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Supporting Information

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- 1) Materials;
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- 3) Tables S1-S2;
- 4) Figures S1-S33;

1) Materials

TPE-BPA was synthesized according to our previous report (*ACS Appl. Mater. Interfaces* **2016**, *8*, 27987–27995).

Triethyldodecylamonium bromide (DEAB), trimethyldodecylamonium bromide (DTAB), tripropyldodecylamonium bromide (DPAB), tributyldodecylamonium bromide (DBAB), cetyltriethylamonium bromide (CEAB), cetyltrimethylamonium bromide (CTAB) were recrystallized five times from acetone. The purities of the surfactants were examined and no surface tension minima were found in the surface tension curves. Other reagents were of AR grade, and were purchased from Beijing Chemical Reagents Company. The aqueous solutions were prepared using Milli-Q water of 18 MΩ.

Azo-DPA was synthesized in a similar approach:



Synthesis of compound 2. 136g of sodium ethanol was dissolved in 500 mL of ethanol, the obtained solution was divided into two uniform parts for standby application. 58g of anhydrous acetone and 150g of diethyl oxalate (compound 1) were mixed in a 3L flask, slowly added into one of stocked sodium ethanol solution at room temperature, during the adding process, the temperature had a distinct increase, the solution gradually became thick and separated out plenty of yellow solid. Then, dropwise added other 160 g of diethyl oxalate and remaining part of sodium ethylate into the reaction liquid. The colour of the reaction liquid became dark. Continue stirring for 30 minutes, the reaction liquid had a large number of solid precipitation. Heat the reaction liquid to 120° C, after distilling 150 mL of ethanol, add 300 mL of concentrated hydrochloric acid and 800 mL of water, the mixture was reacted under 100° C for 20 hours. The reaction mixture was cooled to room temperature and filtered, after water washing and drying, 120 g of compound 2 was obtained. ¹HNMR (400 MHz, DMSO), δ (TMS, ppm): 6.96 (s, 2H).

Synthesis of compound 3. 50 g of compound 2 was dissolved in 250 mL of ammonia, reacted 4 hours under 100°C, in the process, adding 20 mL ammonia in the reaction liquid every 1 hour. The reaction mixture was filtered, and the solvent was evaporated under vacuum. The residue and 10g of activated carbon were refluxed in 500 mL of water for 30 minutes. HCl solution was then added to precipitate the product. The mixture was filtered, and washed with water several times. After drying, 45g compound 3 (white solid) was obtained. ¹H NMR (400 MHz, DMSO), δ (TMS, ppm): 7.56 (s, 2H).

Synthesis of compound 4. 45g of compound 3 and 5mL sulfuric acid were refluxed in 450 mL of ethanol for 4 hours. The solution was cooled to room temperature and NaHCO₃ solution was then added to tune the pH to 7. After evaporating most of the ethanol, extracting the product with ethyl acetate. The mixture was filtered, and washed with water several times. After drying and recrystallization, 35g compound 4 was obtained. ¹H NMR (400 MHz, CDCl3), δ (TMS, ppm):7.20 (s, 2H),4.37~4.42(m, 4H), 1.34~1.43(m, 6H).

Synthesis of compound 6. 50g of compound 5 was dissolved in 500Ml of HCl(1M). The solution was cooled to 0-5°C with ice-salt bath and 31.5g of NaNO₂ was added carefully. At 0°C, 1L of ice methanol was added into the reaction mixture slowly. Then, 165mL phenol-NaOH solution was added into above mixture, the reaction mixture was warmed to room temperature and reacted for 2h under continuous stirring. After filtration and solvent evaporation, the product was purified by recrystallization using ethanol/water (1:9) as solvent. Hereto, 32g compound 6 was obtained. ¹H NMR (400 MHz, CDCl3), δ (TMS, ppm): 10.10 (s, 2H), 7.7(d, 4H), 6.9(d, 4H).

