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Supporting Information

Co-assembly of two types of complementary dendritic units into amphiphilic supramolecular complexes capable of hosting guest molecules

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Table S1 Mole extinction coefficients (ε) at λ_{max} of three dyes in water and chloroform

	Aqueous phase		Chloroform phase	
	ε（L/mol/cm）	λ_{max} (nm)	ε（L/mol/cm）	λ_{max} (nm)
MO	2.28×10^4	465	2.56×10^4	420
EY	3.97×10^4	512	4.10×10^4	536
FS	5.33×10^4	487	5.57×10^4	502

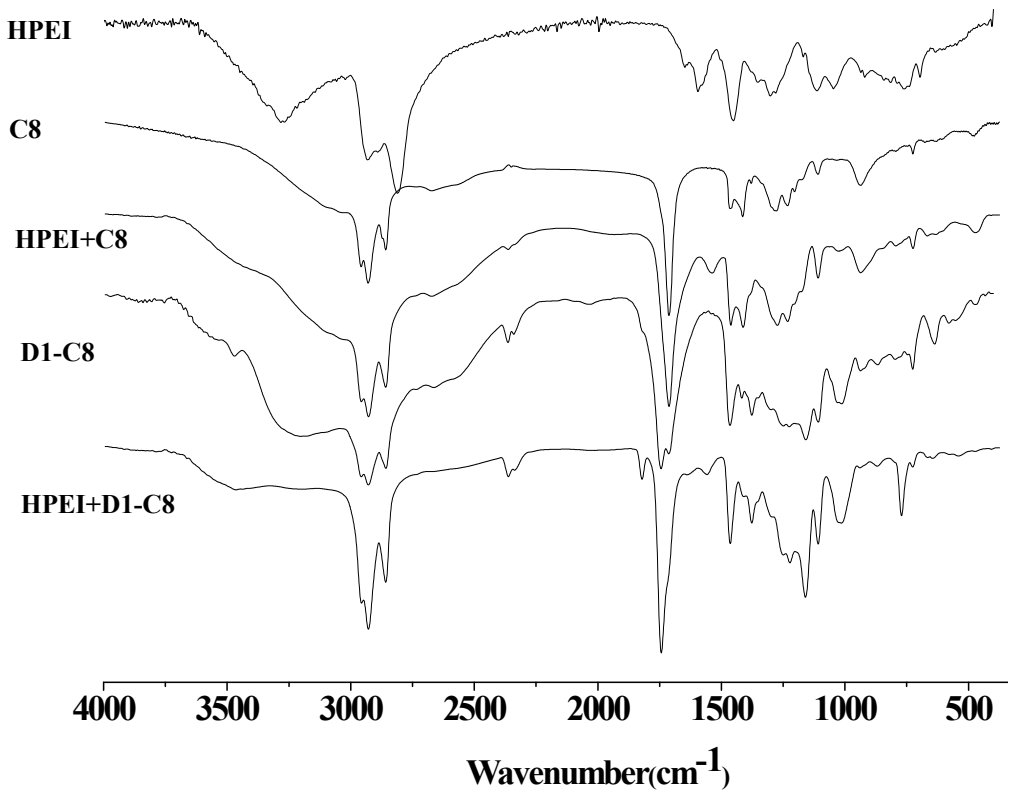


Fig. S1 Transmission FT-IR spectra of HPEI, octoic acid (C8), HPEI+C8-0.54 complex, D1-C8, HPEI+D1-C8-0.54 complex, the 0.54 is the ratio of [COOH]/[N].

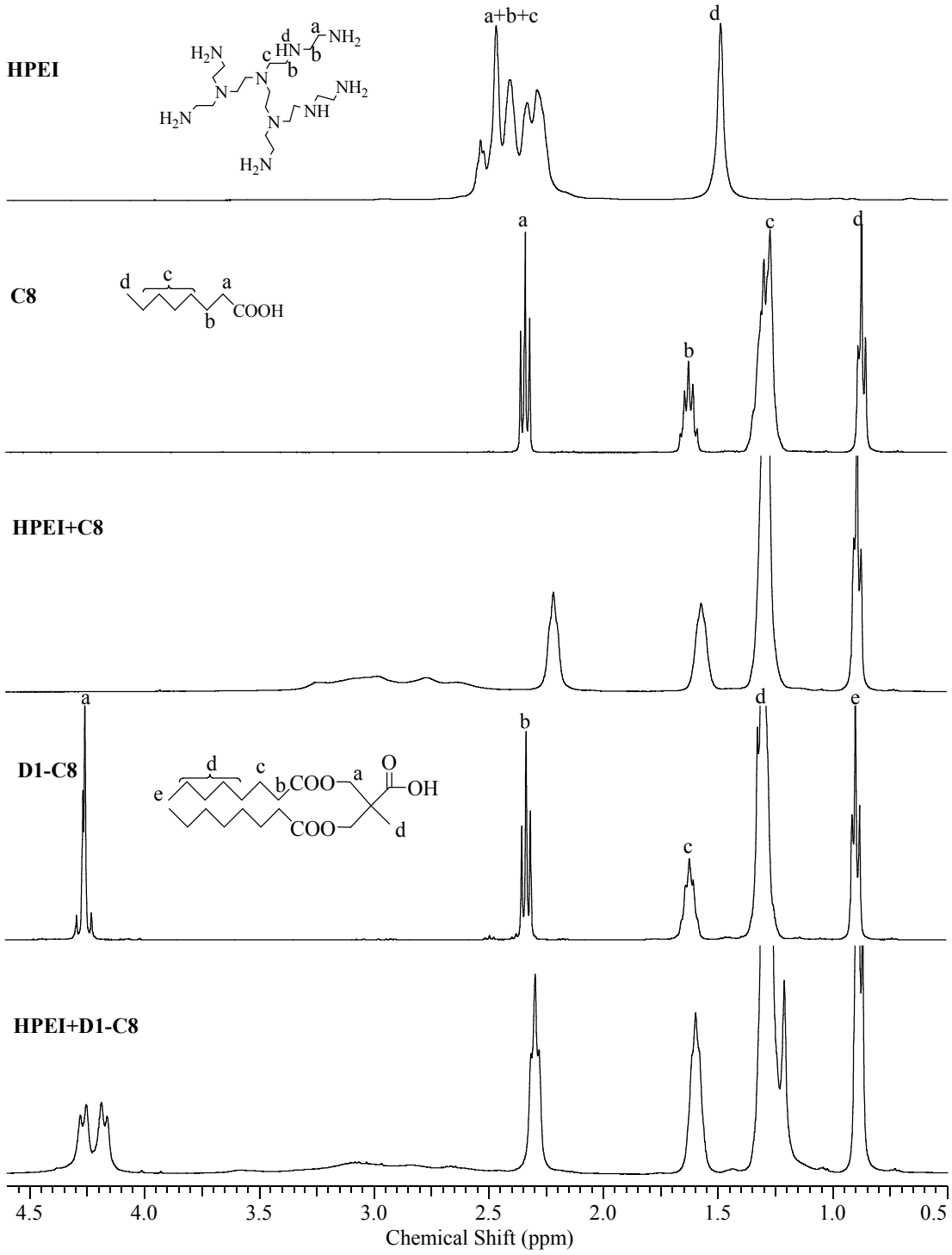


Fig. S2 ^{1}H NMR spectra of HPEI, octoic acid (C8), HPEI+C8-0.54 complex, D1-C8, HPEI+D1-C8-0.54 complex, the 0.54 is the ratio of [COOH]/[N].

