Supporting Information

Non-amphiphilic pyrene cored poly(aryl ether) dendron based gels: tunable morphology, unusual solvent effects on the emission and fluoride ion detection by the self-assembled superstructures

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1. Synthetic procedure and characterizations of dendrons

All compounds were synthesized according to reported procedures.¹ ²

1.1. Synthesis of compound II

A solution of 1-pyrenecarboxaldehyde (0.16 g, 0.00071 mole) in methanol was added drop wise to a CHCl₃ solution of compound b (1 g, 0.00071 mole). The mixture was stirred for 3 hours. The resulting precipitate was filtered off by suction and dried under vacuum to yield II (1.05 g, 90.5 %); ¹H NMR (400 MHz, CDCl₃) δ: 4.84-5.05 (m, ArCH₂O, 24H), 6.74-6.79 (m, ArH, 6H), 7.21-7.36 (m, ArH & PhH, 47H), 7.99 (s, PyH, 3H), 8.09-8.14 (m, PyH, 3H), 8.12-8.19(d, J = 8 Hz, PyH, 1H), 8.71(s, PyH, 2H), 9.05 (s, CH=N, 1H), 9.15 (s, CONH, 1H); ¹³C NMR (100 MHz, DMSO-d₆) δ: 70.61, 70.82, 71.16, 74.88, 74.98, 106.98, 107.57, 107.61, 108.74, 127.15, 127.55, 127.74, 128.13, 128.31, 128.46, 128.63, 128.88, 128.95, 128.98, 130.24, 130.78, 131.12, 131.30, 131.77, 131.89, 133.84, 133.98, 134.80, 134.93, 137.25, 137.41, 148.36, 151.90, 152.54, 168.29; MS (MALDI-TOF): m/z Calcd for C₁₀₈H₈₈N₂O₁₃: 1620.62, found: 1660.14[M+K]+.
1.2 Synthesis of compound III

A solution of 1-pyrenecarboxaldehyde (0.66 g, 0.0029 mole) in methanol was added drop wise to a CHCl₃ solution of compound c (1 g, 0.0029 mole) under nitrogen atmosphere. The mixture was stirred for 3 hours. The resulting precipitate was filtered off by suction and dried under vacuum to yield III (1.56 g, 93.9 %); ^1^H NMR (400 MHz, DMSO-d₆) δ: 5.19 (s, ArCH₂O, 4H), 6.95 (s, ArH, 1H), 7.26-7.49 (m, ArH & PhH, 12H), 8.11 (t, PyH, J = 7.6 Hz, 1H), 8.24 (m, PyH, 2H), 8.35 (t, PyH, J = 8.0 Hz, 4H), 8.57 (d, PyH, J=8.0 Hz, 1H), 8.79 (d, PyH, J = 9.2 Hz, 1H), 9.51 (s, CH=N, 1H), 11.95(s, CONH, 1H); ^13^C NMR (100 MHz, DMSO-d₆) δ: 69.99, 103.29, 107.72, 124.24, 124.86, 125.08, 125.21, 125.56, 125.73, 126.90, 128.17, 128.31, 128.41, 128.07, 131.13, 131.75, 138.09,144.58, 159.58, 168.4; HRMS (ES+): m/z Calcd for C₃₈H₂₈N₂O₃: 560.2100, found: 561.2189[M+H]^+.

1.3 Synthesis of compound IV

A solution of 1-pyrenecarboxaldehyde (0.298 g, 0.0013 mole) in methanol was added drop wise to a CHCl₃ solution of compound d (1 g, 0.0013 mole). The mixture was stirred for 3 hours. The
resulting precipitate was filtered off by suction and dried under vacuum to yield IV (1.2 g, 92.4 %); $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$: 5.06 (s, ArCH$_2$O, 8H), 5.11 (s, ArCH$_2$O, 4H), 6.63 (s, ArH, 2H), 6.73 (s, ArH, 4H), 6.92 (s, ArH, 1H), 7.23-7.42 (m, ArH & PhH, 22H), 8.19 (t, PyH, $J = 6.0$ Hz, 1H), 8.22 (m, PyH, 2H), 8.34 (t, PyH, $J = 6.0$ Hz, 4H), 8.57 (d, PyH, $J = 8.0$ Hz, 2H), 8.78 (d, PyH, $J = 6.0$ Hz, 2H), 9.50 (s, CH=N, 1H) 11.98 (s, CONH, 1H). $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$: 70.28, 101.80, 106.56, 125.51, 126.20, 127.30, 127.70, 127.77, 127.96, 128.17, 128.37, 128.58, 128.73, 128.74, 129.09, 130.49, 131.39, 136.86, 139.00, 160.29, 160.35, 168. MS (MALDI-TOF): m/z Calcd for C$_{66}$H$_{52}$N$_2$O$_7$: 984.37, found: 1008.2[M+Na]$^+$, 1024.4[M+K]$^+$.

