

## **Polymerization-induced self-assembly of liquid crystalline ABC triblock copolymers with long solvophilic chain**

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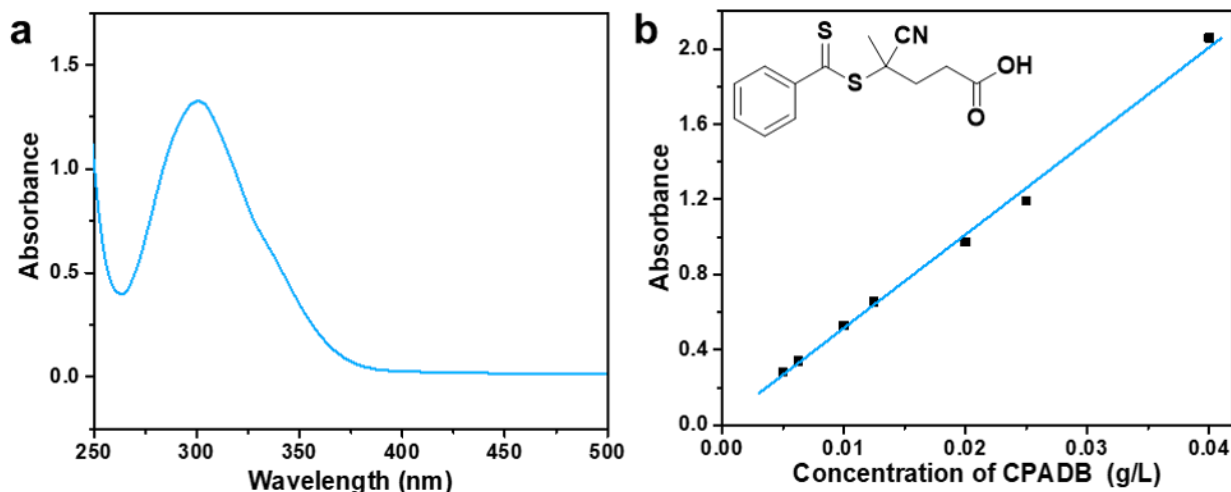
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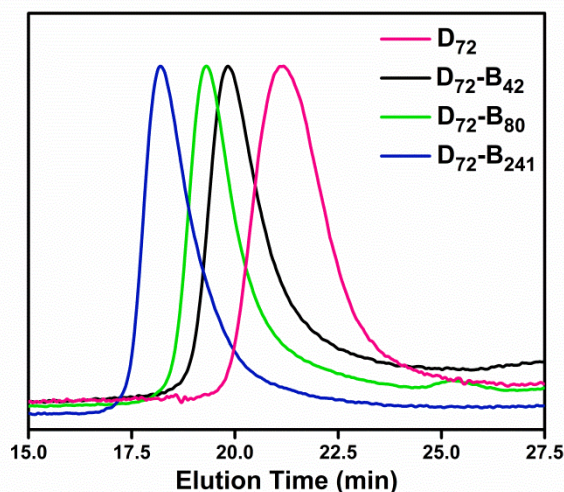
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**Fig. S1.** a) Ultraviolet–visible spectrum of PDMA<sub>72</sub> solution (solvent: THF; concentration: 1.0 mg mL<sup>-1</sup>). b) Absorbance of gradient solutions of CPADB in THF at 301 nm.



**Fig. S2.** SEC trace of PDMA<sub>72</sub> and D<sub>72</sub>-B<sub>x</sub> (x = 42, 80, 241) copolymers.

**Table S1.** Molecular and size characteristics of diblock copolymers D<sub>72</sub>-B<sub>x</sub>.

Entry	Molar feed ratio (BzMA/PDMA)	DP <sub>BzMA</sub> <sup>a</sup>	Monomer conversion <sup>b</sup>	$M_{n, SEC}$ /kDa <sup>c</sup>	$\bar{D}$ <sup>d</sup>	Diameter /nm <sup>e</sup>	PDI <sup>e</sup>
D <sub>72</sub> -B <sub>42</sub>	50	42	83%	10.8	1.22	23.35	0.130
D <sub>72</sub> -B <sub>80</sub>	100	80	83%	16.2	1.19	29.94	0.037
D <sub>72</sub> -B <sub>241</sub>	250	241	96%	33.6	1.23	56.98	0.056

