# Unconventional hydrogen-bond-directed hierarchical co-assembly between perylene bisimide and azobenzene-functionalized melamine†

**Shiki Yagai,*[a,b] Saori Hamamura,‡[a] Hao Wang,[c] Vladimir Stepanenko,[c] Tomohiro Seki,[a] Kanako Unoike,[a] Yoshihiro Kikkawa,[d] Takashi Karatsu,[a] Akihide Kitamura[a] and Frank Würthner*[c]**

*Received 30th June 2009, Accepted 23rd July 2009*
*First published as an Advance Article on the web 3rd August 2009*
**DOI: 10.1039/b912809c**

**Co-assembly of ditopic perylene bisimide and azobenzene-functionalized melamine occurs with an unconventional stoichiometric ratio, providing well-defined nanostructures with a helically-coiled architecture where perylene chromophores are packed in desirable J-type arrangements.**

Well-defined nanostructures composed of optically and electronically addressable molecular elements are attractive as active modules for miniaturizing optoelectronic devices.[1] In nature, highly sophisticated photophysical functionalities on the nanoscale are achieved by complexation of functional dye molecules by polypeptide scaffolds, or by self-assembly of functional dyes through the synergetic action of various noncovalent interactions.[2] The tailoring of such demanding dye-incorporated nanostructures *via* a supramolecular approach[3] is thus a challenging, albeit an interesting, research topic.[4] Most of the previous efforts in this area, however, have been primarily focused on self-assemblies composed of one dye component and one self-complementary structure-directing building block.[5,6] A very often applied supramolecular motif of this brick-and-mortar approach has apparently been the combination of bisimide chromophores (brick) and melamines (mortar).[5-7] In addition, there are only a few examples where the effect of non-stoichiometric ratios of the two components on self-assembly has been elucidated.[8,9] In general, it is assumed that the directionality and strength of hydrogen bonds ensure robust supramolecular motifs, *i.e.* triple hydrogen bonds between melamine and imide building blocks, and that accordingly any non-stoichiometric excess should be expelled from the 1:1 self-assembled composite material. However, some recent examples have demonstrated that, in particular, the involvement of chromophores with strong $\pi$–$\pi$-stacking ability can direct the formation of stoichiometrically mismatched supramolecular architectures.[9] Unfortunately, such mismatched assemblies have failed to afford well-defined nanostructures and are therefore considered as less appealing. We herein report the formation of structurally highly defined self-assembled nanostructures with an unconventional composition ratio of two complementary hydrogen-bonding dyes, *i.e.* perylene bisimide (PBI) **1**[5d] and melamine-linked azobenzene **2**[10] (Fig. 1).[11] Most importantly, we found that the outcome of this self-assembly strongly depends on the addition protocol of the two components, and the temperature and time period of self-assembly. Our results point at more complex self-assembly pathways than commonly taken into consideration by "supramolecular design" based on intermolecular Gibbs binding energies between particular ligand–receptor pairs.

Since **1** and **2** possess ditopic complementary triple-hydrogen-bonding modules, our initial expectation was that the most stable

