Electronic Supplementary Information

Fluorinated Tolane Dyads with Alkylene Linkage: Synthesis and Evaluation of Photophysical Characteristics

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Table of contents

1. Synthetic procedure

1-1. Preparation of 1-bromo-4-(methoxymethoxy)benzene

In a two-necked round-bottomed flask, equipped with a Teflon®-coated stirrer bar, was placed 4-bromophenol (3.7 g, 21 mmol) and ethyldiisopropylamine (5.3 g, 41 mmol) in CH_2Cl_2 (25 mL). The solution was cooled to 0 °C and added dropwise chloromethyl methyl ether (MOMCl, 1.9 g, 24 mmol), and the whole was stirred at room temperature for 20 h. After 20 h, organic layer was washed with an aqueous NaOH solution (1.5 mol L^{-1}, 30 mL, two times), extracted with EtOAc (30 mL, three times). Organic layer collected was dried over anhydrous Na_2SO_4, which was separated by filtration. The filtrate was evaporated in vacuo and subjected to silica-gel column chromatography to obtain the desired title compound (3.60 g, 16.6 mmol, 78%) as a colorless oil.

1-Bromo-4-(methoxymethoxy)benzene

Yield: 78% (Colorless oil), ^{1}H NMR ($CDCl_3$): δ 3.46 (s, 3H), 5.14 (s, 2H), 6.93 (d, J = 9.0 Hz, 2H), 7.38 (d, J = 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 55.9, 94.4, 114.1, 118.0, 132.3, 156.4. The spectral data were fully in accordance with the reported data.[1]

1-2. Preparation of 1-(methoxymethoxy)-4-[2-(trimethylsilyl)ethyn-1-yl]benzene

In a two-necked round-bottomed flask, equipped with a Teflon®-coated stirrer bar, reflux condenser, was placed 1-bromo-4-(methoxymethoxy)benzene (3.60 g, 16.6 mmol), trimethylsilylacetylene (2.4 g, 25 mmol), $Cl_2Pd(PPh_3)_2$ (0.61 g, 0.87 mmol), PPh_3 (0.24 g, 0.91 mmol), CuI (0.33 g, 1.7 mmol) in Et_3N (90 mL), and the suspended solution was stirred at reflux for 21 h. After being stirred for 21 h, precipitate formed during reaction was separated by atmospheric filtration, and the filtrate was poured into saturated aqueous NH_4Cl solution. Crude product was extracted with EtOAc (three times) and the organic layer combined was washed with brine (once). Organic layer collected was dried over anhydrous Na_2SO_4, which was separated by filtration. The filtrate was evaporated in vacuo and subjected to silica-gel column chromatography to obtain the desired title compound (1.96 g, 8.4 mmol, 50%) as a yellow oil.

1-(Methoxymethoxy)-4-[2-(trimethylsilyl)ethyn-1-yl]benzene

Yield: 50% (Yellow oil); ^{1}H NMR ($CDCl_3$): δ 0.24 (s, 9H), 3.46 (s, 3H), 5.17 (s, 2H), 6.95 (d, J = 8.8 Hz, 2H), 7.40 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 0.02, 55.8, 94.1, 94.3, 105.2, 115.2, 116.4, 133.4, 157.4. The spectral data were fully in accordance with the reported data.[2]

1.3. Preparation of 4-(methoxymethoxy)phenylacetylene (3)

In a round-bottomed flask, equipped with a Teflon®-coated stirrer bar, was placed 1-(methoxymethoxy)-4-[2-(trimethylsilyl)ethyn-1-yl]benzene (1.96 g, 8.4 mmol) and potassium carbonate (1.81 g, 13 mmol) in MeOH (40 mL). The whole was stirred at room temperature for 3 h. After stirring for 3 h, organic layer was poured into saturated aqueous NH_4Cl solution. Crude product extracted with EtOAc (three times) and organic layer combined was washed with brine (once). Organic layer collected was dried over anhydrous Na_2SO_4, which was separated by filtration. The filtrate was evaporated in vacuo and subjected to silica-gel column chromatography to obtain the desired **3** (1.27 g, 7.8 mmol, 94%) as a yellow oil.

4-(Methoxymethoxy)phenylacetylene (3)

Yield: 94% (Yellow oil); ^{1}H NMR ($CDCl_3$): δ 3.02 (s, 1H), 3.47 (s, 3H), 5.18 (s, 2H), 6.98 (d, J = 8.8 Hz, 2H), 7.44 (d, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$): δ 56.2, 76.2, 83.6, 94.3, 115.5, 116.2, 133.7, 157.7. The spectral data were fully in accordance with the reported data.[3]

[1] An, P.; Shi, Z.–F.; Dou, W.; Cao, X.–P.; Zhang, H.–L. *Org. Lett.* **2010**, *12*, 4364–4367.
[2] Krause, M.; Ligneau, X.; Stark, H.; Garbarg, M.; Schwartz, J.–C.; Schunack, W. *J. Med. Chem.* **1998**, *41*, 4171–4176.
[3] Smeyanov, A.; Schmidt, A. *Synth. Commun.* **2013**, *43*, 2809–2816.

2. NMR Spectra

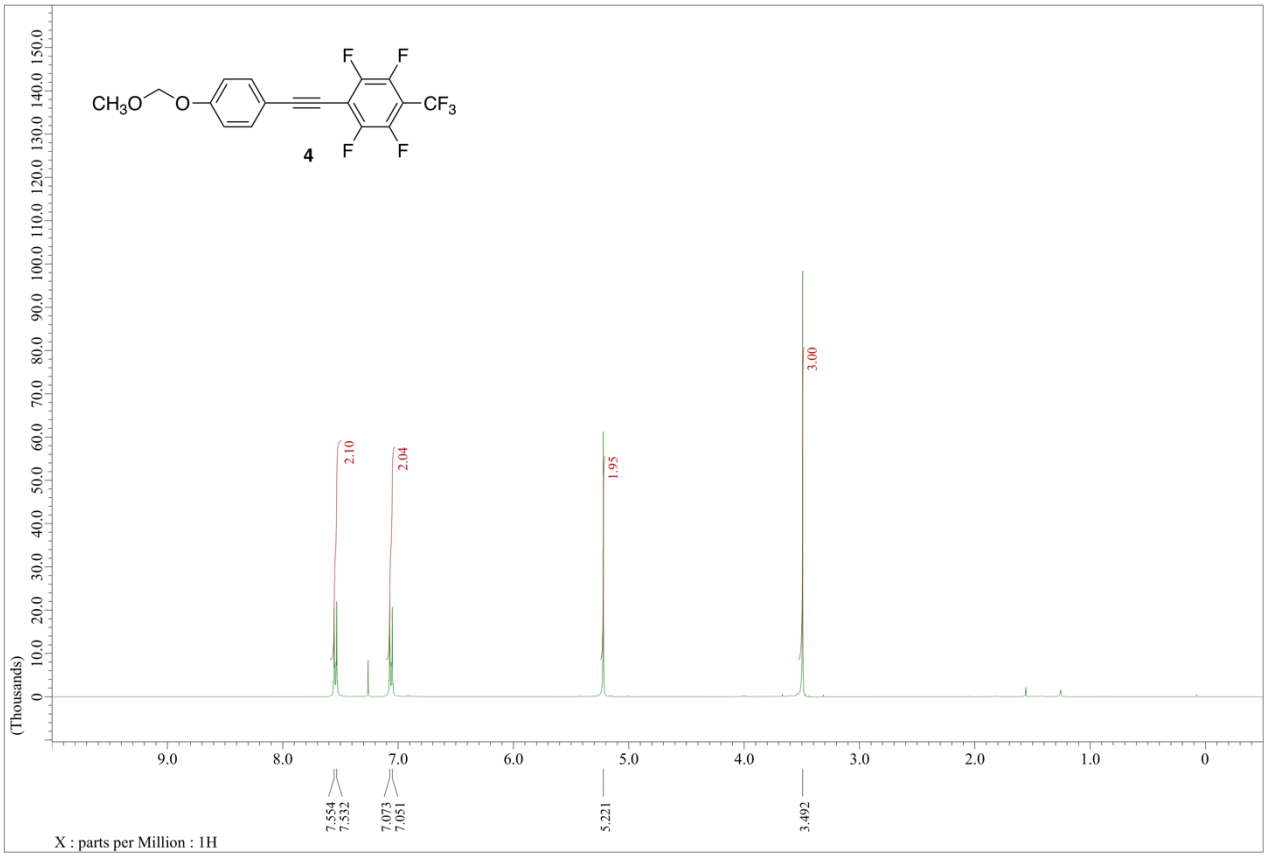


Figure S1. ^{1}H NMR spectrum of **4** (Solvent: $CDCl_3$)

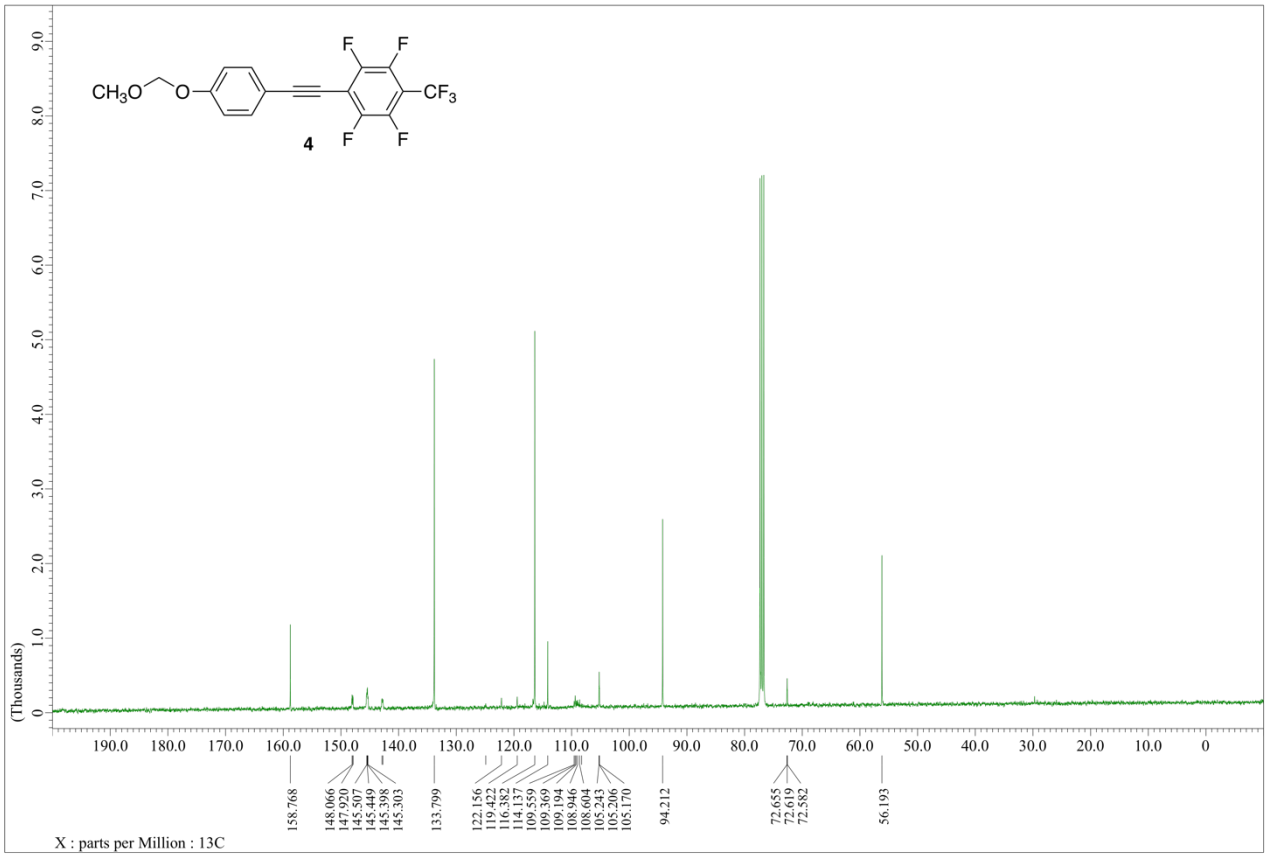


Figure S2. ^{13}C NMR spectrum of **4** (Solvent: $CDCl_3$)

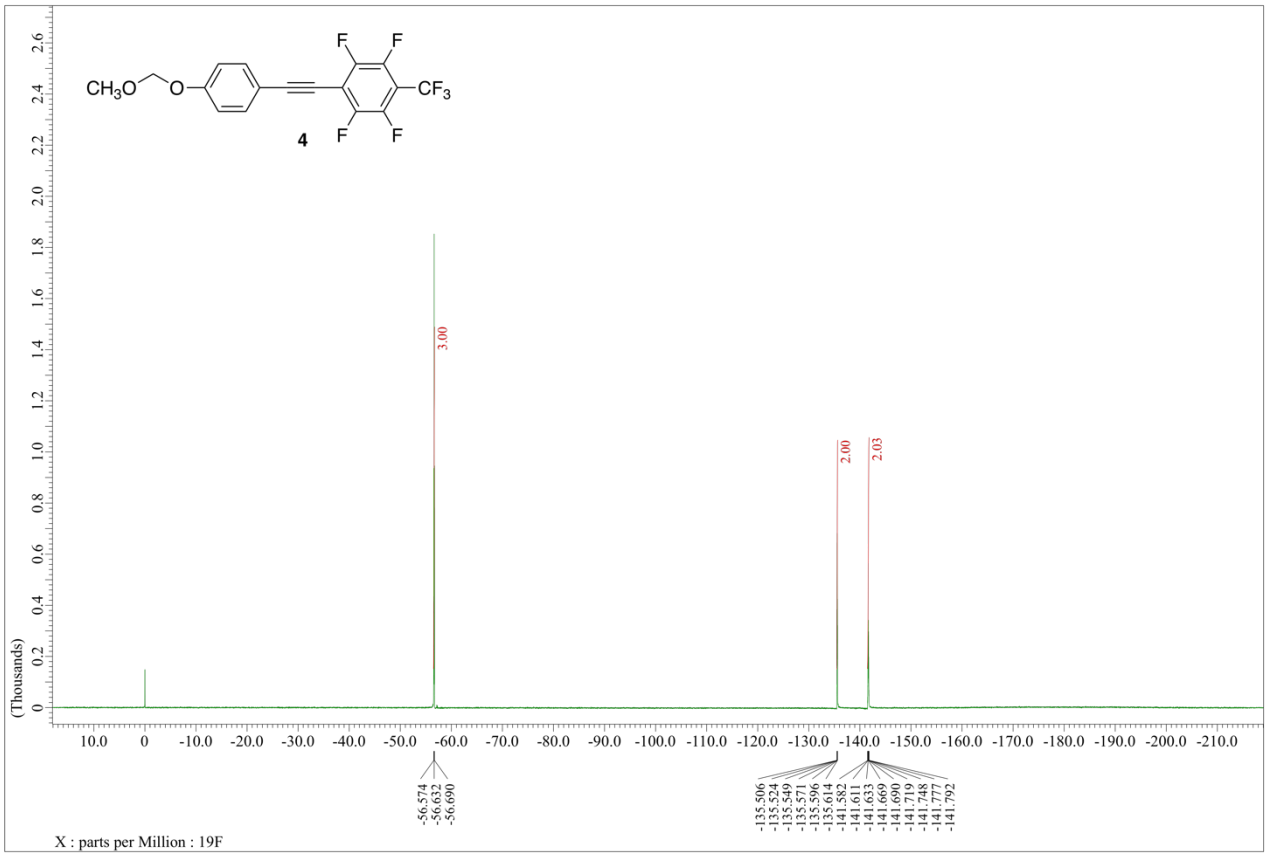


Figure S3. ^{19}F NMR spectrum of **4** (Solvent: $CDCl_3$)

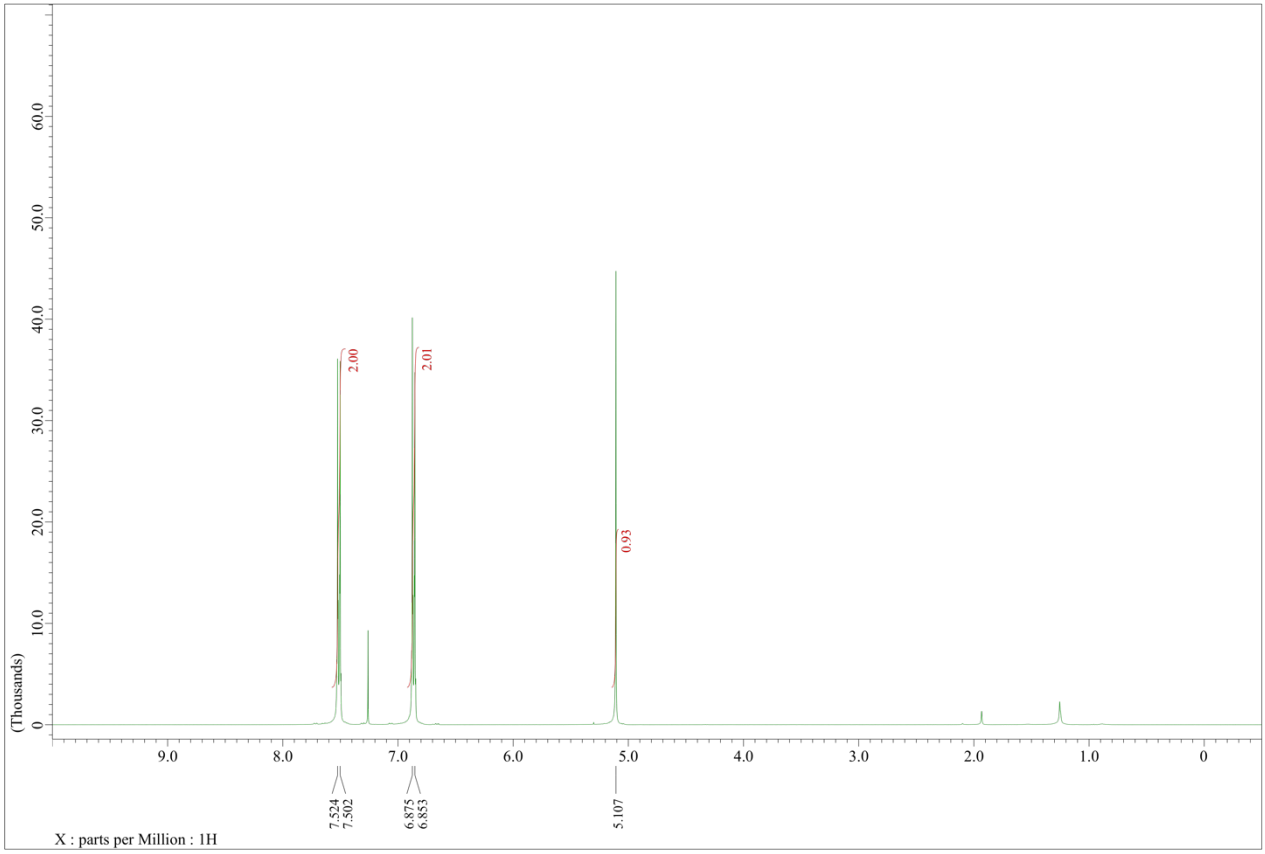


Figure S4. ^{1}H NMR spectrum of **5** (Solvent: $CDCl_3$)

