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A Two-Component Hydrogelator from Citrazinic Acid and Melamine: Synthesis, Intriguing Role of Reaction Parameters and Iodine Adsorption Study

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ABSTRACT

Herein, we have implemented an intimate grinding-mixing protocol (GMP) for the synthesis of a new hydrogelator from citrazinic acid and melamine. Ground mixture upon sonication, just for few second, in a suitable solvent/mixed-solvent system finally results in a gel matrix. Citrazinic acid, is decorated with ureidopyrimidone functionality and melamine is enriched with amino-pyridine functionality. Therefore, the necessary non-covalent interactions (like hydrogen bonding and π-π stacking) become a part-and-parcel, bringing a nanofibrous gel material in existence. A thorough and complete solvent dependent gelation investigation suggests that water must be present as the sole solvent or one of the members of other mixed-solvent system to successfully result in gel formation. The gel shows entangled network morphology. Different micro-analytical studies (FTIR, Powder XRD, FESEM, TEM, Rheology etc.) have been conducted for complete characterizations of the gel sample. The gel also exhibits its stimuli responsive behaviour towards different interfering chemical parameters like pH, selective anions etc. Again, it is worth mentioning that here GMP plays a key role to strongly initiate and improvise solid state self-assembly. Different non-covalent interactions procure the suitable hydrogen-bonded motif which presumably propagates upon activation in solution phase after mild sonication favouring spontaneous formation of fibrous architectures. It was also noticed that without grinding, the solid state interactions are

jeopardized and only partial gel structure prevails. Finally the available porosity in the gel framework and the enriched π-electron density within, make the gel a suitable host for adsorption of guest molecules. This information provoked us to study the reversible adsorption-desorption equilibrium of molecular iodine within the dried-gel matrix. The guest, iodine entrapment into the host occurs both from the solution and also from gas phase iodine. The complete analysis suggests that our material presents a high storage capacity of this halogen species. Therefore the study prescribes that the synthesized hydrogel material could be a suitable candidate for application in synthetic organic chemistry and would find an avenue to solve other environmental issues also.

INTRODUCTION

Gels are principally self-assembled, viscoelastic materials and in present days they are gaining increasing attention owing to their promising applications in different branches of science and technology including catalysis, sensing, environmental pollution abatement, sorption, optoelectronics, magnetism, drug delivery and so on.[1] These soft materials are usually fabricated with some typically selected molecules/ligands (called low-molecular weight gelator or LMWG) which can preferentially introduce different supramolecular and non-covalent interactions through an efficient entrapment of solvent molecules into their interstitial positions. And it has been regularly identified that the gelation process is typically a solvent dependent phenomena[2] and hence the gels are broadly classified as organogel (gelation of organic solvent) and hydrogel (gelation of water). Though other different parameters (e.g. nature of the gelator molecules, pH, temperature, selective metal ions and anions, selective complexing agents etc.) are also shown to play vital role in gelation or regulate stability.[3] Syntheses of hydrogels are now-a-days additionally favoured owing to their preferential and facile implementations in biological and environmental areas. Different attempts have been made and successfully executed for the design of new molecular skeletons which will efficiently result in hydrogelation. Among the extensive assortments of such skeletal motifs, molecules encompassing urea and/or ureido-type functionalities in their structural backbones are the promising candidates to ensure the favourable construction of the gel networks and fibrilar assemblies in aqueous medium.[4,1h] These archetypal functionalities have been shown to effectively introduce the different non-covalent interactions essential to construct the self-assembled nanofibres in the gelation process.

Melamine, a commercially available molecule with ‘triazine’ ring in its structural-scaffold has been employed recently as a successful gelator candidate in assistance with another different molecule.[5] The second molecule is chosen in such a way so that it can easily form stable hydrogen-bonded motif. Therefore the choice of the second candidate is very selective and thus provides a wide scope to explore new molecules enabling the gelation with melamine. We have employed citrazinic acid (CZA), a heterocyclic compound having a pyridine backbone with two hydroxy substitutions at C–2 and C–6 respectively and a carboxylic acid group substitution at the C–4 position of the molecule, as the other member.

Given the biological need of iodine in medical science as well as its other relevance,[6] adsorption and storage of this molecular halogen is a focused theme in today’s advance materials research community. Therefore a variety of functional materials, though few in numbers, including metal-organic frameworks (MOFs), coordination polymers (CPs), porous-organic frameworks (POFs), zeolitic inorganic clusters (referred as ‘Zeoball’), chalcogenide aerogels and polysulfide-ion intercalated layered double hydroxide (LDH) materials have been recently explored to meet this purpose.[7] Hence there is still a wide scope to make use of other functional materials to accomplish the perspective.

Here we have taken melamine and citrazinic acid collectively in a definite molar ratio and they were ground well after thorough mixing in the solid state following grinding-mixing protocol (GMP). The ground mixture (or the two-component gelator system) was then sonicated just for a few seconds in a suitable solvent/mixed-solvent system and a whitish-yellow coloured gel resulted in immediately. The gel phase, confirmed preliminary, through the widely acclaimed “inversion of the glass vial” technique. Solvent dependent gelation study suggests that water should be present as one of the essential component in the solvent/mixed-solvent system for efficient gelation. Effects of grinding and sonication were also studied in the event of gelation. The gel was stable at acidic/neutral pH but dissolves in alkaline pH. Rheological studies suggest the significantly higher gelation behaviour of the synthesized material. Again, the dried-gel shows considerable porosity. The material is also enriched with π electrons cloud as evidenced from the skeletal characters of the constituents. These features jointly made it a suitable host for adsorption of guest molecules. It was noticed that the dried-gel matrix shows efficient adsorption behaviour as well as storage platform for molecular iodine in its interior porous architectures. To the best of our knowledge such high level adsorption of molecular iodine as well as its storage for long-time scale in a supramolecular hydrogel matrix is novel and reported here for first time.

EXPERIMENTAL SECTION

Materials: All the reagents were of analytical grade and used without further purification. Citrazinic acid and melamine were purchased from Aldrich. The sodium/potassium salts of fluoride, chloride, bromide, iodide, sulfate, nitrate, thiosulfate, thiocyanate, cyanide, dihydrogen-phosphate, hydrogen-phosphate, sulfide and nitrite, hydrochloric acid and sodium hydroxide were purchased from Merck, India. The different solvents (methanol, ethanol, isopropanol, acetonitrile, dimethylformamide, dichloromethane, benzene, toluene, chloroform, diethyl ether and n-heptane) were purchased from Sisco Research Laboratories (SRL), India.

All glassware were cleaned using aqua-regia, subsequently rinsed with a copious amount of double distilled water and dried well prior to use. Double distilled water was used throughout the course of the experiment**.**

Preparation of the gel:

In preparation of the two-component gel, 1 mmol citrazinic acid (CA) and 1 mmol melamine (MA) were weigh-out and taken together in an agate mortar. The mixture was ground well for about half-an hour and a whitish-yellow solid fine powder mass was (CAMA) obtained. A desired quantity (10 mg) of the powder was placed in a glass vial and 1 mL of the desired solvent was added to it. The suspension was sonicated for a while (few seconds only) in an ultrasonic bath and shaken occasionally to get a well-dispersed suspension of the mixture. Here it is worth mentioning that for non-aqueous solvent (primarily chosen for well dispersion of the grinded mixture), addition of just few drops of water molecules (50-100 μL) to the well-dispersed suspension further followed by sonication just for few seconds immediately resulted in a whitish-yellow coloured gel. The gel state was primarily confirmed (i.e. before performing the rheological experiments which ultimately supports the characteristics of a gel as a new synthesized hybrid material) by the retardation of flow of the materials upon "inversion of the glass vial". The typical gelation was found to strictly depend on the quantity (equivalent) of CAMA added to a definite volume of the solvent/solvent mixture.

