

Figure 2. Ground-state (a) and excited-state (b) CD spectra of Ru(bpy)₃²⁺ taken with the transient CD apparatus.¹ The ground-state spectrum is in excellent agreement with the previously reported spectrum taken with a conventional CD spectrometer.¹⁹ The excited-state spectrum is the average of 64 measurements of signals in a window from 10 to 70 nm after the laser pulse. Sufficient laser power was used to ensure complete ground-state depletion.

a spectrum taken on a conventional CD spectrometer.¹⁹ Note that each point in the spectrum represents a total of 3.2- μ s exposure time. The comparable spectrum taken on a conventional CD spectrometer would require a time constant on the order of 1 s. Work is now proceeding to incorporate a photodiode array detection system to facilitate more efficient collection of CD spectra.

Figure 2b is the excited-state CD spectrum obtained by averaging signals for 60 ns after the laser pulse. Sufficient laser power was used to ensure complete depletion of the ground state as determined by the laser power dependence of the signal. There is no postlaser CD signal within experimental error ($|\Delta\epsilon| \leq 2$) from 450 to 480 nm, a region that lacks significant excited-state absorption. The transient absorption reported by Creutz et al.¹⁰ at 420 nm shows no significant circular dichroism. The CD of the 370-nm transient absorption is very small ($\Delta\epsilon \approx 3$), while a moderate CD is observed centered at 312 nm ($\Delta\epsilon \approx -15$).^{9,10}

The near-zero magnitude of the 370-nm band is consistent with a single ligand localized $\pi^*\pi^*$ transition. This CD is even less than that reported for the single phen localized $\pi\pi^*$ transition of Co(en)₂(phen)⁺ ($\Delta\epsilon \approx 10$).¹⁸ The moderate CD at 315 nm does not persist into the red, though the excited-state absorption is reported to go as far as 330 nm.¹⁰ Hence the CD implies that the absorption band consists of at least two transitions, one being much more strongly CD active than the other. The magnitude of the $\Delta\epsilon$ of this CD-active band is on the order of the interligand $\pi\pi^*$ CD of the ground-state absorption of Co(bpy)₂(NO₂)₂.¹⁷ Moreover, the transition occurs in a region in which bipyridyl ligand $\pi\pi^*$ transitions are seen. Hence, we tentatively assign this band as interligand $\pi\pi^*$ absorption of the two unreduced ligands. However, a LMCT $d^5\pi^* \rightarrow d^6\pi\pi^*$ transition is also expected to occur in the transient spectrum and this assignment cannot be ruled out. Taken together, our assignments support previous descriptions of the lowest MLCT excited state of Ru(bpy)₃²⁺ as having the transferred electron localized on a single ligand.^{10,20-23}

(19) Gillard, R. D.; Hill, R. E. E.; Muskill, R. *J. Chem. Soc. A* 1970, 707.

(20) Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* 1979, 101, 4391.

Acknowledgment. We thank Dr. V. Miskowski for useful discussions of this work and J. Smallberries for the loan of an oscillation overthrunder. We also thank the National Institutes of Health for financial support under Grants EY00983 and GM35158.

(21) Bradley, P. G.; Kress, N.; Hornberger, B. A.; Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* 1981, 103, 7441.

(22) Kober, E. M.; Sullivan, B. P.; Meyer, T. *J. Inorg. Chem.* 1984, 23, 2098.

(23) Carlin, C. M.; DeArmond, M. K. *J. Am. Chem. Soc.* 1985, 107, 53.

Electron Transfer through Aromatic Spacers in Bridged Electron-Donor-Acceptor Molecules

H. Heitele and M. E. Michel-Beyerle*

Institut für Physikalische und Theoretische Chemie, Technische Universität München 8046 Garching, Federal Republic of Germany

Received May 7, 1985

Recently, linked electron-donor-acceptor systems¹ have been shown to be useful for a critical test of mechanisms and theories of electron-transfer processes.² Among the factors, which determine the rates of electron-transfer processes, are the exothermicity of the reaction, the distance between donor and acceptor, and the nature of the medium or of the spacer between them.

The question of interest in this paper is the potential influence of the spacer between electron donor and electron acceptor on the electron transfer.³

With this goal we synthesized⁴ four linked donor-acceptor compounds (1-4), in which dimethylaniline acts as the donor and (excited) pyrene or anthracene as the acceptor.

