

Cooperative Recognition of C₆₀-Ammonium Substrates by a Ditopic Oligophenylenevinylene/Crown Ether Host

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Dedicated to the memory of Dr. Bernard Dietrich

Abstract: A new fullerene derivative with an ammonium subunit has been prepared. Its ability to form supramolecular complexes with oligophenylenevinylene derivatives bearing one or two crown ether moieties has been evidenced by electrospray mass spectrometry, and UV-visible and luminescence spectroscopy experiments. Interestingly, the assembly of the C₆₀-ammonium cation with the oligophenylenevinylene derivative bearing two crown ether moieties leads to the cooperative formation of the 2:1 complex owing to intramolecular fullerene–fullerene interactions.

Keywords: cooperative phenomena • crown compounds • fullerenes • pi-conjugated system • supramolecular chemistry

Introduction

Photochemical molecular devices based on the combination of C₆₀ with π -conjugated oligomers have generated significant research activities in the past few years.^[1] In particular, such fullerene-donor arrays have shown interesting excited state properties^[2] and have been used as photovoltaic materials in solar cells.^[3] Whereas a wide range of covalently linked fullerene/ π -conjugated oligomer systems have been reported so far,^[1–3] research focused on related noncovalent assemblies has been probed to a lesser degree.^[4] The use of weak molecular interactions rather than covalent bonds for

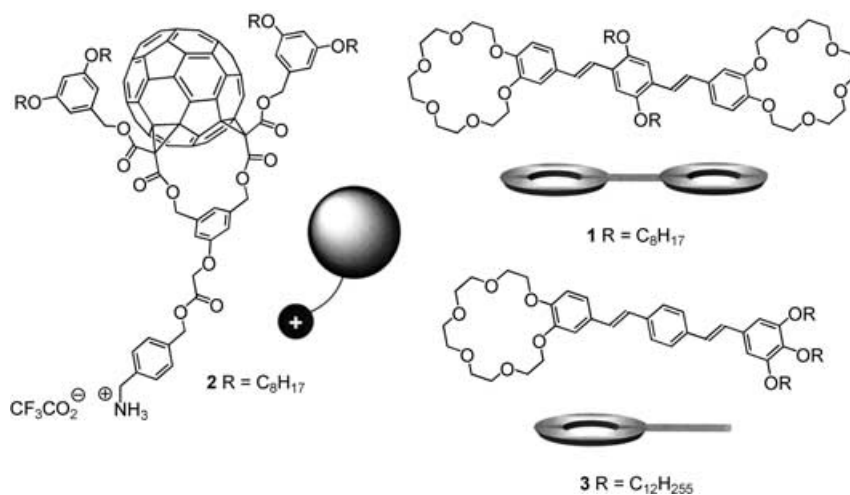
assembling donor and acceptor molecules is, however, particularly attractive,^[5] as illustrated, for example, by numerous noncovalently linked porphyrin–fullerene dyads.^[6] As part of our research on compounds combining C₆₀ with π -conjugated oligomers, we have recently shown that a fullerene derivative bearing an ammonium unit is able to form a supramolecular complex with an oligophenylenevinylene (OPV)/crown ether conjugate by using the well-known ammonium/crown ether interaction.^[7] In this paper, we now report on the assembly of the C₆₀-ammonium cation **2** with an OPV derivative bearing two crown ether moieties **1**. For the sake of comparison, monotopic ligand **3**^[7] with only one crown ether subunit has also been studied. Interestingly, the selective and directional recognition of the ammonium substrates by the ditopic ligand leads to the *cooperative self-assembly* of the 2:1 complex thanks to intramolecular fullerene–fullerene interactions.

