Electronic Supplementary Information

for

Tunable, Luminescent, and Self-healing Hybrid Hydrogels of Polyoxometalates and Triblock Copolymers Based on Electrostatic Assembly

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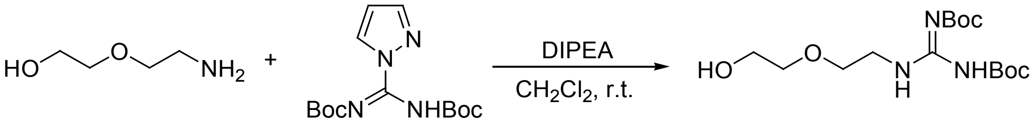
1. Experimental Section

1.1 Materials and Measurements

$Na_9EuW_{10}O_{36}\cdot 32H_2O$ was prepared as described by Yamase.[S1] *N,N′*-bis(tert-butoxycarbonyl)-1*H*-pyrazole-1-carboxamidine, 2-(2-aminoethoxy) ethanol, and *N,N*-diisopropylethylamine were purchased from Tokyo Chemical Industry Co. and used without further purification. Copper (I) bromide (CuBr) was purified by stirring with glacial acetic acid for 2 hours, filtrating, and then washing with glacial acetic acid, ethanol and diethyl ether in succession, finally stored in glove box before use. *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA), poly(ethylene glycol) ($M_n \approx$ 10 000 g/mol) was purchased from Sigma-Aldrich Ltd and used without further purification. Methacryloyl chloride was purchased from Sinopharm Chemical Reagent Co. Ltd and purified by distillation under reduced pressure. Unless otherwise noted, the other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd.

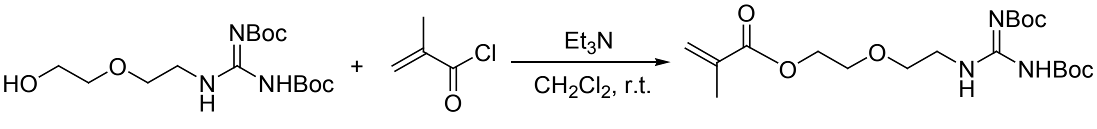
^1H and ^{13}C NMR spectra were recorded on a Bruker 400 AVANCE Ⅲ spectrometer operating at 400.23 and 100.65 MHz, using $CDCl_3$ as solvent. High-resolution mass spectra (HRMS) were performed by the ESI ionization technique (using a quadrupole analyzer). A commercial laser light scattering spectrometer (Brookhaven Inc, Holtsville, NY) equipped with a BI-200SM goniometer and a BITurboCorr digital correlator was used to perform both static light scattering (SLS) and dynamic light scattering (DLS) over a scattering angle range of 20 to 150°. A 100 mW vertically polarized solid-state laser (GNI, Changchun, China) operating at 532 nm was used as light source. The intensity time-correlation function was analyzed by the CONTIN method. Rheological measurements were performed using a rheometer (MCR 301, Anton Paar) with cone plate geometry with a cone angle 2º and a diameter of 25 mm. The hydrogels were placed between the cone plate and the platform with special care to avoid evaporation of water. Oscillatory rheological measurements were performed in the linear viscoelastic regime at 25 ºC. The strain was kept at 0.8% to ensure the linearity of dynamic viscoelasticity and the frequency was varied from 0.1 to 100 rad/s. The recovery property of the hydrogels in response to applied shear forces was probed as the following procedure: 50% (600 s) → 0.8% (600 s) → 50% (600 s) → 0.8% (600 s) → 50% (600 s) → 0.8% (1200 s). Cryo-TEM was performed at -178 °C with a 200 kV accelerating voltage. In order to avoid evaporation of water, the sample preparation was conducted in an environmental chamber having relative air humidity of 100%. A small amount of the hydrogel (~ 3 μL) was placed onto a holey carbon grid, and the excess hydrogel was swept off by filter papers, followed by immediate plunging of the samples into liquid ethane at its melting temperature (-174 °C). The vitrified samples were then stored in liquid nitrogen until they were transferred to a cryogenic sample holder (Gatan 626) and examined with a JEM 2200FS TEM (200 KeV) equipped with a Gatan multiscan CCD at about –178 °C. Photoluminescence measurements were performed on an FLS 920 Steady State & Time-resolved Fluorescence Spectrometer (Edinburgh Instruments Ltd.). Photoluminescence quantum yields (PLQY) were measured by absolute PL quantum yield measurement system C9920-02 at the excitation wavelength of 280 nm. Small-angle X-ray scattering (SAXS) measurements were performed using a SAXSess (Anton Paar) equipped with Kratky block-collimation system. The scattering pattern was recorded on an imaging plate (IP) with a pixel size of 42.3×42.3 μm^2 which extended to the high-angle range (the q range covered by the IP was from 0.06 to 29 nm^{-1}). Background subtraction and desmearing were conducted by using SAXSquant 3.6 software. The pairdistance distribution function (PDDF) of scattering curves was calculated using the generalized indirect Fourier transform (GIFT)[S2] program included in the SAXSess software package.

