View Article Online View Journal

# ChemComm

# Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: G. -. --, V. Wakchaure, K. C. Ranjeesh, C. A. Ralph Abhai and S. B. Sukumaran, *Chem. Commun.*, 2017, DOI: 10.1039/C7CC02994B.



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 **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, 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.



rsc.li/chemcomm

Published on 08 June 2017. Downloaded by State University of New York at Binghamton on 08/06/2017 14:21:22.



# Journal Name

# COMMUNICATION

# Cascade Energy Transfer and Tunable Emission from Nanosheet Hybrids: Locating Acceptor Molecules Through Chiral Doping

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

Goudappagouda, <sup>a,b</sup> Vivek Chandrakant Wakchaure, <sup>a,b</sup> Kayaramkodath Chandran Ranjeesh, <sup>a,b</sup> Chalona Antony Ralph Abhai, <sup>c</sup> Sukumaran Santhosh Babu<sup>a,b\*</sup>

DOI: 10.1039/x0xx00000x

www.rsc.org/

Light harvesting donor-acceptor assemblies are indispensable to efficiently tap photons. In an attempt to improve the light harvesting efficiency of an acceptor doped assembly, we design and synthesize a donor-acceptor-donor triad which exhibit an exceptional intramolecular energy transfer with excellent efficiency. Moreover, a facile cascade energy transfer (energy funnelling) is observed in the presence of a series of second acceptors (63-91% efficiency) with tunable emission colours. Selfassembled nanosheets formed by the triad in the presence of acceptors, exhibit cascade energy transfer assisted tunable emission. In addition, use of chiral acceptors induce chirality to the triad and results in the formation of chiral nanosheets along with cascade energy transfer. Here chiral induction, nanosheet formation and cascade energy transfer in the presence of chiral acceptor is used as a tool to probe the intercalation of acceptor molecules in the donor scaffold.

The focus on alternate energy sources has aroused interest in the development of new organic functional assemblies for solar light harvesting and conversion.<sup>1</sup> Natural as well as artificial light-harvesting systems utilize ordered chromophore arrays to efficiently and unidirectionally transfer absorbed radiation.<sup>2</sup> In these assemblies, chromophores are placed at optimum distances with appropriate orientations in space using specific noncovalent interactions.<sup>3</sup> By mimicking natural photosynthetic system, numerous studies using artificial analogues focusing on self-assembled multichromophoric arrays are reported.<sup>2c,d,4a</sup> In this direction, dendrimers, gels, polymers, organic-inorganic hybrids etc. have been widely investigated for energy transfer (ET) studies.<sup>4</sup> Intriguingly, tailor-made organic donor-acceptor (D-A) assemblies have attracted wide attention due to favourable ET features<sup>5</sup> and subsequently became the active components in electronic devices and other related applications.<sup>6</sup>

Cascade energy transfer (CET) is highlighted as a unique phenomena involving active participation of individual components to direct energy towards the most suitable acceptor moiety and hence to tune the emission color from blue to red or even white.<sup>7-9</sup> However, most of the reported CET systems are complex and exhibit best performance in solution or gel state which limits further demonstration of these materials.<sup>8,10</sup> In the recent past, many research groups have focused on CET in multichromophoric assemblies equipped with energetically favourable and suitably placed D-A units.<sup>7,8</sup> Research groups of Fréchet and Müllen independently demonstrated sequential ET in dendritic multichromophoric systems.<sup>8</sup> In another strategy, the donor scaffolds are doped with acceptors to facilitate energy transfer.<sup>5d</sup> However, a clear evidence for the location of acceptor molecules in the doped energy transfer systems is nearly impossible. In the context of favourable donor-acceptor distance for efficient energy transfer, probing the acceptor location in donor matrix is always desirable to improve design strategies. Here we report efficient intramolecular ET in a donor-acceptor-donor (D-A-D) triad DADT, which exhibit CET assisted tunable emission with various second acceptors. Chiral acceptors enabled to locate the acceptors in the hybrid assembly and thereby to reveal the reason for efficient cascade energy transfer.