RESULTS AND DISCUSSION

Typical selection of specific ligands is an essential criterion for the design and engineered fabrication of a new gel material. And in this context, the ligands (or the gelators) preferentially enabling different non-covalent interactions like hydrogen bondings, vander Waals interaction, π....π interaction etc. usually been inherited and talked about so-far for the generation of one-dimensional architectures suitable for gelation . The gelators encompassing urea and/or ureidopyrimidone functionalities are the promising candidates to ensure the favourable construction of such soft-functional materials (hydrogel/organogel/metallogel) as has been well documented by Steed et al.[4] and also by other research groups[4]. Ligands with thiourea functionality have also been explored recently ensuring gelation.[1j,k,m] This tradition therefore opens up an avenue to welcome new molecular systems bearing the above functionalities in their structural skeleton to promote the scope of gelation and subsequent applications. Here we have employed citrazinic acid collectively with melamine in studying the gelation behaviour. The molecules were subjected to ground together through grinding-mixing protocol (GMP) and finally the feasibility of the ground mixture (or more specifically, the two-component gelator system) was found suitable to study the gelation strategy.

Synthesis

In preparation of the gel, citrazinic acid and melamine (1:1 mmolar ratio) were ground well which then resulted in a whitish-yellow solid powder mass (CAMA) (Fig. 1a). A desired quantity of the powder, taken in a suitable solvent/mixed-solvent system, was sonicated just for few seconds, it immediately results in the formation of a whitish-yellow coloured gel for which the gel state was primarily confirmed through the widely acclaimed “inversion of the glass vial” technique (Fig. 1b). Here it is worth mentioning that water molecule should present as an essential component either in neat (i.e. purely water medium) or in mixed-solvent system (i.e. methanol-H_2O; ethanol-H_2O; CH_3CN-H_2O) to trigger the gelation. In the mixed-solvent system 50-100 μL of water was used. The rest part (950-900 μL) was the organic solvent as described above. Therefore the ratio of non-aqueous solvents to water was 19:1 – 9:1 (v/v). In non-aqueous solvent system, the gelator (CAMA) either loses solvents or flows freely indicating the partial/weak gelation resulting from the less population of the formed gel fibers in the non-aqueous solvent medium. Therefore water molecules play a fundamental role in the gel formation protocol from the two-component gelator. Here it is worth noting that the gel prepared in CH_3CN-H_2O solvent system was employed for the different experimental studies.

FTIR

Fig. 2 shows the FTIR spectrum of melamine, citrazinic acid and the air-dried gel in single window. For melamine, the –NH_2 vibrational modes (N–H stretching mode) appear at ~3476 cm^{-1} and 3416 cm^{-1}. Similarly the bands in the ~1430-1700 cm^{-1} range presents the CN stretching and NH_2 bending vibrations. The bands at lower wavenumber region (e.g. 810 cm^{-1}, 1022 cm^{-1}) presents ring deformation modes.

On other hand, for citrazinic acid, the modes, arising principally from the torsion, stretching and bending vibrations of the pyridine ring moiety and the externally attached –OH group of the molecule, are identified. We observed two broad IR bands at ~3116 and ~2920 cm^{-1} which appears due to the N–H and C–H vibrations. The broadening of the vibrational signatures may primarily signify the presence of more than one forms of the CZA molecule in the solid state. Again we observed a medium intense band at ~990 cm^{-1} with the weak appearance of a band at ~1060 cm^{-1}. These two bands (deformation mode of N–H vibration) along with the broad band at ~ 3113 cm^{-1} advocate that here the N–H bond is involved in H-bonding. Two strong bands were observed at ~1695 and ~1605 cm^{-1}. These vibrations are from $\nu_{C=O}$ of the keto group of the imine tautomeric form and from $\nu_{C=C}$ of the ring. Similarly the two strong bands at ~1310 and 1250 cm^{-1} were noticed and these bands appear owing to the $\nu_{C–O}$ and $\nu_{C–N}$ vibrational modes. Therefore this result supports the existence of tautomeric form of CZA even in its solid phase. Again the bands at ~1415 and ~1530 cm^{-1} are from $\nu_{S \text{ and }} \nu_{as}$vibrational modes of the –COOH moiety. The splitted bands at ~1467 and ~1485 cm^{-1} emerge from the $\delta_{N–H}$ and $\nu_{C=N}$ modes of vibrations. The different vibrational bands at lower frequency window present the torsional modes and bending modes of different vibrations.

However, the spectral signatures of the individuals (melamine and CZA) are significantly changed in FTIR spectrum of the air-dried gel. There were distinctive alterations in the peak positions and their intensities of the major vibrations involving the –N–H and –COOH moieties. This clearly indicates the preferential engagements of the different functional groups of the gelator components in the gel formation.

Powder X-ray Diffraction

The PXRD pattern of the dried gel is shown in Fig. 3a.The pattern clearly differs from the patterns of its individual components and even from the pattern of the physical mixture (Fig.

3b). We can observe the presence of a broad and most intense peak at 27.8° associated with a shoulder peak at 25.7°. Few other less intense peaks are also observed at low-angle (eg. at 8.7, 11.6, 13.1, 15, 17.6 and 19.4°) though we hardly observed any diffraction above 40°. These features suggest the low-crystalline nature of the sample. However the closely-spaced low-angle peaks prescribe a large unit cell consistent with the extended hydrogen bonded patterns in the crystal packing through the employment of unsymmetrical hydrogen bonding fragments of the citrazinic acid molecule. The most intense peak at 27.8° corresponds to a *d* spacing of 3.3 Å and as reported in the literature,[8] this value is very close to typical π–π stacking interactions in the crystalline materials (either in single crystals or in hydrogel) involving melamine as one of the essential structural counterparts. This peak position has also been observed for hydrogels involving guanosine/bromo-guanosine molecules and has been reported as the result of allied stacking interactions.[8] Therefore, the above identity in the diffraction pattern with the reported results indicates a similar type of bonding/packing patterns within the gelator components in our case.

Electron Microscopy

Fig. 4 presents the typical FESEM images of the as-synthesized gel (gel obtained from 10 mg CAMA in 1 mL acetonotrile in presence of 100μL H_2O following the method described in synthesis). The panoramic image in Fig. 4a is an overview of the high-yield grown dense fibrillar network. The morphology is comprised of intertwined nanofibres which spontaneously self-assemble to form the network structure. The fibres are several micrometers long. The individual fibres are also observed to simultaneously assemble to result in bundled aggregates (Fig. 4b). Along with the fibrillar morphology, formation of micrometer long nanobelts was also observed. Fig. 4c presents the TEM images of the gel where the long, entwined fibres are clearly observed. The ultrathin natures of the fibres are also clearly noted from these TEM images. Close inspection of the images also reveals porous interior of the nanofibres/nanobelts (Fig. 4d). The FESEM images of the gels for other two different ratio of citrazinic acid and melamine, (3:1) and (1:3) respectively, are presented in Fig. S1 though no major morphological alterations were noticed. Fibrous aggregates were commonly observed in every case.

