Electronic Supplementary Information

Scaleable two-component gelator from phthalic acid

derivatives and primary alkyl amines: Acid-base interaction in

the cooperative assembly

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Characterization of single-component gelators P



R = C_nH_{2n+1} (n = 8, 10, 12, 14, 16, 18)

P (n = 8). White solid (1.32 g, 68%); ¹H NMR (CD₃OD, 400 MHz): δ = 7.95 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.59 (dt, *J* = 7.6, 0.8 Hz, 1H), 7.51 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.41 (dd, *J* = 7.6, 0.8 Hz, 1H), 3.33 (t, *J* = 6.8 Hz, 2H), 1.65-1.58 (m, 2H), 1.40-1.32 (m, 10H); 0.92 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (CD₃OD, 100 MHz): δ = 172.8, 169.2, 140.1, 132.9, 131.3, 130.7, 130.4, 128.8, 41.1, 33.0, 30.5, 30.1, 28.1, 23.7, 14.5; ESI-HRMS Calcd for C₁₆H₂₄NO₃⁺ [M+H⁺]: 278.1751; Found: 278.1747.

P (n = 10). White solid (1.48 g, 69%); ¹H NMR (CD₃OD, 400 MHz): δ = 7.95 (dd, J = 7.6, 0.8 Hz, 1H), 7.59 (dt, J= 7.2, 1.2 Hz, 1H), 7.51 (dt, J = 7.6, 1.2 Hz, 1H), 7.41 (dd, J = 7.6, 0.8 Hz, 1H), 3.33 (t, J = 7.2 Hz, 2H), 1.65-1.58 (m, 2H), 1.38-1.31 (m, 14H); 0.91 (t, J = 6.8 Hz, 3H); ¹³C NMR (CD₃OD, 100 MHz): δ = 172.8, 169.3, 140.1, 132.9, 131.3, 130.8, 130.4, 128.8, 41.1, 33.1, 30.7, 30.5, 30.4, 30.1, 28.1, 23.7, 14.5; ESI-HRMS Calcd for C₁₈H₂₈NO₃⁺ [M+H⁺]: 306.2064; Found: 306.2061.

P (n = 12). White solid (2.20 g, 67%); ¹H NMR (CD₃OD, 400 MHz): δ = 7.94 (dd, J = 7.6, 0.8 Hz, 1H), 7.59 (dt, J= 7.6, 1.6 Hz, 1H), 7.51 (dt, J= 8.0, 1.6 Hz, 1H), 7.41 (dd, J = 7.6, 0.8 Hz, 1H), 3.33 (t, J= 7.2 Hz, 2H), 1.64-1.59 (m, 2H), 1.42-1.30 (m, 18H); 0.90 (t, J = 6.4 Hz, 3H); ¹³C NMR (CD₃OD, 100 MHz): δ = 172.9, 169.3, 140.1, 133.0, 131.3, 130.8, 130.4, 128.8, 41.1, 33.1, 30.8, 30.8, 30.7, 30.5, 30.5, 30.1, 28.1, 23.7, 14.4; ESI-HRMS Calcd for C₂₀H₃₂NO₃⁺ [M+H⁺]: 334.2377; Found: 334.2373.

P (n = 14). White solid (1.81 g, 76%); ¹H NMR (CD₃OD, 400 MHz): δ = 7.95 (d, *J* = 7.2 Hz, 1H), 7.58 (dt, *J* = 7.2, 0.8 Hz, 1H), 7.51 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.41 (d, *J* = 6.8 Hz, 1H), 3.33 (t, *J* = 7.2 Hz, 2H), 1.65-1.58 (m, 2H), 1.38-1.30 (m, 22H); 0.91 (t, *J* = 6.4 Hz, 3H); ¹³C NMR (CD₃OD, 100 MHz): δ = 172.8, 169.3, 140.1, 132.9, 131.3, 130.9, 130.4, 128.8, 41.1, 30.8. 30.8, 30.7, 30.5, 30.5, 30.1, 28.2, 23.7, 14.5; ESI-HRMS Calcd for C₂₂H₃₆NO₃⁺ [M+H⁺]: 362.2690; Found: 362.2688.