Absorption spectrum of **DADT** (Figure 1a, Scheme S1, S2) in dichloromethane (DCM) solution, shows peaks corresponding to the donor (TPE) and acceptor (BPA) moieties having maxima at 320, 450 and 472 nm (Figure 1b). Emission spectrum consists of major contribution from BPA with a maximum located at 492 nm (Figure 1c, S1) and a minor TPE emission (Figure S2; inset). A thin film of **DADT** has shown a broad, red shifted absorption and emission spectra, indicating aggregate formation on surface (Figure 1b, 1c). The disappearance of TPE emission in **DADT** thin film points to possible ET between TPE and BPA in the triad and hence justifies the molecular design (Figure 1c). A good spectral overlap integral ( $J(\lambda) = 2.67 \times 10^{13}$ 

<sup>&</sup>lt;sup>a.</sup> Organic Chemistry Division, National Chemical Laboratory (CSIR-NCL), Pune-411008, India.

<sup>&</sup>lt;sup>b.</sup> Academy of Scientific and Innovative Research (AcSIR), New Delhi-110020, India.
<sup>c</sup> School of Chemical Sciences, Mahatma Gandhi University, Kottayam-686560, India.

<sup>&</sup>lt;sup>+</sup> Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

DOI: 10.1039/C7CC02994B Journal Name

### COMMUNICATION

Published on 08 June 2017. Downloaded by State University of New York at Binghamton on 08/06/2017 14:21:22.

(solution) and 3.22 x 10<sup>13</sup> (thin film) M<sup>-1</sup>cm<sup>-1</sup>nm<sup>4</sup>) exists between TPE emission and BPA absorption, which allows the triad to efficiently transfer energy from TPE to BPA (Figure 1d, S2).<sup>11</sup> Wavelength dependent emission lifetime decay profile of BPA in DADT thin film shows a faster decay at the lower wavelengths than the longer wavelength emission of BPA, indicating the presence of strong energy migration among (BPA of DADT) aggregates after energy transfer (Figure 1e). An efficient ET with almost complete disappearance of the donor emission in DADT could be ascribed to, i) optimum Förster distance in the covalently linked D-A units (centre to centre distance of ~2 nm) and ii) high spectral overlap integral between TPE emission and BPA absorption. Since the donor emission is absent both in solution and thin films, ET experiments were cross checked with that of 1, 2 (Scheme S3) and their physical mixture 1+2 (2:1) (Figure S3, Table S1). Compared to 1 and 2, solution and thin film of the physical mixture showed a weak energy transfer, keeping the donor emission still active. In contrast to 1+2, a complete donor fluorescence quenching in DADT ascertains the significance of optimum D-A distance favouring ET. Time-resolved experiments of DADT thin films on nanosecond timescale indicated a faster triexponential decay with a lifetime of 0.43 ns (18.70%), 1.8 ns (51.79%) and 8.6 ns (29.51%) (Figure S4, Table S1). An increase in the lifetime of BPA moiety in DADT thin film compared to that of 2 supports ET in DADT (Table S1).



Fig. 1. (a) Chemical structure of DADT. Normalized (b) absorption and (c) emission spectra of DADT in DCM solution and thin film ( $\lambda_{ex} = 320$  nm for solution and 340 nm for thin film). (d) Spectral overlap integral between emission of 1 and absorption of BPA of DADT in thin film. (e) Wavelength dependent fluorescence lifetime decay profile of DADT thin film ( $\lambda_{ex} = 374$  nm, IRF = instrument response function). Inset shows the fluorescence lifetime decay profiles of DADT thin film monitored at 490 nm (O) and at 600 nm ( $\Delta$ ), showing growth at the initial time scale.

Second acceptor molecules such as diketopyrrolepyrrole (DPP), Rhodamine B (RB), perylenebisimide (PBI-1), Nile red (NR) and Rubrene (RBn) derivatives (Scheme S4) having good spectral overlap integrals of their absorption peaks with **DADT** emission are chosen for energy tapping (Figure S5, S6). Even though the thin film absorption spectrum covers 300 to 650 nm due to contributions from three different chromophore units (Figure S7), emission spectrum shows complete quenching of TPE and moderate quenching of BPA emissions when **DADT** is excited at 340 nm ( $\lambda_{max}$  of TPE absorption) in the presence of the acceptors (Figure 2a, 2b, S8). ET in **DADT** thin films with second acceptors was found to be extremely efficient and an optimum ET performance was observed at 10 mol% of the acceptors. Interestingly, a CET with strong second acceptor emission from 550 to 700 nm was observed upon exciting the TPE unit of **DADT**. This could be attributed to the sequential ET from TPE to BPA and then to the second acceptor molecules. The energy gradient present in three chromophores enabled a stepwise ET from the high to the low energy absorbing molecules.



