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Hydrogen-Bonding Directed Assembly and Gelation of Donor–Acceptor Chromophores: Supramolecular Reorganization from a Charge-Transfer State to a Self-Sorted State

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Gelation^[1] of various functional π systems^[2] has been extensively studied due to the possibility of modulating their photophysical properties in the gel state. Donor-acceptor (D-A) charge-transfer (CT) interactions have been utilized to generate many elegant supramolecular materials, such as rotaxanes and catenanes,[3] synthetic ion channels,^[4] liquid crystals,^[5] folded oligomers,^[6] polymers,^[7] and organogels.^[8] Recently we have demonstrated self-sorting^[9] in a mixed assem-



Scheme 1. Structure of various donor and acceptor building blocks.

bly of a bis(amide)-functionalized dialkoxynaphthalene (DAN) donor and a naphthalenediimide (NDI) acceptor due to synergistic effect of hydrogen bonding and π stacking.^[10a] Control experiments indicated that if the number of methylene groups (*n*) between the DAN/NDI chromophore and the amide functionality can be adjusted so that *n*-NDI = (n+2)-DAN, then alternate co-stacking of the D–A chromophore could also be achieved. However, in the previously reported D–A pair (**DAN-2+NDI-0**),^[10a] although a CT band was visible in solution, no gelation could be observed, probably due to highly rigid assembly of NDI chromophore.^[10b] Thus to achieve CT gelation we have explored a new D–A pair **DAN-4+NDI-2** (Scheme 1) in which the rigidity of the acceptor unit is reduced due to the inclusion of additional methylene units. In this communication we reveal CT-

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interaction-mediated gelation of this D–A pair in a moderately nonpolar solvent tetrachloroethylene (TCE) and also demonstrate the serendipitous discovery that when the solvent was changed to a less polar methylcyclohexane (MCH), the CT gel switched over to thermodynamically stable selfsorted gel within few hours.

Self-assembly of NDI-2+DAN-4 (1:1, total concentration=25 mM) was performed in TCE. The compounds were soluble only at elevated temperature to generate a colorless solution, which when cooled down to room temperature produced a deep red gel (Figure 1 a) clearly suggesting alternate co-stacking of the donor and acceptor chromophores. NDI-2 and DAN-4 individually also showed spontaneous gelation under identical conditions (Figure 1).



Figure 1. Left: SEM picture of the CT-gel (1:1 mixture of NDI-2 + DAN-4) in TCE; Right: Photographs of gels in TCE derived from a) NDI-2 + DAN-4 (1:1), b) NDI-2, c) DAN-4, d) NDI-2 + DAN-2. Total gelator concentration = 25 mM in each case.

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To confirm that distance between the two amide groups in D and A indeed is critical for the CT interaction, we tested the gelation of the **NDI-2+DAN-2** pair and observed gelation without appearance of any red color (Figure 1d), suggesting lack of alternate co-stacking. The morphology of the CT gel was examined by scanning electron microscopic (SEM) studies that revealed the presence of micrometer long entangled bundles of fibers (Figure 1, width of smallest fiber = 62 nm), which is typical of a good gelator. To understand the influence of hydrogen bonding on the self-assembly and gelation we examined the effect of MeOH, a hydrogen-bonding competing solvent, on the UV/Vis spectra of the **NDI-2+DAN-4** mixture (Figure 2).



Figure 2. a) Effect of MeOH on the CT band of **NDI-2+DAN-4** (1:1, total concentration = 5 mM) in TCE. b) Gel (in TCE, conc. 25 mM) to sol transition in presence of 7% (v/v) MeOH.

In TCE there is a broad absorption band ($\lambda_{max} = 550 \text{ nm}$) that is characteristic of CT interactions between the NDI and DAN chromophores.^[6] With an increasing amount of MeOH, the intensity of the CT band gradually decreased and finally disappeared at only 7.0% (v/v) MeOH/TCE (Figure 2 a). Consequently, when 7.0% MeOH was added to the CT gel, the red color disappeared with concomitant transformation of the gel to homogeneous solution (Figure 2 b). This clearly indicates that hydrogen bonding is the most-influential factor for the self-assembly and in its absence, the CT interaction alone is not adequate for gelation.

