

# Electronic Supplementary Information (ESI)

## Fluoride-triggered phase transition of metallogels for on-demand *in situ* containment of fluids

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### Experimental Section

**General Considerations.** All reagents were obtained from commercial suppliers and used as received unless otherwise noted. All air-sensitive manipulations were carried out under argon atmosphere by standard Schlenk-line techniques. The compounds **1**<sup>1</sup>, and **5**<sup>2</sup> were prepared according to literature procedures.

**Physical Measurements.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Varian/Oxford As-500 (500 MHz) Spectrophotometer. Chemical shifts in the <sup>1</sup>H NMR spectra were reported in parts per million (ppm) on the  $\delta$  scale with respect to the internal standard of tetramethylsilane ( $\delta = 0.00$  ppm), or peak of residual chloroform ( $\delta = 7.26$  ppm). Data for <sup>1</sup>H NMR spectra were reported as follows: chemical shift, multiplicity (*s*, singlet; *br*, broad; *d*, doublet; *m*, multiplet), coupling constant in Hertz (Hz) and integration. Data for <sup>13</sup>C NMR spectra were reported as chemical shift in ppm from the peak of residual chloroform ( $\delta = 77.16$  ppm). High-resolution electrospray ionization (ESI) mass spectra were obtained on an ESI-Q-TOF mass spectrometer (Compact, Bruker Daltonics Inc). FT-IR spectra were recorded on a Shimadzu IRTracer-100 FT-IR Spectrophotometer. FESEM studies were carried out on a JSM-7800F Prime (JEOL), operating at 1–10 kV. To minimize sample charging, samples were coated with a thin layer of Pt before measurements. EDX mapping was carried out with SDD type 80 mm<sup>2</sup> EDX X-MAS detector (Horiba), coupled with FESEM (Hitachi, SU-8020). Time-dependent gelation processes were monitored by using an Ocean Optics FLAME-S-XR1 spectrometer with a DH-2000-BAL deuterium-halogen light source. Fluorescence spectra were recorded on a Photon Technology International QuantaMaster 400 Spectrofluorometer with FelixGX software.

### 4,4'-Bis((trimethylsilyl)oxy)-[1,1'-biphenyl]-3,3',5,5'-tetracarbaldehyde

**O,O,O,O-tetra(trimethylsilyl) tetraoxime (2a).** A flame-dried 100 mL round-bottom flask was charged with **1** (1.00 g, 2.79 mmol) and a magnetic stir bar. The reaction vessel was purged with argon, and anhyd DMF (20 mL) was delivered to the vessel. Trimethylsilyl chloride (2.80 mL, 22.3 mmol) was added in a single portion via syringe, and imidazole (3.05 g, 44.654 mmol)

<sup>1</sup> J. Kim and D. Lee, *Chem. Sci.*, 2019, **10**, 3864–3872.

<sup>2</sup> A. Eiji, C. Mitsuyoshi, Y. Atsushi, S. Yoshiteru and S. Ken-ichi, *Chem. Lett.*, 2000, **29**, 678–679.

was added in a single portion. The reaction mixture was stirred under argon atmosphere at r.t. for 24 h, and poured into H<sub>2</sub>O (100 mL). The precipitate was isolated by filtration, and washed with H<sub>2</sub>O (200 mL). The residual material was extracted into hexane (100 mL), dried over anhyd MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure to afford **2a** as an off-white solid (1.05 g, yield = 49%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K): δ 8.43 (s, 4H), 8.11 (s, 4H), 0.28 (s, 36H), 0.27 (s, 18H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 298 K): δ 151.97, 150.00, 133.50, 126.24, 125.42, 77.16, 31.07, 1.48, 0.63, -0.48. FT-IR (ATR, cm<sup>-1</sup>): 2961, 1436, 1341, 1250, 1211, 1071, 1022, 943, 873, 841, 752, 690. HRMS (ESI) calcd for C<sub>34</sub>H<sub>62</sub>N<sub>4</sub>O<sub>6</sub>Si<sub>6</sub> [M + H]<sup>+</sup> 791.3358, found 791.3360.

**4,4'-Bis((*tert*-butyldimethylsilyl)oxy)-[1,1'-biphenyl]-3,3',5,5'-tetracarbaldehyde *O,O,O,O*-tetra(*tert*-butyl-dimethylsilyl) tetraoxime (**2b**).** A flame-dried 100 mL round-bottom flask was charged with **1** (0.53 g, 1.48 mmol) and a magnetic stir bar. The reaction vessel was purged with argon, and anhyd DMF (10 mL) was delivered to the vessel. Portions of *tert*-butyldimethylsilyl chloride (1.69 g, 11.2 mmol) and imidazole (1.53 g, 22.4 mmol) were added sequentially. The reaction mixture was stirred under argon atmosphere at r.t. for 24 h, and poured into H<sub>2</sub>O (50 mL). The precipitate was isolated by filtration, and washed with H<sub>2</sub>O (100 mL). The residual material was extracted into hexane (50 mL), dried over anhyd MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure to afford **2b** as an off-white solid (1.10 g, yield = 75%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K): δ 8.45 (s, 4H), 8.02 (s, 4H), 1.08 (s, 18H), 0.97 (s, 36H), 0.23 (s, 24H), 0.14 (s, 12H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 298 K): δ 151.84, 150.11, 133.99, 126.30, 125.53, 77.16, 26.22, 26.06, 25.86, 18.66, 18.30, -2.79, -3.85, -4.96. FT-IR (ATR, cm<sup>-1</sup>): 2944, 2913, 2893, 2875, 1467, 1455, 1356, 1292, 1227, 1061, 986, 919, 849, 767, 722. HRMS (ESI) calcd for C<sub>52</sub>H<sub>98</sub>N<sub>4</sub>O<sub>6</sub>Si<sub>6</sub> [M + H]<sup>+</sup> 1043.6175, found 1043.6175.

**4,4'-Bis((triisopropylsilyl)oxy)-[1,1'-biphenyl]-3,3',5,5'-tetracarbaldehyde *O,O,O,O*-tetratriisopropylsilyl tetraoxime (**2c**).** A flame-dried 100 mL round-bottom flask was charged with **1** (0.50 g, 1.40 mmol) and a magnetic stir bar. The reaction vessel was purged with argon, and anhyd DMF (10 mL) was delivered to the vessel. Portions of triisopropylsilyl chloride (2.40 mL, 11.2 mmol) and imidazole (1.52 g, 22.4 mmol) were added sequentially. The reaction mixture was stirred under argon atmosphere at r.t. for 24 h, and poured into H<sub>2</sub>O (50 mL). The precipitate was filtered and washed with H<sub>2</sub>O (100 mL). The residual material was extracted into hexane (50 mL), dried over anhyd MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure, affording **2c** as an off-white solid (1.03 g, yield = 57%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K): δ 8.55 (s, 4H), 7.84 (s, 4H), 1.27 (m, 18H), 1.10 (d, J = 7.4 Hz, 108H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 298 K): δ 153.08, 150.17, 150.15, 134.66, 126.51, 125.31, 18.03, 17.86, 13.70, 12.08, 12.06. FT-IR (ATR, cm<sup>-1</sup>): 2958, 2883, 1449, 1380, 1258, 1129, 1052, 1021, 1006, 924, 914, 784, 759, 694, 672, 558, 453. HRMS (ESI) calcd for C<sub>70</sub>H<sub>134</sub>N<sub>4</sub>O<sub>6</sub>Si<sub>6</sub> [M + H]<sup>+</sup> 1295.8992, found 1295.8992.

