



Dynamic switching between binding sites in the complexation of macrocyclic ‘push–pull’ chromophores to lanthanides

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ABSTRACT

The introduction of a 1,3-diacetylpyridine moiety, as an additional binding niche in a macrocyclic receptor ligand containing a conjugated, push–pull malonate functionality, leads to, in addition to the 1:1 binding stoichiometry, the equilibrium formation of multiple complexes, specifically 1:2, 2:1, and 3:1 ligand:metal complexes with lanthanide trications. Various binding modes elicit distinctive responses in the visible region, which enhance the potential recognition of lanthanide ions. This paper also highlights the usefulness of a full factor analysis in the elucidation of complex binding phenomena.

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1. Introduction

There is a great deal of interest in trivalent lanthanide complexes because of their unique optical properties such as line-like emission spectra and long luminescence lifetimes. These properties can be exploited in a wide variety of applications from optical amplification of lasers¹ to *in vivo* luminescence bioassays.² The most successful macrocyclic ligands developed in recent years for these applications with lanthanide cations are based mainly on polydentate azamacrocycles with chelating carboxylate arms, which then encapsulate lanthanide ions with very high stability constants, but little selectivity.³ Other studies have demonstrated the possibility of complexing lanthanide ions with polydentate ligands such as podands,⁴ calix[4]arene derivatives,⁵ or dendrimers.⁶ These ligands typically avail at least 8–9 hard donor atoms, like O and N atoms, to fill the first coordination sphere of the ion.

Lanthanide ions are also widely used in organic catalysis, functioning as Lewis acids. Their relatively weak coordination to organic moieties facilitates high turnover numbers. One of the added values

of the use of lanthanides in this context is the possibility, given their high coordination number, of simultaneously coordinating both the reagent (usually bidentate) and a co-catalyst (both bidentate or tridentate). 1,3-Dicarbonyl units (either as reagents, malonate derivatives, or catalysts in the form of chiral bisoxazolines) and 1,3-pyridinediacetyl units are amongst the most popular organic moieties used in this context.⁷

In this paper, we report on the design, synthesis and complexation of a novel macrocyclic architecture, in which both the above mentioned moieties are embedded into a covalent cyclic skeleton.

2. Results and discussion

We have recently reported that ‘push–pull’ chromophores, built around conjugated 1,3-dicarbonyl moieties, behaving as soft ligands, are able to form stable complexes in organic solutions with lanthanides such as Eu³⁺, introduced as its triflate salt (Fig. 1).⁸

More specifically, we have observed the formation of a stable 1:1 Eu(III):ligand complex with compounds **1** and **2** in MeCN solutions. The association constants could be readily ascertained via spectrophotometric titration as the intramolecular charge transfer (ICT) band of either ligand redshifts about 100 nm upon complexation with the Eu³⁺ cation, and clear isosbestic points persist for the entire range of the titration. The crown ether structure of

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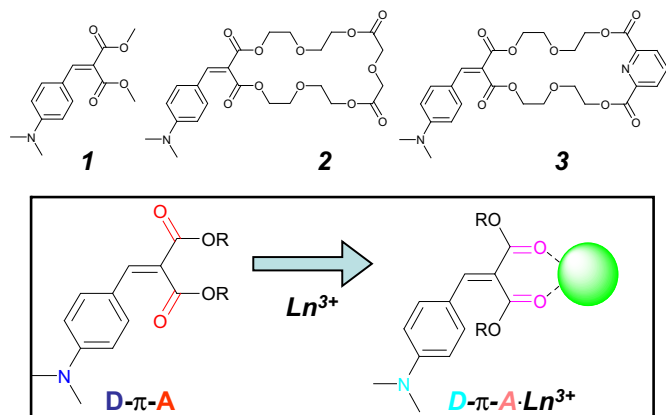
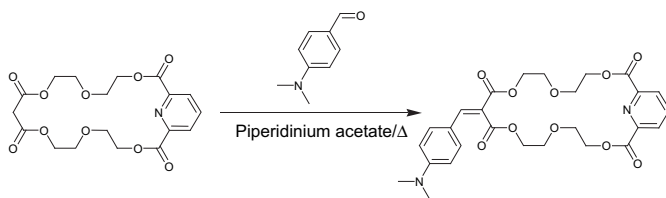


