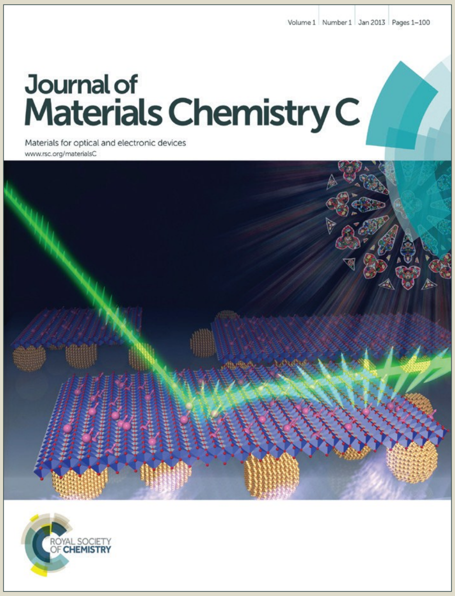
Journal of Materials Chemistry C

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/materialsC

Journal of Materials Chemistry C

ARTICLE

Triphenylamine-functionalized tetraphenylpyrazine: facile preparation and multifaceted functionalities

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Ming Chen,[a] Han Nie,[b] Bo Song,[b] Lingzhi Li,[a] Jing Zhi Sun,[a] Anjun Qin*[ab] and Ben Zhong Tang*[abc]

Aggregation-induced emission (AIE) is a unique photo-physical phenomenon and has become an emerging and hot research area. With the enthusiastica effects paid by the researchers, hundreds of AIE-active luminogens (AIEgens) have been generated but heterocyclic AIEgens are rarely reported. Recently, we enriched the family of AIEgens and reported a pyrazine-based AIEgen of tetraphenylpyrazine (TPP), which could be facilely functinalized by post-synthetic strategy. In this work, we further expanded the TPP-based AIE system by covalently attaching one, two or four electron-donating triphenylamine moiety to the TPP core via Suzuki coupling, and TPP-TPA, TPP-2TPA and TPP-4TPA were produced, respectively. Thanks to their donor-π-acceptor structures, these luminogens exhibit multi-functional properties, such as excellent thermal stability (up to 504 ^{o}C), large molar absorptivity, bright emission in the solid states (the quantum yields up to 35.2%), solvatochromism, high two-photon absorption cross-sections (up to 480 GM). Furthermore, using TPP-TPA as emitting layer, a triple-layer device was fabricated and turn-on voltage, maximum luminance, current efficiency, power efficiency, and external quantum efficiency of 3.7 V, 17459 cd m^{-2}, 5.49 cd A^{-1}, 3.18 lm W^{-1} and 2.88 % were realized, respectively. These results indicate a huge potential to develop high-tech applications based on these TPP-based AIEgens.

Introduction

Over the past decades, organic fluorophores have drawn much attention especially in the areas of optoelectronic and biological fields, due to their high emission efficiency, tuneable emission colour, facile post-functionalization and low toxicity, etc.[1] However, traditional fluorophores generally suffer from the aggregation-caused quenching (ACQ) effect: they are highly emissive in dilute solution but become weakly or non-emissive in high concentration or condensed phases like aggregate or solid states due to their planar conjugated structures. The ACQ effect has reduced the performance of traditional fluorophores when used in optoelectronic devices and as bio-probes etc.[2] To alleviate this negative effect and to obstruct the formation of excimers or exciplexes upon aggregation, various approaches, such as physical doping or chemical modification with bulky groups have been adopted.[3] Nevertheless, the difficulties for precise control of doping concentration and avoidance of phase separation between host and guest during usage could not be ignored, whereas, in the latter case, tedious synthetic procedures and lengthened operating time are also involved. In other words, these methods met with limited success.

One possible permanent strategy to solve this difficulty is to enable the intrinsic aggregation process of fluorophores to play positive roles in enhancing emission. In 2001, we indeed observed such unique phenomenon: the multiple phenyl-substituted silole derivatives are non-emissive when molecularly dissolved but induce to emit intensely upon aggregation. Since the emission was induced by aggregation, we thus defined it as “aggregation-induced emission (AIE)”.[4] The propeller-shaped AIE luminogens (AIEgens) drives them to dissipate the excited state energy via intramolecular rotation of their peripheral rotators in dilute solution, whereas, in aggregate state this rotation is greatly restricted and the radiative transition channel is opened up. Accordingly, the mechanism of restriction of intramolecular rotation (RIR) was proposed and has thoroughly proved by plenty of experimental and theoretical studies.[5]

Excited by the AIE concept and enlightened by RIR mechanism, researchers have designed and synthesized hundreds of AIEgens especially based on the cores of silole,[6] tetraphenylethene (TPE),[7] distyrylanthracene (DSA),[8] and

---

[a] *MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China. E-mail: qinaj@zju.edu.cn or msqinaj@scut.edu.cn (A.J.Q.).*
[b] *Guangdong Innovative Research Team, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China.*
[c] *Department of Chemistry, Institute for Advanced Study, Institute of Molecular Functional Materials, Hong Kong Branch of Chinese National Engineering Research Center for Tissue Restoration and Reconstruction, and State Key Laboratory of Molecular Neuroscience, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong China. E-mail: tangbenz@ust.hk (B.Z.T.).*

