Supporting Information

Cyclodextrin-based supramolecular polymeric nanoparticles for next generation gas separation membranes

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1. Experimental section

1.1 Methods:

Synthesis of 3-azidopropyl anthrancene-9-carboxylate

3-Azidopropyl anthracene-9-carboxylate was synthesised according to the literature.[1] ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 2.09 (*quin*, 2H, *J* = 6.4 Hz, CH_2), 3.45 (*t*, 2H, *J* = 5.2 Hz, OCH_2), 4.67 (t, 2H, *J* = 5.2 Hz, CH_2N_3), 7.44-7.54 (*m*, 4H, 4ArH), 7.99-8.01 (*m*, 4H, 4Ar*H*), 8.48 (*s*, 1H, Ar*H*) ppm.

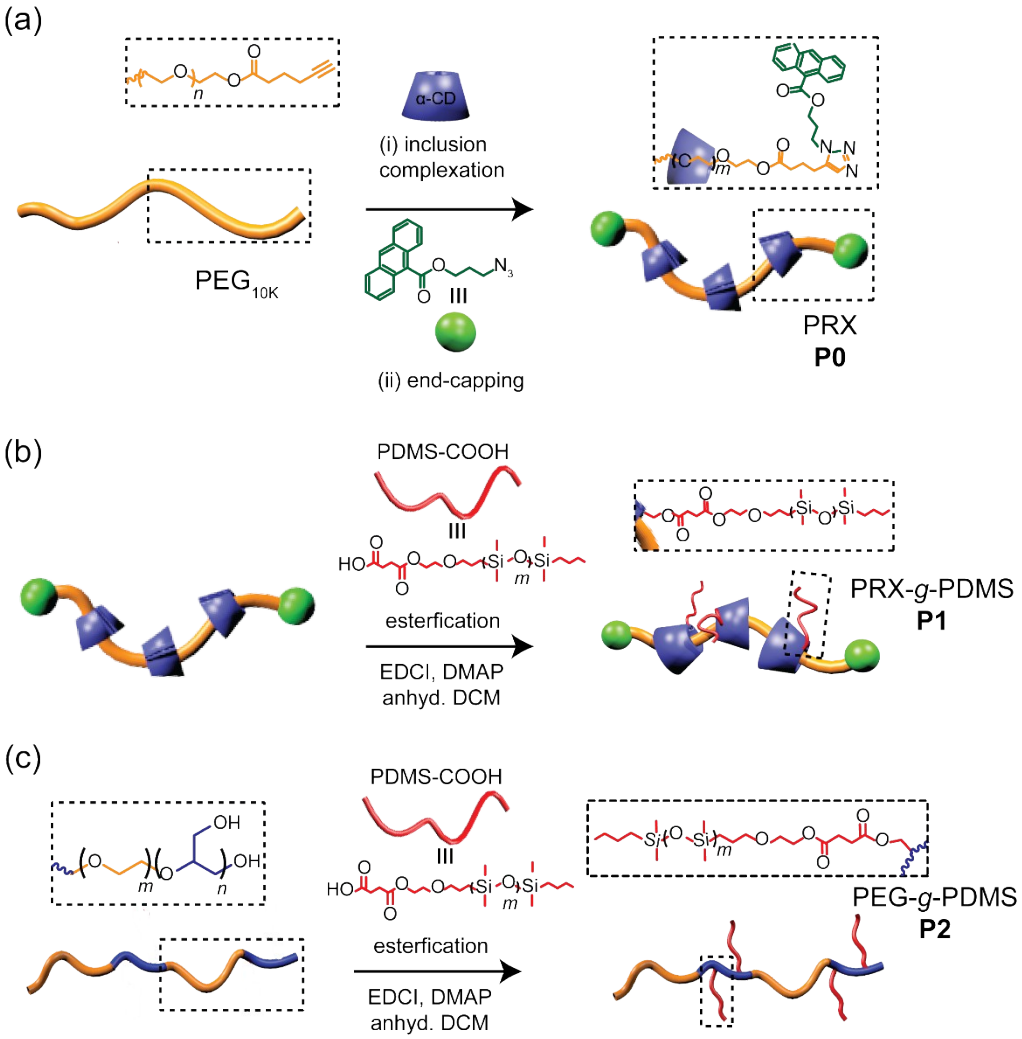
Synthesis of α,ω-dialkyne PEG_{10K}

α,ω-Dialkyne PEG_{10K} was synthesised according to the literature.[2] ^{1}H NMR (400 MHz, d_6-DMSO): δ_H 1.69 (*quin*, *J* = 7.2 Hz, $CH_2CH_2CH_2$ end-group), 2.20 (*dt*, *J* = 2.8 & 7.2 Hz, -CCH_2 end-group), 2.40 (*t*, *J* = 7.2 Hz, CH_2CO end-group), 2.80 (*t*, *J* = 2.8 Hz, C≡C*H* end-group), 3.69–3.30 (*m*, CH_2O), 4.14–4.11 (*m*, CH_2OCO end-group) ppm. MALDI ToF MS: M_n = 11.3 kDa, GPC-MALLS (DMF): PDI = 1.32.

1.2 Density Experiments

Densities of dense membranes were determined by the buoyancy method according to the literature [3] in hexane with a known density of 0.659 g.mL^{-1} at 20 °C. The following equation was used to calculate density where W_a and W_h is the membrane weight in air and hexane, respectively. Membranes were dried in a vacuum oven at 40°C for 24 h before being weight in air.

$$\rho = \frac{W_a}{W_a - W_h}\rho_{solvent}$$



Scheme S1. Synthetic outline showing the prepartion of the SNP precursors **(a)** PRX **P0**, **(b)** PRX-*g*-PDMS **P1** and **(c)** PEG-*g*-PDMS **P2**.

