Supplementary Material

Effect of Fluoroalkyl-Substituent in Bistolane-Based Photoluminescent Liquid Crystals on Their Physical Behavior

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1. NMR Spectra

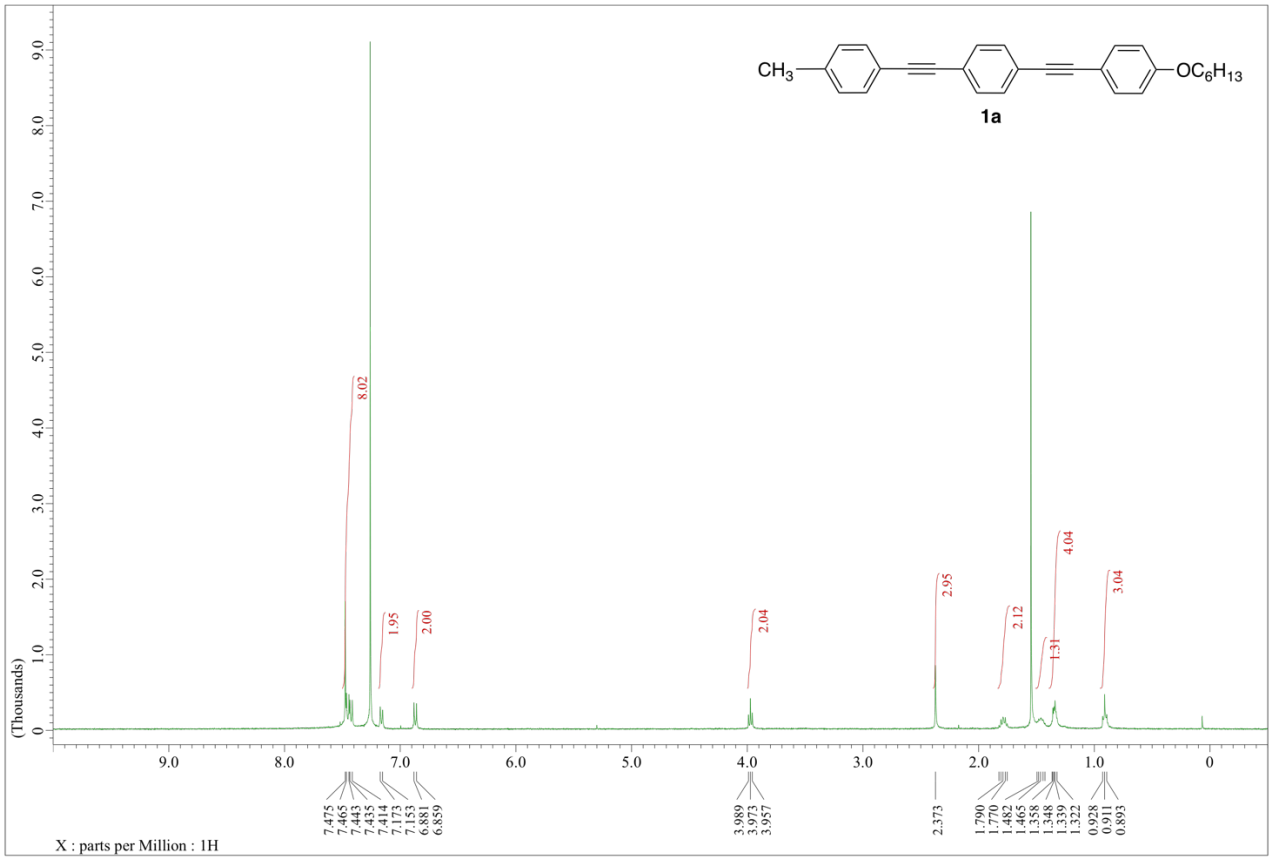


Figure S1. ^{1}H NMR spectrum of **1a** (solvent: $CDCl_3$).

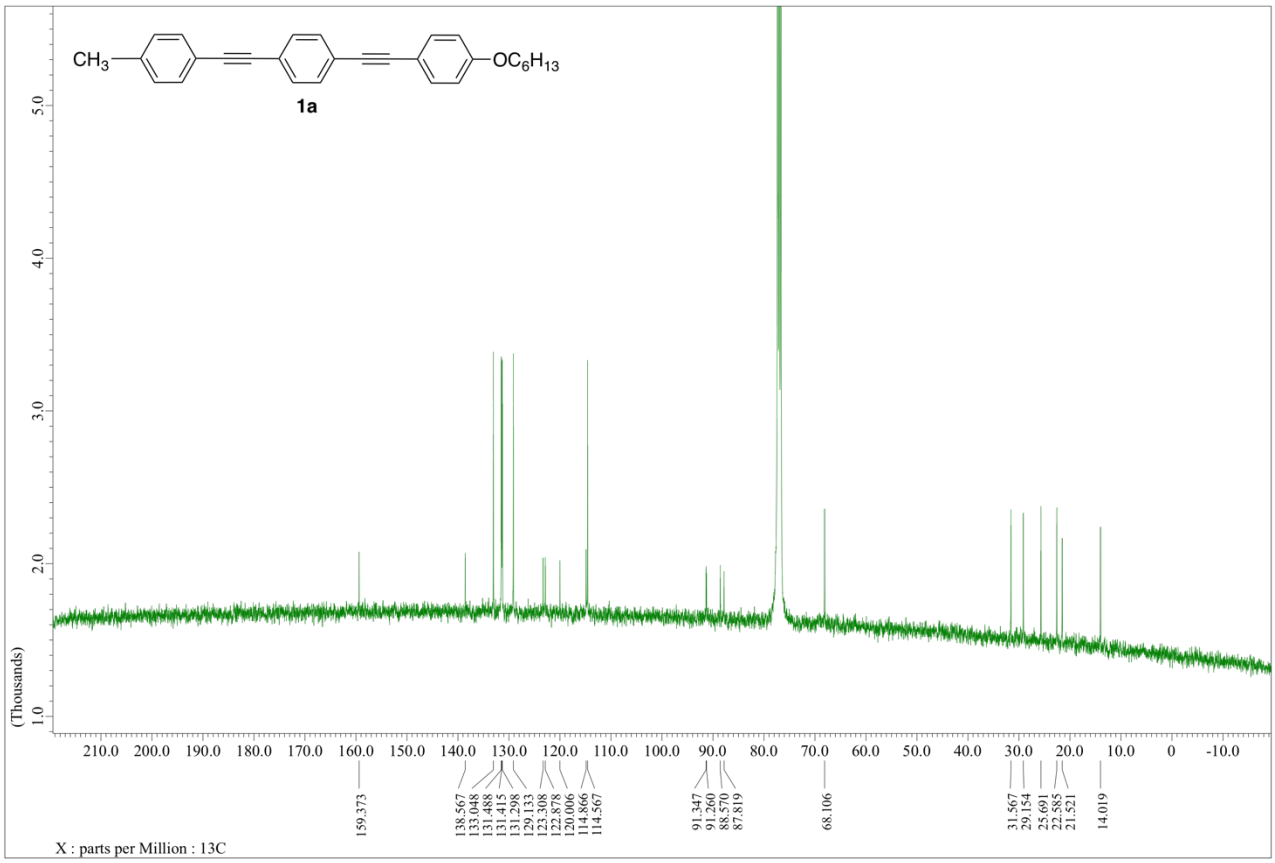


Figure S2. ^{13}C NMR spectrum of **1a** (solvent: $CDCl_3$).

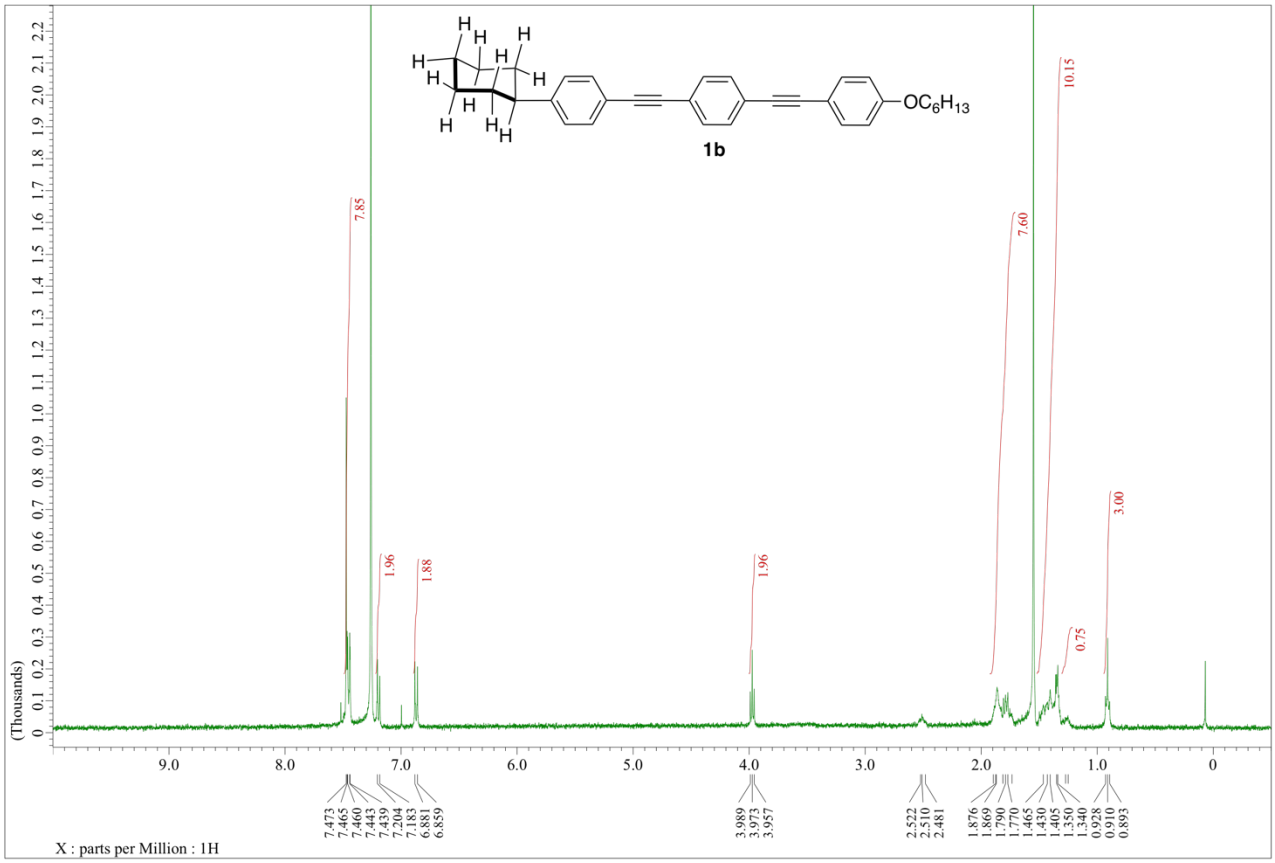


Figure S3. ^{1}H NMR spectrum of **1b** (solvent: $CDCl_3$).

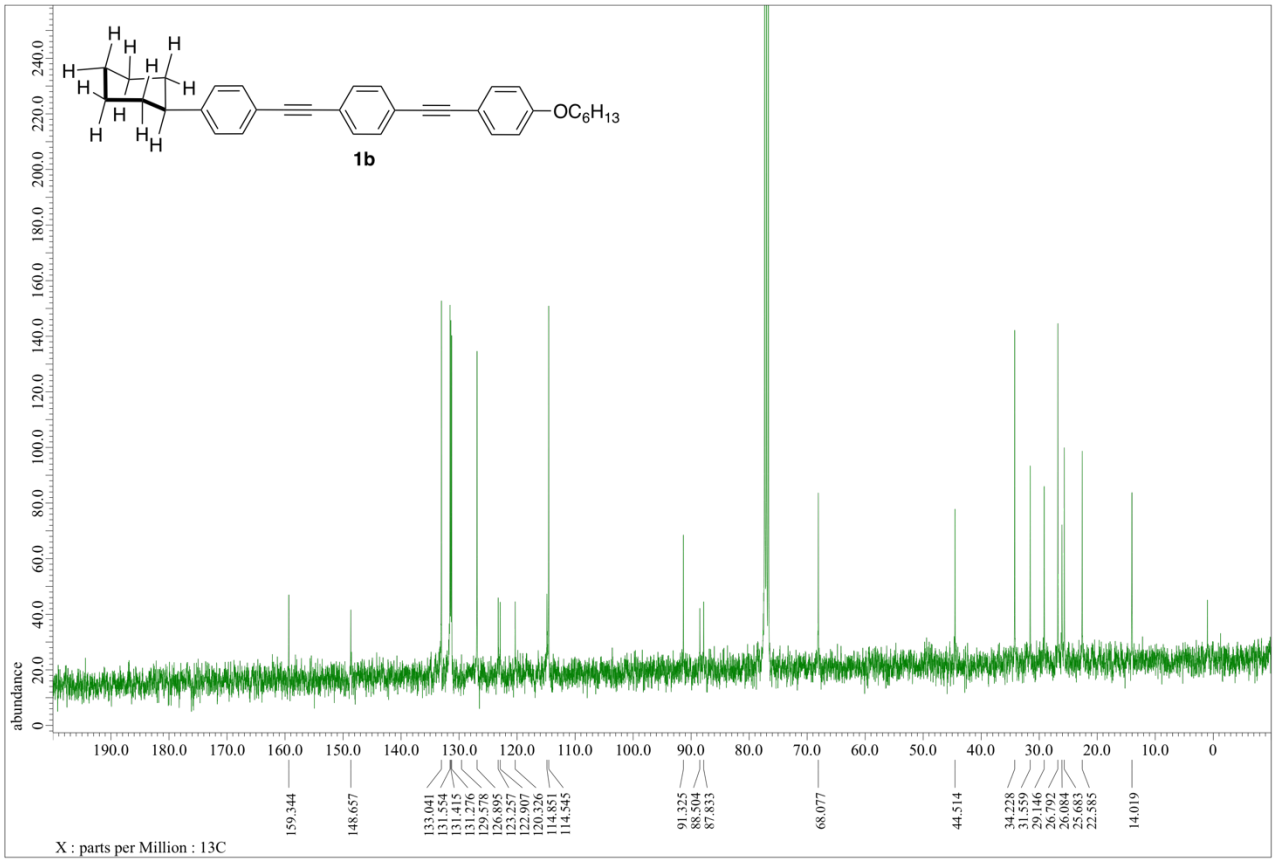


Figure S4. ^{13}C NMR spectrum of **1b** (solvent: $CDCl_3$).

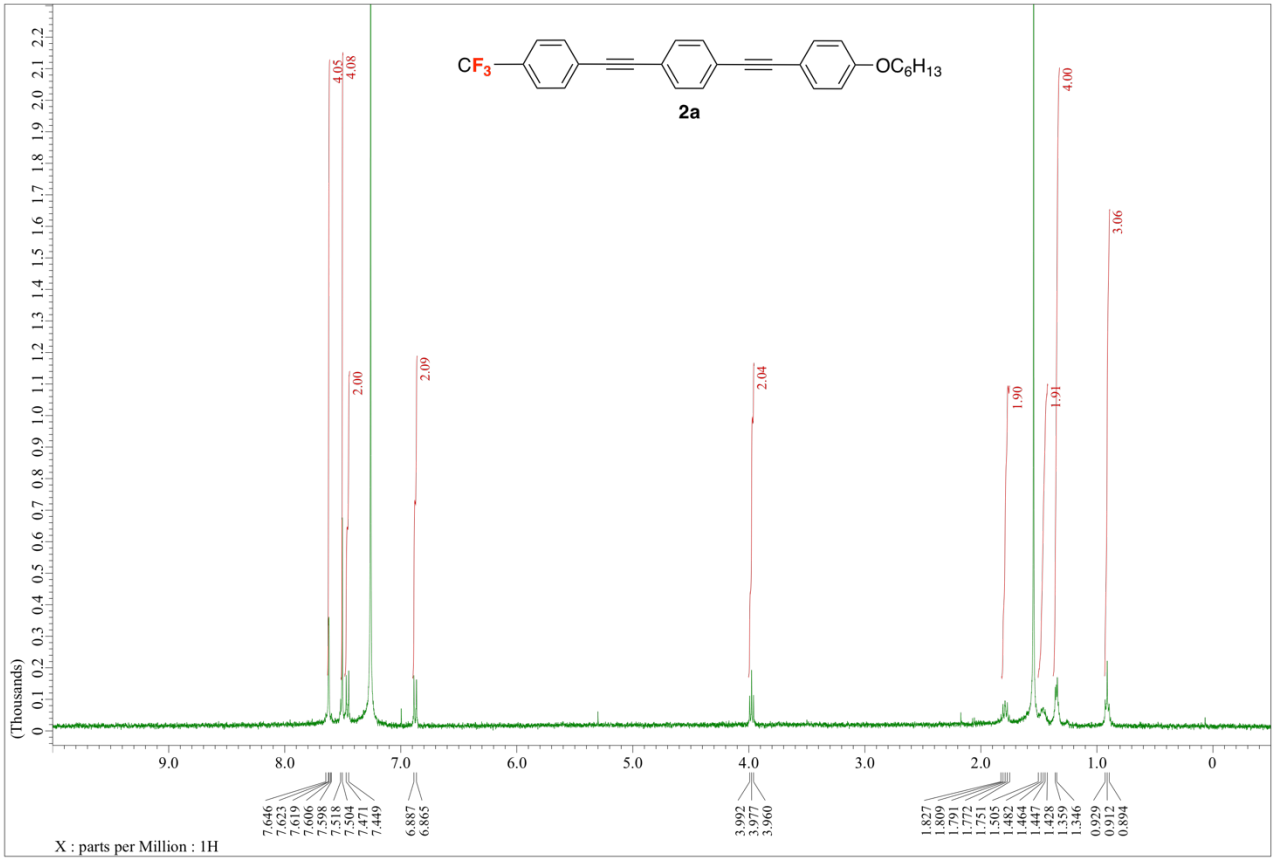


Figure S5. ^{1}H NMR spectrum of **2a** (solvent: $CDCl_3$).