**Fig. 2.** Emission spectrum of **DADT** thin films with varying amounts of (a) DPP and (b) RB ( $\lambda_{ex}$  = 340 nm). (c) Photograph of **DADT**-RB thin films with varying amounts of RB under UV light (365 nm). Fluorescence lifetime decay profile of **DADT** thin film with increasing amounts of (d) DPP and (e) RB ( $\lambda_{ex}$  = 374 nm,  $\lambda_{mon}$  = 526 nm). Insets show the fluorescence lifetime decay profile of the acceptors in the absence (O) and presence ( $\Delta$ ) of **DADT**. monitored at 580 nm for DPP and 600 nm for RB.

The efficient ET in thin films could be due to favourable aggregate formation assisted energy migration in thin films as well as the conformational flexibility provided by the alkyl linker between BPA and TPE, which brings the ET partners in close proximity.<sup>12</sup> ET efficiency among the second acceptors is varied as 91%, 63%, 78%, 77% and 70% for DPP, RB, PBI-1, NR and RBn, respectively (Figure 2a, 2b, S8). The relatively quenched emission of the acceptors exhibited enhanced emission due to sensitization via energy transfer (for instance, NR). By taking DPP into consideration as the best acceptor candidate, excitation of TPE at 340 nm results in intramolecular ET efficiency of ~99%<sup>7b</sup> and out of that, 91% of energy is intermolecularly transferred to DPP. Upon increasing the amount of acceptors, a reasonably efficient CET resulted in tunable emission color from green (0 mol%) to yellow (3 mol%), brown (7 mol%) and red (10 mol%) (Figure 2c). Even though, there have been various methods to obtain tunable emission,<sup>13</sup> one such study using an ET efficient triad and varieties of other acceptors has rarely been attempted.

Published on 08 June 2017. Downloaded by State University of New York at Binghamton on 08/06/2017 14:21:22.

### Journal Name

Fluorescence lifetime decay of the BPA emission was considerably decreased with increasing amounts of the second acceptors and thus ruled out the trivial ET mechanisms (Figure 2d, 2e, S9, Table S3). In addition, a temporal growth observed for fluorescence lifetime decay of second acceptors (for instance, insets of Figure 2d, 2e for DPP and RB, respectively), in the presence of DADT at an early time scale also points to the initial singlet excited state population build-up before radiative decay associated with Förster ET. In the case of second acceptors, wavelength of excitation with minimum absorption was chosen to minimize the contribution of direct excitation towards ET assisted emission (Figure S10). As anticipated, the ET efficiency in solution was very low compared to that of thin films (Figure S11, S12). ET studies were conducted in different concentrations of DADT in DCM (eg.  $1 \times 10^{-5}$  and  $5 \times 10^{-5}$  M) and exhibited consistent results. Since our main focus is thin films of DADT prepared from 1 mM DCM solution, all energy transfer studies in solution were conducted at the same concentration.

The excellent ET in thin films inspired us to know about the D-A interactions, however, it is extremely challenging to detect that in thin films. Hence self-assembly of DADT was monitored by adding DCM solution to excess methanol, typically, 10 µL DCM solution (1 mM) of DADT was added to 3 mL of MeOH and the resulting aggregate solution was drop casted on Silicon substrate for analysis. In the presence of second acceptors such as PBI-1 and DPP (up to 10 mol%), DADT exclusively formed nanosheet structures in large numbers (Figure 3). However, DADT, PBI-1 and DPP alone form ill-defined random structures under similar experimental conditions (Figure S13, S14). DADT assembly formation is efficient up to 10 mol% of PBI-1 loading and further addition resulted in phase separation. The presence of PBI-1 in the nanosheets is confirmed by the characteristic red emission of PBI-1, when the nanosheets are excited at 352 nm and monitored in the red window, 573 nm in fluorescence imaging (Figure S15). The optical microscopy (OM) (Figure 3a), transmission electron microscopy (TEM) (Figure 3b, S16) and scanning electron microscopy (SEM) (Figure S17) images showed the presence of layered nanosheets. Elemental mapping for carbon, nitrogen and oxygen confirmed the uniform distribution of PBI-1 throughout the nanosheets (Figure 3c-e). Detailed AFM imaging showed the presence of nanosheets with varying heights in multiple of 5 nm (Figure 3f, 3g, S18, S19) and this might be due to the extended aggregation of initially formed monolayer assembly (~5 nm height) (Figure S20). The formation of nanosheets was monitored with time and immediate drop casting of the solution showed that nanosheet formation is spontaneous (Figure S21). Thus formed nanosheets grow in size and height with time and optical microscope images confirmed the formation of larger nanosheets upon ageing (Figure S21). XRD profile of the sheets showed two peaks with d-spacing of 3.39 and 4.06 Å, might be due to the intermolecular  $\pi$ -stacking distance between central BPA moieties in the same layer and interdigitating TPE moieties of adjacent layers (Figure S22). Similar nanosheet structures were formed by **DADT**-DPP coassembly also (Figure \$23).



