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Removal of toxic dyes from aqueous medium using adenine based bicomponent hydrogel†

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By utilizing hydrogen bonding and π–π stacking interactions, we have demonstrated the construction of three dimensional adenine based gel networks due to the self assembly with complementary tricarboxylic acid derivatives which were designed and unambiguously characterized with the help of NMR, HRMS, and FTIR. Upon cooling the homogeneous aqueous solution of adenine and tricarboxylic acid, it formed hydrogels which were thermoreversible in nature and characterized by various instrumental techniques such as OM, FESEM, TEM, AFM, FL, XRD, FT-IR, rheology *etc.* Networks of belts in the hydrogel were clearly observed and the dimension of belt depended on the tricarboxylic acid used. The intermolecular hydrogen bonds which were considered to be the driving force for the formation of stable gel were confirmed by FT-IR studies. In spite of the absence of symmetry either in bpca or adenine, these two moieties surprisingly produced gels and it was due to the symmetrical position of complementary interaction sites between adenine and tricarboxylic acids. The mechanical strength of the hydrogel network as revealed by rheological study depended on the tricarboxylic acid used in the two-component systems and also on the composition of fixed pair. These kind of hydrogels have potential to be utilized as inexpensive materials for the treatment of waste water containing organic dyes (methylene blue, rhodamine 6G and crystal violet) that are widely used in textile as well as dye industries.

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Introduction

Recently, supramolecular gels have received considerable attention both as a case of self-assembly and phase separation, and in creating ''smart'' materials.[1–3] The gel state is characterized by its solid-like properties despite being largely liquid in composition.[4,5] Conventional polymeric gels are formed by cross-linked covalent polymers which are able to swell and trap many times their own weight in solvent.[6] In contrast, supramolecular gels are generally formed from low-molecular weight organic compounds which utilize noncovalent interactions to self-assemble into supramolecular networks capable of trapping solvent. Because such gels are held together by multiple weak and therefore reversible interactions, supramolecular gels are a particularly responsive and tunable form of soft matter. The abnormal changes in viscosity carried out by gelation can be triggered by a vast range of stimuli such as changes in temperature, sonication,[7] oxidation,[8] pH,[9] addition of anions,[10] and irradiation with light.[11] A wide variety of chemical species have been shown to exhibit gelation including surfactants,[12] sugars,[13] fatty acids,[14] and amino acids,[15] amongst many others.[4,5,16] The bottom-up fabrication of ordered superstructures using specific noncovalent interactions is more appealing to generate new functional materials that are achievable by nanometer-scale manipulation.[17,18] The incorporation of multi noncovalent interactions can increase the stability and robustness of the ordered superstructures,[19] and simultaneously the reversible and dynamic nature of these noncovalent interactions can allow supramolecular materials to respond to external stimuli.[20] Utilizing the facile approach, well-defined nanostructures such as nanofibers, nanoribbons, helical structures, nanotubes, *etc.*, have been created.[21–23]

Among the family of gels, the growth of low molecular weight hydrogels (LMWH) has advanced in many fields ranging from cosmetic products to pharmaceuticals to gene delivery, due to their characteristics of biocompatibility and biodegradation. In addition, the development of an ever-increasing spectrum of functional hydrogelators continues to broaden the versatility of hydrogel applications. LMWH now play a critical role in many tissue engineering scaffolds, biosensor and biological microelectro-mechanical systems, and drug carriers.[24] In contrast to single component organo gel systems, new gelation systems comprising of two components have been developed.[14,25,26] In these systems, both components that serve as gelators are held together by noncovalent interactions. The most important feature of the two-component systems is the ease with which the properties and structures of the gel can be modulated by changing the molar ratio of the two components or by changing one of the

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two components. Excellent examples of a dendritic building block based on an amino acid in combination with an aliphatic diamine have been reported by Smith *et al.*[26], who studied the properties and structures of the resulting gel.

Adenine, a purine nucleobase, is an important naturally occurring nitrogen heterocycle present in nucleic acids DNA and RNA. Several reports are present in the literature describing adenine metal coordinated crystals and adenine derivatives used for molecular recognition.[27] In this study, we report a two-component gel system in which three acid groups and aromatic cores act as hydro gelators in the process of self-assembly. The compositions of the two components have a pronounced effect on the gel properties and on rheological properties. However, to the best of our knowledge, almost no studies have been concerned about adenine based hydrogels except one recent example from our group.[28] Making adenine based hydrogels and subsequent potential application of these gels will be interesting.

Textile, paper, plastics, and cosmetic industries use a wide variety of dyes to colour their products and discharge large amount of effluents including dyes which are very toxic and could cause serious ecological problems. These dyes can cause some harmful effects, such as heartbeat increase, vomiting, shock, cyanosis *etc.* Methods of dye removal from industrial waste waters could require many processes such as biological treatment, coagulation, flotation, electrochemical techniques, adsorption, and oxidation. Within these methods, adsorption is more preferred due to high efficiency, easy handling, and availability of different adsorbents. Hydrogels possessing different functional groups have been investigated for this purpose.[29] Regarding this it should be mentioned here that gelator molecules containing both hydrophobic and hydrophilic groups can adsorb the dye molecules very efficiently. As our moieties fulfil the above criteria, the produced hydrogel has been successfully applied for the purification of dye contaminated water.

Experimental section

Materials and instruments

4-Bromoacetophenone, $K_2S_2O_7$, 5-amino isophthalic acid, bis(pinacolato)diborane, and $PdCl_2$ were purchased from Aldrich. $NaNO_2$, KOAc and all other chemicals and solvents

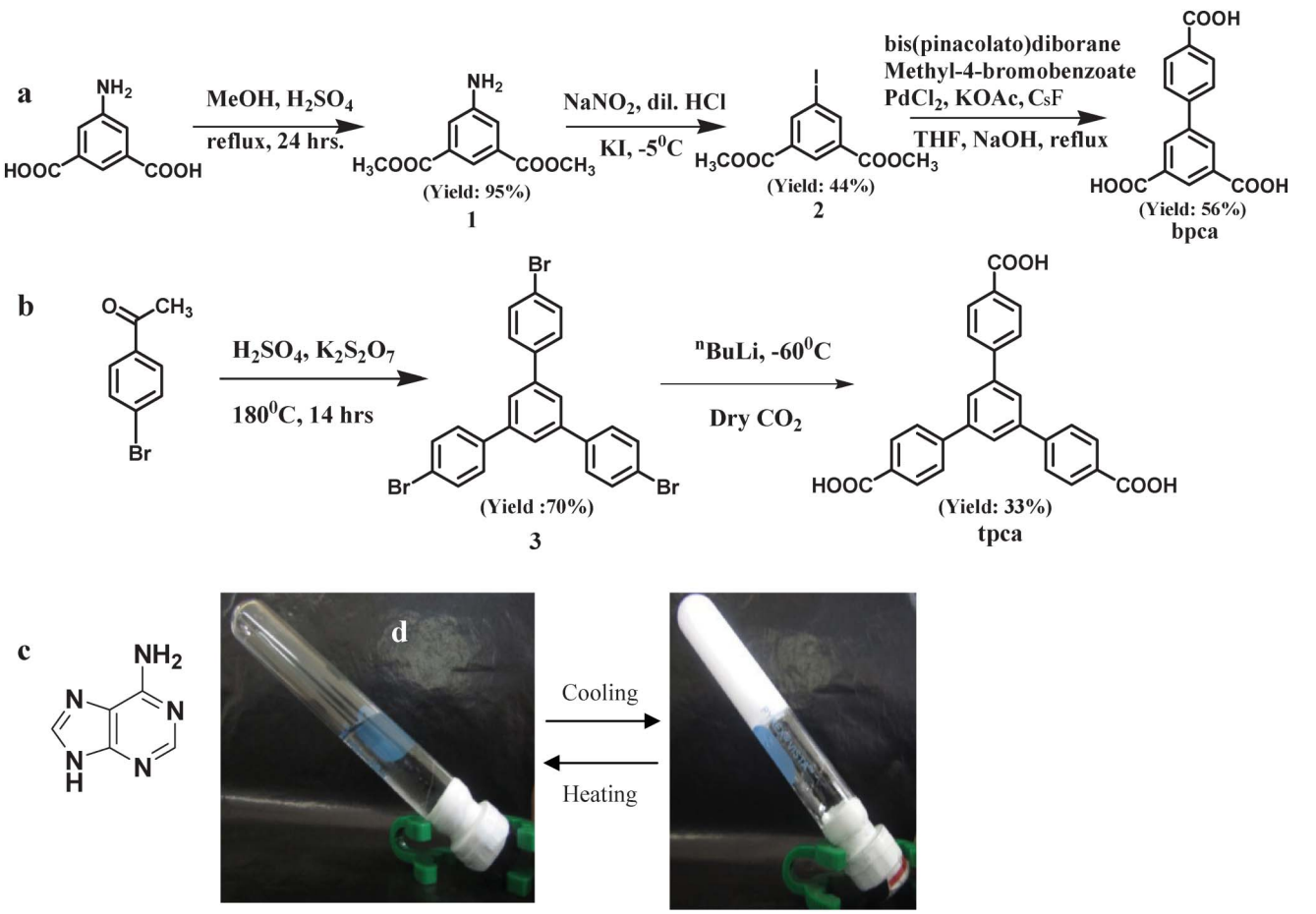


Fig. 1 (a) Synthesis scheme of biphenyl-3,4′,5-tricarboxylic acid (bpca). (b) Synthetic scheme of 1,3,5-tris(4-carboxyphenyl)benzene (tpca). (c) Chemical structure of adenine (ADN). (d) Representative photo of inverted solution and gel of ADN/bpca 11 (0.41% w/v) [inner diameter of the glass tube is 10 mm].

were purchased from Merck. HPLC grade water from Spectrum was purchased and used as gelling medium.

