

Luminescence and Theoretical Studies of Cu(tripod)X [tripod = 1,1,1-Tris(diphenylphosphanylmethyl)ethane; X[−] = Halide, Thiophenolate, Phenylacetylde]

Valeri Pawlowski,^{[a],[‡]} Günther Knör,^[a] Christian Lennartz,^{*[b]} and Arnd Vogler^{*[a]}

Keywords: Electronic spectra / Luminescence / Copper complexes / Phosphane ligands / Quantumchemical calculations

Complexes of the type Cu^I(tripod)X [tripod = 1,1,1-tris(diphenylphosphanylmethyl)ethane; X[−] = Br[−], I[−], PhS[−], PhC≡C[−]] are phosphorescent in solution and in the solid state ($\lambda_{\text{max}} \approx 465$ nm). Calculations show that the emissive triplet is of mixed MLCT/LLCT character. The emission is facilitated by the rigid tetrahedral structure, which is imposed by the tripod ligand. Accordingly, a distortion towards a square-planar geometry, which should occur upon MLCT excitation, is pre-

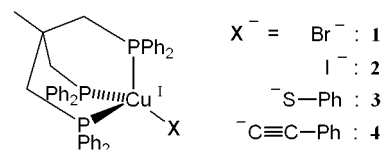
vented. On the other hand, in the triplet state the phenyl substituents of the phosphane ligands undergo a rotation which favours radiationless deactivation. As a result, the emission efficiency is relatively small in solution, but much higher in the solid state owing to the rigidity of the lattice.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2005)

Introduction

The luminescence of transition metal complexes is a rapidly expanding research field.^[1,2] Potential applications such as optical sensors or OLEDs (organic light-emitting diodes) have stimulated many studies in this area.^[3,4] The appearance of a luminescence at room temperature is largely restricted to complexes of metals which belong to the second and third transition row, while complexes of first-row transition metals are frequently not emissive under ambient conditions. However, there is one notable exception. A variety of mononuclear and polynuclear Cu^I complexes are luminescent at room temperature in solution or in the solid state.^[5–8] In particular, mononuclear complexes with polypyridine ligands have attracted much interest.^[8,9] These compounds are characterized by emissive low-energy MLCT (metal-to-ligand charge transfer) states. (Phosphane)Cu^I complexes constitute another group of luminescent compounds^[5] which, however, have not been investigated to the same extent as (polypyridine)Cu^I complexes. In particular, the nature of the emitting excited states of (phosphane)Cu^I complexes is not clear at all. The present study was undertaken to gain more insight into the excited-state properties of (phosphane)Cu^I complexes and to define structural requirements for potential applications. Com-

plexes of the type Cu^I(tripod)X [tripod = 1,1,1-tris(diphenylphosphanylmethyl)ethane; X[−] = Br[−], I[−], PhS[−], PhC≡C[−]] were expected to serve this purpose (Scheme 1).



Scheme 1.

The rigid structure of these complexes,^[10] which is imposed by the tripod ligand, should facilitate this work. These complexes are kinetically stable, soluble in a variety of organic solvents and volatile at higher temperatures without decomposition. Moreover, the rigidity of the compounds prevents extensive excited-state distortions. Accordingly, calculations of the frontier orbitals may be sufficient to characterize the lowest-energy excited state. In addition, the lack of flexibility could block radiationless deactivations and increase the luminescence efficiency. Finally, the rigidity should reduce the Stokes shift. As a result, the emission is expected to undergo a blue-shift. In this context, it should be mentioned that for certain applications such as OLEDs blue triplet emitters are requested, but are not yet available to the same extent as green and red molecular phosphors.

Results and Discussion

Experimental Results

The neutral compounds Cu(tripod)X [X[−] = Br[−], I[−], PhS[−], PhC≡C[−]] were readily obtained as white or slightly yellow-

[a] Institut für Anorganische Chemie, Universität Regensburg, 93040 Regensburg, Germany
E-mail: arnd.vogler@chemie.uni-regensburg.de

[b] BASF AG, Computational Chemistry and Biology, GVC/C-A30, 67057 Ludwigshafen, Germany
E-mail: christian.lennartz@basf-ag.de

