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Light Induced E-Z Isomerization in a Multi-responsive Organogel : Elucidation from ¹H NMR Spectroscopy

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A multiresponsive organogel of (E) -N'-(anthracene-10-ylmethylene)-3,4,5-tris(dodecyloxy) benzohydrazide (I) shows a decrease of fluorescence intensity, decrease of mechanical strength and change in gel morphology on irradiation with a wavelength of 365nm. This is attributed to the E-Z isomerization across the C=N bond of I as evidenced from ¹H NMR spectroscopy.

Last few years have witnessed an incredible boom in research for the development of functional soft materials engineered from molecular self assembly.¹ In this context low-molecular-weight organogelators (LMOGs) have attracted immense research interest as they posses ample applications in light harvesting,^{2,3} sensing, photovoltaics,⁵ functional material, etc.^{6,7} Organogels are fabricated by the self assembly of a LMOG constituting a three dimensional network structure by various non-covalent interactions like Hbonding, π -stacking, van der Waals forces and thus immobilizing a large amount of solvent molecules.8 One most amazing advantage of supramolecular organogels is their stimuli-responsiveness and apart from thermo-responsiveness they are also sensitive to photochemical,⁹ chemical¹⁰ and mechano-chemical stimuli.¹¹ Amongst all, light is the most significant stimulus as its wavelength, polarization directions and intensity can be easily controlled. Azobenzene is the most common photoresponsive moiety amongst all others and there are several reports on photosensitive properties of azobenzene containing organogelators.7,12-14 Very recently, the light driven isomerization of molecules having imine functional group has drawn great attention in solution state,¹⁵ however, yet there exists no report of photoisomerization of organogelators containing an imine (C=N) functional group in the semisolid gel state. Here we report the light driven behavior of such an organogel with a proof from ¹H NMR spectroscopy for the first time to our knowledge. We have synthesized and characterized a LMOG (E) -N'-(anthracene-10-ylmethylene)-3,4,5 tris(dodecyloxy) benzohydrazide (I) (Fig. 1a) encompassing an anthracene moiety attached to the 3,4,5-tris(dodecyloxy) benzohydrazide core (SI). The

LMOG has been elegantly designed so that it contains H-bonding, π -stacking, and van der Waals interacting motifs required for an organogelator. The I organogel is yellowish green colored, transparent, thermoreversible with a minimum gelation concentration of 0.05% (w/v) in methyl cyclohexane indicating it to be a supergelator and all the studies reported here are carried out using methyl cyclohexane. It is also highly fluorescent (Fig. 1b) which is also retained in the xerogel state (Fig. 1d) and exhibits mechanoresponsive behavior (Fig. 1e). The effect of prolonged UV-irradiation on the photophysical, mechanical and morphological



Fig. 1 (a) Structure of molecule I. (b) digital image of I gel under UV light. (c, d) digital image of I xerogel under normal and UV light respectively. (e) Schematic representation of mechanoresponsive and thermoreversible behavior of I in methyl cyclohexane.

properties of the I gel is studied and a detailed ¹H NMR investigation indicates that the changes in all these properties stem from E-Z type of isomerisation across C=N bond upon UV-irradiation. Thus the novelty of this work is that the newly synthesized molecule I is a supergelator for a large number of organic solvents (table S1) and the organogel produced in methyl cyclohexane is thermoresponsive, mechanoresponsive, fluorescent and undergoes E-Z type of isomerization across the C=N bond upon UV-irradiation altering the gel properties.

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Experimental details of synthesis and charaterization of I and its organogel, Table of gelation test, FTIR, WAXS, SEM, TEM, Fluorescence, Rheological data. See DOI: 10.1039/x0xx00000x

In the FTIR spectra (Fig. S1) the -NH stretching peak of secondary amide of I powder at 3184 cm⁻¹ has shifted to 3178 cm⁻¹ and the

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>C=O stretching peak of amide of I powder at 1644 cm⁻¹ has shifted to 1640 cm⁻¹ in the xerogel state indicating intermolecular hydrogen bonding between the >C=O group with –NH group. It is evident from WAXS patterns (Fig. S2) that pure I powder exhibits some small peaks characterizing very low crystallinity which are absent in I xerogel suggesting that gelation brings in completely amorphous structure. The WAXS patterns of the xerogel shows broad peaks at $2\theta = 10.9^{\circ}$, 13.8° and 21.8° corresponding to d values at 8.0, 6.4 and 4.07 Å, respectively and the last d value corresponds to the π - π