Synthesis

All synthesis procedures for tricarboxylic acids were carried out according to Fig. 1a, b. All the compounds were fully characterized by mass spectrometry, ^{1}H-NMR spectroscopy (300 MHz), and ^{13}C-NMR spectroscopy (300 MHz).

Synthesis of 1,3-dimethyl-5-aminobenzene-1,3-dicarboxylate (1)

5-amino isophthalic acid (2.0 g, 11.04 mmol) was dissolved in methanol (50 mL). Concentrated sulfuric acid (2 mL) was added slowly and the solution was refluxed for 24 h. After removing the solvent, the residue was dissolved in chloroform (150 mL) and washed twice with saturated bicarbonate, and the solvent was removed under reduced pressure to receive the desired product 1 as a white powder (yield: 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.90 (s, 6H), 7.51 (s, 2H), 8.04 (s, 1H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 52.4, 119.8, 120.7, 131.6, 146.8, 166.6 ppm. HRMS: calcd for $C_{10}H_{11}NO_4$ 209.20, found 210.01 (MH^+), 231.9 (MNa^+).

Dimethyl-5-iodobenzene-1,3-dicarboxylate (2)

A solution of sodium nitrite (8.28 g, 0.12 mol) in water (150 mL) was added to a suspension of 1,3-dimethyl-5-aminobenzene-1,3-dicarboxylate (1) (25.11 g, 0.12 mol) in 20% HCl (75 mL) at -5 °C. Toluene (200 mL) and then a solution of potassium iodide (40.32 g, 0.48 mol) in water (100 mL) were slowly added to the suspension. After the addition, the reaction mixture was stirred for 12 h and afterward refluxed for 1 h. The organic layer was separated and washed three times with water, dried over $MgSO_4$, filtered, and concentrated in vacuum. The crude product was purified by column chromatography (silica gel, ethyl acetate/hexane, 3 : 7 v/v) and recrystallized from methanol, giving 2 as light-brown crystals. Yield 44%.^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.95 (s, 6H), 8.53 (d, 2H), 8.61 (t, 1H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 52.6, 93.4, 129.8, 132.3, 142.4, 164.7 ppm.

Biphenyl-3,4′,5-tricarboxylic acid (bpca)

A mixture of dimethyl 5-iodobenzene-1,3-dicarboxylate (2) (320 mg, 1.00 mmol), bis(pinacolato)diborane (279 mg, 1.10 mmol), potassium acetate (294 mg, 3.00 mmol), $PdCl_2$(dppf) (24 mg,

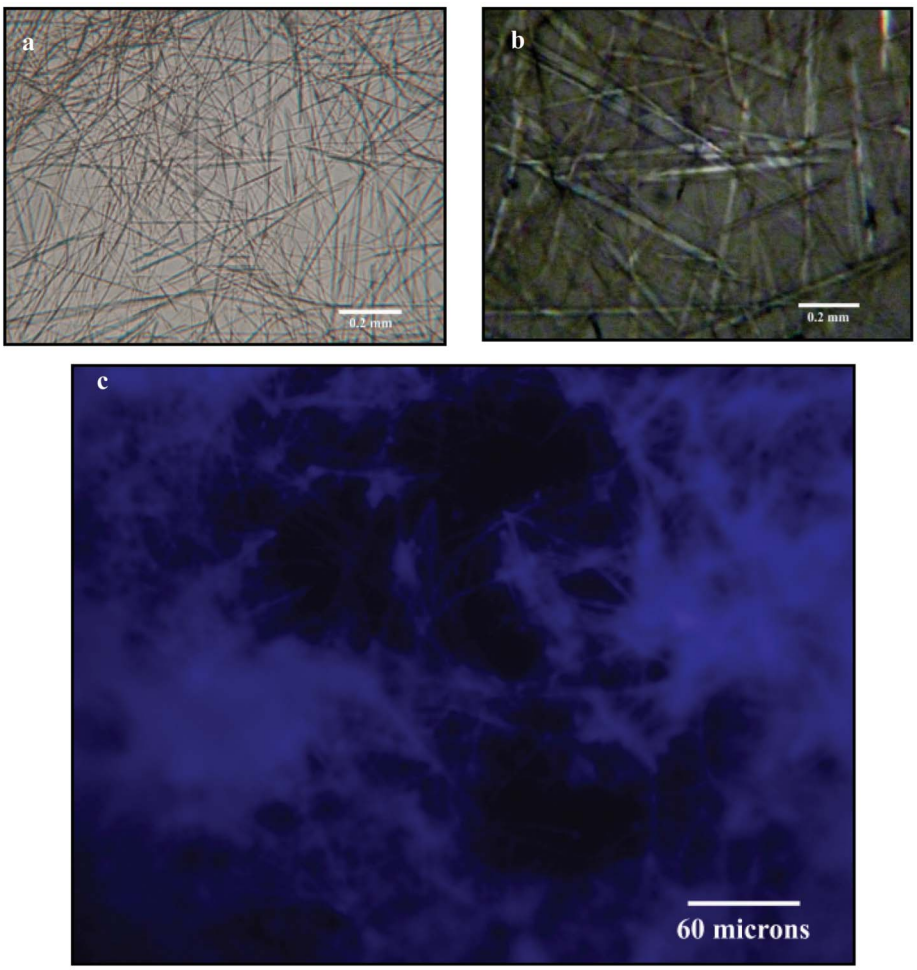


Fig. 2 (a) Optical image, (b) optical image under polarized light and (c) fluorescence image of dried gel under excitation at 380 nm [ADN : bpca = 1 : 1, (0.41% w/v), a slice of gel was cast on a glass slide and dried under air prior to taking image].

0.03 mmol), and dried DMF (6 mL) was stirred at 80 °C for 2 h. After cooling at room temperature, methyl-4-bromobenzoate (640 mg, 2.00 mmol), $PdCl_2$(dppf) (24 mg, 0.03 mmol), and CsF (456 mg, 3.0 mmol; dissolved in 2.5 mL of water) were added. The mixture was stirred at 80 °C overnight and afterward extracted several times with diethyl ether. The organic layer was dried with $MgSO_4$, and the solvent was removed and the crude product was purified by column chromatography (silica

