

Supporting Information

A Bis-exTTF Macrocyclic Receptor that Associates C₆₀ with Micromolar Affinity

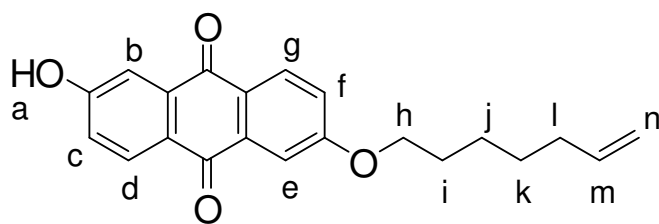
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1. Synthesis and characterization

General. All solvents were dried according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere. Flash chromatography was performed using silica gel (Merck, Kieselgel 60, 230-240 mesh, or Scharlau 60, 230-240 mesh). Analytical thin layer chromatography (TLC) was performed using aluminium-coated Merck Kieselgel 60 F254 plates. Melting points were determined on a Gallenkamp apparatus. NMR spectra were recorded on a Bruker Avance 300 (¹H: 300 MHz; ¹³C: 75 MHz) a Bruker Avance 500 (¹H: 500 MHz; ¹³C: 125 MHz) or a Bruker AvanceIII 700 (¹H: 700 MHz; ¹³C 175 MHz) spectrometers at 298 K, unless otherwise stated, using partially deuterated solvents as internal standards. Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet, b = broad. Electrospray ionization mass spectra (ESI-MS) and Matrix assisted Laser desorption ionization (coupled to a Time-of-Flight analyzer) experiments (MALDI-TOF) were recorded on a HP1100MSD spectrometer and a Bruker REFLEX spectrometer, respectively.

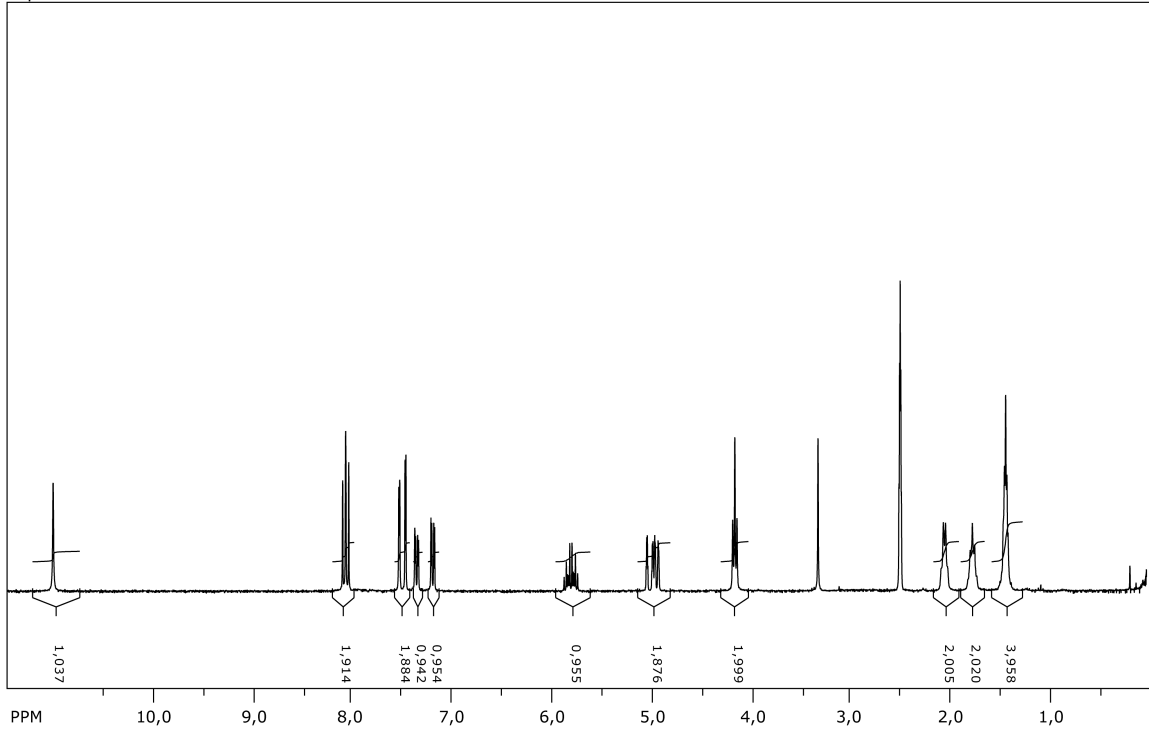


Chemical Formula: $C_{21}H_{20}O_4$
Molecular Weight: 336,38

Anthraflavic acid 3.33 g (12.5 mmol) was dissolved with sonication in 450 mL of dry DMF. Then, 1.73 g (12.5 mmol) of dry K_2CO_3 , 2.21 g (12.5 mmol) of 7-bromo-1-heptene, and a catalytic amount of NaI were added and the mixture heated to reflux for 2 h. The crude reaction was poured into ice-cold 1 M aqueous HCl, and filtrated. The solid was redissolved in CH_2Cl_2 and washed with water (2x), the organic fraction was dried over $MgSO_4$, the solvent evaporated, and the resulting product subjected to column chromatography (CH_2Cl_2 to $CH_2Cl_2:CH_3OH$ 2%) to obtain the pure product as a light yellow solid in 47% yield.

Mp 80-82 °C; 1H NMR (d_6 -DMSO, 300 MHz) δ 11.02 (brs, 1H, H_a), 8.09 (d, $J = 8.5$ Hz, 1H, H_g), 8.06 (d, $J = 8.1$ Hz, 1H, H_d), 7.54 (d, $J = 2.7$ Hz, 1H, H_e), 7.48 (d, $J = 2.7$ Hz, 1H, H_b), 7.36 (dd, $J = 2.7$ Hz, $J = 8.5$ Hz, 1H, H_f), 7.20 (dd, $J = 2.7$ Hz, $J = 8.1$ Hz, 1H, H_c), 5.81 (m, 1H, H_m), 4.98 (m, 2H, H_n), 4.16 (t, $J = 6.7$ Hz, 2H, H_h), 2.04 (m, 2H, H_i), 1.77 (m, 2H, H_i), 1.44 (m, 4H, H_{j+k}). ^{13}C NMR (d_6 -DMSO, 75 MHz) δ 182.26, 181.90, 164.33, 164.09, 139.53, 136.35, 130.71, 130.27, 127.20, 126.07, 121.94, 121.26, 115.68, 113.10, 111.48, 69.22, 33.98, 29.13, 28.81, 25.77. MS m/z : calcd. for $C_{21}H_{19}O_4$ $[M-H^+]$ 335.1 found ESI (neg.) $[M-H^+]$ 335.0.

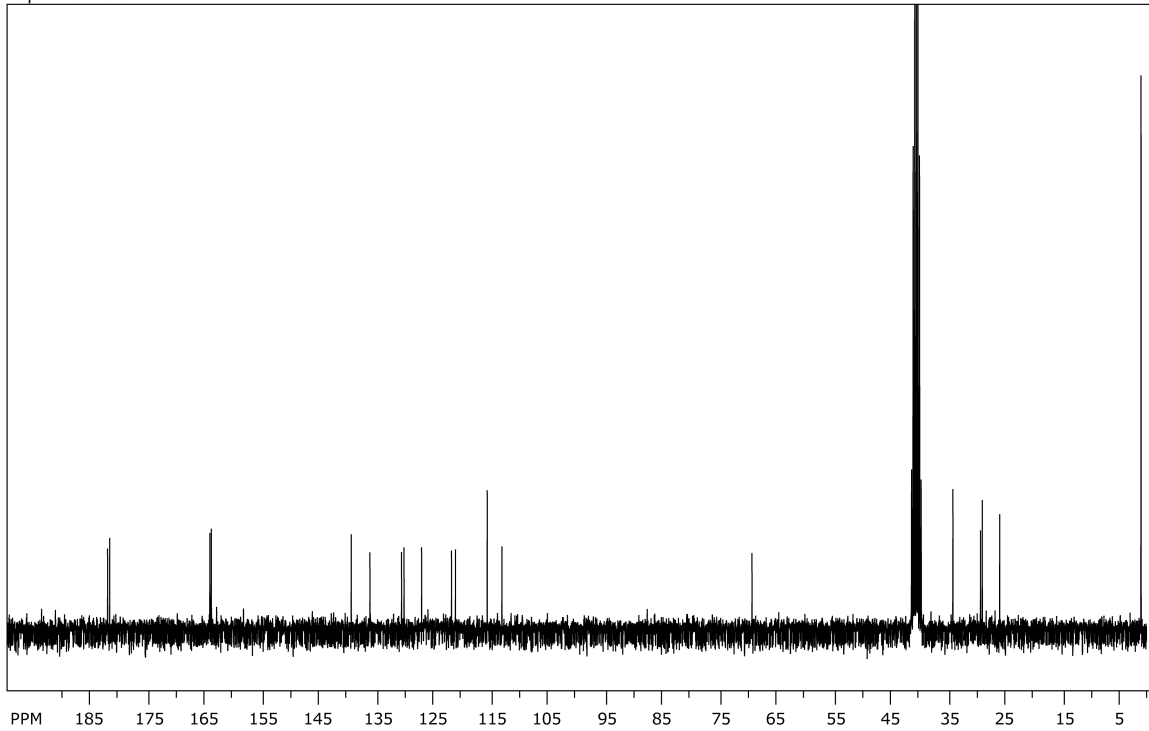
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SpinWorks 3:



