CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201000596

Self-Sorted Assembly in a Mixture of Donor and Acceptor Chromophores

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Abstract: A simple and novel supramolecular approach for orthogonal self-assembly of donor and acceptor chromophores has been demonstrated. Suitably designed 1,5-dialkoxynaphthalene (DAN) and naphthalene tetracarboxylic acid diimide (NDI) derivatives were used as the donor and acceptor systems, respectively. The molecular design for self-sorting relies upon the precise control over the placement of the self-complementary hydrogen-bonding units (amide functionality) with respect to the individual chromophore. By design, the distances between the two amide groups in the donor and acceptor chromophores are not identical, and consequently the effect of the hydrogen-bonding interaction cannot be maximised in the case of alternate donor–acceptor-type π-stacking. Thus a relatively weak charge-transfer interaction is expected to be sacrificed, and segregated assembly among the individual chromophores should be enforced by virtue of the much stronger effects of hydrogen bonding and π–π stacking. Detailed spectroscopic studies were carried out to probe the mode of self-assembly in various derivatives of the DAN–NDI donor–acceptor pairs to establish the utility of the molecular design as a generalised one for orthogonal self-assembly.

Keywords: chromophores · charge transfer · donor–acceptor systems · self-assembly · self-sorting

Introduction

Electron-rich (donor) and -deficient (acceptor) aromatic π systems often form charge-transfer (CT) complexes,[1] which have been extensively utilised to generate many elegant supramolecular structures, such as organogels,[2] synthetic ion channels,[3] rotaxanes,[4] catenanes,[5] folded oligomers[6] and polymers,[7] liquid crystalline materials[8] and dendritic assembly.[9] However, little is known regarding the self-sorting[10] of individual chromophores in the donor–acceptor mixture, which is highly relevant in the context of organic electronic device applications, such as in bulk heterojunction solar cell, for efficient charge-separation and charge-carrier mobility.[11] In the recent past, Venkataraman and co-workers have demonstrated the segregated assembly of donor and acceptor π systems based on mutually phobic aliphatic fluorocarbon–hydrocarbon interactions in the solid state.[12a] More recently, Shinkai and co-workers have reported self-sorting of bis-amide-functionalised perylene bisimide (PBI) and tetraamide-functionalised oligothiophene (OT) chromophores in solution[12b] by using the inherent difference in the self-assembly propensities of the two chromophores, which arises from the difference in the number of peripheral amide functionalities involved in hydrogen-bonding interactions. The drawback of this approach is that the equilibrium constant for self-assembly of either the donor or acceptor chromophore must be significantly weaker than for the other one. Further, the shape and size of the PBI and OT chromophores are very different, and thus it is possible, even in the absence of hydrogen bonding, that they form orthogonal self-assembled structures under suitable condition, as demonstrated by Meijer and co-workers in the case of functionalised PBI and oligo(*p*-phenylenevinylene) chromophores.[12c]

Herein, we introduce a novel and versatile strategy for self-sorted assembly in a mixture of donor and acceptor chromophores in solution, based on specific directional supramolecular interactions. The design is based on linking the individual chromophores with two amide functionalities in such a manner so that the distances between the two amide functionality are different in the donor and acceptor systems. We envisaged that such a molecular design will ensure that in case of alternate donor–acceptor type π stack-

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201000596.

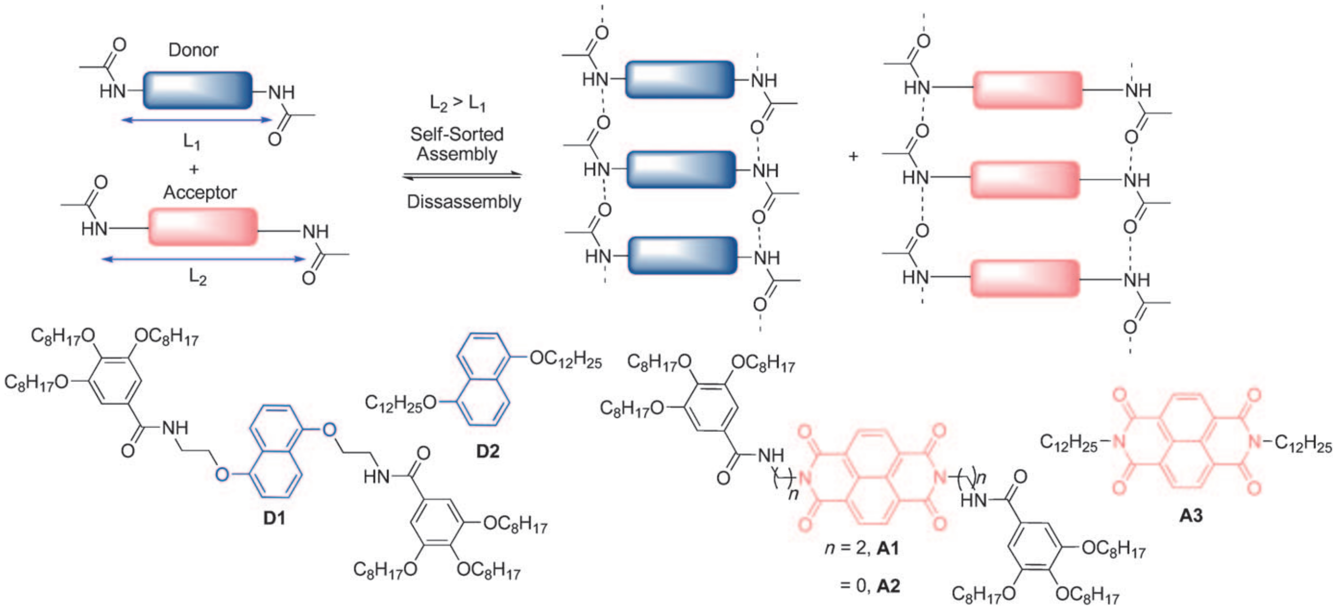
ing, intermolecular hydrogen-bonding interactions between the amide groups cannot operate simultaneously because of geometrical constraint. On the other hand it is also expected that given a choice, the mode of self-assembly will be dictated by the relatively stronger hydrogen-bonding interaction rather than weak CT interactions. Thus in the process of self-assembly the donor and acceptor chromophores would sacrifice the weak CT interaction to gain the synergistic effect of π–π stacking and hydrogen bonding, which can be achieved only in the case of segregated assembly (Scheme 1).

To test this hypothesis we studied the self-assembly of 1,5-dialkoxynaphthalene (DAN) derivative **D1** and naphthalene-1,4,5,8-tetracarboxylic acid diimide (NDI) derivative **A1** (Scheme 1) as donor and acceptor chromophores, respectively. The peripheral trioctyloxybenzamide groups were incorporated to improve the solubility of **A1** and **D1** in non-polar solvents, in which the effect of the hydrogen-bonding interaction should be realised to a greater extent. We chose the DAN–NDI donor–acceptor pair because formation of their co-assembly aided by a CT interaction is well-established[3–6] and if they behave in an opposite manner in our system it will strongly justify the utility of the present approach for self-sorting of donor–acceptor systems in solution.

