meso-meso Linked Dimer of Antiaromatic Tetraoxa Isophlorin

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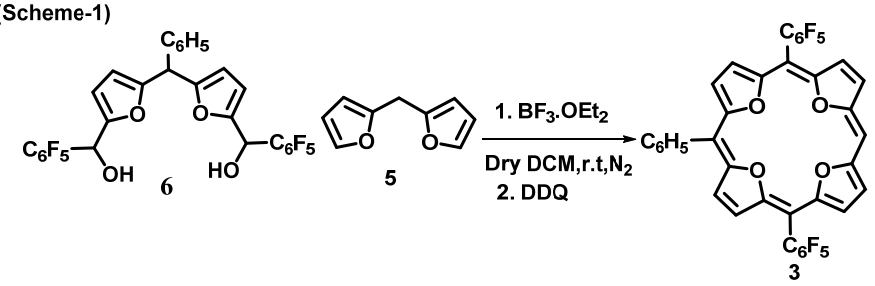
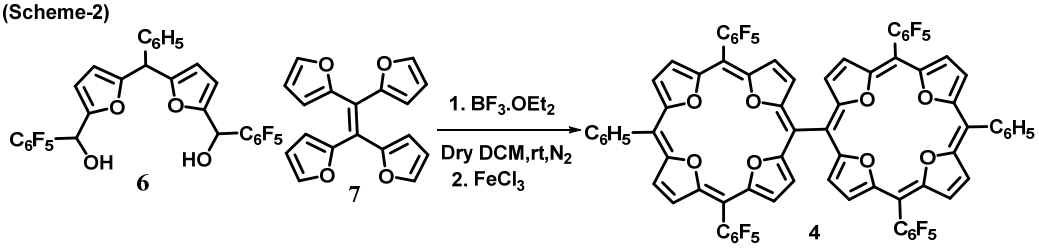
EXPERIMENTAL METHODS

All reagents and solvents were of commercial reagent grade and were used without further purification except where noted. Dry CH_2Cl_2 was obtained by refluxing and distillation over P_2O_5. Synthesis was carried out under an inert atmosphere using standard Schlenk line techniques. Column chromatography was performed by open-column gel permeation chromatography with Bio-Beads S-X1 (BIO-RAD). ^1H NMR and ^{19}F NMR spectra were recorded on a JEOL 400 MHz and BRUKER 500 MHz spectrometers. Chemical shifts (δ) are reported in parts per million (ppm). Electronic spectra were recorded on a Perkin-Elmer λ-950 ultraviolet–visible (UV–vis) spectro-photometer. High Resolution Mass spectra were obtained using WATERS G2 Synapt Mass Spectrometer. Single-crystal diffraction analysis data were collected at 100K with a BRUKER KAPPA APEX II CCD Duo diffractometer (operated at 1500 W power: 50 kV, 30 mA) using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å).

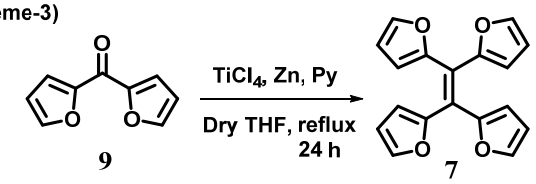
(Scheme-1)



(Scheme-2)



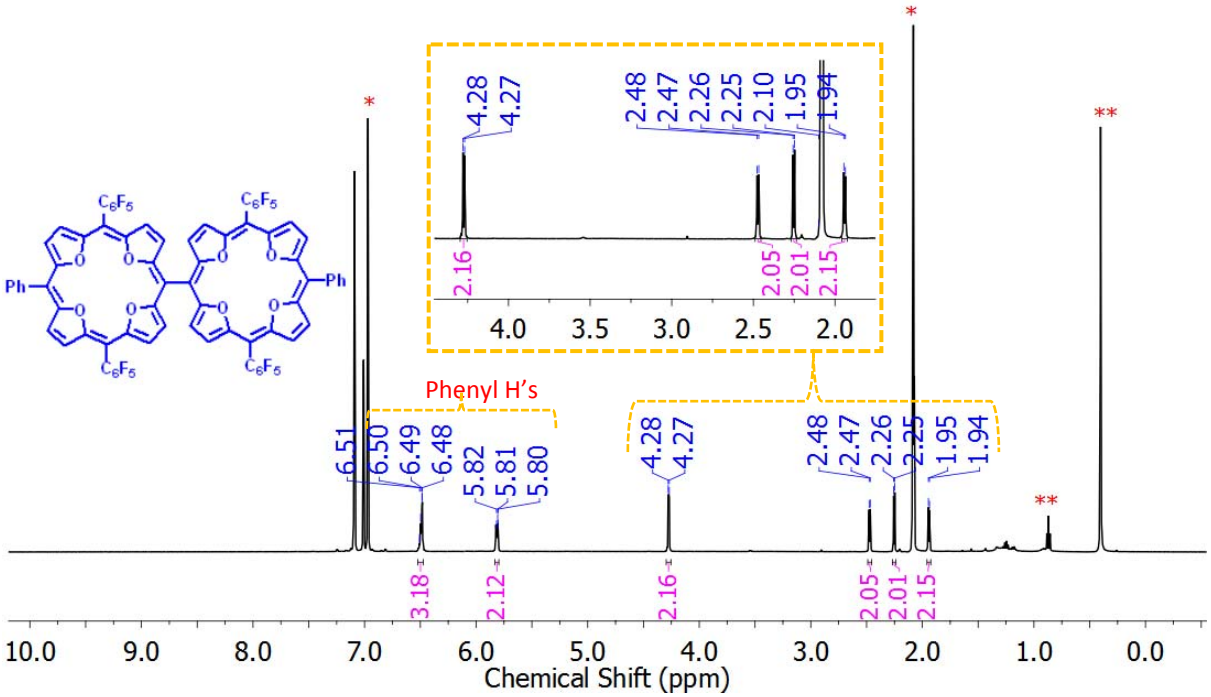
(Scheme-3)



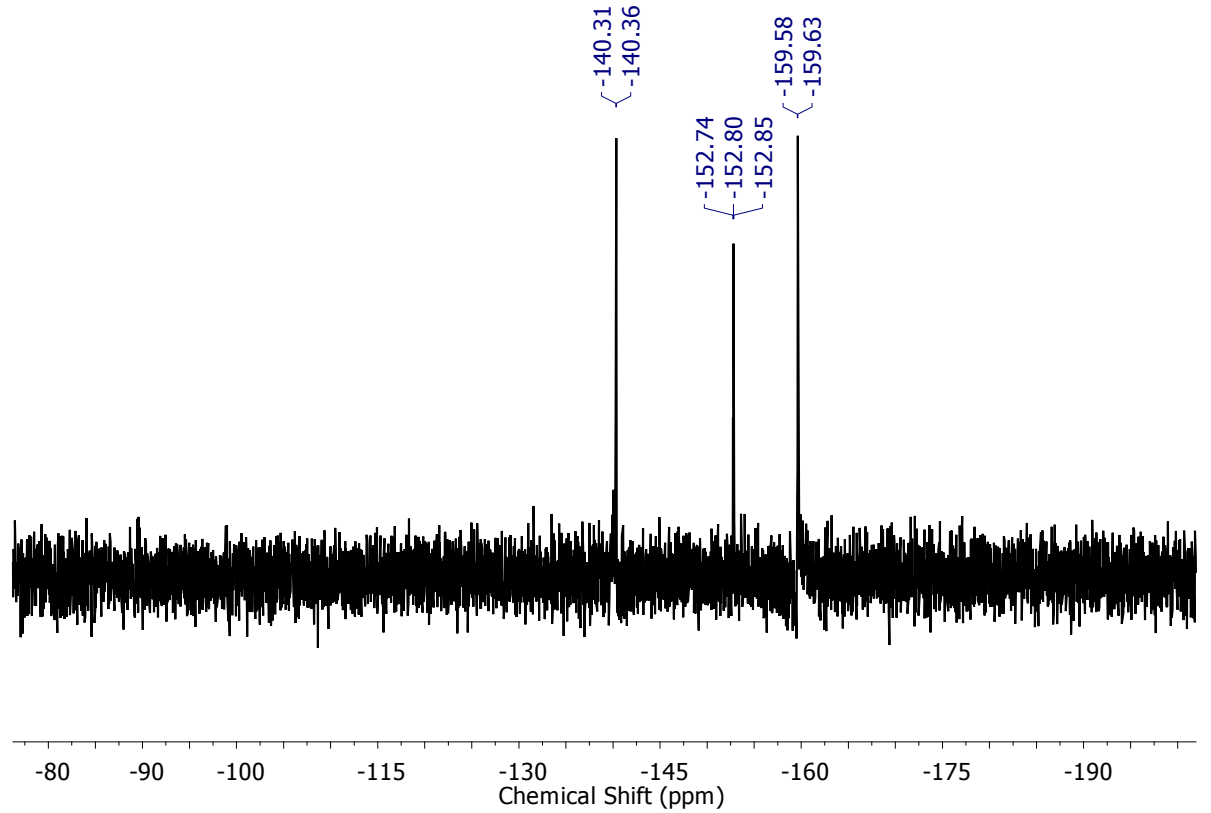
Synthetic procedure for 4:

A mixture of tetrafuroethene[3] **7**, (146 mg, 0.5 mmol) and the difuromethanediol **6**, (616 mg, 1 mmol) were stirred in 100 ml dry dichloromethane. The solution was bubbled with argon for 10 min. $BF_3.OEt_2$ (60µl, 0.5 mmol) was added under dark, and the resulting solution was stirred for 2h. After adding ten equivalents of $FeCl_3$ under inert atmosphere, solution was stirred for additional one hour. The reaction mixture was passed through a short basic alumina column. This mixture was separated by repeated size exclusion column chromatography by using toluene as eluent. A brown colour band obtained was identified as **4** in 30mg, 4.1% yield.

