

## *ESI*

# Amphiphilic hyperbranched copolymers bearing hyperbranched core and dendritic shell: syntheses, characterization and guest encapsulation performances

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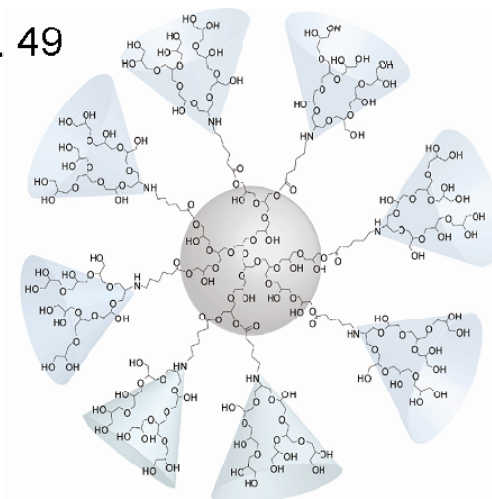
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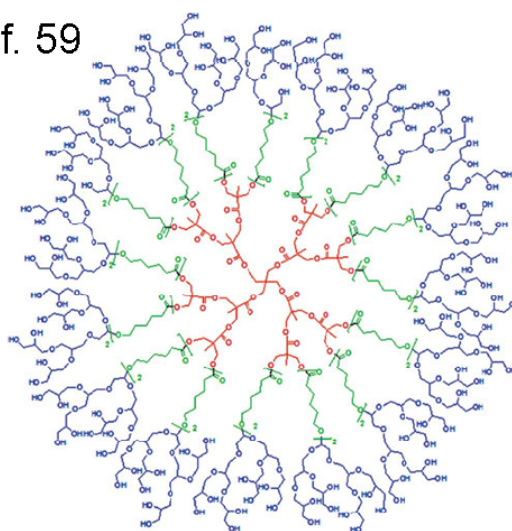
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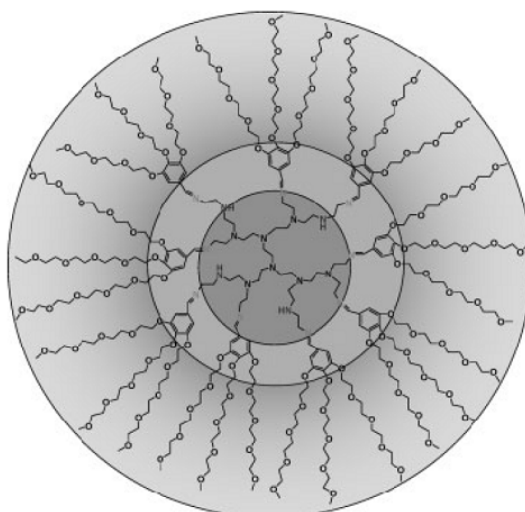
