Inorg. Chem. **2007**, *46*, 9912–9918

Urea-Based Ruthenium(II)–Polypyridyl Complex as an Optical Sensor for Anions: Synthesis, Characterization, and Binding Studies

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Received July 21, 2007

A new ruthenium(II) complex [Ru(bpy)$_2$(1-(6-nitro-[1,10]phenanthrolin-5-yl)-3-(4-nitrophenyl)-urea)] (bpy = 2,2′-bipyridyl) was synthesized and characterized using standard analytical and spectroscopic techniques. Detailed absorption, emission, and ^{1}H NMR spectral studies revealed that this receptor molecule acts as a sensor for F^-, CH_3COO^-, and $H_2PO_4^-$ in acetonitrile solution. Binding of these anions caused an appreciable change in the color of the acetonitrile solution, which could be detected with the naked eye. At relatively lower concentration of anions, 1:1 H-bonded adduct was formed; however, at higher concentration, classical Brønsted acid–base-type reaction prevailed. The relative binding affinity of different anions toward this receptor was evaluated and was rationalized with quantum chemical calculations. Narrowing of the gap between the highest occupied molecular orbital and lowest unoccupied molecular orbital energy levels on deprotonation of the receptor molecule caused a faster decay of the luminescence lifetime for the $Ru_{d\pi} \rightarrow L_{\pi^*}/bpy_{\pi^*}$-based triplet excited state.

Introduction

Discriminatory binding of ions is an important area of research in terms of ion detection, transport, and sensing. These have direct relevance in the fields of chemistry, biology, and environmental science.[1] Currently, there is a surge of interest in the development of specific sensor molecules, which are able to act as chromogenic sensors for a certain analyte.[1,2] Sensor molecules should fundamentally have a receptor component, specific for a selected analyte and also a signaling unit to translate the analyte-binding-induced changes into an output signal. These changes could be probed through changes in redox potential, ^{1}H NMR chemical shifts, and/or additional spectral properties.[2−4] Among the sensor molecules where changes in spectral properties are used for probing the analyte-receptor binding, fluorescence-based sensors have received wider attention to achieve the high sensitivity and low analyte detection limit.[4,5] However, recently, the design and development of sensitive colorimetric sensors have received more attention owing to the facile visual recognition of a particular analyte.[2,6,7] It is known that halides and various oxyanions form H-bonded adducts with different H-bond donor functionalities,[1,2] such

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(1) (a) Martinez-Manez, R.; Sancenon, F. *Chem. Rev.* **2003**, *103*, 4419. (b) Bowman-James, K. *Acc. Chem. Res.* **2005**, *38*, 671. (c) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486. (d) Gale, P. A. *Coord. Chem. Rev.* **2003**, 1. (e) Suksai, C.; Tuntulani. T. *Top. Curr. Chem.* **2005**, *255*, 163. (f) Gale, P. A. *Acc. Chem. Res.* **2006**, *39*, 465. (g) Amendola, V.; Esteban-Gómez, D.; Fabbrizzi, L.; Licchelli, M. *Acc. Chem. Res.* **2006**, *39*, 343. (h) Gunnalauhsson, T.; Glynn, M.; Tocci, G. M.; Kruger, P. E.; Pfeffer, F. M. *Coord. Chem. Rev.* **2006**, *250*, 3094.

(2) (a) Bondy, C. R.; Loeb, S. J. *Coord. Chem. Rev.* **2003**, *240*, 77. (b) Choi, K.; Hamilton, A. D. *Coord. Chem. Rev.* **2003**, *240*, 101. (c) Gale, P. A. *Coord. Chem. Rev.* **2003**, *240*, 191. (d) Suksai, C.; Tuntulani, T. *Chem. Soc. Rev.* **2003**, *32*, 192. (e) Beer, P. D. *Acc. Chem. Res.* **1998**, *31*, 71. (f) Sessler, J. L.; Davis, J. M. *Acc. Chem. Res.* **2001**, *34*, 989. (g) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Hauxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515. (h) Hartley, J. H.; James, T .D.; Ward, C. J. *J. Chem. Soc., Perkin Trans 1* **2000**, 3155. (i) Jose, D. A.; Mishra, S.; Ghosh, A.; Shrivastav, A.; Mishra, S. K.; Das, A. *Org. Lett.* **2007**, *9*, 1979.

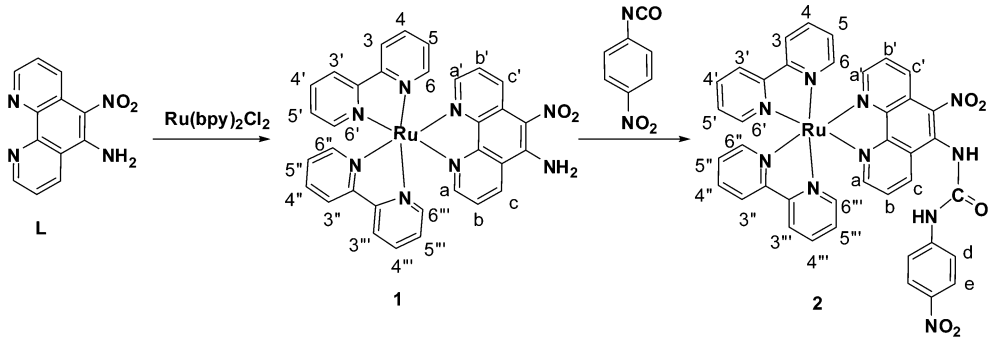
(3) (a) Lee, C. H.; Lee, J. S.; Na, H. K.; Yoon, D. W.; Miyji, H.; Cho, W. S.; Sessler, J. L. *J. Org. Chem.* **2005**, *70*, 2067. (b) Ghosh, T.; Maiya, B.; Wong, M. W. *J. Phys. Chem. A* **2004**, *108*, 11249. (c) Mizukami, S.; Nagano, T.; Urano, Y.; Odani, A.; Kikuchi, K. *J. Am. Chem. Soc.* **2002**, *124*, 3902. (d) Otón, F.; Tárraga, A.; Velasco, M. D.; Espinosa, A.; Molina, P. *Chem. Commun.* **2004**, 1658. (e) Anzenbacher, P., Jr.; Try, C. A.; Miyaji, H.; Jursíková, K.; Lynch, V. M.; Marquez, M.; Sessler, J. L. *J. Am. Chem. Soc.* **2000**, *122*, 10268.

