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High hole mobility of 1,2-bis[4'-(diphenylamino)biphenyl-4-yl]-1,2-diphenylethene in field effect transistor†

Zujin Zhao,^{ab} Zhefeng Li,^c Jacky W. Y. Lam,^a Jose-Luis Maldonado,^d Gabriel Ramos-Ortiz,^d Yang Liu,^a Wangzhang Yuan,^a Jianbin Xu,^e Qian Miao*^c and Ben Zhong Tang*^a

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Triphenylamine-functionalized tetraphenylethene shows aggregation-induced emission feature with unity solid-state fluorescence efficiency. Its amorphous film can function in a p-type FET device with field effect mobility up to $2.6 \times 10^{-3} \text{ cm}^2/\text{Vs}$.

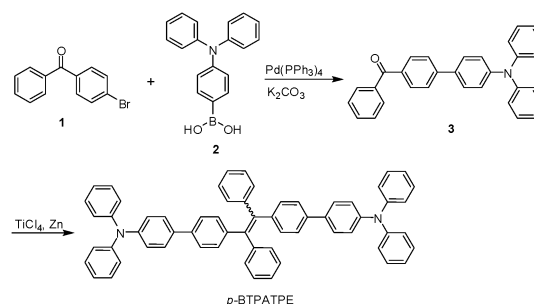
Design and synthesis of novel organic molecules for optoelectronic devices, such as organic light-emitting diodes (OLEDs), field effect transistors (FETs), and solar cells, have been a critical research topic for several decades. In 2001, we discovered that a series of propeller-like luminogens exhibit a novel phenomenon of aggregation-induced emission (AIE).¹ An example of such luminogens is represented by tetraphenylethene (TPE), which is non-emissive in solution but emits intensely by aggregate formation due to the restriction of intramolecular rotation.^{2,3} Since then, many AIE luminogens with different structures and emission colors have been designed and prepared. By melting AIE units with conventional chromophores at molecular level, new AIE molecules with efficient solid-state photoluminescence (PL) and useful functional properties are generated, from which OLEDs with outstanding performances have been fabricated.⁴

Triphenylamine (TPA) and its derivatives have been widely studied as active materials for OLEDs and solar cells due to their good PL and hole-transporting properties.⁵ However, TPA-based materials have rarely been utilized to fabricate FETs, perhaps due to their amorphous nature in the solid state, which is unfavorable for efficient charge transport.⁵ Zhu *et al.*⁶ synthesized TPA-based macrocycles, whose FET devices constructed from their amorphous films exhibited a

mobility of $2.3 \times 10^{-3} \text{ cm}^2/\text{Vs}$ and a current on/off ratio of 10^5 . However, their linear analogue showed only inferior performances with low mobilities (10^{-4} – $10^{-5} \text{ cm}^2/\text{Vs}$).⁷ Recently, we succeeded in creating a new AIE luminogen (2TPATPE or *p*-BTPATPE) by capping the TPE core with TPA peripheries. OLED utilizing *p*-BTPATPE as light-emitting and hole-transporting material is constructed, which exhibits maximum luminance and efficiencies of 33 700 cd/m², 13.0 cd/A, 11.0 lm/W, and 4.4%.^{4d} Such good results are attributable to its efficient solid-state PL and high hole mobility and stimulate us to investigate its FET application in this work.

p-BTPATPE was synthesized by Suzuki coupling of **1** with **2** catalyzed by Pd(PPh₃)₄ in basic medium followed by McMurry reaction of the resultant product **3** in the presence of TiCl₄ and Zn dust (Scheme 1). Detailed procedures and characterization data are given in the Electronic Supplementary Information. Unlike the recent reported synthetic route, which was based on Suzuki coupling of **2** with 1,2-bis(4-bromophenyl)-1,2-diphenylethene,^{4d} the present one can generate the desirable product in a higher isolation yield.

p-BTPATPE shows an absorption maximum at 357 nm with a molar absorptivity of $46\,500 \text{ M}^{-1} \text{ cm}^{-1}$ in dilute THF solution (Fig. 1A). Its PL spectrum in THF (10 μM) exhibits only noisy signals. The absolute fluorescence quantum yield (Φ_F) measured by a calibrated integrating sphere is as low as 1.8%, corroborating that *p*-BTPATPE is a genuinely weak emitter when molecularly dissolved in solution. Addition of poor solvents such as water into its THF solution has aggregated its molecules and enhanced its emission (Fig. 2A). Clearly, the emission of *p*-BTPATPE is induced by aggregate formation,



Scheme 1 Synthetic route to TPA-functionalized TPE.

^a Department of Chemistry, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China.

E-mail: tangbenz@ust.hk

^b College of Material, Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou 310036, China^c Department of Chemistry, The Chinese University of Hong Kong, Shatin New Territories, Hong Kong, China.

