Supporting Information

Hyperbranched Poly（ether amine)@Poly (vinylidenene fluoride) Porous Membrane (hPEA@PVDF) for Selective Adsorption and Molecular Filtration of Hydrophilic dyes

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1. Experimental

1.1 Materials

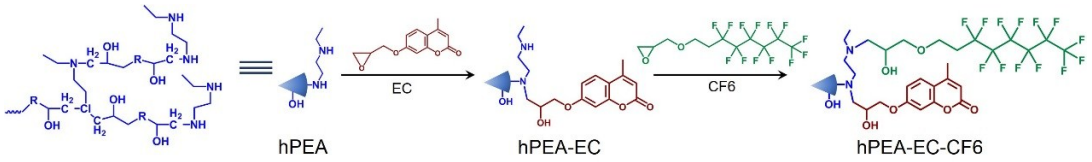
Hyperbranched poly(ether amine) (hPEA211)[1] and 7-(2,3-expoxypropyloxy) coumarin (EC)[2] were synthesized according to our previous work. 3-(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyloxy)-1,2-Epoxypropane(CF6, TCI), Poly(Vinylidene Fluoride) (PVDF, Aldrich) were used as received without further purification. The water-soluble dyes Rose Bengal (RB), Erythrosin B (ETB), Eosin B (EB), 4,5,6,7-tetrachlorofluorescein (TCF), Fluorescein (FR), 4', 5'-dibromofluorescein (DBF), Calcein (Cal), Methylene blue (MB), Acid red 27(AR), Bismarck brown (BBY), Ponceau S (PS) and Evans blue (EVB) used in this study were supplied by Sinopharm Chemical.

1.2 Synthesis of hPEA-EC-CF6

hPEA-EC-CF6 was synthesized according to Scheme S1. Firstly, EC (0.033 mol) and hPEA 211(0.010 mol in term of its structure units) were stirred and refluxed in ethanol (20 mL) for 24 h to synthesize hPEA-EC. Secondly,CF6 (0.066 mol) was add to the reactants above, stirred and refluxed for another 24h to ensure that CF6 was introduced into hPEA-EC. The whole reaction was operated in a 50-mL two-necked flask under the protection of nitrogen. And the mole ratio of reactants was presented as n(hPEA211):n(EC):n(CF6)=3:1:2. After that, most of the ethanol was removed by reduced pressure distillation at 60℃, and the mixture left was poured into n-hexane. After removing the supernatant, the precipitate was collected and dried in vacuum to obtain hPEA-EC-CF6.

2. Results

2.1 Synthesis and characterization of hPEA-EC-CF6



Scheme S1. Synthesis process of hPEA-EC-CF6

The synthesis process of hPEA-EC-CF6 was shown in Scheme S1. Firstly, EC, which was known as a photo-crosslinker, was introduced into the hPEA211 backbone. Then the hydrophobe (CF6) was branched onto hPEA-EC to obtain hPEA-EC-CF6. Both EC and CF6 were grafted into hPEA through nucleophilic substitution/ring-opening reaction. As shown in Fig. S1, according to our previous research[19], the peaks appeared at 2.4-7.8 ppm assigned to the coumarin groups, which indicated that EC was successfully grafted into hPEA. While the spectrum of hPEA-EC-CF6 was similar to that of hPEA-EC. That might be ascribed to the few peaks of H atoms in CF6 which might be covered by the peaks of hPEA-EC. In the FT-IR spectrum of hPEA-EC (Fig. S2), there were two new peaks appearing at 1612 cm^{-1} and 1724 cm^{-1} compared with hPEA. The peak of C=O usually appears in the region of 1950 cm^{-1}-1600 cm^{-1} and the signal of the conjugated C=C was in the region of 1680 cm^{-1}-1560 cm^{-1}. Therefore, the peak at 1612 cm^{-1} was assigned to conjugated C=C in coumarin moiety (EC), and the peak at 1724 cm^{-1} could be assigned to C=O of EC. These new peaks proved that EC was successfully introduced into hPEA. Besides, in hPEA-EC-CF6 spectrum, the signals appeared at 1241 cm^{-1} and 1203cm^{-1} could be assigned to C-F in CF6, which confirmed that CF6 was successfully grafted.