Solvent Effect

The solvent gelation ability of the bi-component gelator (CAMA) system was studied in a couple of pure and mixed solvents. Here it is worth noting that the solvents employed were either polar protic or polar aprotic in nature due to the insolubility of the gelator system in common nonpolar solvents. Fig. S2 presents the corresponding FESEM images of the materials (obtained after gelation/partial gelation/pecipitation of CAMA with the corresponding solvents or mixed-solvents systems). It was interesting to note that fibrous morphology was observed in only water or in mixed-solvent systems having water as one of the components (Fig.S2a, S2b and S2c). In other solvent systems like in only methanol, methanol-DMF and only DMF, the morphology alters distinctively (Fig.S2d, S2e and S2f). Here it is also important to note that in these solvent systems we did not observed stable gel formation. Only partial gelation (in methanol) or precipitation (in DMF and methanol-DMF) was noticed. It is now well known that large volumes of appropriate solvent molecules are trapped in the interstitial sites of the assembled nanofibres and directs the gel formation. Table S1 presents the complete observation of the experimental results which clearly depicts that delicate balance of the Kamlet-Taft solvent parameters primarily contribute to the state of the gelation.[9,2d] The table also shows the utmost protogenic ability of water. Hence it is anticipated that strong hydrogen bonding ability of water molecules play the key function in the gel formation. The available protons of the gelator backcone interact with water (solvent) through hydrogen bonding and help in propagation of the parent molecular assembly. This continuous propagation in all directions finally brings about extensive formation of hydrogen-bonded network and results in formation of the gel. But this propagation could only be favoured in protic medium through hydrogen bonding assembly. Water molecules being the stronger hydrogen bond donors, could assist the propagation most efficiently. Hence, the gelation is strongly favoured in aqueous medium. However weak hydrogen bond donor systems (eg. CH_3OH, C_2H_5OH. iPrOH etc.) could also perform the job (propagation of the assembly) but less competently than water and results in either weak or partial gelation. Therefore to achieve the stable gel formation in mixed-solvent system, the presence of water as an essential component of the mixed-solvent system is readily understandable. This proposition could also be corroborated from the observation that in methanol-water solvent system, the grinded mixture (CAMA) form gel with fibrous architectures (Fig. S2b) whereas in pure methanol, the formation of nano-bundles composed of relatively short-length nanowires were observed throughout (Fig. S2d). Thus the competence of hydrogen-bonding of the entrapped solvent molecules plays the critical role in formation of the robust gel network.[2]

An Overview on the Gel Formation: Reviewing the Function of Grinding and Sonication

To have an insight into the gelation process by the two-component hydrogelator, we go through the literatures which suggests that the gelator molecules favour the formation of one-dimensional nanostructure/fibre (instead of crystallisation or precipitation as most commonly be observed/expected) through hierarchical self-assembly aided with different non-covalent interactions like hydrogen bonding and π-stacking.[10] These nanofibres finally entangle throughout and form the supramolecular gel. However, the gelation process is typically solvent dependent. Therefore the simultaneous and thoughtful selections of gelator molecules with suitable structural backbone to trigger the aforesaid supramolecular interactions as well as the choice of appropriate solvent systems are the essential parameters to support the favourable formation of the gel. Here our consideration about both the components (citrazinic acid and melamine) of the gelator provides the appropriate platform to successfully impart the non-covalent interactions directed self-assembly. The molecular structure of CZA which appears as yellow powder in the solid state is shown in Fig. S3. However, the molecule can also exist as keto-imine tautomeric form.[11] The pKa values for the acidic –COOH and the phenolic –OH groups of the CZA molecule are reported to be 4.0 (±0.04) and 11.04 (±0.01) respectively. The molecule, is decorated with ureidopyrimidone functionality and therefore favours the hydrogen-bonded assembly with the other member, melamine, through the formation of 'supramolecular synthon' [–N–H(melamine)••••O=C<(citrazinic acid) and –N–H(citrazinic acid)••••N(melamine)]. This synthon majorly drives the self-assembly and has been observed for other systems as well as in complementary nucleobase pairs. Thus the hydrogen bonding assembly between citrazinic acid and melamine could be considered as the prototypes of different 'donor-acceptor' arrangements.[12] Such plausible interactions with their theoretical understandings have been nicely interpreted by Steed et al. for hydrogelation with uric acid-melamine systems.[12a] Our assembly also favours such π–π stacking interactions through the suitable molecular components (CZA and MA).

Here it is worth noting that we first weigh out equimolar mixture of citrazinic acid and melamine and then the grinding-mixing protocol (GMP)[13] was followed. The ground mixture was then sonicated a little in suitable solvent system as mentioned earlier which spontaneously results in hydrogelation. We have also characterized the ground mixture (gelator) by FTIR and XRD analyses. Here it is worth noting that the XRD pattern of the ground mixture (Fig. S4a) shows the presence of diffraction peak at 27.8° (marked in the figure). This peak resembles the main diffraction peak of the XRD profile of the dry gel. This clearly suggests the true precursor nature of the ground mixture for the formation of the hydrogel. The powder XRD pattern of the un-ground physical mixture of melamine and citrazinic acid is also presented in Fig.S4b. The difference in the diffraction patterns in Fig. S4a and S4b clearly suggests that the ground mixture, synthesized following the grinding-mixing protocol (as described in our MS), is not the simple physical mixture of citrazinic acid and melamine (also in 1:1 ratio) and indeed a new compound (gelator) which spontaneously forms gel in aqueous solvent. Again, the FTIR pattern (Fig. S4c) also differs from the FTIR patterns of citrazinic acid and melamine. It was also noticed that if the solids (CZA and MA) were just mixed thoroughly without grinding and then subjected to sonication in the properly chosen solvent, surprisingly the structures change from fibrous entangled network structures to rod-like nanostructures (Fig.S5). From these experimental results we could conclude that the grinding-mixing protocol for citrazinic acid-melamine (in 1:1 molar ratio) in fact leads to the formation of a new compound (gelator) which spontaneously forms gel in aqueous solvent. Thus this mechanochemistry[13] plays a vital role at the first stage to strongly initiate the solid state self-assembly through different non-covalent interactions which particularly propagates in solution phase through activation under mild sonication and favour the spontaneous formation of fibrous architectures. Without grinding, the solid state interactions become redundant and thus the weak interactions in solution phase prefer only the formation of rod-like nanostructures.

Here it is worth mentioning that the sonication also plays a key role in the gelation event.[14] Without sonication, the gelation occurs but then it took hours. It is presumed that the sonication assists the partial dissolution and/or bubble-collapse strategy of the two-component gelator. The gelator in solid state is principally insoluble in the recommended solvent systems where the molecular counterparts remain hydrogen bonded as mentioned earlier. Thus sonication-assisted dissolution of the little quantities of the above gelator instigates the rapid aggregation of the gelator with the employed solvent systems. This spontaneous and prompt aggregation under the non-equilibrium condition ultimately favours in the formation of the fibrous networks over crystallization to occur. Solvent molecules also play a major role in the gelation process which has been discussed in the previous section (‘solvent effect’).

Again, we have taken a mixture of citrazinic acid and melamine (1:1 mmolar ratio) without grinding. 1 mL water was added and then the suspension was heated just to boiling followed by cooling to room temperature. We observed the formation of aggregate which flows partially when we used the “inversion of the glass vial” technique. This refers to the partial gelation of the mixture (without grinding) in neat water under heating-cooling technique. However, in case of mixed solvent system (CH_3CN-H_2O), no such partial gelation was observed under this technique. The mixture (citrazinic acid-melamine) forms precipitate (Fig. S6). Therefore, our GMP methodology produces a gelator which could spontaneously form gel in neat water or aqueous solvent system (eg. CH_3CN-H_2O).

Schematic Illustration of Molecular Knitting and Theoretical Study

We have made an attempt to show the typical association of citrazinic acid and melamine taking into account of some possible models (Scheme 1) and their corresponding geometry optimizations. Scheme 1 presents the possible hydrogen-bonded assembly of citrazinic acid and melamine. Here we have shown the occurrence of ‘ureidopyrimidone’ functionality derived synthon (Model 1, 2 and 3 respectively). It is also worth noting that this synthon typically helps the molecules (citrazinic acid and melamine) to approach in proximity. Other possible mode of hydrogen bondings are also shown in the different model structures.

