

Fullerene Ylidene Malonate Supramolecular Triads

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This paper describes the synthesis and characterization of novel covalently bound fullerene ylidene malonate dyads in which the linker between the two units is a di-, tri-, or tetra-ethylene glycol unit. The synthesis involves a stepwise, convergent addition of the two components to bis(malonate crown ethers) of increasing overall dimensions through (i) Knoevenagel condensation with (dimethylamino)benzaldehyde and (ii) subsequent Bingel functionalization of the free malonate moiety with C₆₀. These dyads have been spec-

troscopically characterized and studied by UV/Vis spectroscopy. Their ability to form stable complexes with europium triflate, thus forming a complex three-component supramolecular system with UV/Vis absorption characteristics clearly dependent on the overall distance between the interacting units, has been assessed quantitatively.

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Introduction

Compounds combining several photoactive and electroactive species are the subject of active current investigation, since they can exhibit particular new material properties from the electrochemical and photochemical points of view. Monofunctionalized C₆₀ compounds, thanks to their remarkable electron-accepting properties upon photoexcitation, have been incorporated into a wide variety of molecular structures, containing photoactive or electroactive counterparts, to form molecular dyads^[1] and triads.^[2] Well-established methods for the monofunctionalization of C₆₀ have greatly contributed to the attainment of such complex structures for study of their physical and chemical properties.^[3] More recently, C₆₀ has also been introduced in combination with electroluminescent organic conjugated polymers as a component for organic solar cells, with increasingly promising results in terms of overall efficiency.^[4]

In view of the tuneability and of the thermodynamic reversibility of supramolecular interactions, reports relating to systems combining two interacting moieties linked through a noncovalent bond have also begun to appear in the literature.^[5] In particular, one of us has recently reported the synthesis of a methanofullerene bearing an 18-crown-6 derivative, and its photoinduced interaction with an aminoxyl ammonium cation as a guest.^[5c,5d]

We have recently reported that malonate ester and crown ether derivatives functionalized with π -electron-donating conjugated substituents to form ylidene malonate moieties are able to form 1:1 complexes with Lewis acid like metal cations, such as Eu³⁺ in the form of its triflate salt (Fig-

ure 1).^[6,7] The complexation of the metal cation with the 1,3-dicarbonyl system is inferred from NMR and UV/Vis spectroscopic studies, but is also immediately evident from the colorimetric change upon formation of the 1:1 adduct, due to the marked shift of the intramolecular charge-transfer (ICT) band of the “push-pull” chromophore upon binding.

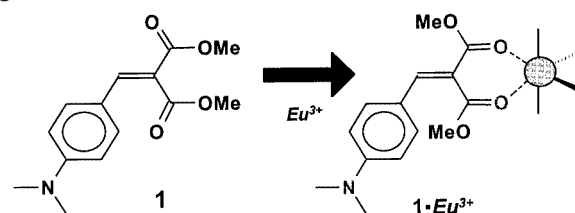


Figure 1. Binding of Eu³⁺ to π -extended “push-pull” compounds

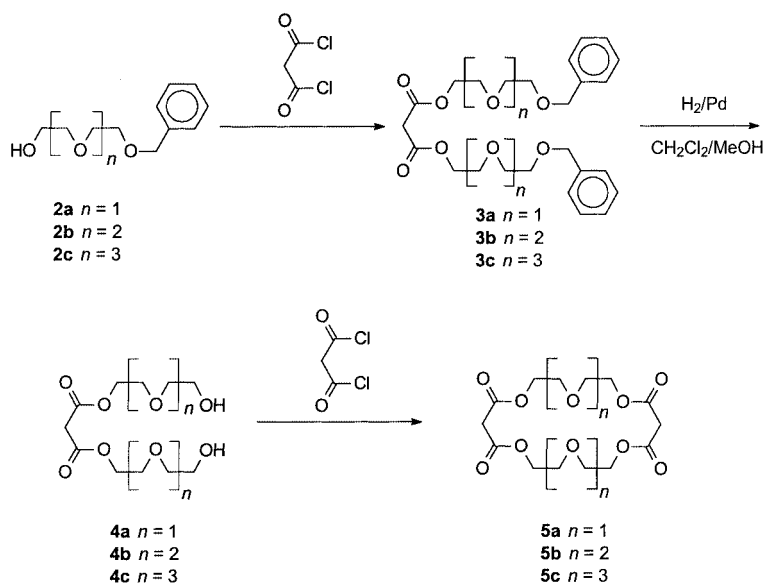
In this paper we describe the synthesis of novel crown ethers containing two malonate units spaced by ethylene glycols of increasing lengths; their stepwise, convergent functionalization to introduce a C₆₀ unit and a π -extended “push-pull” system, and a detailed study of the UV/Vis complexation properties of these novel compounds with europium triflate in organic solutions.

Results and Discussion

Synthesis of the Components

The synthesis of the macrocyclic components is described in Scheme 1. The monobenzyl-protected oligoethylene glycols, synthesized and purified as previously reported,^[8] were treated with malonyl dichloride to give compounds

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Scheme 1. Synthesis of bis(malonate crown ethers) **5a–c**

3a–c, which were purified by column chromatography. Deprotection by hydrogenolysis gave compounds **4a–c** in quantitative yields; these were used directly for the macrocyclization reaction with malonyl dichloride under high-dilution conditions to give crown ethers **5a–c** in good yields (44, 37 and 35% for **5a**, **5b** and **5c**, respectively), after a simple purification procedure and recrystallization.

Crown ether **5a** could also be prepared, according to a procedure reported in the literature,^[9a] by dibutyltin oxide mediated macrocyclization starting from diethylene glycol and malonyl dichloride. The yields of the reaction, however, were consistently substantially lower than those reported (15–20% vs. 33%) and problems were encountered in the removal of the tin by-products. In this case, however, larger cyclic oligomers (the trimeric form) could also be isolated in low yields and unequivocally characterized by mass spectrometry.

