Electronic Supplementary Information

3,6-Fluoren[5]arenes: synthesis, structure and complexation with fullerenes C_{60} and C_{70}

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1. Materials and methods

Compound **1** was prepared according to literature procedure.[S1] Other reagents were commercially available and used as received. Flash column chromatography was performed on 100-200 mesh silica gel. NMR spectra were recorded on the Brucker® Avance III 500 MHz NMR spectrometers. The ionization methods used in high-resolution mass spectrometry were electrospray ionization (ESI) and matrix-assisted laser desorption/ ionization (MALDI). The fluorescence spectra were recorded on HITACHI® F-7000 Fluorescence Spectrometer at room temperature.

2. Experimental procedure for 2-6

Compound **2**: A mixture of 2,7-dihydroxyfluorene (1.00 g, 5.00 mmol), K_2CO_3 (3.46 g, 25.00 mmol) and 1-bromobutane (1.64 g, 12.00 mmol) were dissolved in acetonitrile (100mL). The mixture was stirred at 80 °C in oil bath for 12 h and then quenched with water. The organic layer was separated, washed with brine three times, and dried with anhydrous $MgSO_4$. The organic layer was evaporated and then purified by flash column chromatography on silica gel (dichloromethane/*n*-hexane, 1:1, v/v) to afford compound **2** as a white solid (1.52 g, 98 %), m.p.: 68 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, J = 8.1 Hz, 2H), 6.86 (dd, J = 8.2, 2.4 Hz, 2H), 4.05 (t, J = 6.5 Hz, 4H), 3.75 (s, 2H), 1.86-1.77 (m, 4H) 1.58-1.51 (m, 4H) 1.00 (t, J = 7.4 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.7, 143.0, 136.3, 125.5, 113.9, 105.5, 68.1, 35.4, 31.5, 19.3, 13.9; ESI-HRMS(*m/z*): $[M+H]^+$ calcd. for $C_{21}H_{27}O_2$, 311.2011; found: 311.2003.

Compound **3**: To a solution of 3,6-dimethoxyfluorene **1** (1.13 g 5.00 mmol) in anhydrous THF (50 mL) at -78 °C, *n*-butyllithium (4.8 mL 12 mmol; 2.5 M in hexane) was added dropwise under N_2 atmosphere. The mixture was stirred at -78 °C for 30 min, and 1-bromobutane (1.51 g, 11 mmol) was added dropwise to the mixture. The solution was allowed to warm to room temperature and stirred for 4 h and then quenched with water. The organic layer was separated, washed with brine three times, and dried with anhydrous $MgSO_4$. The organic layer was evaporated and then purified by flash column chromatography on silica gel (dichloromethane/*n*-hexane, 1:2, v/v) to afford compound **3** as a colorless oil (1.52 g, 90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21 (d, J = 5.1 Hz, 2H), 7.19 (s, 2H), 6.86 (dd, J = 8.3, 2.2 Hz, 2H), 3.89 (s, 6H), 1.93-1.88 (m, 4H), 1.08 (h, J = 7.3 Hz, 4H), 0.68 (t, J = 7.4 Hz, 6H), 0.66-0.58 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.0, 143.7, 142.1, 123.4, 113.3, 104.6, 55.5, 53.7, 40.2, 26.0, 23.1, 13.9; ESI-HRMS(*m/z*): $[M+H]^+$ calcd. for $C_{23}H_{20}O_2$, 339.2324; found: 339.2316.

Compound **4**: To a solution of 3,6-dimethoxyfluorene **1** (1.37 g, 6.05 mmol) and paraformaldehyde (0.91 g, 30.25 mmol) in anhydrous CH_2Cl_2 (500 mL) was added $BF_3 \cdot Et_2O$ (1 mL) in dropwise. The mixture was stirred at room temperature for 2 min and then quenched with saturated $NaHCO_3$ solution. The organic layer was separated, washed with brine three times, and dried with anhydrous $MgSO_4$. The organic layer was evaporated and then purified by flash column chromatography on silica gel (dichloromethane/*n*-hexane, 2:1, v/v) to afford compound **4** as a white solid (1.01 g, 73 %), m.p.: > 300 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 (s, 10H), 7.07 (s, 10H), 4.06 (s, 10H), 3.94 (s, 30H), 3.55 (s, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.1, 141.1, 136.1, 128.2, 126.5, 101.7, 56.0, 35.8, 30.1; MALDI-TOF-HRMS(*m/z*): $[M]^+$ calcd. for $C_{80}H_{70}O_{10}$, 1190.4969; found, 1190.4958.

Compound **5**: To a solution of **2** (1.00 g, 3.22 mmol) and paraformaldehyde (0.48 g, 16.10 mmol) in anhydrous CH_2Cl_2 (300 mL) was added $BF_3 \cdot Et_2O$ (0.5 mL) in dropwise. The mixture was stirred at room temperature for 2 min and then quenched with saturated $NaHCO_3$ solution. The organic layer was separated, washed with brine three times, and dried with anhydrous $MgSO_4$. The organic layer was evaporated and then purified by flash column chromatography on silica gel (dichloromethane/*n*-hexane, 2:1, v/v) to afford compound **5** as a white solid (0.74 g, 71 %), m.p.: 264 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.20 (s, 10H), 7.09 (s, 10H), 4.10-4.05 (m, 30H), 3.53 (s, 10H), 1.82-1.75 (m, 20H), 1.52-1.44 (m, 20H), 0.94 (t, J = 7.4 Hz, 30H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.6, 141.0, 135.8, 128.6, 126.5, 102.6, 68.3, 35.7, 31.7, 27.1, 19.5, 14.0; MADLI-TOF-HRMS(*m/z*): $[M]^+$ calcd. for $C_{110}H_{130}O_{10}$, 1611.9698; found: 1611.9684.

Compound **6**: To a solution of **3** (1.00 g, 3.22 mmol) and paraformaldehyde (0.48 g, 16.10 mmol) in anhydrous CH_2Cl_2 (300 mL) was added $BF_3 \cdot Et_2O$ (0.5 mL) in dropwise. The mixture was stirred at room temperature for 2 min and then quenched with saturated $NaHCO_3$ solution. The organic layer was separated, washed with brine three times, and dried with anhydrous $MgSO_4$. The organic layer was evaporated and then purified by flash column chromatography on silica gel (dichloromethane/*n*-hexane, 2:1, v/v) to afford compound **6** as a white solid (0.74 g, 71 %), m.p.: 184 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.12 (s, 10H), 6.92 (s, 10H), 4.03 (s, 30H), 3.88 (s, 10H), 1.74-1.64 (m, 20H), 1.47 (m, 20H), 0.98-0.88 (t, 30H), 0.64-0.52 (m, 50H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.6, 141.0, 135.8, 128.6, 126.5, 102.6, 68.3, 35.7, 31.7, 27.1, 19.5, 14.0; MALDI-TOF-HRMS(*m/z*): $[M]^+$ calcd. for $C_{120}H_{150}O_{10}$, 1752.1263; found: 1752.1234.

3. NMR spectra of 2-6

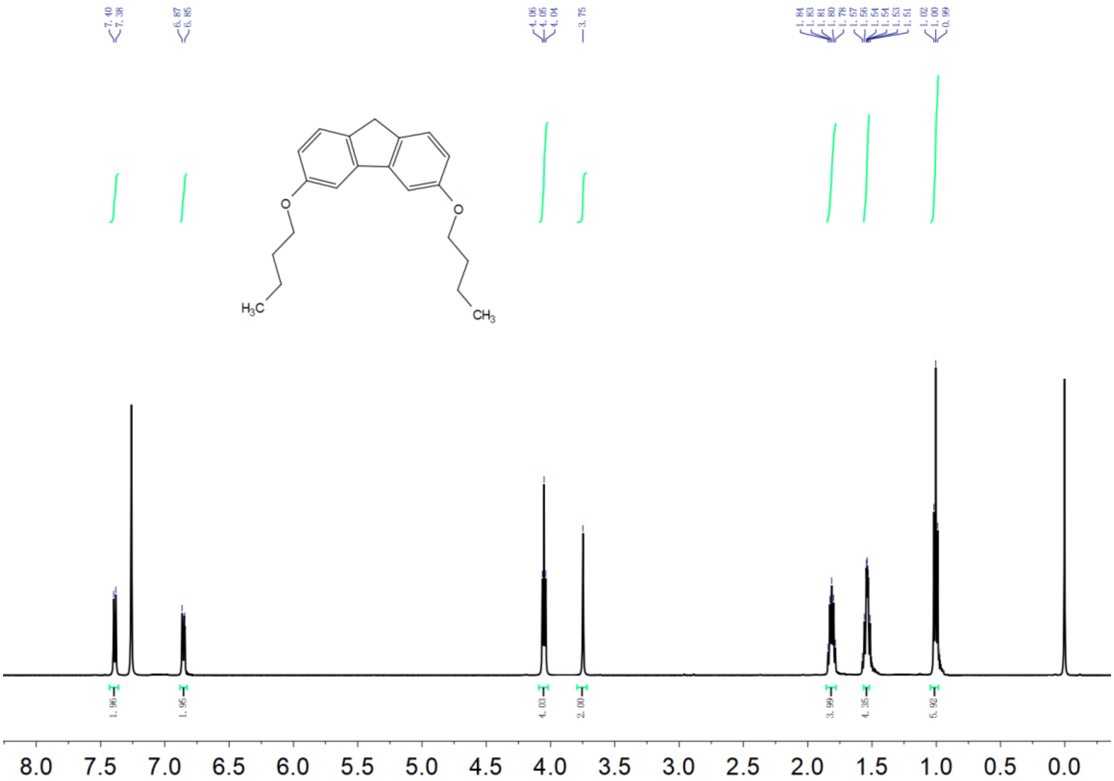


Fig. S1 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **2**.

