Ruthenium Complexes

Selective Sensing of Phosphates by a New Bis-heteroleptic Ru^{II} Complex through Halogen Bonding: A Superior Sensor over Its Hydrogen-Bonding Analogue

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Dedicated to Professor Parimal K. Bharadwaj on the occasion of his 65th birthday

Abstract: The selective phosphate-sensing property of a bisheteroleptic Ru^{\parallel} complex, $1[PF_6]_2$, which has a halogenbonding iodotriazole unit, is demonstrated and is shown to be superior to its hydrogen-bonding analogue, $2[PF_6]_2$. Complex $1[PF_6]_2$, exploiting halogen-bonding interactions, shows enhanced phosphate recognition in both acetonitrile and aqueous acetonitrile compared with its hydrogen-bonding analogue, owing to considerable amplification of the Ru^{\parallel} -center-based metal-to-ligand charge transfer (MLCT) emission response and luminescence lifetime. Detailed solution-state studies reveal a higher association constant, lower limit

of detection, and greater change in lifetime for complex 1 in the presence of phosphates compared with its hydrogenbonding analogue, complex 2. The ¹H NMR titration study with $H_2PO_4^-$ ascertains that the binding of $H_2PO_4^-$ occurs exclusively through halogen-bonding or hydrogen-bonding interactions in complexes $1[PF_6]_2$ and $2[PF_6]_2$, respectively. Importantly, the single-crystal X-ray structure confirms the first ever report on metal-assisted second-sphere recognition of $H_2PO_4^-$ and $H_2P_2O_7^{2-}$ with 1 through a solitary C–I···anion halogen-bonding interaction.

Introduction

Substantial research efforts have been devoted to the recognition of anions, particularly phosphate, because of the significant roles played by the latter in chemical, biological, medical, and environmental processes.^[1] Although anion coordination chemistry has been enriched greatly by hydrogen-bonding (HB) interactions over recent years,^[1e,f,2] the potential of charge-assisted halogen bonding (XB) interactions for selective anion recognition is still a flourishing topic in the area of supramolecular chemistry.^[3] Halogen bonding is a directional, noncovalent attractive interaction, which generally arises between the positive region of the electrostatic potential surface of an electrophilic halogen atom and the negative sites of a Lewis base such as N, O, S, P, or halogen functionalities and π -electron donors.^[3,4] Disruption of electron density through the formation of a carbon-halogen (C-X) bond leads to the development of a positive electrostatic potential,^[5] whereas the strength of halogen bonding depends on the polarizability of the halogen attached to the receptor.^[4, 5c, 6] Again, the majority of receptors designed for phosphates are mainly concerned with coulombic interactions, metal coordination, and hydrogen

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201604049.

Chem. Eur. J. 2016, 22, 1 – 10 Wiley Onlir

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bonding.^[1g,2d,7] In general, the XB receptors developed to date display excellent selectivity for halides over oxo anions.^[3b,g,8] However, there have been very few reports showing the recognition of phosphates through charge-assisted XB interactions.^[3g,9]

On the other hand, among the traditional luminescent metal complexes for the recognition of anions, Ru^{II} complexes derived from bidentate chelating ligands^[10,11b,16c] are particularly attractive because of their interesting photophysical, photochemical, and electrochemical properties associated with the metal-to-ligand charge-transfer (MLCT) excited states.^[10c, 11b,c, 15b] In our recently published articles we have shown the selective recognition of phosphates by bis-heteroleptic Ru^{II} complexes of click-derived triazole-pyridine and phenanthroline hybrid ligands through C–H-anion interactions. $\ensuremath{^{[12]}}$ Complexation with the Ru^{II} center enhances the acidity of the triazole C–H proton and makes it an effective anion recognition unit, and the recognition event is understood easily through the change in photophysical properties of the Ru^{II} complexes.^[10a-c] However, metal-complex-based second-sphere anion recognition through XB interactions is yet to be explored. Beer et al. have reported recognition of halides through solitary charge-assisted XB interactions using a Ru^{II} or Re^I-bipyridyl complex-based rotaxane host system.^[3h,8d] However, direct attachment of the XB subunit to the metal center has not yet been explored.