Synthesis of compound 7. 5g of compound 6 was dissolved in 50mL of DMF, 16g of K_2CO_3 and 12g $C_4H_8Br_2$ were added into above solution, the mixture was stirring for 24h under room temperature and a N_2 atmosphere. After reaction, the reaction mixture was extracted with CH_2Cl_2 , then the organic phase was washed with NaCl solution. After filtration and solvent evaporation, the product was purified by silica gel column. Hereto, 5.2g compound 7 was obtained. ¹H NMR (400 MHz, CDCl3), δ (TMS, ppm): 7.8(d, 4H), 7.1(d, 4H), 4.1(t, 4H), 3.5(t, 4H), 1.9(m, 8H).

Synthesis of compound 8. 5.2g of compound 7, 5.5g of compound 4 and 7g of K_2CO_3 were refluxed in 50mLof 2-butanone for 3 days. After filtration and solvent evaporation, the product was purified by silica gel column. Hereto, 5g of compound 8 was obtained. ¹H NMR (400 MHz, CDCl3), δ (TMS, ppm):7.86~7.88 (d, 4H),7.82(d, 4H), 6.98(d, 4H),4.13~4.25(m,8H),4.0(m,8H),2.0(m,8H),1.3(m,12H).

Synthesis of compound 9. 5g of compound 8 was dissolved in mixed solvent which composed of THF: acetonitrile, methanol= 5:1:1, then conducting a hydrolysis reaction by adding KOH solution. Hereto, 5g of compound 9 was obtained. ¹H NMR (400MHz, DMSO), δ (TMS, ppm): 7.81~7.83(d, 4H),7.7(d, 4H), 7.1(d, 4H),4.3(m,4H),4.1(m,4H),1.9(m,8H). Elemental analysis: C (56.86%),H (4.71%), N (7.67%), C₃₄H₃₂N₄O₁₂·2H₂O; calcd: C (56.35%),H (5.01%), N (7.73%).

2) Methods

Film and Powder Formation. To an aqueous solution of TPE-BPA, an aqueous solution of DEAB were added in sequence, at final concentrations of 0.2 mM for TPE-BPA and 3.2 mM for DEAB. On addition of the 0.2 mM $Zn(NO_3)_2$, white precipitates were formed. After an hour for aging, the precipitates were collected together from the suspensions by simply decanting the supernatant. The collected precipitates were then treated with four aforementioned parallel ways: (1) incubated in humid environment; (2) kept in dry environment after vacuum dried; (3) subjected to moisture after vacuum dried; (4) compressed under a pressure of 0.7 MPa for 10 seconds at room temperature. (1), (3) led the solids to 2.0-2.5 mm thick transparent films, and (4) led to 200-250 µm thick transparent films, whereas (2) resulted in white powders. The films with compositions of TPE-BPA/DPAB/Zn(NO₃)₂, TPE-BPA/DBAB/Zn(NO₃)₂, TPE-BPA/DEAB/Co(NO₃)₂, TPE- $BPA/DEAB/Ni(NO_3)_2$, TPE-BPA/DEAB/Cu(NO₃)₂, TPE-BPA/DEAB/TA and Azo-DPA/DEAB/Zn(NO₃)₂ were formed via similar strategies, just by replacing the corresponding compound mentioned in the TPE-BPA/DEAB/ $Zn(NO_3)_2$ system with the target one.

Film Damage, Healing and Remolding. Films of TPE-BPA⁸⁻•4DEA⁺•2Zn²⁺ were cut into two separate pieces with a razor blade. Two pieces of such cut films were then brought to contact edge-to-edge or face-to-face in humid environment for self-healing process. For healing under load, the pieces were overlaid face-to-face or on the edge, and pressed to contact with the pressure about 0.7 MPa. The self-healing process took 12 hours to happen, while the instant healing process only took with 10 seconds. Remolding of the film was carried out by dropping 15 microliter water to a film about 5mm×5 mm, then press the two films face to face. Following with desired bending or folding, the remolded film can be made into diversified structures.

Elemental Analysis. The elemental analysis of the film was carried out with energy dispersive spectroscopy (EDS) measurement. The weight ratios of C, N and H were collected from a vario EL elemental analyzer (Elementar Analysensysteme GmbH). The weight ratios of O and Zn were collected from EDS on a Hitachi S4800 microscope at an acceleration voltage of 10 kV.

