J. Am. Chem. Soc. 1990, 112, 7395–7396

Effect on MLCT Excited States of Electronic Delocalization in the Acceptor Ligand

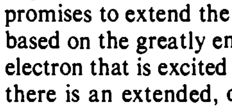
Stephen Boyde, Geoffrey F. Strouse, Wayne E. Jones, Jr.,
and Thomas J. Meyer*

Department of Chemistry, The University of North Carolina
Chapel Hill, North Carolina 27599-3290

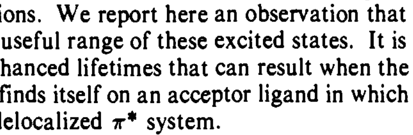
Received April 9, 1990

The metal to ligand charge transfer (MLCT) excited states of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridyl) and related polypyridyl complexes of Ru^{II}, Os^{II}, or Re^{I} have been utilized extensively as sensitizers of photochemical electron transfer.[1] A fundamental limitation exists in the ability of these complexes to utilize low-energy visible or very near infrared light. Their lifetimes are dictated largely by nonradiative processes, and the rates of these processes increase as the energy gap between excited and ground state decreases.[2] This means that, although systematic procedures are available for preparing complexes that absorb low-energy light, the resulting excited states are short-lived and difficult to exploit in photochemical reactions. We report here an observation that promises to extend the useful range of these excited states. It is based on the greatly enhanced lifetimes that can result when the electron that is excited finds itself on an acceptor ligand in which there is an extended, delocalized π^* system.

Compared to $[Ru(dmb)_3]^{2+}$ (dmb = 4,4′-dimethyl-2,2′-bipyridine),[3a] the ligand-bridged complex $[(dmb)_2Ru(\mu\text{-bbpe})Ru(dmb)_2]^{4+}$ (bbpe = *trans*-1,2-bis(4′-methyl-2,2′-bipyridyl-4-yl)ethene) has a new absorption feature at 500 nm (ϵ = 25 800 M^{-1} cm^{-1}) in CH_3CN in addition to a $d\pi \rightarrow \pi^*$(dmb) transition at 460 nm (ϵ = 12 650 M^{-1} cm^{-1}). The complex emits at 750 ± 5 nm compared to 640 ± 5 nm for $[Ru(dmb)_3]^{2+*}$. In cyclic voltammograms in 0.1 M $[N(n\text{-}C_4H_9)_4](PF_6)$–$CH_3CN$, the following waves appear: (1) a single, unresolved, two-electron wave for the $Ru^{III/II}$ couples at 1.16 V vs the saturated sodium chloride calomel electrode (SSCE) (ΔE_p = 70 mV); (2) two one-electron, bbpe-based reductions, the first at −1.04 V and the second at −1.30 V; and (3) a two-electron, unresolved dmb-based reduction wave at −1.65 V. The first dmb-based reduction in $[Ru(dmb)_3]^{2+}$ occurs at −1.40 V under the same conditions.



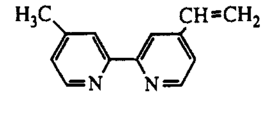
(dmb)



(bbpe)

The bbpe ligand was prepared by a condensation reaction between 4-methyl-2,2′-bipyridyl-4′-carboxaldehyde and the ylide (4′-methyl-2,2′-bipyridyl-4-yl)methyltriphenylphosphonium bromide.[4] The ligand-bridged complex was prepared by the reaction between bbpe and $[Ru(dmb)_2Cl_2]$[5] in ethylene glycol in a 1:2 ratio.[4]

