ChemComm

Cite this: Chem. Commun., 2011, 47, 8934-8936

COMMUNICATION

Chiral induction by helical neighbour: spectroscopic visualization of macroscopic-interaction among self-sorted donor and acceptor π -stacks[†]

Mijanur Rahaman Molla, Anindita Das and Suhrit Ghosh*

Received 28th February 2011, Accepted 24th May 2011 DOI: 10.1039/clcc11178g

Supramolecular induction of chirality to a π -stacked dialkoxynaphthalene (DAN)-fiber (made of achiral building blocks) from a neighbouring helical naphthalenediimide (NDI)-fiber is reported. CD-studies helped in understanding the nature of co-assembly in the donor-acceptor chromophore mixture from molecular to macroscopic scale.

Helical assembly plays a key role in many elegant functions performed by biopolymers in living systems with ultimate perfection. Chemists have been fascinated to study helicity in polymeric¹ and supramolecular systems² to mimic such biological objects, if not by function, then at least from structural aspects. In supramolecular systems, most often helicity is originated from asymmetric building blocks by transfer of chirality from molecular to macroscopic scale. It is well established that even a very small fraction of a chiral building block is sufficient to induce chirality in the entire supramolecular or polymeric assemblies by the so-called "sergeant-and-soldiers" effect.³ Induction of chirality in 1-D supramolecular assemblies has also been observed by external perturbations using various types of physical and chemical interactions,⁴ chiral solvent,⁵ and even vortex effect ⁶ generated by unidirectional magnetic stirring.

We have recently demonstrated self-sorting⁷ among bis-amide functionalized dialkoxynaphthalene (**DAN-1**, Scheme 1) donor and naphthalenediimide (**NDI-2**, Scheme 1) acceptor due to hydrogen-bonding and π -stacking.⁸ To gain further insight into this interesting phenomenon herein we have studied self-assembly



Scheme 1 Structure of the various chromophores.

of a structurally similar NDI-chromophore containing an asymmetric centre in the peripheral alkyl chain (NDI-1, Scheme 1) with achiral DAN-1 by circular dichroism (CD), which revealed chirality transfer from the acceptor-stacks to the donor-stacks. To the best of our knowledge, as yet there is no report of such unique chirality induction by helical neighbours, which in turn helped in spectroscopic visualization of the nature of macroscopic level organization among the molecularly self-sorted donor and acceptor supramolecular π -stacked fibers.

Self-assembly of **NDI-1** was studied by absorption spectroscopy (Fig. 1a) by varying the solvent from CHCl₃ to methylcyclohexane (MCH). In CHCl₃ well resolved absorption bands are seen in the range of 300–400 nm due to π – π * transition polarized along the long axis of the chromophore, suggesting the presence of monomers. With increasing amount of MCH, the spectra remained almost invariant till 80:20 MCH–CHCl₃ and beyond this point with further increase in MCH composition, a strong hypochromic shift with concomitant red shift (~3 nm) was observed suggesting π -stacked assembly.^{8,9} The mole fraction of the aggregate (α_{agg})⁸ is plotted as a function of solvent composition in Fig. 1b and from this plot the α_{50} (critical solvent composition where $\alpha_{agg} = 0.5$) was estimated to be 83% (v/v) MCH–CHCl₃.



Fig. 1 Solvent dependent UV/vis spectra (a) and variation of α_{agg} with solvent composition (b) for NDI-1 at rt; Variation of CD spectra of NDI-1 with solvent (c) and temperature (d) (solvent = 95:5 MCH–CHCl₃). Concentration of NDI-1 = 0.5 mM. Arrows in (a) indicate spectral variation from CHCl₃ to MCH.

Indian Association for the Cultivation of Science, Polymer Science Unit, 2A & 2B Raja S. C. Mullick Rd., Kolkata, India. E-mail: psusg2@iacs.res.in; Fax: +91 33 2473 2805; Tel: +91 33 2473 4971

[†] Electronic supplementary information (ESI) available: Synthesis, characterization, detail experimental procedure and additional spectral data related to probing self-assembly. See DOI: 10.1039/c1cc11178g

