Supramolecular Complexation Behavior of Novel Cyclotrivera-trylene Derivatives with Benzoate Pendants with C_{60}

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Four novel cyclotriveratrylene (CTV) derivatives with three benzoate pendants bearing different aliphatic chains have been prepared in good yields, starting from CTV. The complexation behavior of these CTV derivatives towards C_{60} in arene solvents has been measured by UV-visible spectroscopy and high complexation constants are obtained. It is observed that the complexation is promoted pronouncedly by introducing methyl ester groups to the aromatic pendants, while this promoting effect is reduced when the methyl groups are replaced by longer alkyl groups.

Keywords   Cyclotriveratrylene, fullerene, complexation, supramolecules, benzoate pendant

Introduction

In recent years there have been considerable interests in developing supramolecular complexes between fullerenes and different organic receptors.[1] Though solid state complexes between fullerenes and a variety of π-electron rich compounds and synthetic macrocyclic receptors have been extensively investigated,[2] relatively few macrocyclic molecules have been observed to lead to strong complexation in organic solutions.[3] Cyclotriveratrylenes (CTVs) are a class of cyclic oligomers which can be conveniently prepared from vanillyl alcohol. Mainly because of the pioneering research by Collet *et al.*, CTVs have been widely utilized as building blocks to construct various receptors for recognizing small organic molecules.[4] Recently Matsubara *et al.* have reported that CTVs with acylated phenolic OH groups can form stable 1:1 complexes with fullerenes in organic sol-

vents.[3d-3f] The main driving force for complex formation has been believed to be the weak π-π interactions between fullerenes and both the concave CTV and the attached aromatic pendants. In this paper, we wish to report our synthesis of a new class of CTV derivatives with benzoate groups of different lengths as pendants and their efficient association ability towards C_{60}.

