

Anion-triggered melamine based self-assembly and hydrogel

Jiang-Shan Shen,^a Qing-Guo Cai,^b Yun-Bao Jiang,^b Hong-Wu Zhang*^a

^a *Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China*

^b *Department of Chemistry, College of Chemistry and Chemical Engineering, and the MOE Key Laboratory of Analytical Sciences, Xiamen University, Xiamen 361005, China*

Fax: (+86)592-619-0773; Tel: (+86)592-619-0773; E-mail: hwzhang@iue.ac.cn

Supporting Information

Chemicals and characterizations

All chemicals commercially available at AR grade were used as received.

Infrared (IR) spectra were conducted on Nicolet AVATAR FT-IR360 spectrophotometer. X-Ray powder diffractions (XRD) were performed on Panalytical X'pert PRO diffractometer equipped with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at room temperature. Field emission scanning electron microscopy (FESEM) experiments were carried out on HITACHI S-4800 working at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) experiments were performed on HITACHI H-7650 system. Elemental analysis data were obtained on Vario EL III analyzer. For XRD, IR, and elemental analysis characterization, samples were prepared by freeze-drying the original hydrogels under vacuum at $-80 \text{ }^\circ\text{C}$, the corresponding xerogels were then washed several times by water to remove free ions and melamine and then dried in vacuum at room temperature.

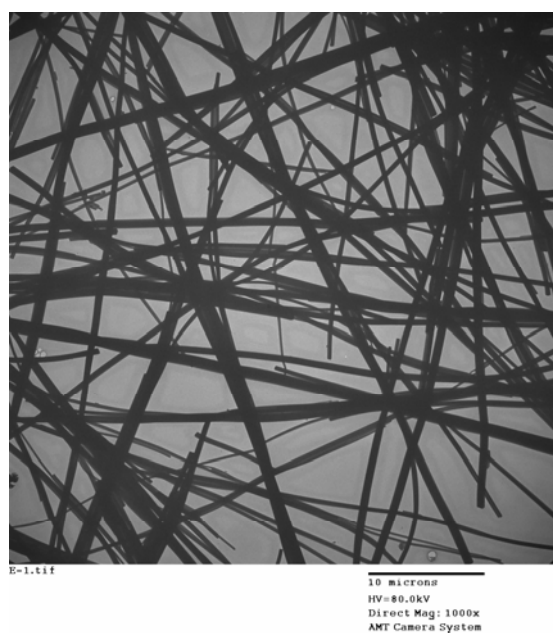


Fig. S1 TEM image of melamine (M) xerogel from the corresponding original hydrogel of protonated M triggered by PO_4^{3-} . The scale bar is $10\ \mu\text{m}$.

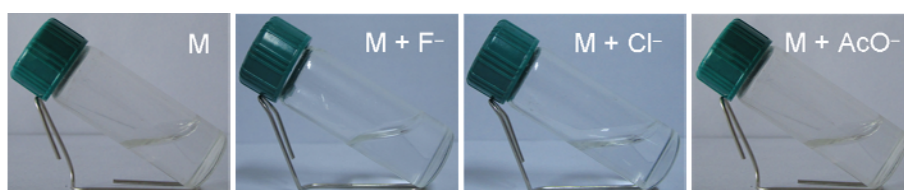


Fig. S2 No gelation of protonated melamine (M) could be observed in the presence of F^- , Cl^- , and AcO^- , respectively. The molar ratio of anion to M was 6:1 and the total concentration was 700 mM, and pH was 2-5.

Table S1. Experimental conditions and observations of melamine (M)-anion systems

Anions	[anion] / mM	[M] / mM	[anion] / [M]	pH	observation
F ⁻	600	100	6 : 1	ca.2-5	Sol
Cl ⁻	600	100	6 : 1	ca.2-5	Sol
NO ₃ ⁻	300	50	6 : 1	ca.2-5	Gel
PO ₄ ³⁻	600	100	6 : 1	ca.2-5	Gel
SO ₄ ²⁻	450	75	6 : 1	5	Gel
ATP	100	100	1 : 1	ca.2-5	Gel
AcO ⁻	600	100	6 : 1	ca.2-5	Sol

