

Electronic Supplementary Information (ESI)

Multi-Stimuli-Responsive Behaviours of Fluorenone-Based Donor– Acceptor–Donor Triads in Solution and Supramolecular Gel States

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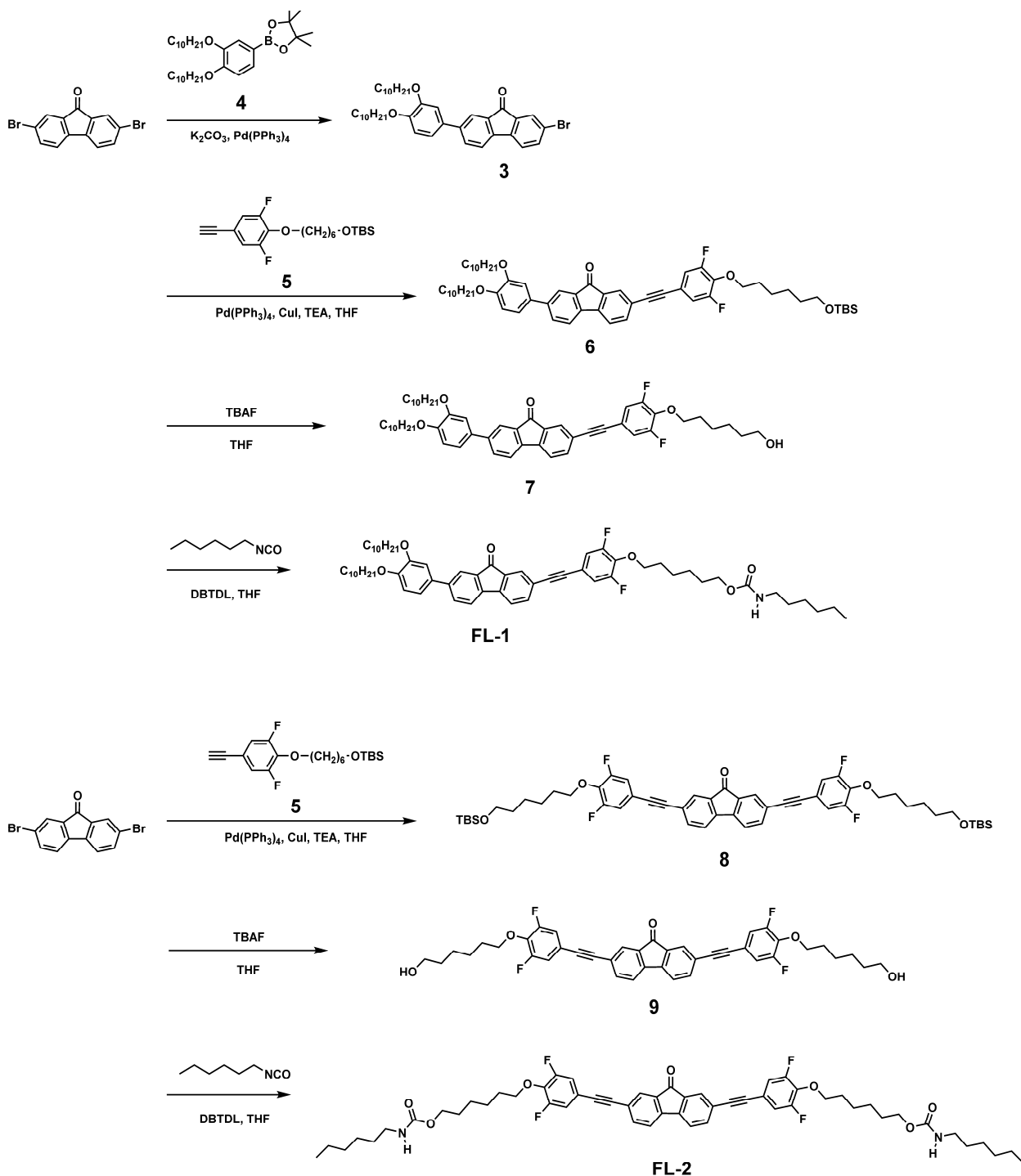
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S-1. Synthesis



Scheme S1 Synthetic route of fluorenone-based D-A-D triads **FL-1** and **FL-2**.

All reactions were performed under argon atmosphere in a well-dried three-necked flask equipped with a magnetic stirring bar. Fluorenone-based D-A-D triads **FL-1** and **FL-2** were synthesized as shown in Scheme S1. The mono-substituted intermediate compound **3** was synthesized via the Suzuki-Miyaura reaction between 2,7-dibromo-9-fluorenone and 3,4-bis(decyloxy)phenylboronic acid pinacol ester **4**. The Sonogashira-Hagihara cross

coupling reaction of compound **3** with using phenylacetylene derivative **5** was afforded to the compound **6**.^{S1,S2} The following deprotection of TBS unit by tetrabutylammonium fluoride (TBAF) gave hydroxy-terminated precursor **7**. The bilaterally symmetrical intermediate **8** was synthesized via the Sonogashira-Hagihara cross-coupling reaction between 2,7-dibromo-9-fluorenone and phenylacetylene derivative **5**. The D-A-D triads **9** bearing two hydroxy-extremities was obtained by the deprotection reaction using TBAF. The target compounds **FL-1** and **FL-2** were synthesized via urethanation between hexylisocyanate and corresponding hydroxy compounds **7** and **9**, respectively.

2-Bromo-7-[3',4'-bis(decyloxy)phenyl]-9-fluorenone (**3**)

To a stirred solution of 3,4-bis(decyloxy)phenylboronic acid pinacol ester **4** (4.75 g, 9.19 mmol, 1.00 eq.), 2,7-dibromo-9-fluorenone (4.66 g, 13.8 mmol, 1.50 eq.), and Pd(PPh₃)₄ (426 mg, 0.36 mmol, 0.04 eq.) in dry THF (200 mL) was added K₂CO₃ aqueous solution (4 M, 70 mL, 276 mmol) under argon atmosphere. The reaction mixture was refluxed for 40 hours. After cooling to room temperature, the product was extracted with chloroform (100 mL ×1, 50 mL ×3). The collected organic fractions were combined and dried over Na₂SO₄. After filtration and evaporation, the crude product was purified by the silica gel column chromatography (eluent: *n*-hexane/THF = 10/1; v/v). and recrystallization from THF/ethyl acetate to give compound **3** as an orange solid (1.84 g, 2.84 mmol, 31% yield).

¹H NMR (400 MHz, CDCl₃): δ [ppm] = 7.86 (d, 1H, *J* = 1.6 Hz), 7.78 (d, 1H, *J* = 1.8 Hz), 7.69 (dd, 1H, *J* = 7.8, 1.8 Hz), 7.62 (dd, 1H, *J* = 7.9, 1.8 Hz), 7.53 (d, 1H, *J* = 7.7 Hz), 7.40 (d, 1H, *J* = 7.9 Hz), 7.16-7.12 (m, 2H), 6.95 (d, 1H, *J* = 8.0 Hz), 4.10-4.01 (m, 4H), 1.90-1.80 (m, 4H), 1.54-1.43 (m, 4H), 1.43-1.20 (m, 24H), 0.92-0.84 (m, 6H); ¹³C NMR (100 MHz, CDCl₃): δ [ppm] = 192.6, 149.5, 143.0, 142.6, 141.8, 137.2, 136.1, 134.4, 133.0, 132.5, 127.6, 122.8, 122.7, 121.7, 120.8, 119.4, 114.0, 112.5, 69.5, 69.3, 31.9, 29.7, 29.6, 29.4, 29.4, 29.3, 26.1, 22.7, 14.1.

Compound **6**

To a stirred suspension of compound **3** (1.71 g, 2.64 mmol, 1.00 eq.), compound **5** (1.03 g, 2.80 mmol, 1.06 eq.), CuI (6.4 mg, 0.034 mmol, 0.01 eq.), and Pd(PPh₃)₄ (35 mg, 0.030 mmol, 0.01 eq.) in dry THF (100 mL) was added triethylamine (TEA, 30 mL) under argon atmosphere. The mixture was refluxed for 23 hours. After monitoring the reaction progress by TLC, CuI (5.6 mg, 0.029 mmol, 0.01 eq.), and Pd(PPh₃)₄ (32 mg, 0.028 mmol, 0.01 eq.) were added. The mixture was further refluxed for 13 hours. After cooling to room temperature, the reaction mixture was filtered to remove the insoluble residue. The volatile components were evaporation under reduced pressure from the filtrate. Then, the resultant residue was purified by silica gel column chromatography (eluent: *n*-hexane/chloroform = 2/1→1/2; v/v) and dried *in vacuo* to afford **6** as an orange solid (1.03 g, 1.10 mmol, 42% yield).

¹H NMR (400 MHz, CDCl₃): δ [ppm] = 7.88 (d, 1H, *J* = 1.4 Hz), 7.78 (d, 1H, *J* = 0.88 Hz), 7.70 (dd, 1H, *J* = 7.8, 1.8 Hz), 7.63 (dd, 1H, *J* = 7.7, 1.5 Hz), 7.56 (d, 1H, *J* = 7.8 Hz), 7.52 (d, 1H, *J* = 7.7 Hz), 7.17-7.13 (m, 2H), 7.07 (d, 2H, *J* = 8.8 Hz), 6.96 (d, 1H, *J* = 8.1 Hz), 4.18 (t, 2H, *J* = 6.5 Hz), 4.10-4.02 (m, 4H), 3.62 (t, 2H, *J* = 6.5 Hz), 1.91-1.80 (m, 4H), 1.78 (quintet, 2H, *J* = 7.1 Hz), 1.59-1.21 (m, 34H), 0.90 (s, 9H), 0.92-0.85 (m, 6H), 0.05 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ [ppm] = 193.1, 155.6 (dd, *J* = 247.0, 7.1 Hz), 149.5, 149.5, 144.1, 142.7, 142.0, 137.8, 136.8, 135.1, 134.6, 133.0, 132.5, 127.4, 123.2, 122.7, 121.0, 120.3, 119.4, 117.1, 115.6 (dd, *J* = 17.1, 7.3 Hz), 114.0, 112.5, 89.4, 88.8, 77.3, 77.2, 77.0, 76.7, 74.8, 69.6, 69.3, 63.1, 32.7, 31.9, 30.0, 29.7, 29.6, 29.4, 29.4, 29.3, 26.1, 26.0, 25.5, 25.4, 22.7, 18.4, 14.1, -5.3.

Compound **7**

TBS-protected compound **6** (888 mg, 0.95 mmol, 1.00 eq.) was dissolved in dry THF (80 mL). After the mixture was cooled in ice bath, a solution of TBAF in THF (ca. 1.0 M, 3.3 mL, 3.50 eq.) was slowly added to the mixture for over 15 minutes at to 0 °C. Then, the mixture was gradually warmed to room temperature and stirred for 16 hours. The product was washed with sat.NH₄Cl aq. (50 mL ×3), brine (50 mL) and H₂O (50 mL). The collected organic fractions were combined and dried over Na₂SO₄. After filtration and evaporation, the crude product was

recrystallized from THF/methanol, and dried *in vacuo* to afford **7** as an orange solid (739 mg, 0.90 mmol, 95% yield).

¹H NMR (400 MHz, CDCl₃): δ [ppm] = 7.88 (d, 1H, *J* = 1.4 Hz), 7.78 (d, 1H, *J* = 0.9 Hz), 7.70 (dd, 1H, *J* = 7.8, 1.8 Hz), 7.62 (dd, 1H, *J* = 7.7, 1.5 Hz), 7.55 (d, 1H, *J* = 7.9 Hz), 7.52 (d, 1H, *J* = 7.7 Hz), 7.18-7.12 (m, 2H), 7.07 (d, 2H, *J* = 8.8 Hz), 6.95 (d, 1H, *J* = 8.1 Hz), 4.18 (t, 2H, *J* = 6.5 Hz), 4.11-4.00 (m, 4H), 3.67 (t, 2H, *J* = 6.5 Hz), 1.91-1.72 (m, 6H), 1.67-1.19 (m, 34H), 0.93-0.83 (m, 6H); ¹³C NMR (100 MHz, CDCl₃): δ [ppm] = 193.1, 155.6 (dd, *J* = 247.2, 6.8 Hz), 149.5, 149.5, 144.1, 142.7, 142.0, 137.8, 136.7, 135.1, 134.6, 133.0, 132.5, 127.4, 123.2, 122.7, 121.0, 120.3, 119.4, 117.2, 115.6 (dd, *J* = 17.2, 7.3 Hz), 114.0, 112.5, 89.4, 88.7, 77.3, 77.2, 77.0, 76.7, 74.8, 69.6, 69.3, 62.9, 32.7, 31.9, 29.9, 29.7, 29.6, 29.4, 29.4, 29.3, 26.1, 25.5, 25.4, 22.7, 14.1.

Compound **8**

To a stirred suspension of 2,7-dibromo-9-fluorenone (769 mg, 2.28 mmol, 1.00 eq.), compound **5** (1.99 g, 5.41 mmol, 2.37 eq.), CuI (10 mg, 0.054 mmol, 0.02 eq.), and Pd(PPh₃)₄ (59 mg, 0.051 mmol, 0.02 eq.) in dry THF (80 mL) was added TEA (80 mL) under argon atmosphere. The mixture was refluxed for 26 hours. After cooling to room temperature, the reaction mixture was filtered to remove the insoluble residue. The volatile components were evaporation under reduced pressure from the filtrate. Then, the resultant residue was purified by silica gel column chromatography (eluent: *n*-hexane/chloroform = 1/1→2/3→1/2; v/v), and dried *in vacuo* to afford **8** as an orange solid (1.62 g, 1.78 mmol, 78% yield).