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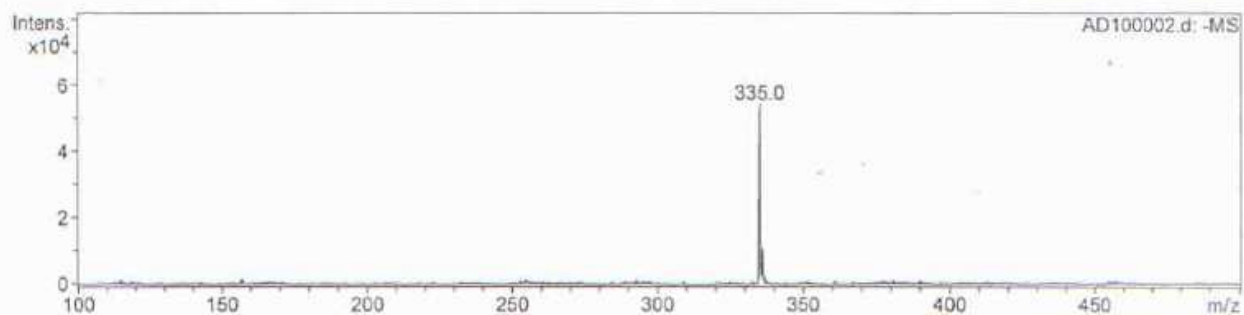
Mass Spectrum List Report

Analysis Info

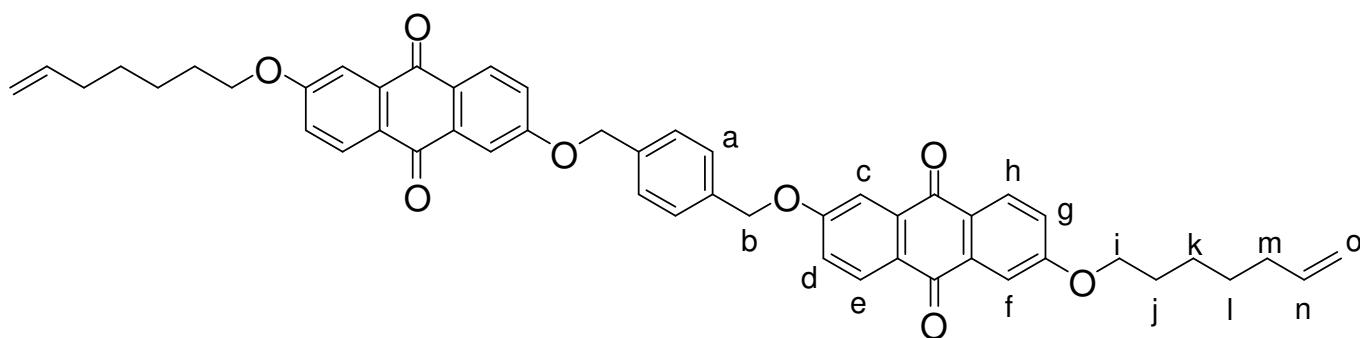
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Method VETTER06.M Operator Dr. Nour Kayali
Sample Name AD1 Instrument Esquire-LC_00126
Comment DIRECTO, EN DCM+MeOH

Acquisition Parameter

Ion Source Type ESI Ion Polarity Negative Alternating Ion Polarity n/a
Mass Range Mode Std/Normal Scan Begin 100.00 m/z Scan End 500.00 m/z
Capillary Exit -75.4 Volt Skim 1 -9.4 Volt Trap Drive 40.4
Accumulation Time 1000 μ s Averages 16 Spectra Auto MS/MS Off



#	m/z	I	FWHM	S/N
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2	335.9	10611	0.3	72.3
3	336.9	1756	0.3	12.0

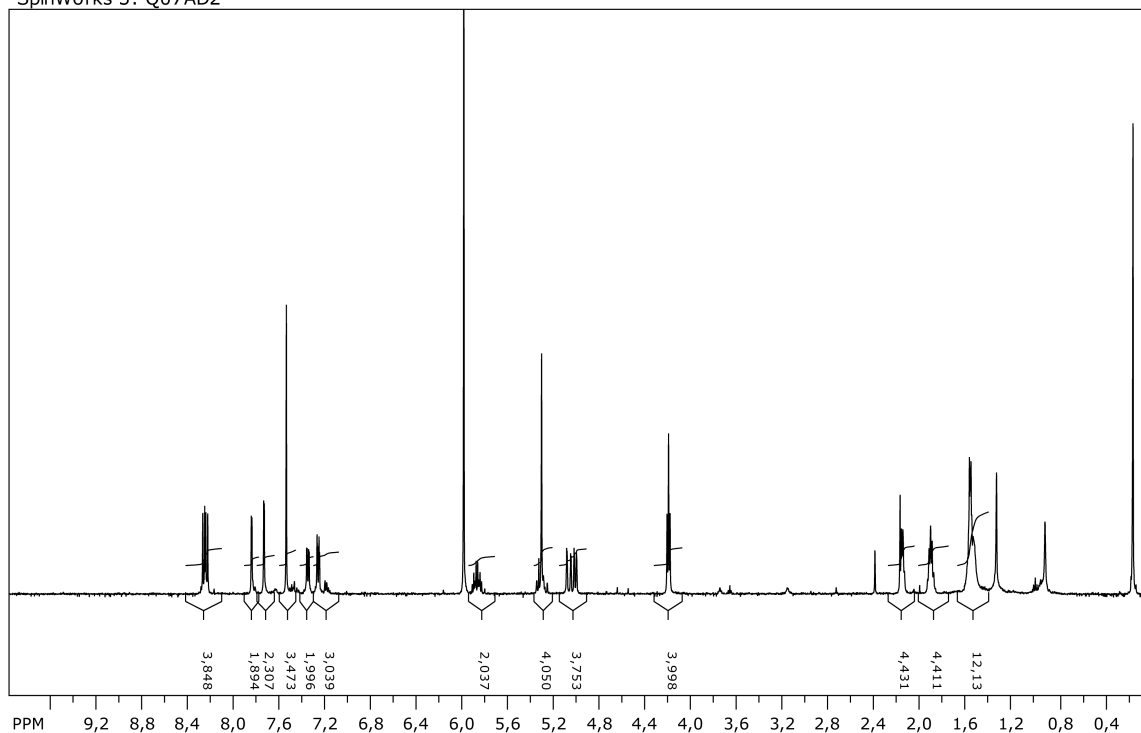


Chemical Formula: $C_{50}H_{46}O_8$
 Molecular Weight: 774,90

1.23 g (8.91 mmol) of dry K_2CO_3 , 1.17 g (4.46 mmol) of α - α' dibromo-p-xylene, and a catalytic amount of sodium iodide were added to a solution of 2.69 g (8.0 mmol) of the monoalkylated anthraflavic acid in 20–25 mL of dry N,N-dimethylformamide. The solution was heated to 60 °C for 4 h, and the resulting suspension was filtrated. The solid obtained was washed successively with methanol and diethylether to remove unreacted starting materials, to yield pure compounds without further purification ($y = 67\%$). The insolubility of this compound at room temperature forced us to characterize it at 353 K in $C_2D_2Cl_4$.

Mp 275-278 °C; 1H NMR ($C_2D_2Cl_4$, 500 MHz, 353 K) δ 8.28 (d, $J = 8.3$ Hz, 2H, H_h), 8.25 (d, $J = 8.3$ Hz, 2H, H_e), 7.86 (d, $J = 2.6$ Hz, 2H, H_f), 7.75 (d, $J = 2.5$ Hz, 2H, H_c), 7.56 (s, 4H, H_a), 7.37 (dd, $J = 2.6$ Hz, $J = 8.3$ Hz, 2H, H_g), 7.28 (dd, $J = 2.5$ Hz, $J = 8.3$ Hz, 2H, H_d), 5.89 (m, 2H, H_n), 5.32 (brs, 4H, H_b), 5.05 (m, 4H, H_o), 4.21 (t, $J = 6.6$ Hz, 4H, H_i), 2.16 (m, 4H, H_m), 1.91 (m, 4H, H_j), 1.55 (m, 8H, H_{k+l}). ^{13}C NMR ($C_2D_2Cl_4$, 125 MHz, 353 K) δ 181.85, 181.72, 164.02, 163.41, 138.46, 136.00, 135.90, 135.78, 129.56, 128.06, 127.66, 126.99, 120.91, 120.69, 120.21, 114.39, 111.35, 111.03, 70.24, 68.80, 33.26, 28.74, 28.39, 25.25. MS m/z : calcd. for $C_{50}H_{47}O_8$ $[M+H^+]$ 775.32 found MALDI-TOF 775.32.

