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C_2 Symmetrical double chromophores: cooperativity effects in lanthanide ion complexation †

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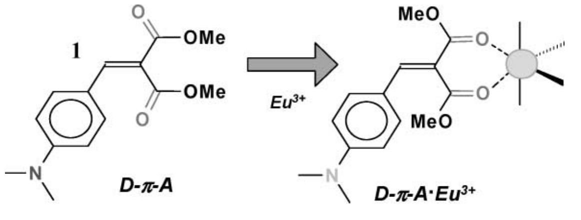
We describe the synthesis and characterization of C_2 symmetrical double chromophores, in which two identical chromophores are linked through ethylene glycol spacers of increasing lengths. The complexation ability of the *trans* stereopure form for each diastereoisomeric pair showed how the two chromophores, when the spacer unit is comprised of a diethylene or a triethylene glycol moiety, are able to interact in a positive way, stabilizing the resulting complexes when compared with single chromophore analogous compounds.

Introduction

There is a standing interest in the synthesis of π-extended organic chromophores strongly absorbing in the UV/Vis region for a variety of applications in materials science, such as second order non linear optical (NLO) devices, two photon absorbing dyes, optical limiting materials.[1–3] 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 supramolecular, reversible 1 : 1 complexes with Lewis acid-like metal cations, such as Eu^{3+}, as its triflate salt, in organic solvents.[4] The complexation of the metal cation with the 1,3-dicarbonyl system is inferred by NMR and UV/Vis spectroscopic studies, and 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.



We have adapted this principle, through the use of bis-malonate crown ethers,[5] to the convergent synthesis of two component systems, containing both a π-extended chromophoric system and a fullerene derivative at increasing distances, and demonstrated how these covalent systems are able to form stable complexes with Eu^{3+} triflate salt. Such supramolecular triads showed very interesting UV/Vis properties, essentially dependent on the relative distance between the two covalently linked π-extended and fullerene moieties.[6]

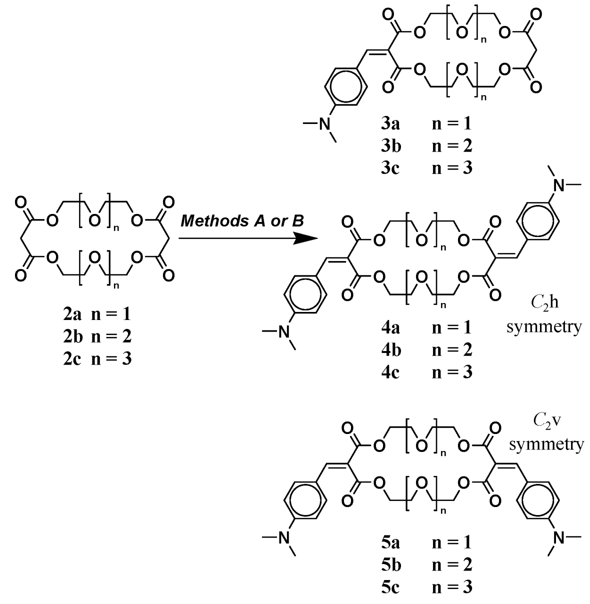
In this paper, we describe the synthesis and characterization of C_2 symmetrical double chromophores, in which two identical chromophores are linked through ethylene glycol spacers of increasing lengths; we also report the X-ray characterization of the diastereopure forms and their relative ability to form complexes with Eu^{3+} triflate.

Results and discussion

Synthesis of the components

The synthesis was performed according to Scheme 1. Crown ethers **2** and crown ether derivatives **3** were described in a previous paper.[6,7] Compounds **4**–**5** could be obtained from the corresponding crown ethers **2** using an excess of *N*,*N*-dimethylaminobenzaldehyde *via* a Knoevenagel condensation catalyzed by piperidinium acetate. The reactions were carried out in different conditions: at room temperature, with the presence of molecular sieves (Method B), *via* kinetic control; or in refluxing benzene, with a Dean–Stark apparatus in order to azeotropically remove H_2O produced by the reaction, under thermodynamic control (Method A). The products could be purified by removing excess reagents by column chromatography. Initial ^1H NMR spectroscopy in $CDCl_3$ of the crude compounds obtained by column separation showed only one set of signals attributable to each of the symmetry-related sets of protons of the products.

