

Solvent effect on hierarchical assembly of 2-aminooctane-functionalized naphthalenediimide†

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Hierarchical assembly of 2-aminooctane-functionalized naphthalenediimide (NDI) was investigated *via* a solvent displacement method. That is, a good solvent (ethyl acetate) of NDI was fast dispersed into a poor solvent (methanol, methanol + water, or water). The NDI assemblies with varied scale, shape, and aggregation were formed and fully characterized by SEM, TEM, EDX, UV-vis, and fluorescence. The results demonstrated that the use of a mixture of two poor solvents can provide fine-tuning of intermolecular interactions. In addition, to reveal the structure–property correlation, the *I*–*V* characteristics of the as-obtained NDI architectures were explored.

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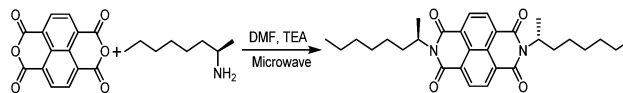
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Introduction

Organic semiconductors have received great interest due to their unique electrical and optical properties. Their performance not only relates to the chemical structures of molecules but also depends on the degree of molecular ordering in the solid state.^{1–3} Therefore, strategies that can improve and optimize the molecular ordering are urgently needed. Self-assembly is among the most promising strategies, and has generated numerous architectures with varied shapes and molecular ordering, such as wires,⁴ belts,⁵ helices,⁶ vesicles,⁷ and sheets.⁸ However, it is still a great challenge to prepare materials with the desired scale, shape, and aggregation. This is due to the variety of chemical structures of molecules and complexity of intermolecular interactions involved. In addition, compared to the more common p-type counterparts, only limited studies were carried out for the self-assembly of n-type semiconductors.

Naphthalenediimides (NDIs) are among the most promising n-type small-molecule semiconductors used in organic electronics^{9–14} and are ideal blocks for constructing artificial photo-systems.^{15–17} The planarity and high π -acidity of NDI molecules are ideal for face-to-face π stacking, which provide continuous pathway for better transport of charge-carrier mobility. To date, a variety of methods including solvent evolution,¹⁸ solvent vapour diffusion,¹⁹ and solvent displacement^{20,21} have been used to form assembled objects. Among them, the solvent displacement



Scheme 1 Chemical structure and synthesis route of 2-aminooctane-functionalized naphthalenediimide.

method, in which good and poor solvents of targeted molecules are mixed together, is highly desired due to its fine-tuning of assembling parameters. It is noted that generally only single poor solvent are taken into account for controlling the morphology and dimension of self-assembled structures.

Herein, we report the preparation of hierarchical structures of 2-aminooctane-functionalized naphthalenediimide (NDI) *via* a solvent displacement method. The targeted NDI was synthesized by a facile microwave-assisted reaction (Scheme 1). Substitution of chiral alkyl chains enhances the solubility of NDI, while do not change the electronic structures significantly, since two nitrogen are at node of π orbitals. To form NDI assemblies, a good solvent (ethyl acetate) containing NDI was dispersed into a poor solvent (methanol, methanol + water, or water). The use of mixed poor solvents provides fine-tuning of intermolecular interactions. The as-obtained NDI assemblies were fully characterized by means of SEM, TEM, EDX, UV-vis, and fluorescence and had the varied scale, shape, and aggregation. In addition, the *I*–*V* characteristics of the NDI assemblies were investigated to reveal the structure–property correlation. The effect of chirality on the self-assembly process and electronic properties could be also explored, which was out of scope to this work.

Experimental section

Materials synthesis

Naphthalenetetracarboxylic dianhydride (Nda, 97%) and (*R*)-2-aminooctane (99%) were pursued from Aldrich Company. Ethyl

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acetate, methanol, dimethylformamide (DMF), and triethylamine (TEA) were purchased from Alfa Company. The deionized (DI) water (18.2 MΩ) was used. All the chemicals were used without further purification.

