Supporting Information to

Strong π-delocalization and Substitution effect on Electronic Properties of Dithienylpyrrole-containing bipyridine Ligands and Corresponding Ruthenium Complexes

By

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Fluoresence of the free ligands

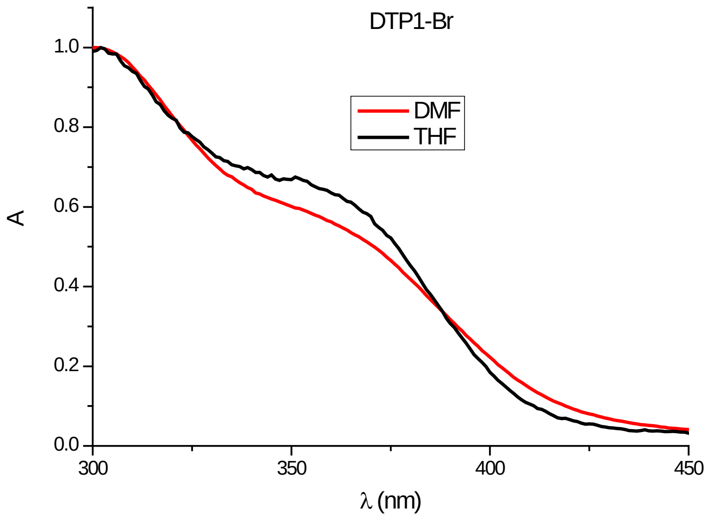

Fig.S1. Normalized absorption spectrum of DTP1-Br in DMF (red) and THF (black)

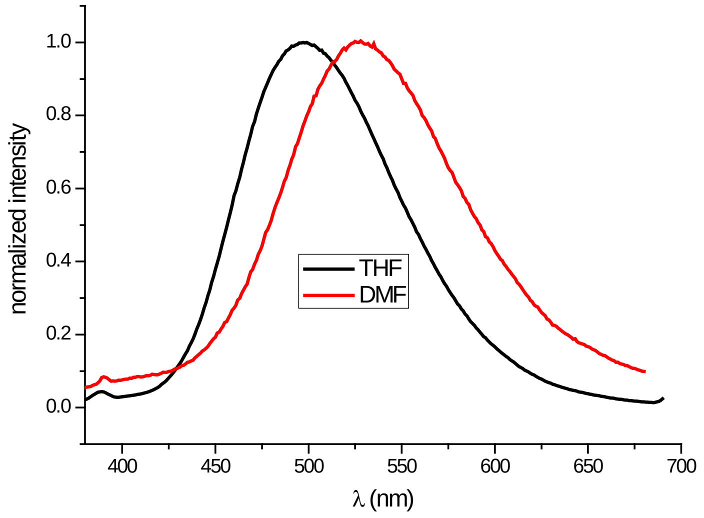

Fig. S2. Typical DTP-1 ligand emission in DMF (red) and in THF (black). Above it is shown the DTP1- Br. A 30 nm red shift is generally observed.

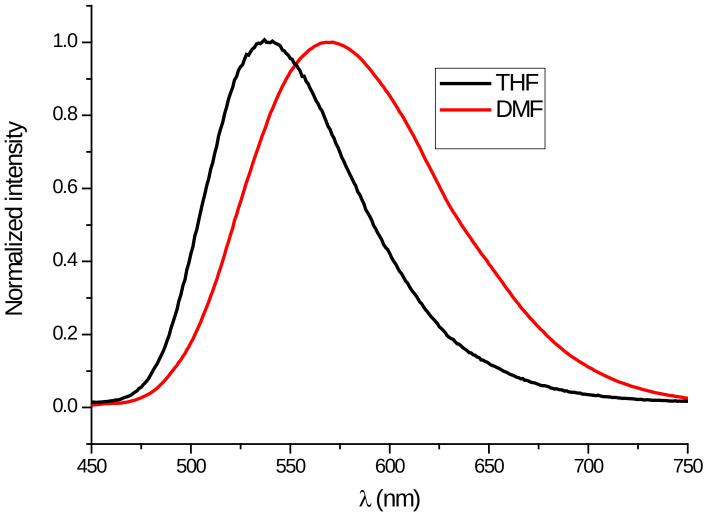

Fig. S3. Typical DTP-2 ligand emission in DMF (red) and in THF (black). Above it is shown the DTP2-F.

