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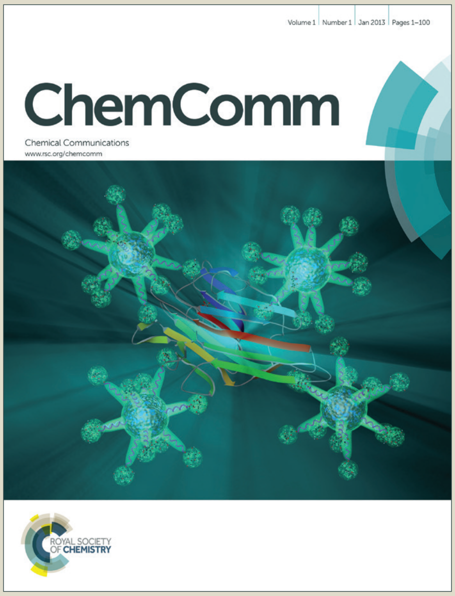

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Tuning of multiple luminescence output and white-light emission from a single gelator molecule through ESIPT coupled AIEE process

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Unique example of ESIPT coupled AIEE process, associated with a single molecule (1), is utilized for generating multiple luminescent color (blue-green-white-yellow). *J*-aggregated state of 1 forms a luminescent gel in THF and this luminescent property is retained even in solid state.

Luminescent nanostructures derived from small organic molecules or achieved from supramolecular assembly of various functional π-conjugated molecules has attracted considerable attention due to their potential applications in color tuneable displays,[1] optoelectronic devices,[2] chemical sensors,[3] and many related fields.[4] Soft materials with tuneable luminescence responses are important for developing multiple color emitting devices. Such responses are generally achieved by appropriate modulation of energies of the frontier orbitals through systematic structural modification of luminophore or in presence of an appropriate external stimuli,[5a-d] as well as through mixing of several discrete compounds with different luminescence outputs.[5e] However, example of such a response from a single molecule is scanty in the contemporary literature. Further, an ideal white-light emitter demands simultaneous emission of three primary RGB (red, green and blue) colors or at least two complementary colors with nearly similar distribution of intensities covering the entire visible wavelength range from 400 to 700 nm.[6a] Due to the technological relevance and demand for optical devices with tuneable light emission, specially white-light emission, there has been a significant surge in research interest in recent past. Förster resonance energy-transfer (FRET) between donor and acceptor components have been used to achieve white-light emitting organic assemblies in gels,[6a-b] solution,[5d,6c] nanoparticales,[6d-e] nanofiber,[6f] and in solid state.[6g] But the use of multiple components with proper control for the FRET process in generating white-light emission is argued as a relatively complicated process. Processes like excited state intramolecular proton transfer (ESIPT),[7a-b] and aggregation induced emission (AIE) or aggregation induced emission enhancement (AIEE)[7c-d] for organic molecules have been utilized for generating tuneable luminescence responses and in some instances white-light emission. ESIPT process generally results an excited keto tautomer (K^*) with abnormal emission property and large stokes shift relative to that is observed for the normal excited enol form (E^*).[7a] Dual emission (E^*/K^*) is also expected over the wide wavelength range if the proton transfer is not quantitative and this has been utilized for generating white light emission.[8] However, such reports are scarce. Tang and his co-workers were first to report that certain class of luminophores exhibited AIE in their aggregated state,[7c] contrary to the luminescence behaviour of the common organic fluorophores. Aggregation process helped such molecules to pack efficiently through a π-π stack interaction, which eventually blocked the non-radiative deactivation pathway through restricted intramolecular rotations (RIR). This accounted for an improved luminescence response in the aggregated state and was also utilized for developing certain luminescent gels.[9]

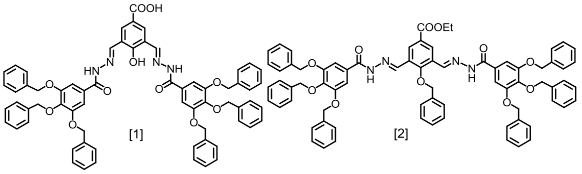


Fig.1. Molecular structure of the synthesized two new compound **1** and **2**.

