Anion-recognition studies of a Re(I)-based square containing the dipyridyl-amide ligand

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The molecular square $[Re(CO)_3Cl(\mathbf{L})]_4$ (**1**) containing the dipyridyl-amide ligand, *N*,*N*′-4-dipyridyloxalamide (**L**), was constructed from $Re(CO)_5Cl$ and **L** for the purpose of anion-recognition studies. Upon addition of fluoride anions to a THF solution of **1**, a remarkable spectral change is observed, and indeed a new absorption band grows at *ca.* 348 nm. We reasoned that upon addition of fluoride, the hydrogen bonds between F^- and –NH groups of **L** would first form and increase the electron densities of nitrogen atoms. This in turn increases the conjugation throughout the **L** ligand, which is responsible for the new growing absorption band. Finally, a proton-transfer process occurs upon addition of excess F^- anions, corroborated by the ^1H NMR titration experiment due to the occurrence of HF_2^-. The binding constants based on a 1 : 1 complex (**1**–X^-, X^- = anions) follow the order: $F^- > CN^- > OAc^- > Cl^- > Br^-$, PF_6^-, BF_4^-, ClO_4^-, NO_3^- and HSO_4^-. The most electronegative F^- anion shows the largest binding constant, followed by CN^-, OAc^- and Cl^- anions. The less electronegative Br^- anion and bigger PF_6^-, BF_4^-, ClO_4^-, NO_3^- and HSO_4^- anions do not show any binding affinity with **1**. The control titrations carried out using **L** and the same series of anions showed that the basicity of anions also possibly lends some contribution to the sensing events. However, the binding affinity of **1** toward various anions can be mostly correlated with the electronegativity as well as cavity size of the molecular square, and hence **1** can be expected to be a sensor for F^-.

Introduction

The coordinative-bond approach has been extensively used in the construction of coordination polymers with a wide range of one-, two- and three-dimensional infinite solid-state coordination networks[1] as well as discrete supramolecular architectures.[2] Moreover, it is also possible, in parallel, to use highly directional hydrogen bonds as a means of controlling self-assembly in supramolecular systems. Indeed, a variety of discrete and infinite coordination architectures with hydrogen-bonded frameworks have been achieved in the last decade.[3] In this regard, the combination of the coordinative-bond approach, hydrogen bonding and/or other weak interactions (*i.e.*, π···π interactions) has recently been recognized as a very powerful and versatile strategy in material synthesis. In 1990, a paradigm example by Fujita *et al.*[4a] of a supramolecular system, $[(en)Pd(4,4'\text{-bpy})]_4(NO_3)_8$ (en = ethylenediamine, 4,4′-bpy = 4,4′-bipyridine), was first synthesized and characterized in a self-assembly reaction by the combination of equimolar amounts of $Pd(en)(NO_3)_2$ and 4,4′-bpy; its molecular structure was further determined by X-ray diffraction confirming a molecular-square structure.[4b] Later, $[Re(CO)_3Cl(diimine)]_4$ complexes (diimine = pyrazine, 4,4-bipyridine, 1,2-bis(4-pyridyl)ethylene or other linear spacers) reported by the Hupp group[5] represent another interesting family of neutral molecular squares with tunable cavity sizes depending on the linear spacers used. In the meantime, Hupp *et al.* have obtained an interesting class of Mn(I) and Re(I) rectangles *via* a two-step synthesis,[6] whereas a handful of examples of Re(I)-based rectangles were also reported by Lu *et al.* by a two-step synthesis or one-pot preparation.[7] Applications including chemical sieving, sensing and catalysis based on supramolecular systems have been found, including some very exciting results.[8]

Organic amides have long been proved to be very useful in self-assembly through hydrogen bonding, and the assembled products have relevance to biological systems. With reference to the work reported by Ghadiri *et al.*,[9] cyclic oligoamides can be utilized as useful building units to give interesting nanotubes or zeolite-like frameworks through inter-ring and/or inter-tube NH···O=C hydrogen bonding, representing potentially a new family of functional materials. However, the related studies based on metal-containing cyclic amides are still in its infancy. Puddephatt *et al.* pioneered an intriguing work based on this novel idea toward the construction of a Pt(II)-based supramolecular structure by taking advantage of dipyridyl-amides (*N*-pyridin-4-yl-isonicotinamide) as bridging ligands and Pt^{II} ions as a connector in the assembly process.[10] The complex cation appears to be a rare example of a triangular structure that further forms a dimeric architecture through the NH···O=C hydrogen bonding and Pt···O=C interactions, and thus it suggests that a biomimetic approach

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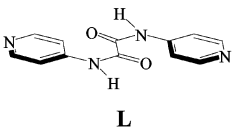
to organization of the coordination networks holds considerable promise in this research field.