Here, we report two new bis-heteroleptic Ru^{II} complexes with iodotriazole and triazole C–H groups as XB and HB donor units to compare their potentiality toward the binding of phosphate through XB and HB interactions, respectively. We

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show that the complex exploiting XB provides stronger binding toward $H_2PO_4^-$ than its HB analogue in both acetonitrile and the aqueous acetonitrile mixed solvent system. Moreover, XB-assisted phosphate binding has been studied extensively in solution, which is further supported by single-crystal X-ray diffraction studies. To the best of our knowledge, this is the first ever report on metal-assisted second-sphere phosphate binding through solitary XB interactions.

Results and Discussion

Designing aspect of complex

In our recently published articles we have shown selective sensing of phosphates by rigidification of the flexible framework of sensors in which the binding event was mainly attributable to the C-H-manion interactions. The triazole C-H unit was the main phosphate-coordinating unit in these complexes. These studies show that coordination of the pyridine-triazole unit with the Ru^{II} center serves the dual purpose of enhancing the anion-coordinating ability of the triazole C-H group and helping in establishing the anion recognition phenomenon through the change in photophysical properties of the Ru^{II} complexes.^[12] At this juncture, it would be appropriate to incorporate an XB subunit in the complex structure to explore the effect of an XB donor group on the sensing of phosphates. Accordingly, we have designed a new bis-heteroleptic Ru^{II} complex, $1[PF_6]_2$, comprising the iodotriazole group, and its HB analogue, **2**[PF₆]₂, for anion-sensing studies (Scheme 1).



Scheme 1. Chemical structures of the two Ru^{II} complexes.

Synthesis and characterization

Compounds L1, L2, and *cis*-[Ru(phen)₂Cl₂] were synthesized according to the reported literature procedures.^[13,14] The ruthenium(II) complexes, 1[PF₆]₂ and 2[PF₆]₂, were synthesized by heating ligands L1 or L2 at reflux with *cis*-[Ru(phen)₂Cl₂] in an ethanol/water (2:1, v/v) mixture under an argon atmosphere for 24 h, followed by exchange of Cl⁻ with PF₆⁻ (Scheme 2). Both the complexes were characterized fully by ¹H, DEPT-135, ¹³C, ¹H-¹H COSY, ¹H-DEPT-135 HSQC, and ¹H-¹³C HMBC NMR spectroscopy (Figures S1–S12, Supporting Information), electrospray ionization mass spectrometry (ESI-MS; Figures S13 and

S14, Supporting Information), and elemental analysis techniques. Finally, single-crystal X-ray diffraction analysis confirmed the structures of both complexes.

Photophysical studies

The presence of the anion-coordinating iodotriazole (C-I) group and photoresponsive Ru^{II} center in 1[PF₆]₂ allows us to explore its anion-binding affinities by observing the extent of perturbation of its photophysical properties in the presence of various anions such as F^- , Cl^- , AcO^- , BzO^- , NO_3^- , HCO_3^- , HSO₄⁻, HO⁻, HP₂O₇³⁻, H₂PO₄⁻, and so on. The absorption spectrum of complex 1[PF₆]₂ shows three characteristic bands at 262, 403, and 445 nm (Figure S15, Supporting Information). The MLCT bands at 403 and 445 nm can be attributed to $Ru(d\pi) \rightarrow phenanthroline and Ru(d\pi) \rightarrow pyridine-triazole charge$ transfer transitions.^[10b,c,11b,15] Practically no change in the typical MLCT band at 445 nm is observed upon the addition of ten equivalents of the anions into 40 µm acetonitrile solutions of $1[PF_6]_2$ (Figure S16, Supporting Information), except for $H_2PO_4^$ and $HP_2O_7^{3-}$. The addition of $H_2PO_4^{-}$ and $HP_2O_7^{3-}$ causes a slight redshift in the MLCT band of $1[PF_6]_{2}$, indicating an interaction between 1 and the corresponding anions. The slight redshift of the MLCT bands can be visualized from the point of lowering of the MLCT band energies owing to a slight increase in the electron density at the metal center through C-I-manion interactions.^[11b, 16c]

Complex $1[PF_6]_2$ is very weakly emissive (quantum yield: 0.0027) and is found to exhibit a broad luminescence band at 585 nm upon excitation at its MLCT absorption maximum of 403 nm (Figure S15, Supporting Information). However, excitation at either 403 or 445 nm results in similar emission behavior, indicating that the emission occurs from the same triplet MLCT excited state.^[10a] The intensity of the broad centered weak emission band increases only in the presence of $H_2PO_4^-$ (17-fold) and $HP_2O_7^{3-}$ (5-fold), whereas the addition of other competitive anions promotes no change in the PL spectrum even at high concentrations (10 equiv; Figure 1).