Synthesis

The synthesis of 1,4,5,8-naphthalenediimide was similar to the literature.²² All reactions were performed in a microwave system (2.45 GHz, 300 W, Discover S-Class, CEM). In a typical process, 100 mg Nda, 129 mg (*R*)-2-aminooctane, 4 mL DMF, 0.08 mL TEA were mixed in a microwave vial, sonicated, and sealed with a Teflon cap. The vial was transferred into the microwave reactor and heated at 140 °C for 1 h. The solvent was removed under the reduced pressure and the residue was purified by the column chromatography on silica gel with hexane/chloroform (3/4) as the eluent. The product was a light yellow solid with a yield of 40%.

To form supramolecular architectures, the as-obtained yellow NDI powder was dissolved into ethyl acetate by sonication at 40 °C, fast injected into poor solvent, and stirred for 15 min. The final solution was stored for 9 days without disturbance at room temperature, and the precipitates were collected at the bottom.

Characterization

The product was characterized by ¹H nuclear magnetic resonance (HNMR, Varian MR 400 spectrometer operating at 400 MHz), and high resolution mass spectrometry (HRMS, Varian ProStar LC240).

(*R,R*)-(+)-2,7-Bis-(1-methyl-octyl)benzo[1*mn*] [3,8] phenanthro-line-1,3,6,8-tetraone: ¹H NMR (400 MHz, CDCl₃, δ): 8.72 (s, 4H), 5.26 (m, 2H), 2.13–2.21 (m, 2H), 1.87–1.93 (m, 2H), 1.58 (d, *J* = 8 Hz, 6H), 1.21–1.32 (m, 16H), 0.83 (t, *J* = 8 Hz, 6H). HRMS (ESI) *m/z* calculated for [C₃₀H₃₈N₂O₄Na]⁺, [Mina]⁺, 513.272; found 513.272.

Self-assembled structures of NDI were characterized by means of scanning electron microscopy (SEM, Quanta 400 FEG), transmission electron microscopy (TEM, Tecnai G2 F20 S-Twin), energy dispersive X-ray spectroscopy (EDX) equipped with TEM, UV-vis spectroscopy (PE Lambda 750s), and X-ray diffraction (XRD, Bruker D8 Advance X-ray Diffractometer).

Device fabrication

Bottom-contact devices were fabricated to test charge transport of supramolecular architectures of NDIs. Finger electrodes with an interval of 5 μm, a width of 20 μm, and a length of 200 μm were fabricated on SiO₂/Si substrate by standard photoetching process followed by Ti/Au deposition and liftoff. One drop of NDI dispersion was drop-cast on the electrodes. To remove the solvent thoroughly and enhance the contact between NDIs nanostructures and Au electrodes, the device was annealed at 100 °C for 20 min. Current–voltage characteristics of the devices were recorded with Keithley 4200 SCS and SUSS PM8 probe station in a shielded box at room temperature. All measurements were performed at ambient conditions.

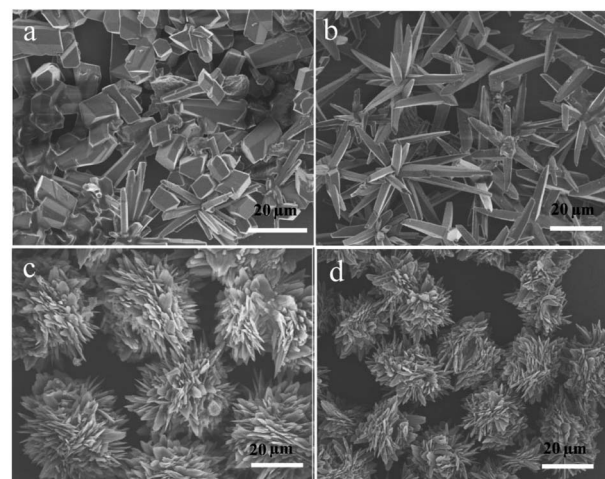


Fig. 1 SEM images of hierarchical architectures of NDI. The concentrations of NDI are (a) 0.5 mM, (b) 1 mM, (c) 3 mM, and (d) 5 mM. The volume ratio of ethyl acetate to methanol was fixed at 1 : 20.

