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Synthesis and Characterisation of Novel Ruthenium(II) Bipyridyl and Ferrocenoyl Cavitand Receptors for the Recognition of Anionic Guests

Isabelle Dumazet and Paul D. Beer*

Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, U.K.

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Abstract

Novel ruthenium(II) bipyridyl and ferrocenoyl resorcinarene cavitand receptors have been prepared. The ruthenium(II) bipyridyl modified resorcinarene 4 has been shown by UV visible absorption and fluorescence emission spectroscopy to bind chloride, acetate and benzoate anions with a preference for carboxylate anions.

Keywords: anion binding, cavitands, molecular recognition

Introduction

The recognition of anionic guest species of biochemical, medical and environmental importance is an area of intense current interest [1]. As a consequence of their unique topological frameworks, the calixarenes and resorcinarenes are attractive host molecules to modify for the recognition of anionic guest species [2]. Indeed, Reinhoudt and co-workers [3] have recently described the complexation of (thio)urea-functionalised resorcinarene cavitands with halide anions. The ability of such calixarene type systems to optically or electrochemically sense anions is relatively rare [4]. We report here the synthesis of new redox- and photoactive resorcinarene cavitand receptors that contain respectively four ruthenium(II) bipyridyl and four ferrocenoyl moieties. Preliminary anion binding investigations reveal that 4 complexes and senses via MLCT fluorescence emission enhancement chloride, acetate and benzoate.

Results and Discussion

Synthesis of anion receptors

The condensation of four equivalents of 4-chlorocarbonyl-4'-ethoxycarbonyl-2,2'-bipyridine **2** with tetrakis(aminomethyl)cavitand **1** [5] in dry dichloromethane in the presence of triethylamine afforded a crude product which was purified via column chromatography to give tetrakis(4-amidomethyl-4'-ethoxycarbonyl-2,2'-bipyridine)cavitand **3** as a light-brown powder in 36% yield. The tetrakis(ruthenium(II) bipyridyl) cavitand receptor **4** was obtained by refluxing **3** with four equivalents of $[RuCl_2(bipy)_2] . 2H_2O$ in a mixture of ethanol and water, followed by purification on Sephadex LH-20 column chromatography and precipitation of the complex on addition of ammonium hexafluorophosphate (Scheme 1).