Results and Discussion

Synthesis: The preparation of compound **1** is depicted in Scheme 1. Reaction of bis-phosphonate **5**^[8] with aldehyde **4**^[9] in the presence of *t*BuOK in THF afforded the bis(benzocrown ether) derivative **1** in 93% yield. Both ¹H and ¹³C NMR spectra are in full agreement with the centrosymmetric structure of **1**. In particular, a coupling constant of about 17 Hz for the AB system corresponding to the vinylic

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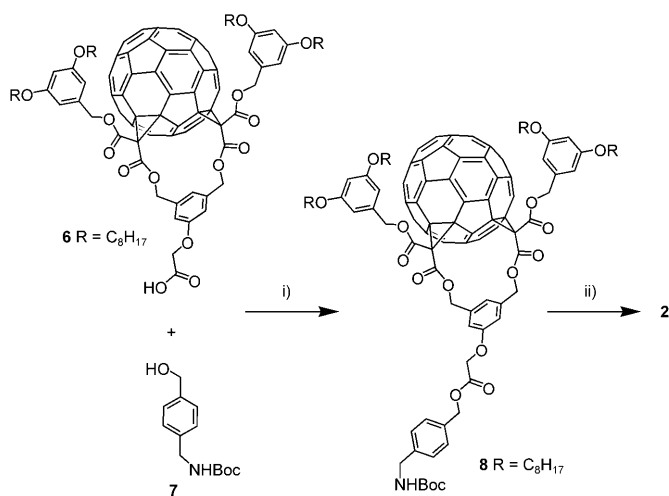
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Scheme 1. Reagents and conditions: i) *t*BuOK, THF, 0°C to RT (93%).

protons in the ^1H NMR spectrum confirmed the *E* stereochemistry of both double bonds in **1**.

The preparation of fullerene derivative **2** is shown in Scheme 2. The C_{5v} -symmetrical fullerene bis-adduct precursor **6** was obtained in ten steps according to a previously reported procedure.^[10] The synthesis of the *tert*-butyloxycarbonyl (Boc)-protected amine **8** was achieved from **6** and **7**^[7] under esterification conditions by using *N,N'*-dicyclohexyl-



Scheme 2. Reagents and conditions: i) DCC, DMAP, HOBt, CH_2Cl_2 , 0°C to RT (61%); ii) CF_3COOH , CH_2Cl_2 , RT (86%).

carbodiimide (DCC), 4-dimethylaminopyridine (DMAP) and 1-hydroxybenzotriazole (HOBt). Finally, removal of the Boc group with $\text{CF}_3\text{CO}_2\text{H}$ afforded the targeted derivative **2** as its trifluoroacetate salt in 86% yield.

Binding studies: The ability of fullerene derivative **2** to form supramolecular complexes with the OPV/crown ether conjugates **1** and **3** was first evidenced by electrospray mass spectrometry (ES-MS). The positive ES mass spectrum recorded from a 1:1 mixture of **2**

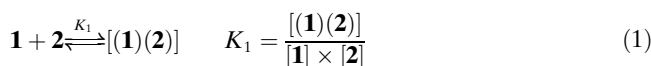
and **3** displayed only one singly charged ion peak at $m/z = 2983.8$ assigned to the 1:1 complex after loss of the trifluoroacetate counteranion (calculated $m/z = 2983.8$). Similarly, the peak corresponding to the supramolecular complex $[(\mathbf{1})(\mathbf{2})_2]$ after loss of the two trifluoroacetate counteranions was observed at $m/z = 2417.8$ (calculated $m/z: 2417.9$) in the spectrum obtained from a mixture of **1** (1 equiv) and **2** (2 equiv). To quantify the interactions between the OPV-based hosts and the C_{60} -ammonium guest, the complexation between **2** and both OPV/crown ether conjugates was further investigated in CH_2Cl_2 by UV-visible absorption binding studies. Thus, titrations of the crown ether derivatives with the ammonium substrate were carried out. The spectral changes occurring upon successive addition of **2** to a CH_2Cl_2 solution of **1** or **3** were monitored; the binding constants derived from these data are summarized in Table 1.

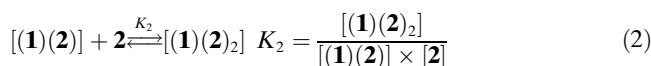
Table 1. Successive stability constants for the OPV- C_{60} conjugates determined in CH_2Cl_2 at $25.0 \pm 0.2^\circ\text{C}$.^[a,b]

	3	1
indirect luminescence titration ^[a,c]		
$\log K_1$	4.80(4)	5.0(1)
$\log K_2$	–	5.6(1)
UV-visible absorption titration ^[b,c]		
$\log K_1$	5.9(8)	5.6(8)
$\log K_2$	–	6.5(2)

