

Supporting Information for

Meta–Para–Linked Octaaza[1₈]cyclophanes and Their Polycationic States

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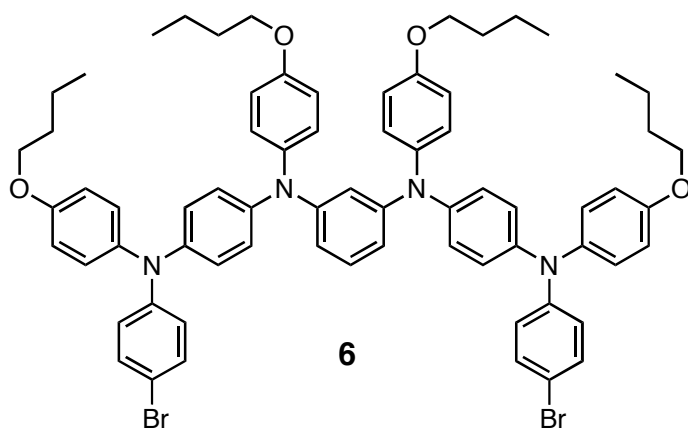
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General Experimental Methods

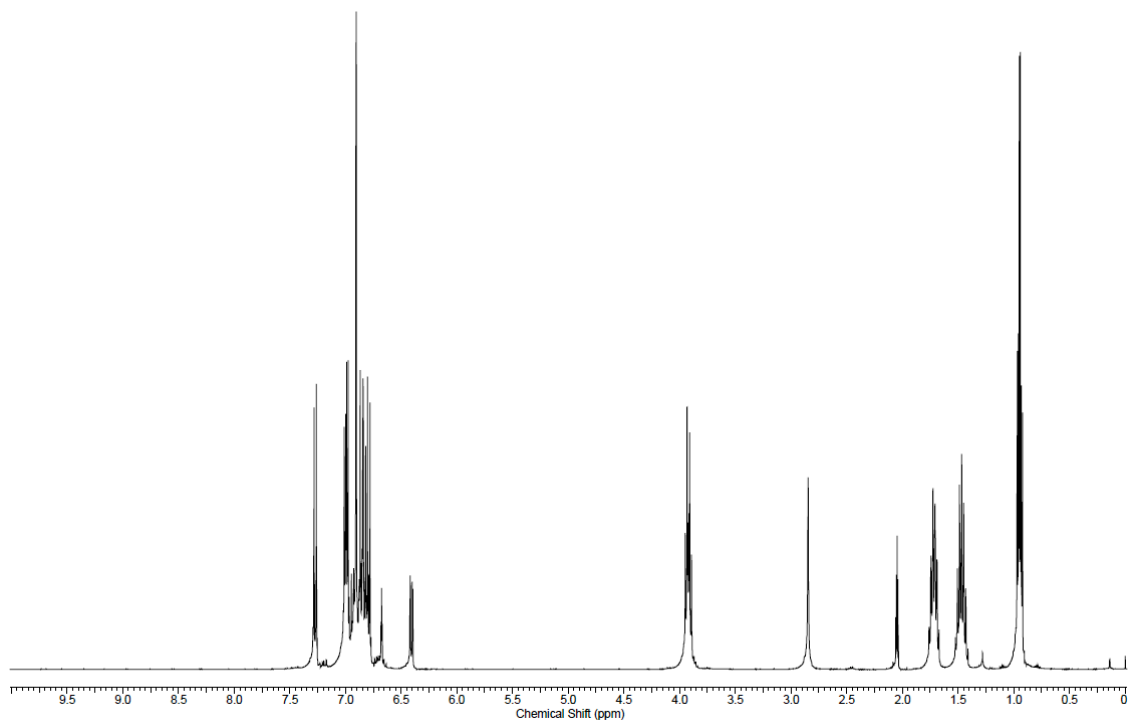
Column chromatography was performed with silica gel (neutral (pH 7.0±0.5) spherical grain 40-100 μm in diameter). Elemental analyses were performed by Center for Organic Elemental Microanalysis, Kyoto University. ^1H and ^{13}C NMR spectra were recorded by a 400 MHz FT-NMR spectrometer. Variable-temperature ^1H NMR spectra were recorded by a 300 MHz FT-NMR spectrometer. Chemical shifts of NMR spectra are determined relative to internal tetramethylsilane (TMS) standard (δ), and are given in parts per million (ppm). Low resolution (LR) fast-atom-bombardment (FAB) mass spectra (MS) were obtained on a double-focusing mass spectrometer with *m*-nitrobenzyl alcohol as a matrix. High-resolution electrospray ionization (ESI) mass spectra were acquired using a mass spectrometer equipped with an orbitrap mass analyzer. UV-Vis-NIR absorption spectra were obtained with a double beam spectrometer.

^1H - and ^{13}C -NMR Spectra for Compounds 2, 3, and 6

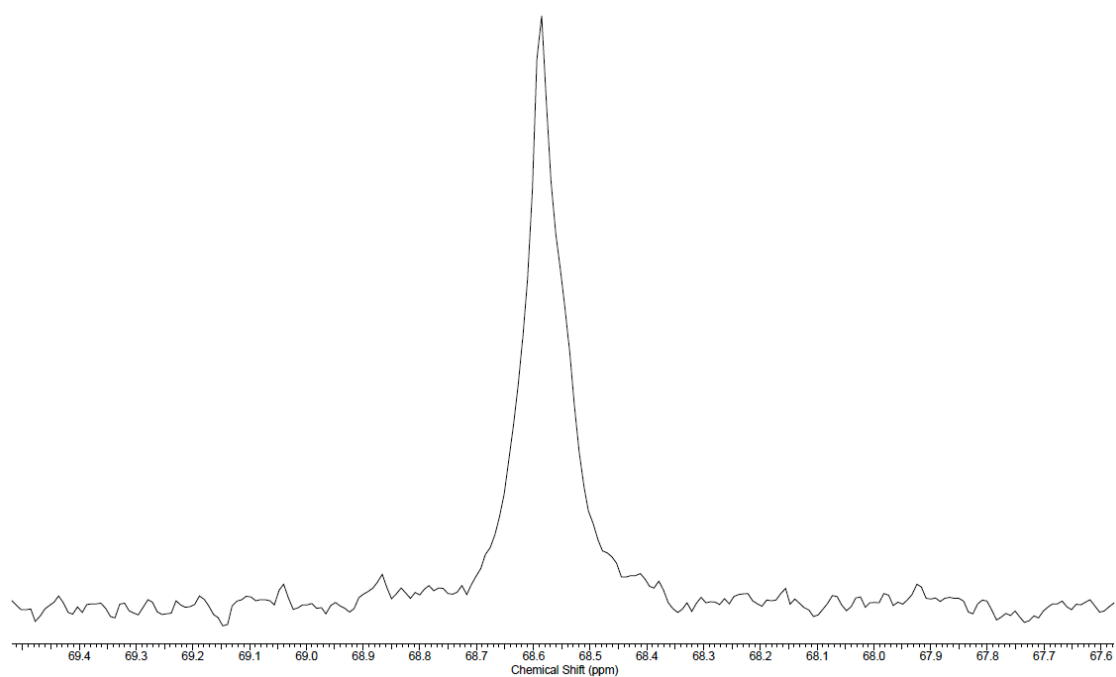
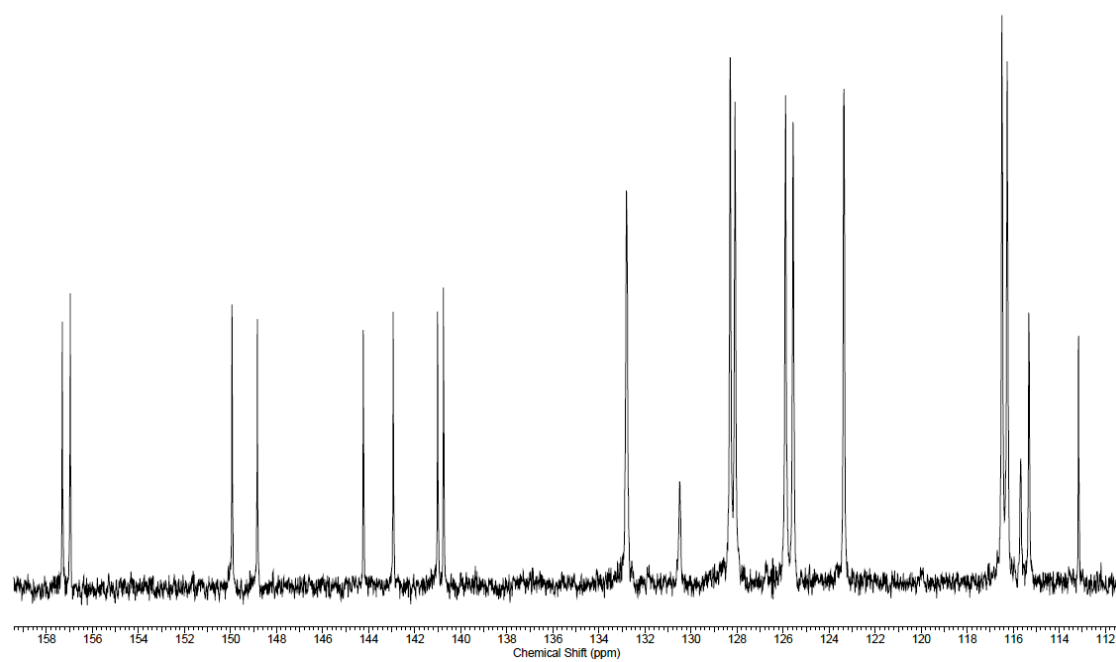
Compound 6

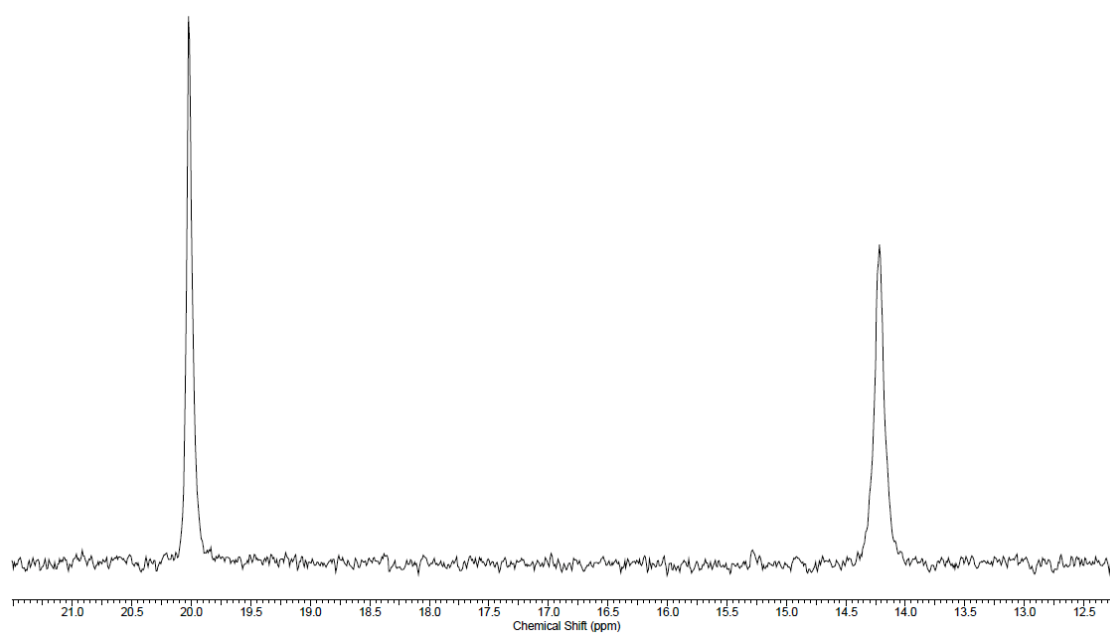
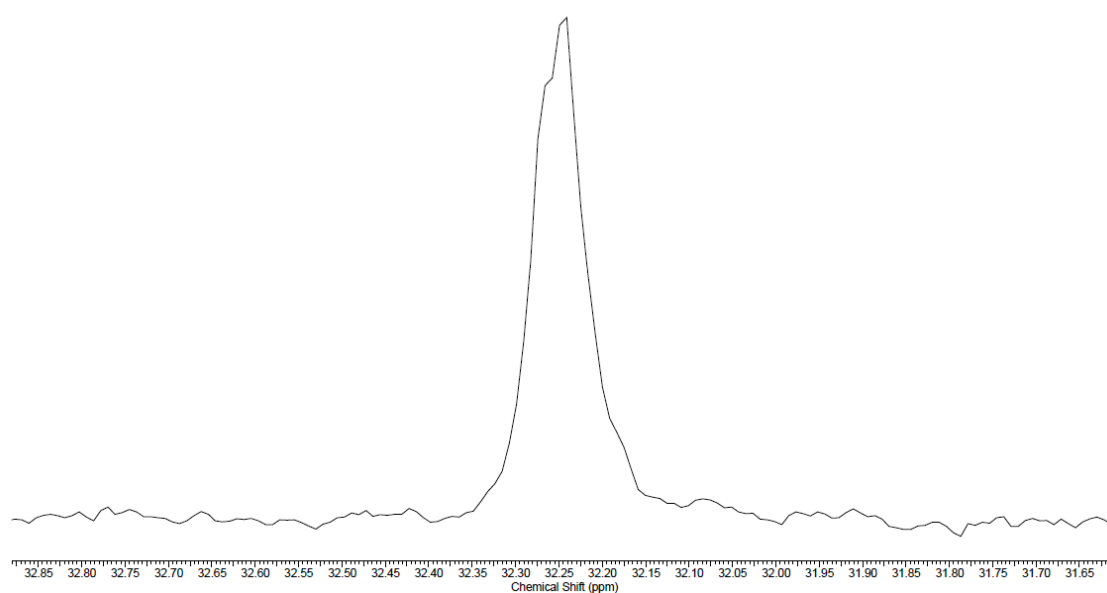