[‡] Present address: Institute of Molecular and Atomic Physics, National Academy of Science of Belarus, 220072 Minsk, Belarus

ish solids by reaction of the corresponding copper(I) precursors CuX with the tridentate phosphane ligand tripod (Scheme 1). Their monomeric composition was confirmed by elemental analysis, and in the case of the halide derivatives **1** and **2** also by conductivity and molecular weight measurements.^[11]

While the electronic spectrum of the tripod ligand in CH₂Cl₂ exhibits a featureless ultraviolet band at $\lambda_{\text{max}} = 251$ nm, the absorption spectra of the corresponding copper complexes display their maxima in the 300 nm spectral region (Figure 1). These bands are rather intense ($\epsilon = 13650 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda_{\text{max}} = 298$ nm for **2** in CH₂Cl₂) and significantly red-shifted in the order of $4000\text{--}6500 \text{ cm}^{-1}$ from the absorption of free tripod. In the case of the thiophenolate derivative **3**, an additional splitting of the main absorption band occurs with two well-resolved peaks at 270 and 290 nm.

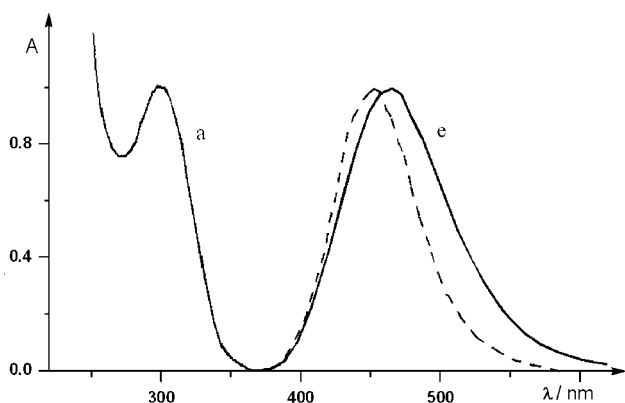


Figure 1. Electronic absorption (a) and emission (e) spectra of Cu(tripod)I (**2**) at room temperature and at 77 K (dashed curve). Absorption: $7.36 \times 10^{-5} \text{ M}$ in CH₂Cl₂, 1-cm cell. Emission: $\lambda_{\text{exc}} = 300$ nm, solid and in toluene matrix, intensity in arbitrary units.

All of the Cu(tripod)X complexes **1–4** exhibit an intense blue emission with peaks around 465 nm when excited with ultraviolet light in the solid state. This feature is shown in Figure 1 for Cu(tripod)I (**2**) with $\lambda_{\text{max}} = 462$ nm. At 77 K in a low-temperature toluene matrix, the luminescence maximum of **2** is blue-shifted to $\lambda_{\text{max}} = 453$ nm and the spectrum is slightly narrowed, while no significant structuring or larger change of shape of the emission band is observed (Figure 1). In argon-saturated dichloromethane solution, the luminescence of compound **2** shows a broad maximum with $\lambda_{\text{max}} = 465$ nm. A rather low quantum yield of $\phi = 8 \times 10^{-4}$ is obtained in CH₂Cl₂ relative to quinine sulfate as a standard, and the luminescence in solution is found to be only moderately quenched by dioxygen. A quite similar behaviour is observed for the corresponding bromide derivative **1**.

The thiophenolate complex **3** also shows a blue emission at $\lambda_{\text{max}} = 465$ nm in the solid state, but in contrast to the halide derivatives **1** and **2**, a green luminescence with a significantly shifted, structureless band at $\lambda_{\text{max}} = 508$ nm is dominant in dichloromethane solution (Figure 2). As a solid compound, the luminescence spectrum of the phenylace-

tylide complex **4** displays a conspicuous structuring with a rather sharp maximum at 465 nm and a clearly resolved shoulder in the region of 510 nm. The peak separation of about 2000 cm^{-1} approximately matches the C≡C stretching frequency of the ligand X. In solution, however, a broad and nearly structureless band with $\lambda_{\text{max}} = 475$ nm is present in the organometallic derivative **4** as well. The spectroscopic data for all of the copper(I) complexes **1–4** in the solid state and in dichloromethane solution are summarized in Table 1.