**4,4'-Bis((*tert*-butyldimethylsilyl)oxy)-[1,1'-biphenyl]-3,3',5,5'-tetracarbaldehyde (**4**).** A flame-dried 50 mL Schlenk flask was charged with **5** (0.105 g, 0.336 mmol) and a magnetic stir bar. The vessel was purged with argon, and anhyd DMF (5 mL) was delivered to the vessel. Anhyd triethylamine (0.11 mL, 0.81 mmol) was added in a single portion via syringe, and DMAP (9 mg, 0.07 mmol) was added in a single portion. A solution of *tert*-butyldimethylsilyl chloride (0.13 g, 0.84 mmol) in anhyd DMF (3 mL) was added dropwise to the mixture over a period of 20 min. The reaction mixture was stirred at r.t. for 24 h, and poured into sat'd aq NH<sub>4</sub>Cl (50 mL). The precipitate was isolated by filtration, washed with H<sub>2</sub>O (20 mL), and extracted into CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and acetone (20 mL) sequentially. The combined extracts were dried over anhyd MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure to afford **4** as a pale yellow solid (0.137 g, yield = 77%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  10.41 (s, 4H), 8.33 (s, 4H), 1.11 (s, 18H), 0.21 (s, 12H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  188.22, 160.40, 133.11, 132.62, 132.26, 129.90, 25.78, 18.68, -4.31. FT-IR (ATR,  $\text{cm}^{-1}$ ): 2948, 2929, 2860, 1687, 1596, 1573, 1470, 1450, 1391, 1293, 1262, 1230, 1075, 950, 900, 838, 823, 806, 779, 719, 666, 561, 497. HRMS (ESI) calcd for  $\text{C}_{28}\text{H}_{38}\text{O}_6\text{Si}_2$   $[\text{M} + \text{Na}]^+$  549.2099, found 549.2096.

**4,4'-Bis((*tert*-butyldimethylsilyl)oxy)-[1,1'-biphenyl]-3,3',5,5'-tetracarbaldehyde tetraoxime (3).** A 25 mL round-bottom flask was charged with **4** (49 mg, 95  $\mu\text{mol}$ ) and a magnetic stir bar. MeOH (5 mL) was added in a single portion, and  $\text{NH}_2\text{OH}\cdot\text{HCl}$  (132 mg, 190  $\mu\text{mol}$ ) and NaOAc (156 mg, 190  $\mu\text{mol}$ ) were added successively to the mixture. The reaction mixture was heated at reflux for 2 h, and concentrated under reduced pressure. The residue was dispersed in EtOAc (50 mL) and washed with  $\text{H}_2\text{O}$  (50 mL  $\times$  2). The organic layer was dried over anhyd  $\text{MgSO}_4$ , filtered, and concentrated under reduced pressure. The residual material was purified by flash column chromatography on  $\text{SiO}_2$  ( $\text{CH}_2\text{Cl}_2$ :MeOH = 95:5, v/v) to afford **3** as a pale yellow solid (30 mg, yield = 54%).  $^1\text{H}$  NMR (500 MHz, acetone- $d_6$ , 298 K):  $\delta$  10.54 (s, 4H), 8.39 (s, 4H), 8.06 (s, 4H), 1.12 (s, 18H), 0.20 (s, 12H).  $^{13}\text{C}$  NMR (125 MHz, acetone- $d_6$ , 298 K):  $\delta$  151.98, 145.47, 134.54, 126.91, 125.72, 26.21, 19.07, -3.79. FT-IR (ATR,  $\text{cm}^{-1}$ ): 3468, 2954, 2928, 2856, 1737, 1714, 1427, 1390, 1303, 1257, 1212, 1082, 1011, 960, 901, 882, 839, 783, 717, 682. HRMS (ESI) calcd for  $\text{C}_{28}\text{H}_{42}\text{N}_4\text{O}_6\text{Si}_2$   $[\text{M} + \text{Na}]^+$  609.2535, found 609.2539.

**X-ray Crystallographic Studies on 2b.** Single crystals of **2b** were prepared by slow evaporation of hexane solution of this material. A colorless crystal (approximate dimensions 0.075  $\times$  0.156  $\times$  0.197  $\text{mm}^3$ ) was placed onto a nylon loop with Paratone-N oil, and mounted on an XtaLAB AFC12 (RINC): Kappa dual home/near diffractometer. The data collection was carried out using Cu  $K\alpha$  radiation and the crystal was kept at  $T = 93$  K. A total of 53203 reflections were measured ( $5.102^\circ \leq 2\theta \leq 159.326^\circ$ ). The structure was solved with SHELXT<sup>3</sup> using Intrinsic Phasing, and refined with SHELXL<sup>4</sup> refinement package of OLEX2.<sup>5</sup> A total of 13663 unique reflections were used in all calculations. The final  $R1$  was 0.0415 ( $I \geq 2\sigma(I)$ ) and  $wR2$  was 0.1147 (all data). CCDC 2042527 contains the supplementary crystallographic data for this structure.

**X-ray Crystallographic Studies on 2c.** Single crystals of **2c** were prepared by slow evaporation of hexane solution of this material. A colorless crystal (approximate dimensions 0.053  $\times$  0.084  $\times$  0.154  $\text{mm}^3$ ) was placed onto a nylon loop with Paratone-N oil, and mounted on an XtaLAB AFC12 (RINC): Kappa dual home/near diffractometer. The data collection was carried out using Cu  $K\alpha$  radiation and the crystal was kept at  $T = 93$  K. A total of 47578 reflections were measured ( $5.618^\circ \leq 2\theta \leq 159.158^\circ$ ). The structure was solved with SHELXT<sup>3</sup> using Intrinsic Phasing, and refined with SHELXL<sup>4</sup> refinement package of OLEX2.<sup>5</sup> A total of 16502 unique reflections were used in all calculations. The final  $R1$  was 0.0458 ( $I \geq 2\sigma(I)$ ) and  $wR2$  was 0.1278 (all data). CCDC 2042528 contains the supplementary crystallographic data for this structure.

<sup>3</sup> G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3–8.

<sup>4</sup> G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3–8.

<sup>5</sup> O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339–341.

