Quantitative description of MLCT transitions in ruthenium polypyridyl complexes probed by two-photon absorption spectroscopy

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Abstract. Quantitative two-photon absorption (2PA) cross section and 2PA spectrum measurements were used to determine the molecular electric dipole change in the metal-to-ligand charge-transfer transition of ruthenium(II) tris-complexes of 2,2'-bipyridine ($[Ru(bpy)_3]^{2+}$) and 1,10-phenanthroline ($[Ru(phen)_3]^{2+}$) in several solvents.

1 Introduction

Ruthenium(II) polypyridyl complexes are well studied systems with the ability to form metal-to-ligand charge-transfer (MLCT) excited states with visible light absorption. This charge-transfer makes these complexes useful for numerous applications, but also makes them sensitive to local electric fields due to the formation of a dipole moment, $\Delta\mu$.

Quantitative two-photon absorption (2PA) spectroscopy is a versatile technique that can measure changes of permanent electric dipole moment.[1,2] We investigated the 2PA spectra of $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ dissolved in water (H_2O), dimethylsulfoxide (DMSO), acetonitrile (ACN), and dichloromethane (DCM), and use a two-level model of 2PA applied to the lowest-energy transitions to estimate the value of $\Delta\mu$ in different solvents.

2 Results and Discussion

The 2PA cross-sections over the wavelength range of $680 - 1020$ nm for $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ are shown as solid lines in Figure 3. Applying the two-state model of 2PA[1] to the lowest-energy transitions, we can evaluate the difference in the ground- and excited state dipole moments according to the equation:

$$|\Delta\mu| = \frac{13650}{n^2 + 2} \sqrt{\frac{n}{\lambda} \frac{\sigma_{2PA}(2\lambda)}{\varepsilon_{1PA}(\lambda)}}, \tag{1}$$

where n is the index of refraction, ε_{1PA} is the molar absorption coefficient at wavelength λ, and σ_{2PA} is the 2PA cross section at twice that wavelength. The calculated $\Delta\mu$ values

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(Table 1) are in the range 5 – 8 D and show a decrease with decreasing solvent polarity. Our all-optical measurements agree with previous electroabsorption measurements,[3,4] but are the first to show the dipole moment solvent dependence for both complexes, which is important in their function as a charge-transfer photosensitizers.
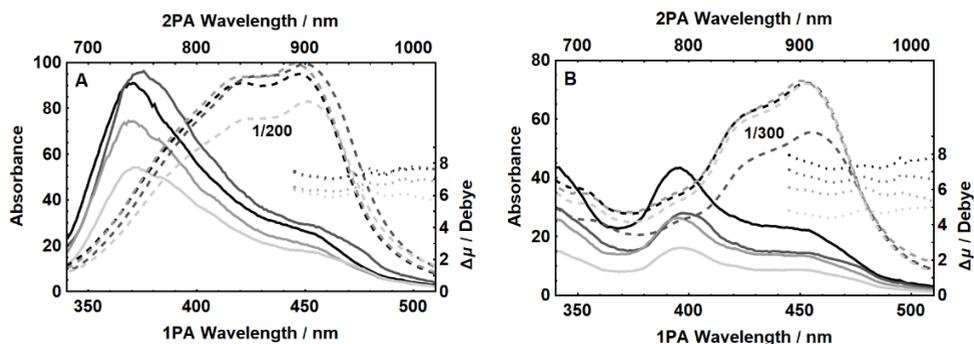

Fig 1. Absorption spectra collected for $[Ru(phen)_3]^{2+}$ (A) and $[Ru(bpy)_3]^{2+}$ (B) in H_2O (Black), DMSO (Dark-Gray), ACN (Mid-Gray), and DCM (Light-Gray). 2PA (solid lines) are in units of Goeppert-Mayer (GM), and 1PA molar absorption coefficients ($M^{-1}cm^{-1}$, dashed lines) are scaled for comparison. The calculated dipole moment ($\Delta\mu$) is displayed with units on the right-hand axis.

Table 1. Comparison of the 1PA molar absorption coefficient (ε) and 2PA cross section (σ) at λ_{max} for both complexes in the four solvents studied, as well as the relative permittivity (ε_r) for each solvent.

Solvent	ε_r	$[Ru(bpy)_3]^{2+}$			$[Ru(phen)_3]^{2+}$		
		ε (M^{-1} cm^{-1})	σ (GM)	$|\Delta\mu|$ (D)	ε (M^{-1} cm^{-1})	σ (GM)	$|\Delta\mu|$ (D)
H_2O	78	14450[a]	56	7.4	19000[a]	83	7.4
DMSO	47	11100[b]	32	6.6	19900[e]	93	7.4
CAN	36	14600[c]	27	6.0	19900[d]	73	6.6
DCM	9	14400[e]	26	4.5	16600[e]	54	6.0

[a]ref [5], [b]ref [6], [c]ref [7], [d]ref [8], [e]ref [9].

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