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A Xanthene–Benzimidazole Receptor with Multiple H-Bond Donors for Carboxylic Acids

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The combination of two benzimidazole moieties with a spacer formed by a leucine unit and a xanthene skeleton provides an efficient receptor for neutral guests with oxygen atoms such as sulfoxides, ketones, or alcohols. ^{1}H NMR and UV spectroscopic techniques have been used to evaluate its binding ability. These experiments indicated the largest association constants for carboxylic acids and different binding stoichiometries. The structures of these different complexes were studied both in solution and in the solid state. Fluorescence of anthracenecarboxylic acid is strongly quenched in the presence of receptor **1**, and therefore, this system could be used to sense the presence of stronger carboxylic acids and anions like chloride.

Introduction

Since Henderson's[1] first proposal of the existence of an "oxyanion hole" in the crystal structure of an acyl-chymotrypsin, many high-resolution enzyme structures have evidenced the presence of such a preorganized environment. Generally, acceptor oxygen atoms like carbonyl groups[2–11] are stabilized by setting two (or three) strong linear H-bonds when bound at the active site. In many cases, the hydrogen-bond donors are two NH groups of peptide residues.

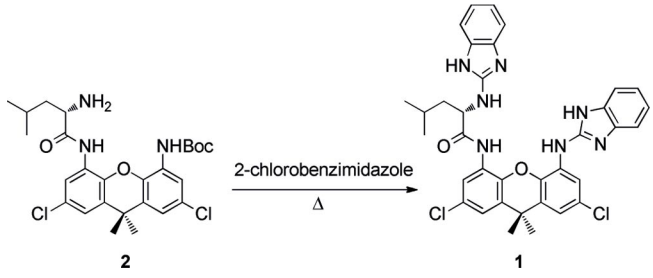
Despite their small molecular weight compared to enzymes, derivatives of the 4,5-diamino-9,9-dimethylxanthene developed by Rebek[12] have proved to be reasonable mimics for oxyanion holes, as shown by X-ray analysis.[13,14] Attaching functional groups containing NH hydrogen-bond donors to the xanthene scaffold has been exploited to achieve preorganized cavities and to bind target anions.[15–22]

Our interest in this field has led us to develop several compounds based on the xanthene framework and suitably functionalized for oxyanion hole mimics.[22–26] Herein, we report the synthesis and H-bond donor ability of related receptor **1** made up of two benzimidazole units linked through a spacer formed by a xanthene unit and a leucine residue. Combination of these fragments (oxyanion hole mimic and benzimidazole) affords a preorganized binding site containing multiple H-bond donors. In addition, the observed changes in the fluorescence emission of anthracenecarboxylic acid upon complexation make its application as a fluorescent sensor feasible.

Results and Discussion

Synthesis

Receptor **1** was synthesized in a single step by treating a previously described material, spacer **2**,[26] with 2-chlorobenzimidazole in sulfolane (Scheme 1). After recrystallization, compound **1** was isolated in 84% yield.



2 1

Scheme 1. Synthesis of receptor **1** from spacer **2** in one synthetic step.

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Solid-State and Solution Studies with Methanol, Acetone, and DMSO

Due to its oxyanion hole-like structure, receptor **1** was able to form complexes in chloroform with neutral organic compounds such as methanol, acetone, or DMSO. The complex with DMSO was especially relevant, as it crystallized from a DMSO/water solution. As shown in the X-ray structure (Figure 1), a molecule of DMSO is bound to the receptor through three intermolecular H-bonds directed towards the sulfoxide oxygen (see the Supporting Information for the X-ray structure data).