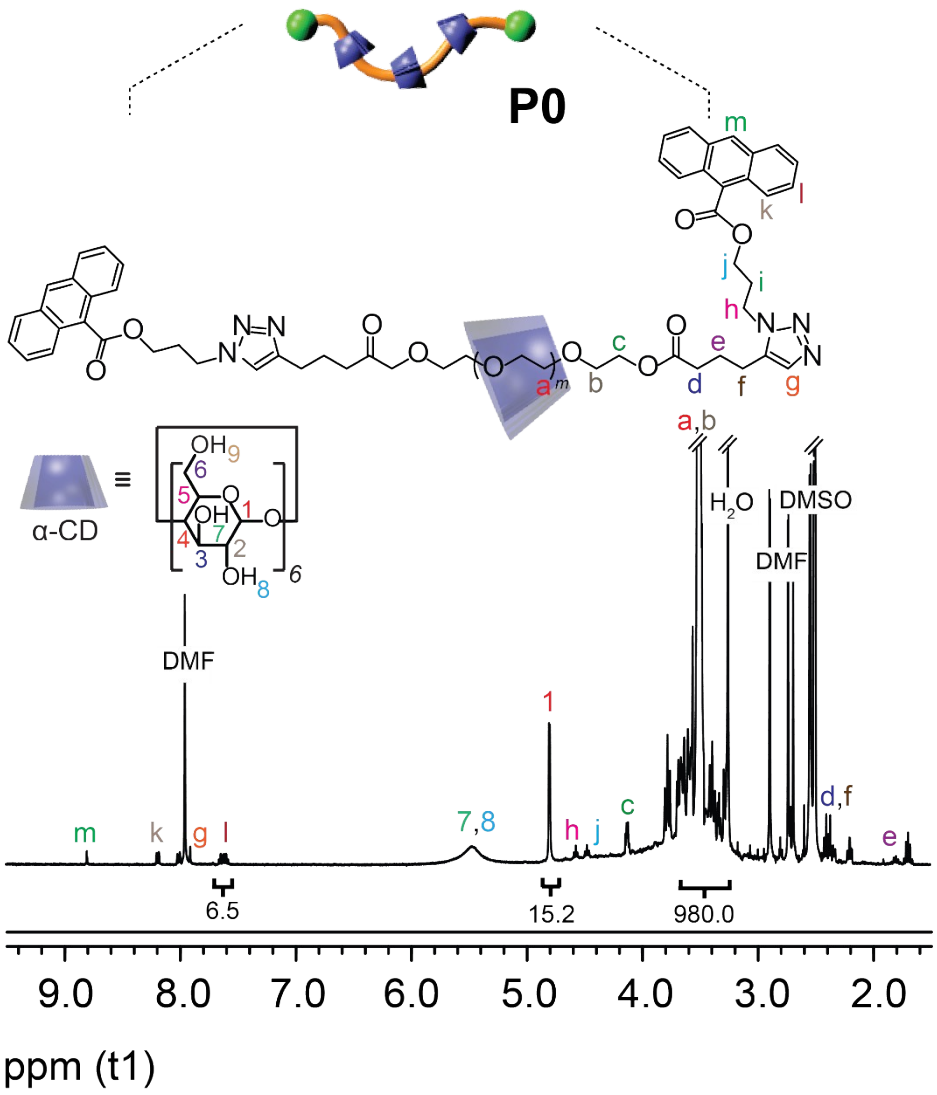


Figure S1. ^{1}H NMR spectrum (d_6-DMSO, 400 MHz) of anthracene end-capped polyrotaxane **P0**.

