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A generalized supramolecular strategy for self-sorted assembly between donor and acceptor gelators†

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An effective supramolecular strategy for self-sorting between naphthalene-diimide (NDI) acceptor and dialkoxy-naphthalene (DAN) donor organogelators is reported. The concept is based on mismatch in the placement of the two amide functionalities in the donor and acceptor chromophores so that self-sorting ensured maximum effect of H-bonding.

In the recent past there has been considerable interest in H-bonding mediated self-assembly of various organic π-systems[1] and utilizing them as building blocks[2] for gelation[3] due to their potential application in optoelectronic devices.[4] In this context, self-sorting[5] among electron-rich (donor) and electron-deficit (acceptor) aromatic compounds is desirable because this will allow formation of distinct p- and n-type bundles of fibres that further intermix and generate multiple junction points for efficient electron transfer and transport of charge carriers. However, the difficulty associated with such practice is the possibility of an alternative mode of assembly, *i.e.* charge-transfer (CT) interaction mediated alternate donor–acceptor stacking,[6] and thus examples related to self-sorting among donor–acceptor chromophores are still limited.[7] Recently we have demonstrated hydrogen (H)-bonding mediated orthogonal self-assembly,[8] in a mixture of bis-amide functionalized NDI-acceptor and DAN-donor, where mutual recognition between similar chromophores took place to maximize the effect of H-bonding. Nevertheless, the strategy was found to be too sensitive on many parameters, and even minor structural variation of the building block or change in solvent polarity altered the mode of assembly from self-sorting to alternate D–A co-stacking.[9] Herein we reveal a versatile supramolecular strategy for self-sorted assembly between donor and acceptor chromophores and demonstrate the concept using a classical DAN–NDI donor–acceptor pair.

In the present design, we appended the donor and acceptor chromophores with two amide functionalities but deliberately changed their positions in the individual chromophores (Fig. 1). In **DAN-1**, the two amide groups were symmetrically placed on both arms while for **NDI-1** they were located on one side of the chromophore. We envisaged that in such a case, the number of intermolecular H-bonds among the amide functionalities of the neighbouring chromophores can be maximized in self-sorting, and thus the possibility of mixed D–A alternate stacking can be eliminated. **NDI-2**, a structural isomer of **NDI-1** is used as a control molecule which is known to form alternate D–A stacks with **DAN-1**, as H-bonding is geometrically allowed in the CT-state for this D–A pair.[9] Gelation of the individual chromophores were checked in methylcyclohexane (MCH) where both **NDI-1** and **DAN-1** showed spontaneous gelation (Fig. 1) with a critical gelation concentration (CGC) of 1.23 and 2.0 mM, respectively.[10] Morphologies of self-assembled structures were examined by transmission electron microscopy (TEM) where micrometre long crosslinked-fibres were observed (Fig. S1†) which is typical of an efficient gelator. We examined gelation of the **NDI-1** + **DAN-1** (1 : 1) pair and observed formation of a light-yellow gel (Fig. 1), and no red color (which is the characteristic of CT-interaction between NDI and DAN chromophores) appeared during gelation, suggesting that there is no molecular mixing among the NDI and DAN chromophores. Contrary to this, the **DAN-1** + **NDI-2** pair produced an intense red gel (Fig. 1) indicating formation of CT-interaction among the alternately stacked NDI and DAN chromophores.

Clear indication of self-sorting from gelation experiments prompted us to probe the self-assembly quantitatively by spectroscopic experiments. Fig. 2a shows solvent and temperature-dependent variations in absorption spectra of **NDI-1**. The spectrum in $CHCl_3$ represents the monomeric form with well-resolved absorption bands in the range of 300–400 nm due to π–π* transition along the long axis of **NDI-1** monomers. By contrast, in highly non-polar medium such as MCH–$CHCl_3$ (95 : 5) a strong hypochromic shift with significant bathochromic

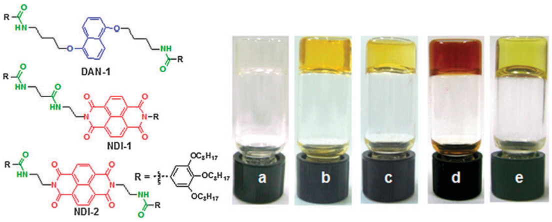

Fig. 1 Left: Structure of the amide-functionalized chromophores. Right: Photos of gels in MCH (*c* = 10 mM) formed by **DAN-1** (a), **NDI-1** (b), **DAN-1** + **NDI-1** (c), **DAN-1** + **NDI-2** (d) and **NDI-2** (e).

