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Synthesis and Excited-State Properties of a Novel Ruthenium Nucleoside: 5-[Ru(bpy)$_2$(4-m-4′-pa-bpy)]$^{2+}$-2′-deoxyuridine

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The synthesis and photophysical properties of a novel ruthenium-modified nucleoside are reported. The key synthetic step to 5-[Ru(bpy)$_2$(4-m-4′-pa-bpy)]$^{2+}$-2′-deoxyuridine involves the Pd(0)-catalyzed cross-coupling of a propargylamine-derivatized Ru(bpy)$_3$$^{2+}$ and 3′,5′-dibenzoyloxy-2′-deoxy-5-iodouridine. The long-lived ^{3}MLCT excited state (1300 ns) of 5-[Ru(bpy)$_2$(4-m-4′-pa-bpy)]$^{2+}$-2′-deoxyuridine has an emission maximum centered at 640 nm. Step-scan Fourier transform infrared (S^{2}FTIR) time-resolved spectroscopy reveals the excited-state electron to be localized on the modified bipyridine with the excited-state dipole oriented toward the 2′-deoxyuridine.

Introduction

Transition metal adducts of nucleic acids are studied as probes of nucleic acid structure and function, artificial nucleases, and as metallopharmaceuticals.[1−13] The two primary modes of metal complex binding are intercalation and coordination. Intercalation is a common binding motif for d^6 and d^8 metal complexes containing polyaromatic diimine ligands (e.g., dipyridophenazine).[8,11,12,20−25] Alternatively, a number of coordination sites are available for a metal complex on the nucleobase, ribose, or phosphate of a nucleotide or oligonucleotide. For example, metallonucleobase coordination complexes can be formed by ligation of the metal complex to a purine amine, such as cis-[Pt(NH$_3$)$_2$Cl$_2$] with the N7 of guanosine.[14−19] Our interest, however, focuses on covalently attaching metal complexes to the nucleobases at non-hydrogen bonding sites. These metallonucleosides serve as models for the corresponding metallo-oligonucleotides.[26−28,55] We are using d^6 metal diimine complexes such as Ru(bpy)$_3$$^{2+}$ since these complexes possess several favorable electronic properties including (1) spectroscopically distinguishable metal redox states, (2) tunable electronic structures, (3) energetic excited states, (4) long lifetimes in fluid solution ($\tau \approx 1$ μs), (5) high quantum yields, and (6) photochemical stability.[29,30] Furthermore, these metal chromophores are widely used to study a number of photophysical processes including energy- and electron-transfer reactions in supramolecular inorganic assemblies[29,31−36] and biological systems.[21,37−42] Herein, we report the synthesis, electrochemistry, and spectroscopy (UV−vis, emission, time-resolved step-