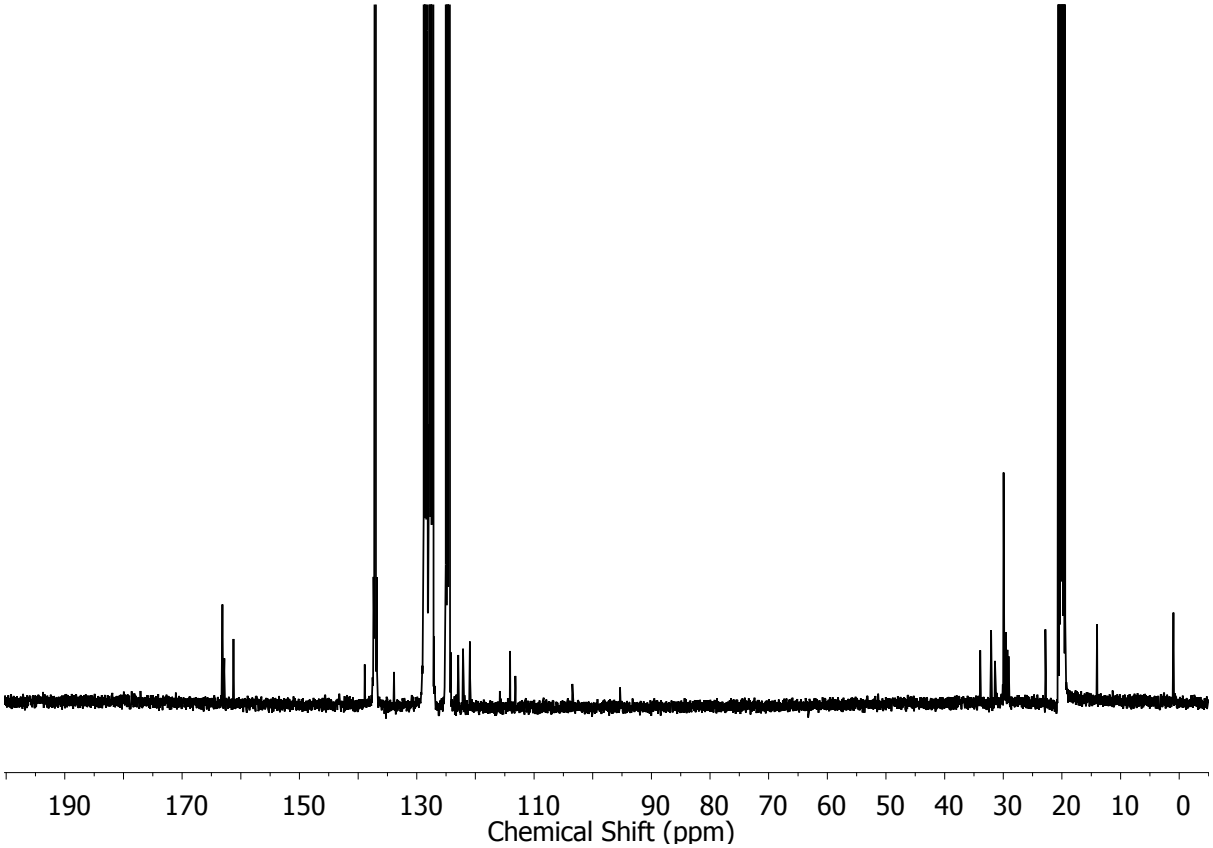
^{1}H NMR (500 MHz, Toluene-d_8) δ 6.49(dd, J=9.0, 3.2Hz, 3H), 5.81 (dd, J = 7.5, 2.3 Hz, 2H), 4.27 (d, J = 4.8 Hz, 2H), 2.47 (d, J = 4.8 Hz, 2H), 2.25 (d, J = 4.8 Hz, 2H), 1.94 (d, J=4.8 HZ, 2H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -140.31 (d), -152.82 (t), -159.61 (d). **UV-vis** (CH_2Cl_2): λmax(ε): 371(103822). **HRMS** m/z: Calcd. for $C_{38}H_{14}F_{10}O_4$: 1447.1386; observed: 1447.1332 (100.0%, M+H). **Crystal data:** $C_{76}H_{26}F_{20}O_8$, 2(C_{61}) (Mr = 2912.19), cubic, space group F d -3 (no. 203) , a = 57.756(6) Å, b = 57.756(6) Å, c = 57.756(6) Å, α = 90.00° β = 90.00° γ = 90.00°, V = 192656(58) Å^3, Z = 112, T = 100(2) K , D_{calcd} = 1.205g cm^{-3}, R_1 = 0.1296 (I>2s(I)), R_w (all data) = 0.1940, GOF = 1.557.



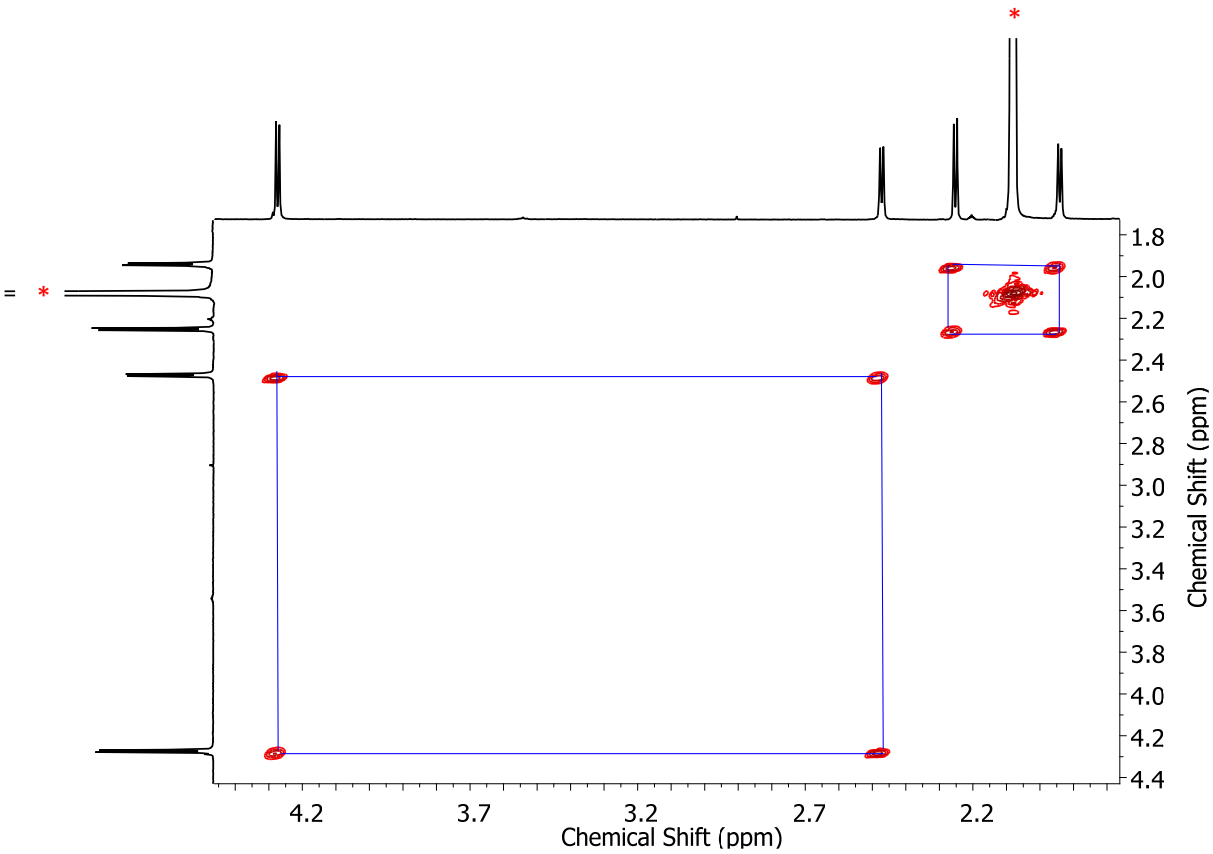
S1: ^{1}H NMR spectrum of **4** in Toluene-d_8 at 298*K,* (*Toluene-d_8, **H_20, and Hexane).



