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Contrasting Self-Assembly and Gelation Properties among Bis-urea- and Bis-amide-Functionalised Dialkoxynaphthalene (DAN) π Systems

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Precise control over the spatial arrangement of various functional chromophores[1] plays an important role in modulating the inter-chromophoric interactions and consequently the photophysical properties. The motivation to study these properties stems from the desire to understand the effect of molecular-level interactions on macroscopic properties because of the relevance in organic electronic device applications.[2] In the recent past, there have been many efforts aimed towards developing suitable supramolecular strategies for achieving long-range order in the self-assembled structure of various π systems, such as p-[3] and n-type[4] semiconductors, push–pull-type chromophores,[5] and donor–acceptor charge-transfer systems.[6] The design of the building blocks in most of these systems ensure that self-assembly can be facilitated by gaining the synergistic effect of several non-covalent forces, such as π–π interactions, hydrogen bonding, dipole–dipole interactions, and the hydrophobic effect. In most cases, the role of hydrogen-bonding functionalities has been restricted only to strengthen the propensity for self-assembly, except for a few recent examples in which the nature of the chromophore arrangements could be drastically changed (H- vs. J-type aggregation) by varying the peripheral functional groups[7] or the hydrogen-bonding motif.[8]

Amide and urea are the two most common self-complementary hydrogen-bonding motifs and have been extensively used for various dye assemblies.[3–5] However, to the best of our knowledge there have not been any studies to exclusively compare the influence of these two functionalities in deciding the chromophoric arrangements in the self-assembled structure. The question we asked is whether, due to the mismatch in number of hydrogen-bonding (−NH···O−) interaction sites, they only differ in terms of providing differential stability to the self-assembled structure or are they also capable of altering the mode of the chromophoric arrangements? To answer this question, we have synthesised two derivatives of the dialkoxynaphthalene (DAN) π system, namely, DAN-U and DAN-A (Scheme 1), which differ only in amide and urea functionalities. Herein, we report the contrasting solution self-assembly and gelation behaviour of DAN-U and DAN-A and our studies related to understanding the correlation between these two phenomena.

Firstly, we studied the self-assembly in solution by solvent-dependent absorption spectroscopy. In a recent report we have shown that DAN-A forms H-type π stacks in non-polar medium such as methylcyclohexane (MCH)/$CHCl_3$ (95:5).[9] However, DAN-U was found to be insoluble in $CHCl_3$ at room temperature and so to avoid ambiguity in the comparative self-assembly studies in solution, herein we have used a THF and MCH solvent composition.

In Figure 1a, we show the UV-visible absorption spectral changes of DAN-A as a function of solvent composition. With gradual addition of non-polar solvent MCH to the solution of the chromophore in THF, there was almost no change in the absorption spectra until around 80 % MCH/THF (v/v), which suggested no π stacking. Further addition of MCH caused drastic changes in the absorption spectra; the intensity of the major bands at 313 and 326 nm reduced by ≈60 % with a slight blueshift and the peaks became significantly broader, suggesting formation of H aggregates (Figure 1a, inset) as a result of hydrogen bonding and π stacking. When similar experiments were performed with DAN-U, to our surprise, we noticed distinctly different spectral changes. In THF, which is a polar, hydrogen-bonding competing solvent, the absorption spectrum was almost identical to that of DAN-A, suggesting presence of monomeric chromophores. However, with an increasing amount of MCH, the major absorption bands at 326 and 313 nm exhibited strong hyperchromic shifts (absorption intensities at 326 nm increased by almost 200 % from THF to 95:5 MCH/THF) along a with small bathochromic shift of about 3 nm for both peaks and the modified spectrum became more