A few AIE or AIEE responsive single molecules could also exhibited multiple color emission either due to different conformation and/or packing modes in aggregated state, or due to a change in the degree of aggregation.[10] In some instances, these resulted white-light emission.[5c-d,11] Few recent reports discuss about ESIPT active molecules with AIEE properties.[12] However, to the best of our knowledge there is no report that has discussed about ESIPT coupled AIEE process for a single molecule for developing tuneable multiple luminescence color (blue, green, yellow and white) at room temperature. In this communication we have reported such a phenomena using a newly synthesized poly(aryl ether) dendron based gelator molecule (compound-**1**, Fig.1). Its luminescence color was found to change from blue-green-white and then eventually to yellow with gradual increase of water percentage into its THF solution. Interestingly, **1** showed an intense yellow color emission in gel, powder and in thin film states. Synthesis and all characterization details for **1** (Fig.1), are provided in supporting information.† Compound **1** with a flexible and freely rotatable acylhydrazone spacer and a free -OH group, participated in an intramolecular six membered hydrogen-bond (H-bond) formation with N_{Imine} atom. To investigate the specific role of the ESIPT process on the luminescence responses, model compound **2** was synthesized.†

Absorption spectrum (Fig.2a) for **1** (10 μM) was recorded in pure THF and band maxima at 306 nm (ε = 4.69 x 104 $M^{-1}cm^{-1}$) and 355 (ε = 1.7 x 104 $M^{-1}cm^{-1}$) nm with two shoulders at 320 and 372 nm were observed. On gradual addition of water into its THF solution, intensities of all absorption bands were found to decrease due to formation of molecular aggregates and eventually in THF-water (1:9; v/v) solution a distinct red shift of 10 and 12 nm (Fig.2a & SI Fig.S10) was observed for the absorption band at 355 and 372 nm, respectively. Such bathochromic shifts for the absorption bands were anticipated on *J*-type aggregation.[5b,11b] To test the stability of the aggregated structures we had performed variable-temperature UV-Vis studies for the THF-water solution (3:7, v/v) of **1**. Results of these studies revealed that absorption spectral pattern and thus, the aggregated structure remained almost invariant till 70°C (SI Fig.S11). This confirmed high thermal stability for the *J*-aggregated structures. Results of the thermo gravimetric analysis confirmed that **1** was stable up to 280°C (SI Fig.S12).

Steady state luminescence spectrum for **1** was studied carefully to understand the effect of ESIPT coupled AIEE process that could be operational. Luminescence spectra of **1** were recorded with varying the composition of THF-water mixtures (100:0 to 1:99; v/v) with effective [**1**] as 10 μM (Fig.2b). Broad emission band with two maxima at 454 and 487 nm (λ_{Ext} of 365 nm) was observed In THF solution.

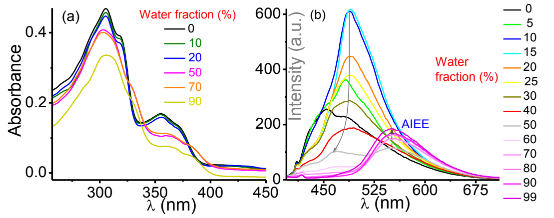
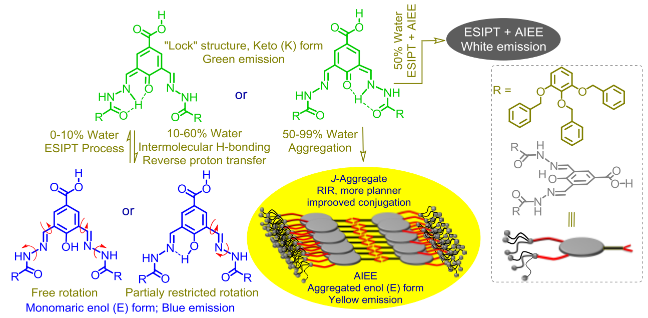


Fig.2. (a) UV-Vis and **(b)** luminescence spectra of **1** (10 μM) in THF and THF-water mixed solvent medium (λ_{Ext} = 365 nm was used for luminescence studies).

In THF-water (9:1, v/v) solution, an appreciable increase in emission intensity was observed at 487 nm. On further increase in water fraction, bleaching of the emission band with maximum at 487 nm was observed with small associated blue shifts (Fig.2b); while a subsequent new emission band at ~551 nm appeared. This new band was evident for THF-water solvent mixture having composition of 1:1 (v/v). Emission band with maximum at 487 nm eventually disappeared for THF-water solution having water content ≥ 70% (v/v). Band at 551 nm became more intense on further increase in the water (Fig.2b) content. Thus, an eventual Stroke's shift of 186 nm was observed.

