

## Supporting information

### The Synthesis, Self-assembly and pH-responsive Fluorescent Enhancement of Alternating Amphiphilic Copolymer with Azobenzene Pendants

*Jiacheng Wu, Binbin Xu, Zhenghui Liu, Yuan Yao\*, Qixin Zhuang and Shaoliang Lin\**

Shanghai Key Laboratory of Advanced Polymeric Materials, Key Laboratory for  
Ultrafine Materials of Ministry of Education, School of Materials Science and  
Engineering, East China University of Science and Technology, Shanghai 200237,  
China

\*Corresponding authors: [slin@ecust.edu.cn](mailto:slin@ecust.edu.cn) (S.L.); [yaoyuan@ecust.edu.cn](mailto:yaoyuan@ecust.edu.cn) (Y.Y.).

# Experimental

## Materials

N-Phenyldiethanolamine (NPDA, 98%, Adamas), pyridine (99%, Adamas), p-toluenesulfonyl chloride (TsCl, 99%, Adamas), p-anisidine (99%, Adamas), fluoroboric acid (40% in water, Adamas), bis[2-(2-hydroxyethoxy)ethyl] ether (99%, Adamas), potassium tert-butoxide (99%, Adamas), sodium nitrite (99%, Adamas), copper(I) bromide (99%, Adamas), and N,N,N',N'',N'''-pentamethyl-diethylenetriamine (PMDETA, 99%, Adamas) were used as received. All the solvents, including tetrahydrofuran (THF), N,N'-dimethylformamide (DMF), pyridine, petroleum ether and ethyl acetate were analytic reagents and obtained from Adamas without further purification. Deionized water was obtained from a Millipore water purification system. A dialysis bag (Membracel, 3500 Dalton cutoff) was provided by Serva Electrophoresis GmbH.

## Synthesis of NPDAOTs

In a typical procedure, NPDA (5.0 g, 27.6 mmol, 1.0 eq) was dissolved in dry pyridine (60 ml). TsCl (12.7 g, 66.3 mmol, 2.4 eq) was then added slowly into the solution with modest stirring at 0 °C. As the reaction mixture was allowed to reach room temperature, the reaction became slightly exothermic and the reaction mixture became turbid. After 3 h, pyridine was removed by rotary evaporation. A large amount of ice water was added under continuous stirring to give a white solid. The solid was filtered and washed by cold methanol to yield phenylazanediy bis(ethane-2,1-diyl) bis(4-methylbenzenesulfonate) (NPDAOTs, 8.5 g, 63%).

## Synthesis of NPDA-N<sub>3</sub>

To a solution of NPDAOTs (1.5 g, 3.07 mmol, 1.0 eq) in DMF (10 ml) at room temperature was added NaN<sub>3</sub> (2.0 g, 30.8 mmol, 10.0 eq). This solution was stirred under nitrogen atmosphere at 80 °C for 12 h, and then was cooled down to room temperature and filtered to remove excess salts. The obtained yellow oil was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and extracted with H<sub>2</sub>O three times. The organic phase was then dried with Na<sub>2</sub>SO<sub>4</sub> and the CH<sub>2</sub>Cl<sub>2</sub> was removed to produce NPDA-N<sub>3</sub> (0.6 g, 84%).

## Synthesis of NAzoOMe-N<sub>3</sub>

p-Anisidine (4.0 g, 32.5 mmol, 1.0 eq) was dissolved in fluoroboric acid (40%, 15.7 ml) at 0 °C. Sodium nitrite (2.5 g, 35.7 mmol, 1.1 eq) ice water solution was added dropwise. Then the mixture was stirred at 0 °C for 45 min. The solid was filtered and washed with cool ether for several times, yielding a pale pink solid anisidine diazonium salt (4.6 g, 64%).

Anisidine diazonium salt (1.9 g, 8.7 mmol, 1.0 eq) and NPDA-N<sub>3</sub> (2.0 g, 8.7 mmol, 1.0 eq) was dissolved in DMF (10 ml) respectively at 0 °C. The resultant mixture was stirred at 0 °C overnight. The mixture was treated with H<sub>2</sub>O and extracted by CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was washed with brine and dried with Na<sub>2</sub>SO<sub>4</sub>. The crude product was purified by silica gel chromatography eluted with PE : EA=7:1 to yield an orange solid (1.2 g, 38%).