Figure 1. The compounds used in this study (top), and the mode of binding between the chromophore and the lanthanide cation (green sphere).

chromophore **2** stabilizes the 1:1 complex with **2** ($\log K_a = 3.8 \text{ M}^{-1}$) relative to that with **1** ($\log K_a = 2.6(1) \text{ M}^{-1}$)⁹ presumably as a result of the additional coordination of one of the polyether oxygen atoms, likely the one belonging to the diglycolyl moiety.¹⁰

We now introduce and compare ligand **3** (obtained from a Knoevenagel condensation of the corresponding malonate crown ether,¹¹ Scheme 1). It incorporates a 2,6-pyridinediacetyl moiety as an additional stabilizing functionality in the binding of lanthanide ions, while preserving the overall crown ether structure at 22 atoms as in the case of **2**.



Scheme 1. Synthesis of chromophore **3**.

Spectrophotometric titration of compound **3** with $\text{Eu}(\text{OTf})_3$ in MeCN solutions showed an increase in the band associated with the ICT band of the complex (centered at 480 nm, see Fig. 2), and a decrease in the $\pi-\pi^*$ band of the free ligand (centered at 377 nm), similarly to what is observed for **1** and **2**. However, unlike

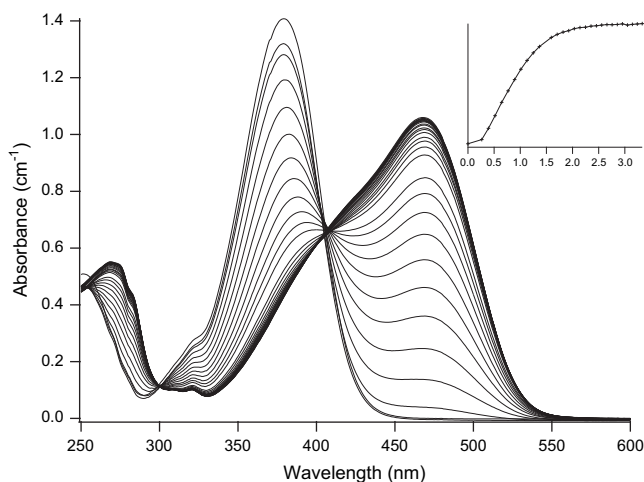


Figure 2. Spectroscopic data for the titration of macrocycle **3** ($5 \times 10^{-5} \text{ M}$) with $\text{Eu}(\text{OTf})_3$ ($0.15 \times 10^{-4} \text{ M}$). Inset: Absorbance profile at 480 nm as a function of europium equivalents.

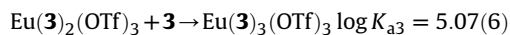
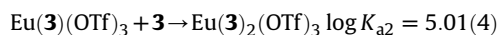
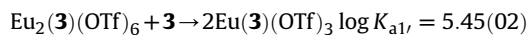
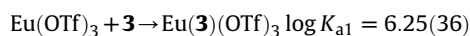
the results with compound **2**, no clear isosbestic points exist throughout the titration range. A close inspection reveals at least two distinct isosbestic points around 400 nm (404 and 414 nm). The shift in spectral curves from one isosbestic point to the other appears to be centered around the addition of one equivalent of $\text{Eu}(\text{OTf})_3$ titrant. This clearly indicates the presence of multiple equilibria in solution resulting from the introduction within the crown ether structure of a second binding niche for lanthanide ions.

The lack of isosbestic points that persist throughout the titration suggests that there are at least two possible complexes between ligand and metal. Not surprisingly, modeling the titration profile at 480 nm (see Fig. 2, inset) as a 1:1 binding event gave poor results.

The shape of this profile is sigmoidal, which is not only indicative of multiple equilibria, but also generally associated with positive cooperativity.^{12–15} Fitting with the Hill equation (see Table S1) yields a mathematically satisfactory result: a Hill coefficient of 3.2 and a binding constant of $\log K_a = 4.0$. A profile for the reverse titration of lanthanide with **3** yields a Hill coefficient of 1.2 and a binding constant of $\log K_a = 3.5$.

