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Soluble conjugated porous organic polymer: efficient white light emission in solution, nanoparticles, gel and transparent thin film

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Tetraphenylcyclopentadiene based a multifunctional, solution processable, fluorescent, ultramicroporous polymer exhibiting high hydrogen uptake was employed for encapsulation of dyes to obtain enhanced white light emission in solution, nanoparticles, gel and transparent thin film. Hybrid nanoparticles showed a quantum yield of 35% with high color rendering index.

White light emitting (WLE) materials have gained significant attention because of its multi-stimuli responsive properties and applications in lighting and display devices.[1-3] The extensive use of hazardous mercury vapour in commercial white light emitting devices like fluorescent lamps possesses a serious threat to the environment. Thus, the development of a cost-effective, environmentally benign and convenient protocol for solid state white light emission with high quantum efficiency is in increasing demand. The WLE system can be obtained with the combination of three primary colors blue, green and red or only blue and yellow covering the wavelength range of 400-800 nm.[4,5] The typical WLE material is designed using the combination of multichromophoric components or a single molecular material with multifunctional emitters.[6,7] Various kinds of materials based on small organic molecules, π-conjugated polymers and porous solids like metal-organic frameworks (MOFs) have been explored for white light emission.[1-8]

Currently, the conjugated porous organic polymers (CPOPs) have emerged as fascinating materials with diverse applications in gas storage, catalysis, light harvesting, energy storage and chemo/bio-sensing.[9-18] In addition to high thermal and hydrothermal stabilities due to the covalent bonds, the unique combination of π-electron conjugation as well as porosity makes CPOPs highly promising for multifunctional applications.[12] The porous structures affect the efficiency of energy transfer between the polymer and encapsulated dyes leading to the tuning of fluorescence including white light emission.[19] However, due to the lack of solution processability of CPOPs, fabrication of white light emitting system with high quantum yield still remain a challenge. As proposed by Cooper and coworkers, processability has now been considered as an important functional property of new porous materials.[20] Thus, imparting solution processability in CPOPs and utilizing them for efficient white light generation is an important research problem to address.

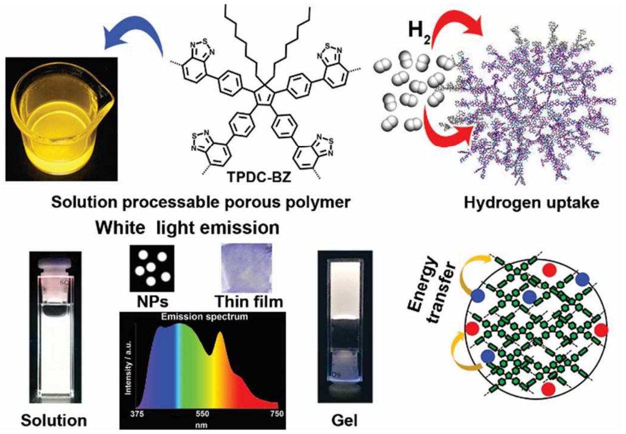

Fig. 1 The schematic illustration depicting the versatile use of a strongly fluorescent and soluble porous organic polymer (TPDC-BZ) for hydrogen uptake and efficient white light emission in solution, nanoparticles (NPs), gel and thin film, by utilizing energy transfer between the polymer and encapsulated dyes.

We have synthesized a strongly fluorescent, soluble CPOP using tetrakis-(4-bromophenyl)-5,5-dioctyl cyclopentadiene (TBDC) and benzothiadiazole (BZ). The polymer (TPDC-BZ, Fig. 1) exhibited ultramicroporosity and an appreciable H_2 uptake capacity. This communication focusses on the fabrication of efficient WLE systems in four different forms viz. solution, aqueous dispersion of nanoparticles, gel as well as the transparent thin film by incorporating suitable fluorescent dyes in TPDC-BZ polymer matrix (Fig. 1). The excited state processes were elucidated by time-resolved emission spectra

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measurements. Even though very few examples of fabrication of WLE materials based on porous polymers exist,[19,21] to the best of our knowledge, the present study is the first report on implementation of solution processable CPOP for the efficient generation of white light as many as four different forms.

