Double layer 3D codes: fluorescent supramolecular polymeric gels allowing direct recognition of the chloride anion using a smart phone

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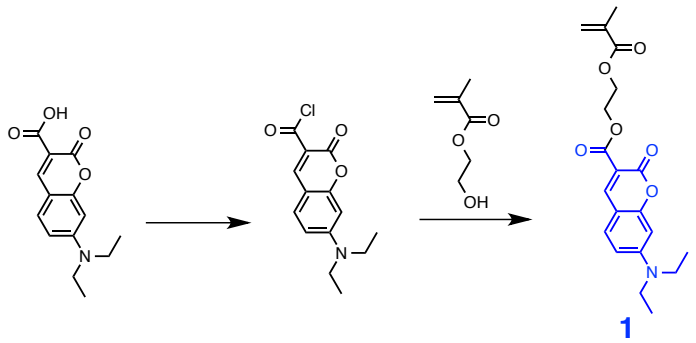
Electronic Supplementary Information

1. Materials and methods

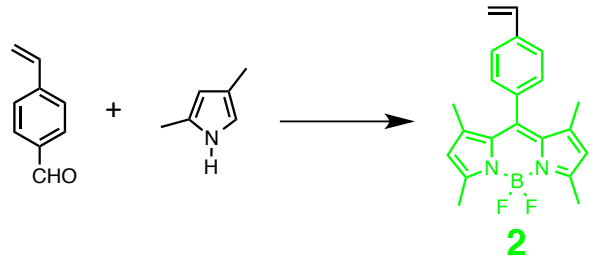
One- and two-dimensional nuclear magnetic resonance (NMR) spectra were recorded on Agilent MR 400, and Varian Inova 500 instruments. The instrumental parameters for the NMR spectrometer were as follows: Field: 400 MHz; sweep width: 8223.685 Hz; number of scans: 16; temperature: 298 K. ESI Mass spectra were obtained on an Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS or a Thermoscientific TSQ Quantum GC/MS. Fluorescence measurements were performed on a Perkin-Elmer Luminescence Spectrophotometer LS 50B or a Gilden Photonics Ltd. fluorimeter. Rheological experiments were performed using a rheometer (AR 2000EX, TA instrument) with a Peltier plate in the frequency sweep mode (25 °C). Tensile tests were performed using a tensile Hounsfield machine equipped with a 5-N load cell. The experiments were performed at room temperature using a deformation rate of 100 mm min^{-1}. The black nitrile substrate used in the present experiments was cut from a standard laboratory glove. The commercially available smartphone "app" used in the present studies was COLORCODE^{TM} and at the time the work was performed could be downloaded for free from the Apple app store.

2. Synthesis of the monomers for polymerization



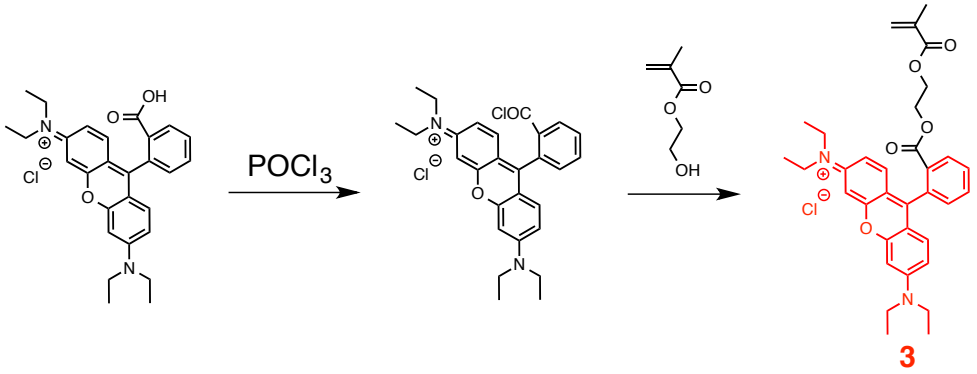
Monomer **1**: Under nitrogen, 7-(diethylamino)-2-oxo-2H-chromene-3-carboxylic acid (998 mg, 3.8 mmol) was added to dry liquid $SOCl_2$ (15 mL) and the resulting suspension was stirred at room temperature for 3 hours. The mixture was then filtered. The solid material isolated in this way was washed with ether to afford 898 mg of a yellow solid, 7-(diethylamino)-2-oxo-2H-chromene-3-carbonyl chloride (yield 84 %), which was immediately taken forward for use in the ensuing synthetic steps.

Under nitrogen, Et_3N (0.2 ml) was added to a solution of 2-hydroxyethyl methacrylate (199 mg, 1.5 mmol) in CH_2Cl_2 (10 mL). A solution of 7-(diethylamino)-2-oxo-2H-chromene-3-carbonyl chloride (279 mg, 1.0 mmol) in CH_2Cl_2 (20 mL) was then added dropwise to the first solution with stirring. After stirring for 24 h, the reaction mixture was washed with water (100 mL). The organic phase was separated off and dried over anhydrous Na_2SO_4. After removal of the solids by filtration, the solvent was removed under reduced pressure. The crude product obtained in this way was purified by column chromatography (silica gel, CH_2Cl_2: acetone = 9:1, v/v, eluent) to afford 310 mg of **1** in 83% yield.[1] ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.49 (s, 1H), 7.55 (d, J = 8.4 Hz, 1H), 6.80 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 6.50 (d, J = 2.0 Hz, 1H), 6.12 (s, 1H), 5.64 (s, 1H), 4.45-4.55 (m, 4H), 3.58 (q, J = 6.8 Hz, 4H), 1.93 (s, 3H), 1.25 (t, J = 6.8 Hz, 6H).



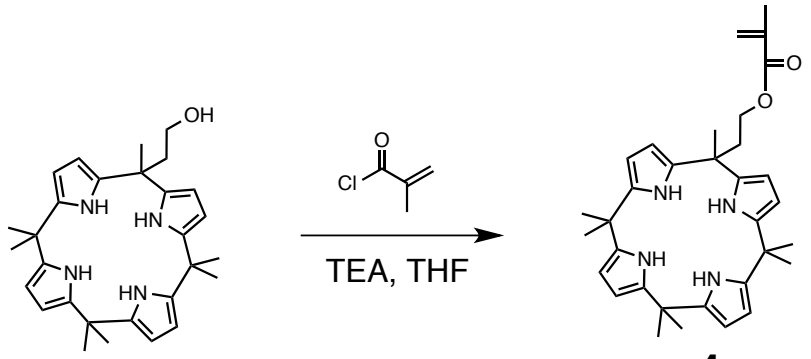
Monomer **2**: 4-Vinylbenzaldehyde (529 mg, 4.00 mmol) and 2,4-dimethylpyrrole (761 mg, 8.00 mmol) were dissolved in 500 mL dry and degassed CH_2Cl_2 (N_2 was bubbled through the CH_2Cl_2