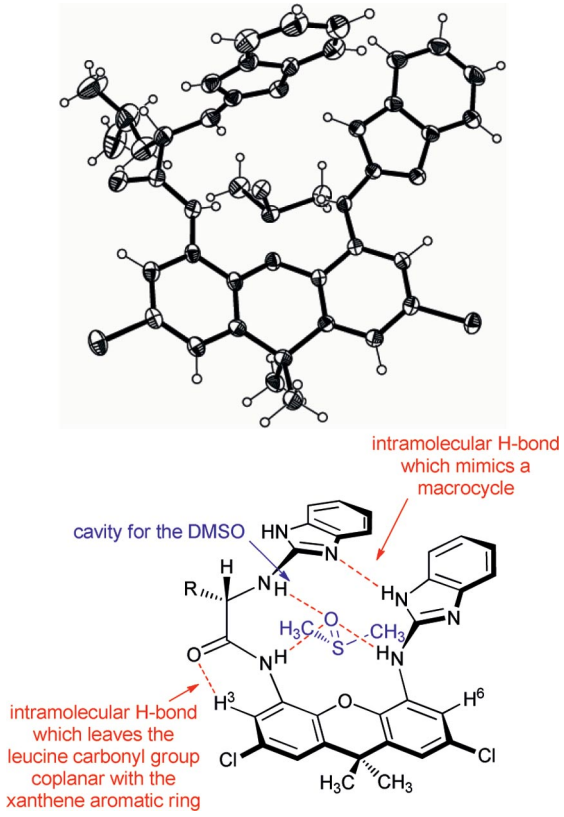


Figure 1. (Top) X-ray structure and (bottom) representation of the complex of receptor **1** with DMSO. Thermal ellipsoids are drawn at the 50% probability level.

Another interesting feature was the formation of an intramolecular H-bond between both benzimidazoles, which looks like a macrocycle in this associate. The existence of this intramolecular H-bond induces the phenyl groups of the xanthene moiety to form a large dihedral angle (27°). Furthermore, the carbonyl group of leucine is almost coplanar with the proximal phenyl ring of the xanthene (angle 2.5°) due to the formation of another intramolecular H-bond between this carbonyl oxygen and the aromatic H^3 (Figure 1). This hydrogen essentially disappears inside the van der Waals radii of the oxygen and carbon C^3.

The binding properties of receptor **1** were investigated by ^1H NMR spectroscopy in $CDCl_3$ at 293 K. In a typical titration experiment, the concentration of **1** was kept constant ($c = 3 \times 10^{-3}$ M) while the amount of guest was increased. The results of these studies are shown in Table 1. The most striking feature of these complexes was the very different chemical shifts of H^3, moving from 8.03 ppm in methanol to 8.95 ppm in acetone.

Table 1. Calculated association constants and observed chemical shifts for H^3 in deuteriochloroform.

Entry	Guest	K_{ass} (M^{-1})	δ_{H^3} (ppm)
1	none		8.20
2	methanol	58	8.03[a]
3	DMSO	40	8.69[a]
4	acetone	20	8.95[a]

[a] Value calculated by extrapolation of the experimental data.

Although high-quality crystals from the acetone complex could not be obtained, it was possible to crystallize the receptor from water/methanol. The compound crystallizes with a molecule of water and a molecule of methanol. The X-ray analysis of these crystals revealed that receptor **1** may adopt different conformations upon complexation with oxygen atoms (Figure 2, see the Supporting Information for the X-ray structure data).

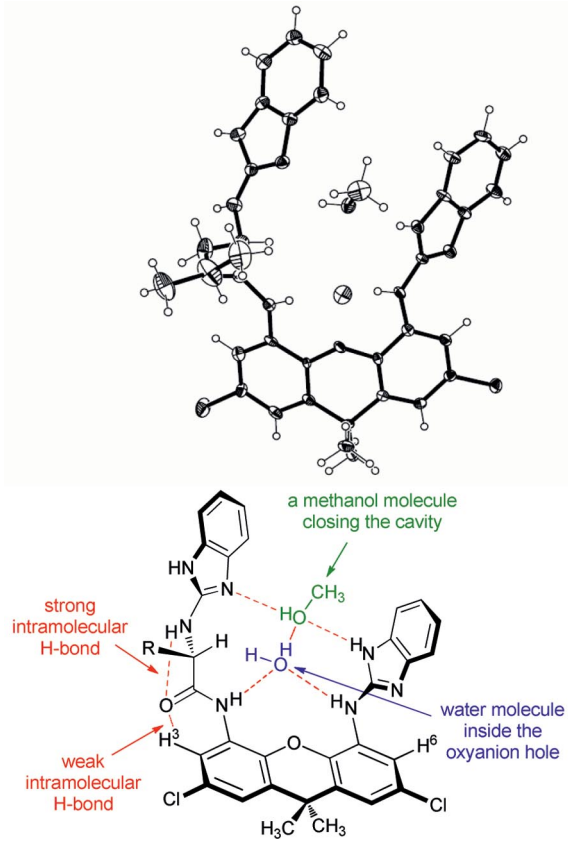


Figure 2. (Top) X-ray structure and (bottom) representation of compound **1** showing methanol and water molecules. Thermal ellipsoids are drawn at the 50% probability level.

