Electronic Supplementary Material (ESI) for Soft Matter.

Electric Supporting Information

Large-scale preparation of 3D patchy surface with dissimilar dendritic amphiphiles

Yanyan Feng, Yujia Wan, Ming Jin, and Decheng Wan*

Department of Polymer Materials
School of Materials Science and Engineering, Tongji University
4800 Cao-an Rd, Shanghai 201804, China

*corresponding author, wandecheng@tongji.edu.cn

Table of contents

1.1. Glycidyl-capped PPG

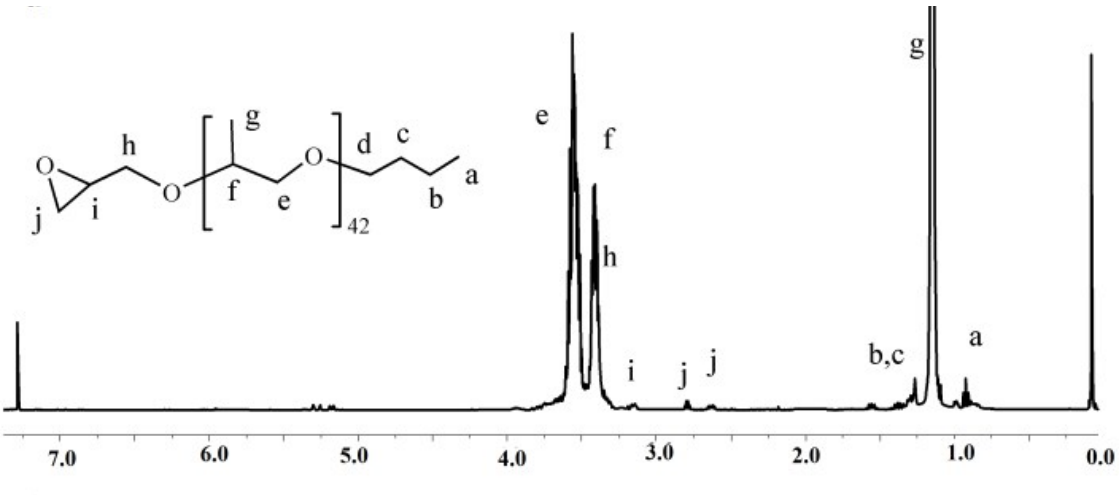

Figure S1. ^{1}H NMR spectrum of glycidyl-capped PPG.

1.2. ^{1}H NMR of PEI-N^{+}@PPG1

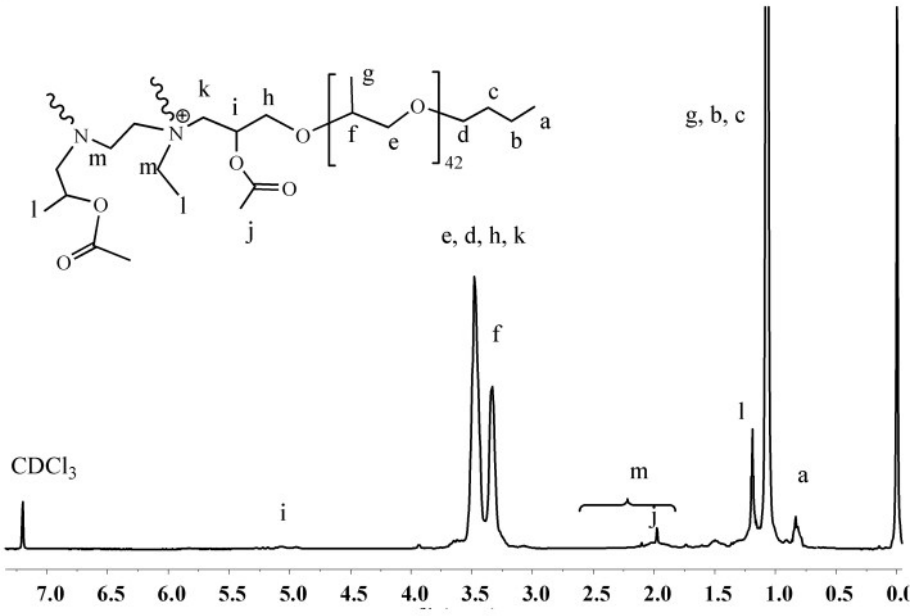

Figure S2. ^{1}H NMR spectrum of PEI-N+@PPG1.