**Table S1.** X-ray Crystallographic Data of **2b** and **2c**.

	<b>2b</b>	<b>2c</b>
Chemical formula	C <sub>52</sub> H <sub>98</sub> N <sub>4</sub> O <sub>6</sub> Si <sub>6</sub>	C <sub>70</sub> H <sub>134</sub> N <sub>4</sub> O <sub>6</sub> Si <sub>6</sub>
Formula weight	1043.88	1296.34
Crystal system	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
Color of crystal	colorless	colorless
a (Å)	11.96430(10)	15.9929(3)
b (Å)	16.5858(2)	16.1504(3)
c (Å)	17.56880(10)	17.3188(4)
$\alpha$ (°)	90.5290(10)	79.449(2)
$\beta$ (°)	98.8760(10)	65.041(2)
$\gamma$ (°)	109.3500(10)	78.584(2)
Volume (Å <sup>3</sup> )	3243.16(6)	3950.27(15)
<i>Z</i>	2	2
<i>R</i> <sub>int</sub>	0.0349	0.0348
Final <i>R</i> indices [ <i>I</i> ≥ 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0415, <i>wR</i> 2 = 0.1132	<i>R</i> 1 = 0.0458, <i>wR</i> 2 = 0.1243
Final <i>R</i> indices [all data]	<i>R</i> 1 = 0.0434, <i>wR</i> 2 = 0.1147	<i>R</i> 1 = 0.0512, <i>wR</i> 2 = 0.1278
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.121	1.099

**Synthesis of Metallogels.** Solution samples of **2a**, **2b**, and **2c** (0.14 M in CH<sub>2</sub>Cl<sub>2</sub>, 0.12 mL, 17 μmol) were delivered to 2 mL vials. A solution of Zn(acac)<sub>2</sub>·xH<sub>2</sub>O (0.14 M in CH<sub>2</sub>Cl<sub>2</sub>, 0.36 mL, 50 μmol, 3 equiv) was added to each of the vials, and Et<sub>3</sub>N (15 μL, 102 μmol) was added in a single portion to afford clear light yellow solutions. To the pre-mixture, tetrabutylammonium fluoride (1.4 M in CH<sub>2</sub>Cl<sub>2</sub>, 0.07 mL, 102 μmol, 6 equiv) was added quickly via syringe. The solution became turbid and gelled to produce a yellow opaque material.

**Gelation Rate Measurements.** Stock solutions were prepared according to the following procedure. A CH<sub>2</sub>Cl<sub>2</sub> solution of silyl-protected ligand (**2a**, **2b**, or **2c**; 0.14 M, 0.12 mL, 17 μmol) was placed in a 2 mL vial. To this vial, a portion of Zn(acac)<sub>2</sub>·xH<sub>2</sub>O (0.14 M in CH<sub>2</sub>Cl<sub>2</sub>, 3.6 mL, 0.50 mmol, 3 equiv) was added, followed by the addition of Et<sub>3</sub>N (0.15 mL, 1.02 mmol) to afford a clear light yellow solution. This pre-mixture (1.6 mL) was transferred to a dual-path UV–vis cuvette and placed inside the sample holder. The intensity of panchromatic light (λ = 300–700 nm) penetrating the sample was measured. A CH<sub>2</sub>Cl<sub>2</sub> solution of tetrabutylammonium fluoride (1.4 M, 0.23 mL, 6 equiv) was added quickly in a single portion via a syringe needle placed at the center of the solution. The gelation process was monitored by recording changes in the transmittance of the panchromatic light.

**Rheological Measurements.** Viscoelastic properties of the metallogels were determined by using a rheometer (Discovery Hybrid HR-3 rheometer, TA Instruments, USA). For time-dependent measurements, a pre-mixture containing **2a**, **2b** or **2c** in CH<sub>2</sub>Cl<sub>2</sub> (3.4 mL; see above for the sample preparation) was delivered to a 70 mL vial. The height of the rotating plate was adjusted to come into contact with the solution surface, and an angular frequency of 10 rad s<sup>-1</sup> was maintained. Concurrently, tetrabutylammonium fluoride (1.0 M in THF, 0.7 mL) was added via a syringe, and

the storage modulus ( $G'$ ) and loss modulus ( $G''$ ) were recorded (Fig. S4). The resulting gel materials were isolated to eliminate the influence of remaining fluid, and their mechanical properties were measured using a rotating disk (Fig. S2). Frequency sweeps of gels were performed in the angular frequency range of 0.1 to 100  $\text{rad s}^{-1}$  at strain (1%) in the linear region.

**Selectivity Studies.** A pre-mixture containing **2b** in  $\text{CH}_2\text{Cl}_2$  (0.8 mL; see above for the sample preparation) was delivered to 1.5 mL vials. To each of these vials, solution samples of  $\text{TBA}^+\text{X}^-$  ( $\text{X}^- = \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{PF}_6^-, \text{ClO}_4^-, \text{BF}_4^-, \text{OAc}^-, \text{OTf}^-, \text{and NO}_3^-$ ) in  $\text{CH}_2\text{Cl}_2$  (1.4 M, 0.12 mL, 6 equiv) were added in a single portion. Gelation was checked by inversion tests (Fig. 3a), in which the vial was turned upside down to see if the mixture flowed.

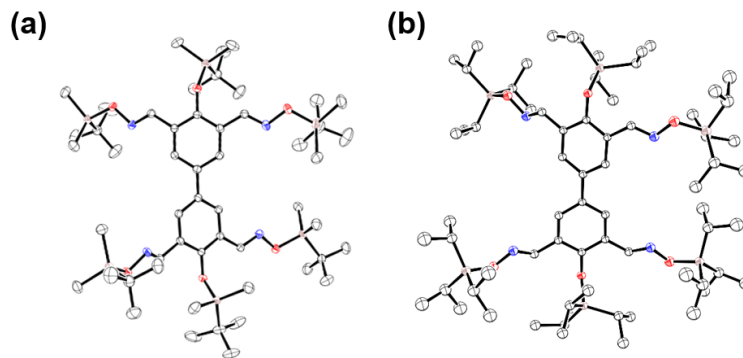
**Effect of Cation on Gelation.** A pre-mixture containing **2b** in  $\text{CH}_2\text{Cl}_2$  (0.8 mL; see above for the sample preparation) was delivered to 1.5 mL vials. Solution samples of tetrabutylammonium fluoride (1.4 M in  $\text{CH}_2\text{Cl}_2$ , 0.12 mL, 6 equiv) and CsF (1.4 M in MeOH, 0.12 mL, 6 equiv) were added to each vial in a single portion. Gelation was checked by inversion tests (Fig. 3b), in which the vial was turned upside down to see if the mixture flowed.

**Effect of Metal Source on Gelation.** A solution of **2b** (0.14 M in  $\text{CH}_2\text{Cl}_2$ , 0.12 mL, 17  $\mu\text{mol}$ ) was divided into 1.5 mL vials. Different metal acetylacetonate complexes ( $\text{Fe}(\text{acac})_3$  and  $\text{Co}(\text{acac})_3$ : 0.09 M in  $\text{CH}_2\text{Cl}_2$ , 0.36 mL, 33  $\mu\text{mol}$ , 2 equiv;  $\text{Co}(\text{acac})_2$ ,  $\text{Cu}(\text{acac})_2$ , and  $\text{Zn}(\text{acac})_2 \cdot x\text{H}_2\text{O}$ : 0.14 M in  $\text{CH}_2\text{Cl}_2$ , 0.36 mL, 50  $\mu\text{mol}$ , 3 equiv) were added to each vial. A portion of  $\text{Et}_3\text{N}$  (15  $\mu\text{L}$ , 100  $\mu\text{mol}$ ) was added in a single portion to each vial. Following this, tetrabutylammonium fluoride (1.4 M in  $\text{CH}_2\text{Cl}_2$ , 0.07 mL, 100  $\mu\text{mol}$ ) was introduced into each vial using a syringe. Gelation was checked by inversion tests (Fig. 3c), in which the vial was turned upside down to see if the mixture flowed.