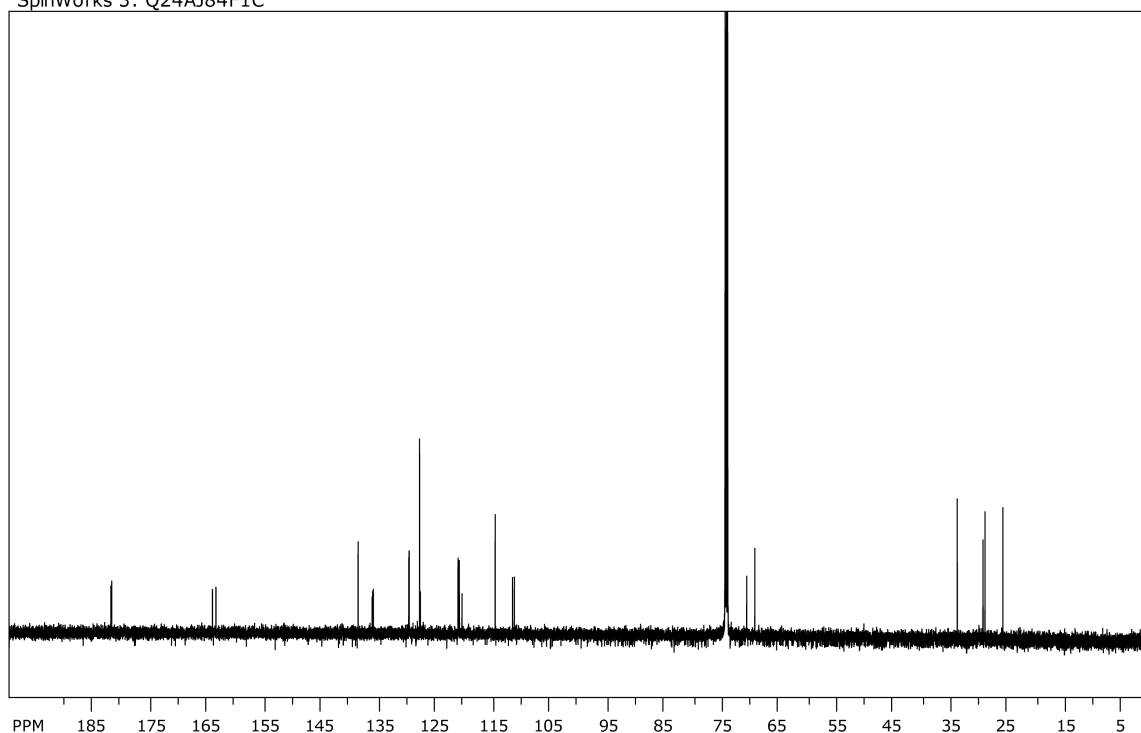
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 number of scans: 4

freq. of 0 ppm: 500,129681 MHz
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 Hz/cm: 199,686 ppm/cm: 0,39926

SpinWorks 3: Q24AJ84F1C



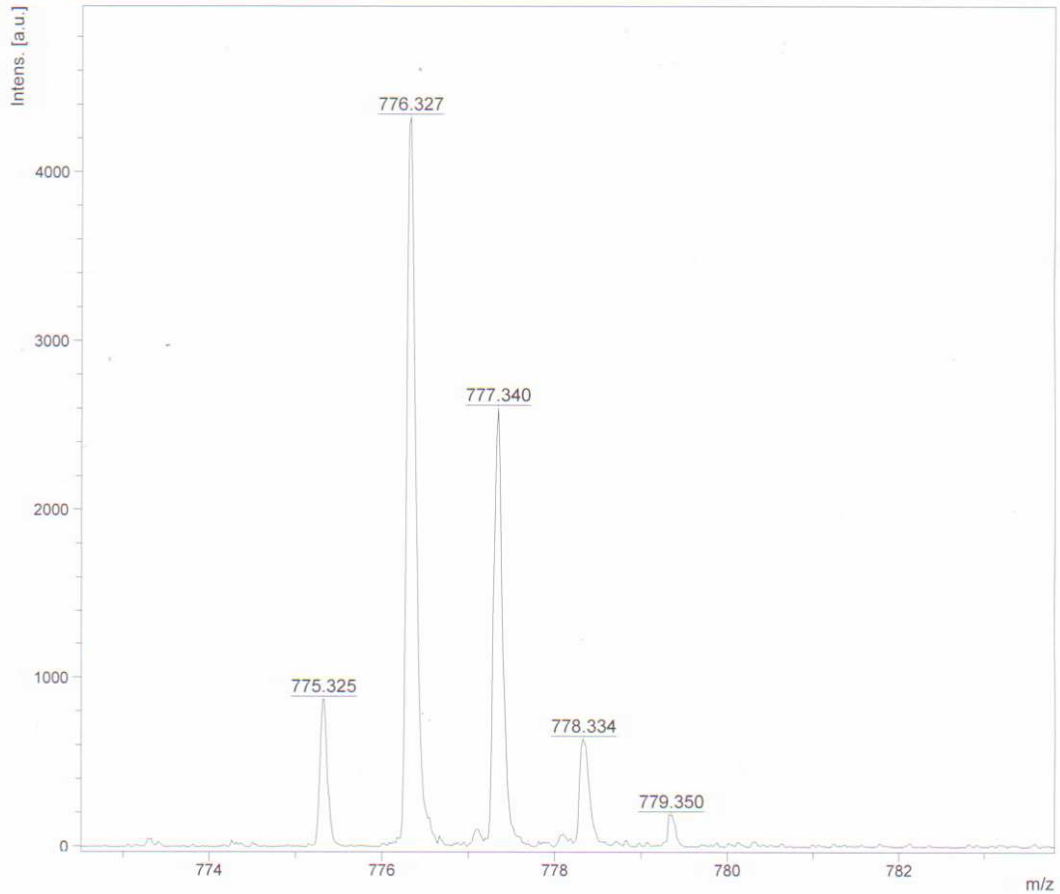
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Comment 1

Comment 2

DICLOROMETANO



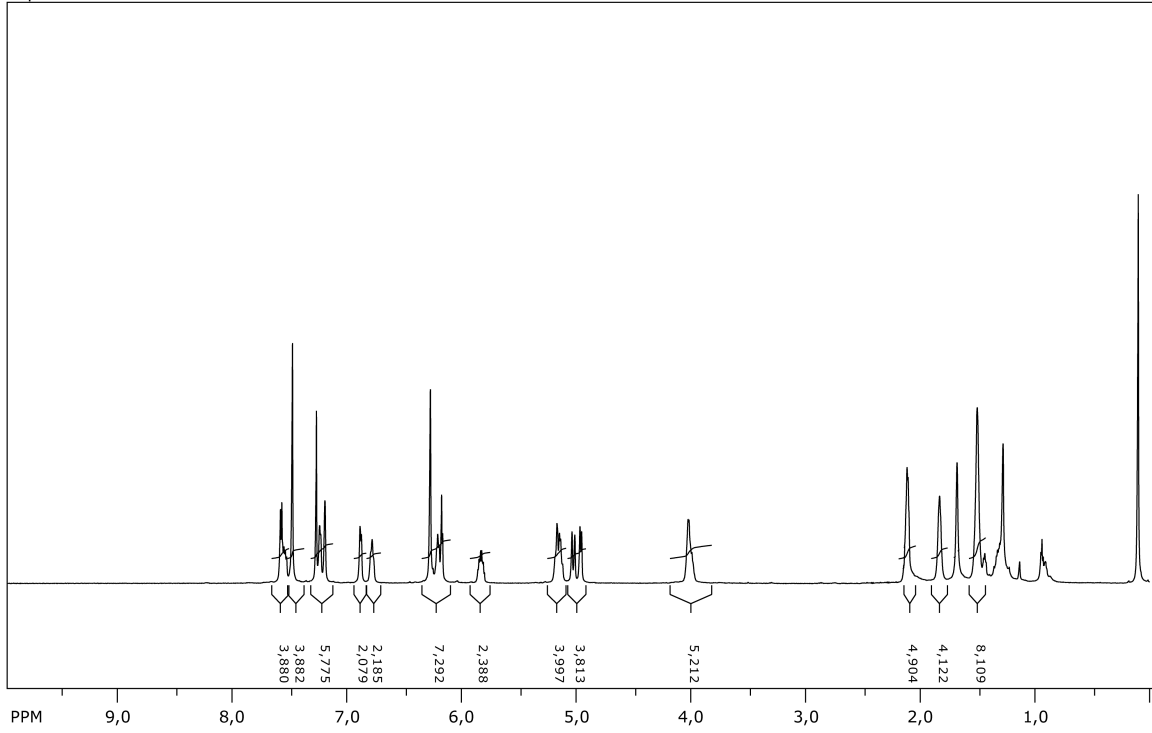
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Date of acquisition 2009-09-08 13:39:56
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Voltage polarity POS
Number of shots 500
Name of spectrum used for calibration
Calibration reference list used