Tab.S1 Emission properties of the free ligands in THF

Compound	λem-max (nm)[a]	τ(ns)[b]
DTP$_1$-H	501	1.25
DTP$_1$-Br	497	1.64
DTP$_1$-F	498	1.57
DTP$_1$-Hex	498	1.68
DTP$_2$-F	538	1.44
DTP$_2$-Me	540	1.57
DTP$_2$-Hex	541	1.57

[a] Emission maxima in THF . [b] In the case of biexponential decay (DTP1 series) the average amplitude weighted lifetime was given.

Tab. S2 Emitting properties of the DTP-2 series in DMF.

Compound	λem-max (nm)	(amplitude%) τ_1(ns) (amplitude%) τ_2(ns)	$\tau_{average}$(ns)[a]
DTP$_2$-F	570	(94.63 %) 0.32 (5.37 %) 2.213	0.420
DTP$_2$-Me	571	(91 %) 0.3704 (8.75 %) 2.07	0.519
DTP$_2$-Hex	571	(92.57 %) 0.39 (7.43 %) 2.08	0.517

[a] The singlet excited state decay becomes biexponential in DMF. Here the average amplitude weighted lifetime is reported.

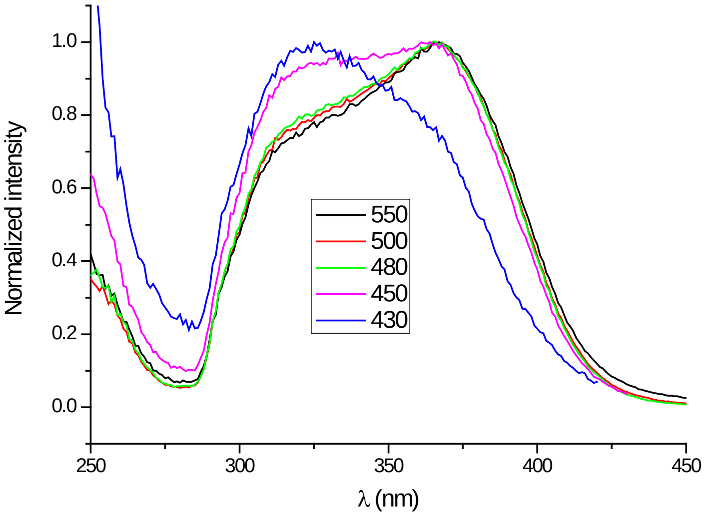

Fig. S4. Typical excitation spectrum of the DTP 1 series (DTP1-F is reported here as an example) in THF. The spectrum varies as a function of the observation wavelength. The 367 nm band gradually decreases in intensity with respect to the 323 nm as the the observation is moved from the red part of the emission band (550 nm) to the blue (430 nm).

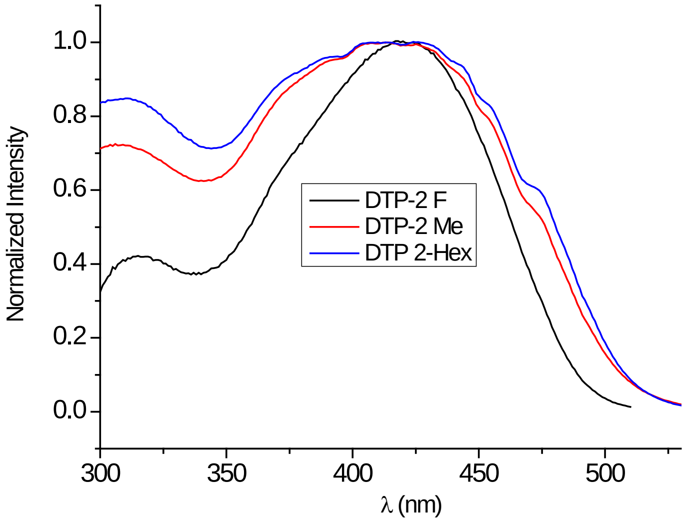

Fig. S5. Typical excitation spectrum of the DTP 2 series in THF. A close agreement with the absorption spectrum can be noticed.