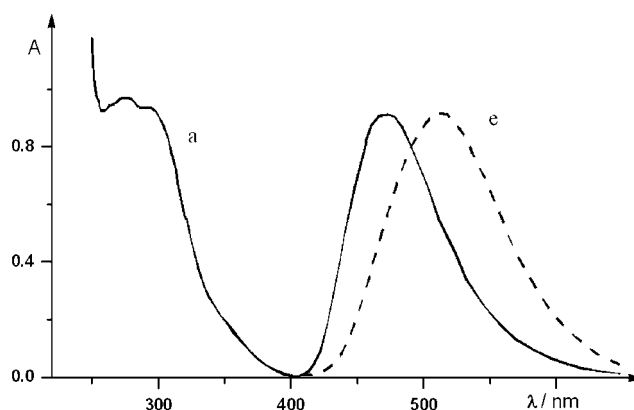


Figure 2. Electronic absorption (a) and emission (e) spectrum of Cu(tripod)SPh (**3**) at room temperature. Absorption: CH₂Cl₂, 1-cm cell. Emission: $\lambda_{\text{exc}} = 300$ nm, solid and in CH₂Cl₂ solution (dashed curve), intensity in arbitrary units.

Table 1. Absorption and emission maxima of Cu(tripod)X at room temperature.

X	λ_{max} [nm] (CH ₂ Cl ₂)	λ_{em} [nm] (solid)	λ_{em} [nm] (CH ₂ Cl ₂)
Br	296	462	462
I	298	461	465
SPh	270, 290	465	508
C≡CPh	297	465, 510	475

Discussion

The compounds Cu(tripod)X are monomeric and tetrahedral.^[10,11] They are kinetically stable in distinction to other Cu^I complexes with monodentate or bidentate phosphane ligands, which undergo dissociation and dimerization in solution.^[12,13] The electronic spectra of various (arylphosphane)Cu^I complexes have been reported.^[5] However, assignments for the lowest-energy excited states seem to be controversial. In most cases it has been suggested that these states are of the phosphane IL (intraligand) type. This excitation involves the promotion of an electron from the Cu–P σ -bond into π^* -orbitals, which are partially delocalized over the aryl substituents. Since the lone-pair of the free phosphane is stabilized by coordination, a blue-shift of this transition should take place. However, this has been frequently not observed. Generally, the lowest-energy transitions of such (arylphosphane)Cu^I complexes are very close to those of the free ligands, sometimes at somewhat higher

and sometimes at slightly lower energies. The longest-wavelength absorptions of Cu(tripod)X (Table 1) are assigned to spin-allowed transitions in agreement with their high intensities.

Generally, the luminescence of Cu^I complexes is a phosphorescence, but occasionally a delayed fluorescence at shorter wavelengths has also been observed.^[14–17] In the case of Cu(tripod)X complexes, the emission is certainly a phosphorescence, since it does not overlap with the absorption spectrum. Moreover, at low temperatures Cu(tripod)X complexes do not show a new long-wavelength emission, although the appearance of a phosphorescence should be favoured under these conditions.

Quantum chemical calculations were carried out for all complexes to determine the electronic character of the emission. TD-DFT calculations of the T₁-state at the T₁-geometry based on the singlet orbitals showed that the electronic character of the state is dominated by a one-electron transition from HOMO to LUMO (weight of the leading configurations > 0.95). Therefore the interpretation is based on HOMO and LUMO taken from the singlet wave function calculated at the T₁-state geometry (Figure 3).

The character of the HOMO is dominated by the d-p- π -antibonding interaction between Cu and X. Additionally, there is an antibonding interaction between the phosphane lone pair and the copper d-orbital. The LUMO is mainly localized on the phenyl rings and displays π^* character (e_{2u} benzene-type). Accordingly, the electronic character of the transition is best described as MLCT(Cu^I $\rightarrow$ phosphane) + LLCT(X[−] $\rightarrow$ phosphane). This is shown in Figure 4 for X = I, but is qualitatively very similar for the other Cu(tripod)-X complexes.

Comparison of the calculated geometries of the singlet ground state and triplet state (Table 2) shows that the main geometrical changes are due to rotations of the phenyl groups in the case of X = Br, I. The maximum rotation angles found among the phenyl groups amount to 50° and 35° for Br[−] and I[−], respectively. The rms distances of all atoms add up to 68 pm and 49 pm, respectively. The Cu–Br/Cu–I bond length is slightly shortened (2.9/3.7 pm) in the triplet state due to the depopulation of the Cu–Br/Cu–I antibonding orbital. Distortions are substantially lower in the case of X = SPh. The maximum rotation is found on the thiophenyl group and amounts to 12° (rms d = 26 pm).

