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Luminescent Cyclometalated Iridium(III) Polypyridine Complexes Containing a Thiourea Moiety: Synthesis, Characterization, Photophysics, Electrochemistry and Anion-Binding Properties

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A series of new luminescent cyclometalated iridium(III) polypyridine thiourea complexes $[Ir(N\text{-}C)_2(N\text{-}N)](PF_6)$ [HN-C = 2-phenylpyridine (Hppy), N-N = *N*-ethyl-*N′*-1,10-phenanthrolin-5-yl thiourea (phen-TU-Et) (**1a**), *N*-phenyl-*N′*-1,10-phenanthrolin-5-yl thiourea (phen-TU-Ph) (**1b**), *N*-(1-adamantanemethyl)-*N′*-1,10-phenanthrolin-5-yl thiourea (phen-TU-MeA) (**1c**); HN-C = 7,8-benzoquinoline (Hbzq), N-N = phen-TU-Et (**2a**), phen-TU-Ph (**2b**), phen-TU-MeA (**2c**); HN-C = 2-phenylquinoline (Hpq), N-N = phen-TU-Et (**3a**), phen-TU-Ph (**3b**), phen-TU-MeA (**3c**)] have been synthesized and characterized. The photophysical and electrochemical properties of these complexes have been investigated. On the basis of the photophysical and electrochemical data, the nature of the emissive states has been assigned. The thiourea moieties of the complexes allow them to act as receptors for anions; the binding of OAc^-, F^-, and $H_2PO_4^-$ to the complexes has been investigated by emission titrations.

Introduction

Recognition of anions is an interesting area of research because of the important roles of anions in industrial and biological processes and environmental science. Hydrogen-bonding interactions have been commonly used in the development of artificial anion receptors;[1–9] for example, traditional amide-based receptors have been employed as hydrogen-bond donors to bind various anions.[1–5] Recently, the thiourea moiety has attracted much attention because of its specific binding of F^- and oxyanions such as OAc^- and $H_2PO_4^-$.[6–9] It has been attached to various organic chromophores and fluorophores to produce effective anion sensors.[6–8]

The photophysics and photochemistry of luminescent iridium(III) polypyridine complexes have attracted much attention recently.[10–25] This interest originates from the successful use of these complexes as dopants in the fabrication of light-emitting diode devices.[16a,16e] Some luminescent iridium(III) polypyridine complexes have been developed as luminescent sensors for various analytes, including oxygen,[11c] proton,[17a] and alkali and alkaline-earth metal cations.[23d] However, the use of luminescent iridium(III) polypyridine complexes as anion sensors is very limited.[17b] With our recent interest in using luminescent iridium(III) polypyridine complexes as biological labeling reagents and probes,[25] we envisage that incorporation of a thiourea moiety into these complexes can afford a new anion-sensory system. Herein, we report the synthesis, characterization, photophysics, and electrochemistry of a series of new luminescent cyclometalated iridium(III) polypyridine thiourea complexes $[Ir(N\text{-}C)_2(N\text{-}N)](PF_6)$ [HN-C = 2-phenylpyridine (Hppy), N-N = *N*-ethyl-*N′*-1,10-phenanthrolin-5-yl thiourea (phen-TU-Et) (**1a**), *N*-phenyl-*N′*-1,10-phenanthrolin-5-yl thiourea (phen-TU-Ph) (**1b**), *N*-(1-adamantanemethyl)-*N′*-1,10-phenanthrolin-5-yl thiourea (phen-TU-MeA) (**1c**); HN-C = 7,8-benzoquinoline (Hbzq), N-N = phen-TU-Et (**2a**), phen-TU-Ph (**2b**), phen-TU-MeA (**2c**); HN-C = 2-phenylquinoline (Hpq), N-N = phen-TU-Et (**3a**), phen-TU-Ph (**3b**), phen-TU-MeA (**3c**)] (Scheme 1). The emission and electrochemical properties of these complexes have been compared to those of their amine and isothiocyanate counterparts $[Ir(N\text{-}C)_2(N\text{-}N)](PF_6)$ [HN-C = Hppy, N-N = 5-amino-1,10-phenanthroline ($phen\text{-}NH_2$) (**1d**), 5-isothiocyanato-1,10-phenanthroline (phen-ITC) (**1e**); HN-C = Hbzq, N-N = $phen\text{-}NH_2$ (**2d**), phen-ITC (**2e**); HN-C = Hpq, N-N = $phen\text{-}NH_2$ (**3d**), phen-ITC (**3e**)] (Scheme 1).[25a,25c] The binding of anions including OAc^-, F^-, and $H_2PO_4^-$ to the thiourea complexes has been investigated by emission titrations.

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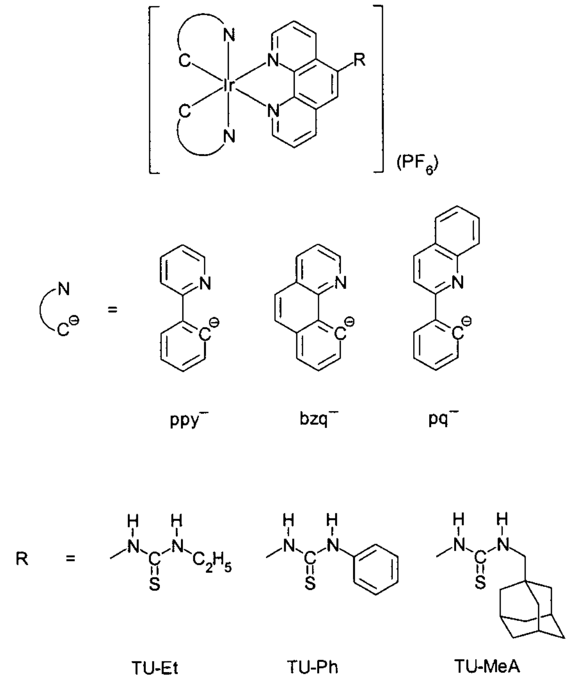

N-C$^-$ = ppy$^-$; R = TU-Et (**1a**), TU-Ph (**1b**), TU-MeA (**1c**), NH$_2$ (**1d**), NCS (**1e**)
N-C$^-$ = bzq$^-$; R = TU-Et (**2a**), TU-Ph (**2b**), TU-MeA (**2c**), NH$_2$ (**2d**), NCS (**2e**)
N-C$^-$ = pq$^-$; R = TU-Et (**3a**), TU-Ph (**3b**), TU-MeA (**3c**), NH$_2$ (**3d**), NCS (**3e**)

Scheme 1. Structures of the iridium(III) polypyridine complexes.

Results and Discussion

Synthesis

The isothiocyanate group of [Ir(N-C)$_2$(phen-ITC)](PF$_6$) reacts readily with primary amines to form thiourea linkages. We have used these luminescent complexes as labeling reagents for amine-containing biological molecules.[25a,25c] All the cyclometalated iridium(III) thiourea complexes in the current work were prepared by the reaction of [Ir(N-C)$_2$-(phen-ITC)](PF$_6$) with the corresponding amines. To investigate the effects of the substituent of the thiourea moiety on the photophysical, electrochemical, and anion-binding properties of the target complexes, we have employed an electron-donating ethyl group and an electron-withdrawing phenyl ring as the substituents. Additionally, a relatively bulky 1-adamantanemethyl unit has also been employed. All the iridium(III) thiourea complexes were characterized by ^{1}H NMR spectroscopy, positive-ion ESI-MS, IR spectroscopy, and gave satisfactory microanalysis.