solvent for 30 min prior to use), and 10 drops of TFA were added dropwise. The resulting red solution was stirred at room temperature in the dark overnight. After chloranil (992 mg, 4.00 mmol) was added, the reaction mixture was stirred for additional 6 h, followed by the addition of 6 mL of Et_3N and 6 mL of BF_3•OEt_2. After stirring for a further 30 min, the reaction mixture was washed three times with water and dried over Na_2SO_4. After filtration to remove the solids, the volatiles were evaporated off and the resulting residue was purified by flash column chromatography (silica gel, CH_2Cl_2: petroleum ether = 1:2, v/v, eluent) to give **2** as an orange solid (144 mg, 10%).[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.8 Hz, 2H), 7.25 (d, J = 8.8 Hz, 2H), 6.79 (m, 1H), 6.00 (s, 2H), 5.88 (d, J = 17.6 Hz, 1H), 5.38 (d, J = 10.9 Hz, 1H), 2.58 (s, 6H), 1.44 (s, 6H).



Monomer **3**: Under nitrogen, phosphorus oxychloride (0.3 mL) was added dropwise to a solution of rhodamine B (479 mg, 1.0 mmol) in dichloromethane (10 mL). The solution was then heated at reflux for 4 h. After cooling, the volatiles were evaporated off under vacuum to give rhodamine B acid chloride,[3] which was not purified and used for the next step immediately.

Under nitrogen, Et_3N (0.2 mL) was added to a solution of 2-aminoethyl methacrylate hydrochloride (248 mg, 1.5 mmol) in CH_2Cl_2 (10 mL). The above solution of rhodamine B acid chloride (497 mg, 1.0 mmol) in CH_2Cl_2 (20 mL) was then added dropwise to the first solution with stirring. After 24 h, the mixture was washed with water (100 mL) and the organic layer was dried over anhydrous Na_2SO_4 and filtered. The volatiles were evaporated off under reduced pressure. The crude product obtained in this way was purified by column chromatography (silica gel, ethyl acetate: methanol = 2 : 1, v/v, eluent) to afford 308 mg of **3** in 52% yield.[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30–6.80 (m, 10H), 6.02 (s, 1H), 5.55 (s, 1H), 4.29 (t, J = 6.8 Hz, 2H), 4.19 (t, J = 6.8 Hz, 2H), 3.63 (q, J = 7.2 Hz, 8H), 1.88 (s, 3H), 1.33 (t, J = 7.2 Hz, 12H).



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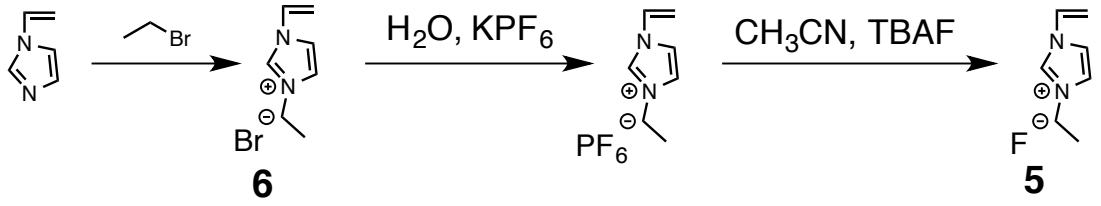
Monomer **4**: In a 100 mL round bottom flask, ethyl hydroxycalix[4]pyrrole (0.5191 g, 1.13 mmol) was dissolved in dry tetrahydrofuran (50 mL) and placed under an atmosphere of nitrogen gas. To this solution was added freshly distilled triethylamine (0.20 mL, 1.43 mmol) and the resulting mixture was stirred for 10 minutes at room temperature and then cooled to 0 °C with an ice-water bath. To the cooled solution was added methacryloyl chloride (0.13 mL, 1.16 mmol) dropwise over 15 minutes. The reaction was then allowed to stir while warming to room temperature over 2 hours. Upon consumption of the starting material, the reaction was quenched with water (30 mL). The excess THF was removed and the water layer was extracted with dichloromethane (3 × 20 mL) and the combined organic layers were then washed with saturated aqueous sodium bicarbonate (2 × 20 mL) and brine (1 × 30 mL). The organic layer was then dried over sodium sulfate, decanted, and the excess solvent removed *in vacuo*. The resulting crude brown solid was then purified by column chromatography (silica gel; eluent: dichloromethane). After removal of the excess solvent, product **4** (0.3883 g, 65% yield) was obtained as a fluffy white powder (65% yield);[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (s, 4H), 6.02 (t, J = 1.2 Hz, 1H), 5.90 (m, 8H), 5.52 (t, J = 1.6 Hz, 1H), 4.02 (t, J = 7.2 Hz, 2H), 2.23 (t, J = 7.2 Hz, 2H), 1.90 (s, 3H), 1.49 (s, 21H).