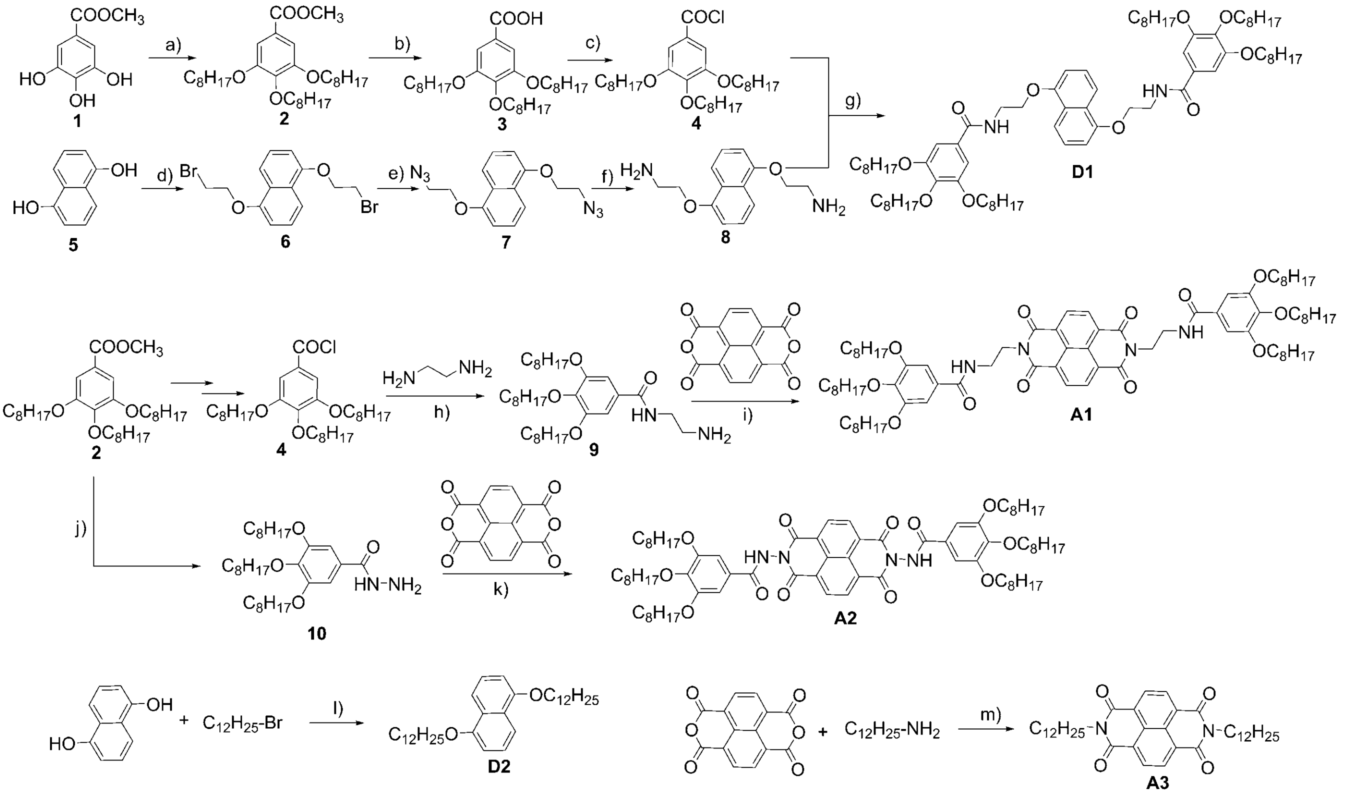
Results and Discussion

Synthetic routes for various donor and acceptor chromophores are depicted in Scheme 2. 3,4,5-Trioctyloxybenzoylchloride (**4**) was synthesised from commercially available 3,4,5-trihydroxymethylbenzoate by following a literature procedure.[10e] Diamine-functionalised donor intermediate **8** was synthesised from 1,5-dialkoxynaphthalene in a few standard synthetic steps and was reacted with compound **4** to give **D1** in 68% isolated yield. Compound **D2** was synthesised in a single step by alkylation of 1,5-dialkoxynaphthalene with dodecylbromide and isolated in 65% yield. For the synthesis of **A1**, acid chloride **4** was reacted with excess ethylenediamine to produce intermediate compound **9**, which was reacted with naphthalene tetracarboxylic acid dianhydride to generate acceptor compound **A1** in 70% yield. For the synthesis of **A2**, a slightly different procedure was followed in which 3,4,5-trioctyloxymethylbenzoate was directly reacted with excess hydrazine hydrate to generate the intermediate compound **10**, which was then coupled with naphthalene tetracarboxylic acid dianhydride to produce **A2** in 81% yield. Compound **A3** was synthesised by reaction of naphthalene tetracarboxylic acid dianhydride with dodecylamine and was isolated in 71% yield.

Self-assembly of **A1** and **D1** was studied by solvent-dependent variations in their UV/Vis absorption spectra (Figure 1). Chloroform is known to be benign for rigid π systems,[10e, 12c] whereas in the non-polar solvent methylcyclohexane (MCH), both π–π stacking and hydrogen-bonding interaction should be more favourable. The absorption spectrum of **A1** in $CHCl_3$ is compared with that in MCH/$CHCl_3$ (95:5; v/v)[13] in Figure 1a. In $CHCl_3$, well-resolved bands can be seen in the range of $\lambda = 300$ to 400 nm due to a π–π* transition polarised along the long axis of the monomeric NDI chromophores.[14] In MCH/$CHCl_3$ (95:5), a decrease in the absorbance intensity (≈60%) was observed for all the major bands along with significant broadening of the spectrum which clearly suggests π–π stacking among the NDI chromophores.[15] Similarly, a distinct hypochromic shift was



Scheme 1. Top: Schematic representation of the proposed self-sorted assembly of donor and acceptor chromophores; bottom: the structures of the various molecules studied.



Scheme 2. Synthetic routes for various donor and acceptor chromophores. Reagents and conditions: a) *n*-octyl bromide, K_2CO_3, DMF, 80 °C, 88 %; b) KOH, EtOH/H_2O, 100 °C, 81 %; c) $SOCl_2$, CH_2Cl_2, RT; d) 1,2-dibromoethane (excess), CH_3CN, K_2CO_3, 26 %; e) NaN_3, DMF, 100 °C, 93 %; f) H_2 (55 psi), 10 % Pd/C, EtOAc, 95 %; g) Et_3N, CH_2Cl_2, 0 °C→RT, 68 %; h) CH_2Cl_2, 0 °C→RT, 56 %; i) DMF, 140 °C, 70 %; j) hydrazine hydrate, MeOH/THF, 70 °C, 96 %; k) DMF, 140 °C, 81 %; l) KOH, TBAB, H_2O, 95 °C, 65 %; m) DMF, 140 °C, 71 %.