Fig. 3 (a) OM and (b) TEM images of DADT-PBI-1 hybrid nanosheets. Elemental mapping of the hybrid sheets for (c) carbon, (d) nitrogen and (e) oxygen. (f) AFM image of the DADT-PBI-1 hybrid sheet with (g) height profile for the marked line in the AFM image.

In order to locate the acceptor intercalation in hybrid nanosheets, CET has been attempted in a D-A assembly of DADT and chiral acceptors. Similar to PBI-1, CET was observed in DADT-PBI-2R/S (Scheme S5) in solution (Figure S24-S27) as well as in thin films (Figure S28, S29, Table S4). In addition, DADT formed chiral nanosheet assembly in the presence of PBI-2R and PBI-2S (Figure S30, S31). Surprisingly, circular dichroism (CD) spectra of DADT-chiral PBI assembly showed exciton coupled mirror image CD spectra with an enhanced CD intensity for  $\pi$ - $\pi$ \* transition of TPE ( $\lambda_{max}$  = 315 nm) in **DADT** (Figure 4a), indicating the preferable intercalation of chiral PBIs in the TPE region of **DADT** layered sheet assembly (Figure S32) and leading to chiral induction at that particular absorption part (Figure 4a, 4b).<sup>14</sup> Both reduced energy transfer efficiency (Figure S33), layered hybrid sheet formation and CD signal at the TPE absorption region points to possible selective interaction of chiral PBIs within TPE units and placing it in a geometrically unfavourable position for energy transfer to BPA. In short, energy transfer and self-assembly studies of DADT with chiral PBIs strongly support the possibility of intercalation of the second acceptor molecules in the interlayer region of nanosheet hybrids (Figure S32). The specific intercalation of PBIs in the locking cites of TPE is supported by the AFM images with varying heights. The initially formed single layer assemblies are joined together by the intercalated PBIs. Even though the CD signal enhancement is not remarkable, it enables to point out the possible intercalation mode of acceptor molecules. Hence chiral PBIs act as a probe to monitor the location of acceptor molecules in the donor scaffold. The overall processes involving CET assisted tunable emission and chiral induction of DADT and second acceptor assemblies is schematically demonstrated in Figure 4c. We strongly believe that CET and chiral induction in a multi-fluorophoric assembly is a rare observation and this

Page 4 of 4

will eventually enable to tune circularly polarized luminescence.



Fig. 4 (a) CD and (b) UV-Vis spectra of DADT-PBI-2R and DADT-PBI-2S co-assembly. (c) Schematic of DADT self-assembly with chiral and achiral acceptors leading to formation of self- and co-assembled nanosheets exhibiting cascade energy transfer assisted tunable emission and chiral induction.

In conclusion, we have demonstrated CET assisted tunable emission of a new D-A-D triad based hybrids and probed the location of acceptor molecules in the assembly through chiral doping. Triad justified the molecular design with optimum Förster distance, resulting in extremely efficient intramolecular ET. The presence of favorable D-A spectral overlap integral and aggregation greatly assisted to obtain such high ET efficiency in thin films. Moreover, facile CET is observed in the presence of a series of second acceptors with good spectral overlap integral and thereby enabled to tune emission colors. In addition, the non-emitting acceptor (alone) molecules exhibited sensitized emission via energy transfer. Since the overall energy transfer efficiency is very high, this strategy can be employed in luminescent solar concentrators. Selfassembled hybrid nanosheets formed by the triad in the presence of chiral and achiral acceptors using a solventantisolvent method also exhibited CET assisted tunable emission. Chiral doping enabled to achieve chiral induction, tunable emission colors and to identify the acceptor location in the coassembly. Currently, we work on circularly polarized luminescence of the CET assisted D-A systems.

