Photophysical properties of the photosensitizer [Ru(bpy)$_2$(5-CNphen)]$^{2+}$ and intramolecular quenching by complexation of Cu(II)

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Abstract

The lifetime of the ^{3}MLCT emitting state of [Ru(bpy)$_2$(5-CNphen)]$^{2+}$ (bpy = 2,2′-bipyridine, 5-CNphen = 5-cyano-1,10-phenanthroline) has been determined in CH$_3$CN by flash photolysis and TCSPC techniques. The obtained value, $\tau = 2.2\,\mu$s, points to its potential use as a photosensitizer in molecular devices. The transient spectrum shows that this excited state can be formulated as a metal-to-ligand charge transfer state. Static and dynamic quenching of the complex luminescence by Cu^{2+} ions is observed. The static and dynamic components were evaluated by measuring emission intensities and lifetimes at different [Cu^{2+}]. The combined quenching results point to a strong ground state complexation of Cu^{2+} ($K_{eq} = 7500\,$M^{-1} for 1:1 complex) with the nitrile group of 5-CNphen. At high [Cu^{2+}], a short-lived component of the decay has been detected, with $k_{et} = 4.0 \times 10^9\,$s^{-1}. This value is compared to the electron transfer rate constant in the encounter complex of the bimolecular quenching, which was obtained from the dynamic quenching rate constant.
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1. Introduction

Ruthenium polypyridine complexes have been extensively studied and have recently been employed for a variety of potential applications in areas, such as artificial photosynthesis [1–6], molecular electronic devices [7–11], analytical biochemistry [12–15], molecular machines [16–19] and dye sensitized photoelectrochemical cells [20]. The detection of long-lived excited states by light excitation is a desirable property for several of these applications, but especially bioanalytical devices. We recently described the preparation and physicochemical properties of a photosensitizer in this class having a cyano substituent for potential coordination to a second metal [21]: [Ru(bpy)$_2$(5-CNphen)]$^{2+}$ (bpy = 2,2′-bipyridine, 5-CNphen = 5-cyano-1,10-phenanthroline), **1**. The complex emits at room temperature in CH$_3$CN with a quantum yield and

lifetime similar to that of [Ru(bpy)$_3$]$^{2+}$. When incorporating a pentaammmineruthenim(III) as an electron acceptor group in the derived dinuclear mixed-valent complex [(bpy)$_2$Ru^{II}(5-CNphen)Ru^{III}(NH$_3$)$_5$]$^{5+}$, the emission is almost completely quenched, a fact that was attributed to a rapid metal-to-metal intramolecular electron transfer process [21]. In this work, we report on the lifetime and the nature of the lowest-energy excited state of [Ru(bpy)$_2$(5-CNphen)]$^{2+}$ and address the possibilities of having both static and dynamic quenching by Cu^{2+} ions, and of measuring the direct intramolecular electron transfer rate constant for the pre-formed complex in acetonitrile solutions at high [Cu^{2+}].

2. Results and discussion

The photophysical behavior of complex **1** was examined by transient absorption spectroscopy and by steady state and time resolved luminescence spectroscopy. The excited state difference spectrum is shown in Fig. 1 for **1** following excitation into the MLCT absorption of the complex at 450 nm. The transient

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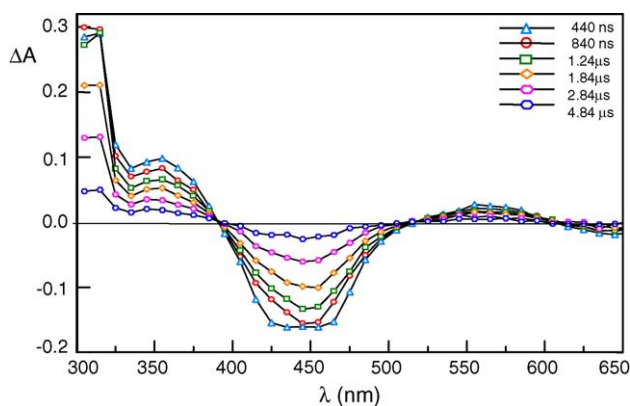*E-mail address:* nkatz@arnet.com.ar (N.E. Katz).