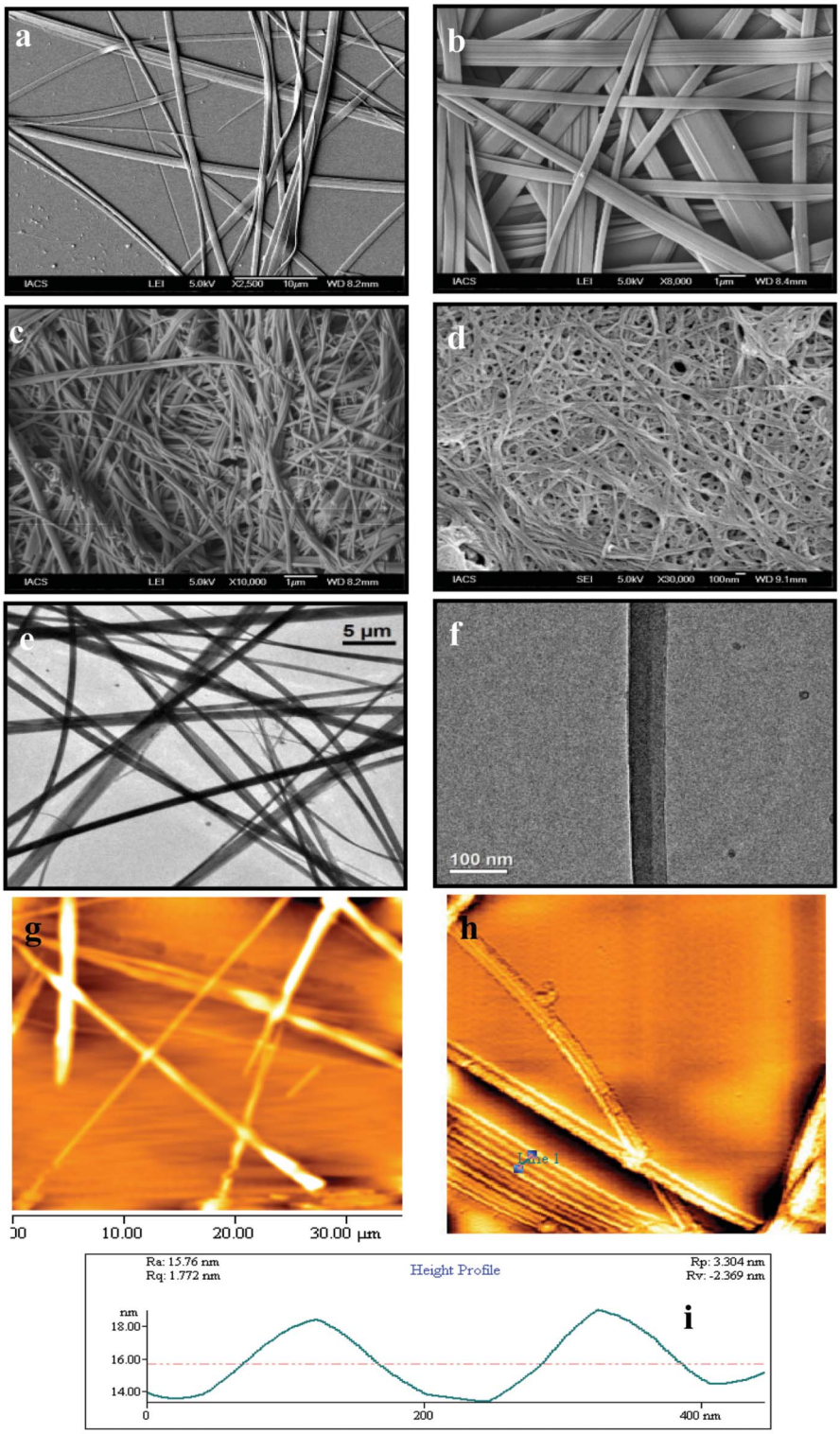


Fig. 3 (a,b) FE-SEM images of ADN/bpca11 dried gel, (c,d) ADN/tpca11 dried gel. TEM images of ADN/bpca11 dried gel (e,f). AFM topographs of dried gel cast on a freshly cleaved mica surface, (g) ADN/bpca11 gel, 0.41% w/v, (h) ADN/tpca11 gel, 0.53% w/v, and (i) corresponding height profile.

gel, ethyl acetate/hexane, 3 : 7 v/v). Subsequently it was hydrolyzed as follows. A mixture of biphenyl-3,4′,5-methyltricarboxylate (0.96 g, 2.5 mmol), THF (40 mL), and NaOH (1.6 g, 40 mmol) dissolved in water (40 mL) was refluxed for 1 h, the organic solvent was removed under reduced pressure, and the aqueous solution was refluxed again for 4 h. The reaction mixture was cooled and acidified with 50% H_2SO_4 to get the precipitate which was filtered, washed and dried to obtain bpca as a white powder. Yield 56%. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.86–7.87 (d, 2H), 8.04–8.06 (d, 2H), 8.41 (s, 2H), 8.48 (s, 1H), 13.28 (s, 3H) ppm. ^{13}C NMR (300 MHz, DMSO-d_6): δ = 127.1, 129.47, 130.4, 131.4, 132.2, 140, 142.4, 166.3, 167 ppm. MS (MALDI-TOF) calcd 286.05 found 309.1 $[M + Na]^+$. FTIR: 3262, 1739, 1695, 1610, 1455, 1394, 1279 cm^{-1}.

Synthesis of 1,3,5-tri(4-bromophenyl)benzene (3)

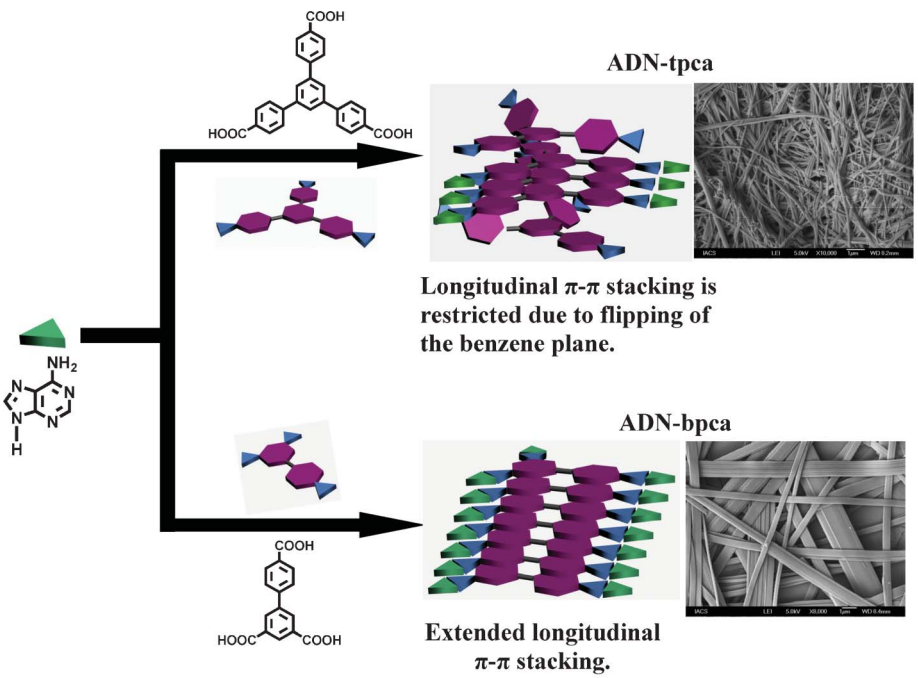
4-Bromoacetophenone (10 g, 50.25 mmol), 0.5 mL of H_2SO_4(c) and $K_2S_2O_7$ (15 g, 59 mmol) were heated at 180 °C for 14 h under nitrogen atmosphere. The resulting crude solid was cooled to room temperature and refluxed in 50 mL of dry EtOH for 1 h and then cooled to room temperature. The solution was filtered and the resulting solid was refluxed in 50 mL of H_2O, giving a pale-yellow solid that was filtered. The crude product was dried under vacuum and recrystallized in $CHCl_3$. Yield: 70%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (d, 6H), 7.60 (d, 6H), 7.68 (s, 3H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 122.2, 125.1, 129,132.2, 139.7, 141.6 ppm.

Synthesis of 1,3,5-tris(4-carboxyphenyl)benzene (tpca)

1,3,5-Tri(4-bromophenyl)-benzene (3 g, 5.52 mmol) was dissolved in 40 mL of anhydrous THF under N_2 atmosphere. The stirred solution was cooled to −60 °C and a 1.6 M solution of *n*-BuLi in hexane (10.5 mL, 16.3 mmol) was added dropwise. A red to light-green precipitation of the aryl lithium derivative was formed. Predried gaseous carbon dioxide was passed into the mixture at −60 °C to give a colorless precipitate of the lithium salt. The mixture was allowed to warm and was quenched with 50% aqueous acetic acid. The solid product was filtered and recrystallized from acetic acid to give 0.8 g (33%) of white microcrystals. ^{1}H NMR (DMSO-d_6): δ = 8.06 (s, 12 H), 8.09 (s, 3 H) ppm, ^{13}C NMR (300 MHz, DMSO-d_6): δ = 125.6, 127.4, 129.9, 130.0, 140.8, 143.8, 167.2 ppm. MS (MALDI-TOF) calcd 438.1 found 439.2 $[M + H]^+$. FTIR: 3071, 2985, 1691, 1608, 1419, 1318, 1294, 1245 cm^{-1}.

