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Controlled Synthesis of a New, Soluble, Conjugated Metallopolymer Containing Ruthenium Chromophoric Units

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Conjugated polymers have been of interest because of their electrical conductivity.[1,2] More recently, metal-derivitized conjugated systems and new polymer systems have been developed that are better able to coordinate metal centers.[3−5] The rationale is metalated derivatives could combine the rich electro- and photochemical activities of the metal complex with the long-range conjugation properties of the polymer, thus leading to systems capable of performing electro- or photoinduced very-long-range electron transfer. These systems could also have applications as donor−acceptor type conjugated systems, or electro- and photochemical manipulation of the metal centers on the polymer could represent switchable molecular wires responding to external stimuli.[6] We report here the synthesis and characterization of a new bipyridine-containing conjugated polymer system, poly[1-(2,2′-bipyridine-4-yl)-1,4-diazabutadiene-4,4′-diyl] (polyazabpy), and its polymetalated ruthenium complex.[7]

A number of metalated polymer systems containing ruthenium have been reported and have found use in light absorption[8−11] and multielectron redox chemistry,[9] as well as applications in a number of electron- and energy-transfer systems.[10−12] The majority of these, however, are nonconjugated, saturated polymer systems, in which the polymer backbone acts as a spacer for the pendent chromophores, quenchers, and relays but plays no part in the communication among these sites. These systems are also developed either by copolymerization of the desired active sites[12] or by binding the desired groups to reactive substituents on a preformed polymer sample,[8−11] both routes giving nonordered copolymers with random loading. Our synthetic method (Scheme 1) provides a well-ordered π-conjugated polymer which allows metal coordination directly to the polymer backbone. This will hopefully provide increased communicative abilities along the polymer backbone to provide stronger interaction between coordinated active sites.

A related conjugated polymer, poly(2,2′-bipyridine-5,5′-diyl) (PBpy), and its ruthenium complex were recently reported.[5] As for the previously discussed polymers, the polymerization and metalation of PBpy have little control. Like most conjugated polymers, PBpy has very low solubility, and all characterization must be carried out in formic acid. Metalation of PBpy is also somewhat difficult since maximum loading levels reported are 5 mol % of Ru per bpy unit.[5b]

Our polymer system lacks most of these problems. Polyazabpy has limited solubility but is readably soluble in solvents such as DMF and DMSO, allowing greater flexibility in our synthetic methods and characterization. Reaction of the polymer with a stoichiometric amount of $Ru(bpy)_2(O_3SCF_3)_2$ in refluxing DMF gives us a completely metalated polymer with ∼100% loading (Scheme 1).[13] Also, due to the mild conditions needed for the polymerization step, it is possible first to coordinate the Ru to the active monomer and then to initiate polymerization to form the metalated polymer. Both routes to the metalated species give polymers with identical characteristics.

The unmetalated polymers were characterized by ^{1}H NMR in DMSO-d_6. The unmetalated and metalated polymers were not sufficiently soluble in either DMSO-d_6 or DMF-d_3 to obtain ^{13}C data. The peaks in the ^{1}H NMR spectrum were broadened as expected for a polymeric sample.[9] Four major peaks of the spectrum were clearly observed which correspond to three bipyridyl protons at $\delta = 8.2$, 7.6, and 6.7 ppm, respectively, and an imine proton resonance at $\delta = 8.4$ ppm. The region between 4 and 5 ppm showed multiplets of smaller magnitude corresponding to defect sites and cross-linking as described by Euler.[4] A resonance assigned to aldehydic end groups was observed at 10.6 ppm. The length of the polymers is estimated to be 20 repeat units as deduced from the ratio of integrated peak intensities of aldehyde protons to polypyridyl protons.

