Sonication-Induced, Solvent-Selective Gelation of a 1,8-Napthalimide-Conjugated Amide: Structural Insights and Pollutant Removal Applications

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MATERIALS AND METHODS

All chemicals were purchased from commercial suppliers and used without further purification. All UV/Visible absorption spectra were recorded on a Varian Cary 50 Bio UV-Visible spectrophotometer. Fluorescence spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer. 1H NMR spectra were obtained using a Bruker Avance III spectrophotometer operating at 400 MHz, and were referenced to signals from the deuterated solvents. All fluorescence spectra were integrated vs. wavenumber on the X-axis using OriginPro 2020. All curve fitting was done using OriginPro curve fitting options for both linear and non-linear curve fitting. The morphologies of the reported amides were investigated using scanning electron microscopy (TESCAN MAIA3 Triglav). Polarized optical microscopic images were taken at 20-fold magnification (ZEISS, Axioscope 5 with polarizer and CCD camera). The rheological measurements were done on a MCR 102 rheometer (Anton Paar, Modular Compact Rheometer) with a steel parallel plate geometry having 40 mm diameter at 25 °C. The rheometer was attached to a Peltier circulator thermo cube in order to control the temperature accurately. All circular dichroism experiments were done on JASCO spectrophotometer.
SYNTHETIC PROCEDURES

**Synthesis of Compound 1**

![Chemical Structure](image)

**Scheme S1.** Overall synthetic scheme executed in order to obtain compound 1

**Synthesis of compound S2:**

991 mg (5 mmol, 1 eq.) of 1,8-napthalic anhydride (compound S1) and 656 mg (5 mmol, 1 eq.) of 6-aminocaproic acid (Acp-OH) were measured into a round-bottomed flask and dissolved in anhydrous DMF (20 mL). The reaction mixture was heated to 140 °C under an inert (argon) atmosphere, and stirred at that temperature for five hours. After five hours, the solution was allowed to cool to room temperature and a light-yellow solid precipitated from solution. This solid was filtered using Whatman #1 filter paper and washed several times with a methanol-water mixture to obtain 1.36 grams of compound S2 (4.3 mmol, 86.2% yield) as a light yellow solid. 

1H NMR (400 MHz, CDCl3, δ in ppm): 10.76 (s, 1 H, -COOH), 8.60-8.58 (m, 2 H, Ar-H), 8.21-8.19 (d, J = 8.0 Hz, 2 H, Ar-H), 7.76-7.73 (t, J = 4.0, 8.0 Hz, 2 H, Ar-H), 4.20-4.17 (t, J = 4.0, 8.0 Hz, 2 H, ε-Acp-H), 2.40-2.36 (t, J = 8.0, 16.0 Hz, 2 H, α-Acp-H), 1.81-1.71 (m, 4 H, β, δ-Acp-H), 1.69-1.45 (m, 2 H, γ-Acp-H). 

13C NMR (125 MHz, CDCl3, δ in ppm): 179.10, 164.26, 133.87, 131.57, 131.21, 128.14, 126.91, 122.74, 40.11, 36.76, 27.70, 26.51, 24.35. LC-MS: m/z calcd for C18H17NO4: 311.12; found: [M+H]+ = 312.10.

**Synthesis of compound 1:**

1.30 g (4.18 mmol, 1 eq.) of compound S2 was dissolved in a mixture of dichloromethane and dimethylformamide (DMF) (25 mL dichloromethane; 10 mL DMF) and cooled to 0 °C by using an ice bath. After that, 867 mg (4.20 mmol, 1.005 eq.) of N,N'-dicyclohexylcarbodiimide (DCC) and 644 mg (4.20 mmol, 1.005 eq.) of hydroxybenzotriazole (HOBt) were added. After 5 minutes, 546 μL (4.50 mmol, 1.08 eq.) of NH2-CH2-Ph was added dropwise to the reaction mixture. The reaction mixture was allowed to gradually warm to room temperature and stirred at room temperature for 48 hours. After 48 hours, dichloromethane was evaporated under reduced pressure, and the remaining residue was dissolved in 60 mL of ethyl acetate. The solid N,N'-dicyclohexylurea (DCU) was removed via filtration. The organic filtrate was then washed with 2 M HCl (3 x 50 mL) and a saturated sodium chloride solution (i.e., brine) (2 x 50 mL), and then dried over anhydrous sodium sulfate. The organic solvent was removed under reduced pressure to obtain compound 1 as a yellowish-white solid. Purification was done by silica gel chromatography (60-120 mesh size) with an ethyl acetate: hexanes mixture (1:3 ethyl acetate: hexanes; vol/vol), leading to the isolation of 900 mg of compound 1 (2.25 mmol, 54% yield). 

1H NMR (400 MHz, CDCl3, δ in ppm): 8.59-8.57 (d, J = 8.0 Hz, 2 H, Ar-H), 8.22-8.20 (d, J = 8.0 Hz, 2 H, Ar-H), 7.77-7.73 (t, J = 8.0, 16.0 Hz, 2 H, Ar-H), 7.34-7.24 (m, 6 H, -NH and Ar-H), 4.45-4.44 (d, J = 4.0 Hz, 2 H, α-CH2-Ph), 4.19-4.16 (t, J = 4.0, 8.0 Hz, 2 H, ε-Acp-H), 2.29-2.25 (m, 2 H, α-Acp-H), 1.81-1.74 (m, 4 H, β, δ-Acp-H), 1.52-1.47 (m, 2 H, γ-Acp-H). 