Because of the possible rotations around the σ -bonds at the methylene groups, the absolute distance between donor and acceptor is not fixed,⁵ whereas the difference of the distances in the biphenyl bridged (2, 4) compared with the phenyl bridged compounds (1, 3) is definite (4 Å).

The fluorescence lifetimes of the compounds (1-6, Figure 1) were measured by time-resolved photon counting. The pyrene or anthracene moiety was excited at a wavelength of 337 nm by using a flashlamp (ORTEC 9362) with a pulse width of 2.7 ns (fwhm). At this wavelength, the absorption of the dimethylanilino group and of the spacers is negligible. Singlet energy transfer from excited pyrene or anthracene to the dimethylanilino group is impossible for energetic reasons. In time-resolved experiments, the fluorescence light was not spectrally resolved except by the

(1) (a) Joran, A. D.; Leland, B. A.; Geller, G. G.; Hopfield, J. J.; Dervan, P. B. *J. Am. Chem. Soc.* 1984, 106, 6090-6092. (b) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* 1984, 106, 3047-3049. (c) Wasielewski, M. R.; Niemczyk, M. P. *J. Am. Chem. Soc.* 1984, 106, 5043-5045. Wasielewski, M. R.; Niemczyk, M. P.; Pewitt, E. P. *J. Am. Chem. Soc.* 1985, 107, 1080-1082.

(2) (a) Marcus, R. A. *J. Chem. Phys.* 1964, 43, 679-701. (b) Kestner, N. R.; Logan, J.; Jortner, J. *J. Phys. Chem.* 1974, 78, 2148-2166. (c) Van Duyne, R. P.; Fischer, S. F. *J. Phys. Chem.* 1974, 78, 183-197. (d) Ulstrup, J. "Charge Transfer Processes in Condensed Media"; Springer-Verlag: Berlin, 1979; and references therein. (e) Newton, M. O.; Sutin, N. *Annu. Rev. Phys. Chem.* 1984, 35, 437-480 and references therein.

(3) (a) McConnell, H. M. *J. Chem. Phys.* 1961, 35, 508-515. (b) Kuznetsov, A. M.; Ulstrup, J. *J. Chem. Phys.* 1981, 75, 2047-2055 and references therein. (c) Larson, S. *J. Am. Chem. Soc.* 1981, 103, 4034-4040. (d) Fischer, S. F.; Nussbaum, I. In "Antennas and Reaction Centres of Photosynthetic Bacteria; Structure, Interaction and Dynamics"; Michel-Beyerle, M. E., Ed.; Springer: Berlin, in press.

(4) Heitele, H.; Michel-Beyerle, M. E.; Wegner, G., manuscript in preparation.

(5) In the most extended conformation the donor-acceptor distances are 7.5 and 11.5 Å from edge to edge.

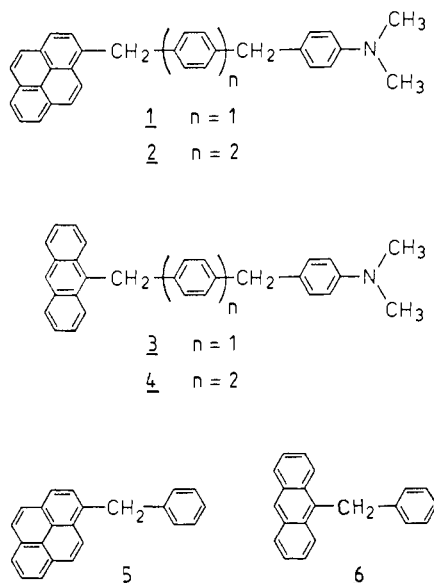


Figure 1. Bridged donor-acceptor systems 1-4 and reference substances 5,6.