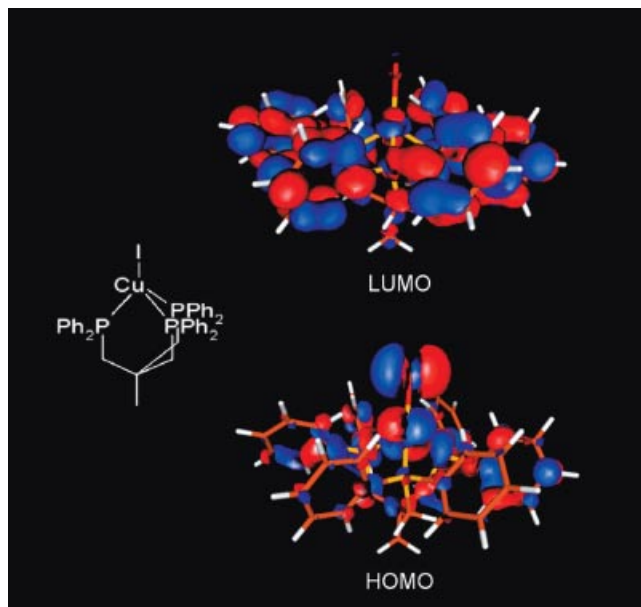


Figure 3. Frontier orbitals of Cu(tripod)I (2): HOMO (bottom) and LUMO (top).

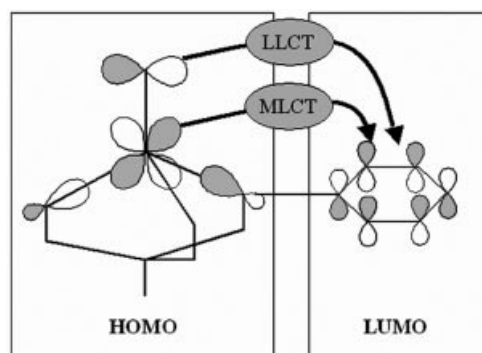


Figure 4. Schematic representation of the electronic transition. Only one of the six phenyl groups is shown.

The Cu–S bond is shortened by 4.7 pm in the triplet state. Nearly no distortions are found for X = C $\equiv$ C–Ph (rms d = 11 pm; elongation of the Cu–C bond: 3.9 pm). In all cases

Table 2. Calculated geometries of the singlet ground states and triplet states of Cu(tripod)X.

Parameter	X = I		X = Br		X = SPh		X = CCPh	
	singlet	triplet	singlet	triplet	singlet	triplet	singlet	triplet
Cu–X ^[a]	2.584	2.547	2.380	2.351	2.283	2.236	1.909	1.870
Cu–P1 ^[b]	2.307	2.310	2.301	2.358	2.323	2.306	2.319	2.317
Cu–P2 ^[b]	2.303	2.322	2.301	2.298	2.305	2.346	2.322	2.325
Cu–P3 ^[b]	2.304	2.372	2.229	2.344	2.342	2.370	2.324	2.372
max (C _{ph} –C _{ph}) ^[c]	1.416	1.425	1.416	1.416	1.414	1.420	1.413	1.415
max (phtor) ^[d]	35		50		12 ^[e]		2	
rms d ^[f]	0.49		0.68		0.26		0.11	

[a] Distance in Å. [b] Distance between Cu and P atoms of the tripod ligand in Å. [c] Maximum C–C distance in Å observed in the phenyl rings. [d] Maximum changes in torsional angles [°] of phenyl groups found on comparison of singlet and triplet geometry. [e] Thiophenyl group. [f] Root-mean-square distance variation in Å of all atoms in an alignment of singlet and triplet structure.

Table 3. Emission maxima, orbital energies and calculated dipole moments of Cu(tripod)X.