¹H NMR (400 MHz, CDCl₃): δ [ppm] = 7.78 (d, 2H, *J* = 0.8 Hz), 7.64 (dd, 2H, *J* = 7.8, 1.5 Hz), 7.53 (d, 2H, *J* = 7.7 Hz), 7.06 (d, 4H, *J* = 8.8 Hz), 4.18 (t, 4H, *J* = 6.5 Hz), 3.63 (t, 4H, *J* = 6.5 Hz), 1.78 (quintet, 4H, *J* = 7.0 Hz), 1.60-1.34 (m, 12H), 0.90 (s, 18H), 0.05 (s, 12H); ¹³C NMR (100 MHz, CDCl₃): δ [ppm] = 191.9, 155.6 (dd, *J* = 247.2, 6.8 Hz), 143.4, 137.9, 136.9, 134.5, 127.5, 123.9, 120.7, 116.9, 115.7 (dd, *J* = 17.0, 7.4 Hz), 89.2, 89.2, 74.8, 63.1, 32.7, 30.0, 26.0, 25.5, 25.4, 18.4, -5.3.

Fluorenone-based D-A-D triad **FL-1**

To a stirred solution of compound **7** (687 mg, 0.84 mmol, 1.00 eq.) in dry THF (20 mL) were added hexyl isocyanate (0.3 mL, 2.08 mmol) at room temperature. Then, dibutyltin dilaurate (0.1 mL, 0.17 mmol) was immediately added to the reaction mixture under argon atmosphere. The reaction mixture was stirred for 16 hours at room temperature. The crude product was extracted with chloroform (100 mL) and washed with H₂O (100 mL ×3). The collected organic fractions were combined and dried over Na₂SO₄. After filtration and evaporation, the product was recrystallized from THF and *n*-hexane with small amount of methanol, and dried *in vacuo* to afford **FL-1** as an orange solid (680 mg, 0.17 mmol, 85% yield).

¹H NMR (400 MHz, CDCl₃): δ [ppm] = 7.88 (d, 1H, *J* = 1.4 Hz), 7.78 (d, 1H, *J* = 1.5 Hz), 7.70 (dd, 1H, *J* = 7.8, 1.8 Hz), 7.63 (dd, 1H, *J* = 7.7, 1.5 Hz), 7.56 (d, 1H, *J* = 7.8 Hz), 7.53 (d, 1H, *J* = 7.8 Hz), 7.18-7.12 (m, 2H), 7.07 (d, 2H, *J* = 8.8 Hz), 6.96 (d, 1H, *J* = 8.2 Hz), 4.61 (s, 1H), 4.18 (t, 2H, *J* = 6.4 Hz), 4.12-4.01 (m, 6H), 3.21-3.10 (m, 2H), 1.91-1.74 (m, 6H), 1.71-1.59 (m, 2H), 1.54-1.21 (m, 40H), 0.93-0.84 (m, 9H); ¹³C NMR (100 MHz, CDCl₃): δ [ppm] = 193.1, 156.8, 155.6 (dd, *J* = 247.1, 7.0 Hz), 154.4, 154.3, 149.5, 149.5, 144.1, 142.7, 142.0, 137.8, 136.7, 135.1, 134.6, 133.0, 132.5, 127.3, 123.2, 12, , 121.0, 120.3, 119.4, 117.2, 115.6 (dd, *J* = 17.1, 7.3 Hz), 114.0, 112.5, 89.4, 88.7, 77.3, 77.2, 77.0, 76.7, 74.7, 69.6, 69.3, 64.7, 41.0, 31.9, 31.5, 30.0, 29.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.0, 26.4, 26.1, 25.6, 25.4, 22.7, 22.6, 14.1, 14.0; HRMS (ESI): molecular weight: 948.2898 (C₆₀H₇₉F₂NO₆); m/z calcd. for [C₆₀H₈₀F₂NO₆]⁺: 948.5948 ([M+H]⁺); found. 948.5949.

Fluorenone-based D-A-D triad **FL-2**

To a stirred solution of compound **9** (621 mg, 0.81 mmol, 1.00 eq.) in dry THF (60 mL) were added hexyl isocyanate (0.6 mL, 4.43 mmol) at room temperature. Then, dibutyltin dilaurate (0.2 mL, 0.37 mmol) was immediately added to the reaction mixture under argon atmosphere. The reaction mixture was stirred for 20 hours at room temperature. The crude product was extracted with chloroform (100 mL) and washed with H₂O (100 mL ×3). The collected organic fractions were combined and dried over Na₂SO₄. After filtration and evaporation, the

product was recrystallized from THF and methanol, and dried *in vacuo* to afford **FL-2** as a yellow solid (744 mg, 0.79 mmol, 87% yield).

^1H NMR (400 MHz, CDCl_3): δ [ppm] = 7.79 (d, 2H, J = 0.9 Hz), 7.64 (dd, 2H, J = 7.7, 1.5 Hz), 7.54 (d, 2H, J = 7.8 Hz), 7.07 (d, 4H, J = 8.7 Hz), 4.62 (s, 2H), 4.18 (t, 4H, J = 6.4 Hz), 4.06 (t, 4H, J = 6.5 Hz), 3.24-3.04 (m, 4H), 1.78 (quintet, 4H, J = 7.0 Hz), 1.72-1.59 (m, 4H), 1.56-1.22 (m, 24H), 0.88 (t, 6H, J = 6.8 Hz); ^{13}C NMR (100 MHz, CDCl_3): δ [ppm] = 191.9, 155.6, 143.5, 137.9, 136.8, 134.5, 127.5, 124.0, 120.7, 117.1, 115.7, 89.2, 89.2, 74.7, 64.7, 41.1, 31.5, 30.0, 29.9, 29.0, 26.4, 25.6, 25.4, 22.6, 14.0; HRMS (ESI): molecular weight: 939.1016 ($\text{C}_{55}\text{H}_{62}\text{F}_4\text{N}_2\text{O}_7$); m/z calcd. for $[\text{C}_{55}\text{H}_{63}\text{F}_4\text{N}_2\text{O}_7]^+$: 939.4566 ($[\text{M}+\text{H}]^+$); found. 939.4566.

S-2. Gelation Properties

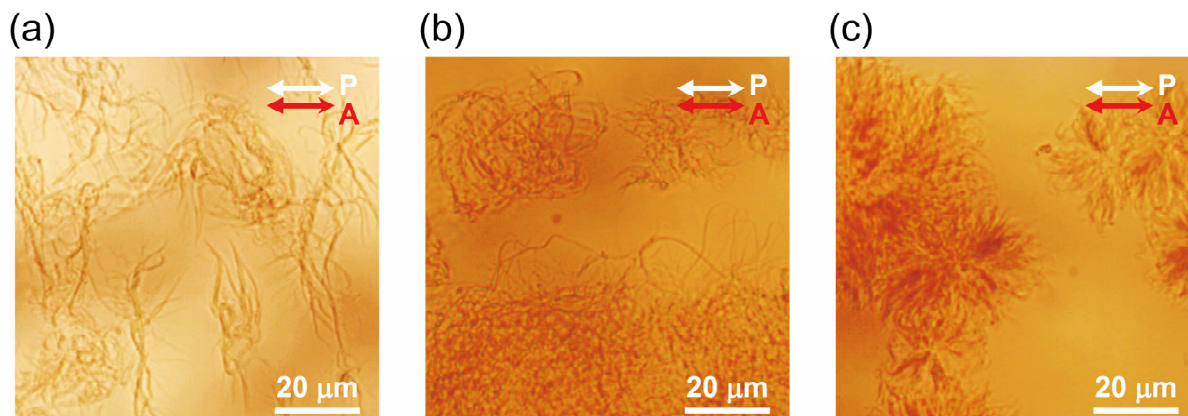


Fig. S1 POM images of organogels composed of **FL-1** in the open nicol arrangement: (a) *n*-decane gel (20 g L⁻¹), (b) *n*-dodecane gel (20 g L⁻¹), and (c) DB gel (50 g L⁻¹). The images were adjusted the brightness and contrast on equal terms in order to improve visibility.

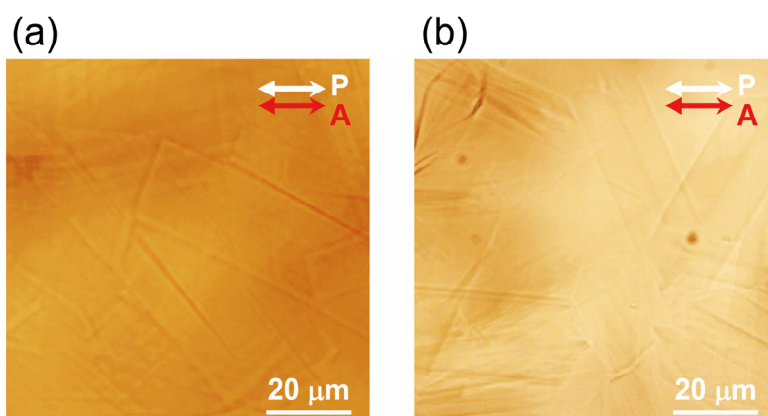


Fig. S2 POM images of organogels composed of **FL-2** in the open nicol arrangement: (a) DB gel (20 g L⁻¹), and (b) DES gel (50 g L⁻¹). The images were adjusted the brightness and contrast on equal terms in order to improve visibility.

S-3. Liquid-Crystalline Properties

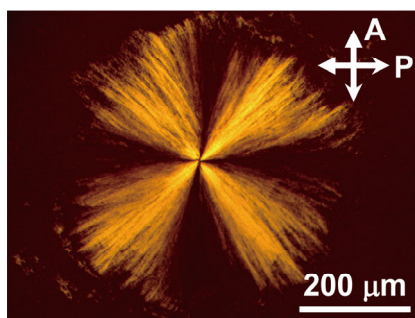


Fig. S3 A POM image of FL-1 in the Cr₂ phase (25 °C).

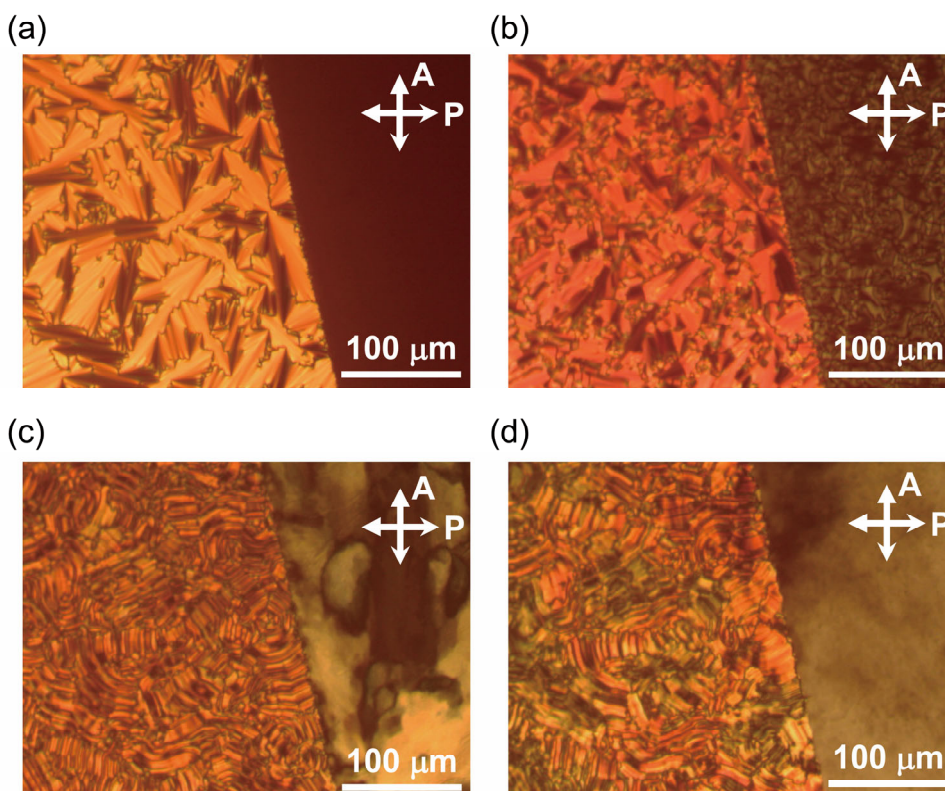


Fig. S4 POM images of FL-2 in the (a) S_A phase (170 °C), (b) S_C phase (150 °C), (c) M phase (135 °C), and (d) Cr₂ phases (100 °C) on cooling process.

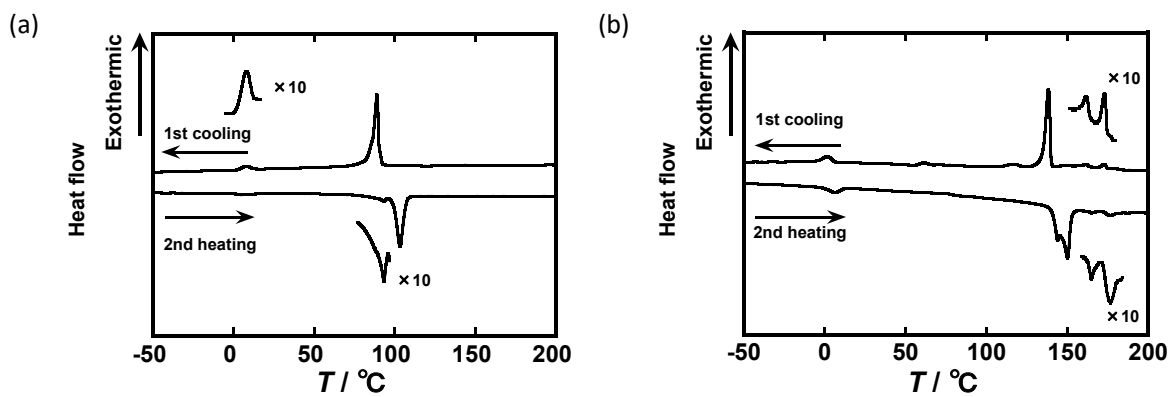


Fig. S5 DSC thermograms of (a) FL-1 and (b) FL-2. The scanning rates are 10 °C min⁻¹.