The selective recognition and sensing of biologically or environmentally important anions by artificial receptors has emerged recently as a key research topic in supramolecular chemistry.[11] In this regard, the design and synthesis of receptors sensitive to the anion–receptor interactions and capable of exhibiting either a chromogenic and/or fluorogenic response are of current interest. Methodologies for the efficient detection and quantitative determination of anions are being developed, and a variety of molecular sensors for anions have been synthesized and designed in the last decade.[12] In particular, the sensing of fluoride, the smallest anion, has attracted attention because of its important role in numerous biological processes.[13] The nature of the anion–receptor interaction can be electrostatic or hydrogen bonding. In the latter case, the receptor must provide hydrogen-bond donor groups, in most cases the –NH group of carboxyamides, sulfonamides, ureas, thioureas and pyrroles.[14] Receptors based on hydrogen bonding are expected to interact principally with anions containing the most electronegative atoms, *i.e.*, fluoride and oxygen, and the sensing events may be achieved by either hydrogen-bond formation[12*a–h*] and/or proton transfer.[12*g,i*] However, the basicity of anions also possibly plays an important role in the sensing events.[12*i*]

The use of Re(I) pyridyl amides in the detection of anions was initially pioneered by Beer and coworkers.[15] The Re(I) pyridyl amide containing a crown ether was shown to be selective for acetate over chloride, which reflected the different basicities of the anions. Interestingly, the presence of bound potassium had a positive cooperative effect on anion binding. Thus, the anion binding affinity can be enhanced by the presence of potassium, *via* electrostatic and conformational effects. Lees *et al.* have recently reported new luminescent Re(I) dipyridyl-amide based receptors, $[\{(Bu^t_2bpy)Re(CO)_3\}_2(\mu\text{-}\mathbf{L1})](PF_6)_2$ and $[\{(Bu^t_2bpy)Re(CO)_3\}_2(\mu\text{-}\mathbf{L2})](PF_6)_2$ (Bu^t_2bpy = 4,4′-di-*tert*-butylbipyridine, **L1** = *N*,*N*′-dipyridin-4-yl-isophthalamide, **L2** = pyridine-2,6-dicarboxylic acid pyridin-4-ylamide),[12*a,b*] for a variety of anions, and these artificial receptors show high affinities for halides, cyanide and acetate anions. This may pave a new way for the design and synthesis of anion sensors based on Re(I) dipyridyl-amide supermolecules, and thus the above findings prompted us to initiate this study to search for new supramolecular hosts for anions.



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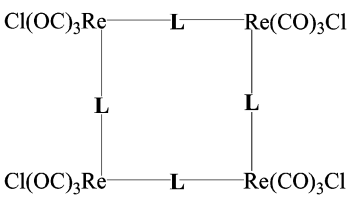

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We[16] and other groups[3*h–k*] have successfully demonstrated the important role of hydrogen-bonding interactions in crystal-engineering studies for metal-containing pyridyl-amide systems, and the amide–amide hydrogen bonding significantly increases the supramolecular complexity in the solid state. Indeed, several reports related to anion sensors also primarily rely on the key idea regarding anion–receptor interactions in pyridyl-amide systems.[12*a–c,j*] We report herein anion-recognition studies of a Re(I)-based square containing the dipyridyl-amide ligand, *N*,*N*′-4-dipyridyl oxalamide (**L**).

Experimental section

General information

All reactions were performed under a nitrogen atmosphere and solvents for syntheses (analytical grade) were purified by literature methods. NMR spectra were recorded on Bruker DPX 400 MHz NMR and Varian-Unity INOVA-500 MHz NMR spectrometers. Samples were prepared in deuterated solvents with the usual standards. UV-vis spectra were recorded on a Shimadzu UV-310PC spectrophotometer, and solid-state emission spectra were recorded on a SPEX Fluorolog-2 spectrophotometer. *N*,*N*′-4-dipyridyl oxalamide (**L**)[17] was prepared by the literature method. The anions (X) used in this study are all in $[Bu_4N]X$ salts.

Synthesis

***N*,*N*′-4-Dipyridyl oxalamide (L).** 4-Pyridylamine (1.88 g, 20 mmol) was put into a 250 ml of a two-necked bottle under an atmosphere of nitrogen, and it was then heated with stirring at 150 °C for 1 h after addition of oxalic acid diethyl ester (1.46 ml, 10 mmol). The reaction can be recrystallized from acetone to give rise to a pure and white solid with a 93% yield. MS (FAB): [M], *m*/*z*= 242, 10%. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ 7.96 [d, J = 6.0 Hz, 2H, NCH_2], 8.63 [d, J = 6.4 Hz, 2H, $C(CH)_2$], 11.35 [s, H, N*H*]. ^{13}C NMR (400 MHz, DMSO-d_6, 25 °C): δ 114.55, 144.60, 150.65, 159.14. FT-IR (KBr): ν_{NH} = 3224 and $\nu_{C=O}$ = 1694 cm^{-1}. Anal. Calcd (%) for $C_{12}H_{10}N_4O_2$: C, 59.50; H, 4.16; N, 23.13. Found (%): C, 59.35; H, 3.98; N, 23.37.

$[Re(CO)_3Cl(L)]_4$ (1). This was synthesized by reacting 100 mg (0.276 mmol) of $Re(CO)_5Cl$ with 67 mg (0.276 mmol) of **L1** in 100 mL of 3 : 1 THF–toluene. The reaction solution was then heated with stirring at 60 °C for 48 h, whereupon a pale-yellow solid was formed. After cooling, the solid was collected on a glass frit, washed with hexanes, dried under vacuum and obtained with a *ca.* 70% yield. Typically, no further purification was needed. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ 8.01 [d, J = 6.8 Hz, 2H, NCH_2], 8.59 [d, J = 6.4 Hz, 2H, $C(CH)_2$], 11.50 [s, H, N*H*]. FT-IR: ν_{NH}=3232 cm^{-1}, $\nu_{C\equiv O}$ = 2027 cm^{-1}, $\nu_{C\equiv O}$ = 1904 cm^{-1}, $\nu_{C=O}$ = 1613 cm^{-1}. ESI-MS: $[M - 4Cl]^{4+}$, *m*/*z*= 513.0, 20.6%; $[M - Cl]^+$, *m*/*z*= 2153.0, 7.1%; $[M]^+$, *m*/*z*= 2190.0, 5.7%. Anal. Calcd (%) for $C_{60}H_{40}Cl_4N_{16}O_{20}Re_4$: C, 32.88; H, 1.84; N, 10.23. Found (%): C, 32.83; H, 2.13; N, 10.01.

