# Spectroscopic, microscopic and first rheological investigations in charge-transfer interaction induced organogels<sup>†</sup>

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This article describes two-component charge-transfer interaction mediated organogels (CT-gels) derived from anthracene carboxamides obtained from 2-amino-2-hydroxymethyl-1.3-propanediol (TRIS), and 2,3-dialkoxyanthracenes as donors, with 2,4,7-trinitrofluorenone (TNF) as the common acceptor. We demonstrate the versatility of TNF as an electron acceptor in the formation of these gels. The effect of subtle changes in the donor structure on the gelation ability has been investigated by varying the alkyl chain length in the dialkoxyanthracene donors, and by varying the position of the TRIS substituent in the anthracene carboxamide donors. Distinct differences have been observed in the nature of the CT-gels based on these two kinds of anthracene donors. It has been reported in the literature that 2,3-dialkoxyanthracenes form gels on their own in various aliphatic hydrocarbons and alcohols for linear alkyl chains bearing at least 6 carbon atoms ( $C_6$ ). In the present study, it is shown that the CT-complex of these molecules with TNF is able to gel many alcoholic and a few hydrocarbon solvents. Also, in the presence of TNF, the 2,3-dialkoxyanthracenes ( $C_4$ – $C_5$ ) which were non-gelators on their own at ambient temperatures, form CT-gels in a number of alcohols. The other series of gelators discussed, the anthracene carboxamides, require the mandatory presence of TNF to form gels. This donor-acceptor complex forms gels in various aliphatic alcohols. Interestingly, the formation of these CT-gels requires rapid cooling in most of the cases. Thermal stability studies with both types of CT-gels indicate an optimum stoichiometry of 1 : 1 between the donor and the acceptor. Dynamic rheological experiments reveal these gels as viscoelastic soft materials, with the mechanical strength of these gels depending on the amount of TNF present. This provides a means to tune the strength of the gel by varying the doping concentration of the acceptor.

# Introduction

Low molecular mass organic compound based gels (LMOG) have attracted much interest in recent years<sup>1</sup> for their immense potential in the design of novel nanomaterials, which may find use in optoelectronics,<sup>2</sup> in sensing applications,<sup>3</sup> as templates for nanoparticles<sup>4</sup> and various inorganic nanostructures.<sup>5</sup> A small amount of the gelator (typically <1 wt%) dissolved in an organic solvent self-assembles through non-covalent interactions such as van der Waals, H-bonding,  $\pi$ - $\pi$  stacking, donor-acceptor interactions *etc.* to form an entangled fibrous network, trapping and immobilizing the bulk solvent (>99%). These supramolecular gels have advantages over (covalent) polymeric gels since the interactions involved are reversible, and hence the gel can be reversibly broken and re-formed, usually by temperature control.

Of particular interest are two-component gels<sup>6</sup> where the two molecular units form a complex through self-complementary interactions, which further self-assemble hierarchically to form the gel nanostructure.

The presence of two components in the gel provides scope for structural tuning of the gel by altering the functionalities in the individual components, thereby controlling the interactions in the complex, and eventually modulating the gel strength, stability and other properties. One of the first reports by Hanabusa et al. utilized intermolecular hydrogen bonding interactions between barbituric acid and pyrimidine to obtain two-component organogels.7 Shinkai and co-workers reported that the optical, thermal properties and the morphology of the benzene gel of a thymidinebased organogelator could be modulated in the presence of its complementary polynucleotide in the gel medium through A-T hydrogen bonding interactions.8 In 2001, Smith et al. reported a dendritic two-component organogel with carboxylic acid-containing dendritic peptides and alkyl diamines.9 An interesting example of a two-component organogelation has been reported by Weiss and co-workers. They showed that bubbling CO<sub>2</sub> through a solution of primary and secondary aliphatic amines in organic solvents led to reversible gelation due to the formation of ammonium carbamates.10

Donor-acceptor interaction mediated formation of gels constitute a special class of two-component gels where a complex is formed through partial charge transfer between the two components – a relatively electron rich molecule (donor) and an electron deficient molecule (acceptor). The gel formation is

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driven by this charge transfer interaction, and the complex generally absorbs in the visible region (in a relatively non-polar solvent), leading to the intensification of the color upon forming the gel. Such donor-acceptor promoted organogelation may stabilize the organization of the functionalities of its molecular components which otherwise may not individually be able to form stable supramolecular assemblies.<sup>11,12</sup> The CT-interaction may often lead to stronger gels relative to the gels derived from one of the components and modulate the optical properties of the resultant self-assembly.<sup>13</sup> This has the potential to expand the scope of the applications of these CT-gels as functional materials in fields as diverse as thermochromics and optoelectronics. Besides, the donor-acceptor charge transfer interaction is a demonstration of specific molecular recognition, which may enable these gels to act as sensors.14 The first example of donoracceptor interaction promoted organogelation was reported by us,11,12 in which a variety of pyrene derivatives were found to form strongly colored gels in organic solvents in the presence of an equivalent amount of 2,4,7-trinitrofluorenone (TNF). Since our initial work, there have been quite a few other reports on donor-acceptor interaction promoted gel formation in organic solvents.13