^1H NMR (acetone- d_6)

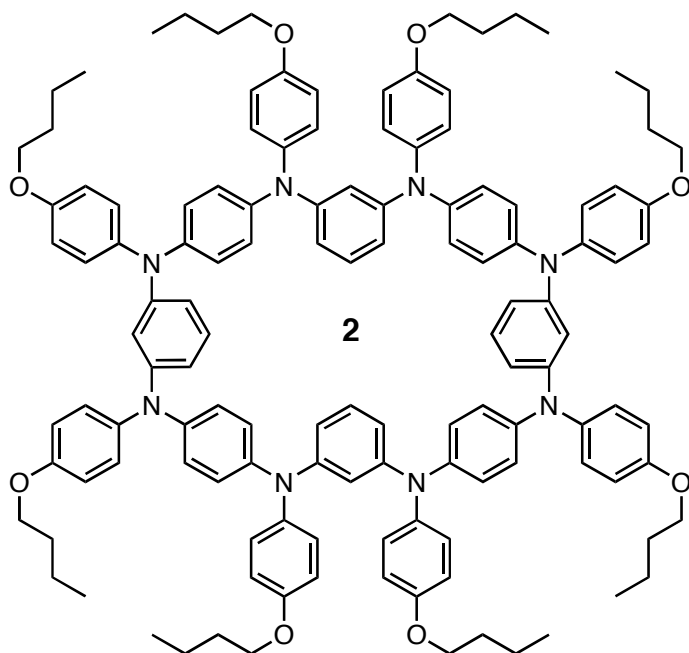


^{13}C NMR (acetone- d_6)

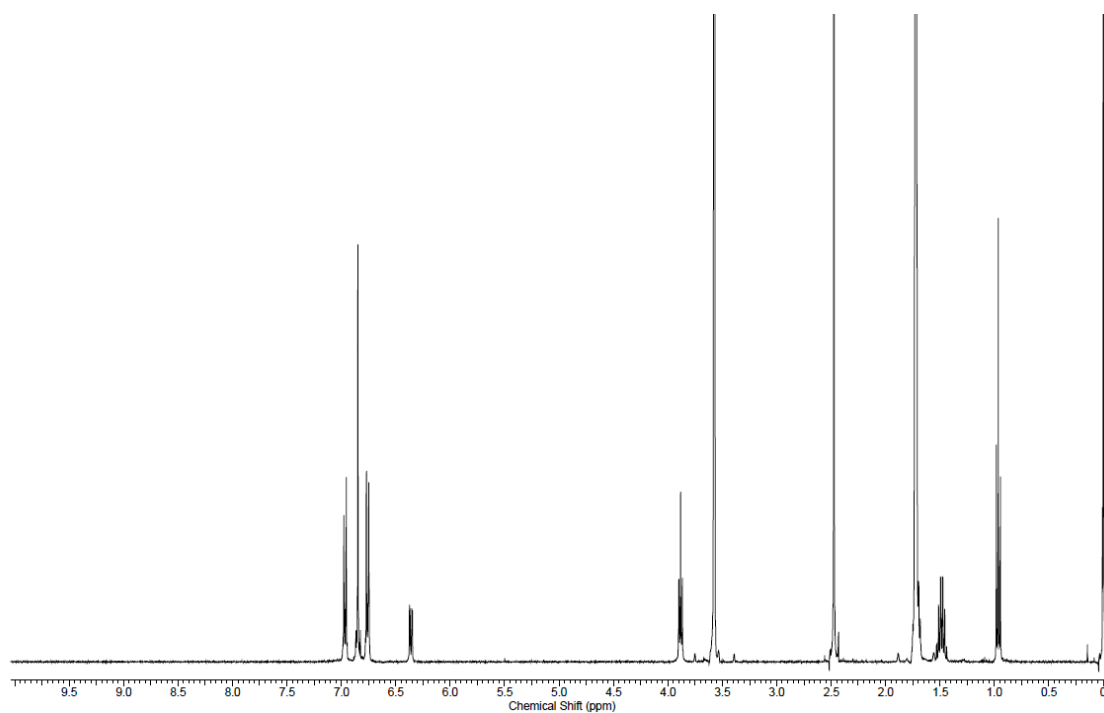




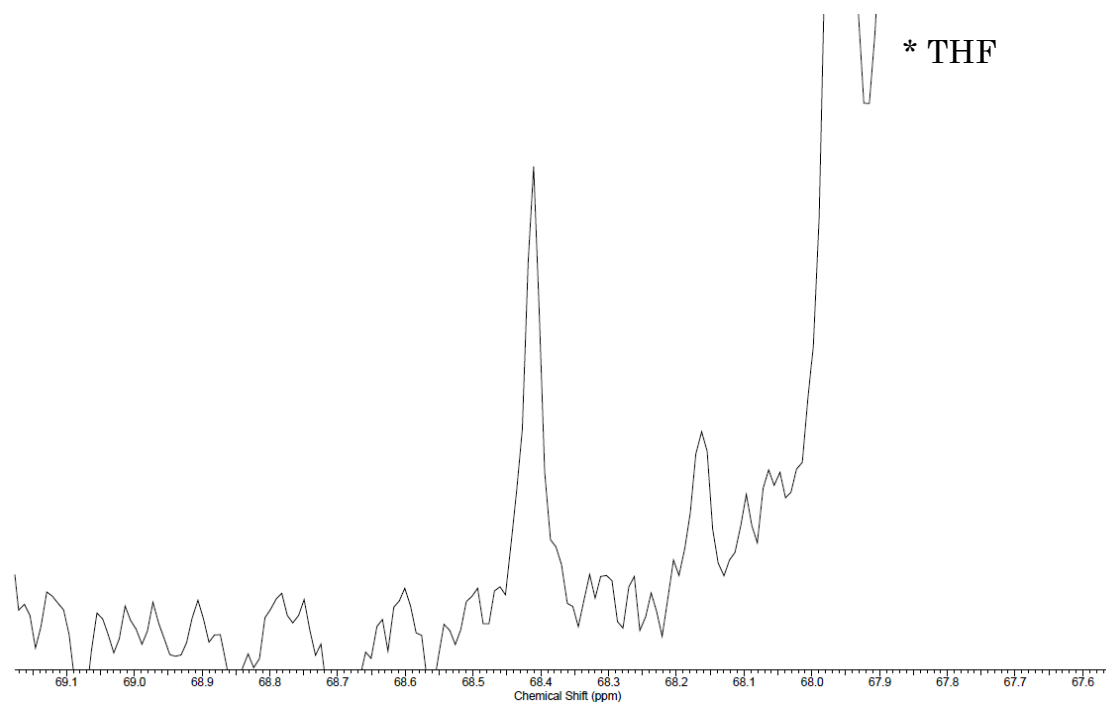
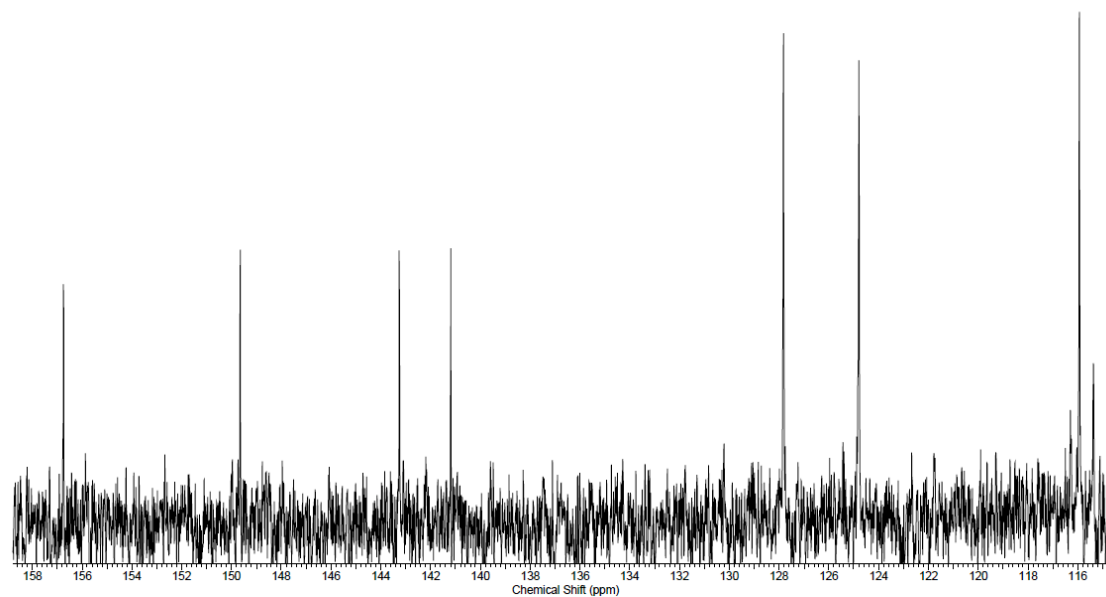
Compound 2

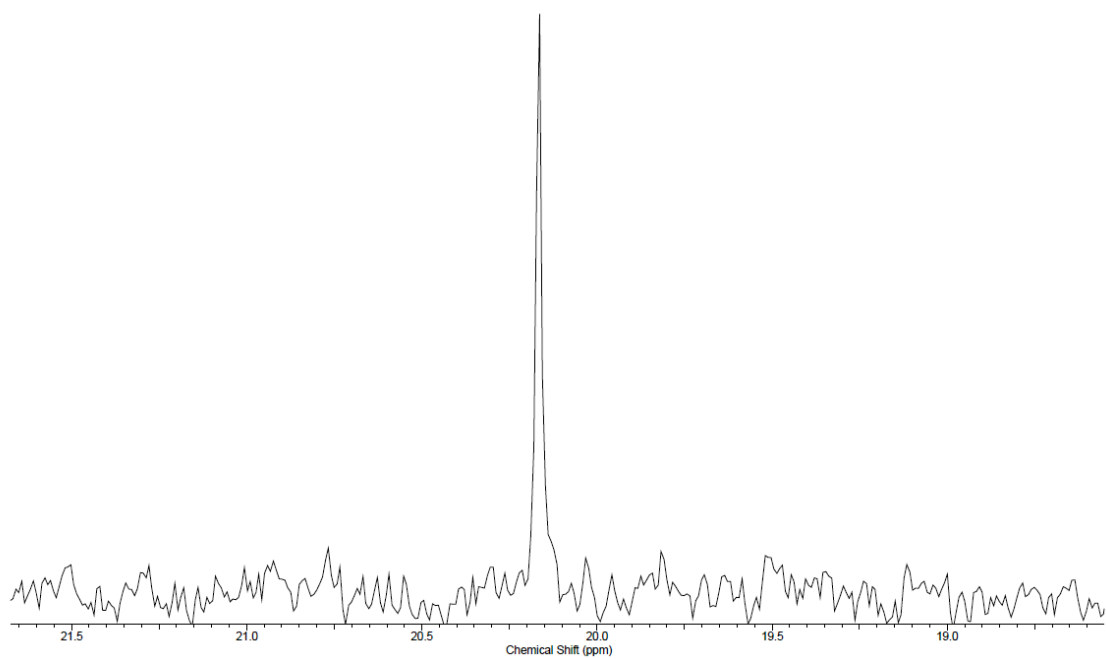
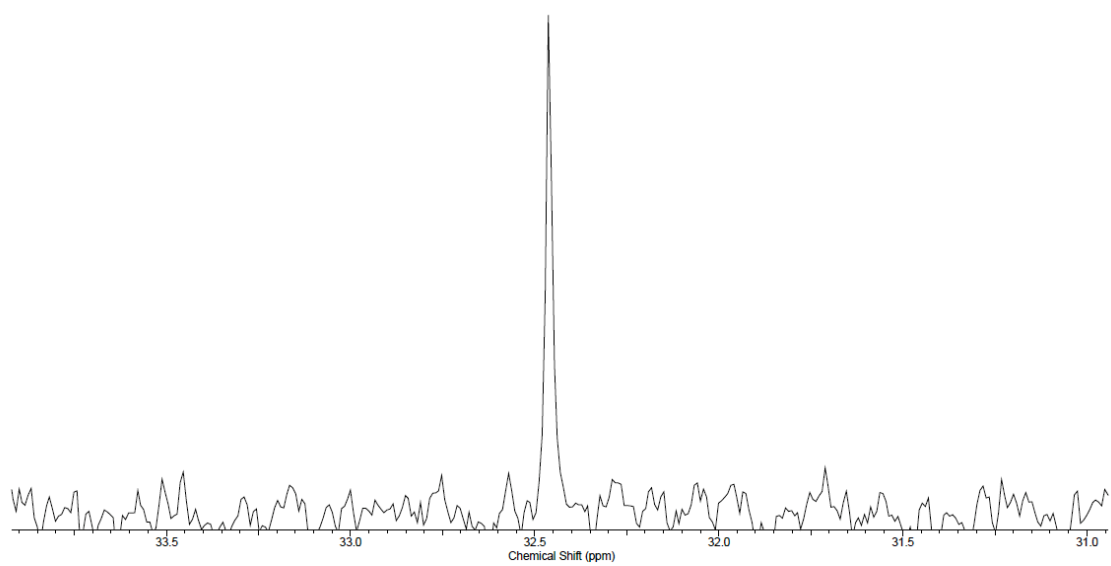


