Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Effect of Internal Oxygen Substituents on the Properties of Bowl-Shaped Aromatic Hydrocarbons

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1. Instrumentation and materials

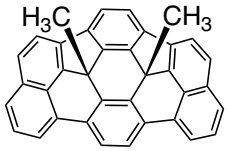
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra were recorded on a Bruker Varian INOVA-500 spectrometer. ^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra were recorded on a JEOL JNM-ECA600II spectrometer. Chemical shifts were reported as the delta scale in ppm relative to $CHCl_3$ (δ = 7.26 ppm) for ^{1}H NMR and $CDCl_3$ (δ = 77.16 ppm) for ^{13}C NMR. UV/vis absorption spectra were recorded on a JASCO V 670 spectrometer. High-resolution atmospheric pressure chemical ionization time-of-flight (APCI-TOF) mass spectra was taken on a Bruker micrOTOF instrument using a positive ionization mode. X-ray data were obtained using a Rigaku CCD diffractometer (Saturn 724 with MicroMax-007) with Varimax Mo optics. Cyclic voltammograms were obtained under the following conditions; solvent: CH_2Cl_2, electrolyte: 0.1 M Bu_4NPF_6, working electrode: Pt, counter electrode: Pt, reference electrode: $Ag/AgNO_3$, scan rate: 0.01 V/s.

All calculations were carried out using the Gaussian 16 software package.[エラー! 参照元が見つかりません。] Initial geometry for the calculations of **5**, **6**, **7**, and **6**@C_{60} were obtained from the X-ray crystal structure. The initial geometry of **8** was obtained by replacing the hydrogen atoms of optimized **6** with anisyl groups. The opt, freq, and TD-DFT calculations of **5**, **6**, **7**, and **8** were performed by density functional theory (DFT) method with restricted B3LYP[2] level, employing basis sets 6-31G(d). The structural optimization of **5**@C_{60} and **6**@C_{60} were performed with restricted B3LYP-D3 level, employing basis sets 6-31G(d), where the starting geometries were given by their X-ray crystal structures. The NMR calculations of **6**@C_{60} were performed with restricted B3LYP level, employing basis sets 6-31G(d). The second-generation ALMO-EDA calculations were conducted at the ωB97M-V/def2-TZVPPD level implemented in the Q-Chem 6.0.0 program package.[3]

Compounds **5** and **6** were prepared according to the literature.[4] TfOH and iodomethane were purchased from Tokyo Chemical Industry Co., Ltd. Anisole was purchased from FUJIFILM Wako Pure Chemical Co. *n*-Butyllithium in hexane was purchased from Kanto Chemical Co., INC. Fullerene C_{60} was purchased from Materials Technologies Research Ltd. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

2. Experimental procedures and compound data

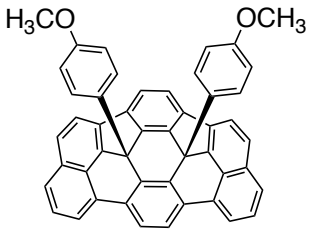
Dimethyl-*as*-indaceno[3,2,1,8,7,6-*ghijklm*]terrylene (7)



Compound **6** (21 mg, 46 μ mol) was placed in a two-necked 50 mL glass flask filled with N_2. To the flask, Et_2O (6.0 mL) were added. After stirring at 0 °C, *n*-BuLi (1.6 M, 0.4 mL) was added. The reaction mixture was stirred at 0 °C for 30 min. MeI (0.4 mL, 6.4 mmol) was added to the mixture. The reaction mixture was stirred at room temperature for 30 min. The reaction was quenched with water (2.0 mL). Et_2O was removed by rotary evaporator. The reaction mixture was extracted with EtOAc. The organic phase was washed with brine and dried over Na_2SO_4. After removing the solvent, purification by silica-gel column chromatography (CH_2Cl_2/hexane as eluent) afforded **7** (11.4 mg, 25.1 μmol, 54%) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$, 295 K): δ = 7.73 (d, J = 7.2 Hz, 2H), 7.55 (d, J = 8.2 Hz, 2H), 7.54 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H), 7.50 (s, 2H), 7.30 (s, 2H), 7.25 (dd, J = 7.2 Hz, J = 8.2 Hz, 2H), 2.39 (s, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 296 K): δ = 154.3, 151.1, 138.8, 138.3, 137.5, 132.5 132.1, 131.6, 127.6, 126.9, 126.7, 125.0, 123.7, 120.6, 120.3, 49.1, 31.0 ppm (One signal due to sp^2 carbons is missing due to overlapping.); HRMS (APCI-TOF): $[M+H]^+$ Calcd for $C_{36}H_{21}$ 453.1638; Found 453.1633; IR ν_{max} (neat): 2957 (w), 1576 (w), 1504 (w), 1446 (w), 1182 (w), 826 (s), 810 (s), 779 (s), 754 (s), 697 (w), 613 (w), 547 (w), 455 (w), 431 (m) cm^{-1}; m.p. >250 °C (dec.).

Di(*p*-methoxyphenyl)-*as*-indaceno[3,2,1,8,7,6-*ghijklm*]terrylene (8)



Compound **5** (25 mg, 52 μ mol) was placed in a two-necked 50 mL glass flask filled with N_2. To the flask, CH_2Cl_2 (1.0 mL) and anisole (5.0 mL) were added. After the mixture was stirred at room temperature for 1 min, TfOH (0.02 mL, 0.23 mmol) was added. After the mixture was stirred at room temperature for 1.5 h, the reaction was quenched with NEt_3. The reaction mixture was

extracted with CH_2Cl_2. The organic phase was washed with brine and dried over Na_2SO_4. After removing the solvent, purification by silica-gel column chromatography (CH_2Cl_2/hexane as eluent) afforded **8** (14 mg, 22 μmol, 41%) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$, 297 K): δ = 7.75 (d, J = 6.6 Hz, 2H), 7.65 (s, 2H), 7.48–7.54 (m, 6H), 7.35–7.36 (m, 6H), 7.22 (dd, J_1 = 8.3 Hz, J_2 = 7.2 Hz, 2H), 6.50 (d, J = 9.0 Hz, 4H), 3.61 (s, 6H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 295 K): δ = 158.1, 153.3, 149.9, 138.9, 138.5, 137.2, 133.4, 133.3, 132.7, 131.9, 128.6, 127.6, 127.3, 127.2, 126.6, 125.1, 123.5, 120.7, 120.2, 113.5, 55.3 ppm; HRMS (APCI-TOF): $[M+H]^+$ Calcd for $C_{48}H_{29}O_2$ 637.2162; Found 637.2137; IR ν_{max} (neat): 2960 (w), 1606 (w), 1505 (m), 1461 (w), 1248 (m), 1181 (w), 1096 (w), 1031 (m), 794 (m), 756 (w) cm^{-1}; m.p. 208 °C.

3. NMR spectra

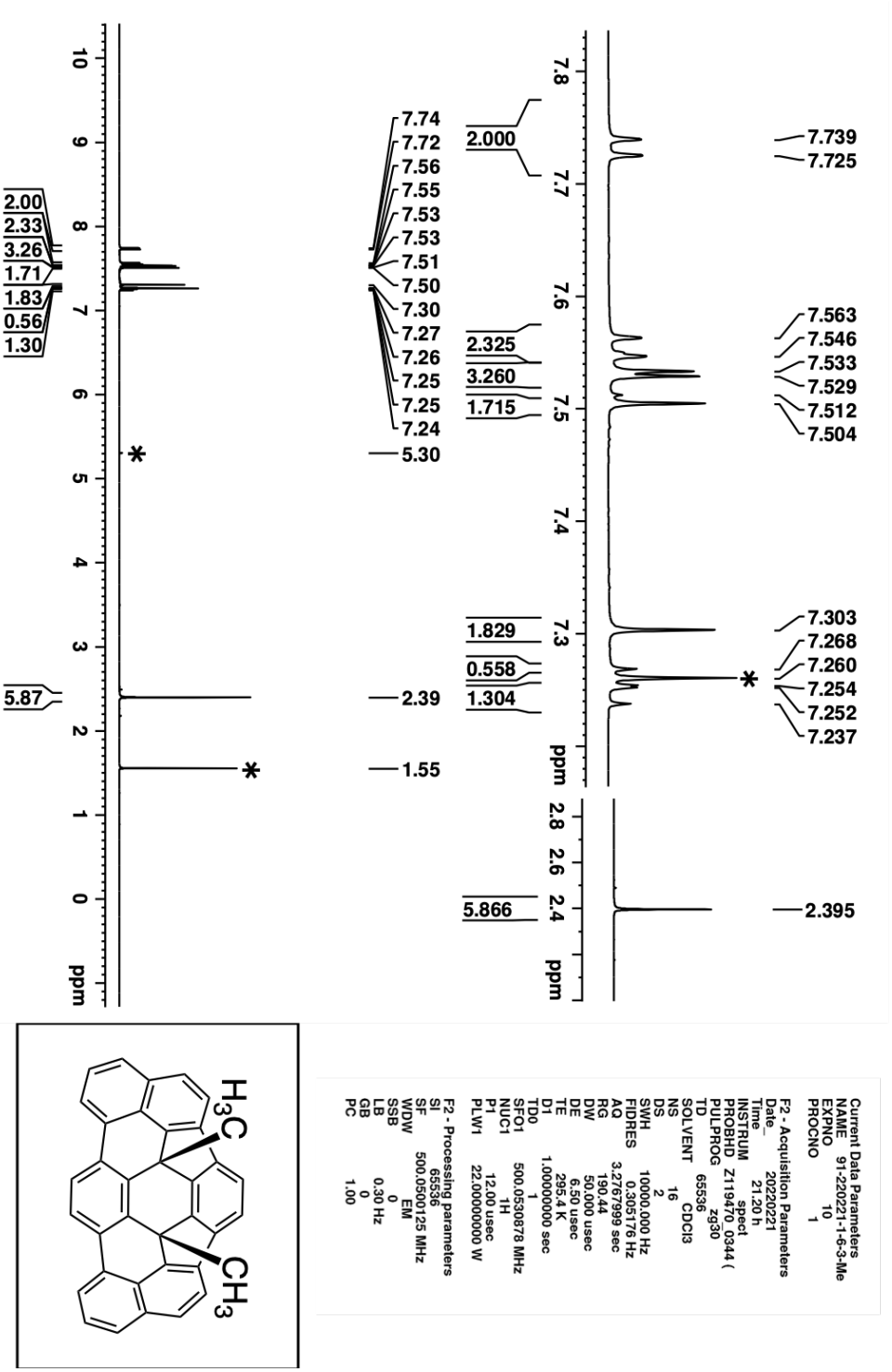


Figure S1. ^{1}H NMR spectrum of **7** in $CDCl_3$ at 22 °C (* indicates solvent peaks).

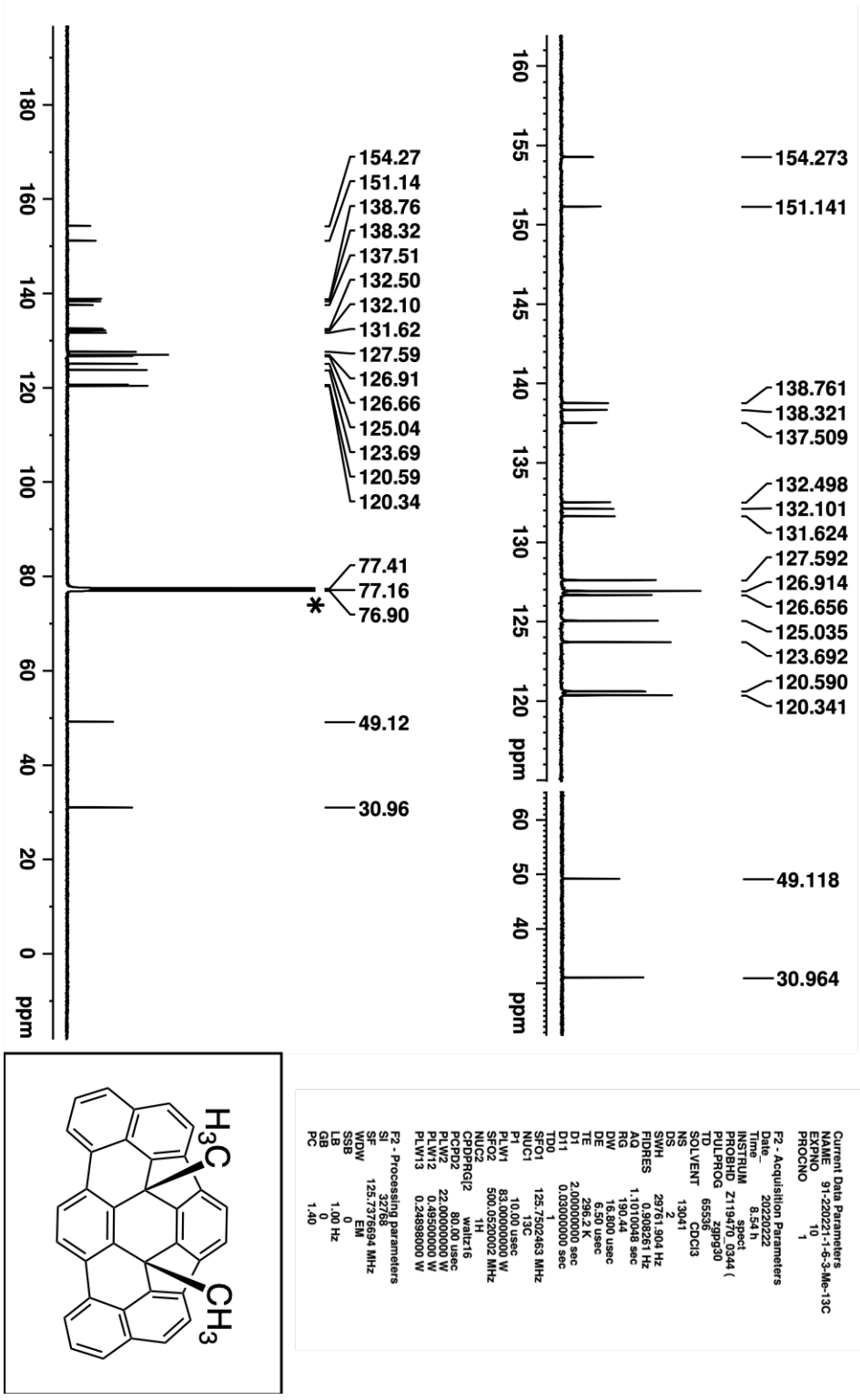


Figure S2. ^{13}C NMR spectrum of **7** in $CDCl_3$ at 23 °C (* indicates solvent peaks).

