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Luminescently Tagged 2,2′-Bipyridine Complex of Fe^{II}: Synthesis and Photophysical Studies of 4-[*N*-(2-Anthryl)carbamoyl]-4′-methyl-2,2′-bipyridine

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The anthracene lumiphore was linked to the chelating ligand 2,2′-bipyridine, forming 4-[*N*-(2-anthryl)carbamoyl]-4′-methyl-2,2′-bipyridine (bpyAnth). Coupling through an amide linkage provides some electronic isolation of the anthracene lumiphore. Electrochemistry suggested little change of the anthracene oxidation whether free (1.35 V) linked to 2,2′-bipyridine as bpyAnth (1.30 V) or appended to Fe^{II} (1.29 V). The bpyAnth ligand retained the structured luminescence characteristic of anthracene at 375, 400, 419, and 441 nm. This anthracene emission persists even when bpyAnth is complexed to an Fe^{II} center. The complex $[Fe(bpyAnth)_3]^{2+}$ is emissive, in marked contrast to typical polyazine iron(II) complexes. This bpyAnth ligand serves as a luminescently tagged analogue of 2,2′-bipyridine, useful for coordination to a variety of metals.

Polypyridine transition-metal complexes are efficient light absorbers, and many display interesting photophysical properties.[1] The prototypical $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) displays an intense metal-to-ligand charge-transfer (MLCT) absorption in the visible region, and the ^{3}MLCT state is emissive at room temperature. Supramolecular complexes derived from related Ru light absorbers have found utility as molecular devices.[2] While $[Fe(bpy)_3]^{2+}$ is an efficient MLCT light absorber, it is not emissive.[3] The $Fe(d\pi) \rightarrow bpy(\pi^*)$ MLCT state is rapidly deactivated by low-lying ligand-field (LF) states.[3a,b]

The development of a lumiphore-tagged bpy ligand could provide for emissive complexes, even in the presence of rapid nonradiative deactivation pathways. A successful lumiphore must be electronically uncoupled, retaining its emissive characteristics. Complexation of a luminescently tagged bpy to Fe^{II} provides an efficiently deactivated MLCT state to probe lumiphore coupling to the MLCT state. This report focuses on the preparation of 4-[*N*-(2-anthryl)carbamoyl]-4′-methyl-2,2′-bipyridine (bpyAnth) and its complexation to Fe^{II}.

A common approach for luminescence tagging is to link organic lumiphores to species of interest.[4−11] Anthracene is often employed because of its high quantum yield (ϕ) and long excited-state lifetimes (τ).[12] Incorporation of electronically coupled anthracene into metal complexes has also been investigated to extend MLCT excited-state lifetimes.[4,6−8,11] Chelating ligands electronically coupled to anthracene have been used as metal complexation indicators through luminescence quenching.[5]

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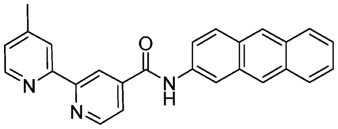

Figure 1. Tagged bpy ligand 4-[*N*-(2-anthryl)carbamoyl]-4′-methyl-2,2′-bipyridine (bpyAnth).

Quenching of a lumiphore tag's emission by an Fe center depends on the efficiency of energy transfer between the tag and metal-based states.[10,13−15] Few emissive Fe complexes have been reported; most consist of an emissive tag linked to a ligand on the Fe center.[10,13−15] Schmehl et al. recently reported a $Ru(tpy)_2-Fe(tpy)_2-Ru(tpy)_2$ complex (tpy = 2:2′,6′:2′′-terpyridine) linked together by conjugated tethers.[15] The complex has a low-lying, emissive intraligand excited state that can be populated by energy transfer from the $Fe(d\pi) \rightarrow tpy(\pi^*)$ MLCT state.