Fig. 2 SEM (a and b) and AFM (c and d) images of I before and after photoirradiation respectively.

stacking distance. It is evident from the FESEM (Fig. 2a), AFM (Fig. 2c) and TEM (Fig. S3) images that the I gel posses three dimensional fibrous network morphology. The average diameter of the fibers is 45 ± 8 nm and their length is of several micrometers and the fibrils are intertwined with each other (Fig. S4). DSC thermograms of the I gel at a concentration of 3% (w/v) (Fig. S5) exhibits a melting peak at 49° C and its broad nature indicates the polydispersed nature of the aggregates.¹⁶ On cooling the I gel shows an exothermic peak at 35° C indicating hysterisis in the melting and gelation temperatures surmising first order nature of the gelation process.¹⁷

Fig. S6 displays the rheological properties of the I gel (1.0 % (w/v))at 25 ^oC. Frequency sweep experiment of the I gel (Fig. S6a) reveals that G'>G'' and is independent of frequency in a wide frequency region indicating the gel nature of the sample. Stress sweep experiments (Fig. S6b) of the I gel indicates that the G' and G'' cross each other at an oscillator stress of 4 Pa indicating the breaking of the gel to a sol state. Our newly designed I organogel exhibit the unique property of thixotropy (Fig. 1e) and for a quantitative estimation of it we have performed time sweep experiments under both a low strain of 0.1 % and a high strain of 100 % (Fig. S6c). However it is noticeable that in the first, third and fifth steps the values of G' are almost the same which indicates that the I gel is completely recoverable after being destroyed by mechanical force. For a gel to be certified as thixotropic, presence of supramolecular interactions and driving forces for propagating in more than one dimension is indispensable. These criteria can be fulfilled by small molecular weight gelator with negligible crystallinity. $^{18}\ \mathrm{Both}\ \mathrm{the}\ \mathrm{I}$ powder and the I xerogel has prominent amorphous structure as evident from the XRD patterns (Fig. S2) which facilitate its thixotropic behavior. The long fibers produced by assembly of the I molecules are connected with each other at the junction points by the supramolecular interaction. On application of mechanical force these junction points become ruptured causing the transformation to the sol state. Due to the presence of a large number of different supramolecular interacting sites in the I molecule which also operates on the fibre surface as residual force causes quick regeneration of network junction reforming the gel.

Fig. 3a displays the UV-vis spectra of I solution (10^{-5} M) and gel (0.1 % w/v) in methyl cyclohexane. Two peaks at 367 and 387 nm in the absorption spectra of the I solution corresponds to the π - π^{*} and n- π^{*} transitions of I molecule. Both these peaks are red shifted to 371 and 389 nm, respectively, in the I gel. This type of red shift in the π -



Fig. 3 (a) UV-vis spectra of I solution (10⁻⁵ M) and gel (0.1 % w/v) in methyl cyclohexane. (b) Fluorescence spectra of I sol (0.025% w/v) and gel (0.1% w/v) for excitation at 370 nm.

 π transition peak indicates π stacking between the anthracene and benzene units during gelation which is also evident from the XRD patterns. Also the red shift in the absorption bands may indicate the formation of J type aggregates in the gel state where the molecular planes are stacked side by side.¹⁹ Fig. 3b shows the fluorescence spectra of I solution (0.025% w/v) and it's gel (0.1% w/v) for excitation at 370 nm. It is clearly evident from the figure that the fluorescence intensity of the gel is ~6 times higher than that of the solution. Also there is a 14 nm red shift of the emission peak in the gel state than that of the solution supporting the J type aggregate formation.²⁰ The I molecule is fluorescence active due to the presence of the anthracene moiety and in solution phase there is a possibility of dynamic free rotation of the anthracene rotor which causes the non-radiative annihilation of the excited state. Consequently, the solution state of the I molecule is less fluorescent, but in the gel state the molecules are closely packed by H bonding and π -stacking interactions causing restriction of intramolecular rotation decreasing the quenching of exitonic decay through the non-radiative paths and hence fluorescence intensity increases.²¹ Temperature dependent fluorescence spectra are used to support the above hypothesis (Fig. S7). The fluorescence intensity of the I gel decreases with increase in temperature and the peak position also gets blue shifted. With increasing temperature the inception of breaking of the self assembly occurs and above ~50° C the intensity decreases sharply due to the breaking of network structure.