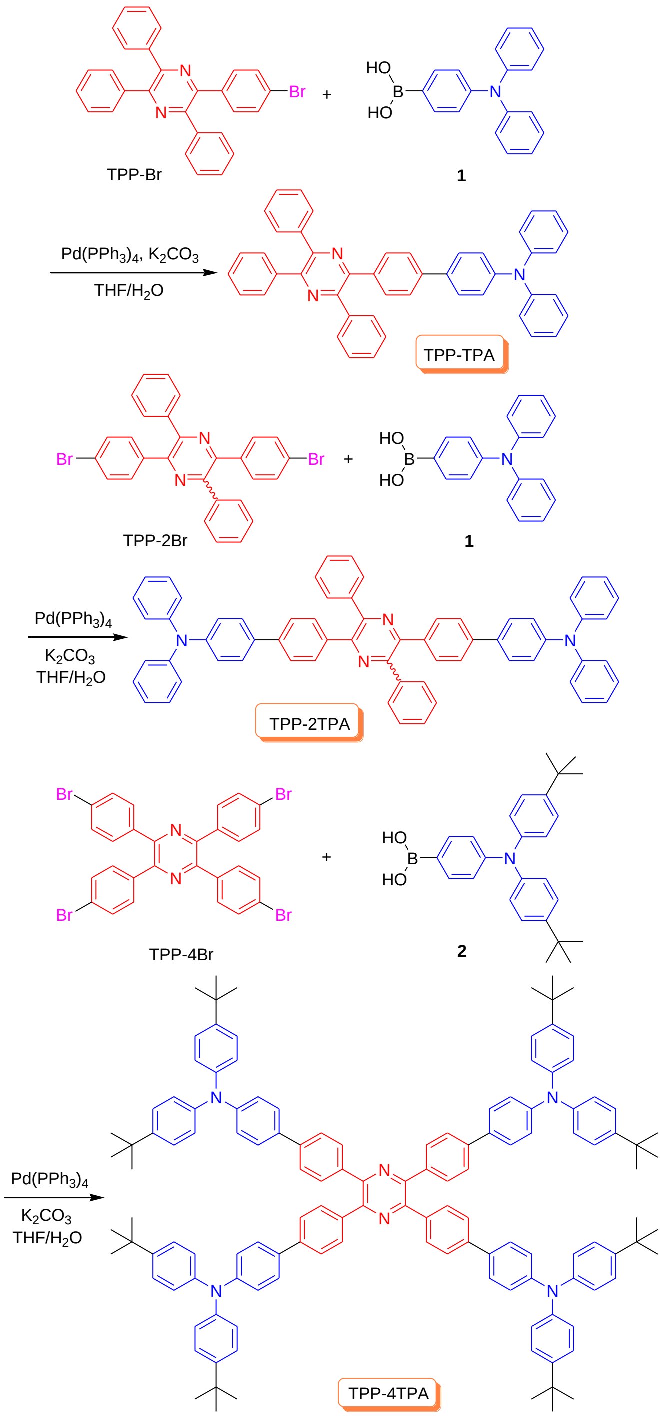
Electronic Supplementary Information (ESI) available: [^{1}H and ^{13}C NMR spectra, HRMS spectra, absorption and photoluminescence spectra, CV curves, TGA and DSC curves]. See DOI: 10.1039/x0xx00000x tetraphenyl-1,4-butadiene (TPBD),[9] etc. However, the heterocycle-based AIE cores with diverse electronic property, are still rare but in great demand because they could further expand the functionalities and promote high-tech applications in organic light-emitting diode (OLED), fluorescent sensor and biological imaging, and so on.[10] Very recently, we successfully generated a new type of such AIEgen of tetraphenylpyrazine (TPP), which possesses lots of charming advantages, such as easy preparation, facile modification, excellent stability, tuneable emission colour and definite luminescent mechanism.[11] It is thus envisioned that TPP could also act as another powerful AIE core, and attract considerable interests in materials and biological sciences.

To demonstrate its versatility as an AIE core, in this paper, we further expanded its family by covalently bonding with triphenylamine (TPA) moiety, which is well-known for its luminescent property, electron-dotation ability, and hole-transporting capability.[12] However, most of TPA derivatives suffer from the ACQ effect. A powerful strategy to enable TPA moiety to increase the emission efficiency in the solid state is to covalently bind it to an AIE core, like TPE.[13] More importantly, the remaining charge-transporting ability makes the new generated luminogens perform much better when used in OLED. In addition, thanks to its electron-donating property, the molecules containing TPA units and electron-withdrawing groups are always in association with large two-photon absorption cross-sections, which is exceedingly desirable for bio-imaging and photodynamic therapy applications.[14] Indeed, three TPP-based molecules of TPP-TPA, TPP-2TPA, and TPP-4TPA, in which one, two and four TPA moieties are covalently attached to the TPP core, show multi-functional properties and are potentially applicable in OLED and two-photon absorption materials, etc.

Results and discussion

Synthesis

To obtain TPP-based luminogens with flexible structures, the intermediates of Br-substituted TPPs are indispensable. Besides TPP-2Br (the structure was shown in Scheme 1), which has been reported in our recent work,[11] another two intermediates of TPP-Br and TPP-4Br (Schemes 1, their synthetic procedures are given in Electronic Supplementary Information, ESI†) were prepared in a facile way in this paper.[15,16] The TPP-based luminogens were then prepared by classical Suzuki coupling. Among which, TPP-TPA and TPP-2TPA were obtained by the reaction of TPP-Br and TPP-2Br with commercially available 4-(diphenylamino)-phenylboronic acid (**1**) in moderate yields, respectively. However, the product yielded from TPP-4Br and **1** was insoluble probably due to its rigidity. Delightfully, TPP-4TPA was successfully obtained by the reaction of TPP-4Br and isobutyl-decorated **1**, that is, the compound **2**.[17] TPP-TPA, TPP-2TPA TPP-4TPA and their intermediates were fully characterized by spectroscopy techniques and satisfactory analysis data corresponding to their structures were obtained (Fig. S1-S20, ESI†).



Scheme 1. Synthetic routes to TPP-TPA, TPP-2TPA and TPP-4TPA.