## Synthesis of dipropargyl tetraethylene glycol (PAEG<sub>4</sub>)

Potassium tert-butoxide (4.9 g, 44.0 mmol, 2.2 eq) was dissolved in THF (100 ml) at 0 °C under nitrogen atmosphere. Bis[2-(2-hydroxyethoxy)ethyl] Ether (3.9 g, 20.0 mmol, 1.0 eq) was added

slowly with a syringe under robust stirring. After half an hour, 3-bromopropyne (5.2 g, 44.0 mmol, 2.2 eq) was added through injection. Then mixture was stirred at 0 °C for 3 h. The crude product was purified by silica gel chromatography and eluted with PE : EA=3:2 to yield an pale yellow oil (PAEG<sub>4</sub>, 3.6 g, 66%).

### **Synthesis of P(EG<sub>4</sub>-*a*-NAzoOMe)**

In a typical procedure, CuBr (5.0 mg, 0.04 mmol, 0.05 eq) and NAzoOMe-N<sub>3</sub> (281.0 mg, 0.8 mmol, 1.1 eq) were first added to a 10 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum for degassing and kept under N<sub>2</sub>. Next, PAEG<sub>4</sub> (186.0 mg, 0.7 mmol, 1.0 eq), PMDETA (12.0 μL, 0.07 mmol, 0.1 eq) and DMF (3 mL) were charged via a gastight syringe. The flask was degassed by three cycles of freeze-pump-thaw, and followed by immersing the flask into an oil bath at 35 °C. The coupling reaction lasted for 24 h and was terminated by immersing the flask into liquid N<sub>2</sub>. The mixture was diluted by DMF and passed through a neutral alumina column to remove the residual copper catalyst. The solution was concentrated and precipitated into plenty of cold ether for three times to obtain poly(tetraethylene glycol-*a*-N,N-bis(2-(1H-1,2,3-triazol-1-yl)ethyl)-4-((4-methoxyphenyl)diazenyl)aniline (P(EG<sub>4</sub>-*a*-NAzoOMe), 245.0 mg, 52%).

### **Preparation of P(EG<sub>4</sub>-*a*-NAzoOMe) aggregates**

The aggregation solutions were prepared by using a dialysis method. To a solution of 0.1 mg mL<sup>-1</sup> P(EG<sub>4</sub>-*a*-NAzoOMe) in DMSO, 2 mL of deionized water was added dropwise under mild stirring to form the self-assembled aggregates. Subsequently, the micelle solution was under dialysis against deionized water to remove organic solvents.

### **pH sensitivity study**

For characterizing the pH sensitivity of P(EG<sub>4</sub>-*a*-NAzoOMe), 12 M HCl aqueous solution was added to the micelle solution to tune the pH value, and was then constantly stirred for at least 12 h at room temperature before measurement.

### **Fluorescence emission study**

For characterizing fluorescence emission behavior of P(EG<sub>4</sub>-*a*-NAzoOMe) aggregates, micelle aqueous solutions with different pH value were stirred overnight at room temperature before measurement. 378 nm UV light was used as the excitation. The micelle aqueous solutions with different pH value were irradiated upon 450 nm blue light for 1 h and then performed the same operation with the excitation of 378 nm UV light for charactering the fluorescence emission behavior of the micelles with *cis*- state azobenzenes.