Despite the potential merit of the mathematical fit, Ercolani has revisited several systems previously reported to show positive cooperativity, and warned about a judgment on cooperativity on the basis of Scatchard and Hill plots.¹⁶ Clearly, given that this system involves a multivalent receptor (the lanthanide cation, which can coordinate more than one macrocycle), and a multitopic ligand (macrocycle **3**, possessing two different binding sites), the sensibility of the fitting parameters is highly questionable. Titrating **3** with $\text{Gd}(\text{OTf})_3$ also gives a sigmoidal titration profile similar to that observed for $\text{Eu}(\text{OTf})_3$, and the same values in terms of binding constants.¹⁷

To better ascertain the species present and the thermodynamic relationships between them, a set of absorbance data like those shown in Figure 2 for $\text{Eu}(\text{OTf})_3$ titrated with **3** was modeled using a factor analysis program called Sivvu, which takes into account all available wavelengths, and can potentially account for any set of equilibria.¹⁸ Indeed, unrestricted factor analysis on the forward titration reveals that there are at least five and not more than seven absorbing species that contribute to the data.¹⁹ The analysis on data from the reverse titration (ligand into metal) indicates five major absorbers. These likely include species with metal to ligand ratios of 1:1, 2:1, 1:2, 1:3, and 0:1. To verify this, the dataset for the forward titration was modeled according to the following equilibria:



This model fitted the data extremely well (though the possibility of a 2:2 complex cannot be eliminated). The binding constants are a result of least-squares refinement. The root-mean-square of the residuals over all of the spectroscopic data points was just 0.0022. The error values associated with the binding constants were calculated by re-optimizing the model with 19% of the absorbance data randomly ignored.²⁰ These six ($\text{Eu}(\text{III})$ is a minor absorber) equilibrium-restricted factors account for 99.76% of the data, whereas six unrestricted factors could account for 99.787%. No seventh factor could be found that decreased this gap. The dataset

from the reverse titration was also modeled with these chemical equilibria and yielded corroborating results (see Fig. S7).

As expected, these binding constants are higher than the values attained when just 1:1 binding was assumed since the presence of other species depletes the effective amounts of reactants. It is also clear that the pyridine moiety is involved in the binding, as convincingly demonstrated by comparison of K_{a1} value for ligand **3** with the K_a values obtained for ligands **1** and **2**.

Figure 3 shows the evolving concentration values for the species in solution for the forward and reverse titrations, which demonstrate the extent to which multiple species co-exist in each solution.

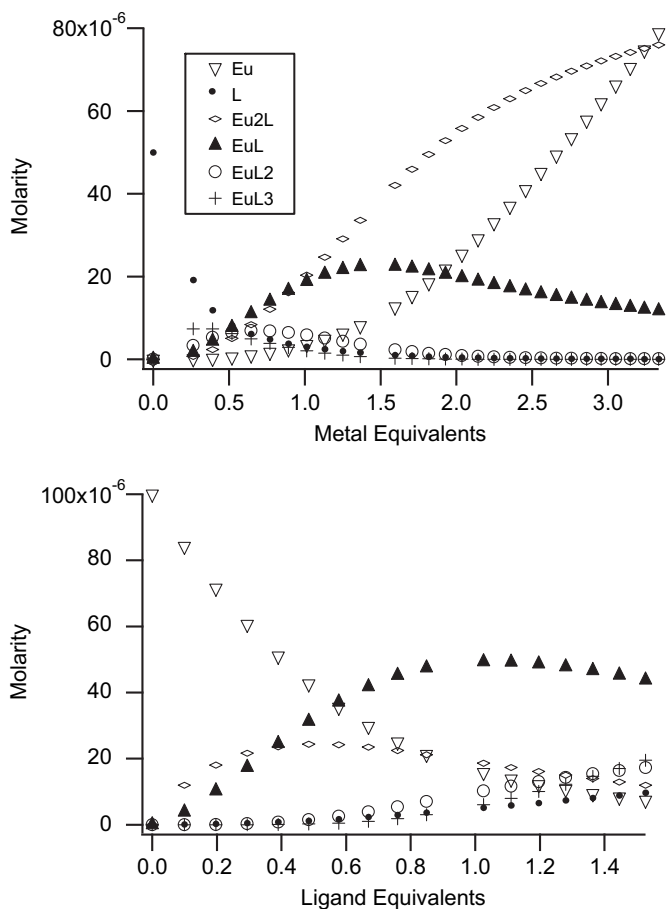


Figure 3. Concentration profiles for the six absorbers that were found to exist in MeCN solutions of **3** upon titration with Eu(OTf)₃ (top), and in solutions of Eu(OTf)₃ upon titration with **3** (bottom).