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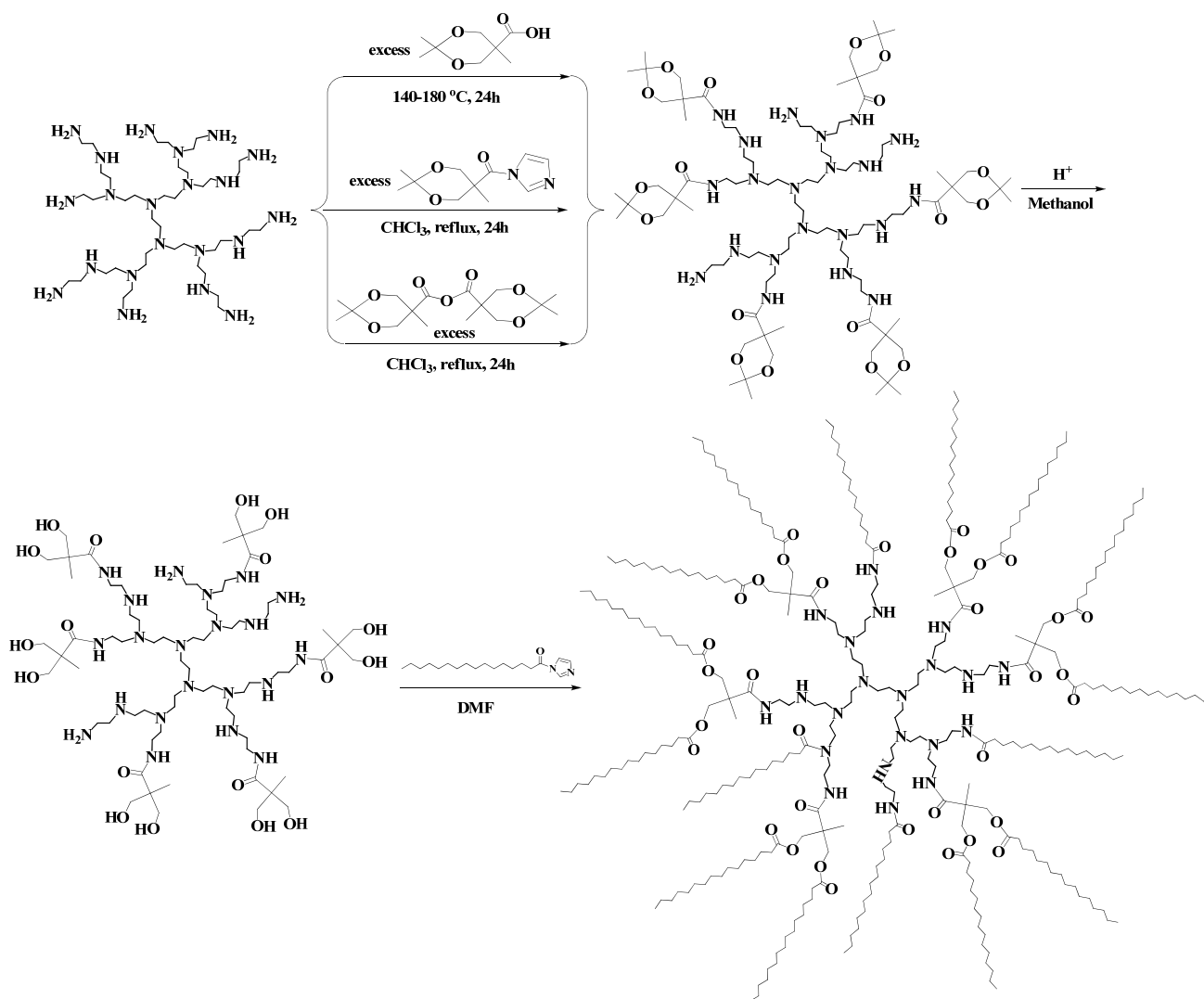
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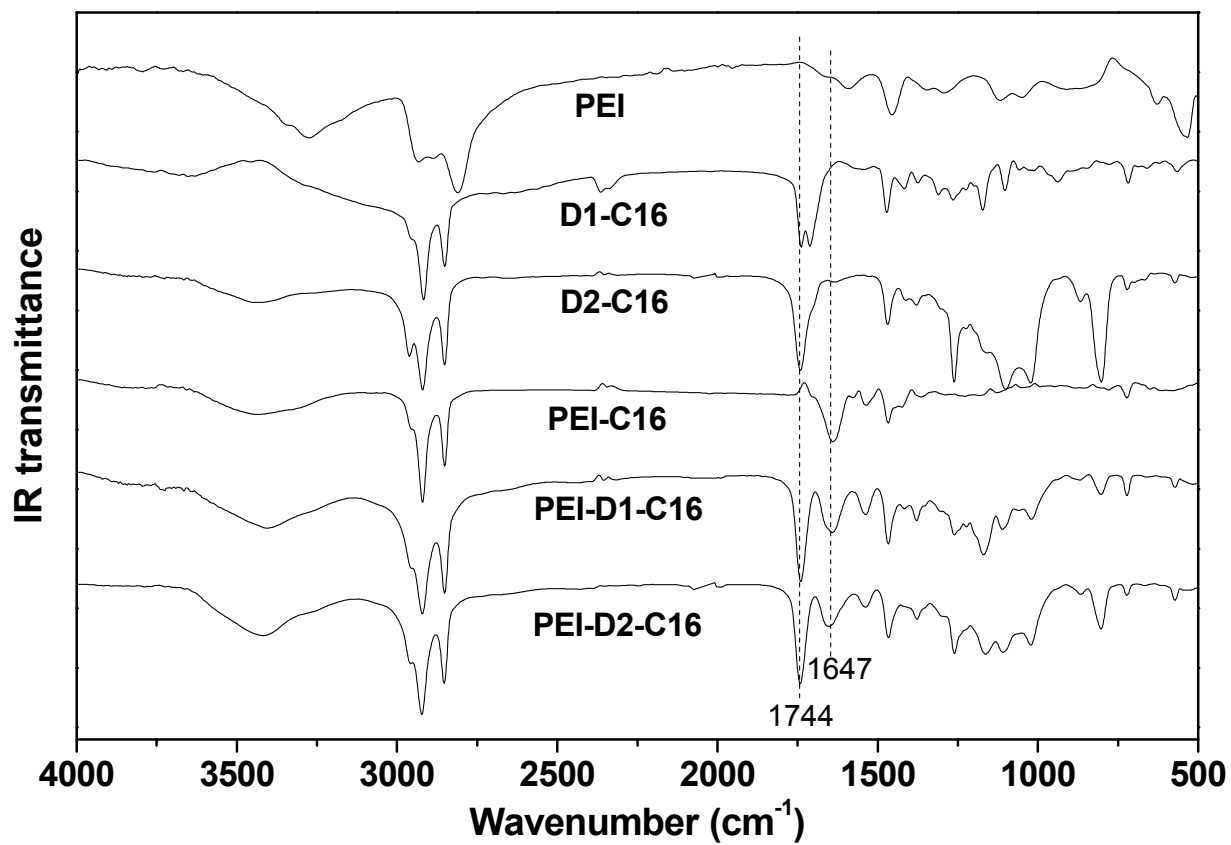
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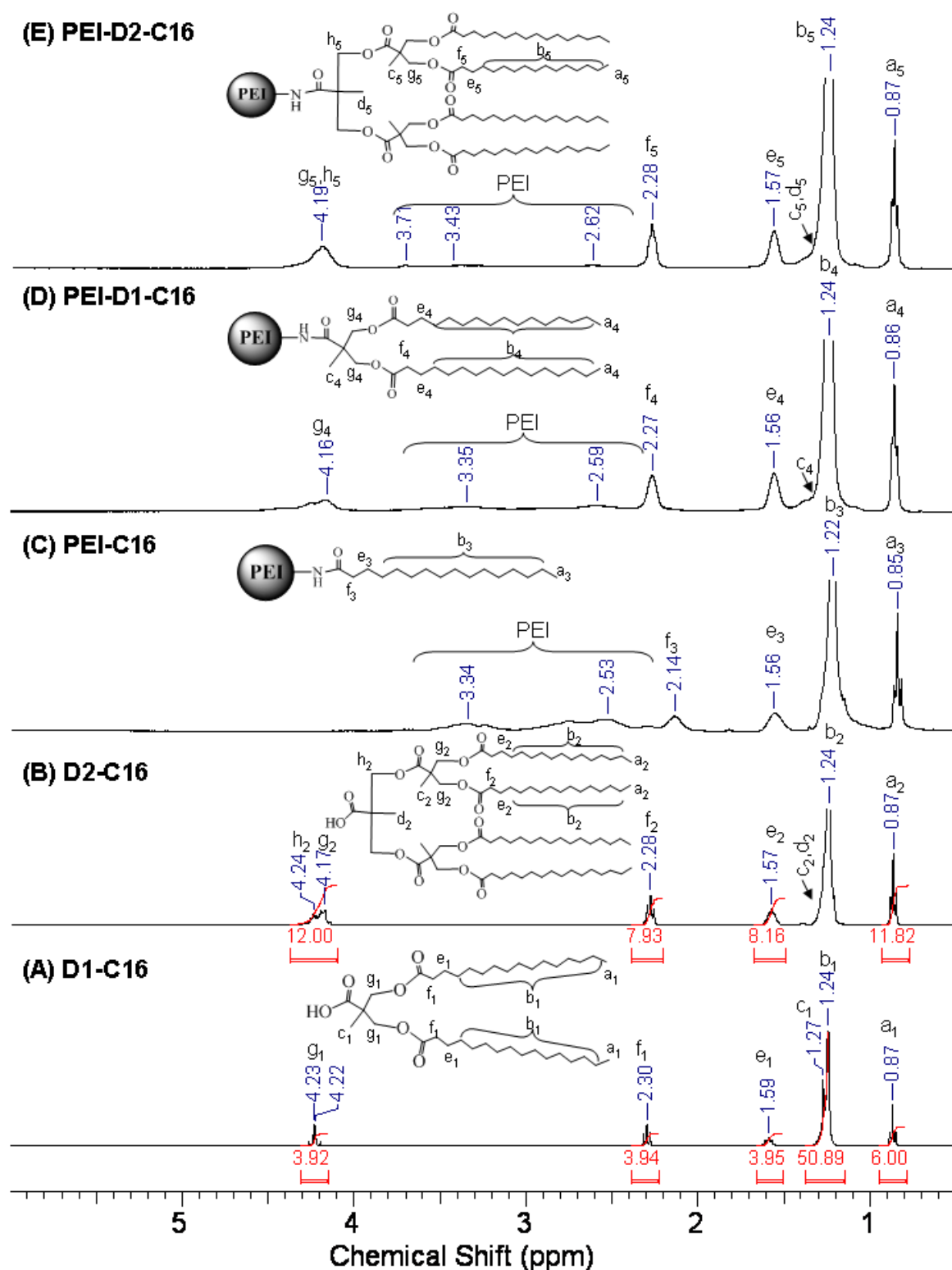
**Fig. S1** Illustration of the typical nanocarriers with branched core and shell