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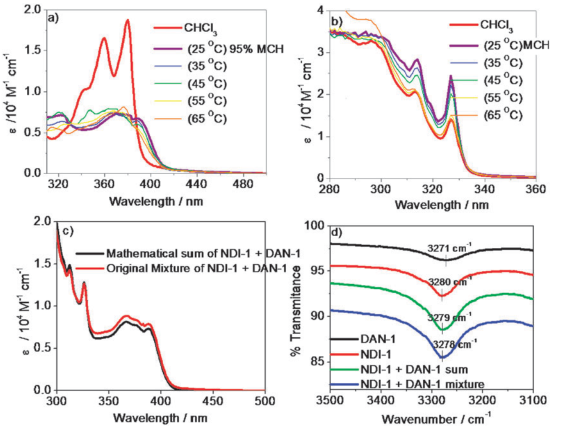

Fig. 2 Solvent and temperature dependent UV/vis spectra of (a) **NDI-1** (c = 0.1 mM) and (b) **DAN-1** (c = 2.5 mM); (c) UV/Vis spectrum of **NDI-1** + **DAN-1** (1 : 1) in MCH–$CHCl_3$ (95 : 5) and the mathematical sum of the individual spectra (c = 0.2 mM); (d) IR-spectra of various gels in MCH (c = 2.5 mM for individual chromophores).

shift (10 nm) was observed, suggesting offset stacking of **NDI-1** chromophores on top of each other. [11] Similarly for **DAN-1** distinct differences were noticed when its absorption spectra in $CHCl_3$ were compared with that in MCH (Fig. 2b). The major absorption bands at 327 and 314 nm experienced a hyperchromic shift with concomitant very small bathochromic shift and the aggregated spectrum in MCH became more sharp than the monomeric spectrum in $CHCl_3$.[12] Such opposite spectral behavior compared to those observed for self-assembled **NDI-1** (Fig. 2a) eliminates the possibility of face-to-face π-stacking among **DAN-1** chromophores.[13] This can be attributed to the electrostatic repulsion among the electron-rich DAN chromophores when they are stacked on top of each other.[14] It is noteworthy that for DAN π-systems, generally edge-to-face[15] or side-by-side (same plane)[16] chromophoric arrangements have been observed in their solid-state structures. In the present case, as the geometry of the stacked-assembly is expected to be greatly influenced by the restriction imposed due to H-bonding among the amide groups (as evidenced by IR studies), side-by-side chromophore arrangements is more likely. However, in the absence of a crystal structure of a suitable model chromophore we refrain from proposing an exact geometry for the self-assembled DAN chromophores. Thermal stabilities of the individual self-assembled structures of **NDI-1** and **DAN-1** were compared by variable-temperature UV-vis studies. For **NDI-I**, even at 65 °C there was no significant change in the aggregated spectrum (Fig. 2a) indicating very strong self-assembly. Conversely, for **DAN-1** (Fig. 2b), thermal dissociation took place at much lower temperature (45 °C), indicating weaker self-assembly, which can be attributed to electrostatic repulsion among the donor chromophores[17] as well as increase in the spacer length between the chromophore and the amide groups.[18] We then examined spectral behavior of **NDI-1** + **DAN-1** (1 : 1) pair in MCH–$CHCl_3$ (95 : 5) (Fig. 2c) and noted the absorption spectrum of the mixture was nearly identical with the mathematical summation of the aggregated spectra of individual chromophores confirming no molecular interaction between the donor and acceptor chromophores in the mixture. Besides, the absence of a CT-band in the range of 450–500 nm (Fig. S3†) also discounted the probability of CT-interaction mediated alternate co-stacking. To test the ability of the design to tolerate stoichiometric imbalance of the two chromophores, absorption spectra of the D–A mixture were recorded with varying molar ratios of **NDI-1** and **DAN-1**, while keeping the total chromophore concentration constant.[8] From these data absorbance at 388 and 326 nm, due to the NDI and DAN chromophores, were plotted as a function of mole fraction of **DAN-1** and a perfect linear plot was observed (Fig. S4†) which would not have been possible if molecular mixing had occurred in presence of excess of any of the components.

As the self-sorting is based on H-bonding, we further probed self-assembly by FT-IR. The NH-stretching frequency of the amide group was recorded for individual gels and their mixtures. Lower stretching frequency in MCH (Fig. 2d) compared to $CHCl_3$ (Fig. S5†) was observed in all three gels as expected for H-bonding. The IR spectrum due to NH-stretching frequency in the self-sorted (**NDI-1** + **DAN-1**) yellow gel was compared with mathematical summation of those of the individual gels and was found to be nearly identical (Fig. 2d), further confirming self-sorting of the individual components in the mixed gel.

