Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Photomechanochromic vs Mechanochromic Fluorescence of a Unichromophoric Molecular Solid: Multicolour Fluorescence Patterning

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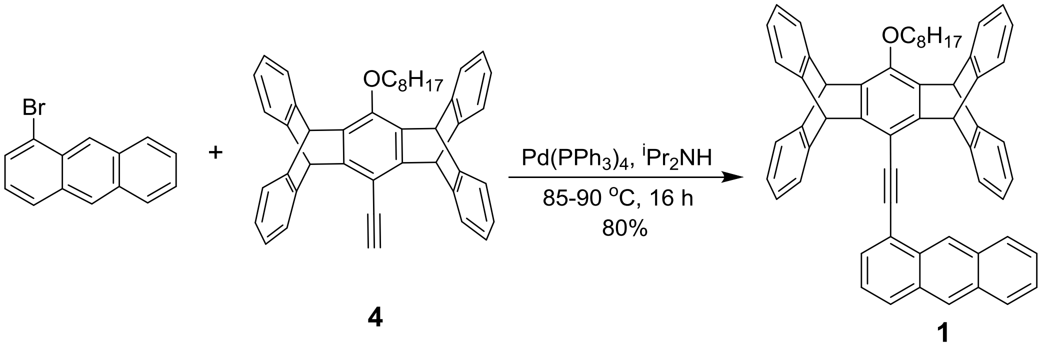
CONTENTS

Synthesis and Reactions

Synthesis of Compound 1. Under argon atmosphere 1-bromoanthracene (102 mg, 0.40 mmol), compound **4** (232 mg, 0.40 mmol) and $Pd(PPh_3)_4$ (46.0 mg, 0.04 mmol) were taken in 15 mL of degassed diisopropylamine. The mixture was refluxed at 85-90 °C for 16 h. After cooling to room temperature, the solvent was removed under reduced pressure and the crude product was purified by column chromatography with hexane/DCM (4:1) eluent to produce yellow solid **1** (240 mg, 80%): Mp: > 300 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.27 (s, 1H), 8.58 (s, 1H), 8.16-8.12 (m, 3H), 8.03-8.01 (d, *J* = 8.0 Hz, 1H), 7.63-7.56 (m, 3H), 7.45-7.41 (m, 4H), 7.37-7.33 (m, 4H), 6.98-6.96 (m, 8H), 6.06 (s, 2H), 5.73 (s, 2H), 4.02-3.99 (t, *J* = 7.2 Hz, 2H), 2.08-2.00 (m, 2H), 1.73-1.65 (m, 2H), 1.53-1.39 (m, 8H), 0.97-0.94 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.9, 146.0, 145.2, 145.1, 135.6, 132.4, 132.1, 131.4, 130.2, 129.3, 128.5, 128.2, 127.2, 126.2, 126.0, 125.3, 124.9, 124.0, 123.5, 121.5, 111.2, 93.0, 90.4, 76.2, 52.6, 48.4, 32.0, 30.6, 29.6, 29.4, 26.4, 22.7, 14.2; IR (KBr): 3067, 3020, 2925, 2853, 2353, 1460, 1388, 1299 cm^{-1}; HRMS (MALDI-TOF): m/z calculated for $C_{58}H_{46}O$ ([M]$^+$): 758.3543; found: 758.3518.

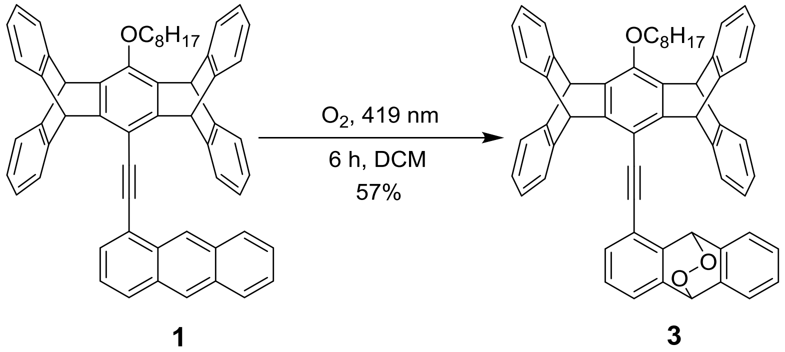


Scheme S1. Synthesis of compound **1.**

Synthesis of Compound 2. The thin solid film of compound **1** (Y form, 40.0 mg, 0.05 mmol) sandwiched by two quartz plates were irradiated with UV light at 365 nm for 12 h. After irradiation, the solid compound over the glass plate was dissolved in DCM and concentrated. The solid mass was purified by column chromatography to produce pale yellow solid **2** (34.0 mg, 85%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.50 (t, *J* = 6.5 Hz, 8H), 7.43-7.39 (m, 10H), 7.34-7.32 (d, *J* = 7.5 Hz, 2H), 7.24 (s, 2H), 7.11-6.99 (m, 24H), 6.08 (s, 4H), 5.78 (s, 4H), 5.65-

5.62 (d, *J* = 11.0 Hz, 2H), 4.99-4.96 (d, *J* = 11.0 Hz, 2H), 4.05-4.01 (t, *J* = 6.8 Hz, 4H), 2.10-2.03 (m, 4H), 1.75-1.68 (m, 4H), 1.51-1.41 (m, 16H), 0.99-0.95 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.9, 145.8, 145.2, 145.1, 145.1, 143.7, 143.2, 142.5, 135.6, 129.3, 127.4, 127.2, 126.5, 126.4, 126.2, 126.0, 125.4, 125.4, 123.8, 123.7, 122.0, 111.2, 93.5, 88.5, 76.2, 53.4, 52.7, 51.7, 48.4, 32.0, 30.6, 29.6, 29.4, 26.4, 22.7, 14.2; IR (KBr): 3447, 3067, 2926, 2854, 2364, 2333, 1629, 1477, 1384 cm^{-1}; HRMS (MALDI-TOF): m/z calculated for $C_{116}H_{93}O_2$ ($[M+H]^+$): 1517.7170; found: 1517.7186.

Synthesis of compound 3. A solution of compound **1** (30.0 mg, 0.04 mmol) in dry DCM (15 mL) under oxygen was irradiated by 419 nm light in a photoreactor at ambient temperature for 6 h. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography (hexane/ethyl acetate = 4:1) to produce the endoperoxide **3** as white solid (18.0 mg, 57%). Mp: 207-209 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71-7.69 (d, *J* =8.0 Hz, 1H), 7.58-7.52 (m, 3H), 7.46-7.42 (t, *J* =7.6 Hz, 1H), 7.40-7.34 (m, 10H), 6.98-6.95 (m, 8H), 6.77 (s, 1H), 6.17 (1H, s), 5.88 (s, 2H), 5.72 (s, 2H), 4.01-3.98 (t, *J* =6.8 Hz, 2H), 2.07-2.00 (m, 2H), 1.72-1.65 (m, 2H), 1.53-1.39 (m, 8H), 0.98-0.95 (t, *J* =6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.2, 146.1, 145.0, 144.9, 139.6, 138.6, 138.0, 137.5, 135.7, 131.0, 128.3, 128.0, 125.3, 123.9, 123.9, 123.6, 123.5, 119.2, 110.3, 90.3, 89.6, 79.1, 77.7, 76.2, 52.5, 48.3, 31.9, 31.6, 30.6, 29.6, 29.4, 26.4, 22.7, 14.1; IR (KBr): 3068, 3018, 2928, 2856, 2365, 2248, 1637, 1457, 1300, 1270, 1083, 909, 742, 560 cm^{-1}; HRMS (MALDI-TOF): m/z calculated for $C_{58}H_{46}O_3$ ($[M]^+$): 790.3441; found: 790.3435.



Scheme S2. Synthesis of compound **3.**

Thermal conversion of 2 to 1. The pure photodimer **2** (20.0 mg, 0.01 mmol) was reversed back to **1** (17.0 mg, 95%) by heating at 165 ^{o}C for 2 h. The reaction rate constant was determined by 400 MHz ^{1}H NMR spectroscopy in $CDCl_3$ (Figure S13). Seven sets of sandwiched glass plates (1.0 cm × 1.0 cm) with 2.0 mg of compound **2** were placed over the hot plate with uniform heating at 165 ^{o}C. To monitor the conversion, one set of the sample was removed intermittently after heating for 10, 20, 30, 40, 60, 80, and 120 min, respectively. The signals near 5.8 ppm were used to calculate the relative ratio of the monomer **1** and photodimer **2**. The plot of ln([**2**] in percentage) against the reaction time (min) yielded a straight line with a slope of -0.0146 min^{-1} that corresponded to the rate constant and gave the half-life ($t_{1/2} = \ln 2/k$) of 47.5 min (Figure S12).