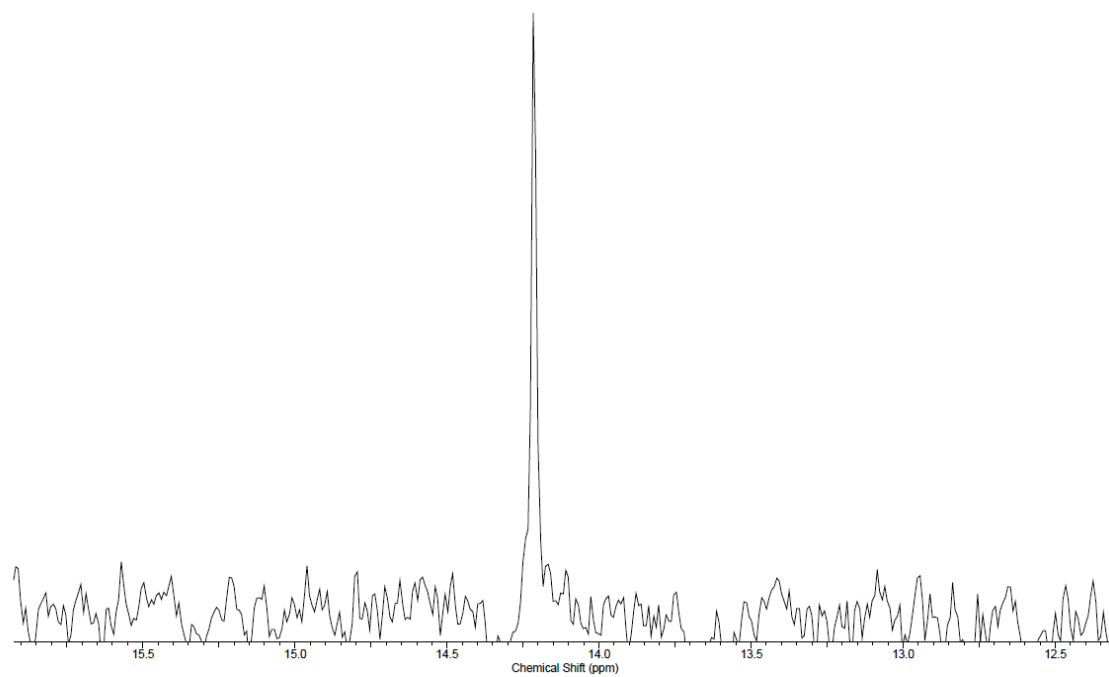
¹H NMR (tetrahydrofuran-*d*₈)



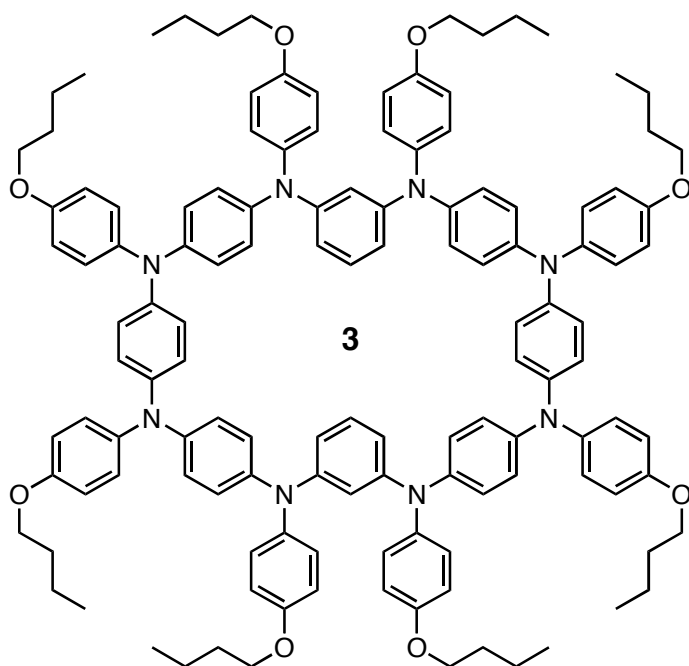
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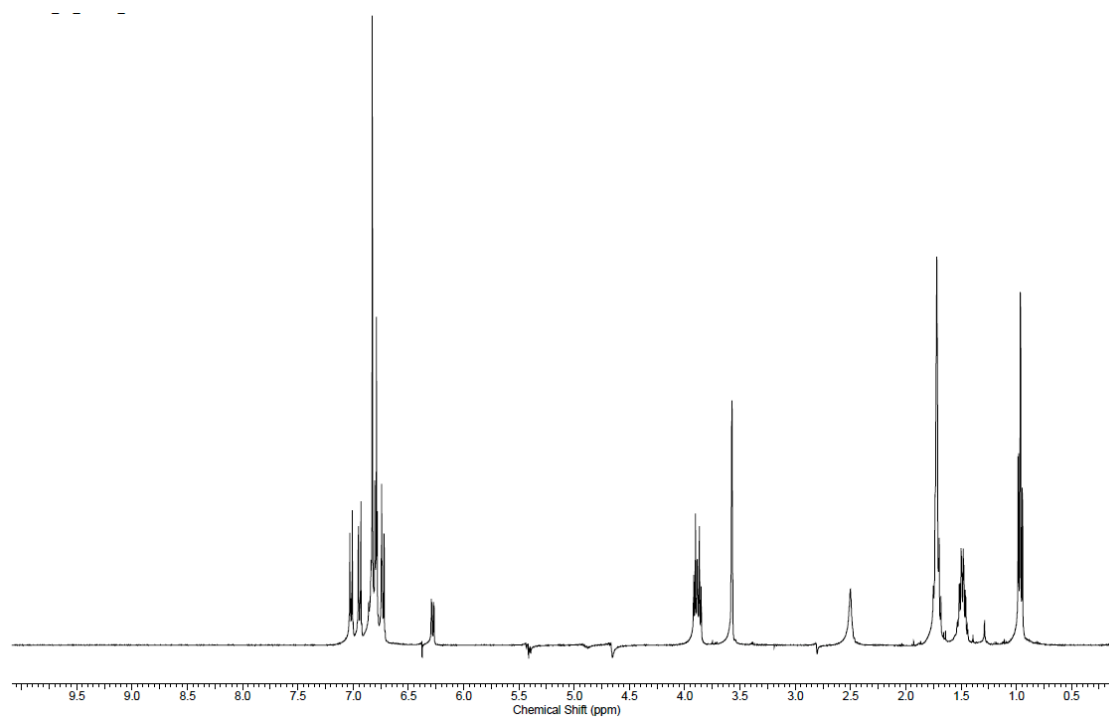




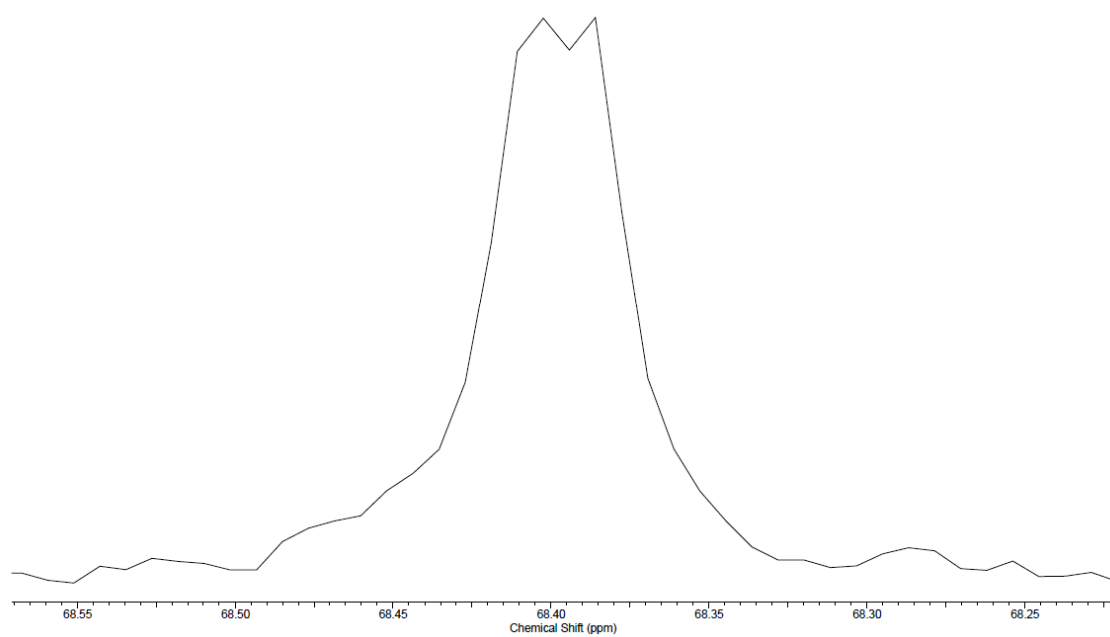
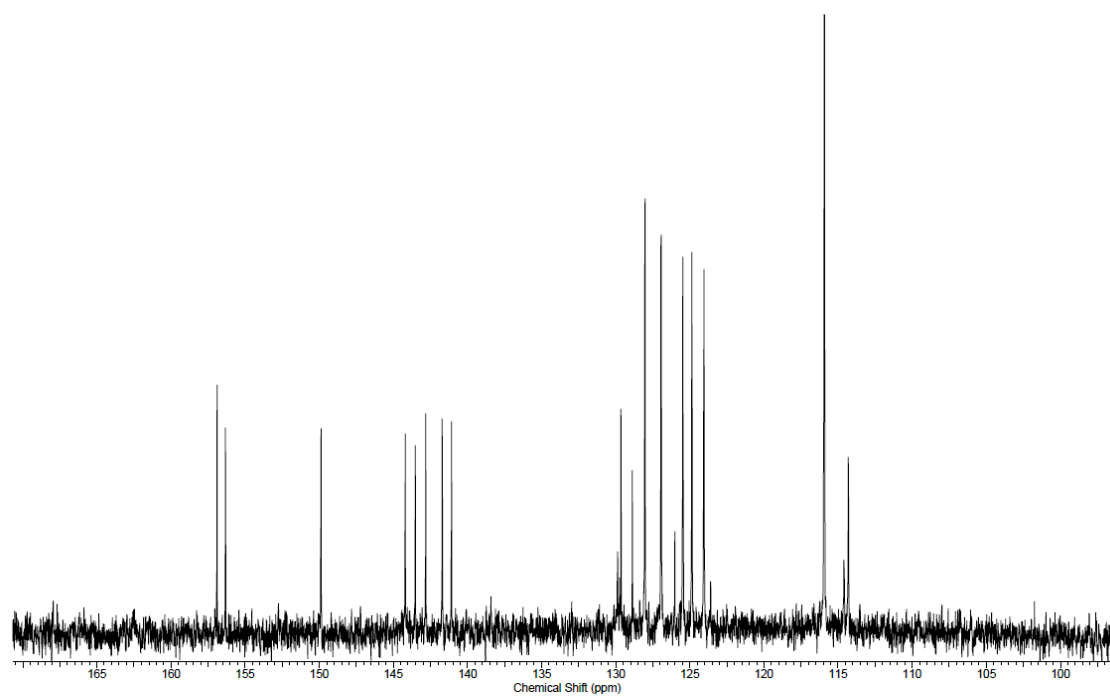
Compound 3

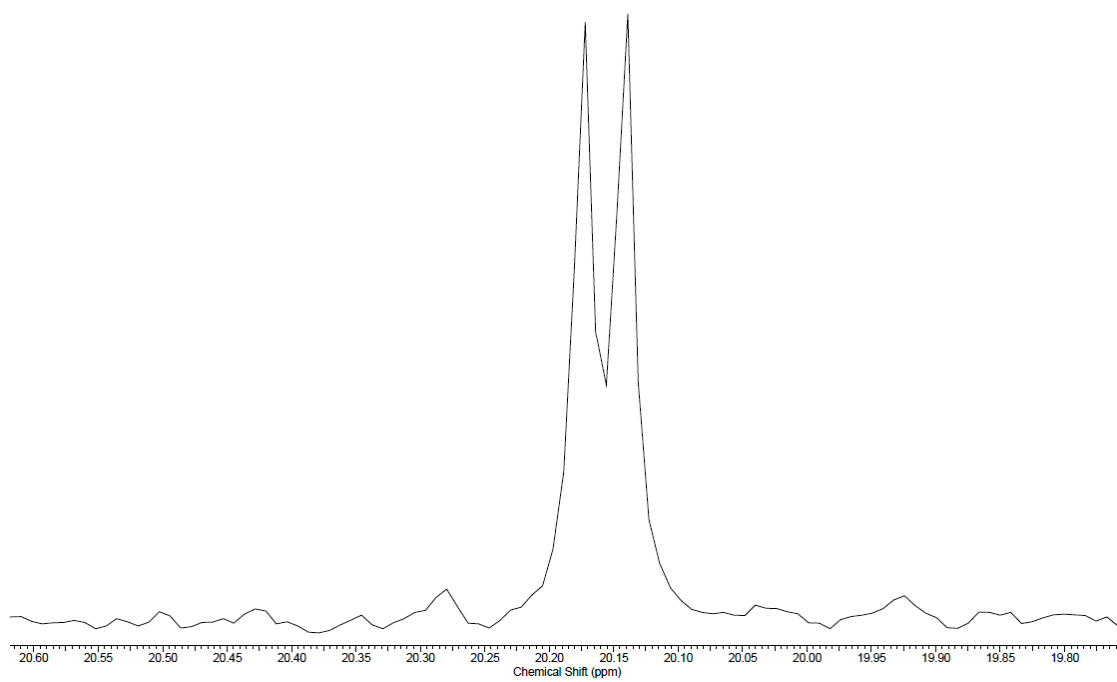
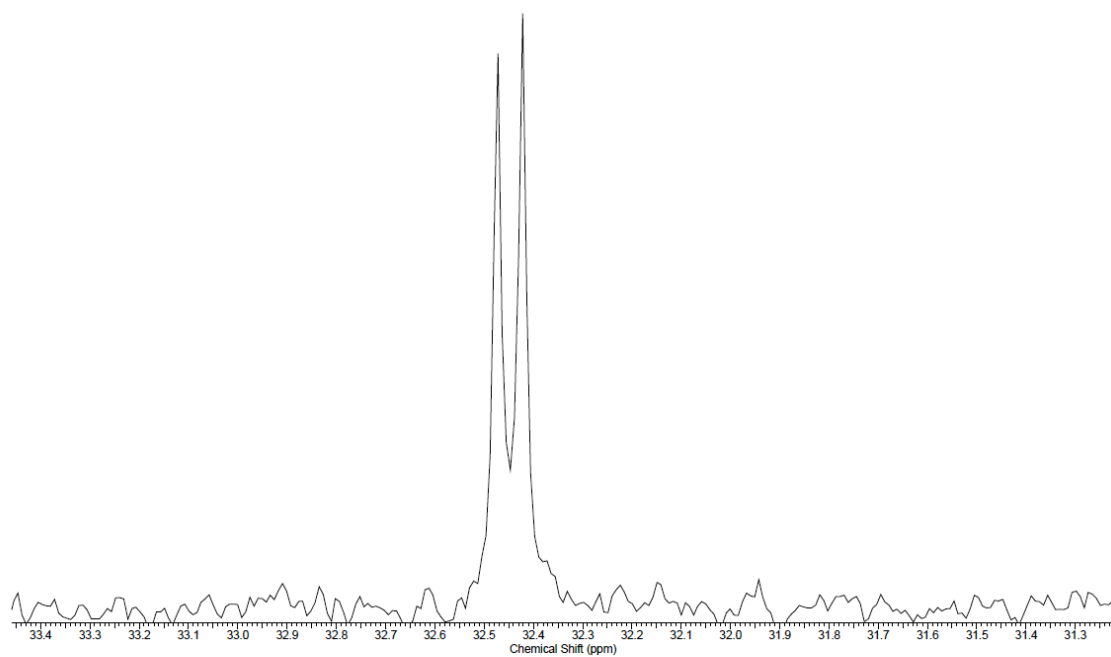


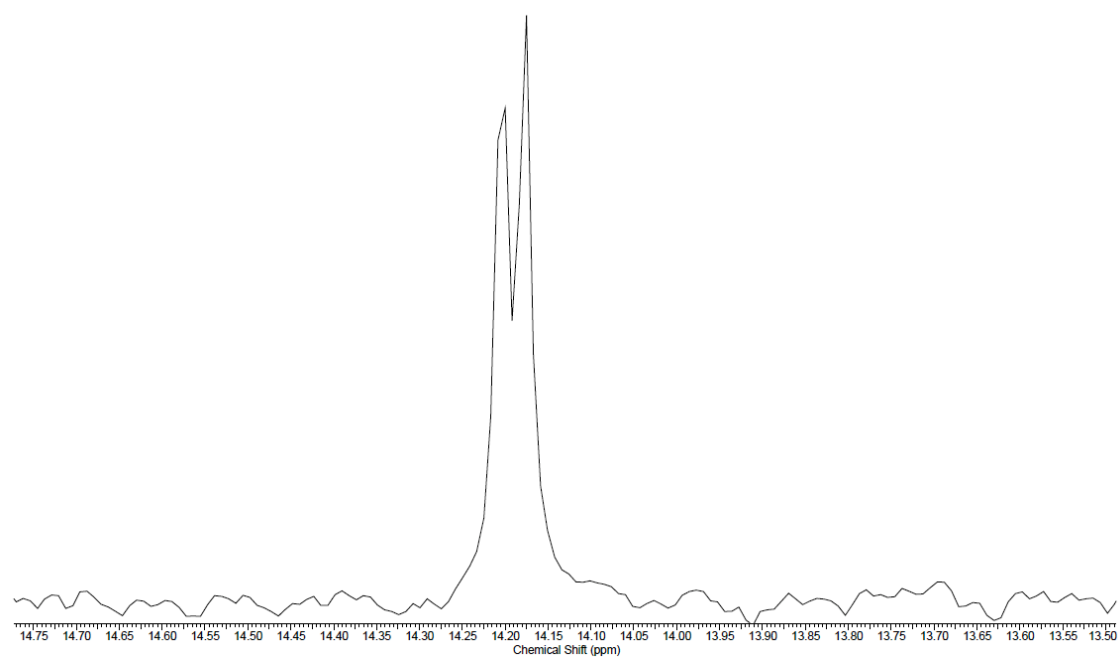
¹H NMR (tetrahydrofuran-*d*₈)



^{13}C NMR (tetrahydrofuran- d_8)







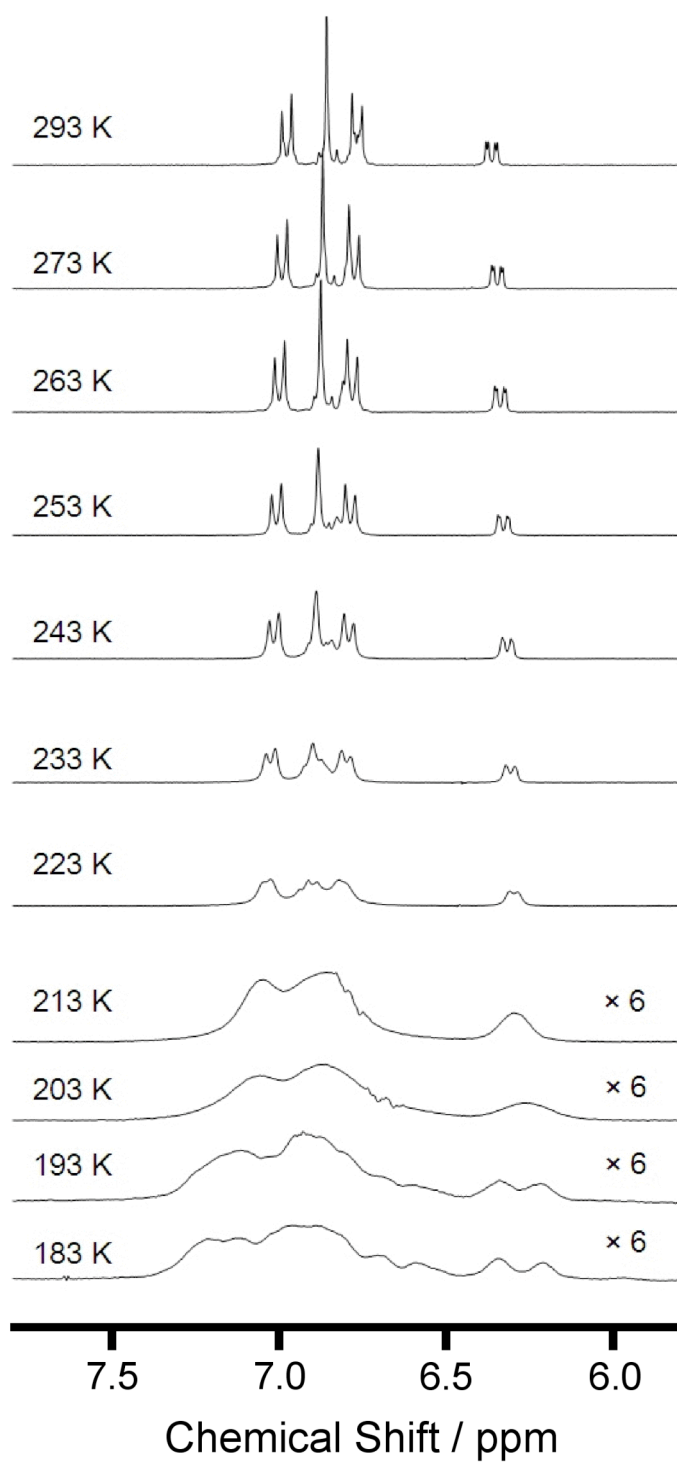


Figure S1. Variable-temperature ^1H NMR spectra (300 MHz, tetrahydrofuran- d_8) of **2**.

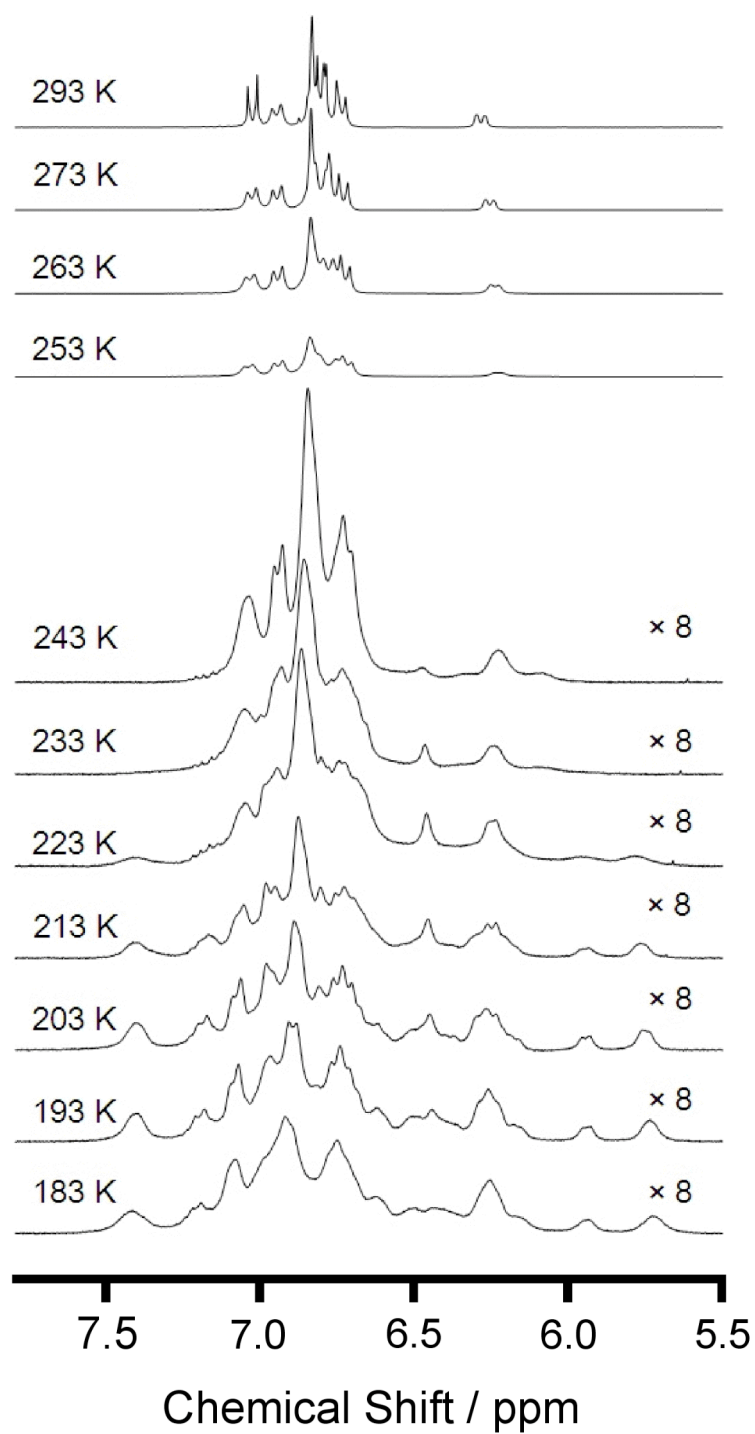


Figure S2. Variable-temperature ^1H NMR spectra (300 MHz, tetrahydrofuran- d_8) of **3**.

DFT Calculations of **2'** and **3'**

To check the influence of optimized macrocyclic structures in **2** and **3** by replacing long *n*-butoxy groups with short methoxy groups, we carried out semi-empirical AM1 (Austin model 1)^[S1] calculations on both **2**, **2'**, **3**, and **3'**. As shown in Figures S3 and S4, the replacement of long alkyl chains with short ones did not affect the optimized structures. Thus we conducted performed the DFT calculations of the model compounds **2'** and **3'** with methoxy groups. In addition, prior to the DFT calculations on the most and the next stable conformers of **2'** and **3'**, we performed the semi-empirical AM1 calculations on possible conformers of **2'** and **3'**. For **2'**, four conformers are possible depending on the orientations of four *meta*-phenylene rings: all the four rings are up to the molecular plane (C_4 conformer), the four rings are alternately up and down to the molecular plane (D_{2d} conformer), one ring is solely down to the molecular plane (C_s conformer), and the adjacent two rings are up and the others are down to the molecular plane (C_{2h} conformer) (Figure S5). As a consequence, the relative energies for C_4 , D_{2d} , C_s , and C_{2h} conformers were predicted to be 0.0, 0.99, 1.18, 1.27 kcal mol⁻¹, respectively, as compared to the C_4 conformer. In contrast, in the AM1 optimizations on **3'**, it was found that the C_{2v} - and C_s -symmetric conformers were only possible (Figure S4 (a) and (c)). Contrary to the DFT results, the C_{2v} conformer lay 0.31 kcal mol⁻¹ above the C_s conformer.

DFT calculations were performed with using a hybrid Hartree–Fock/density functional theory (HF/DFT) method (B3LYP).^[S2] Full geometrical optimization of **2'** and **3'** were carried out under C_4 and C_{2v} symmetrical constraints, respectively and furthermore, their local minimum structures were confirmed by performing subsequent frequency analyses. The possibility for the other conformations was tested. The next lowest energy conformers for **2'** and **3'** were found to be in D_{2d} and C_s symmetry, respectively. All the computations employed the 6-31G* basis set.^[S3] All these computational approaches are implemented in Gaussian 09 package of ab initio MO calculation.^[S4] We have also calculated with the more reliable Minnesota density functional (M06-2X), which has improved performance for main-group thermochemistry, barrier heights, and noncovalent interactions as compared with the popular B3LYP functional.^[S5] For the M06-2X functional, the 6-31G** basis set was employed.^[S3] As a result, the relative energies between two competing conformers were

estimated to be 5.18 and 0.02 kcal mol⁻¹ for **2'** and **3'**, respectively. On the other hand, the M06-2X optimized geometries for two conformers were similar with the B3LYP ones (Figure S6). In addition, the MO energy diagrams similar to those for B3LYP/6-31G* calculations were obtained for the M06-2X/6-31G* calculations (Figure S7).

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- [S1] Dewar, M. J. S.; Zebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.
- [S2] K. Ragavachari, *Theor. Chim. Acc.* **2000**, *103*, 361 and references cited therein.
- [S3] W. J. Hehre, L. Radom, P.v. R. Schleyer, J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, **1986**.
- [S4] M. J. Frisch, *et al.*, Gaussian 09 (Revision C.01), Gaussian, Inc., Wallingford CT, **2009**.
- [S5] (a) Zhao, Y.; Truhlar, D. G. *J. Chem. Phys.* **2006**, *125*, 194101. (b) Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157. (c) Zhao, Y.; Truhlar, D. G. *Chem. Phys. Lett.* **2011**, *502*, 1.

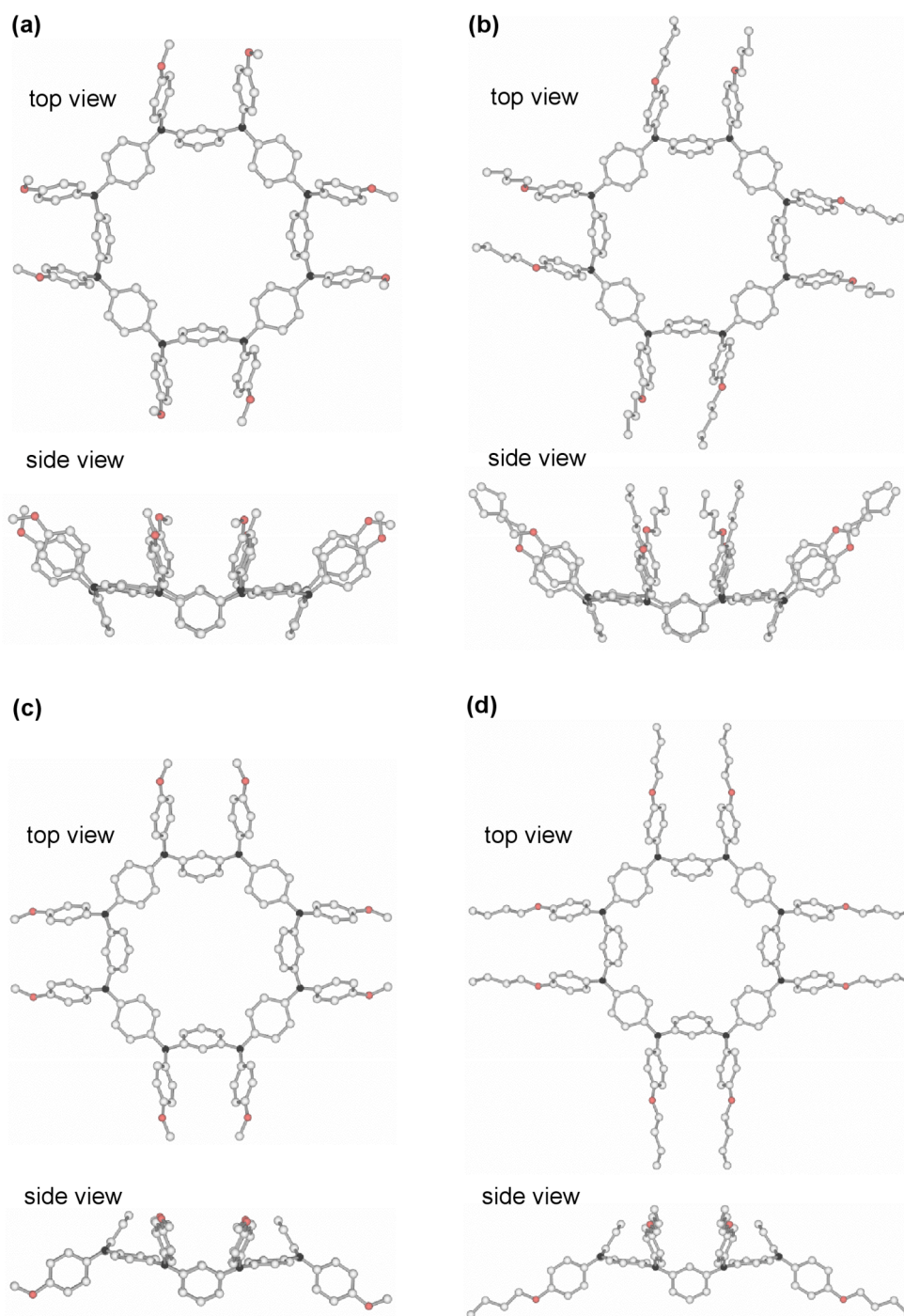
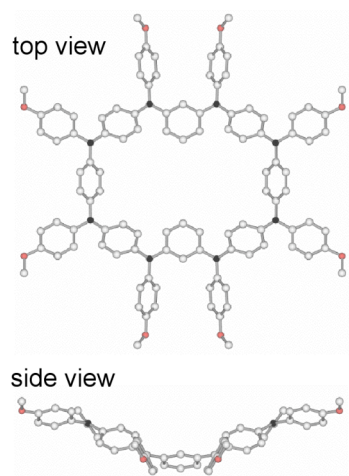
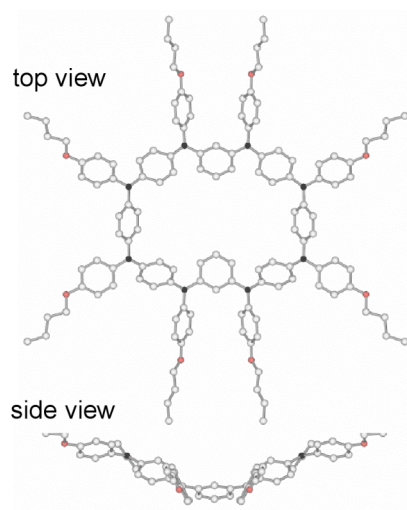


Figure S3. AM1-optimized structures of the C_4 - and D_{2d} -conformers for the model compounds **2'** ((a) and (c)) and for **2** ((b) and (d)).

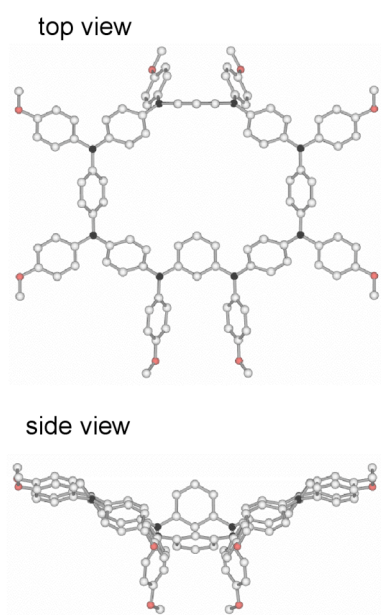
(a)



(b)



(c)



(d)

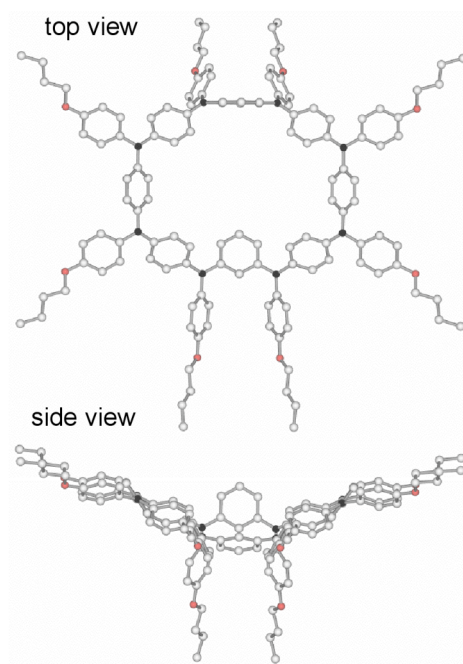


Figure S4. AM1-optimized structures of the C_{2v} - and C_s -conformers for the model compounds **3'** ((a) and (c)) and for **3** ((b) and (d)).

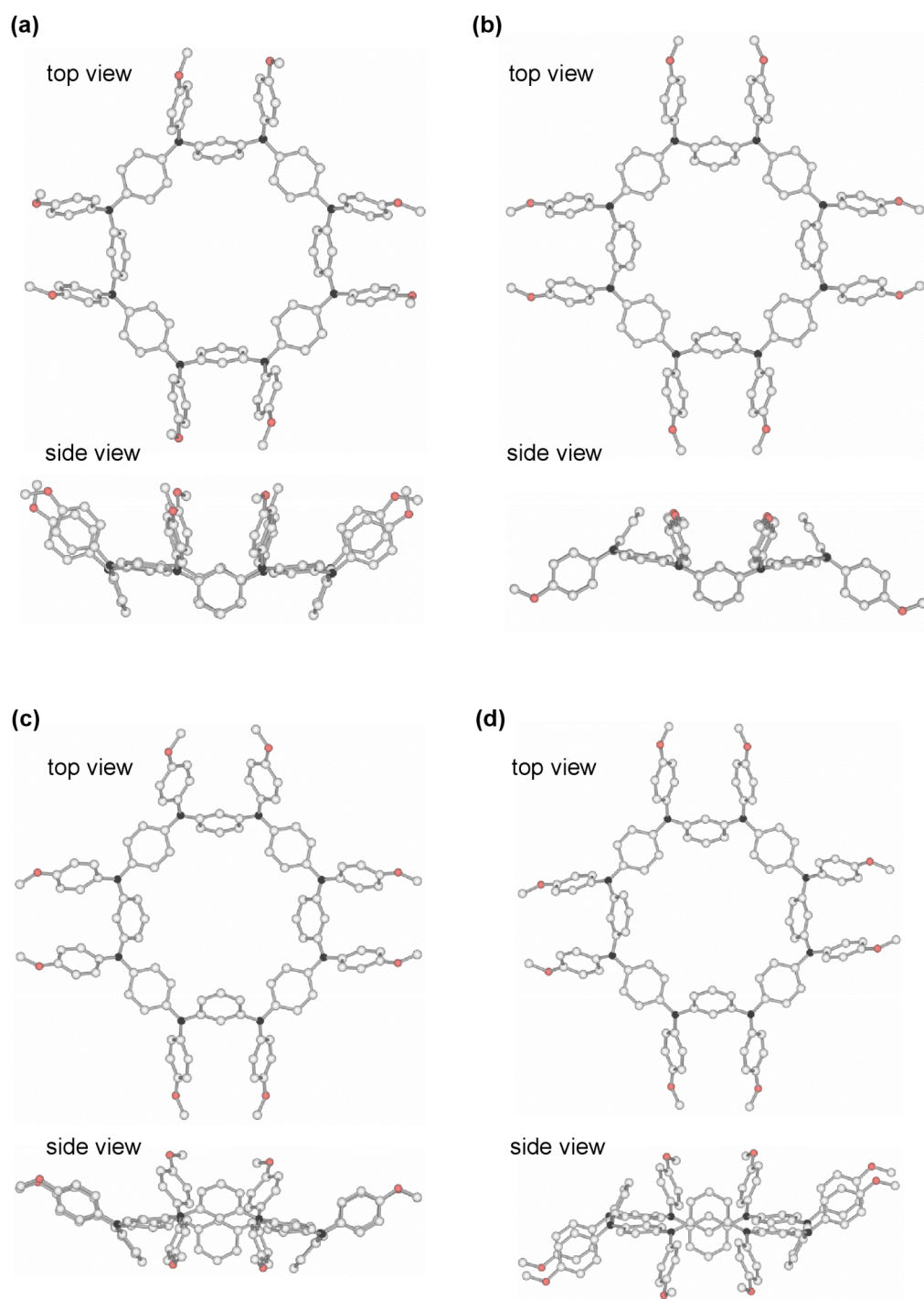


Figure S5. AM1-optimized structures of the model compounds **2'**: (a) C_{4-} , (b) D_{2d-} , (c) C_{s-} , and (d) C_{2h-} -conformers.

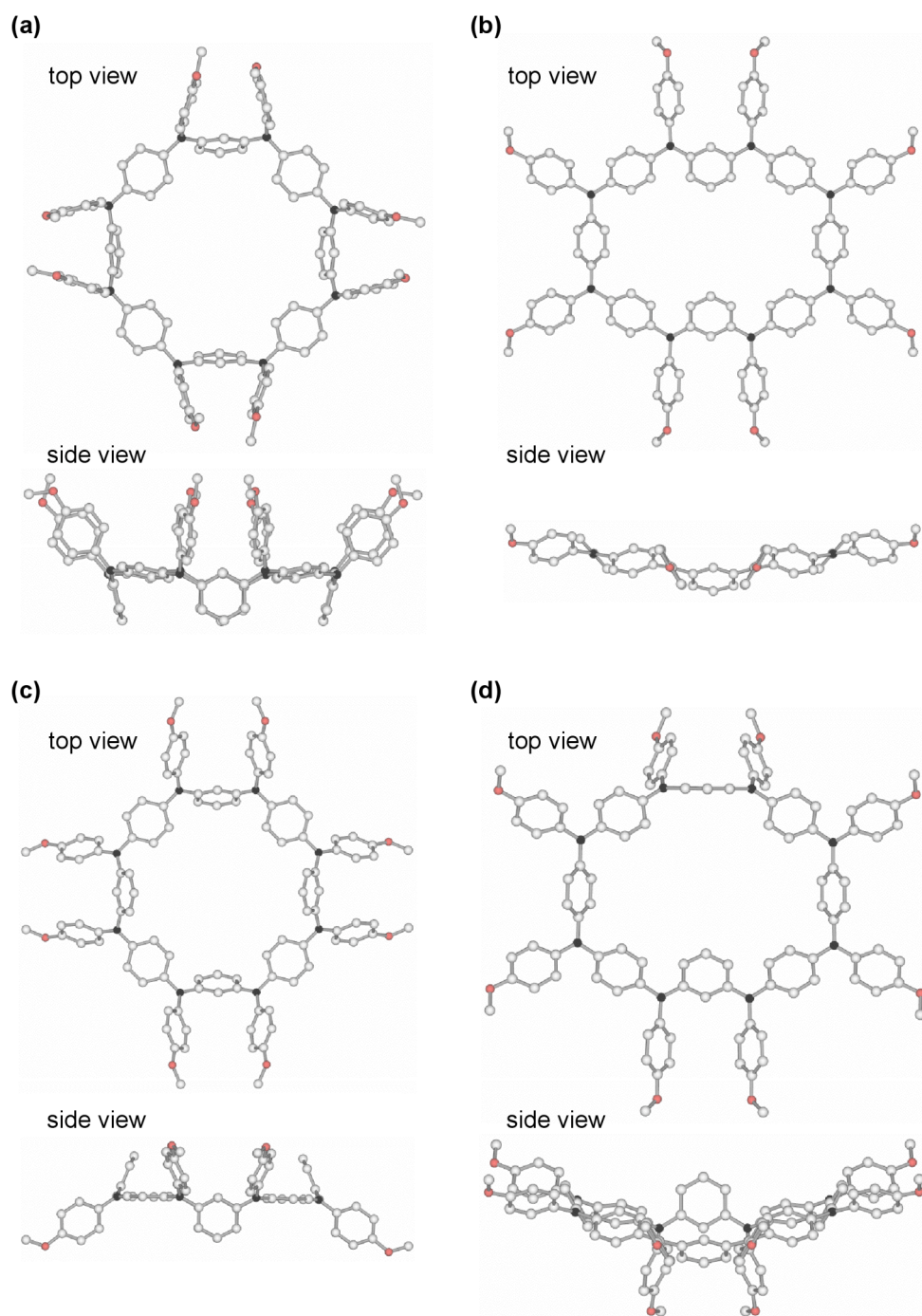


Figure S6. M06-2X-optimized structures of the model compounds **2'** and **3'**: the lowest energy conformers for (a) **2'** (C_4) and (b) **3'** (C_{2v}), and the next lowest energy conformers for (c) **2'** (D_{2d}) and (d) **3'** (C_s)

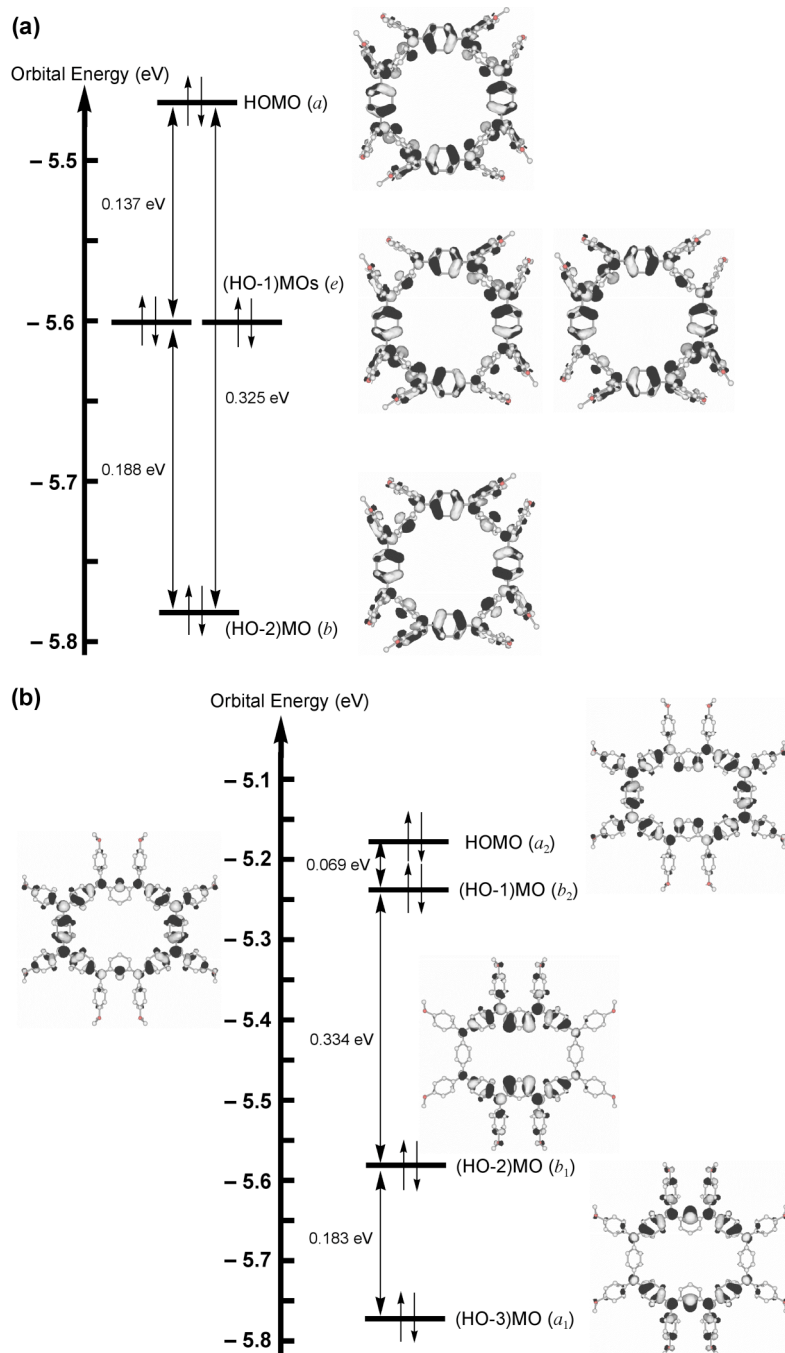


Figure S7. Relative energy levels of the frontier Kohn–Sham molecular orbitals for the model compounds (a) **2'** and (b) **3'** based on calculations at the M06-2X/6-31G** level.

Optimized geometry of **2'** (C_4)

E = -5055.75681357 hartree

The number of imaginary frequencies: 0

C	-1.508193	6.275505	-0.845753
N	-0.226288	6.889214	-0.828981
C	-2.678377	7.043047	-0.962415
C	-1.637785	4.881929	-0.736617
C	-2.889205	4.277116	-0.749949
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H	-2.964433	3.199131	-0.650842
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C	4.277116	2.889205	-0.749949
C	6.437997	3.931548	-0.97579
C	5.042954	4.059942	-0.872379
H	4.270046	0.74815	-0.627335
H	3.199131	2.964433	-0.650842
H	8.12191	2.601002	-1.056079
H	7.04956	4.822363	-1.080118
N	4.420162	5.336132	-0.888544
C	8.050283	0.002938	-0.037432
C	6.270224	-0.855861	-1.509426
C	4.969209	6.413528	-0.139139
C	5.755548	-0.67323	-2.803785
C	6.133041	-2.103833	-0.884366
C	5.495788	-3.165988	-1.539895
C	5.110326	-1.728938	-3.444535
C	4.983147	-2.974448	-2.833405
H	6.506021	-2.243208	0.124123
H	5.862526	0.289217	-3.292743
H	4.721717	-1.584978	-4.449415
H	4.492445	-3.796599	-3.343531
C	4.996498	7.71215	-0.67876
C	5.495788	6.216025	1.142117
C	6.04939	7.273896	1.867158
C	5.523722	8.771682	0.045205
C	6.060431	8.562756	1.324043
H	5.479408	5.222194	1.578176
H	6.450863	7.079658	2.855336
H	4.598419	7.882422	-1.674311
H	5.546033	9.774823	-0.369502

O	6.565882	9.671092	1.947479
C	8.168046	0.557619	1.249548
C	9.104804	-0.77927	-0.522168
C	10.241379	-1.021288	0.251818
C	9.305763	0.341743	2.0143
C	10.351372	-0.455222	1.526436
H	9.03397	-1.210512	-1.515858
H	11.03317	-1.63939	-0.155851
H	7.358895	1.162786	1.645878
H	9.399404	0.769226	3.007911
O	11.420533	-0.615063	2.364637
C	7.119445	9.511584	3.242336
C	12.498147	-1.423153	1.923576
H	12.176893	-2.454937	1.726841
H	12.967141	-1.014671	1.018013
H	13.226911	-1.421881	2.736551
H	6.37123	9.151858	3.961654
H	7.971976	8.818856	3.235949
H	7.463542	10.502072	3.546566

Optimized geometry of **2'** (D_{2d})

E = -5055.75539454 hartree

The number of imaginary frequencies: 0

C	-3.454955	5.459187	0.068609
N	-2.448549	6.457958	0.140913
C	-4.81703	5.800392	0.023379
C	-3.115763	4.09609	0.045162
H	-2.071194	3.804311	0.079424
H	-5.106647	6.846434	0.042532
C	-2.624963	7.59425	0.978701
C	-1.218266	6.269443	-0.546005

C	-1.213737	5.823237	-1.877823
C	0.000001	6.487806	0.112266
C	1.218268	6.269443	-0.546005
C	0.000001	5.595991	-2.523351
C	1.213739	5.823237	-1.877823
H	0	6.808742	1.147944
H	-2.155002	5.655016	-2.390317
H	0.000001	5.258498	-3.556587
H	2.155004	5.655016	-2.390316
C	3.115765	4.09609	0.045163
C	4.81703	5.800392	0.02338
C	3.454957	5.459187	0.06861
H	2.071196	3.804311	0.079425
H	5.106647	6.846434	0.042534
N	2.448551	6.457958	0.140913
C	2.624964	7.59425	0.978701
C	5.459187	3.454956	-0.06861
C	5.800392	4.81703	-0.02338
C	4.09609	3.115764	-0.045163
H	3.804312	2.071195	-0.079425
H	6.846434	5.106647	-0.042534
C	-4.09609	3.115764	-0.045164
C	-5.800392	4.81703	-0.023381
C	-5.459187	3.454956	-0.068611
H	-3.80431	2.071195	-0.079426
H	-6.846434	5.106647	-0.042536
N	-6.457958	2.44855	-0.140915
C	-7.59425	2.624963	-0.978703
N	-6.457958	-2.44855	-0.140915
C	-7.59425	-2.624964	-0.978703
C	-6.269443	-1.218267	0.546003
C	-5.823238	-1.213738	1.877821