Extensive crosslinking in the network polymers reduces solubility. Hence, a simple, easily attainable fabrication method resulting in soluble CPOP with high surface area is desirable. In this study, we developed highly porous and strongly fluorescent soluble CPOP by employing A_4 + B_2 type Suzuki-Miyaura polycondensation between TBDC and 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) (Scheme S5, see ESI†). The resultant polymer TPDC-BZ was found to be soluble in common organic solvents like toluene, tetrahydrofuran (THF), chloroform ($CHCl_3$) and dichloromethane (DCM). The long alkyl chains in tetraphenyl)-5,5-dioctyl cyclopentadiene (TPDC) impart flexibility and help to solubilize the polymer. High surface area, solution processability and strong low-energy fluorescence open up the possibilities of multifunctional applications using TPDC-BZ (*vide infra*).

The FTIR spectrum of TPDC-BZ show the characteristic bands corresponding to aliphatic C-H stretching (2850 cm^{-1} and 2925 cm^{-1}), C_{Ar}-H stretching (3046 cm^{-1}) and aromatic C=C stretching (1482 cm^{-1}, Fig. S1†). ^1H NMR spectrum of TPDC-BZ compared with that of constituent monomers clearly indicates similar resonances in addition to other resonances demonstrating polycondensation between the monomers (Fig. S4†). ^{13}C NMR of TPDC-BZ shows the peaks at 153 and 155 ppm attributed to benzothiadiazole moiety and the peaks at 14 to 35 ppm correspond to the aliphatic carbons of TPDC core (Fig. S5†). The weight average molecular weight (*Mw*) of TPDC-BZ was found to be 5.4 kDa with a polydispersity index of 1.5 as determined by gel permeation chromatography (GPC, Fig. S6). The thermogravimetric analysis (TGA) indicates that the polymer is thermally stable up to 370 ^{o}C (Fig. S7†). The surface morphology of the TPDC-BZ as characterized by field emission scanning electron microscopy (FESEM), reveal globular morphology with rough surfaces (Fig. S8†).

Nitrogen sorption profile of TPDC-BZ was found to follow type (II) adsorption isotherm (Fig. 2a). At low-pressure region, high gas uptake indicates microporous nature of the polymer. The Brunauer-Emmett-Teller (BET) surface area of TPDC-BZ were estimated to be 610 m^2 g^{-1} (Fig. 2a, Fig. S9a). The micropore surface area and external surface area were found to be 330 m^2 g^{-1} and 280 m^2 g^{-1} respectively as determined by t-plot method (Fig. S10). TPDC-BZ was obtained by rapid precipitation of chloroform solution to ultracold methanol. It has been observed by researchers that rapidly precipitated polymers show high surface area because of the inefficient packing.[22] During the course of precipitation, the collapsing of pores is restricted due to relatively smaller strut length,[23] as is the case in TPDC-BZ leading to its higher surface area.

The pore volume of TPDC-BZ is 0.73 cm^3 g^{-1} at a relative pressure of P/P_0 = 0.99. The pore size was found to be 0.7 nm as determined by nonlocal density functional theory (NLDFT) method indicating ultramicroporous nature (Fig. 2a, inset). The hydrogen sorption profile show type III adsorption isotherm. H_2 uptake by TPDC-BZ was found to be 143 cm^3 g^{-1} (6.4 mmol g^{-1} or 1.3 wt% at 1 bar, 77 K, Fig. 2b). H_2 uptake capacity of TPDC-BZ is higher than the reported soluble CPOP like SCMP1 (3.9 mmol g^{-1}, S_{BET} = 505 m^2 g^{-1})[20a] and comparable to insoluble microporous polymers having similar surface areas under identical conditions such as CPOP-7 (1.5 wt%, S_{BET} = 1430 m^2 g^{-1}),[9d] BB-POP-3 (1.1 wt%, S_{BET} = 560 m^2 g^{-1}),[9f] BDT-2 (1.5 wt%, S_{BET} = 571 m^2 g^{-1}).[12] The efficient hydrogen uptake by TPDC-BZ is attributed to its small pore size. It has been observed that small pores facilitate the interactions of hydrogen molecules with pore walls leading to higher enthalpies of adsorption.[24]

