ELECTRONIC SUPPLEMENTARY INFORMATION

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

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Analytical Methods:

Field Emission Scanning Electron Microscopy (FESEM): The morphology of the samples were analyzed by field emission scanning electron microscopy (FESEM) using (Supra 40, Carl Zeiss Pvt. Ltd.) microscope at an accelerating voltage 20 kV.

- Sample was prepared by placing a tiny amount of the air-dried gel material over the carbon coated sample holder and was gold coated prior to FESEM analyses.

Transmission Electron Microscopy (TEM): TEM analyses of the samples were carried out on a Hitachi H-9000 NAR transmission electron microscope, operating at 80 kV.

- Samples were prepared by sonicating the air-dried gel material in methanol and then placing a drop of solution on a carbon coated copper grid followed by solvent evaporation in vacuum.

Fourier Transform Infrared Spectroscopy (FTIR): FTIR spectra were collected in KBr pellet in reflectance mode with Nexus 870 Thermo-Nicolet instrument coupled with a Thermo-Nicolet Continuum FTIR Microscope.

X-ray diffraction (XRD): XRD patterns of the air-dried gel and other materials were recorded in a Philips PW-1710 X-ray diffractrometer (40 kV, 30 mA) using Cu *Kα* radiation (λ=1.5418 Å) in the 2*θ* range of 1°-70° at a scanning rate of 0.5˚ min^{-1}.

Rheology: The rheological properties of the gel were achieved with an advanced rheometer (AR 2000, TA Instruments, USA) using cone plate geometry on a peltier plate. The diameter of the plate was 40 mm and angle was 4º with a plate gap of 121µm. The gel samples were placed on the plate and stress sweep experiment at a constant frequency at 25°C and frequency sweep measurements at a constant stress in the linear viscoelastic range were carried out to get the storage or elastic modulus (G′) and loss or viscous modulus (G″) values of the gel materials.

Computational Details: The theoretical calculations were carried out using Gaussion-09 suite software. The geometry optimization for different structure has been obtained from the B3LYP/6-31+g(d,p) level of theory in the Linux operating system.

Reference:

Gaussian 09, Revision D.01, M. J. Frisch and G. W. Trucks and H. B. Schlegel and G. E. Scuseria and M. A. Robb and J. R. Cheeseman and G. Scalmani and V. Barone and B. Mennucci and G. A. Petersson and H. Nakatsuji and M. Caricato and X. Li and H. P. Hratchian and A. F. Izmaylov and J. Bloino and G. Zheng and J. L. Sonnenberg and M. Hada and M. Ehara and K. Toyota and R. Fukuda and J. Hasegawa and M. Ishida and T. Nakajima and Y. Honda and O. Kitao and H. Nakai and T. Vreven and Montgomery, {Jr.}, J. A. and J. E. Peralta and F. Ogliaro and M. Bearpark and J. J. Heyd and E. Brothers and K. N. Kudin and V. N. Staroverov and R. Kobayashi and J. Normand and K. Raghavachari and A. Rendell and J. C. Burant and S. S. Iyengar and J. Tomasi and M. Cossi and N. Rega and J. M. Millam and M. Klene and J. E. Knox and J. B. Cross and V. Bakken and C. Adamo and J. Jaramillo and R. Gomperts and R. E. Stratmann and O. Yazyev and A. J. Austin and R. Cammi and C. Pomelli and J. W. Ochterski and R. L. Martin and K. Morokuma and V. G. Zakrzewski and G. A. Voth and P. Salvador and J. J. Dannenberg and S. Dapprich and A. D. Daniels and Ö. Farkas and J. B. Foresman and J. V. Ortiz and J. Cioslowski and D. J. Fox**,** Gaussian, Inc., Wallingford CT, 2009.

