Supporting Information

Gelation-driven selection in dynamic covalent C=C/C=N exchange

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Chemicals and instruments

All the chemicals were purchased from commercial chemical suppliers and used as received. Reagents: 4-hydroxybenzaldehyde (98%) was purchased from Alfa Aesar; bromoethane (99%) was purchased from Fluka; 1-bromobutane (99%), 1-bromooctane (99%), 1-Bromodecane (98%), 1-bromohexadecane (97%), 1-bromooctadecane (96%), 3,5-dihydroxybenzaldehyde (98%), 3,4,5-trihydroxybenzoate (98%), 1,3-dimethylbarbituric acid (99%), benzylamine (99%), L-proline (99%) and pyridinium chlorochromate (PCC, 98%) were purchased from Aldrich; $LiAlH_4$ (95%) was purchased from Acros; K_2CO_3 (99.8%) and $MgSO_4$ (99.2%) were purchased from VWR Prolabo Chemicals. Solvents: DMF (99.8%), THF (99%), dichloromethane (99.9%), chloroform (99-99.4%), and hexane (97.0%) were purchased from Aldrich. Deuterated solvents ($CDCl_3$: 99.80% D, water < 0.01%;

CD_3CN: 99.80% D; DMSO-d_6: 99.80% D, water < 0.02%; MeOD: 99.80% D, water < 0.03%; EtOD: 99.00% D, water < 0.3%) were purchased from *Euriso-Top* and used without further purification except $CDCl_3$, which was passed through a column of activated alumina (aluminium oxide *90* active basic).

^1H nuclear magnetic resonance (^1H NMR) spectra were recorded with a Bruker 400 spectrometer operated at 400 MHz and ^{13}C nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a Bruker 400 spectrometer operated at 101 MHz. Accurate mass data were obtained with a Bruker Technologies 10204 Accurate-Mass Q-TOF LC/MS instrument and Bruker MicroTOF (HRMS on Bruker MicroTOF-Q), with electrospray ionization. Nominal precision of the HRMS analysis is 10 ppm. Scanning electron microscopy (SEM) images were taken by QUANTA FEG 250 microscope with 5 kV operating voltage. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX 2500/PC X-ray diffractometer with CuKα radiation (λ = 0.15418 nm). The rheological properties were studied on a TA instrument (AR2000 Rheometer) equipped with a stainless steel plate of 40 mm diameter. The samples were sandwiched between the two plates with a gap of 0.5 mm throughout the experiments.

Method of preparing samples for SEM:

The silicon substrates used here were first treated in hot sulphuric acid–hydrogen peroxide solution (v/v, 7 : 3), then cleaned with water and ethanol, and stored in ethanol for further use. The silicon substrates were dried with nitrogen before use. The organogels were prepared by wiping a small amount of gel samples onto a silicon substrate followed by naturally evaporating the solvent. The solvents used here were ethanol and DMSO.

Gelation experiment:

In a typical gelation test, a weighed amount of the gelator was mixed with a measured volume of the selected solvent in a test tube, which was capped and heated until the compound dissolved. After that, the test tube was put in a room temperature environment for a while. Finally the test tubes were inverted to observe whether the content of the tube could still flow or not, thus the formation of gel (G), precipitate (P), or solution (S) was determined.

Method to determine T_{gel} and MGC:

The gel to sol transition temperature (T_{gel}) was measured by the 'inverse flow method'.[1] Specifically, after the gel formed, the test-tube was placed in an oil-bath and the bath was warmed gradually at the rate of about 1℃ per minute. The temperature at which the sol fell to the bottom of the test-tube was taken to be the melting point.

The MGC is the lowest possible gelator concentration needed to form a stable gel. A lower MGC is desired to minimize the amount of gelator material needed to form gels. Here we used 1 mg gelator and added solvents gradually from 100 μL until it did not form a gel, then we calculated the MGC for the gelators.

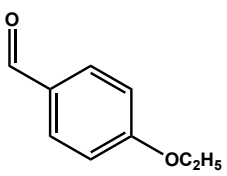
General procedure for C=C/C=N exchange:

Equimolar amounts of Knoevenagel and imine were mixed in the solution, and the final solution was 10 mM for each starting component. The %-composition of the reactions at different time was determined by integration of the corresponding ^{1}H-NMR signals.

General procedure for the synthesis of aldehydes:

To a 250 mL round-bottom flask equipped with a magnetic stirrer, 4-hydroxybenzaldehyde (0.305 g, 2.5 mmol) (or 0.345 g 3,5-dihydroxybenzaldehyde for two chains) and K_2CO_3 (0.691 g, 5.0 mmol) were dissolved in DMF (80 mL), and then RBr (5.0 mmol, 0.545 g bromoethane, 0.685 g 1-bromobutane, 0.965 g 1-bromooctane, 1.527 g 1-bromohexadecane, or 1.667 g 1-bromooctadecane for one chain; 7.5 mmol, 2.290 g 1-bromohexadecane for two chains; R: alkyl chain) was added dropwise. The reaction mixture was heating at 80°C for 24 h, and then the reaction mixture was cooled to room temperature and filtered. The solvent was extracted with chloroform (3×50 mL).The combined extracts were washed with water three times (3×50 mL) and dried over anhydrous $MgSO_4$ and the solvent was evaporated via rotary evaporation. The crude product was further purified by silica gel (40-63 μm) column chromatography using hexane-chloroform (5:1; v:v) as eluting solvents

4-ethoxybenzaldehyde:[2]

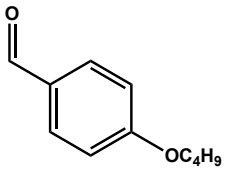


Colorless oil. Yield: 88.9%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H, -CHO), 7.82 (d, J = 8.8 Hz, 2H, -Ar), 6.98 (d, J = 8.7 Hz, 2H, -Ar), 4.12 (t, J = 10.5 Hz,

2H, -OCH_2), 1.45 (t, J = 7.0 Hz, 3H, -CH_3).

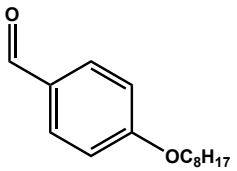
4-butoxybenzaldehyde:[2]



Pale Yellow oil. Yield: 87.6%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 1H, -CHO), 7.83 (d, J = 8.8 Hz, 2H, -Ar), 6.99 (d, J = 8.7 Hz, 2H, -Ar), 4.05 (t, J = 6.5 Hz, 2H, -OCH_2), 1.89 – 1.74 (m, 2H, -CH_2), 1.55 – 1.42 (m, 2H, -CH_2), 0.99 (t, J = 7.4 Hz, 3H, -CH_3).