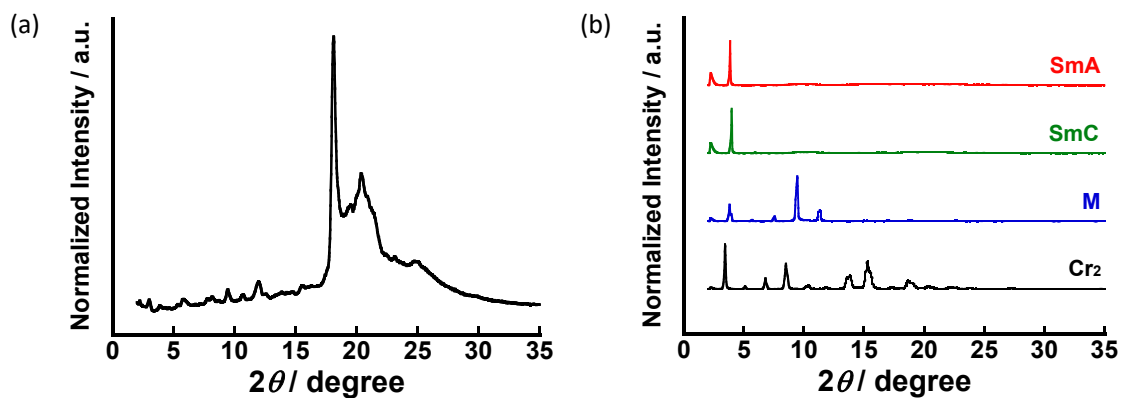


Fig. S6 Variable temperature XRD profiles of (a) FL-1 at room temperature and (b) FL-2 at the appropriate temperature.

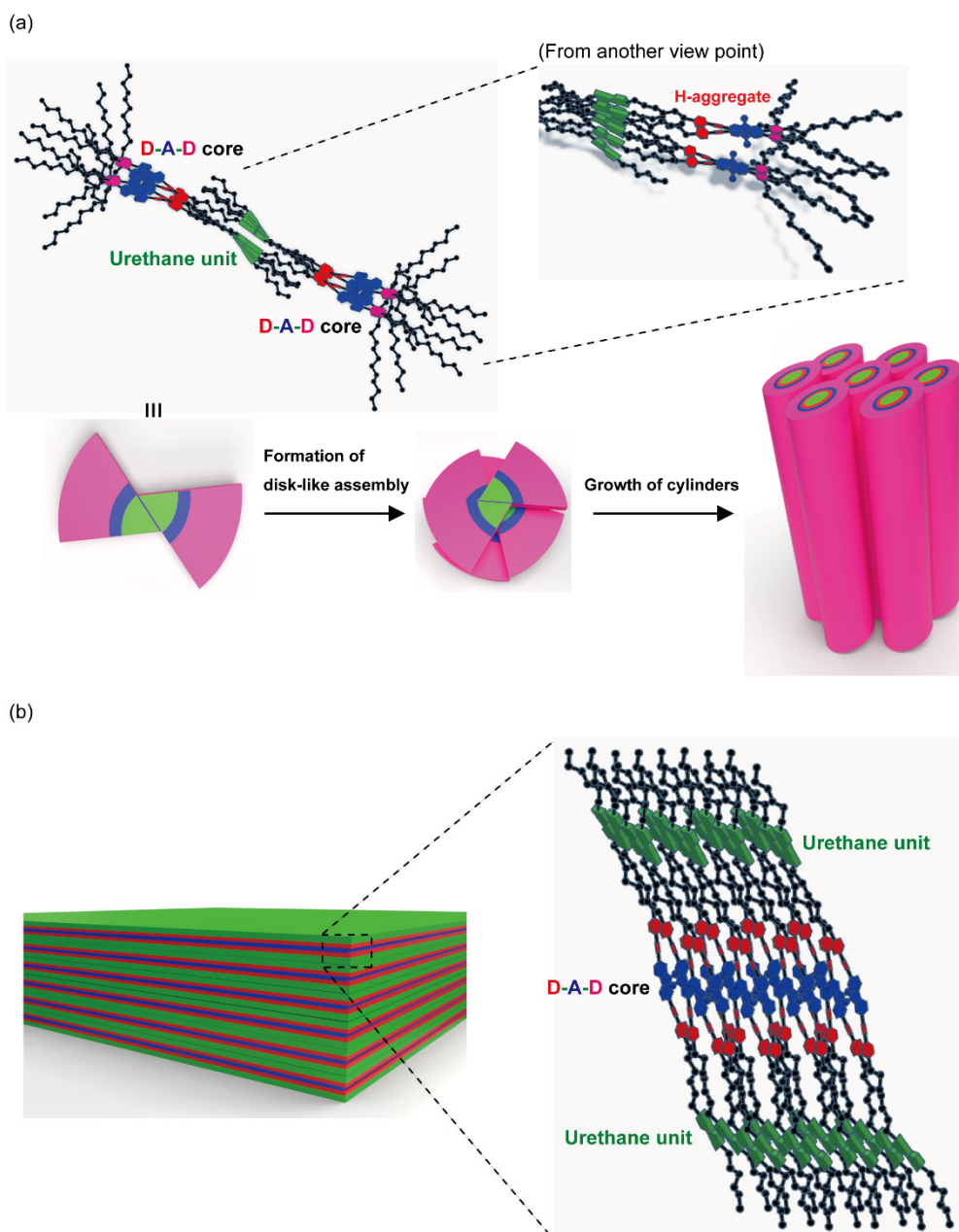


Fig. S7 Schematic illustrations of one of the possible molecular packing in the high-ordered phases of (a) FL-1 and (b) FL-2.

S-4. Intermolecular Hydrogen Bonding

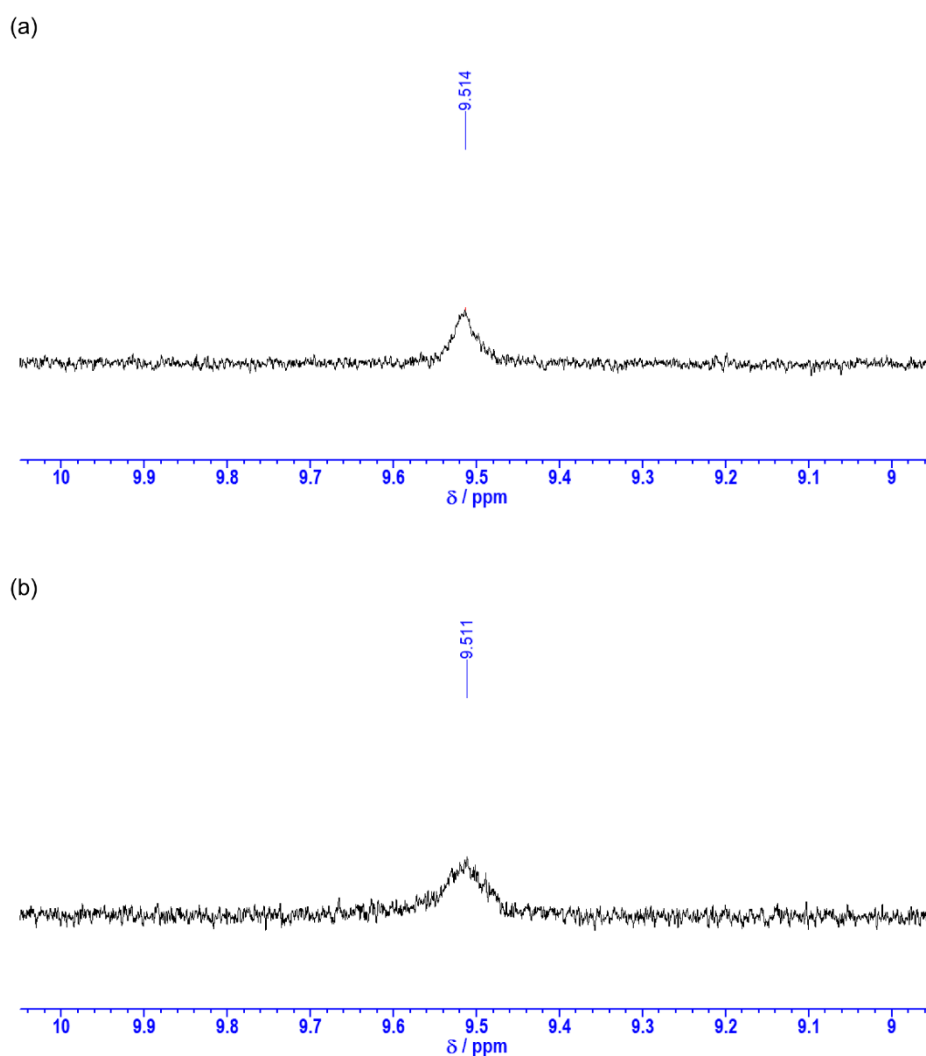


Fig. S8 ^1H NMR spectra of (a) FL-1, and (b) FL-2 in $\text{DMSO-}d_6/\text{CDCl}_3$ (5/1; v/v).

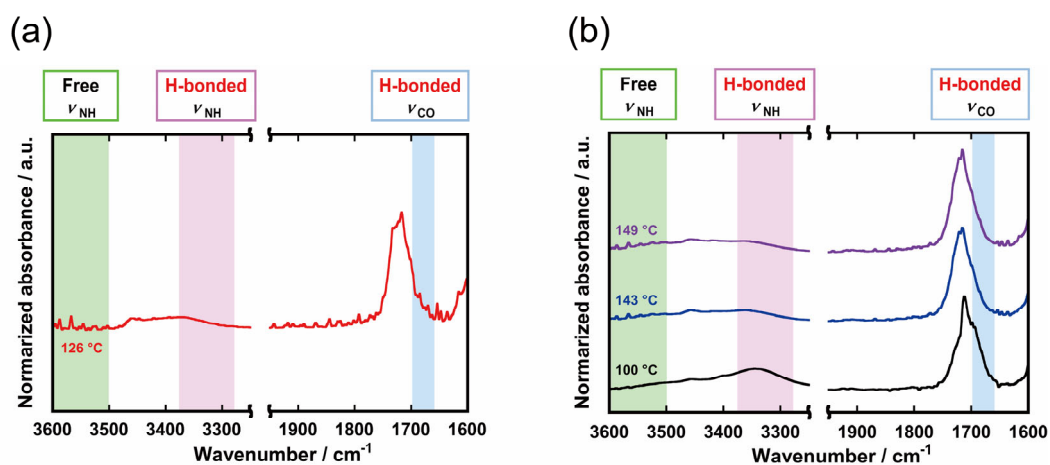


Fig. S9 Variable temperature FT-IR spectra of the films of (a) FL-1 in the IL phase (126 °C), and (b) FL-2 in the S_C phase (149 °C), M phase (143 °C) and Cr_2 phase (100 °C) on cooling process.

S-5. Density functional theory (DFT) calculations

The density functional theory (DFT) calculations were carried out by using a Gaussian R 09W (Version 9.5) software.⁵³ The accompanied Gauss View 5.0 software was used for visualization of calculation results. The calculation for the analogues of the fluorenone-based D–A–D triads **FL-1** and **FL-2** at the electrically neutral state were based on the generalized gradient approximation B3LYP functional,^{54,55} in conjunction with a 6-31G(d,p) basis set.^{56,57} To avoid the overestimation of the extent of wave function delocalization by DFT methods, initial molecular geometries for the DFT calculations were optimized by energy minimization on the basis of molecular mechanics calculation (MMFF94) with Avogadro (Version 1.2.0) software. All flexible side chains of **FL-1** and **FL-2** were replaced with short alkyl groups to reduce computational burden.

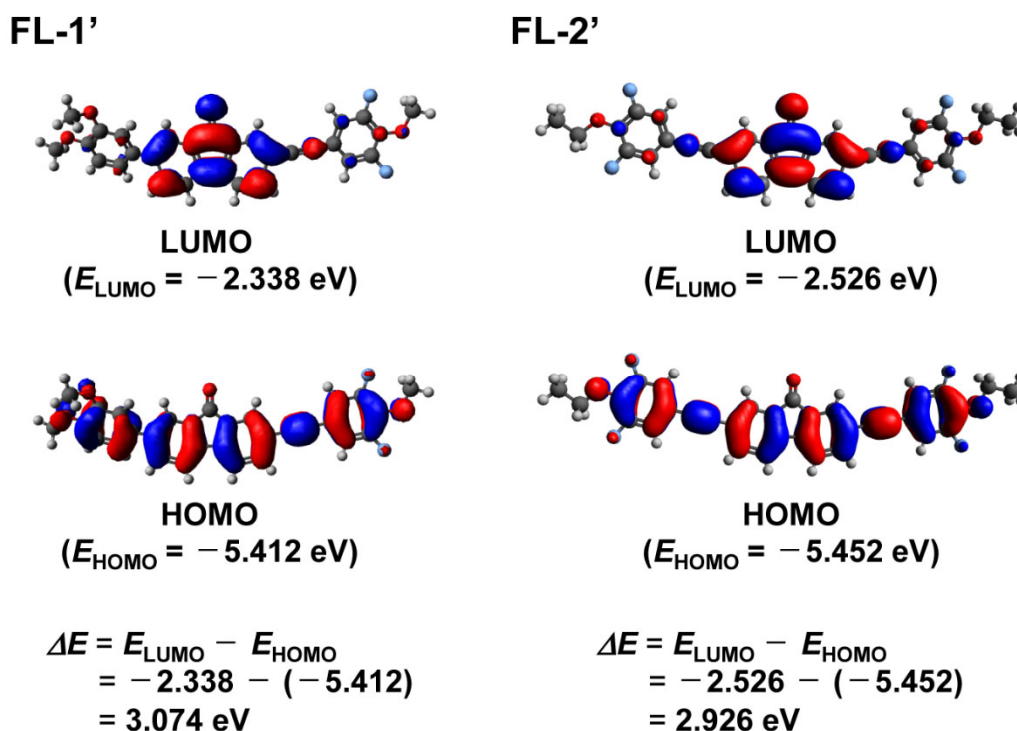


Fig. S10 HOMO and LUMO distributions and estimated energy levels for analogous molecules of **FL-1** and **FL-2** by DFT calculation at the B3LYP/6-31G(d,p) level.