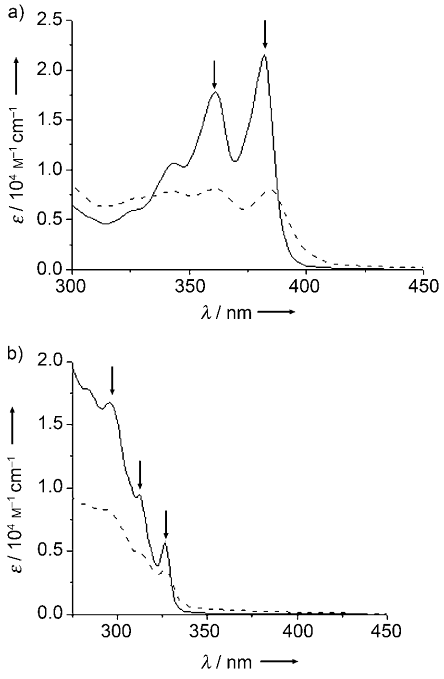


Figure 1. UV/Vis spectra of a) **A1** and b) **D1** in $CHCl_3$ (——) and MCH/$CHCl_3$ (95:5; -----). Concentration of chromophore = 0.1 mM and *T* = 25 °C.

observed for all the major bands of **D1** in the UV/Vis spectrum in MCH/$CHCl_3$ (95:5) compared with that in pure $CHCl_3$ (Figure 1b) due to self-assembly.[16]

To elucidate the role of hydrogen bonding in self-assembly as depicted in Scheme 1, we examined the effect of MeOH, a protic hydrogen-bonding-competing solvent, on the spectral properties of **A1** and **D1**.[17] The spectral variations are shown in Figure 2. It can be seen that with gradual addition of MeOH to a solution of either **A1** (Figure 2a) or **D1** (Figure 2c) in MCH/$CHCl_3$ (95:5) the UV/Vis spectrum changed drastically for both chromophores, and after the addition of a certain amount of MeOH the spectra almost resembled that of the respective monomeric chromophores. Such a dramatic effect of MeOH on disassembly clearly demonstrates the strong influence of hydrogen-bonding interactions on the self-assembly process. In Figure 2b, the variation in the absorbance of **A1** at $\lambda = 382$ nm is plotted against amount of MeOH and it can be seen that as an increasing amount of MeOH is added, the absorbance gradually increases and almost reaches saturation at ≈5 % MeOH (v/v). Similarly, for **D1** the change in absorbance at $\lambda = 312$ nm is plotted as a function of MeOH in Figure 2d; in this case the saturation was achieved after the addition of only ≈1 % (v/v) MeOH, probably because of the reduced stability of the aggregates[6e] in this case as compared with the **A1** assembly.

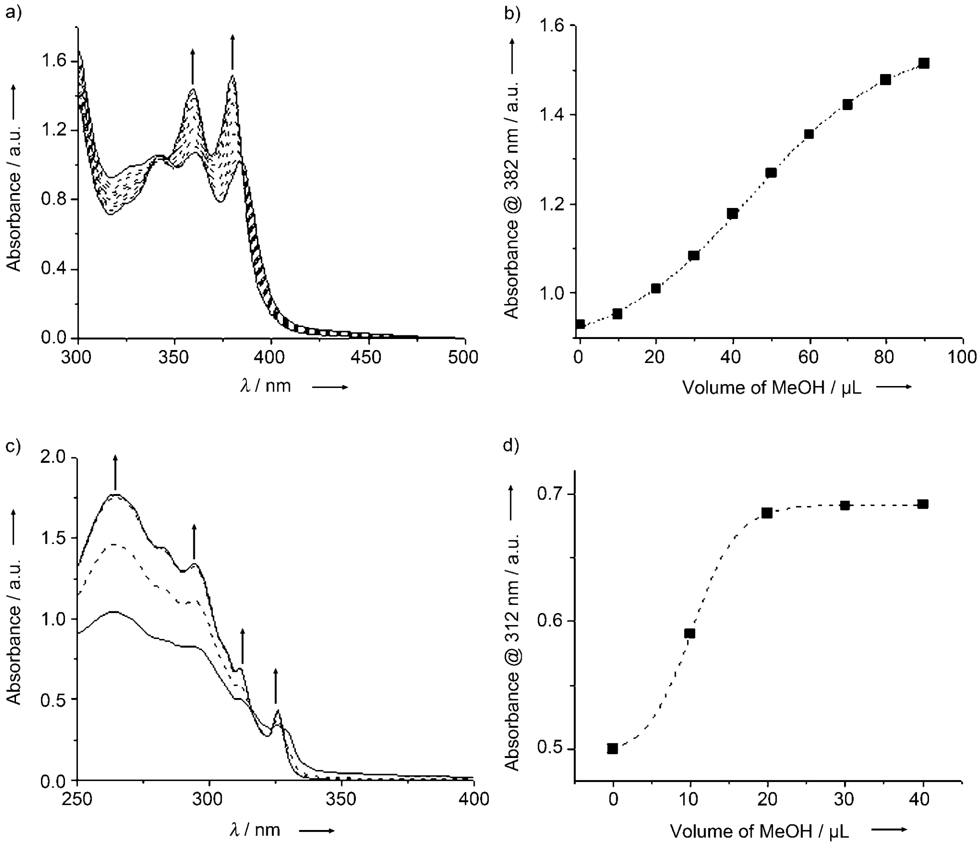


Figure 2. Variation in the UV/Vis spectra of a) **A1** and c) **D1** in MCH/CHCl$_3$ (95:5) as a result of gradual addition of MeOH; arrows indicate the spectral changes with increasing amount of MeOH; initial concentration of chromophore = 0.1 mм, volume of the solution = 1.8 mL, path length of the cuvette = 1 cm, T = 25 °C. Variation in the absorbance at b) $\lambda = 382$ nm in Figure 2a and d) $\lambda = 312$ nm in Figure 2c as a function of volume of added MeOH.

Then we examined the spectral behaviour of the equimolar mixture of **A1** and **D1** in MCH/CHCl$_3$ (95:5). It can be seen in Figure 3a that the spectrum of the mixture of **A1** and **D1** is almost identical to that generated by mathematical summation of the spectra of the individual chromophores, which suggests that the presence of **D1** or **A1** has no influence on the self-assembly of **A1** or **D1**, respectively. More significantly, the spectrum of the mixture does not exhibit any CT absorption band (Figure 3b) in the range of $\lambda =$ 450 to 600 nm, which eliminates the possibility of donor–acceptor-type π-stacking between NDI and DAN chromophores.[3–6] These observations unambiguously support the self-sorted assembly of individual chromophores as depicted in Scheme 1.

To gain further insight into the self-assembly process, we carried out variable-temperature UV/Vis absorption experiments of **A1**, **D1** and an equimolar mixture of **A1** and **D1** in MCH/CHCl$_3$ (95:5). The spectral variations of **A1** and **D1** are shown in Figure 4a and b, respectively. It can be seen that in both cases the spectral features gradually change from aggregated to monomeric chromophores with increasing temperature, as expected for reversible self-assembly process. Further, we carried out variable-temperature experiments with a 1:1 mixture of **A1** and **D1** and found significant hyperchromic shifts of all the major bands with increasing temperature (Figure 4c) as expected for the aggregate to monomer conversion. From the temperature-dependent absorption spectra, the stabilities of the π-stacked assemblies of **A1** and **D1** were estimated by calculating the respective $\alpha_{\mathrm{agg}}(T)$ (mole fraction of aggregate at temperature T) values by using Equation (1):[10e]

$$\alpha_{\mathrm{agg}}(T) \approx \frac{A(T) - A_{\mathrm{mon}}}{A_{\mathrm{agg}} - A_{\mathrm{mon}}} \tag{1}$$

in which A_{agg}, A_{mon} and A(T) are the absorbance at a particular wavelength in the UV/Vis spectra for the fully aggregated, monomeric and in-between state at temperature T, respectively. The calculations were first carried out for the spectral data obtained from the experiments with individual chromophores (Figure 4a and b). For both **A1** and **D1**, the UV/Vis spectra in MCH/CHCl$_3$ (95:5) at 25 °C and in CHCl$_3$ were considered to reflect the fully aggregated state and the monomeric state, respectively. The intensity of the bands at $\lambda = 382$ and 312 nm were considered for the calculation of the $\alpha_{\mathrm{agg}}(T)$ value of **A1** and **D1**, respectively. The α_{agg} values estimated from these calculations are plotted as a function of temperature in Figure 2d, and from these plots the values of $\alpha_{50}(T)$ (the temperature at which $\alpha_{\mathrm{agg}} = 0.5$) were found to

