Electronic supplementary information

A new class of amide-based organogels: from oil spill recovery to self-assembly structure analysis

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Experimental Details

1. Materials

Kerosene and DMTMM were purchased from Macklin (P.R. China). Paraffin oil (its density is 0.830–0.860 g/cm^3), benzene, toluene and cyclohexane are purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, P.R. China), undecane, dodecane, tridecane, tetradecane, pentadecane, hexadecane, p-aminobenzoic acid，ethanol，THF, n-tridecane, n-tetradecane, 2-aminopropane-1,3-diol， ethyl acetate，palmitoyl chloride, oleoyl chloride, stearoyl chloride, methanol and sodium hydroxide are all accessible from Aladdin (Shanghai, P.R. China). Acetone was purchased from Qingdao Zhengye Reagent Instrument Co., Ltd. A neighborhood gas station provided the diesel (0#). Other solvents were purchased from local distributors. All reagents were not further purified.

2. Synthesis

Compound 4-stearamidobenzoic acid: 30.00 mL acetone/water (volume ratio: 1:1) solution was added to a three-necked flask with 25.00 mmol p-aminobenzoic acid and 1.00 g NaOH. The reaction mixture was cooled to 0-15 °C. Then 26.00 mmol stearoyl chloride and 10 ml acetone was added dropwise, the reaction mixture was adjusted with NaOH about pH = 8-10, the temperature is slowly raised to 20.00-25.00 °C. After the solution is added dropwise, then the solution stayed at 25.00°C, monitored by TLC. The temperature was decreased to 0.0-15.0°C after the response has passed, and 1.00 mol·L^{-1} HCl was added dropwise to pH= 1-2. After an hour， the white solid was collected by filtration. The white solid was washed with deionized water. Yield: 9.25 g (22.92 mmoL 91.67 %).

Compounds 4-oleamidobenzoic acid and compound 4-palmitamidobenzoic acid were made using the same procedure.

Compound 4-oleamidobenzoic acid: Yield: 9.07 g (22.59 mmoL 90.34%)

Compound 4-palmitamidobenzoic acid: Yield: 8.97 g (23.88 mmoL 95.54%)

Compound N-(1,3-dihydroxypropan-2-yl)-4-stearamidobenzamide (A_{18}, Fig. S1 and S2): A_{18} was synthesized according to the literature[1, 2]. 2.00 g (5.95 mmoL) 2-aminopropane-1,3-diol and 5.95 mmoL 4-stearamidobenzoic acid and (4,6-dimethoxy-1,3,5-triazin-2-yl) DMTMM was added to 80.0 mL THF in a three-necked flask. The reaction mixture was stirred at room temperature and monitored by TLC. After the reaction is finished, Filtration was used to collect the solid, which was then washed with ethanol. The filter cake was recrystallized with ethanol. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.05 (s, 1H), 7.80 (t, J = 7.9 Hz, 3H), 7.68 – 7.62 (m, 2H), 4.64 (t, J = 5.7 Hz, 2H), 3.94 (dq, J = 7.8, 5.7 Hz, 1H), 3.51 (t, J = 5.8 Hz, 4H), 2.54 – 2.48 (m, 3H), 2.32 (t, J = 7.4 Hz, 2H), 1.59 (p, J = 7.2 Hz, 2H), 1.24 (s, 28H), 0.90 – 0.82

(m, 3H). Yield: 1.61 g (3.38 mmoL 68.16%).

Compound N-(1,3-dihydroxypropan-2-yl)-4-oleamidobenzamide (B_{18}, Fig S3 and S4): B_{18} was synthesized according to the literature[1, 2]. 2 g (4.98 mmoL) 4-oleamidobenzoic acid, 5.98 mmoL of 2-aminopropane-1,3-diol and 5.98 mmoL DMTMM in 50 ml methanol were added to three-necked flask. The reaction mixture was stirred at room temperature and monitored by TLC. After the reaction is finished, Filtration was used to collect the solid, which was then washed with ethanol. The filter cake was recrystallized with ethanol.^{1}H NMR (400 MHz, DMSO-d_6) δ 10.06 (s, 1H), 7.88 – 7.76 (m, 3H), 7.66 (d, J = 8.3 Hz, 2H), 5.38 – 5.30 (m, 2H), 4.62 (s, 2H), 3.95 (p, J = 6.4 Hz, 1H), 3.52 (d, J = 5.5 Hz, 4H), 2.32 (t, J = 7.4 Hz, 2H), 1.97 (dt, J = 19.0, 5.8 Hz, 4H), 1.59 (t, J = 7.1 Hz, 2H), 1.35 – 1.15 (m, 22H), 0.84 (d, J = 6.7 Hz, 3H). Yield: 1.47 g (3.10 mmoL 62.18%).