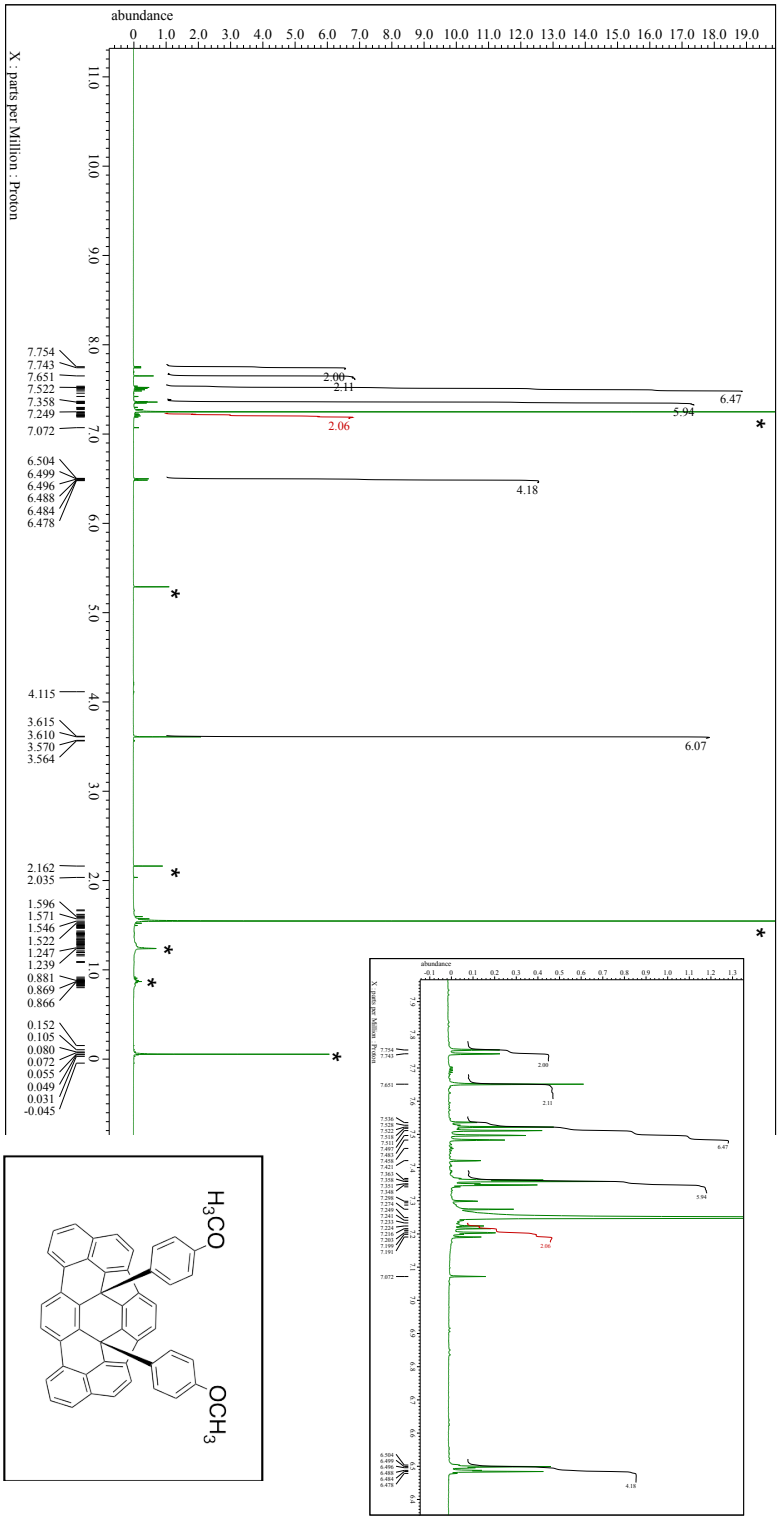


Figure S3. ^{1}H NMR spectrum of **8** in $CDCl_3$ at 24 °C (* indicates solvent and impurity peaks).

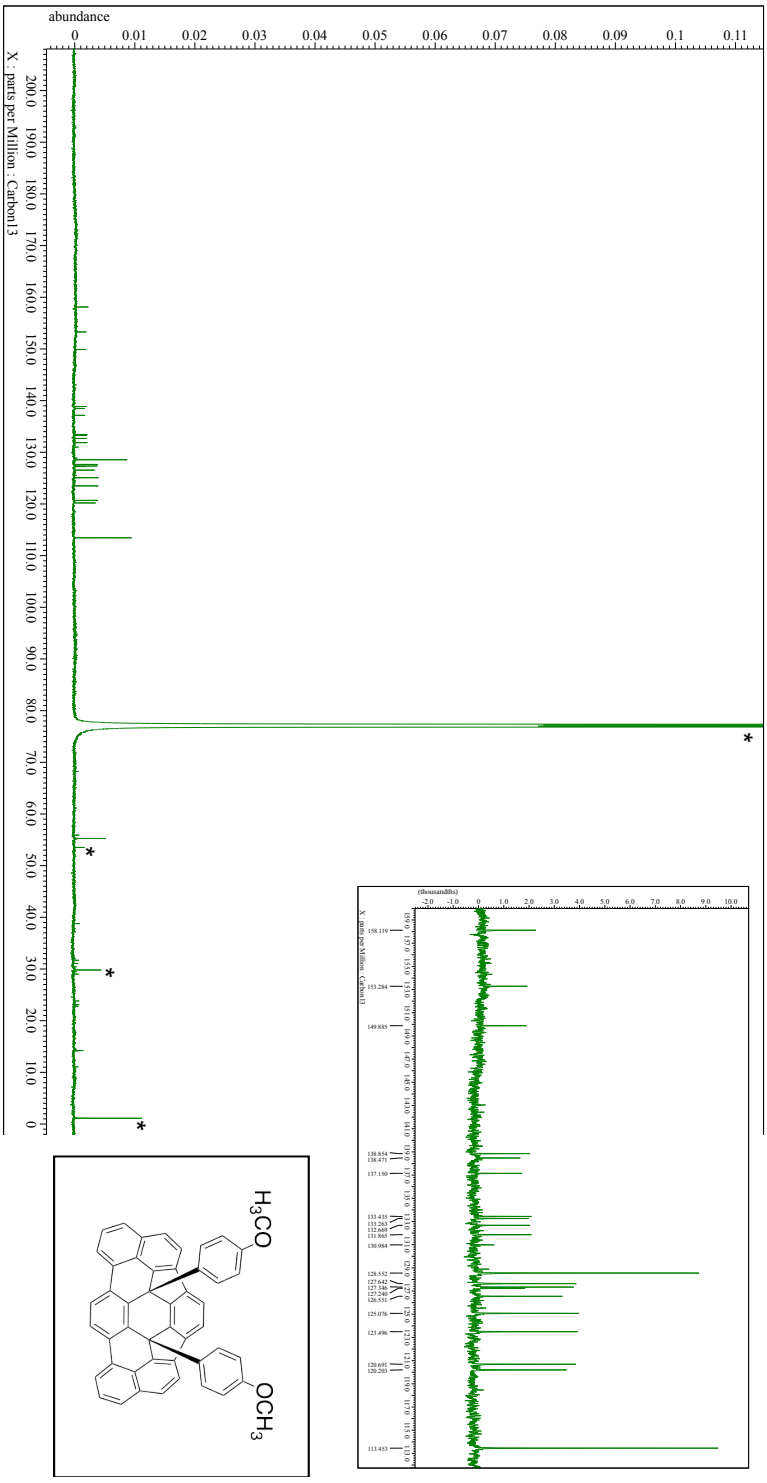


Figure S4. ^{13}C NMR spectrum of **8** in $CDCl_3$ at 22 °C (* indicates solvent peaks).

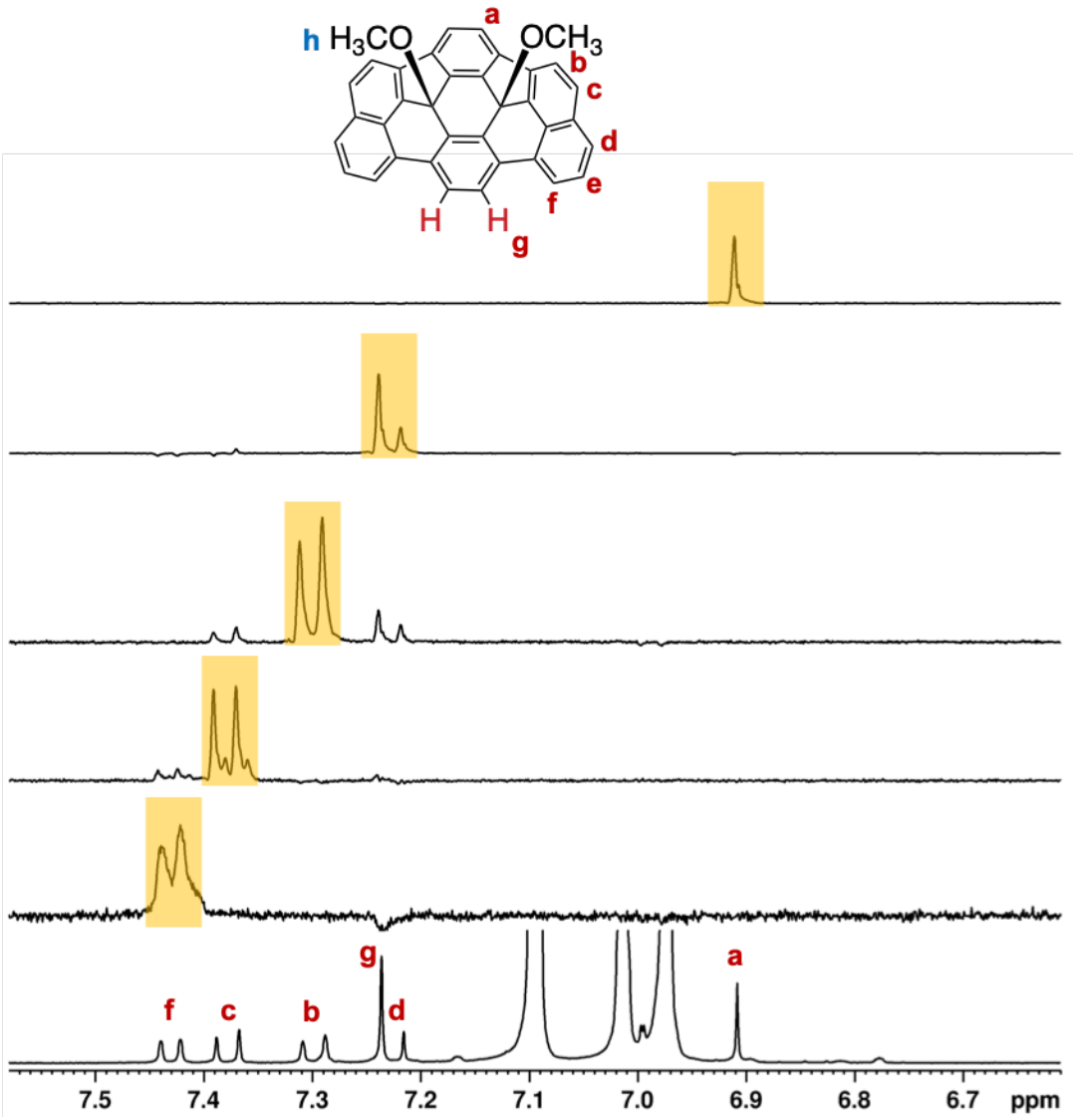


Figure S5. 1D selective NOESY of **5** in toluene-d_8 (yellow boxes indicate irradiated signals.).

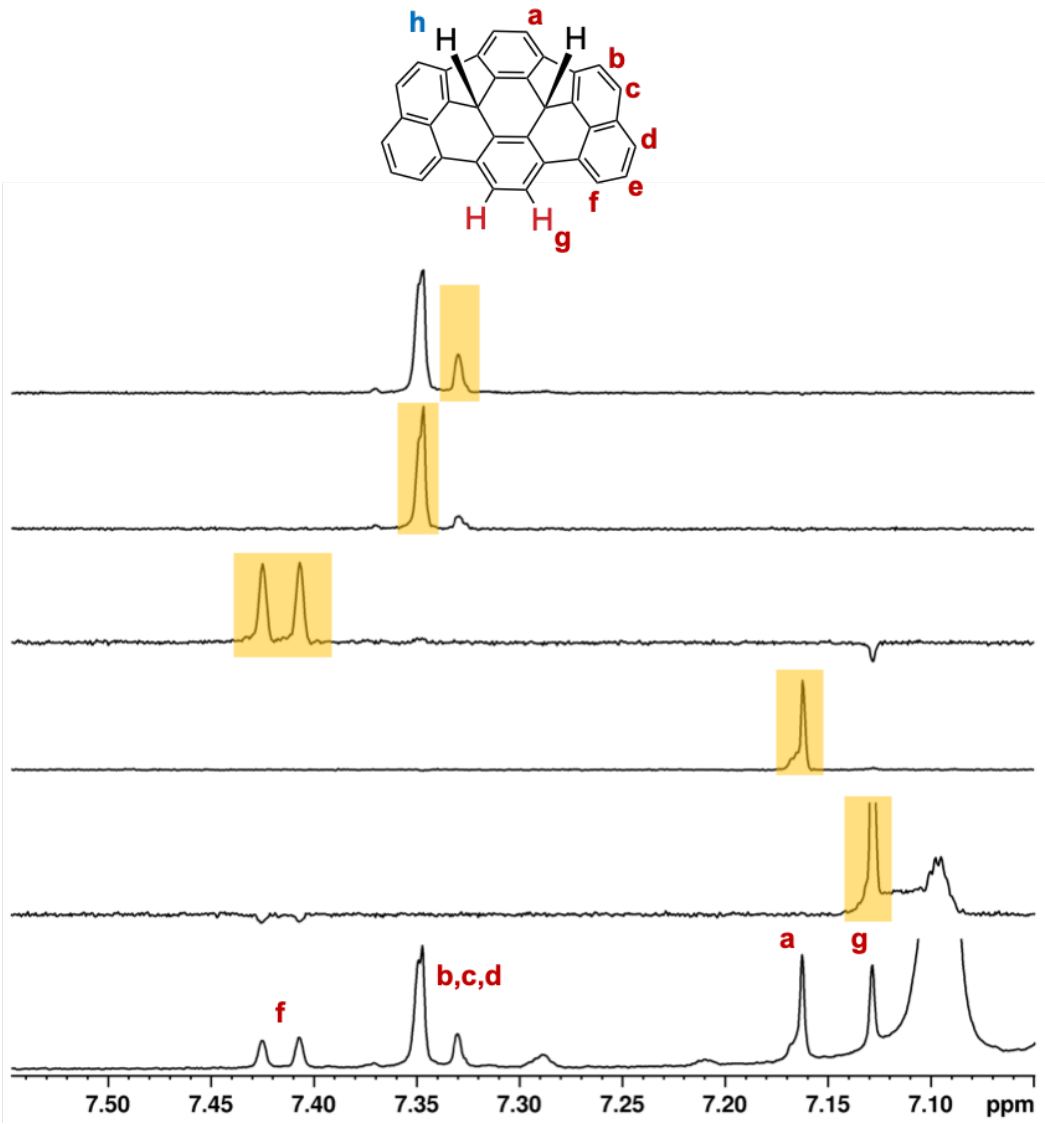


Figure S6. 1D selective NOESY of **6** in toluene-d_8 (yellow boxes indicate irradiated signals.).