X	λ_{em} [eV] (exp.)		λ_{em} [eV] (calcd.) ^[a]		Orbital energy [eV]		Dipole [D]	
	solid	CH ₂ Cl ₂	unshifted	shifted ^[b]	HOMO	LUMO	S ₀	T ₁
Br	2.68	2.68	1.53	2.68	-3.78	-2.21	7.30	6.50
I	2.69	2.67	1.62	2.78	-3.88	-2.22	8.50	6.96
SPh	2.67	2.44	1.31	2.46	-3.46	-2.14	8.70	2.50
C≡CPh	2.67	2.61	2.00	3.16	-3.91	-1.90	8.03	5.83

[a] TD-DFT/TZVP. [b] Energies shifted by 1.16 eV to fit the emission energy of X = Br, since this method is known to yield systematical red-shifts.

there is a slight increase of the P–Cu bond length in the triplet state.

The calculated emission energies of Cu(tripod)X with X = I, Br and SPh were found to be systematically red-shifted. Therefore, we added a constant shift of 1.16 eV to facilitate a comparison with the experimental values (Table 3). This shifting behaviour may be understood by the fact that standard approximate exchange-correlation functionals suffer from an artificial stabilization of CT states due to the wrong asymptotic behaviour of the corresponding exchange-correlation functionals.^[18] We performed additional single-CI calculations (TZVP basis set) in order to determine the character of the lowest excited state for X = Br. Although this method only gives qualitative results for energies, it does not suffer from the artificial stabilization of charge-transfer states. We found that the CT state actually is the lowest-lying state in Cu(tripod)Br. Therefore, the relative TD-DFT energies should reflect the right trend. Indeed, the shifted TD-DFT energies nicely correlate with the observed phosphorescence energies of Cu(tripod)X with X = I, Br and SPh (Table 3). The red-shift observed for the thiophenolate complex is caused by a greater destabilization of the HOMO which contains a rather large sulfur contribution.

For the phenylacetylide complex, there is a distinct discrepancy between the calculated and the observed phosphorescence energies. While in comparison to other Cu(tripod)-X complexes a blue-shift is calculated, a red-shift is indeed observed. Probably, here the TD-DFT calculation fails to describe the first excited state correctly due to the problems already mentioned above. For phenylacetylide complexes, such as (PR₃)Au(C≡C-Ph),^[19] an IL (phenylacetylide) phosphorescence occurs at energies which are comparable to the calculated transition energies (Table 3). It is conceivable that contrary to the calculation, the emission of Cu(tripod)(C≡C-Ph) now originates from the phenylacetylide IL triplet, which in reality is located below the MLCT/LLCT triplet. Therefore, the artificial stabilization of the CT states may result in a qualitatively wrong picture here.

The mixed MLCT/LLCT character of the lowest-energy excited state of Cu(tripod)I does not only follow from the present calculations; it is also supported by previous calculations on related systems.^[20] Moreover, similar conclusions have been drawn for the assignment of the lowest-energy electronic transition in tetranuclear copper(I) clusters.^[6,7] In this context it should be kept in mind that the structures of Cu^I complexes in their MLCT states are planar and not tetrahedral as in their ground states.^[21–26] The rigidity of Cu(tripod)X is expected to facilitate the emission since radi-

ationless transitions are hampered when the flexibility including excited-state distortions is restricted. Indeed, all four Cu(tripod)X complexes are luminescent in solution and at room temperature (Table 1). However, in solution at room temperature the efficiency is still rather low. We suggest that the rotations of the phenyl groups at the phosphane ligand, which take place in the lowest triplet state, favour radiationless deactivations. In the solid state the phosphorescence of Cu(tripod)X is much more intense and shifts to shorter wavelengths. This is certainly a consequence of a diminished flexibility in the lattice of the solid compound. However, since the extent of structural changes in the solid state is not well defined, the calculations should be better compared with the emission spectrum in solution. While the formal assignments of MLCT/LLCT transitions are certainly appropriate, the actual amount of charge redistribution seems to be rather small as indicated by the dipole moments (Table 3). Accordingly, a distinct solvent-dependent shift is neither expected nor observed.

In conclusion, the complexes Cu(tripod)X are characterized by a blue emission, which originates from a mixed MLCT (Cu^I → tripod)/LLCT (X[−] → tripod) triplet. Owing to the rigid structure imposed by the tripod ligand, this phosphorescence appears not only in the solid state, but also at room temperature in solution.

