Molecular "Light Switch" for DNA: $Ru(bpy)_2(dppz)^{2+}$

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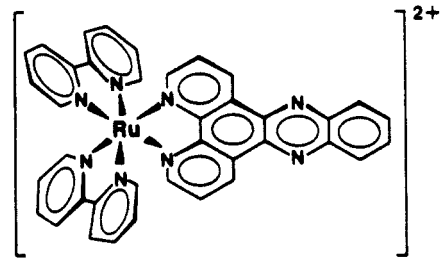
Received January 8, 1990

Considerable research has focused on the development of nonradioactive probes for nucleic acids.[1] On the basis of the well-characterized photophysical properties of ruthenium polypyridyls,[2] we earlier developed $Ru(phen)_3^{2+}$ (phen = 1,10-phenanthroline) and its derivatives as spectroscopic probes for DNA structure.[3-5] Extensive photophysical studies[4] indicate that $Ru(phen)_3^{2+}$ bound to double-helical DNA displays an increase in luminescence owing to intercalation; emission from the metal-to-ligand charge transfer (MLCT) excited state decays as a biexponential with one lifetime of 2 μs attributed to the intercalative form and a second lifetime of 0.6 μs (indistinguishable from the free species) assigned to the surface-bound form.[6] This enhancement in luminescence, coupled to shape- and symmetry-selective binding, has been useful in probing nucleic acid conformations and in the development of new phototherapeutics.[4,7,8] However, the background luminescence of the free form, the relatively weak binding, and the extent of enhancement on binding appeared insufficient for the broader application of the ruthenium complexes as general nonradioactive nucleic acid probes. Here we report the application of a novel transition-metal complex as a true molecular "light switch" for DNA. This probe is $Ru(bpy)_2(dppz)^{2+}$ (bpy = 2,2′-bipyridine, dppz = dipyrido[3,2-*a*:2′,3′-*c*]phenazine),[9] which shows no photoluminescence in aqueous solution at ambient temperatures, but displays intense photoluminescence in the presence of double-helical DNA, to which the complex binds avidly.[10]

Table I. Luminescence[a] of $Ru(bpy)_2(dppz)^{2+}$ in the Absence and Presence of Polynucleotides

solvent	DNA[b]	rel luminescence[c] (steady state)	λ_{em},[d] nm	τ,[e] ns
H_2O		0.0		
50 mM NaCl/5 mM Tris, pH 7.0		0.0		
2-propanol		1.0	622	210
methanol		0.23	610	30
50 mM NaCl/5 mM Tris, pH 7.0	calf thymus	0.61	632	75, 259
50 mM NaCl/5 mM Tris, pH 7.0	poly[d(GC)]	0.72	628	75, 250
50 mM NaCl/5 mM Tris, pH 7.0	poly[r(AU)]	0.09	650	
20 mM NaCl/2 mM Tris, pH 7.0/4 μM $Co(NH_3)_6^{3+}$	Z-poly[d(GC)]	0.79	640	
20 mM NaCl/2 mM Tris, pH 7.0/4 μM $Co(NH_3)_6^{3+}$	calf thymus	0.61	632	

[a] All measurements were conducted at 25 °C with $Ru(bpy)_2(dppz)^{2+}$ at 10 μM. [b] The concentration of DNA used was 100 μM nucleotides. [c] The luminescence spectra were measured by using an SLM 8000C spectrofluorimeter with excitation at 482 nm. Values are given for the maximum intensity found relative to that found in 2-propanol at 622 nm. [d] Wavelength with maximum emission (uncorrected for photomultiplier tube response) upon excitation at 482 nm. [e] Emission lifetimes were determined by deconvolution of biexponential decay traces in single photon counting experiments as described previously.[4] Values given have an estimated uncertainty of 10%.