Electronic Absorption and Emission

The electronic absorption spectroscopic data of the iridium(III) thiourea complexes are listed in Table 1. The electronic absorption spectra of complexes **1a**, **2a**, and **3a** in CH$_2$Cl$_2$ are shown in Figure 1. All the complexes showed intense spin-allowed intra-ligand (^{1}IL) ($\pi\rightarrow\pi^*$) (N-N and N-C$^-$) absorption bands at around 252–348 nm (ε of the order of 10^4 M^{-1} cm^{-1}) and spin-allowed metal-to-ligand charge-transfer (^{1}MLCT) [dπ(Ir)$\rightarrow\pi^*$(N-N and N-C$^-$)] absorption shoulders at around 370–521 nm. Similar to related cyclometalated iridium(III) polypyridine systems,[10–16,17a,17c–17e,18–24] spin-forbidden ^{3}MLCT [dπ(Ir)$\rightarrow\pi^*$(N-N and N-C$^-$)] absorption tailing was also observed in a lower-energy region (ca. 518–550 nm) due to spin-orbital coupling associated with the iridium(III) center. It is noteworthy that the absorption data of the complexes with the same cyclometalating ligand but different substituents on the thiourea moiety (i.e. ethyl, phenyl or 1-adamantanemethyl) are very similar, thus indicating that these substituents do not substantially affect the energy levels of the π^* orbitals of the diimine ligands.

Table 1. Electronic absorption spectroscopic data of the iridium(III) polypyridine thiourea complexes at 298 K.

Complex	Medium	λ_{abs} [nm] (ε [M^{-1} cm^{-1}])
1a	CH$_2$Cl$_2$	255 (71500), 266 sh (65785), 278 sh (49880), 333 sh (16710), 380 sh (9615), 466 sh (1155)
	CH$_3$CN	252 (70060), 266 sh (59590), 279 sh (43780), 332 sh (16520), 375 sh (9100), 465 sh (1205)
1b	CH$_2$Cl$_2$	254 (68330), 266 (66960), 282 sh (50175), 332 sh (18330), 375 sh (11605), 463 sh (1550)
	CH$_3$CN	253 (62645), 266 sh (59160), 284 sh (42560), 332 sh (16390), 375 sh (10140), 463 sh (1405)
1c	CH$_2$Cl$_2$	256 (62640), 268 sh (57860), 332 sh (16890), 370 sh (10950), 464 sh (1855)
	CH$_3$CN	253 (64400), 268 sh (55870), 332 sh (16440), 370 sh (10210), 464 sh (1817)
2a	CH$_2$Cl$_2$	257 (60335), 282 sh (32620), 328 (20330), 405 sh (6355)
	CH$_3$CN	254 (55390), 277 sh (31940), 326 (19420), 408 sh (5500)
2b	CH$_2$Cl$_2$	257 (51405), 284 sh (29295), 330 (17935), 403 sh (5490)
	CH$_3$CN	254 (56525), 280 sh (35375), 323 (21390), 408 sh (5720)
2c	CH$_2$Cl$_2$	256 (72380), 284 sh (37600), 328 (24410), 410 sh (7040)
	CH$_3$CN	253 (74020), 280 sh (39225), 325 (25525), 408 sh (6975)
3a	CH$_2$Cl$_2$	262 sh (58600), 273 (62095), 333 (29025), 348 sh (26165), 433 (6915), 519 sh (655)
	CH$_3$CN	262 sh (62475), 274 (65435), 332 (27140), 346 sh (24660), 427 (6650), 520 sh (685)
3b	CH$_2$Cl$_2$	262 (60590), 284 sh (55450), 333 (26340), 347 sh (23070), 436 (5590), 518 sh (510)
	CH$_3$CN	262 (61690), 280 sh (57675), 331 (26275), 348 sh (22535), 432 (5725), 521 sh (550)
3c	CH$_2$Cl$_2$	263 (69450), 280 sh (63150), 334 (30505), 346 sh (26895), 436 (6700), 520 sh (705)
	CH$_3$CN	262 (68875), 280 sh (61795), 334 (29170), 348 sh (25115), 432 (6430), 520 sh (720)

Upon irradiation, all the iridium(III) thiourea complexes displayed intense and long-lived green to orange luminescence under ambient conditions and in low-temperature alcohol glass. The emission data of these complexes and their amine (**1d**–**3d**) and isothiocyanate (**1e**–**3e**) counterparts are summarized in Table 2. The emission spectra of

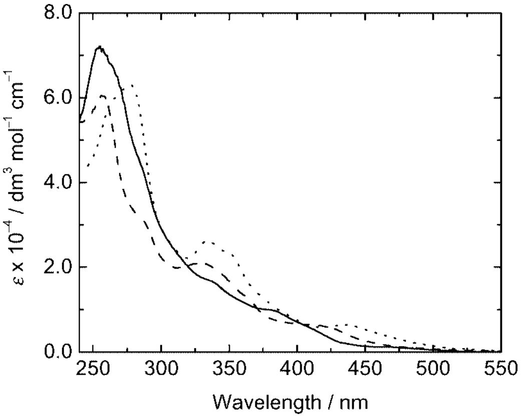

Figure 1. Electronic absorption spectra of complexes **1a** (—) **2a** (---), and **3a** (···) in CH_2Cl_2 at 298 K.

complexes **1a**, **2a**, and **3a** in degassed CH_2Cl_2 at 298 K and in alcohol glass at 77 K are shown in Figures 2, 3, and 4, respectively. The emission of the ppy$^-$ (**1a**–**1c**) and bzq$^-$ (**2a**–**2c**) thiourea complexes occurred at a lower energy with a shorter excited-state lifetime and lower emission quantum yield in more polar CH_3CN than in less polar CH_2Cl_2 (Table 2). These findings suggest that the emissive states bear a high parentage of triplet MLCT [dπ(Ir)→π*(N-N)] character.[10,11b–11f,13a,14a,15,16,17c–17e,19a,20–24,25a,25c,25d,25f] This assignment is supported by the observations that the iridium(III) thiourea complexes emitted at lower energy than complexes **1d** and **2d**, which contain an electron-donating amine group on the diimine ligand, and at higher energy than complexes **1e** and **2e**, which contain an electron-withdrawing isothiocyanate group on the diimine ligand. Interestingly, in fluid solutions at 298 K the emission spectra of all the pq$^-$ complexes **3a**–**3c** showed very similar structural features, with an emission maximum at around 558–563 nm and a shoulder at around 584–588 nm (Table 2 and Figure 4). The independence of the nature of the diimine ligands on the emission behavior is further reflected by the fact that the phen-NH_2 complex **3d** and the phen-ITC complex **3e** also exhibited very similar emission energies (Table 2). The excited-state lifetimes of the pq$^-$ thiourea complexes varied from around 3.11 to 1.27 μs and are much longer than those of their ppy$^-$ and bzq$^-$ counterparts. On the basis of these observations, we propose that the emissive states of these pq$^-$ complexes are essentially triplet IL (π→π*) (pq$^-$) in nature, perhaps with mixing of some ^{3}MLCT [dπ(Ir)→π*(pq$^-$)] character. Similar ^{3}IL emission has been observed for related iridium(III) pq$^-$ systems.[25c,25d]

Upon cooling to 77 K, the emission bands of the ppy$^-$ (**1a**–**1c**) and bzq$^-$ (**2a**–**2c**) thiourea complexes showed large hypsochromic shifts (Table 2, Figure 2 and Figure 3), which is a typical feature of common iridium(III) ^{3}MLCT emitters.[10a,10c,11b,11c,11e,11f,13a,14b,15,16b–16e,17c,19a,20a,21,22,25a,25c,25d,25f] Bi-exponential emission decays were observed; the longer- and shorter-lived counterparts are ascribed to ^{3}MLCT excited states involving the cyclometalating and di-

Table 2. Photophysical data of the iridium(III) polypyridine complexes.