Results and discussion

Though many functional groups could be used as pendants attached to the CTV scaffold, we chose to synthesize compounds 6a, 6b, 6c, and 6d with the benzoate unit of different lengths for our purpose. Compound 6e was also prepared for the purpose of comparison with the above compounds. CTV receptors 6a, 6c, and 6d were prepared from coupling reactions of an excess quantity of bromides 4a, 4c, and 4d with the readily available CTV derivative 5[5] in acetonitrile in the presence of potassium carbonate, as shown in Scheme 1. All the bromides were prepared from toluic acid 1. Compound 1 was first converted to their esters 3a, 3c, 3d in high yields by being heated in the corresponding alcohol in the presence of catalytic amount of sulfuric acid. The bromination of 3a, 3c, 3d with N-bromosuccimide (NBS) or bromine in chloroform afforded the corresponding bromides 4a[6] 4c, and 4d in good yields. Scheme 2 shows the synthesis of CTV derivative 6b. Compound 6a was first quantitatively hydrolyzed in the presence of potassium carbonate to the intermediate acid
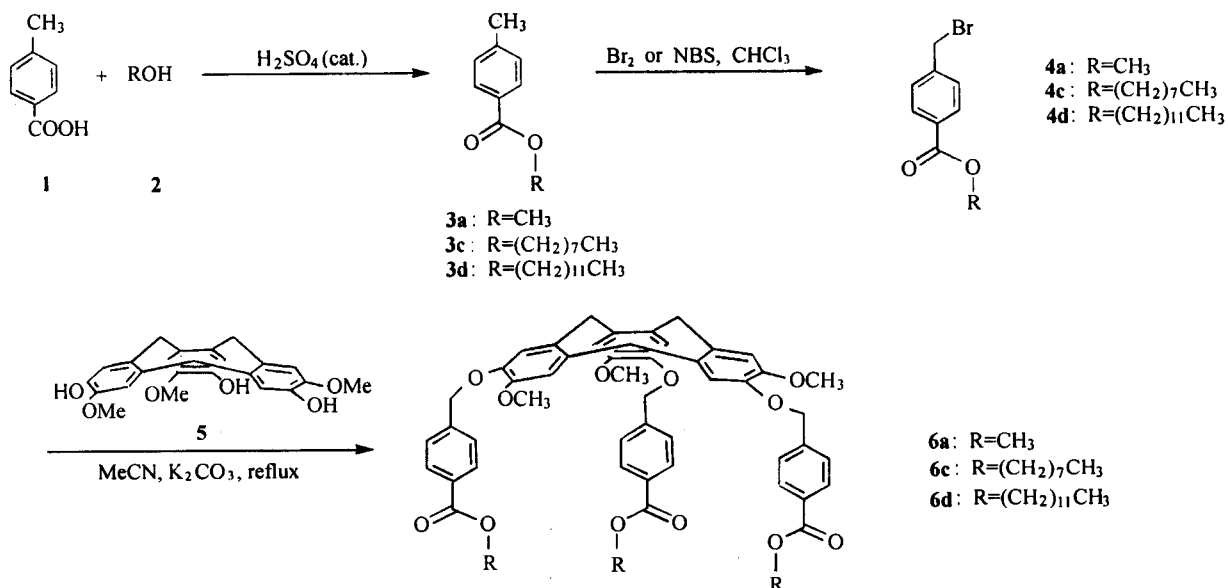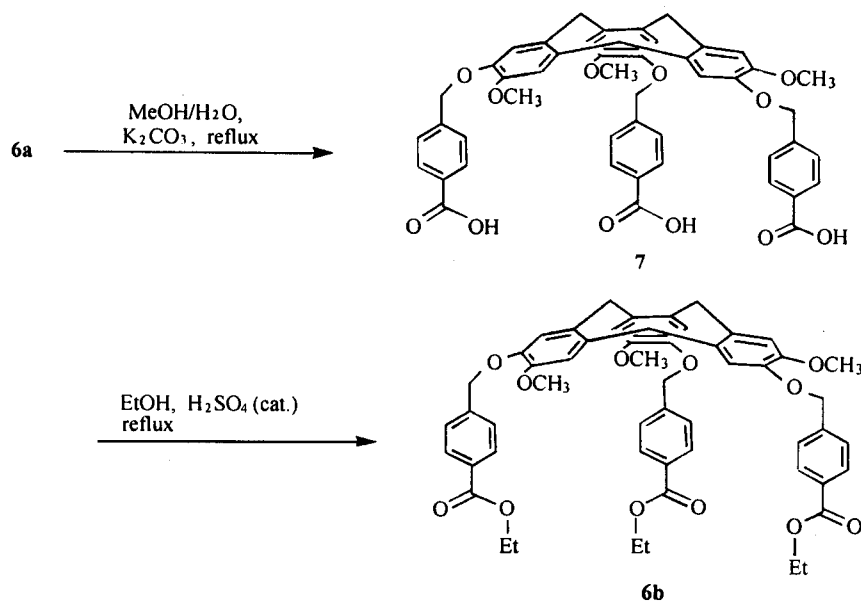
7, which was then esterified by refluxing in ethanol in the presence of sulfuric acid, to afford compound **6b** in high yield. The preparation of **6e** from CTV and benzyl bromide is shown in Scheme 3.

Scheme 1

3a : R=CH₃
3c : R=(CH₂)₇CH₃
3d : R=(CH₂)₁₁CH₃

4a : R=CH₃
4c : R=(CH₂)₇CH₃
4d : R=(CH₂)₁₁CH₃

6a : R=CH₃
6c : R=(CH₂)₇CH₃
6d : R=(CH₂)₁₁CH₃

Scheme 2

All the CTV receptors **6a**, **6b**, **6c**, **6d**, and **6e** were characterized by the ¹H NMR and Mass spectra, and gave correct elemental analysis data. The bowl shapes of the CTV skeletons in these compounds were proven by ¹H NMR spectra, which displayed the typical AB signals for the ArCH₂Ar protons of a bowl-shaped CTV skeleton.