Table I. Fluorescence Lifetimes in Hexane (τ_{hex}) and Acetonitrile (τ_{MeCN}) and Intramolecular Electron Transfer Rates (k_{ET}) in Acetonitrile^a

compd	τ_{hex} , ns	τ_{MeCN} , ns	$k_{\text{ET}} \times 10^{-8}$, s ⁻¹
1	274 ± 15	1.2 ± 0.1 ^b	8.3 ± 0.7
2	279 ± 15	28.5 ± 1.5	0.30 ± 0.02
3	4 ± 0.2	0.13 ± 0.03 ^b	76 ± 18
4	4.3 ± 0.2	2.1 ± 0.1	3.4 ± 0.3
5	287 ± 10	204 ± 7	
6	4.4 ± 0.2	7.5 ± 0.4	

^aAverages and error limits result from two or three measurements each. ^bMeasurements together with Dr. W. Rettig at the Berliner Elektronensynchrotron (Bessy).

use of a filter to cut off light with a wavelength shorter than 390 nm. The measurements were performed in hexane and acetonitrile at room temperature. The samples were deoxygenated by several thaw-freeze-pump cycles. The concentrations used were 1-5 × 10⁻⁵ M; to eliminate excimer or exciplex formation in the samples with long fluorescence lifetimes, the concentrations were varied between 10⁻⁵ and 10⁻⁴ M and the lifetimes were obtained by extrapolation to infinite dilution according to the Stern-Volmer relation. The intermolecular quenching constant for compounds 1 and 2 in hexane was found to be (1.6 ± 0.2) × 10¹⁰ M⁻¹ s⁻¹. The fluorescence decay was single exponential in all cases. The results are compared with the reference substances (5, 6) and are summarized in Table I.

In the nonpolar solvent hexane, the lifetimes of the donor-acceptor systems are identical with those of the corresponding reference substances, whereas in acetonitrile a strong quenching of the fluorescence is observed, depending on the donor-acceptor distances. No evidence of an (intramolecular) exciplex emission was found.

Given the well-known properties of a homogeneous solution of anthracene- and pyrene/dimethylaniline in various solvents,⁶ the fluorescence quenching in acetonitrile is interpreted as intramolecular electron transfer. The corresponding rates, summarized in Table I, are obtained from the fluorescence quenching data by using the relation: $k_{\text{ET}} = \tau^{-1} - \tau_{\text{ref}}^{-1}$ with k_{ET} = electron-transfer rate, τ = lifetime of the bridged compound, and τ_{ref} = lifetime of the reference substance.

(6) Knibbe, H.; Staerk, H.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1968**, *72*, 257-263. Rehm, D.; Weller, A. *Z. Phys. Chem. Neue Folge* **1970**, *69*, 183-200.

The free enthalpies ΔG of the electron transfer in hexane and acetonitrile are approximately +1.1 and -0.5 eV⁷ for the pyrene as well as the anthracene derivatives. This explains the absence of intramolecular quenching in hexane.

The most important result for both bridged systems is the decrease of the rate by a factor of 22 to 27 when the distance is increased by 4 Å. This is in striking contrast to recent experimental findings^{1a} in systems using an aliphatic spacer. In this case, an increase of the distance by 4 Å leads to a decrease of the rate by a factor of at least 100.

We attribute the large difference of this ratio for aromatic and aliphatic spacers to the occurrence of electron transfer via superexchange^{3a,c} which is mediated by the spacer. If for phenyl- and biphenyl-bridged compounds the superexchange mechanism holds, theory in its most elementary form predicts that $k_{\text{ET}}(2)/k_{\text{ET}}(1) = k_{\text{ET}}(4)/k_{\text{ET}}(3) \approx (\beta/\Delta E)^2$, where β is the resonance integral between the spacer units and ΔE corresponds to the (average) energy difference between the spacer and the donor and acceptor states. Our experimental data for $k_{\text{ET}}(2)/k_{\text{ET}}(1)$ imply, that for our aromatic spacer $|\beta/\Delta E| \approx 1/5$. On the other hand, for aliphatic spacers one expects^{3a} considerably smaller values for $|\beta/\Delta E|$, accounting for their lower efficiency in mediating electron transfer.