Table S1. Photophysical data of compound **1** and **2** in dilute DCM solutions and in various solid-state forms.[a]

Form	λ_{fl} (nm)	Φ_{fl}	τ_1 (A_1)	τ_2 (A_2)	τ_3 (A_3)	<τ> (ns)
Y (powder)	591	0.17	63.6 (0.60)	25.1 (0.35)	0.1 (0.05)	47.0
Y (crystal)	585	0.20	59.1 (0.99)	5.6 (0.01)		58.6
$\mathrm{W_{Yg}}$	453, 575	0.12				
$\mathrm{B_{Yg}}$	453	0.11	11.1 (0.14)	2.6 (0.40)	0.5 (0.46)	2.8
$\mathrm{G_{Yv}}$	542	0.17	89.7 (0.74)	32.2 (0.23)	0.9 (0.02)	73.8
$\mathrm{W_{Yi}}$	439, 573	0.08				
$\mathrm{B_{Yi}}$	439	0.06	9.0 (0.12)	2.3 (0.65)	0.2 (0.22)	2.6[b]
G (powder)	538	0.19	68.8 (0.93)	9.2 (0.07)		64.4
$\mathrm{C_{Gg}}$	480	0.13	12.8 (0.59)	2.2 (0.41)		8.5
$\mathrm{G_{Gv}}$	530	0.15	76.8 (0.89)	16.7 (0.12)		70.3
G (crystal)	534[c]	0.09	47.2 (0.75)	3.8 (0.25)		36.5
$\mathrm{O_{Gi}}$	540, 600[c]	0.05	47.9 (0.49)	8.8 (0.51)		28.1
$\mathrm{R_{Gi}}$	540, 604[c]	0.02	43.1 (0.33)	7.7 (0.67)		19.2
2	341[b]	0.03[b]	3.9 (0.33)	1.4 (0.67)		2.2[b]
1-DCM	415	0.66	3.7 (1.00)			
2-DCM	329[b]	0.93[b]	1.3 (1.00)[b]			

[a] Excitation wavelength (λ_{ex}) is 380 nm, unless otherwise noticed. For lifetime measurements, the emission wavelength are monitored at the corresponding λ_{fl}; [b] λ_{ex}=300 nm; [c] λ_{ex} = 430 nm.

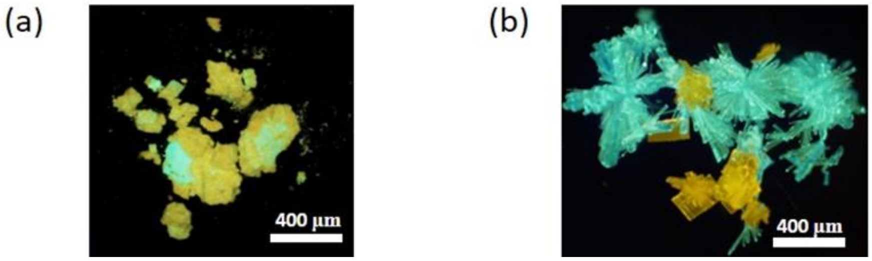


Figure S1. (a) Powder of **1** after evaporation of solvent. (b) Mixture of Y and G crystalline form obtained through slow evaporation of compound **1** in DCM/MeOH mixture (Photographs are taken under 340-390 nm UV source).

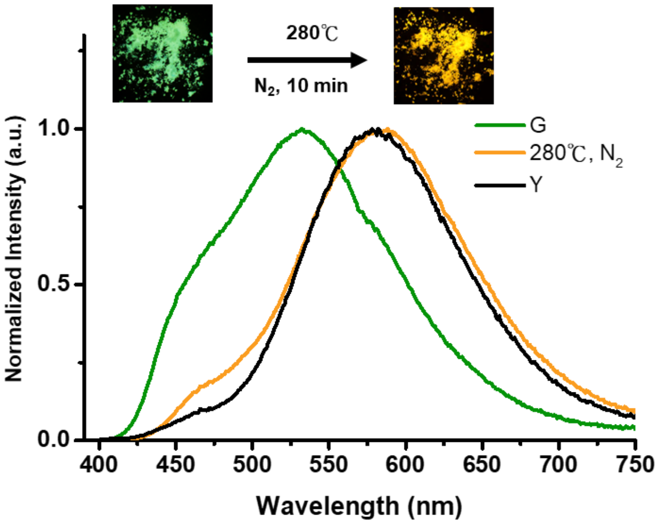


Figure S2. Photographs and emission spectra (excitation wavelength is 380 nm) of the thermal G (green line)-to-Y (orange line) transformation at 280°C for 10 min under nitrogen environment. The fluorescence spectrum of the pristine Y form (black line) is also shown for comparison.

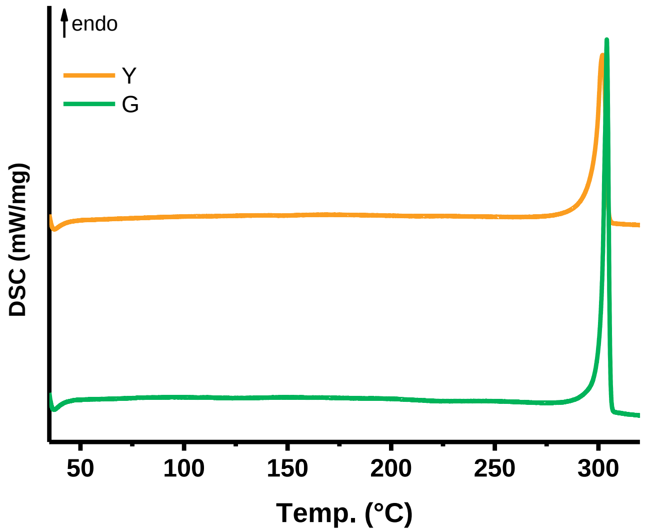


Figure S3. DSC analysis diagram of the Y and G forms under nitrogen atmosphere. Heating rate is 5 °C /min.

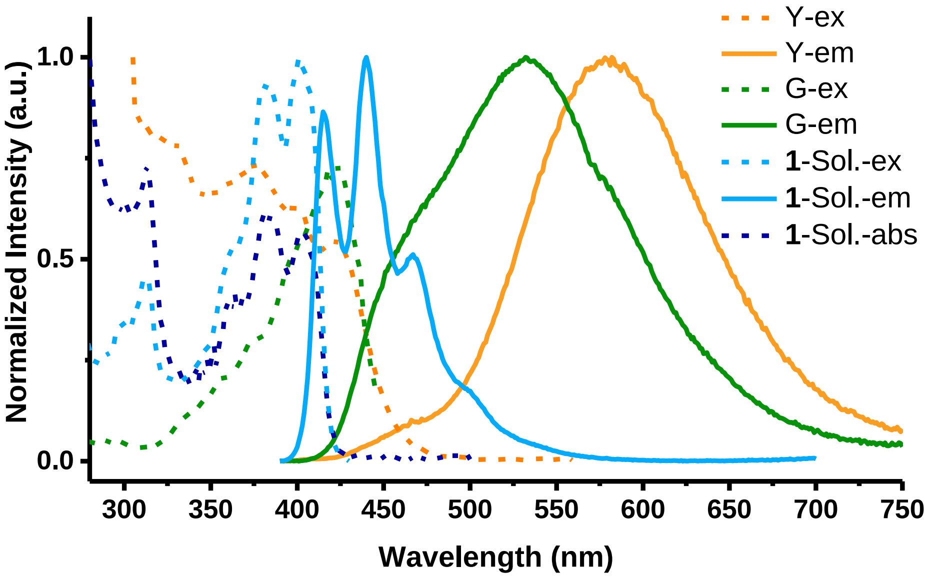


Figure S4. Normalized fluorescence excitation and emission spectra of **1** in the Y (orange lines) and G (green lines) forms and in DCM solution (blue lines). For comparison, the absorption spectrum of **1** in DCM is included.

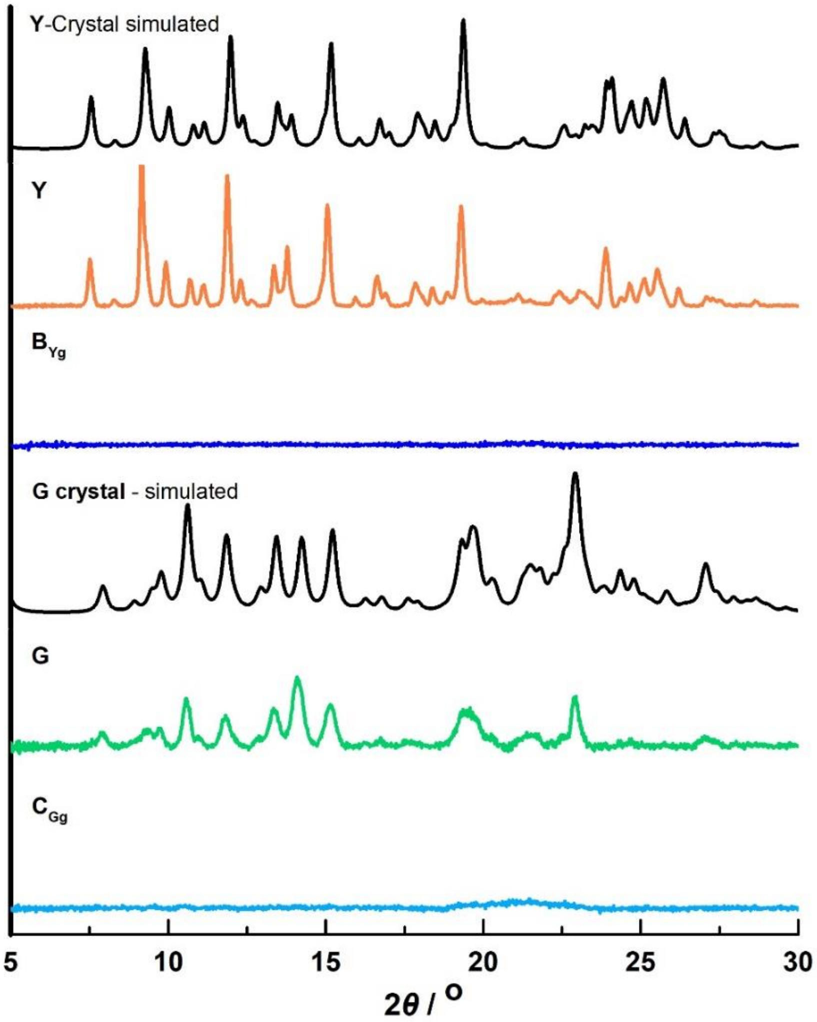


Figure S5. Powder XRD data of the Y and G forms and the corresponding ground B_{Yg} and C_{Gg} forms of **1.**

