Supporting Information

Dual-Sensing Full-Color-Tunable Polymeric Optical Nanosensor

as Full-Spectrum Colorimetric and Ultra-Sensitive

Thermometric Array

Qiang Yan, Jinying Yuan*, Yan Kang, Zhinan Cai, Lilin Zhou and Yingwu Yin

Key Lab of Organic Optoelectronic & Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing, 100084, China.

1. Experimental Section

Materials.

N-isopropylacrylamide (NIPA, Acros, 98%) was recrystallized from benzene and *n*-hexane (1:3). 2-Hydroxyethyl methacrylate (HEMA, Acros, 98%) and Methacrylic acid (MAA, Acros, 98%) were treated by passing through a column of alumina for removal of inhibitor and then was distilled in a vacuum. Tetra(*p*-carboxylic phenyl) porphyrin (TCPP, 99.8%) was purchased from Aldrich Company. Dicyclohexylcarbodiimide (DCC, Alfa Aesar, 99%) 2,2-Azobis(isobutyronitrile) (AIBN, Alfa Aesar, 98%), 4-dimethaminopyridine (DMAP, Fluka, 99%) were used as received. All solvent were used as received.

Charaterization.

Fourier Transform Infrared Spectroscopy (FT-IR). The absorption spectra were recorded on a AVATAR 360 ESP FT-IR spectrometer and the results were collected at 30 scans with a spectral resolution of 1 cm^{-1} .

Nuclear Magnetic Resonance (NMR). ¹H NMR spectra for the polymer structural analysis were obtained from a JEOL JNM-ECA300 spectrometer with CDCl₃ as the solvent. The chemical shifts were relative to tetramethylsilane at $\delta = 0$ ppm for protons.

Gel Permeation Chromatography (GPC). The molecular weight $(M_{n,GPC})$ and molecular weight distribution (M_w/M_n) were measured on a Viscotek TDA 302 gel permeation chromatograph equipped with two columns (GMHHR-H and M Mixed Bed). THF was used as the eluent at a flow rate of 1 mL/min at 30 °C. A series of low polydispersity polystyrene standards were employed for the GPC calibration.

UV-vis Spectroscopy (UV-vis). The UV-vis absorption of the polymeric optical nanosensor solutions were acquired on a UV 2100 UV-visible spectrophotometer (Shimadzu, Japan) at the wavelength scanning from 250 nm to 750 nm using a cuvette. The turbidity upon temperature were measured on a fixed wavelength at $\lambda = 650$ nm.

Dynamic Light Scattering (DLS). A commercial spectrometer (ALV/DLS/SLS-5022F) equipped with a multi-tau digital time correlator (ALV5000) and a 22 mW He-Ne laser ($\lambda_0 = 632$ nm) as the light source was used. In dynamic light scattering (DLS) experiments, scattering light was collected at a fixed angle of 90° for duration of ~10 min. Average radius $\langle R_h \rangle$ and particle size distributions $\langle f_h \rangle$ were computed using cumulants analysis and CONTIN routines. In static light

scattering, we can obtain the apparent weight-average molar mass $\langle M_{w, app} \rangle$, aggregated number $\langle N_{agg} \rangle$, and gyration radius $\langle R_g \rangle$ of assemblies from the angular dependence of the excess absolute scattering intensity, known as Rayleigh ratio $R_{vv}(q)$, as

$$\frac{KC}{R_{w}(q)} \approx \frac{1}{M_{w}} (1 + \frac{1}{3} < R_{g}^{2} > q^{2}) + 2A_{2}C$$

in which $K = 4\pi^2 n^2 (dn/dC)^2 / (N_A \lambda_0^4)$ and $q = (4\pi n/\lambda_0) sin(\theta/2)$ with N_A , dn/dC, n, and λ_0 being the Avogardro number, the specific refractive index increment, the solvent refractive index, and the wavelength of laser light in a vacuum, respectively; and A_2 is the second virial coefficient.

Surface Tension Measurement. Surface tension measurements were engaged on a high-sensitive micro-electromechanical balance system (Dataphysics DCAT21, Germany). The plate used to detect the surface tension is with a length of 19.9 mm and a width of 0.2 mm. The motor speed to drive the plate is 1.00 mm/s.

Synthetic Route.



Scheme S1. The Synthetic Route of Triblock Copolymer PNIPA-b-PHEMA-b-PMAA (1) bearing TCPP groups at PHEMA pendant.

