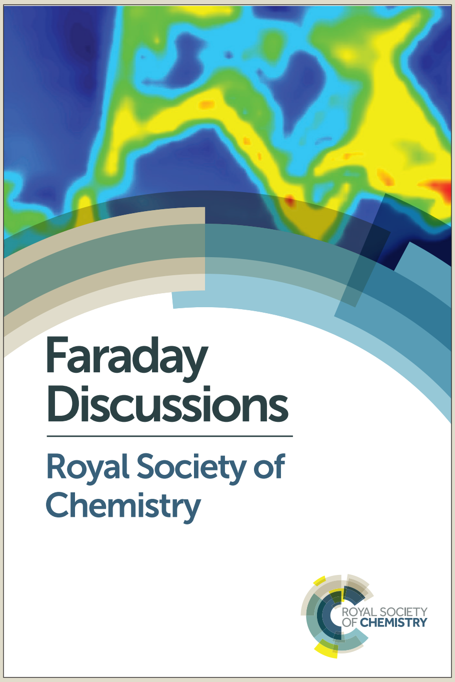
View Article Online
View Journal

Faraday Discussions

Accepted Manuscript

This manuscript will be presented and discussed at a forthcoming Faraday Discussion meeting. All delegates can contribute to the discussion which will be included in the final volume.

Register now to attend! Full details of all upcoming meetings: http://rsc.li/fd-upcoming-meetings



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

This article can be cited before page numbers have been issued, to do this please use: L. Li, H. Nie, M. Chen, J. Z. Sun, A. Qin and B. Z. Tang, *Faraday Discuss.*, 2016, DOI: 10.1039/C6FD00163G.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/faraday_d

View Article Online
DOI: 10.1039/C6FD00163G

Journal Name

RSCPublishing

COMMUNICATION

Aggregation-enhanced emission active tetraphenylbenzene-cored efficient blue light emitter

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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

A tetraphenylbenzene (TPB) cored luminophore of TPB-AC with aggregation-enhanced emission characteristics was designed and synthesized. TPB-AC could be potentially applied in fabrication of high performance organic light-emitting diodes (OLED) with blue light emission.

Organic light-emitting diodes (OLED) have drawn considerable attention for their huge commercial value in full-colour display and lighting applications.[1] While, for the former, red, green and blue (RGB) are three elementary colours, of which the efficient blue emissive materials is the most difficult to obtain because of the high energy gap, which is hard for charge injection and lack of the balance of charge transport.[2] However, the blue light plays a critical role in creating white light and phosphosphoresence with long wavelength emission via energy transfer.[3] Thus, it's of great importance to develop blue OLED materials with high efficiency, and there is still a broad space for researchers to explore.

In conventional blue-emissive organic emitters, anthracene, pyrene, fluorene and carbazole derivatives etc. have received wide interests.[4] Most of these fluorophores have planar conjugated conformation, thus the fluorescence quenching and wavelength change via excimer formation in their condensed phases cannot be avoided.[5] To alleviate this problem, several physical and chemical approaches have been developed. For example, blue emitters have been doped in host materials to dilute their concentration and to enhance their emission. In addition, branched chains, bulky cyclics and spiro links have been introduced on the rigid conjugated structure to supress the formation of aggregates.[6] However, such processes always need fussy skills and pay unnecessary price because molecule aggregation is a natural process.

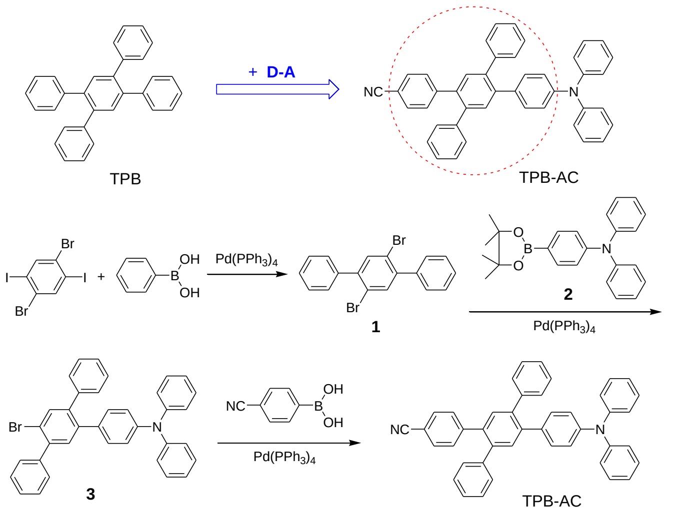
Delightfully, the usage of aggregates to enhance the fluorophore emission was realized by Tang et al. in 2001. They found that a series of fluorophores, such as hexaphenylsilole (HPS), tetraphenylethene (TPE) and their derivatives emit greatly in the aggregate states but give no or weak emission in their dilute solution, thus they coined this unique phenomenon as "aggregation-induced emission (AIE)".[7] The AIE has boosted the real-world application of AIE-active luminogens (AIEgens) in the fields of OLED and biological imaging, etc.[8]