S-6. Absorption and Photoluminescent Properties

Table S1 Absorption and photoluminescent properties of **FL-1** and **FL-2** in various solvents.

Solvent	FL-1			FL-2		
	$\lambda_{\text{abs}} / \text{nm}$ ($\epsilon / \text{M}^{-1} \text{cm}^{-1}$)	$\lambda_{\text{em}} / \text{nm}$ ^a	PLQY ^b	$\lambda_{\text{abs}} / \text{nm}$ ($\epsilon / \text{M}^{-1} \text{cm}^{-1}$)	$\lambda_{\text{em}} / \text{nm}$ ^a	PLQY ^b
<i>n</i> -Hexane / Chloroform (9/1; v/v)	299 (6.6×10 ⁴)	404	0.071	299 (6.9×10 ⁴)	383	0.195
	345 (4.8×10 ⁴)	581		350 (5.9×10 ⁴)	402	
	442 (4.4×10 ³)			431 (5.8×10 ³)	546	
Toluene	303 (5.4×10 ⁴)	428	0.234	302 (5.6×10 ⁴)	387	0.489
	348 (4.3×10 ⁴)	567		354 (5.4×10 ⁴)	409	
	448 (4.0×10 ³)			437 (5.5×10 ³)	537	
THF	302 (6.2×10 ⁴)	420	0.164	302 (7.3×10 ⁴)	381	0.464
	349 (4.6×10 ⁴)	581		352 (6.1×10 ⁴)	402	
	448 (4.2×10 ³)			435 (5.7×10 ³)	537	
Ethyl acetate	300 (6.4×10 ⁴)	419	0.171	301 (7.7×10 ⁴)	385	0.394
	345 (4.6×10 ⁴)	581		350 (6.2×10 ⁴)	540	
	448 (4.2×10 ³)			438 (5.5×10 ³)		
Chloroform	303 (6.4×10 ⁴)	435	0.013	304 (7.1×10 ⁴)	391	0.074
	348 (4.5×10 ⁴)	620		353 (5.7×10 ⁴)	572	
	450 (3.7×10 ³)			445 (5.0×10 ³)		
<i>N,N</i> -Dimethylformamide (DMF)	304 (5.7×10 ⁴)		0.021	305 (6.6×10 ⁴)	383	0.211
	349 (4.2×10 ⁴)	452		354 (5.6×10 ⁴)	401	
	454 (3.7×10 ³)			441 (4.9×10 ³)	555	
Acetonitrile / Chloroform (9/1; v/v)	301 (6.7×10 ⁴)	452	0.025	302 (7.8×10 ⁴)	396	0.131
	346 (4.7×10 ⁴)	623		352 (6.2×10 ⁴)	563	
	448 (3.8×10 ³)			436 (5.2×10 ³)		
Ethanol / Chloroform (9/1; v/v)	301 (6.8×10 ⁴)		0.015	303 (8.1×10 ⁴)	396	0.014
	346 (4.5×10 ⁴)	435		351 (6.3×10 ⁴)	601	
	448 (3.3×10 ³)			437 (5.1×10 ³)		

a) The photoexcitation at the absorption maximum around 350 nm.

b) The excitation wavelength is 365 nm.

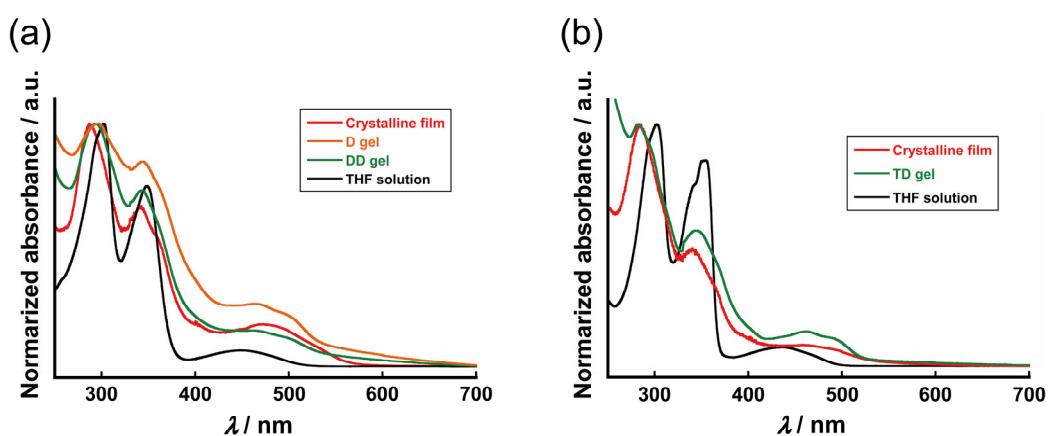


Fig. S11 UV-Vis spectra of (a) **FL-1** and (b) **FL-2** in the THF solution, organogels and crystalline films.

Table S2 Absorption and photoluminescent properties of organogels of **FL-1** and **FL-2**.

Solvent	FL-1		FL-2	
	$\lambda_{\text{abs}} / \text{nm}$	$\lambda_{\text{em}} / \text{nm}^{\text{a}}$	$\lambda_{\text{abs}} / \text{nm}$	$\lambda_{\text{em}} / \text{nm}^{\text{a}}$
THF solution (10 μM)	302, 349, 448	420, 581	302, 352, 435	381, 402, 537
Toluene solution (10 μM)	303, 348, 448	428, 567	302, 354, 437	387, 409, 537
Crystalline film	287, 343, 473	–	285, 341, 458	–
<i>D</i> gel	297, 345, 466	570	–	–
<i>DD</i> gel	293, 343, 465	569	–	–
<i>DB</i> gel	298, 346, 468	571	285, 343, 459	554
<i>TD</i> gel	–	–	283, 345, 463	–

a) The photoexcitation at the absorption maximum around 365 nm.

b) The excitation wavelength is 365 nm.

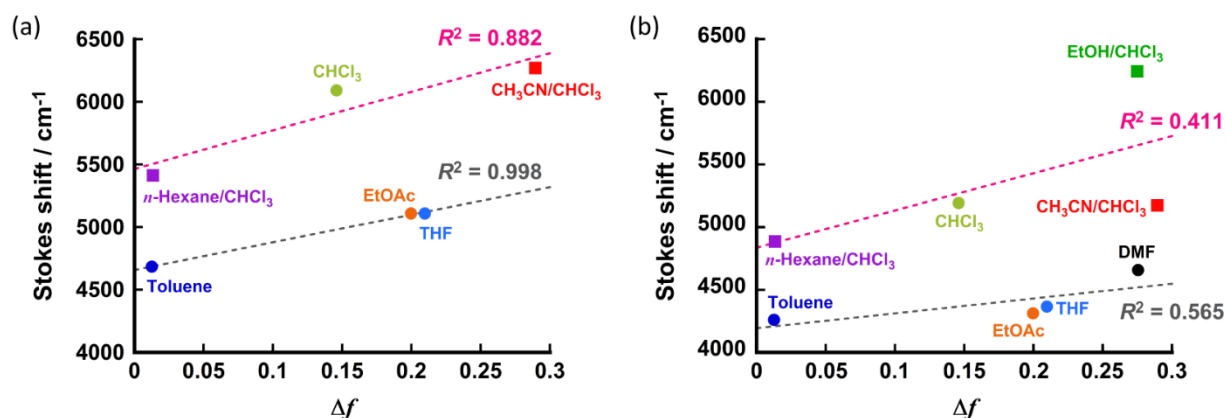


Fig. S12 Lippert-Mataga plots for (a) FL-1 and (b) FL-2. The value of Δf as a parameter for orientational polarity was determined by $f(\varepsilon) - f(n)$.⁵⁸ Each value of $f(\varepsilon)$ and $f(n)$ of the mixed solvents were determined as weighted average values of $f(\varepsilon)$ and $f(n)$ for the constituent solvents, respectively. The Stokes shift was determined as the difference between wavenumbers of CT absorption and emission maxima ($\nu_{\text{abs, CT}} - \nu_{\text{em, TICT}}$).

Table S3 Fluorescence lifetime of FL-1 and FL-2 in various solvents.

Solvent	FL-1		FL-2	
	$\lambda_{\text{det}} / \text{nm}^a$	τ / ns^b	$\lambda_{\text{det}} / \text{nm}^a$	τ / ns^b
<i>n</i> -Hexane / Chloroform (9/1; v/v)	400	0.56 (0.21) ^c , 1.26 (0.79)	385	0.72 (1.00)
	580	1.52 (0.80), 2.36 (0.20)	400	0.78 (1.00)
			550	0.90 (0.09), 4.33 (0.91)
Toluene	430	1.22 (1.00)	410	0.72 (1.00)
	565	0.85 (0.07), 5.45 (0.93)	535	1.26 (0.11), 8.63 (0.89)
THF	420	1.49 (1.00)		
	580	1.55 (0.12), 4.22 (0.88)	540	1.37 (0.07), 9.46 (0.93)
Ethyl acetate	420	1.31 (1.00)	390	0.83 (1.00)
	580	2.68 (0.39), 4.05 (0.61)	540	1.02 (0.07), 9.10 (0.93)
Chloroform	440	1.21 (0.54), 1.85 (0.49)	390	0.83 (1.00)
	620	0.58 (1.00)	570	1.45 (0.79), 1.98 (0.21)
<i>N,N</i> -Dimethylformamide (DMF)	450	0.70 (0.41), 2.67 (0.59)	400	0.83 (0.46), 1.08 (0.54)
			555	1.50 (0.09), 5.54 (0.91)
Acetonitrile / Chloroform (9/1; v/v)	450	2.55 (1.00)	400	0.94 (0.97), 1.90 (0.03)
	620	0.22 (0.99), 2.84 (0.01)	560	1.36 (0.12), 3.22 (0.88)
Ethanol / Chloroform (9/1; v/v)	435	0.37 (0.54), 1.77 (0.46)	400	1.00 (1.00)

a) Detection wavelength.

b) The excitation wavelength is 365 nm.

c) The values in parentheses are amplitudes of exponential decay components.

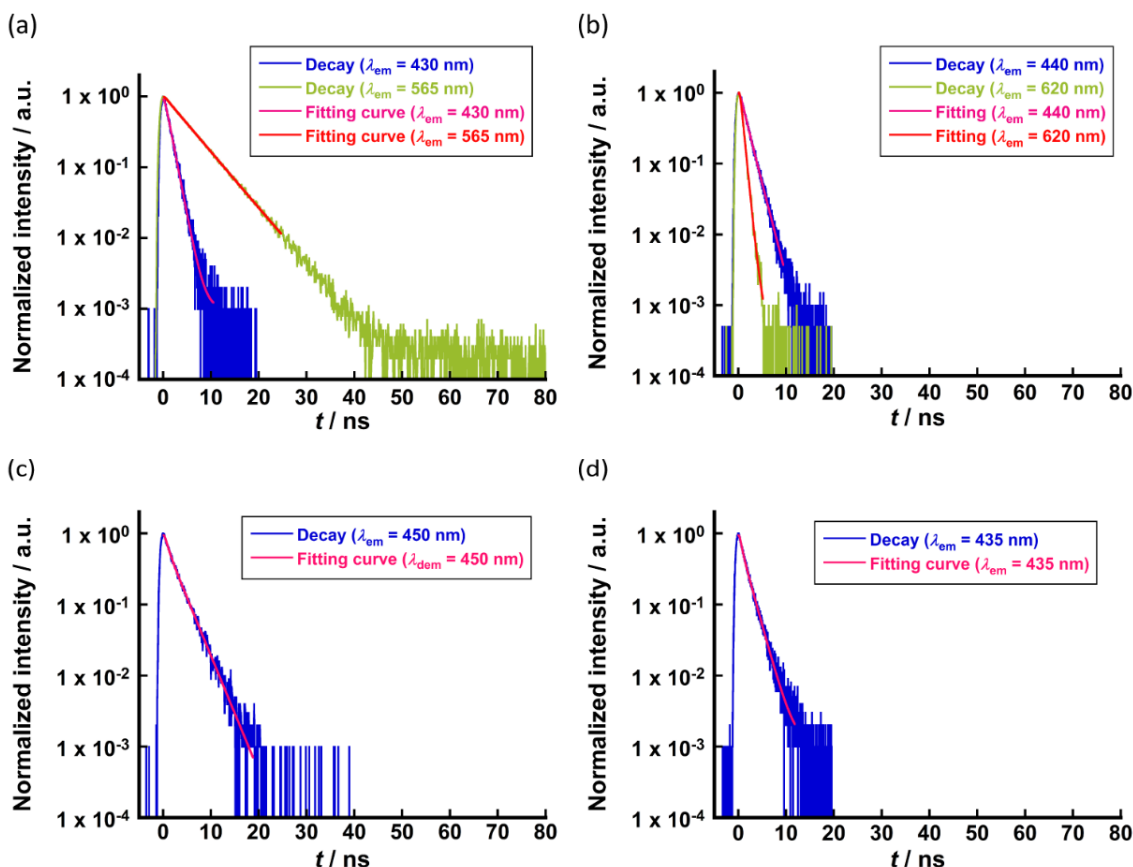


Fig. S13 Emission decay profiles of FL-1 in solutions (10 mM) diluted by (a) toluene, (b) chloroform, (c) DMF and (d) ethanol / chloroform (9/1; v/v). The excitation wavelength is 365 nm.