The superexchange for the aromatic spacers phenyl and biphenyl involves the participation of (virtual) anionic and/or cationic states of the bridging elements which correspond to the (formal) structures donor-spacer⁺-acceptor⁻ (I) or donor⁺-spacer⁻-acceptor* (II). The charge transfer in these (virtual) states does not imply a corresponding internal or solvent reorganization (except electronic polarization). The value of ΔE for structure I can then be approximated as the energy difference between structure I and excited I using a Born-Haber cycle: $\Delta E \sim \text{IP} - \text{EA} + P + C - \Delta E^*$, where IP = gas phase ionization potential of the spacer, EA = electron affinity of the acceptor, P = electronic polarization energy of the medium for structure I, ΔE^* = excitation energy ($S_0 \rightarrow S_1$) of the acceptor, and C = Coulomb energy of structure I. This relation gives $\Delta E \sim 1-1.5$ eV for structure I; an analogous estimate for structure II yields $\Delta E \sim 4-5$ eV.⁸ These simple energetic considerations indicate that the energy difference ΔE involving structure I is considerably lower than that of structure II. Thus, the contribution of hole transfer to the superexchange mechanism should be predominant. Furthermore, $\Delta E \sim 1-1.5$ eV suggests $\beta \sim 0.2-0.3$ eV for the exchange integral between the two phenyl rings of the biphenyl spacer.

Our results demonstrate the participation of specific spacers in electron-transfer processes. The superexchange mechanism will be put to test by changing the energy levels of the spacer at a fixed donor-acceptor distance. Measurements with such modified compounds are in progress.

Acknowledgment. We are highly indebted to Dr. Jürgen Vogel and Prof. S. Schneider in this institute for the kind permission to use their single-photon-timing apparatus for the lifetime measurements. It is also a pleasure to thank Prof. J. Jortner, Tel

(7) ΔG is calculated from the excitation energy ΔE^* of the acceptor, the electrochemical reduction potential $E_0(A/A^-)$ of the acceptor, the oxidation potential $E_0(D/D^+)$ of the donor, the Coulomb energy C of the ion pair, and (in hexane) a correction for the solvation energy ΔP in different solvents: $\Delta G = E_0(D/D^+) - E_0(A/A^-) - \Delta E^* + C (+ \Delta P)$. For D = N,N-dimethyl-p-toluidine, $E_0(D/D^+) \approx +0.7$ eV; A = 9-methyl-anthracene, $\Delta E^* = 3.2$ eV, $E_0(A/A^-) \approx -2.0$ eV; A = 1-methyl-pyrene, $\Delta E^* = 3.3$ eV, $E_0(A/A^-) \approx -2.1$ eV (redox potentials measured in MeCN versus SCE); in MeCN C > -0.05 eV, in hexane $\Delta P + C \sim 1.6$ eV; see also: Schulz, M. Dissertation, Göttingen, 1974. Weller, A. *Z. Phys. Chem. Neue Folge* **1982**, *133*, 93-98.

(8) Estimate of ΔE for structure I of compound 1: IP ~ 8.5 eV (for p-xylylene), EA ~ 0.6 eV (for pyrene), $\Delta E^* \approx 3.3$ eV; C = $-e^2/d\epsilon \sim -1.3$ eV, d ≈ 6 Å (=center to center distance between pyrene and the phenyl spacer), $\epsilon \sim 1.8$ (=optical dielectric constant of MeCN); P = $e^2/2(r_+^{-1} + r_-^{-1})(\epsilon^{-1} - 1) \sim -2.2$ eV, $r_+ \approx r_- \approx 3\text{Å}$ (=effective radii of the ion); this gives $\Delta E \sim 1.1$ eV. For structure II: $\Delta E \sim \text{IP} - \text{EA} + P + C$ with IP ~ 7.1 eV (for the donor dimethylaniline), EA ~ -1.4 eV (for the phenyl spacer), C ~ -1.6 eV, P ~ -2.5 eV; this gives $\Delta E \sim 4.4$ eV. Values for IP and EA were taken from: Gutmann, F.; Lyons, L. E. "Organic Semiconductors"; Wiley: Inc.: New York, 1967.

Aviv, for stimulating and helpful discussions of the results. Financial support from the Deutsche Forschungsgemeinschaft and the Stiftung Volkswagenwerk as well as the Alfred Krupp von Bohlen und Halbach-Stiftung is gratefully acknowledged.