[a] **3**: $\lambda_{\text{exc}} = 372 \text{ nm}$; $[\mathbf{3}]_{\text{tot}} = 8.15 \times 10^{-7} \text{ M}$; $0 \leq [\mathbf{2}]_{\text{tot}}/[\mathbf{3}]_{\text{tot}} \leq 13.32$. **1**: $\lambda_{\text{exc}} = 398 \text{ nm}$ $[\mathbf{1}]_{\text{tot}} = 8.12 \times 10^{-7} \text{ M}$; $0 \leq [\mathbf{2}]_{\text{tot}}/[\mathbf{1}]_{\text{tot}} \leq 16.74$. [b] **3**: $l = 2 \text{ cm}$; $[\mathbf{3}]_{\text{tot}} = 4.07 \times 10^{-6} \text{ M}$; $0 \leq [\mathbf{2}]_{\text{tot}}/[\mathbf{3}]_{\text{tot}} \leq 3.7$. **1**: $l = 2 \text{ cm}$; $[\mathbf{1}]_{\text{tot}} = 4.06 \times 10^{-6} \text{ M}$; $0 \leq [\mathbf{2}]_{\text{tot}}/[\mathbf{1}]_{\text{tot}} \leq 6.8$. [c] The errors correspond to standard deviations given as 3σ .

In the case of **1**, the processing of the spectrophotometric data^[6a] led to the determination of two binding constants defined by the equilibria given in Equations (1) and (2).





High stability constants ($\log K_1 = 5.6 \pm 0.8$ and $\log K_2 = 6.5 \pm 0.2$) were found, but due to weak spectral variations, the binding constants were obtained with high errors. Therefore, we decided to take advantage of the efficient quenching of the OPV emission by the C_{60} moiety^[7] upon complexation of **2** with **1** or **3** to determine the K values by luminescence titrations. At this point, it must be emphasized that both intra- and intermolecular quenching processes occur upon addition of **2** to solutions of **1** or **3** in CH_2Cl_2 . All the luminescence experiments were therefore carried out in the presence and in the absence of base in order to always have a suitable reference.^[6a] Indeed, the use of 1,4-diazabicyclo-[2.2.2]octane (DABCO) as a base allows the deprotonation of the ammonium residue in **2** and thereby prevents any recognition processes between the OPV/crown ether conjugates and the fullerene derivative. The partial decrease of luminescence intensity observed in the presence of DABCO (Figure 1) accounts for intermolecular quenching processes

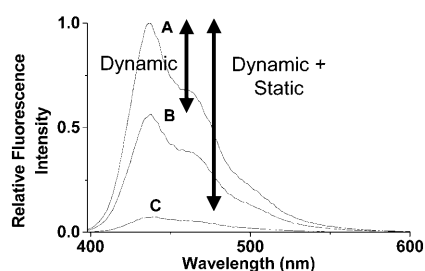


Figure 1. Intra- (static) and intermolecular (dynamic=collisional quenching and reabsorption of the OPV emission by the fullerene derivative) interactions between **1** and **2**. Solvent: CH_2Cl_2 ; $T = 25.0 \pm 0.2^\circ C$; $\lambda_{ex} = 398$ nm; emission and excitation slit widths = 2.8 nm; A) $[1]_{tot} = 8.12 \times 10^{-7}$ M; B) $[2]_{tot}/[1]_{tot} = 16.34$ (+0.02% DABCO (by weight)); C) $[2]_{tot}/[1]_{tot} = 16.34$.

and reabsorption of the OPV luminescence by the fullerene derivative. In contrast, protonation of the terminal amino unit in **2** triggers the recognition event and leads to a larger decrease in luminescence due to both the intramolecular photoinduced processes within the supramolecular assembly and the intermolecular events (collisions and reabsorption). It is worth noting that the luminescence properties of mixtures of **1** and **2** upon addition of DABCO were found to be exactly the same as those of a model mixture of compounds **1** and **8**, which are unable to associate. Indeed, the ammonium function of the fullerene derivative is protected by a Boc group in **8**; this group inhibits any recognition process between **8** and its crown ether partner **1**. This control experiment clearly revealed that even if the concentration of DABCO is rather high under our experimental conditions, its influence as an OPV static or dynamic quencher can be excluded.