Results and discussion

Fig. 1 presents a set of SEM images of hierarchical architectures of NDI, which are prepared by a rapid dispersion of ethyl acetate solution of NDI (“good” solvent) into methanol (“poor” solvent). The concentration of NDI in ethyl acetate is varied from 0.5 to 5 mM, while the volume ratio of ethyl acetate to methanol is fixed at 1 : 20. Different shapes of NDI architectures are observed, indicating that the concentration plays an important role in the self-assembling process. At lower concentration, block-like structures (Fig. 1a) with the length of tens of micrometers and the width of 3–10 μm are formed, which was attributed to slow growth of NDIs. Increasing the concentration to 1 mM, needle-like structures (Fig. 1b) are formed. Apparently, there is a substantial increase of length and decrease of width of needle-like structures compared with block-like ones. At a concentration of 3 mM, flower-like structures (Fig. 1c) with the average size of about 30 μm are formed. Similar aggregates are observed when the volume ratios of ethyl acetate to methanol are varied from 1 : 5 to 1 : 50 (Fig. S3†). Further increasing the concentration does not change the overall morphology but causes a substantial decrease of dimension of flower-like structures. For instance, at a concentration of 5 mM, the average size of flower-like structures (Fig. 1d) is reduced to about 20 μm. This is reasonable that more nuclei are formed when the concentration is higher. As a result, the number of flower-like structures increases, whereas their sizes decrease accordingly.

Fig. 2a shows a high-magnified SEM image of a single flower-like structure of NDI. It can be seen that the NDI flower consists of numerous flakes, which are randomly oriented and connected with each other. Each flake has a thickness of 50–100 nm and a length of 3–5 μm. Fig. 2b and c show a TEM image of nanoscale flakes and the corresponding SAED pattern. The observation of the well-defined pattern indicates a perfect crystalline feature. No change of the SAED pattern is observed for different parts of the same nanoflake, implying that the whole flake is a single crystal. This feature is vital for potential

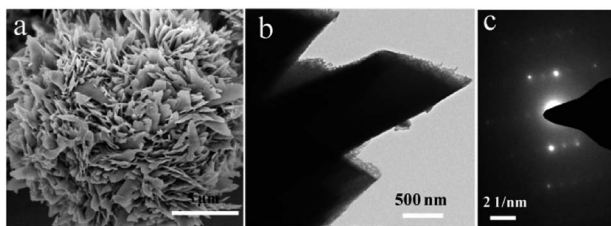


Fig. 2 (a) High magnified SEM image a single flower-like structure of NDI. (b) TEM image of several flakes in an NDI flower. (c) The corresponding SAED pattern of a single flake.

applications in electric devices. In addition, the EDX spectrum (Fig. S4†) clearly reveals carbon and nitrogen elements in flower-like structures.

To understand the growth mechanism, time-lapsed experiments are carried out to monitor the evolution of flower-like structures. Fig. 3 shows a set of SEM images acquired at different growth time. When ethyl acetate is added into poor solvent, microphase separation takes place at first due to the low solubility of NDIs in the mixed solvent.²³ The NDI-rich phase forms spherical droplets, in which the nanoscale flakes are formed (Fig. 3a). This is related to the nucleation of the primary structures. This process depends not only on the coordination of attractive forces between the NDI molecules, but also the balance of interactions between the NDI and solvent molecules. After ~ 2 days of assembly, the solution becomes turbid and a small collection of yellow products, which are composed of both nanoscale flakes and star-like structures, (Fig. 3b) appear at the bottom of bottles. Note that the number and size of nanoscale flakes have increased remarkably compared with the initial ones. As time passed, the number of star-like assembly increased significantly (Fig. 3c). In the later stage, thin nanoflakes start to grow directly on these star-like structures. The number of nanoscale flakes increases with time. Finally, the nanoflakes are coalescent with each other and star-