1.2 Synthesis of 2-[2-(*N,N′*-di-*tert*-butoxycarbonylguanidino)ethoxy] ethanol (1)



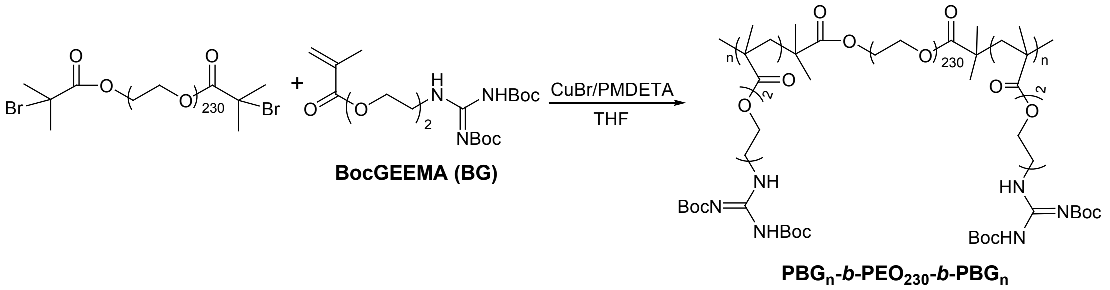
A solution of *N,N′*-bis(tert-butoxycarbonyl)-1*H*-pyrazole-1-carboxamidine (2.00 g, 6.44 mmol) in DCM (10 mL) was added dropwise to a stirred solution of 2-(2-aminoethoxy) ethanol (0.68 g, 6.44 mmol) and *N,N*-diisopropylethylamine (2.50 g, 19.3 mmol) in DCM (20 mL). The mixture was stirred overnight, and the reaction solution was diluted with DCM (30mL) and washed successively with 0.15 N HCl (3 × 40 mL), 0.15 N $NaHCO_3$ (3 × 40 mL), and brine (2 × 50 mL). The organic layer was dried over Na_2SO_4, and the concentrated under reduced pressure to provide the desired compound which was purified by chromatography on silica gel using DCM/EtOAc (2/1, v/v) as an eluent to give **1** (1.81 g, 81%) as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.49 (s, 9H), 1,50 (s, 9H), 2,45 (br, s, OH, 1H), 3.62 (m, 4H), 3.68 (m, 2H), 3.76 (m, 2H), 8.84 (br, s, NH, 1H), 11.49 (br, s, NH, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 28.1, 28.3, 40.4, 61.9, 69.0, 72.4, 79.5, 83.5, 153.3, 156.1, 163.3. HRMS: cacld for $C_{15}H_{30}N_3O_6$ (MH^+) 348.2132, found 348.2129.

1.3 Synthesis of 2-[2-(*N,N′*-di-*tert*-butoxycarbonylguanidino)ethoxy] ethyl methacrylate (BocGEEMA, BG)



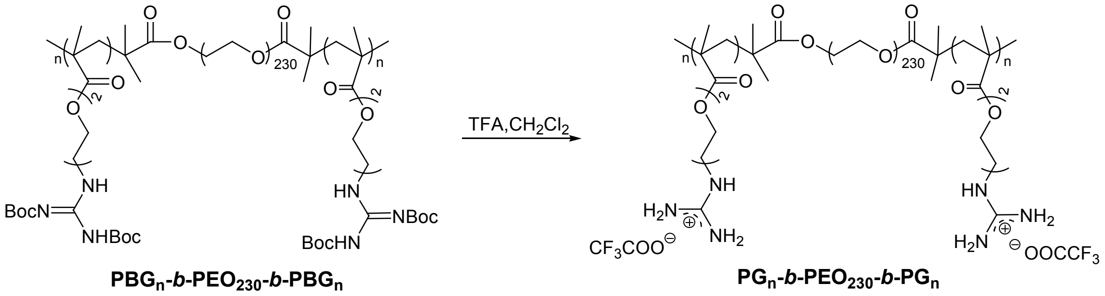
To a solution of **1** (1.81 g, 5.21 mmol) and Et_3N (1.1 mL, 7.82 mmol) in dry DCM (20 mL), placed ice-water bath under nitrogen atmosphere, methacryloyl chloride (0.60 g, 5.73 mmol) in DCM (10 mL) was added dropwise with a dropping funnel. After stirring at 0 °C for 30 min, the mixture was stirred for 6 h at room temperature, and then quenched with water. The reaction mixture was diluted with DCM (40 mL) and washed successively with 0.2 N HCl (3 × 50 mL), 0.2 N $NaHCO_3$ (3 × 50 mL), and brine (2 × 50 mL). The organic layer was dried over Na_2SO_4, and concentrated under reduced pressure to provide **2** (1.60 g, 74%) as a colorless oil which was purified by chromatography on silica gel using DCM/EtOAc (15/1, v/v) as eluent. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.49 (s, 9H), 1.51 (s, 9H), 1.95 (s, 3H), 3.64 (m, 2H), 3.68 (m, 2H), 3.74 (t, $J = 4.80$ Hz, 2H), 4.31 (t, $J = 4.80$ Hz, 2H), 5.57 (m, 1H), 6.15 (m, 1H), 8.71 (br, s, NH, 1H), 11.47 (br, s, NH, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 18.3, 28.0, 28.3, 40.7, 63.9, 68.9, 69.4, 79.4, 83.0, 125.8, 136.1, 153.0, 156.2, 163.4, 167.3. HRMS: cacld for $C_{19}H_{34}N_3O_7$ (MH^+) 416.2387, found 416.2391.

