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Solvent-dependent, bimodal self-assembly of a flexible, amphiphilic LMWG results in a chargetransfer hydrogel and organogel with different nano-morphologies and the hydrogel is used as nanocatalyst for Knoevenagel condensation reaction.

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y of an amphiphilic gelator to hydroge

explored base-type catalytic site.<sup>7</sup> However, inaccessibility of

catalytic sites due to small pore size or pore blocking often

limit their activity. In this respect hydrogels of amide-

functionalized LMGWs are superior as wide pores of gel-

network facilitate easy diffusion of reactive species towards the catalytic sites.<sup>8</sup> Since hydrogels are metal-free and contain

huge amount of water within, they are environmentally more benign compared to MOFs. Moreover, hydrogel-nanocatalysts

could host different hydrophilic substrates on their outer

surface and their high surface-to-volume ratio could facilitate

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Published on 11 October 2016. Downloaded by Cornell University Library on 12/10/2016 01:32:57.

Bimodal self-assembly of an amphiphilic gelator to hydrogelnanocatalyst and organogel of different morphologies and photophysical properties

we design a flexible, amphiphilic LMWG consists of donor and acceptor  $\pi$ -chromophores which self-assembles to hydrogel and organogel with different nano-morphologies. Different mechanisms of self-assembly evolve charge transfer (CT) emission in hydrogel and LMWG-based emission in organogel. Moreover, the hydrogel-nanostructure with surface exposed amide groups is explored for catalyzing Knoevenagel condensation reactions.

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Over a past few decades, there has been a growing interest in the development of hydrogels or organogels from the selfassembly of low molecular weight gelators (LMWGs).<sup>1</sup> Owing to the dynamic behaviour and high processability, such supramolecular gels exhibit impending applications in diverse fields, including tissue engineering, bio-medicine, optoelectronics.<sup>2</sup> Although many elegant design strategies have been implemented to construct a number of LMWGs, it is still a daunting task to design a prior a LMWG which can act as both organogelator and hydrogelator.<sup>3</sup> This is because a critical balance between hydrophobicity and hydrophilicity is required to design such LMWG. In this regard, a novel strategy would be to design an amphiphilic LMWG with donor and acceptor  $\pi$ chromophores, connected by flexible alkylamide chain. Selfassembly of such LMWG not only advances the possibility to form CT gel, but also could result in different nanostructures of hydrogel and organogel depending upon polarity of the solvent medium.<sup>4</sup> By considering the extensive opto-electronic applications of supramolecular CT nanostructures, it is worth to design such LMWGs which can pave the way towards adaptive soft-material.<sup>5</sup>

Knoevenagel condensation is an important base-catalyzed reaction in research and industry.<sup>6</sup> Till date, many amide functionalized metal organic frameworks (MOFs) or microporous organic polymers (MOPs) are utilized as heterogeneous Knoevenagel catalysts because amide is a well-

wing such such hydrogel as heterogeneous catalyst for Knoevenagel condensation is yet to be accounted. Herein, we design a new  $C_3$ -symmetrical LMWG (L) with a 4,4',4"-[1,3,5-phenyltri(methoxy)]-tris-benzene (tmb) core, connected to three 2,2':6',2"-terpyridyl (tpy) moieties through flexible alkylamide chain. The self-assembly of L in aqueous and organic medium result in hydrogel (HG) and organogel (OG) with nanosphere and nanofiber morphologies, respectively. The HG exhibits CT emission, whereas the OG shows normal LMWG-based emission. Due to the presence of surface-exposed amide selfty to es of the conic



 $\ensuremath{\mathsf{Scheme}}\xspace1$  Schema 1 Schematic showing the self-assembly of L to hydrogel and organogel and their catalytic activity.

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Electronic Supplmentary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x



**Fig.1** (a) Photograph of **HG** hydrogel under day light and UV-light. (b) FESEM image of **HG** xerogel, inset showing FESEM image of single nanosphere. (c) TEM image of **HG** xerogel. (d) High resolution TEM image of HG xerogel. (d) PXRD of **HG** xerogel. (f) Mechanism of self-assembly of **L** in **HG**. (g) UV-Vis spectra of methanolic solution of **L** (10<sup>-5</sup>, Black), solid L (Red) and **HG** xerogel (Blue). (h) Emission spectra of methanolic solution of **L** (10<sup>-5</sup>, Red), solid **L** (Blue) and **HG** xerogel (Black).

groups,  $\mathbf{H}\mathbf{G}$  is exploited as heterogeneous nanocatalyst in Knoevenagel condensation reaction (Scheme 1).