Further confirmation of the role of the pyridine moiety can be seen in the wavelength dependent color for each of the metal/ligand complexes, which are simply determined simultaneously with the optimization of the binding constants without any *a priori* knowledge of absorptivity values. Figure 4 shows the calculated molar absorptivity curves for the five absorbing species. The two major bands (~380 nm and ~475 nm) help distinguish between the two binding sites of **3** (1,3-diacetylpyridine and π -chromophore). By comparison with the behavior of model compounds **1** and **2**, it is evident that coordination at the π -chromophore brings about the formation of a new band around 475 nm, whereas coordination to the 1,3-diacetylpyridine, as reported in the literature, does not.²¹ Thus, coordination of the lanthanide cation by the 1,3-diacetylpyridine does not alter the spectrum around 450 nm.

Not surprisingly, the peak intensity for complexes with one, two, or three ligands per metal increase with ligand equivalents.

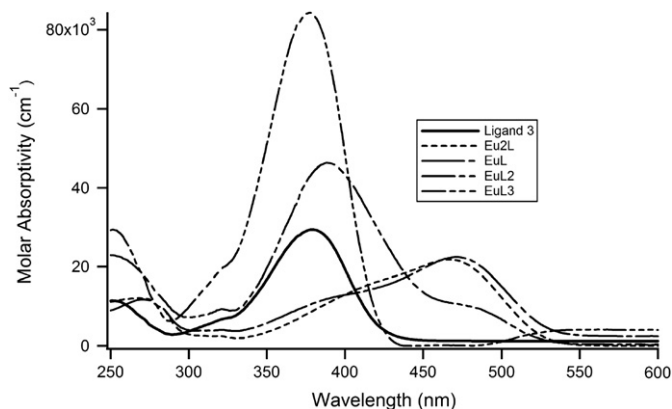


Figure 4. Refined molar absorptivity curves for the five dominant absorbers that were found to exist in MeCN solutions of Eu(OTf)₃ and macrocycle **3**.

Furthermore, these peak absorbances shift monotonically from 472 nm down to 389 nm and finally 378 nm, which is nearly the peak absorbance for the ligand by itself (377 nm). This observation suggests that the mode of binding in these three complexes is quite distinct. Eu(**3**)₃(OTf)₃ is likely formed by the coordination of three pyridine moieties to the metal, leaving the three π -chromophores electronically unperturbed. This is consistent with lesser steric demand of the pyridine moieties compared to that of the π -chromophore end of the ligand. By comparison, the absorption around 475 nm for the 1:2, 1:1, and 2:1 complexes indicates that the π -chromophore is coordinated directly to the metal. Eu(**3**)₂(OTf)₃ appears to have each of its two ligands coordinated in distinct modes: one through the pyridine moiety that augments the band below 400 nm, and one through the π -chromophore that leads to the new band at 475 nm. Eu(**3**)₃(OTf)₃ presumably has one ligand coordinated through both ends (a 2:2 complex is also possible), which is further established with the addition of a second metal cation to form Eu₂(**3**)(OTf)₆ that does not shift the peak positions significantly as it also involves a ligand coordinated through both the pyridine moiety and the π -chromophore, but now to two separate metal cations.

Doing a proper full factor analysis and fitting all wavelengths makes it clear that the sigmoidal shape of the titration profile at 480 nm is not the result of cooperativity, but rather competition between two binding sites (and the accompanying difference in absorption of the resulting complexes) of the macrocyclic scaffold. The first one, the diacetylpyridine, is spectroscopically silent at this wavelength, and it is mainly involved in the binding process in the presence of excess ligand **3**; the second one, the π -chromophore, spectroscopically active at this wavelength, is mainly involved at higher lanthanide/macrocycle molar ratios.²¹

In order to corroborate this model, mass spectrometry was carried out on a variety of MeCN solutions of lanthanide in the presence of ligand **3**. With excess ligand present (Fig. 5a), major peaks were found for [EuL(OTf)₂]⁺, [EuL₂]³⁺, and [EuL₂(OTf)]²⁺; and minor peaks were found for [EuL(OTf)₂]⁺, [EuL₂(OTf)₂]⁺, [EuL₃]³⁺, and [EuL₃(OTf)]²⁺. With excess metal present (Fig. 5b), major peaks were found for [EuL(OTf)]²⁺, and [EuL(OTf)₂]⁺; and minor peaks were found for [EuL]³⁺, [Eu₂L(OTf)₂]⁴⁺, [Eu₂L(OTf)₃]³⁺, [Eu₂L(OTf)₅]⁺.