Our attempt on theoretical calculations gives a brief idea on the possible modes of hydrogen-bonded gluing of citrazinic acid and melamine. The calculations were carried out using Gaussion-09 suite software. The geometry optimizations for different structures have been obtained from the B3LYP/6-31+g(d,p) level of theory. From the optimized structures and the corresponding energy values, it is recommended that ureidopyrimidone’ functionality among the two molecules, citrazinic acid and melamine, brings the molecules close enough to favour their association. Again the carboxylic acid groups between two citrazinic acid moiety also facilitates to extend/propagate the supramolecular communications through hydrogen bonding interactions.

Rheology

Supramolecular gels are viscoelastic materials and their gel strength are characterized by storage (G') and loss modulus (G''), respectively. In the gel state, the frequency independent storage modulus (G') shows higher value relative to the loss modulus (G'') and $G'(\omega) \sim \omega^0$, where ω is the angular frequency. Apart from the verification of gel formation, the mechanical strength, fragility (σ^*, minimum stress required to rupture the gel), elasticity (G' -

G″) and stiffness (*G′/G″*) of the gel could be measured from the rheological data. The dynamic frequency sweep experiment of the as-synthesized gel is shown in Fig.5a where we could observe a wide linear viscoelastic region (LVR) with frequency. A considerably higher *G′* value (~510000 Pa or ~$5.1\text{x}10^5$ Pa) than that of *G″* (~13000 Pa or ~$1.3\text{x}10^4$ Pa) also observed which confirm its gel nature. The oscillator stress sweep experimental data is shown in Fig. 5b and we observed a very high fragility (σ*) ~2600 Pa which indicating very high stress is required to rupture the gel structure. The mechanical strength (*G′*), elasticity (*G′-G″*) and stiffness (*G′/G″*), of the supramolecular gel are ~510000 Pa, ~497000 Pa and 39.3 respectively.

Stimuli Responsive Behaviour of the Gel: Effect of pH and Interfering Ions

The present supramolecular gel was stable only in acidic and neutral pH condition (as confirmed by the ‘vial-inversion’ practice) as in low/medium pH, higher degree of protonation of the corresponding ‘amine’ nitrogen of the constituent molecules (CA and MA) helps in extensive hydrogen bonding to stabilize the coordination-gel assembly. However in alkaline condition (pH>10), the successive deprotonation cause the immediate disruption of the assembly and irreversibly transform the gel into a sol phase. Such pH regulated assembly-disassembly for hydrogels has been illustrated for other types of gelators.[15]

The synthesized hydrogel shows chemical responsive behaviour towards selective inorganic anions. For example, when we added aqueous solution (1 mL) of sodium/potassium salts of some anions (F^-, Cl^-, Br^-, I^-, SO_4^{2-}, NO_3^-, $S_2O_3^{2-}$, SCN^-, CN^-, $H_2PO_4^-$, HPO_4^{2-}, S^{2-} and NO_2^-), we observed an immediate dissolution of the gel matrix selectively in presence of only two ions, cyanide and sulfide (Fig. S7). However, the other salts remain innocent to do the job even when kept for a couple of days. Our present hydrogel system is enriched with extensive hydrogen bonding interactions. We presume that the ions, sulfide and cyanide, can selectively disrupt the hydrogen-bondings and thus cause an immediate dissolution of the hydrogel matrix. The specific selectivity of these two ions might be explained by taking into account of the respective pKa values (Table S2) of the conjugate acids of the ions (these ions are practically base or more precisely Brønsted base in nature). From the table it is clearly understood that HCN and HS^- are weak acids (highest pKa values among the series; marked in cyano colour) among the series (HF to HNO_2). Therefore, the respective conjugate bases (CN^- and S^{2-}) are strong in comparison to the other conjugate bases (F^-, Cl^-, Br^-, I^-, SO_4^{2-}, NO_3^-, $S_2O_3^{2-}$, SCN^-, $H_2PO_4^-$, HPO_4^{2-} and NO_2^-) as explainable from Brønsted-Lowry acid-base theory. Hence it is expected that these two ions would be strong proton acceptors compared to others and thus will disrupt the hydrogen bondings more favorably compared to the other anions. Such ion-responsive behaviour has been observed for some other hydrogels as well as metallogel and organogel systems.[16]

Porosity Measurement

Quantification of the porosity of the air dried gel was achieved with BET gas sorptometry measurement in view of the nitrogen adsorption/desorption isotherm (Fig. 6) and the BJH pore-size distribution (inset in Fig.6). The isotherm can be categorized as type III/V with a narrow hysteresis loop in the relative pressure (P/P_0) range 0.4-1.0. Hysteresis at desorption moment often results from hindered desorption. The BET specific surface area is found to be 61.5 m^2g^{-1}, and the average pore diameter, as calculated from the BJH pore-size distribution plot (found to be 31.2 Å), addresses the presence of mostly mesopores within the gel framework with the pore-size distribution centered at ~31 Å. Here the significant value of the observed surface area could also be corroborated from the observed porous interiors within the gel fibrils as already discussed in the TEM analysis.

Adsorption and Release of Iodine: Kinetic and Mechanistic Aspects

The accountable porosity of our dried-gel material makes it an excellent host to efficiently accommodate molecular iodine through adsorption. We immersed 80 mg of the dried-gel powder in a hexane solution of iodine (2 mL $3x10^{-2}$ M) and noticed that the colour of the material (originally off-white) started to change instantaneously and goes to chocolate-brown. Fig. 7 presents the digital image of the dried-gel material just before the adsorption and after completion/saturation of the process. Fig. 8 presents the colour of the solution taken-off from the parent solution (iodine + dried-gel as adsorbent) in a time-scale of 0, 2 and 16 h which clearly demonstrates the continuous uptake of molecular iodine by the gel matrix from solution phase. Therefore incorporation of the halogen molecules in the host framework is clearly indicated from this sorption study as presented in the image. We carried out FTIR and PXRD studies of the iodine-adsorbed dried gel powder. The similarity in the IR spectrum of the two samples (dried gel powder and I_2-adsorbed dried gel powder) suggests that there is no structural rearrangement of the gel-framework before and after iodine-adsorption takes place (Fig. S8a). Similarly, the XRD patterns indicate the preservation of the crystalline nature of the gel-framework before and after iodine-adsorption (Fig. S8b). But we noted changes in the powder X-ray diffraction profile of the iodine-adsorbed gel to that of only dried-gel. It is presumable that the product is turned into an over-doped iodine salt with an approximate composition of (gel-I_n). This salt is unstable and excess iodine is released with time when the material is exposed in open air. After 24 h we carried out XRD study of this material. The profile (Please see Fig. S8b) presents the XRD pattern of the iodine-adsorbed air-dried gel with an approximate composition of (gel-I). When, the iodine-adsorbed gel powder was taken in ethanol (3 mL), slow release of iodine from the host to the solvent was noticed (Fig. 9). Colour of the solvent gradually changes from colourless to light-yellow to brown. However complete release was not observed even after a week which recommends the material to be a smart host for storage of iodine molecules.

Our host matrix was also capable to adsorb iodine from its vapour phase. Thus, when we placed the dried-gel powder (20 mg) along with few solid iodine granules (100 mg) in a closed vial at room temperature (~25° C) the immediate colour change of the gel powder was evident. The colour gradually deepens form light-yellow to dark-brown. After keeping for 20 h, the iodine-adsorbed dark-brown powder was separated from the granules manually and then kept in an opened-mouth small container. Then, we noted the weight of the material in different time interval. From this time-dependent experiment, the iodine-adsorption capacity as well as the iodine storage capacity was calculated and found to be ~1.1 g/g of the host material and 600 mg/g after 24 h respectively (both are calculated at RT and atmospheric pressure). This remarkable intake of iodine (~1.1 g/g of the host gel) in gel-framework is even higher than that of the commercially well-acclaimed zeolite-13X (0.32-0.38g/g) and activated carbon (~0.84 g/g). This result could be attributed to the comparative pore sizes of the dried gel matrix (31.2Å) and molecular iodine (2.67Å) which indicates the trouble-free entry of the guest molecules into the porous framework. Additionally the abundant π-electrons within the molecular backbones of the gel also prefer the adsorption through π....I–I interactions.[7] Recently some research groups have reported high-adsorption capacity for iodine for porous metal-organic and organic-framework as well as in few other functional materials as already discussed.[7] Nevertheless such high level adsorption of molecular iodine as well as its storage for a long-time period by a supramolecular hydrogel matrix is hitherto unknown.