The crown ethers showed good solubility characteristics in common organic solvents, and could be treated with *p*-(dimethylamino)benzaldehyde in order to introduce the π -extended “push-pull” system by Knoevenagel condensation (compounds **6a–c**, Scheme 2). The reaction was conducted in toluene in the presence of piperidinium acetate as a catalyst. We found that addition of a slight excess of crown ether with respect to the aldehyde was the best method to obtain the highest yields of monofunctionalized vs. difunctionalized compounds.^[10]

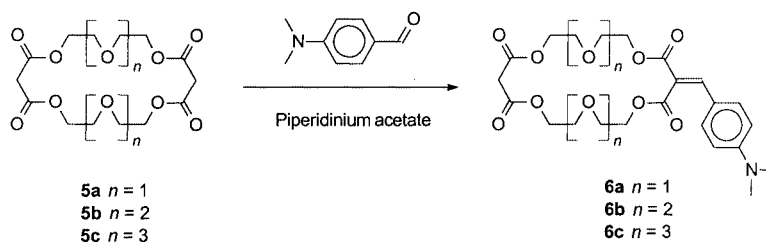
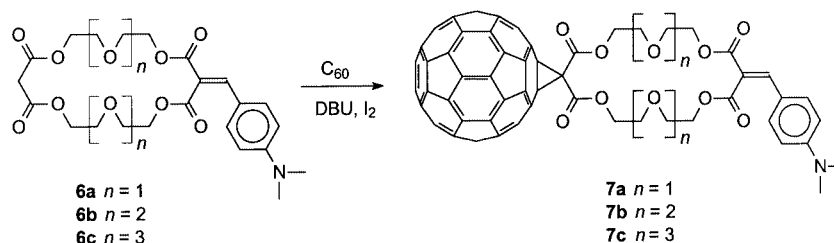
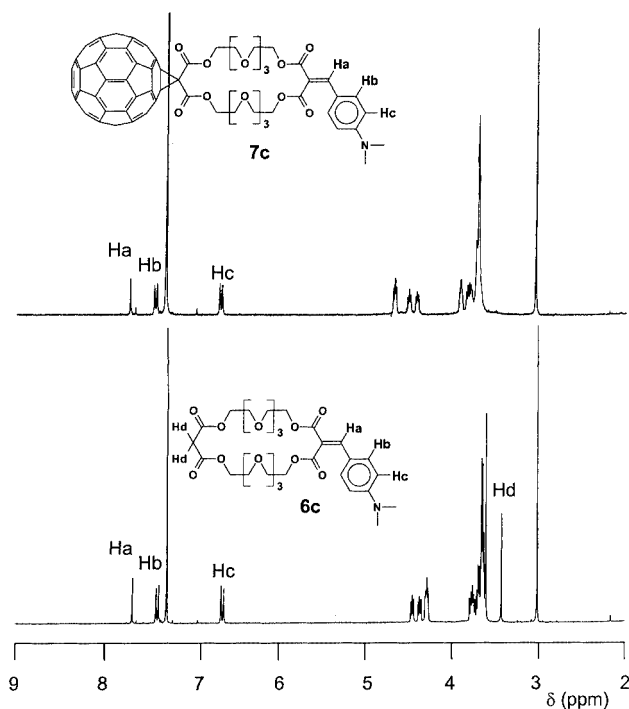
After purification and characterization, the compounds were subjected to the Bingel cyclopropanation procedure^{[3][5b]} for the introduction of C_{60} (Scheme 3). The adducts **7a–c** were then subjected to purification by column chromatography in order to remove small amounts of disubstituted monofullerenated derivatives, followed by precipitation in MeOH and centrifugation. Yields after purifica-

tion were in the order of 35–40%; we believe these yields to be satisfactory in view of the ability of C_{60} to undergo multiple addition in the Bingel reaction,^[11] and also because of the instability of the ylide malonate moiety to strong bases. Compounds **7a–c** were then fully characterized and identified by NMR spectroscopy and by mass spectrometry.

Typical 1H NMR spectra of the precursor **6c** and the fullerene derivative **7c** are shown in Figure 2. The peak corresponding to the free malonate functionality proton resonances ($\delta = 3.45$ ppm) is, as would be expected, present in **6c** and absent in **7c**; the proton resonances corresponding to the “push-pull” aromatic portion do not seem to experience any detectable shift on comparison of **6c** and **7c**. The same applies throughout the series of compounds **6** and **7**, indicating that no substantial π - π stacking interactions are occurring between the two covalently linked π -extended surfaces.

UV/Vis Spectroscopy

Compounds **6a–c** and **7a–c** were all characterized by UV/Vis spectroscopy. The monofunctionalized compounds **6a–c** exist as yellow solids and glasses and each possess an intense intramolecular charge-transfer (ICT) band centred at 380 nm, with molar absorptivity (see also Table 1) in the order of 25000. Upon the introduction of C_{60} , λ_{max} for this transition is slightly shifted (375 nm), but the molar absorptivity remains of the same order of magnitude as above. Since UV/Vis absorption spectra of a methanofullerene derivative bearing an 18-crown-6 derivative^[5c] revealed a very low residual absorbance at 380 nm ($\epsilon_{380} < 2000$), we believe the intensity of the absorption band at this wavelength can be mostly attributed to the ICT of the π -extended “push-pull” system.