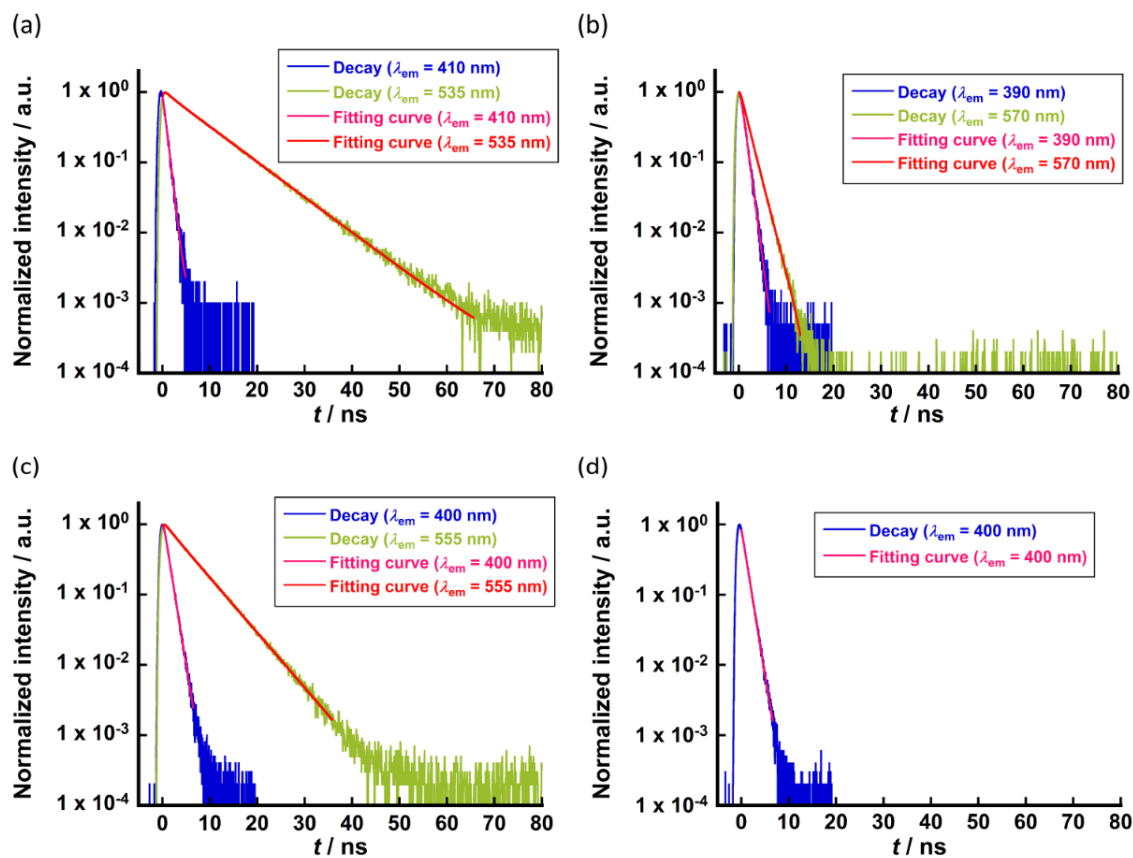


Fig. S14 Emission decay profiles of FL-2 in solutions (10 mM) diluted by (a) toluene, (b) chloroform, (c) DMF and (d) ethanol / chloroform (9/1; v/v). The excitation wavelength is 365 nm.

S-7. Acid-Responsive Behaviours

Table S4 Acid-responsive fluorescent behaviours of FL-1 and FL-2 in the toluene solution.

Sample	<i>D</i> gel of FL-1	<i>DB</i> gel of FL-2
	PLQY ^a	PLQY ^a
Initial toluene solution (10 μ M)	0.234	0.489
TFA (10 ⁴ eq.)-added solution	0.014	0.033
TEA (10 ⁴ eq.)-neutralized solution	0.080	0.260

a) The excitation wavelength is 365 nm.

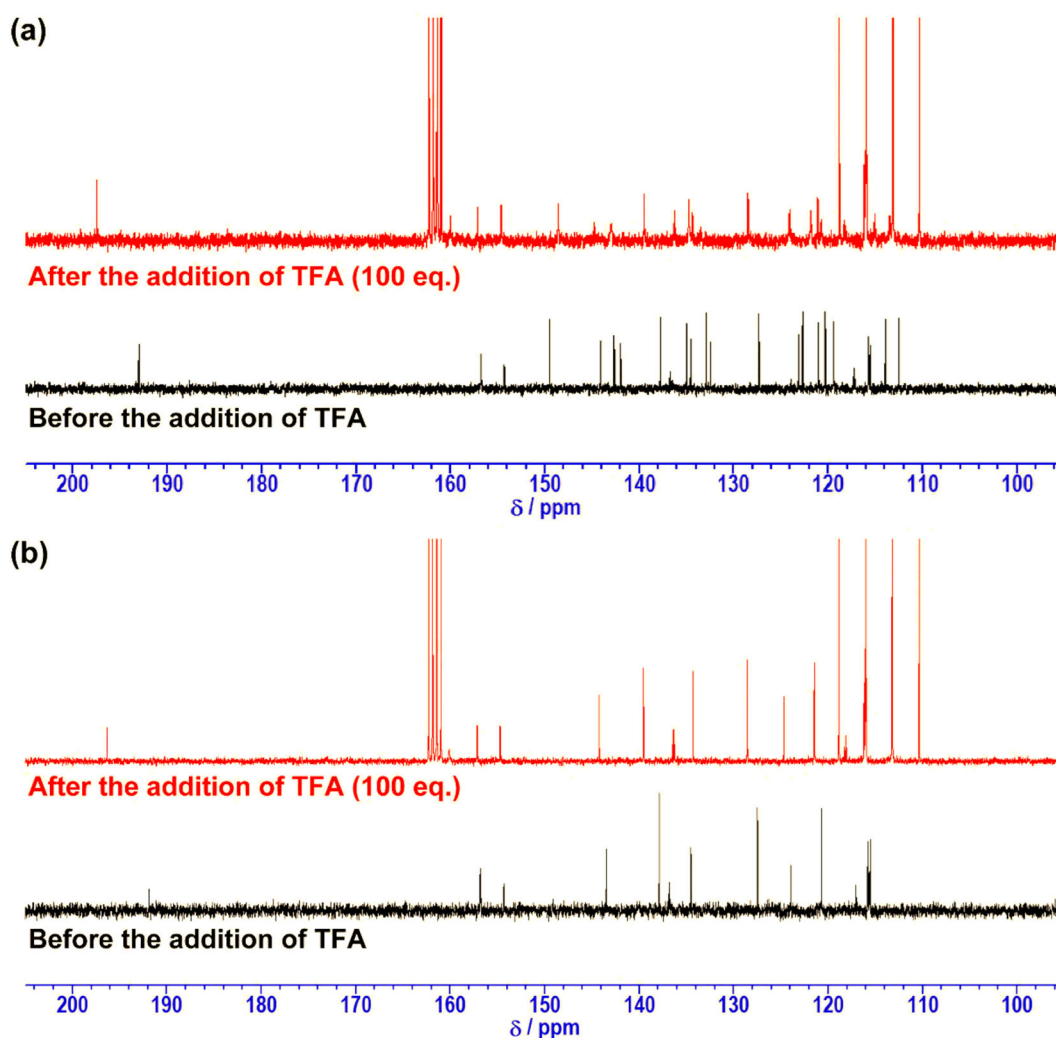


Fig. S15 Variations in ¹³C NMR spectra of (a) FL-1 and (b) FL-2 when an excess amount of TFA (100 eq.) was added to the solution in CDCl₃.

Table S5 Acid-responsive fluorescent behaviours of **FL-1** and **FL-2** in organogel states.

Sample	<i>D</i> gel of FL-1			<i>DB</i> gel of FL-2		
	PLQY ^a	$\lambda_{\text{det}} / \text{nm}^{\text{b}}$	$\tau / \text{ns}^{\text{a}}$	PLQY ^a	$\lambda_{\text{det}} / \text{nm}^{\text{b}}$	$\tau / \text{ns}^{\text{a}}$
Initial	0.139	550	2.69 (0.08) ^c , 9.30 (0.92)	0.198	550	6.97 (0.33) ^c , 13.9 (0.67)
Acidified by TFA (1.0 eq.)	0.058	590	4.68 (0.18), 8.01 (0.82)	0.221	550	5.93 (0.12), 12.2 (0.88)
Neutralized by TEA (1.0 eq.)	0.140	550	3.11 (0.09), 9.21 (0.91)	0.209	550	8.98 (0.27), 13.9 (0.73)

a) The excitation wavelength is 365 nm.

b) Detection wavelength.

c) The values in parentheses are amplitudes of exponential decay components.

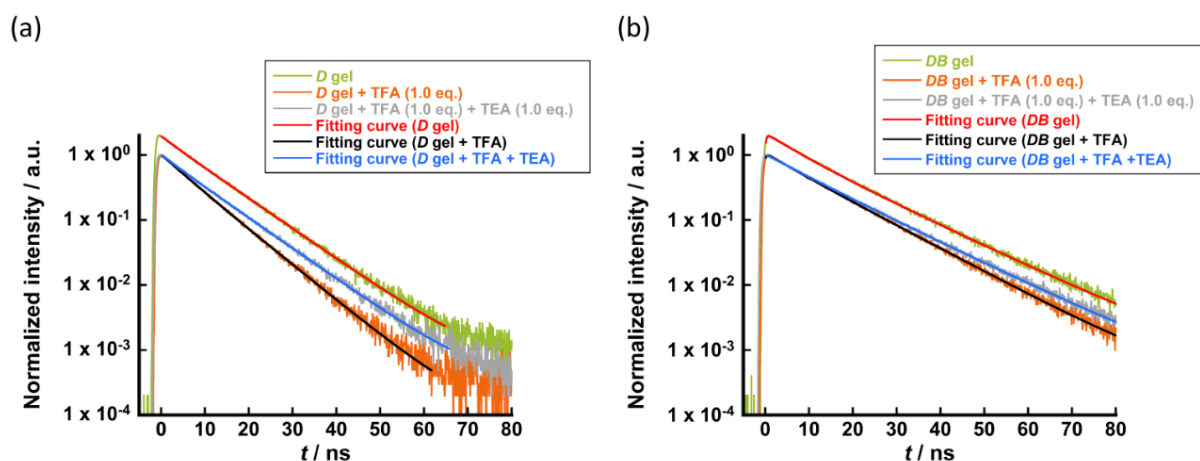


Fig. S16 Variations in emission decay profiles for (a) *D* gel of **FL-1** and (b) *DB* gel of **FL-2** after the addition of TFA (1.0 eq.) and following neutralization by TEA (1.0 eq.). The excitation wavelength was 365 nm. The emission decays were monitored at the wavelength shown in Table S4.

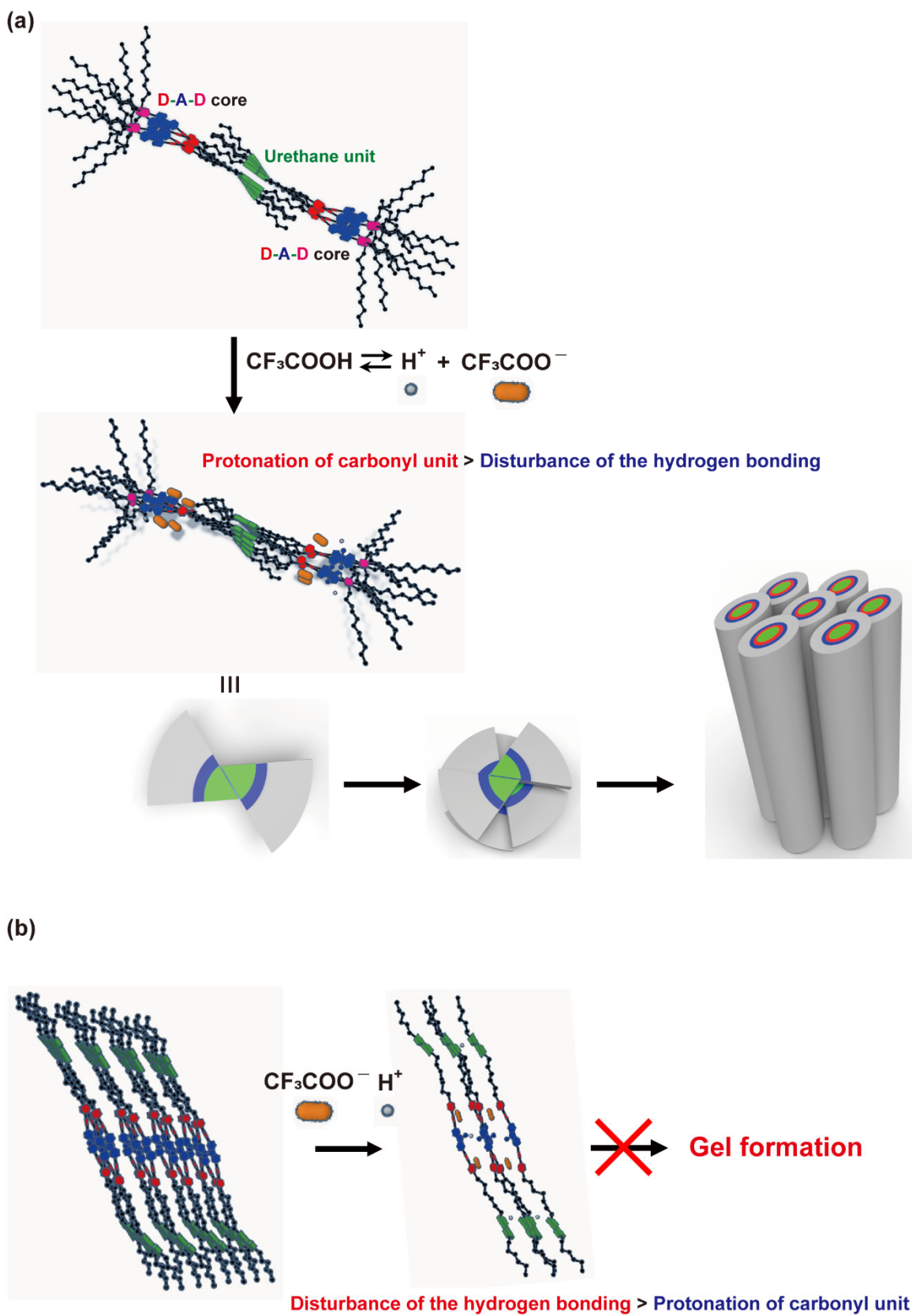


Fig. S17 Schematic illustrations of distinct TFA-responsive behaviors in organogels of (a) FL-1 and (b) FL-2.