Microscopy

The morphology of the gel was observed through an optical microscope (Leitz, Biomed) under perfectly crossed polarizers and taking the picture through a digital camera (Leica D-LUX 3). FESEM experiments were performed by placing a small portion of gel samples on a microscope cover glass. Samples were dried in air and vacuum successively and coated with platinum prior to observation. Micrographs were recorded by using a Jeol Scanning Microscope JSM-6700F. TEM images were taken using a JEOL electron microscope operated at an accelerating voltage of 200 kV and these samples were prepared through placing the gel-phase material on a TEM grid (300 mesh carbon-coated Cu grid). AFM topologies were recorded using atomic force microscopy (Veeco, model AP0100) in noncontact mode at a tip resonance frequency of 300 kHz. Samples for the imaging were prepared by drop casting the solution on freshly cleaved mica surface at the required concentrations at ambient conditions.



Scheme 1 Plausible modelling for the formation of different size of belt for different gel and their growth in the longitudinal direction.

Fluorescence microscopy and spectroscopy

Gel-phase material was placed on a glass microscope slide, dried, and examined under a fluorescence microscope (OLIMPUS BX-61) in 40X magnification at excitation 360 nm. Fluorescence spectral studies of ADN/bpca and ADN/tpca gel samples prepared in a sealed cuvette were carried out in a Horiba Jobin Yvon Fluoromax 3 instrument. The gel samples were directly prepared in a quartz cell of 1 cm path length. Fluorescence excitation acquisition and emission acquisition were taken in slit width of 2/2 nm and scan rate was 0.2 s.

XRD study

The WAXS studies of the dried gels were performed by a Seifert X-ray diffractometer (C-3000) using nickel filtered Cu-Kα radiation with a parallel beam optics attachment. The instrument was operated at a 35 kV voltage and a 30 mA current and was calibrated with standard silicon sample. The samples were scanned from $2\theta = 2^\circ$ at the step scan mode (step size 0.03°, preset time 2 s), and the diffraction pattern was recorded using a scintillation counter detector.

Rheology

Rheological experiments were performed with an AR 2000 advanced rheometer (TA Instruments) using cone plate geometry in a Peltier plate. The plate diameter was 40 mm, with a cone angle of 2 degrees. Two types of experiments were performed: (i) by frequency sweep and (ii) by strain sweep methods. The frequency sweep experiments were made at 25 °C at constant 1% strain. The strain sweep experiment was performed at 25 °C at a constant frequency of 2 rad s^{-1}.

FTIR spectroscopy

FT-IR spectra of bpca, tpca and dried gels were recorded using KBr pellets of samples in an FTIR-8400S instrument (Shimadzu). All sample were diluted with KBr and pelletized prior to the experiment. Two independent experiments were performed for each sample.

Results and discussion

Molecules chosen here for gelation studies were adenine (ADN), 1,3,5-tris(4-carboxyphenyl)benzene (tpca),[30] Biphenyl-3,4′,5-tricarboxylic acid (bpca).[31] These two tricarboxylic acids were synthesized according to Fig. 1a, b and characterized by ^{1}H-NMR, HRMS, and FTIR. All these components have three complementary binding sites through hydrogen bonding either C=O···H–N or C–O–H···N. Both of the above two acids have the strong possibility to form gel with adenine through supramolecular interactions. The gelation ability is primarily observed by a ''stable to inversion of the test-tube'' method and it will be later proved by rheology. Appropriate amount of tpca/bpca and ADN were taken into water at room temperature and these mixtures were heated to form transparent liquid, then cooled to room temperature to observe whether immobile gel formed or not in the inverted test-tube. It has shown in the Fig. 1d that the complete gelations of tpca/bpca with adenine have occurred in water within 5 min. With the increase of the temperature to T_{gel} (93 °C), the stable gel is transformed into sol phase, and the clear solution is finally obtained. The process could be reversed to form the hydrogel by cooling the solution to room temperature. The cycle has been repeated many times and the gelation ability is not affected, indicating a fully thermoreversible nature.

Optical microscope images (Fig. 2a, b) show the formation of a fibrillar network like structure with each fibre having a length of several millimetres. These long fibers are formed due to extended intermolecular H-bonding between ADN and tricarboxylic acids. The dried gels prepared by the deposition of a gel sample followed initially by drying in air and finally in vacuum are observed under an electron microscope. As shown in Fig. 3, the field emission scanning electron microscope (FE-

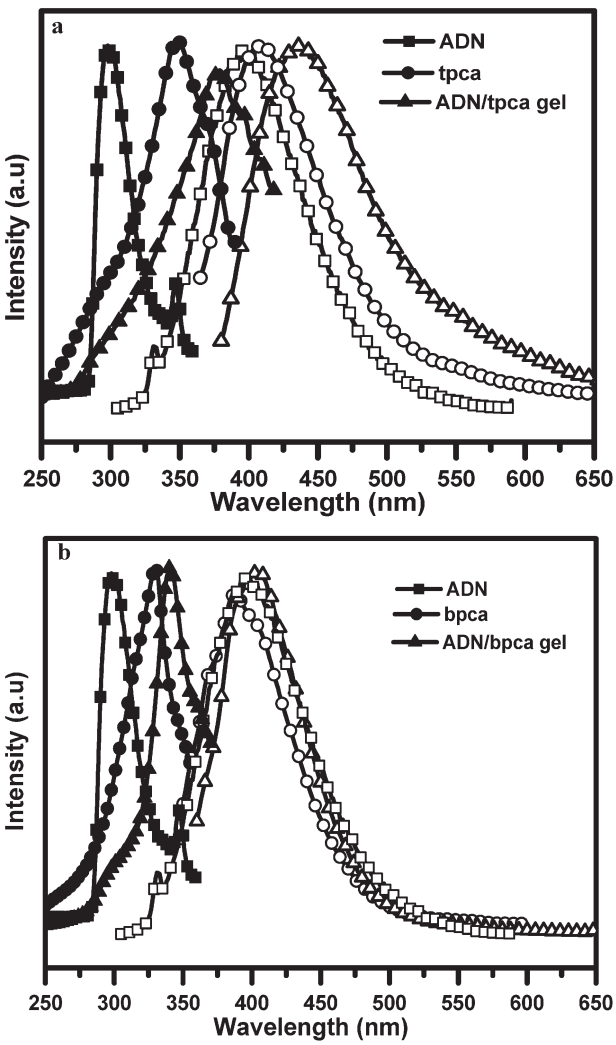


Fig. 4 (a) Fluorescence excitation (filled symbol) and emission spectra (vacant symbol) of pure ADN, pure tpca and ADN/tpca gel at room temperature [pathlength 10 mm]. λ_{ex} for the emission spectra of ADN = 280 nm, tpca = 370 nm, and ADN/tpca gel = 370 nm. (b) Fluorescence excitation (filled symbol) and emission spectra (vacant symbol) of pure ADN, pure bpca and ADN/bpca gel. λ_{ex} for the emission spectra of ADN = 280 nm, bpca = 340 nm, and ADN/bpca gel = 340 nm.

SEM) images demonstrate the network of belts that are formed by self-assembled nanofibers for all gels. Careful investigations of these images at higher magnification (Fig. 3a–d) reveal that belts having a width of 20–100 nm are then assembled to form fatty belts having width of above 1–2 μm and a length of several micrometers. Belts like network structures are observed for both gels having different molar ratio of adenine and tricarboxylic acids.[32] The formations of such belt like morphology is due to the long range inter molecular hydrogen bonding interaction between ADN and tricarboxylic acids. It is very interesting that ADN/tpca produces slim belts whereas ADN/bpca forms fatty belts in all compositions. ADN/tpca could self-assemble into nanoscale fibrous structures with regular fiber diameters of *ca.* 20–100 nm whereas ADN/bpca shows fibers having large diameter (500–600 nm). The formation of such different size belts for the two different gels can be explained from Scheme 1. As there is large probability for the flipping of the single bond (C_{sp2}–C_{sp2}) between two benzene ring in case of tpca, extended longitudinal π–π stacking is restricted for the ADN-tpca gel system and a slim belt is formed. However, for the ADN-bpca system the probability of non-planarity of the benzene plane is much lower and the extended longitudinal π–π stacking that occurs is responsible for fatty belt formation. Transmission electron microscopy (TEM) images of dried gels prepared directly on a carbon coated Cu-grid reveal the formation of supramolecular nanobelts (50–60 nm in width) which have created a three-dimensional network (Fig. 3e, 3f). Therefore hydrogelation has occurred by immobilizing water molecules in the nanospaces of the three-dimensional networks. AFM topology (Fig. 3g, 3h) clearly reveals the presence of belt like morphology in the dried gel. Individual belts are bundled up to form fatty belts having large width of ~1 μm. The AFM height image in Fig. 3h, 3i shows the clear layer by layer assembly of the belts.