Quantum yields calculated for $1[PF_6]_2$ as well as in the presence of various anions in acetonitrile are listed in Table S1 (Supporting Information). The presence of flexible side arms in $1[PF_6]_2$ results in a lowering of its quantum yield (ϕ_f ; Figure S17, Supporting Information) by a factor of 23 compared with the standard ($[Ru(bpy)_3](PF_6)_2$; $\phi_f = 0.062$). The ϕ_f value of $1[PF_6]_2$ remains almost unperturbed in the presence of various anions, but increases 17-fold and 5-fold in the presence of $H_2PO_4^-$ and $HP_2O_7^{3-}$, respectively. This may be caused by the lowering of the non-radiative decays through rotational and vibrational relaxation pathways by rigidification of the framework upon selective binding of $H_2PO_4^-$ and $HP_2O_7^{3-}[^{2d}, ^{11b}, 16]$

To gain a quantitative insight into the receptor–anion interactions, we performed UV/Vis and PL titrations of $1[PF_6]_2$ with $H_2PO_4^-$ and $HP_2O_7^{3-}$. Upon gradual addition of increasing amounts of $H_2PO_4^-$ and $HP_2O_7^{3-}$ to $1[PF_6]_2$ (40 µM in acetonitrile), the absorption bands at 403 and 445 nm decreased, and a well-defined single isosbestic point appeared at 455 nm (Figure 2a and Figure S18, Supporting Information). This indicates

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Scheme 2. Synthetic procedure for the two Ru^{II} complexes.



Figure 1. Changes in the PL (10 μ M) spectrum of 1[PF₆]₂ in the presence of various anions (10 equiv) in acetonitrile at room temperature.

the presence of a single equilibrium between the non-complexed (free complex 1) and complexed species (phosphate adduct of complex 1). The UV/Vis titration data show a saturation point at the addition of one equivalent of $H_2PO_4^-$ and HP₂O₇³⁻ (Figure S19, Supporting Information). During PL titration, upon incremental addition of $H_2PO_4^{-}/HP_2O_7^{3-}$ into $1[PF_6]_2$ (10 µm in acetonitrile), the intensity of the broad centered emission band at 585 nm is continually enhanced up to the addition of one equivalent of the guest anion with a slight redshift (5 nm) of the emission maxima (Figure 2b and Figure S20, Supporting Information). No further change in the emission intensity is observed beyond this, indicating a saturation point (Figure S21, Supporting Information). Job's plot analyses suggest 1:1 host-quest stoichiometric binding between $1[PF_6]_2$ and H₂PO₄^{-/}HP₂O₇³⁻ (Figure S22, Supporting Information). The PL titration data of $1[PF_6]_2$ with $H_2PO_4^-$ and $HP_2O_7^{3-}$ fit well with the 1:1 binding model (Figure S23, Supporting Information), and apparent 1:1 association constant values are obtained as 1.94×10^5 and $5.6 \times 10^4 \,\text{m}^{-1}$ for $1[\text{PF}_6]_2$ with $\text{H}_2\text{PO}_4^{-1}$ and $\text{HP}_2\text{O}_7^{3-}$, respectively, by fitting the respective titration data to a nonlinear 1:1 curve-fitting model.^[7c,I]

The selectivity of $1[PF_6]_2$ toward $H_2PO_4^-$ over other anions was verified by adding one equivalent of $H_2PO_4^-$ to the acetonitrile solution of $1[PF_6]_2$ in the presence of ten equivalents of other competitive anions. As expected, the selectivity and emission enhancement remained unperturbed in the presence of all the anions (Figure 3 a). The PL intensity change $(I-I_0)$ of $1[PF_6]_2$ shows a good linear response against increasing concentration of $H_2PO_4^-$, and the detection limit is found to be as low as approximately 0.018 µM on the basis of specific quantitative analyses (Figure 3 b and Figure S24, Supporting Information).

