

# Supporting Information

## Investigation of Pyridine/Propargyl Bromide Reaction and Strong Fluorescence Enhancements of the Resultant Poly(propargyl pyridinium bromide)

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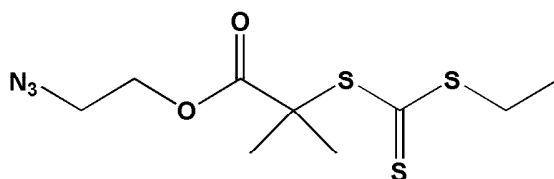
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### S1. Characterization of molecular weight of PPPB

The weight-average molecular weight ( $M_w$ ) of PPPB was determined by multiangle laser light scattering (MALLS) measurement in a GPC-MALLS system. The  $dn/dc$  value of PPPB in DMF was 0.197 mL/g.

### S2. Synthesis and characterization of PPPB-PNIPAM

*N*-isopropylacrylamide (NIPAM, Adamas Reagent Co., Ltd., 98%) and Azodiisobutyronitrile (AIBN, Shanghai No.4 Reagent & H.V. Chemical Co., Ltd.) were purified by recrystallization in *n*-hexane and methanol, respectively. The RAFT agent 2-azidoethyl-2-(ethylthiocarbonothioylthio)-2-methyl propanoate (EMP- $N_3$ ) (Scheme S1) was synthesized according to literature.<sup>1</sup> CuBr (Sinopharm Chemical Reagent Co., Ltd.) was washed by excess acetic acid, ethanol and ethyl ether successively prior to use. *N,N,N',N',N''*-Pentamethyldiethylene triamine (PMDETA) was purchased from Aldrich and used as received. *N,N'*-dimethylformamide (DMF) and 1,4-dioxane were distilled under reduced pressure before use.



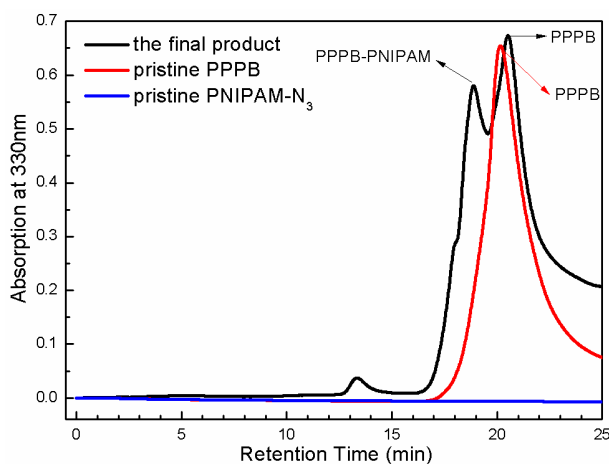
**Scheme S1.** Chemical structure of EMP- $N_3$

PNIPAM bearing an azide group at the end (PNIPAM-N<sub>3</sub>) was synthesized according to following procedures: *N*-isopropylacrylamide (4.82g, 42.6mmol), EMP-N<sub>3</sub> (50mg, 0.17mmol) and AIBN (2.8mg, 0.017mmol) were dissolved in 1,4-dioxane (6.5mL) in a 25 mL Schlenk flask. The reaction mixture was degassed by three freeze-pump-thaw cycles. Subsequently, the flask was immersed in an oil bath at 60 °C for 12 h. The polymerization was terminated by freezing the flask with liquid nitrogen. The product (PNIPAM-N<sub>3</sub>) was purified by three cycles of dissolution with tetrahydrofuran (THF) and precipitation with excess ethyl ether. The weight-average molecular weight ( $M_w$ ) and the polydispersity index ( $M_w/M_n$ ) of PNIPAM-N<sub>3</sub> were determined to be  $1.13 \times 10^4$  and 1.10 respectively by the GPC-MALLS system.

The click reaction between PPPB and PNIPAM-N<sub>3</sub> was conducted by mixing PPPB (240mg, 0.0027mmol), CuBr (7.8mg, 0.054mmol), PNIPAM-N<sub>3</sub> (92mg, 0.0081mmol) and PMDETA (10.5μL, 0.051mmol) in DMF (40mL) in a 60 mL Schlenk flask. The reaction mixture was degassed by three freeze-pump-thaw cycles. Subsequently, the flask was immersed in an oil bath at 70 °C for 100 h. The final product of the click reaction was precipitated by an excess amount of ethyl ether and dried under a vacuum. The final product was a mixture of PPPB-PNIPAM, PNIPAM and PPPB.