Among the reported AIEgens, TPE, silole, distyrylanthracene, triphenylethene, tetraphenylpyrazene, tetraphenyl-1,4-butadiene *etc.* are the most used ones for these applications.[9-14] To enrich the family of AIEgens and to realize broad applications especially in the area of OLED, new AIEgens should be further explored according to the AIE mechanism of restriction of intramolecular motion (RIM, including rotation and vibration).[15] In our previous work, we established an unambiguous structure-property relationship of polyphenyls through turning the number and position of substituted phenyl rings on the benzene core.[16] During the study, we found tetraphenylbenzene (TPB) is AIE-active and suitable for decoration to furnish desirable functionalities. TPB is structurally similar to TPE with the double-bond replaced by the benzene ring, thus, TPB possesses a better thermal stability than TPE, with its decomposition temperature higher than 30 ^{o}C.[17] In addition, TPB emits at 380 nm in the aggregate state. It provides a good platform to generate deep blue emitters by enlarging the conjugation or introduction of donors and acceptors, which is hard for TPE to fulfil this application because it already emits at 445 nm.[18] Thus, it is very attractive to achieve efficient and stable deep-blue solid emitters based on TPB via molecular engineering.

Alone this line, we decorated TPB core with electron-donating diphenylamino and electron-accepting cyano groups and generated a new emitter named TPB-AC (Scheme 1). It is worth noting that the triphenylamine moiety in TPB-AC is widely used in blue OLED as hole transporting materials. As shown in Scheme 1, TPB-AC was prepared in three steps, all of which are finished by Suzuki reactions in comparatively high yields. The chemical structures of the intermediates and product were characterized spectroscopically and satisfactory results corresponding to their structures were obtained. Their ^{1}H and ^{13}C NMR and high resolution Mass spectra were shown in electronic supplementary information (ESI†, Fig. S1-S5).

Afterward, the thermal property of TPB-AC was evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen atmosphere (Fig. S6, ESI†). The TGA measurement showed that TPB-AC possesses an excellent thermal stability with 5% loss of its weight at temperature as high as 365 ^{o}C, which is about 100 ^{o}C higher than that of TPB itself, manifesting that subtle structural modification will greatly improve the thermal stability of TPB derivatives. Whereas, in the DSC curve, there is no phase transition occurred except for a melting peak at 253

View Article Online
DOI: 10.1039/C6FD00163G



Scheme 1. Tailor rule from TPB to TPB-AC and synthetic route to TPB-AC.

°C for the first scan, suggesting that TPB-AC is hard to crystalize, which will be especially advantageous in OLED applications.

Next, we investigated the photo-physical property of TPB-AC. Due to its donor-π-acceptor structure, the maximum absorption (λ_{ab}) of TPB-AC was observed at 342 nm, which is bathochromically shifted in comparison with that of TPB (Fig. S7, ESI†). Unlike TPB, TPB-AC emits intensely both in solution and solid states but with ref-shift of its peak.

