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ARTICLE TYPE

Naphthalene linked pyridyl urea as supramolecular gelator: A new insight in naked eye detection of I^- in the gel state with semiconducting behaviour

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The gelation and anion responsive behavior of some 3-aminopyridine-based urea molecules **1-5** have been examined. Of the different pyridyl ureas, compounds **1** and **2** form instant gel from DMSO/H_2O and DMF/H_2O solvents. Between the gels **1** and **2**, only the gel state of **2** has been noted, for the first time, to detect iodide ion over a series of other anions through a colour change involving no phase transformation. Furthermore, the gel state of **2** is poor semiconductor and the presence of iodide ion considerably enhances its conductivity that varies with temperature.

Introduction

The design and synthesis of small low molecular weight gelators (LMWG) capable of forming supramolecular gels draws considerable attention, not only because of numerous applications of gels, but also due to poor understanding of gelling behaviour of gelators with structural diversities.[1] Various non-covalent interactions such as hydrogen bonds, π-π stacking, metal coordination, and van der Waals interactions etc., are involved during organization of the small molecule gelators into three dimensional networks that enable organic solvent or water molecules to be trapped under appropriate conditions to form supramolecular gels.[2] Molecules of this class bear different functional groups that take part in non-covalent interactions for their organization. Out of several functional entities, urea and thiourea groups are of special attention because they form directed, strong hydrogen bonds[3] that regulate the molecules to form aggregate. Urea-based oregano gelators having pyridyl groups in the backbone exhibit unique properties in gel chemistry. The gelation abilities of these molecules depend on the hydrogen bonding interactions of the urea moieties, coupled to the spacers of different kinds. Steed *et. al.,* have already shaded light on this topic.[4] In their report, they have unveiled the different possibilities of hydrogen-bonded networks of pyridyl ureas in solution and solid states. The gelation abilities of such compounds either alone or in presence of metal ions[1a,4] and carboxylic acids[4c,d] are also explored by Steed *et. al.* and others. Inspite of reasonable progress,[1a,4] the use of pyridyl ureas in the formation of anion-responsive supramolecular gels is unexplored and thus challenging.

During our ongoing work on ion recognition using chemosensors,[5] we wish to shed light on anion responsive behaviour of the gel states of some simple pyridyl ureas **1**-**5** (Fig. 1). It is to note that the urea molecules **1**,[6a-b] **3**[3b] and **5**[6c] are reported earlier by Steed and other groups. However, compound **2** which is the main focus of this manuscript is new and exhibits excellent anion responsive behaviour in its gel state. Of the urea molecules, **1** and **2** display excellent gelation abilities in several aqueous organic solvents. Interestingly, while the hydrogels of both **1** and **2** are thermo reversible, pH responsive and hydrogel of **2** is observed to be the good detector of iodide ion through a color change, a new observation for the first time.

Iodide recognition by artificial synthetic receptor is an important aspect in supramolecular chemistry. Iodide is an important halide linked with several biological processes such as neurological activity and thyroid function.[7] In this horizon, although there are very few reports on fluorescent recognition of iodide,[8] till date no report on naked eye detection of iodide using gel phase of small molecular weight supramolecular gelators is known in the literature.

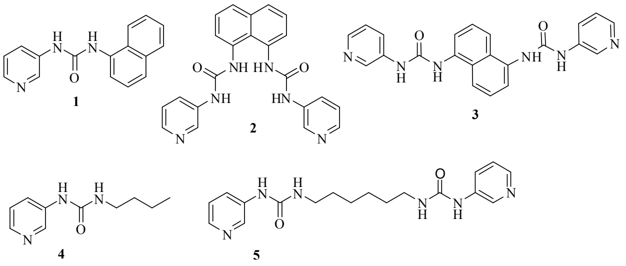

Fig. 1 Structures of 3-aminopyridyl ureas **1**-**5**.

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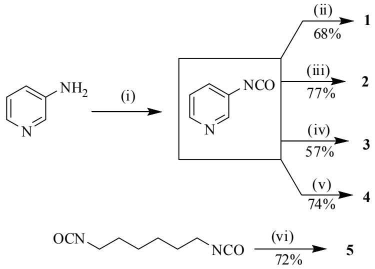
†Electronic Supplementary Information (ESI) available: experimental details and spectroscopic data, gelation profile, SEM image and different plots, pH responsive behaviour, anion responsive nature of **1**, interference study, binding constant determination, fluorescence spectra for **1** and **2** See http://dx.doi.org/10.1039/b000000x/

In addition to pH and iodide ion responsiveness, the hydrogels of **1** and **2** are weakly semiconducting. In presence of iodide ion the conductivity of the hydrogel of **2** that varies with temperature is considerably enhanced. Low molecular –weight organic gels often possess semiconducting properties which render them unique materials for different electronic applications.[9] Semiconducting properties of the gels usually arises due to self-organization of the gelators under the influence of weak forces. The tuning of these weak forces controls the spatial arrangement of individual molecular component within the aggregates. Such arrangements may establish a long-range charge delocalization within the gel matrix[10] and imparts the semiconducting property. The strength of such electrical properties is influenced by the π-surface of the gelators that contribute to the stacking interaction. Addition of some dopants sometimes reinforces the semiconducting property of the gels presumably by inducing a subtle arrangement of the gelators in the gel matrix.