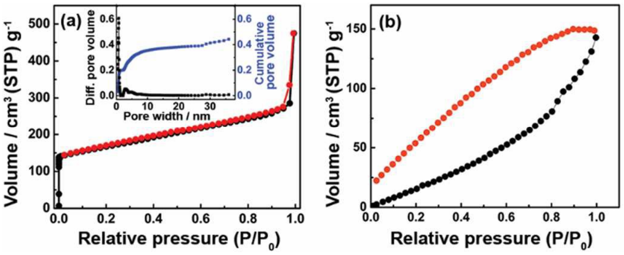

Fig. 2 (a) Nitrogen sorption isotherm of TPDC-BZ at 77 K; inset: pore size distribution estimated using NLDFT method (black squares: differential pore volume and blue squares: cumulative pore volume). (b) H_2 sorption isotherm of TPDC-BZ at 77 K. Black circles: adsorption and red circles: desorption.

The electronic absorption spectrum of TPDC-BZ in THF shows peaks at 305 and 388 nm (Fig. S12†). Absorption peaks at UV region are presumably due to $\pi-\pi^*$ transition of the conjugated framework. Absorption and excitation spectra were found to be similar in solvents of varying polarity (Table S1†). TPDC-BZ polymer showed strong yellow fluorescence in THF (ϕ_F = 46%) with a peak at 577 nm (Fig. 1 and 3a). Emission spectra depict a considerable red shift as the solvent polarity increases; emission maximum shifts from 550 nm in toluene to 600 nm in DCM (Fig. 3a). Such positive solvatochromism in emission indicates a highly polar excited state, presumably originating from the benzothiadiazole moiety.[13]

TPDC-BZ can provide a promising scaffold for encapsulating dyes due to its porous nature. Therefore, a blue emitting dye 5-octyl-1,2,3,4,5-pentaphenyl-1,2-cyclopentadiene (OPCP, Scheme S6, $\lambda_{em}^{max} = 435\,nm$) was mixed with yellow fluorescent TPDC-BZ. 0.5 mg mL^{-1} of TPDC-BZ and 0.1 M OPCP in THF were used as stock solution. The concentration of blue and yellow emitting solution was optimized to get the white light emission (Fig. S13†). Three parameters to evaluate the quality of white light are Commission Internationale de l'Eclairage (CIE) coordinates (x = 0.33, y = 0.33), color rendering index (CRI†) and correlated color temperature (CCT†).[1,8] The CIE color coordinates of x = 0.34, y = 0.31 were obtained for WLE solution (ϕ_F = 14%) containing 5 μM of OPCP in 2.5 mL of TPDC-BZ solution (Fig. S13d†). The CRI value was found to be 84 (Fig. S13e†). The CCT for WLE solution is 5290 K, which is close to that of daylight and in the range of electronic flashlight. Lifetime measurements of WLE solution suggest that there is no significant energy transfer (ET) between OPCP and TPDC-BZ (Fig. S13f and Table S2†).

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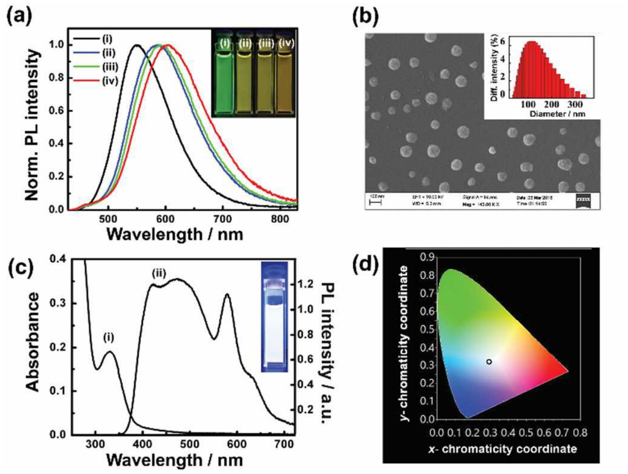