The electron acceptor, TNF (Chart 3), used in our earlier studies, is known in the literature to form strong charge transfer complexes with three, four and five membered aromatic rings.<sup>15</sup> In the present work, we demonstrate that the charge transfer interaction of TNF with anthracenes can be utilized to access a variety of anthracene-based organogelators, which can gel a range of organic solvents. We discuss here two distinct classes of charge transfer organogels derived from (a) anthracene TRIScarboxamides (3-5, Chart 1), and (b) a series of 2,3-dialkoxyanthracenes (7-11, Chart 2) in the presence of TNF as the common acceptor. We had earlier reported the use of 2-amino-2hydroxymethyl-1,3-propanediol (TRIS) group for modulating the solubility profiles of bile acid derivatives,16 which were potent hydrogelators. Extending the concept to organogelators, the design of the first series of gelators involved attaching TRIS with anthracene through an amide linkage. The amide functionality is known to participate in directional H-bonding, and the hydroxyls of TRIS are expected to improve the solubility of these molecules in protic solvents. The second series, 2,3-dialkoxyanthracenes,<sup>17</sup> has already been reported as non-hydrogen bonding gelators of a variety of aliphatic hydrocarbons and alcohols on their own.

Interestingly, the present study revealed that the gelation properties of these molecules can be significantly modulated, and in some cases enhanced, in the presence of TNF.

# Experimental

#### Materials

All starting materials were of commercial grade and purchased from Aldrich or Fluka, and were used without further purification.

#### Characterization and instrumentation

NMR spectra were recorded on a 300 MHz (JEOL Lambda-300) and 400 MHz (Bruker) in DMSO-d<sub>6</sub> and CDCl<sub>3</sub>. Absorption spectra were recorded on Shimadzu UV 2100 and Perkin-Elmer

Lambda 35 spectrophotometers. IR and fluorescence spectra were recorded on JASCO-70 FT-IR and Perkin Elmer LS-50 B spectrophotometers, respectively. Dynamic rheological measurements were done on the gels on an AR 1000 rheometer (TA instruments) using a plate-plate geometry. HRMS was recorded on Micromass O-TOF. Microanalyses were done on a Carlo Erba Strumentazione CHNS Analyser-model 1106 and Flash EA 1112. Transmission electron micrographs of the xerogels were obtained using a TECNAI T-20 electron microscope operating at 160 kV. Scanning electron micrographs were recorded on a FEI-Quanta 200 electron microscope. Melting points were recorded on a Buchi Melting Point B-540 apparatus. The confocal fluorescence microscopy (CFM) measurements were performed on a Picoquant Microtime 200 using SPAD detectors (MPD) and a Ti-Sa laser chain from Coherent.

The synthesis, characterization and the details of the experiments are given in the electronic supplementary information (ESI).<sup>†</sup>

#### **Gelation properties**

#### The tris-substituted derivatives (1-6)

Among the tris derivatives with 2–4 benzene rings, the naphthalene derivatives 1 and 2 did not form CT complexes with TNF, and they did not gel any of the solvents tested (data not shown). The pyrene derivative 6 formed a red CT complex with TNF in aliphatic alcohols, but no gelation was observed. Only compounds 3–5 were found to be gelators.

Common to all these gelators was the observation that none of them was able to form gels *in the absence of* TNF. All the three anthracene derivatives formed charge-transfer gels in aliphatic alcohols in the presence of varying amounts of TNF, typically at concentrations below 1 wt%. Depending on the position of the TRIS carboxamide on the anthracene backbone, distinct differences in the gelation behavior of the compounds **3–5** were observed. While compound **3** formed gels in aliphatic alcohols ranging from 1-octanol to 1-dodecanol both by 'normal cooling' (the hot sols were allowed to cool under ambient conditions) and 'rapid cooling' (hot sol at 120 °C was dipped in an ice-water bath for 1-octanol gels; for 1-decanol and 1-undecanol gels, the hot sol was dipped in a water bath maintained at 15 °C; for 1-dodecanol gels, a water bath maintained at ~25 °C was used), compound **4** 

**Table 1** Results of the gelation studies (rapid cooling) with compounds **3**, **4** and **5** in the presence (1 : 1 mole ratio) and absence of **TNF** in aliphatic alcohols, toluene and n-dodecane<sup>a</sup>