Complex	Medium (T [K])	λ_{em} [nm]	τ_o [μs]	Φ
1a	CH_2Cl_2 (298)	584	0.81	0.32
	CH_3CN (298)	587	0.34	0.12
	glass[a] (77)	516, 540 sh	49.93 (9%), 5.73 (91%)	
1b	CH_2Cl_2 (298)	577	0.97	0.13
	CH_3CN (298)	588	0.47	0.068
	glass[a] (77)	531	49.54 (9%), 5.48 (91%)	
1c	CH_2Cl_2 (298)	585	0.98	0.11
	CH_3CN (298)	593	0.43	0.032
	glass[a] (77)	522, 553 sh	49.38 (10%), 5.50 (90%)	
1d[b]	CH_2Cl_2 (298)	564	9.52	0.43
	CH_3CN (298)	568	11.38	0.079
	glass[a] (77)	560 (max), 602, 658 sh	286.21	
1e[b]	CH_2Cl_2 (298)	598	0.77	0.29
	CH_3CN (298)	608	0.41	0.079
	glass[a] (77)	512 (max), 552, 594 sh	93.52 (32%), 14.58 (68%)	
2a	CH_2Cl_2 (298)	581	1.13	0.20
	CH_3CN (298)	590	0.45	0.039
	glass[a] (77)	520 (max), 539, 574 sh	48.04 (21%), 4.82 (79%)	
2b	CH_2Cl_2 (298)	580	1.11	0.15
	CH_3CN (298)	588	0.56	0.041
	glass[a] (77)	505, 540 (max), 575 sh	47.79 (28%), 4.78 (72%)	
2c	CH_2Cl_2 (298)	587	0.87	0.13
	CH_3CN (298)	593	0.37	0.040
	glass[a] (77)	508 sh, 520 (max), 539	47.64 (30%), 5.30 (70%)	
2d[b]	CH_2Cl_2 (298)	568	6.65	0.26
	CH_3CN (298)	567	25.02	0.015
	glass[a] (77)	506 sh, 562 (max), 606, 666 sh	260.30	
2e[b]	CH_2Cl_2 (298)	597	0.67	0.12
	CH_3CN (298)	607	0.32	0.046
	glass[a] (77)	511 (max), 553, 600 sh	51.83 (23%), 4.48 (77%)	
3a	CH_2Cl_2 (298)	558, 587 sh	3.11	0.44
	CH_3CN (298)	561, 584 sh	2.58	0.11
	glass[a] (77)	545 (max), 587, 640 sh	6.10	
3b	CH_2Cl_2 (298)	558, 584 sh	2.64	0.44
	CH_3CN (298)	563, 588 sh	2.31	0.21
	glass[a] (77)	544 (max), 587, 631 sh	6.65	
3c	CH_2Cl_2 (298)	562, 587 sh	2.06	0.28
	CH_3CN (298)	562, 587 sh	1.27	0.22
	glass[a] (77)	545 (max), 587, 632 sh	6.07	
3d[b]	CH_2Cl_2 (298)	555, 599 sh	4.07	0.36
	CH_3CN (298)	559, 599 sh	5.99	0.17
	glass[a] (77)	540 sh, 570, 615 sh, 681 sh	389.15	
3e[b]	CH_2Cl_2 (298)	560, 599 sh	1.50	0.25
	CH_3CN (298)	559, 599 sh	1.13	0.17
	glass[a] (77)	540 (max), 582, 626 sh	4.96	

[a] EtOH/MeOH (4:1, v/v). [b] From ref.[25c]

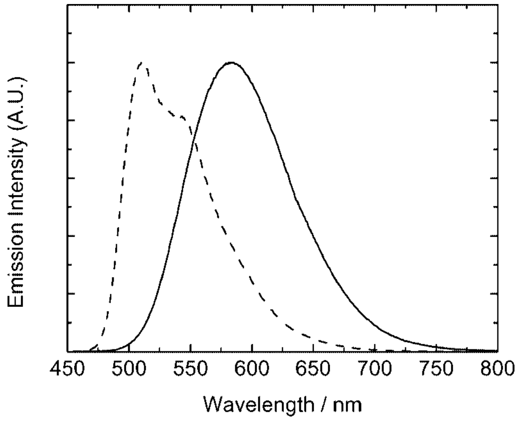

Figure 2. Emission spectra of complex **1a** in CH_2Cl_2 at 298 K (—) and in EtOH/MeOH (4:1, v/v) at 77 K (---).

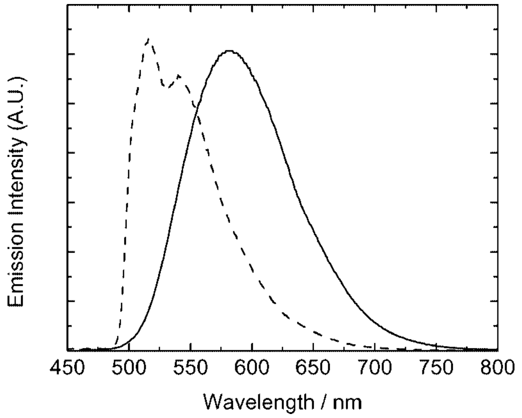

Figure 3. Emission spectra of complex **2a** in CH_2Cl_2 at 298 K (—) and in EtOH/MeOH (4:1, v/v) at 77 K (---).

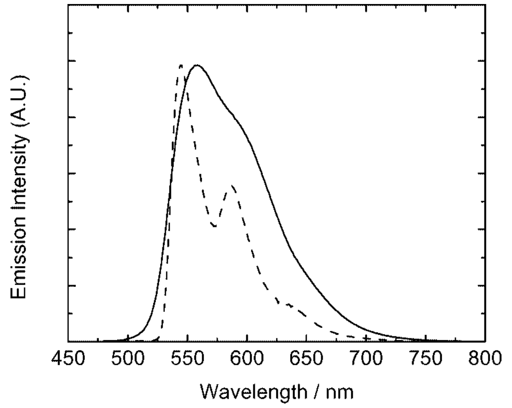

Figure 4. Emission spectra of complex **3a** in CH_2Cl_2 at 298 K (—) and in EtOH/MeOH (4:1, v/v) at 77 K (---).

imine ligands, respectively.[10,13a] On the contrary, the emission bands of the pq$^-$ thiourea complexes **3a**–**3c** only showed small blue shifts upon cooling to 77 K (Table 2 and Figure 4). The complexes displayed very similar and vibronically structured emission spectra with an excited-state lifetime of about 6 μs in alcohol glass at 77 K. It is conceivable that the nature of the emissive states is essentially ^{3}IL ($\pi \rightarrow \pi^*$) (pq$^-$), probably mixed with some ^{3}MLCT [dπ(Ir)$\rightarrow\pi^*$(pq$^-$)] character.