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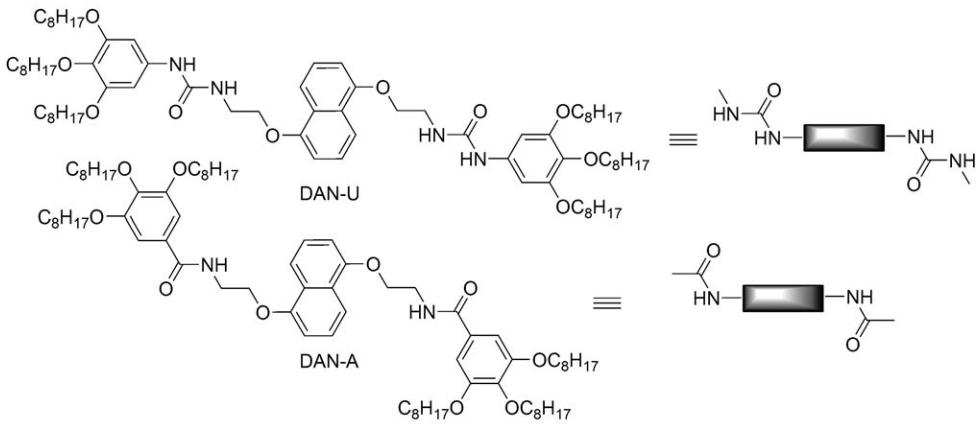

Scheme 1. Structure of the chromophores.

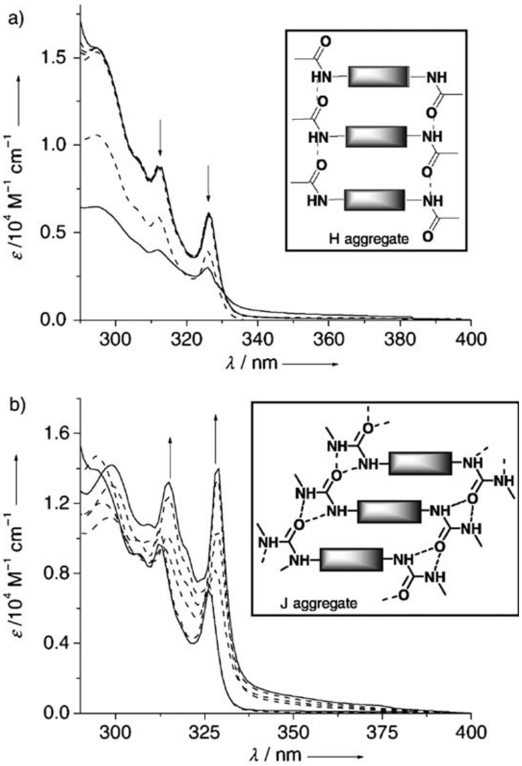

Figure 1. Solvent-dependent absorption spectra of DAN-A (a) and DAN-U (b): Arrows indicate direction of spectral changes from THF to MCH. Inset: schematic representation of the proposed mode of chromophore assembly (hydrogen bonding is shown with a dashed bond). Concentration of the chromophore = 0.1 mM and temperature = 25 °C.

sharp (full width at half maxima reduced to 3 nm from 6 nm) compared with the monomeric spectrum in THF. These spectral changes clearly suggest that DAN-U forms J aggregates[10] in non-polar media wherein the chromophores are arranged with a longitudinal displacement along the long axis (Figure 1 b, inset).

Just to highlight the fact that the mode of self-assembly of DAN-A and DAN-U are completely different, we compared the UV-visible spectra of two extreme cases (monomeric and fully aggregated) for both chromophores in Figure 2 a. It can be noted that in THF, in which both chromophores remain as monomers, the absorption spectra (indicated by dotted lines) are very similar in nature and the extinction coefficients (ε) for the lowest energy band at 326 nm are 6000 and 6900 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$ for DAN-A and DAN-U, respective-