In transient absorbance difference spectra of $[(dmb)_2Ru(\mu\text{-bbpe})Ru(dmb)_2]^{4+}$, $[Ru(dmb)_3]^{2+}$, or $[Ru(bpy)_2(vbpy)]^{2+}$ in CH_3CN, $\pi \rightarrow \pi^*$ transitions appear for the reduced dmb or vbpy ligands at 360–380 nm along with the expected bleaches in the $d\pi \rightarrow \pi^*$ (bpy, dmb, vbpy) region at ~450 nm.[3,6] The spectra were acquired 50 ns after 460-nm laser flash photolysis (~6-ns pulses at <4 mJ/pulse) by using an apparatus that has been described elsewhere.[3b] For the ligand-bridged complex, an additional, intense absorption feature appeared at 580 ± 5 nm. It was present at the earliest observation times, <5 ns, and decayed with the same lifetime, τ (CH_3CN, 298 ± 2 K) = 1.31 ± 0.05 μs, as the emission, independent of the exciting or monitoring wavelengths. Related, low energy absorption features have been found for singly reduced 4,4′-bipyridine or bipyridinium cations,[7] and for the MLCT excited states of complexes containing 4,4′-bipyridine-type ligands where the added electron is thought to be delocalized over both pyridyl rings.[8] After an extended photolysis period there was no sign of trans → cis isomerization at bbpe.[9]



(vbpy)

From the available evidence, we conclude that the lowest lying excited state in $[(dmb)_2Ru(\mu\text{-bbpe})Ru(dmb)_2]^{4+*}$ is a MLCT state in which the excited electron is on the bbpe ligand. This conclusion is based on the absence of trans → cis isomerization at bbpe upon photolysis, the pattern of features that appear in the transient absorbance difference spectrum, the red-shifted emission maximum, and the more positive potential for the first ligand-based reduction (−1.07 V vs −1.48 V) compared to $[Ru(dmb)_3]^{2+}$. In the related, ligand-bridged complex $[(dmb)_2Ru(\mu\text{-dstyb})Ru(dmb)_2]^{4+}$ (dstyb is 1,4-bis[2-(4′-methyl-2,2′-bipyridyl-4-yl)ethenyl]benzene), it has been concluded that low-lying MLCT and $\pi\pi^*$ states coexist and are in equilibrium.[10]

In the bbpe-based MLCT state in $[(dmb)_2Ru(\mu\text{-bbpe})Ru(dmb)_2]^{4+}$, a double mixed valency exists. One is at the metals, Ru^{II}–Ru^{III}. The second is at the bpy groups of the bbpe ligand, $bpy\text{–}bpy^{\bullet-}$, eq 1. On the basis of the appearance of the new

$$[(dmb)_2Ru^{II}(\mu\text{-bbpe})Ru^{II}(dmb)_2]^{4+} \xrightarrow{h\nu} [(dmb)_2Ru^{II}(\mu\text{-bbpe}^{\bullet-})Ru^{III}(dmb)_2]^{4+*} \quad (1)$$

absorption feature at 580 nm in the transient spectrum, it can be inferred that the excited electron is delocalized over both of the bipyridyl groups in the bbpe ligand. There is extensive electronic coupling between these groups as demonstrated by the 0.26-eV difference between the $E_{1/2}$ values for the two one-electron, bbpe-based reductions at −1.04 and −1.30 V.[11] Electronic coupling

---

(1) (a) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163. (b) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; Von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85. (c) Krause, R. A. *Struct. Bonding* (*Berlin*) **1987**, *67*, 1. (d) Kalayanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159. (e) Sutin, N.; Creutz, C. *Pure Appl. Chem.* **1980**, *52*, 2717.

(2) (a) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1576. (b) Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630.

(3) (a) Boyde, S.; Strouse, G. F.; Jones, W. E., Jr.; Meyer, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 8305. (b) Danielson, E., in preparation.

(4) The preparation and characterization of the ligand and the complex will be published elsewhere. The information is available as supplementary material.

(5) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.

(6) Creutz, C.; Chou, M.; Netzel, T. L.; Okamura, M.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 1309.

(7) (a) Kihara, H.; Gondo, Y. *J. Raman Spectrosc.* **1986**, *17*, 263. (b) Henning, J. C. M. *J. Chem. Phys.* **1966**, *44*, 2139. (c) Ebbesen, T. W.; Ferraui, G. *J. Phys. Chem.* **1983**, *87*, 3717. (d) Mackay, R. A.; Landolph, J. R.; Pozionck, E. J. *J. Am. Chem. Soc.* **1971**, *93*, 5626. (e) Hestaer, R. E.; Suzuki, S. *J. Phys. Chem.* **1982**, *86*, 4626. (f) Johnson, C. S.; Gutowsky, H. S. *J. Chem. Phys.* **1963**, *39*, 58. (g) Hoffman, H. J.; Cimiraglia, R.; Tomasi, J. *J. Chem. Res., Synop.* **1987**, 48.