Transient spectra of Zn^{2+}-Ligand adducts[1]

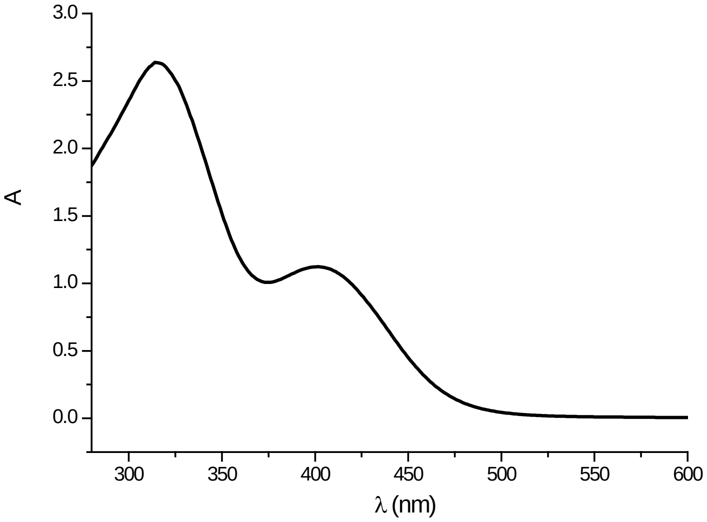

Fig.S6 Zn^{2+} DTP 1-F adduct in concentrated solution (typical concentration used for laser flash photolysis experiments)

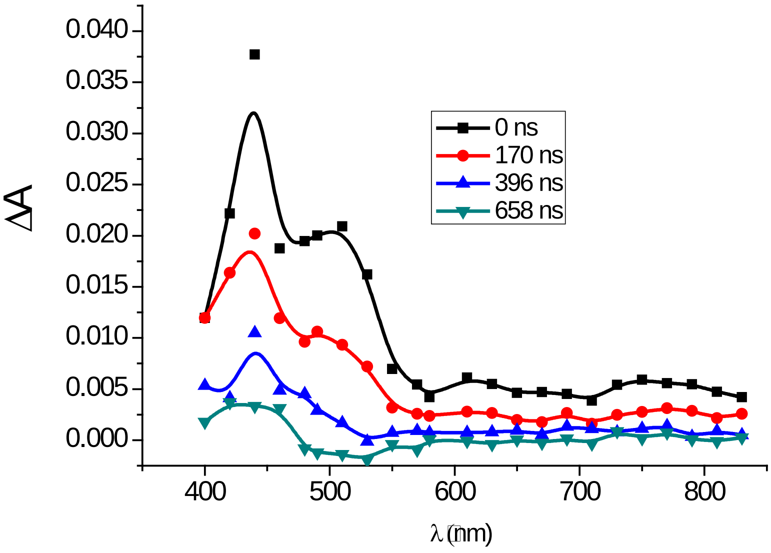

Fig.S7 Transient triplet absorption of the Zn^{2+} DTP 1-F adduct following 355 nm laser excitation.

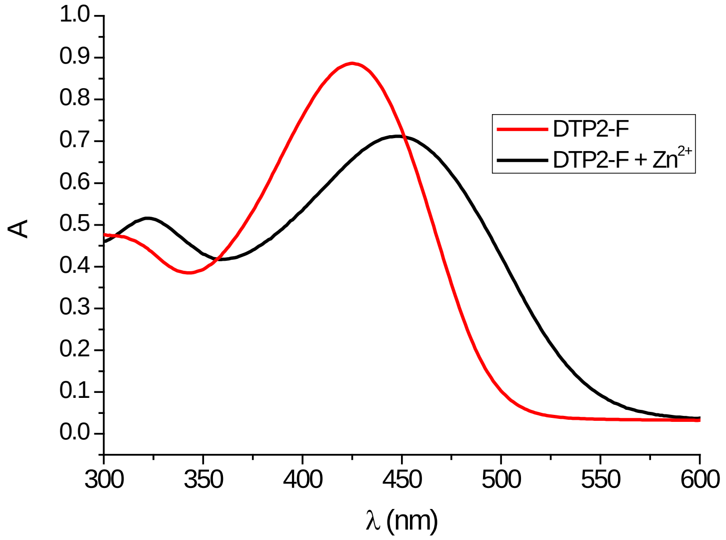

Fig. S8. Zn^{2+} DTP 2-F adduct in concentrated solution (typical concentration used for laser flash photolysis experiments) compared to the absorption spectrum of the free ligand