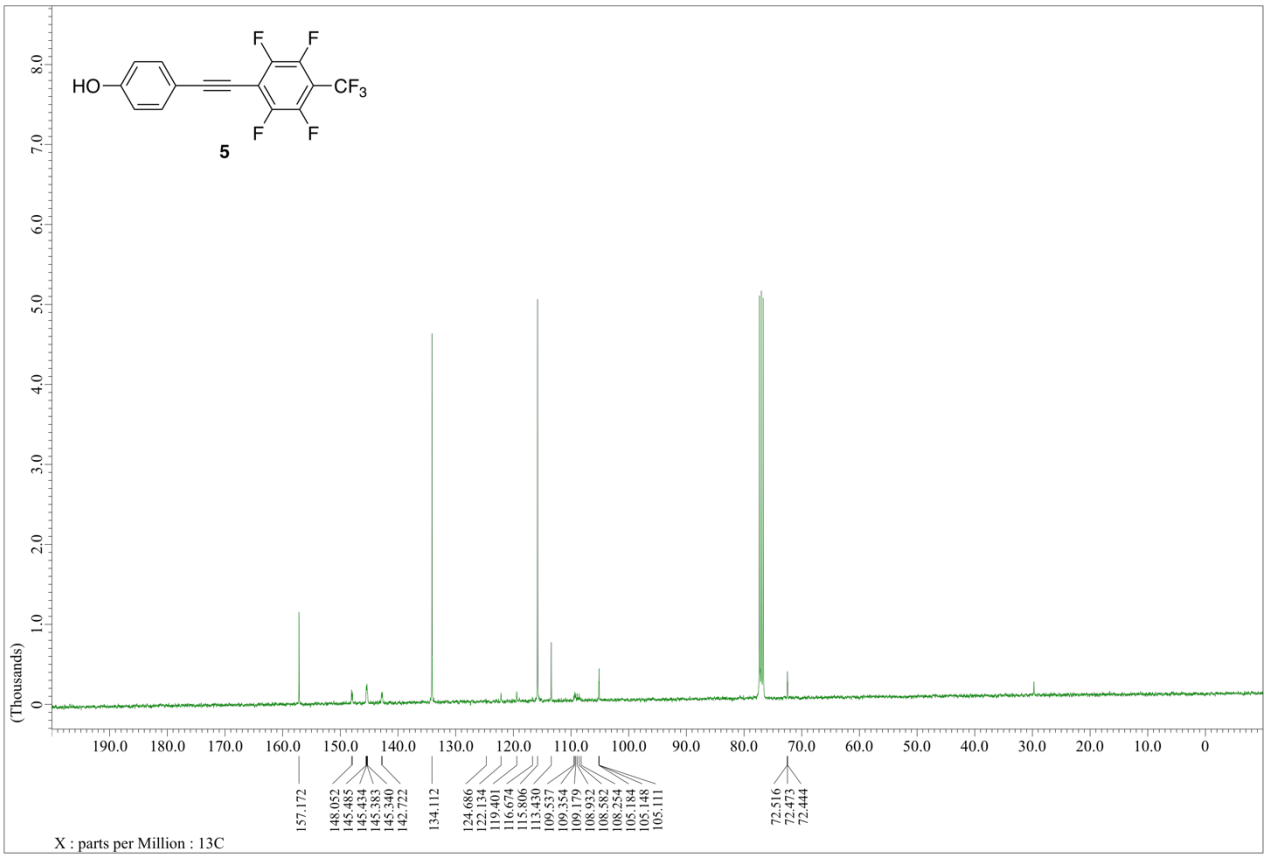


Figure S5. ^{13}C NMR spectrum of **5** (Solvent: $CDCl_3$)

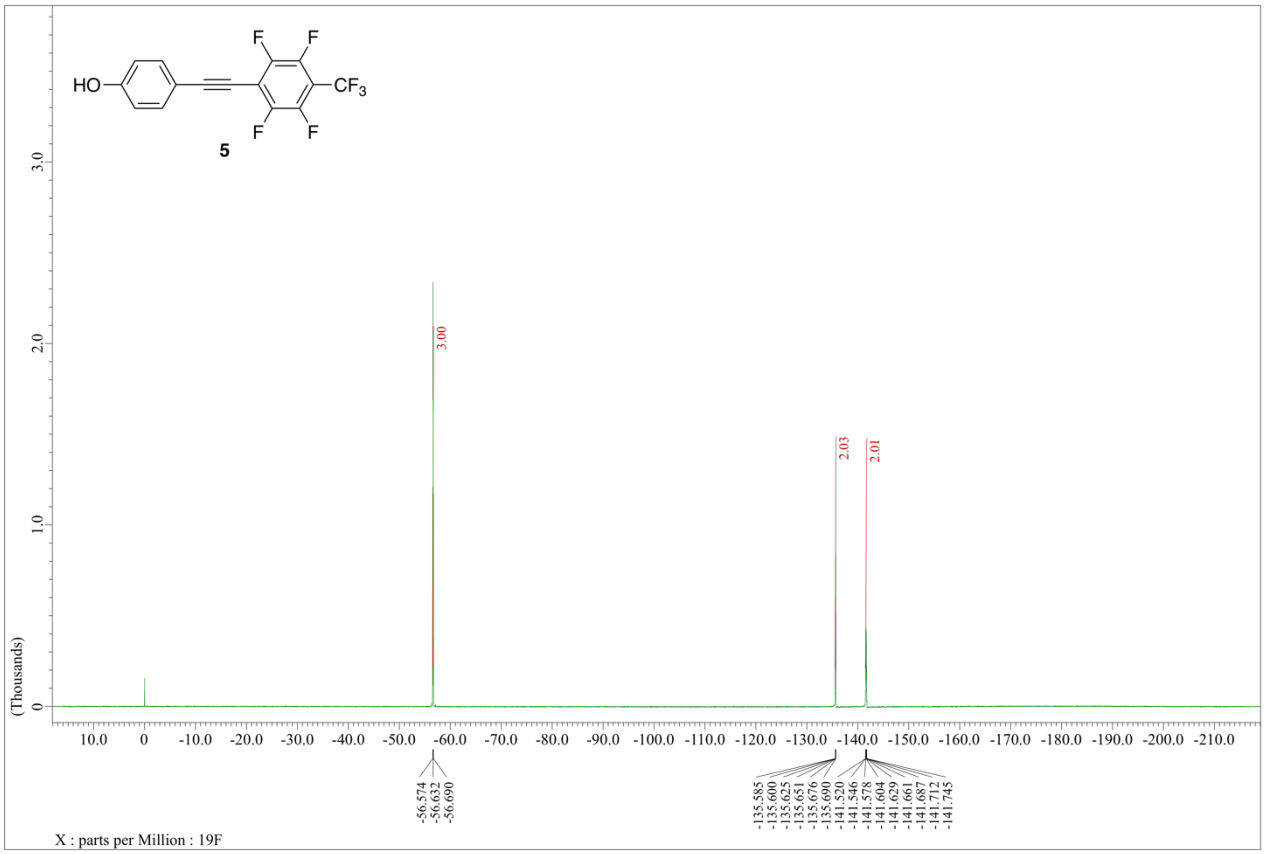


Figure S6. ^{19}F NMR spectrum of **5** (Solvent: $CDCl_3$)

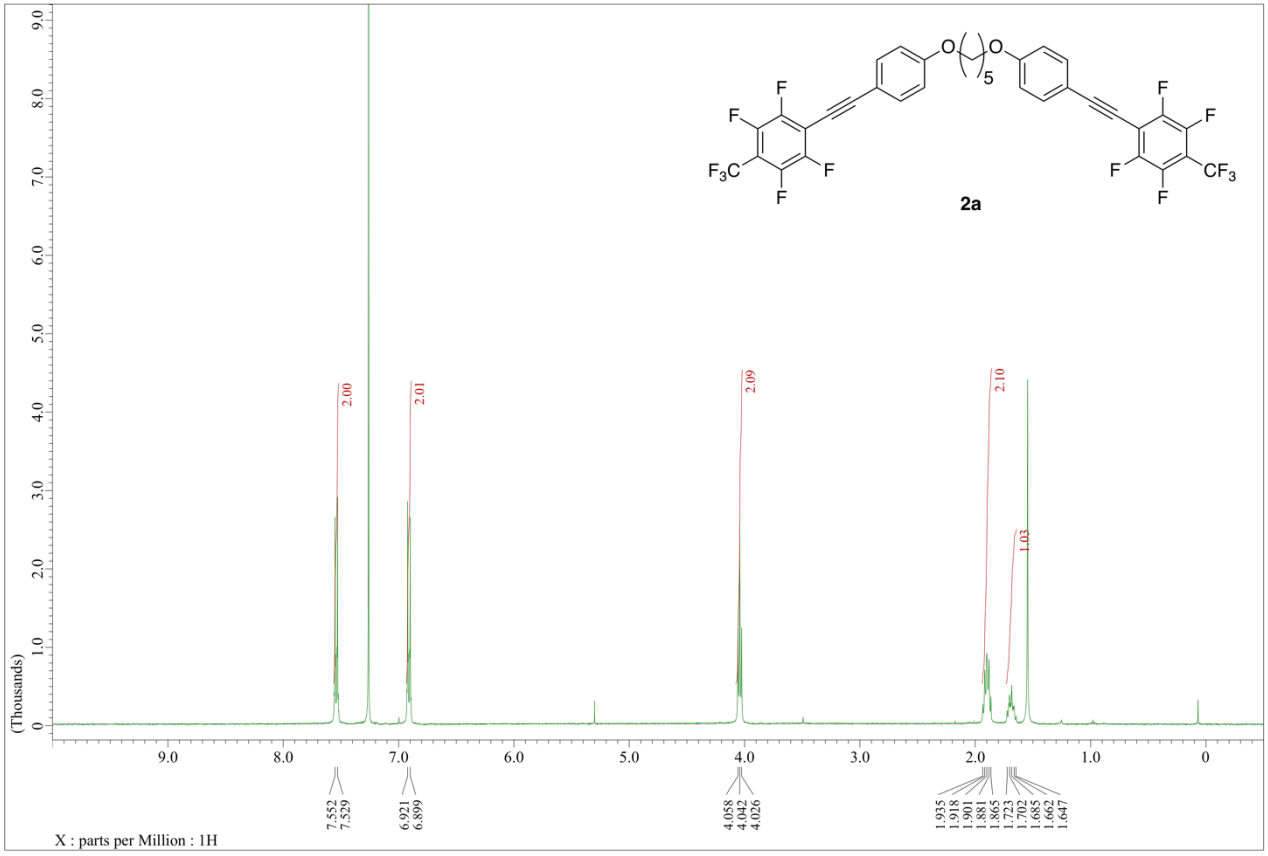


Figure S7. ^{1}H NMR spectrum of **2a** (Solvent: $CDCl_3$)

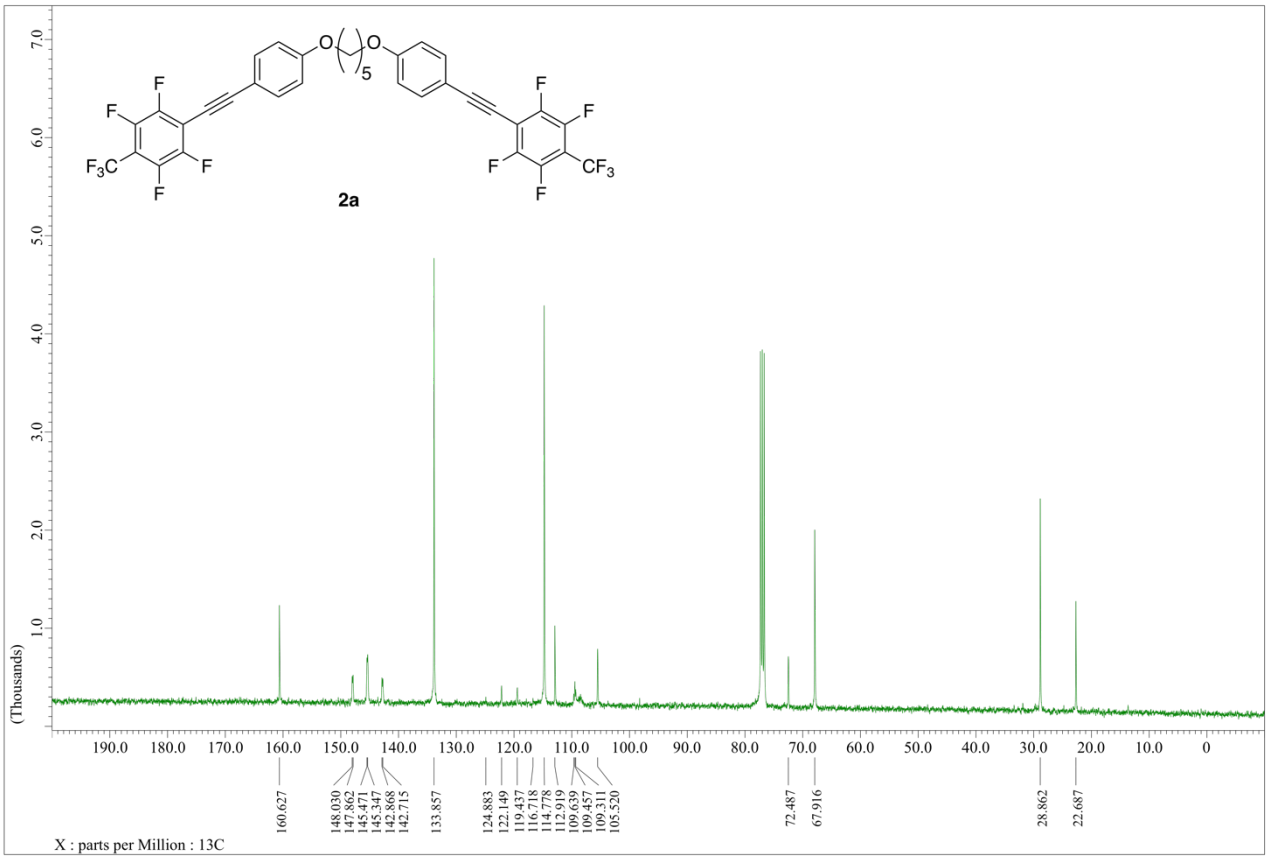


Figure S8. ^{13}C NMR spectrum of **2a** (Solvent: $CDCl_3$)

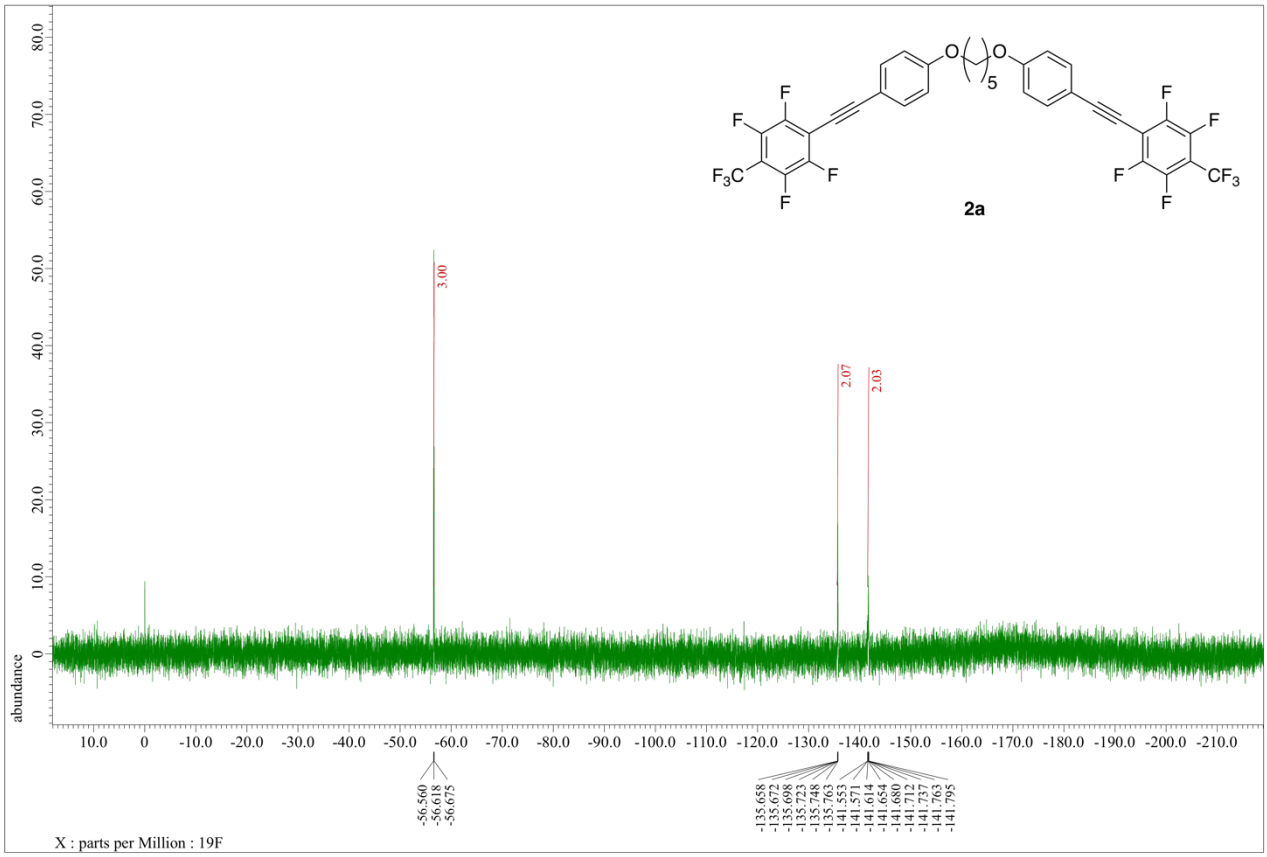


Figure S9. ^{19}F NMR spectrum of **2a** (Solvent: $CDCl_3$)