Results and discussion

The reported compounds **1**, **3** and **4** were synthesized by coupling of different amines with 3-pyridyl isocyanate, obtained from the reaction of 3-aminopyridine with triphosgene (Scheme 1). Compound **2**, a new analogue of **3** was obtained following the same reaction protocol. Compound **5**, reported earlier by Steed *et al.*,[6c] was obtained from the reaction of 1,6-diisocyanato-hexane with 3-aminopyridine in dry CH_2Cl_2. All the compounds were characterized by usual spectroscopic techniques.



Scheme 1. Reagents and conditions: (i) dry CH_2Cl_2, triphosgene, Et_3N, rt, 1h; (ii) 1-naphthyl amine, dry CH_2Cl_2, rt, 16h; (iii) naphthalene-1,8-diamine, dry CH_2Cl_2, rt, 24h; (iv) naphthalene-1,5-diamine, dry DMF and dry CH_2Cl_2 mixture solvent, rt, 26h; (v) *n*-butyl amine, dry CH_2Cl_2, rt, 16h; (vi) 3-aminopyridine, dry CH_2Cl_2, Et_3N, rt, 24h.

Close observation of the structures in Fig. 1 reveals that 3-aminopyridyl urea is connected to different aromatic and aliphatic scaffolds. Depending on the position, the pyridyl urea motif may assume different orientations. This may result in different types of hydrogen bonded networks in solution. Thus the gelation propensity of the compounds in different solvents were studied (Table 1S). While compound **1** exhibited gelation in CH_3OH/H_2O and $DMSO/H_2O$, compound **2** formed stable gel from $DMSO/H_2O$ and DMF/H_2O solvent combinations. Morphologies of gels from $DMSO/H_2O$ show fibrous networks as confirmed from SEM images (Fig. 2). Structural differences between the two compounds left a significant effect on the morphology of the gels. While hydrogel of **1** is comprised of very thin, irregular, twisted fibres with a large number of void spaces to trap the solvents (Fig. 2a), compound **2** in gel state exhibits long, more regularly, closely spaced fibres to form the 3D network for solvent trapping *via* surface tension (Fig. 2b).

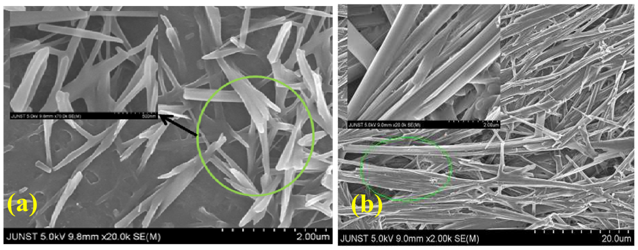


Fig. 2 SEM images of xerogels of (a) **1** and (b) **2** prepared from DMSO – water (1:2, v/v).

To our belief, compound **1** under the influence of hydrogen bonding of the urea groups, π-stacking of the naphthyl units and role of water in linking the pyridine ring nitrogens[11] make a possible cross-linked arrangement in solution to undergo gelation (Fig. 3a). Likewise, compound **2** may follow linear packing arrangements involving the urea motifs in different ways shown in Fig. 3b and 3c. Instead of linear polymeric arrangement, the molecules of **2** may assume columnar packing involving similar weak non covalent forces as cited in Fig. 3b and 3c.

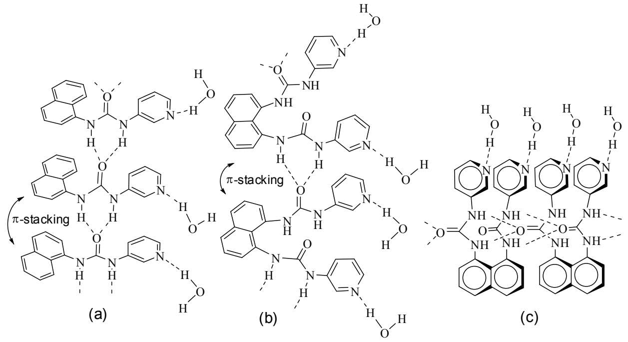


Fig 3 Suggested modes of interaction: (a) for **1**, (b) and (c) for **2** to form the networks in solution.