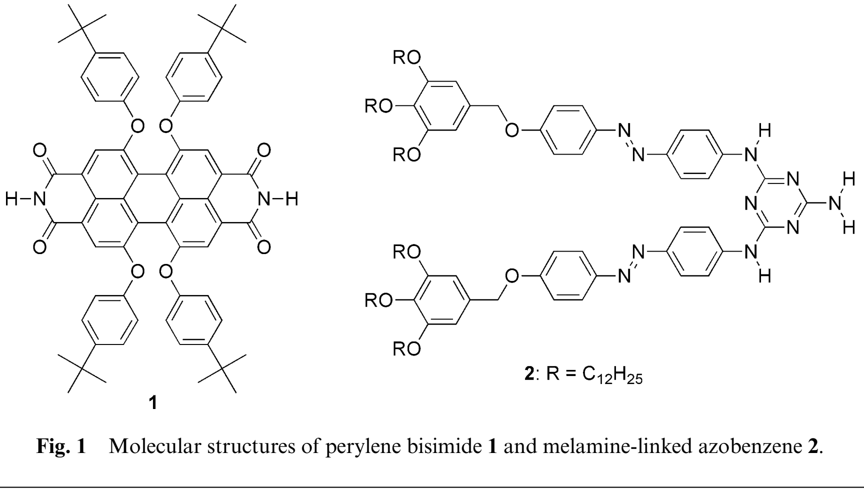

**Fig. 1** Molecular structures of perylene bisimide **1** and melamine-linked azobenzene **2**.

---

[a] *Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan. E-mail: yagai@faculty.chiba-u.jp; Fax: (+81) 43-290-3401*
[b] *PRESTO, Japan Science Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan*
[c] *Universität Würzburg, Institut für Organische Chemie and Röntgen Research Center for Complex Material Systems, Am Hubland, 97074, Würzburg, Germany. E-mail: wuerthner@chemie.uni-wuerzburg.de; Fax: (+49) 931-318-4756*
[d] *Photonics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8562, Japan*

† Electronic supplementary information (ESI) available: Experimental details, UV/vis titration of **2** with **1**, DLS data, temperature-dependent UV/vis spectra of assembly. See DOI: 10.1039/b912809c

‡ Present address: Hitachi, Ltd. Production Engineering Research Laboratory, 292 Yoshida-cho, Totsuka-ku, Yokohama 244-0817, Japan.

composite of these two dyes should be the 1:1 co-assembly $\cdots\equiv\mathbf{2}\equiv\mathbf{1}\equiv\mathbf{2}\equiv\mathbf{1}\equiv\cdots$, where '≡' represents triple hydrogen bonds between imide and melamine moieties. Such molecular arrays are either polymeric or cyclic oligomers,[7] which further organize into higher-order structures through $\pi$-stacking interactions. The components **1** and **2** were thus mixed at a molar ratio of 1:1 in dichloromethane, and after evaporation of the solvent redissolved in nonpolar methylcyclohexane (MCH). Dynamic light scattering (DLS) of the resulting solution, however, did not show any large assemblies at $[\mathbf{1}] = 5 \times 10^{-5}$ M. This solution exhibited a conspicuously different absorption spectrum in the visible range compared to that of the monomeric state of **1** in dichloromethane (blue and red spectra in Fig. 2a, respectively). Thus, a rather broad band with a maximum at 577 nm and distinct shoulders at around 540 and 600 nm was observed. Such spectral features are indicative of the presence of different stacking arrangements of the PBI dyes in a complex self-assembled architecture or, more likely, co-existing architectures.[7a] Atomic force microscopy (AFM) images of samples prepared from a 1:1 mixture of **1** and **2** in MCH ($[\mathbf{1}] = 5 \times 10^{-5}$ M) spin-coated onto highly oriented pyrolytic graphite (HOPG) showed small assemblies with ill-defined morphologies of less than 50 nm size (Fig. 3a). In analogy to the closely related system reported recently,[9b] it is therefore conceivable that **1** and **2** do not form a single defined nanostructure by employing complementary triple hydrogen-bonding interactions.

