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ARTICLE

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N,N'-Di-[(1-naphthyl)-*N,N'*-diphenyl]-1,1'-biphenyl-4,4'-diamine (NPB) possesses high thermal and morphological stability and is one of the well-known hole-transporting material for the fabrication of organic light-emitting diodes (OLEDs). Modification of NPB by covalent integration of tetraphenylethene (TPE) into its structure dramatically changes its emission behavior: the resulting adduct (TPE-NPB) is highly emissive in the aggregated state, showing a novel phenomenon of aggregation-induced emission (AIE). The adduct is thermally and morphologically stable. Non-doped multilayer electroluminescence (EL) devices using TPE-NPB as emitting layer was fabricated, which emitted green light with maximum luminance and current efficiency of 11981 cd/m² and 11.9 cd/A. Even better device performances are observed in bilayer device without NPB. Our strategy takes the full advantage of the AIE property in the solid state and retains the inherent properties of conventional luminophores. It opens a new avenue in the development of stable and efficient solid-state fluorescent materials for OLED application.

Introduction

Development of efficient luminescent materials in the solid state is important for various photonic applications such as organic light-emitting diodes (OLEDs)¹ and transistors,² organic lasers,³ and fluorescent sensors or probes.⁴ However, many conventional π -conjugated fluorophores are highly emissive in solutions but become faintly emissive in the condensed phase due to the severe intermolecular interaction,⁵ which promotes the formation of detrimental species such as excimers and exciplexes. An example of such fluorophores is given by perylene, in which its efficient blue emission (fluorescence quantum yield in cyclohexane = 94%) is almost quenched completely in the aggregated state.⁶ Such aggregation-caused quenching effect (ACQ) has limited and complicated their high-technological applications. Because of this, in optical and electronic devices, they are normally utilized as dopants

at low concentration in host materials.⁷ However, to achieve an optimum device performance, careful control on the dopant concentration is required.⁸ Performance degradation due to phase separation upon heating is also a problem.⁹ Thus, emitting layer made of a single component with no ACQ effect is in urgent demand.

On the other hand, to further enhance the device performance, it is desirable to have emitters with both efficient solid-state emission and good charge-transporting properties. These features lead to simpler fabrication procedures, overall improved device stability and a lower production cost compared to the multilayer OLEDs.¹⁰ Arylamines, such as *N,N'*-bis(3-methylphenyl)-*N,N'*-diphenylbenzidine (TPD), are well-known hole-transporting materials. TPD has been frequently utilized in the early OLED study, for its outstanding hole-transporting capability.¹¹ However, TPD suffers from low glass transition temperature ($T_g = 60$ °C), and is found to crystallize at ambient temperature within few hours after

vacuum deposition.^{7a} The low morphological stability of TPD greatly decreases the stability and lifetime of the devices. Structural modification by replacing two out of the four phenyl rings of TPD attached to the nitrogen atoms by naphthalene rings creates *N,N'*-di-[(1-naphthyl)-*N,N'*-diphenyl]-1,1'-biphenyl)-4,4'-diamine (NPB)¹² which retains the high hole mobility of TPD, but exhibits a much enhanced glass transition temperature ($T_g = 98\text{ }^\circ\text{C}$)^{7a} and hence a stable thin-film morphology.¹³ Although NPB possesses the abovementioned inherent advantages, it is not a good emitter in the solid state due to π - π stacking between its molecules.¹⁴ Thus, it would be nice to create new fluorescent molecules that possess the advantage of NPB but overcome its shortcoming as a non-doped emitter.

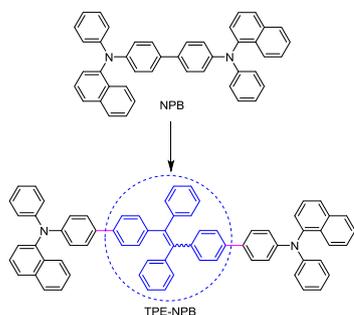


Chart 1 Chemical structures of NPB and TPE-NPB.