It is important to note that the emission properties of these cyclometalated iridium(III) polypyridine complexes are sensitive to the substituents on the diimine ligands. In most cases, the emission energies of the complexes follow the order: phen-NH_2 > phen-thiourea > phen-ITC, which is indicative of the involvement of ^{3}MLCT [dπ(Ir)$\rightarrow\pi^*$(N-N)] character in the emissive states. On the contrary, variation of the substituent of the thiourea moiety does not result in any substantial difference of the emission properties of the thiourea complexes (Table 2). It appears that the thiourea bridge does not facilitate electronic communication and its substituent cannot profoundly perturb the electronic structures of the diimine ligand and the iridium(III) complex.

Electrochemistry

The electrochemical properties of the iridium(III) thiourea complexes have been studied by cyclic voltammetry. The electrochemical data of these complexes and the phen-NH_2 and phen-ITC analogs are listed in Table 3. All the iridium(III) thiourea complexes showed an irreversible wave at about +1.08 to +1.19 V vs. SCE, which is assigned to the oxidation of the thiourea groups because similar waves are absent in the cyclic voltammograms of the phen-NH_2 and phen-ITC complexes (Table 3). An additional quasi-reversible oxidation couple appeared at about +1.21 to +1.31 V, attributable to the metal-centered $Ir^{IV/III}$ oxidation.[10a,10c,11–13,14a,15b,15c,19a,19b,23a,24b,24c,25] The lower reversibility of these couples compared to that of typical iridium(III) polypyridine complexes could be a result of the irreversible thiourea-based oxidation that occurred at lower potentials. The iridium(III) thiourea complexes exhibited the first reduction waves at about –1.32 to –1.37 V vs. SCE. These waves are assigned to the reduction of the diimine ligands. This assignment agrees with the find-

Table 3. Electrochemical data of the iridium(III) polypyridine complexes in CH_3CN (0.1 M TBAP) at 298 K (glassy-carbon working electrode; sweep rate: 100 $mV\,s^{-1}$; all potentials vs. SCE).

Complex	Oxidation, $E_{1/2}$ or E_a [V]	Reduction, $E_{1/2}$ or E_c [V]
1a	+1.12,[a] +1.27[b]	–1.36,[a] –1.61,[b] –2.30[a]
1b	+1.19,[a] +1.27[b]	–1.34,[a] –1.57,[b] –2.28[a]
1c	+1.12,[a] +1.26[b]	–1.36,[a] –1.61,[b] –2.45[a]
1d[c]	+1.27[a]	–1.45,[a] –2.24,[b] –2.53[a]
1e[c]	+1.27	–1.21,[a] –1.48, –1.98,[a] –2.43[a]
2a	+1.08,[a] +1.21[b]	–1.36,[a] –2.10,[b] –2.34[a]
2b	+1.13,[a] +1.21[b]	–1.36,[a] –1.61,[b] –2.08,[a] –2.32[a]
2c	+1.09,[a] +1.21[b]	–1.34,[a] –1.63,[b] –2.08,[a] –2.32[a]
2d[c]	+1.13[b]	–1.42,[b] –1.69,[b] –2.00,[a] –2.29[a]
2e[c]	+1.15	–1.20,[a] –1.47,[a] –2.08,[a] –2.37[a]
3a	+1.13,[a] +1.31[b]	–1.37,[a] –1.90,[a] –2.27[a]
3b	+1.14,[a] +1.30[b]	–1.37,[a] –1.56,[b] –1.90,[a] –2.04,[a] –2.24[a]
3c	+1.12,[a] +1.27[b]	–1.32,[a] –1.58,[b] –1.88,[a] –2.04,[a] –2.27[a]
3d[c]	+1.25[a]	–1.45, –1.75,[b] –1.99,[b] –2.35[b]
3e[c]	+1.28	–1.20,[a] –1.45,[b] –1.87,[b] –2.56[a]

[a] Irreversible waves. [b] Quasi-reversible couples. [c] From ref.[25c]

ings that the potentials of these waves are less negative than those of the phen-NH_2 (ca. –1.42 to –1.45 V) and more negative than the phen-ITC analogs (ca. –1.20 to –1.21 V) due to the electron-donating and -withdrawing properties of the amine and isothiocyanate groups, respectively. Whilst most diimine-based reductions of cyclometalated iridium(III) polypyridine complexes are reversible in nature (see references cited above), the irreversibility of these waves suggests the possible involvement of thiourea in the reduction process. Again, variation of the substituent of the thiourea moiety does not cause much difference in the reduction potentials of these complexes (Table 3), thus confirming that the π* orbitals of the diimine ligand are not strongly affected by the substituents on the other side of the thiourea linkage. Other irreversible and distorted waves appeared at lower potentials; these are assigned to reduction of the cyclometalating ligands.

Anion-Binding Properties

Since the OAc^-, F^-, and $H_2PO_4^-$ ions are well known to bind to thiourea,[6–9] we have studied their binding to the iridium(III) thiourea complexes. The absorption spectra of the complexes did not exhibit any changes in the presence of these three ions. It is therefore likely that the binding does not significantly alter the π* energy levels of the diimine ligands and hence the energies of the ^{1}IL and ^{1}MLCT transitions. Emission titrations have been performed to study the anion-binding properties of the complexes. As an example, the luminescence spectral traces for complex **3c** in CH_3CN upon addition of OAc^-, F^-, and $H_2PO_4^-$ ions are illustrated in Figures 5(a), 6(a), and 7(a), respectively. The emission intensities of all the iridium(III) thiourea complexes in the current work were reduced in the presence of these three anions. These findings are attributed to binding of the anions to the thiourea moieties because no changes were observed for the control complexes [Ir(N-C)$_2$(phen)](PF$_6$) (N-C$^-$ = ppy$^-$, bzq$^-$, pq$^-$).[26] It is worth mentioning that the emission energies of the thiourea complexes were not altered upon the binding events, thereby suggesting that the uptake of the anions by the thiourea moieties did not increase the π* levels of the diimine ligands. To a certain extent, this is in agreement with the independence of the emission properties of the complexes on the substituents of the thiourea moieties (see above). We tentatively ascribe the observed emission quenching to a more efficient nonradiative deactivation pathway. Similar anion-induced emission quenching has also been observed in the luminescent rhenium(I) polypyridine thiourea complexes that we reported previously.[9]

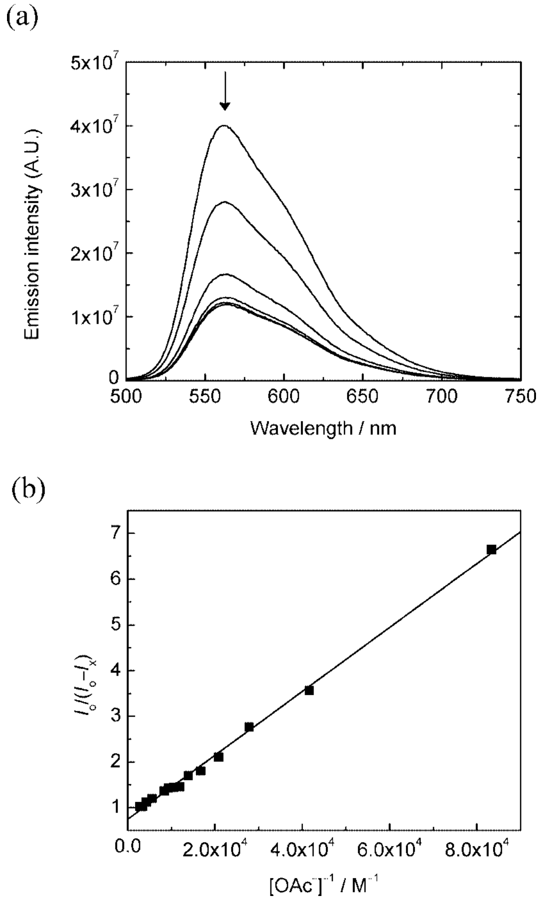

Figure 5. (a) Luminescence spectral traces of complex **3c** (120 μM) in CH_3CN (0.1 M TBAP) upon addition of OAc^- at 298 K. The concentrations of OAc^- were 0, 24, 48, 72, 96, and 120 μM, respectively. (b) A plot of $I_o/(I_o - I_x)$ vs. $[OAc^-]^{-1}$ (■) and the theoretical fit on the basis of a 1:1 binding stoichiometry (—).

