a-c**.

The HOMO energy was deduced from the oxidation onset potential and calculated by the equation: $E_{HOMO} = -E_{oneset}$ -4.93 (eV) as -5.30, -5.28, -5.21 and -5.20 eV for **1a-d**, respectively. A slight improvement of HOMO energies from **1a** to **1b** and **1c** are consistent with above computation results, verifying the donor effects on HOMO.

3.4. Absorption Abilities

Fig.4(a) plots the absorption spectra of **1a-d** in dichloromethane solutions. The absorption band between 260 and 400 nm can be ascribed to π - π * electronic transitions of aryl groups and azobenzne bands [59]. The absorption maxima of **1a-d** locates at around 464 nm, 489 nm, 491 nm and 506 nm, respectively. This absorption is attributed to HOMO-LUMO transition according to the computation results and influenced by the degree of ICT. Decreased stokes shifts of 1a-d in cyclohexane and benzene (Table S1) suggest that the ICT degree reduces from 1a to 1d. Since the acceptor unit is almost the same for four compounds, the maxima absorption wavelength changes with the donor units. **1d** has the longest absorption band at 506 nm. Methyl group is electron donating, leading to a 15 nm bathochromic shift of **1b** in comparison with **1a**. A further 2 nm bathochromic shift is found in **1c** by substitution of both methyl groups in **1b** for octyloxyl groups. The optical energy gap (Eg) is 2.19, 2.12, 2.11 and 2.04 eV for **1a-d**, respectively. This agrees with computation results and declares that enhanced ICT may reduce the energy gap.

The absorption spectra of **1a-d** films were also measured by spin-coating the chlorobenzene solution onto a glass substrate at a speed of 1500 rpm. As shown in Fig.4(b), the absorption peaks especially the longest band become wider for films in comparison with those obtained in solution, indicative of intermolecular interactions. An obvious red-shift by 47 nm and a clearly reduced Eg by 0.23 eV were observed for **1b** in films while the red-shift and Eg variation were within 20 nm and 0.20 eV for other compounds (**1a**, **1c-d**, **4a-d** and sprio-OMeTAD) as shown in Table S2. Since the films are prepared in similar thickness, a great improve of the absorption ability is discovered for **1b** for the absorbance of **1b** in films is similar as that of **1c** and larger than that of **1a** and **1b** in films whereas the absorbance of **1b** in solutions is distinctly below that of **1c** and **1d** in solutions. All these phenomena demonstrate that, among these compounds, **1b** has the strongest

intermolecular interaction, which enhances its absorption ability especially for the longer wavelength.

3.5. Application in perovskite solar cells

The electrochemical diagram of TiO₂, CH₃NH₃PbI₃ and compounds **1a-d** are shown in Fig.5(a). The HOMOs of **1a-d** are between that of CH₃NH₃PbI₃ (-5.44 eV) and Au (-5.10 eV), indicative of the possibility of **1a-d** as the hole transfer materials for perovskite solar cells. The LUMOs of **1a-d** are also higher than that of CH₃NH₃PbI₃ (-3.93 eV), showing a possible transfer electron from **1a-d** to CH₃NH₃PbI₃. Then we fabricated perovskite solar cells using **1a-d** as the HTM. The cross-sectional SEM image is shown in Fig.5(b). The J-V curves are shown in Fig.6(a) and the photovoltaic parameters are listed in Table 1.

Perovskite solar cells with compounds **1a-d** as HTM show an adequate photovoltaic performance with a PCE of 7-9 %. The highest V_{oc} , J_{sc} and PCE are achieved with compound **1b** as 917.1 mV, 15.96 mA·cm⁻² and 9.02 %, respectively. The V_{oc} depends on the gap (Eg oc) between the HOMO of HTMs and the quasi-Fermi level of the TiO₂. Therefore the relatively low Eg oc leads to a relatively low V_{oc} for compound **1c** and **1d**. The difference of J_{sc} may be relative to the absorption ability and hole mobility of HTMs as well as the charge transportation ability at interfaces. The IPCE spectra in Fig.6(b) record higher efficiency in the range of 400-550 nm, corresponding to the absorption peaks of compounds **1a-d**. This indicates that light absorption from compound **1a-d** also contribute to the photocurrent. Above discussions reveal that compound **1b** has the highest absorption ability in films, corresponding to its highest J_{sc} . And here the hole mobility, which was obtained with the film processed in same procedure and same film thickness as the preparation of solar cells, is found to increase from **1a** to **1d** (Table 1 and Fig S3). However,