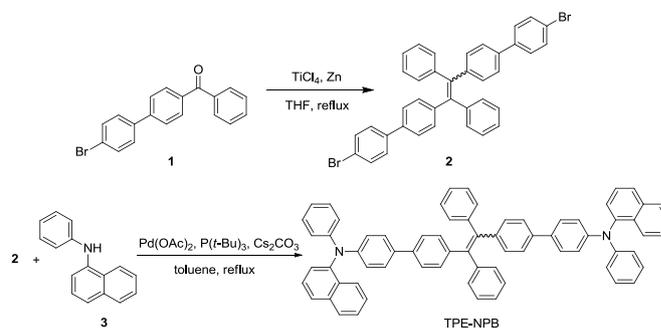
Since 2001, we have developed a novel class of organic luminogens with aggregation-induced emission (AIE) characteristics.¹⁵ These luminogens are non-emissive in dilute solutions but start to luminesce intensely when aggregated. Tetraphenylethene (TPE) is an archetypal AIE luminogen with a simple structure but exhibits a splendid AIE effect.¹⁶ Incorporation of TPE as a spacer into NPB is anticipated to generate a twisted and nonplanar adduct with properties of both components, i.e. AIE and hole-transporting as well as high thermal and morphological stability (Chart 1).

In this paper, we explored such possibility. As anticipated, TPE-NPB is AIE-active and is thermally and morphologically stable. It possesses a non-planar conformation, which effectively hampers π - π stacking and endows it with a high fluorescence quantum yield (Φ_F) of 98%. Efficient OLEDs using TPE-NPB as emitter and hole-transporting layer (HTL) are constructed, which exhibit outstanding performances. The performance of OLED device without NPB as HTL was even better than that of the device with NPB as HTL. These results demonstrate a good example for the creation of stable and efficient luminescent materials for OLED application.

Results and Discussion

TPE-NPB was facilely synthesized according to the synthetic routes shown in Scheme 1. The key intermediate **2** was prepared by McMurry coupling of 4-benzoyl-4'-bromobiphenyl catalyzed by TiCl_4/Zn in reflux tetrahydrofuran (THF). Amination of **2** with *N*-phenyl-1-naphthylamine, a commercially available chemical, was mediated by $\text{Pd}(\text{OAc})_2$ in basic medium, furnishing the desired

product TPE-NPB in satisfactory yield. We have previously prepared a similar compound (2TPATPE) from TPE and triphenylamine but its synthesis involves a more complicated procedure.^{10b} All the intermediates and product were characterized by standard spectroscopic techniques, from which satisfactory analysis data corresponding to their chemical structures were obtained. Details are provided in the Experimental Section and examples of spectra are shown in Fig. S1 and S2 in the Supporting Information. TPE-NPB shows a good solubility in common organic solvents, such as toluene, dichloromethane, chloroform and THF, but is insoluble in water. The absorption spectra of NPB and TPE-NPB in THF are peaked at 339 nm and 340 nm, respectively, indicative of similar conjugation between the two molecules (Table 1).



Scheme 1 Synthetic routes to TPE-NPB.

We first investigated the photoluminescence (PL) of NPB in THF and its mixture with water. The dilute THF solution of NPB emits a blue fluorescence at $\sim 450\text{ nm}$. Addition of water into the THF solution has slightly weakened the light emission and shifted the emission maximum to $\sim 460\text{ nm}$ (Fig. 1). The emission becomes strong again when the water content exceeds 70%, and overall a slight PL enhancement was observed.

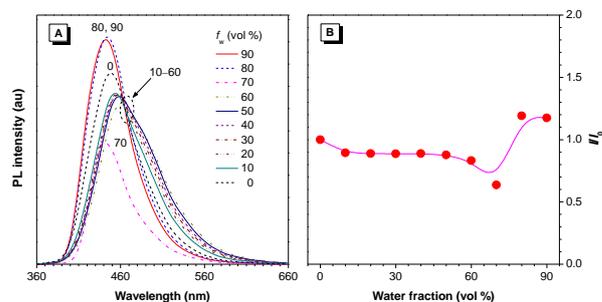


Fig. 1 (A) PL spectra of NPB in THF and water mixtures with different water fractions (f_w). (B) Plot of relative PL intensity (I/I_0) versus the composition of THF/water mixture of NPB. I_0 = emission intensity in pure THF solution. Concentration: 10 μM ; excitation wavelength: 340 nm.