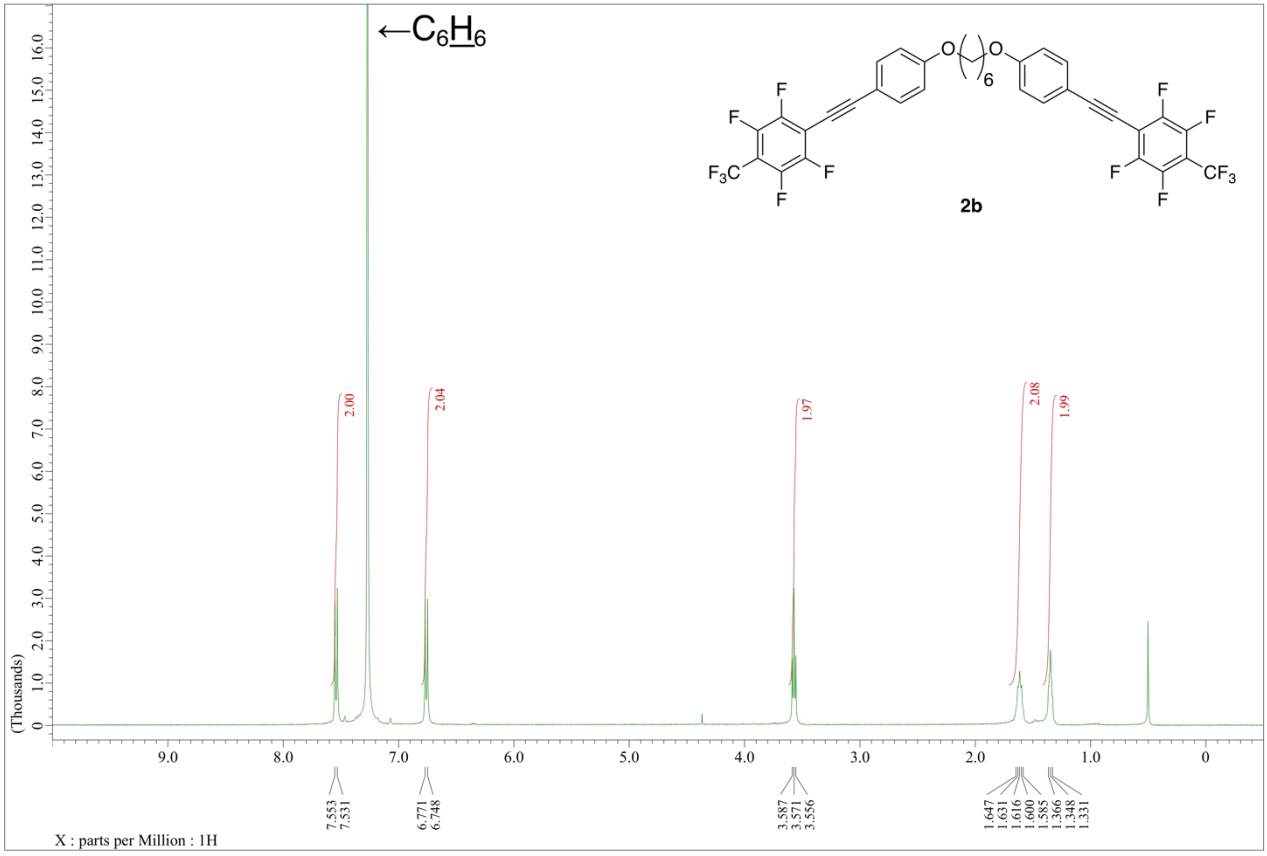


Figure S10. ^{1}H NMR spectrum of **2b** (Solvent: C_6D_6)

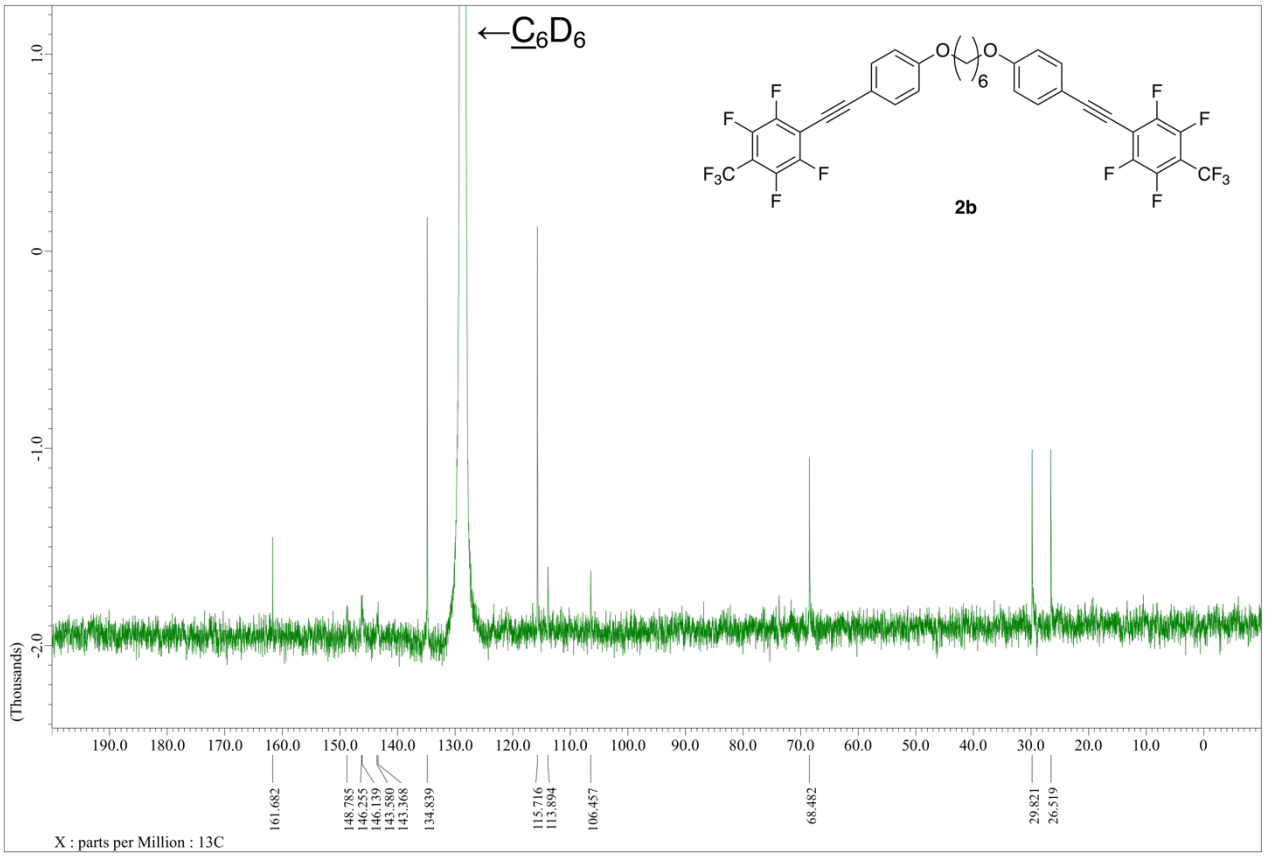


Figure S11. ^{13}C NMR spectrum of **2b** (Solvent: C_6D_6)

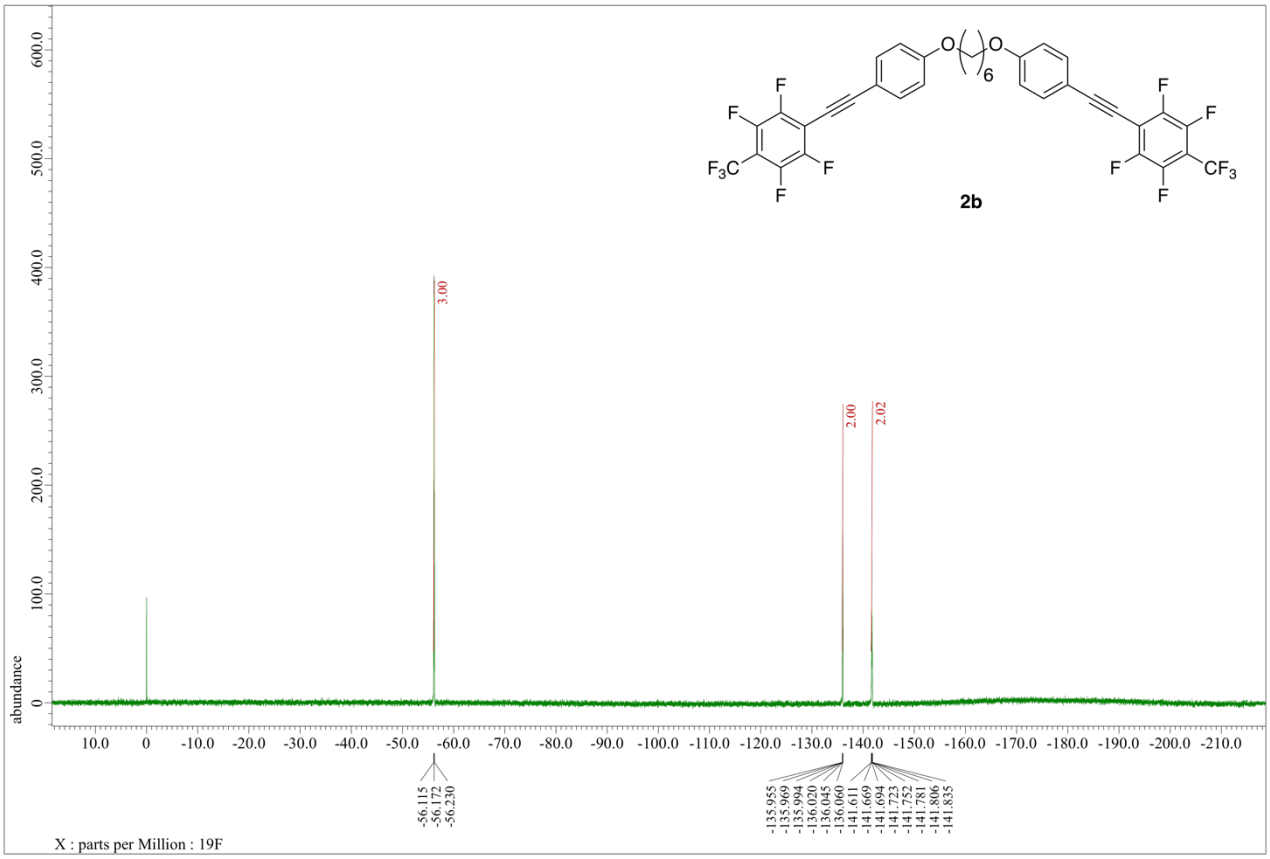


Figure S12. ^{19}F NMR spectrum of **2b** (Solvent: C_6D_6)

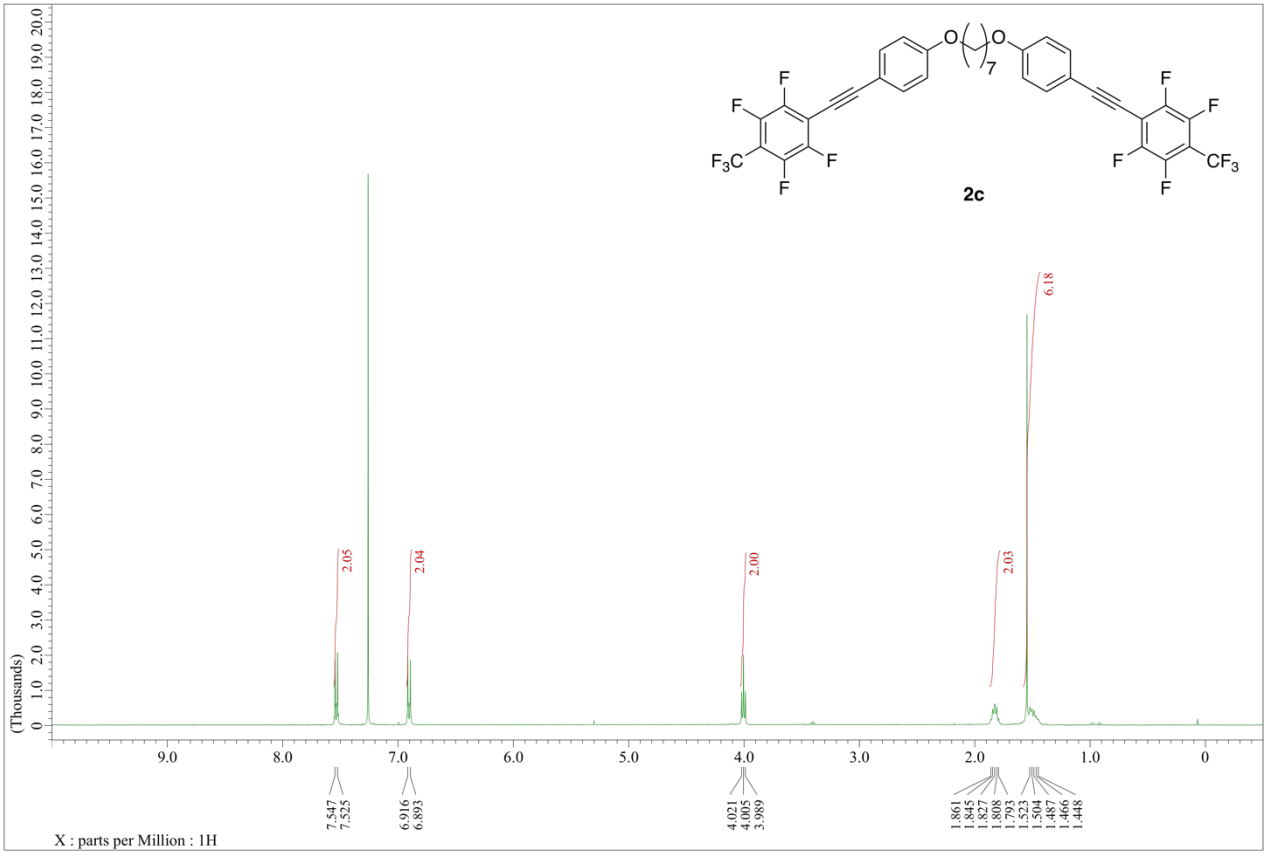


Figure S13. ^{1}H NMR spectrum of **2c** (Solvent: $CDCl_3$)

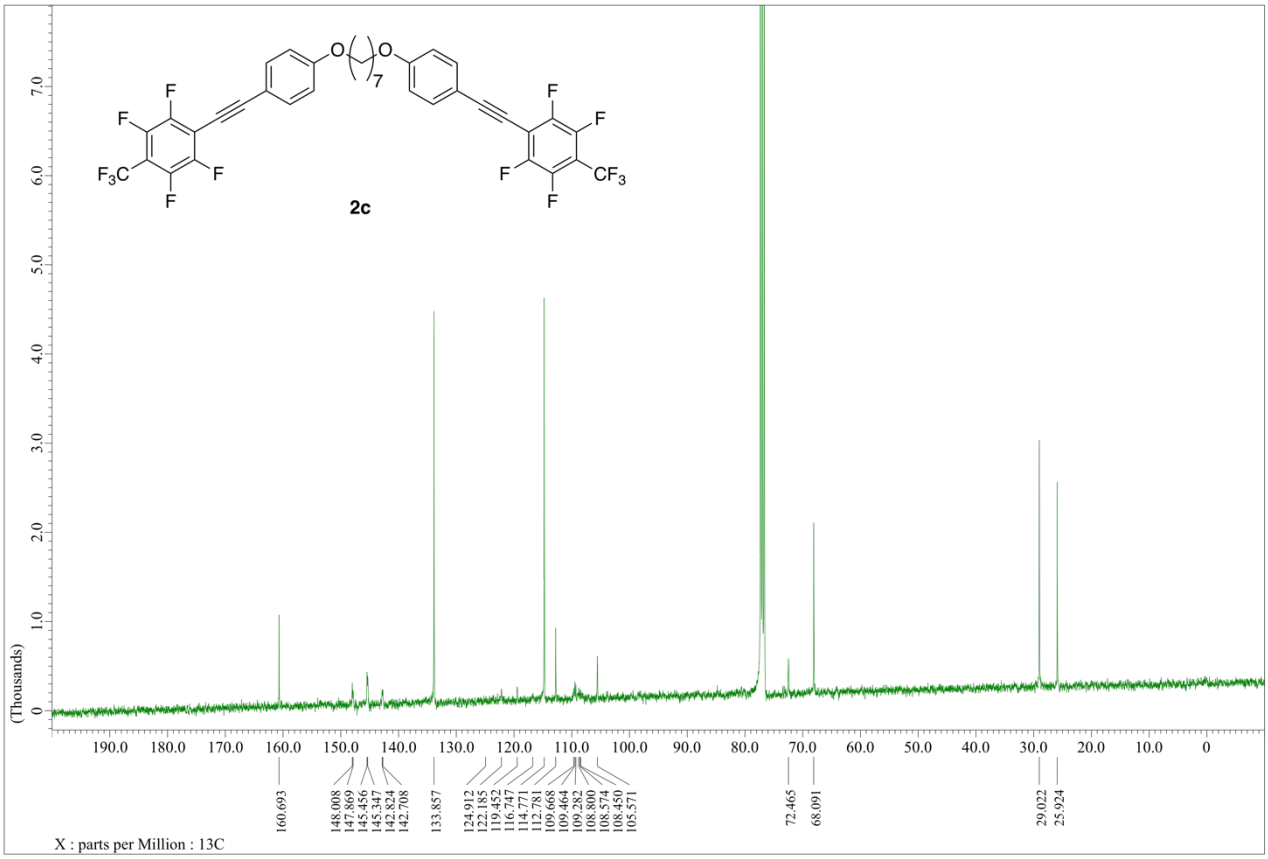


Figure S14. ^{13}C NMR spectrum of **2c** (Solvent: $CDCl_3$)