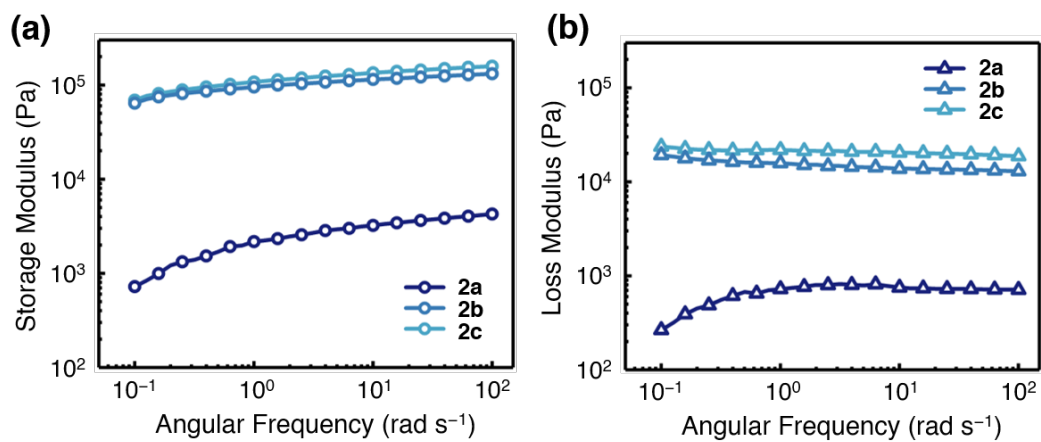
**Preparation of Xerogels.** Xerogel samples were prepared by washing the metallogels with  $\text{CH}_2\text{Cl}_2$  to remove soluble components, and mounted on copper tape for SEM analysis (Fig. S3). Xerogels of **2a**, **2b** and **2c** showed similar structures composed of small particles.

**Measurements in Flow Systems.** In the flow system depicted in Fig. 6a,  $\text{CH}_2\text{Cl}_2$  (50 mL) was delivered to a reservoir and allowed to flow down until a constant flow rate was reached. After depleting the reservoir, 5 mL of pre-mixture (**2a**, **2b**, or **2c**) was quickly loaded into the reservoir. Once the pre-mixture filled the flow system and a constant flow rate was established, tetrabutylammonium fluoride (1.0 M in THF, 0.5 mL) was added via a syringe. Time-dependent changes in the flow rate were recorded using a flowmeter. Images of fluorescence change (Fig. 6c) were monitored and recorded under a UV lamp ( $\lambda = 365 \text{ nm}$ ) as schematically shown in Fig. S4.

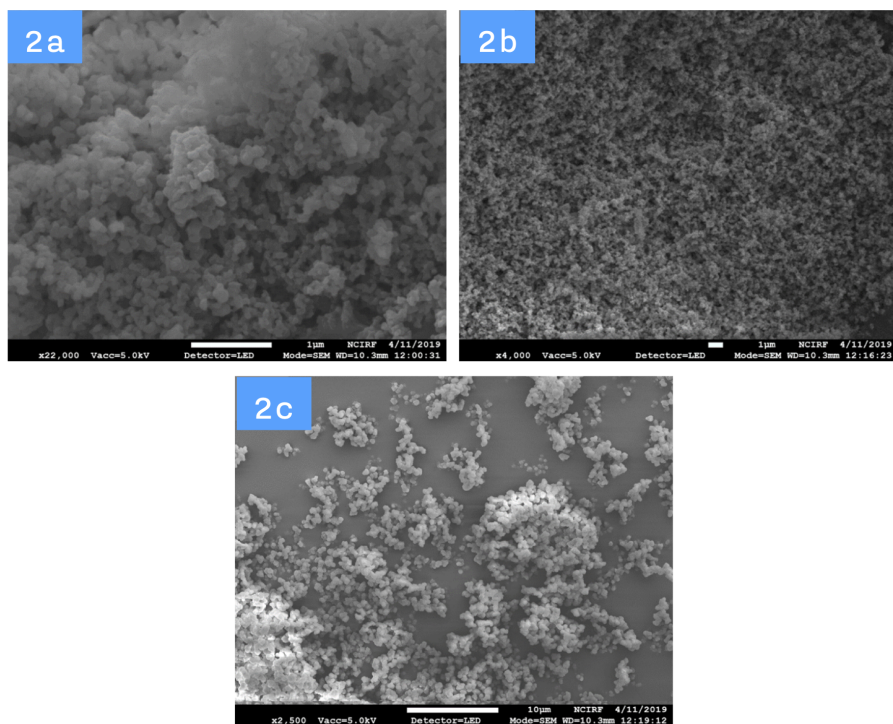
**Gelation–Degelation Switching in the Flow System.** In the flow system depicted in Fig. 7b,  $\text{CH}_2\text{Cl}_2$  (50 mL) was delivered to a reservoir and allowed to flow down until a constant flow rate was reached. After depleting the reservoir, 5 mL of a pre-mixture of **2a** was quickly loaded into the reservoir. Once the pre-mixture filled the flow system and a constant flow rate was established, tetrabutylammonium fluoride (1.0 M in THF, 0.2 mL) was added via a syringe. As the flow rate decreased to its minimum, HBr (33 wt% in AcOH, 0.5 mL) was introduced. This process was repeated three times, and the time-dependent changes in flow rate were recorded using a flowmeter.



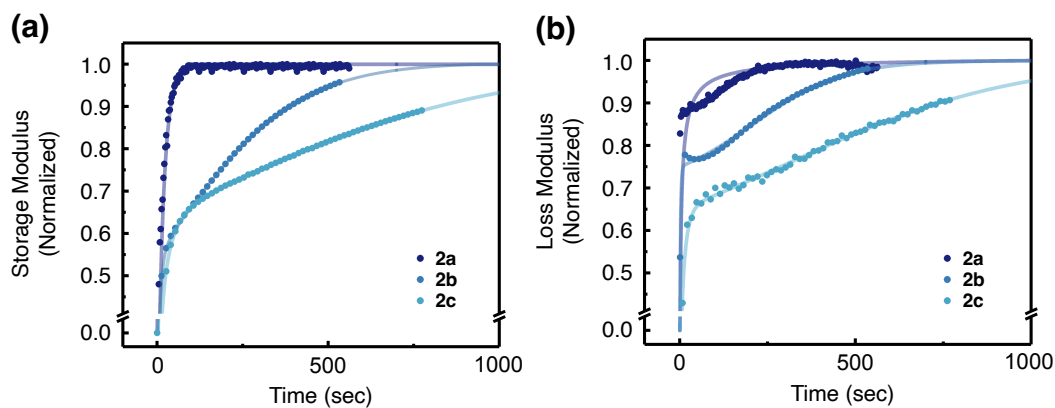
**Fig. S1.** ORTEP diagrams of (a) **2b** and (b) **2c** with thermal ellipsoids at the 50% probability level.



