PAPER

Using tetraphenylethene and carbazole to create efficient luminophores with aggregation-induced emission, high thermal stability, and good hole-transporting property†‡

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Tetraphenylethene (TPE) is an archetypal luminogen that exhibits a phenomenon of aggregation-induced emission (AIE), while carbazole is a conventional chromophore which shows the opposite effect of aggregation-caused quenching (ACQ) of light emission in the condensed phase. Melding the two units at the molecular level generates a group of new luminescent materials that suffer no ACQ effect but depict high solid-state fluorescence quantum yields up to unity, demonstrative of the uniqueness of the approach to solve the ACQ problem of traditional luminophores. All the TPE–carbazole adducts are thermally and morphologically stable, showing high glass-transition temperatures (up to 179 °C) and thermal-degradation temperatures (up to 554 °C). Multilayer electroluminescence devices with configurations of ITO/NPB/emitter/TPBi/Alq$_3$/LiF/Al are constructed, which exhibit sky blue light in high luminance (up to 13 650 cd m^{-2}) and high current and external quantum efficiencies (up to 3.8 cd A^{-1}, and 1.8%, respectively). The devices of the luminogens fabricated in the absence of NPB or hole-transporting layer show even higher efficiencies up to 6.3 cd A^{-1} and 2.3%, thanks to the good hole-transporting property of the carbazole unit.

Introduction

Great efforts have been made to develop efficient solid-state emitters for their potential applications in the fabrication of practically useful optoelectronic devices such as organic light-emitting diodes (OLEDs). A thorny obstacle to the development of OLEDs is the aggregation-caused quenching (ACQ) effect: the efficient luminescence processes of many conventional luminophores in dilute solutions are often weakened or even totally exterminated when their molecules aggregate due to the formation of detrimental species such as excimers and exciplexes in the condensed phase.[1] Various chemical, physical, and engineering approaches have been proposed to hamper the formation of luminogenic aggregates and mitigate the ACQ effect. However, in most cases, these processes have met with only limited success because they are basically working against a natural process as aggregate formation is an intrinsic process when luminogenic molecules are located in close vicinity in the solid state.[2]

In 2001, we observed a phenomenon of aggregation-induced emission (AIE)[3,4] that is exactly opposite to the ACQ effect. Unlike conventional luminophores, the AIE luminogens are almost non-fluorescent when molecularly dissolved in good solvents but emit intensely when aggregated as nanoparticles in poor solvents or fabricated as thin films in the solid state. Among the AIE luminogens, tetraphenylethene (TPE) is an archetypal luminophore with a simple molecular structure but possesses outstanding AIE effect.[5] Through a series of designed experiments and theoretical calculations, the AIE effect of TPE is identified to be caused by the restriction of intramolecular rotation (IMR). In the solution state, the rotation of the multiple phenyl rings of TPE has consumed the excited state energy through the nonradiative process. In the aggregate state, the IMR process is restricted, which blocks the nonradiative relaxation channel and hence makes the molecule highly emissive.[6,7] Recent research shows that TPE is a very interesting and useful molecule, and its derivatives have been extensively investigated and explored their high-tech applications in biological[8,9] and

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environmental sciences.[10] Recently, a new structural design strategy to solve the ACQ problem of traditional luminophores without causing any side effects is developed.[11] By decorating the ACQ chromophores with AIE units, new luminogens with AIE characteristics are generated. An example of such molecules is represented by 9-[4-(1,2,2-triphenylvinyl)phenyl]carbazole (TPECa, Chart 1), which is non-emissive in the solution state but exhibits the fluorescence quantum yield of unity in the aggregate state.[6d] To further verify the applicability of such strategy and explore more efficient solid-state emitters, in this work, we prepared counterparts of TPECa by attaching the TPE unit to carbazole at different positions. We have chosen carbazole as the ACQ component because of its high thermal stability and good hole-transporting property. Thus, adducts containing such chromophores are anticipated to show good thermal stability and bifunctional property. In this paper, we present their synthesis as well as their materials properties.

Results and discussion

Synthesis

We designed the molecular structures of a group of TPE–carbazole adducts and elaborated multi-step reaction routes for their synthesis (Scheme 1). Intermediates 1–4,[12] 6,[10c] and 7[11a] were prepared according to the literature methods. Suzuki coupling reactions of 7 with 1, 4, and 2 catalyzed by Pd(PPh₃)₄ in basic medium gave the target products TPECaP, BTPECaP, and TTPECaP, respectively, in ~54 to 71% yields. The procedures for their synthesis are described in detail in the Experimental section. The structure and purity of the products were characterized by standard spectroscopic methods and elemental analysis with satisfactory results. Single crystals of TPECaP were grown from its methanol/dichloromethane mixture and analyzed by X-ray diffraction crystallography. All the products dissolve readily in common organic solvents, such as THF, toluene, chloroform, and dichloromethane, but are insoluble in methanol and water.
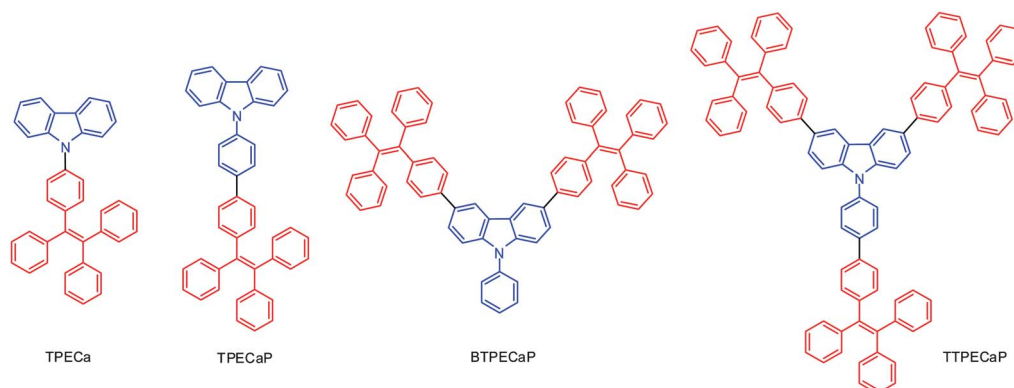
Optical properties