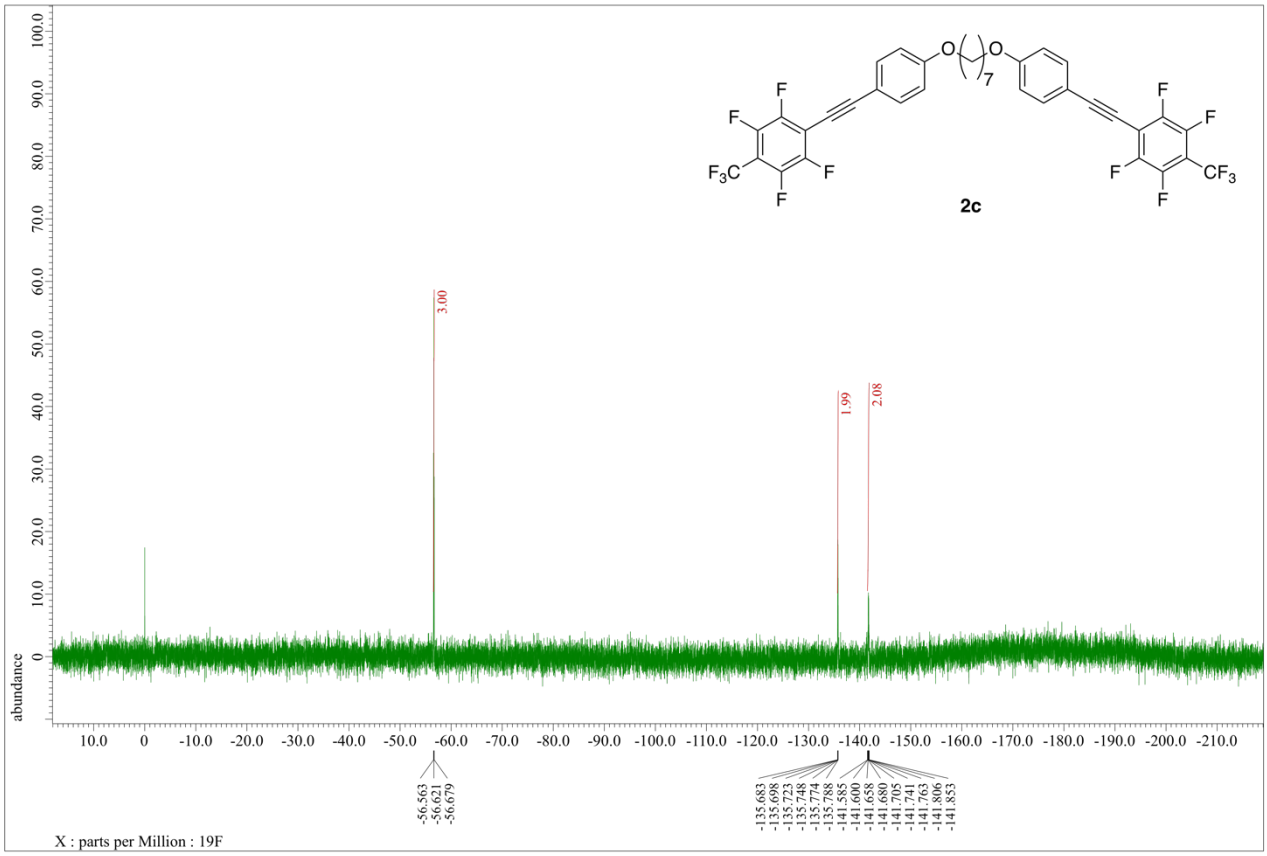


Figure S15. ^{19}F NMR spectrum of **2c** (Solvent: $CDCl_3$)

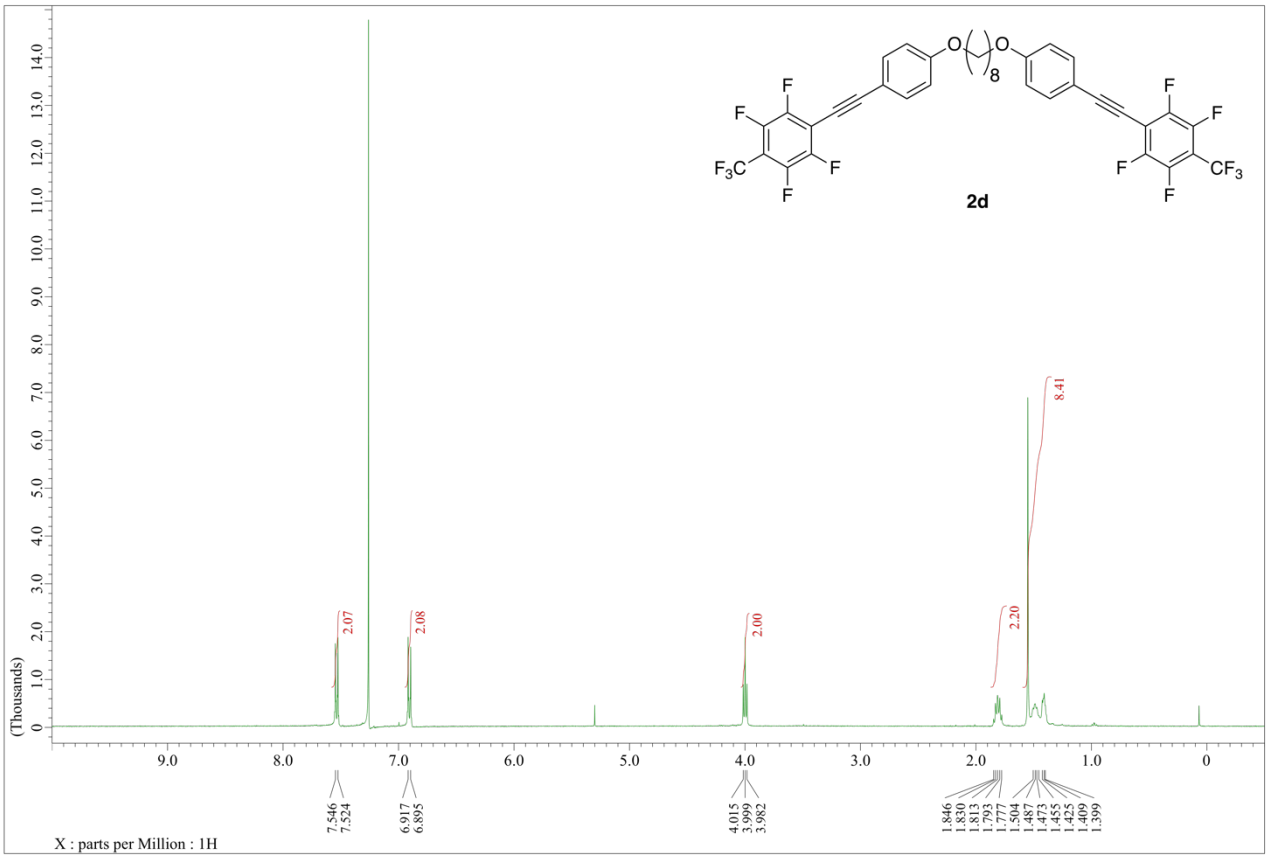


Figure S16. ^{1}H NMR spectrum of **2d** (Solvent: $CDCl_3$)

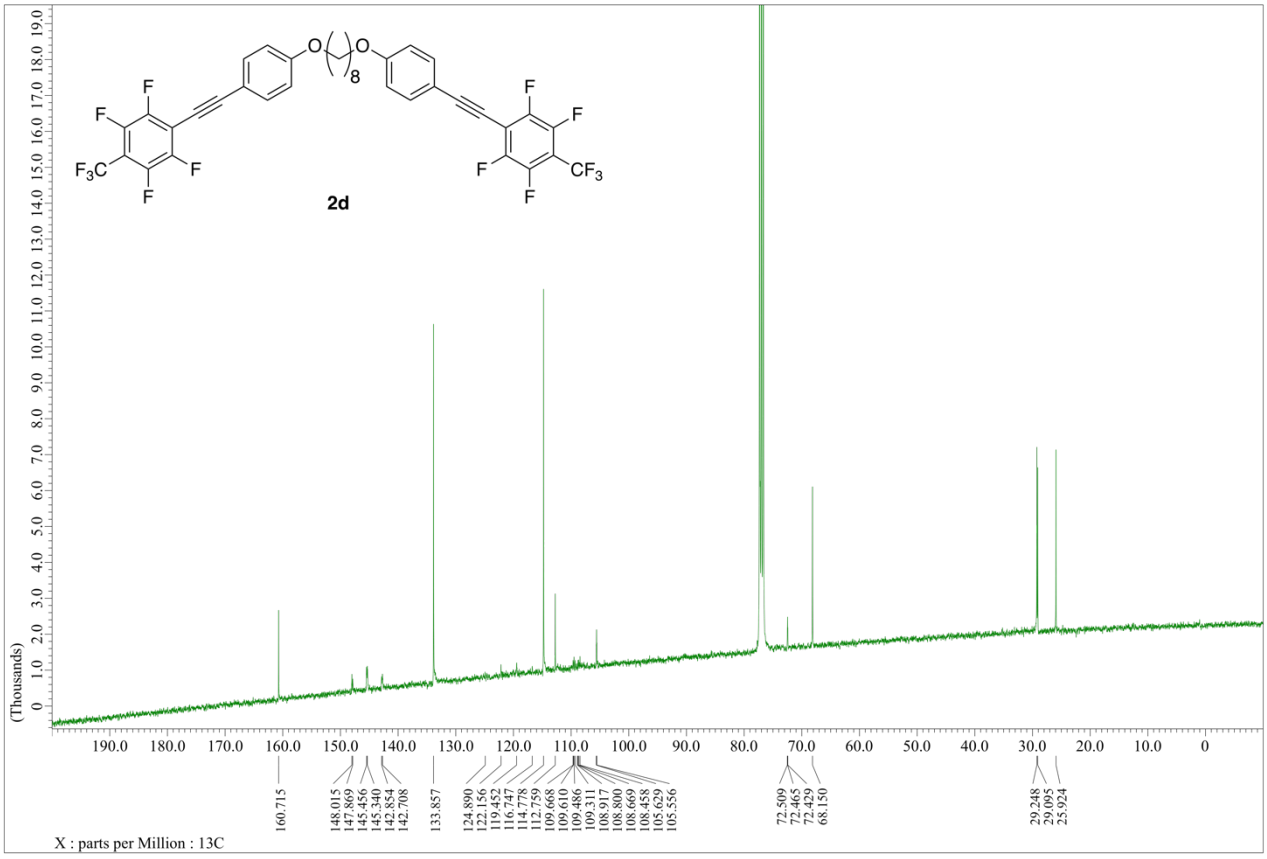


Figure S17. ^{13}C NMR spectrum of **2d** (Solvent: $CDCl_3$)

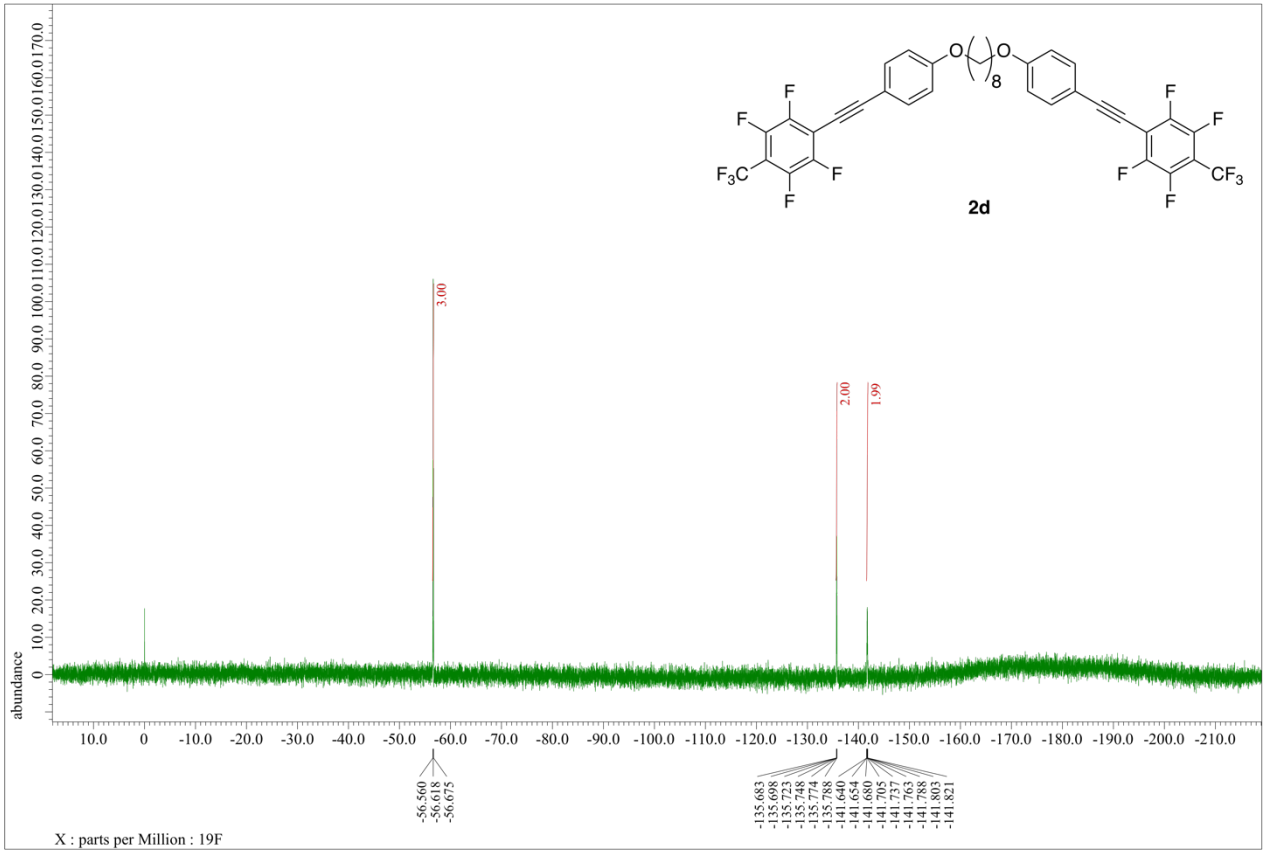


Figure S18. ^{19}F NMR spectrum of **2d** (Solvent: $CDCl_3$)

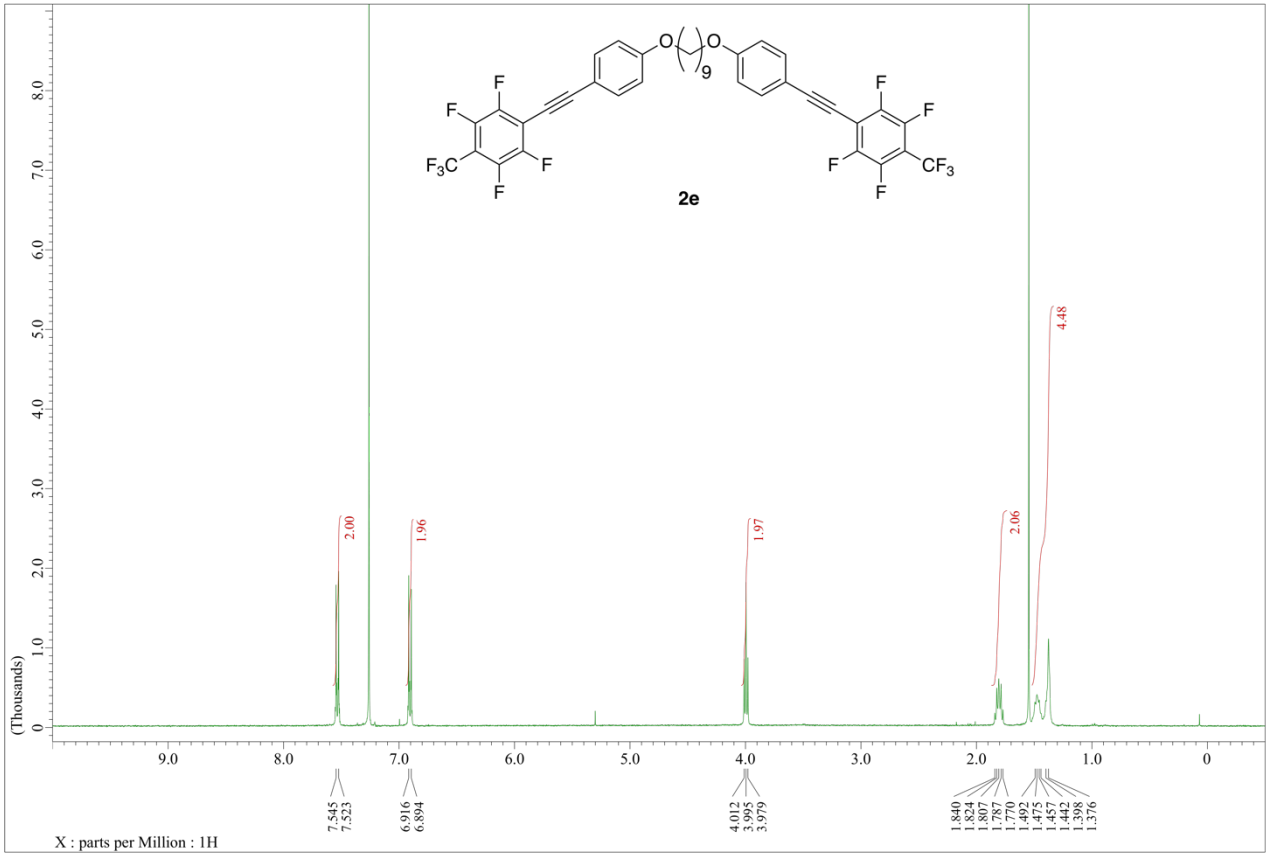


Figure S19. ^{1}H NMR spectrum of **2e** (Solvent: $CDCl_3$)