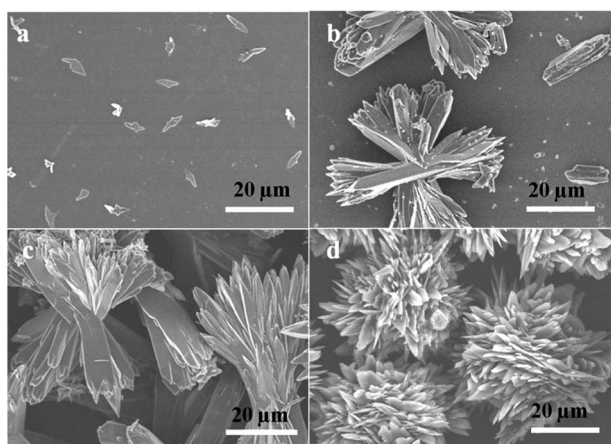


Fig. 3 SEM images of the evolution of flower-like structures. The growth time was: (a) 1 day, (b) 2 days, (c) 5 days, and (d) 9 days. The volume ratio of ethyl acetate to methanol was fixed at 1 : 20, and the concentration of NDI in ethyl acetate was 3 mM.

like objects turn into flower-like structures (Fig. 3d). The above processes are derived by systemic effects of π - π interaction and hydrogen bonding.²⁴

The solvent polarity is known to play an important role in self-assembling process. Different from flower-like structures, sheet-like structures (Fig. 4d) are formed when water is used as poor solvent. More importantly, self-assembled structures of NDI can be tuned from flower to nanosheet when a mixture of two poor solvents of methanol and water are used and their volume ratios are varied. The solution becomes turbid immediately after the injection of ethyl acetate solution of NDI into methanol + water. The white products appear at the bottom of bottle after 2 days of assembly. This process is much faster than that in methanol. Moreover, with the water content of 20%, star-like structures (Fig. 4a) are formed. In comparison with the flower-like ones, the number of flakes in each star-like object is lower, and the thickness of flakes is also thinner. Further increase in the water content results in forming sheet-like structures. Careful inspection also reveals that the overall shape, thickness, and size of sheet-like structures are changed with water content. For instance, with a water content of 33%, the sizes of nanosheets (Fig. 4b) are 2–3 μm . With water content of 50%, the sizes of nanosheets reach 4–7 μm (Fig. 4c). On the basis of above results, it is tentatively concluded that the use of mixed poor solvent provide additional tuning of intermolecular interactions. As a consequence, the NDI architectures with the aimed scale, shape, and aggregation are obtained.

To understand the diversity of NDI architectures upon the variation of volume ratios of methanol to water, the UV-vis absorption (Fig. 5a) and fluorescence spectra (Fig. 5b) of NDI molecules are investigated. The absorption spectrum in ethyl acetate shows three characteristic peaks in the range of 325–375 nm. When dispersed in poor solvent of (methanol, methanol + water, and water), dramatic changes occur in the