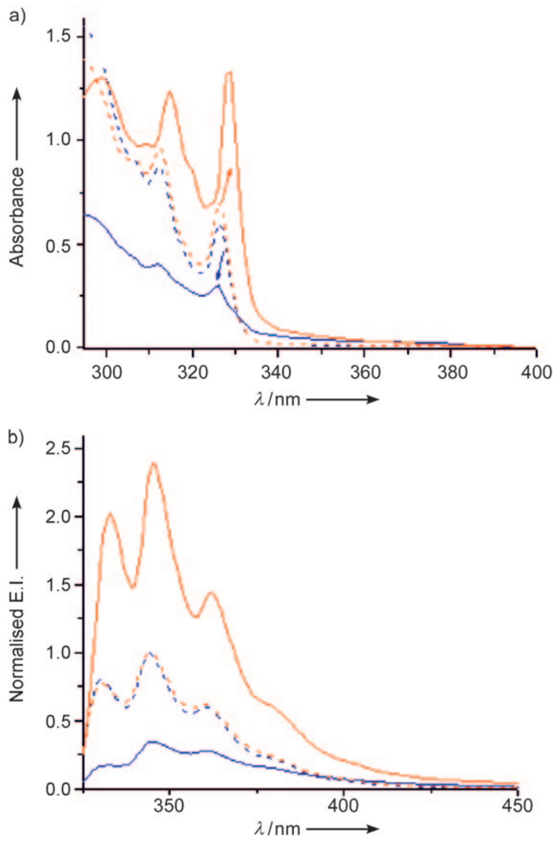

Figure 2. Solvent-dependent absorption (a) and emission (b) spectra ($\lambda_{ex} = 295$ nm) of DAN-A (blue) and DAN-U (red). Dotted lines indicate spectra recorded in THF and solid lines indicate spectra recorded in MCH/THF (95:5). Concentration = 0.1 mM, Temperature = 25 °C.

ly. Going from THF to MCH/THF (95:5) the two spectra changed completely in opposite directions. There was a hypochromic shift along with a blueshift (indicated by the blue arrow in Figure 2a) for H-aggregated DAN-A, whereas a hyperchromic shift along with a redshift (indicated by the red arrow) for DAN-U was observed. As a result, the value of ε for the lowest energy band in the aggregated state was found to be 13400 $\text{M}^{-1}\text{cm}^{-1}$ for DAN-U, which is astonishingly high relative to that for DAN-A (2900 $\text{M}^{-1}\text{cm}^{-1}$).

The self-assembly of the two chromophores were also probed by fluorescence spectra. In Figure 2b, the emission spectra of the two chromophores were compared in the monomeric (in THF) and aggregated (MCH/THF) states. Going from THF to MCH, for DAN-U the emission intensity increased by 2.5 times with peak sharpening, which is a well-known signature for J aggregates.[10] In contrast, the fluorescence of DAN-A was found to be almost quenched with peak broadening as a result of aggregation, which further supports that the mode of self-assembly in these two chromophores is significantly different.

Apart from the difference in amide and urea functionality, the two chromophores also differ in the number of atoms (n) in between the DAN chromophore and the 3,4,5-trialkoxy benzene ring ($n=4$ and 5 for DAN-A and DAN-U, respectively), which may influence in the packing of the two chromophores due to the change in the conformational angle between the two aromatic units. We chose these two systems because we wanted to keep the number of methylene units the same between the DAN chromophore and the hydrogen-bonding functionalities to avoid confusion regarding the odd–even effect[11] of the spacer moiety. However, to examine this effect we synthesised another amide-functionalised control molecule, DAN-A′ (Figure 3)[12] in which $n=5$. Solvent-dependant UV-visible studies (Figure 3) revealed that going from polar (THF) to non-polar solvents (MCH), there was a significant reduction (the intensity of the band at 326 nm reduced to 57 %) in the peak intensity in conjunction with peak broadening. These spectral variation are similar to those observed for DAN-A, and thus suggests similar aggregation properties for both amide-containing chromophores.