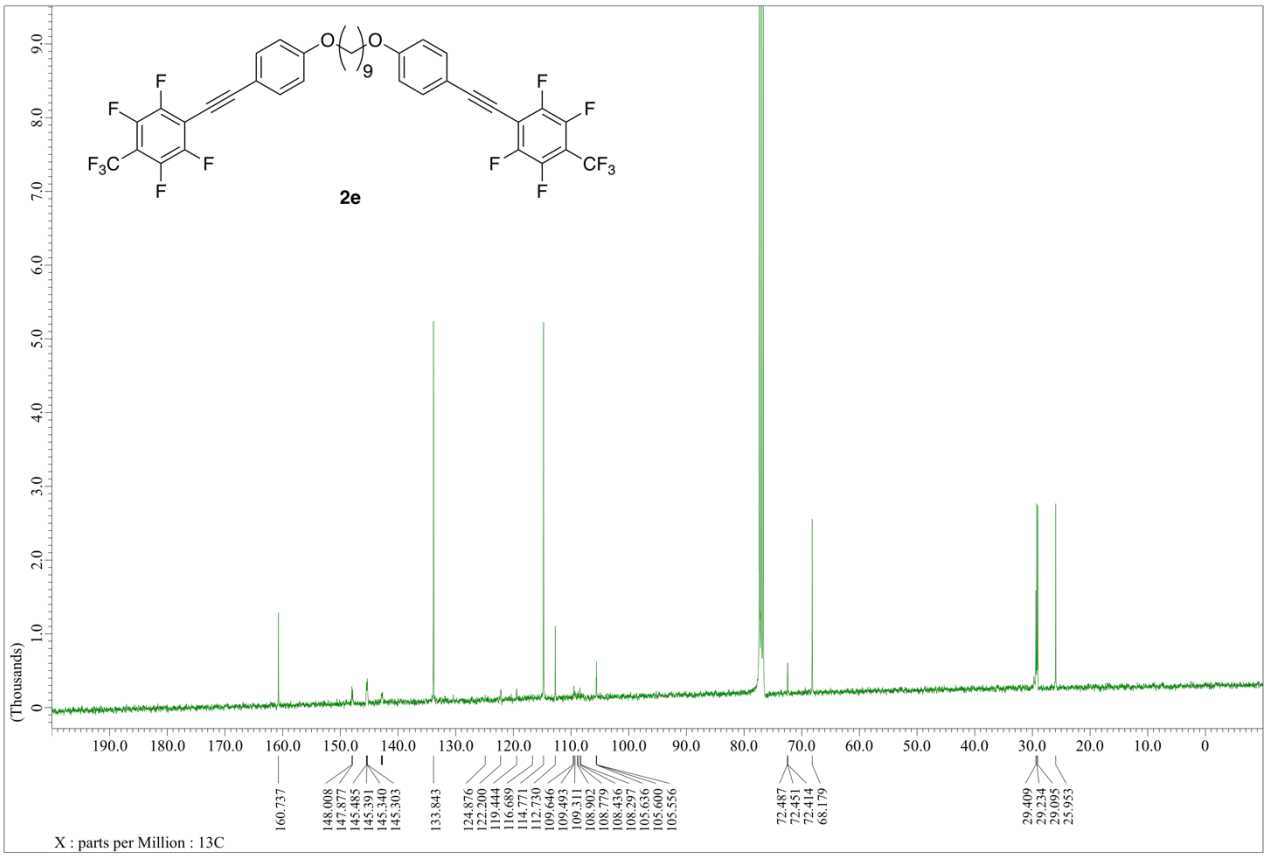


Figure S20. ^{13}C NMR spectrum of **2e** (Solvent: $CDCl_3$)

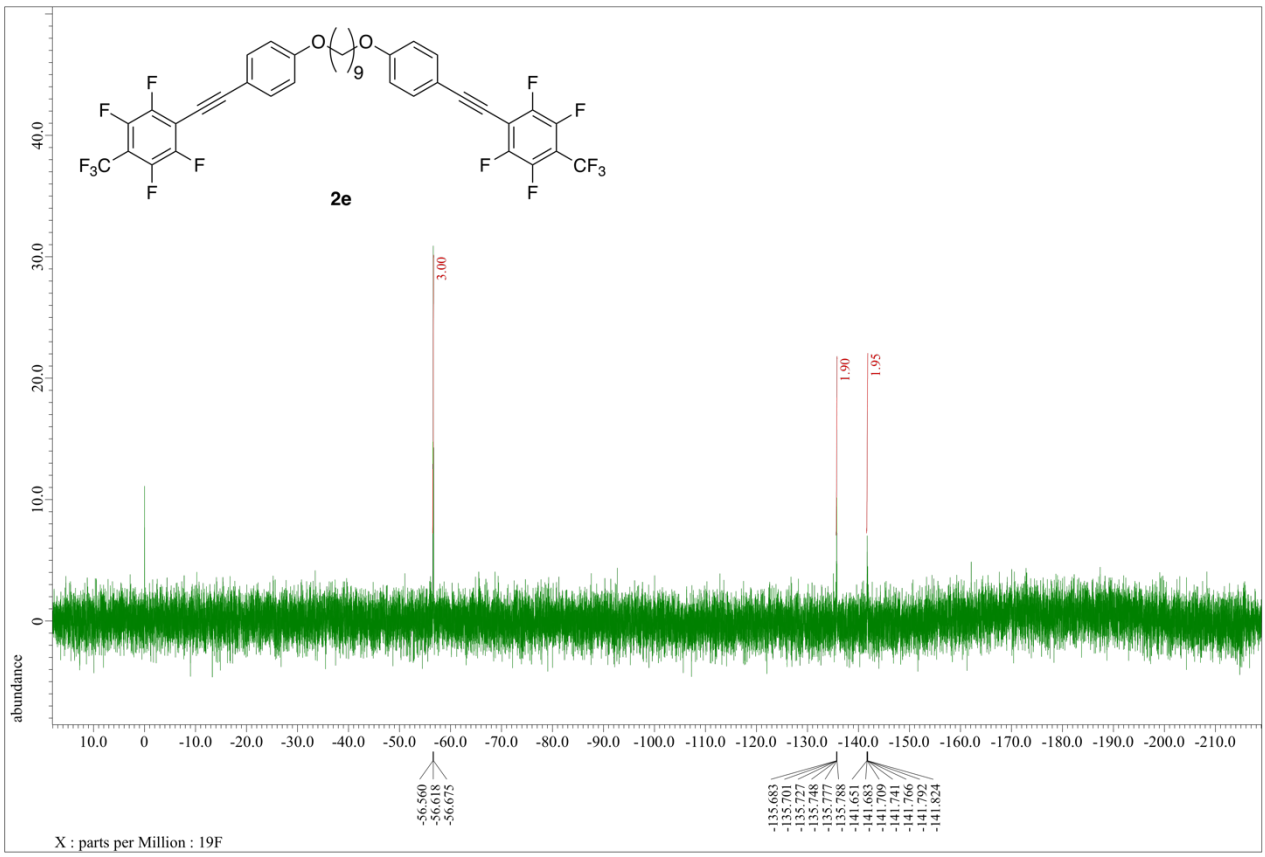


Figure S21. ^{19}F NMR spectrum of **2e** (Solvent: $CDCl_3$)

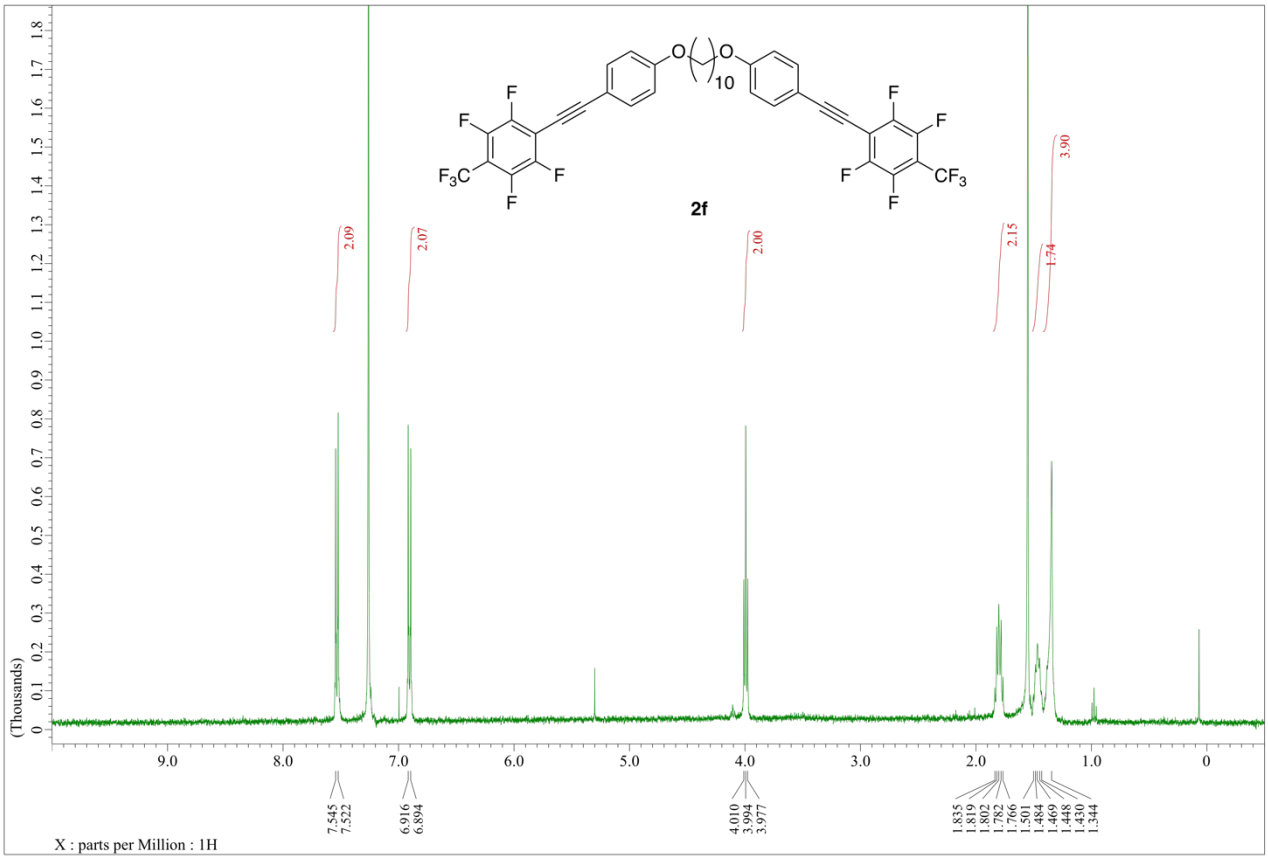


Figure S22. ^{1}H NMR spectrum of **2f** (Solvent: $CDCl_3$)

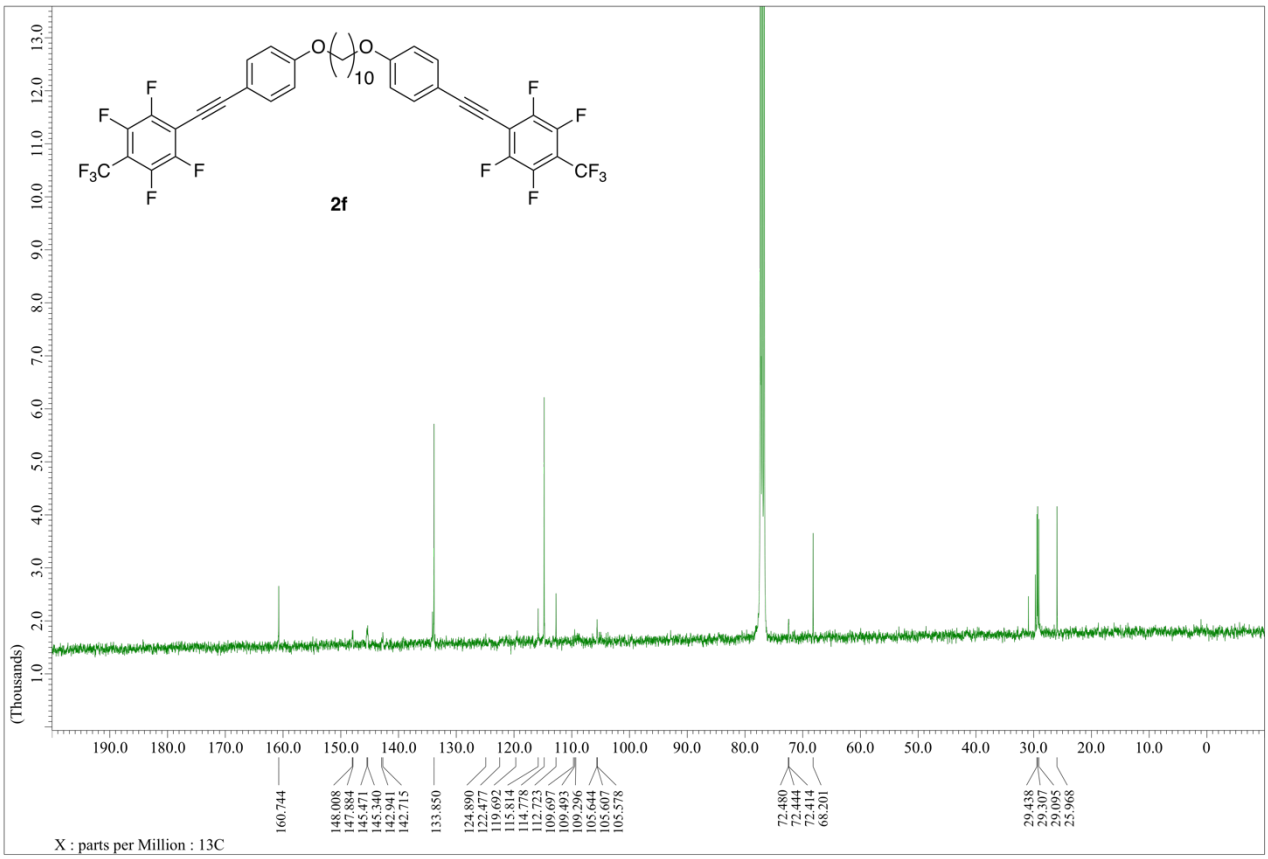


Figure S23. ^{13}C NMR spectrum of **2f** (Solvent: $CDCl_3$)

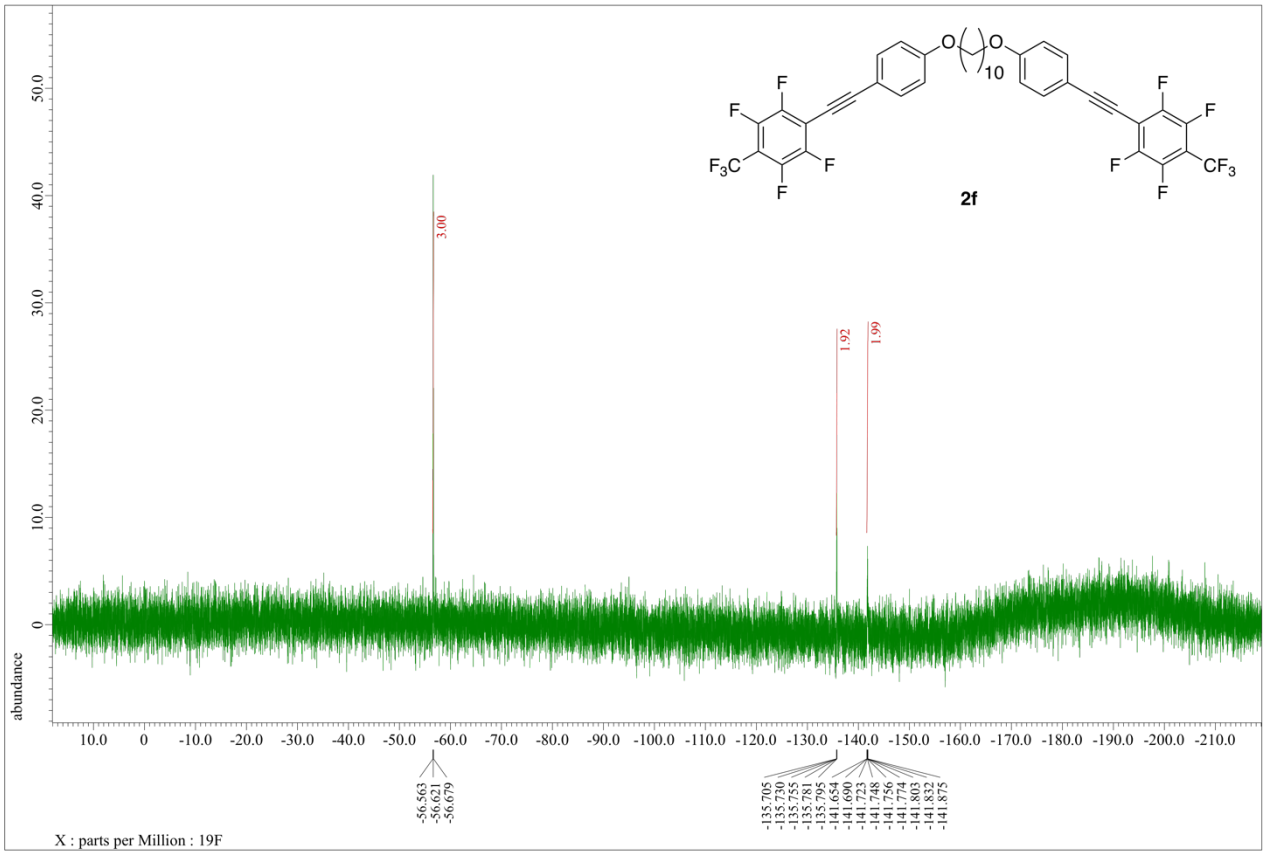


Figure S24. ^{19}F NMR spectrum of **2f** (Solvent: $CDCl_3$)

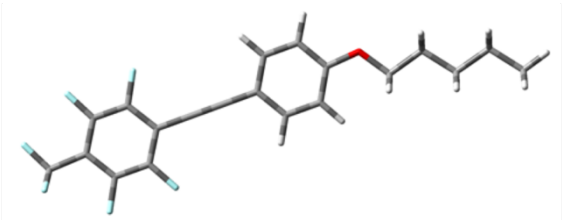
3. Quantum chemical calculation

All computations were performed using density functional theory (DFT) and the Gaussian 16 (Revision B.01) software package. Geometry optimizations were executed using the CAM-B3LYP hybrid functional and the 6-31+G(d) basis set with the implicit solvation model (conductor-like polarizable continuum model (CPCM)) for CH_2Cl_2. The vertical excitation energies and dipole moments of optimized structures were calculated using the time-dependent DFT (TD-DFT) method at the same level of theory.

Table S1. Calculated photophysical data in ground S_0 and excited S_1 states.

