Ligand-to-Ligand Charge Transfer in (2,2′-Biquinoline)bis(cyclopentadienyl)zirconium(IV) – Absorption and Emission in the Visible Range

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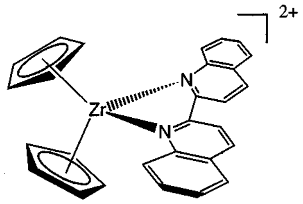
The lowest energy electronic transition of [(cyclopentadienyl)$_2$Zr^{IV}(2,2′-biquinoline)]$^{2+}$, which appears in absorption at λ_{max} = 360 nm and in emission at λ_{max} = 518 nm, is of the Cp$^-$ → biq ligand-to-ligand charge-transfer-type.

Coordination compounds which contain reducing and oxidizing ligands are frequently characterized by long-wavelength ligand-to-ligand charge-transfer (LLCT) absorptions in their electronic spectra[1][2]. Such optical electron transfer between two ligands is a special type of light-induced charge separation which plays an important role in areas such as artificial photosynthesis[3] and nonlinear optics[4]. In the case of LLCT a metal mediates the electronic interaction between donor and acceptor. Appropriate acceptor ligands include 1,2-diimines (e.g. 2,2′-bipyridyl), while anions such as thiolates can be donor ligands. As yet little attention has been paid to organometallic compounds, although recently photoreactive LLCT states have been identified in complexes with alkyl anions as donor ligands[5][6][7][8]. However, in general, the large potential of organometallic compounds for optical LLCT has not yet been utilized. The present report includes an investigation of novel features such as $C_5H_5^-$ ligands as donors and an early transition metal as a template and mediator. Moreover, we report on emission from a LLCT state of an organometallic compound, which we believe to be a new observation. Finally, some intriguing analogies between our target compound and the photosynthetic reaction center will be mentioned.

The desired complex [Cp$_2$Zr(biq)]$^{2+}$ (Cp$^-$ = $C_5H_5^-$ and biq = 2,2′-biquinoline) was designed taking into account the following considerations. Cp$^-$ is a suitable donor ligand as indicated by the appearance of long-wavelength LMCT absorptions in the spectra of complexes such as Cp$_2$Fe$^+$[2][9][10][11] or CpReO$_3$[2][12]. The metallocene moiety Cp$_2$M^{IV} (M = Ti, Zr, Hf) provides an obliquely oriented pair of Cp$^-$ ligands and a d^0 metal center, which can provide no interference from low-energy LF and MLCT states. Moreover Zr^{IV}, in contrast to Ti^{IV}, is barely oxidizing[2][13]. Accordingly, low-energy Cp$^-$ → Zr^{IV} LMCT transitions do not occur. 1,2-Diimines such as 2,2′-bipyridyl (bipy) or 9,10-phenanthroline (*o*-phen) are well-known electron acceptors in CT transitions[9][10][14][15]. Complexes of the type [Cp$_2$Ti^{IV}(diimine)]$^{2+}$, with bipy and *o*-phen, have been prepared previously[16]. Unfortunately, the corresponding Zr^{IV} complexes are not stable, and undergo a dissociation owing to the tendency of Cp$_2$ZrL$_2$ complexes to expand their coordination sphere to Cp$_2$ZrL$_3$[17][18][19]. However, if bulkier ligands are introduced Cp$_2$ZrL$_2$ complexes become stable because access to a further ligand is blocked[18]. As a bidentate diimine the ligand biq meets this requirement, and the complex [Cp$_2$Zr(biq)]$^{2+}$ is prepared by the reaction of Cp$_2$Zr(THF)(CF$_3$SO$_3$)$_2$[19] with biq. Mixing of the colourless solutions leads to the precipitation of a bright yellow crystalline material.



The electronic spectrum of [Cp$_2$Zr(biq)]$^{2+}$ (Figure 1) shows absorptions at λ_{max} = 360 (ε/dm^3 mol^{-1} cm^{-1} = 7700), 341 (8800), 329 (7400), 315 (5300), 304 (sh, 4300), 262 nm (20400). The bands at 341, 329, 315, 304, and 262 nm appear at almost the same wavelength as those of free biq and are thus attributed to intraligand (IL) transitions. However, while Cp$_2$Zr^{IV} compounds such as Cp$_2$ZrCl$_2$ and related complexes are colourless, [Cp$_2$Zr(biq)]$^{2+}$ is bright yellow owing to a new absorption at λ_{max} = 360 nm which extends into the visible spectral region. The complex is solvatochromic, and the longest wavelength absorption undergoes a blue shift with increasing solvent polarity (Figure 2[20]). This band is assigned to an LLCT transition[1][2] from the (Cp$^-$)$_2$ donor ligands to the biq acceptor, and the intensity of the band is consistent with this assignment. Complexes of the type Cp$_2$M^{IV}L$_2$ with M = Ti, Zr, and Hf including [Cp$_2$Ti(diimine)]$^{2+}$ are pseudotetrahedral[16] (C_{2v}). The highest occupied orbitals of such Cp$_2$ML$_2$ compounds

Figure 1. Electronic absorption (a,– – – – –) and emission (e, ·······) spectra of $2.18 \cdot 10^{-5}$ M $[Cp_2Zr(biq)]^{2+}$ at room temp. under argon in THF in a 1-cm cell; emission: $\lambda_{exc} = 380$ nm, intensity in arbitrary units