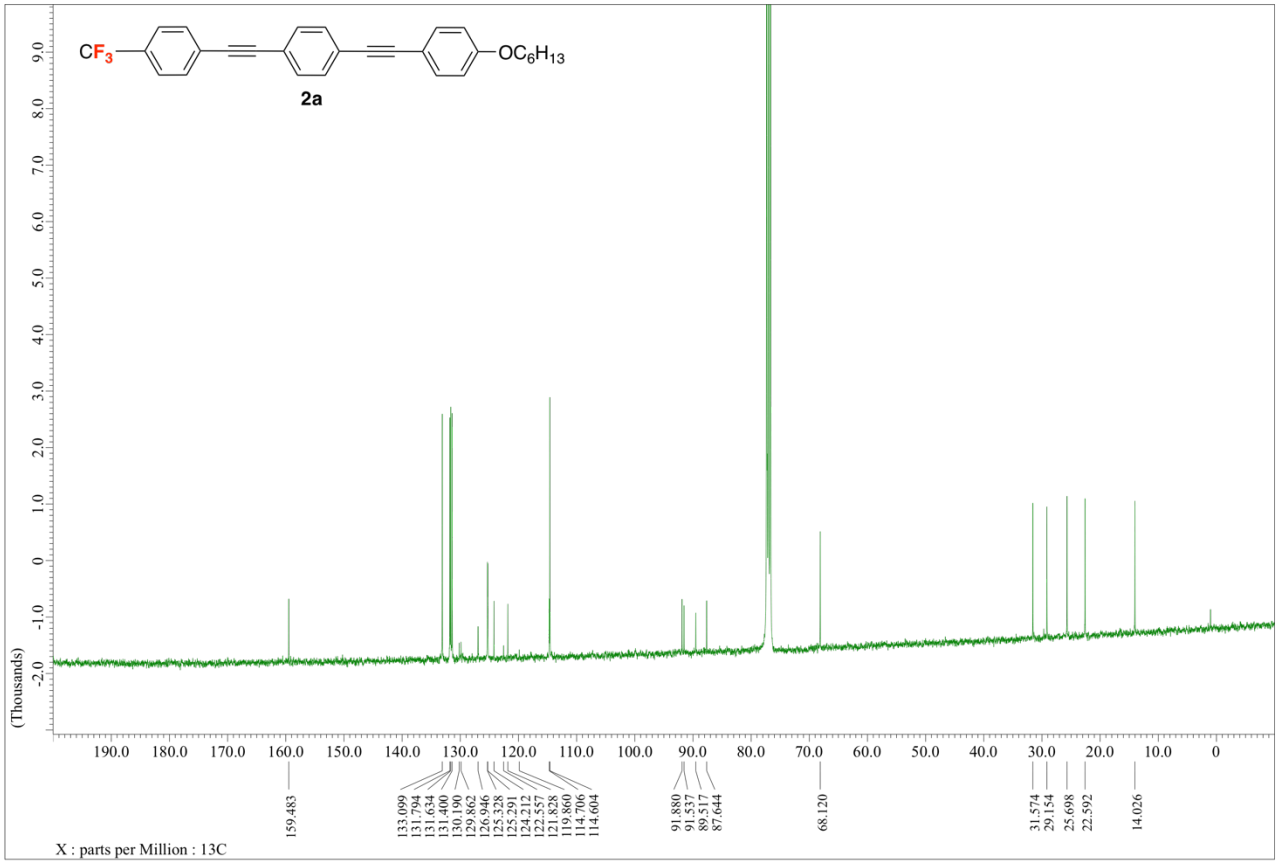


Figure S6. ^{13}C NMR spectrum of **2a** (solvent: $CDCl_3$).

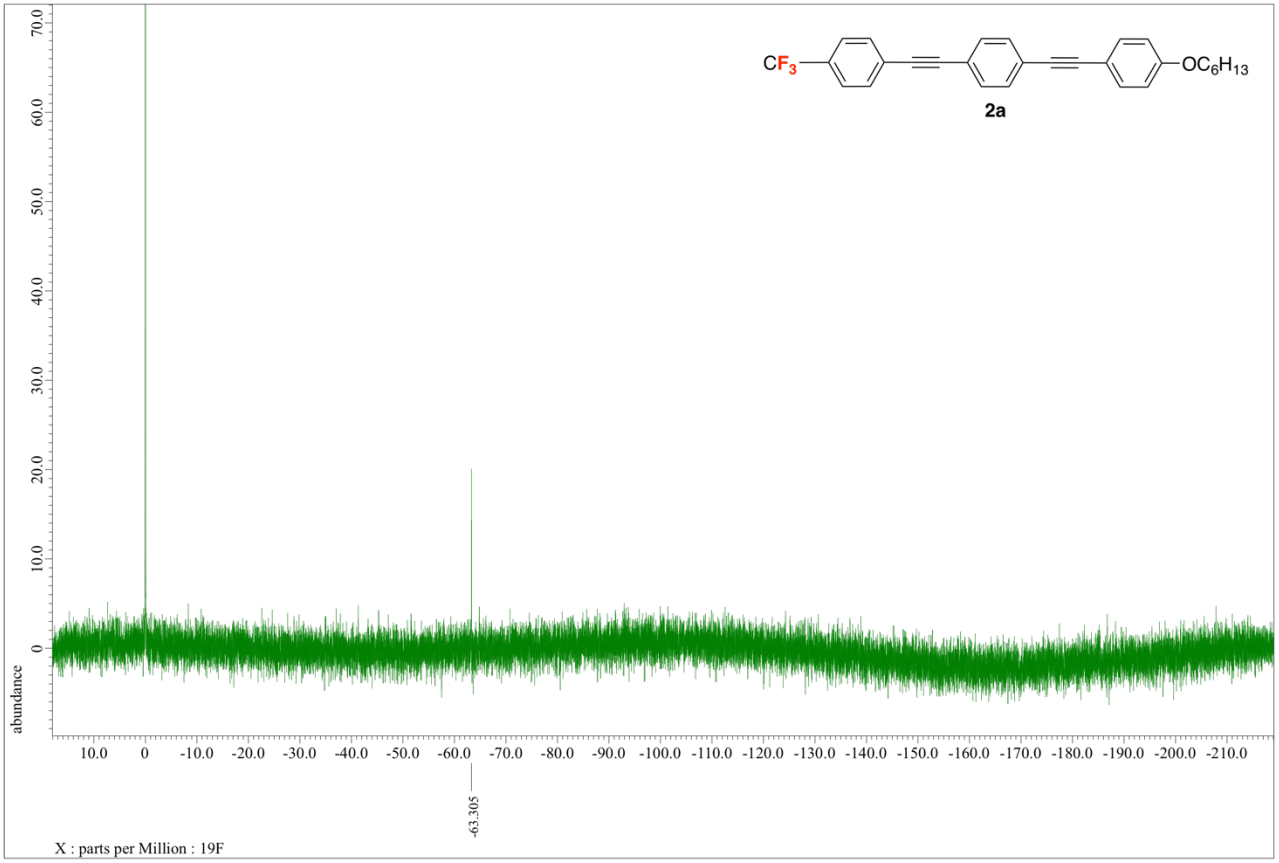


Figure S7. ^{19}F NMR spectrum of **2a** (solvent: $CDCl_3$; Internal reference: $CFCl_3$).

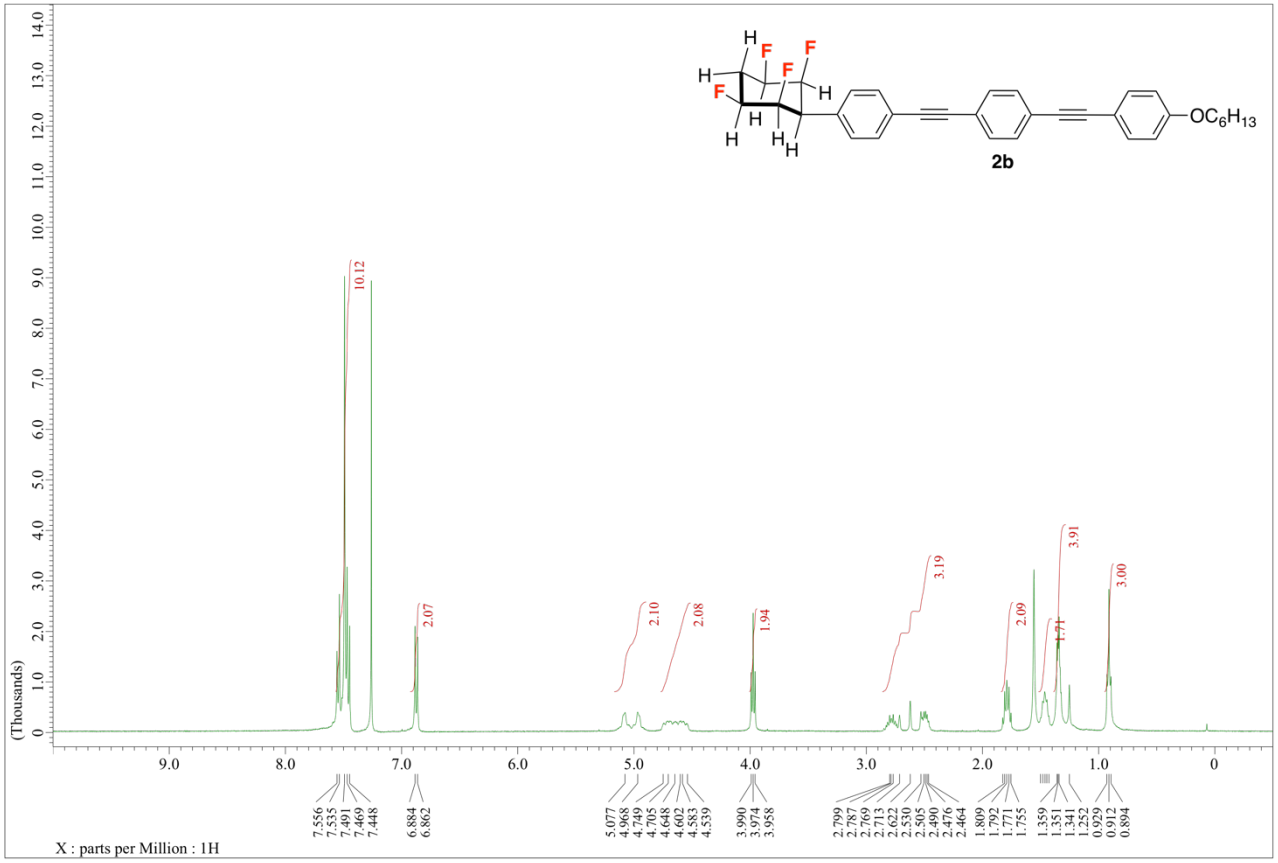


Figure S8. ^{1}H NMR spectrum of **2b** (solvent: $CDCl_3$).

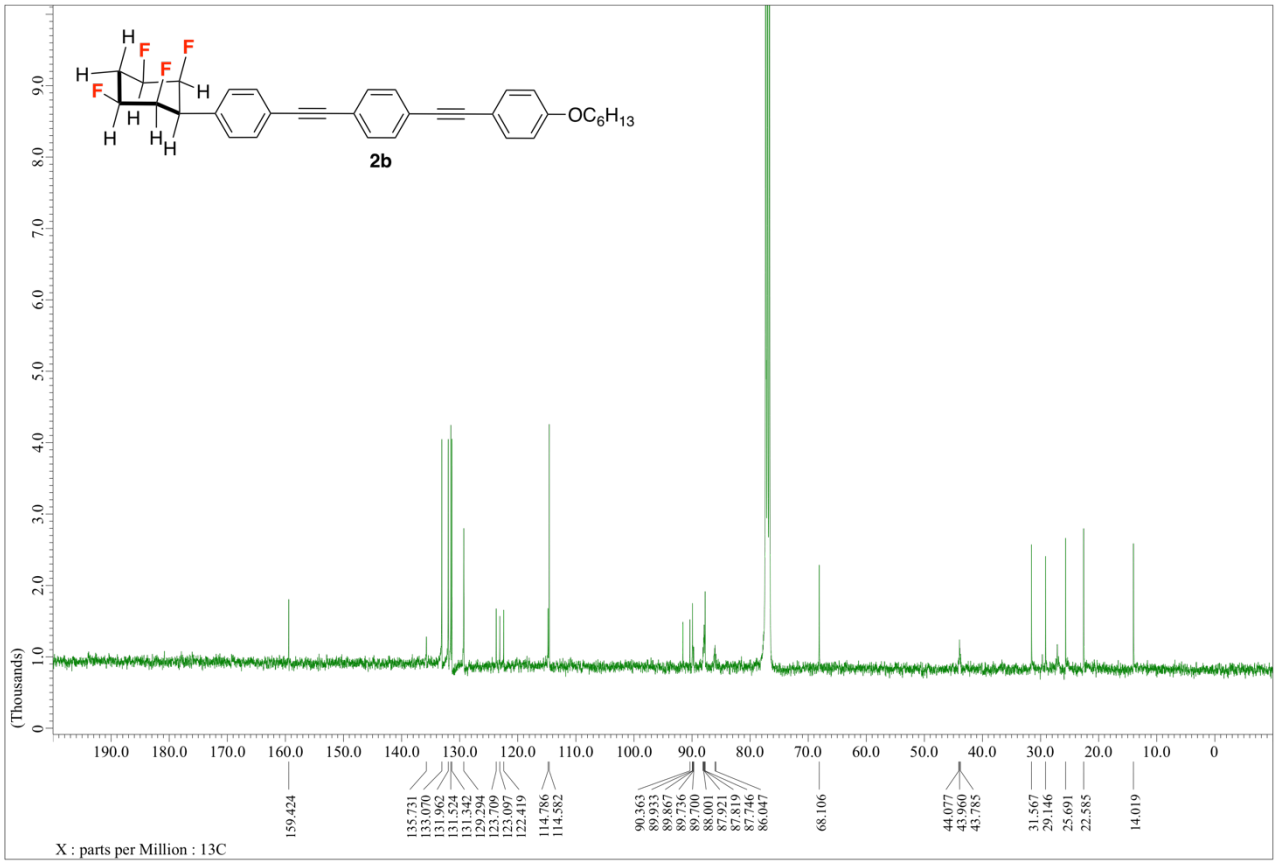


Figure S9. ^{13}C NMR spectrum of **2b** (solvent: $CDCl_3$).

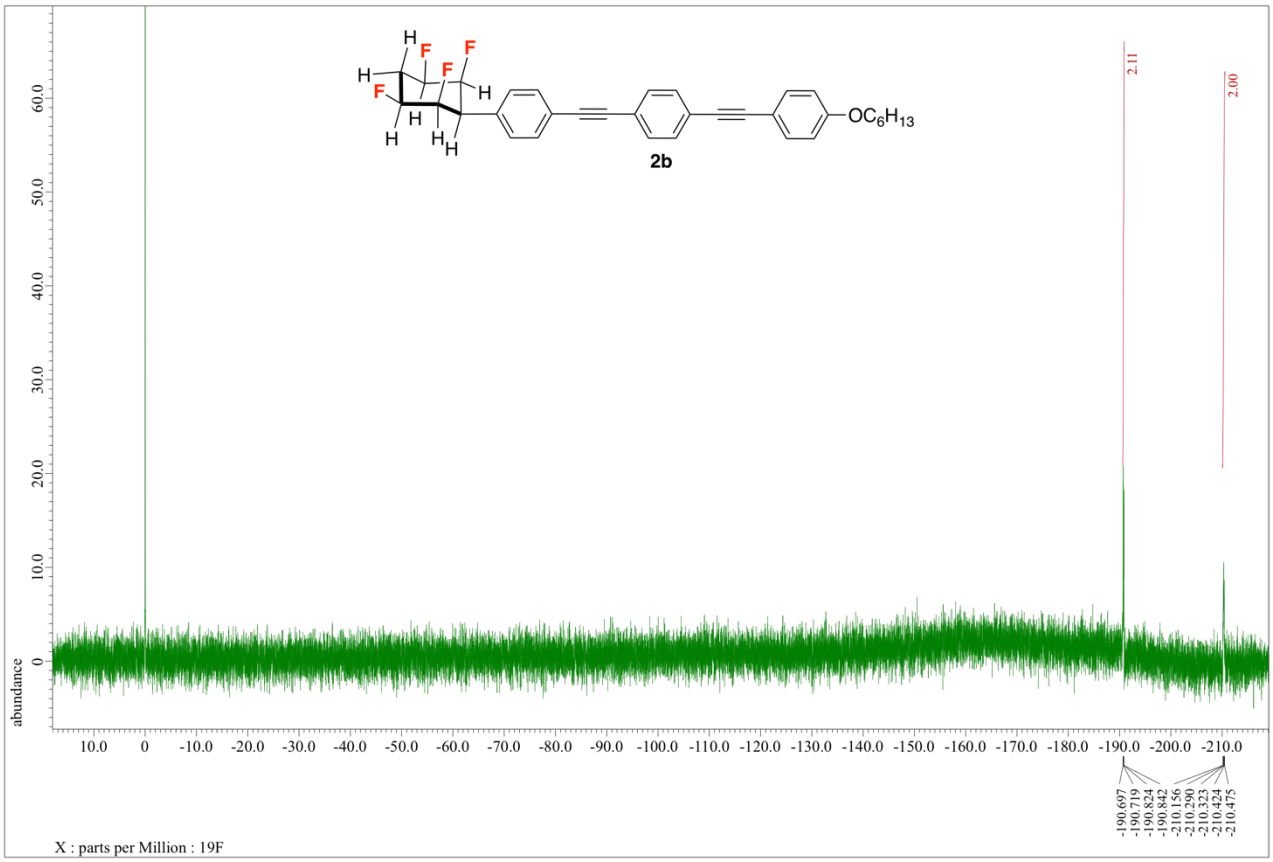


Figure S10. ^{19}F NMR spectrum of **2b** (solvent: $CDCl_3$; Internal reference: $CFCl_3$).

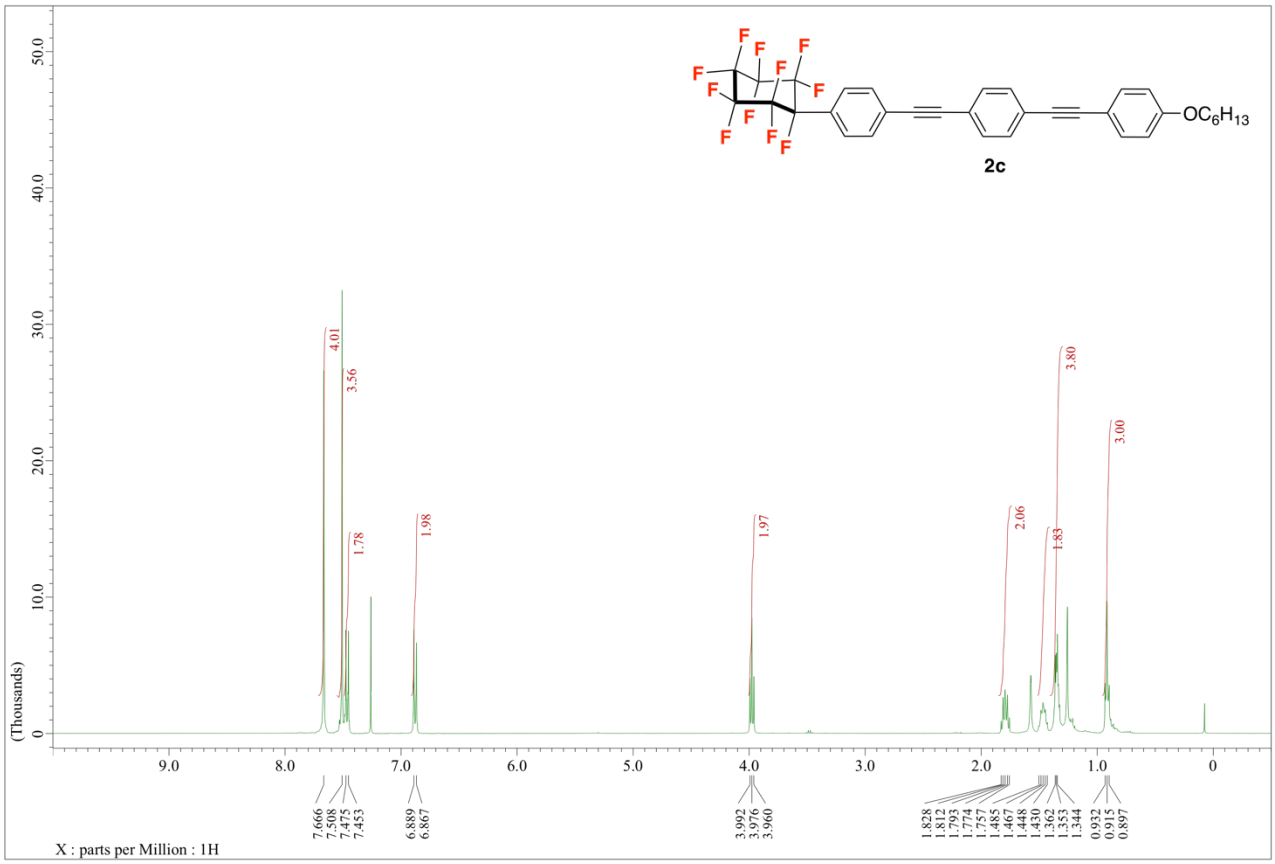


Figure S11. ^{1}H NMR spectrum of **2c** (solvent: $CDCl_3$).