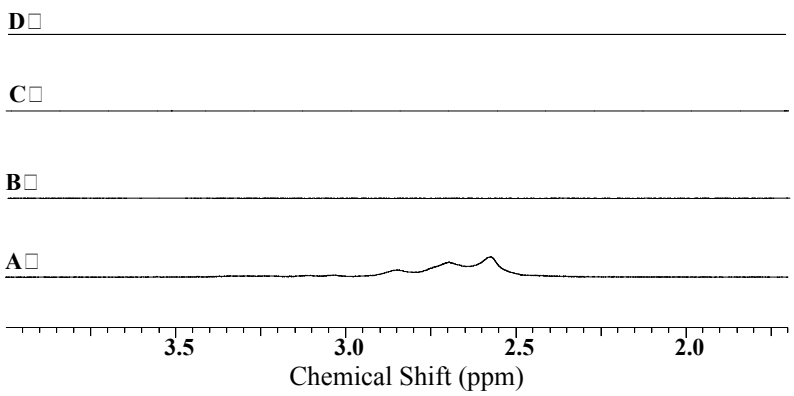
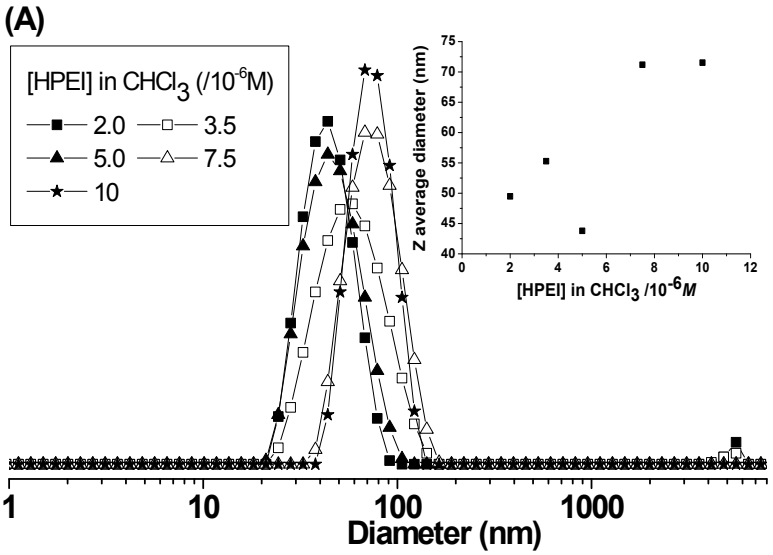
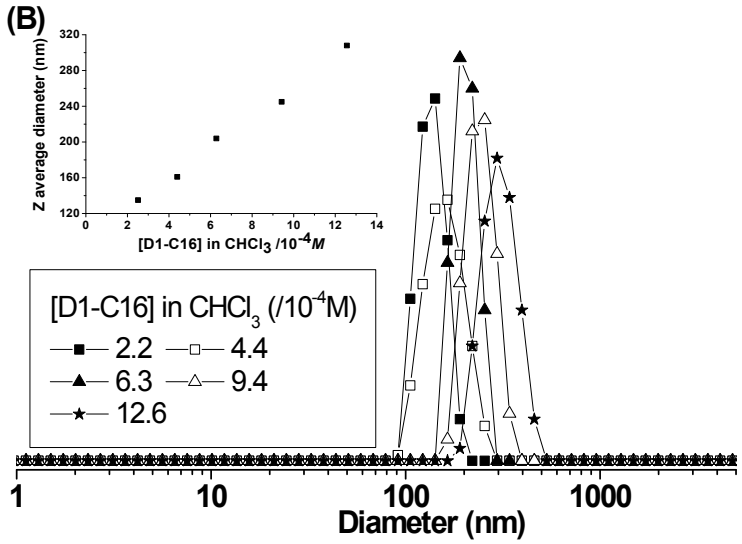
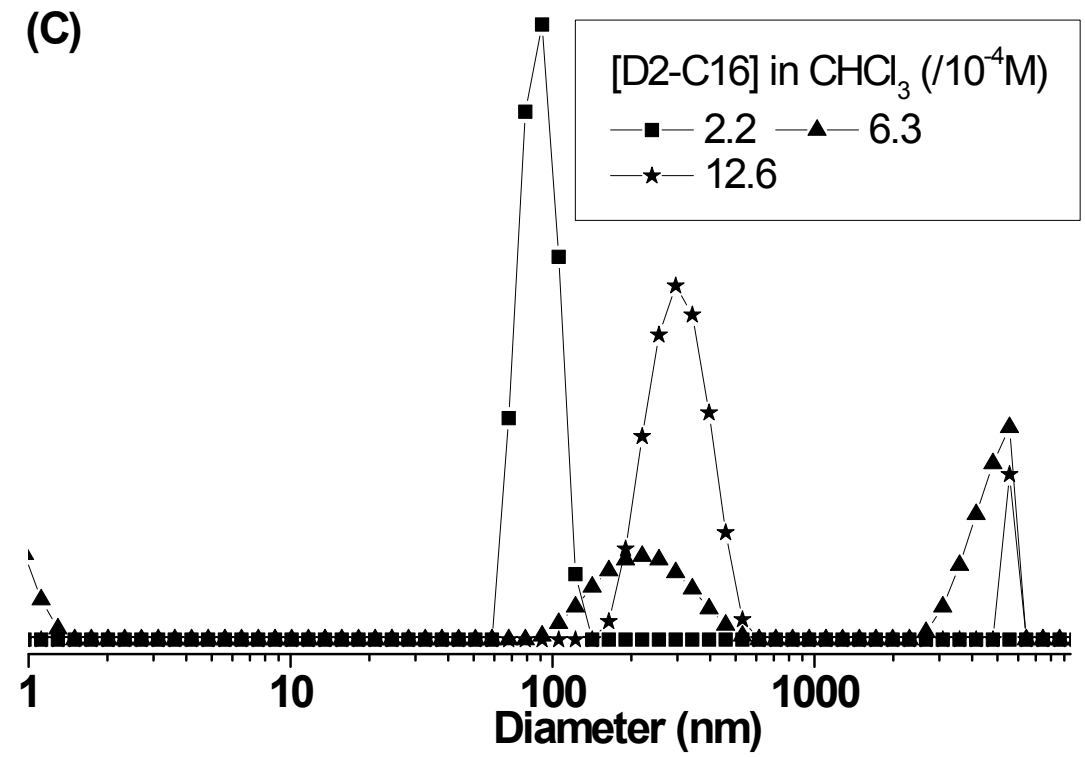
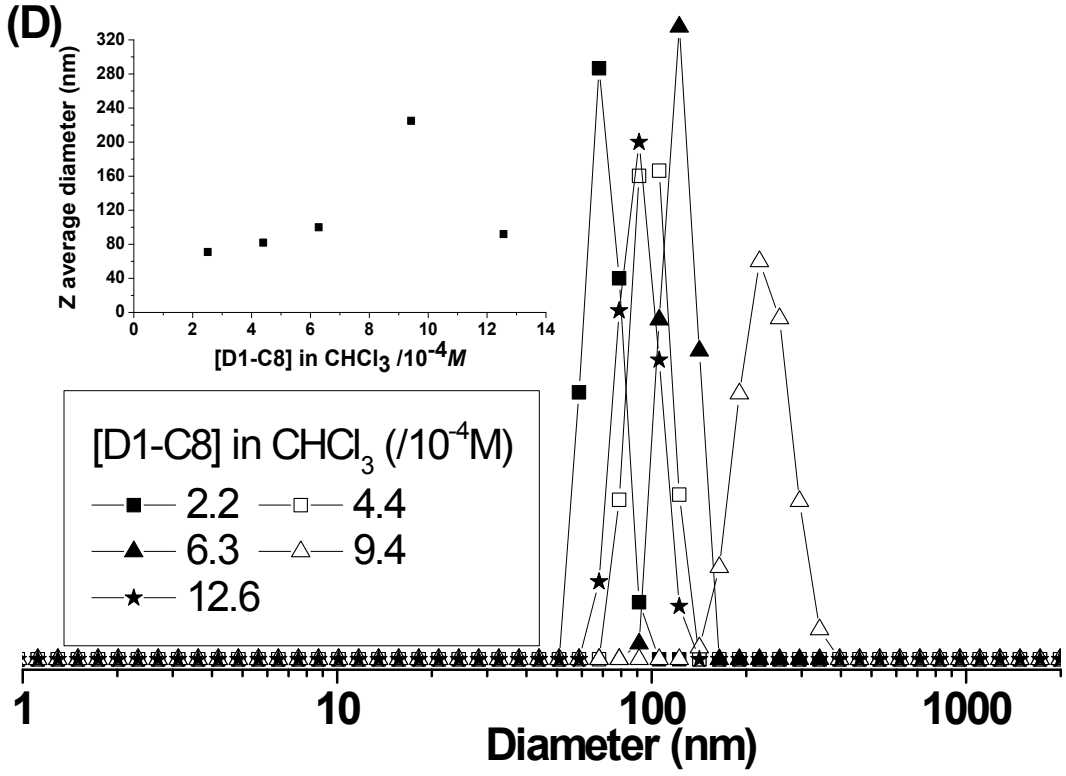