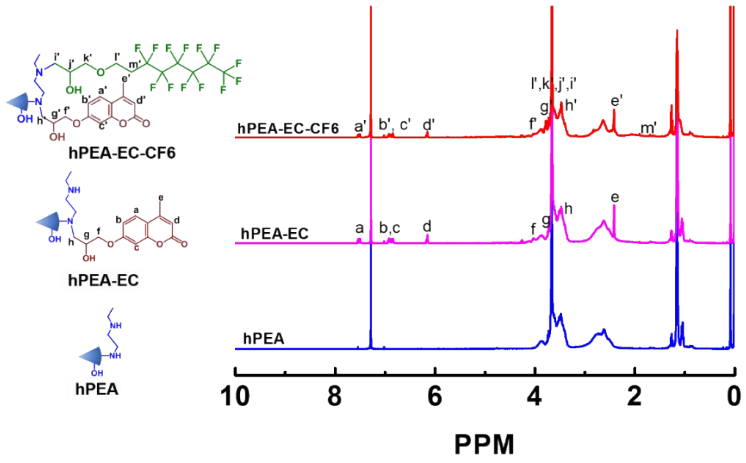


Fig. S1. ^{1}H-NMR spectra of hPEA, hPEA-EC and hPEA-EC-CF6 in $CDCl_3$.

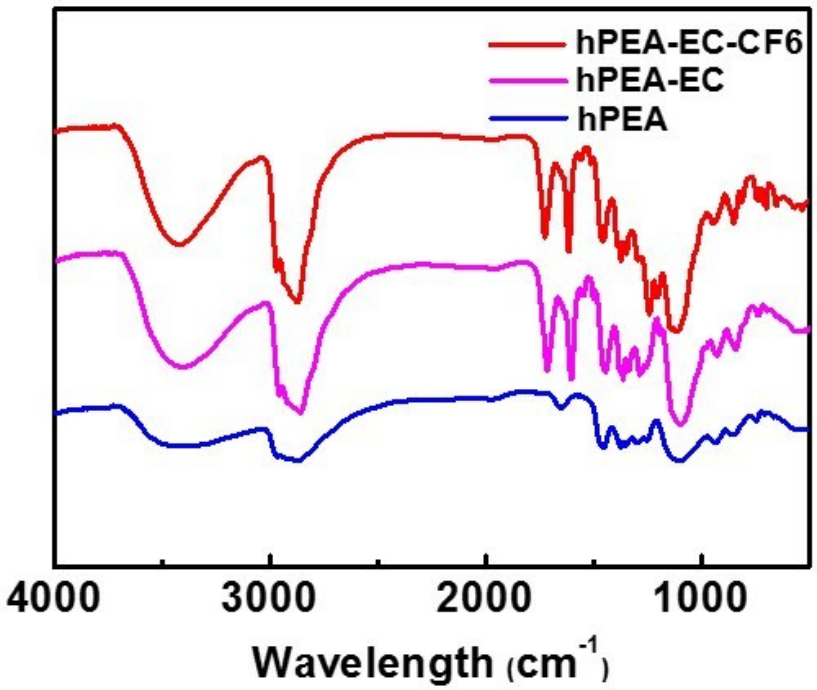


Fig. S2. FT-IR Spectra of hPEA211, hPEA-EC and hPEA-EC-CF6.

2.2 Characterization of hPEA@PVDF membranes

Table S1 Average pore size, porosity and thickness of hPEA@PVDF and pure PVDF membranes.

Sample	Average pore size [nm]	Porosity [%]	Thickness [μm]
PVDF	121	71.3	96.3
P10@hPEA2.5	80.0	76.6	246
P10@hPEA3.3	152	78.8	276
P10@hPEA5.0	167	78.5	281
P10@hPEA10	172	77.9	309
P15@hPEA5.0	46.7	73.3	254

Porosity of the membrane (ε) refers to the amount of void space that the membrane contains. It was calculated from the bulk density of the membrane ($\rho_{membrane}$) and the density of hPEA@PVDF membrane ($\rho_{composite}$), using the following equation[3]:

$$\varepsilon = 1 - \frac{\rho_{membrane}}{\rho_{composite}} \times 100\% = 1 - \frac{\frac{M_{membrane}}{V_{membrane}}}{\rho_{PVDF} \times (1 - hEPA\%) + \rho_{hPEA} \times hEPA\%} \times 100\% \quad (1)$$

where $M_{membrane}$ (g) is the mass of a hPEA@PVDF membrane segment, $V_{membrane}$(cm^3) is the volume of the membrane segment, and its thickness was determined by a thickness tester (GS-702N type D, Teclock, Japan). ρ_{PVDF} and ρ_{hPEA} (g cm^{-3}) are the density of PVDF and hPEA, and ρ_{PVDF} is 1.77 g cm^{-3}, ρ_{hPEA} is 1.00 g cm^{-3}.