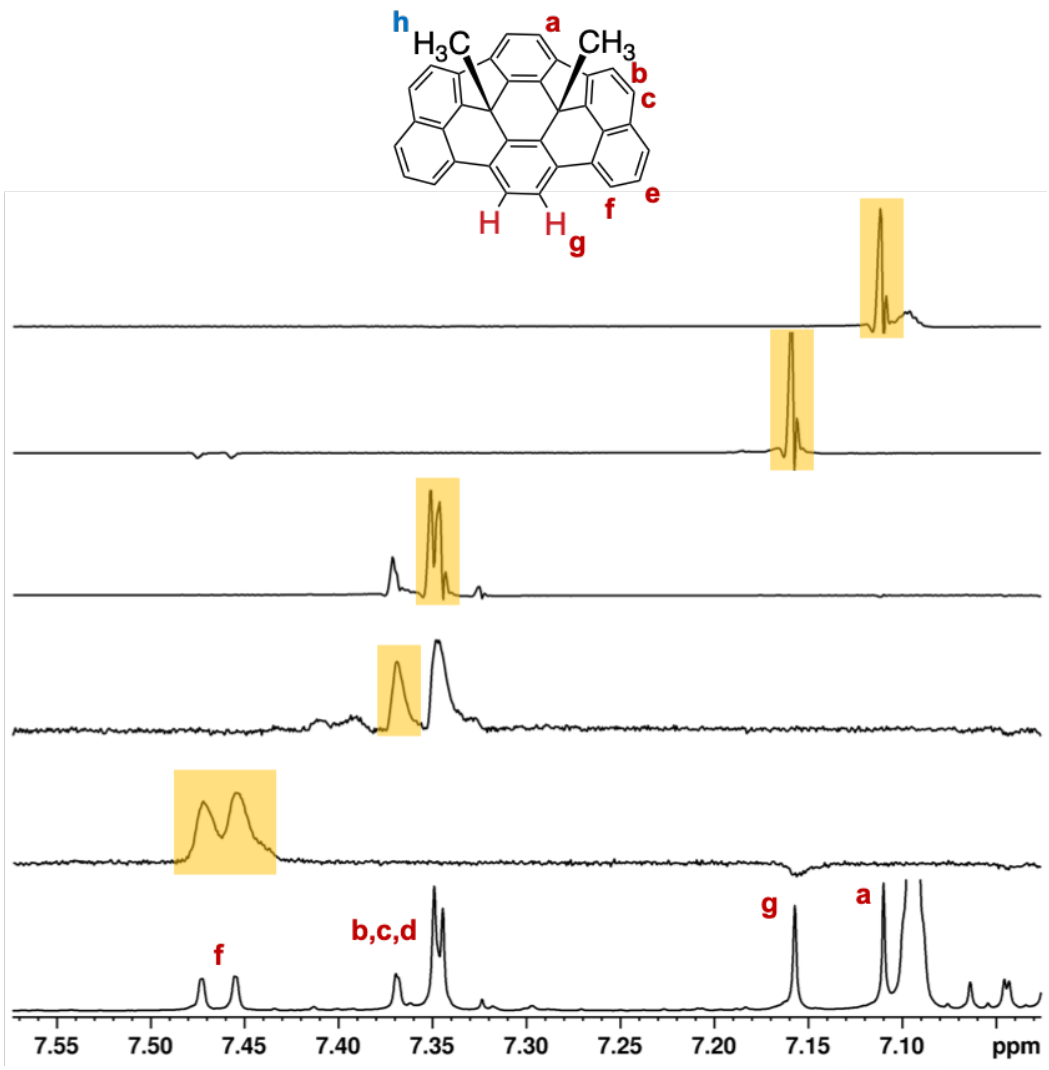


Figure S7. 1D selective NOESY of **7** in toluene-d_8 (yellow boxes indicate irradiated signals.).

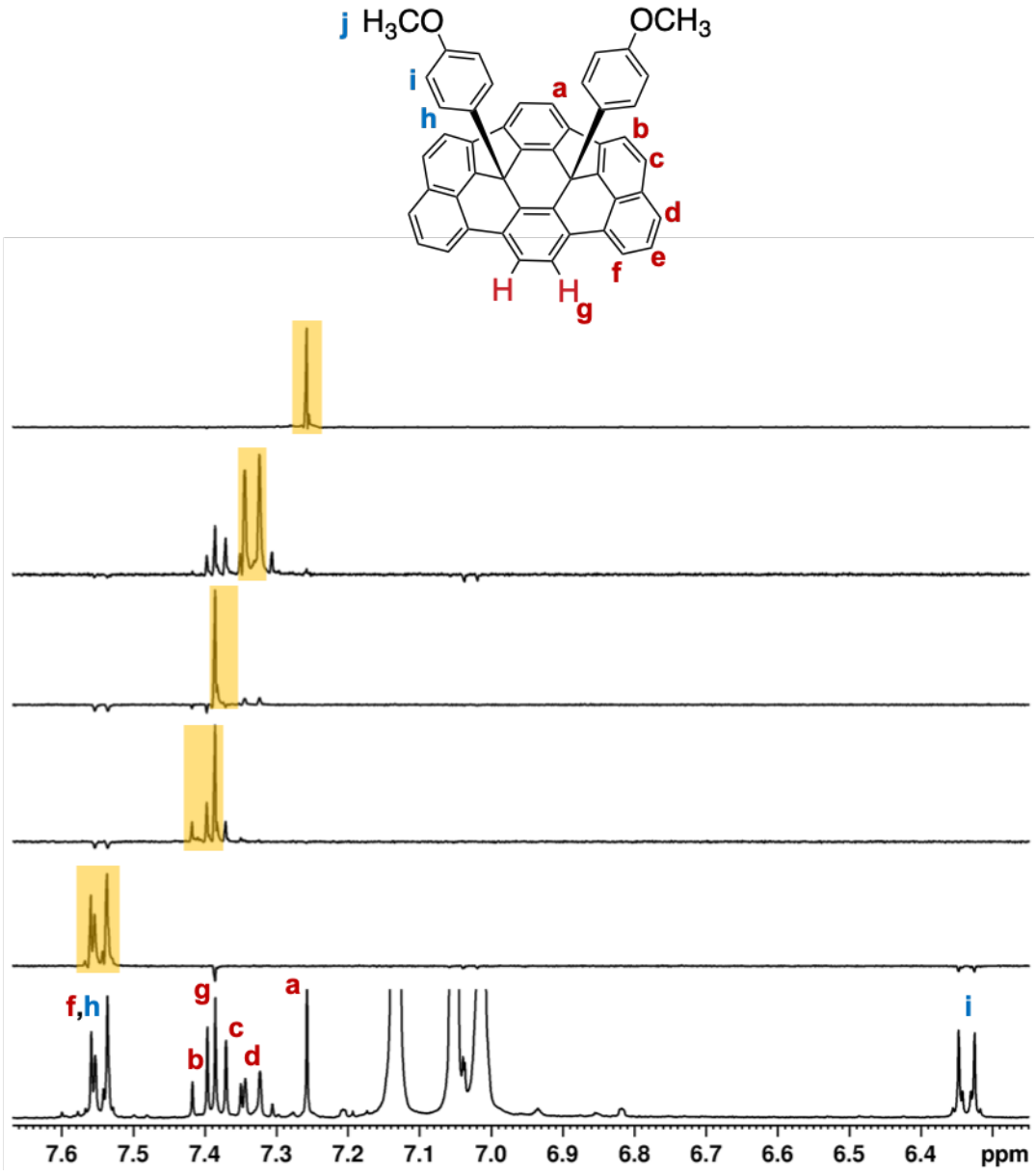


Figure S8. 1D selective NOESY of **8** in toluene-d_8 (yellow boxes indicate irradiated signals.).

4. Mass spectra

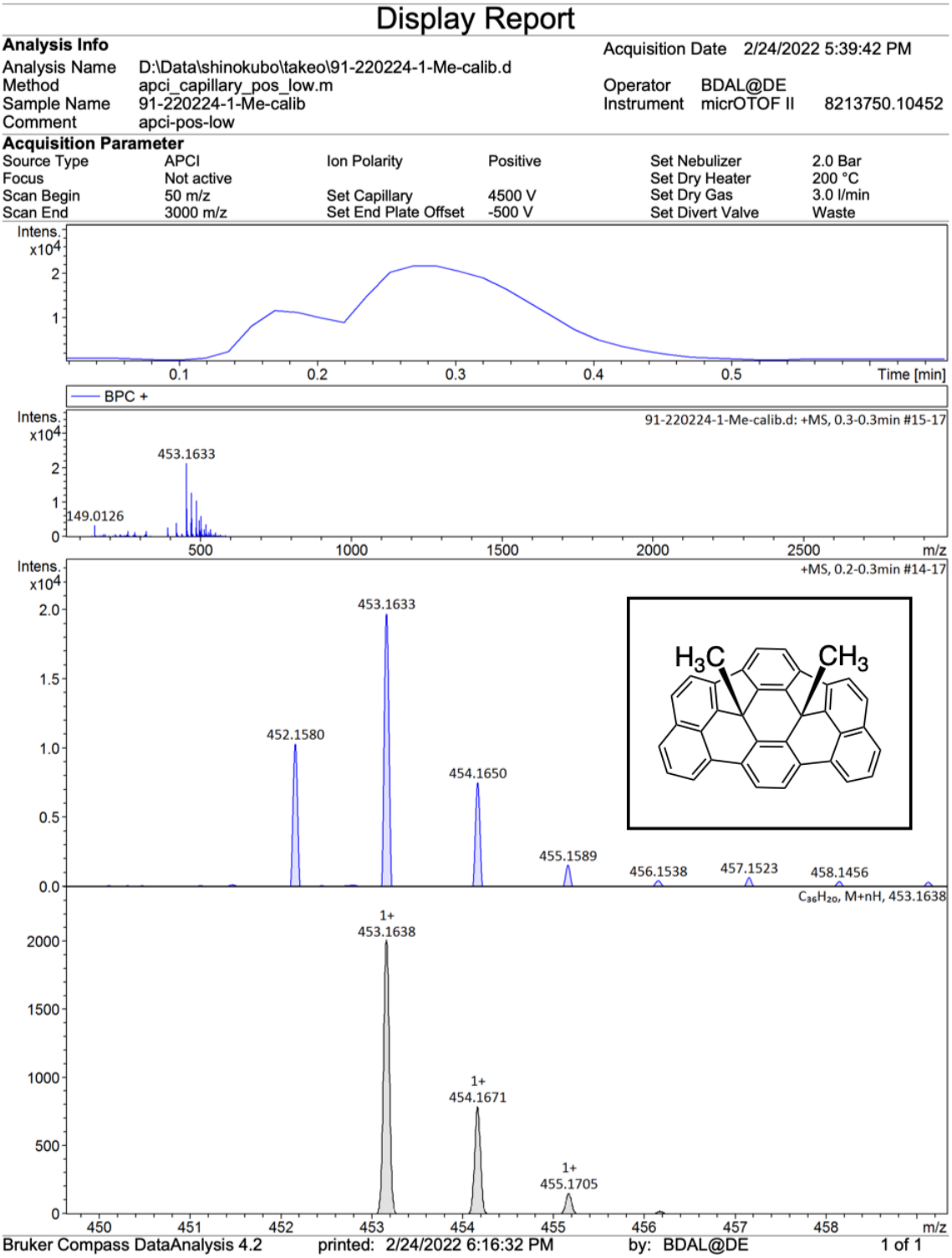


Figure S9. APCI-TOF MS spectrum of **7**.

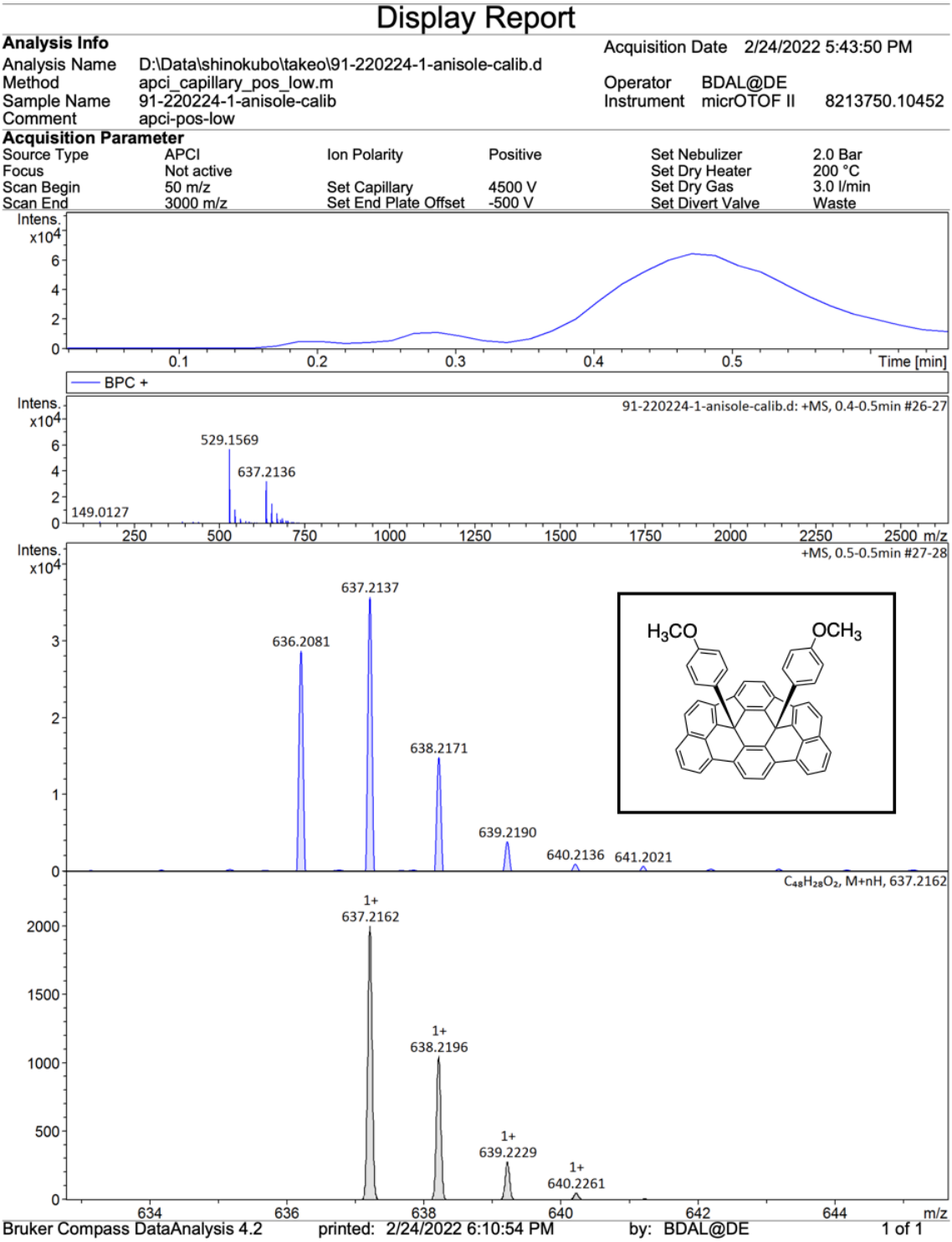


Figure S10. APCI-TOF MS spectrum of **8**.