We further examined the gelation in an aliphatic hydrocarbon solvent, MCH, in which hydrogen-bonding interactions are expected to be even stronger and observed spontaneous gelation with an intense red color (Figure 3). However, much to our surprise, unlike in TCE, in this case the red color gradually faded away and completely disappeared in about 5 h to produce a yellowish gel (Figure 3). Consequently with increasing time the CT band in the UV/Vis spectrum disappeared with concomitant increase in the base-line intensity (Figure S1a in the Supporting Information), which is probably due to the increased opaqueness of the switched gel. To examine the mode of assembly in the modified yellow gel, we compared the absorption bands appearing due to $n-\pi^*$ and $\pi-\pi^*$ transitions in the D-A mixture with that of the mathematical sum of the aggregated spectra for the individual D and A chromophores (Figure S1b in the



Figure 3. Photograph of the gel (1:1 NDI-2+DAN-4 in MCH, total concentration = 10 mM) at various time intervals.

Supporting Information) and found them to be almost identical. This simple experiment reveals the self-sorted assembly of the individual chromophores in the modified yellowish gel.

Furthermore we examined the effect of concentration and temperature on this unprecedented reorganization phenomenon in the gel state (Figure 4). The variation of the scattering intensity^[11] at 700 nm was monitored as a function of time at two different temperatures (Figure 4a) and gelator concentrations (Figure 4b). It can be clearly seen that in both cases, the scattering intensity increased and then finally saturated. It is evident that the process is much faster at the lower concentration and higher temperature. This is expected as the re-organization of the chromophores from the CT state to the self-sorted one will be facilitated at lower con-



Figure 4. Variation of scattering intensity @ 700 nm in the UV absorption spectra of the dynamic gel (**DAN-4+NDI-2** (1:1) in MCH) at two different temperatures and concentrations. Concentration of gelator=5 mM; path-length of cuvette=1 mm.

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centration due to less rigidity of the medium and at higher temperature due to more available energy.

To rationalize this supramolecular transformation, we examined the FT-IR spectra of the gel in MCH (Figure 5a). The freshly prepared red gel exhibited a broad band due to the N–H stretching of the amide functionality at 3309 cm^{-1} ,



Figure 5. a) Selected region of the IR spectra of the CT-gel (NDI-2+DAN-4, concentration = 10 mM) in MCH as a function of time. b) Rheological data in MCH for the gel (4.0 wt%) before (triangles) and after reorganization (circles).

which gradually shifted towards lower values and finally saturated at 3271 cm^{-1} after 6 h. Note that by this time the red gel also has been switched over to the yellow one (Figure 3). It is also interesting to note (Figure 5a) that the final stretching frequency of the reorganized gel almost exactly matches the mathematical sum^[12] of the IR spectrum of the individual donor and acceptor gels (indicated as "sum spectrum" in Figure 5a), which confirms that reorganization eventually leads to self-sorting.

We also compared the rheological properties of the CT and self-sorted gels in a stress-amplitude sweep measurement (Figure 5b). For both samples, the storage modulus (G') is initially higher than the loss modulus (G''), which is typical of a gel phase.^[13] With increasing stress, both G' and G'' remained invariant up to a certain point and then deviated and crossed each other. This crossover point is considered as the yield stress (σ_y) ,which is a measure of the robustness of the gel. The value of σ_y for the self-sorted gel was found to be 30.6 Pa, which is almost 30-fold higher than that of the CT gel (1.17 Pa); this result supports the findings of the IR experiment that stronger hydrogen bonding is achieved due to the reorganization.

Table 1. Gelation data in TCE and MCH.

NDI-2	DAN-4	NDI-2+DAN-4 (1:1)
0.75	11.0	3.0
0.91	2.0	_[d]
75	31	72
$> 105^{[b]}$	65	> 39 ^[c]
	NDI-2 0.75 0.91 75 >105 ^[b]	NDI-2 DAN-4 0.75 11.0 0.91 2.0 75 31 >105 ^[b] 65

[a] Concentration of the gelator = 20 mM. [b] Solvent started boiling beyond this temperature. [c] T_g varied significantly with time, please see the Supporting Information (Table S1) for details. [d] The data could not be retrieved due to dynamic nature of the gel.