Solvent	3	3/TNF	4	4/TNF	5	5/TNF
methanol	s	Р	Р	Р	Р	Р
1-propanol	S	Р	Р	G	Р	Р
1-butanol	S	Р	Р	G	Р	Р
1-pentanol	S	Р	Р	G	Р	Р
1-octanol	Р	G	Р	G	Р	G
1-decanol	Р	G	Р	Р	Р	G
1-undecanol	Р	G	Р	Р	Р	G
1-dodecanol	Р	G	Р	Р	Р	Р
toluene	Р	Р	Р	Р	Ι	Ι
n-dodecane	Ι	Ι	Р	Ι	Ι	Ι

<sup>a</sup> G: gel, P: precipitate, I: insoluble.

formed gels in alcohols (1-propanol to 1-octanol) only through rapid cooling. Both the gels were deep red in color, showing the CT band at ~530 nm in the absorption spectra (*vide infra*). However, the CT-gels derived from compound **5** (also formed only through rapid cooling) were deep brown in color. These gels showed CT band at ~570 nm in the absorption spectra (*vide infra*). Unlike the CT-gels from **3**, which broke down over a period of 2–10 h, the CT-gels from **4** and **5** were stable for months, although they become translucent over time. All these charge transfer gels can form at quite low concentrations of the donor molecule, *e.g.*, the critical gelation concentration for compound **4** to form CT gel in 1-octanol was ~0.16 wt %. The results of the gelation experiments are summarized in Table 1.

#### 2,3-Di-n-alkoxyanthracenes (7-11)

2,3-Di-n-alkoxyanthracene derivatives (having 6-16 carbons on the alkoxy chains) were reported to be good gelators of a variety of organic solvents (alkanes, alcohols, amines and nitriles).<sup>18</sup> The derivatives with 10-12 carbon chains were found to be the most efficient. But with decreasing chain length, the gelation ability became weaker. This interesting chain length dependent gelation ability of these derivatives made us investigate the modulation of their gelation properties by TNF. We started with the didecyloxy derivative 7 (DDOA) which is the most efficient and most explored gelator in the series. When DDOA was heated in the presence of TNF (1:1 mole ratio) in alcoholic solvents (except MeOH), the hot sols initially assumed a light brown color and on keeping at room temperature, they formed dark brown gels. The intensification of the color suggested that DDOA was able to form a charge transfer complex with TNF which participates in the gelation process. This behavior was observed in a variety of alcohols ranging from ethanol to 1-decanol, and in alkanes such as n-hexane and n-dodecane. A few interesting points emerged from these studies. Firstly, the gels of DDOA in branched alcohols (isopropanol, 2-butanol) have been reported to be weaker than in their linear analogues,17 but the CT-gels were stronger in these branched alcohols. Secondly, in MeOH where DDOA forms gels most efficiently (its critical gelation concentration is 0.6 mM in MeOH), the brown coloration did not appear. A yellowish gel was obtained at a much higher concentration (probably DDOA formed a gel of its own and TNF was just dispersed within the gel network). These results suggested a modulation of the gelation property of DDOA by TNF and

**Table 2** Results of the gelation studies with compounds **7**, **8**, **9** and **10** in the presence (1:1) of **TNF** in aliphatic alcohols and n-dodecane<sup>*a*</sup>

Solvent	7/TNF	8/TNF	9/TNF	10/TNF
1-propanol	G	G	G	
isopropanol	Ğ	Ğ	Ğ	Р
1-butanol	Ğ	Ğ	Ğ	
2-butanol	G	G	G	
t-butanol	G	G	G	Р
1-pentanol	G	G	G	Р
1-octanol	G	G	G	Р
1-decanol	G	G	G	
n-dodecane	G	G	G	Р
<sup><i>a</i></sup> G: gel, P: prec	cipitate, I: insol	uble.		

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this prompted us to investigate the behavior of the smaller chain derivatives in the presence of TNF. 2,3-Di-n-(heptyloxy)anthracene (8) is a much weaker gelator than DDOA and with chains shorter than  $C_6$ , they become non-gelators at ambient temperatures. However, in the presence of TNF, the *weaker gelator* 2,3-diheptyloxy (8) and the *non-gelator* 2,3-dibutyloxyanthracenes (9) were found to transform into efficient gelators of alcohols and hydrocarbons. Subsequent studies revealed that the alkoxy derivatives with  $C_1$ - $C_3$  did not show any gelation even in the presence of TNF. The results are summarized in Table 2.