Thermal stability

After confirming their structures, we investigated the thermal stability of obtained luminogens by thermogravimetric analysis (TGA) with a heating rate of 10 °C/min under nitrogen (Fig. S21, ESI†). The temperatures for 5% weight loss (T_d) of TPP-TPA and TPP-2TPA were recorded to be as high as 402 and 504 °C, respectively, due to their fully conjugated aromatic structures. It is worth noting that these values are higher than the TPE-TPA and TPE-2TPA, which were reported to be 360 and 430 °C,

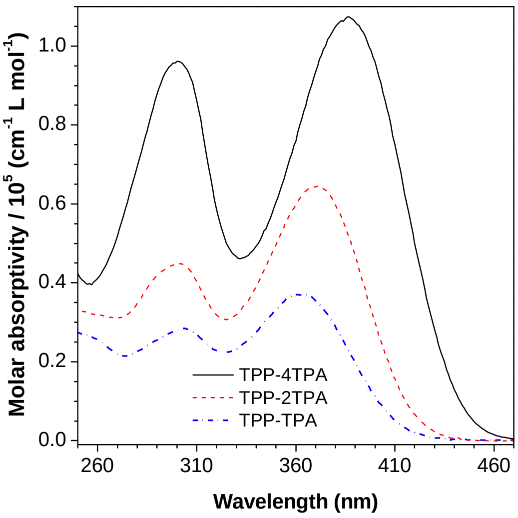


Fig. 1 UV-vis spectra of TPP-TPA, TPP-2TPA and TPP-4PTA in THF.

respectively,[18] further confirming that the TPP core possesses highly thermal stability. Unexpectedly, TPP-4TPA began to decompose at a temperature of 171 °C and followed by a second decomposition temperature of over 500 °C. After a careful inspection, we ascribe the first weight loss of TPP-4TPA to the isobutyl groups on its periphery, whereas, the central aromatic moieties remain intact until the temperature reaches 500 °C. The high thermal stability of TPP-based luminogens potentially enables them to find broad applications.

Photo-physical properties

We first investigated the absorption properties of these luminogens in dilute THF solutions. As shown in Fig. 1, with increasing the numbers of TPA moieties, the maximum absorption (λ_{ab}) of TPP-TPA, TPP-2TPA and TPP-4TPA red-shifted from 363 to 387 nm, suggesting that the molecular conjugation could be slightly influenced by increasing electron-donating groups. In contrast, the molar absorptivity of TPP-TPA, TPP-2PTA and TPP-4TPA enhanced linearly and is nearly proportional to the attached numbers of TPA moieties. This phenomenon could be attributed to the multiple intramolecular charge-transfers between TPA moieties to TPP cores. More acceptor (A) and donor (D) pairs, more molar absorptivity could be achieved.

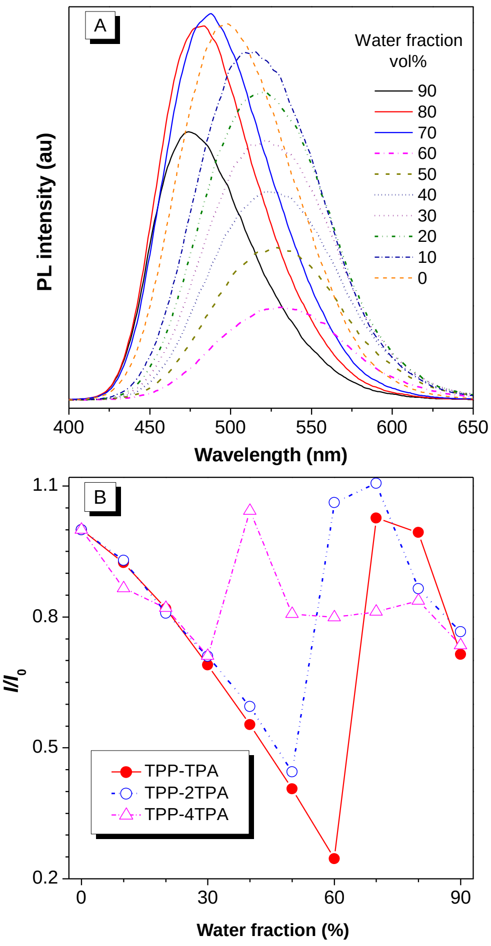


Fig. 2 (A) PL spectra of TPP-TPA in THF/water mixtures with different water fractions; λ_{ex} = 363 nm; concentration: 10 µM. (B) Changes of relative PL intensity of TPP-TPA, TPP-2TPA and TPP-4TPA in THF/water mixtures with different water fraction.

TPP is AIE-active, whether these TPP-based luminogens are also AIE-active? To answer this question, we studied their photoluminescence (PL) spectra in THF/water mixtures with different water fractions. As shown in Fig. 2 and Fig. S22 (ESI†), TPP-TPA emits at 498 nm in dilute THF solution. After addition of poor solvent (*i.e.* water), the emission of the system weakened with red-shift of their peaks at the same time. Specifically, more than 75% of its fluorescence intensity was quenched and a bathochromic shift about 34 nm could be discerned at the water fraction (f_w) of 60%. Afterwards, remarkable fluorescence enhancement with blue-shift of peaks was recorded. The decrease in fluorescence intensity and red-shift of its peaks is due to the twisted intramolecular charge-transfer (TICT) effect of TPP-TPA in the gradually strengthened polar mixed solvent of THF/water with higher fraction of polar water.[19] Whereas, the enhanced emission and blue-shift peak could be attributed to the aggregate formation due to the worsened solvating power of the aqueous mixture and less impact of the polarity of solvent on the TPP-TPA. Simultaneously, the rotation of the phenyl rings of TPP-TPA was greatly restricted in the aggregate state, and thus the unique aggregation-enhanced emission (AEE) was occurred. The weaker emission of TPP-TPA in the THF/water mixtures with f_w of 80 and 90% than that in 70% is probably due to the difference of aggregate morphology.[20]

The similar D-A structures of TPP-2TPA and TPP-4TPA also enable them to have ACQ plus AEE effects dominated by the TICT and RIR, respectively (Fig.S23 and S24, ESI†). Nevertheless, there are some evident differences between them (Fig. 2B). For example, from TPP-TPA, TPP-2TPA to TPP-4TPA, the enhanced molecular rigidity has greatly decreased the solubility, and thus led to the formation of aggregates at lower f_w. In addition, the AEE effect was discounted obviously