Fig. 3 (a) Emission spectra of TPDC-BZ solution in (i) toluene, (ii) THF, (iii) $CHCl_3$ and (iv) DCM (inset: photographs of TPDC-BZ in the corresponding solvents upon irradiation with UV light at 365 nm depicting color tunable emission). (b) FESEM image of nanoparticles; inset: DLS profile of the aqueous dispersion of nanoparticles. (c) Spectral characteristics of WLE nanoparticle dispersion: (i) absorption, (ii) emission (λ_{ex} = 340 nm) spectra; inset: photograph of WLE nanoparticles under irradiation at 365 nm. (d) The chromaticity diagram (CIE 1931) of WLE nanoparticles (x = 0.29, y = 0.32).

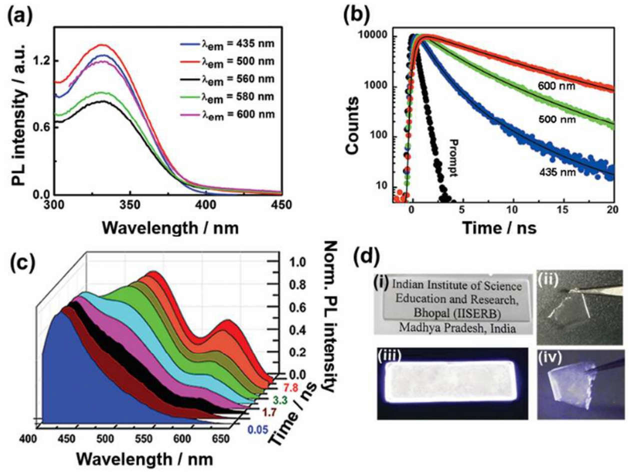

Fig. 4 (a) Excitation spectra of nanoparticle dispersions monitored at different emission wavelengths. (b) Zoomed view of fluorescence decay profiles (λ_{ex} = 340 nm) of nanoparticle dispersions at different emission wavelengths. (c) Time-resolved emission (TRES) spectra of an aqueous dispersion of nanoparticles with the wavelength range from 400-650 nm and delay time from 54 ps to 7.8 ns. (d) Photographs of (i) transparent gel coated on a quartz plate and (ii) free standing thin film in day light. (iii) Gel coated quartz plate and (iv) thin film exhibiting white light emission under UV light.

It is envisioned that constrained environment of nanoparticles may facilitate the excitation energy migration between the polymer and encapsulated dyes (Fig. S11). WLE nanoparticles were prepared by reprecipitation method involving OPCP, TPDC-BZ, and perylene red (PR). The optimized concentration of OPCP (0.4 mM), PR (0.01 mM) and TPDC-BZ (0.5 mg mL^{-1}) in THF solution was rapidly injected into ultrapure water (Millipore MilliQ, resistivity = 18 MΩ cm). The FESEM images of nanoparticles revealed nearly spherical morphology with average particle size ranging from 80-110 nm (Fig. 3b). The particle size distribution obtained from dynamic light scattering (DLS) measurements resembles that obtained from the FESEM images (Fig. 3b, inset).

The nanoparticle dispersions show absorption maxima at 340 nm which corresponds to OPCP (Fig. 3c). Upon exciting at 340 nm, the nanoparticle dispersion showed broad emission covering the entire visible region from 400-700 nm (Fig. 3c and S14a†). The photograph of an aqueous dispersion of nanoparticles under the illumination of UV light of 365 nm reveals bright white emission (Fig. 3c, inset). The CIE color coordinates of nanoparticles were found to be x = 0.29, y = 0.32 (Fig. 3d) with significantly high CRI of 93 (Fig. S14b†). The absolute quantum yield of WLE nanoparticles was 35%. The quantum yield of WLE nanoparticles is higher compared to WLE materials involving insoluble porous polymer like TMBPT-Ir-a (5.2%)[21] and CP-CMPw (8.8%)[19b] and comparable to that using MOFs like Ir-MOF (20.4%)[5a] and MOF-253 (33%).[5b]