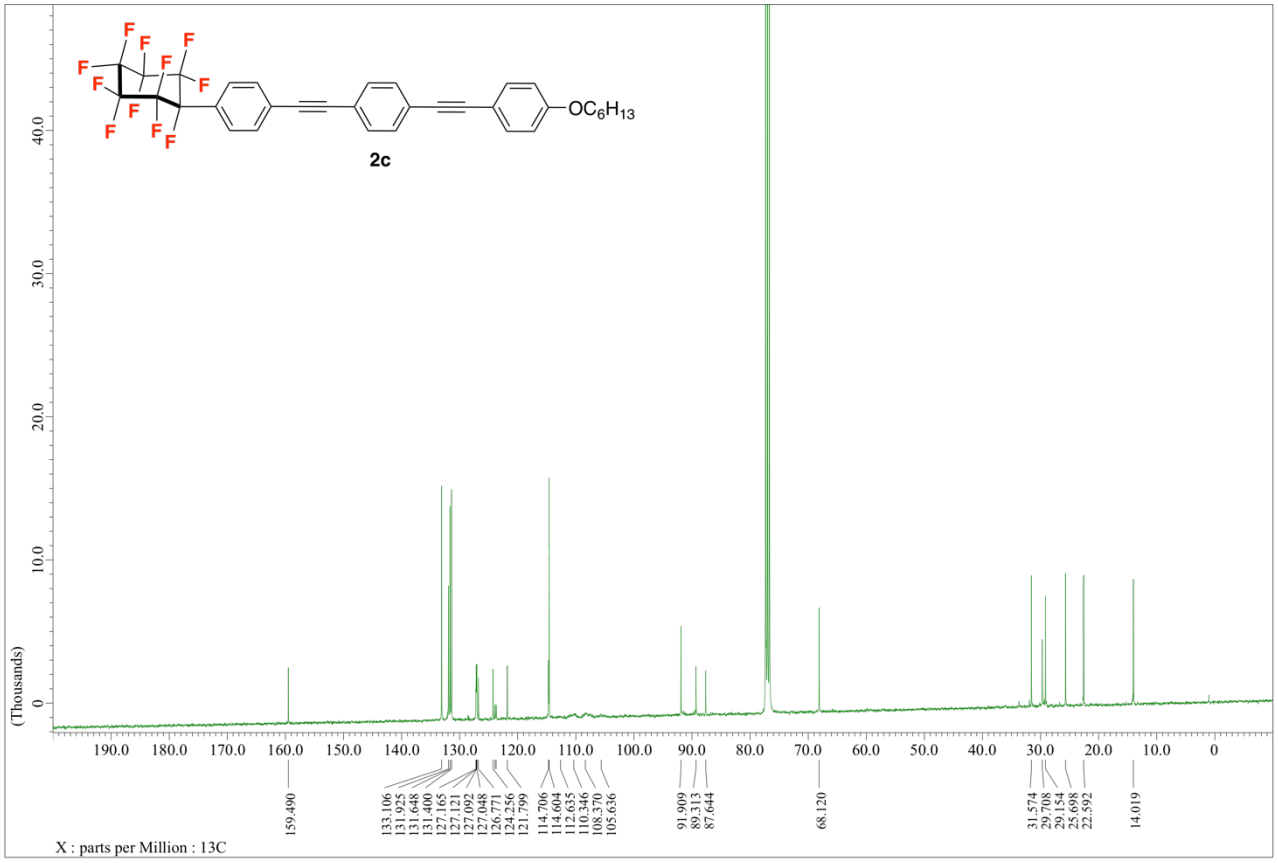


Figure S12. ^{13}C NMR spectrum of **2c** (solvent: $CDCl_3$).

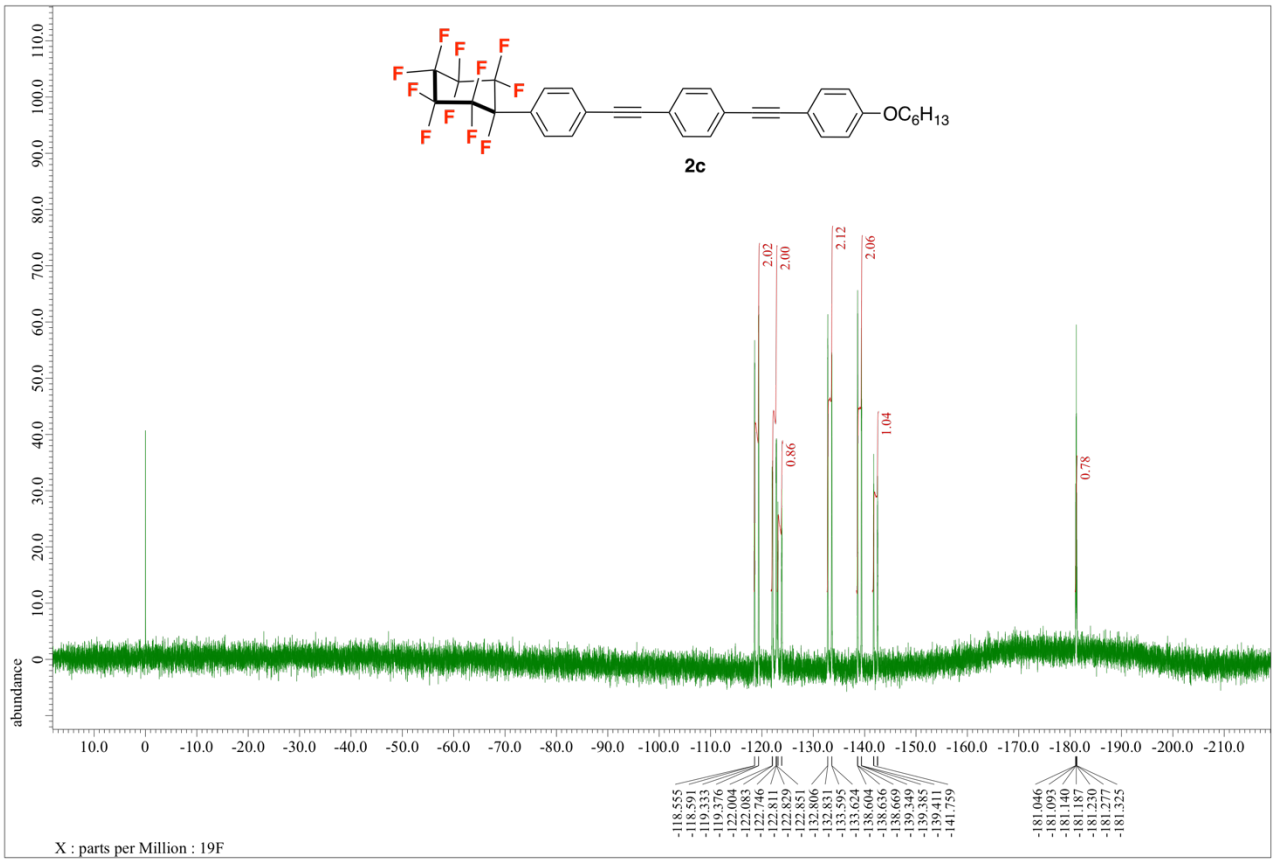


Figure S13. ^{19}F NMR spectrum of **2c** (solvent: $CDCl_3$; Internal reference: $CFCl_3$).

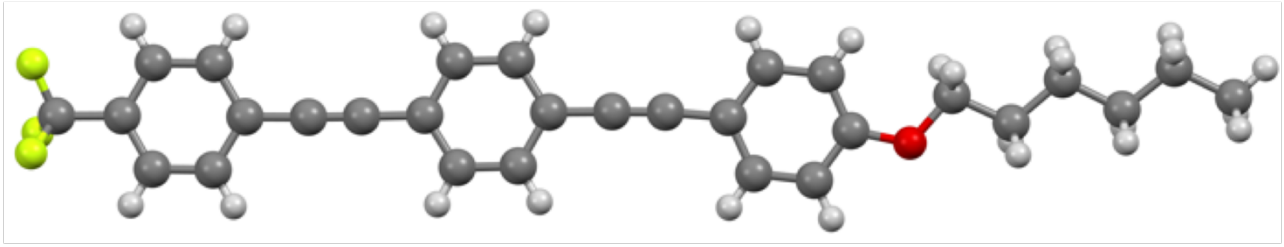
2. Crystallography

Table S1. Crystallographic data

	2a	**2c**
CCDC No.	2065068	2065069
Empirical formula	$C_{29}H_{25}F_3O$	$C_{34}H_{25}F_{11}O$
Formula weight	446.49	658.54
Temperature [K]	173(2)	173(2)
Crystal color / Habit	Colourless / Rod	Colourless / Block
Crystal size [mm]	0.19 x 0.10 x 0.09	0.24 x 0.22 x 0.12
Crystal system	monoclinic	Monoclinic
Space group	*Cc*	$P2_1$
a [Å]	51.666(2)	10.7246(3)
b [Å]	7.3498(3)	7.5494(2)
c [Å]	6.1422(3)	36.5923(8)
α [°]	90	90
β [°]	92.441(4)	91.468(2)
γ [°]	90	90
V [Å^3]	2330.29(17)	2961.70(13)
Z	4	4
R [$F^2 > 2\sigma(F^2)$] [a]	0.0320	0.0320
wR (F^2) [b]	0.0893	0.0825

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

(a)



(b)

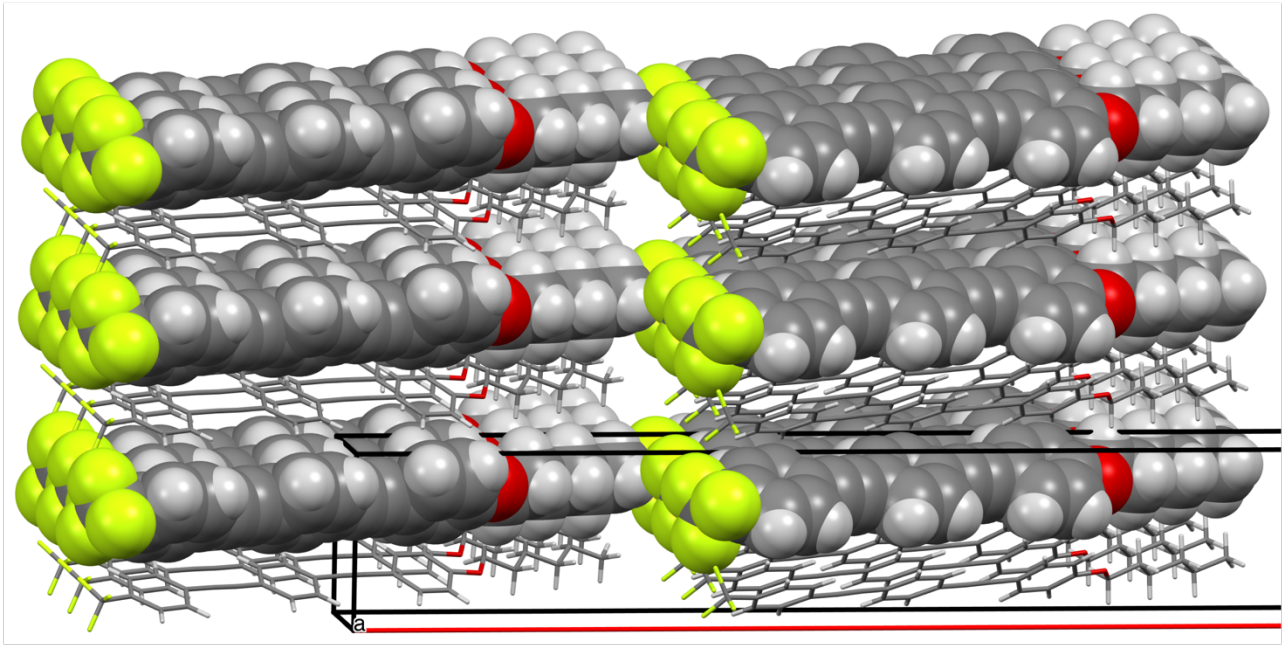


Figure S14. (a) Crystal structures and (b) packing structures of **2a**.

(a)

(b)

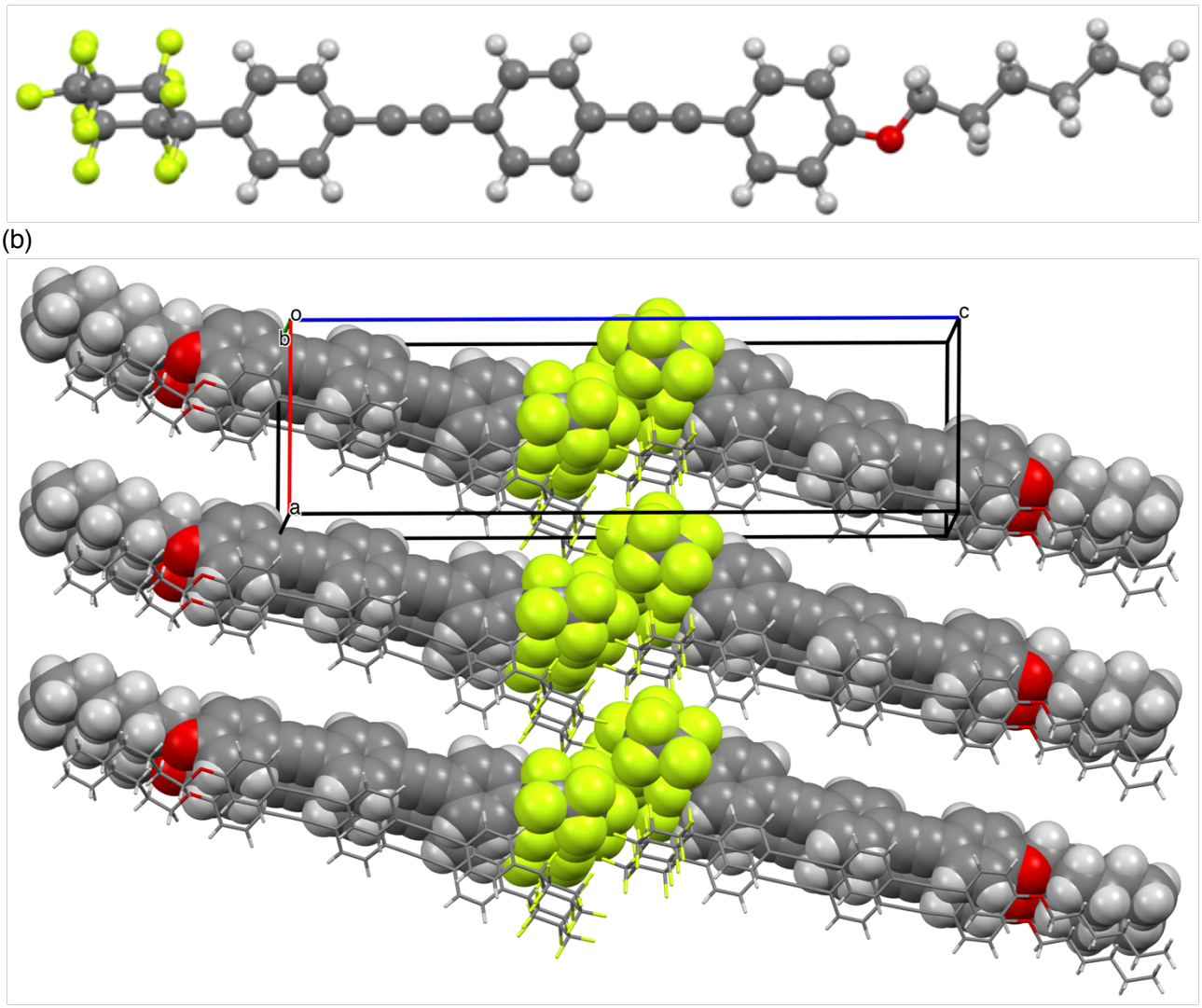
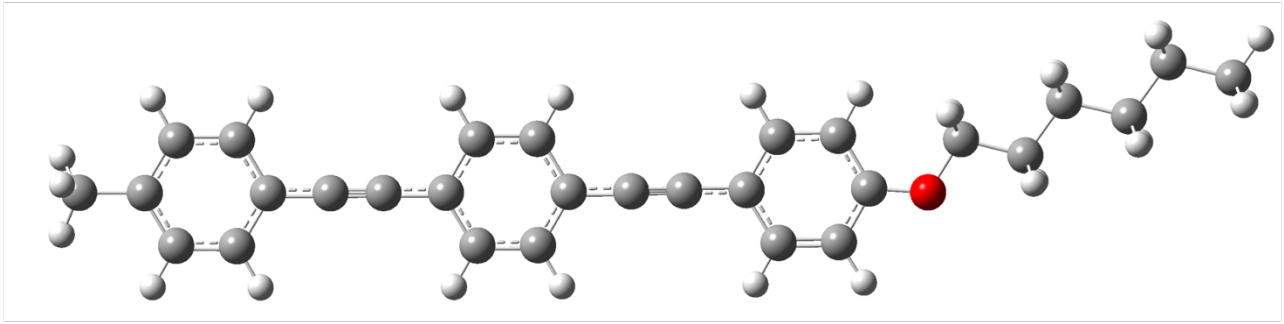


Figure S15. (a) Crystal structures and (b) packing structures of **2c**.

3. Quantum chemical calculation

All computations were performed using the Gaussian 16 (*Revision* B.01) software package. Geometry optimizations were carried out using the hybrid meta GGA functional (M06-2X) 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 self-consistent field (TD-SCF) approximation at the same level of theory.

Compound **1a** (R = CH_3)



SCF Done: E(RM062X) = -1196.59584706 A.U. after 7 cycles
Dipole moment (field-independent basis, Debye):
X= 0.9606 Y= -1.7952 Z= -0.0406 Tot= 2.0365

TD-SCF approximation (Energy calculation) at M06-2X/6-31+G(d) with CPCM (CH_2Cl_2)
Excited State 1: Singlet-A 3.7531 eV 330.35 nm f=2.4831 <S**2>=0.000
104 ->107 0.13791
105 ->106 0.67914

TD-SCF approximation (Optimization calculation) at M06-2X/6-31+G(d) with CPCM (CH_2Cl_2)
Excited State 1: Singlet-A 3.0201 eV 410.54 nm f=2.6800 <S**2>=0.000
104 ->107 -0.11500
105 ->106 0.68998

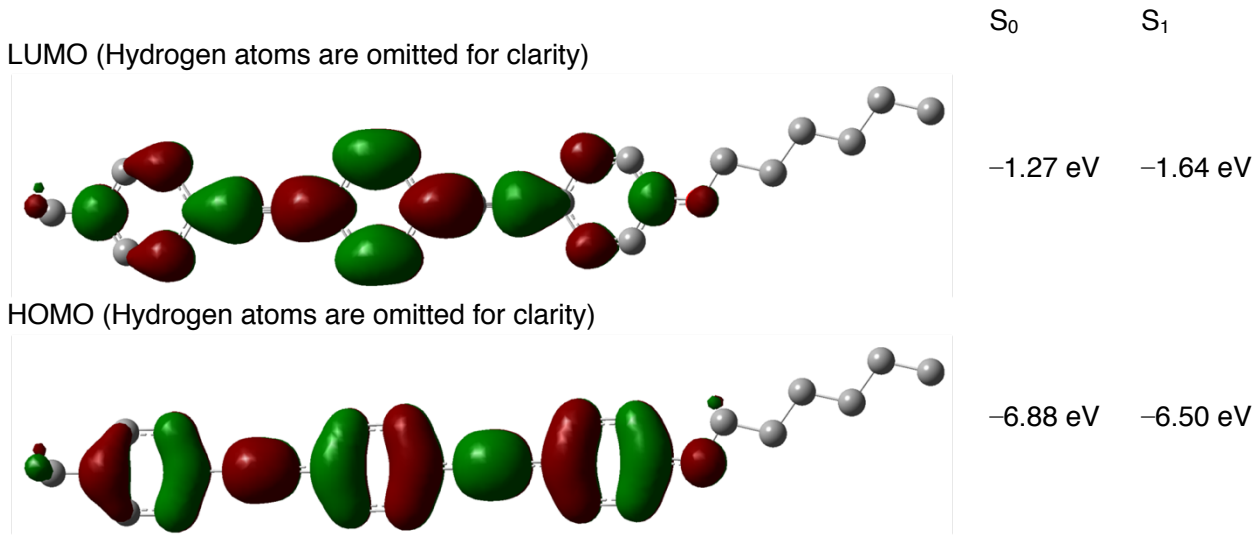


Figure S16. Optimized structure, HOMO and LUMO of **1a** and their orbital energies (eV). Computed with M06-2X/6-31+G(d).