Fig. 1A shows the absorption spectra of the TPE–carbazole adducts in THF solutions. All the luminogens exhibit absorption maxima at ~342 nm, associated with the π–π* transitions of the molecules, indicating that they possess similar effective
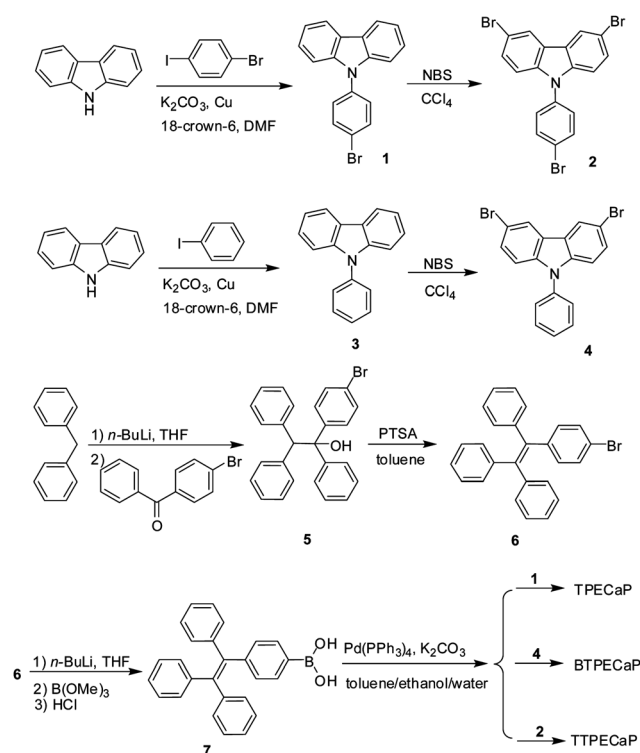

Scheme 1 Synthetic routes to the TPE–carbazole adducts.

conjugation length. The molar absorptivities become higher with the increase of the TPE units. The photoluminescence (PL) spectra of the new luminogens in dilute THF solutions exhibit only noisy signals without discernible peaks. The fluorescence quantum yields (Φ_F) of TPECaP, BTPECaP, and TTPECaP estimated using 9,10-diphenylanthracene are merely 0.068, 0.263, and 0.095% (Table 1), indicating that they are genuinely weak emitters when molecularly dissolved in good solvents. Such values are close to that of TPECa (0.045%) but are much lower than those of carbazole (37%)[13] and carbazole-based chromophores,[14] suggesting that the TPE unit in TPECaP, BTPECaP, and TTPECaP works as a PL quencher in the solution state.[11]

Whereas the TPE–carbazole adducts are almost non-fluorescent in solutions, they become strong emitters in the aggregate state. Fig. 1B shows their PL spectra in the solid film state. When their thin films are photoexcited, intense PL emissions at

Chart 1 Molecular structures of the TPE–carbazole adducts.
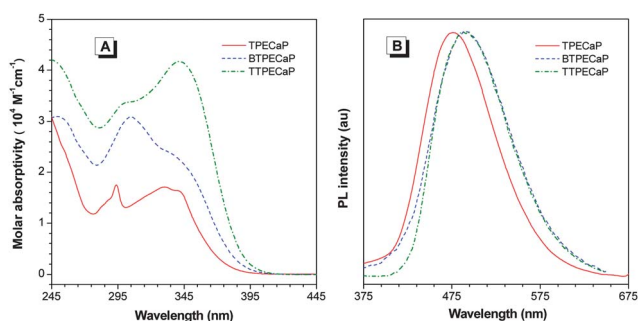
Fig. 1 (A) Absorption and (B) PL spectra of the TPE–carbazole adducts (A) in THF solutions (10 μM) and (B) in thin films.
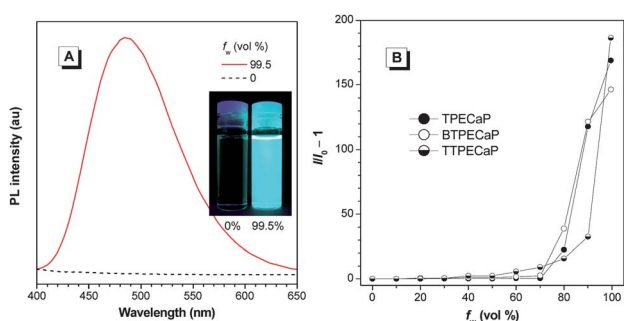
Table 1 Optical and thermal properties of the TPE–carbazole adducts[a]

	λ_{abs}/nm	λ_{em}/nm		Φ_F/%		T_g/T_d
	Soln	Cryst	Film	Soln	Film	°C
TPECa[b]	340	440	468	0.045	100	nd/315
TPECaP	342	455	476	0.068	100	112/402
BTPECaP	341	nd	490	0.263	100	147/479
TTPECaP	342	nd	491	0.095	100	179/554

[a] Abbreviation: λ_{abs} = absorption maximum, λ_{em} = emission maximum, Soln = solution (10 μM in THF), Cryst = crystals, Film = drop-casted film, Φ_F = fluorescence quantum yield in THF solution estimated using 9,10-diphenylanthracene (Φ_F = 90% in cyclohexane) as standard, and that in solid film measured by integrating sphere, T_g = glass-transition temperature, T_d = onset decomposition temperature, nd = not determined. [b] Data taken from ref. 6d for comparison.

476–491 nm are observed. The associated Φ_F values of solid films measured by integrating sphere reach 100%, revealing that these molecules are AIE-active.

To further confirm the AIE characteristics of the new luminogens, we added water, a non-solvent for the luminogens, into their THF solutions and studied the PL change. The PL spectra of TTPECaP in THF/water mixtures with 0 and 99.5% water fractions (f_w) are given in Fig. 2A as an example. The PL intensity remains almost unchanged at low f_w values but starts to

increase afterwards. The emission intensity reaches its maximum at a f_w value of 99.5%. Similar phenomena are also observed in TPECaP and BTPECaP (Fig. 2B). Clearly, the emissions of the TPE–carbazole adducts are induced by aggregate formation, thus truly verifying their AIE characteristics. In dilute solution, the rotation of the multiple phenyl peripheries against the olefin double bond of the TPE unit of the molecules has quenched the light emission of the carbazole core. In the aggregate state, the IMR process is restricted, thus allowing the molecules to emit intensely. Clearly, the attachment of AIE unit to ACQ dye has created a series of new AIE luminogens with efficient PL in the solid state.