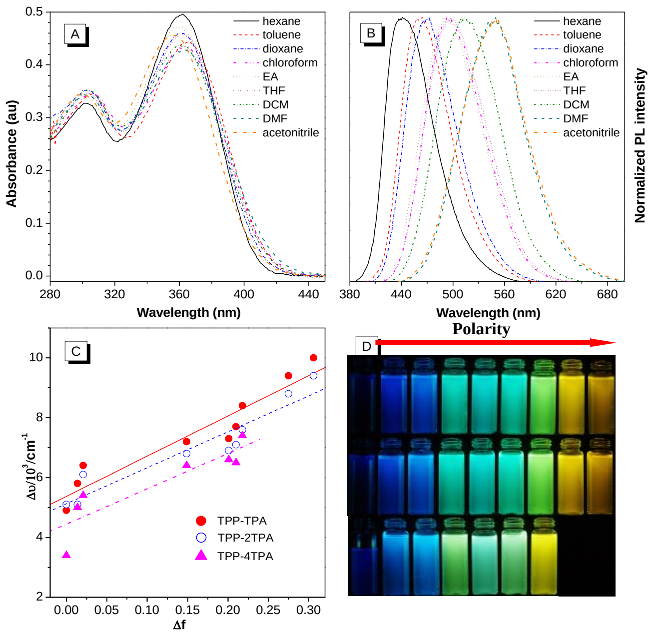


Fig. 3 UV-vis spectra (A) and normalized PL spectra (B) of TPP-TPA in solvent with various polar parameters. (C) Plot of Stokes shift ($\Delta\nu$) of TPP-TPA, TPP-2TPA and TPP-4TPA versus Δf of their solutions. (D) Photographs of TPP-TPA, TPP-2TPA and TPP-4TPA (from top to bottom) in solvents with increased polar parameters (from left to right) taken under the irradiation of 365 nm UV light.

with the increase of TPA moieties because more TPA groups attached to TPP core might generate larger free volume, in which the rotation of the phenyl rings could not be restricted efficiently after aggregation.[21] This explanation was proven by the absolute quantum yield (Φ_F) measurement. The values of TPP-TPA, TPP-2PTA and TPP-4TPA in solid states were recorded to be 35.2, 16.5 and 12.4 %, respectively (Table S1, ESI†).

Solvatochromism

The sensitivity of these TPP-based luminogens to the polar solvents was further confirmed by measuring their photo-physical property in various organic solvents with different polarities ranging from the low-polar hexane to high-polar acetonitrile. The UV-vis spectra of TPP-TPA showed that its absorption profiles changed little and were nearly free from the influence of solvent polarity. Contrarily, distinct changes in emission colour were observed in these luminogens. For example, when TPP-TPA was dissolved in hexane, it emits a deep blue light at 441 nm. However, further increase of solvent polarity remarkably red-shifted its emission. The bathochromic shift was identified as large as 108 nm in solvents from hexane to acetonitrile. Moreover, similar solvatochromism was also observed in TPP-2TPA and TPP-4TPA (Fig. 3, and Fig S25 and S26, ESI†).

Subsequently, we quantitatively analysed the influence of solvent polarity, characterized by Δf, on Stokes shift with Lippert-Mataga equation:[22]

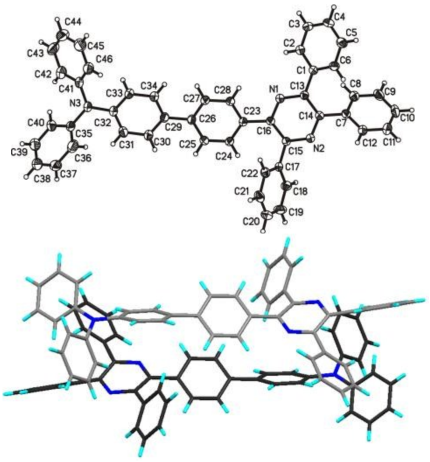


Fig. 4 ORTEP drawing of TPP-TPA and the packing of adjacent molecules in crystal cell.

$$\Delta\nu \equiv \nu_{\mathrm{ab}} - \nu_{\mathrm{em}} = \frac{2\Delta f}{hca^3}\left(\mu_{\mathrm{e}} - \mu_{\mathrm{g}}\right)^2 + const$$

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$

where $\Delta\nu$ is the Stokes shift, h is the Planck constant, c is the speed of light, a is the radius of the chromophore, μ_e and μ_g are the dipole moments in the excited (e) and ground (g) states, Δf is the solvent polarity parameter, and ε and n are the dielectric constant and refractive index of the solvent, respectively. According to the plots of $\Delta\nu$ *vs* Δf, TPP-TPA, TPP-2TPA and TPP-4TPA exhibit notable positive slope after linear fitting, with their values deduced to be 13454, 12026 and 11827, respectively (Fig.3C). These results suggest that much effective intramolecular charge transfer process could take place from the electron-donating TPA to electron-withdrawing TPP units in these luminogens.

Single crystal structure

The single crystal structure and relevant packing information are crucial for further understanding the photo-physical behaviour of molecules. Fortunately, a single crystal of TPP-TPA (CCDC 1419384) suitable for X-ray diffraction analyse was obtained by slow evaporation of chloroform/methanol mixture. Fig. 4 shows the ORTEP drawing of TPP-TPA and the packing of adjacent molecules in the crystal cell. Owing to respective propeller-like and cone-shaped TPP and TPA moieties, the whole molecule adopts a twisted conformation. Moreover, the molecules are loosely stacked in an antiparallel fashion, suggesting the TPP-TPA is a polar molecule. Meanwhile, this conformation also makes TPP-TPA easy to boost the emission in aggregate state as intramolecular motion is suppressed by steric effect of adjacent molecules to open up the irradiative transition channel.