5. Crystal data

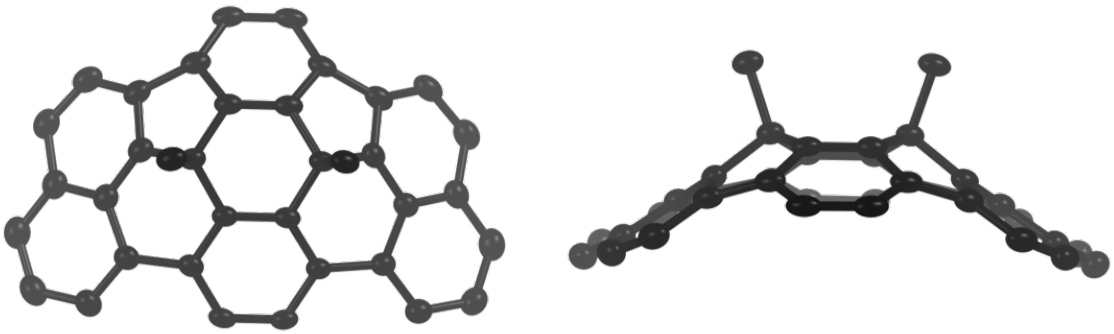
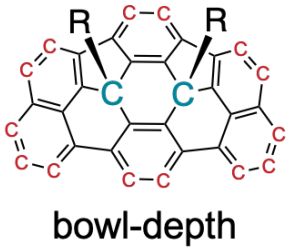
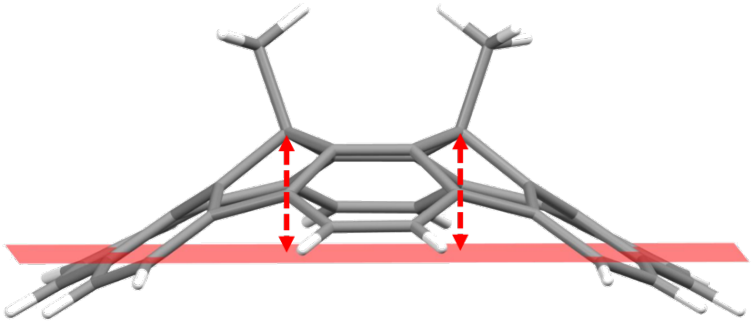


Figure S11. X-ray crystal structure of **7**. Thermal ellipsoids are shown at the 50% probability level. All hydrogen atoms are omitted for clarity.





	5 (R = OCH_3)	**6** (R = H)	**7** (R = CH_3)
bowl depth (Å)	1.99	1.98	2.05

Figure S12. Bowl depths of **5**, **6**, and **7**.

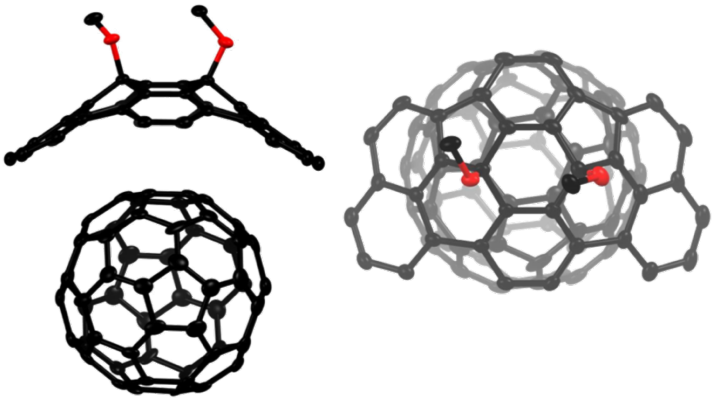


Figure S13. X-ray crystal structure of C_{60}@**5**. Thermal ellipsoids are shown at the 50% probability level. All hydrogen atoms are omitted for clarity.

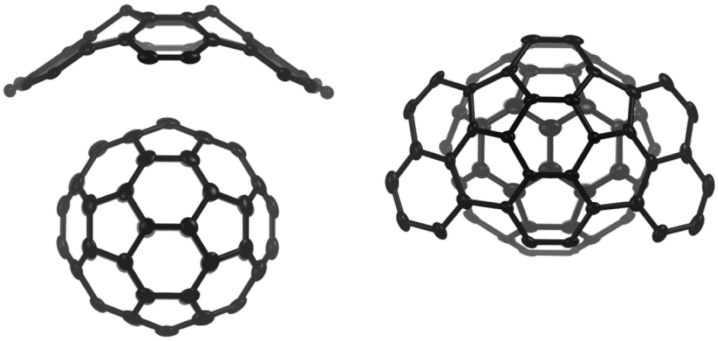


Figure S14. X-ray crystal structure of C_{60}@**6**. Thermal ellipsoids are shown at the 50% probability level. All hydrogen atoms are omitted for clarity.

Table S1. Crystallographic data of **7**, **C_{60}@5**, and **C_{60}@6**.

compound	**7**	**C_{60}@5**	**C_{60}@6**
Formula	$C_{36}H_{20}$	$C_{96}H_{20}O_2$	$C_{94}H_{16}$
Formula weight	452.56	1205.21	1145.16
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	*Aba2* (No. 41)	$P2_1/c$ (No. 14)	$P2_1/m$ (No. 11)
Crystal color	yellow	brown	black
Crystal description	prism	prism	plate
a [Å]	26.9226(9)	13.3342(2)	9.7684(2)
b [Å]	23.7598(8)	19.0108(3)	17.8451(4)
c [Å]	6.8227(2)	22.7010(4)	13.4530(3)
α [°]	—	—	—
β [°]	—	91.784(1)	96.000(2)
γ [°]	—	—	—
V [Å^3]	4364.3(2)	5751.77(16)	2332.25(9)
Z	8	4	4
d_{calcd} [g cm^{-3}]	1.377	1.551	1.631
R_1 ($I > 2\sigma(I)$)	0.0653	0.0488	0.0573
wR_2 (all data)	0.1655	0.1289	0.1604
Goodness-of-fit	1.036	1.010	1.056
Temperature [K]	93	93	93
Solvent	CH_2Cl_2/hexane	toluene	toluene/hexane
CCDC No	2270014	2270012	2270013

6. Cyclic voltammograms

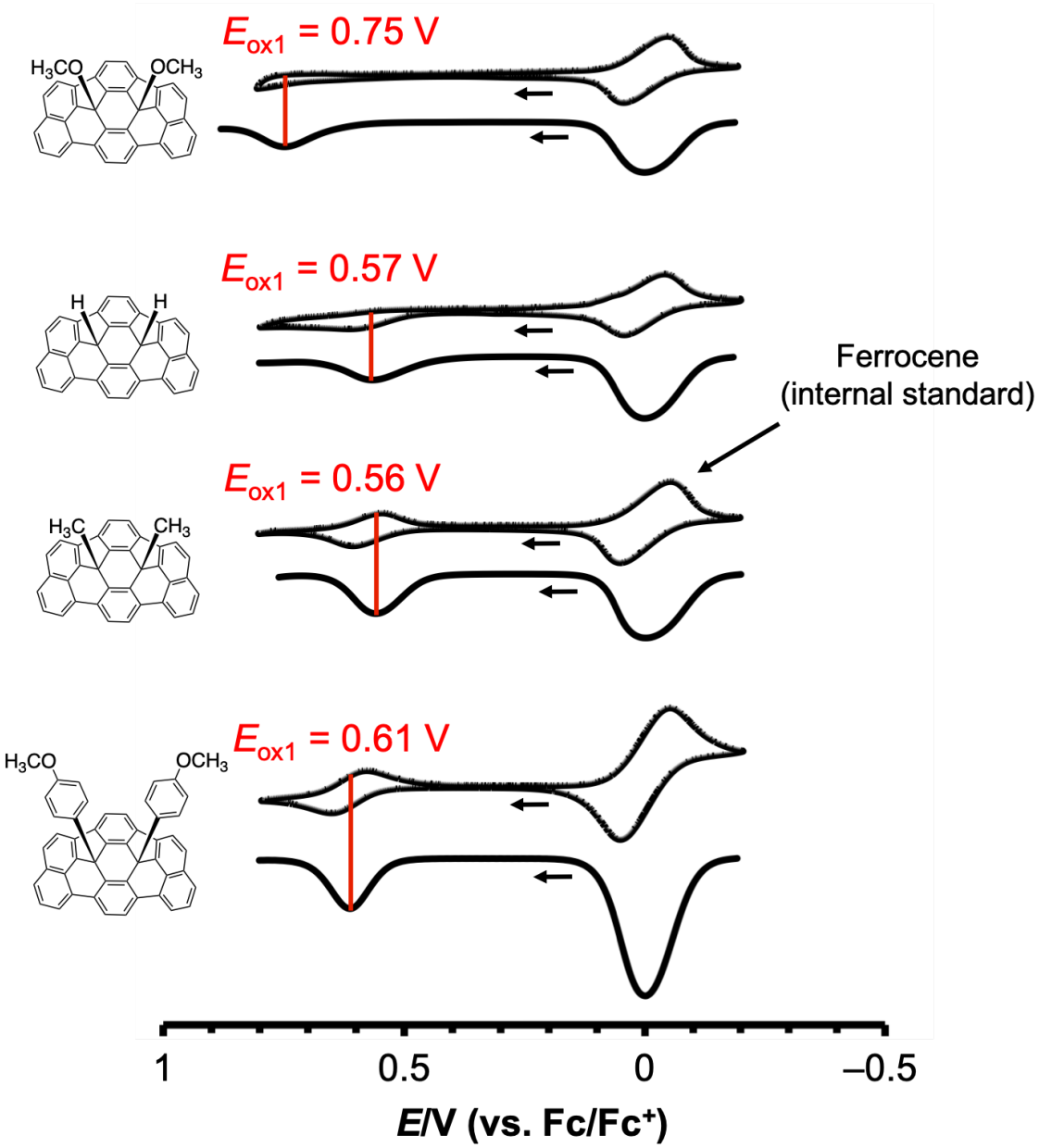


Figure S15. Cyclic voltammograms and differential pulse voltammograms of **5**, **6**, **7**, and **8**.

7. DFT calculations

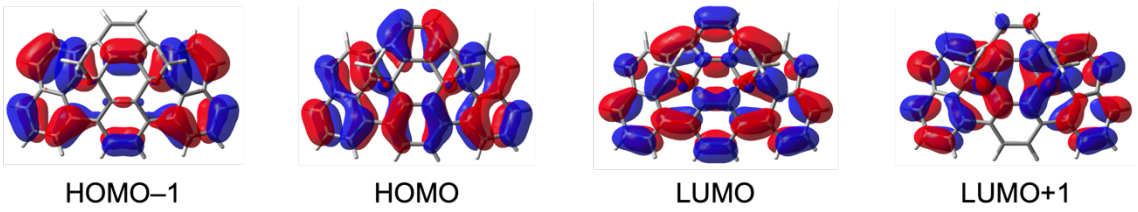


Figure S16. Calculated molecular orbitals of **5** at the B3LYP/6-31G(d) level.

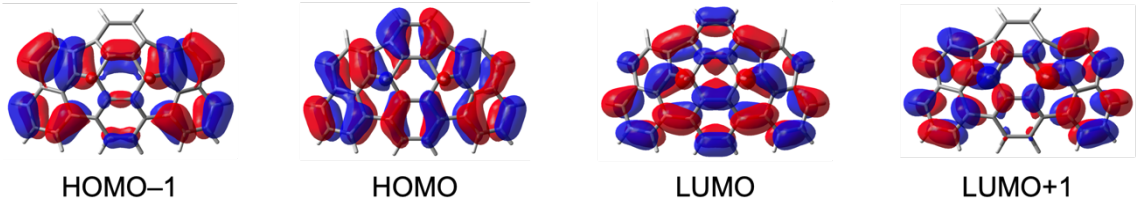


Figure S17. Calculated molecular orbitals of **6** at the B3LYP/6-31G(d) level.

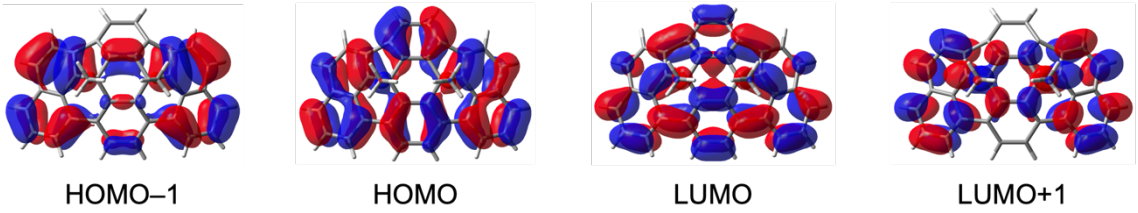


Figure S18. Calculated molecular orbitals of **7** at the B3LYP/6-31G(d) level.

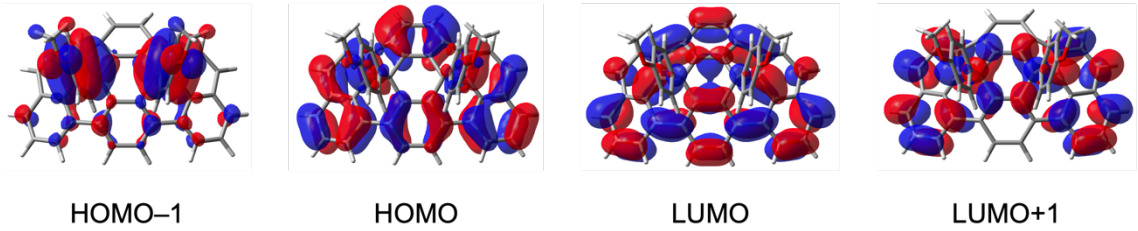


Figure S19. Calculated molecular orbitals of **8** at the B3LYP/6-31G(d) level.

Table S2. Cartesian coordinate and geometry of **5**.

