Supplementary Information

SANS, SAXS and Light Scattering Investigations of pH-Responsive Dynamic Combinatorial Mesophases

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Synthesis of Dynablocks

**Fig. S 1** General synthesis of amine functionalized peg.

- **a)** PEGₙOH (1.0 equiv.), p-toluencesulfonyl chloride (1.2 equiv.), pyridine, 0 °C, 4 – 8 h
- **b)** PEGₙOTs 6-8 (1.0 equiv.), 9 (2.5 equiv.), K₂CO₃ (3.5 equiv.), CH₃CN, reflux, 6 – 8 h
- **c)** PEGₙOTs 6-7 (1.0 equiv.), 10 (2.0 equiv.), K₂CO₃ (3.0 equiv.), CH₃CN, reflux, 6 – 8 h
- **d)** Compounds 11-15 (1.0 equiv.), NH₂aq (45 equiv.), THF, r.t., 4 - 8 h.
Fig. S 2 Synthesis of aromatic phtalimid 9 and benzylic phtalimid 10.

2-(4-hydroxyphenyl)isoindoline-1,3-dione 9: \textit{p}-aminophenol (1.0 equiv.), phtalic anhydride (1.0 equiv.), DMF, 90°C, 6 h, 9: 90%.

2-(4-hydroxybenzyl)isoindoline-1,3-dione 10: 4-hydroxybenzylalcohol (1.0 equiv), Phtalimide (1.2 equiv.), PPh\(_3\) (1.5 equiv.), DIAD (1.2 equiv.), THF, 8 h, 10: 54%.

Description of chemical products 1-15

1: \textsuperscript{1}H NMR in CDCl\(_3\): 6.75 (d, \(J = 0.0\) Hz, 2H), 6.62 (d, \(J = 8.0\) Hz, 2H), 4.04 (t, \(J = 4.8\) Hz, 2H), 3.80 (t, \(J = 4.6\) Hz, 2H), 3.64 (m, 22H), 3.54 (m, 2H), 3.37 (s, 3H); ESI-MS: calcd C\(_{21}\)H\(_{37}\)NO\(_8\) 432.26 [M+H]\(^{+}\); found 432.51.

2: \textsuperscript{1}H NMR in CDCl\(_3\): 6.73 (d, \(J = 8.0\) Hz, 2H), 6.62 (d, \(J = 8.0\) Hz, 2H), 4.05 (t, \(J = 4.8\) Hz, 2H), 3.80 (t, \(J = 4.8\) Hz, 2H), 3.65 (m, 40H), 3.37 (s, 3H).

3: \textsuperscript{1}H NMR in CDCl\(_3\): 6.74 (d, \(J = 8.0\) Hz, 2H), 6.64 (d, \(J = 8.0\) Hz, 2H), 4.05 (t, \(J = 4.4\) Hz, 2H), 3.81 (t, \(J = 4.4\) Hz, 2H), 3.65 (m, 60H), 3.37 (s, 3H).

4: \textsuperscript{1}H NMR in CDCl\(_3\): 7.19 (d, \(J = 8.4\) Hz, 2H), 6.87 (d, \(J = 8.4\) Hz, 2H), 4.10 (t, \(J = 4.8\) Hz, 2H), 3.83 (m, 2H), 3.79 (s, 2H), 3.65 (m, 24H), 3.36 (s, 3H); \textsuperscript{13}C NMR in CDCl\(_3\): 159.97, 157.47, 128.24, 113.61, 70.87, 69.51, 58.01, 29.61; ESI-MS: calcd C\(_{22}\)H\(_{39}\)NO\(_8\) 446.27 [M+H]\(^{+}\); found 446.52.