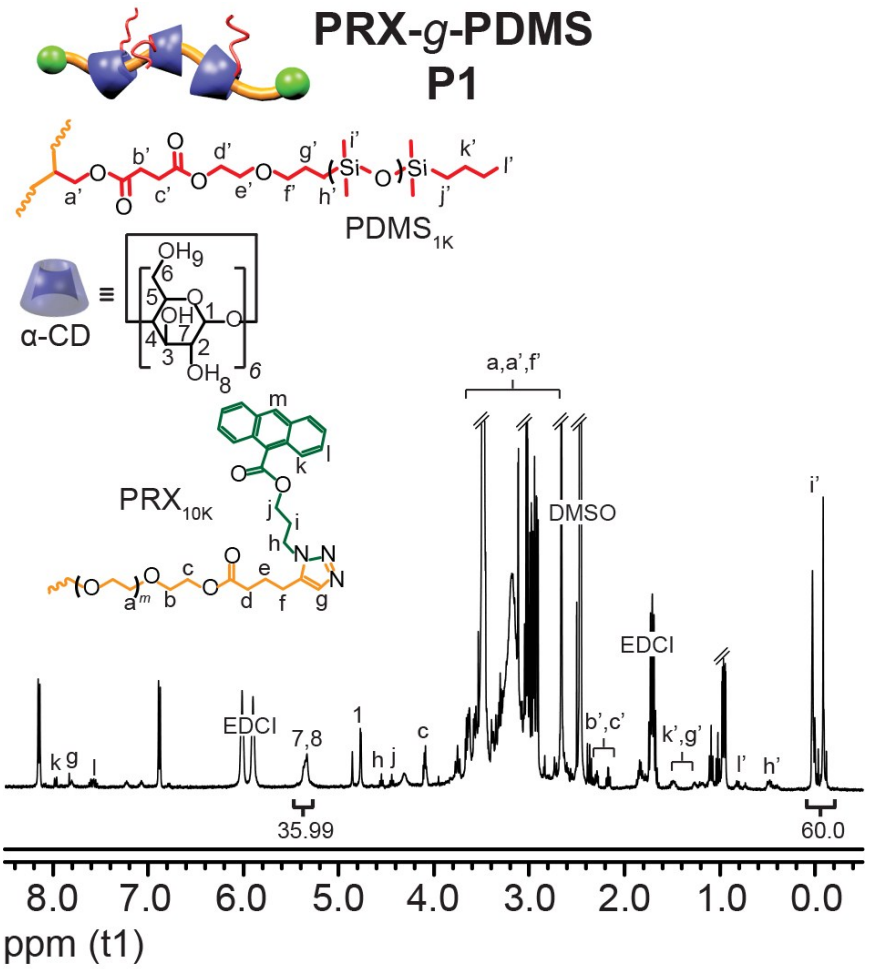


Figure S2. ^{1}H NMR spectrum (d_6-DMSO, 400 MHz) of the PDMS functionalised PRX **P1**.