13C NMR (125 MHz, CDCl3, δ in ppm): 172.84, 164.22, 138.35, 133.91, 131.22, 128.69, 128.16, 127.83, 127.46, 126.93, 122.68, 40.64, 36.44, 29.69, 26.56, 25.26. LC-MS: m/z calcd for C22H24N2O3: 400.18; found: [M+H]+ = 401.20
Synthesis of Compound 2

**Scheme S2.** Overall synthetic scheme executed in order to obtain compound 2

**Synthesis of compound S4:**
991 mg of 1,8-naphthalic anhydride S1 (5 mmol, 1.0 eq.) and 0.766 g of compound S3 (5.2 mmol, 1.04 eq.) were dissolved in 20 mL of anhydrous DMF. The reaction mixture was heated to 140 °C for 5 hours under an inert (argon) atmosphere. After five hours, the solution was cooled to room temperature, and the resulting light-yellow precipitate was filtered using Whatman filter paper (#1). The residue was washed several times with a methanol-water mixed solvent system to obtain compound S4 in 88.8% yield (1.47 g, 4.44 mmol).

\[ ^1H \text{NMR (400 MHz, DMSO-}d_6, \delta \text{ in ppm)}: 12.87 (s, 1H, -COOH), 8.52-8.46 (m, 4H, Ar-H), 7.88-7.87 (m, 4H, Ar-H), 7.48-7.45 (m, 2H, Ar-H), 5.31 (s, 2H, }^\alpha-\text{CH}_2-\text{Ph}). \]

\[ ^13C \text{NMR (125 MHz, DMSO-}d_6, \delta \text{ in ppm)}: 167.04, 163.48, 142.35, 134.60, 131.33, 131.02, 129.52, 129.43, 127.48, 127.39, 127.26, 121.87, 42.82. \]

**Synthesis of compound 2:**
1.40 g (4.18 mmol, 1.0 eq.) of compound S4 was dissolved in a mixed dichloromethane-dimethylformamide solvent system (25 mL dichloromethane; 10 mL dimethylformamide). The reaction mixture was cooled to 0 °C using an ice bath, and 867 mg of N,N′-dicyclohexylcarbodiimide (DCC) (4.20 mmol, 1.005 eq.) and 644 mg of hydroxybenzotriazole (HOBt) (4.20 mmol, 1.005 eq.) were added. After 5 minutes, 600 μL of n-hexylamine (4.50 mmol, 1.08 eq.) was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred at room temperature for 48 hours. After 48 hours, the dichloromethane was evaporated and the resulting residue was dissolved in ethyl acetate (60 mL), followed by filtering of the N,N-dicyclohexylurea (DCU) byproduct. The organic filtrate was washed with 2 M HCl (3 x 50 mL) and brine (2 x 50 mL), dried over anhydrous sodium sulfate, and filtered to remove the sodium sulfate. The resulting solution was concentrated under reduced pressure to provide compound 2 as a yellowish-white solid. Purification by silica gel chromatography (60-120 mesh size silica) with an ethyl acetate and hexane solvent mixture (1:3 ethyl acetate: hexanes, vol/vol) provided compound 2 as a yellowish-white solid in 63.4% yield (1.10 grams, 2.65 mmol).

\[ ^1H \text{NMR (400 MHz, CDCl}_3, \delta \text{ in ppm)}: 8.60-8.58 (m, 2H, Ar-H), 8.21-8.19 (d, J = 8.0 Hz, 2H, Ar-H), 7.76-7.74 (d, J = 8.0 Hz, 2H, Ar-H), 7.68-7.66 (m, 2H, Ar-H), 7.57-7.55 (d, J = 8.0 Hz, 2H, Ar-H), 6.16 (s, 1H, -NH), 5.39 (s, 2H, }^\alpha-\text{CH}_2-\text{Ph}), 3.41-3.36 (m, 2H, Hex-CH_2), 1.59-1.52 (m, 2H, Hex-CH_2), 1.34-1.25 (m, 6H, Hex-CH_2), 0.87-0.84 (t, J = 4.0, 8.0 Hz, 2H, Hex-CH_2). \]

\[ ^13C \text{NMR (125 MHz, CDCl}_3, \delta \text{ in ppm)}: 167.41, 164.15, 140.70, 134.20, 133.85, 131.59, 131.51, 128.93, 128.16, 126.97, 122.42, 43.21, 40.08, 31.43, 29.52, 26.58, 22.49, 13.95. \]

**LC-MS:** m/z calcd for C_{26}H_{26}N_{2}O_{3}: 414.19; found: [M+H]^+ = 415.20 and [2M+H]^+ = 829.40.
Synthesis of compound 15:

Scheme S3. Synthesis of compound 15

For the synthesis of compound 15, we followed the same synthetic procedures used to obtain compound 1. NMR results for amide 15. $^1$H NMR (400 MHz, CDCl$_3$, $\delta$ in ppm): 8.54-8.52 (d, $J = 8.0$ Hz, 2 H, Ar-H), 8.17-8.15 (d, $J = 8.0$ Hz, 2 H, Ar-H), 7.72-7.68 (t, $J = 8.0$, 16.0 Hz, 2 H, Ar-H), 7.27-7.20 (m, 4 H, Ar-H), 6.46 (s, 1 H, -NH), 4.41-4.39 (d, $J = 8.0$ Hz, 2 H, $\alpha$-CH$_2$-Ph), 4.22-4.19 (t, $J = 4.0$, 8.0 Hz, 2 H, $\gamma$-Gabu-H), 2.32-2.29 (m, 2 H, $\beta$-Gabu-H), 2.11-2.07 (m, 2 H, $\alpha$-Gabu-H). $^{13}$C NMR (125 MHz, CDCl$_3$, $\delta$ in ppm): 172.50, 164.60, 138.55, 134.25, 131.77, 131.54, 128.78, 128.36, 127.99, 127.52, 127.12, 122.64, 43.83, 39.79, 34.16, 24.55. LC-MS: m/z calcd for C$_{23}$H$_{20}$N$_2$O$_3$: 372.15; found: [M+H]$^+$ = 373.10.