IR spectra before and after modification: Figure s3.

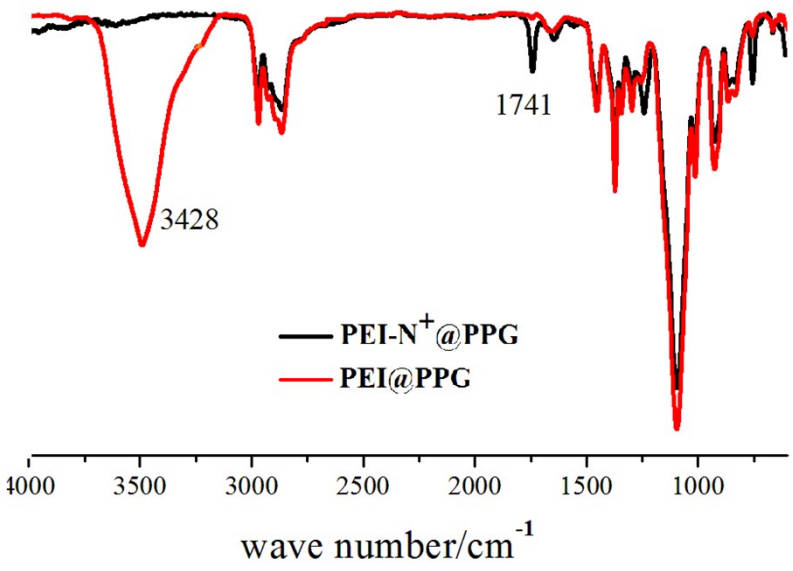

Figure S3. IR spectra of PEI@PPG1 (black line) and PEI-N^+@PPG1 (red line).

1.3. MIP characterization of polyHIPE-N^+/S^-

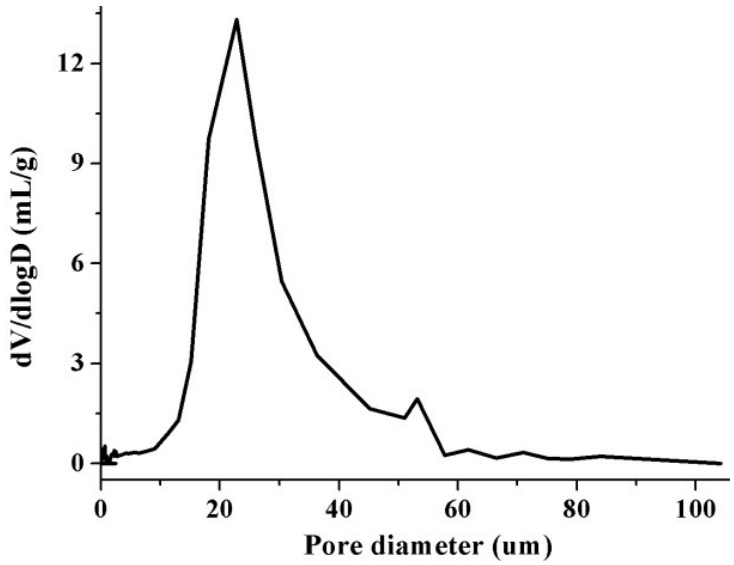

Figure S4. Size distribution of the pores of polyHIPE measured by MIP.

1.4. Unimolecularity of PEI@PPG2 and PEI-N^+@PPG1

Measurement of dye encapsulating capacity determined the unimolecularity of an amphiphile. Typically, excess MOs in water (10^{-4} M) were sufficiently exposed to PEI@PPG samples at diverse concentration (10^{-6}–10^{-9} M) in toluene, after full phase equilibration, the amounts of MOs transferred to the chloroform phase were determined by UV/Vis measurement. The MOs transferred per PEI@PPG was plotted against

concentration of the latter, where the reflecting point represents the critical aggregation concentration (CAC).