6 **5**

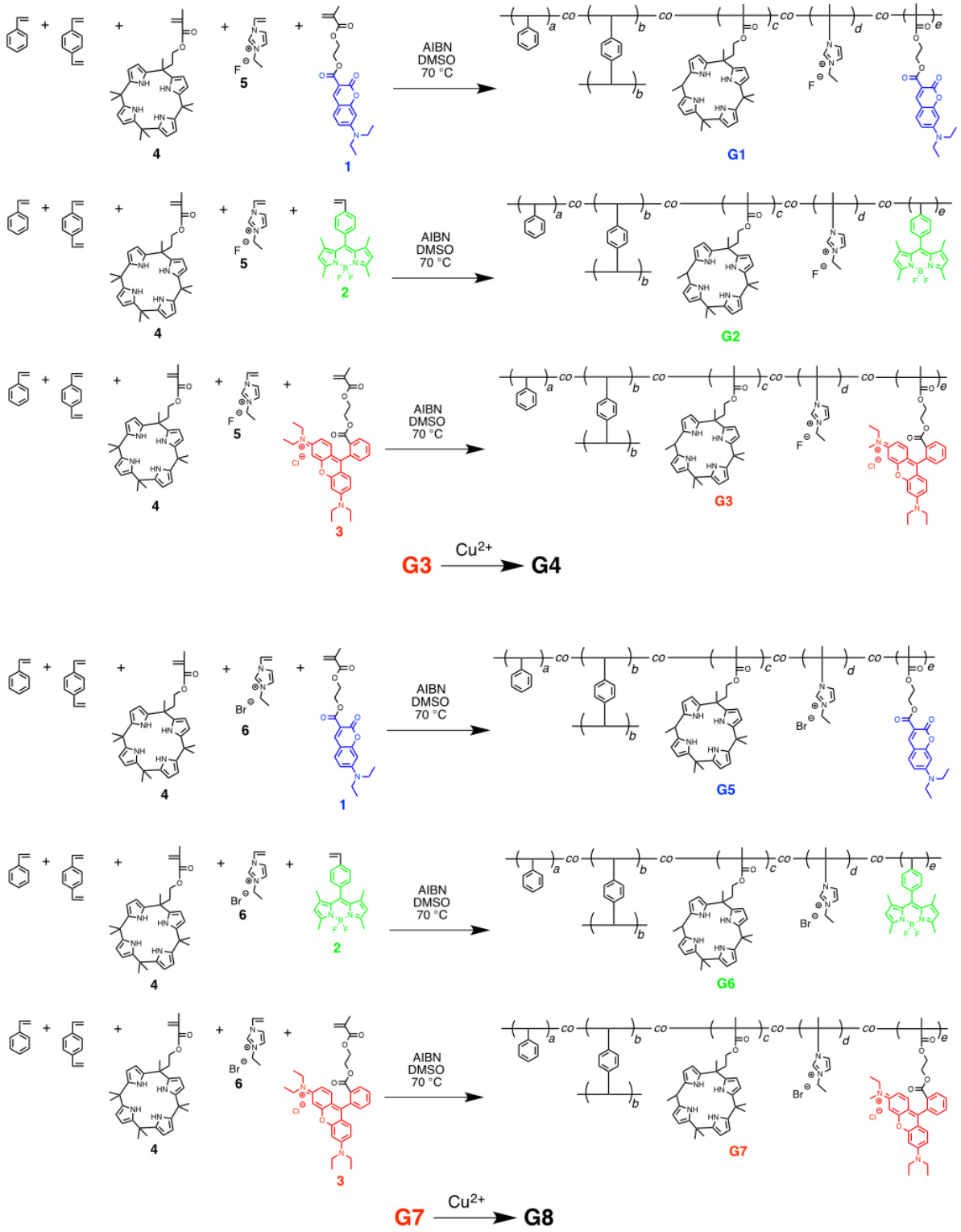
Monomer **6**:[6] Under a nitrogen atmosphere, a mixture of 1-vinylimidazole (2.82 g, 30 mmol) and bromoethane (3.85 g, 36 mmol) in acetone (15 mL) was heated at reflux for 48 hours. The product (3.84 g, 63% yield) was precipitated via the addition of ether, filtrated, and dried at room

temperature under vacuum. ^{1}H NMR (400 MHz, d_6-DMSO): 9.77 (s, 1H), 8.31 (s, 1 H), 8.05 (s, 1H), 7.37 (dd, 1H), 6.05 (dd, 1H), 5.44 (dd, 1H), 4.28 (q, 2H), 1.47 (t, 3H).

Monomer **5**:[7]

To monomer **6** (3.000 g, 0.014 mol) as an aqueous solution, KPF_6 (2.577 g, 0.014 mmol) was added and stirred at room temperature for 24 h. The precipitate was washed with water three times and dried under vacuum at room temperature.[7a] The obtained precipitate was further dissolved in CH_3CN, and excess tetrabutylammonium fluoride (TBAF) was introduced. This led to formation of a precipitate, which was collected by filtration and washed with CH_3CN to afford monomer **5** (1.17 g, 59%) as a white solid.[7b] ^{1}H NMR (400 MHz, d_6-DMSO): 9.77 (s, 1H), 8.31 (s, 1 H), 8.05 (s, 1H), 7.37 (dd, 1H), 6.05 (dd, 1H), 5.44 (dd, 1H), 4.28 (q, 2H), 1.47 (t, 3H).

3. Synthesis and characterization of the fluorescent polymeric gels



Scheme S1. Synthetic routes to the fluorescent polymeric gels used in this study.

G1: Styrene (208 mg, 2.00 mmol), *p*-divinylbenzene (1.30 mg, 0.01 mmol), **4** (211 mg, 0.40 mmol), **5** (28.4 mg, 0.20 mmol), **1** (1.49 mg, 0.004 mmol), and azobisisobutyronitrile (AIBN) (0.33 mg, 0.002 mmol) were dissolved in DMSO (0.5 mL). The solution was purged with argon gas for 30 min and was then heated at 70 °C overnight to give a gel. The gel obtained in this way was repeatedly washed with $CHCl_3$ to remove DMSO over the course of two days.

G2: Styrene (208 mg, 2.00 mmol), *p*-divinylbenzene (1.30 mg, 0.01 mmol), **4** (211 mg, 0.40 mmol), **5** (28.4 mg, 0.20 mmol), **2** (1.40 mg, 0.004 mmol), and azobisisobutyronitrile (AIBN) (0.33 mg, 0.002 mmol) were dissolved in DMSO (0.5 mL). The solution was purged with argon gas for 30 min and was then heated at 70 °C overnight to give a gel. The gel obtained in this way was repeatedly washed with $CHCl_3$ to remove DMSO over the course of two days.

G3: Styrene (208 mg, 2.00 mmol), *p*-divinylbenzene (1.30 mg, 0.01 mmol), **4** (211 mg, 0.40 mmol), **5** (28.4 mg, 0.20 mmol), **3** (2.36 mg, 0.004 mmol), and azobisisobutyronitrile (AIBN) (0.33 mg, 0.002 mmol) were dissolved in DMSO (0.5 mL). The solution was purged with argon gas for 30 min and was then heated at 70 °C overnight to give a gel. The gel obtained in this way was repeatedly washed with $CHCl_3$ to remove DMSO over the course of two days.

G4: This gel was obtained by covering gel **G3** with excess $Cu(CH_3COO)_2$ powder (10.0 mg).

G5: Styrene (208 mg, 2.00 mmol), *p*-divinylbenzene (1.30 mg, 0.01 mmol), **4** (211 mg, 0.40 mmol), **6** (162 mg, 0.80 mmol), **1** (1.49 mg, 0.004 mmol), and azobisisobutyronitrile (AIBN) (0.33 mg, 0.002 mmol) were dissolved in DMSO (0.5 mL). The solution was purged with argon for 30 min and was then heated at 70 °C overnight to give a gel. The gel obtained in this way was repeatedly washed with $CHCl_3$ over the course of two days to remove DMSO.

G6: Styrene (208 mg, 2.00 mmol), *p*-divinylbenzene (1.30 mg, 0.01 mmol), **4** (211 mg, 0.40 mmol), **6** (162 mg, 0.80 mmol), **2** (1.40 mg, 0.004 mmol), and azobisisobutyronitrile (AIBN) (0.33 mg, 0.002 mmol) were dissolved in DMSO (0.5 mL). The solution was purged with argon gas for 30 min and was then heated at 70 °C overnight to give a gel. The gel obtained in this way was repeatedly washed with $CHCl_3$ over the course of two days to remove DMSO.