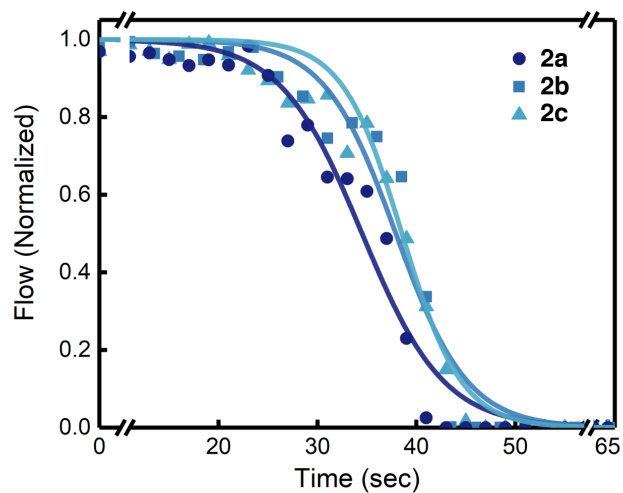
**Fig. S2.** (a) Storage modulus, and (b) loss modulus of zinc metallogels prepared by adding F<sup>-</sup> ions into a premix solution of pre-gelators (**2a**, **2b**, or **2c**) and Zn<sup>2+</sup> in CH<sub>2</sub>Cl<sub>2</sub> at  $T = 273$  K.



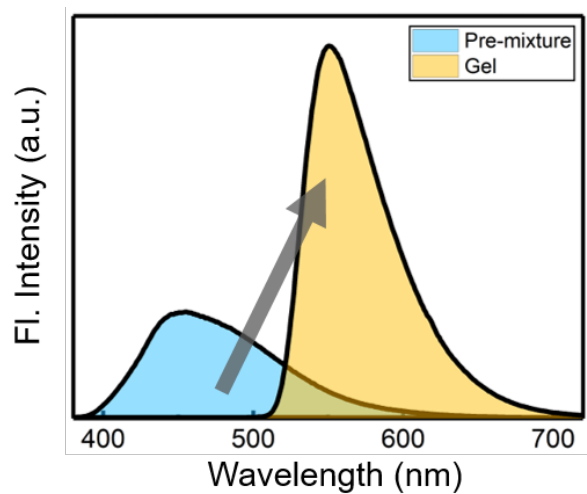
**Fig. S3.** SEM images of xerogels from **2a**, **2b**, and **2c**.



**Fig. S4.** Time-dependent changes in the normalized (a) storage modulus, and (b) loss modulus of pre-gel solutions of pre-gelators (**2a**, **2b**, or **2c**) and  $\text{Zn}^{2+}$  in  $\text{CH}_2\text{Cl}_2$  following the addition of  $\text{F}^-$  ions ( $t = 0$ ) at  $T = 273$  K.  $\omega = 10$  rad  $\text{s}^{-1}$ ; strain = 1%. Solid lines serve as visual guides.

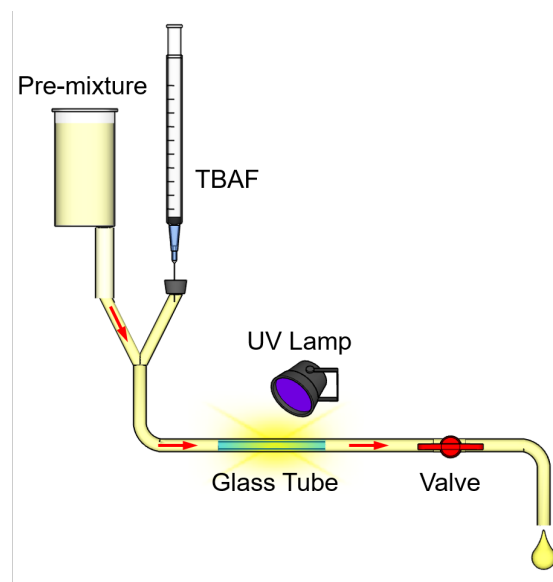


**Fig. S5.** Time-dependent changes in the normalized flow rate upon adding  $F^-$  ions into a draining premix solution of pre-gelators (**2a**, **2b**, or **2c**) +  $Zn^{2+}$  in  $CH_2Cl_2$ . Solid lines serve as visual guides.

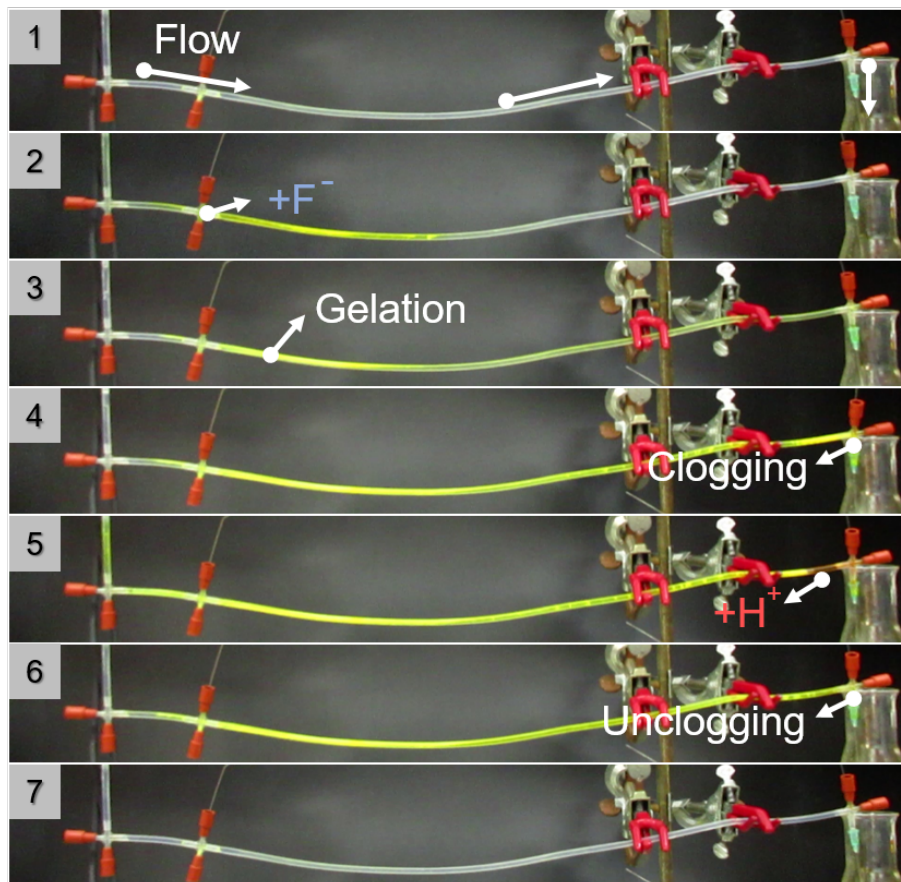


**Fig. S6.** Fluorescence spectra of pre-mixture (shaded in blue) and metallogel (shaded in yellow) of **2b** in  $CH_2Cl_2$  at 298 K ( $\lambda_{ex} = 365$  nm).