Treatment of the emission titration data of all the iridium(III) thiourea complexes and the three anions using a 1:1 binding model gave satisfactory fits.[27] Plots of $I_o/(I_o - I_x)$ vs. $[A^-]^{-1}$ (A^- = OAc^-, F^-, $H_2PO_4^-$) for complex **3c** and the corresponding theoretical fits are shown in Figures 5(b), 6(b), and 7(b), respectively. The $\log K_s$ values for the binding of all the iridium(III) thiourea complexes and the three anions in CH_3CN have been determined from the fitting (Table 4). The $\log K_s$ values for the binding of OAc^- range from 4.03 to 4.35 and are larger than those for F^- (from 3.13 to 3.73) and $H_2PO_4^-$ (from 3.12 to 3.68). Importantly, variation of the cyclometalating ligands and the substituents of the thiourea moieties did not lead to any noticeable difference in the anion-binding properties of the complexes. The minor role of the cyclometalating ligands on the anion-binding behavior is reasonable. However, the use of various thiourea substituents of different electronic and structural properties was expected to affect the anion-binding affinities of the complexes. Our experimental results indicate, however, that these effects are minimal. A possible reason is that these thiourea substituents can only control the electronic density of one of the two NH groups of the thiourea moiety, and that the bulky adamantane unit does not hamper the binding properties owing to the flexible methylene linkage. Overall, the iridium(III) thiourea complexes revealed a stronger affinity for OAc^- than for the F^- and $H_2PO_4^-$ ions (Table 4). A similar trend has been observed for a related naphthalimide-thiourea conjugate [$\log K_s$ = 4.47 (OAc^-), 3.80 (F^-), 3.48 ($H_2PO_4^-$) in DMSO][8f] and a

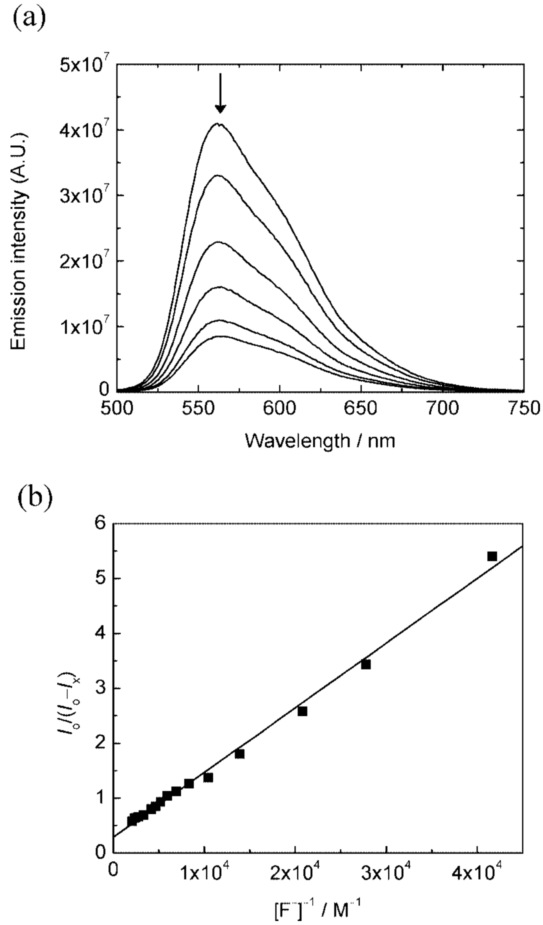

Figure 6. (a) Luminescence spectral traces of complex **3c** (120 μM) in CH_3CN (0.1 M TBAP) upon addition of F^- at 298 K. The concentrations of F^- were 0, 24, 48, 72, 96, and 120 μM, respectively. (b) A plot of $I_o/(I_o - I_x)$ vs. $[F^-]^{-1}$ (■) and the theoretical fit on the basis of a 1:1 binding stoichiometry (—).

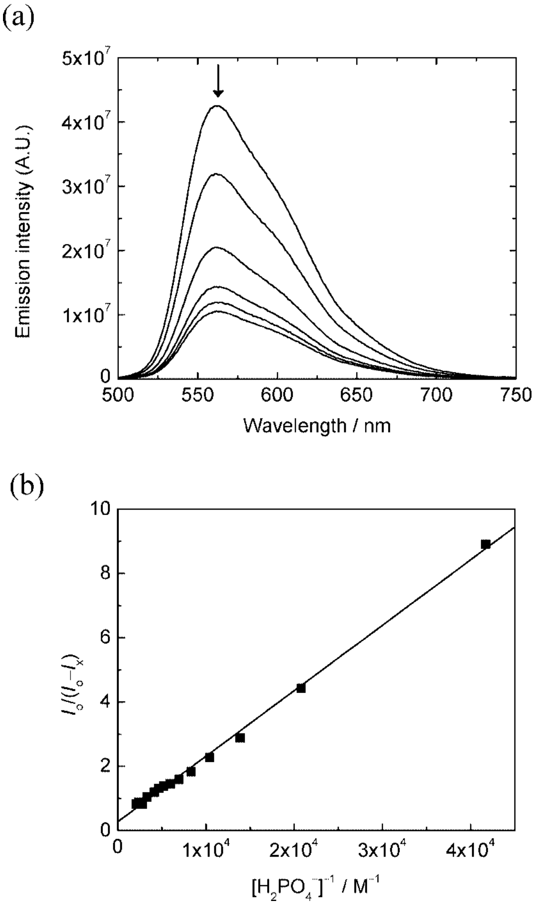

Figure 7. (a) Luminescence spectral traces of complex **3c** (120 μM) in CH_3CN (0.1 M TBAP) upon addition of $H_2PO_4^-$ at 298 K. The concentrations of $H_2PO_4^-$ were 0, 24, 48, 72, 96, and 120 μM, respectively. (b) A plot of $I_o/(I_o - I_x)$ vs. $[H_2PO_4^-]^{-1}$ (■) and the theoretical fit on the basis of a 1:1 binding stoichiometry (—).

rhenium(I) polypyridine anthraquinone thiourea complex [$\log K_s$ = 4.61 (OAc^-), 3.66 (F^-), 3.70 ($H_2PO_4^-$) in CH_3CN].[9] It is likely that this preferential binding of OAc^- ion is associated with the basicity of the anions [pK_a = 4.75 (HOAc), 3.45 (HF), 2.12 (H_3PO_4) in aqueous solution at 298 K].[28] The binding affinities of the iridium(III) thiourea complexes to F^- and $H_2PO_4^-$ are very similar. The geometry of the anions appears to contribute strongly to the stabilities of the receptor–anion adducts,[29] with the trigonal OAc^- and tetrahedral $H_2PO_4^-$ ions fitting the trigonal planar shape of the thiourea unit better than the spherical F^- ion. Thus, it is likely that the binding affinities of the iridium(III) thiourea complexes to OAc^-, F^-, and $H_2PO_4^-$ are a combined effect of the basicity and molecular geometry of the guest ions.