Scheme 2. Synthesis of monofunctionalized crown ethers **6a–c**Scheme 3. Synthesis of fullerened derivatives **7a–c**Figure 2. ^1H NMR spectra (CDCl_3 , 300 MHz) of monofunctionalized compound **6c** (bottom), and its fullerened derivative **7c** (top)

Examples of spectrophotometric titrations of compounds **6a–c** and **7a–c** with $\text{Eu}(\text{OTf})_3$ are shown in Figure 3. All titration profiles showed clear, well-defined isosbestic points, indicating the presence of a unique mode of binding in solution,^[12] and could be fitted against a model equation for a 1:1 binding equilibrium by a nonlinear fitting program

(see Exp. Sect.). A $\text{CHCl}_3/\text{MeCN}$ (1:1) mixture was used throughout the titrations in order to solubilize both the fullerened derivatives, which are only sparingly soluble in MeCN, and $\text{Eu}(\text{OTf})_3$, which is not soluble in CHCl_3 . Selected examples of fitting curves and titration data, based on values taken either from the descending ICT of the free compound or from the increasing ICT band of the complex with $\text{Eu}(\text{OTf})_3$, are shown in Figure 4.

Titrations of compounds **6a–c** are very similar in their behaviour: upon complexation, a marked bathochromic shift in the ICT occurs as a consequence of the additional polarisation of the “push-pull” system; λ_{max} of this band is remarkably constant in all these compounds and is located at 480 nm, indicating very similar geometries of interaction of the metal cation with the 1,3-dicarbonyl conjugated moiety of the crown ether. In order to ascertain possible macrocyclic stabilization effects in the binding of the metal cation, the binding constant in pure MeCN was also measured in the case of compound **6b**. As shown in Table 1 (Entry 4 vs. 1), the binding constant of **6b** in pure MeCN is, as should be expected, lower than that measured in $\text{MeCN}/\text{CHCl}_3$, but also essentially identical to that measured for **1**,^[6] thus indicating a negligible stabilization effect from the ethylene glycol oxygen atoms in the binding of $\text{Eu}(\text{OTf})_3$. The same observation could be applied to compound **6a**, since its complexation constant in $\text{MeCN}/\text{CHCl}_3$ is basically identical to that of **6b**.

There is, however, an increase in stability in the 1:1 complex, in which the cavity of the macrocycle is substantially enlarged (compound **6c**, Entry 5 vs. 2 and 3); λ_{max} of the ICT band upon complexation is not detectably different from those recorded for **6a** and **6b**, indicating that the main mode and geometry of coordination in all cases seem to be

Table 1. Thermodynamic stability constants between functionalized crown ethers **6** and **7** and Eu(OTf)₃ in CHCl₃/MeCN (1:1) at 25 °C

Entry ^[a]	Compound	$\epsilon_{\text{free ligand}}$ ^[b]	$\log K_a$	λ_{max} [nm]	$\epsilon_{\text{complex}}$ ^[c]
1	1 ^[d] ^[e]	33100 (380) ^[d]	2.60 ± 0.05 ^[d,e]	478 ^[d]	7600(480 nm) ^[d,e]
2	6a	28100 (380)	3.1 ± 0.1	480	6800 ± 400 (480 nm)
3	6b	22800 (380)	2.9 ± 0.1	480	6900 ± 1200 (480 nm)
4	6b ^[d]	22100 (380) ^[d]	2.7 ± 0.2 ^[d]	480 ^[d]	9600(480 nm) ^[d]
5	6c	20100 (380)	4.65 ± 0.05	480	13300 ± 3800 (480 nm)
6	7a	17100 (375)	2.75 ± 0.05	480	N.a. (480 nm) ^[f]
7	7b	46100 (375)	2.7 ± 0.2	480	7200 ± 1000 (480 nm)
8	7c	39500 (375)	3.1 ± 0.1	480	9800 ± 400 (480 nm)

[a] All values for the stability constants are in M⁻¹. The values reported are the average of four independent titrations, with all nonlinear regressions giving high confidence outputs ($r^2 > 0.99$). [b] Molar absorptivity and λ_{max} (in parentheses) for the intermolecular charge-transfer (ICT) band related to the free ligand. [c] Molar absorptivity at λ_{max} (in parentheses) for the intramolecular charge-transfer (ICT) band related to the complex with Eu(OTf)₃. [d] As determined in MeCN. [e] Data taken from ref.^[6] [f] Not applicable. The ICT was too weak in intensity to provide reliable results for the molar absorptivity and K_a to fit the data taken at this wavelength to the equation shown in the Exp. Sect. See also text for details.