Synthesis of compound 16:

Scheme S4. Synthesis of compound 16

For the synthesis of compound 16, we followed the same synthetic procedure used to obtain compound 2. NMR results for compound 16. $^1$H NMR (400 MHz, CDCl$_3$, $\delta$ in ppm): 8.63-8.61 (d, $J = 8.0$ Hz, 2 H, Ar-H), 8.24-8.22 (d, $J = 8.0$ Hz, 2 H, Ar-H), 7.87-7.74 (t, $J = 8.0$, 16.0 Hz, 4 H, Ar-H), 7.57-7.53 (d, $J = 8.0$, 2 H, Ar-H), 6.02 (s, 1 H, -NH), 5.41 (s, 2 H, $\alpha$-CH$_2$-Ph), 3.45-3.00 (m, 2 H, $\alpha$-bu-H), 1.60-1.53 (m, 2 H, $\beta$-bu-H), 1.42-1.35 (m, 2 H, $\gamma$-bu-H), 0.95-0.88 (m, 2 H, $\delta$-bu-H). $^{13}$C NMR (125 MHz, CDCl$_3$, $\delta$ in ppm): 167.51, 164.34, 140.91, 139.06, 134.38, 134.22, 131.80, 129.25, 128.33, 127.14, 122.74, 43.42, 39.94, 31.88, 20.27, 13.90. LC-MS: m/z calcd for C$_{24}$H$_{22}$N$_2$O$_3$: 386.16; found: [M+H]$^+$ = 387.10 and [2M+H]$^+$ = 773.30.
DETAILED EXPERIMENTAL PROCEDURES

EXPERIMENTAL PROCEDURES FOR AGGREGATION STUDIES

The molecular recognition and self-assembly of the reported naphtalic anhydride (NA)-based compounds 1 and 2 were studied by concentration dependent UV-visible and fluorescence spectroscopy. The concentration of the compounds ranged from 4.51 x 10^{-2} mM to 11.88 x 10^{-2} mM. UV-visible spectra were integrated from 250-400 nm using OriginPro software (with wavenumbers on the X-axis). Fluorescence spectra were measured from excitation at 330 nm, and integrated from 340-500 nm using OriginPro software (with wavenumbers reported on the X-axis).

EXPERIMENTAL PROCEDURES FOR SOLID-STATE FTIR STUDIES

Compounds 1 and 2, as well as the gel obtained from sonicating a solution of compound 1 in toluene for 90 seconds, were examined using solid-state FTIR spectroscopy. A small amount of all compounds was ground by hand with a mortar and pestle. The resulting solid-state mixture consisted of the compounds with KBr salt, and pellets were formed from this mixture using a hydraulic pressure apparatus. To measure the solid-state FTIR spectra of the samples, first a background correction scan was conducted in air. Then, the sample pellets were placed in the FTIR spectrometer and the spectra were acquired. All data were saved as ASCII files and fitted using Microsoft Excel software.

EXPERIMENTAL PROCEDURES FOR GELATION STUDIES

Gelation studies were conducted by sonicating a solution of compound 1 or 2 ([1] = [2] = 10 mg/mL) for 90 seconds (for sonication-induced gel formation) or by heating the solution of compound in a specified solvent to 90-100 °C for 2-3 minutes followed by slowly cooling the mixture to room temperature (for heat-induced gel formation). Minimum gelation concentrations were determined by varying the concentration of the compound and measuring the ability of the resulting solution to form gels. The existence of a gel was determined by inverting the vial containing the solution and observing if the material remained at the top of the vial (indicating formation of a gel) or if it fell to the bottom of the vial (indicating the absence of a gel).

EXPERIMENTAL PROCEDURES FOR DYE ABSORBANCE OVER TIME STUDIES

Dye absorbance studies were conducted by mixing a solution of compound 1 ([1] = 10 mg/mL) with o-xylene (0.75 mL) to create a gel, followed by adding a solution of the dye (compounds 10-14) ([dye] = 1 mg/mL in water). The UV-visible spectrum of the dye as a function of time was measured using a Varian Cary 50 Bio UV-Visible spectrophotometer, and recorded from 200-700 nm.

EXPERIMENTAL PROCEDURES FOR STUDIES OF GEL REUSABILITY

To check reusability, a gel formed from compound 1 in o-xylene (20 mg/mL) was treated with tap water containing rhodamine B (2 mg/mL). After effective absorption of the dye over 50 hours, the gel was treated with a dilute solution of sodium bicarbonate solution and the resulting solution was extracted with multiple portions of ethyl acetate. This led to partitioning of the compounds between the layers, with the aqueous-soluble dye remaining in water and the gelator compound dissolving in the organic solution. The combined organic layer was separated, washed with brine (6-7 times), and dried over sodium sulfate, followed by removal of the ethyl acetate under reduced pressure to obtain the solid product. The mass of the recovered compound was determined, followed by using the recovered compound to re-prepare the organogel. The resulting organogel was again treated with tap water containing the rhodamine B dye ([rhodamine B] = 2 mg/mL).

EXPERIMENTAL PROCEDURES FOR MICROSCOPIC IMAGING EXPERIMENTS

A small amount of gel (compound 1 in toluene), a solution of compound 1 in 1,2-dichlorobenzene, a solution of compound 2 in toluene, and a solution of compound 2 in 1,2-dichlorobenzene were placed on a previously cleaned silicon wafer. The samples were dried via slow evaporation of the solvent, and then kept...
under vacuum at room temperature for two days. The materials were coated with gold, and the micrographs were taken using SEM instruments.