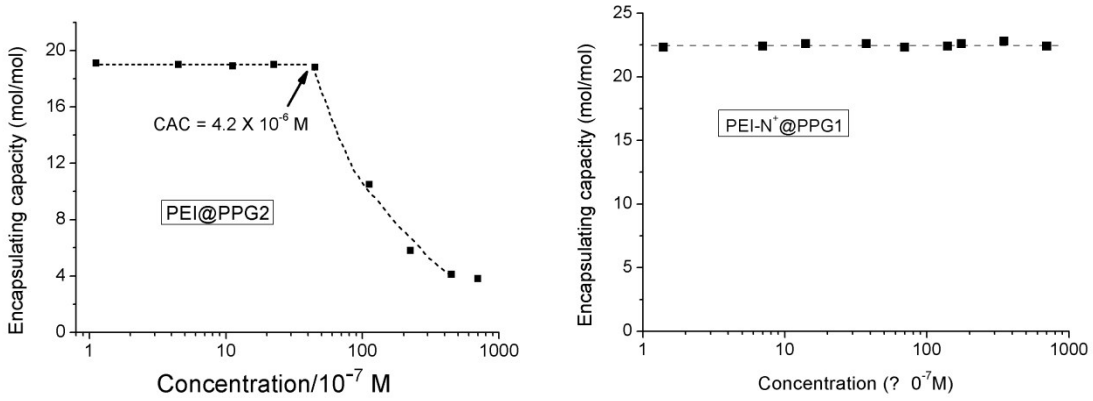

Figure S5. Dependence of the MO-encapsulating capacity on concentration of the dendritic amphiphile of PEI@PPG2 or PEI-N$^+$@PPG1. Conditions: biphasic extraction of aqueous MOs with diverse amount of the dendritic amphiphile in toluene; pH ~7.

1.5. Simultaneous adsorption of anionic and cationic guests by polyHIPE

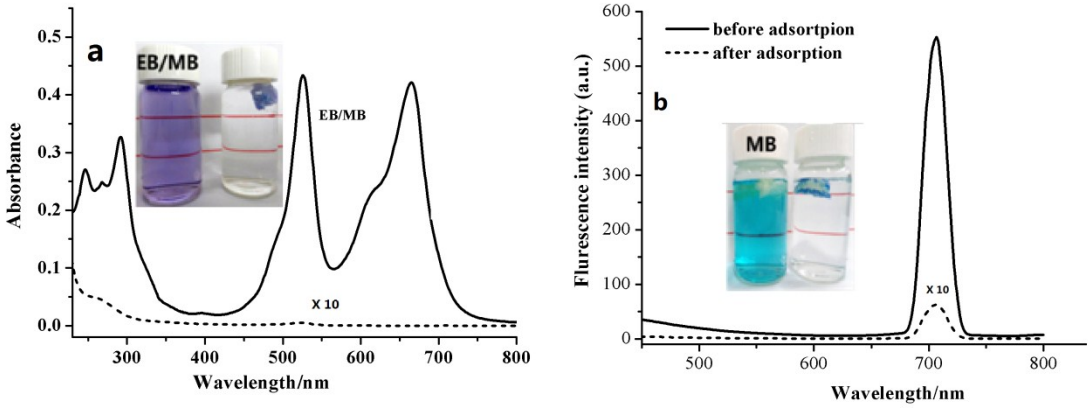

Figure S6. UV/vis signal of EB/MB before and after treatment with the adsorbent (a), and for MB detected by fluorescence (b). Conditions: pH = 11; the water sample after treatment was 10-fold concentrated before detection.

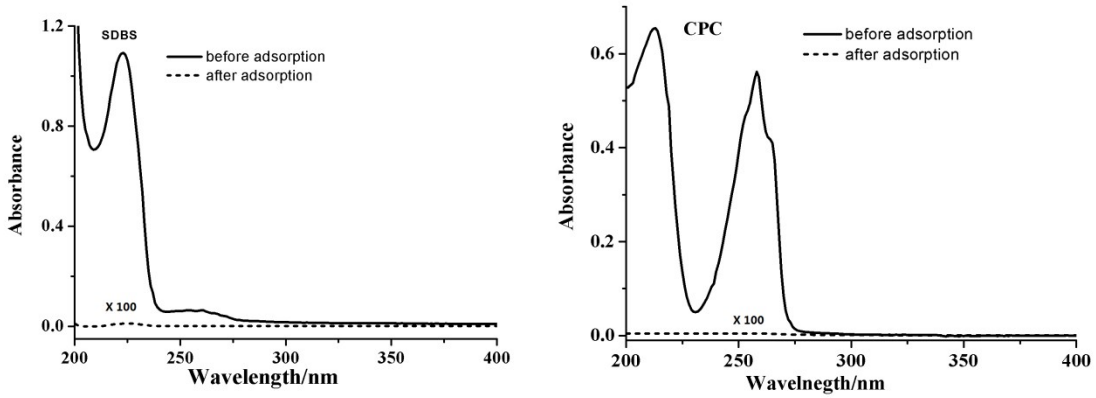

Figure S7. UV-vis spectra of sodium dodecyl benzene sulfate (SDBS) (Left) and cetylpyridium chloride (CPC) (Right) before and after adsorption by excess dosage of polyHIPE at pH 11. Conditions: pH = 11; $[SDBS]_0 = 0.9 \times 10^{-4}$ M; $[CPC]_0 = 1.24 \times 10^{-4}$ M; treated water samples were 100-fold concentrated prior to detection.