Pyrophosphate Formation via a Phosphoramidate Intermediate in Polyammonium Macrocycle/Metal Ion-Catalyzed Hydrolysis of ATP

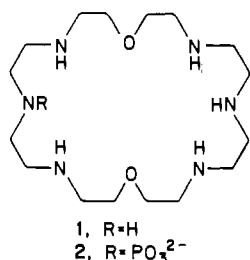
P. G. Yohannes, Mathias P. Mertes,[†] and Kristin Bowman Mertes*

Departments of Chemistry and Medicinal Chemistry
University of Kansas, Lawrence, Kansas 66045

Received July 1, 1985

The ATP phosphotransferases, hydrolases, and synthetases, crucial enzymes in the biological energy cycle, often require mono- or divalent metal ions in order to carry out their function.¹ A major portion of the model studies have therefore focused on metal-ATP interactions to elucidate the role of the metal ion.² More recently, models for the enzyme substrate reaction were examined employing polyammonium macrocycles and ATP.³ By melding the two foci, a metal-ATP-polyammonium macrocycle system which even more closely resembles its biological counterpart has been examined in this laboratory. The results of these initial studies, in which not only enhanced rates of ATP hydrolysis but also the formation of pyrophosphate are observed, are described herein.

The hexaazadioxo macrocycle, [24]-N₆O₂ (**1**) catalyzes the



hydrolysis of ATP at pH 7.6 via the formation of the intermediate phosphoramidate species **2**, which subsequently hydrolyzes to give inorganic phosphate.³ This macrocycle has also been found to mediate in the formation of pyrophosphate during the hydrolysis of acetyl phosphate.⁴

The investigation of the effect of the biologically significant metal ions, Ca(II), Mg(II), and Zn(II), added to **1** in this laboratory has revealed a striking metal-dependent influence on ATP

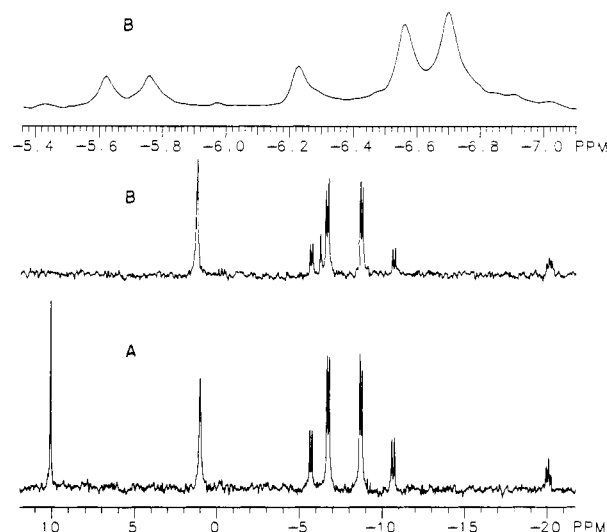


Figure 1. ³¹P NMR of 0.010 M ATP, 0.015 M [24]-N₆O₂-6HBr (**1**-6HBr), and 0.015 M CaBr₂ in 10% D₂O/H₂O at pH 4.5 and 22 °C: (A) at 22 °C with pH adjusted to 4.5 after partial hydrolysis for 38 min at 70 °C at pH 7.6; (B) after 24 h at pH 4.5 at 22 °C. The chemical shift assignments: ATP, α, -10.71, β, -20.12, γ, -5.72; ADP, α, -8.72, β, -6.75; pyrophosphate, -6.22; orthophosphate and AMP +1.0; and phosphoramidate **2**, +10.07 ppm relative to an external standard of 85% H₃PO₄.

Table I. Observed First-Order Rate Constants for the Hydrolysis of ATP and the Maximum Observed Concentrations of the Phosphoramidate **2** in a Solution Containing 0.010 M ATP and 0.015 M [24]-N₆O₂ (**1**) at pH 7.6 and 70 °C upon the Addition of 0.015 M Divalent Metal Bromides^a

MBr ₂ addtns	k _{obsd} , min ⁻¹	2 , M (min) ^b
none	0.023	0.0021 (25)
MgBr	0.023	0.0030 (36)
CaBr ₂	0.043 ^c	0.0035 (17)
ZnBr ₂	0.0039	0.0013 (60)

^aSolutions (0.5 mL) in a 5-mm NMR tube were heated to 70 °C in the NMR probe (Varian XL 300). ³¹P NMR integrals were measured from the proton-decoupled spectra programmed for 450 acquisitions (6 min) spaced by 1 min. The integral values and the observed rate constants are accurate to ±10%. ^bThe maximum observed concentration of the transient phosphorylated macrocycle **2** as determined from the ³¹P NMR integral for this species at +10.0 ppm relative to an external standard of 85% H₃PO₄. ^cCalcium phosphate precipitated at this pH.