In THF solution, compound **1** could actually adopt various conformations due to several combinations for C-C/N-N or even $C=N_{Imine}$ bond rotations/isomerisation with board range of torsional angles (Scheme-1). Such rotations or conformational changes are expected to favour the non-radiative deactivation of the excited state, which should have resulted in a nominal emission quantum yield for THF solution of **1**. However, presence of bulky poly(aryl ether) dendron groups and preformed six membered H-bond between -OH and N_{imine} centres (Scheme-1) were expected to partially restrict the above referred rotations and/or isomerisation process(es), which could be accounted for the observed week and board emission spectra in pure THF (Fig.2b). In addition ESIPT process is known to be sensitive towards media polarity. In hydrocarbon and non-polar solvents, emission band with large Stokes shift is generally observed, which is attributed to the emission from excited keto form (K^*) of two tautomers. In protic or polar solvent, generally enol (E) form gets stabilized through formation of intermolecular hydrogen bonds with solvent molecules. This accounted for emission band from E^* with normal Stokes shift value before undergoing ESIPT.[7a]



Scheme-1 Changes of configuration of **1** from twisted ground state to more planer excited state, and finally *J*-aggregated rigid structure through ESIPT coupled AIEE processes with the variation of water fraction to its THF solution.

Relative intensities of these two emission bands are expected to vary according to the media polarity and structure for the respective luminophore. For the present study, **1** could exist in **E** as well as in **K** form in THF, a solvent with moderate polarity. Thus, two emission maxima at 454 and 487 nm (λ_{Ext} = 365 nm) in pure THF solution were attributed to monomeric E^* and K^* form, respectively. Interestingly, excitation spectrum recorded for **1** using λ_{Ems} of 454 and 487 nm in pure THF was significantly different from its corresponding absorption spectrum (SI Fig.S13a-b). This confirmed that the final emitting state(s) is/are different from the one that accounted for emission at 454 and 487 nms. This new emission could arise from the follow-up ESIPT process. On addition of water to the THF solution of **1**, the media polarity was enhanced and this was expected to favour the emission from E^* at 454 nm with normal Stokes shift, which was contrary to our observation (Fig.2b). In THF-water solvent mixture with maximum 15% water content, emission band at 487 nm was prominent, which was linked to the emission from K^*. This unusual phenomenon could be explained if one considers the possibility of the compound to adopt a planar structure due to RIR. Water was a non-solvent for **1** and this would help molecules of **1** to aggregate in presence of ~10 or 15 % water (v/v). Such aggregation was expected to impose certain restriction on the intermolecular torsional motions and would help molecules to eventually attain somewhat planner structures that were conducive for the proton transfer from –OH to N_{imine} atom on photoexcitation.[12b] This ESIPT process was expected to fully restrict the intra molecular rotation and helped molecules of **1** to attain a "lock" structure (Scheme-1), which accounted for the shift in the prominent band maxima from 454 to 487 nm, (Fig.2b) with enhanced emission band from K^*. As it was observed in case of pure THF, fluorescence excitation spectra (λ_{Ems} = 487 nm) for solution having ~10% water also yielded similar results (SI Fig.S14a-b, *vide infra*). With further increase of the media polarity by gradual addition of water, intermolecular H-bonding was preferred over the intramoleculr H-bonding process and thus, one would expect E-form to prevail over the K-form. Hence, for solution having increasingly higher water content (~20 to 60%), the emission band with maxima at 487 nm was found to bleach gradually along with a distinct blue shift (Fig.2b). This signified the transformation from K to E tautomer. For ~ 50% water content, an additional emission band at 551 nm was observed (Fig.2b). Degree of aggregation for **1** was expected to be more significant in solution having higher water content. For water content ≥ 50 %, such extensive aggregation was expected to restrict all the C-C/N-N bond rotation or C=N bond isomerization and molecules of **1** would attain a more planner structure (Scheme-1). This should enhance molecular planarity and conjugation, which subsequently induced the red shifted emission band maxima at 551 nm with Stroke's shift of 186 nm (Fig.2b). Thus, this emission band with high Stroke's shift value was assigned as AIEE band of the aggregated E form of **1**.[11] In case of (~50%) water contain we have also record fluorescence excitation spectra (using two different λ_{Ems} of 468 and 551 nm). Excitation spectrum (λ_{Ems} of 468 nm) was different from its absorption spectrum (SI Fig.S15a-b), whereas that obtained for λ_{Ems} of 551 nm was identical to its absorption spectrum. This further confirmed that E-form for **1** was stabilized in its aggregated states in solution having water content ≥ 50 %. Results of the electronic spectral studies (Fig.2a) revealed a *J*-type aggregation (Scheme-1). Thus, both the ESIPT and AIEE processes were operational for solution with ~50% water content and accounted for a broad emission spectrum with two emission maxima at 468 and 551 nm, respectively. On further increase of water fraction (~60 to 99%), AIEE process prevailed over the ESIPT process and a gradual growth in emission band intensity with λ_{Max} at 551 nm was observed for normal AIEE process involving E form. For solution with 90% water content fluorescence excitation spectrum (λ_{Ems} of 551 nm) matched with the corresponding absorption spectrum (SI Fig.S16a-b), which again confirmed that only E form of **1** existed in aggregated states. Molecule **2** was used for control experiments and failed to show any such spectral changes for identical experiment (SI Fig.S18).