Interestingly, this charge transfer interaction driven gelation phenomenon was observed only with 2,3-dialkoxy anthracene derivatives. Several other alkoxy derivatives of anthracene<sup>19</sup> shown in Chart 4, 9-n-decyloxy (12), 1,2-di-n-decyloxy (13), 1,5di-n-decyloxy (14) and 9,10-di-n-decyloxy (15), did not form gels in the presence of TNF. Even the derivatives with 2,3-methylenedioxy (16) and 2,3-ethylenedioxy (17) substituents also did not form gels in any of the organic solvent tested. In all these cases the charge transfer complexes either precipitated out or remained in solution.

Therefore, for the charge transfer interaction promoted gelation, the following structural aspects in the anthracene moiety are important: (1) the *n*-alkoxy substituents must be in the 2 and







Chart 3



3 positions, and (2) *n*-alkoxy substituents with alkyl chains >  $C_3$  are required.

### Thermal stability of gels

The thermal stability of the gels was determined by inverted test tube method. Sealed tubes containing gels were kept upside down in a thermostated water bath and the temperature of the water bath was raised slowly ( $\sim 2 \ ^{\circ}C \ min^{-1}$ ) until the gel fell under gravity.

#### Optimum stoichiometry of the donor and the acceptor

As we have observed previously in the case of the pyrene derived CT gels,<sup>12</sup> the maximum thermal stability was obtained when the components were present in a 1 : 1 mole ratio. To determine the optimum stoichiometry for these anthracene derived CT gels,  $T_{gel}$  was determined by varying the concentration of TNF at a constant concentration of the donor. The thermal stability reached a maximum at ~1 : 1 mole ratio of the donor and acceptor. At higher acceptor to donor ratios, the gel melting point again started to decrease (the extent depends on the specific gelling systems). It is possible that the excess TNF (acceptor) precipitates out in the gel matrix, compromising the strength of the gels. The general conclusion drawn from these experiments is



**Fig. 1** Variation of the gel melting temperature of (a) 1-octanol gel of 5/ **TNF** (maintaining a fixed concentration of 15.4 mM of 5) and (b) 2-BuOH gel of 7/**TNF** (maintaining a fixed concentration of 5.1 mM of 7).

that for both these two classes of anthracene derivatives, the optimum stoichiometry is 1 : 1 (Fig. 1).

After determining the optimum stoichiometry for these CT gels, the thermal stability profile of the CT gels in different solvents and the variation of the  $T_{gel}$  against concentration in a particular solvent (in which the thermal stability is highest) for each derivative were evaluated maintaining a 1 : 1 mole ratio of the two components.

# CT-gels derived from 3-5

All the gels showed high thermal stability in aliphatic alcohols, with  $T_{gel}$  above 60 °C (Fig. 2). For **3** and **4**, the thermal stability of the CT gels was generally higher with increasing the chain length of the alcohol. For example, for the gels of **4/TNF**,  $T_{gel}$  followed the order 1-octanol > 1-pentanol ~ 1-propanol. The **3/TNF** gels showed similar trend 1-dodecanol ~ 1-decanol > 1-octanol. However this trend is reversed for **5/TNF** gels: 1-undecanol ~ 1-decanol < 1-octanol. A plot of  $T_{gel}$  as a function of the CT gelator concentration (donor and acceptor present in 1 : 1 mole ratio) for all the three systems showed a linear increase in thermal stability with concentration (Fig. 3), which is a general observation for many of the gels derived from the self-assembly of small-size organic molecules.<sup>20</sup> It is observed that **4/TNF** gels in 1-octanol have higher gel melting temperature compared to



Fig. 2 Bar diagram showing the gel melting temperatures of the charge transfer gels of 3/TNF (black), 4/TNF (blue) and 5/TNF (red) in different aliphatic alcohols. The concentration of each component in the gel was 15.4 mM (for 3 and 4) and 14.7 mM (for 5).



**Fig. 3** Variation of  $T_{gel}$  with the gelator concentration for the 1-decanol gels of **3/TNF** (1 : 1) (blue triangle), 1-octanol gels of **4/TNF** (1 : 1) (black square) and **5/TNF** (1 : 1) (red circle). The linear fits to the corresponding data points are also shown.

**5/TNF** gels. The data for **3/TNF** correspond to the gels in 1-decanol, because this CT complex forms stronger gel in 1-decanol than in 1-octanol.

### CT-gels from 7-9

As mentioned previously, DDOA has been reported to form stronger gels in linear alcohols.<sup>17</sup> But the CT-gels obtained in branched alcohols, especially in isopropanol, were found to be stronger. The same trend was observed for the diheptyloxy (8) and dibutyloxy (9) derivatives. In terms of the thermal stability, the charge transfer gels formed from these three anthracene derivatives (didecyloxy, diheptyloxy and dibutyloxy) did not show significant differences, except in 2-butanol (Fig. 4).