X-ray crystallography

Suitable crystals were mounted on glass capillaries. Data collection was carried out on a Bruker SMART CCD diffractometer with Mo radiation (0.71073 Å) at 150 K. A preliminary orientation matrix and unit cell parameters were determined from 3 runs of 15 frames each, each frame corresponding to 0.3° scan in 20 s, followed by spot

Table 1 Crystallographic data of **L**

	L
Empirical formula	$C_{12}H_{10}N_4O_2$
Formula weight	242.24
Crystal system	Monoclinic
Space group (No.)	$P2_1/c$ (14)
a/Å	8.373(1)
b/Å	14.700(1)
c/Å	9.176(1)
β/°	98.917(2)
V /Å^3	1115.8(1)
Z	4
F(000) (e)	504
μ (*Mo-Kα*) (mm^{-1})	0.103
T/K	150(1)
λ/Å	0.71073
Reflections collected	9828
Independent reflections	2558 (R_{int} = 0.042)
Observed reflections ($Fo \geq 2\sigma(Fo)$)	2114
Refined parameters	163
Goodness-of-fit on F^2	1.068
R^a, $R_w{}^b$ ($I \geq 2\sigma(I)$)	0.049, 0.112
R^a, $R_w{}^b$ (all data)	0.062, 0.119

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR_2 = \{[\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma[w(F_o{}^2)^2]\}^{1/2}$.

integration and least-square refinement. Data were measured using an ω scan of 0.3° per frame for 20 s until a complete hemisphere had been collected. Cell parameters were retrieved using SMART[18a] software and refined with SAINT[18b] on all observed reflections. Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS.[18c] The structure was solved by direct methods with the SHELXS-97[18d] program and refined by full-matrix least-squares methods on F^2 with SHELXL-97.[18e] All non-hydrogen atomic positions were located in difference Fourier maps and refined anisotropically. Hydrogen atoms were constrained to the ideal geometry using an appropriate riding model. Detailed data collection and refinement of **1** is summarized in Table 1.†

Results and discussion

The Re(I)-based square (**1**) of the dipyridyl-amide ligand, *N*,*N*′-4-dipyridyl oxalamide (**L**), has been synthesized and characterized for the purpose of anion-recognition studies. **1** was prepared by reacting $Re(CO)_5Cl$ with equimolar amounts of dipyridyl-amide ligands (**L**) in 3 : 1 THF–toluene at 60 °C for 48 h, respectively, with a yield of *ca.* 70%. Indeed, this is a typical method to synthesize neutral Re(I)-based supermolecules.[5b,8a] Suitable single crystals were grown by ether diffusion into a DMF solution of **L**. Unfortunately, single crystals of **1** of a good quality suitable for single-crystal X-ray analysis have not yet been obtained, but **1** has been fully characterized by ESI-MS, EA, ^{1}H NMR and FTIR analyses. **1** is formed by a self-assembly reaction, and it is air stable both in solution and in the solid state. In addition, **1** is weakly emissive in the solid state, but non-emissive in solution.

† CCDC 618524. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b613508k

Description of crystal structure of L

The perspective view of **L1** is shown in Fig. 1(a). The 2-D extended structure through intermolecular hydrogen-bonding interactions [N(1)···N(4) 3.059 Å; N(2)···N(3) 3.139 Å] observed in the solid state is shown in Fig. 1(b), which features a grid-typed and corrugated sheet structure. Surprisingly, the nitrogen atoms of pyridyl groups instead of the oxygen atoms of amide groups are involved in hydrogen-bonding interactions with the –NH groups, although the oxygen atom is more electronegative than the nitrogen atom. Interestingly, the 2-D structure is further stacked to form a porous structure with a rectangular channel of *ca.* 10.60 × 7.20 Å^2 as shown in Fig. 1(c).

Spectroscopic and solid-state luminescence properties

Spectroscopic and solid-state luminescence data are listed in Table 2, and the absorption spectrum of **1** measured in THF is shown in Fig. 2. In general, **1** shows higher-energy absorptions at *ca.* 231 and 264 nm. Based on the similarity to the absorptions of **L**, these higher-energy absorptions are most likely ascribed to intraligand (IL) transitions. In addition to the higher-energy absorptions, **1** also shows a lower-energy absorption at *ca.* 315 nm. As a matter of fact, the molecular square, $[Re(CO)_3Cl(4,4'\text{-bpy})]_4$ (4,4′-bpy = 4,4′-bipyridine), shows a low-energy absorption at *ca.* 348 nm,[5b,8a] which is ascribed to a metal-to-ligand charge-transfer (MLCT) transition. Thus, the *ca.* 315 nm absorption of **1** is tentatively assigned to an MLCT transition in origin, probably mixing with some IL character. However, the blue shift in the absorption energy for **1** may be due to a higher-energy π* orbital of **L**, which most likely results from less coplanarity and conjugation compared with that of 4,4′-bpy.

