

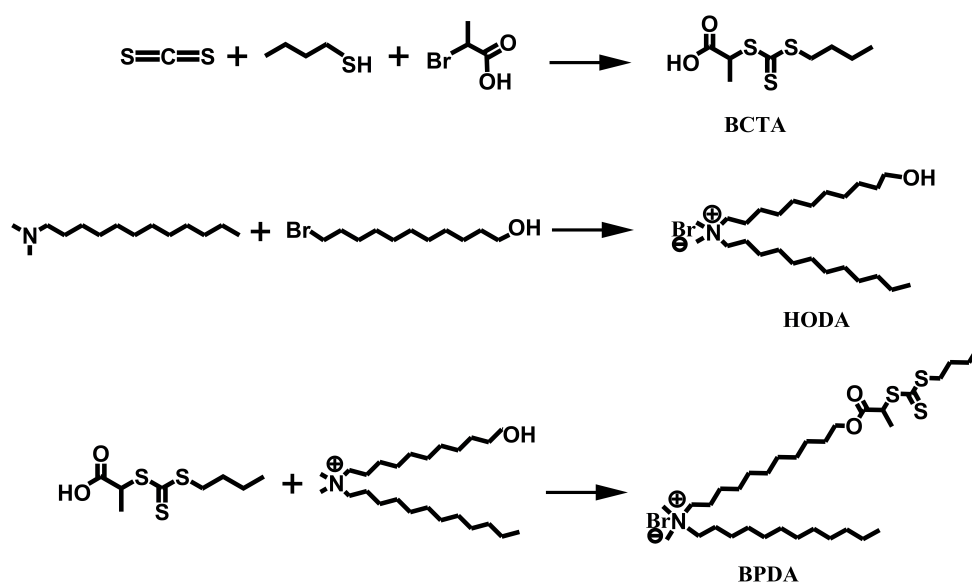
## Supporting information

### Structurally Dependent Self-assembly and Luminescence of Polyoxometalate-cored Supramolecular Star Polymers

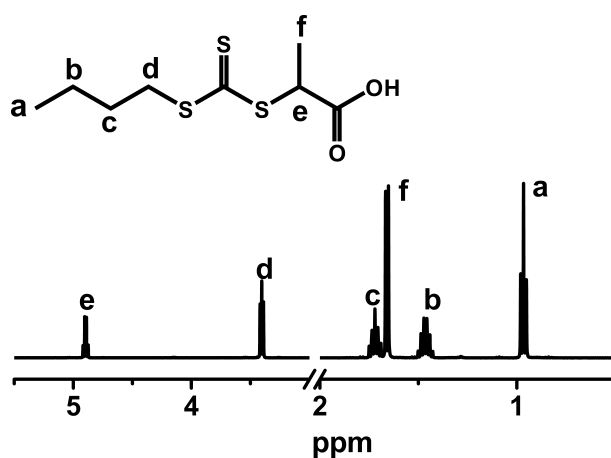
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**Scheme S1.** Synthesis route of the bifunctional surfactant BPDA.



**Fig. S1**  $^1\text{H}$  NMR spectrum of BCTA.

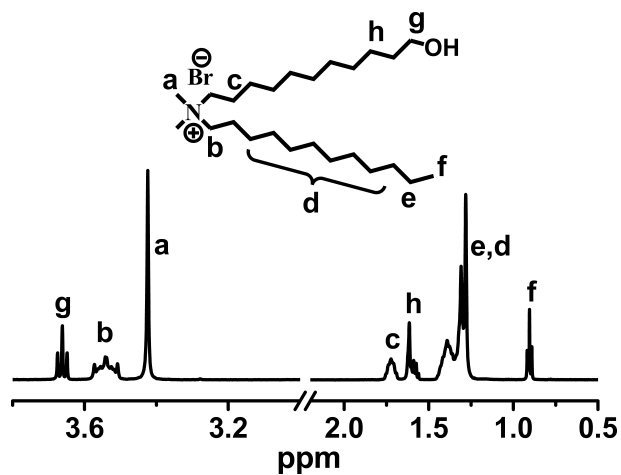


Fig. S2 <sup>1</sup>H NMR spectrum of HODA.