The π-stacking effect of the naphthalene motifs in **1** and **2** imparts stability to the network. Under the similar conditions, compounds **4** and **5** devoid of naphthalene groups were unable to form gel in different solvents (Table 1S) and thereby indicated the key role of aromatic stacking. On the other hand, inspite of the presence of naphthyl unit, compound **3** (isomer of **2**) did not exhibit gelation. We, therefore, presume that not only the aromatic π-stacking but also the alignment of the pyridyl ureas in forming hydrogen bonded cross-linked network in solution is crucial. It is mentionable that although compound **5** did not form gel, its copper complex as reported by Steed *et al.*, forms colored gel.[6c]

A shouldering at 324 nm in UV-vis spectrum of **1** in the gel state in comparison to its sol state in DMSO: H_2O (1:2, v/v) is likely to be due to the formation of aggregate in the gel (Fig. 4a). In fluorescence, a weak emission at 374 nm in the sol state of **1** was significantly intensified in the gel state showing the emission at 365 nm (Fig. 4b). This fluorescence enhancement is due to aggregation formed and is in accordance with the observation reported by several groups. Similarly, in **2** the appearance of a much prominent peak at 327 nm in UV (Fig. 4c) and a broad peak

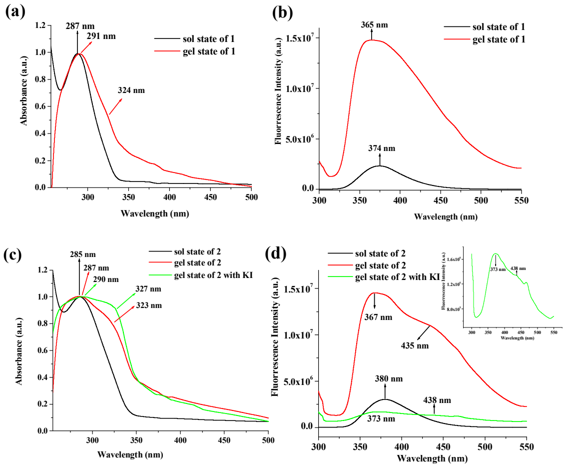


Fig. 4 Comparison of UV-vis (a) and (b) fluorescence spectra of **1** in the sol and gel states; Comparison of UV-vis (c) and (d) fluorescence spectra of **2** in the sol and gel states [solvent combination for sol state: DMSO: H_2O (1:2, v/v)].

at 435 nm in emission with much broadening (Fig. 4d) corroborated the formation of stronger aggregates than the case with gelator **1**. In this aggregate, π-stacking interaction of the naphthalenes presumably influences to form excimer that shows emission at 435 nm. However, in both **1** and **2**, the increase of fluorescence intensity for the gel states over their sol states was assigned to the phenomenon of aggregation-induced enhanced emission (AIEE).[12] Upon aggregation the gelator molecules lose their mobility that results in the suppression of the nonradiative decay of the fluorophore in the gelator. In Fig. 4d, the quenching of fluorescence of the gel state of **2** containing I^- ion is attributed to the heavy atom effect of I^- ion.[13]

For better understanding the nature of emission, fluorescence decay (Fig. 2S and 3S) and excitation spectra were measured. In time resolved emission, while the decay profile for **1** in sol state monitored at 370 nm was fitted monoexponentially, in gel state it was fitted with two components $\tau_1 = 0.68$ ns (83%) and $\tau_2 = 2.08$ ns (17%). The component 0.68 ns is attributed to the radiative lifetime of naphthalene and the component 2.08 ns is accounted for the excimer originated from the naphthalene-naphthalene stacking. In comparison, fluorescence decays for **2** in the sol and gel states monitored at 370 nm were fitted with monoexponential decay. The fluorescence decay monitored at 450 nm for gel **2** exhibited biexponential decay with the components $\tau_1 = 1.56$ ns (72%) and $\tau_2 = 6.23$ ns (28%). Table 1 represents the decay profile in details and the results indicate that the lifetime of the fluorophore naphthalene in the urea molecules **1** and **2** increases in the gel state compared to their sol states. The components originated from the aggregation also show significant increase in lifetime. The same was true for gel **2** containing KI.

The excitation spectra of both the gels of **1** and **2** did not correspond in shape or position to their absorption spectra (Fig. 4S, 5S and 6S). These differences provided evidence for the 'trapping' or localization of excitation in the aggregate.[14] The excitation spectra of **1** and **2** in the sol states also did not superimposable with their respective absorption spectra and the spectral appearance were similar to that of the cases noted in gel states. These findings indicate that in solution there is no single species in the ground state. Instead some aggregated forms coexist with the sole species.

Table 1. Fluorescence decay time (τ) with preexponential factors (c) for **1** and **2** in sol and gel states ($\lambda_{ex} = 295$ nm) in DMSO: H_2O (1:2, v/v).

Compounds (State)	**λ_{em} (nm)**	**τ_1(c) in ns**	**τ_2(c) in ns**	**τ_{av} in ns**	**χ^2**
1 (Sol state)	370	0.34 (100%)	-	-	1.11
1 (Gel state)	370	0.68 (83%)	2.08 (17%)	0.92	1.18
2 (Sol state)	370	0.32 (100%)	-	-	1.20
2 (Gel state)	370	1.84 (100%)	-	-	1.16
2 (Gel state)	450	1.56 (72%)	6.23 (28%)	2.86	1.16
2 with KI (Gel state)	370	0.70 (100%)	-	-	1.02
2 with KI (Gel state)	450	1.32 (82%)	8.14 (18%)	2.54	1.12

To realize the role of urea functional groups in non covalent interaction to establish the network for gelation, we recorded the FTIR spectra of the compounds **1** and **2** in their amorphous and gel states. Comparison of the FTIR spectra for the amorphous and gel states of both **1** and **2** reveals that urea carbonyl stretching frequency in each case moves to the lower region by 4 cm^{-1} unit (Fig. 5). This undoubtedly indicates the involvement of the urea groups in hydrogen bonding to establish a cross linked network in the solution.

