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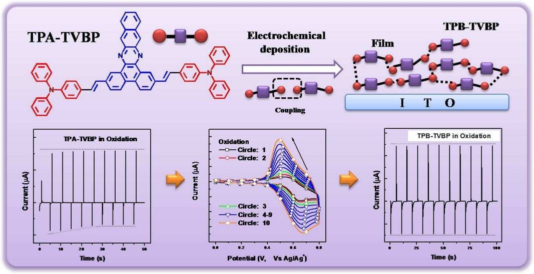
A Triphenylamine-capped Solution-Processable Wholly Aromatic Organic Molecule with Electrochemical Stability and Its Potential Application in Photovoltaic Devices

TOC：

TPA-TVBP, as a TPA-capped model material, exhibited a surprising harvest in potential OPV application because of its electrochemical stability in solution and film by the cyclic voltammetry and potential switching step measurements.

TOC figure



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ARTICLE TYPE

A Triphenylamine-capped Solution-Processable Wholly Aromatic Organic Molecule with Electrochemical Stability and Its Potential Application in Photovoltaic Devices

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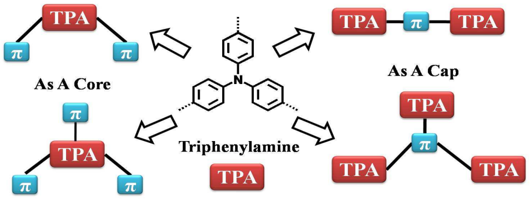
A triphenylamine-capped solution-processable wholly aromatic conjugated molecule, **TPA-TVBP**, was designed and synthesized. It exhibited a high thermodynamic stability and good film forming ability as expected, originating from the absent of alkyl and alkoxyl moieties. The triphenylamine cap provided a good solubility because of three-dimensional propeller structure and a donor moiety to construct the organic D-π-A molecule with electron-deficient tribenzo[a,c,i]phenazine moiety as the acceptor. The special electrochemical stability was discussed through cyclic voltammetry and potential switching step measurements, and the photo current generation in photovoltaic device application was described further. Simple bulk heterojuction photovoltaic cells were fabricated using **TPA-TVBP** and **PCBM**, and the higher short circuit current and fill factor than the similar structures were achieved. Based on the mechanism of the photocurrent generation, the molecule **TPA-TVBP** would be a good model molecule to investigate the electrochemistry properties of the triphenylamine-capped material in photovoltaic device application.

Introduction

Solution-processable molecules have attracted increasing attention in organic light-emitting diodes (**OLED**) and organic photovoltaic (**OPV**) devices.[1] With respect to their polymer counterparts, small molecule compounds presenting a better reproducibility of synthesis and easier purification, together with their precise (monodisperse) chemical structures facilitate the establishment of structure-properties relationships.[2] Their solution processability offers the possibility of avoiding the troublesome high-precision mask alignment during vacuum deposition process, particularly to produce large-area colour display and solar panels.[3] Based on the development of OLED and OPV materials for possible commercial applications, some of alkyl and alkoxyl moieties are introduced to enhance solution processability, which is beneficial to adjust the efficiency and reduce fabricating cost.[4] However, these alkyl and alkoxyl moieties can be readily decomposed than their aryl block for their instability under the sun and oxygen. Therefore, the wholly aromatic organic molecule should be a better choice to extend service life of photoelectric material.[5] Generally, the wholly aromatic structure possesses high photo-thermal stability and robust morphology, while the solubility remains a key issue.[6]

The triphenylamine (**TPA**) moiety possesses three-dimensional propeller structure, which can effectively avoid molecular aggregation and is usually chosen as a block to increase solution-processability,.[7] TPA has been reported as a good p-doping unit in photoelectric research and used as hole-injection and transport moiety.[8,9] As shown in Scheme-1, many solution-processable molecules containing **TPA** reported exhibit excellent performance in photoelectric devices,[10] while their reversibility (stability) in redox process is ignored, which is important for their service life.