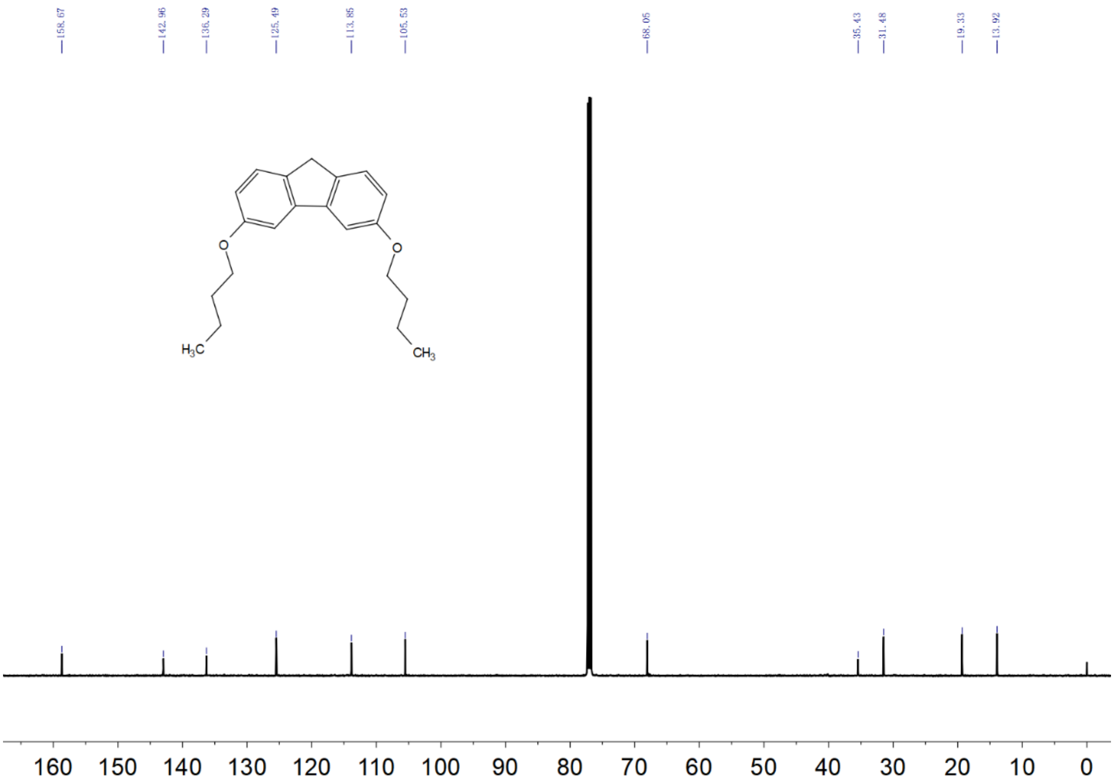


Fig. S2 ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **2**.

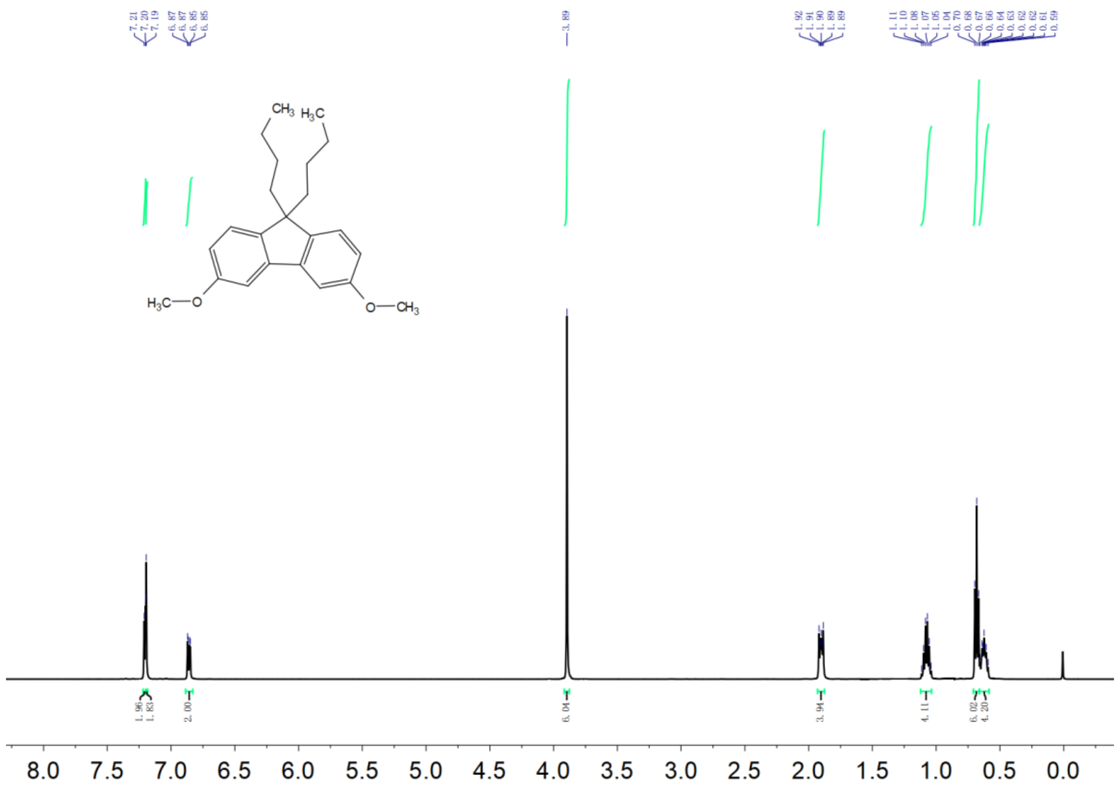


Fig. S3 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **3**.

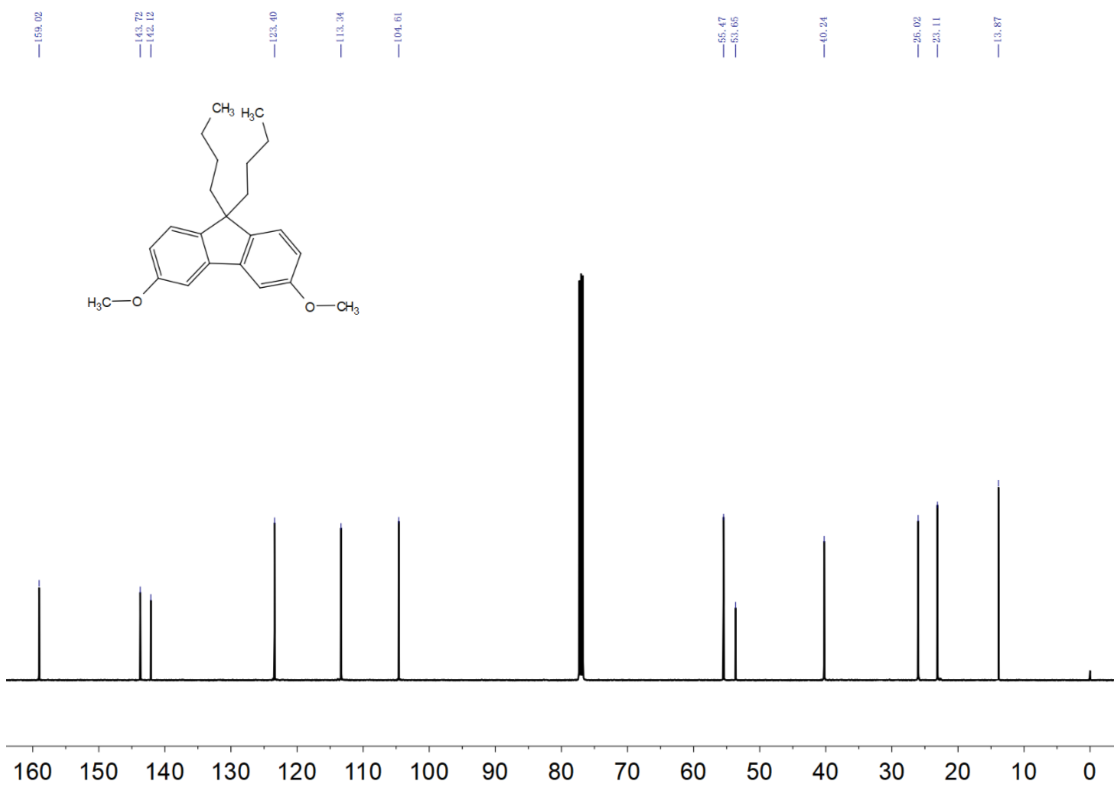


Fig. S4 ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **3**.

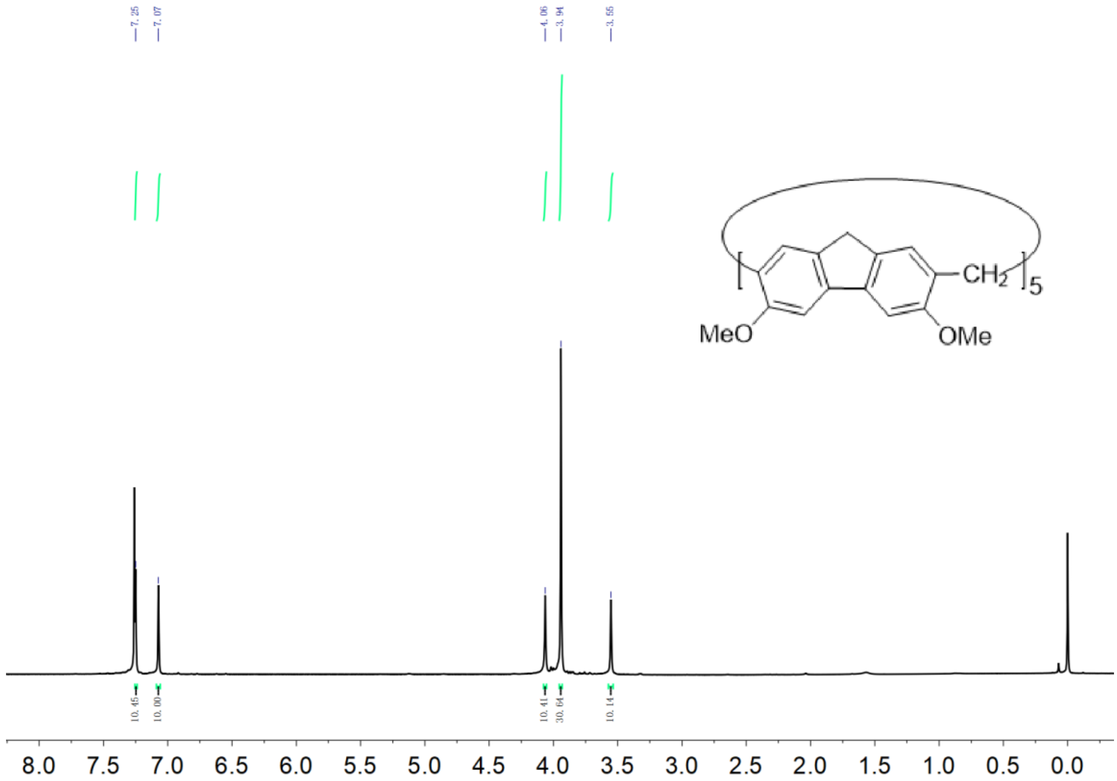


Fig. S5 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **4**.