The doping of these CT gels with the non-gelator alkoxy derivatives of anthracene (maintaining the net concentration of the donor as constant) led to some interesting observations. When 2,3-di-alkoxy derivatives (dimethoxy 11 and dipropyloxy 10, both non-gelators) were incorporated replacing 50% of the gelator derivative 7, the thermal stability of the resulting gels did not vary significantly whereas the incorporation of structurally dissimilar dialkoxy derivatives (14 and 15) led to a decrease in the thermal stability as shown in Table 3. These results suggest strong structural recognition at a molecular level in the formation of the supramolecular aggregates and the replacement of the gelling agent by 14 or 15 within the supramolecular organization.

# Variable temperature absorption spectral study of CT gels

The gelation process in these two-component gels is driven by the charge transfer interaction, as indicated by the intensification of



Fig. 4 Bar diagram showing the gel melting temperatures of the charge transfer gels of 7/TNF (black), 8/TNF (red) and 9/TNF (blue) in different aliphatic alcohols. The concentration of each component was 10 mM for all the gels.

**Table 3** Comparison of  $T_{gel}$  of the CT gels (with TNF) of DDOA andDDOA/non-gelator dialkoxy anthracene derivatives

Anthracene derivatives (conc in mM)	TNF/mM	Tg/°C	
7 (10)	10	65	
7(5) + 11(5)	10	68	
7(5) + 10(5)	10	64	
7(5) + 14(5)	10	57	
7 (5) + 15 (5)	10	54	

the color when the gels form from the pale yellow/light brown sols. All these gels showed intense charge transfer bands in the visible region, which were absent in the sol. The **3/TNF** and **4/TNF** gels (deep red, Fig. 6) show the CT band at  $\sim$ 530 nm, whereas the CT band appeared at  $\sim$ 570 nm for the **5/TNF** gels (deep brown). The gels of the charge transfer complexes based on 2,3-dialkoxyanthracene donors were dark brown (Fig. 6) in color, similar to the **5/TNF** gels. However, they showed two characteristic maxima (473 nm and 583 nm) in the absorption spectra (Fig. 5a). The change in the intensity of these two bands with temperature was monitored in variable temperature experiments (Fig. 5b).

As seen from Fig. 5b, the intensity of both the bands decreased gradually with an increase in the temperature and a similar pattern was observed for didecyloxy 7 and dibutyloxy 9. This dual spectrum might correspond to the occurrence of two different CT complexes (of distinct geometry or stoichiometry); further investigations beyond the scope of this study will be necessary for understanding this. In any case, these observations confirm the importance of the charge transfer interaction in the self-assembly process.

#### Variable temperature fluorescence studies

These charge transfer gels in general showed a significant quenching of the anthracene emission in the gel state, compared to the sol state, because of the strong charge transfer interaction with TNF in the gel (Fig. 7a). As seen in absorption, the lowestlying excited state is indeed a charge transfer state, which is wellknown to be weakly or non-emissive. When the fluorescence intensity was monitored in variable temperature experiments, the initial increase of the donor emission was gradual with increasing



**Fig. 5** (a) Charge transfer band for **7/TNF** (1 : 1 mole ratio) gel in i-PrOH (8.2 mM). (b) Temperature dependence of **8/TNF** CT-band (1 : 1 mole ratio) gel (0.33%, 8.2 mM) in i-PrOH.



**Fig. 6** 1-Octanol gel of **4/TNF** (1 : 1), 8 mM in both donor (**4**) and the acceptor (**TNF**) (left) and i-PrOH gel of **7/TNF** (1 : 1), 8 mM in both donor (**7**) and acceptor (**TNF**) (right).



**Fig. 7** (a) Emission spectra of **9/TNF** (1 : 1) in gel (25 °C) and in sol (65 °C) in i-PrOH (6.8 mM,  $\lambda_{ex} = 345$  nm). (b) Comparison of variable temperature emission spectra of **7/TNF** and **8/TNF** gels in i-PrOH ( $\lambda_{ex} = 345$  nm).

temperature. But when the temperature approached the melting point of the system, the increase was more significant, though the extent of increment varied from one system to another as illustrated in Fig. 7b. This provides a tool for probing the gel to sol transition as a function of temperature.

# Microstructures of the CT gels

## Electron microscopy

The morphology of the xerogels of these charge transfer systems was investigated by electron microscopy. An interconnected fibrous network of the gel aggregates was observed (Fig. 8a) for the charge transfer gels of **4/TNF**. Gels of **8/TNF** and **9/TNF** in solvents such as isopropanol and 1-pentanol also showed entangled fibrous structure (Fig. 8b). However, in case of **7/TNF** only broken fibers could be observed (Fig. 8c). TEM investigation of the xerogel obtained from i-PrOH gel of **8/TNF** (1 : 1) showed that the average diameter of the fibers was in the range of 50–80 nm (Fig. 8d).