**EXPERIMENTAL PROCEDURES FOR RHEOLOGY EXPERIMENTS**

Small amounts of the gel were used to examine the mechanical strength of the gels. We prepared gels of compound 1 in toluene, \(\alpha\)-xylene, and \(m\)-xylene, and performed oscillatory frequency sweep experiments to measure the storage modulus (\(G'\)) and loss modulus (\(G''\)) of the gel, using the experimental setup detailed in “Materials and Methods,” above. The variation of \(G'\) and \(G''\) were monitored as a function of angular frequency at a constant strain value of 0.01%.

**EXPERIMENTAL PROCEDURES FOR CD EXPERIMENTS**

To investigate supramolecular chirality and chirality changes in compounds 1 and 2, we conducted circular dichroism experiments. First solutions of compounds 1 and 2 were prepared in methanol ([1] = [2] = 4.51 \(\times\) \(10^{-2}\) mM). After a baseline correction was run using methanol, the samples were run, and the CD spectra were recorded.
SUMMARY TABLES
SUMMARY TABLES OF AGGREGATION STUDY DATA

Table S1. Integrated UV-visible absorbance of compounds 1 and 2 as a function of increasing concentrations<sup>a</sup>

| [1] = [2] (mM) | Integrated absorbance of 1 | Integrated absorbance of 2 |
|----------------|----------------------------|----------------------------|
| 4.51 x 10⁻²    | 0.38 ± 0.0009              | 0.37 ± 0.0003              |
| 5.44 x 10⁻²    | 0.45 ± 0.0005              | 0.45 ± 0.0003              |
| 6.63 x 10⁻²    | 0.53 ± 0.0021              | 0.53 ± 0.0000              |
| 7.28 x 10⁻²    | 0.61 ± 0.0004              | 0.60 ± 0.0004              |
| 8.20 x 10⁻²    | 0.68 ± 0.0001              | 0.68 ± 0.0000              |
| 9.12 x 10⁻²    | 0.76 ± 0.0002              | 0.76 ± 0.0005              |
| 10.04 x 10⁻²   | 0.84 ± 0.0003              | 0.84 ± 0.0003              |
| 10.96 x 10⁻²   | 0.92 ± 0.0018              | 0.92 ± 0.0004              |
| 11.88 x 10⁻²   | 1.00 ± 0.0035              | 1.00 ± 0.0005              |

<sup>a</sup> Absorbance spectra were integrated vs. wavenumber on the X-axis, from 250-500 nm, using OriginPro software. All values represent the average of at least two trials. The compounds were dissolved in chloroform.

Table S2. Integrated fluorescence emission spectra of compounds 1 and 2 as a function of increasing concentrations<sup>a</sup>

| [1] = [2] (mM) | Integrated emission of 1 | Integrated emission of 2 |
|----------------|--------------------------|--------------------------|
| 4.51 x 10⁻²    | 0.60 ± 0.002             | 0.69 ± 0.003             |
| 5.44 x 10⁻²    | 0.68 ± 0.003             | 0.76 ± 0.004             |
| 6.63 x 10⁻²    | 0.74 ± 0.004             | 0.82 ± 0.013             |
| 7.28 x 10⁻²    | 0.80 ± 0.010             | 0.86 ± 0.005             |
| 8.20 x 10⁻²    | 0.85 ± 0.002             | 0.91 ± 0.007             |
| 9.12 x 10⁻²    | 0.90 ± 0.001             | 0.94 ± 0.006             |
| 10.04 x 10⁻²   | 0.94 ± 0.006             | 0.97 ± 0.004             |
| 10.96 x 10⁻²   | 0.97 ± 0.001             | 0.98 ± 0.005             |
| 11.88 x 10⁻²   | 1.00 ± 0.003             | 1.02 ± 0.023             |

<sup>a</sup> Fluorescence spectra were integrated vs. wavenumber on the X-axis, from 340-600 nm, using OriginPro software. All values represent the average of at least two trials. The compounds were dissolved in chloroform.
### SUMMARY TABLES OF GELATION STUDY DATA

#### GELATION OF COMPOUND 1

**Table S3.** Summary table of gelation properties of compound 1 in the presence of various organic solvents

| Solvent          | Sonication | Heating-Cooling | Minimum Gel Concentration (MGC) |
|------------------|------------|-----------------|---------------------------------|
| Toluene          | Gel        | Clear Solution<sup>d</sup> | 5.8 mg/mL                       |
| o-Xylene         | Gel        | Clear Solution<sup>d</sup> | 4.9 mg/mL                       |
| m-Xylene         | Gel        | Clear Solution<sup>d</sup> | 5.1 mg/mL                       |
| p-Xylene         | Gel        | Clear Solution<sup>d</sup> | 5.2 mg/mL                       |
| Mesitylene       | Gel        | Clear Solution<sup>d</sup> | 5.0 mg/mL                       |
| Ethylbenzene     | Gel        | Clear Solution<sup>d</sup> | 4.8 mg/mL                       |
| Benzene          | Sol-gel<sup>c</sup> | Clear Solution<sup>d</sup> | N/A<sup>b</sup>               |
| Chlorobenzene    | Sol-gel<sup>c</sup> | Clear Solution | N/A<sup>b</sup>               |
| Bromobenzene     | Sol-gel<sup>c</sup> | Clear Solution | N/A<sup>b</sup>               |
| Iodobenzene      | Sol-gel<sup>c</sup> | Clear Solution | N/A<sup>b</sup>               |
| 1,2-Dichlorobenzene | Sol-gel<sup>c</sup> | Clear Solution | N/A<sup>b</sup>               |
| Nitrobenzene     | Sol-gel<sup>c</sup> | Clear Solution | N/A<sup>b</sup>               |
| Cyclohexane      | Insoluble  | Insoluble       | N/A<sup>b</sup>               |
| n-Hexane         | Insoluble  | Insoluble       | N/A<sup>b</sup>               |
| n-Heptane        | Insoluble  | Insoluble       | N/A<sup>b</sup>               |
| Methanol         | Clear Solution | Clear Solution | N/A<sup>b</sup>               |
| Ethanol          | Clear Solution | Clear Solution | N/A<sup>b</sup>               |
| Acetonitrile     | Clear Solution | Clear Solution | N/A<sup>b</sup>               |
| Ethyl Acetate    | Clear Solution | Clear Solution | N/A<sup>b</sup>               |
| Acetone          | Clear Solution | Clear Solution | N/A<sup>b</sup>               |
| Dichloromethane  | Clear Solution | Clear Solution | N/A<sup>b</sup>               |