$Ru(bpy)_2(dppz)^{2+}$ appeared to be a prime candidate for application as a spectroscopic probe for nucleic acids owing to its shape[7] and the sensitivity of its excited-state properties to environment.[9] While the complex does not luminesce in aqueous solution, it shows appreciable solvatochromic luminescence in ethanol (λ_{exc} = 482 nm, λ_{em} = 610 nm), acetonitrile (λ_{exc} = 482 nm, λ_{em} = 615 nm) and 2-propanol (λ_{exc} = 482 nm, λ_{em} = 622 nm) (Table I). Electrochemical and photophysical measurements of $Ru(bpy)_2(dppz)^{2+}$ in its ground and excited states show that the charge transfer is directed from the metal center to the phenazine ring, and the major nonradiative deactivation pathway for the complex likely involves the protonation of the phenazine nitrogen atoms in the excited state.[9] Not surprisingly owing to the extended planar structure of the dppz ligand[7c] and in contrast to $Ru(bpy)_3^{2+}$,[4] $Ru(bpy)_2(dppz)^{2+}$ binds to double-helical DNA by intercalation; topoisomerase assays[11] indicate an unwinding angle of 30 ± 11° per ruthenium bound. Given the preferential charge transfer onto the intercalating dppz ligand, the luminescence of the bound complex therefore provides a sensitive reporter of its helical environment.

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Preparations[9,12] of $Ru(bpy)_2(dppz)^{2+}$ (10 μM) in buffered aqueous solutions show no detectable luminescence. In the presence of 100 μM calf thymus DNA, however, luminescence, with emission centered at 632 nm and comparable in intensity to that found in 2-propanol (where $\Phi \geq 0.02$),[13] is apparent (Table I). For comparison, $\Phi(Ru(bpy)_3^{2+}) = 0.042$ for photoluminescence in aqueous solution,[2] both in the presence of DNA and in its absence; there is no detectable spectroscopic perturbation for $Ru(bpy)_3^{2+}$ by DNA under physiological conditions. Single photon counting experiments at 25 °C reveal a biexponential decay of emission from $Ru(bpy)_2(dppz)^{2+}$ bound to DNA with a short-lived component of 75 ns and a longer lived component of 259 ns.[14] As with $Ru(phen)_3^{2+}$,[4] the anionic solution quencher of the ruthenium complex, $Fe(CN)_6^{4-}$, preferentially quenches the short-lived component; we therefore assign the longer lived component as the less accessible, tightly intercalated form.[15]

The extent of enhancement on DNA binding is perhaps best illustrated in steady-state luminescence experiments (Figure 1). In the presence of 100 μM poly[d(GC)·d(GC)] (B form), intense emission centered at 628 nm is observed, whereas in the absence of polynucleotide, no emission is detectable. We estimate from our limits of detection the enhancement factor upon binding to DNA to be $>10^4$. Similar results are evident with Z-form poly[d(GC)·d(GC)]; here the relative intensity is still greater and the emission maximum is shifted to 640 nm.[16] Interestingly, only weak emission (λ_{em} = 650 nm) is apparent in the presence of poly[r(AU)·r(AU)], an A-form helical polymer. Given that $Ru(phen)_3^{2+}$ does not appear to intercalate into synthetic double-stranded RNA (there is no long-lived luminescent component in emission, for example),[4] these results suggest that it may be the tightly intercalated interaction that is primarily responsible for preserving emission in the dppz complex.

These results point also to the selective nature of $Ru(bpy)_2(dppz)^{2+}$ as a molecular switch, responding sensitively to the subtle changes in the structure of the helix. As can be seen in Table I, variations as a function of DNA substrate are detected not only in the intensity of photoluminescence but also in the emission maximum. With B-form polymers, poly[d(GC)·d(GC)] and mixed-sequence calf-thymus DNA show emission maxima at 628 and 632 nm, respectively; with the Z- and A-form helices, the maximum shifts to still longer wavelengths (640 and 650 nm for the Z- and A-form polymers, respectively). It is not clear whether it is the electronic character of the DNA bases and its overlap with the phenazine ring, the accessibility of the phenazine ring to protonation, or some mixture thereof that is responsible for the novel luminescent properties associated with the interaction with the helix.

