ChemComm

Anion recognition through hydrogen bonding: a simple, yet highly sensitive, luminescent metal-complex receptor

Shih-Sheng Sun and Alistair J. Lees*

Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13902-6016, USA. E-mail: alees@binghamton.edu

Received (in Irvine, CA, USA) 5th June 2000, Accepted 26th July 2000

A new luminescent rhenium(I) polypyridyl-based receptor for a variety of inorganic anions has been designed and synthesized and this artificial receptor shows high affinities for halides, cyanide and acetate anions with binding constants as high as 10^4–10^5 M^{-1} and a detection limit as low as 10^{-8} M in CH_2Cl_2 solution.

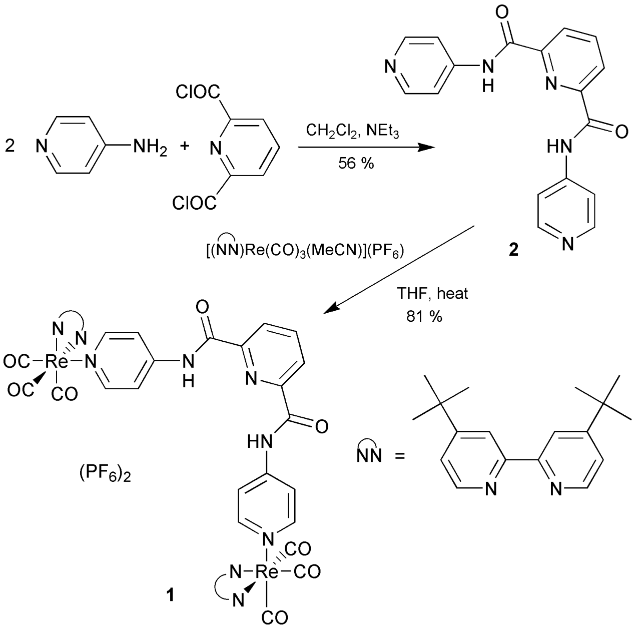
The design and synthesis of efficient artificial receptors for selective binding of biologically or environmentally important anionic species is an emerging field with many applications.[1,2] A variety of synthetic receptors have been designed and studied for their binding strength and selectivity toward different anions. These have included Lewis acids,[1] protonated polyammonium macrocycles,[1] pyrroles,[3] guanidiniums,[4] metalloreceptors[1] and amides.[1] However, many of these receptors have very elaborate structures that typically require multiple synthetic steps with relatively low overall yields which make it impractical to prepare them on a large scale. There are only a few structurally simple receptors exhibiting both sensitivity and selectivity.[5]

Nature provides many examples of proteins utilizing hydrogen bonding for binding substrates. The incorporation of luminescent chromophores into the receptor which are sensitive to interactions between the receptor and analytes has gained considerable attention due to their high sensitivity and detection limit.[6] Although there have been several literature reports concerning luminescence-based anion detection,[6,7] the highly sensitive luminescence-based halide and cyanide sensory systems are much rarer.[7] Thus, we embarked on designing a very simple and easily prepared luminescent metal complex integrated with an amide moiety functioning as a hydrogen bonding site. We report herein, the synthesis and binding properties of this highly sensitive and selective luminescent anion receptor, $[\{(Bu^t{}_2bpy)Re(CO)_3\}_2(\mu\text{-}L)](PF_6)_2$ **1**, ($Bu^t{}_2$bpy = 4,4′-di-*tert*-butylbipyridine).

The synthesis of L and complex **1** is shown in Scheme 1. The bridging ligand **2** was prepared in 56% yield from 2 equivalents of 4-aminopyridine and 2,6-pyridinedicarbonyl dichloride. Subsequent reaction of **2** and 2 equivalents of $[(MeCN)(Bu^t{}_2bpy)Re(CO)_3](PF_6)$[8] in refluxing THF, followed by recrystallization from CH_2Cl_2–pentane, afforded a bright yellow crystalline solid **1**† in 81% yield.

The N–H protons of complex **1** exhibit a chemical shift δ 10.59 in $CDCl_3$. The very downfield chemical shift indicates the presence of strong intramolecular hydrogen bonding between the N–H protons and nitrogen in the central pyridine. This results in ligand **2** having an approximate right angle geometry[9,10] and the converged structure of complex **1** renders it as an effective anion receptor through hydrogen bonding. In deoxygenated CH_2Cl_2 solution, complex **1** exhibited intense absorption bands in the near UV to visible spectral region (λ_{max} = 254, 281 and 380 nm, ε_{max} = 63600, 61500 and 7700 M^{-1} cm^{-1}, respectively) and a very strong luminescence at 536 nm with quantum yield of 0.37 and lifetime of 0.48 μs.