<sup>a</sup> [1] = 10 mg/mL; sonication occurred using a water sonicator for 1-2 minutes; heating-cooling occurred according to the following procedure: 10 mg of each compound in 1 mL of a selected solvent was measured into a closed vial. Then the vial was heated using a hot air gun until all components dissolved. After that, the vial was removed from heat and allowed to cool to room temperature undisturbed.

<sup>b</sup> N/A = not applicable; no gel formation occurred

<sup>c</sup> The term “sol-gel” refers to a state of neither a clear liquid nor the formation of a gel; rather a cloudy mixture forms from which a solid precipitates after 2-3 hours.

<sup>d</sup> Clear solution form during heating and precipitate out after 2-3h.

#### LACK OF GELATION OF COMPOUND 2

**Table S4.** Summary table of gelation properties of compound 2 in the presence of various organic solvents

| Solvent          | Sonication | Heating-Cooling | Minimum Gel Concentration (MGC) |
|------------------|------------|-----------------|---------------------------------|
| Ethanol          | Clear Solution | Clear Solution | N/A<sup>b</sup>               |
| Acetonitrile     | Clear Solution | Clear Solution | N/A<sup>b</sup>               |
| Ethyl Acetate    | Clear Solution | Clear Solution | N/A<sup>b</sup>               |
| Acetone          | Clear Solution | Clear Solution | N/A<sup>b</sup>               |
| Dichloromethane  | Clear Solution | Clear Solution | N/A<sup>b</sup>               |
| Solvent          | Sonication | Heating-Cooling | Minimum Gel Concentration (MGC) |
|------------------|------------|-----------------|---------------------------------|
| Toluene          | Sol-gel<sup>c</sup> | Clear solution<sup>d</sup> | N/A<sup>b</sup>                |
| o-Xylene         | Sol-gel<sup>c</sup> | Clear solution<sup>d</sup> | N/A<sup>b</sup>                |
| m-Xylene         | Sol-gel<sup>c</sup> | Clear solution<sup>d</sup> | N/A<sup>b</sup>                |
| p-Xylene         | Sol-gel<sup>c</sup> | Clear solution<sup>d</sup> | N/A<sup>b</sup>                |
| Mesitylene       | Sol-gel<sup>c</sup> | Clear solution<sup>d</sup> | N/A<sup>b</sup>                |
| Ethylbenzene     | Sol-gel<sup>c</sup> | Clear Solution<sup>d</sup> | N/A<sup>b</sup>                |
| Benzene          | Sol-gel<sup>c</sup> | Clear solution<sup>d</sup> | N/A<sup>b</sup>                |
| Chlorobenzene    | Sol-gel<sup>c</sup> | Clear solution   | N/A<sup>b</sup>                |
| Bromobenzene     | Sol-gel<sup>c</sup> | Clear solution   | N/A<sup>b</sup>                |
| Iodobenzene      | Sol-gel<sup>c</sup> | Clear solution   | N/A<sup>b</sup>                |
| 1,2-Dichlorobenzene | Sol-gel<sup>c</sup> | Clear solution | N/A<sup>b</sup>                |
| Nitrobenzene     | Sol-gel<sup>c</sup> | Clear Solution   | N/A<sup>b</sup>                |
| Cyclohexane      | Insoluble   | Insoluble        | N/A<sup>b</sup>                |
| n-Hexane         | Insoluble   | Insoluble        | N/A<sup>b</sup>                |
| n-Heptane        | Insoluble   | Insoluble        | N/A<sup>b</sup>                |
| Methanol         | Clear solution | Clear solution | N/A<sup>b</sup>                |
| Ethanol          | Clear solution | Clear solution | N/A<sup>b</sup>                |
| Acetonitrile     | Clear solution | Clear solution | N/A<sup>b</sup>                |
| Ethyl Acetate    | Clear solution | Clear solution | N/A<sup>b</sup>                |
| Acetone          | Clear solution | Clear solution | N/A<sup>b</sup>                |
| Dichloromethane  | Clear solution | Clear solution | N/A<sup>b</sup>                |

<sup>a</sup> [2] = 10 mg/mL; sonication occurred using water sonicator for 1-2 minutes; heating-cooling occurred according to the procedure detailed above.

<sup>b</sup> N/A = not applicable; no gel formation occurred

<sup>c</sup> The term “sol-gel” refers to a state of neither a clear liquid nor the formation of a gel; rather a cloudy mixture forms from which a solid precipitates after 2-3 hours.

<sup>d</sup> Clear solution form during heating and precipitate out after 2-3h.

**LACK OF GELATION OF COMPOUND 15**

**Table S5.** Summary table of gelation properties of compound 15 in the presence of various organic solvents<sup>a</sup>
| Solvent          | Sonication   | Heating-Cooling | Minimum Gel Concentration (MGC) |
|------------------|--------------|-----------------|--------------------------------|
| Toluene          | Precipitated | Clear solution^d| N/A^b                           |
| o-Xylene         | Precipitated | Clear solution^d| N/A^b                           |
| m-Xylene         | Precipitated | Clear solution^d| N/A^b                           |
| p-Xylene         | Precipitated | Clear solution^d| N/A^b                           |
| Mesitylene       | Precipitated | Clear solution^d| N/A^b                           |

^a [15] =10 mg/mL; sonication occurred using water sonicator for 1-2 minutes; heating-cooling occurred according to the procedure detailed above.