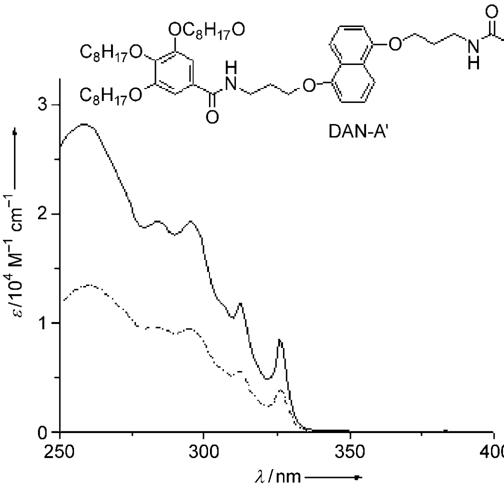

Figure 3. Solvent-dependent (——: THF, •••••: MCH/THF (95:5)) absorption spectra of DAN-A′. Concentration of the chromophore = 0.1 mM and temperature = 25 °C.

From this experiment, it appears that the difference in number of atoms between the aromatic units is not responsible, at least directly, for the observed difference in the mode of self-assembly between DAN-A and DAN-U. However, that does not confirm that the amide versus urea functionality is the only reason for contrasting self-assembly because there are also other structural differences between these two molecules that cannot be completely decoupled. For example, the carbonyl functionality, involved in hydrogen bonding, is not located in identical chemical environments with respect to the aromatic units in both cases. In case of DAN-A, it is the terminal unit that is directly linked to the benzene ring, whereas that is not true for DAN-U. Thus, although the experiments indicate the amide versus urea functionality plays a crucial role in deciding the mode of self-assembly, one cannot completely rule out the possibility of additional influences of other structural differences as described above on the contrasting self-assembly between these two molecules.

Now we estimated the propensity for self-assembly in these two systems by calculating the mole fraction of aggregate (α_{agg}) values as a function of solvent composition from the variation in their absorption spectra (Figure 1a and b) by using Equation (1):[7]

$$\alpha_{\text{agg}} \approx \frac{A_{\text{mix}} - A_{\text{mon}}}{A_{\text{agg}} - A_{\text{mon}}} \tag{1}$$

The absorbance at 326 nm at the lowest and highest MCH/THF ratios were taken as the values for A_{mon} and A_{agg}, respectively. A_{mix} is the absorbance at 326 nm at a given solvent mixture. It can be clearly seen in Figure 4 that for DAN-U the aggregate formation starts at a much lower MCH/THF ratio, suggesting the relatively high tendency to form aggregates compared with DAN-A. From these plots the α_{agg}^{50} (solvent composition at which $\alpha_{\text{agg}} = 0.5$) values were

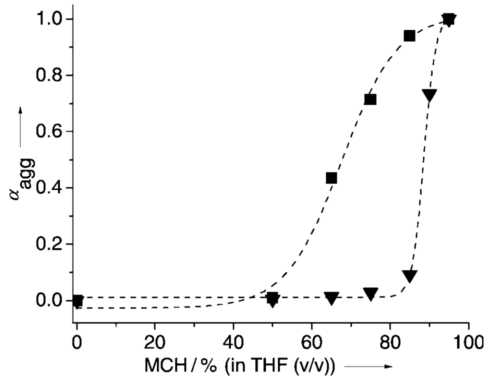

Figure 4. Plot of α_{agg} as a function of solvent composition for DAN-U (■) and DAN-A (▼).

estimated to be 68 and 88% MCH/THF for DAN-U and DAN-A, respectively. This significant difference was attributed to the stronger hydrogen-bonding interaction in the urea functionality than in the amide.

To ascertain that hydrogen bonding is indeed responsible for self-assembly, we examined the effect of MeOH, a hydrogen-bonding competing solvent, in the absorption spectra of both chromophores (Figure 5). It was observed that even in the presence of very little MeOH, the assembled structure was completely destroyed and the monomeric spectrum could be recovered. For DAN-A the monomeric spectrum could be regenerated in the presence of only about 1% (v/v) MeOH in 95:5 MCH/THF, whereas to obtain the same for DAN-U, about 11% (v/v) MeOH was required. These differences corroborate well with the conclusion drawn from the observed differences in their α_{agg}^{50} values and clearly suggest stronger self-assembly for J-aggregated DAN-U.