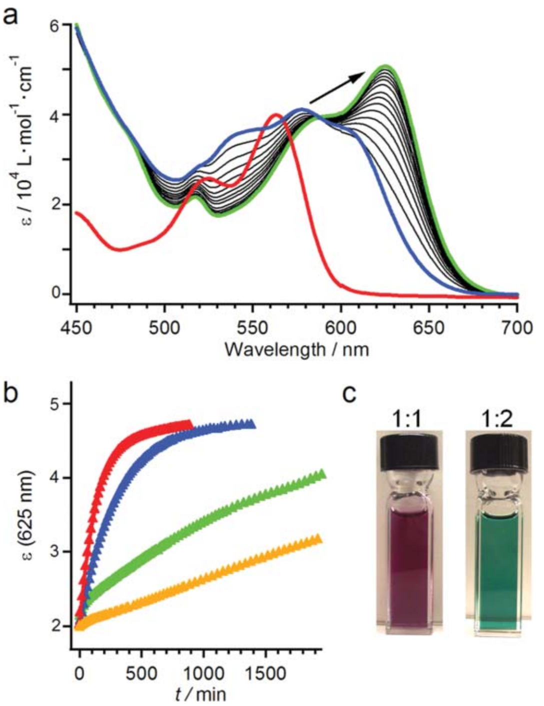

**Fig. 2** UV/vis data of pure **1** and mixtures of **1** and **2** in MCH. (a) Red line, the spectrum of monomeric **1** ($[\mathbf{1}] = 1.25 \times 10^{-6}$ M); blue line, the spectrum of a 1:1 mixture of **1** and **2** once mixed in dichloromethane ($[\mathbf{1}] = 1.25 \times 10^{-5}$ M); blue-to-green lines, time-dependent spectral change (0 to 890 min) upon addition of 3 equiv. of **2**. (b) Time-dependent changes of ε at 625 nm in the UV/vis spectral change of the above 1:1 mixture upon addition of 0.5 (orange), 1 (green), 2 (blue) and 3 equiv. (red) of **2**. (c) Photographs of MCH solutions of 1:1 and thermodynamically equilibrated 1:2 assemblies ($[\mathbf{1}] = 1.0 \times 10^{-4}$ M).

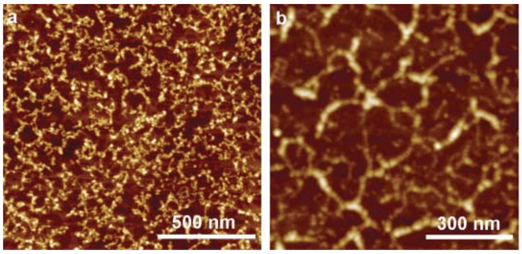

**Fig. 3** AFM height images of (a) a 1:1 mixture and (b) a 1:1.5 mixture of **1** and **2**, spin-coated from their MCH solutions onto HOPG ($[\mathbf{1}] = 5 \times 10^{-5}$ M); $z$ scale: 6 nm in (a) and 10 nm in (b).

To our surprise, the addition of excess amounts of **2** to this 1:1 stoichiometric solution triggers the transition into assemblies showing a more red-shifted absorption band at 630 nm, which is characteristic for J-aggregated tetraphenoxy-substituted PBIs (blue to red spectra, Fig. 2a).[6e,12] This process was not instantaneous but required a substantial equilibration time of about 15 h at 20 °C for $[\mathbf{1}] = 1.25 \times 10^{-5}$ M after addition of 3 equiv. of **2**. For smaller amounts of **2**, this process became even slower which points at a kinetically hindered reorganization process between the supramolecular species involved (Fig. 2b). As a result of the spectral transition, the solution color turns from purple to green (Fig. 2c).

To determine the exact stoichiometry for the formation of the J-aggregate state, UV/vis spectra of **1** ($c = 2.5 \times 10^{-6}$ M) were recorded in the presence of varying amounts of **2** after thermal treatment to achieve thermodynamically equilibrated solutions (Fig. 4). A plot of absorbance at 630 nm *versus* molar ratios revealed that a 1:1.5 ratio of **1** and **2** is required for the stacking of PBI **1** dyes in the J-aggregate state (inset in Fig. 4). This unconventional complexation ratio between ditopic complementary hydrogen-bonding modules was further confirmed by a reverse titration of **2** ($c = 1.5 \times 10^{-5}$ M) with **1** (see Fig. S1†). These experiments clearly show that an excess of melamine units is required for the organization of all PBI **1** molecules in a J-type aggregation mode.