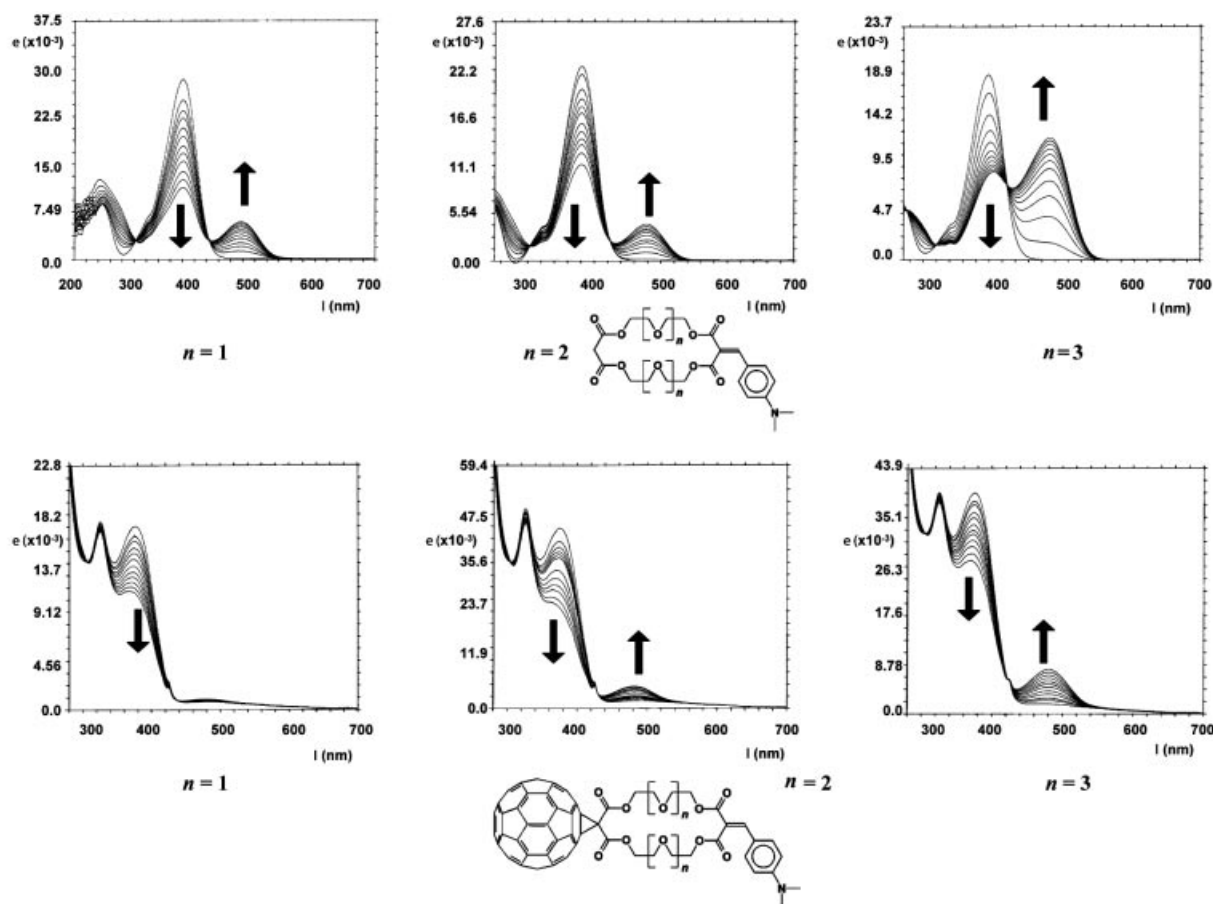


Figure 3. UV/Vis spectroscopic titrations of compounds **6a–c** and compounds **7a–c** in CHCl₃/MeCN (1:1); the arrows indicate the disappearance, with addition of increasing amounts of Eu(OTf)₃, of the intramolecular charge-transfer (ICT) band associated with compounds **6a–c** and dyads **7a–c**, and increase of new ICT bands associated with the 1:1 complexes with Eu(OTf)₃

very similar, and consistent with the model proposed for compound **1** and illustrated schematically in Figure 1.

The titration profiles related to compounds **7a–c** with Eu(OTf)₃ are shown in Figure 3 (bottom row). In the cases of compounds **7a** and **7b**, the relative thermodynamic

stability constants for the 1:1 binding with Eu(OTf)₃ are comparable. In the case of compound **7c**, analogously to what was observed for **6c**, the association constant is consistently larger. Furthermore, on comparing the series of compounds **7** to **6**, the introduction of C₆₀ brings about a

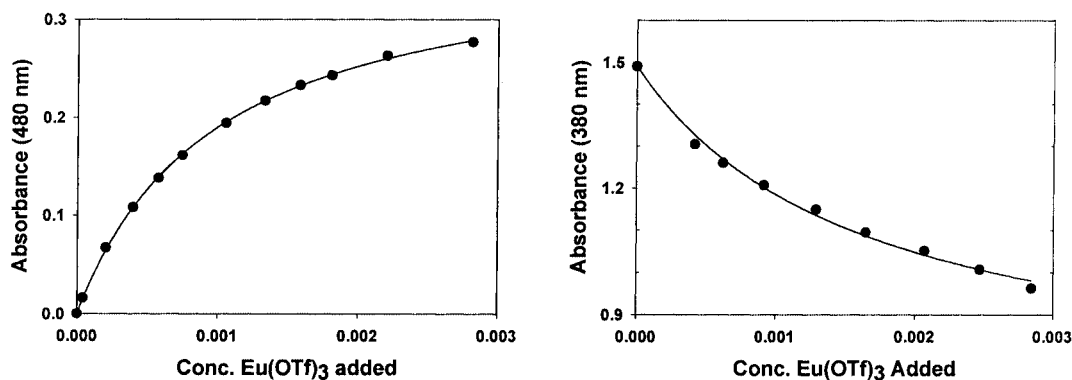


Figure 4. Selected examples of titration profiles for compounds **6b** (left) and **7a** (right) with Eu(OTf)₃; titrations were conducted and evaluated under the conditions reported in the Exp. Sect. and summarized in Table 1

reduction in the relative stability constants, probably as a result either of conformational locking of the crown ether (because of the introduction of the cyclopropane-fullerenated substituent) or of steric interactions; once again, the predominant mode of coordination of the metal cation seems to be directed to the 1,3-dicarbonyl π -conjugated system.

A point of great interest is represented by the dramatic reduction in the intensity of the ICT upon complexation with Eu³⁺ in the case of compound **7a** (Figure 3, bottom left corner). Since the maximum of this band is still located at 480 nm, one can exclude effects such as π - π stacking phenomena, which would result in an energetic change, and therefore also a change of λ_{max} in the UV/Vis spectrum for this transition. One stimulating possible explanation is that the overall geometry of the molecule is severely perturbed upon complexation and renders this spectroscopic transition formally forbidden by symmetry consideration, and only weakly allowed by vibronic coupling;^[13] in the case of **7a**, in which the ring size is probably too small for the methanofullerene moiety to flip freely around the complexed Eu(OTf)₃, the overall symmetry plane of the molecule is effectively lost. In the cases of **7b** and **7c**, possessing overall longer ethylene glycol spacers between the two units, in contrast, the average symmetry plane of the molecule is still present even upon complexation.