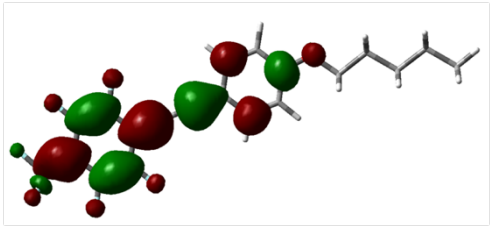
	S_0 state				*S_1 state*		
	Transition	Energy [nm]	*f*		Transition	Energy [nm]	*f*
1b	HOMO→LUMO (91%)	315	1.368		HOMO→LUMO (91%)	390	1.6341
2a	HOMO–1→LUMO (45%) HOMO→LUMO+1 (45%)	315	2.5817		HOMO→LUMO (94%) HOMO–1→LUMO+1 (91%)	389 322	1.6569 1.4782
2b	HOMO–1→LUMO (45%) HOMO→LUMO+1 (45%)	315	2.7947		HOMO→LUMO (94%) HOMO–1→LUMO+1 (91%)	389 323	1.6559 1.4819

Optimized Geometry in S_0 ground state

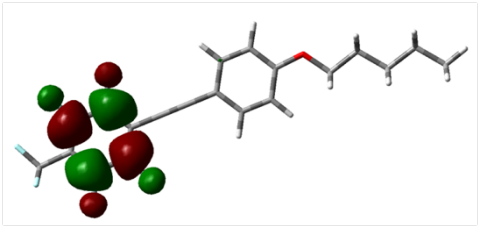


E(RCAM-B3LYP) = –1544.65951023 Hartree

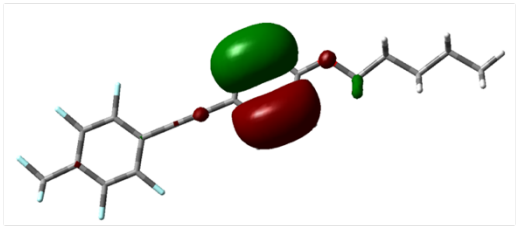
Dipole moment (Debye): X= 7.4314 Y= –0.8586 Z= –0.0001 Tot= 7.4809



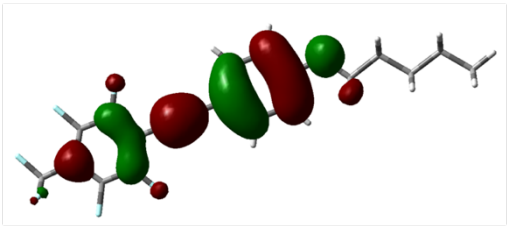
LUMO (–1.31 eV)



LUMO+1 (–0.39 eV)



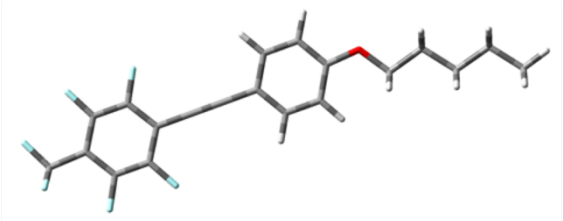
HOMO–1 (–8.96 eV)



HOMO (–7.51 eV)

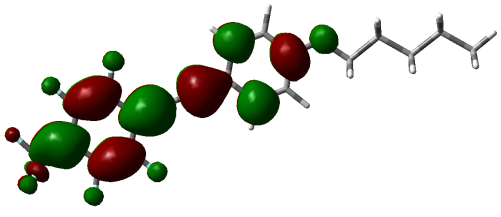
Figure S25. Optimized Geometry, HOMO and LUMO Distribution of **1b** in S_0 ground state.

Optimized Geometry in S_1 excited state

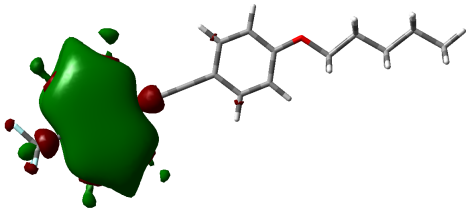


E(RCAM-B3LYP) = –1544.64805556 Hartree

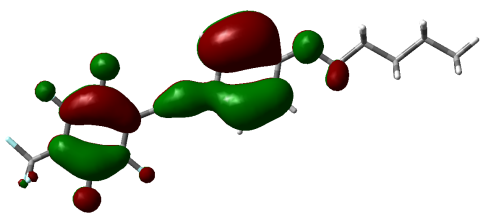
Dipole moment (Debye): X= –10.1133 Y= –0.6736 Z= 0.0000 Tot= 10.1357



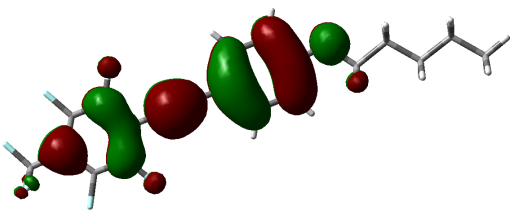
LUMO (–1.69 eV)



LUMO+1 (0.40 eV)



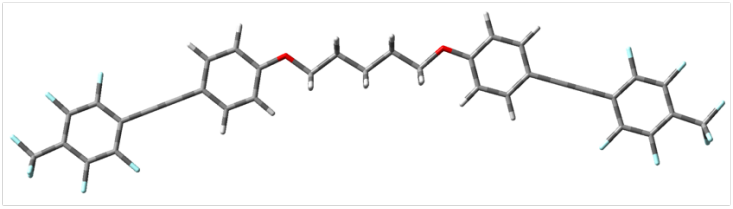
HOMO–1 (–9.11 eV)



HOMO (–7.22 eV)

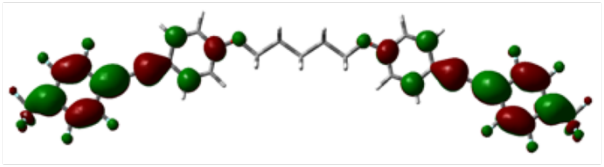
Figure S26. Optimized Geometry, HOMO and LUMO Distribution of **1b** in S_1 ground state.

Optimized Geometry in S_0 ground state

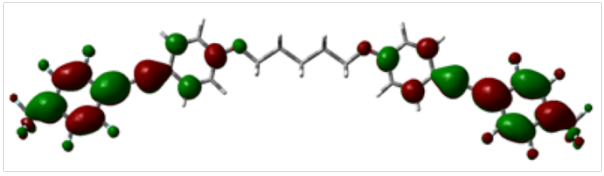


E(RCAM-B3LYP) = –2891.67495791 Hartree

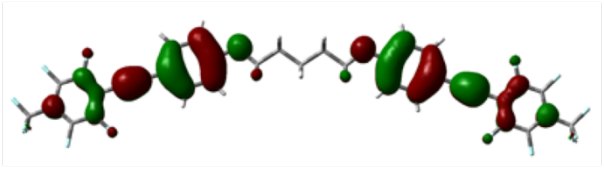
Dipole moment (Debye): X= 0.0000 Y= –1.5790 Z= –0.2446 Tot= 1.5978



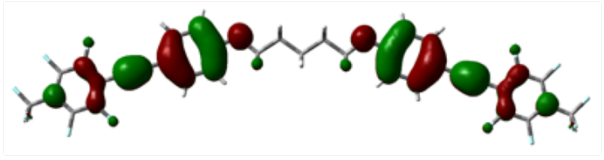
LUMO (–1.3221 eV)



LUMO+1 (–1.3219 eV)



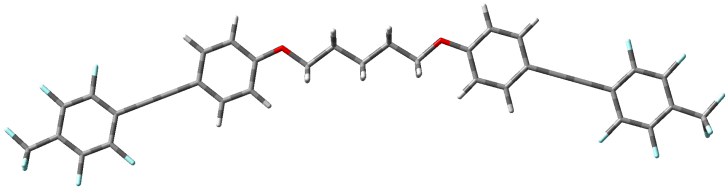
HOMO–1 (–7.5336 eV)



HOMO (–7.5297 eV)

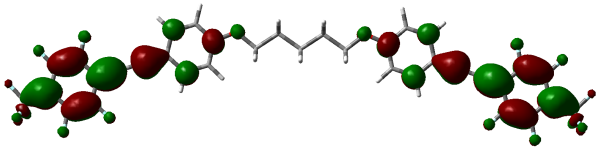
Figure S27. Optimized Geometry, HOMO and LUMO Distribution of **2a** in S_0 ground state.

Optimized Geometry in S_1 excited state

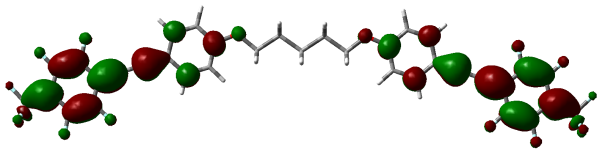


E(RCAM-B3LYP) = –2891.66346495 Hartree

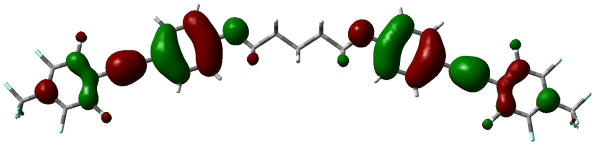
Dipole moment (Debye): X= –2.5690 Y= –2.2237 Z= –0.3568 Tot= 3.4164



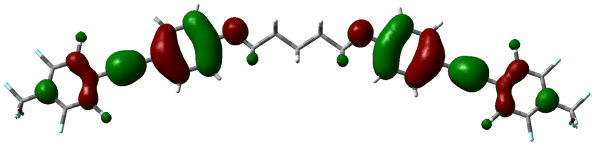
LUMO (–1.70 eV)



LUMO+1 (–1.32 eV)



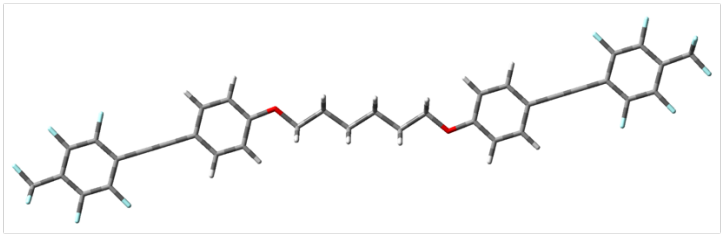
HOMO–1 (–7.54 eV)



HOMO (–7.24 eV)

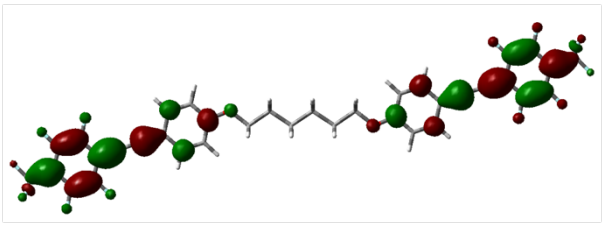
Figure S28. Optimized Geometry, HOMO and LUMO Distribution of **2a** in S_1 ground state.

Optimized Geometry in S_0 ground state

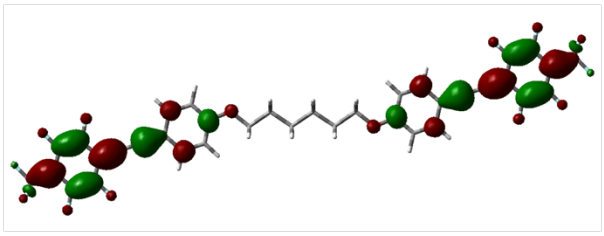


E(RCAM-B3LYP) = –2930.96502089 Hartree

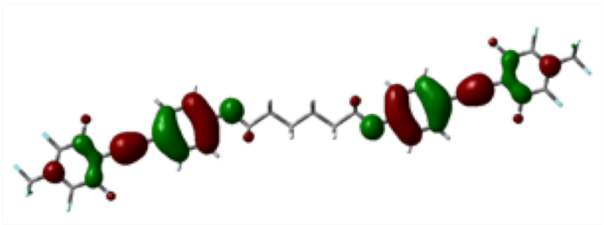
Dipole moment (Debye): X= 0.0000 Y= 0.0000 Z= 0.0000 Tot= 0.0000



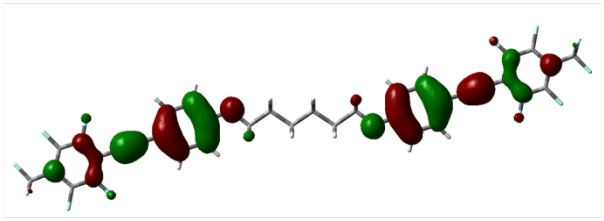
LUMO (–1.3186 eV)



LUMO+1 (–1.3184 eV)



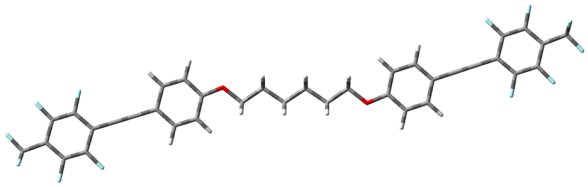
HOMO–1 (–7.525 eV)



HOMO (–7.523 eV)

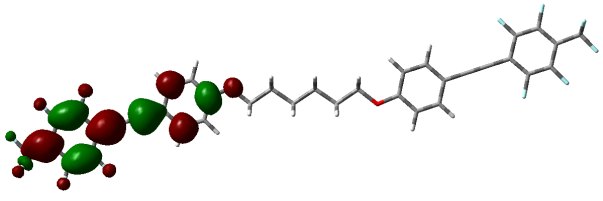
Figure S29. Optimized Geometry, HOMO and LUMO Distribution of **2b** in S_0 ground state.

Optimized Geometry in S_1 excited state

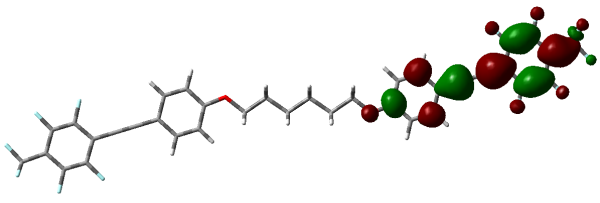


E(RCAM-B3LYP) = –2930.95354945 Hartree

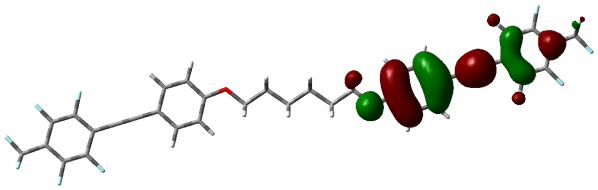
Dipole moment (Debye): X= 2.6621 Y= 0.1149 Z= 0.0003 Tot= 2.6646



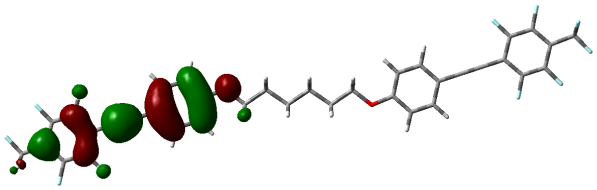
LUMO (–1.70 eV)



LUMO+1 (–1.32 eV)



HOMO–1 (–7.53 eV)



HOMO (–7.23 eV)

Figure S30. Optimized Geometry, HOMO and LUMO Distribution of **2b** in S_0 ground state.

Table S2. Cartesian Coordinates of **1b** (S_0 state)

No.	Atom No.	Type	Coordinates (Angstroms) x	y	z
1	6	0	-2.560621	0.102992	0.000025
2	6	0	-3.186619	-1.146996	0.000059
3	6	0	-4.560997	-1.264072	0.000042
4	6	0	-5.393718	-0.145832	-0.000011
5	6	0	-4.779390	1.103163	-0.000044
6	6	0	-3.399003	1.218102	-0.000026
7	9	0	-2.445065	-2.259619	0.000109
8	9	0	-5.097177	-2.490325	0.000077
9	9	0	-5.489060	2.234840	-0.000096
10	9	0	-2.865232	2.444576	-0.000062
11	6	0	-1.149042	0.230085	0.000036
12	6	0	0.056221	0.338173	0.000038
13	6	0	1.475677	0.467928	0.000038
14	6	0	2.078468	1.739007	0.000164
15	1	0	1.455681	2.627607	0.000264
16	6	0	3.453623	1.862654	0.000163
17	1	0	3.925989	2.839430	0.000262
18	6	0	4.266044	0.720289	0.000033
19	6	0	3.680485	-0.549048	-0.000095
20	1	0	4.286666	-1.445983	-0.000197
21	6	0	2.295766	-0.666015	-0.000091
22	1	0	1.844434	-1.652892	-0.000191
23	8	0	5.599778	0.944764	0.000045
24	6	0	6.495986	-0.170238	-0.000065
25	1	0	6.311077	-0.783424	-0.890485
26	1	0	6.311079	-0.783597	0.890237
27	6	0	7.912099	0.369256	-0.000009
28	1	0	8.048951	1.006663	0.882032
29	1	0	8.048984	1.006775	-0.881965
30	6	0	8.952347	-0.750365	-0.000058
31	1	0	8.802246	-1.391463	0.879556
32	1	0	8.802267	-1.391373	-0.879742
33	6	0	10.388359	-0.227413	-0.000013
34	1	0	10.538742	0.413580	-0.878626
35	1	0	10.538707	0.413512	0.878656
36	6	0	11.427580	-1.346187	-0.000038
37	1	0	11.319955	-1.984246	0.884839
38	1	0	11.319957	-1.984205	-0.884945
39	6	0	-6.884188	-0.358182	-0.000030
40	9	0	-7.274604	-1.061363	1.082554
41	9	0	-7.578058	0.785828	-0.000084
42	9	0	-7.274564	-1.061440	-1.082580
43	1	0	12.446422	-0.944770	-0.000028

Table S3. Cartesian Coordinates of **1b** (S_1 state)