Table 4. $\log K_s$ values for the binding of anions by the iridium(III) polypyridine thiourea complexes in CH_3CN (0.1 M TBAP) at 298 K.

Complex	OAc^-	F^-	$H_2PO_4^-$
1a	4.02	3.13	3.34
1b	4.35	3.12	3.46
1c	4.03	3.16	3.16
2a	4.17	3.14	3.45
2b	4.19	3.73	3.68
2c	4.16	3.24	3.26
3a	4.03	3.18	3.13
3b	4.10	3.23	3.12
3c	4.03	3.38	3.14

Conclusions

This paper describes the synthesis, characterization, photophysics, electrochemistry, and anion-binding properties of a series of new luminescent cyclometalated iridium(III) polypyridine thiourea complexes. The emission intensities of all the complexes were reduced upon addition of anions OAc^-, F^-, and $H_2PO_4^-$. The binding stoichiometries were determined to be 1:1 in all cases, and the $\log K_s$ values ranged from 3.12 to 4.35. The binding affinity of the iridium(III) thiourea complexes for OAc^- was higher than those for F^- and $H_2PO_4^-$, which is a combined effect of the basicity and molecular geometry of the anions. Interestingly, the substituents of the thiourea moieties did not affect the photophysical, electrochemical, and anion-binding properties of the complexes, probably due to insufficient communication between these substituents and the diimine ligand. Nevertheless, these thiourea complexes are the first systematic design of specific anion receptors derived from luminescent cyclometalated iridium(III) polypyridine complexes. The development of related luminescent transition metal complexes as anion receptors is in progress.

Experimental Section

Materials and Reagents: All solvents were of analytical grade and were purified according to published procedures.[30] Ethylamine (2 M in THF) (International Laboratory), aniline (Aldrich), 1-adamantanemethylamine (International Laboratory), tetra-*n*-butylammonium acetate (TBAOAc; Aldrich), tetra-*n*-butylammonium fluoride (TBAF; Acros), and tetra-*n*-butylammonium dihydrogen phosphate (TBAH$_2$PO$_4$; Aldrich) were used without purification. Tetra-*n*-butylammonium hexafluorophosphate (TBAP; Aldrich) was recrystallized from hot ethanol twice and dried in vacuo at 110 °C before use.

Synthesis: A mixture of [Ir(N-C)$_2$(phen-ITC)](PF$_6$) (HN-C = Hppy, Hbzq, Hpq; 0.12 mmol)[25c] and the corresponding amine (ethylamine, aniline, 1-adamantanemethylamine; 0.12 mmol) in acetone (30 mL) was stirred at room temperature under an inert atmosphere of nitrogen in the dark for 12 h. Recrystallization of the products from a mixture of acetone and diethyl ether gave air-stable orange-yellow crystals.

[Ir(ppy)$_2$(phen-TU-Et)](PF$_6$) (1a): Yield: 93 mg (84%). ^{1}H NMR (300 MHz, [D$_6$]acetone, 298 K, relative to TMS): δ = 9.37 (s, 1 H, phen-N*H*), 8.86 (t, J = 8.4 Hz, 2 H, 6-H of pyridyl ring of ppy$^-$), 8.47 (s, 1 H, 6-H of phen), 8.45 (dd, J = 5.0 and 1.2 Hz, 1 H, 2-H of phen), 8.38 (dd, J = 5.0 and 1.5 Hz, 1 H, 9-H of phen), 8.25 (d, J = 8.2 Hz, 2 H, 3-H of pyridyl ring of ppy$^-$), 8.10–8.02 (m, 2 H, 3-H and 8-H of phen), 7.96–7.89 (m, 4 H, 4-H of pyridyl ring and 3-H of phenyl ring of ppy$^-$), 7.81 (t, J = 4.9 Hz, 1 H, Et-N*H*), 7.72 (d, J = 5.0 Hz, 1 H, 7-H of phen), 7.65 (d, J = 5.9 Hz, 1 H, 4-H of phen), 7.11–6.94 (m, 6 H, 5-H of pyridyl ring and 4-H and 5-H of phenyl ring of ppy$^-$), 6.45 (d, J = 7.6 Hz, 2 H, 6-H of phenyl ring of ppy$^-$), 3.72–3.63 (m, 2 H, C*H*$_2$CH$_3$), 1.21 ppm (t, J = 6.2 Hz, 3 H, CH$_2$C*H*$_3$). IR (KBr): $\tilde{\nu}$ = 3367 (m, N–H), 1269 (m, C=S), 844 (s, PF$_6^-$) cm^{-1}. Positive-ion ESI-MS: ion cluster at *m*/*z* 783 [*M*]$^+$. $C_{37}H_{30}F_6IrN_6PS\cdot 0.5H_2O$ (936.94): calcd. C 47.43, H 3.33, N 8.97; found C 47.43, H 3.27, N 8.98.

[Ir(ppy)$_2$(phen-TU-Ph)](PF$_6$) (1b): Yield: 88 mg (75%). ^{1}H NMR (300 MHz, [D$_6$]acetone, 298 K, relative to TMS): δ = 10.43 (s, 1 H, phen-N*H*), 10.31 (s, 1 H, Ph-N*H*), 9.11 (d, J = 8.2 Hz, 1 H, 6-H of pyridyl ring of ppy$^-$), 8.81 (d, J = 8.5 Hz, 1 H, 6-H of pyridyl ring of ppy$^-$), 8.55 (s, 1 H, 6-H of phen), 8.42 (d, J = 5.0 Hz, 1 H, 2-H of phen), 8.37 (d, J = 5.0 Hz, 1 H, 9-H of phen), 8.24 (d, J = 8.2 Hz, 2 H, 3-H of pyridyl ring of ppy$^-$), 8.06–7.99 (m, 2 H, 3-H and 8-H of phen), 7.95–7.88 (m, 4 H, 4-H of pyridyl ring and 3-H of phenyl ring of ppy$^-$), 7.73–7.67 (m, 4 H, 4-H and 7-H of phen and 2-H and 6-H of Ph), 7.38 (t, J = 7.6 Hz, 2 H, 3-H and 5-H of Ph), 7.20 (t, J = 7.0 Hz, 1 H, 4-H of Ph), 7.10–6.94 (m, 6 H, 5-H of pyridyl ring and 4-H and 5-H of phenyl ring of ppy$^-$), 6.45 ppm (d, J = 6.7 Hz, 2 H, 6-H of phenyl ring of ppy$^-$). IR (KBr): $\tilde{\nu}$ = 3374 (m, N–H), 1268 (m, C=S), 844 (s, PF$_6^-$) cm^{-1}. Positive-ion ESI-MS: ion cluster at *m*/*z* 829 [*M*]$^+$. $C_{41}H_{30}F_6IrN_6PS\cdot H_2O$ (994.00): calcd. C 49.54, H 3.24, N 8.45; found C 49.78, H 3.49, N 8.25.