the J_{sc} of **1c** is higher than that of **1d**. Therefore we assume that the charge transportation ability at interfaces is significant for high performance pervoskite solar cells. The higher HOMO of compounds **1a-d** than that of CH₃NH₃PbI₃ allows hole injection from compounds **1a-d** to CH₃NH₃PbI₃, thus contributing to J_{sc} . A match of HOMO potentials between CH₃NH₃PbI₃ and the HTM can achieve relatively high J_{sc} . Results by Karl Leo et al. indicate that the most appropriate ionization potential of HTMs is around 5.3 eV for triphenylamine modified spiro-derivatives[60]. Herein similar HOMO energy of **1b** may also contribute to the higher J_{sc} of **1b** than **1a**.

Furthermore, the solubility of **1a-d** is low in common organic solvents. Chlorobenzene is a relatively good solvent for them. Thus, during the device fabrication, chlorobenzene was employed to dissolve **1a-d** and the concentration is as low as 5 mg·mL⁻¹. Even so, films of **1a-d** exhibit many cracks, which is adverse to the exciton separation at the interface of $CH_3NH_3PbI_3$ and HTMs as well as the hole transportation within HTM layer. For comparison, under the same fabrication process, we fabricated perovskite solar cells using compound **4b** as the HTM and results are also given in Table 1. Compound **4b** shows similar HOMO energy to **1b**, but better solubility and filming ability than **1a-d**. It is found that their contrast device has a comparable PCE (7.61 %) to that of compound **1a** and **1d**, but obviously less than that of **1b**. As comparing with that of **4b**, **1b** shows obviously higher hole mobility and better light absorption ability. However, the J_{se} is found only a bit higher with **1b** than **4b**. All these suggest the significance of filming ability for this kind of HTMs.

Spiro-OMeTAD was also employed as the HTM without any dopants to fabricate perovskite solar cells. As shown in Table 1, the V_{oc} of spiro-OMeTAD is a bit lower than that of **1b** due to its a bit higher HOMO (-5.22 eV). However, devices of spiro-OMeTAD present an obviously

improved J_{sc} (18.25 mA·cm⁻²), and thus a higher PCE (11.46 %). This is attributed to a higher hole mobility and better light absorption ability of spiro-OMeTAD. In experiments, we found the hole mobility and photovoltaic parameters change little as we improved the film thickness by increasing its concentration to 20 mg·mL⁻¹. It can be reasonably attributed to its good solubility and filming ability, which reduce the effect of charge transportation at interfaces. This further declares the importance of filming ability for this kind of HTMs.

4. Summary

In conclusion, a novel series of triphenylamine modified azobenzenes **1a-d** have been synthesized and studied theoretically and experimentally. An intramolecular charge transfer(ICT) from both triphenylamine or indoline units (donor) to the central azobenzene unit (acceptor) is revealed, suggesting a D-A-D structure for these dyes. Both computational and experimental results indicate that stronger electron donating ability of the donor may enhance the degree of ICT, and improve their HOMO energies. An electron donating groups at the donor such as methyl in **1b** and octyloxyl in **1c** may reduce their electrochemical stability and optical energy gap, but improve their light absorption ability and hole mobility. The intermolecular interaction also affects their absorption ability in films. But as they are applied to perovskite solar cells, their solubility and filming ability of **1a-d** lead to an inadequate PCE of respect solar cells. The highest PCE was obtained as 9.02 % with perovskite solar cells using **1b** as the HTM. High performance is expected as the solubility and filming ability of triphenylamine-based azobenzene are improved.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at

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Scheme 1. The synthetic route for azobenzene-derivatives