(4) (a) Lu, H.; Xu, W.; Zhang, D.; Zhu, D. *Chem. Commun.* **2005**, 4777. (b) Curiel, D.; Beer, P. D.; Cowley, A.; Sambrook, M. R.; Szemes, F. *Chem. Commun.* **2004**, 1162. (c) Li, Z.-B; Lin, J.; Zhang, H.-C.; Sabat, M.; Hyacinth, M.; Pu, L. *J. Org. Chem.* **2004**, *69*, 6284. (d) Cho, E. J.; Moon, J. W.; Ko, S. W.; Lee, J. Y.; Kim, S. K.; Yoon, J.; Nam, K. C. *J. Am. Chem. Soc.* **2003**, *125*, 12376. (e) Xu, G. X.; Tarr, M. A. *Chem. Commun.* **2004**, 1050. (f) Curiel, D.; Cowley, A.; Beer, P. D. *Chem. Commun.* **2005**, 236.

(5) (a) Melaimi, M.; Gabbai, F. *J. Am. Chem. Soc.* **2005**, *127*, 9680. (b) Xu, S.; Chen, K.; Tian, H. *J. Mater. Chem.* **2005**, *15*, 2676. (c) Costero, A. M.; Manuel, C.; Pablo, G.; Salvador, G. *Chem. Commun.* **2006**, 761.

10.1021/ic701447g CCC: $37.00
Published on Web 10/20/2007

Scheme 1: Reaction Scheme Followed for the Synthesis of Complex **2**



as urea,[6,8] thiourea,[8] amide,[9] pyrrole,[9] indole,[4f,10] and pyrimidine.[11] Among different anions, the presence of excess F^- is known to cause deprotonation at the H-bond donor receptor center through the formation of the highly stable HF_2^- species.[3b,6,12,13] In this regard, the acidity of the H atom that participates in the H-bond formation with the anionic analyte is crucial.[6c,1g] In certain cases, CH_3COO^- and $H_2PO_4^-$ are also known to cause this deprotonation.[12b,14] However, metal-complexed-based anion sensors are not very common in the literature. In such cases, detection has been observed through the changes in the redox potential, ^{1}H NMR chemical shifts, or luminescence spectral patterns.[15] Examples of the spectral change in the visible region in ruthenium(II)−polypyridyl complexes are rare.[16] Herein, we report a new ruthenium(II)−polypyridyl-based urea receptor **2** (Scheme 1) for the colorimetric recognition of ions such as F^- among halides and CH_3COO^- and $H_2PO_4^-$ among oxoanions. Emission spectral studies showed that the emission intensity was completely quenched or "*switched off*" in the presence of an excess of F^-, CH_3COO^-, and $H_2PO_4^-$. At relatively lower concentration of these anions, 1:1 H-bonded adduct formation takes place, whereas at higher concentration, Brønsted acid−base reaction prevailed. Various association and deprotonation constants were evaluated from different spectral titration studies. The binding affinity of these anions with the receptor (**2**) was rationalized at the *ab initio* RHF/6-31G* level of theory.

Experimental Section

Materials and Methods. Chemicals. $Ru(^{\prime}bpy)_2Cl_2{\cdot}2H_2O$ (bpy = 2,2′-bipyridyl) was prepared following standard literature procedure. $RuCl_3{\cdot}xH_2O$, ′bpy, 1,10-phenanthroline, $[^tBu_4N]PF_6$, and 1-isocyanato-4-nitrobenzene were purchased from Aldrich Chemical Co. (U.S.A.) and used as received. All solvents were distilled and dried for the following procedures. 5-Nitro-1,10-phenanthroline and 5-nitro-6-amino-1,10-phenanthroline (**L**) were synthesized following the known literature procedures.[17]

Analytical Measurements. ^{1}H NMR spectra were recorded on a Bruker 200 MHz FT NMR (model: Advance-DPX 200) spectrometer at room temperature (RT, 25 °C). The chemical shifts (δ) and coupling constant (J) values are given in parts per million

(6) (a) Jose, D. A.; Kumar, D. K.; Ganguly, B.; Das, A. *Org. Lett*. **2004**, *6*, 3445. (b) Jose, D. A.; Kumar, D. K.; Ganguly, B.; Das, A. *Tetrahedron Lett.* **2005**, *46*, 5343 and references therein. (c) Jose, D. A.; Singh, A.; Das, A.; Ganguly, B. *Tetrahedron Lett*. **2007**, *48*, 3695. (d) Louise, S. E.; Gale, P. A.; Light, M. E.; Quesada, R. *Chem. Commun*. **2006**, 965. (e) Lin, Z.-H.; Ou, S.-J.; Duan, C.-Y.; Zhang, B.-G.; Bai, Z.-P. *Chem. Commun.* **2006**, 624. (f) Suresh, M.; Jose, D. A.; Das, A. *Org. Lett.* **2007**, *9*, 441. (g) Jose, D. A.; Kumar, D. K.; Kar, P.; Verma, S.; Ghosh, A; Ganguly, B.; Ghosh, H. N.; Das, A. *Tetrahedron* **2007**. doi: 10.1016.j.tet.2007.09.008.

(7) (a) Cho, E. J.; Ryu, B. J.; Lee, Y. J.; Nam, K. C. *Org. Lett.* **2005**, *7*, 2607. (b) Gunnalogsson, T.; Jensen, P.; Kruger, P. E. *Org. Lett.* **2005**, *7*, 5357. (c) Azenbacher, P.; Palacious, M. A.; Jursikova, K.; Marquez, M. *Org. Lett.* **2005**, *7*, 5027. (d) Gunnlaugsson, T.; Kruger, P. E.; Jensen, P.; Tierney, J.; Ali, H. D. P.; Hussey, G. M. *J. Org. Chem.* **2005**, *70*, 10875 and references therein. (e) Vázquez, M.; Fabbirizi, L.; Taglietti, A.; Pedrido, R. M.; González, N.; Bermezo, M. R. *Angew. Chem., Int. Ed*. **2004**, *43*, 1962.