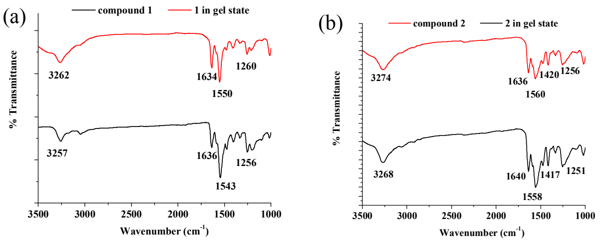


Fig. 5. FTIR spectra in amorphous and gel states of **1** (a) and (b) **2**.

Both gels of **1** and **2** derived from DMSO/H_2O showed sharp T_g. A plot of T_g vs. W/V clearly reveals that the higher the gelator concentrations greater are the stabilities of the gels (Fig. 6a). Thermal stability of hydrogel of **2** is relatively greater than the hydrogel of **1**. The viscoelastic behaviour of the gel of **2** was characterised by rheological measurements, in which the storage modulus G' and the loss modulus G'' were measured as a functions of strain and frequency. As shown in Fig. 6b, the G' was around four times greater than G'', which indicated the

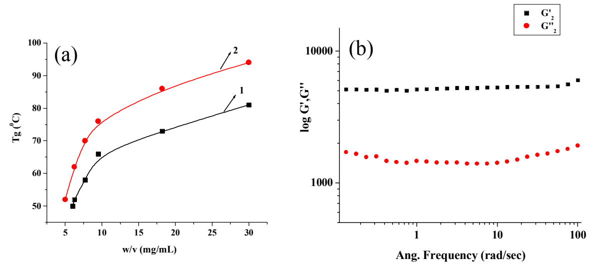


Fig. 6. (a) Variation of gel melting temperature (T_g) with increasing concentration of gelators; (b) Rheological data for DMSO: H_2O (1:2, v/v) gel of **2**.

dominant elastic character of the hydrogel exhibiting the clear thixotropic property.[15]

Hydrogels of both **1** and **2** were observed to be pH responsive. While in strong acidic environment the gels are broken, they started to appear when the pH of the medium lies in the range 5 to 6 for **2** and 6 to 7 for **1** (Fig. 8S).

Since anions are known to compete with the urea hydrogen bonds,[16] we were keen to know whether anions can induce the breaking of hydrogen bonds and π-stack assisted assemblies of both **1** and **2**. Interestingly, while the gel of **1** from DMSO/H_2O was insensitive to anions (Fig. 9S), under identical condition the gel state of **2** was responsive selectively to iodide ion. In presence of iodide ions (counter cations: tetrabutylammonium, potassium and sodium; Fig. 10S), the gel state of **2** exhibited sharp reddish brown coloration with time showing no phase transformation and distinguished it from other anions examined (Fig. 7). A similar observation was noticed when the DMF/H_2O gel of **2** was undertaken in the study. However, the color intensity of the gel was dependent on the amount of the gelators (Fig. 11S) as well as the concentration of KI (Fig. 8) taken in the study. It was observed that iodide ion of ~10^{-2} M was much efficient in bringing intense color of the gel. This iodide-induced colored gel remained unchanged for more than three months.

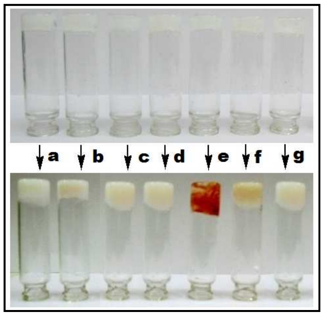


Fig. 7 Photograph showing the changes in DMSO: H_2O (1:2, v/v) gels of **2** (10 mg/ mL) after keeping contact with 1 mL aqueous solution of different anions ($c = 9.5 \times 10^{-2}$ M as K^+ salt) for 2h. Similar finding was observed when gels were prepared by adding aqueous solution of respective anion ($c = 9.5 \times 10^{-2}$ M as K^+ salt) to the DMSO solution of **2** in 2:1 (H_2O:DMSO) ratio [a = HSO_4^-, b = AcO^-, c = Cl^-, d = Br^-, e = I^-, f = F^- and g = $H_2PO_4^-$].