Addition of different halides or inorganic polyatomic anions (as tetrabutylammonium salts) into a 1×10^{-5} M solution of complex **1** was observed to cause different degrees of quenching of the luminescence intensities.‡ The N–H protons in ^1H NMR spectra all showed significant downfield shifts (> 1.5 ppm), indicating the strong hydrogen bonding formation between the amide protons of complex **1** and the anions. Fig. 1



Scheme 1

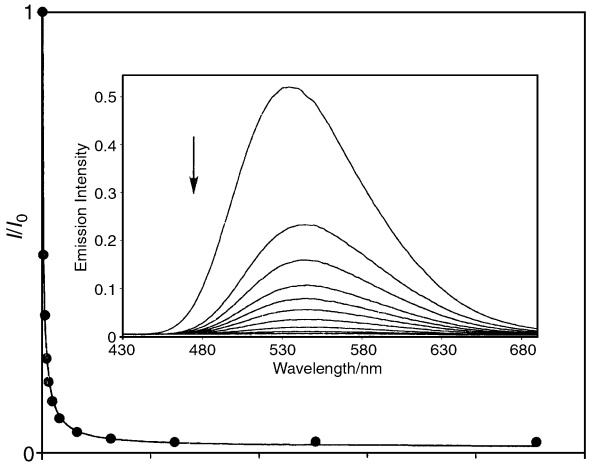


Fig. 1 Titration curve of the addition of F^- anion (as tetrabutylammonium salt). The inset shows the change of the emission intensity of complex **1** in CH_2Cl_2 solution upon addition of F^- anion. Excitation wavelength is 360 nm.

DOI: 10.1039/b004541l

Table 1 Binding constants K_b determined by luminescence titration in CH_2Cl_2 at 298 K

Anion	K_b/M^{-1}
CN^-	8.80×10^5
F^-	3.82×10^5
Cl^-	3.99×10^4
Br^-	3.90×10^4
I^-	1.49×10^5
OAc^-	3.41×10^4
$H_2PO_4^-$	1.47×10^2
NO_3^-	63.4
ClO_4^-	8.4

shows a typical titration curve for the luminescence intensity upon addition of F^- to a CH_2Cl_2 solution of **1**.§ The curve was determined to fit well to a 1:1 binding isotherm.[11] Concomitant with the quenching, the luminescence wavelength slightly red-shifted from 536 to 546 nm. Table 1 summarizes the binding constants measured for complex **1** toward different anions. Clearly, this molecule shows strong binding affinity toward halides, cyanide or acetate anions, only moderate binding affinity toward dihydrogen phosphate and very weak binding affinity to nitrate or perchlorate anions.

The overall order determined for binding affinity is: $CN^- > F^- > I^- > Cl^- \approx Br^- \approx OAc^- >> H_2PO_4^- > NO_3^- > ClO_4^-$. This finding is significant as it is not common for charged receptors to exhibit such outstanding selectivity for anion species.[12] In fact, the combination of interactions involving electrostatic force, hydrogen bonding strength and steric effects all apparently influence the binding affinities toward anions in complex **1**. Importantly, the sensitivity of complex **1** is so high that the emission intensity can be effectively quenched by as much as 10% even in the presence of only 10^{-8} M cyanide or fluoride anions.

The origin of the emission quenching upon addition of anions is not certain at this stage. The red shift of the emission band, however, indicates that the emission quenching is associated with a change in the energy of the excited state and, thus, the enhancement of nonradiative decay.

In summary, complex **1** represents a simple and easy to prepare luminescent anion sensory system. The strong binding affinity and high selectivity of complex **1** for certain anions also may make it a promising candidate for many other different applications besides sensors, such as homogeneous catalysis[13] and membrane transport.[14] Currently, we are working on anion binding studies in H-bonding competitive solvents such as MeCN as well as modifying the dipyridyl ligands so that the receptors will be soluble in aqueous solvents. These results are expected to be intriguing given the fact that most biologically and environmentally important anions are only soluble in aqueous environments.

We are grateful to the U. S. Department of Energy (Grant DE-FG02-89ER14039) for support of this research.