C	1.424552	-2.489398	-0.467886
C	0.710386	-3.409505	-1.2466
H	1.221367	-4.042086	-1.968257
C	-0.710368	-3.409496	-1.246583
H	-1.221352	-4.041919	-1.968372
C	-1.424528	-2.489433	-0.467834
C	-0.679014	-1.704753	0.440752
C	-1.440563	-0.500562	0.935721
C	-0.697533	0.797863	0.709611
C	-1.442793	1.964414	0.431318
C	-0.698416	3.148385	0.268313
H	-1.208772	4.081417	0.047319
C	0.698478	3.148383	0.268314
H	1.208826	4.081422	0.047318
C	1.442869	1.964419	0.431304
C	0.697621	0.797869	0.709593
C	1.440536	-0.500621	0.935836
C	0.678974	-1.704675	0.44056
C	2.623445	-0.571394	0.024095
C	2.739302	-1.785326	-0.644677
C	3.885796	-1.970742	-1.456655
H	4.053344	-2.904121	-1.987556
C	4.806484	-0.936803	-1.576848
H	5.703099	-1.092341	-2.172494
C	4.582511	0.359177	-1.019523
C	5.407946	1.496531	-1.236303
H	6.341341	1.390574	-1.783792
C	5.004035	2.7332	-0.775166
H	5.63777	3.600098	-0.941777
C	3.738982	2.926064	-0.157816
H	3.427723	3.940638	0.075106
C	2.896288	1.85697	0.092351
C	3.401392	0.551147	-0.245356
C	-2.623274	-0.571326	0.023716
C	-2.739266	-1.785337	-0.64479
C	-3.885893	-1.970802	-1.456597
H	-4.053625	-2.904238	-1.987336
C	-4.806538	-0.936821	-1.576777
H	-5.703222	-1.092386	-2.172316
C	-4.582492	0.359198	-1.019568
C	-5.407952	1.496559	-1.23623
H	-6.341411	1.390636	-1.783621
C	-5.00402	2.733202	-0.775037
H	-5.637799	3.600085	-0.941558
C	-3.738958	2.926085	-0.157714
H	-3.427759	3.94064	0.075382
C	-2.896214	1.856988	0.092302
C	-3.401291	0.55122	-0.245543
O	1.789317	-0.504528	2.332223
C	2.485668	-1.649784	2.79814
H	3.465694	-1.768482	2.315979
H	1.905998	-2.571667	2.649458
H	2.633704	-1.49123	3.869359
O	-1.790366	-0.504059	2.331887
C	-2.485127	-1.650123	2.798124
H	-1.903943	-2.571154	2.650246
H	-3.464773	-1.770654	2.315554
H	-2.633971	-1.491197	3.869179

Negative frequency = zero

Sum of electronic and thermal free energies = -1533.907478 Hartree

Table S3. Cartesian coordinate and geometry of **6**.

C	-1.427137	2.646742	0.308425
C	-0.708149	3.6872	-0.30739
H	-1.219781	4.436151	-0.906808
C	0.70823	3.687203	-0.307371
H	1.219909	4.436248	-0.906639
C	1.42722	2.646758	0.308498
C	0.679823	1.732544	1.079928
C	1.434948	0.476525	1.384193
C	0.698355	-0.79143	1.005625
C	1.44304	-1.898378	0.542663
C	0.698192	-3.043458	0.196353
H	1.209173	-3.929981	-0.167985
C	-0.698181	-3.043444	0.196307
H	-1.209168	-3.929948	-0.16805
C	-1.443017	-1.898359	0.542626
C	-0.698336	-0.791423	1.005613
C	-1.434955	0.476521	1.384131
C	-0.679806	1.732537	1.079933
C	-2.630095	0.67925	0.522506
C	-2.739528	1.979714	0.034195
C	-3.890545	2.280827	-0.738689
H	-4.059411	3.282986	-1.123796
C	-4.809218	1.276705	-1.013581
H	-5.706658	1.518304	-1.578333
C	-4.58231	-0.088543	-0.657882
C	-5.405547	-1.182246	-1.040667
H	-6.338444	-0.99682	-1.567531
C	-5.003475	-2.474257	-0.765967
H	-5.637789	-3.306155	-1.060155
C	-3.740751	-2.757366	-0.18125
H	-3.42938	-3.795185	-0.100531
C	-2.898039	-1.736608	0.225371
C	-3.402662	-0.392753	0.082939
C	2.630169	0.679255	0.522707
C	2.739586	1.979704	0.034259
C	3.890507	2.280775	-0.738766
H	4.0593	3.282932	-1.123922
C	4.809159	1.276648	-1.013694
H	5.706551	1.518191	-1.578537
C	4.582275	-0.088574	-0.657863
C	5.405497	-1.182268	-1.040704
H	6.338341	-0.996799	-1.567641
C	5.003412	-2.474283	-0.766054
H	5.637653	-3.306203	-1.060335
C	3.740701	-2.757355	-0.181268
H	3.429277	-3.795165	-0.100686
C	2.898056	-1.736609	0.225479
C	3.402685	-0.392737	0.083057
H	1.739554	0.424272	2.444554
H	-1.739741	0.424252	2.444428

Negative frequency = zero

Sum of electronic and thermal free energies = -1304.944077 Hartree

Table S4. Cartesian coordinate and geometry of **7**.

C	-1.422303	2.620234	0.039775
C	-0.707879	3.643723	-0.604436
H	-1.221351	4.370188	-1.229507
C	0.708015	3.643716	-0.604438
H	1.221482	4.370192	-1.229502
C	1.422416	2.620195	0.039757
C	0.680582	1.725897	0.843246
C	1.450711	0.4847	1.200656
C	0.699771	-0.787225	0.839671
C	1.440154	-1.910215	0.403146
C	0.697671	-3.065787	0.091843
H	1.209723	-3.96042	-0.250573
C	-0.697733	-3.065777	0.091849
H	-1.2098	-3.960386	-0.250595
C	-1.440187	-1.910195	0.403171
C	-0.699777	-0.787219	0.839678
C	-1.450722	0.484711	1.200643
C	-0.680555	1.725898	0.843279
C	-2.617262	0.657715	0.284302
C	-2.728439	1.944315	-0.234846
C	-3.87136	2.224471	-1.027109
H	-4.036857	3.216442	-1.439342
C	-4.787286	1.213167	-1.28467
H	-5.679049	1.439027	-1.864767
C	-4.563932	-0.14102	-0.88766
C	-5.384826	-1.245471	-1.243034
H	-6.312056	-1.076297	-1.785246
C	-4.988246	-2.528516	-0.921156
H	-5.621343	-3.368594	-1.194137
C	-3.732874	-2.794507	-0.313205
H	-3.425818	-3.829767	-0.19246
C	-2.891797	-1.76164	0.06607
C	-3.390657	-0.423579	-0.128394
C	2.617325	0.657671	0.28445
C	2.728556	1.944245	-0.23472
C	3.871464	2.224415	-1.027015
H	4.036906	3.216399	-1.439233
C	4.787365	1.213117	-1.284584
H	5.679133	1.4389	-1.8647
C	4.563955	-0.14108	-0.88759
C	5.384802	-1.245524	-1.243055
H	6.312036	-1.076331	-1.785249
C	4.988193	-2.528584	-0.921235
H	5.621256	-3.368666	-1.194273
C	3.732819	-2.794557	-0.313297
H	3.425722	-3.829809	-0.192601
C	2.891776	-1.761677	0.066044
C	3.390696	-0.423629	-0.128314
C	1.931892	0.455345	2.680263
H	2.497313	1.363825	2.912552
H	1.081733	0.389827	3.365429
H	2.578296	-0.411513	2.850738
C	-1.932163	0.45522	2.680115
H	-1.082151	0.3894	3.365444
H	-2.497405	1.363799	2.912461
H	-2.578773	-0.411533	2.850364

Negative frequency = zero

Sum of electronic and thermal free energies = -1383.518601 Hartree

Table S5. Cartesian coordinate and geometry of **8**.

C	1.421376	-0.962456	2.664568
C	0.707979	-1.38412	3.798041
H	1.222749	-1.842116	4.63903
C	-0.707947	-1.384085	3.79806
H	-1.222717	-1.842052	4.639063
C	-1.421353	-0.96239	2.664605
C	-0.679286	-0.366981	1.621387
C	-1.449994	-0.255209	0.330983
C	-0.700135	-0.914141	-0.818883
C	-1.439533	-1.602274	-1.809604
C	-0.697336	-2.182039	-2.856423
H	-1.210421	-2.7248	-3.644858
C	0.6972	-2.182049	-2.856447
H	1.21025	-2.724812	-3.644902
C	1.439441	-1.602299	-1.80965
C	0.700085	-0.91416	-0.818901
C	1.449995	-0.255263	0.330947
C	0.67931	-0.367007	1.621372
C	2.628781	-1.110017	0.699583
C	2.734994	-1.352385	2.066195
C	3.878845	-2.060995	2.514171
H	4.037034	-2.254351	3.571974
C	4.803306	-2.519971	1.586079
H	5.697677	-3.03206	1.933243
C	4.579282	-2.42649	0.178505
C	5.399342	-3.016767	-0.820997
H	6.330284	-3.501809	-0.537406
C	4.995859	-2.997522	-2.14142
H	5.627683	-3.449437	-2.90137
C	3.732834	-2.477846	-2.529228
H	3.417557	-2.601481	-3.561637
C	2.895865	-1.877752	-1.603621
C	3.402864	-1.752873	-0.262586
C	-2.628808	-1.109915	0.69965
C	-2.735002	-1.352261	2.066267
C	-3.878873	-2.060815	2.514276
H	-4.037049	-2.254148	3.572085
C	-4.80337	-2.519769	1.58621
H	-5.697757	-3.031816	1.9334
C	-4.579367	-2.426325	0.178632
C	-5.399465	-3.016594	-0.820844
H	-6.33042	-3.501596	-0.537227
C	-4.996003	-2.997395	-2.141274
H	-5.627856	-3.449305	-2.901203
C	-3.732965	-2.477774	-2.529114
H	-3.417709	-2.601448	-3.561524
C	-2.89596	-1.877687	-1.603535
C	-3.402931	-1.75276	-0.262494
C	-1.904139	1.193788	0.010953
C	-2.34354	2.030147	1.041722
C	-1.937607	1.698071	-1.296497
C	-2.800446	3.325401	0.793668
H	-2.331073	1.673187	2.067244
C	-2.389249	2.986258	-1.56118
H	-1.603144	1.083303	-2.124762
C	-2.825451	3.811698	-0.518379
H	-3.127646	3.938939	1.625515
H	-2.408579	3.374548	-2.574819
C	1.904178	1.193723	0.010925
C	2.344158	2.029851	1.041636
C	1.937063	1.698243	-1.296445
C	2.801071	3.325106	0.793607
H	2.332155	1.6727	2.067097

C	2.388702	2.986438	-1.5611
H	1.602143	1.083662	-2.124663
C	2.825493	3.811652	-0.51836
H	3.12874	3.938436	1.625424
H	2.407578	3.374917	-2.574675
O	3.249521	5.059806	-0.879879
O	-3.24952	5.059842	-0.879892
C	-3.698862	5.93444	0.140716
H	-2.905313	6.148766	0.869304
H	-3.985082	6.860472	-0.361861
H	-4.570406	5.526151	0.670122
C	3.699367	5.934268	0.14062
H	3.985507	6.860307	-0.361993
H	2.906134	6.148646	0.869531
H	4.571072	5.525839	0.669652

Negative frequency = zero

Sum of electronic and thermal free energies = -1995.873522 Hartree

Table S6. Cartesian coordinate and geometry of C_{60}@**5**.

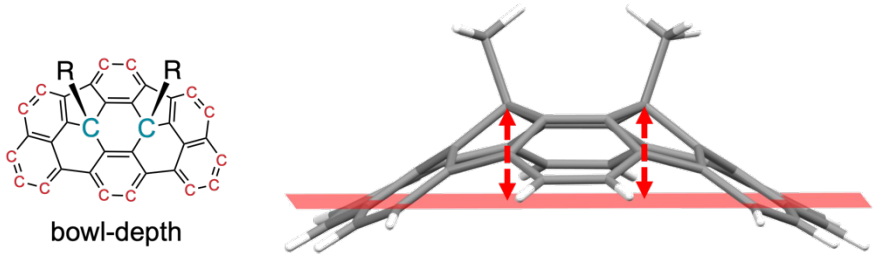
O	6.091628	-1.69025	-0.06737
O	5.972871	2.176723	0.105725
C	3.407435	-2.755633	-1.908954
C	3.729934	-1.305011	-2.071879
C	3.861505	-2.516754	0.479953
C	3.360891	-3.280617	-0.568815
C	4.728363	-1.326272	0.232144
C	4.509748	-0.581715	1.527217
C	4.237769	-0.566909	-0.97949
C	2.633712	-4.458192	-0.227801
C	2.896247	-3.568913	-2.905546
H	2.891943	-3.237175	-3.939652
C	3.48095	-2.654544	1.810432
C	3.321918	-0.550761	-3.188409
H	2.913151	-1.05234	-4.060062
C	3.676942	1.578962	-2.025502
C	4.489296	0.776013	1.549092
C	3.807666	-1.354782	2.482409
C	3.287892	3.006823	-1.814974
C	3.294691	0.84475	-3.164531
H	2.862499	1.358297	-4.017771
C	4.21731	0.829507	-0.95508
C	3.238049	-0.673284	3.563613
H	2.667125	-1.209928	4.316689
C	2.307735	-4.825095	-2.599532
H	1.923602	-5.430395	-3.415861
C	2.368291	-4.699669	1.154058
H	1.801027	-5.588681	1.418728
C	2.140118	-5.25203	-1.297943
H	1.606477	-6.174436	-1.083556
C	3.21416	3.481533	-0.457633
C	2.741179	3.828494	-2.78523
H	2.756652	3.533603	-3.83038
C	2.554887	3.88328	2.277998
H	2.227871	4.008943	3.306219
C	3.754383	1.486208	2.528772
C	7.062073	1.269852	-0.009116
H	7.94771	1.892034	-0.163239
H	7.191326	0.673462	0.90449
H	6.943532	0.578959	-0.851466
C	3.211195	0.746898	3.585766
H	2.617606	1.236666	4.353137
C	2.43258	4.611854	-0.079089
C	3.368519	2.788842	1.899925
C	4.677968	1.576418	0.282632
C	3.75004	2.709439	0.566206
C	2.720976	-3.79896	2.15227
H	2.398646	-3.972481	3.175007
C	6.770862	-2.412084	0.950623
H	7.782208	-2.58118	0.572847
H	6.826032	-1.840996	1.88827
H	6.29688	-3.381137	1.15719
C	1.904106	5.417459	-1.123432
H	1.329263	6.30714	-0.879197
C	2.093134	5.044104	-2.438414
H	1.683101	5.659021	-3.234727
C	2.156963	4.796806	1.309119
H	1.548589	5.649142	1.601589
C	-1.807883	0.003535	-3.426741
C	-0.529688	0.028567	-2.866398
C	-0.07105	1.211602	-2.155087
C	-0.906303	2.322492	-2.033279
C	-2.238242	2.294761	-2.615093