S-8. ^1H and ^{13}C NMR Spectra

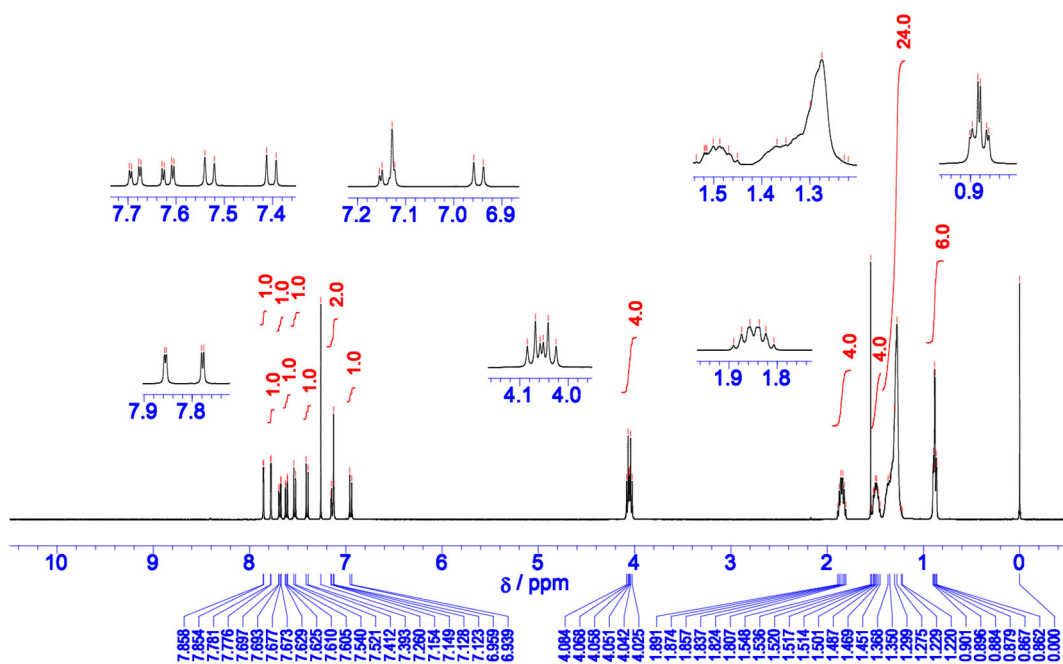


Fig. S18 ^1H NMR spectrum of 3.

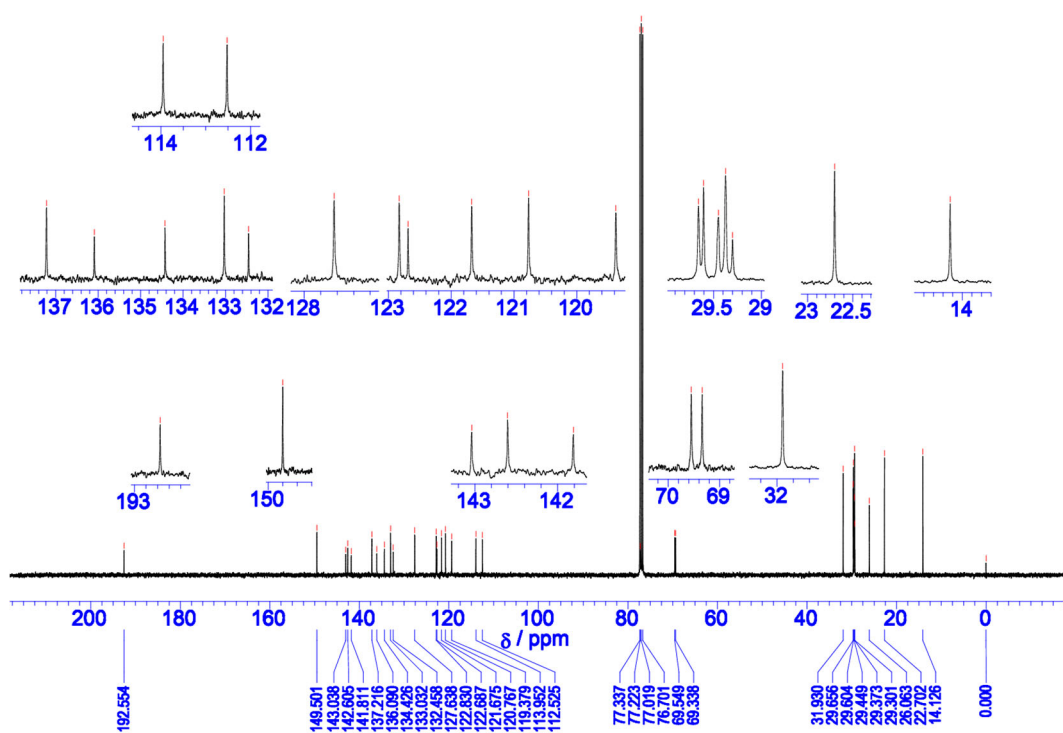


Fig. S19 ^{13}C NMR spectrum of 3.

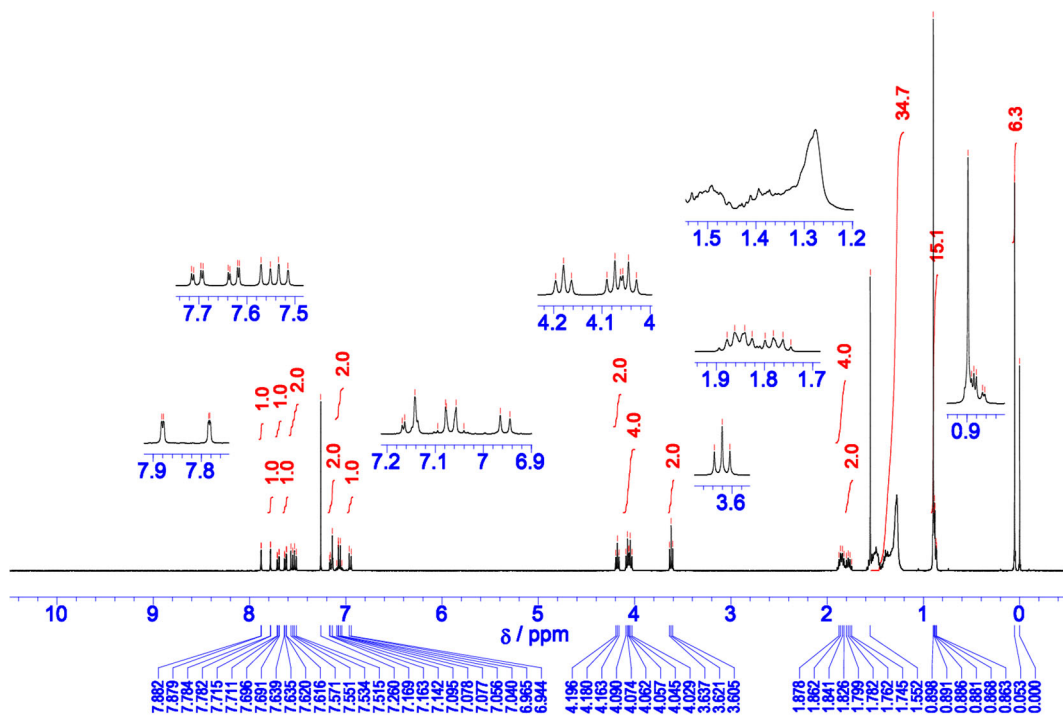


Fig. S20 ^1H NMR spectrum of 6.

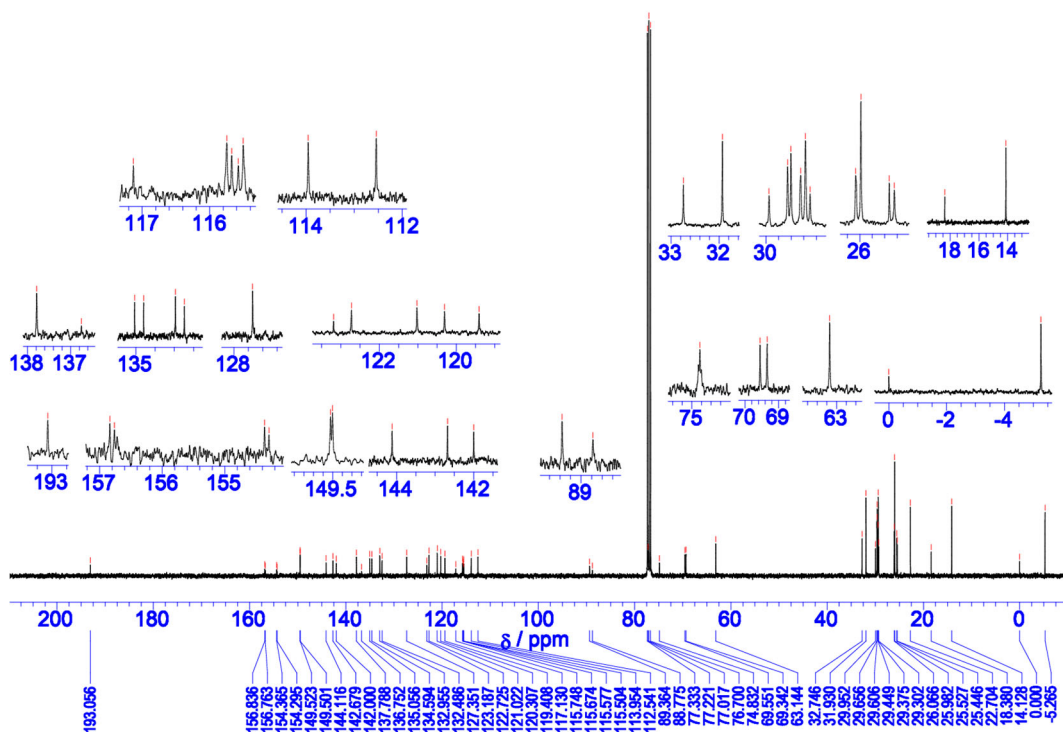


Fig. S21 ^{13}C NMR spectrum of 6.

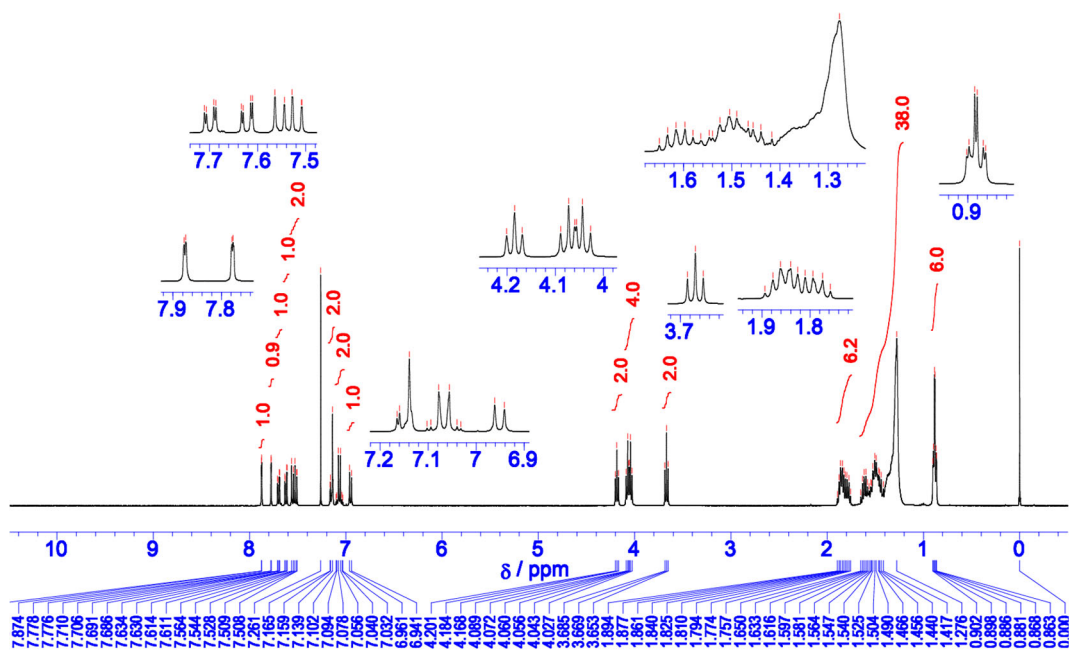


Fig. S22 ^1H NMR spectrum of 7.