Average pore size of the top surface was determined via SEM images of the surface. Pore diameters were measured and the averages were recorded. And pore size, porosity and thickness of hPEA@PVDF and pure PVDF membranes are listed in Table S1.

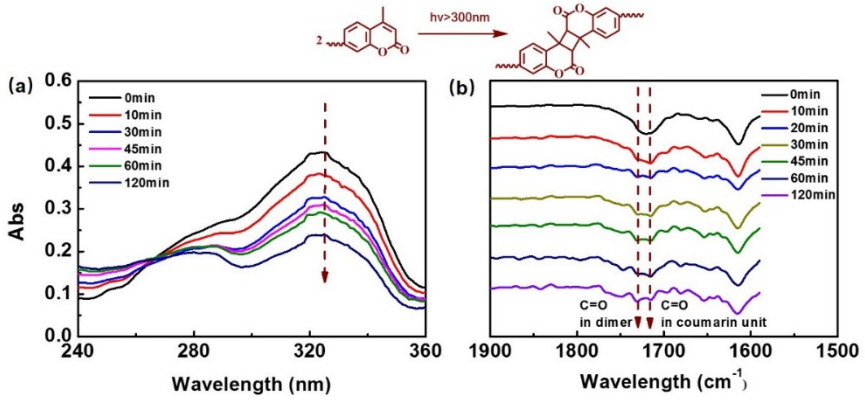


Fig. S3. To trace cross-linking process of P10@hPEA2.5: (a)UV−vis absorption spectra of hPEA photodimerization kinetics at different irradiation times by 365 nm UV light. (b) FT-IR spectra and C=O shift after UV irradiation.

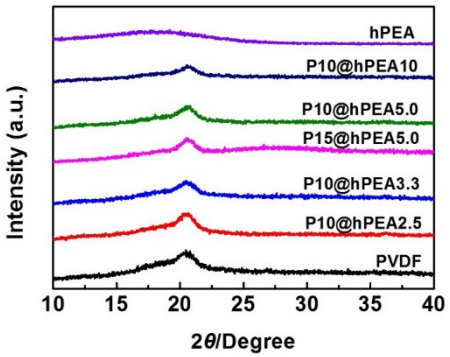


Fig. S4. WAXD curves of hPEA/PVDF membranes, as well as hPEA and PVDF.

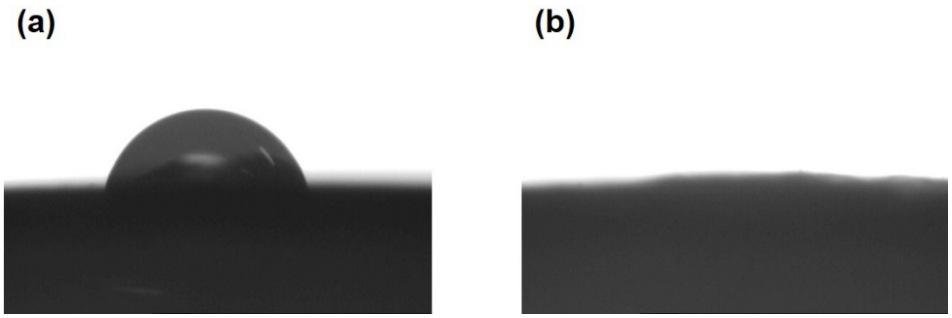


Fig. S5. Contact angles of (a) pure PVDF membrane and (b) P15@hPEA5.0 membrane.