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(1) Sigel, A.; Sigel, H. *Probing of Nucleic Acids by Metal Ion Complexes of Small Molecules*; Marcel Dekker Inc.: New York, 1996; Vol. 33, p 678.
(2) Sigel, A.; Sigel, H. *Interactions of Metal Ions with Nucleotides, Nucleic Acids, and their Constituents*; Marcel Dekker Inc.: New York, 1996; Vol. 32, p 814.
(3) Tullius, T. D. *Metal−DNA Chemistry*; American Chemical Society: Washington, DC, 1988; Vol. 402.
(4) O'Halloran, T. V. *Science* **1993**, *261*, 715−725.
(5) Stubbe, J.; Kozarich, J. W.*Chem. Rev.* **1987**, *87*, 1107−1136.
(6) Magda, D.; Crofts, S.; Lin, A.; Miles, D.; Wright, M.; Sessler, J. L. *J. Am. Chem. Soc.* **1997**, *119*, 2293−2294.
(7) Magda, D.; Miller, R. A.; Sessler, J. L.; Iverson, B. L. *J. Am. Chem. Soc.* **1994**, *116*, 6, 7439−7440.
(8) Bashkin, J. K.; Frolova, E. I.; Sampath, U. *J. Am. Chem. Soc.* **1994**, *116*, 5981−5982.
(9) Modak, A. S.; Gard, J. K.; Merriman, C. M.; Winkeler, K. A.; Bashkin, J. K.; Stern, M. K. *J. Am. Chem. Soc.* **1991**, *113*, 283−291.
(10) Wang, G.; Bergstom, D. E. *Tetrahedron Lett.* **1993**, *34*, 6721−6724.
(11) Sigman, D. S. *Acc. Chem. Res.* **1986**, *19*, 180−186.
(12) Chen, C. B.; Sigman, D. S. *J. Am. Chem. Soc.* **1988**, *110*, 6570−6572.
(13) Abrams, M. J.; Murrer, B. A. *Science* **1993**, *261*, 725−730.
(14) Takahara, P. M.; Frederick, C. A.; Lippard, S. J. *J. Am. Chem. Soc.* **1996**, *118*, 12309−12321.
(15) Sherman, S. E.; Lippard, S. J. *Chem. Rev.* **1987**, *87*, 1153−1181.
(16) Green, M.; Garner, M.; Orton, D. M. *Transit. Met.* **1992**, *17*, 164−176.
(17) Hambley, T. W. *Coord. Chem. Rev.* **1997**, *166*, 181−223.
(18) Margiotta, N.; Habtemariam, A.; Sadler, P. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1185−1186.
(19) Metzger, S.; Lippert, B. *J. Am. Chem. Soc.* **1996**, *118*, 12467−12468.
(20) Jennette, K. W.; Lippard, S. J.; Vassiliades, G. A.; Bauer, W. R. *Proc. Nat. Acad. Sci. U.S.A.* **1974**, *71*, 3839−3843.
(21) Holmlin, R. E.; Dandliker, P. J.; Barton, J. K. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2714−2730.
(22) Friedman, A. E.; Chambron, J. C.; Sauvage, J. P.; Turro, N. J.; Barton, J. K. *J. Am. Chem. Soc.* **1990**, *112*, 4960−4962.
(23) Turro, C.; Bossmann, S. H.; Jenkins, Y.; Barton, J. K.; Turro, N. J. *J. Am. Chem. Soc.* **1995**, *117*, 9026−9032.
(24) Peyratout, C. S.; Aldridge, T. K.; Crites, D. K.; McMillin, D. R. *Inorg. Chem.* **1995**, *34*, 4484−4489.
(25) Liu, F.; Meadows, K. A.; McMillin, D. R. *J. Am. Chem. Soc.* **1993**, *115*, 6699−6704.
(26) A preliminary account of this work was reported at the 216th ACS National Meeting, 1998, and at the 23th International Conference on Coordination Chemistry, 1998.
(27) Please see the work of Sigman (ref 12), Bashkin (refs 8 and 9), and Bergstrom (ref 10) for elegant examples of diimine labeled nucleosides (attachment site either the phosphate or nucleobase).
(28) Hurley, D. J.; Tor, Y. *J. Am. Chem. Soc.* **1998**, *120*, 2194−2195.
(29) Balzani, V.; Juris, A.; Venturi, M.; Campagne, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759−833.
(30) Damrauer, N. H.; Cerullo, G.; Yeh, A.; Boussie, T. R.; Shank, C. V.; McCusker, J. M. *Science* **1997**, *275*, 54−57.
(31) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85−277. The excited reduction and oxidation state potentials were estimated using $E = E^{0/-} + E^{00}$ and $E = E^{+/0} - E^{00}$, respectively.
(32) Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. *Acc. Chem. Res.* **1998**, *31*, 26−34.
(33) Balzani, V.; Barigelletti, F.; Decola, L. *Topics Curr. Chem.* **1990**, *158*, 31−71.
(34) Gratzel, M.; Kalyanasundaram, K. *Curr. Sci.* **1994**, *66*, 706−714.
(35) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163−170.
(36) Dupray, L. M.; Devenney, M.; Striplin, D. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1997**, *119*, 10243−10244.

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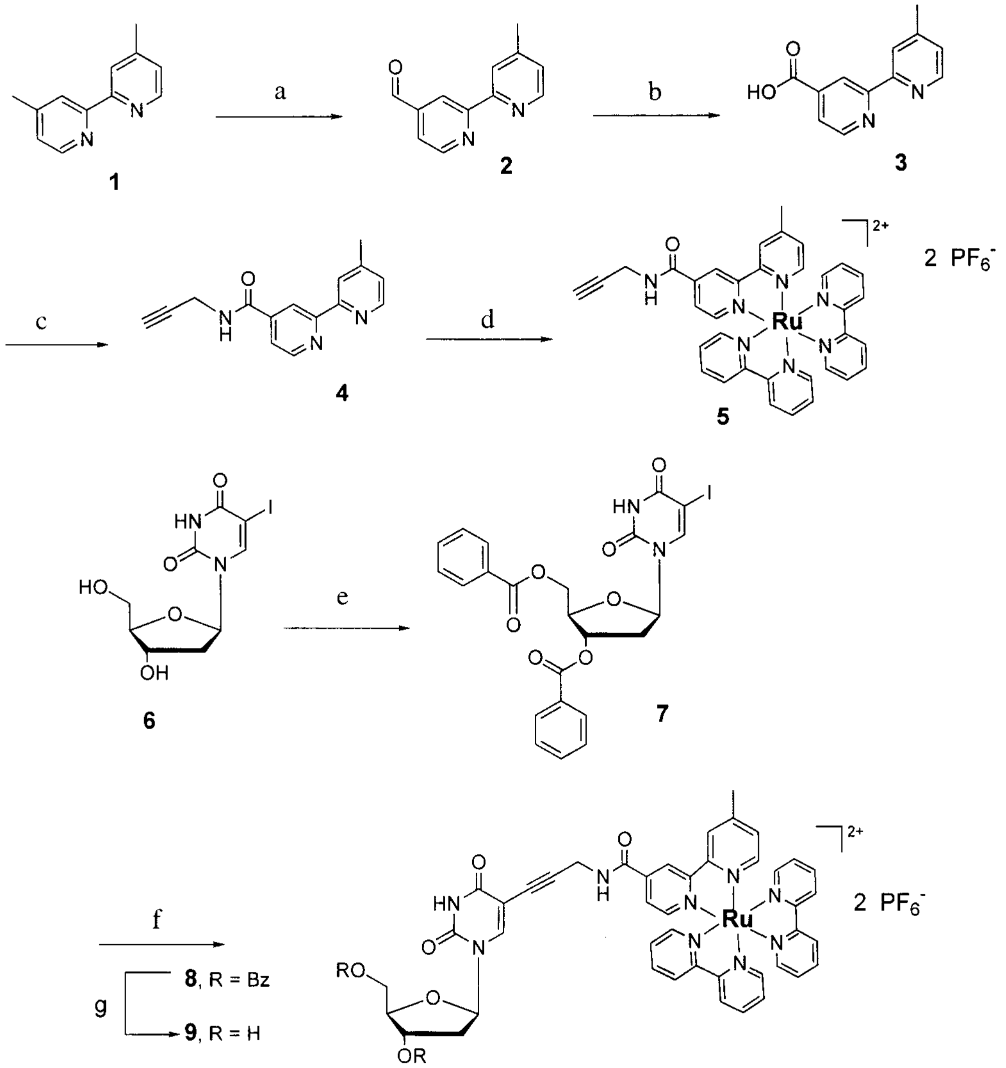
Scheme 1 Synthesis of 5-[Ru(bpy)$_2$(4-m-4′-pa-bpy)]$^{2+}$-2′-deoxyuridine[a]