^b N/A = not applicable; no gel formation occurred

^c The term “sol-gel” refers to a state of neither a clear liquid nor the formation of a gel; rather a cloudy mixture forms from which a solid precipitates after 2-3 hours.

^d Clear solution formed during heating, and a solid precipitates out after 2-3 hours.

**LACK OF GELATION OF COMPOUND 16**

**Table S6.** Summary table of gelation properties of compound 16 in the presence of various organic solvents^a^
| Compound                  | Form          | Solution  | N/A  |
|---------------------------|---------------|-----------|------|
| Ethylbenzene              | Precipitated  | Clear Solution<sup>d</sup> | N/A<sup>b</sup> |
| Benzene                   | Precipitated  | Clear solution<sup>d</sup> | N/A<sup>b</sup> |
| Chlorobenzene             | Precipitated  | Clear solution | N/A<sup>b</sup> |
| Bromobenzene              | Precipitated  | Clear solution | N/A<sup>b</sup> |
| Iodobenzene               | Precipitated  | Clear solution | N/A<sup>b</sup> |
| 1,2-Dichlorobenzene       | Precipitated  | Clear solution | N/A<sup>b</sup> |
| Nitrobenzene              | Precipitate   | Clear Solution | N/A<sup>b</sup> |
| Cyclohexane               | Insoluble     | Insoluble  | N/A<sup>b</sup> |
| n-Hexane                  | Insoluble     | Insoluble  | N/A<sup>b</sup> |
| n-Heptane                 | Insoluble     | Insoluble  | N/A<sup>b</sup> |
| Methanol                  | Clear solution| Clear solution | N/A<sup>b</sup> |
| Ethanol                   | Clear solution| Clear solution | N/A<sup>b</sup> |
| Acetonitrile              | Clear solution| Clear solution | N/A<sup>b</sup> |
| Ethyl Acetate             | Clear solution| Clear solution | N/A<sup>b</sup> |
| Acetone                   | Clear solution| Clear solution | N/A<sup>b</sup> |
| Dichloromethane           | Clear solution| Clear solution | N/A<sup>b</sup> |

<sup>a</sup> [16] = 10 mg/mL; sonication occurred using water sonicator for 1-2 minutes; heating-cooling occurred according to the procedure detailed above.

<sup>b</sup> N/A = not applicable; no gel formation occurred

<sup>c</sup> The term “sol-gel” refers to a state of neither a clear liquid nor the formation of a gel; rather a cloudy mixture forms from which a solid precipitates after 2-3 hours.

<sup>d</sup> Clear solution formed during heating, and a solid precipitates out after 2-3 hours.
**SUMMARY TABLES OF DYE ABSORBANCE SPECTRA OVER TIME**

**Table S7.** Summary table of integrated absorbance spectra of methyl orange 10 as a function of time in the presence of a gel formed from compound 1 and o-xylene\(^a\)

| Time       | Methyl orange integrated absorbance |
|------------|------------------------------------|
| 0 hrs      | 0.98 ± 2.4E-7                      |
| 2 hours    | 1.00 ± 2.4E-7                      |
| 5 hours    | 0.99 ± 2.4E-7                      |
| 12 hours   | 0.79 ± 5.6E-5                      |
| 24 hours   | 0.72 ± 5.1E-5                      |
| 32 hours   | 0.46 ± 1.1E-7                      |
| 48 hours   | 0.40 ± 9.8E-8                      |
| 60 hours   | 0.39 ± 9.4E-8                      |

\(^a\) The compound 1-derived gel was formed by mixing 7.5 mg of compound 1 with 0.75 mL of o-xylene. Integration was done from 250-500 nm, using wavenumbers on the X-axis and OriginPro software. [10] = 1 mg/mL in water. All values represent an average of at least two trials.

**Table S8.** Summary table of integrated absorbance spectra of methyl violet 11 as a function of time in the presence of a gel formed from compound 1 and o-xylene\(^a\)

| Time       | Methyl violet integrated absorbance |
|------------|------------------------------------|
| 0 hrs      | 1.00 ± 9.5E-7                      |
| 2 hours    | 0.94 ± 9.0E-7                      |
| 5 hours    | 0.93 ± 8.8E-7                      |
| 12 hours   | 0.94 ± 8.9E-7                      |
| 32 hours   | 0.61 ± 4.3E-4                      |
| 56 hours   | 0.22 ± 2.1E-7                      |
| 72 hours   | 0.26 ± 2.4E-7                      |

\(^a\) The compound 1-derived gel was formed by mixing 7.5 mg of compound 1 with 0.75 mL of o-xylene. Integration was done from 250-500 nm, using wavenumbers on the X-axis and OriginPro software. [11] = 1 mg/mL in water. All values represent an average of at least two trials.

**Table S9.** Summary table of integrated absorbance spectra of rhodamine B 12 as a function of time in the presence of a gel formed from compound 1 and o-xylene\(^a\)

| Time       | Rhodamine B integrated absorbance |
|------------|----------------------------------|
| 0 hrs      | 1.00 ± 1.0E-6                    |
| 2 hours    | 0.38 ± 5.3E-4                    |
| 5 hours    | 0.22 ± 3.2E-4                    |
| 12 hours   | 0.18 ± 2.5E-4                    |
| 24 hours   | 0.10 ± 1.4E-4                    |

\(^a\) The compound 1-derived gel was formed by mixing 7.5 mg of compound 1 with 0.75 mL of o-xylene.
The compound 1-derived gel was formed by mixing 7.5 mg of compound 1 with 0.75 mL of o-xylene. Integration was done from 250-500 nm, using wavenumbers on the X-axis and OriginPro software. [12] = 1 mg/mL in water. All values represent an average of at least two trials.

