## **Supporting Information**

## Schizophrenic poly(*ɛ*-caprolactone)s: synthesis, self-assembly and

## fluorescent decoration

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**Fig. S1** <sup>1</sup>H NMR spectra of (a) 4-*N*-benzyl formate-piperidone and (b) 4-*N*-benzyl formate-piperilactone (NPIL) in CDCl<sub>3</sub>.



Fig. S2 <sup>13</sup>C NMR spectrum of monomer NPIL.



Fig. S3 Conversion vs time for the ring-opening polymerization of the cyclic lactone NPIL.



Fig. S4 SEC traces of macro-initiator PBCL<sub>25</sub> and copolymer PBCL<sub>25</sub>-*b*-PNPIL<sub>50</sub>.



**Fig. S5** DSC curves of homopolymer PBCL<sub>25</sub>, PNPIL<sub>50</sub> and block copolymer PBCL<sub>25</sub>-*b*-PNPIL<sub>50</sub>.



Fig. S6 The hydrodynamic diameter of  $PCCL_{25}$ -*b*-PPIL<sub>50</sub> at different pHs. Sample concentration was 0.5 mg/mL.



**Fig. S7** The hydrodynamic diameter and zeta potential of  $PCCL_{25}$ -*b*-PPIL<sub>50</sub> copolymer (0.5 mg/mL) in NaCl aqueous solution with different salt concentrations. (A) at pH 5, (B) at pH 8, respectively.



**Fig. S8** (A) UV-vis absorption spectra of 1-(hydroxymethyl)pyrene in precipitated solution as a function of precipitation times and (B) the absorbance at 345 nm of pyrene derivatives in each precipitation time. The inset in (A) shows UV-vis absorption spectrum of free 1-(hydroxymethyl)pyrene in diethyl ether at 0.001mg/mL.



**Fig. S9** <sup>1</sup>H NMR spectra of (a) 1-(hydroxymethyl)pyrene, (b)  $PCCL_{25}$ -*b*-PPIL<sub>50</sub> and (c)  $PCCL_{25}$ -*b*-PPIL<sub>50</sub>-*g*-Py in DMSO-d6. The inset in (d) shows photograph of the partial sample for pyrene-labeled copolymer under UV irradiation (365 nm).



**Fig. S10** UV-vis absorption spectra of pyrene-labeled copolymer aqueous solution (0.1 mg/mL) (A) UV irradiation (365 nm) for different time and (B) at different pHs.



**Fig. S11** (A) UV-vis absorption spectra of FITC in ethanol as a function of washing times and (B) the absorbance at 278 nm of FITC in each washing time.



**Fig. S12** <sup>1</sup>H NMR spectra of (a) FITC, (b)  $PCCL_{25}$ -*b*-PPIL<sub>50</sub> and (c)  $PCCL_{25}$ -*b*-PPIL<sub>50</sub>-*g*-FITC in DMSO-d6.