No.	Atom No.	Type	Coordinates (Angstroms) x	y	z
1	6	0	2.521532	0.105140	-0.000009
2	6	0	3.189467	-1.163168	0.000031
3	6	0	4.548883	-1.264884	0.000038
4	6	0	5.399012	-0.136295	0.000007
5	6	0	4.760272	1.121786	-0.000032
6	6	0	3.397730	1.238933	-0.000039
7	9	0	2.441547	-2.277918	0.000061
8	9	0	5.102039	-2.491396	0.000075
9	9	0	5.479740	2.255769	-0.000062
10	9	0	2.847369	2.464149	-0.000077
11	6	0	1.157235	0.223517	-0.000015
12	6	0	-0.084454	0.331144	-0.000020
13	6	0	-1.449697	0.449023	-0.000025
14	6	0	-2.084582	1.741208	-0.000069
15	1	0	-1.463055	2.629759	-0.000100
16	6	0	-3.445108	1.846457	-0.000073
17	1	0	-3.934913	2.814329	-0.000106
18	6	0	-4.257812	0.683738	-0.000032
19	6	0	-3.661010	-0.598407	0.000011
20	1	0	-4.272253	-1.491942	0.000042
21	6	0	-2.294407	-0.714250	0.000014
22	1	0	-1.831460	-1.694926	0.000048
23	8	0	-5.571542	0.900659	-0.000038
24	6	0	-6.494802	-0.203873	0.000004
25	1	0	-6.313171	-0.813435	0.891982
26	1	0	-6.313178	-0.813498	-0.891933
27	6	0	-7.897410	0.366710	-0.000010
28	1	0	-8.021460	1.005481	-0.882513
29	1	0	-8.021452	1.005544	0.882448
30	6	0	-8.957243	-0.734901	0.000034
31	1	0	-8.819095	-1.378153	-0.879740
32	1	0	-8.819087	-1.378090	0.879853
33	6	0	-10.382720	-0.183761	0.000021
34	1	0	-10.520571	0.459767	0.878714
35	1	0	-10.520580	0.459703	-0.878717
36	6	0	-11.442673	-1.282819	0.000067
37	1	0	-11.347328	-1.922659	-0.884859
38	1	0	-11.347319	-1.922595	0.885038
39	6	0	6.870720	-0.343190	0.000018
40	9	0	7.291268	-1.054133	-1.080213
41	9	0	7.570454	0.802539	-0.000017
42	9	0	7.291262	-1.054064	1.080296
43	1	0	-12.453453	-0.861713	0.000056

Table S4. Cartesian Coordinates of **2a** (S_0 state)

No.	Atom No.	Type	Coordinates (Angstroms) x	y	z
1	6	0	11.406040	0.294422	0.010782
2	6	0	11.732940	1.651802	-0.060098
3	6	0	13.044171	2.079055	-0.034141
4	6	0	14.107281	1.182331	0.063163
5	6	0	13.791569	-0.171564	0.133198
6	6	0	12.473941	-0.598068	0.107014
7	9	0	10.759743	2.563861	-0.154390
8	9	0	13.288830	3.392924	-0.104535
9	9	0	14.737945	-1.109412	0.228301
10	9	0	12.231509	-1.911554	0.177878
11	6	0	10.060495	-0.150422	-0.012090
12	6	0	8.911115	-0.528387	-0.029082
13	6	0	7.557462	-0.974846	-0.046731
14	6	0	7.255813	-2.348346	-0.009483
15	1	0	8.061999	-3.073517	0.031173
16	6	0	5.943848	-2.778427	-0.023662
17	1	0	5.702966	-3.835952	0.005261
18	6	0	4.896178	-1.848808	-0.074733
19	6	0	5.181091	-0.481027	-0.113357
20	1	0	4.388959	0.255838	-0.154017
21	6	0	6.503912	-0.055287	-0.099355
22	1	0	6.721901	1.007368	-0.128988
23	8	0	3.646856	-2.368224	-0.082650
24	6	0	2.523287	-1.485273	-0.120798
25	1	0	2.571173	-0.874410	-1.030581
26	1	0	2.555637	-0.818367	0.749442
27	6	0	1.267986	-2.334559	-0.103829
28	1	0	1.276409	-2.961018	0.796040
29	1	0	1.283799	-3.010170	-0.967288
30	6	0	0.000000	-1.481971	-0.131876
31	1	0	-0.000002	-0.797853	0.727043
32	1	0	0.000002	-0.853516	-1.032280
33	6	0	-1.267987	-2.334560	-0.103835
34	1	0	-1.283795	-3.010168	-0.967296
35	1	0	-1.276413	-2.961020	0.796032
36	6	0	-2.523288	-1.485274	-0.120808
37	1	0	-2.555641	-0.818370	0.749433
38	1	0	-2.571169	-0.874408	-1.030590
39	8	0	-3.646857	-2.368224	-0.082668
40	6	0	-4.896179	-1.848809	-0.074751
41	6	0	-5.181092	-0.481028	-0.113371
42	1	0	-4.388960	0.255838	-0.154027
43	6	0	-6.503913	-0.055288	-0.099369
44	1	0	-6.721902	1.007367	-0.128998
45	6	0	-7.557462	-0.974847	-0.046749
46	6	0	-7.255813	-2.348347	-0.009506
47	1	0	-8.062000	-3.073518	0.031146
48	6	0	-5.943849	-2.778428	-0.023685
49	1	0	-5.702967	-3.835953	0.005234
50	6	0	-8.911116	-0.528388	-0.029099
51	6	0	-10.060495	-0.150423	-0.012104
52	6	0	-11.406040	0.294422	0.010772
53	6	0	-11.732940	1.651802	-0.060094
54	6	0	-13.044170	2.079056	-0.034130
55	6	0	-14.107281	1.182332	0.063166
56	6	0	-13.791569	-0.171565	0.133188
57	6	0	-12.473942	-0.598069	0.106998
58	9	0	-10.759742	2.563862	-0.154378
59	9	0	-13.288829	3.392926	-0.104510
60	9	0	-14.737946	-1.109412	0.228285
61	9	0	-12.231510	-1.911556	0.177849
62	6	0	-15.509790	1.729147	0.087199
63	9	0	-15.773827	2.437912	-1.029358
64	9	0	-15.686647	2.565435	1.130374
65	9	0	-16.444072	0.776078	0.181222
66	6	0	15.509791	1.729146	0.087184
67	9	0	15.686644	2.565467	1.130333
68	9	0	16.444072	0.776079	0.181241
69	9	0	15.773834	2.437876	-1.029395

Table S5. Cartesian Coordinates of **2a** (S_1 state)

No.	Atom No.	Type	Coordinates (Angstroms) x	y	z
1	6	0	11.381841	0.268738	0.014119
2	6	0	11.754021	1.651289	-0.055350
3	6	0	13.056789	2.051987	-0.028749
4	6	0	14.133253	1.142042	0.068018
5	6	0	13.787419	-0.224247	0.135917
6	6	0	12.484980	-0.640655	0.110093
7	9	0	10.779982	2.570126	-0.148590
8	9	0	13.326291	3.368241	-0.097224
9	9	0	14.737989	-1.168120	0.228897
10	9	0	12.217775	-1.955073	0.177719
11	6	0	10.077627	-0.147926	-0.007600
12	6	0	8.889564	-0.524512	-0.026052
13	6	0	7.582620	-0.935699	-0.043211
14	6	0	7.240613	-2.332383	0.028545
15	1	0	8.037979	-3.064222	0.095376
16	6	0	5.934968	-2.729133	0.013564
17	1	0	5.664786	-3.778321	0.067653
18	6	0	4.892160	-1.771607	-0.072498
19	6	0	5.198888	-0.393271	-0.146228
20	1	0	4.410186	0.345358	-0.213880
21	6	0	6.508112	0.015280	-0.132285
22	1	0	6.749142	1.071123	-0.188318
23	8	0	3.655633	-2.267334	-0.077205
24	6	0	2.517189	-1.390661	-0.146617
25	1	0	2.574592	-0.809742	-1.073738
26	1	0	2.547943	-0.704667	0.707083
27	6	0	1.273053	-2.253830	-0.112721
28	1	0	1.286348	-2.859323	0.800938
29	1	0	1.296116	-2.946674	-0.961832
30	6	0	-0.001058	-1.410687	-0.159724
31	1	0	-0.008460	-0.711795	0.686994
32	1	0	-0.003838	-0.798799	-1.071279
33	6	0	-1.261556	-2.273803	-0.119356
34	1	0	-1.273033	-2.959935	-0.974445
35	1	0	-1.263664	-2.888959	0.788241
36	6	0	-2.523492	-1.434400	-0.144529
37	1	0	-2.560064	-0.758760	0.718748
38	1	0	-2.576756	-0.833394	-1.060570
39	8	0	-3.639397	-2.325854	-0.096154
40	6	0	-4.892958	-1.815869	-0.087718
41	6	0	-5.188327	-0.450717	-0.136294
42	1	0	-4.402134	0.291910	-0.186443
43	6	0	-6.514303	-0.034902	-0.119901
44	1	0	-6.740493	1.025793	-0.157025
45	6	0	-7.560524	-0.961984	-0.055321
46	6	0	-7.248291	-2.332797	-0.008710
47	1	0	-8.048734	-3.063723	0.041103
48	6	0	-5.933117	-2.753031	-0.025025
49	1	0	-5.684121	-3.808445	0.011297
50	6	0	-8.917434	-0.525487	-0.034703
51	6	0	-10.069406	-0.155741	-0.014840
52	6	0	-11.417976	0.279791	0.011617
53	6	0	-11.754416	1.634738	-0.060775
54	6	0	-13.068470	2.053016	-0.031143
55	6	0	-14.125014	1.149150	0.071384
56	6	0	-13.799759	-0.202398	0.143105
57	6	0	-12.479310	-0.619875	0.113246
58	9	0	-10.787827	2.553268	-0.160056
59	9	0	-13.322396	3.365024	-0.102952
60	9	0	-14.739310	-1.146509	0.243423
61	9	0	-12.227527	-1.931494	0.185895
62	6	0	-15.531199	1.686376	0.099398
63	9	0	-15.803165	2.393299	-1.016393
64	9	0	-15.710745	2.521428	1.143098
65	9	0	-16.458657	0.726953	0.195995
66	6	0	15.522403	1.670202	0.092983
67	9	0	15.731708	2.518363	1.135164
68	9	0	16.456475	0.710955	0.186334
69	9	0	15.818403	2.393106	-1.020075

Table S6. Cartesian Coordinates of **2b** (S_0 state)

No.	Atom No.	Type	Coordinates (Angstroms) x	y	z
1	6	0	1.788625	-0.786625	-0.000061
2	1	0	1.676899	-1.428784	0.881933
3	1	0	1.676902	-1.428758	-0.882074
4	6	0	0.706110	0.291915	-0.000047
5	1	0	0.830307	0.937503	-0.879815
6	1	0	0.830306	0.937480	0.879737
7	6	0	-0.706111	-0.291917	-0.000056
8	1	0	-0.830303	-0.937489	-0.879835
9	1	0	-0.830311	-0.937497	0.879717
10	6	0	-1.788625	0.786623	-0.000057
11	1	0	-1.676902	1.428769	0.881947
12	1	0	-1.676899	1.428770	-0.882060
13	6	0	-3.182748	0.192192	-0.000060
14	1	0	-3.343713	-0.427854	-0.890388
15	1	0	-3.343718	-0.427852	0.890269
16	8	0	-4.119701	1.272399	-0.000065
17	6	0	-5.444391	0.998150	-0.000055
18	6	0	-5.982159	-0.292058	-0.000050
19	1	0	-5.343003	-1.165857	-0.000053
20	6	0	-7.361633	-0.460285	-0.000040
21	1	0	-7.776213	-1.463133	-0.000036
22	6	0	-8.223153	0.642458	-0.000036
23	6	0	-7.668021	1.935032	-0.000043
24	1	0	-8.323348	2.799891	-0.000040
25	6	0	-6.298417	2.109609	-0.000052
26	1	0	-5.862432	3.103159	-0.000056
27	6	0	-9.636953	0.460665	-0.000026
28	6	0	-10.837561	0.309758	-0.000017
29	6	0	-12.244049	0.134619	-0.000004
30	6	0	-12.827562	-1.135709	-0.000021
31	6	0	-14.197291	-1.298669	-0.000008
32	6	0	-15.066935	-0.208961	0.000021
33	6	0	-14.495034	1.059962	0.000038
34	6	0	-13.119257	1.221032	0.000026
35	9	0	-12.049092	-2.222691	-0.000050
36	9	0	-14.692279	-2.542040	-0.000024
37	9	0	-15.242282	2.167061	0.000069
38	9	0	-12.626854	2.464578	0.000043
39	6	0	-16.549390	-0.471594	0.000037
40	9	0	-16.915524	-1.187499	1.082546
41	9	0	-16.915550	-1.187488	-1.082471
42	9	0	-17.281329	0.648418	0.000052
43	6	0	3.182748	-0.192193	-0.000052
44	1	0	3.343722	0.427823	0.890296
45	1	0	3.343708	0.427882	-0.890361
46	8	0	4.119701	-1.272399	-0.000094
47	6	0	5.444391	-0.998151	-0.000069
48	6	0	5.982159	0.292057	-0.000038
49	6	0	6.298417	-2.109610	-0.000081
50	6	0	7.361633	0.460284	-0.000018
51	1	0	5.343003	1.165857	-0.000030
52	6	0	7.668021	-1.935033	-0.000062
53	1	0	5.862432	-3.103159	-0.000106
54	6	0	8.223153	-0.642459	-0.000029
55	1	0	7.776214	1.463132	0.000007
56	1	0	8.323348	-2.799892	-0.000071
57	6	0	9.636953	-0.460667	-0.000009
58	6	0	10.837561	-0.309759	0.000009
59	6	0	12.244049	-0.134620	0.000029
60	6	0	12.827561	1.135709	0.000020
61	6	0	13.119258	-1.221032	0.000059
62	6	0	14.197290	1.298669	0.000041
63	6	0	14.495035	-1.059962	0.000079
64	6	0	15.066935	0.208961	0.000081
65	6	0	16.549390	0.471596	0.000083
66	9	0	14.692278	2.542040	0.000014
67	9	0	12.049091	2.222690	-0.000015
68	9	0	15.242284	-2.167060	0.000096
69	9	0	12.626856	-2.464579	0.000064
70	9	0	17.281329	-0.648415	0.000323
71	9	0	16.915498	1.187701	1.082467
72	9	0	16.915574	1.187291	-1.082550

Table S7. Cartesian Coordinates of **2b** (S_1 state)

No.	Atom No.	Type	Coordinates (Angstroms) x	y	z
1	6	0	-1.795713	0.690526	0.000085
2	1	0	-1.690172	1.332465	0.882580
3	1	0	-1.690173	1.332469	-0.882408
4	6	0	-0.705401	-0.380645	0.000082
5	1	0	-0.824365	-1.026722	-0.879847
6	1	0	-0.824361	-1.026723	0.880012
7	6	0	0.701412	0.216126	0.000078
8	1	0	0.819859	0.862526	-0.879783
9	1	0	0.819864	0.862527	0.879938
10	6	0	1.792655	-0.853538	0.000075
11	1	0	1.686307	-1.496487	0.882115
12	1	0	1.686297	-1.496491	-0.881962
13	6	0	3.181787	-0.247352	0.000065
14	1	0	3.337555	0.373969	-0.890304
15	1	0	3.337566	0.373973	0.890429
16	8	0	4.127161	-1.319944	0.000061
17	6	0	5.449822	-1.035025	0.000052
18	6	0	5.977056	0.259454	0.000042
19	1	0	5.330886	1.128091	0.000041
20	6	0	7.355155	0.438819	0.000032
21	1	0	7.761627	1.444974	0.000023
22	6	0	8.225517	-0.656950	0.000032
23	6	0	7.680848	-1.953953	0.000043
24	1	0	8.343107	-2.813513	0.000043
25	6	0	6.312665	-2.139577	0.000053
26	1	0	5.884747	-3.136630	0.000061
27	6	0	9.637835	-0.463699	0.000020
28	6	0	10.837165	-0.303045	0.000009
29	6	0	12.242203	-0.116551	-0.000016
30	6	0	12.815420	1.158458	-0.000036
31	6	0	14.183776	1.332553	-0.000061
32	6	0	15.062290	0.249932	-0.000066
33	6	0	14.500650	-1.023591	-0.000046
34	6	0	13.126207	-1.195792	-0.000021
35	9	0	12.028071	2.239133	-0.000032
36	9	0	14.668548	2.579983	-0.000079
37	9	0	15.256804	-2.124659	-0.000049
38	9	0	12.643882	-2.443364	-0.000003
39	6	0	16.542621	0.524525	-0.000093
40	9	0	16.903096	1.243451	1.082457
41	9	0	16.903059	1.243441	-1.082661
42	9	0	17.283729	-0.589490	-0.000101
43	6	0	-3.181649	0.080092	0.000083
44	1	0	-3.346062	-0.534362	0.892047
45	1	0	-3.346059	-0.534362	-0.891881
46	8	0	-4.133849	1.159070	0.000081
47	6	0	-5.441627	0.906882	0.000079
48	6	0	-6.003872	-0.390692	0.000074
49	6	0	-6.284666	2.047666	0.000081
50	6	0	-7.366980	-0.542760	0.000069
51	1	0	-5.368995	-1.267665	0.000073
52	6	0	-7.641931	1.906415	0.000076
53	1	0	-5.820580	3.028145	0.000085
54	6	0	-8.242141	0.597770	0.000069
55	1	0	-7.803890	-1.535292	0.000064
56	1	0	-8.286744	2.778198	0.000077
57	6	0	-9.603742	0.444132	0.000060
58	6	0	-10.842406	0.305401	0.000046
59	6	0	-12.203433	0.154359	0.000019
60	6	0	-12.841090	-1.129395	-0.000010
61	6	0	-13.105892	1.267346	0.000010
62	6	0	-14.197810	-1.263022	-0.000033
63	6	0	-14.465344	1.118193	-0.000014
64	6	0	-15.074059	-0.154671	-0.000022
65	6	0	-16.540675	-0.396230	-0.000070
66	9	0	-14.722071	-2.502014	-0.000077
67	9	0	-12.067155	-2.226096	-0.000021
68	9	0	-15.211252	2.234783	-0.000029
69	9	0	-12.584458	2.505036	0.000022
70	9	0	-17.267254	0.732446	0.000093
71	9	0	-16.943774	-1.117324	1.080024
72	9	0	-16.943764	-1.117000	-1.080391

4. Crystal Structure

Single crystal of **2a** was obtained by recrystallization from $CDCl_3$. The obtained single crystal was mounted on a glass fiber. X-ray diffraction patterns were recorded on a Rigaku XtaLabMini diffractometer or a Rigaku Saturn 724 diffractometer equipped with a VariMax Mo optic system using Cu$K\alpha$ radiation (λ = 1.54187 Å). The reflection data were integrated, scaled, and averaged using the *CrysAlilsPro* (ver. 1.171.38.46, Rigaku Oxford Diffraction, 2015). Empirical absorption corrections were applied using the *SCALE3 ABSPACK* scaling algorithm (*CrysAlisPro*). The structures were solved by a directed method (*SHELXT-2014/5*) and refined using a full-matrix least square method on F^2 for all reflections (*SHELXL-2014/7*). The crystallographic data were deposited into the Cambridge Crystallographic Data Centre (CCDC) database (CCDC 2011588 for **2a**). These data can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.