[a] Reagents: (a) SeO$_2$, dioxane, 40% yield; (b) AgNO$_3$, NaOH, 77% yield; (c) propargyl amine·HCl, DCC, HOBt, DIPEA, DMF, 82% yield; (d) Ru(bpy)$_2$Cl$_2$, 70% aq. CH$_3$CH$_2$OH, 82% yield; (e) benzoyl chloride, C$_5$H$_5$N, 95% yield; (f) **5**, Pd(PPh$_3$)$_4$, CuI, TEA, DMF, 79% yield; (g) NH$_3$/CH$_3$OH, 90% yield.

scan Fourier transform infrared, transient absorption), of 5-[Ru(bpy)$_2$(4-m-4′-pa-bpy)]$^{2+}$-2′-deoxyuridine, a novel metallonucleoside.

Results and Discussion

A convergent synthetic approach was used to construct the 5-[Ru(bpy)$_2$(4-m-4′-pa-bpy)]$^{2+}$-2′-deoxyuridine, **9**, as outlined in Scheme 1. First, 4,4′-dimethyl-2,2′-bipyridine, **1**, was oxidized with SeO$_2$ to afford 4′-methyl-2,2′-bipyridine-4-carboxaldehyde, **2**, in 40% yield.[43,44] Compound **2** was oxidized to the carboxylic acid, **3**, using AgNO$_3$, in 77% yield. Dicyclohexylcarbodiimide (DCC/HOBt method) was then used to couple 4′-methyl-2,2′-bipyridine-4-carboxylic acid and propargylamine hydrochloride to yield the propargylamide-derivatized bipyridine, **4** (4-m-4′-pa-bpy), in 80% yield. The resulting modified bipyridine, 4-m-4′-pa-bpy, was then reacted with Ru(bpy)$_2$Cl$_2$ to form the tris-bipyridine complex, **5**. The starting halonucleoside, 5-iodo-2′-deoxyuridine, **6**, was protected with benzoyl chloride in pyridine to give the 3′,5′-dibenzoyloxy-protected nucleoside, **7**, in 95% yield.[45] The ruthenium complex, **5**, and 3′,5′-dibenzoyloxy-2′-deoxy-5-iodouridine, **7**, were Pd(0) cross-coupled using Pd(PPh$_3$)$_4$ to afford the ruthenium(II)-nucleoside, **8**, in 85% yield.[46,47] Benzoyl deprotection of **8** by methanolic ammonia yielded 5-[Ru(bpy)$_2$(4-m-4′-pa-bpy)]$^{2+}$-2′-deoxyuridine, **9**.

The final product, 5-[Ru(bpy)$_2$(4-m-4′-pa-bpy)]$^{2+}$-2′-deoxyuridine, was isolated and recrystallized from acetonitrile and ether as the PF$_6^-$ salt. Reverse-phase HPLC analysis of this product showed one band (C18 column; CH$_3$CN; 20 min run; monitoring at 254 and/or 450 nm). A fast atom bombardment mass spectrum (FAB-MS) of **9** showed the parent ion minus

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(37) Telser, J.; Cruickshank, K. A.; Schanze, K. S.; Netzel, T. L. *J. Am. Chem. Soc.* **1989**, *111*, 7221−7226.

(38) Winkler, J. R.; Gray, H. B. *Chem. Rev.* **1992**, *92*, 369−379.

(39) Gray, H. B.; Winkler, J. R. *Annu. Rev. Biochem.* **1996**, *65*, 537−561.

(40) McLendon, G. *Acc. Chem. Res.* **1988**, *21*, 160−167.

(41) Winkler, J. R.; Nocera, D. G.; Yocom, K. B.; Bordignon, E.; Gray, H. B. *J. Am. Chem. Soc.* **1982**, *104*, 5798−5800.