As they should exist in two separate diastereoisomers, namely a *trans* form **4**, possessing a C_{2h} symmetry molecular



Scheme 1 *Reagents and conditions*: *Method A*: Benzene, Δ, Dean–Stark, 24 h; *Method B*: CH_2Cl_2, room temperature, 4 Å molecular sieves, 5 d.

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† Electronic supplementary information (ESI) available: chemical shifts for diastereoisomeric pairs **4/5** in C_6D_6 solutions (300 MHz). See http://www.rsc.org/suppdata/ob/b4/b403494e/

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Table 1 Diastereoisomeric ratio as determined by relative integration in C_6D_6 at 25 °C[a]

Entry	Method	% Diastereoisomer **4** (C_{2h})	% Diastereoisomer **5** (C_{2v})
1	**A**	60 (**4a**)	40 (**5a**)
2	**A**	55 (**4b**)	45 (**5b**)
3	**A**	50 (**4c**)	50 (**5c**)
4	**B**	55 (**4a**)	45 (**5a**)
5	**B**	40 (**4b**)	60 (**5b**)
6	**B**	50 (**4c**)	50 (**5c**)

[a] Relative integration of ratios of peak heights was conducted on those sets of signals for which the two diastereoisomeric forms were clearly distinguishable.

point group, and a *cis* form **5**, possessing a C_{2v} symmetry molecular point group, we would have expected two such sets of signals. Indeed, melting points of the initial mixtures were rather broad, and a second inspection by ^{1}H NMR spectroscopy using C_6D_6 as the solvent revealed a nice separation of several sets of signals into two closely related sets of unequal height and integration for all the diastereoisomeric couples **4**–**5** (in Fig. 1 bottom, the ^{1}H NMR spectrum of **4b**–**5b** mixture is reported as an example). After careful fractional crystallization of the mixtures from EtOH (in the case of the diethylene glycol spaced diastereoisomers **4a** and **5a** and triethylene glycol spaced diastereoisomers **4b** and **5b**), we were able to obtain solids which could be identified by sharp melting point intervals, and simple ^{1}H NMR spectra in C_6D_6 (Fig. 1, top).

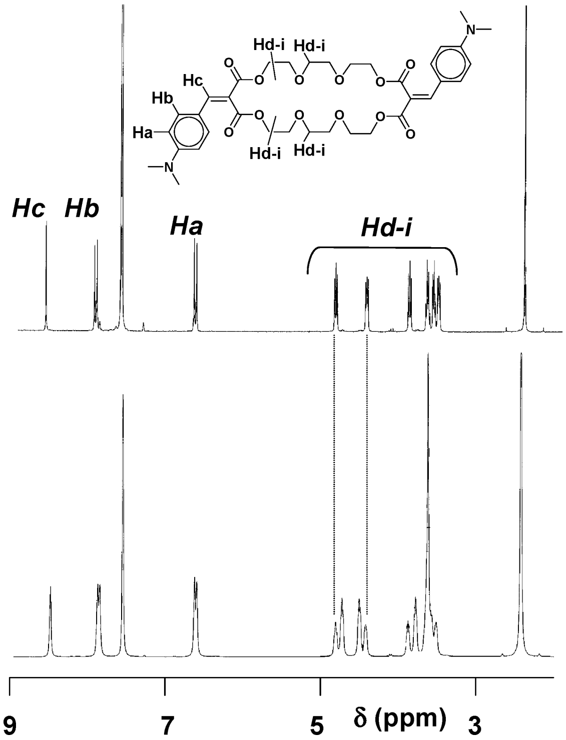

Fig. 1 ^{1}H NMR (C_6D_6) of pure **4b** (top), obtained after fractional crystallization from EtOH, and of a **4b**–**5b** mixture (bottom) after initial column chromatography (entry 5 in Table 1).

