

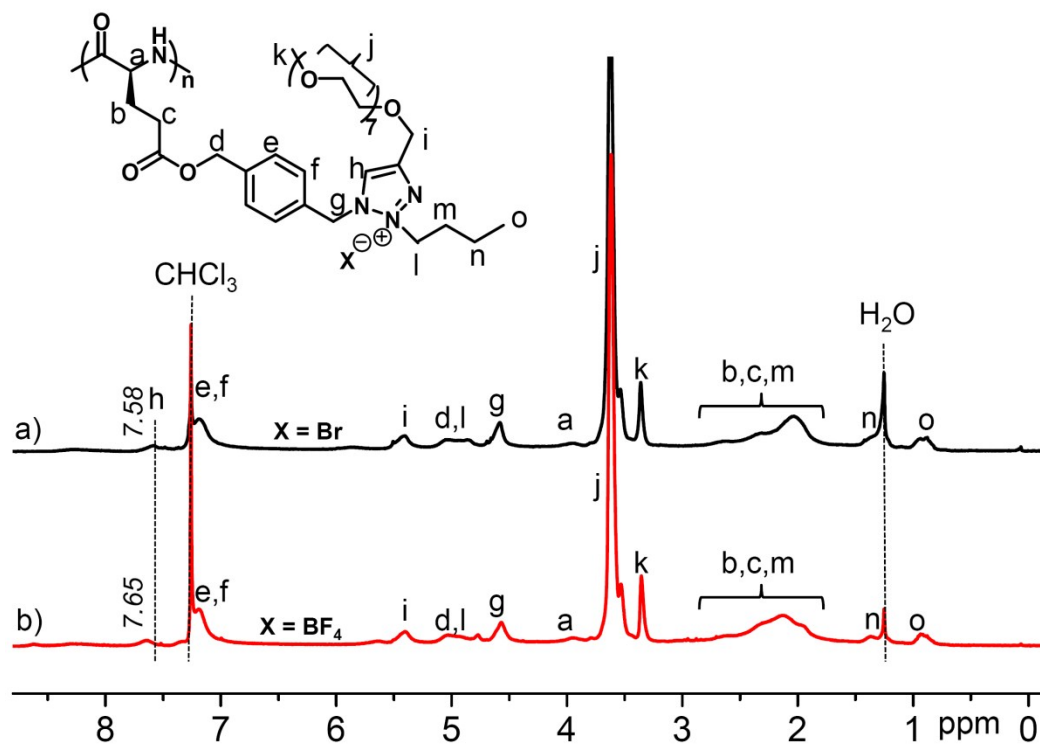
Supporting Information

**Synthesis and LCST-Type Phase Behavior of Water-Soluble Polypeptide with  
Y-Shaped and Charged Side-Chains**

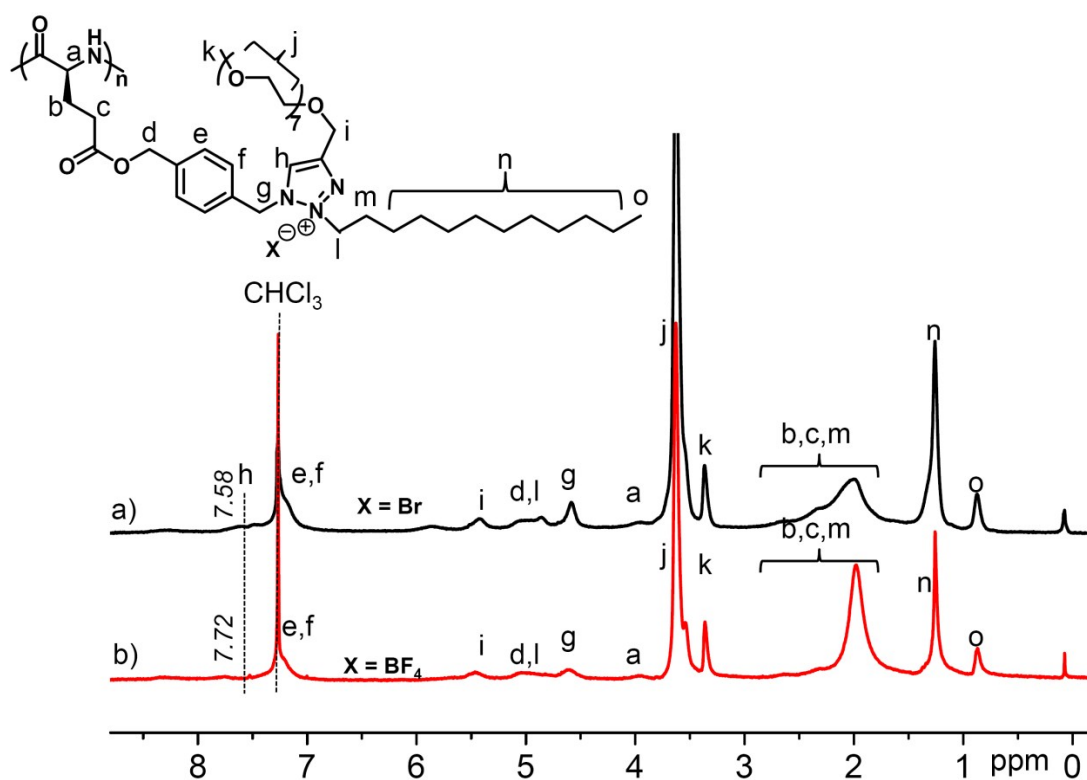
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**Figure S1.**  $^1\text{H}$  NMR spectra of PMBLG-OEG<sub>7</sub>/C<sub>4</sub>-X (X = Br or BF<sub>4</sub>) in CDCl<sub>3</sub>.



**Figure S2.**  $^1\text{H}$  NMR spectra of PMBLG-OEG<sub>7</sub>/C<sub>12</sub>-X (X = Br or BF<sub>4</sub>) in CDCl<sub>3</sub>.

Table S1. Elemental analysis results of PMBLG-OEG<sub>7</sub>/C<sub>m</sub>-BF<sub>4</sub> samples.

| Samples                                                  | C (%) |       | H (%) |       | N (%) |       | O (%) |       |
|----------------------------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
|                                                          | Calcd | Found | Calcd | Found | Calcd | Found | Calcd | Found |
| PMBLG-OEG <sub>7</sub> /C <sub>4</sub> -BF <sub>4</sub>  | 52.77 | 52.53 | 7.21  | 7.25  | 7.03  | 7.07  | 22.09 | 22.33 |
| PMBLG-OEG <sub>7</sub> /C <sub>6</sub> -BF <sub>4</sub>  | 53.89 | 53.69 | 7.46  | 7.49  | 6.79  | 6.83  | 21.34 | 21.75 |
| PMBLG-OEG <sub>7</sub> /C <sub>12</sub> -BF <sub>4</sub> | 56.82 | 57.60 | 8.10  | 8.14  | 6.16  | 6.18  | 19.36 | 19.67 |