C	-2.679596	1.15982	-3.297682
C	-4.037583	0.678617	-3.104752
C	-4.005135	-0.774723	-3.114154
C	-2.626985	-1.192181	-3.312889
C	-2.135191	-2.315115	-2.645022
C	-0.80322	-2.290677	-2.06314
C	-0.018722	-1.141819	-2.170114
C	0.750422	-0.680293	-1.027048
C	0.718351	0.770217	-1.017798
C	0.646478	1.458112	0.191908
C	-0.223465	2.614713	0.318818
C	-0.982588	3.040528	-0.770518
C	-2.36174	3.455511	-0.57243
C	-3.137613	2.995441	-1.712559
C	-4.441538	2.533475	-1.528617
C	-4.90075	1.351598	-2.239204
C	-5.766947	0.599382	-1.346655
C	-5.735808	-0.795558	-1.35565
C	-4.837174	-1.496708	-2.25758
C	-4.3254	-2.666026	-1.562247
C	-3.002124	-3.066699	-1.751734
C	-2.206179	-3.50629	-0.617405
C	-0.847011	-3.02764	-0.809785
C	-0.107416	-2.582307	0.285225
C	0.709974	-1.386533	0.173552
C	0.634934	-0.670289	1.433484
C	0.603796	0.72296	1.442419
C	-0.290412	1.425507	2.347614
C	-0.803907	2.594949	1.651055
C	-2.126022	2.996325	1.841203
C	-2.921655	3.435571	0.706158
C	-4.27912	2.952863	0.897205
C	-5.024123	2.512006	-0.19725
C	-5.843132	1.316429	-0.084653
C	-5.885599	0.609881	1.117785
C	-5.85308	-0.843137	1.108395
C	-5.779567	-1.531541	-0.10304
C	-4.907909	-2.687764	-0.230842
C	-4.143655	-3.108965	0.858067
C	-2.766033	-3.528131	0.66121
C	-1.990503	-3.068464	1.802142
C	-0.687686	-2.605808	1.617551
C	-0.226669	-1.423785	2.329365
C	-1.088169	-0.750798	3.19704
C	-1.120606	0.703737	3.20651
C	-2.500186	1.12055	3.401943
C	-2.992123	2.242996	2.733769
C	-4.322883	2.216482	2.150139
C	-5.109578	1.069004	2.25806
C	-4.597723	-0.100058	2.953346
C	-5.057047	-1.281843	2.242908
C	-4.219895	-2.391479	2.120349
C	-2.889087	-2.366008	2.703949
C	-2.44758	-1.231333	3.386573
C	-3.319347	-0.075055	3.513251

Table S7. Cartesian coordinate and geometry of C_{60}@**6**.

C	4.616438	-0.698719	-0.884041
C	4.82546	-0.679789	1.63384
C	3.726946	-0.697632	-3.105171
H	3.324084	-1.206087	-3.975538
C	5.052355	-1.439978	0.363124
H	6.104255	-1.754318	0.252064
C	4.100793	-1.441162	-1.96896
C	3.662589	-3.383114	-0.434656
C	3.740305	-2.881475	-1.784204
C	4.187038	-2.626868	0.610503
C	4.096128	-1.421769	2.587528
C	3.759377	-2.720756	1.934015
C	3.532733	-0.707773	3.658606
H	2.957205	-1.223025	4.422845
C	2.947572	-3.830143	2.279327
H	2.596488	-3.967849	3.298134
C	2.577077	-4.732673	1.29321
H	1.968657	-5.593324	1.559812
C	2.877161	-4.522347	-0.087738
C	3.215726	-3.693091	-2.776343
H	3.235736	-3.376314	-3.814933
C	2.37102	-5.314298	-1.152635
H	1.797726	-6.210832	-0.930545
C	2.577393	-4.920175	-2.459439
H	2.183601	-5.526044	-3.270814
C	4.616387	0.69888	-0.884037
C	4.825407	0.679937	1.633843
C	3.726896	0.69775	-3.105167
H	3.323997	1.206181	-3.97553
C	5.052261	1.440151	0.363132
H	6.104149	1.754541	0.252081
C	4.100689	1.441301	-1.968951
C	3.662426	3.383238	-0.43465
C	3.740126	2.881594	-1.78419
C	4.186888	2.626993	0.610511
C	4.09602	1.421863	2.58753
C	3.759171	2.72082	1.934011
C	3.532676	0.70782	3.658607
H	2.957111	1.223024	4.42285
C	2.947338	3.83019	2.279333
H	2.596065	3.967773	3.29809
C	2.576867	4.732739	1.293229
H	1.968396	5.593356	1.559826
C	2.876994	4.522463	-0.087711
C	3.215449	3.693172	-2.776313
H	3.235413	3.37638	-3.814898
C	2.370745	5.314366	-1.152588
H	1.79745	6.210896	-0.930484
C	2.577064	4.920225	-2.459396
H	2.183178	5.526048	-3.270761
C	-0.262889	-1.426363	2.641698
C	-3.111946	-0.698444	-3.335135
C	-0.887663	-2.602939	2.058098
C	0.70664	-0.726687	1.924265
C	-1.279977	-0.697466	3.383579
C	-3.735568	-0.725983	3.138673
C	-0.512312	-3.032454	0.784078
C	-2.532614	-1.423605	3.257979
C	-4.127944	-1.424937	-2.591692
C	-2.290257	-2.60036	2.438578
C	-3.261075	-3.032137	1.533324
C	-1.522824	-3.482483	-0.159276
C	-5.495405	-1.175916	-0.553236

C	-1.859537	-1.426325	-3.211887
C	-3.879862	-3.032325	-0.736106
C	-2.101243	-2.602414	-2.392309
C	-2.869433	-3.481919	0.207769
C	0.121293	-2.306399	-1.361775
C	-3.503575	-2.601323	-2.008895
C	1.099802	-1.176361	0.599577
C	-4.513105	-2.304493	1.408941
C	-4.745837	-1.175474	2.195258
C	-4.895505	-2.304649	0.006477
C	0.501294	-2.304251	0.040767
C	-5.103793	-0.727071	-1.879039
C	-1.130558	-3.033565	-1.486462
C	-5.737569	0.000149	0.265815
C	-0.657088	-0.728016	-3.091564
C	-5.370299	0.000389	1.611928
C	0.352316	-1.176747	-2.146896
C	1.343605	-0.000205	-0.219302
C	0.972513	-0.000445	-1.562329
C	-0.262781	1.427134	2.641159
C	-3.111891	0.69719	-3.335395
C	-0.887471	2.603539	2.057108
C	0.706691	0.727115	1.923991
C	-1.279924	0.698597	3.383318
C	-3.735513	0.727208	3.138397
C	-0.512092	3.032543	0.782929
C	-2.532506	1.424785	3.257438
C	-4.127835	1.424041	-2.592232
C	-2.290062	2.601207	2.43759
C	-3.260848	3.032728	1.532177
C	-1.522565	3.482312	-0.160591
C	-5.495323	1.175891	-0.553682
C	-1.859429	1.425024	-3.212428
C	-3.879639	3.032108	-0.737252
C	-2.101048	2.601447	-2.393295
C	-2.869171	3.48197	0.206455
C	0.121446	2.305643	-1.362639
C	-3.503383	2.600603	-2.009883
C	1.099912	1.176286	0.599145
C	-4.512936	2.305131	1.408073
C	-4.745744	1.176422	2.194812
C	-4.895334	2.304788	0.005606
C	0.501458	2.303972	0.039885
C	-5.103742	0.726518	-1.879316
C	-1.130333	3.03286	-1.487609
C	-0.657034	0.726669	-3.09184
C	0.352411	1.175681	-2.147349



	5 (R = OCH_3)	**6** (R = H)	**7** (R = CH_3)	**8** (R = $C_6H_4OCH_3$)
bowl-depth (Å)	2.00	1.97	2.02	2.05

Figure S20. Bowl-depths of **5**, **6**, **7**, and **8** in their optimized structures.

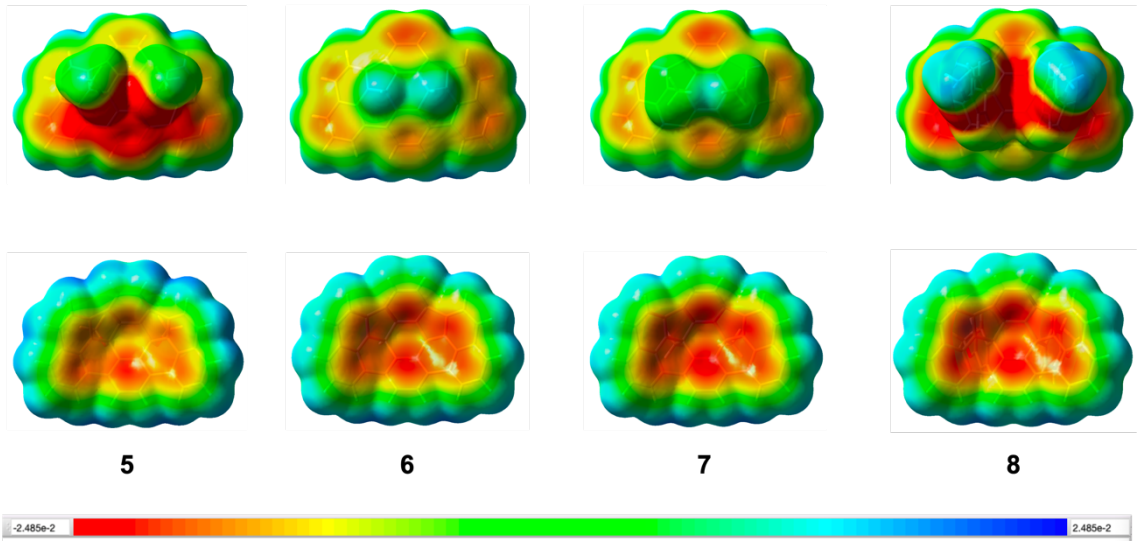


Figure S21. Calculated electron potential maps of **5**, **6**, **7**, and **8**.

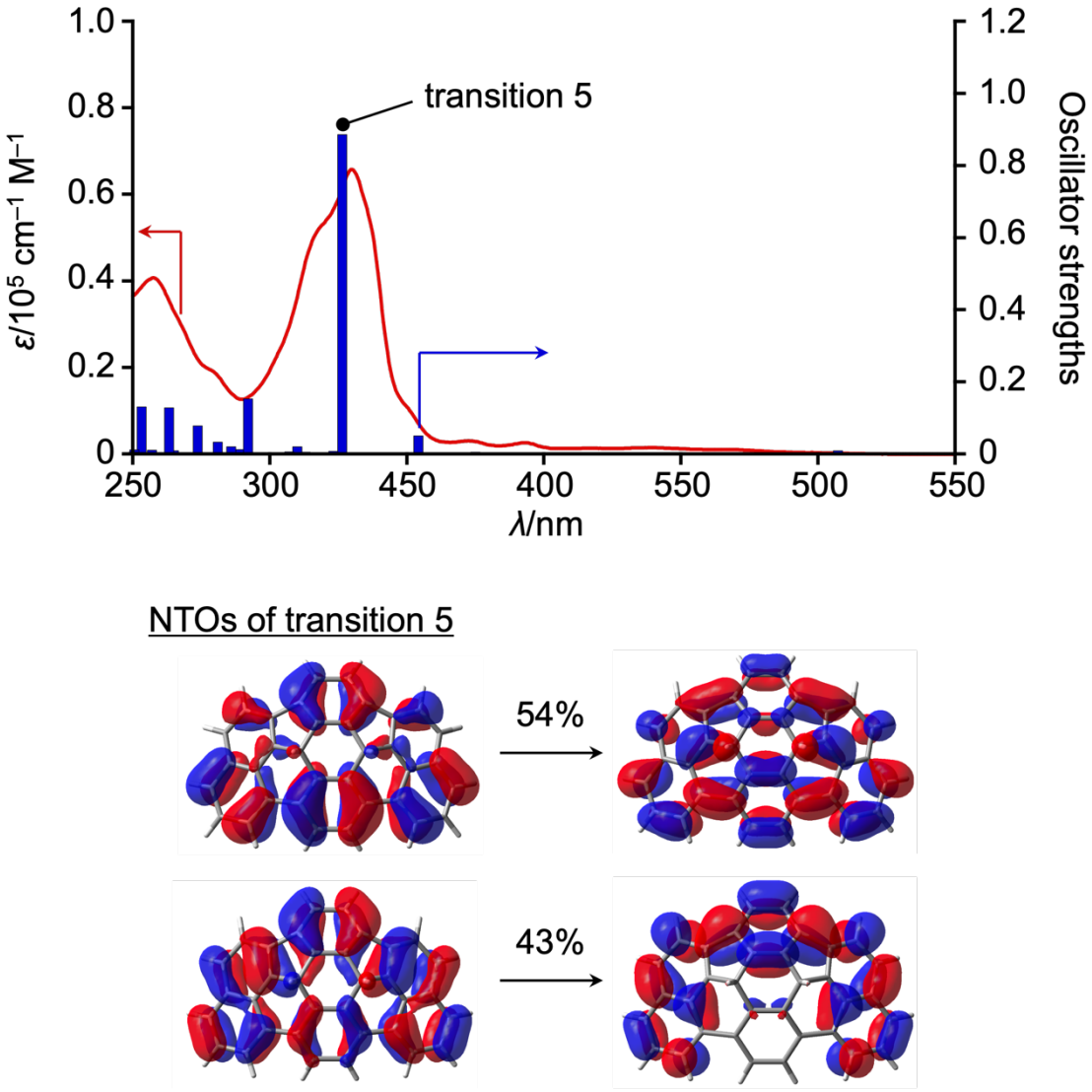


Figure S22. Experimental absorption spectrum (red line) and calculated oscillator strengths (blue bars) of **5**.