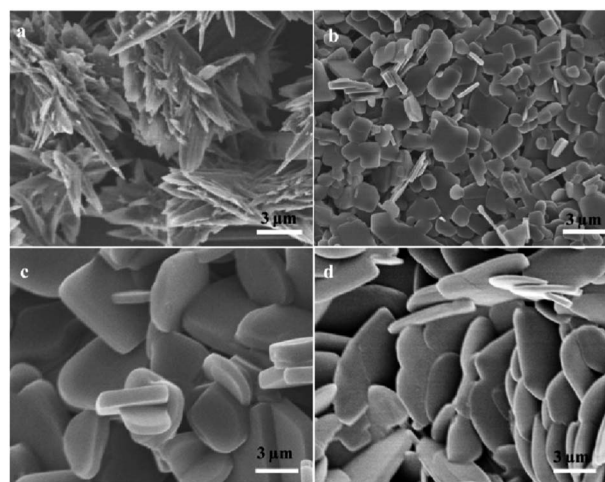


Fig. 4 SEM images of hierarchical architectures of NDI collected after 9 days of assembly. The poor solvents was (a) methanol + water ($v/v = 4 : 1$), (b) methanol + water ($v/v = 2 : 1$), (c) methanol + water ($v/v = 1 : 1$), and (d) water. The volume ratio of ethyl acetate to poor solvent was fixed at 1 : 20, and the concentration of NDI in ethyl acetate was 3 mM.

absorption spectra. This indicates that NDI molecules undergo aggregation due to the limited solubility. No new absorption peaks observed at longer wavelength implies the weak π - π interaction in the aggregate of NDI. A small red shift is attributed to the formation of J-type assembly with the longitudinal displacement along the long axis of chromophores.^{25,26} Moreover, the characteristic absorption peaks of NDI almost disappeared when the volume ratio of water to methanol is larger than 1 : 1. This is due to a fast growth of NDI aggregate, facilitated by water. The fluorescence spectra (Fig. 5b) further confirm this observation. The spectrum in ethyl acetate reveals a monomeric emission peak at ~ 455 nm. When dispersed in poor solvent, the intensity of the emission spectra is significantly quenched. Moreover, a new broad emission peak appears at ~ 550 nm, which is similar to the report.²⁶ The above results demonstrate that the NDI molecules have strong tendency to form aggregates in poor solvents with higher polarity and lower solubility.

In general, non-covalent forces are the driving force for molecular self-assembly. In the present study, the NDI molecule is made from naphthalenediimide and 2-amino-octane (Scheme 1). That is, the strong π - π interaction between the naphthalene planes and the hydrophobic interaction between the alkyl chains should be taken into account for the self-assembly of NDI. Moreover, the interaction between solvent molecules and NDI is the other factor, which counterbalances the intermolecular interactions (especially the hydrophobic interaction between side chains), and affects the molecular assembly. When dispersed in water, there is a strong hydrophobic effect. The alkyl chains tend to attach to each other to reduce its surface expose to the water and in turn weakens the π - π interaction of naphthalenes. Thus, the effective packing of NDI molecules along one dimension is prohibited and sheet-like structures are formed. As for flower-like structure, its formation seems to be associated with the NDI nucleation at the initial stage when dispersed in methanol. The alkyl chains are likely to be exposed to a solvent medium. A nucleus composed of radially arranged NDIs is formed to achieve nanoscale flake driven by the attractive forces, hence flower-like structures are produced. On the other hand, the balance between different forces could be delicately controlled by carefully adjusting the volume ratio

of methanol to water. The variation of different morphologies of sheet, star, and flower were realized.

To understand the correlation between assembled structures and electronic properties, I - V characteristics of flower- and sheet-like structures of NDI are explored and compared. Fig. 6a shows a representative configuration of prototype device, while the inset in Fig. 6b presents a photograph of as-constructed devices. Hierarchical architectures of NDI are firmly connected to Au electrodes with a channel length of *ca.* 5 μm . A larger slope of flower-like structure is obtained, which is indicative of a better conductance than that of sheet-like ones (Fig. 6b). At an applied voltage of -15 V, the current of flower-like structure reach 1 nA, which is in the same order of organic nanostructures in the literatures,^{27,28} while the current of sheet-like one is only 52 pA. At the same time, the conductivity of flower-like structure is about $4.1 \times 10^{-9} \text{ S m}^{-1}$, which is higher than that of the sheet-like ones with $3.2 \times 10^{-10} \text{ S m}^{-1}$. This significant enhancement is probably attributed to the higher crystallinity with well-ordered π - π stacking structure as evidenced in SAED (Fig. 2 and S5†), which benefits the improvement of charge-carrier transport.²⁹ Nevertheless, the current of the flower-like structure is still lower. This is possibly due to the poor contact between NDI architectures and Au electrodes as well as the anisotropic charge transporting in 3-D architectures. Meanwhile, the multiple crystal junctions is also another reason to lower the conductivity. Importantly, the above results demonstrates that it is an effective way to enhance the electric property *via* controlled self-assembly to prepare ordered hierarchical structures of NDIs.