1.4 Synthesis of the PBocGEEMA-*b*-PEO-*b*-PBocGEEMA (PBG-*b*-PEO-*b*-PBG) triblock polymers



A typical procedure for the preparation of a ABA triblock copolymer PBG-*b*-PEO-*b*-PBG by ATRP was illustrated as follows: Br-PEO-Br (0.23 g, 2.31 × 10^{-5}mol), BocGEEMA (0.46 g, 1.11 × 10^{-3}mol), copper (I) bromide (13.24 mg, 9.23 × 10^{-5}mol), PMDETA (15.59 mg, 9.23 × 10^{-5}mol), and dry THF (3 mL) were added into a glass tube. The mixture in the tube was degassed by three freeze-vacuum-thaw cycles. The tube was sealed under vacuum and then immersed into a water bath thermostated at 35 °C. After the polymerization proceeded for 3 h, the reaction was quenched by immersed the tube to the liquid nitrogen. The polymerization mixture was diluted with THF and precipitated in hexanes. The polymer was then dissolved in THF (10 mL) and precipitated in hexane (150 mL) three times. The copper catalyst was removed by dissolving the polymer in 2 M KCl solution containing 10 mM EDTA at pH = 3, and extracted two times with DCM (50 mL). The organic layers were combined and washed with 2 M KCl solution (50 mL) containing 10 mM EDTA at pH = 3 to remove the copper catalyst thoroughly. The organic layer was dried over Na_2SO_4, concentrated under reduced pressure, then dissolved in THF (10 mL), and precipitated in hexane (150 mL). After drying in vacuum, the polymer was obtained as a white powder (0.45 g, yield: 65%). Gel permeation chromatography analysis results (polystyrene standards): $M_{n,\,GPC}$ = 24100 g/mol and the polydispersity index (PDI) = 1.18. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm), 0.96 (m, 3H; CH_3), 1.49 (s, 18 H, $(CH_3)_3C$), 1.76 (m, 2H; CH_2), 3.64 (bs, 41H; OCH_2CH_2O of both EO and BG units), 4.09 (s, 2H, $COOCH_2$), 8.58 (s, 1H; NH), 11.50 (s, 1H; NH). The number of PBG units in this ABA triblock copolymer was 13, calculated from its ^{1}H NMR spectrum.

1.5 Synthesis of the PGEEMA-*b*-PEO-*b*-PGEEMA (PG-*b*-PEO-*b*-PG) triblock polymers



PBG-*b*-PEO-*b*-PBG (0.45 g, $M_{n,\,GPC}$ = 24100 g/mol, PDI = 1.18) was dissolved in a 100 mL flask with 20 mL of dry DCM, followed by the addition of trifluoroacetic acid (20 mL), and the resulting solution was stirred for 6 h at room temperature. The volatiles in the reaction mixture were removed using a rotavapor, and then the residues were dissolved in MeOH, evaporated again by a rotavapor. This process was repeated an additional two times to remove CF_3COOH as much as possible. The polymer was then dissolved in THF (12 mL), precipitated in hexanes/diethyl ether (v/v = 3/1, 200 mL), and dried in high vacuum. Complete deprotection of the Boc groups was confirmed by the disappearance of the ^{1}H NMR signal at $\delta = 1.49$ ppm of *tert*-Boc. ^{1}H NMR (D_2O): δ (ppm), 1.00 (m, 3H; CH_3), 1.85 (m, 2H; CH_2), 3.36 (s, 2H; CH_2-N), 3.64 (bs, 39H; OCH_2CH_2O of both EO and G units), 4.13 (s, 2H, $COOCH_2$).

1.6 Preparation of hybrid hydrogels

All the hydrogels were prepared at a charge stoichiometric point of macroanionic EuW_{10} and cationic PG-*b*-PEO-*b*-PG copolyelectrolytes. In a typical procedure of hydrogelation, 0.32 mL of an aqueous solution of EuW_{10} (36 mg, 10 wt%) was added into 0.63 mL of aqueous solution of copolyelectrolyte (PG_{13}-*b*-PEO_{230}-*b*-PG_{13}, 70 mg, 10 wt%), and then mixed under vigorous stirring. The solution mixture became completely gelation within 1 minute, forming a self-standing hydrogel.

2. Characterization of the triblock copolymers

Gel Permeation Chromatography (GPC) was performed to determine the relative molecular weight of the triblock copolymer PBG-*b*-PEO-*b*-PBG, and the results were illustrated in Fig. S1. GPC was carried out at room temperature using Waters 515 HPLC pump with a Waters 2410 refractive-index detector. THF was used as the eluent at a flow rate of 1.0 mL/min at 35 ºC. All GPC curves were calibrated against a series of monodispersed polystyrene standards.

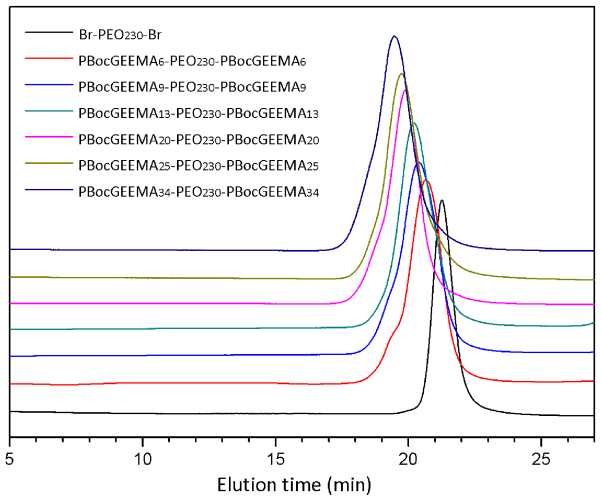


Fig. S1, GPC traces of PEO macroinitiator and PBG-*b*-PEO-*b*-PBG triblock copolymers.

Take copolymer PBG_{34}-PEO_{230}-PBG_{34} as a typical example, the degree of polymerization (DP) of the triblock copolymer was calculated from the integral values of the peak located at 4.09 ppm (peak d, -$COOCH_2$- of BG) to the peak of PEO (3.64 ppm), see Fig. S2. Taking into account the integral values of PEO overlaid into three -CH_2- units of BG, thus, the DP was determined by eq 1:

$$\mathrm{DP} = \frac{2\times I_d}{(I_{PEO}-3I_d)} \times 230 \qquad (1)$$

Where I_{d} and I_{PEO} represent the integral value of the peak d and PEO. The calculated molecular weight based on NMR ($M_{\mathrm{n,\,NMR}}$) was given by eq 2:

$$M_{n,NMR} = 10000 + DP \times 415.44 \qquad (2)$$

where 10000 and 415.44 are the molecular weights of PEG macroinitiator and the BG monomer, respectively. Detailed experimental conditions and the average molecular weights by GPC and NMR were given in Table S1.