(42) Isied, S. S.; Worosila, G.; Atherton, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 7659−7661.

(43) Peck, B. M.; Ross, G. T.; Edwards, S. W.; Meyer, G. I.; Meyer, T. J.; Erickson, B. W. *Int. J. Peptide Protein Res.* **1991**, *38*, 114−123.

(44) Kus, P.; Knerr, G.; Czuchajowski, L. *J. Heterocyclic Chem.* **1990**, *27*, 1161−1166.

(45) Amarnath, V.; Broom, A. D. *Chem. Rev.* **1977**, *77*, 183-217.

(46) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *50*, 4467−4470.

(47) Hobbs, J. F. W. *J. Org. Chem.* **1989**, *54*, 3420−3422.

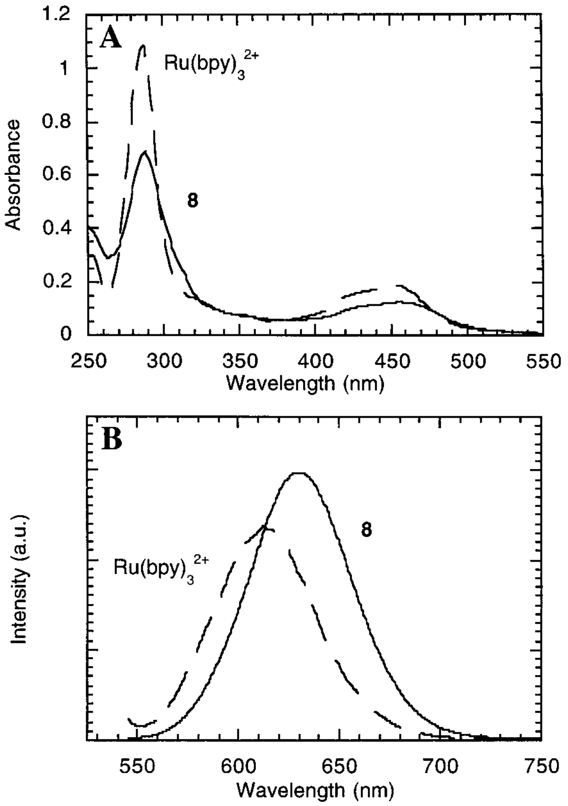

Figure 1. Electronic absorption (A) and emission spectra (B) of Ru(bpy)$_3^{2+}$ and **8** in CH$_3$CN. Absorption and emission spectra recorded at 298 K (10^{-6} M chromophore concentration for the emission experiments; excitation at 450 nm).

one PF_6^- and two PF_6^- confirming formation of this ruthenium-modified nucleoside. A ^{1}H NMR spectrum of 5-[Ru(bpy)$_2$(4-m-4′-pa-bpy)]$^{2+}$-2′-deoxyuridine in CD$_3$CN also confirmed the product.

From the onset, a number of both inorganic and nucleic acid synthetic hurdles must be overcome to successfully synthesize this ruthenium-labeled 2′-deoxyuridine. Two important considerations in our synthetic approach were (1) to efficiently attach the metal complex to the halonucleoside in high yield using a well-precedented Pd(0) cross-coupling reaction,[46−48] and (2) to ensure sufficient solubility in organic solvents for the handling and purification of this large complex (>1000 molecular weight) using the noncoordinating PF_6^- counterion. The alternative linear synthetic approach of first covalently coupling the bipyridine to the nucleoside followed by reaction with Ru(bpy)$_2$Cl$_2$ was attempted, but abandoned at an early stage in our synthetic work. Not surprisingly, the major problem was the low yield and multiple products from the Pd(0) cross-coupling reaction between the bipyridine ligand and 5-iodo-2′-deoxyuridine.[28] Protection of the 3′,5′-hydroxyls of 5-iodo-2′-deoxyuridine with benzoyl groups, which also increased the solubility, was needed to achieve efficient Pd(0) cross-coupling.

The metal-to-ligand charge-transfer band (^{1}MLCT-^{1}A$_1$) of 5-[Ru(bpy)$_2$(4-m-4′-pa-bpy)]$^{2+}$-2′-deoxyuridine was observed in the visible region with a maximum at 450 nm similar to Ru(bpy)$_3^{2+}$ as shown in Figure 1A. At higher energy, the $\pi-\pi^*$ transitions of the pyrimidine and bipyridine were observed at 254 and 280 nm, respectively. Excitation of the MLCT band of **8** produced an emission centered at 640 nm (^{3}MLCT excited state; $E^{00} \approx 1.9$ eV), slightly red-shifted relative to Ru(bpy)$_3^{2+}$ (Figure 1B). The emission maximum of **9** moved to 675 nm in phosphate buffer (5 mM sodium phosphate 50 mM NaCl; pH = 7). The emission lifetime was measured to be 1362 ns in CH$_3$CN and 485 ns in phosphate buffer at room temperature (Figure 2A). A cyclic voltammogram of **8** (in CH$_3$CN, 0.1 M TBA$^+$PF$_6^-$) revealed a quasi-reversible reduction at −1.28 V corresponding to reduction of the bipyridine ligand and a reversible oxidation at 1.0 V for Ru(II/III) vs NHE. The excited-state reduction and oxidation potentials of ruthenium-labeled 2′-deoxyuridine complex were estimated to be ≈0.6 and −0.9 V, respectively, consistent with previously synthesized Ru(bpy)$_3^{2+}$ derivatives.[29,31]