(8) (a) Koulov, A. V.; Lambert, T. N.; Shukla, R.; Jain, M.; Boon, M. J.; Smith, B. D.; Li, H.; Sheppard, D. N.; Joos, J.-B.; Clare, J. P.; Davis, A. P. *Angew. Chem., Int. Ed*. **2003**, *42*, 4931. (b) Bondy, C. R.; Gale, P. A.; Loeb, S. J. *J. Am. Chem. Soc.* **2004**, *126*, 5030. (c) Kwon, J. Y.; Jang, Y. J; Kim, S. K.;. Lee, K.-H.; Kim, J. S.; Yoon, J. *J. Org. Chem.* **2004**, *69*, 5155. (d) Zhang, S.; Echegoyen, L. *J. Am. Chem. Soc.* **2005**, *127*, 2006. (e) Clare, J. P.; Ayling, A. J.; Joos, J.-B.; Sission, L. A.; Magro, G.; Pérez-Payán, M. N.; Lambert, T. N.; Shukla, R.; Smith, B. D.; Davis, A. P. *J. Am. Chem. Soc.* **2005**, *127*, 10739. (f) Li, C.; Munenori, N.; Masayuki, T.; Shinkai, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 6371. (g) Kim, S. K.; Singh, N. J.; Kim, S. J.; Swamy, K. M. K.; Kim, S. H.; Lee, K.-H.; Kim, K. S.; Yoon, J. *Tetrahedron* **2005**, *61*, 4545. (h) Kwon, J. Y.; Singh, N. J.; Kim, H.; Kim, S. K.; Yoon, J. *J. Am. Chem. Soc.* **2004**, *126*, 8892. (i) Turner, D. R.; Paterson, M. J.; Steed, J. W. *J. Org. Chem.* **2006**, *71*, 1598.

(9) (a) Nishiyabu, R.; Anzenbacher, P., Jr. *Org. Lett*. **2006**, *8*, 359. (b) Nielsen, K. A.; Cho, W.-S.; Lyskawa, J.; Levillain, E.; Lynch, V. M.; Sessler, J. L.; Jeppesen, J. O. *J. Am. Chem. Soc*. **2006**, 128, 2444 and reference therein. (c) Sessler, J. L.; Katayev, E.; Pantos, G. D.; Scherbakov, P.; Reshetova, M. D.; Khrustalev, V. N.; Lynch, V. M.; Ustynyuk, Y. A. *J. Am. Chem. Soc*. **2005**, *127*, 11442. (d) Sessler, J. L.; Camiolo, S.; Gale, P. A. *Coord. Chem. Rev*. **2003**, *240*, 17. (e) Gale, P. A. *Chem. Commun*. **2005**, 3761. (f) Evgeny, A. K; DanPantos, G.; Reshetova, M. D.; Khrustalev, V. N.; Lynch, V. M; Ustynyuk, Y. A.; Sessler, J. L. *Angew. Chem., Int. Ed.* **2005**, *44*, 7386. (g) Kang, S. O.; Powell, D.; Day, V. W.; Bowman-James, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 1921.

(10) Chang, K.-J.; Dohyun Moon, D.; Lah, M. S.; Jeong, K. S. *Angew. Chem., Int. Ed.* **2005**, *44*, 7926.

(11) Cui, Y.; Mo, H.-J.; Chen, J.-C.; Niu, Y.-L.; Zhong, Y.-R.; Zheng, K.-C.; Ye B.-H. *Inorg. Chem.* **2007**, *46*, 6427.

(12) (a) Boiocchi, M.; Del, Boca, L.; Gomez, D. E.; Fabbrizzi, L.; Licchelli, M.; Monazani, E. *J. Am. Chem. Soc*. **2004**, *126*, 16507. (b) Gomez, D. E.; Fabbrizzi, L.; Licchelli, M.; Monazani, E. *Org. Biomol. Chem*. **2005**, *3*, 1495.

(13) (a) Peng, X.; Wu, Y.; Fan, J.; Tian, M.; Han, K. *J. Org. Chem*. **2005**, *70*, 10524.(b) Gomez, D. E.; Fabbrizzi, L.; Liccheli, M. *J. Org. Chem.* **2005**, *70*, 5717. (c) Gronert, S. *J. Am. Chem. Soc.* **1993**, *115*, 10258.

(14) (a) Boicchi, M.; Boca, L. D.; Gómez, D. E.; Fabbrizzi, L.; Licchelli, M.; Monzani, E. *Chem.—Eur. J*. **2005**, *11*, 3097. (b) Esteban-Gómez, D.; Fabbrizzi, L.; Licchelli, M.; Sacchi, D. *J. Mater. Chem.* **2005**, *15*, 2670.

(15) Rice, C. R. *Coord. Chem. Rev*. **2006**, *250*, 3190.

(16) (a) Mizuno, T.; Wei, W.-H.; Eller, L. R.; Sessler, J. L. *J. Am. Chem. Soc*. **2002**, *124*, 1134. (b) Lin, Z. H.; Zhao, Y.-G.; Duan, C. Y.; Zhang, B. G.; Bai, Z. P. *Dalton. Trans.* **2006**, 3678. (c) Jose, A. D.; Kar, P.; Koley, D.; Ganguly, B.; Thiel, W.; Ghosh, H. N.; Das, A. *Inorg. Chem*. **2007**, *46*, 5576.

(17) Amouyal, E.; Homsi, A.; Chambron, J.-C.; Sauvage, J.-P. *J. Chem. Soc., Dalton Trans.* **1990**, 1841.

and hertz, respectively, throughout this work unless mentioned otherwise. Tetramethylsilane (TMS) was used as an internal standard for all ^{1}H NMR studies. Electrospray ionization mass spectrometry (ESI MS) measurements were carried out on a Waters QTof-Micro instrument. Microanalyses (C, H, N) were performed using a Perkin-Elmer 4100 elemental analyzer. Infrared spectra were recorded as KBr pellets using a Perkin-Elmer Spectra GX 2000 spectrometer. UV−vis spectra were obtained by using either Shimadzu UV-3101 PC or Cary 500 Scan UV−vis−NIR spectrometers. Room-temperature emission spectra were obtained using a Perkin-Elmer LS 50B luminescence spectrofluorimeter.

The fluorescence quantum yields, ϕ_f, were estimated in appropriate solvents (as specified) using the integrated emission intensity of $Ru(bpy)_3Cl_2$ ($\phi_f = 0.042$ in H_2O at RT) as referenced[18] via

$$\phi_f = \phi_f' (I_{sample}/I_{std})(A_{std}/A_{sample})(\eta^2_{sample}/\eta^2_{std})$$

where ϕ_f' is the absolute quantum yield for the $Ru(bpy)_3Cl_2$, used as reference; I_{sample} and I_{std} are the integrated emission intensities; A_{sample} and A_{std} are the absorbances at the excitation wavelength, and η^2_{sample} and η^2_{std} are the respective refractive indices.

A time-correlated single-photon-counting laser flash instrument (Mini τ; Edinburgh Instruments) was used for recording the luminescence decay profile for receptor **2**, in CH_3CN and in the presence of added anionic analytes. Emission at 600 nm was monitored as a function of time, following excitation by a 440 nm picosecond laser diode having a pulse width of 20 ps. Air-equilibrated solutions were used for recording the luminescence lifetime.