(8) (a) Chen, P. Y.; Dannielson, E.; Meyer, T. J. *J. Phys. Chem.* **1988**, *92*, 3708. (b) Schanze, K. S.; Neyhart, G. A.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 2182. (c) Tapolsky, G.; Duesing, R.; Meyer, T. J. *J. Phys. Chem.* **1989**, *93*, 3885. (d) Chen, P. Y.; Curry, M.; Meyer, T. J. *Inorg. Chem.* **1989**, *28*, 2271.

(9) After photolysis in CH_2Cl_2 (298 ± 5 K) at energies greater than the energy of the ligand absorption bands ($\lambda < 400$ nm) for periods >24 h, there was no evidence for either trans → cis isomerization or decomposition of the bbpe ligand by ^1H NMR or UV–visible spectroscopy.

(10) Shaw, J. R.; Webb, R. T.; Schmehl, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 1117.

(11) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.

(12) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278.

(13) (a) Caspar, J. V.; Westmoreland, T. D.; Allen, G. H.; Bradley, P. G.; Meyer, T. J.; Woodruff, W. F. *J. Am. Chem. Soc.* **1984**, *106*, 3492. (b) Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 3722. (c) Caspar, J. Ph.D. Thess, University of North Carolina at Chapel Hill, 1982. (d) Lumpkin, R. S. Ph.D. Thesis, University of North Carolina at Chapel Hill, 1987.

(14) (a) Bixon, M.; Jortner, J. *J. Chem. Phys.* **1968**, *48*, 715. (b) Freed, K. F.; Jortner, J. *J. Chem. Phys.* **1970**, *52*, 6272. (c) Engleman, R.; Jortner, J. *Mol. Phys.* **1970**, *18*, 145. (d) Freed, K. F. *Top. Curr. Chem.* **1972**, *31*, 65.

0002-7863/90/1512-7395$02.50/0

between the metal ions is small as shown by the unresolved, single $Ru^{III/II}$ wave at $E_{1/2}$ = 1.16 V.[12]

The lifetime of the bbpe-based MLCT state in $[(dmb)_2Ru(\mu\text{-}bbpe)Ru(dmb)_2]^{4+}$, 1.31 ± 0.05 μs in CH_3CN at 298 ± 2 K, is surprisingly long. Lifetimes of MLCT excited states characteristically decrease with the energy gap between the excited and ground states.[2] Yet, for $[Ru(dmb)_3]^{2+}$, which has a significantly higher energy gap, E_{em} = 15 600 cm^{-1} compared to 13 300 cm^{-1}, the lifetime is 950 ± 30 ns under the same conditions. For $[Ru(bpy)_2(py)Cl]^+$ (py = pyridine), where there is a comparable emission energy (752 ± 5 nm, 13 300 cm^{-1}), the lifetime is 44 ± 3 ns under the same conditions. On the basis of the results of temperature-dependent lifetime studies, at 157 ± 2 K in 4:1 (v:v) ethanol–methanol, there are no complications from low-lying dd states.[16] Under these conditions, lifetimes, as determined by emission decay, were 1.97 ± 0.07 μs for $[(dmb)_2Ru(\mu\text{-}bbpe)Ru(dmb)_2]^{4+*}$ and 104 ± 4 ns for $[Ru(bpy)_2(py)Cl]^{+*}$.

The extended lifetime for the bbpe complex appears to be a consequence of electronic delocalization in bbpe acting as the acceptor ligand. Emission spectral profiles in 4:1 (v:v) ethanol–methanol at 157 ± 2 K or 298 ± 2 K could be fit[13] satisfactorily by including contributions from an averaged ν(bpy) mode ($h\nu$ = 1350 cm^{-1}), an averaged low-frequency mode ($h\nu$ = 350 cm^{-1}), and the solvent. On the basis of this analysis, the electron-vibrational coupling constant, S, for ν(bpy) was 0.72 ± 0.05 for $[Ru(bpy)_2(py)Cl]^{+*}$ and 0.60 ± 0.05 for $[(dmb)_2Ru(\mu\text{-}bbpe)Ru(dmb)_2]^{4+*}$. The quantity S is related to the change in equilibrium displacement between the excited and ground states, ΔQ_e, the reduced mass, M, and the angular frequency, ω (=$2\pi\nu$), by eq 2. On the basis of the smaller value of S, the structural change in the acceptor ligand is decreased for $(dmb)_2Ru(\mu\text{-}bbpe)Ru(dmb)_2]^{4+*}$. This is a further indication that delocalization over both bpy's has occurred. The decrease in S and ΔQ_e with enhanced delocalization must be a consequence of decreased electron–electron repulsion in the acceptor ligand.