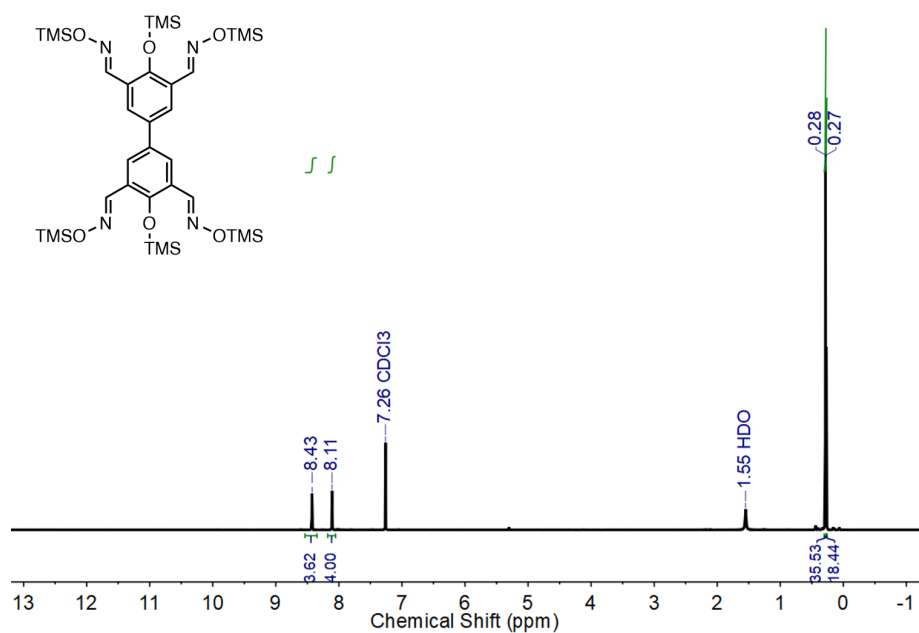




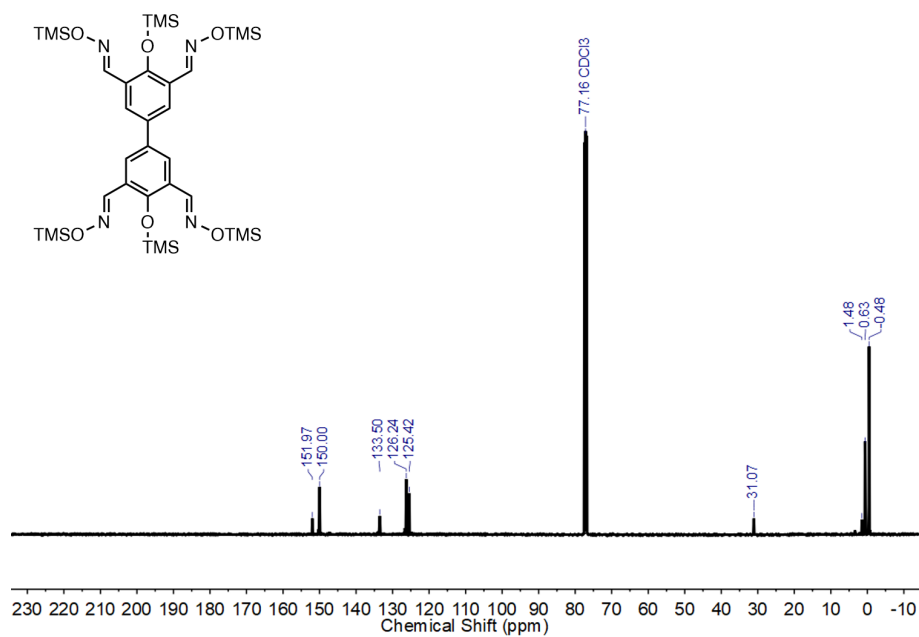
**Fig. S7.** Schematic diagram of an experimental setup to take time-lapse images of fluorescence changes in the fluidic system.



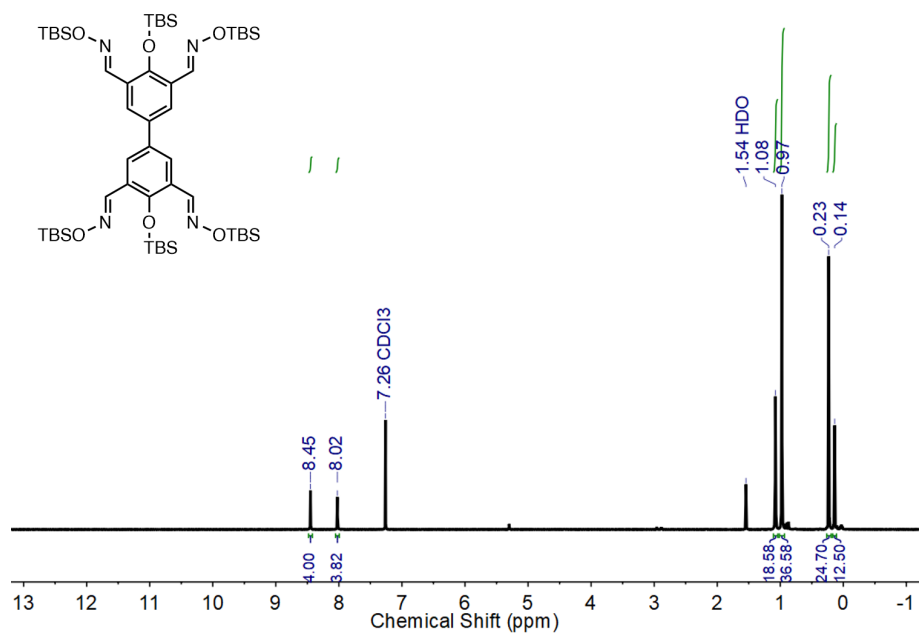
**Fig. S8.** Time-lapse photographic images showing the clogging–unclogging cycle driven by the alternate introduction of fluoride and acid into the flow system.