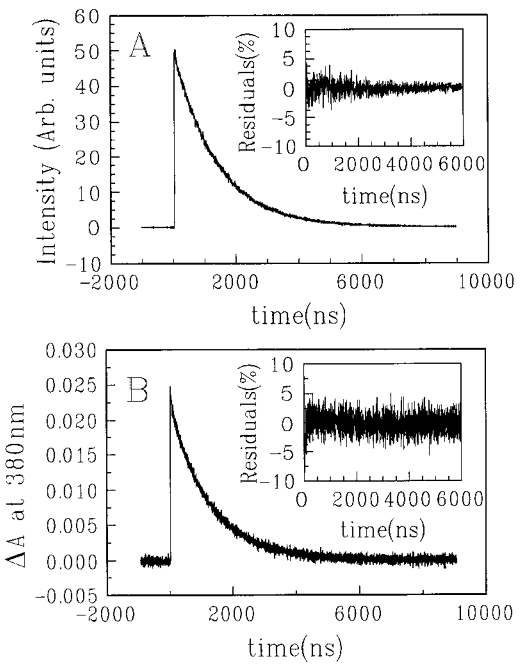

Figure 2. (A) Emission decay trace monitored at 620 nm for **8** after 460 nm pulse excitation. Insert shows the residuals in % between the experimental curve and the best monoexponential fit. (B) Decay of the transient absorption at 380 nm for **8** after pulse excitation at 460 nm. Insert shows the residuals in % between the experimental curve and the best monoexponential fit.

Transient absorption spectra were obtained by exciting a degassed solution of **8** in CH$_3$CN with a 460-nm laser pulse. The characteristic absorption band for the ruthenium tris-bipyridine radical anion was observed at 380 nm ($\tau = 1232$ ns; Figure 2B). Time-resolved step-scan Fourier transform infrared (S^{2}FTIR) spectroscopy with 10 ns time resolution was next used to probe the excited state of this ruthenium nucleoside.[49−52] Ground-state and ΔA infrared spectra of **5** and **8** are shown in Figure 3. The ground-/excited-state infrared ν(C=O) band energies for **5** and **8** are 1679/1647 and 1677/1642 cm^{-1}, respectively. The large negative ν shift (≈33 cm^{-1}) indicates considerable C=O character in the lowest π^* level in which the excited state is localized, with the excited-state dipole oriented toward the uridine. In addition, the excited state contains significant metal−ligand polarization.[53,54] This specific

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(48) de Meijere, A.; Meyer, F. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2379−2411.

(49) Omberg, K. M.; Smith, G. D.; Kavaliunas, D. A.; Chen, P.; Treadway, J. A.; Schoonover, J. R.; Palmer, R. A.; Meyer, T. F. *Inorg. Chem.* **1999**, *38*, 951−956.

(50) Schoonover, J. R.; Strouse, G. F.; Dyer, R. B.; Bates, W. D.; Chen, P.; Meyer, T. J. *Inorg. Chem.* **1996**, *35*, 273−274.

(51) Palmer, R. A. *Spectroscopy* **1993**, *8*, 26−36.

(52) Palmer, R. A.; Chao, J. L.; Dittmar, R. M.; Gregoriou, V. G.; Plunkett, S. E. *Appl. Spectrosc.* **1993**, *47*, 1297−1310.

(53) Treffert-Ziemelis, S. M.; Golus, J.; Strommen, D. P.; Kincaid, J. R. *Inorg. Chem.* **1993**, *32*, 3890−3894.

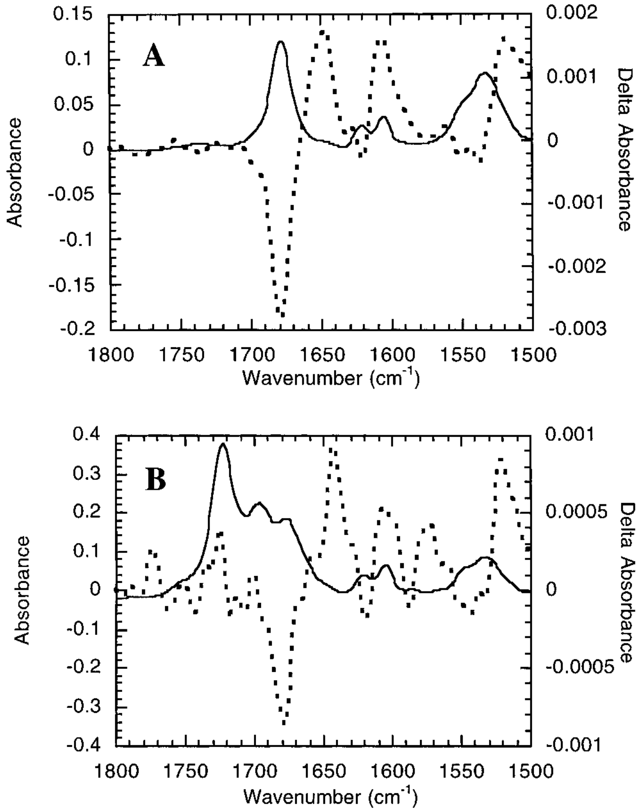

Figure 3. FT-IR ground state (solid line) and laser induced Δ*A* spectra (dashed line) in CD_3CN of **5** (A) and **8** (B).