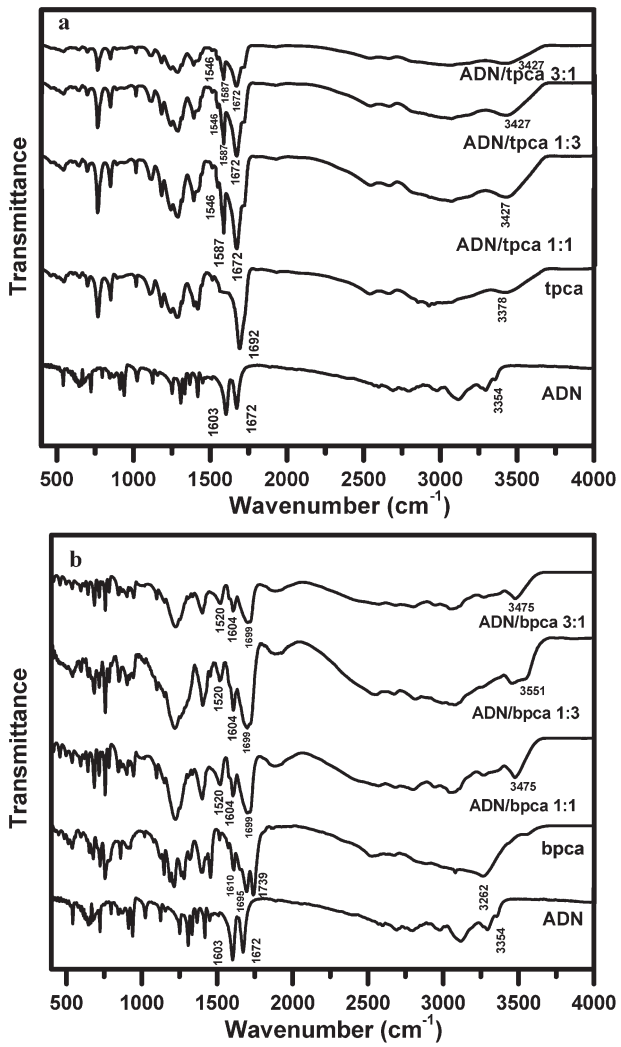


Fig. 5 (a) FTIR plot of pure adenine (ADN), pure tpca, ADN/tpca11, ADN/tpca13, and ADN/tpca31 dried gel. (b) FTIR plot of pure adenine (ADN), pure bpca, ADN/bpca11, ADN/bpca13, and ADN/bpca31 dried gel.

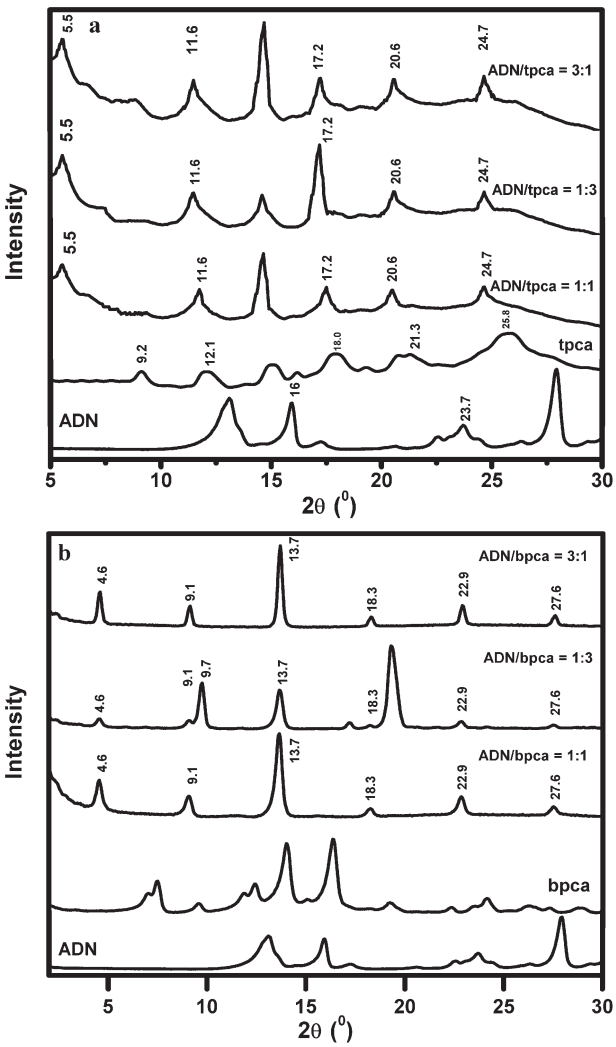


Fig. 6 (a) WAXS of pure adenine (ADN), pure tpca, ADN/tpca11, ADN/tpca13, and ADN/tpca31 dried gel, all the gels were caste on glass slide and dried under air. (b) WAXS of pure adenine (ADN), pure bpca, ADN/bpca11, ADN/bpca13, and ADN/bpca31 dried gel, all the gels were cast on a glass slide and dried under air.

As the optical density of gel at any composition is above the instrumental limit of a UV-Vis spectrophotometer, we have performed the fluorescence excitation and emission spectroscopy of the pure compounds in water and their hydrogels are shown in Fig. 4. Only adenine in water produces the excitation and emission peaks at 297 nm and 395 nm respectively, whereas only tpca produces the excitation and emission peaks at 348 nm and 407 nm respectively. bpca exhibits the excitation and emission peaks at 328 nm and 385 nm respectively. However, after making the gel by mixing ADN with tpca/bpca solutions in 1 : 1 ratio, excitation and emission spectra generate new peaks at 379 nm and 436 nm for ADN-tpca, and 341 nm and 405 nm for ADN-bpca gel, respectively. The red shift of excitation and emission peaks for tpca/bpca occurs after gel formation and it is due to the definite arrangement of adenine in the gel. To investigate the luminescence properties of the gel, fluorescence microscopy of all the dried gels has performed. Under the microscope, it clearly generates blue fluorescent gel networks upon excitation at 380 nm (Fig. 2c).

A low-molecular-weight gelator forms self-assembled nanofibers or nanotapes in a supramolecular gel through hydrogen bonding and π–π interactions, which can be analyzed by FTIR spectroscopy. FTIR spectra of tpca, bpca, adenine and gels are presented in Fig. 5. Typical IR stretching bands arising from the non-hydrogen bonded acid groups in tpca/bpca are observed around 1692/1739 cm^{-1}, whereas the same in the dried gels have appeared around 1672/1699 cm^{-1} respectively. So the carboxylic acid groups show a large shifting of frequency, from 1692 to 1672 cm^{-1} and 1739 to 1699 cm^{-1}, that indicates the strong intermolecular hydrogen bonding in gel state.[33] Similarly for adenine, two strong bands at around 1672 cm^{-1}(C=N) and 1603 cm^{-1} (R–NH_2 bending) and a weak band at 3354 cm^{-1} (ν_{N-H}, amine ADN) appeared in the pure