**Fig. 8** SEM images of the charge transfer gels of (a) **4/TNF** in 1-butanol, (b) **9/TNF** in 1-pentanol and (c) **7/TNF** in i-PrOH. (d) TEM image for a xerogel of **8/TNF** (1 : 1) in i-PrOH.

#### Confocal fluorescence microscopy

Confocal fluorescence microscopy (CFM) images were taken for both 7 and 7/TNF gels in isopropanol. This technique is nondestructive, allows imaging of the solvated fibers and had already been used for the study of 7 in the presence of traces of trinitrobenzene.<sup>21</sup> As shown by fluorescence spectroscopy, the emission of the 7/TNF gels is weaker as compared to 7. CFM allows within an area of the gel (e.g.  $20 \times 20 \mu m$ ) to determine whether emission intensities are fluctuating. The image (Fig. 9a) shows that the fluorescence stems exclusively from the fibers, and the local variations of intensity are attributed to changes in the fiber sizes (besides, some darker fibers are out of focus). Fig. 9b and 9c, obtained in the 7/TNF gels with more intense laser excitation, show comparable intensity fluctuations within the fibers as in 7. Since no particularly bright fibers are observed, this indicates that TNF is dispersed in all the fibers that have been imaged and quenches their fluorescence. Moreover, comparable fiber network morphologies were observed for 7 and 7/TNF at both 1:0.5 and 1:1 stoichiometries. The solvated fiber network is well preserved and the widths of the fibers are similar in the presence or absence of TNF (limited by optical diffraction, *i.e.*  $\leq$  230 nm). Larger fibers or bundles seen by electron microscopy could not be observed by this technique, as they might be too weakly emissive or not present in solvated organogels.

# **Rheology of CT gels**

The CT gels derived from the two different classes of anthracene derivatives were characterized by dynamic rheology. Gels are viscoelastic materials and so they can both store and dissipate energy (characterized by storage modulus G' and loss modulus G'' respectively). The three important parameters obtained from dynamic rheology are elasticity (G'), fragility ( $\sigma^*$ ) and stiffness



**Fig. 9** Fluorescence confocal microscope intensity images  $(20 \times 20 \,\mu\text{m})$  of 8 mM organogels in i-PrOH (a) 7, (b) 7/TNF 1 : 0.5, (c) 7/TNF 1 : 1. The widths of the solvated fibres is typically  $\leq 230 \,\text{nm}$  (optical diffraction limit) in a, b and c.  $\lambda_{\text{ex}}$  385 nm,  $\lambda_{\text{em}} > 405 \,\text{nm}$ .

(G'/G''). All the rheology experiments were performed in 1-octanol or 1-decanol to minimize solvent evaporation during the experiments.

#### Dynamic frequency sweep experiments

Dynamic frequency sweep experiments at a small value of applied stress were performed for all the CT gels and they showed a consistently higher value for the storage modulus (G') over the loss modulus (G''), which is typical for viscoelastic soft solids (Fig. 10). The ratio of (G'/G'') is ~18–24 for CT gels of **3**, **4** and **5** and 9–14 for the CT gels of **7**, **8** and **9** (Table 4). It suggests that the dissipation of energy is more for the CT gels of 2,3-dia-lkoxyanthracenes *via* viscous mechanisms.

When we compare the CT gels of 7, 8 and 9 in 1-octanol, no particular trend was observed on going from didecyloxy (7) to dibutyloxy (9) derivative (Table 4). For example, 7/TNF gel showed the lowest value of elasticity (G') whereas 8/TNF and 9/ TNF exhibited similar values. In terms of stiffness of the gel, 9/ TNF shows the lowest value but comparable values were observed for 7/TNF and 8/TNF.

The 1-octanol gel of **4/TNF** (1:1) showed higher G' values (Table 4) compared to the **5/TNF** gel in the frequency sweep experiment, indicating higher elasticity, which also correlates well with their thermal stability (*vide supra*). However, although the 1-octanol gel of **3/TNF** (1:1) showed a significantly lower melting temperature (64 °C), a higher value of G' (8336 Pa) indicated higher mechanical strength.



**Fig. 10** Dynamic frequency sweep experiment (0.01 Hz to 10.0 Hz @ constant stress of 1.0 Pa) for **7/TNF** (1 : 1) gel in 1-octanol (open circles for G' and closed circles for G'').

