

Electronic Supporting Information (ESI)

Excited State Behaviour of Substituted Dipyridophenazine Cr(III) Complexes in the Presence of Nucleic Acids

Michał Wojdyla, Jayden A. Smith, Suni Vasuvedan, Susan J. Quinn
and John M. Kelly

| Complex | Absorption band position [nm] | | | |
|---|-------------------------------|------|---|-----|
| [Cr(phen) ₂ (dppz)][Cl] ₃ | 271 | 280 | 360 ($\epsilon=13\ 900\ M^{-1}cm^{-1}$) | 377 |
| [Cr(phen) ₂ (Me ₂ dppz)][Cl] ₃ | 270 | 286 | 371($\epsilon=12\ 200\ M^{-1}cm^{-1}$) | 389 |
| [Cr(phen) ₂ (F ₂ dppz)][Cl] ₃ | 270 | ~281 | 357 ($\epsilon=11\ 500\ M^{-1}cm^{-1}$) | 376 |

Table S1. Absorption bands position of [Cr(phen)₂X₂dppz](Cl)₃ (X=H, Me, F).

| [Cr(phen) ₂ (X ₂ dppz)][CF ₃ SO ₃] ₃ | Peak No. | Peak Type | Area | FWHM/nm | Center/nm |
|--|----------|-----------|-------|---------|-----------|
| X=H | 1 | Gaussian | 861 | 15 | 698 |
| | 2 | Lorentz | 22577 | 12 | 730 |
| | 3 | Lorentz | 5683 | 22 | 746 |
| | 4 | Lorentz | 2571 | 61 | 801 |
| X=Me | 1 | Gaussian | 912 | 15 | 697 |
| | 2 | Lorentz | 25226 | 12 | 729 |
| | 3 | Lorentz | 6335 | 22 | 746 |
| | 4 | Lorentz | 1905 | 40 | 805 |
| X=F | 1 | Gaussian | 1161 | 16 | 697 |
| | 2 | Lorentz | 26585 | 12 | 729 |
| | 3 | Lorentz | 6689 | 22 | 745 |
| | 4 | Lorentz | 3432 | 59 | 805 |

Table S2. Multipeaks fitting parameter results for emission spectra of [Cr(phen)₂(X₂dppz)][CF₃SO₃]₃ (X=H, Me, F)

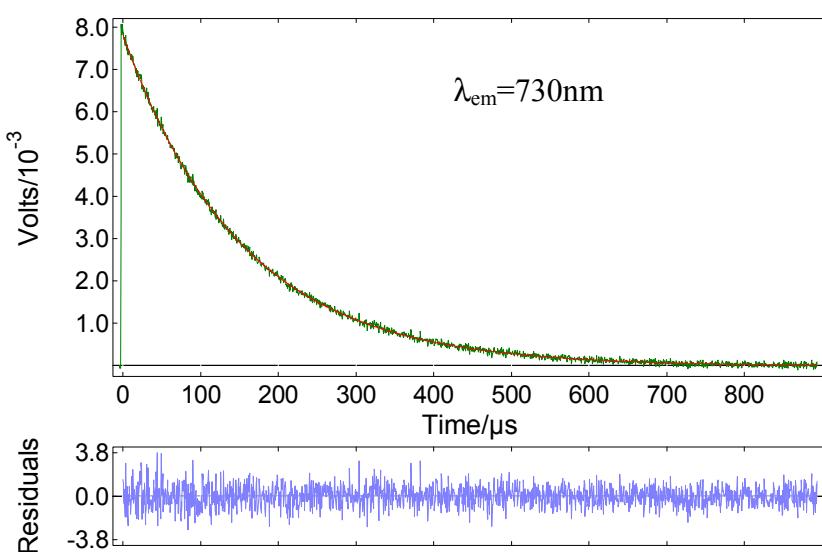


Fig. S1. Monoexponential fit (red line) to photoluminescence decay curve of N_2 purged $10\ \mu\text{M}$ water solution of $[\text{Cr}(\text{phen})_2(\text{F}_2\text{dppz})](\text{CF}_3\text{SO}_3)_3$ ($\lambda_{\text{ex}}=308\ \text{nm}$, $\lambda_{\text{em}}=730\ \text{nm}$)