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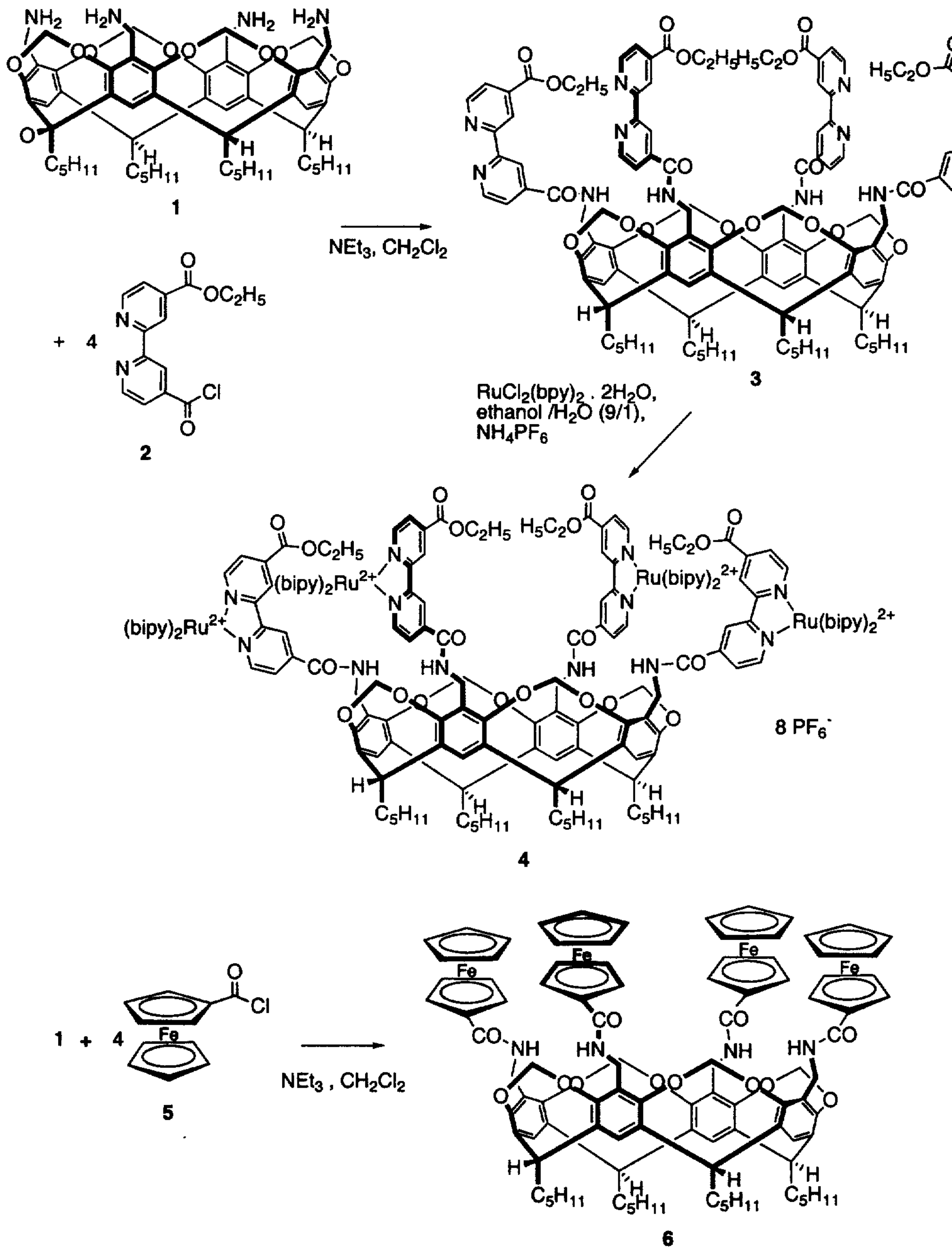
1
+ 4
2
NEt3, CH2Cl2
3
RuCl2(bpy)2 . 2H2O,
ethanol /H2O (9/1),
NH4PF6
4
8 PF6-
1 + 4
5
NEt3 , CH2Cl2
6

Scheme 1

Using a similar synthetic procedure, the condensation of 4 equivalents of (chlorocarbonyl)ferrocene with (aminomethyl)cavitand **1** in dry dichloromethane in the presence of triethylamine gave tetrakis(ferrocenylamidomethyl)cavitand **6** which, after column chromatographic purification, was isolated as a yellow powder in 36% yield. Both new receptors were characterized by ^{1}H NMR, mass spectrometry and elemental analysis.[1]

Anion Coordination Investigations.

The recognition of anions in solution was initially investigated by ^{1}H NMR. The addition of two equivalents of tetrabutylammonium chloride to a CD_3CN solution of **4** resulted in significant amide and bipyridyl-H_3 downfield proton shifts of up to 0.64 ppm. Similar observations were observed with acetate and benzoate. Unfortunately precipitation problems thwarted stability constant values being obtained from these ^{1}H NMR titration experiments. In the case of **6** analogous ^{1}H NMR titration studies in CD_2Cl_2 with chloride revealed large perturbations of both the receptor's cyclopentadienyl and amide protons. EQNMR [6] analysis of the titration data gave a 1:1 stoichiometric stability constant value of 66 M^{-1} for the chloride complex which in comparison with the chloride stability constant of 4.7 M^{-1} exhibited by butylaminocarbonylferrocene [7] suggests the four ferrocenoyl amide linked moieties of the cavitand cooperate in the binding of the halide guest anion.