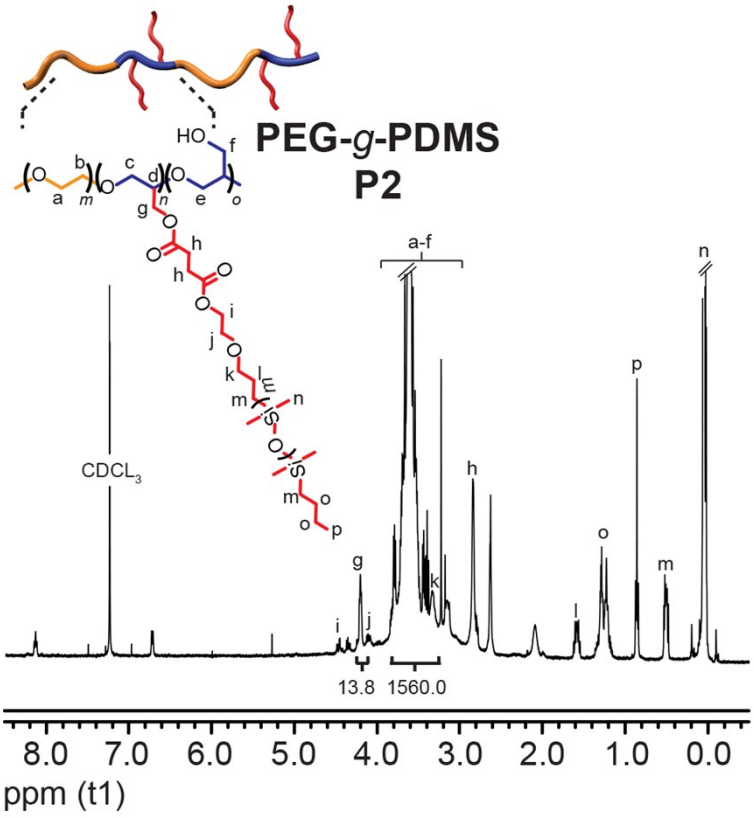


Figure S3. ^{1}H NMR spectrum (d_6-DMSO, 400 MHz) of the PEG-*g*-PDMS **P2**.

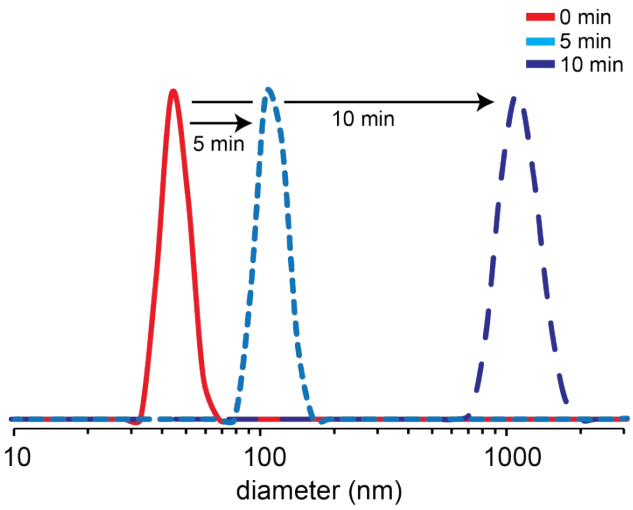


Figure S4. Kinetic study of **SNP1** using DLS measurements (number) at 0, 5 and 10 min at 25 °C after self-assembly at 40 °C.

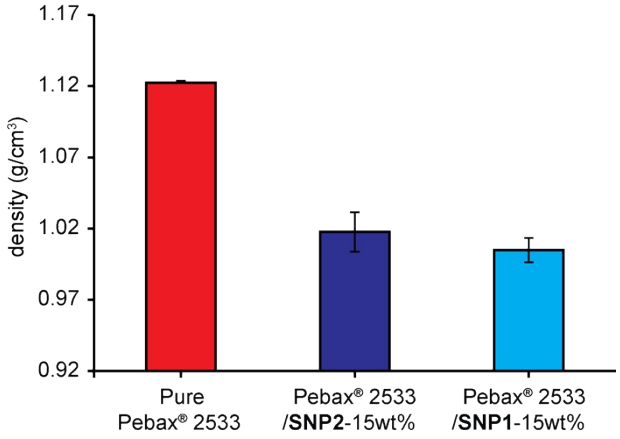


Figure S5. Density of the pure Pebax® 2533, Pebax® 2533/**SNP2**-15wt% and Pebax® /**SNP1**-15wt% dense membranes.