Upon photoexcitation at 300–350 nm, **1** shows a weak emission at *ca.* 544 nm in the solid state. Since **L** shows a high-energy emission at 300–400 nm, the emission at *ca.* 544 nm should have different excited states. In $[Re(CO)_3Cl(4,4'\text{-bpy})]_4$,[5b,8a] the complex emits at *ca.* 632 nm and is ascribed to an MLCT transition. The emission at *ca.* 544 nm is again blue-shifted with respect to the *ca.* 632 nm emission as the absorption trend, and most likely they have the same MLCT excited state, MLCT. The blue shift in absorption and emission energies with respect to $[Re(CO)_3Cl(4,4'\text{-bpy})]_4$ should also be due to less coplanarity and conjugation of **L** compared with that of 4,4′-bpy.

Anion-recognition studies

A THF solution of **1** was titrated with a solution of a $[Bu_4N]F$ salt in THF. Upon addition of the F^- anions from 0 to 30 equivalents, a remarkable spectral change with unclear isosbestic points was observed. Since there is no clear isosbestic point, the spectral change is not indicative of a clean reaction. However, the spectral change can be divided into two parts (from 0 to 4 equivalents and from 5 to 30 equivalents of the F^- anions added), which are shown in Fig. 3(a) and 3(b), respectively. As shown in Fig. 3(a), the spectral change with two isosbestic points at *ca.* 244 and 323 nm shows a decrease in the absorptions at *ca.* 264 and 315 nm concomitant with an increase in the absorption at *ca.* 338 nm from 0 to 4

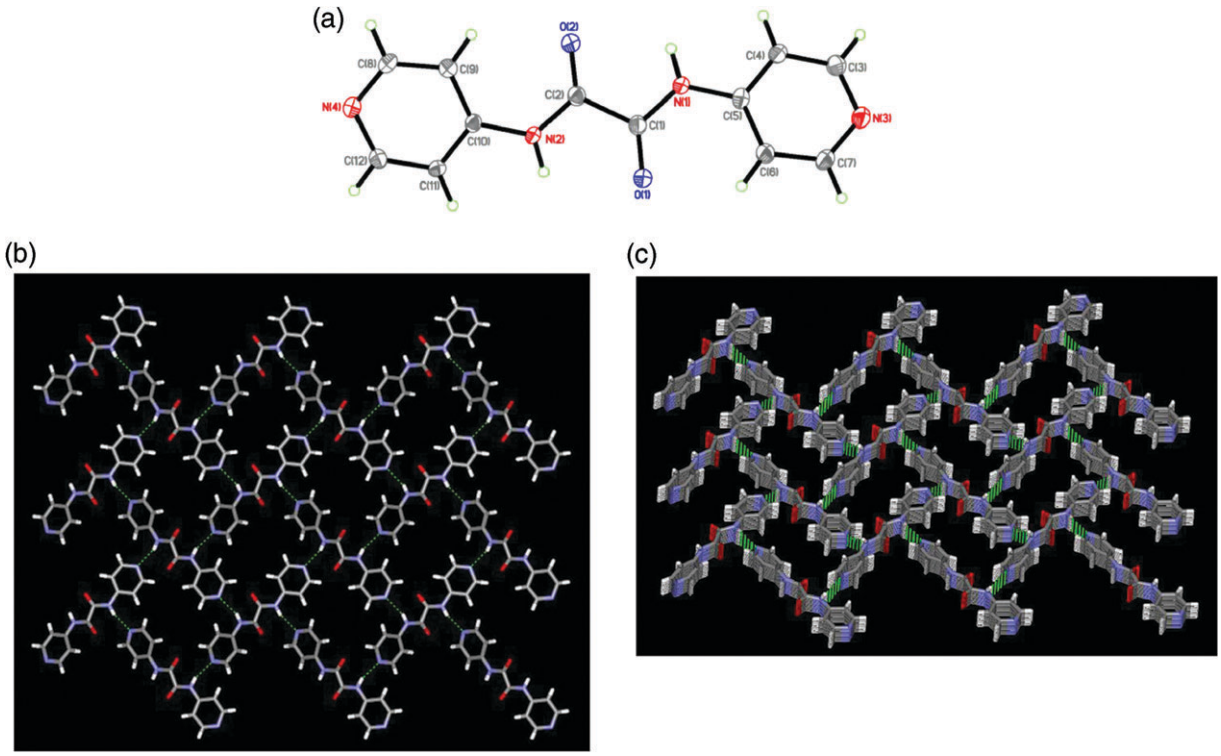

Fig. 1 (a) Molecular structure of **L1**. ORTEP diagram shows 50% probability ellipsoids. (b) its 2-D extended framework through hydrogen bonding, and (c) 3-D porous framework showing a 1-D channel structure with a dimension of *ca.* 10.60 × 7.20 Å^2 in the solid state (viewing through the *c* axis).

equivalents of the F^- anions added. For the spectral change from 5 to 30 equivalents of the F^- anions added in Fig. 3(b), only one unclear isosbestic point at *ca.* 315 nm can be observed entailing with an increase in the absorption at *ca.* 348 nm, red-shifted from the absorption at *ca.* 338 nm. CN^- and OAc^- anions show a similar but less pronounced effect. The absorption spectrum of **1** can be recovered while CF_3COOH is added into the solution in the presence of 30 equivalents of F^- (or CN^-, OAc^-) anions as shown in Fig. 3(c). Addition of Cl^- anions only shows a minor effect on the spectral change as shown in Fig. 3(d). Besides the anions above, addition of other anions (Br^-, PF_6^-, BF_4^-, ClO_4^-, NO_3^- and HSO_4^-) does not show any effect on the absorption spectra of **1**, even when 50 equivalents of anions have been added.