Experimental Procedures. Synthesis of $Ru(bpy)_2(L)(PF_6)_2$ (1). The procedure adopted for synthesizing compound **1** was similar to that of an earlier reported method.[19] The analytical data matched the proposed compound well. ^{1}H NMR (200 MHz, CD_3CN, TMS, δ (ppm)): 8.97 (dd, 1H, $J = 8.8$ Hz, 1 Hz Hc′), 8.84 (dd, 1H, $J =$ 8.6 Hz, 1.1 Hz, Hc), 8.53 (d, 2H, $J = 6.4$ Hz, H_5, $H_{5'}$), 8.49 (d, 2H, $J = 5.6$ Hz, $H_{5''}$, $H_{5'''}$), 8.19 (d, 1H, $J = 5.4$ Hz, Ha′), 8.08 (d, 2H, $J = 4.8$ Hz, $H_{6,}$ $H_{6'}$), 8.01 (d, 2H, $J = 8.2$ Hz, $H_{6''}$, $H_{6'''}$), 7.79 (d, 1H, $J = 4.6$ Hz, H_a), 7.74 (d, 1H, $J = 8.8$ Hz, $H_{b'}$), 7.63 (d, 1H, $J = 8$ Hz, H_b), 7.57 (d, 2H, $J = 8$ Hz, H_4, $H_{4'}$), 7.45 (d, 2H, $J =$ 7.2 Hz, $H_{4''}$, $H_{4'''}$), 7.42 (d, 1H, $J = 6$ Hz, H_3), 7.27−7.33 (m, 3H, $H_{3'}$, $H_{3''}$, $H_{3'''}$). FTIR (KBr; ν/cm^{-1}) 3362, 1627, 1527, 1445, 1261, 1172, 839, 763, 557. ESI-MS: m/z 798 ($M^+ - PF_6$) (∼20%), 653 ($M^+ - 2PF_6$) (∼100%). Elemental anal. Calcd for $C_{32}H_{24}N_8O_2RuP_2F_{12}\cdot H_2O$: C 40.73, H 2.56, N 11.88. Found: C 40.4, H 2.7, N 11.7.

Synthesis of $Ru(bpy)_2$(1-(6-nitro-[1,10]phenanthrolin-5-yl)-3-(4-nitrophenyl)-urea)$(PF_6)_2$ (2). Compound **1** (150 mg, 0.164 mM) was dissolved in a dry and distilled minimum volume of acetonitrile. 1-Isocyanato-4-nitrobenzene (40.0 mg, 0.244 mM) was dissolved in dried THF and added dropwise slowly through an additional funnel to the above solution of **1**. The whole system was kept in a dinitrogen atmosphere for 2 days. Then the solvent was evaporated. The crude product was subjected to column chromatography, where the stationary phase is alumina grade (III) and the eluent is 50% CH_3CN in toluene, followed by recrystallization in an acetonitrile−ether mixture. Yield: 80 mg (44%). ^{1}H NMR (200 MHz, CD_3CN, TMS, δ (ppm)): 8.63 (d, 1H, $J = 8.2$ Hz, $H_{c'}$), 8.53 (t, 4H, $J = 6.8$ Hz, $H_{5,5',5'',5'''}$), 8.42 (d, 1H, $J = 8.6$ Hz, H_c), 8.22 (d, 1H, $J' = 5.2$ Hz, $H_{a'}$), 8.11 (d, 2H, $J = 9.4$ Hz, $H_{6,\ 6'}$), 8.02 (d, 2H, $J = 7.6$ Hz, H_e), 7.81 (d, 1H, $J = 5.2$ Hz, H_a), 7.75−7.61 (m, 6H, H_b, $H_{b'}$, $H_{4,4',4'',-4'''}$), 7.6 (d, 2H, $J = 7.2$ Hz, $H_{6'',6'''}$), 7.42 (m, 4H, $H_{3,3',3'',3'''}$), 7.0 (d, 2H, $J = 9.2$ Hz, H_d). FTIR (KBr; ν/cm^{-1}): 3573, 1596, 1539, 1503, 841 (br, PF_6), 762, 556. ESI-MS: m/z 961 ($M^+ - PF_6$) (∼7%), 985 ($M^+ - PF_6 + Na^+$) (∼20%), 1105 (M^+) (1%). Elemental anal. Calcd for $C_{39}H_{28}N_{10}O_5Ru$: C 57.28, H 3.45, N 17.13. Found: C 57.8, H 3.6, N 17.6.

Computational Details. All the calculations were performed using the *Jaguar* program suite.[20] The calculations were performed employing the RHF/6-31G* level of theory. For computational simplicity, only the phenanthroline moiety was modeled with different anions.

Spectrophotometric Titration. A 1.0×10^{-4} M solution of the complex **2** in acetonitrile was prepared and stored in the dark. This solution was used for all spectroscopic studies after appropriate dilution. Solutions of 1.0×10^{-3} M tetrabutyl ammonium (TBA) salts of the respective anions were prepared in dried and distilled acetonitrile and were stored under an inert atmosphere. All titration experiments were performed using 2.0×10^{-5} M solutions of complex **2** and various concentrations of anions ($2.0-100.0 \times 10^{-6}$ M) in the same solvent. Affinity constants were evaluated after calculating the concentrations of the respective species, free **2**, A^- (A^- is F^-/ $H_2PO_4^-$/ CH_3COO^-), and associated complexes, e.g., $\mathbf{2}\cdot\mathbf{A}^-$ (1:1 complex of receptor **2** and $\mathbf{A}^-$). The effect of the ionic strength on the affinity constant was also examined by repeating the studies at various (0−0.1 M [nBu$_4$N]ClO_4) supporting electrolyte concentrations. Affinity constants were evaluated from the collected absorbance data of the titration curve using 540 nm as the probe wavelength, and the equation $K_a = [LA^-]/\{[L]_{free}\text{-}[A^-]_{free}\}$ was used for all calculations (Supporting Information).

Luminescence Titration. The standard solutions given above were also used for the luminescence titration studies. For all measurements, $\lambda_{ext} = 455$ nm with an excitation and emission slit width of 10/10 or 15/15 nm. All titration experiments were performed using 2.0×10^{-5} M solutions (air-equilibrated) of complex **2** in air-equilibrated acetonitrile solutions (2.0×10^{-6} to 5.0×10^{-3} M) of various anions.

Results and Discussion

Synthesis, Physicochemical, and Photophysical Studies. Urea functionality in compound **2** was generated by reacting 1-isocyanato-4-nitrobenzene with the pendant amino functionality of **1** in a dry acetonitrile−THF mixture.[6a,b] Pure complexes **1** and **2** were isolated through column chromatography and a recrystallization process. Intermediate ligands and the ruthenium(II)−polypyridyl complexes were characterized by standard analytical techniques.