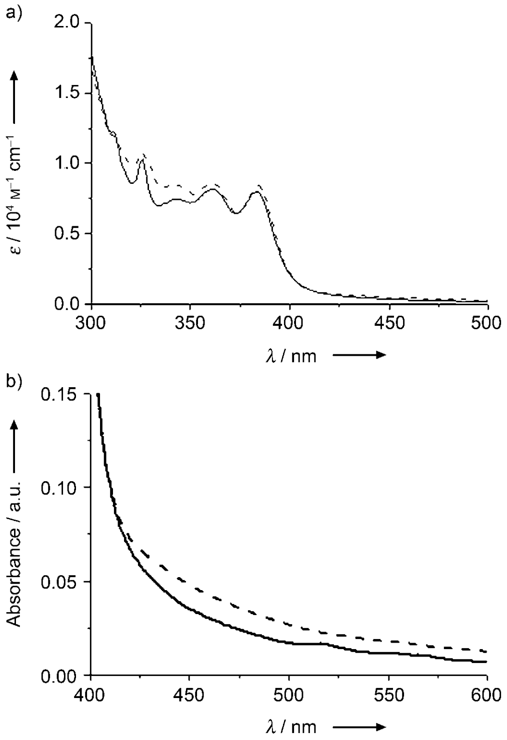


Figure 3. a) UV/Vis spectrum and b) CT region of the spectra of **A1**+**D1** (1:1) in MCH/CHCl$_3$ (95:5; ——) and the mathematical sum of the individual spectrum (-----). Concentration of chromophore = 0.1 mM in each measurements and T = 25 °C.

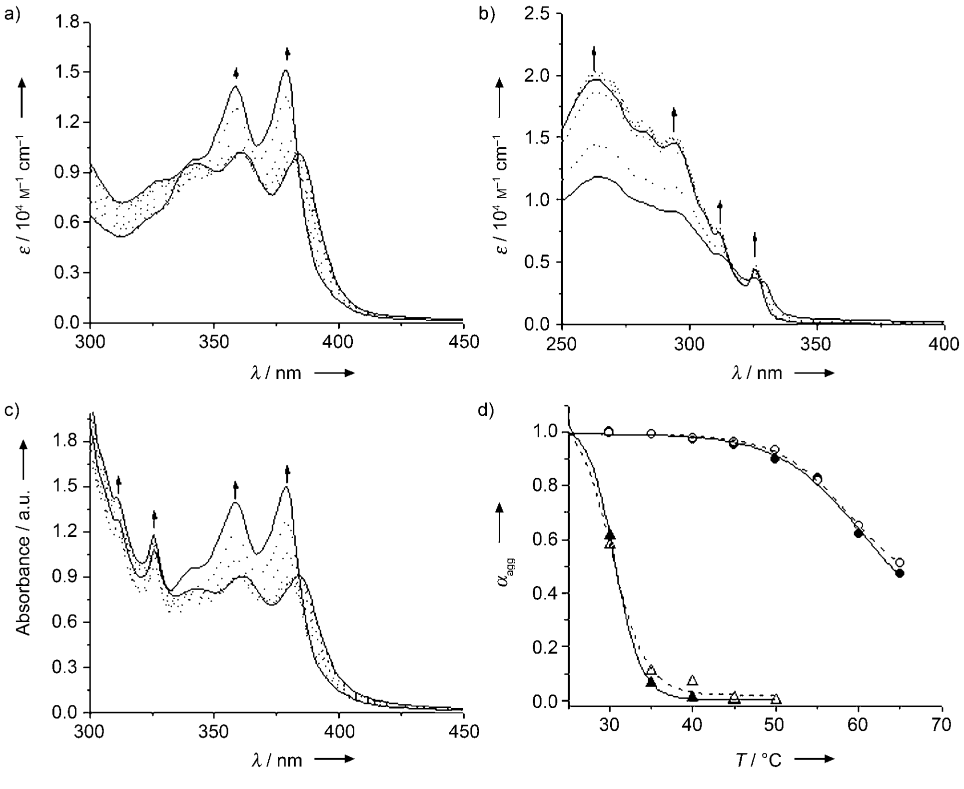


Figure 4. Temperature-dependent UV/Vis absorption spectra of a) **A1** (T = 25–65 °C), b) **D1** (T = 25–50 °C) and c) a 1:1 mixture of **A1**+**D1** (T = 25–65 °C) in MCH/CHCl$_3$ (95:5) at a concentration of 0.1 mM (individual chromophores); arrows indicate spectral changes upon increasing temperature. d) Variation in α_{agg} as a function of temperature; ●: **A1** only, ○: **A1** in mixture, ▲: **D1** only, △: **D1** in mixture.

be 64 and 31 °C for **A1** and **D1**, respectively. Such a low $\alpha_{50}(T)$ value for **D1** compared with **A1** is attributed to the lower stability of the donor–donor π-stacked assembly due to electrostatic repulsion, and is consistent with the literature report.[6e] Independently, the α_{agg} values for **A1** and **D1** were calculated from the spectral variations of their mixed solution (Figure 4c) by monitoring the absorbance at λ = 382 and 312 nm,[19] respectively, and plotted in Figure 2d. Remarkably, for both **A1** and **D1** the plot of α_{agg} versus T based on the data obtained from the individual experiments and the mixed experiment looks almost identical (Figure 4d). This striking similarity of the temperature-dependent aggregate-to-monomer conversion profile provides strong evidence for the proposed self-sorted assembly of individual chromophores in the donor–acceptor mixed system.

So far we have discussed self-sorting of **D1** and **A1** from an equimolar mixture only. We also wanted to examine the effect of the stoichiometric imbalance of the two chromophores on their self-assembly. Therefore, we studied the UV/Vis absorption spectra of **D1**+**A1** in MCH/CHCl$_3$ (95:5) at different relative molar ratios of the two chromophores, with the total concentration kept constant (Figure 5a). The absorbance of the mixed spectra at λ = 382 nm is solely due to **A1** and is not affected by the absorbance of the **D1**, but it was not possible to identify such a separate band for **D1** in the mixed spectra. Therefore, to get the spectral contribution of **D1** alone (inset Figure 5a), the spectrum of **A1** was subtracted from the corresponding mixed spectrum in each mixture by using Equation (2):

$$S_{\mathbf{D1}} = S_{\text{mixed}} - (\alpha_{\mathbf{A1}} \times S_{\mathbf{A1}}) \qquad (2)$$

in which $S_{\mathbf{D1}}$, S_{mixed}, $S_{\mathbf{A1}}$ and $\alpha_{\mathbf{A1}}$ are the modified donor spectrum, original spectrum of the mixture, spectrum of **A1** only and mole fraction of **A1** in the mixture, respectively. The absorbance at λ = 382 nm (for **A1**) in the mixed spectra and that at λ = 325 nm (for **D1**) in the subtracted spectra were plotted as a function of mole fraction of **D1** in Figure 5b. If there were a CT interaction between the donor–acceptor chromophores at higher stoichiometric imbalance, a deviation from linearity would have been observed. However, that possibility could be completely eliminated because at least in the range of **D1**/**A1** = 1:4 to **D1**/**A1** = 4:1 both the plots behave linearly (see Figure 5b).