Fig. S3 The H^1 NMR in water phase after extracted with the chloroform solutions of (A)HPEI, (B)HPEI+C16, (C)HPEI+D1-C16, (D)HPEI+D2-C16.






(C)
[D2-C16] in CHCl3 (/10-4M)
2.2
6.3
12.6
1
10
100
1000
Diameter (nm)


(D)
Z average diameter (nm)
[D1-C8] in CHCl3 /10-4M
[D1-C8] in CHCl3 (/10-4M)
2.2
4.4
6.3
9.4
12.6
1
10
100
1000
Diameter (nm)

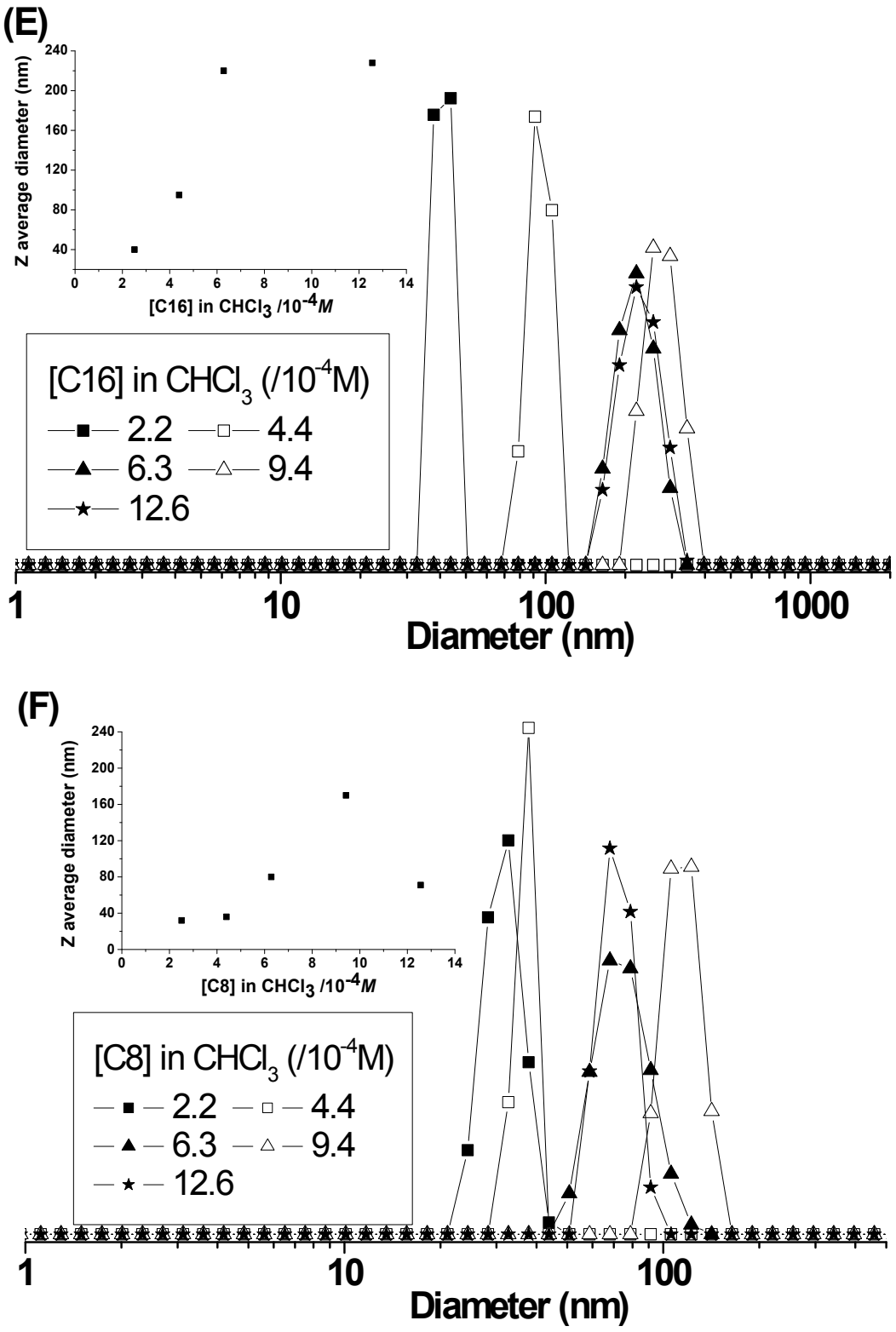


Fig. S4 The typical DLS profiles of different concentration of (A) HPEI, (B) D1-C16, (C) D2-C16, (D) D1-C8, (E) C16 and (F) C8 in chloroform.