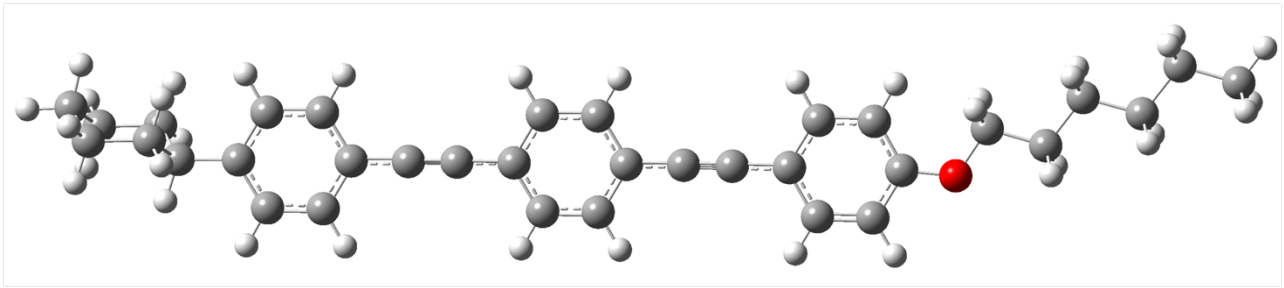
Table S2. Cartesian Coordinates of **1a** (S_0 state)

No.	Atom No.	Type	Coordinates (Angstroms) x	y	z
1	6	0	13.656952	-1.010561	0.005347
2	1	0	13.864652	-0.398711	-0.879818
3	1	0	14.359902	-1.849515	0.006577
4	1	0	13.863065	-0.397448	0.890007
5	6	0	12.207444	-1.492606	0.004397
6	1	0	12.029143	-2.125911	-0.874865
7	1	0	12.027582	-2.124664	0.884238
8	6	0	11.206099	-0.338603	0.00269
9	1	0	11.383975	0.294906	-0.878101
10	1	0	11.382482	0.296205	0.882845
11	6	0	9.75219	-0.808007	0.001812
12	1	0	9.577156	-1.442088	-0.87867
13	1	0	9.575659	-1.440695	0.882997
14	6	0	8.759054	0.353534	0.00005
15	1	0	8.919102	0.984867	0.882959
16	1	0	8.920458	0.983361	-0.883687
17	6	0	7.324297	-0.136109	-0.000616
18	1	0	7.121273	-0.745657	-0.891492
19	1	0	7.119936	-0.744095	0.891025
20	8	0	6.470085	1.00561	-0.002246
21	6	0	5.129757	0.806853	-0.002591
22	6	0	4.338226	1.965467	-0.003725
23	1	0	4.830426	2.933043	-0.004298
24	6	0	2.95799	1.867159	-0.004039
25	1	0	2.350756	2.767239	-0.004863
26	6	0	2.329171	0.607194	-0.003262
27	6	0	3.129565	-0.542093	-0.002227
28	1	0	2.658346	-1.520356	-0.001632
29	6	0	4.519746	-0.452383	-0.001881
30	1	0	5.108462	-1.361961	-0.001039
31	6	0	0.901568	0.503768	-0.003359
32	6	0	-0.309686	0.416209	-0.003273
33	6	0	-1.736761	0.307875	-0.002856
34	6	0	-2.540329	1.460984	-0.000731
35	1	0	-2.0699	2.439272	0.000415
36	6	0	-3.923701	1.354081	0.000014
37	1	0	-4.538937	2.248423	0.001733
38	6	0	-4.540526	0.09139	-0.001377
39	6	0	-3.737168	-1.061728	-0.003659
40	1	0	-4.207747	-2.039957	-0.004774
41	6	0	-2.353937	-0.954908	-0.004368
42	1	0	-1.738722	-1.849244	-0.006034
43	6	0	-5.967662	-0.019697	-0.000275
44	6	0	-7.177967	-0.116313	0.001395
45	6	0	-8.605745	-0.234893	0.002724
46	6	0	-9.418216	0.909023	0.010704
47	1	0	-8.956958	1.892113	0.016588
48	6	0	-10.804123	0.783801	0.01491
49	1	0	-11.420082	1.67964	0.024145
50	6	0	-11.418394	-0.473253	0.009187
51	6	0	-10.600197	-1.610634	0.004069
52	1	0	-11.057515	-2.5973	0.004776
53	6	0	-9.215007	-1.500871	-0.000111
54	1	0	-8.594073	-2.391776	-0.002648
55	6	0	-12.919282	-0.607497	-0.012862
56	1	0	-13.253408	-1.410996	0.650175
57	1	0	-13.404778	0.321415	0.297427
58	1	0	-13.271087	-0.848093	-1.022543

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

No.	Atom No.	Type	Coordinates (Angstroms) x	y	z
1	6	0	-13.640161	-0.971979	-0.009374
2	1	0	-13.843839	-0.356555	0.874235
3	1	0	-14.35003	-1.805063	-0.009699
4	1	0	-13.840055	-0.359091	-0.895607
5	6	0	-12.194768	-1.46618	-0.00558
6	1	0	-12.022811	-2.098982	0.875283
7	1	0	-12.019079	-2.101552	-0.883856
8	6	0	-11.184008	-0.320416	-0.005125
9	1	0	-11.357578	0.316392	0.8741
10	1	0	-11.353911	0.313828	-0.886914
11	6	0	-9.734178	-0.802298	-0.001429
12	1	0	-9.565369	-1.435524	0.880797
13	1	0	-9.561829	-1.438269	-0.880996
14	6	0	-8.732011	0.351623	-0.00125
15	1	0	-8.885536	0.981796	-0.885983
16	1	0	-8.888768	0.984389	0.881064
17	6	0	-7.302408	-0.151608	0.002023
18	1	0	-7.102224	-0.757732	0.895254
19	1	0	-7.099287	-0.760729	-0.888504
20	8	0	-6.436649	0.985371	0.001507
21	6	0	-5.105016	0.788612	0.00299
22	6	0	-4.311757	1.955745	0.001373
23	1	0	-4.810948	2.91977	-0.000766
24	6	0	-2.939633	1.865657	0.002352
25	1	0	-2.332815	2.765712	0.000998
26	6	0	-2.292738	0.593628	0.005041
27	6	0	-3.110153	-0.569522	0.006904
28	1	0	-2.63583	-1.54599	0.009053
29	6	0	-4.490545	-0.477223	0.00589
30	1	0	-5.082967	-1.384582	0.007315
31	6	0	-0.903635	0.494932	0.005554
32	6	0	0.333235	0.406078	0.005599
33	6	0	1.708716	0.30395	0.005077
34	6	0	2.542822	1.480793	0.001688
35	1	0	2.065586	2.456084	-0.000051
36	6	0	3.903388	1.376958	0.000484
37	1	0	4.521918	2.269408	-0.002205
38	6	0	4.550275	0.090184	0.002674
39	6	0	3.718108	-1.085395	0.006461
40	1	0	4.19608	-2.060382	0.008278
41	6	0	2.357441	-0.984404	0.00758
42	1	0	1.739456	-1.87717	0.01028
43	6	0	5.930445	-0.015044	0.001014
44	6	0	7.162845	-0.112565	-0.001137
45	6	0	8.559235	-0.227544	-0.003541
46	6	0	9.388198	0.924052	-0.010595
47	1	0	8.927411	1.907332	-0.014984
48	6	0	10.767693	0.794792	-0.015754
49	1	0	11.385877	1.68936	-0.023776
50	6	0	11.385653	-0.465967	-0.012168
51	6	0	10.563917	-1.60705	-0.00813
52	1	0	11.02421	-2.592556	-0.01015
53	6	0	9.184277	-1.503115	-0.00298
54	1	0	8.564346	-2.394689	-0.001442
55	6	0	12.883736	-0.600078	0.011389
56	1	0	13.219802	-1.404114	-0.650922
57	1	0	13.370641	0.329114	-0.29636
58	1	0	13.236876	-0.842889	1.021318

Compound **1b** (R = *cyclo*-C_6H_{11})



SCF Done: E(RM062X) = -1391.87434008 A.U. after 7 cycles
Dipole moment (field-independent basis, Debye):
X= -0.6931 Y= -1.7924 Z= -0.0282 Tot= 1.9220

TD-SCF approximation (Energy calculation) at M06-2X/6-31+G(d) with CPCM (CH_2Cl_2)
Excited State 1: Singlet-A 3.7461 eV 330.97 nm f=2.5923 <S**2>=0.000
123 ->126 -0.14019
124 ->125 0.67889

TD-SCF approximation (Optimization calculation) at M06-2X/6-31+G(d) with CPCM (CH_2Cl_2)
Excited State 1: Singlet-A 3.0168 eV 410.98 nm f=2.7434 <S**2>=0.000
123 ->126 -0.11596
124 ->125 0.68990

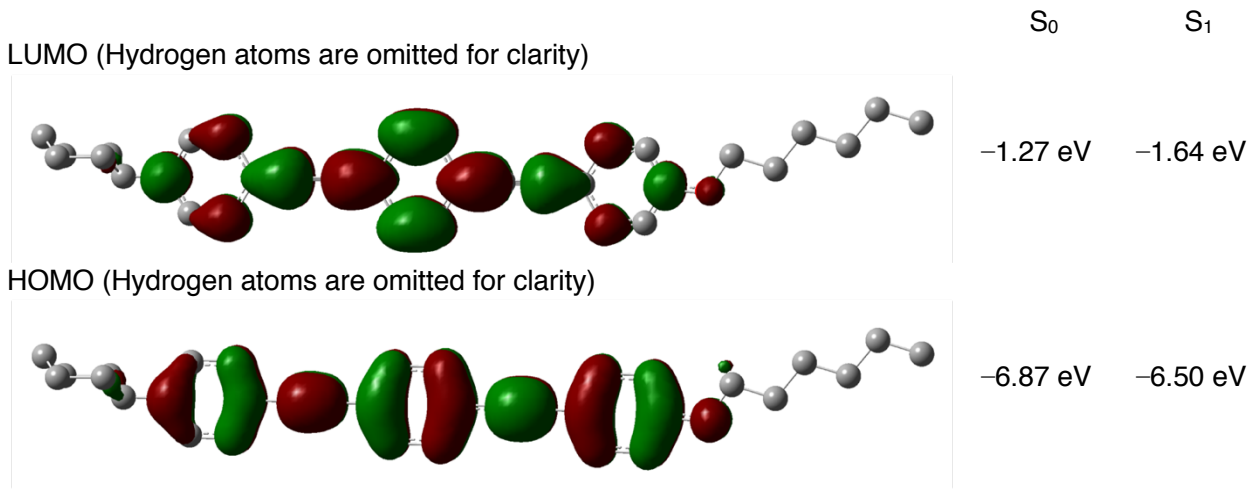


Figure S17. HOMO and LUMO of **1b** and their orbital energies (eV). Computed with M06-2X/6-31+G(d).

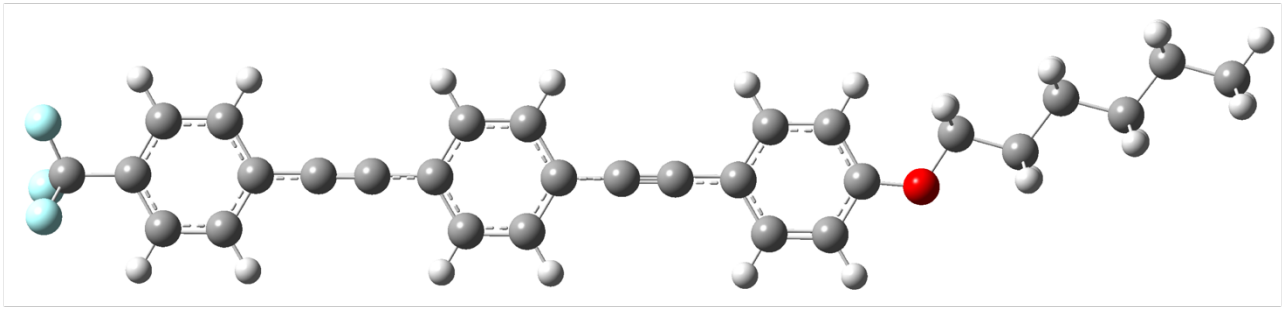
Table S4. Cartesian Coordinates of **1b** (S_0 state)

No.	Atom No.	Type	Coordinates (Angstroms) x	y	z
1	6	0	-15.877998	-1.232366	-0.126765
2	1	0	-16.120489	-0.603789	0.737599
3	1	0	-16.566819	-2.082944	-0.127691
4	1	0	-16.069106	-0.643488	-1.031032
5	6	0	-14.421374	-1.689507	-0.07419
6	1	0	-14.206812	-2.339455	-0.932962
7	1	0	-14.257227	-2.298221	0.824958
8	6	0	-13.439728	-0.518754	-0.073744
9	1	0	-13.601752	0.090701	-0.974366
10	1	0	-13.652986	0.13345	0.785275
11	6	0	-11.978588	-0.962099	-0.020641
12	1	0	-11.767744	-1.616869	-0.877803
13	1	0	-11.816209	-1.56688	0.882586
14	6	0	-11.006906	0.217292	-0.02826
15	1	0	-11.15385	0.817362	-0.934938
16	1	0	-11.204463	0.87159	0.83004
17	6	0	-9.563438	-0.24279	0.025971
18	1	0	-9.369407	-0.81227	0.944893
19	1	0	-9.325578	-0.880864	-0.835867
20	8	0	-8.733561	0.916382	0.001046
21	6	0	-7.389372	0.748134	0.023606
22	6	0	-6.75088	-0.495237	0.087777
23	1	0	-7.318824	-1.417188	0.126221
24	6	0	-5.358932	-0.552529	0.102472
25	1	0	-4.865615	-1.518615	0.151334
26	6	0	-4.585157	0.613749	0.054187
27	6	0	-5.242689	1.857559	-0.00769
28	1	0	-4.656119	2.770475	-0.045243
29	6	0	-6.624614	1.923664	-0.022497
30	1	0	-7.138811	2.878479	-0.071438
31	6	0	-3.155448	0.54625	0.063203
32	6	0	-1.94209	0.495431	0.066455
33	6	0	0.157745	-0.791119	0.138835
34	1	0	-0.419012	-1.708641	0.201204
35	6	0	1.544366	-0.839996	0.131723
36	1	0	2.055624	-1.795922	0.188554
37	6	0	2.298425	0.343077	0.050225
38	6	0	1.628971	1.576658	-0.022004
39	1	0	2.205909	2.49406	-0.084808
40	6	0	0.242546	1.625591	-0.015009
41	1	0	-0.268729	2.581457	-0.072392
42	6	0	-0.511915	0.442333	0.064542
43	6	0	3.728914	0.293182	0.038475
44	6	0	4.942342	0.252916	0.025161
45	6	0	6.374249	0.209482	0.007584
46	6	0	7.052794	-1.019702	0.063369
47	1	0	6.481918	-1.941763	0.121065
48	6	0	8.441611	-1.05503	0.044432
49	1	0	8.943534	-2.018685	0.087745
50	6	0	9.197957	0.123777	-0.029491
51	6	0	8.512981	1.342737	-0.084486
52	1	0	9.079011	2.269501	-0.142546
53	6	0	7.122343	1.393723	-0.06692
54	1	0	6.608137	2.349243	-0.110752
55	6	0	10.709489	0.081717	-0.051945
56	6	0	11.288208	-0.545363	1.228406
57	6	0	12.818819	-0.553946	1.201601
58	6	0	13.346465	-1.279069	-0.038872
59	6	0	12.775609	-0.662852	-1.318367
60	6	0	11.244959	-0.653797	-1.293126
61	1	0	11.068524	1.120701	-0.102799
62	1	0	10.846763	-0.183306	-2.200278
63	1	0	14.442024	-1.250796	-0.05883
64	1	0	13.054979	-2.338249	0.011947
65	1	0	10.920419	0.001221	2.105205
66	1	0	13.185352	0.482715	1.197563
67	1	0	13.140448	0.369806	-1.416245
68	1	0	10.876762	-1.690038	-1.282887
69	1	0	10.922907	-1.57854	1.319923
70	1	0	13.205948	-1.023901	2.112992
71	1	0	13.131802	-1.210079	-2.198711

Table S5. Cartesian Coordinates of **1b** (S_1 state)

No.	Atom No.	Type	Coordinates (Angstroms) x	y	z
1	6	0	15.849018	-1.229888	0.066254
2	1	0	16.078419	-0.604489	-0.803954
3	1	0	16.540295	-2.078453	0.062026
4	1	0	16.050015	-0.636458	0.965385
5	6	0	14.39326	-1.691647	0.03453
6	1	0	14.191527	-2.337754	0.899281
7	1	0	14.219554	-2.305389	-0.85937
8	6	0	13.408353	-0.523663	0.040459
9	1	0	13.580014	0.091182	0.935555
10	1	0	13.608457	0.124302	-0.824884
11	6	0	11.948094	-0.971937	0.00853
12	1	0	11.749332	-1.620309	0.873354
13	1	0	11.776577	-1.584072	-0.887929
14	6	0	10.973612	0.205325	0.018048
15	1	0	11.130234	0.814105	0.917117
16	1	0	11.15759	0.851512	-0.849186
17	6	0	9.531987	-0.261474	-0.013543
18	1	0	9.327032	-0.841772	-0.92271
19	1	0	9.302577	-0.885135	0.860411
20	8	0	8.696393	0.897603	0.003429
21	6	0	7.359974	0.73725	-0.009576
22	6	0	6.710773	-0.51047	-0.048011
23	1	0	7.277837	-1.433671	-0.071122
24	6	0	5.328198	-0.564173	-0.056762
25	1	0	4.827103	-1.526725	-0.086119
26	6	0	4.543544	0.62072	-0.027437
27	6	0	5.225388	1.873742	0.00965
28	1	0	4.643785	2.790024	0.031908
29	6	0	6.599439	1.92555	0.01821
30	1	0	7.125182	2.874905	0.047187
31	6	0	3.151927	0.562414	-0.033088
32	6	0	1.912956	0.513963	-0.035351
33	6	0	-0.163673	-0.799066	-0.069216
34	1	0	0.419062	-1.7148	-0.09714
35	6	0	-1.527332	-0.847302	-0.065821
36	1	0	-2.04267	-1.802722	-0.091066
37	6	0	-2.313326	0.359121	-0.028485
38	6	0	-1.616814	1.619504	0.003192
39	1	0	-2.200179	2.534911	0.030548
40	6	0	-0.253321	1.670349	-0.00018
41	1	0	0.261488	2.626017	0.024468
42	6	0	0.534431	0.462613	-0.035513
43	6	0	-3.696338	0.309341	-0.022184
44	6	0	-4.932011	0.265989	-0.0153
45	6	0	-6.331934	0.219582	-0.005896
46	6	0	-7.021589	-1.022332	-0.034588
47	1	0	-6.447586	-1.943717	-0.064797
48	6	0	-8.404367	-1.057604	-0.024092
49	1	0	-8.904865	-2.022944	-0.046255
50	6	0	-9.169655	0.123449	0.014747
51	6	0	-8.485912	1.349902	0.042922
52	1	0	-9.058462	2.274182	0.073268
53	6	0	-7.101774	1.410792	0.033251
54	1	0	-6.592365	2.369567	0.055623
55	6	0	-10.677961	0.075022	0.027408
56	6	0	-11.245443	-0.583804	-1.243921
57	6	0	-12.776163	-0.600028	-1.227719
58	6	0	-13.309404	-1.301302	0.02382
59	6	0	-12.751365	-0.654456	1.293667
60	6	0	-11.22063	-0.638071	1.280358
61	1	0	-11.043449	1.112641	0.053327
62	1	0	-10.832164	-0.146174	2.180197
63	1	0	-14.405208	-1.278382	0.035075
64	1	0	-13.012072	-2.359734	-0.001984
65	1	0	-10.874491	-0.053818	-2.129401
66	1	0	-13.148053	0.434506	-1.248813
67	1	0	-13.122219	0.378093	1.366635
68	1	0	-10.84703	-1.672241	1.294825
69	1	0	-10.873468	-1.616468	-1.310323
70	1	0	-13.153559	-1.091487	-2.131893
71	1	0	-13.111023	-1.18452	2.183143