Conclusion

In summary, hierarchical assembly of functionalized NDI was investigated *via* a solvent displacement method. That is, a good solvent (ethyl acetate) containing NDI was fast dispersed into a poor solvent (methanol, methanol + water, or water). The NDI assemblies with the varied scale, shape, and aggregation were formed and fully characterized by SEM, TEM, EDX, UV-vis, and fluorescence. The results demonstrated that the use of a mixture of two poor solvents could provide fine-tuning of intermolecular interactions. In addition, to reveal the structure-property correlation, the I - V characteristics of the as-obtained NDI architectures were explored.

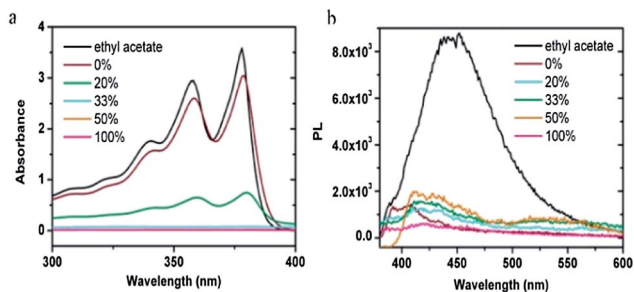


Fig. 5 (a) UV-vis absorption and (b) fluorescence spectra ($\lambda_{\text{ex}} = 342$ nm) of NDI in ethyl acetate and in different mixed solvents (methanol-water) with increasing percentage of added water. The ratio of ethyl acetate/poor solvents is fixed at 1 : 20, and the concentration of NDI in ethyl acetate is 3 mM.

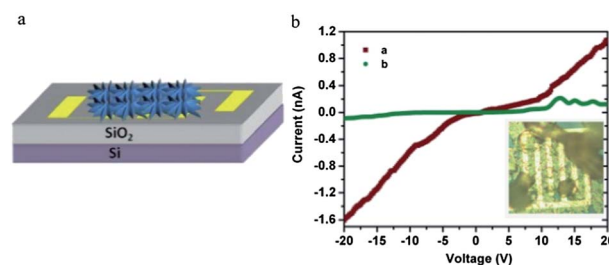


Fig. 6 (a) A schematic depiction of the device based on NDI hierarchical architectures. (b) I - V curves of flower-like (red square) and sheet-like structures (green circle). The inset shows a typical photograph image of NDIs nanostructure-based device.