The excitation spectra of WLE nanoparticle dispersion monitored at different emission wavelengths corresponding to emission maximum of OPCP, TPDC-BZ and PR revealed a common peak at 340 nm relating to the absorption maximum of OPCP (Fig. 4a). This result indicates the ET from OPCP to TPDC-BZ and PR. Further, the processes were investigated by time-correlated single photon counting (TCPSC) measurements (Fig. S17†). The decay time of donor monitored at 435 nm was found to decrease in WLE nanoparticles (τ_{avg} = 1.7 ns) compared to that of pristine aqueous dispersion of OPCP (τ_{avg} = 3.1 ns). The average decay time of TPDC-BZ (3.6 ns at 500 nm) and PR (8.4 ns at 600 nm) was increased in WLE nanoparticles compared to respective aqueous dispersions (Table S3†). The decay profiles of nanoparticles monitored at the emission wavelengths of TPDC-BZ and PR show negative pre-exponentials relating to rise time of 300 and 400 ps, respectively (Fig. 4b). The rise time correlates closely with the shortest decay component of 400 ps of donor OPCP at 435 nm, confirming the ET from excited OPCP to TPDC-BZ and PR.

Time-resolved emission spectra (TRES) further provide an intimate picture of ET processes.[25] TRES were recorded using 340 nm diode laser. Emission spectra of WLE nanoparticle dispersion collected at different delay time is shown in Fig. 4c. The characteristic emission of OPCP at 435 nm is dominant at initial gated time up to 1.15 ns, which arises because of the direct excitation of OPCP. With the increase of delay time, emission at 435 nm decreases due to the depopulation of the excited state. Further, with longer gated time up to 7.8 ns, the spectrum is mainly dominated by emission at 500 and 600 nm, corresponding to TPDC-BZ and PR respectively (Fig. 4c and S18†). Such correlated decrease of the intensity in blue region and increase in green and red regions with time corroborate the results obtained from TCSPC measurements and unambiguously prove the ET from OPCP to TPDC-BZ and PR.

WLE gel was prepared using agarose gelator. Aliquot of nanoparticle dispersion was taken in agarose gelator and was allowed to cool. WLE gel showed broad emission (ϕ_F = 14%) in the visible region with the characteristic peaks of OPCP, TPDC-BZ, and PR (Fig. 1 and S19a†) having CIE coordinates of x = 0.31, y = 0.28 with CRI value of 79 (Fig. S19b and c†). The excitation spectra revealed that the Förster type resonance

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energy transfer (FRET) is retained in the gel (Fig. S19d†). TRES measurement was also substantiated the same. The temporal evolution of peaks at 500 and 600 nm with a concomitant decrease of emission at 435 nm was observed (Fig. S20†).

Solution processable polymers and hybrid materials with excellent white light emission are important for device fabrication. Therefore, the thin film was fabricated by coating the WLE gel on a quartz plate (Fig. 4d). Remarkably, the entire thin film was highly transparent with a transmittance of 95-97% in 500-800 nm (Fig. S21†) and showed strong white light emission under the illumination of UV light (Fig. 4d). The transparent thin film was peeled off from the substrate to obtain the free-standing WLE thin film (ϕ_F = 8%, Fig. 4d). The CIE coordinates of WLE thin film (0.33, 0.32) is very close to that of pure white light with CRI value of 82 and CCT 5481 K promising for applications in warm white light emitting devices (Fig. S22 and Table S4†).