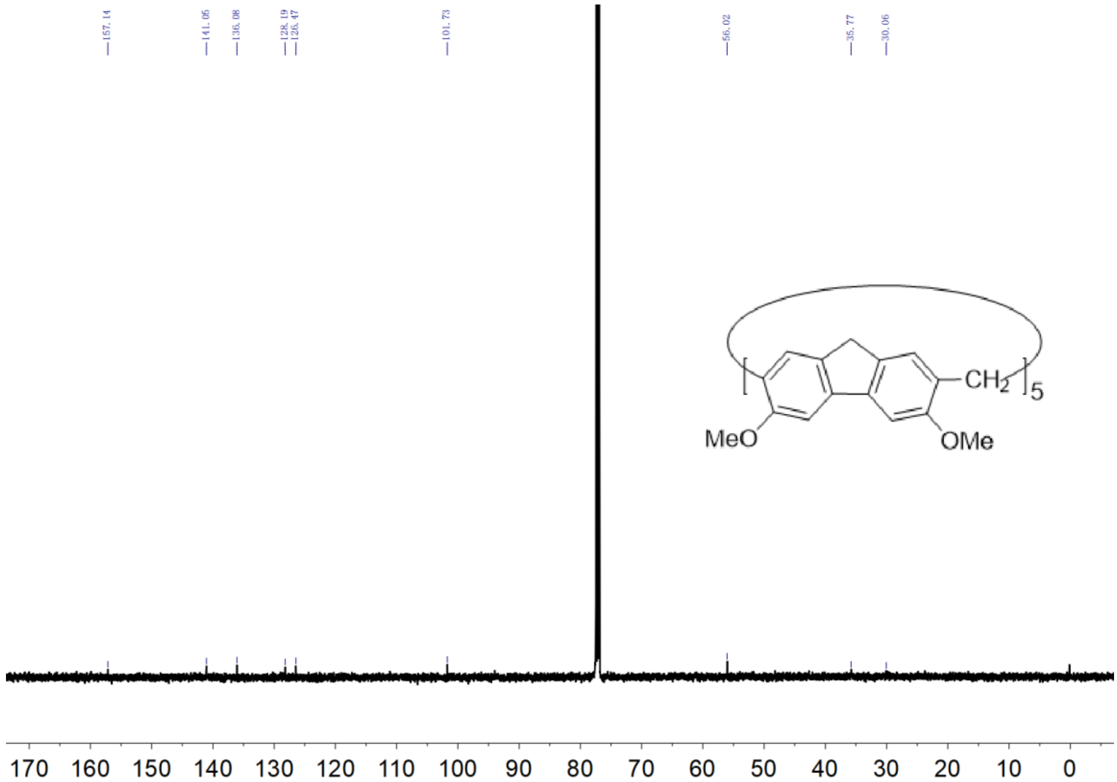


Fig. S6 ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **4**.

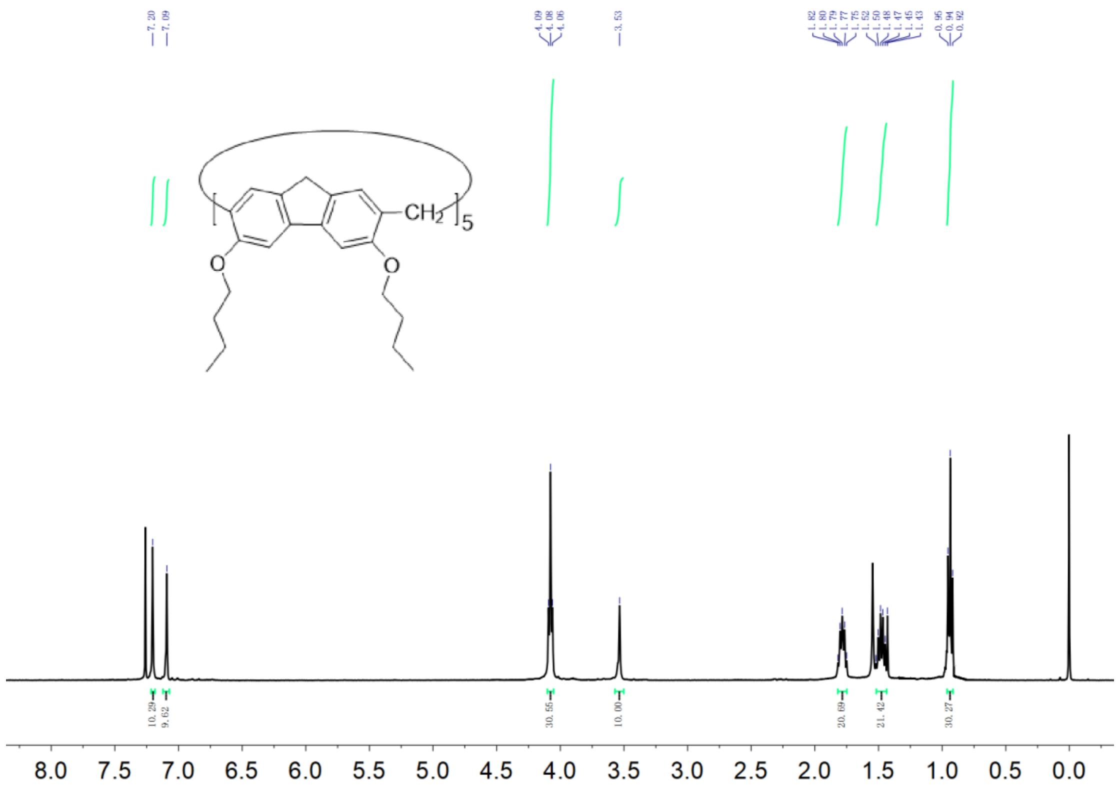


Fig. S7 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **5**.

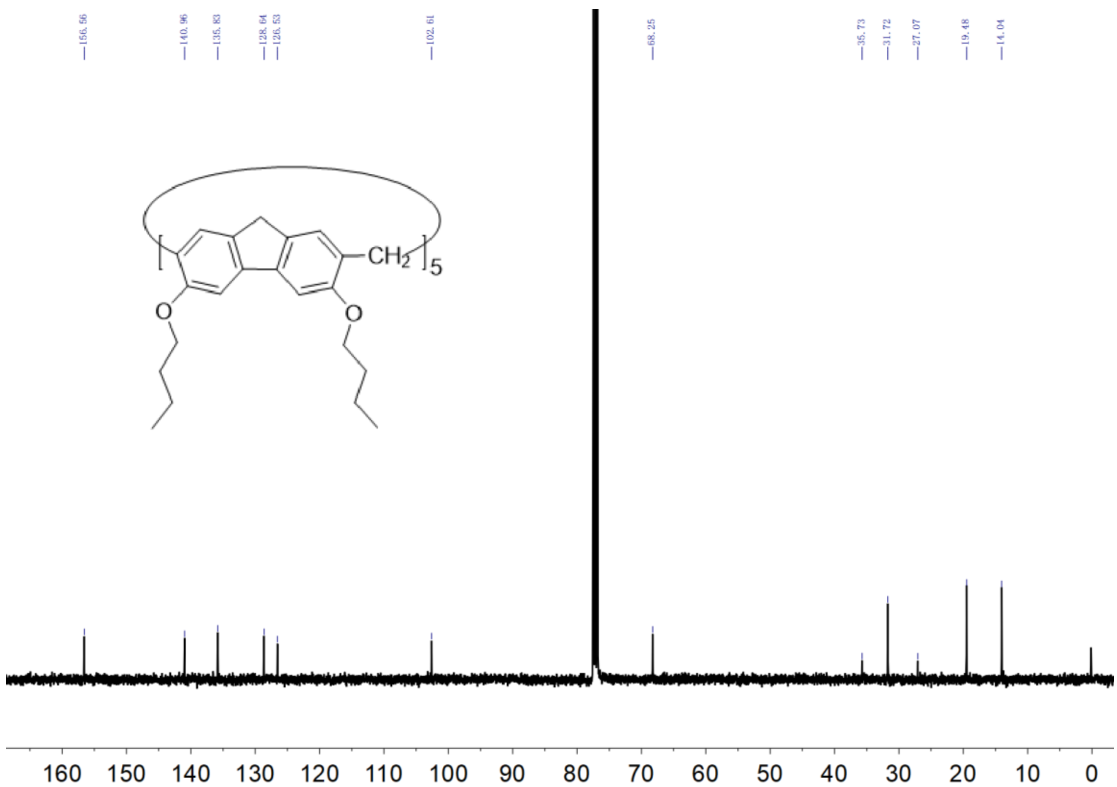


Fig. S8 ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **5**.