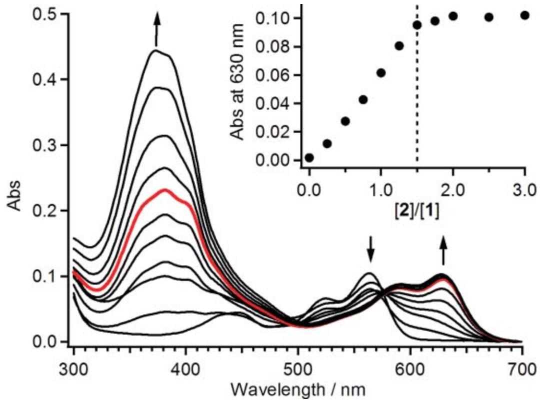

**Fig. 4** UV/vis spectra of MCH solutions containing constant amounts of **1** ($[\mathbf{1}] = 2.5 \times 10^{-6}$ M) and various amounts of **2** ($[\mathbf{2}] = 0$ to $7.5 \times 10^{-6}$ M). Each solution was obtained by mixing the two components directly in MCH and the spectra were taken after heating at 90 °C to obtain a thermodynamically stable state. Arrows indicate the increase of **2**. Red spectra are the spectra at $[\mathbf{2}]/[\mathbf{1}] = 1.5$. Inset: plot of absorbance at 630 nm *versus* $[\mathbf{2}]/[\mathbf{1}]$. Dotted line indicates $[\mathbf{2}]/[\mathbf{1}] = 1.5$.

DLS experiments of the 1:1.5 mixture revealed that these self-assemblies with J-type PBI stacks have increased hydrodynamic diameters of 79 nm for [**1**] = $5 \times 10^{-5}$ M solution at 20 °C (Fig. S2†). AFM images of the 1:1.5 mixture ([**1**] = $5 \times 10^{-5}$ M) also clearly showed an enlargement of the assemblies compared to those of the 1:1 mixture (Fig. 3b). Globular assemblies with diameters ranging from 17 to 42 nm are observed that preferentially stick together to afford coil-like morphologies. Temperature-dependent UV/vis measurements of 1:1.5 mixtures revealed a fully reversible transition between the J-aggregate state and the molecularly dissolved state (Fig. S3†). Transition temperatures of 84, 78 and 56 °C were observed for solutions with [**1**] = $5 \times 10^{-5}$, $1.4 \times 10^{-5}$ and $2.5 \times 10^{-6}$ M, respectively, demonstrating higher stabilities of these aggregates compared to closely related systems based on PBI **1** and oligo(*p*-phenylenevinylene)s (OPVs).[9b] This is quite remarkable since the π-stacking ability of azobenzene is much weaker than that of OPVs, which virtually excludes the one-dimensional J-type stacking of a small hydrogen-bonded species.[6e] We rather propose the formation of supramolecular polymers such as ···≡**1**≡**2**=**2**≡**1**≡**2**≡···, where additional modules **2** are inserted into alternate hydrogen-bonded arrays of **1** and **2** by forming melamine–melamine double hydrogen bonds ('=').[8] Such supramolecular polymers featuring relatively flexible double hydrogen bonds may allow J-type stacking of perylene chromophores between supramolecular polymer chains.[13]

Whilst the spectroscopic studies indicated that a stationary state with optimized J-type packing of all PBI **1** chromophores was accomplished at a 1:1.5 ratio of the two components, AFM investigations revealed that a further insertion of **2** into the supramolecular polymers enabled the formation of an even more defined nanostructure (with identical J-type PBI packing according to UV/vis spectroscopy). At a 1:2 ratio of **1** and **2**, a considerable number of well-defined fibrous nanostructures could be visualized by AFM imaging ([**1**] = $5 \times 10^{-5}$ M, Fig. 5a), illustrating the formation of only one type of extended nanostructure. High-resolution imaging suggests the formation of tightly-coiled helical nanostructures with an average helical pitch of 6.0 nm and contour lengths in the range of 100–200 nm (Fig. 5b–d). The helical sense appears not to be biased, which is reasonable in the absence of any chiral sources. The average width of these coils is 12.0 ± 2.0 nm, whereas the average height is 3.8 ± 0.4 nm. This significant difference between the two dimensions could be attributed to the presumably hollow structure of the coils that is susceptible to deformation through evaporation process.

