Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION

for

Inversion of donor-acceptor roles in photoinduced intervalence charge transfers

by

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Experimental details

Materials. $RuRu^{2-}$, $RuOs^{2-}$, $RuFe^{2-}$ and **$RuNCS^{+}$** were prepared according to published procedures.[1,2] Anhydrous DMSO was provided by Sigma Aldrich and used as supplied.

Methods. Excitation and emission spectra were recorded in a PTI-QuantaMaster or a Cary Eclipse spectrofluorimeter. Quantum yields were measured in argon-saturated solutions using $[Ru(bpy)_3]^{2+}$ ($\varphi = 0.095$[3] in ACN at 25 °C). Fluorescence lifetimes were determined through the time-correlated single photon counting (TCSPC) technique using a Fluorolog 3 (Horiba Jobin Yvon). All measurements were conducted under argon atmosphere. The time profiles were recorded at 700 nm. Ultrafast transient absorption (TA) experiments were conducted using an amplified Ti:sapphire fs laser system (Clark MXR CPA2101 and 2110, 1kHz, FWHM = 150 fs, λ_{exc} = 505 nm, 200-300 nJ per pulse) with TA pump / probe Helios and EOS detection systems from Ultrafast Systems. For the picosecond to nanosecond experiments (Helios), white light was generated focusing a fraction of the fundamental 775 nm output onto a 2 mm sapphire disk (~430−760 nm) or a 1 cm sapphire disk (~800−1600 nm). A magic angle configuration was employed to avoid rotational dynamics. Excitation pulses of 505 nm wavelength were generated by a NOPA. Bandpass filters with ± 5 or ± 10 nm were used to ensure low spectral width and to exclude 775 nm photons. For the nanosecond to microsecond experiments (EOS), white light (~370 to >1600 nm) was generated by a built-in photonic crystal fiber supercontinuum laser source with a fundamental of 1064 nm at 2 kHz output frequency and pulse width of approximately 1 ns. All measurements were conducted in a 2 mm quartz cuvettes under argon atmosphere. Obtained data were treated by global and target analyses using the R-package TIMP and GloTarAn.[4–6]

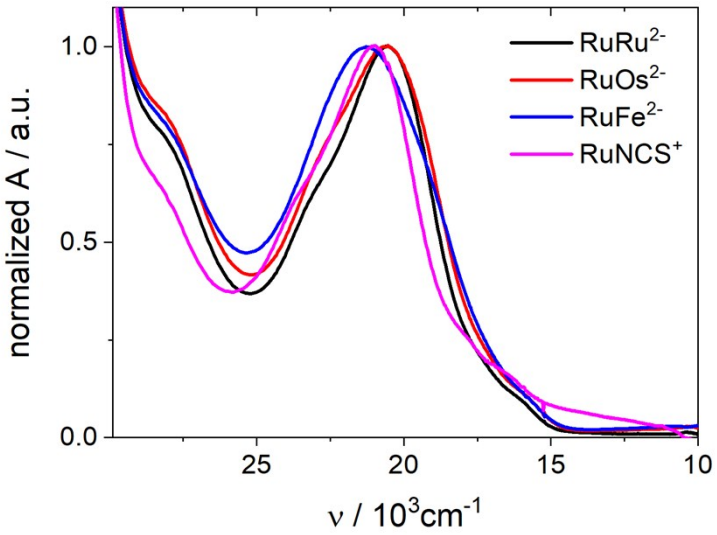

Figure S1. UV-vis absorption spectra of **RuRu^{2-}**, **RuOs^{2-}**, **RuFe^{2-}** and **RuNCS^{+}** in water at room temperature.

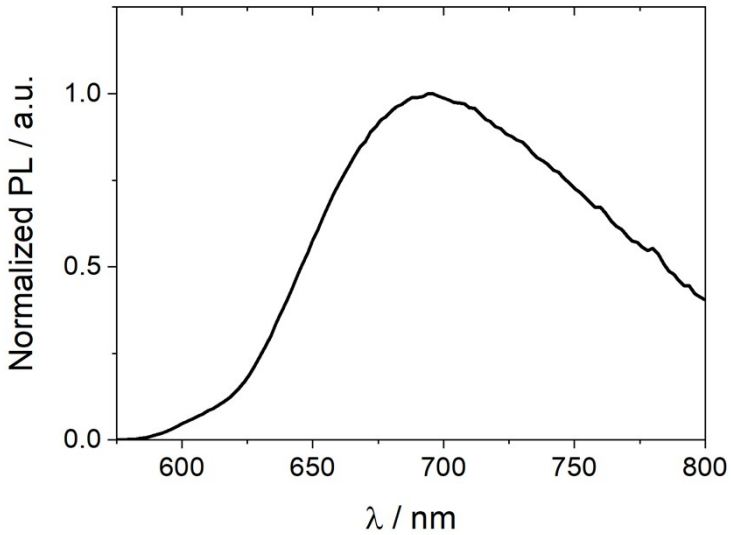

Figure S2. Normalized emission spectrum of **RuNCS^{+}** in water at room temperature.