Compounds N-(1,3-dihydroxypropan-2-yl)-4-palmitamidobenzamide (A_{16}, Fig S5 and S6) were made using the same procedure. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.10 (d, J = 41.0 Hz, 1H), 7.91 – 7.76 (m, 3H), 7.68 (dd, J = 19.8, 8.6 Hz, 2H), 4.63 (d, J = 5.7 Hz, 2H), 3.52 (t, J = 4.9 Hz, 1H), 3.40 – 3.28 (m, 4H), 2.51 (p, J = 1.8 Hz, 2H), 2.32 (td, J = 7.4, 5.3 Hz, 2H), 2.06 (t, J = 7.4 Hz, 1H), 1.59 (t, J = 7.2 Hz, 2H), 1.24 (s, 24H), 0.85 (d, J = 7.0 Hz, 3H).Yield：2.07 g (4.61 mmoL 86.64%).

References

1. M. Kunishima, C. Kawachi, K. Hioki, K. Terao and S. Tani, *Tetrahedron*, 2001, **57**, 1551-1558.
2. M. Kunishima, C. Kawachi, J. Monta, K. Terao, F. Iwasaki and S. Tani, *Tetrahedron*, 1999, **55**, 13159-13170.

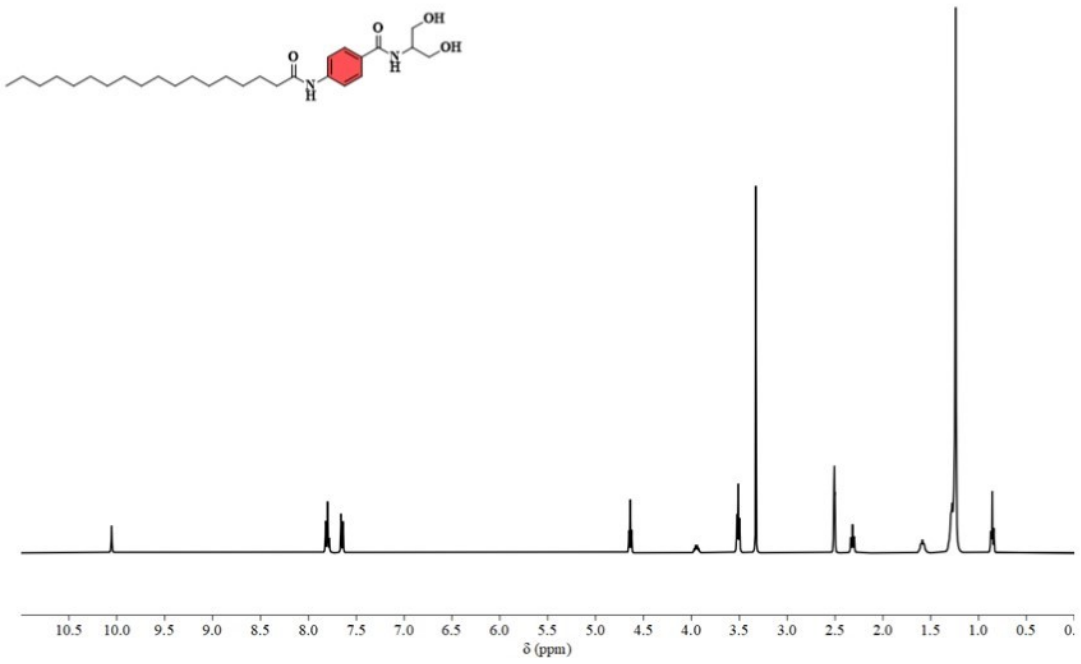

Fig. S1 ^{1}H NMR spectrum of A_{18} in DMSO-d_6 solvent.

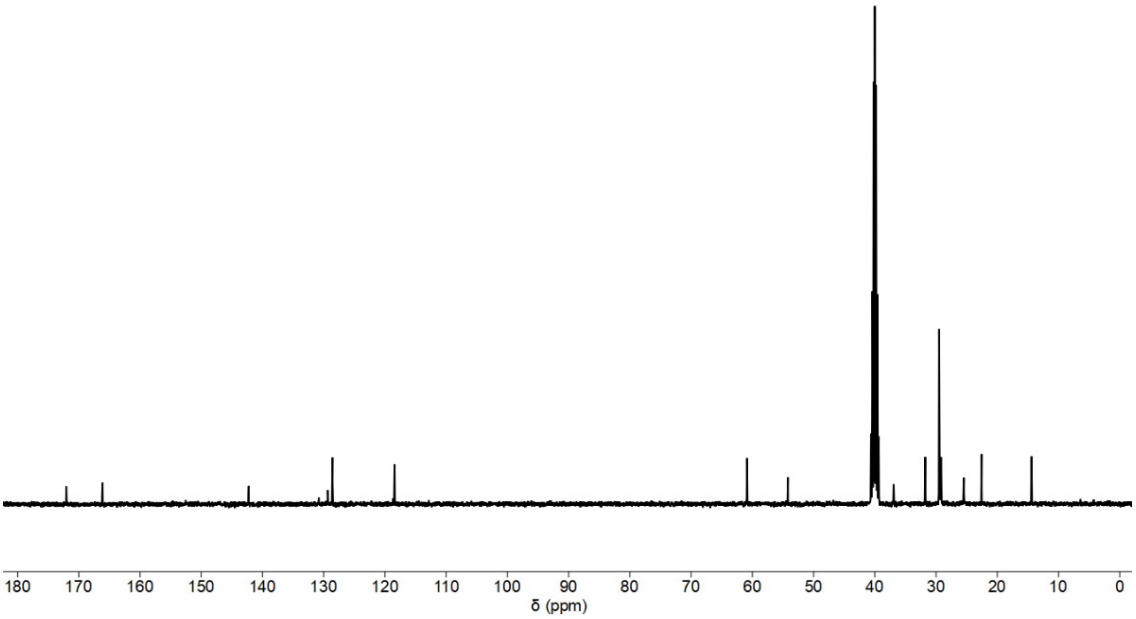

Fig. S2 ^{13}C NMR spectrum of A_{18} in DMSO-d_6 solvent.