Fluorescence Measurements. The fluorescence spectra of the solutions were recorded on a Hitachi F-7000 fluorescence spectrometer ($\lambda_{ex} = 365$ nm). The fluorescence spectra of the films were recorded on a Nanolog FL3-2iHR fluorescence spectrometer ($\lambda_{ex} = 365$ nm). The photos for the fluorescent samples were taken under 365 nm UV light from a Spectroline FC-100F fan-cooled, long wave UV lamp.

Confocal Laser Scanning Microscopy (CLSM). CLSM measurements were conducted on a A1R-si CLSM (Nikon Co.) with a laser of UV405 nm. The samples were observed directly without any staining. The films were placed on clean coverslips for CLSM observations. The 3D images and videos were reconstructed using the NIS-Elements C image analysis software.

Polarizing Optical Microscopy (POM). The photographs of birefringence were taken with a LV100N Polarizing Microscope (Nikon Co.) in ambient environment at room temperature. Samples were photographed at $\theta = 0$ and 45°, respectively, where θ is the angle between the analyzer and the alignment direction of the sample.

Fourier Transform Infrared (FTIR) Spectroscopy. FTIR spectra were obtained using a Nicolet Magna-IR 750 spectrophotometer (Thermo Scientific Co.). The method of SMART iTR was ART. Scanning speed was 1.0 cm⁻¹. The liquid samples were prepared by dropping solutions onto clean quartz plates and dried in the air. The film samples were prepared by placing on clean quartz plates.

X-ray Photoelectron Spectroscopy (XPS). XPS spectra were recorded on an AXIS-Ultra Imaging Photoelectron Spectrometer from Kratos Analytical Ltd., using monochromatic Al-

K α radiation in a vacuum of 2×10^{-8} Pa. The liquid samples were vacuum-dried on clean silicon wafers. The film samples were placed on clean silicon wafers.

2D X-ray Diffraction (2D XRD). The 2D XRD patterns of the powder and films were recorded in the transmission mode on a Bruker D8 Discover diffractometer with a Vantec500 as the 2D detector. The background scattering was recorded and subtracted from the sample pattern. XRD measurements were performed using a Rigaku Dmax-2400 diffractometer with Cu K α radiation. The solid samples were placed on clean glass slides. The particle size *D* in each sample was estimated using Scherrer equation:

$$D = \frac{K\gamma}{(B-B')\cos\theta}$$

Where *K* is a constant taken as 0.89, *B* is the half height width of the scattering peak at the diffraction angle θ . In this study, the strongest peak corresponding to d_1 is taken for calculation. Since the particle in the membrane is very small, the *B*' is not corrected for the estimated calculation.

Small Angle X-ray Scattering (SAXS). SAXS measurements were performed by SAXSess (Anton-Paar, Austria) with Cu K_{α} radiation. The films or the powders were measured in situ. q is the scattering vector, where $q = 4\pi \sin(\theta) / \lambda$ and 2θ is the scattering angle.

Cryogenic Transmission Electronic Microscopy (Cryo-TEM). For cryo-TEM studies, a sample droplet of 2μ L was put on a lacey carbon film covered copper grid (Science Services, Munich, Germany), which was hydrophilized by glow discharge (Solarus, Gatan, Munich, Germany) for 30s. Most of the liquid was then removed with blotting paper, leaving a thin film stretched over the lace holes. The specimen was instantly shock frozen by rapid immersion into liquid ethane and cooled to approximately 90 K by liquid nitrogen in a temperature-and humidity controlled freezing unit (Leica EMGP, Wetzlar, Germany). The temperature and humidity were monitored and kept constant in the chamber during all sample preparation steps. The specimen was inserted into a cryo transfer holder (CT3500, Gatan,