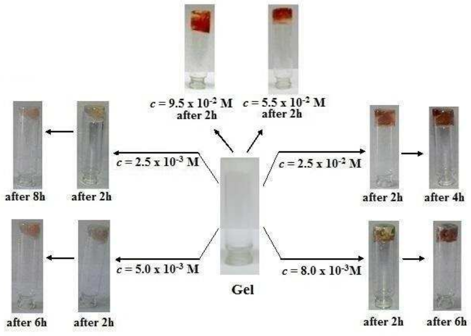


Fig. 8 Photograph showing the color changes in the DMSO: H_2O (1:2, v/v) gels of **2** (10 mg/ mL) with time on contact with 1 mL aqueous solution of KI of different concentrations;

A linear increase in T_g with the added amount of KI in Fig. 9a further depicts the I^- ion dependence stability of the gel. SEM images of the gel of **2** either in presence of KI (Fig. 12S) or in presence of TBAI (Fig 9b) reveal the more fibrous network than the gel with no I^- ion. As reason, we strongly believe that the cooperative hydrogen bonding interactions of the pyridyl ureas in **2** with iodide ion or pyridine ring nitrogen bonded water-iodide supramolecular interaction[17] pack the gelators of **2** efficiently due to which the stacking interaction among the naphthalene units is reinforced. In this context, in presence of I^-, the broadening of the emission at 436 nm of **2** with significant quenching (Fig. 4d) supports more aggregation of the gelators compared to the gel state of **2** containing no I^- ions. This is in contrast to **1** which contains one pyridyl urea. Iodide binding-induced close packing of gelators of **2** possibly influences the charge transfer interaction that results in color formation in the gel state. In the event, the possibility of formation of I_3^- ions (in situ generation either through oxidation of I^- in presence of DMSO[18a] or photooxidation of I^- in the gel phase) and its involvement in charge transfer complex formation cannot be ruled out. To gain insight into this fact, we recorded the UV-vis spectrum of the iodide-induced colored gel of **2** by dissolving in DMSO (Fig. 10). A band at 370 nm in the spectrum probably intimates the presence of I_3^- ions[18b] that coexist with I^- ions in the gel network.

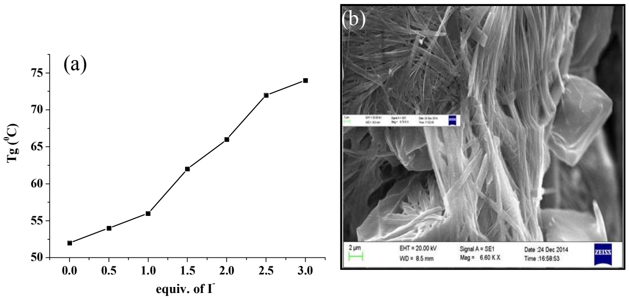


Fig. 9 (a) Variation of gel melting temperature (T_g) of DMSO: H_2O (1:2, v/v) gel of **2** (5 mg/ mL) with increasing amount of KI (c = 0.2 M); (b) SEM image of the gel of **2** containing TBAI.

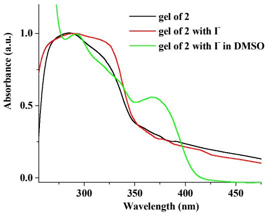


Fig. 10 Normalized UV-Vis spectra of the gel of **2** under different conditions.

Interestingly, when this colored gel was impregnated with aqueous solution of $AgNO_3$ (c = 0.5 M) and was kept for longer time (~ 16 h) the intensity of reddish brown colour was slowly reduced due to loss of I^-/I_3^- ions as Ag- complexes from the gel medium (Fig. 11).

The iodide-induced color change of the gel state was also noticed in the presence of other halides. In the study, an almost colorless gel of **2** from DMSO/H_2O exhibited a faint brown color in the presence of 100 μL of each solution of KF, KCl and KBr (c = 0.2 M). But addition of 500 μL of KI (c = 0.2 M) solution to this medium brought about reddish brown coloration. This suggested the negligible interference of other halides in the sensing process

(Fig. 11b). This was also true in case of DMF/H_2O gel of **2** (Fig. 13S).

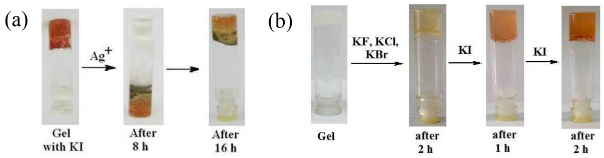


Fig. 11 (a) Photograph showing the color change of iodide treated gel of **2** in the presence of $AgNO_3$ (c = 0.5 M); (b) Photograph showing selectivity of the hydrogel of **2** (in DMSO: H_2O, 1:2 v/v, 10 mg/ mL) towards I^- in presence of other halides.

It is further to be pointed out that I^--induced colored gel of **2** loses its color on heating. On cooling, the transparent, colorless sol was slowly transformed into gel with its original reddish brown coloration (Fig. 12). This observation underlines the fact that I^-/I_3^- chelation-based arrangements of molecules of **2** are presumably destroyed on heating and charge transfer no longer exists in the sol state. But on cooling, the original arrangement of molecules is set up due to which charge transfer-induced coloration is further noticed in the gel state.