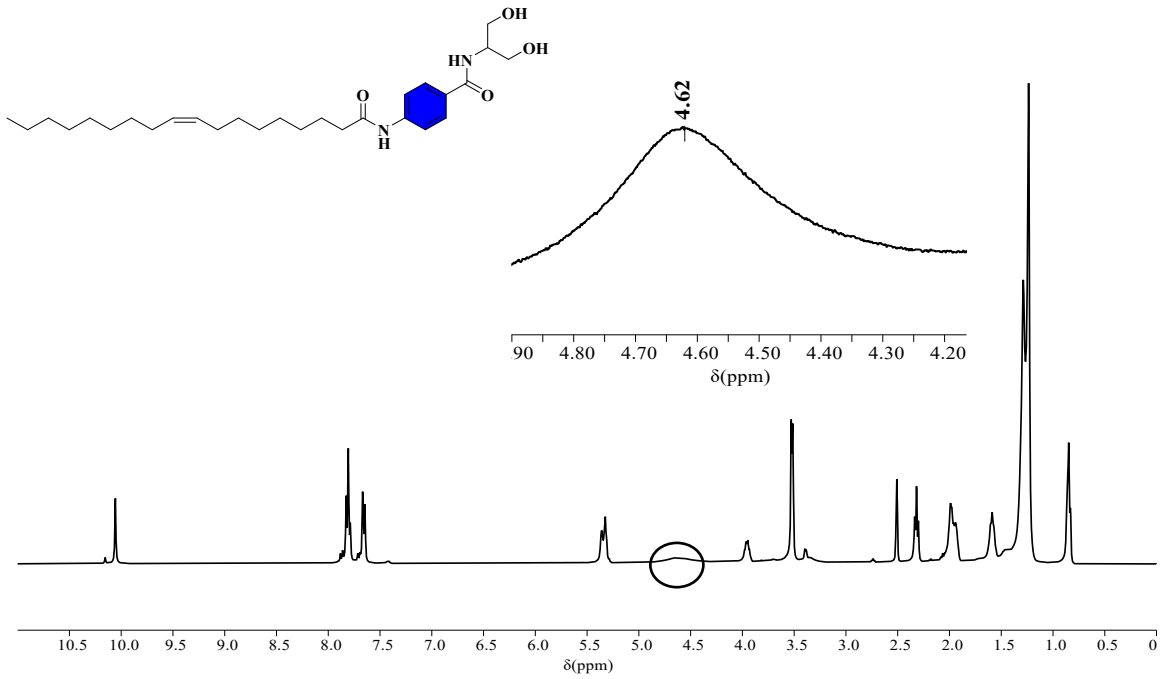

Fig. S3 ^{1}H NMR spectrum of B_{18} in DMSO-d_6 solvent.

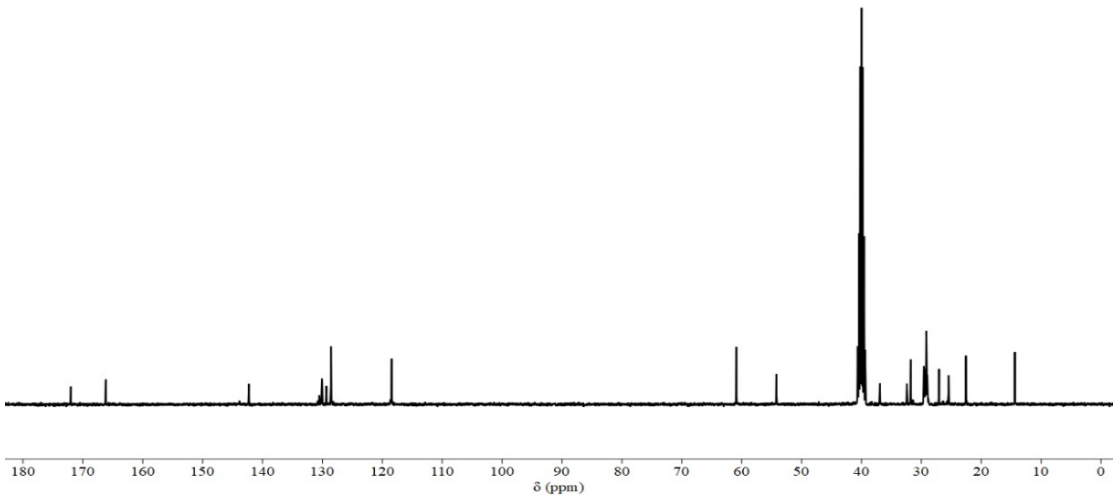

Fig. S4 ^{13}C NMR spectrum of B_{18} in DMSO-d_6 solvent.

