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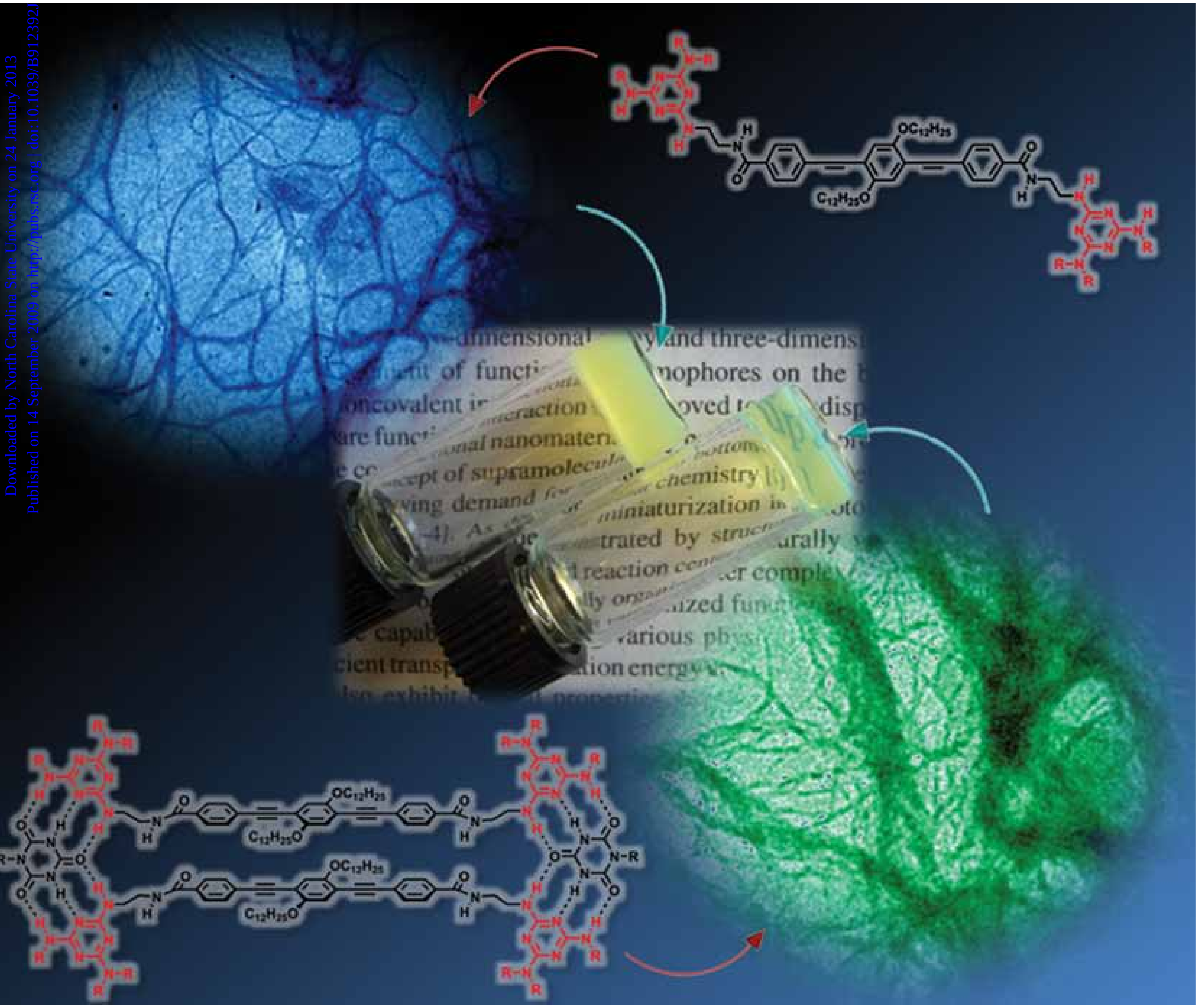

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Role of complementary H-bonding interaction of a cyanurate in the self-assembly and gelation of melamine linked tri(*p*-phenyleneethynylene)s†