Conclusions

This work describes the synthesis of novel symmetrical malonate crown ethers incorporating ethylene glycol units of varying lengths. Obtained in good yields after simple recrystallization of the reaction mixtures, these compounds are useful scaffolds for the construction of molecular dyads, incorporating C₆₀ and “push-pull” systems, and, upon complexation with Eu(OTf)₃, of supramolecular three-component systems. Their spectroscopic properties are clearly dependent on the overall distance between the two covalently linked components, and are drastically modified by the coordination of the Eu(OTf)₃ to the 1,3-dicarbonyl π -

conjugated system. The presence of the C₆₀ unit is not detrimental to efficient coordination of the metal cation to these conjugated systems. Given the noteworthy emission properties of europium,^[14] and the potential of fullerene derivatives in optical applications,^[15] we aim to explore the use of this novel class of compounds for material applications.

Experimental Section

General Remarks: All commercially available compounds were purchased from Aldrich and used as received. Benzene (Na), THF (CaH₂) and CH₂Cl₂ (CaH₂) were dried and distilled before use. Compound **1**,^[6] triethylene glycol monobenzyl ether **2b**^[8] and tetraethylene glycol monobenzyl ether **2c**^[8] were prepared according to literature procedures. ¹H and ¹³C NMR spectra were recorded from solutions in CDCl₃ or CD₃CN with Bruker 200 or AMX 300 instruments with the solvent residual proton signal or tetramethylsilane (TMS) as a standard. Infrared spectra were recorded with a Perkin–Elmer 881 instrument from NaCl disks. Mass spectra were recorded with an Electrospray Ionization instrument LCQ Decca (ThermoFinnigan). The UV/Vis spectroscopic studies were conducted with a Perkin–Elmer Lambda 5 spectrophotometer. Melting points were recorded with a Büchi 510 apparatus and are uncorrected.

General Procedure for the Preparation of Diols 4a–c: A solution of oligoethylene glycol monobenzyl ether (81 mmol) in dry benzene (30 mL) was added dropwise at 35–40 °C over a 1-h period to a solution of malonyl chloride (5.6 g, 40 mmol) in dry benzene (50 mL). The solution was then heated under reflux for an additional 2 h. After it had then cooled to room temperature, H₂O (50 mL) and a saturated aqueous NaHCO₃ solution were added until neutrality. The aqueous phase was extracted with Et₂O (3 × 70 mL) and dried (MgSO₄). The crude product was purified by column chromatography (SiO₂; C₆H₁₂/EtOAc). Pd (10 wt-% on activated carbon, ca. 10 wt-% relative to substrate) was added to a solution of the malonate ester of diethylene glycol monobenzyl ether (8 mmol) in dry EtOH (30 mL), and the resulting suspension was subjected to hydrogenolysis at room temperature and pressure with vigorous stirring. After filtration, the solvent was removed in vacuo to give the product (in nearly quantitative yield), which was used for the following steps without further purification.

Compound 4a: This compound was produced from diethylene glycol monobenzyl ether (**2a**) (16 g, 81.6 mmol) and malonyl chlor-

ide (5.6 g, 40 mmol). Purified by column chromatography (SiO_2 ; $\text{C}_6\text{H}_{12}/\text{EtOAc}$, 70:30), **3a** was obtained as a pale yellow oil (13.9 g, 75%). IR: $\tilde{\nu} = 1740\text{ cm}^{-1}$ ($\nu_{\text{C=O}}$). ^1H NMR (CDCl_3): $\delta = 7.4\text{--}7.2$ (m, 10 H, ArH), 4.6 (s, 4 H, $-\text{CH}_2\text{--Ph}$), 4.3 (m, 4 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$), 3.8–3.6 (m, 12 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$ and $-\text{OCH}_2\text{CH}_2\text{O}-$), 3.45 (s, 2 H, $-\text{OOCCH}_2\text{COO}-$). From **3a** (3.68 g, 8 mmol), **4a** was obtained as a colourless oil (2.17 g, 97%). IR: $\tilde{\nu} = 3240$ (ν_{OH}), 1735 cm^{-1} ($\nu_{\text{C=O}}$). ^1H NMR (CDCl_3): $\delta = 4.4\text{--}4.3$ (m, 4 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$), 3.65 (m, 4 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$), 3.45 (s, 2 H, $-\text{OOCCH}_2\text{COO}-$), 3.3–3.2 (m, 8 H, $-\text{OCH}_2\text{CH}_2\text{O}-$), 2.85 (s, 2 H, $-\text{OH}$).

Compound 4b: This compound was produced from **2b** (15.5 g, 65 mmol) and malonyl dichloride (4.5 g, 32 mmol). Purified by column chromatography (SiO_2 ; $\text{C}_6\text{H}_{12}/\text{EtOAc}$, 40:60), **3b** was obtained as a clear oil (13.9 g, 80%). IR: $\tilde{\nu} = 1754\text{ cm}^{-1}$ ($\nu_{\text{C=O}}$). ^1H NMR (CDCl_3): $\delta = 7.4\text{--}7.2$ (m, 10 H, ArH), 4.55 (s, 4 H, $-\text{CH}_2\text{--Ph}$), 4.3–4.2 (m, 4 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$), 3.75–3.6 (m, 20 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$ and $-\text{OCH}_2\text{CH}_2\text{O}-$), 3.42 (s, 2 H, $-\text{OOCCH}_2\text{COO}-$) ppm. From **3b** (4.38 g, 8 mmol), **4b** was obtained as a colourless oil (2.8 g, 95%). IR: $\tilde{\nu} = 3330$ (ν_{OH}), 1754 cm^{-1} ($\nu_{\text{C=O}}$). ^1H NMR (CDCl_3): $\delta = 4.35$ (m, 4 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$), 3.79–3.71 (m, 20 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$ and $-\text{OCH}_2\text{CH}_2\text{O}-$), 3.40 (s, 2 H, $-\text{OOCCH}_2\text{COO}-$), 2.9 (s, 2 H, $-\text{OH}$) ppm.