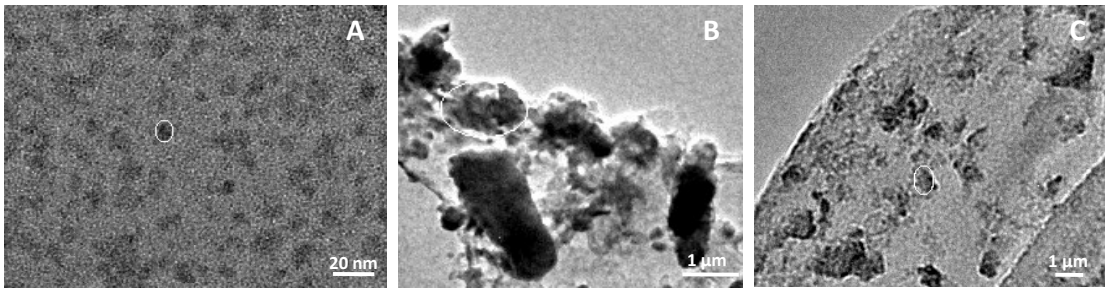
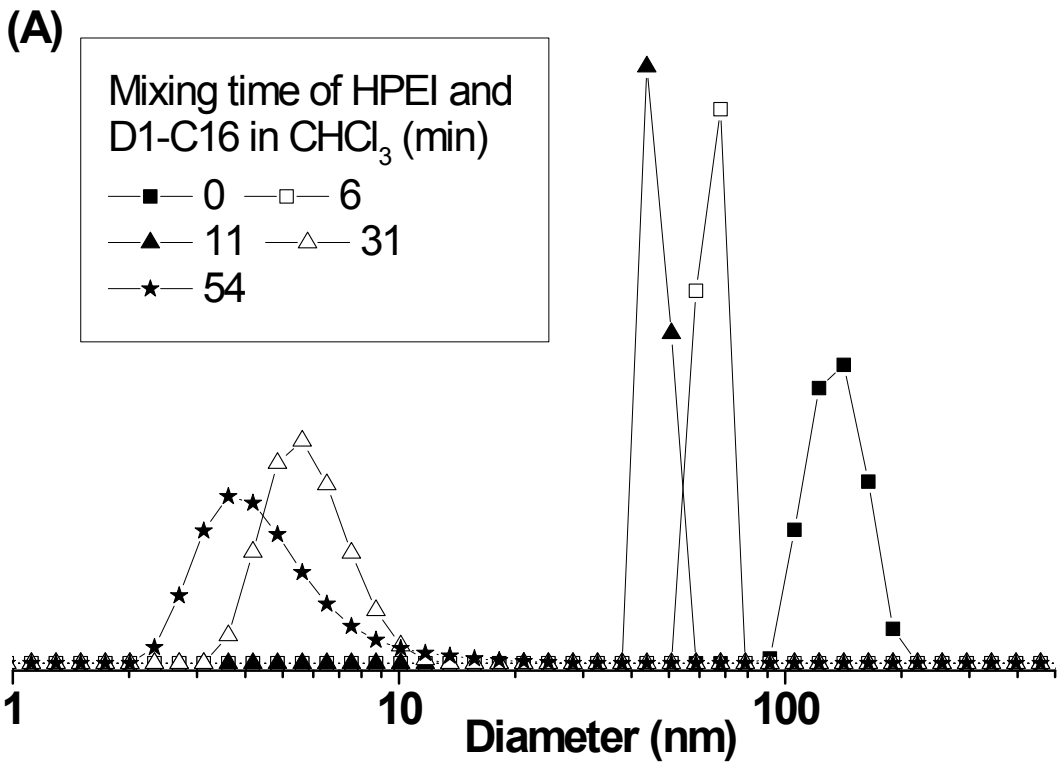


Fig. S5 The morphology of the complex architecture and its aggregates were determined by TEM measurements. A: HPEI+D1-C16 in chloroform; B: HPEI+D1-C16 chloroform solution contacted with water; C: HPEI+D1-C16 chloroform solution contacted with MO aqueous solution. The concentration of D1-C16 is 6.28×10^{-4} mol/L, and the concentration of HPEI is 5×10^{-6} mol/L; the [COOH]/[N] ratio of complex is 0.54.



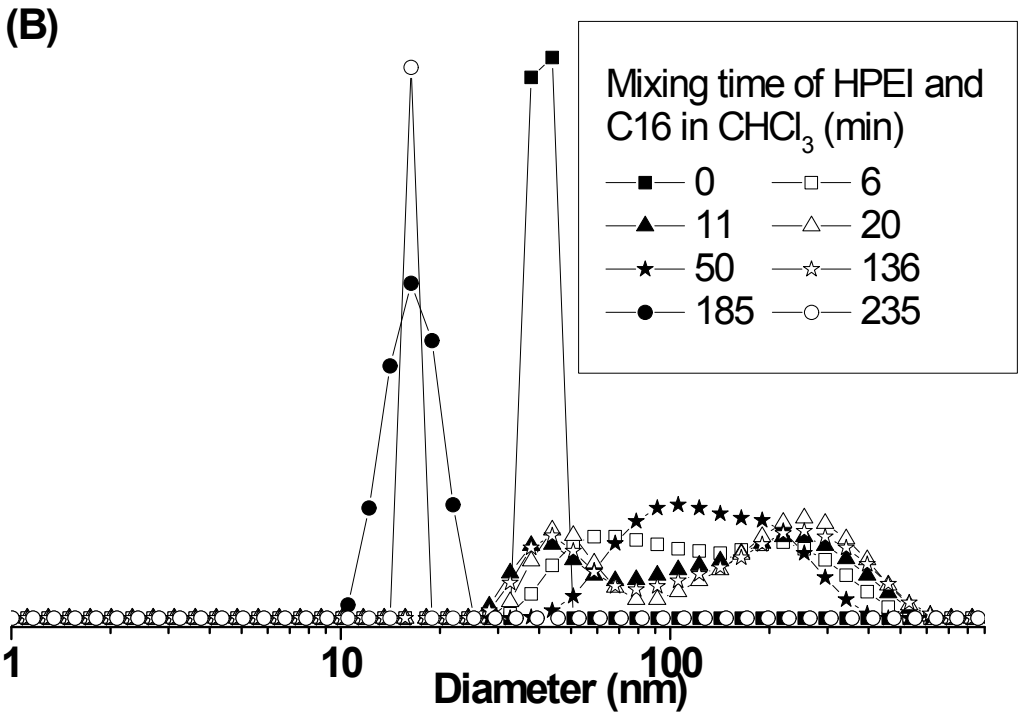


Fig. S6 The typical evolution of DLS profiles of the mixture of HPEI with (A) D1-C16 and (B) C16 in chloroform at different time ([HPEI]=2.0×10^{-6}M, [COOH]/[N]=0.73)

Table S2 The main diameter of supramolecular complexes and their precursors.

Abbreviation	[COOH]/[N][a]	Con. of HPEI (/10^{-6} M)	Before mixing			Complex (nm)[d]	Organic phase after shaking with water (no MO)(nm)[e]	Organic phase (contains MO) after encapsulation (nm)[f]
			HPEI (nm)[b]	Hydrophobic molecules	(nm)[c]			
HPEI+ D2-C16	0.54	2	30.3	D2-C16	85.0	17.6	943	827.8
		5	37.2		234.7	14.2	1311	1569
HPEI+ D1-C16	0.27	10	64.9	D1-C16	141.9	8.5	810	2410
	0.54	2	30.3		134.7	6.2	1930	1055
		5	37.2		141.9	9.8	1834	1837
		10	64.9		220.7	5.4	1792	1183
	0.73	10	64.9		127.4	13.0	1114	2164
HPEI+C16	0.27	10	64.9	C16	226.6	7.4	687	1654
	0.54	2	30.3		483.5	13.8	1827	1023
		5	37.2		226.6	6.8	3570	1089
		10	64.9		188.4	4.6	1231	1519
	0.73	10	64.9		386.1	10.1	1591	3702

[a][COOH]/[N] represents the ratio of carboxylic acid to the total amino groups of HPEI; [b,c]The diameter of monomer in chloroform before mixing respectively. [d]The diameter of complex in chloroform. [e]The diameter of complex in chloroform phase after shaking with water and resting. [f]The diameter of complex in chloroform phase after shaking with MO aqueous solutions and resting. [b,c,d,e,f]The results are all obtained by Nano ZS.