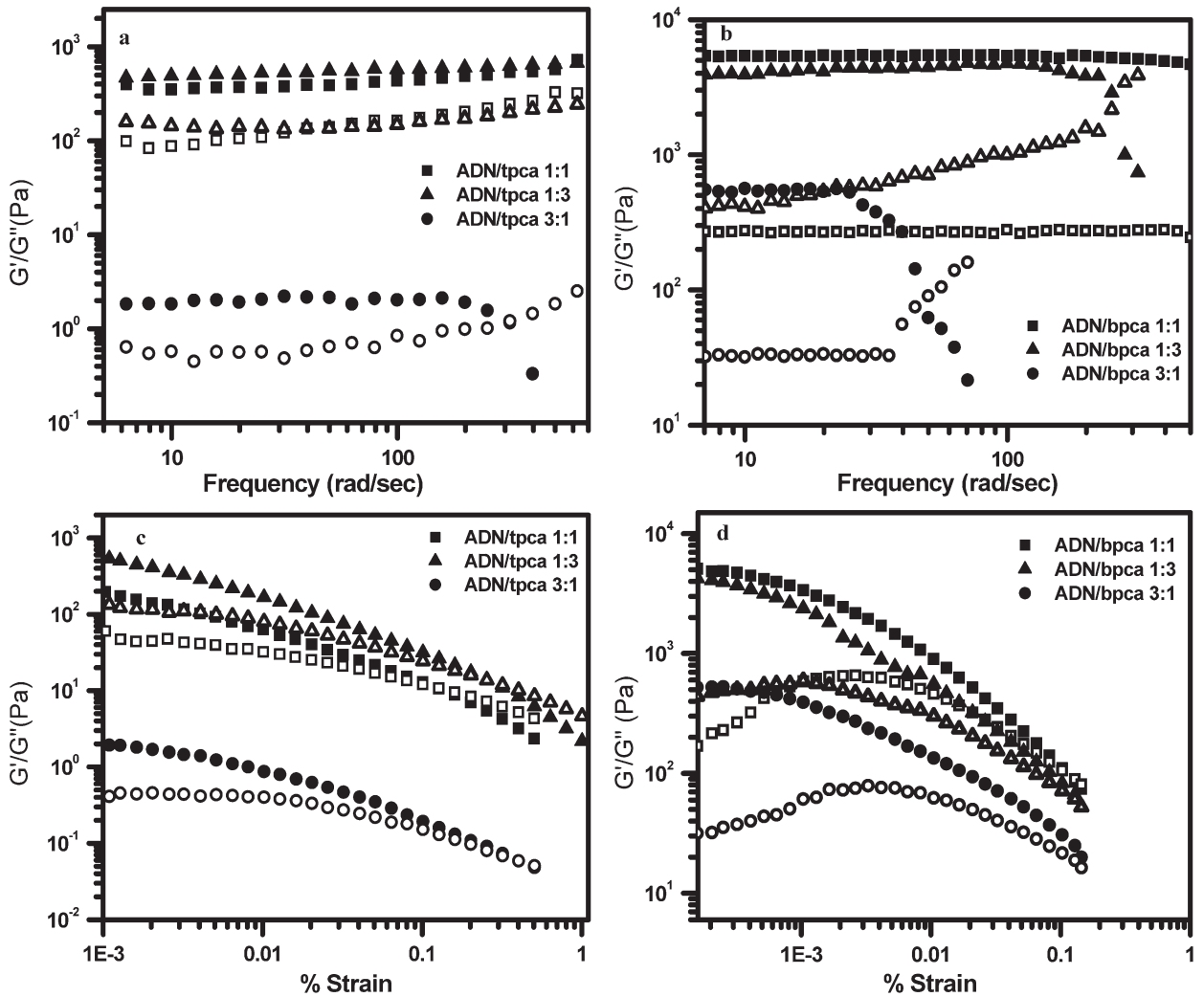


Fig. 7 (a) Rheological studies (frequency sweep) of hydrogels of different molar ratio at room temperature of ADN/tpca system. (b) Rheological studies (frequency sweep) of hydrogels of different molar ratio at room temperature of ADN/bpca systems. (c) Rheological studies (strain sweep) of hydrogels of different molar ratio at room temperature of ADN/tpca systems. (d) Rheological studies (strain sweep) of hydrogels of different molar ratio at room temperature of ADN/bpca systems, (filled symbol indicates *G′* and corresponding vacant symbol indicates *G′′*).

state. Whereas in the gel state the first two bands are shifted to a lower frequency (1587 cm^{-1} and 1546 cm^{-1} for ADN/tpca gel or 1604 cm^{-1} and 1520 cm^{-1} for ADN/bpca gel), surmising the reduction of electron density on ring due to its involvement of hydrogen bonding with tpca/bpca. This result clearly indicates hydrogen-bonding-induced hydrogelation of adenine with tpca/bpca similar to a common hydrogelator previously reported.[26b,26e] From the FTIR spectroscopy, it can be surmised that adenine and tpca/bpca are self-assembled into nanofibers through a number of hydrogen-bonding interactions. In our previous report, it was observed that only 1,3,5-benzene tricarboxylic acid (1,3,5-B) formed a gel among three isomers of benzene tricarboxylic acids.[28] It was due to the symmetrical position of complementary interaction sites between adenine and 1,3,5-B. In the present instance, bpca, as well as adenine, does not have molecular symmetry, still these two produce gel in water. The symmetrical position of hydrogen bonding interaction sites have oriented these two moieties to produce short fibers which are entangled together to form a network of belts which ceases the flow of water upon tilting the gel tube. The intermolecular hydrogen bonds are the driving force for the formation of stable gel.

X-ray powder diffraction has been frequently used for ascertaining the molecular packing of gelator molecules in gel networks. Fig. 6a, b show the XRD pattern of ADN, tpca and bpca in powdered state and those in dried gel states, which had been prepared from the gels of ADN/tpca/water. Clearly, the XRD traces are all characterized by a group of well-resolved reflections showing that the samples are all crystalline in nature. The ADN/tpca dried gels in the Fig. 6a indicates the presence of the main diffraction peaks (2θ = 5.5°, 11.6°, 14.7°, 17.2°, 20.6°, 24.7°). The corresponding *d*-values are 1.6, 0.76, 0.60, 0.50, 0.40, and 0.36 nm respectively, and the interlayer distance is 1.6 nm. Further examination of any trace of ADN/bpca dried gel (Fig. 6b) indicates the presence of the main diffraction peaks (2θ = 4.6°, 9.1°, 13.7°, 18.3°, 22.9°, 27.6°). The corresponding *d*-values are 1.9, 0.97, 0.64, 0.48, 0.38, and 0.32 nm respectively that follow a ratio of 1 : 1/2 : 1/3 : 1/4 : 1/5 : 1/6, indicating layer stacking of assemblies[34] and the interlayer distance is 1.9 nm.

Rheological studies of gels are an important technique to prove the formation of gel as gelation involves a transition from a viscous fluid (sol state) to a semi-solid state (gel). The viscoelastic behaviour of a system is generally characterized by the storage modulus (G') and loss modulus (G''). In an oscillatory amplitude sweep experiment, G' represents the ability of the deformed gel to restore its original geometry (*i.e.* measurement of elastic behaviour in solid-like gel), and G'' indicates the tendency of a material to flow under stress (*i.e.* measurement of fluidity in gel). The dynamic modulus of hydrogel system can be described by the relation between the oscillatory stress and strain

where, G' (storage modulus) = $\frac{\sigma_o}{\varepsilon_o}\cos\delta$

G'' (loss modulus) = $\frac{\sigma_o}{\varepsilon_o}\sin\delta$

'ε_o & δ_o' represent the amplitude of strain and stress. 'δ' is the phase difference between them and is equal to "ωt" (frequency of oscillation at time 't'). In the sol state, $G''(\omega) > G'(\omega)$ ($G' \sim \omega^2$ and $G'' \sim \omega$; ω the angular frequency) and in the gel state $G'(\omega) > G''(\omega)$ (G' and $G'' \sim \omega^{\circ}$), demonstrating the dominant elastic behavior of the system.[10,35] All three gels (Fig. 7a, b) have been subjected to frequency sweep measurements under a constant strain of 1% and it is apparent from Fig. 7a that in the frequency range of 1 to 500 rad s^{-1}, ADN/tpca 1 : 1 and ADN/tpca 1 : 3 gels show elastic storage moduli, G', which are always greater than the associated loss moduli (G'') in the said frequency zone whereas similar for ADN/tpca 3 : 1 in the frequency range 1 to 350 rad s^{-1}. In Fig. 7b for ADN/bpca 1 : 1, it is from 1 to 500 rad s^{-1}, for ADN/bpca 1 : 3, 1 to 250 rad s^{-1}, and for ADN/bpca 3 : 1, it is lowest, only 1 to 50 rad s^{-1}. It indicates that the viscoelastic behaviours of these gels are dominated by an elastic nature and are dependent on the composition. This kind of mechanical behaviour is generally a characteristic feature observed for soft materials. However, it is also clear from Fig. 7a, b that the 3 : 1 composition gives the least stable gel for both systems. Similarly, strain sweep measurements (Fig. 7c, d) under a constant frequency 2 rad s^{-1} reveal that G' is not always greater than G'' in the entire range of the strain sweep. At a lower value of strain, G' is greater than G''. After a certain strain is applied to the gel, it is transformed to a sol as indicated by reversal of G' and G'' in the plot.