C	-6.487806	0.000000	-0.112268
C	-6.269443	1.218267	0.546003
C	-5.595992	0.000000	2.523349
C	-5.823238	1.213738	1.877821
H	-6.808742	0.000000	-1.147946
H	-5.655017	-2.155003	2.390316
H	-5.258499	0.000000	3.556585
H	-5.655017	2.155003	2.390315
C	3.169991	7.46798	2.269013
C	2.255526	8.868937	0.535259
C	2.408185	9.99153	1.351765
C	3.346887	8.582359	3.076665
C	2.963245	9.854636	2.628441
H	1.839523	8.984507	-0.460808
H	2.106114	10.961708	0.973746
H	3.456917	6.486624	2.633142
H	3.767761	8.488433	4.073007
O	3.171377	10.883343	3.506331
C	-3.169991	7.46798	2.269012
C	-2.255524	8.868937	0.535259
C	-2.408184	9.99153	1.351764
C	-3.346887	8.582359	3.076664
C	-2.963244	9.854636	2.62844
H	-1.839521	8.984507	-0.460808
H	-2.106113	10.961708	0.973745
H	-3.456916	6.486624	2.633141
H	-3.767761	8.488433	4.073006
O	-3.171377	10.883343	3.50633
C	-7.467979	3.169991	-2.269015
C	-8.868937	2.255525	-0.535262
C	-9.99153	2.408184	-1.351768
C	-8.582359	3.346886	-3.076668

C	-9.854636	2.963244	-2.628444
H	-8.984507	1.839522	0.460806
H	-10.9617	2.106113	-0.973749
H	-6.486623	3.456916	-2.633143
H	-8.488431	3.76776	-4.073009
O	-10.88334	3.171376	-3.506334
C	-7.467979	-3.169991	-2.269014
C	-8.868937	-2.255525	-0.535261
C	-9.99153	-2.408185	-1.351767
C	-8.582359	-3.346888	-3.076667
C	-9.854636	-2.963245	-2.628443
H	-8.984507	-1.839522	0.460806
H	-10.9617	-2.106114	-0.973748
H	-6.486623	-3.456917	-2.633142
H	-8.488431	-3.767762	-4.073008
O	-10.88334	-3.171378	-3.506333
C	-12.18883	-2.798455	-3.103869
C	-12.18883	2.798453	-3.10387
C	-2.798454	12.188838	3.103866
C	2.798454	12.188838	3.103867
H	-12.51488	-3.355367	-2.214753
H	-12.25697	-1.721496	-2.895828
H	-12.84407	-3.044376	-3.94186
H	-12.25697	1.721494	-2.895828
H	-12.51488	3.355366	-2.214754
H	-12.84407	3.044374	-3.941861
H	-1.721495	12.256972	2.895824
H	-3.355366	12.514883	2.21475
H	-3.044375	12.844074	3.941857
H	3.355367	12.514883	2.214751
H	1.721495	12.256972	2.895825
H	3.044375	12.844074	3.941858

C	3.454957	-5.459187	0.068611
N	2.448551	-6.457958	0.140915
C	4.81703	-5.800392	0.023381
C	3.115765	-4.09609	0.045164
H	2.071196	-3.804311	0.079426
H	5.106647	-6.846434	0.042536
C	2.624964	-7.59425	0.978703
C	1.218268	-6.269443	-0.546003
C	1.213739	-5.823238	-1.877821
C	0.000001	-6.487806	0.112268
C	-1.218266	-6.269443	-0.546003
C	0.000001	-5.595992	-2.523349
C	-1.213737	-5.823238	-1.877821
H	0.000000	-6.808742	1.147946
H	2.155004	-5.655017	-2.390315
H	0.000001	-5.258499	-3.556585
H	-2.155002	-5.655017	-2.390316
C	-3.115763	-4.09609	0.045163
C	-4.81703	-5.800392	0.02338
C	-3.454955	-5.459187	0.06861
H	-2.071194	-3.804311	0.079425
H	-5.106647	-6.846434	0.042534
N	-2.448549	-6.457958	0.140915
C	-2.624963	-7.59425	0.978703
C	-5.459187	-3.454956	-0.06861
C	-5.800392	-4.81703	-0.02338
C	-4.09609	-3.115764	-0.045163
H	-3.80431	-2.071195	-0.079425
H	-6.846434	-5.106647	-0.042534
C	4.09609	-3.115764	-0.045162
C	5.800392	-4.81703	-0.023379
C	5.459187	-3.454956	-0.068609

H	3.804312	-2.071195	-0.079424
H	6.846434	-5.106647	-0.042532
N	6.457958	-2.44855	-0.140913
C	7.59425	-2.624964	-0.978701
N	6.457958	2.44855	-0.140913
C	7.59425	2.624963	-0.978701
C	6.269443	1.218267	0.546005
C	5.823237	1.213738	1.877823
C	6.487806	0.000000	-0.112266
C	6.269443	-1.218267	0.546005
C	5.595991	0.000000	2.523351
C	5.823237	-1.213738	1.877823
H	6.808742	0.000000	-1.147944
H	5.655016	2.155003	2.390316
H	5.258498	0.000000	3.556587
H	5.655016	-2.155003	2.390317
C	-3.169991	-7.467979	2.269014
C	-2.255524	-8.868937	0.535261
C	-2.408184	-9.99153	1.351767
C	-3.346887	-8.582359	3.076667
C	-2.963244	-9.854636	2.628443
H	-1.839521	-8.984507	-0.460806
H	-2.106113	-10.9617	0.973748
H	-3.456916	-6.486623	2.633142
H	-3.767761	-8.488431	4.073008
O	-3.171377	-10.88334	3.506333
C	3.169991	-7.467979	2.269015
C	2.255526	-8.868937	0.535262
C	2.408185	-9.99153	1.351768
C	3.346887	-8.582359	3.076668
C	2.963245	-9.854636	2.628444
H	1.839523	-8.984507	-0.460806

H	2.106114	-10.9617	0.973749
H	3.456917	-6.486623	2.633143
H	3.767761	-8.488431	4.073009
O	3.171377	-10.88334	3.506334
C	7.46798	-3.169991	-2.269012
C	8.868937	-2.255525	-0.535259
C	9.99153	-2.408185	-1.351764
C	8.582359	-3.346888	-3.076664
C	9.854636	-2.963245	-2.62844
H	8.984507	-1.839522	0.460808
H	10.961708	-2.106114	-0.973745
H	6.486624	-3.456917	-2.633141
H	8.488433	-3.767762	-4.073006
O	10.883343	-3.171378	-3.50633
C	7.46798	3.169991	-2.269013
C	8.868937	2.255525	-0.535259
C	9.99153	2.408184	-1.351765
C	8.582359	3.346886	-3.076665
C	9.854636	2.963244	-2.628441
H	8.984507	1.839522	0.460808
H	10.961708	2.106113	-0.973746
H	6.486624	3.456916	-2.633142
H	8.488433	3.76776	-4.073007
O	10.883343	3.171376	-3.506331
C	12.188838	2.798453	-3.103867
C	12.188838	-2.798455	-3.103866
C	2.798454	-12.18883	3.10387
C	-2.798454	-12.18883	3.103869
H	12.514883	3.355366	-2.214751
H	12.256972	1.721494	-2.895825
H	12.844074	3.044374	-3.941858
H	12.256972	-1.721496	-2.895824

H	12.514883	-3.355367	-2.21475
H	12.844074	-3.044376	-3.941857
H	1.721495	-12.25697	2.895828
H	3.355367	-12.51488	2.214754
H	3.044375	-12.84407	3.941861
H	-3.355366	-12.51488	2.214753
H	-1.721495	-12.25697	2.895828
H	-3.044375	-12.84407	3.94186

Optimized geometry of **3'** (C_{2v})

E = -5055.75697963 hartree

The number of imaginary frequencies: 0

C	0.000000	5.831247	-1.044345
H	0.000000	2.565167	-3.107579
H	0.000000	6.734352	-0.445618
C	0.000000	3.480103	-2.520477
C	0.000000	-5.831247	-1.044343
H	0.000000	-2.565168	-3.107578
H	0.000000	-6.734352	-0.445616
C	0.000000	-3.480103	-2.520476
C	-1.220706	5.254946	-1.425048
C	-1.215842	4.063795	-2.171327
N	-2.441240	5.871669	-1.050560
C	-3.571350	5.093729	-0.682125
C	-4.861110	5.467201	-1.093610
C	-5.974856	4.725205	-0.716960
C	-5.842117	3.580313	0.085601
C	-4.551911	3.202871	0.492415
C	-3.437611	3.946567	0.116984
N	-6.984656	2.836686	0.482268
C	-6.329973	0.695373	-0.535791

C	-6.959156	1.417670	0.492030
C	-7.579028	0.695202	1.524633
C	-8.166807	3.522796	0.881705
C	-2.538393	7.293760	-1.020386
H	-2.153153	3.612164	-2.476908
H	-4.987179	6.343147	-1.722060
H	-6.961067	5.028068	-1.054395
H	-4.425833	2.328681	1.123521
H	-2.452336	3.645435	0.458425
H	-5.854418	1.231716	-1.350946
H	-8.058168	1.231679	2.337468
C	-9.427408	3.122830	0.402708
C	-8.104771	4.612885	1.757028
C	-9.258885	5.300256	2.139834
C	-10.580580	3.786237	0.796909
C	-10.507900	4.884934	1.665889
H	-7.140841	4.933381	2.140013
H	-9.169068	6.143158	2.815736
H	-9.494841	2.282057	-0.280574
H	-11.554870	3.478809	0.429549
O	-11.701020	5.474421	1.982680
C	-2.109110	8.065721	-2.114188
C	-3.074352	7.953005	0.090458
C	-3.198810	9.344054	0.114804
C	-2.208006	9.449351	-2.088687
C	-2.760003	10.101831	-0.976339
H	-3.406719	7.370847	0.944490
H	-3.624298	9.819477	0.991311
H	-1.694956	7.568218	-2.985651
H	-1.876637	10.049699	-2.930209
O	-2.827060	11.465108	-1.058894
C	-3.371681	12.174207	0.040171

C	-11.682860	6.586507	2.860451
H	-4.415072	11.887898	0.230767
H	-2.784690	12.017089	0.955354
H	-3.333228	13.230130	-0.234580
H	-11.275740	6.319499	3.845233
H	-11.099740	7.420418	2.446315
H	-12.723340	6.897006	2.974061
C	1.220706	5.254946	-1.425048
C	1.215842	4.063795	-2.171326
N	2.441240	5.871669	-1.050560
C	3.571350	5.093729	-0.682124
C	4.861110	5.467201	-1.093609
C	5.974856	4.725205	-0.716958
C	5.842117	3.580313	0.085602
C	4.551911	3.202871	0.492416
C	3.437611	3.946567	0.116985
N	6.984656	2.836686	0.482269
C	6.329973	0.695373	-0.535789
C	6.959156	1.417670	0.492032
C	7.579028	0.695202	1.524635
C	8.166807	3.522796	0.881707
C	2.538393	7.293760	-1.020385
H	2.153153	3.612164	-2.476907
H	4.987179	6.343147	-1.722058
H	6.961067	5.028068	-1.054393
H	4.425833	2.328681	1.123522
H	2.452336	3.645435	0.458426
H	5.854418	1.231716	-1.350944
H	8.058168	1.231679	2.337471
C	9.427408	3.122830	0.402711
C	8.104771	4.612885	1.757030
C	9.258885	5.300256	2.139836

C	10.580589	3.786237	0.796912
C	10.507902	4.884934	1.665892
H	7.140840	4.933381	2.140015
H	9.169068	6.143158	2.815738
H	9.494841	2.282057	-0.280571
H	11.554871	3.478809	0.429552
O	11.701021	5.474421	1.982683
C	2.109110	8.065721	-2.114187
C	3.074352	7.953005	0.090459
C	3.198810	9.344054	0.114805
C	2.208006	9.449351	-2.088686
C	2.760003	10.101831	-0.976338
H	3.406719	7.370847	0.944491
H	3.624298	9.819477	0.991312
H	1.694956	7.568218	-2.985650
H	1.876637	10.049699	-2.930208
O	2.827060	11.465108	-1.058893
C	3.371681	12.174207	0.040172
C	11.682867	6.586507	2.860455
H	4.415072	11.887898	0.230768
H	2.784690	12.017089	0.955355
H	3.333228	13.230130	-0.234579
H	11.275744	6.319499	3.845236
H	11.099747	7.420418	2.446318
H	12.723348	6.897006	2.974064
C	-1.220706	-5.254946	-1.425047
C	-1.215842	-4.063796	-2.171326
N	-2.441240	-5.871669	-1.050559
C	-3.571350	-5.093729	-0.682124
C	-4.861110	-5.467201	-1.093609
C	-5.974856	-4.725205	-0.716958
C	-5.842117	-3.580313	0.085602

C	-4.551911	-3.202871	0.492416
C	-3.437611	-3.946567	0.116985
N	-6.984656	-2.836686	0.482268
C	-6.329973	-0.695373	-0.535791
C	-6.959156	-1.417670	0.492030
C	-7.579028	-0.695202	1.524633
C	-8.166807	-3.522796	0.881706
C	-2.538393	-7.293760	-1.020384
H	-2.153153	-3.612164	-2.476907
H	-4.987179	-6.343147	-1.722058
H	-6.961067	-5.028068	-1.054393
H	-4.425833	-2.328681	1.123522
H	-2.452336	-3.645435	0.458426
H	-5.854418	-1.231716	-1.350946
H	-8.058168	-1.231679	2.337469
C	-9.427408	-3.122830	0.402709
C	-8.104771	-4.612885	1.757029
C	-9.258885	-5.300255	2.139835
C	-10.580580	-3.786237	0.796910
C	-10.507900	-4.884934	1.665890
H	-7.140841	-4.933380	2.140014
H	-9.169068	-6.143157	2.815737
H	-9.494841	-2.282057	-0.280573
H	-11.554870	-3.478809	0.429550
O	-11.701020	-5.474420	1.982681
C	-2.109110	-8.065721	-2.114185
C	-3.074352	-7.953005	0.090460
C	-3.198810	-9.344054	0.114807
C	-2.208006	-9.449351	-2.088684
C	-2.760003	-10.101830	-0.976336
H	-3.406719	-7.370847	0.944492
H	-3.624298	-9.819477	0.991314

H	-1.694956	-7.568219	-2.985649
H	-1.876637	-10.049690	-2.930206
O	-2.827060	-11.465100	-1.058891
C	-3.371681	-12.174200	0.040174
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H	-11.275740	-6.319498	3.845235
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C	1.215842	-4.063796	-2.171325
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C	2.538393	-7.293760	-1.020383
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C	8.104771	-4.612885	1.757032
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H	3.406719	-7.370847	0.944493
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H	1.876637	-10.049690	-2.930206
O	2.827060	-11.465100	-1.058890
C	3.371681	-12.174200	0.040175
C	11.682867	-6.586506	2.860456
H	4.415072	-11.887890	0.230771
H	2.784690	-12.017080	0.955358
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H	11.275744	-6.319498	3.845238
H	11.099747	-7.420417	2.446320
H	12.723348	-6.897005	2.974066

Optimized geometry of **3'** (C_s)

$E = -5055.75693542$ hartree

The number of imaginary frequencies: 0

C	6.025335	0.450801	-0.000001
H	6.257947	-3.407781	0.000001
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C	-5.452503	1.280154	0.000000
H	-1.931911	2.870795	0.000000
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C	4.960805	-0.325800	5.926809
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H	2.292115	-1.543099	4.216255
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H	1.564061	0.721932	5.899593

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C	4.528673	-3.047264	7.702187
C	5.186776	-3.661895	8.769934
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C	4.892696	-3.279001	10.083213
H	4.751893	-3.357824	6.686098
H	5.910393	-4.442306	8.563213
H	2.592707	-0.856414	9.425360
H	3.733109	-1.975369	11.331510
O	5.465738	-3.817581	11.201853
C	6.088378	2.843271	3.119835
C	8.053898	1.835639	2.157231
C	8.739264	3.047168	2.271573
C	6.769693	4.044077	3.257994
C	8.100541	4.159148	2.830666
H	8.559664	0.972241	1.736090
H	9.768886	3.102949	1.936692
H	5.054805	2.768271	3.442820
H	6.283438	4.916941	3.682477
O	8.677258	5.387578	3.003495
C	10.018773	5.559149	2.584126
C	6.427329	-4.844400	11.030402
H	10.703061	4.893488	3.127722
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H	10.273876	6.596936	2.807512
H	5.997073	-5.723591	10.531871
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C	-3.546261	2.151755	1.215799
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C	-4.773062	0.811387	3.569173
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C	-4.403702	0.777195	5.973331
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C	-9.095615	0.640136	3.202264

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O	-11.026450	2.104013	2.822956
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C	-6.672396	-2.605505	11.676494
H	-11.640830	0.888167	4.406837
H	-11.853690	0.186951	2.774887
H	-12.894090	1.535223	3.312135
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C	6.077333	-0.238823	-1.219597
C	6.159074	-1.641778	-1.214986
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C	5.259976	-0.007395	-3.534225
C	5.728754	0.110508	-4.852927
C	4.960803	-0.325799	-5.926814
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C	3.254409	-1.076316	-4.401075
C	4.003296	-0.601721	-3.330241
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H	6.283438	4.916939	-3.682479
O	8.677253	5.387567	-3.003500
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H	10.703058	4.893486	-3.127722
H	10.131325	5.383408	-1.504973
H	10.273865	6.596931	-2.807514
H	5.997064	-5.723595	-10.531870
H	7.294971	-4.494809	-10.454420

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C	-3.546258	2.151751	-1.215799
N	-5.491577	1.291802	-2.441832
C	-4.773061	0.811386	-3.569174
C	-5.086822	1.260178	-4.862746
C	-4.403703	0.777197	-5.973336
C	-3.378219	-0.172272	-5.833357
C	-3.060163	-0.616833	-4.539630
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C	-6.903160	1.466852	-2.539729
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H	-4.657339	1.146177	-6.962241
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H	-5.021066	-1.980665	-7.120345
H	-6.279492	-2.534570	-9.154662
H	-1.965245	-0.111172	-9.487038
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C	-7.509812	2.659368	-2.107865
C	-7.715441	0.464016	-3.078643
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C	-8.882824	2.833066	-2.205616
C	-9.688744	1.827231	-2.759309
H	-7.262341	-0.463740	-3.414255
H	-9.692107	-0.157603	-3.630270
H	-6.892291	3.449428	-1.692093
H	-9.355960	3.751049	-1.871217
O	-11.026450	2.104011	-2.822958
C	-11.887340	1.115644	-3.360683
C	-6.672391	-2.605506	-11.676480
H	-11.640830	0.888169	-4.406840
H	-11.853700	0.186950	-2.774885
H	-12.894090	1.535225	-3.312126
H	-6.576369	-3.603250	-11.226670
H	-7.440531	-2.039958	-11.131300
H	-6.975857	-2.709709	-12.720080

Electrochemical Measurements

The redox properties were evaluated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in CH_2Cl_2 solution at 298 K with 0.1 M tetra-*n*-butylammonium tetrafluoroborate (TBABF₄) as supporting electrolyte (scan rate 100 mV s⁻¹) using an electrochemical analyzer. A three-electrode assembly was used, which was equipped with platinum disk (2 mm²), a platinum wire, and Ag/0.01 M AgNO₃ (acetonitrile) as the working electrode, the counter electrode, and the reference electrode, respectively. The redox potential were referenced against a ferrocene/ferrocenium (Fc^{0/+}) redox potential measured in the same electrolytic solution.

Spectroelectrochemical Measurements

Spectroelectrochemical measurements were carried out with a custom-made optically transparent thin-layer electrochemical (OTTLE) cell (light pass length = 1 mm) equipped with a platinum mesh, a platinum coil, and a silver wire as the working electrode, the counter electrode, and the pseudo-reference electrode, respectively. The potential was applied with an electrochemical analyzer.

ESR Measurements

ESR spectra were recorded on a X-band ESR spectrometer, in which temperature was controlled by a variable-temperature unit in the range of 120-300 K. A Mn²⁺/MnO solid solution was used as a reference.

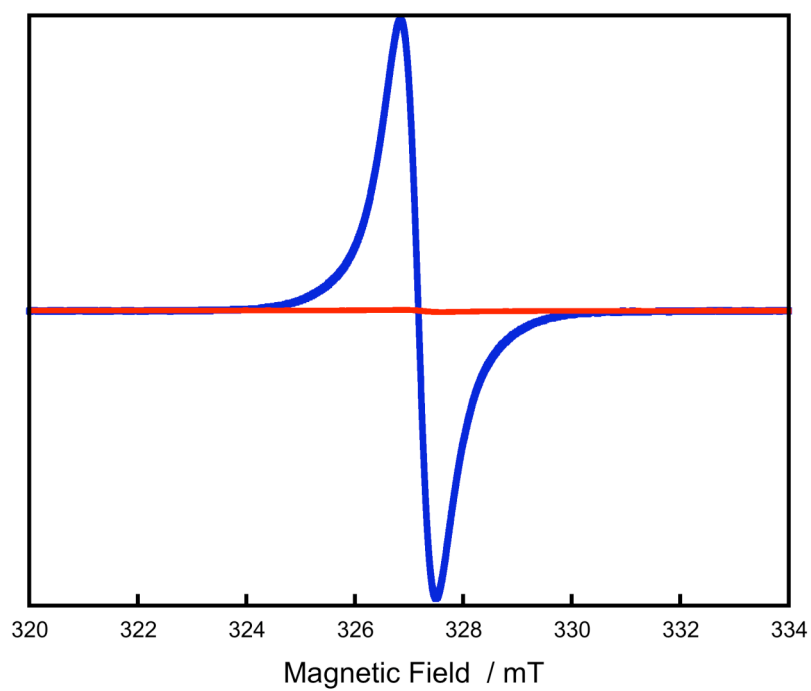
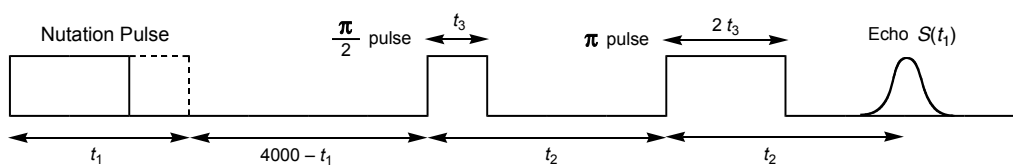


Figure S8. ESR spectra of **3** treated by 2 molar equiv of Magic Blue (blue line) and 4 molar equiv of Magic Blue (red line) in the same volume of CH_2Cl_2 at 123 K. The comparison between these two spectra supports the closed-shell diamagnetic state of $\mathbf{3}^{4+}$ in CH_2Cl_2 solution.

Pulsed ESR Measurements

The magnetic moments with distinct spin quantum numbers (S) precess with their specific nutation frequency (ω_{nut}) in the presence of a microwave irradiation field and a static magnetic field. The nutation frequency for a transition from $|S, M_S\rangle$ to $|S, M_S + 1\rangle$ can be expressed as $\omega_{\text{nut}} = [S(S+1) - M_S(M_S + 1)]^{1/2} \omega_0$ under certain conditions. This indicates that ω_{nut} can be scaled with the total spin quantum number S and the spin magnetic quantum number M_S in the unit of ω_0 ($= \omega_{\text{doublet}}$). For determination of spin-multiplicity for high-spin molecules by using the pulsed ESR technique, see: a) J. Isoya, H. Kanda, J. R. Norris, J. Tang, M. K. Brown, *Phys. Rev. B* **1990**, *41*, 3905; b) A. V. Astashkin, A. Schweiger, *Chem. Phys. Lett.* **1990**, *174*, 595; c) K. Sato, M. Yano, M. Furuichi, D. Shiomi, T. Takui, K. Abe, K. Itoh, A. Higuchi, K. Katsuma, Y. Shiota, *J. Am. Chem. Soc.* **1997**, *119*, 6607; d) H. Bock, K. Gharagozloo-Hubmann, M. Sievert, T. Prisner, Z. Havlas, *Nature* **2000**, *404*, 267; e) A. Ito, H. Ino, K. Tanaka, K. Kanemoto, T. Kato, *J. Org. Chem.* **2002**, *67*, 491.

Pulsed ESR measurements were carried out on a X-band FT ESR spectrometer, in which temperature was controlled by temperature controller combined with a continuous-flow cryostat. The microwave pulse power of 10 mW provided by the microwave bridge was boosted to level of 1 kW using a traveling wave tube (TWT) amplifier. The ESTN measurements were performed by the three-pulse sequence shown below. The two-pulse ($\pi/2 - \pi$ pulses) electron spin-echo signal $S(t_1)$ was detected by increasing the width (t_1) of the nutation pulse. We employed appropriate phase cycles in order to suppress undesirable signals and artifacts which arise from an inaccurate pulse length.^[S6,S7] The observed signal $S(t_1, B)$ as a function of external magnetic field B is converted into a nutation frequency $S(\omega_{\text{nut}}, B)$ spectrum. The parameters used for the measurements were $t_2 = 400$ ns, $t_3 = 8$ ns for 2^{4+} and 12 ns for 2^{2+} and 3^{2+} . The signals observed at ca. 14 MHz in Figure 8 are due to the electron spin echo envelope modulation (ESEEM),^[S8] which results from weak interaction with proton nuclei ($I = 1/2$) originating from the solvent molecules surrounding the paramagnetic species.



[S6] J.-M. Fauth, A. Schweiger, L. Braunschweiler, J. Forrer, R. R. Ernst, *J. Magn. Res.* **1986**, 66, 74.

[S7] C. Gemperle, G. Aebli, A. Schweiger, R. R. Ernst, *J. Magn. Res.* **1990**, 88, 241.

[S8] W. B. Mims, *Phys. Rev. B* **1972**, 5, 2409.