### **Characterization**

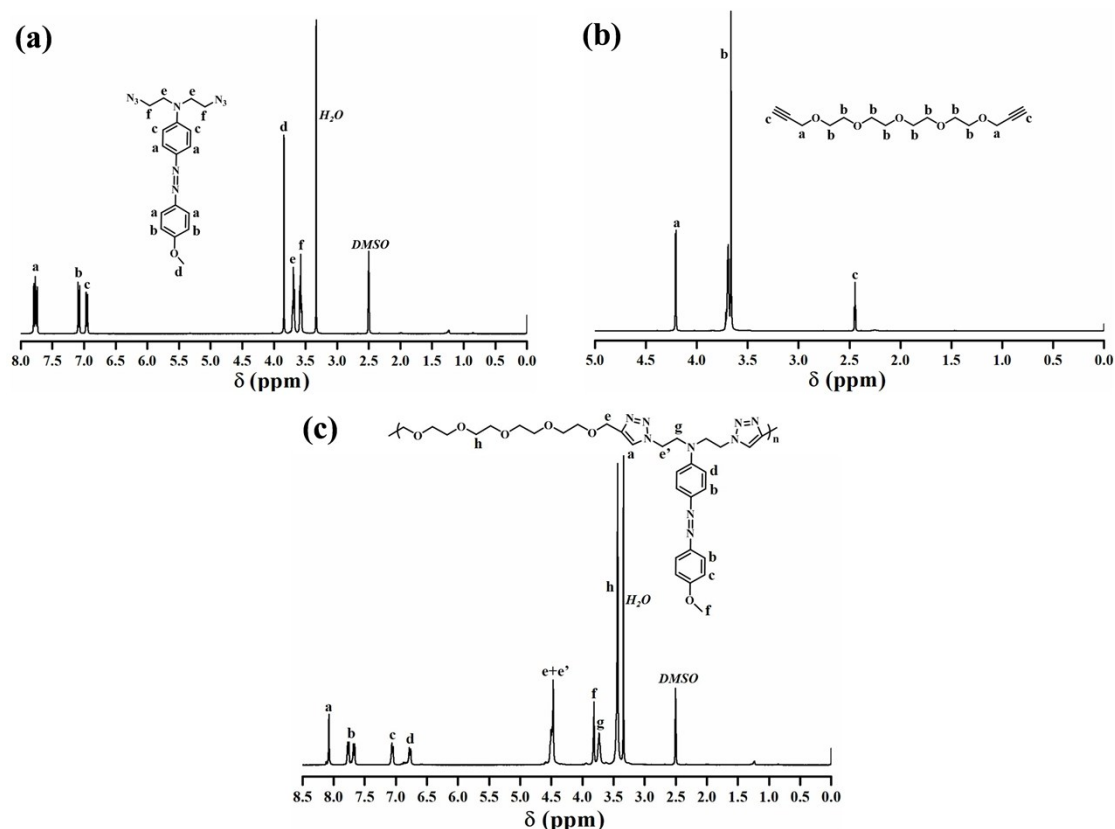
<sup>1</sup>H NMR was recorded by MERCURY plus 400 spectrometer (Varian, Inc., USA) at 30 °C in DMSO-*d*<sub>6</sub> with tetramethylsilane internal standard. The molecular weight and distribution were investigated by gel permeation chromatography (GPC) on a PerkinElmer Series 200 system at 50 °C, and DMF was used as the eluent and the flow rate was 1.0 mL min<sup>-1</sup>. Polystyrene was used as the calibration. The photo-isomerization was induced by irradiation with a high-intensity lamp (Uvata UP114). The UV-Vis spectra of the samples were measured over different irradiation time

intervals using a UV-Vis spectrophotometer (UV-2550 SHIMADZU). Scanning electron microscopy (SEM) measurements were performed on a HITACHI S-4800 at an accelerating voltage of 15.0 kV. The samples were prepared by dropping the aggregates' solution onto a silicon wafer, followed by ambient drying. The samples were sputtered gold before observation. Transmission electron microscopy (TEM) observation was carried on JEM-1400F instrument (JEOL) with the accelerating voltage of 200 kV. The samples were prepared by dropping the solution onto a copper grid coated with carbon film and then dried in ambient. Radius of hydrodynamic measurements  $\langle R_h \rangle$  were recorded by dynamic light scattering (DLS) according to our previous work.<sup>1</sup>

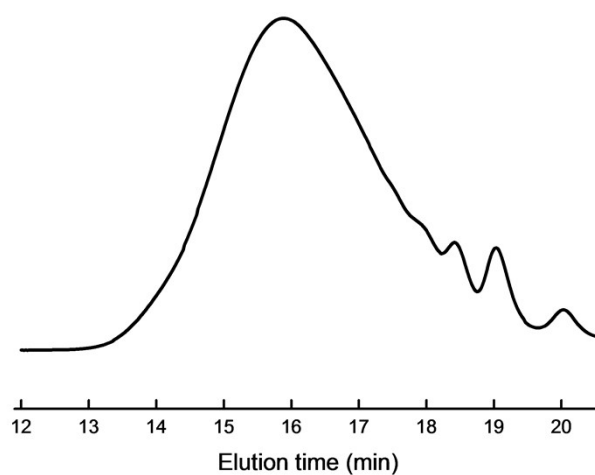
## Characterization of NAzoOMe-N<sub>3</sub> and PAEG<sub>4</sub>