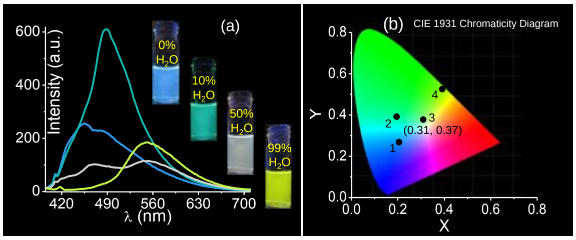


Fig.3. (a) Changes of emission spectra of **1** (10µM) with varying water content in THF-water medium, Inset: Photographs showing luminescent colours on irradiation with 365 nm light with different water content; (b) CIE chromaticity diagram for blue (1), green (2), white (3) and yellow (4) emission, respectively.

In absence of -OH proton, this molecule had a little chance to form an analogous "lock" structure like **1** (Scheme-1) through ESIPT processes at relatively lower water content. With further increase of water content (~70-99%), an insignificant board emission band was observed at 481 nm (SI Fig.S18), which was attributed to an AIE effect. To confirm that ESIPT process was really operational, luminescence spectra of **1** (10µM) was recorded in solvents with different polarities and band maximum was found to be red shifted with decrease in the solvent polarity (SI Fig.S19). This corroborated our presumption that ESIPT process was operational under appropriate condition.

Visually detectable luminescence color was also examined carefully on irradiation with 365 nm UV light. This was found to change from blue-green-white-yellow (Fig.3a inset), respectively, for **1** with the change in THF-water ratio to 100:0, 9:1, 1:1 and 1:99. Luminescence spectra recorded for solution having ~ 50% water covered the entire visible range (~ 400–700 nm) and this accounted for a white-light emission (Fig.3a). CIE coordinates were also calculated using luminescence data to check purity of the white-light and this fell in the range of (0.31, 0.37), which was very close to pure white-light (0.33, 0.33). CIE coordinates for other luminescent colors are shown in Fig. 3b.

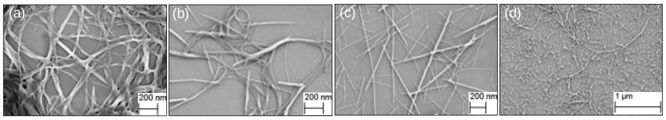


Fig.4. Solvent dependent FESEM images of **1** (100µM) having (a) 0, (b) 10, (c) 50 and (d), 90 % water content in THF.

To understand conformational changes associated with **1** for varying water content in THF-water medium, field emission scanning electron microscopic (FESEM) studies were performed (Fig.4). In THF and in THF-water (9:1, v/v) mixture, entangled fibre-like aggregates were observed (Fig.4a-b). Nano rod shaped aggregates were obtained for THF-water (1:1, v/v) mixture, while marine habitats like nanostructure were observed in THF-water (1:9, v/v) medium (Fig.4c-d). These also supported our argument on changes in conformation and aggregation pattern on increase in water content in the THF-water medium.