The effect of water addition on the PL property of TPE-NPB in THF is more obvious. As shown in Fig. 2, the PL spectrum of TPE-NPB is basically a flat line parallel to the abscissa in pure THF. The spectral pattern remains unchanged at water content up to 60%. Afterwards, the PL intensity rises swiftly. The higher the water fraction, the stronger is the emission intensity. The emission

intensity reaches its maximum value at 90% water content, which is 96-fold higher than that in pure THF solution. This indicates that the PL of TPE-NPB is enhanced by aggregate formation, or in other words, it is AIE-active. Measurement on its fluorescence quantum yields in the solution and solid states also support the above conclusion. The Φ_F in pure THF is merely 1.1%, while in the solid state, it reaches 98.0%, which is much higher than those of NPB (26.5%) and TPE (49.2%).¹⁷

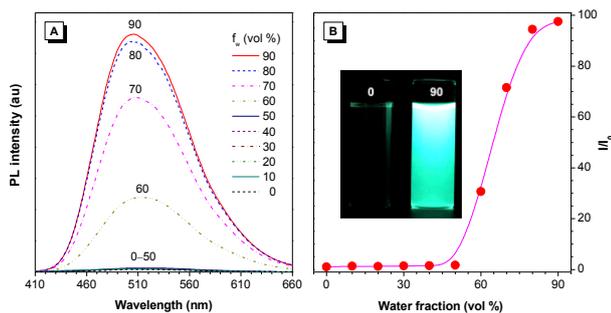


Fig. 2 (A) PL spectra of TPE-NPB in THF and water mixtures with different water fractions (f_w). (B) Plot of relative PL intensity (I/I_0) versus the composition of THF/water mixture of TPE-NPB. I_0 = emission intensity in pure THF solution. Concentration: 10 μ M; excitation wavelength: 340 nm. Inset in (B) are the fluorescent photographs at $f_w = 0$ and 90% taken under 365 nm UV irradiation from a handheld UV lamp.

The thermal properties of TPE-NPB are investigated by TGA and DSC analyses. As shown in Fig. 3, TPE-NPB show a high thermal stability, losing 5% of its weight at 466 $^{\circ}$ C, which is higher than those of NPB (435 $^{\circ}$ C) (Fig. S3) and 2TPATPE at the 1,2-positions (361 $^{\circ}$ C).^{10b}

Table 1 Optical and thermal properties of NPB and TPE-NPB^a

Compound	λ_{ab}/nm	E_g/eV	λ_{em}/nm			$T_d/T_g/^{\circ}\text{C}$
			soln	aggr	film	
NPB	339	3.0	449	443	443	435/98 ^b
TPE-NPB	340	3.02	511	505	506	466/149

^aAbbreviation: λ_{ab} = absorption maximum in THF, E_g = energy band gap calculated from the onset of the absorption spectrum, λ_{em} = emission maximum in THF solution (soln), THF/water mixture (1:9 by volume) (aggr) and solid thin film, T_d = temperature for 5% weight loss, T_g = glass transition temperature. ^bData taken from ref 7a.

DSC analysis of TPE-NPB in the second heating scan detects a glass transition temperature (T_g) at 149 $^{\circ}$ C (Fig. 3), which is higher than those of NPB ($T_g = 98$ $^{\circ}$ C) and 2TPATPE ($T_g = 119$ $^{\circ}$ C).^{10b} No transition peak associated with crystallization was observed when the fluorophore was heated up to 250 $^{\circ}$ C. The bulky non-planar TPE unit in TPE-NPB may hinder close packing between molecules in the solid state, thus making the luminogen non-crystalline in nature. Luminogenic materials with high thermal and morphological stability are beneficial to the stability and lifetime of optoelectronic devices. TPE-NPB possesses such advantages as well as efficient solid-state emission. This makes it promising for the fabrication of efficient EL devices.

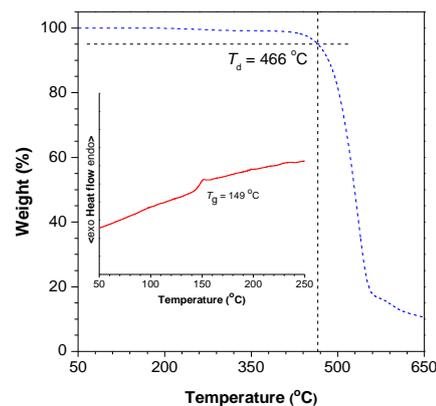


Fig. 3 TGA thermogram of TPE-NPB recorded under nitrogen at a heating rate of 10 $^{\circ}$ C/min. Inset: DSC curve of TPE-NPB recorded during the second heating scan.