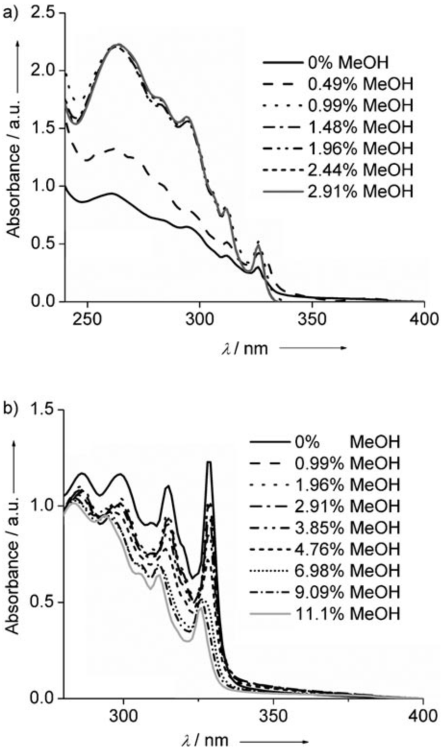

Figure 5. Effect of gradual addition of MeOH on the absorption spectra of the self-assembled structure of DAN-A (a) and DAN-U (b) in 95% MCH/THF. Concentration = 0.1 mM, Temperature = 25 °C.

The stabilities of these two types of self-assembled structures could also be compared by variable-temperature UV-visible studies.[13] For DAN-A, the aggregated spectrum could be reversibly converted to the monomeric species at relatively low temperatures (40 °C), suggesting a very weak nature of the assembly, which is in accordance with the observations made by Iverson and Cubberley for DAN chromophores.[14] However, for J-aggregated DAN-U, there was negligible change in the absorption spectra even at 65 °C, reiterating the fact that stronger self-assembly occurred. The observed difference may not only be due to stronger hydrogen bonding, but the slipped geometry of the chromophores in the J-type assembly could also contribute to less electrostatic repulsion among the adjacent chromophores compared with that for the face-to-face π stacking in the H-type assembly.

Self-assembly often leads to gelation at higher concentrations.[15,3–6] Gelation with chromophoric building blocks such as ours provides the opportunity to study self-assembly separately by spectroscopic methods at a concentration below the critical gelation concentration (CGC) and understand the effect of the nature of inter-chromophoric interactions on gelation.[16] Thus, we were curious to know the effect of the remarkable differences in the self-assembly of DAN-U and DAN-A on their gelation properties. Gelation of these two chromophores was studied in ten common organic solvents of different natures and the results are presented in Table 1. J-aggregated DAN-U was found to be an excellent gelator for various types of solvents, such as aliphatic (MCH), aromatic (toluene, benzene, 1,2-dichlorobenzene), chlorinated (chloroform, TCE, tetrachloromethane) and even hydrogen-bonding solvents (THF). The CGC values in all of the solvents were found to be very low (< 1.0 wt% except for THF) and particularly in aromatic solvents[17] they were found to be extremely low (< 0.1 wt%). It is noteworthy that gelators with such low CGC values are often called super-gelators[18] to emphasise their extraordinary gelation ability.

Table 1. Gelation data for DAN-A and DAN-U.[a]

Solvent	DAN-U	CGC [wt%]	DAN-A	CGC [wt%]
toluene	G	0.06	G	1.39
benzene	G	0.07	S	–
1,2-dichlorobenzene	G	0.05	S	–
MCH	G	0.32	G	0.46
cyclohexane	GP	–	G	1.14
TCE[b]	G	0.40	S	–
$CHCl_3$	G	0.30	S	–
CCl_4	G	0.29	G	0.76
THF	G	1.20	S	–
dioxane	P	–	S	–

[a] G = gel, GP = gel-like precipitate, P = precipitate, S = soluble. [b] TCE = tetrachloroethylene.