Instrument Info

Instrument type ultraflexTOF/TOF

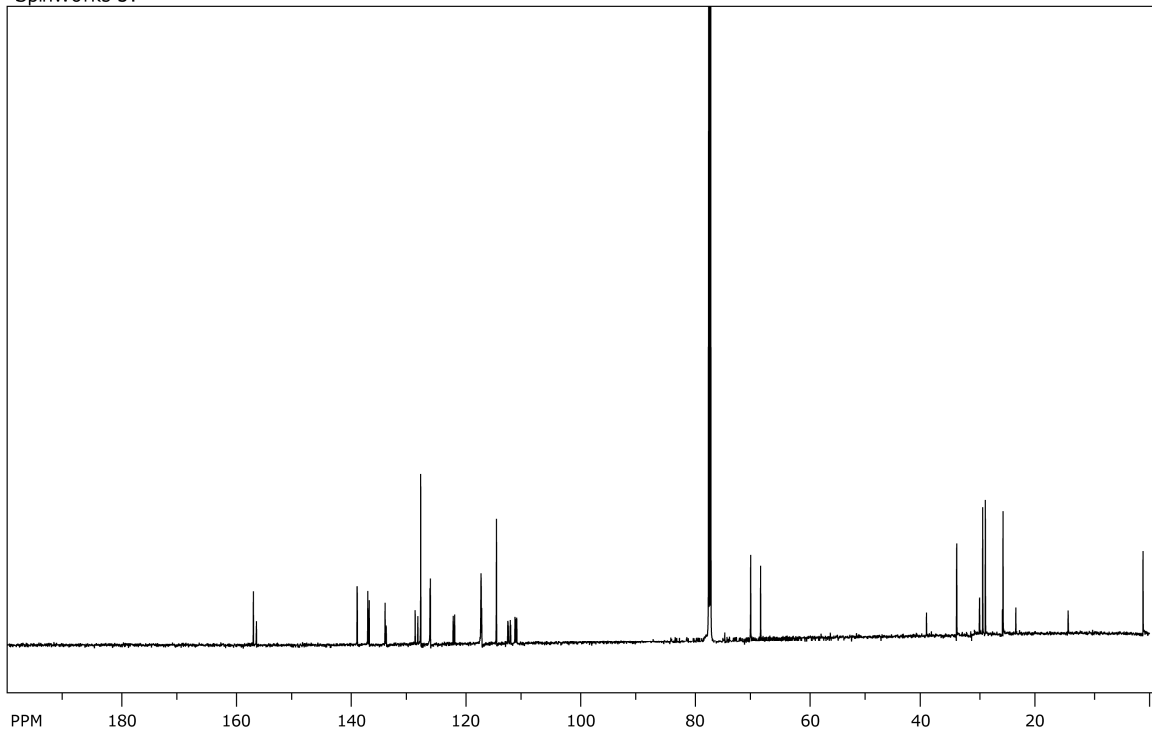
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number of scans: 1

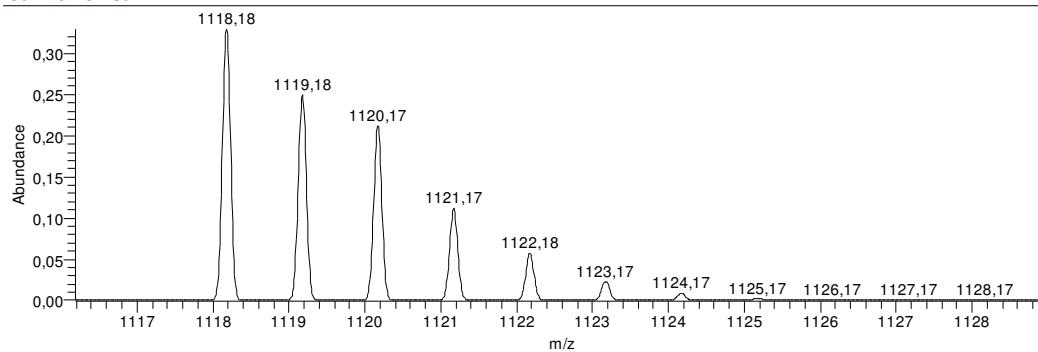
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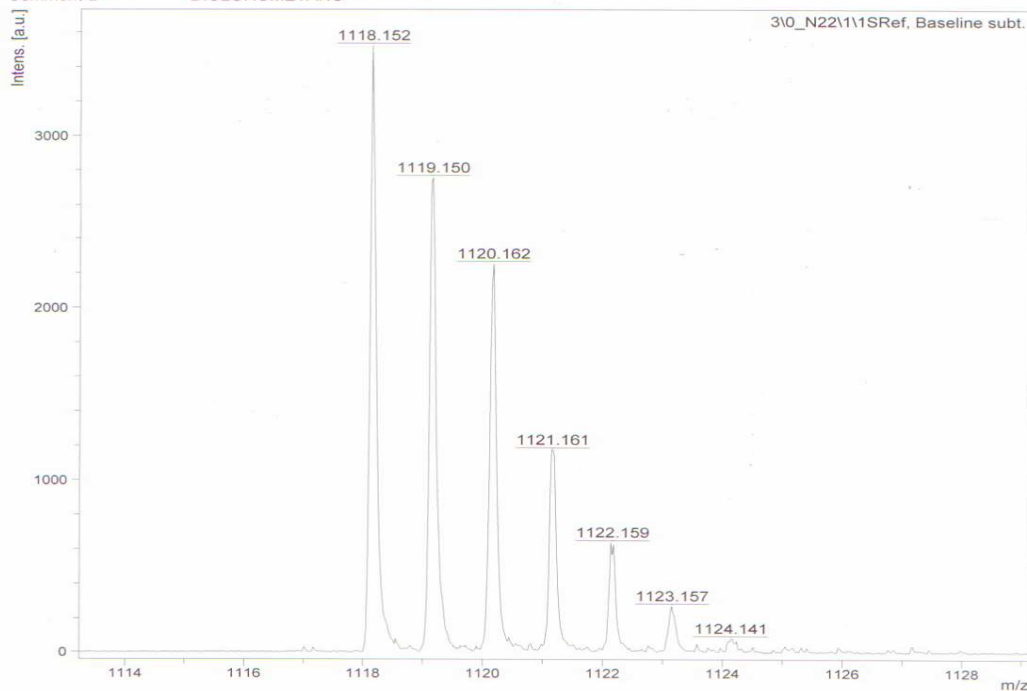
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C62H54O4S8
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at 5% height
Charges 1
Chrg dist 0
Ions 73606
Min Ion Ab. 1e-020
Min Ions 5000
Max Ions. 20000

D:\Data\UCM\2009\2009-09\03-02-Q07AD2\0_L23\3\0_N22\1

Comment 1
Comment 2

DICLOROMETANO

3\0_N22\1\1SRef, Baseline subt.

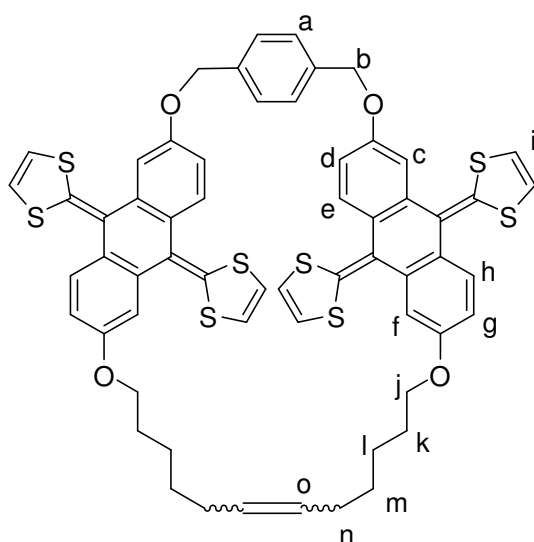


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Number of shots 200
Name of spectrum used for calibration
Calibration reference list used

Instrument Info

Instrument type ultraflexTOF/TOF



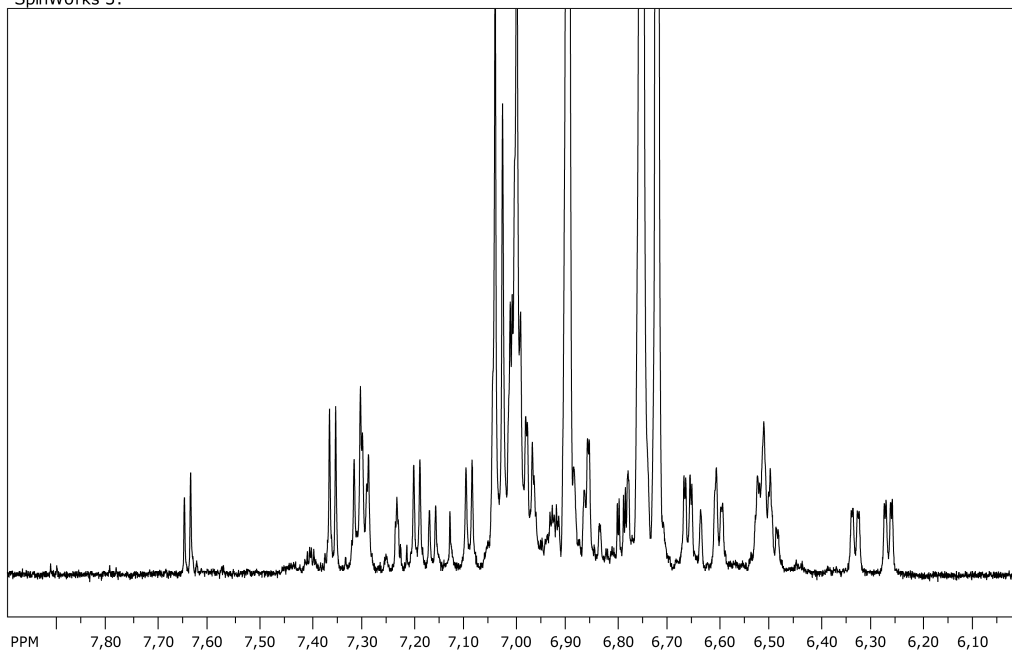
Chemical Formula: $C_{60}H_{50}O_4S_8$
 Molecular Weight: 1091,557

A catalytic amount of Grubb's 1st generation catalyst was added to a solution of the linear precursor **1** in dry and degassed CH_2Cl_2 . The solution was stirred at room temperature and its progress monitored by TLC (Hex: CH_2Cl_2 2:1). The reaction proceeds spot to spot until it is close to completion, when unidentified polar spots start to appear on the TLC. The reaction is then stopped, filtered through a pad of Celite, the solvent evaporated under reduced pressure, and the crude subjected to column chromatography on silica gel (Hex: CH_2Cl_2 2:1) to yield the product as an inseparable mixture of *E/Z* isomers ($y = 90\%$). The product shows complicated 1H NMR, consistent with an asymmetric molecule in several conformations in slow chemical exchange at NMR timescale. We have obtained a sufficiently well-resolved spectrum on a Bruker AvanceIII 700 MHz in chlorobenzene- d_5 , and fully assigned it based on COSY and TOCSY experiments (see below). Lettering corresponds to that shown above. No distinction between isomers or conformers has been made.