CONCLUSIONS

In conclusion, we have reported synthesis of a melamine based hydrogel. Melamine, when ground together with citrazinic acid results in a fine yellowish-white/off-white powdered mass. Sonication of this gelator powder in suitable solvent system immediately results in the formation of a gel. The gel shows the presence of fibrous-network morphology throughout. The participation of different non-covalent interactions (like hydrogen bonding and π- π stacking) prevails in the gel backbone which offers strength to the gel matrix. Here the molecules, citrazinic acid and melamine, are constructed with building units like ureidopyrimidone moiety and amino-pyridine functionality and hence these molecules strongly favour the association through the formation of hydrogen-bonded supramolecular synthon. We have also analyzed the necessity of different reaction parameters/conditions (grinding, sonication, solvent effect etc.) concerned with the formation of the hydrogel. The gel also exhibits its stimuli responsive behaviour towards different interfering chemical parameters (pH, selective anions etc.). The dried-gel provides mesoporous interior which was substantiated with the porosity measurement. Finally we have employed the dried-gel matrix as an efficient candidate for adsorption and storage of molecular iodine. It was observed that the adsorption of iodine into the material occurs both from solution and gas phases of iodine as well. The material could also release iodine reversibly but here it is worth mentioning that, even after prolonged time, complete desorption of iodine from the gel matrix could not occur and thus the material shows a high storage capacity/affinity for this halogen. Reversible adsorption-desorption of iodine and its superior storage capacity by a supramolecular hydrogel matrix is hitherto unknown and thus opens up the opportunities to exploit the material for other related environmental issues and may be in iodination reaction.

ELECTRONIC SUPPLEMENTARY INFORMATION (ESI) AVAILABLE:

Complete analytical methods and sampling techniques, computational details, FESEM image of the hydrogel in methanol-water solvent system having citrazinic acid/melamine molar ratio (3:1) and (1:3) respectively, FESEM image of the materials synthesized from the two-component gelator in different solvent systems, molecular structure of citrazinic acid, PXRD patterns of ground mixture and physical (un-ground) mixture of melamine and citrazinic acid as well as FTIR pattern of the ground mixture, FESEM image of the material synthesized from the two-component gelator under un-ground condition, Digital image showing the partial gelation of the physical mixture (unground) in neat water under heating-cooling technique and precipitation in mixed solvent system (CH_3CN-H_2O), anion-responsive behaviour of the gel, comparative FTIR and PXRD patterns of iodine-adsorbed gel and air-dried gel and Table S1 and Table S2.

ACKNOWLEDGEMENTS

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Figure Captions

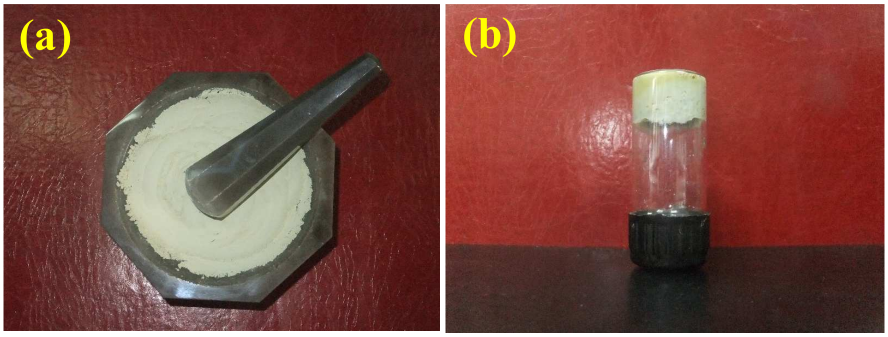


Fig. 1 (a) Ground mixture of citrazinic acid and melamine after solid state grinding in an agate mortar and (b) the standard 'vial-inversion' technique to support the gel formation.

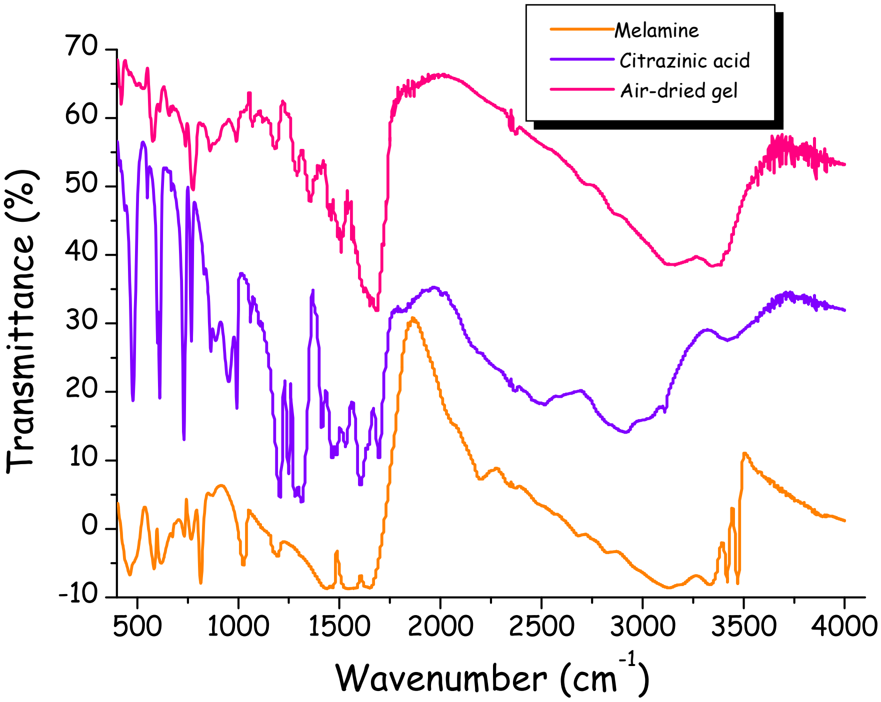


Fig. 2 FTIR spectrum of air-dried gel along with the principle gelator components, melamine and citrazinic acid respectively.