Results and discussion

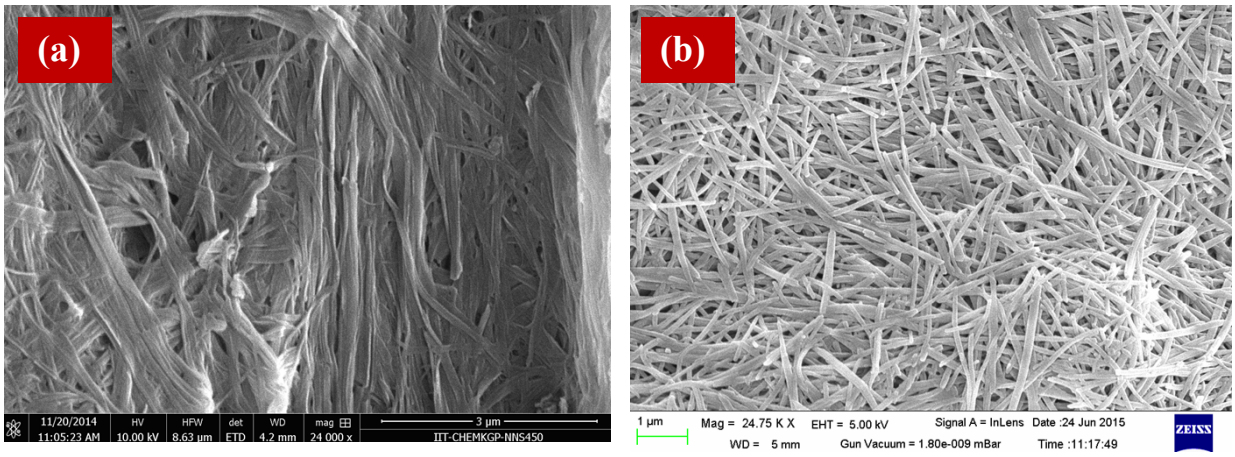

Fig. S1 FESEM images of the hydrogels in methanol-water solvent system where citrazinic acid/melamine molar ratio are (3:1; "a") and (1:3; "b") respectively showing no major morphological alterations from the gel morphology synthesized in (1:1) molar ratio.

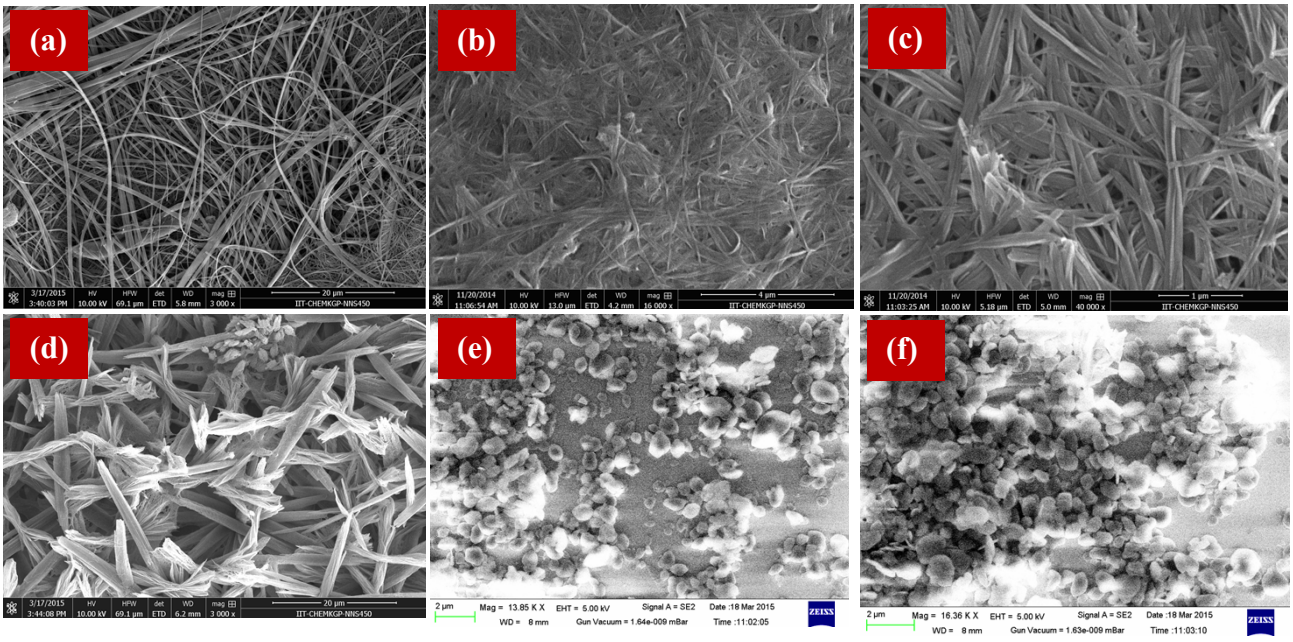

Fig. S2 FESEM images of the gels synthesized from the citrazinic acid-melamine gelator (molar ratio = 1:1) prepared in a couple of pure and mixed solvents. (a) Dimethylformamide-Water (b) Methanol-Water (c) Water (d) Methanol (e) Methanol-Dimethylformamide (f) Dimethylformamide. The images clearly reflect that water plays key role in the formation of fibrous architectures of the gel. In non-aqueous solvent system the complete gelation was not observed.