Due to the presence of imine functionality in I there is a possibility of E-Z type of isomerization on UV- irradiation that may alter the physical properties of the gel which is studied by different spectroscopic techniques. The gels were irradiated with a wavelength of 365 nm and the physical properties of the gels were monitored with respect to irradiation time. UV-vis spectra of the I

gel at 0.2% (w/v) concentration (Fig. 4a) exhibits a decrease in the absorbance values with increase in photoirradiation time. To investigate the change in fluorescence property of the I gel with

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photoirradiation we have measured the fluorescence emission of the I gel (0.6 % w/v) for irradiation with 356nm at different time intervals (Fig. 4b). It is manifested from the figure that the fluorescence intensity of the I gel decreases sharply with increasing irradiation time with a concomitant blue shift of the emission maxima. These changes in absorbance and fluorescence intensities of the I gel upon photoirradiation may be explained as follows. I can exist in two isomeric forms: E and Z. The E form is more stable and normally the compound is a mixture of the two isomers with the E form dominating. With photoirradiation with a wavelength of 365 nm the compound transforms into the Z isomer (Scheme 1). In the Z isomer the intermolecular H bonding between the >C=O group and -NH group becomes prohibited due to steric interference of the anthracene moiety (Scheme 1). This disturbs the aggregation of the I molecules which in turn prevents the π stacking phenomenon. Hence the delocalization of the π electrons and consequently the change in dipole moment value decreases. ²² The



Fig. 4 (a) UV-vis spectra of I gel (0.2% w/v) with irradiation (at 365 nm) time. (b) Variation of Fluorescence spectra of I gel (0.6% w/v) upon irradiation at 365 nm at different time interval.

transition moment integral thus decreases causing the gradual lowering of the absorbance values with irradiation time. The decrease in fluorescence intensity and a blue shift of the emission maxima also occurs due to the disaggregation of the I molecules upon photoirradiation. We have also performed rheological experiments on the I gel (1% (w/v)) with increase in photoirradiation time to investigate the changes in the gel strength after photoirradiation. Frequency sweep experiments of the I gels at different time intervals after photoirradiation are carried out (Fig. S8) and the G' values are plotted against irradiation time (Fig. S9). The results clearly manifests that the G' value hence gel strength decreases with increasing photoirradiation time. Also it is important to note that on photoirradiation the thixotropic property of the gel is lost. Morphological studies are carried out on the I gel after 5 hours of irradiation to observe if there is any change in morphology of the I gel occurs with photoirradiation. It is evident from the SEM image (Fig. 2b) that the fibers of the I gel are disintegrating causing lesser density of fibres and forming tiny spherical aggregates coming from breaking of the fibres. The AFM result shown in Fig. 2d and Fig.S10 is very interesting showing how the fibres are disintegrating into tiny particles on irradiation. The reason for this breaking of the fibrillar morphology of the gel is responsible for the lower gel strength and lower fluorescence intensity. Though the process of transformation is of molecular origin, we may consider it as a phase change from fiber to disintegrated spherical morphology. This spherical aggregates of Z isomers are energetically more stable and prohibits its reversible transition to E isomer under thermal and visible light conditions. We have used Avrami equation for this process of changing the fluorescence intensity with irradiation time and we have calculated the rate constant k (0.151 min⁻¹) of E-Z isomerization from the intercept of Fig. S11 using fluorescence spectra (Fig. 4b).²³ The possibility of optical dimerization of the



Scheme 1. Schematic representation of aggregation and disaggregation of compound I (E-isomer) and II (Z-isomer) respectively.

anthracene moiety is discarded because of the absence of peak for the m/z value at 1755 (mass of the dimer) in the MALDI-TOF spectra (Fig.S12) of I gel after 24 hr of UV-irradiation.