The electrochemical property and energy levels of TPE-NPB are investigated by cyclic voltammetry. In our experiment, the working and reference electrodes are glass carbon and Hg/HgCl₂, respectively, with tetra-*n*-butylammonium hexafluorophosphate (0.1 M in dichloromethane) as the supporting electrolyte. Using such set-up, ferrocene ($E_{\text{ferrocene}}$) was found to oxidize at 0.42 V (Fig. S4), while the oxidation onset potential (E_{onset}) of TPE-NPB occurs at 0.77 eV. Applying the equation: $\text{HOMO} = -(E_{\text{onset}} + 4.8 - E_{\text{ferrocene}})$ eV, the HOMO of TPE-NPB is calculated to be -5.15 eV, which is slightly higher than that of NPB (HOMO = -5.3 eV).¹⁸ This suggests that TPE-NPB possesses a good hole-transporting property, presumably due to the fine contribution from the NPB unit. The LUMO of TPE-NPB can be obtained by subtraction of the optical band gap energy (E_g) estimated from the onset absorption wavelength from the HOMO value and is located at -2.15 eV.

To get further insight into the photophysical property of TPE-NPB, density functional theory calculations are carried out using a suite of the Gaussian 03 program. The nonlocal density functional of B3LYP with 6-31G(d) basis sets was used for the calculation. The optimized structures and orbital distributions of HOMO and LUMO energy levels of TPE-NPB are shown in Fig. 4. TPE-NPB adopts a propeller-like conformation. The torsion angle between the central plane of the TPE core and the adjacent phenyl rings is $\sim 34^{\circ}$. The dihedral angles between any phenyl ring and the vinyl core of the TPE unit are $\sim 50^{\circ}$ (Tables S1). The dihedral angles between any two aryl rings of arylamine substituents in TPE-NPB range from $\sim 63^{\circ}$ to $\sim 83^{\circ}$ (Table S1). The non-planar conformation of TPE-NPB should prevent close molecular packing in the solid state, leading to efficient fluorescence in the condensed phase. The LUMO of TPE-NPB is dominated by the orbitals from the TPE core. In contrast, the electron cloud of the HOMO is located mainly on the arylamino functionalities and partly on the TPE core. Such orbital distributions reveal an intrinsic intramolecular charge transfer property of the dye molecule.

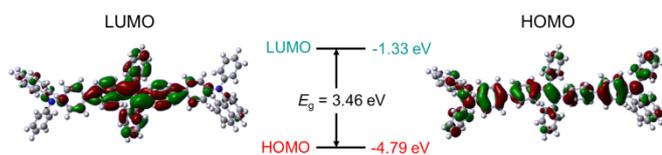


Fig. 4 Optimized geometries and molecular orbital amplitude plots of HOMO and LUMO levels of TPE-NPB calculated using the B3LYP/6-31G(d) basis set.

The efficient solid emission and good thermal and morphological stability of TPE-NPB prompt us to study its EL property. We first fabricated a single-layer EL device with a configuration of ITO/TPE-NPB(100 nm)/LiF/Al(100 nm). The device emits at 516 nm, exhibiting maximum current density of 1072 mA/cm² and maximum luminance (L_{\max}) of 588 cd/m² (Fig. S5). This demonstrates that TPE-NPB possesses a good charge transporting property, even though these results are preliminary. To improve the device performance, we fabricated a multilayer EL device with a configuration of ITO/NPB(40 nm)/TPE-NPB(20 nm)/TPBi(40 nm)/LiF(1 nm)/Al(100 nm) (Device I), where NPB functions as hole-transporting layer (HTL) and 2,2',2''-(1,3,5-benzinetriyl)tris(1-phenyl-1-*H*-benzimidazole) (TPBi) serves as both electron-transporting and hole-blocking material. Device I emits at 512 nm, which is slightly red-shifted from the PL peak of TPE-NPB film (506 nm) but far from the EL peak of NPB (440 nm)¹⁹ and TPBi (400 nm).^{9c} This confirms that the EL is indeed from the emitting layer. The device turns on at a low bias of 3.7 V, emitting brilliantly with maximum luminance (L_{\max}) of 11981 cd/m² and maximum current efficiency ($\eta_{C,\max}$), power efficiency ($\eta_{P,\max}$) and external quantum efficiency ($\eta_{\text{ext,max}}$) of 11.9 cd/A, 8.9 lm/W and 4.0%, respectively (Fig. 5). Such high EL performance is impressive and outperforms the result reported previously.²⁰