Electrochemical, spectroscopic, emission lifetime, and quantum yield data for polyazabpy and its Ru(II) complexes are summarized in Table 1. The electrochemical data for $[Ru(bpy)_2(dabpy)]^{2+}$ show a reductive wave at -1.4 V vs SCE assigned to a bpy reduction, and by inference the lowest lying MLCT excited state will be bpy localized.[14a] The $[Ru(bpy)_2(dabpy)]^{2+}$, $[\{(Ru(bpy)_2\}_2(DAB)]^{4+}$, and $[(polyazabpy)Ru(bpy)_2]_x^{(2x)+}$ ions are short-lived and weaker emitters relative to $[Ru(bpy)_3]^{2+}*$.[14b,15] The enhanced rate constants for excited state decay in the dabpy-

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(1) *Conjugated Conducting Polymers*, Kiess, H., Ed.; Springer Series in Solid State Sciences, Vol. 102; Springer-Verlag: New York, 1992.

(2) (a) The literature on this topic is too vast to be cited exhaustively.[2b] Lead review article references are given as Supporting Information. (b) Patil, A. O.; Heeger, A. J.; Wudl, F. *Chem. Rev.* **1988**, *88*, 183 and all references therein.

(3) (a) The literature on this topic is too vast to be cited exhaustively.[3b] Lead article references are given as Supporting Information. (b) Deronzier, A.; Moutet, J.-C. *Acc. Chem. Res.* **1989**, *22*, 249.

(4) (a) Euler, W. B. *Polyhedron* **1991**, *10* (8), 859 and references therein.[4b] (b) Lead article references are given as Supporting Information.

(5) (a) Yamamoto, T.; Zhou, Z.; Kanbara, T.; Maruyama, T. *Chem. Lett.* **1990**, 223. (b) Yamamoto, T.; Yoneda, Y.; Maruyama, T. *J. Chem. Soc., Chem. Commun.* **1992**, 1652.

(6) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304.

(7) Elemental analyses of these polymeric systems provide few useful data because of incomplete combustion. FAB and ^{1}H NMR studies of the polymer, polyazabpy, are consistent with the structure shown in Scheme 1.

(8) (a) Calvert, J. M.; Meyer, T. J. *Inorg. Chem.* **1981**, *20*, 27. (b) Forster, R. J.; Vos, J. G. *Macromolecules* **1990**, *23*, 4372.

(9) (a) DeArmond, M. K.; Tait, C. D.; Gex, J. N.; Wertz, D. W.; Hanck, K. W. *J. Phys. Chem.* **1989**, *93*, 977. (b) Sun, Y.; DeArmond, M. K. *Inorg. Chem.* **1994**, *33*, 2004. (c) Worl, L. A.; Strouse, G. F.; Younathan, J. N.; Baxter, S. M.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 7571.

(10) Rabek, J. F. In *New Trends in the Photochemistry of Polymers*; Allen, N. S., Rabek, J. F., Eds.; Elsevier: New York, 1985; pp 265−288.

(11) (a) Kaneko, M.; Yamada, A. *Adv. Polym. Sci.* **1984**, *55*, 1. (b) Baxter, S. M.; Jones, W. E.; Danielson, E.; Worl, L.; Strouse, G.; Younathan, J.; Meyer, T. J. *Coord. Chem. Rev.* **1991**, *111*, 47. (c) Jones, W. E.; Baxter, S. M.; Strouse, G. F.; Meyer, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 7363.

(12) (a) Ennis, P. M.; Kelly, J. M.; O'Connell, C. M. *J. Chem. Soc., Dalton Trans.* **1986**, 2485. (b) Ennis, P. M.; Kelly, J. M. *J. Phys. Chem.* **1989**, *93*, 5735.

(13) Loading was determined by comparison of the extinction coefficients of the Ru → bpy MLCT transition between the monomeric and polymeric species.