To determine the binding constants of both complexes, fluorescence titrations were performed and analyzed according to the modified Stern–Volmer equations [Eq. (3) for **3** and Eq. (4) for **1**] given here.

$$F^0/F = (1 + K_{SV}[2])(1 + K_1[2]) \quad (3)$$

$$F^0/F = (1 + K_{SV}[2])(1 + K_1[2] + K_1K_2[2]^2) \quad (4)$$

In these equations F^0 is the normalized fluorescence intensity of the OPV derivative (**1** or **3**) in the absence of the **2**, F is the fluorescence intensity of the OPV derivative (**1** or **3**) in the presence of **2**, $[2]$ is the molar concentration of fullerene derivative **2**, and K_{SV} the pseudo Stern–Volmer constant. The K_{SV} values for both **1** [$(1.6 \pm 0.2) \times 10^4 M^{-1}$] and **3** [$(1.8 \pm 0.2) \times 10^5 M^{-1}$] were determined from the luminescence titrations carried out under the same experimental conditions in the presence of DABCO according to classical Stern–Volmer treatment.^[11] It is important, however, to note here that the K_{SV} values thus obtained do not correspond to the Stern–Volmer constant of a collisional intermolecular quenching process, since a large part of the decrease in emission intensity is actually due to the reabsorption of the OPV luminescence by the fullerene derivative.

The nonlinear least square fits^[12] of the luminescence data allowed the determination of the binding constants values for both **1** and **3** (Table 1). The fitting of the experimental data obtained for the binding of **2** to **1** according to Equation (4) is shown in Figure 2.

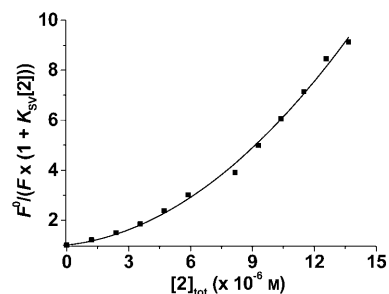


Figure 2. Luminescence titration ($F^0/(F \times (1 + K_{SV}[2]))$) of **1** by **2**. Solvent: CH_2Cl_2 ; $T = 25.0 \pm 0.2^\circ C$; $\lambda_{ex} = 398$ nm; $\lambda_{ana} = 437$ nm; emission and excitation slit widths = 2.8 nm; $[1]_{tot} = 8.12 \times 10^{-7}$ M. The full line corresponds to the nonlinear least squared fit of experimental data according to Equation (4).

The K values determined from indirect luminescence titration are 0.6–1 order of magnitude lower than those obtained from the spectrophotometric titrations (Table 1). These differences can be explained by the weak spectral variations observed in the ground state. However, several key points can be proposed at this stage. It is worth noting that the close values of $\log K_1$ for the monotopic (**3**) and ditopic ligands (**1**). Even if the experimental conditions are different, a strong stabilization of about two orders of magnitude is observed, when the $\log K_1$ values (**1** and **3**) are compared

to those measured for complexes formed between crown ether derivatives and ammonium, alkylammonium, or arylammonium in ethanol or acetonitrile (3.03 ± 0.10 ($C_5H_5NH^+$) $< \log K < 3.59 \pm 0.10$ (NH_4^+)).^[5c,13] Moreover, a sizeable stabilization is also observed with respect to ground-state charge-transfer complexes formed by bis(crown)stilbene and alkyldiammonium or bis(ammonium)viologen substrates ($1.13 < \log K < 9.08$).^[14] A sum of secondary weak interactions like π - π stacking or hydrophobic associations between host **1** or **3** and guest **2** may be proposed to explain this stronger coordination.

For the binding of **2** to the bis(crown ether) substrate **1**, the ratio $K_2/K_1 \approx 4$ is significantly larger than 0.25, which is the value expected for a statistical model of two identical binding sites.^[15] This observation clearly indicates that the stability of the supramolecular complex $[(1)(2)_2]$ is significantly higher than that of its analogue $[(1)(2)]$ due to cooperative recognition processes (Figure 3).