localization of the excited electron on the uridine-substituted bipyridine of 5-[Ru(bpy)$_2$(4-m-4′-pa-bpy)]$^{2+}$-2′-deoxyuridine as opposed to delocalization over all three bipyridines should facilitate directional electron-transfer reactions in this novel ruthenium nucleoside.

Conclusions

In summary, the facile preparation of a ruthenium-labeled nucleoside is reported. Spectroscopic studies of 5-[Ru(bpy)$_2$-(4-m-4′-pa-bpy)]$^{2+}$-2′-deoxyuridine show that (1) favorable photophysical properties associated with Ru(bpy)$_3^{2+}$, such as being a potent oxidant and reductant in its excited state and possessing a significant excited state lifetime, are retained; (2) the excited electron is localized on the uridine-modified bipyridine; (3) the excited-state dipole is directed toward the nucleoside; and (4) the excited state is long lived. We are currently determining the generality of this synthetic approach to other metallonucleosides and the site-specific incorporation of these compounds in oligonucleotides.[55]

Experimental Procedures

All solvents were dried and distilled prior to use. Absorption spectra were measured on a Hewlett-Packard 8452 diode array spectrometer. Emission spectra were recorded on a Perkin-Elmer LS50B. Reverse-phase HPLC was performed on a Ranin HPLC with a C18 column monitoring at 254 and/or 450 nm. Electrochemical measurements were performed using a EG&G Princeton Applied Research electrochemical apparatus. [Abbreviations: DCC, dicyclohexylcarbodiimide; HOBt, 1-hydroxybenzotriazole; DIPEA, *N,N*-diisopropylethylamine; DMF, dimethylformamide; TEA, triethylamine.]

Syntheses. 4′-Methyl-2,2′-bipyridine-4-carboxaldehyde, 2.[43] SeO_2 (3.48 g, 31.4 mmol) was added to a solution of 4,4′-dimethyl-2,2′-bipyridine (**1**, 5.27 g, 28.6 mmol) in dioxane (150 mL) and refluxed for 24 h. The solution was then filtered hot, and the dioxane was removed by rotary evaporation. Next the residue was dissolved in ethyl acetate and filtered to remove additional solid material. The ethyl acetate layer was subsequently extracted with 1 M Na_2CO_3(2 × 100 mL) to remove additional carboxylic acid and 0.3 M $Na_2S_2O_5$ (3 × 100 mL) to form the aldehyde bisulfite. The combined aqueous extracts were adjusted to pH 10 with Na_2CO_3 and extracted with CH_2Cl_2 (4 × 100 mL). Evaporation of solvent yielded 1.9 g (40%) of a pure white solid compound, mp 132 °C; ^1H NMR ($CDCl_3$) δ 2.45 (s, 3H, CH_3); 7.15−8.8 (m, 6H, py); 10.1 (s, 1H, CHO); FAB-MS calculated for $C_{12}H_{10}N_2O$ $[M]^+$ 198.22, found $[M + H]^+$ 199.2.

4′-Methyl-2,2′-bipyridine-4-carboxylic acid, 3.[43] A solution of $AgNO_3$ (3.15 g) in water (32 mL) was added to a suspension of 4′-methyl-2,2′-bipyridine-4-carboxaldehyde (**2**, 3.5 g, 15 mmol) in 95% EtOH (150 mL). The suspension was stirred rapidly, and 1 M NaOH (79 mL) was added dropwise over 20 min to form Ag_2O. The dark black solution was stirred for an additional 15 h. Finally, the EtOH was removed by rotary evaporation, and the remaining water solution was filtered to remove Ag_2O. The residue was washed with 1.3 M NaOH (2 × 20 mL) and H_2O (20 mL). The combined filtrates were extracted with CH_2Cl_2 to remove unreacted aldehyde and adjusted to pH 3.5 with 1:1 (v/v) 4 N HCl/AcOH to afford a white compound. The product precipitated overnight at −10 °C, and the compound was collected and dried to afford 2.9 g (77%), mp 274 °C; ^1H NMR (DMSO) δ 2.5 (s, 3H, CH_3); 7.15−9 (m, 6H, py); FAB-MS calculated for $C_{12}H_{10}N_2O_2$ $[M]^+$ 214.22, found $[M + H]^+$ 215.1.