**Table 4** Dynamic rheology of CT gels. The G' and G'' values shown in the table are obtained from frequency sweep experiments performed at a fixed stress of 1.0 Pa for the CT gels (1 : 1) of 7, 8 and 9 (10 mM of donor) and 6.0 Pa for the CT gels for 3, 4 and 5 (15.4 mM for 3 and 4, and 14.7 mM for 5). The values are at f = 1.0 Hz. The  $\sigma^*$  values shown are obtained from stress sweep experiments at a fixed frequency of 1.0 Hz. (Error  $\pm$  10–15%)

System	G' (Pa)	G'' (Pa)	G'/G''	σ* (Pa)
3/TNF	8300	500	17	245
4/TNF	4300	180	24	150
5/TNF	2900	150	20	170
7/TNF	900	70	13	42
8/TNF	4000	275	14	295
9/TNF	4200	450	9	140

#### Stoichiometry dependent mechanical strength

We have discussed earlier that the thermal stability of these CT gels is dependent on the stoichiometry. A similar trend is expected in the mechanical strength of these CT gels, too. When the dynamic frequency sweep experiment was performed with 8/ TNF (1 : 0.5) gel in 1-octanol, the values of dynamic moduli (G', G'') obtained were one order in magnitude lower than those obtained from the 8/TNF gel (1 : 1) in 1-octanol. Similarly, the 4/TNF (1 : 0.5) gel in 1-octanol showed ~2.5 times reduced value of G' and the gel started to flow at considerably lower applied stress (Fig. S4, ESI†). So, a possible way of modulating the mechanical strength and the flow property of these CT gels is to vary the ratio of the donor and the acceptor.

#### Dynamic stress sweep experiments

When the CT gels were subjected to an ascending stress ramp, above a particular value of stress ( $\sigma^*$ , yield stress), the gels broke down and flow occurred. From these dynamic stress sweep experiments (performed at f = 1.0 Hz, the stress sweep for 9/TNF is shown in Fig. 11), it was found that 7/TNF gel was the most fragile among the CT gels of 7, 8 and 9. It started flowing at a relatively low stress of 42 Pa whereas the yield stress values for 8/TNF and 9/TNF (Table 4) and 7 (530 Pa) were significantly higher. G' and G'' of 7/TNF are also one order of magnitude lower than in 7 without TNF (1 wt% in 1-octanol).<sup>22</sup> A comparative study of the CT-gels of 3, 4 and 5 showed that the 3/TNF gel has the highest yield stress (245 Pa). The 1-octanol gels obtained from 4/TNF and 5/TNF showed comparable yield stress values (Table 4). However, both these gels are more fragile than the 3/TNF gel.

#### Variable temperature rheology

The gel-sol transition temperature can be estimated by using rheology. It is done by following the dynamic moduli as a function of temperature at a fixed frequency and at a low enough stress amplitude so that the perturbation caused to the system is minimum. When this experiment was performed for a gel of 8/ TNF (1 : 1, 10 mM of each component, Fig. 12), the values of the dynamic moduli initially decreased gradually and then at a point the decrease became sharper which can be considered as the gel-sol transition point. It was satisfying to note that the value of the transition temperature obtained from this experiment was close



**Fig. 11** Dynamic stress sweep experiment (@1.0 Hz) for **9/TNF** (1 : 1) gel in 1-octanol (open squares for G' and closed squares for G'').



Fig. 12 The dynamic moduli as function of temperature for 8/TNF (1 : 1) gel in 1-octanol (open circles for G' and closed circles for G'') at f = 1.0 Hz,  $\sigma = 0.5$  Pa and at a heating rate of 0.5 °C min<sup>-1</sup>.

to that obtained from the inverted test tube experiments (the values obtained from these experiments differed by only a few degrees).

# Discussion

The present study on anthracene based charge transfer gels illustrates the versatility of TNF as an acceptor molecule in the gelation process. The charge transfer interaction is the driving force for gelation, which is supported by the appearance of a strong CT absorption band in the visible region. For the anthracene carboxamide-based gelators 3-5, CT complex formation is a prerequisite for the gelation to occur. The naphthalene carboxamides fail to show any gelation because the formation of a CT complex with TNF is not favorable probably due to  $\pi$ -surface mismatch. However, the pyrene-based carboxamide 6, although it forms CT complex with TNF, fails to form gels. This indicates that CT complex formation may be an essential condition for this class of gelators, but it is not the sole determining factor. Moreover, most of the gels from anthracene carboxamides form only by rapid cooling. Slow cooling results in the precipitation of the CT complex. This observation suggests that kinetics plays an important role in the gelation, and these gels can be essentially regarded as metastable states. The position of the TRIS substituent on the anthracene skeleton has a profound effect on the stability of the gels. For example, the gels derived from 3/TNF were stable only for a few hours, whereas 4/TNF and 5/TNF gels were stable for weeks. Such effects of the substituent position on gel stability is a fairly common observation in many gels derived from low molecular mass species, both single component and two component gels.