Notes and references

† IR ($\nu_{C\equiv O}$, CH_2Cl_2): 2032, 1928. δ_H (300 MHz, $CDCl_3$): 10.59 (s, 2 H, NH), 8.91 (d, 4 H, J_{HH} 5.9 Hz, $H^{6,6'}$-$Bu^t{}_2$bpy), 8.34 (d, 2 H, J_{HH} 7.7 Hz, H_m-py), 8.28 (s, 4 H, $H^{3,3'}$-$Bu^t{}_2$bpy), 8.04 (t, 1 H, J_{HH} 7.6 Hz, H_p-py), 7.93 (d, 4 H, J_{HH} 6.4 Hz, H_α-py), 7.81 (d, 4 H, J_{HH} 6.6 Hz, H_β-py), 7.67 (d, 4 H, J_{HH} 7.1 Hz, $H^{5,5'}$-$Bu^t{}_2$bpy), 1.46 (s, 36 H, CH_3). δ_C(360 MHz, $CDCl_3$): 196.3, 192.0, 166.3, 162.7, 155.8, 152.6, 152.1, 148.0, 147.7, 139.7, 126.6, 126.4, 122.0, 117.1, 36.3, 30.3. ES-MS: *m/z* 1540.2 (calc. *m/z* 1541.6 for $[M - PF_6^-]^+$) and 698.6 (calc. 698.3 for $[M - 2PF_6^-]^{2+}$). Anal. Calc for $C_{59}H_{61}N_9O_8Re_2P_2F_{12}$: C, 42.02; H, 3.65; N, 7.47. Found: C, 41.80; H, 3.62; N, 7.26%.

‡ The binding studies were conducted in air-equilibrated CH_2Cl_2 solution. We found the emission intensities were *ca.* 10% lower than those in deoxygenated CH_2Cl_2 solutions. However, the resultant I/I_0 and fitted binding constants toward different anions did not change upon deaeration.

§ Luminescence titrations were carried out by adding CH_2Cl_2 solutions of anions to complex **1** in CH_2Cl_2. Emission spectra were collected on a SLM 48000S spectrophotometer. Fitting was carried out using eqn. (1), as described by Connors (see ref. 11).

$$I/I_0 = (1 + (k_f/k_s)K_b[L])/(1 + K_b[L]) \qquad (1)$$

Here, I and I_0 represent the emission intensity and k_f and k_s are the proportionality constants for the bound complex and free complex **1**, respectively, and K_b is the binding constant.

1 P. D. Beer and D. K. Smith, *Prog. Inorg. Chem.*, 1997, **46**, 1 and references therein.

2 F. P. Schmidtchen and M. Berger, *Chem. Rev.*, 1997, **97**, 1609.

3 P. A. Gale, J. L. Sessler, V. Král and V. Lynch, *J. Am. Chem. Soc.*, 1996, **118**, 5140.

4 E. F. Scott, V. Arman, S. Kincaid and A. D. Hamilton, *J. Am. Chem. Soc.*, 1993, **115**, 369.

5 K. Kavallieratos, S. R. de Gala and R. H. Crabtree, *J. Am. Chem. Soc.*, 1997, **119**, 2325.

6 A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher and T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515 and references therein.

7 C. R. Cooper, N. Spencer and T. D. James, *Chem. Commun.*, 1998, 1365; C. B. Black, B. Andrioletti, A. C. Try, C. Ruiperez and J. L. Sessler, *J. Am. Chem. Soc.*, 1999, **121**, 10438.

8 J. V. Caspar and T. J. Meyer, *J. Phys. Chem.*, 1983, **87**, 952.

9 A. P. Bisson, V. M. Lynch, M.-K. C. Monahan and E. V. Anslyn, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2340.

10 C. A. Hunter and L. D. Sarson, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2313; K.-S. Jeong, Y. L. Cho, J. U. Song, H.-Y. Chang and M.-G. Choi, *J. Am. Chem. Soc.*, 1998, **120**, 10982.

11 K. A. Connors, *Binding Constants*, John Wiley & Sons, New York, 1st edn., 1987.

12 D. E. Kaufmann and A. Otten, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1832.

13 D. A. Bell and E. V. Anslyn, *Comprehensive Supramolecular Chemistry*, ed. J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vogtle and J.-M. Lehn, Pergamon, Oxford, 1996, vol. 2, ch. 14 and references therein; P. Tecilla, S.-K. Chang and A. D. Hamilton, *J. Am. Chem. Soc.*, 1990, **112**, 9586; K. Kavallieratos and R. H. Crabtree, *Chem. Commun.*, 1999, 2109.

14 F. de Jong and H. C. Visser, *Comprehensive Supramolecular Chemistry*, ed. J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vogtle and J.-M. Lehn, Pergamon, Oxford, 1996, vol. 10, ch. 2 and references therein; L. A. J. Chrisstoffels, F. de Jong and D. N. Reinhoudt, *Chem. Eur. J*, 2000, **6**, 1376.