### Characterization of P(EG<sub>4</sub>-*a*-NAzoOMe)

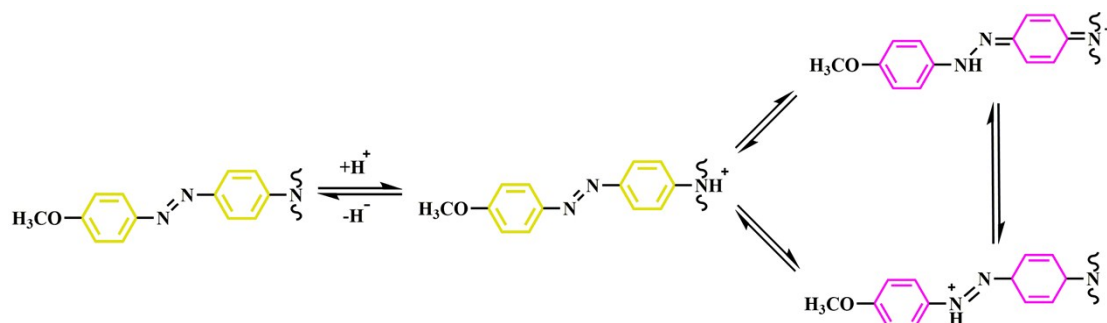
<sup>1</sup>H NMR of monomer N<sup>1</sup>-(2-azidoethyl)-N<sup>1</sup>-(4-((4-methoxyphenyl) diazenyl)phenyl)ethane-1,2-diamine (NAzoOMe-N<sub>3</sub>) (see Fig. S1a): (DMSO-*d*<sub>6</sub>)  $\delta$  (ppm) 7.82 (m, 4H, ArH labeled as a), 7.08 (m, 2H, ArH labeled as b), 6.95 (m, 2H, ArH labeled as c), 3.80 (s, 3H, CH<sub>3</sub>OAr, labeled as d), 3.65 (t, 4H, -CH<sub>2</sub>N, labeled as e), 3.55 (t, 4H, -CH<sub>2</sub>N<sub>3</sub>, labeled as f). <sup>1</sup>H NMR of monomer dipropargyl tetraethylene glycol (PAEG<sub>4</sub>) (see Fig. S1b): (CDCl<sub>3</sub>)  $\delta$  (ppm) 4.19 (d, 4H, OCH<sub>2</sub>-C $\equiv$ , labeled as a), 3.70 (m, 16H, -OCH<sub>2</sub>CH<sub>2</sub>O-, labeled as b), 2.45 (t, 2H, HC $\equiv$ C-, labeled as c). <sup>1</sup>H NMR of P(EG<sub>4</sub>-*a*-NAzoOMe) (see Fig. S1c): (DMSO-*d*<sub>6</sub>)  $\delta$  (ppm) 8.08 (ArH of triazole, labeled as a), 7.70-7.80 (ArH, labeled as b), 7.10 (ArH, labeled as c), 6.82 (ArH, labeled as d), 4.48-4.51 (OCH<sub>2</sub>-triazole, labeled as e and e'), 3.82 (CH<sub>3</sub>OAr, labeled as f), 3.75 (-CH<sub>2</sub>-N, labeled as g), 3.48 (-OCH<sub>2</sub>CH<sub>2</sub>O-, labeled as h).



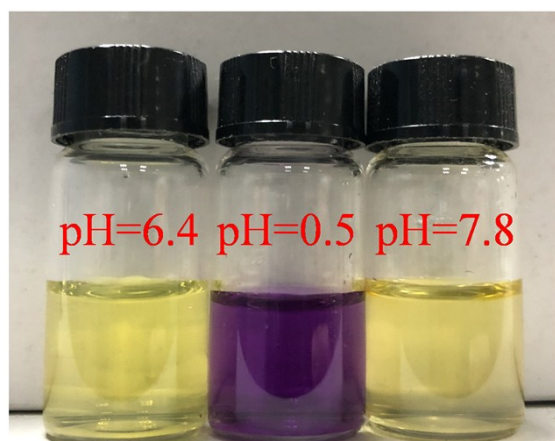
**Fig. S1**  $^1\text{H}$  NMR spectra of (a) NAzoOMe- $\text{N}_3$  monomer, (b) PAEG $_4$  monomer and (c) P(EG $_4$ -*a*-NAzoOMe).



**Figure S2.** GPC curve of P(EG $_4$ -*a*-NAzoOMe).



**Fig. S3** Protonation of tertiary amines and rearrangement of -NAzoOMe structure through intramolecular proton transfer.



**Fig. S4** The obvious color variation of LCM aqueous solutions through reversible pH transition

by adding  $H^+$  and  $OH^-$ .

## References

- (1) Wang, Y.; Lin, S.; Zang, M.; Xing, Y.; He, X.; Lin, J.; Chen, T. Self-Assembly and Photo-Responsive Behavior of Novel  $ABC_2$ -type Block Copolymers Containing Azobenzene Moieties. *Soft Matter* **2012**, *8*, 3131-3138.