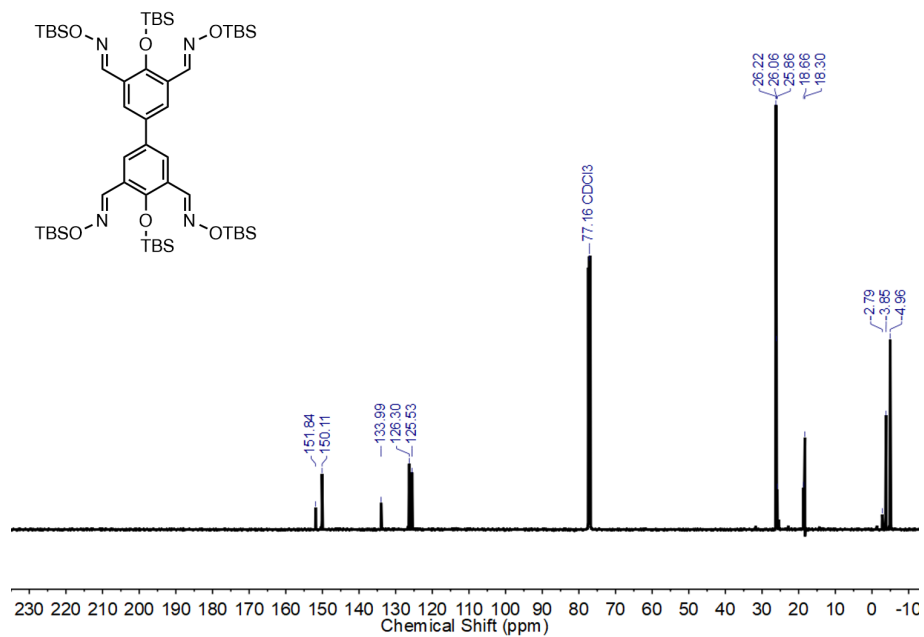
**Fig. S9.**  $^1\text{H}$  NMR (500 MHz) spectrum of **2a** in  $\text{CDCl}_3$  ( $T = 298$  K).



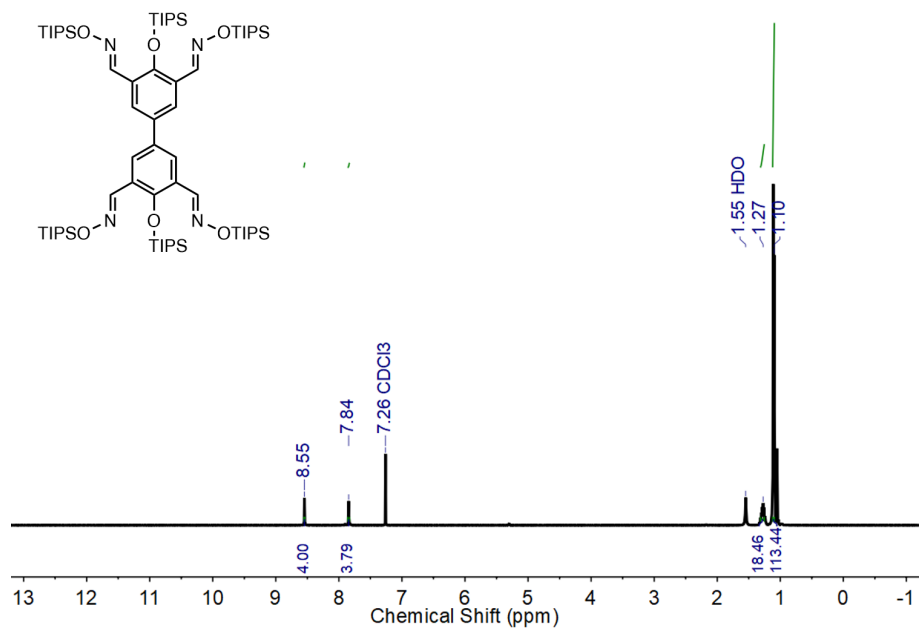
**Fig. S10.**  $^{13}\text{C}$  NMR (125 MHz) spectrum of **2a** in  $\text{CDCl}_3$  ( $T = 298$  K).



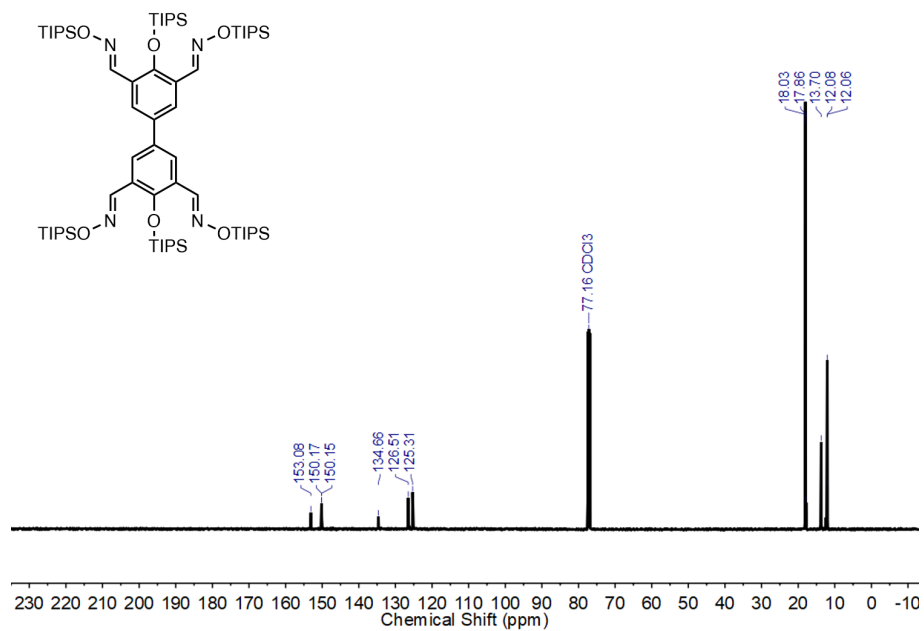
**Fig. S11.** <sup>1</sup>H NMR (500 MHz) spectrum of **2b** in CDCl<sub>3</sub> (*T* = 298 K).



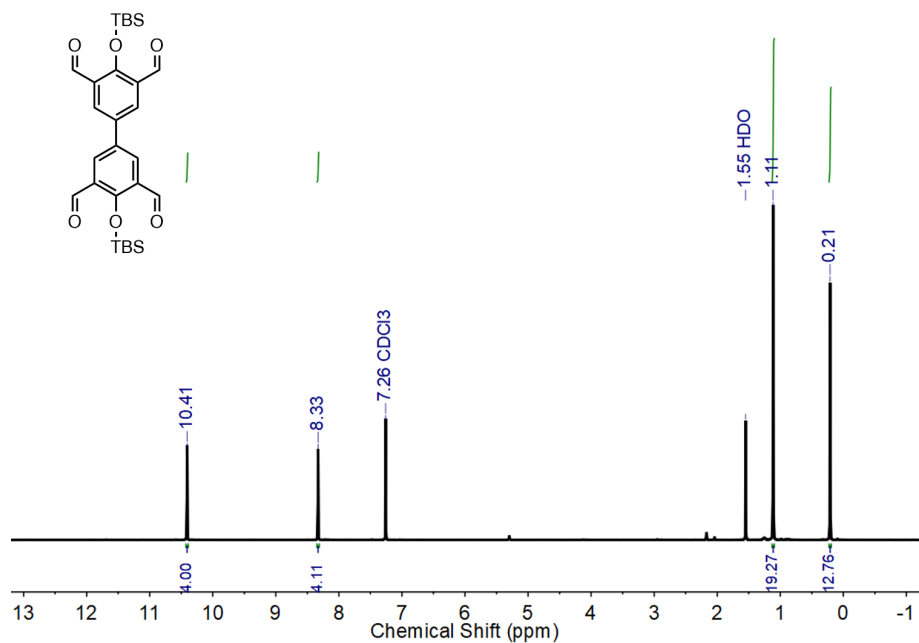
**Fig. S12.** <sup>13</sup>C NMR (125 MHz) spectrum of **2b** in CDCl<sub>3</sub> (*T* = 298 K).