To give a clear perception of emission behaviour of TPB-AC, we investigated its PL behaviours in THF/water mixtures with different water fractions (f_w). As can been in Figure 1, TPB-AC emits intensely at 479 nm in diluted THF solution. After adding 10% volume ratio of water, the emission intensity was weakened with its maximum emission wavelength (λ_{em}) red-shifted by 16 nm. Such trend sustainedly unchanged until the f_w was up to 60% with a change of λ_{em} about 47 nm and PL intensity decreased by 4.7-fold. Although the emission intensity continued to weaken with $f_w = 70\%$, its emission peak began to shift hypsochromically. Since then, the light emission is invigorated and intensified greatly accompanying with gradual blue-shift of λ_{em} with further increasing f_w. Compared to the intensity in the THF/water mixtures with f_w of 70%, the emission is increased by 11.6-fold. According to these results, we can conclude that TPB-AC features the unique characteristics of aggregation-enhanced emission. Such trend in change of PL intensity was also in consistent with the result of quantum yields tested in THF/water mixtures (Fig. S8, ESI†). It is worth noting that such emission phenomenon was reported frequently in donor-acceptor system by our group before. When $f_w \leq 60\%$, increase of f_w just improves the solvent polarity of mixed solvents, which have led the molecules to have the twisted intramolecular charge transfer (TICT) process and quench the emission. When a large amount of water ($f_w \geq 70\%$) was added, aggregates were formed because of the worsened solvating ability of the mixture solvents. Thus, the emission from the locally excited (LE) state was observed. In other words, an aggregation-induced LE state emission is activated.[19] Moreover, the intramolecular rotations of the phenyl rings of TPB-AC were also restricted. These two effects together induce TPB-AC to enhance its emission and to blue-shift its peaks.

Besides, we also examined the lifetime (τ) of TPB-AC both in THF and thin-solid film, with their τ values deduced to be 3.19 and 3.14 ns, respectively, indicating that the emissive species belongs to fluorescence (Fig. S9, ESI†).

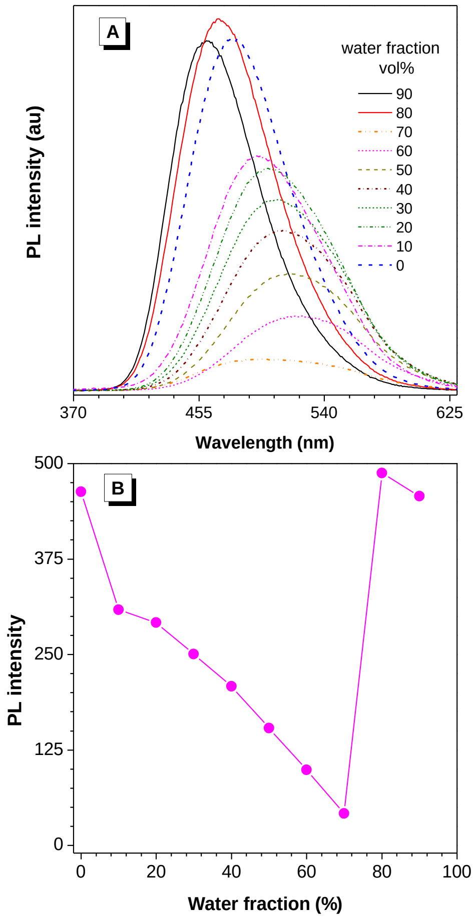


Figure 1. (A) PL spectra and (B) changes in PL intensity of TPB-AC in THF/water mixtures with different water fraction; λ_{ex}=341 nm; concentration = 10 μM.

Similar to other fluorophores with donor-π-acceptor structures, TPB-AC also shows the unique solvatochromism effect.[20] As depicted in Figure 2A, the λ_{em} of TPB-AC changed dramatically from 418 to 535 nm with increasing solvent polarity from hexane to DMF (Fig. S10, ESI†). However, the variation of polarity has less influence on λ_{ab}. The large solvatochromism can be attributed to intramolecular charge-transfer (ICT) process. The influence of solvent polarity parameter (Δf) on Stokes shift could be calculated via Lippert-Mataga equation shown below:

$$\Delta\upsilon \equiv \boldsymbol{v_{ab}} - \boldsymbol{v_{em}} = \frac{2\Delta f}{hac^3}\left(\boldsymbol{\mu_e}-\boldsymbol{\mu_g}\right)^2 + \boldsymbol{const}$$