The luminescence response of the metalloreceptor $(1[PF_6]_2)$ upon binding with various anions is further confirmed through time-resolved emission studies (Figure 4a and Table 1). Complex $1[PF_6]_2$ displays biexponential decay, with an initial luminescence lifetime of approximately 5 ns followed by a relatively longer-lived component with an excited-state lifetime of around 9 ns. Comparing the lifetime data with those of previously reported complexes, one can say that the first component may be attributed to the ³MLCT state based on the phenanthroline unit, whereas the second component originates from the equilibrium with the triplet state of the pyridine-triazole moiety, which repopulates the ³MLCT state after the initial emission.^(10b, 11e)

The addition of various anionic guests, except $H_2PO_4^-$ and $HP_2O_7^{3-}$, does not change the decay pattern or the lifetime of $1[PF_6]_2$ (Figure 4a and Table 1). In the presence of $H_2PO_4^-$ and $HP_2O_7^{3-}$, the lifetimes of both the components increase in general. On further addition of these anions, the lifetime of the first component decreases, whereas that of the second component increases. The bi-exponential decay pattern in the presence of $H_2PO_4^-/HP_2O_7^{3-}$ indicates the presence of two distinct luminescent species; the one with the shorter lifetime can be assigned as the free metalloreceptor, and the other is the $H_2PO_4^-/HP_2O_7^{3-}$ adduct of the receptor, with a longer lifeti-

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Figure 2. a) UV/Vis (40 $\mu m)$ and b) PL (10 $\mu m)$ titration of $1[PF_6]_2$ with $H_2PO_4^-$ (0–1.5 equiv) in acetonitrile at room temperature.

Table 1. Lifetimes of $1[PF_6]_2$ and $1[PF_6]_2$ in the presence of various anions (3 equiv) in acetonitrile at 25 °C.				
Entry	Lifetime [ns]	Entry	Lifetime [ns]	
1[PF ₆] ₂	5.78	$1[PF_6]_2 + BzO^-$	5.85	
$1[PF_6]_2 + F^-$	5.99	$1[PF_6]_2 + HCO_3^-$	5.66	
$1[PF_6]_2 + CI^-$	5.92	$1[PF_6]_2 + NO_3^-$	5.67	
$1[PF_6]_2 + Br^-$	5.88	$1[PF_6]_2 + HSO_4^-$	6.65	
$1[PF_6]_2 + I^-$	5.96	$1[PF_6]_2 + HP_2O_7^{3-}$	34.20	
$1[PF_6]_2 + AcO^-$	5.79	$1[PF_6]_2 + H_2PO_4^-$	108.55	

me.^[11b] Combination of the above two components leads to the overall enhancement in lifetime. The increase in the lifetime of $1[PF_6]_2$ with $H_2PO_4^{-}/HP_2O_7^{3-}$ can be explained by the lowering of the chances of rotational/vibrational relaxation modes of non-radiative decay through rigidification in the receptor framework upon complexation with the aforementioned anions, which leads to stabilization of the ³MLCT state of the complexes, and hence, increases the energy gap of the ³MLCT level with the corresponding non-emitting metal-cen-



Figure 3. a) Selectivity graph of $1[PF_6]_2$ (10 μM) with $H_2PO_4^-$ in the presence of other anions in acetonitrile. Color code: Light gray bars correspond to $1[PF_6]_2$ in the presence of all anions; dark gray bars correspond to $1[PF_6]_2$; in the presence of all anions and $H_2PO_4^-$. Codes used: A) Only $1[PF_6]_2$; B) F⁻; C) Cl⁻; D) Br⁻; E) I⁻; F) AcO⁻; G) BzO⁻; H) NO₃⁻; I) HCO₃⁻; J) HO⁻; K) ClO₄⁻; L) HSO₄⁻; M) HP_2O₇³⁻; N) H₂PO₄⁻. b) Calibration curve for $H_2PO_4^-$ over the concentration range 0 to 5.0 μM derived from the PL titration with $1[PF_6]_2$ (10 μM).

tered excited state (${}^{3}MC$).^[10b,11b,16c] This change in the lifetime and decay pattern of complex 1[PF₆]₂ continues up to the addition of one equivalent of H₂PO₄⁻/HP₂O₇³⁻ and stops beyond that, supporting the 1:1 host-guest stoichiometry obtained from UV/Vis and PL titration data (Figure 4b, and Figure S25 and Table S2, Supporting Information). Again, between H₂PO₄⁻ and HP₂O₇³⁻, the former is proved to cause a better change in the decay pattern and lifetime of 1[PF₆]₂, which makes complex 1[PF₆]₂ a suitable lifetime-based sensor for H₂PO₄⁻ over HP₂O₇³⁻ and other competitive anions in acetonitrile.