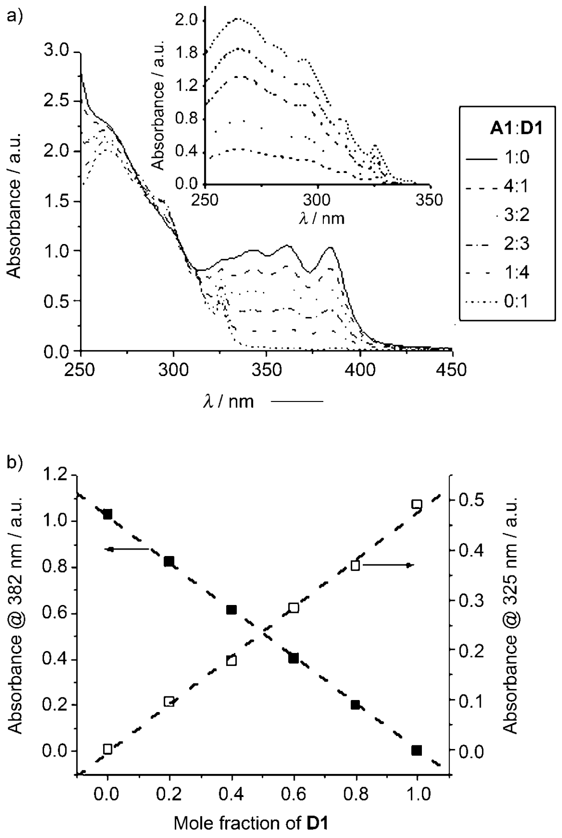


Figure 5. a) UV/Vis absorption spectra of **A1**+**D1** at various ratios in MCH/$CHCl_3$ (95:5); inset: the subtracted spectra for **D1** only, as obtained by using Equation (2). b) Plot of absorbance as a function of the mole fraction of **D1**. Total chromophore concentration was 0.1 mm.

To understand the packing of the chromophores in the π-stacked assemblies, we carried out molecular modelling studies for generating energy-minimised structures of **A1** and **D1** (Figure 6a and b, respectively).[20] The distance between the amide hydrogen atom of a particular chromophore and the carbonyl oxygen of the immediately neighbouring chromophore (indicated as red dashed lines in Figure 6) was found to be 2.01 and 2.05 Å for **A1** and **D1**, respectively, which is well within the limit of the hydrogen-bonding distance. The π–π stacking distance between two NDI chromophores in the **A1** assembly (Figure 6a) was found to be 3.41 Å, which exactly matches that observed in the crystal structure of NDI.[21] For the **D1** assembly, the chromophores were packed with significant rotational displacement along the long axis and the interplanar perpendicular distance between the two π planes was found to be 3.88 Å, which suggests weak π–π interactions between the DAN chromophores. To further support our hypothesis regarding the basis of the observed self-sorting, we wanted to identify suitable alternate derivatives of the same donor–acceptor pair as controlled molecules in which the relative distances between the two amide functionalities in donor and acceptor chromophores are mutually adjusted so that intermolecular hydrogen bonding is feasible in the case of alternate donor–acceptor π stacking. To predict the molecular structure, we carried out energy-minimisation calculations with different DAN and NDI derivatives, in which the donor was fixed as **D1** and the acceptor was modified from **A1** by changing only the number of methylene groups between the NDI chromophore and the trioctyloxybenzamide groups. We found that in case of alternately stacked **D1** and **A2** (Scheme 1), the distance among the amide hydrogen and carbonyl oxygen of the amide groups between the neighbouring chromophores was 2.04 Å (Figure 6c), which is well below the limit of hydrogen-bonding interaction distance (2.45 Å). If this prediction is indeed true, one should expect an alternate donor–acceptor-type assembly in the **A2**+**D1** mixture due to the synergistic effect of CT and hydrogen-bonding interactions, unlike the self-sorting in the **A1**+**D1** system. To check this, we synthesised **A2** (Scheme 1). Self-assembly of **A2** alone was examined by comparing its absorption spectrum in MCH/$CHCl_3$ (95:5) with that in $CHCl_3$ and π-stacking was evident of **A2** from spectral changes that were similar to those of **A1** (Figure 7a). It is worth noting that in case of **A2**, the functional group should be called hydrazide instead of amide, although the NHCO moiety responsible for hydrogen-bonding remains same. To confirm that the self-assembly in **A2** is also primarily driven by hydrogen bonding, we examined the effect of MeOH on the spectrum of the self-assembled chromophore. In Figure 7b, it can be seen that the aggregated spectrum clearly changes into the monomeric spectrum on gradual addition of MeOH, and thus the involvement of hydrogen bonding on the self-assembly is supported. We then examined the nature of the co-assembly between **A2** and **D1**. When **A2** was mixed with **D1** in MCH/$CHCl_3$ (95:5), an orange-coloured solution formed spontaneously (Figure 8a), which clearly suggests an alternate donor–acceptor-type π-stacking system. As expected from a cursory observation, a broad CT band appeared at $\lambda = 550$ nm in the UV/Vis spectrum (Figure 8b, inset) owing to the donor–acceptor interaction among DAN and NDI chromophores.[6] It is worth noting that no orange colouration (Fig-

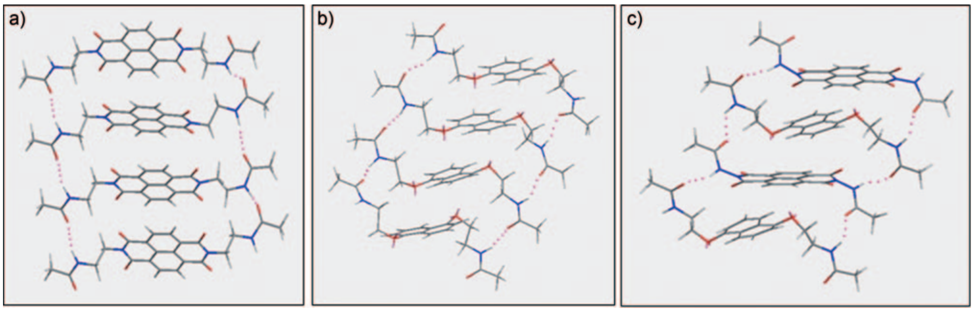


Figure 6. Packing model of a) **A1**, b) **D1** and c) **A2**+**D1**.