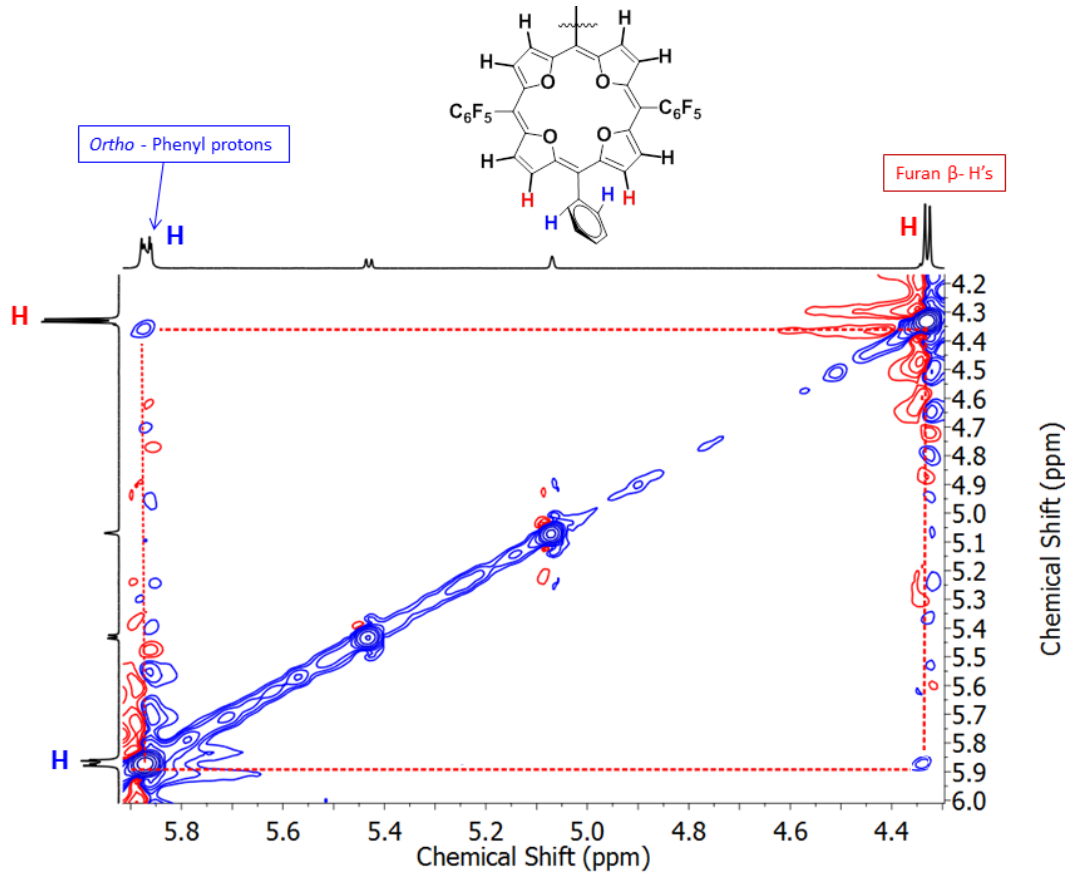
S2: ^{19}F NMR spectrum of **4** in $CDCl_3$ at 298*K*



S3: ^{13}C NMR spectrum of **4** in Toluene-d_8 at 298K

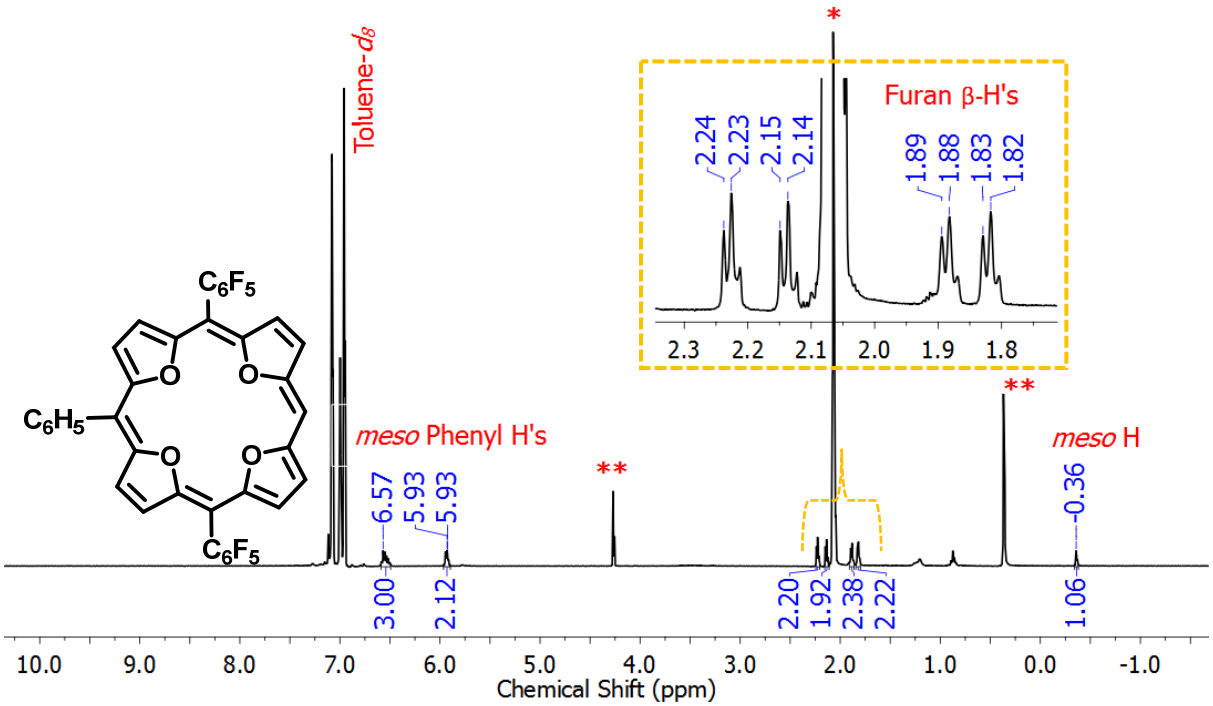


S4: ^{1}H-^{1}H COSY spectrum of **4** in Toluene-d_8 at 298K

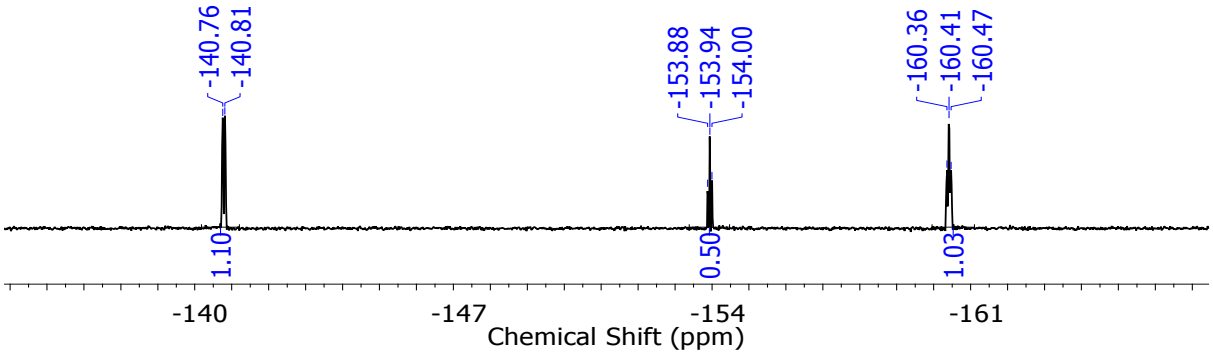


S5: NOESY spectrum of **4** in Toluene-d_8 at 298K

Synthetic procedure for 3:
A mixture of mesofree difuromethane **5**, (148 mg, 1 mmol) and the difuromethanediol **6**, (616 mg, 1 mmol) were stirred in 100 ml dry dichloromethane. The solution was bubbled with argon for 10 min. $BF_3.OEt_2$ (0.12 ml, 1 mmol) was added under dark, and the resulting solution was stirred for 2h. After adding five equivalents of DDQ under inert atmosphere, solution was stirred for additional one hour. The reaction mixture was passed through a short basic alumina column. This mixture was separated by repeated size exclusion column chromatography by using toluene as eluent. A brown color band obtained was identified as **3** in 60 mg 8% yield.
^{1}H NMR (400 MHz, Toluene-d_8) δ 6.57 (s, 3H), 5.93 (d, J = 1.3 Hz, 2H), 2.23 (t, J = 5.1 Hz, 2H), 2.13 (dd, J = 10.2, 4.5 Hz, 2H), 1.91 – 1.86 (m, 2H), 1.82 (t, J = 5.1 Hz, 2H), -0.36 (s, 1H). **^{19}F NMR** (376 MHz, Chloroform-d) δ -140.79 (d, J = 21.6 Hz), -153.94 (t, J = 21.7 Hz), -160.41 (t, J = 21.1 Hz). **UV-vis** (CH_2Cl_2): $\lambda_{max}(\varepsilon)$: 357(91411), 322(79800). **HRMS** m/z: Calcd. for $C_{38}H_{14}F_{10}O_4$: 724.0732; observed: 724.0725 (100.0%, M+).



S6: ^{1}H NMR spectrum of **3** in Toluene-d_8 at 298*K*, (*Toluene-d_8, **H_20 and CH_2Cl_2).