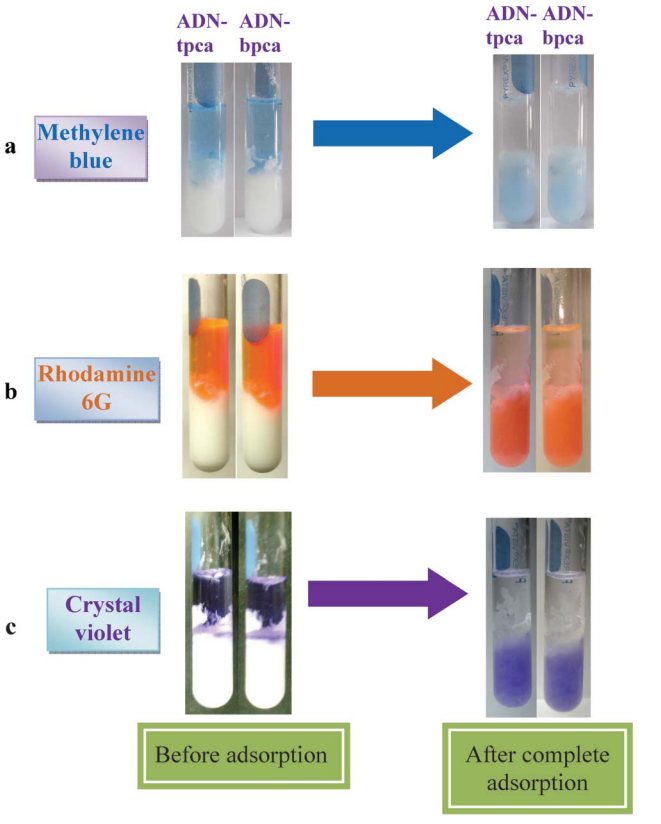


Fig. 8 Photographs of the hydrogels before and after the removal of dyes (a) methylene-blue, (b) rhodamine-6G, and (c) crystal violet.

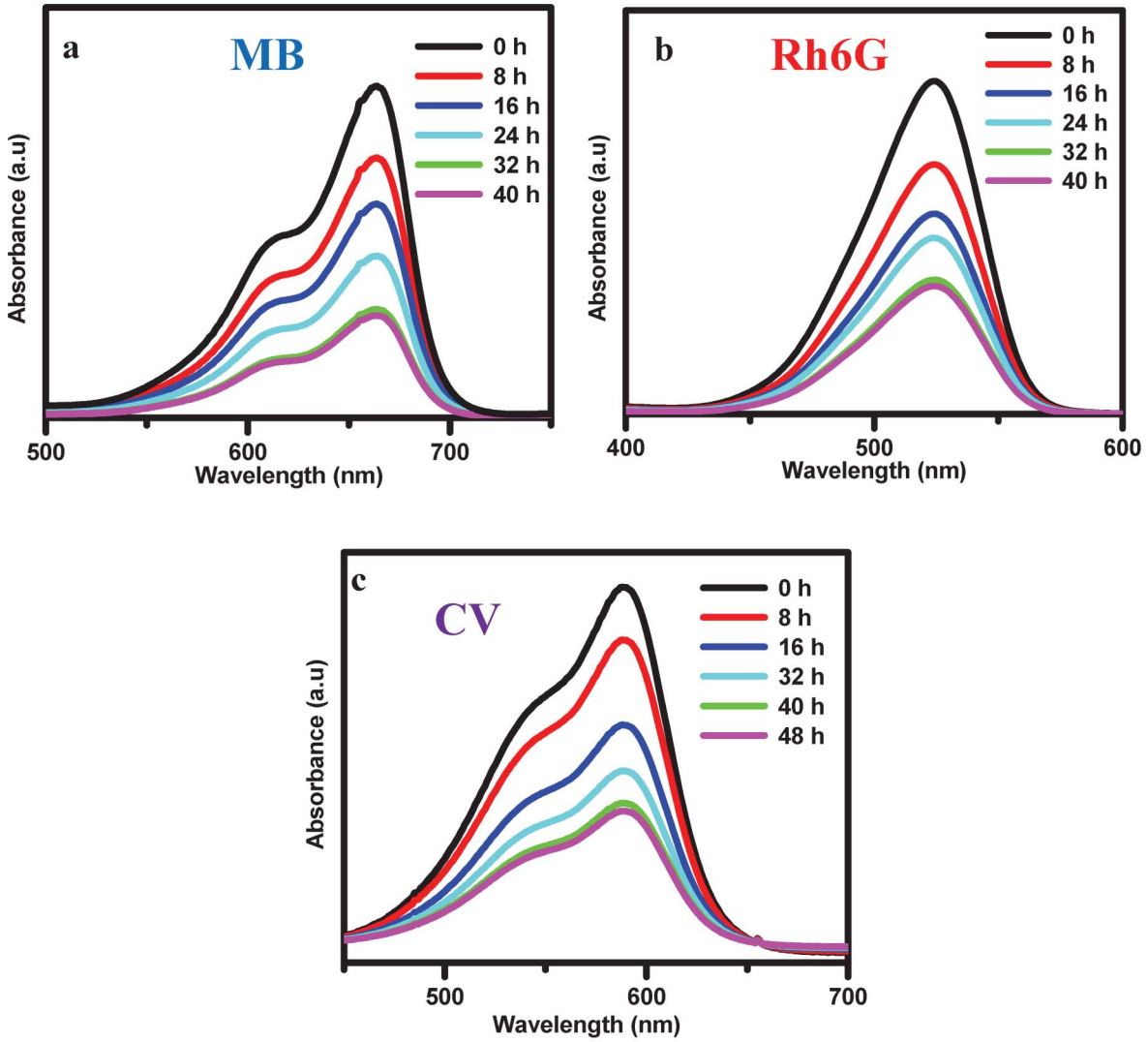


Fig. 9 UV-Vis spectra of dye solution kept contact with ADN-tpca hydrogel (a) methylene blue, (b) rhodamine 6G and (c) crystal violet after indicated hours.

Adsorption of dye molecules from their respective aqueous solution was monitored by UV-visible spectroscopy and dye uptake capacities of the hydrogels were determined by batch kinetic sorption experiments. The adsorption capacity, Q (milligram dye per gram gelator), of gelators was calculated by using the following expression:

$$Q(\mathrm{mg/g}) = \frac{(C_i\text{-}C_e)V}{m}$$

where, C_i and C_e are the initial and equilibrium concentrations of dye (mg L^{-1}), respectively, V is the volume of the solution added (L) and m is the amount of gelator (g). To study the adsorption properties of these specific gelators, we chose three dyes (methylene blue (MB), rhodamine 6G (Rh6G) and crystal violet (CV)) which have absorption bands above 450 nm for the determination of the relative dye uptake of the gelators. In this regard, these hydrogels were very efficient to adsorb three different aqueous solutions of dyes. The process of dye uptake by the hydrogel is shown in Fig. 8, which shows photographs of MB, Rh6G, and CV removal for the two sets of hydrogels, ADN-tpca, and ADN-bpca after 48 h. For the measurement of the kinetics of dye extraction by the gelators, hydrogels were first prepared and then these gels were kept in contact with the aqueous solution of dyes. Fig. 9 (c) shows the maximum number of CV dye molecules can be removed from water within 48 h. Similarly the times taken for the removal of dyes like MB and Rh6G dyes are 32 h and 40 h respectively. Plots of λ_{max} as a function of time for the two gel systems of the three different dyes are presented in Fig. 10 which reveals a significant difference in both the relative dye extraction and maximum dye uptake for the gel systems. From Fig. 11, it is observed that the ADN-tpca gel system is a more efficient bi-component gel system for the absorption of dye than the ADN-bpca system. It is also noticeable that the dye adsorp-