**Scheme S1.** Attempt to the synthesis of amphoteric copolymer bearing PEI core and branched shell



**Fig. S2** FTIR spectra of the amphiphilic copolymers and their precursors



**Fig. S3** Typical  $^1\text{H}$  NMR spectra of (A) D1-C16, (B) D2-C16, (C) PEI-C16 (PL-2), (D) PEI-D1-C16 (PD1-3) and (E) PEI-D2-C16 (PD2-1)

**Table S1.** The derived structural parameters of the obtained amphiphilic hyperbranched polymers according to the elemental analysis results

Polymer	Elemental analysis (%)				$DA$	$DS_{(C16)}$	$M_n / 10^4$
	C	H	N	O			
PD2-1	62.52	12.75	3.1	21.63	0.27	1.08	9.2
PD1-1	58.08	12.71	5.54	23.67	0.28	0.56	4.9
PD1-2	68.22	13.54	4.84	13.4	0.39	0.78	6.4
PD1-3	68.42	13.2	4.23	14.15	0.46	0.92	7.3
PL-1	66.8	14.04	11.18	7.98	0.31	0.31	2.7
PL-2	70.01	13.78	8.55	7.66	0.47	0.47	3.6
PL-3	74.47	13.08	6.84	5.61	0.67	0.67	4.7

<sup>a</sup>  $DA$  represents degree of amidation relative to the total amino groups of PEI; <sup>b</sup>  $DS_{C16}$  represents degree of substitution of C16 chain relative to the total amino groups of PEI.