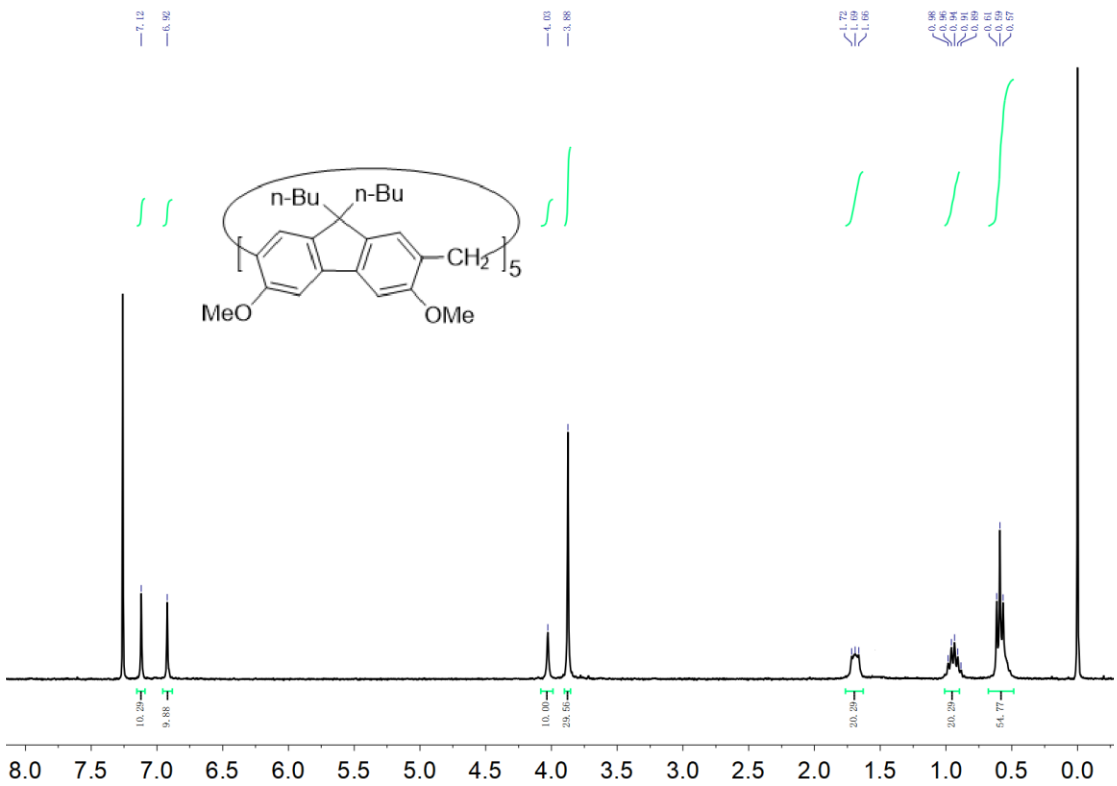


Fig. S9 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **6**.

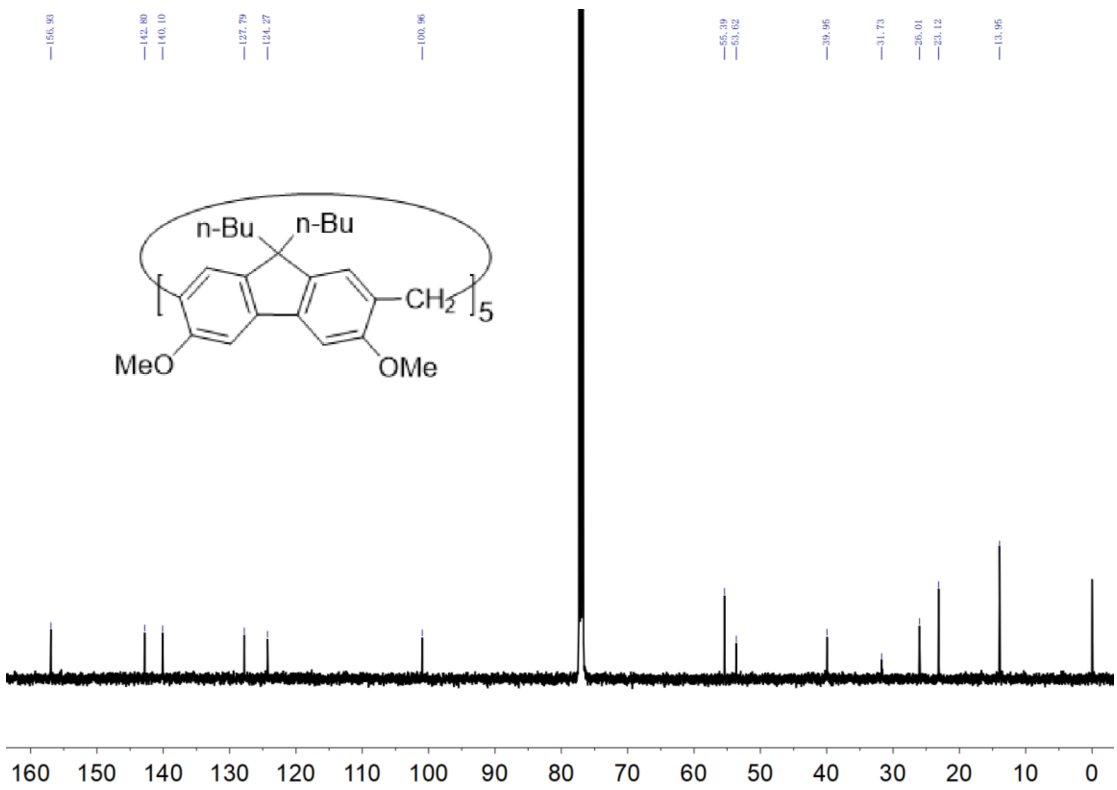


Fig. S10 ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **6**.

4. Variable-temperature ^{1}H NMR spectra of 5

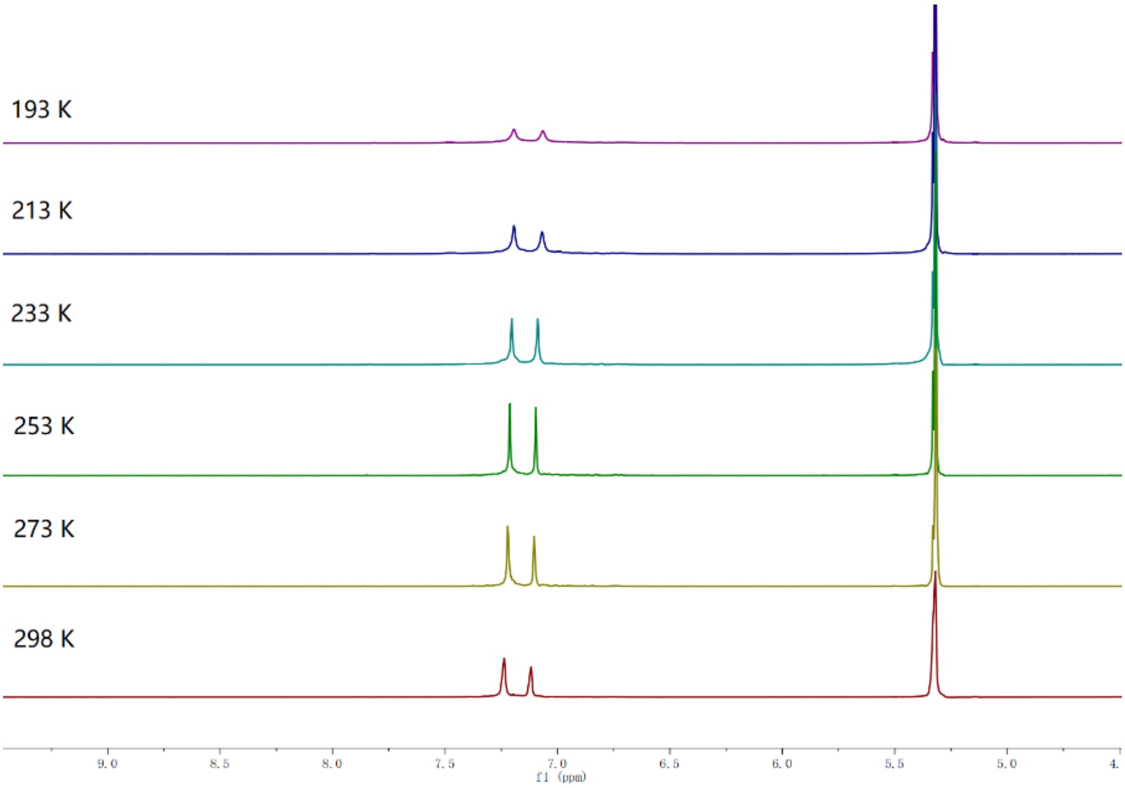


Fig. S11 Truncated variable-temperature ^{1}H NMR spectra of **5** (CD_2Cl_2, 500 MHz, 298 K-193 K).

5. Color change of C_{60}@5

Fig. S12 Solution of C_{60} (left), C_{60} mixed with one equivalent of **5** (mid) and **5** (right), 1.0×10^{-3} M in toluene.

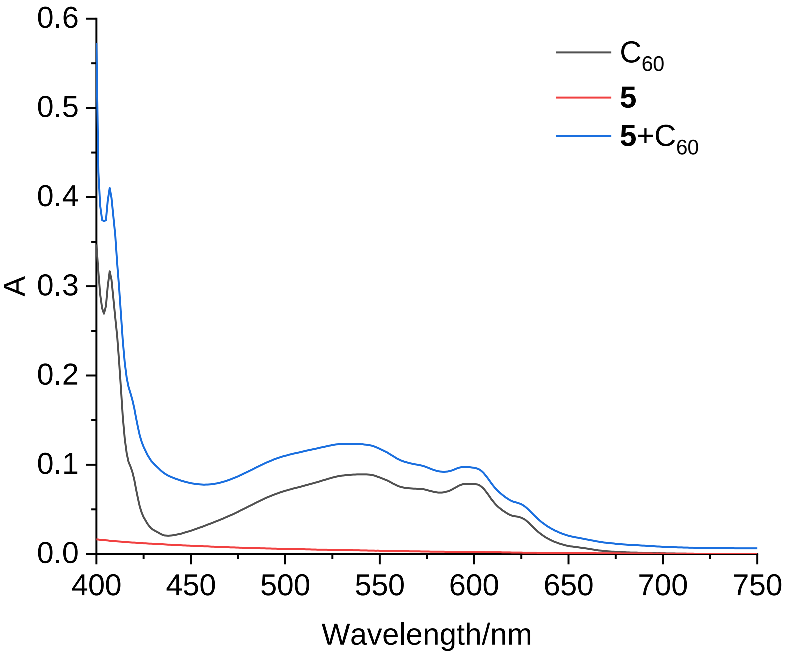


Fig. S13 UV/Vis spectra of **5** and C_{60} (1.0×10^{-4} M) in the absence and presence of 1.0 eq. **5** in toluene at 298K.

6. Determination of the association constants by fluorescence titration experiments

Job's plot. A solution of fullerene in toluene (1.0×10^{-5} M) and a solution of **5** in toluene (1.0×10^{-5} M) were mixed in a different ratio to prepare 11 samples. The emission spectra (λ_{ex} = 330 nm) were measured for each sample, and the emission at 343 nm was monitored.