In summary, we find $Ru(bpy)_2(dppz)^{2+}$ to be a highly sensitive spectroscopic reporter of double-helical DNA. In aqueous solution, luminescence is detectable only when $Ru(bpy)_2(dppz)^{2+}$ has intercalated in (or is perhaps otherwise shielded by) the nucleic acid structure. The emission characteristics furthermore sensitively distinguish both in terms of intensity and emission maximum the different helical forms of the polynucleotide. We therefore conclude that $Ru(bpy)_2(dppz)^{2+}$ can serve as a true molecular "light switch" for DNA structures, and tethered onto oligonucleotides,[18] the complex may be useful as a sensitive, nonra-

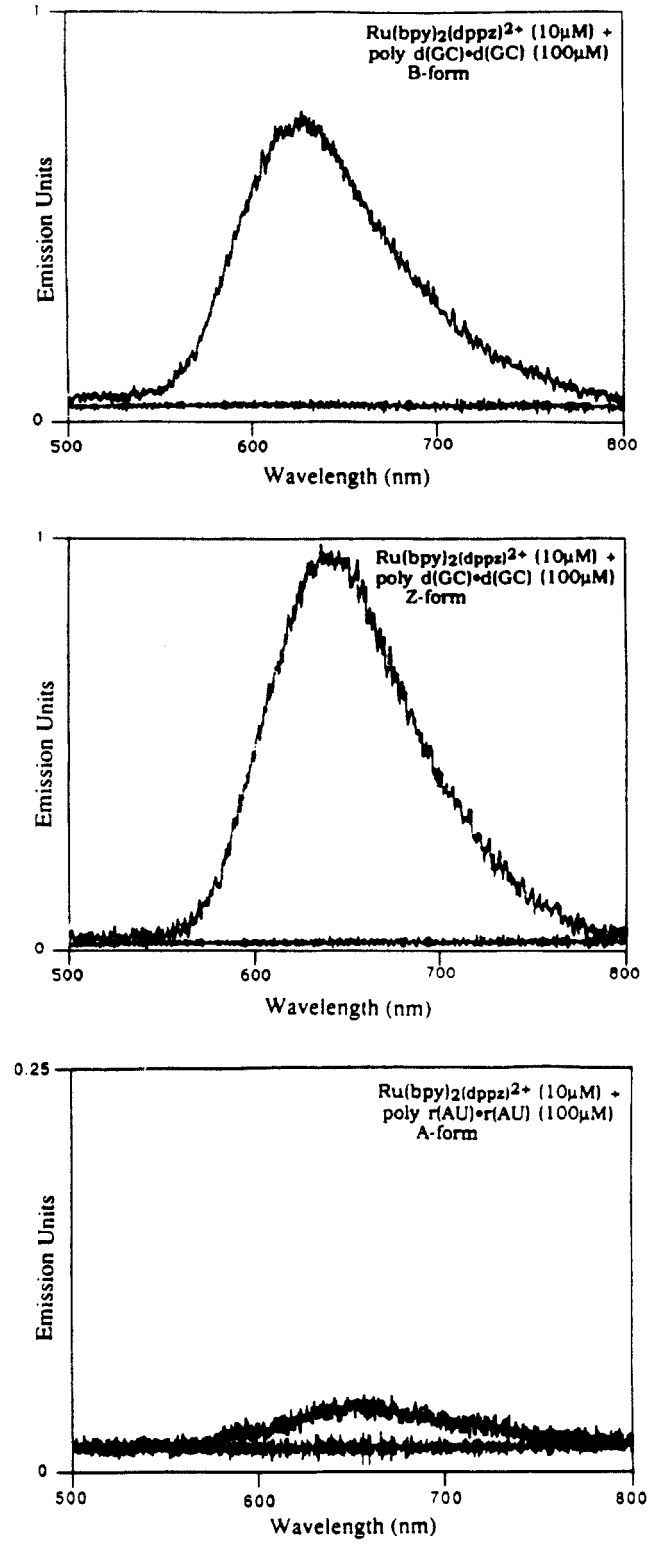

Figure 1. Steady-state emission spectra of $Ru(bpy)_2(dppz)^{2+}$ (10 μM) in the absence and presence of B-form (top), Z-form (middle), and A-form (bottom) double-helical nucleic acids. In each case in the absence of polynucleotide, only the base-line spectrum, the same level of emission as detected with pure solvent, is obtained for the ruthenium complex in 50 mM NaCl/5 mM Tris, pH 7.0, at 25 °C. In the presence of B-DNA, 100 μM poly[d(GC)·d(GC)] has been added. For the spectrum in the presence of Z-DNA, 100 μM poly[d(GC)·d(GC)] has also been added, but the buffer (both in the presence and in the absence of DNA) contains instead 20 mM NaCl/2.0 mM Tris/4 μM $Co(NH_3)_6^{3+}$, pH 7.0, to promote Z formation. For the spectra of $Ru(bpy)_2(dppz)^{2+}$ (10 μM) taken in the absence (base line) and presence of A-form poly[r(AU)·r(AU)] (100 μM), the buffer employed is again 50 mM NaCl/5.0 mM Tris, pH 7.0. Note that for the A-form panel, higher sensitivity (4×) was employed to record both spectra.

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(13) This quantum yield for photoluminescence is based upon comparison to that of $Ru(bpy)_3^{2+}$ in aqueous solution.[2]

(14) The 259-ns component accounted for 66% of the emission.

(15) The short-lived component may correspond, as with $Ru(phen)_3^{2+}$,[4] to a surface-bound mode in the minor groove or to an alternate binding mode in which the dppz ligand is less shielded than if tightly intercalated.