Fig. 1. Transient spectra at different times of $^{*}[\text{Ru(bpy)}_2(\text{5-CNphen})]^{2+}$ in CH$_3$CN, at room temperature ($\lambda_{\text{exc}} = 450$ nm).

spectrum shows strong bleaching with a minimum at 450 nm, and excited state absorption with maxima at 355 and 555 nm. The spectrum is typical of Ru(II) diimine complexes, exhibiting bleaching of the ground state MLCT absorption and excited state absorption which is typical of the diimine radical anion [3]. Since the coordinated 5-CNphen ligand has a reduction potential that is significantly more positive than bpy [21], the lowest-energy excited state can be assigned to the Ru(II) d(π) $\rightarrow$ π^{*} (5-CNphen) MLCT state. The measured lifetime in N$_2$ purged CH$_3$CN at room temperature is $\tau = 2.2\ \mu$s; a typical decay from transient absorption data and the single exponential fit of ΔA ($= A_{\text{ES}} - A_{\text{GS}}$) at 450 nm is shown in Fig. 2. The value of τ measured by time resolved emission (time correlated single photon counting) is nearly the same ($\tau = 2.0\ \mu$s), thus confirming that the excited states observed by absorption and luminescence are the same. It should be noted that τ of **1** is almost three times longer than that of [Ru(bpy)$_2$(phen)]$^{2+}$ ($\tau = 0.76\ \mu$s in CH$_3$CN at 298 K) [22], which may be related to an increase in the energy gap between the emissive ^{3}MLCT state and the metal centered (^{3}LF) state that serves as a thermally activated non-radiative decay pathway in a large number of Ru(II) diimine complexes [23]. This characteristic has been established for various Ru(II) diimine complexes that have two good sigma donating diimine ligands (i.e. bpy) and one significantly better π acceptor ligand (i.e. CNphen). It has also been established that the greater
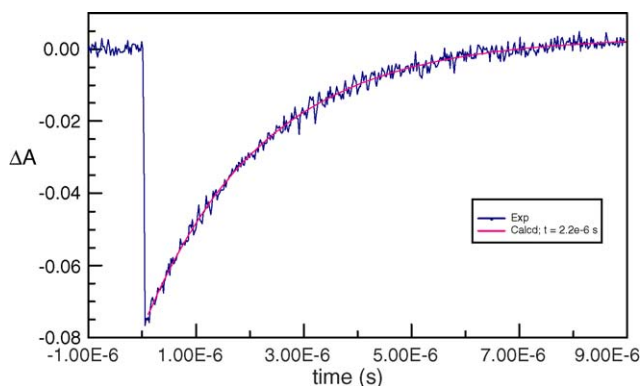
rigidity of polypyridine rings usually increases the lifetimes of MLCT excited sates in ruthenium complexes [24].

In previous work with this complex, it was found that a Ru$^{\text{III}}$(NH$_3$)$_5$ moiety covalently binds to the nitrile group of 5-CNphen and effectively quenches the emission of the ^{3}MLCT state by a factor of 5 [21]. The complex is stable in solution and has been isolated and characterized crystalographically. The observed quenching suggests that complex **1** may be useful as a sensor for metals that form labile complexes in solution by binding to the non-coordinated CN of the CNphen ligand and causing unique changes in the luminescence. In earlier work, Demas et al. illustrated that the weak emission of [Ru(bpy)$_2$(CN)$_2$] was quenched by coordination of Cu(II) to the cyano ligands directly bound to the Ru [26]. Also, examples exist of metal ion sensing in complexes exhibiting changes in chromophore MLCT emission following binding of the metal of interest to coordination sites that are remotely attached to the chromophore [25].