Compound **2a** (R = CF_3)



SCF Done: E(RM062X) = -1494.25488395 A.U. after 7 cycles
Dipole moment (field-independent basis, Debye):
X= 6.1945 Y= -1.4880 Z= -0.0717 Tot= 6.3712

TD-SCF approximation (Energy calculation) at M06-2X/6-31+G(d) with CPCM (CH_2Cl_2)
Excited State 1: Singlet-A 3.7172 eV 333.54 nm f=2.3994 <S**2>=0.000
116 ->118 -0.14513
116 ->119 -0.10752
117 ->118 0.65997
117 ->119 -0.13713

TD-SCF approximation (Optimization calculation) at M06-2X/6-31+G(d) with CPCM (CH_2Cl_2)
Excited State 1: Singlet-A 2.9739 eV 416.91 nm f=2.6217 <S**2>=0.000
116 ->119 -0.10285
117 ->118 0.68245

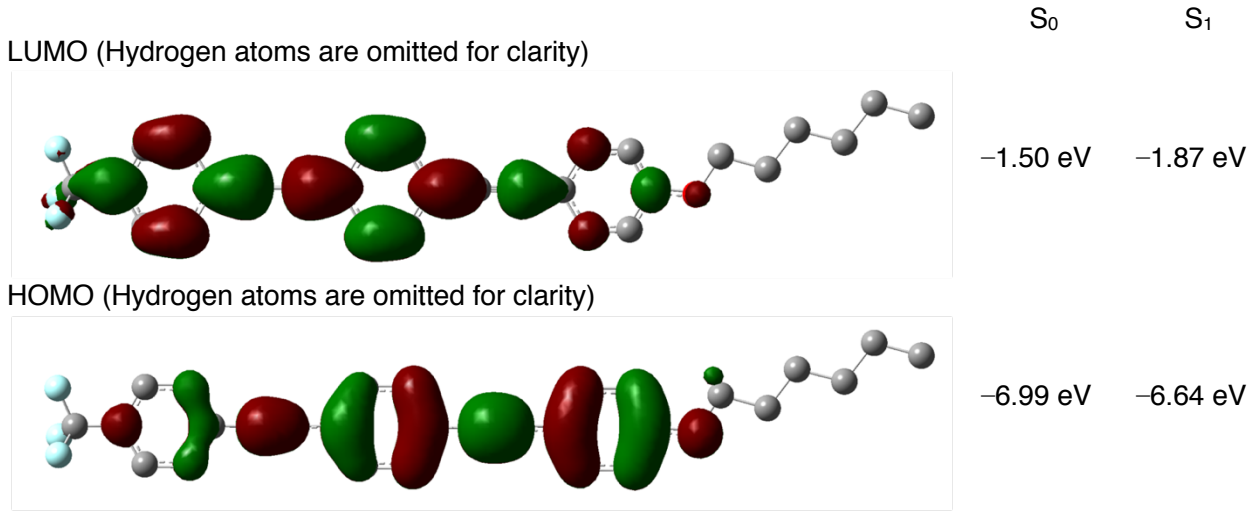


Figure S18. HOMO and LUMO of **2a** and their orbital energies (eV). Computed with M06-2X/6-31+G(d).

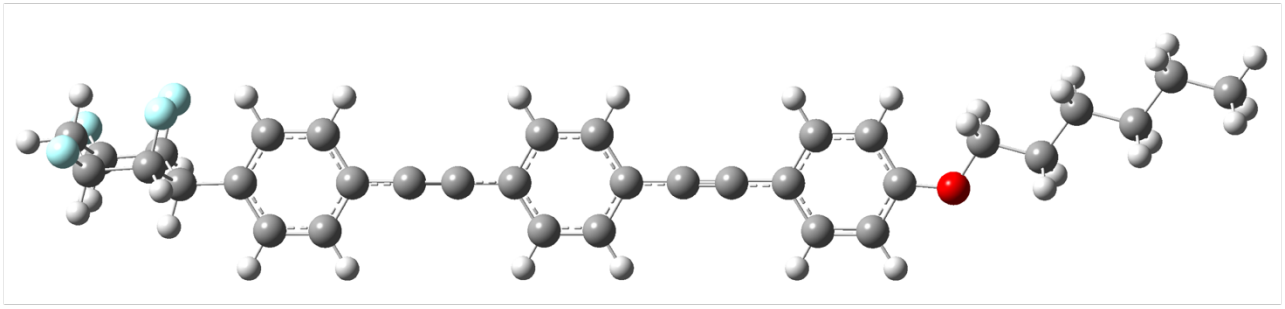
Table S6. Cartesian Coordinates of **2a** (S_0 state)

No.	Atom No.	Type	Coordinates (Angstroms) x	y	z
1	6	0	15.028334	-1.041558	-0.024738
2	1	0	15.230439	-0.43547	-0.91514
3	1	0	15.73052	-1.881139	-0.023104
4	1	0	15.241112	-0.423097	0.854605
5	6	0	13.578414	-1.52223	-0.012636
6	1	0	13.393455	-2.160849	-0.88666
7	1	0	13.404056	-2.148569	0.872376
8	6	0	12.578228	-0.367238	-0.0147
9	1	0	12.750851	0.260659	-0.900535
10	1	0	12.761163	0.272786	0.860325
11	6	0	11.123801	-0.834933	-0.003035
12	1	0	10.942176	-1.47415	-0.878452
13	1	0	10.95228	-1.461938	0.88317
14	6	0	10.132382	0.328048	-0.005476
15	1	0	10.298593	0.964104	0.872883
16	1	0	10.289615	0.952636	-0.893665
17	6	0	8.696734	-0.158866	0.00476
18	1	0	8.487417	-0.772967	-0.881487
19	1	0	8.495828	-0.761118	0.901043
20	8	0	7.84517	0.984966	0.001105
21	6	0	6.504584	0.790297	0.005638
22	6	0	5.716891	1.951613	-0.000935
23	1	0	6.212357	2.917473	-0.008803
24	6	0	4.3365	1.857827	0.002229
25	1	0	3.732066	2.759767	-0.00317
26	6	0	3.703796	0.59978	0.012084
27	6	0	4.500177	-0.552264	0.019078
28	1	0	4.025715	-1.528921	0.02686
29	6	0	5.890583	-0.467051	0.015994
30	1	0	6.476501	-1.378419	0.021598
31	6	0	2.275977	0.502351	0.014039
32	6	0	1.064204	0.42297	0.014713
33	6	0	-0.363667	0.329501	0.014164
34	6	0	-1.15289	1.492625	0.005801
35	1	0	-0.670499	2.464949	0.000657
36	6	0	-2.53718	1.402254	0.003627
37	1	0	-3.142353	2.303345	-0.00322
38	6	0	-3.166959	0.146286	0.009762
39	6	0	-2.379154	-1.017046	0.01881
40	1	0	-2.861725	-1.989346	0.023721
41	6	0	-0.994843	-0.926418	0.020994
42	1	0	-0.389878	-1.827575	0.027615
43	6	0	-4.595211	0.053538	0.005594
44	6	0	-5.806093	-0.02464	0.000714
45	6	0	-7.235293	-0.114709	-0.006828
46	6	0	-8.016836	1.053362	-0.018708
47	1	0	-7.530512	2.023263	-0.021364
48	6	0	-9.401926	0.964979	-0.030466
49	1	0	-10.004404	1.868365	-0.043073
50	6	0	-10.014846	-0.289513	-0.030788
51	6	0	-9.252721	-1.455906	-0.016571
52	1	0	-9.735964	-2.427175	-0.018391
53	6	0	-7.864903	-1.368809	-0.005787
54	1	0	-7.261828	-2.27073	0.001431
55	6	0	-11.513973	-0.358977	-0.007271
56	9	0	-12.073048	0.519044	-0.862481
57	9	0	-12.012594	-0.064364	1.212726
58	9	0	-11.980248	-1.576598	-0.330072

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

No.	Atom No.	Type	Coordinates (Angstroms) x	y	z
1	6	0	15.005227	-0.997848	-0.034327
2	1	0	15.199298	-0.392426	-0.926951
3	1	0	15.715808	-1.830301	-0.031725
4	1	0	15.213576	-0.374712	0.842761
5	6	0	13.56035	-1.493284	-0.017721
6	1	0	13.379992	-2.136196	-0.889532
7	1	0	13.394197	-2.118685	0.8695
8	6	0	12.548753	-0.348282	-0.020986
9	1	0	12.713082	0.278716	-0.908964
10	1	0	12.726782	0.295894	0.85194
11	6	0	11.09934	-0.831226	-0.005111
12	1	0	10.922351	-1.474267	-0.878559
13	1	0	10.935828	-1.457221	0.883199
14	6	0	10.097063	0.322647	-0.008676
15	1	0	10.257718	0.961831	0.868214
16	1	0	10.246015	0.946087	-0.898864
17	6	0	8.667982	-0.181203	0.005009
18	1	0	8.459166	-0.795122	-0.880471
19	1	0	8.470258	-0.779159	0.903862
20	8	0	7.801977	0.957998	0.000179
21	6	0	6.473676	0.768474	0.006787
22	6	0	5.686852	1.941685	-0.000952
23	1	0	6.192424	2.902099	-0.011066
24	6	0	4.315662	1.858504	0.003824
25	1	0	3.711948	2.760453	-0.002456
26	6	0	3.664384	0.58829	0.01663
27	6	0	4.474188	-0.580876	0.025069
28	1	0	3.993204	-1.553898	0.035194
29	6	0	5.853488	-0.496229	0.02027
30	1	0	6.442425	-1.405638	0.026914
31	6	0	2.276574	0.497035	0.019889
32	6	0	1.039384	0.417521	0.021299
33	6	0	-0.336935	0.329317	0.021048
34	6	0	-1.154819	1.516008	0.009767
35	1	0	-0.665531	2.485099	0.00299
36	6	0	-2.516392	1.427471	0.007049
37	1	0	-3.125597	2.326024	-0.001908
38	6	0	-3.17546	0.147794	0.015335
39	6	0	-2.358824	-1.037533	0.028077
40	1	0	-2.848453	-2.006467	0.035053
41	6	0	-0.997064	-0.951843	0.030853
42	1	0	-0.388191	-1.850596	0.040035
43	6	0	-4.556515	0.059516	0.009934
44	6	0	-5.789705	-0.019875	0.003636
45	6	0	-7.186622	-0.108824	-0.006273
46	6	0	-7.988704	1.065683	-0.023119
47	1	0	-7.505369	2.037301	-0.027131
48	6	0	-9.367078	0.971514	-0.037778
49	1	0	-9.970881	1.874475	-0.053525
50	6	0	-9.986711	-0.286776	-0.037222
51	6	0	-9.216186	-1.455135	-0.016757
52	1	0	-9.699758	-2.426731	-0.016347
53	6	0	-7.834639	-1.373149	-0.00299
54	1	0	-7.233331	-2.27642	0.008301
55	6	0	-11.479429	-0.356035	-0.013106
56	9	0	-12.045577	0.522584	-0.86745
57	9	0	-11.989865	-0.060572	1.206422
58	9	0	-11.948982	-1.574698	-0.334376

Compound **2b** (R = *cyclo*-$C_6H_7F_4$)



SCF Done: E(RM062X) = -1788.73140181 A.U. after 7 cycles
Dipole moment (field-independent basis, Debye):
X= -2.4454 Y= -4.1108 Z= -0.7287 Tot= 4.8384

TD-SCF approximation (Energy calculation) at M06-2X/6-31+G(d) with CPCM (CH_2Cl_2)
Excited State 1: Singlet-A 3.7460 eV 330.97 nm f=2.5521 <S**2>=0.000
139 ->142 -0.13050
140 ->141 0.67335

TD-SCF approximation (Optimization calculation) at M06-2X/6-31+G(d) with CPCM (CH_2Cl_2)
Excited State 1: Singlet-A 3.0128 eV 411.53 nm f=2.7099 <S**2>=0.000
139 ->142 -0.11190
140 ->141 0.68808

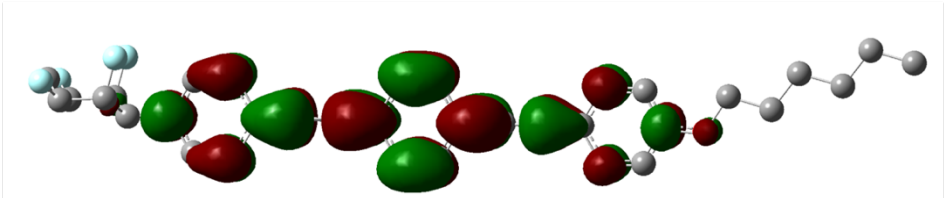
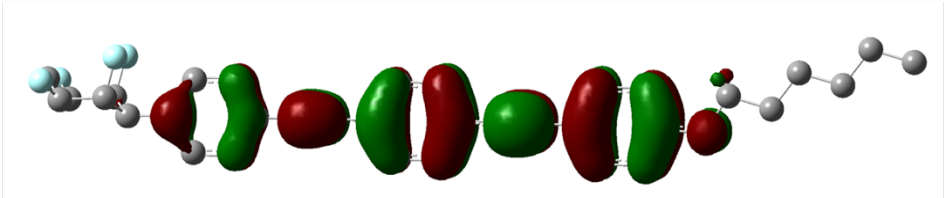
	S_0	S_1
LUMO (Hydrogen atoms are omitted for clarity)		
	−1.35 eV	−1.72 eV
HOMO (Hydrogen atoms are omitted for clarity)		
	−6.93 eV	−6.56 eV

Figure S19. HOMO and LUMO of **2b** and their orbital energies (eV). Computed with M06-2X/6-31+G(d).

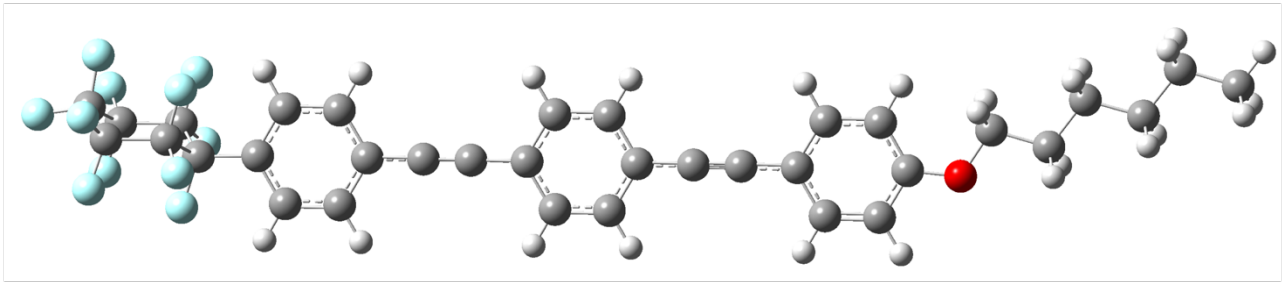
Table S8. Cartesian Coordinates of **2b** (S_0 state)

No.	Atom No.	Type	Coordinates (Angstroms) x	y	z
1	6	0	-17.229632	1.454061	-0.003392
2	1	0	-17.447495	0.905531	-0.926798
3	1	0	-17.896233	2.321201	0.037703
4	1	0	-17.477096	0.798969	0.839609
5	6	0	-15.761153	1.871866	0.046526
6	1	0	-15.56996	2.441368	0.965809
7	1	0	-15.540828	2.548516	-0.789873
8	6	0	-14.810128	0.677488	-0.010755
9	1	0	-15.030086	-0.002044	0.825087
10	1	0	-14.998287	0.107905	-0.932158
11	6	0	-13.337511	1.081191	0.04123
12	1	0	-13.149219	1.645731	0.965235
13	1	0	-13.119511	1.76348	-0.024117
14	6	0	-12.396771	-0.121314	-0.024117
15	1	0	-12.602391	-0.80403	0.809784
16	1	0	-12.568474	-0.680806	-0.952143
17	6	0	-10.941454	0.299633	0.032684
18	1	0	-10.694939	0.964089	-0.806532
19	1	0	-10.724646	0.828343	0.970687
20	8	0	-10.141663	-0.878303	-0.044472
21	6	0	-8.793664	-0.745407	-0.021866
22	6	0	-8.123362	0.47814	0.085396
23	1	0	-8.667426	1.41225	0.159679
24	6	0	-6.73046	0.499273	0.097044
25	1	0	-6.212247	1.449899	0.179707
26	6	0	-5.987002	-0.683911	0.003062
27	6	0	-6.676229	-1.90741	-0.102724
28	1	0	-6.113506	-2.833081	-0.176192
29	6	0	-8.05944	-1.937572	-0.114812
30	1	0	-8.598205	-2.876441	-0.196949
31	6	0	-4.556119	-0.651895	0.011147
32	6	0	-3.341943	-0.628027	0.014619
33	6	0	-1.220648	0.617277	0.132109
34	1	0	-1.781751	1.54171	0.226339
35	6	0	0.166495	0.642564	0.127405
36	1	0	0.694297	1.586809	0.217916
37	6	0	0.899427	-0.550019	0.004401
38	6	0	0.209707	-1.768783	-0.111815
39	1	0	0.770969	-2.693104	-0.206639
40	6	0	-1.1774	-1.79407	-0.106821
41	1	0	-1.705096	-2.7383	-0.197766
42	6	0	-1.911105	-0.601321	0.014231
43	6	0	2.330619	-0.523051	-0.005132
44	6	0	3.544157	-0.498601	-0.016286
45	6	0	4.976489	-0.470342	-0.032091
46	6	0	5.667095	0.743284	0.114002
47	1	0	5.105924	1.663988	0.241078
48	6	0	7.057065	0.772242	0.096557
49	1	0	7.572099	1.719003	0.21074
50	6	0	7.792628	-0.409596	-0.06817
51	6	0	7.099648	-1.616858	-0.212614
52	1	0	7.65406	-2.543186	-0.341029
53	6	0	5.70986	-1.654882	-0.195479
54	1	0	5.186529	-2.599211	-0.309071
55	6	0	9.307375	-0.415902	-0.093969
56	6	0	9.89237	0.367069	-1.277275
57	9	0	9.533866	1.711702	-1.191376
58	6	0	11.411146	0.293309	-1.278641
59	9	0	11.889651	1.072343	-2.328207
60	6	0	12.002059	0.795714	0.028957
61	6	0	11.450964	-0.044362	1.170016
62	9	0	11.966253	0.423965	2.375177
63	6	0	9.933184	0.019806	1.237869
64	9	0	9.577502	1.335564	1.531027
65	1	0	9.625752	-1.457271	-0.242371
66	1	0	9.557822	-0.598755	2.058512
67	1	0	13.091985	0.718831	0.000744
68	1	0	11.724937	1.844349	0.177955
69	1	0	9.487771	-0.007318	-2.222285
70	1	0	11.716847	-0.739329	-1.483049
71	1	0	11.758647	-1.092415	1.077053