Mass spectrometry therefore helps confirm the identify all of the species that comprise the model of the spectrophotometric data. Similar to ligand **2**, for which the most abundant species in the gas phase was [Eu(2)(OTf)₂]⁺, [Eu(3)(OTf)₂]⁺ is still one of the most abundant species present in the MS data.^{8a} This suggests that the first coordination sphere of the europium cation in MeCN consists of all three triflate counterions, which are bidentate, and ligand in a tridentate binding mode. The coordination of **2** then involves a 'soft' ligand, the conjugated malonate, and a hard ligand, one of

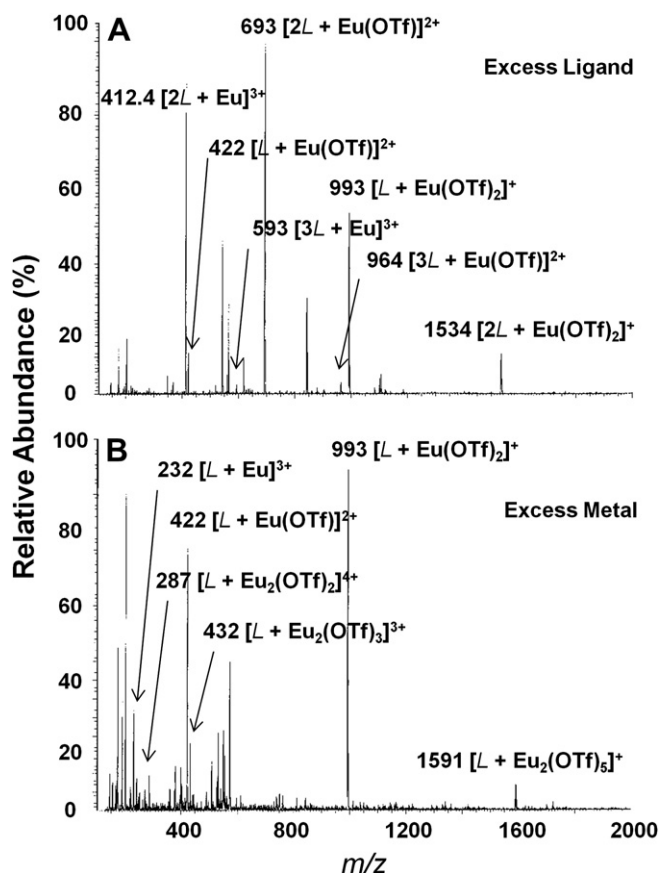


Figure 5. Mass spectrometry experiments for mixtures of ligand **3** (L , 0.001 M) and $\text{Eu}(\text{OTf})_3$. A: 0.5 equiv of $\text{Eu}(\text{OTf})_3$. B: 3.0 equiv.

the ether oxygens.²² As this dual binding mode is unusual, mass spectrometric experiments were carried out in MeCN with ligand **2** and equimolar quantities of five Ln(III) triflate salts (Ln=La, Ce, Eu, Gd, Yb) in order to ascertain possible marked differences in the binding mode of the trivalent lanthanides. The experiment confirmed in all cases the presence of a 1:1 complex in which two triflate counterions are clearly involved in the first coordination sphere in the gas phase (see Fig. S1).

Interest in lanthanide luminescence owes to their sharp emissive behavior in solution when suitably excited in the UV/Vis region through an antenna chromophore. The presence of the conjugated push-pull moiety in **1–3**, directly involved in the coordination sphere of the lanthanide complex suggests they might work as antenna chromophores. The ligands **1–3** showed very weak emissive behavior in solution upon excitation of the lowest energy $\pi-\pi^*$ absorption transition (in all cases with maxima at 380 nm). Upon addition of $\text{Eu}(\text{OTf})_3$, excitation at 380 nm did not result in line-like emission from the europium ion (Fig. S8).²³ A similar, non-emissive response was obtained by using an excitation wavelength positioned on the absorption band of the 1,3-pyridinediacetyl moieties (280 nm).²⁴ The dual nature of ligand **3**, and the complex speciation occurring in solution complicates the use of these cyclic chromophores for optimal luminescence behavior.