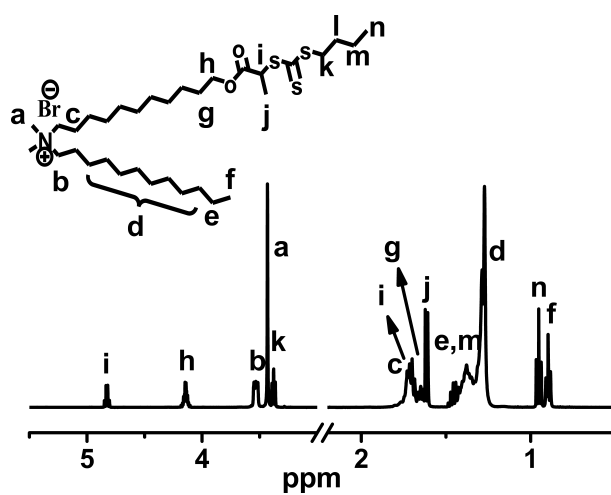


Fig. S3 <sup>1</sup>H NMR spectrum of BPDA.

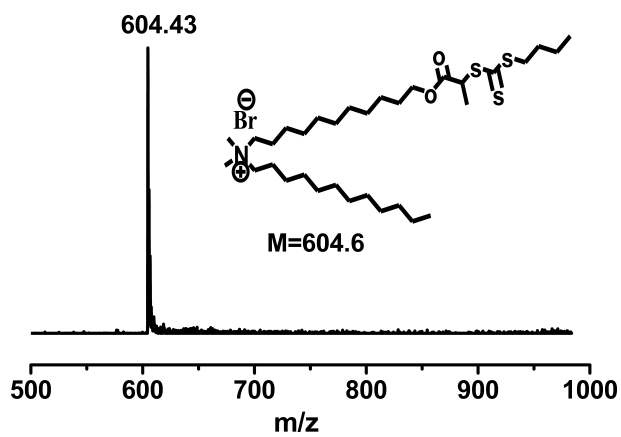
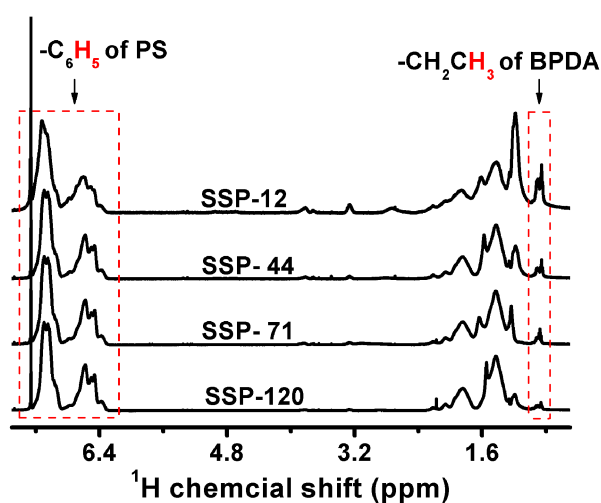


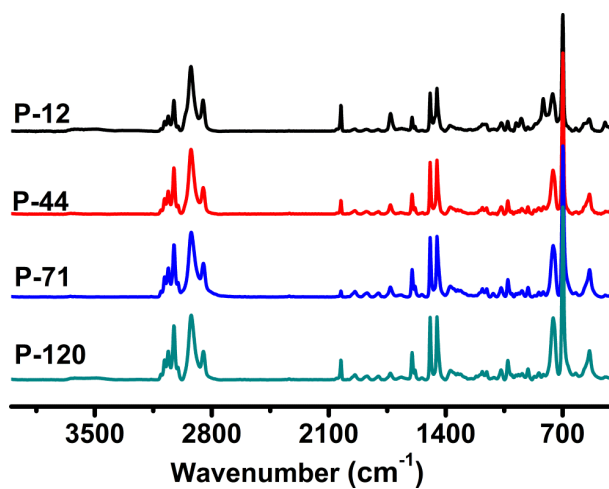
Fig. S4 MALDI-TOF result of the BPDA.