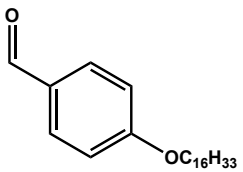
4-(octyloxy)benzaldehyde:[3]



Pale yellow oil. Yield: 92.2%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H, -CHO), 7.81 (d, J = 8.8 Hz, 2H, -Ar), 6.98 (d, J = 8.7 Hz, 2H, -Ar), 4.03 (t, J = 6.6 Hz, 2H, -OCH_2), 1.84 – 1.77 (m, 2H, -CH_2), 1.49 – 1.42 (m, 2H, -CH_2), 1.34– 1.28 (m, 8H, -CH_2), 0.88 (t, J = 6.8 Hz, 3H, -CH_3).

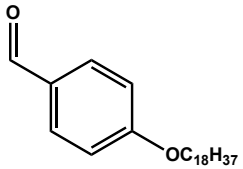
4-(hexadecyloxy)benzaldehyde:[4]



White solid. Yield: 79.7%. m.p. 38.2-40.3℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H, -CHO), 7.82 (d, J = 8.8 Hz, 2H, -Ar), 6.99 (d, J = 8.7 Hz, 2H, -Ar), 4.03 (t, J = 6.6 Hz, 2H, -OCH_2), 1.84 – 1.77 (m, 2H, -CH_2), 1.49 – 1.21 (m, 26H, -CH_2), 0.88 (t, J = 6.8 Hz, 3H, -CH_3).

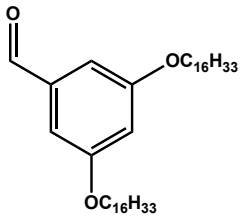
4-(octadecyloxy)benzaldehyde:[5]



White solid. Yield: 78.7%. m.p. 58.5-60.8℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 1H, -CHO), 7.82 (d, J = 8.8 Hz, 2H, -Ar), 6.99 (d, J = 8.7 Hz, 2H, -Ar), 4.03 (t, J = 6.6 Hz, 2H, -OCH_2), 1.87 – 1.72 (m, 2H, -CH_2), 1.52 – 1.40 (m, 2H, -CH_2), 1.36 – 1.17 (m, 28H, -CH_2), 0.88 (t, J = 6.8 Hz, 3H, -CH_3).

3,5-bis(hexadecyloxy)benzaldehyde:[4]

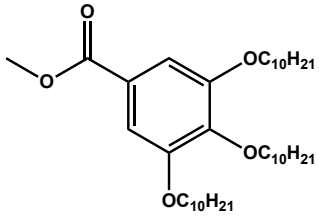


White solid. Yield: 82.6%. m.p. 56.7-58.3℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H, -CHO), 6.98 (d, *J* = 2.3 Hz, 2H, -Ar), 6.69 (t, *J* = 2.3 Hz, 1H, -Ar), 3.98 (t, *J* = 6.6 Hz, 4H, -OCH_2), 1.85 – 1.70 (m, 4H, -CH_2), 1.52 – 1.38 (m, 4H, -CH_2), 1.37 – 1.16 (m, 48H, -CH_2), 0.88 (t, *J* = 6.8 Hz, 6H, -CH_3).

Methyl 3,4,5-tris(decyloxy)benzoate:[6]

To a 250mL round-bottom flask equipped with a magnetic stirrer, methyl 3,4,5-trihydroxybenzoate (0.921 g, 5.0 mmol) and K_2CO_3 (2.764 g, 20.0 mmol) were dissolved in DMF (80 mL), and then 1-bromodecane (3.683 g, 20.0 mmol) was added dropwise. The reaction mixture was heating at 80°C for 24 h, then the reaction mixture was cooled to room temperature and filtered. The solvent was extracted with chloroform (3×50 mL).The combined extracts were washed with water three times (3×50 mL) and dried over anhydrous $MgSO_4$ and the solvent was evaporated via rotary evaporation. The crude product was further purified by silica gel (40-63 μm) column chromatography using dichloromethane as eluting solvents.



Pale yellow oil. Yield: 54.7%.

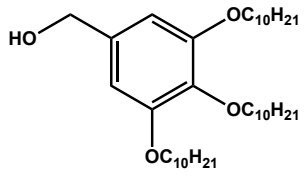
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (s, 2H, -Ar), 4.01 (m, 6H, -OCH_2), 3.88 (s, 3H,-OCH_3), 1.88 – 1.68 (m, 6H, -CH_2), 1.54 – 1.41 (m, 6H, -CH_2), 1.39 – 1.22 (m, 36H, -CH_2), 0.88 (t, *J* = 6.8 Hz, 9H, -CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.08, 152.96, 142.53, 124.79, 108.14, 73.62, 69.31, 52.22, 32.08, 32.06, 30.47, 29.87, 29.81, 29.78, 29.73, 29.71, 29.64, 29.53, 29.49, 29.45, 26.22, 26.20, 22.83, 14.24.

(3,4,5-tris(decyloxy)phenyl)methanol[6]

$LiAlH_4$ (0.3 g, 4.0 mmol) was suspended in dry THF (10 mL), and the solution of methyl 3,4,5-tris(decyloxy)benzoate (2.4 g, 2.0 mmol) in THF (5 mL) was added slowly dropwise at 0 °C in an ice-water bath. After all of the THF solution had been

added, the ice-water bath was removed and the temperature was increased to 30 °C. The reagents were stirred at 30 °C for 20 h. Subsequently, a small quantity of H_2O was added to consume the unreacted $LiAlH_4$. Then, hydrochloric acid was used to neutralize the reaction. The mixture was extracted three times by adding dichloromethane. Next, the liquid ballistic under layers was obtained, dried over $MgSO_4$, and filtered to remove the solvent. The product was further purified by silica gel (40-63 μm) column chromatography using dichloromethane as eluting solvents.