Scheme 3

$$5 \xrightarrow[\text{MeCN, reflux}]{\text{BzBr, K}_2\text{CO}_3}$$

6e
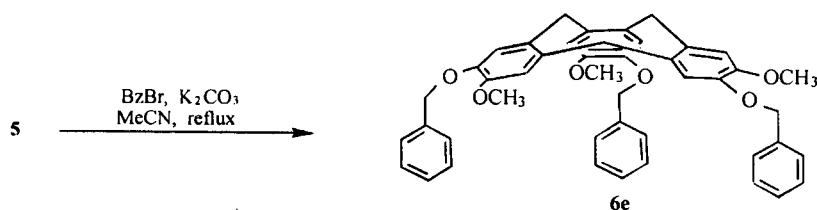
In order to determine the complexation behavior of these CTV derivatives with C_{60}, the stoichiometry of the comlexes between them and C_{60} was investigated with the method of continuous variations. The Job's plot[7] has a maximum at a mole fraction of ~ 0.5, indicative of a 1:1 complex. The absorption spectral change of C_{60} showed an isosbestic point at ~ 587 cm^{-1}. The binding constants of the complexes of **6a—e** with C_{60} in benzene, toluene, or p-xylene were determined at 25 ℃ by measuring the intensity of absorption at 437—438 nm^{-1}. Application of the Benesi-Hildebrand treatment of the spectrophotometric measurements produced the complexation constants,[3d-f, 8] shown in Table 1.

Table 1 Association constants (K, M^{-1}) of CTV receptors **6a-e** with C_{60} at 25 ℃ in arene solvents

CTVs	Benzene	Toluene	p-Xylene
6a	$(9.5 \pm 0.9) \times 10^3$	$(4.9 \pm 0.4) \times 10^4$	$(4.1 \pm 0.2) \times 10^4$
6b	$(4.8 \pm 0.3) \times 10^3$	$(2.5 \pm 0.1) \times 10^4$	$(2.3 \pm 0.2) \times 10^3$
6c	$(7.7 \pm 0.3) \times 10^3$	$(1.2 \pm 0.2) \times 10^4$	$(5.4 \pm 0.4) \times 10^3$
6d	$(2.5 \pm 0.3) \times 10^3$	$(8.3 \pm 0.3) \times 10^3$	$(1.7 \pm 0.2) \times 10^3$
6e	$(1.6 \pm 0.1) \times 10^3$	$(8.7 \pm 0.4) \times 10^3$	$(4.4 \pm 0.1) \times 10^3$

The large complexation constants exhibited in Table 1 reveal that the separation distance between the bowl-shaped CTV unit and the pendant aromatic unit is quite appropriate for efficient encapsulation of C_{60}. It can be found that all the compounds **6a—e** display higher binding ability in toluene than that in benzene or p-xylene, possibly reflecting its relatively higher polarity. Among the ester derivatives, the methyl ester **6a** exhibits the largest complexation constant of $(4.9 \pm 0.4) \times 10^4$ M^{-1} in toluene. It can also be found that the complexation constants decrease with the increase of the aliphatic chain length and even the ethyl derivative **6b** has pronouncedly lower binding ability than **6a**. This general trend demonstrates that the longer aliphatic chains mainly exert steric hindrance on the complexation and do not have the so-called chain effect, which usually promoted the formation of the complexes and had been often revealed in highly polar solutions.[9] The results seem rational considering that the complexation interactions between the CTV receptors and C_{60} were mainly driven by the weak π-π aromatic stacking in arene solvents rather than in highly polar aqueous solution, where a considerably large hydrophobic interaction of the aliphatic chains would be expected to facilitate the complex formation.[10]

In conclusion, we have developed one novel class of CTV receptors with three benzoate pendants for efficient encapsulation of C_{60} via π-π stacking interactions in arene solvents. The existence of methyl ester groups in the benzoate pendants substantially promotes the formation of the complexes, resulting in the largest binding constants, while the receptors bearing ester groups with longer aliphatic chains show lower binding ability, which is attributed to their large steric hindrance.