Mp 215–217 °C; 1H NMR (chlorobenzene- d_5 , 700 MHz, 298 K) δ 7.64 (d, $J = 8.4$ Hz, 0.25H, H_h), 7.36 (d, $J = 8.4$ Hz, 0.75H, H_h), 7.31 (d, $J = 8.4$ Hz, 0.50H, H_e), 7.29 (d, $J = 8.4$ Hz, 0.50H, H_e), 7.23 (s, 0.25H, H_f), 7.19 (d, $J = 8.4$ Hz, 0.75H, H_h), 7.16 (d, $J = 8.4$ Hz, 0.25H, H_h), 7.09 (d, $J = 8.4$ Hz, 0.50H, H_e), 7.04 (s, 3H, H_a), 7.02 (s, 1H, H_a), 7.00 (d, $J = 2.3$ Hz, 0.50H, H_e), 6.99 (s, 0.50H, H_f), 6.98 (d, $J = 2.3$ Hz, 0.50H, H_f), 6.96 (d, $J = 2.3$ Hz, 0.75H, H_f), 6.88 (s, 0.25H, H_c), 6.86 (s, 0.25H, H_c), 6.85 (d, $J = 2.3$ Hz, 0.75H, H_c), 6.83 (m, 0.25H, H_c), 6.79 (dd, $J = 8.3$ Hz, $J = 2.4$ Hz, 0.25H, H_g), 6.77 (s, 0.25H, H_c), 6.66 (dd, $J = 8.4$ Hz, $J = 2.4$ Hz, 0.50H, H_g), 6.63 (s, 0.25H, H_c), 6.60 (dd, $J = 8.4$ Hz, $J = 2.4$ Hz, 1H, H_d), 6.51 (m, 1.5H, H_g), 6.33 (dd, $J = 8.4$ Hz, $J = 2.3$ Hz, 0.50H, H_d), 6.26 (dd, $J = 8.5$ Hz, $J = 2.3$ Hz, 0.50H, H_d), 5.63 (d, $J = 6.6$ Hz, 0.50H, H_i), 5.57 (m, 1H, H_i), 5.47 (m, 1H, H_i), 5.24 (d, $J = 6.6$ Hz, 0.50H, H_i), 5.19 (d, $J = 6.6$ Hz, 0.50H, H_i), 5.16 (m, 0.75H, H_o), 5.13 (m, 1.25H, H_o), 5.09 (d, $J = 6.6$ Hz, 0.5H, H_i), 4.98–4.87 (m,

4H, H_b), 3.59 (m, 4H, H_j), 1.79 (m, 4H, H_n), 1.44 (m, 4H, H_k), 1.19 (m, 8H, H_{l+m}). ¹³C NMR (chlorobenzene-*d*₅, 175 MHz, 298 K) δ 157.52, 156.49, 156.25, 156.02, 138.90, 137.56, 137.49, 137.39, 137.31, 137.09, 136.95, 132.47, 130.89, 130.65, 127.28, 127.21, 127.10, 121.84, 121.43, 117.20, 117.09, 117.00, 116.93, 116.72, 116.66, 116.57, 114.31, 113.70, 112.83, 112.33, 111.89, 111.84, 111.76, 111.66, 111.39, 111.20, 111.01, 110.52, 69.21, 69.07, 68.23, 68.02, 37.91, 35.13, 34.55, 34.17, 33.21, 32.63, 32.51, 32.40, 31.44, 29.84, 29.63, 29.41, 29.14, 27.69, 27.23, 27.02, 25.38, 25.32. MS *m/z*: calcd. for C₆₀H₅₀O₄S₈ [M⁺] 1090.1 found MALDI-TOF 1090.2 HRMS *m/z*: calcd. for C₆₀H₅₀O₄S₈ [M⁺] 1090.1475 [M²⁺] 545.0738 found ESI (pos.) 1090.1372; 545.0732.

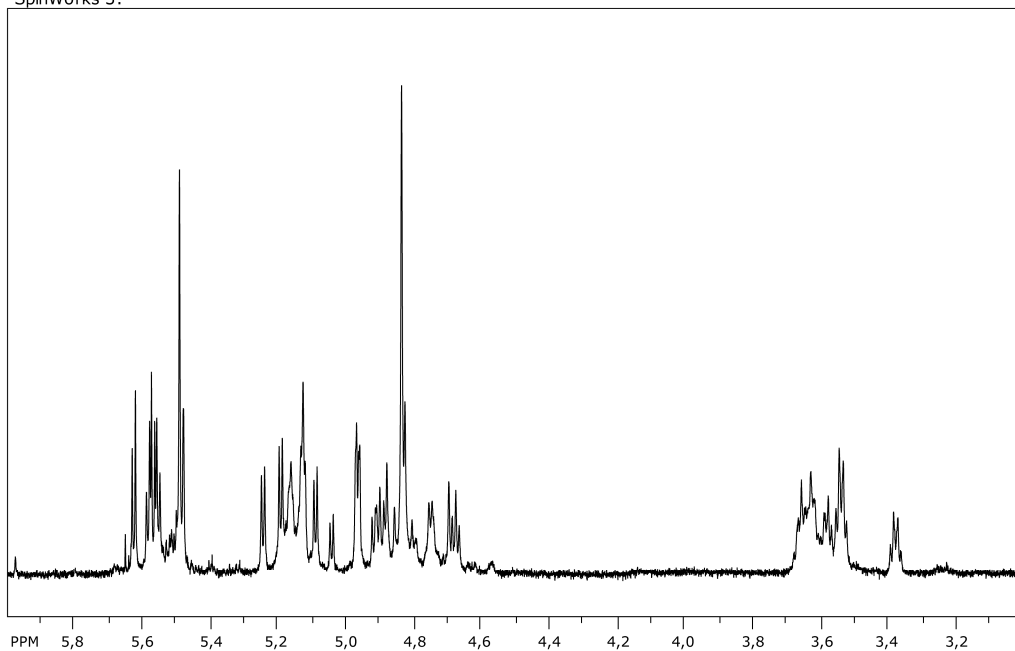
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number of scans: 4

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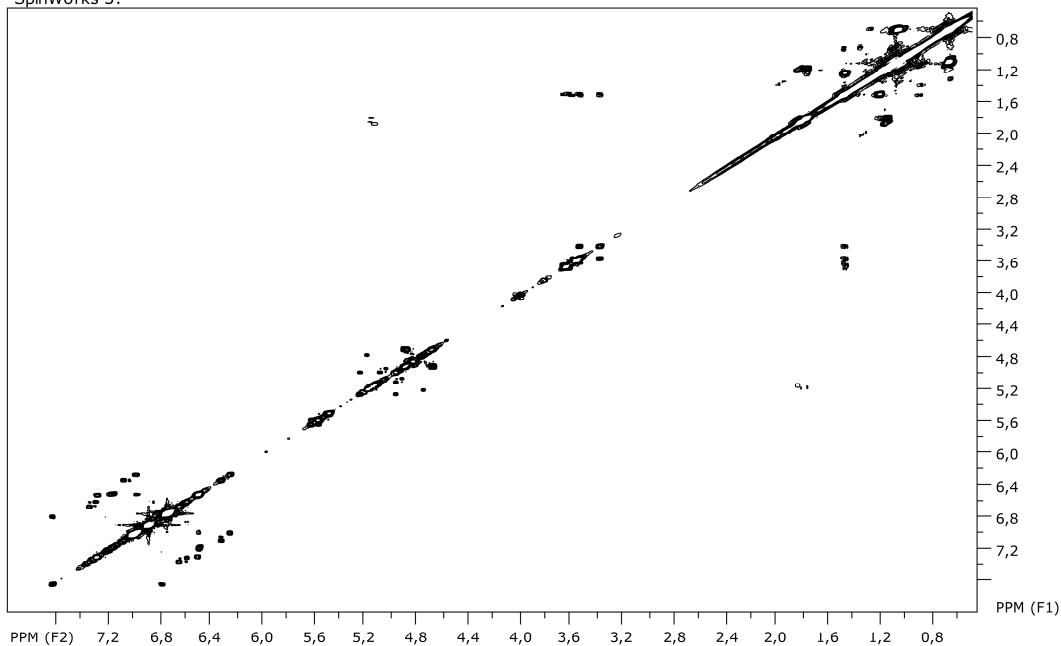
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number of scans: 4