1.6. Adsorption kinetics and mechanism

The adsorption data are analyzed by the first-order rate equation (Lagergren model):

$$\text{Ln } (Q_e - Q_t) = \ln Q_e - k_1 t,$$

where Q_e and Q_t are the amounts of the dyes (EB) adsorbed (mg g^{-1}) at equilibrium and at contact time t (h), respectively, k_1 (h^{-1}) is the rate constant. The linear fitting was shown in Figure 6c with a regression coefficient of $R^2 = 0.990$. From the fitting line, Q_e (theoretic) = 66.0 mg g^{-1} is derived from the intercept, and $k_1 = 0.028$ h^{-1} is derived from the slope.

The experimental data were also fitted by the pseudo-second order kinetic model:

$$t/Q_t = 1/(k_2 Q_e^2) + (1/Q_e)t,$$

where k_2 (g mg^{-1} h^{-1}) is the rate constant of pseudo-second order adsorption reaction. The linear fitting of t/Q_t versus t was shown in Figure 6b with $R^2 = 0.999$. Q_e (theoretic) = 55.5 mg g^{-1} and $k_2 = 0.0016$ (g mg^{-1} h^{-1}) are derived from the fitting data.

One can find that from R^2 and from comparison the Q_e (theoretic) with the experimental Q_e = 50 mg g^{-1} that the adsorption kinetics follows a pseudo-second order model. This is somewhat out of expectation in view that electrostatic interaction between the cationic adsorbent and anionic EB is important, and chemical interaction between them seems impossible. Probably, the adsorption is initially driven by electrostatic attraction, but

subsequent entrance of an EB molecule into the aggregated dendritic amphiphile involves much conformation adjustment, rendering the second step rate-determining.

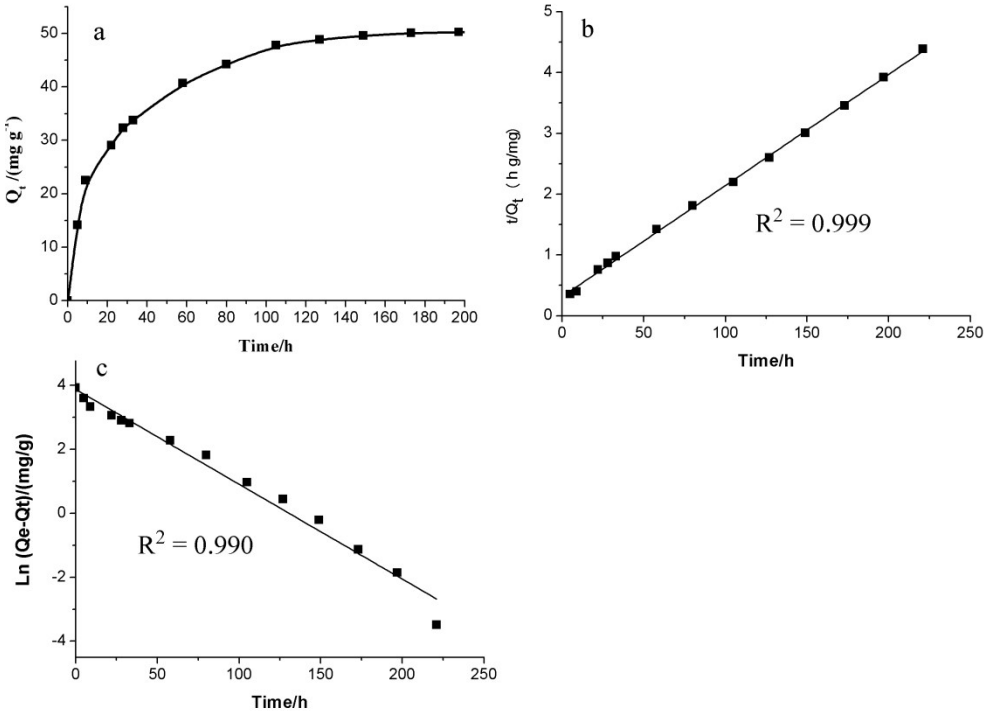

Figure S8. adsorption of EB by polyHIPE-N+ against time (a) and data analysis with Lagergren's pseudo-first-order model (b) or with pseudo second-order model (c). Curve in a is obtained by best fitting; pH 7.