P (n = 16). White solid (1.91 g, 74%); ¹H NMR (CD₃OD/CDCl₃(4/1), 400 MHz): δ = 7.94 (d, J = 7.6 Hz, 1H), 7.56 (t, J = 7.2 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.40 (d, J = 7.6 Hz, 1H), 3.33 (t, J = 6.4 Hz, 2H), 1.63-1.59 (m, 2H), 1.36-1.28 (m, 26H); 0.89 (t, J = 6.0 Hz, 3H); ¹³C NMR (CD₃OD/CDCl₃(4/1), 100 MHz): δ = 172.5, 169.1, 139.7, 132.8, 131.1, 130.4, 130.2, 128.5, 40.9, 32.8, 30.6, 30.5, 30.5, 30.3, 30.3, 29.8, 27.9, 23.5, 14.5; ESI-HRMS Calcd for C₂₄H₄₀NO₃⁺ [M+H⁺]: 390.3008; Found: 390.3003.

P (n = 18). White solid (1.93 g, 70%); ¹H NMR (CD₃OD/CDCl₃ (4/1), 400 MHz): δ = 7.91 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.53 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.47 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.41 (dd, *J* = 7.6, 1.2 Hz, 1H), 3.33 (t, *J* = 7.2 Hz, 2H), 1.64-1.56 (m, 2H), 1.34-1.26 (m, 30H); 0.87 (t, *J* = 6.4 Hz, 3H); ¹³C NMR (CD₃OD/CDCl₃ (4/1), 100 MHz): δ = 172.1, 169.5, 138.9, 132.3, 130.8, 130.1, 128.3, 40.8, 32.6, 30.3, 30.3, 30.2, 30.0, 30.0, 29.6, 27.7, 23.3, 14.4; ESI-HRMS Calcd for C₂₆H₄₄NO₃⁺ [M+H⁺]: 418.3316; Found: 418.3312.

NMR Spectroscopy



Fig. S1 ¹H NMR of **P** ($n_P = 8$) in CD₃OD.



Fig. S2 ¹³C NMR of **P** ($n_P = 8$) in CD₃OD.



Fig. S3 ¹H NMR of **P** ($n_P = 10$) in CD₃OD.



Fig. S4 ¹³C NMR of **P** (n_P =10) in CD₃OD.



Fig. S5 ¹H NMR of **P** (n_P =12) in CD₃OD.



Fig. S6 ¹³C NMR of **P** (n_P = 12) in CD₃OD.



Fig. S7 ¹H NMR of **P** ($n_P = 14$) in CD₃OD.



Fig. S8 C^{13} NMR of **P** ($n_P = 14$) in CD₃OD.



Fig. S9 ¹H NMR of **P** ($n_P = 16$) in CD₃OD/CDCl₃ (4/1).



Fig. S10 ¹³C NMR of **P** ($n_P = 16$) in CD₃OD/CDCl₃ (4/1).



Fig. S11 ¹H NMR of **P** (n_P = 18) in CD₃OD/CDCl₃ (4/1).



Fig. S12 ¹³C NMR of **P** ($n_P = 18$) in CD₃OD/CDCl₃ (4/1).

The establishment of the best mole ratio

Table S1 Gelation abilities (MGC values in wt%) of **PA** ($n_P = n_A = 16$) with changing mole ratio in diesel.

Mole ratio	1:0.15	1:0.2	1:0.25	1:0.3	1:0.35	1:0.4	1:0.45	1:0.5	1:0.6	1:0.8	1:0.9	1:1	1:1.2
MGC (wt%)	3.27	1.84	1.53	1.35	1.20	0.83	1.01	1.01	2.93	1.38	1.15	0.92	1.76

Table S2 Gelation abilities (MGC values in wt%) of **PA** ($n_P = n_A = 18$) with changing mole ratio in paraffin oil.

Mole ratio	1:0.1	1:0.2	1:0.3	1:0.4	1:0.5	1:0.6	1:0.7	1:0.8	1:0.9	1:1	1:1.1	1:1.2	1:1.3
MGC (wt%)	0.28	0.23	0.33	0.43	0.49	0.62	1.14	1.87	1.00	1.04	1.01	1.21	0.85

X-ray diffraction data of *n*-hexadecane xerogel of P and PA



Fig.S13 XRD spectra of a: *n*-hexadecane xerogel of **P** ($n_P = 16$), b: *n*-hexadecane xerogel of **PA** ($n_P = n_A = 16$, 1:0.4)

Large-scale gelation test



Fig. S14 Gelation of 500 ml diesel with the crude products: A mixture of phthalic anhydride and 1-hexadecylamine (mole ratio was 1:1.4) was stirred in the acetone for six hours, the crude products can gel 500ml diesel in the beaker at 14.8 mg/ml (1.73 wt%).