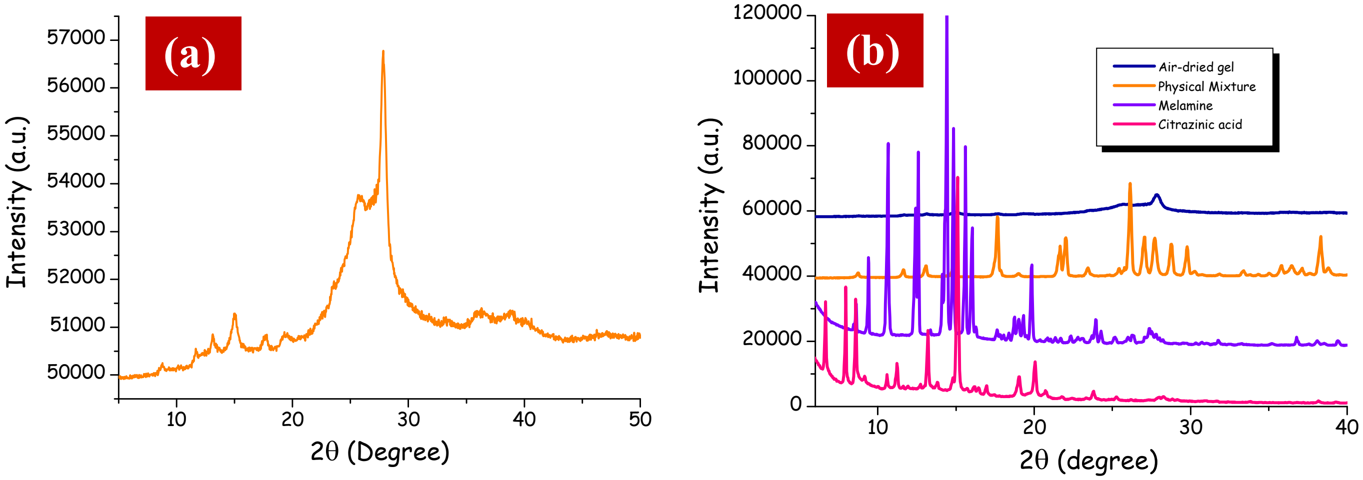


Fig. 3 (a) PXRD pattern of the air-dried gel showing the appearance of intense peak at 27.8° corresponds to the typical π–π stacking interactions in the crystalline materials and (b) PXRD patterns of air-dried gel, physical mixture of melamine and citrazinic acid, melamine and citrazinic acid respectively in a single window showing the distinct crystalline nature of the synthesized gel material from the other three.

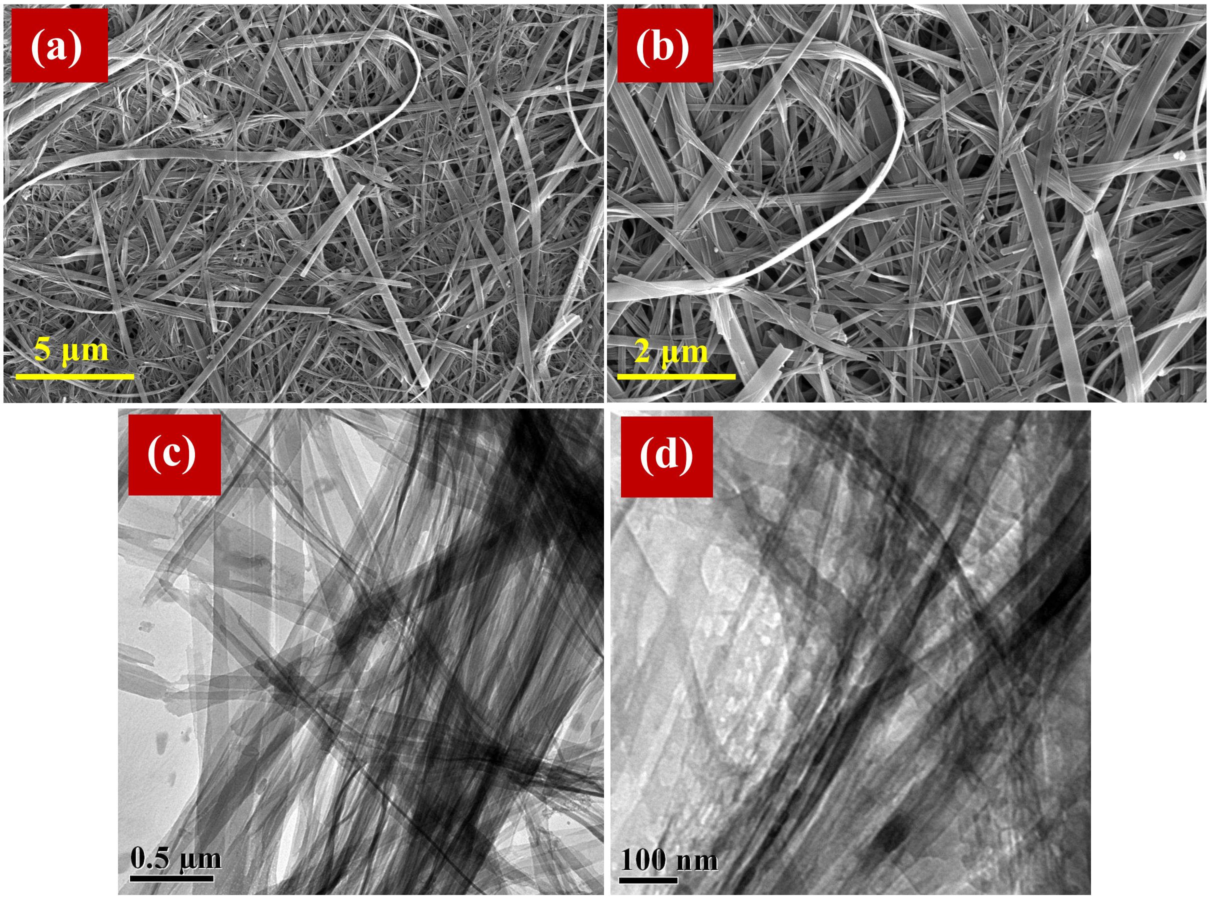
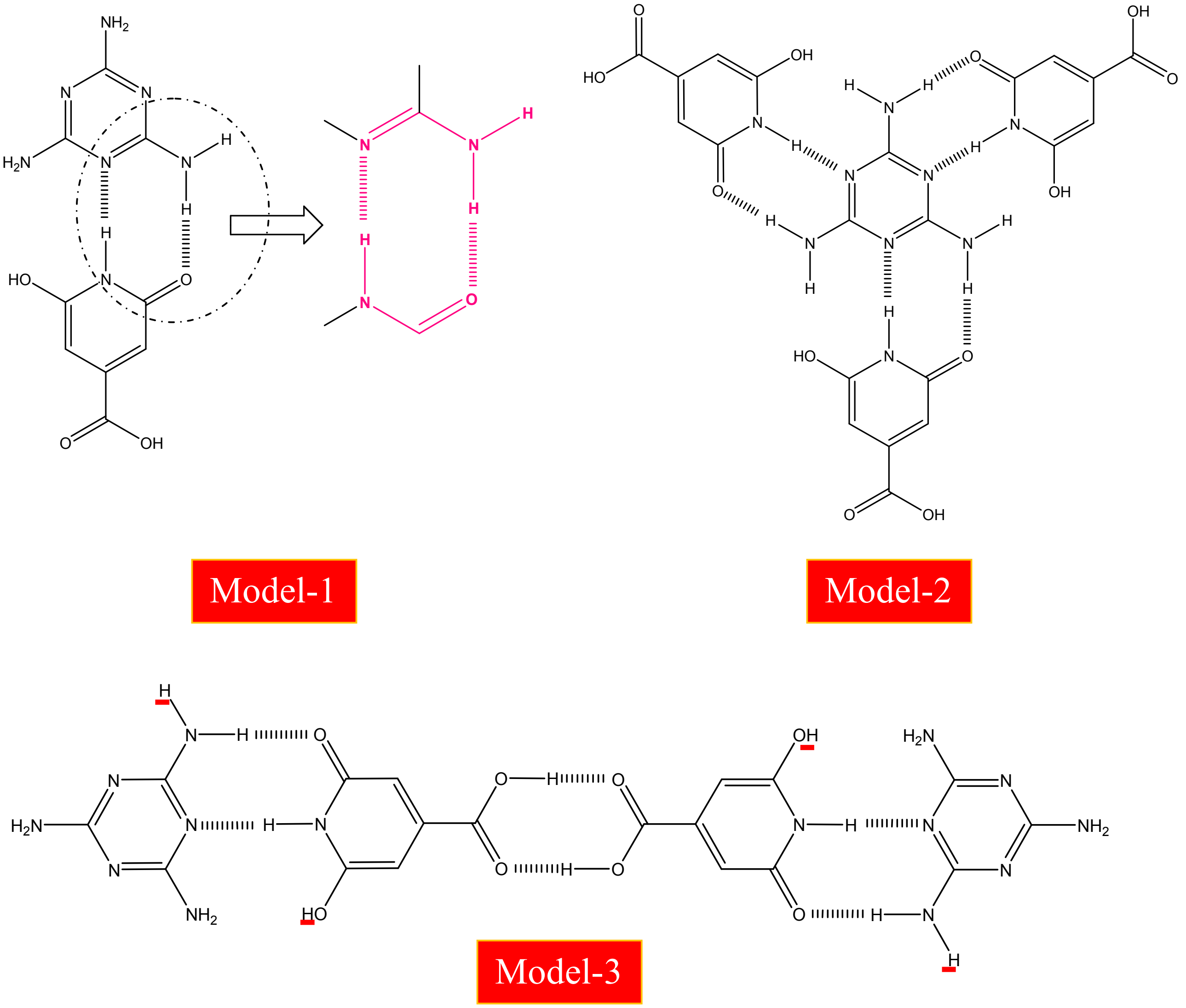