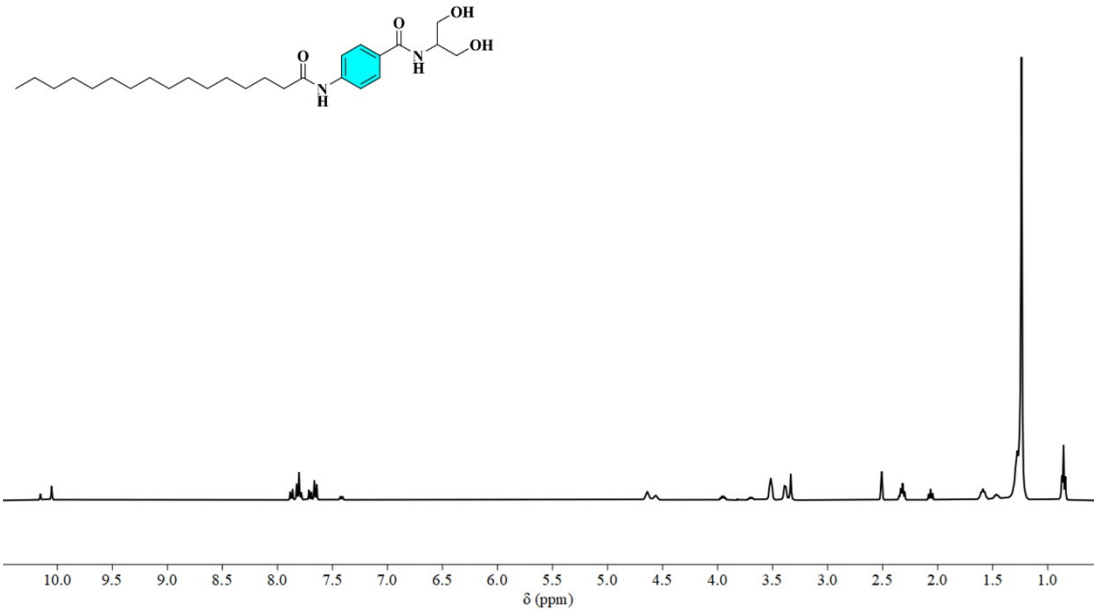

Fig. S5 ^{1}H NMR spectrum of A_{16} in DMSO-d_6 solvent.

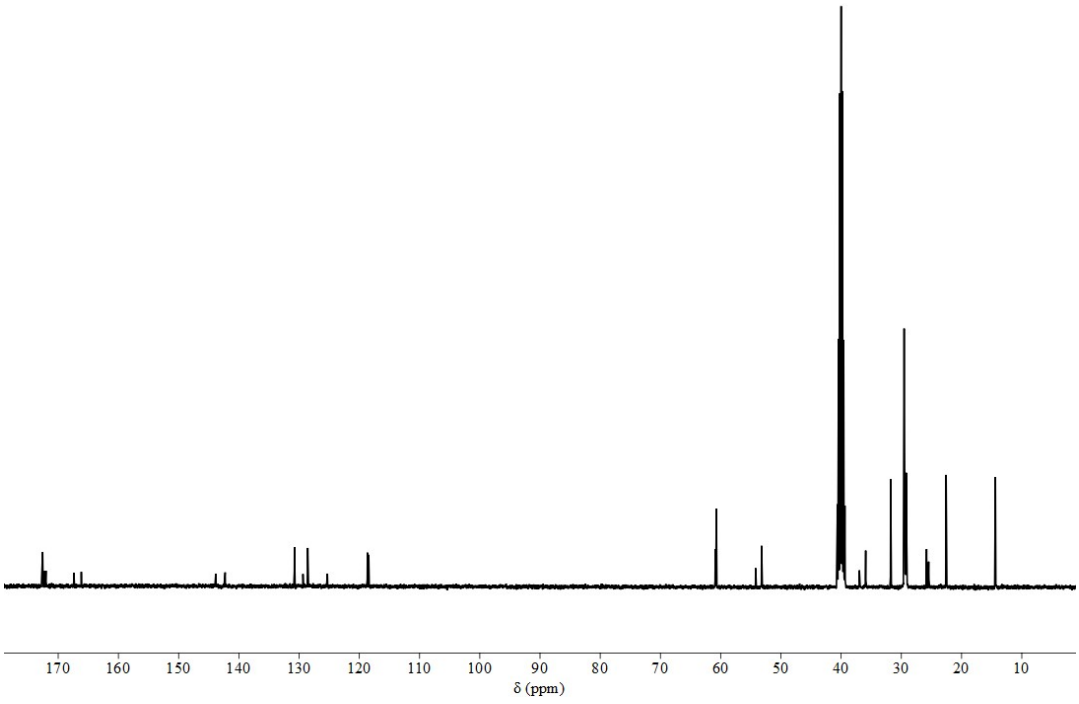

Fig. S6 ^{13}C NMR spectrum of A_{16} in DMSO-d_6 solvent.