Fluorescence titration. Data were fitted by using the following equation:

$F_0/F_{cal} = 1+K_a[G]$

Here, F_0, F_{cal}, K_a, [G] are fluorescence intensity of host before the addition of guest, calibrated fluorescence intensity, the association constant and concentration of guest, respectively.[S2]

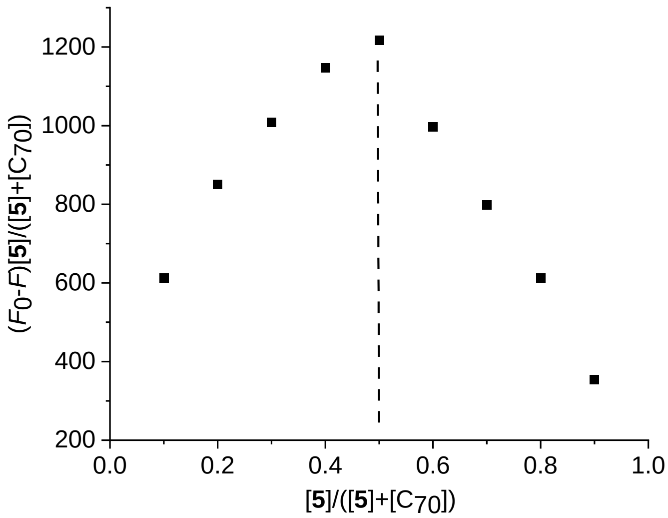


Fig. S14 Job's plot of **5** and C_{70} in toluene, 298 K, [**5**] + [C_{70}] = 1.0×10^{-5} M.

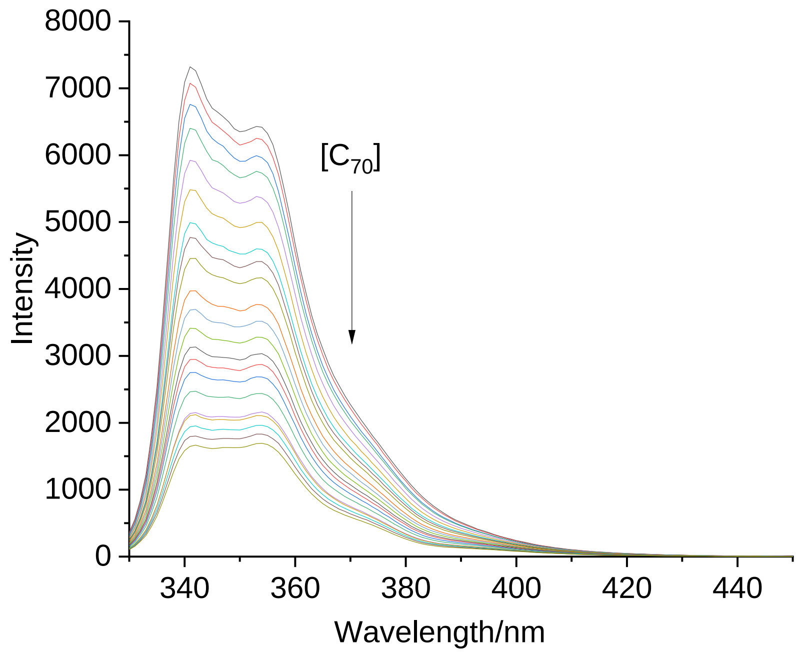


Fig. S15 Emission spectra (λ_{ex} = 330 nm) of **5** (1.0×10^{-5} M) in the presence of C_{70} in toluene, [C_{70}] from top to bottom are 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0 ($\times$ 10^{-5} M), 298 K.

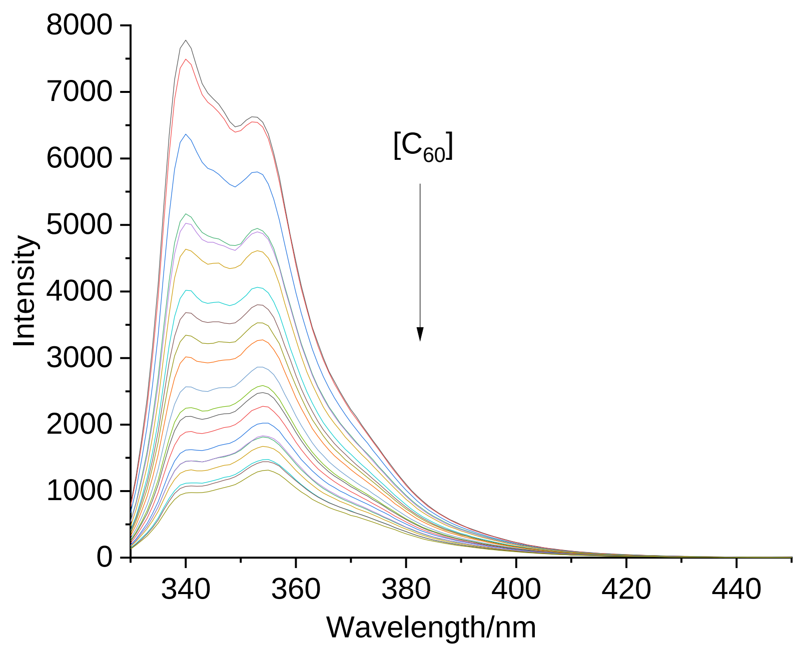


Fig. S16 Emission spectra (λ_{ex} = 330 nm) of **4** (1.0×10^{-5} M) in the presence of C_{60} in toluene, [C_{60}] from top to bottom are 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0 ($\times10^{-5}$ M), 298 K.

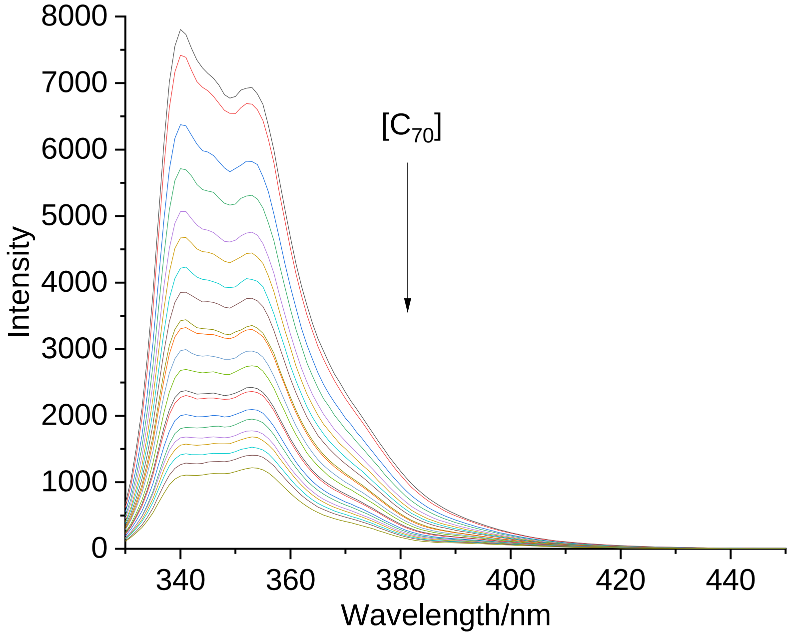


Fig. S17 Emission spectra (λ_{ex} = 330 nm) of **4** (1.0×10^{-5} M) in the presence of C_{70} in toluene, [C_{70}] from top to bottom are 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0 ($\times10^{-5}$ M), 298 K.

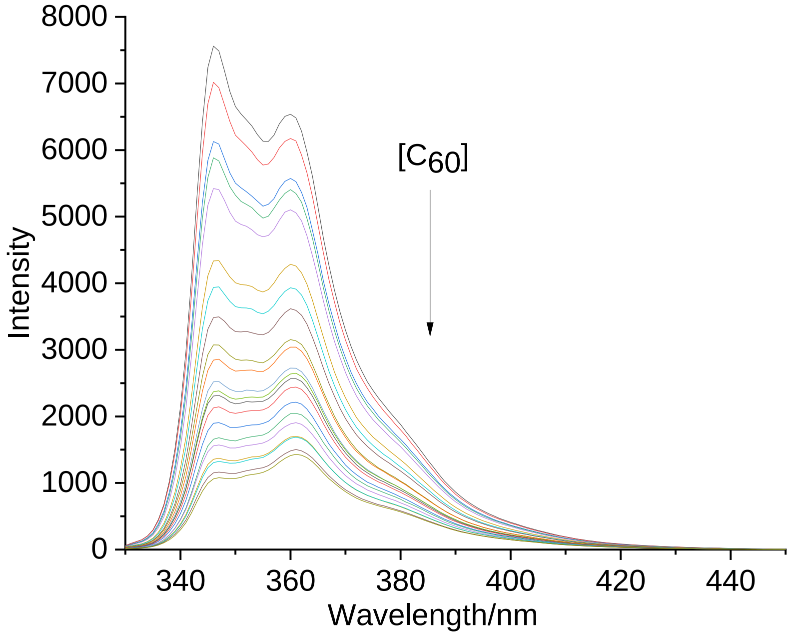


Fig. S18 Emission spectra (λ_{ex} = 330 nm) of **6** (1.0×10^{-5} M) in the presence of C_{60} in toluene, [C_{60}] from top to bottom are 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0 ($\times10^{-5}$ M), 298 K.

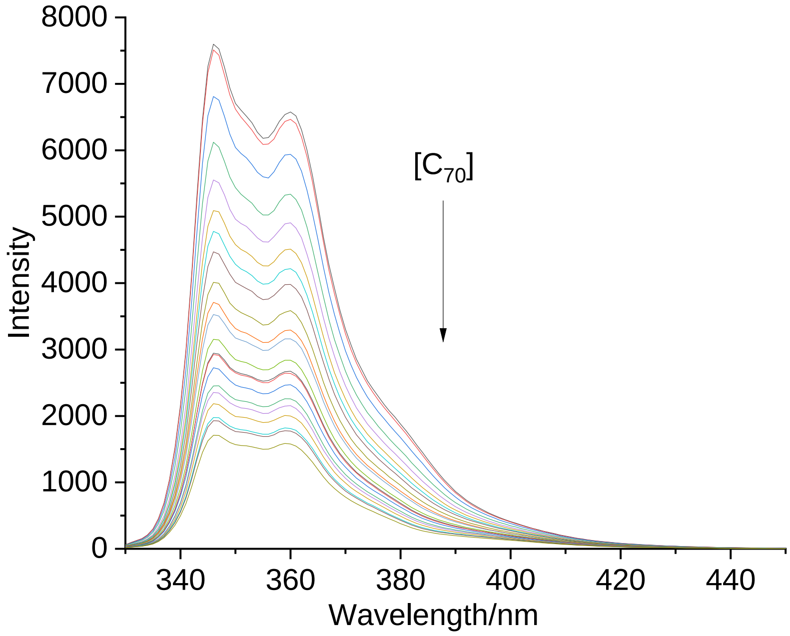


Fig. S19 Emission spectra (λ_{ex} = 330 nm) of **6** (1.0×10^{-5} M) in the presence of C_{70} in toluene, [C_{70}] from top to bottom are 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0 ($\times10^{-5}$ M), 298 K.