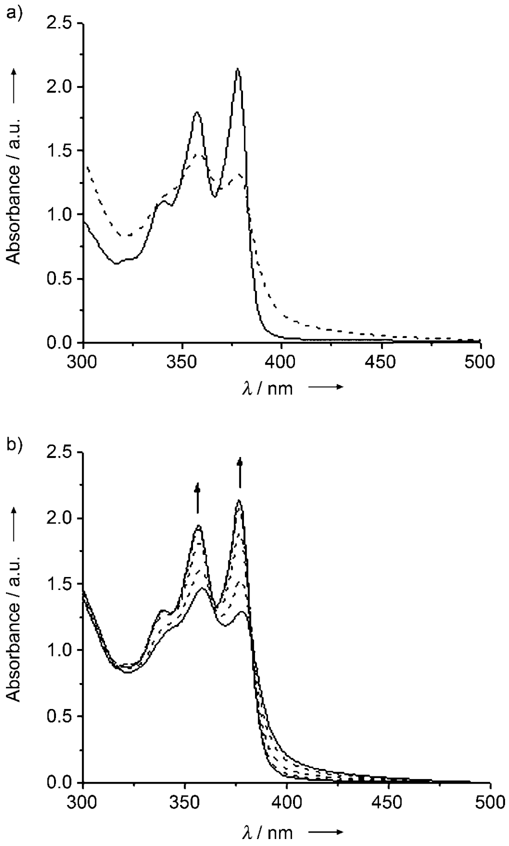


Figure 7. a) UV/Vis spectra of **A2** (concentration = 0.1 mM) in $CHCl_3$ (——) and MCH/$CHCl_3$ (95:5; -----) at 25 °C; b) Effect of MeOH addition (0–3 % v/v) on the UV/Vis spectra of **A2** in MCH/$CHCl_3$ (95:5); arrows indicate spectral changes with increasing amounts of MeOH.

ure 8a) and no CT band were visible in the UV/Vis spectrum of the self-sorting mixture, that is, **A1+D1** (Figure 3b). Furthermore, the UV/Vis spectrum of **A2+D1**, unlike **A1+D1**, does not match with the calculated spectrum generated by mathematical summation of the individual spectrum (Figure 8b). We also compared the CT region of the UV/Vis spectra of **A2+D1** with that of **A1+D1** at a significantly higher concentration (0.5 mM), and even there found the appearance of an intense CT band only in the former case but not for the latter mixture (Figure 9a). To ascertain that hydrogen bonding is indeed involved in the donor–acceptor-type self-assembly, we carried out the MeOH addition ex-

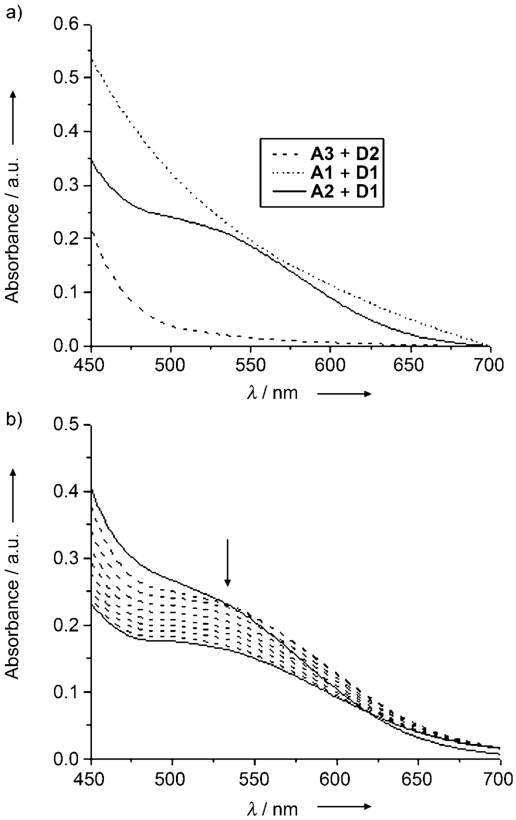


Figure 9. a) CT region of the UV/Vis spectra of equimolar mixtures of **A3+D2** (-----) **A1+D1** (•••••) and **A2+D1** (——) in MCH/$CHCl_3$ (95:5); total chromophore concentration = 0.5 mM and T = 25 °C. b) Effect of MeOH addition (0–5 %) on the CT band of **A2+D1** (1:1) in MCH/$CHCl_3$ (95:5); arrows indicate spectral changes with increasing MeOH.

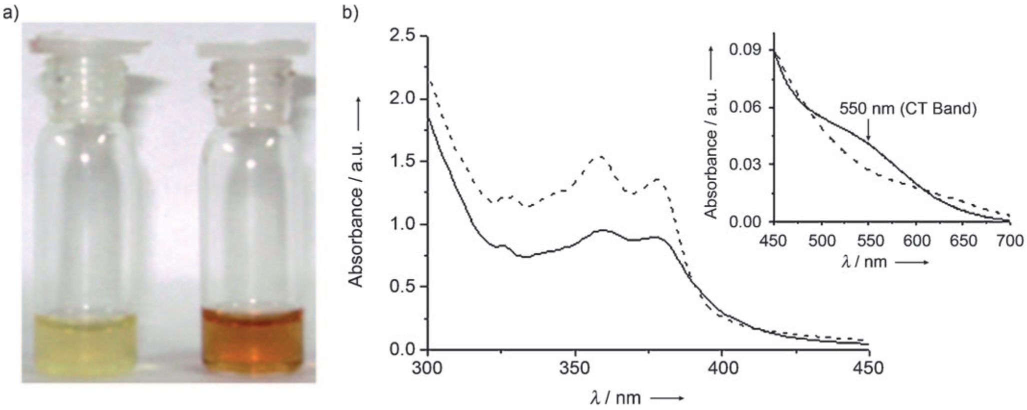


Figure 8. a) Photograph of **A1+D1** (1:1; left) and **A2+D1** (1:1; right) in MCH/$CHCl_3$ (95:5); total chromophore concentration = 0.5 mM. b) UV/Vis spectrum of **A1+D1** (1:1) in MCH/$CHCl_3$ (95:5; ——) and the mathematical sum of the individual spectra (-----); inset: the CT region of the spectra; concentration of each chromophore = 0.1 mM and T = 25 °C.

periment and found that the intensity of the CT-band decreased rapidly with increasing amounts of MeOH (Figure 9b). However, the CT interaction is known to be inherently weak in polar media,[1] and thus the observed effect of MeOH might not be only due to the breaking of hydrogen bonding. To unambiguously demonstrate the role of hydrogen bonding, we synthesised two other controlled molecules **A3** and **D2** (Scheme 1) that were devoid of any amide functionality. In the UV/Vis spectra of **A3**+**D2** (1:1), no CT band (Figure 9a) and no indication of π stacking (Figure S2 in the Supporting Information) was observed, which suggests that hydrogen bonding is essential for self-assembly in the present system, at least in the concentration range at which the experiments were performed (0.1–0.5 mM).

Conclusion

In conclusion, we have demonstrated a simple, novel and versatile supramolecular approach for the self-sorted assembly of donor and acceptor chromophores in solution. The design is based on molecular-level control over the placement of self-complementary hydrogen-bonding units (amide functionality) with respect to the individual chromophore. The distances between the two amide groups in the donor and acceptor chromophores are not identical and consequently the number of hydrogen-bonding interactions cannot be maximised in the case of alternate donor–acceptor-type π stacking. Thus by virtue of the much stronger hydrogen-bonding and π–π-stacking effects, the relatively weak CT interaction is sacrificed and self-sorting among the individual chromophores could be enforced. In a controlled experiment in which the distance between the two amide bonds was almost identical for two different types of chromophores, alternate donor–acceptor-type π stacking was observed. We believe the findings of this work and its relevance to various other interdisciplinary research fields will significantly add to the ongoing effort to correlate the supramolecular organisation of various functional π systems to their macroscopic properties.[22] We are now testing the scope of this approach for specific supramolecular organisations of n- and p-type semiconductors and studying the charge-transport properties of self-sorted blends.

Experimental Section

Materials and methods: The solvents and reagents were received from commercial sources and purified by standard methods.[23] For UV/Vis spectroscopy experiments, spectroscopy-grade solvents were used. ^{1}H NMR spectra were recorded by using a Bruker DPX-300 MHz NMR spectrometer, and all the spectra were calibrated against TMS. UV/Vis spectra were recorded by using a Perkin–Elmer Lambda 25 spectrometer equipped with a Peltier system for variable-temperature experiments.