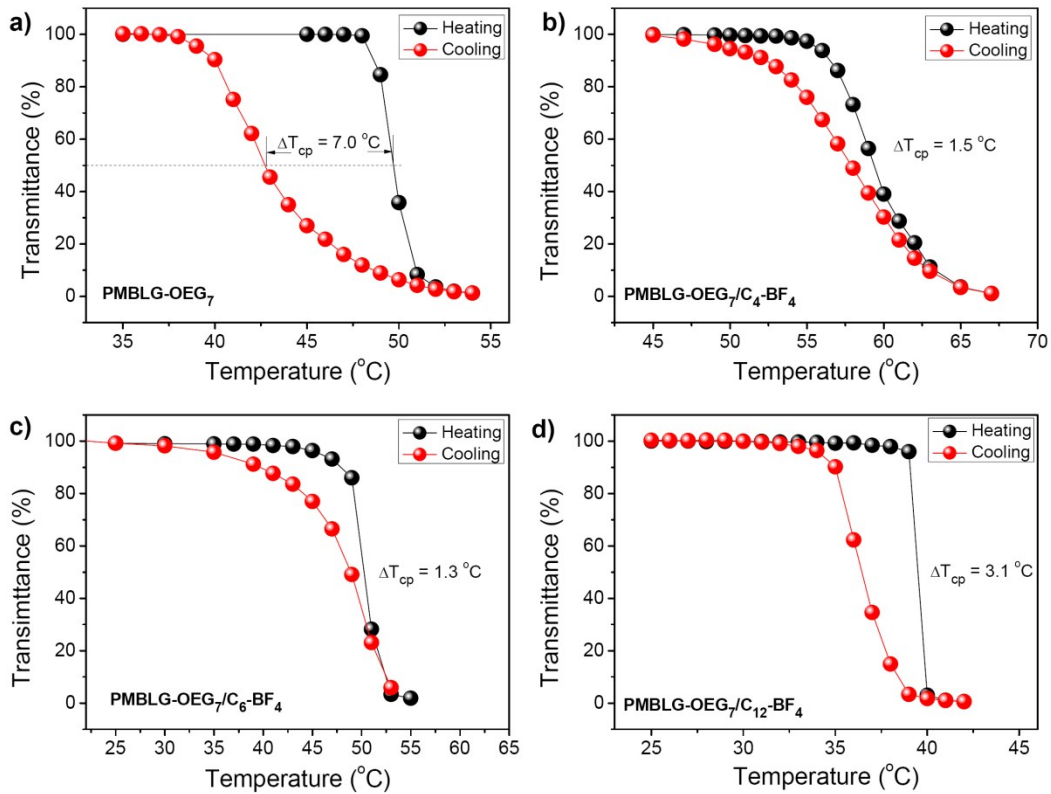
Table S2. Solubility characteristics of PMBLG-OEG<sub>7</sub> and PMBLG-OEG<sub>7</sub>/C<sub>m</sub>-X samples in various solvents.

| Solvents         | PMBLG<br>-OEG <sub>7</sub> | PMBLG-OEG <sub>7</sub> /C <sub>m</sub> -Br |       |        | PMBLG-OEG <sub>7</sub> /C <sub>m</sub> -BF <sub>4</sub> |       |        |
|------------------|----------------------------|--------------------------------------------|-------|--------|---------------------------------------------------------|-------|--------|
|                  |                            | m = 4                                      | m = 6 | m = 12 | m = 4                                                   | m = 6 | m = 12 |
| DMSO             | S                          | S                                          | S     | S      | S                                                       | S     | S      |
| DMF              | S                          | S                                          | S     | S      | S                                                       | S     | S      |
| H <sub>2</sub> O | L                          | S                                          | S     | S      | L                                                       | L     | L      |
| MeOH             | S                          | S                                          | S     | S      | S                                                       | S     | S      |
| EtOH             | S                          | S                                          | S     | S      | S                                                       | S     | S      |
| THF              | S                          | I                                          | I     | I      | I                                                       | I     | I      |
| EAc              | I                          | I                                          | I     | I      | I                                                       | I     | I      |
| DEE              | I                          | I                                          | I     | I      | I                                                       | I     | I      |
| TCM              | S                          | S                                          | S     | S      | S                                                       | S     | S      |
| DCM              | S                          | S                                          | S     | S      | S                                                       | S     | S      |
| Hexane           | I                          | I                                          | I     | I      | I                                                       | I     | I      |