Crystal structure

In order to have a better understanding of the photophysical properties of the present luminogens, we investigated the packing arrangements of the TPE–carbazole adducts in the crystal state. However, only crystals of TPECaP can be grown from its methanol/dichloromethane mixture. Fig. 3 shows the ORTEP drawing of TPECaP and its representative repeatable units. The phenyl plane next to the carbazole ring is highly twisted. The TPECaP molecules are stacked in a head to head fashion, where the carbazole and TPE units pile up separately at different sides. Such kind of stacking pattern is somewhat similar to that of H-aggregate[4a,15] but strictly it is not the case as the two adjacent carbazole units lay in an almost mutually perpendicular direction. C–H⋯π hydrogen bond with a distance of 2.989 Å is formed between the carbazole hydrogen atom in one molecule and the π-electron cloud of the central core of the carbazole ring
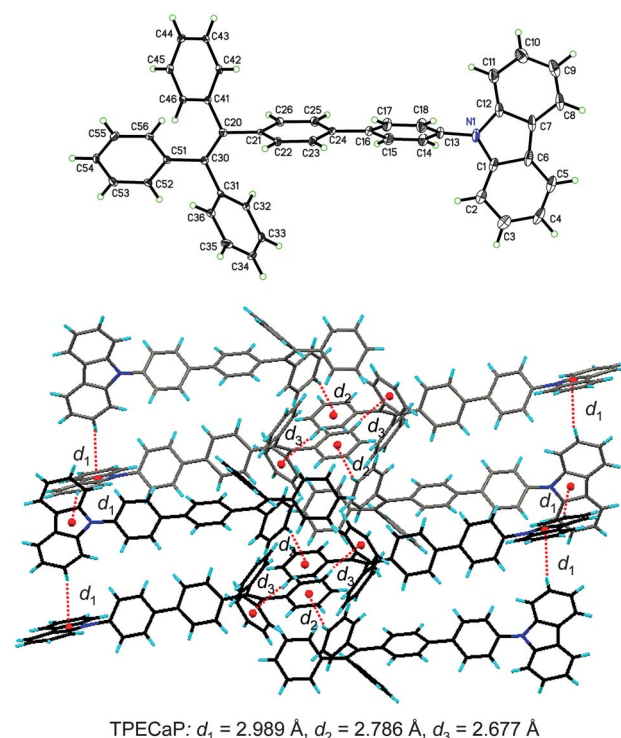

Fig. 2 (A) PL spectra of TTPECaP in THF/water mixtures with 0 and 99.5% water fractions (f_w). (B) Plots of ($I/I_0 - 1$) values *versus* water fractions in THF/water mixtures of TPECaP, BTPECaP, and TTPECaP. I_0 was the PL intensity in pure THF solution. The inset in panel A: photos of TTPECaP in THF/water mixtures ($f_w = 0$ and 99.5%) taken under the illumination of a UV lamp.

TPECaP: d_1 = 2.989 Å, d_2 = 2.786 Å, d_3 = 2.677 Å

Fig. 3 ORTEP drawing of TPECaP and molecular packing and C–H⋯π hydrogen bonds formed between the adjacent molecules of TPECaP in the crystal state. The solvent molecules are omitted for clarity.

in the adjacent molecule. Meanwhile, multiple C–H⋯π hydrogen bonds with distances of 2.786 and 2.677 Å are also formed between the TPE units of adjacent TPECaP molecules. All these collective effects help rigidify the molecular conformation and have locked the molecular rotation. The excited state energy consumed by the IMR process is thus greatly reduced, enabling TPECaP to emit intensely in the solid state. The crystal of TPECaP emits a strong blue light at 453 nm, which is 21 nm blue-shifted from that of its thin film. Similar phenomena have been observed in TPECa and other TPE derivatives[5,6d,11a] and is presumably caused by conformational adjustment of their molecules by twisting their aromatic rings to fit into the crystalline lattices. Since there is no such constraint in the amorphous films, the TPECaP molecules may have adopted a more planar conformation and arranged randomly, thus leading to red-shift in the PL spectrum.

Theoretical calculation

To have a deep insight on the optical behaviors of the TPE–carbazole adducts, the geometrical and electronic properties of TPECaP, BTPECaP, and TTPECaP are studied by density functional theory using B3LYP hybrid functional theory with a 6-31G(d) basis set. Their optimized structures and HOMO and LUMO orbital distributions are given in Fig. 4. The TPE units are twisted from the plane of the carbazole core in all the molecules, which prevents emission quenching caused by π–π stacking interaction. Whereas the HOMOs of all the luminogens are dominated by the orbitals from the carbazole core and part of the TPE unit, the orbitals of the LUMOs are located mainly on the TPE unit. The carbazole cores in TPECaP and TTPECaP show almost no contribution to the LUMOs. We infer that the IMR process of the TPE unit can effectively consume the excited

state energy, resulting in non-emissive nature of the luminogens in the solution state. Other AIE-active TPE derivatives also show similar electronic structures. In our previous work, we found that when TPE units were attached as substituents to some electron-withdrawing chromophores such as benzo-2,1,3-thiadiazole, the generated luminogens exhibit reasonably high Φ_F values in the solution state.[16] For example, 4,7-bis[4-(1,2,2-triphenylvinyl) phenyl]benzo-2,1,3-thiadiazole (BTPETD) shows a Φ_F value of 61% in dilute solution. Theoretical calculation shows that the orbitals of the LUMO of BTPETD are densely populated in the benzo-2,1,3-thiadiazole core. In this case, the IMR process of the TPE unit may have thus little influence on the relaxation process of the excited state. As a result, whether the light emission of a TPE-substituted ACQ chromophore in solution will be quenched by the IMR process of its TPE unit should relate closely to the electron cloud distribution in the LUMO and the electronic structure of the ACQ component. Systematic investigation on the validity of this hypothesis through theoretical calculations and photophysical property measurements of a vast variety of TPE derivatives is in progress in our labs.

Thermal stability

To investigate the thermal properties of the TPE–carbazole adducts, differential scanning calorimetry (DSC) measurement and thermogravimetric analysis (TGA) were carried out. As shown in Fig. 5, TPECaP, BTPECaP, and TTPECaP are thermally stable and show high onset degradation temperatures (T_d) ranging from 402 to 554 °C (Table 1). They also possess good morphological stability, as suggested by their high glass-transition temperatures (T_g) of 112, 147, and 179 °C, respectively. The T_g and T_d values well correlate with the number of TPE units in the molecular structure, which is understandable as the TPE unit
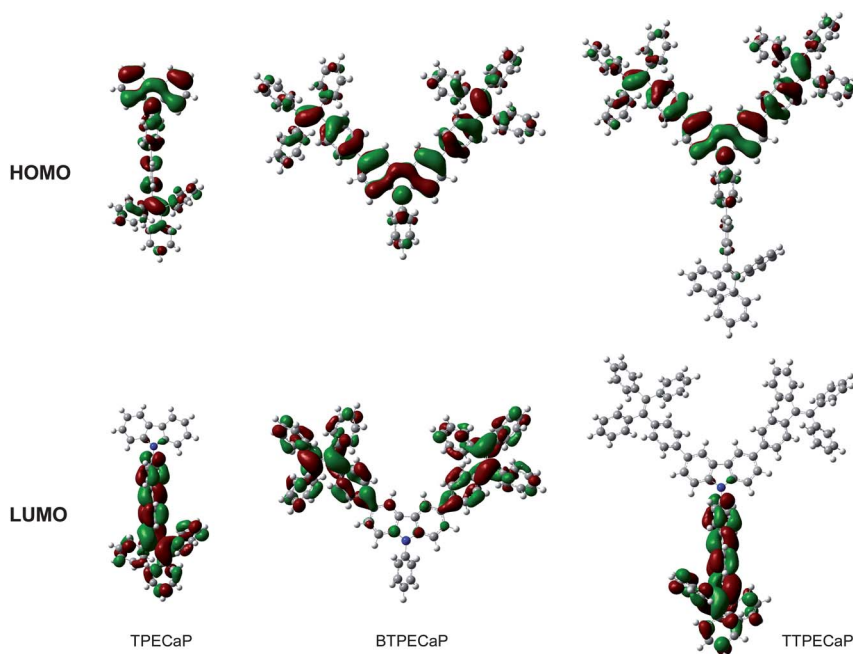
Fig. 4 Optimized molecular structures and molecular orbital amplitude plots of HOMOs and LUMOs of the TPE–carbazole adducts calculated using the B3LYP/6-31G(d) basis set.
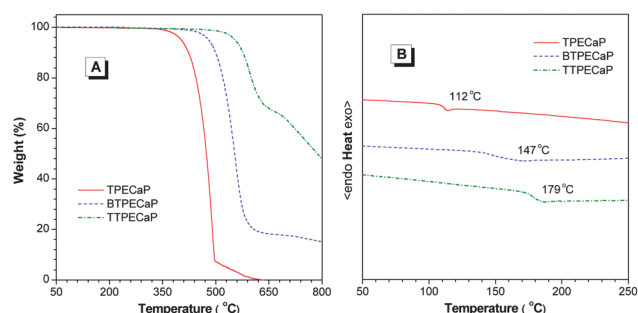
Fig. 5 (A) TGA thermograms and (B) DSC curves (second heating scan) of the TPE–carbazole adducts recorded under nitrogen at a heating rate of 10 °C min⁻¹.