UV/Vis spectroscopic studies: Stock solutions of different chromophores were made in $CHCl_3$ (2 mM). An aliquot (1 mL) was taken and was added to an appropriate amount of MCH to adjust the desired solvent composition and final concentration. The solutions were allowed to equilibrate at RT for 2 h before spectral measurements. For variable-temperature experiments, a solution (2 mL) of a particular chromophore in MCH/$CHCl_3$ (95:5) was heated and allowed to equilibrate for 15 min equilibrium at the desired temperature before each measurement.

Synthesis and characterisation: Synthesis of various compounds has been achieved by following procedures reported in the literature.[10e,15b,25] New compounds have been characterised by using ^{1}H NMR and UV/Vis spectroscopies, melting point (if solid), MS (ESI) and elemental analysis, whereas previously reported compounds have been characterised by ^{1}H NMR and UV/Vis spectroscopies and melting point analysis (if solid). Synthetic procedures for the new and final compounds are described here and rest are included in the Supporting Information.

1,5-Bis(2-azidoethoxy)naphthalene (7): Compound **6** (2.762 g, 7.38 mmol,) and NaN_3 (9.599 g, 147.68 mmol) were dissolved in dry DMF (45 mL), and the reaction mixture was stirred at 100 °C for 12 h under an N_2 atmosphere. The reaction was stopped, cooled to RT and poured into ice-cold H_2O (100 mL) to give an off-white solid, which was filtered. The obtained solid was washed several times with H_2O and dried under vacuum to afford the desired product (2.05 g, 93 %). M.p. 117–120 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta=7.907$ (d, $J=8.7$ Hz, 2 H), 7.393 (t, $J=8.1$ Hz, 2 H), 6.851 (d, $J=7.8$ Hz, 2 H), 4.327 (t, $J=5.1$ Hz, 4 H), 3.728 ppm (t, $J=5.1$ Hz, 4 H); FTIR (KBr): $\tilde{\nu}=2104.19\,\text{cm}^{-1}$ for azide stretching; UV/Vis (CH_2Cl_2): λ_{max} (ε)=326 (5150), 312 (6862), 295 (8976), 285 nm ($7074\,\text{M}^{-1}\text{cm}^{-1}$); MS (ESI): m/z calcd for $C_{14}H_{17}N_6O_2$: 301.14 $[M+3\text{H}]^+$; found: 301.02; elemental analysis calcd (%) for $C_{14}H_{14}N_6O_2$: C 56.37, H 4.73, N 28.17; found: C 56.42, H 4.87, N 28.26.

2-[1-(2-Aminoethoxy)naphthalen-5-yloxy)ethanamine] (8): 10 % Pd/C catalyst (200 mg) was added to a solution of compound **7** (2.014 g, 6.75 mmol) in EtOAc (45 mL), and the reaction mixture was mechanically stirred at RT under H_2 (55 psi) for 5 h. The reaction was stopped, the catalyst was filtered through Celite, and the filtrate was concentrated to afford the crude product as an off-white solid (1.58 g, 95 %). M.p. 83–85 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta=7.862$ (d, $J=8.5$ Hz, 2 H), 7.365 (t, $J=8.0$ Hz, 2 H), 6.856 (d, $J=7.5$ Hz, 2 H), 4.168 (t, $J=5.0$ Hz, 4 H), 3.221 ppm (t, $J=5.0$ Hz, 4 H); FTIR (KBr): $\tilde{\nu}=2104.19\,\text{cm}^{-1}$ peak for azide is absent; UV/Vis (THF/CH_2Cl_2 1:1): λ_{max} (ε)=326 (5043), 312 (6539), 296 (7929), 285 nm ($6103\,\text{M}^{-1}\text{cm}^{-1}$); MS (ESI): m/z calcd for $C_{14}H_{19}N_2O_2$: 247.14 $[M+\text{H}]^+$; found: 247.07; elemental analysis calcd (%) for $C_{14}H_{18}N_2O_2$: C 68.27, H 7.37, N 11.37; found: C 68.36, H 7.38, N 11.44.

Compound D1: A solution of compound **4** (0.8 g, 1.52 mmol) in dry CH_2Cl_2 (5 mL) was added to an ice-cold solution of compound **8** (0.15 g, 0.608 mmol) and Et_3N (0.4 mL) in dry CH_2Cl_2 (10 mL). The reaction mixture was then stirred in the ice bath for another 2 h, and then at RT for 12 h. The mixture was diluted with CH_2Cl_2 (20 mL) and washed with H_2O (3×30 mL) and brine (1×30 mL). The organic layer was dried over anhyd Na_2SO_4, and the solvent was evaporated to afford the crude product, which was purified by using column chromatography with silica gel as the stationary phase and 5 % EtOAc in CH_2Cl_2 as the eluent to get the pure product as an off-white solid (5.06 g, 68 %). M.p. 110 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta=7.870$ (d, $J=8.5$ Hz, 2 H), 7.365 (t, $J=8$ Hz, 2 H), 6.954 (s, 4 H), 6.892 (d, $J=7.5$ Hz), 6.537 (t, $J=6$ Hz, 2 H), 4.342 (t, $J=5$ Hz, 4 H), 4.031–3.947 (m, 16 H), 1.827–1.692 (m, 12 H), 1.465–1.266 (m, 60 H), 0.875 ppm (t, $J=6.5$ Hz, 18 H); ^{13}C NMR ($CDCl_3$): $\delta=167.71$, 154.17, 153.19, 141.42, 129.32, 126.74, 125.43, 114.46, 106.05, 77.06, 73.55, 69.40, 67.27, 39.69, 31.93, 30.35, 29.54, 26.11, 22.70, 14.11 ppm; UV/Vis (THF): λ_{max} (ε)=326 (5085), 312 (7652), 295 (13677), 283 (15361), 262 nm ($20594\,\text{M}^{-1}\text{cm}^{-1}$); MS (ESI): m/z calcd for $C_{76}H_{123}N_2NaO_{10}$: 1246.92 $[M+\text{Na}+\text{H}]^+$; found: 1247.20; elemental analysis calcd (%) for $C_{76}H_{122}N_2O_{10}$: C 74.59, H 10.05, N 2.29; found: C 74.63, H 10.04, N 2.35.

Compound A1:[15b] Compound **9** (240 mg, 0.445 mmol) and 1,4,5,8-naphthalenetetracarboxylic bisanhydride (41 mg, 0.15 mmol) were placed in a round-bottomed flask with dry DMF (10 mL) and the reaction mixture was stirred for 6 h at 140 °C under a N_2 atmosphere. Then the solution was allowed to cool to RT and placed in the refrigerator for 30 min to give an orange solid, which was filtered, and the obtained solid was washed with MeOH several times. The product was further purified by column chromatography by using silica gel as stationary phase and

$CHCl_3$ as the eluent to obtain the pure product as a yellow solid (0.14 g, 70 %). M.p. 140 °C; ^{1}H NMR (300 MHz, $CDCl_3$,TMS): δ = 8.75 (s, 4H), 6.91 (s, 4H), 4.55 (t, 4H), 4.02–3.89 (m, 16H), 1.84–1.71 (m, 12H), 1.30–1.27 (m, 60H), 0.89–0.87 ppm (m, 18H); ^{13}C NMR ($CDCl_3$): δ = 166.57, 151.99, 140.09, 130.07, 127.96, 125.85, 125.55, 104.49, 76.25, 75.99, 75.74, 72.45, 68.21, 60.80, 39.22, 38.73, 32.24, 30.88, 30.10, 29.30, 28.68, 28.49, 28.36, 28.34, 28.28, 28.20, 25.04, 21.65, 13.05 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 382 (26785), 361 (21429), 344 nm (13513 $M^{-1}cm^{-1}$); MS (ESI): m/z calcd for $C_{80}H_{120}N_4NaO_{12}$: 1351.88 $[M+Na]^+$; found: 1352.01; elemental analysis calcd (%) for $C_{80}H_{120}N_4O_{12}$: C 72.25, H 9.10, N 4.21; found: C 72.19, H 9.16, N 4.27.