2. Plots of solvent parameters Vs CGC value

Fig. S1 Effect of solvent polarity parameters a) Dielectric constant ($\varepsilon$), and b) Reichart’s parameter ($E_T$) on the CGC value for the compound IV.
Fig. S2 Effect of individual Kamlet–Taft parameter on the CGC value for the compound IV
CGC values a) $\alpha$ vs CGC, b) $\beta$ vs CGC, and c) $\pi^*$ vs CGC.

3. FT-IR spectrum of gel

Fig. S3 FT-IR spectrum of the xerogel formed from compound IV in CHCl$_3$. 
4. Powder-XRD Patterns

![Powder-XRD Patterns](image)

**Fig. S4** Powder XRD pattern of xerogel formed from a) compound I, b) compound II, c) compound III, and d) compound IV in CHCl₃.

5. Plot of phase transition temperature vs concentration

The gel-sol phase transition temperature ($T_{gel}$) was estimated to be in between 53-63 °C in THF–water mixture (0.2-1.2 wt%). The gel transition temperature increases as the concentration of the gel increases. Plot shows the linear relation between the gel transition temperature and the gel concentration for the first generation AB₂ type dendron derivatives in THF–water mixture (1:1)
Fig. S5 Effect of concentration on the gel–sol phase-transition temperature ($T_{gel}$) of compound III in THF: water mixture, measured by ball dropping method.

6. SEM images of xerogel and spherical aggregate

Fig. S6 SEM images of compound IV; a) larger vesicle formation from smaller vesicles in CHCl$_3$-MeOH, b) fibre formation from vesicles, c) finer formation in CHCl$_3$-hexane (above CGC), and d) fibre formation from compound I in THF-water.
7. Dynamic light scattering data

Fig. S7 Dynamic light scattering histograms of compounds II and IV in CHCl₃-MeOH (1: 1; v/v): [II]=[IV]=1x10⁻⁵ M for (a) and (c), and [II]=[IV]=1x10⁻⁴ M for (b) and (d).

7. AFM images of xerogel and spherical aggregates

Fig. S8 AFM images of xerogel formed from a) compound I, b) compound III, c) compound II and d) compound IV in CHCl₃.
Fig. S9 AFM images of a) compound II in CHCl₃-MeOH (below CGC), b) vesicle to fibre conversion for compound II, and c) xerogel formed from compound IV in CHCl₃-hexane (above CGC).

8. AFM images of spiral and helical structure

Fig. S10 AFM images of gel formed from toluene: a) compound I, b) compound III, and c) compound II.

9. CD spectrum

Fig. S11 CD spectrum of compound I in toluene.
10. TEM images of vesicles and gels

Fig. S12 TEM images of xerogel formed from a) compound I, b) compound III, c) compound II and d) compound IV in CHCl₃.
Fig. S13 TEM images of a) compound IV in CHCl₃-hexane (1x10⁻⁵ M), b) compound IV in CHCl₃-hexane (1x10⁻⁴), c) compound IV in CHCl₃-hexane (1x10⁻⁵ M) with higher magnification, d) compound IV in CHCl₃-MeOH (1x10⁻⁵ M) with higher magnification, e) compound II from CHCl₃-MeOH (1x10⁻⁵ M), and f) xerogel formed from compound II in CHCl₃-MeOH.
11. Steady state fluorescence spectra

Fig. S14 Emission spectra of compounds I, II, and III in the gel phase (formed from CHCl₃) (red traces in a, b and c, respectively), and in CHCl₃ solution (1x10⁻⁴ M) (black traces in a, b and c, respectively). (d) Emission spectra of compound II (gel) formed from toluene (black), CHCl₃-MeOH (red) and CHCl₃-Hexane mixtures.

12. Fluorescence decay trace

Fig. S15 Fluorescence decay of gel formed from compound IV in CHCl₃
13. UV-vis absorption spectra of compounds I, II and III in presence of various anions

Fig. S16 UV-vis absorption spectra of a) compound I (5×10^{-5} M), b) compound II (5×10^{-5} M), and c) compound III (5×10^{-5} M) in the presence of 1 equiv of various anions in THF.

14. $^1$HNMR spectra in the presence of and absence of fluoride ion

Fig. S17 $^1$H NMR spectra of compound I in DMSO-d$_6$: (a) in the presence and (b) in the absence of 1 equiv. of F$^-$ ion
16. Reference: