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Supporting Information

Synthesis of Tetrasilatetrathia[8]circulenes through C–I and C–H Silylation

Shuhei Akahori,[1] Tetsuaki Fujihara,[2] Yasushi Tsuji,[2] Hiroshi Shinokubo[1], and Yoshihiro Miyake[1]*

[1]Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8603, Japan

[2]Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University Kyoto 615-8510 (Japan)

E-mail: miyake@chembio.nagoya-u.ac.jp

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1. NMR and MS spectra

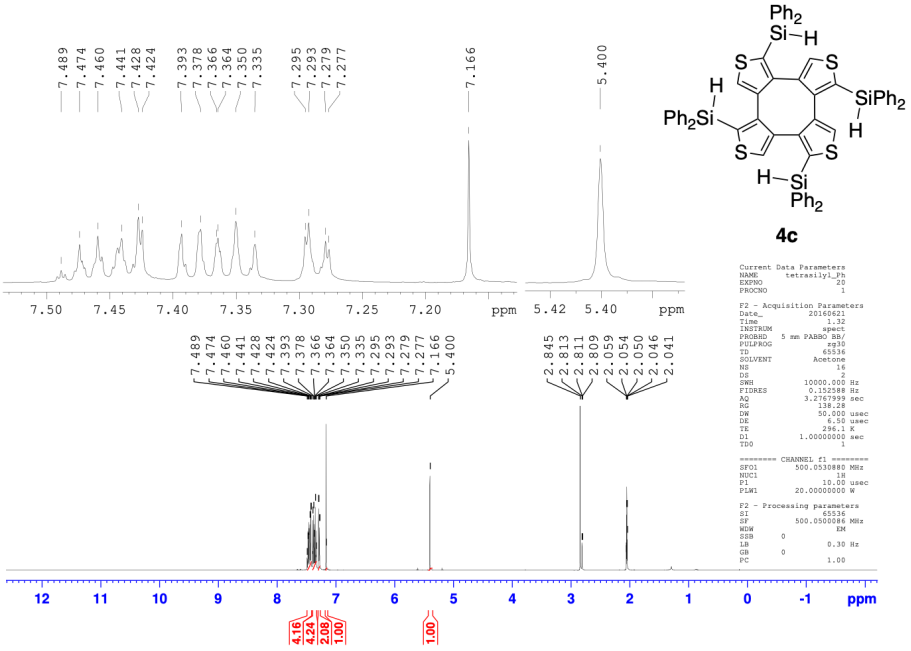


Figure S1. ^{1}H NMR spectrum of **4c** in acetone-d_6.

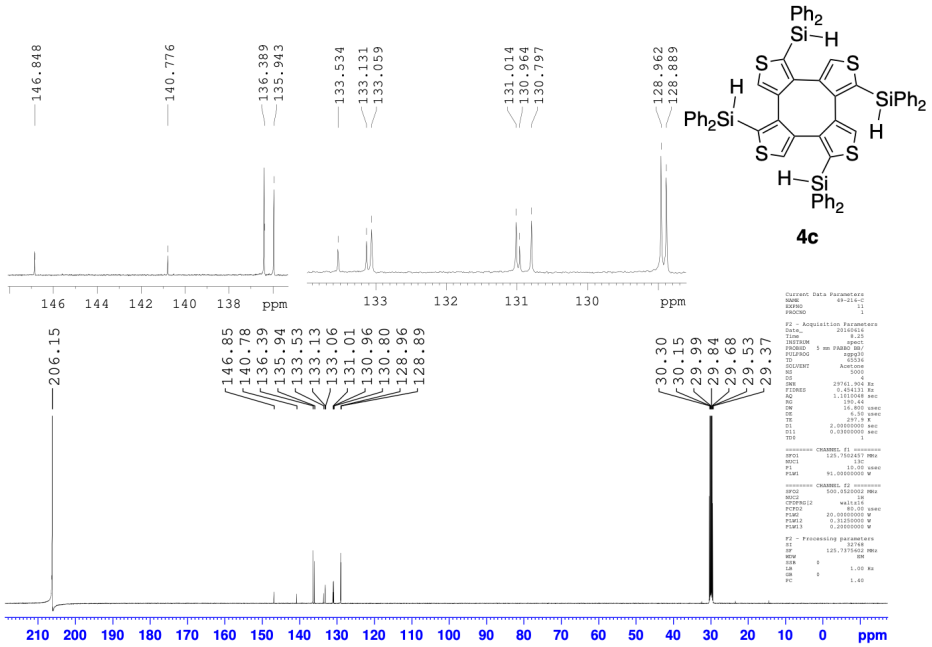


Figure S2. ^{13}C NMR spectrum of **4c** in acetone-d_6.

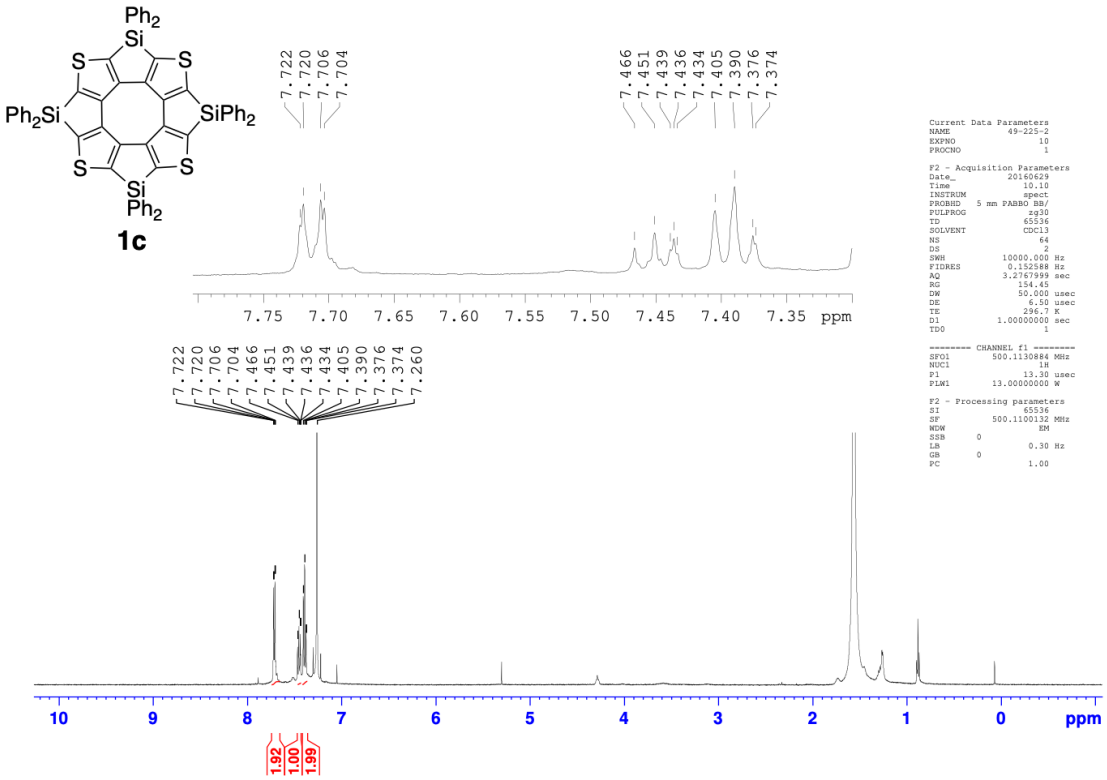


Figure S3. ^{1}H NMR spectrum of **1c** in $CDCl_3$.

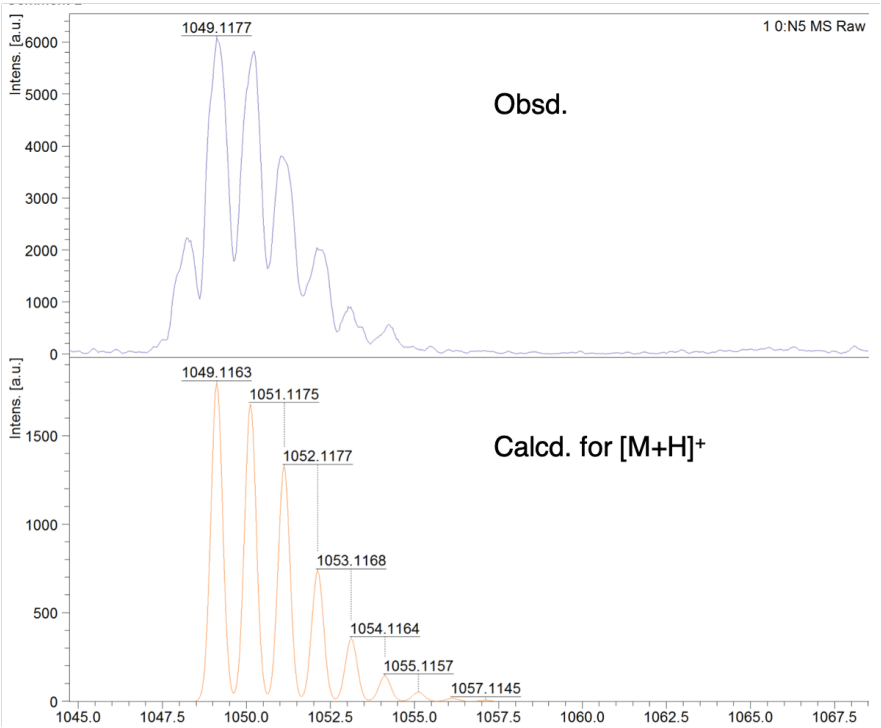


Figure S4. MALDI-TOF-MS spectrum of **1c**.

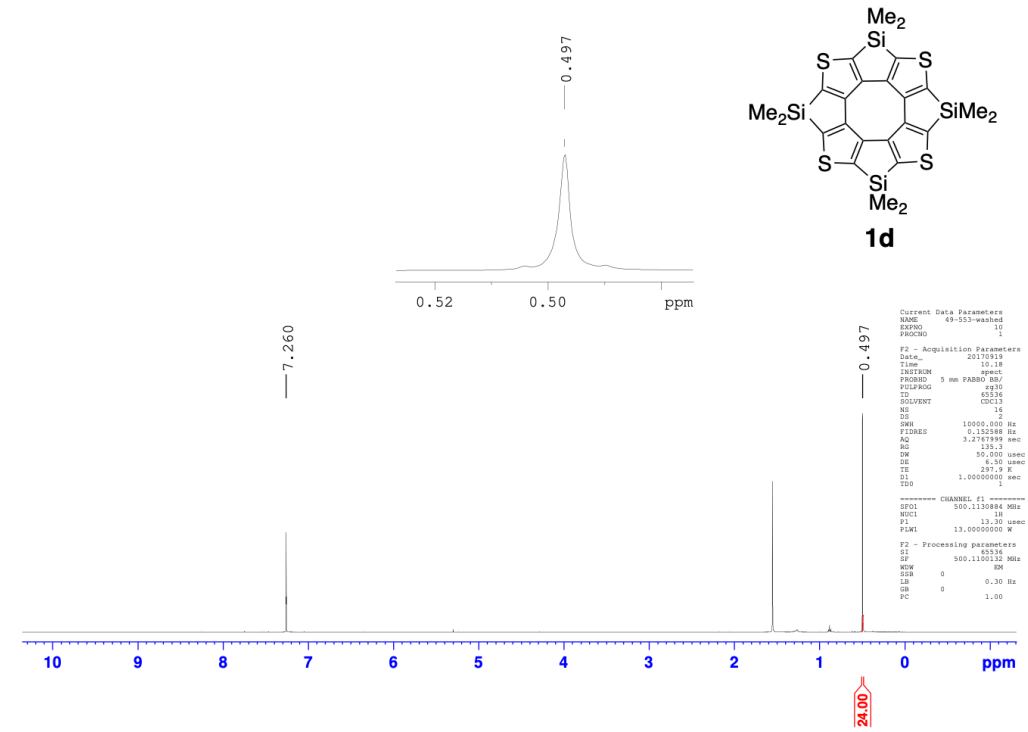


Figure S5. ^{1}H NMR spectrum of **1d** in $CDCl_3$.

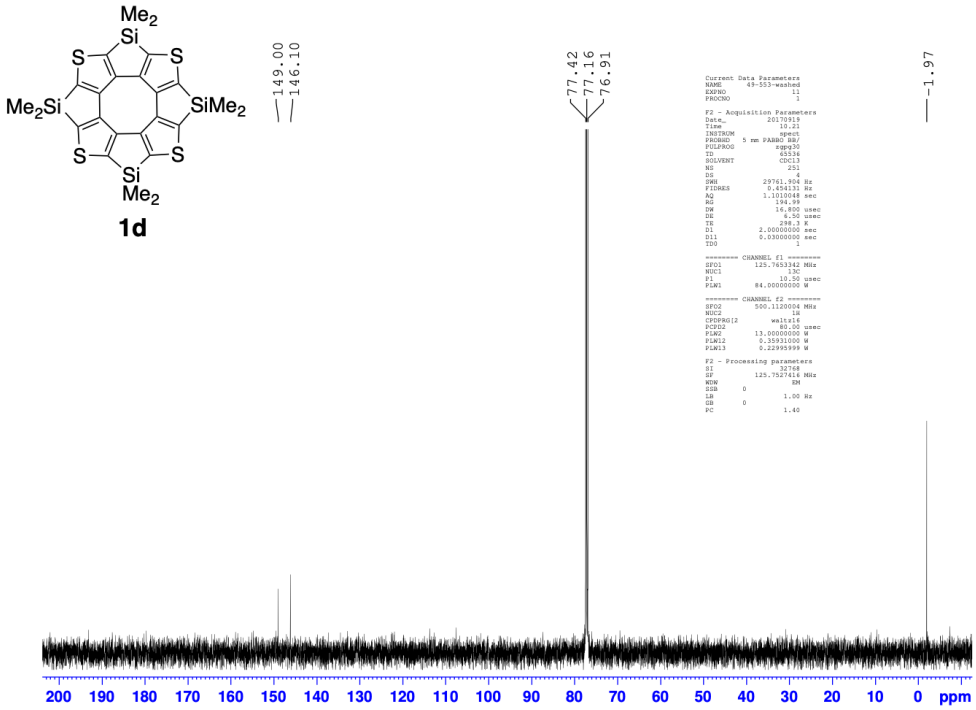


Figure S6. ^{13}C NMR spectrum of **1d** in $CDCl_3$.

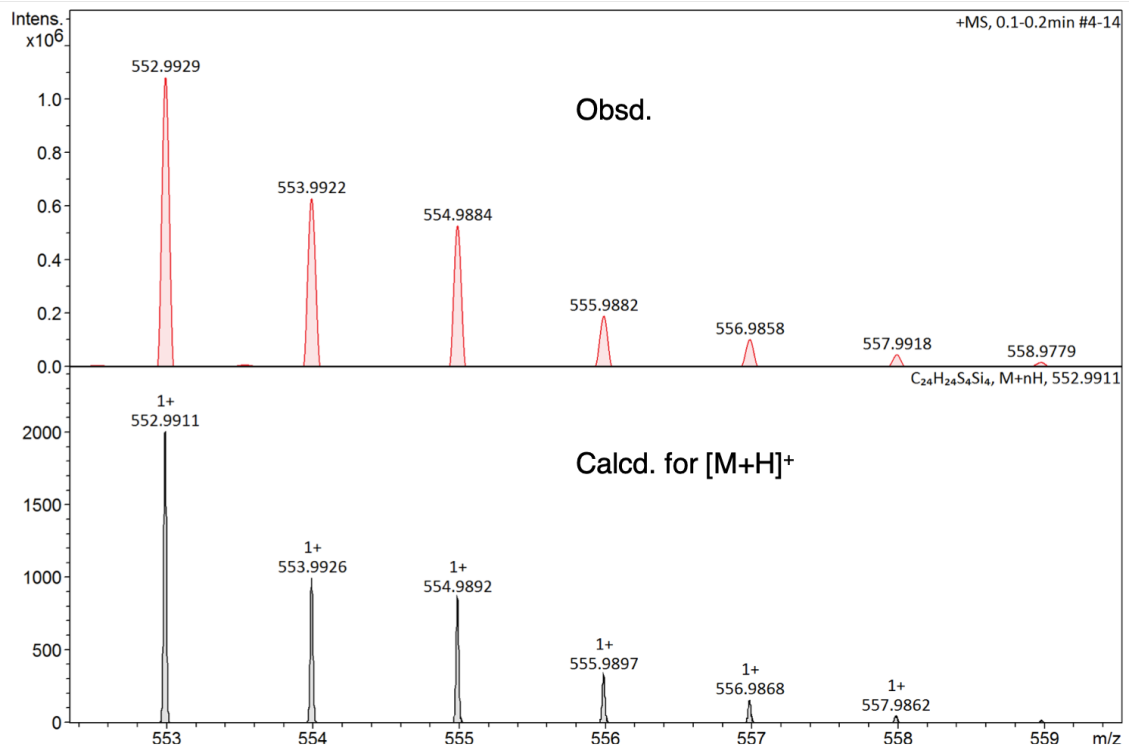


Figure S7. APCI-MS spectrum of **1d**.

2. X-ray diffraction (XRD) analysis

X-ray diffraction data for **1d** were taken on a Rigaku CCD diffractometer (Rigaku VariMax Saturn) with Varimax Mo optics using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The structures were solved using a direct method (SHELXT) and refined by a full-matrix least-squares method on F^2 for all reflections using the programs of SHELXL-2014. All non-hydrogen atoms of **1d** were refined with anisotropic displacement parameters. The hydrogen atoms were placed in idealized positions and refined as riding models with the relative isotropic displacement parameters. Crystallographic data for the structures of **1d** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-2067909. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

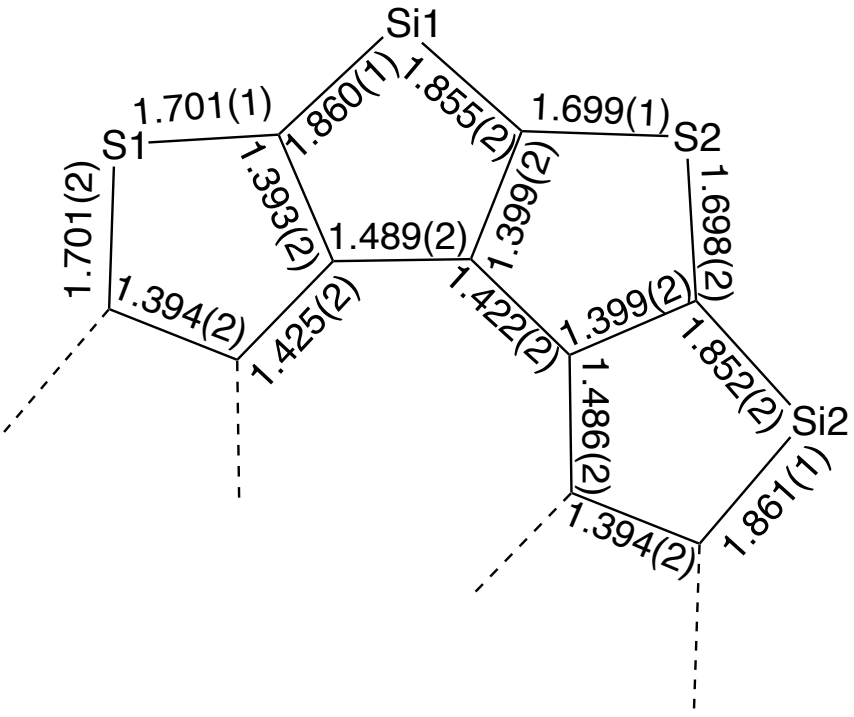


Figure S8. Bond length (Å) of **1d**.

Table S1. Crystallographic data of **1d**.

	1d
empirical formula	$C_{24}H_{24}S_4Si_4$
Temperature (ºC)	−180
crystal system	monoclinic
space group	$P2_1/c$ (#14)
a (Å)	11.2688(2)
b (Å)	10.4466(1)
c (Å)	11.8834(2)
α (°)	90
β (°)	104.966(2)
γ (°)	90
V (Å^3)	1351.47(4)
Z	2
D (g/cm^3)	1.359
R_1 ($I > 2\sigma(I)$)	0.0317
wR_2 (all data)	0.0861
GOF	1.081

3. DFT calculations

All calculations were performed using the Gaussian 09 program.[S1] Initial geometries of **1c** and **1d** were obtained calculated from the X-ray structure of **1d**. Full optimization was performed without any symmetric restriction with Becke's three-parameter hybrid exchange functional and the Lee–Yang–Parr correlation functional (B3LYP)[S2] and the 6-31G(d) basis set for C, H, Si, and, S atoms. The oscillator strengths of the model compounds for **1c** and **1d** were calculated by the TD-DFT method at the B3LYP/6-31+G(d,p) level.

Table S2. Calculated coordinates and geometry of **1c**.

S	4.255081	-0.238426	0.000072
S	-4.254815	0.238367	0.000067
S	0.238535	4.254907	-0.001178
S	-0.238293	-4.254977	-0.001306
Si	2.930298	-3.278124	-0.000061
Si	3.278209	2.93013	-0.000766
Si	-2.930057	3.278049	-0.000194
Si	-3.277942	-2.930194	-0.001188
C	-1.40765	-2.99765	-0.013013
C	-3.135944	-1.06418	0.010523
C	0.617337	-1.80968	0.001484
C	2.997769	-1.407815	-0.011871
C	1.729522	-0.815527	-0.004986
C	-1.064025	3.136057	0.009606
C	1.407911	2.997582	-0.013107
C	1.064268	-3.136133	0.009776
C	-1.729261	0.81546	-0.00496
C	-0.617081	1.809614	0.001398
C	1.809767	0.617163	0.001517
C	0.815613	1.729342	-0.005499
C	3.136213	1.064103	0.010181
C	-1.809511	-0.617237	0.001758
C	-2.997499	1.40774	-0.0121

C	-0.815354	-1.729422	-0.005256
C	4.058324	3.664996	-1.547879
C	5.439741	3.929569	-1.608782
C	3.287896	3.918721	-2.697774
C	6.029232	4.423989	-2.773034
H	6.063884	3.756516	-0.735078
C	3.873498	4.416154	-3.862738
H	2.217984	3.727539	-2.681728
C	5.245861	4.668807	-3.902463
H	7.09798	4.621277	-2.797349
H	3.258167	4.608322	-4.73798
H	5.70297	5.057239	-4.809055
C	4.093406	3.621849	1.548144
C	4.510512	4.965124	1.611244
C	4.257473	2.826618	2.697539
C	5.065321	5.494477	2.777222
H	4.410102	5.605631	0.737994
C	4.814675	3.351913	3.864235
H	3.948653	1.784571	2.679542
C	5.218774	4.687489	3.906162
H	5.380473	6.534544	2.80336
H	4.935277	2.718055	4.739037
H	5.653797	5.097508	4.814113
C	3.621071	-4.094399	1.548669
C	4.966584	-4.503757	1.615152
C	2.822651	-4.267818	2.694438
C	5.494897	-5.06017	2.780803
H	5.609891	-4.395865	0.744834
C	3.346964	-4.826568	3.860859
H	1.77895	-3.964838	2.674051
C	4.684676	-5.223037	3.906102
H	6.536725	-5.369215	2.809524

H	2.710624	-4.95434	4.732838
H	5.093892	-5.659379	4.813777
C	3.665984	-4.057187	-1.547354
C	3.93882	-5.437034	-1.606466
C	3.911347	-3.287391	-2.69949
C	4.433256	-6.025674	-2.77118
H	3.772034	-6.060575	-0.731138
C	4.408762	-3.872085	-3.864887
H	3.713657	-2.218632	-2.68473
C	4.66976	-5.242964	-3.902812
H	4.63695	-7.093252	-2.79413
H	4.594541	-3.257218	-4.741833
H	5.05821	-5.699385	-4.809745
C	-4.056944	-3.663999	-1.549369
C	-5.436598	-3.937723	-1.608469
C	-3.28733	-3.90684	-2.702161
C	-6.025256	-4.430669	-2.773783
H	-6.059931	-3.77272	-0.732652
C	-3.872069	-4.40264	-3.86818
H	-2.218711	-3.708408	-2.687392
C	-5.242756	-4.664577	-3.906069
H	-7.092705	-4.635016	-2.796771
H	-3.257403	-4.586512	-4.745667
H	-5.699181	-5.051707	-4.813562
C	-4.094277	-3.622561	1.546798
C	-4.503703	-4.9681	1.61212
C	-4.267142	-2.825213	2.693403
C	-5.059944	-5.497419	2.777408
H	-4.396339	-5.61049	0.741069
C	-4.825706	-3.350529	3.85946
H	-3.964	-1.781537	2.673838
C	-5.222387	-4.688224	3.903516

H	-5.369225	-6.539203	2.805208
H	-4.953201	-2.71501	4.73208
H	-5.65849	-5.098251	4.810944
C	-3.666055	4.057239	-1.547239
C	-3.937473	5.437366	-1.606496
C	-3.913415	3.287356	-2.698892
C	-4.432351	6.026216	-2.770905
H	-3.769304	6.060965	-0.731467
C	-4.411184	3.872286	-3.864009
H	-3.716865	2.218385	-2.684061
C	-4.670702	5.243438	-3.902102
H	-4.634995	7.093991	-2.793943
H	-4.598337	3.257399	-4.740648
H	-5.059586	5.699991	-4.808781
C	-3.620923	4.09371	1.548846
C	-4.966332	4.503448	1.615184
C	-2.822915	4.265499	2.695144
C	-5.495023	5.058491	2.781328
H	-5.609122	4.397065	0.744306
C	-3.347552	4.823038	3.862
H	-1.779188	3.962619	2.674558
C	-4.685249	5.219635	3.907209
H	-6.536774	5.367806	2.809993
H	-2.711513	4.949702	4.734359
H	-5.094764	5.654862	4.815287

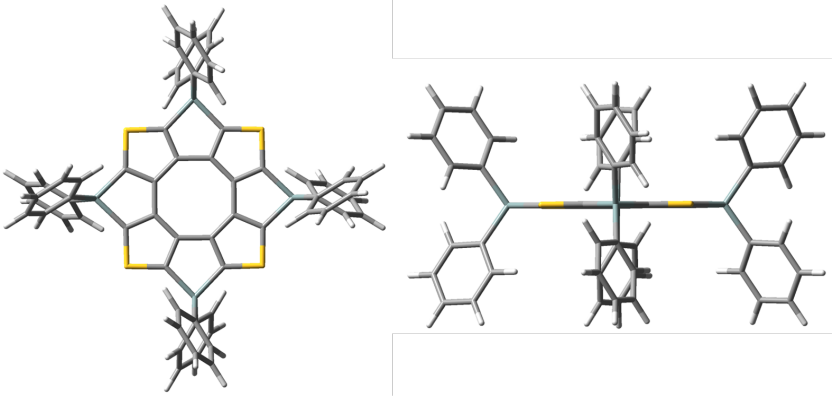
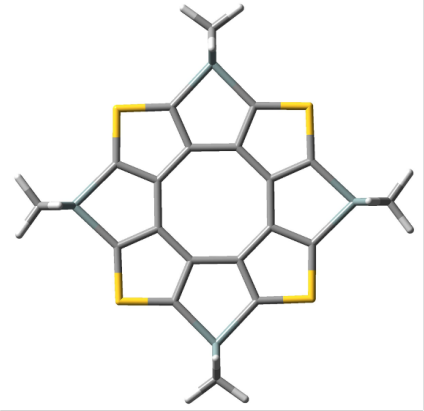
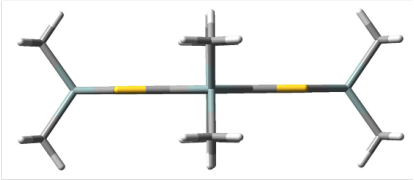


Table S3. Calculated coordinates and geometry of **1d**.

S	1.30338	4.057942	0.000456
S	-1.30338	-4.057943	-0.00024
S	-4.057942	1.30338	0.00035
S	4.057942	-1.30338	-0.000594
Si	3.910389	2.009014	-0.000092
Si	-2.009014	3.910389	0.000617
Si	-3.910389	-2.009015	0.000092
Si	2.009014	-3.91039	-0.000582
C	2.546779	-2.119617	-0.000442
C	0.240205	-3.304708	-0.000387
C	1.908802	0.141544	-0.000219
C	2.119617	2.546778	0.000269
C	1.226579	1.46943	0.000106
C	-3.304708	-0.240205	0.000079
C	-2.546779	2.119617	0.00044
C	3.304708	0.240205	-0.000399
C	-1.226579	-1.46943	-0.000021
C	-1.908802	-0.141544	0.00006
C	-0.141544	1.908802	0.000213
C	-1.46943	1.226579	0.000233
C	-0.240205	3.304708	0.000397
C	0.141544	-1.908802	-0.000235
C	-2.119617	-2.546779	0.000039
C	1.46943	-1.226579	-0.000275
C	2.498822	-4.865089	1.551687
H	2.0046	-5.843611	1.584699
H	3.5812	-5.039247	1.582773
H	2.218019	-4.312736	2.454228
C	2.498627	-4.864736	-1.55313
H	3.581078	-5.038348	-1.584701
H	2.004883	-5.843504	-1.585997

H	2.21716	-4.312454	-2.455509
C	4.864656	2.499134	-1.552528
H	5.038224	3.581602	-1.583771
H	5.843443	2.00544	-1.585585
H	4.31235	2.217925	-2.454972
C	-2.498861	4.865091	-1.551638
H	-3.581319	5.038698	-1.583015
H	-2.005134	5.843873	-1.584343
H	-2.217515	4.313027	-2.454187
C	-2.498587	4.864734	1.553178
H	-2.004361	5.843248	1.586342
H	-3.580961	5.038884	1.584467
H	-2.217648	4.312173	2.45555
C	4.86517	2.498315	1.552288
H	5.84368	2.004057	1.585099
H	5.039357	3.580678	1.583711
H	4.31285	2.217238	2.454766
C	-4.864916	-2.49879	-1.552293
H	-5.038511	-3.581248	-1.583734
H	-5.843698	-2.00507	-1.58509
H	-4.31275	-2.217403	-2.454767
C	-4.864911	-2.498657	1.552524
H	-5.843416	-2.004407	1.585605
H	-5.039092	-3.581027	1.583739
H	-4.312442	-2.217776	2.45497





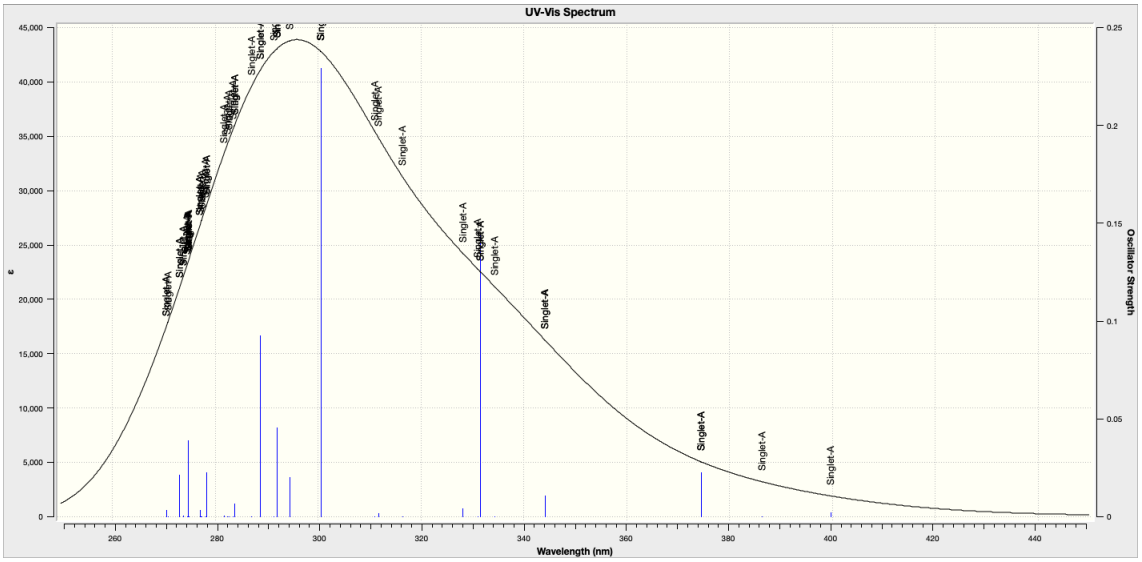


Figure S9. Simulated absorption spectra of **1c** calculated at the B3LYP/6-31+G(d,p).

Table S4. Selected wavelengths, oscillator strengths, and compositions of major electronic transitions of **1c**.

Excited State	1:	Singlet-A	3.1018 eV	399.71 nm	f=0.0021
272 -> 273		0.70457			
Excited State	2:	Singlet-A	3.2092 eV	386.34 nm	f=0.0000
271 -> 273		0.69855			
Excited State	3:	Singlet-A	3.3106 eV	374.50 nm	f=0.0224
270 -> 273		0.69631			
Excited State	4:	Singlet-A	3.3107 eV	374.49 nm	f=0.0224
269 -> 273		0.69631			
Excited State	5:	Singlet-A	3.6029 eV	344.12 nm	f=0.0105
272 -> 274		0.67283			
272 -> 275		0.11810			
Excited State	6:	Singlet-A	3.6030 eV	344.11 nm	f=0.0105
272 -> 274		-0.11811			
272 -> 275		0.67283			
Excited State	7:	Singlet-A	3.7082 eV	334.35 nm	f=0.0000
269 -> 274		0.41307			
269 -> 275		-0.27215			

270 -> 274 0.27308

270 -> 275 0.41421

Excited State 8: Singlet-A 3.7391 eV 331.58 nm f=0.1440

271 -> 274 0.65739

271 -> 275 0.17478

Excited State 9: Singlet-A 3.7392 eV 331.58 nm f=0.1439

271 -> 274 -0.17477

271 -> 275 0.65732

Excited State 10: Singlet-A 3.7454 eV 331.03 nm f=0.0000

269 -> 274 0.38766

269 -> 275 -0.26919

270 -> 274 -0.26911

270 -> 275 -0.38591

272 -> 276 0.22182

Excited State 11: Singlet-A 3.7779 eV 328.18 nm f=0.0040

269 -> 274 0.24284

269 -> 275 0.36910

270 -> 274 -0.36878

270 -> 275 0.24375

271 -> 276 0.29523

271 -> 284 0.11538

Excited State 12: Singlet-A 3.9183 eV 316.42 nm f=0.0000

269 -> 274 -0.13062

270 -> 275 0.13050

272 -> 276 0.64396

Excited State 13: Singlet-A 3.9772 eV 311.74 nm f=0.0015

269 -> 274 -0.12168

269 -> 275 -0.18518

270 -> 274 0.18853

270 -> 275 -0.12410

271 -> 276 0.60098

271 -> 284 0.18771

Excited State 14: Singlet-A 3.9857 eV 311.07 nm f=0.0000

269 -> 274 0.28216

269 -> 275 0.40525

270 -> 274 0.40344

270 -> 275 -0.28110

Excited State 15: Singlet-A 4.1254 eV 300.54 nm f=0.2290

269 -> 276 -0.24467

270 -> 276 0.53701

271 -> 277 0.10294

272 -> 274 0.11545

272 -> 277 0.28443

Excited State 16: Singlet-A 4.1255 eV 300.53 nm f=0.2292

269 -> 276 0.53699

270 -> 276 0.24493

271 -> 278 -0.10265

272 -> 275 0.11552

272 -> 278 0.28415

Excited State 17: Singlet-A 4.2093 eV 294.55 nm f=0.0200

269 -> 277 -0.17851

269 -> 278 -0.10863

270 -> 277 0.10918

270 -> 278 -0.17874

271 -> 284 -0.15388

272 -> 279 0.60381

Excited State 18: Singlet-A 4.2449 eV 292.08 nm f=0.0011

269 -> 277 -0.12847

269 -> 282 0.12694

270 -> 278 0.12761

270 -> 283 0.12696

271 -> 281 -0.16364

272 -> 280 0.61448

Excited State 19: Singlet-A 4.2455 eV 292.04 nm f=0.0447

269 -> 276 0.15197

269 -> 279 -0.16223

269 -> 280 -0.11113

270 -> 276 -0.23739

270 -> 279 0.10840

272 -> 277 0.56757

Excited State 20: Singlet-A 4.2456 eV 292.03 nm f=0.0454

269 -> 276 -0.23940

269 -> 279 -0.10971

270 -> 276 -0.15429

270 -> 279 -0.16492

270 -> 280 0.11074

272 -> 278 0.57355

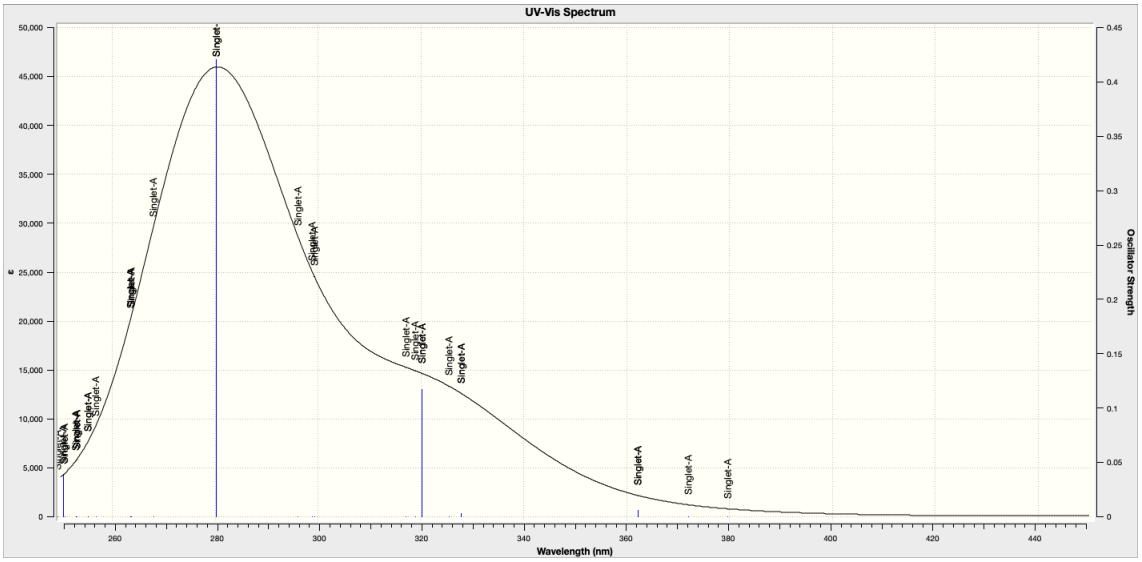


Figure S10. Simulated absorption spectra of **1d** calculated at the B3LYP/6-31+G(d,p).

Table S5. Selected wavelengths, oscillator strengths, and compositions of major electronic transitions of **1d**.

Excited State 1: Singlet-A 3.2651 eV 379.72 nm f=0.0000

144 ->145 0.70556

Excited State 2: Singlet-A 3.3326 eV 372.03 nm f=0.0000

143 ->145 0.69694

144 ->148 0.11055

Excited State 3:	Singlet-A	3.4228 eV	362.23 nm	f=0.0061
142 ->145	0.69253			
Excited State 4:	Singlet-A	3.4228 eV	362.23 nm	f=0.0061
141 ->145	0.69253			
Excited State 5:	Singlet-A	3.7813 eV	327.89 nm	f=0.0031
142 ->148	0.14453			
144 ->146	0.68320			
Excited State 6:	Singlet-A	3.7813 eV	327.89 nm	f=0.0031
141 ->148	-0.14453			
144 ->147	0.68320			
Excited State 7:	Singlet-A	3.8092 eV	325.48 nm	f=0.0000
141 ->146	0.26532			
141 ->147	0.42100			
142 ->146	0.42102			
142 ->147	-0.26531			
Excited State 8:	Singlet-A	3.8714 eV	320.26 nm	f=0.1174
141 ->148	-0.13944			
143 ->146	0.67692			
Excited State 9:	Singlet-A	3.8714 eV	320.26 nm	f=0.1174
142 ->148	0.13944			
143 ->147	0.67692			
Excited State 10:	Singlet-A	3.8877 eV	318.92 nm	f=0.0000
141 ->146	-0.20206			
141 ->147	0.45489			
142 ->146	-0.45488			
142 ->147	-0.20209			
Excited State 11:	Singlet-A	3.9095 eV	317.14 nm	f=0.0000
141 ->146	0.38407			
141 ->147	-0.24202			
142 ->146	-0.24200			
142 ->147	-0.38406			
143 ->148	0.28816			
Excited State 12:	Singlet-A	4.1420 eV	299.33 nm	f=0.0000

141 ->146	-0.17333			
141 ->147	0.10924			
142 ->146	0.10928			
142 ->147	0.17325			
143 ->148	0.64306			
Excited State 13:	Singlet-A	4.1481 eV	298.90 nm	f=0.0000
141 ->146	0.45004			
141 ->147	0.19996			
142 ->146	-0.19994			
142 ->147	0.45007			
Excited State 14:	Singlet-A	4.1869 eV	296.12 nm	f=0.0000
143 ->145	-0.10883			
144 ->148	0.69280			
Excited State 15:	Singlet-A	4.4239 eV	280.26 nm	f=0.4205
141 ->148	0.10021			
142 ->148	0.65149			
143 ->147	-0.14604			
144 ->146	-0.15113			
Excited State 16:	Singlet-A	4.4239 eV	280.26 nm	f=0.4205
141 ->148	0.65149			
142 ->148	-0.10021			
143 ->146	0.14604			
144 ->147	0.15114			
Excited State 17:	Singlet-A	4.6261 eV	268.01 nm	f=0.0000
141 ->151	0.17500			
142 ->150	0.17500			
144 ->149	0.64817			
Excited State 18:	Singlet-A	4.7020 eV	263.69 nm	f=0.0000
141 ->151	0.18294			
142 ->150	-0.18294			
143 ->149	0.62608			
144 ->152	0.16256			
Excited State 19:	Singlet-A	4.7033 eV	263.61 nm	f=0.0000

142 ->149	0.45551			
142 ->152	-0.13046			
143 ->150	-0.20318			
144 ->150	0.46010			
Excited State 20:	Singlet-A	4.7033 eV	263.61 nm	f=0.0000
141 ->149	0.45551			
141 ->152	0.13046			
143 ->151	0.20319			
144 ->151	0.46010			

4. References

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