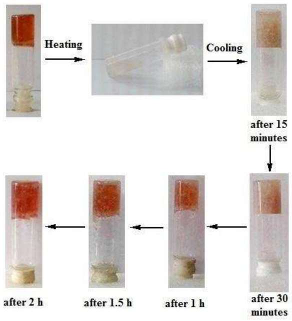


Fig. 12 Photograph showing the change in colour of the KI containing gel of **2** in DMSO: H_2O (1:2, v/v) upon heating and cooling.

The iodide specific interaction of **2** in solution was realized from greater quenching in emission of **2** in the presence of tetrabutyl ammonium iodide (TBAI) in DMSO: H_2O (1:2, v/v) (Fig. 13a). Other anions showed weak interaction (Fig. 13b). However, small change in emission of **1** upon adding iodide ions suggested its weak interaction in solution (Fig. 14S). UV-vis titration of the solution of **2** with TBAI did not produce any color of the solution and also any charge transfer band in the spectra (Fig. 15S and 16S). Even the absence of peak in between 340 nm to 370 nm during titration indicated the mere existence of I_3^- in solution. This is in contrast to the findings in the gel state (Fig. 10). These observations enable us to conclude that I^-/I_3^-- induced charge transfer only exist in the gel state.

The Benesi-Hildebrand plot[19] of the change in emission intensity of **2** against the reciprocal of the TBAI concentration gave a linear fit, characteristic of 1:1 complexation from which the association constant was estimated as 5.34 x 10^2 M^{-1} (Fig. 17S). ^1H NMR spectrum of **2** in the presence of equiv. amount of TBAI in d_6-DMSO/D_2O mixture solvent was observed to be negligibly perturbed and thereby suggested very weak or almost no interaction of I^- into the urea binding site. In this context, it is thus believed that in fluorescence, I^- ion-induced quenching of emission of **2** in solution phase is maximally due to heavy atom effect[13] rather than strong hydrogen bonding interaction.

In order to gain insight into the current conductivity of the gels, we measured the current (I)–voltage (V) characteristics of the gels of **1** and **2** at room temperature (Fig. 14a). A nonlinear increase in current with increase in voltage within the measured voltage range indicated the ideal semiconducting nature of each gel. This semiconducting nature of the gels may be attributed to the π-π stacking interaction of the naphthalene units within the gel matrix which was confirmed by comparison of the UV-visible and emission spectra of **1** and **2** in their sol and gel states. Possibly due to the greater π-stacking interaction of the naphthalenes in the gel state, the gel state of **2** with much fibrous character shows better semiconducting properties than the gel of **1**. It is to note that the observed semiconducting property of the gel state of **2** is almost independent of solvent. Interestingly, the gel state of **2** containing KI shows more than ten order increase in current at a particular voltage with respect to that of the normal gel. Such increase in current in presence of KI may be ascribed to the formation of I^- ion binding induced charge transfer complex in the gel matrix. This is similar to the report on the semiconducting property of the perylene-iodine charge transfer complex observed by Uchida *et al.*[20] The temperature dependency of the electrical behavior of the gel state of **2** in presence of KI shows thermally activated semiconducting nature (Fig. 14b). This semiconducting behavior persists upto temperature close to T_g of the gel above which rapid fall in current is observed. This occurs seemingly due to the disruption of the charge transfer complex that exists in the gel state.

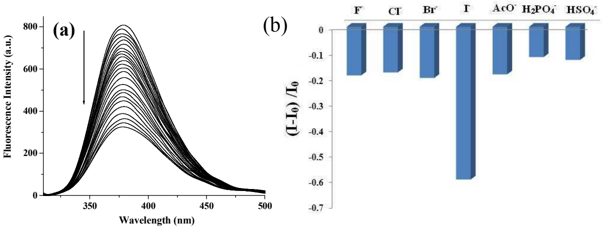


Fig. 13 (a) Emission titration spectra of **2** (c = 3.85 x 10^{-5} M) upon addition of TBAI (c = 1.54 x 10^{-3} M) (upto 30 equiv) in DMSO: H_2O (1:2, v/v); (b) Change in fluorescence ratio (λ_{ex} = 290 nm) of **2** (c = 3.85 x 10^{-5} M) at 378 nm upon addition of 30 equiv. amounts of anions (c = 1.54 x 10^{-3} M) in DMSO: H_2O (1:2, v/v).

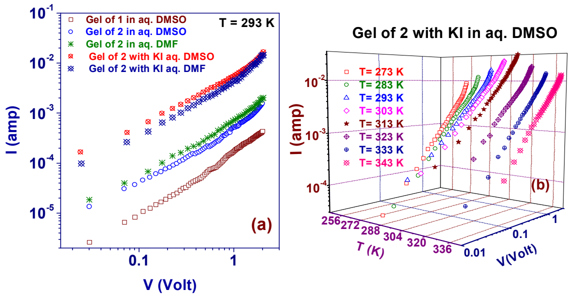


Fig. 14 (a) Comparison of **I**-V characteristics of gels of **1** and **2** at room temperature, plotted in log-log scale; (b) I-V characteristics of gel of **2** with KI, in the temperature range 273–343 K, plotted in log-log scale.