Theoretical calculations

To gain insight into the molecular structures of TPP-based luminogens, theoretical calculations were performed. The density function theory (DFT) with a B3LYP/6-31G (d) basis set was used and the results of molecular energy levels are shown in Fig. 5 and Table S2 (ESI†). We can see that the electron

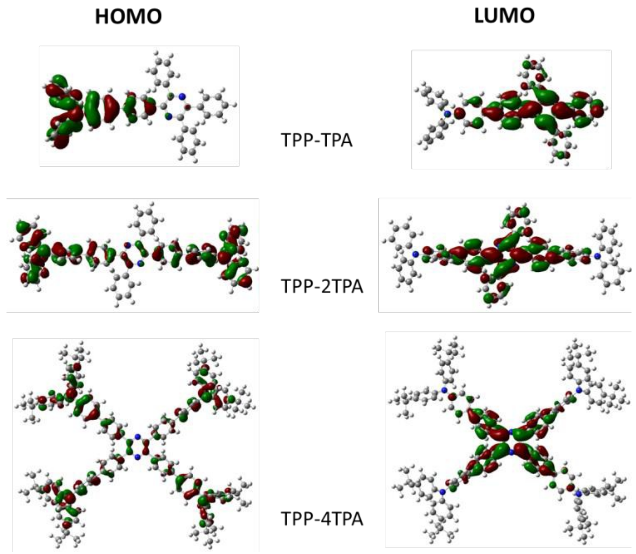


Fig. 5 Optimized molecular conformation and molecular orbital amplitude plots of HOMO and LUMO energy levels of TPP-TPA, TPP-2TPA and TPP-4TPA. One of the two isomers of TPP-2TPA was used.

clouds of HOMOs and LUMOs of these luminogens are mainly located on TPA and TPP groups, respectively, demonstrating a remarkable charge separation between ground and excited states. From the calculation, we can also conclude that more D-A pairs in the molecules, more charge separation is involved, which further confirms our observation and explanation about the photo-physical properties of TPP-based luminogens.

Electrochemical property

Besides theoretically evaluation, we also used cyclic voltammograms (CV) technique to measure their energy level experimentally. From the voltammogram curves shown in Fig. S27 (ESI†), the oxidization peaks with onset potentials of TPP-TPA, TPP-2TPA and TPP-4TPA at 0.66, 0.57 and 0.47 eV, respectively, could be easily observed in a positive scan direction, which is responsive to electron-rich TPA moieties in these luminogens. More TPA groups involved, more potential of oxidation happens in these luminogens. We thus infer that electronic property of ground state is mainly controlled by TPA moieties in these luminogens.

From the CV measurements, the HOMO energy levels of TPP-TPA, TPP-2TPA and TPP-4TPA were calculated to be -5.04, -4.95 and -4.85 eV, respectively. Such high values are comparable to typical TPA derivatives and endow them with hole-transporting ability. By subtracting the optical band gap energies (estimated from the absorption spectra) from HOMO energy levels, all the LUMO of them were deduced to be *ca.* 2.0 eV, which are much higher than TPP (-2.58 eV) (Table S2, ESI†).

Two-photon absorption

The molecules with D-π-A structures usually exhibit large two-photon absorption cross-sections (σ_{TPA}). We thus measured these values by employing two-photon excited fluorescence technique at the wavelength range of 700-900 nm. The results

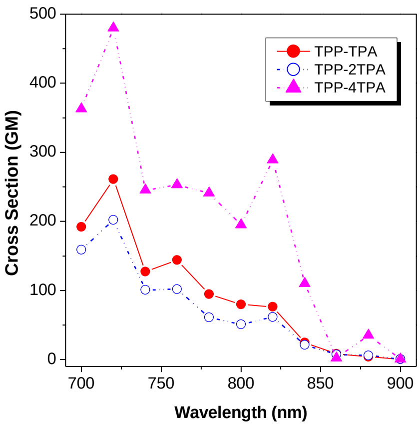


Fig. 6 The plots of two-photon absorption cross section (σ_{TPA}) of TPP-TPA, TPP-2PTA and TPP-4TPA *vs* excitation wavelength in dichloromethane. The concentrations of TPP-TPA, TPP-2TPA, TPP-4TPA are 6.37, 5.28 and 2.77 μM, respectively.

show that TPP-TPA, TPP-2TPA and TPP-4TPA emit with peaks at 532, 535 and 561 nm, respectively, upon exciting by a laser in the wavelength range of 700-900 nm. These peaks are about 20 nm red-shifted compared to the one-photon excited fluorescence, which probably caused by the system errors of varying apparatus (Fig. S28, ESI†). Moreover, another important value of σ_{TPA} was also calculated. From Fig. 6, we can see that the σ_{TPA} values of TPP-based luminogens changed with the molecular structures as well as the excitation wavelengths. Furthermore, both TPP-TPA and TPP-2TPA possess similar σ_{TPA} values, whereas, that of TPP-4TPA is almost 2 times higher than those of TPP-TPA and TPP-2PTA, and the highest value of 480 GM was deduced. In addition, by choosing σ_{TPA} at 800 nm as criterion, which is a mature and most used laser source for biological imaging, the values of TPP-TPA, TPP-2TPA and TPP-4TPA were tested to be 80, 51, an 195 GM, respectively. It is worthy to note that these values are still superior to that of coumarin and fluorescein, whose values are generally in the range of 36 to 45 GM.[23]

Electroluminescence

Thanks to the high emission of TPP-TPA in the solid state, we used it as emitting layer to fabricate OLEDs. A typical triple-layer device with configuration of ITO/NPB (60 nm)/TPP-TPA (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al (Device I) was fabricated. (NPB = 4,4-bis(1-naphthylphenylamino)biphenyl, functions as the hole-transporting layer; TPBi = 2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-*H*-benzimidazole, functions as electron-transporting layer). The results show that device I emits a sky blue light at 482 nm with its EL spectrum resembling the PL spectrum of TPP-TPA in solid film, indicating that the charges could transport in balance and excitions were successfully combined in the emitting layer (Fig. 7A). Moreover, the device also performed well with the turn-on voltage and maximum luminance, current efficiency, power efficiency, and external quantum efficiency of 3.7 V, 17459 cd m^{-2}, 5.49 cd A^{-1}, 3.18 lm W^{-1} and 2.88 %, respectively, which is almost identical to multilayer devices using TPE-TPA as emitting layer (Fig. 7B and Table 1).[18]

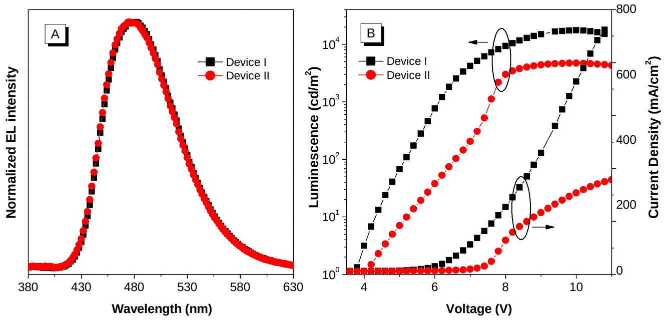


Fig. 7 (A) EL spectra of devices I and II using TPP-TPA as emitting layers. (B) Luminescence and current density versus voltage characteristics of TPP-TPA based devices.