For a comparison between the sensing abilities of $1[PF_6]_2$ (with the XB iodotriazole unit) and its HB analogue $2[PF_6]_2$, de-

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Figure 4. Time-resolved luminescence decays of $1[PF_6]_2$ (10 μ M) in acetonitrile solution at 25 °C: a) upon addition of various anions as their corresponding tetrabutylammonium salts, and b) upon addition of increasing amounts of TBAH₂PO₄.

tailed photophysical studies were performed for 2[PF₆]₂ (Figures S26–S38 and Tables S3–S5, Supporting Information). The combined solution-state output for complexes $1[PF_6]_2$ and **2**[PF₆]₂ is summarized in Table S6 (Supporting Information). This clearly shows that $2[PF_6]_2$ selectively senses $H_2PO_4^-$ similarly to 1[PF₆]₂; however, the degree of emission enhancement (sixfold), apparent 1:1 association constant ($5.59 \times 10^4 \,\text{m}^{-1}$), sensitivity (0.05 $\mu\text{m})\text{,}$ and lifetime enhancement (sixfold) are much lower in the case of $2[PF_6]_2$. Here, it is important to mention that our previously reported methyl-substituted pyridine-triazole-based Ru^{II} complex, $2'[PF_6]_2$, which is structurally quite similar to complex 2[PF₆]₂, the benzyl-substituted one, also showed similar outputs in the presence of $H_2PO_4^{-}$. Thus, changing the appending methyl group in $2'[PF_6]_2$ to a benzyl group in 2[PF₆]₂ does not perturb the basic photophysical properties (UV/Vis, PL) or the anion-sensing behavior.

The selectivities of complexes $1[PF_6]_2$ and $2[PF_6]_2$ toward $H_2PO_4^-$ over other competitive anions and $HP_2O_7^{3-}$ can be attributed to the high basicity and high charge density of $H_2PO_4^-$, which assist the formation of strong adducts between host and guest. However, the higher degree of enhancement in case of $1[PF_6]_2$ than in $2[PF_6]_2$ with $H_2PO_4^-$ can be rational-

ized by comparing the mode of $H_2PO_4^-$ binding through two distinct noncovalent interactions, that is, C–I...anion XB interactions in $1[PF_6]_2$ and C–H...anion HB interactions in $2[PF_6]_2$.

Moreover, to examine the effect of water on the luminescence sensing behaviors of the XB and HB receptors toward $H_2PO_4^-$ and $HP_2O_7^{3-}$, we performed analogous PL experiments in 5%, 10%, 15%, and 20% water/acetonitrile mixed solvents (Figure 5 and Figures S39–S41, Supporting Information). It was observed that the XB receptor $1[PF_6]_2$ is capable of sensing $H_2PO_4^-$ and $HP_2O_7^{3-}$ in up to 20% water/acetonitrile mixtures through moderate changes in PL intensities. The degree of emission enhancement is reduced upon switching from anhydrous acetonitrile to aqueous acetonitrile owing to the hydration of the anion in the aqueous medium.

Further, trianionic HP₂O₇³⁻ shows weak binding with XB and HB receptors in aqueous acetonitrile compared with H₂PO₄⁻, probably owing to its higher hydration energy than that of H₂PO₄⁻. The apparent 1:1 association constant and lower limit of detection values for 1[PF₆]₂ with H₂PO₄⁻ are calculated as $1.46 \times 10^4 \text{ m}^{-1}$ and 0.28 μ m, respectively, in 20% water/acetoni-



Figure 5. PL titration of $1[PF_6]_2$ (10 μ M) with $H_2PO_4^-$ (0–1.5 equiv) in a) 15% water/acetonitrile, and b) 20% water/acetonitrile at room temperature.

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trile (Figure S42, Supporting Information). Interestingly, although the HB analogue (2[PF₆]₂) shows a change in emission behavior with $H_2PO_4^{-}$ and $HP_2O_7^{3-}$ in 5% water/acetonitrile, it fails to give signaling output in the presence of the aforementioned anions in water/acetonitrile mixtures of 10% or above. Thus, complex $1[PF_6]_2$ with the XB donor group is proved to be a better sensor for the detection of $H_2PO_4^{-}$ over $HP_2O_7^{3-}$ and other competitive anions than its HB analogue $2[PF_6]_2$ in acetonitrile and aqueous acetonitrile mixed solvent.