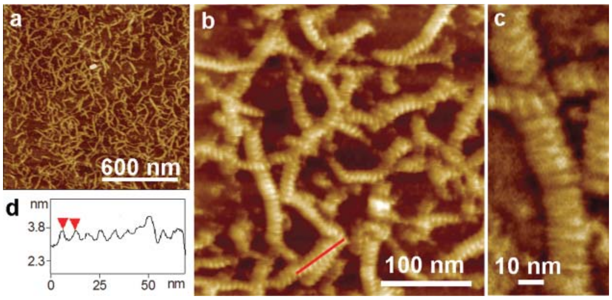

**Fig. 5** (a,b) AFM height and (c) phase images of a 1:2 mixture of **1** and **2** spin-coated from a MCH solution ([**1**] = $5 \times 10^{-5}$ M) onto HOPG; *z* scale: 12 nm in (a) and 8 nm in (b). (d) The cross section along the red line in (b).

A possible packing model for these 1:2 self-assemblies is depicted in Fig. 6. From UV/vis, DLS and AFM studies, it is obvious that the addition of **2** to the 1:1 mixture (small assemblies) enables growth into more extended species. At the 1:2 molar ratio of **1** and **2**, all the melamine moieties should exist as dimers (Fig. 6a). The *syn* orientation both in the dimeric segments (**2**=**2**) and in two adjacent melamine units separated by **1** with respect to the azobenzene side chains allows polymeric strands of ···≡**1**≡**2**=**2**≡**1**≡**2**=**2**≡**1**≡**2**=**2**≡··· to form a helically-elongated structure (Fig. 6b). Molecular modelling shows that the outer width of such a helical structure with extended alkyl chains is *ca.* 9.0 nm, which is in good agreement with the diameters of the coils by taking into account the morphological deformation. By assuming a π–π-stacking distance of 0.5 nm between PBI cores, intertwining of about twelve strands is calculated for the generation of a closely packed self-assembled tube composed of J-aggregated PBI **1** chromophores. Such a tube is surrounded by azobenzene units with dodecyl chains pointing outwards, which is highly favorable in aliphatic solvents (Fig. 6c). We would like to point out that the proposed model is still quite speculative but is in accordance with all our available data.

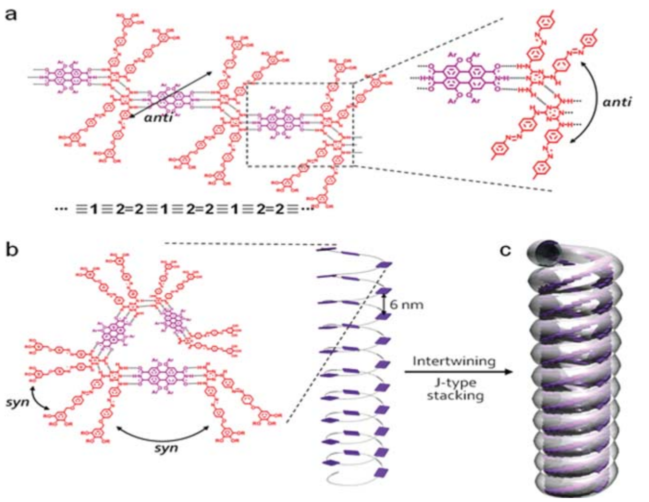

**Fig. 6** Possible organization for the 1:2 co-assemblies of **1** and **2**. (a) One-dimensional linear hydrogen-bonded supramolecular co-polymer (···≡**1**≡**2**=**2**≡**1**≡**2**=**2**≡**1**≡**2**=**2**≡···), where the orientations of neighbouring **2** molecules and of those separated by **1** is *anti* with respect to the azobenzene side chains. (b) The resulting polymeric strand can take a helical tubular architecture by adopting *syn* orientations. In the cartoon presentation, PBI chromophores are indicated by purple squares, which are spatially arranged along the hydrogen-bonded strand represented by the grey wire. (c) Twelve helical strands are intertwined to form coils, which is accompanied by the J-type stacking of PBI chromophores.