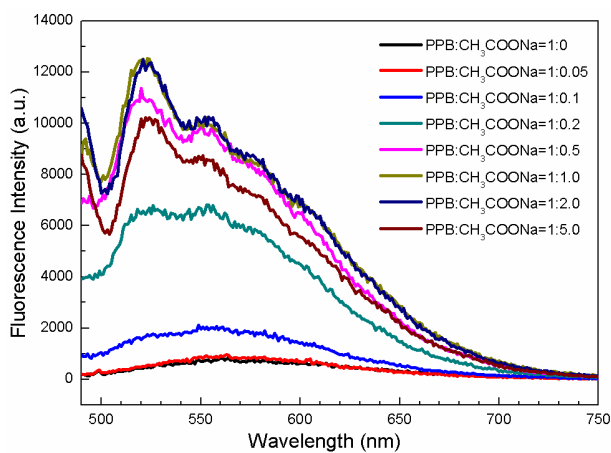
UV-vis detector in the GPC system was used to confirm the signal of PPPB. The detected wavelength was 330 nm. In Figure S1, two peaks appear on the GPC trace of the

final product: the peak at 18.9 min could be attributed to PPPB-PNIPAM and another peak at 20.5 min is assigned to PPPB.



**Figure S1.** Spectra of GPC trace recorded by UV-vis detector of pristine PPPB, pristine PNIPAM- $N_3$  and the final product of click reaction.

### S3. Fluorescence emission of PPPB in DMSO with addition of $CH_3COONa$



**Figure S2.** Fluorescence emission spectra of PPPB/ $CH_3COONa$  mixtures in DMSO (the concentration of PPPB is 0.2 mg/mL) at different PPB/ $CH_3COONa$  molar ratios ( $\lambda_{ex}$  =

482 nm). “PPB:CH<sub>3</sub>COONa” in the inset represents molar ratio of the pyridinium in PPPB to CH<sub>3</sub>COONa.

**S4. Photographs of PPPB in DMF and DMSO before and after addition of anions**



**Figure S3.** Bright-field photographs of PPPB solutions (0.2mg/mL) in DMF without and with addition of anions at the pyridinium/anion molar ratio of 1:1. (A: PPPB, B: PPPB+NaCl, C: PPPB+NaNO<sub>3</sub>, D: PPPB+CH<sub>3</sub>COONa, E: PPPB+HCOONa)



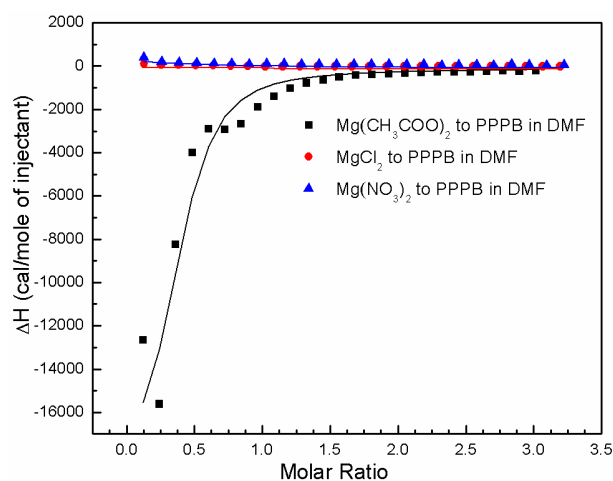
**Figure S4.** Bright-field photographs of PPPB solutions (0.2mg/mL) in DMSO without and with addition of anions at the pyridinium/anion molar ratio of 1:1. (A: PPPB, B: PPPB+NaCl, C: PPPB+NaNO<sub>3</sub>, D: PPPB+CH<sub>3</sub>COONa, E: PPPB+HCOONa)

#### **S5. Mixing DNA aqueous solution with PPPB in DMF**

0.132 mL DNA aqueous solution at 5.0 mg/mL was added dropwise into 1.868 mL PPPB solution in DMF at 0.2 mg/mL. In the final mixture solution, the volume fraction of water is 6.6% and the molar ratio of phosphate/pyridinium is 1/1.

#### **S6. ITC measurements of the enthalpy changes caused by titrating PPPB in DMF with MgCl<sub>2</sub>, Mg(NO<sub>3</sub>)<sub>2</sub> and Mg(CH<sub>3</sub>COO)<sub>2</sub>, respectively**

Experimental titration curves were analyzed with the Origin LLC ITC 7.0 program. The PPPB solutions (PPPB in DMF, 0.18 mg/mL, in the calorimeter cell) were titrated by the respective magnesium salt solutions (concentrations of Cl<sup>1-</sup>, NO<sub>3</sub><sup>1-</sup> and CH<sub>3</sub>COO<sup>1-</sup> in DMF were setting to be 16.9 mM, 17.1 mM and 16.0 mM respectively) at 25.00 ± 0.01 °C. Each solution was degassed for 20 min by shaking under a vacuum at 20 °C prior to experiments. Titration was carried out by 25 injections of 250 µL with a spacing time of 300 seconds for each assay. Blank titration experiments were also done to measure the heat of dilution of the titrant and subtracted from the corresponding ITC data. The raw ITC data were processed using the Origin software (Origin Lab) to obtain binding isotherms (Figure S5).