Polypyridine metal complexes have been coupled to DNA fragments, peptide chains, carbon nanotubes, and each other using amide linkers.[16] The amide linker has not been extensively investigated to couple an organic lumiphore to a free ligand. The electronic isolation of an amide linkage has been suggested by the attachment of anthracene to a Ru^{II}-bound bpy.[4] The reported luminescence data indicated separate $anth(\pi \rightarrow \pi^*)$ and $Ru(d\pi) \rightarrow bpy(\pi^*)$ CT emissive states. We developed a preparation of the free ligand, bpyAnth, and coordination to Fe^{II}, reported herein as a study of the utility of bpyAnth as a luminescently tagged analogue of bpy (Figure 1).

The ligand bpyAnth was prepared by a modification of the synthetic method used to modify the Ru-bound 4-carboxy-4′-methyl-2,2′-bipyridine ligand.[4a,b] Commercially available 4,4′-dimethyl-2,2′-bipyridine was selectively oxidized to 4-carboxy-4′-methyl-2,2′-bipyridine with selenium dioxide.[16a] Carboxylic acid activation with *N*,*N*′-diisopropylcarbodiimide and anhydrous 1-hydroxybenzotriazole followed by condensation with 2-aminoanthracene in dimethylformamide (DMF) afforded the title ligand. The crude product was suspended in cold acetone and filtered to give 67% yield of pure bpyAnth. The ^1H NMR spectrum of bpyAnth was well-resolved, and proton assignments were made with the aid of $^1H-^1H$ correlation spectroscopy (COSY).[4a,17]

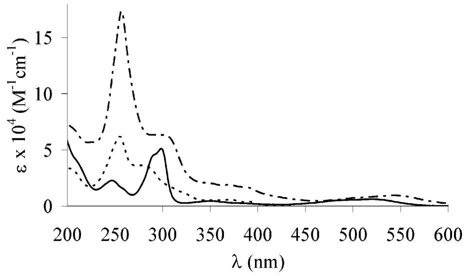

Figure 2. Electronic absorption spectroscopies of bpyAnth (···), $[Fe(bpy)_3]^{2+}$ (—), and $[Fe(bpyAnth)_3]^{2+}$ (− · −) in acetonitrile.′′′

Table 1. Electrochemical Data for Anthracene and Anthracene-Tagged Compounds[a]

compound	$E_{1/2}$ (V)[b,c]	assign
anthracene	1.35[d]	anth
bpyAnth	1.30[d]	anth
	−1.50	$bpy^{0/-}$
$[Fe(bpy)_3](PF_6)_2$	1.12	$Fe^{2+/3+}$
	−1.19, −1.40, −1.69	$bpy^{0/-}$
$[Fe(bpyAnth)_3](PF_6)_2$	1.29[d]	anth
	−1.01, −1.19, −1.39	$bpy^{0/-}$

[a] Pt working electrode, 0.1 M Bu_4NPF_6. Reported potentials vs Ag/AgCl (−0.44 mV vs ferrocene); bpy = 2,2′-bipyridine; bpyAnth = 4-[*N*-(2-anthryl)carbamoyl]-4′-methyl-2,2′-bipyridine. [b] Oxidations measured in CH_3CN. [c] Reductions measured in DMF. [d] Irreversible oxidation reported as E_p.

Table 2. Photophysical Properties of Anthacene-Tagged Compounds and Related Model Systems[a]

compound	λ_{max}^{em} (nm)
anthracene	372, 394, 417, 441, 471 (sh)
bpyAnth	375, 400, 419, 441, 470 (sh)
$[Fe(bpyAnth)_3]^{2+}$	442, 471, 502 (sh)

[a] Emission measured at room temperature (excited at 337 nm) in MeOH. bpy = 2,2′-bipyridine; bpyAnth = 4-[*N*-(2-anthryl)carbamoyl]-4′-methyl-2,2′-bipyridine.