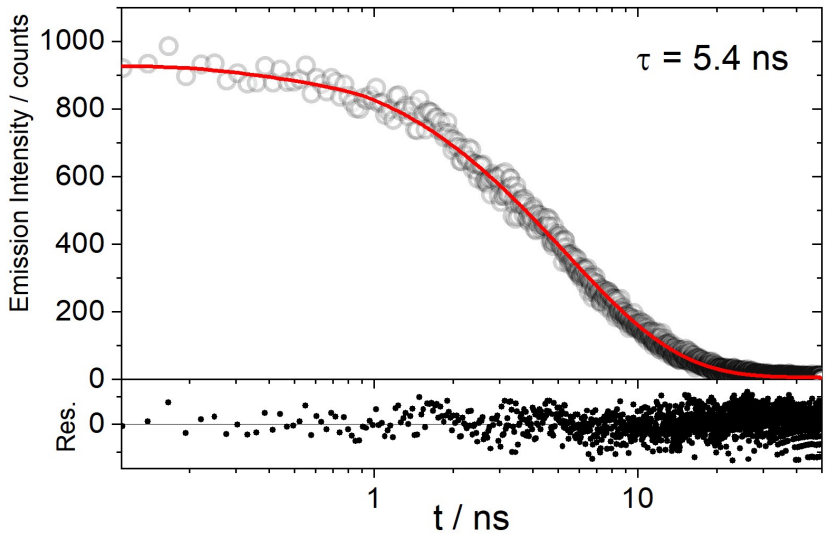

Figure S3. TCSPC emission lifetime of **RuNCS**$^{+}$ in water at room temperature (black dots) and monoexponential fitting (red curve).

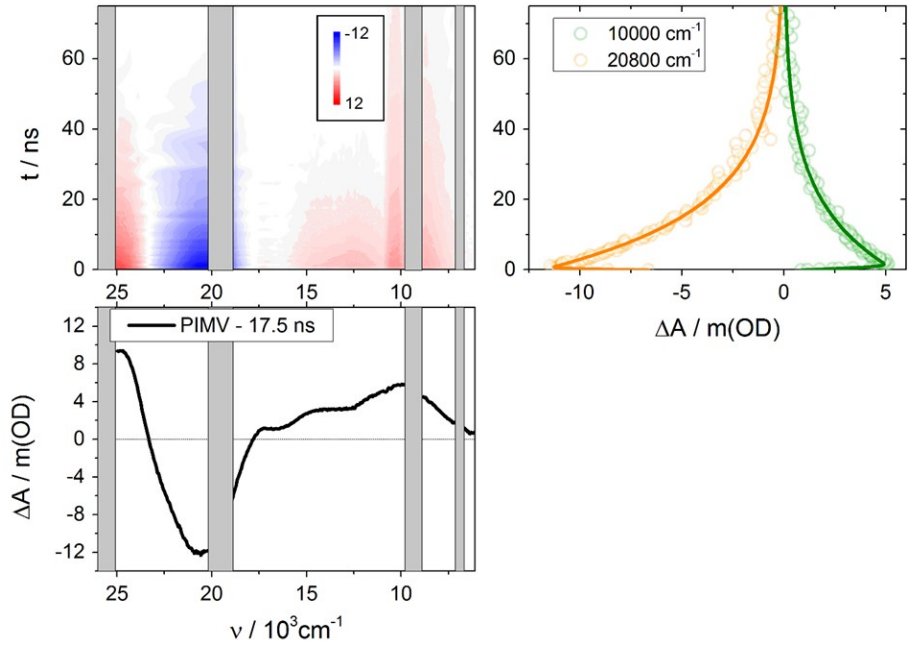

Figure S4. Upper left: Differential absorption 3D map obtained from nanosecond pump-probe experiments (λ_{exc}= 505 nm) for **RuRu**$^{2-}$ in water at room temperature. Upper right: Time absorption profiles (open circles) and corresponding fittings from global analysis (solid lines). Bottom left: Decay-associated differential spectra.