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

Where, Δv 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. The linear dependence of Δv *vs* Δf together with the large slope of the Δf–Δv plot (the fitting ratio is 18360, Fig. 2B) suggests that the ICT excited state has a larger dipolar moment than the ground state due to the substantial charge redistribution, which is probably derived from the relaxation of the initially formed Franck-Condon excited state instead of direct transition from the ground state.[21]

View Article Online
DOI: 10.1039/C6FD00163G

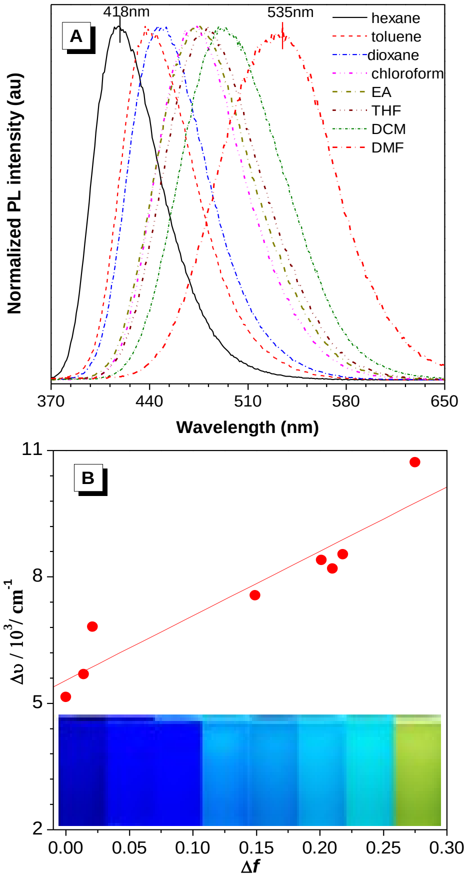
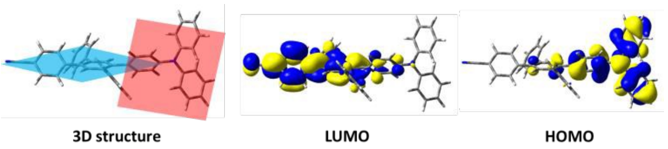


Figure 2. PL spectra (A) of TPB-AC (concentration = 10 μM, λ_{ex}= 341 nm) in solvents with different polarity parameters (Δ*f*). (B) Plot of Stokes shift (Δυ) of TPB-AC versus solvent polarity parameter (Δ*f*) of their solutions. Inset: light emission of TPB-AC solutions in hexane (left) toluene, dioxane, chloroform, ethyl acetate, THF, dichloromethane, and *N,N*-dimethylformamide (right). The photographs were taken under illumination of a hand-hold 365 nm UV lamp.



3D structure LUMO HOMO

Figure 3. Optimized molecular structure and frontier orbitals of TPB-AC.

We try to growth single crystal of TPB-AC to further understand the molecular and electronic structure but unfortunately failed, mostly due to the excellent morphological stability of molecule as described above. We thus in turn performed the theoretical calculation using DFT/B3LYP/6-31G(d). The simulated 3D structure indicates that TPB-AC adopts a twisted conformation and almost perpendicular orientation between the donor and the acceptor moieties, and the LUMO and HOMO localized on donor and acceptor moieties, respectively, with only a little electron cloud overlapping, This result may probably be caused by large dihedral angle and contrary electron property of these two units. Moreover, the energy level of LUMO and HOMO was calculated to be -1.62 and -5.03 eV, respectively, which is very close to the experimental results (-1.96 and -5.18 eV, respectively) tested by Cyclic Voltammetry (Fig. S11, ESI†). The theoretical and experimental analyses also demonstrate that the introduction of electron-donating group contributed more to TPB-AC with its E_{HOMO} elevated obviously, while electron-drawing cyano group has less influence on variation of energy level.

Table 1. EL performance of TPB-AC based devices.

	V_{on} [b] (V)	L [a] (cdm^{-2})	η_{C} [a] (cdA^{-1})	η_{P} [a] (lmW^{-1})	EQE[a]	CIE (x,y)[c]
I	4.0	4748	2.94	2.19	2.43	(0.15, 0.14)
II	3.2	4629	3.25	3.06	2.92	(0.15, 0.12)

[a] The luminescence (L), 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. [c] CIE coordinates at 100 mA/cm^2. Device configuration: I: ITO/NPB (60 nm)/TPB-AC (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al; II: ITO/NPB (40 nm)/TPB-AC (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al.