Experimental

Melting points were uncorrected. ^{1}H NMR spectra were recorded at 300 MHz on a Brucker AM300 instrument with CDCl$_3$ as the solvent and the internal standard, unless noted otherwise. Mass spectra (MS) were recorded on an F-MAT212 instrument. All experiments were carried out under nitrogen atmosphere. Elemental

analysis was carried out at the SIOC analytical center. CTV **5**[5] and methyl toluate **3a**[11] were prepared according to the literature methods. The solvents were dried by using standard methods and toluic acid, octanol, and lauryl alcohol were used as received. The UV absorption spectra were recorded on a Perkin-Elmer UV-vis Lambda spectrometry.

Octyl p-toluate (**3c**)

p-Toluic acid (1.36 g, 10.0 mmol) was dissolved in hot 1-octanol (**2c**, 10 mL) and several drops of H_2SO_4 were added. The solution was refluxed with stirring for 8 h and the product directly purified by column chromatography on silica gel using ether/ethyl acetate (9 : 1) as the eluent. Compound **3c** (2.36 g) was obtained in 95% yield as a colorless oil. ^1H NMR δ: 0.91 (t, J = 6.93 Hz, 3H, CH_3), 1.30—1.49 (m, 10 H, $(CH_2)_5$), 1.72—1.81 (m, 2H, OCH_2CH_2), 2.40 (s, 3H, $ArCH_3$), 4.30 (t, J = 6.8 Hz, 2H, OCH_2), 7.25 (d, J = 8.0 Hz, 2H, ArH) and 7.95 (d, J = 8.0 Hz, 2H, ArH). MS $m/z(\%)$: 249 (M^+ + H). Anal. Calcd $C_{16}H_{24}O_2$: (248.4): C 77.38, H 9.74; found: C 77.61, H, 10.03.

Lauryl p-toluate (**3d**)

This oily compound **3d** was prepared in 98% yield from compound **1** and lauryl alcohol (**2d**) employing the same procedure as that described for compound **3c**. ^1H NMR δ: 0.88 (t, J = 6.8 Hz, 3H, CH_2CH_3), 1.17—1.44 (m, 18H, $(CH_2)_9$), 1.70—1.79 (m, 2H, OCH_2CH_2), 2.38 (s, 3H, $ArCH_3$), 4.29 (t, J = 6.7 Hz, 2H, OCH_2), 7.20 (d, J = 7.8 Hz, 2H, ArH) and 7.93 (d, J = 7.8 Hz, 2H, ArH). MS $m/z(\%)$: 305 (M^+). Anal. Calcd $C_{20}H_{32}O_2$(304.5): C 78.89, H 10.59; found: C 79.05, H 10.54.

Methyl 4-(bromomethyl)benzoate (**4a**)

Methyl *p*-toluate **3a** (1.50 g, 10.0 mmol) was dissolved in tetrachloromethane (25 mL) and bromine (0.90 g, 11.0 mmol) added. The mixture was lighted with stirring by a tungsten lamp (150 W) for 6 h. The solution was then washed with water (5 mL × 2) and saturated brine solution (5 mL), and dried over sodium sulfate. After the solvent was stripped off, the resulting

residue was purified by column chromatography on silica gel using ether/ethyl acetate (1:1) as the eluent. 2.00 g of 4a as a colorless needle in 86% yield. m.p. 53—55℃. ^1H NMR δ: 3.92 (s, 3H, CH_3), 4.49 (s, 2H, CH_2Br), 7.46 (d, J = 4.8 Hz, 2H, ArH), 8.00 (d, J = 4.8 Hz, 2H, ArH). MS $m/z(\%)$: 228 (M^+).

Octyl 4-(bromomethyl)benzoate (**4c**)

Octyl *p*-toluate **3c** (2.25 g, 9.00 mmol) was dissolved in tetrachloromethane (25 mL) and NBS (1.76 g, 10.0 mmol) added. The mixture was lighted with stirring by a 150 W of tungsten lamp for 1 h. The solid produced was filtered off, and the organic phase was washed with water (5 mL × 2) and saturated brine solution (5 mL), and dried over sodium sulfate. After the solvent was removed with a rotavapor, the residue obtained was subject to column chromatography on silica gel with ether/ethyl acetate (4:1) as the eluent. 2.16 g of compound **4c** was obtained as a colorless oil in 73% yield. ^1H NMR δ: 0.88 (t, J = 6.9 Hz, 3H, CH_3), 1.28—1.45 (m, 10H, $(CH_2)_5$), 1.71—1.83 (m, 2H, OCH_2CH_2), 4.32 (t, J = 6.6 Hz, 2H, OCH_2), 4.51 (s, 2H, CH_2Br), 7.46 (d, J = 8.2 Hz, 2H, ArH) and 8.03 (d, J = 8.3 Hz, 2H, ArH). MS $m/z(\%)$: 329 (M^+ + H). Anal. Calcd for $C_{16}H_{23}O_2Br$ (327.3): C 58.72, H 7.08; found: C 58.28, H, 7.23.