As shown, a water molecule was located within the molecular cavity of receptor **1**, setting two linear H-bonds within the oxyanion-hole backbone. Comparison with the previous X-ray structure for the DMSO adduct (Figure 1) demonstrated a different binding pattern for the leucine

NH; instead of binding to the oxygen of the guest, an intramolecular H-bond with the leucine carbonyl is preferred in this case (Figure 2). In addition, both benzimidazoles were bridged through H-bonds to the methanol molecule, thus preventing the formation of the intramolecular H-bond between these heterocycles displayed in Figure 1.

Finally, X-ray analysis of the structure in Figure 2 revealed another difference concerning the strength of the intramolecular H-bond established between the leucine carbonyl group and the aromatic H^3. As a result of the conformational change, the carbonyl group of the leucine and the nearest phenyl ring of the xanthene moiety are no longer coplanar, with a dihedral angle equal to 15°. This explains the weaker H-bond and also the NMR absorption at higher fields for H^3 (Table 1) in this associate.

Solid-State and Solution Studies with Carboxylic Acids

^{1}H NMR Direct Titrations in Methanol and Deuteriochloroform

Carboxylic acids[27–33] are suitable substrates for receptor **1**, as they fulfil the designed criteria for binding; the carbonyl group fits perfectly into the oxyanion hole, whereas further stabilization appears due to the strong interaction between the acidic hydroxy group and the basic benzimidazole nitrogen. Even in the highly competitive solvent methanol, the complexes were formed as shown in Table 2.

Table 2. Association constants for the complexes of **1** and several carboxylic acids in CD_3OD.

Entry	Guest	K_{ass} (M^{-1})
1	decanoic acid	12
2	toluic acid	50
3	anthracenecarboxylic acid	100
4	pyrenecarboxylic acid	130

Attempts to measure the association constants of **1** with decanoic or toluic acids in deuteriochloroform suggested more than one equilibrium (for NMR titration curves see the Supporting Information). The addition of increasing amounts of guest during the ^{1}H NMR titrations led to non-coordinated movement of protons.

Solid-State and Solution Studies with Fluorescent Guest, as Anthracenecarboxylic Acid

The use of the anthracene moiety in the development of fluorescent photoinduced electron transfer (PET) sensors is well documented.[34–37] Interestingly, anthracenecarboxylic acid offered us the possibility to learn more about the structure of the complexes between receptor **1** and carboxylic acids in chloroform solution. This guest is highly fluorescent at 470 nm ($c = 3 \times 10^{-5}$ M), and its light emission was strongly quenched in the complex; two equivalents of receptor **1** quench 90% of the emission at 470 nm (Figure 3), at least under the diluted conditions used in the fluorescence experiments.

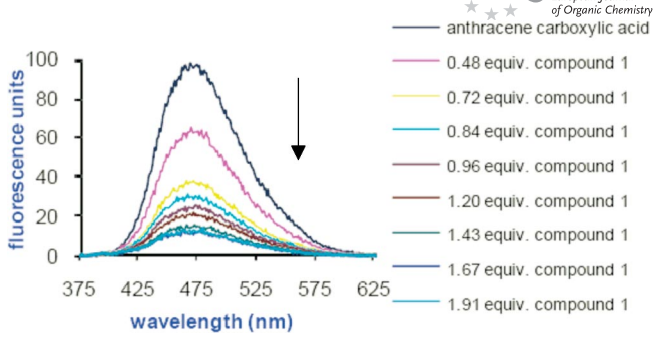


Figure 3. Quenching of anthracenecarboxylic acid fluorescence upon addition of receptor **1**.

The fluorescent emission allowed the measurements of a large association constant ($K_{ass} = 1.8 \times 10^6$ M^{-1}). Under these highly diluted conditions ([compound **1**] = 3×10^{-5} M) a single equilibrium could be detected. The 1:1 complex crystallized from methanol/water, and the X ray structure of this adducts was obtained (Figure 4). As shown, the carbonyl group of the anthracenecarboxylic acid sets two oxyanion-like H-bonds with the xanthene NHs, whereas the other oxygen atom of the carboxylic group points towards the benzimidazole attached to the leucine unit (see the Supporting Information for the X-ray structure data).