Munich, Germany) and transferred to a Zeiss EM922 Omega energy-filtered TEM (EFTEM) instrument (Carl Zeiss Microscopy, Jena, Germany). Examinations were carried out at temperatures around 90 K. The TEM instrument was operated at an acceleration voltage of 200 kV. Zero-loss-filtered images (DE = 0 eV) were taken under reduced dose conditions (100-1000 e/nm2). The images were recorded digitally by a bottom-mounted charge-coupled device (CCD) camera system (Ultra Scan 1000, Gatan, Munich, Germany) and combined and processed with a digital imaging processing system (Digital Micrograph GMS 1.9, Gatan, Munich, Germany). The images were taken very close to focus or slightly under the focus (some nanometers) due to the contrast enhancing capabilities of the in-column filter of the employed Zeiss EM922 Omega. In EFTEMs, deep underfocused images can be totally avoided.

Transmission Electron Microscopy (TEM). TEM images were recorded on a JEM-2100F transmission electron microscope. The liquid samples were prepared by dropping solutions onto copper grids coated with Formvar film. Excess water was removed by filter paper, and the samples were stained with uranyl acetate if there was no metal element within them, and then they were dried in ambient environment at room temperature for TEM observations at an acceleration voltage of 120 kV. The film samples were prepared to sections of approximately $2-3 \mu m$ thickness by ultramicrotomy, and were observed by TEM at an acceleration voltage of 200 kV.

Scanning Electron Microscopy (SEM). SEM measurements were performed using a Hitachi S4800 microscope at an acceleration voltage of 1.0 kV. The films or the powders were placed on clean silicon wafers for SEM observations.

Atomic Force Microscopy (AFM). AFM measurements were conducted on a VEECO D3100 AFM with a tapping mode under ambient conditions. The films were placed on clean coverslips for AFM observations.

8

Mechanical Tests. The mechanical properties of the films of TPE-BPA⁸⁻•4DEA⁺•2Zn²⁺ were tested by a WDW3020 electronic universal testing machine in ambient environment at room temperature. Stress-strain data were collected with a strain rate of 1 mm/min. The film thickness ranges from 200-250 μ m. The unit of length within the drawing is millimeter. All mechanical tests were conducted on dumbbell-shaped samples. Samples undergoing different remolding times, which were from the same original film, were used to measure the outstanding healing ability of the materials.

Development of Prototype LEDs. UV LEDs (365 ± 5 nm) with flat top window, purchased from Lumex Opto/Components Inc., were used without additional modifications to prepare our LEDs. The window was cleaned with distilled water and ethanol. Blue light-emitting sample was prepared by depositing the TPE-BPA/DBAB/Zn(NO₃)₂ precipitates on the flat top surface of the LED and then compressed in situ to produce a film coated on the window. Pink light-emitting sample was prepared by similar strategy, where the TPE-BPA/DBAB/Zn(NO₃)₂ precipitates are formed from a Rhodamine B aqueous solution (0.2 mM). 20 mA of direct current was applied to light the LEDs. 10 mM EDTA was used to rinse the films coated on the top of UV LEDs.

Other Methods. ¹H NMR spectra were acquired in CDCl₃ or D₂O using an AVANCE III Bruker 500 MHz NMR spectrometer; chemical shifts (δ) are expressed in parts per million relative to an internal TMS standard. Mass spectra were obtained using a Solarix XR Bruker fourier transform ion cyclotron resonance mass spectrometer. TGA experiments were carried out under nitrogen on TA Instrument Q600 SDT at a heating rate of 10 °C/min. DSC experiments were carried out under nitrogen on TA Instrument Q100 DSC at a heating rate of 3 °C/min.

3) Table S1-S2

Table S1. Comparison between the experimental and theoretical value of the elements in the TPE-BPA⁸⁻•4DEA⁺•2Zn²⁺ film. Experimental results were obtained from EDX measurements.

TPE-BPA ⁸⁻ • 4DEA ⁺ • 2Zn ²⁺	w(C)/w(N)	w(O)/w(Zn)
Theoretical	15.23	2.94
Experimental	14.90	2.80

Table S2. Comparison between the experimental and theoretical value of the elements in the $Azo^{4} \cdot 2DEA^{+} \cdot Zn^{2+}$ film. Experimental results were obtained from EDX measurements.