In the case of **4a** and **4b**, good quality crystals could be grown by slow evaporation of their AcOEt solutions, and the stereochemistry of the compounds could be unequivocally identified by X-ray crystallographic analysis (*vide infra*). In the case of the diastereoisomeric pair **4c** and **5c**, the mixture could be again purified by fractional crystallization from EtOH to obtain a pure compound with a sharp melting point interval, but good quality crystals for X-ray analysis could not be obtained. Differences in the chemical shifts for the diastereoisomeric **4a**–**5a** and **4b**–**5b** pairs were quite small and without a pattern to predict the stereochemical configuration of the **4c**–**5c** pair with reasonable certainty on this basis (see Supplementary Information). The mixtures contained in the mother liquors were enriched in the **5** diastereoisomeric compounds, which could not however be obtained in pure form. The use of a polar solvent for the crystallization process in all cases, however, is a strong hint that the less polar compound, which should be the *trans* product (the two chromophores are oriented in such a way that the molecular dipole moment should be almost nil), is the one that crystallized out preferentially, and therefore we will refer to the compound obtained from the **4c**–**5c** pair, as **4c** from now on.

As TLC or HPLC chromatography in several solvent mixtures was revealed to be of no use for the separation of the diastereoisomeric couples, we relied on ^{1}H NMR spectroscopy in C_6D_6 to quantitate the diastereoselectivity in the reaction formation for **4** and **5**. The results are shown in Table 1. It is evident that in thermodynamic conditions (method A in Table 1) there is a preference for the *trans* form **4a** (entry 1 in Table 1), probably as a consequence of the fact that the steric repulsion between the two forming and bulky chromophores is minimized. This situation is clearly reminiscent of the diastereoselectivities observed between *cis* and *trans* forms in C=C bond forming reactions under thermodynamic conditions. There is also a fading of the observed diastereoselectivities as the two bulky forming chromophores are further apart (entries 2 and 3, Table 1). Under kinetic conditions (method B), the situation is less straightforward (entries 4–6 in Table 1).

Possible supramolecular interactions between the catalyst (a secondary ammonium salt) and the crown ether might play an important role at room temperature in directing the diastereoselectivities observed.[8] Purified mixtures obtained under kinetic conditions (entries 4 and 5) were subjected to heating at reflux in toluene in the presence of catalytic amounts of piperidinium acetate. In both cases, we obtained traces of starting crown ethers **2** and monofunctionalized compounds **3**, to indicate that a retro-Knoevenagel mechanism is in place; furthermore, the diastereoisomeric ratio was clearly shifted towards the *trans* form (after these experiments, the ratio was 67 : 33 for **4a**–**5a** and 50 : 50 for **4b**–**5b**).

UV/Vis studies

The double chromophores **4a**–**c** were all characterized by UV/Vis spectroscopy. The relevant spectroscopic data of the free ligands are reported in Table 2. The compounds **4a**–**c** possess an intense intramolecular charge-transfer (ICT) band centered at 380 nm in all cases, with molar absorptivities (Table 2), in the order of 70 000. The molar absorption coefficients for the free ligands were also very similar, but substantially higher than the ones measured for model single chromophores **3a**–**c**.

The binding ability of double chromophores **4a**–**c** was investigated using Eu(OTf)$_3$, a previously reported useful probe for the relative complexation ability of these systems, as a ligand.[4–6]

Examples of spectrophotometric titrations of compounds **4a**–**c** with Eu(OTf)$_3$ are shown in Fig. 2. All titration profiles showed well defined isosbestic points, indicating a unique mode of binding present in solution, and could be fitted against a model equation for a 1 : 1 binding equilibrium using the