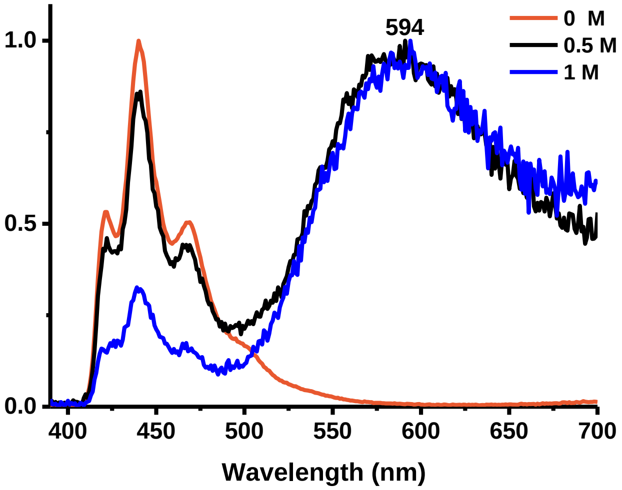


Figure S6. Normalized fluorescence spectra of **1** (4×10^{-4} M) in toluene in the absence (red line) and presence of 0.5 M (black line) and 1.0 M (blue line) of pMDMA.

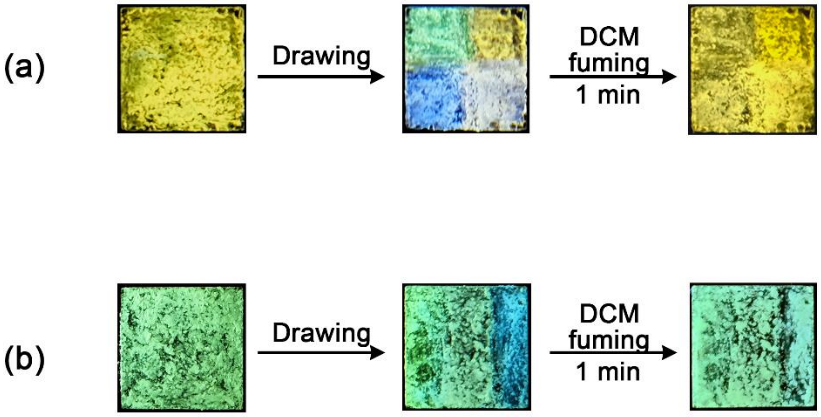


Figure S7. Reversible MFC and VFC properties of the (a) Y and (b) G forms of **1**.

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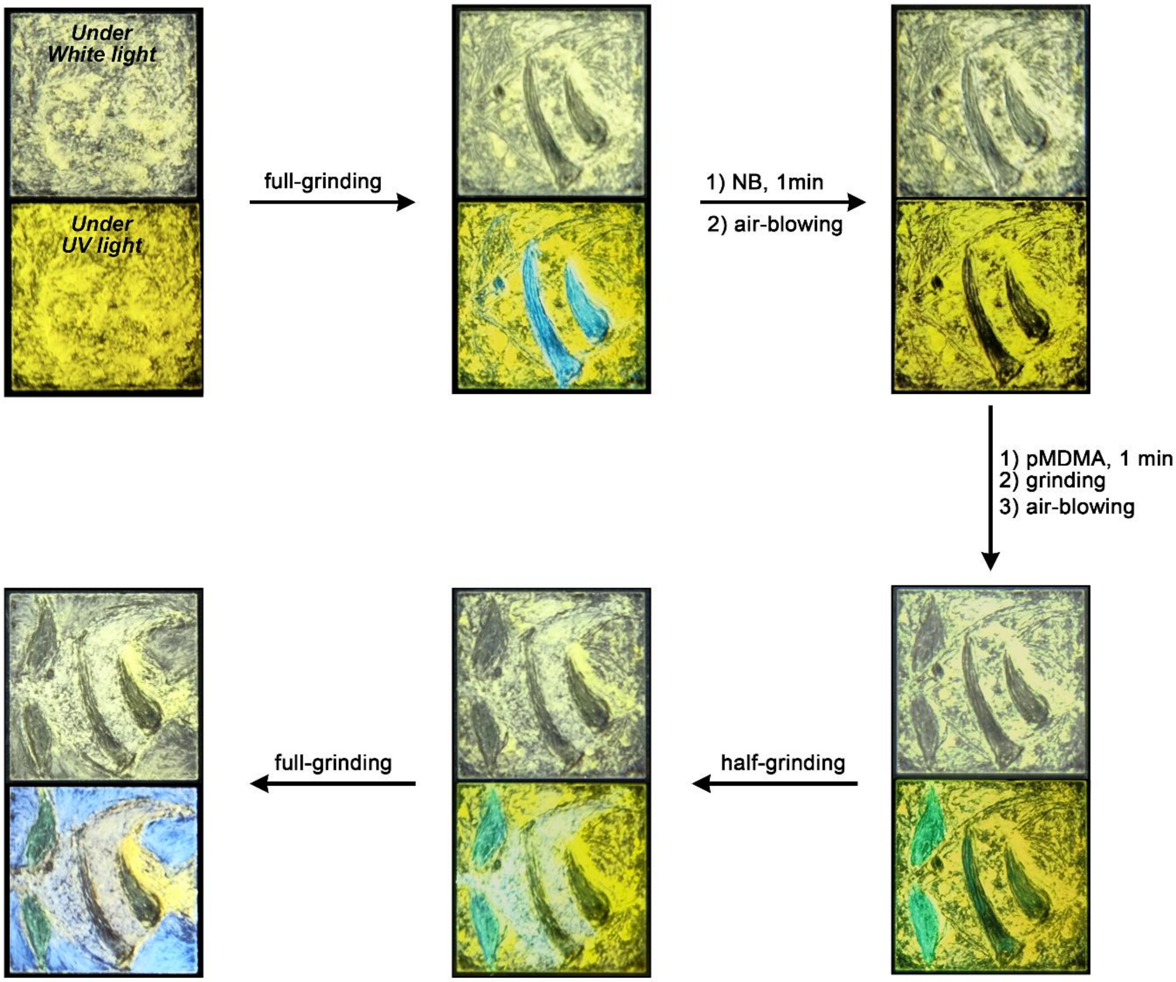


Figure S8. Detailed procedure and images of the MFC- and VFC-based multicolor fluorescence patterning of the "angelfish" (upper: under room light; bottom: under UV light). First, the powder film (1.5 × 1.5 cm) was scratched to draw "stripes and eye" into the $\mathrm{B_{Yg}}$ form. The film was set in a vial containing cotton soaked with nitrobenzene (NB) for 1 min to convert the $\mathrm{B_{Yg}}$ form to the $\mathrm{K_{Yv}}$ form. Next, the film was blown with air for 15 sec to clean the surface before being fumed with the *p*-methyl-*N*,*N*-dimethylaniline (pMDMA) vapor. The "aquatic plant" was drawn immediately after the pMDMA fuming to afford the $\mathrm{G_{Yv}}$ form. After being blown with air for 15 sec, the film was drawn with the "fish body" by partial grinding followed by the drawing of the "water" background by full grinding.