**Table S10.** Summary table of integrated absorbance spectra of rhodamine 6G 13 as a function of time in the presence of a gel formed from compound 1 and o-xylene

| Time    | Rhodamine 6G integrated absorbance |
|---------|-----------------------------------|
| 32 hours| 0.02 ± 3.1E-5                     |
| 48 hours| 0.01 ± 1.2E-5                     |

**Table S11.** Summary table of integrated absorbance spectra of thioflavin T 14 as a function of time in the presence of a gel formed from compound 1 and o-xylene

| Time    | Thioflavin T integrated absorbance |
|---------|-----------------------------------|
| 0 hrs   | 1.00 ± 2.2E-7                     |
| 2 hours | 1.00 ± 2.3E-7                     |
| 5 hours | 1.00 ± 2.3E-7                     |
| 24 hours| 0.89 ± 2.0E-7                     |
| 32 hours| 0.80 ± 1.8E-7                     |
| 48 hours| 0.54 ± 1.2E-7                     |
| 60 hours| 0.40 ± 5.6E-4                     |
| 72 hours| 0.40 ± 5.7E-4                     |

**Table S12.** Summary of quantitative coloration of the compound 1 - o-xylene gels after removal of dyes from contaminated aqueous solutions

| Dye      | Red value | Green value | Blue value |
|----------|-----------|-------------|------------|
| Methyl Orange | 191.5    | 156.3       | 57.7       |
| Compound         | Value 1 | Value 2 | Value 3 |
|------------------|---------|---------|---------|
| Methyl Violet    | 39.6    | 19.0    | 69.3    |
| Rhodamine B      | 222.0   | 77.7    | 124.8   |
| Rhodamine 6G     | 213.3   | 70.0    | 69.5    |
| Thioflavin T     | 192.3   | 179.0   | 110.0   |

*a* RGB analysis was performed using ImageJ (imagej.nih.gov) with an RGB analysis plug-in, using photographs taken under ambient light.
SUMMARY FIGURES
SUMMARY FIGURES OF SPECTRAL DATA FOR SYNTHESIZED COMPOUNDS

Compound S2:
Mass Spectrum (MS):

Figure S1. Mass spectrum (MS) of compound S2
$^1$H NMR Spectrum:

Figure S2. $^1$H NMR spectrum of compound S2

$^{13}$C NMR Spectrum:

Figure S3. $^{13}$C NMR spectrum of compound S2
Compound 1:
Mass Spectrum (MS):

Figure S4. Mass spectrum (MS) of compound 1
$^1$H NMR Spectrum:

![H NMR spectrum of compound 1](image)

**Figure S5.** $^1$H NMR spectrum of compound 1

$^{13}$C NMR Spectrum:

![C NMR spectrum of compound 1](image)

**Figure S6.** $^{13}$C NMR spectrum of compound compound 1
Figure S7. HRMS of compound 1
Compound **S4**:  
Mass Spectrum (MS):

**Figure S8.** Mass spectrum (MS) of compound S4
$^1$H NMR Spectrum:

![$^1$H NMR spectrum of compound S4](image)

**Figure S9.** $^1$H NMR spectrum of compound S4

$^{13}$C NMR Spectrum:

![$^{13}$C NMR spectrum of compound S4](image)

**Figure S10.** $^{13}$C NMR spectrum of compound S4
Compound 2:
Mass Spectrum (MS):

Figure S11. Mass spectrum (MS) of compound 2
$^1$H NMR Spectrum:

Figure S12. $^1$H NMR spectrum of compound 2

$^{13}$C NMR Spectrum:

Figure S13. $^{13}$C NMR spectrum of compound 2
Figure S14. HRMS of compound 2
Compound 15:

Figure S15. $^1$H NMR spectrum of compound 15

Figure S16. $^{13}$C NMR spectrum of compound 15
Figure S17. HRMS of compound 15

Compound 16:

Figure S18. $^1$H NMR spectrum of compound 16
Figure S19: $^{13}$C NMR spectrum of compound 16

Figure S20. HRMS of compound 16
SUMMARY FIGURES OF AGGREGATION STUDY DATA

**Figure S21.** UV-visible absorption spectra of compound 1 in chloroform with varying concentrations

**Figure S22.** Summary of the UV-visible absorption spectra of compound 1 in chloroform with varying concentrations, indicating a slight hypsochromic shift

**Figure S23.** UV-visible absorption spectra of compound 2 in chloroform with varying concentrations
Figure S24. Summary of the UV-visible absorption spectra of compound 2 in chloroform with varying concentrations

Figure S25. Fluorescence emission spectra of compound 1 in chloroform with varying concentrations

Figure S26. Summary of the fluorescence emission spectra of compound 1 in chloroform with varying concentrations
Figure S27. Fluorescence emission spectra of compound 2 in chloroform with varying concentrations

Figure S28. Summary of the fluorescence emission spectra of compound 2 in chloroform with varying concentrations
SUMMARY FIGURES OF GELATION STUDIES

GELATION OF COMPOUND 1

**Figure S29.** Photograph of compound 1 in various aromatic solvents under ambient light. (Left to right: toluene, o-xylene, p-xylene, benzene, 1,2-dichlorobenzene).

**Figure S30.** Photograph of compound 1 in various aromatic solvents after inversion of the vials under ambient light. (Left to right: toluene, o-xylene, p-xylene, benzene, 1,2-dichlorobenzene).

**Figure S31.** Photograph of compound 1 in various aromatic solvents after inversion of the vials under 365 nm irradiation with a hand-held TLC lamp. (Left to right: toluene, o-xylene, p-xylene, benzene, 1,2-dichlorobenzene).
Figure S32. Absorbance spectra of compound 1 in the presence of toluene before and after sonication.