Mechanistic investigation by ¹H NMR experiments

To obtain mechanistic information on the binding mode of the two receptors ($1[PF_6]_2$ and $2[PF_6]_2$) with various anions, we performed ¹H NMR titration experiments involving the gradual addition of aliquots of the anions to a solution of the receptors in [D₆]DMSO. There was no shift in any proton signal in the ¹H NMR spectrum of $1[PF_6]_2$ in the presence of $H_2PO_4^-$ (Figure 6 a), which implies that the binding of $H_2PO_4^-$ with 1 occurs through the C-I-manion XB interaction only, without the assistance of any proton. On the other hand, the addition of $H_2 PO_4^{-}$ and $HP_2 O_7^{\,3-}$ promotes a significant downfield shift of the triazole C–H proton of $2[PF_6]_2$, from 9.29 to 9.77 ppm $(\Delta \delta = 0.48 \text{ ppm})$ and 9.57 ppm $(\Delta \delta = 0.28 \text{ ppm})$, respectively, whereas the other protons are not affected. This indicates that complex 2[PF₆]₂ provides C–H…anion HB interactions toward the binding of H₂PO₄⁻/HP₂O₇³⁻ (Figure 6b and Figure S43, Supporting Information). However, the addition of other competitive anions does not induce any noticeable change in the ¹H NMR spectrum of $2[PF_6]_2$, except for very high amounts of F⁻ and AcO⁻ (Figure S44, Supporting Information) owing to the acid-base interaction between the acidic triazole C-H proton and these highly basic anions.

For confirmation of whether the anion-recognition processes in solution could involve the formation of polymeric supramolecular structures, ¹H DOSY NMR spectroscopic experiments were performed in a 9:1 CD₃CN/CD₃OD solution of 1[PF₆]₂ before and after the addition of one equivalent of $H_2PO_4^-$ and $HP_2O_7^{3-}$. Interestingly, the diffusion coefficient of the free complex (1[PF₆]₂; $1.52 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$) decreases significantly upon the addition of one equivalent of $H_2PO_4^-$ (6.37×10⁻⁹ m²s⁻¹) and $HP_2O_7^{3-}$ (6.72×10⁻⁹ m²s⁻¹), indicating the formation of polymeric supramolecular structures in solution. It is evident from the diffusion spectroscopic data that the sizes of the phosphate adducts of complex 1 in solution are significantly larger than that of the free complex. The similar diffusion coefficients for all the peaks in the ¹H DOSY NMR spectra (Figure S45–S47, Supporting Information) of the H₂PO₄^{-/}/HP₂O₇³⁻ adducts of complex 1 suggest the formation of a single polymeric species for these two phosphate adducts in solution.

³¹P NMR experiments

 ^{31}P NMR spectra of free $\text{H}_2\text{PO}_4^{-}$ and $\text{HP}_2\text{O}_7^{\,3-}$ as well as those in the presence of one equivalent of $1[PF_6]_2$ and $2[PF_6]_2$ were recorded in [D₆]DMSO using triphenylphosphine (PPh₃) as external standard (-4.8 ppm in [D₆]DMSO). The ³¹P signal of free



Figure 6. ¹H NMR titration profile of a) $1[PF_6]_2$ (7 mm) and b) $2[PF_6]_2$ (6.7 mm) upon addition of increasing amounts of $H_2PO_4^-$ (0–2.0 equiv) in [D₆]DMSO.