2.3 Adsorption experiments

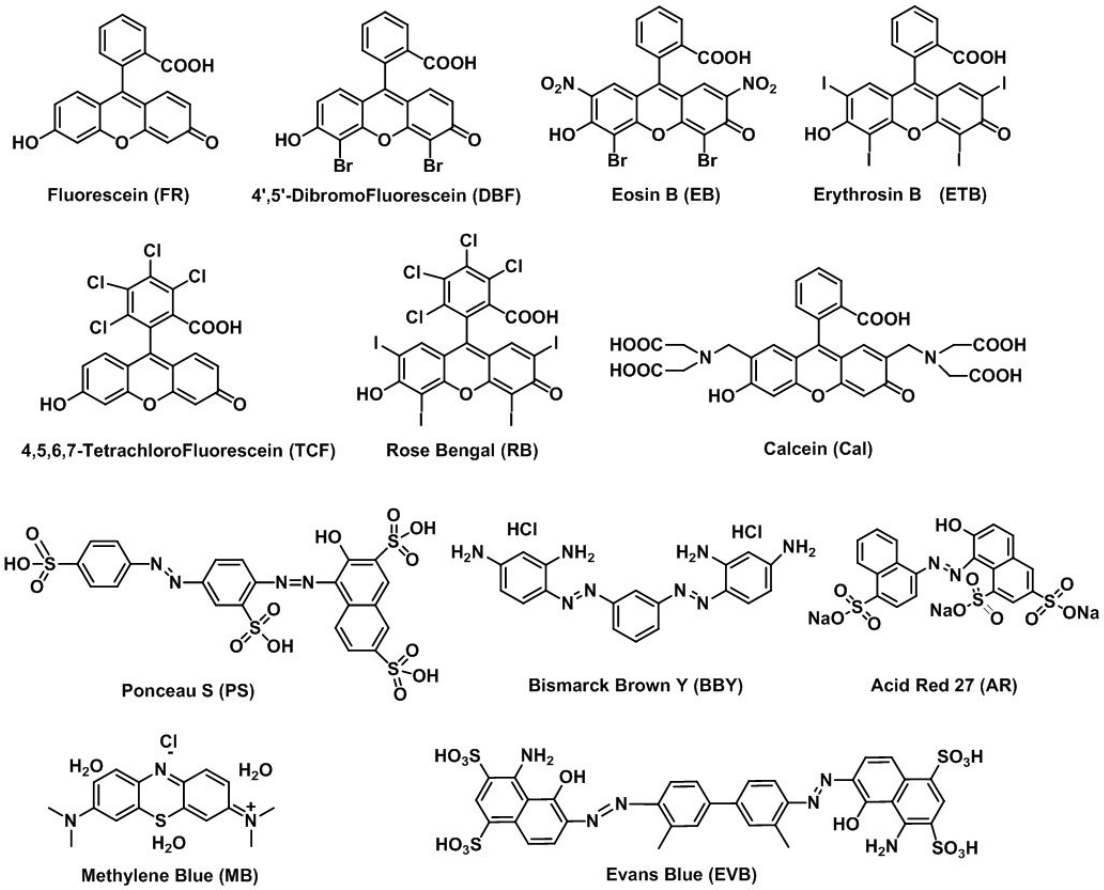


Fig. S6. Structures and abbreviations of twelve hydrophilic dyes.

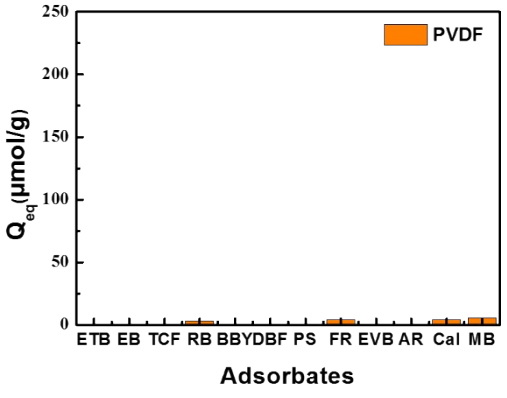


Fig. S7. Saturated adsorption capacities of PVDF membranes (Fluorescein dyes were dissolved in phosphate buffer, azo dyes and MB were in deionized water at 25 °C; 15 mL of dye solution with concentration of 300 μmol L^{-1}, adsorbent 15mg, adsorption time 48 h).

In the adsorption kinetic experiment, the uptake rate of each adsorbent was described by pseudo-secondorder adsorption model, which was generated by plotting t/Qt to t, the equations are given as follows:

$$\frac{t}{Q_t} = \frac{t}{Q_{eq}} + \frac{1}{kQ_{eq}^2} \quad (1)$$

where Q_t and Q_{eq} (μmol g^{-1}) are the absorbate uptakes at time t (min) and at equilibrium, respectively, and k (g μmol^{-1} min^{-1}) is the second-order rate constant.