Electronic spectra recorded for **2** in acetonitrile are shown in Figure 1. The electronic spectra recorded for this complex in acetonitrile are shown in Figure 1. The observed transition bands at 280, 340, and 455 nm were assigned to the predominantly intraligand bpy/L-based $\pi \rightarrow \pi^*$, interligand bpy/L-based $\pi \rightarrow \pi^*$ and $d\pi_{Ru} \rightarrow \pi^*_{bpy}/\pi^*_L$ transitions, respectively.[16c,21] On excitation at the $d\pi_{Ru} \rightarrow \pi^*_{bpy}/\pi^*_L$-based metal-to-ligand charge transfer (MLCT) transition band (455 nm), this air-equilibrated acetonitrile solution of this compound was found to be luminescent and the emission

(18) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.
(19) Ishow, E.; Gourdon, A.; Launay, J.-P.; Chiorboli, C.; Scandola, F. *Inorg. Chem.* **1999**, *38*, 1504.
(20) *Jaguar*, version 5.5; Schrodinger, Inc.: Portland, OR, 2004.
(21) Lachaud, F.; Quaranta, A.; Pellegrin, Y.; Dorlet, P.; Charlot, M.-F.; Un, S.; Leibl, W.; Aukauloo, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 1536.

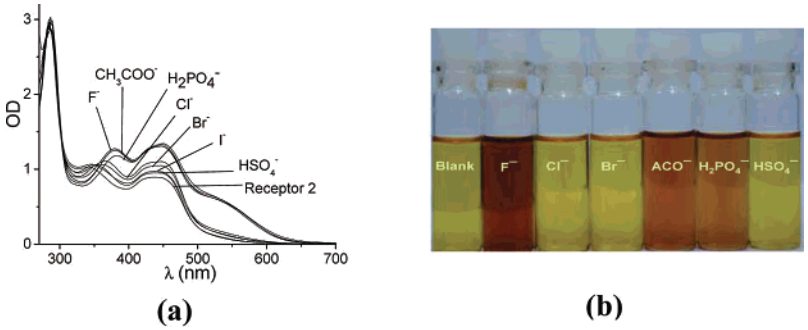


Figure 1. (a) Change in UV−vis spectra of receptor **2** (4.65×10^{-5} M) after the addition of different anions ($\sim 2.5 \times 10^{-4}$ M) in CH_3CN solution. (b) Color change of the acetonitrile solution of **2** in the presence of an excess of various anions.

spectrum displayed a characteristic emission peak (slit width 10/10 nm) at 598 nm (quantum yield 0.022 with respect to $Ru(bpy)_3(PF_6)_2$). On excitation at the 420 nm wavelength of the air-equilibrated acetonitrile solution of **2**, the time-correlated single-photon-counting luminescence decay experiments revealed a biexponential decay. The kinetic profile was best fit with time constants 135 ± 6 (42%) and 240 ± 7 (58%) ns ($\chi^2 = 1.04$). Two lifetimes (135 and 240 ns) can be attributed to the triplet state of the ruthenium(II)−complex involving L and bpy ligands, respectively. The shorter component (135 ns) can be attributed to the triplet state of the $Ru_{d\pi} \rightarrow L_{\pi^*}$-based MLCT transition, and the longer component can be attributed to the $Ru_{d\pi} \rightarrow bpy_{\pi^*}$-based MLCT transition. Furthermore, support for this assignment came from the luminescence decay kinetic profile recorded for the excited triplet state for $Ru(bpy)_3^{2+}$ under the identical experimental conditions, which could best be fit with a single-exponential decay of time constant 265 ns ($\chi^2 = 1.02$). The presence of the biexponential decay implies that internal conversion between the two triplet MLCT excited states is slow. The nonradiative channel is expected to be more active for the H-bond donor urea-based ligand (L), and as a result, the excited-state lifetime will be shorter as compared with the one involving bpy. Such a phenomena is known for ruthenium(II)−polypyridyl complexes with H-bond donor 2,2-bipyridyl derivatives.[16c,22] This was further confirmed when the lifetime of the excited state for **2** was evaluated in other solvent with different H-bond accepting ability. In dichloromethane, the kinetic profile was best fit with time constants 360 ± 13 (29%) and 651 ± 17 (71%) ns ($\chi^2 = 1.09$). CH_2Cl_2, being a poor H-bond acceptor, reduces the possibility of deactivation via the nonradiative pathway involving the $Ru_{d\pi} \rightarrow L_{\pi^*}$-based triplet excited state, and an overall increase in the lifetime of the excited state along with the increase in the decay component through $Ru_{d\pi} \rightarrow bpy_{\pi^*}$-based triplet excited state were observed. Furthermore, based on the proposition made by Wrighton et al.,[22c] a possibility exists for excited state **2** to be in an equilibrated mixture of protonated and deprotonated forms of L due to changed acidity in the excited state. Thus, the presence of two completely distinct species with overlapping spectra and different excited-state lifetimes could also explain the biexponential kinetics.

Absorption Titration. Preliminary studies revealed a detectable change in color from pale yellow to orange on the addition of the TBA salt solution of F^- (TBAF), CH_3COO^- (TBAA), and $H_2PO_4^-$ (TBAP) (1 equiv) to the acetonitrile solution of **2**. No such change could be detected when a similar experiment was repeated for other anions like Cl^- (TBAC), Br^- (TBAB), I^- (TBAI), and HSO_4^- (TBAS). Furthermore, this change was more prominent when F^-/ CH_3COO^-/ $H_2PO_4^-$ was added in excess; the color changed to reddish brown. This observation tends to suggest that there could be two equilibrium processes associated with the binding of these three anions to complex **2**. The absorption spectra of **2** in the absence and presence of 1.25 equiv of various anions are shown in Figure 1. No detectable change in absorption and emission spectrum for $Ru(bpy)_3^{2+}$ on the addition of the TBA salt of $F^-/CH_3COO^-/H_2PO_4^-$ revealed that the urea functionality of **2** is actually involved in H-bond formation with these three anions.

Systematic changes in the electronic spectra on the addition of standard A^- solutions ($0.2-8.0 \times 10^{-5}$ M in CH_3CN) to the acetonitrile solution of **2** (2.0×10^{-5} M) are shown in Figure 2.

The absorption band at 340 nm shifted to ca. 398 nm, and a hyperchromic shift from 455 to 580 nm with an isosbestic point at around 348 nm was observed on the addition of ca. 1.2 equiv of A^- (Figure 2). A broad absorption band with maxima at ca. 545 nm developed, with a concomitant increase in the absorption value at 440 nm. However, on the addition of an even higher concentration of A^-, further changes in the spectral pattern occurred, with a new isosbestic point at ca. 300 nm. It is worth mentioning that due to the presence of different strongly absorbing species in equilibrium, the isosbestic points are not as clear they should have been—however, these two isosbestic points signify the presence of two distinctly different equilibrium processes (eqs 1 and 2)

$$2 + A^- \rightleftharpoons 2\cdots A^-; \quad K_a \tag{1}$$

$$2\cdots A^- + A^- \rightleftharpoons 2_{-H+}{}^- + AH\cdots A^-; \quad K_d \tag{2}$$

The spectra recorded for the receptor molecule **2** in the presence of a large excess of $F^-/CH_3COO^-/H_2PO_4^-$ were

(22) Balzani, V.; Juris, A.; Venturi, M. *Chem. Rev.* **1996**, *96*, 759. (b) Kalyanasundaram, K.; Gratzel, M.; Nazeeruddin, M. K. *Dalton Trans.* **1991**, 343. (c) Giordano, P. J.; Randolph Bock, C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 6960.

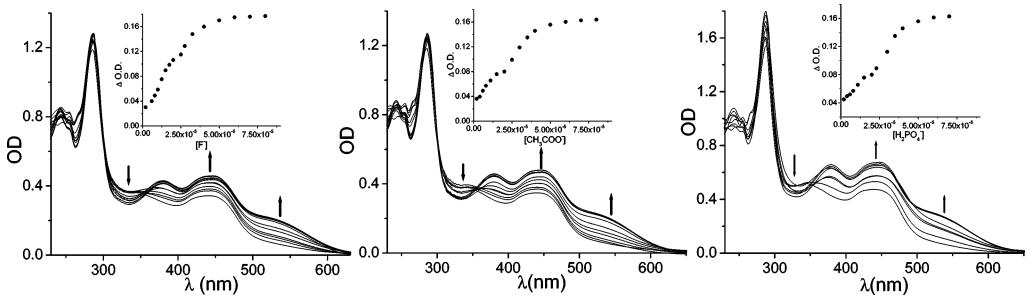


Figure 2. UV−vis titration of receptor **2** (2.0×10^{-5} M) in acetonitrile solution with (a) F^- (2.0×10^{-6} M to 8.0×10^{-5} M), (b) CH_3COO^- (2.0×10^{-6} M to 8.5×10^{-5} M), and (c) $H_2PO_4^-$ (2.0×10^{-6} M to 8.3×10^{-5} M). Insets: Corresponding titration profile for each titration.

Table 1. Binding Constant Values Calculated from UV−Vis Titration[a,b]

anion	K_a (M^{-1}) ($\times 10^4$)	K_d (M^{-1}) ($\times 10^4$)
F^-	22 (±1)	6.1 (±0.3)
CH_3COO^-	19 (±2)	5.97 (±0.4)
$H_2PO_4^-$	8.7 (±0.5)	1.2 (±0.1)

[a] *t*-Butyl salts of the respective anions were used for the studies. [b] The *K* value reported is the average of the six independent data evaluated from each individual UV−vis titration data for the respective receptor and anion. Confidence limits for the respective *K* values are also shown.

found to be similar to the species $[2_{-H+}]^-$, generated by treatment with $[NBu^t_4]OH$ in acetonitrile. This confirms the deprotonation of the receptor **2** at higher levels of $[F^-]/[CH_3COO^-]/[H_2PO_4^-]$.

Formations of the H-bonded adduct and the deprotonation phenomena were also evident from spectrofluorimetric and ^1H NMR titrations (vide infra). The two equilibriums involved are shown in eqs 1 and 2. K_a reflects the relative affinity/stability of the H-bonded adduct (**2**···$\mathbf{A}^-$), while K_d is the composite constant that involves the equilibrium of the deprotonation of **2**, protonation of A^-, and the formation of the higher anion aggregate. High thermodynamic stability of an anion aggregate such as HF_2^- is proposed by several researchers and is believed to be the driving force for the deprotonation process.[1g,3b,6] The formation of the similar complexes ca. $[H_3PO_4\cdots H_2PO_4^-]$ and $[CH_3COOH\cdots CH_3COO^-]$ was also reported earlier.[14] Respective equilibrium constants (K_a and K_d) were evaluated from the spectrophotometric titration with various analytes and are shown in Table 1. Experimentally obtained K_a values ($F^- > CH_3COO^- > H_2PO_4^-$) basically reflect the affinity of these conjugate bases for protonation.[23] It is worth mentioning here that the absence of any observable shift in the electronic spectra of **2** on the addition of $Cl^-/Br^-/HSO_4^-$ does not exclude the possibility of any weaker interaction that may exist between **2** and these anions. This was confirmed by luminescence and ^1H NMR studies.

Emission Titrations. The effect of various anions on the emission spectra of **2** was investigated in air-equilibrated acetonitrile solution, and the results are shown in Figure 3.

In the absence of any anion, the emission spectrum of **2** displayed a characteristic emission peak at 598 nm (relative quantum yield for receptor **2** was found to be 0.022 with respect to $Ru(bpy)_3(PF_6)_2$) upon exciting at $Ru_{d\pi} \rightarrow L_{\pi^*}$/

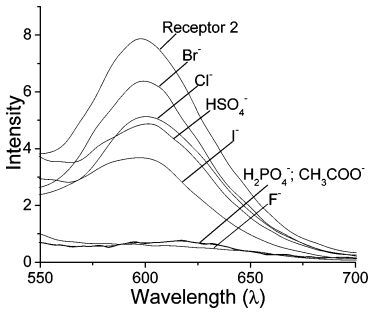


Figure 3. Emission spectra of receptor **2** (4.65×10^{-5} M) in the absence and presence of respective anions (1.5×10^{-4} M) in acetonitrile solution.

bpy_{π^*}-based MLCT band at 440 nm. An almost complete quenching of emission intensity was observed on the addition of 1.2 equiv of F^-, CH_3COO^-, and $H_2PO_4^-$, while a complete quenching was observed on the addition of an excess of these three anions. No appreciable quenching was observed on the addition of other anionic analytes (Figure 3).

The values were found to be in good agreement with those determined from spectrophotometric titrations. Affinity constants for Cl^-, Br^-, and HSO_4^- were found to be [3.0 (±0.2)] × 10^3, [1.4 (±0.1)] × 10^3, and [2.0 (±0.1)] × 10^3, respectively. Thus, the binding values of these anions were 2 orders of magnitude lower.