7. NMR studies of complexation between 5 with fullerenes C_{60} and C_{70}

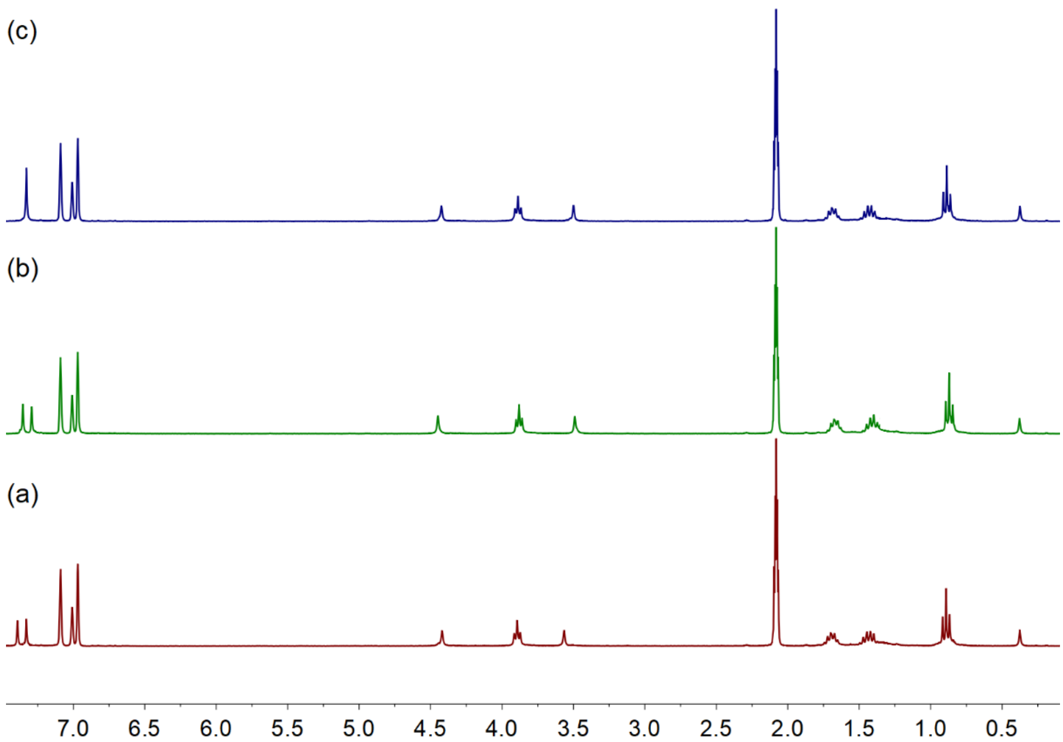


Fig. S20 [1]H NMR spectra (300 MHz, d_8-toluene, 298K) of (a) **5** with 1.0 equiv. of C_{60}, (b) free **5** and (c) **5** with 1.0 equiv. of C_{70}, [**5**]$_0$ = 1.0 mM.

8. Crystallographic data of 6

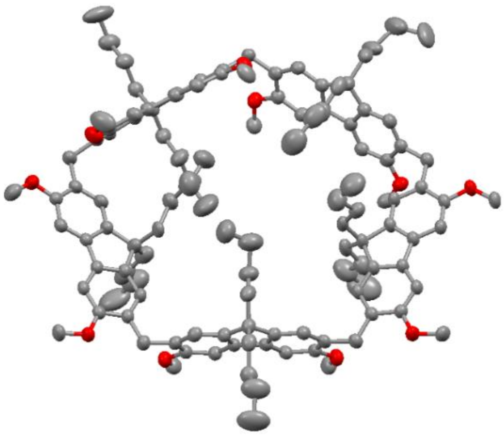


Fig. S21 ORTEP view (the thermal ellipsoids are displayed at a 50% probability) of **6**. Solvent molecules and hydrogen atoms were omitted for clarity.

Table S2. Crystal data and structure refinement for **6** (CCDC 2044335).

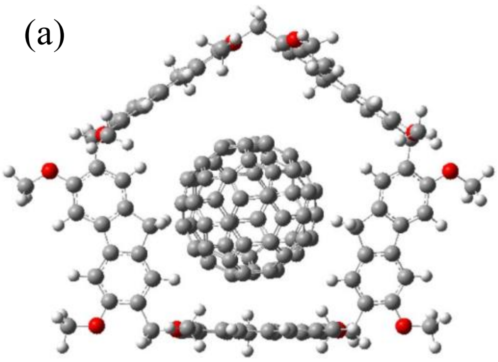
Empirical formula	$C_{123}H_{153}Cl_9O_{10}$
Formula weight	2110.49
Temperature/K	169.99(11)
Crystal system	triclinic
Space group	P-1
a/Å	12.9917(4)
b/Å	21.9009(5)
c/Å	22.5682(3)
α/°	95.436(2)
β/°	95.461(2)
γ/°	92.331(2)
Volume/Å^3	6355.4(3)
Z	2
ρ_{calc}g/cm^3	1.103
μ/mm^{-1}	2.214
F(000)	2248.0
Crystal size/mm^3	0.22 × 0.14 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.378 to 151.74
Index ranges	$-16 \le h \le 16, -27 \le k \le 27, -27 \le l \le 27$
Reflections collected	93801
Independent reflections	25361 [R_{int} = 0.0670, R_{sigma} = 0.0598]
Data/restraints/parameters	25361/543/1457
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0930, wR_2 = 0.2534
Final R indexes [all data]	R_1 = 0.1256, wR_2 = 0.2809

Largest diff. peak/hole / e Å^{-3}	0.73/-0.75
Empirical formula	$C_{123}H_{153}Cl_9O_{10}$
Formula weight	2110.49
Temperature/K	169.99(11)
Crystal system	triclinic
Space group	P-1

9. Calculations of complexation between 4 with fullerenes C_{60} and C_{70}

Calculations were performed with the Gaussian 09 program.[S3] Geometry optimizations of all stationary points were performed with the B3LYP-D3 functional,[S4-S5] which has been proven to be suitable to describe the dispersion effects. The 6-31G(d) basis set was applied for all elements. Frequency calculations at the same level were performed to confirm each stationary point to be a minimum structure.

(a)



(b)

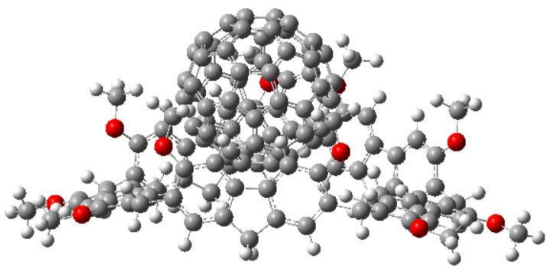


Fig. S22 (a) Top view and (b) side view of optimized structure of C_{60}@**4**.

The atomic coordinates of C_{60}@**4**:

C	-6.77038548	-2.98358315	-3.02235774
C	-6.73199944	-3.42977519	-1.67895848
C	-5.74043923	-4.30814145	-1.23258301
C	-4.76880008	-4.74139107	-2.14014908
C	-4.78637615	-4.30618063	-3.47585860
C	-5.78484091	-3.43673832	-3.90523985
C	-3.62363117	-5.64080230	-1.95621412
C	-2.93567652	-5.74578127	-3.17677521
C	-3.62681163	-4.91474799	-4.23951528
C	-3.18650225	-6.34123268	-0.82973338
C	-2.04005147	-7.13846647	-0.92928482
C	-1.31564260	-7.23344436	-2.14213639
C	-1.79560190	-6.53686533	-3.25771373
O	-7.72883735	-2.94201021	-0.87759540
O	-1.55502521	-7.88039758	0.11288087
C	-7.86120024	-2.04101637	-3.47646166

C	-5.62904631	5.83723453	-1.29385533
C	-7.00280272	5.85902738	-1.63595742
C	-7.67428859	4.70489681	-2.04689170
C	-6.96058560	3.50351041	-2.11279342
C	-5.59929792	3.46246080	-1.77141483
C	-4.94415647	4.62276836	-1.36847637
C	-7.38639627	2.15286625	-2.50118973
C	-6.28615692	1.28738344	-2.39015041
C	-5.06603941	2.05240453	-1.92038863
C	-8.62862632	1.67198493	-2.92742048
C	-8.75139957	0.31451671	-3.23577944
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C	-6.42708778	-0.06338447	-2.69422716
O	-7.60003460	7.09087592	-1.53319135
O	-9.91791573	-0.26072431	-3.67522428
C	-4.96997164	7.14286769	-0.86655041
C	1.23873240	-7.24729891	-2.12631034
C	1.96151624	-7.17672085	-0.91089539
C	3.11071998	-6.38522165	-0.79578222
C	3.55539166	-5.67118480	-1.91078106
C	2.87380563	-5.75922772	-3.13621451
C	1.72783082	-6.53993525	-3.23105096
C	4.70513329	-4.77431327	-2.07827723
C	4.73752532	-4.33218144	-3.41158918
C	3.57836681	-4.92537786	-4.18771639
C	5.66779939	-4.34686346	-1.15857962
C	6.66810759	-3.47100422	-1.59104857
C	6.72833357	-3.02792831	-2.93452109
C	5.74821597	-3.47126461	-3.82858069
O	1.47290143	-7.93564717	0.11727459
O	7.65345462	-2.98483646	-0.77446940
C	7.83605972	-2.10123159	-3.38054247
C	-0.04230422	-8.06615054	-2.24172372
C	7.63010436	-0.62425752	-3.06924084
C	8.72183163	0.26177439	-3.23501833
C	8.60077890	1.62952958	-2.97574928
C	7.36304860	2.12389383	-2.55149117
C	6.26644623	1.26105997	-2.39395762
C	6.40564980	-0.09998338	-2.64966625
C	6.93928939	3.48708074	-2.20657706
C	5.58289157	3.45550793	-1.84537093
C	5.05089346	2.04038062	-1.93688479
C	7.65073756	4.69157787	-2.19256610
C	6.98240839	5.85778630	-1.81130373