Table 1 EL performance of devices based on TPP-TPA.

	λ_{EL} (nm)	V_{on} (V)^b	L_{max} (cd/m^2)^a	η_C (cd/A)^a	η_P (lm/W)^a	EQE^a (%)
I	482	3.7	17459	5.49	3.18	2.88
II	476	4.0	4692	4.72	3.53	2.52

[a] The maximum luminescence (L_{max}), current efficiency (η_C), power efficiency (η_P) and external quantum efficiency are the maximum values of the devices. [b] V_{on} is the turn-on voltage at 1 cd/m^2.

TPP-TPA possesses high-lying HOMO energy level, which is anticipated to possess good hole-transporting ability besides serving as emitting layer. We thus simplified the device configuration by removing HTL but thickening the emitting layer to 80 nm (Table 1). Unfortunately, the device performance is not as good as we expected although its EL spectrum is quite similar to that of device I, suggesting that other factors, such as molecular planarity and morphological homogeneity might be involved to influence the hole-transporting property of TPP-TPA.

Conclusions

In this work, by covalently binding electron-donating TPA moieties to the electron-accepting TPP core via Suzuki coupling, three luminogens of TPP-TPA, TPP-2TPA and TPP-4TPA were successfully obtained. Thanks to their D-π-A structures, these luminogens exhibit multiple functional properties. They possess large molar absorptivity, show strong emission intensity in the solid states, perform distinct solvatochromism, and exhibit high two-photon absorption cross-sections. Moreover, these luminogens are thermally stable because of their conjugated aromatic structures. Based on the high absolute quantum yield (35.2%) of TPP-TPA in the solid state, a triple-layer device using it as EML was fabricated, which gave high performance with a low V_{on} of 3.7 V, high L_{max} of 17459 cd/m^2 and good EQE of 2.88 %. This work not only furnishes a promising platform for the preparation of TPP-based luminogens with mutable structures, high emission, and multifaceted functionalities, but also demonstrates the possibility of applying these AIEgens in high-tech areas.

Acknowledgements

This work was partially supported by the key project of the Ministry of Science and Technology of China (2013CB834702), the National Science Foundation of China (21490571, 21222402 and 21174120), and the Research Grants Council of Hong Kong (16301614) and Innovation and Technology Commission (ITC-CNERC14S01). A.J.Q. and B.Z.T. thank the support from Guangdong Innovative Research Team Program (201101C0105067115) and the Fundamental Research Funds for the Central Universities (2015ZY013).

Notes and references

1 (a) C. H. Chien, C. K. Chen, F. M. Hsu, C. F. Shu, P. T. Chou and C. H. Lai, *Adv. Funct. Mater.*, 2009, **19**, 560; (b) L. Zöphel, V. Enkelmann and K. Müllen, *Org. Lett.*, 2013, **15**, 804; (c) J. P. Anderson, B. L. Reynolds, K. Baum and G. Williams, *Nano. Lett.*, 2010, **10**, 788; (d) S. You, Q. Cai, Y. Zheng, B. He, J. Shen, W. Yang and M. Yin, *ACS Appl. Mater. Interfaces*, 2014, **6**, 16327.

2 J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley, London, 1970.

3 (a) S. A. Swanson, G. M. Wallraff, J. P. Chen, W. Zhang, L. D. Bozano, K. R. Cater, J. R. Salem, R. Villa and J. C. Scott, *Chem. Mater.*, 2003, **15**, 2305; (b) H. J. Cho, D. H. Hwang, J. I. Lee, Y. K. Jung, J. H. Park, J. Lee, S. K. Lee and H. K. Shim, *Chem. Mater.*, 2006, **18**, 3780; (c) K. Y. Pu, B. Zhang, Z. Ma, P. Wang, X. Y. Qi, R. F. Chen, L. H. Wang, Q. L. Fan and W. Huang, *Polymer*, 2006, **47**, 1970; (d) S. Xiao, M. Nguyen, X. Gong, Y. Cao, H. Wu, D. Moses and A. J. Heeger, *Adv.Funct. Mater.*, 2003, **13**, 25; (e) Y. Zou, J. Zou, T. Ye, H. Li, C. Yang, H. Wu, D. Ma, J. Qin and Y. Cao, *Adv.Funct. Mater.*, 2013, **23**, 1781; (f) Z. Li, B. Jia, Z. Wu, P. Liu, L. Ma, X. Lei, D. Wang, G. Zhou, H. Hu and X. Hou, *J. Mater. Chem. C*, 2013, **1**, 2183.

4 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.

5 (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. Sung, K. S. Wong, P. Gao, I. D. Williams, H. S. Kwok and B. Z. Tang, *J. Phys. Chem B*, 2005, **109**, 10061; (c) Y. Ren, J. W. Y. Lam, Y. Dong, B. Z. Tang and K. S. Wong, *J. Phys. Chem. B*, 2005, **109**, 1135; (d) A. Qin, J. W. Y. Lam, F. Mahtab, C. K. W. Jim, L. Tang, J. Z. Sun, H. H. Y. Sung, I. D. Williams and B. Z. Tang, Appl. Phys. Lett., 2009, **94**, 253308; (e) T. Zhang, Y. Jiang, Y. Niu, D. Wang, Q. Peng and Z. Shuai, *J. Phys. Chem. A*, 2014, 118, 9094; (f) Q. Wu, Q. Peng, Y. Niu, X. Gao and B. Z. Tang, *J. Phys. Chem. A*, 2012, **116**, 3881; (g) S. L. Deng, T. L. Chen, W. L. Chien and J. L. Hong, *J. Mater. Chem. C* 2014, **2**, 651.