is mainly constructed from aromatic rings. Generally, lumino-genic materials constructed from carbazole show higher T_gs and T_ds than those fabricated from triphenylamine.[17] For example, the T_g and T_d of 3TPETPA, an AIE luminogen with triphenyl-amine core decorated with three TPE units, are 143 and 359 °C, respectively,[11b] which are much lower than those of TTPECaP (179 and 554 °C, respectively). The good thermal and morpho-logical stabilities of these luminogens are advantageous for the construction of stable and durable optoelectronic devices.

Electroluminescence

While we have studied the AIE property of TPECa in our previous paper, its application in OLEDs has yet to be explored. We thus investigated the electroluminescence (EL) of TPECa as well as the new luminogens by fabrication of multilayer EL devices with a configuration of ITO/NPB (60 nm)/emitter (20 nm)/TPBi (10 nm)/Alq₃ (30 nm)/LiF (1 nm)/Al (100 nm) (device I) by vapor deposition processes, in which N,N-bis(1-naphthyl)-N,N-diphenylbenzidine (NPB) functioned as a hole-transporting layer, TPE–carbazole adducts served as emitting layers, 2,2′,2″-(1,3,5-benzinetriyl)tris(1-phenyl-1-H-benzimidazole) (TPBi) worked as hole-blocking layer, and tris(8-hydroxyquinolinolato) aluminium (Alq₃) functioned as electron-transporting layer. The EL device of BTPECaP is not available due to its poor film-forming property. Table 2 summarizes the EL performances of the devices. TPECaP and TTPECaP show similar EL spectra with peak maxima at ∼488 nm. The EL spectra resemble the PL spectra of their films, indicating that both EL and PL originate from the same radiative decay of the singlet excitons. TPECa,

however, exhibits bathochromically shifted EL compared with PL of its film, probably due to the microcavity effect. OLEDs based on these luminogens show good performances. The device fabricated from TPECaP is turned on at a low voltage of 3.8 V and exhibits a maximum luminance (L_{max}) of 11 060 cd m⁻² (Fig. 6). The maximum current ($\eta_{C,max}$), power ($\eta_{P,max}$), and external quantum efficiencies ($\eta_{ext,max}$) attained by the device are 3.5 cd A⁻¹, 2.9 lm W⁻¹, and 1.7%, respectively. Devices based on TPECa and TTPECaP exhibit slightly better perfor-mances with higher L_{max}, $\eta_{C,max}$, and $\eta_{ext,max}$ values up to 13 650 cd m⁻², 3.8 cd A⁻¹, and 1.8%, respectively. These values are much better than those of the 3TPATPE-based device[11b] and also superior to those of devices based on luminogens con-structed from carbazole core and conventional planar ACQ chromophores,[12b,18] thanks to the AIE feature of the TPE unit. The EL results of TPE–carbazole adducts, although prelimi-nary, suggest that these AIE luminogens are promising candi-dates for OLEDs.

Materials that possess multiple functional properties, such as light-emitting and hole- and/or electron-transporting capabili-ties, are more useful for high-tech applications and in great demand because they can simplify the device structure and facilitate fabrication procedures. Carbazole is a representative building block that can be used to construct materials with both light-emitting[19] and hole-transporting properties.[20] As a result, the electron-donating ability of the carbazole core may endow the present luminogens with good hole-transporting property. To explore the application of these AIE luminogens as bifunc-tional materials, OLED of TPECaP with a configuration of ITO/TPECaP (80 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm) (device II) was constructed, where TPECaP served as both light-emitting and hole-transporting layers. Device II based on TPECaP emits at 496 nm (Fig. 6A), which is close to the EL peak in device I. This indicates that the EL originates from the TPECaP layer. However, device II exhibits much better performances. It emits more intensely with luminance up to 12 930 cd m⁻², exhibiting higher $\eta_{C,max}$, $\eta_{P,max}$, and $\eta_{ext,max}$ values of 5.5 cd A⁻¹, 3.8 lm W⁻¹, and 2.2%, respectively. Device III of TTPECaP fabricated in the absence of NPB or hole-transporting layer also shows better performances. It is turned on at a low voltage of 3.6 V, exhibiting a high $\eta_{P,max}$ of 4.1 lm W⁻¹, a $\eta_{C,max}$ of 6.3 cd A⁻¹ and a $\eta_{ext,max}$ of 2.3%. Evidently, the carbazole core retains its good hole-transporting property after being substituted with TPE, enabling TPECaP and TTPECaP to perform well as bifunctional materials in OLEDs.

Table 2 EL properties of the TPE–carbazole adducts[a]

Active layer	λ_{EL}/nm	V_{on}/V	L_{max}/cd m⁻²	$\eta_{P,max}$/lm W⁻¹	$\eta_{C,max}$/cd A⁻¹	$\eta_{ext,max}$/%
TPECa[I]	484	4.0	7508	2.7	3.8	1.8
TPECaP[I]	488	3.8	11 060	2.9	3.5	1.7
TTPECaP[I]	488	4.0	13 650	2.1	3.8	1.8
TPECaP[II]	496	4.4	12 930	3.8	5.5	2.2
TTPECaP[III]	490	3.6	9048	4.1	6.3	2.3