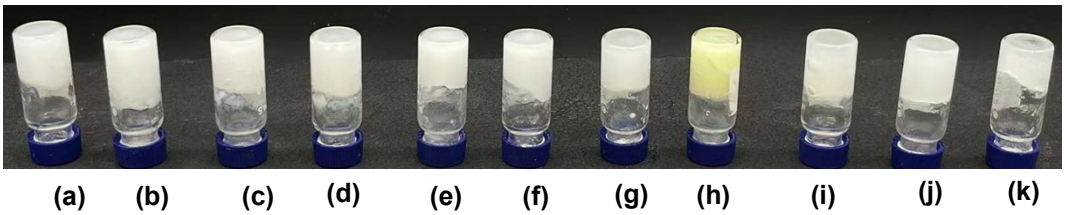

Fig. S7 The gelation test of A_{16} in (a) Cyclohexane, (b) Dodecane, (c) Tridecane, (d) Tetradecane, (e) Pentadecane, (f) Hexadecane, (g) Paraffin, (h) Diesel, (i) Kerosene, (j) Benzene, (k) Toluene.

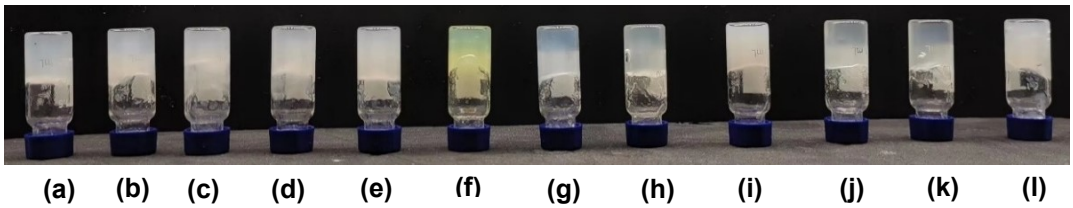

Fig. S8 The gelation test of B_{18} in (a) Paraffin, (b) Dodecane, (c) Tridecane, (d) Tetradecane, (e) Pentadecane, (f) Diesel, (g) Kerosene, (h) Toluene, (i) Dichloromethane, (j) Benzene, (k) Xylene, (l) Hexadecane.

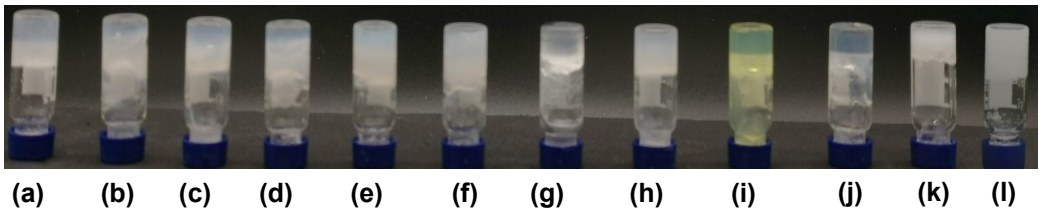

Fig. S9 The gelation test of A_{18} in (a) Cyclohexane, (b) Dodecane, (c) Tridecane, (d) Tetradecane, (e) Pentadecane, (f) Hexadecane, (g) Xylene, (h) Paraffin, (i) Diesel, (j) Kerosene, (k) Dichloromethane, (l) Acetone.

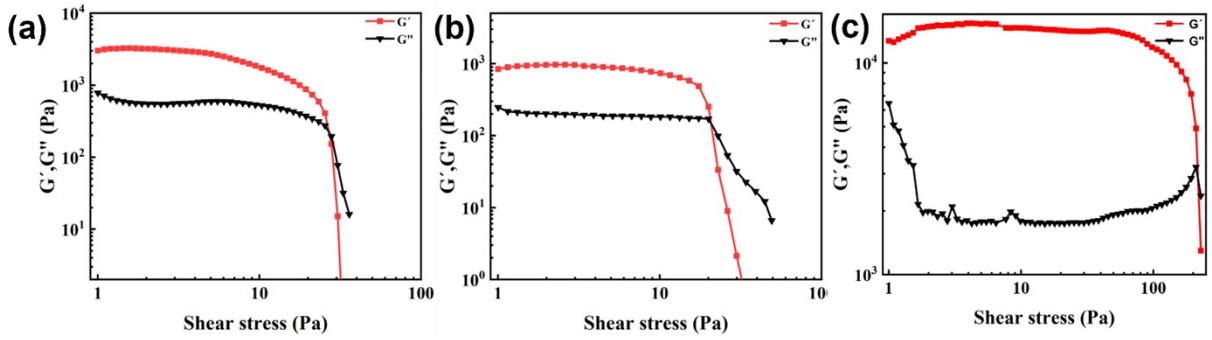

Fig. S10 Stress sweep of organogel (1.00% w/v) in dodecane: (a) A_{16}, (b) B_{18} and (c) A_{18} at 25 °C.