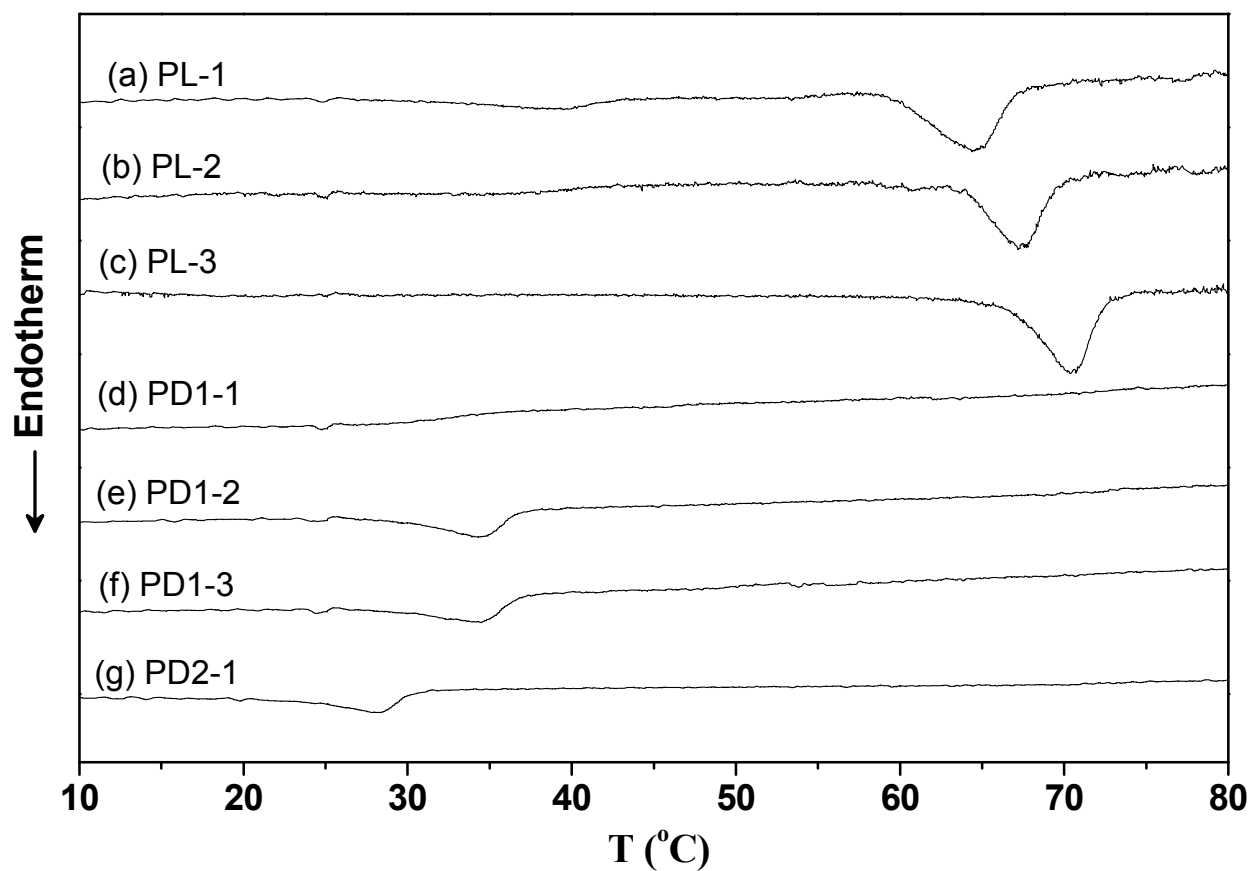


Fig. S4 DSC diagrams of the obtained amphiphilic hyperbranched copolymers in the second-heating run