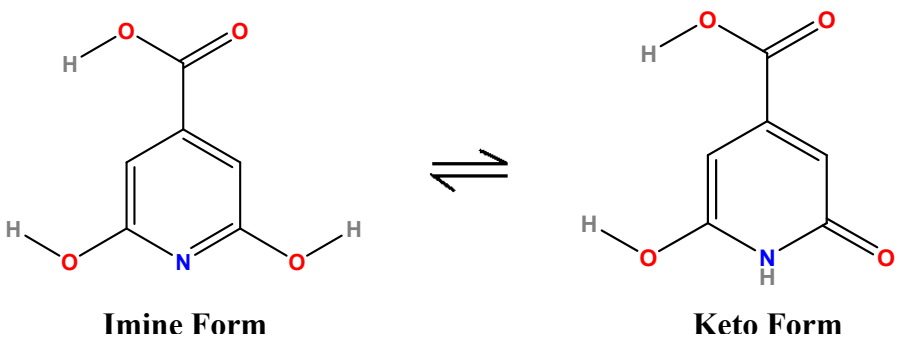

Fig. S3 Molecular structure of citrazinic acid showing the presence of both keto and imine form in its equilibrium.

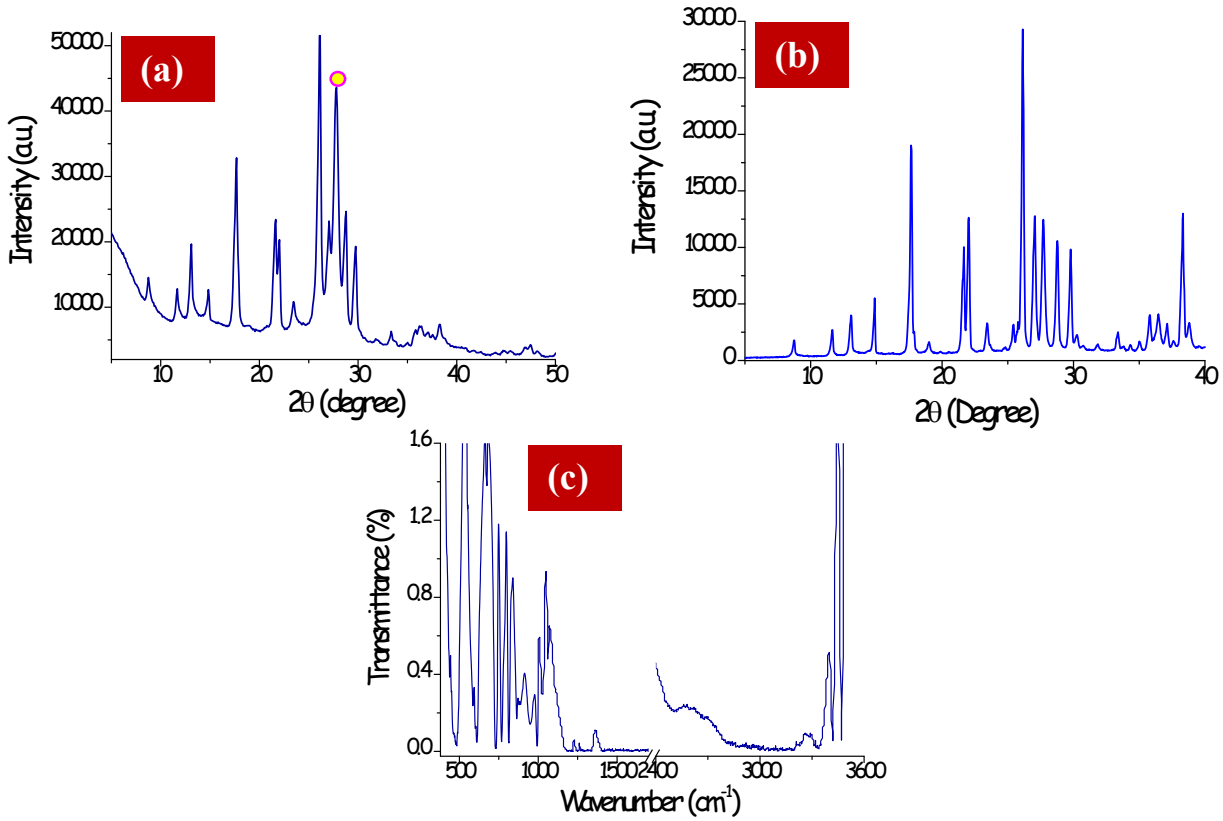

Fig. S4 PXRD patterns of (a) ground mixture (b) physical (un-ground) mixture of melamine and citrazinic acid. (c) FTIR pattern of the ground mixture. The XRD pattern of the ground mixture (Fig. S4a) shows the presence of diffraction peak at 27.8° (marked in the figure). This peak resembles the main diffraction peak of the XRD profile of the dry gel (Fig. 3a).

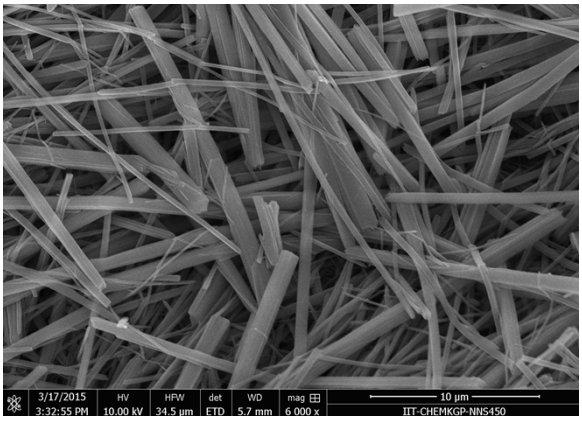

Fig. S5 FESEM image of the physical mixture of citrazinic acid and melamine (in un-ground condition) after sonication in acetonitrile-water mixed solvent system. Here instead of formation of fibrous architectures, rod-like nanostructures were observed, clearly indicating the key role of solid-state grinding in the synthetic protocol (as described in MS).