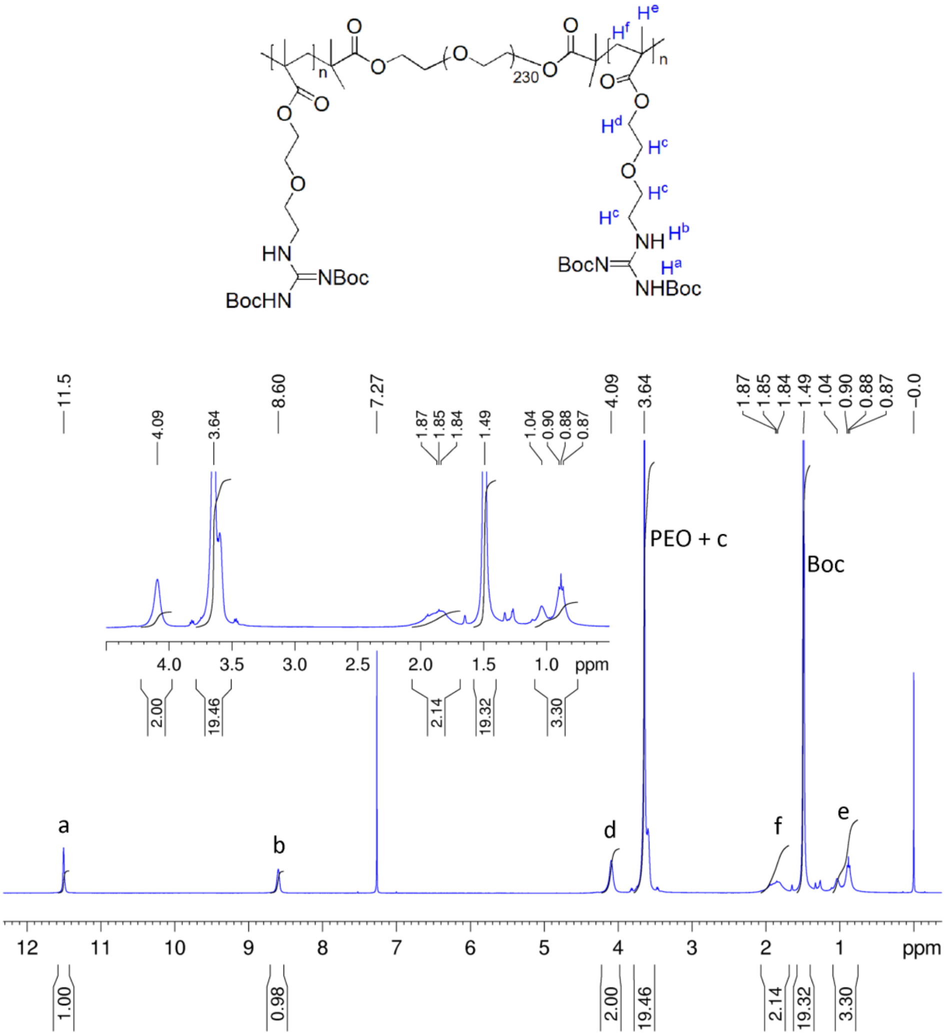


Fig. S2, Typical ^{1}H NMR spectrum of the triblock copolymer PBG$_{34}$-PEO$_{230}$-PBG$_{34}$ in CDCl$_3$.

Table S1, Experimental conditions[a] and characterizations of the ABA triblock copolymers synthesized by the ATRP method

no.	sample	$[M]_0/[I]_0$ [b]	time (h)	$M_{n,\,GPC}$ [c]	$M_{n,\,NMR}$ [d]	$M_{w,\,GPC}$	M_w/M_n [e]
1	PBG_6-PEO_{230}-PBG_6	24	1.5	20,900	15,000	24,800	1.18
2	PBG_9-PEO_{230}-PBG_9	24	2	23,200	17,500	27,700	1.19
3	PBG_{13}-PEO_{230}-PBG_{13}	48	3.5	24,100	20,800	28,300	1.18
4	PBG_{20}-PEO_{230}-PBG_{20}	60	4	31,000	26,600	38,300	1.23
5	PBG_{25}-PEO_{230}-PBG_{25}	90	5.5	34,000	30100	41,600	1.22
6	PBG_{34}-PEO_{230}-PBG_{34}	90	7	41,900	38,200	52,700	1.25

[a] [Initiator]: [PMDETA]: [Cu(I)Br] = 1: 4: 4. Polymerization temperature is 35 °C. [b] Feed molar ratio of the monomer $[M]_0$ to initiator $[I]_0$. [c] Number-average molecular weight, determined by GPC. [d] M_n(NMR) determined by ^{1}H NMR. [e] Polydispersity determined by GPC.

3. Figure and Tables

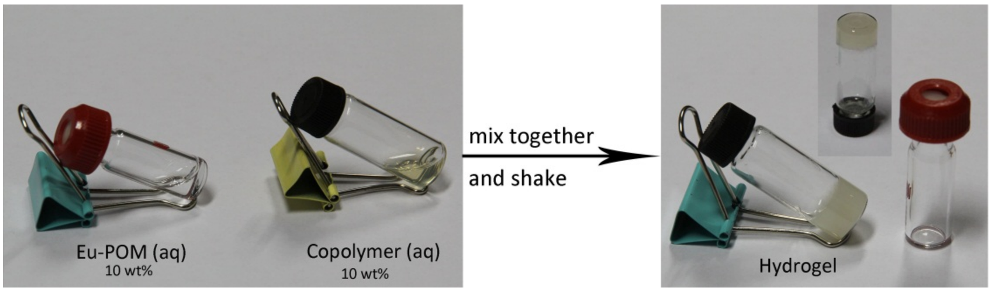


Fig. S3, Photographs of an aqueous solution of EuW_{10}, triblock copolymer (PG_{13}-*b*-PEO_{230}-*b*-PG_{13}), and a supramolecular hybrid hydrogel. The hydrogel formed spontaneously when mixing two aqueous solutions of EuW_{10} and copolymer together.