4′-Methyl-2,2′-bipyridine-4-propargylamide, (4-m-4′pa-bpy) 4. 4′-Methyl-2,2′-bipyridine-4-carboxylic acid (**3**, 0.22 g, 1 mmol), propargylamine hydrochloride, (0.092 g, 1 mmol), HOBt (0.15 g, 1 mmol), and DIPEA (0.21 mL) were dissolved in dry DMF (15 mL) and cooled to 0 °C. DCC (0.25 g, 1.2 mmol) was dissolved in DMF (3 mL) and added dropwise to the reaction mixture. The mixture was stirred at room temperature overnight. The DCU formed was filtered off, and the solvent was removed by vacuum distillation. The remaining solid compound was dissolved in ethyl acetate, washed with $NaHCO_3$ (5%), 0.5 N HCl, and brine, and dried over sodium sulfate. The solvent was removed by rotary evaporation and the compound was purified by column chromatography using 2% methanol in chloroform as eluent (0.19 g; 76%), mp 146 °C; ^1H NMR (DMSO) δ 2.4 (s, 3H, CH_3); 2.5 (s, 1H, CH); 4 (s, 2H, CH_2); 7.25−8.8 (m, 6H, py); 9.4 (s, 1H, NH); FAB-MS calculated for $C_{15}H_{13}N_3O$ $[M]^+$ 251.29, found $[M + H]^+$ 252.11.

Ruthenium(II) Bis(bipyridine)(4-methyl-4′-propargylamidebipyridine)bis(hexafluorophosphate), 5. Ru(bpy)$_2$Cl$_2$ (0.15 g, 0.3 mmol) was added to a solution of 4′-methyl-2′,2′-bipyridine-4-propargylamide (**4**, 0.08 g, 0.3 mmol) in 70% ethanol/H_2O (25 mL) and refluxed for 10 h. Next, the reaction mixture was cooled and ethanol was removed in vacuo. After standing for 4 h at room temperature, the solution was filtered and the solid compound washed with cold water. A saturated aqueous solution of NH_4PF_6 was added until no further precipitate was observed. The mixture was kept at room temperature for an additional 2 h and then finally filtered, washed with cold water and ether, and dried overnight to give 0.45 g (82%) of a pure orange compound. ^1H NMR (DMSO) δ 2.4 (s, 3H, CH_3); 2.5 (s, 1H, CH); 4.1 (s, 2H, CH_2); 7.4−9.2 (m, 22H, bpy); UV−vis (CH_3CN) λ_{max} 246, 288, and 454 nm; FAB-MS calculated for $C_{35}H_{29}N_7ORuP_2F_{12}$ $[M - 2PF_6^-]^+$ 664.74, $[M - PF_6^-]^+$ 809.7, found $[M - 2PF_6^-]^+$ 665.2, $[M - PF_6^-]^+$ 810.2.

3′,5′-Dibenzoyloxy-2′-deoxy-5-iodouridine, 7. 2′-Deoxy-5-iodouridine (6 mmol) was dissolved in dry pyridine and cooled to 0 °C. Benzoyl chloride (36 mmol) was added slowly while the reaction stirred for 12 h at room temperature. The solvent was then removed, and the crude material was dissolved in $CHCl_3$ (150 mL), washed with 0.5 N HCl and water, and dried over Na_2SO_4. Silica gel column chromatography afforded a white crystallinic solid in 80% yield. ^1H NMR (DMSO) δ 2.15 (t, 2H, C-2′); 3.6 (m, 2H, C-5′); 3.8 (m, 1H, C-3′); 4.2 (m, 1H, C-4′); 6.2 (t, 1H, C-1′); 7.2−7.9 (m, 10H, 2Ph); 8.2 (s, 1H, C-6); FAB-MS calculated for $C_{23}H_{19}N_2O_7$ $[M]^+$ 562.3, found $[M + H]^+$ 563.3.

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(54) Danzer, G. D.; Golus, J. A.; Kincaid, J. R. *J. Am. Chem. Soc.* **1993**, *115*, 8643−8648.

(55) Khan, S. I.; Beilstein, A. E.; Grinstaff, M. W. *Inorg. Chem.* **1999**, *38*, 418−419.

3′,5′-Dibenzoyloxy-5-[ruthenium(II) (bpy)$_2$(4-methyl-4′-propargylamidebipyridine)]$^{2+}$ 2′-Deoxyuridinebis(hexafluorophosphate), 8. **7** (0.5 g 0.89 mmol), **5** (0.8 g, 0.8 mmol), Pd(PPh$_3$)$_4$ (0.11 g, 0.089 mmol), and CuI (0.4 g, 0.18 mmol) were dissolved in dry DMF (15 mL) and degassed with N$_2$. Triethylamine (0.7 mL) was added, and the reaction mixture stirred for 8 h.[46] The solvent was then removed under reduced pressure. The crude product obtained was dissolved in acetonitrile and passed through a Sephadex column. The first 10 mL of eluent was collected and concentrated. Next the solid was dissolved in acetonitrile and the addition of dry ether gave an orange precipitate. The compound was filtered and dried to yield the ruthenium modified 2′-deoxyuridine (0.95 g, 79%). UV−vis CH$_3$CN λ_{max} 290, 454 nm; ^{1}H NMR (DMSO) δ 2.5 (s, 3H, CH$_3$); 2.8 (m, 2H, C-2′); 3.1 (m, 2H, C-5′); 4.25 (bs, 2H, CH$_2$); 4.6 (m, 1H, C-3′); 5.6 (m, 1H, C-4′); 6.2 (t, 1H, C-1′); 7.3−8.9 (m, 32H, Ph + bpy); 9.1 (s, 1H, C-6); FAB-MS calculated for $C_{58}H_{47}N_9O_8RuP_2F_{12}$ $[M - 2PF_6^-]^+$ 1099.1, $[M - PF_6^-]^+$ 1244.1, found $[M - 2PF_6^-]^+$ 1099.2, $[M - PF_6^-]^+$ 1244.1.