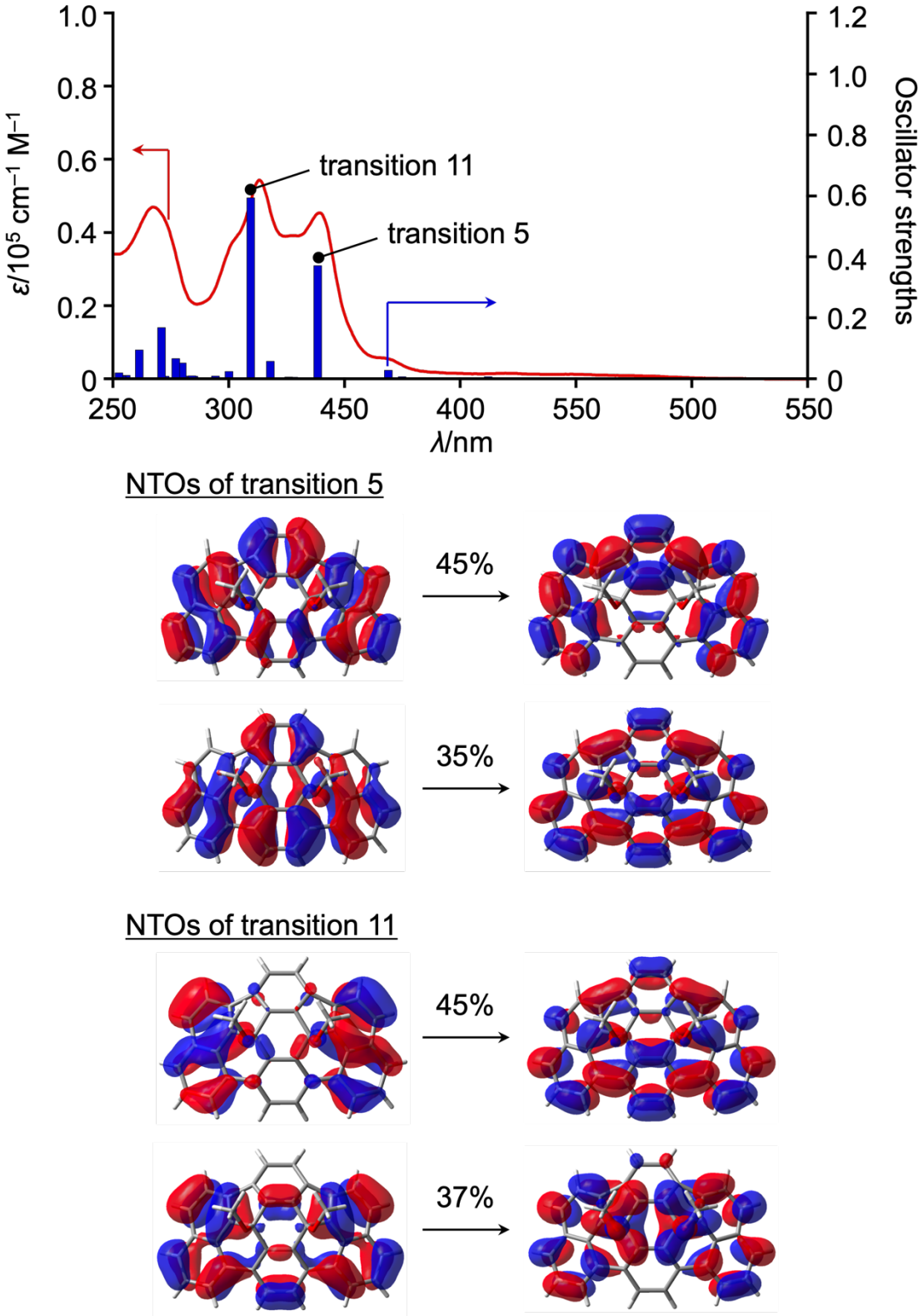


Figure S23. Experimental absorption spectrum (red line) and calculated oscillator strengths (blue bars) of **5**.

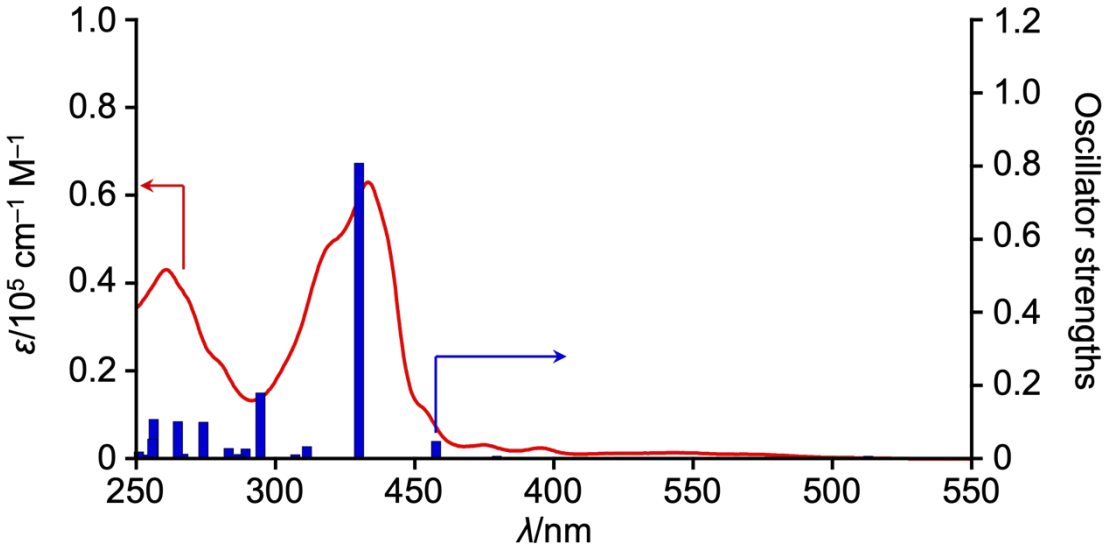


Figure S24. Experimental absorption spectrum (red line) and calculated oscillator strengths (blue bar) of **7**.

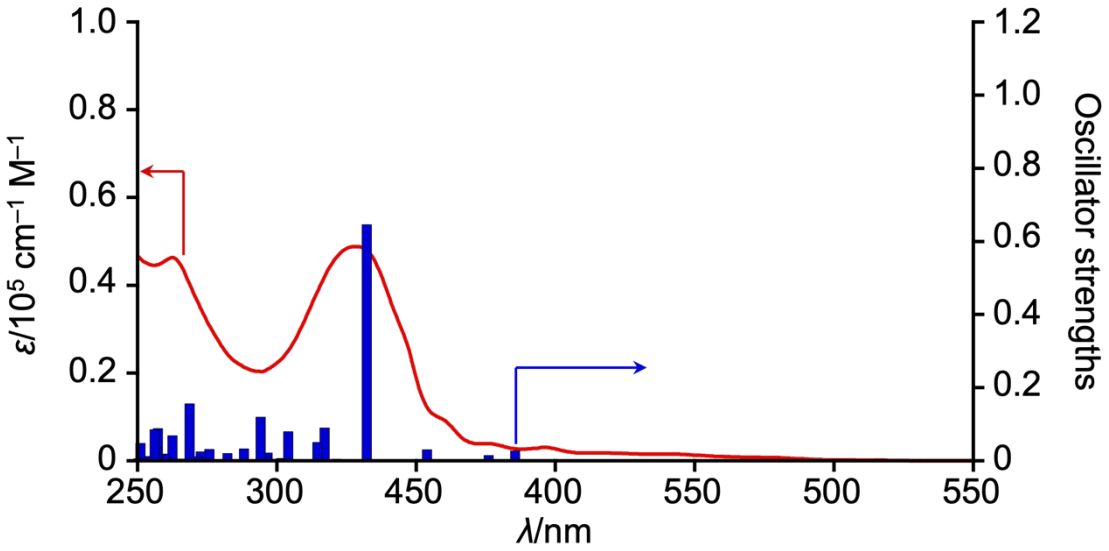
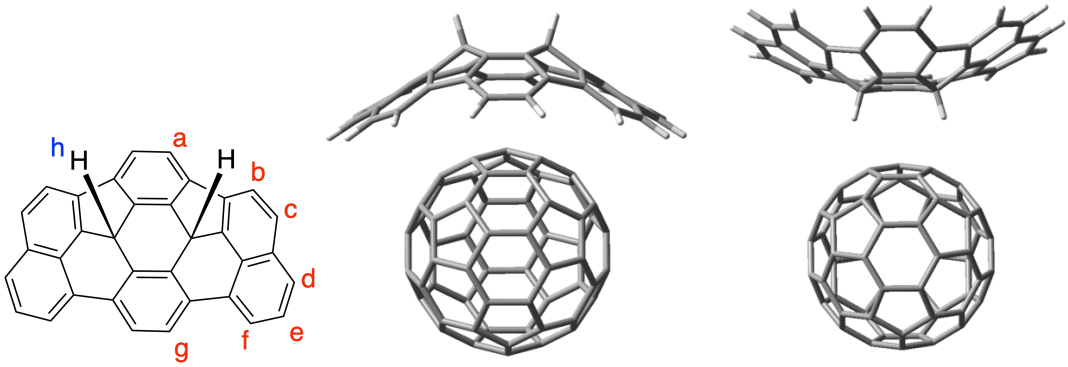


Figure S25. Experimental absorption spectrum (red line) and calculated oscillator strengths (blue bars) of **8**.

Table S8. Experimental and calculated chemical shift changes (Δδ) of **6** upon fullerene binding.



(concave) (convex)

Position	Δδ/ppm		
	Exp.	Calc. (concave)	Calc. (convex)
a	0.03	0.05	0.03
b	—	–0.11	0.03
c	—	0.07	0.02
d	—	0.21	0.03
e	—	0.04	0.01
f	0.01	–0.01	–0.03
g	0.07	0.18	–0.06
h	0.03	0.13	0.16

8. Fullerene binding

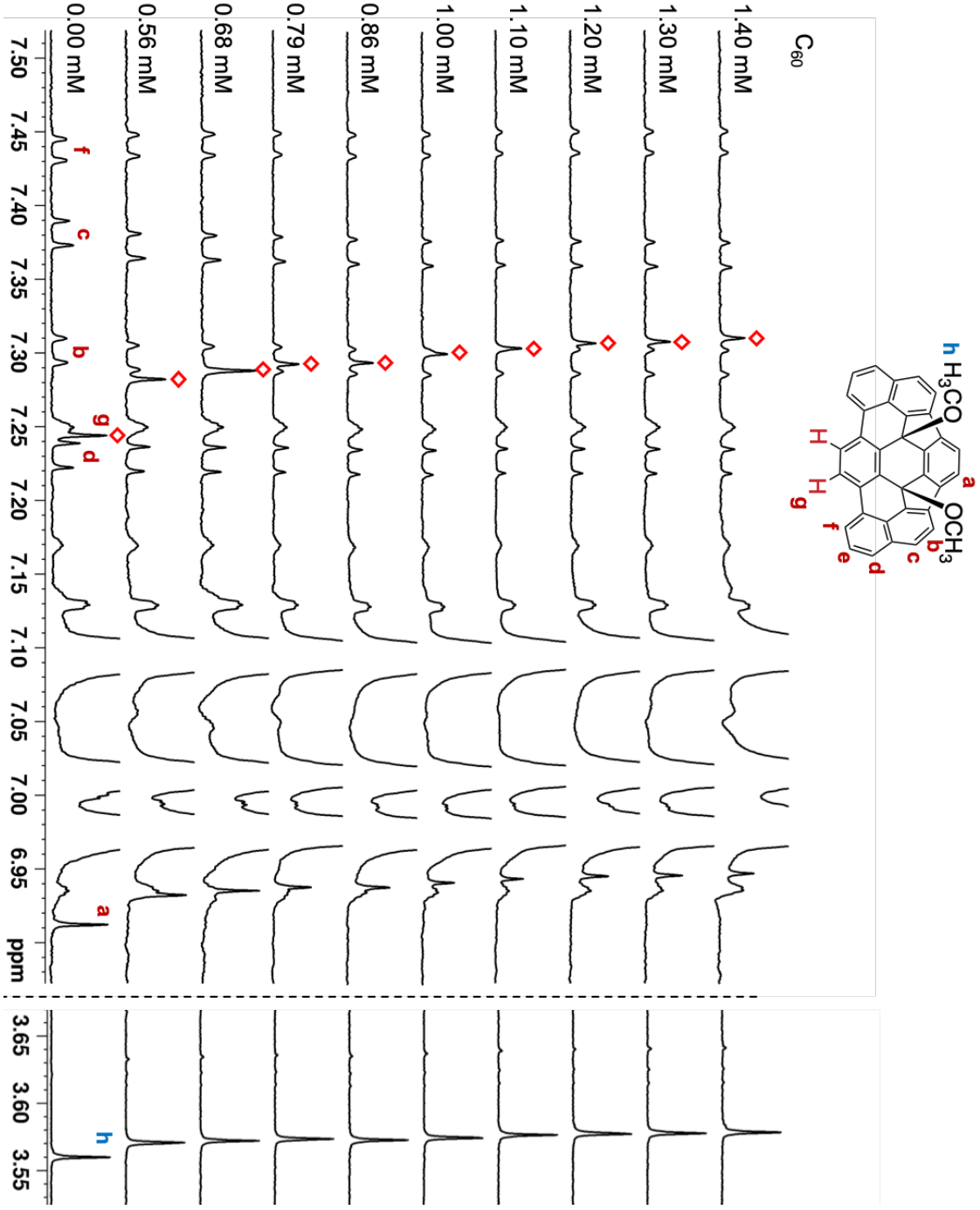
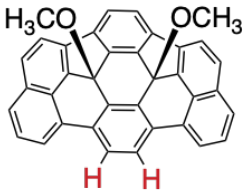


Figure S26. The change of ^{1}H NMR chemical shifts of **5** in toluene-d_8 at 303 K.

Table S9. Parameters given by the curve fitting of the change of ^{1}H NMR chemical shifts of **5**.