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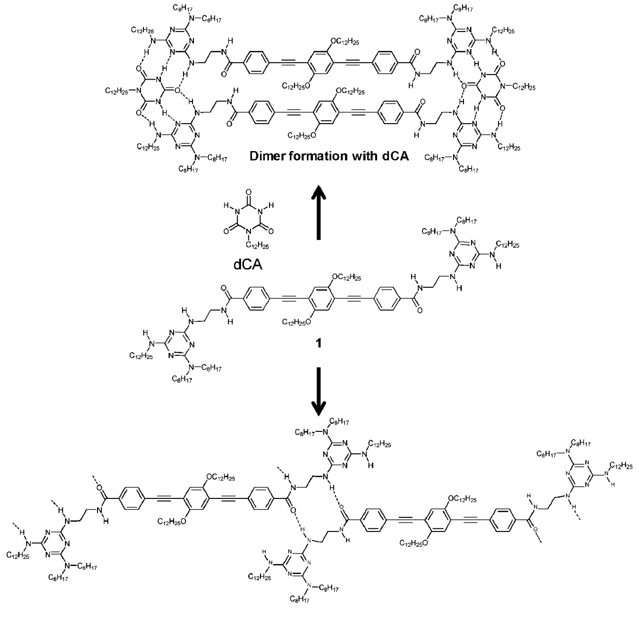
Melamine-functionalized tri(*p*-phenyleneethynylene) 1 self-assembles to form opaque and weak gels in aliphatic solvents which turned transparent and stable upon addition of a cyanurate, affording supramolecular nanostructures with distinct physical properties.

Complex superstructures of organized biopolymers are created by the interplay of complementary hydrogen-bonding interactions. While nature uses amide hydrogen-bonding in protein organization, complementary double and triple hydrogen-bonding interactions between heteroaromatic components are used in transferring genetic information of nucleic acids.[1] Thus, multiple hydrogen-bonding interactions are vital in determining the structure and properties of supramolecular architectures.[2] In recent years, complementary hydrogen-bonding between heterocyclic compounds has been exploited to regulate the structure and properties of functional chromophores.[3,4] Due to strong propensity for π-stacking, linear π-conjugated systems when functionalized with H-bonding moieties are known to form diverse supramolecular architectures.[5,6] Recently, we and others have been exploring the use of *p*-phenyleneethynylene systems for the creation of a variety of supramolecular architectures.[7,8] In the present study we demonstrate the self-assembly of a dual hydrogen-bonding system **1** based on melamine linked tri(*p*-phenyleneethynylene) (TPE) in the absence and presence of a complementary cyanurate (**dCA**) (Scheme 1).

In methylcyclohexane, **1** (1×10^{-5} M) showed an emission maximum at 407 nm (see ESI†). The absence of significant solvent dependence on the maximum suggests that this compound exists as monomeric species under low concentration. When aliquots of the ditopic **dCA** was added to the solution of **1** at a concentration of 1×10^{-5} M, the emission was gradually quenched and red-shifted, both characteristics diagnostic for electronic interaction between the π-conjugated molecules (Fig. 1(a)). Quenching of the emission was saturated when 1 equiv. of **dCA** was added (Fig. 1(a), inset). The emission intensity is decreased upon increasing the temperature to 45 °C, whereas above 45 °C, the emission intensity is enhanced (Fig. 1(b) and (d)). Interestingly, in the case of the self-assembly of **1** alone, the fluorescence of the molecule did not vary much under similar experimental conditions. This is clear from the plots of the fluorescence intensities of **1** in the absence and presence of **dCA** at different temperatures (Fig. 1(c) and (d)).

Hierarchical self-assembly of compound **1** under higher concentrations resulted in blue emitting gels in aliphatic solvents such as hexane and methylcyclohexane. The critical gelator concentration (CGC) in methylcyclohexane is 3 mM. The gel is turbid which indicates the tendency of the aggregates to precipitate or to form aggregates of large size which may scatter light (Fig. 2(a)). In this case, the gel melting temperature (T_{gel}) at the CGC is found to be 38 °C which gradually increased with concentration. Remarkably, in the case of the 1 : 1 complex **1·dCA**, a transparent gel is formed in aliphatic solvents (Fig. 2(a)). The CGC of **1·dCA** in methylcyclohexane is 2 mM. In this case the T_{gel} is found to be 42 °C which is 4 °C higher than that of **1** alone indicating that the **1·dCA** gel is stabilized by the complementary H-bonding interaction with cyanurates. A comparison of the plots of T_{gel} against



Scheme 1 The self-assembly pathways of **1** and **1·dCA**.