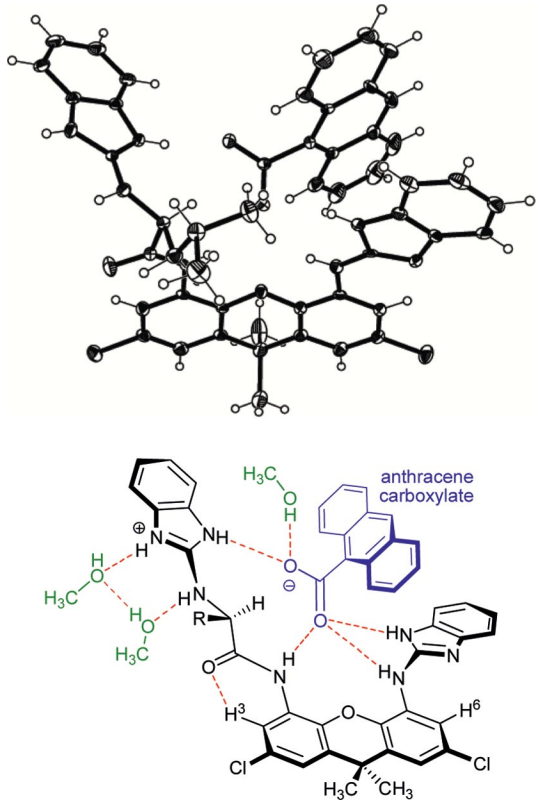


Figure 4. (Top) X-ray structure and (bottom) representation of **1** and anthracenecarboxylic acid. Solvent (methanol) molecules are omitted for clarity in the ORTEP diagram. Thermal ellipsoids are drawn at the 50% probability level.

This receptor conformation resembles that previously described for the associate with the water molecule (Figure 2), because the NH of leucine prefers to form an intermolecular H-bond with a methanol molecule rather than binding the guest. From the lengths of the O–C anthracenecarboxylic acid and the C–N benzimidazole bonds, one can know that proton transfer has taken place from the carboxylic acid to the benzimidazole ring. This proton transfer was unexpected considering the optical properties of anthracenecarboxylic acid. No emission of the anthracenecarboxylate below 450 nm was detected. The characteristic carboxylate emission was also not observed for other fluorescent carboxylic acids such as the pyrene derivative tested, but under more-concentrated conditions, such as those used in NMR experiments, it is not possible to rule out that proton transfer has taken place. In addition, for the pyrenecarboxylic acid, no quenching in its light emission after complexation was detected.

UV Spectroscopy Experiments of 1 in the Presence of Acetic, Chloroacetic, and Trichloroacetic Acids

UV experiments showed, however, that compound **1** ($c = 5 \times 10^{-5}$ M in $CHCl_3$) underwent protonation with chloroacetic acid and even diprotonation with trichloroacetic acid (Figure 5).

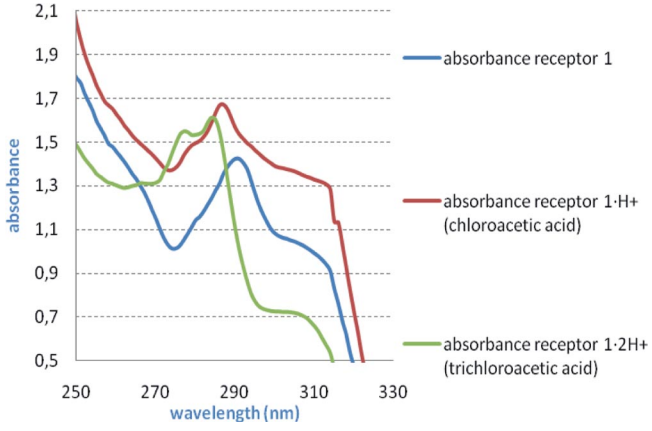


Figure 5. Changes in UV spectra of **1** when mixed with chloroacetic and trichloroacetic acid in $CHCl_3$.

A fourfold excess of acetic acid led to slight protonation of **1** and only with a high acetic acid concentration did complete proton transfer take place (see the Supporting Information for X-ray crystal structure data).

Crystallization from methanol of a mixture of receptor **1** and two equivalents of chloroacetic acid yielded the 1:1 adduct. X-ray analysis revealed, as the most striking feature, proton transfer to the benzimidazole linked to the xanthene and not to the more basic benzimidazole attached to the leucine (Figure 6, see the Supporting Information for X-ray crystal structure data).