Compound 4c: This compound was produced from **2c** (8.7 g, 31 mmol) and malonyl dichloride (2 g, 14.3 mmol). Purified by column chromatography (SiO_2 ; $\text{C}_6\text{H}_{12}/\text{EtOAc}$, 30:70), **3c** was obtained as a clear oil (7.3 g, 80%). IR: $\tilde{\nu} = 1735$, 1752 cm^{-1} ($\nu_{\text{C=O}}$). ^1H NMR (CDCl_3): $\delta = 7.4\text{--}7.2$ (m, 10 H, ArH), 4.55 (s, 4 H, $-\text{CH}_2\text{--Ph}$), 4.3–4.2 (m, 4 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$), 3.75–3.6 (m, 28 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$ and $-\text{OCH}_2\text{CH}_2\text{O}-$), 3.45 (s, 2 H, $-\text{OOCCH}_2\text{COO}-$) ppm. From **3c** (5.1 g, 8 mmol), **4c** was obtained as a colourless oil (3.5 g, 96%). IR: $\tilde{\nu} = 3330$ (ν_{OH}), 1735 , 1752 cm^{-1} ($\nu_{\text{C=O}}$). ^1H NMR (CDCl_3): $\delta = 4.3$ (m, 4 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$), 3.72–3.6 (m, 28 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$ and $-\text{OCH}_2\text{CH}_2\text{O}-$), 3.46 (s, 2 H, $-\text{OOCCH}_2\text{COO}-$), 2.79 (s, 2 H, $-\text{OH}$) ppm.

General Procedure for the Synthesis of Crown Ethers: The reaction was conducted under high-dilution conditions by slow addition, from two identical dropping funnels, of solutions of the appropriate diol and malonyl dichloride in dry toluene/THF (1:1, 80 mL) and toluene (80 mL), respectively, into toluene (400 mL) at 55°C . Additions were carried out over a period of 8–10 h. The reaction vessel was equipped with an NaOH trap. The reaction mixture was vigorously stirred for 2 d, and then cooled to room temperature. After neutralisation, the solvent was distilled off in vacuo, and the waxy residue was thoroughly washed with Et_2O to provide **5a–c** as white solids.

Compound 5a: This compound was produced from diol **4a** (5.17 g, 20 mmol) and malonyl dichloride (3.1 g, 22 mmol) and was obtained as white needles (3.1 g, 44%). M.p. $88\text{--}89^\circ\text{C}$ (EtOAc) (ref.^[9a] $67\text{--}69^\circ\text{C}$). ^1H NMR and mass spectroscopic data are identical to those reported in the literature.^[9b] ^{13}C NMR (CDCl_3): $\delta = 166.6$, 69.2 , 65.1 , 42.0 ppm.

Compound 5b: This compound was produced from diol **4b** (5.5 g, 15 mmol) and malonyl dichloride (2.3 g, 16 mmol) and was obtained as white prisms (2.95 g, 37%). M.p. $80\text{--}81^\circ\text{C}$ (EtOAc). IR: $\tilde{\nu} = 1728\text{ cm}^{-1}$ ($\nu_{\text{C=O}}$). ^1H NMR (CDCl_3): $\delta = 4.32$ (m, 8 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$), 3.72 (m, 8 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$), 3.67 (m, 8 H, $-\text{OCH}_2\text{CH}_2\text{O}-$), 3.47 (s, 4 H, $-\text{OOCCH}_2\text{COO}-$) ppm. ^{13}C NMR (CDCl_3): $\delta = 166.2$, 70.4 , 68.6 , 64.4 , 41.2 ppm. MS (EI): m/z

$(\%) = 459.4$ (100) $[\text{M} + \text{Na}]^+$. $\text{C}_{18}\text{H}_{28}\text{O}_{12}$ (436.2): calcd. C 49.54, H 6.42; found C 49.32, H 6.74.

Compound 5c: This compound was produced from diol **4c** (5.25 g, 11.5 mmol) and malonyl dichloride (1.83 g, 13 mmol) and was obtained as white needles (2.10 g, 35%). M.p. $59\text{--}60^\circ\text{C}$ (iPrOH). IR: $\tilde{\nu} = 1744$, 1725 cm^{-1} ($\nu_{\text{C=O}}$). ^1H NMR (CDCl_3): $\delta = 4.32$ (m, 8 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$), 3.72 (m, 8 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$), 3.67 (m, 16 H, $-\text{OCH}_2\text{CH}_2\text{O}-$), 3.47 (s, 4 H, $-\text{OOCCH}_2\text{COO}-$) ppm. ^{13}C NMR (CDCl_3): $\delta = 166.3$, 70.3 , 68.5 , 64.4 , 61.2 , 41.0 ppm. MS (EI): m/z ($\%$) = 563.4 (42) $[\text{M} + \text{K}]^+$, 547.4 (100) $[\text{M} + \text{Na}]^+$. $\text{C}_{22}\text{H}_{36}\text{O}_{14}$ (524.5): C 50.37, H 6.92; found C 50.05, H 7.10.

Preparation of Monofunctionalized 6a–c: A solution of the crown ether (1 mmol) and piperidinium acetate (10 mg) in dry benzene (20 mL) was brought to reflux in a flask fitted with a Dean–Stark apparatus. A solution of *p*-(dimethylamino)benzaldehyde (0.8 mmol) in dry benzene (20 mL) was added dropwise over a 2-h period. Heating under reflux was maintained for an additional 24 h. The solvent was removed in vacuo and the residue was purified by column chromatography. By-products obtained from condensation on both malonate moieties were also isolated and characterized and will be described elsewhere.