The synthesis of L is carried out via amide coupling between 4,4',4"-[1,3,5-phenyl-tri(methoxy)]-tris-benzoic acid and 2,2':6',2"-terpyridin-4'-yl-propane-1,3-diamine (Fig. S1-S3).<sup>2e</sup> Methanolic solution of L (10<sup>-5</sup> M) shows a broad absorption band at 250-320 nm which could be assigned to the  $\pi\text{-}\pi^*$ transition of the tmb core and terminal tpy moieties (Fig. S4-S6). Upon excitation at 280 nm, the same solution exhibits blue emission with maxima at 420 nm which could be considered as combined emission from tmb and tpy groups of L (Fig. S4-S6). Gelation propensity of L is thoroughly checked in various solvents. The solution of L (9 mg/ml) in H<sub>2</sub>O/MeOH mixture forms the translucent hydrogel (HG) at room temperature (Fig. 1a). Upon shaking, HG is transformed into a sol, which again turned back to a gel on resting, thereby confirming its thixotropic nature. Insight into the morphology of HG is obtained by recording field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) images of corresponding xerogel. FE-SEM and TEM images of HG xerogel reveal the presence of nanospheres with 700±100 nm diameter (Fig. 1b, 1c, S7 and S8). High resolution TEM image shows that surface of the nanospheres consists of layered sheets (Fig. 1d). Formation of the nanosphere occurs through a two-step hierarchical self-assembly process as shown in Fig. 1f.<sup>9</sup> First, in polar solvent the molecules are assembled through intermolecular  $\pi$ - $\pi$  stacking between the tmb and tpy moieties and result in extended 2D sheets. As time proceeds, the  $\pi$ -stacked tmb and tpy groups tend to minimize their contact with H<sub>2</sub>O/MeOH due to hydrophobic effect, whereas amide groups present on the sheets tend to be exposed towards the polar medium due to H-bonding with H<sub>2</sub>O/MeOH. As a result, sheets are folded to nanospheres whose exterior are decorated with amide groups. The presence of  $\pi$ - $\pi$  stacking in **HG** is supported by powder X-ray diffraction (PXRD) which shows peak at  $2\theta$ = 24.5°,

corresponding to the *d*-spacing value of 3.6 Å (Fig. 1e and S9).Comparison of fourier transform infrared (FTIR) spectra of HG xerogel with L, does not exhibit significant change in -N-H and -C=O stretching frequency which indicates no H-bonding interaction between L and gelation is driven by only  $\pi\text{-}\pi$ stacking/hydrophobic interaction between tmb and tpy groups (Fig. S10). UV-Vis spectrum of HG xerogel exhibits maxima at 290 nm and a broad shoulder at 410 nm which could be attributed to the interligand CT transition between  $\pi$ -stacked tmb ( $\pi$ -donor) and tpy groups ( $\pi$ -acceptor) (Fig. 1g). Similar Ar→tpy intraligand charge transfer (ILCT) transition is reported for many Zn<sup>2+</sup> complexes of Ar-tpy derivatives.<sup>10</sup> Upon exciting at 290 nm HG xerogel shows cyan emission with maxima at  $\lambda$ = 478 nm (Fig. 1h). Moreover, the intensity of the emission maxima increases upon excitation at 400 nm, further indicating CT based emission in HG (Fig. S11). Excitation spectra show presence of ground state interaction, thus ruling out the possibility of excited state exciplex formation (Fig. S12).<sup>11</sup> To further confirm the CT interaction, the absorption and emission spectra of L in MeOH/H2O mixture are recorded by gradually adding H<sub>2</sub>O in the MeOH solution of L. With incremental addition of H<sub>2</sub>O, the absorption spectra of L show appearance of a new peak at 410 nm, suggesting intermolecular CT interaction of aggregated L in mixed solvent (Fig. S13). The corresponding emission spectra ( $\lambda_{ex}$ =400 nm) exhibit red shift of the emission maxima at 420 nm with increase in intensity, confirming CT emission of aggregated L in mixed solvent (Fig. S14). Comparison of absorption spectra of HG xerogel with solid L, shows that the CT band at 410 nm becomes more prominent in HG (Fig. 1g). This result indicates that the CT interaction between the  $\pi$ - $\pi$  stacked tmb and tpy groups becomes prominent in the ordered assembly of HG. Confocal fluorescence microscopy images of HG xerogel confirm the formation of cvan emissive nanospheres with an average diameter of 700±100 nm (Fig. S15).

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Fig. 2 (a) Photograph of OG organogel under day light and UV-light. (b) FESEM image of OG xerogel. (c) TEM image of OG xerogel. (d) Mechanism of self-assembly of L in OG. (e) PXRD of OG xerogel. (f) UV-Vis and emission spectra of OG xerogel.