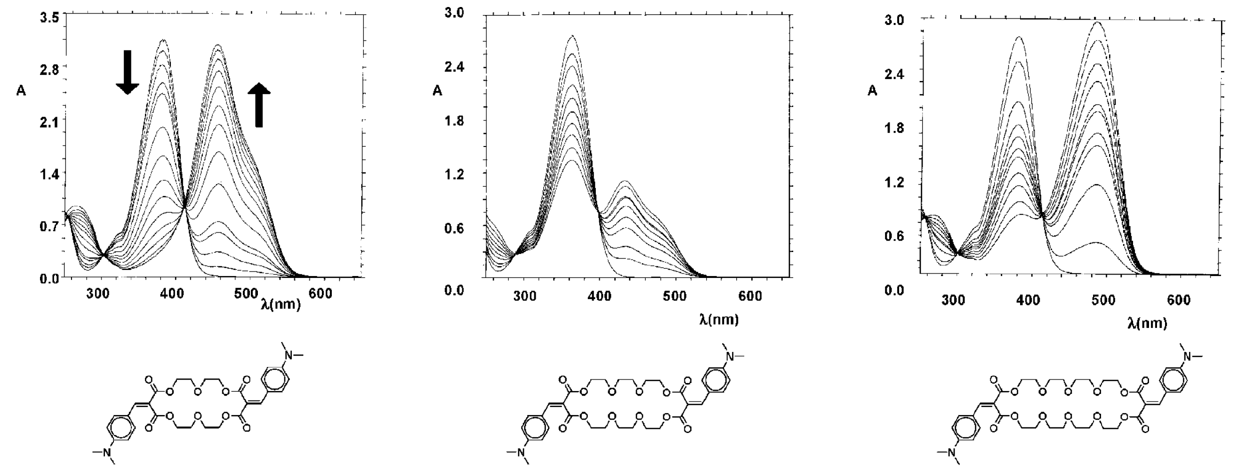

Fig. 2 UV/Vis titrations of **4a–c** with $Eu(OTf)_3$ in MeCN at 25 °C.

Table 2 Thermodynamic stability constants between functionalized crown ethers **3** and **4** and $Eu(OTf)_3$ in MeCN at 25 °C as determined by UV/Vis titrations[a]

Entry	Compound	$\varepsilon_{\text{free ligand}}$[b]	Log K_a	$\lambda_{\text{max complex}}$ (nm)
1[c]	**1**	33100	2.60 ± 0.05	478
2[c, d]	**3a**	28100	3.1 ± 0.1	480
3	**4a**	69000	4.7 ± 0.1	455
4[c]	**3b**	22100	2.7 ± 0.2	480
5[c, d]	**3b**	22800	2.9 ± 0.1	480
6	**4b**	66400	4.1 ± 0.2	448
7[c, d]	**3c**	20100	4.65 ± 0.05	480
8	**4c**	68200	4.65 ± 0.05	480

[a] All values for the stability constants are in M^{-1}. The values reported are the average of four independent titrations, with all nonlinear regression giving high confidence outputs ($r^2 > 0.99$). [b] Molar absorptivity and λ_{max} (at 380 nm in all cases) for the intermolecular charge-transfer (ICT) band related to the free ligand. [c] Data taken from Reference 6. [d] Data measured in $CHCl_3$–MeCN 1 : 1.

equation reported in the experimental section. Compounds **4a–c** show, upon complexation, a marked shift in the ICT towards longer wavelengths, which occurs as a consequence of the additional polarization of the "push–pull" system after coordination of the metal ion to the acceptor 1,3-dicarbonyl system. A similar behavior has been detailed for the complexation of **1** with $Eu(OTf)_3$: it has been shown by NMR spectroscopic studies ‡ that the metal cation is bound by both carbonyls of the malonate moiety, giving rise to a large bathochromic shift for the λ_{max} of the ICT band upon complex formation (entry 1 in Table 2). As shown in Table 2, however, the λ_{max} for this band upon complex formation is variable in the dichromophoric compounds (455 and 448 nm for **4a** and **4b**, and 480 nm for **4c**), indicating a dissimilar geometry of interaction of the metal cation with the 1,3-dicarbonyl conjugated moiety of the crown ether. The titration profiles in the case of **4a** and **4b** show (Fig. 2, left and middle) shoulders well above 500 nm.

The values of the thermodynamic binding constants, also reported in Table 2, show interesting results: the two sites are not formally independent, as demonstrated from the results for **4a** and **4b** when compared with **3a** and **3b**. If no cooperation was in place, a purely statistical factor would enhance the stability constant by a factor of 2 (0.30 in Log units).[9] These data seem to suggest a binding situation in which the metal cation is stabilized by both chromophores on the molecule. This observation is supported also by the reduced value of the λ_{max} of this band. The not optimal interaction of each π-extended moiety coordinating the metal cation could be a consequence of the fact that it is bound by both of them. The net result is an overall stabilization of the system, with binding constants for **4a** and **4b** which are vastly superior to the single chromophore analogues **3a** and **3b**.

The titration profile for compound **4c** shows a profile which is very similar to the ones already reported for **3c**, both in terms of the absolute thermodynamic value and in terms of the λ_{max} of this band. In this case, the two chromophores are too far away to interact in a convergent, positive way. A statistical effect cannot be excluded, since the values in entries 7 and 8 refer to slightly different solvent mixtures (MeCN–$CHCl_3$ *vs.* MeCN). The effect of these different solvent mixtures on the overall stability constants, however, is small (entries 4 *vs.* 5 in Table 2), and cannot be accounted for by the large increase in stability recorded in the case of compounds **4a** and **4b**.