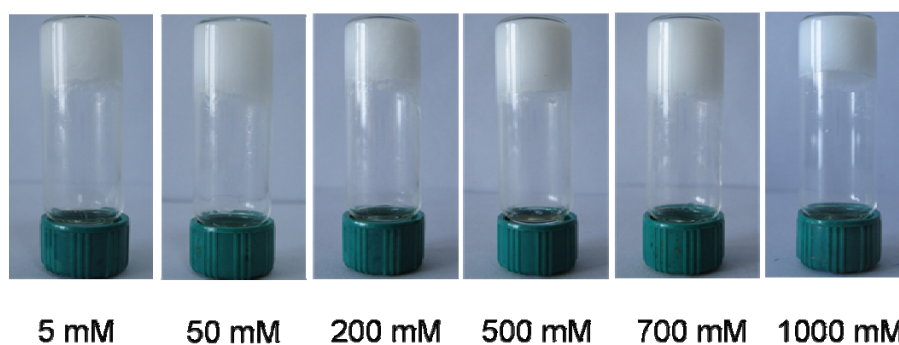


Fig. S3 Ionic strength effect on the hydrogelation of protonated melamine (M) triggered by NO₃⁻. NaCl concentration varied from 5 to 1000 mM. The molar ratio of NO₃⁻ to M was 6:1 and the total concentration of M-NO₃⁻ was 700 mM. pH was 2-5.

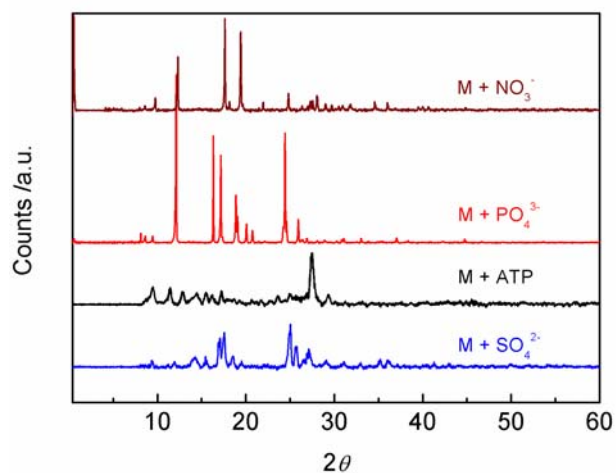


Fig. S4 X-ray diffraction patterns of the xerogels from the corresponding original hydrogels of protonated melamine (M) triggered by NO₃⁻, PO₄³⁻, SO₄²⁻, and ATP, respectively.

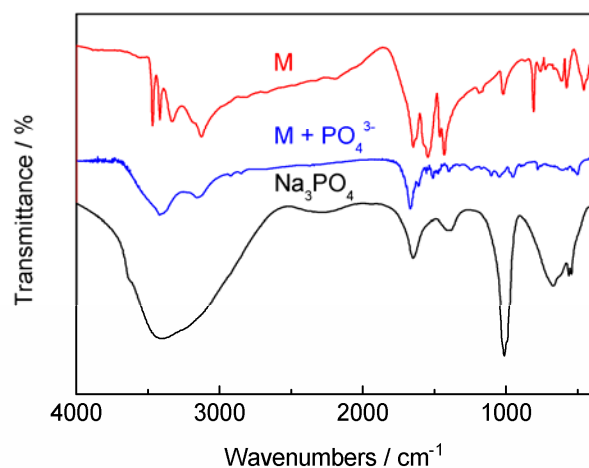


Fig. S5 IR spectra in KBr pellet of melamine (M), Na₃PO₄, and M(H⁺)_m-PO₄³⁻ xerogel from the corresponding original hydrogel of protonated melamine triggered by PO₄³⁻

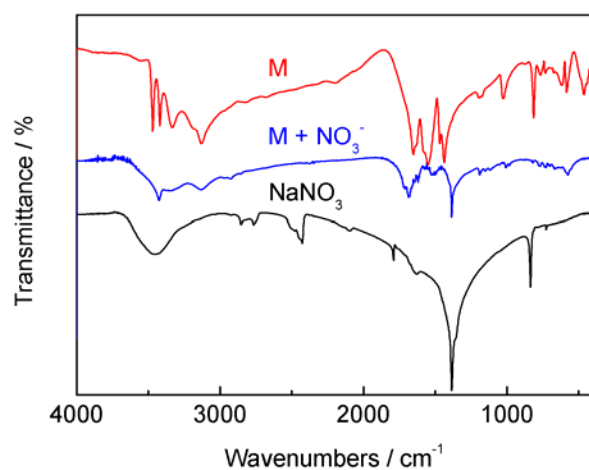


Fig. S6 IR spectra in KBr pellet of melamine (M), NaNO₃, and M(H⁺)_m-NO₃⁻ xerogel from the corresponding original hydrogel of protonated melamine triggered by NO₃⁻