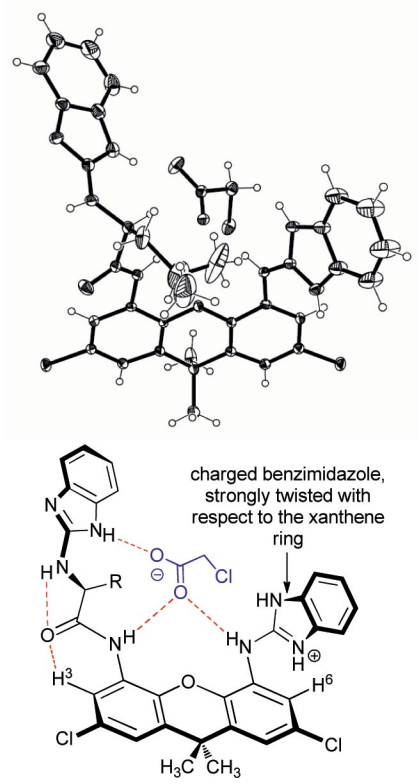


Figure 6. X-ray structure (top) and representation (bottom) of the associate with chloroacetic acid. Thermal ellipsoids are drawn at the 50% probability level.

The solid state may be responsible for this curious effect; due to the presence of the new proton the benzimidazole linked to the xanthene moiety is now strongly twisted with respect to the main plane of the xanthene backbone with a dihedral angle equal to 36° instead of the previous angle of 5°.

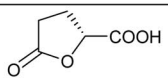
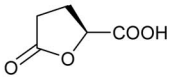
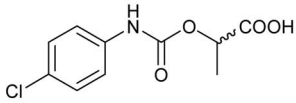
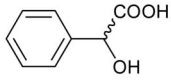
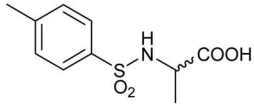
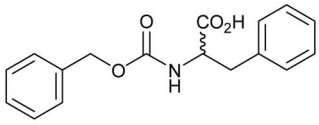
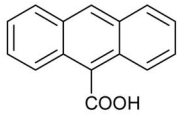
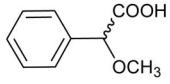
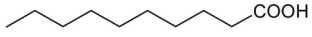
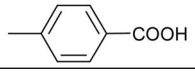
^{1}H NMR Competitive Titrations in Deuteriochloroform

Different carboxylic acids have been tested and their association constants evaluated through ^{1}H NMR competitive experiments with anthracenecarboxylic acid (Table 3).

1:2 Stoichiometry for the Complexes with 5-Oxotetrahydrofuran-2-Carboxylic Acid

The best association constants correspond to 5-oxotetrahydrofuran-2-carboxylic acids (Table 3, Entries 1 and 2). These lactones strongly split the ^{1}H NMR signals of racemic receptor **1**, shifting the leucine methyl groups to negative ppm values. This effect is more dramatic for (*R*)-5-oxotetrahydrofuran-2-carboxylic acid, resulting in an upfield shift of one of the methyl groups to –0.20 ppm. This fact might indicate some chiral recognition; nevertheless, a competitive titration led to a small value, around 3, for the association constant ratio. The analysis through CPK models suggested the formation of an additional H-bond with the lactone oxygen in the complex. However, X-ray analysis of

Table 3. Association constants of **1** and several carboxylic acids in $CDCl_3$ determined by competitive experiments (see the Experimental Section).

Entry	Guest	K_{ass} (M^{-1})
1		5.7×10^7
2		1.9×10^7
3		9.5×10^6
4		6.8×10^6
5		3.8×10^6
6		3.8×10^6
7		$1.8\times10^{6[a]}$
8		1.2×10^6
9		3.8×10^5
10		2.7×10^5

[a] Determined by absolute experiments.

the strong complex with the (*R*)-5-oxotetrahydrofuran-2-carboxylic acid showed no evidence of such H-bond. The structure of this associate is nevertheless interesting, as it corresponds to a 1:2 stoichiometry, in which one carboxylate fills the oxyanion hole while the other forms an ion pair with the leucine benzimidazole (Figure 7; see also the Supporting Information). The presence of more than one lactone molecule in the associates could also be confirmed by ^1H NMR experiments (see the Supporting Information).

Development of a Fluorescent Sensor

As already shown, the receptor–anthracenecarboxylic acid system might be exploited for the development of fluorescent sensors. Because the natural fluorescence of anthracenecarboxylic acid is quenched in the complex, better guests able to displace anthracenecarboxylic acid should regenerate its strong light emission. This is the case of some neutral guests as chloroacetic or trichloroacetic acids and many others shown in Table 3.