Azo ⁴⁻ •2DEA ⁺ •Zn ²⁺	<i>w</i> (C)/ <i>w</i> (N)	<i>w</i> (O)/ <i>w</i> (Zn)
Theoretical	10.00	2.94
Experimental	9.80	3.01

4) Figures S1-S33



Figure S1. (a) Fluorescence spectra of TPE-BPA/DEAB mixed systems at different molar ratios. ([TPE-BPA] = 0.2 mM) (b) The ratios of fluorescence enhancement for TPE-BPA at various [DEAB]/[TPE-BPA].



Figure S2. Fluorescence spectra of a TPE-BPA/DEAB mixed system, before and after the addition of $Zn(NO_3)_2$. ([TPE-BPA] = 0.2 mM, [DEAB] = 3.2 mM, [Zn(NO_3)_2] = 0.4 mM)



Figure S3. XPS spectra of (a) Zn 2p peaks for $Zn(NO_3)_2$ and the precipitates, and (b) O 1s peaks for TPE-BPA/DEAB irregular clusters and the precipitates.



Figure S4. FTIR spectra of TPE-BPA and the precipitates (1800 - 1200 cm⁻¹).



Figure S5. TEM image of the aggregates obtained in the supernatant of TPE-BPA/DEAB/Zn(NO₃)₂ system.



Figure S6. SAXS results of the transparent films (1) (3), the powder precipitates (2), and the film made by pressing.



Figure S7. XRD results of TPE-BPA, DEAB, TPE-BPA/DEAB clusters, and TPE-BPA/DEAB/Zn(NO₃)₂ precipitates.



Figure S8. FTIR spectrum of the precipitates $(3100 - 2700 \text{ cm}^{-1})$. The two bands in this figure correspond to the asymmetric and symmetric vibrations. Because the ordered packing of the alkyl chains should be expected around 2920 cm⁻¹ and 2850 cm⁻¹ for asymmetric and symmetric vibration, respectively, the present 2854 and 2925 cm⁻¹ suggest that DEAB molecules didn't packed orderly in the film.



Figure S9. 2D ¹HNMR result for the system of TPE-BPA/DEAB (1/16) solution. It is clear that no correlation occurs between DEAB and TPE-BPA.



Figure S10. Illustration of the possible molecular packing if the chain of DEAB is perpendicular to the TPE-BPA plane. Two peroids corresponding to distances of 2.88 nm and 2.0 nm should be expected in XRD, which disagrees with the results in Figure 1j and Figure S8. Therefore, this type of molecular packing is ruled out.



Figure S11. 2D XRD pattern for the spontaneously formed film.



Figure S12. TEM image of the cross-section of the transparent films.



Figure S13. POM images of the transparent films and the powder precipitates, which are processed through protocol (1), (2), (3) and under pressure.



Figure S14. TGA result of the pressed film (30 - 210 °C).



Figure S15. 2D XRD pattern for the film formed under a pressure of 0.7 MPa.



Figure S16. (a) DSC results of the transparent films (1) (3), the powder precipitates (2), and the film made by pressing (10 - 140 °C). (b) DSC results of the transparent film (-70 - 140 °C), showing a T_g at around 20 °C. (The T_g would not appear on the heating curve if the last cooling temperature was not under -30 °C.)



Figure S17. Slices of 3D CLSM scan of the cuts within the films, (a) before and (b) after the healing process.



Figure S18. Fluorescence spectra of the supernatants of a piece of film placing in pure water, in 10 mM EDTA solution and in 10 mM EDTA solution which is treated with extra $Zn(NO_3)_2$ then.



Figure S19. Photos of the spontaneously formed transparent film in water at different aging times. The precipitates were not separated from the supernatants, and allow standing still for (a) 0 hour, (b) 48 hours and (c) 96 hours. The photos are taken under daylight and 365 nm UV light.



Figure S20. Mechanical tests for the hardness and tensile stress of the film. When the TPE-DEAB-Zn film was fully dried, it would be a little bit difficult to fold or stretch the film. However, the tensile strength of the film remains unchanged.