[a] Device configuration: [I]ITO/NPB (60 nm)/emitter (20 nm)/TPBi (10 nm)/Alq₃ (30 nm)/LiF (1 nm)/Al (100 nm), [II]ITO/TPECaP (80 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm), and [III]ITO/TTPECaP (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm) Abbreviations: 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 $\eta_{ext,max}$ = maximum external quantum efficiency.
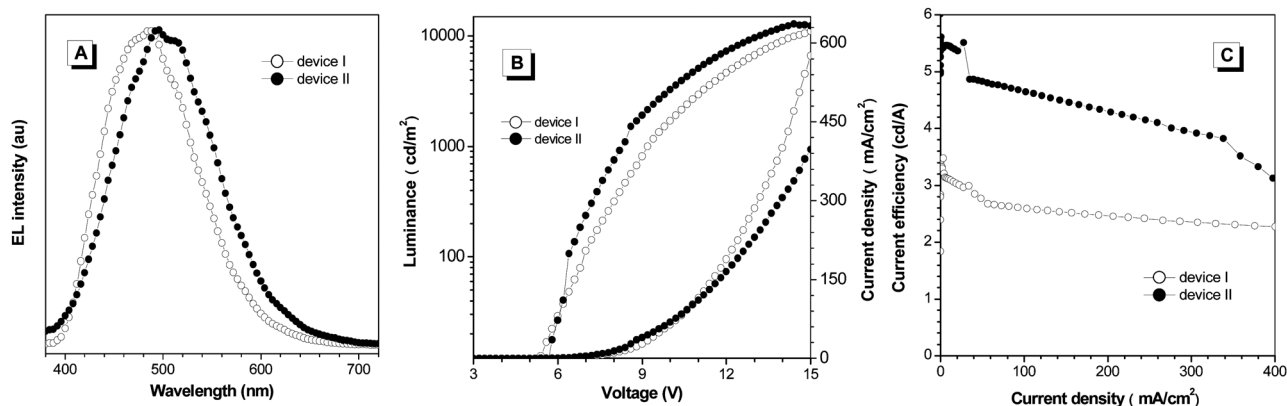
Fig. 6 (A) EL spectra, (B) change in luminance and current density with the applied bias, and (C) plots of current efficiency *versus* current density in multilayer EL devices of TPECaP with a configuration of ITO/NPB/TPECaP/TPBi/Alq₃/LiF/Al (device I) and ITO/TPECaP/TPBi/LiF/Al (device II).
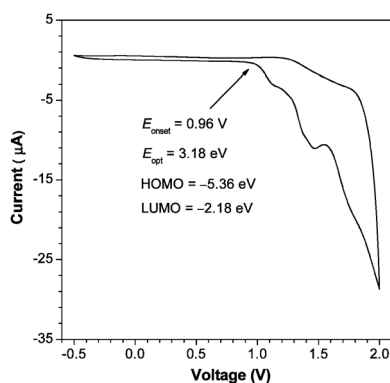
Fig. 7 Cyclic voltammogram of TPECaP measured in dichloromethane containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate. Scan rate: 100 mV s⁻¹.

Fig. 7 shows the cyclic voltammogram of TPECaP. The HOMO energy level of TPECaP can be estimated from the onset oxidation potential and is equal to −5.36 eV. The LUMO energy level can be obtained by subtraction of the optical band gap (obtained from the onset absorption wavelength) from the HOMO energy level and is calculated to be −2.18 eV.[21] The HOMO energy level of TPECaP is slightly higher than that of NPB (−5.4 eV),[22] indicating that TPECaP is in favor of hole injection and transportation. The use of NPB as an additional hole-transporting layer is thus not necessary in the device fabrication and could even be harmful because it may break the charge balance in the EL device. These data attest that the present luminogens are excellent hole-transporting materials, in addition to being highly emissive in the solid state. This helps to simplify the device structure, shorten the fabrication process, and lower production costs.

Conclusions

In this work, new AIE luminogens are constructed from TPE and carbazole and their electronic, thermal, and optical properties are investigated. All the molecules are almost non-fluorescent in solutions but become strong emitters when aggregated in poor solvents or fabricated as thin films in the solid state. Attachment

of TPE unit to the carbazole core has quenched its light emission in solution due to the active IMR process but endowed the resultant molecules with salient AIE characteristics. Preliminary results from theoretical calculation imply that the IMR process of the TPE units works more effectively to consume excited state energy when the orbitals of the LUMOs of the molecules are distributed mainly on the TPE units. Multiple C–H⋯π hydrogen bonds formed between the TPE and carbazole units in the solid state help to restrict the IMR process efficiently and boost the Φ_F values of the luminogens to unity. The TPE–carbazole adducts show high thermal and morphological stabilities, whose T_gs and T_ds are comparable or higher than those of adducts constructed from TPE and triphenylamine. Efficient OLEDs using these AIE luminogens as active layers are fabricated, which show good device performances. The carbazole unit shows merits in improving the thermal stability of the materials and their device performances, making the present luminogens function as both light-emitting and hole-transporting materials. The results obtained here manifest that the ACQ problem of conventional chromophores can be solved without causing an adverse effect by introduction of the AIE unit into their molecular structures. The present work not only gives further insight into the mechanism of the AIE phenomenon but also demonstrates the applicability of the new approach for creating efficient materials for optics and electronics.

Experimental

General information

THF was distilled from sodium benzophenone ketyl under dry nitrogen immediately prior to use. All other chemicals and reagents were purchased from Aldrich and used as received without further purification. ¹H and ¹³C NMR spectra were measured on a Bruker AV 300 spectrometer in deuterated chloroform using tetramethylsilane (TMS; $\delta = 0$) as internal reference. UV spectra were measured on a Milton Roy Spectronic 3000 Array spectrophotometer. PL spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. Elemental analysis was performed on an Elementary Vario EL analyzer. The high resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 mass spectrometer operated in MALDI-TOF

mode. Thermogravimetric analysis (TGA) was carried on a TA TGA Q5000 instrument under dry nitrogen at a heating rate of 10 °C min^{-1}. Thermal transitions were investigated by differential scanning calorimetry (DSC) using a TA DSC Q1000 instrument under dry nitrogen at a heating rate of 10 °C min^{-1}. The ground-state geometries were optimized using the density functional theory with B3LYP hybrid functional at the basis set level of 6-31G(d). All the calculations were performed using the Gaussian 03 package. Cyclic voltammetry was performed at room temperature with use of a standard three-electrode electrochemical cell in dichloromethane containing tetra-*n*-butylammonium hexafluorophosphate (0.1 M). The working and reference electrodes were platinum and Ag/AgCl. The reference electrode was checked *versus* ferrocene as internal standard as recommended by IUPAC. All the solutions were deaerated by bubbling nitrogen gas for a few minutes prior to the electrochemical measurements.