Fig. 4 FESEM images of the hydrogel at (a) low and (b) high magnifications; (c) TEM image of the gel showing the ultrathin, long and entangled gel fibrils; (d) High magnification TEM image of the nano fibres reveals the porous interior of the gel structures.



Scheme 1. Schematic presentation of hydrogen bonded assembly between citrazinic acid and melamine (Model-1, 2 and 3 respectively). Citrazinic acid is decorated with ureidopyrimidone functionality and therefore favours the hydrogen-bonded assembly with the other member, melamine, through the formation of 'supramolecular synthon' [–N–H(melamine)••••O=C<(citrazinic acid) and –N–H(citrazinic acid)••••N(melamine)] (encircled and magnified view; Model-1). This synthon majorly drives the self-assembly and has been observed for the other systems (Model-2 and 3). The underlined protons (shown in Model-3) are available for H-bonding with protic solvent (eg. water).

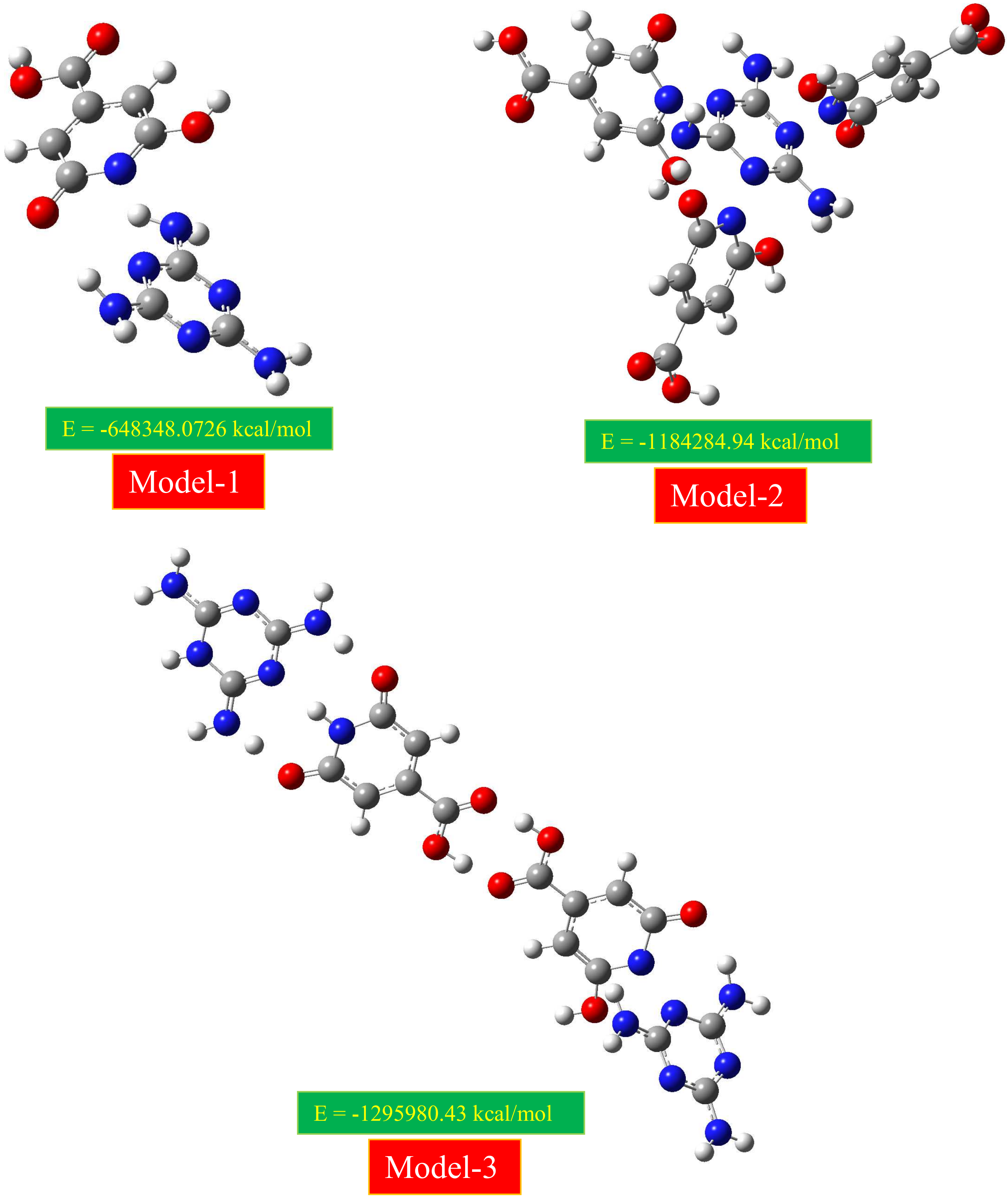


Fig. 5 DFT optimized molecular models. The theoretical calculations were carried out using Gaussion-09 suite of software. The geometry optimization for different structure has been

obtained from the B3LYP/6-31+g(d,p) level of theory. The optimization energy has been presented for each model.

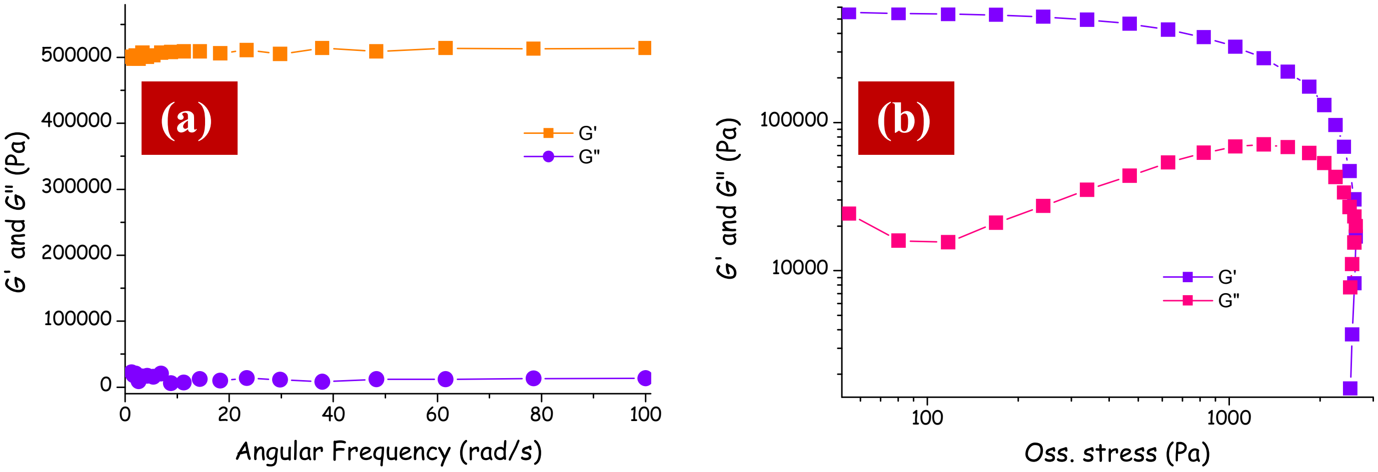


Fig. 6 (a) Storage (*G′*) and Loss (*G″*) modulus vs. angular frequency; (b) Storage (*G′*) and Loss (*G″*) modulus vs. oscillator stress at constant frequency.

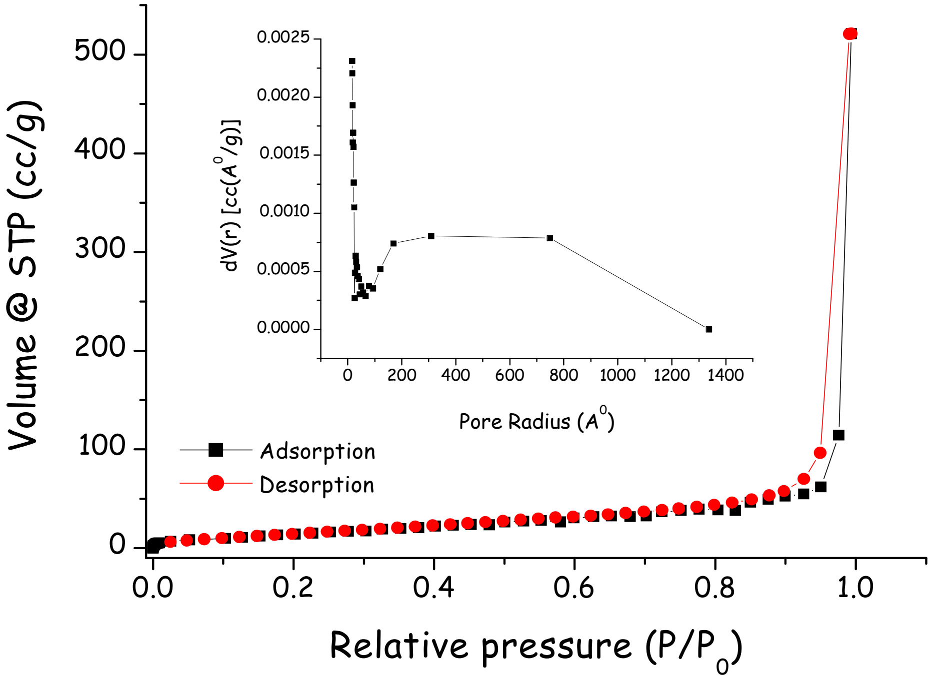


Fig. 7 Nitrogen adsorption and desorption isotherms of the air-dried gel. The insets display the corresponding poresize distribution plot.

Fig. 8 Digital images of the dried-gel material (a) just before the adsorption and (b) after completion/saturation of the adsorption process indicating the continuous uptake of molecular iodine by the gel matrix from solution phase.

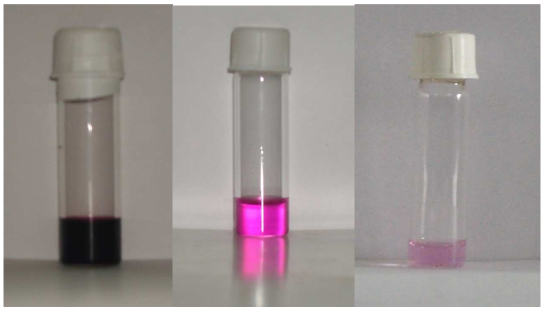


Fig. 9 Digital images showing the colour of the solution taken-off from the mother solution (iodine + dried-gel as adsorbent) in a time-scale of 0, 2 and 16 h (from left to right respectively) which clearly demonstrates the continuous uptake of molecular iodine by the gel matrix from solution phase.

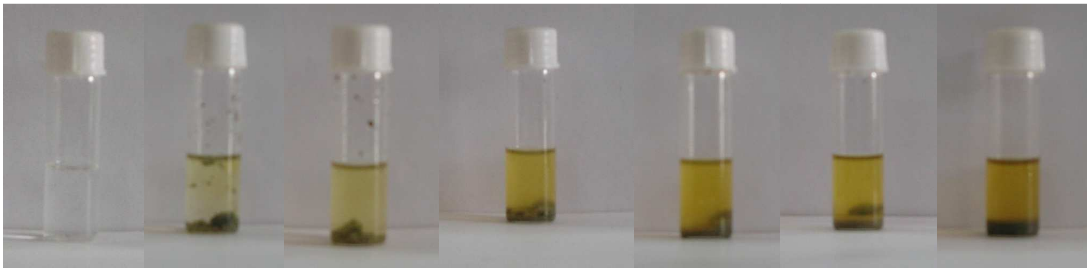


Fig. 10 Digital images showing the spontaneous release of iodine from the iodine-adsorbed gel when it was immersed in ethanol.

Graphical Abstract

A Two-Component Hydrogelator from Citrazinic Acid and Melamine: Synthesis, Intriguing Role of Reaction Parameters and Iodine Adsorption Study

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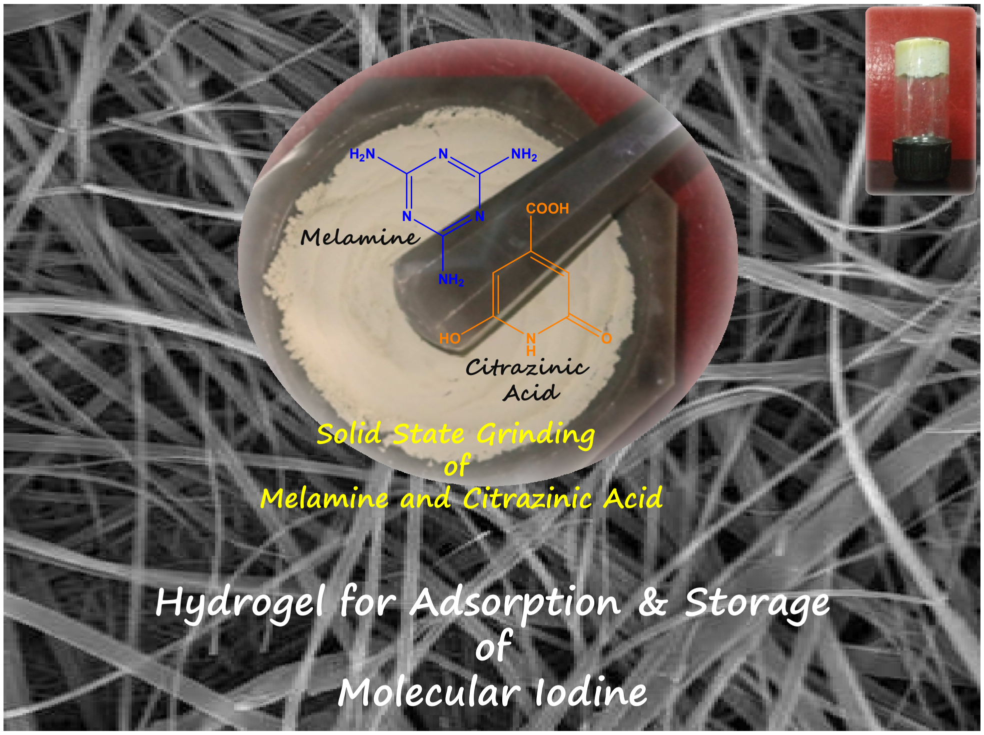

Melamine and citrazinic acid, upon solid state grinding, produced a two-component gelator which selectively gelates water or a mixed-solvent system having water as one of the solvents. The hydrogel, in air-dried condition, shows considerable porosity and acts as a suitable host for adsorption and storage of molecular iodine.