 $H_2PO_4^-$ at 1.85 ppm is shifted downfield to 3.72 ppm and 3.23 ppm in the presence of $1[PF_6]_2$ and $2[PF_6]_2$, respectively (Figure 7 a). Similarly, it is observed that the initial ³¹P signals of free HP₂O₇³⁻ at -3.31 and -7.44 ppm are shifted downfield significantly to 1.85 and -3.95 ppm in the presence of $1[PF_6]_2$ and 1.45 and -3.98 ppm upon the addition of $2[PF_6]_2$ (Figure 7 b). This downfield shifting of the ³¹P signals of free HP₂O₇³⁻ ($\Delta\delta$ = 5.16 and 3.49 ppm with 1[PF₆]₂ and $\Delta\delta$ = 4.76 and 3.46 ppm with $2[PF_6]_2$) and $H_2PO_4^-$ ($\Delta\delta$ = 1.87 and 1.38 ppm with $1[PF_6]_2$ and $2[PF_6]_2$, respectively) in the presence of $1[PF_6]_2$ and $2[PF_6]_2$ indicates that the binding of $H_2PO_4^-$ and $HP_2O_7^{3-}$ occurs through the participation of neighboring oxygen centers of P in $H_2PO_4^{-}$ and $HP_2O_7^{3-}$.

Single-crystal X-ray structural studies

Single crystals suitable for X-ray diffraction of complexes 1 and 2 with PF₆⁻ counter anions were grown by diffusing diethylether into acetone/THF (9:1, v/v) solutions of the complexes at approximately 10 °C. Both 1[PF₆]₂ and 2[PF₆]₂ are found to crystallize in the triclinic crystal system with $P\bar{1}$ space group. The Ru^{II} centers adopt a distorted octahedral geometry through co-

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Figure 7. Partial ³¹P NMR spectra of a) TBAH₂PO₄ and b) TBA₃HP₂O₇ in the presence of 1[PF₆]₂ and 2[PF₆]₂; PPh₃ as external standard (-4.8 ppm in [D₆]DMSO).

ordination with two ancillary phenanthrolines and one triazolepyridine ligand (Figure 8). The Ru-N bond lengths and N-Ru-N angles (Tables S7 and S8, Supporting Information) are in line with the previously reported Ru^{II} polypyridyl complexes.^[10b,c, 11b, 12, 16c] Analysis of the crystal packing reveals that both the complexes form noncovalent 3D networks through C-I-F and C-H-F interactions (Figure S48, Supporting Information). To obtain solid-state support of phosphate binding with complex 1 we attempted to crystallize $H_2PO_4^{-}$ and $HP_2O_7^{3-}$ adducts of 1. Single crystals of X-ray diffraction quality of dihydrogen phosphate and pyrophosphate adducts of complex 1, namely $1[H_2PO_4]_2$ and $1_2[H_2P_2O_7]_2$, were grown by slow evaporation of complex 1 with the corresponding phosphates as their tetrabutylammonium salts from an acetonitrile/methanol (9:1, v/v) mixture. Crystallographic parameter details of complex 3 $(1[H_2PO_4]_2)$ and complex 4 $(1_2[H_2P_2O_7]_2)$ are listed in Table S9 (Supporting Information).

 $1[H_2PO_4]_2$ and $1_2[H_2P_2O_7]_2$ crystallize in triclinic crystal systems with the P1 space group (Figure 9 and Figure S49, Supporting Information), in which the geometry around the Ru^{II} centers remains similar to that in the free complexes (Tables S10 and S11, Supporting Information). Interestingly, in these two structures, phosphate or pyrophosphate is bound by strong and directional XB interactions between the iodine atom of the iodotriazole group and the oxygen atom of the corresponding phosphates. The XB distances (O--I) are found



Figure 8. Single-crystal X-ray structures: a) complex 1 and b) complex 2 with PF_6^- counter anions (thermal ellipsoids drawn at the 30% probability level).

to be 2.833 and 2.801 Å in 1[H₂PO₄]₂ and 1₂[H₂P₂O₇]₂, respectively, and the XB angles (C–I···O) are observed as 178.58° and 177.72° for $1[H_2PO_4]_2$ and $1_2[H_2P_2O_7]_2$, respectively. Importantly, these XB (O--I) distances are 81% and 80% of the sum of their van der Waals radii in 1[H₂PO₄]₂ and 1₂[H₂P₂O₇]₂, respectively (Table S12, Supporting Information). This clearly designates a noticeably strong and directional XB interaction, as observed in previously reported systems.[3g,9a] Interestingly, apart from halogen bonding, the oxygen atoms of the phosphate anion are also involved in the formation of a hydrogen-bonded polymeric assembly of phosphates, which results in the development of infinite anionic chains. On the other hand, the pyrophosphate adduct shows 2:2 host-guest stoichiometry between complex 1 and $H_2P_2O_7^{2-}$, in which apart from the C–I--O XB interaction, the pyrophosphate anion is involved in a hydrogen-bonded dimeric assembly. Analysis of the crystal packing in $1[H_2PO_4]_2$ and $1_2[H_2P_2O_7]_2$ reveals the formation of a 3D network through C-I-O XB interactions between the O atoms of $H_2PO_4^{-}/H_2P_2O_7^{2-}$ and the iodine center of complex 1 (Figure S50, Supporting Information).

