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Evidence of aggregation induced emission enhancement and keto-enol-tautomerism in a gallic acid derived salicylideneaniline gel[†]

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A novel salicylideneaniline type fluorescent organogelator based on a 3,4,5-(tri-dodecyloxy)benzoyl group immobilizes aromatic solvents. The resulting gels show enhancement in emission and thermochromic/non-photochromic behaviour during sol-to-gel transition.

Low-molecular-mass organic gelators (LMOGs) have attracted much attention because of their unique properties and potential uses in various fields of research and industry.¹ Intermolecular hydrogen-bonding and other weak non-covalent interactions (*e.g.* van der Waals, π - π stacking and solvophobic effect, charge-transfer, metal–ligand coordination *etc.*) are the driving forces which bring about the supramolecular assemblies. Non-covalent 'cross-links' and physical entanglements among such assemblies create a three-dimensional network where the solvent is immobilized.²

Salicylideneanilines (anils) have recently received particular interest because of their excellent photochromic,³ thermochromic,⁴ solvatochromic⁵ and liquid-crystalline properties.⁶ Metal–salen based complexes are also widespread in the literature because of their extensive applications in catalysis and industry.⁷ The packing of the anils confirmed the general trend: thermochromic = "close-packed-structure" and photochromic = "open-structure".⁸ In thermochromic anils, the salicylaldimine group is involved in intramolecular H-bonding and the structural motif is arranged in a planar conformation which introduces π – π stacking with short inter-planar distances (3.5 Å). In the photochromic anils, only the latter moiety is planar and it forms an intramolecular H-bond, whereas the aniline ring is rotated by ~50° with respect to this plane, thus limiting their close proximity.⁸

Recently, cholesterol based photochromic/thermochromic salicylideneaniline type organogelators were introduced by Lu and co-workers.⁹ There are a number of examples of 3,4,5-(tri-dodecyloxy)benzoyl derivatives based on salicylideneanilines and

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Fig. 1 (a) Molecular structure of 3,4,5-(tri-dodecyloxy)benzamide based salicylideneaniline (1) with H-bonding donors/acceptors and (b) a photograph of the organogel of 1 in toluene at 2 mM.

metal–salen complexes that exhibit excellent liquid-crystalline properties.⁶ But, there is no report of supramolecular gelation induced by such salicylideneanilines. Herein, we report the first example of a new thermochromic salicylideneaniline type organogelator consisting of a 3,4,5-(tri-dodecyloxy)benzoyl group.

Firstly, the gelation ability of compound 1 (Fig. 1) was confirmed in different aromatic hydrocarbons by the "stable-to-inversion protocol of a test tube" method. It formed gel in aromatic solvents such as benzene and toluene (minimum gelator concentration [mgc] = 2 mM). Presence of four sets of -NH-(C=O) linkages in 1 promotes facile intermolecular H-bonding mediated association leading to gelation (see below). However, it was soluble in CH_2Cl_2 , $CHCl_3$ and THF and was insoluble either in ethanol or in *n*-butanol.

To discern the microstructures formed by the gel of 1 in toluene, scanning electron microscopy (SEM) was performed. It showed the presence of fibrous networks (Fig. 2a). The morphology of the gel observed by atomic force microscopy (AFM) (Fig. 2b) was in agreement with the SEM analysis. Distinct fibrous structures (0.2–0.3 μ m) along with bundles were clearly visible.