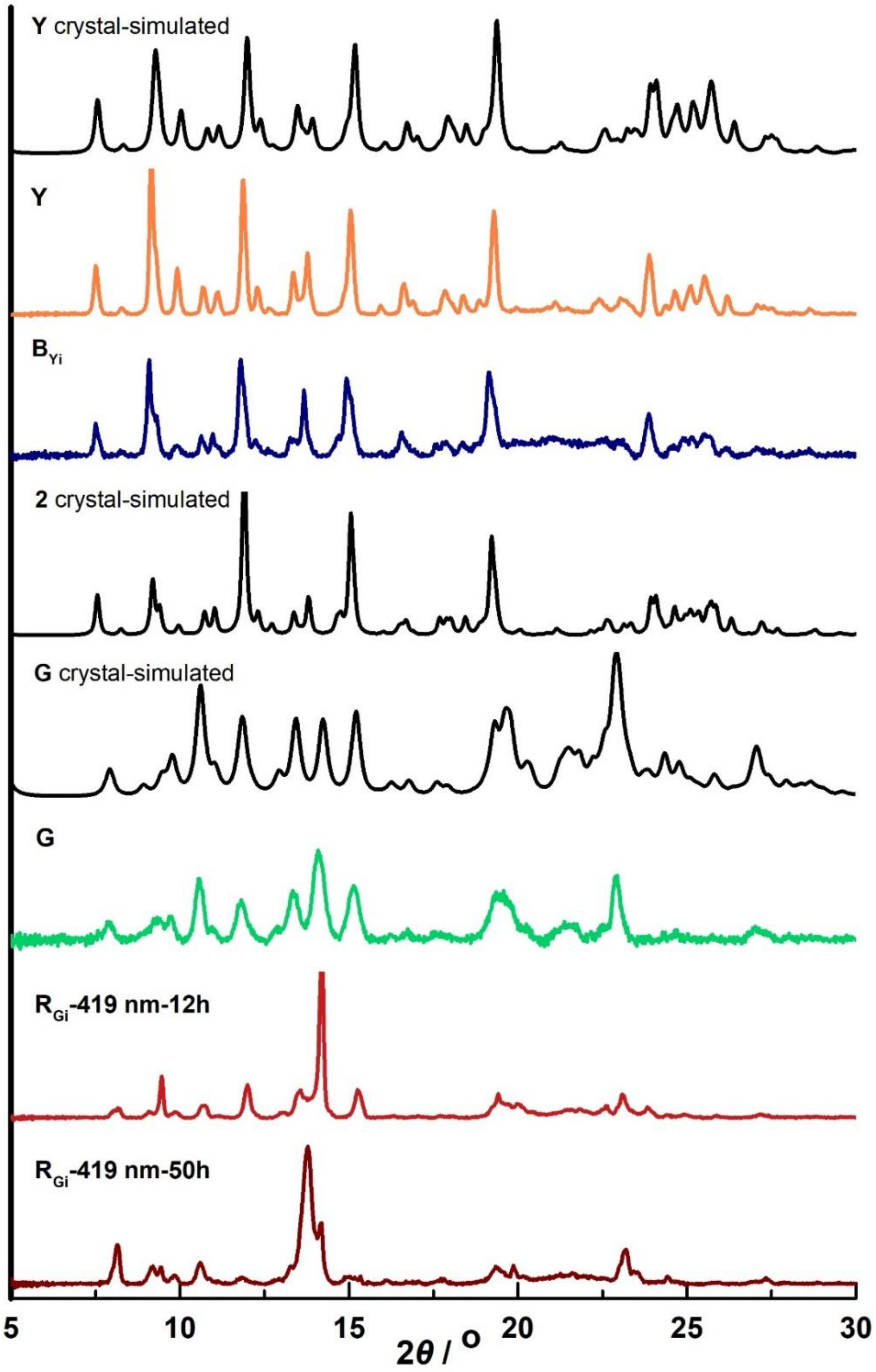


Figure S9. PXRD patterns of the Y, B$_{Yi}$ form, **2**, G form and the R$_{Gi}$ forms, the latter of which were prepared by 419-nm irradiation of the G form for 12 and 50 h. The simulated PXRD patterns of the single crystals are included for comparison.

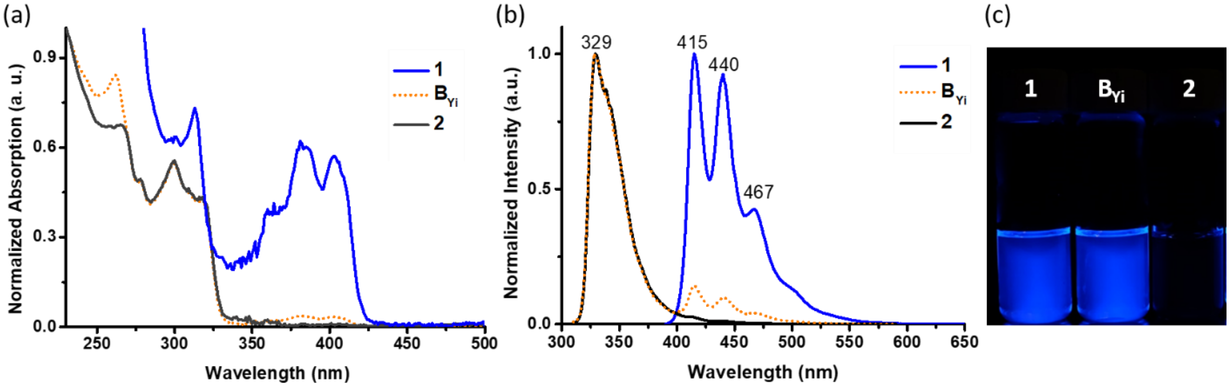


Figure S10. (a) Absorption and (b) emission spectra and (c) photos of fluorescence for **1**, **2**, and B_{Yi} in DCM solution.

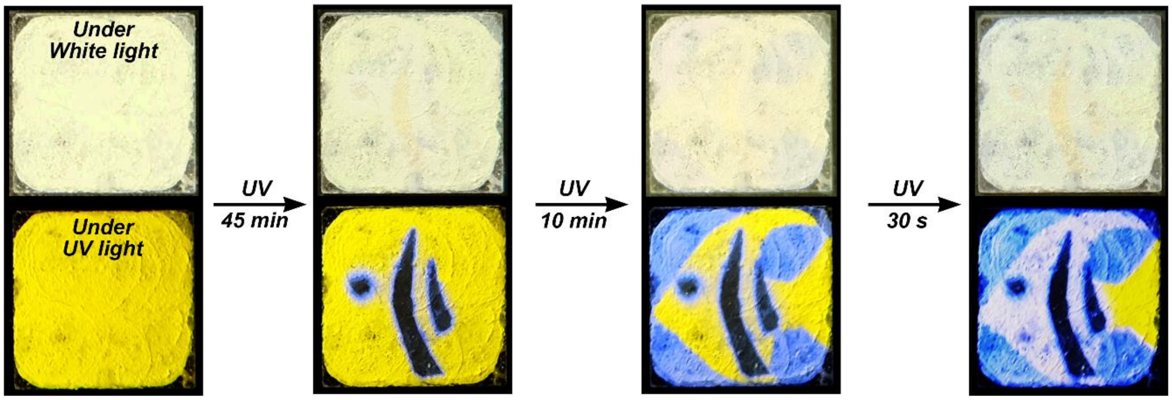


Figure S11. Detailed photochromic fluorescence patterning procedure and photographs of a drop-cast film of the Y form of **1** (upper: under room light; bottom: under UV light). The patterning was carried out with a broadband (340-390 nm) UV light with the use of a paper-made photomask. First, a paper-made photomask that exposed the shape of "stripes and eye" was used to cover the film during UV irradiation (340-390 nm), which turned the exposed area to the K_{Yi} form. Next, a photomask that covered the whole fish was used to generate the blue background (the B_{Yi} form). Finally, a photomask that covered the "fish tail" was used to generate the white stripes of the W_{Yi} form by controlling irradiation time.

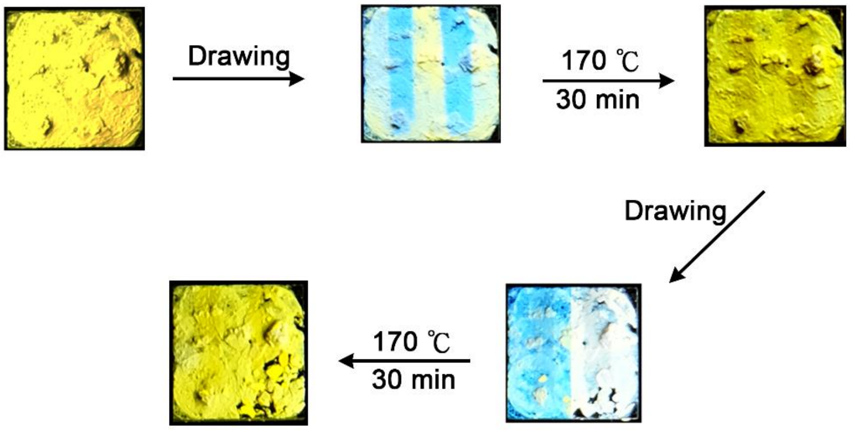


Figure S12. Thermal reversibility of the photochromic fluorescence of the Y form of **1**.

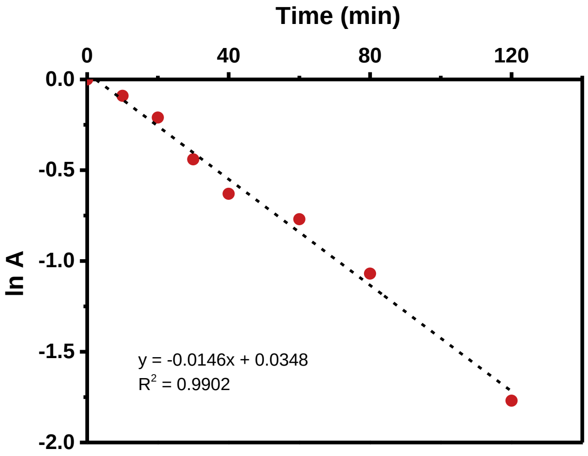


Figure S13. Plot of ln(A) against heating time (min), where A is the percentage of compound **2** in the samples after different time interval of heating. The rate of constant (*k*) for the thermal **2** → **1** conversion is 14.6 × 10^{-3} min^{-1}, corresponding to a half-life ($t_{1/2}$ = ln2/*k*) of 47.5 min.