X-Ray crystallography

The molecular structure of compound **4a**, as determined by X-ray diffraction techniques, is shown in Fig. 3.

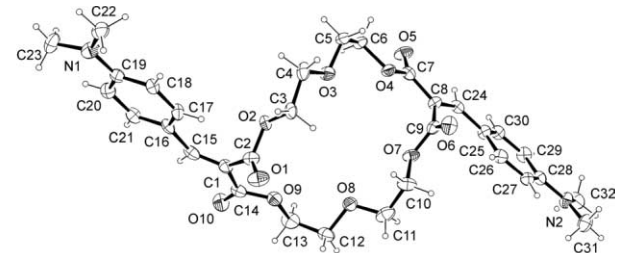

Fig. 3 ORTEP view of **4a** with displacement ellipsoids drawn at 30% probability level. The water molecule has been omitted for clarity.

All bond lengths and angles are in good agreement with standard values. For example, the average Csp^3–O is 1.426 Å, while the average Csp^2–O is 1.363 Å and the average Csp^2=O is 1.187 Å. Both π-extended groups are essentially planar as expected. The mean deviation from the least-squares plane calculated using all ten atoms is 0.036 Å and 0.035 Å for the two groups, respectively. It is worth noting that the angle formed between the two groups is 49.2(3)°. Most of the torsion angles in the crown ether ring are in either a *gauche* or *anti* conformation. The macrocycle assumes a quite irregular rectangular geometry [O2 ··· O9 3.34(1) Å; O3 ··· O8 5.12(2) Å; O4 ··· O7 3.34(1) Å; apex–apex distance: C1 ··· C8 8.27(2) Å]. If a least-squares plane is calculated through all the atoms of the crown ether, an average deviation of 0.72 Å is calculated for the contributing atoms. The crystal packing is maintained by van der Waals forces and hydrogen bonds involving the water molecule and oxygen atoms O1 and O8: O1 ··· O11 3.018(37) Å; O8 ··· O11 2.880(38) Å.

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‡ See reference 4 below and in particular references 6 and 8 therein.

The crystal structure of compound **4b** is characterized by the presence of a center of symmetry which lies in the center of the crown ether ring. As a consequence, half of the formula unit comprises the asymmetric unit (Fig. 4).

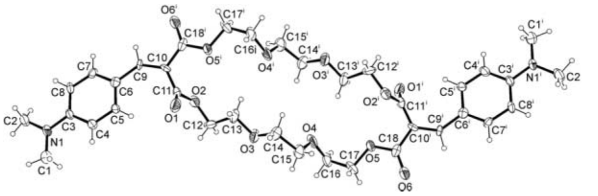

Fig. 4 ORTEP view of **4b** with displacement ellipsoids drawn at 30% probability level. Symmetry codes: (i) $-x$, $-y$, $-z$.

Overall, the macrocycle is flat; the mean deviation from the best plane calculated using all 30 atoms is in fact 0.51 Å. All bond lengths and angles are in agreement with standard values [mean Csp^3–O 1.426 Å; mean Csp^2–O 1.346 Å; mean Csp^2=O 1.241 Å; mean Csp^3–Csp^3 1.485 Å]. The cavity is characterized by the following distances: O2 ··· O5^i 2.90(1) Å; O4 ··· C13^i 3.53(1); C13 ··· O4^i 3.53(1) Å; O5 ··· O2^i 2.90(1) Å; apex–apex distance: C10 ··· C10^i 12.75(3) Å. Most of the C–O–C–C torsion angles lie close to 180° (*anti* conformation), but C11–O2–C12–C13 and C15–O4–C16–C17 are in the *gauche* conformation; two O–C–C–O torsion angles adopt the *gauche* geometry, while the third (O2–C12–C13–O3) is *anti*. No significant deviation from theoretical values has been observed. The π-extended groups are planar [mean deviation from the least-squares plane calculated using ten atoms 0.024 Å; maximum deviation 0.059 Å] and lie parallel to each other. In the crystal packing the crown molecules are ordered into parallel layers. The crystal is maintained by van der Waals forces.