3. Conclusions

We have reported the construction of a novel chemical architecture, obtained by joining together two very different, yet pre-organized, binding moieties, into a single ligand suitable for the complexation of lanthanide cations. This ligand shows the ability to form numerous architectures with various stoichiometries, which

were fully characterized via spectrophotometric titration and mass spectrometry. Upon modification of the ligand **3** structure, and in particular by realizing covalently bound dimeric macrocycles, it should be possible to form colored, dynamic, stoichiometry-switchable supramolecular polymers in a lanthanide-driven self-assembly process.²⁵

Ligands with multiple binding modes, especially ones with differing UV/Vis properties (e.g., silent or active at a particular wavelength), can falsely support a hypothesis of cooperative binding. This study strongly testifies to the usefulness of full factor analysis in the interpretation of complex binding events. Modeling the full range of absorbance data with Sivvu allowed for simultaneous thermodynamic and spectroscopic characterization that then even helped to sort out the competing binding modes of the ligand.

4. Experimental section

4.1. General

All commercially available compounds were used as received. Lanthanide Triflate salts were stored under nitrogen. THF (Na), CH_2Cl_2 (CaH₂), and MeCN (CaH₂) were dried and distilled before use. Compounds **1** and **2** were prepared according to literature procedures.^{8a} Column chromatography was performed on silica gel (0.040–0.063 μm). FTIR spectra were recorded using a KBr diffuse reflectance accessories. ¹H and ¹³C NMR spectra were recorded from solutions in CDCl_3 or CD_3CN on 200 or 300 MHz instruments with the solvent residual proton signal as a standard. Mass spectra were recorded using an Electrospray Ionization instrument LCQ Decca (ThermoFinnigan). Melting points are uncorrected.

4.1.1. Compound 3. The corresponding malonate crown ether¹² (411 mg, 1 mmol), *p*-dimethylaminobenzaldehyde (150 mg, 1 mmol) and piperidinium acetate (10 mg) in toluene (50 mL) were heated under reflux for 24 h with a Dean–Stark apparatus. The solvent was then removed in vacuo and the product purified by column chromatography (SiO_2 ; $\text{AcOEt}/\text{Me}_2\text{CO}$: 9/1) to give **3** as a yellow solid (324 mg, 60%). Mp: 152–154 °C (AcOEt). IR (cm^{-1})=1720 ($\nu_{\text{C}=\text{O}}$), 1704 ($\nu_{\text{C}=\text{O}}$). ¹H NMR (CDCl_3) δ =8.31 (m, 2H; PyH), 7.98 (t, 1H; PyH), 7.57 (s, 1H; $-\text{CH}=\text{C}-$), 7.37 (m, 2H; Ar-H), 6.65 (m, 2H; Ar-H), 4.6–4.37 (m, 8H; $-\text{COOCH}_2\text{CH}_2\text{O}-$), 4.07–3.8 (m, 8H; $-\text{COOCH}_2\text{CH}_2\text{O}-$), 3.05 (s, 6H; $-\text{N}(\text{CH}_3)_2$). ¹³C NMR (CD_3CN) δ =167.3, 164.9, 164.8, 164.6, 152.3, 148.0, 142.7, 138.5, 131.8, 128.0, 127.9, 119.2, 119.0, 117.3, 111.6, 69.0, 68.8, 68.7, 68.6, 65.3, 64.8, 64.4, 39.2. UV (MeCN): λ_{max} =378 (35,520), 250 (10,340), 226 (12,280). MS (EI, relative %)=565.3 (100) $[\text{M}+\text{Na}]^+$, 543.3 (27) $[\text{M}+\text{H}]^+$, 542.3 (14) $[\text{M}]^+$. Anal. calcd for $\text{C}_{27}\text{H}_{30}\text{N}_2\text{O}_{10}$ C, 59.8%, H, 5.6%, N, 5.2%; found C, 59.5%, H, 5.8%, N, 5.2%.

Acknowledgements

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Supplementary data

General procedure for the determination of the binding constants, additional graphs; additional mass spectrometric analysis. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.10.024.

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