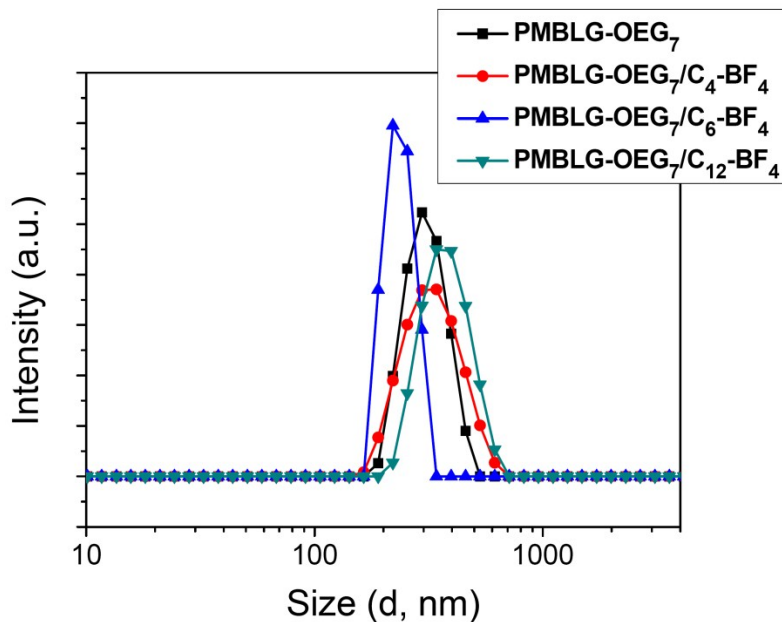
DMSO = dimethyl sulphoxide; DMF = *N,N*-dimethylformamide; MeOH = methanol; EtOH = ethanol; THF = tetrahydrofuran; EAc = ethyl acetate; DEE = diethyl ether; TCM = trichloromethane; DCM = dichloromethane; S = soluble; I = insoluble; L = LCST-type phase transition (concentration = 10 mg·mL<sup>-1</sup>).

Table S3. Mean residual ellipticity ( $[\theta]_{222}$ ) and fractional helicity ( $f_H$ ) of PMBLG-OEG<sub>7</sub> and PMBLG-OEG<sub>7</sub>/C<sub>m</sub>-X samples in DI-H<sub>2</sub>O (0.05 mg·mL<sup>-1</sup>).

| Name                                                     | $[\theta]_{222}$ | $f_H$ (%) |
|----------------------------------------------------------|------------------|-----------|
| PMBLG-OEG <sub>7</sub>                                   | -32,411          | 91        |
| PMBLG-OEG <sub>7</sub> /C <sub>4</sub> -Br               | -20,800          | 61        |
| PMBLG-OEG <sub>7</sub> /C <sub>6</sub> -Br               | -16,981          | 51        |
| PMBLG-OEG <sub>7</sub> /C <sub>12</sub> -Br              | -14,018          | 44        |
| PMBLG-OEG <sub>7</sub> /C <sub>4</sub> -BF <sub>4</sub>  | -23,177          | 67        |
| PMBLG-OEG <sub>7</sub> /C <sub>6</sub> -BF <sub>4</sub>  | -18,005          | 54        |
| PMBLG-OEG <sub>7</sub> /C <sub>12</sub> -BF <sub>4</sub> | -14,987          | 46        |



**Figure S3.** The plots of transmittance at  $\lambda = 500$  nm versus temperature for the aqueous solutions of (a) PMBLG-OEG<sub>7</sub> and (b-d) PMBLG-OEG<sub>7</sub>/C<sub>m</sub>-BF<sub>4</sub> ( $m = 4, 6,$  and  $12$ ) in DI-H<sub>2</sub>O (polymer concentration =  $10 \text{ mg}\cdot\text{mL}^{-1}$ ).



**Figure S4.** DLS size distribution plots of PMBLG-OEG<sub>7</sub> and PMBLG-OEG<sub>7</sub>/C<sub>m</sub>-BF<sub>4</sub> ( $m = 4, 6,$  and  $12$ ) at the temperatures above respective  $T_{cp}$ s. (polymer concentration =  $1 \text{ mg}\cdot\text{mL}^{-1}$ )

Table S4. DLS results of resulting polypeptides in DI-H<sub>2</sub>O above respective T<sub>cp</sub> (polymer concentration = 1 mg·mL<sup>-1</sup>).

| Name                                                     | Diameter (nm) | PDI <sup>a</sup> |
|----------------------------------------------------------|---------------|------------------|
| PMBLG-OEG <sub>7</sub>                                   | 331.7         | 0.183            |
| PMBLG-OEG <sub>7</sub> /C <sub>4</sub> -BF <sub>4</sub>  | 290.3         | 0.378            |
| PMBLG-OEG <sub>7</sub> /C <sub>6</sub> -BF <sub>4</sub>  | 221.3         | 0.109            |
| PMBLG-OEG <sub>7</sub> /C <sub>12</sub> -BF <sub>4</sub> | 349.6         | 0.201            |

<sup>a</sup> Distribution of polymer aggregates in the solvents.