Synthesis of S-1-dodecyl-S'-(α,α'-dimethyl-α''-acetic acid) thrithiocarbonate (TTC).

S-1-dodecyl-S'-(α, α '-dimethyl- α ''-acetic acid) trithiocarbonate was synthesized according to the literature.^[1] 1-Dodecanethiol (20.2 g, 0.10 mol), tricaprylylmethylammonium chloride (1.0 g, 0.0025 mol), and acetone (58.0 g, 1.0 mol) were added into a flask, then cooled to 0 °C under a nitrogen atmosphere. Sodium hydroxide solution (50%) (8.4 g, 0.105 mol) was added over 10 min. After the mixture was stirred for additional 20 min, carbon disulfide (7.6 g, 0.10 mol) in acetone (10.0 g) was added over 30 min, and the color turned red gradually. After chloroform (17.8 g, 0.15

mol) was added, 50% sodium hydroxide solution (40 g) was added dropwise over 20 min. The mixture was stirred overnight. Water (200 mL) was added, followed by 80 mL of concentrated HCl to acidify the aqueous solution. After removing acetone, the solid was collected, and then stirred in 300 mL of 2-propanol. The undissolved solid was filtered off. The 2-propanol solution was concentrated, and the resulting solid was recrystallized from hexane to afford 17.2 g of yellow crystalline solid (yield: 47%). ¹H NMR (CDCl₃, ppm): 11.1 (s, 1H), 3.2 (t, 2H), 1.70-1.82 (s, 6H), 1.61–1.72 (m, 2H), 1.30–1.52 (m, 18H), 0.89 (t, 3H).

Synthesis of PNIPA via RAFT polymerization.

TTC (36.4 mg, 0.1 mmol), AIBN (3.4 mg, 0.02 mmol), NIPA (5.65 g, 50.0 mmol), and 25 mL THF solvent were added into a 50 mL round-bottom flask, followed by three freeze-vacuum-thaw cycles. The flask was immersed into an oil bath at 60 °C with magnetic stirring. After reaction for 12 h, the flask was cooled to room temperature and opened to the air. The polymer was diluted in 25 mL THF and then precipitated in *n*-hexane three times for removal of unreacted NIPA monomer. The slight yellow polymer obtained was dried in vacuum oven for 48 h (conversion: 49%). $M_{n,GPC} = 26300 \text{ g/mol}, M_{n,NMR} = 28800 \text{ g/mol}, M_w/M_n = 1.14$. IR (KBr, cm⁻¹): 3290~3520 (v_{N-H}), 1648 (v_{NH-C=O}). ¹H NMR (CDCl₃, ppm): 11.1 (s, 1H in TTC), 6.12–6.73 (br, 251H, -N**H**- in PNIPA), 3.99 (s, 251H, N-C**H**(CH₃)₂ in PNIPA), 3.2 (t, 2H in TCC), 2.10–2.35 (m, 753H, -[C**H**₂-C**H**]_n- in PNIPA), 1.77 (s, 6H in TCC), 1.60–1.69 (m, 2H in TCC), 1.10 (s, 1452H, -CH(C**H**₃)₂ in PNIPA), 0.89 (t, 3H in TCC).

Synthesis of PNIPA-b-PHEMA via sequential RAFT polymerization.

Above product (2.88 g, 0.10 mmol), AIBN (4.3 mg, 0.025 mmol), HEMA (0.65 g, 5.0 mmol), and 25 mL THF were added into a 50 mL flask, followed by three freeze-vacuum-thaw cycles. The polymerization was carried out at room temperature for 4 h with strongly stirring. After reaction, the flask was cooled to temperature and opened to air. The crude product was dissolved in 5 mL THF, and then precipitated in diethyl ether three times for removal excessive HEMA monomer. The resultant product was dried in vacuum for 24 h (conversion: 32%). $M_{n,GPC} = 29200$ g/mol, $M_{n,NMR} = 30900$ g/mol, $M_w/M_n = 1.16$. IR (KBr, cm⁻¹): 3258~3722 (v_{N-H} and v_{O-H}), 1728 (v_{C=O} in PHEMA), 1648 (v_{NH-C=O} in PNIPA). ¹H NMR (CDCl₃, ppm): 11.1 (s, 1H in TTC), 6.12–6.73 (br, 251H, -NH- in PNIPA), 4.77 (s, 16H, -CH₂OH in PHEMA), 3.99 (s, 251H, N-CH(CH₃)₂ in PNIPA), 3.86 (m, 32H, -COOCH₂- in PHEMA), 3.54 (m, 32H, -COOCH₂- in PHEMA), 3.2 (t, 2H in TCC), 1.64–2.38 (m, 806H, -[CH₂-CH]_n- in PHEMA and PNIPA), 1.77 (s, 6H in TCC), 1.60–1.69 (m, 2H in TCC), 1.10 (s, 1452H, -CH(CH₃)₂ in PNIPA), 0.61–1.02 (m, 48H, -CH₃ in PHEMA).