- Fig 1. (top) ORTEP diagram (50 % probability, other hydrogen atoms without hydrogen bonding are omitted for clarity) of compound 1a. (below) 1a molecules showing planarity and its three-dimensional packing structure.
- **Fig 2.** HOMO–LUMO frontier molecular orbitals and corresponding energies of **1a-d** calculated by DFT at a B3LYP/6-31G(d,p) in dichloromethane

Fig 3. CV curves of compounds 1a-d in dichloromethane vs Ag/AgNO₃

- Fig 4. (a) Absorption spectra of compound 1a-d in dichloromethane $(5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1})$ and (b) in films prepared by spin-coating the chlorobenzene solution (5 mg/mL) onto glass slides at a spin speed of 1500 rpm.
- Fig 5. (a)Energy level diagram of HTMs applied in perovskite solar cells. HOMO energies of la-d were determined from CV curves via the oxidation onset potentials and LUMO energies of la-d were obtained by subtracting the optical energy gap from the HOMO energies. Others are from the literatures[61]. (b) cross-sectional SEM image of the FTO/TiO₂/CH₃NH₃PbI₃/HTMs film (chlorobenzene solution).
- Fig 6. (a) J-V curves for the perovskite solar cells with azobenzene-HTMs and (b) corresponding IPCE spectra
- Table 1. Photovoltaic performance of perovskite solar cells based on azobenzenes and

 Spiro-OMeTAD under AM 1.5G (100mW cm⁻²) illumination



(3) LiAlH₄, tetrahydrofuran, N₂, rf, 2h





Fig 1. (top) ORTEP diagram (50 % probability, other hydrogen atoms without hydrogen bonding are omitted for clarity) of compound **1a**. (below) **1a** molecules showing planarity and its

three-dimensional packing structure.



Fig 2. HOMO-LUMO frontier molecular orbitals and corresponding energies of 1a-d calculated

by DFT at a B3LYP/6-31G(d,p) in dichloromethane.



Fig 3. CV curves of compounds 1a-d in dichloromethane vs Ag/AgNO₃



Fig 4. (a) Absorption spectra of compound 1a-d in dichloromethane $(5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1})$ and (b) in

films prepared by spin-coating the chlorobenzene solution (5 mg/mL) onto glass slides at a spin

speed of 1500 rpm.



Fig 5. (a)Energy level diagram of HTMs applied in perovskite solar cells. HOMO energies of **1a-d** were determined from CV curves via the oxidation onset potentials and LUMO energies of **1a-d** were obtained by subtracting the optical energy gap from the HOMO energies. Others are from the literatures[61]. (b) cross-sectional SEM image of the FTO/TiO₂/CH₃NH₃PbI₃/HTMs film (chlorobenzene solution).



Fig 6. (a) J-V curves for the perovskite solar cells with azobenzene-HTMs and (b) corresponding

IPCE spectra

Table 1. Photovoltaic performance of perovskite solar cells based on azobenzenes and

Compound	Hole Mobility (cm ² V ⁻¹ s ⁻¹)	$J_{\rm SC}({\rm mA}{\cdot}{\rm cm}^{-2})$	V _{oc} (mV)	FF	η
1a	1.90×10 ⁻⁵	14.01	903.3	0.591	7.48%
1b	4.11×10 ⁻⁵	15.96	917.1	0.616	9.02%
1c	8.98×10 ⁻⁵	14.45	896.2	0.625	8.10%
1d	1.15×10 ⁻⁴	13.88	896.2	0.616	7.66%
4b	1.21×10 ⁻⁵	15.43	875.3	0.562	7.61%
Spiro-OMeTAD	1.90×10^{-4}	18.25	910.7	0.690	11.46%

Spiro-OMeTAD under AM 1.5G (100mW cm⁻²) illumination

Highlights

- Four new triphenylamine modified azobenzene dyes were synthesized.
- Donor-acceptor-donor structure was characterized for these dyes.
- HOMO, light absorption ability and hole mobility can be improved by varying the substitutions.
- The dyes display applications in pervoskite solar cells as hole transport materials.

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