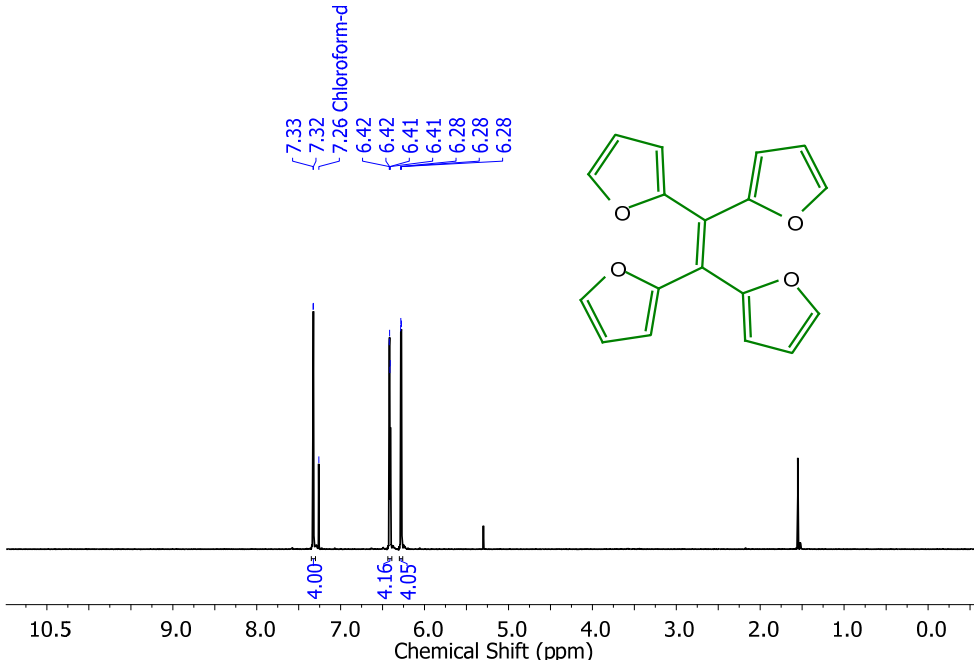


S7: ^{19}F NMR spectrum of 724 in Toluene-d_8 at 298*K*

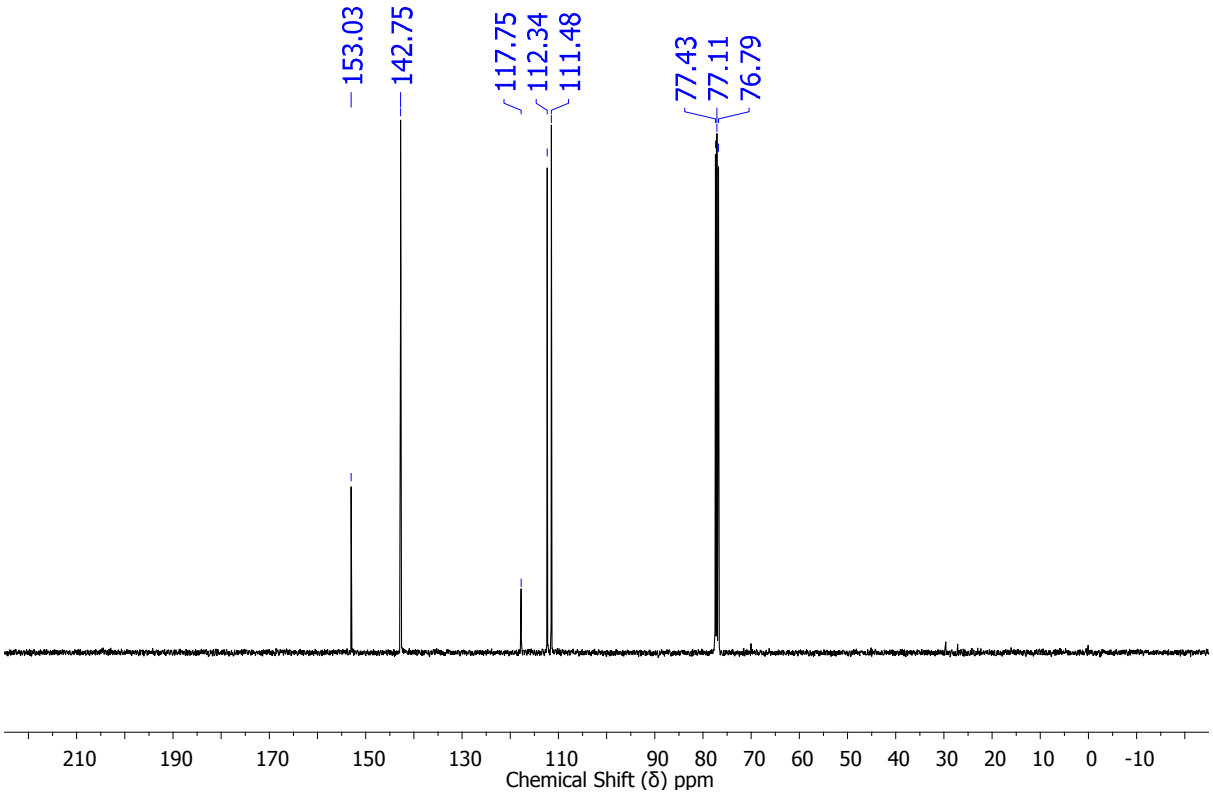
Synthetic procedure for 7:

To a mixture of Zn dust (19.26g) in dry THF (200 ml) TiCl4 (16.4 ml, 150 mmol) was carefully added and argon was bubbled through it. The resulting black slurry was refluxed for 2 hrs, then add pyridine 11.78ml at room temperature and again reflux 1h. A solution of compound **9** (2 g, 12 mmol) in THF (100 ml) was added drop wise to the black slurry and the resulting mixture was refluxed for 12 hr. The reaction mixture was cooled to 0 °C and quenched by the addition of distilled water (200 ml). The organic phase was extracted in $CHCl_3$, washed with water and concentrated under reduced pressure. The compound **7** was purified by column chromatography on silica gel (100-200 Mesh) eluted with hexane yielded in 20%.

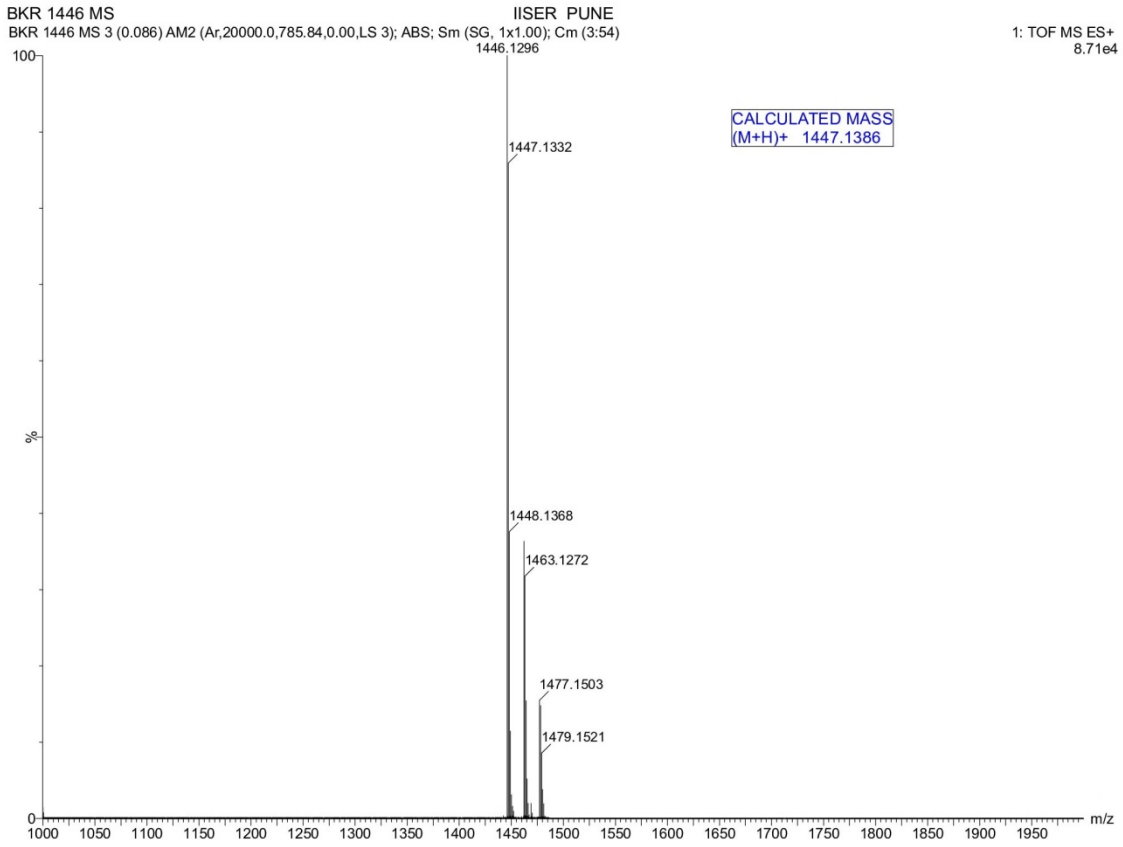
^{1}H NMR (400 MHz, CDCl3) δ 7.33 (d, J = 2.0 Hz, 4H), 6.42 (d, J = 2.0 Hz, 4H), 6.28 (m, 4H); **HRMS** m/z: Calcd. for $C_{18}H_{12}O_4$: 293.0814; observed: 293.0811 (100.0%, M+).