The most striking feature in the F^- titration is a decrease in the absorption at *ca.* 315 nm concomitant with an increase in the absorption at *ca.* 338 nm and further red-shifted to *ca.* 348 nm. The former is previously assigned to an MLCT band, and the latter is a new absorption band growing with an increasing amount of F^- anions added. We reasoned that addition of F^- anions in a THF solution of **1** could cause both hydrogen-bonding and proton-transfer processes to occur based on the above spectral change. For the first part of the titration experiment, the clear isosbestic points observed are suggestive of a hydrogen-bonding process. Since there are no clear isosbestic points for the second part, this may be explained by the combination of hydrogen-bonding and proton-transfer processes simultaneously occurring in the solution. CN^- and OAc^- anions are expected to behave as F^- anions due to similar spectral changes. The new band at *ca.*

Table 2 Spectroscopic and solid-state luminescence data of **1**

Compound	λ_{abs} (nm)/ε (dm^3 mol^{-1} cm^{-1})	λ_{em} (nm)[a] solid state (rt)
1[b]	231/102 000 264/130 300 315/84 480	544

[a] Photoexcitation for solid-state samples are at 300–350 nm. [b] The solvent used for the absorption spectrum measurement is THF.

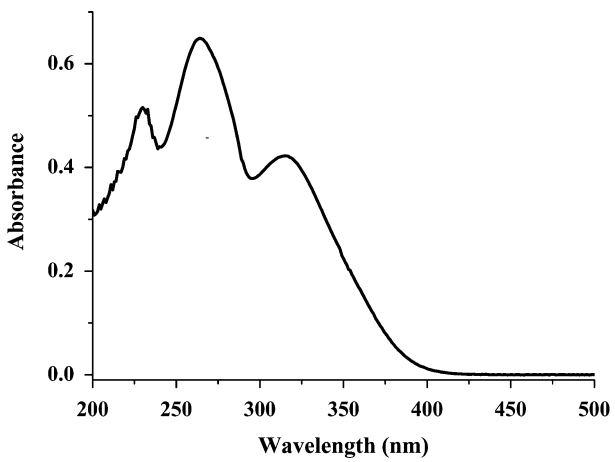

Fig. 2 The absorption spectrum of **1** is measured in THF at a concentration of 5 × 10^{-6} M.