Experimental Section

Materials: All solvents used for spectroscopic measurements were of spectrograde quality. CuBr, CuI, CuSPh, CuC≡CPh and the tripodal ligand 1,1,1-tris(diphenylphosphanylmethyl)ethane were commercially available (Aldrich and Strem) and used without further purification. The title compounds were obtained by the following synthetic routes.

Cu(tripod)Br (1): In a procedure different from the published route,^[11,27] a solution of CuBr (0.16 g, 1.1 mmol) and tripod (0.71 g, 1.1 mmol) in 40 mL of acetonitrile was refluxed for 20 min, and then cooled to room temperature. The resulting white precipitate was collected by filtration, washed with acetonitrile and diethyl ether, and dried yielding 0.77 g (88%). C₄₁H₃₉BrCuP₃ (768.12): calcd. C 64.11, H 5.12, Br 10.40; found C 64.02, H 5.06, Br 9.61.

Cu(tripod)I (2): Similar to the bromide complex **1**, a solution of CuI (0.10 g, 0.5 mmol) and tripod (0.32 g, 0.5 mmol) in 20 mL of acetonitrile was refluxed for 20 min, and then cooled to room temperature. The resulting white precipitate was collected by filtration, washed with acetonitrile and diethyl ether, and dried yielding 0.32 g (73%). C₄₁H₃₉CuIP₃ (815.12): calcd. C 60.41, H 4.82, I 15.57; found C 60.23, H 4.57, I 15.23.

Cu(tripod)SPh (3): A suspension of CuSPh (0.26 g, 1.5 mmol) and tripod (0.96 g, 1.5 mmol) in 60 mL of acetonitrile was stirred at room temperature for 10 min and then kept under reflux for 90 min. After filtration of the hot, yellowish mixture, the solution was reduced to a small volume and cooled to room temperature. The resulting white precipitate was collected by filtration, washed with ethanol, and dried to yield 0.77 g (64%). $C_{47}H_{44}CuP_3S$ (797.39): calcd. C 70.79, H 5.56, S 4.02; found C 70.26, H 4.79, S 3.38.

Cu(tripod)C≡CPh (4): According to the published procedure,^[28] a suspension of $CuC\equiv CPh$ (0.25 g, 1.5 mmol) and tripod (0.96 g, 1.5 mmol) in 60 mL of benzene was stirred at ambient temperature for 24 h. After filtration from a dark green material, the pale yellow solution was concentrated to dryness. The residue was dissolved in toluene and petroleum ether was added. The resulting slightly yellowish precipitate was isolated by filtration, washed with petroleum ether and diethyl ether, and then dried to yield 0.96 g (81%). $C_{49}H_{44}CuP_3$ (789.34): calcd. C 74.56, H 5.62; found C 74.74, H 5.64.

Instrumentation: Absorption spectra were measured with a Shimadzu 2100 spectrophotometer. Emission spectra were recorded with a Hitachi 850 spectrofluorometer equipped with a Hamamatsu 928 photomultiplier for measurements up to 900 nm.

Calculations: Geometries and energies were calculated according to the density functional theory involving the BP86 functional^[29] in combination with a split-valence basis set with polarisation functions on all heavy atoms [SV(P)]^[30]. Triplet states were optimized according to the unrestricted KS approach. Time-dependent density functional calculations were performed with the same functional in combination with a valence triple zeta basis set (TZVP^[31]). For iodine an effective core potential with relativistic corrections (ecp-46-mwb: derived from a multi-electron fit to the quasirelativistic Wood-Boring total valence energies) was employed^[32]. Resolution of identity techniques^[33] were used throughout. All calculations were carried out with the TURBOMOLE software package.^[34]

Acknowledgments

Financial support of the Regensburg group by BASF is gratefully acknowledged.

- [1] A. Vogler, H. Kunkely, *Top. Curr. Chem.* **2001**, 213, 143.
- [2] D. M. Roundhill, *Photochemistry and Photophysics of Metal Complexes*, Plenum, New York, **1994**.
- [3] J. N. Demas, B. A. DeGraff, *Coord. Chem. Rev.* **2001**, 211, 317.
- [4] H. Yersin, *Top. Curr. Chem.* **2004**, 241, 1.
- [5] C. Kutal, *Coord. Chem. Rev.* **1990**, 99, 213.
- [6] P. C. Ford, A. Vogler, *Acc. Chem. Res.* **1993**, 26, 220.