With this in mind, we have performed quenching experiments in CH$_3$CN with Cu^{2+}, a metal ion capable of reacting with the ^{3}MLCT state of complex **1** via energy or electron transfer. Earlier work has shown that Cu^{2+} quenches the emission of various Ru(II) diimine complexes effectively by a diffusional process in aqueous solution. In this system, there is also competitive binding of the Cu^{2+} to the CN of the CNphen ligand and the solvent. Fig. 3 shows Stern–Volmer plots for Cu^{2+} quenching obtained from luminescence intensity and lifetime data. While the lifetime dependence on [Cu^{2+}] follows classical linear Stern–Volmer behavior ($K_{\text{sv}} = 5900\ \text{M}^{-1}$; Fig. 3), the intensity quenching data exhibits a strong upward curvature. From the linear lifetime quenching Stern–Volmer plot, the second-order rate constant for bimolecular reaction of Cu^{2+} with the ^{3}MLCT state of the CNphen complex is $2.7 \times 10^9\ \text{M}^{-1}\ \text{s}^{-1}$. The Stern–Volmer constant in this system ($K_{\text{sv}} = 5.9 \times 10^3\ \text{M}^{-1}$) is almost 17 times higher than that of the Demas system ($K_{\text{sv}} = 340\ \text{M}^{-1}$ for CuSO$_4$ in H$_2$O) [26], which results not only from the longer lifetime of **1** but also by the higher quenching rate constant ($k_{\text{q}} = 2.7 \times 10^9\ \text{M}^{-1}\ \text{s}^{-1}$). The higher bimolecular quenching rate constant very likely reflects the higher redox potential difference between both metal centers in this system relative to that studied by Demas.
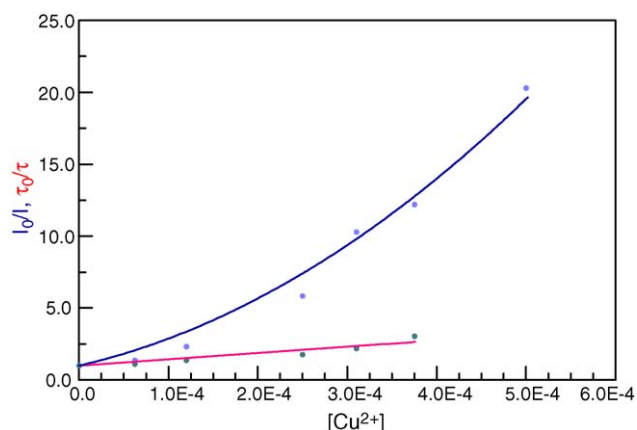

Fig. 2. Exponential fit of the time evolution of the absorbance difference for the excited state $^{*}[\text{Ru(bpy)}_2(\text{5-CNphen})]^{2+}$ at $\lambda = 450$ nm.

Fig. 3. Dependence of I_0/I and τ_0/τ for $^{*}[\text{Ru(bpy)}_2(\text{5-CNphen})]^{2+}$ on [Cu^{2+}].

The curvature in the intensity quenching data may result from formation of a ground state complex between the CNphen complex and Cu^{2+}. The intensity quenching data can then be fit to obtain an estimate of the association equilibrium constant for Cu^{2+} with the CNphen complex. If it is assumed that $[(bpy)_2Ru(phenCNCuL_n)]^{4+}$ ($L_n = CH_3CN$) is non-emissive (or at least that the quantum yield for emission is more than an order of magnitude lower than the parent complex) and that dynamic bimolecular quenching by Cu^{2+} contributes to the overall observed intensity quenching, the modified Stern–Volmer expression below can be used to obtain the equilibrium constant, K_{eq}.

$$\frac{I_0}{I} = (1 + K_{sv}[Cu^{2+}])(1 + K_{eq}[Cu^{2+}]) \tag{1}$$

The average value of K_{eq} obtained in this way is $7500\,M^{-1}$, assuming 1:1 complex formation between Cu^{2+} and the CNphen complex. The results are similar to those reported in the earlier work of Demas et al. concerning quenching of the luminescence of $[Ru(phen)_2(CN)_2]$ by Cu^{2+} in water [26], although the K_{eq} value for the CNphen complex in CH_3CN is ca. 28 times higher than the equilibrium constant for association of $Ru(phen)_2(CN)_2$ and Cu^{2+} in aqueous solution [26]. This higher affinity may be attributed to differences in solvent or possibly to the greater basicity of the free N of a CN^- group bonded to phen relative to that of a CN^- group bonded to Ru(II) [27,28]. The pK_a of $[(bpy)_2Ru(CN)_2]$ was measured by Peterson and Demas to be -0.14 in water [27]. For comparison, the pyridine of cyanopyridine was determined by Ford and Clarke to have a pK_a of 2.72 and the pK_a of the cyano moiety is therefore lower [28,30]. Thus, both the coordinated cyanide and the cyano of cyanopyridine are very weak bases in aqueous solution and the difference in binding affinity is more likely related to the relative lability of water versus acetonitrile. It is also interesting that Cu^{2+} binds well to the CNphen ligand in a coordinating solvent that is structurally similar and the association equilibrium is best expressed as a substitution of CNphen for solvent bound to Cu^{2+}.