In contrast, H-aggregated DAN-A showed gelation in only a few cases of all tested solvents (Table 1). Such contrasting gelation properties can be attributed to the vast differences in the nature (J- vs H-aggregation) and the propensity for self-assembly among DAN-U and DAN-A. Please note that strikingly similar results for J- and H-aggregated perylenebisimide (PBI) organogelators have been recently reported by Würthner and co-workers.[19] To compare the thermal stability of the gels, we determined the gel-to-sol melting temperatures for DAN-U and DAN-A in MCH at a fixed concentration (4.0 mM) and they were found to be 94 and 59 °C, respectively, which clearly revealed much higher thermal stability in the former case. The morphology of the self-assembled fibres responsible for gelation was examined by AFM studies. The AFM images of DAN-A and DAN-U are shown in Figure 6. In both cases the formation of micrometer long fibres is clearly visible, as commonly observed for gelation. The heights of the smallest fibres were found to be 3.3 and 4.3 nm, for DAN-U and DAN-A, respectively. From a cursory observation it appears that the extent of cross-linking among the DAN-U fibres is less than those for DAN-A.

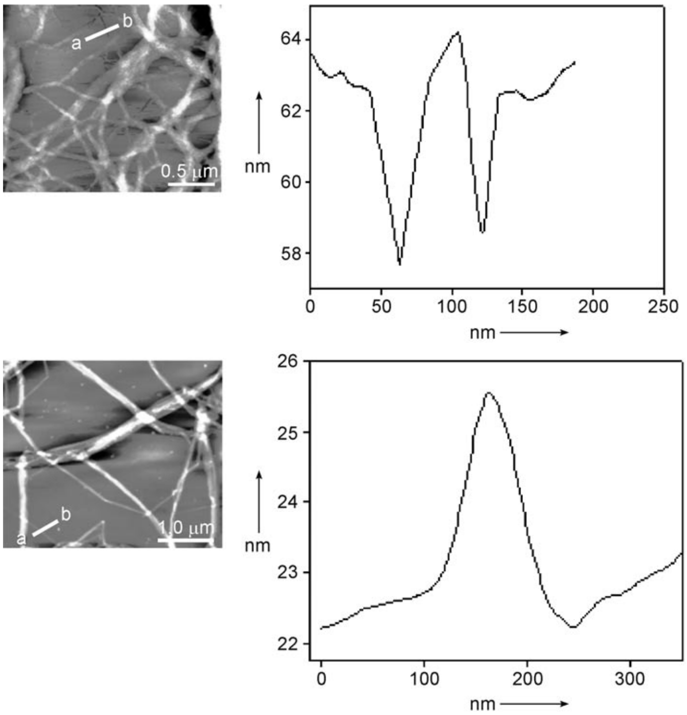

Figure 6. AFM height images of DAN-A (top) and DAN-U (bottom) in 90 % MCH/THF (concentration = 0.05 mm). In the right-hand side the cross-sectional analyses from a–b are shown for the respective images.

We also examined the flow behaviour of the two types of gels by comparing their rheological properties (Figure 7).[20] It can be seen for both systems that initially G′ (storage modulus) was higher than G″ (loss modulus), suggesting the presence of a gel phase. With a gradual increase in applied stress, both G′ and G″ remained invariant and then beyond a certain stress they deviated from linearity.

The stress at which deviation occurred is defined as the yield stress and gels begin to flow above this point.[20] The yield stress for DAN-A and DAN-U were estimated to be 11.7 and 2.6 Pa, respectively. The ratio of G′/G″ was also found to be higher for DAN-A (11.2 Pa) than that for DAN-U (6.7 Pa). To confirm that this result is not just one exception, we also compared the rheological data for both gels in another solvent, toluene, and even in this case similar trends were observed.[13] Thus, the rheological data clearly revealed better mechanical stability for DAN-A gels, which contradicts the rest of the observations in which we have shown stronger self-assembly, more versatile gelation and higher thermal stability for the DAN-U gelator. To understand the reason behind this apparent anomaly, we proposed the following hypothesis, which is shown in Figure 8: The building block self-assembles to generate elongated fibres (step 1), which at higher concentrations entangle and trap the solvent molecules to show gelation.[13f] Various physical properties of the gel thus depend on both the strength of self-assembly as well as the nature of the self-assembled fibres. Since DAN-U has much stronger self-assembly properties than DAN-A, it forms elongated fibres in various solvents at lower concentrations and also the thermal stability is much higher.