Furthermore, it was observed that self-assembly could be completely destroyed by addition of ~5% (v/v) MeOH to the chromophore solution in 95:5 MCH-CHCl₃ (Fig. S1a, ESI[†]) suggesting strong influence of H-bonding. The value of $\alpha_{50}(T)$ (temperature at which $\alpha_{agg} = 0.5$) for self-assembly in 95:5 MCH-CHCl₃ was estimated to be 60 °C from variabletemperature UV/vis experiments (Fig. S1, ESI⁺). Similar to recently reported NDI-2,¹⁰ NDI-1 also showed very efficient gelation ability¹¹ in non-polar organic solvents with extremely low critical gelation concentration (0.55 wt% in cyclohexane). Further the self-assembly of NDI-1 was probed by CD. In CHCl₃ where the NDI-1 chromophores remain as monomers, no CD band was observed, but in 95:5 MCH/CHCl₃ an intense positive Cotton effect was observed (Fig. 1c) in the region of 300-400 nm which corresponds to the absorption due to $\pi - \pi^*$ transition polarized along the long axis (band 1) of NDI. The observed positive Cotton effect was attributed to the formation of *P*-type helical assembly based on previously reported systems.¹² We further noticed that in presence of 5% (v/v) MeOH, the CD-band completely disappeared (Fig. 1c), clearly suggesting that the CD-band originates due to selfassembly. A variable-temperature CD-experiment (Fig. 1d) revealed the Cotton effect even at 60 °C suggesting very good thermal stability of the helical assembly. Atomic force microscopy (AFM) images of NDI-1 (sample prepared from solution in 95:5 MCH-CHCl₃) revealed micrometre long fibrils (Fig. 2) with average height and diameter of 5.9 ± 0.5 and 70.6 \pm 1 nm, respectively. However, the resolution of the images does not allow us to assign helicity conclusively.

Having established the self-assembly of NDI-1 alone we now examined the co-assembly pattern for a mixture of **NDI-1** + **DAN-1**. **NDI-1** is structurally almost identical to NDI-2 except in one of the three peripheral alkyl chains which contains the chiral centre, and thus it is expected to show similar self-sorting behaviour⁸ with **DAN-1**. This was confirmed by comparing the UV/vis spectrum of NDI-1 + DAN-1 (1:1) in 95:5 MCH–CHCl₃ with that generated by mathematical summation of the spectra of the two individual components (Fig. S2, ESI[†]), and both were found to be almost identical, suggesting self-sorting. Furthermore, absence of any chargetransfer absorption band in the spectrum of the mixture (Fig. S2, ESI[†]) confirmed lack of alternate co-assembly between donor and acceptor chromophores. Now we examined the co-assembly by CD (Fig. 3a). In CHCl₃, NDI-1 + DAN-1 (1:1) mixture does not show any CD-signal due to lack of

1 μm100 nmFig. 2 (a) AFM height-images of NDI-1 in cyclohexane (conc. =0.05 mM); inset: photo of the NDI-1 gel in cyclohexane at 0.55 wt%;(b) zoomed region of the AFM-image shown in (a).



Fig. 3 (a) CD spectra of NDI-1 and its mixture with DAN-1 under various conditions. (b) Variation of CD intensity at 386 nm (solely due to NDI-1) with temperature for NDI-1 alone and NDI-1 + DAN-1 (1:1) in 95: 5 MCH–CHCl₃. Concentration of individual chromophore = 0.5 mM.

aggregation. However an intense positive Cotton effect was observed (green line) in 95:5 MCH-CHCl₃ suggesting helical self-assembly. Surprisingly in the CD-spectrum of the mixture, in addition to the NDI-1 band at 386 nm, additional bands were observed (orange line) in the region of 320-340 nm which correspond to the **DAN-1** absorption in the aggregated state⁸ although the chromophore does not contain any chiral center. To confirm that the new band appears due to self-assembly of DAN-1, the CD spectrum of the mixture was examined at an intermediate temperature (55 °C) where self-assembly of NDI-1 should remain intact, but the relatively less-stable π -stacked assembly DAN-1 should be converted to monomers.8,13 In Fig. 3a, it can be clearly seen that at 55 °C the additional bands in the CD-spectrum corresponding to the donor-absorption disappear (blue line) and the spectrum is very similar to that observed for NDI-1 alone (black line). This clearly demonstrates that the new band in the 320-340 nm region indeed corresponded to the self-assembly of DAN-1. Further we carried out variabletemperature CD-experiments of the NDI-1 + DAN-1 mixture (Fig. S3[†]) and compared the variation of intensity at 386 nm (DAN molecule does not absorb in this region) with that for NDI-1 alone (Fig. 3b). An almost identical nature of the curve in both cases14 confirmed no significant interference of the neighboring chromophoric-stack on the strength of selfassembly for NDI chromophore, which is governed by interchromophoric interaction among the NDI building blocks. To explain this we considered the possibility of chiral induction by the "sergeant-and-soldiers" effect due to insertion of small fraction of chiral NDI-1 into the achiral DAN-1 stack. In such a situation, one would expect appearance of a CT-band due to donor-acceptor interaction. To check this we examined the UV/vis spectra of DAN-1 mixed with 5% and 10% of NDI-1 but no CT-band was visible in either case (Fig. S6[†]). However, one may argue that intrinsically weak and broad CT-bands may not be detectable at very low concentration. However, when we mixed the same amount of NDI-1 (5% and 10%) in DAN-4¹⁵ (see Fig. S5[†] for structure), we could trace a distinct CT-band (Fig. S6⁺) clearly suggesting even at this concentration it is detectable. Thus we eliminate the possibility of chiral induction by "sergeant-and-soldiers" effect in the present study and propose the following hypothesis (Scheme 2). Individual donor and acceptor chromophores self-assemble in orthogonal fashion as revealed from UV/vis studies. Such self-sorted NDI- and DAN-homo-aggregates do not macroscopically differentiate among them because both types of fibers are encased with similar hydrocarbon chains. Thus clustering of individual