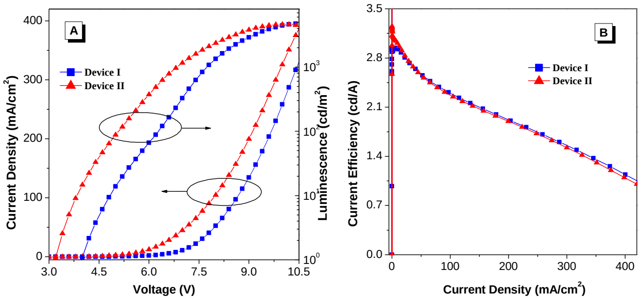


Figure 4. (A) Current density and luminescence versus voltage characteristic of TPB-AC based devices; (b) Current efficiency versus voltage characteristic of TPB-AC based devices. Device configuration: I: ITO/NPB (60 nm)/TPB-AC (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al; II: ITO/NPB (40 nm)/TPB-AC (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al.

As we discussed aforementioned, TPB-AC emits intensely in the aggregate state. Similarly, its nanoparticles, film and powder also show strong emission with absolute photoluminescence quantum efficiency of 61.33, 49.59, and 69.4%, respectively. Thus, TPB-AC is an ideal material to fabricate deep blue OLED in combination with its maximum emission at right 452 nm in the film state.

Keep this in mind, we fabricated two devices with TPB-AC as emitting layers with structure configuration of ITO/NPB (60/40 nm)/TPB-AC (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al, where*N,N*-bis(1-naphyhyl)-*N,N*-diphenylbenzidine (NPB) and 2,2′,2′′-(1,3,5-benzine-triyl)tris(1-phenyl-1-*H*-benzimidazole) (TPBi) act as hole-transporting layer and electron-transporting layer, respectively.

The difference between devices I and II is the hole-transporting layer: the former (60 nm) is 20 nm thicker than that of the latter. The electroluminescence (EL) performances of devices are summarized in Table 1 and Figure 4. Both devices show their EL at 458 nm, about 6 nm red-shifted compared to that of PL spectra in film. Such little change in emissive wavelength can be usually attributed to a microcavity effect. Device I is turned on at 4.0 V and exhibits a L_{max} of 4848 cdm^{-2}, a $\eta_{\mathrm{C,max}}$ of 2.94 cd A^{-1}, a $\eta_{\mathrm{P,max}}$ of 2.19 lm W^{-1} and a $\eta_{\mathrm{ext,max}}$ of 2.43%. After optimizing the structure, Device II performs better, with its V_{on} as low as 3.2V and $\eta_{\mathrm{C,max}}$ up to 2.92%. In addition, Device II exhibits a much better color purity in blue with its CIE$_{(x,\ y)}$ coordination (0.15, 0.12) at 100 mA cm^{-2}. All these results indicates an OLED fabricated with TPB-AC as emitting layer can perform efficiently with deep blue EL and is suitable for photoelectric application. In addition, we also tried to simplify the device configuration through making TPB-AC function both as emitting and hole-transporting layers because the incorporated TPA often elevates the HOMO energy and facilitates the hole transporting in the devices. However, this attempt met with some difficulties and is getting on with investigation in our laboratory.

View Article Online
DOI: 10.1039/C6FD00163G

Conclusions

In summary, a TPB derivative of TPB-AC was designed and synthesized by incorporation of electron-donating diphenylamino group and electron-withdrawing cyano groups, which exhibits the unique AEE feature. TPB-AC is thermally stable and emits strongly in the condensed phases with high quantum efficiency. The OLEDs fabricated with TPB-AC as emitting layers perform efficiently with deep blue emission, indicative of its potential application in optoelectronic field.

This work was partially supported by the National Science Foundation of China (21525417and 21490571); the key project of the Ministry of Science and Technology of China (2013CB834702), The National Program for Support of Top-Notch Young Professionals, and the Innovation and Technology Commission (ITC-CNERC14SC01). A.J.Q. and B.Z.T. thank the support from the National Science Foundation of Guangdong Province (2016A030312002) and Guangdong Innovative Research Team Program (201101C0105067115).