[Ir(ppy)$_2$(phen-TU-MeA)](PF$_6$) (1c): Yield: 89 mg (77%). ^{1}H NMR (300 MHz, [D$_6$]acetone, 298 K, relative to TMS): δ = 9.44 (s, 1 H, phen-N*H*), 8.86 (dd, J = 8.8 and 5.6 Hz, 2 H, 6-H of pyridyl ring of ppy$^-$), 8.52 (s, 1 H, 6-H of phen), 8.45 (d, J = 4.4 Hz, 1 H, 2-H of phen), 8.38 (d, J = 4.4 Hz, 1 H, 9-H of phen), 8.25 (d, J = 8.2 Hz, 2 H, 3-H of pyridyl ring of ppy$^-$), 8.10–8.01 (m, 2 H, 3-H and 8-H of phen), 7.99–7.89 (m, 4 H, 4-H of pyridyl ring and 3-H of phenyl ring of ppy$^-$), 7.73–7.63 (m, 3 H, 4-H and 7-H of phen and CH$_2$-N*H*), 7.11–6.95 (m, 6 H, 5-H of pyridyl ring and 4-H and 5-H of phenyl ring of ppy$^-$), 6.45 (d, J = 7.3 Hz, 2 H, 6-H of phenyl ring of ppy$^-$), 2.83 (s, 2 H, C*H*$_2$NH), 1.97 (s, 3 H, CH of adamantane), 1.76–1.61 ppm (m, 12 H, CH$_2$ of adamantane). IR (KBr): $\tilde{\nu}$ = 3387 (m, N–H), 1266 (m, C=S), 844 (s, PF$_6^-$) cm^{-1}. Positive-ion ESI-MS: ion cluster at *m*/*z* 903 [*M*]$^+$. $C_{46}H_{42}F_6IrN_6PS$ (1048.1): calcd. C 52.71, H 4.04, N 8.02; found C 52.58, H 3.98, N 8.25.

[Ir(bzq)$_2$(phen-TU-Et)](PF$_6$) (2a): Yield: 75 mg (64%). ^{1}H NMR (300 MHz, [D$_6$]acetone, 298 K, relative to TMS): δ = 10.66 (s, 1 H, phen-N*H*), 9.19 (d, J = 5.9 Hz, 1 H, 2-H of phen), 8.95 (s, 1 H, Et-N*H*), 8.71 (d, J = 7.6 Hz, 2 H, 6-H and 9-H of phen), 8.50 (d, J = 6.7 Hz, 2 H, 4-H of bzq$^-$), 8.39 (d, J = 5.3 Hz, 1 H, 4-H of phen), 8.29 (d, J = 4.4 Hz, 1 H, 7-H of phen), 8.16 (d, J = 4.1 Hz, 2 H, 2-H of bzq$^-$), 8.00 (d, J = 8.8 Hz, 2 H, 6-H of bzq$^-$), 7.92–7.86 (m, 4 H, 5-H of bzq$^-$ and 3-H and 8-H of phen), 7.59 (d, J = 7.9 Hz, 2 H, 7-H of bzq$^-$), 7.46 (t, J = 5.3 Hz, 2 H, 3-H of bzq$^-$), 7.23 (t, J = 7.3 Hz, 2 H, 8-H of bzq$^-$), 6.47 (d, J = 6.5 Hz, 2 H, 9-H of bzq$^-$), 3.65–3.63 (m, 2 H, C*H*$_2$CH$_3$), 1.29–1.20 ppm (m, 3 H, CH$_2$C*H*$_3$). IR (KBr): $\tilde{\nu}$ = 3365 (m, N–H), 1266 (m, C=S), 847 (s, PF$_6^-$) cm^{-1}. Positive-ion ESI-MS: ion cluster at *m*/*z* 831 [*M*]$^+$. $C_{41}H_{30}F_6IrN_6PS\cdot H_2O$ (994.00): calcd. C 49.54, H 3.24, N 8.45; found C 49.44, H 3.24, N 8.17.

[Ir(bzq)$_2$(phen-TU-Ph)](PF$_6$) (2b): Yield: 86 mg (70%). ^{1}H NMR (300 MHz, [D$_6$]acetone, 298 K, relative to TMS): δ = 9.88 (s, 1 H, phen-N*H*), 9.77 (s, 1 H, Ph-N*H*), 8.99 (d, J = 7.6 Hz, 1 H, 2-H of phen), 8.83 (d, J = 7.9 Hz, 1 H, 9-H of phen), 8.52 (d, J = 7.3 Hz, 2 H, 4-H of bzq$^-$), 8.47 (s, 1 H, 6-H of phen), 8.43 (d, J = 5.0 Hz, 1 H, 4-H of phen), 8.37 (d, J = 4.1 Hz, 1 H, 7-H of phen), 8.19 (d, J = 4.4 Hz, 1 H, 2-H of bzq$^-$), 8.11 (d, J = 5.6 Hz, 1 H, 2-H of bzq$^-$), 8.03–7.86 (m, 7 H, 2-H, 3-H and 8-H of phen and 5-H and 6-H of bzq$^-$), 7.66–7.59 (m, 4 H, 2-H and 6-H of Ph and 7-H of bzq$^-$), 7.50–7.38 (m, 4 H, 3-H and 5-H of Ph and 3-H of bzq$^-$), 7.24 (t, J = 7.6 Hz, 3 H, 4-H of Ph and 8-H of bzq$^-$), 6.48 ppm (d, J = 7.3 Hz, 2 H, 9-H of bzq$^-$). IR (KBr): $\tilde{\nu}$ = 3395 (m, N–H), 1262 (m, C=S), 847 (s, PF$_6^-$) cm^{-1}. Positive-ion ESI-MS: ion cluster at *m*/*z* 879 [*M*]$^+$. $C_{45}H_{30}F_6IrN_6PS\cdot 0.5H_2O$ (1033.0): calcd. C 52.32, H 3.02, N 8.14; found C 52.19, H 3.28, N 8.08.

[Ir(bzq)$_2$(phen-TU-MeA)](PF$_6$) (2c): Yield: 95 mg (72%). ^{1}H NMR (300 MHz, [D$_6$]acetone, 298 K, relative to TMS): δ = 10.80 (s, 1 H, phen-N*H*), 9.24 (d, J = 6.7 Hz, 1 H, 2-H of phen), 8.83 (s, 1 H, CH$_2$-N*H*), 8.77 (s, 1 H, 6-H of phen), 8.69 (d, J = 6.5 Hz, 1 H, 9-H of phen), 8.51 (dd, J = 3.5 and 7.3 Hz, 2 H, 4-H of bzq$^-$), 8.40 (d, J = 3.8 Hz, 1 H, 4-H of phen), 8.30 (d, J = 5.0 Hz, 1 H, 7-H of phen), 8.16 (t, J = 4.5 Hz, 2 H, 2-H of bzq$^-$), 8.01 (dd, J = 7.0 and 1.8 Hz, 2 H, 6-H of bzq$^-$), 7.94–7.86 (m, 4 H, 3-H and 8-H of phen and 5-H of bzq$^-$), 7.60 (d, J = 7.6 Hz, 2 H, 7-H of bzq$^-$), 7.46 (dd, J = 5.0 and 2.6 Hz, 2 H, 3-H of bzq$^-$), 7.24 (t, J = 7.6 Hz, 2 H, 8-H of bzq$^-$), 6.48 (d, J = 7.3 Hz, 2 H, 9-H of bzq$^-$), 2.83 (s, 2

H, C*H₂*NH), 1.97 (s, 3 H, CH of adamantane), 1.68–1.67 ppm (m, 12 H, CH_2 of adamantane). IR (KBr): ṽ = 3439 (m, N–H), 1266 (m, C=S), 847 (s, PF_6^-) cm^{-1}. Positive-ion ESI-MS: ion cluster at *m*/*z* 950 [*M*]$^+$. $C_{50}H_{42}F_6IrN_6PS$ (1096.2): calcd. C 54.79, H 3.86, N 7.67; found C 54.99, H 3.99, N 7.92.