$$S = (1/2)(M\omega/h)(\Delta Q_e)^2 \qquad (2)$$

The decrease in S is sufficient to account, to a large degree, for the enhanced lifetime in $[(dmb)_2Ru(\mu\text{-}bbpe)Ru(dmb)_2]^{4+*}$ compared to $[Ru(bpy)_2(py)Cl]^{+*}$ at 157 K. From radiationless decay theory and the energy gap law,[14] the nonradiative decay rate constant, k_{nr}, is predicted to vary with S, the energy gap (E_0), and $h\nu$ as shown in eq 3.[13b,14] For $h\nu$ = 1350 cm^{-1}, E_0 = 13 780 cm^{-1}, and S = 0.72 or 0.60, the decrease in k_{nr} between $[Ru(bpy)_2(py)Cl]^{+*}$ and $[(dmb)_2Ru(\mu\text{-}bbpe)Ru(dmb)_2]^{4+*}$, calculated by using eq 3, is 17 in 4:1 (v:v) ethanol–methanol at 157 ± 2 K. The parameters used in the calculations were those obtained by spectral fitting. The decrease observed experimentally was 19. The origin of the effect is a decrease in vibrational overlap between the vibrational wave functions for the ν(bpy) acceptor modes between the excited and ground states as ΔQ_e decreases.

$$k_{nr} \propto e^{-S} e^{-\gamma E_0/h\nu} \qquad (3)$$

$$\gamma = (\ln E_0/Sh\nu) - 1$$

Compared to related complexes having comparable energy gaps, we find that lifetimes for the MLCT excited states of $[Ru(dmb)_2(bbpe)]^{2+}$, $[Os(bpy)_2(bbpe)]^{2+}$, $[(bpy)_2Os(\mu\text{-}bbpe)Os(bpy)_2]^{4+}$, $[Re(bbpe)(CO)_3Cl]^+$, or $[Cl(CO)_3Re(\mu\text{-}bbpe)Re(CO)_3Cl]^{2+}$ are all lengthened. These observations and the sometimes anomalous lifetime behavior observed for other MLCT excited states[10,15] point to what could be a general approach to enhancing excited-state lifetimes based on introducing increased delocalization in the acceptor ligand.

Our results have important implications for the design of MLCT based photosensitizers. They open the possibility of preparing complexes that have significant light absorptivities much further into the red while, at the same time, maintaining lifetimes that are accessible to electron-transfer quenchers.

Acknowledgment. Financial support from the Department of Energy (DE-FG05-86ER13633) and from the SERC for postdoctoral support (S.B.) is gratefully acknowledged.

Supplementary Material Available: The preparations and characterizations of the bbpe ligand and complex (3 pages). Ordering information is given on any current masthead page.

---

(15) (a) Juris, A.; Campagna, S.; Bidd, I.; Lehn, J.-M.; Ziessel, R. *Inorg. Chem.* **1988**, *23*, 4007. (b) Ruminski, R.; Kiplinger, J.; Cookcroft, T.; Chase, C. *Inorg. Chem.* **1989**, *24*, 370.

(16) For both complexes, excited-state lifetimes as measured by transient emission are nearly temperature independent over the range 150–200 K (Murtaza, Z., unpublished results).

