Electronic Supplementary Information

for

pH-Responsive Inorganic-Organic Hybrid Supramolecular

Hydrogels with Jellyfish-like Switchable Chromic Luminescence

Haibing Wei, ^{*a*}[‡] Nan Shi, ^{*a*}[‡] Jinlong Zhang, ^{*a,b*} Yan Guan, ^{*a*} Jie Zhang, ^{*a*} and Xinhua

Wan*^a

^{*a*} Beijing National Laboratory for Molecular Sciences, Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P.R. China. E-mail: jz10@pku.edu.cn; xhwan@pku.edu.cn.

^b State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, P.R. China.

1. Experimental Section

1.1 Materials and Measurements

Na₉DyW₁₀O₃₆·xH₂O was prepared as described by Caronado.^[1] The macroinitiator Br-PEO₂₃₀-Br ($M_n \sim 10000$ g/mol) was synthesized according to the reported method.^[2] N,N-dimethylaminoethyl methacrylate (DMAEMA) was purchased from Heowns, Tianjin, and purified by distillation under reduced pressure over calcium hydride. 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 the 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. Unless otherwise noted, the other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd.

¹H NMR spectrum was recorded on a Bruker 400 AVANCE III spectrometer operating at 400.23 MHz, using CDCl₃ as the solvent. The number average molecular

weights (M_n) and polydispersity indices (PDIs) of polymers were measured by gel permeation chromatography (GPC) with THF or DMF (containing 0.02 M LiBr) as an eluent. GPC with THF as the eluent was equipped with a Waters 2414 refractive index detector, a Waters 1525 binary HPLC pump, and three Waters Styragel HT columns (HT2, HT3, and HT4). Temperature was set at 35 °C with a flow speed of 1.0 mL/min and PS standards were used for calibration. GPC with DMF as the eluent was equipped with a Waters 2489 refractive index detector, a Waters 1515 binary HPLC pump, and three Waters Styragel HR columns (HR1, HR3, and HR4). Temperature was set at 35 °C with a flow speed of 1.0 mL/min and polystyrene standards were used for calibration. Rheological measurements were performed using a rheometer (MCR 301, Anton Paar) with cone plate geometry with a cone angle 2° 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 °C. The strain was kept at 0.8% to ensure the linearity of dynamic viscoelasticity and the frequency was varied from 1 to 100 rad/s. The recovery property of the hydrogels in response to applied shear forces was probed as the following procedure: 400% (600 s) $\rightarrow 0.8\%$ $(600 \text{ s}) \rightarrow 400\% (600 \text{ s}) \rightarrow 0.8\% (600 \text{ s}) \rightarrow 400\% (600 \text{ s}) \rightarrow 0.8\% (1200 \text{ s}).$ TEM images were obtained on a JEM 2100 instrument operating at an acceleration voltage of 200 kV. The specimen was prepared by drop-casting the sample solution or hydrogel onto a carbon-coated copper grid for about 1 minute. The excess liquid or hydrogel was blotted away with a strip of filter papers followed by water wash three times, and the sample grid was dried in air. Photoluminescence (PL) spectra were carried out on HORIBA Jobin Yvon Nanolog FL3-2iHR spectrometer by an integrating sphere system at the excitation wavelength of 280 nm. Photoluminescent lifetimes at room temperature were measured by time-correlated single-photon counting using an FLS 920 Steady State & Time-resolved Fluorescence Spectrometer (Edinburgh Instruments Ltd.). Small-angle X-ray scattering (SAXS) measurements were performed using a SAXSess (Anton Paar) equipped with Kratky blockcollimation system. The scattering pattern was recorded on an imaging plate (IP) with

a pixel size of 42.3×42.3 μ m² which extended to the high-angle range (the *q* range covered by the IP was from 0.06 to 29 nm⁻¹). We carefully loaded the DyW₁₀/PG₃₅-*b*-PEO₂₃₀-*b*-PG₃₅ solution and hydrogel samples for SAXS measurement into a quartz capillary with a diameter of 1 mm at ambient temperature. The scattering curve of pure water filled in the same capillary was measured as the background. Background subtraction and desmearing were conducted by using SAXSquant 3.6 software. The pair distance distribution function (PDDF) of scattering curves was calculated using the generalized indirect Fourier transform (GIFT)^[S3] program included in the SAXSess software package.