Electronic Absorption and Fluorescence Emission Spectra.

Ruthenium(II) polypyridyl complexes exhibit well known luminescence properties [8] and it was of interest to probe the optical anion recognition behaviour of **4** using electronic absorption and fluorescence emission spectroscopy. In acetonitrile solution **4** displays the characteristic MLCT absorption band at λ_{max} = 463 nm, $\varepsilon = 5.8 \times 10^4$ $M^{-1}cm^{-1}$, which because of the electron withdrawing characteristics of the amide groups is bathochromically shifted relative to $[Ru(bpy)_3]$ $[PF_6]_2$ (λ_{max} = 452 nm, $\varepsilon = 1.43 \times 10^4$ $M^{-1}cm^{-1}$) [9]. The addition of anions led to significant perturbations of notably the receptor's MLCT absorption bands and using SPECFIT analysis [10] of the titration data,[2] stability constants were determined. Table 1 shows the cavitand **4** forms stable 1:1 complexes with chloride, benzoate and acetate, with the receptor displaying a selectivity preference for the carboxylate anions over chloride.

Anions	Log K^a
Chloride	3.4
Benzoate	4.4
Acetate	4.3

Table 1. Stability Constant data for **4** with anions in acetonitrile at 296K, ^{a} Errors estimated to be <5%.

Fluorescence emission spectroscopic measurements were also undertaken to probe anion binding.

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[1] Compound **3** : MS (FAB) m/z 1951 $[M+H]^+$, 1973 $[M+Na]^+$; ^{1}H NMR ($CDCl_3$) : δ 8.89 (s, 4H, bpyH_3), 8.76 (dd, 8H, J 2.2Hz, bpy$H_{5,5'}$), 8.58 (s, 4H, bpy$H_{3'}$), 7.85 (d, 4H, J 4.5Hz, bpyH_6), 7.69 (d, 4H, J 4.6Hz, bpy$H_{6'}$), 7.11 (s, 4H, H_{ar}), 7.02 (b t, 4H, NH), 6.09 (d, 4H, J 6.8Hz, OCH_2O), 4.78 (t, 4H, C_{ar}-CH-C_{ar}), 4.48-4.38 (m, 20H, OCH_2O, OCH_2CH_3 and CH_2NH), 2.18 (m, 8H, C_5H_{11}), 1.29 (m, 36H, C_5H_{11} and OCH_2CH_3), 0.65 (t, 12H, C_5H_{11}) ; Anal. Calc. for $C_{112}H_{116}O_{20}N_{12}$ + 4 H_2O : C, 66.52% ; H, 6.18% ; N, 8.31% ; Found C, 66.34% ; H, 5.83% ; N, 8.04%. Compound **4** : MS (ES) m/z 1946.5 $[M-4PF_6^-]^{4+}$, 450.3 $[M-8PF_6^-]^{8+}$; ^{1}H NMR (CD_3CN) : δ 9.00(b t, 4H, NH), 8.84 (s, 4H, H_{ar}), 8.53-8.50 (m, 20H, bpyH), 8.10-8.05 (m, 16H, bpyH), 7.95 (d, 4H, J 6.0Hz, bpyH), 7.90 (d, 4H, J 6.1Hz bpyH), 7.82 (dd, 4H, bpy), 7.69 (m, 20H, bpyH), 7.44-7.37 (m, 20H, bpyH), 6.01 (d, 4H, J 6.9Hz, OCH_2O), 4.66 (b t, 8H, CH_2NH), 4.28 (b t, 4H, C_{ar}-CH-C_{ar}), 4.23 (b s, 8H, OCH_2CH_3), 3.91 (d, 4H, J 6.8Hz, OCH_2O), 2.08 (m, 8H, C_5H_{11}), 1.18-1.38 (m, 36H, C_5H_{11} and OCH_2CH_3), 0.90 (t, 12H, C_5H_{11}) ; Anal. Calc. for $C_{192}H_{180}O_{20}N_{28}Ru_4P_8F_{48}$ + 5 H_2O : C, 47.46% ; H, 3.94% ; N, 8.08% ; Ru 8.40% ; Found C, 47.78% ; H, 4.41% ; N, 8.03% ; Ru 8.11%. Compound **6** : MS (FAB) m/z 1803 $[M+Na]^+$; ^{1}H NMR ($CDCl_3$) : δ 7.08 (s, 4H, Har), 6.19 (b t, 4H, NH), 6.07 (d, 4H, J 6.8Hz, OCH_2O), 4.81 (t, 4H, C_{ar}-CH-C_{ar}), 4.64 (s, 8H, Fc H), 4.46 (d, 4H, J 7.1Hz, OCH_2O), 4.39 (d, 4H, J 5.4Hz, CH_2-NH) 4.32 (s, 8H, Fc H), 4.12 (s, 20H, Fc H), 2.18 (m, 8H, C_5H_{11}), 1.29 (m, 24H, C_5H_{11}), 0.65 (t, 12H, C_5H_{11}) ; Anal. Calc. for $C_{100}H_{108}O_{12}N_4Fe_4$ + H_2O : C, 66.75% ; H, 6.16% ; N, 3.11% Found C, 66.36% ; H, 6.54% ; N, 2.99%.