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Scheme 1

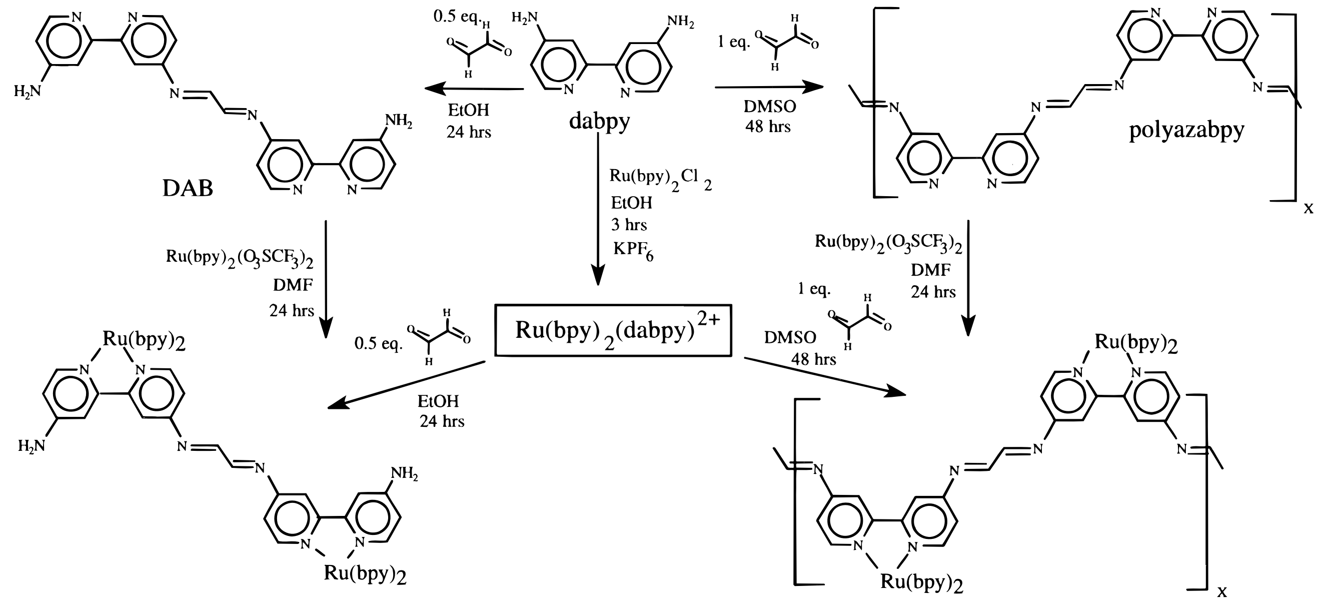

Table 1. Electrochemical/Photophysical Data (DMF, 295 K)

compound	$E_{1/2}$, V (ΔE_p, mV)	λ_{max}^{abs}, nm	λ_{max}^{em}, nm	ϕ_{em}^{f}	τ_{em}, ns
$[Ru(bpy)_3](PF_6)_2$	1.26 (60) −1.26 (70) −1.44 (70) −1.71 (70)	453[a] (452[c])[d]	610[e] (626[c])[d]	0.063[c] (0.062[c])[d]	912[b] (920[c])[d]
$[Ru(bpy)_2(dabpy)](PF_6)_2$	0.94 (60) −1.43 (60) −1.64 (80)	485 (480)[d]	675[e] (666)[d]	0.0046 (0.010)[d]	144
$[\{Ru(bpy)_2\}_2DAB](PF_6)_4$	1.01 (120) −0.83 (260) −1.35 (60) −1.59 (90)	480	666[e]	0.0055	130
$[(polyazabpy)Ru(bpy)_2]_x$-$(PF_6)_{2x}$	0.99 (190) −0.83 (290) −1.49 (150) −1.66 (160)	465 (br)	666[e]	0.0015	111
polyazabpy	1.04 (170) −0.81 (150) −1.10 (irr)		500[e]		