Synthesis of PNIPA-b-PHEMA-b-PMAA via sequential RAFT polymerization.

Above product (1.55 g, 0.05 mmol), AIBN (1.7 mg, 0.01 mmol), MAA (1.29 g, 15.0 mmol), and 25 mL THF were added into a 50 mL flask, followed by three freeze-vacuum-thaw cycles. The polymerization was carried out at room temperature for 24 h with strongly stirring. After reaction, the flask was cooled to temperature and opened to air. The crude product was precipitated in vast mixture of diethyl ether and methanol (10:1) three times for removal of excessive MAA monomer. The resultant triblock copolymer was dried in vacuum for 24 h (conversion: 54%). $M_{n,GPC} = 41300$ g/mol, $M_{n,NMR} = 44600$ g/mol, $M_w/M_n = 1.20$. IR (KBr, cm⁻¹): 3120~3785 (v_{N-H}, v_{O-H}, and v_{COOH}),

1728, 1720 ($v_{C=O}$ in PHEMA and PMAA), 1648 ($v_{NH-C=O}$ in PNIPA). ¹H NMR (CDCl₃, ppm): 11.1 (s, 1H in TTC), 6.12–6.73 (br, 251H, -N*H*- in PNIPA), 4.77 (s, 16H, -CH₂O*H* in PHEMA), 3.99 (s, 251H, N-C*H*(CH₃)₂ in PNIPA), 3.86 (m, 32H, -COOC*H*₂- in PHEMA), 3.54 (m, 32H, -COOC*H*₂C*H*₂- in PHEMA), 3.2 (t, 2H in TCC), 1.64–2.38 (m, 966H, -[C*H*₂-C*H*]_n- in PHEMA, PNIPA and PMAA), 1.77 (s, 6H in TCC), 1.60–1.69 (m, 2H in TCC), 1.12 (s, 1452H, -CH(C*H*₃)₂ in PNIPA), 0.57–0.98 (m, 203H, -C*H*₃ in PHEMA and PMAA).

Synthesis of PNIPA-*b*-PHEMA-*b*-PMAA triblock copolymer bearing TCPPs pendant groups at PHEMA block via coupling reaction.

A typical example was as follows. The triblock copolymer PNIPA-b-PHEMA-b-PMAA (0.89 g, 20.0 µmol), TCPP (0.25 mg, 0.32 mmol), DCC (69.0 mg, 0.34 mmol), and DMAP (39.0 mg, 0.32 mmol) were dissolved in 20 mL of anhydrous methylene chloride, and the reaction was performed at room temperature for 48 h under nitrogen atmosphere. The byproduct dicyclohexylcarbodiurea was removed by filtration, and the filtered solution was evaporated to dryness. The solid was dissolved in chloroform, and the solution was extracted with a diluted NaOH solution (pH = 10.0, 10 mL) to remove unreactive TCPP. The polymer was still soluble in CHCl₃. Then, the pure copolymer stayed in CHCl₃ solution can be obtained through firstly performing in diluted acid solution to recover the COOH groups at polymer backbone and then precipitating from diethyl ether (yield: 90%). $M_{n,GPC} = 50900 \text{ g/mol}, M_{n,NMR} = 56450 \text{ g/mol}, M_w/M_n = 1.22.$ ¹H NMR (CDCl₃, ppm): 10.2-11.1 (br, COOH in TTC, attached TCPP and PMAA), 8.79 (m, 48H, -CH=CH- in TCPP), 8.35 (s, 48H, -CH=CH- in TCPP), 8.01 (s, proton in benzyl), 6.12–6.73 (br, 251H, -NHin PNIPA), 4.77 (s, 16H, -CH₂OH in PHEMA), 3.99 (s, 251H, N-CH(CH₃)₂ in PNIPA), 3.86 (m, 32H, -COOCH₂- in PHEMA), 3.54 (m, 32H, -COOCH₂CH₂- in PHEMA), 3.2 (t, 2H in TCC), 1.64–2.38 (m, 966H, -[CH₂-CH]_n- in PHEMA, PNIPA and PMAA), 1.77 (s, 6H in TCC), 1.60–1.69 (m, 2H in TCC), 1.12 (s, 1452H, -CH(CH₃)₂ in PNIPA), 0.57–0.98 (m, 203H, -CH₃ in PHEMA and PMAA).