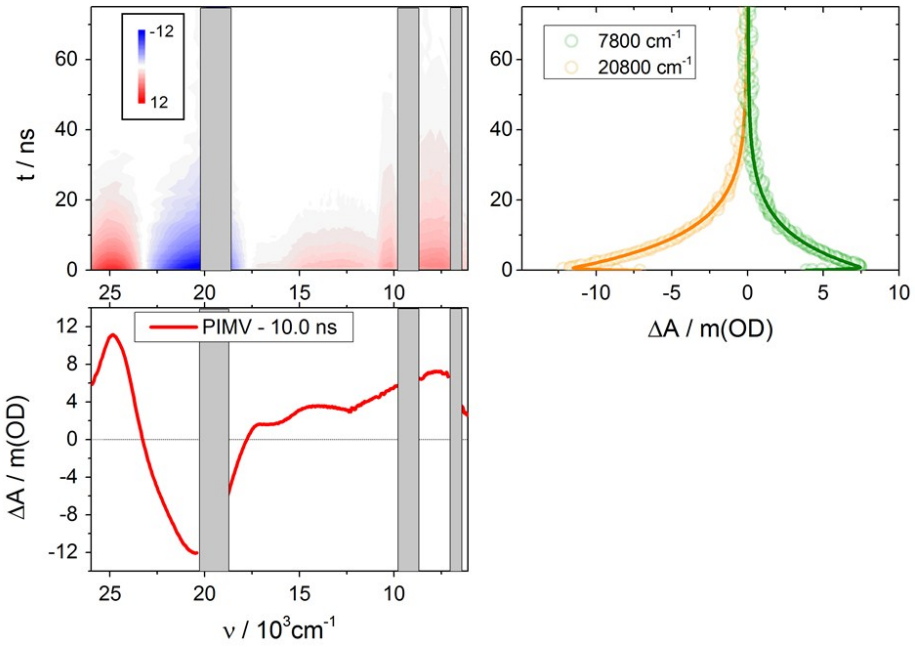

Figure S5. Upper left: Differential absorption 3D map obtained from nanosecond pump-probe experiments (λ_{exc}= 505 nm) for **RuOs^{2-}** in water at room temperature. Upper right: Time absorption profiles (open circles) and corresponding fittings from global analysis (solid lines). Bottom left: Decay-associated differential spectra.

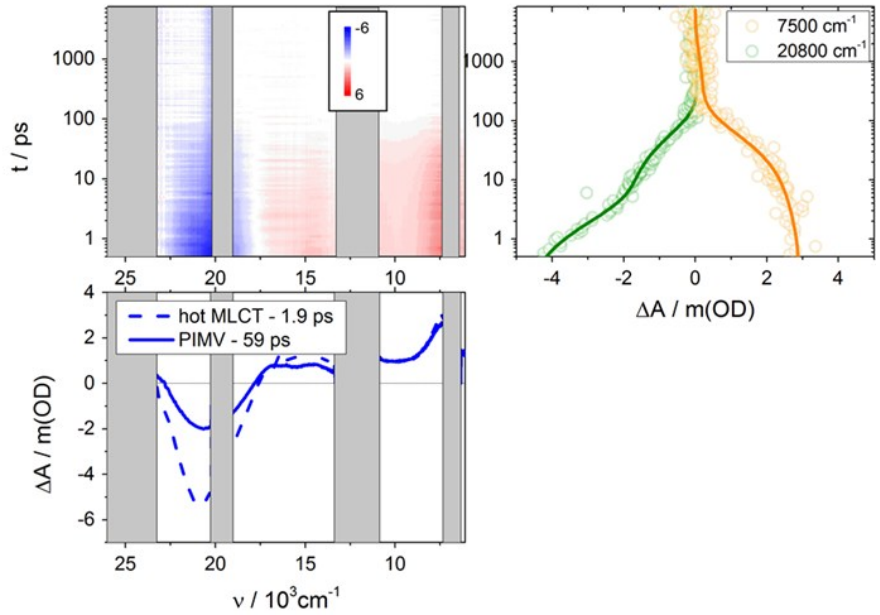

Figure S6. Upper left: Differential absorption 3D map obtained from picosecond pump-probe experiments (λ_{exc}= 505 nm) for **RuFe^{2-}** in water at room temperature. Upper right: Time absorption profiles (open circles) and corresponding fittings from global analysis (solid lines). Bottom left: Decay-associated differential spectra.