^{1}H NMR Titration. Furthermore, we have recorded the ^1H NMR spectra for **2** in CD_3CN in the absence and presence of varying concentrations of anions. The ^1H NMR titrations carried out in CD_3CN solution in the presence of different anions are shown in Figure 4. Receptor **2** was found to have a limited solubility in DMSO.

This restricted our choice in recording the ^1H NMR spectra in CD_3CN, and no signal for the −NH proton was observed for receptor **2**. Hence, we have assigned the shifts of certain aromatic protons only. A significant downfield shift for H(c′) and H(c) protons was observed upon the addition of F^- (Scheme 1), whereas there is an upfield shift for H(d) protons. Similar shifts were also observed on the addition of CH_3COO^-. The formation constant of the 1:1 adduct (eq 1) for F^- and CH_3COO^- was also evaluated from ^1H NMR titrations (Supporting Information) and was found to be in good agreement ($K_a(F^-) = [2.24 \pm 0.10] \times 10^5$; $K_a(CH_3COO^-) = [2.0 \pm 1] \times 10^5$) with those obtained otherwise. For $H_2PO_4^-$, evaluation of the association constant value was not possible, as the complex was found to precipitate on adding this anion during the ^1H NMR experiment. The experimentally obtained relative binding

(23) Steiner, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 48.

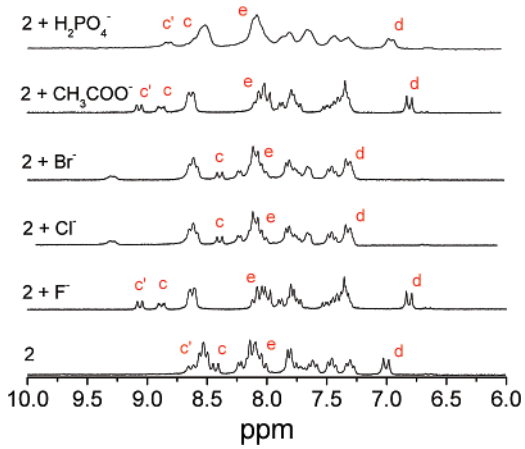


Figure 4. Partial ^{1}H NMR (200 MHz) spectra of **2** in the presence of different anions in CD_3CN at room temperature.

affinity of various anions toward receptor **2**, as determined by different spectroscopic methods, was further rationalized by quantum mechanical calculations.

Quantum Chemical Calculations. To rationalize the relative affinity of the receptor **2** toward various anionic analytes, *ab initio* quantum chemical calculations have been performed.[20] The structure of **2** and its complexes with F^-, Cl^-, Br^-, CH_3COO^-, $H_2PO_4^-$, and HSO_4^- were optimized at the Hartree−Fock RHF/6-31G* level of theory (Figure 5).[6a−c,g] For computational simplicity, receptor **2** was modeled as the phenanthroline moiety only. The calculated structural parameters of **2** and its adducts with the respective anions explain the observed chemical shifts.

Optimized structures for **2** and the corresponding complex with anions reveal that a C−H···O-type interaction exists, which accounts for the observed downfield shifts of c′ (Figure 5). The distance between the c′ proton and one of the O atoms of the $-NO_2$ group decreases (from 2.336 to 2.219, 2.232, 2.234, 2.235, 2.24, and 2.244 Å for F^-, Cl^-, Br^-, CH_3COO^-, $H_2PO_4^-$, and HSO_4^-, respectively) on interaction with these anions and that results in a stronger C−H···O type interaction in the complexed state. Similarly, the C−H···A^- distance follows the order F^- > CH_3COO^- > $H_2PO_4^-$ and thereby the interaction with the c protons (Figure 5).

The corresponding nonbonded distances are 2.01, 2.27, and 2.36 Å, respectively. In the optimized parent structure, we find that one of the NH− bonds is intramolecularly hydrogen bonded with the $-NO_2$ group (Figure 5). However, to maximize the interaction with the anions, the urea moiety rotates, and consequently, the hydrogen bond is ruptured in each case (Figure 5). The calculated binding energies (ΔE) support the observed trend that fluoride binds preferentially in comparison to other anions studied here. This observed trend was found in agreement with the recent report on this type of anion sensors.[2,14,24]

Luminescence Decay Studies. In one of our recent reports,[16c] we have shown through detailed TD-DFT studies on related ruthenium(II)−polypyridyl complexes that deprotonation at the substituted bpy ligand caused an increase in the highest occupied molecular orbital (HOMO) energy of the deprotonated ligand and this favored a predominant interligand charge transfer ($L_\pi \rightarrow bpy_{\pi^*}$) transition with some minor contribution from the $Ru_{d\pi} \rightarrow L_{\pi^*}/bpy_{\pi^*}$ transitions. It may be presumed that similar phenomena will prevail here, and this is expected to narrow the energy gap between the excited triplet state and the HOMO of the deprotonated Ru complex, which accounts for the new absorption bands at longer wavelengths. Thus, according to the energy gap law[25] one would expect a faster decay of the excited triplet state owing to the narrowing of the energy gap between the excited triplet and ground singlet states, which is exactly what we