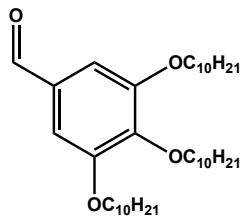
White solid. Yield: 65.0%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.56 (s, 1H), 4.59 (d, J = 5.8 Hz, 1H), 4.02 – 3.89 (m, 3H), 1.86 – 1.69 (m, 3H), 1.52 – 1.40 (m, 4H), 1.36 – 1.20 (m, 21H), 0.88 (t, J = 6.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.44, 137.78, 136.16, 105.53, 77.16, 73.59, 69.27, 65.84, 32.09, 32.07, 30.48, 29.90, 29.83, 29.80, 29.77, 29.75, 29.66, 29.57, 29.50, 26.29, 26.25, 22.84, 14.26.

3,4,5-tris(decyloxy)benzaldehyde:[7]

To a mixture of PCC (0.99 g, 4.5 mmol) and CH_2Cl_2 (10 mL) was added (3,4,5-tris(decyloxy)phenyl)methanol (1.73 g, 3.0 mmol) in 5 mL of CH_2Cl_2 at 0 C. The mixture was stirred at room temperature overnight. After the solvent was removed at reduced pressure, the residue was purified by a chromatography on silica gel (40-63 μm) using chloromethane as eluting solvents give the product.



White solid. Yield: 62.8%. m.p. 34.2-35.5℃.

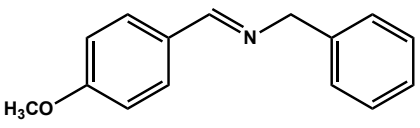
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H, -CHO), 7.08 (s, 2H, -Ar), 4.04 (m, 6H, -OCH_2), 1.88 – 1.78 (m, 4H, -CH_2), 1.74 (m, 2H, -CH_2), 1.47 (m, 6H, -CH_2), 1.40 – 1.21 (m, 36H, -CH_2), 0.88 (t, J = 6.7 Hz, 9H, -CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.43, 153.67, 144.02, 131.59, 108.01, 73.78, 69.39, 32.08, 32.06, 30.49, 29.86, 29.81, 29.77, 29.73, 29.69, 29.52, 29.49, 29.41, 26.21, 26.17, 22.83, 14.25.

General procedure for the synthesis of imines:

Equimolar amounts of benzylamine (0.054 g, 0.5 mmol) and aldehyde (0.5 mmol) were dissolved in ethanol (~3 mL), and heated to reflux for 8 hours. After moving solvent via rotary evaporation and drying under vacuum, the products were got as solid or oil.

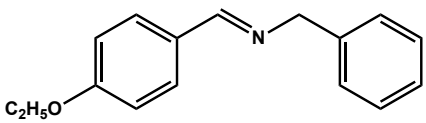
(E)-N-(4-methoxybenzylidene)-1-phenylmethanamine (**I'**):[8]



Pale yellow solid. Yield: 60.8%. m.p. 29.2-30.6℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H, -CH=N), 7.79 – 7.71 (m, 2H, -Ar), 7.38 – 7.30 (m, 4H, -Ar), 7.26 (emerged in CDCl3, 1H, -Ar), 6.93 (d, J = 8.8 Hz, 2H, -Ar), 4.79 (s, 2H, -CH_2), 3.85 (s, 3H, -CH_3).

(E)-N-(4-ethoxybenzylidene)-1-phenylmethanamine (**I-2**):



White solid. Yield: 68.2%. m.p. 52.6-54.3℃.

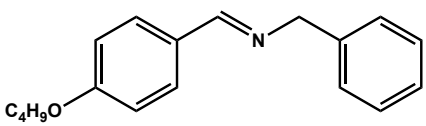
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H, -CH=N), 7.72 (d, J = 8.7 Hz, 2H, -Ar), 7.35-7.33 (m, 4H, -Ar), 7.28 – 7.23 (m, 1H, -Ar), 6.92 (d, J = 8.7 Hz, 2H, -Ar), 4.79 (s, 2H, -CH_2), 4.07 (q, J = 7.0 Hz, 2H, -OCH_2), 1.43 (t, J = 7.0 Hz, 3H, -CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.39, 161.19, 139.72, 129.90, 129.06, 128.52, 128.02, 126.95, 114.55, 77.16, 65.03, 63.61, 14.82.

LC-MS (m/z) calcd. for [$C_{16}H_{17}NO+H^+$] 240.14; found. 240.02

Elemental Analysis: C, 80.30; H, 7.16; N, 5.85; O, 6.69; found: C, 80.23; H, 7.08; N, 5.87; O, 6.82

(E)-N-(4-butoxybenzylidene)-1-phenylmethanamine (**I-4**):

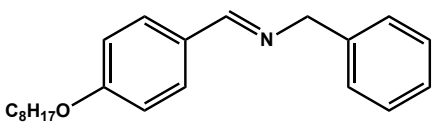


Orange oil. Yield: 75.2%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H, -CH=N), 7.71 (d, J = 8.7 Hz, 2H, -Ar), 7.40 – 7.28 (m, 4H, -Ar), 7.27 (m,1H, -Ar), 6.92 (d, J = 8.7 Hz, 2H, -Ar), 4.79 (s, 2H, -CH_2), 4.00

(t, J = 6.5 Hz, 2H, -OCH_2), 1.84 – 1.73 (m, 2H, -CH_2), 1.50 (m, 2H, -CH_2), 0.98 (t, J = 7.4 Hz, 3H, -CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.42, 161.40, 139.67, 129.88, 128.94, 128.63, 128.48, 127.99, 126.92, 114.54, 67.80, 64.96, 31.28, 19.26, 13.90.
LC-MS (m/z) calcd. for [$C_{18}H_{21}NO+H^+$] 268.17; found. 268.06.

(E)-N-(4-(octyloxy)benzylidene)-1-phenylmethanamine (**I-8**):

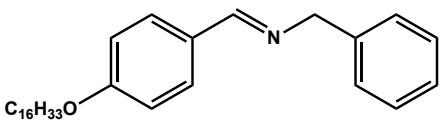


White solid. Yield: 78.8%. m.p. 42.1-43.4℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H, -CH=N), 7.71 (d, J = 8.8 Hz, 2H, -Ar), 7.35 – 7.32 (m, 4H, -Ar), 7.28 – 7.23 (m, 1H, -Ar), 6.92 (d, J = 8.8 Hz, 2H, -Ar), 4.79 (s, 2H, -CH_2), 3.99 (t, J = 6.6 Hz, 2H, -OCH_2), 1.88 – 1.70 (m, 2H, -CH_2), 1.46 (m, 2H, -CH_2), 1.39 – 1.14 (m, 8H, -CH_2), 0.89 (t, J = 6.9 Hz, 4H, -CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.46, 139.77, 129.92, 129.05, 128.56, 128.07, 126.99, 114.62, 68.24, 65.10, 31.94, 29.47, 29.36, 29.32, 26.14, 22.78, 14.23.
LC-MS (m/z) calcd. for [$C_{22}H_{29}NO+H^+$] 324.23; found. 324.12.