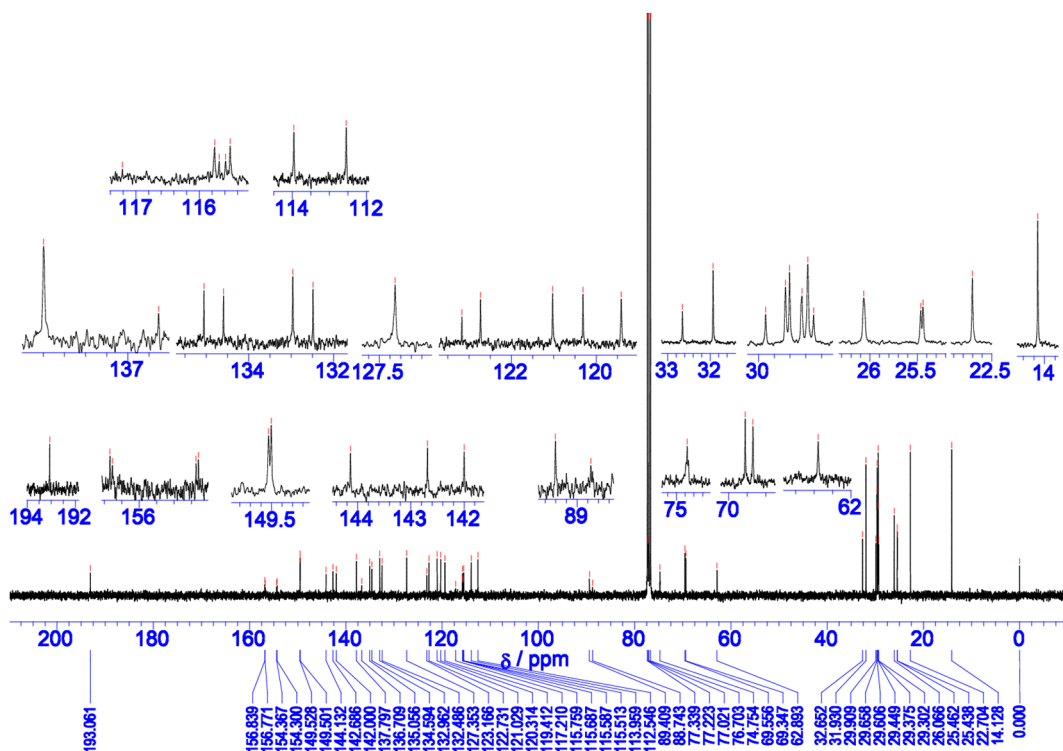


Fig. S23 ^{13}C NMR spectrum of 7.

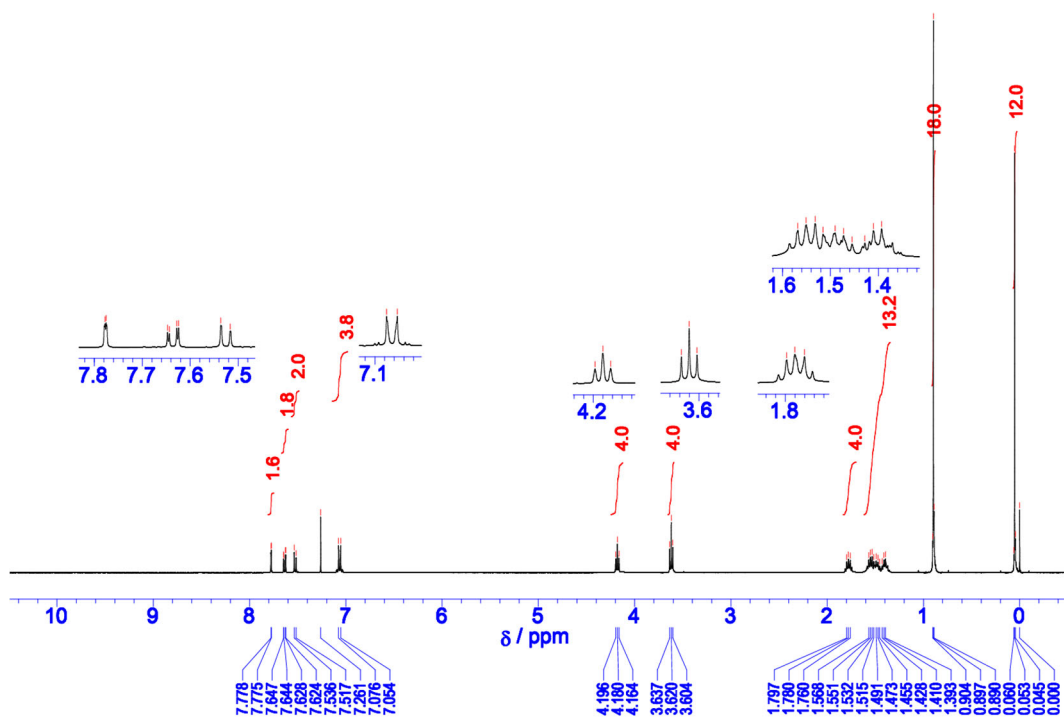


Fig. S24 ^1H NMR spectrum of **8**.

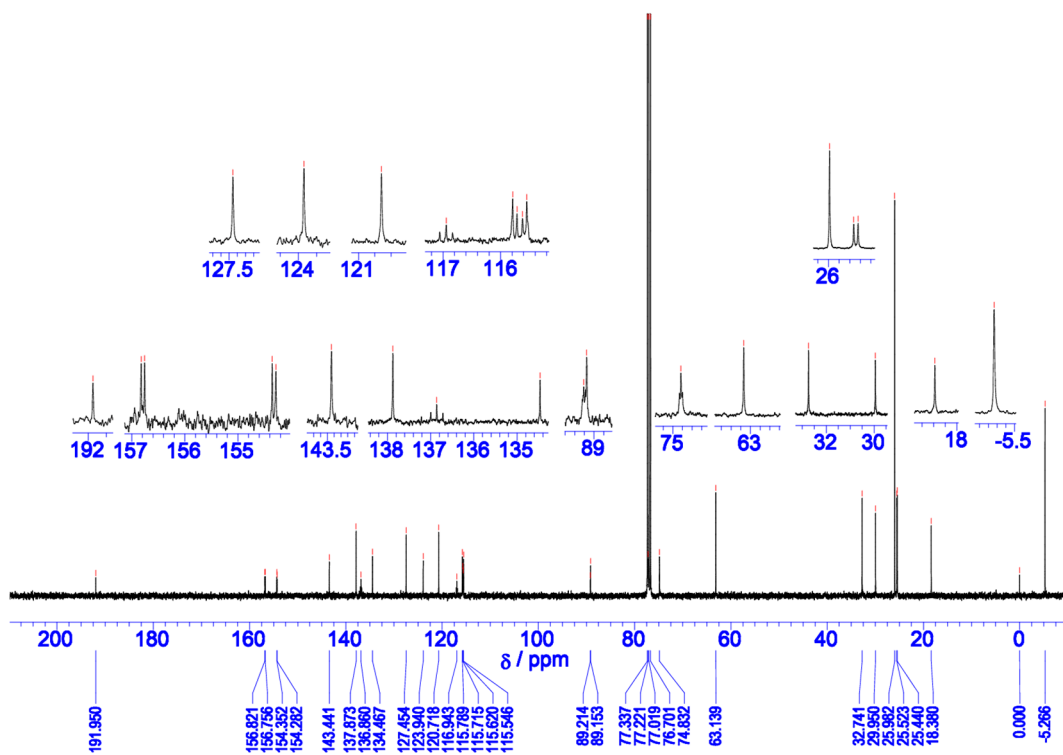


Fig. S25 ^{13}C NMR spectrum of **8**.

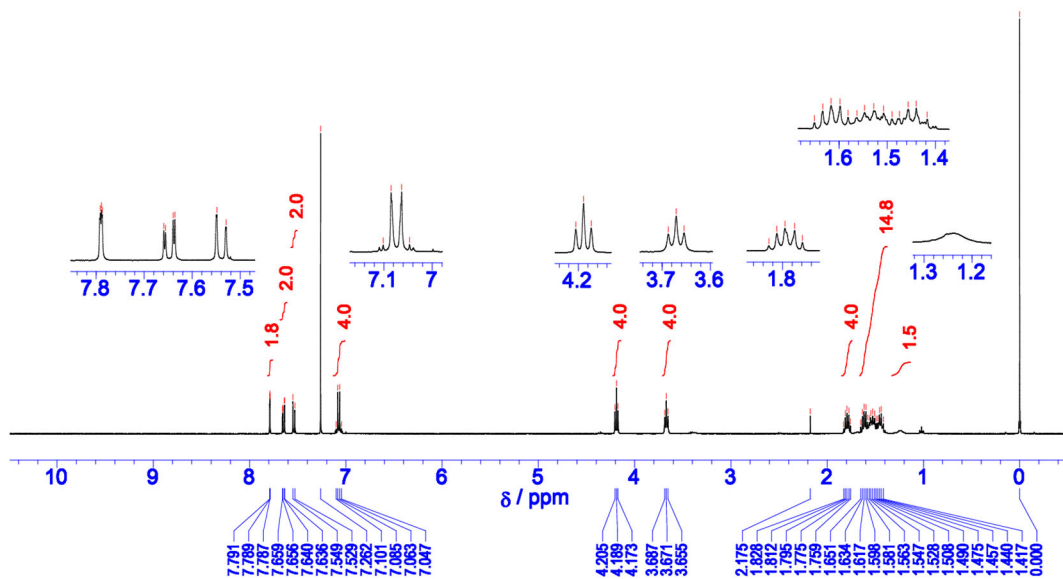


Fig. S26 ^1H NMR spectrum of **9**.

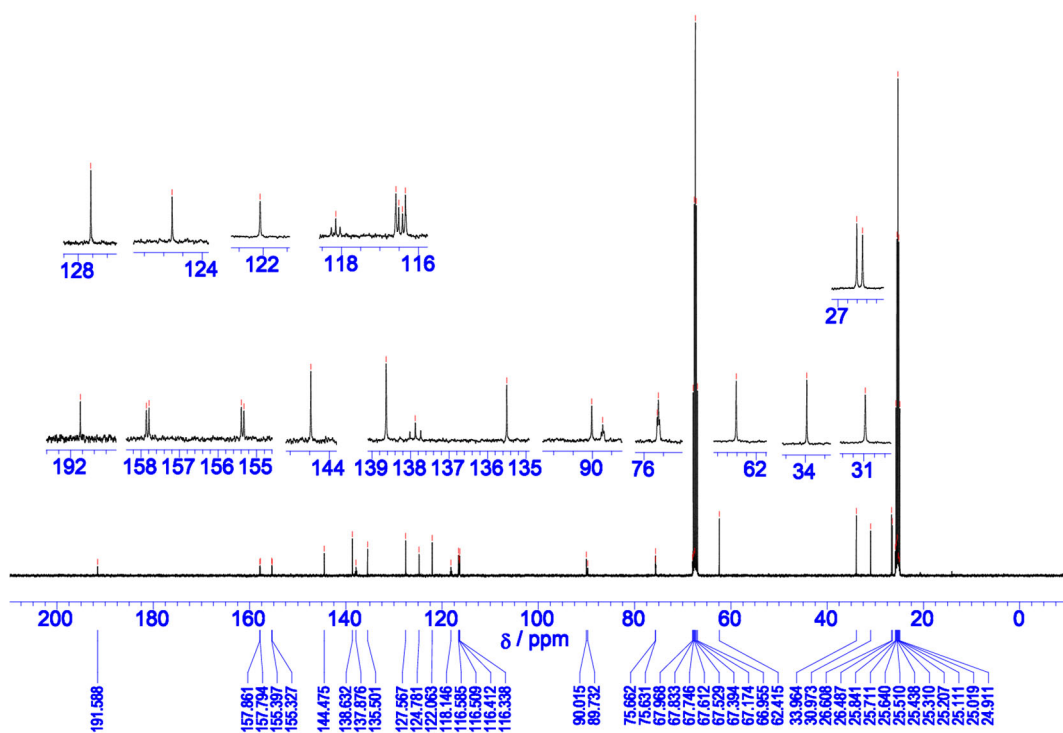


Fig. S27 ^{13}C NMR spectrum of **9**.

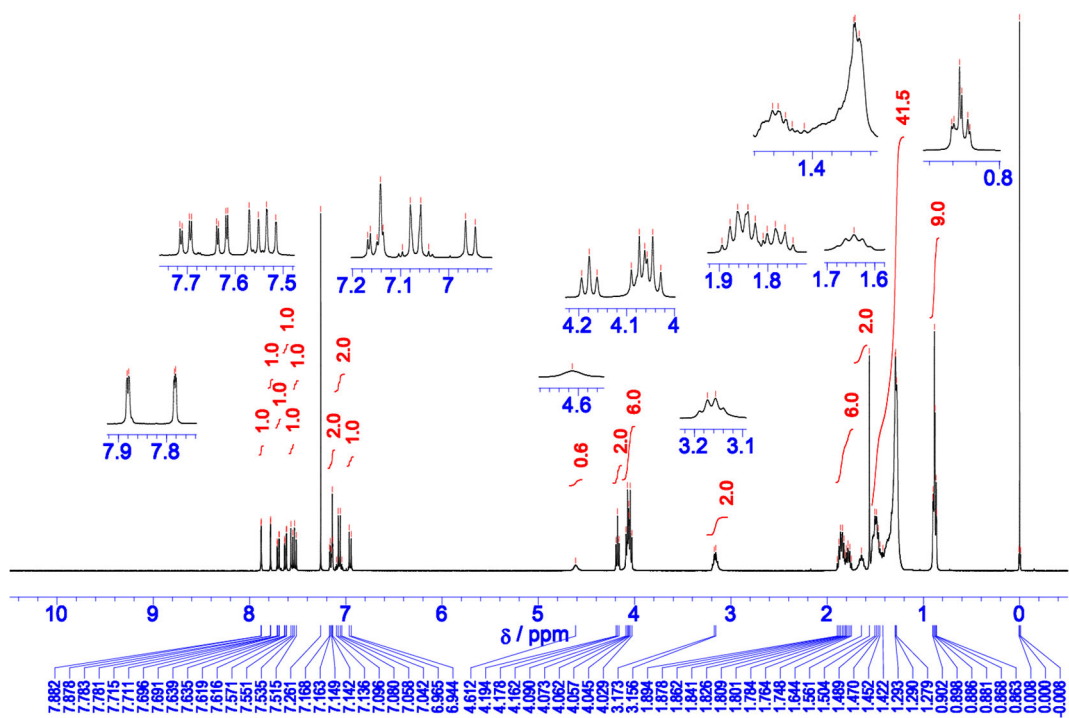


Fig. S28 ^1H NMR spectrum of FL-1.