Heating solution of L (8 mg/ml) in CHCl<sub>3</sub>/THF mixture followed by cooling results in an opaque organogel (OG) (Fig. 2a). FESEM and TEM images of OG xerogel reveal the typical fibrous morphology (Fig. 2b, 2c and S16). Nanofibers are several micrometer long with an average diameter of 80-100 nm. The presence of nanorings is also observed which are formed by coiling of nanofibers. In CHCl<sub>3</sub>/THF mixture, selfassembly of L is driven by complementary H-bonding interaction between amide groups and  $\pi$ - $\pi$  stacking between tmb cores of neighbouring L and results in 1D fibril (Fig. 2d). These fibrils upon aggregation form fibers which further entangle to form fibrous gel architecture. The presence of Hbonding and  $\pi$ - $\pi$  stacking in **OG** is supported by PXRD and FTIR. Comparison of FTIR spectra of L and OG xerogel exhibits decrease in -C=O and -N-H stretching frequencies from 1693  $cm^{-1}$  to 1688  $cm^{-1}$  and from 3436  $cm^{-1}$  to 3420  $cm^{-1}$ respectively, indicating the presence of intermolecular Hbonding between the amide groups of L (Fig. S17). PXRD analysis of **OG** xerogel exhibits broad peck at  $2\theta$ = 21.7°, corresponding to d = 4.0 Å which indicates the  $\pi$ - $\pi$  stacking in organogel (Fig. 2e and S18). Absorption spectrum of OG xerogel shows maxima around 290 nm. The xerogel exhibits a blue emission with maxima at 430 nm ( $\lambda_{ex}$ =290 nm), originating from both tmb and tpy, similar to the methanolic solution of L (Fig. 2f). This also suggests that self-assembly of L is different in **HG** and **OG**. Oscillatory strain and frequency sweep measurements on HG and OG show that storage modulus (G') is higher than the loss modulus (G") over a long range of strain (%) indicating viscoelastic nature of the gels (Fig. S19-S22). Interestingly, the G' value of OG is two-fold higher than the G' value of **HG** indicating greater mechanical strength of **OG** compared to **HG**.



Table 1 The catalytic reactions and the results with varying substituent on the aldehydes.

The presence of free amide groups on the exterior of nanosphere of HG xerogel prompted us to study its catalytic activity towards the Knoevenagel condensation of aldehydes and active methylene compounds. In a typical condensation reaction p-nitrobenzaldehyde (1 equiv), malononitrile (1 equiv), and HG xerogel (1 mol %) are taken in dry THF and stirred at 40°C under inert conditions. Formation of product is confirmed by <sup>1</sup>H-NMR and GC-MS analysis (Fig. S23, S24). The quantitative analysis of the product conversion is monitored by a GC-MS analyser at regular intervals of times. The reaction kinetics shows a sharp increase in conversion (69%) in 20 minutes, after 2 h 90% conversion of product is observed and after 4 h almost all aldehyde is converted to product (99%) (Fig. S25). However, no detectable amount of product is obtained, when L is used as catalyst under the similar reaction condition. This suggests that the direct contacts of the substrate with the amide groups present on the surface of nano-spheres are essential for catalytic activities. The catalytic activity of HG xerogel towards different p-substituted benzaldehyde (X = H, NO<sub>2</sub>, Cl, CH<sub>3</sub> and OCH<sub>3</sub>) is studied and the conversion results are summarized in Table 1. (Fig. S26-S29). Although the conversion of product is significant for X= H, NO<sub>2</sub> and Cl, the yield is reduced for X= CH<sub>3</sub>, OCH<sub>3</sub>. This suggests that electron withdrawing group (NO2, Cl) at the para-position of benzaldehyde enhances the electrophilicity of the carbonyl carbon and thereby increases its reactivity.<sup>12</sup> However, the electron donating group (OCH<sub>3</sub>, CH<sub>3</sub>) reduces the electrophilicity of the carbonyl carbon and therefore exhibits lesser yield. The catalyst could be reused for at least 4 cycles. TEM images of the catalyst after 4th cycle show retention of morphology. The size distribution histogram plots of HG xerogel before and after the catalytic reaction also indicate

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that the sizes of nanosphere are unchanged after reaction (Fig. S30, S31). The PXRD of **HG** xerogel do not change after immersing it in THF at 40 °C (**HG@THF**), thus confirming its stability (Fig.S32). To further prove that the surface exposed amide groups are essential for the catalytic activity, we have performed same catalytic reactions with nanofiber **OG** xerogel. Interestingly, no conversion of product is observed even after 12 hours. This suggests that **OG** xerogel cannot catalyze the reaction. Stability of **OG** xerogel in THF at 40 °C (**OG@THF**) is confirmed by PXRD and TEM (Fig S33, S34). Since the amide groups are not exposed on the surface of nano-fiber, the reactants could not access the catalytic sites and therefore reaction did not occurred. This further supports our conjecture of different self-assembly of **L** in two different solvent systems as discussed earlier.

The preceding results demonstrate design of a LMWG which can self-assemble in both aqueous and organic medium resulting into hydrogel and organogel, respectively. Hydrogel shows unique spherical morphology and CT emission. However, the organogel shows typical fibrous morphology. The nanospheres of hydrogel are utilized for catalysing Knoevenagel condensation reaction, whereas the nano-fibers of organogel fail to show catalytic activity due to inaccessibility of free amide groups. This work would open up a new perspective to rationally design LMWG that can form both organogel and hydrogel and explore their catalytic applications. Furthermore, the effect of metal ion coordination on self-assembly of this LMWG and their properties can be explored.

TKM is grateful to the Department of Science and Technology (DST, Project No. MR-2015/001019), Government of India (GOI) and JNCASR for financial support. PS is thankful to Council of Scientific and Industrial Research (CSIR), GOI for fellowship.

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