5: \textsuperscript{1}H NMR in CDCl\(_3\): 7.21 (d, \(J = 8.4\) Hz, 2H), 6.88 (d, \(J = 8.4\) Hz, 2H), 4.10 (t, \(J = 4.8\) Hz, 2H), 3.84 (t, \(J = 4.8\) Hz, 2H), 3.79 (s, 2H), 3.64 (m, 40H), 3.37 (s, 3H).
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6: $^1$H NMR in CDCl$_3$: 7.76 (d, $^3J = 8.4$ Hz, 2H), 7.31 (d, $^3J = 8.3$ Hz, 2H), 4.12 (t, $^3J = 4.8$ Hz, 2H), 3.66 (t, $^3J = 5.0$ Hz, 2H), 3.58 (brm, 2H), 3.34 (s, 3H), 2.41 (s, 3H); $^{13}$C NMR in CDCl$_3$: 144.66, 132.90, 129.70, 127.84, 71.80, 70.60, 70.47, 70.43, 70.37, 69.13, 68.54, 58.88, 21.50. Anal. calcd. for C$_{22}$H$_{38}$O$_{10}$S: C 53.42, H 7.74, S 6.48; found C 52.65, H 7.82, S 5.93; ESI-MS: calcd for C$_{22}$H$_{38}$O$_{10}$S 495.22 [M+H]$^+$; found 495,45.

7: $^1$H NMR in CDCl$_3$: 7.76 (d, $^3J = 8.4$ Hz, 2H), 7.30 (d, $^3J = 8.3$ Hz, 2H), 4.12 (t, $^3J = 4.8$ Hz, 2H), 3.64 (t, $^3J = 5.0$ Hz, 2H), 3.62 (m, 6H), 3.60 (m, 4H), 3.54 (m, 4H), 3.51 (m, 2H), 3.34 (s, 3H), 2.41 (s, 3H); $^{13}$C NMR in CDCl$_3$: 144.77, 133.02, 129.82, 127.96, 71.92, 70.75, 70.57, 70.51, 69.25, 68.67, 59.01, 21.63; ESI-MS: calcd for C$_{30}$H$_{54}$SO$_{14}$ 688.34 [M+H$_2$O]$^+$; found 688.58.

8: $^1$H NMR in CDCl$_3$: 7.79 (d, $^3J = 8.4$ Hz, 2H), 7.33 (d, $^3J = 8.3$ Hz, 2H), 4.14 (t, $^3J = 4.8$ Hz, 2H), 3.67 (t, $^3J = 4.8$ Hz, 2H), 3.64 (m, 6H), 3.62 (m, 4H), 3.60 (m, 4H), 3.56 (m, 4H), 3.53 (m, 2H), 3.37 (s, 3H), 2.44 (s, 3H); $^{13}$C NMR in CDCl$_3$: 144.78, 133.05, 129.83, 127.99, 71.94, 70.75, 70.57, 70.51, 69.25, 68.69, 59.04, 21.66; ESI-MS: calcd for C$_{40}$H$_{74}$SO$_{19}$ 908.47 [M+H$_2$O]$^+$; found 908.90.

9: $^1$H NMR in CDCl$_3$: 7.94 (m, 2H), 7.78 (m, 2H), 7.30 (d, $^3J = 8.8$ Hz, 2H), 6.95 (d, $^3J = 8.8$ Hz, 2H); $^1$H NMR in DMSO: 9.77 (s, 1H), 7.93 (m, 2H), 7.88 (m, 2H), 7.21 (d, $^3J = 8.7$, 2H), 6.88 (d, $^3J = 8.7$, 2H); $^{13}$C NMR in DMSO: 167.43, 157.32, 134.64, 131.61, 128.84, 123.31, 122.85, 115.42; Anal. calcd. for C$_{14}$H$_9$NO$_3$: C 70.29, H 3.79, N 5.86; found C 67.70, H 4.06, N 5.80.

10: $^1$H NMR in CDCl$_3$: 7.83 (m, 2H), 7.69 (m, 2H), 7.33 (d, $^3J = 8.5$ Hz, 2H), 6.76 (d, $^3J = 8.5$ Hz, 2H), 4.77 (s, 2H), 4.74 (s, 1H); $^{13}$C NMR in CDCl$_3$: 168.10, 155.20, 134.64, 131.61, 128.84, 123.31, 122.85, 115.42; Anal. calcd. for C$_{15}$H$_{11}$NO$_3$: C 71.14, H 4.38, N 5.53; found C 70.71, H 4.45, N 5.68; HRMS (ESI-TOF): calcd for C$_{15}$H$_{11}$NO$_3$ 260.089 [M+Li]$^+$; found 260.090.