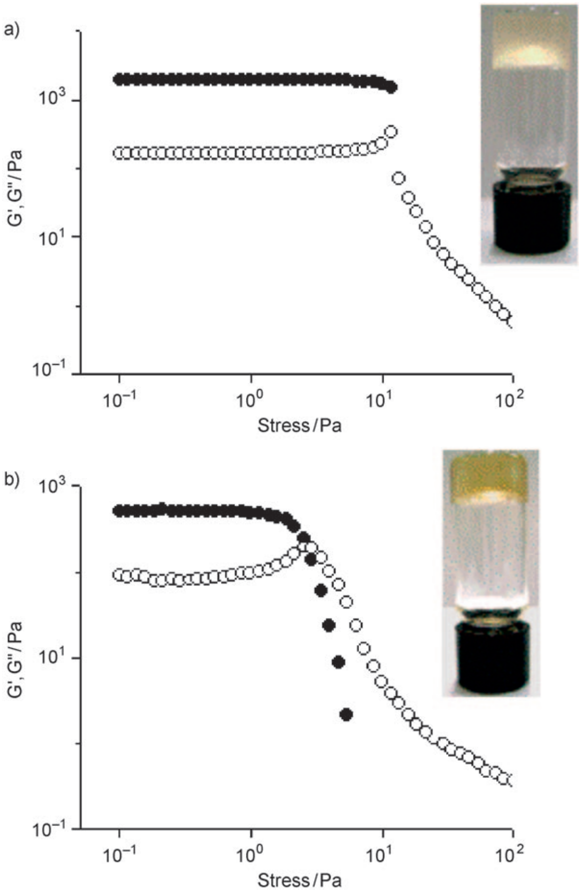

Figure 7. Rheological data for DAN-A (a) and DAN-U (b) gels in MCH. ●: G′, ○: G″. Concentration = 3 wt %, and temperature = 25 °C. Insets show respective gel (4.0 mm) pictures. In 7a, for G′ no points are visible after the yield stress because the value became negative and thus in the log plot it is not visible.

Thus gelation in this case happens in a wide range of solvents with higher thermal stability and lower CGC values. However, due to strong hydrogen-bonding interaction, the DAN-U fibres are expected to be stiffer and thus cannot undergo extensive entanglement.[21] On the other hand, DAN-A forms more coil-like flexible fibres due to weaker hydrogen-bonding interaction and thus formation of an entangled network structure is more facile in this case. Consequently, with increasing stress it is easier to disintegrate the compa-

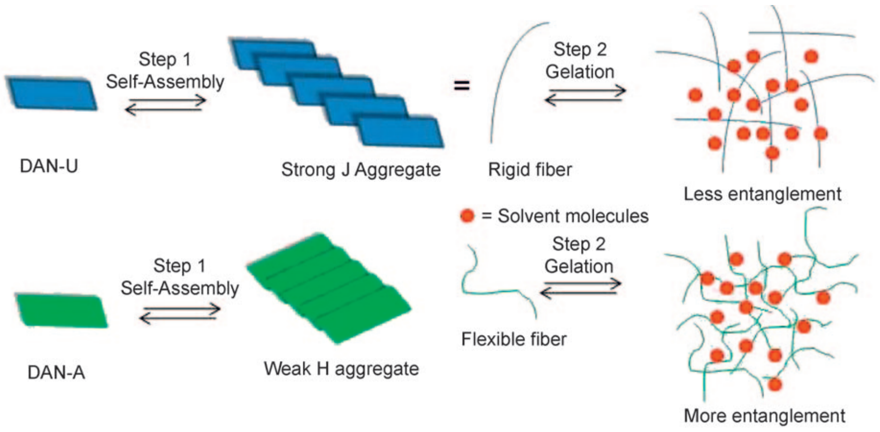

Figure 8. Schematic presentation of the proposed hypothesis regarding the steps of gelation for the two systems.

ratively less-entangled DAN-U gel network than that of DAN-A.