G7: Styrene (208 mg, 2.00 mmol), *p*-divinylbenzene (1.30 mg, 0.01 mmol), **4** (211 mg, 0.40 mmol), **6** (162 mg, 0.80 mmol), **3** (2.36 mg, 0.004 mmol), and azobisisobutyronitrile (AIBN) (0.33 mg, 0.002 mmol) were dissolved in DMSO (0.5 mL). The solution was purged with argon gas for 30 min and was then heated at 70 °C overnight to give a gel. The gel obtained in this way was repeatedly washed with $CHCl_3$ over the course of two days to remove DMSO.

G8: This gel was obtained by covering gel **G7** with excess $Cu(CH_3COO)_2$ powder (10.0 mg).

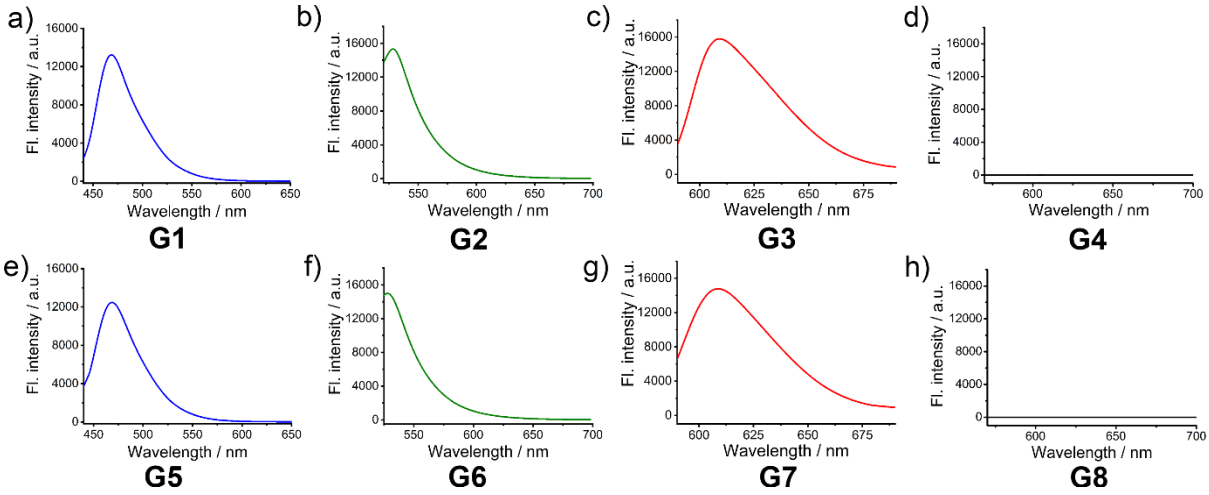


Fig. S1. Fluorescence emission spectra (λ_{ex} = 365 nm) of a) **G1**, b) **G2**, c) **G3**, d) **G4**, e) **G5**, f) **G6**, g) **G7**, and h) **G8**.

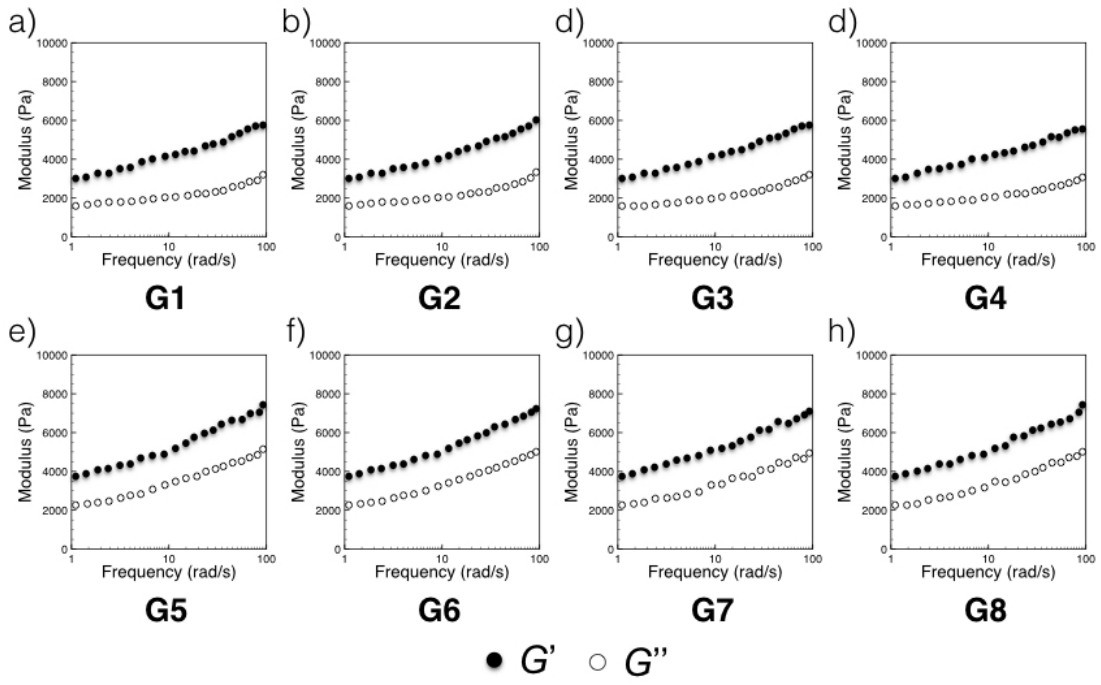


Fig. S2. Plots of P_a *versus* scanning frequency from 1 to 100 rad/s (2% strain, 25 °C) and the corresponding *G*′ and *G*″ curves for a) **G1**, b) **G2**, c) **G3**, d) **G4**, e) **G5**, f) **G6**, g) **G7**, and h) **G8**.