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SpinWorks 3:



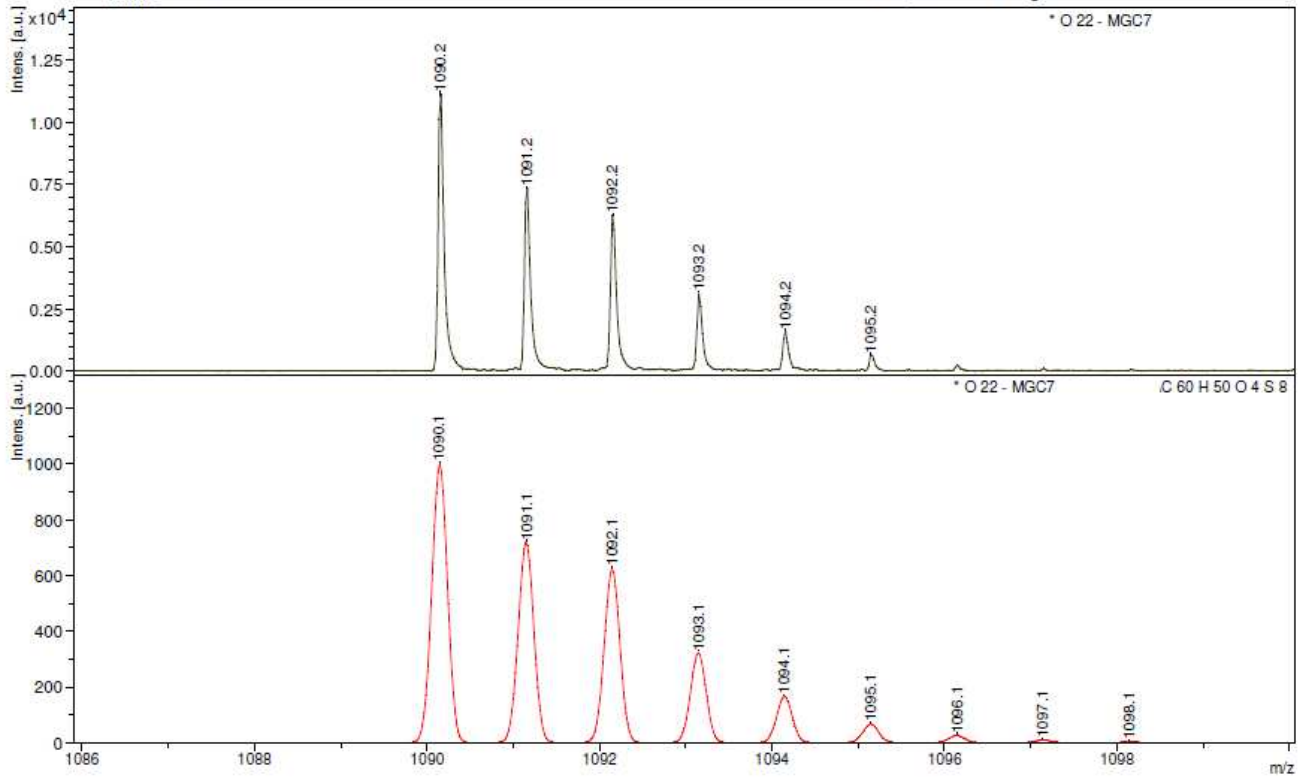
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number of scans: 8

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window function: Sine
shift: 0,0 degrees
Hz/cm: 219,924 ppm/cm: 0,31410

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processed size: 1024 complex points
window function: Sine
shift: 0,0 degrees
Hz/cm: 353,388 ppm/cm: 0,50472

Muestra MGC7
Matriz DCTB

Ensayo MALDI (ULTRAFLEX III)
D:\Data\U-006\o 22 - mgc7

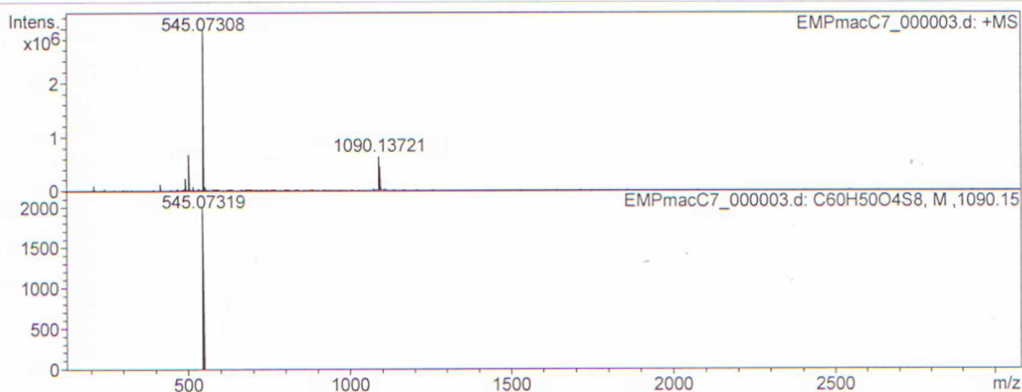


Mass Spectrum List Report

Analysis Info

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DIRECTO, EN DCM+MeOH+acn al 2%ac. form.			

Acquisition Parameter



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489.34037		46681	62906
491.28040		250705	60879
492.28388		71129	60673
502.09089		700486	59197
502.59263		482066	60234
503.08754		171700	67646
503.09616		116095	71571
503.35569		205444	58786
503.58999		109564	64514
504.35963		55742	58161
514.22353		93582	58852
517.34327		82864	60177
533.36622		45490	62644
545.07308		3148014	56183
545.55768		113029	45833
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545.58530		165145	76983
546.07040		959664	28843
546.57216		710295	56917
547.07455		182773	33499
547.38212		189467	55461
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548.38504		61151	54006
551.22516		53683	55508
553.07053		84128	58447
553.57252		53036	52645
582.41310		44574	55329
585.53315		42800	49839
590.05263		65350	53332
591.29270		86452	52481
591.40749		161292	50392
592.41125		56780	51650
626.34839		133475	49240
627.35212		51306	51541

2. Estimation of the binding constants through UV-vis titrations

Binding constants towards C₆₀:

In a typical experiment, we prepared stock solutions of the macrocyclic receptor **2** at a concentration of approximately 1×10^{-5} M. Those solutions were utilized as solvents in the C₆₀ solution (1×10^{-4} M), to ensure working at constant concentration of host. Aliquots of the fullerene solution were added to the host solution and UV-vis spectra recorded at room temperature on a Cary UV-50 spectrophotometer. Determination of the binding constants towards C₆₀ was carried out utilizing Specfit software and by non-linear least-squares analysis of the Δ Abs at both 425 nm and 478 nm against the concentration of the fullerene, utilizing OriginPro 7.5 (OriginLab corporation) and the binding isotherm:

$$dabs=dmax*((1+Ka*G+Ka*H)-((1+Ka*G+Ka*H)^2-4*Ka^2*H*G)^{0.5})/(2*Ka*H)$$

In this case, plots of Δ Abs at 425 nm tend to overestimate the binding constants, so we have routinely utilized Δ Abs at 478 nm. Experiments were repeated three times. The value of $\log K_a$ of **2** vs C₆₀ obtained through this method is 6.1 ± 0.2 . An example of titration of **2** vs C₆₀ and its fit for the binding isotherm are provided in the main text. The analysis of the spectral data utilizing Specfit software provided a value of $\log K_a = 6.5 \pm 0.5$, identical within the error limits.

Binding constants towards C₇₀:

In a typical experiment, we prepared stock solutions of the macrocyclic receptor **2** at a concentration of approximately 1×10^{-5} . Those solutions were utilized as solvents in the C₇₀ solution (3.5×10^{-5} M), to ensure working at constant concentration of host. Aliquots of the fullerene solution were added to the host solution and UV-vis spectra recorded at room temperature on a Cary UV-50 spectrophotometer.

Due to the high degree of spectral overlap, analyses of the UV-vis data were performed utilizing Specfit software, which afforded a value of $\log K_a = 8.4 \pm 2.5$.