Elemental Analysis: C, 81.69; H, 9.04; N, 4.33; O, 4.95; found: C, 81.68; H, 8.98; N, 4.33; O, 5.01.

(E)-N-(4-(hexadecyloxy)benzylidene)-1-phenylmethanamine (**I-16**):

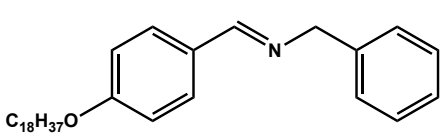


White solid. Yield: 66.7%. m.p. 55.5-56.5℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H, -CH=N), 7.72 (d, J = 8.4 Hz, 2H, -Ar), 7.39 – 7.28 (m,4H, -Ar), 7.28 – 7.23 (m, 1H, -Ar), 6.92 (d, J = 8.8 Hz, 2H, -Ar), 4.79 (s, 2H, -CH_2), 3.99 (t, J = 6.6 Hz, 2H, -OCH_2), 1.85 – 1.71 (m, 2H, -CH_2), 1.48 – 1.38 (m, 2H, -CH_2), 1.38 – 1.15 (m, 24H, -CH_2), 0.88 (t, J = 6.9 Hz, 3H, -CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.48, 139.77, 129.93, 129.06, 128.57, 128.08, 127.00, 114.63, 68.26, 65.11, 32.07, 29.84, 29.81, 29.74, 29.71, 29.53, 29.51, 29.34, 26.15, 22.84, 14.26.
LC-MS (m/z) calcd. for [$C_{30}H_{45}NO+H^+$] 436.36; found. .436.31.

Elemental Analysis: C, 82.70; H, 10.41; N, 3.21; O, 3.67; found: C, 82.60; H, 10.37; N, 3.25; O, 3.78.

(E)-N-(4-(octadecyloxy)benzylidene)-1-phenylmethanamine (**I-18**):



White solid. Yield: 73.7%. m.p. 61.1-62.5℃.

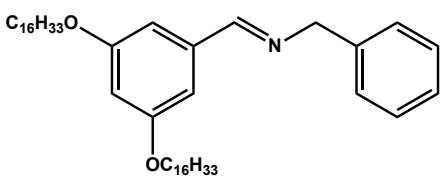
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H, -CH=N), 7.71 (d, *J* = 8.8 Hz, 2H, -Ar), 7.33 (d, *J* = 4.7 Hz, 4H, -Ar), 7.30 – 7.22 (m, 1H, -Ar), 6.91 (d, *J* = 8.8 Hz, 2H, -Ar), 4.79 (s, 2H, -CH_2), 3.99 (t, *J* = 6.6 Hz, 2H, -OCH_2), 1.89 – 1.72 (m, 2H, -CH_2), 1.50 – 1.39 (m, 2H, -CH_2), 1.40 – 1.19 (m, 28H, -CH_2), 0.88 (t, *J* = 6.8 Hz, 3H, -CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.49, 139.77, 129.94, 129.06, 128.58, 128.08, 127.01, 114.64, 68.26, 65.11, 32.07, 29.85, 29.81, 29.74, 29.71, 29.53, 29.51, 29.34, 26.16, 22.84, 14.27.

LC-MS (m/z) calcd. for [$C_{32}H_{49}NO+H^+$] 464.39; found. 464.35.

Elemental Analysis: C, 82.88; H, 10.65; N, 3.02; O, 3.45; found: C, 82.39; H, 10.57; N, 3.04; O, 4.00.

(E)-N-(3,5-bis(hexadecyloxy)benzylidene)-1-phenylmethanamine (**I-(16)$_2$**):



White solid. Yield: 82.1%. m.p. 57.0-58.3℃.

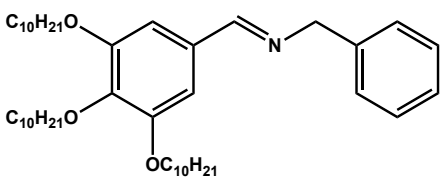
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.43 – 7.30 (m, 4H), 7.27 (m, 1H), 6.91 (s, 2H), 6.52 (s, 1H), 4.82 (s, 2H), 3.96 (t, *J* = 6.6 Hz, 4H), 1.82 – 1.70 (m, 4H), 1.48 – 1.38 (m, 4H), 1.38 – 1.12 (m, 48H), 0.88 (t, *J* = 6.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.30, 160.63, 139.37, 138.20, 128.62, 128.14, 127.13, 106.61, 104.51, 68.38, 65.07, 32.08, 29.85, 29.82, 29.76, 29.73, 29.54, 29.52, 29.39, 26.18, 22.84, 14.27.

HRMS (ESI, m/z) calcd. for [$C_{46}H_{77}NO_2+H^+$] 676.61; found. .676.60

Elemental Analysis: C, 81.72; H, 11.48; N, 2.07; O, 4.73; found: C, 81.73; H, 11.32; N, 1.98; O, 4.97.

(E)-1-phenyl-N-(3,4,5-tris(decyloxy)benzylidene)methanamine (**I-(10)$_3$**):



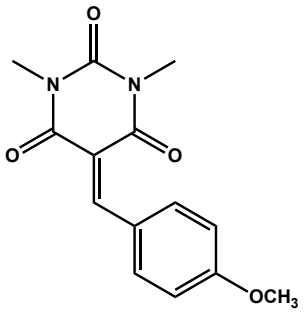
Pale orange oil. Yield: 91.9%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.43 – 7.29 (m, 4H), 7.29 – 7.18 (m, 1H), 6.98 (s, 2H), 4.80 (s, 2H), 4.10 – 3.93 (m, 6H), 1.89 – 1.67 (m, 6H), 1.53 – 1.39 (m, 6H), 1.28 (m, 36H), 0.88 (t, *J* = 6.8 Hz, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.06, 153.47, 140.80, 139.44, 131.35, 128.58, 128.12, 127.08, 106.75, 73.60, 69.30, 64.99, 32.07, 32.05, 30.47, 29.87, 29.81, 29.77, 29.72, 29.53, 29.52, 29.48, 26.22, 22.82, 14.24.
HRMS (ESI, m/z) calcd. for [$C_{44}H_{73}NO_3$+H^+] 664.57; found. 664.56.