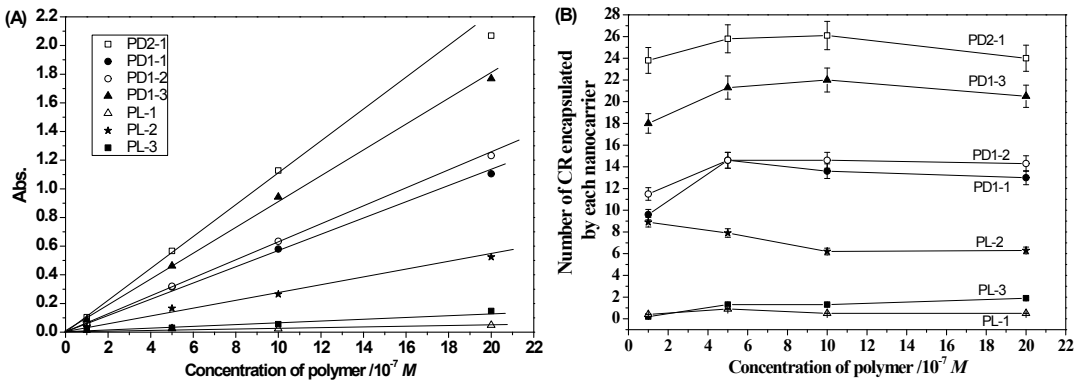


Fig. S7 The effect of polymer concentration on (A) the absorbance intensity of CR at in chloroform, (B) the encapsulation capacity of the nanocarrier (initial concentration

of CR in water is 0.30 mg/mL)

PD2-1, PD1-1, PD1-2, PD1-3, PL-1, PL-2 and PL-3 are corresponding covalent chemical compounds HPEI-D2-C16-0.27, HPEI-D1-C16-0.27, HPEI-D1-C16-0.54, HPEI-D1-C16-0.73, HPEI-C16-0.27, HPEI-C16-0.54 and HPEI-C16-0.73 respectively. When the concentration of polymer is less than 1×10^{-6}mol/L , the number of dyes in organic solutions increased linearly with the enlargement of polymer concentration and the trend lines through original point without exception (Fig. S6A). All the polymers are unimolecule morphology of nanocapsules. In addition, the capacity of dye encapsulation is unaffected by the concentration of polymers (Fig. S6B).

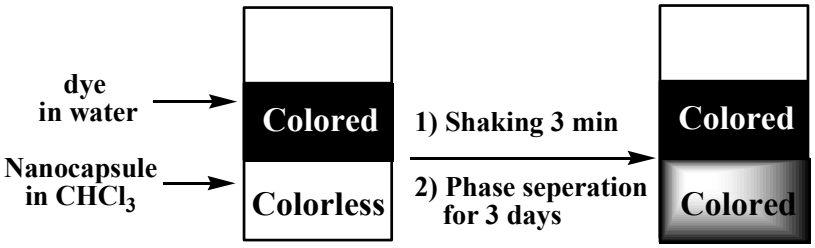
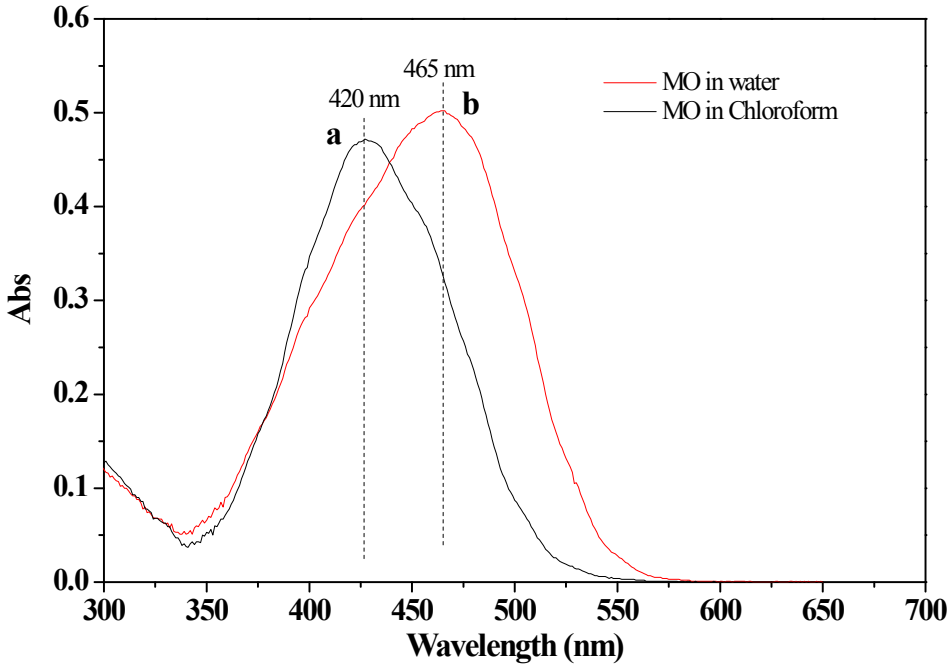
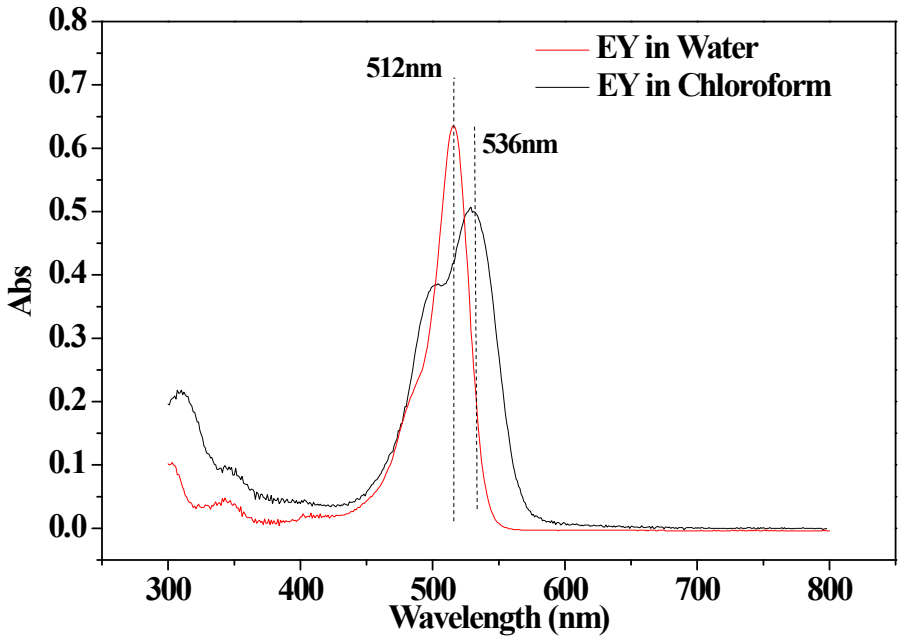


Fig. S8 Illustration of liquid-liquid encapsulation protocol


0.6
0.5
0.4
0.3
0.2
0.1
0.0
Abs
300
350
400
450
500
550
600
650
700
Wavelength (nm)
465 nm
420 nm
a
b
MO in water
MO in Chloroform


0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Abs
300
400
500
600
700
800
Wavelength (nm)
512nm
536nm
EY in Water
EY in Chloroform