In an attempt to correlate this hypothesis with molecular-level interactions, we carried out solvent-dependent fluorescence anisotropy studies[22] for both systems (Figure 9). It

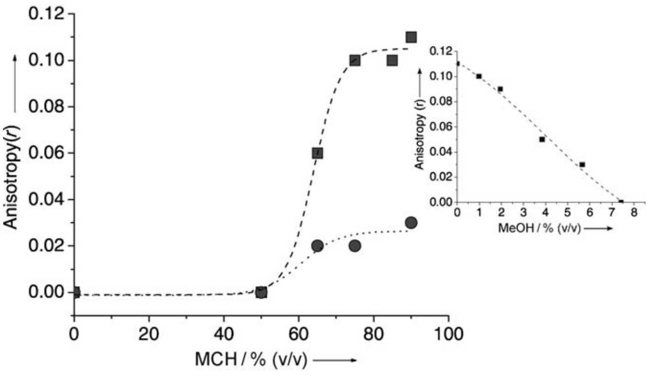

Figure 9. Solvent-dependent (MCH/THF) fluorescence anisotropy studies of DAN-A (●) and DAN-U (■) at 25 °C. Inset: effect of MeOH on the anisotropy values of DAN-U at 95:5 MCH/THF. Concentration = 0.1 mM, $\lambda_{ex} = 295$ nm, $\lambda_{em} = 344$ nm.

can be seen that for both DAN-U and DAN-A, the anisotropy values are very close to zero in THF, suggesting the presence of freely tumbling monomeric chromophores. However, when the relative amount of MCH was increased gradually, beyond about 65 % MCH/THF, the anisotropy value for DAN-U started increasing significantly and finally reached a value of 0.11. It is noteworthy that the inflection point in this plot is almost identical to that observed for the solvent dependent α_{agg} plot (Figure 4), which indicates that the enhanced anisotropy is directly related to self-assembly.

For DAN-A there was also a certain increase in the anisotropy value beyond a certain solvent composition. However, the significantly higher anisotropy value (0.11) of DAN-U than DAN-A (0.03) clearly suggests a more rigid chromophore assembly in the former case than the later. To further confirm that the observed increase in the anisotropy values for DAN-U is indeed due to self-assembly, we added MeOH to the solution and found a sharp decrease in the value (Figure 9, inset). Previously, we have shown that in the presence of MeOH disassembly occurs (Figure 5 b) and thus this experiment undoubtedly demonstrates that the increase in the anisotropy is indeed due to the self-assembly.

In conclusion, we have demonstrated distinct differences in the mode of self-assembly between bis-amide- and bis-urea-functionalised DAN chromophores. The urea-functionalised system formed J aggregates in solution with a superior self-assembling propensity and thermal stability than the H-aggregated amide-functionalised system. The contrasting self-assembly behaviour resulted in significantly different gelation properties for the two systems. The urea-functionalised system showed gelation in versatile organic solvents with much greater thermal stability and lower CGC, whereas the amide-functionalised DAN building block formed gels with higher mechanical stability. The observed anomaly was explained by comparing the difference in rigidity of the two types of self-assembled fibres. To the best of our knowledge, such a drastic difference in self-assembly (H vs. J aggregate) of amide- and urea-functionalised chromophores are not known.[23] We believe that the present study, which aims towards understanding the relationship between molecular structure and macroscopic properties, will add valuable information to the ongoing effort to study the supramolecular assembly of various other functional π systems in the context of organic electronic device applications.[24] Currently, we are exploring the utility of this structural variation in tuning the self-assembling properties of other DAN-related chromophores[25] and also other types of functional π systems.

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Keywords: dialkoxynaphthalene · gels · hydrogen bonds · organogels · self-assembly

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