Compound 6a: This compound was produced from crown ether **5a** (520 mg, 1.5 mmol) and *p*-(dimethylamino)benzaldehyde (150 mg, 1 mmol), purified by column chromatography (SiO_2 ; toluene/MeCN, 4:1 to 2:1) and obtained as a yellow solid (130 mg, 230 mg of recovered **5a**, 79%). M.p. $97\text{--}99^\circ\text{C}$ (EtOH). IR: $\tilde{\nu} = 1720\text{ cm}^{-1}$ ($\nu_{\text{C=O}}$). ^1H NMR (CDCl_3): $\delta = 7.69$ (s, 1 H, $-\text{CH}=\text{C}-$), 7.4 (m, 2 H, Ar-H), 6.65 (m, 2 H, Ar-H), 4.46–4.37 (m, 4 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$), 4.31 (m, 4 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$), 3.84–3.75 (m, 8 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$), 3.44 (s, 2 H, $-\text{OOCCH}_2\text{COO}-$), 3.05 [s, 6 H, $-\text{N}(\text{CH}_3)_2$] ppm. ^{13}C NMR (CDCl_3): $\delta = 167.7$, 166.6 , 166.0 , 164.7 , 151.9 , 143.8 , 132.2 , 132.0 , 119.8 , 118.7 , 111.8 , 111.5 , 69.3 , 69.0 , 68.8 , 65.1 , 64.8 , 64.6 , 41.8 , 39.8 ppm. UV/Vis ($\text{CHCl}_3/\text{MeCN}$, 1:1): λ_{max} (ϵ) = 380 nm (28100). $\text{C}_{23}\text{H}_{29}\text{NO}_{10}$ (479.3): calcd. C 57.61, H 6.10, N 2.92; found C 57.4, H 6.25, N 2.8. MS (EI): m/z ($\%$) = 480.5 (23) $[\text{M} + \text{H}]^+$, 502.4 (100) $[\text{M} + \text{Na}]^+$.

Compound 6b: This compound was produced from crown ether **5b** (440 mg, 1 mmol) and *p*-(dimethylamino)benzaldehyde (120 mg, 0.8 mmol), purified by column chromatography (SiO_2 ; $\text{C}_6\text{H}_{12}/\text{EtOAc}$, 30:70) and obtained as a yellow oil (300 mg, 150 mg of recovered **5b**, 80%). IR: $\tilde{\nu} = 1720\text{ cm}^{-1}$ ($\nu_{\text{C=O}}$). ^1H NMR (CDCl_3): $\delta = 7.65$ (s, 1 H, $-\text{CH}=\text{C}-$), 7.38 (m, 2 H, Ar-H), 6.65 (m, 2 H, Ar-H), 4.48–4.40 (m, 4 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$), 4.32 (m, 4 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$), 3.83–3.6 (m, 16 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$), 3.42 (s, 2 H, $-\text{OOCCH}_2\text{COO}-$), 3.05 (s, 6 H, $-\text{N}(\text{CH}_3)_2$) ppm. ^{13}C NMR (CDCl_3): $\delta = 167.5$, 166.1 , 164.6 , 151.7 , 143.4 , 131.8 , 119.9 , 118.8 , 111.4 , 70.5 , 70.4 , 68.9 , 68.6 , 68.6 , 64.5 , 64.4 , 64.3 , 41.3 , 39.8 ppm. UV/Vis ($\text{CHCl}_3/\text{MeCN}$, 1:1): λ_{max} (ϵ) = 380 nm (22800). $\text{C}_{27}\text{H}_{37}\text{NO}_{12}$ (567.2): calcd. C 57.14, H 6.52, N 2.47; found C 56.87, H 6.72, N 2.32.

Compound 6c: This compound was produced from crown ether **5c** (520 mg, 1 mmol) and *p*-(dimethylamino)benzaldehyde (100 mg, 0.7 mmol), purified by column chromatography (SiO_2 ; toluene/MeCN, 2:1 to 1:1) and obtained as a yellow oil (270 mg, 140 mg of recovered **5c**, 60%). IR: $\tilde{\nu} = 1720\text{ cm}^{-1}$ ($\nu_{\text{C=O}}$). ^1H NMR (CDCl_3): $\delta = 7.68$ (s, 1 H, $-\text{CH}=\text{C}-$), 7.40 (m, 2 H, Ar-H), 6.64 (m, 2 H, Ar-H), 4.48–4.39 (m, 4 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$), 4.32 (m, 4 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$), 3.79–3.62 (m, 24 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$), 3.46 (s, 2 H, $-\text{OOCCH}_2\text{COO}-$), 3.05 [s, 6

H, $-\text{N}(\text{CH}_3)_2$ ppm. ^{13}C NMR (CDCl_3): δ = 167.4, 166.2, 164.5, 151.1, 143.1, 131.8, 121.0, 119.6, 112.1, 70.4, 68.8, 68.6, 64.5, 41.2, 40.3 ppm. UV/Vis ($\text{CHCl}_3/\text{MeCN}$, 1:1): λ_{max} (ϵ) = 380 nm (20100). MS (EI): m/z (%) = 694.5 (41) $[\text{M} + \text{K}]^+$, 678.6 (100) $[\text{M} + \text{Na}]^+$. $\text{C}_{31}\text{H}_{45}\text{NO}_{14}$ (655.3): calcd. C 56.78, H 6.92, N 2.14; found C 57.05, H 6.72, N 2.25.

General Procedure for the Preparation of Methanofullerenes: A solution of DBU (0.5 mmol) in toluene (5 mL) was added dropwise to a solution of the crown ether (0.2 mmol), C_{60} (0.2 mmol) and I_2 (0.2 mmol) in toluene (130 mL). Stirring under nitrogen was continued for 12 h. The product was purified by column chromatography (SiO_2 ; toluene, then toluene/*i*PrOH, 98:2), and then dissolved in a minimum amount of CH_2Cl_2 , precipitated with MeOH and centrifuged. The solvent was then removed and the solid was dried under high vacuum.