Notes and references

[a] *MOE Key Laboratory of Macromolecule Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China.*

[b] *State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China.*

[c] *Department of Chemistry, Hong Kong Branch of National Engineering Research Center for Tissue Restoration & Reconstruction, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong China.*

† Electronic Supplementary Information (ESI) available: Experimental section, schemes, characterization spectra, detailed detection procedures, full data. See DOI: 10.1039/c000000x/

1 (a) C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, 1987, **51**, 913; (b) J. E. Anthony, *Chem. Rev.*, 2006, **106**, 5028.

2 (a) W. Li, L. Yao, H. Liu, Z. Wang, S. Zhang, S. Zhang, R. Xiao, H. Zhang, P. Lu, B. Yang and Y. Ma, *J. Mater. Chem. C*, 2014, **2**, 4733; (b) C. Chien, C. Chen, F. Hsu, C. Shu, P. Chou and C. Lai, *Adv. Funct. Mater.*, 2009, **19**, 560.

3 (a) K. V. Rao, K. K. R. Datta, M. Eswaramoorthy and S. J. George, *Adv. Mater.*, 2013, **25**, 1713; (b) J. Ye, C. Zheng, X. Ou, X. Zhang, M. Fung and C. Lee, *Adv. Mater.*, 2012, **24**, 3410.

4 (a) Y. H. Kim, H. C. Jeong, S. H. Kim, K, Yang and S. K. Kwon, *Adv. Funct. Mater.*, 2005, **15**, 1799; (b) T. M. Figueira-Fuarte and K. Mllen, *Chem. Rev.*, 2011, **111**, 7260; (c) W. Huang, L. Chi, W. Chen, Y. Chen, S. Chou and K. Wong, *J. Mater. Chem.*, 2010, **20**, 10113; (d) A. L. Fischer, K. E. Linton, K. T. Kamtekar, C. Pearson, M. R. Bryce and M. C. Petty, *Chem. Mater.*, 2011, **23**, 1640.

5 (a) Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Soc. Rev.*, 2011, **40**, 5361; (b) Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Commun.*, 2009, 4332.

6 (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. Cho, D. Hwang, J. Lee, Y. Jung, J. Park, J. Lee, S. Lee and H. Shim, *Chem. Mater.*, 2006, **18**, 3780.

7 (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) Y. Dong, J. W. Y. Lam, A. Qin, J. Liu, Z. Li and B. Z. Tang, *Appl. Phys. Lett.*, 2007, **91**, 011111-1.

8 (a) J. Mei, N. L. C. Leung, R. T. K. Kwok, J. W. Y. Lam, B. Z. T. *Chem. Rev*. 2015, **115**, 11718; (b) Z. Zhao, J. W. Y. Lam, B. Z. Tang, *J. Mater. Chem.*, 2012, **22**, 23726; (c) D. Ding, K. Li, B. Liu and B. Z. Tang, *Acc. Chem. Res.*, 2013, **46**, 2441.

9 (a) 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; (b) R. E. Scalise, P. A. Caradonna, H. J. Tracy, J. L. Mullin, A. E. Keirstead, *J. Inorg. Organomet. Polym. Mater*. 2014, **24**, 431; (c) J. Liu, J. W. Y. Lam and B. Z. Tang, *J. Inorg. Organomet. Polym. Mater*. 2009, **19**, 249.

10 (a) 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; (b) X. G. Gu, J. J. Yao, G. X. Zhang, C. Zhang, Y. L. Yan, Y. S. Zhao, D. Q. Zhang, *Chem. Asian J*. 2013, **8**, 2362; (c) X. Zhang, Z. Chi, X. Zhou, S. Liu, Y. Zhang and J. Xu, *J. Phys. Chem. C.*, 2012, **116**, 23629; (d) R. Misra, T. Jadhav, B. Dhokale, S. M. Mobin, *Chem. Commun.* 2014, **50**, 9067; (e) K. R. Ghosh, S. K. Saha, Z. Y. Wang, *Polym. Chem*. 2014, **5**, 5638; (f) W. Dong, T. Fei, A. Palma-Cando, U. Scherf, *Polym. Chem*. 2014, **5**, 4048.