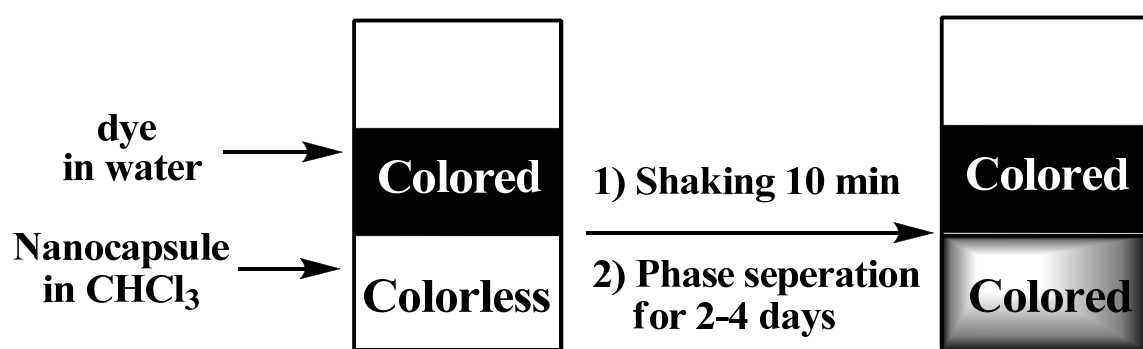
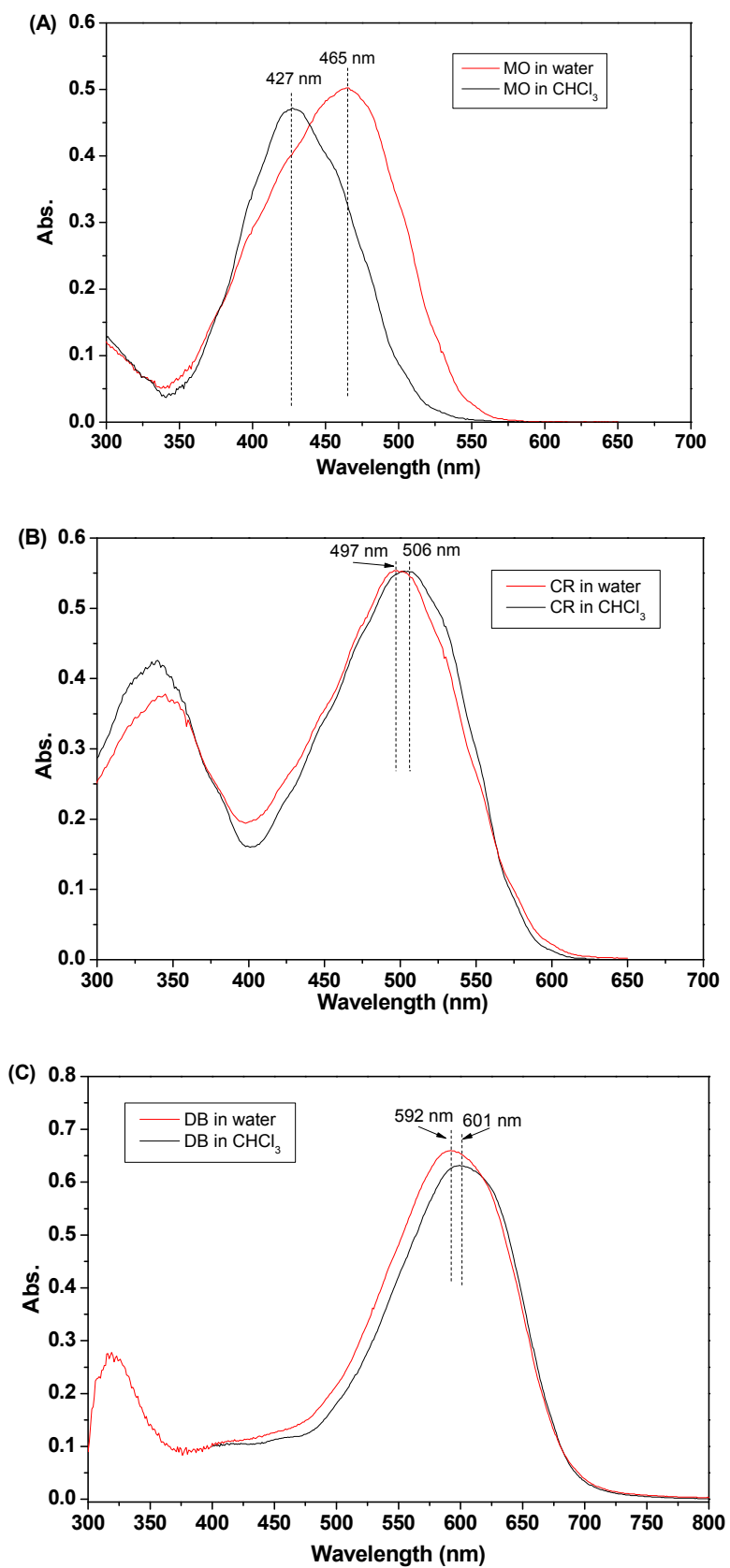