**Table S1.** Elemental analysis results of the four EuW<sub>10</sub>-cored SSP.

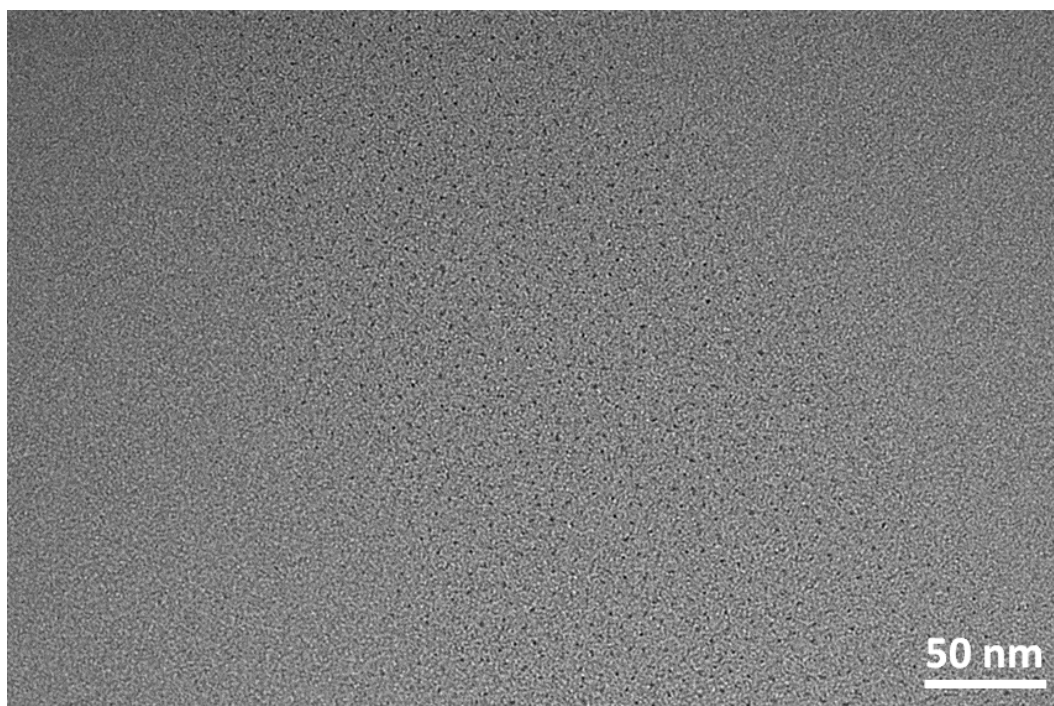
	C (%)	H (%)	N (%)
Experimental results of BCTA	40.63	5.93	-
Calculated value of (C <sub>8</sub> H <sub>14</sub> O <sub>2</sub> S <sub>3</sub> )Molecular weight: 238.0	40.30	5.91	-
Experimental results of HODA	64.69	11.34	2.86
Calculated value of C <sub>25</sub> H <sub>54</sub> NOBr Molecular weight: 463.4	64.62	11.71	3.01
Experimental results of BPDA	56.82	9.42	2.01
Calculated value of C <sub>33</sub> H <sub>66</sub> NO <sub>2</sub> S <sub>3</sub> .H <sub>2</sub> O Molecular weight: 703.0	56.38	9.75	1.99
Experimental results of SSP-12	69.43	7.07	0.89
Calculated value of (C <sub>33</sub> H <sub>66</sub> NO <sub>2</sub> S <sub>3</sub> ) <sub>9</sub> ((C <sub>8</sub> H <sub>8</sub> ) <sub>12</sub> ) <sub>7</sub> EuW <sub>10</sub> O <sub>36</sub> Molecular weight: 16760.6	69.44	7.61	0.75
Experimental results of SSP-44	82.65	7.52	0.29
Calculated value of (C <sub>33</sub> H <sub>66</sub> NO <sub>2</sub> S <sub>3</sub> ) <sub>9</sub> ((C <sub>8</sub> H <sub>8</sub> ) <sub>44</sub> ) <sub>7</sub> EuW <sub>10</sub> O <sub>36</sub> Molecular weight: 40090.0	82.76	7.69	0.31
Experimental results of SSP-71	85.94	7.52	0.25
Calculated value of (C <sub>33</sub> H <sub>66</sub> NO <sub>2</sub> S <sub>3</sub> ) <sub>9</sub> ((C <sub>8</sub> H <sub>8</sub> ) <sub>71</sub> ) <sub>7</sub> EuW <sub>10</sub> O <sub>36</sub> Molecular weight: 59774.2	85.86	7.70	0.21
Experimental results of SSP-120	88.16	7.63	0.20
Calculated value of (C <sub>33</sub> H <sub>66</sub> NO <sub>2</sub> S <sub>3</sub> ) <sub>9</sub> ((C <sub>8</sub> H <sub>8</sub> ) <sub>120</sub> ) <sub>7</sub> EuW <sub>10</sub> O <sub>36</sub> Molecular weight: 95497.3	88.25	7.72	0.13