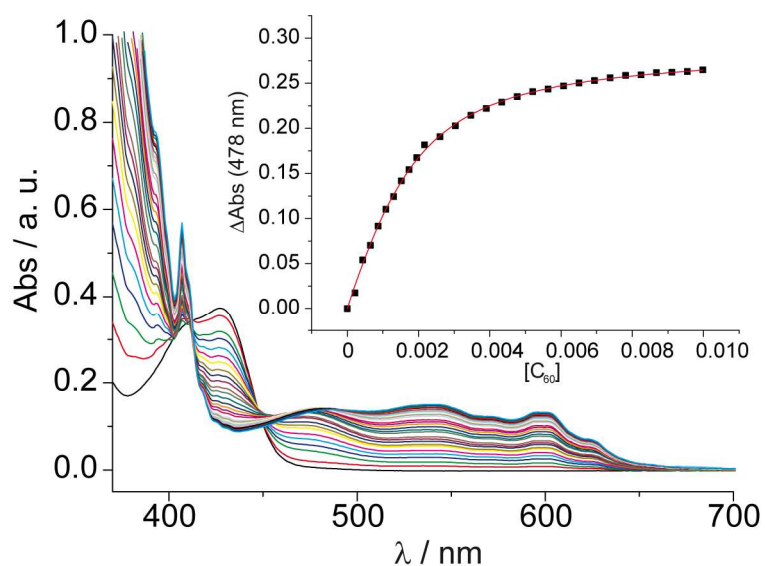


Figure S1. Spectral changes in a UV-vis titration experiment of the linear precursor **1** vs. C_{60} in PhCl at room temperature, and binding isotherm (inset, $K_a = 1271 \pm 101 \text{ M}^{-1}$, $R^2 = 0.999$).

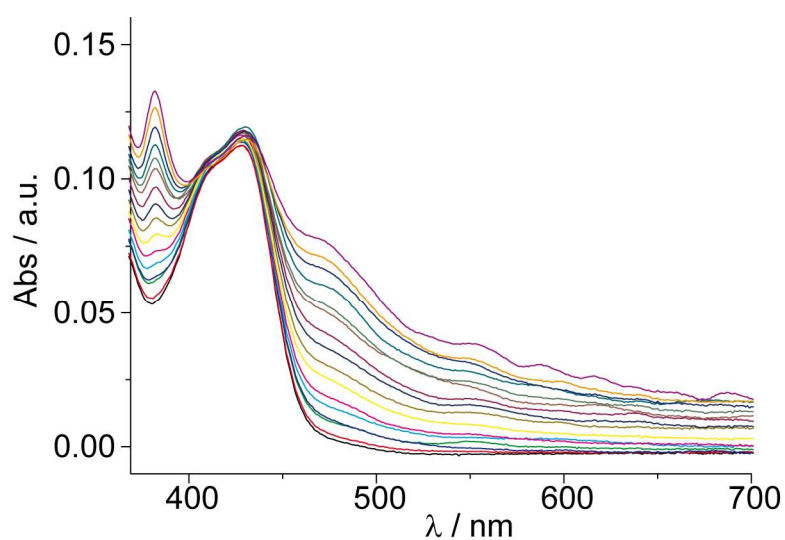


Figure S2. Spectral changes in a UV-vis titration experiment of **2** vs. C_{70} in PhCl at room temperature.

3. Theoretical calculations

Theoretical calculations were carried out within the density functional theory (DFT) approach by using the D.02 revision of the Gaussian 03 suite of programs.¹ Geometry optimizations were performed making use of Becke's "half-and-half" functional, BH&H,² and the 6-31G** basis set.³ The BH&H functional is an *ad hoc* mixture of exact Hartree-Fock (HF) and local density approximation (LDA) exchange, coupled with Lee, Yang, and Parr's (LYP) expression⁴ for the correlation energy. The attractiveness of the BH&H functional to calculate supramolecular associations is that it successfully reproduces the results of highly-accurate post-HF methods for π -stacked complexes.⁵⁻⁹ Waller et al.⁵ found that the BH&H functional provides a binding energy for the archetypal parallel-displaced benzene dimer in good agreement with the best available high-level computational methods. Truhlar et al.⁷ have recently reported a very comprehensive study of a large database of non-covalent interacting systems using different functionals and concluded that the BH&H functional gives good performance for dispersion-dominated interactions. A similar conclusion is stated by Hobza et al.⁸ in a very recent study on small peptides for which the interaction is dominated by dispersion forces. The different conformations of macrocycle **2** were also optimized using Becke's three-parameter B3LYP exchange-correlation functional² and the 6-31G** basis set. The B3LYP functional was not employed to calculate the supramolecular complexes because it fails in describing dispersion forces and does not properly account for stacking π - π interactions.¹⁰

Association binding energies were firstly obtained at the BH&H/6-31G** level by fully optimizing the geometry (intra- and intermolecular parameters) of the supramolecular complex. Binding energies were afterwards recalculated using the more extended 6-31+G** basis set,¹¹ which includes diffuse functions on the heavy atoms, and the 6-31G**-optimized geometries. The basis set superposition error (BSSE) was calculated using the counterpoise correction approach.¹² The BSSE is a spurious contribution to the interaction energy arising from the improved description of the molecular fragment A in the complex A•••B due to the assistance of the basis set located in fragment B, and vice versa. The counterpoise method corrects the interaction energy of the complex A•••B by computing the energies of the isolated fragments A and B with exactly the same basis set (both in number and location) as used to compute the complex A•••B.

Figure S3 sketches two energy-minimized structures calculated for the **2**•C₆₀ associate at the BH&H/6-31G** level (structure A corresponds to that displayed in Figure 2 in the main text). Structures A and B in Figure S1 show a similar disposition of the exTTF moieties and the central xylylene unit around C₆₀, and mainly differ in the conformation of the alkyl chain that closes the macrocycle. Macrocycle **2** indeed presents a high flexibility due to the alkyl chain and to the relative orientation of the exTTF units, and multiple minima can be envisaged for the molecular associate.

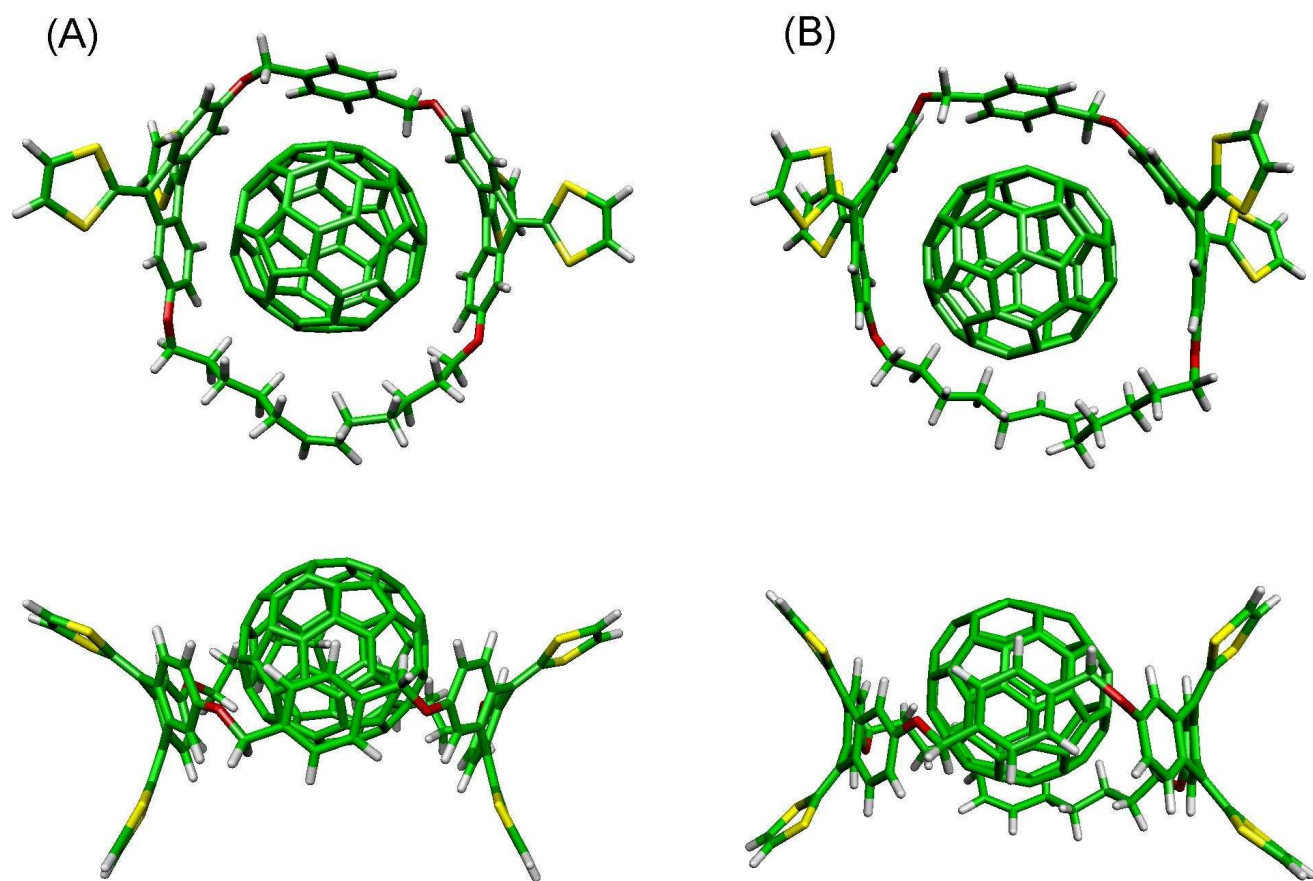


Figure S3. Top view (top) and side view (bottom) of two energy-minimized structures (A and B) calculated for the $2 \cdot C_{60}$ associate at the BH&H/6-31G** level.