Fig. S5 Illustration of liquid-liquid encapsulation protocol



**Fig. S6** The UV-vis spectra of MO, CR and DB in water and complexes of MO, CR and DB with polymers in chloroform



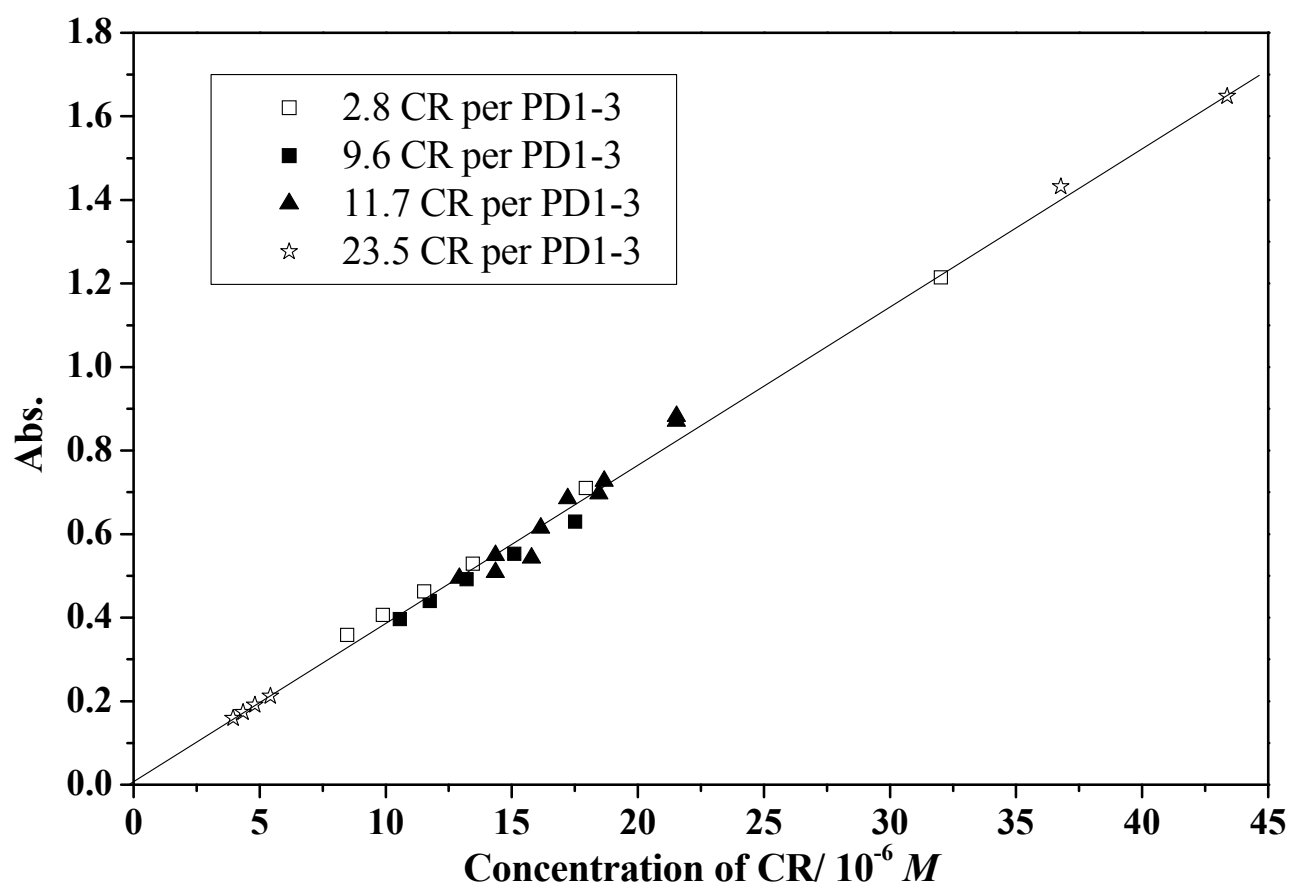
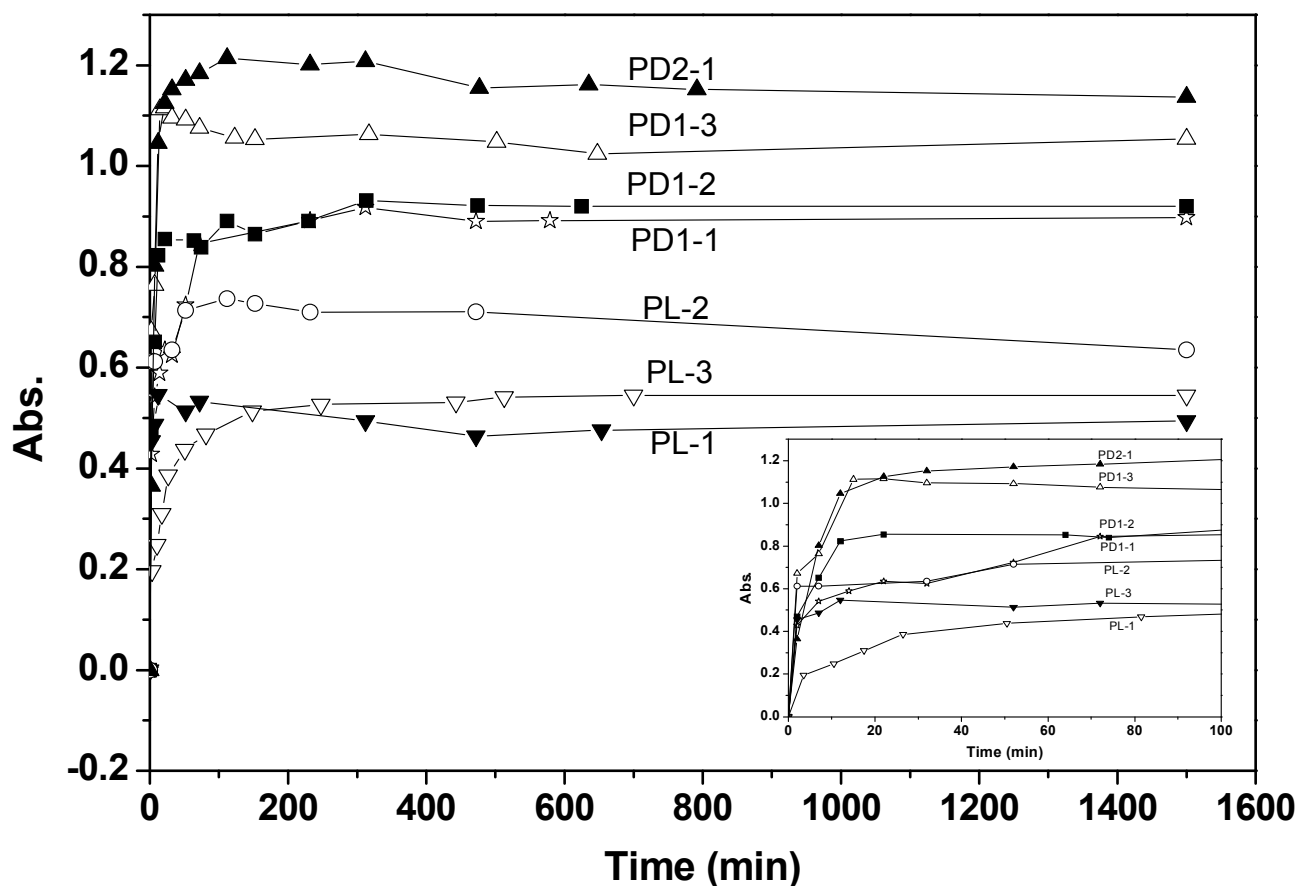
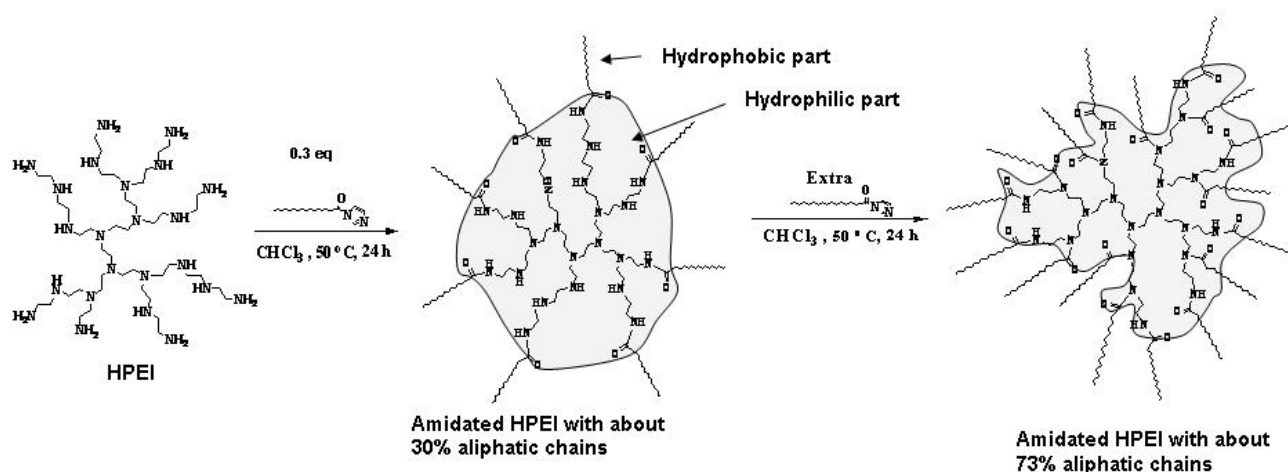