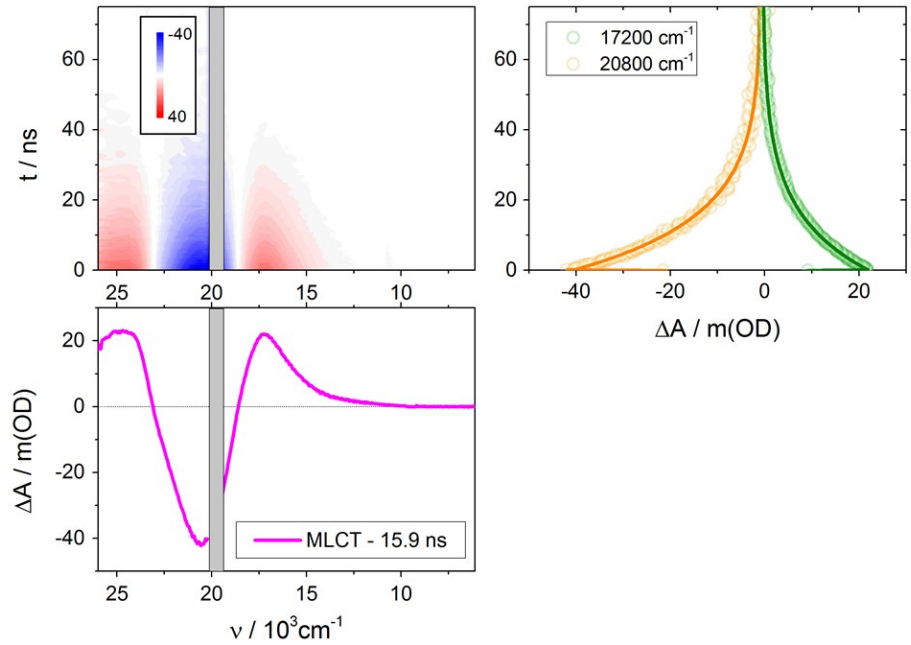

Figure S7. Upper left: Differential absorption 3D map obtained from nanosecond pump-probe experiments (λ_{exc}= 505 nm) for **RuNCS$^+$** in DMSO at room temperature. Upper right: Time absorption profiles (open circles) and corresponding fittings from global analysis (solid lines). Bottom left: Decay-associated differential spectra.

Table S1. Time constants extracted from global analyses of transient absorption experiments for **RuRu^{2-}** , **RuOs^2** , **RuFe^{2-}** and **RuNCS$^+$** exciting at 505 nm, and TCSPC lifetimes.

Compound	Solvent	Transient Absorption		TCSPC
		τ_1 / ps (k_1 / ps^{-1})	τ_2 / ps (k_2 / ps^{-1})	τ_{em} / ps
RuRu^{2-}	water	-	17500 (5.72±0.08) x10^{-5}	16600
RuOs^{2-}	water	-	10000 (9.99±0.01) x10^{-5}	9300
RuFe^{2-}	water	1.9 (0.52±0.01)	59 (0.0170±0.0001)	-
RuNCS$^+$	DMSO	-	15900 (6.31±0.02) x10^{-5}	14400

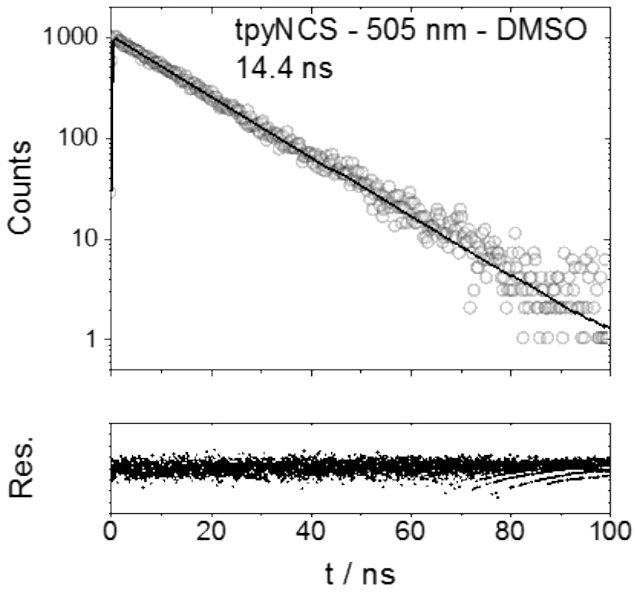

Figure S8. TCSPC emission lifetime of **RuNCS**$^{+}$ in DMSO at room temperature (black dots) and monoexponential fitting (black curve).

References

(1) Cadranel, A.; Alborés, P.; Yamazaki, S.; Kleiman, V. D.; Baraldo, L. M. Efficient Energy Transfer via the Cyanide Bridge in Dinuclear Complexes Containing Ru(II) Polypyridine Moieties. *Dalt. Trans.* **2012**, *41* (17), 5343–5350. https://doi.org/10.1039/c2dt11869f.

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