To obtain further insights into the interactions among the salicylideneaniline chromophores in the gel state, temperaturedependent absorption spectra of the gelator 1 (2 mM) were recorded in toluene. The intensity of the broad absorption in the range 200–500 nm increased monotonically with the increase in temperature. This was a consequence of gel-to-sol transition, weakening the interactions between the chromophores and the

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Fig. 2 (a) SEM and (b) AFM images of toluene gel of 1 at a concentration of 2 mM.

transition temperature (~50 °C) was calculated from the A_{350} vs. temperature plot (Fig. S1, ESI[†]). Relative to the sol, gelator **1** showed a red-shift of ~8 nm in the gel phase, indicating a *J*-type aggregation.¹⁰ This phenomenon was further supported by the observation of a blue-shift in the absorption characteristics of **1** in toluene during dilution (Fig. S2, ESI[†]). This observation suggests that H-bonding among the amide linkages and probably π - π stacking are responsible for the rigidity of supramolecular structural motifs, which leads to the formation of *J*-aggregates. Concentration-dependent IR-spectroscopy revealed significant shifts of the –NH stretching frequency to higher wavenumber on dilution, indicating the weakening of the H-bonding interaction (Fig. S3, ESI[†]). The N–H band appeared at 3275 cm⁻¹ in 'strong' gel (2 mM), 3305 cm⁻¹ in 'weak' gel (1 mM) and shifted to 3310 cm⁻¹ in the sol state (0.2 mM).¹¹

To explore the photochromic behaviour, the toluene gel of 1 was exposed to 365 nm UV light for a long time (>1 h) at room temperature. But, even after this UV-visible spectra remained invariant and a gel-to-sol transition did not occur. Interestingly, a greenish yellow gel of 1 in toluene was rendered colourless at 77 K and was converted to nearly colourless sol at 353 K. These may be attributed to the low population of the keto form in sol. In order to investigate this equilibrium process further, temperature-dependent UV-Vis spectroscopy was performed at the mgc. Unfortunately, it became difficult to detect the NH absorption band near 500 nm at such a high gelator concentration because of the broad nature of the absorption spectra. So, we investigated this phenomenon at lower concentration (0.27 mM) of the gelator molecule. But, it is notable that the intensity of absorption near 500 nm in the UV-Vis spectra of 1 in toluene at mgc starts to decrease at 45 °C and is completely diminished at 75 °C (Fig. S1, ESI⁺).

Accordingly, we prepared a toluene solution of 1 (0.27 mM) and froze it in liquid nitrogen. A greenish yellow solution at 298 K was converted to a colourless solid at 77 K. This was then allowed to thaw naturally and the colourless solid started to regain its greenish yellow colour (Fig. 3a). UV-Vis spectra were recorded during warming at a time interval of 2 min (Fig. S4, ESI[†]). The absorption in the range of 450–500 nm became stronger with increasing temperature. This phenomenon indicates that the tautomeric equilibrium markedly shifts to the E–OH form at the liq. nitrogen temperature. The greenish yellow solution of 1 in toluene also started to lose its colour on heating and turned nearly into a colourless solution at 353 K, illustrating a very low population of the E–NH form. Fig. S5 (ESI[†]) shows the temperature-dependent changes in absorption



Fig. 3 (a) Photographs of the colourless sol at 353 K, yellow gel at 298 K and colourless solid gel at 77 K of 1 in toluene at 2 mM. (b) Keto–enol tautomerism of thermochromic salicylideneanilines and (c) temperature-dependent partial ¹H-NMR spectra of 1 in $[D_6]$ benzene at 2 mM.

spectra of **1** in toluene at 0.27 mM. Absorption intensity in the range 450–500 nm decreased with increasing temperature, elucidating a low population of the NH form at higher temperature.

Keto-enol-tautomerism of 1 (Fig. 3b) associated with the sol-gel transition was further investigated by temperaturedependent ¹H-NMR spectroscopy, which is an efficient tool for following the process of aggregation.¹² Interestingly, ¹H-NMR spectra of 1 in $[D_6]$ benzene at the mgc (2 mM) showed significant differences from that of the ¹H-NMR spectra in CDCl₃. Fig. 3c shows NMR signals near $\delta = 13.7$. These originated from a combination of two closely spaced peaks, which can be interpreted from the presence of an equilibrium between the enol (-OH) and the keto (-NH) form. Both peaks were of equal intensity in the gel phase at 25 °C and the peak that appeared at more downfield was assigned to the OH form because of higher electronegativity of O than that of N. However, the relative intensity of the peak associated with the enol form became stronger and sharper with increasing temperature. This suggests that the gel phase of 1 contains an approximately equal population of the enol and keto forms and the population of the enol form increases with increasing temperature during the gel-to-sol transition. The same interpretation may be applied to explain a similar behaviour of the NMR signals at $\delta \approx 8$ which were assigned to the H' of the enol form and H" of the keto form. It indicates that the enol and keto forms of 1 coexist in solution while in the gel the OH form predominates in the sol phase. Ogawa and Arai¹³ proposed that the energy differences between the ground states of the OH and NH forms in solution are too large to allow enol to convert to the keto form. However, here the NH form is stabilized in the aggregates of the gel phase. This lowers the energy barrier between the OH and NH forms than that in the solution, which in turn favors the proton tautomerization leading to the formation



