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Spectroscopy of Ru(II) polypyridyl complexes used as intercalators in DNA: Towards a theoretical study of the light switch effect

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Abstract

The absorption spectroscopy of $[Ru(phen)_2dppz]^{2+}$ and $[Ru(tap)_2dppz]^{2+}$ (phen = 1,10-phenanthroline, tap = 1,4,5,8-tetraazaphenanthrene; dppz = dipyridophenazine) complexes used as molecular light switches by intercalation in DNA has been analysed by means of Time-Dependent Density Functional Theory (TD-DFT). The electronic ground state structures have been optimized at the DFT (B3LYP) level of theory. The absorption spectra are characterized by a high density of excited states between 500 nm and 250 nm. The absorption spectroscopy of $[Ru (phen)_2dppz]^{2+}$ in vacuum is characterized by metal-to-ligand-charge-transfer (MLCT) transitions corresponding to charge transfer from Ru(II) either to the phen ligands or to the dppz ligand with a strong MLCT ($d_{Ru} \rightarrow \pi^*_{dppz}$) absorption at 411 nm. In contrast, the main feature of the lowest part of the vacuum theoretical spectrum of $[Ru(tap)_2dppz]^{2+}$ between 522 nm and 400 nm is the presence of various excited states such as MLCT ($d_{Ru} \rightarrow \pi^*_{TAP}$), ligand-to-ligand-charge-transfer LLCT ($\pi_{dppz} \rightarrow \pi^*_{TAP}$) or intra-ligand IL ($\pi_{dppz} \rightarrow \pi^*_{dppz}$) states. When taking into account solvent corrections within the polarizable continuum model (PCM) approach (H_2O, CH_3CN) the absorption spectrum of $[Ru(tap)_2dppz]^{2+}$ is dominated by a strong absorption at 388 nm (CH_3CN) or 390 nm (H_2O) assigned to a ^{1}IL ($\pi_{dppz} \rightarrow \pi^*_{dppz}$) corresponding to a charge transfer from the outside end of the dppz ligand to the site of coordination to Ru(II). These differences in the absorption spectra of the two Ru(II) complexes have dramatic effects on the mechanism of deactivation of these molecules after irradiation at about 400 nm. In particular, the electronic deficiency at the outside end of the dppz ligand created by absorption to the ^{1}IL state will favour electron transfer from the guanine to the Ru(II) complex when it is intercalated in DNA.

Keywords: Spectroscopy; Ruthenium polypyridyl; Photophysics; Theoretical chemistry; DNA intercalators

1. Introduction

Increasing attention has been devoted to the design of new transition metal complexes as potential probes for nucleic acids since the discovery in 1990 of $[Ru(bpy)_2(dppz)]^{2+}$ highly sensitive luminescent reporter of double-helical DNA [1]. The investigation of photophysical, electrochemical and structural properties of novel Ru(II) complexes in the presence and absence of DNA has pointed to their potential as "molecular light switches" [2,3]. It has been found that the photoluminescence quantum yields of these complexes are extremely sensitive to the environment [1–3]. In particular, when DNA is added to an aqueous solution of the complexes the yield of emission increases dramatically. It was proposed that few triplets metal-to-ligand-charge-transfer (MLCT) $d_{Ru} \rightarrow \pi^*_{dppz}$ excited states give rise to the DNA light switch effect in these systems [4–6]. Moreover, the luminescent parameters are remarkably sensitive to the DNA structure and binding modes at intercalation [1–3]. The chemical properties of these coordinatively saturated molecules which are water soluble and inert to substitution make them excellent compounds as diagnostic and therapeutic agents [2]. These molecules have also been exploited in the study of electron transfer between the base pairs of DNA. As illustrated by a recent review article on ruthenium polypyridyl chemistry [7] this area of research has opened the route to a wide range of applications in various fields. Experiments reported on $[Ru(tap)_2dppz]^{2+}$ and $[Ru(phen)_2dppz]^{2+}$ have shown that these Ru(II) complexes strongly bind to dou-

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ble helical DNA being very efficient “molecular light switches” [4,8–14]. Linear dichroism spectroscopy [8–10], steady-state as well as time-resolved absorption/emission spectroscopy and laser flash photolysis experiments [4,11,12] have investigated the properties of $[Ru(tap)_2L]^{2+}$ (L = bpy, phen, tap, dppz) and of $[Ru(phen)_2dppz]^{2+}$ in DNA, in different solvents (H_2O, CH_3CN, H_2O/CH_3CN mixture) and in various double-stranded synthetic polynucleotides, such as $[poly(dA\text{-}dT)]_2$ and $[poly(dG\text{-}dC)]_2$. The first example of *reversible* DNA light switch has been recently accomplished for $[Ru(byp)_2(tpphz)]^{2+}$ (tpphz = tetrapyrido phenazine) [15]. The experimental spectrum of $[Ru(phen)_2dppz]^{2+}$ is characterized by an absorption in the visible region assigned to a metal-to-ligand-charge-transfer MLCT transition ($\lambda_{max} = 440$ nm) and to an intraligand IL transition localized on the dppz chromophore ($\lambda_{max} = 372$ nm; $\varepsilon = 21\,800\ M^{-1}\ cm^{-1}$) [13]. The emission yield is undetectable in water, but moderate in acetonitrile and increases when the complex is intercalated to DNA or bound to polynucleotides [4,11,12]. The efficient quenching of luminescence in water has been proposed to be due to fast hydrogen bonding of solvent to the phenazine aza nitrogens of the dppz anion radical (formed in the MLCT states) [16–18]. Methyl substitution effects on the radiative and solvent quenching rate constants on $[Ru(phen)_2dppz]^{2+}$ have been investigated by Olofsson et al. [19]. When the distant benzene ring of the dppz ligand is substituted by methyl groups a dramatic increased luminescence lifetimes and quantum yield in polyol solvents is observed. A similar effect, but less dramatic is observed when the substituted complexes are intercalated in DNA. The substitution has no effect on the position and intensity of the MLCT band at 440 nm, but the perturbation of the dppz chromophore is significant in the IL band [19]. Pure enantiomers Δ and Λ of $[Ru(phen)_2dppz]^{2+}$ have been synthesized and it has been shown that the Δ enantiomer is primarily responsible for the luminescence enhancement upon DNA binding reported for the racemate [14]. Interestingly, a recent study has shown that the luminescence of both the Δ and Λ forms of the $[Ru(phen)_2dppz]^{2+}$ is enhanced not only upon intercalation with DNA but also when the metal complexes bind to single stranded oligonucleotides [20].