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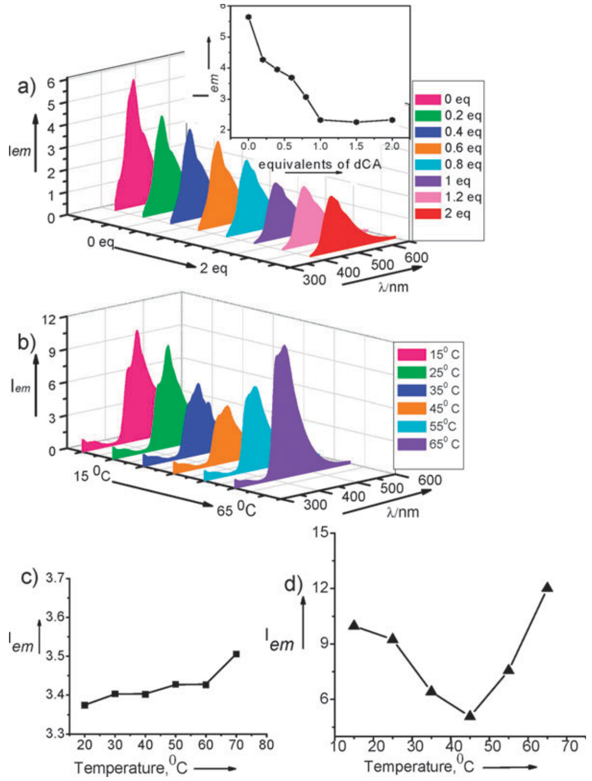

Fig. 1 (a) Change in the fluorescence intensity of **1** ($c = 1 \times 10^{-5}$ M) with different aliquots of **dCA** ($c = 1 \times 10^{-5}$ M) and (b) variable-temperature emission spectra of the 1 : 1 complex **1·dCA** at 1×10^{-5} M; (c) and (d) are temperature-dependent plots of the fluorescence intensity changes of **1** and for 1 : 1 complex **1·dCA**, respectively.

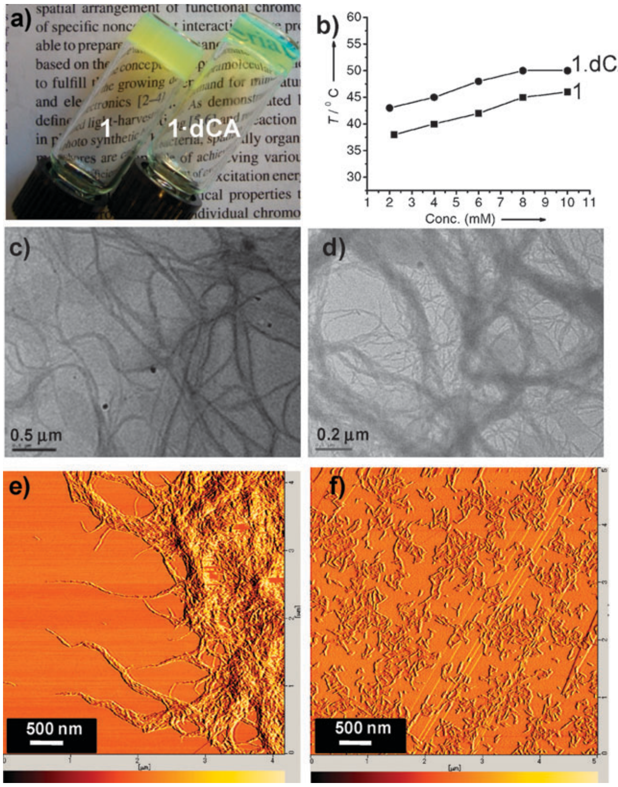

Fig. 2 (a) Photographs of the gels in methylcyclohexane in the absence and presence of **dCA**. (b) Gel melting temperature of **1** and **1·dCA** at different concentrations; (c) and (d) TEM images of **1** in the absence and presence of **dCA**, respectively; (e) and (f) AFM images of **1** in the absence and presence of **dCA**, respectively.

concentration is shown in Fig. 2(b). The enhanced stability of the gels is rationalized by the synergistic effect of the complimentary H-bonding with cyanurates as well as the π-stacking of the TPE moieties.

Transmission electron microscopy (TEM) images of a drop casted dilute solution of **1** showed fibrous networks. The average width of fibers is *ca.* 100 nm (Fig. 2(c)). These fibers must have originated from the bundling of the one-dimensional polymeric chains of **1** arising from amide–amide hydrogen-bonding and π stacking. This observation is further confirmed by atomic force microscopic (AFM) measurements of the diluted gels in methylcyclohexane showing bundles of fibers (Fig. 2(e)). The size of the smallest fiber is approximately around 40 ± 5 nm. On the other hand, TEM images of a dilute solution of **1·dCA** showed thinner fibers of 20 ± 5 nm (Fig. 2(d)) in width which are more compatible with the solvent. In presence of solvent in the gel state, these thin fibers may be uniformly dispersed. As a result, the gel is optically transparent, which is in sharp contrast to the gel of **1** alone. When drop-casted on a TEM grid, these thin and short fibers may entangle and agglomerate as can be seen in the TEM images. AFM images in this case convincingly showed the formation of very short fibers with a length of *ca.* 200–250 nm and width of *ca.* 50 ± 5 nm (Fig. 2(f)).