Lauryl 4-(bromomethyl)benzoate (**4d**)

This compound **4d** was prepared in 72% yield as a white solid from compound **3d** and bromine using the same procedure as that described for compound **4c**. m.p. 38—40℃. ^1H NMR δ: 0.89 (t, J = 6.9 Hz, 3H, CH_3), 1.27—1.49 (m, 18H, $(CH_2)_9$), 1.68—1.81 (m, 2H, OCH_2CH_2), 4.32 (t, J = 6.7 Hz, 2H, OCH_2), 4.49 (s, 2H, CH_2Br), 7.48 (d, J = 8.4 Hz, 2H, ArH) and 8.03 (d, J = 8.4 Hz, 2H, ArH). MS $m/z(\%)$: 384 (M^+ + H). Anal. Calcd for $C_{20}H_{31}O_2Br$ (383.4): C 62.66, H 8.15; found: C 62.74; H, 8.24.

2, 7, 12-Tri (4-methoxycarbonylbenzyloxy)-3, 8, 13-trimethoxy-10, 15-dihydro-5H-tribenzo [a, d, g] cyclononene (**6a**)

A suspension of CTV **5** (2.40 g, 5.90 mmol), K_2CO_3 (5.00 g, 36.2 mmol) and **4a** (8.00 g, 35.2 mmol) in CH_3CN (200 mL) was refluxed with stirring for 48 h. The solvent was then removed under reduced pressure. The resulting residue was triturated in CH_2Cl_2 (50 mL). The solution was washed with water (10 mL × 2), satuated brine solution (10 mL), and dried (Mg-SO_4). After the solvent was distilled off, the resulting residue was recrystallized from CH_2Cl_2/MeOH, affording 4.30 g of compound **6a** as a white flaky crystal (85%). mp 175—176℃. ^1H NMR δ: 3.62 (s, 9H, CO_2CH_3), 3.49 (d, $J = 13.5$ Hz, 3H, $ArCH_2Ar$), 3.85 (s, 9H, OCH_3), 4.66 (d, $J = 13.5$ Hz, 3H, $ArCH_2Ar$), 5.15(s, 6H, OCH_2), 6.98 and 7.15(s, s, 6H, ArH), 7.55(d, $J = 8.3$ Hz, 6H, ArH), and 7.94 (d, $J = 8.3$ Hz, 6H, ArH). MS $m/z(\%)$: 852 (M^+). Anal. Calcd $C_{51}H_{48}O_{12}$(853.0): C 71.81, H 5.68; found: C 71.70, H, 5.63.

2, 7, 12-*Tri* (4-*n-octoxycarbonylbenzyloxy*)-3, 8, 13-*trimethoxy*-10, 15-*dihydro-5H-tribenzo* [*a* , *d* , *g*] *cyclononene* (**6c**)

This compound **6c** was prepared in 50% yield as a white powder using the same procedure as that described for **6a**. m.p. 118—119℃. ^1H NMR δ: 0.88 (t, $J = 6.7$ Hz, 3H, CH_2CH_3), 1.28—1.42 (m, 10H, $(CH_2)_5$), 1.74—1.79 (m, 2H, OCH_2CH_2), 3.46 (d, $J = 13.8$ Hz, 3H, $ArCH_2Ar$), 3.67 (s, 9H, OCH_3), 4.31 (t, $J = 6.6$ Hz, 6H, OCH_2CH_2), 4.66 (d, $J = 13.8$ Hz, 3H, $ArCH_2Ar$), 5.15 (s, 6H, OCH_2Ar), 6.64 and 6.79 (s, s, 6H, ArH), 7.49 (d, $J = 8.2$ Hz, 6H, ArH) and 8.02 (d, $J = 8.2$ Hz, 6H, ArH). MS $m/z(\%)$: 1187 (M^+ + CH_3CN). Anal. Calcd $C_{72}H_{90}O_{12}$(1147.6): C 75.36, H 7.91; found: C 75.62, H, 7.90.