(16) Unlike other DNA-intercalating species such as ethidium,[17] $Ru(bpy)_2(dppz)^{2+}$ does not promote a Z–B transition, as the spectral differences seen here support. See: Friedman, A. E.; Kumar, C. V.; Turro, N. J.; Barton, J. K., to be submitted.

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dioactive, luminescent DNA probe in both heterogeneous and homogeneous assays.

Acknowledgment. We are grateful to the NIH (GM33309 to J.K.B. and NRSA Fellowship CA08518 to A.E.F.), the NSF (CHE85-13521 to N.J.T.), the AFOSR (88-0043 to N.J.T.), and the CNRS (to J.-C.C. and J.-P.S.) for their financial support of this research.

Synthesis and Characterization of the First Example of a Metallacarborane That Incorporates an Alkaline-Earth Metal: The Molecular Structure of *closo*-1,1,1,1-$(MeCN)_4$-1,2,4-$CaC_2B_{10}H_{12}$[1]

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Received January 24, 1990

The organometallic chemistry of the alkaline-earth metals has received particular attention in recent years.[2-10] In this context, high yield synthesis routes to the cyclopentadienyl[2-8] and cyclooctatetraenediyl[10] complexes of calcium, strontium, and barium have been developed and the molecular structures of $(C_5Me_5)_2Ba$,[6] $(C_5H_5)_2Ca$,[2] $[(C_5Me_5)Ca(\mu\text{-}I)(THF)_2]_2$,[9] and $[C_5H_3\text{-}1,3\text{-}(SiMe_3)_2]_2M(THF)$[8] (M = Ca or Sr) have been established crystallographically. The desolvated species possess polymeric structures in the solid state [for example, $(C_5Me_5)_2Ba$[6] and $(C_5H_5)_2Ca$[2]], are monomeric in the gas phase [for example, $(C_5Me_5)_2M$ (M = Ca,[3,5] Sr,[11] or Ba[11])], and the solvated species are either dimeric or monomeric in the solid state.[8,9] However, there is no previous report of a discrete metallacarborane cluster that incorporates an alkaline-earth metal. We here report the high-yield synthesis and characterization of such a metallacarborane as well as the molecular structure of the novel calcium carborane complex, *closo*-1,1,1,1-$(MeCN)_4$-1,2,4-$CaC_2B_{10}H_{12}$, the first structurally authenticated example of an alkaline-earth metallacarborane.