FT-IR measurements of the gels confirm the contribution of the amide groups to the formation of the fibrous structures. A gel of **1** in methylcylohexane (3 mM) exhibited IR bands corresponding to the carbonyl and the N–H stretchings of the free amide groups at 1633 and 3288 cm^{-1}, respectively (see ESI†). In the case of the **1·dCA** gel, the former band is shifted to 1712 cm^{-1} and the latter band completely disappeared from the original position (see ESI†). It can be assumed that the latter band is embedded in a broad band at around 3310 cm^{-1} involving the NH stretching of CA.

The observed changes in the fluorescence emission, gelation properties and morphological differences of **1** in the absence and presence of **dCA** could be explained in analogy to a previous study on the self-assembly of perylene bisimide.[6g] In the case of **1·dCA**, the formation of a 2 : 2 dimer is invoked during the initial stage of the self-assembly (Fig. 3). In this dimer, the molecule **1** is strongly bonded in an H-type fashion through twelve H-bonds. These dimers may further self-assemble to form hierarchical structures in a J-type fashion through amide H-bonding. The variable-temperature fluorescence changes thus could be explained by the selective breakage of the inter-aggregate J-type amide–amide hydrogen bonds upon increasing temperature up to 45 °C, thereby forming the H-type dimer with more favourable π-overlap, which reduces the fluorescence intensity. The H-dimers subsequently dissociate into individual components upon a further increase of temperature (45–90 °C), resulting in a strong fluorescence from molecularly dissolved TPE chromophores. In the case of **1** alone, initially, a linear supramolecular polymeric assembly could be favored through amide–amide

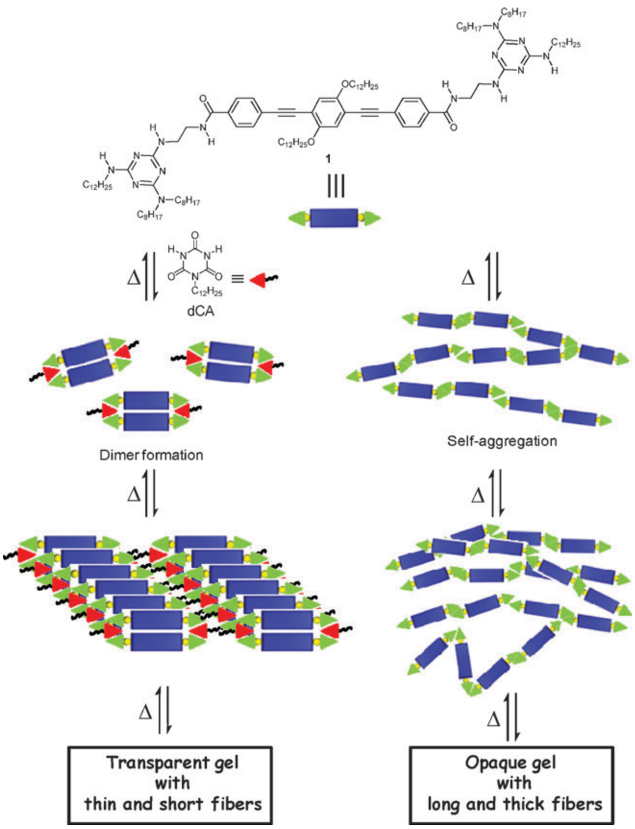

Fig. 3 Cartoon representations of the different self-assembly processes of **1** in the absence and presence of **dCA**.

H-bonding. In such a situation, interchromophore interaction is minimised, as indicated by the variable-temperature fluorescence studies which did not show any considerable variation (see ESI†). Under higher concentration, these noncovalent polymer chains may undergo further aggregation leading to the gelation of the solvents.

In conclusion, we have demonstrated the role of a cyanurate in the self-assembly of a melamine-linked TPE thereby modifying the physical properties and morphological features of the resultant supramolecular gels. The fluorescence changes of the TPE moiety and the difference in the morphology and physical properties of the gels indicate that the molecule **1** self-assembles to form 1D supramolecular polymers in the absence of dCA, whereas in the presence of **dCA**, H-type dimers are formed during the initial stages of the self-assembly. This strategy can be applied to other functional chromophores to diversify their self-assembly pattern, morphologies, and optical and electronic properties.

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