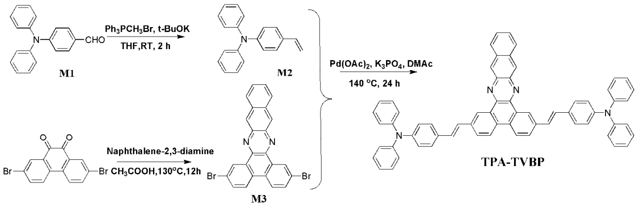


Scheme 1 The common structures of TPA and its derivatives in OPVs

Tribenzo[a,c,i]penazine (**TBP**) is a famous liquid crystal molecule, which has good thermo and environmental stability. The low electron injection barrier and the reversible re-dox progress in reduction are suitable for balancing the carries transport.[11] Recently, we designed a model molecule to investigate the electrochemical stability of the **TPA**-capped material in OPV application. With **TPA** unit, we chose **TBP** as an accepter unit to construct the wholly aromatic organic D-π-A molecule **TPA-TVBP** (Scheme 2), which is consisting of a rigidity moiety of **TBP** and a flexibility moiety of **TPA** via conjugated bridge.[12] To be expected, **TPA-TVBP** exhibits good solution-processability and space-charge-separation capability, high thermodynamic stability and good film forming ability. The stable electrochemical property in doping state is discussed by cyclic voltammetry and potential switching step measurements further. Here, we report its synthesis, characterization and primary photovoltaic application as a solution-processable **OPV** material.

Synthesis and Characterization

Design and Synthesis



Scheme. 2 The synthesis route of **TPA-TVBP**

As shown in Scheme-1, **TPA-TVBP** was synthesized via cross-coupling of 2,7-dibromotribenzo[a,c,i]phenazine (**M3**) with two equivalents of 4-*N,N*-diphenylaminostyrene (**M2**) under typical Heck reaction conditions, catalyzed by $Pd(OAc)_2$ and K_3PO_4.[13] **M2** was prepared as the literature reported, and **M3** was started from 2,7-dibromophenanthrene-9,10-dione and naphthalene-2,3-diamine by a similar method as described in our previous report with a little revision.[14] The NMR spectrum of **TPA-TVBP** was shown in Fig.1, and all of the peaks observed in the aromatic range were corresponded well to its expected structure as marked.

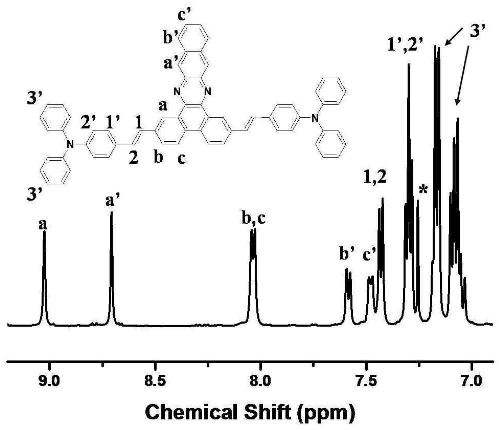


Fig.1 ^{1}H NMR spectrum **TPA-TVBP** in the aromatic range

Thermal Properties

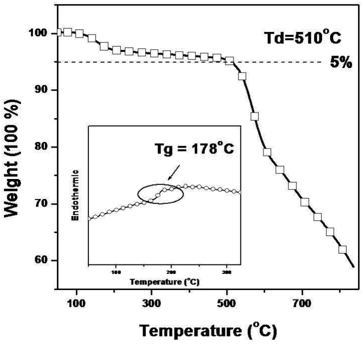


Fig.2 The TGA and DSC (insert) graphs of **TPA-TVBP**

Thermal properties of the molecule were investigated using thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC) at a heating rate of 10°C/min under nitrogen atmosphere (Fig.2). The molecule showed a small weight loss (<5%) at 510°C, and before 200°C, the lost weight, which may be due to the lost of the trapped solvent (DMAC) in the material. The Tg values were measured to be 178°C (Fig.2 inserted), and this implied the **TPA-TVBP** molecule exhibited glass phase property. Such high T*d* and T*g* indicate that **TPA-TVBP** could form morphologically stable amorphous films upon thermal evaporation, which is very important for its application in OLED and OPV.[15]

Photophysical Properties

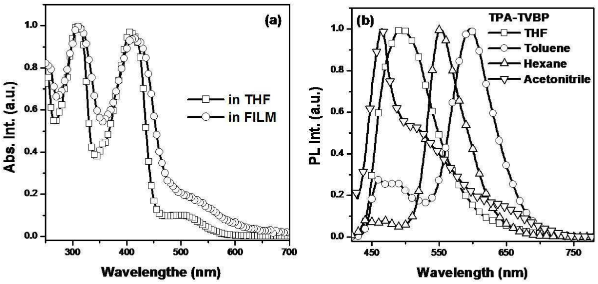


Fig. 3 Normalized absorption spectra of **TPA-TVBP** in THF and film (a) and the emission spectra in different polarity solvent (b)