Putidaredoxin Reduction of Cytochrome P-450$_{cam}$: Dependence of Electron Transfer on the Identity of Putidaredoxin's C-Terminal Amino Acid

Matthew D. Davies, Ling Qin, Jennifer L. Beck,[†]
Kenneth S. Suslick, Hideo Koga,[‡] Tadao Horiuchi,[‡] and
Stephen G. Sligar[*]

School of Chemical Sciences
University of Illinois at Urbana-Champaign
Urbana, Illinois 61801
Faculty of Pharmaceutical Sciences, Kyushu University
Maidashi, Higashi-ku, Fukuoka 812, Japan

Received April 2, 1990

Considerable experimental and theoretical efforts have been made to determine the effect of exothermicity, distance, and protein medium on the rate of biological electron transfer.[1,2] We have discovered that the interprotein electron transfer from site-specific variants of putidaredoxin (a 2Fe–2S ferredoxin) is strongly affected by the presence or absence of a C-terminal aromatic residue. Activity is maintained when the wild-type C-terminal tryptophan is replaced by other aromatic residues but is lost upon nonaromatic replacement or deletion.

Putidaredoxin functions in the *Pseudomonas putida* camphor hydroxylase electron-transfer chain as a one-electron shuttle between an NADH-dependent flavoprotein and the terminal acceptor, cytochrome P-450$_{cam}$. This enzyme system catalyzes the first catalytic step whereby *P. putida* ATCC strain 17453 can use camphor as its sole source of carbon and energy.[3] The C-terminal tryptophan of putidaredoxin is known to be solvated, independently mobile, accessible to carboxypeptidase cleavage, and near an anionic surface domain.[4] Preliminary NMR structure

---

[*] To whom correspondence should be addressed.

[†] Present address: Research School of Chemistry, Australian National University, Canberra, Australia.

[‡] Kyushu University.

(1) For reviews, see: (a) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265–322. (b) Scott, R. A.; Mauk, A. G.; Gray, H. B. *J. Chem. Educ.* **1985**, *62*(11), 932–938. (c) Mayo, S. L.; Ellis, W. R., Jr.; Crutchley, R. J.; Gray, H. B. *Science* **1986**, *233*, 948–952. (d) Kuki, A.; Wolynes, P. G. *Science* **1987**, *236*, 1647–1652. (e) McLendon, G. *Acc. Chem. Res.* **1988**, *21*, 160–167.

(2) (a) Takano, T.; Kallai, O. B.; Swanson, R.; Dickerson, R. E. *J. Biol. Chem.* **1973**, *248*(15), 5234–5255. (b) Pielak, G. J.; Mauk, A. G.; Smith, M. *Nature (London)* **1985**, *313*, 142–154. (c) Cheung, E.; Taylor, K.; Kornblatt, J. A.; English, A. M.; McLendon, G.; Miller, J. R. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 1330–1333. (d) Conklin, K. T.; McLendon, G. *Inorg. Chem.* **1986**, *25*, 4804–4806. (e) Liang, N.; Pielak, G. J.; Mauk, A. G.; Smith, M.; Hoffman, B. M. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 1249–1252. (f) Wendoloski, J. J.; Matthew, J. B.; Salemme, F. R. *Science* **1987**, *238*, 794–797. (g) Hoffman, B. M.; Ratner, M. A. *J. Am. Chem. Soc.* **1987**, *109*, 6237–6243. (h) Axup, A. W.; Albin, M.; Mayo, S. L.; Crutchley, R. J.; Gray, H. B. *J. Am. Chem. Soc.* **1988**, *110*, 435–439. (i) Liang, N.; Mauk, A. G.; Pielak, G. J.; Johnson, J. A.; Smith, M.; Hoffman, B. M. *Science* **1988**, *240*, 311–313. (j) Brunschwig, B. S.; Sutin, N. *J. Am. Chem. Soc.* **1989**, *111*, 7454–7465.

(3) (a) Tyson, C. A.; Lipscomb, J. D.; Gunsalus, I. C. *J. Biol. Chem.* **1972**, *247*(18), 5777–5784. (b) Hedegaard, J.; Gunsalus, I. C. *J. Biol. Chem.* **1965**, *240*, 4038–4043.

(4) Sligar, S. G.; DeBrunner, P. G.; Lipscomb, J. D.; Namtvedt, M. J.; Gunsalus, I. C. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*(10), 3906–3910.

0002-7863/90/1512-7396$02.50/0