6 (a) Y. Dong, J. W. Y. Lam, A. Qin, Z. Li, J. Liu, J. Sun, Y. Dong and B. Z. Tang, *Chem. Phys. Lett.*, 2007, **446**, 124; (b) H. Shi, J. Liu, J. Geng, B. Z. Tang and B. Liu, *J. Am. Chem. Soc.*, 2012, **134**, 9569; (c) Z. Zhao, Z. Wang, P. Lu, C. Y. K. Chan, D. Liu, J. W. Y. Lam, H. H. Sung, I. D. Williams, Y. Ma and B. Z. Tang, *Angew. Chem. Int. Ed.*, 2009, **48**, 7608. (d) L. Chen, Y. B. Jiang, H. Nie, P. Lu, H. H. Y. Sung, I. D. Williams, H. S. Kwok, F. Huang, A. J. Qin, Z. J. Zhao, B. Z. Tang, *Adv. Funct. Mater.*, 2014, **24**, 3621; (e) R. E. Scalise, P. A. Caradonna, H. J. Tracy, J. L. Mullin and A. E. Keirstead, *J. Inorg. Organomet. Polym., Mater.* 2014, **24**, 431; (f) J. Mei, J. Wang, J. Z. Sun, H. Zhao, W. Z. Yuan, C. M. Deng, S. M. Chen, H. H. Y. Sung, P. Lu, A. J. Qin, H. S. kwok, Y. G. Ma, I. D. Williams and B. Z. Tang, *Chem. Sci.,*

2012, **3**, 549; (g) J. Liu, J. W. Y. Lam and B. Z. Tang, *J. Inorg. Organomet. Polym. Mater.,* 2009, **19**, 249; (h) Z. Zhao, B. He and B. Z. Tang, *Chem. Sci.*, 2015, **6**, 5347.

7 (a) Y. Dong, J. W. Y. Lam, A. Qin, J. Liu, Z. Li and B. Z. Tang, *Appl. Phys. Lett.*, 2007, **91**, 011111; (b) H. Zhang, H. Li, J. Wang, J. Z. Sun, A. Qin and B. Z. Tang, *J. Mater. Chem. C*, 2015, **3**, 5162; (c) H. T. Feng, S. Song, Y. C. Chen, C. H. Shen and Y. S. Zheng, *J. Mater. Chem. C*, 2014, **2**, 2353; (d) X. Liu, J. Jiao, X. Jiang, J. Li, Y. Cheng and C. Zhu, *J. Mater. Chem. C*, 2013, **1**, 4713. (e) Z. Zhao, J. W. Y. Lam and B. Z. Tang, *J. Mater. Chem.* 2012, **22**, 23726; (f) J. Huang, N. Sun, Y. Dong, R. Tang, P. Lu, P. Cai, Q. Li, D. Ma, J. Qin and Z. Li, *Adv. Funct. Mater.*, 2013, **23**, 2329; (g) X. G. Gu, J. J. Yao, G. X. Zhang, C. Zhang, Y. L. Yan, Y. S. Zhao and D. Q. Zhang, *Chem. Asian J.,* 2013, **8**, 2362; (h) X. Zhang, Z. Chi, X. Zhou, S. Liu, Y. Zhang and J. Xu, *J. Phys. Chem. C.*, 2012, **116**, 23629; (i) J. Ma, T. T. Lin, X. Y. Pan and W. Z. Wang, *Chem. Mater.* 2014, **26**, 4221; (j) R. Misra, T. Jadhav, B. Dhokale and S. M. Mobin, *Chem. Commun.,* 2014, **50**, 9067; (k) K. R. Ghosh, S. K. Saha and Z. Y. Wang, *Polym. Chem*., 2014, **5**, 5638; (l) W. Dong, T. Fei, A. Palma-Cando and U. Scherf, *Polym. Chem*., 2014, **5**, 4048; (m) J. Li, Y. Li, C. Y. K. Chan, R. T. K. Kwok, H. Li, P. Zrazhevskiy, X. Gao, J. Z. Sun, A. Qin and B. Z. Tang, *Angew. Chem. Int. Ed.,* 2014, **53**, 13518; (n) Z. Chang, Y. Jiang, B. He, J. Chen, Z. Yang, P. Lu, H. S. Kwok, Z. Zhao, H. Qiu and B. Z. Tang, *Chem. Commun.*, 2013, **49**, 594.

8 (a) J. He, B. Xu, F. Chen, H. Xia, K. Li, L. Ye and W. Tian, *J. Phys. Chem. C*, 2009, **113**, 9892; (b) X. Q. Zhang, Z. G. Chi, B. J. Xu, L. Jiang, X. Zhou, Y. Zhang, S. W. Liu and J. R. Xu, *Chem. Commun*., 2012, **48**, 10895; (c) H. Li, X. Zhang, Z. Chi, B. Xu, W. Zhou, S. Liu, Y. Zhang and J. Xu, *Org. Lett.*, 2011, **13**, 556; (d) L. Bu, M. Sun, D. Zhang, W. Liu, Y. Wang, M. Zheng, S. Xue and W. Yang, *J. Mater. Chem. C*, 2013, **1**, 2028; (e) N. Song, D. X. Chen, M. C. Xia, X. L. Qiu, K. Ma, B. Xu, W. Tian and Y. W. Yang, *Chem. Commun*., 2015, **51**, 5526; (f) B. Xu, J. B. Zhang, S. Q. Ma, J. L. Chen, Y. J. Dong and W. J. Tian, *Prog. Chem.*, 2013, **25**, 1079;

9 (a) J. W. Chen, B. Xu, X. Y. Ouyang, B. Z. Tang and Y. Cao, *J. Phys. Chem. A*, 2004, **108**, 7522; (b) Y. Ezhumalai, T. H. Wang and H. F. Hsu, *Org. Lett.*, 2015, **17**, 536; (c) T. Han, Y. J. Zhang, X. Feng, Z. G. Lin, B. Tong, J. B. Shi, J. G. Zhi and Y. P. Dong, *Chem. Commun*., 2013, **49**, 7049; (d) Y. X. Guo, X. Feng, T. Y. Han, S. Wang, Z. G. Lin, Y. P. Dong and B. Wang, *J. Am. Chem. Soc*., **2014**, *136*, 15485.