So far, multiple hydrogen-bonding interactions have been applied as a supramolecular construction kit with a high degree of fidelity. In this study, however, we have demonstrated that mismatched stoichiometries may afford the thermodynamically more stable species and that elevated temperatures or prolonged time periods may be required to overcome kinetic barriers upon incorporation of dyes with extended π-surfaces. Similarly, complex self-assembly processes may be expected for any kind of extended supramolecular architecture formed by multiple binding events as provided in the present case by hydrogen bonding and

$\pi$–$\pi$ stacking. Although at first glance the often desired simplicity of "programmed" self-assembly seems to be miscarried under such conditions, new exciting prospects arise that include more advantageous organization and stability (as shown here with properly J-packed PBI dyes) or responsiveness of the system to external stimuli (photoswitching of the azobenzene subunits in the various self-assembled states will be investigated in the future).

## Acknowledgements

We would like to thank Prof. Hitoshi Tamiaki and Dr Michio Kunieda for DLS analysis. H.W. thanks the Humboldt foundation for a postdoctoral fellowship. This work was partially supported by the Ministry of Education, Science, Sports and Technology of Japan, Grant-in-Aid for Scientific Research (B) (No. 20350061).

## Notes and references

1 F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer and A. P. H. J. Schenning, *Chem. Rev.*, 2005, **105**, 1491.

2 *Light-Harvesting Antennas in Photosynthesis, Advances in Photosynthesis and Respiration series*, ed: B. R. Green and W. W. Parson, Kluwer Academic Publishers, Dordrecht, 2003, Vol. 13.

3 J.-M. Lehn, *Supramolecular Chemistry, Concept and Perspectives*, VCH, Weinheim, 1995.

4 (*a*) *Supramolecular Dye Chemistry*, F. Würthner, Ed.; *Top. Curr. Chem.*, 2005, **258**; (*b*) S. Yagai, *J. Photochem. Photobiol. C: Photochem. Rev.*, 2006, **7**, 164.

5 For some examples of hydrogen-bonded self-assemblies composed of one dye component and one self-complementary structure-directing building block: (*a*) T. M. Bohanon, S. Denzinger, R. Fink, W. Paulus, H. Ringsdorf and M. Weck, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 58; (*b*) N. Kimizuka, T. Kawasaki, K. Hirata and T. Kunitake, *J. Am. Chem. Soc.*, 1995, **117**, 6360; (*c*) N. Kimizuka, S. Fujikawa, H. Kuwahara, T. Kunitake, A. Marsh and J.-M. Lehn, *J. Chem. Soc., Chem. Commun.*, 1995, 2103; (*d*) F. Würthner, C. Thalacker, A. Sautter, W. Schartl, W. Ibach and O. Hollricher, *Chem.–Eur. J.*, 2000, **6**, 3871; (*e*) F. Würthner, S. Yao, B. Heise and C. Tschierske, *Chem. Commun.*, 2001, 2260; (*f*) S. Yagai, T. Kinoshita, M. Higashi, K. Kishikawa, T. Nakanishi, T. Karatsu and A. Kitamura, *J. Am. Chem. Soc.*, 2007, **129**, 13277; (*g*) S. Yagai, S. Mahesh, Y. Kikkawa, K. Unoike, T. Karatsu, A. Kitamura and A. Ajayaghosh, *Angew. Chem., Int. Ed.*, 2008, **47**, 4691; (*h*) S. Yagai, S. Kubota, K. Unoike, T. Karatsu and A. Kitamura, *Chem. Commun.*, 2008, 4466.

