Heteroditopic Ligand Accommodating a Fused Phenanthroline and a Schiff Base Cavity as Molecular Spacer in the Study of Electron and Energy Transfer

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Supporting Information

SalCu

Chart S1

Figure S1: CV of SalCu in Acetonitrile

Figure S2: UV-Vis modification upon first oxidation at 1.0 V vs SCE
Additional Photophysical Experiments:

Excitation of Ru-complexes in the UV with intense laser flashes could lead to formation of solvated electrons which typically show broad absorption band in 500-900 nm spectral region [D. Meisel, M.S. Matheson, W.A. Mulac, J. Rabani, J. Phys. Chem. 1977, 81, 1449-1455; E.J. Hart, J.W. Bong, J. Am. Chem. Soc. 1962, 84, 4090-4095]. The underlying mechanism is a two-photon process implying excitation of the excited (MLCT) state which has a strong absorption around 360 nm [K. Miedlar, P.K. Das, J. Am. Chem. Soc., 1982, 104, 7462-7469]. This process depends strongly on the excitation energy. The energy dependence of the absorption changes of [Ru(bpy)$_3$]$^{2+}$ measured at 450 nm and 800 nm (Fig. S3) shows that the energy dependence is identical for both wavelengths demonstrating that in the red spectral region a biphotonic process does not significantly contribute to the spectrum. As a further control, experiments were performed using excitation wavelengths in the visible spectral region where the excited state of [Ru(bpy)$_3$]$^{2+}$ does not absorb (440 nm, 532 nm). In both cases the presence of a broad absorption band in the red and near infrared region was confirmed (shown for 532 nm excitation in Fig. S4). We would like to stress that for the other complexes investigated in this work, Ru(bpy)$_2$(DPSalH$_2$)$_2$ and Ru(bpy)$_2$(DPSalCu)$_2$, the probability of double excitation with a nanosecond laser flash is negligible because of the very short lifetime of their excited states being about four orders of magnitude shorter than in the case of [Ru(bpy)$_3$]$^{2+}$.

![Fig. S3: Energy dependence of the absorption changes due to bleaching of the ground state (450 nm, circles) and due to absorption of the excited state in the far-red region (800 nm,)](image-url)
stars) upon excitation of \( \text{Ru(bpy)}_3 \) in argon saturated EtOH (OD\(_{355}=0.31 \)) with UV flashes from a nanosecond laser (355 nm). An excitation energy of 5 mJ has been used for recording the spectrum in Fig. 11.

![Absorption spectrum](image-url)

Fig. S4: Spectrum of flash-induced absorption changes upon excitation with a nanosecond laser flash (532 nm, 30 mJ) of \([\text{Ru(bpy)}_3]^2+\) in argon saturated EtOH (OD\(_{530}=0.08 \)). Amplitudes of absorbance changes were taken about 0.5 µs after the flash and were corrected for the emission. The small negative absorption change near 600 nm is probably an artefact due to non-perfect correction for emission which has its maximum at this wavelength. For the other complexes investigated in this work, \([\text{Ru(bpy)}_2(\text{DPSalH})]^2+\) and \([\text{Ru(bpy)}_2(\text{DPSalCu})]^2+\), the yield of emission is orders of magnitudes smaller (see Fig. 10) and does not interfere with the absorption change measurements.
Figure S5: Time resolved absorption changes at 460 nm (○) and 820 nm (●) upon excitation with nanosecond laser flashes at 440 nm for [Ru(bpy)$_2$(DPSalH$_2$)]($\text{ClO}_4$)$_2$, in the absence of MV$^{2+}$ on an extended time scale.