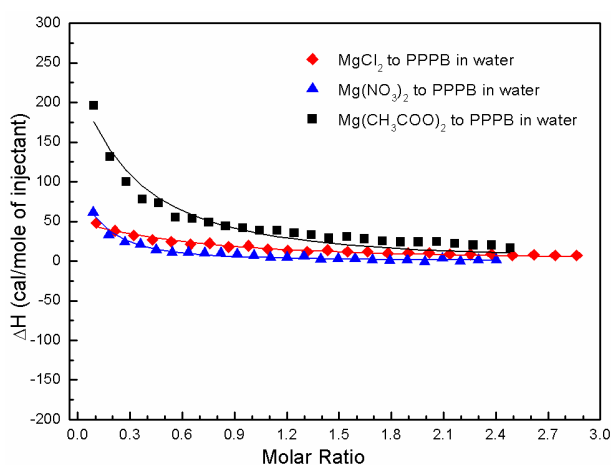
**Figure S5.** Binding isotherms corresponding to the titrations of solutions of the respective magnesium salts ( $\text{Mg}(\text{CH}_3\text{COO})_2$ ,  $\text{MgCl}_2$  or  $\text{Mg}(\text{NO}_3)_2$  in DMF) into PPPB solution (0.18 mg/mL) in DMF at 25 °C. The solid lines represent the results of non-linear least-square fitting of the experimental data using the single-site model.

$\Delta H$  is the normalized enthalpy change caused by mixing PPPB with anion at the pyridinium/anion molar ratio of 1:1. The values of  $\Delta H$  for PPPB/ $\text{Cl}^{1-}$ , PPPB/ $\text{NO}_3^{1-}$  and PPPB/ $\text{CH}_3\text{COO}^{1-}$  in DMF were calculated based on the data exhibited in Figure S5 to be 38.2 cal/mol, 179.9 cal/mol and -5811.3 cal/mol respectively.

**S7. ITC measurements of the enthalpy changes caused by titrating PPPB in water with  $\text{MgCl}_2$ ,  $\text{Mg}(\text{NO}_3)_2$  and  $\text{Mg}(\text{CH}_3\text{COO})_2$ , respectively**

The PPPB solutions (PPPB in water, 0.244 mg/mL, in the calorimeter cell) were titrated by the aqueous solutions of the respective magnesium salts (concentrations of  $\text{Cl}^{1-}$ ,

$\text{NO}_3^{1-}$  and  $\text{CH}_3\text{COO}^{1-}$  in the solutions were 18.9 mM, 15.9 mM and 16.4 mM, respectively) at  $25.00 \pm 0.01^\circ\text{C}$ . Details about parameter settings and instrument operations for the ITC measurements were the same as those mentioned above. The raw ITC data were also processed using the Origin software (Origin Lab) to obtain binding isotherms (Figure S6).

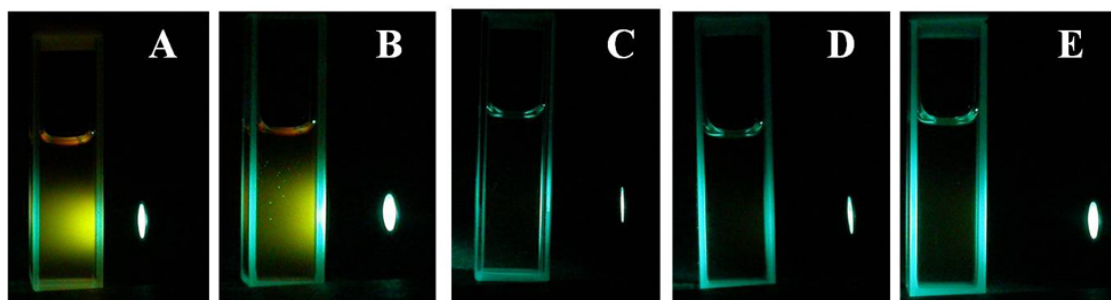


**Figure S6.** Binding isotherms corresponding to the titrations of aqueous solutions of  $\text{MgCl}_2$ ,  $\text{Mg}(\text{NO}_3)_2$ , or  $\text{Mg}(\text{CH}_3\text{COO})_2$  into the aqueous solution of PPPB (0.244 mg/mL) at  $25^\circ\text{C}$ . The solid lines represent the results of non-linear least-square fitting of the experimental data using the single-site model.