5-[(4-Methyl-4′-propargylamidebipyridine)(bpy)$_2$ruthenium(II)]$^{2+}$ 2′-Deoxyuridinebis(hexafluorophosphate), 9. **8** (1 g) was suspended in methanolic ammonia and left for 2 days at room temperature with occasional shaking. The solvent was removed by rotary evaporation. The compound was dissolved in a minimum volume of acetonitrile and precipitated with dry ether to yield a dark orange color compound, **9** (0.77 g 90%). UV−vis CH$_3$CN λ_{max} 290, 454 nm; ^{1}H NMR (DMSO) δ 2.5 (s, 3H, CH$_3$); 4.2 (s, 2H, CH$_2$); 6.15 (t, 1H, C-1′); 7.3−8.8 (m, 22H, bpy); 8.9 (s, 1H, C-6); FAB-MS calculated for $C_{44}H_{39}N_9O_6RuP_2F_{12}$ $[M - 2PF_6^-]^+$ 890.9, $[M - PF_6^-]^+$ 1035.8, found $[M - 2PF_6^-]^+$ 890.3, $[M - PF_6^-]^+$ 1036.3. One peak was observed in an HPLC trace (C18 column, CH$_3$CN and TEAA buffer).

Lifetimes. A Laser Photonics LN1000 nitrogen laser LN102 dye laser (coumarin 460 dye, exciton) was used as the irradiation source. The emission was monitored at right angle with a Macpherson 272 monochromator and Hammamatsu R666-10 PMT. The signal was processed by a LeCroy 7200A transient digitizer interfaced with an IBM-PC. The excitation wavelength was 460 nm and the monitoring wavelength was 620 nm. Power at the sample was 120 μJ/pulse as measured by a Molectron J3-09 power meter. The measured instrument lifetime response is 10 ns (fwhm). The acquired emission decay curves were analyzed by locally written software based on the Marquardt algorithm.

Transient Absorbance Spectra. A Surelite II-10 (continuum) Nd:YAG-OPO system was used as the excitation source. The excitation beam from the laser irradiated the sample perpendicularly to an optical axis of an Applied Photophysics laser kinetic spectrometer with a 250 W pulsed Xe lamp, f3.4 monochromator, and Hammamatsu PMT. The output from the PMT was coupled to LeCroy 7200A oscilloscope and analyzed as described for the lifetime measurements. Electronic synchronization and control of the experiment was achieved by electronics of local design. The excitation wavelength was 460 nm and the power at the sample was 3 mJ/pulse as measured by a Molectron J3-09 power meter.

S^{2}FTIR. The transient data reported here were measured on a step-scan modified Bruker IFS88 spectrometer with a standard globar source and dry air purge. The samples were dissolved in CD$_3$CN to give an absorbance between 0.125 and 0.5 in a 250 mm path length cell for the amide band analyzed. Samples were deoxygenated by sparging with argon for 60 min and were loaded into a CaF$_2$ window cell by syringe under argon.

The samples were excited using the third harmonic (355 nm, 10 ns, 10 Hz, 3 mJ/pulse) from a Q-switched Quanta-Ray DCR-1A Nd:YAG laser. The laser excitation and data acquisition were synchronized with a Stanford Research model DG535 pulse generator. An AC/DC-coupled photovoltaic Kolmar Technologies mercury cadmium telluride (MCT) detector with a 50 MHz preamplifier and an effective rise time of ∼20 ns was used to sample the transmitted infrared signal. The AC signal was further amplified by a Stanford Research model SR445 preamplifier (×250) before being directed to a personal computer equipped with a 100/200 MHz PAD82a transient digitizer. The DC signal was sent directly to the digitizer to be used for phase correction of the AC signal. The data were processed using Bruker Instruments’ Opus 3.0 software.

To minimize data collection times, the spectral window observed was limited to 1150 to 2250 cm^{-1} by the CaF$_2$ cell windows and a germanium low-pass filter placed over the detector window. The interferogram response before and after each laser flash was digitized at 10 ns intervals, and in a typical experiment, data from 240 laser flashes were averaged at each point. Data collection time was approximately 2 h. The ΔA spectra were calculated from the single beam ΔI transforms by the relation $\Delta A(\upsilon,t) = -\log[1 + \Delta I(\upsilon,t)/I(\upsilon)]$, where $I(\upsilon)$ is the detected intensity before laser excitation and $\Delta I(\upsilon,t)$ is the change in intensity at time, t. For the ΔA “snapshots”, several post-excitation time slices were averaged for greater signal-to-noise.

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