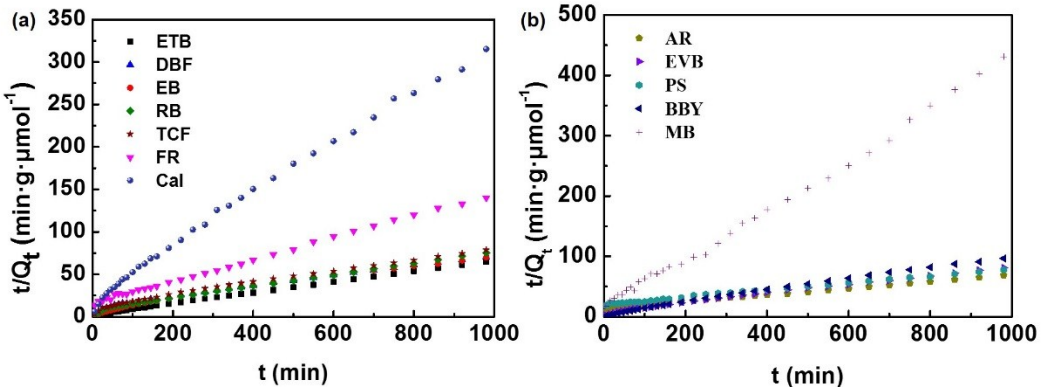


Fig. S8. Pseudo-second-order adsorption kinetics of (a) fluorescein dyes and (b) azo dyes and MB. (Fluorescein dyes were dissolved in phosphate buffer (pH=7.2), azo dyes and MB were in deionized water; 15mL dye solution with concentration of 40 μmol L^{-1}; adsorbent 30 mg).

Table S2. Kinetics parameters describing the adsorption of twelve dyes onto P15@hPEA5.0 membranes.

Dye	$Q_{eq,ex}$ [μmol g^{-1}]	k [g μmol min^{-1}]	$Q_{eq,cal}$ [μmol g^{-1}]	R^2
ETB	15.1	0.0642	15.6	0.999
DBF	13.9	0.0647	15.5	0.989
EB	14.0	0.0685	14.6	0.986
RB	13.0	0.0700	14.3	0.995
TCF	12.5	0.0719	13.9	0.988
FR	7.01	0.128	7.79	0.998
Cal	3.11	0.307	3.26	0.996
AR	14.3	0.055	18.2	0.992
EVB	12.1	0.078	12.9	0.993
PS	12.8	0.059	16.9	0.997
BBY	10.2	0.098	10.2	0.997
MB	2.27	0.409	2.45	0.996

The Langmuir and Freundlich isotherm models were applied to analyze the equilibrium adsorption data and determine the adsorption mechanism. The Langmuir and Freundlich isotherm are given as follows:

$$\frac{C_{eq}}{Q_{eq}} = \frac{C_{eq}}{Q_{max}} + \frac{1}{K_L Q_{max}} \quad (2)$$

$$lnQ_{eq} = lnK_F + b_F lnC_{eq} \quad (3)$$

where Q_{eq} (μmol g^{-1}) is Langmuir maximum adsorption capacity, C_{eq} (μmol L^{-1}) is the equilibrium concentration of the dyes in the solution, Q_{max} (μmol g^{-1}) is the maximum capacity of the hPEA@PVDF membranes, K_L (L μmol^{-1}) is the Langmuir adsorption constant and related to the energy of adsorption, K_F is the Freundlich constant, acts as an indicator of the adsorption capacity, b_F is the adsorption intensity.