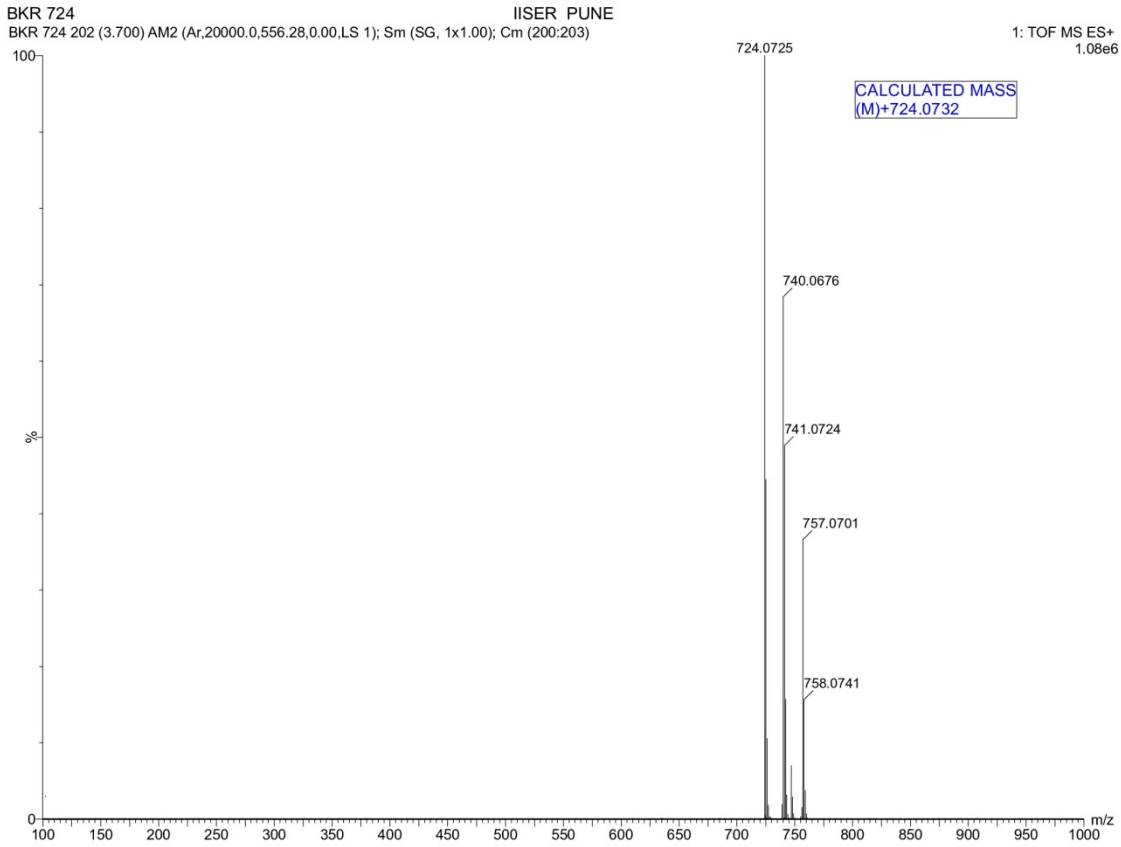
S8: ^{1}H NMR spectrum of **7** in CDCl3 at 298*K.*



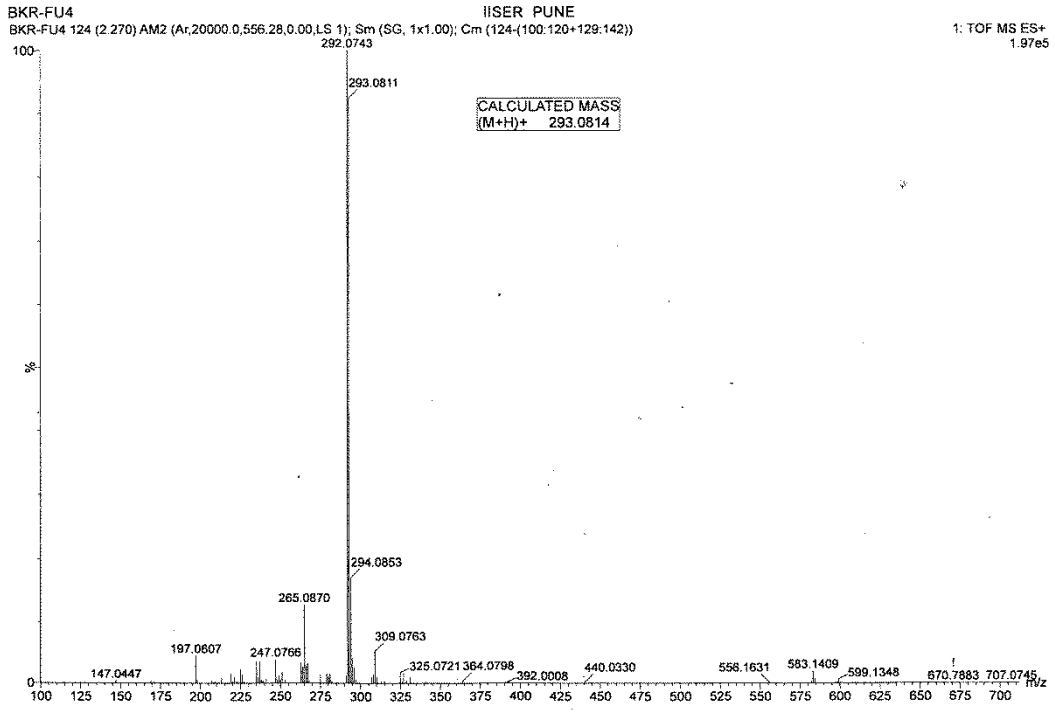
S9: ^{13}C NMR spectrum of **7** in $CDCl_3$ at 298*K.*



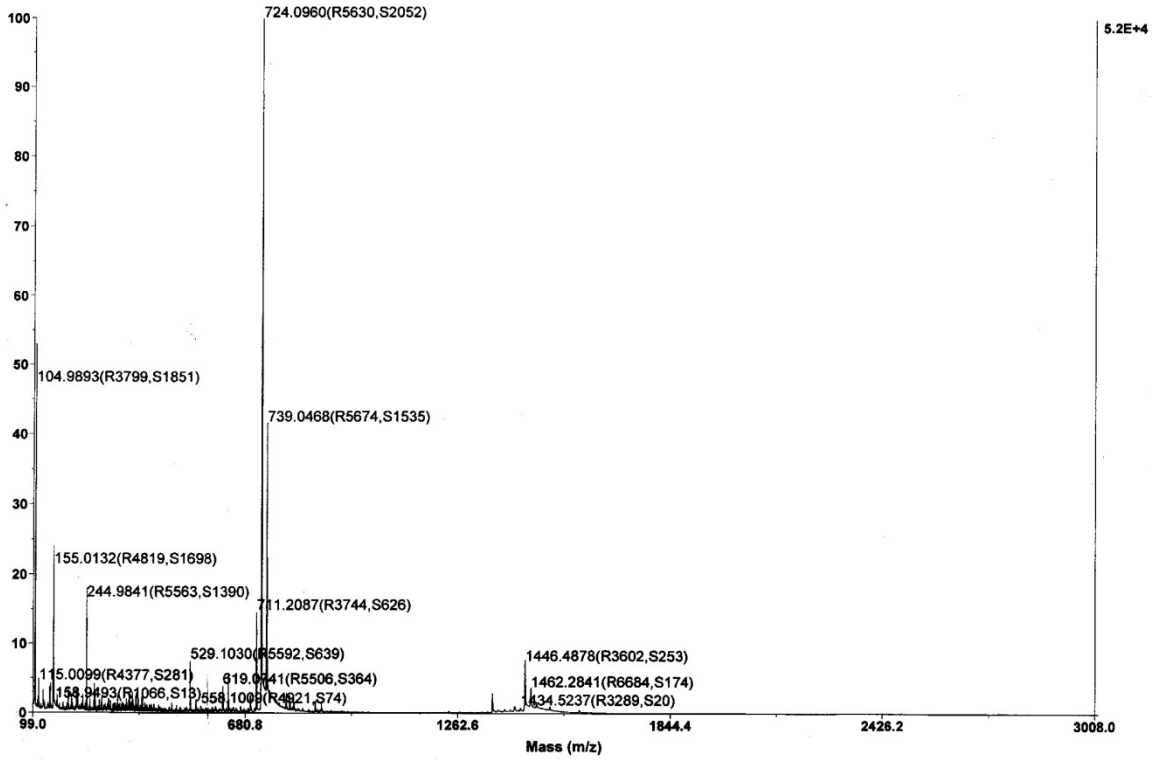
S10: HR-ESI-TOF mass spectrum of **4**.