Benefited from its donor-acceptor structure linked with conjugated bridge as designed, **TPA-TVBP** showed a broad absorption band covering the wavelength range from 250 to 650 nm (Fig.3a), which is favorable for the application in photovoltaic devices.[16] The normalized optical absorption spectra of **TPA-TVBP** in dilute (10^{-5} M) THF solutions exhibited two strong absorption peaks at 308, 406 nm and an absorption band at 505 nm respectively. In film state, they were red-shifted to 312, 414, and 535 nm, respectively. The absorption edge of the film extended to 650 nm, from which the corresponding optical energy gap (Eg opt) was calculated to be 1.9eV.

TPA-TVBP showed a low and broad emission band at 495 nm in THF (10^{-5} M), while the emission of its film was too weak to be observed with a band around the 650 nm. Solvatochromism experiments of the **TPA-TVBP** were done in different polarity solvents and some fluorescence spectra were split two parts obviously, which might be originated from the donor part and the

ICT state. When increasing solvent polarity, the emission maximum of **TPA-TVBP** was blue-shifted, from 596 nm in hexane, 551 nm in toluene, 494 nm in THF to 462 nm in acetonitrile, accompanying the full width at half maximum (FWHM) significantly broadened from 150 nm in hexane to 300 nm in acetonitrile. Such a change indicated that the dipole moment or the molecule excited state structure of **TPA-TVBP** had been affected by the solvent, inducing the change of intramolecular charge and energy transfer progress.[17] Meanwhile, it suggested that the quinoxaline structure (**TBP**) had strong electron-withdraw ability and was suitable to construct the space charge separation system, which was also approved by the data of electrochemistry and molecule simulation discussed below.

Theoretical Calculations and molecule simulation

The electronic properties of compound **TPA-TVBP** had been investigated by theoretical calculations. Calculations were done using the restricted B3LYP/6-31G(d)* functions. The orbital distribution of HOMO and LUMO levels of neutral molecule **TPA-TVBP** were shown in Fig. 4. The HOMO state density mainly distributed on the two triphenylamine (**TPA**) moieties and phenanthrene part of tribenzo[a,c,i]phenazine moiety. The electron density of LUMO was mainly localized at naphthalene part of the tribenzo[a,c,i]phenazine moiety. This was a strong proof of space-charge-separation and could greatly enhance exciton dissociation and decrease the recombination of charged species to increase the light-current intensity at the electrode.

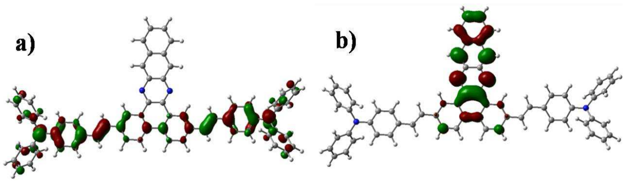


Fig 4.The calculated HOMO (a) and LUMO (b) orbital distributuion

The optimized geometry of **TPA-TVBP** indicated that the two **TPA** moieties at the end of the molecule were in 3-D spatial arrangement. The nonplanar conformation of **TPA-TVBP** could be beneficial to increase solution-processability and forming amorphous film ability. While the obvious planer structure of **TVBP** indicated that the molecule would be prone to aggregate in proper condition, and increase the charge mobility when they aggregated in blend. Such a molecular structure balanced rigidity and flexibility, determining its excellent film forming abilities,

Morphology

As expected, **TPA-TVBP** was soluble in common organic solvents such as THF, toluene, and chlorobenzene. High quality amorphous film could be obtained by spin-coating from solution as shown in Fig-4. The AFM images of **TPA-TVBP** film on an indium-tin-oxide (ITO) substrate (10mg/ml in chlorobenzene, 1000rps), revealed that the surface roughness was 0.6 nm, the same to the polymer roughness. This proved that the planer unit had no influence on film morphology. After annealing at 90 °C in N_2 atmosphere for 30 min, the film was kept unchanged. It suggested that the film of the molecule was suitable for applications as thin film devices with good film-forming ability and morphological stability under Joule heat and sunlight irradiation during operation. This was derived from the all aromatic structure and high thermodynamic stability of the wholly aromatic structure. When the annealing temperature was improved to 160 °C in N_2 atmosphere for 10 min, the roughness changed only form 1.09 nm to 1.69 nm.