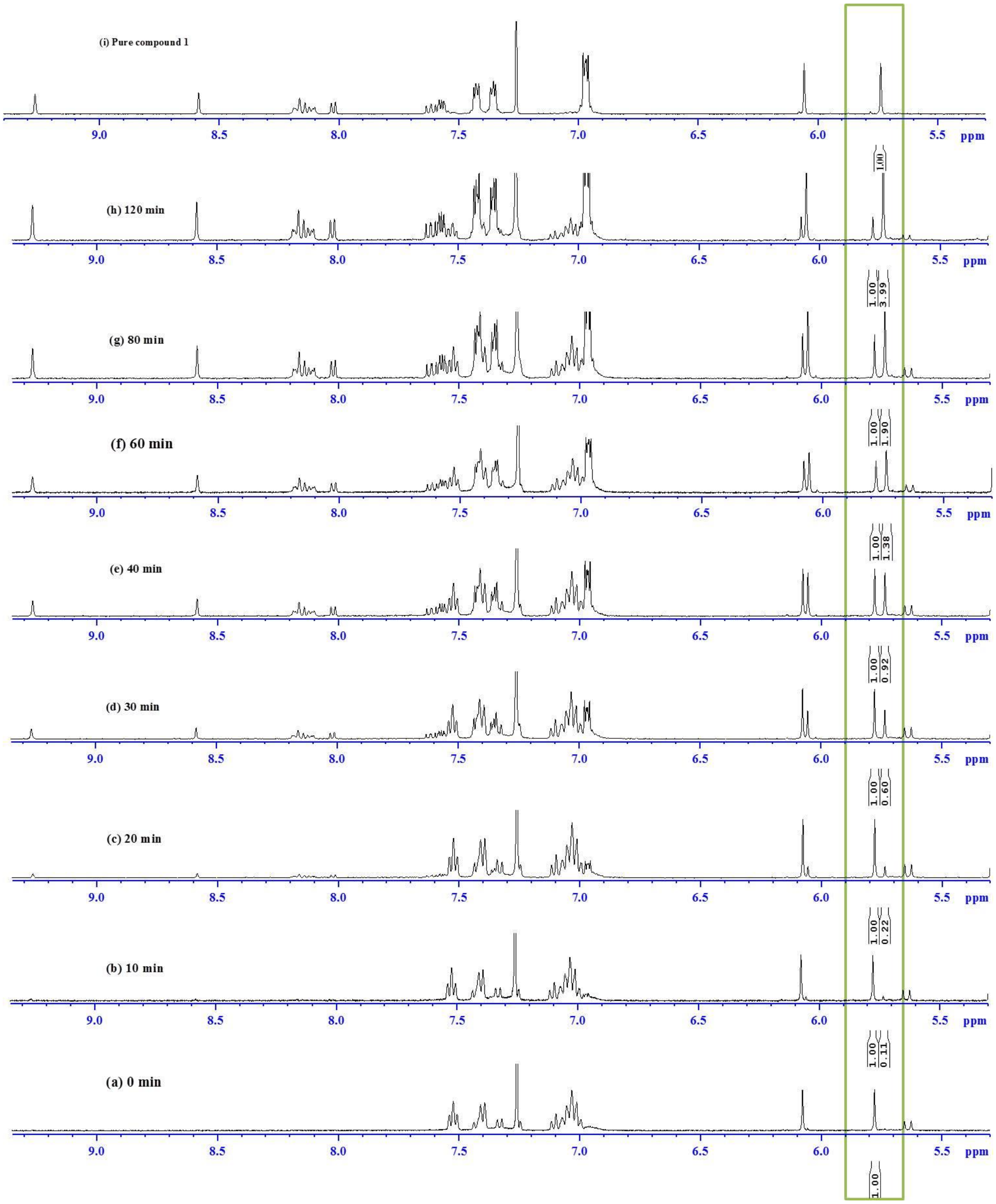


Figure S14. ^{1}H NMR (400 MHz, $CDCl_3$) spectra in the region 5.30-9.35 ppm for **2** upon heating at 165 ℃ for (a) 0, (b) 10, (c) 20, (d) 30, (e) 40, (f) 60, (g) 80, and (h) 120 min in the solid-state. Spectrum (i) is from pure **1** for comparison.

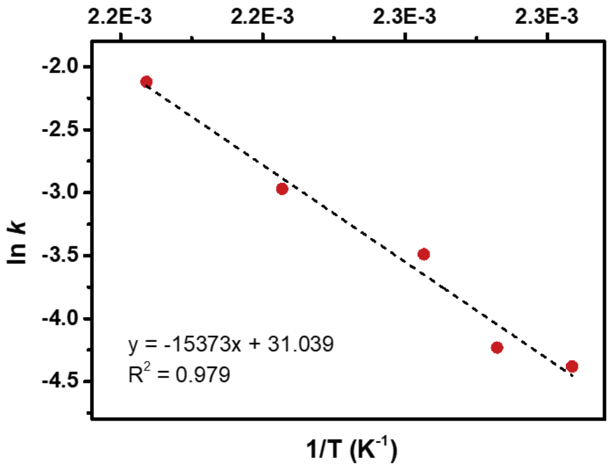


Figure S15. Arrhenius plot of the solid-state cycloreversion of **2** monitored at 160, 165, 170 ,180 and 190°C. The activation energy (E_a) is 127.8 kJ mol^{-1} (30.6 kcal mol^{-1}).

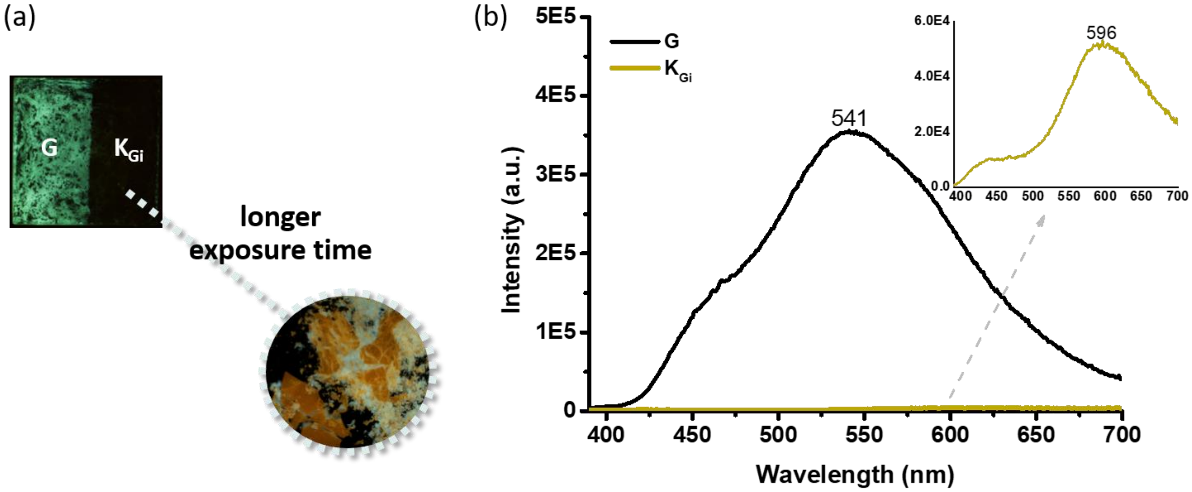
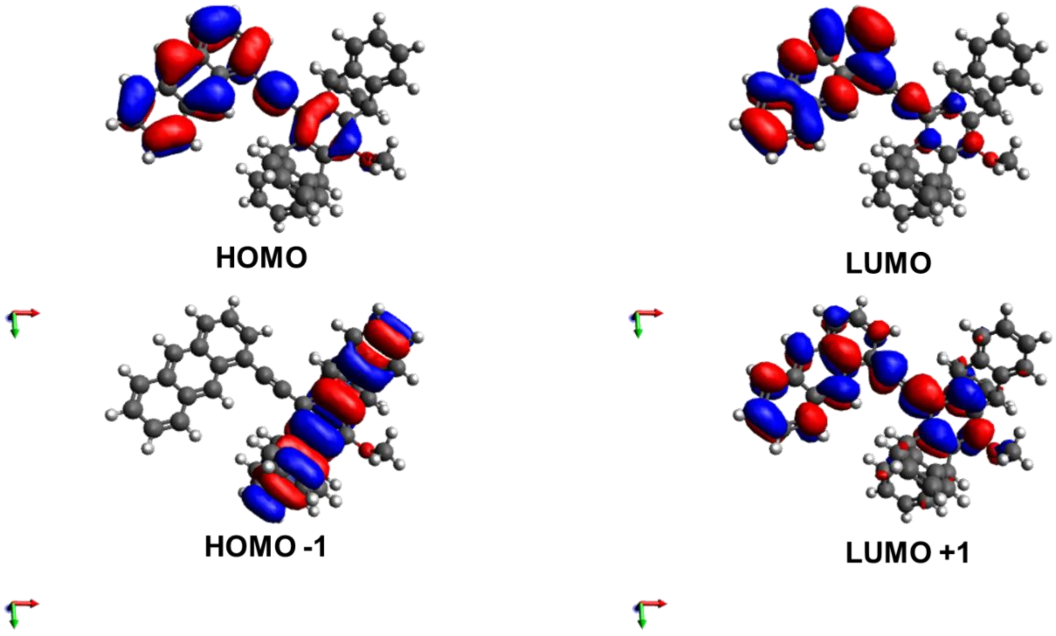


Figure S16. The (a) photographs and (b) fluorescence spectra (λ_{ex} = 380 nm) of the powdered G form before and after photoirradiation (λ_{ex} = 340-390 nm).