Compound 7a: This compound was produced from crown ether **6a** (77 mg, 0.16 mmol), C_{60} (115 mg, 0.16 mmol), I_2 (41 mg, 0.16 mmol) and DBU (61 mg, 0.4 mmol) and was obtained as a dark red solid (50 mg, 26%). M.p. > 250 °C. ^1H NMR (CDCl_3): δ = 7.72 (s, 1 H, $-\text{CH}=\text{C}-$), 7.4 (m, 2 H, Ar-*H*), 6.65 (m, 2 H, Ar-*H*), 4.63 (m, 4 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$), 4.56–4.43 (m, 4 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$), 4–3.88 (m, 8 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$), 3.05 [s, 6 H, $-\text{N}(\text{CH}_3)_2$] ppm. ^{13}C NMR (CDCl_3): δ = 164.8, 163.4, 152.0, 145.1, 144.6, 144.0, 143.8, 142.9, 142.1, 141.8, 140.8, 139.0, 137.5, 132.1, 119.8, 118.6, 111.5, 69.6, 69.1, 69.0, 68.8, 66.8, 66.4, 65.0, 64.8, 39.9 ppm. UV/Vis ($\text{CHCl}_3/\text{MeCN}$, 1:1): λ_{max} (ϵ) = 375 nm (17100).

Compound 7b: This compound was produced from crown ether **6b** (90 mg, 0.16 mmol), C_{60} (150 mg, 0.21 mmol), I_2 (43 mg, 0.17 mmol) and DBU (64 mg, 0.42 mmol), and was obtained as a dark red solid (70 mg, 35%). M.p. > 250 °C. ^1H NMR (CDCl_3): δ = 7.72 (s, 1 H, $-\text{CH}=\text{C}-$), 7.4 (m, 2 H, Ar-*H*), 6.65 (m, 2 H, Ar-*H*), 4.66 (m, 4 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$), 4.54–4.39 (m, 4 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$), 3.96–3.73 (m, 16 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$ and $-\text{OCH}_2\text{CH}_2\text{O}-$), 3.05 [s, 6 H, $-\text{N}(\text{CH}_3)_2$] ppm. ^{13}C NMR (CDCl_3): δ = 167.8, 164.8, 163.4, 151.6, 145.3, 145.2, 145.1, 144.9, 144.7 $\times$ 3, 144.6, 143.9, 143.6, 143.1, 143.0 $\times$ 2, 142.2, 141.9 $\times$ 2, 141.0, 139.3, 132.1, 112.1, 71.4, 72.0, 70.8, 70.6, 70.1, 70.0, 69.9, 66.4, 65.7, 64.5, 40.3 ppm. UV/Vis ($\text{CHCl}_3/\text{MeCN}$, 1:1): λ_{max} (ϵ) = 375 nm (46100). MS (EI): m/z (%) = 1309.4 (47) $[\text{M} + \text{Na}]^+$.

Compound 7c: This compound was produced from crown ether **6c** (120 mg, 0.18 mmol), C_{60} (144 mg, 0.2 mmol), I_2 (51 mg, 0.2 mmol) and DBU (61 mg, 0.4 mmol), and was obtained as a dark red solid (67 mg, 27%). M.p. > 250 °C. ^1H NMR (CDCl_3): δ = 7.72 (s, 1 H, $-\text{CH}=\text{C}-$), 7.4 (m, 2 H, Ar-*H*), 6.65 (m, 2 H, Ar-*H*), 4.64 (m, 4 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$), 4.52–4.38 (m, 4 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$), 3.93–3.65 (m, 16 H, $-\text{COOCH}_2\text{CH}_2\text{O}-$ and $-\text{OCH}_2\text{CH}_2\text{O}-$), 3.05 [s, 6 H, $-\text{N}(\text{CH}_3)_2$] ppm. ^{13}C NMR (CDCl_3): δ = 167.7, 164.8, 163.5, 145.3, 145.3, 145.2, 145.0, 144.8, 144.7, 144.0, 143.1, 143.1, 143.0, 142.3, 141.9, 141.0, 139.2, 139.1, 132.1, 71.5, 70.9, 70.8, 70.8, 70.8, 69.2, 68.9, 68.9, 66.4, 65.0, 65.0, 64.8, 64.7, 64.7, 52.0, 43.3, 43.3 ppm. UV/Vis ($\text{CHCl}_3/\text{MeCN}$, 1:1): λ_{max} (ϵ) = 375 nm (39500). MS (EI): m/z (%) = 1397.5 (100) $[\text{M} + \text{Na}]^+$.

General Procedure for the Determination of the Association Constants: MeCN (Carlo Erba UV/Vis spectroscopic grade) was used for the determination of the stability constants by UV/Vis spectrophotometry. A Mettler H31 analytical balance (with a precision of 10^{-4} g) was used to weigh the samples for the stock solutions. Aliquots of these stock solutions were then taken by high-precision Hamilton syringes to prepare the cuvette samples for spectrophotometric analyses. The titration experiments were conducted as fol-

lows. To a stock solution of crown ether (solution A) in MeCN were added several aliquots of a solution (solution B) made up of the metal salt (at higher concentration) dissolved in solution A, in order to maintain the crown ether at the same, constant concentration. Stock solutions A were in the range 5×10^{-5} to 8×10^{-5} , whereas stock solutions B were in the range 6×10^{-5} to 2×10^{-2} for $\text{Eu}(\text{OTf})_3$. After each addition, the UV/Vis spectrum in the 250–700-nm region was recorded, and absorbances at selected wavelengths were measured. By use of a nonlinear fitting curve program, the plot of A against the metal concentration x was fitted by Equation (1), thus affording the value of the association constant k_a , where A is the measured absorbance, x is the total concentration of titrant (usually metal salt) added, ϵ_c is the molar absorptivity of the complex, ϵ_s is the molar absorptivity of the substrate at the desired wavelength, which could be directly determined, C is the total concentration of the titrate (which is a constant quantity, usually the crown ether), and k_a is the association constant for the 1:1 complex.

$$A = (\epsilon_c - \epsilon_s) \frac{k_a(C+x) + 1 - \{[k_a(C+x) + 1]^2 - 4k_a^2Cx\}^{0.5}}{2k_a} + \epsilon_s C \quad (1)$$

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