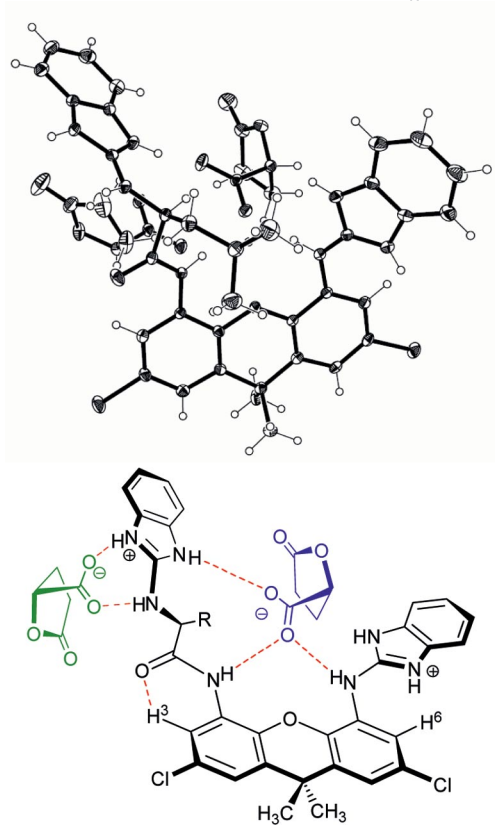


Figure 7. (Top) X-ray structure and (bottom) representation of the 1:2 complex between (*S*)-**1** and (*R*)-5-oxotetrahydrofuran-2-carboxylic acid. Both benzimidazole moieties of the receptor are protonated. Thermal ellipsoids are drawn at the 50% probability level.

Logically, anionic guests should also be analyzed within this system. The choice is, however, limited, because basic anions generate anthracenecarboxylate, which has its own fluorescence properties. Nonbasic anions did not show the necessary affinity for this system; for example, neither iodide nor bromide displaced anthracenecarboxylic acid at all. The exception was chloride, but the response of the system was unexpected. Fluorescence of anthracenecarboxylic acid did not change upon titration with chloride, but if the complex anthracenecarboxylic acid–compound **1** was previously formed, the presence of chloride altered the light emission from that for the neutral carboxylic acid at 470 nm to that corresponding to the carboxylate emission below 450 nm, with small changes in the fluorescence intensity (see the Supporting Information). Apparently, chloride favors proton transfer from anthracenecarboxylic acid to the aminobenzimidazole inside the complex, yielding an associate with three components.

Conclusions

In summary, a new compound based on the xanthene framework and functionalized with multiple hydrogen-bond donors has been synthesized and its ability to associate neutral substrates was evaluated through ^1H NMR titrations

and fluorescent methods. Association constants for carboxylic acids are, in the most favorable cases, in the range 10^6 to 10^7. The geometry of these complexes has been fully elucidated by X-ray diffraction studies, revealing different recognition patterns and intramolecular H-bonds. Due to the several possibilities for intramolecular H-bond formation, receptor **1** can adopt different conformations. In combination with anthracenecarboxylic acid it may provide an interesting sensor for the detection of other carboxylic acids or anions such as chlorides.

Experimental Section

General: Melting points were measured with a Stuart Scientific SM3P capillary apparatus. Optical rotations were determined with a Perkin–Elmer digital polarimeter 341. ^{1}H and ^{13}C NMR spectra were recorded with Bruker Model WP-200-SY or Varian Model Mercury VS. 2000 spectrometers in deuterated chloroform/methanol (4:1). IR spectra were recorded with a Nicolet IR100 spectrometer. Mass spectra were determined with a Applied Biosystems QSTAR XL. X-ray spectra were recorded with a Bruker Kappa APEX II. UV spectra were taken with a UNICAM HeλIOSα VI 0.6. Fluorescence measurements were studied with a Shimadzu RF-5301PC series. Absolute titration were carried out by fluorescence techniques adding increasing amounts of receptor **1** to a solution of anthracenecarboxylic acid and observing fluorescent quenching of anthracenecarboxylic acid signal. Competitive titrations were carried out by NMR techniques adding increasing amounts of receptor **1** of a mixture of anthracenecarboxylic acid and other guest observing chemical shift changes of the both carboxylic acids (for a more detailed explanation, see the Supporting Information). The binding stoichiometry of the complexes studied in this work has been determined, when possible, by Job plots[38] or by the relative integration of the ^{1}H NMR signals of guest and receptor **1**, from solutions of accurate concentrations. They were confirmed by X-ray spectroscopy when crystals of the complexes could be obtained.