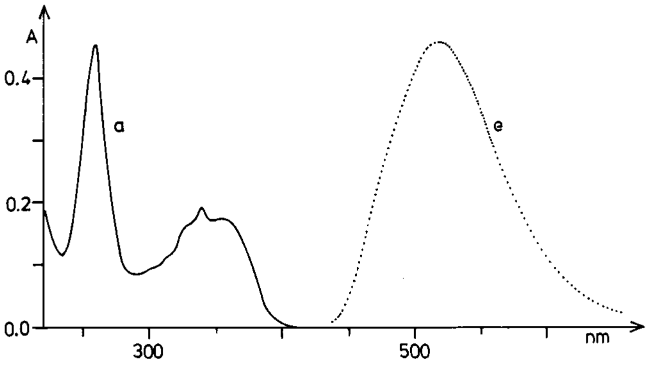
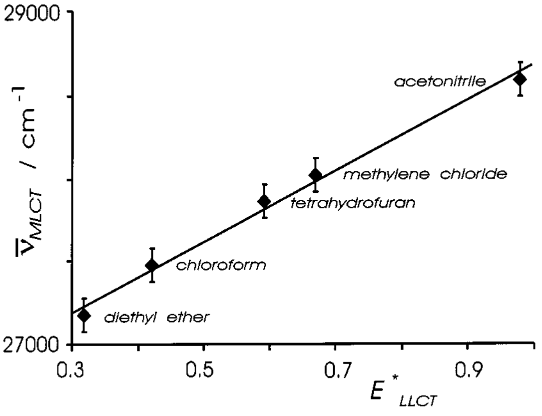


Figure 2. Energies of the LLCT absorption ($\tilde{\nu}_{max}$) of $[Cp_2Zr(biq)]^{2+}$ plotted against solvent parameters E^*_{MLCT}[20]



are derived from the Cp^- ligands and are of the b_2, b_1, a_2, and a_1 symmetry in close energetic proximity[21]. The LUMO is a π* orbital (b_1) at the diimine ligand. While the $b_2 \rightarrow b_1$ transition is forbidden the other $Cp^- \rightarrow$ biq LLCT transitions ($b_1 \rightarrow b_1$, $a_2 \rightarrow b_1$ and $a_1 \rightarrow b_1$) are allowed[22].

The cation $[Cp_2Zr(biq)]^{2+}$ shows a bright yellow/green luminescence at $\lambda_{max} = 518$ nm in solution (Figure 1) and 524 nm in the solid state at room temp. The quantum yield of the emission is $\phi = 0.01$ (calibrated by comparison with rhodamine B)[23]. This luminescence is not of the intraligand (biq) type, and this is indicated by the absence of any vibrational structure at 77 K, since at low temperatures structured bands are typical for intraligand emissions[24][25]. The excitation spectrum matches the absorption spectrum and it is concluded that the luminescence originates from the lowest energy LLCT excited state, which is most likely to be a triplet state, in agreement with the general behavior of diamagnetic complexes with metals of the second transition row.

In summary, the lowest energy transition of $[Cp_2Zr(biq)]^{2+}$ is of the LLCT type and involves an electron transfer from the $(Cp^-)_2$ moiety to biq (absorption) and back (emission). The complex shares some remarkable features with the photosynthetic reaction center, which is characterized by a pair of two bacteriochlorophyll molecules in close proximity but in an oblique orientation. In the primary photochemical step this "special pair" undergoes a light-induced electron transfer to an electron acceptor. A variety of models have been developed to mimic the initial charge separation in the reaction center. In $[Cp_2Zr(biq)]^{2+}$ the special pair corresponds to both $C_5H_5^-$ ligands, which are also planar π-electron systems in an oblique orientation. However, in both the natural system and artificial models[3] charge separation takes place by excited-state electron transfer, whilst in our organometallic model it occurs as an optical transition since the metal facilitates an electronic coupling of donor and acceptor.

Other aspects of our observations may be also of interest as metallocene dihalides are well known to exhibit antitumor activity[26][27]. Since extended planar ligands can intercalate in DNA[28] the luminescence of $[Cp_2Zr(biq)]^{2+}$ and related compounds may be utilized to monitor such interactions. In this context it should be also mentioned that a few reports on the luminescence of some other d^0 complexes[29][30][31][32][33] including metallocene derivatives[34][35][36] have appeared recently. In these cases the emission apparently originates from LMCT excited states.

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Experimental Section

General: Absorption spectra: Hewlett Packard 8452A diode array spectrophotometer, spectrograde solvents. – Emission and excitation spectra: Hitachi 850 spectrofluorometer equipped with a Hamamatsu 928 photomultiplier for measurements up to 900 nm. – Luminescence spectra: Corrected for monochromator and photo-multiplier efficiency variations. Absolute emission quantum yields were determined by comparison of the integrated emission intensity with that of Rhodamine B under identical conditions such as exciting wavelength, optical density, and apparatus parameters.

Preparation of $[Cp_2Zr(biq)(CF_3SO_3)_2]$: All solvents were dried and saturated with argon. The starting chemicals were used as purchased without further purification. A solution of 1.28 g ($5 \cdot 10^{-3}$ mol) of $AgCF_3SO_3$ in 10 ml of THF was added to a solution of 0.73 g ($2.5 \cdot 10^{-3}$ mol) of Cp_2ZrCl_2 in 10 ml of THF. The combined solutions were stirred for 30 min. AgCl precipitated and was removed by filtration. A solution of 1.02 g ($4 \cdot 10^{-3}$ mol) of biq in 40 ml of THF was added to the filtrate under strirring. The solution immediately turned intensely yellow and yellow crystals started to deposit. After 1 h, the crude product was collected by filtration and washed with a little THF/ether, and dried under vacuum. The product was purified by repeated recrystallization from THF/ether, yield: 0.6 g (31%). – $C_{30}F_6H_{22}N_2O_6S_2Zr$ (775.86): calcd. C 46.44, H 2.86, N 3.61; found C 46.52, H 2.98, N 3.69.

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