4. Self-healing properties of the gels based on rheological data and cut/heal tests

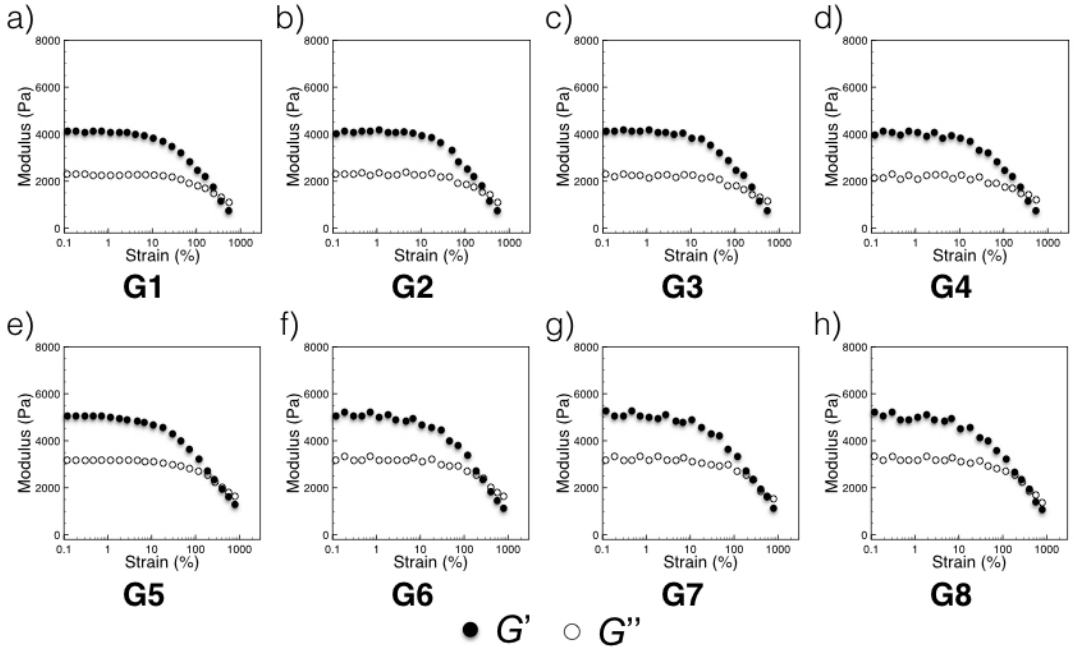


Fig. S3. Strain-dependent oscillatory shear measurements of a) **G1**, b) **G2**, c) **G3**, d) **G4**, e) **G5**, f) **G6**, g) **G7**, and h) **G8** at 10 rad/s.

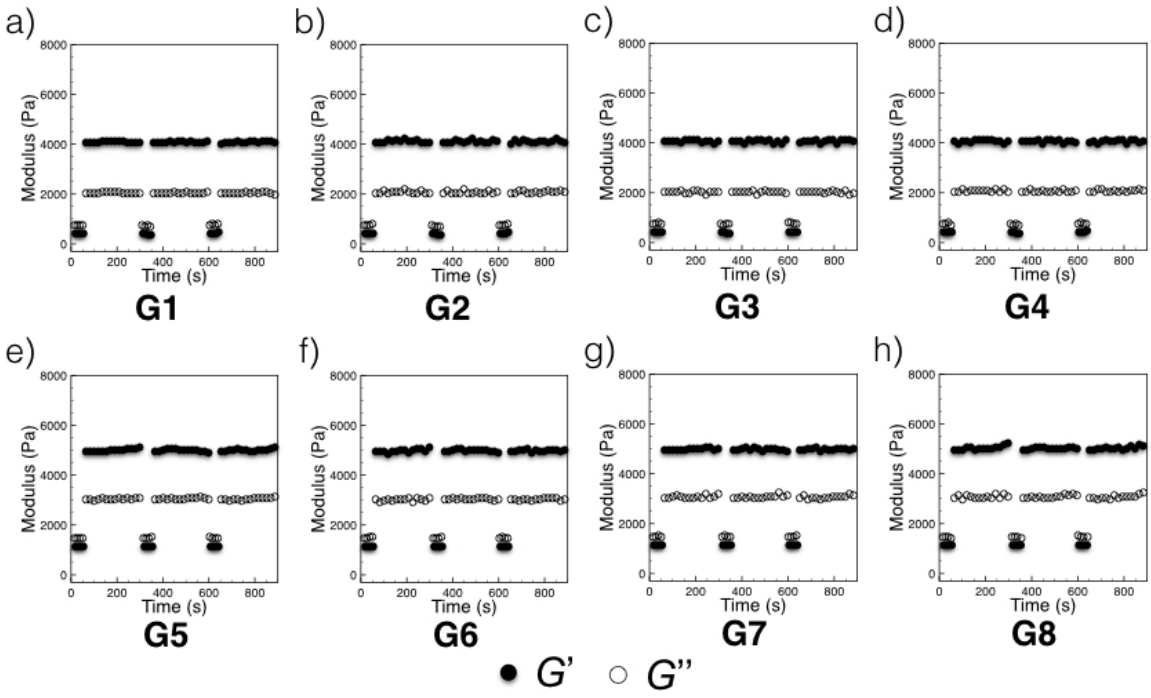


Fig. S4. Step-rate time-sweep measurements of a) **G1**, b) **G2**, c) **G3**, d) **G4**, e) **G5**, f) **G6**, g) **G7**, and h) **G8**: The gels were first subjected to 500% strain for 60 s, then 1% strain for 240 s. Three cycles of strain and relaxation were performed. The scanning frequency was 10 rad/s, 25 °C.