- [7] P. C. Ford, E. Cariati, J. Bourassa, *Chem. Rev.* **1999**, 99, 3625.
- [8] D. R. McMillin, K. M. McNett, *Chem. Rev.* **1998**, 98, 1201.
- [9] K. Kalyanasundaram, *Photochemistry of Polypyridine and Porphyrin Complexes*, Academic Press, London, **1992**, p. 293.
- [10] D. J. Fife, H. J. Mueh, C. F. Campana, K. W. Morse, *Acta Crystallogr., Sect. C* **1993**, 49, 1714.
- [11] L. Sacconi, S. Midollini, *J. Chem. Soc., Dalton Trans.* **1972**, 1213.
- [12] D. J. Fife, W. M. Moore, K. W. Morse, *Inorg. Chem.* **1984**, 23, 1684.
- [13] P. Comba, C. Katsichtis, B. Nuber, H. Pritzkow, *Eur. J. Inorg. Chem.* **1999**, 777.
- [14] M. T. Buckner, D. R. McMillin, *J. Chem. Soc., Chem. Commun.* **1978**, 759.
- [15] M. T. Buckner, T. G. Matthews, F. E. Lytle, D. R. McMillin, *J. Am. Chem. Soc.* **1979**, 101, 5846.
- [16] J. R. Kirchhoff, R. E. Gamache, M. W. Blaskie, A. A. Del Pagio, R. K. Lengel, D. R. McMillin, *Inorg. Chem.* **1983**, 22, 2380.
- [17] Z. A. Siddique, Y. Yamamoto, T. Ohno, K. Nozaki, *Inorg. Chem.* **2003**, 42, 6366.
- [18] A. Dreuw, M. Head-Gordon, *J. Am. Chem. Soc.* **2004**, 126, 4007.
- [19] H.-Y. Chao, W. Lu, Y. Li, M. C. W. Chan, C.-M. Che, K.-K. Cheung, N. Zhu, *J. Am. Chem. Soc.* **2002**, 124, 14696.
- [20] P. Aslanidis, P. J. Cox, S. Divanidis, A. C. Tsiapis, *Inorg. Chem.* **2002**, 41, 6875.
- [21] D. Felder, J. F. Nierengarten, F. Barigeletti, B. Ventura, N. Armaroli, *J. Am. Chem. Soc.* **2001**, 123, 6291.
- [22] C. T. Cunningham, J. J. Moore, K. L. H. Cunningham, P. E. Fanwick, D. R. McMillin, *Inorg. Chem.* **2000**, 39, 3638.
- [23] M. T. Miller, P. K. Gantzel, T. P. Karpishin, *Inorg. Chem.* **1999**, 38, 3414.
- [24] K. Shinozaki, Y. Kaizu, *Bull. Chem. Soc. Jpn.* **1994**, 67, 2435.
- [25] S. Sakaki, H. Mitsuani, Y. Kase, *Inorg. Chem.* **1992**, 31, 4375.
- [26] L. X. Chen, G. Jennings, T. Liu, D. J. Gosztola, J. P. Hessler, D. V. Scaltrito, G. J. Meyer, *J. Am. Chem. Soc.* **2002**, 124, 10861.
- [27] M. I. García-Sejío, P. Sevilano, R. O. Gould, D. Fernández-Ancá, M. E. García-Fernández, *Inorg. Chim. Acta* **2003**, 355, 206.
- [28] K. Hiraki, Y. Fuchita, Y. Morita, *Bull. Chem. Soc. Jpn.* **1978**, 51, 2012.
- [29] J. P. Perdew, *Phys. Rev. B* **1986**, 33, 8822; A. D. Becke, *Phys. Rev. A* **1988**, 36, 3098.
- [30] A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, 97, 2571.
- [31] A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, 100, 5829.
- [32] P. Schwerdtfeger, M. Dolg, W. H. E. Schwarz, G. A. Bowmaker, P. D. W. Boyd, *J. Chem. Phys.* **1989**, 91, 1762.
- [33] K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, 97, 119.
- [34] R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Cölmel, *Chem. Phys. Lett.* **1989**, 162, 165.

Received: November 17, 2004
Published Online: June 22, 2005