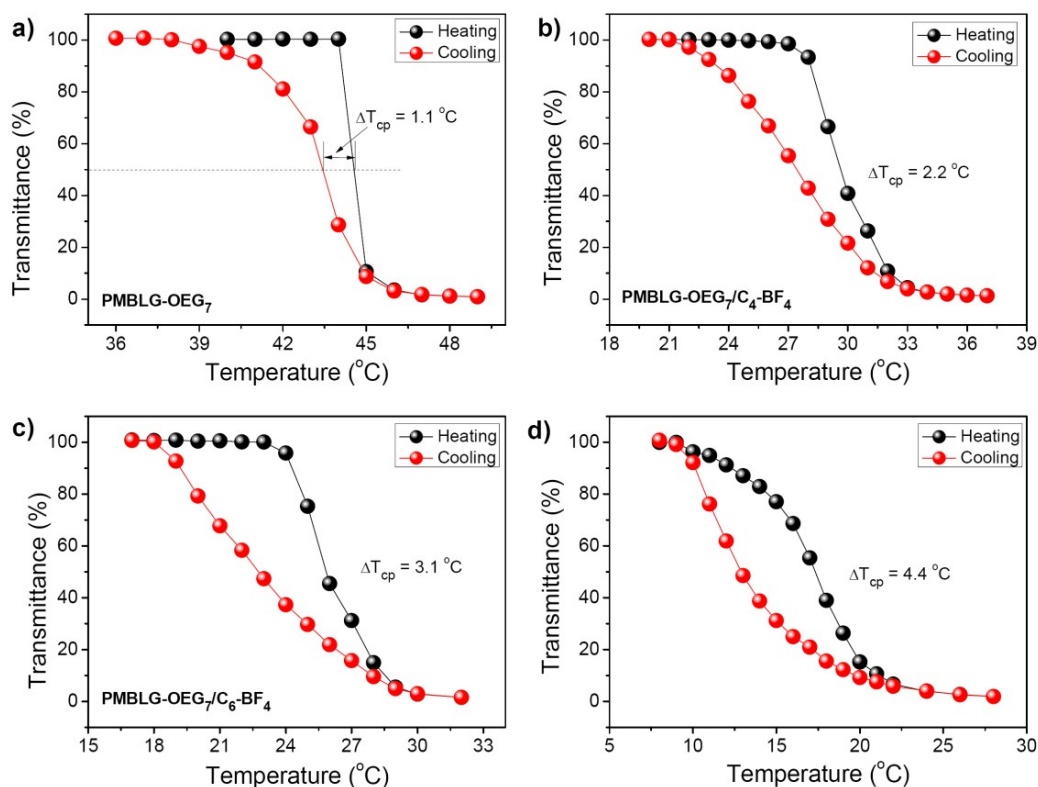
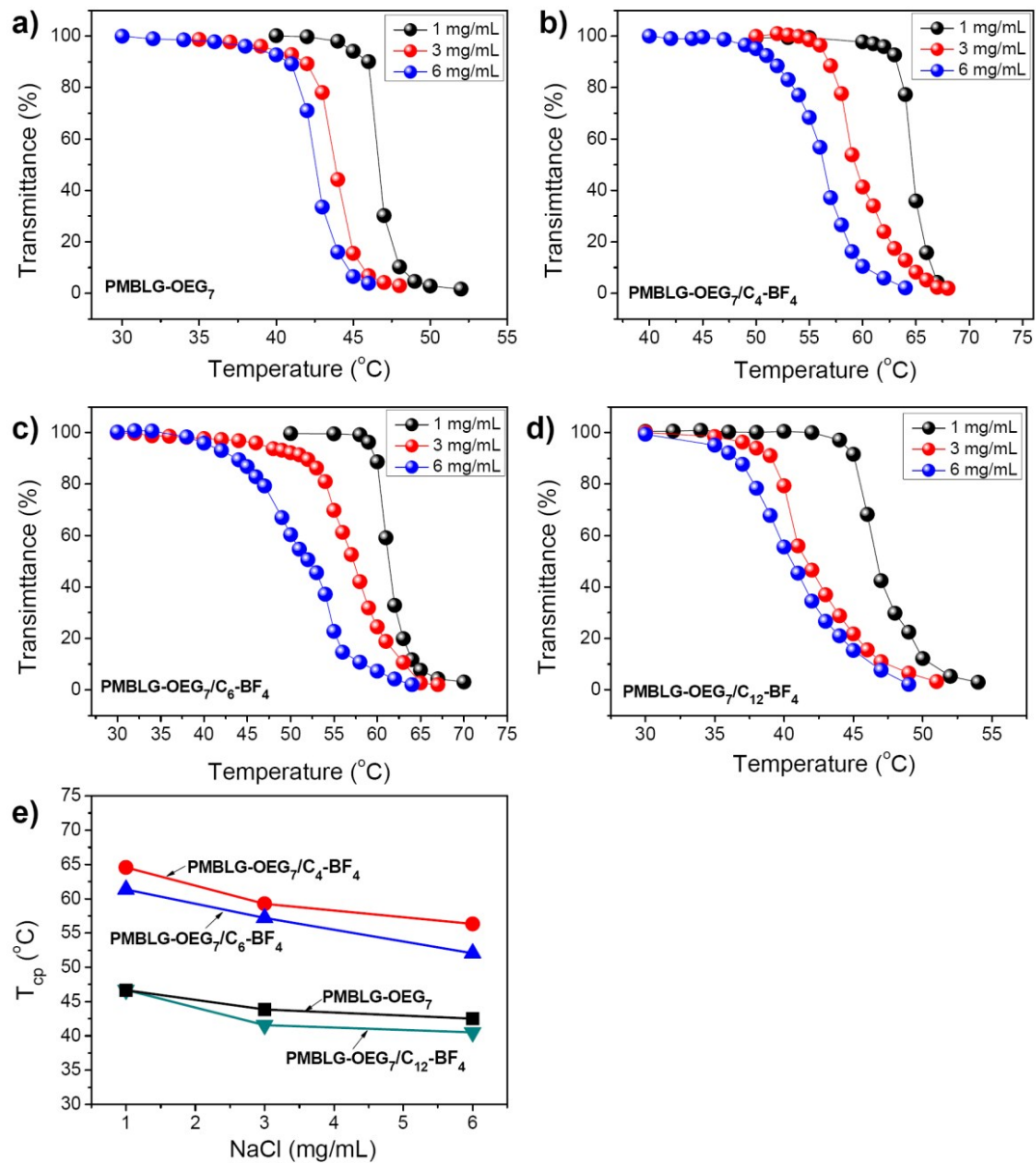