Conclusion

In conclusion, we have thus thrown light on some pyridyl urea – based some small molecular systems **1**-**5** of which naphthyl motif appended urea molecules **1** and **2** exhibit excellent gelation properties from aqueous organic solvents. Non gelation behavior of **3** (isomer of **2**) under identical conditions signifies that correct alignment of the pyridyl urea groups around naphthalene motif is essential to establish a cross-linked hydrogen bonded network in solution. The gels of **1** and **2** are pH responsive and in particular, the gel state of **2** shows anion responsive behavior. Among the different halides and other anions taken in the study, only iodide ion is sensed by the gel state of **2** through a marked change in color (from colorless to reddish brown) *via* the formation of charge transfer complex. In comparison, no change in color of the solution phase of **2** was noticed in the presence of iodide ion. To our opinion, the cross linked network of the gel phase has some role in formation of charge transfer complex. Another interesting point is while anions are usually gel breaker[21] either due to strong noncovalent interaction or deprotonation of the functional groups of the gelator, iodide ion in the present case does not show any phase change of the gel. To the best of our knowledge, such naked-eye detection of iodide by gel state without showing any phase transformation is a first time report in the literature. Furthermore, while the gel phase of **2** itself is poor semiconductor, the iodide containing gel of **2** shows greater conductivity that varies with temperature.

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Experimental

1-Naphthalen-1-yl-3-pyridin-3-yl-urea (1):[6a-b]
To a stirred solution of triphosgene (0.18 g, 0.62 mmol), in 4 mL dry CH_2Cl_2, 3-aminopyridine (0.16 g, 1.7 mmol) dissolved in 20 dry CH_2Cl_2, was added dropwise using a dropping funnel for 30 min. After complete addition of 3–aminopyridine, Et_3N (0.59 ml, 4.25 mmol) was added and stirred for another 40 min. Then 1-naphthylamine (0.27 g, 1.89 mmol) in dry CH_2Cl_2, was added to the reaction mixture and stirred. Stirring was continued for 16 h. After completion of reaction, CH_2Cl_2 was evaporated off and water was added to the residue. The aqueous layer was extracted with 2% MeOH in $CHCl_3$ (25 mL x 3) and dried over anhydrous Na_2SO_4. Purification of the crude mass by silica gel column chromatography using petroleum ether/ethyl acetate (2:3, v/v) as eluent gave the product **1** (0.3 g, 68%), mp 220-222 ^{0}C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.30 (s, 1H), 8.97 (s, 1H), 8.72 (s, 1H), 8.28 (d, 1H, J = 4.80 Hz), 8.19 (d, 1H, J = 8 Hz), 8.09-8.00 (m, 3H), 7.75 (d, 1H, J = 8 Hz), 7.69-7.60 (m, 2H), 7.55 (t, 1H, J = 8 Hz), 7.40 (dd, 1H, J_1 = 8 Hz, J_2 = 4 Hz); 13C NMR (100 MHz, d_6-DMSO): δ 153.5, 143.3, 140.3, 137.0, 134.4, 134.1, 128.8, 126.7, 126.4, 126.3, 125.6, 124.1, 123.9, 121.8, 118.6 (one carbon is unresolved); FTIR: ν cm-1 (KBr): 3263, 1642, 1587, 1555, 1414, 1264; Mass: (LCMS) 264.0 (M+1)$^+$.

1-Pyridin-3-yl-3-[8-(3-pyridin-3-yl-ureido)-naphthalen-1-yl]-urea (2):
To a stirred solution of triphosgene (0.89 g, 3.01 mmol) in 10 mL dry CH_2Cl_2 , 3-aminopyridine (0.77 g, 8.19 mmol) dissolved in 40 mL CH_2Cl_2 was added dropwise over 30 minutes followed by the addition of Et_3N (2.72 mL, 20.40 mmol). The reaction mixture was then allowed to stir for another 30 minutes. Then naphthalene-1,8-diamine (0.5 g, 3.16 mmol), dissolved in 10 mL CH_2Cl_2, was added dropwise from a dropping funnel. The reaction mixture was allowed to stir for further 24 h. After completion of reaction, a white precipitate appeared. This was filtered off and washed with warm CH_2Cl_2 followed by diethyl ether to have pure compound **2** in 77% yield (0.97 g), mp 202-206 ^{0}C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.22 (s, 2H), 8.86 (s, 2H), 8.52 (s, 2H), 8.10 (d, 2H, J = 4.4 Hz), 7.83 (d, 2H, J = 8 Hz), 7.77(d, 2H, J = 8 Hz), 7.63(d, 2H, J = 8 Hz), 7.48 (t, 2H, J = 8 Hz), 7.21 – 7.18 (m, 2H); ^{13}C NMR (d_6-DMSO, 100 MHz): 153.9, 142.9, 140.2, 137.1, 136.0, 133.8, 126.1, 125.9, 125.4, 123.8, 123.6 (one carbon is unresolved); FTIR (KBr) ν cm^{-1}: 3268, 1640, 1558, 1417; Mass (EI): 399.2 (M +1)$^+$; Anal Calcd for $C_{22}H_{18}N_6O_2$: C, 66.32, H, 4.55, N, 21.09. Found: C, 66.41, H, 4.64, N, 20.96.