The addition of THF solutions of $Na_2[nido\text{-}7,9\text{-}C_2B_{10}H_{12}]$[1,12] to THF solutions of CaI_2 at room temperature over a period of 0.5 h affords a colorless complex, which is insoluble in THF but soluble in other coordinating solvents such as MeCN or DMF. Recrystallization of this complex from $MeCN/Et_2O$ produces colorless needle-like crystals; the X-ray study showed it to have the formulation $Ca(C_2B_{10}H_{12})(MeCN)_4$ (**1**).[13] The complex **1** is extremely air- and moisture-sensitive. The presence of the $[nido\text{-}7,9\text{-}C_2B_{10}H_{12}]^{2-}$ fragment in the complex **1** is supported by the fact that the known $[nido\text{-}9,12\text{-}C_2B_{10}H_{13}]^-$ (^1H and ^{11}B NMR, vide infra) is produced upon exposure to moisture/H_2O.[14-16] Complex **1** serves as a source of $[nido\text{-}7,9\text{-}C_2B_{10}H_{12}]^{2-}$ by its reaction with $YbI_2(MeCN)_2$ in MeCN to afford the known[17] *closo*-1,1,1,1-$(MeCN)_4$-1,2,4-$YbC_2B_{10}H_{12}$ in quantitative yield.

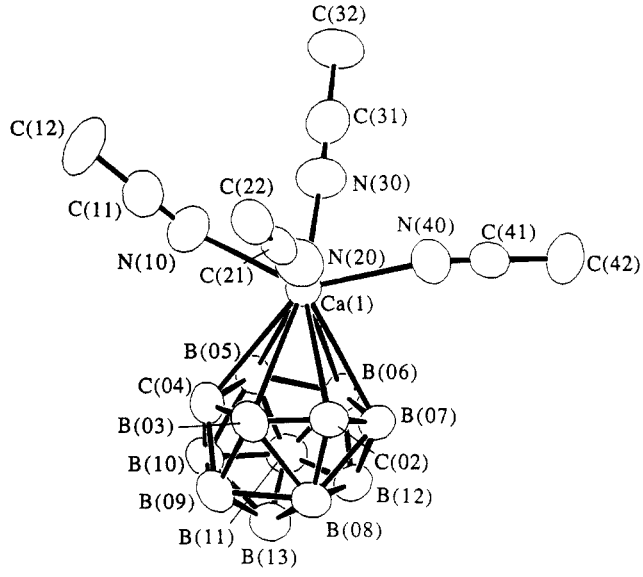

Figure 1. The molecular structure of *closo*-1,1,1,1-$(MeCN)_4$-1,2,4-$CaC_2B_{10}H_{12}$ (**1**). All hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å): Ca(1)–N(10), 2.471 (5); Ca(1)–N(20), 2.431 (5); Ca(1)–N(30), 2.476 (5); Ca(1)–N(40), 2.508 (5); Ca(1)–C(2), 2.701 (5); Ca(1)–B(3), 2.879 (6); Ca(1)–C(4), 2.895 (5); Ca(1)–B(5), 2.649 (6); Ca(1)–B(6), 2.828 (6); Ca(1)–B(7), 2.935 (6); C(2)–B(3), 1.518 (7); C(2)–B(7), 1.515 (7); C(2)–B(8), 1.734 (7); C(2)···B(9), 2.789 (7); C(2)···B(12), 2.814 (8); C(4)–B(3), 1.638 (8); C(4)–B(5), 1.701 (7); C(4)–B(9), 1.692 (8); C(4)–B(10), 1.691 (7); B(3)···B(8), 2.037 (9); B(3)–B(9), 1.840 (8); B(3)···B(10), 2.935 (8); B(5)–B(6), 1.739 (7).