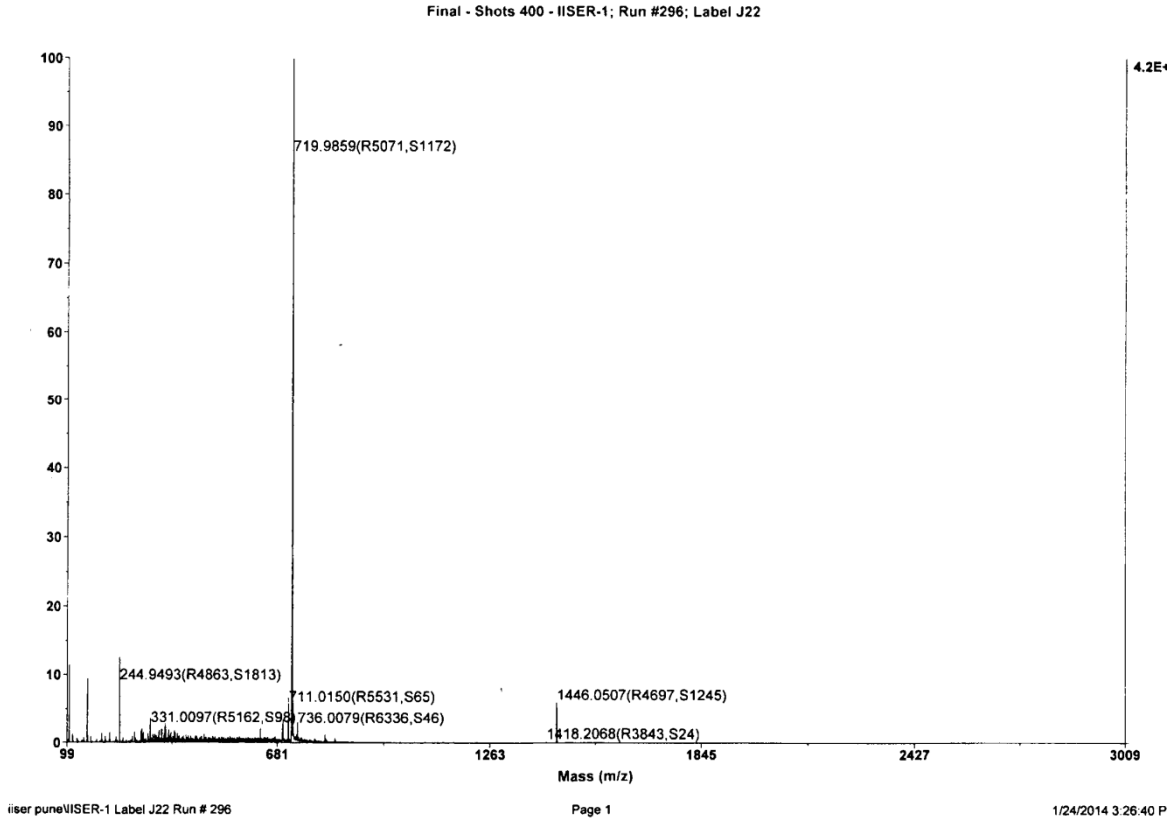
S11: HR-ESI-TOF mass spectrum of **3**.



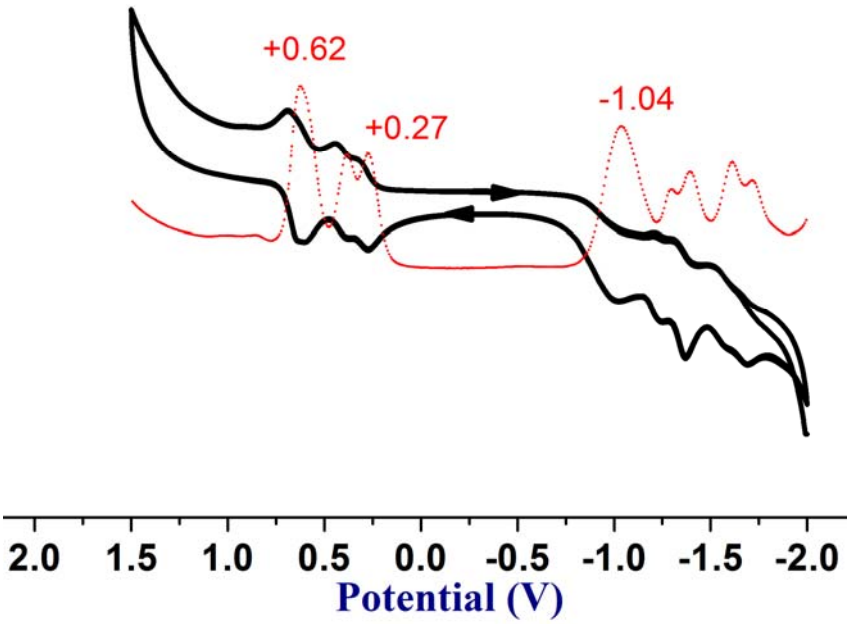
S12: HR-ESI-TOF mass spectrum of **7**.



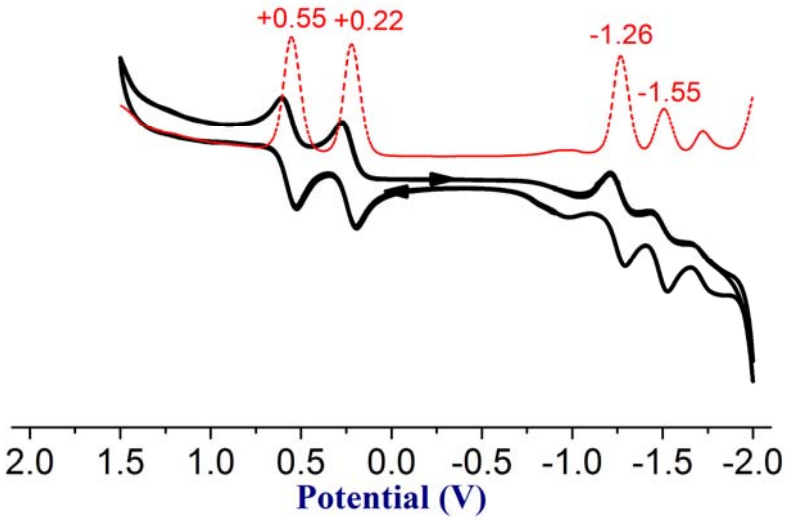
S13: MALDI TOF-TOF mass spectrum revealed a minute formation of the dimer **4** during the initial few minutes of the reaction.



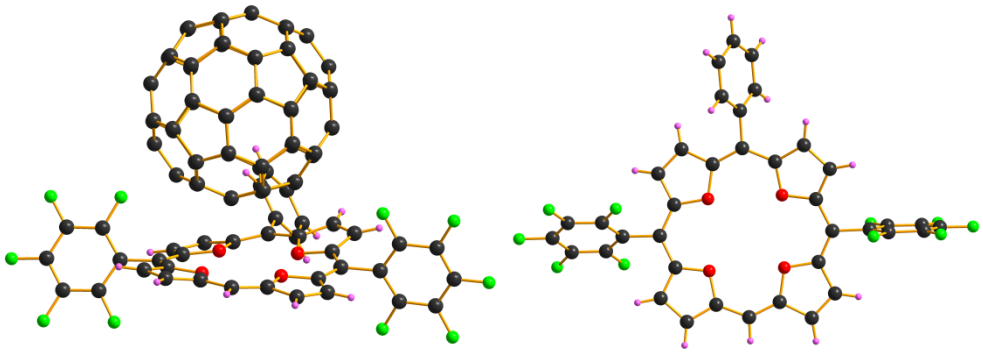
S14: MALDI TOF-TOF mass spectrum of **4.C_{60}** cocrystals revealed two different m/z vales corresponding to the dimer **4** and the **C_{60}**-fullerene.



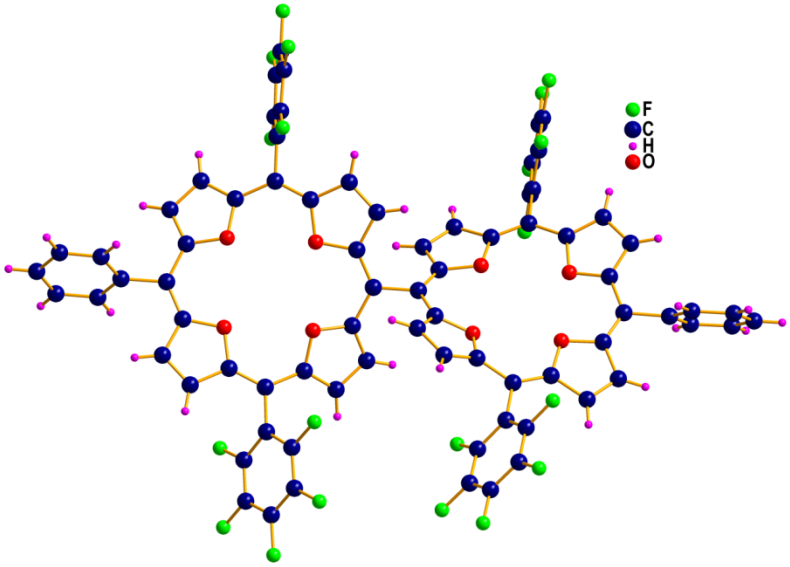
S15: Cyclic (black) and Differential Pulse (red) voltammograms of **4** in dichloromethane containing 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte recorded at a 50 mV s^{-1} scan rate.