General procedure for the synthesis of Knoevenagel condensation products:

Equimolar of 1,3-dimethylbarbituric acid (0.078 g, 0.5 mmol) and corresponding aldehyde (0.5 mmol) were dissolved in ethanol (~3 mL), then a catalyst amount of L-proline (10%) was added. The solution was refluxed for about 4 hours. After cooling the solution, precipitate was filtered. After drying under vacuum, the products were isolated as solid.

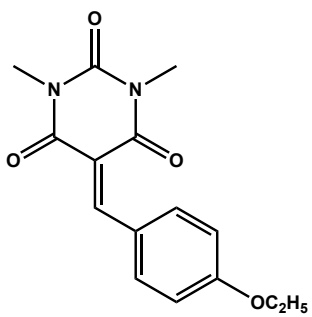
5-(4-methoxybenzylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (**K**):[9]



Yellow solid. Yield: 84.2%. m.p. 148.4-149.4℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H, -CH=C), 8.33 (d, *J* = 8.8 Hz, 2H, -Ar), 6.98 (d, *J* = 9.0 Hz, 2H, -Ar), 3.91 (s, 3H, -CH_3), 3.42 (s, 3H, -CH_3), 3.40 (s, 3H, -CH_3).

5-(4-ethoxybenzylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (**K'-2**):[10]

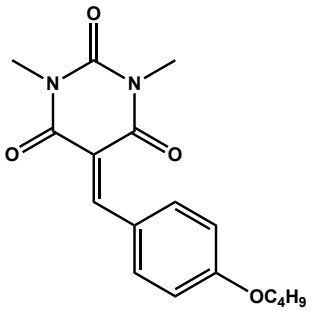


Yellow solid. Yield: 67.6%. m.p. 175.0-176.5℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H, -CH=C), 8.33 (d, *J* = 8.9 Hz, 2H, -Ar), 6.96 (d, *J* = 9.0 Hz, 2H, -Ar), 4.14 (q, *J* = 7.0 Hz, 2H, -OCH_2), 3.42 (s, 3H, -CH_3), 3.40 (s, 3H, -CH_3), 1.46 (t, *J* = 7.0 Hz, 3H, -CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.86, 163.16, 161.03, 158.82, 151.44, 138.16, 125.39, 114.43, 114.11, 64.04, 29.06, 28.38, 14.66.

5-(4-butoxybenzylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (**K'-4**):



Yellow solid. Yield: 74.7%. m.p. 127.9-129.2℃.

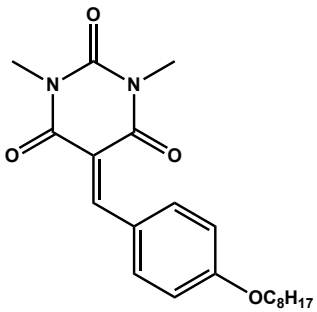
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H, -CH=C), 8.33 (d, *J* = 8.9 Hz, 2H, -Ar), 6.96 (d, *J* = 9.0 Hz, 2H, -Ar), 4.07 (t, *J* = 6.5 Hz, 2H, -OCH_2), 3.42 (s, 3H, -CH_3), 3.40 (s, 3H, -CH_3), 1.88 – 1.71 (m, 2H, -CH_2), 1.62 – 1.42 (m, 2H, -CH_2), 0.99 (t, *J* = 7.4 Hz, 3H, -CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.15, 163.24, 161.09, 158.96, 151.51, 138.19, 125.39, 114.51, 114.11, 68.25, 31.13, 29.11, 28.43, 19.24, 13.87.

LC-MS (m/z) calcd. for [$C_{17}H_{20}N_2O_4$+H^+] 317.15; found. 317.06.

Elemental Analysis:C, 64.54; H, 6.37; N, 8.86; O, 20.23; found: C, 64.60; H, 6.31; N, 8.85; O, 20.24.

1,3-dimethyl-5-(4-(octyloxy)benzylidene)pyrimidine-2,4,6(1H,3H,5H)-trione (**K'-8**):



Yellow solid. Yield: 76.3%. m.p. 96.1-97.3℃.

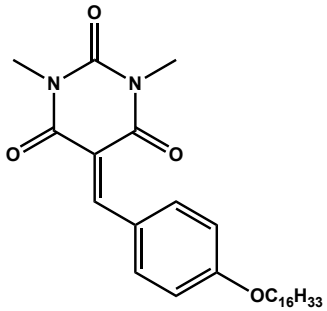
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H, -CH=C), 8.33 (d, *J* = 8.8 Hz, 2H, -Ar), 6.96 (d, *J* = 9.0 Hz, 2H, -Ar), 4.06 (t, *J* = 6.6 Hz, 2H, -OCH_2), 3.42 (s, 3H, -CH_3), 3.40 (s, 3H, -CH_3), 1.88 – 1.76 (m, 2H, -CH_2), 1.50 – 1.40 (m, 2H, -CH_2), 1.37 – 1.22 (m, 8H, -CH_2), 0.89 (s, 3H, -CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.13, 163.20, 161.06, 158.90, 151.47, 138.19, 125.36, 114.48, 114.07, 68.55, 31.86, 29.36, 29.27, 29.08, 28.40, 26.01, 22.71, 14.16.

LC-MS (m/z) calcd. for [$C_{21}H_{28}N_2O_4$+H^+] 373.21; found. 373.09.

Elemental Analysis:C, 67.72; H, 7.58; N, 7.52; O, 17.18; found: C, 67.61; H, 7.52; N, 7.47; O, 17.40.

5-(4-(hexadecyloxy)benzylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (**K'-16**):



Yellow solid. Yield: 66.1%. m.p. 101.4-102.7℃.