Table S1. Gas separation performance of the selective layer of TFC membranes at 35 °C and 340 kPa.

Entry	Sample code	Additive (wt%)	Selective Layer		
			J (CO_2)[a] (GPU)	P (CO_2)[b] (Barrer)	CO_2/N_2 Selectivity
1	Pebax®	0	556	167	27
2	Pebax®/**SNP0**-15wt%	15	-	-	-
3	Pebax®/**SNP1**-10wt%	10	1,000	300	27
4	Pebax®/**SNP1**-15 wt%	15	1,420	426	25
5	Pebax®/**SNP1**-20 wt%	20	1,990	597	22
6	Pebax®/**SNP1**-30 wt%	30	3,310	993	19
7	Pebax®/**SNP2**-15 wt%	15	-	-	-
8	Pebax®/**CD**-15 wt%	15	-	-	-
9	Pebax®/**PDMS**-15 wt%	15	-	-	-

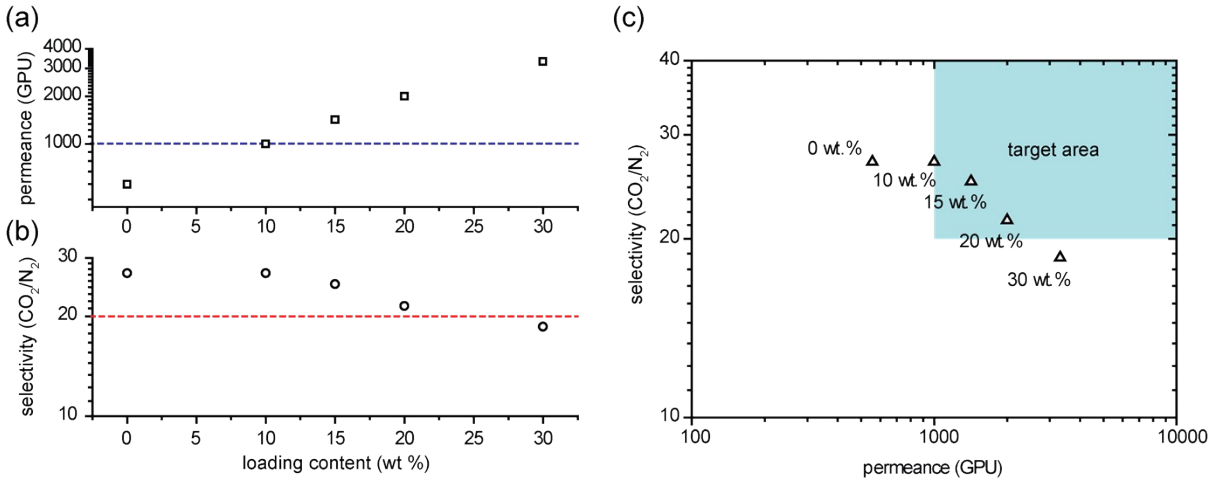


Figure S6. (a) CO_2 permeance and **(b)** CO_2/N_2 selectivity of the selective layer of TFC membranes as a function of **P1** content (wt% relative to Pebax®) determined at 35 °C and 340 kPa. **(c)** Trade-off plot between CO_2/N_2 selectivity and CO_2 permeance for Pebax® and Pebax®/**SNP1** TFC membranes. The target area is that proposed by Merkel *et al.*[1]

References

1. J. M. Ren, J. T. Wiltshire, A. Blencowe, G. G. Qiao, *Macromolecules*, **2011**, 44, 3189-3202
2. S. Tan, A. Blencowe, K. Ladewig, G. G. Qiao, *Soft Matter*, **2013**, 9, 5239-5250
3. A. Car, C. Stropnik, W. Yave, K-V. Peinemann, *Journal of Membrane Science*, **2008**, 307, 88.

[1] T. C. Merkel, H. Lin, X. Wei, R. Baker, *Journal of Membrane Science* **2010**, *359*, 126.