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Stereoselective optical sensing of dicarboxylate anions by an induced-fit type Ru(II) receptor

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Abstract

An induced-fit type Ru(II) receptor **1** has been synthesized in which, upon approach of dicarboxylates, a highly flexible tetraamide binding site is organized to complement their chemical structures. Stereoselective optical sensing has been demonstrated by virtue of the luminescence response of **1** to the binding of *cis*/*trans*-1,4-cyclohexanedicarboxylates.

Optical and electrochemical sensing of anionic species in aqueous and nonaqueous media is an area of great interest in current research.[1–4] Beer recently described photo- and redox-responsive anion receptors, based on Lewis acidic centres and amide binding sites.[5] In particular, macrocyclic Ru(II) receptors showed electrochemical and optical sensing of anions with high binding selectivity.[6] As part of our own efforts to develop new photoresponsive anion receptors,[7] we have designed an induced-fit type Ru(II) receptor **1** in which, upon approach of dicarboxylates, conformational changes occur to organize a binding site for achieving optimal complexation. Here we report the synthesis and binding properties of the Ru(II) receptor **1**, and present stereoselective optical sensing of dicarboxylate anions.

Mono-*N*-acetylation of 4,4′-methylenedianiline, followed by coupling to 4,4′-bis(chlorocarbonyl)-2,2′-bipyridine[8] at room temperature in the presence of Et_3N in *N*,*N*′-dimethylacetamide (DMAC), gave tetraamide bipyridine in 48% yield. Tetraamide bipyridine reacted with $Ru(bpy)_2Cl_2$[9] (bpy = 2,2′-bipyridine) at 100°C in 90% DMAC for 24 h to give **1** in 35% yield.[10]

The UV–vis titrations with aromatic and aliphatic dicarboxylates in DMSO showed clear structure dependence. In a series of 1,*x*-$(CO_2^-)_2C_6H_4$ ($x = 2$–4) and $^-{}_2OC(CH_2)_nCO_2^-$ ($n = 1$–8), isophthalate ($x = 3$), terephthalate ($x = 4$), adipate ($n = 4$) and pimelate ($n = 5$) caused a slight blue shift of the MLCT band with distinct isosbestic points, whereas the other dicarboxylates provided

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no isosbestic points. Alicyclic dicarboxylates such as 1,3-adamantane- and 1,4-cyclohexanedicarboxylates ($n = 3, 4$) caused the most pronounced changes in the MLCT band with isosbestic points.

Optical sensing of dicarboxylates was more dramatically demonstrated by virtue of the luminescence response to the complexation (Table 1). Addition of iso- or tere-phthalate to a solution of **1** in DMSO resulted in a slight blue shift and a marked increased intensity of the MLCT emission band. A similar spectral change was observed upon addition of *p*-toluene but it was much less pronounced. Interestingly, the luminescence spectrum of **1** decreased by 3–5% until 1 equiv. of adipate or pimelate was added to the DMSO solution, and then increased by 16–19%. There was no increase but a significant decrease of emission intensity ($\Delta I = -15\%$) upon addition of 1,3-adamantanedicarboxylate. Interestingly, the emission intensity of the MLCT emission band of **1** was enhanced in the presence of *trans*-1,4-cyclohexanedicarboxylate but diminished by the *cis*-isomer. The magnitude and the direction of the emission intensity change was strikingly guest geometry-dependent. Such optical properties have not hitherto been observed for Ru(II) receptors with a preorganized amide binding site to complement the size and shape of anions.