Figure S33. Absorbance spectra of compound 1 in the presence of 1,2-dichlorobenzene before and after sonication.

Figure S34. Photograph of compound 1 mixed with o-xylene and water after sonication for one minute under ambient light, showing the formation of a phase-selective gel with the o-xylene layer exclusively. ([1] = 10 mg/mL; 1 mL o-xylene; 1 mL water).
Figure S35. Photograph of compound 1 mixed with o-xylene and water after a heating and cooling cycle under ambient light, showing that gel formation does not occur. ([1] = 10 mg/mL; 1 mL o-xylene; 1 mL water).

LACK OF GELATION OF COMPOUND 2

Figure S36. Photograph of compound 2 in various aromatic solvents under ambient light. (Left to right: toluene, o-xylene, p-xylene, benzene, 1,2-dichlorobenzene).

Figure S37. Photograph of compound 2 in various aromatic solvents after inversion of the vials under ambient light. (Left to right: toluene, o-xylene, p-xylene, benzene, 1,2-dichlorobenzene).

Figure S38. Photograph of compound 2 in various aromatic solvents after inversion of the vials under 365 nm irradiation with a hand-held TLC lamp. (Left to right: toluene, o-xylene, p-xylene, benzene, 1,2-dichlorobenzene).
LACK OF GELATION OF COMPOUND 15

**Figure S39.** Photograph of compound 15 in various aromatic solvents after inversion of the vials under ambient light. (Left to right: toluene, o-xylene, mesitylene, benzene, 1,2-dichlorobenzene, iodobenzene, nitrobenzene).

LACK OF GELATION OF COMPOUND 16

**Figure S40.** Photograph of compound 16 in various aromatic solvents after inversion of the vials under ambient light. (Left to right: toluene, o-xylene, mesitylene, benzene, 1,2-dichlorobenzene, iodobenzene, nitrobenzene).
SUMMARY FIGURES OF DYE ABSORBANCE SPECTRA OVER TIME

**Figure S41.** Change in the UV-visible absorbance over time of a methyl orange-containing aqueous solution treated with a gel composed of compound 1.

**Figure S42.** Summary of the changes in the UV-visible absorbance over time of a methyl orange-containing aqueous solution treated with a gel composed of compound 1.

**Figure S43.** Change in the UV-visible absorbance over time of a methyl violet-containing aqueous solution treated with a gel composed of compound 1.
**Figure S44.** Summary of the changes in the UV-visible absorbance over time of a methyl violet-containing aqueous solution treated with a gel composed of compound 1.

**Figure S45.** Change in the UV-visible absorbance over time of a rhodamine B-containing aqueous solution treated with a gel composed of compound 1.

**Figure S46.** Summary of the changes in the UV-visible absorbance over time of a rhodamine B-containing aqueous solution treated with a gel composed of compound 1.
Figure S47. Change in the UV-visible absorbance over time of a rhodamine 6G-containing aqueous solution treated with a gel composed of compound 1.

Figure S48. Summary of the changes in the UV-visible absorbance over time of a rhodamine 6G-containing aqueous solution treated with a gel composed of compound 1.

Figure S49. Change in the UV-visible absorbance over time of a thioflavin T-containing aqueous solution treated with a gel composed of compound 1.
**Figure S50.** Summary of the changes in the UV-visible absorbance over time of a thioflavin T-containing aqueous solution treated with a gel composed of compound 1.

**Figure S51.** Photograph of the xylene-compound 1 gels under ambient light after removal of the dyes from a contaminated aqueous solution. (Left to right: methyl orange, methyl violet, rhodamine B, rhodamine 6G, and thioflavin T).

**Figure S52.** Summary of the recovery of compound 1 after its use in the removal of rhodamine B from water.
**Figure S53.** SEM images of: (a) compound 1 forming an entangled fibrous network in the gel formed from toluene; (b) compound 1 forming microspheres from 1,2-dichlorobenzene; (c) compound 2 forming a sheet-like structure from its mixture with toluene; and (d) compound 2 forming a crystal flower-like morphology from its mixture with 1,2-dichlorobenzene.
SUMMARY FIGURES OF POLARIZED OPTICAL MICROSCOPE IMAGES

Figure S54. Polarized optical microscope images of a compound 1 xerogel formed from o-xylene: (a) without the use of the polarizer and (b) with the use of the polarizer. After the absorption of rhodamine B, microscopic images of the same compound 1 – o-xylene xerogel: (c) without the use of the polarizer; and (d) with the use of the polarizer.

Figure S55: Polarized Optical Microscopy (POM) images of: (a) compound 1 forming an entangled fibrous network in the gel formed from o-xylene; (b) compound 1 forming microspheres from 1,2-dichlorobenzene; (c) compound 2 forming a crystal structure from o-xylene; and (d) compound 2 forming a crystal flower-like morphology from its mixture with 1,2-dichlorobenzene.
Figure S56. Illustration of solid state FTIR spectroscopy results for compound 1, a compound 1-derived gel formed from a mixture of o-xylene and compound 2.
SUMMARY FIGURES OF RHEOLOGY EXPERIMENTS RESULTS

Figure S57. Summary of rheology measurements of the gel formed from compound 1 in (a) o-xylene and (b) m-xylene. The storage modulus $G'$ of the gel was found to be larger than the loss modulus $G''$, which is indicative of an elastic rather than a viscous material.
SUMMARY FIGURES OF CD EXPERIMENTS RESULTS

**Figure S58.** Solution-state CD spectra of compounds 1 and 2 in a methanol solution. ([1] = [2] = 4.51 x 10^{-2} mM)
SUMMARY FIGURES OF SELF-HEALING EXPERIMENTS

Figure S59. Photograph of the self-healing experiment. A small portion of gel with Rhodamine B-absorbed dye (pink coloration in the above figure) merged after 15 minutes to another portion of gel without the dye.