Conclusions

We have reported the synthesis and characterization of covalently bound double chromophoric compounds, in which the distance between the π-extended moieties is gradually increasing. Although an unequivocal attribution of the stereochemistry for compound **4c** could not be obtained, and we could not obtain any of the stereochemically pure *cis* compounds **5**, the diastereopure forms **4a** and **4b** showed that a cooperative mechanism is in place in the formation of supramolecular complexes with Eu^{3+} salts, that is when the two chromophores are not too far apart. The thermodynamic values for these hosts are the highest we recorded within this class of compounds,[4–6] auguring well for their possible use in functional devices.

Experimental

General remarks

All commercially available compounds were purchased from Aldrich and used as received. THF (CaH_2), MeCN (CaH_2) and CH_2Cl_2 (CaH_2) were dried and distilled before use. Crown ethers **2a**, **2b** and **2c** and monofunctionalized derivatives **3a**, **3b** and **3c** were described in a previous paper. ^{1}H and ^{13}C NMR spectra were recorded from solutions in $CDCl_3$ or C_6D_6 on an AMX300 with the solvent residual proton signal or tetramethylsilane (TMS) as a standard. Infrared spectra were recorded on a Perkin Elmer 881 using NaCl disks with the compound dissolved in Nujol when using solids and neat compound when using oils. Mass spectra were recorded using an Electrospray Ionization instrument LCQ Decca (Thermofinnigan). The UV/Vis spectroscopic studies were conducted on a Perkin Elmer Lambda 5 spectrophotometer. Melting points were recorded on a Büchi 510 apparatus and are uncorrected.

Preparation of bisfunctionalized 4a–c and 5a–c. Method A

A solution of the crown ether (1 mmol), piperidinium acetate (30 mg) and *p*-dimethylaminobenzaldehyde (2.5 mmol) in dry benzene (30 mL) was heated under reflux for 24 h with a Dean–Stark apparatus in order to azeotropically remove water. The solvent was then removed *in vacuo* and the residue was purified by column chromatography. **Method B.** A solution of the crown ether (1 mmol), piperidinium acetate (30 mg) and *p*-dimethylaminobenzaldehyde (2.5 mmol) in dry CH_2Cl_2 (30 mL) was stirred for 5 d in the presence of 4 Å molecular sieves.

Compounds 4a and 5a

From crown ether **2a** (348 mg, 1 mmol) and *p*-dimethylaminobenzaldehyde (224 mg, 1.5 mmol). The diastereoisomeric mixture was separated from excess reagents and byproducts by column chromatography (SiO_2; C_6H_{12}–AcOEt 50 : 50) and obtained as a yellow solid (580 mg, 95%). The diastereoisomer **4a** could be obtained in pure form by fractional crystallization (EtOH, 116 mg, 19% overall yield). Mp (EtOH) = 218–220 °C. IR (cm^{-1}) = 1727, 1704 ($\nu_{C=O}$). ^{1}H NMR ($CDCl_3$): δ = 7.66 (s, 1H; –CH=C–), 7.38 (m, 2H; Ar-H), 6.55 (m, 2H; Ar-H), 4.5–4.3 (m, 4H; $-COOCH_2CH_2O-$), 3.8–3.72 (m, 4H; $-COOCH_2CH_2O-$), 3.05 (s, 6H; $-N(CH_3)_2$). ^{13}C NMR ($CDCl_3$) δ = 167.9, 164.8, 151.9, 143.8, 132.0, 119.9, 118.6, 111.5, 69.3, 69.1, 65.2, 64.7, 39.9. UV/Vis (MeCN): λ_{max} = 380 (62000), 247 (17700). Anal. calcd. for $C_{32}H_{38}O_{10}N_2 \cdot H_2O$: C 61.14%, H 6.41%, N 4.46%; found: C 60.58%, H 6.03%, N 4.89%. MS (EI, relative %) = 633 ([M + Na]$^+$, 21%), 611 ([M + H]$^+$, 100%).