Table S9. Cartesian Coordinates of **2b** (S_1 state)

No.	Atom No.	Type	Coordinates (Angstroms) x	y	z
1	6	0	17.205562	-1.412732	-0.028012
2	1	0	17.411473	-0.876154	-0.961113
3	1	0	17.880354	-2.273068	0.020969
4	1	0	17.453187	-0.742926	0.803271
5	6	0	15.741457	-1.843225	0.039191
6	1	0	15.562406	-2.400842	0.968129
7	1	0	15.521108	-2.533931	-0.785592
8	6	0	14.779317	-0.658312	-0.028251
9	1	0	14.998699	0.034875	0.796381
10	1	0	14.955695	-0.100278	-0.958954
11	6	0	13.310962	-1.074988	0.039783
12	1	0	13.1342	-1.628236	0.972757
13	1	0	13.093275	-1.770243	-0.782998
14	6	0	12.359723	0.118881	-0.035327
15	1	0	12.563718	0.813649	0.788737
16	1	0	12.520404	0.66737	-0.971682
17	6	0	10.909768	-0.316368	0.035728
18	1	0	10.661134	-0.990399	-0.794343
19	1	0	10.69974	-0.831136	0.982244
20	8	0	10.096626	0.856391	-0.052304
21	6	0	8.759076	0.726707	-0.022865
22	6	0	8.083594	-0.502158	0.102398
23	1	0	8.631461	-1.433363	0.186087
24	6	0	6.701118	-0.525018	0.119168
25	1	0	6.178813	-1.471819	0.214857
26	6	0	5.942189	0.673021	0.011463
27	6	0	6.650167	1.906557	-0.111783
28	1	0	6.087752	2.831308	-0.194084
29	6	0	8.024268	1.927726	-0.127858
30	1	0	8.570901	2.860833	-0.222275
31	6	0	4.551252	0.644528	0.022632
32	6	0	3.311107	0.621469	0.027595
33	6	0	1.21172	-0.64621	0.153219
34	1	0	1.777321	-1.567931	0.249867
35	6	0	-0.15261	-0.668867	0.148703
36	1	0	-0.686236	-1.609879	0.241844
37	6	0	-0.914547	0.545773	0.01911
38	6	0	-0.195735	1.787296	-0.101424
39	1	0	-0.762028	2.708688	-0.197809
40	6	0	1.168513	1.813497	-0.096087
41	1	0	1.701474	2.754943	-0.188111
42	6	0	1.932641	0.596752	0.029318
43	6	0	-2.298908	0.520241	0.008023
44	6	0	-3.534235	0.496548	-0.004643
45	6	0	-4.935632	0.470571	-0.022483
46	6	0	-5.644213	-0.752803	0.103995
47	1	0	-5.085295	-1.67671	0.217818
48	6	0	-7.02855	-0.77558	0.083432
49	1	0	-7.546121	-1.723025	0.182151
50	6	0	-7.76794	0.412116	-0.064788
51	6	0	-7.069049	1.623941	-0.188994
52	1	0	-7.624522	2.551858	-0.303806
53	6	0	-5.685058	1.665764	-0.16912
54	1	0	-5.162504	2.612359	-0.266957
55	6	0	-9.280288	0.420138	-0.092723
56	6	0	-9.867481	-0.350707	-1.284209
57	9	0	-9.511076	-1.696803	-1.211768
58	6	0	-11.386194	-0.275172	-1.286148
59	9	0	-11.865149	-1.042306	-2.344579
60	6	0	-11.979119	-0.790552	0.01532
61	6	0	-11.428199	0.037463	1.165075
62	9	0	-11.945618	-0.442201	2.365155
63	6	0	-9.910516	-0.028341	1.233972
64	9	0	-9.556104	-1.347157	1.51485
65	1	0	-9.59772	1.463338	-0.231268
66	1	0	-9.536017	0.582011	2.061075
67	1	0	-13.068966	-0.712322	-0.013201
68	1	0	-11.703064	-1.840907	0.153849
69	1	0	-9.46185	0.032646	-2.225116
70	1	0	-11.690349	0.759982	-1.479892
71	1	0	-11.734887	1.08667	1.082214

Compound **2c** (R = *cyclo*-C_6F_{11})



SCF Done: E(RM062X) = -2483.21281812 A.U. after 15 cycles
Dipole moment (field-independent basis, Debye):
X= 6.5726 Y= -1.5297 Z= -0.1280 Tot= 6.7494

TD-SCF approximation (Energy calculation) at M06-2X/6-31+G(d) with CPCM (CH_2Cl_2)
Excited State 1: Singlet-A 3.7060 eV 334.55 nm f=2.5054 <S**2>=0.000
167 ->169 -0.15147
167 ->170 -0.10587
168 ->169 0.65782
168 ->170 -0.14135

TD-SCF approximation (Optimization calculation) at M06-2X/6-31+G(d) with CPCM (CH_2Cl_2)
Excited State 1: Singlet-A 2.9696 eV 417.51 nm f=2.6890 <S**2>=0.000
167 ->170 -0.10222
168 ->169 0.68182

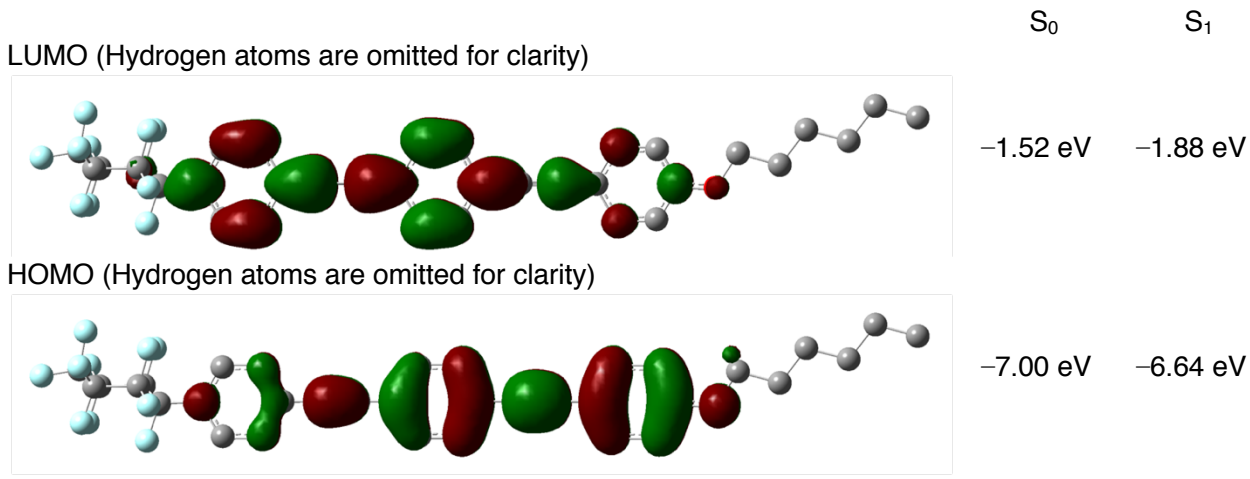


Figure S20. HOMO and LUMO of **2b** and their orbital energies (eV). Computed with M06-2X/6-31+G(d).

Table S10. Cartesian Coordinates of **2c** (S_0 state)

No.	Atom No.	Type	Coordinates (Angstroms) x	y	z
1	6	0	19.086837	-1.411039	0.038264
2	1	0	19.335285	-0.738865	-0.790877
3	1	0	19.760203	-2.272336	-0.013845
4	1	0	19.294061	-0.87787	0.973043
5	6	0	17.621913	-1.838655	-0.029757
6	1	0	17.400653	-2.531639	0.792896
7	1	0	17.441566	-2.39308	-0.960379
8	6	0	16.661697	-0.652413	0.041702
9	1	0	16.839664	-0.097351	0.973929
10	1	0	16.882037	0.042902	-0.780942
11	6	0	15.192443	-1.065807	-0.026808
12	1	0	14.973736	-1.762597	0.794507
13	1	0	15.014527	-1.61707	-0.960828
14	6	0	14.242747	0.128921	0.050721
15	1	0	14.405457	0.676206	0.987609
16	1	0	14.447983	0.824972	-0.772158
17	6	0	12.790736	-0.301229	-0.020094
18	1	0	12.582932	-0.81933	-0.966014
19	1	0	12.543821	-0.977831	0.809202
20	8	0	11.982607	0.870394	0.067118
21	6	0	10.635844	0.729472	0.034412
22	6	0	9.973756	-0.496976	-0.090078
23	1	0	10.52405	-1.426885	-0.170815
24	6	0	8.581158	-0.526383	-0.110774
25	1	0	8.069195	-1.479136	-0.206698
26	6	0	7.830102	0.651365	-0.009184
27	6	0	8.51104	1.877921	0.113853
28	1	0	7.942166	2.79931	0.193345
29	6	0	9.89384	1.916241	0.13525
30	1	0	10.426431	2.857357	0.230668
31	6	0	6.399651	0.611358	-0.026861
32	6	0	5.185675	0.581946	-0.038349
33	6	0	3.06924	-0.670767	-0.162839
34	1	0	3.633669	-1.593855	-0.24926
35	6	0	1.682258	-0.699974	-0.165829
36	1	0	1.157236	-1.645895	-0.25453
37	6	0	0.946636	0.491729	-0.052943
38	6	0	1.631118	1.7135	0.147982
39	1	0	1.066427	2.636445	0.147982
40	6	0	3.017989	1.742404	0.063978
41	1	0	3.542874	2.688263	0.153389
42	6	0	3.755147	0.550661	-0.046818
43	6	0	-0.484251	0.461632	-0.050242
44	6	0	-1.697381	0.436663	-0.043889
45	6	0	-3.128741	0.410083	-0.030958
46	6	0	-3.818291	-0.808554	-0.126739
47	1	0	-3.260548	-1.735148	-0.213894
48	6	0	-5.206744	-0.837228	-0.10909
49	1	0	-5.711513	-1.792821	-0.182544
50	6	0	-5.928247	0.35733	0.004313
51	6	0	-5.24891	1.57473	0.098477
52	1	0	-5.799724	2.503754	0.18672
53	6	0	-3.859763	1.601635	0.080935
54	1	0	-3.335389	2.548647	0.15536
55	9	0	-7.897474	1.673142	0.146678
56	6	0	-7.443232	0.377217	0.034765
57	6	0	-8.084716	-0.155916	-1.270271
58	9	0	-7.685672	-1.425825	-1.491986
59	9	0	-7.685147	0.608335	-2.29906
60	6	0	-9.63346	-0.162295	-1.250961
61	9	0	-10.076732	-0.796748	-2.347936
62	9	0	-10.08747	1.102003	-1.269682
63	6	0	-10.206243	-0.873321	-0.004781
64	9	0	-9.955285	-2.190645	-0.114712
65	9	0	-11.532272	-0.682462	0.038099
66	6	0	-9.578693	-0.366611	1.312683
67	9	0	-9.976113	-1.168454	2.313437
68	9	0	-10.02691	0.877214	1.55122
69	6	0	-8.030714	-0.357708	1.265378
70	9	0	-7.625938	-1.645139	1.265213
71	9	0	-7.584355	0.235369	2.383928

Table S11. Cartesian Coordinates of **2c** (S_1 state)

No.	Atom No.	Type	Coordinates (Angstroms) x	y	z
1	6	0	19.053437	-1.379291	0.027372
2	1	0	19.296049	-0.698067	-0.796067
3	1	0	19.733921	-2.234448	-0.032185
4	1	0	19.256345	-0.852441	0.966645
5	6	0	17.592211	-1.818763	-0.044118
6	1	0	17.376826	-2.520233	0.772845
7	1	0	17.416424	-2.366916	-0.979286
8	6	0	16.622328	-0.641042	0.037093
9	1	0	16.795794	-0.092004	0.973657
10	1	0	16.836365	0.062455	-0.780165
11	6	0	15.156736	-1.066806	-0.034287
12	1	0	14.943838	-1.770846	0.782225
13	1	0	14.983262	-1.612609	-0.972226
14	6	0	14.197964	0.120334	0.05168
15	1	0	14.355975	0.662259	0.992259
16	1	0	14.396395	0.822876	-0.767078
17	6	0	12.751091	-0.324216	-0.021616
18	1	0	12.543565	-0.834314	-0.970975
19	1	0	12.505971	-1.003265	0.805116
20	8	0	11.930125	0.84401	0.0724
21	6	0	10.595646	0.709835	0.038986
22	6	0	9.92551	-0.522327	-0.091178
23	1	0	10.47756	-1.450891	-0.175163
24	6	0	8.543968	-0.549644	-0.11232
25	1	0	8.024348	-1.497456	-0.211811
26	6	0	7.781961	0.646236	-0.004854
27	6	0	8.483314	1.882711	0.123841
28	1	0	7.91634	2.804567	0.206252
29	6	0	9.856617	1.909028	0.144801
30	1	0	10.400329	2.843274	0.243239
31	6	0	6.391498	0.61252	-0.022109
32	6	0	5.152269	0.585318	-0.033546
33	6	0	3.05892	-0.689107	-0.165362
34	1	0	3.62845	-1.609	-0.254967
35	6	0	1.694668	-0.716003	-0.168257
36	1	0	1.163817	-1.658536	-0.260269
37	6	0	0.92982	0.497522	-0.048642
38	6	0	1.643281	1.741987	0.07069
39	1	0	1.073439	2.661746	0.159845
40	6	0	3.007421	1.77151	0.073766
41	1	0	3.538055	2.714201	0.165287
42	6	0	3.773277	0.556346	-0.042474
43	6	0	-0.453542	0.468773	-0.045387
44	6	0	-1.689165	0.443677	-0.038891
45	6	0	-3.088005	0.417335	-0.025901
46	6	0	-3.796367	-0.808989	-0.136548
47	1	0	-3.240306	-1.735705	-0.235127
48	6	0	-5.178423	-0.833611	-0.118419
49	1	0	-5.683424	-1.788602	-0.203474
50	6	0	-5.908678	0.361841	0.009998
51	6	0	-5.222347	1.581602	0.118374
52	1	0	-5.774727	2.509088	0.21774
53	6	0	-3.839838	1.614988	0.100994
54	1	0	-3.31851	2.563004	0.186232
55	9	0	-7.87767	1.673232	0.17148
56	6	0	-7.418333	0.37934	0.041264
57	6	0	-8.064324	-0.136215	-1.270687
58	9	0	-7.662417	-1.402047	-1.512417
59	9	0	-7.670098	0.643744	-2.290187
60	6	0	-9.612737	-0.14757	-1.251217
61	9	0	-10.056578	-0.766989	-2.357242
62	9	0	-10.070873	1.115737	-1.251508
63	6	0	-10.183557	-0.877612	-0.015683
64	9	0	-9.929378	-2.192819	-0.143851
65	9	0	-11.510608	-0.691661	0.029684
66	6	0	-9.557563	-0.387191	1.308189
67	9	0	-9.955199	-1.203228	2.298156
68	9	0	-10.009821	0.852201	1.56326
69	6	0	-8.009901	-0.373288	1.261463
70	9	0	-7.602828	-1.660389	1.245536
71	9	0	-7.56809	0.204932	2.389996

4. Phase Transition Behavior

4.1. DSC and PXRD

The thermodynamic behavior was determined using a differential scanning calorimeter (DSC, SHIMADZU DSC-60 Plus; Kyoto, Japan) at heating and cooling rates of 5.0 °C min^{-1} under N_2 atmosphere. Liquid crystalline structures were evaluated by an FR-E X-ray diffractometer attached with an R-axis IV two-dimensional (2D) detector (Rigaku, Tokyo, Japan). 0.3 mm collimated Cu *K*α radiation (λ = 1.54187 Å) was used as an X-ray beam, and the camera length was set at 300 mm. The powder sample was loaded into a thin wall glass capillary tube for XRD analysis (ϕ 1.0–2.5 mm, Hilgenberg GmbH), and the n annealed up to isotropic temperature under vacuum. The glass capillary was set onto a ceramic heater attached to the FR-E sample holder. Exposure time of the X-ray beam was 5–60 min.

(a)

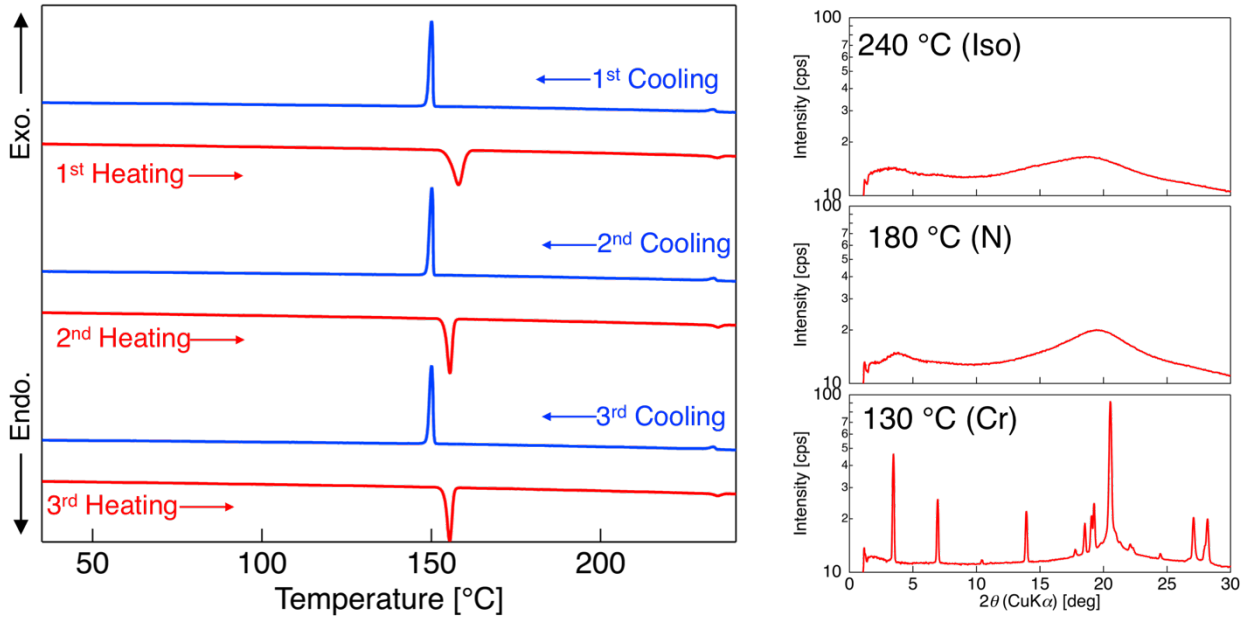


Figure S21. DSC thermogram of **1a** under N_2 atmosphere (scan rate: 5.0 °C min^{-1}) and PXRD pattern.