6 For some examples of hydrogen-bonded self-assemblies composed of two different chromophores, see: (*a*) N. D. McClenaghan, C. Absalon and D. M. Bassani, *J. Am. Chem. Soc*, 2003, **125**, 13004; (*b*) C.-H. Huang, N. D. McClenaghan, A. Kuhn, J. W. Hofstraat and D. M. Bassani, *Org. Lett.*, 2005, **7**, 3409; (*c*) H. Nakade, B. J. Jordan, H. Xu, G. Han, S. Srivastava, R. R. Arvizo, G. Cooke and V. M. Rotello, *J. Am. Chem. Soc.*, 2006, **128**, 14924; (*d*) F. Würthner, J. Schmidt, M. Stolte and R. Wortmann, *Angew. Chem., Int. Ed.*, 2006, **45**, 3842; (*e*) F. Würthner, Z. Chen, F. J. M. Hoeben, P. Osswald, C.-C. You, P. Jonkheijm, J. van Herrikhuyzen, A. P. H. J. Schenning, P. P. A. M. van der Schoot, E. W. Meijer, E. H. A. Beckers, S. C. J. Meskers and R. A. J. Janssen, *J. Am. Chem. Soc.*, 2004, **126**, 10611.

7 (*a*) G. M. Whitesides, E. E. Simanek, J. P. Mathias, C. T. Seto, D. Chin, M. Mammen and D. M. Gordon, *Acc. Chem. Res.*, 1995, **28**, 37; (*b*) C. Fouquey, J.-M. Lehn and A.-M. Levelut, *Adv. Mater.*, 1990, **2**, 254; (*c*) K. Ariga and T. Kunitake, *Acc. Chem. Res.*, 1998, **31**, 371; (*d*) R. F. M. Lange, F. H. Beijer, R. P. Sijbesma, R. W. W. Hooft, H. Kooijman, A. L. Spek, J. Kron and E. W. Meijer, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 969; (*e*) W. T. S. Huck, R. Hulst, P. Timmerman, F. C. J. M. van Veggel and D. N. Reinhoudt, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1006.

8 (*a*) C. Thalacker and F. Würthner, *Adv. Funct. Mater.*, 2002, **12**, 209; (*b*) P. Jonkheijm, A. Miura, M. Zdanowska, F. J. M. Hoeben, S. De Feyter, A. P. H. J. Schenning, F. C. De Schryver and E. W. Meijer, *Angew. Chem., Int. Ed.*, 2004, **43**, 74.

9 (*a*) S. Yagai, T. Seki, T. Karatsu, A. Kitamura and F. Würthner, *Angew. Chem., Int. Ed.*, 2008, **47**, 3367; (*b*) F. J. M. Hoeben, J. Zhang, C. C. Lee, M. J. Pouderoijen, M. Wolffs, F. Würthner, A. P. H. J. Schenning, E. W. Meijer and S. D. Feyter, *Chem.–Eur. J.*, 2008, **14**, 8579.

10 (*a*) S. Yagai, T. Nakajima, T. Karatsu, K. Saitow and A. Kitamura, *J. Am. Chem. Soc.*, 2004, **126**, 11500; (*b*) S. Yagai, T. Nakajima, K. Kishikawa, S. Kohmoto, T. Karatsu and A. Kitamura, *J. Am. Chem. Soc.*, 2005, **127**, 11134.

11 For the self-assembly of covalently connected perylene bisimide–azobenzene dyads, see: Y. Fenga and W. Feng, *Opt. Mater.*, 2008, **30**, 876.

12 T. E. Kaiser, H. Wang, V. Stepanenko and F. Würthner, *Angew. Chem., Int. Ed.*, 2007, **46**, 5541.

13 For the organization of supramolecular polymers, see: (*a*) L. Brunsveld, B. J. Folmer, E. W. Meijer and R. P. Sijbesma, *Chem. Rev.*, 2001, **101**, 4071; (*b*) A. T. ten Cate and R. P. Sijbesma, *Macromol. Rapid Commun.*, 2002, **23**, 1094.