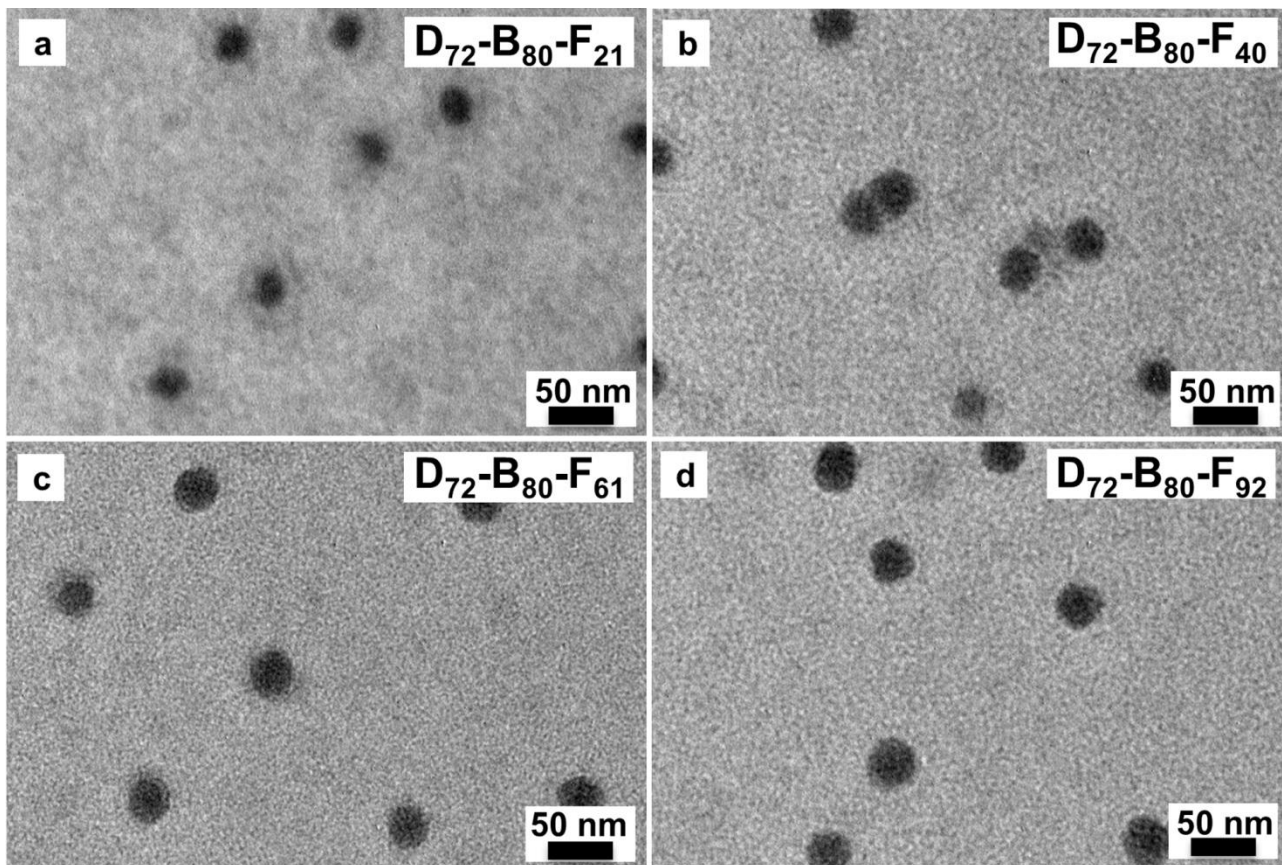
<sup>a</sup> Determined by <sup>1</sup>H NMR spectra;

<sup>b</sup> Calculated by <sup>1</sup>H NMR spectra;