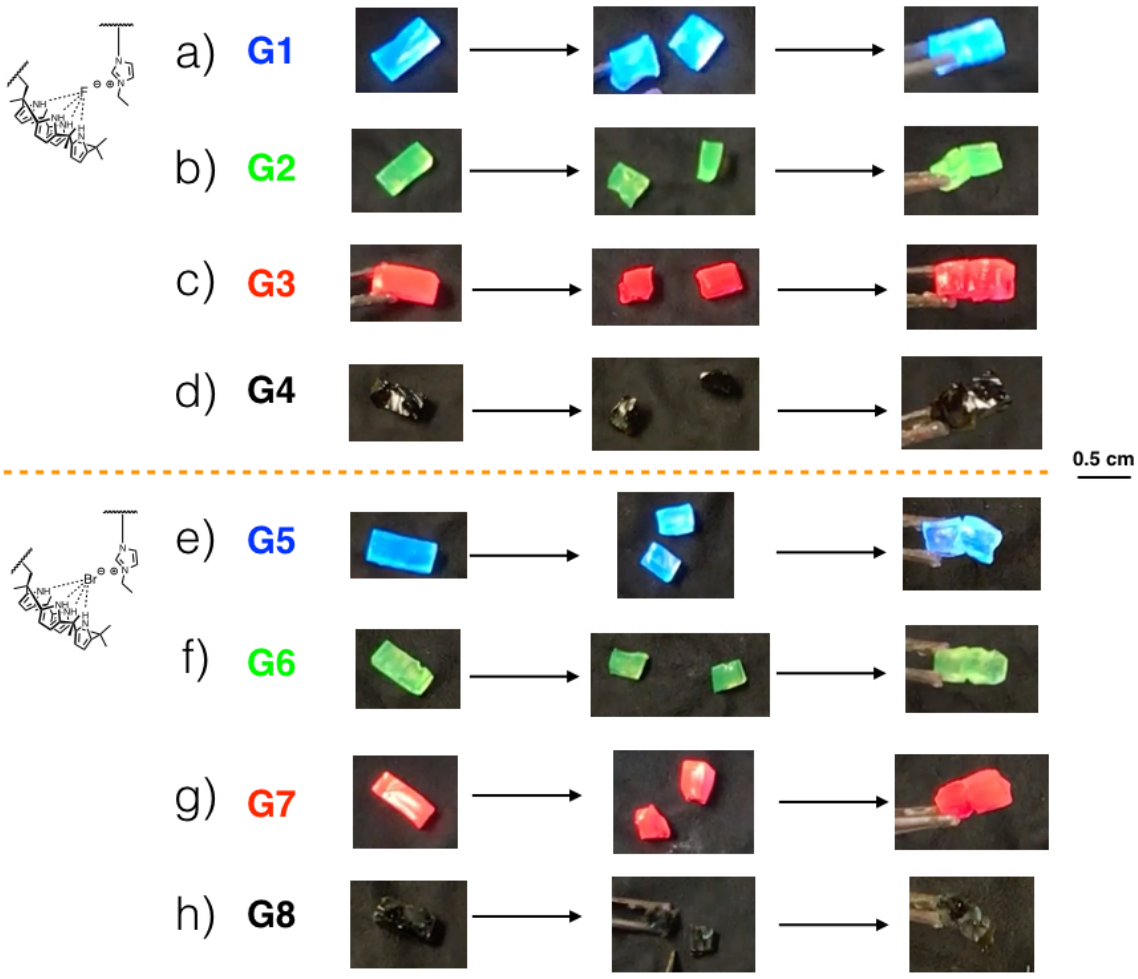


Fig. S5. Cut/heal tests of a) **G1**, b) **G2**, c) **G3**, d) **G4**, e) **G5**, f) **G6**, g) **G7**, and h) **G8** taken under a UV lamp (λ_{ex} = 365 nm, scale bar = 0.5 cm).

The presence of supramolecular cross-linking interactions was expected to endow gels **G1**–**G8** with the ability to self-heal as discussed in the main text. To test this, strain-dependent oscillatory rheology experiments were carried out at a scan frequency of 10 rad/s (Figure S3). Gel **G1** was examined as a representative example (Figure S3a). It was found that both G' and G'' were relatively stable over a strain range of 0.1% to 20%. Moreover, over this regime, G' always proved much larger than G''. However, starting from 20% strain G' decreased dramatically, while G'' began to decrease when the strain was >50%. G' decreased faster than G'', and a G'/G'' crossover point was observed around 300% strain. When the strain was increased further, G'' became larger than G', reflecting damage to the gel. Step-strain rheological measurements of G' and G'' were then carried out in an effort to probe whether self-healing of the gel structure occurs. This was done by alternating between high

(500% for 60 s) and low (1% for 240 s) strain (Figure S4). Under high strain conditions (500%, 10 rad/s), G'' proved larger than G'. However, under low strain conditions (1%, 10 rad/s), G' was found to be larger than G'' again, indicating recovery of the gel state. In fact, the supramolecular polymeric gel was found to revert to its original G'/G'' state within seconds, with the recovery behavior proving reproducible over three cycles involving different levels of strains. On this basis, we conclude that **G1** is able to self-heal quickly on the laboratory time scale. Support for this conclusion came from direct cut/heal tests as discussed below.

As shown in Figure S5a and Movie S1, **G1** could be easily cut into two pieces. The resulting fragments were then brought into physical contact at room temperature. The two pieces rejoined to produce a single entity within seconds. The healed gel could be lifted up off the black nitrile substrate used for these experiments and held against its own weight without breaking apart. The combined rheological, cut/heal, and weight bearing integrity tests were thus all consistent with the fact that **G1** could recover its initial gel-like state after being subject to strain or physical rupture. Similar strain-dependent oscillatory rheological experiments, step-strain rheological measurements, and cut/heal tests were carried out for **G2**-**G8** (Figures S3-S5, and Movie S1). In analogy to what was found for **G1**, these studies provided support for the conclusion that these fluorescent gels also self-heal. Importantly, the optical properties of the healed gels proved essentially identical to those of the as-prepared materials.