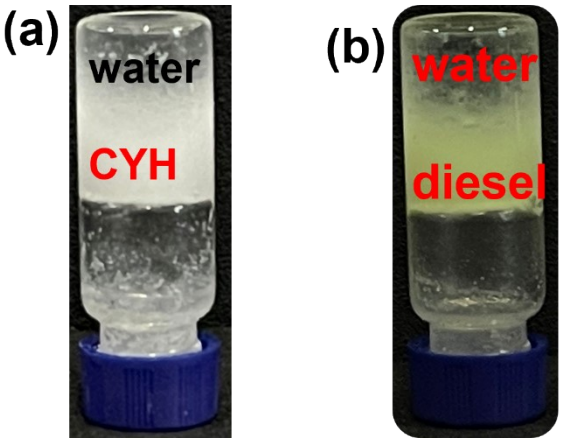

Fig. S11 (a) Organogel in cyclohexene -water mixture (volume: water: CYH = 1:1) and (b) organogel in diesel-water mixture (volume ratio: water: diesel = 1:1), CYH = cyclohexene.

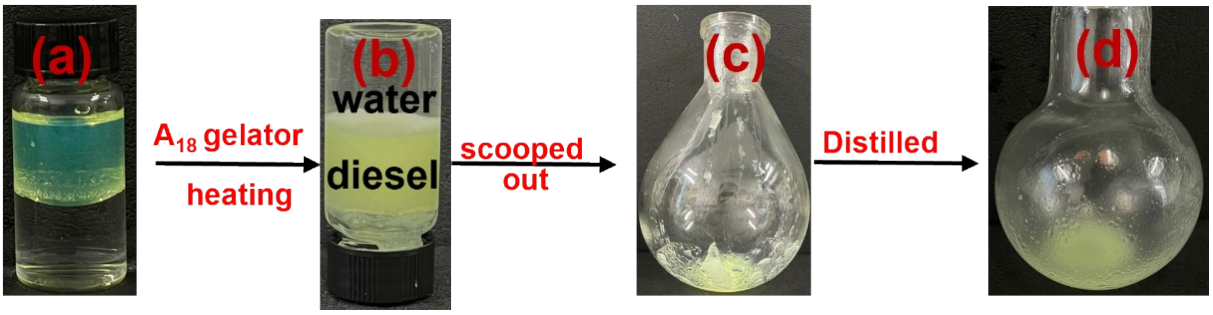

Fig. S12 (a) Diesel-water mixture, (b) formation of organogel, (c) transfer of the diesel organogel to a flask with a circular bottom and (d) recovery of diesel by vacuum distillation from the organogel.

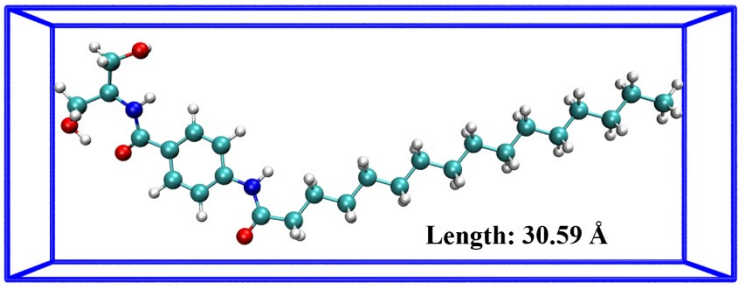

Fig. S13 Structure and length of A_{16}.

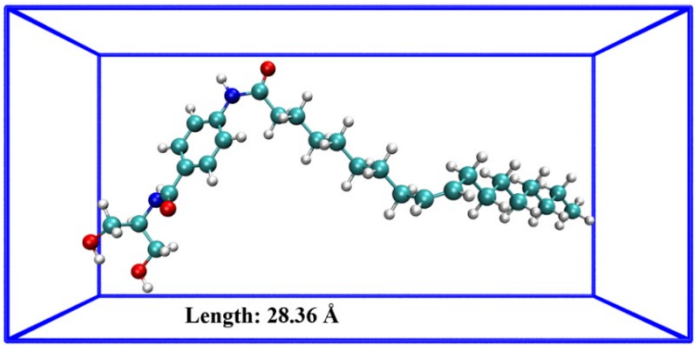

Fig. S14 Structure and length of B_{18}.

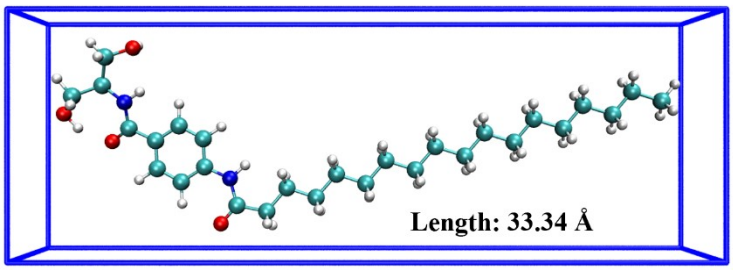

Fig. S15 Structure and length of A_{18}.