Transition	Wavelength	Oscillator Strength	CI%
S_1 (HOMO → LUMO)	435.63 nm	0.3247	98.69
S_2 (HOMO-1 → LUMO)	379.96 nm	0.0201	98.61
S_3 (HOMO-1 → LUMO) (HOMO → LUMO+1)	357.82 nm	0.0212	87.57 10.26

Figure S17. DFT (B3LYP/6-31+G(d, p))-optimized and TDDFT (B3LYP/6-31+G(d,p))-derived frontier orbitals and the energy, oscillator strength, and configuration interactions for the lowest electronic excited states of **1**. Note that the octyl group is replaced with a methyl group to accelerate the calculations.

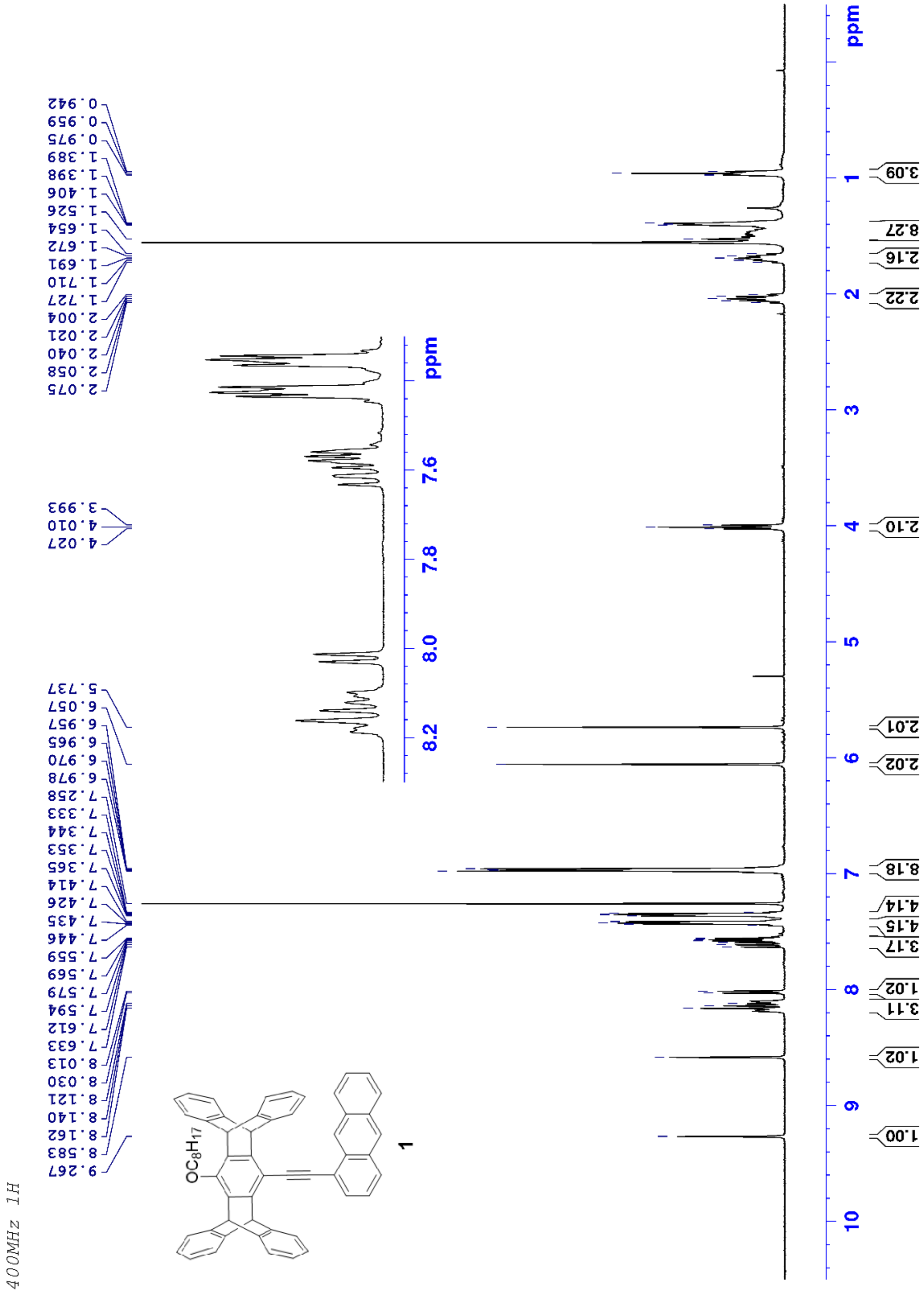


Figure S18. ^{1}H-NMR spectrum of compound **1** (400 MHz, $CDCl_3$).

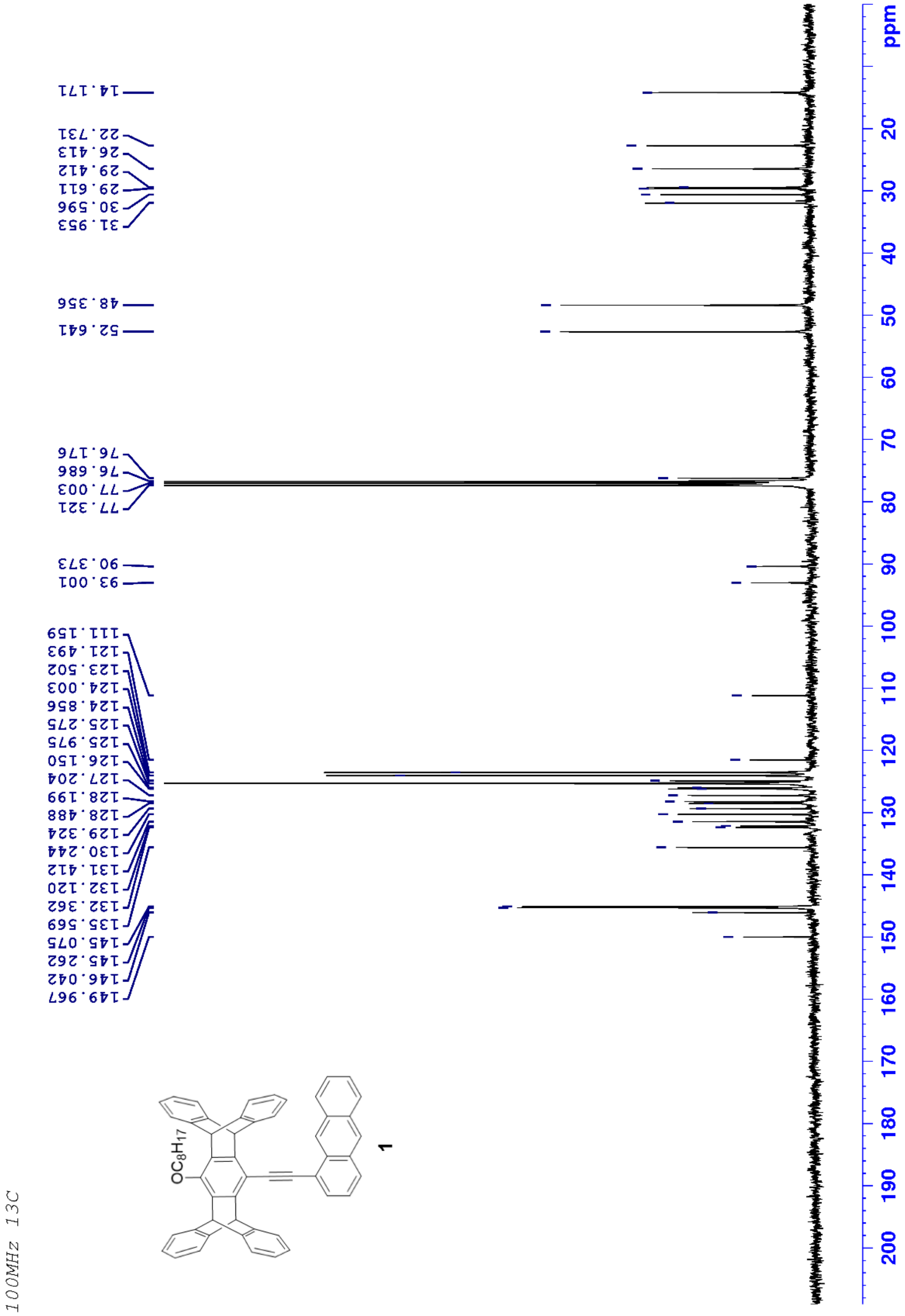


Figure S19. ^{13}C-NMR spectrum of compound **1** (100 MHz, $CDCl_3$).