3,4,5-Tris(octyloxy)benzohydrazide (10):[24] Compound **2** (615.0 mg, 1.18 mmol) and hydrazine monohydrate (2.9 mL, 59.0 mmol) were placed in a round-bottomed flask and dissolved in MeOH (10 mL) and THF (3 mL). The reaction mixture was stirred at 70 °C for 12 h. The heating was stopped, the reaction mixture was allowed to cool to RT, the volatiles were removed under reduced pressure, and the product was dissolved in CH_2Cl_2 (25 mL) and washed with H_2O (3×25 mL). The organic layer was dried over anhyd Na_2SO_4, and the solvent was evaporated to get crude product, which was purified by column chromatography by using silica gel as the stationary phase and 5 % MeOH in CH_2Cl_2 as the eluent to get the pure product as a colourless waxy material (0.597 g, 96 %). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 6.92 (s, 2H), 4.06–3.97 (m, 6H), 1.83–1.68 (m, 6H), 1.48–1.45 (m, 6H), 1.31–1.29 (m, 24H), 0.90–0.86 ppm (m, 9H); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 266 nm (7459 $M^{-1}cm^{-1}$); MS (ESI): m/z calcd for $C_{31}H_{56}N_2NaO_4$: 543.40 $[M+Na]^+$; found: 543.55; elemental analysis calcd (%) for $C_{31}H_{56}N_2O_4$: C 71.49, H 10.84, N 5.38; found: C 71.44, H 10.89, N 5.43.

Compound A2: Compound **10** (500 mg, 0.96 mmol) and 1,4,5,8-naphthalenetetracarboxylic bisanhydride (103 mg, 0.384 mmol) were placed in a round-bottomed flask along with dry DMF (10 mL), and the reaction mixture was stirred for 6 h at 140 °C under a N_2 atmosphere. The reaction mixture was allowed to cool to RT, poured into H_2O (100 mL) and then extracted with CH_2Cl_2 (2×20 mL). The combined organic layer was washed with H_2O (2×50 mL), dried over anhyd Na_2SO_4, and the solvent was evaporated to afford the crude product as a brown solid, which was purified by column chromatography by using silica gel as stationary phase and $CHCl_3$ as eluent to obtain the pure product as a yellow solid (0.396 g, 81 %). M.p. 138–140 °C; ^{1}H NMR (300 MHz, $CDCl_3$,TMS): δ = 6.92 (s, 2H), 4.04–4.00 (m, 6H), 1.86–1.73 (m, 6H), 1.49–1.45 (m, 6H), 1.34–1.24 (m, 24H), 0.90–0.87 ppm (m, 9H); ^{13}C NMR ($CDCl_3$,): δ = 160.76, 153.29, 142.32, 131.72, 126.82, 125.63, 106.35, 77.27, 77.01, 76.76, 73.59, 69.36, 31.91, 31.84, 30.36, 29.55, 29.38, 29.36, 29.30, 26.09, 22.7, 22.67, 14.09 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 378 nm (20846), 358 nm (17722), 340 nm (10832 $M^{-1}cm^{-1}$); MS (ESI): m/z calcd for $C_{76}H_{113}N_4O_{12}$: 1273.83 $[M+H]^+$; found: 1274.00; elemental analysis calcd (%) for $C_{76}H_{112}N_4O_{12}$: C 71.67, H 8.86, N 4.40; found: C 71.73, H 8.91, N 4.45.

1, 5-Bis(dodecyloxy)naphthalene (D2):[25] 1,5-Dihydroxynaphthalene (0.4 g, 2.499 mmol), KOH (0.370 g, 6.607 mmol) and tetrabutyl ammonium bromide (0.510 g, 1.582 mmol) were dissolved in H_2O (3 mL) and stirred at RT for 30 min. Dodecylbromide (3.2 mL, 10.07 mmol) was added to this solution, and the solution was stirred at 95 °C for 24 h. The reaction was stopped, and on cooling to RT the product precipitated as a yellow solid. The solid was filtered, then washed with H_2O and then repeatedly washed with hexane to get the pure compound as shiny yellow solid (0.531 g, 65 %). M.p. 69–70 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 7.84 (d, J = 8.3 Hz, 2H), 7.34 (t, J = 8.2 Hz, 2H), 6.82 (d, J = 7.6 Hz, 2H), 4.12 (d, J = 6.4 Hz, 4H), 1.94–1.87 (m, 4H), 1.31–1.27 (m, 36H), 0.88 ppm (t, J = 4.4 Hz, 6H); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 327 (5345), 313 (5881), 298 (6008), 287 nm (6221 $M^{-1}cm^{-1}$); MS (ESI): m/z calcd for $C_{34}H_{57}O_2$: 497.43 $[M+H]^+$; found: 497. 54; elemental analysis calcd (%) for $C_{34}H_{56}O_2$: C 82.20, H 11.36; found: C 82.27, H 11.32.

Compound A3: Dodecylamine (500 mg, 2.7 mmol) and 1,4,5,8-naphthalenetetracarboxylic dianhydride (322 mg, 1.2 mmol) in dry DMF (15 mL) were stirred at 140 °C for 6 h. The reaction mixture was allowed to cool to RT, and the solution was placed in the refrigerator for 30 min to get a cream-coloured solid product. The solution was filtered and washed with MeOH, and the obtained solid was further purified by column chromatography by using silica gel as the stationary phase and $CHCl_3$ as the eluent to obtain the pure product as an off-white solid (0.520 g, 72 %). M.p. 156–158 °C; ^{1}H NMR (500 MHz, $CDCl_3$,TMS): δ = 8.75 (s, 4H), 4.19 (t, J = 7.5 Hz, 4H), 1.76–1.70 (m, 4H), 1.45–1.41 (m, 4H), 1.37–1.25 (m, 32H), 0.87 ppm (t, J = 7 Hz); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 382 (26138), 360 (21810), 342 nm (12678 $M^{-1}cm^{-1}$); MS (ESI): m/z calcd for $C_{38}H_{55}N_2O_4$: 603.41 $[M+H]^+$; found: 603.65; elemental analysis calcd (%) for $C_{38}H_{54}N_2O_4$: C 75.71; H 9.03; N 4.65; found: C 75.82, H 8.97, N 4.72.

Acknowledgements

We thank the Department of Science and Technology (DST), New Delhi, India, for financial support (Project No: SR/FT/CS-039/2008). S.G. thanks Prof. S. Ramakrishnan, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, for many valuable suggestions to improve the quality of the manuscript. M.R.M. and A.D. thank the IACS and CSIR, respectively, for research fellowships.

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[19] To get the sole contribution of **D1** to the absorption at $\lambda = 312$ nm, the spectrum was subtracted from the **A1** spectrum.

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Received: March 7, 2010