[Ir(pq)$_2$(phen-TU-Et)](PF$_6$) (3a): Yield: 86 mg (70%). ^{1}H NMR (300 MHz, [D$_6$]acetone, 298 K, relative to TMS): δ = 9.24 (s, 1 H, phen-N*H*), 9.03 (d, *J* = 7.8 Hz, 1 H, 2-H of phen), 8.75–8.65 (m, 3 H, 3-H, 8-H and 9-H of phen), 8.58–8.46 (m, 5 H, 4-H, 6-H and 7-H of phen and 3-H of quinolinyl ring of pq$^-$), 8.31 (d, *J* = 7.6 Hz, 1 H, 5-H of quinolinyl ring of pq$^-$), 8.15–7.96 (m, 2 H, 4-H of quinolinyl ring of pq$^-$), 7.89 (s, 1 H, Et-N*H*), 7.81 (d, *J* = 6.7 Hz, 2 H, 8-H of quinolinyl ring of pq$^-$), 7.41–7.21 (m, 6 H, 6-H and 7-H of quinolinyl ring and 3-H of phenyl ring of pq$^-$), 6.95–6.86 (m, 4 H, 4-H and 5-H of phenyl ring of pq$^-$), 6.68 (d, *J* = 7.9 Hz, 2 H, 6-H of phenyl ring of pq$^-$), 3.62–3.58 (m, 2 H, CH_2CH_3), 1.32 ppm (t, *J* = 7.2 Hz, 3 H, CH_2CH_3). IR (KBr): ṽ = 3387 (m, N–H), 1288 (m, C=S), 846 (s, PF_6^-) cm^{-1}. Positive-ion ESI-MS: ion cluster at *m*/*z* 882 [*M*]$^+$. $C_{45}H_{34}F_6IrN_6PS\cdot H_2O$ (1046.1): calcd. C 51.67, H 3.47, N 8.03; found C 51.58, H 3.27, N 8.24.

[Ir(pq)$_2$(phen-TU-Ph)](PF$_6$) (3b): Yield: 96 mg (74%). ^{1}H NMR (300 MHz, [D$_6$]acetone, 298 K, relative to TMS): δ = 10.35 (s, 1 H, phen-N*H*), 10.06 (s, 1 H, Ph-N*H*), 8.95 (d, *J* = 8.5 Hz, 1 H, 2-H of phen), 8.72–8.63 (m, 3 H, 3-H, 8-H and 9-H of phen), 8.58–8.46 (m, 4 H, 4-H and 7-H of phen and 3-H of quinolinyl ring of pq$^-$), 8.31 (dd, *J* = 7.8 and 3.2 Hz, 2 H, 5-H of quinolinyl ring of pq$^-$), 8.22 (s, 1 H, 6-H of phen), 8.06–7.99 (m, 2 H, 4-H of quinolinyl ring of pq$^-$), 7.80 (t, *J* = 6.9 Hz, 2 H, 2-H and 6-H of Ph), 7.65 (d, *J* = 8.8 Hz, 2 H, 8-H of quinolinyl ring of pq$^-$), 7.41–7.13 (m, 9 H, 3-H, 4-H and 5-H of Ph and 6-H and 7-H of quinolinyl ring and 3-H of phenyl ring of pq$^-$), 6.94–6.84 (m, 4 H, 4-H and 5-H of phenyl ring of pq$^-$), 6.69 ppm (d, *J* = 7.6 Hz, 2 H, 6-H of phenyl ring of pq$^-$). IR (KBr): ṽ = 3351 (m, N–H), 1288 (m, C=S), 845 (s, PF_6^-) cm^{-1}. Positive-ion ESI-MS: ion cluster at *m*/*z* 931 [*M*]$^+$. $C_{49}H_{34}F_6IrN_6PS\cdot 1.5\,H_2O$ (1103.12): calcd. C 53.35, H 3.38, N 7.62; found C 53.25, H 3.44, N 7.78.

[Ir(pq)$_2$(phen-TU-MeA)](PF$_6$) (3c): Yield: 106 mg (77%). ^{1}H NMR (300 MHz, [D$_6$]acetone, 298 K, relative to TMS): δ = 10.87 (s, 1 H, phen-N*H*), 9.20 (d, *J* = 8.2 Hz, 1 H, 2-H of phen), 9.00 (s, 1 H, CH_2-N*H*), 8.68 (d, *J* = 4.4 Hz, 1 H, 9-H of phen), 8.60–8.53 (m, 5 H, 3-H, 6-H and 8-H of phen and 3-H of quinolinyl ring of pq$^-$), 8.48–8.44 (m, 2 H, 4-H and 7-H of phen), 8.30 (d, *J* = 8.2 Hz, 2 H, 5-H of quinolinyl ring of pq$^-$), 7.98–7.93 (m, 2 H, 4-H of quinolinyl ring of pq$^-$), 7.78 (d, *J* = 8.2 Hz, 2 H, 8-H of quinolinyl ring of pq$^-$), 7.38–7.20 (m, 6 H, 6-H and 7-H of quinolinyl ring and 3-H of phenyl ring of pq$^-$), 6.92–6.85 (m, 4 H, 4-H and 5-H of phenyl ring of pq$^-$), 6.68 (dd, *J* = 7.6 and 2.3 Hz, 2 H, 6-H of phenyl ring of pq$^-$), 2.83 (s, 2 H, C*H₂*NH), 1.90 (s, 3 H, CH of adamantane), 1.70–1.62 ppm (m, 12 H, CH_2 of adamantane). IR (KBr): ṽ = 3410 (m, N–H), 1288 (m, C=S), 846 (s, PF_6^-) cm^{-1}. Positive-ion ESI-MS: ion cluster at *m*/*z* 1002 [*M*]$^+$. $C_{54}H_{46}F_6IrN_6PS\cdot 0.5\,H_2O$ (1157.26): calcd. C 56.05, H 4.09, N 7.26; found C 56.26, H 4.38, N 7.38.

Instrumentation and Methods: Equipment for characterization and photophysical and electrochemical studies has been described previously.[25c] Luminescence quantum yields were measured by the optically dilute method[31] using an aerated aqueous solution of $[Ru(bpy)_3]Cl_2$ (Φ = 0.028)[32] as the standard solution.

Anion-Binding Studies: Steady-state emission spectral titrations were used to determine the binding constants. A supporting electrolyte (0.1 M TBAP) was present in the titration solutions to maintain a constant ionic strength. The binding constant, K_s, of the anion A$^-$ to the receptor Ir for the following equilibrium

$$\mathrm{Ir} + \mathrm{A}^- \overset{K_s}{\rightleftharpoons} \mathrm{Ir\text{-}A}^-$$

was obtained by fitting the experimental data to Equation (1)[27]

$$\frac{I_o}{I_o - I_x} = \left(\frac{I_o}{I_o - I_\infty}\right)\left(\frac{1}{K_s[\mathrm{A}^-]} + 1\right) \qquad (1)$$

where I_o is the emission intensity of the receptor only, I_x is the emission intensity of the receptor in the presence of the anion at a concentration [A$^-$], and I_∞ is the limiting emission intensity.

Acknowledgments

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