Compounds 4b and 5b

From crown ether **2b** (436 mg, 1 mmol) and *p*-dimethylaminobenzaldehyde (224 mg, 1.5 mmol). The diastereoisomeric mixture was separated from excess reagents and byproducts by column chromatography (SiO_2; C_6H_{12}–AcOEt 30 : 70) and obtained as a yellow solid (628 mg, 90%). The diastereoisomer **4b** could be obtained in pure form by fractional crystallization (EtOH, 125 mg, 18% overall yield). Mp (EtOH) = 166–167 °C. IR (cm^{-1}) = 1730, 1703 ($\nu_{C=O}$). ^{1}H NMR ($CDCl_3$): δ = 7.67 (s, 1H; –CH=C–), 7.37 (m, 2H; Ar-H), 6.63 (m, 2H; Ar-H), 4.49–4.35 (m, 4H; $-COOCH_2CH_2O-$), 3.83–3.72 (m, 4H; $-COOCH_2CH_2O-$), 3.66 (s, 4H; $-OCH_2CH_2O-$), 3.03 (s, 6H; $-N(CH_3)_2$). ^{13}C NMR ($CDCl_3$) δ = 167.8, 164.8, 151.9, 143.7, 132.0, 119.9, 118.9, 111.5, 70.7, 70.5, 69.0, 68.8, 64.6, 39.9. UV/Vis (MeCN): λ_{max} = 380 (70300), 247 (23800). Anal. calcd. for $C_{36}H_{46}O_{12}N_2$: C 61.89%, H 6.59%, N 4.01%; found: C 61.96%, H 6.87%, N 4.21%. MS (EI, relative %) = 699 ([M + H]$^+$, 100%).

Compounds 4c and 5c

From crown ether **2c** (524 mg, 1 mmol) and *p*-dimethylaminobenzaldehyde (224 mg, 1.5 mmol). The diastereomeric mixture was separated from excess reagents and byproducts by column chromatography (SiO_2; AcOEt) as a yellow oil (708 mg, 90%). The diastereoisomer **4c** could be obtained in pure form by fractional crystallization (EtOH, 106 mg, 14% overall yield). Mp (EtOH) = 123–124 °C. IR (cm^{-1}) = 1725, 1705 ($\nu_{C=O}$). ^{1}H NMR ($CDCl_3$): δ = 7.65 (s, 1H; –CH=C–), 7.35 (m, 2H; Ar-H), 6.61 (m, 2H; Ar-H), 4.48–4.31 (m, 4H; $-COOCH_2CH_2O-$), 3.8–3.6 (m, 4H; $-COOCH_2CH_2O-$), 3.60–3.57 (m, 8H; $-OCH_2CH_2O-$), 3.04 (s, 6H; $-N(CH_3)_2$). ^{13}C NMR (C_6D_6) δ = 168.7, 165.8, 152.6, 144.0, 133.0, 121.8, 121.6, 112.6, 71.7, 71.6, 69.9, 69.8, 65.5, 65.4, 40.0. UV/Vis (MeCN): λ_{max} = 380 (64800), 248 (19600). Anal. calcd. for $C_{40}H_{54}O_{14}N_2$: C 61.05%, H 6.91%, N 3.56%; found: C 60.87%, H 6.72%, N 3.32%. MS (EI, relative %) = 787 ([M + H]$^+$, 100%).

Table 3 Crystal and refinement data

	4a	**4b**
Formula	$C_{32}H_{38}N_2O_{10}\cdot 0.3H_2O$	$C_{36}H_{46}N_2O_{12}$
Molecular weight	615.77	698.75
Crystal size (mm)	0.40 × 0.10 × 0.05	0.20 × 0.18 × 0.05
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
a (Å)	11.431(10)	8.186(5)
b (Å)	14.985(15)	18.852(16)
c (Å)	10.19(3)	6.057(15)
α (°)	92.1(2)	96.7(2)
β (°)	104.70(17)	106.03(11)
γ (°)	70.09(9)	80.81(8)
V (Å^3)	1585(6)	884(2)
d_{calc} (g cm^{-3})	1.289	1.312
T (K)	293(2)	293(2)
Radiation, λ (Å)	Mo-K$_\alpha$, 0.71073	Mo-K$_\alpha$, 0.71073
Monochromator	Graphite	Graphite
μ (mm^{-1})	0.097	0.099
Scan type	ω-2θ	ω-2θ
θ range (°)	2–20	2–22
Reflections measured	$-10 < h < 10$	$-8 < h < 8$
	$-14 < k < 14$	$-19 < k < 19$
	$0 < l < 9$	$0 < l < 6$
Standard reflections	3 every 200 reflns	3 every 200 reflns
Tot. reflns measured	3175	2418
Unique reflections	2952	2163
R_{int} [a]	0.0639	0.0732
Refinement type	F^2	F^2
R_1 [b]	0.0854 (1332 reflns)	0.1513 (729 reflns)
R_{all}	0.1944	0.3324
GOF [c]	1.094	1.048
Refined parameters	411	228
Weighting scheme [d]	$1/[\sigma^2 F_o^2 + (0.0846P)^2 + 0.276P]$	$1/[\sigma^2 F_o^2 + (0.186P)^2 + 0.00P]$
(shift/e.s.d.)$_{max}$	0.000	0.000
max., min. $\Delta\rho$ (e Å^{-3})	0.236, −0.217	0.406, −0.406