To explain stability of the CT gel in TCE, we examined gelation of the NDI-2 and DAN-4 individually in both TCE and MCH (Table 1). The critical gelation concentration (CGC) and gel-melting temperature (T_{α}) data (Table 1) indicated much stronger gelation for NDI-2 relative to DAN-4. Poor gelation for the donor is attributed to the relatively weaker hydrogen-bonding interaction, owing to the enhanced flexibility due to the presence of more number of methylene units^[10b,c] between the chromophore and amide functional groups. The D-D self-assembly is further destabilized by electrostatic repulsion among the electron-rich DAN chromophores.^[6] The gelation data in TCE also revealed almost identical thermal stability and even lower CGC for NDI-2 gel relative to those of the CT gel. This is rather surprising, because one would expect the CT interaction to be stronger than A–A π -stacking. Thus to gain further insights about the structural nuances of the A-A homoaggregates and the charge-transfer (D-A) dual aggregates, a preliminary quantum chemical investigation was conducted. The hybrid density functional method, BHLYP was used in conjunction with 6-31G (d, p) basis sets to optimize the molecular geometries for NDI-2 and NDI-2+DAN-4 (Figure 6).^[14,15] The optimized structure for CT-assembly ex-



Figure 6. Optimized molecular geometries of **DAN-4+NDI-2** (top) and **NDI-2** homo-aggregate (bottom) at BHLYP/6-31G (d, p) level of theory. Some of the alkyl and phenyl hydrogen atoms are not shown for clarity.

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hibits intermolecular hydrogen bonding between the amide functionalities of the donor and acceptor chromophores (each 2.08 Å), along with a CT interaction. For assembly of **NDI-2** alone, similar hydrogen-bonding interactions were observed but with significantly shorter bond lengths(1.99 and 1.96 Å). These results clearly suggest that the strength of the hydrogen-bonding interaction is greater in case of A–A homoaggregates compared to the D–A alternate stacking.^[16]

We assume that it is just a coincidence that the strength of (stronger hydrogen bonding + A–A π -stacking) becomes comparable to that of (weaker hydrogen bonding + D–A CT interaction) and thus the thermal stability of the two types of gels (pure **NDI-2** and **NDI-2+DAN-4**) are found to be almost identical (Table 1). However, it is the poor self-assembly of the donor gel that favours the formation of pure CT gel^[17] instead of acceptor gel, because in that case maximum number of amide functionalities linked to both D and A chromophores can be engaged in hydrogen bonding. As we used 1:1 mixture of D and A chromophores, if a mixture of CT and A gels is formed, then many of the D molecules will not take part in aggregate formation, because they cannot form a stable self-assembled structure on their own in TCE, as evident from its poor gelation ability (Table 1).

Next we examined the gelation data in MCH, in which reorganization was observed.^[18] The CGC value for **DAN-4** was found to be 2 mm (Table 1), which is almost four times lower than that in TCE (Table 1), and the T_g (20 mM) was found to be 65 °C, which is more than twice as much as that in TCE (Table 1). Similarly for **NDI-2** also the gelation data indicates stronger self-assembly compared to that in TCE; this fact can be attributed to stronger hydrogen-bonding interaction in hydrocarbon solvent. However, in case of D–A alternate co-stacking we do not anticipate strengthening of hydrogen bonding to such extent, because solvent polarity can only alter the electronic parameters but not the geometrical constraint that was observed in their energy minimized geometry (Figure 6).

This is evident from the observed T_g of the CT gel in MCH (Table 1, and Table S1 in the Supporting Information). It is interesting to note that soon after the formation of the CT gel, the T_g was found to be 39°C, which is even lower than that in TCE (72°C). This can be attributed to the dynamic nature of the system, which inhibits precisely defined self-assembly with long-range order at the early stage of gelation. However, gradually as the gel switched over to the stable self-sorted state, the T_g increased significantly (Table S1 in the Supporting Information).

It is evident from the forgone discussion that self-sorted state is prefered over the alternate co-assembly if the stability of the individual self-assembled structure is higher, as is the case in MCH. To examine whether this can also be established by structural variation of the chromophores instead of solvent variation we examined gelation of **NDI-2** with a different donor **DAN-3**^[10c] (Scheme 1). The rationale behind choosing the new donor is that we anticipated homoaggregates of **DAN-3** to be stronger than **DAN-4**, due to

smaller number of methylene units.^[10b] Of course the distance between the two amide groups in this D-A pair also was found to be comparable. The CGC and T_{g} (at 20 mm concentration) of DAN-3 in TCE were found to be 3.2 mm and 59°C, respectively, which indeed proved superior selfassembly of DAN-3 compared to DAN-4 in TCE. As expected NDI-2+DAN-3 (1:1) produced red CT gel in TCE (total concentration 10 mm), but unlike previous case (NDI-2+DAN-4 in TCE) after 4 h the color completely disappeared suggesting reorganization from CT state to the selfsorted state (Figure S5 in the Supporting Information).^[19] This observation provides further evidence that if the individual self-assembly of both the donor and acceptor chromophores are reasonably strong, eventually the self-sorted state is achieved even though the kinetically controlled CT state is initially formed.