Regarding the adsorption isotherm, experiment is also carried out. The dependence of equilibrium adsorption capacity on equilibrium dye concentration in solution is plotted (Figure 7a). The data were fitted with Freundlich equation:

$$\log Q_e = \log K_F + (1/n) \log C_e,$$

where Q_e is the equilibrium dye concentration on adsorbent (mmol g^{-1}), C_e is the equilibrium solution concentration of the dye (mmol L^{-1}), K_F is the Freundlich constant (mmol g^{-1}), n is the heterogeneity factor. The fitting is shown in Figure 7b, with $R^2 = 0.975$, $K_F = 0.050$ mmol g^{-1} and $n = 4.29$.

The data were also fitted with Langmuir model:

$$1/Q_e = 1/Q_0 + 1/(bQ_0C_e),$$

where Q_e is the amount of dye adsorbed on the adsorbent (mmol g^{-1}), C_e is the equilibrium dye concentration in the solution (mmol L^{-1}), Q_0 is a constant relating to the surface available for the

adsorbate, and b is the Langmuir adsorption constant (L mmol^{-1}).

The fitting yields an R^2 = 0.84 (Figure not shown), suggesting it does not follow a Langmuir model.

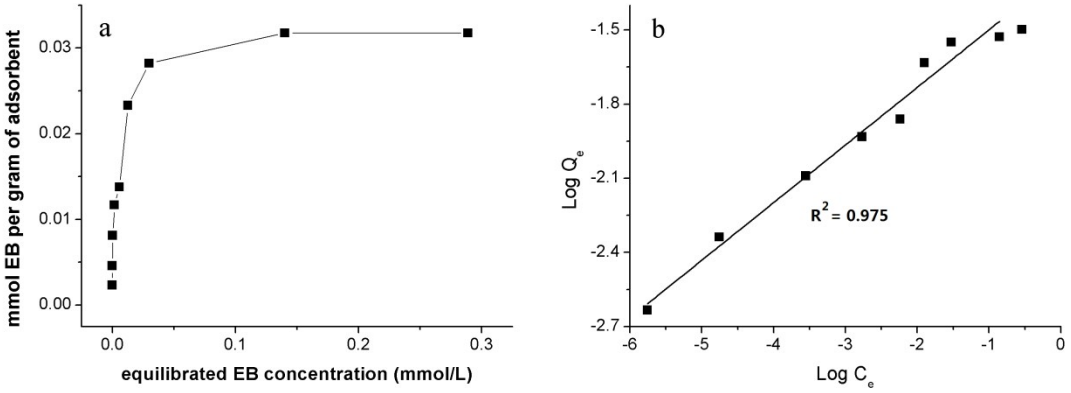

Figure S9. Adsorbing capacity of polyHIPE-N$^+$ on initial concentration of EB (a) and analysis with Freundlich model (b). conditions: pH ~7, temperature 25 °C.

1.7. Adsorbing capacity and pollutant residue

Table s1. Comparison of several polyHIPEs on elimination cationic or anionic pollutant species from water.[a]

adsorbent	Solute[b]	Q_e (mg g-1)[c]	Residue[d]	
			(mol L^{-1})/10^{-9}	(ppb)
polyHIPE-N+/S-	EB	23.5	6.2	4.2
	MB	19.0	1.1	0.35
	SDBS	23.2	8.7	3.0
	CPC	19.5	9.5	3.2
polyHIPE-N$^+$	EB (pH 7)	50.5	5.0	3.5
	SDBS (pH 7)	50.6	8.8	3.1
polyHIPE-S$^-$	MB (pH 7)	40.4	1.2	0.38
	CPC (pH 7)	47.6	9.8	3.2

[a] adsorption at pH 11 unless stated otherwise; [b] EB: erythrosine B; MB: methylene blue; SDBS: sodium dodecyl benzene sulfonate; CPC: cetylpyridinum chloride; [c] adsorbing capacity; [d] with excess adsorbent.