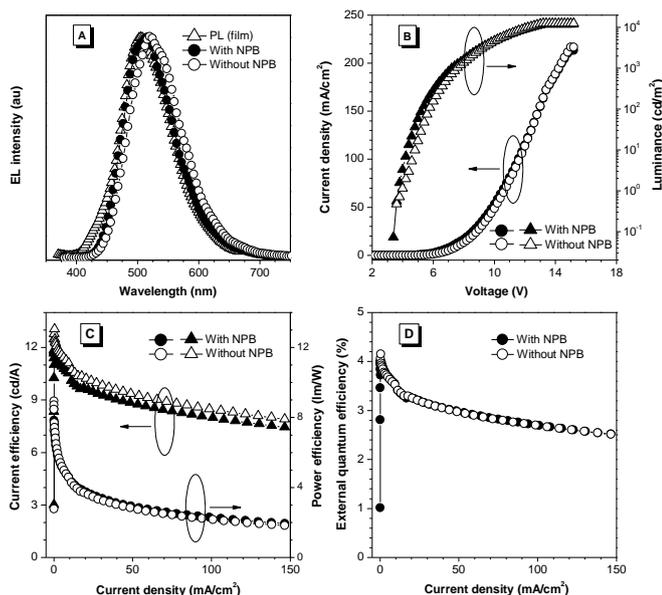


Fig. 5 (A) PL and EL spectra of solid thin film of TPE-NPB. (B) Current efficiency–current density–luminance characteristics of a multilayer EL device of TPE-NPB. Changes in (C) power and current and (D) external quantum efficiencies with the applied current density in a multilayer EL device of TPE-NPB. Device configuration: ITO/(NPB)/TPE-NPB/TPBi/LiF/Al.

Since TPE-NPB possesses hole-transporting arylamino moieties, the application of NPB as an additional HTL may not be necessary or can even be harmful because it may break the charge balance in the EL device. From the energy level diagram shown in Fig. 6, it is possible to further enhance the device performance by removing the NPB layer because it will lower the energy gap between the ITO and the HTL or the emitter from 0.6 eV to 0.45 eV. This decreases the charge injection barrier and is beneficial for hole-transportation. To verify this, Device II containing no NPB as additional HTL was fabricated, which turned on at 3.9 V and emitted more intensely with L_{\max} of 12607 cd/m². The $\eta_{C,\max}$, $\eta_{P,\max}$ and $\eta_{\text{ext,max}}$ reach 13.1 cd/A, 7.8 lm/W and 4.2%, respectively, which are even higher than those of Device I (Table 2). It is noteworthy that the profiles of the EL curves in Device I and II are smooth, which are indicative of their high stability. The above results show that TPE-NPB displays excellent hole transportation and efficient emission in this simplified EL device. Thus, the synthetic procedure adopted in the present work is a win-win strategy, which makes full use of the intrinsic advantages of both TPE and NPB to create AIE luminogens with more efficient solid-state emission, good hole-transporting property and prominent thermal and morphological stability.

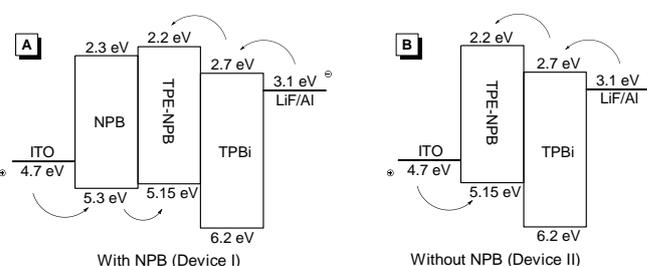


Fig. 6 Energy level diagrams and device configurations of (A) Device I and (B) Device II. Abbreviation: NPB = *N,N'*-Di-[[1-naphthyl)-*N,N'*-diphenyl]-1,1'-biphenyl-4,4'-diamine, TPBi = 2,2',2''-(1,3,5-benzinetriyl)tris(1-phenyl-1-*H* benzimidazole).

Table 2 EL performances of TPE-NPB^a

Device	NPB	λ_{EL} /nm	V_{on} /V	L_{\max} /cd m ⁻²	$\eta_{C,\max}$ /cd A ⁻¹	$\eta_{P,\max}$ /lm W ⁻¹	$\eta_{\text{ext,max}}$ /%
I	✓	512	3.7	11981	11.9	8.9	4.0
II	×	516	3.9	12607	13.1	7.8	4.2

^aDevice configuration: ITO/NPB(40 nm)/TPE-NPB(20 nm)/TPBi(40 nm)/LiF(1 nm)/Al(100 nm) (Device I); ITO/TPE-NPB(60 nm)/TPBi(40 nm)/LiF(1 nm)/Al(100 nm) (Device II). Abbreviation: λ_{EL} = EL maximum, V_{on} = turn-on voltage at 1 cd m⁻², L_{\max} = maximum luminance, $\eta_{P,\max}$ = maximum power efficiency, $\eta_{C,\max}$ = maximum current efficiency and $\eta_{\text{ext,max}}$ = maximum external quantum efficiency.