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Notes and references

- 1 M. R. Molla and S. Ghosh, *Chem. Mater.*, 2011, **23**, 95–105.
- 2 Y. Sun, C. He, K. Sun, Y. Li, H. Dong, Z. Wang and Z. Li, *Langmuir*, 2011, **27**, 11364–11371.
- 3 A. L. Briseno, S. C. Mannsfeld, S. A. Jenekhe, Z. Bao and Y. Xia, *Mater. Today*, 2008, **11**, 38–47.
- 4 M. H. So, V. A. Roy, Z. X. Xu, S. S. Chui, M. Y. Yuen, C. M. Ho and C. M. Che, *Chem. – Asian J.*, 2008, **3**, 1968–1978.
- 5 Y. Che, X. Yang, G. Liu, C. Yu, H. Ji, J. Zuo, J. Zhao and L. Zang, *J. Am. Chem. Soc.*, 2010, **132**, 5743–5750.
- 6 G. D. Pantos, P. Pengo and J. K. Sanders, *Angew. Chem., Int. Ed.*, 2007, **46**, 194–197.
- 7 D. Ke, C. Zhan, A. D. Li and J. Yao, *Angew. Chem., Int. Ed.*, 2011, **50**, 3715–3719.
- 8 K. Liu, Y. Yao, Y. Liu, C. Wang, Z. Li and X. Zhang, *Langmuir*, 2012, **28**, 10697–10702.
- 9 J. H. Oh, S. L. Suraru, W. Y. Lee, M. Könnemann, H. W. Höffken, C. Röger, R. Schmidt, Y. Chung, W. C. Chen and F. Würthner, *Adv. Funct. Mater.*, 2010, **20**, 2148–2156.
- 10 T. D. Bell, S. Yap, C. H. Jani, S. V. Bhosale, J. Hofkens, F. C. De Schryver, S. J. Langford and K. P. Ghiggino, *Chem. – Asian J.*, 2009, **4**, 1542–1550.
- 11 H. E. Katz, J. Johnson, A. J. Lovinger and W. Li, *J. Am. Chem. Soc.*, 2000, **122**, 7787–7792.
- 12 S. V. Bhosale, S. V. Bhosale, M. B. Kalyankar and S. J. Langford, *Org. Lett.*, 2009, **11**, 5418–5421.
- 13 M. Kumar and S. J. George, *Nanoscale*, 2011, **3**, 2130–2133.
- 14 E. B. Namdas, I. D. Samuel, D. Shukla, D. M. Meyer, Y. Sun, B. B. Hsu, D. Moses and A. J. Heeger, *Appl. Phys. Lett.*, 2010, **96**, 043304.
- 15 N. Sakai, J. Mareda, E. Vauthey and S. Matile, *Chem. Commun.*, 2010, **46**, 4225–4237.
- 16 R. Bhosale, J. Mišek, N. Sakai and S. Matile, *Chem. Soc. Rev.*, 2010, **39**, 138–149.
- 17 C. Thalacker, C. Röger and F. Würthner, *J. Org. Chem.*, 2006, **71**, 8098–8105.
- 18 N. B. Kolhe, R. N. Devi, S. P. Senanayak, B. Jancy, K. S. Narayan and S. K. Asha, *J. Mater. Chem.*, 2012, **22**, 15235–15246.
- 19 S. Wang, L. Dossel, A. Mavrinskiy, P. Gao, X. Feng, W. Pisula and K. Mullen, *Small*, 2011, **7**, 2841–2846.
- 20 M. Kumar, N. Jonnalagadda and S. J. George, *Chem. Commun.*, 2012, **48**, 10948–10950.
- 21 S. V. Bhosale, C. Jani, C. H. Lalander and S. J. Langford, *Chem. Commun.*, 2010, **46**, 973–975.
- 22 P. Pengo, G. D. Pantos, S. Otto and J. K. Sanders, *J. Org. Chem.*, 2006, **71**, 7063–7066.
- 23 J. U. Kim, R. Davis and R. Zentel, *J. Colloid Interface Sci.*, 2011, **359**, 428–435.
- 24 M. R. Molla and S. Ghosh, *Chem. – Eur. J.*, 2012, **18**, 9860–9869.
- 25 M. B. Avinash and T. Govindaraju, *Nanoscale*, 2011, **3**, 2536–2543.
- 26 M. R. Molla and S. Ghosh, *Chem. – Eur. J.*, 2012, **18**, 1290–1294.
- 27 B. Mukherjee, K. Sim, T. J. Shin, J. Lee, M. Mukherjee, M. Reeand and S. Pyo, *J. Mater. Chem.*, 2012, **22**, 3192–3200.
- 28 J. S. Hu, H. X. Ji and L. J. Wan, *J. Phys. Chem. C*, 2009, **113**, 16259–16265.
- 29 Y. H. Chou, W. Y. Lee and W. C. Chen, *Adv. Funct. Mater.*, 2012, **22**, 4352–4359.