At high $[Cu^{2+}]$, a short-lived component of the luminescence decay was detected by time correlated single photon counting, as shown in Fig. 4. A fit of this very rapidly decaying
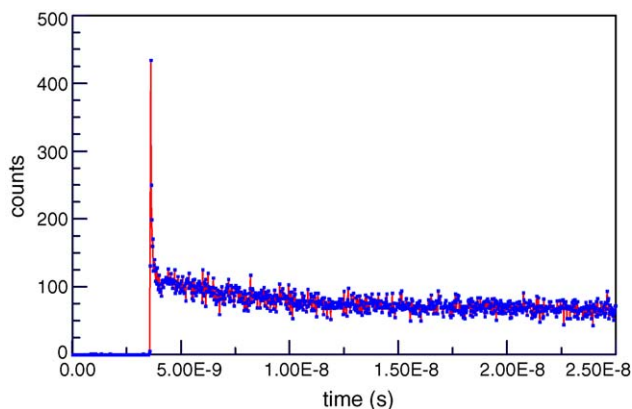

Fig. 4. Short-lived component of the luminescence decay of $^*[Ru(bpy)_2(5\text{-}CNphen)]^{2+}$ at high $[Cu^{2+}]$ (5×10^{-4} M).

portion of this emission gives $k \sim 4.0 \times 10^9\,s^{-1}$. This decay rate constant is close to the instrumental limit of our system and thus represents only a lower limit on the rate constant. This fast decay component very likely results from intramolecular electron transfer from the ^{3}MLCT excited state of the Ru(II) center to the Cu^{2+} of the bound complex; the decay constant for this emission provides a direct measure of the electron transfer rate constant, k_q, as shown in Scheme 1. Earlier, we had examined intramolecular electron transfer from a Ru to bipyridine MLCT state to Cu(II) in a complex having 4-(p-phenylphosphonic acid)-2,2′-bipyridyl bridging ligand; the Cu(II) was bound to the phosphonate; intramolecular electron transfer rate constants were measured by ps time resolved transient absorbance and were found to be 4–$8 \times 10^9\,s^{-1}$ [25]. The $[(bpy)_2Ru(CNphen)]^{2+}$ not bound to Cu^{2+} has a much longer lived decay and the decrease in the longer lifetime component with increasing $[Cu]^{2+}$ results from bimolecular quenching in solution. The bimolecular quenching rate constant measured by lifetime quenching, $2.7 \times 10^9\,M^{-1}\,s^{-1}$ (vide infra) is less than the diffusion limited value expected for the two ions in solution ($\sim 2 \times 10^{10}\,M^{-1}\,s^{-1}$).

A question that arises relates to the nature of the encounter complex formed in association of the photoexcited
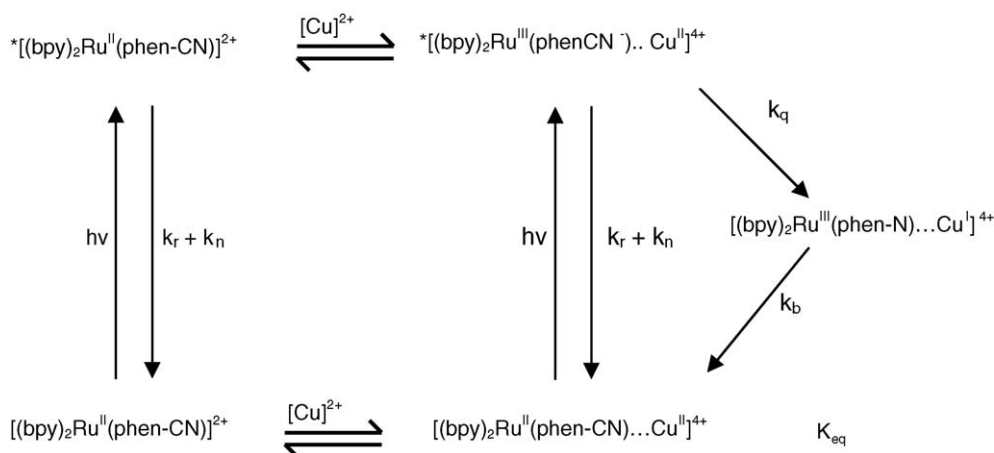
Scheme 1. Static and dynamic quenching of the luminescence of complex **1** by Cu(II).