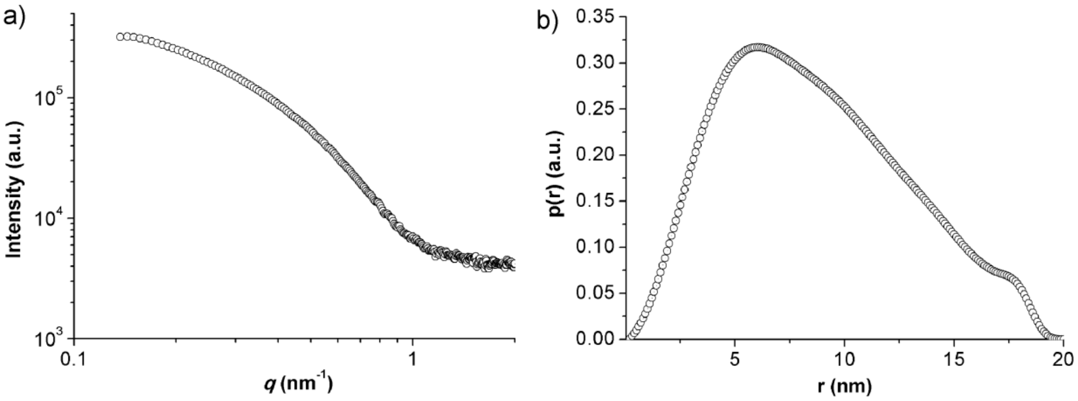


Fig. S4. Small angle X-ray scattering patterns (a) and the corresponding pair distance distribution function (b) obtained for a 1 wt% aqueous dispersion of PG_{34}-PEO_{230}-PG_{34}/EuW_{10} complex. The *p(r)* function indicates that the PG_{34}-PEO_{230}-PG_{34}/EuW_{10} complex contain globular, almost spherical micelles with a diameter of about 20 nm.

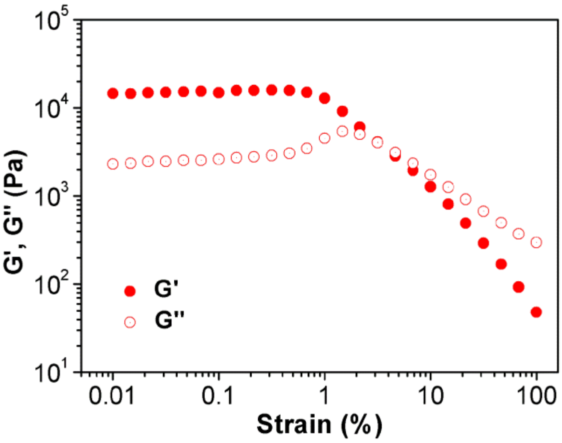


Fig. S5. *G′* and *G″* values of a PG_{20}-PEO_{230}-PG_{20}/EuW_{10} hydrogel on a strain sweep. The hydrogel samples were prepared at a solid concentration of 15 wt%.

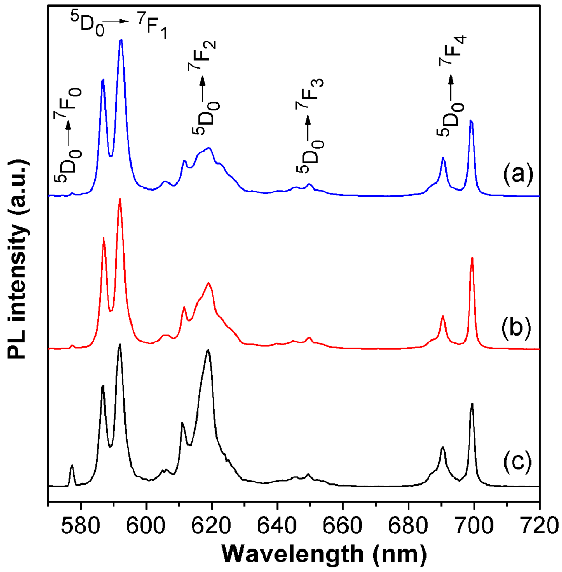


Fig. S6. Emission spectra of EuW_{10} crystal (a), the hybrid hydrogel (b), and EuW_{10} in 8 wt% aqueous solution (c) at an excitation wavelength of 280 nm. The hydrogel was prepared of PG_{34}-PEO_{230}-PG_{34} and EuW_{10} aqueous solution at a solid concentration of 15wt%.

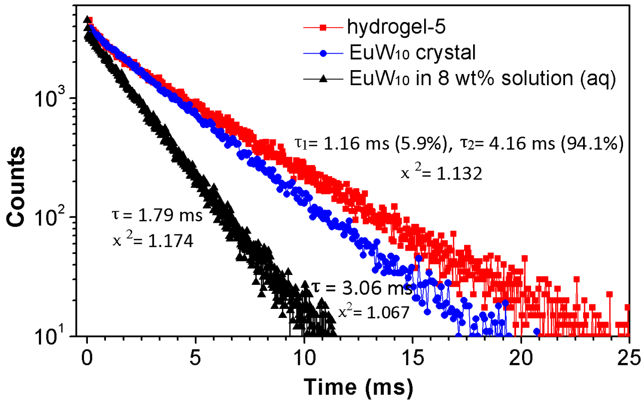


Fig. S7. Emission decay curves of the hybrid hydrogel, EuW_{10} crystal, and EuW_{10} in 8 wt% aqueous solution at an excitation wavelength of 280 nm. The hydrogel was prepared of PG_{34}-PEO_{230}-PG_{34} and EuW_{10} aqueous solution at a solid concentration of 15wt%.