Conclusions

In this paper, TPE-NPB was synthesized and its optical properties were investigated. The dye molecule shows a typical AIE characteristic and improved quantum yields than its parent NPB and TPE molecules. It enjoys high thermal and morphological stability. Non-doped multilayer EL devices are constructed, which show outstanding performances. The bilayer device without NPB as HTL exhibits even better performances than the one with NPB as HTL. These results demonstrate that covalent integration of AIE unit into conventional chromophores is a good strategy to generate efficient solid-state

emitters with novel functional properties. Such method takes the full advantage of AIE property in the solid state and retains other functional properties of the chromophores. Through such strategy, it is expected that new AIE luminogens with new and/or enhanced functional properties will be created.

Experimental

Materials. THF was distilled from sodium benzophenone ketyl under dry nitrogen immediately prior to use. NPB was purchased from Luminescence Technology Crop. Other chemicals and reagents were purchased from Aldrich and used as received without further purification.

Instruments. ^1H and ^{13}C NMR spectra were measured on a Bruker AV 300 spectrometer in CDCl_3 using tetramethylsilane (TMS; $\delta = 0$) as internal reference. High resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 mass spectrometer operating in MALDI-TOF mode. Elemental analysis was performed on a ThermoFinnigan Flash EA1112. UV spectra were measured on a Milton Roy 5 Spectronic 3000 Array spectrophotometer. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. The solution fluorescence quantum yields (Φ_{F}) were determined by using 9,10-diphenylanthracene ($\Phi_{\text{F}} = 90\%$ in cyclohexane) as standard. The absorbance of the solutions was kept below 0.1 to avoid the internal filter effect. The Φ_{F} values of solid thin films were measured by using a calibrated integrating sphere. The thermal properties of TPE-NPB and NPB were evaluated on TA Instruments TGA Q5000 and DSC Q1000 under nitrogen at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$.

Preparation of nanoaggregates. Stock THF solutions of the compounds with a concentration of 10^{-4} M were prepared. Aliquots of the stock solution were transferred to 10 mL volumetric flasks. After appropriate amounts of THF were added, water was added dropwise under vigorous stirring to furnish 10^{-5} M solutions with different water contents (0–90 vol %). The PL measurements of the resulting solutions were then performed immediately.

Synthesis of 2. 4-Benzoyl-4'-bromobiphenyl (4.2 g, 12.5 mmol), Zn dust (3.5 g, 54 mmol) and THF (125 mL) were added to a 250 mL two-necked round bottom flask under nitrogen. The solution was cooled to $-78\text{ }^\circ\text{C}$, into which TiCl_4 (4.75 g, 25 mmol) was added. After reflux for 36 h, the reaction mixture was cooled to room temperature and concentrated by vacuum. Chloroform (300 mL) was added to dissolve the product and the mixture was filtered under vacuum suction. The filtrate was concentrated and the crude product was purified on a silica gel column using petroleum ether/chloroform as eluent. A white solid was obtained in 90% yield (3.6 g). ^1H NMR (300 MHz, CDCl_3), δ (TMS, ppm): 7.52–7.49 (m, 4H), 7.42–7.39 (m, 4H), 7.36–7.29 (m, 4H), 7.14–7.04 (m, 14H). HRMS (MALDI-TOF): m/z 642.0381 (M^+ , calcd 642.0381).

Synthesis of TPE-NPB. Under nitrogen, a mixture of **2** (706 mg, 1.1 mmol), *N*-phenyl-1-naphthylamine (569.4 mg, 2.6 mmol), Cs_2CO_3

(2.28 g, 7 mmol), $\text{Pd}(\text{OAc})_2$ (11.2 mg, 0.05 mmol), tri-*tert*-butylphosphine (30.3 mg, 0.15 mmol) and toluene (40 mL) was heated at $40\text{ }^\circ\text{C}$ for 2 h. The reaction mixture was then heated at $110\text{ }^\circ\text{C}$ for 24 h. After the mixture was cooled to room temperature, water (30 mL) and chloroform (200 mL) were added. The organic layer was separated, washed with brine, dried over anhydrous MgSO_4 and evaporated to dryness under reduced pressure. The crude product was purified by silica gel column chromatography using hexane/chloroform mixture as eluent, affording a pale yellow solid in 61% yield (620 mg). ^1H NMR (300 MHz, CDCl_3), δ (TMS, ppm): 7.92 (d, $J = 8.5\text{ Hz}$, 2H), 7.88 (d, $J = 8.1\text{ Hz}$, 2H), 7.76 (d, $J = 8.2\text{ Hz}$, 2H), 7.49–7.42 (m, 4H), 7.39–7.27 (m, 12H), 7.22–7.17 (m, 4H), 7.10–7.00 (m, 22H), 6.93 (t, $J = 7.3\text{ Hz}$, 2H). ^{13}C NMR (75 MHz, CDCl_3), δ (TMS, ppm): 148.23, 147.67, 143.84, 143.37, 142.18, 140.56, 138.30, 135.26, 133.50, 131.76, 131.43, 131.18, 129.10, 128.38, 127.72, 127.61, 127.33, 127.19, 126.49, 126.40, 126.33, 126.13, 125.58, 125.48, 124.23, 122.10, 121.86, 121.69, 121.67. HRMS (MALDI-TOF): m/z 918.3826 (M^+ , calcd 918.3974). Anal. Calcd For $\text{C}_{70}\text{H}_{50}\text{N}_2$: C, 91.47; H, 5.48; N, 3.05. Found: C, 91.21; H, 5.66; N, 3.01.

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Notes and references

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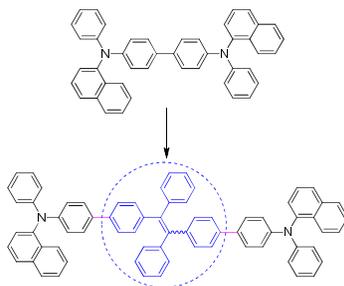
- (a) P. Schouwink, A. H. Schafer, C. Seidel, H. Fuchs, *Thin Solid Films*, 2000, **372**, 163; (b) T. W. Kwon, M. M. Alam, S. A. Jenekhe, *Chem. Mater.*, 2004, **16**, 4657.

- 2 (a) F. Cicoira, C. Santato, *Adv. Funct. Mater.*, 2007, **17**, 3421; (b) J. Zaumseil, H. Sirringhaus, *Chem. Rev.*, 2007, **107**, 1296.
- 3 (a) M. D. McGehee, A. J. Heeger, *Adv. Mater.*, 2000, **12**, 1655; (b) I. D. W. Samuel, G. A. Turnbull, *Chem. Rev.*, 2007, **107**, 1272.
- 4 (a) S. W. Thomas, G. D. Joly, T. M. Swager, *Chem. Rev.*, 2007, **107**, 1339; (b) L. Basabe-Desmonts, D. N. Reinhoudt, M. Crego-Calama, *Chem. Soc. Rev.*, 2007, **36**, 993; (c) M. S. Meaney, V. L. McGuffin, *Anal. Bioanal. Chem.*, 2008, **391**, 2557; (d) Y. Liu, K. R. Wang, D. S. Guo, B. P. Jiang, *Adv. Funct. Mater.*, 2009, **19**, 2230; (e) W. C. Wu, C. Y. Chen, Y. Q. Tian, S. H. Jang, Y. N. Hong, Y. Liu, R. R. Hu, B. Z. Tang, Y. T. Lee, C. T. Chen, W. C. Chen, A. K. Y. Jen, *Adv. Funct. Mater.*, 2010, **20**, 1413; (f) W. Qin, D. Ding, J. Z. Liu, W. Z. Yuan, Y. Hu, B. Liu, B. Z. Tang, *Adv. Funct. Mater.*, 2012, **22**, 771.
- 5 (a) S. A. Jenekhe, J. A. Osaheni, *Science*, 1994, **265**, 765; (b) R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Logdlund, W. R. Salaneck, *Nature*, 1999, **397**, 121; (c) M. Shimizu, T. Hiyama, *Chem. Asian J.*, 2010, **5**, 1516.
- 6 J. B. Birks, *Photophysics of Aromatic Molecules*. Wiley-Interscience, London, 1970.
- 7 (a) C. H. Chen, J. Shi, C. W. Tang, *Macromol. Symp.*, 1998, **125**, 1; (b) W. C. Wu, H. C. Yeh, L. H. Chan, C. T. Chen, *Adv. Mater.*, 2002, **14**, 1072.
- 8 H. C. Yeh, S. J. Yeh, C. T. Chen, *Chem. Commun.*, 2003, 2632.
- 9 (a) S. C. Chang, G. He, F. C. Chen, T. F. Guo, Y. Yang, *Appl. Phys. Lett.*, 2001, **79**, 2088; (b) G. Y. Zhong, Z. Xu, J. He, S. T. Zhang, Y. Q. Zhan, X. J. Wang, Z. H. Xiong, H. Z. Shi, X. M. Ding, W. Huang, X. Y. Hou, *Appl. Phys. Lett.*, 2002, **81**, 1122; (c) J. R. Gong, L. J. Wan, S. B. Lei, C. L. Bai, X. H. Zhang, S. T. Lee, *J. Phys. Chem. B*, 2005, **109**, 1675.
- 10 (a) S. L. Tao, L. Li, J. S. Yu, Y. D. Jiang, Y. C. Zhou, C. S. Lee, S. T. Lee, X. H. Zhang, O. Y. Kwon, *Chem. Mater.*, 2009, **21**, 1284; (b) Y. Liu, S. M. Chen, J. W. Y. Lam, P. Lu, R. T. K. Kwok, F. Mahtab, H. S. Kwok, B. Z. Tang, *Chem. Mater.*, 2011, **23**, 2536.
- 11 (a) M. Stolka, J. F. Yanus and D. M. Pai, *J. Phys. Chem.*, 1984, **88**, 4707; (b) Y. Hamada, T. Sano, M. Fujita, T. Fujii, Y. Nishio and K. Shibata, *Jpn. J. Appl. Phys.*, 2, 1993, **32**, 514; (c) Y. Shirota, Y. Kuwabara, D. Okuda, R. Okuda, H. Ogawa, H. Inada, T. Wakimoto, H. Nakada, Y. Yonemoto, S. Kawami and K. Imai, *J. Lumin.*, 1997, **72–74**, 985.
- 12 S. A. VanSlyke, C. H. Chen, C. W. Tang, *Appl. Phys. Lett.*, 1996, **69**, 2160.
- 13 K. L. Tong, S. K. So, H. F. Ng, L. M. Leung, M. Y. Yeung, C. F. Lo, *Synthetic Met.*, 2004, **147**, 199.
- 14 J. A. Cheng, P. J. Cheng, *J. Chem. Crystallogr.*, 2010, **40**, 557.
- 15 J. D. Luo, Z. L. Xie, J. W. Y. Lam, L. Cheng, H. Y. Chen, C. F. Qiu, H. S. Kwok, X. W. Zhan, Y. Q. Liu, D. B. Zhu, B. Z. Tang, *Chem. Commun.*, 2001, 1740.
- 16 (a) Y. N. Hong, J. W. Y. Lam, B. Z. Tang, *Chem. Commun.*, 2009, 4332; (b) Y. N. Hong, J. W. Y. Lam, B. Z. Tang, *Chem. Soc. Rev.*, 2011, **40**, 5361.
- 17 Z. J. Zhao, S. M. Chen, J. W. Y. Lam, C. K. W. Jim, C. Y. K. Chan, Z. M. Wang, P. Lu, C. M. Deng, H. S. Kwok, Y. G. Ma, B. Z. Tang, *J. Phys. Chem. C*, 2010, **114**, 7963.
- 18 Z. J. Zhao, S. M. Chen, C. M. Deng, J. W. Y. Lam, C. Y. K. Chan, P. Lu, Z. M. Wang, B. B. Hu, X. P. Chen, P. Lu, H. S. Kwok, Y. G. Ma, H. Y. Qiu, B. Z. Tang, *J. Mater. Chem.*, 2011, **21**, 10949.
- 19 W. F. Xie, Y. Zhao, C. A. Li, S. Y. Liu, *Semicond. Sci. Tech.*, 2005, **20**, 57.
- 20 A. Saitoh, N. Yamada, M. Yashima, K. Okinaka, A. Senoo, K. Ueno, D. Tanaka, R. Yashiro, *SID Int. Symp. Dig. Tech. Pap.*, 2004, **35**, 150.

Crafting NPB with tetraphenylethene: a win-win strategy to create stable and efficient solid-state emitter with aggregation-induced emission feature, high hole-transporting property and efficient electroluminescence

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A win-win strategy to create efficient solid-state emitters for OLED application is proposed.