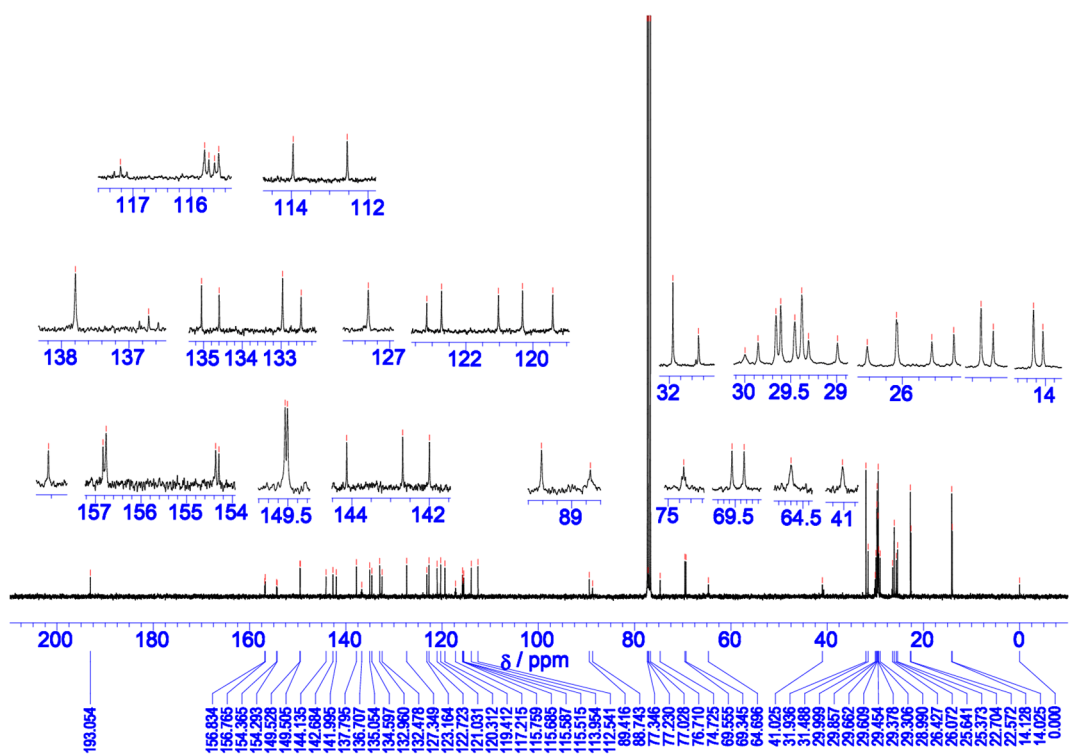


Fig. S29 ^{13}C NMR spectrum of FL-1.

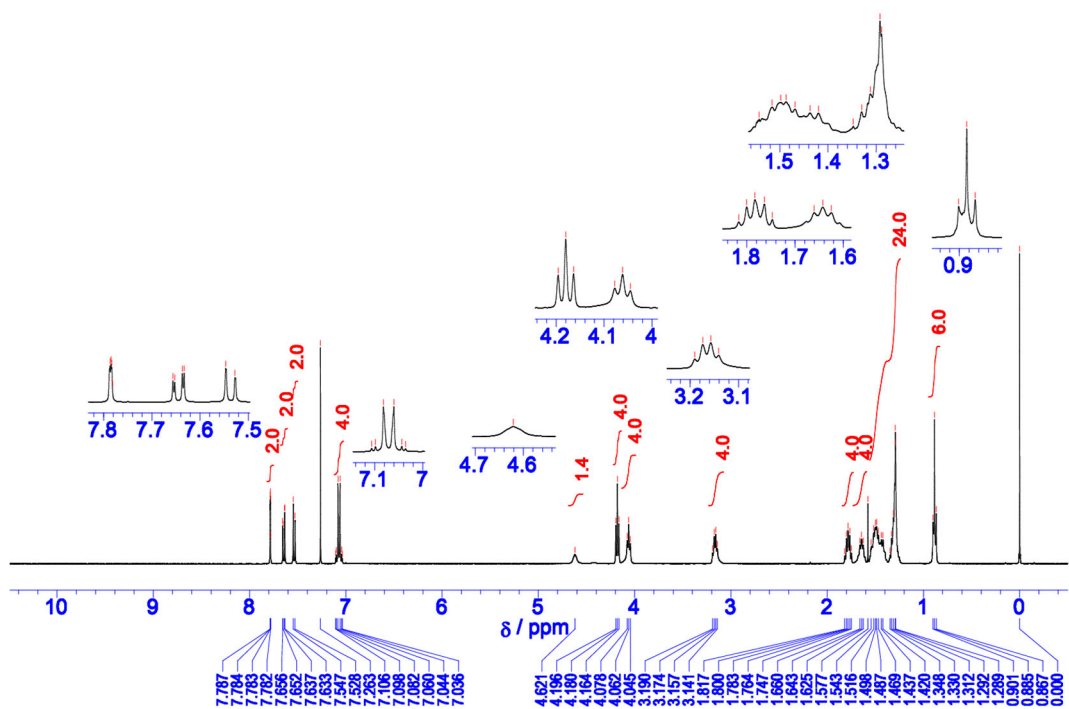


Fig. S30 ¹H NMR spectrum of FL-2.

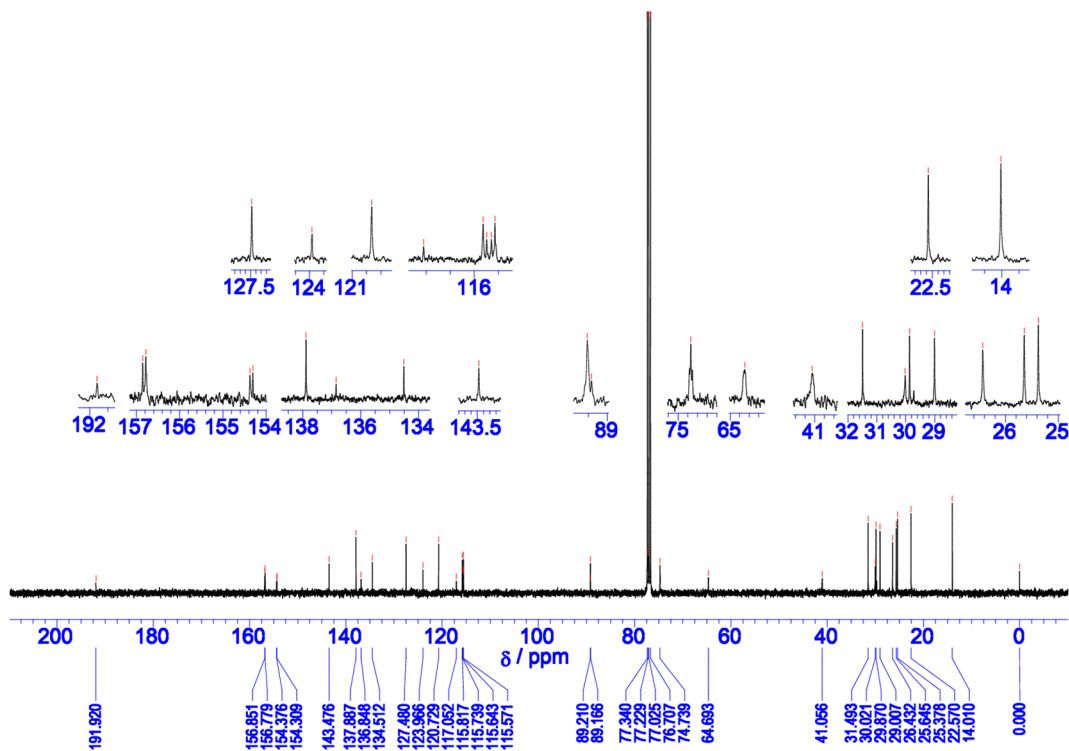


Fig. S31 ¹³C NMR spectrum of FL-2.

Formula [M+H] ⁺	Theoretical m/z	Found m/z	RDB	Delta m/z (ppm)	Resolution
C ₆₀ H ₈₀ F ₂ NO ₆	948.5948	948.5949	21.0	0.1	29554

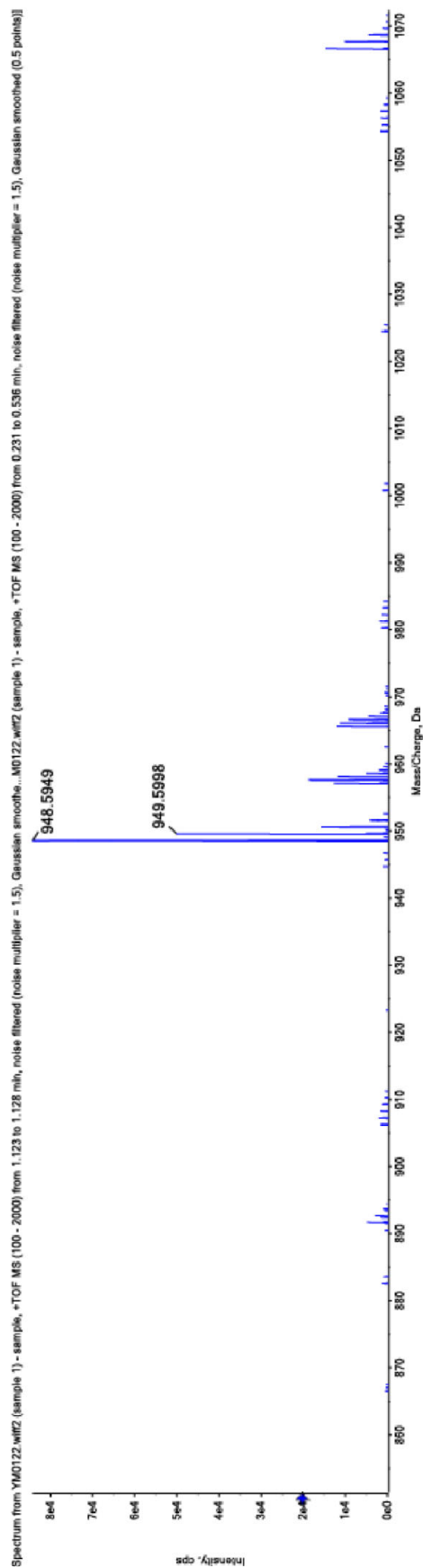


Fig. S32 High resolution ESI mass spectrum of FL-1.

Formula	Theoretical <i>m/z</i>	Found <i>m/z</i>	RDB	Delta <i>m/z</i> (ppm)	Resolution
<chem>C55H63F4N2O7</chem>	939.4566	939.4566	24.0	0.0	29607

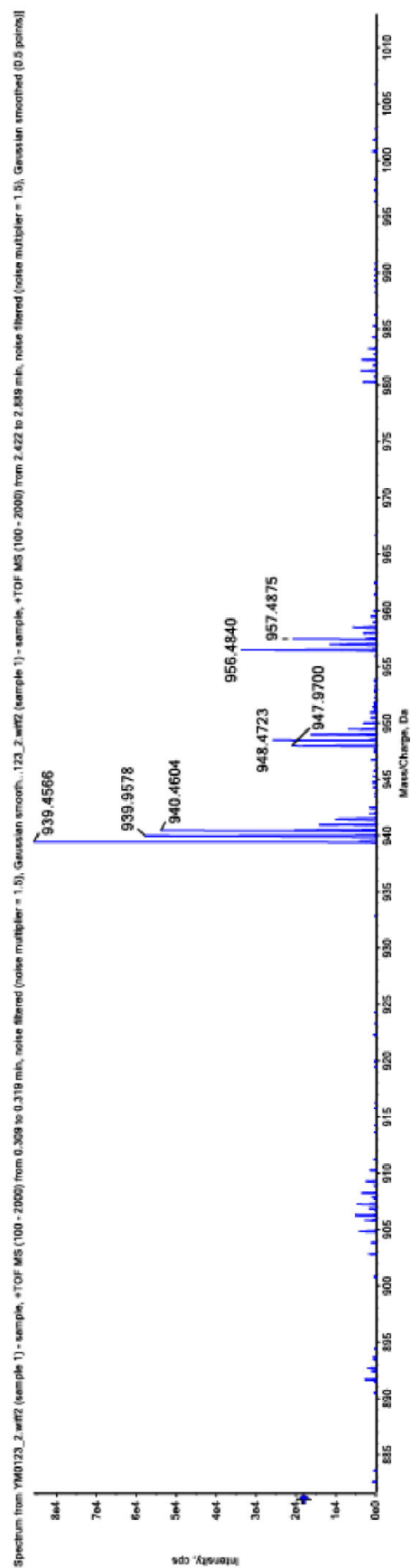


Fig. S33 High resolution ESI mass spectrum of FL-2.

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