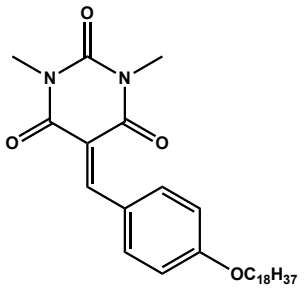
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H, -CH=C), 8.33 (d, *J* = 9.0 Hz, 2H, -Ar), 6.96 (d, *J* = 9.0 Hz, 2H, -Ar), 4.06 (t, *J* = 6.6 Hz, 2H, -OCH_2), 3.42 (s, 3H, -CH_3), 3.40 (s, 3H, -CH_3), 1.87 – 1.76 (m, 2H, -CH_2), 1.51 – 1.40 (m, 2H, -CH_2), 1.39 – 1.22 (m, 24H, -CH_2), 0.88 (t, *J* = 6.8 Hz, 3H, -CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.20, 163.28, 161.13, 159.00, 151.56, 138.21, 125.46, 114.56, 114.18, 68.62, 32.04, 29.81, 29.77, 29.70, 29.66, 29.47, 29.45, 29.15, 29.13, 28.45, 26.07, 22.80, 14.21.

HRMS (ESI, m/z) calcd. for [$C_{29}H_{44}N_2O_4$+H^+] 485.34; found. 485.33.

Elemental Analysis: C, 71.87; H, 9.15; N, 5.78; O, 13.20; found: C, 71.81; H, 9.10; N, 5.77; O, 13.32.

1,3-dimethyl-5-(4-(octadecyloxy)benzylidene)pyrimidine-2,4,6(1H,3H,5H)-trione (**K'-18**):



Yellow solid. Yield: 64.2%. m.p. 104.0-105.1℃.

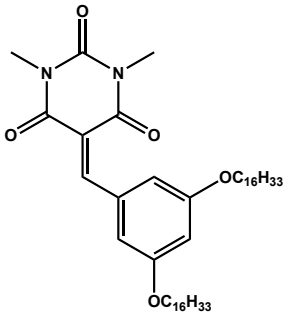
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H, -CH=C), 8.33 (d, *J* = 8.9 Hz, 2H, -Ar), 6.96 (d, *J* = 8.9 Hz, 2H, -Ar), 4.06 (t, *J* = 6.5 Hz, 2H, -OCH_2), 3.42 (s, 3H, -CH_3), 3.40 (s, 3H, -CH_3), 1.89 – 1.75 (m, 2H, -CH_2), 1.50 – 1.37 (m, 2H, -CH_2), 1.37 – 1.16 (m, 28H, -CH_2), 0.88 (t, *J* = 6.6 Hz, 3H, -CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.21, 163.30, 161.14, 159.02, 151.57, 138.22, 125.47, 114.57, 114.19, 68.63, 32.05, 29.82, 29.78, 29.71, 29.67, 29.48, 29.46, 29.16, 29.14, 28.46, 26.07, 22.81, 14.22.

HRMS (ESI, m/z) calcd. for [$C_{31}H_{48}N_2O_4$+H^+] 513.37; found. 513.36.

Elemental Analysis:C, 72.62; H, 9.44; N, 5.46; O, 12.48; found: C, 72.37; H, 9.39; N, 5.46; O, 12.78.

5-(3,5-bis(hexadecyloxy)benzylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (**K'-(16)$_2$**):



Yellow solid. Yield: 76.4%. m.p. 90.7-92.2℃.

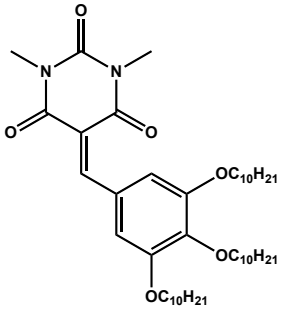
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H, -CH=C), 7.26 (s, 2H, -Ar), 6.63 (s, 1H, -Ar), 3.98 (t, *J* = 6.5 Hz, 4H, -OCH_2), 3.42 (s, 3H, -CH_3), 3.38 (s, 3H, -CH_3), 1.84 – 1.71 (m, 4H, -CH_2), 1.52 – 1.40 (m, 4H, -CH_2), 1.38 – 1.18 (m, 48H, -CH_2), 0.88 (t, *J* = 6.8 Hz, 6H, -CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.74, 160.37, 159.95, 159.67, 151.40, 134.15, 117.76, 111.90, 107.03, 68.49, 32.07, 29.84, 29.76, 29.55, 29.51, 29.31, 29.25, 28.63, 26.18, 22.83, 14.26.

HRMS (ESI, m/z) calcd. for [$C_{45}H_{76}N_2O_5$+H^+] 725.59; found. 725.58.

Elemental Analysis: C, 74.54; H, 10.56; N, 3.86; O, 11.03; found: C, 74.28; H, 10.50; N, 3.68; O, 11.54.

1,3-dimethyl-5-(3,4,5-tris(decyloxy)benzylidene)pyrimidine-2,4,6(1H,3H,5H)-trione (**K'-(10)$_3$**):



Yellow solid. Yield: 72.9%. m.p. 49.4-50.3℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H, -CH=C), 7.68 (s, 2H, -Ar), 4.12 (t, *J* = 6.6 Hz, 2H, -OCH_2), 4.04 (t, *J* = 6.4 Hz, 4H, -OCH_2), 3.42 (s, 3H, -CH_3), 3.40 (s, 3H, -CH_3), 1.92 – 1.78 (m, 6H, -CH_2), 1.53 – 1.42 (m, 6H, -CH_2), 1.41 – 1.20 (m, 36H, -CH_2), 0.88 (t, *J* = 6.8 Hz, 9H, -CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.23, 160.92, 159.57, 152.40, 151.48, 144.06, 127.29, 115.27, 114.40, 73.88, 69.37, 32.04, 30.50, 29.84, 29.77, 29.71, 29.65, 29.54, 29.51, 29.47, 29.39, 29.23, 28.58, 26.24, 26.11, 22.80, 14.22.

HRMS (ESI, m/z) calcd. for [$C_{43}H_{72}N_2O_6$+H^+] 713.55; found. 713.54.

Elemental Analysis: C, 72.43; H, 10.18; N, 3.93; O, 13.46; found: C, 72.48; H, 10.17; N, 3.82; O, 13.53.