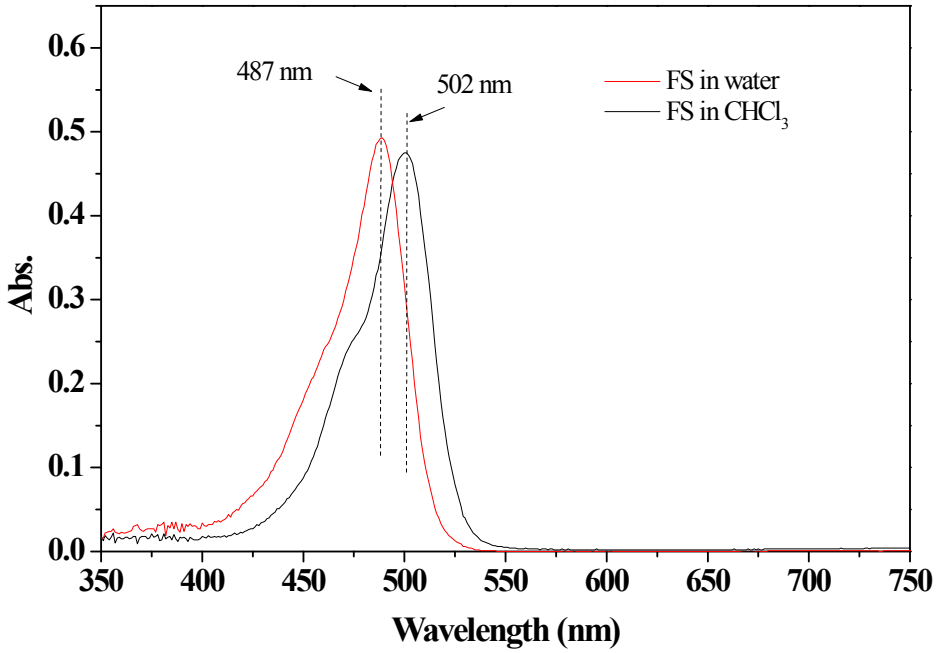
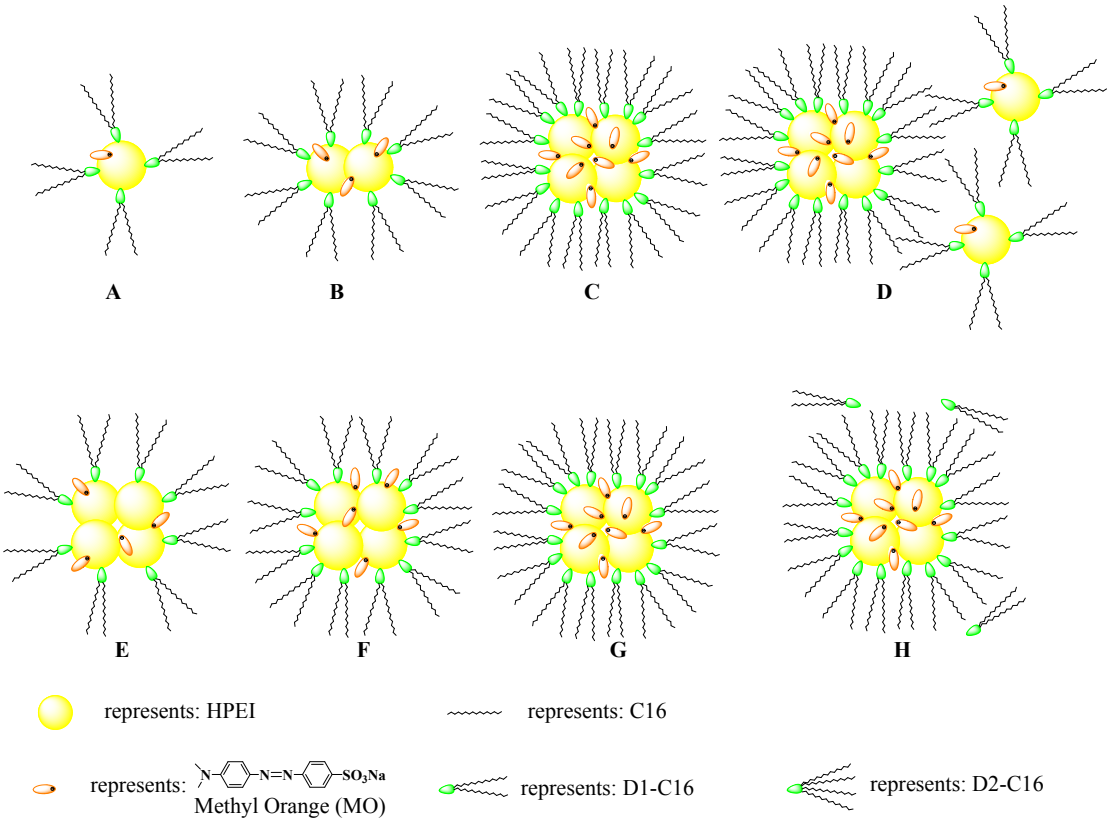
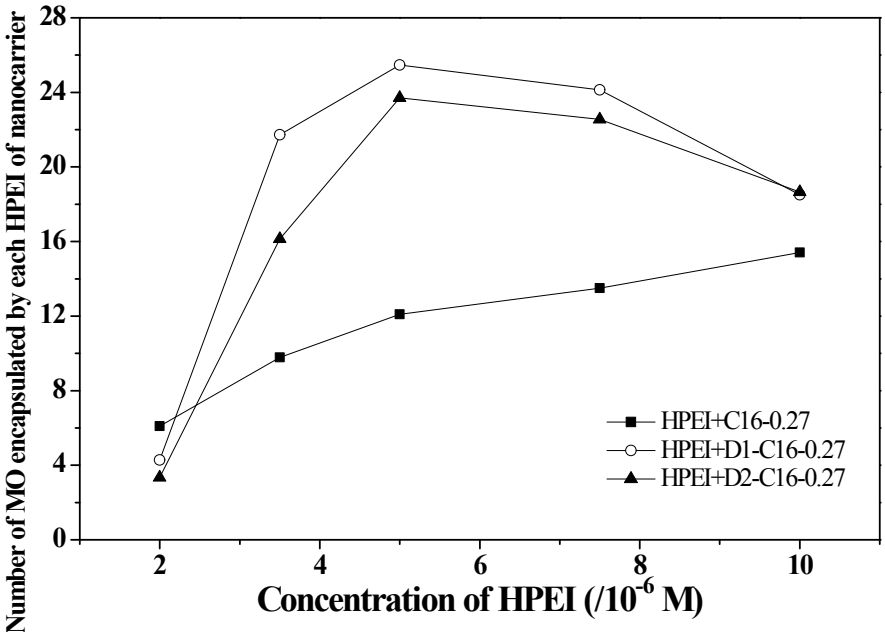