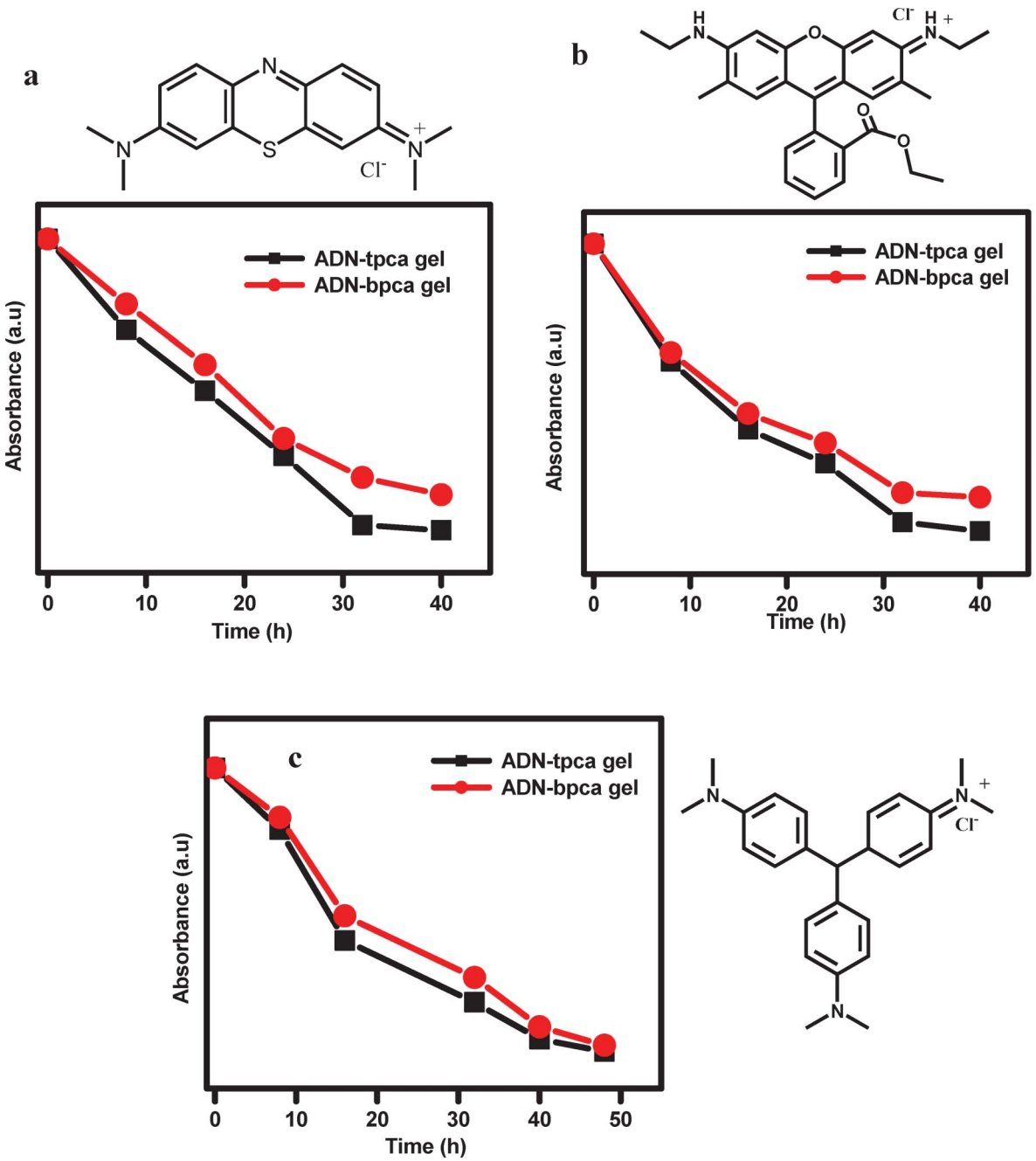


Fig. 10 Plots of λ_{max} *vs.* time (a) methylene-blue absorption at λ_{max} = 664 nm, (b) rhodamine-6G absorption at λ_{max} = 524 nm, and (c) crystal violet absorption at λ_{max} = 590 nm. Corresponding structures of the dyes are attached with the graphs, respectively.

tion efficiency of CV is very large (98.2%) compared to those of the other two dyes, MB (76.1%) and Rh6G (82.4%) for the ADN-tpca gel system (Table 1). This may be due to the hydrophobic interaction between the gelators and dye molecules in a proper way. These results indicate that our hydrogels are efficient to remove toxic dye molecules from water.

Conclusion

In the present manuscript, we have reported the gelation abilities and physical properties of adenine with two different tricarboxylic acids. Upon cooling the pre-warmed solution of adenine and 1,3,5-tris(4-carboxyphenyl)benzene (tpca) or biphenyl-3,4′,5-tricarboxylic acid (bpca) in water, hydrogels were formed which were thermo-reversible in nature and were characterized with the help of various instrumental techniques such as OM, FESEM, HRTEM, AFM, FL. XRD, FT-IR, rheology

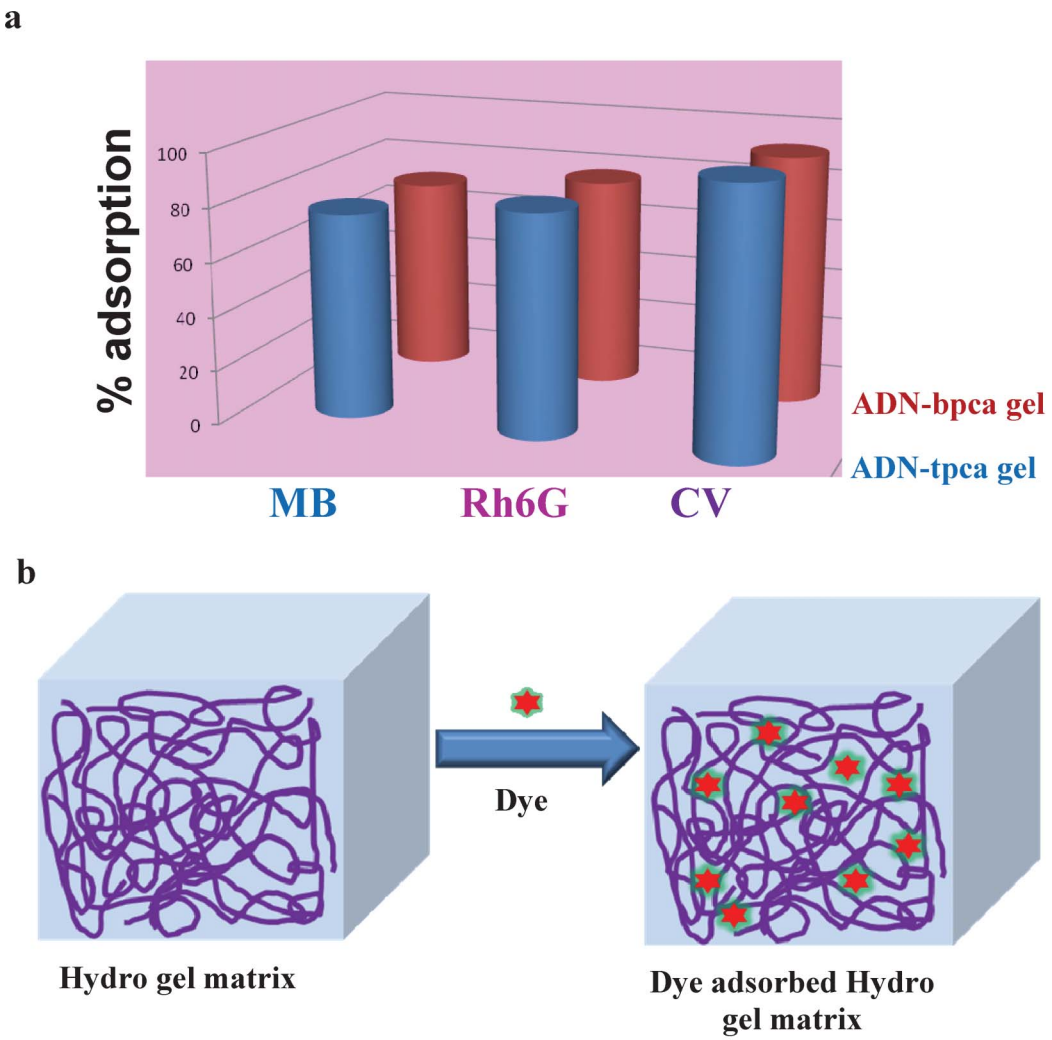


Fig. 11 (a) Graphical representation of the percentage of adsorption of dyes into the hydro gel matrix (computed from Fig. 9). (b) Schematic representation of the dye adsorption by the hydro gel fibers.

etc. The entangled network composed of belts in the hydrogel was observed and the dimensions of the belt depended on the tricarboxylic acid used. The intermolecular hydrogen bonds which were considered to be the driving force for the formation of a stable gel were confirmed by FT-IR studies. In spite of the absence of symmetry either in bpca or adenine, these two moieties surprisingly have produced gels and it is due to the symmetrical position of complementary interaction sites. The mechanical strength of the hydrogel network as revealed by rheological study depends on the tricarboxylic acid used in the two-component systems and also on the composition of the fixed pair. These hydrogels were able to sequester over 0.6 mg of dye per mg of gelator from aqueous solution, with the ADN-tpca gel achieving a higher level of dye adsorption for crystal violet dye than for other dyes. These structure property relationship studies hold the future promise for the realization of inexpensive and highly effective purification systems for waste water.

Table 1 Adsorption data for hydrogels using various dyes

Name of dye	Wavelength (nm) of light absorption maximum of dye solution only	Initial aqueous concentration of the corresponding dyes [mM] (mg mL^{-1})	Quantity of the adsorbed dye in mg per mg of the gelators	
			ADN-tpca gel	ADN-bpca gel
Methylene blue	664	1.0 (0.319)	6.34	6.02
Rhodamine 6G	524	1.0 (0.479)	7.21	7.18
Crystal violet	590	1.0 (0.407)	7.86	7.48

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