Table S12. Phase transition behavior of **1a** determined by DSC

	Phase transition	Temperature [°C]	Enthalpy (*ΔH*) [kJ mol^{-1}]	Entropy (*ΔS*) [J mol^{-1} K^{-1}]
1st Heating	Cr–N N–Iso	155 232	38.3 1.91	89.6 3.77
1st Cooling	Cr–N N–Iso	151 234	–29.0 –1.56	–68.6 –3.09
2nd Heating	Cr–N N–Iso	154 233	30.3 1.64	70.9 3.26
2nd Cooling	Cr–N N–Iso	151 234	–28.8 –1.66	–68.0 –3.28
3rd Heating	Cr–N N–Iso	154 233	29.8 1.66	69.8 3.28
3rd Cooling	Cr–N N–Iso	151 234	–28.4 –1.44	–67.1 –2.85

(b)

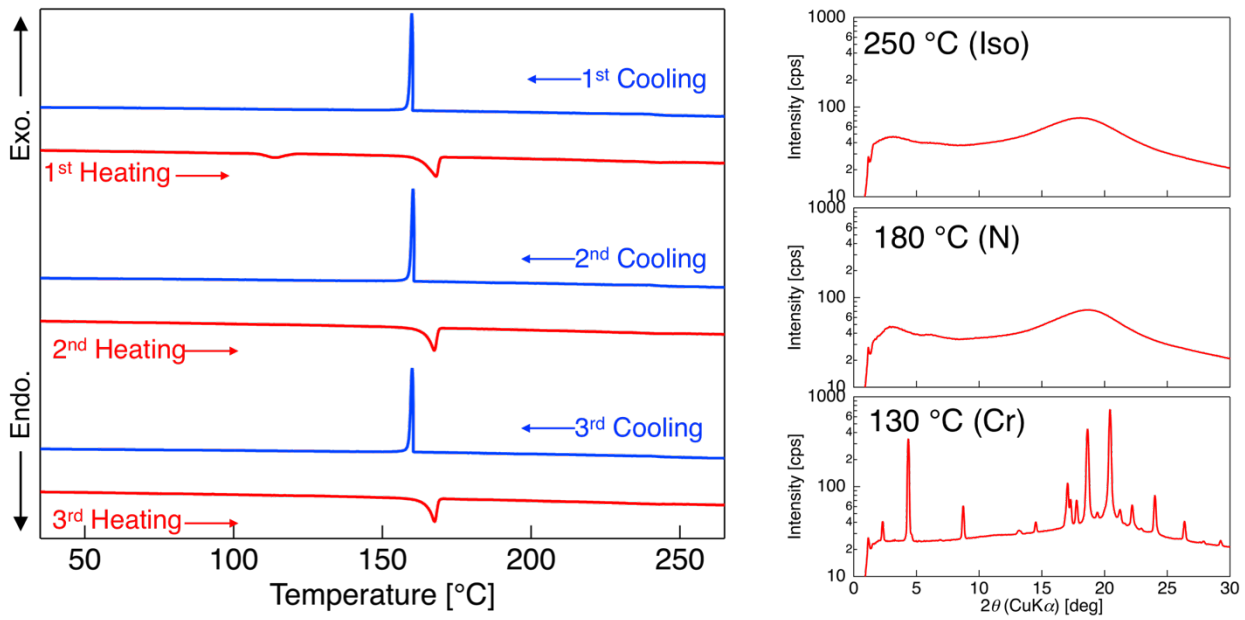


Figure S22. DSC thermogram of **1b** under N_2 atmosphere (scan rate: 5.0 °C min^{-1}) and PXRD pattern.

Table S13. Phase transition behavior of **1b** determined by DSC

	Phase transition	Temperature [°C]	Enthalpy (ΔH) [kJ mol^{-1}]	Entropy (ΔS) [J mol^{-1} K^{-1}]
1st Heating	Cr1–Cr2 Cr2-N N–Iso	108 163 239	8.07 24.2 1.30	21.1 55.6 2.54
1st Cooling	Cr–N N–Iso	160 242	–22.5 –1.00	–51.9 –1.94
2nd Heating	Cr–N N–Iso	164 239	22.9 2.48	52.4 4.84
2nd Cooling	Cr–N N–Iso	160 243	–21.9 –1.26	–50.6 –2.44
3rd Heating	Cr–N N–Iso	165 237	22.8 1.67	52.2 3.28
3rd Cooling	Cr–N N–Iso	160 242	–21.1 –1.05	–48.6 –2.04

(c)

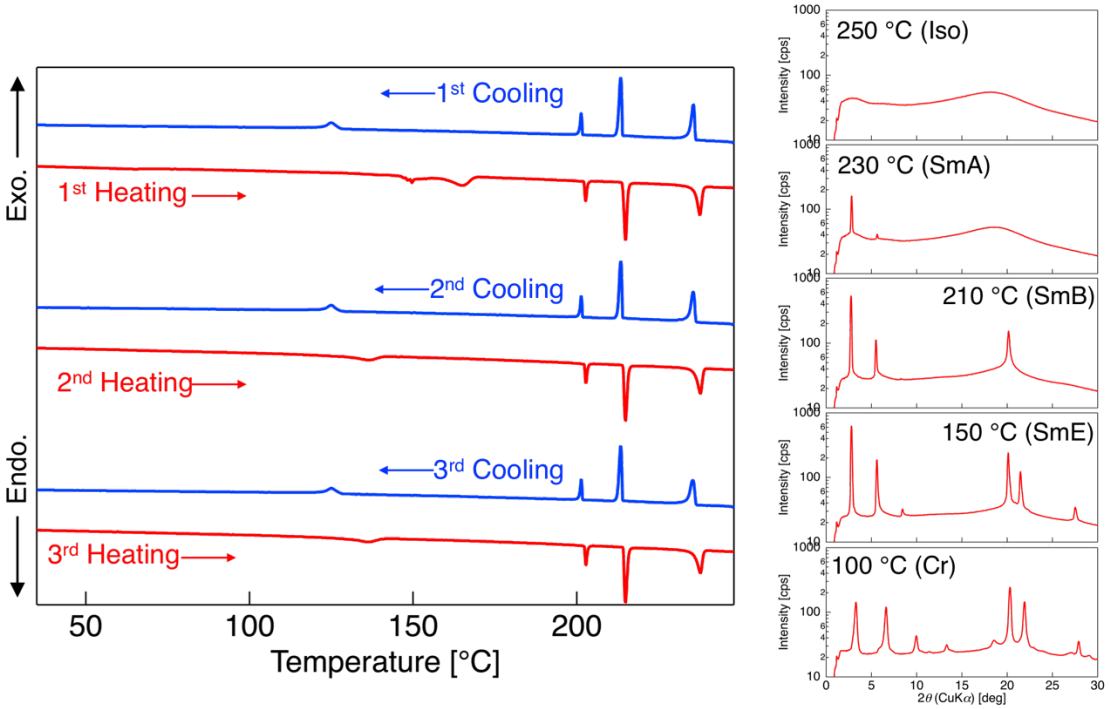


Figure S23. DSC thermogram of **2a** under N_2 atmosphere (scan rate: 5.0 °C min^{-1}) and PXRD pattern.

Table S14. Phase transition behavior of **2a** determined by DSC

	Phase transition	Temperature [°C]	Enthalpy (ΔH) [kJ mol^{-1}]	Entropy (ΔS) [J mol^{-1} K^{-1}]
1st Heating	Cr^1–Cr^2	147	17.1	40.8
	Cr^2–SmE	158	–	–
	SmE–SmB	202	2.56	5.38
	SmB–SmA	214	9.70	19.9
	SmA–Iso	236	8.84	17.4
1st Cooling	Cr^1–SmE	129	–3.91	–9.76
	SmE–SmB	202	–2.40	–5.06
	SmB–SmA	214	–9.11	–18.7
	SmA–Iso	236	–8.58	–16.8
2nd Heating	Cr–SmE	130	5.40	13.4
	SmE–SmB	202	2.43	5.11
	SmB–SmA	214	9.26	19.0
	SmA–Iso	236	8.19	16.1
2nd Cooling	Cr–SmE	127	–3.94	–9.85
	SmE–SmB	202	–2.39	–5.03
	SmB–SmA	214	–8.76	–18.0
	SmA–Iso	236	–7.93	–15.6
3rd Heating	Cr–SmE	130	5.92	14.7
	SmE–SmB	202	2.38	5.01
	SmB–SmA	214	9.06	18.6
	SmA–Iso	236	8.05	15.8
3rd Cooling	Cr–SmE	128	–3.79	–9.44
	SmE–SmB	202	–2.35	–4.95
	SmB–SmA	214	–8.57	–17.6
	SmA–Iso	236	–7.72	–15.2

(d)

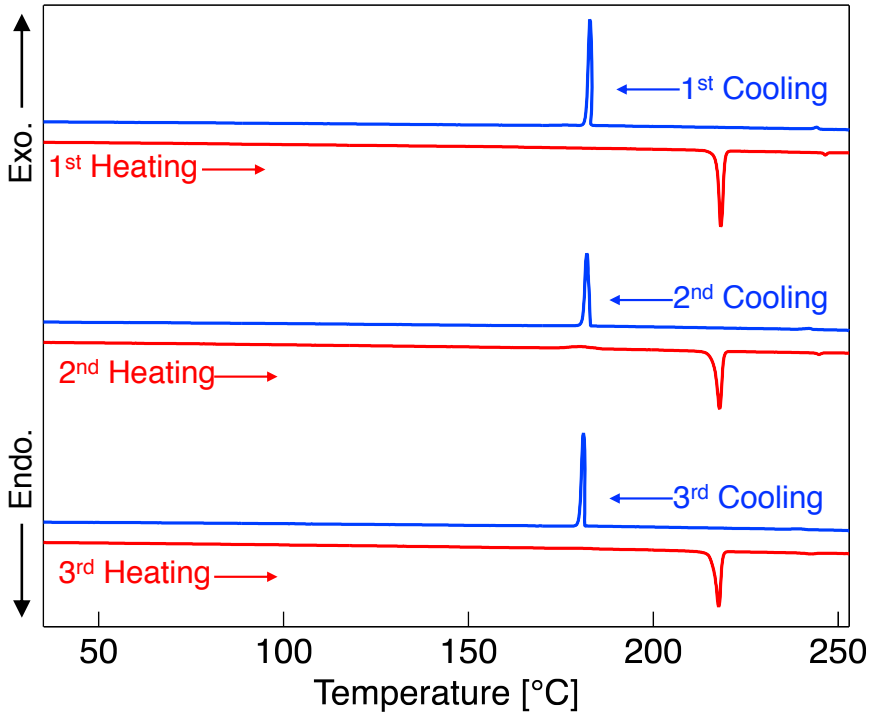


Figure S24. DSC thermogram of **2b** under N_2 atmosphere (scan rate: 5.0 °C min^{-1}).

Table S15. Phase transition behavior of **2b** determined by DSC

	Phase transition	Temperature [°C]	Enthalpy (ΔH) [kJ mol^{-1}]	Entropy (ΔS) [J mol^{-1} K^{-1}]
1st Heating	Cr–SmA N–Iso	217 246	40.9 0.96	83.5 1.86
1st Cooling	Cr–N N–Iso	183 245	–27.0 –0.92	–59.3 –1.78
2nd Heating	Cr^1–Cr^2 Cr^2–N N–Iso	175 216 244	–4.64 39.3 1.00	–10.4 80.4 1.93
2nd Cooling	Cr^1–N N–Iso	183 243	–30.9 –0.95	–67.8 –1.85
3rd Heating	Cr^1–Cr^2 Cr^2–N N–Iso	176 216 240	–0.94 38.4 1.13	–2.10 78.6 2.21
3rd Cooling	Cr^1–N N–Iso	181 241	–26.4 –0.82	–58.2 –1.60

(e)

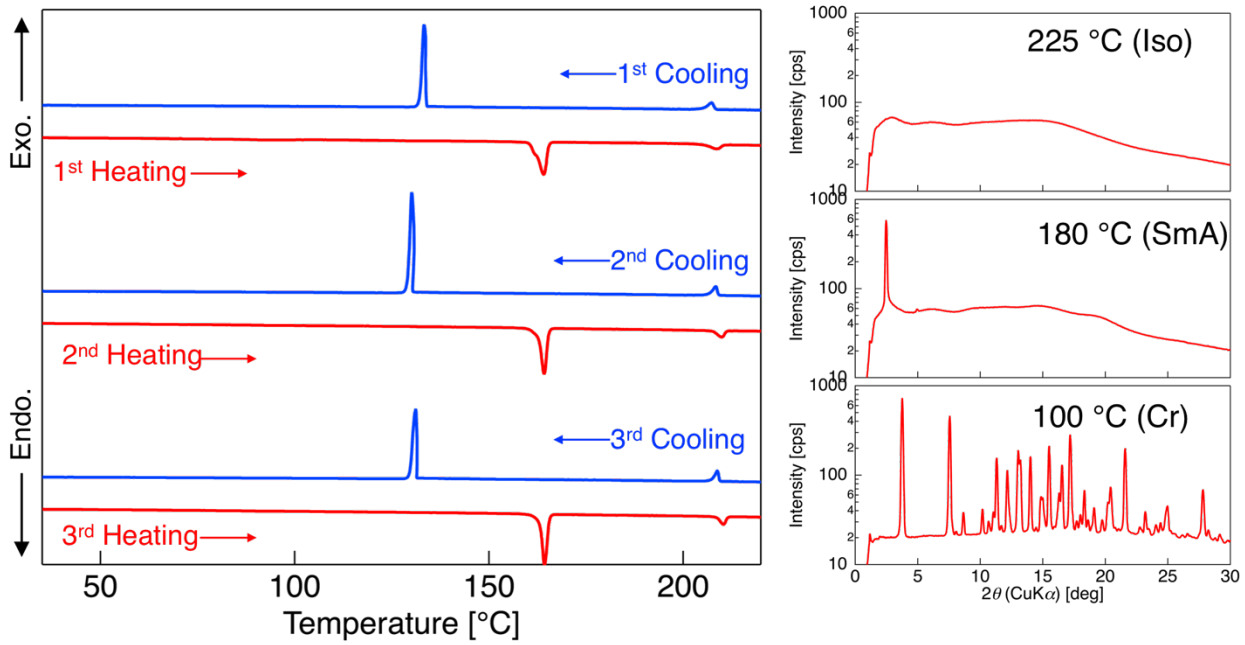


Figure S25. DSC thermogram of **2c** under N_2 atmosphere (scan rate: 5.0 °C min^{-1}) and PXRD pattern.

Table S16. Phase transition behavior of **2c** determined by DSC

	Phase transition	Temperature [°C]	Enthalpy (ΔH) [kJ mol^{-1}]	Entropy (ΔS) [J mol^{-1} K^{-1}]
1st Heating	Cr–SmA SmA–Iso	161 206	28.4 4.83	65.5 10.1
1st Cooling	Cr–SmA SmA–Iso	134 208	–23.8 –4.45	–58.5 –9.25
2nd Heating	Cr–SmA SmA–Iso	163 209	28.1 4.50	64.5 9.37
2nd Cooling	Cr–SmA SmA–Iso	131 209	–22.6 –4.50	–55.9 –9.33
3rd Heating	Cr–SmA SmA–Iso	163 209	28.0 4.58	64.1 9.50
3rd Cooling	Cr–SmA SmA–Iso	131 209	–22.8 –4.40	–56.3 –9.12

4.2. POM

Polarizing optical microscopy (POM) was carried out using an Olympus BX53 microscope (Tokyo, Japan) equipped with a cooling and heating stage (Linkam Scientific Instruments, 10002L; Surrey, UK).

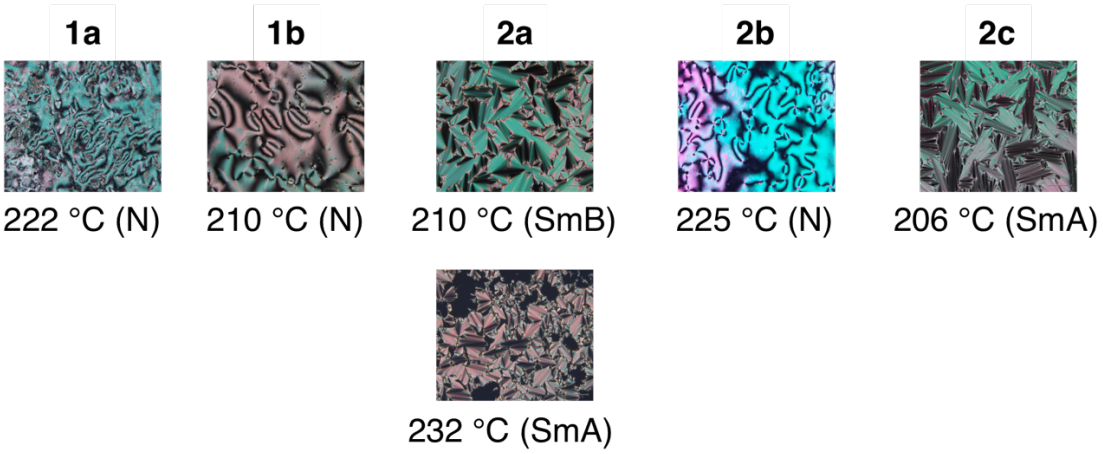
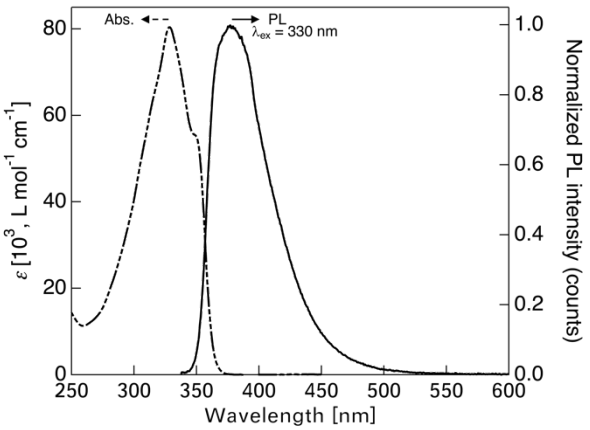


Figure S26. Microphotographs for optical texture images of LC phases for **1a**, **1b**, and **2a**–**c** observed by POM.