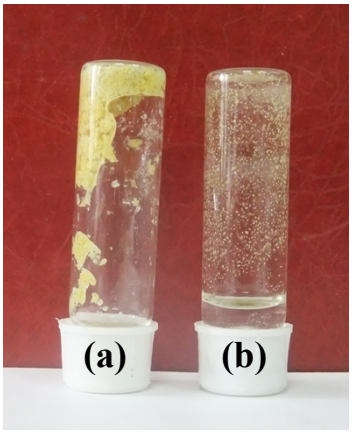

Fig. S6 Partial gelation of the physical mixture (unground) in neat water under heating-cooling technique. However, in case of mixed solvent system (CH_3CN-H_2O), no such partial gelation was observed under this technique. The mixture (citrazinic acid-melamine) forms precipitate.

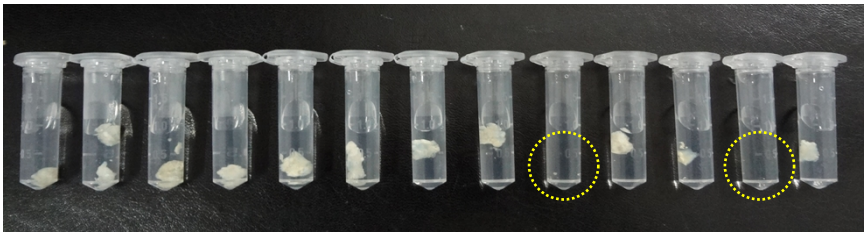

Fig. S7 The response of the air-dried gel (the off-white monolith in the tube) towards sodium/potassium salt of some anions. ***From left-to-right***: F^-, Cl^-, Br^-, I^-, SO_4^{2-}, NO_3^-, $S_2O_3^{2-}$, SCN^-, CN^-, $H_2PO_4^-$, HPO_4^{2-}, S^{2-} and NO_2^-. The immediate dissolution of the gel matrix takes place selectively in presence of only two ions, cyanide and sulfide (encircled in the figure).