10 For reviews, see: (a) Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Commun.*, 2009, 4332; (b) Y. Hong, J. W. Y. Lam, and B. Z. Tang, *Chem. Soc. Rev.*, 2011, **40**, 5361; (c) A. J. Qin, J. W. Y. Lam, B. Z. Tang, *Prog. Polym. Sci.*, 2012, **37**, 182; (d) M. Wang, G. Zhang, D. Zhang, D. Zhu and B. Z. Tang, *J. Mater. Chem.*, 2010, **20**, 1858; (e) Z. Chi, X. Zhang, B. Xu, X. Zhou, C. Ma, Y. Zhang, S. Liu and J. Xu, *Chem. Soc. Rev.*, 2012, **41**, 3878; (f) Z. Zhao, J. W. Y. Lam and B. Z. Tang, *J. Mater. Chem.*, 2012, **22**, 23726; (g) J. Mei, Y. N. Hong, J. W. Y. Lam, A. J. Qin, Y. H. Tang, B. Z. Tang, *Adv. Mater.*, 2014, **26**, 5429; (h) R. T. Kwok, C. W. T. Leung, J. W. Y. Lam and B. Z. Tang, *Chem. Soc. Rev.*, 2015, **44**, 4228; (i) H. Wang, E. Zhao, J. W. Y. Lam and B. Z. Tang, *Mater. Today*, 2015, **18**, 365; (j) M. Chen, J. Z. Sun, A. Qin and B. Z. Tang, *Chinese Sci. Bull.*, 2015, DOI: 10.1360/N972015-00760; (k) Z. Li and A. Qin, *National Sci. Rev.*, 2014, **1**, 22.

11 M. Chen, L. Li, H. Nie, J. Tong, L. Yan, B. Xu, J. Z. Sun, W. Tian, Z. Zhao, A. Qin and B. Z. Tang, *Chem. Sci.*, 2015, **6**, 1932.

12 (a) C. W. Ko, Y. T. Tao, A. Danel, L. Krzemińska, and P. Tomasik, *Chem. Mater.*, 2001, **13**, 2441; (b) H. F. Yang, W. F. Su and Y. Chen, *New J. Chem.*, 2011, **35**, 1219; (c) E. Bellmann, G. E. Jabbour, R. H. Grubbs and N. Peyghambarian, *Chem. Mater.*, 2000, **12**, 1349; (d) Q. Y. Chen, L. Kong, Y. P. Tian, X. Y. Xu, L. M. Yang, G. B. Zhang, W. B. Jia and J. X. Yang, *Rsc Adv.*, 2014, **4**, 18981.

13 (a) W. Z. 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; (b) 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.

14 (a) W. Qin, D. Ding, J. Liu, W. Z. Yuan, Y. Hu, B. Liu and B. Z. Tang, *Adv. Funct. Mater.*, 2012, **22**, 771; (b) W. Qin, K. Li, G. Feng, M. Li, Z. Yang, B. Liu and B. Z. Tang, *Adv. Funct. Mater.*, 2014, **24**, 635; (c) W. Huang, F. Tang, B. Li, J. Su and H. Tian, *J. Mater. Chem. C*, 2014, **2**, 1141; (d) W. Huang, H. Wang, L. Sun, B. Li, J. Su and H. Tian, *J. Mater. Chem. C*, 2014, **2**, 6834.

15 S. Cacchi, G. Fabrizi, A. Goggiamani, A. Iazzetti and R. Verdiglione, *Synthesis*, 2013, **45**, 1701.

16 H. Ren, J. Li, T. Zhang, R. Wang, Z. Gao and D. Liu, *Dyes Pigments*, 2011, **91**, 298.

17 N. S. Nandurkar, M. J. Bhanushali, M. D. Bhor and B. M. Bhanage, *Tetrahedron Lett.*, 2007, **48**, 6573.

18 Y. Liu, S. M. Chen, J. W. Y. Lam, P. Lu, R. T. K. Kwok, F. Mahtab, H. S. Kwok and B. Z. Tang, *Chem. Mater.*, 2011, **23**, 2536.

19 (a) R. Hu, E. Lager, A. Aguilar-Aguilar, J. Liu, J. W. Y. Lam, H. H. Y. Sung, I. D. Williams, Y. Zhong, K. S. Wong, E. Peña-Cabrera and B. Z. Tang, *J. Phys. Chem. C,* 2009, **113**, 15845; (b) E. Wang, J. W. Y. Lam, R. Hu, C. Zhang, Y. S. Zhao and B. Z. Tang, *J. Mater. Chem. C*, 2014, **2**, 1801; (c) M. Chen, L. Li, H. Nie, Y. Shi, J. Mei, J. Wang, J. Z. Sun, A. Qin and B. Z. Tang, *Chem. Commun.*, 2015, **51**, 10710.

20 (a) X. Luo, J. Li, C. Li, L. Heng, Y. Q. Dong, Z. Liu, Z. Bo and B. Z. Tang, *Adv. Mater.*, 2011, **23**, 3261; (b) Z. Chen, J. Zhang, M. Song, J. Yin, G. A. Yu and S. H. Liu, *Chem. Commun.*, 2015, **51**, 326.

21 (a) L. Qian, B. Tong, J. Shen, J. Shi, J. Zhi, Y. Q. Dong, F. Yang, Y. P. Dong, J. W. Y. Lam, Y. Liu and B. Z. Tang, *J. Phys. Chem. B,* 2009, **113**, 9098; (b) Y. Dong, J. W. Y. Lam, A. Qin, Z. Li, J. Sun, H. H. Y. Sung, I. D. Williams and B. Z. Tang, *Chem. Commun.*, 2007, 40.

22 A. Qin, J. W. Y. Lam, H. Dong, W. Lu, C. K. W. Jim, Y. Dong, M. Häussler, H. H. Y. Sung, I. D. Williams, G. K. L. Wong and B. Z. Tang, *Macromolecules,* 2007, **40**, 4879.

23 N. S. Makarov, M. Drobizhev and A. Rebane, *Opt. Express*, 2008, **16**, 4029.

Journal of Materials Chemistry C

ARTICLE

Table of content