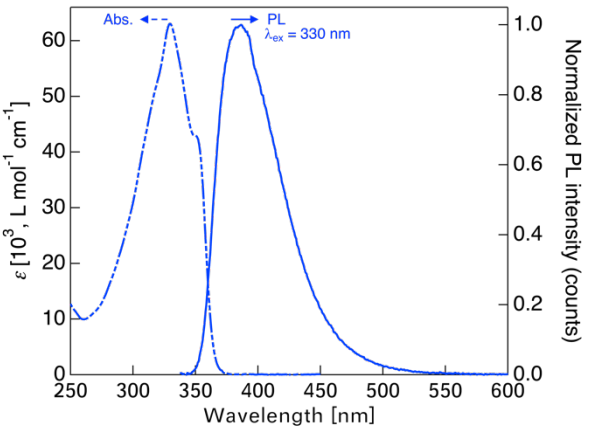
5. Photophysical Behavior

5.1. CH_2Cl_2 solution

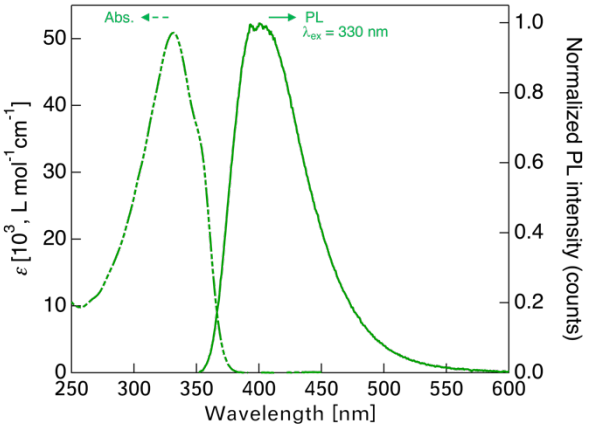
(a) **1a**



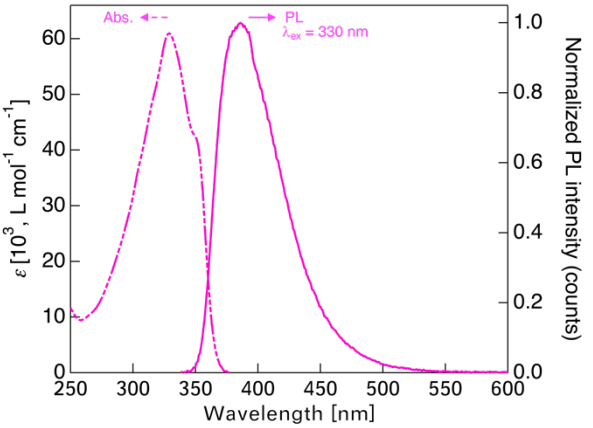
(b) **1b**



(c) **2a**



(d) **2b**



(e) **2c**

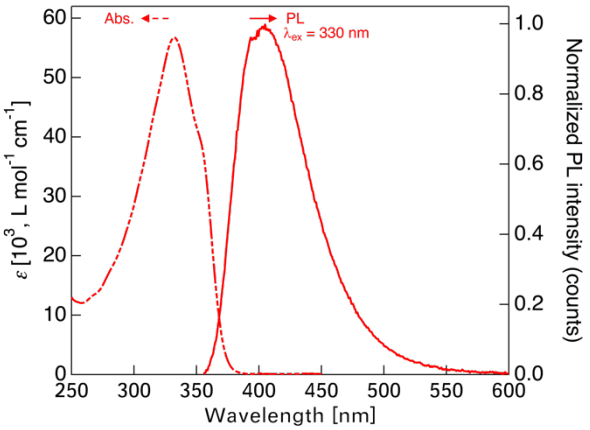


Figure S27. UV-vis absorption spectra (left axis) and photoluminescence spectra (right axis) for (a) **1a**, (b) **1b**, (c) **2a**, (d) **2b** and (e) **2c**. Concentration: UV-vis absorption measurement: 1.0×10^{-5} mol L^{-1} and PL: 1.0×10^{-6} mol L^{-1}.

5.2. Solvent Effect

5.2.1. Absorption and PL spectra of 1a in various solvent

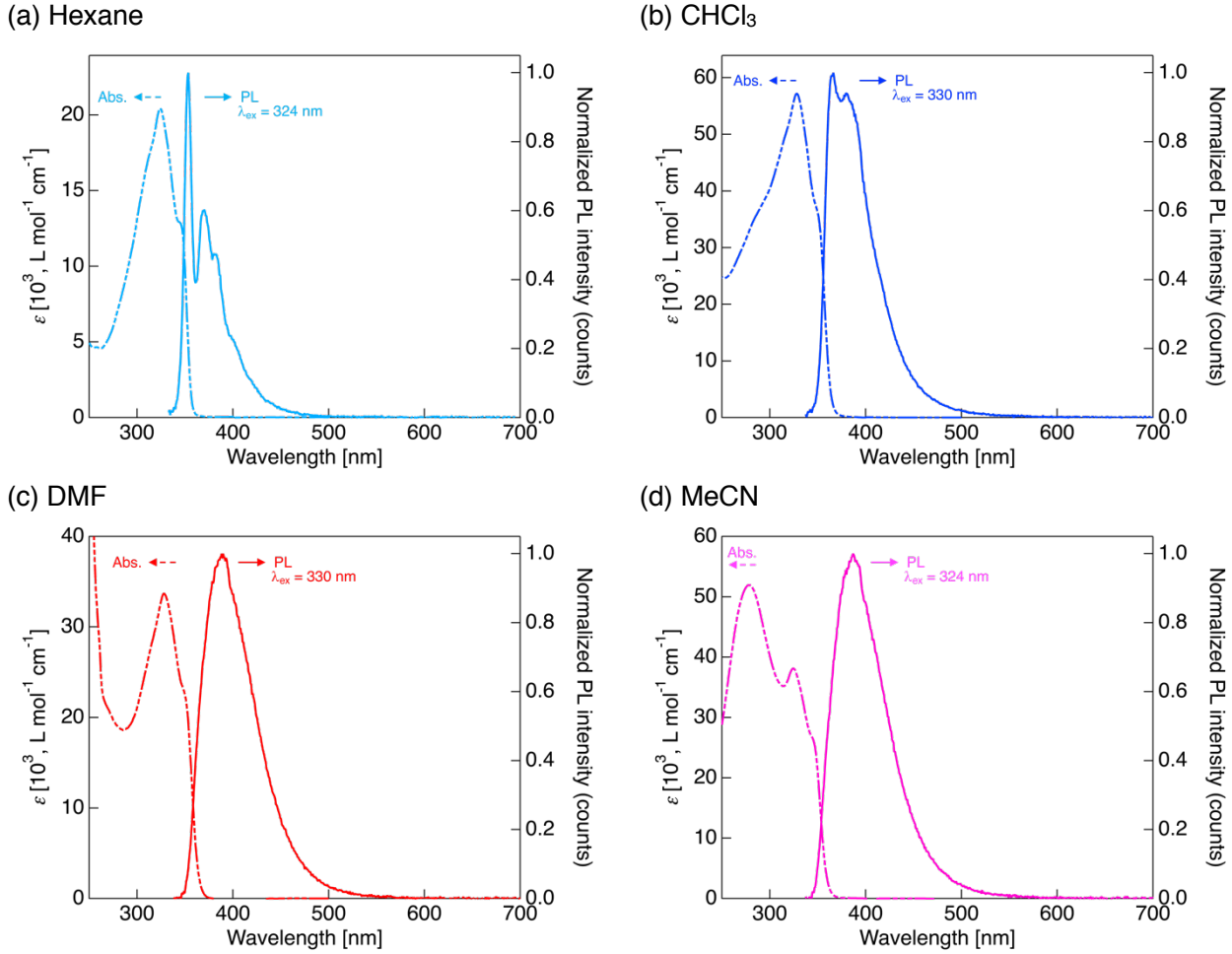


Figure S28. UV-vis absorption spectra (left axis) and photoluminescence spectra (right axis) of **1a** in (a) hexane, (b) $CHCl_3$, (c) DMF and (d) MeCN. Concentration: UV-vis absorption measurement: 1.0×10^{-5} mol L^{-1} and PL: 1.0×10^{-6} mol L^{-1}.

Table S17. Polarizability and Stokes' shift obtained from general solvent effect.

	Relative permitivity	Reflactive index	Δf	ν_{abs} (cm^{-1})	ν_{PL} (cm^{-1})	$\Delta\nu$ (cm^{-1})
Hexane	1.8799	1.3749	-0.0013777	30864	28293	2571
$CHCl_3$	4.806	1.4429	0.14912754	30488	27299	3189
CH_2Cl_2	8.93	1.424	0.2171701	30488	26531	3957
DMF	36.71	1.428	0.27521461	30581	25656	4925
MeCN	35.94	1.344	0.30460935	30864	25856	5008

5.2.2. Absorption and PL spectra of 2a in various solvent

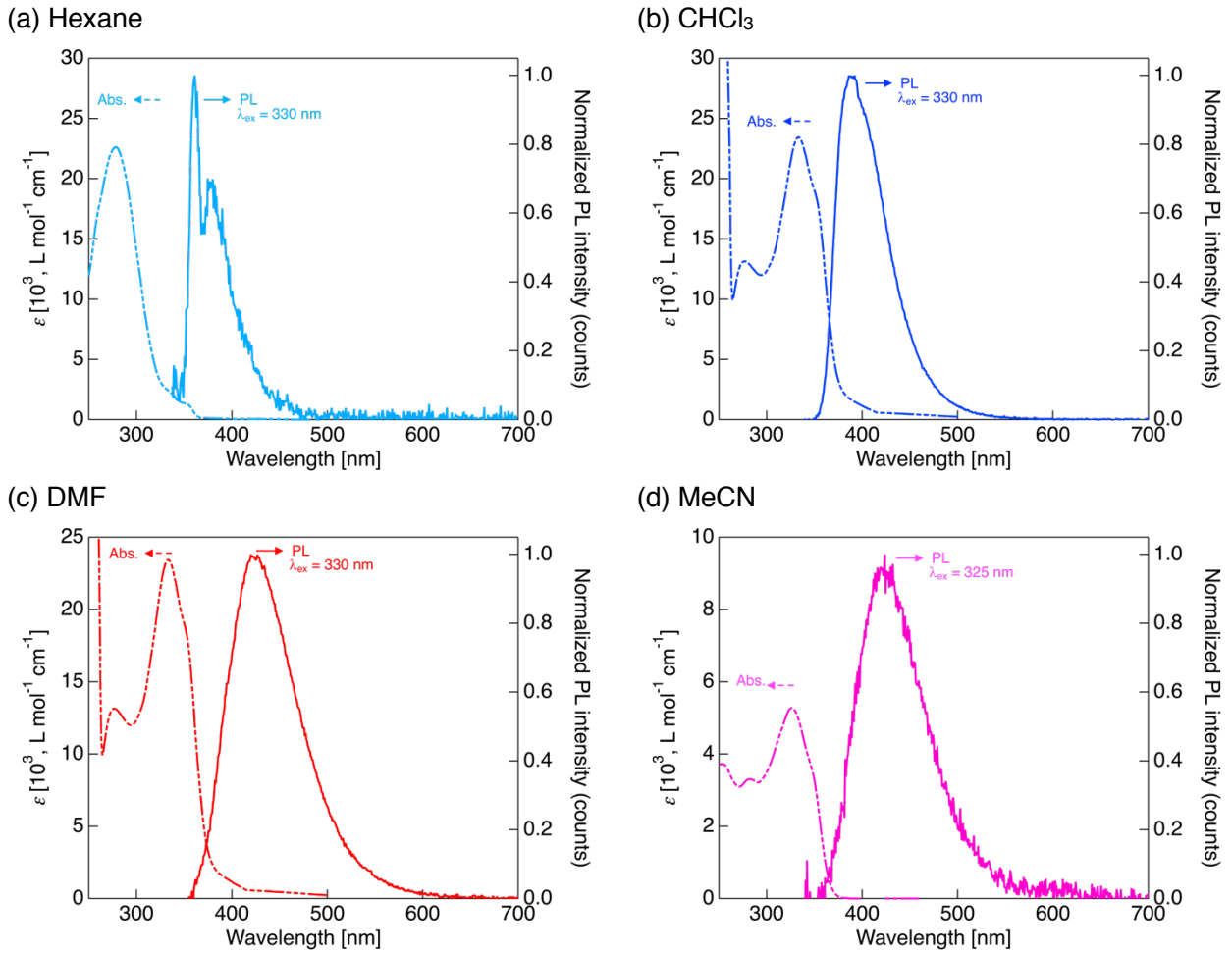


Figure S29. UV-vis absorption spectra (left axis) and photoluminescence spectra (right axis) of **2a** in (a) hexane, (b) $CHCl_3$, (c) DMF and (d) MeCN. Concentration: UV-vis absorption measurement: 1.0×10^{-5} mol L^{-1} and PL: 1.0×10^{-6} mol L^{-1}.

Table S18. Polarizability and Stokes' shift obtained from general solvent effect.

	Relative permitivity	Refractive index	Δf	ν_{abs} (cm^{-1})	ν_{PL} (cm^{-1})	$\Delta\nu$ (cm^{-1})
Hexane	1.8799	1.3749	-0.0013777	29586	27699	1887
$CHCl_3$	4.806	1.4429	0.14912754	30120	25756	4364
CH_2Cl_2	8.93	1.424	0.2171701	30201	24978	5223
DMF	36.71	1.428	0.27521461	30030	23641	6389
MeCN	35.94	1.344	0.30460935	30675	23599	7076

5.2.3. Lippert-Mataga plot

The Lippert-Mataga plot was constructed by using the relation

$$\nu_{abs} - \nu_{PL} = [2(\mu_e - \mu_g)^2/hca^3]\Delta f + (\nu_{abs} - \nu_{PL})^\circ \qquad \text{(Eq. 1)}$$

where $\nu_{abs} - \nu_{PL}$ is the Stokes' shift, the superscript "°" indicates the absence of solvent, μ_g and μ_e are dipole moments in the ground and the excited states, respectively, D (1D = 1.0x10^{-18} cm$^{5/2}$ g$^{1/2}$ s^{-1}); h is the Planck constant (h = 6.626x10^{-27} erg s); c is the rate of light in vacuum (c = 2.998x10^{-10} cm s^{-1}). a is Onsager cavity radius. The Onsagar radius (a) was estimated by DFT calculation using Gaussian 16 with M06-2X/6-31+G(d) level of theory: a = 6.01 Å for **1a** and 6.20 Å for **2a**. The orientation polarizability Δf is defined as

$$\Delta f = [(\varepsilon - 1)/(2\varepsilon + 1)] - [(n^2 - 1)/(2n^2 + 1)] \qquad \text{(Eq. 2)}$$

where ε and n are solvent dielectric constant and refractive index, respectively.

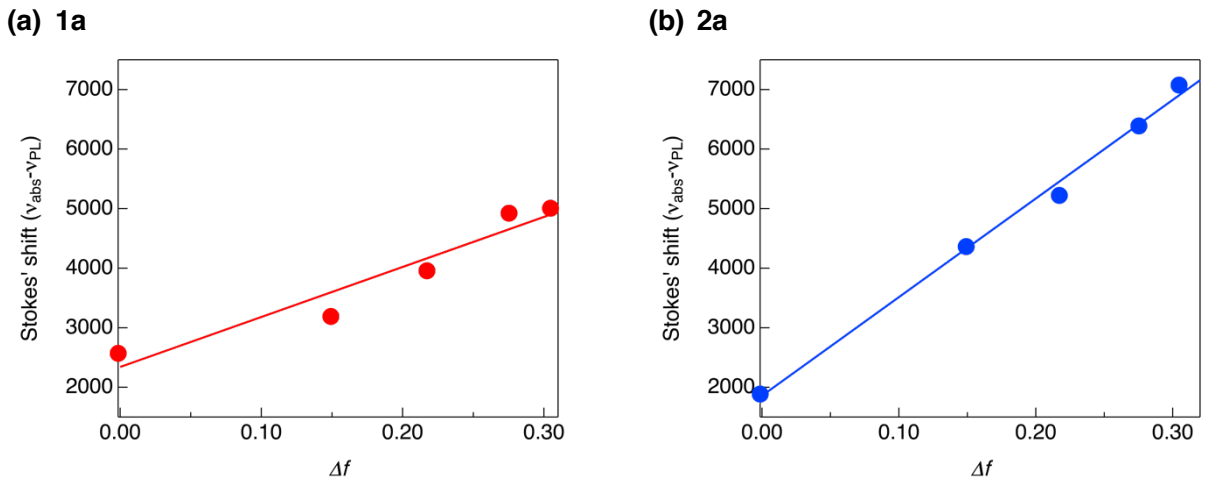


Figure S30. Lippert-Mataga plot for (a) **1a** and (b) **2a**.

5.3. Crystal

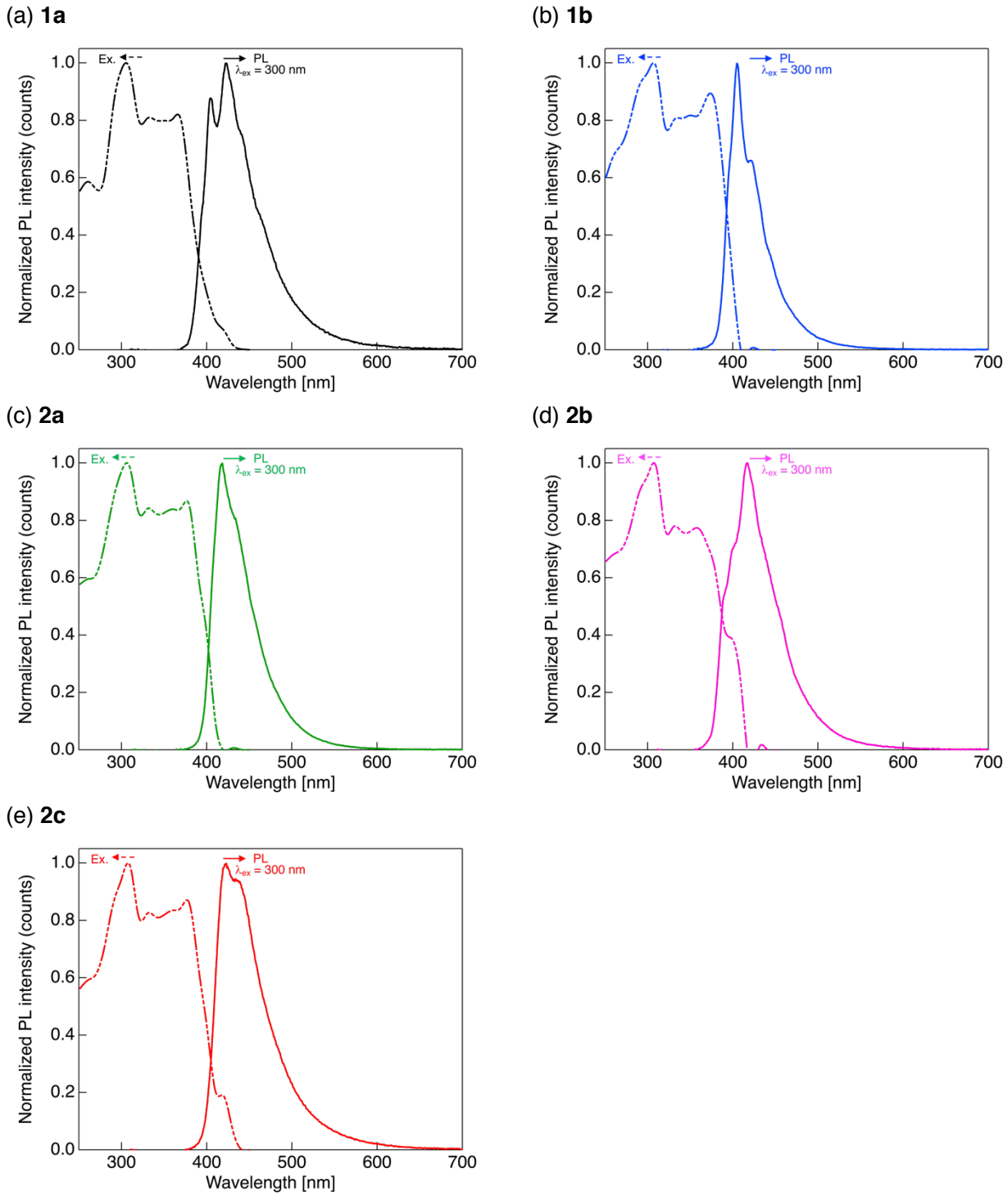


Figure S31. Excitation and photoluminescence spectra for (a) **1a**, (b) **1b**, (c) **2a**, (d) **2b** and (e) **2c** in crystalline samples. Excitation spectra were obtained for detection of PL at the maximum PL wavelength.