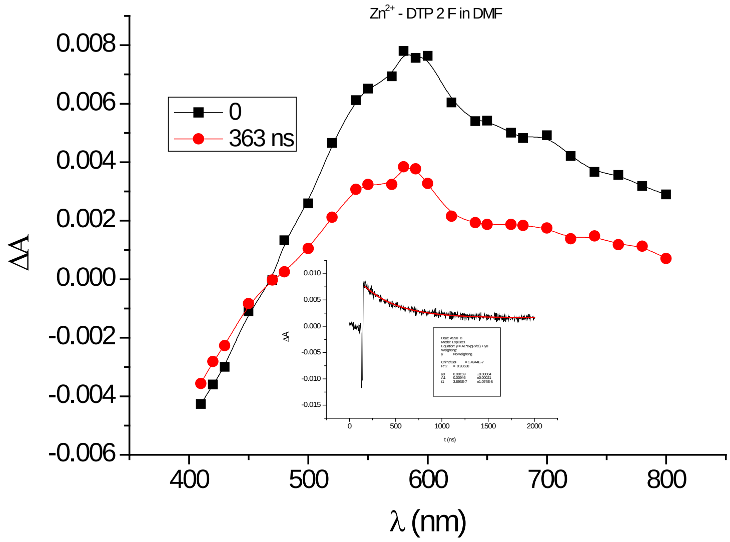

Fig.S9. Transient triplet absorption of the Zn^{2+} DTP 2-F adduct following 355 nm laser excitation

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[1] $Zinc^{2+}$ adducts were directly obtained in DMF solution, without isolation, by reacting the ligand with a ≈ 10 fold excess of solid $Zn(ClO_4)_2$ (Aldrich). The reaction was instantaneous. No spectral changes were observed after prolonged laser flash photolysis experiments.

Emitting properties of the Ru(II) homoleptic properties

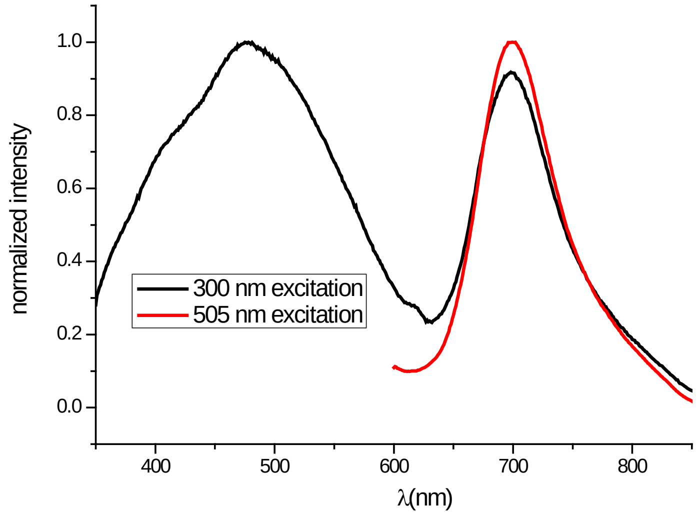

Fig. S10. Typical emission spectrum of the Ru-DTP1 series (Ru-DTP1 F) in DMF upon 300 nm and (505 nm excitation)

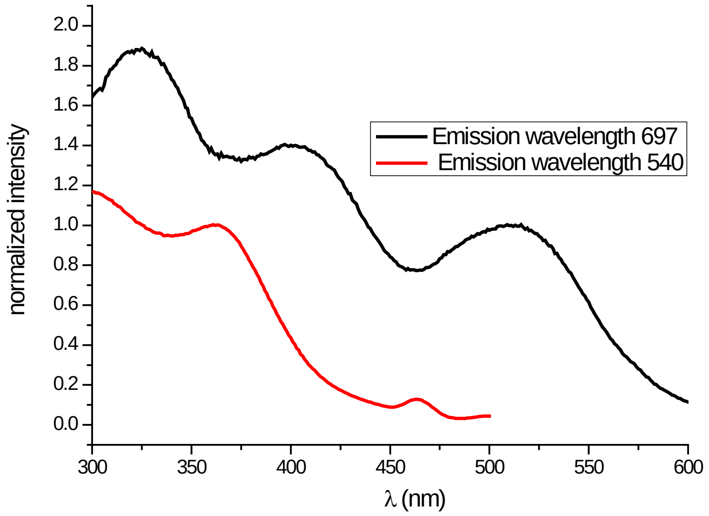

Fig. S11. Excitation spectrum of Ru-DTP1 F in DMF recorded by observing at 540 nm (red) and at the 697 nm black.