C	5.61423744	5.84467868	-1.44740713
C	4.93089787	4.62738551	-1.47250926
O	9.88333918	-0.32860195	-3.66762764
O	7.57786514	7.09372432	-1.75952089
C	4.95895139	7.16159680	-1.04955758
C	3.48273866	7.09055455	-0.73357586
C	3.03861520	6.71601871	0.55724684
C	1.67586325	6.63809149	0.86348101
C	0.74448525	6.93824469	-0.13542585
C	1.16670918	7.31681163	-1.42138483
C	2.52550034	7.38951519	-1.70848657
C	-0.72384982	6.93357639	-0.10849852
C	-1.19516323	7.31081907	-1.37778115
C	-0.03168793	7.58932035	-2.30726470
C	-1.61598613	6.62595063	0.92318796
C	-2.98974231	6.69633051	0.66758232
C	-3.48306388	7.07304301	-0.60454068
C	-2.56382234	7.37774883	-1.61389263
O	4.03453013	6.44406468	1.45692419
O	-3.94943773	6.41418485	1.60301078
C	8.94505569	7.19844490	-2.11276956
C	11.02870058	0.48538964	-3.84189303
C	7.63047981	-3.33946455	0.59683851
C	2.16813015	-7.93750845	1.35023327
C	-2.25826015	-7.86689620	1.34101999
C	-7.73781902	-3.31078883	0.48983156
C	-11.06815074	0.55581217	-3.79757539
C	-8.97201113	7.20447963	-1.86465573
C	-3.53789400	6.06214820	2.91220614
C	3.67456974	6.06683660	2.77416855
H	-5.71946989	-4.64933978	-0.20438832
H	-5.81293101	-3.09456163	-4.93752862
H	-2.96362563	-4.14800362	-4.66273230
H	-3.96753538	-5.52860873	-5.08467468
H	-3.73175099	-6.26892612	0.10371424
H	-1.25960317	-6.62564413	-4.19983211
H	-7.97129456	-2.12511318	-4.56572061
H	-8.81962168	-2.36159988	-3.05746995
H	-8.72532103	4.73394866	-2.30976837
H	-3.88975560	4.59775735	-1.11059403
H	-4.67192905	1.65825031	-0.97372859
H	-4.24082030	1.99733233	-2.64375966
H	-9.47483292	2.34299667	-3.01681229
H	-5.58193530	-0.73930087	-2.60298108

H	-5.15804052	7.89239858	-1.64450467
H	-5.48471803	7.51325726	0.02659678
H	3.65377677	-6.33016155	0.14002178
H	1.19407450	-6.61186483	-4.17585315
H	2.92464644	-4.14951870	-4.60904217
H	3.91909672	-5.53563340	-5.03545796
H	5.63381240	-4.69017382	-0.13143889
H	5.79100757	-3.12814474	-4.86005483
H	8.78061391	-2.41515557	-2.92614483
H	7.97770851	-2.21505326	-4.46337163
H	-0.03934206	-8.56656028	-3.21699413
H	-0.05118186	-8.83887648	-1.47323184
H	9.44455488	2.29790316	-3.10132570
H	5.56275077	-0.77296212	-2.52287182
H	4.66929965	1.67974685	-0.97212329
H	4.21680686	1.95808834	-2.64743387
H	8.69782529	4.71366105	-2.47139978
H	3.88058390	4.60856203	-1.19829457
H	5.50098668	7.56883341	-0.18898041
H	5.11397669	7.88269151	-1.86102411
H	1.34323769	6.34975847	1.85360333
H	2.86561173	7.67925815	-2.70030524
H	-0.04666774	6.94086110	-3.19390692
H	-0.04107749	8.62255195	-2.68069918
H	-1.24549484	6.33414393	1.89875724
H	-2.94204398	7.66828439	-2.59158924
H	9.20621138	8.25249232	-2.00385024
H	9.58323969	6.59920712	-1.45013877
H	9.12167299	6.88900162	-3.15130904
H	11.82522627	-0.18068009	-4.17800279
H	10.86427071	1.26159323	-4.60085420
H	11.33316197	0.96587430	-2.90279854
H	8.47546480	-2.82369400	1.05556180
H	6.70150814	-3.01398183	1.08309616
H	7.74837140	-4.42170968	0.74018370
H	1.62282681	-8.62322638	2.00100984
H	3.20029372	-8.29493254	1.23668651
H	2.18327555	-6.94130079	1.81088351
H	-1.71561070	-8.54196354	2.00497551
H	-2.27949628	-6.86446801	1.78781027
H	-3.28884930	-8.22813857	1.22540192
H	-8.59138092	-2.79728967	0.93498514
H	-7.86126898	-4.39417313	0.61908232
H	-6.81933194	-2.99302267	1.00020693

H	-11.86891684	-0.09940721	-4.14476685
H	-11.35682021	0.99889386	-2.83538526
H	-10.91964588	1.36108989	-4.52904960
H	-9.23366658	8.25354141	-1.71602381
H	-9.16182002	6.93060628	-2.91080852
H	-9.60028449	6.58136644	-1.21470446
H	-4.45434080	5.90461451	3.48314567
H	-2.94728061	5.13700614	2.91932482
H	-2.95258741	6.86285825	3.38313581
H	4.61268180	5.91613105	3.31067561
H	3.09333460	6.85054594	3.27757442
H	3.10014521	5.13151479	2.78632035
C	-2.88370400	-2.18665567	1.37620225
C	-2.88226591	-2.79848445	2.69473767
C	-1.90579703	-3.73921624	3.02648808
C	-0.89058753	-4.10811577	2.05325704
C	-0.89053431	-3.51809677	0.78845024
C	-1.90690372	-2.53869648	0.44379143
C	-3.27265222	-1.78495086	3.66096563
C	-1.27994485	-3.70478793	4.33793591
C	0.36271780	-4.29989029	2.76426843
C	0.36143144	-3.09996129	0.18096494
C	-1.28305226	-1.51508276	-0.37762080
C	-3.27493381	-0.79487167	1.52801650
C	1.56481122	-3.28661060	0.86123587
C	1.56536329	-3.89796425	2.18003193
C	2.57544668	-2.24251980	0.85033602
C	2.57618158	-3.23140266	2.98421909
C	-2.67231009	-1.75278156	4.92071716
C	0.12213017	-4.05148120	4.17575346
C	3.20116778	-2.20813563	2.16200476
C	1.09317363	-3.41162107	4.94757391
C	-1.65530270	-2.73207579	5.26553518
C	0.11884813	-1.86211574	-0.53993724
C	-1.65925843	-0.17954683	-0.23344050
C	-2.28890180	-0.48097853	5.51068179
C	-2.67475133	0.18804067	0.73957783
C	-3.51485951	-0.54667837	2.93963793
C	-0.64889756	0.86531541	-0.24397152
C	-2.29043747	1.45915030	1.33062751
C	-3.14702957	0.67443398	3.50662345
C	2.34482090	-2.99336067	4.33962805
C	1.08882837	-0.85943772	-0.55075653
C	-0.64393763	-2.06600871	6.06911879

C	-1.03925118	1.87774894	0.72235904
C	-2.52367006	1.69834314	2.68536787
C	-2.52189709	0.70792608	4.81811332
C	-1.51136714	1.75265707	4.80749317
C	-1.03557497	-0.67471757	6.22062266
C	0.70226638	-2.39913948	5.91394264
C	1.71301449	-1.35446724	5.90317034
C	-1.51251342	2.36519890	3.48903534
C	-0.30967335	2.76711746	2.90455313
C	0.94361303	2.57349296	3.61559498
C	-0.06867373	2.51927377	1.49293873
C	2.34207451	-1.05344433	0.15875447
C	1.33669252	-0.01864349	6.04792836
C	0.69694944	0.53177301	-0.39881401
C	1.70734747	1.19815710	0.40493875
C	-0.06529764	0.32806489	6.21023284
C	2.72815784	-1.72201084	4.93012358
C	3.32813125	-0.73936572	4.14155413
C	-0.30800803	1.56626453	5.48905146
C	0.94415914	1.98489815	4.88124352
C	1.33284778	2.17216870	1.33108003
C	1.95936048	2.20554429	2.64234645
C	1.96056476	1.00501993	5.22619037
C	2.72442565	0.21820342	0.75012232

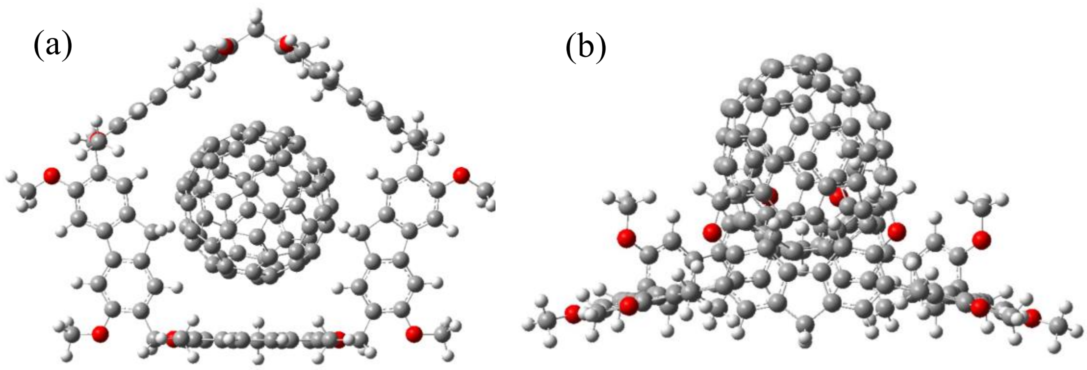

Fig. S23 (a) Top view and (b) side view of optimized structure of C_{70}@**4**.