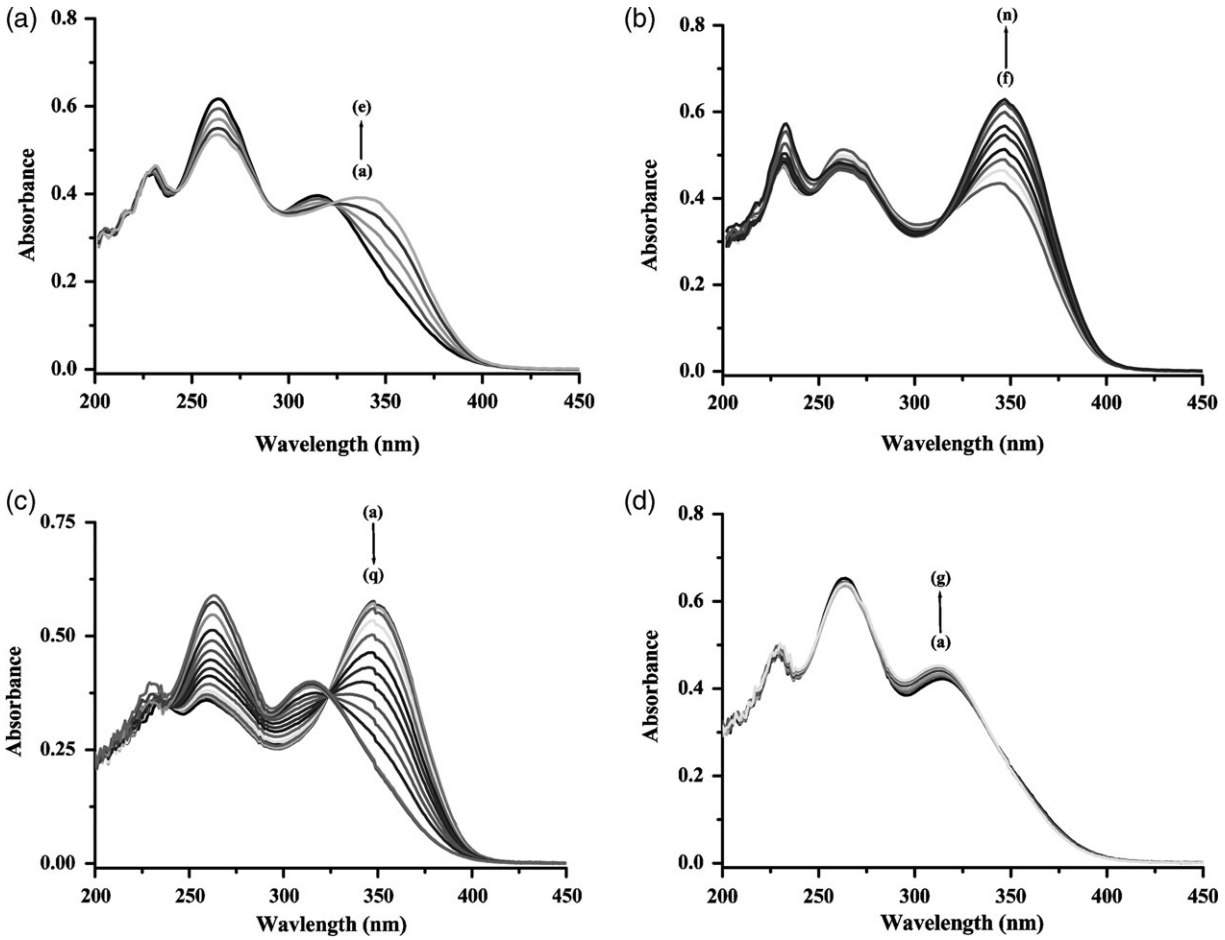

Fig. 3 The spectral change of **1** at a concentration of 5×10^{-6} M in THF is measured upon addition of (**a**) (a) 0, (b) 1.0, (c) 2.0, (d) 3.0, (e) 4.0 equivalents of F^- anions, (**b**) (f) 5.0, (g) 6.0, (h) 7.0, (i) 8.0, (j) 9.0, (k) 10.0, (l) 20.0, (m) 25.0, (n) 30.0 equivalents of F^- anions, (**c**) the titration of **1** in DMSO-d_6 (10^{-2} M) by a solution of CF_3COOH in the presence of 30 equivalents of F^- anions. The spectra were recorded after the addition of (a) 0, (b) 0.5, (c) 1.0, (d) 2.0, (e) 3.0, (f) 4.0, (g) 5.0, (h) 6.0, (i) 7.0, (j) 7.5, (k) 8.0, (l) 8.5, (m) 9.0, (n) 9.5, (o) 10.0, (p) 20.0, (q) 30.0 equivalents of F^- anions, and (**d**) (a) 0, (b) 0.5, (c) 1.0, (d) 5.0, (e) 10.0, (f) 20.0, (g) 30.0 equivalents of Cl^- anions.

348 nm is comparable in energy to that of 1-benzyl-3-(toluene-4-sulfonylamino)pyridinium upon addition of F^- anions,[12i] which is suggested to correspond to a neat proton transfer. In this context, we reasoned that upon addition of F^- anions, the hydrogen bonds between F^- and –NH groups of **L** in **1** would form first and increase the electron densities of nitrogen atoms, and hence increase the conjugation throughout the **L** ligand. This conjugation is expected to reduce the π* orbital energy of **L** and to concomitantly cause a red shift for the MLCT transition energy, a common phenomenon observed in several anion-sensing systems.[12a–c]

At last, a proton-transfer process occurs upon addition of excess F^- anions (at least five equivalents). This will be referred to again in the ^{1}H NMR titration section. The stoichiometry in the reaction between **1** and various anions (F^-, CN^-, OAc^- and Cl^-) with TBA salts was confirmed to be 1 : 1 from a Job's plot. A standard curve-fitting method was utilized for the A_{360} *vs.* $[Bu_4N]X$ plot to evaluate the binding constants for the 1 : 1 complex (**1**–X^-),[19] and hence the binding constants for **1** toward various anions can be calculated and are summarized in Table 3 with experimental errors.

Further insights into the nature of anion–receptor interactions were provided by analysis of the ^{1}H NMR spectra. Fig. 4(a) and (b) show the spectra for the titration of a DMSO-d_6 solution of **1** with a DMSO-d_6 solution of $[Bu_4N]F$. Upon addition of the fluoride salt the –NH signal at $\delta = 11.50$ ppm first slightly shifts upfield, Then, over the course of the addition of one to five equivalents of F^-, this signal broadens and finally disappears. Correspondingly, the signals of the

Table 3 Binding constants (K_b) for **1** and **L** toward various anions determined by absorption titration in THF at 298 K

Anions	K_b/M^{-1} (**1**)	K_b/M^{-1} (**L**)
F^-	11 790 ± 580	1090 ± 70
CN^-	4610 ± 170	6200 ± 260
OAc^-	2250 ± 150	3540 ± 190
Cl^-	350 ± 20	60 ± 15
Br^-, PF_6^-, BF_4^-, ClO_4^-, NO_3^- and HSO_4^-	ND[a]	ND[a]

[a] Changes in UV-vis spectra were not enough to calculate binding constants.