[(bpy)$_2$Ru(CNphen)]$^{2+}$ with Cu^{2+} in CH$_3$CN in the bimolecular quenching process. For instance, does the encounter complex formed in this collisional quenching involve association of the Cu^{2+} ion with the CNphen ligand? Since, we have an approximate value of the excited state electron transfer rate constant for [(bpy)$_2$Ru(phenCNCuL_n)]$^{4+}$ from the fast component of the luminescence decay, it is worthwhile to determine an approximate value of k_{et} in the bimolecular quenching. The mechanism is presumed to involve diffusion of the ions together to form an encounter complex and electron transfer (with rate constant k_{et}) within the encounter complex. If it is assumed that the electron transfer event is sufficiently exergonic that back electron transfer to the excited state does not occur, the observed bimolecular rate constant will be related to the diffusional rate constant and k_{et} by the expression below (Eq. (2)).

$$\frac{1}{k_{obs}} = \frac{1}{k_{diff}} + \frac{1}{k_{et}K_{assoc}} \tag{2}$$

Here, k_{diff} is the rate constant for diffusion together of the ions and K_{assoc} is the equilibrium constant for their association. The value of k_{diff} can be estimated from the Debye–Smoluchowski equation (Eq. (3)) and the association equilibrium constant can be

$$k_{diff} = \left[\frac{2RT}{3000\eta}\right]\left[\frac{(r_{Ru} + r_{Cu})^2}{r_{Ru}r_{Cu}}\right]b[\exp(b) - 1]^{-1},$$
$$b = \frac{Z_{Ru}Z_{Cu}e^2}{4\pi\varepsilon_0 d\varepsilon k_b T} \tag{3}$$

approximated from the Fuoss equation (Eq. (4)). In these equations, η is the solution

$$K_{assoc} = \left[\frac{4\pi Nr^3}{3000}\right]\exp\left(\frac{Z_a Z_b e^2}{r\varepsilon k_b T}\right) \tag{4}$$

viscosity (P), r and Z represent the radii (cm) and the charge, respectively, of the two reacting ions, d the sum of the radii of the ions (cm), ε_0 the permittivity of space, ε the dielectric constant of the solvent, e the charge on the electron (C) and k_b is the Boltzman constant. Using these expressions, a value of 1.1×10^9 s^{-1} is calculated for the electron transfer rate constant in the encounter complex assuming the radii of the Ru complex and the Cu^{2+} species in solution are 8 and 2 Å, respectively. The margin of error of the value is at least a factor of 2, but it is interesting that this calculated value is somewhat lower than the lower limit value measured for the photoinduced electron transfer rate constant obtained from direct excitation of the ground state complex in which the Cu^{2+} is very likely bound to the CN of the CNphen ligand. The implication is that the outer sphere excited state electron transfer, involving collisions with random orientation, is somewhat slower than electron transfer in the CN-bridged coupled donor–acceptor complex.

To conclude, we have demonstrated that efficient association of a cyano substituent of phenanthroline between two different redox active metal centers gives rise not only to an efficient quenching of emission from the triplet excited MLCT state, but also allows the direct determination of an intramolecular electron transfer rate constant [29]. In addition, it should be noted that the long-lived emission of **1** allows its possible use as a photosensitizer in molecular devices.

3. Experimental

The complex [Ru(bpy)$_2$(5-CNphen)](PF$_6$)$_2$ was prepared by modification of a literature method [21].

Emission spectra were recorded with a Shimadzu RF-5301 PC spectrofluorometer, provided with 1-cm fluorescence cells. Solutions were purged with Ar for 15 min prior to luminescence measurements.

TCSPC and flash photolysis experiments were carried out as described before [25].