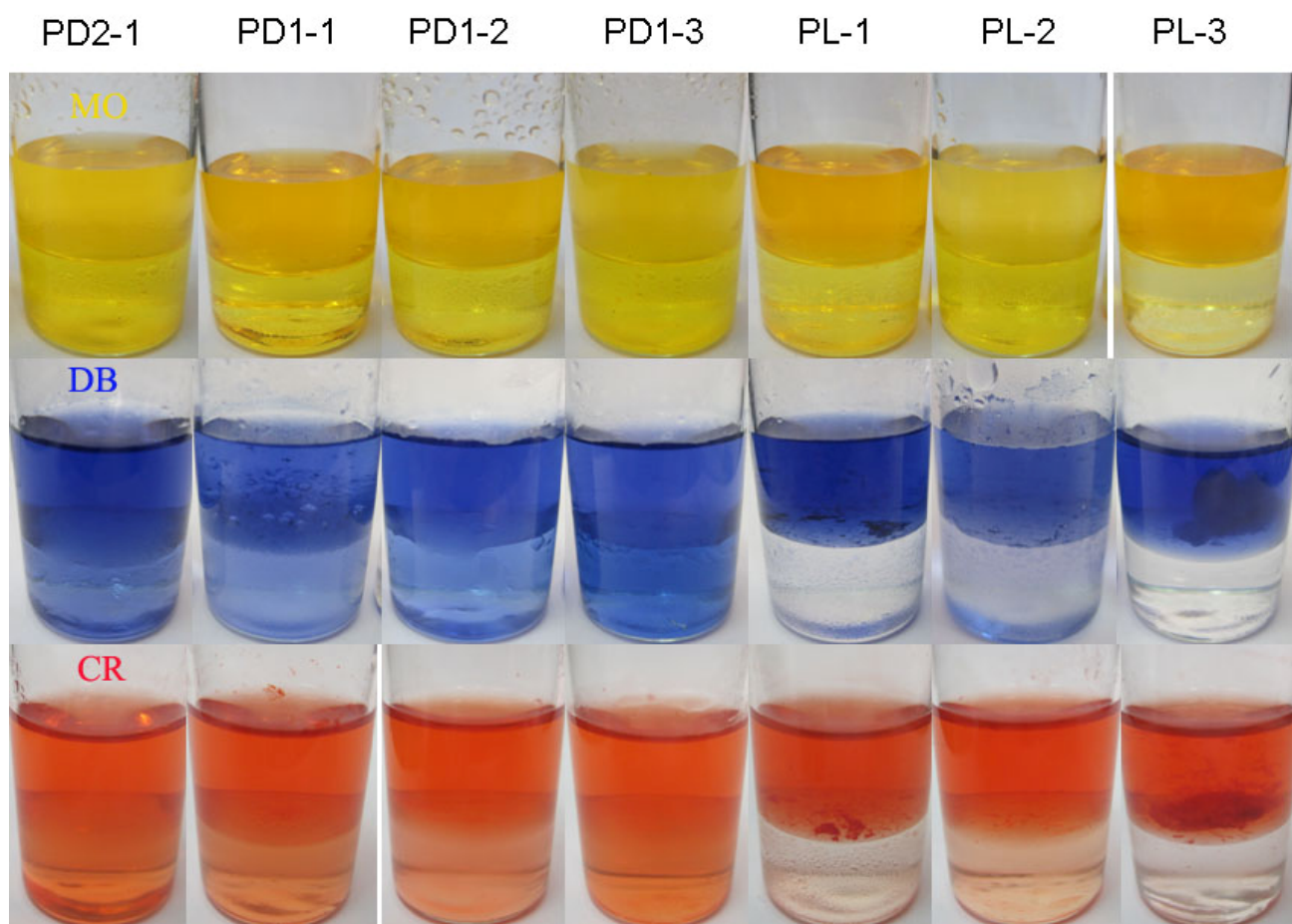
Fig. S7 The typical plots of the intensity of maximal UV-vis absorbance of CR encapsulated by PD1-3 in chloroform versus the concentration of CR