The bpyAnth ligand displays spectroscopic and redox properties of both the bpy and anthracene subunits. The electronic absorption spectrum of bpyAnth contains characteristic transitions for both bpy (278 nm) and anthracene (256 nm) with a weaker, structured-anthracene absorption at 340−378 nm (Figure 2). The electrochemistry of free bpyAnth was consistent with anthracene- and amido-substituted bpy. A reversible reduction at −1.69 V was consistent with a stabilized π^* orbital on bpy. An irreversible anthracene oxidation dominated at 1.30 V (Table 1). Excited-state properties are also consistent with an amido-substituted anthracene.[18] Free bpyAnth showed an intense structured-anthracene-based emission (Table 2).

Metal binding of bpyAnth was investigated, showing its utility as a luminescent tag binding to Fe^{II} to produce $[Fe(bpyAnth)_3](PF_6)_2$. A total of 3 equiv of free bpyAnth was stirred in ethanol with $FeSO_4{\cdot}7H_2O$. The addition of water and acetonitrile followed by filtration to remove free ligand gave a solution of $[Fe(bpyAnth)_3]SO_4$, which

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(17) ^1H NMR $[(CD_3)_2C{=}O]$: δ 10.25 (1H, bs), 8.99 (1H, dd, J = 1.6 and 0.8 Hz), 8.89 (1H, dd, J = 5.0 and 0.8 Hz), 8.81 (1H, d, J = 1.8 Hz), 8.60 (1H, dd, J = 4.9 and 0.5 Hz), 8.53 (2H, s), 8.38 (1H, m), 8.11 (1H, d, J = 9.1 Hz), 8.07 (2H, m), 7.99 (1H, dd, J = 5.0 and 1.8 Hz), 7.87 (1H, dd, J = 9.1 and 2.0 Hz), 7.50 (2H, m), 7.32 (1H, ddd, J = 5.0, 1.6, and 0.8 Hz), 2.49 (3H, s).

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precipitated as a hexafluorophosphate salt in 95% yield. The purity of $[Fe(bpyAnth)_3](PF_6)_2{\cdot}2H_2O$ was determined by CHN analysis and a comparison of the ^1H NMR spectrum of a nearly saturated solution of the complex with that of free bpyAnth.[19] The ^1H NMR spectrum of $[Fe(bpyAnth)_3]^{2+}$ showed two magnetically inequivalent amido protons at 10.1 ppm that may represent facial and meridinal isomers.

The electronic absorption spectroscopy of $[Fe(bpyAnth_3]$-$(PF_6)_2$ is characteristic of $[Fe(bpy)_3]^{2+}$ and the linked anthracene tag (Figure 2). The UV region of the absorption spectrum of $[Fe(bpyAnth)_3]^{2+}$ closely resembles that of bpyAnth, with the relative extinction coefficients being three times the corresponding absorption of the free ligand. The MLCT of the tagged complex is red-shifted compared to $[Fe(bpy)_3]^{2+}$ in acetonitrile (542 nm), consistent with a stabilized π^*-acceptor orbital on bpyAnth.

The redox properties of $[Fe(bpyAnth)_3](PF_6)_2$ are summarized in Table 1. Binding to Fe^{II} had little effect on the anthracene oxidation. $[Fe(bpyAnth)_3]^{2+}$ displays an irreversible oxidation at 1.29 V, correlating well with values for anthracene-based processes.[9,20−22] The reversible Fe^{II}/Fe^{III} oxidation seen for $[Fe(bpy)_3]^{2+}$ at 1.12 V is not observed for the tagged complex, presumably because of overlap with the anthracene oxidation. The three coupled $bpy^{0/-}$ reductions of $[Fe(bpyAnth)_3]^{2+}$ (−1.01, −1.19, and −1.39 V) are shifted from those of $[Fe(bpy)_3]^{2+}$ (−1.19, −1.40, and −1.69 V) (Table 2).