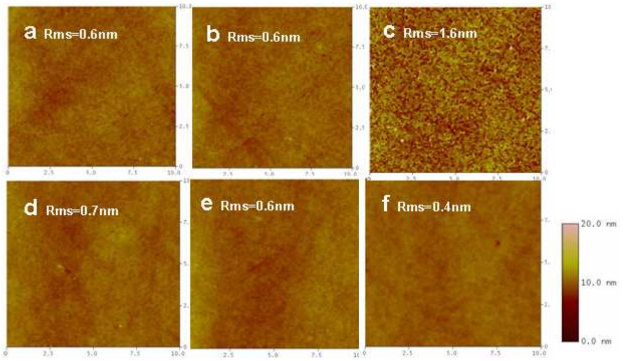


Fig 5. The AFM of **TPA-TVBP** (a) at room temperature, (b) annealing at 90 °C, (c) annealing at 160 °C. The AFM of **TPA-TVBP** : **PCBM** (1:1) (d) at room temperature, (e) annealing at 90 °C, (f)annealing at 160 °C.

As shown in Fig. 5, the blend film of **TPA-TVBP** and **PCBM** (on ITO substrate 10mg/ml in chlorobenzene, 1000rps), revealed that the surface roughness was only 0.7 nm, which implied the **PCBM** had no influence on the film of **TPA-TVBP**. Significantly, the blend became even flatter than original spin-coated film after annealing at 90 °C and 160 °C in N_2 atmosphere for 30 min and 10 min, respectively. This may be properly ascribed to the restrained aggregation of **PCBM** doping. All of this proved that the wholly aromatic structure **TPA-TVBP** was suitable as a better film material with solution-processable ability.

Electrochemical Properties

a. Measurment of Energy Level

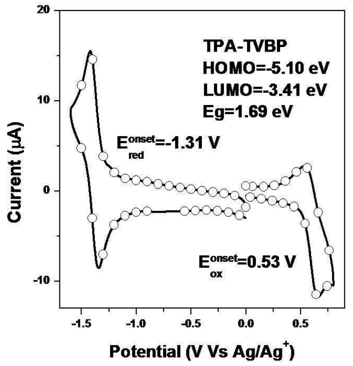


Fig. 6. The CV curve of TPA-TVBP in in CH_2Cl_2 and DMF solution.

The electrochemical behavior and the electrochemical energy levels of the **TPA-TVBP** were investigated by cyclic voltammetry (CV) in a standard three-electrode electrochemical cell. The CV measurement in solution was conducted in CH_2Cl_2 and DMF 1:1 with 0.1 M tetra-n-butylammonium hexafluorophosphate ($n\text{-}Bu_4NPF_6$) as electrolyte at room temperature. HOMO and LUMO level were estimated using the energy level of the ferrocene (Fc) reference (4.8 eV) and calibrated with $E_{1/2}(Fc/Fc^+) = 0.11$ V.[18]

As shown in Fig. 6, in the positive potential region there was one couple of oxidation/re-reduction peak with the onset oxidation potential (E^{onset}_{ox}) at 0.53 V vs Ag wire which was from **TPA** unit. [19a] And a couple of reduction peak in the negative potential region with onset reduction potential (E^{onset}_{red}) at -1.30 V vs Ag wire was observed, which is affirmed from the TBP unit. This was consistent with the result of molecular simulation fact that HOMO was localized at **TPA** unit and LUMO was localized at TBP unit. HOMO and LUMO levels were calculated to be -5.10 eV and -3.41 eV, respectively, and the electrochemical band gap was 1.69 eV.