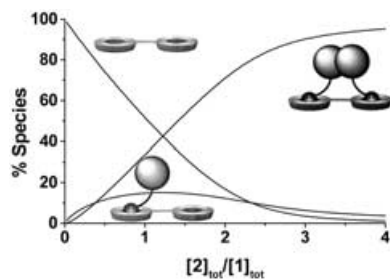


Figure 3. Distribution curves of the oligophenylenevinylene- C_{60} conjugates versus the concentration of **2**. Solvent: CH_2Cl_2 ; $T = 25.0 \pm 0.2^\circ C$; $[1]_{tot} = 4.0 \times 10^{-6} M$; the stability constants determined by fluorescence (Table 1) were taken into account in the calculations.

The apparent bulkiness of substrate **2** is minimized thanks to a long and flexible spacer between the C_{60} core and the terminal ammonium unit. Therefore, the ditopic host **1** is capable of accommodating two C_{60} -ammonium guests either in *syn* or *anti* manner (Figure 4).

Our thermodynamic data suggest a *syn* structure in which the two C_{60} units could strongly interact through π - π stacking interactions, as demonstrated by its ability to self-aggregate, whereas a statistical behavior is expected for an *anti*

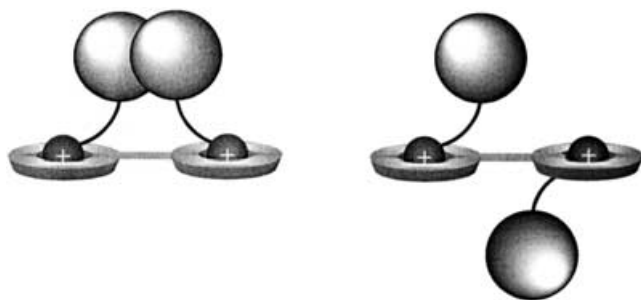


Figure 4. Schematic representation of the *syn* (left) and *anti* (right) conformers of the supramolecular complex $[(1)(2)_2]$.

organization for which no stabilizing interactions could take place.

Conclusion

A new fullerene derivative with an ammonium subunit has been prepared. Its ability to form supramolecular complexes with OPV derivatives bearing one or two crown ether moieties has been evidenced by electrospray mass spectrometry, and UV-visible and luminescence spectroscopy experiments. Interestingly, the assembly of the C_{60} -ammonium cation with the OPV derivative bearing two crown ether moieties leads to the cooperative formation of the 2:1 complex, owing to intramolecular fullerene-fullerene interactions. In conclusion, this work paves the way towards the construction of new stable noncovalent supramolecular arrays, combining π -conjugated systems and fullerene units. Upon a suitable choice of the molecular components, new supramolecular architectures displaying interesting photoinduced intercomponent processes can be designed. Work in this direction is under progress in our laboratories.

Experimental Section

General: All reagents were used as purchased from commercial sources without further purification. Compounds **3**,^[16] **4**,^[9] **5**,^[8] **6**,^[10] and **7**^[7] have been prepared according to previously reported procedures. Solvents were dried using standard techniques prior to use. All reactions were performed in standard glassware under an inert argon atmosphere. Evaporation was done using water aspirator and drying in vacuo at 10^{-2} Torr. Column chromatography: Merck silica gel 60, 40–63 μm (230–400 mesh). TLC: Precoated glass sheets with silica gel 60 F₂₅₄ (Merck), visualization by UV light. Melting points were determined on an electrothermal digital melting point apparatus and are uncorrected. UV-visible spectra (λ_{max} in nm (ϵ)) were measured on a Hitachi U-3000 spectrophotometer. IR spectra (cm^{-1}) were determined on an ATI Mattson Genesis Series FTIR instrument. NMR spectra were recorded on a Bruker AM 300 (300 MHz) with solvent signal as reference. Mass spectrometry measurements were carried out on a Bruker BIFLEXTM matrix-assisted laser desorption time-of-flight mass spectrometer (MALDI-TOF).