Table S2, Storage modulus *G′*, the decay lifetimes τ_1 and τ_2, and the absolute PL quantum yield φ_{PL} of hydrogels with different NaCl concentrations.[a]

no.	C_{NaCl} (mol/L)	*G′* (KPa)[b]	τ_1 (ms)	τ_2 (ms)	$\varphi_{PL (\%)}$
1	0	11.7	0.74	3.90	18.5
2	0.2	11.6	0.93	3.93	18.8
3	0.4	10.6	1.26	4.19	19.1
4	0.8	7.43	0.59	3.96	19.4
5	1.6	5.23	0.76	3.88	18.8

[a] The hydrogels were prepared by 9.1 wt% PG_{20}-PEO_{230}-PG_{20}, 5.9 wt% EuW_{10}, and 85.0 wt% water or NaCl solution; [b] the rheological measurement performs at the frequency of 2 rad/s.

Table S3, Storage modulus *G′*, decay lifetimes τ_1 and τ_2, and the absolute PL quantum yield φ_{PL} of hydrogels at various copolymer concentrations.[a]

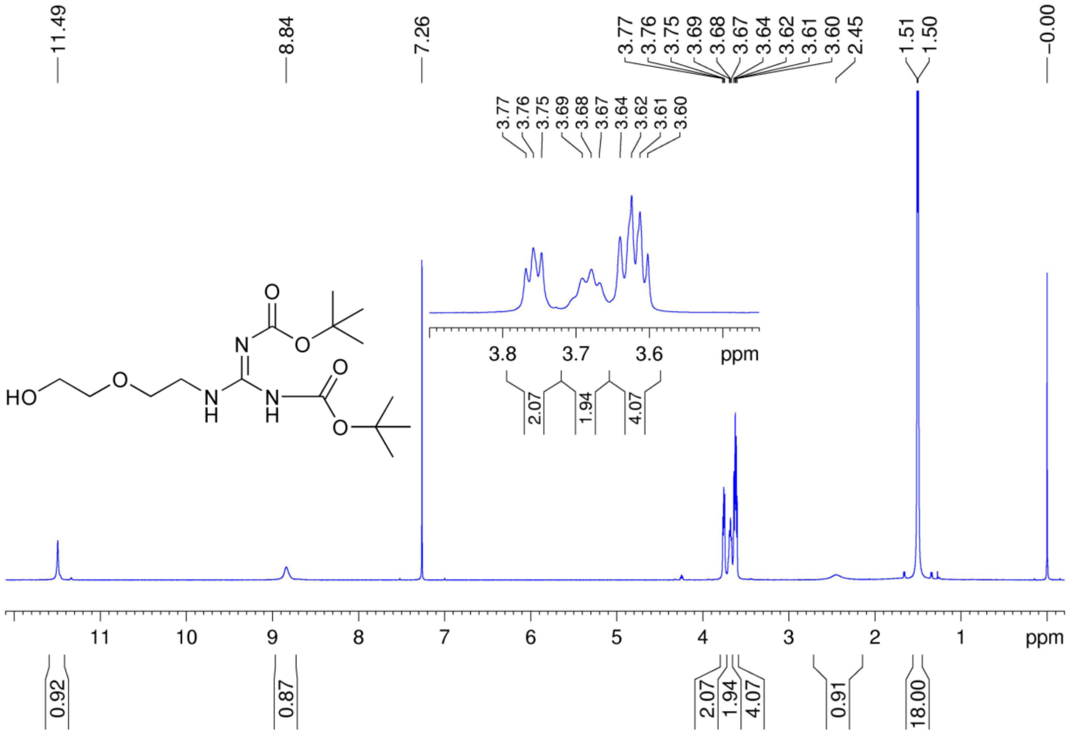
no.	$C_{copolymer}$ (wt%)	*G′* (KPa)[b]	τ_1 (ms)	τ_2 (ms)	$\varphi_{PL (\%)}$
1	9.10	11.7	0.74	3.90	18.5
2	4.90	3.73	0.72	3.99	19.0
3	3.06	1.37	0.84	3.93	18.8

[a] The hydrogel was prepared by PG_{20}-PEO_{230}-$PG_{20}$with various concentrations (3.1-9.1 wt%) a charge stoichiometric point; [b] the rheological measurement performs at the frequency of 2 rad/s.