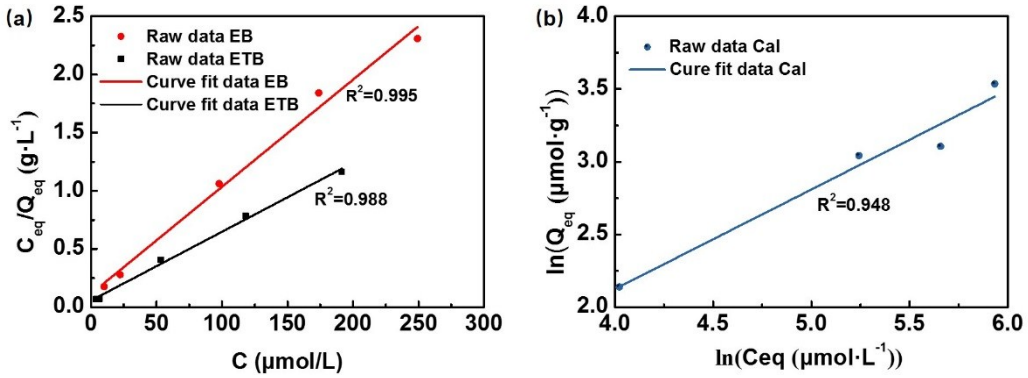


Fig. S9. (a) Linearized Langmuir isotherms of ETB and RB and (b) Linearized Freundlich isotherms of Cal onto P15@hPEA5.0 membranes at 25 °C and pH 7.2.

Table S3. Langmuir adsorption isotherm constants of ETB and EB and Freundlich isotherm constants of Cal onto P15@hPEA5.0 membranes

	Langmuir parameters				Freundlich parameters		
Dye	Q_{max} [μmol g^{-1}]	K_L [L μmol^{-1}]	R^2	Dye	K_F	b_F	R^2
ETB	169	0.104	0.988	Cal	0.543	0.684	0.948
EB	109	0.0806	0.995				

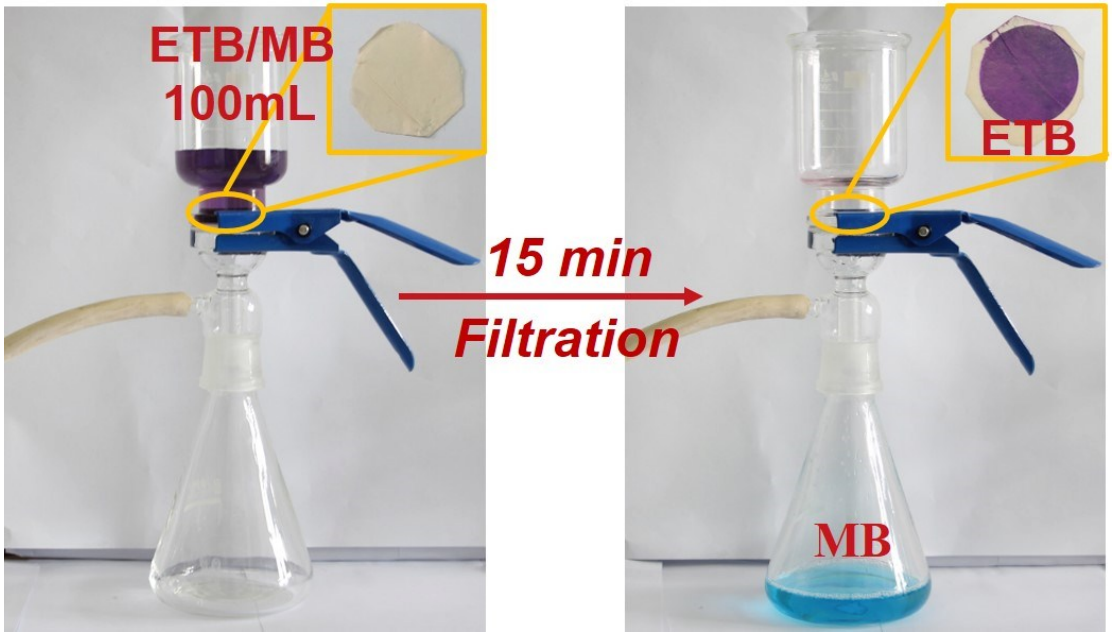


Fig. S10. Equipment for molecular filtration and photographs before and after filtering ETB/MB solution by P15@hPEA5.0 membrane, and inset is the photograph of P15@hPEA5.0 membrane before and after filtration.

References

1. B. Yu, X. Jiang, G. Yin and J. Yin, *J. Polym. Sci. Part A: Polym.Chem.*, 2010, **48**, 4252-4261.
2. P. Zhang, J. Yin and X. Jiang, *Langmuir.*, 2014, **30**, 14597-14605.
3. C. Y. Lai, A. Groth, S. Gray and M. Duke, *J. Membr. Sci.*, 2014, **449**, 146-157.