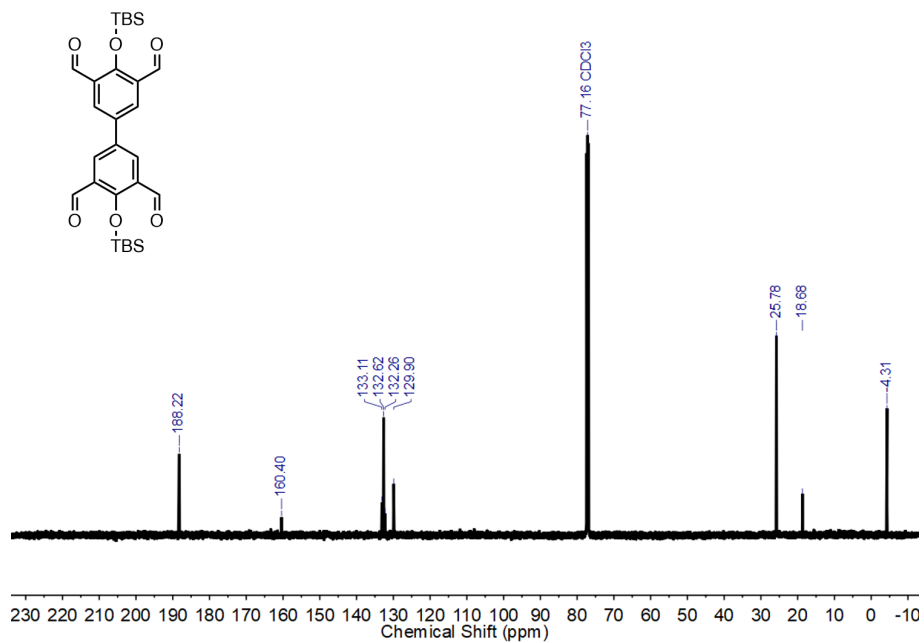
**Fig. S13.** <sup>1</sup>H NMR (500 MHz) spectrum of **2c** in CDCl<sub>3</sub> (*T* = 298 K).



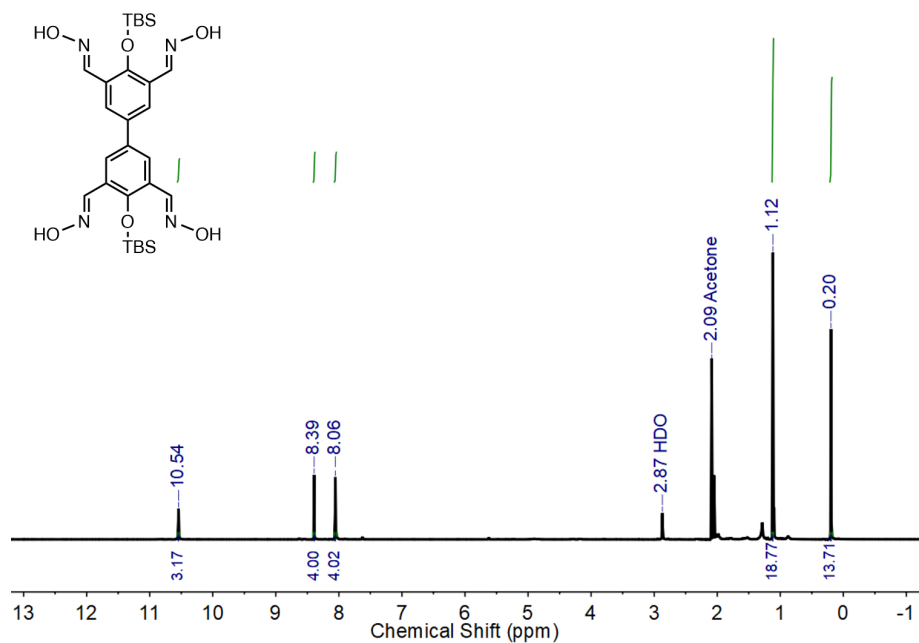
**Fig. S14.** <sup>13</sup>C NMR (125 MHz) spectrum of **2c** in CDCl<sub>3</sub> (*T* = 298 K).



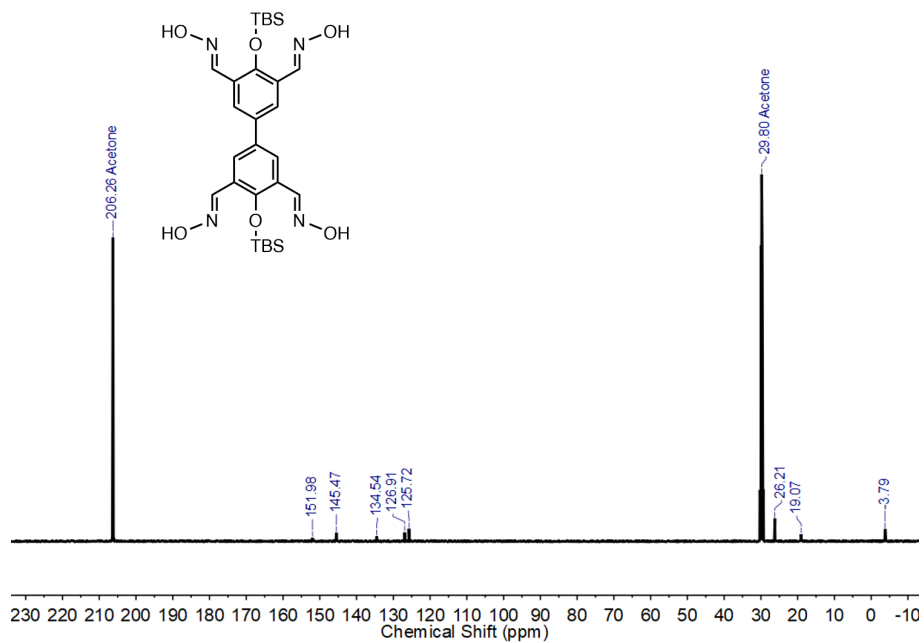
**Fig. S15.**  $^1\text{H}$  NMR (500 MHz) spectrum of **4** in  $\text{CDCl}_3$  ( $T = 298$  K).



**Fig. S16.**  $^{13}\text{C}$  NMR (125 MHz) spectrum of **4** in  $\text{CDCl}_3$  ( $T = 298$  K).



**Fig. S17.**  $^1\text{H}$  NMR (500 MHz) spectrum of **3** in acetone- $d_6$  ( $T = 298$  K).



**Fig. S18.**  $^{13}\text{C}$  NMR (125 MHz) spectrum of **3** in acetone- $d_6$  ( $T = 298$  K).