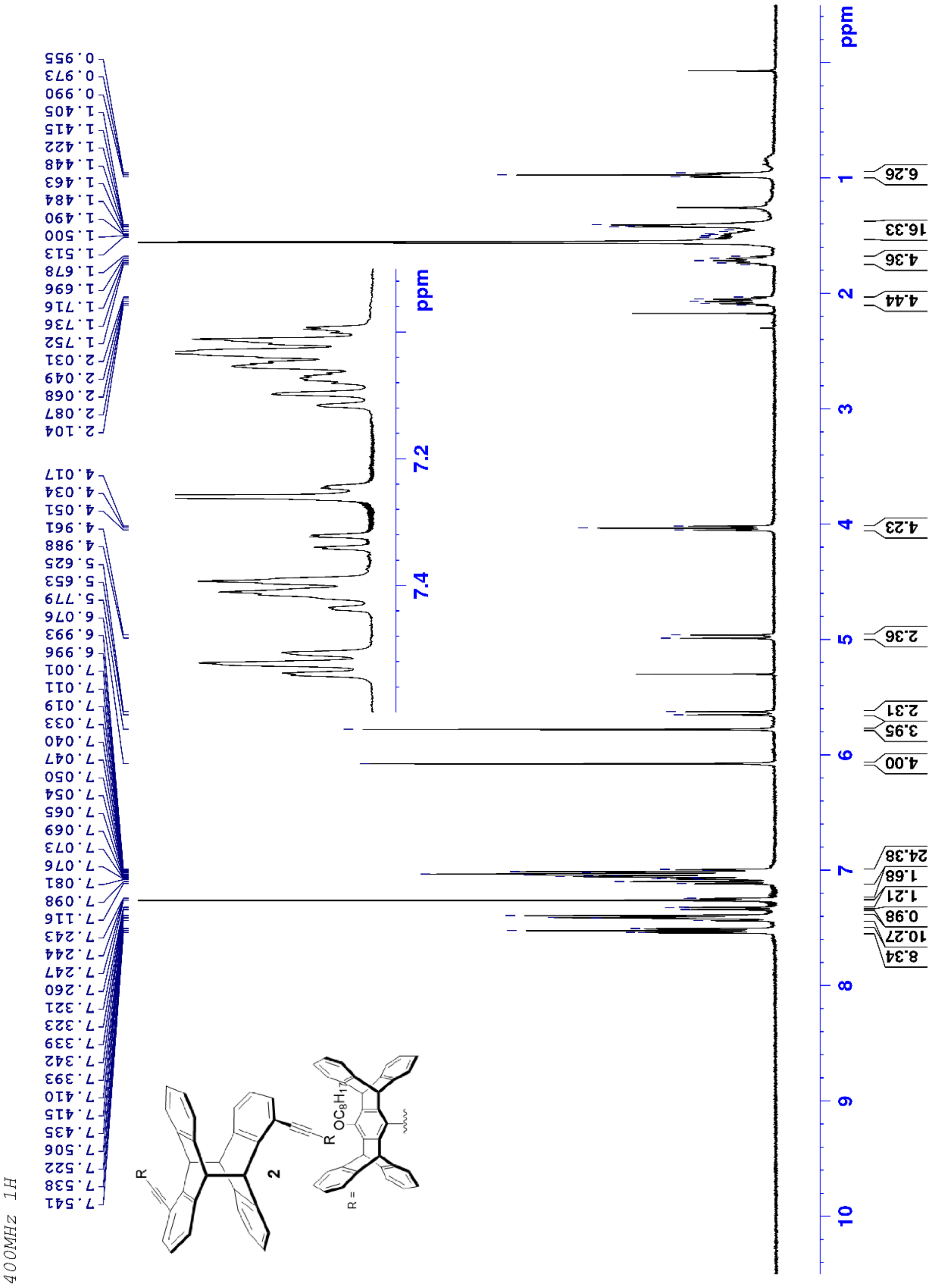


Figure S20. ^{1}H-NMR spectrum of compound **2** (400 MHz, $CDCl_3$).

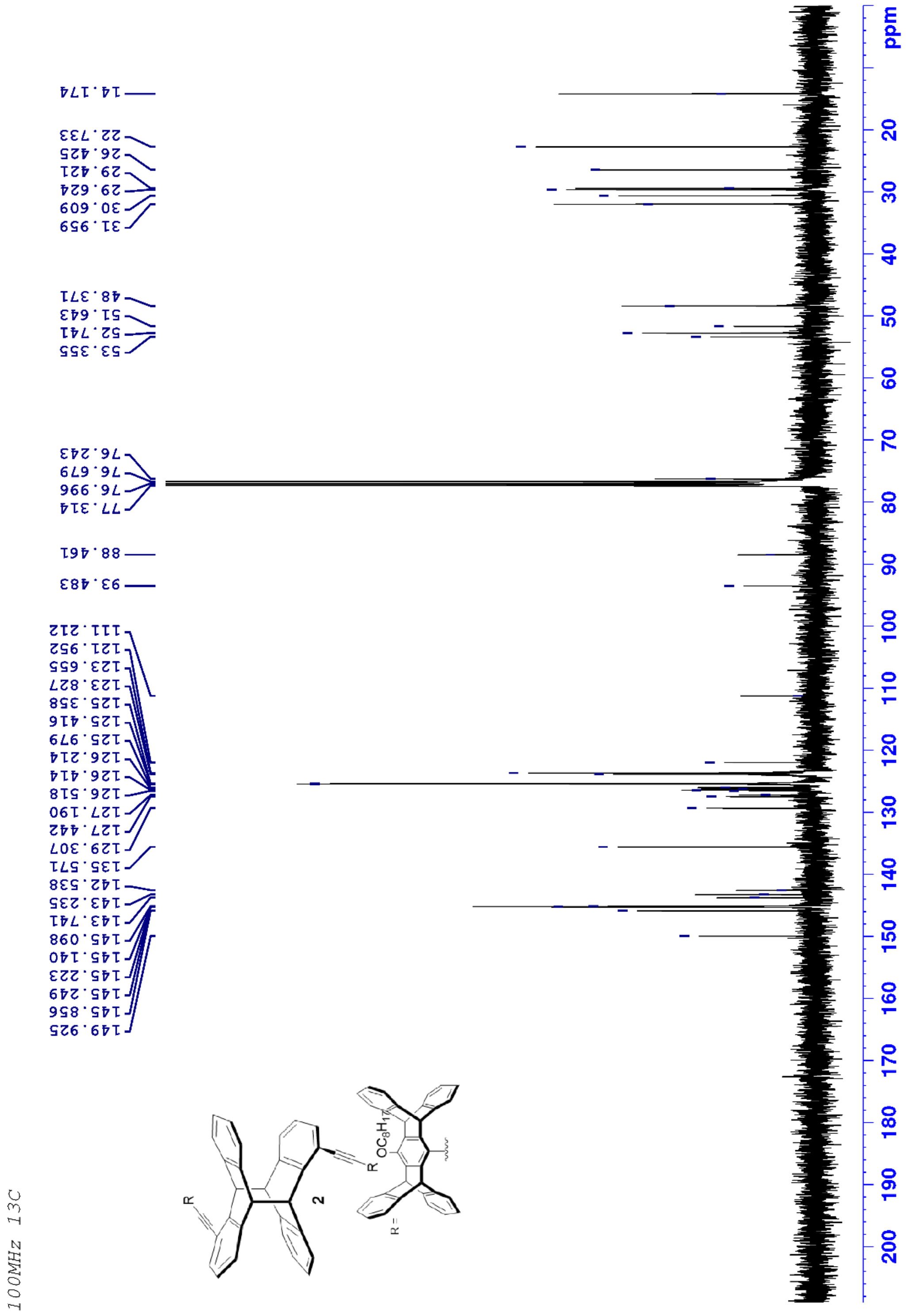


Figure S21. ^{13}C-NMR spectrum of compound **2** (100 MHz, $CDCl_3$).