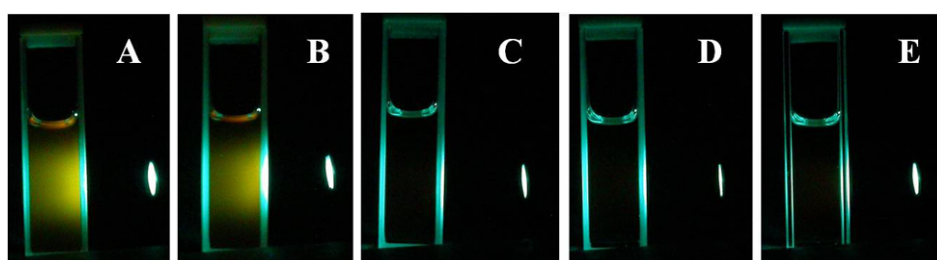
The  $\Delta H$  values for  $\text{PPPB}/\text{Cl}^{1-}$ ,  $\text{PPPB}/\text{NO}_3^{1-}$  and  $\text{PPPB}/\text{CH}_3\text{COO}^{1-}$  in water were calculated to be 26.5 cal/mol, 19.4 cal/mol and 78.3 cal/mol respectively.

#### **S8. Fluorescence emission photographs and the quantum yields of PPPB solutions with and without addition of anions:**





**Figure S7.** Fluorescence emission photographs of PPPB solutions (0.2mg/mL) in DMF without and with addition of anions at the pyridinium/anion molar ratio in solution of 1:1. Each solution inside the 1 cm cuvette was irradiated with visible light (470 nm, 30 mW/cm<sup>2</sup>, CCS HLV-24) which was placed on the right side of the cuvette. (A: PPPB+CH<sub>3</sub>COONa, B: PPPB+HCOONa, C: PPPB+NaCl, D: PPPB+NaNO<sub>3</sub>, E: PPPB)



**Figure S8.** Fluorescence emission photographs of PPPB solutions (0.2mg/mL) in DMSO without and with addition of anions at the pyridinium/anion molar ratio in solution of 1:1. Each solution inside the 1 cm cuvette was irradiated with visible light (470 nm, 30 mW/cm<sup>2</sup>, CCS HLV-24) which was placed on the right side of the cuvette. (A: PPPB+CH<sub>3</sub>COONa, B: PPPB+HCOONa, C: PPPB+NaCl, D: PPPB+NaNO<sub>3</sub>, E: PPPB).

Fluorescence quantum yields ( $\Phi_F$ ) were determined according to the following equation:

$$\Phi_F = \Phi_{FR} \left( \frac{F A_R}{F_R A} \right) \left( \frac{n}{n_R} \right)^2$$

Where  $\Phi_{FR}$  is the fluorescence quantum yield of a reference compound (rhodamine 6G,  $\Phi_{FR} = 95\%$  in ethanol).  $F$  and  $F_R$  are the integrated values of fluorescence spectra for the samples and reference,  $A$  and  $A_R$  are the respective absorbances at the excitation wavelength, and  $n$  and  $n_R$  are the refractive indices of solvents. According to the equation above, the quantum yields of PPPB solution with addition of anions at the pyridinium/anion molar ration of 1:1 are calculated and the results are listed below:

In DMF: For PPPB,  $\Phi_F = 1.38\%$ ; For PPPB+CH<sub>3</sub>COONa,  $\Phi_F = 9.62\%$ ; For PPPB+HCOONa,  $\Phi_F = 6.76\%$ ; For PPPB+NaOH,  $\Phi_F = 7.28\%$ ; For PPPB+Na<sub>2</sub>SiO<sub>3</sub>,  $\Phi_F = 8.72\%$ ; For PPPB+Na<sub>3</sub>PO<sub>4</sub>,  $\Phi_F = 8.26\%$ .

In DMSO: For PPPB,  $\Phi_F = 0.86\%$ ; For PPPB+CH<sub>3</sub>COONa,  $\Phi_F = 7.44\%$ ; For PPPB+HCOONa,  $\Phi_F = 5.22\%$ ; For PPPB+NaOH,  $\Phi_F = 4.29\%$ ; For PPPB+Na<sub>2</sub>SiO<sub>3</sub>,  $\Phi_F = 5.70\%$ ; For PPPB+Na<sub>3</sub>PO<sub>4</sub>,  $\Phi_F = 6.84\%$ .

## References

- (1) Liu, J. Y.; Nie, Z. H.; Gao, Y.; Adronov, A.; Li, H. M. *J. Polym. Sci., Part A: Polym. Chem.* 2008, 46, 7187-7199.