Self-assembly was also probed by solvent and temperature-dependent ^{1}H NMR experiments. In Fig. 3, we show a part of the NMR spectra where at least one signal from the DAN (Ha) and NDI (Hb) ring proton could be assigned unambiguously. In $CDCl_3$, where the chromophores remain in monomeric form, sharp signals for both Ha and Hb could be observed. However in MCH where strong self-assembly was noticed, signals corresponding to neither Ha nor Hb could be observed. Thus to overcome this problem we chose TCE as the solvent for NMR in which the self-assembly is inherently weak compared to MCH.[9] As anticipated at 30 °C in TCE the DAN proton Ha appeared at 7.60 ppm which is significantly upfield shifted compared to that in $CHCl_3$ (7.82 ppm) suggesting self-assembly. However, the Hb signal could not be seen at 30 °C even in TCE, which further confirms very strong self-assembly for **NDI-1**. We also examined the NMR spectrum of the mixed gel (**NDI-1** + **DAN-1**) at 30 °C where Ha protons are visible but no signal for Hb was seen. Interestingly the chemical shift (δ) for

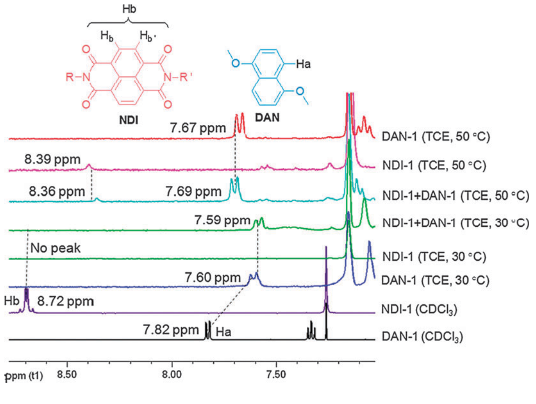

Fig. 3 Solvent- and temperature-dependent proton NMR spectra (selected region) of various gels and their mixtures. For TCE, 10% C_6D_6 was used for locking the signal.

Ha in the mixture (7.59 ppm) nearly matched with that of Ha protons (7.60 ppm) when the experiment was carried out with **DAN-1** only. This clearly suggests that in the mixed system both **NDI-1** and **DAN-1** maintain their identity in terms of self-assembly. However as no signal due to Hb could be observed, the experiments were performed at slightly higher temperature (50 °C) hoping that slight destabilization of the aggregates will cause appearance of Hb protons. In Fig. 3 it can be seen indeed that the Hb signal is now visible at 8.36 ppm whereas the Ha signal appeared at 7.69 ppm. Both these signals still were significantly upfield shifted compared to those in $CDCl_3$, suggesting the existence of self-assembly, even at 50 °C. More importantly, when the signals for Ha and Hb were compared with the corresponding signals for the experiments with individual gels, the respective chemical shift values were found to be almost identical, clearly illustrating orthogonal self-assembly of **NDI-1** and **DAN-1** in their mixture. Further for **DAN-1**, going from $CDCl_3$ to TCE, we observed a downfield shift of the peak due to the amide proton, which at elevated temperature experienced an upfield shift (Fig. S6†) as one would expect for formation and disruption of H-bonding, respectively. At no stage did we observe splitting of the amide peak so indicating that both the amides were equally involved in H-bonding.

Having demonstrated self-sorting for the (**NDI-1** + **DAN-1**) pair we tested gelation of **NDI-1** with various bis-amide functionalized DAN-derivatives (Fig. S7†) with varying distance between the two amide groups, and for all tested D–A pairs, yellowish gels were observed in MCH (Fig. S7†) without appearance of any red color, clearly suggesting versatility of the current approach which was the major drawback of our previous design.[8,9] We further examined the validity of this design in various structurally different non-polar solvents (aromatic, chlorinated and hydrocarbon), and in every occasion self-sorting was observed as indicated by formation of a yellow gel (Fig. S8†).

In summary, we have illustrated a versatile molecular design for H-bonding mediated orthogonal-assembly between aromatic donor and acceptor chromophores. The molecular design relies on placing two self-complementary H-bonding functionalities (amide) symmetrically in the donor building block while unsymmetrically in the acceptor one, so that for alternate co-stacking, not all the amides can participate in H-bonding. As H-bonding is stronger than CT-interaction, self-sorting was observed for all the tested donor–acceptor pairs with related structures. To best of our knowledge this is the most effective design for self-sorting because, in principle, it is applicable universally to any donor–acceptor pair without compromising the stability of individual assembly.

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