[a] $R_{int} = \Sigma |F_o^2 - F_o^2(\text{mean})| / \Sigma [F_o^2]$. [b] $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ (calculated on reflections with $I > 2\sigma_I$). [c] $\text{GOF} = S = [\Sigma [w(F_o^2 - F_c^2)^2]/(n - p)]^{0.5}$, where n is the number of reflections and p is the total number of parameters refined. [d] $P = [\text{Max}(F_o^2,0) + 2F_c^2/3]$

General procedure for the determination of the association constants

Distilled MeCN was used for the determination of the stability constants by UV/Vis spectrophotometry. In the titration experiments, to a stock solution of crown ether (solution A) in MeCN, were added several aliquots of a solution (solution B) formed by the metal salt (at higher concentration) dissolved in solution A, in order to maintain the crown ether host always at the same, constant concentration. Stock solutions A were in the range (4×10^{-5} – 5×10^{-5}), whereas stock solutions B were *ca.* 10^{-2} for Eu(OTf)$_3$. After each addition the UV/Vis spectra in the region 250–700 nm were recorded and absorbances at selected wavelengths measured. By employing a nonlinear fitting curve program (Sigmaplot®), the plot of A against the metal concentration x was fitted by equation 1, thus affording the value of the association constant K_a and of the molar absorptivity of the complex ε_c.

$$A = (\varepsilon_c - \varepsilon_s)\frac{K_a(C + x) + 1 - [[K_a(C + x) + 1]^2 - 4K_a^2 Cx]^{0.5}}{2K_a} + \varepsilon_s C \qquad (1)$$

[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 (and in the cases reported here is always 0), 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.]

X-Ray crystallographic studies

Good quality crystals of compounds **4a** and **4b** were grown by slow evaporation from AcOEt. The crystal and molecular structures of **4a** and **4b** have been determined by X-ray diffraction methods. Unit cell parameters and intensity data were obtained on a Philips PW1100 four-circle diffractometer at room temperature using graphite-monochromatized Mo-K$_\alpha$ radiation. Calculations were performed with the WinGX-97 software.[10] Crystal data and the most relevant parameters used in the crystallographic study are reported in Table 3.§

Cell dimensions were determined by least-squares fitting of 24 centered reflections monitored in the ranges $5.04° < \theta < 12.47°$ for **4a** and $4.93° < \theta < 11.01°$ for **4b**. Correction for Lp was applied. For both crystals, no suitable reflections for a ψ-scan were found in the $80° < \phi < 90°$ and the empirical absorption correction was not applied. Both structures were solved by SIR-92[11] and refined by full-matrix least-squares using SHELX-97.[12] In both cases, the non hydrogen atoms were refined anisotropically while hydrogen atoms were inserted in the calculated positions and refined with an isotropic displacement factor proportional to that of their neighbouring atom.

In the crystal structure of compound **4a** one water molecule is also present; the oxygen atom was refined with partial occupancy (0.3) while the hydrogen atoms were not located in the difference Fourier maps and were then disregarded.

The poor quality of the **4b** crystal did not allow the achievement of a good resolution for the structural model. Nevertheless, the molecular conformation of the compound

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§ CCDC reference numbers 233251–233252. See http://www.rsc.org/suppdata/ob/b4/b403494e/ for crystallographic data in.cif or other electronic format.

in the solid state has been revealed; no chemically unacceptable bond lengths or angles were found and the final difference Fourier maps were featureless, thus confirming the reliability of the model.

Atomic scattering factors were taken from International Tables for X-ray Crystallography.[13] Diagrams of the molecular structure were produced by the ORTEP program.[14]

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