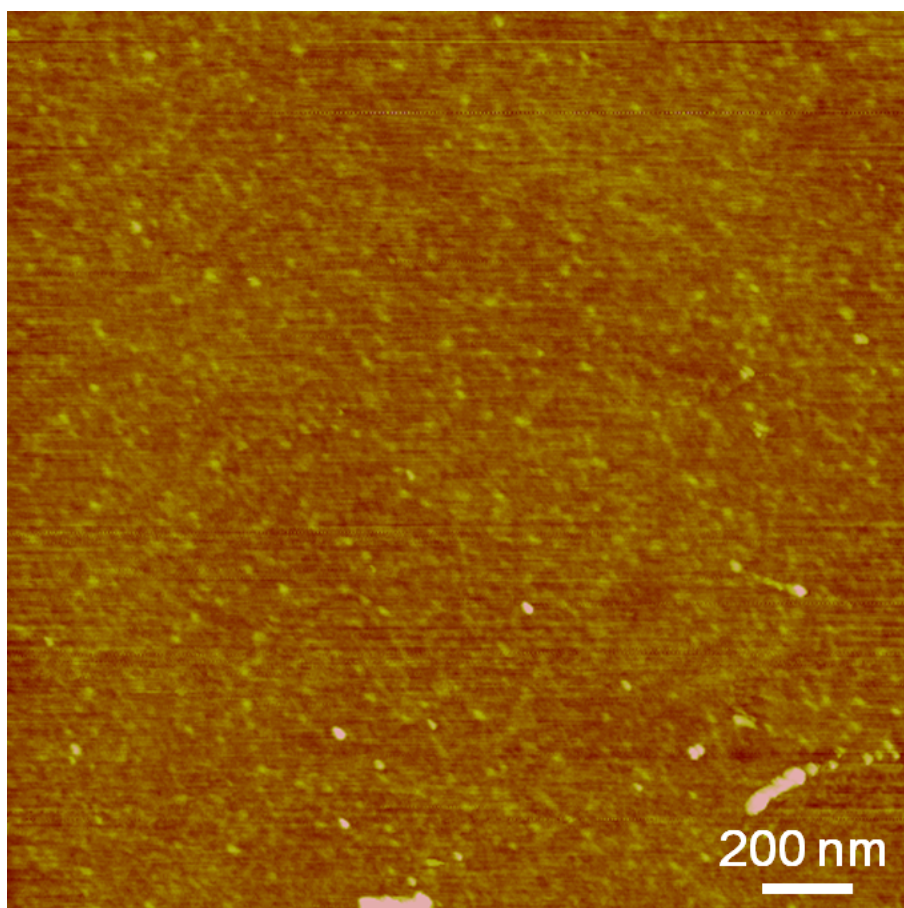
**Fig. S5** <sup>1</sup>H NMR spectra of the four EuW<sub>10</sub>-cored SSP in CDCl<sub>3</sub>.