	Peripheral proton		
T/K	K_{assoc}/M^{-1}	$\Delta\delta_{max}$/ppm	R^2
303	884 ± 46	0.1240	0.9973
313	745 ± 44	0.1181	0.9971
323	638 ± 44	0.1118	0.9968
333	532 ± 44	0.1086	0.9963
343	477 ± 40	0.0999	0.9966

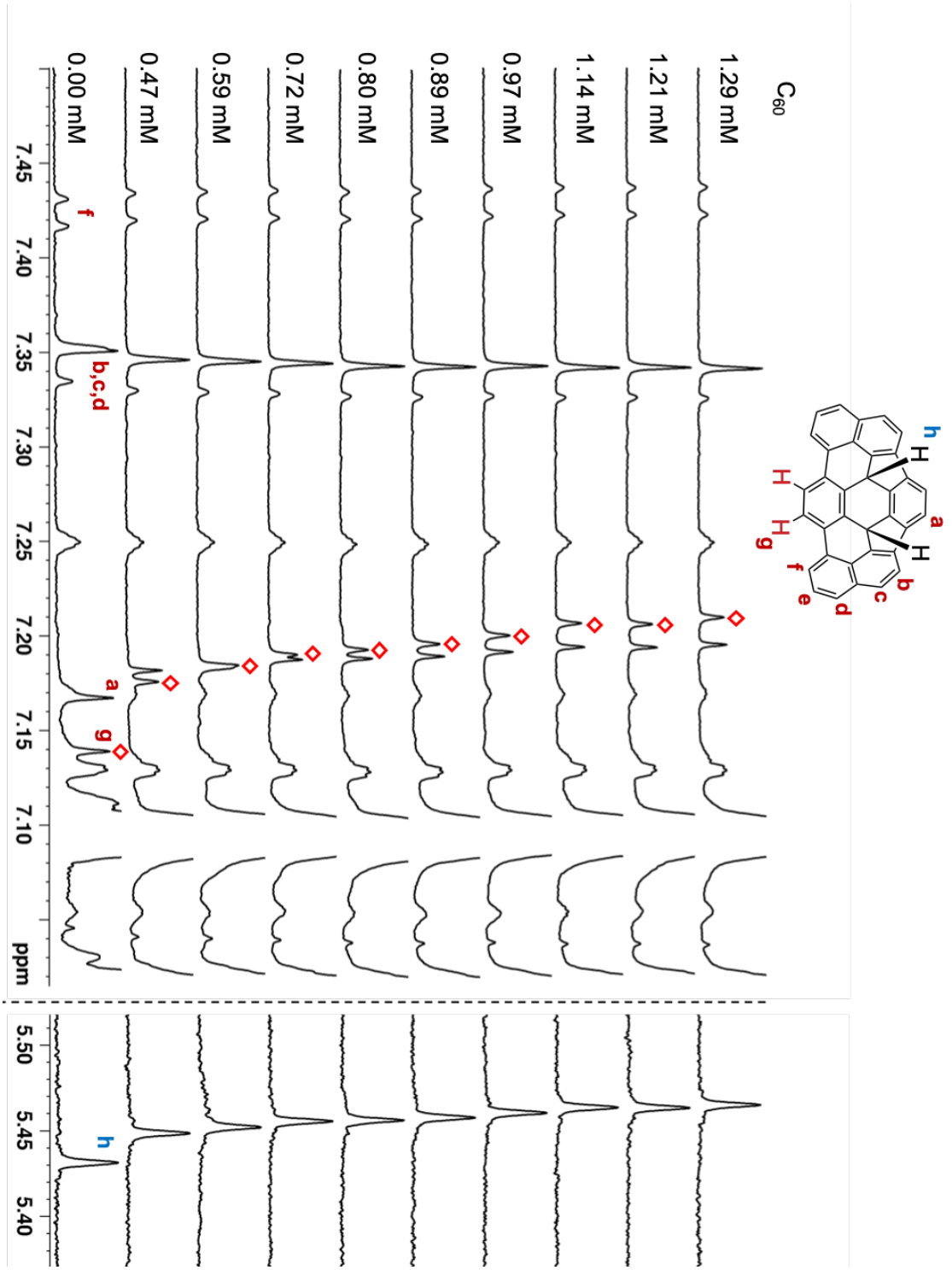
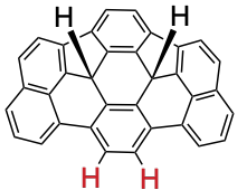


Figure S27. The change of ^{1}H NMR chemical shifts of **6** in toluene-d_8 at 303 K.

Table S10. Parameters given by the curve fitting of the change of ^{1}H NMR chemical shifts of **6**.



	Peripheral proton		
T/K	K_{assoc}/M^{-1}	$\Delta\delta_{max}$/ppm	R^2
303	918 ± 72	0.1350	0.9950
313	713 ± 60	0.1335	0.9956
323	606 ± 56	0.1258	0.9956
333	518 ± 55	0.1194	0.9952
343	425 ± 51	0.1148	0.9952

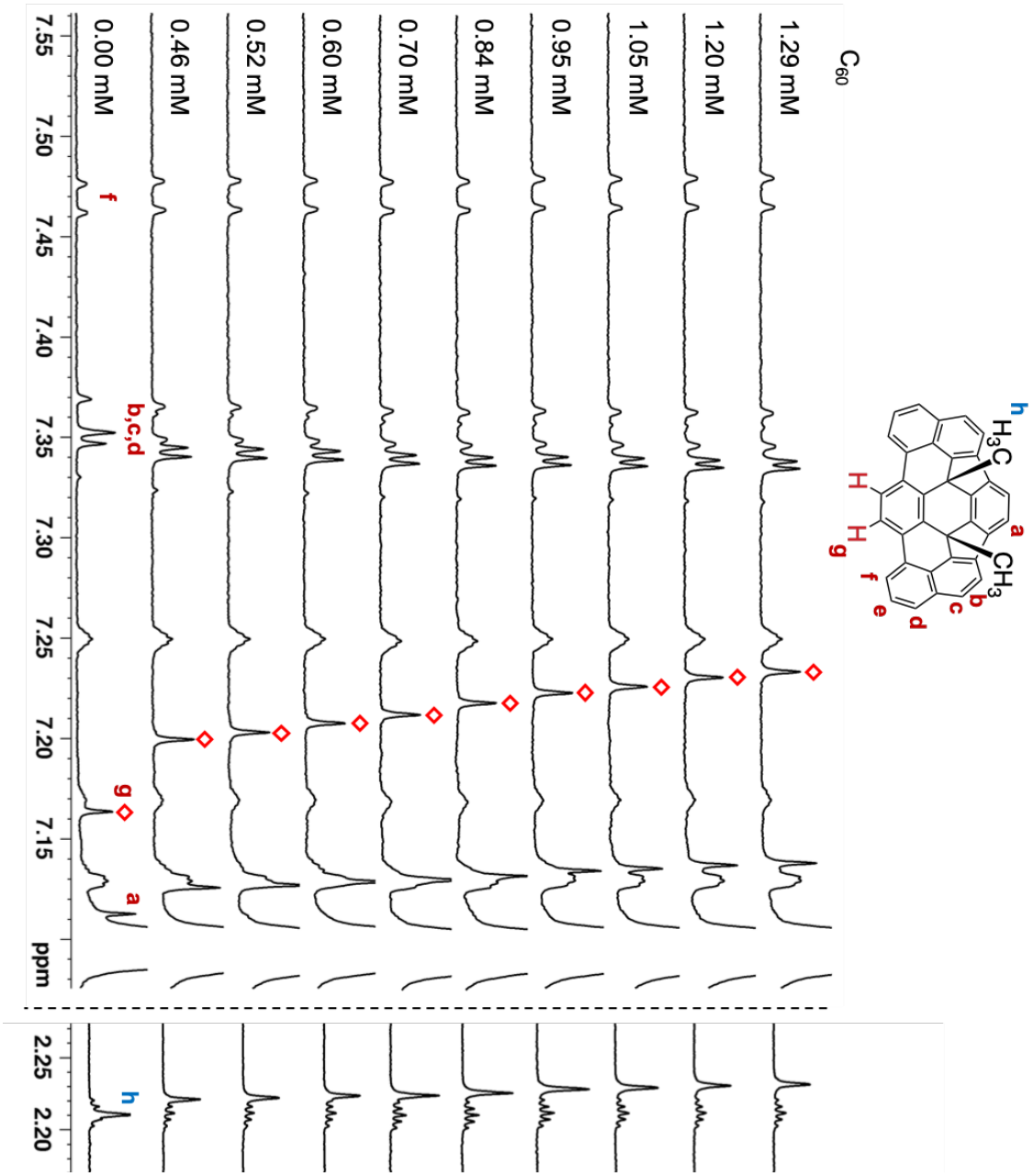
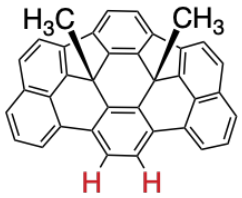


Figure S28. The change of ^{1}H NMR chemical shifts of **7** in toluene-d_8 at 303 K.

Table S11. Parameters given by the curve fitting of the change of ^{1}H NMR chemical shifts of **7**.



	Peripheral proton		
T/K	K_{assoc}/M^{-1}	$\Delta\delta_{max}$/ppm	R^2
303	865 ± 15	0.1363	0.9998
313	710 ± 15	0.1324	0.9997
323	584 ± 14	0.1296	0.9997
333	489 ± 14	0.1264	0.9997
343	406 ± 12	0.1231	0.9998

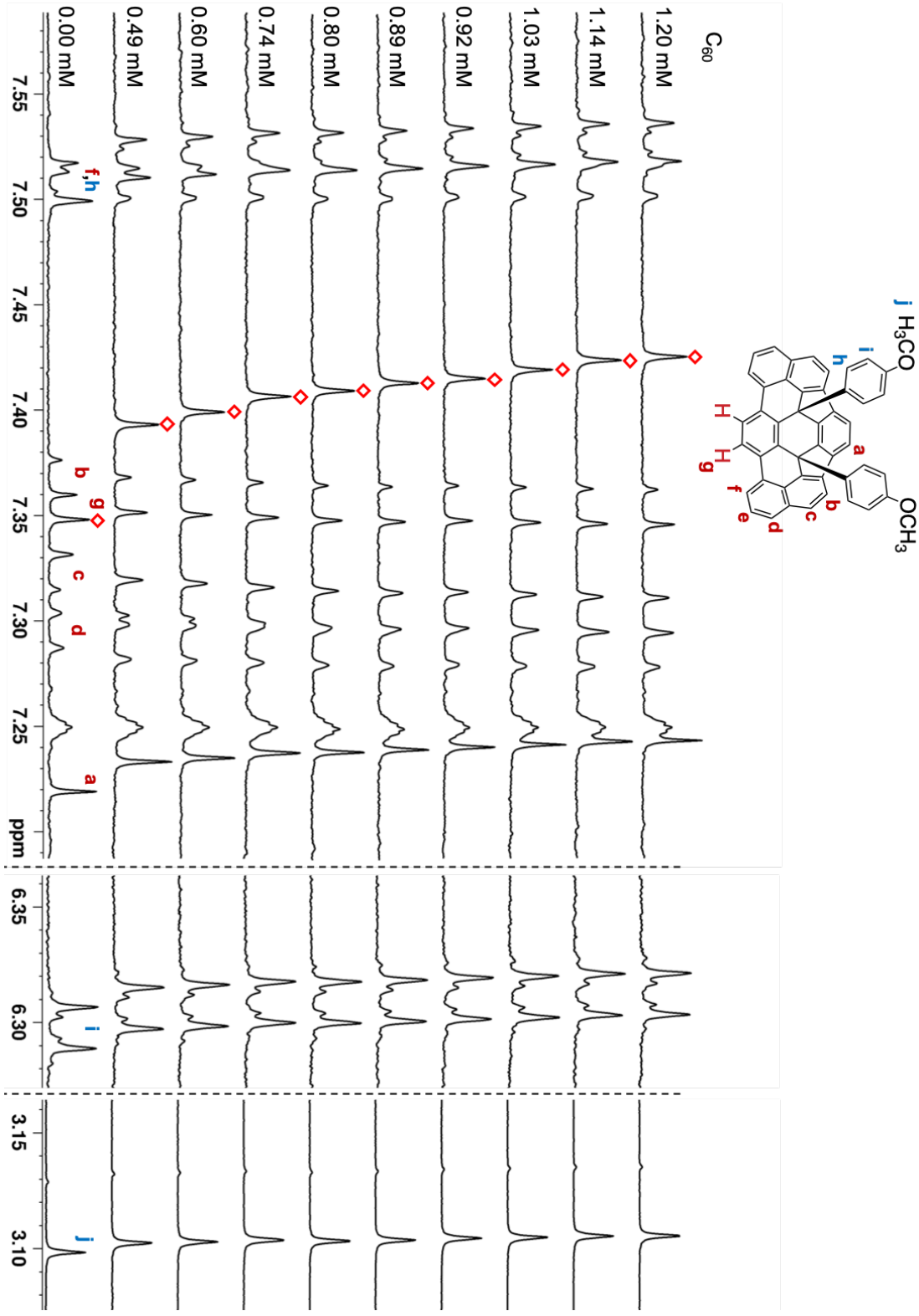
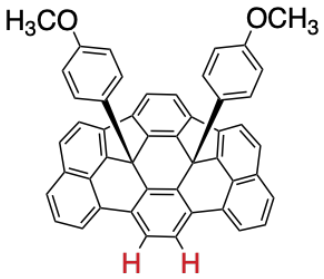


Figure S29. The change of ^{1}H NMR chemical shifts of **8** in toluene-d_8 at 303 K.

Table S12. Parameters given by the curve fitting of the change of ^{1}H NMR chemical shifts of **8**.



	Peripheral proton		
T/K	K_{assoc}/M^{-1}	$\Delta\delta_{max}$/ppm	R^2
303	964 ± 14	0.1488	0.9998
313	777 ± 12	0.1468	0.9998
323	646 ± 12	0.1434	0.9998
333	530 ± 10	0.1414	0.9998
343	431 ± 10	0.1400	0.9998

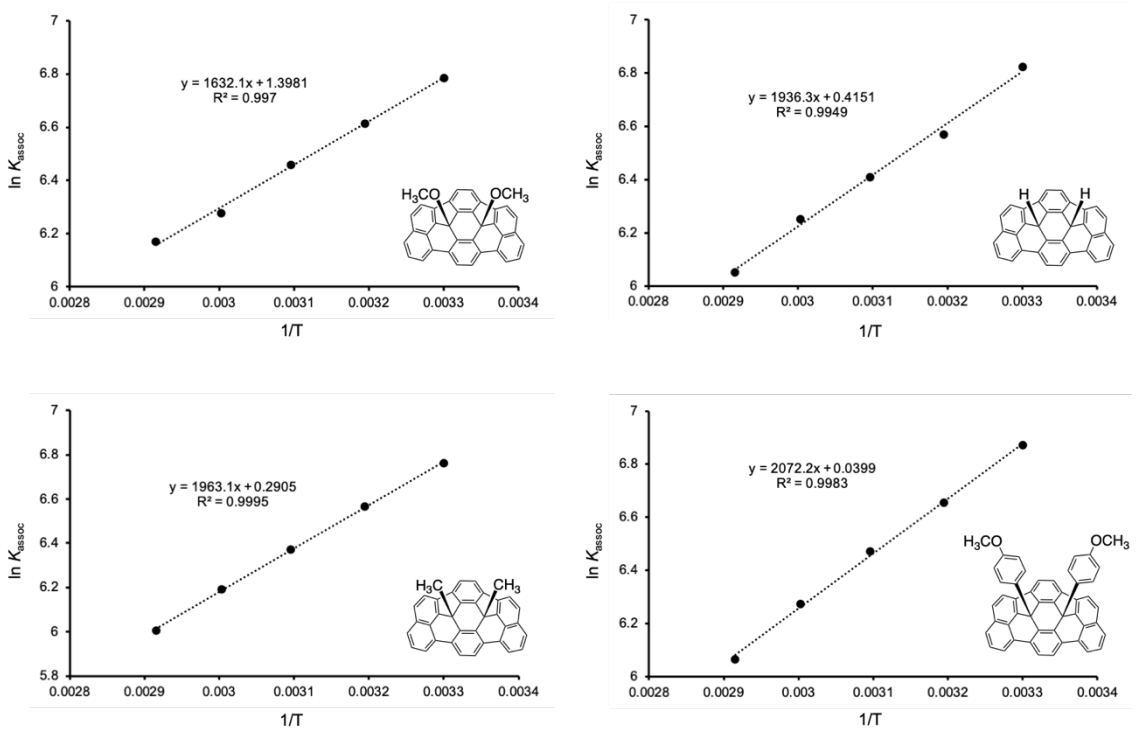


Figure S30. van't Hoff plots of **5**, **6**, **7**, and **8**.

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