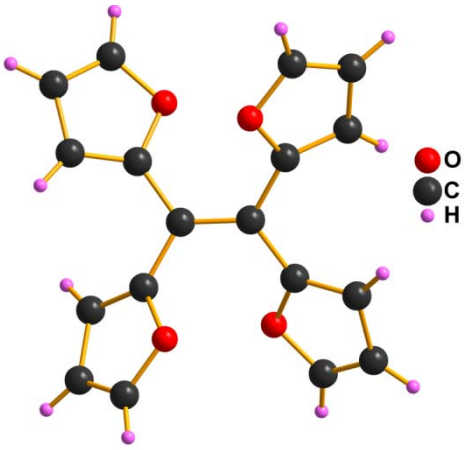
S16: Cyclic (black) and Differential Pulse (red) voltammograms of **3** in dichloromethane containing 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte recorded at a 50 mV s^{-1} scan rate.



S17: Molecular structure of isophlorin **3** along with C_{60} side view (left) and isophlorin **3** without C_{60} top view (right).



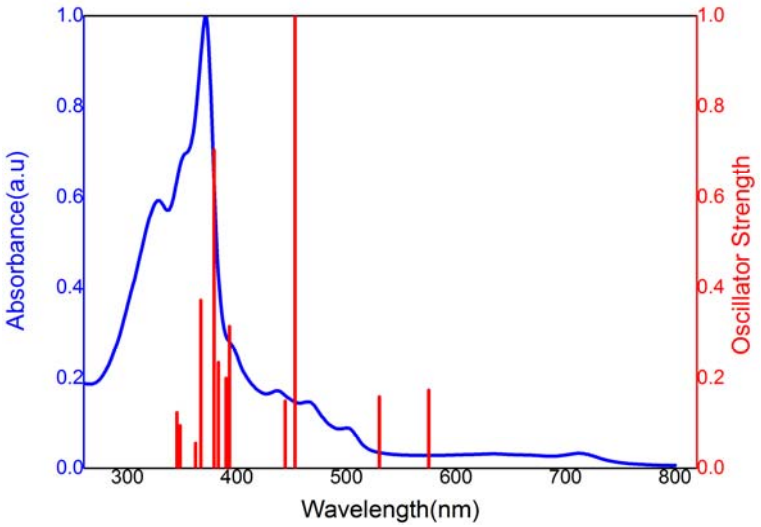
S18: Molecular structure of **4** (C_{60} has omitted for clarity).



S19: Molecular structure of **7.**

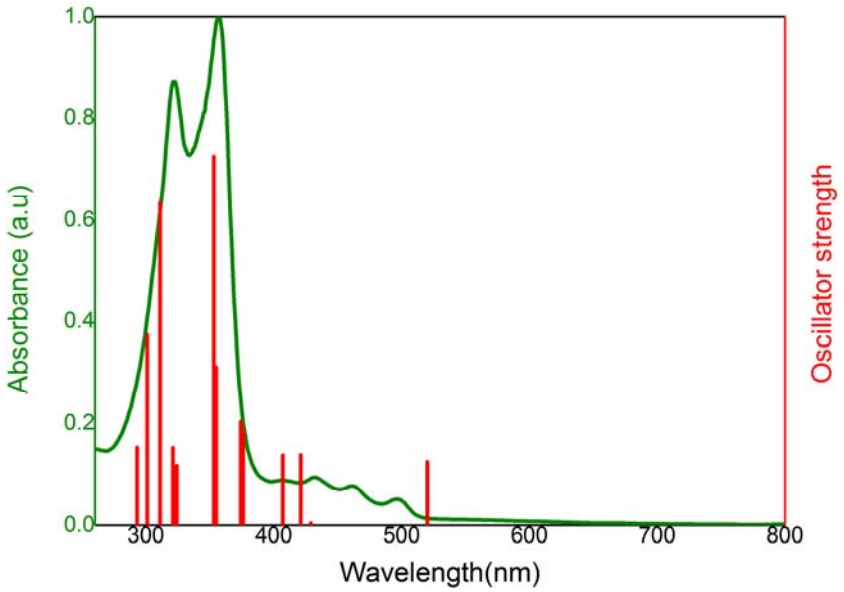
Density Functional Theory (DFT) Calculations

Quantum mechanical calculations were performed with the Gaussian09 [2] program suite using a High Performance Computing Cluster facility of IISER PUNE. All calculations were carried out by Density functional theory (DFT) with Becke's three-parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP) and 6-31G(d,p) basis set for all the atoms were employed in the calculations. The molecular structures obtained from single crystal analysis were used for geometry optimization. To verify the optimized structures frequency calculations were performed where no imaginary frequency was found. To simulate the steady-state absorption spectra, the time-dependent TD-DFT calculations were employed on the optimized structures. Molecular orbital contributions were determined using GaussSum 2.2.Program package. The global ring centres for the NICS (0) values were designated at the non weighted mean centres of the macrocycles. The NICS (0) value was obtained with gauge independent atomic orbital (GIAO) method based on the optimized geometries.



Energy (cm-1)	Wavelength (nm)	Osc. Strength(f)	Major contribtions
12402.47312	806.2908021	0.2584	H-1->L+1 (80%), HOMO->LUMO (19%)
17362.01056	575.97016	0.1731	HOMO->L+2 (89%)
18840.43504	530.7733064	0.1584	H-2->L+1 (15%), H-1->L+2 (32%), HOMO->L+3 (45%)
22038.44544	453.752513	1.0239	H-2->LUMO (65%), H-1->L+3 (15%)
22501.41088	444.416577	0.1489	H-4->LUMO (14%), H-3->LUMO (47%), H-2->L+1 (32%)
25431.64336	393.2109246	0.3142	H-5->L+1 (11%), H-4->LUMO (17%), H-1->L+6 (11%), HOMO->L+7 (33%)
25592.95536	390.7325223	0.1997	H-4->L+1 (41%), H-1->L+7 (12%), HOMO->L+6 (37%)
26062.37328	383.6949111	0.2338	H-5->L+1 (69%), HOMO->L+7 (14%)
26374.512	379.1539347	0.7043	H-4->L+1 (36%), HOMO->L+6 (31%)
27189.94416	367.7830282	0.3715	H-4->LUMO (19%), H-2->L+1 (10%), HOMO->L+7 (39%)
28984.54016	345.0115111	0.1238	H-1->L+11 (17%), HOMO->L+12 (49%)

S20: Selected TD-DFT (B3LYP/6-31G(d,p)) calculated energies, oscillator strengths and compositions of the major electronic transitions of **4.**



Energy (cm-1)	Wavelength (nm)	Osc. Strength(f)	Major contributions
19203.38704	520.7414702	0.1254	H-1->LUMO (24%), HOMO->L+1 (76%)
23724.15584	421.5113097	0.1386	H-1->LUMO (13%), HOMO->L+3 (82%)
24513.77808	407.9338553	0.1381	H-2->LUMO (76%), HOMO->L+8 (19%)
26529.37152	376.9407049	0.1851	H-1->LUMO (10%), HOMO->L+4 (17%), HOMO->L+5 (37%), HOMO->L+6 (30%)
26672.9392	374.9118132	0.2028	H-1->LUMO (10%), HOMO->L+4 (16%), HOMO->L+5 (29%), HOMO->L+6 (38%)
28090.87168	355.9875291	0.3102	H-1->LUMO (13%), HOMO->L+6 (16%), HOMO->L+7 (55%)
28274.76736	353.6722291	0.7255	H-1->LUMO (26%), HOMO->L+1 (10%), HOMO->L+6 (13%), HOMO->L+7 (38%)
30852.53312	324.1224946	0.1177	H-6->LUMO (17%), H-5->LUMO (73%)
31074.33712	321.8089564	0.1524	H-6->LUMO (75%), H-5->LUMO (16%)
32139.80288	311.1406762	0.634	H-2->LUMO (12%), H-1->L+1 (16%), HOMO->L+8 (44%), HOMO->L+10 (15%)
33179.45872	301.3912941	0.3735	H-1->L+1 (21%), HOMO->L+8 (19%), HOMO->L+10 (31%)
34102.96992	293.2295933	0.1531	H-8->LUMO (88%)

S21: Selected TD-DFT (B3LYP/6-31G(d,p)) calculated energies, oscillator strengths and compositions of the major electronic transitions of **3.**

Macrocycle	NICS(0) ppm	Huckel 4nπ rule
3	30.38	Antiaromatic
4	12.90	Antiaromatic

S22 : Computational parameters to classify ring current effects in 20π monomer **3** and dimer **4** determined from NICS calculations.