Device fabrication

The devices were fabricated on 80 nm ITO coated glass with a sheet resistance of 25 Ω □$^{-1}$. Prior to loading into the pretreatment chamber, the ITO-coated glasses were soaked in ultrasonic detergent for 30 min, followed by spraying with de-ionized water for 10 min, soaking in ultrasonic de-ionized water for 30 min, and oven-baking for 1 h. The cleaned samples were treated by perfluoromethane plasma with a power of 100 W, gas flow of 50 sccm, and pressure of 0.2 Torr for 10 s in the pretreatment chamber. The samples were transferred to the organic chamber with a base pressure of 7×10^{-7} Torr for the deposition of NPB, emitter, TPBi, and Alq$_3$. The samples were then transferred to the metal chamber for cathode deposition which composed of lithium fluoride (LiF) capped with aluminium (Al). The light-emitting area was 4 mm^2. The current density–voltage characteristics of the devices were measured by a HP4145B semiconductor parameter analyzer. The forward direction photons emitted from the devices were detected by a calibrated UDT PIN-25D silicon photodiode. The luminance and external quantum efficiencies of the devices were inferred from the photocurrent of the photodiode. The EL spectra were obtained by a PR650 spectrophotometer. All the measurements were carried out under air at room temperature without device encapsulation.

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 (0–99.5 vol%). The PL measurements of the resultant solutions were then performed immediately.

X-Ray crystallography

Crystal data for TPECaP (CCDC 836364): $C_{44}H_{31}N \cdot CH_2Cl_2$, M_W = 658.62, monoclinic, P2(1)/c, a = 21.295(2), b = 16.3989(19), c = 9.7404(11) Å, β = 98.263(2), V = 3366.2(7) Å^3, Z = 4, D_c = 1.300 g cm^{-3}, μ = 0.227 mm^{-1} (MoKα, λ = 0.71073), $F(000)$ = 1376, T = 173(2) K, 18 495 measured reflections, 5854 independent reflections (R_{int} = 0.0405), GOF on F^2 = 1.045, R_1 = 0.0886, wR_2 = 0.1743 (all data), Δe 0.740 and −0.348 e Å^{-3}.

Synthesis

9-[4′-(1,2,2-Triphenylvinyl)biphenyl-4-yl]-9H-carbazole (TPE-CaP). A mixture of **1** (0.32 g, 1 mmol), **7** (0.41 g, 1.1 mmol), Pd(PPh$_3$)$_4$ (0.058 g, 0.05 mmol), and potassium carbonate (0.55 g, 4.0 mmol) in 100 mL of toluene/ethanol/water (8/1/1 v/v/v) was heated to reflux for 24 h under nitrogen. The mixture was then poured into water and extracted with dichloromethane. The organic layer was washed with water and dried over magnesium sulfate. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography using hexane/dichloromethane mixture as eluent. White solid; yield 71% (0.4 g). ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 8.14 (d, 2H, J = 8.1 Hz), 7.79 (d, 2H, J = 9.0 Hz), 7.60 (d, 2H, J = 8.4 Hz), 7.48–7.38 (m, 6H), 7.30–7.25 (m, 2H), 7.16–7.05 (m, 17H). ^{13}C NMR (75 MHz, CDCl$_3$), δ (TMS, ppm): 144.5, 144.0, 142.1, 141.6, 141.2, 140.3, 138.7, 137.5, 132.6, 132.0, 131.9, 128.9, 128.5, 128.4, 128.0, 127.3, 127.2, 126.9, 126.7, 124.0, 121.0, 120.7, 110.5. HRMS: *m/z* 573.2451 (M$^+$, calcd 573.2457). Anal. Calcd for C$_{44}$H$_{31}$N: C, 92.11; H, 5.45; N, 2.44. Found: C, 91.85; H, 5.40; N, 2.36%.

9-Phenyl-3,6-bis[4-(1,2,2-triphenylvinyl)phenyl]-9H-carbazole (BTPECaP). The procedure was analogous to that described for TPECaP. Pale green solid; yield 66%. ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 8.33 (d, 2H, J = 1.5 Hz), 7.64–7.59 (m, 6H), 7.50–7.47 (m, 5H), 7.43 (d, 2H, J = 8.4 Hz), 7.15–7.03 (m, 34H). ^{13}C NMR (75 MHz, CDCl$_3$), δ (TMS, ppm): 144.7, 144.6, 142.9, 141.8, 141.5, 141.5, 140.2, 138.2, 133.5, 132.5, 132.1, 132.0, 130.7, 128.5, 128.4, 128.4, 127.6, 127.2, 127.1, 126.9, 126.0, 124.7, 119.2, 110.9. HRMS: *m/z* 903.3847 (M$^+$, calcd 903.3865). Anal. Calcd for C$_{70}$H$_{49}$N: C, 92.99; H, 5.46; N, 1.55. Found: C, 92.52; H, 5.39; N, 1.45%.

9-[4′-(1,2,2-Triphenylvinyl)biphenyl-4-yl]-3,6-bis[4-(1,2,2-triphenylvinyl)phenyl]-9H-carbazole (TTPECaP). The procedure was analogous to that described for TPECaP. Pale green solid; yield 54%. ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 8.33 (d, 2H, J = 1.5 Hz), 7.79 (d, 2H, J = 8.1 Hz), 7.64–7.60 (m, 4H), 7.49–7.44 (m, 8H), 7.17–7.05 (m, 51H). ^{13}C NMR (75 MHz, CDCl$_3$), δ (TMS, ppm): 144.6, 144.5, 144.4, 144.3, 143.9, 142.7, 142.0, 141.6, 141.3, 141.1, 140.5, 140.2, 139.1, 138.5, 137.3, 133.8, 132.7, 132.6, 132.2, 132.1, 128.9, 128.5, 128.4, 127.7, 127.2, 127.1, 127.0, 126.9, 126.1, 124.7, 119.3, 110.8. HRMS: *m/z* 1234.3140 (M$^+$, calcd 1234.5307). Anal. Calcd for C$_{96}$H$_{67}$N: C, 93.40; H, 5.47; N, 1.13. Found: C, 93.42; H, 5.31; N, 1.05%.

References

1 (a) J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley, London, UK, 1970; (b) I. Capek, *Adv. Colloid Interface Sci.*, 2002, **97**, 91; (c) S. W. Thomas III, G. D. Joly and T. M. Swager, *Chem. Rev.*, 2007, **107**, 1339; (d) F. Mancin, P. Scrimin, P. Tecilla and U. Tonellato, *Coord. Chem. Rev.*, 2009, **253**, 2150.

2 (a) T. M. Swager, *Acc. Chem. Res.*, 2008, **41**, 1181; (b) A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz and A. B. Holmes, *Chem. Rev.*, 2009, **109**, 897; (c) J. Liu, J. W. Y. Lam and B. Z. Tang, *Chem. Rev.*, 2009, **109**, 5799.

3 (a) J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu and B. Z. Tang, *Chem. Commun.*, 2001, 1740; (b) B. Z. Tang, X. Zhan, G. Yu, P. P. S. Lee, Y. Liu and D. Zhu, *J. Mater. Chem.*, 2001, **11**, 2974; (c) Z. Zhao, Z. Wang, P. Lu, C. Y. K. Chan, D. Liu, J. W. Y. Lam, H. H. Y. Sung, I. D. Williams, Y. Ma and B. Z. Tang, *Angew. Chem., Int. Ed.*, 2009, **48**, 7608; (d) J. Liu, J. W. Y. Lam and B. Z. Tang, *J. Inorg. Organomet. Polym. Mater.*, 2009, **19**, 249; (e) Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Soc. Rev.*, 2011, **40**, 5361; (f) A. Qin, J. W. Y. Lam and B. Z. Tang, *Prog. Polym. Sci.*, 2012, **37**, 182.