Figure S21. Variation of the emission colors of the film with the doping amount of rhodamine B. From left to right: [Rhodamine B]=0, 0.01. 0.02, 0.4 mM. [TPE-BPA]=0.2 mM for all the films.



Figure S22. Photos of the transparent and fluorescent films made in (a) the TPE-BPA/DEAB/Co(NO₃)₂ system, (b) the TPE-BPA/DEAB/Ni(NO₃)₂ system and (c) the TPE-BPA/DEAB/Cu(NO₃)₂ system at the mixture of 1:16:1, which are under daylight and 365 nm UV light.



Figure S23. XRD pattern for the film obtained with TPE-BPA/DEAB/Co(NO₃)₂ system, TPE-

BPA/DEAB/Ni(NO₃)₂ and TPE-BPA/DEAB/Cu(NO₃)₂.



Figure 24. (a) Molecular structure of the Azo-DPA, and (b) the photos of the films generated in the system of Azo-DPA/DEAB/Zn.



Figure S25. EDX analysis for the composition in film formed with Azo ligand, DEAB, and Zn^{2+} . The obtained weight ratio of C:N:Zn corresponds the composition of $Azo^{4-}:DEA^+:Zn^{2+} = 1:2:1$. The data in the table S2 shows the theoretical and experimental composition of the film, respectively.



Figure S26. XRD pattern for the film obtained from the film of $Azo^{4-}:DEA^{+}:Zn^{2+}=1:2:1$. Lamellar structures are formed as well, and the thickness of a single layer is 3.3 nm, which is the extending lenth of the azo ligand.



Figure S27 (a) Molecular structure of the tannic acid (TA), and (b) the photos of the films generated in the system of TPE-BPA/TA/DEAB.



Figure S28. XRD pattern for the film of TPE-BPA/DEAB/TA .



Figure S29. (a) Photos of the film made in the TPE-BPA/DPAB/ $Zn(NO_3)_2$ system at the mixture of 1:16:1, which are under daylight and 365 nm UV light. (b) Photos of the film made in the TPE-

BPA/DBAB/Zn(NO₃)₂ system at the mixture of 1:16:1, which are under daylight and 365 nm UV light.



Figure S30. (a) Fluorescence spectra of TPE-BPA/DTAB mixed systems at different molar ratios. ([TPE-BPA] = 0.2 mM) (b) The ratios of fluorescence enhancement for TPE-BPA at various [DTAB]/[TPE-BPA]. (c) Cryo-TEM image of the irregular clusters formed by TPE-BPA/DTAB at the molar ratio of 1:8. (d) Photos of the precipitates collected from the TPE-BPA/DTAB/Zn(NO₃)₂ system at the mixture of either 1:8:1 or 1:16:1, which are under daylight and 365 nm UV light.



Figure S31. (a) Molecular structure of the CEAB. (b) Fluorescence spectra of TPE-BPA/CEAB mixed systems at different molar ratios. ([TPE-BPA] = 0.2 mM) (c) The ratios of fluorescence enhancement for TPE-BPA at various [CEAB]/[TPE-BPA]. (d) Fluorescence spectra of the TPE-BPA/CEAB solution system, before and after the addition of $Zn(NO_3)_2$ ([TPE-BPA] = 0.2 mM, [CEAB] = 3.2 mM, [Zn(NO_3)_2] = 0.2 mM). TEM image of the TPE-BPA/CEAB vesicles, (e) before and (f) after the addition of $Zn(NO_3)_2$. No precipiates are formed in the system, so that no film can be generated.





Figure S32. TPE-BPA/Zn(NO₃)₂ in water and dried without surfactant. Coordination between TPE-BPA and Zn^{2+} results in precipitation in water. The dried precipitates do not form bulk film even under load.



Figure S33. Addition of DEAB into the precipitate system of TPE-BPA/ $Zn(NO_3)_2$ in water. The amount of precipitates increases on addition of 16 eqv. DEAB to the TPE-BPA/ $Zn(NO_3)_2$ system, and the separated precipitates can form a film under load.