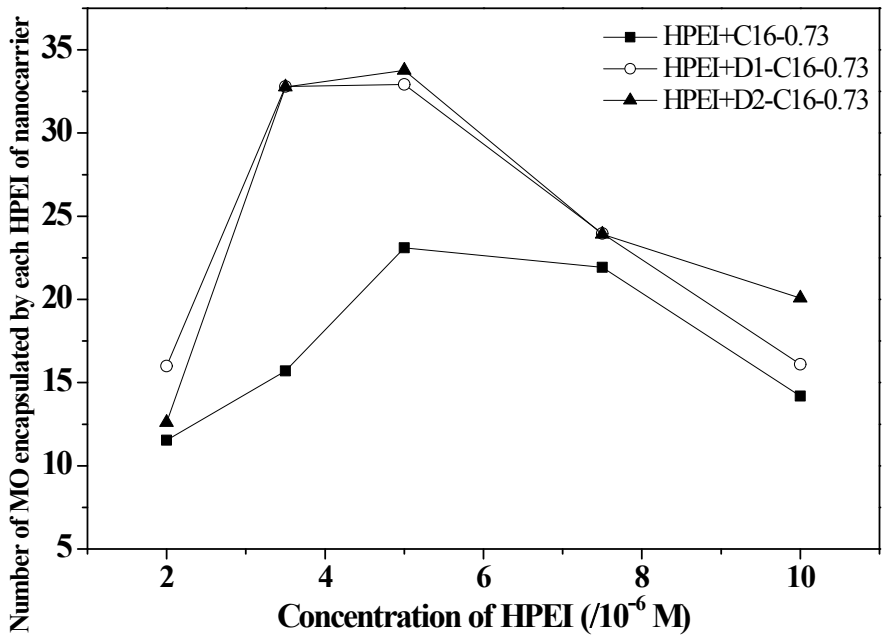
Fig. S9 The UV-vis spectra of MO, EY and FS in water and complexes of MO, EY and FS with complexes in chloroform.



Scheme S1 Exemplifed as D1-C16 and complex HPEI-D1-C16. (A)(B)(C): Under the fixed [COOH]/[N], the growth process of formed aggregate in the chloroform with the increase of the HPEI concentration. (D): When the aggregate grows to a certain degree, its size and ability of

encapsulation are both no further change with the increase of HPEI concentration. From (E) to (G): the complex ratio of [COOH]/[N] increased successively, the contrast of encapsulated ability about the formed aggregates under the same concentration of HPEI. (H): When the ratio of [COOH]/[N] is up to a certain value, the peripheral carbon chain density of the aggregate would be saturated, and the encapsulated ability would hardly change even if more carboxyl acid molecules joined.





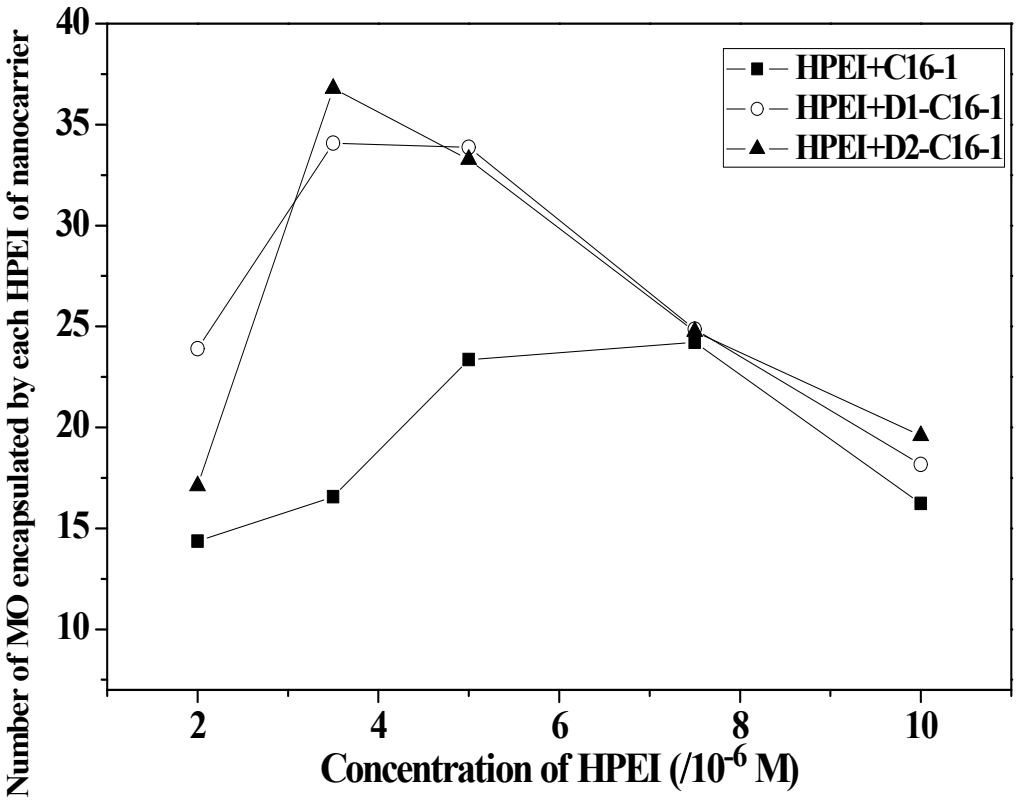


Fig. S10 The effect of HPEI concentration on the encapsulation capacity of the nanocarrier (initial concentration of MO in water is 2.14×10^{-4} mol/L, the ratio of [COOH]/[N] is 0.27, 0.73 and 1.0)

Table S3 The Saturated Concentration of complex in chloroform.

[COOH]/[N]	HPEI+C16 $\times10^{-6}$ M	HPEI+D1-C16 $\times10^{-6}$ M	HPEI+D2-C16 $\times10^{-6}$ M
0.27	10	5	5
0.54	7	5	4.5
0.73	5	3.5	3.5
1	5	3.5	3.5

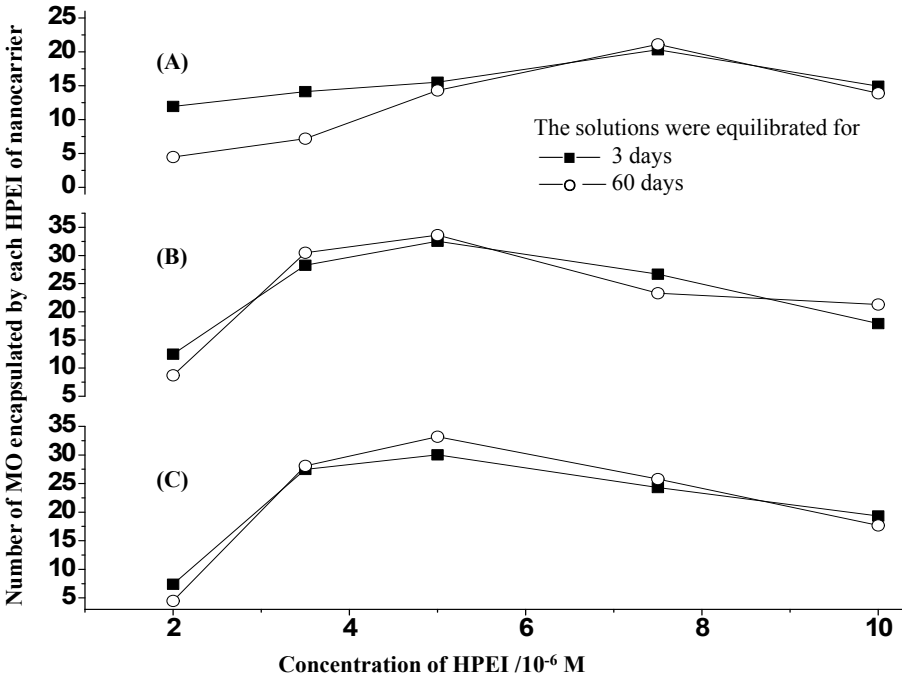


Fig. S11 The effect of HPEI concentration on the encapsulation capacity of the nanocarrier after the solutions equilibrating for 3 days and 60 days. (A): HPEI+C16-0.54; (B): HPEI+D1-C16-0.54; (C): HPEI+D2-C16. (The ratio of [COOH]/[N] is 0.54)