FTIR spectra were recorded for **1** and **2** as KBr pellet (SI Fig.S20 & SI Table.S1). For **1**, an intense and sharp band for stretching frequency of –C=N appeared at 1656 cm^{-1}, while a much weaker band at 1606 cm^{-1} was observed for **2** (SI Fig.S20). This was attributed to a conformationally rigid structure for **1** and flexible structure for **2**, where –C=N bond isomerization was possible. Additionally, respective stretching frequency of $-C=O_{Amide}$ for **1** and **2** appeared at 1619 cm^{-1} and 1643 cm^{-1} (SI Fig.S20), also suggested that the strength of the hydrogen bonding in **2** was less as compared to that of **1**. All these results indicated that **1** adopted a rigid and planner structure.

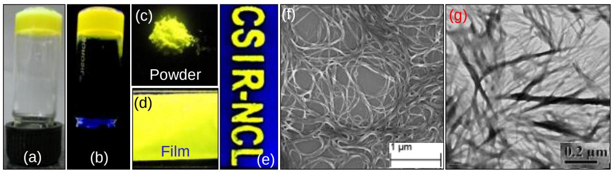


Fig.5. (a) Photographs of the THF gel of **1** in daylight, (b), (c), (d) and (e) are photographs of the THF gel, solid powder, thin film and a write-up using compound **1** under UV light (365 nm) irradiation, respectively; (f) & (g) are the FESEM and TEM images of the gel obtained for compound **1** in THF solution.

Compound **1** was sparingly soluble in THF at ambient temperature and was found to dissolve completely on gentle heating.† A yellow color opaque gel was formed (CGC is 1.0 wt. %) upon cooling to room temperature and this was confirmed by inverted vial method (Fig.5a) as well as by rheological studies (SI Fig.S24).† Bright yellow fluorescence was observed (Fig.5b) from this gel, when exposed to a UV light (365 nm). While, **2** failed to give gel (SI Fig.S21) under identical condition. This perhaps revealed the role of the pendent -COOH functionality in **1** for gel formation. Importantly, powder and a thin film of **1** on glass plate as well as a print "CSIR-NCL" on silica gel plate (Thickness 0.2 mm & Pore size of 60 Å on Aluminium plate) using THF solution of **1** were found to be strongly emissive on irradiation with 365 nm light (Fig.5c-e). Such property has relevance for energy efficient display devices. FESEM and TEM experiments of the gel obtained from **1** (Fig.5f-g) in THF shows the formation of nano scale fibrous architecture with diameter range of 50 - 150 nm and several micrometer of length.

To gain additional insight about the modes of molecular packing, X-ray powder diffraction (XRPD) were recorded for small as well as for wide angle regions of air dried THF gel of **1**. In the small angle region peak at $2\theta = 3.1°$ with a d spacing value of 28.5 Å (D) (SI Fig.S25a) was followed by several other peaks in wide angle region (SI Fig.S25b) in a periodical order with d spacing values 13.8 Å (D/2), 9.5 Å (D/3), 7.1 Å (D/4), 5.5 Å (D/5), 4.8 Å (D/6) was observed. These data suggested that, molecules of **1** were self-assembled into lamellar fashion in gel state.[9d] In wide angle region two more peaks at $2\theta = 20.1°$ and 23.9° for respective d spacing value of 4.4 Å and 3.7 Å were observed. This suggested the presence of hydrogen bonding and π-π staking interactions of dendrons in the gel fiber.[4c]

In aggregated state **1** adopted a more planer π-conjugated structure. This led us to examine the electrical conductivity of the gel obtained from **1** at room temperature by following the two-probe method with drop casting the **1** (10 mg/mL of THF) on the surface of an ITO glass. The corresponding *I-V* plot (SI Fig.S26) was obtained. In low voltage region (-2.5 to 5.5 V), a linear plot was obtained, however deviation from the linearity was observed for higher voltage region and this indicates the semiconducting nature of **1**.[9d,11b]

In summary, we have demonstrated that ESIPT coupled AIEE process could be utilized for tuning luminescence color of a single molecular over a wide energy range (blue-green-white-yellow). To the best of our knowledge no such example for a single molecule is available in contemporary literature. Interestingly, compound **1** exhibits bright yellow color luminescence in gel. Gel structure is characterized morphologically as well as structurally. Photophysical studies and XRPD pattern revealed *J*-type lamellar arrangement attain among molecules of **1**. Finally the solid state emitting capabilities and semiconducting nature of compound **1** may be exploited for organic field-effect transistors (OFETs) and OLEDs device fabrication.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Synthesis, characterization data, Uv-vis, luminescence & FTIR spectra, rheological study, PXRD data, *I-V* characteristic plot. See DOI: 10.1039/c000000x/

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