In this context, note that Resnati et al. first reported structural evidence of phosphate recognition by charge-assisted XB in-

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Figure 9. Single-crystal X-ray structures of a) infinite propagated chain of halogen-bonded dihydrogen phosphate adduct of complex 1, and b) pyrophosphate adduct of complex 1. Short contacts involving anions are shown as dashed black lines.

teractions, but that is the only solid-state structural evidence of phosphate binding through XB interactions to date.^[9a] Again, to the best of our knowledge, the crystal structures of $1[H_2PO_4]_2$ and $1_2[H_2P_2O_7]_2$ constitute the first ever report of metal-complex-based second-sphere phosphate recognition through solitary XB interactions. Both $1[H_2PO_4]_2$ and $1_2[H_2P_2O_7]_2$ were further characterized by ESI-MS techniques, and good fits of the experimental isotope patterns with their respective simulated patterns are observed (Figure S51, Supporting Information).

Assuming a spherical shape of the crystal structure, we calculated the molecular diameter of the 2:2 dimeric supramolecular assembly between complex **1** and $H_2P_2O_7^{2-}$ by averaging the dimensions of the major and minor axes (Figure S52 and Table S13, Supporting Information). Interestingly, this value (16.40 Å) matches quite well with the diameter obtained in solution from the ¹H DOSY NMR experiment (16.66 Å). This result suggests that the 2:2 dimeric adduct, that is, (1:1 receptor/anion)₂, between complex **1** and $H_2P_2O_7^{2-}$ observed in the solid-state investigation also exists as a stable species in solution.

Conclusions

In summary, an XB-based highly sensitive luminescence "OFF-ON" chemosensor, $1[PF_6]_2$, has been developed, which can detect $H_2PO_4^{-}/HP_2O_7^{3-}$ selectively at very low concentrations, even in the presence of excess amounts of other competitive anions. The HB analogue of $1[PF_6]_2$, that is, $2[PF_6]_2$, shows simi-

lar sensing behavior. However, the detailed solution-state studies performed in this work strongly establish the superiority of $1[PF_6]_2$ over $2[PF_6]_2$ as a phosphate sensor. Mechanistic investigation using NMR titration experiments has confirmed the key functioning modes in the complexes: C–I---anion XB interactions in $1[PF_6]_2$ and C–H---anion HB interactions in $2[PF_6]_2$. Finally, single-crystal X-ray structural analyses corroborated the binding of $H_2PO_4^{-}/H_2P_2O_7^{2-}$ with complex 1 through solitary C–I---anion XB interactions. This is the first ever report of metal-assisted second-sphere phosphate binding through solitary C–I---anion XB interactions.

Experimental Section

The synthetic procedures and characterization of the complexes and other experimental details are provided in the Supporting Information.

Acknowledgements

P.G. gratefully acknowledges the Science and Engineering Research Board (SERB; EMR/2016/000900), India, for financial support and the Alexander von Humboldt Foundation for donating a Fluorimeter. B.C. and S.S. would like to thank CSIR, India, for research fellowships. The authors acknowledge Koushik Sarkar and Saptarshi Mondal IACS, Kolkata, India, for their help in solving the crystal structure of complex **4** and in the fitting of PL titration data, respectively.

Keywords: C–H…anion interaction • halogen bonding • phosphates • ruthenium • X-ray diffraction

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Received: August 25, 2016 Published online on ■■ ■, 0000





FULL PAPER

Ruthenium Complexes

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Selective Sensing of Phosphates by a New Bis-heteroleptic Ru^{II} Complex through Halogen Bonding: A Superior Sensor over Its Hydrogen-Bonding Analogue



Tipping the balance: Selective "OFF-ON" luminescent sensing, based on halogen bonding, of dihydrogen phosphate, and its superiority over the C– H…anion interaction are demonstrated (see figure). Solid-state second-sphere recognition of dihydrogen phosphate through solitary halogen-bonding interactions is also shown.

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