### Acknowledgements

Goudappagouda, VCW and KCR acknowledge UGC, India for fellowship. We thank Prof. H. N. Gopi, IISER Pune for CD spectral measurements. This work is supported by SERB Govt. of India, GAP312826.

- (a) G. D. Scholes, G. R. Fleming, A. Olaya-Castro and R. van Grondelle, *Nat. Chem.*, 2011, **3**, 763; (b) N. S. Lewis and D. G. Nocera, *Proc. Natl Acad. Sci. USA*, 2006, **103**, 15729; (c) M. S. Dresselhaus and I. L. Thomas, *Nature*, 2001, **414**, 332.
- (a) T. Mirkovic, E. E. Ostroumov, J. M. Anna, R. van Grondelle, Govindjee and G. D. Scholes, *Chem. Rev.*, 2016, DOI: 10.1021/acs.chemrev.6b00002; (b) G. R. Fleming, G. S. Schlau-Cohen, K. Amamath and J. Zaks, *Faraday Discuss.*, 2012, **155**, 27; (c) S.

Fukuzumi and K. Ohkubo, *J. Mater. Chem.*, 2012, **22**, 4575; (d) J. Barber and B. Andersson, *Nature*, 1994, **370**, 31.

- (a) V. Novoderezhkin and R. van Grondelle, *Phys. Chem. Chem. Phys.*, 2010, **12**, 7352; (b) M. R. Wasielewski, *Acc. Chem. Res.*, 2009, **42**, 1910; (c) X. Hu, A. Damjanović, T. Ritz and K. Schulten, *Proc. Natl. Acad. Sci.* USA, 1998, **95**, 5935.
- (a) A. Harriman, *Chem. Commun.*, 2015, **51**, 11745; (b) X. Zhang, Y. Zeng, T. Yu, J. Chen, G. Yang and Y. Li, *J. Phys. Chem. Lett.*, 2014, **5**, 2340; (c) V. K. Praveen, C. Ranjith and N. Armaroli, *Angew. Chem. Int. Ed.*, 2014, **53**, 365; (d) P. D. Frischmann, K. Mahata and F. Würthner, *Chem. Soc. Rev.*, 2013, **42**, 1847; (e) K. V. Rao, K. K. R. Datta, M. Eswaramoorthy and S. J. George, *Chem. Eur. J.*, 2012, **18**, 2184; (f) C. Vijayakumar, V. K. Praveen, K. K. Kartha and A. Ajayaghosh, *Phys. Chem. Chem. Phys.*, 2011, **13**, 4942; (g) C. Vijayakumar, V. K. Praveen, A. Ajayaghosh, *Adv. Mater.*, 2009, **21**, 2059; (h) A. Ajayaghosh, V. K. Praveen, C. Vijayakumar and S. J. George, *Angew. Chem. Int. Ed.*, 2007, **46**, 6260.
- (a) H. A. M. Ardona and J. D. Tovar, *Chem. Sci.*, 2015, **6**, 1474; (b) C. Giansante, G. Raffy, C. Schäfer, H. Rahma, M.-T. Kao, A. G. L. Olive and A. D. Guerzo, *J. Am. Chem. Soc.*, 2011, **133**, 316; (c) B. Albinsson and J. Mårtensson, *Phys. Chem. Chem. Phys.*, 2010, **12**, 7338; (d) A. P. H. J. Schenning, E. Peeters and E. W. Meijer, *J. Am. Chem. Soc.*, 2000, **122**, 4489.
- (a) M. Wang and F. Wudl, *J. Mater. Chem.*, 2012, 22, 24297; (b) Y. Yamamoto, *Sci. Technol. Adv. Mater.*, 2012,13, 033001; (c) G. M. Farinola and R. Ragni, *Chem. Soc. Rev.*, 2011, 40, 3467; (d) A. P. H. J. Schenning and E. W. Meijer, *Chem. Commun.*, 2005, 3245.
- (a) D. Okada, T. Nakamura, D. Braam, T. D. Dao, S. Ishii, T. Nagao, A. Lorke, T. Nabeshima and Y. Yamamoto, *ACS Nano*, 2016, **10**, 7058; (b)