At the BH&H/6-31G** level, structure A is calculated to have a binding energy of -34.52 kcal/mol and is predicted to be more stable than structure B, for which a binding energy of -31.49 kcal/mol is obtained. The higher stability of structure A is due to the more closely wrapping of the fullerene unit by the exTTFs, the xyllylene linker, and the alkyl chain. In structure A, the benzene rings of both the exTTF and the xyllylene units are all oriented parallel to the fullerene surface and maximize the π - π interactions between the receptor and C_{60} (see Figure S3). This is not the case for structure B, for which the benzene rings are tilted with respect to the C_{60} surface and the alkyl chain is less accommodated around C_{60} . When using the more extended 6-31+G** basis set, the value calculated for the association binding energy of structure A is -31.64 kcal/mol and diminishes to -24.13 kcal/mol when the correction for the BSSE ($+7.51$ kcal/mol) is added.

As mentioned above, macrocycle **2** presents a highly flexible structure due to the different conformations that the alkyl chain can adopt, and to the possible orientations of the exTTF units with respect to the central xyllylene linker. Figure S4 sketches five energy-minimized conformations (M1 to M5) calculated

for **2** at the BH&H/6-31G** level, although other conformational minima could be found. B3LYP/6-31G** calculations lead to similar minimum-energy conformations. The exTTF units always adopt a butterfly- or saddle-like structure, in which the central ring of the anthracene units folds into a boat conformation and the benzene and dithiole rings point to opposite directions. Structures M1 and M2 in Figure S4 present the same disposition of the exTTF units, with the dithiole rings pointing outwards of the macrocycle, and mainly differ in the conformation adopted by the alkyl chain. In structure M3 the exTTF units approach each other and the alkyl chain is completely folded. Structures M4 and M5 present a different orientation of the exTTF units, with one or the two exTTFs pointing inwards the macrocycle, and appear to be less adequate to host C₆₀. Indeed, the centre of the macrocycle is completely crowded in structure M5.

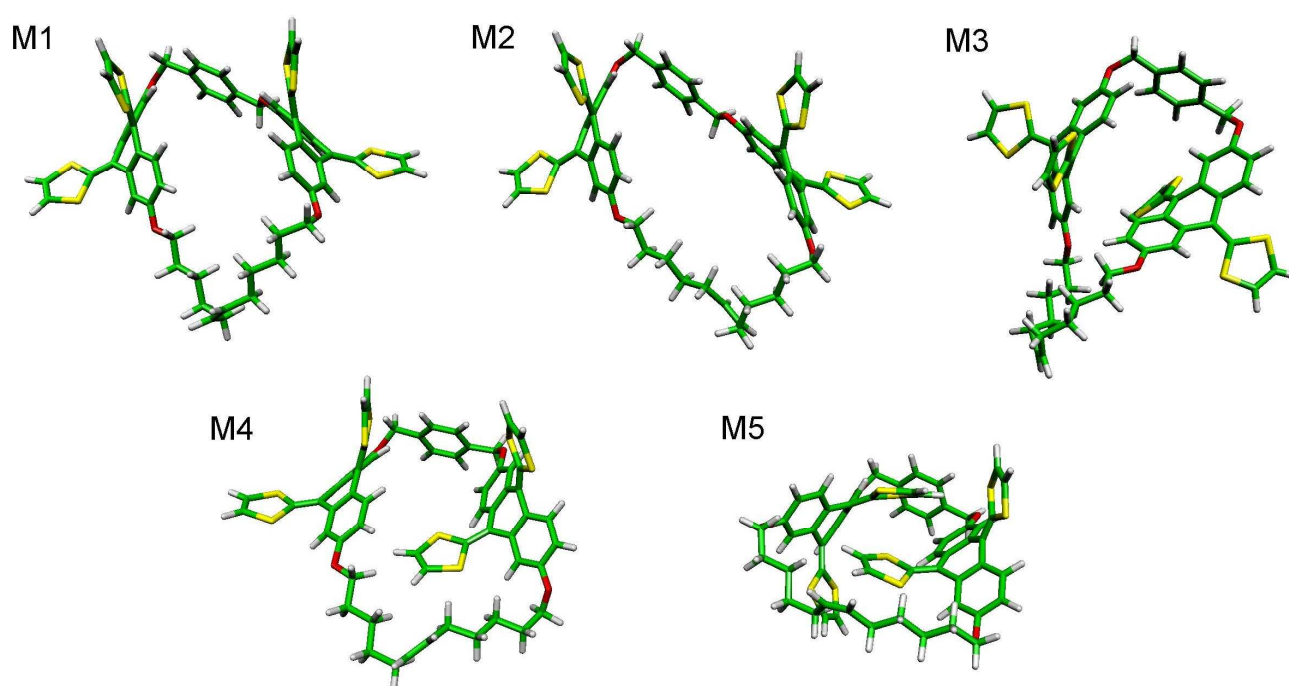


Figure S4. BH&H/6-31G**-optimized conformations calculated for macrocycle **2**.

At the B3LYP/6-31G** level, structures M1–M3 are predicted to be close in energy in a range of 3.24 kcal/mol and structures M4 and M5 are calculated to lie at higher energies (4.74 and 10.33 kcal/mol, respectively). The BH&H/6-31G** approach fails in predicting the relative energy of these conformations since it obtains the crowded structure M5 as the most stable. Structures M1–M5 were also optimized in the presence of the solvent (chlorobenzene) making use of the polarized continuum model (PCM) approach.^{13,14} At the B3LYP/6-31G** level, structure M1 is obtained to be the most stable and structures M2 and M3 lie very close in energy (0.60 and 3.38 kcal/mol, respectively). A mixture of conformations

has therefore to be expected for macrocycle **2** in solution. Among these minimum-energy conformations, only some of them like M1 and M2 show geometries that can be easily reorganized to accommodate C₆₀. Indeed, optimization of **2** starting from the geometry it shows in structures A and B of the **2**•C₆₀ associate leads to conformations M1 and M2, respectively.

Figure S5 displays the energy-minimized structures calculated for the **2**•C₇₀ associate at the BH&H/6-31G** level. The structure was optimized starting from structure A of **2**•C₆₀ and substituting C₆₀ by C₇₀. When C₇₀ is introduced horizontally with its long axis in the plain of the macrocycle, intermolecular interactions occur at too much short distances and C₇₀ is moved out the cavity of the macrocycle (Figure S5 left). When C₇₀ is introduced vertically (Figure S5 right), it stays inside the macrocycle and an association binding energy of -35.91 kcal/mol is computed at the BH&H/6-31G** level. This energy is slightly larger than that predicted for the **2**•C₆₀ associate (-34.52 kcal/mol), in agreement with the higher association constant found experimentally for **2**•C₇₀. Association binding energies were calculated as the difference between the total energy of the complex and the sum of the total energies of the receptor and the fullerene. The energy used for the receptor was that computed for **2** using the optimized geometry it shows in the associate. We employed this energy instead of that calculated for the fully-relaxed macrocycle because the BH&H/6-31G** approach does not provide a correct description of the conformational behavior of **2**. When the energy of the fully-relaxed structure M1 is used, the binding energies calculated at the BH&H/6-31G** level for **2**•C₆₀ and **2**•C₇₀ decrease to -21.05 and -22.53 kcal/mol, respectively.

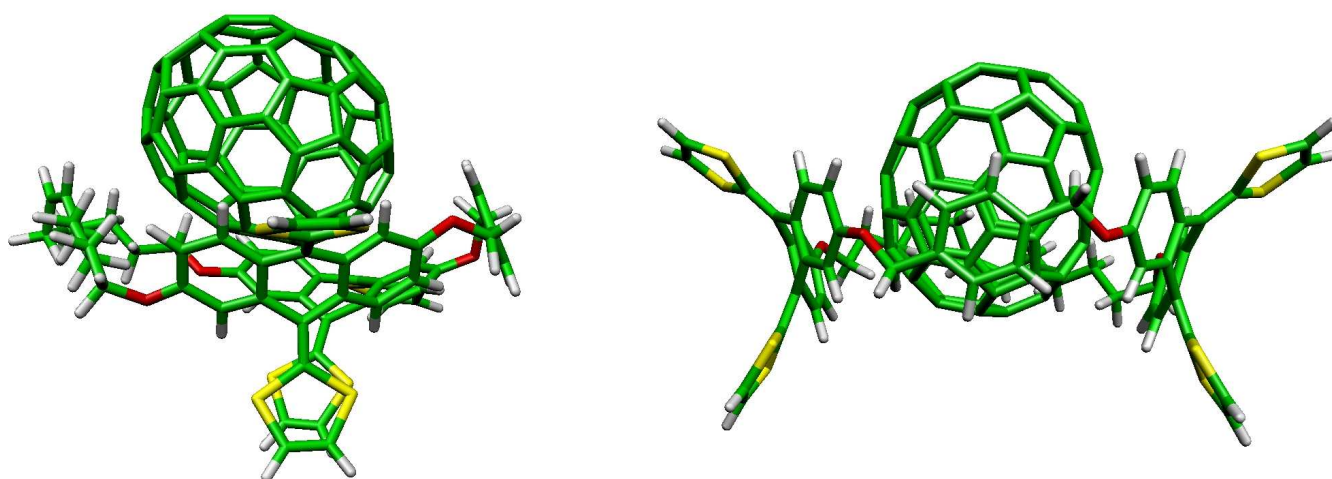


Figure S5. Energy-minimized structures calculated at the BH&H/6-31G** level for the **2**•C₇₀ associate.

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