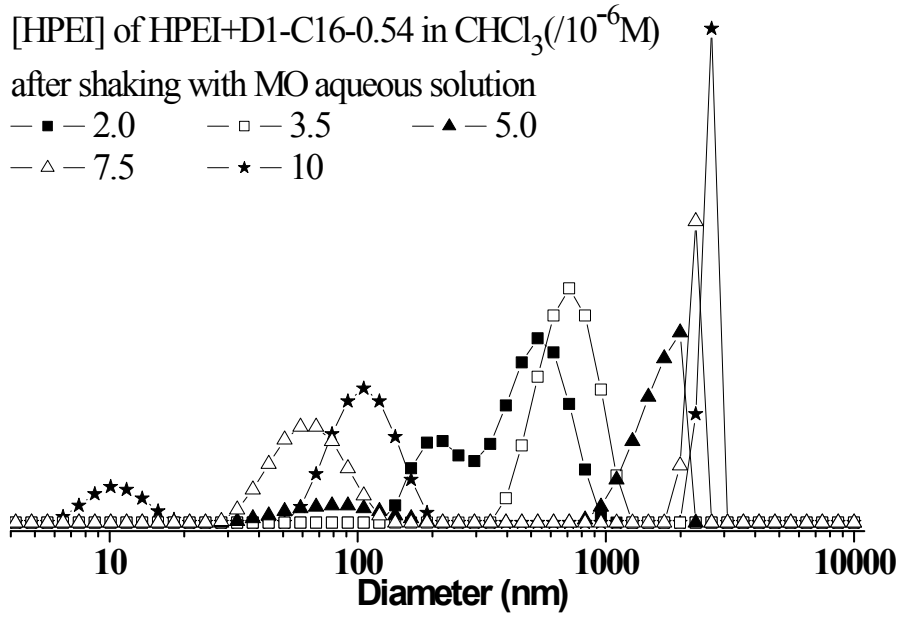


Fig. S12 The effect of HPEI concentration on the distribution of size after the solutions equilibrating for 60 days.

Table S4 The Saturated Ratio of [COOH]/[N] of complex in chloroform.

HPEI Concentration	HPEI+C16	HPEI+D1-C16	HPEI+D2-C16
2.0×10^{-6} M	＞1	＞1	＞1
3.5×10^{-6} M	1	0.73	1
5.0×10^{-6} M	0.73	0.54	0.73
7.5×10^{-6} M	0.54	0.27	0.27
1.0×10^{-5} M	＜0.27	＜0.27	＜0.27

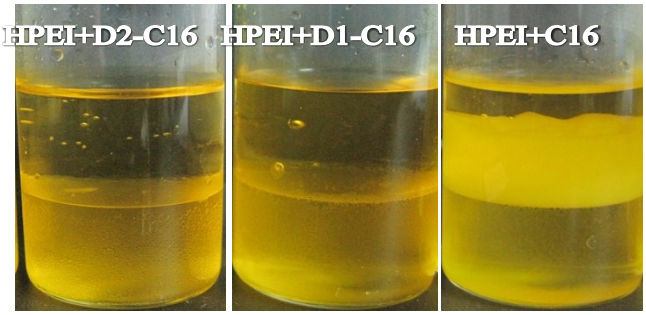


Fig. S13 Images of liquid-liquid encapsulation of different complexes for MO (Upper phase: water; lower phase: chloroform; HPEI concentration is around 5×10^{-6} M; [COOH]/[N] of complexes is all 0.73)

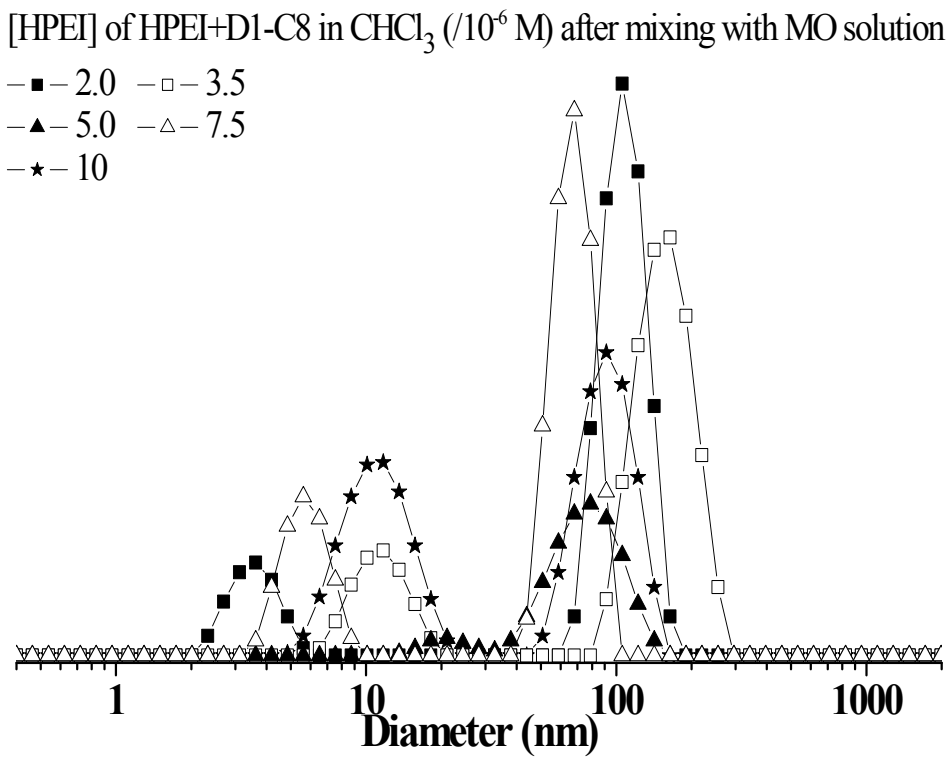


Fig. S14 The effect of HPEI concentration of HPEI+D1-C8-0.54 on the distribution of size.

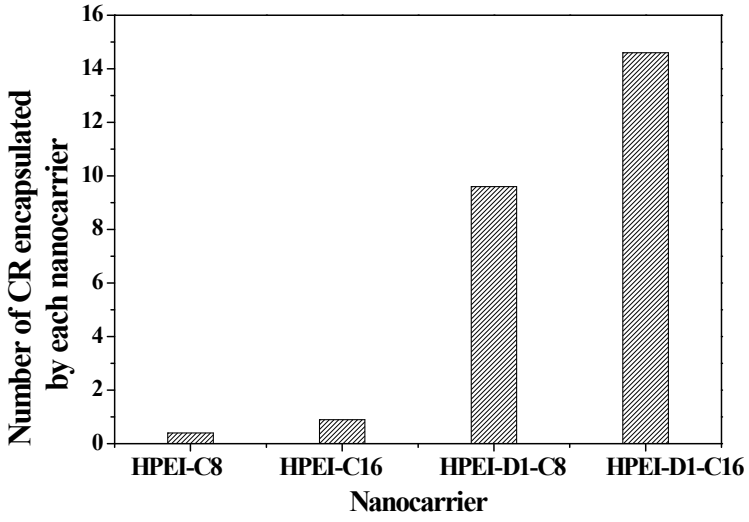


Fig. S15 Effect of the chain length of the shell of the covalent polymers on their guest encapsulation capacity.