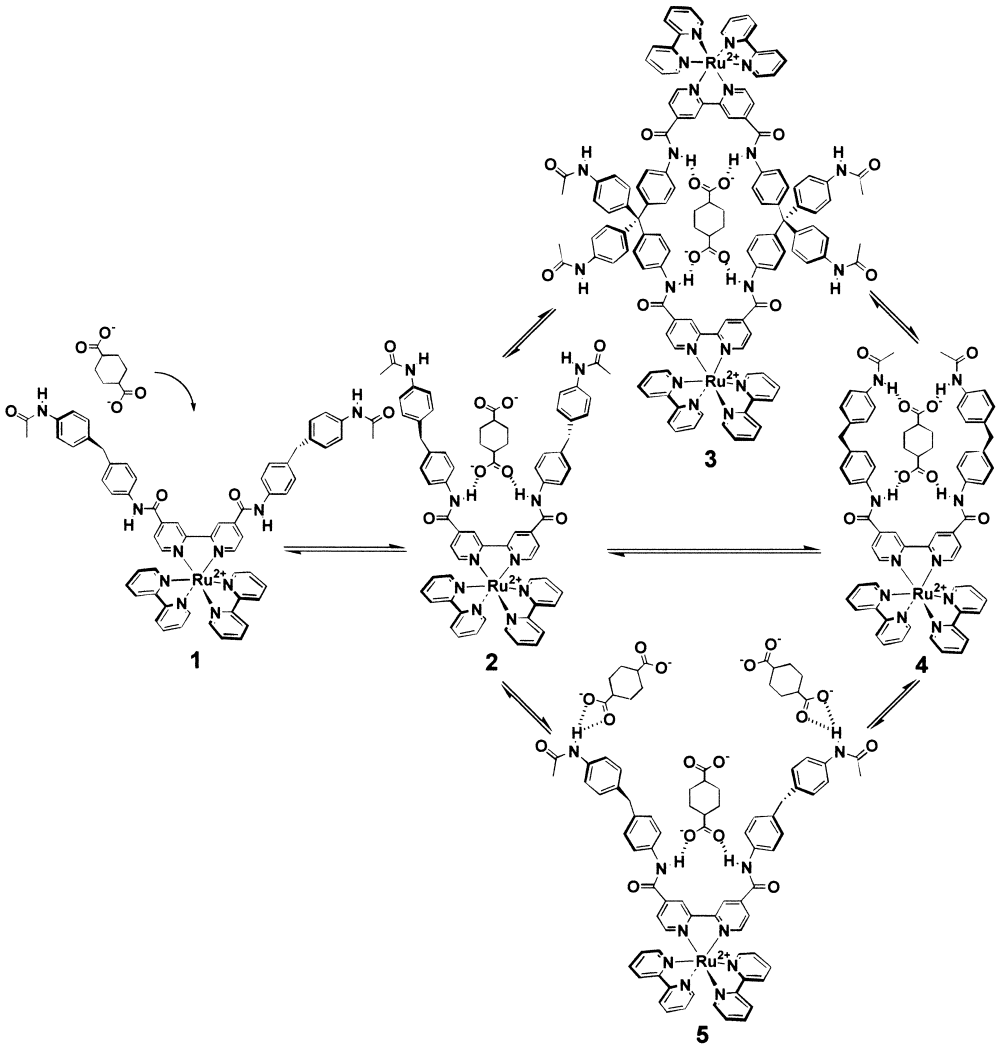
Table 1
Binding constants and luminescence changes of **1** with carboxylate anions in DMSO at 293 K[a]

Substrate (n)[b]	H : G[c]	$K_a(M^{-1})$		$\Delta I(\%)$[d]
		^{1}H-NMR	UV-Vis	
isophthalate^{2-}(3)	1 : 1	$>10^4$	76000	20
terephthalate^{2-}(4)	1 : 1	$>10^4$	74000	21
p-toluate$^-$	1 : 1	850	—[e]	5
adipate^{2-}(4)	1 : 1	$>10^4$	95000	16
pimelate^{2-}(5)	1 : 1	$>10^4$	102000	11
1,3-adamantanedicarboxylate^{2-}(3)	2 : 1	K_1=25000, K_2=79	—[e]	−15
cis-1,4-cyclohexanedicarboxylate^{2-}(4)	2 : 1	K_1=56000, K_2=60	—[e]	−20
trans-1,4-cyclohexanedicarboxylate^{2-}(4)	2 : 1	K_1=54000, K_2=80	—[e]	5

[a]Carboxylates were used as their Et_4N^+ or Bu_4N^+ salts. [b]The number of carbons between carboxylate groups. [c]The Job plots were performed using the inner amide N*H* and 3,3'-byp C*H* resonances of the tetraamide bipyridine. [d]Excited at the isosbestic wavelength. $\Delta I = (I - I_0)/I_0$ where I_0 and I are the emission intensities in the absence and in the presence of 10 equiv. of guest molecules, respectively. [e]No binding constants determined.