   B. G. Park, D. H. Hong, H. Y. Lee, M. Lee and D. Lee, *Chem. Eur. J.*, 2016, **22**, 6610; (c) O. A. Bozdemir, S. Erbas-Cakmak, O. O. Ekiz, A. Dana and E. U. Akkaya, *Angew. Chem. Int. Ed.* 2011, **50**, 10907; (d) E. Fron, L. Puhl, I. Oesterling, C. Li, K. Müllen, F. C. De Schryver, J. Hofkens and T. Vosch, *ChemPhysChem*, 2011, **12**, 595; (e) F. Camerel, G. Ulrich, P. Retailleau and R. Ziessel, *Angew. Chem. Int. Ed.*, 2008, **47**, 8876; (f) K. Sugiyasu, N. Fujita and S. Shinkai, *Angew. Chem. Int. Ed.*, 2004, **43**, 1229; g) M. Berggren, A. Dodabalapur, R. E. Slusher and Z. Bao, *Nature*, 1997, **389**, 466.
- (a) T. Weil, E. Reuther and K. Müllen, *Angew. Chem. Int. Ed.*, 2002, 41, 1900; (b) J. M. Serin, D. W. Brousmiche and J. M. J. Fréchet, *Chem. Commun.*, 2002, 2605; (c) A. Adronov and J. M. J. Fréchet, *Chem. Commun.*, 2000, 1701; (d) S. L. Gilat, A. Adronov and J. M. J. Fréchet, *Angew. Chem. Int. Ed.*, 1999, 38, 1422.
- (a) C. Gu, N. Huang, F. Xu, J. Gao and D. Jiang, *Sci. Rep.*, 2015, 5:8867, DOI: 10.1038/srep08867; (b) S. S. Babu, M. J. Hollamby, J. Aimi, H. Ozawa, A. Saeki, S. Seki, K. Kobayashi, K. Hagiwara, M. Yoshizawa, H. Möhwald and T. Nakanishi, *Nat. Commun.*, 2013, **4**, 1969, doi:10.1038/ncomms2969; (c) S. S. Babu, J. Aimi, H. Ozawa, N. Shirahata, A. Saeki, S. Seki, A. Ajayaghosh, H. Möhwald and T. Nakanishi, *Angew. Chem. Int. Ed.*, 2012, **51**, 3391.
- 10 a) X. Zhang, Y. Zeng, T. Yu, J. Chen, G. Yang and Y. Li, *J. Phys. Chem. Lett.*, 2014, **5**, 2340; b) A. Ajayaghosh, C. Vijayakumar, V. K. Praveen, S. S. Babu and R. Varghese, *J. Am. Chem. Soc.*, 2006, **128**, 7174;
- 11 J. R. Lakowicz, (Ed.) in Principles of Fluorescence Spectroscopy, 3rd edn, Springer, New York, 2006, Ch. 13, 443-472.
- 12 C. V. Suneesh and K. R. Gopidas, *J. Phys. Chem. C*, 2009, **113**, 1606.
- (a) S. Sekiguchi, K. Kondo, Y. Sei, M. Akita and M. Yoshizawa, *Angew. Chem. Int. Ed.*, 2016, **55**, 6906; (b) C. Pan, K. Sugiyasu, Y. Wakayama, A. Sato and M. Takeuchi, *Angew. Chem. Int. Ed.*, 2013, **52**, 10775; (c) Y. Sagara and T. Kato, *Nat. Chem.*, 2009, **1**, 605.
- (a) C. Roche, H.-J. Sun, P. Leowanawat, F. Araoka, B. E. Partridge, M. Peterca, D. A. Wilson, M. E. Prendergast, P. A. Heiney, R. Graf, H. W. Spiess, X. Zeng, G. Ungar and V. Percec, *Nat. Chem.*, 2016, **8**, 80; (b) V. Percec, S. D. Hudson, M. Peterca, P. Leowanawat, E. Aqad, R. Graf, H. W. Spiess, X. Zeng, G. Ungar and P. A. Heiney, *J. Am. Chem. Soc.*, 2011, **133**, 18479; (c) M. Liu, L. Zhang and T. Wang, *Chem. Rev.*, 2015, **115**, 7304.