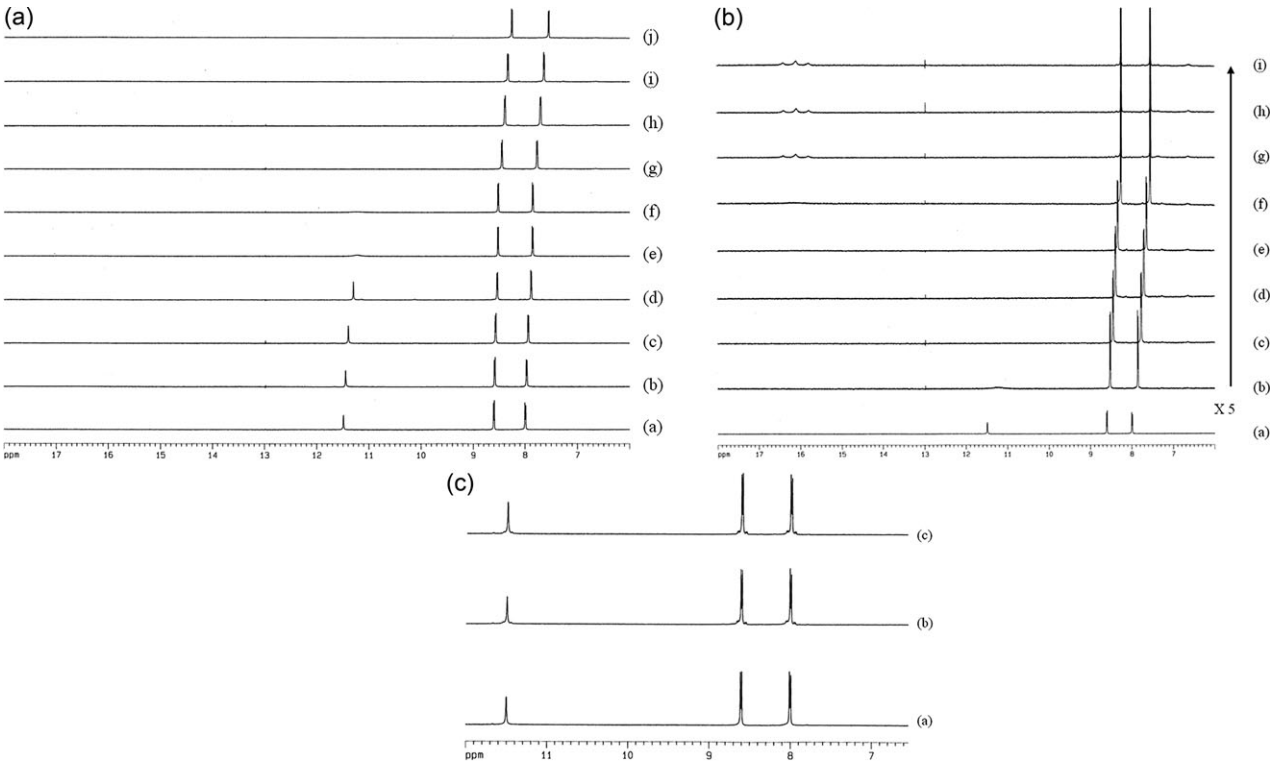

Fig. 4 The ^{1}H NMR spectral titration of **1** in DMSO-d_6 (10^{-2} M) was measured by a standard solution of tetrabutylammonium salts in DMSO-d_6. The spectra were recorded after the addition of (**a**) (a) 0, (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8, (f) 1.0, (g) 2.0, (h) 3.0, (i) 4.0, (j) 5.0 equivalents of F^- anions, (**b**) (a) 0, (b) 1.0, (c) 2.0, (d) 3.0, (e) 4.0, (f) 5.0, (g) 10.0, (h) 20.0, (i) 30.0 equivalents of F^- anions, (**c**) (a) 0, (b) 1.0, (c) 5.0 equivalents of Cl^- anions.

pyridyl protons also shift slightly upfield, with the greatest shift observed to be $\Delta\delta = 0.13$ ppm. In fact, the addition of five equivalents of F^- produces a weak triplet signal at $\delta = 16.05$ ppm, characteristic of the occurrence of HF_2^- signal, and this signal gradually grows up to the addition of 30 equivalents of F^-. Recently, a similar phenomenon indicative of the proton transfer process have been reported by Sun *et al.* based on dipyrrolylquinoxaline-containing conjugated polymers.[12g] Thus, the explanation that upon addition of F^- anions, the hydrogen bonds between F^- and –NH groups would form first and then perform the proton-transfer process upon addition of at least 5 equivalents of F^- anions can be corroborated in light of the UV-vis and ^{1}H NMR titration experiments. Similar phenomena have been observed for the ^{1}H NMR titration of CN^- and OAc^- anions, except that no HF_2^- is observed. Indeed, the –NH signal can be recovered upon addition of CF_3COOH in the presence of 30 equivalents of F^- anions.

However, a different behavior was observed with the remaining anions and a representative spectrum obtained in the titration of **1** with $[Bu_4N]Cl$ in DMSO-d_6 is shown in Fig. 4(c). In contrast to the results for F^-, CN^- and OAc^-, the –NH signal of **1** did not disappear upon addition of even 5 equivalents of the Cl^- anions, and it remains unchanged in terms of the chemical shift and regardless of the ratio of compounds in the titration. In addition, the presence of Cl^- anions did not exert any effect on the protons on the pyridyl rings.