(*S*)-2-(1*H*-Benzo[*d*]imidazol-2-ylamino)-*N*-{5-(1*H*-benzo[*d*]imidazol-2-ylamino)-2,7-dichloro-9,9-dimethyl-9*H*-xanthen-4-yl}-4-methylpentanamide (1): A suspension of spacer **2**[26] (2.1 g, 4.0 mmol) and 2-chlorobenzimidazole (1.3 g, 8.5 mmol) in sulfolane (3.0 mL) was kept under an atmosphere of argon at 135 °C for 5 h. After this time no more gas evolution could be detected. The cold reaction mixture was then poured over methanol (15 mL) and added to a well-stirred 2% aqueous sodium hydroxide solution (150 mL). The resulting precipitate was separated and purified by recrystallization from chloroform/ethyl acetate to yield pure compound **1** (2.2 g, 84%) as a white powder. M.p. 265–269 °C. $[\alpha]_D^{20}$ = –20.3 (*c* = 2.3, methanol). ^{1}H NMR (200 MHz, $CDCl_3$/MeOD = 4:1, 25 °C): δ = 8.28 (d, ^4J = 2 Hz, 1 H, H^3), 8.09 (d, ^4J = 2 Hz, 1 H, H^6), 7.50–7.15 (br. s, 4 H, H$^{4''}$, H$^{7''}$, H$^{4'''}$, H$^{7'''}$), 7.05 (d, ^4J = 2 Hz, 3 H, H^1, H$^{5'''}$, H$^{6'''}$), 6.93 (d, ^4J = 2 Hz, 3 H, H^8, H$^{5''}$, H$^{6''}$), 4.51 (dd, ^3J = 10 Hz, ^3J = 4 Hz, 1 H, H$^{2'}$), 1.70–1.57 (m, 3 H, H$^{3'}$, H$^{4'}$), 1.51 (s, 3 H, CH_3-C-CH$_3$), 1.47 (s, 3 H, CH$_3$-C-CH_3), 0.81 (d, ^3J = 6 Hz, 6 H, CH_3-CH-CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$/MeOD = 4:1, 25 °C): δ = 172.3 (C=O), 154.2 (C=NR), 150.2 (C=NR), 138.4 (ArC), 137.5 (ArC), 131.3 (ArC), 130.7 (ArC), 129.2 (ArC), 128.9 (ArC), 128.6 (ArC), 126.3 (ArC), 121.3 (ArCH), 119.2 (ArCH), 118.6 (ArCH), 117.1 (ArCH), 56.0 (CH), 41.8 (CH$_2$), 34.8 (C), 32.1 (CH$_3$), 30.9 (CH$_3$), 24.7 (CH), 22.5 (CH$_3$), 21.6 ppm (CH$_3$). IR (Nujol): $\tilde{\nu}$ = 3364, 1683, 1631, 1586, 1268, 1200, 736 cm^{-1}. MS (EI+, 70 eV): *m*/*z* = 654.2 [M + H]$^+$, 676.2 [M + Na]$^+$. $C_{35}H_{33}Cl_2N_7O_2 + H_2O$ (752.60): calcd. C 62.50, H 5.24, N 14.58; found C 62.42, H 5.22, N 14.48. The structure of compound **1** was confirmed by X-ray diffraction.

Supporting Information (see footnote on the first page of this article): ^{1}H NMR, ^{13}C NMR, IR, and mass spectra of receptor **1**; ORTEP diagrams and X-ray crystal structure data; ^{1}H NMR chemical shifts in $CHCl_3$ of receptor **1** protons in the presence of increasing amounts of decanoic, (*R*)-5-oxotetrahydrofuran-2-carboxylic, and (*S*)-5-oxotetrahydrofuran-2-carboxylic acid; fluorescence titrations of anthracenecarboxylic and pyrenecarboxylic acid with receptor **1**; UV spectra of receptor **1** with acetic, chloroacetic, and trichloroacetic acid; fluorescent titration of the complex anthracenecarboxylic acid–compound **1** with chloride; Job plot; stereoviews images of X-ray structures; evaluation of binding constants through competitive titrations.

Acknowledgments

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