Encouraged by the excellent gelation ability of **PA** in the diesel and paraffin oil, we were eager to know whether **PA** were good candidates for efficient phase-selective gelation in biphase mixture. We then investigated the phase-selective gelation process using a conventional heating-cooling method. In a typical experiment, gelator **PA** ($n_P = n_A = 16$, **P**:**A** = 1:0.4, 0.85 wt%) was added to a mixture of water (1 mL) and diesel (1 mL) in a vial and solubilized by heating. The resultant mixture was allowed to cool spontaneously and gelation of refined oil occurred while the aqueous phase was left intact. Furthermore, to examine the robustness of the phase- selective gelation property, we performed the process under different oil-water ratios and different types of aqueous solution (35% NaCl and 10% Acid Red 18). It was clear from the images (Fig. S16) that the presence of NaCl or Acid Red 18 ions did not affect the phase-selective gelation progress, which indicated the steady of our PSGs for practical application.



Fig. S16 Phase-selective gelation of paraffin oil and diesel in the presence of 10% Acid Red 18 solution (a and b), in the presence of 35% NaCl solution (c and d).



Fig. S17 Rheological studies for 1: recovered diesel-gel from biphase mixture (6 wt%, $n_P = n_A = 10$, **P**: **A** = 1:0.4); 2: normal diesel-gel without petroleum ether (6 wt%, $n_P = n_A = 10$, **P**: **A** = 1:0.4); 3: normal diesel-gel with petroleum ether (6 wt%, $n_P = n_A = 10$, **P**: **A** = 1:0.4). (a) stress sweep, (b) frequency sweep. Adding of the petroleum ether reduced the mechanical properties of the gel.



Fig. S18 a) Diesel solution of gelator **PA** ($n_P = n_A = 10$, **P**:**A** = 1:0.4) was spread over a crude-oil/water mixture (20 mL:400 mL). b) Gelation of the crude-oil layer after 5 min. c) Removal of the crude-oil gel with a sieved scoop. d) The removed crude-oil gel. The mass fraction of gelator used was 8 wt% to produce enough gel solidity.



Fig. S19 Representative frames of the 5 ns MD simulation (1024 frames) of the **PA**-complex in *n*-hexadecane molecules (*n*-hexadecane molecules were hidden).



Fig. S20 MD simulation of PA complex and the H-bonding network in it.

Field-emission scanning electron microscope pictures





Benzene xerogel of $P(n_P = 8)$

Benzene xerogel of PA ($n_P = n_A = 8$, P : A = 1:0.4) best ratio



Benzene xerogel of P (n_P = 16)



Benzene xerogel of PA (n_P = n_A = 16, P : A = 1:0.2)



Benzene xerogel of **PA** ($n_P = n_A = 16$, **P** : **A** = 1:0.4)



Benzene xerogel of PA ($n_P = n_A = 16$, P : A = 1:0.6) best ratio



Toluene xerogel of $P(n_P = 8)$



Toluene xerogel of **PA** ($n_P = n_A = 8$, **P** : **A** = 1:0.4) best ratio



Toluene xerogel of P (n_P = 16)



Toluene xerogel of **PA** ($n_P = n_A = 16$, **P** : **A** = 1:0.4)



Toluene xerogel of PA ($n_P = n_A = 16$, P : A = 1:0.2) best ratio



Toluene xerogel of **PA** ($n_P = n_A = 16$, **P** : **A** = 1:0.6)

From the above SEM picture we can see that: 1) for the single-component xerogel, when the carbon-chain length became longer, the structure formed thinner and longer, 2) the addition of *n*-alkyamine **A** made the structure formed longer than the corresponding single-component xerogel, 3) for the two-component xerogel, the enhancements of the ratio of **P** and **A** made the structure formed thinner.