4 (a) B. K. An, S. K. Kwon, S. D. Jung and S. Y. Park, *J. Am. Chem. Soc.*, 2002, **124**, 14410; (b) J. Seo, J. W. Chung, E.-H. Jo and S. Y. Park, *Chem. Commun.*, 2008, 2794; (c) S. Kim, Q. Zheng, G. He, D. J. Bharali, H. E. Pudavar, A. Baev and P. N. Prasad, *Adv. Funct. Mater.*, 2006, **16**, 2317; (d) Z. Ning, Z. Chen, Q. Zhang, Y. Yan, S. Qian, Y. Cao and H. Tian, *Adv. Funct. Mater.*, 2007, **17**, 3799; (e) Y. Li, F. Li, H. Zhang, Z. Xie, W. Xie, H. Xu, B. Li, F. Shen, L. Ye, M. Hanif, D. Ma and Y. Ma, *Chem. Commun.*, 2007, 231; (f) R. Deans, J. Kim, M. R. Machacek and T. M. Swager, *J. Am. Chem. Soc.*, 2000, **122**, 8565; (g) S. J. Toal, D. Magde and W. C. Trogler, *Chem. Commun.*, 2005, 5465; (h) C. J. Bhongale and C. S. Hsu, *Angew. Chem., Int. Ed.*, 2006, **45**, 1404; (i) K. Shiraishi, T. Kashiwabara, T. Sanji and M. Tanaka, *New J. Chem.*, 2009, **33**, 1680.

5 (a) Y. Dong, J. W. Y. Lam, A. Qin, J. Sun, J. Liu, Z. Li, S. Zhang, J. Sun, H. S. Kwok and B. Z. Tang, *Appl. Phys. Lett.*, 2007, **91**, 011111; (b) Z. Zhao, S. Chen, X. Shen, M. Faisal, Y. Yu, P. Lu, J. W. Y. Lam, H. S. Kwok and B. Z. Tang, *Chem. Commun.*, 2010, **46**, 686.

6 (a) Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Commun.*, 2009, 4332; (b) W. Wang, T. Lin, M. Wang, T.-X. Liu, L. Ren, D. Chen and S. Huang, *J. Phys. Chem. B*, 2010, **114**, 5983; (c) V. S. Vyas and R. Rathore, *Chem. Commun.*, 2010, **46**, 1065; (d) Z. Zhao, P. Lu, J. W. Y. Lam, Z. Wang, C. Y. K. Chan, H. H. Y. Sung, I. D. Williams, Y. Ma and B. Z. Tang, *Chem. Sci.*, 2011, **2**, 672.

7 (a) J. Chen, C. C. W. Law, J. W. Y. Lam, Y. Dong, S. M. F. Lo, I. D. Williams, D. Zhu and B. Z. Tang, *Chem. Mater.*, 2003, **15**, 1535; (b) Z. Li, Y. Dong, B. Mi, Y. Tang, M. Häussler, H. Tong, Y. Dong, J. W. Y. Lam, Y. Ren, H. H. Y. Sun, K. S. Wong, P. Gao, I. D. Williams, H. S. Kwok and B. Z. Tang, *J. Phys. Chem. B*, 2005, **109**, 10061; (c) G. Yu, S. Yin, Y. Liu, J. Chen, X. Xu, X. Sun, D. Ma, X. Zhan, Q. Peng, Z. Shuai, B. Z. Tang, D. Zhu, W. Fang and Y. Luo, *J. Am. Chem. Soc.*, 2005, **127**, 6335; (d) S. Dong, Z. Li and J. Qin, *J. Phys. Chem. B*, 2009, **113**, 434.

8 (a) Y. Hong, C. Feng, Y. Yu, J. Liu, J. W. Y. Lam, K. Q. Luo and B. Z. Tang, *Anal. Chem.*, 2010, **82**, 7035; (b) Y. Liu, Y. Yu, J. W. Y. Lam, Y. Hong, M. Faisal, W. Yuan and B. Z. Tang, *Chem.–Eur. J.*, 2010, **16**, 8433; (c) H. Tong, Y. Hong, Y. Dong, M. Haeussler, J. W. Y. Lam, Z. Li, Z. Guo and B. Z. Tang, *Chem. Commun.*, 2006, 3705; (d) Y. Hong, M. Haeussler, J. W. Y. Lam, Z. Li, K. K. Sin, Y. Dong, H. Tong, J. Liu, A. Qin, R. Renneberg and B. Z. Tang, *Chem.–Eur. J.*, 2008, **14**, 6428.

9 (a) M. Wang, G. Zhang, D. Zhang, D. Zhu and B. Z. Tang, *J. Mater. Chem.*, 2010, **20**, 1858; (b) M. Wang, X. Gu, G. Zhang, D. Zhang and D. Zhu, *Anal. Chem.*, 2009, **81**, 4444; (c) L. Peng, G. Zhang, D. Zhang, J. Xiang, R. Zhao, Y. Wang and D. Zhu, *Org. Lett.*, 2009, **11**, 4014; (d) T. Sanji, K. Shiraishi, M. Nakamura and M. Tanaka, *Chem.–Asian J.*, 2010, **5**, 817.

10 (a) Q. Chen, D. Zhang, G. Zhang, X. Yang, Y. Feng, Q. Fan and D. Zhu, *Adv. Funct. Mater.*, 2010, **20**, 3244; (b) L. Tang, J. K. Jin, A. Qin, W. Z. Yuan, Y. Mao, J. Mei, J. Z. Sun and B. Z. Tang, *Chem. Commun.*, 2009, 4974; (c) Z. Zhao, S. Chen, J. W. Y. Lam, C. Y. K. Chan, C. K. W. Jim, Z. Wang, C. Wang, P. Lu, H. S. Kwok, Y. Ma and B. Z. Tang, *Pure Appl. Chem.*, 2010, **82**, 863; (d) Z. Zhao, S. Chen, J. W. Y. Lam, C. K. W. Jim, C. Y. K. Chan, Z. Wang, P. Lu, H. S. Kwok, Y. Ma and B. Z. Tang, *J. Phys. Chem. C*, 2010, **114**, 7963; (e) P. Lu, J. W. Y. Lam, J. Liu, C. K. W. Jim, W. Yuan, N. Xie, Y. Zhong, Q. Hu, K. S. Wong, K. K. L. Cheuk and B. Z. Tang, *Macromol. Rapid Commun.*, 2010, **31**, 834; (f) Y. You, H. Yang, J. W. Chung, J. H. Kim, Y. Jung and S. Y. Park, *Angew. Chem., Int. Ed.*, 2010, **49**, 3757; (g) A. Qin, L. Tang, J. W. Y. Lam, C. K. W. Jim, Y. Yu, H. Zhao, J. Z. Sun and B. Z. Tang, *Adv. Funct. Mater.*, 2009, **19**, 1891; (h) B. Xu, Z. Chi, X. Zhang, H. Li, C. Chen, S. Liu, Y. Zhang and J. Xu, *Chem. Commun.*, 2011, **47**, 11080; (i) D. Li, J. Yu and R. Xu, *Chem. Commun.*, 2011, **47**, 11077.