^{1}H NMR titrations were carried out with the dicarboxylates which produced absorption spectral changes going through isosbestic points on the UV–vis titrations. Addition of the dicarboxylate to a solution of **1** in DMSO-d_6 led to chemical shift changes in all of the tetraamide bipyridine protons. The inner amide N*H* and the 3,3′-bpy C*H* shifted downfield by 2.03–2.77 and 0.22–0.56 ppm, respectively. The important downfield shift of 0.41–0.63 ppm was also observed in the outer amide N*H*. There are two possible complexation processes **1**→**2**→**4** and **1**→**2**→**5** to explain these changes (Scheme 1). However, the outer amide N*H* shifted downfield only by 0.13 ppm when *p*-toluate, incapable of forming the complex **4**, was added to a solution of **1** in DMSO-d_6. These results suggest that the induced-fit type complex **4** could be formed upon binding of dicarboxylate anions. Additional changes were observed in the ^{1}H NMR titrations. Both chemical shift changes of the inner amide N*H* and the 3,3′-bpy CH reached a plateau near 1–2 equiv. of dicarboxylates, whereas no saturation characteristics were observed in the chemical shift changes of the outer

amide N*H*, reflecting the complex **4** as being in equilibrium with the complex **2**. Monitoring the chemical shift changes of the outer amide N*H* as a function of dicarboxylate concentration led to the sigmoidal titration curves. This indicates that the induced-fit type complex **4** undergoes further conformational changes to form the 1:3 complex **5** on increasing the concentration of dicarboxylates. Binding to alicyclic dicarboxylates formed a 2:1 receptor to anion complexes **3** under receptor excess conditions. In fact, the 3,3′-bpy C*H* initially shifted downfield until 0.5 equiv. of the alicyclic dicarboxylate was added to the solution; inflection occurred and then moved upfield.



Scheme 1.

All titration curves were analyzed by using nonlinear curve-fitting procedures[11] and the calculated binding constants were corrected in Table 1. Dicarboxylates form complexes of much higher stability with **1** than monocarboxylates, reflecting a major role of electrostatic interactions in anion binding. A variety of aromatic and aliphatic dicarboxylates are bound with considerable

stability ($K_a > 10^4$ M). The high adaptability of **1** to guest structures is also reflected in the poor binding selectivity. Despite their closely similar binding constants, the Ru(II) receptor **1** is capable of optically discriminating between the geometrical isomers of 1,4-cyclohexanedicarboxylate. Under the luminescence titration conditions, the formation of the complex **3** was negligible because of the low binding constants ($K_2 < 100$ M^{-1}). Neither complexes **2** or **5** are likely to produce different luminescence signals for these geometrical isomers. The stereoselective optical sensing of 1,4-cyclohexanedicarboxylates would result from the formation of the induced-fit type complex **4**. The induced-fit complexation rigidifying the receptor structure and thereby inhibiting non-radiation decay processes can induce intensity enhancement of the MLCT emission band of **1**. However, receptor conformations induced by 1,3-adamantane- and *cis*-1,4-cyclohexane-dicarboxylates might open non-radiation decay channels via vibrational relaxation and excitation, which compete with the enhanced radiation decaying processes.[12]

In conclusion, we have shown that an induced-fit binding site incorporated in the photoactive Ru(II) centre can produce the stereoselectivity in optical sensing of dicarboxylate anions. Further investigation is in progress to clarify the effect of guest-induced conformational changes on the optical sensing mechanism.

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