Figures and Tables:

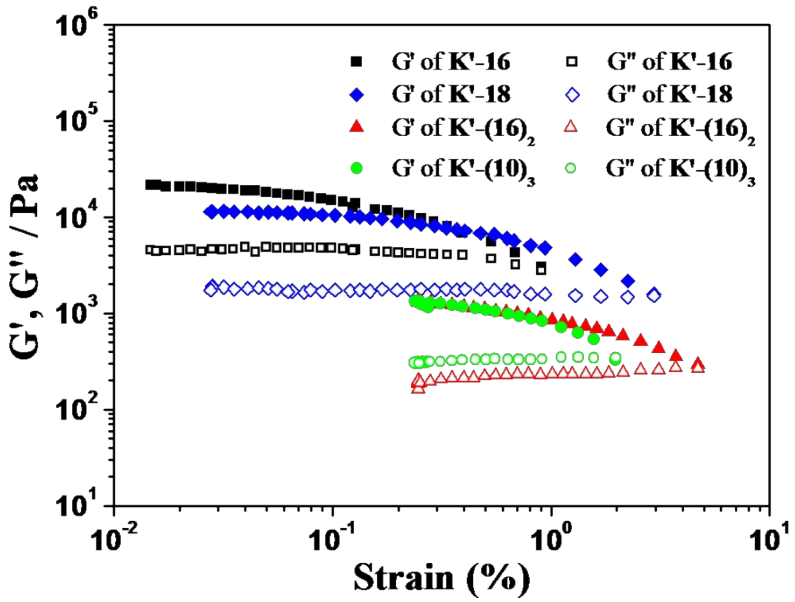


Figure S1. Amplitude dependencies of the storage modulus (G') and loss modulus (G") of gels formed by **K'-16**, **K'-18**, **K'-(16)$_2$** and **K'-(10)$_3$**. 2 wt% in ethanol (**K'-16**, **K'-18**, **K'-(10)$_3$**) and DMSO (**K'-(16)$_2$**). The frequency is 1 Hz.

Solvents	^{1}H-NMR signals[a] /ppm											
	K	**K'-2**	**K'-4**	**K'-8**	**K'-16**	**K'-18**	**I'**	**I-2**	**I-4**	**I-8**	**I-16**	**I-18**
$CDCl_3$	3.91	4.15	4.07	4.06	4.06	4.06	3.85	4.07	4.00	3.99	3.98	3.99
CD_3CN	3.89	4.16	-	-	-	-	3.82	4.08	-	-	-	--
CD_3CN-EtOD[b]	3.89	4.15	-	-	4.09	4.10	3.82	4.07	-	-	4.00	4.01
DMSO	3.88	4,16	-	-	-	-	3.80	4.07	-	-	-	-

[a] recorded signals of -OCH_3 for **K** and **I'**, -OCH_2 for other compounds. [b] CD_3CN : EtOD = 9:1, (v/v).

Table S1. Comparison of ^{1}H-NMR signals for different compounds in different solvents.

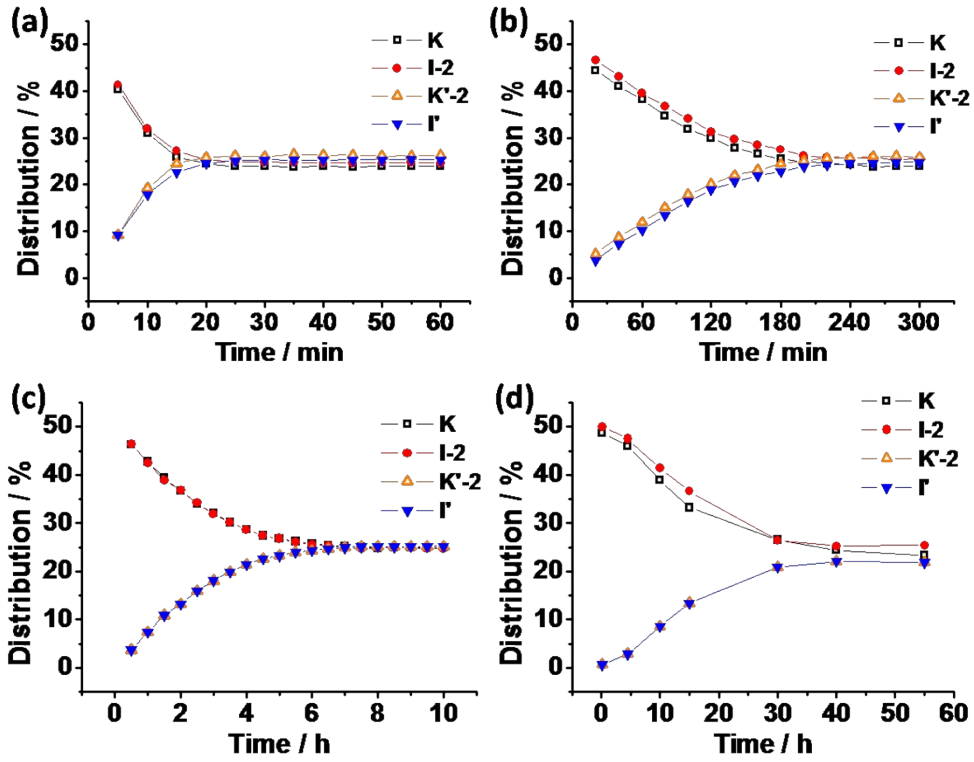


Figure S2. Distribution of **K**, **I-2, K'-2** and **I'** changed with time in different solvents at 22℃. (a) chloroform; (b) acetonitrile; (c) acetonitrile-ethanol (9:1); (d) DMSO.

Entry	Chain Length	t_f/min	$t_{1/2}$/min	Compound distribution [%]				
				K	**I-n**	**K'-n**	**I'**	Hydrolysis
1	$-OC_2H_5$	15-20	6	23.9	24.6	26.3	25.2	-
2	$-OC_4H_9$	15-20	4	24.0	23.6	26.6	25.9	-
3	$-OC_8H_{17}$	15-20	5	23.9	24.0	26.2	25.9	-
4	$-OC_{16}H_{33}$	20-25	8	24.2	23.9	26.0	25.0	-

5	$-OC_{18}H_{37}$	20-25	8	23.9	24.0	26.2	25.9	-

Table S2. Influence of chain length on reaction time and equilibrium. The time for full exchange/reaching equilibrium t_f is estimated from the moment where no change is observed any more. The time for half-exchange $t_{1/2}$ is obtained by integration of the =CH proton signals.