Compound 1: *t*BuOK (0.9 g, 8 mmol) was added under argon to a stirred solution of aldehyde **4** (2.50 g, 7.34 mmol) and phosphonate **5** (2.12 g, 3.34 mmol) in dry THF (15 mL) at $0^\circ C$. The mixture was warmed to RT and stirred for 3 h. A small portion of H_2O was slowly added, the mixture was filtered over celite, the crude product was eluted with CH_2Cl_2 , and the solvent was removed under reduced pressure. Recrystallisation from $CHCl_3/EtOH$ (4:1) yielded **1** as a yellow solid (3.17 g, 93%). UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 398 (7791), 344 nm (3539); 1H NMR (300 MHz, $CDCl_3$, $25^\circ C$): δ = 0.89 (t, $^3J(H,H) = 7$ Hz, 6H), 1.30 (m, 16H), 1.55 (m, 4H), 1.87 (m, 4H), 3.70 (s, 8H), 3.73 (m, 8H), 3.79 (m, 8H), 3.95 (m, 8H), 4.04 (t, $^3J(H,H) = 7$ Hz, 4H), 4.21 (m, 8H), 6.87 (d, $^3J(H,H) = 8$ Hz, 2H), 7.04 (d, $^3J(H,H) = 16$ Hz, 2H), 7.09 (m, 6H), 7.32 ppm (d, $^3J(H,H) = 16$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, $25^\circ C$): δ = 14.06, 22.62, 26.26, 29.28, 29.39, 29.49, 31.80, 69.13, 69.19, 69.56, 69.65, 69.69, 70.76, 70.84, 110.59, 112.09, 114.08, 120.23, 121.85, 126.78, 128.35, 131.70, 148.77, 149.04, 150.92 ppm; elemental analysis calcd (%) for $C_{58}H_{86}O_{14}$: C 69.16, H 8.61; found: C 69.19, H 8.74.

Compound 8: DCC (570 mg, 2.8 mmol) was added to a stirred solution of carboxylic acid **6** (250 mg, 0.14 mmol), alcohol **7** (330 mg, 1.4 mmol), and DMAP (17 mg, 0.14 mmol) in CH_2Cl_2 (40 mL) at $0^\circ C$. After 1 h, a catalytic amount of HOBT was added. The mixture was allowed to slowly

warm to RT and then stirred for 3 d, the produced solid was filtered off, and the solution was evaporated. Column chromatography (SiO₂, 100:0.5 CH₂Cl₂/MeOH) yielded **8** (170 mg, 61%) as a red glassy product. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 0.89 (t, ³J(H,H) = 6 Hz, 12H), 1.27 (m, 40H), 1.47 (s, 9H), 1.73 (m, 8H), 3.86 (t, ³J(H,H) = 6 Hz, 8H), 4.33 (d, ³J(H,H) = 6 Hz, 2H), 4.71 (s, 2H), 4.91 (brs, 1H), 5.00 (d, ²J(H,H) = 12 Hz, 2H), 5.22 (s, 2H), 5.29 (AB, ²J(H,H) = 12 Hz, 4H), 5.76 (d, ²J(H,H) = 12 Hz, 2H), 6.37 (t, ⁴J(H,H) = 2 Hz, 2H), 6.48 (d, ⁴J(H,H) = 2 Hz, 4H), 6.77 (brs, 2H), 7.14 (brs, 1H), 7.32 ppm (m, 4H); ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ = 14.10, 22.67, 26.09, 28.39, 29.26, 29.38, 31.82, 49.01, 65.52, 66.83, 67.07, 68.11, 68.69, 70.55, 101.64, 107.15, 112.62, 116.26, 127.68, 128.86, 134.11, 134.40, 135.81, 136.13, 136.54, 137.80, 138.38, 139.65, 140.00, 141.06, 141.15, 142.29, 142.69, 143.17, 143.59, 143.75, 143.97, 144.16, 144.32, 144.60, 144.93, 145.00, 145.18, 145.35, 145.60, 145.73, 146.08, 147.33, 147.45, 147.48, 148.62, 157.82, 160.39, 162.59, 168.36 ppm.