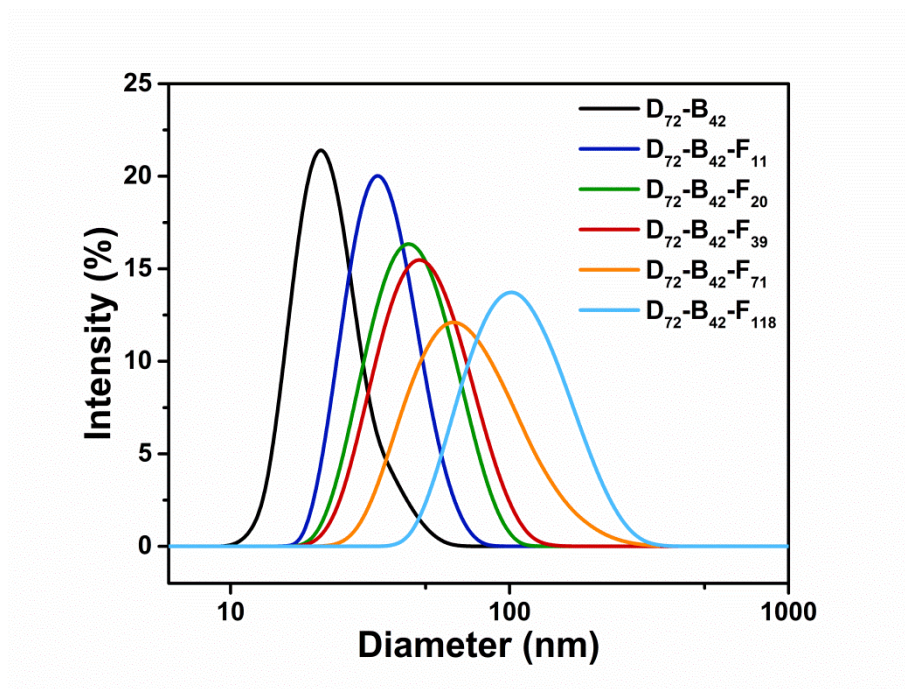
<sup>c</sup> Characterized by SEC;

<sup>d</sup>  $\bar{D} = M_w/M_n$ ;

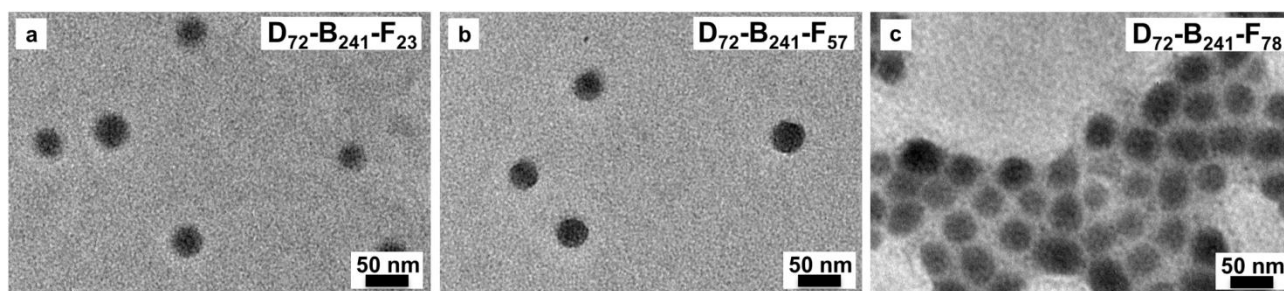
<sup>e</sup> Hydrodynamic diameter measured by DLS.



**Fig. S3.** TEM images of a)  $D_{72}-B_{80}-F_{21}$ , b)  $D_{72}-B_{80}-F_{40}$ , c)  $D_{72}-B_{80}-F_{61}$ , and d)  $D_{72}-B_{80}-F_{92}$  assemblies unstained.



**Fig. S4.** DLS characterization of  $D_{72}-B_{42}$  and  $D_{72}-B_{42}-F_y$  ( $y = 11, 20, 39, 71, 118$ ) assemblies in ethanol.



**Fig. S5.** TEM images of a)  $D_{72}\text{-}B_{241}\text{-}F_{23}$ , b)  $D_{72}\text{-}B_{241}\text{-}F_{57}$  and c)  $D_{72}\text{-}B_{241}\text{-}F_{78}$  assemblies unstained.