5. Tensile behavior of the gels

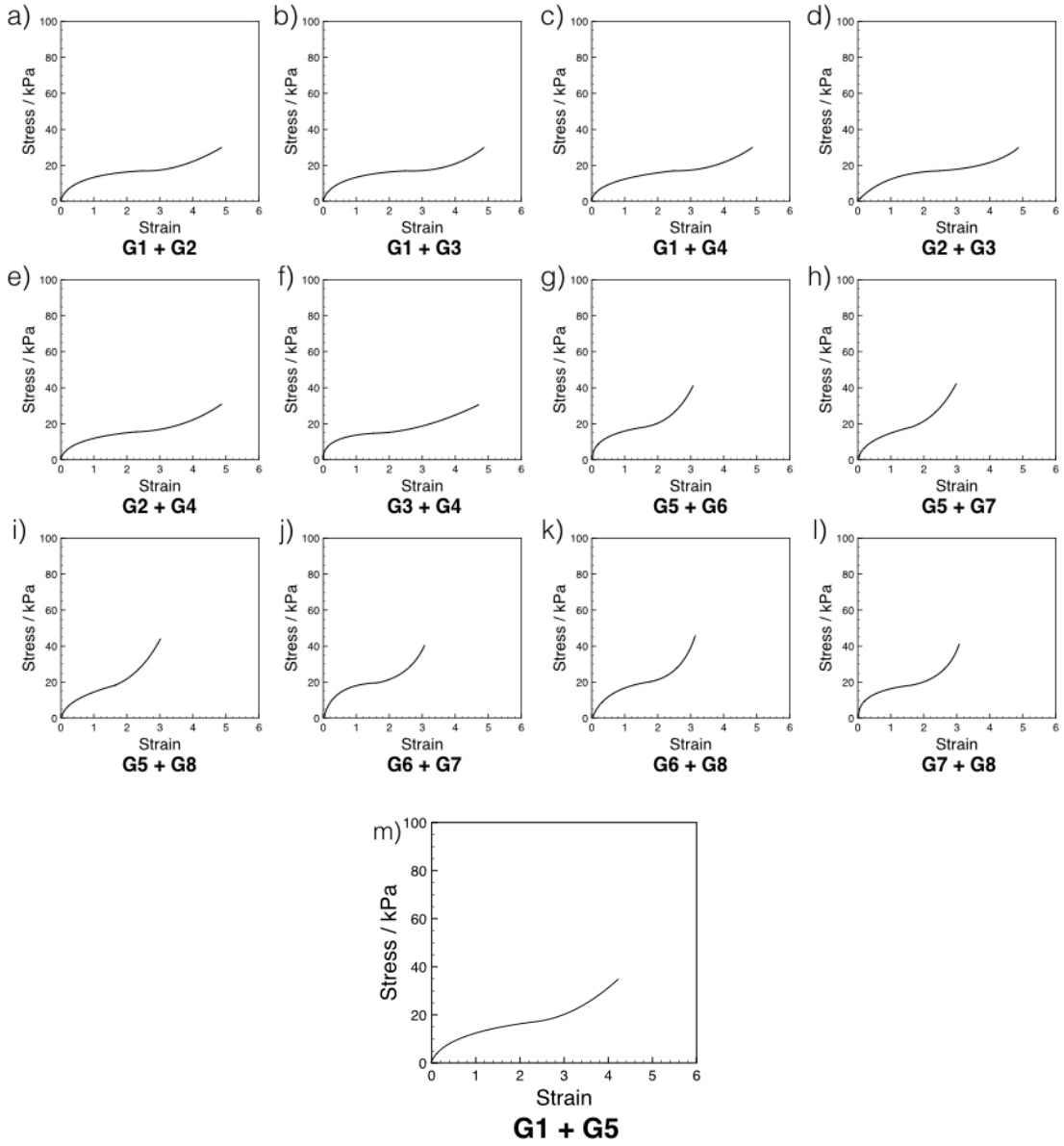


Fig. S6. The tensile stress–strain curves of a) (**G1** + **G2**), b) (**G1** + **G3**), c) (**G1** + **G4**), d) (**G2** + **G3**), e) (**G2** + **G4**), f) (**G3** + **G4**), g) (**G5** + **G6**), h) (**G5** + **G7**), i) (**G5** + **G8**), j) (**G6** + **G7**), k) (**G6** + **G8**), l) (**G7** + **G8**), and m) (**G1** + **G5**) (strain rate: 100 mm/min, 25 °C).

To characterize quantitatively the adhesion strength of gels **G1**-**G8**, stretching studies were carried out. Tensile stress–strain curves were obtained (Figure S6). Figures S6a-S6f show the adhesion strength of any two gels among **G1**-**G4**, and Figures S6g-S6l reflect the adhesion strength of any

two gels among **G5-G8**. A selected adhesive gel (**G1** + **G5**) was then tested to characterize quantitatively the adhesion strength between the two layers.

6. Responsiveness of the double layer code in TBACl solutions with different concentrations

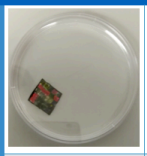
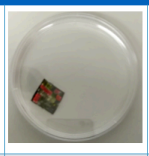
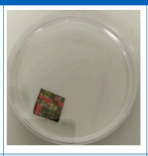
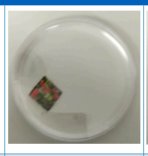
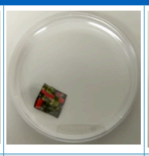
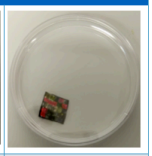
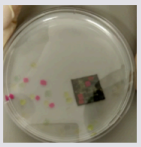
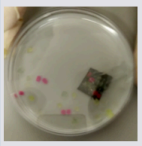
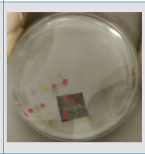
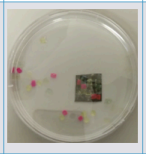
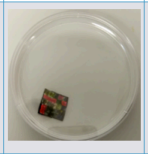
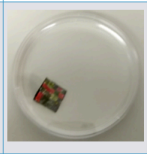
TBACl (mM)	20	15	10	8	6	4	2
Before							
After							
Responsiveness	Yes	Yes	Yes	Yes	Yes	No	No

Table. S1. Responsiveness of the double layer code when treated with chloroform solutions containing different concentrations of TBACl for 20 mins.

7. ^{1}H NMR spectra of the monomers

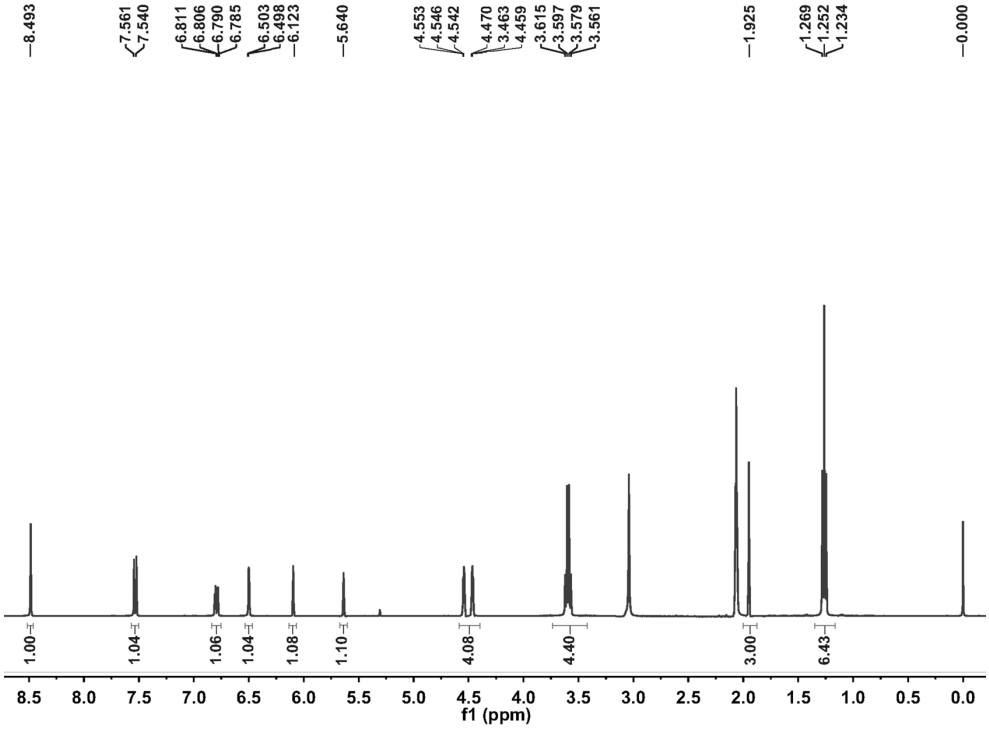


Fig. S7. The ^{1}H NMR ($(CD_3)_2CO$, 400 MHz, 298 K) spectrum of **1**.