b. Electrochemical Stability in Solution

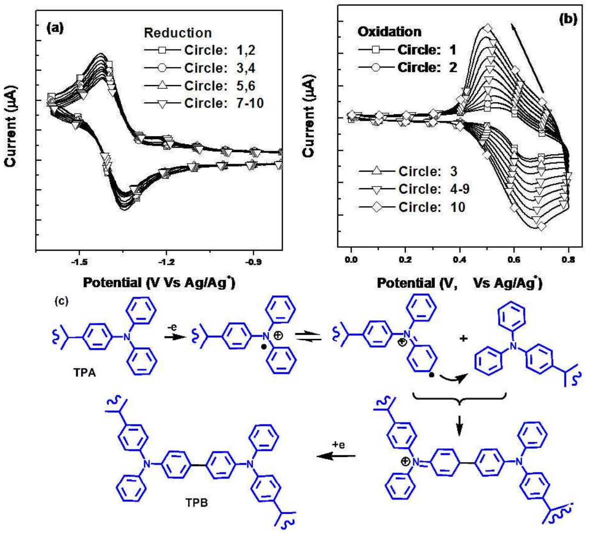


Fig.7. Repetitive cyclic voltammograms of the reduction of **TPA-TVBP** in a 1.0 mM solution (a) and oxidation (b) with 0.1 M **TBAP** on a Pt electrode, V) 0.1 V s-1; (c). The cross-linking mechanism of dimerization reaction from **TPA** to **TPB**

Interestingly, when the repetitive cyclic voltammograms were performed in solution, the reduction was kept unchanged on subsequent scans, meaning **TPA-TVBP** at the anion state was very stable and the doping/dedoping process was completely reversible as shown Fig 7a. During the oxidation process, on subsequent scans in the potential range of 0 V to +0.80 V, the peak current was gradually increased, and in the successive cycles the potential was decreased (Fig. 7b). As shown in Fig. 7c, the **TPA-TVBP** radical cation formed by oxidation was involved in a dimerization reaction, indicating the cross-linking between the **TPA** units and the growth of tetraphenylbenzidine (**TPB**). The oxidation potential was gradually decreased because the more extended π-electron delocalization of **TPB** unit. The electrochemical processes could be described by an **EC_2E** mechanism[19]. That meant the molecule in solution would be electro-deposited on electrode to form the film[20].

c. Electrochemical Stability in Film

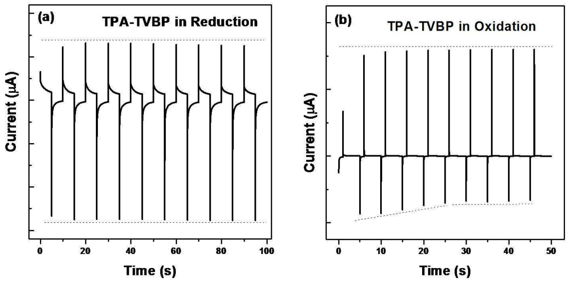


Fig. 8. Potential switching step of the reduction (a) and oxidation (b) of **TPA-TVBP** in spin-coating film.

To discuss the stability of the **TPA-TVBP** film, the method of potential switching step was introduced,[21] which was widely applied in electrochromism to validate the stability of molecules. **TPA-TVBP** was spin-coated on ITO surface to form the film. Its reduction state was switched by stepping the potential between -1.6 and -0.2 V during oxidation with time intervals of 10 s and between -0.8 and 0.8 V during oxidation with time intervals of 5 s, and the current was monitored versus time. As shown in Figure 8, the current transient shapes of the oxidation and reduction current peaks were different, reaching zero in a few seconds during the potential pulses, but the charge injected in both processes were the same. Mostly, the amount of charge (Q) in each current curve in both processes was very similar, in agreement with the stable anodic electrochemical properties of molecule in film[21]. The current kept unchanged in the successive cycles during the reduction process (Fig. 8a). But during the oxidation process (Fig. 8b), on subsequent scans, the peak current was increased firstly, indicating the cross-linking reaction happened between the **TPA** units. And then it was gradually decreased in the successive cycles, which was normally observed and suggested the dimerization reaction was finished[23]. This showed that the electropolymerization process could also form the **TPB-TVBP** film in the solid state.

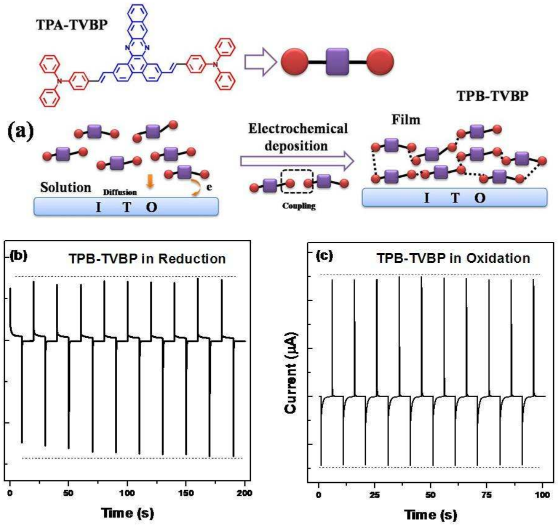


Fig. 9. (a) The preparation of the electrochemical deposition film (**TPB-TVBP**); and the potential switching step of the reduction (b) and oxidation (c) of **TPB-TVBP**.