E-mail: miaoqian@cuhk.edu.hk

^d Centro de Investigaciones en Óptica, A.P. 1-948, 37000 León, Gto., México^e Department of Electronic Engineering, The Chinese University of Hong Kong, Shatin New Territories, Hong Kong, China

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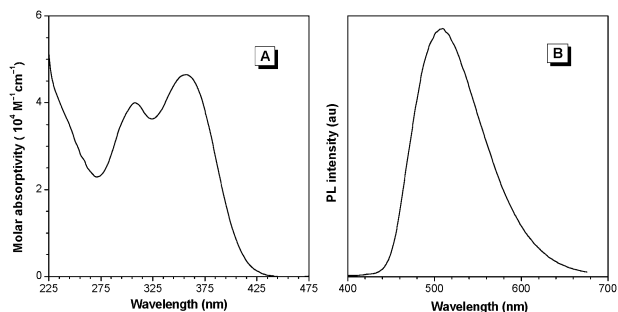


Fig. 1 (A) Absorption spectrum of *p*-BTPATPE in dilute THF solution (10 μ M) and (B) PL spectrum of thin film of *p*-BTPATPE.

in other words, it is AIE-active.^{4d} The thin film of *p*-BTPATPE also emits intensely at 509 nm (Fig. 1B). The associated Φ_F value is 100%, which is more than 2-fold higher than that of unsubstituted TPE (49.2%), presumably due to the electronic communication between the TPA and TPE units.

Cyclic voltammetry analysis of *p*-BTPATPE detects two peaks at 1.00 and 1.41 V associated with the oxidation of its TPA unit (Fig. 2B). The process is reversible and two corresponding peaks are observed at 0.85 and 1.30 V in the backward scan. The HOMO energy level of *p*-BTPATPE can be determined from its onset oxidation potential ($E_{\text{onset}}^{\text{ox}}$) based on the value of -4.8 eV for ferrocene as internal standard with respect to zero vacuum level.⁸ The $E_{\text{onset}}^{\text{ox}}$ of *p*-BTPATPE is found at 0.75 eV, from which a HOMO value of -5.15 eV is derived. The HOMO energy level is close to the workfunction of metallic gold (-5.1 eV), suggesting that *p*-BTPATPE possesses good hole-transporting property, which is advantageous for the fabrication of OLEDs and FETs.⁹ The band gap (E_g) of *p*-BTPATPE can be determined from its onset absorption wavelength and is equal to 2.9 eV. Its LUMO energy level is thus calculated to be -2.25 eV.

We used the time-of-flight (TOF) transient photocurrent technique to investigate the hole-transporting property of *p*-BTPATPE. *p*-BTPATPE-doped poly(styrene) (PS) films (10 μ m) with or without C_{60} were prepared and sandwiched between two ITO-coated glass slides for the measurement. Photogeneration and charge transport could be detected in presence or absence of fullerene C_{60} . The efficient PL emission of *p*-BTPATPE in the solid state suggests that the probability for exciton generation is high in its photophysical process.

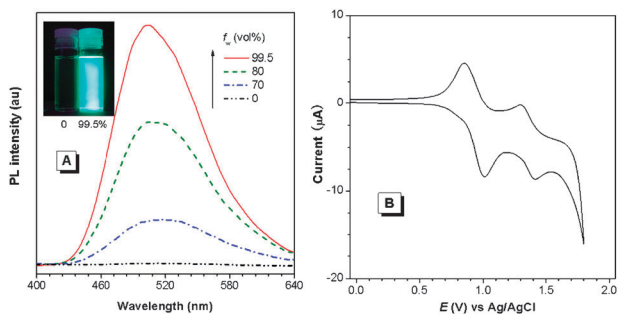


Fig. 2 (A) PL spectra of *p*-BTPATPE in THF/water mixtures with different water fractions (f_w). Inset: photos of *p*-BTPATPE in pure THF and THF/water mixture ($f_w = 99.5\%$) taken under the illumination of a UV lamp. (B) Cyclic voltammogram of *p*-BTPATPE measured in dichloromethane containing 0.1 M Bu_4NPF_6 . Scan rate: 100 mV/s.

Thus, the introduction of C_{60} into the *p*-BTPATPE-doped PS film is to facilitate exciton dissociation and hence increase the efficiency for charge carrier generation owing to its strong electron-accepting capability.¹⁰ As anticipated, the PS/*p*-BTPATPE/ C_{60} composite exhibits a higher photocurrent, which gives a better plot from which the charge mobility can be measured. As shown in Fig. 3, the transient photocurrent for holes increases as the bias voltage becomes higher. The detected photocurrent is dispersive. Since the charge transportation in amorphous films fabricated from organic materials occurs *via* a hopping process, the dispersive behavior can be explained by the presence of traps such as oxygen and water that may arise during the film preparation.¹¹ The transient time determined from the logarithmic plot is 4.3 μ s under an applied electric field of 60 V/ μ m. The hole mobility is estimated to be 5.2×10^{-4} cm^2/Vs , which is higher than that of *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine, a well-known hole-transporting material, under the same measurement conditions.^{10a}