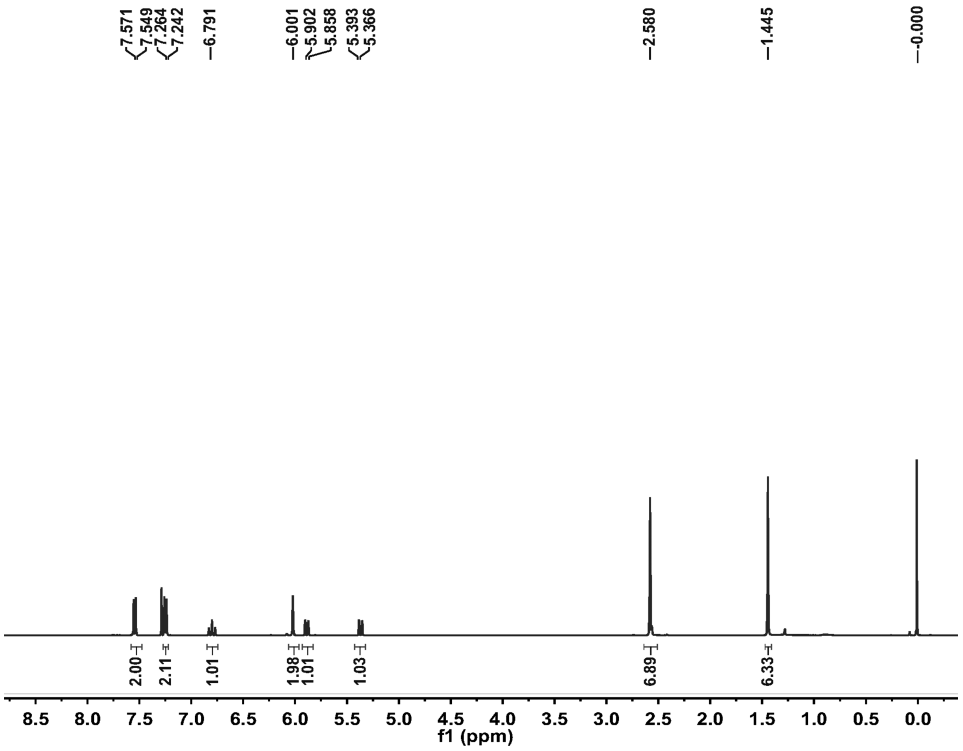


Fig. S8. The ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) spectrum of **2**.

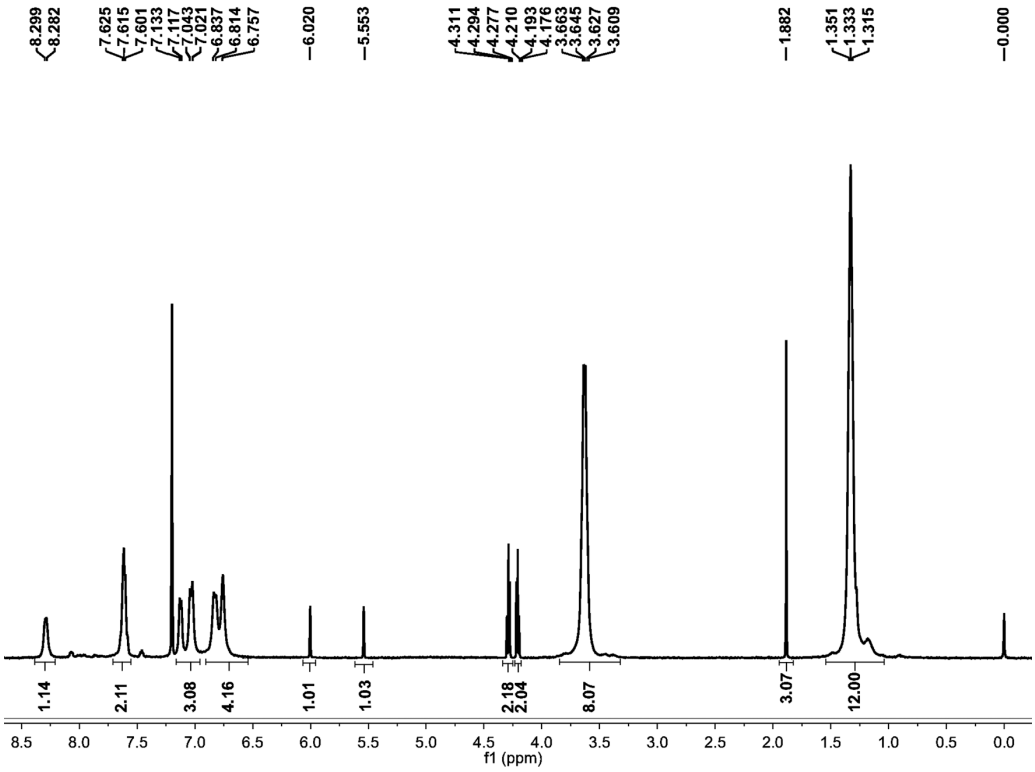


Fig. S9. The ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) spectrum of **3**.

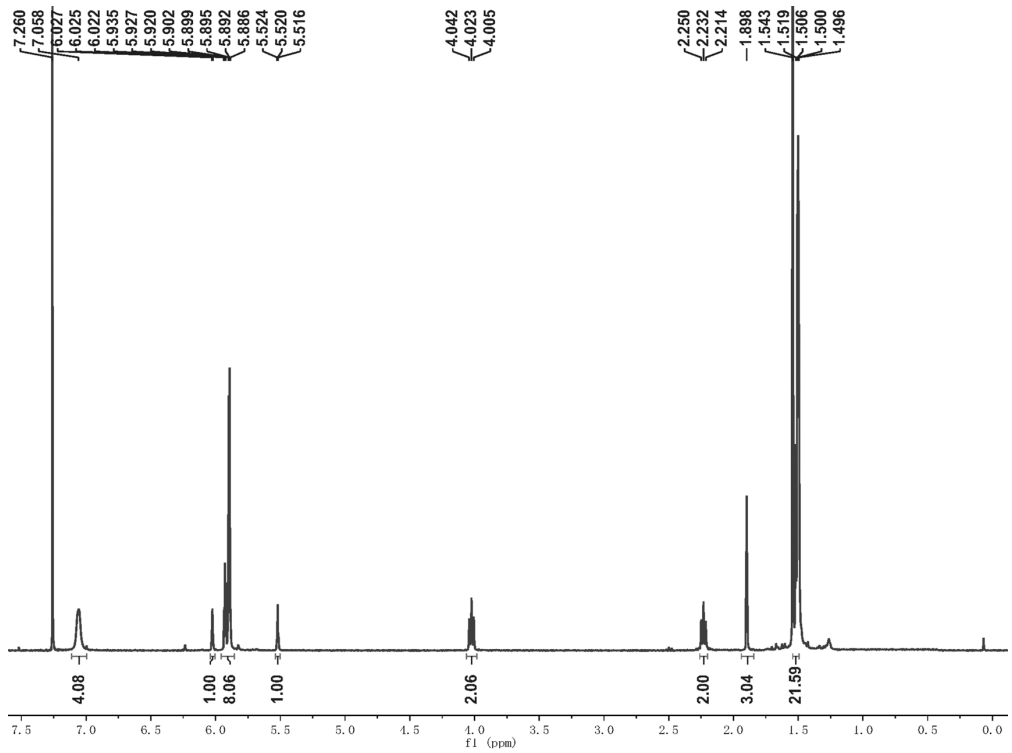


Fig. S10. The ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) spectrum of **4**.

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