2, 7, 12-*Tri* (4-*n-dodecoxycarbonylbenzyloxy*)-3, 8, 13-*trimethoxy*-10, 15-*dihydro-5H-tribenzo* [*a* , *d* , *g*] *cyclononene* (**6d**)

This compound **6d** was prepared in 54% yield as a white powder using the same procedure as that described for preparing compound **6a**. mp 120—122℃. ^1H NMR δ: 0.87(t, $J = 6.9$ Hz, 3H, CH_2CH_3), 1.26—1.43 (m, 18H, $(CH_2)_9$), 1.71—1.81 (m, 2H,

OCH_2CH_2), 3.46(d, $J = 13.8$ Hz, 3H, $ArCH_2Ar$), 3.67(s, 9H, OCH_3), 4.31 (t, $J = 6.7$ Hz, 6H, CO_2CH_2), 4.65(d, $J = 13.8$ Hz, 3H, $ArCH_2Ar$), 5.15(s, 6H, OCH_2Ar), 6.63 and 6.78(s, s, 6H, ArH), 7.49(d, $J = 8.3$ Hz, 6H, ArH) and 8.02(d, $J = 8.3$ Hz, 6H, ArH). MS $m/z(\%)$: 1316(M^+ + H). Anal. Calcd $C_{84}H_{114}O_{12}$ (1315.8): C, 76.68; H, 8.73. Found: C, 76.81; H, 8.87.

2, 7, 12-*Tri* (4-*hydroxycarbonylbenzyloxy*)-3, 8, 13-*trimethoxy*-10, 15-*dihydro-5H-tribenzo* [*a* , *d* , *g*] *cyclononene* (7)

A suspension of **6a** (1.80 g, 2.00 mmol) and K_2CO_3 (2.50 g, 18.0 mmol) in aqueous methanol (MeOH/$H_2O = 7:1$, 150 mL) was refluxed with stirring for 20 h. The solvent was then removed. The residue was treated with aqueous 5 mol/L HCl solution (3 mL) and water (30 mL). The suspended solution was stirred at room temperature overnight and then filtered. The solid obtained was washed with water (5 mL × 3), CH_2Cl_2 (5 mL), and then dried in the air. Compound 7 (1.62 g) was obtained as a grey solid in 100% yield. m.p. > 230℃ (decomp.). ^1H NMR (DMSO-d_6) δ: 3.50 (d, $J = 13.4$ Hz, 3H, $ArCH_2Ar$), 3.64 (s, 9H, OCH_3), 4.67 (d, $J = 13.4$ Hz, 3H, $ArCH_2Ar$), 5.14 (s, 6H, OCH_2), 6.99 and 7.16 (s, s, 6H, ArH), 7.54 (d, $J = 8.3$ Hz, 6H, ArH) and 7.93 (d, $J = 8.19$ Hz, 6H, ArH). MS $m/z(\%)$: 811(M^+ + H). Anal. Calcd $C_{48}H_{42}O_{12}$·$0.5H_2O$ (819.9): C 70.32, H 5.29; found: C 70.38, H 5.32.