1.2 Synthesis of the PDMAEMA-*b*-PEO-*b*-PDMAEMA (PD-*b*-PEO-*b*-PD) triblock polymers



Macroinitiator Br-PEO-Br (0.40 g, 4.00×10^{-5} mol), DMAEMA (0.63 g, 4.02×10^{-3} mol), copper (I) bromide (13.77 mg, 9.60×10^{-5} mol), PMDETA (20.80 mg, 1.20×10^{-4} 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 40 °C. After the polymerization proceeded for 2.5 h, the reaction was quenched by immersing 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 Na₂SO₄, 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 (0.69 g, yield: 67%). Gel permeation chromatography analysis results (polystyrene standards): $M_{n, GPC} = 76900$ g/mol and the polydispersity index (PDI) = 1.34. ¹H NMR (D₂O, 400 MHz): δ (ppm), 0.96 (m, 2.9H; CH₃), 1.88 (m, 1.4H; CH₂), 2.25 (s, 5.9 H, N(CH₃)₂), 2.66 (s, 1.9H; CH₂), 3.63 (b, 13.3H; OCH₂CH₂O of EO unit), 4.09 (s, 2.0H, COOCH₂). The number of PDMAEMA units in this ABA triblock copolymer was 35, calculated from its ¹H NMR spectrum.

1.3 Preparation of DyW₁₀/PD₃₅-*b*-PEO₂₃₀-*b*-PD₃₅ mixture and its hydrogelation

As a typical illustration, 0.18 mL of an aqueous of DyW_{10} (34 mg, 12 wt%) was added into 0.25 mL of aqueous solution of PD_{35} -*b*-PEO₂₃₀-*b*-PD₃₅ (35 mg 12 wt%), and then mixed under vigorous stirring. The viscosity of the polymer solution increases as the DyW_{10} aqueous solution added, but no gelation occurred. However, as 70 µL dilute hydrochloric acid (6.0 wt%) added to the system and vortex shock, the solution mixture became completely gelation within 1 minute, forming a solid-like hydrogel. The pH value of the hydrogel was estimated as 4.0 according to eqs. (1), (2), and (3):

$$K_a = \frac{[\text{DMAEMA}] \bullet [\text{H}^+]}{[\text{DMAEMAH}^+]}$$
(1)

$$[\mathrm{H}^{+}] \approx [\mathrm{DMAEMA}] \tag{2}$$

$$pH = -\log[\mathrm{H}^+] \tag{3}$$

Where [H⁺], [DMAEMA], and [DMAEMAH⁺] are the concentration of hydrogen ion, non-protonated DMAEMA groups and protonated DMAEMA groups in the hydrogel, correspondingly. The pK_a of PDMAEMA was approximately 7.4.



Fig. S1. a) Small angle X-ray scattering patterns of DyW_{10}/PD_{35} -PEO₂₃₀-PD₃₅ complex in sol and gel state, respectively; b) The corresponding pair distance distribution function for the hydrogel. The p(r) function indicates that the DyW_{10}/PD_{35} -PEO₂₃₀-PD₃₅ complex contain globular, almost spherical micelles with a diameter of about 24 nm.



Fig. S2. a) Luminescence spectra of the DyW₁₀ aqueous solution (c = 0.2 mg/mL) with different pH values at an excitation wavelength of 280 nm. b,c) The decay curves and their fitting results of DyW₁₀ in aqueous solution (c = 0.2 mg/mL) at pH = 7.2 and 4.4. The decay lifetimes of the DyW₁₀ aqueous solution at pH = 7.2 and 4.4 are fitted as 5.2 µs ($\chi^2 = 1.402$) and 5.4 µs ($\chi^2 = 1.270$), respectively.



Fig. S3. Emission decay curves of DyW_{10} crystal at an excitation wavelength of 280 nm. The decay lifetime is fitted as ~58 μ s.



Fig. S4. Macroscopical self-healing photographs of the hybrid supramolecular hydrogel (c = 10 wt%). a) Original hydrogel in the vial, b) after damage, c) after free standing for 3 min.

References

S1. M. A. AlDamen, S. Cardona-Serra, J. M. Clemente-Juan, E. Coronado, A. Gaita-Arino, C. Marti-Gastaldo, F. Luis, O. Montero, *Inorg. Chem.*, 2009, 48, 3467.
S2. M. Lemmers, J. Sprakel, I. K. Voet, J. ven der Gucht, M. A. Cohen Stuart, *Angew. Chem. Int Ed.*, 2010, 49, 708.

S3. B. Weyerich, J. Brunner-Popela, O. Glatter, J. Appl. Crystallogr., 1999, 32, 197.