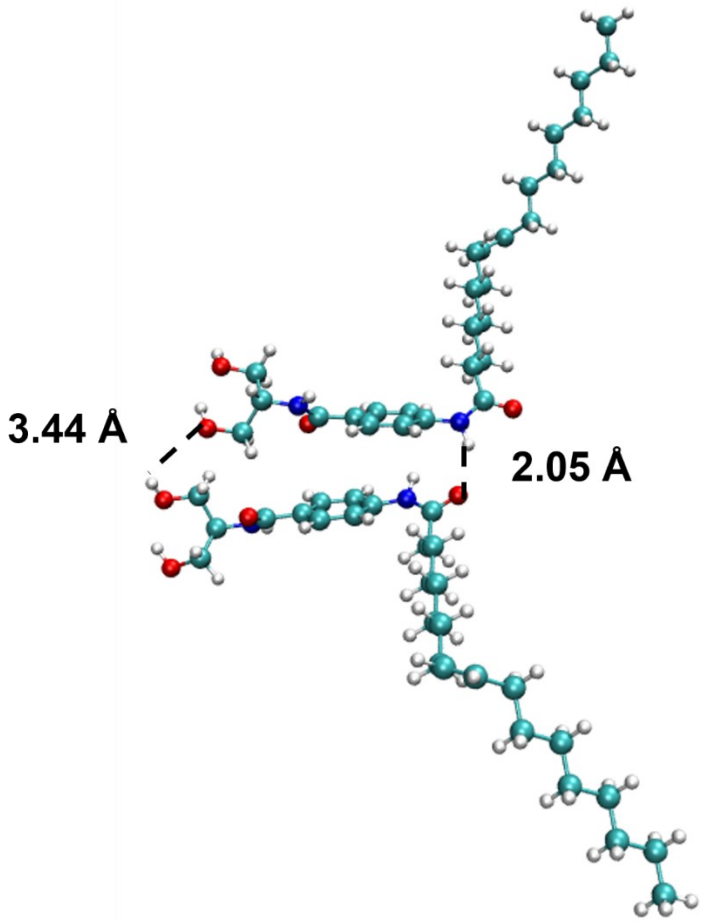

Fig. S16 Dimer structures of B_{18} (consistent with Fig.3e in the main text).

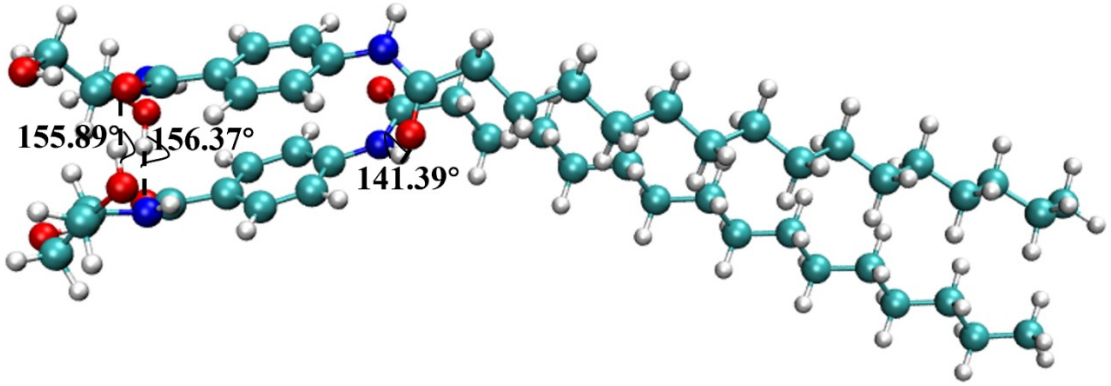

Fig. S17 Important bond angles in the A_{16} dimer.

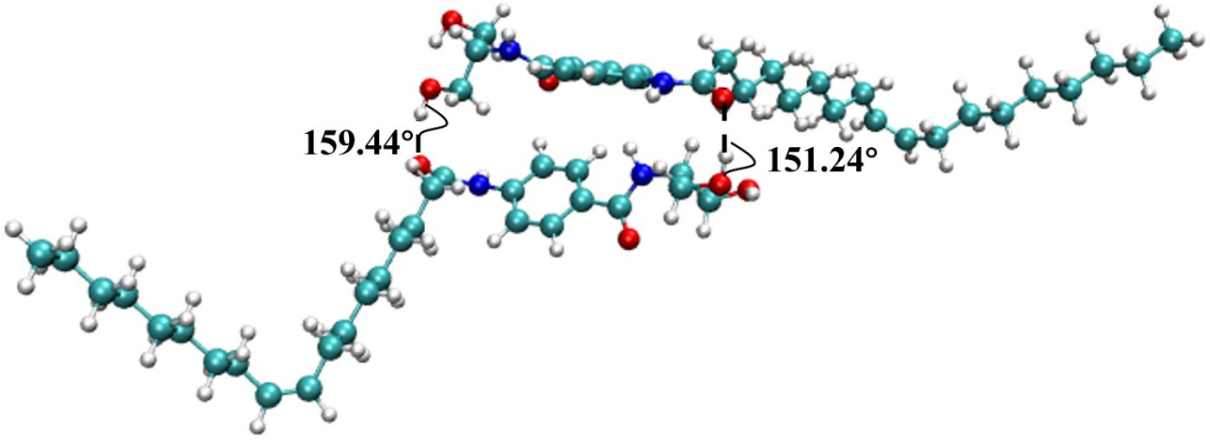

Fig. S18 Important bond angles in the B_{18} dimer.