11 (a) B. Xu, J. B. Zhang, S. Q. Ma, J. L. Chen, Y. J. Dong, W. J. Tian, *Prog. Chem*. 2013, **25**, 1079; (b) X. Q. Zhang, Z. G. Chi, B. J. Xu, L. Jiang, X. Zhou, Y. Zhang, S. W. Liu, J. R. Xu, *Chem. Commun*., 2012, **48**, 10895.

12 (a) X. Zhang, Z. Chi, B. Xu, C. Chen, X. Zhou, Y. Zhang, S. Liu, J. Xu, *J. Mater. Chem*., 2012, *22*, 18505; (b) H. Li, X. Zhang, Z. Chi, B. Xu, W. Zhou, S. Liu, Y. Zhang, J. Xu, *Org. Lett*., 2011, *4*, 556.

13 (a) J. W. Chen, B. Xu, X. Y. Ouyang, B. Z. Tang, Y. Cao, J. Phys. Chem. A. 2004, *108*, 7522; (b) T. Han, Y. J. Zhang, X. Feng, Z. G. Lin, B. Tong, J. B. Shi, J. G. Zhi, Y. P. Dong, *Chem. Commun*. 2013, 49, 7049; (c) Y. X. Guo, X. Feng, T. Y. Han, S. Wang, Z. G. Lin, Y. P. Dong, B. Wang, *J. Am. Chem. Soc*. 2014, *136*, 15485.

14 M. Chen, H. Nie, B. Song, L. Z. Li, J. Z. Sun, A. J. Qin, B. Z. Tang, *J. Mater. Chem. C* 2016, **4**, 2901; (b) M. Chen, L. Z. Li, H. Nie, J. Q. Tong, L. L. Yan, B. Xu, J. Z. Sun, W. J. Tian, Z. J. Zhao, A. J. Qin, B. Z. Tang, *Chem. Sci*. 2015, *6*, 1932; (c) Z. T. Wang, Y. Fang, J. Z. Sun, A. J. Qin, B. Z. Tang, *Sci. China Chem*., 2013, **56**, 1187.

15 J. Mei, Y. N. Hong, J. W. Y. Lam, A. J. Qin, Y. H. Tang, B. Z. Tang, *Adv. Mater*. 2014, **26**, 5429.

16 L. Z. Li, M. Chen, H. K. Zhang, H. Nie, J. Z. Sun, A. J. Qin, B. Z. Tang, *Chem. Commun*. 2015, **51**, 4830.

17 Z. Zhao, S. Chen, J. W. Y. Lam, C. K. W. Jim, C. Y. K. Chan, Z. Wang, P. Lu, C. Deng, H. S. Kwok, Y. Ma and B. Z. Tang, *J. Phys. Chem. C.*, 2010, **114**, 7963.

18 (a) X. J. Zhan, Z. B. Wu, Y. X. Lin, Y. J. Xie, Q. Peng, Q. Q. Li, D. G. Ma, Z. Li, *Chem. Sci*., 2016, **7**, in press; (b)

19 R. Hu, E. Lager, A. Aguilar-Aguilar, J. Liu, J. W. Y. Lam, H. H. S. Sung, I. D. Williams, Y. Zhong, K. S. Wong, E. Pena-Cabrera and B. Z. Tang, *J. Phys. Chem. C*, 2009, **113**, 15845.

20 J. Mei, J. Wang, J. Z. Sun, H. Zhao, W. Yuan, C. Deng, S. Chen, H. H. Y. Sung, P. Lu, A. Qin, H. S. Kwok, Y. Ma, I. D. Williams and B. Z. Tang, *Chem. Sci*., 2012, **3**, 549.

DOI: 10.1039/C6FD00163G

21 (a) H. Y Woo, B. Liu, B. Kohler, D. Korystov, A. Mikhailovsky; G. C. Bazan, *J. Am. Chem. Soc*. 2005, **127**, 14721; (b) A. J. Qin, J. W. Y. Lam, H. C. Dong, W. Lu, C. K. W. Jim, Y. Q. Dong, M. Häussler, H. H. Y. Sung, I. D. Williams, G. K. L. Wong, B. Z. Tang, *Macromolecules* 2007, **40**, 4879.