2. The Measurement of Critical Micelle Concentration (CMC).



Figure S1. The CMC of copolymer 1 is 1.20 g/L measured by surface tension variation.

We have employed a method of the concentration dependence on surface tension to measure the

critical micelle concentration (CMC) of the triblock copolymer (1). According to the Langmuir model for surface adsorption, below the CMC, some of the surfactants adsorb at the water-air interface, and the others disperse into the bulk solution without aggregation; above the CMC, for the interface is fully covered by the surfactants, the surfactants can not adsorb at the interface anymore, and instead, they will aggregate spontaneously in solution by self-organization.^[2] Figure S1 exhibits the change of surface tension with the variation of concentration of copolymer 1 at room temperature. For form of the surfactant, there is a gradual decrease in the surface tension with the increase of concentration. The CMC of copolymer 1 in aqueous solution is ~ 1.20 g/L, indicating a high solubility.

3. The Average Hydrodynamic Radius of Copolymer 1 in Water.



Figure S2. The hydrodynamic radius distribution of the copolymer 1 in aqueous solution. The average hydrodynamic radius (R_h) is ~29.4 nm.

As shown in Figure S2, the average hydrodynamic radius (R_h) of the copolymer 1 in aqueous media is characterized by DLS.^[3] It is observed that the R_h of copolymer 1 is approximately 29.4 nm in water, indicating a spherical micellar structure formed. The narrowly radius distribution (21–36 nm) demonstrates a near dispersive nanoparticles.

4. The Thermochromism of the Copolymer 1 in Water.



Figure S3. The thermochromic UV-vis absorption of copolymer 1 in water at different temperature (blue line: 32 °C, red line: 35 °C).



Figure S4. The turbidity measurement of copolymer 1 in water at various temperature. The thermochromic point of the polymeric optical sensor is 35 °C.

The copolymer **1** in water exhibits relevant UV-vis absorption Soret band of TCPP species ($\lambda_{max} = 434 \text{ nm}$) below 32 °C, and the polymeric optical nanosensor is transparent redbrown solution. Interestingly, when the temperature increases to 35 °C, the Soret band sensitively responds to a dramatic blue-shift from 434 (redbrown) to 406 nm (orange) as shown in Figure S3, which indicates the H-aggregated state formation of TCPP species^[4] that impacts the micro-environment polarity around these chromophores. Moreover, upon heating, the abrupt turbid transition from 100% (32 °C) to 20% (35 °C) (Figure S4) further implies that the copolymer micelles possess phase transformational core-corona micellar structure in which PNIPA as the thermomorphic inner core and PMAA as the hydrophilic corona mediates the shortest PHEMA mid-block bearing TCPP chromophores.

5. The Core-Corona Micelles of Copolymer 1 Monitored by DLS.



Figure S5. $\langle R_h \rangle$ versus temperature curves of the copolymer core-corona micelles by DLS monitor. The $\langle R_h \rangle$ changes from 29.4 (below 32 °C) to 16.3 nm (above 35 °C).

We employed DLS to monitor the core-corona micellar structure and its thermo-responsive phase transition properties. Below the LCST of PNIPA, the micelles are of 29.4 nm and all blocks adopt stretched architectures; while the temperature is above the LCST of PNIPA, they can strongly collapse to 16.3 nm (Figure S5) and result in a dramatic polarity reduction around TCPP species, as a consequence, the synergetic effect of TCPP groups H-aggregates formation and the polarity variation around TCPP species leads to a larger $\pi \rightarrow \pi^*$ absorb isolation that induce the color of the polymeric optical nanosensor change.^[5]

References

- [1] Lai, J. T.; Filla, D.; Shea, R. Macromolecules 2002, 35, 6754
- [2] Omar, A. -A. M. A. J. Chem. Eng. Data 1998, 43, 117.
- [3] Jiang, X. Z.; Ge, Z. S.; Xu, J.; Liu, H.; Liu, S. Y. Biomacromolecules 2007, 8, 3184.
- [4] Shirakawa, M.; Kawano, S-I.; Fujita, N.; Sada, K.; Shinkai, S. J. Org. Chem. 2003, 68, 5037.
- [5] Sawicki, E. J. Org. Chem. 1956, 21, 605.