In summary, TPDC-BZ, a new soluble porous organic polymer having surface area of 610 m^2 g^{-1}, high H_2 uptake capacity (143 cm^3 g^{-1}) and strong color-tunable emission was fabricated. The highly photoluminescent white light emitting solution, nanoparticles, gel and transparent thin film were obtained by encapsulating suitable dyes in the polymer matrix. The CIE coordinates for the WLE materials were very close to those of pure white light with high color rendering indices (Table S4†). The quantum efficiency of white light emitting nanoparticles was found to be as high as 35%. The underlying energy transfer phenomenon was elucidated using time-resolved emission spectra analysis. Compared to existing WLE systems based on porous solids including MOF and porous polymers (Tables S5 and S6†), TPDC-BZ based hybrid materials turned out to be very promising in the cost-effective generation of white light. Moving beyond the gas adsorption properties, the present study paves the way for novel optical applications of solution processable porous organic polymers as potentially useful light emitting materials.

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Notes and references

1 (a) X. Gong, S. Wang, D. Moses, G. C. Bazan and A. J. Heeger, *Adv. Mater.*, 2005, **17**, 2053; (b) N. J. Findlay, J. Bruckbauer, A. R. Inigo, B. Breig, S. Arumugam, D. J. Wallis, R. W. Martin and P. J. Skabara, *Adv. Mater.*, 2014, **26**, 7290.

2 P. Chen, Q. Li, S. Grindy and N. Holten-Andersen *J. Am. Chem. Soc.*, 2015, **137**, 11590.

3 K. V. Rao, K. K. R. Datta, M. Eswaramoorthy and S. J. George, *Adv. Mater.*, 2013, **25**, 1713.

4 (a) S. Basak, Y. S. L. V. Narayana, M. Baumgarten, K. Müllen, and R. Chandrasekar, *Macromolecules*, 2013, **46**, 362; (b) Z. Wang, A. S. Susha, B. Chen, C. Reckmeier, O. Tomanec, R. Zboril, H. Zhong and A. L. Rogach, *Nanoscale*, 2016, **8**, 7197.

5 (a) C. Y. Sun, X. L. Wang, X. Zhang, C. Qin, P. Li, Z. M. Su, D. X. Zhu, G. G. Shan, K. Z. Shao, H. Wu and J. Li, *Nat. Commun.*, 2013, **4**, 2717; (b) Y. Lu and B. Yan, *Chem. Commun.*, 2014, **50**, 15443.

6 Q. W. Zhang, D. Li, X. Li, P. B. White, J. Mecinović, X. Ma, H. Ågren, R. J. M. Nolte, H. Tian and H. Tian, *J. Am. Chem. Soc.*, 2016, **138**, 13541.

7 Q. Y. Yang and J. M. Lehn, *Angew. Chem. Int. Ed.*, 2014, **53**, 4572.

8 G. M. Farinola and R. Ragni, *Chem. Soc. Rev.*, 2011, **40**, 3467.

9 (a) A. I. Cooper, *Adv. Mater.*, 2009, **21**, 1291; (b) T. Ben, H. Ren, S. Ma, D. Cao, J. Lan, X. Jing, W. Wang, J. Xu, F. Deng, J. M. Simmons, S. Qiu and G. Zhu, *Angew. Chem. Int. Ed.*, 2009, **48**, 9457; (c) W. Lu, J. P. Sculley, D. Yuan, R. Krishna, Z. Wei and H. Zhou, *Angew. Chem. Int. Ed.*, 2012, **51**, 7480; (d) Q. Chen, D. Liu, M. Luo, L. Feng, Y. Zhao and B. Han, *Small*, 2014, **10**, 308; (e) K. Sakaushi and M. Antonietti, *Acc. Chem. Res.*, 2015, **48**, 1591; (f) A. A. K. Karunathilake, C. M. Thompson, S. Perananthan, J. P. Ferraris and R. A. Smaldone, *Chem. Commun.*, 2016, **52**, 12881.