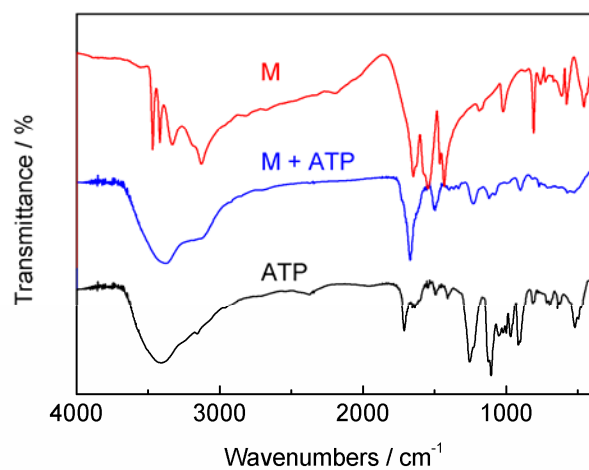


Fig. S7 IR spectra in KBr pellet of melamine (M), ATP, and M(H⁺)_m-ATP xerogel from the corresponding original hydrogel of protonated melamine triggered by ATP

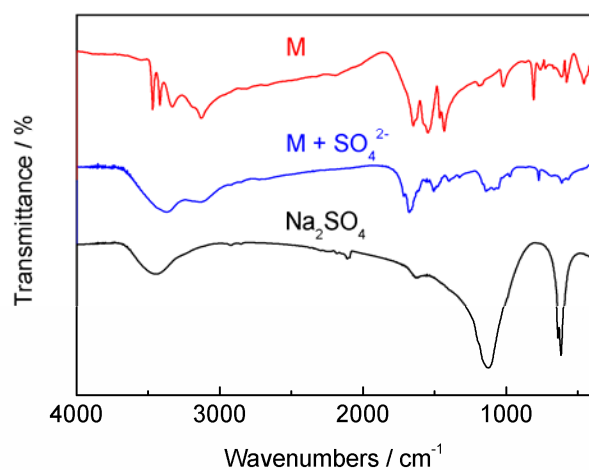


Fig. S8 IR spectra in KBr pellet of melamine (M), Na₂SO₄, and M(H⁺)_m-SO₄²⁻ xerogel from the corresponding original hydrogel of protonated melamine triggered by SO₄²⁻

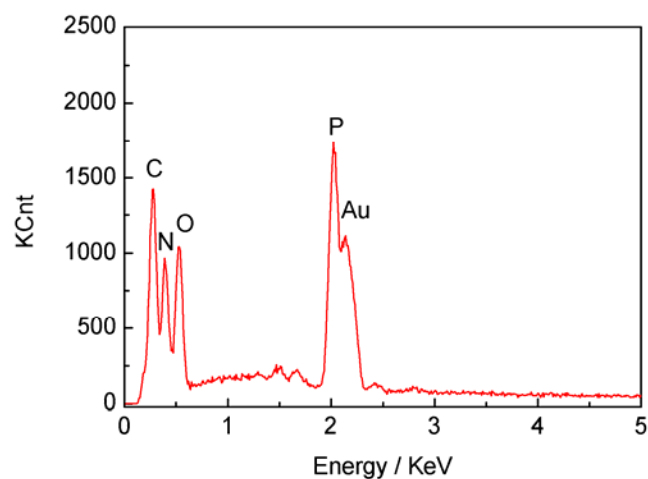


Fig. S9 EDX spectrum of M(H⁺)_m-PO₄³⁻ xerogel from the corresponding original hydrogel of protonated melamine triggered by PO₄³⁻

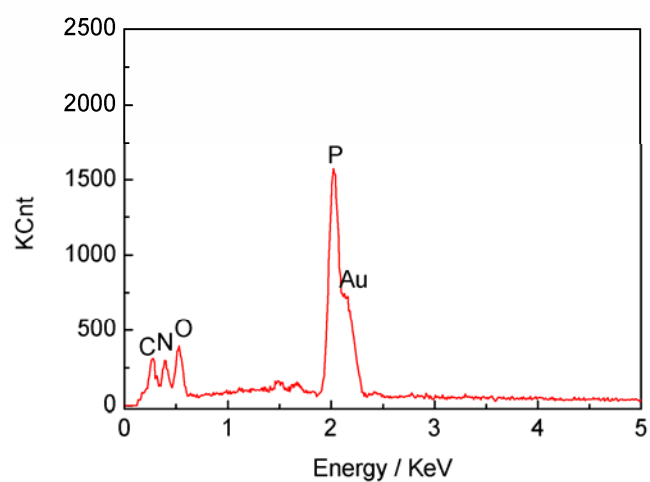


Fig. S10 EDX spectrum of $M(H^+)_m$ -ATP xerogel from the corresponding original hydrogel of protonated melamine triggered by ATP