The complex $[Fe(bpyAnth)_3]^{2+}$ displays a structured emission characteristic of anthracene at room temperature in contrast to typically nonemissive iron(II) polyazine complexes.[23] The $[Fe(bpyAnth)_3]^{2+}$ emission is red-shifted from that of the free ligand (Figure 3). Both bpyAnth and $[Fe(bpyAnth)_3]^{2+}$ emissions display lifetimes of 20 ± 2 ns. The emission of $[Fe(bpyAnth)_3]^{2+}$ displays the characteristic profile of other amido-coupled anthracene metal complexes.[4] Lewis and Liu studied *N*-benzoyl-2-aminoanthracene, which displayed a structured emission reported to come from two emissive states with lifetimes of 7 and 15 ns.[18a] These two emissive states are attributed to rotomers about the *N*-anthracene bond. Similar rotomers would exist in bpyAnth. Metal complexation of bpyAnth could stabilize or selectively quench one fluorescent state, giving the emission profile observed for $[Fe(bpyAnth)_3]^{2+}$. This Fe binding study demonstrates the utility of bpyAnth as a luminescent tag even in the presence of rapidly deactivating LF states (Figure 4).

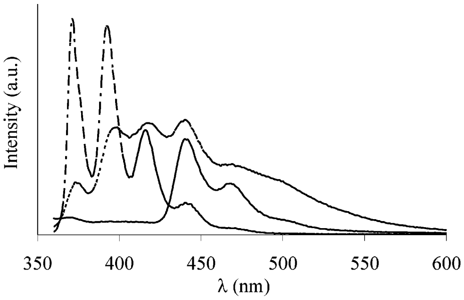

Figure 3. Room-temperature emission spectra of bpyAnth (absorbance-matched; •••), anthracene (spectrum-normalized; — • —), and $[Fe(bpyAnth)_3]^{2+}$ (absorbance-matched; —) in methanol when excited at 337 nm.″

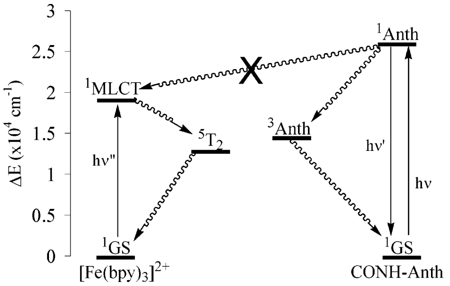

Figure 4. Excited-state energies arising from $[Fe(bpy)_3]^{2+}$ and anthracene portions of $[Fe(bpyAnth)_3]^{2+}$. The ^1MLCT state and anthracene singlet (^1Anth) were determined experimentally. The literature was used to estimate lowest-lying LF ($^5T_2$)[3a,b] and triplet anthracene (^3Anth)[4b,7,12b] states.

The tag retains much of the character of free anthracene, suggesting that bpyAnth is a good candidate for a luminescently tagged analogue to bpy. Studies are underway to form mono-, bis-, and tris-substituted Ru^{II} complexes. This luminescently tagged bpyAnth is of interest for use in biologically active assemblies.[24]

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Supporting Information Available: Syntheses of bpyAnth and $[Fe(bpyAnth)_3](PF_6)_2$, ^1H NMR and $^1H-^1H$ COSY spectra (300 MHz) of bpyAnth with full proton assignments, table of electronic absorption spectral data of anthracene, bpyAnth, $[Fe(bpy)_3](PF_6)_2$, and $[Fe(bpyAnth)_3](PF_6)_2$ in acetonitrile, and square-wave voltammetry of $[Fe(bpy)_3](PF_6)_2$, bpyAnth, and $[Fe(bpyAnth)_3](PF_6)_2$ in 0.1 M Bu_4NPF_6. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) CHN analytical results. Calcd for $FeC_{78}H_{61}N_9O_5P_2F_{12}$: C, 60.50; H, 3.97; N, 8.23. Found: C, 60.09; H, 3.92; N, 8.23.

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