The molecular structure[18] of **1** is illustrated in Figure 1, along with selected interatomic distances. The calcium atom asymmetrically caps the open puckered hexagonal face of the $[nido\text{-}7,9\text{-}C_2B_{10}H_{12}]^{2-}$ ligand. Four acetonitrile ligands are bonded to the calcium atom. The Ca–N bond distances range from 2.43 to 2.51 Å, and calcium–carborane distances fall in the range 2.65–2.94 Å. The Ca(1)–C(2) distance of 2.70 Å compares very well with that reported for the complexes $[C_5H_3\text{-}1,3\text{-}$

(1) Numbers accompanying formulas refer to the positions of the heteroatoms within the *closo*-metallacarborane framework and to the location of the exopolyhedral substituents. Lowest numbers consistent with the molecular geometry are given to carbon in accordance with the inverse periodic order adhered to by the IUPAC Inorganic Nomenclature Committee (see: Adams, R. M. *Pure. Appl. Chem.* **1972**, *30*, 683). The numbering system used for the *nido*-carborane anions described herein is identical with that previously employed (see: Dustin, D. F.; Dunks, G. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1973**, *95*, 1109).

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(13) Data for **1**: IR (Nujol mull, NaCl) ν_{B-H} 2466 (s), 2419 (s, br), ν_{MeCN} 2302 (m), 2273 (s) cm^{-1}; ^1H NMR (CD_3CN, 20 °C, ppm) 4.12 (s, br, carboranyl C–H); ^{11}B NMR (in MeCN, 20 °C; chemical shifts referenced to external $BF_3{\cdot}OEt_2$; peaks upfield of the reference are designated as negative; areas given in parentheses) 2.2 (4), $^1J_{BH}$ = 103 Hz, –6.4 (3), $^1J_{BH}$ = 147 Hz, –17.6 (3), $^1J_{BH}$ = 130 Hz. Anal. Calcd for $C_{10}H_{24}B_{10}N_4Ca$: C, 34.48; H, 6.89; N, 16.09. Found: C, 30.09; H, 7.38; N, 13.30. These values are better suited to $C_8H_{21}B_{10}N_3Ca$, which contains one less MeCN per molecule. Calcd for $C_8H_{21}B_{10}N_3Ca$: C, 31.27; H, 6.84; N, 13.68. We have not been able to obtain satisfactory elemental analyses of **1** due to facile loss of a MeCN ligand during analytical sample preparation. Loss of coordinated solvent molecules from organoalkaline-earth metal complexes is common (refs 3, 4, and 6).

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(18) Crystal data: $C_{10}H_{24}B_{10}N_4Ca$, monoclinic, $P2_1/n$, a = 8.6985 (7) Å, b = 15.825 (1) Å, and c = 15.423 (2) Å, β = 90.106 (3)°, V = 2123 Å^3, Z = 4, μ(Cu Kα) = 25.1 cm^{-1}, D(calcd) = 1.05 g cm^{-3}, T = 298 K, λ = 1.5418 Å, colorless needle specimen, 0.15 × 0.25 × 0.65 mm. A crystal obtained from $MeCN/Et_2O$ solution was sealed in a capillary on a modified Syntex $P\bar{1}$ diffractometer. Data were collected at 298 K in the θ–2θ scan mode. Of the 2177 unique reflections measured, 1676 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. The final discrepancy index was R = 0.050, R_w = 0.070, GOF = 2.55; $\Delta(\rho)$ = 0.2 e Å^{-3}.

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