The atomic coordinates of C_{70}@**4**:

C	-6.745306	-2.633424	-3.438546
C	-6.716079	-3.208061	-2.144852
C	-5.728708	-4.128541	-1.780417
C	-4.747768	-4.468142	-2.717213
C	-4.747777	-3.893525	-3.999544

C	-5.746276	-2.989918	-4.350382
C	-3.608481	-5.387852	-2.616935
C	-2.900686	-5.358334	-3.830396
C	-3.574520	-4.414160	-4.806007
C	-3.194836	-6.216436	-1.571540
C	-2.050631	-7.005384	-1.742408
C	-1.303191	-6.961774	-2.944154
C	-1.760727	-6.139107	-3.980525
O	-7.718398	-2.800884	-1.305907
O	-1.591313	-7.868338	-0.784993
C	-7.843077	-1.665552	-3.816410
C	-5.579598	6.109109	-1.317907
C	-6.945375	6.156466	-1.687897
C	-7.619778	5.023016	-2.148838
C	-6.917729	3.816103	-2.235439
C	-5.565066	3.749452	-1.865455
C	-4.906342	4.889714	-1.414781
C	-7.348331	2.482846	-2.674867
C	-6.260491	1.601725	-2.564637
C	-5.044648	2.337701	-2.040349
C	-8.584747	2.030375	-3.146859
C	-8.712842	0.686040	-3.504952
C	-7.629463	-0.218369	-3.391270
C	-6.406961	0.263357	-2.918206
O	-7.532237	7.390974	-1.559256
O	-9.873001	0.137715	-3.992816
C	-4.915918	7.392905	-0.834812
C	1.250363	-6.971554	-2.945696
C	1.948753	-6.954623	-1.713983
C	3.096991	-6.172878	-1.541567
C	3.563366	-5.410257	-2.614980
C	2.905476	-5.442048	-3.855949
C	1.761645	-6.217339	-4.008474
C	4.716168	-4.507905	-2.719395
C	4.772527	-4.003123	-4.029390
C	3.629111	-4.560322	-4.854118
C	5.662401	-4.126209	-1.763207
C	6.670886	-3.232666	-2.135835
C	6.753046	-2.723066	-3.454460
C	5.789317	-3.122136	-4.386081
O	1.434589	-7.753388	-0.729129
O	7.644449	-2.789915	-1.281561
C	7.867878	-1.775275	-3.833195
C	-0.029014	-7.781555	-3.118729

C	7.666424	-0.320855	-3.426880
C	8.772227	0.560803	-3.490427
C	8.655376	1.907679	-3.137320
C	7.408359	2.385775	-2.722207
C	6.297554	1.528463	-2.666663
C	6.432579	0.187607	-3.014682
C	6.987841	3.725575	-2.293108
C	5.619401	3.686386	-1.981596
C	5.074584	2.289411	-2.197479
C	7.712441	4.915521	-2.166194
C	7.045043	6.059568	-1.721901
C	5.665509	6.038556	-1.404241
C	4.968978	4.836545	-1.543559
O	9.942976	-0.011042	-3.923012
O	7.652175	7.280119	-1.559732
C	5.013627	7.331767	-0.930902
C	3.534024	7.252127	-0.634368
C	3.074828	6.792076	0.623181
C	1.708863	6.710383	0.913198
C	0.789311	7.090290	-0.069320
C	1.226514	7.551014	-1.323001
C	2.588446	7.628877	-1.593536
C	-0.679128	7.101515	-0.053845
C	-1.135428	7.567666	-1.298765
C	0.038813	7.895891	-2.197913
C	-1.583495	6.736965	0.948356
C	-2.954020	6.838797	0.686548
C	-3.432185	7.300543	-0.563064
C	-2.501227	7.662692	-1.542006
O	4.059586	6.444368	1.508777
O	-3.925341	6.507690	1.593392
C	9.031499	7.392095	-1.859604
C	11.103617	0.797171	-3.990177
C	7.596461	-3.205641	0.071807
C	2.130253	-7.849852	0.499506
C	-2.299894	-7.966595	0.436056
C	-7.730736	-3.293353	0.022240
C	-11.011015	0.970458	-4.120371
C	-8.895695	7.529357	-1.915403
C	-3.528990	6.037775	2.870002
C	3.682851	5.964138	2.787441
H	-5.719737	-4.573237	-0.792409
H	-5.765851	-2.546477	-5.343616
H	-2.905343	-3.605014	-5.129204

H	-3.898699	-4.930417	-5.720032
H	-3.758425	-6.251192	-0.647119
H	-1.206564	-6.119952	-4.916009
H	-7.979340	-1.692963	-4.905567
H	-8.792296	-2.007512	-3.393361
H	-8.664261	5.072128	-2.433827
H	-3.857768	4.844318	-1.136979
H	-4.684230	1.914284	-1.093155
H	-4.199556	2.291562	-2.740864
H	-9.421468	2.713432	-3.234241
H	-5.571178	-0.424427	-2.829426
H	-5.091654	8.173638	-1.584170
H	-5.436331	7.731384	0.067955
H	3.620472	-6.158433	-0.593129
H	1.248245	-6.249172	-4.966733
H	2.982203	-3.766383	-5.251636
H	3.986918	-5.130589	-5.722417
H	5.609312	-4.516808	-0.753958
H	5.849799	-2.728905	-5.398610
H	8.807416	-2.122477	-3.393053
H	8.016648	-1.819948	-4.920184
H	-0.030588	-8.201939	-4.131104
H	-0.032671	-8.613860	-2.415181
H	9.509707	2.572718	-3.183270
H	5.579472	-0.482774	-2.965350
H	4.651035	1.863951	-1.277629
H	4.267688	2.272320	-2.943137
H	8.768737	4.943346	-2.407222
H	3.909733	4.812642	-1.306115
H	5.549502	7.679552	-0.041050
H	5.181863	8.102168	-1.693136
H	1.364969	6.359177	1.878792
H	2.940064	7.983854	-2.559830
H	0.025163	7.309119	-3.126536
H	0.043056	8.952121	-2.500385
H	-1.224830	6.379618	1.906308
H	-2.867716	8.019147	-2.502194
H	9.300565	8.431518	-1.663882
H	9.640695	6.736822	-1.223262
H	9.239311	7.158453	-2.912068
H	11.906108	0.145872	-4.340738
H	10.980442	1.628474	-4.696818
H	11.373394	1.204040	-3.006757
H	8.437295	-2.717465	0.566899

H	6.661867	-2.894792	0.556643
H	7.704311	-4.294087	0.168472
H	1.571566	-8.565090	1.105550
H	3.155061	-8.218822	0.359869
H	2.166195	-6.887207	1.025378
H	-1.765176	-8.705581	1.035159
H	-2.316874	-7.010401	0.974859
H	-3.332567	-8.307844	0.283301
H	-8.586050	-2.823195	0.509935
H	-7.854120	-4.384064	0.052094
H	-6.813847	-3.022956	0.562085
H	-11.808366	0.335666	-4.510685
H	-11.322047	1.385410	-3.152641
H	-10.833941	1.797173	-4.820899
H	-9.150279	8.575767	-1.738438
H	-9.066114	7.291275	-2.973586
H	-9.543561	6.892255	-1.299137
H	-4.451870	5.845818	3.419574
H	-2.952423	5.106526	2.798707
H	-2.935340	6.785439	3.412313
H	4.614022	5.754583	3.316184
H	3.109421	6.712259	3.350547
H	3.093712	5.040657	2.716870
C	-0.690430	-1.342188	-1.206389
C	0.613838	-0.704700	-1.211947
C	0.429992	0.695978	-0.877260
C	-0.987820	0.923639	-0.663704
C	-1.680218	-0.335623	-0.867584
C	1.725294	-1.394850	-0.723275
C	2.688185	-0.718949	0.121158
C	2.512439	0.621469	0.441997
C	1.365774	1.344286	-0.067984
C	0.924871	2.234521	0.985207
C	-0.431088	2.453092	1.188627
C	-1.406330	1.790204	0.348822
C	-2.521824	1.430846	1.198794
C	-3.184322	0.225280	1.004136
C	-2.761359	-0.673542	-0.049812
C	-2.891705	-2.020477	0.465807
C	-1.943583	-2.981863	0.142767
C	-0.824965	-2.640245	-0.710539
C	0.329957	-3.347048	-0.198197
C	1.577736	-2.738610	-0.205041
C	-1.482758	-3.908670	1.157455

C	-0.081548	-4.133425	0.946727
C	3.145989	-1.648073	1.134965
C	2.460611	-2.892431	0.934172
C	-3.413287	-1.948355	1.817082
C	-3.594069	-0.564143	2.148510
C	-2.243664	1.890287	2.545031
C	-0.954632	2.521142	2.538683
C	1.808100	2.076526	2.123536
C	2.785779	1.081454	1.789233
C	3.320845	0.211748	2.776820
C	3.507897	-1.207298	2.436991
C	2.119846	-3.730344	2.030046
C	0.797405	-4.376056	2.036274
C	-2.043607	-3.920227	2.463507
C	-3.047139	-2.900695	2.806731
C	-2.712082	1.181414	3.683958
C	-3.413819	-0.094615	3.477550
C	1.337645	2.229218	3.456349
C	-0.099034	2.460240	3.672205
C	3.053649	0.557429	4.128926
C	2.076357	1.552469	4.464376
C	2.728445	-3.416629	3.275345
C	3.413201	-2.172089	3.476068
C	0.185271	-4.658617	3.287356
C	-1.215785	-4.434668	3.498241
C	-0.687581	1.996998	4.879729
C	-1.976423	1.366539	4.885536
C	-3.325849	-1.088417	4.488881
C	-3.144484	-2.472362	4.158069
C	-2.348718	-3.081315	5.205435
C	-1.402084	-4.044579	4.881637
C	0.871058	-4.409627	4.539564
C	2.119236	-3.799808	4.533630
C	3.229204	-1.780135	4.859371
C	3.053492	-0.440481	5.180079
C	1.466600	1.172917	5.723149
C	0.110390	1.391518	5.927521
C	-2.643101	-0.835810	5.742113
C	-1.980863	0.369354	5.937245
C	2.079756	-0.056430	6.180737
C	-0.692103	0.389371	6.597499
C	-2.046554	-2.073257	6.200502
C	-0.111077	-4.041314	5.538148
C	2.438849	-2.794419	5.525614

C	0.189098	-3.067411	6.493312
C	1.493374	-2.429836	6.486996
C	1.309924	-1.029398	6.822544
C	-0.800798	-2.061059	6.832615
C	-0.108034	-0.801464	7.035400

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