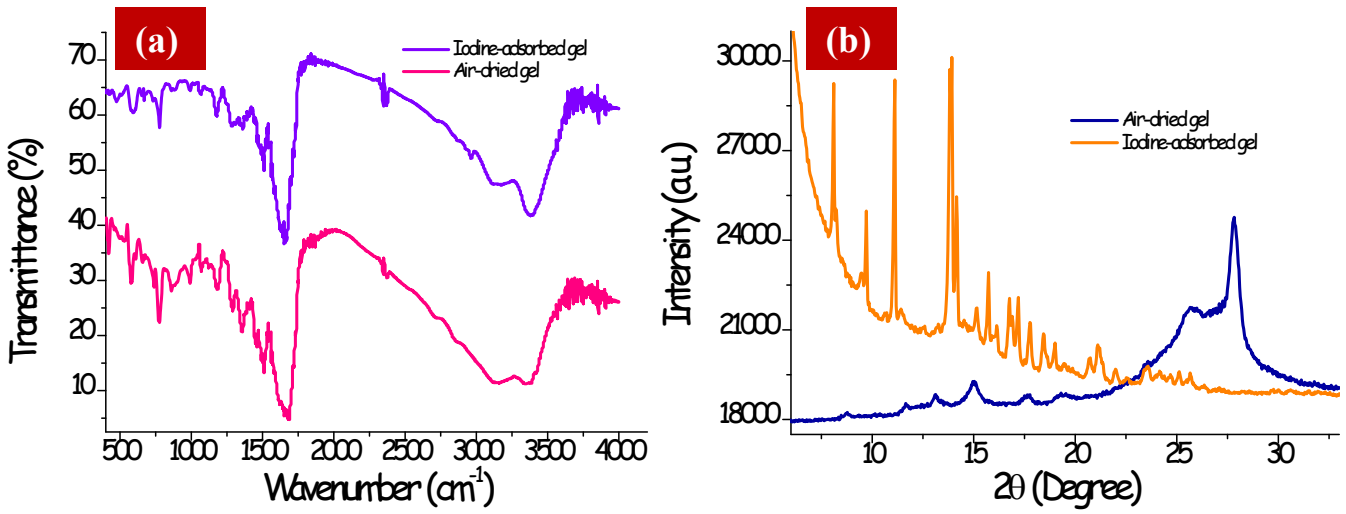

Fig. S8 (a) FTIR spectra of the iodine-adsorbed gel and air-dried gel (b) PXRD patterns of the iodine-adsorbed gel and air-dried gel.

Table S1. Gelation studied in different solvent and mixed-solvent systems with corresponding Kamlet-Taft solvent parameters of the pure solvents*

Entry	Solvent	Phase	Kamlet-Taft parameters		
			α	β	π*
1	H_2O	G	1.17	0.47	1.09
2	H_2O-CH_3OH	G	-	-	-
3	H_2O-DMF	G	-	-	-
4	H_2O-CH_3CN	G	-	-	-
5	H_2O-THF	G	-	-	-
6	CH_3OH	PG	0.98	0.66	0.60
7	EtOH	PG	0.86	0.75	0.54
8	*i*-PrOH	PG	0.76	0.84	0.48
9	Butanol	PG	0.84	0.84	0.47
10	THF	D/P	0.00	0.58	0.55
11	CH_3CN	D/P	0.19	0.40	0.75
12	CH_3OH-DMF	D/P	-	-	-
13	DMF	S	0.00	0.69	0.88
14	Toluene	I	0.00	0.11	0.54
15	$CHCl_3$	I	0.20	0.10	0.58
16	Et_2O	I	0.00	0.47	0.27
17	n-Heptane	I	0.00	0.00	-0.08
18	Benzene	I	0.00	0.10	0.59

***G = Gelation; PG = Partial Gelation; I = Insoluble; D/P = Dispersion and Precipitation; S = Solution**

Table S2. pKa values of different Brønsted acid

Acid	pKa
HF	3.17
HCl	(-)7.00
HBr	(-)9.00
HI	(-)10
H_2SO_4	(-)3.00 (*for 1st deprotonation*)
HNO_3	(-)1.3
$H_2S_2O_3$	0.6 (*for 1st deprotonation*); 1.6 (*for 2nd deprotonation*)
HSCN	4.0
HCN	**9.4**
H_3PO_4	2.12 (*for 1st deprotonation*)
NaH_2PO_4	7.21 (*for 1st deprotonation*)
H_2S	7.0 (*for 1st deprotonation*); **12.89** (*for 2nd deprotonation*)
HNO_2	3.29