10 N. B. McKeown and P. M. Budd, *Chem. Soc. Rev.*, 2006, **35**, 675.

11 (a) P. Kaur, J. T. Hupp and S. T. Nguyen, *ACS Catal.*, 2011, **1**, 819; (b) C. Yang, B. C. Ma, L. Zhang, S. Lin, S. Ghasimi, K. Landfester, K. A. I. Zhang and X. Wang, *Angew. Chem. Int. Ed.*, 2016, **55**, 92025;

12 S. Bandyopadhyay, A. G. Anil, A. James and A. Patra, *ACS Appl. Mater. Interfaces*, 2016, **18**, 27669.

13 B. C. Ma, S. Ghasimi, K. Landfester, F. Vilela and K. A. I. Zhang, *J. Mater. Chem. A*, 2015, **3**, 16064.

14 (a) L. L. Chen, Y. Honsho, S. Seki and D. Jiang, *J. Am. Chem. Soc.*, 2010, **132**, 6742; (b) K. V. Rao, R. Halder and T. K. Maji and S. J. George, *Phys. Chem. Chem. Phys.*, 2016, **18**, 156.

15 (a) A. Patra, J. Koenen and U. Scherf, *Chem. Commun.*, 2011, **47**, 9612; (b) A. Patra and U. Scherf, *Chem. - Eur. J.*, 2012, **18**, 10074.

16 L. Hao, J. Ning, B. Luo, B. Wang, Y. Zhang, Z. Tang, J. Yang, A. Thomas and L. Zhi, *J. Am. Chem. Soc.*, 2015, **137**, 219

17 (a) C. Gu, N. Huang, J. Gao, F. Xu, Y. Xu and D. Jiang, *Angew. Chem. Int. Ed.*, 2014, **53**, 4850; (b) K. Yuan, P. G. Wang, T. Hu, L. Shi, R. Zeng, M. Förster, T. Pichler, Y. Chen and U. Scherf, *Chem. Mater.*, 2015, **27**, 7403; (c) D. Gopalakrishnan and W. R. Dichtel, *Chem. Mater.*, 2015, **27**, 3813; (d) G. Das, B. P. Biswal, S. Kandambeth, V. Venkatesh, G. Kaur, M. Addicoat, T. Heine, S. Verma and R. Banerjee, *Chem. Sci.*, 2015, **6**, 3931;

18 (a) S. Bandyopadhyay, P. Pallavi, A. G. Anil and A. Patra, *Polym. Chem.*, 2015, **6**, 3775; (b) A. Deshmukh, S. Bandyopadhyay, A. James and A. Patra, *J. Mater. Chem. C*, 2016, **4**, 4427.

19 (a) P. Zhang, K. Wu, J. Guo and C. Wang, *ACS Macro Lett.*, 2014, **3**, 1139; (b) B. Bonillo, R. S. Sprick and A. I. Cooper, *Chem. Mater.*, 2016, **28**, 3469.

20 (a) G. Cheng, T. Hasell, A. Trewin, D. J. Adams and A. I. Cooper, *Angew. Chem. Int. Ed.*, 2012, **51**, 12727; (b) A. G. Slater and A. I. Cooper, *Science*, 2015, **348**, 988.

21 J. Liu, K. K. Yee, K. K. W. Lo, K. Y. Zhang, W. P. To, C. M. Che and Z. Xu, *J. Am. Chem. Soc.*, 2014, **136**, 2818.

22 G. Cheng, B. Bonillo, R. S. Sprick, D. J. Adams, T. Hasell and A. I. Cooper, *Adv. Funct. Mater.*, 2014, **24**, 5219.

23 J. X. Jiang, F. Su, A. Trewin, C. D. Wood. H. Niu, J. T. A. Jones, Y. Z. Khimyak and A. I. Cooper, *J. Am. Chem. Soc.*, 2008, **130**, 7710.

24 (a) U. Eberle, M. Felderhoff and F. Schüth, *Angew. Chem. Int. Ed.*, 2009, **48**, 6608; (b) J. Germain, J. M. J. Fréchet and F. Svec, *Small*, 2009, **5**, 1098.

25 (a) X. Zhang, S. Rehm, M. M. S. Sempere and F. Würthner, *Nat. Chem.*, 2009, **1**, 623; (b) C. Vijayakumar, V. K. Praveen and A. Ajayaghosh, *Adv. Mater.*, 2009, **21**, 2059.