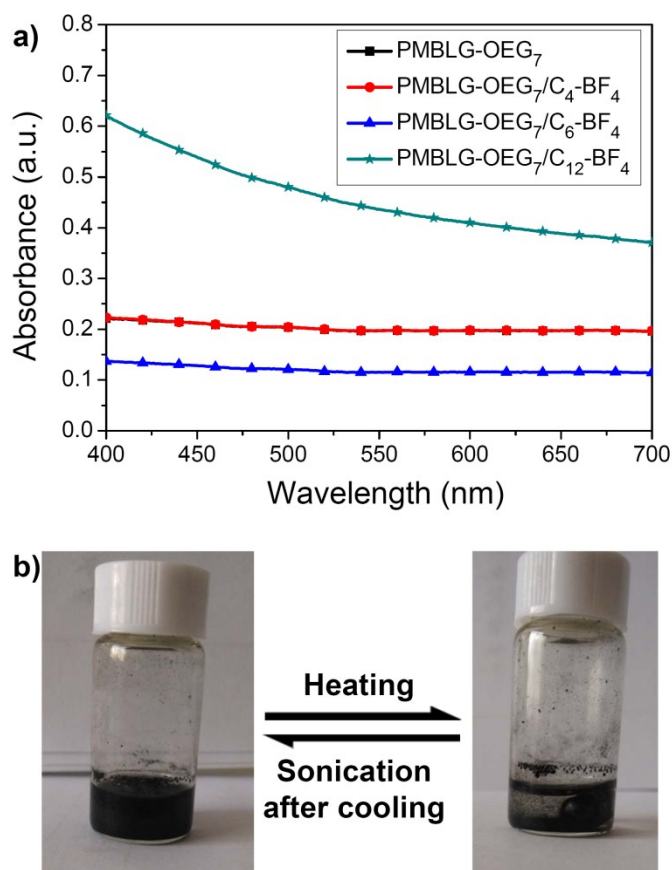