**Fig. S8** The typical plots of the variation of maximal UV-vis absorbance of CR encapsulated by different nanocarrier in chloroform versus the time (polymer concentration is around  $5 \times 10^{-7} \text{M}$ , initial concentration of CR in water is 0.3 mg/mL)



**Fig. S9** Illustration of the decrease of amidated PEI core with the increase of degree of amidation



**Fig. S10** Images of liquid-liquid encapsulation of different polymers for MO, DB and CR (Upper phase: water; lower phase: chloroform; polymer concentration is around  $5 \times 10^{-7} \text{M}$ ; initial concentration of MO, DB and CR is 0.0195, 0.07 and 0.03 mg/mL, respectively)

**Table S2.** Comparison of the encapsulation capacity of the novel nanocarriers in this paper with other similar systems bearing the PEI core and hydrophilic shell

Nanocarrier		MO		CR		Reference
Core	shell	Molar ratio	Weight ratio(%)	Molar ratio	Weight ratio(%)	
PEI10K	D2	55	20	26	20	This paper
PEI10K	D1	51	27	21	22	This paper
PEI4.5K	-CO(CH <sub>2</sub> ) <sub>2</sub> (CF <sub>2</sub> ) <sub>7</sub> CF <sub>3</sub>	—	—	0.5-1.0	—	Ref. 18
PEI4.5K	-CO(CH <sub>2</sub> ) <sub>10</sub> S(CH <sub>2</sub> ) <sub>2</sub> (CF <sub>2</sub> ) <sub>7</sub> CF <sub>3</sub>	—	—	0.1-3.0	—	Ref. 18
PEI25K	=CHC <sub>15</sub> H <sub>31</sub>	—	—	0.6	—	Ref. 21
PEI25K	=C(C <sub>3</sub> H <sub>11</sub> ) <sub>2</sub>	—	—	0.2	—	Ref. 21
PEI1.8K	PCL	4.3-4.9	1.5-3.9	—	—	Ref. 56
PEI10K	PCL	25.2-31.6	1.7-4.0	—	—	Ref. 56
PEI10K-N <sup>+</sup>	PCL	47	7.3	—	—	Ref. 56
PEI10K-N <sup>+</sup>	PCL-C5	71.9	10.7	—	—	Ref. 56
PEI10K-N <sup>+</sup>	-COC <sub>15</sub> H <sub>31</sub>	56.6	—	49.3	—	Ref. 24
PEI25K-N <sup>+</sup>	-COC <sub>15</sub> H <sub>31</sub>	153	—	90.1	—	Ref. 24
PEI10K-N <sup>+</sup> -PO	-OC <sub>12</sub> H <sub>25</sub>	143	—	—	—	Ref. 23
PEI10K-PO	-OC <sub>12</sub> H <sub>25</sub>	70.8	—	—	—	Ref. 23
PEI10K-COOH	-OC <sub>12</sub> H <sub>25</sub>	34.0	—	—	—	Ref. 23