2, 7, 12-*Tri* (4-*ethoxycarbonylbenzyloxy*)-3, 8, 13-*trimethoxy*-10, 15-*dihydro-5H-tribenzo* [*a* , *d* , *g*] *cyclononene* (**6b**)

Compound 7 (1.54 g, 1.90 mmol) was dissolved in EtOH (50 mL) and several drops of H_2SO_4 were added. The solution was then refluxed with stirring for 72 h and the solvent was evaporated under reduced pressure. The residue obtained was triturated in CH_2Cl_2 (100 mL). The organic phase was washed with water (15 mL × 2), saturated brine solution (10 mL), and dried over sodium sulfate. After work-up, 1.53 g of compound **6b** was obtained in 90% yield as a colorless solid. m.p. 73—74℃. ^1H NMR δ: 1.37—1.42 (m, 9H, CH_3), 3.66 (s, 9H, OCH_3), 3.46 (d, $J = 13.8$

Hz, 3H, ArCH$_2$Ar), 4.34—4.42 (m, 6H, CH$_2$), 4.65 (d, J = 13.8 Hz, 3H, ArCH$_2$Ar), 5.16 (s, 6H, OCH$_2$), 6.62 and 6.78 (s, s, 6H, ArH), 7.49 (d, J = 8.2 Hz, 6H, ArH) and 8.05 (d, J = 8.15 Hz, 6H, ArH). MS m/z(%): 894(M$^+$). Anal. Calcd C$_{54}$H$_{54}$O$_{12}$(895.0): C 72.47, H 6.08; Found: C 72.51, H 5.91. Receptor **6a** could be synthesized from compound **7** in the same way in 91% yield.

2,7,12-Tri (benzyloxy)-3,8,13-trimethoxy-10,15-di-hydro-5H-tribenzo[a,d,g]cyclononene (**6e**)

A suspension of CTV **5** (816 mg, 2.00 mmol), K$_2$CO$_3$ (1.80 g, 13.0 mmol), and benzyl bromide (1.13 g, 6.60 mmol) in acetonitrile (75 mL) was refluxed for 48 h. The solvent was evaporated. The residue obtained was taken with dichloromethane (40 mL) and the organic phase washed with water, brine, and dried (MgSO$_4$). After the solvent was distilled, the residue was recrystallyized from CH$_2$Cl$_2$/CH$_3$OH, affording **6e** (0.97 g, 71%) as a white solid. m.p. 150—152℃. ^{1}H NMR δ: 3.47 (d, J = 13.8 Hz, 3H, ArCH$_2$Ar), 3.69 (s, 9H, CH$_3$), 4.67 (d, J = 13.8 Hz, 3H, ArCH$_2$Ar), 5.12 (s, 6H, OCH$_2$), 6.65 and 6.83 (s, s, 6H, ArH), 7.26—7.42 (m, 15H); MS m/z(%): 679 (M$^+$ + H). Anal. Calcd C$_{45}$H$_{42}$O$_6$ · 0.5H$_2$O (686.0): C 78.58, H 6.30; found: C 78.82, H 5.86.

Job Plot

The stoichiometry of the complex between the receptor **6a** and C$_{60}$ was determined by Job's method. Stock solutions 1.2 × 10^{-4} mol/L in **6a** and C$_{60}$ in toluene were prepared. Nine separate portions of the two solutions were added such that their ratio changed from 0 to 1 while maintaining a total concentration of 1.2 × 10^{-4} mol/L and a volume of 3 mL in the sample cell, respectively. Nine absorption spectra were taken and the change in absorption intensity at 438 cm^{-1} was plotted against the mole fraction of **6a**. The largest absorption change was observed at the mole fraction of ~ 0.5.

Measurement of complexation constants

Complexation constants were determined in arene solvents with a Perkin-Elmer UV-vis Lambda spectrometer at 25 ± 1℃. During the dynamic measurements, the concentration of C$_{60}$ was kept at 1.1 × 10^{-4} mol/L in the sample cell and a calculated amount of the CTV derivative was added to the sample cell and the reference cell, and the absorption was recorded. Additional amount of the receptor then added to the cells, and a spectrum was recorded after each addition. The concentration range of the receptors is 0.0—1.2 × 10^{-4} mol/L and usually 6—10 data were collected. The wavelengths for the maximum intensity changes were selected as 437—438 nm. From the absorption intensities at the wavelengths along with the concentrations of the CTV receptors, the complexation constants and errors in Table 1 were calculated using the Benesi Hildebrand equation from a Microcal Origin 5.0 Software.[12]

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