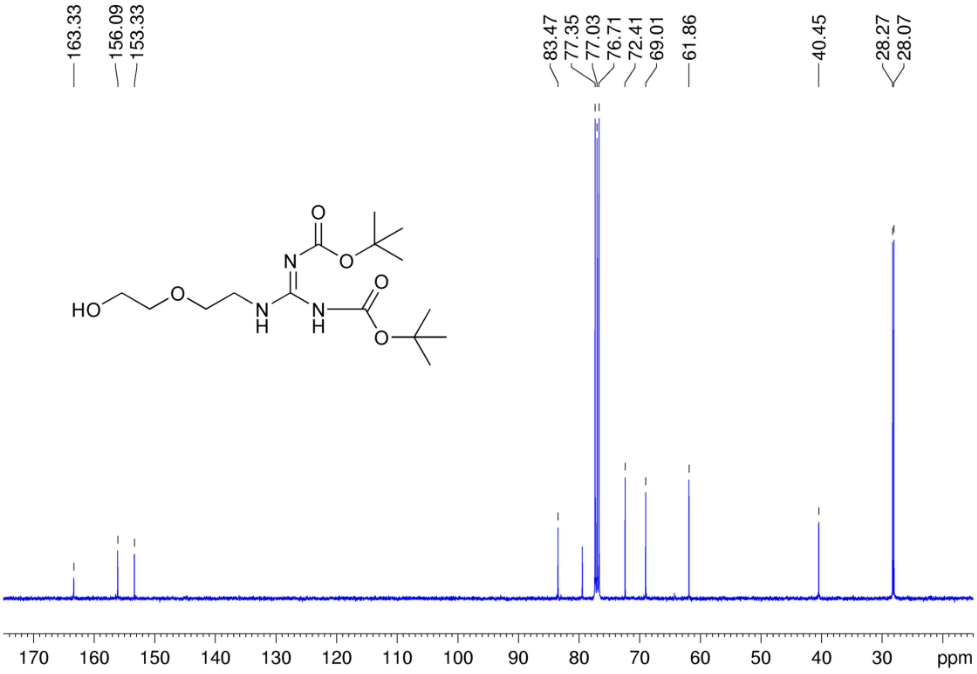
4. References

[S1] M. Sugeta, T. Yamase, *Bull. Chem. Soc. Jpn.,* 1993, **66**, 444.

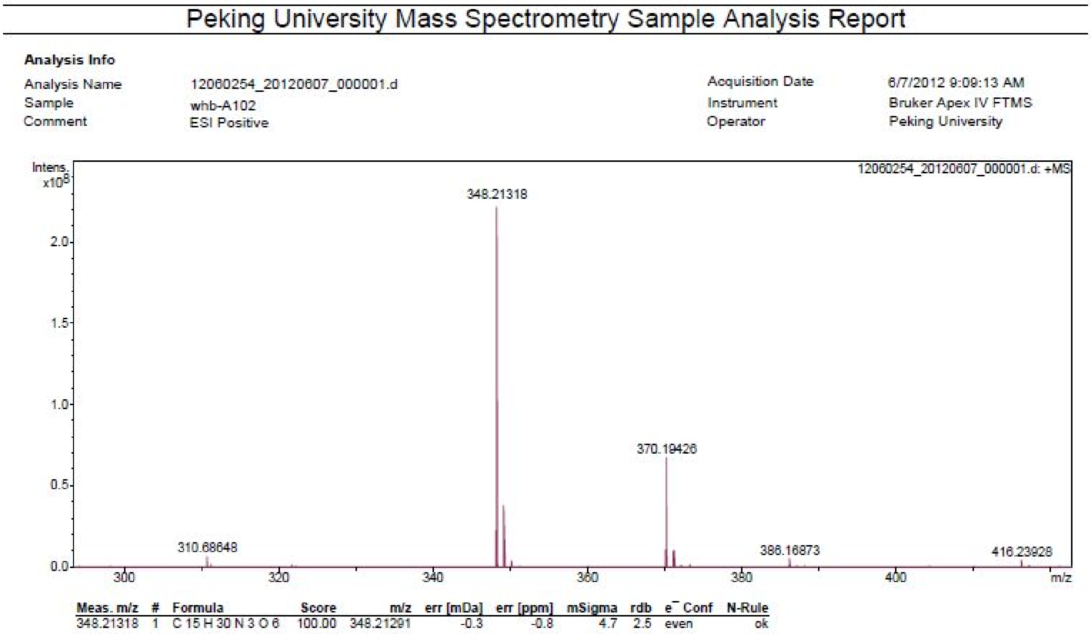
[S2] O. Glatter, *J. Appl. Crystallogr.,* 1977, **10**, 415.



^{1}H NMR spectrum of **1** in $CDCl_3$



^{13}C NMR spectrum of **1** in $CDCl_3$



Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12060254_20120607_000001.d	Acquisition Date	6/7/2012 9:09:13 AM
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Comment	ESI Positive	Operator	Peking University