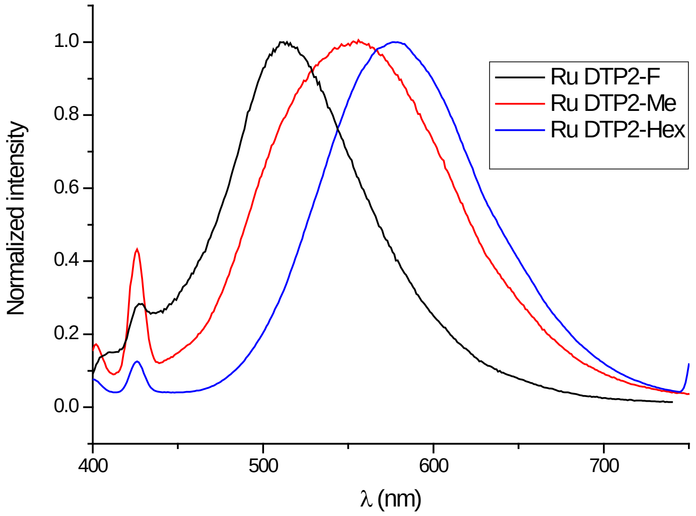

Fig. S12. Emission spectra of the Ru-DTP2 series upon 380 nm excitation. No emission was observed by direct excitation of the low energy band λ > 480 nm)

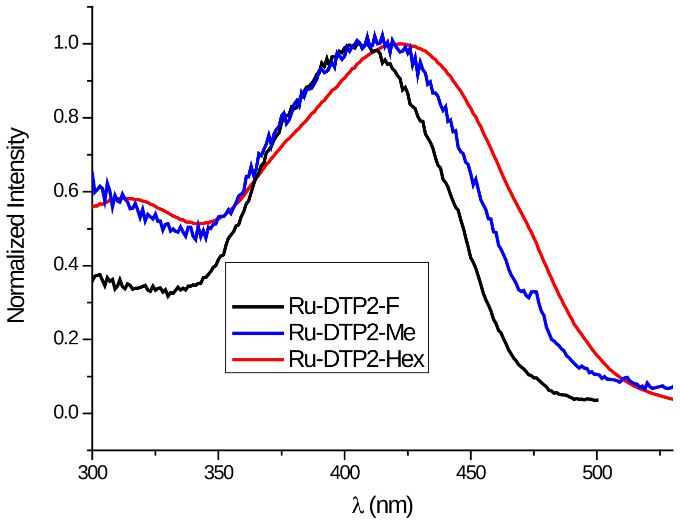

Fig. S13. Excitation spectra of the Ru-DTP2 series confirming the ligand based origin of the observed emission (Fig.S13).

Transient spectra of Ru(II) DTP1 homoleptic complexes upon 355 nm excitation

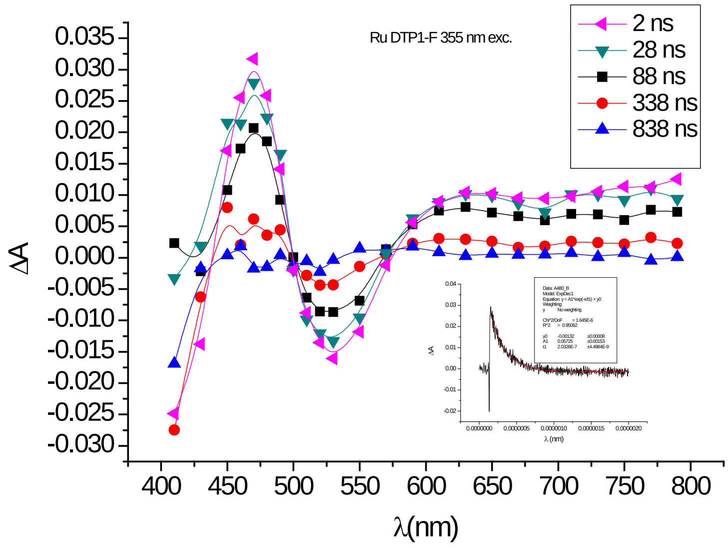

Fig.S14. Transient spectrum of the Ru-DTP 1F upon 355 nm laser excitation