Scheme 2 Schematic of chiral-induction by helical neighbour.

fibers happens indiscriminately which results in chiral induction from the helical NDI-1 fibers to the adjacent DAN-1 fibers through hydrophobic interaction among the peripheral alkyl chains. To support this hypothesis we studied self-assembly of NDI-1 in the presence of another donor DAN-2 (Scheme 1) which contains peripheral oligo-oxyethylene units instead of hydrocarbon chains but in which the remaining part of the molecule is structurally identical to DAN-1. Self-assembly of **DAN-2** alone¹⁶ was primarily investigated by solvent-dependent UV/vis studies (Fig. S4[†]) which indicated J-type π -stacking.¹³ The CD-spectra of NDI-1 + DAN-2 in 95:5 MCH-CHCl₃ was found to be fully matching to that for NDI-1 alone (Fig. S7[†]). This clearly supports the hypothesis that indeed the hydrophobic interaction among the peripheral alkyl chains of the individual fibers is responsible for the observed chiral induction for the (NDI-1 + DAN-1) pair which is not possible for (NDI-1 + DAN-2) because of the immiscibility among hydrocarbon and oligooxyethylene chains.¹⁷

Herein we have probed H-bonding mediated assembly in bis-amide functionalized chiral acceptor (NDI) and achiral donor (DAN) molecules. Due to the mismatch in the distance between the two amide groups, self-sorting was achieved resulting in two types of homo-aggregated fibers. CD-experiments revealed helical assembly for both the donor and acceptor stacks although an asymmetric centre was present only in the acceptor building block. This was attributed to induction of helical-bias from the acceptor-stack to the donor-stack due to mixing of the self-sorted fibers at macroscopic level by hydrophobic interaction among the peripheral alkyl chains. We are exploring this as a general tool for spectroscopic visualization of macroscopic-organization of chromophores and polymeric mixtures which is highly relevant in bulk hetero-junction solar cells.¹⁸

Notes and references

- E. Yishima, K. Maeda, H. Iida, Y. Furusho and K. Nagai, *Chem. Rev.*, 2009, **109**, 6102; J. J. L. M. Cornelissen, A. E. Rowan, R. J. M. Nolte and N. A. J. M. Sommerdijk, *Chem. Rev.*, 2001, **101**, 4039.
- 2 F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer and A. P. H. J. Schenning, *Chem. Rev.*, 2005, **105**, 1491; C. M. Drain, A. Varotto and I. Radivojevic, *Chem. Rev.*, 2009, **109**, 1630.