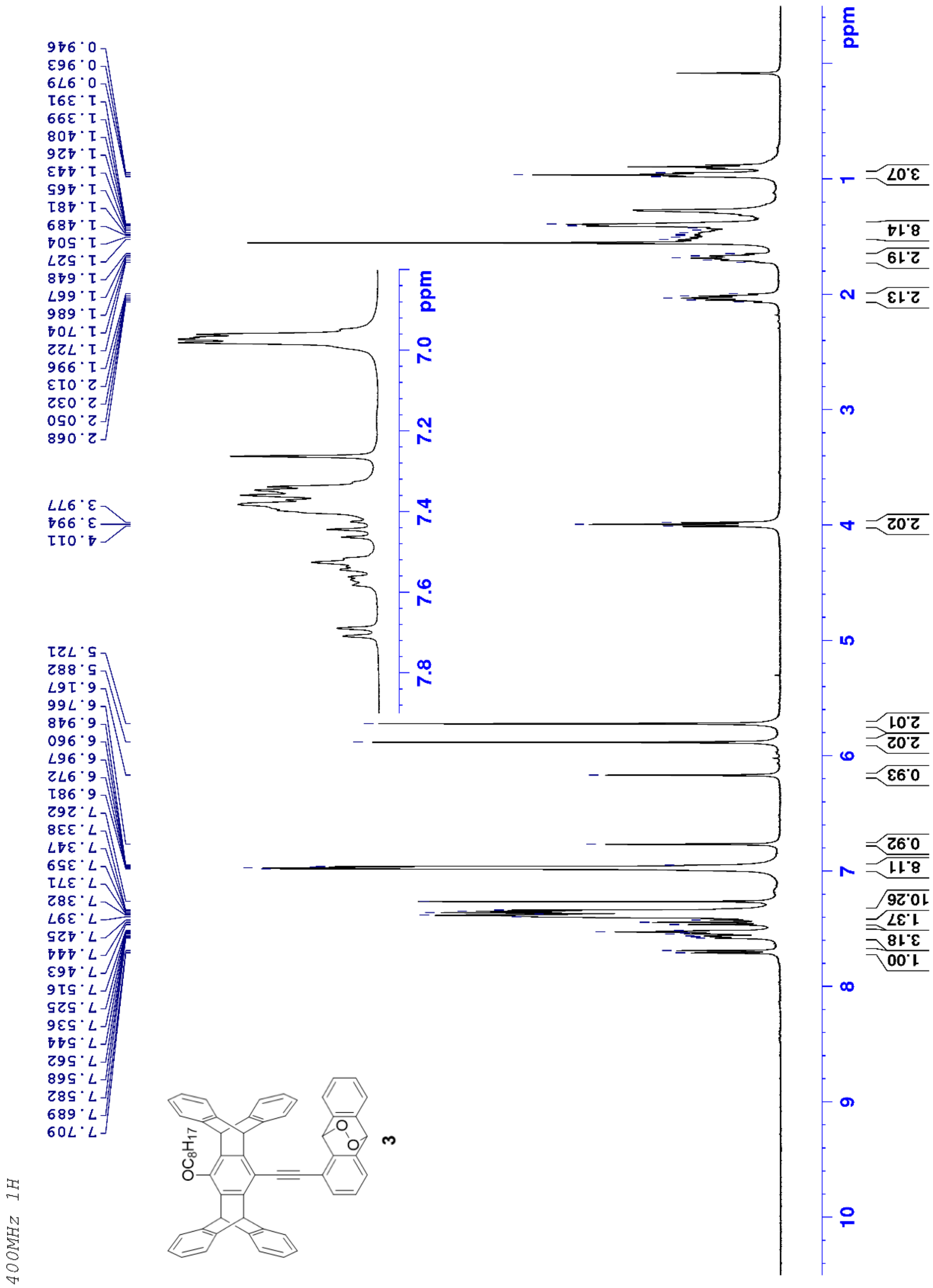


Figure S22. ^{1}H-NMR spectrum of compound **3** (400 MHz, $CDCl_3$).

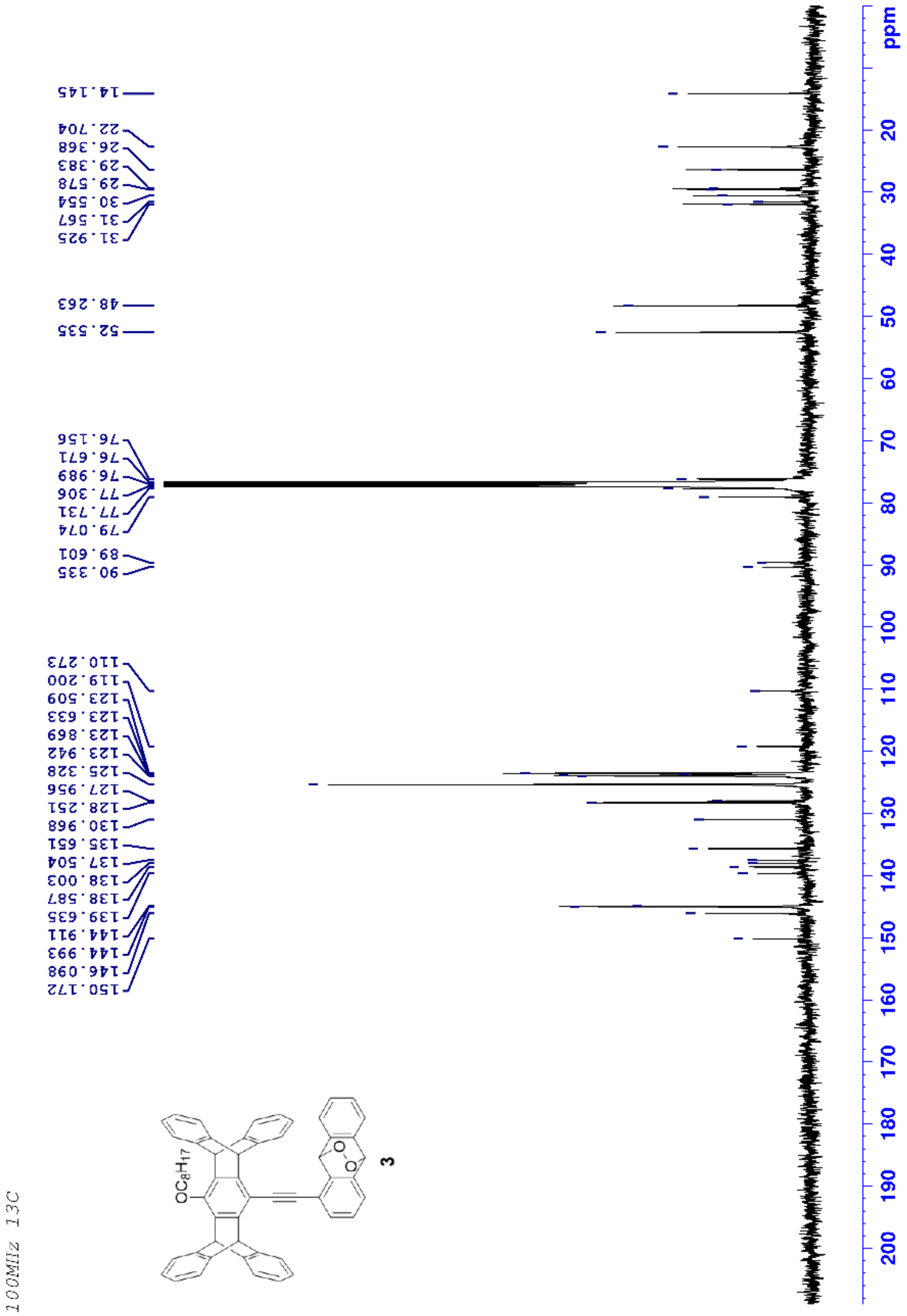


Figure S23. ^{13}C-NMR spectrum of compound **3** (100 MHz, $CDCl_3$).

Coordinates for DFT-optimized 1.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.59241	1.22510	0.04115
2	6	0	1.71546	2.05984	0.04997
3	6	0	3.00520	1.51935	0.02899
4	6	0	3.15457	0.12887	0.02942
5	6	0	2.03295	-0.70733	0.02087
6	6	0	0.72320	-0.17951	0.01891
7	6	0	3.06104	-3.29306	2.30268
8	6	0	3.28237	-2.39503	1.26433
9	6	0	4.40723	-1.55246	1.28027
10	6	0	5.31356	-1.60849	2.33343
11	6	0	5.09255	-2.51537	3.38119
12	6	0	3.97467	-3.35123	3.36610
13	6	0	4.45209	-1.56422	-1.16180
14	6	0	5.39793	-1.63715	-2.17886
15	6	0	5.21202	-2.55245	-3.22649
16	6	0	4.08945	-3.38162	-3.24602
17	6	0	3.13779	-3.30965	-2.21710
18	6	0	3.32351	-2.40281	-1.17951
19	6	0	-1.34708	3.79683	3.44289
20	6	0	-0.22493	4.62694	3.45806
21	6	0	0.69592	4.59291	2.39975
22	6	0	0.47720	3.72463	1.33603
23	6	0	-0.65341	2.88971	1.31997
24	6	0	-1.56601	2.92072	2.36889
25	6	0	-1.60214	3.05954	-2.15412

26	6	0	-1.40569	4.00492	-3.17251
27	6	0	-0.28933	4.84227	-3.15091
28	6	0	0.64892	4.74413	-2.11167
29	6	0	0.45519	3.80421	-1.10515
30	6	0	-0.67227	2.96421	-1.12440
31	6	0	-0.72212	2.00805	0.07006
32	6	0	1.36247	3.54868	0.10003
33	6	0	2.40516	-2.19153	0.02648
34	6	0	4.48034	-0.63702	0.05547
35	6	0	-0.41347	-1.04113	0.00192
36	6	0	-1.35987	-1.81017	-0.01629
37	6	0	-2.43057	-2.74951	-0.03803
38	6	0	-3.81234	-2.30816	-0.05255
39	6	0	-4.85738	-3.30682	-0.07444
40	6	0	-4.50248	-4.69131	-0.08163
41	6	0	-3.18541	-5.07710	-0.06777
42	6	0	-2.14991	-4.10769	-0.04584
43	6	0	-4.16973	-0.95593	-0.04616
44	6	0	-5.51052	-0.54260	-0.05965
45	6	0	-6.55518	-1.53933	-0.08141
46	6	0	-6.19729	-2.89375	-0.08829
47	6	0	-5.88194	0.83909	-0.05235
48	6	0	-7.20155	1.21457	-0.06584
49	6	0	-8.23365	0.22899	-0.08764
50	6	0	-7.91913	-1.10617	-0.09513
51	8	0	4.11403	2.34539	0.05856
52	6	0	4.60164	2.72783	-1.23390
53	1	0	2.18877	-3.94157	2.29291

54	1	0	6.18233	-0.95532	2.34703
55	1	0	5.79476	-2.56414	4.20845
56	1	0	3.80846	-4.04909	4.18169
57	1	0	6.27537	-0.99515	-2.16188
58	1	0	5.94632	-2.61475	-4.02450
59	1	0	3.95037	-4.08672	-4.06043
60	1	0	2.26394	-3.95594	-2.23283
61	1	0	-2.05443	3.82585	4.26666
62	1	0	-0.06080	5.30126	4.29361
63	1	0	1.57198	5.23627	2.41364
64	1	0	-2.43761	2.27134	2.36026
65	1	0	-2.47162	2.40756	-2.17331
66	1	0	-2.12730	4.08367	-3.98049
67	1	0	-0.14442	5.57338	-3.94106
68	1	0	1.51628	5.39963	-2.09363