In conclusion, we have demonstrated spontaneous self-assembly and gelation in a bis(amide)-functionalized donoracceptor chromophore mixture by the synergistic effect of hydrogen bonding and CT interactions/ π -stacking. Two distinctly different modes of assembly (alternate D-A co-assembly versus self-sorting) could be observed depending on marginal variation in structure of the chromophores and/or solvent polarity. When the structure of the chromophore and nature of the solvent provided opportunity for stronger hydrogen bonding, the system adopted the particular mode of assembly in which the effect of hydrogen bonding could be fully realized. Thus the initially formed, kinetically controlled, CT-state (NDI-2+DAN-4 in MCH, NDI-2+DAN-3 in both MCH and TCE) re-organized to more stable selfsorted state, as there was no geometrical constraint for hydrogen bonding. On the other hand, in a moderately nonpolar chlorinated solvent like TCE,^[20] as the strength of the hydrogen-bonding interaction was inherently reduced compared to that in MCH, the CT interaction plays a significant role in deciding the mode of self-assembly and thus longlived CT state was achieved. Of course none of these possibilities arose when the distance between two amide functionalities were very different for the D and A chromophore and in that case (NDI-2+DAN-2) self-sorting was always observed.

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- [11] The baseline intensity of the absorption spectra was found to increase with supramolecular reorganization (Figure S3 in the Supporting Information), probably due to opaque nature of the self-sorted gel. This caused difficulty in monitoring the CT-band intensity as a function of time and thus we followed the increase in the baseline intensity itself at 700 nm, which arises due to scattering to approximately quantify the transformation rate under various conditions with a assumption that the rate of switching is proportional to the change in scattering intensity.
- [12] Solvent dependent (CHCl₃ and MCH) variation in IR spectrum of the individual chromophores clearly indicated hydrogen bonding; see Figure S4 in the Supporting Information for detail.
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- [15] The present calculation is limited by the fact that we have not included solvents Nevertheless, we believe this provides valuable supporting information regarding the geometrical constraints for hydrogen bonding in case of CT gel formation due to miss-match in distance. As here we are only concerned about structural aspects and not the energetic ones, we assume exclusion of solvents does not have much influence on our conclusions. Moreover, all the gelating solvents have very low dielectric constant, hence it is expected that a gas-phase structure would be very similar. More detailed calculations with extended D–A stacks and including solvent molecules are underway and will be published in a subsequent full paper.
- [16] We were also curious to examine the energy minimized structures for the D-A pair NDI-2+DAN-2, in which we always observed self-sorting (Figure S7 in the Supporting Information). In this case we observe a substantially longer hydrogen bond (2.19 Å) between one of the two amide functionalities, while the other one was of very similar length to that observed in the NDI-2+DAN-4. An alternative, almost iso-energetic, minimum was also found that lies only 0.35 kcal mol⁻¹ above the previously discussed structure and in this structure only a single intermolecular hydrogen bond (2.09 Å) between the two interacting moieties could be noted. However, under no circumstances could we arrive at a minimum in which both the amide bonds could be involved in strong hydrogen bonding for the alternate stack of NDI-2 and DAN-2. This corroborates well with the experimental observation, that for this D-A pair we always observed self-sorting and no alternate co-stacking. Alternatively, the distance in D-D aggregates also display slightly longer intermolecular hydrogen bond lengths than their A-A counterparts, but generally slightly shorter than the corresponding D-A species (Figure S8 in the Supporting Information).
- [17] To confirm that the observed CT gel in TCE is not contaminated with individual self-assembly of A and D, we examined the effect of cooling rate on the CT band of the gel (Figure S2 in the Supporting Information); no notable differences were observed. This indirectly supports the hypothesis that only the CT state is formed during gelation. If there were other types of the self-assembly, the relative mole fractions of various types of structures are expected to vary as a function of cooling speed. However, we realize that this is only indirect evidence and does not completely rule out the possibility of co-existence of the CT and self-sorted states. More detail studies to understand these aspects are underway in our laboratory.

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- [19] In this case reorganization also happens in MCH and other hydrocarbon solvents. Detailed kinetics studies are underway to gain further insight.
- [20] The stable CT state was also observed in other non-polar chlorinated solvents (Table S2 in the Supporting Information).

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