For further understanding the electrochemical stability of the

TPB-TVBP, which was formed by the cross-link of **TPA-TVBP** (Fig. 9a), a film on an ITO electrode was got by the way of electro-deposition in CV method from the **TPA-TVBP** solution[24]**.** In the successive scans measurement, the current was increased and the potential changed in the same way as the scan cycles increase. The formed TPB-TVBP film can be treated as the **TPA-TVBP** film by potential switching step method, and the pulse time was tuned twice. The amount of charge in each current curve in two processes was very similar as shown in Fig. 9b-c, and the results suggested the film of TPB-TVBP had better n/p doping capability than the **TPA-TVBP** film. Meanwhile, this method could be applied to the preparation of photo-electro films devices.[23,24]

Actually, the reversible redox progress of the film was important in photovoltaic device. To get a persistent current, the molecule must switch between the doping and neutral state, thus the reversibility of the materials in doping and dedoping process is inherent request for long life-time and high-efficiency device.[25] The electrochemical measurement can reflect the molecule doping and dedoping progress, so the method was introduced to discuss the molecule “bipolar property”.

In n-doping progress of **TPA-TVBP**, the film was very stable by potential switching step measurement from the data above. In p-doping progress, the polymerization might be gained, which meant the **TPA** unit possibly underwent radical cation dimerization and became to be the dimmer **TPB** unit. The film of **TPB-TVBP** exhibited better n/p doping capability than that of **TPA-TVBP**. In other words, if the spin-coating film of **TPA-TVBP** were applied in solar cells, it would possess better electrochemistry properties (stability) even after dimerization reaction happened. This was a surprising harvest for the **TPA**-capped martial.

Photovoltaic properties

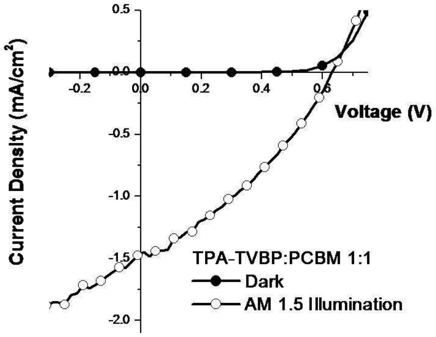


Fig.10. The I-V curve of **TPA-TVBP**/ **PCBM** blend in OPVs.

Based on the above results of **TPA-TVBP**, the photovoltaic property in OPV was attempted to be obtained. Bulk-heterojunction **OPVs** were fabricated based on the spin-coated blend films of **TPA-TVBP** and **PCBM** (1:1, w/w) as the active layer, with LiF/Al as the cathode. Fig. 10 showed the current-voltage (I-V) curves of the **OPVs** in the dark and under AM 1.5 illumination of 100 mW cm^{-2}. The open circuit voltage (V_{OC}), short circuit current (J_{SC}), fill factor (FF) and power conversion efficiency (PCE) of the **OPVs** based on **TPA-TVBP** reached 0.61 V, 1.48 mA cm^{-2}, 0.33 and 0.29% respectively. Although its value was very low, the short circuit current and fill factor were still higher than the similar structures of TPA-TH1[26] and TDOX[27], which was thought to profit from the compositive peculiarity of TPA-TVBP involving the good solution-processability, the space-charge-separation capability, the good thermal and forming film stability, the broad absorption spectrum and especially the stable electrochemistry properties in redox progress. The further optimation in **OPV** with TPA-TVBP as an active layer or with electro-deposited film (TPB-TVBP film) as a functional layer would be reported in the next research work.