The field effect transistors were fabricated by depositing 60 nm-thick *p*-BTPATPE films onto silicon wafers. Before deposition, the silicon surface was treated with a self-assembled monolayer of octadecyltrichlorosilane (OTS) by thermal evaporation under high vacuum. A layer of gold was then applied on the top of the organic layer through a shadow mask to form the top-contact source and the drain electrodes. Doped silicon and 300 nm-thick silicon layer were used as gate electrode and dielectrics, respectively. The *p*-BTPATPE film is amorphous as suggested by the absence of sharp reflections from its X-ray diffractogram. It is also confirmed by its smooth morphology as observed under the atomic force microscope (Fig. 4A). Transistors of *p*-BTPATPE with varied channel length (50, 100 and 150 μ m) and width (1 and 2 mm) are tested in air under ambient conditions. Results show that *p*-BTPATPE works as a p-type semiconductor, and the thin film deposited on the OTS-treated silicon substrate at 80 $^\circ\text{C}$ gives the best device performance. Fig. 4B shows the transfer I - V curve of *p*-BTPATPE obtained under optimized conditions, from which a field-effect mobility of 2.6×10^{-3} cm^2/Vs is obtained in the saturation regime using the equation: $I_{\text{DS}} = (\mu W C_i / 2L)(V_G - V_T)^2$, where C_i is the specific capacitance (11 nF/ cm^2) for the 300 nm-thick OTS-treated silicon wafer.^{12,13}

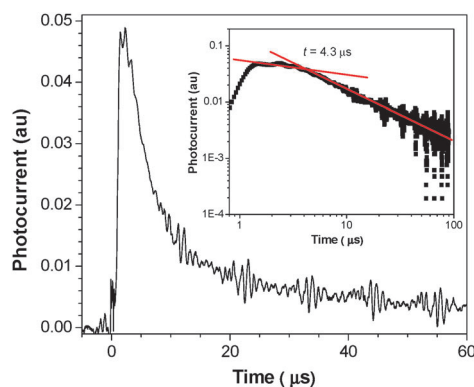


Fig. 3 Transient photocurrent for hole transport in *p*-BTPATPE/PS/ C_{60} composite (50/48.5/1.5 wt%) under an applied electric field of 60 V/ μ m. Inset: logarithmic plot of the photocurrent *versus* time.

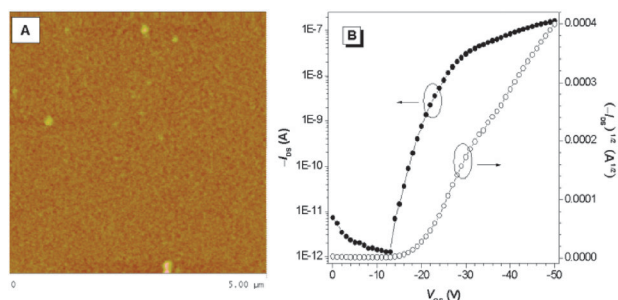


Fig. 4 (A) AFM image of thin film of *p*-BTPATPE deposited on the OTS-treated silicon substrate. (B) Drain current ($-I_{DS}$) and $(-I_{DS})^{1/2}$ versus gate voltage (V_{GS}) at a drain voltage (V_{DS}) of -50 V in a FET device of *p*-BTPATPE with a channel length (L) of $100 \mu\text{m}$ and a channel width (W) of 1 mm .

On/off ratio of the drain current obtained between 0 and -50 V gate bias from the transfer I - V curve is larger than 2×10^4 . The fact that the field effect mobility of *p*-BTPATPE is higher than the hole drift mobility determined through the TOF measurement can be attributed to different films used in the two measurements. The mobility measured from a *p*-BTPATPE-doped PS film in the TOF experiment is affected by many parameters such as the PS matrix and the dopant concentration. It is also limited by the efficiency of charge separation at the interface of *p*-BTPATPE and fullerene. The measured field effect mobility of *p*-BTPATPE is high for amorphous organic semiconductor films,¹⁴ and among the reported values for TPA-based organic semiconductors.^{6,7,15}

In summary, we synthesized an AIE luminogen *p*-BTPATPE by attaching TPA peripheries to a TPE core. Whereas *p*-BTPATPE is weakly emissive in solution, it is induced to emit efficiently in film. *p*-BTPATPE possesses good hole-transporting property, as revealed by its high HOMO energy level (-5.15 eV) and hole mobility ($5.2 \times 10^{-4} \text{ cm}^2/\text{Vs}$) measured by the TOF technique. A p-type FET device utilizing amorphous film of *p*-BTPATPE is fabricated, which shows high field effect mobility up to $2.6 \times 10^{-3} \text{ cm}^2/\text{Vs}$. Combining this with its efficient PL and electroluminescence, *p*-BTPATPE is anticipated to find an array of applications in organic electronics and optics.

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