hydrolysis and on the formation of the phosphoramidate **2** and pyrophosphate. Partial hydrolysis of ATP in a reaction solution of ATP, [24]-N₆O₂-6HBr (**1**-6HBr),⁵ and CaBr₂ in a ratio of 0.67:1:1 at pH 7.6 gave a mixture containing approximately 10% AMP, 70% ADP, and 20% ATP after approximately 35 min at 70 °C. At this point 50% of the phosphate derived from the hydrolysis reaction was present as the phosphorylated ligand **2** and no pyrophosphate peak was observed in the ³¹P NMR spectrum when the pH of the mixture was adjusted to 4.5, in order to dissolve precipitated calcium salts. After standing 24 h at room temperature, the phosphoramidate peak was absent, and, in addition to the formation of inorganic phosphate, approximately 10% of this intermediate was converted to pyrophosphate (Figure 1). The possibility that the pyrophosphate results from attack of water on ATP is unlikely, since it is also formed when no ATP is present in the solution.

While the addition of both Ca(II) and Mg(II) increased the observed percentage of the phosphoramidate **2**, only Ca(II) provided a significant rate acceleration in ATP hydrolysis (Figure 2, Table I), almost doubling the first-order rate constant compared to that of the macrocycle alone. This increase cannot be attributed

[†]Department of Medicinal Chemistry.

(1) (a) Amzel, L. M.; Pedersen, P. L. *Annu. Rev. Biochem.* **1983**, *52*, 801-824. (b) Cohn, M. *Acc. Chem. Res.* **1982**, *15*, 326-332. (c) Eichorn, G. L. *Met. Ions Biol. Syst.* **1980**, *10*, 1-21. (d) Mildvan, A. S. *Adv. Enzymol. Relat. Areas Mol. Biol.* **1979**, *49*, 103-126. (e) Marzilli, L. G. *Prog. Inorg. Chem.* **1977**, *23*, 255-378. (f) Cooperman, B. S. *Met. Ions Biol. Syst.* **1976**, *5*, 79-126.

(2) (a) Milburn, R. M.; Gautam-Basak, M.; Tribolet, R.; Sigel, H. *J. Am. Chem. Soc.* **1985**, *107*, 3315-3321. (b) Bose, R. N.; Cornelius, R. D.; Viola, R. E. *Inorg. Chem.* **1984**, *23*, 1181-1182. (c) Jones, D. R.; Lindoy, L. F.; Sargeson, A. M. *J. Am. Chem. Soc.* **1984**, *106*, 7807-7819. (d) Sigel, H. *Pure Appl. Chem.* **1983**, *55*, 137-144. (e) Sigel, H. In "The Coordination Chemistry of Metalloenzymes"; Bertini, I., Drago, R. S., Luchinat, C. E., Eds.; D. Reidel: Dordrecht, Holland, 1983; pp 65-78. (f) Ramirez, F.; Maracek, J. F. *Pure Appl. Chem.* **1980**, *52*, 2213-2227. (g) Cleland, W. W.; Mildvan, A. S. In "Advances in Inorganic Biochemistry"; Eichorn, G. L., Marzilli, L. G., Eds.; Elsevier/North-Holland: New York/Amsterdam, 1979; Vol. 1, pp 163-191. (h) Imamura, T.; Hinton, D. M.; Bedford, R. L.; Gumpfort, R. I.; Haight, G. P. *J. Inorg. Biochem.* **1979**, *11*, 241-259. (i) Suzuki, S.; Higashiyama, T.; Nakahara, H. *Bioinorg. Chem.* **1978**, *8*, 277-289. (j) Selwyn, M. J. *Nature (London)* **1968**, *219*, 490-493. (k) Miller, D. L.; Westheimer, F. H. *J. Am. Chem. Soc.* **1966**, *88*, 1514-1517.

(3) Hosseini, M. W.; Lehn, J.-M.; Mertes, M. P. *Helv. Chim. Acta* **1983**, *66*, 2454-2466.

(4) Hosseini, M. W.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* **1985**, 1155-1157.

(5) Comarmond, J.; Plumeré, P.; Lehn, J.-M.; Agnus, Y.; Louis, R.; Weiss, R.; Kahn, O.; Morgenstern-Badarau, I. *J. Am. Chem. Soc.* **1982**, *104*, 6330-6340.