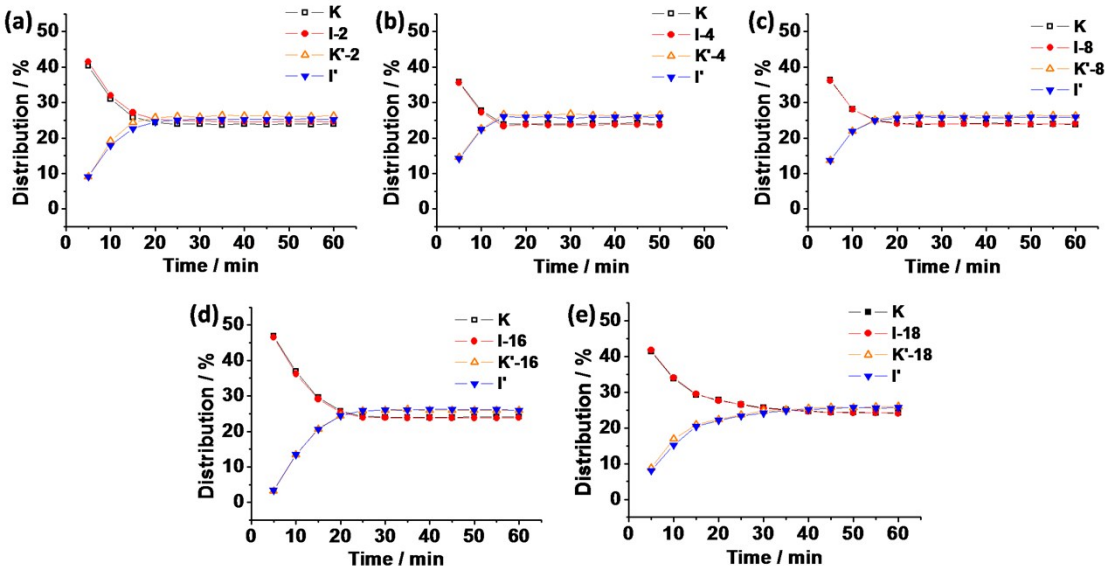


Figure S3. Distribution of **K**, **I-n, K'-n** and **I'** changed with time in chloroform at 22℃. (a) n=2; (b)n=4; (c) n=8; (d) n=16; (e) n=18.

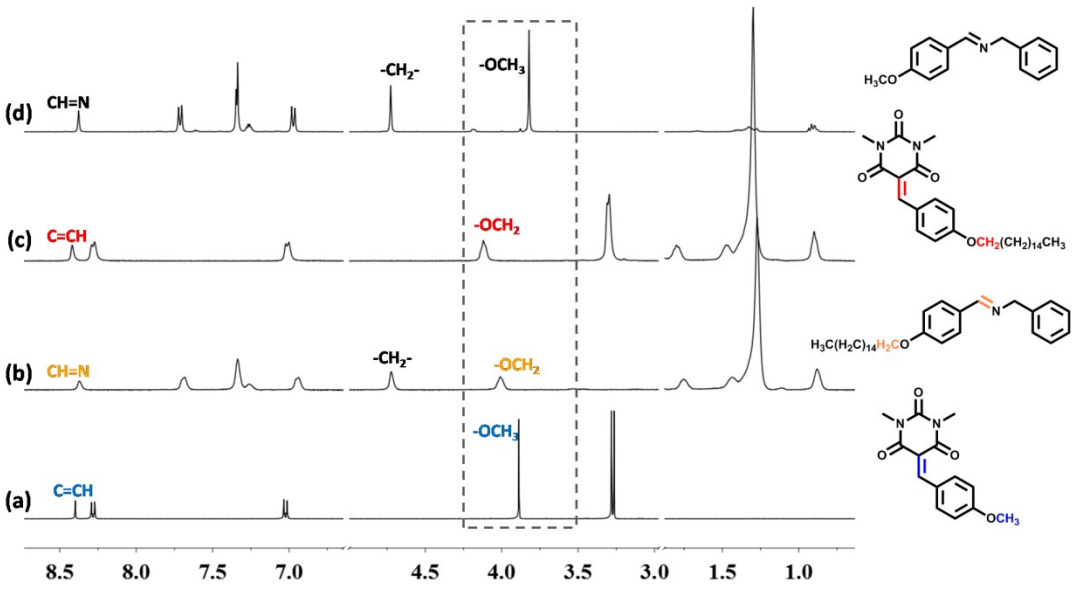


Figure S4. Comparison of ^{1}H NMR signals in $CDCl_3$: (a) **K**, (b) **I-16**, (c) **K'-16**, (d) **I'**. Signals around 4 ppm (shown in the dashed box) were used to analysize the distribution, as signals of C=CH (8.40 ppm for **K**; 8.42 ppm for **K'-16**) or CH=N (8.37 ppm for **I-16**; 8.38 ppm for **I'**) were too close to distinguish.

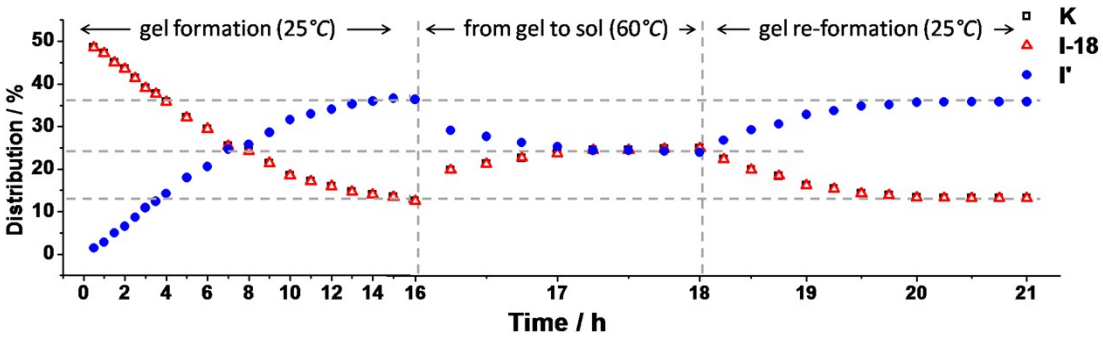


Figure S5. Distribution of **K**, **I-18** and **I'** changed with time in acetonitrile-ethanol (9:1, v/v). Left: started from **K** (10 mM) and **I-18** (10 mM) until gel formed at 25°C; middle: from gel state to sol state at 60°C； right: from sol state to gel state again at 25°C.

References:

[1] J. E. Eldridge and J. D. Ferry, *J. Phys. Chem.*, 1954, **58**, 992-995.

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