Figure S5. The plots of transmittance at  $\lambda = 500$  nm versus temperature for the NaBF<sub>4</sub> aqueous solutions (salt concentration = 5 mg·mL<sup>-1</sup>) of (a) PMBLG-OEG<sub>7</sub> and (b-d) PMBLG-OEG<sub>7</sub>/C<sub>m</sub>-BF<sub>4</sub> (m = 4, 6, and 12) (polymer concentration = 5 mg·mL<sup>-1</sup>).



**Figure S6.** The plots of transmittance at  $\lambda = 500$  nm versus temperature for the NaCl aqueous solutions of (a) PMBLG-OEG<sub>7</sub> and (b-d) PMBLG-OEG<sub>7</sub>/C<sub>m</sub>-BF<sub>4</sub> ( $m = 4, 6,$  and  $12$ ) (salt concentration =  $1, 3, 6$  mg·mL<sup>-1</sup>). (e) The plots of  $T_{cp}$  versus concentrations in NaBF<sub>4</sub> aqueous solution (polymer concentration =  $5$  mg·mL<sup>-1</sup>).



**Figure S7.** (a) UV-vis spectra of polymer/SWCNT/NaCl aqueous solutions (polymers: PMBLG-OEG<sub>7</sub> and PMBLG-OEG<sub>7</sub>/C<sub>m</sub>-BF<sub>4</sub>, salt concentration = 6 mg·mL<sup>-1</sup>, the solutions were diluted 10 times before UV-vis measurement). (b) Optical images of PMBLG-OEG<sub>7</sub>/C<sub>12</sub>-BF<sub>4</sub>/SWCNT/NaCl aqueous solution at room temperature (left) and temperature above the T<sub>cp</sub> (right).

*Table S5.* SWCNT dispersibility in NaCl aqueous solution (salt concentration = 6 mg·mL<sup>-1</sup>) in the presence of PMBLG-OEG<sub>7</sub> and PMBLG-OEG<sub>7</sub>/C<sub>m</sub>-BF<sub>4</sub> (m = 4, 6, and 12).

| Samples                                              | PMBLG-OEG <sub>7</sub> |                    | PMBLG-OEG <sub>7</sub> /C <sub>4</sub> -BF <sub>4</sub> |                    | PMBLG-OEG <sub>7</sub> /C <sub>6</sub> -BF <sub>4</sub> |                    | PMBLG-OEG <sub>7</sub> /C <sub>12</sub> -BF <sub>4</sub> |                    |
|------------------------------------------------------|------------------------|--------------------|---------------------------------------------------------|--------------------|---------------------------------------------------------|--------------------|----------------------------------------------------------|--------------------|
|                                                      | DI-H <sub>2</sub> O    | NaCl <sub>aq</sub> | DI-H <sub>2</sub> O                                     | NaCl <sub>aq</sub> | DI-H <sub>2</sub> O                                     | NaCl <sub>aq</sub> | DI-H <sub>2</sub> O                                      | NaCl <sub>aq</sub> |
| [A] <sub>500</sub> <sup>a</sup>                      | 0.045                  | 0.204              | 0.003                                                   | 0.205              | 0.003                                                   | 0.121              | 0.003                                                    | 0.480              |
| Dispersibility <sup>b</sup><br>(mg·L <sup>-1</sup> ) | 32.6                   | 147.8              | 2.2                                                     | 148.6              | 2.2                                                     | 87.7               | 2.2                                                      | 347.8              |

<sup>a</sup>The absorbance at 500 nm which was determined by UV-vis spectroscopy. Polymer aqueous solutions were diluted 10 times before UV-vis measurement.

<sup>b</sup>Dispersibility = 10 × [A]<sub>500</sub>/0.0138.<sup>1</sup>