11 (a) Z. Zhao, S. Chen, J. W. Y. Lam, P. Lu, Y. Zhong, K. S. Wong, H. S. Kwok and B. Z. Tang, *Chem. Commun.*, 2010, **46**, 2221; (b) W. Yuan, P. Lu, S. Chen, J. W. Y. Lam, Z. Wang, Y. Liu, H. S. Kwok, Y. Ma and B. Z. Tang, *Adv. Mater.*, 2010, **22**, 2159; (c) Y. Liu, S. Chen, J. W. Y. Lam, P. Lu, R. T. K. Kwok, M. Faisal, H. S. Kwok and B. Z. Tang, *Chem. Mater.*, 2011, **23**, 2536; (d) Z. Zhao, S. Chen, C. Deng, J. W. Y. Lam, C. Y. K. Chan, P. Lu, Z. Wang, B. Hu, X. Chen, P. Lu, H. S. Kwok, Y. Ma, H. Qiu and B. Z. Tang, *J. Mater. Chem.*, 2011, **21**, 10949.

12 (a) G.-L. Feng, S.-J. Ji, W.-Y. Lai and W. Huang, *Synlett*, 2006, 2841; (b) Z. Zhao, X. Xu, X. Chen, X. Wang, P. Lu, G. Yu and Y. Liu, *Tetrahedron*, 2008, **64**, 2658.

13 I. B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic Press, New York and London, 1971.

14 (a) Z. Zhao, Y. Zhao, P. Lu and W. Tian, *J. Phys. Chem. C*, 2007, **111**, 6883; (b) Z. Zhao, X. Xu, H. Wang, P. Lu, G. Yu and Y. Liu, *J. Org. Chem.*, 2008, **73**, 594; (c) K. R. J. Thomas, J. T. Lin, Y.-T. Tao and C.-W. Ko, *J. Am. Chem. Soc.*, 2001, **123**, 9404; (d) Z. Yang, Z. Chi, L. Zhou, X. Zhang, M. Chen, B. Xu, C. Wang, Y. Zhang and J. Xu, *Opt. Mater.*, 2009, **32**, 398; (e) Z. Zhao, X. Xu, F. Wang, G. Yu, P. Lu, Y. Liu and D. Zhu, *Synth. Met.*, 2006, **156**, 209; (f) J.-Y. Shen, X.-L. Yang, T.-H. Huang, J. T. Lin, T.-H. Ke, L.-Y. Chen, C.-C. Wu and M.-C. P. Yeh, *Adv. Funct. Mater.*, 2007, **17**, 983.

15 (a) H. Shao and J. R. Parquette, *Chem. Commun.*, 2010, **46**, 4285; (b) K. V. Rao and S. J. George, *Org. Lett.*, 2010, **12**, 2656; (c) A. Kaeser and A. P. H. J. Schenning, *Adv. Mater.*, 2010, **22**, 2985.

16 Z. Zhao, C. Deng, S. Chen, J. W. Y. Lam, W. Qin, P. Lu, Z. Wang, H. S. Kwok, Y. Ma, H. Qiu and B. Z. Tang, *Chem. Commun.*, 2011, **47**, 8847.

17 (a) S. Lamansky, P. Djurovich, D. Murphy, A.-R. Feras, H.-E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest and M. E. Thompson, *J. Am. Chem. Soc.*, 2001, **123**, 4304; (b) K. R. J. Thomas, M. Velusamy, J. T. Lin, Y.-T. Tao and C.-H. Chuen, *Adv. Funct. Mater.*, 2004, **14**, 387; (c) Z. Li, Y. Liu, G. Yu, Y. Wen, Y. Guo, L. Ji, J. Qin and Z. Li, *Adv. Funct. Mater.*, 2009, **19**, 2677; (d) Z. Yang, Z. Chi, T. Yu, X. Zhang, M. Chen, B. Xu, S. Liu, Y. Zhang and J. Xu, *J. Mater. Chem.*, 2009, **19**, 5541.

18 (a) K. R. J. Thomas, J. T. Lin, Y.-T. Tao and C.-W. Ko, *J. Am. Chem. Soc.*, 2001, **123**, 9404; (b) Z. Zhao, X. Xu, L. Xu, G. Yu, P. Lu and Y. Liu, *Synth. Met.*, 2007, **157**, 414.

19 (a) J.-Y. Shen, X.-L. Yang, T.-H. Huang, J. T. Lin, T.-H. Ke, L.-Y. Chen, C.-C. Wu and M.-C. P. Yeh, *Adv. Funct. Mater.*, 2007, **17**, 983; (b) K. R. J. Thomas, M. Velusamy, J. T. Lin, Y.-T. Tao and C.-H. Chuen, *Adv. Funct. Mater.*, 2004, **14**, 387.

20 (a) Q. Zeng, Z. Li, Y. Dong, C. Di, A. Qin, Y. Hong, L. Ji, Z. Zhu, C. K. W. Jim, G. Yu, Q. Li, Z. Li, Y. Liu, J. Qin and B. Z. Tang, *Chem. Commun.*, 2007, 70; (b) V. Promarak, M. Ichikawa, T. Sudyoadsuk, S. Saengsuwan, S. Jungsuttiwong and T. Keawin, *Synth. Met.*, 2007, **157**, 17; (c) J. Li, C. Ma, J. Tang, C.-S. Lee and S. T. Lee, *Chem. Mater.*, 2005, **17**, 615; (d) Q. Zhang, J. Chen, Y. Cheng, L. Wang, D. Ma, X. Jing and F. Wang, *J. Mater. Chem.*, 2004, **14**, 895.

21 (a) S. Chen, X. Xu, Y. Liu, G. Yu, W. Qiu, Y. Ma and D. Zhu, *Adv. Funct. Mater.*, 2005, **15**, 1541; (b) Z. Zhao, J.-H. Li, P. Lu and Y. Yang, *Adv. Funct. Mater.*, 2007, **17**, 2203.

22 (a) S. L. Tao, Z. K. Peng, X. H. Zhang, P. F. Wang, C.-S. Lee and S.-T. Lee, *Adv. Funct. Mater.*, 2005, **15**, 1716; (b) S. Chen, Z. Zhao, B. Z. Tang and H. S. Kwok, *J. Phys. D: Appl. Phys.*, 2010, **43**, 095101.