Conclusion

In summary, the tribenzo[a,c,i]phenazine (**TBP**) was chosen as an accepter unit to construct a wholly aromatic organic D-π-A molecule with **TPA** unit, named **TPA-TVBP** as a model molecular to investigate the electrochemistry stability of the **TPA**-capped material in **OPV** application. **TPA-TVBP** exhibited a good solution-processability and space-charge-separation capability, high thermodynamic stability and good film forming as expected. The special electrochemistry stability was discussed by cyclic voltammetry and potential switching step measurements, and the doping and dedoping progress in **OPV** application was described further. Thus, the result was important not only in terms of developing a new kind of triphenylamine-capped material containing **TBP** unit, but also exploring the TPA moiety as a capped unit in **OPV** film application.

Experimental Part

Materials and measurement

All the reagents and solvents used for the syntheses were purchased from Aldrich or Acros companies and used without further purification. All reactions were performed under a dry nitrogen atmosphere.

The ^{1}H NMR and spectra were recorded on AVANCZ 500 spectrometers at 298K by utilizing deuterated chloroform ($CDCl_3$) or Dimethyl Sulphoxide (DMSO) as solvent and tetramethylsilane (TMS) as standard. The elemental analysis was operated by Flash EA 1112, CHNS-O elemental analysis instrument for these compounds. The MALDI-TOF mass spectra were recorded using an AXIMA-CFRTM plus instrument. UV-vis absorption spectra were recorded on UV-3100 spectrophotometer. Fluorescence measurements were carried out with RF-5301PC. The differential scanning calorimeter (DSC) analysis was determined using a NETZSCH (DSC-204) instrument at 10 ^oC /min under nitrogen flushing. Cyclic voltammetry (CV) were performed with a BAS 100W Bioanalytical Systems, using a glass carbon disk (Φ=3mm) as working electrode, a platinum wire as auxiliary electrode and Ag/Ag^+ as reference electrode. Cyclic voltammetric studies were carried out containing 0.1M [n-NBu_4][BF_4] dried in an oil pump vacuum at 80^{o}C as supporting electrolyte. All solutions were purged with nitrogen stream for 10 min before measurement. The procedure was performed at room temperature and nitrogen atmosphere was maintained over the solution during measurements. The atomic force microscopy (AFM) measurement was conducted on a Nanoscope III (DI, USA) in tapping mode with 100μm scanner.

OPV Device Fabrication and Measurement

The bulk heterojuction photovoltaic cells were fabricated with the active layer consisting of the **TPA-TVBP**:**PCBM** with blend ratios (1:1, w/w). ITO glass was cleaned by detergent, acetone and boiled in H_2O_2. A 50 nm layer of poly(3,4-ethylene dioxythiophene): poly(sty- renesulfonate) (PEDOT: PSS) z(Bayer PVP Al 4083) as a modified layer was spin-coated onto the pre-cleaned ITO glass substrate and then dried at 120 ^{o}C for 15 min on a hot plate. The **TPA-TVBP** was dissolved in chlorobenzene to make 10 mg ml^{-1} solutions, followed by blending with **PCBM** (purchased from Lumtec. Corp) in blend ratios (1:1, w/w). The active layers were obtained by spin-coating the blend solutions and the thickness of films were about 70 nm, as measured with the Ambios Technology XP-2. Finally, the cathode of LiF (0.5 nm)/Al (100 nm) was thermally deposited to finish the device fabrication. The active area was about 5 mm^2. Current-voltage (J-V) characteristics were recorded using a Keithley 2400 Source Meter in the dark and under 100 mW cm^{-2} simulated AM 1.5 G irradiation (Sciencetech SS-0.5 K Solar Simulator). The spectral response was recorded by a SR830 lock-in amplifier under short circuit conditions when devices were illuminated with a monochromatic light from a Xeon lamp. All fabrication and characterizations were performed under ambient atmosphere at room temperature.

Synthesis

4-(diphenylamino)benzaldehyde ***(M1)***

Triphenylamine (5.0 g, 20.2 mmol) was dissolved in distill DMF (15 mL) in a 250 mL two-necked roundbottom flask. Under -20^{o}C in ice-water bath, the phosphorus oxychloride ($POCl_3$, 14.7 mL) was added dropwisely to the mixture with a strong stirrer bar. Then the mixture warmed to 45 ^{o}C for 2 hr until the drop progress stop. This mixture was poured into ice water to stop the reaction with proper pH adjustment (pH=7) with 20% NaOH eq. Formed yellow precipitate and filtered off, and the mixture was recrystallized from ethyl acetate to afford the light-yellow crystal of **M1**. Yield: 89%. ^{1}H NMR ($CDCl_3$, ppm), δ: 7.0-8.0 (m, 14H), 9.8 (s, 1H). MALDI-TOF-MS (m/z): $[M+H]^+$ calcd for $C_{19}H_{15}NO$, 273.1; Found: 273.6. Anal. Calcd for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.12. Found: C, 83.90; H, 6.01; N, 5.07.