- 3 L. J. Prins, P. Timmerman and D. N. Reinhoudt, J. Am. Chem. Soc., 2001, 123, 10153; T. E. Kaiser, V. Stepanenko and F. Würthner, J. Am. Chem. Soc., 2009, 131, 6719; A. Ajayaghosh, R. Varghese, S. Mahesh and V. K. Praveen, Angew. Chem., Int. Ed., 2006, 45, 7729; A. J. Wilson, J. V. Gestel, R. P. Sijbesma and E. W. Meijer, Chem. Commun., 2006, 4404.
- 4 M. M. Green, S. Zanella, H. Gu, T. Sato, G. Gottorelli, F. K. Jha, G. P. Spada, A. M. Schoevaars, B. Feringa and A. Teramoto, J. Am. Chem. Soc., 1998, 120, 9810; A. P. H. J. Schenning, J. v. Herrikhuyzen, P. Jonkheijm, Z. Chen, F. Würthner and E. W. Meijer, J. Am. Chem. Soc., 2002, 124, 10252; S. J. George, Z. Tomović, M. M. J. Smulders, T. F. A. de Greef, P. E. L. G. Leclère, E. W. Meijer and A. P. H. J. Schenning, Angew. Chem., Int. Ed., 2007, 46, 8206; M. P. Thompson and R. P. Lemieux, J. Mater. Chem., 2007, 17, 5068; A. Ajayaghosh, P. Chithra and R. Varghese, Angew. Chem., Int. Ed., 2007, 46, 200; 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.
- G. Celebre, G. D. Luca, M. Maiorino, F. Lemma, A. Ferrarini, S. Pieraccini and G. P. Spada, J. Am. Chem. Soc., 2005, 127, 11736; B. Isare, M. Linares, L. Zargarian, S. Fermandjian, M. Miura, S. Motohashi, N. Vanthuyne, R. Lazzaroni and L. Bouteiller, Chem.-Eur. J., 2010, 16, 173; S. J. George, Z. Tomović, A. P. H. J. Schenning and E. W. Meijer, Chem. Commun., 2011, 47, 3451.
- 6 A. Tsuda, M. A. Alam, T. Harada, T. Yamaguchi, N. Ishii and T. Aida, *Angew. Chem., Int. Ed.*, 2007, **46**, 8198; M. Wolffs, S. J. George, Z. Tomović, S. C. J. Meskers, A. P. H. J. Schenning and E. W. Meijer, *Angew. Chem., Int. Ed.*, 2007, **46**, 8203; S. Ghosh, X.-Q. Li, V. Stepanenko and F. Würthner, *Chem.–Eur. J.*, 2008, **14**, 11343.
- 7 For general references on self-sorting see: A. Pal, S. Karthikeyan and R. P. Sijbesma, J. Am. Chem. Soc., 2010, 132, 7842; J. v. Herrikhuyzen, A. Syamakumari, A. P. H. J. Schenning and E. W. Meijer, J. Am. Chem. Soc., 2004, 126, 10021; K. Mahata, M. L. Saha and M. Schmittel, J. Am. Chem. Soc., 2010, 132, 15933; H. Northrop, Y.-R. Zheng, Ki-Whan Chi and P. J. Stang, Acc. Chem. Res., 2009, 42, 1554; K. Sugiyasu, S.-i. Kawano, N. Fujita and S. Shinkai, Chem. Mater., 2008, 20, 2863; P. Mukhopadhyay, P. Y. Zavalij and L. Isaacs, J. Am. Chem. Soc., 2006, 128, 14093; A. Heeres, C. v. d. Pol, M. Stuart, A. Friggeri, B. L. Feringa and J. v. Esch, J. Am. Chem. Soc., 2003, 125, 14252; J. R. Moffat and D. K. Smith, Chem. Commun., 2009, 316.
- 8 M. R. Molla, A. Das and S. Ghosh, Chem.-Eur. J., 2010, 16, 10084.
- 9 S. V. Bhosale, C. H. Jani and S. J. Langford, *Chem. Soc. Rev.*, 2008, **37**, 331; N. Sakai, J. Mareda, E. Vauthey and S. Matile, *Chem. Commun.*, 2010, **46**, 4225; P. Mukhopadhyay, Y. Iwashita, M. Shirakawa, S.-i. Kawano, N. Fujita and S. Shinkai, *Angew. Chem., Int. Ed.*, 2006, **45**, 1592.
- 10 M. R. Molla and S. Ghosh, Chem. Mater., 2011, 23, 95.
- For recent reviews or organogels, see: M.-O. M. Piepenbrock, G. O. Lloyd, N. Clarke and J. W. Steed, *Chem. Rev.*, 2010, **110**, 1960; A. Ajayaghosh and V. K. Praveen, *Acc. Chem. Res.*, 2007, **40**, 644; P. Dastidar, *Chem. Soc. Rev.*, 2008, **37**, 2699; S. Banerjee, R. K. Das and U. Maitra, *J. Mater. Chem.*, 2009, **19**, 6649; M. Suzuki and K. Hanabusa, *Chem. Soc. Rev.*, 2010, **39**, 455.
- 12 H. Shao, T. Nguyen, N. C. Romano, D. A. Modarelli and J. R. Parquette, J. Am. Chem. Soc., 2009, 131, 16374.
- 13 A. Das and S. Ghosh, Chem.-Eur. J., 2010, 16, 13622.
- 14 As observed in the melting curves, the absolute CD-intensity is slighly different in two cases which probably arises due to difference in total chromophore concentration in two separate experiments.
- 15 Recently we have demonstrated that the relative distances between the two amide groups in this D–A pair allow effective CT-interaction. For details, see: A. Das, M. R. Molla, A. Banerjee, A. Paul and S. Ghosh, *Chem.–Eur. J.*, 2011, **17**, 6061.
- 16 Detail self-assembly studies with **DAN-2** in organic and aqueous medium are underway and will be published elsewhere.
- 17 For segregated chromophore assembly based on side-chain incompatibility, see: T. L. Benanti, P. Saejueng and D. Venkataraman, *Chem. Commun.*, 2007, 692; T. Sakurai, K. Shi, H. Sato, K. Tashiro, A. Osuka, A. Saeki, S. Seki, S. Tagawa, S. Sasaki, H. Masunaga, K. Osaka, M. Takata and T. Aida, *J. Am. Chem. Soc.*, 2008, **130**, 13812.
- 18 J.-L. Brédas, J. E. Norton, J. Cornil and V. Coropceanu, Acc. Chem. Res., 2009, 42, 1691.