S23: Coordinates for optimized structure **4**

S.No	Atom	X	Y	Z
1	F	2.288559	4.874536	-5.277896
2	F	-1.021558	1.624292	-4.247163
3	F	-2.288211	6.640844	3.996436
4	F	2.198476	4.128401	-7.857957
5	F	0.526639	2.120162	-8.657909
6	F	-1.082388	0.881465	-6.829419
7	F	-3.060217	7.30466	6.489551
8	F	0.485054	3.225055	5.786365
9	F	-2.094211	5.928506	8.639818
10	F	-0.323226	3.882951	8.263925
11	C	0.502259	7.491671	-0.378679
12	C	0.675311	3.649096	-3.216036
13	C	1.703648	0.652857	-1.367751
14	H	2.186289	-0.294806	-1.180454
15	O	0.568069	5.368131	-1.541187
16	C	-0.803707	4.555515	7.211389
17	C	0.631315	6.98535	0.969999
18	C	0.518647	8.977923	-0.519673
19	C	0.103311	0.734201	0.624676
20	C	-0.373708	1.495032	1.660743
21	C	0.023562	7.161524	-2.847608
22	H	-0.227621	8.175748	-3.118191
23	C	0.219147	5.659068	2.691155
24	C	0.424142	4.939308	-2.843254
25	C	-0.354498	9.781739	0.235204
26	H	-1.046278	9.309827	0.925505
27	C	0.777859	1.257356	-0.550058
28	C	1.162684	7.598955	2.085803
29	H	1.672811	8.550021	2.096119
30	C	-0.348041	11.167326	0.093792
31	H	-1.038517	11.770153	0.676438
32	C	1.012653	2.561891	-2.312273
33	C	0.899334	6.75159	3.184954
34	H	1.166856	6.91529	4.218258
35	C	1.853193	1.4888	-2.500704
36	H	2.489844	1.325419	-3.357451
37	C	-0.617829	3.299585	2.956698
38	C	-0.209166	2.25307	-5.10817
39	C	-1.360786	2.220984	3.557666
40	H	-1.945006	2.305709	4.461511
41	C	-1.216982	1.128552	2.767035
42	H	-1.65448	0.151263	2.903024

43	C	0.631315	3.284161	-4.655135
44	C	0.537147	11.78052	-0.796691
45	H	0.543506	12.861272	-0.902746
46	C	-0.418915	4.574974	3.411817
47	C	1.410901	9.608556	-1.403405
48	H	2.113113	9.00297	-1.96776
49	C	1.43941	3.894579	-5.624891
50	C	-0.872903	4.905681	4.78851
51	C	1.417517	10.996826	-1.542788
52	H	2.119277	11.465039	-2.22685
53	C	1.407219	3.518787	-6.966368
54	C	0.563788	2.490347	-7.375874
55	C	-0.251896	1.858692	-6.43977
56	C	-2.188304	6.305963	6.306906
57	C	-1.778795	5.952134	5.025696
58	C	-0.397894	4.226264	5.920008
59	C	-1.700584	5.601838	7.406354
60	O	0.366657	2.439177	-1.11292
61	O	-0.062372	2.837453	1.78475
62	O	0.072437	5.783421	1.334839
63	C	0.041786	6.070589	-3.65096
64	H	-0.192071	6.024519	-4.703684
65	C	0.371221	6.738942	-1.514875
66	F	-2.288559	-4.874536	-5.277896
67	F	1.021558	-1.624292	-4.247163
68	F	2.288211	-6.640844	3.996436
69	F	-2.198476	-4.128401	-7.857957
70	F	-0.526639	-2.120162	-8.657909
71	F	1.082388	-0.881465	-6.829419
72	F	3.060217	-7.30466	6.489551
73	F	-0.485054	-3.225055	5.786365
74	F	2.094211	-5.928506	8.639818
75	F	0.323226	-3.882951	8.263925
76	C	-0.502259	-7.491671	-0.378679
77	C	-0.675311	-3.649096	-3.216036
78	C	-1.703648	-0.652857	-1.367751
79	H	-2.186289	0.294806	-1.180454
80	O	-0.568069	-5.368131	-1.541187
81	C	0.803707	-4.555515	7.211389
82	C	-0.631315	-6.98535	0.969999
83	C	-0.518647	-8.977923	-0.519673
84	C	-0.103311	-0.734201	0.624676
85	C	0.373708	-1.495032	1.660743
86	C	-0.023562	-7.161524	-2.847608
87	H	0.227621	-8.175748	-3.118191

88	C	-0.219147	-5.659068	2.691155
89	C	-0.424142	-4.939308	-2.843254
90	C	0.354498	-9.781739	0.235204
91	H	1.046278	-9.309827	0.925505
92	C	-0.777859	-1.257356	-0.550058
93	C	-1.162684	-7.598955	2.085803
94	H	-1.672811	-8.550021	2.096119
95	C	0.348041	-11.167326	0.093792
96	H	1.038517	-11.770153	0.676438
97	C	-1.012653	-2.561891	-2.312273
98	C	-0.899334	-6.75159	3.184954
99	H	-1.166856	-6.91529	4.218258
100	C	-1.853193	-1.4888	-2.500704
101	H	-2.489844	-1.325419	-3.357451
102	C	0.617829	-3.299585	2.956698
103	C	0.209166	-2.25307	-5.10817
104	C	1.360786	-2.220984	3.557666
105	H	1.945006	-2.305709	4.461511
106	C	1.216982	-1.128552	2.767035
107	H	1.65448	-0.151263	2.903024
108	C	-0.631315	-3.284161	-4.655135
109	C	-0.537147	-11.78052	-0.796691
110	H	-0.543506	-12.861272	-0.902746
111	C	0.418915	-4.574974	3.411817
112	C	-1.410901	-9.608556	-1.403405
113	H	-2.113113	-9.00297	-1.96776
114	C	-1.43941	-3.894579	-5.624891
115	C	0.872903	-4.905681	4.78851
116	C	-1.417517	-10.996826	-1.542788
117	H	-2.119277	-11.465039	-2.22685
118	C	-1.407219	-3.518787	-6.966368
119	C	-0.563788	-2.490347	-7.375874
120	C	0.251896	-1.858692	-6.43977
121	C	2.188304	-6.305963	6.306906
122	C	1.778795	-5.952134	5.025696
123	C	0.397894	-4.226264	5.920008
124	C	1.700584	-5.601838	7.406354
125	O	-0.366657	-2.439177	-1.11292
126	O	0.062372	-2.837453	1.78475
127	O	-0.072437	-5.783421	1.334839
128	C	-0.041786	-6.070589	-3.65096
129	H	0.192071	-6.024519	-4.703684
130	C	-0.371221	-6.738942	-1.514875

S24: Coordinates for optimized structure **3**

S.No	Atom	X	Y	Z
1	C	18.000297	25.694128	7.294408
2	C	19.012874	25.851606	8.236299
3	C	19.333499	24.796794	9.088704
4	C	18.634442	23.59761	8.992216
5	C	17.32223	24.479766	7.208124
6	C	17.609889	23.401286	8.054764
7	C	16.901993	22.093683	7.951322
8	C	17.735352	20.985993	7.528252
9	C	18.96176	21.03377	6.901237
10	H	19.473735	21.927018	6.577773
11	C	19.400556	19.698488	6.763965
12	H	20.319986	19.353149	6.317789
13	C	18.421367	18.896026	7.311538
14	C	18.438504	17.459856	7.477106
15	C	17.389628	16.612469	7.702311
16	C	17.446581	15.197053	7.972257
17	H	18.361053	14.634101	8.076431
18	C	16.178536	14.741338	8.08573
19	H	15.859287	13.73405	8.304912
20	C	15.289414	15.86152	7.895512
21	C	13.920388	15.844423	7.894777
22	C	13.008798	16.959349	7.800141
23	C	11.641078	16.951789	7.604261
24	H	11.032857	16.081375	7.412795
25	C	11.208725	18.291936	7.710981
26	H	10.199494	18.667809	7.623155
27	C	12.331977	19.054434	7.954511
28	C	12.413242	20.456844	8.204682
29	H	11.445954	20.928155	8.348903
30	C	13.468284	21.303576	8.296833
31	C	13.432693	22.703286	8.632491
32	H	12.529835	23.246758	8.874915
33	C	14.701283	23.172308	8.597659
34	H	15.04046	24.174393	8.810467
35	C	15.560282	22.076556	8.206269
36	C	13.261523	14.509651	8.001858
37	C	12.495471	14.159849	9.122498
38	C	11.849836	12.930962	9.226019
39	C	11.965469	12.003512	8.192628
40	C	12.721683	12.314868	7.066204
41	C	13.349803	13.555576	6.980092
42	C	19.796798	16.838697	7.349444

43	C	20.071373	15.912958	6.330565
44	H	19.289202	15.658505	5.621851
45	C	21.335905	15.333367	6.214812
46	H	21.530836	14.622456	5.417143
47	C	22.346977	15.673224	7.113635
48	H	23.331396	15.223485	7.023954
49	C	22.088245	16.599543	8.127239
50	H	22.869556	16.867175	8.83262
51	C	20.827112	17.181246	8.241037
52	H	20.628914	17.901087	9.029024
53	F	16.363306	24.368975	6.277326
54	F	17.69331	26.70219	6.469042
55	F	19.672215	27.009803	8.326096
56	F	20.300073	24.948785	10.001816
57	F	18.962502	22.612817	9.837671
58	F	14.060269	13.817241	5.874255
59	F	12.831147	11.427775	6.069845
60	F	11.355814	10.818659	8.28432
61	F	11.132105	12.629291	10.314594
62	F	12.371519	15.018921	10.141687
63	O	14.785663	20.946591	8.065523
64	O	13.438199	18.243385	7.998524
65	O	16.05249	16.99276	7.696239
66	O	17.390305	19.682515	7.770988

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