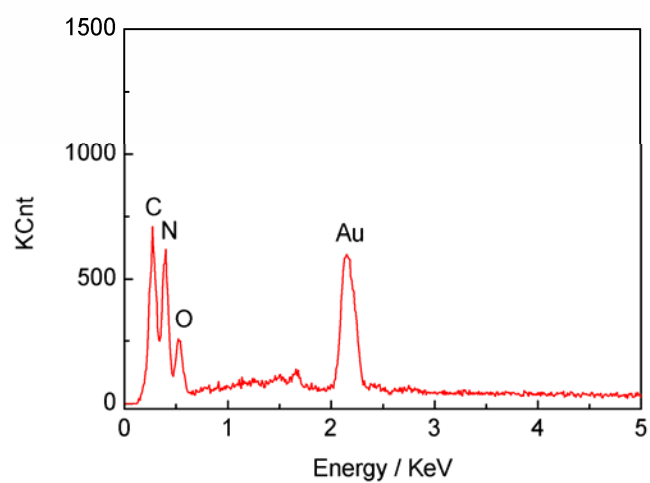


Fig. S11 EDX spectrum of $M(H^+)_m$ - NO_3^- xerogel from the corresponding original hydrogel of protonated melamine triggered by NO_3^-

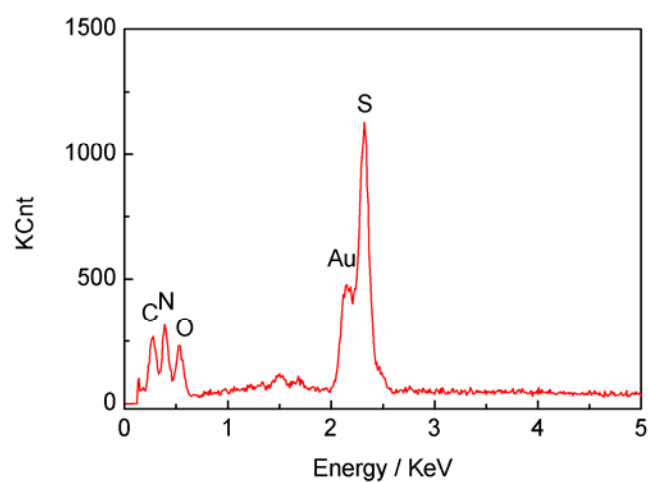


Fig. S12 EDX spectrum of $M(H^+)_m-SO_4^{2-}$ xerogel from the corresponding original hydrogel of protonated melamine triggered by SO_4^{2-}

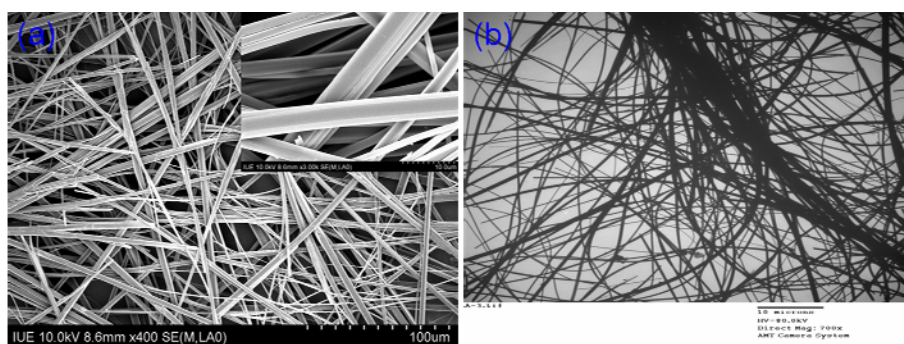


Fig. S13 FESEM (a) and TEM (b) images of melamine - NO_3^- sol system. Molar ratio of melamine to NO_3^- was 1:1 and total concentration was 50 mM. pH was 2-5. The scale bars for (a) and (b) are 100 μm and 10 μm , respectively. The scale bar for inset in (a) is 10 μm .

Table S2. Elemental analysis data of protonated $M(H^+)_m-XO_y^{n-}$ xerogels

Sample name	Weight ^a / [mg]	Content / [%]	$n_M : n_{XO_y^{n-}}$
M-NO ₃ ⁻	1.5680	N: 51.37; C: 18.74; H: 3.224	1:1
	2.6470	N: 51.22; C: 18.78; H: 3.462	1:1
M-PO ₄ ³⁻	2.2220	N: 37.95; C: 16.06; H: 4.404	1:1
	2.4280	N: 37.86; C: 16.02; H: 3.808	1:1
M-ATP	1.9630	N: 31.48; C: 22.60; H: 4.406	2:1
	1.9530	N: 31.21; C: 22.48; H: 4.479	2:1
M-SO ₄ ²⁻	3.6590	N: 44.18; C: 18.89; H: 4.411	3:2
	3.5480	N: 44.07; C: 18.87; H: 4.842	3:2

a. Every sample had two measurements.