[a] Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 2098. [b] Casper, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5583. [c] Mecklenburg, S. L.; McCafferty, D. G.; Schoonover, J. R.; Peek, B. M.; Erickson, B. W.; Meyer, T. J. *Inorg. Chem.* **1994**, *33*, 2974. [d] In CH_3CN. [e] Emission spectal data are uncorrected for instrument response. [f] Emission quantum yields measured relative to $[Ru(bpy)_3]^{2+*}$ were determined using previously described methods and protocols.[11c]

and DAB-based systems are consistent with an increased rate constant for nonradiative (k_{nr}) relaxation, an anticipated effect based on energy gap considerations[16a] and/or intervention of low-lying metal-centered dd states.[16b] The emission lifetimes for $[\{Ru(bpy)_2\}_2(DAB)]^{4+*}$ and $[(polyazabpy)Ru(bpy)_2]_x^{(2x)+*}$ are similar to that for $[Ru(bpy)_2(dabpy)]^{2+*}$, indicating that there are no ground state/excited interactions across the DAB ligand or by adjacent metal centers in the polymeric system. The apparently smaller emission quantum yield for $[(polyazabpy)Ru(bpy)_2]_x^{(2x)+*}$ may indicate that the intersystem crossing efficiency from the ^{1}[MLCT] state to the emissive ^{3}[MLCT] state may be less than unity.[17] Laser flash photolysis and power dependence experiments are currently under investigation to better characterize the excited state processes in $[(polyazabpy)Ru(bpy)_2]_x^{(2x)+*}$.

This new polymer system was synthesized by polymeric condensation fashioned after that of the polymer polyazine, $[-CH{=}N-N{=}CH-]_x$, reported by Euler and co-workers.[4] Polyazine is both isoelectronic and isostructural with polyacetylene, and iodine-doped samples of polyazine have shown high conductivity.[4] Since polymerization is carried out through chemical coupling of a diamine and a dialdehyde, there is substantial synthetic control in designing a desired system. For example, by reacting 2 equiv of the diamine with 1 equiv of the dialdehyde, it is possible to isolate a dimeric species (DAB) as shown in Scheme 1 (left branch). It should be possible to continue selective growth of the polymer by reacting this product with an excess of the dialdehyde to produce aldehyde end groups. Subsequent reaction then with an excess of the diamine will increase the oligomer length by two units. Euler and co-workers have already shown this type of selective growth is possible using this methodology.[4] It is then easy to envision using different monomeric diamine groups for each step. This would allow changing metal centers with each step to produce ordered multimetallic polymeric systems or allow the insertion of various organic diamine units for specific types of desired chemistry. In either case, this system should provide total control over building any number of different well-ordered multimetallic or multicomponent molecular assemblies.

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Supporting Information Available: Additional literature citations for footnotes 2−4 and a textual presentation of synthetic protocols and characterization data for all the materials reported (7 pages). Ordering information is given on any current masthead page.

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(14) (a) There is literature precedent to show that Ru-coordinated dabpy is some 0.4 eV more difficult to reduce than coordinated bpy.[14c] (b) If the excited state is localized on the DAB bridge, the lifetime is expected to be on the microsecond time scale.[14d] (c) Barqawi, K. R.; Llobet, A.; Meyer, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7751. (d) Downard, A. J.; Honey, G. E.; Philips, L. F.; Steel, P. J. *Inorg. Chem.* **1991**, *30*, 2260. (e) Boyd, S.; Strouse, G. F.; Jones, W. E., Jr.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 7395.

(15) Emission lifetimes were determined on a Spex τ−2 multifrequency phase and modulation fluorometer.

(16) (a) Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 3722. (b) The NH_2 substituent is anticipated to stabilize the dd states, giving rise to competitive nonradiative decay via an MLCT−dd state surface crossing.[14d]

(17) Fan, J.; Tysoe, S.; Strekas, T. C.; Gafney, H. D.; Serpone, N.; Lawless, D. *J. Am. Chem. Soc.* **1994**, *116*, 5343.