Compound 2: A solution of **8** (140 mg, 0.07 mmol) and CF₃COOH (6 mL) in CH₂Cl₂ (5 mL) was stirred at RT for 2 h. The mixture was then washed with H₂O and dried over MgSO₄. Evaporation to dryness gave **2** (120 mg, 86%) as a red glassy product. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 0.89 (t, ³J(H,H) = 7 Hz, 12H), 1.29 (m, 40H), 1.72 (m, 8H), 3.84 (t, ³J(H,H) = 6 Hz, 8H), 3.91 (brs, 2H), 4.65 (brs, 2H), 5.03 (d, ²J(H,H) = 12 Hz, 2H), 5.19 (s, 2H), 5.28 (brs, 4H), 5.72 (d, ²J(H,H) = 12 Hz, 2H), 6.32 (s, 2H), 6.46 (s, 4H), 6.75 (s, 2H), 7.14 (s, 1H), 7.32 ppm (brm, 4H); ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ = 14.10, 22.66, 26.08, 29.25, 29.37, 31.80, 49.01, 65.32, 66.45, 66.80, 67.07, 68.09, 68.75, 70.52, 101.64, 107.15, 112.43, 115.97, 127.87, 129.35, 132.43, 134.30, 135.73, 136.01, 136.48, 137.76, 138.52, 139.91, 141.02, 141.13, 142.17, 142.60, 143.15, 143.53, 143.70, 143.90, 144.13, 144.22, 144.57, 144.88, 145.00, 145.15, 145.29, 145.56, 145.69, 146.01, 147.30, 147.44, 148.55, 157.69, 160.36, 162.62, 168.63 ppm; MS (MALDI-TOF): *m/z* calcd for [M-CF₃COO]⁺: 1914.2; found: 1914.

Binding studies: Dichloromethane (MERCK, 99.9% for spectroscopy) and DABCO (FLUKA, 95.0%) were used as received. All stock solutions were prepared by using an AG 245 Mettler Toledo analytical balance (precision 0.01 mg) and the complete dissolution in CH₂Cl₂ was obtained with the help of ultrasonic bath. Their concentrations (≈10⁻⁴ M) were calculated by weight. All the solutions were protected from daylight to avoid any photochemical degradation.

UV-visible titrations: The spectrophotometric titration of **1** (4.06 × 10⁻⁶ M) and **3** (4.07 × 10⁻⁶ M) with **2** were carried out in a Hellma quartz optical cell (2 cm). Microvolumes of a concentrated solution of **2** were added to 4 mL of **1** or **3** with microliter Hamilton syringes (#710 and #750). The [2]_{tot}/[1]_{tot} and [2]_{tot}/[3]_{tot} ratios were varied from 0 to 6.8 and from 0 to 3.7, respectively. Special care was taken to ensure that complete equilibrium was attained. The corresponding UV-visible spectra were recorded from 290 to 600 nm on a Kontron Uvikon 941 spectrophotometer maintained at 25.0 ± 0.2 °C by the flow of a Haake NB 22 thermostat. The spectrophotometric data were processed with SPECFIT^[17] program, which adjusted the stability constants and the corresponding extinction coefficients of the species formed at equilibrium. SPECFIT uses factor analyses to reduce the absorbance matrix and extract the eigenvalues prior to the multiwavelength fit of the reduced data set according to the Marquardt algorithm.^[18] The distribution curves of the OPV-C₆₀ conjugates were calculated using the HALTAFALL program.^[19]

Luminescence titration: Luminescence titrations were carried out on solutions of **1** and **3** with an absorbance smaller than 0.1 at wavelengths > λ_{exc} in order to avoid any errors due to the inner filter effect. The titration of 2 mL of **1** (8.12 × 10⁻⁷ M) or **3** (8.15 × 10⁻⁷ M) were carried out in a 1 cm Hellma quartz optical cell by addition of known microvolumes of solution of **2** with microliter Hamilton syringes (#710 and #750). The [2]_{tot}/[1]_{tot} and [2]_{tot}/[3]_{tot} ratios were varied from 0 to 16.34 and from 0 to 13.32, respectively. The excitation wavelengths were set at 398 ± 1 nm for **1** and 372 ± 1 nm for **3**, and correspond to the maximum absorption of the crown ether hosts. The OPV-centred luminescence spectra were recorded from 400 to 800 nm on a Perkin-Elmer LS-50B spectrophotometer maintained at 25.0 ± 0.2 °C by the flow of a Haake FJ thermostat. The slit width was set at 2.8 nm for both excitation and emission. The same ti-

trations were conducted in the presence of DABCO (0.02% by weight) in order to separate the variation of the luminescence intensity which results from dynamic phenomenon. The data sets were processed with Microcal Origin program.^[12]

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