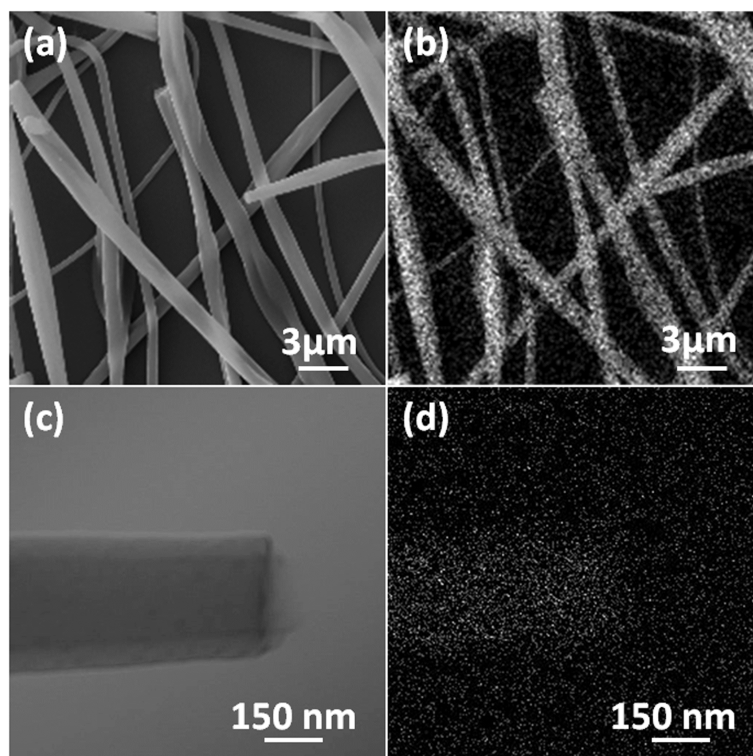
**Fig. S6** FTIR spectra of the four EuW<sub>10</sub>-cored SSP in KBr pellets.



**Fig. S7** TEM image of SSP-12 before being stained by RuO<sub>4</sub>.

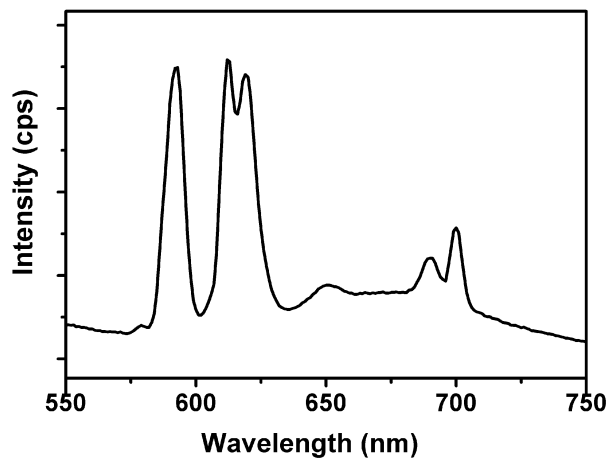


**Fig. S8** AFM image of SSP-120 on silica substrate.



**Fig. S9** (a) SEM image of SSP-120 fibers prepared by electrospinning and (b) its

EDX mapping image by analyzing C element; (c) TEM image of a fiber and (d) its EDX mapping image by analyzing W element. Because the weight content of C and W in SSP-120 are 88.25% and 1.93% respectively, the EDX signal of W is relatively weak.



**Fig. S10** Emission spectrum of SSP-120 fiber prepared by electrospinning at an excitation wavelength of 275 nm.