[2] Typically 7.5×10^{-8} mol of receptor was dissolved in acetonitrile (3ml) (ionic strength 2.5×10^{-3} M made up with TBA PF_6). The guest was added using a microsyringe (as a 7.5×10^{-3} M solution).

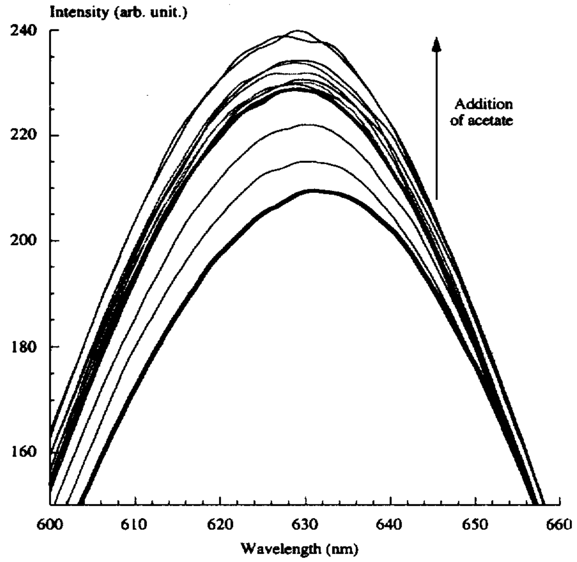

Figure 1. Effect of addition of stoichiometric amounts of acetate on the fluorescence emission spectrum of 4 in acetonitrile.

Compared with $[Ru(bpy)_3][PF_6]_2$, the emission maxima of **4** is bathochromically (red) shifted to longer wavelength respectively from $\lambda_{max} = 609$ nm to $\lambda_{max} = 636$ nm, attributable to the amide moieties.

The addition of excess amounts of anions resulted in significant increases in emission intensity. For example, Figure 1 shows the effect of sequential amounts of acetate on the fluorescence emission spectrum resulting in an increase of 15%. With chloride, an increase of 13% was observed, and with benzoate 11%. In the case of acetate and benzoate, there were small blue shifts (5 and 3 nm respectively) of MLCT band. This anion induced enhancement of emission is also exhibited by acyclic and macrocyclic ruthenium(II) bipyridyl amide receptors [9] [11] and may be explained by the formation of the receptor-anion complex increasing the rigidity of the receptor, thereby disfavouring the nonradiative decay process.

In conclusion, new ruthenium(II) bipyridyl and ferrocenoyl resorcinarene cavitands have been synthesised and shown to bind and in the case of **4** optically sense anions in acetonitrile solutions.

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