4-N,N-diphenylaminostyrene ***(M2)***

5.46 g (20.0 mmol) of 4-(diphenylamino)benzaldehyde (**M1**) and 8.57 g (24.0 mmol) of triphenylmethylphosphonium bromide were dissolved in 50 mL of dry THF. The resulting solution was added dropwise slowly to 280 mg (2.5 mmol) of t-BuOK in 20 ml of dry THF at 0 ^{o}C, then the reaction mixture was warmed to room temperature and stirred under N_2 overnight. The mixture was poured into water and extracted with dichloromethane. The organic phase was washed with water, brine, and dried over $MgSO_4$. After removing the solvent, the product was purified by column chromatography using dichloromethane/petroleum ether (v:v = 1:4) gave M2 (4.06 mg, 73%) as a yellow solid. ^{1}H NMR($CDCl_3$, ppm) δ 5.06 (d, 1H), 5.53 (d, 1H), 6.54 (dd, 1H), 6.92-7.03(m, 10H), 7.15-7.22 (m, 4H). MALDI/TOF MS: Calcd for $C_{20}H_{17}N$ 271.1, Found: 271.6 Anal. Calcd for $C_{20}H_{17}N$: C, 88.52; H, 6.31; N, 5.16. Found: C, 88.46; H, 6.53; N, 5.07.

2,7-dibromotribenzo[a,c,i]phenazine ***(M3)***

In a 100 mL round bottom flask, 2,7-dibromophenanthrene-9,10-dione 2.08 mg (10 mmol) and 3.16 mg (20 mmol) naphthalene-2,3-diamine were placed, then 50 mL glacial acetic acid wad added. The mixture was stirred vigorously at 80 ^{o}C for 4h in air. The whole mixture was then poured into water and then the precipitate was filtered. Then the solid was chromatographed on a silica column using $CHCl_3$ as eluent and recrystallized from DMSO twice to give deep-red needle crystals in 85% yield. $C_{24}H_{12}N_2Br_2$: Calcd. C, 59.05; H, 2.48; Br, 32.74; N, 5.74; Found C, 59.25; H, 2.45; Br, 32.64; N, 5.62. MS(MALDI-TOF): m/z= 488.93 (M^+). ^{1}H NMR (DMSO, ppm): δ 9.24 (dd, 2H), 8.39(s, 2H), 8.30 (d, 2H), 8.08 (d, 2H), 7.68 (d, 4H) , 7.38 (d, 2H).

Synthesis of ***TPA-TVBP***

17.8 mg (0.5 mmol) **M3**, 27.2 mg (1 mmol) **M2**, 5 mg of Pd $(OAc)_2$, and 254.4 mg of K_3PO_4 were added to a 50 mL-flask, and then 5 mL dimethylacetamide (DMAC) was injected by syringe under nitrogen flow. The mixture solution was heated to 140 ^{o}C under the dark and kept at that temperature overnight, and the solution was poured into methanol after cooling to the room temperature. The precipitate was filtered, washed with water, dissolved in methylene chloride, and dried over $MgSO_4$. After column separation (petroleum ether/ ethyl acetate v:v = 3:1), 166 mg deep red powder of **TPA-TVBP** was obtained with a yield of 38%. ^{1}H NMR ($CDCl_3$, ppm): δ 9.02 (s, 2H, naphthalene unit), 8.71 (s, 2H, phenanthrene unit), 8.03 (d, 4H, phenanthrene unit), 7.58 (d, 2H, naphthalene unit), 7.48 (d, 2H, naphthalene unit), 7.43 (d, 2H, C=C), 7.29 (t, 4H, Ph-H of **TPA**), 7.03 (m, 20H, N-Ph-H). MALDI-TOF-MS confirmed the chemical structure of **TPA-TVBP** (m/z): 868. 6, calcd for $C_{64}H_{44}N_4$, 868.36. Anal Calc. for ($C_{64}H_{44}N_4$): C, 88.45; H, 5.10; N, 6.45. Found: C, 88.31; H, 5.32; N, 6.48.

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