Fig. 4 (a) Temperature-dependent changes in the fluorescence spectra of gel **1** in toluene at 2 mM; the inset shows the plot of intensity *vs.* temperature at 525 nm. (b) Photographs of the gel and hot sol of **1** in toluene under 365 nm UV light. (c) SAXD plot of the xerogel of **1**. (d) Molecular packing model in the *xy* plane through stacking with a long period of 5.2 nm and (e) proposed molecular packing of propagation of the aggregates of **1** along the direction (*z*-axis) of the growth of supramolecular fibrous networks.

of the NH form. Surprisingly, the NMR signals at $\delta \approx 8$ and 13.7 were observed as nice single peaks in CDCl₃.

Fig. 4a shows the temperature-dependent changes in the fluorescence spectra of 1 (2 mM) in toluene when excited at 465 nm. The intensity of the peak at 515 nm associated with the sol phase becomes stronger and sharper with decreasing temperature and also red-shifts to 525 nm in the gel phase.¹⁴ Fig. 4b shows a strong green fluorescence emission of the toluene gel of 1 under long UV-light (365 nm) and a weak emission of the hot sol (~80 °C). This phenomenon is ascribed to a combination of *J*-aggregates (head-to-tail arrangement of the fluorophore).¹⁰ The sol-to-gel transition temperature (~50 °C) is calculated from the emission intensity at 525 nm *vs*. temperature plot and the result is in good agreement with the results of the UV-Vis spectroscopy.

Small-angle X-ray diffraction (SAXD) was performed to unveil the mechanism of packing of the supramolecular organization in the xerogel (Fig. 4c). The diffraction pattern shows two peaks at 5.2 nm and 2.6 nm, which are in the ratio of 1:1/2, indicating a lamellar pattern¹⁵ of the aggregates of **1** with an interlayer spacing of 5.2 nm which is less than the double of its molecular length (3.91 nm) as calculated by optimization of geometry of the single molecule using B3LYP/6-31G*. This analysis indicates that the *n*-C₁₂H₂₅ chains interdigitate¹⁶ with each other to introduce van der Waals interactions among the long chains. It thereby renders the salicylideneaniline molecules proximal to develop an extended supramolecular network (Fig. 4d and e).

In conclusion, we have demonstrated that 3,4,5-(tri-dodecyloxy)benzoyl appended salicylideneaniline, 1, acts as an efficient gelator for aromatic solvents. Thermochromism of its toluene gel could be explained by following the equilibrium between the enol (OH) and the keto form (NH) using UV-Vis absorption and temperature-dependent ¹H-NMR spectroscopy. This is the first time it has been possible to investigate keto-enol-tautomerism associated with the gel-to-sol transition of salicylideneaniline by recognizing distinguishable NMR signals of the tautomers. Furthermore, calculation of the molecular length by energy minimization of a single molecule and its comparison with the small-angle X-ray diffraction pattern reveals that gelator molecules arrange themselves in an interdigitated lamellar structure. Thus, the gelation process is attributed to the J-aggregation of the self-assembly promoted by H-bonding, π - π stacking and van der Waals interactions among the individual salicylideneaniline units, which results in an aggregation induced strong green emission in the gel phase.

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