References

[1] N. Sutin, C. Creutz, Pure Appl. Chem. 52 (1980) 2717–2738.
[2] T.J. Meyer, Acc. Chem. Res. 22 (1989) 163–170.
[3] V. Balzani, F. Scandola, Supramolecular Photochemistry, Ellis Horwood, Chichester, 1991.
[4] V. Balzani, A. Juris, M. Venturi, S. Campagna, S. Serroni, Chem. Rev. 96 (1996) 759–833.
[5] V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni, M. Venturi, Acc. Chem. Res. 31 (1998) 26–34.
[6] H. Dürr, S. Bossmann, Acc. Chem. Res. 34 (2001) 905–917.
[7] A. Hatzidimitriou, A. Gourdon, J. Devillers, J.-P. Launay, E. Mena, E. Amouyal, Inorg. Chem. 35 (1996) 2212–2219.
[8] V. Balzani, A. Credi, M. Venturi, Chem. Eur. J. 8 (2002) 5525–5532.
[9] S.G. Camera, H.E. Toma, J. Photochem. Photobiol., A: Chem. 151 (2002) 57–65.
[10] J.P. Sauvage, J.P. Collin, J.C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola, L. Flamigni, Chem. Rev. 94 (1994) 913–993.
[11] M.K. Brennaman, J.H. Alstrum-Acevedo, C.N. Fleming, P. Jang, T.J. Meyer, J.M. Papanikolas, J. Am. Chem. Soc. 124 (2002) 15094–15098.
[12] A.E. Friedman, J.C. Chambron, J.P. Sauvage, N.J. Turro, J.K. Barton, J. Am. Chem. Soc. 112 (1990) 4960–4962.
[13] Y. Jenkins, A.E. Friedman, N.J. Turro, J.K. Barton, Biochemistry 31 (1992) 10809–10816.
[14] R.E. Holmlin, E.D.A. Stemp, J.K. Barton, Inorg. Chem. 37 (1998) 29–34.
[15] L. Li, H. Szmacinski, J.R. Lakowicz, Anal. Biochem. 244 (1997) 80–85.
[16] J.-P. Sauvage, Acc. Chem. Res 31 (1998) 611–619.
[17] V. Balzani, M. Gomez-Lopez, J.F. Stoddart, Acc. Chem. Res. 31 (1998) 405–414.
[18] V. Balzani, A. Credi, F.M. Raymo, J.F. Stoddart, Angew. Chem., Int. Ed. 39 (2000) 3348–3391.
[19] J.F. Stoddart, Acc. Chem. Res. 34 (2001) 410–411.
[20] M.K. Nazeeruddin, S.M. Zakeeruddin, J.-J. Lagref, P. Liska, P. Comte, M. Graetzel, C. Barolo, G. Viscardi, K. Schenk, Coord. Chem. Rev. 248 (2004) 1317–1328.

[21] M.G. Mellace, F. Fagalde, N.E. Katz, I.G. Crivelli, A. Delgadillo, A.M. Leiva, B. Loeb, M.T. Garland, R. Baggio, Inorg. Chem. 43 (2004) 1100–1107.

[22] F. Wu, E. Riesgo, A. Pavalova, R.A. Kipp, R.H. Schmehl, R.P. Thummel, Inorg. Chem. 38 (1999) 5620–5628.

[23] W.M. Wacholtz, R.A. Auerbach, R.H. Schmehl, M. Ollino, W.R. Cherry, Inorg. Chem. 24 (1985) 1758–1760.

[24] J.A. Treadway, B. Loeb, R. Lopez, P.A. Anderson, F.R. Keene, T.J. Meyer, Inorg. Chem. 35 (1996) 2242–2246.

[25] M. Montalti, S. Wadhwa, W.Y. Kim, R.A. Kipp, R.H. Schmehl, Inorg. Chem. 39 (2000) 76–84.

[26] J.N. Demas, J.W. Addington, S.H. Peterson, E.W. Harris, J. Phys. Chem. 81 (1977) 1039–1043.

[27] S.H. Peterson, J.N. Demas, J. Am. Chem. Soc. 101 (1979) 6571–6578.

[28] R.E. Clarke, P.C. Ford, Inorg. Chem. 9 (1970) 495–499.

[29] P.F. Barbara, T.J. Meyer, M.A. Ratner, J. Phys. Chem. 100 (1996) 13148–13168.

[30] A.P. Szecsy, S.S. Miller, A. Haim, Inorg. Chim. Acta 28 (1978) 189–200.