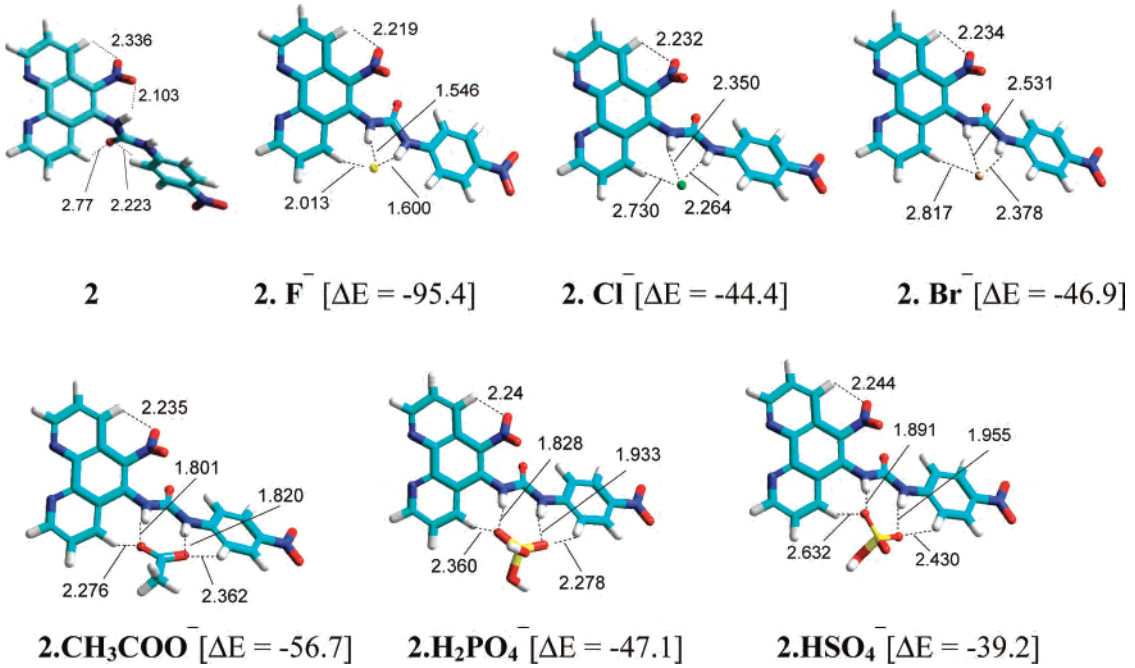


Figure 5. The RHF/6-31G*-optimized geometries for **2** and its complexes with F^-, Cl^-, Br^-, CH_3COO^-, $H_2PO_4^-$, and HSO_4^- anions with corresponding binding energies.

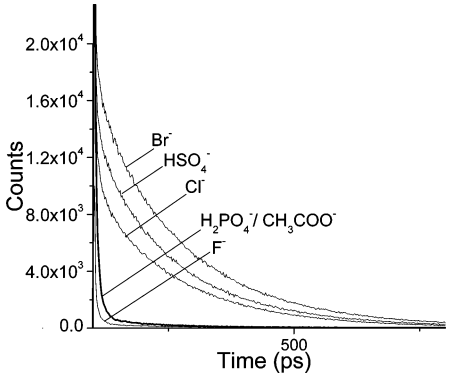


Figure 6. Luminescence decay profile for 1.2×10^{-5} M of **2** in the absence and presence of various anions (1.0×10^{-4} M) in air-equilibrated acetonitrile solution.

have observed in luminescence decay profiles for the deprotonated species ($\mathbf{2}_{-H+}$) in the presence of excess F^- ($\tau_1 = 35 \pm 2$ ns; $\tau_2 = 165 \pm 5$ ns with χ^2 is 1.08)/CH_3COO^- ($\tau_1 = 45 \pm 2$ ns; $\tau_2 = 180 \pm 4$ ns with χ^2 is 1.07)/$H_2PO_4^-$ ($\tau_1 = 43 \pm 2$ ns; $\tau_2 = 170 \pm 5$ ns with χ^2 is 1.09). Furthermore, more effective solvation of the negatively charged adduct ($\mathbf{2}\cdots\mathbf{A}^-$) or deprotonated form ($\mathbf{2}_{-H+}$) might have added to the faster decay of the excited triplet state through radiative pathway.[26] Weaker interaction with other anions was evident from little perturbation of the kinetic profile for **2**; Cl^- ($\tau_1 = 109 \pm 5$ ns; $\tau_2 = 202 \pm 4$ ns with χ^2 is 0.99)/Br^- ($\tau_1 = 130 \pm 3$ ns; $\tau_2 = 229 \pm 5$ ns with χ^2 is 1.06)/HSO_4^- ($\tau_1 = 113 \pm 3$ ns; $\tau_2 = 215 \pm 3$ ns with χ^2 is 1.03) (Figure 6).

Similar faster decay of the luminescence of the $Ru_{d\pi} \rightarrow bp_{\pi^*}$ (bp is substituted bpy)-based excited triplet state is also reported earlier in the luminescence-lifetime-based sensors for anionic analytes.[27]

Conclusions

We have reported a new urea-based ruthenium(II) receptor that can act as colorimetric sensor for F^-, CH_3COO^-, and $H_2PO_4^-$. The binding properties were confirmed by absorption, emission and ^1H NMR spectroscopic techniques. This receptor is one of the rare examples[12a,14a] which can act as a colorimetric sensor for CH_3COO^-. The calculated results support our experimental findings that the receptor binds strongly with F^-, CH_3COO^-, and $H_2PO_4^-$ compared with the other halide and oxyanions studied. Furthermore, the observed chemical shifts upon complexation of these anions were also rationalized by the calculated results. Fluoresence studies showed that the complexation of receptor **2** with F^-, CH_3COO^-, and $H_2PO_4^-$ could completely quench the emission intensity. The luminescence decay profiles for $\mathbf{2}_{-H+}$ (in the presence of excess F^- or CH_3COO^- or $H_2PO_4^-$) and $\mathbf{2}\cdots X^-$ (where X^- is other anions such as Cl^-, Br^-, or HSO_4^-) in picosecond time domain reveal a faster nonradiative decay owing to the better solvation of the anionic adducts or deprotonated form of receptor **2**.

Acknowledgment. The Department of Science and Technology (DST) and Board of Research in Nuclear Science (BRNS), Government of India, supported this work. A.D. and B.G. wish to thank Dr. P. K. Ghosh (CSMCRI, Bhavnagar) for his keen interest in this work.

Supporting Information Available: (1) General formula for calculating binding constants from UV−vis titrations; (2) general formula for calculating binding constants from emission titrations; (3) binding constant values calculated from emission titration; (4) general formula for calculating binding constants from the NMR spectrum; (5) ^1H NMR titration spectra with F^- and CH_3COO^-. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) Santos, C. M. G.; McCabe, T.; Gunnlaugsson, T. *Tetrahedron Lett.* **2007**, *48*, 3135.

(25) (a) Siebrand, W. J. *J. Chem. Phys.* **1966**, *44*, 4055. (b) Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* **1983**, *87*, 952. (c) Chen, P.; Meyer. T. *J. Chem. Rev.* **1998**, *98*, 14 and references therein. (d) Turro, N. J. *Modern Molecular Photochemistry*; The Benzmin/Cummings Publishing Co.: Menlo Park, CA, 1978.

(26) (a) Inoue, H.; Hida, M.; Nakashima, N.; Yoshihara, K. *J. Phys. Chem.* **1982**, *86*, 3184. (b) Yatsuhashi, T.; Nakajima, Y.; Shimada, T.; Inoue, H. *J. Phys. Chem. A* **1998**, *102*, 3018. (c) Onfelt, B.; Olofsson, J.; Lincoln, P.; Nordén, B. *J. Phys. Chem. A* **2003**, *107*, 1000.

(27) Anzebacher, P.; Tyson, D. S.; Jurslkova, K.; Castellano, F. N. *J. Am. Chem. Soc.* **2002**, *124*, 6232.