2,3-Di-n-alkoxyanthracenes (C<sub>6</sub>–C<sub>16</sub>) can form gels on their own (in the absence of TNF), preferably in aliphatic alcohols rather than in hydrocarbons, while with shorter chains (C<sub>2</sub>–C<sub>5</sub>) no organogels are formed. However, compound **9** (C<sub>4</sub>) and C<sub>5</sub> were recently shown to form fibrillar nanoobjects as observed with the gelling components of the series, *i.e.*, C<sub>6</sub>–C<sub>12</sub>. This propensity to produce fibrillar aggregates was found to be connected to their specific molecular packing in triads in the crystalline phase. In contrast, the shortest chains, such as C<sub>2</sub> and C<sub>3</sub>, do not produce any fibrillar aggregates and crystallize in a herringbone structure.<sup>23</sup> Interestingly, our studies show that the incorporation of TNF significantly influences the gelling ability of some of these 2,3dialkoxyanthracenes. Thus, the three tested compounds **7**, **8** and **9** 

form comparable CT gels in aliphatic alcohols and in some aliphatic hydrocarbons in the presence of TNF. Even the nongelator 2.3-dibutyloxyanthracene (9) forms CT gels in aliphatic alcohols. The appearance of a CT-absorption band, the fluorescence quenching and the uniform emission intensity of the fibers shown by confocal fluorescence microscopy indicate that this enhanced gelation is linked to the homogeneous and tight association of TNF with the anthracene derivatives in the nanofibers. In contrast, even in the presence of TNF no gels are formed with  $C_3$ . This supports the hypothesis that the propensity of these derivatives to produce fibrils and gels is connected to their crystalline packing into triads. TNF seems thus to emphasize the predisposition of a molecule to gelate, perhaps without fundamentally altering the molecular packing. A more precise insight on the association of the gelator and TNF require nevertheless a more precise determination of the molecular structure. The thermal stability of the CT gels from the three derivatives 7, 8 and 9 were comparable, suggesting that the presence of TNF not only modulates their normal gelation efficiencies but at the same time also transforms them into gels of similar thermal strengths. The mechanical strengths of these CT-gels are also similar, although 7 is somewhat weakened with the addition of TNF. Though the derivatives having  $C_1$ - $C_3$  chains did not form gels (vide supra) even in the presence of TNF, incorporation of these derivatives into CT gels (replacing the same equivalent of a gelator derivative) did not significantly affect the thermal strengths. In contrast, the incorporation, or lack of incorporation of dialkoxy derivatives having the substitutents in other positions of the anthracene moiety decreases the thermal stability of the resultant gels. These observations suggest that structural similarity between gelating and non-gelating dialkoxy derivatives is required to preserve the original organization of the CT gels.

The general trend observed in these two classes of anthracene derivatives is that both the thermal stability and the mechanical strength of these CT gels are dependent on the stoichiometry of the donor and the acceptor. So, for these gels, a simple tuning of these properties is possible by varying the ratio of the donor and the acceptor.

# Conclusions

We have presented two different classes of anthracene based organogelators, anthracene carboxamides and 2,3-dialkoxyanthracenes, which showed efficient gelation in the presence of acceptor TNF. The two types of charge transfer gels showed distinct differences in their properties. Indeed, the anthracene carboxamides were able to form gels only in the presence of TNF. For the dialkoxy derivatives, the gelation property of the efficient organogelator could be modulated by the addition of TNF, while the weak and non-gelators could actually be transformed into efficient gelators in its presence. Several other dialkoxy derivatives having alkyl substituents not in the 2 and 3 positions did not show gelation in the presence of TNF. These two points illustrate the two major structural aspects necessary for these derivatives to form CT gels- the alkyl chain length and the position of the alkyl substituents. However, the anthracene monocarboxamide donors were able to form CT gels irrespective of the position of the TRIS substituent on the anthracene moiety. The thermal stability of all these gels was found to be maximum with a 1:1 stoichiometry of the donor and the acceptor. The common observation, the intensification of color on going from the sol to the gel phase, supports the crucial role of the charge transfer interaction behind the formation of these gels. The rheological characterization of the gels showed that they behave like viscoelastic soft solids, as has been observed for many other single component supramolecular gels. In summary, we have discussed a new class of charge transfer organogels based on anthracene carboxamides and also presented a detailed study on the modulation of the properties of 2,3-dia-lkoxyanthracene based gels on doping with TNF, the common electron acceptor. We believe that these studies will enable us and others to expand our understanding and the scope of research in the field of two component gels.

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