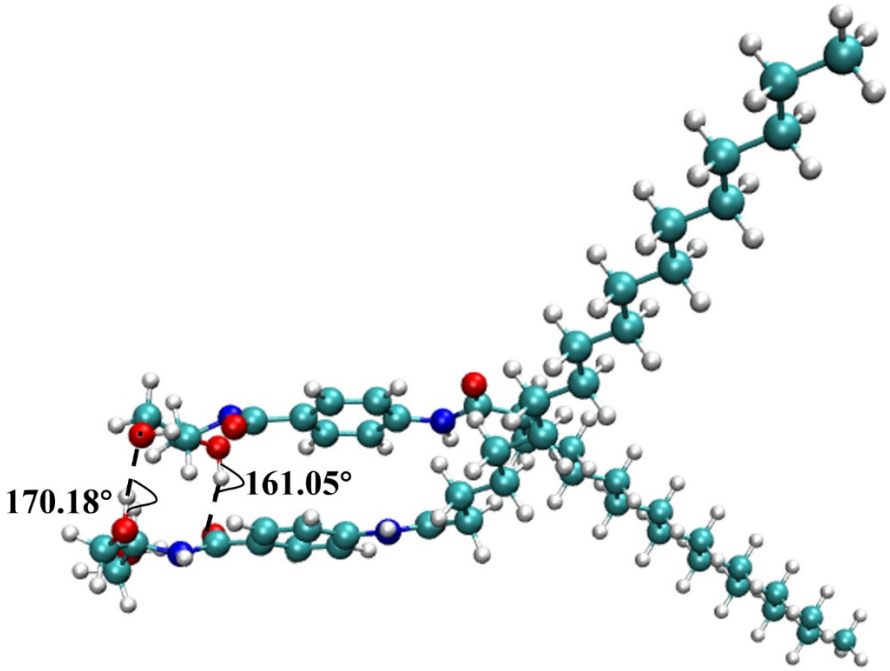

Fig. S19 Important angles in the A_{18} dimer.

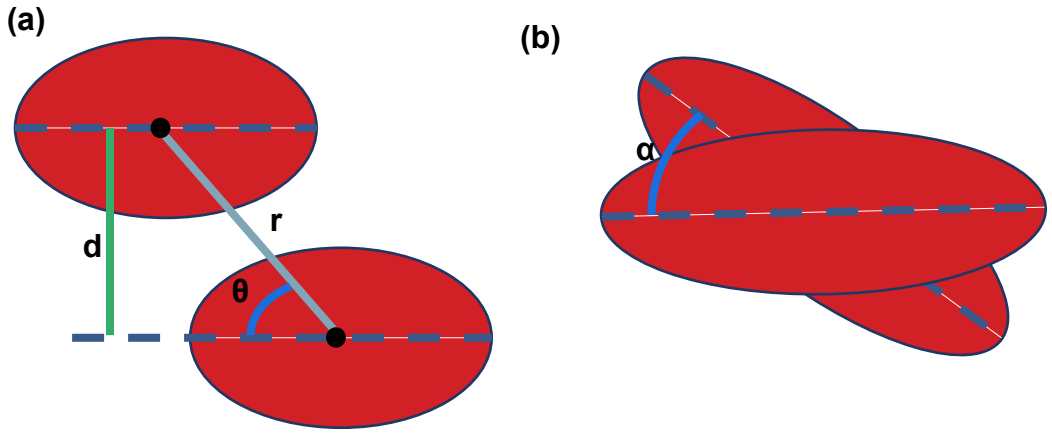

Fig. S20 Schematic diagram of slipping angle (θ) and rotational angle (α) of π-π stacking. d is the spacing between the two benzene rings and r is the distance between the centers of the two benzene rings. For (a) side view, (b) top view. The d represents the distance between the two benzene rings, and the r represents the distance between the centers of the two benzene rings.

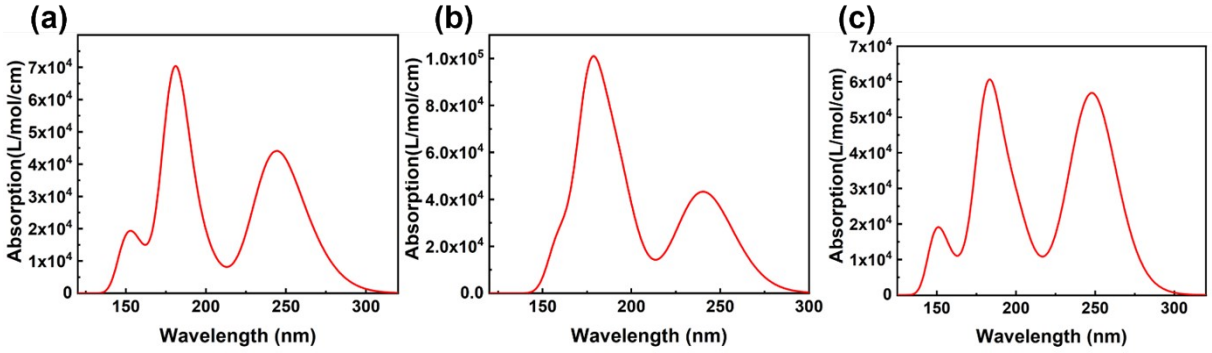

Fig. S21 UV spectroscopy calculated by Gaussian 09 for dimer of (a) A_{16}, (b) B_{18} and (c) A_{18}. TD-DFT was utilized to calculate UV at the M06-2x/6-311G(d,p) level.