Although **1** can not be characterized by X-ray diffraction, at this moment, it is still expected to form a molecular square due to a reaction between $Re(CO)_5Cl$ and a linear bridging ligand **L** used. Several review articles have suggested that linear bridging ligands with two reactive sites which are opposite ($\sim 180°$) would be good candidates for the construction of molecular squares.[2] From Table 5, the binding constants follow the order: $F^- > CN^- > OAc^- > Cl^- > Br^-$, PF_6^-, BF_4^-, ClO_4^-, NO_3^- and HSO_4^-. Fluoride shows the most electronegative nature and the largest binding constant,[12i] followed by CN^-, OAc^- and Cl^-. The less electronegative Br^- and bigger PF_6^-, BF_4^-, ClO_4^-, NO_3^- and HSO_4^- anions do not show any binding affinity with **1** based on the titration experiments with respect to UV-vis absorption and ^{1}H NMR spectra.[20] However, F^- is a weaker base than CN^- and OAc^-, but it has a larger binding constant. This can be probably explained by the fact that for the molecular structures of squares, they are known to be puckered and expected to hydrogen-bond with anions in solution, and thus the cavity size would most likely play an important role in determining binding affinities for a variety of anions studied here. In fact, control titrations carried out using **L** and the same series of anions regarding UV-vis absorption spectra showed a smaller binding constant for F^- (1090 ± 70 M^{-1}) compared with those of CN^- and OAc^- (6200 ± 260, 3540 ± 190 M^{-1}, respectively), which is consistent with the order of basicity. Thus, the anion-binding behavior displayed by **1** appears to be a direct consequence of the appropriate size and shape between **1** and various anions, where hydrogen-bonding may occur in the cavity. The present findings are thus reminiscent of what has been found earlier in the case of anion-binding agents, calix[4x]pyrroles, reported by Sessler *et al.*[12k] In addition,

Lees *et al* have successfully demonstrated that $[(Bu^t_2bpy)Re(CO)_3\}_2(\mu\text{-}\mathbf{L1})](PF_6)_2$ and $[(Bu^t_2bpy)Re(CO)_3\}_2(\mu\text{-}\mathbf{L2})](PF_6)_2$ have strong binding affinities with binding constants as high as 10^4–10^5 M^{-1}.[12a,b] The approximate right angle geometry, converged structure, and cationic character of the complexes render them as effective anion receptors. Indeed, the strong acidity of –NH groups resulting from a metal/ligand ratio of 2 (a metal ion may act as an electron-accepting group through ligand coordination to a metal ion) and the complexes' structural flexibility are most likely to be responsible for the high affinities toward halides through hydrogen bonding. In our study, **1** only shows a moderate affinity toward F^- anions, and this is probably due to a lower metal/ligand ratio of 1 and its neutral character, leading to a weaker acidity of –NH groups. However, **1** shows a moderately selective recognition for halides, *i.e.*, $K_F-/K_{Cl}- = 36$. For Br^- and I^- anions, they do not show any binding affinity with **1**. Actually, the combination of interactions involving electrostatic force, hydrogen bonding strength and steric effects all apparently influences the binding affinity toward anions. Significantly, the binding affinity can be closely correlated with the electronegativity as well as the cavity size of the molecular square in this study, and thus **1** can be expected to act as a sensor for F^- anions. It is noted that the triplet signal at $\delta = 16.05$ ppm, characteristic of the occurrence of HF_2^-, has been observed in this study, suggesting that both hydrogen bonding and proton transfer can happen in the F^- titration experiment for **1**. The above finding is useful to elucidate the F^- sensing events in a metal-containing pyridyl-amide system.

Conclusions

The Re(I)-based square of the dipyridyl-amide ligand, *N*,*N*′-4-dipyridyl oxalamide, has been synthesized and characterized for the purpose of anion-recognition studies. Upon addition of F^- anions to a THF solution of molecular square **1**, a remarkable spectral change with a decrease in the absorption at *ca.* 315 nm concomitant with an increase in the absorption at *ca.* 348 nm has been observed. We reasoned that upon addition of F^- anions, the hydrogen bonds between F^- anions and –NH groups of **L** in **1** would first form and increase the electron densities of nitrogen atoms, and increase the conjugation throughout **L**. This conjugation is expected to reduce the π* orbital energy of **L** and concomitantly to cause a red shift for the MLCT transition energy. Finally, the proton-transfer process occurs upon addition of an excess of F^- anions (at least five equivalents), corroborated by the ^1H NMR titration experiment due to the formation of HF_2^-. The binding constants based on a 1 : 1 complex (**1**–X^-) follow the order: $F^- > CN^- > OAc^- > Cl^- > Br^-$, PF_6^-, BF_4^-, ClO_4^-, NO_3^- and HSO_4^-. Fluoride being the most electronegative nature also shows the largest binding constant. The less electronegative Br^- and bigger anions, PF_6^-, BF_4^-, ClO_4^-, NO_3^- and HSO_4^- do not show any binding affinity with **1**. The control titrations carried out using **L** and the same series of anions showed that the basicity of anions also possibly lends some contribution to the sensing events. However, the binding affinity of **1** toward various anions can be mostly correlated with the electronegativity as well as cavity size of the molecular square, and hence **1** can be expected to be a sensor for F^-. To improve the sensory sensitivity of **1**, studies on the design of cationic molecular squares or cages with pyridyl-amide backbones are in progress.

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20 Since there is an absorption interference by I^-, the spectral change experiment cannot be carried out. However, there are no effects on the signals in the ^1H NMR titration upon addition of I^- anions, suggesting that there is no binding affinity for I^- with **1**.