1-Pyridin-3-yl-3-[5-(3-pyridin-3-yl-ureido)-naphthalen-1-yl]-urea (3)[3b]
To a stirred solution of triphosgene (0.89 g, 3.01 mmol) in 10 mL dry CH_2Cl_2 , 3-aminopyridine (0.77 g, 8.19 mmol) dissolved in 40 mL CH_2Cl_2 was added dropwise over 30 minutes followed by the addition of Et_3N (2.72 mL, 20.40 mmol). The reaction mixture was then allowed to stir for another 30 minutes. Then naphthalene-1,5-diamine (0.5 g, 3.16 mmol), dissolved in 10 mL CH_2Cl_2 containing 10% DMF, was added dropwise from a dropping funnel. The reaction mixture was allowed to stir for further 26 h. After completion of reaction, a white precipitate appeared which was filtered off and washed with warm CH_2Cl_2 followed by diethyl ether to have pure compound **7** in 57% yield (0.71 g, mp above 320 ^{0}C but turns black at 294 ^{0}C). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.38 (s, 2H), 8.98 (s, 2H), 8.66 (s, 2H), 8.21 (d, 2H, J = 4 Hz), 8.02 (t, 4H, J = 8 Hz), 7.91 (d, 2H, J = 8 Hz), 7.58 (t, 2H, J = 8 Hz), 7.36 – 7.34 (m, 2H); FTIR (KBr) ν cm^{-1}: 3280, 1638, 1591, 1558, 1478, 1261.

1-Butyl-3-pyridin-3-yl-urea (4):
To a stirred solution of triphosgene (0.58 g, 1.95 mmol) in 5 mL dry CH_2Cl_2, 3-aminopyridine (0.5 g, 5.31 mmol) dissolved in 30 mL CH_2Cl_2 was added dropwise along with Et_3N (1.85 mL, 13.27 mmol). The reaction mixture was allowed to stir for 1 h. Then *n*-butyl amine (0.46 g, 6.37 mmol), dissolved in 10 mL CH_2Cl_2, was added dropwise from a dropping funnel. The reaction mixture was allowed to stir for further 24 h. After completion of reaction, solvent was evaporated off. The crude mass was extracted with $CHCl_3$ (30 mL x 3). The organic layer was washed with water and dried over Na_2SO_4. Evaporation of the solvent in vacuo gave crude mixture which was chromatographed on a silica gel column using 60% ethyl acetate in petroleum ether as eluent

to give **4** in 74% (0.74 g) yield as gummy product. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.31 (s, 1H), 8.15 (d, 1H, $J = 4.4$ Hz), 8.11 (s, 1H), 8.03 (d, 1H, $J = 8$ Hz), 7.18 – 7.17 (m, 1H), 5.69 (br t, 1H), 3.25 – 3.20 (m, 2H), 1.50 – 1.43 (m, 2H), 1.37 – 1.27 (m, 2H), 0.88 (t, 3H, $J = 8$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): 156.5, 142.8, 140.2, 136.8, 126.4, 123.8, 39.8, 32.1, 20.0, 13.7; FTIR (KBr) ν cm^{-1}: 3296, 2931, 1669, 1534, 1474, 1275; Anal Calcd for $C_{10}H_{15}N_3O$: C, 62.15, H, 7.82, N, 21.74. Found: C, 62.21, H, 7.91, N, 21.59.

N, N'-Hexylene-1,6-diylbis(N'-pyridin-3-ylurea) (5):[6c]

To a stirred solution of 1, 6-diisocyanato-hexane (0.5 g, 2.93 mmol) in 15 mL dry CH_2Cl_2 , a mixture of 3-aminopyridine (0.83 g, 8.92 mmol) and Et_3N (0.94 mL, 7.32 mmol) dissolved in 20 mL CH_2Cl_2 was added and the reaction mixture was allowed to stir for 24 h. After completion of reaction, a white precipitate appeared which was filtered off and washed with warm CH_2Cl_2 followed by diethyl ether to have pure compound **5** in 72% yield (0.76 g, mp 184-186 ^{0}C); ^{1}H NMR ($CDCl_3$ containing one drop of DMSO-d_6, 400 MHz): δ 8.44 (d, 2H, $J = 4$ Hz), 8.27 (s, 2H), 8.13 (dd, 2H, $J_1 = 8$ Hz, $J_2 = 4$ Hz), 8.03 (dd, 2H, $J_1 = 8$ Hz, $J_2 = 4$ Hz), 7.18 – 7.15 (m, 2H), 5.93 (br t, 2H), 3.20 (q, 4H, $J = 8$ Hz), 1.54 – 1.51 (m, 4H), 1.21 – 1.19 (m, 4H); FTIR (KBr) ν cm^{-1}: 3337, 2931, 1638, 1564, 1119; Mass (EI): 357.2 $(M+1)^+$.

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