In an endeavour to enlighten the change in electronic environment of the I molecule and to confirm its isomerization upon photoirradiation at 365 nm wavelength we have carried out ¹H NMR spectrum of the I xerogel in CDCl₃ before (I, E-isomer) and after (II, Z-isomer) 12 hours of photoirradiation (Fig. 5). In the 1 H NMR spectrum of it, signals coming in the range of δ 0.86 to 1.78 represent protons of $\text{-}C_{11}\text{H}_{23}$ group. Methylene protons attached with the 'O' atom in dodecyloxy groups [(-OCH₂-) protons, indicated as 'i'] appear at relatively downfield shifted (4.0 - 4.03 δ) region due to strong electronic withdrawal of electronegative 'O' atom which are again directly connected with aromatic ring. Signal appearing at δ 7.18 is attributed to the ('h') protons. Four protons indicated by 'c' and 'd' are found at δ (7.44 - 7.52) showing a rather complicated multiplicity which is quite expected as both of the 'c' and 'd' protons should primarily show a double doublet pattern. A doublet signal at δ (7.98 - 8.0) is assigned to 'b' protons. Proton 'a' appears as a singlet at δ 8.47. The doublet signal at δ 8.59 may be attributed to the protons 'e'. The broad signal at δ 9.61 is attributed to proton 'g' which is attached with electronegative nitrogen atom and is involved in H-bonding interaction here. Finally the most downfield signal at δ 9.71 is due to proton 'f' which is very much deshielded due to the coupled effect of paramagnetic anisotropic influence of (C=N) bond and very strong electronic withdrawal by electron deficient imine 'N' atom. Irradiation of molecule (I) with photons of 365 nm wavelength transforms into molecule (II) by photoisomerization across (C=N) bond. However in this Z-isomeric form proton signals change their positions. This change in signal position may be related with the change in 'electron' delocalization scenario of the lone pair on (-NH-) nitrogen atom. The said nitrogen atom lone pair is in a cross conjugated situation and therefore may delocalize either within the amide carbonyl group or within anthracene ring through (-N=C<) in the other side. In the trans form (E-isomer) anthracene rings may remain electron rich due to the π – stacking and hence 'electron' delocalization of the said lone pair

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takes place significantly within the amide carbonyl group. This S.M, P.C and P.B acknowledge CSIR for financial support. restricts any marked effect of electron withdrawing carbonyl group



within the aromatic phenyl ring. In contrast, in Z-isomer due to unfavourable orientations of anthracene moieties, π -stacking can't occur effectively and therefore 'electron' delocalization favourably occurs towards the anthracene ring. Also the disposition of the lone pair of the said nitrogen atom is in closer proximity to the anthracene ring. These two reasons may cause a greater delocalization of the lone pair to the anthracene moiety than that of the E isomer. Therefore electron withdrawing effect of carbonyl group on the phenyl ring splits the (-O-CH₂-) group signals (at 3-4 δ) of dodecyloxy groups. The ¹H NMR spectrum shows that $(-O-CH_2)$ signals in case of Z-isomer is split in two signals. The 'j' protons present in more deshielded environment comes at higher δ value (3.81δ) than 'i' protons at 3.50 δ showing as expected (1:2) signal area ratio. Electron withdrawing effect of carbonyl group also shifts the position of ortho protons (h) to downfield direction at 8.6 δ . compared to the E-isomer. Now, in the Z form due to increased steric hindrance, H-bonding with the (-NH-) hydrogen atom is not favoured and this is reflected by the development of signal 'g' at much upfield region (δ 6.39). Now, absence of the above said Hbonding also should place lesser amount of (+ve) charge on the nitrogen atom of (C=N) of any individual molecule and this is reflected by the relative upfield shift of the (-CH=N-) proton 'f' (8.95 δ). Proton 'e' and 'b' appears at δ (8.10 – 8.09) and δ (8.03 – 8.01) respectively showing doublet nature. Proton 'c' appears at δ (7.63 – 7.61) showing almost a triplet multiplicity as expected. However, the signal at δ (7.57 – 7.54) represents a complicated pattern with somewhat increased signal area than that can be expected for 'd' protons. Therefore, this signal may represent a combined signal arising from the merger of signals corresponding to protons 'd' and 'a' as both of these two sets of protons are present in comparably electron shielded environment considering electronic delocalization of nitrogen atom lone pair of (-NH-) group within the anthracene moiety. So it is evident from the ¹H NMR spectra that the loss of aromaticity of anthracene is not occurring here ruling out the probability of photodimerisation of anthracene.

So we have successfully tailored an organic super-gelator with thermo-responsive, mechano-responsive and photo-responsive behaviour and established that the molecule undergoes a E-Z type of isomerization across (C=N) bond upon UV-irradiation at 365 nm wavelength. The thixotropic and fluorescence properties of the gels vary significantly upon UV irradiation and it may find use for sensing and release applications.

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Light induced E-Z Isomerization along imine bond in a multiresponsive organogel of anthracene attached 3,4,5-tris(dodecyloxy) benzohydrazide gelator altering morphology, fluorescence and mechanical properties is elucidated from ¹H NMR spectra.