The behaviour of the tap substituted complexes is characterized by the presence of excited states able to oxidise guanine.

$$[Ru(tap)_2(L)]^{2+*} + G \rightarrow [Ru(tap)_2(L)]^{+} + G^{\bullet +} \qquad (1)$$

This photo-induced electron transfer is a key step in the enhancement of strand breaks and in adducts formation such as nucleobase and mononucleotide derivatives [11]. UV/vis transient experiments on $[Ru(tap)_2dppz]^{2+}$ in aqueous buffer or intercalated in polynucleotides [12] point to the presence of a shoulder between 400 nm and 500 nm and a strong absorption at 278 nm. The strong IL band observed in $[Ru(phen)_2dppz]^{2+}$ and in the free dppz ligand between 350–400 nm is not visible in $[Ru(tap)_2dppz]^{2+}$. In the presence of $[poly(dG\text{-}dC]_2$ the luminescence of $[Ru(tap)_2dppz]^{2+}$ is quenched and $[Ru(tap)_2dppz]^{+}$ is formed within 480 ± 40 ps, through electron transfer from the guanine to the excited state, as evidenced by means of a 400 fs pulse of 400 nm light by Kelly et al. [12].

Most of the theoretical studies performed until now have focus either on the structural or binding aspects [21] or on the nature and position of the low-lying triplet excited states in order to interpret the emission spectroscopy [22–25]. Structural and binding modes have been studied by means of force field approaches showing a classical intercalation for $[Ru(phen)_2dppz)]^{2+}$ [21]. The spectroscopic calculations reported on $[Ru(phen)_2dppz]^{2+}$ were based essentially on semi-empirical methods [22,23] and TD-DFT [24,25] studies. It has been shown that the low-lying MLCT states delocalized over the three ligands in the free complex slightly red-shifted and relocalize on the different ligands (phen or dppz) upon binding to DNA [22]. Recent DFT/TD-DFT analysis have assigned the experimental band characterized at 440 nm to a superposition of two distinct MLCT features, which arise from two groups of transitions, one at ≈450 nm and another at ≈415 nm, which correspond to $d_{Ru} \rightarrow \pi^*_{dppz}$ and $d_{Ru} \rightarrow \pi^*_{phen}$, respectively. The band at ≈372 nm has been assigned to have a dominant MLCT character partially mixed with dppz IL [24]. INDO/SCI calculations completed by TD-DFT on a series of polyazaaromatic Ru(II) complexes have shown that molecules containing π-extended ligands, such as dppz, are characterized by luminescence lifetimes largely dependent on temperature in aprotic solvents. This behaviour has been associated to the presence of low-lying triplet IL states centred mainly on the π-extended ligand [23]. Finally, TD-DFT calculations of the low-lying triplet excited states of $[Ru(bpy)_2dppz]^{2+}$ without and with solvent effects point to the presence of low-lying ^{3}MLCT ($d_{Ru} \rightarrow \pi^*_{bpy}$) states in gas phase which are delocalized within the dppz ligand when solvent correction is included [25]. This effect has been attributed to a change in dipole moment of the molecule. The lowest triplet state has been assigned to a ^{3}IL ($\pi_{dppz} \rightarrow \pi^*_{dppz}$).

The aim of the present study is to analyze and rationalise the absorption/emission spectroscopy in $[Ru(phen)_2dppz)]^{2+}$ and $[Ru(tap)_2dppz]^{2+}$ which are used as DNA intercalators in luminescence experiments. Our objective is to propose a qualitative mechanism able to explain the occurrence of competing processes under visible irradiation, namely luminescence versus electron transfer. For this purpose we performed a detailed investigation of the early stage photophysics (within ∼10 ps) of these two molecules. This is a preliminary step towards the fundamental understanding of the light switch effect in this class of molecules.

2. Computational details

The geometrical structures of $[Ru(L)_2(L')]^{2+}$ complexes (L = L′ = tap; L = phen, L′ = dppz; L = tap, L′ = dppz) were optimized in vacuum for the closed shell electronic ground state at the DFT (B3LYP) [26] level within C_1 symmetry. The following basis sets and pseudopotentials describing the core electrons of the metal centre were used: (i) a full double-ξ D95 basis set (9s, 5p) contracted to [4s,2p] for C and N atoms and (4s) contracted to [2s] for H atoms [27] combined to LanL2DZ effective core potentials and associated valence basis sets for the Ru atom [28] (denoted as BSI); (ii) a polarized split valence 6-31G* basis set