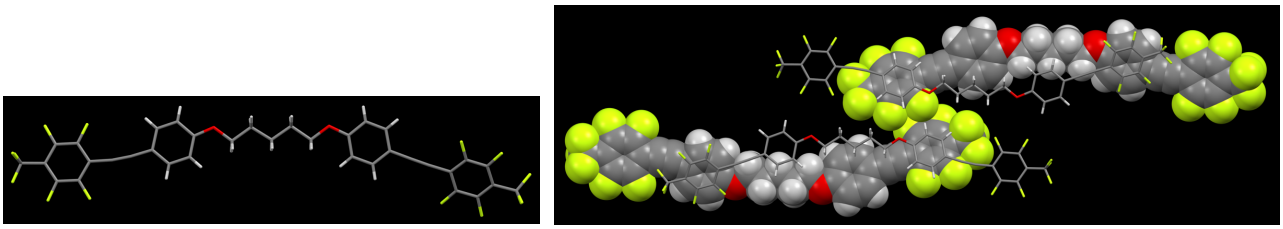


Figure S31. Crystal and the packing structures of **2a**

Table S8. Crystallographic data for **2a**

	2a
CCDC No.	2011588
Empirical formula	$C_{35}H_{18}F_{14}O_2$
Formula weight	736.49
Temperature [K]	293(2)
Crystal color / Habit	Colorless / block
Crystal size [mm]	0.12 x 0.11 x 0.10
Crystal system	Monoclinic
Space group	$P\,2_1/n$
a [Å]	12.4775(9)
b [Å]	14.3824(13)
c [Å]	35.1870(17)
α [°]	90
β [°]	98.060(5)
γ [°]	90
V [Å^3]	6252.2(8)
Z	8
$R\,[F^2>2\sigma(F^2)]$ [a]	0.0702
$wR\,(F^2)$ [b]	0.1689

[a] $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. [b] $wR = \{[\Sigma w(|F_o| - |F_c|)]/\Sigma w|F_o|\}^{1/2}$.

5. PL behavior in CH_2Cl_2 solution

UV-vis absorption spectra were recorded on a JASCO V-500 absorption spectrometer (Tokyo, Japan). Samples for absorption measurements were prepared by dissolving crystalline **2a**–**f** in a common organic solvent to a concentration of 1.0×10^{-5} mol L^{-1} and transferring the solution to a quartz cuvette with an optical path length of 1 cm. Steady-state photoluminescence (PL) spectra and PL quantum yields (PLQYs) in solution and crystalline states were obtained using a JASCO FP-6000 fluorescence spectrometer (Tokyo, Japan) and an absolute PLQY measurement system (Hamamatsu Photonics KK., C11347-01, Hamamatsu, Japan). PL measurements were performed for 1.0×10^{-6} mol L^{-1} solutions using quartz cuvettes with an optical path length of 1 cm. The excitation wavelength (λ_{ex}) corresponded to the maximum absorption wavelength.

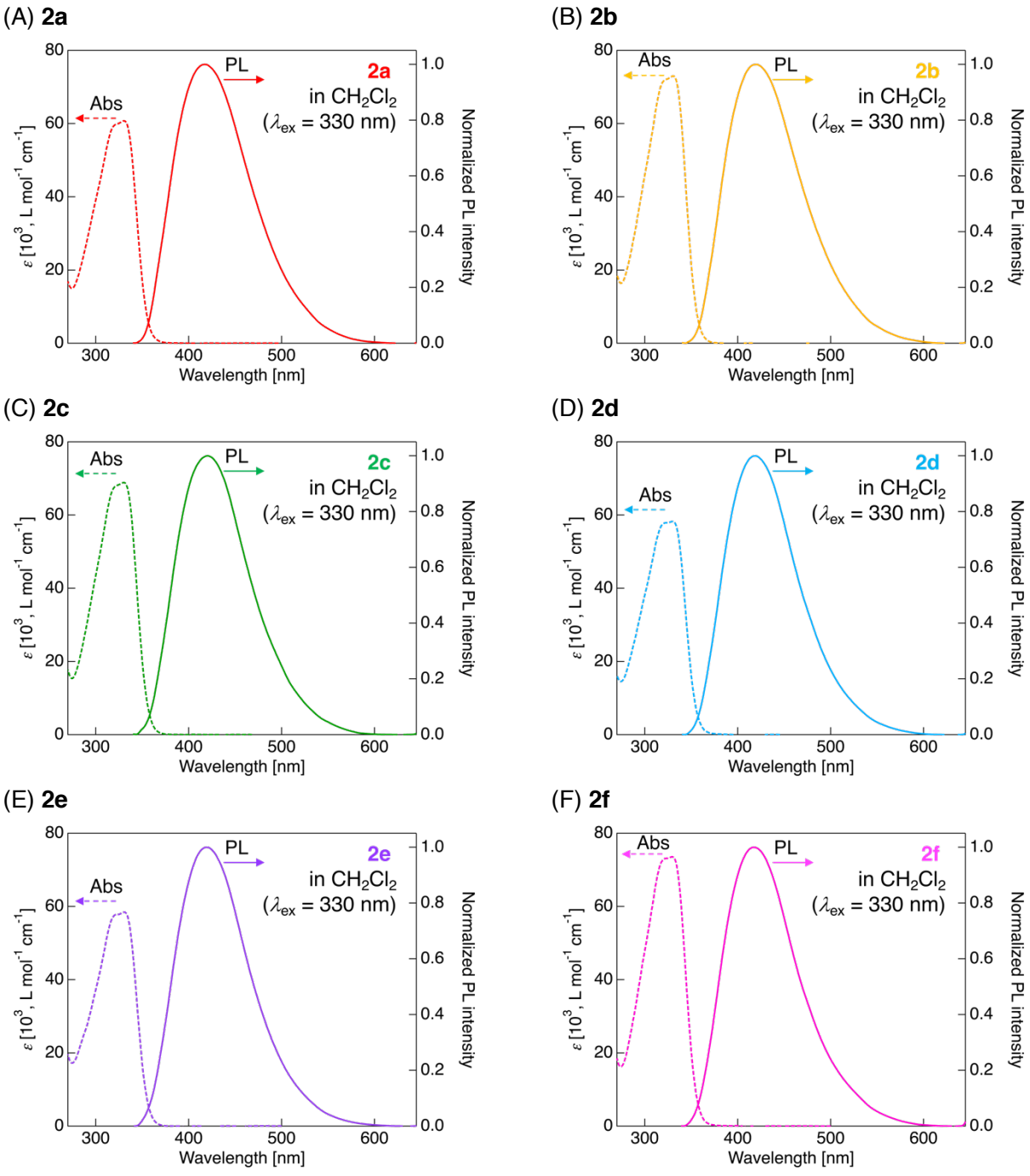


Figure S32. Absorption and PL spectra of (A) **2a**, (B) **2b**, (C) **2c**, (D) **2d**, (E) **2e**, and (F) **2f** in CH_2Cl_2 solution states.

AIE evaluation

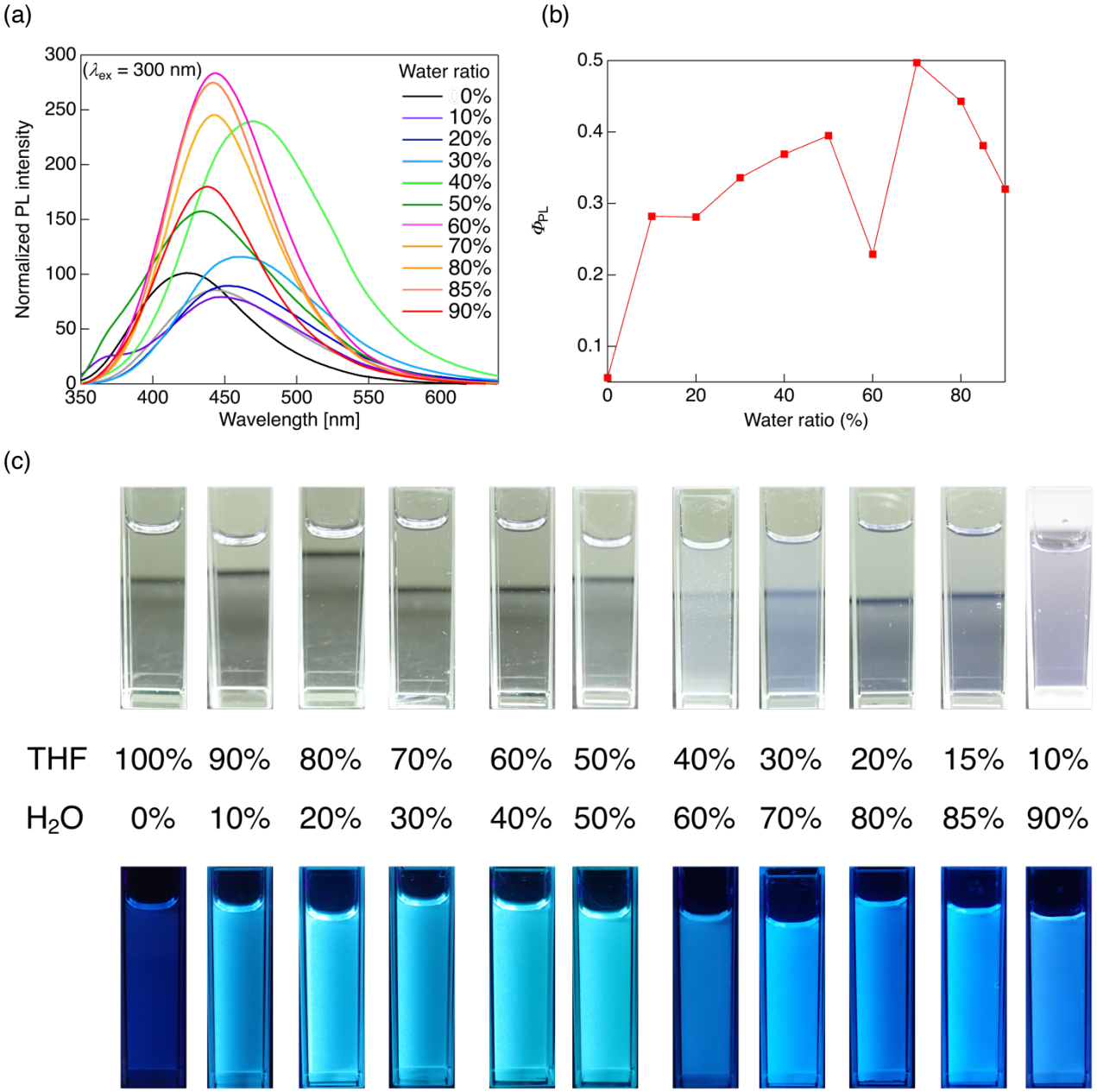


Figure S33. (a) PL spectra of **2a** in a mixed solvent of THF and H_2O. (b) Relationship between water ratio and photoluminescence efficiency (Φ_{PL}). (c) Photoluminescence color of the solution without/with UV irradiation (λ_{ex} = 365 nm).

6. PL behavior in crystalline powder

For excitation and PL measurements, crystalline powder samples were placed between two quartz glass plates, and the samples were placed above a quartz Petri dish and characterized using a calibrated integrating sphere for measurements of PL behavior and PLQY in the crystalline state using a C11347-01 absolute PLQY measurement system (Hamamatsu Photonics KK, Hamamatsu, Japan).

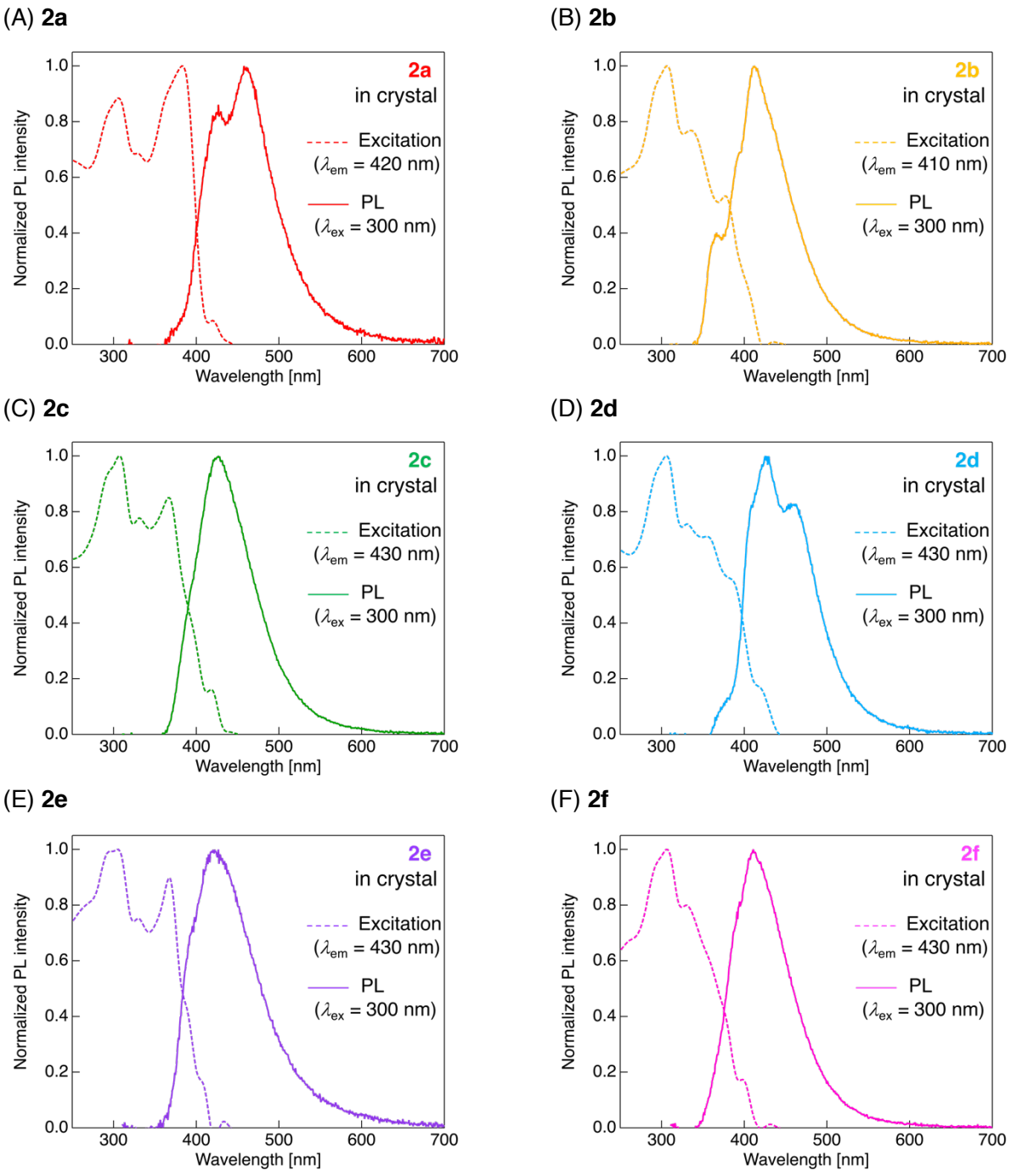
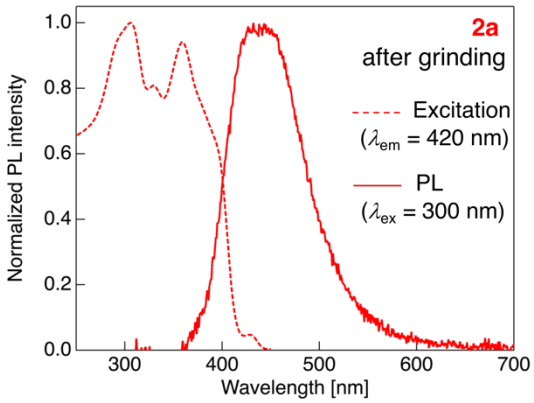


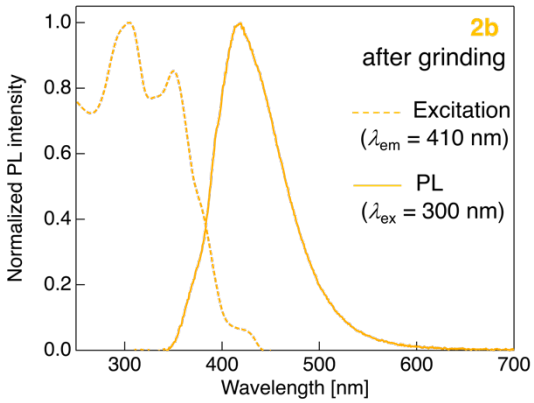
Figure S34. Excitation (dotted line) and PL spectra (solid line) of (A) **2a**, (B) **2b**, (C) **2c**, (D) **2d**, (E) **2e**, and (D) **2f** in crystalline powder states.

7. PL Behavior after mechanical stimulus

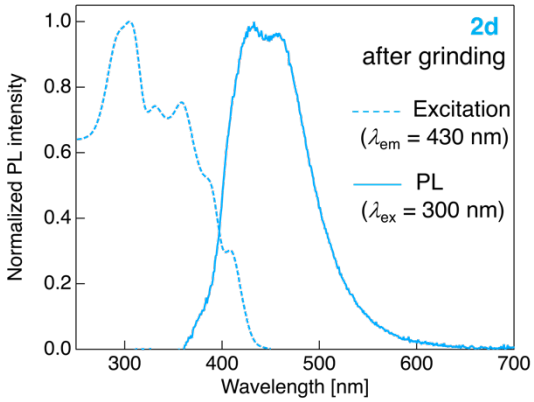
(A) **2a**



(B) **2b**



(C) **2d**



(D)

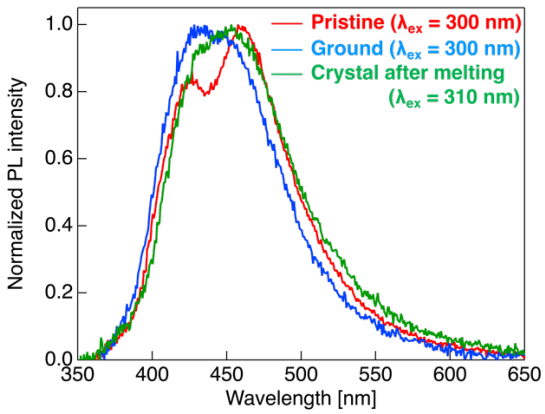


Figure S35: Excitation (dotted line) and PL spectra (solid line) of (A) **2a**, (B) **2b**, and (C) **2d** after mechanical stimulus. (D) Stimuli-responsive PL behavior of **2a**; pristine crystalline powder (red), after grinding (blue), and recrystalline sample after thermal treatment (green).