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
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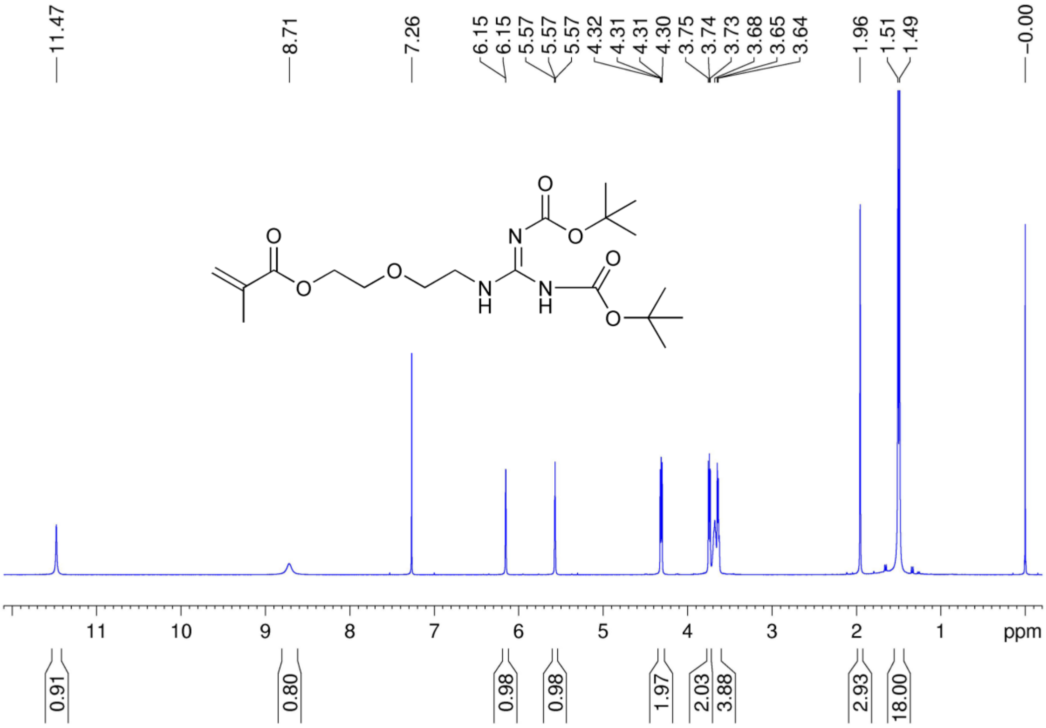
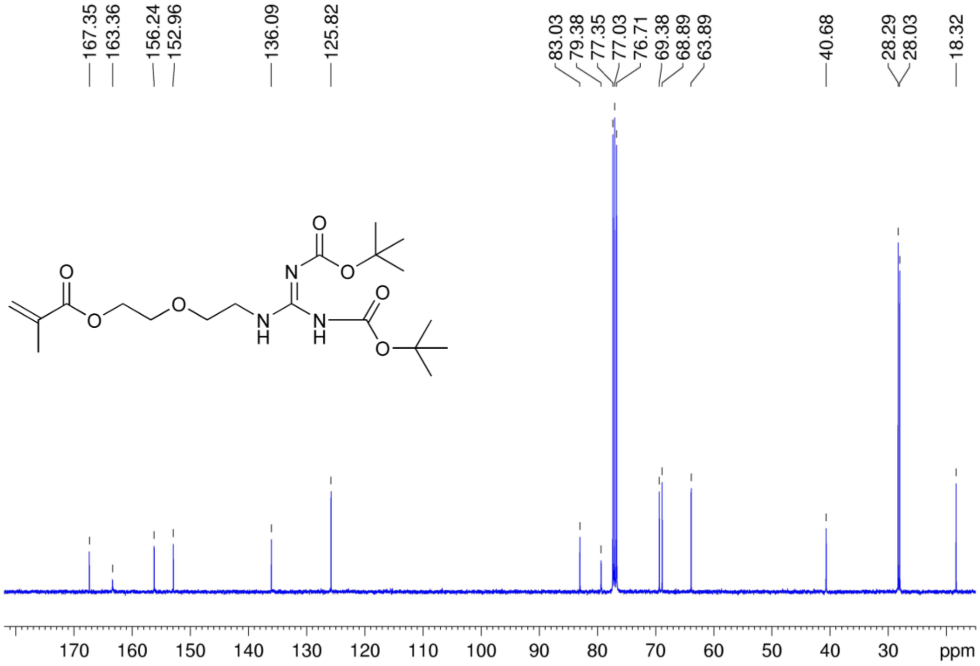
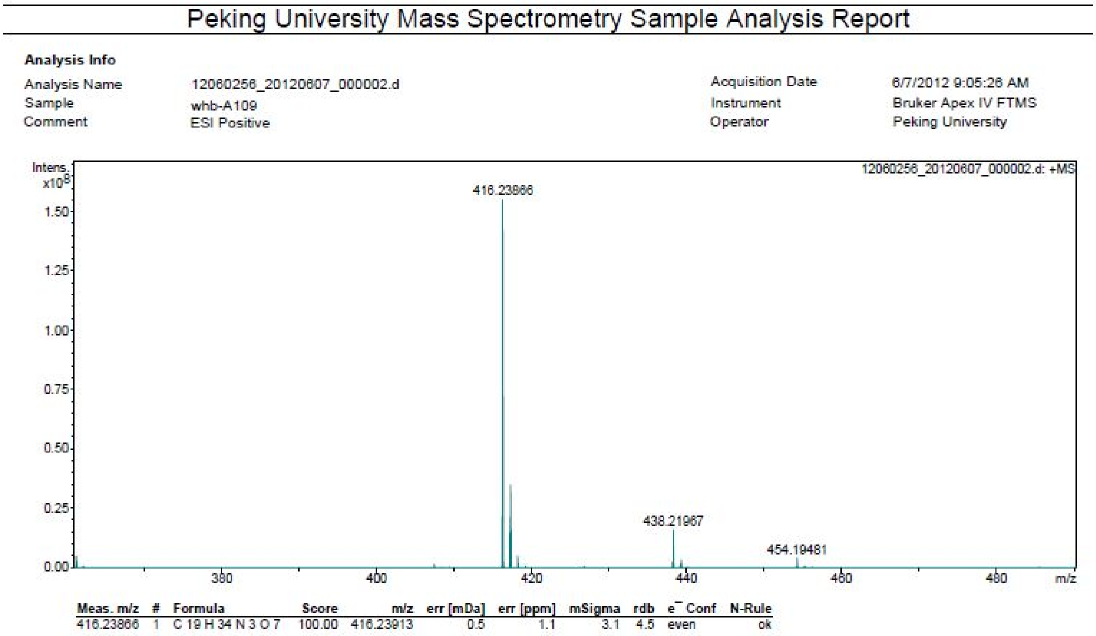
HR mass spectrum of **1**



^{1}H NMR spectrum of monomer **BocGEEMA** in $CDCl_3$



^{13}C NMR spectrum of monomer **BocGEEMA** in $CDCl_3$



Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12060256_20120607_000002.d	Acquisition Date	6/7/2012 9:05:26 AM
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Comment	ESI Positive	Operator	Peking University

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
416.23866	1	C 19 H 34 N 3 O 7	100.00	416.23913	0.5	1.1	3.1	4.5	even	ok

HR mass spectrum of monomer **BocGEEMA**