11: $^1$H NMR in CDCl$_3$: 7.94 (m, 2H), 7.78 (m, 2H), 7.32 (d, $^3J = 9.2$ Hz, 2H), 7.03 (d, $^3J = 9.2$ Hz, 2H), 4.17 (t, $^3J = 5.2$ Hz, 2H), 3.87 (t, $^3J = 5.2$ Hz, 2H), 3.73 (m, 2H), 3.64 (m, 20H), 3.54 (m, 2H), 3.37 (s, 3H); $^{13}$C NMR in CDCl$_3$: 167.54, 158.42, 134.31, 131.82, 127.90, 124.56, 123.68, 115.17, 71.95, 70.92, 70.67, 70.59, 69.65, 67.72, 59.07; ESI-MS: calcd for C$_{29}$H$_{39}$NO$_{10}$ 579.27 [M+H$_2$O]$^+$; found 579.60.

12: $^1$H NMR in CDCl$_3$: 7.82 (m, 2H), 7.69 (m, 2H), 7.35 (d, $^3J = 8.8$ Hz, 2H), 6.83 (d, $^3J = 8.8$ Hz, 2H), 4.77 (s, 2H), 4.07 (t, $^3J = 4.0$ Hz, 2H), 3.81 (t, $^3J = 5.0$ Hz, 2H), 3.62 (m, 2H), 3.53 (m, 2H), 3.36 (s, 3H); $^{13}$C NMR in...
CDCl₃: 168.09, 158.41, 133.94, 132.09, 130.11, 128.70, 123.27, 114.75, 71.96, 70.82, 70.65, 70.57, 69.71, 67.42, 59.06, 41.09.

15: ¹H NMR in CDCl₃: 7.83 (m, 2H), 7.69 (m, 2H), 7.35 (d, ³J = 8.4 Hz, 2H), 6.84 (d, ³J = 8.8 Hz, 2H), 4.77 (s, 2H), 4.08 (t, ³J = 4.0 Hz, 2H), 3.81 (t, ³J = 4.8 Hz, 2H), 3.63 (m, 38H), 3.55 (m, 2H), 3.37 (s, 3H); ¹³C NMR in CDCl₃: 165.88, 157.36, 132.87, 131.14, 129.05, 127.8, 122.29, 113.70, 70.93, 69.56, 58.02, 40.18; ESI-MS: calcd C₃₈H₅₇NO₁₄ 769.39 [M+H2O]+; found 769.72.

Detail of fitting procedures for Dynablocks and for competitive exchanges.

For all the experimental data the fitting procedure is based on a core-shell model with different form factors: spherical or cylindrical micelles. In some cases we observe coexistence between different shapes, thus the total scattering intensity Iₜₒ𝑡(q) can be described as a sum of contributions from the different objects: I(q)=I₁(q)+I₂(q)+I₃(q).

In the Supplementary Information we detailed the fits when coexistences of shapes are involved. Figures S3, S4 and S5 present the SANS curves of Dynablocks 3A, 4A and 5A. To fit the data, we used a combination of spheres form factor and vesicle form factor for 3A and 5A and a combination of cylinder and vesicle for 4A. For each case we added the form factor of rigid chain to account the behavior at high q.

Figures S6 and S7 detail the fits for exchange 2A-5A at pD=8.1 and 9 (S6) and for exchange 3A-4A at all pD (S7).
**Fig. S 3** SANS spectra of Dynablock 3A: the best fit (black solid line) is obtained by a combination of vesicle (--), sphere (--) and rigid chain (....) form factors.

**Fig. S 4** Scattering spectra of Dynablock 4A: the best fit (black solid line) is obtained by a combination of vesicle (--), cylinder (--) and rigid chain (....) form factors. (a) SANS, (b) SAXS.
**Fig. S 5** Scattering spectra of Dynablock 5A: the best fit (black solid line) is obtained by a combination of vesicle (--), sphere (--) and rigid chain (....) form factors. (a) SANS, (b) SAXS.

**Fig. S 6** Scattering spectra for exchange 2A-5A: the best fit (black solid line) is obtained by a combination of vesicle (--), cylinder (--) and rigid chain (....) form factors. (a) pD=8.1, (b) pD=9.
Fig. S 7 Scattering spectra for exchange 3A-4A: the best fit (black solid line) is obtained by a combination of vesicle (---), sphere (--) and rigid chain (....) form factors. (a) pD=6.4, (b) pD=8.9, (c) pD=10.1, (d) pD=10.5.