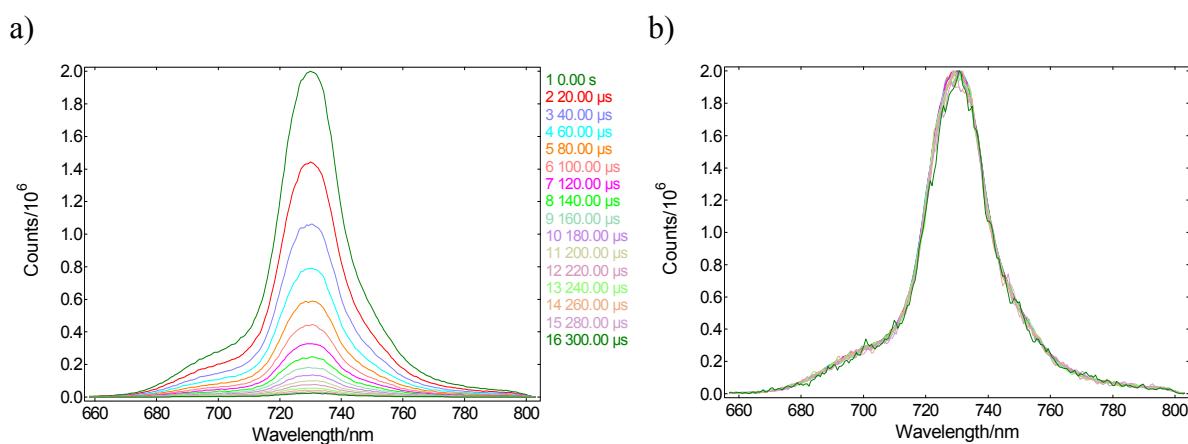


Fig. S2. (a) Time resolved emission spectra (TRES) of $50\ \mu\text{M}$ an air saturated water solution of $[\text{Cr}(\text{phen})_2(\text{F}_2\text{dppz})](\text{CF}_3\text{SO}_3)_3$ recorded using ICCD camera ($\lambda_{\text{ex}}=308\ \text{nm}$, 10 shots averaging per spectrum, gate width $20\ \mu\text{s}$). (b) Normalized TRES. Note: spectral resolution of camera measurements is lower than that of the spectrofluorimeter (see Fig. 2 or Fig. S3 for comparison).

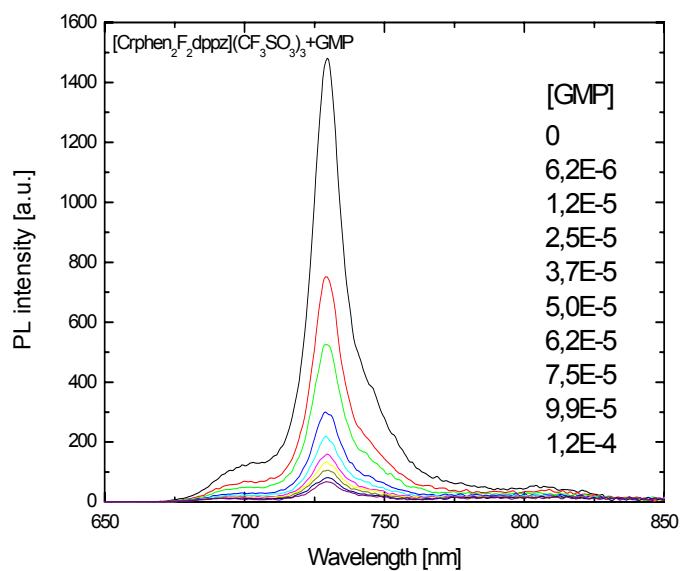


Fig. S3. Emission quenching of 100 mM phosphate buffer solution (pH 7.4) of $[\text{Cr}(\text{phen})_2(\text{F}_2\text{dppz})(\text{CF}_3\text{SO}_3)_3$ (45 μM) in the presence of increasing concentration of GMP.

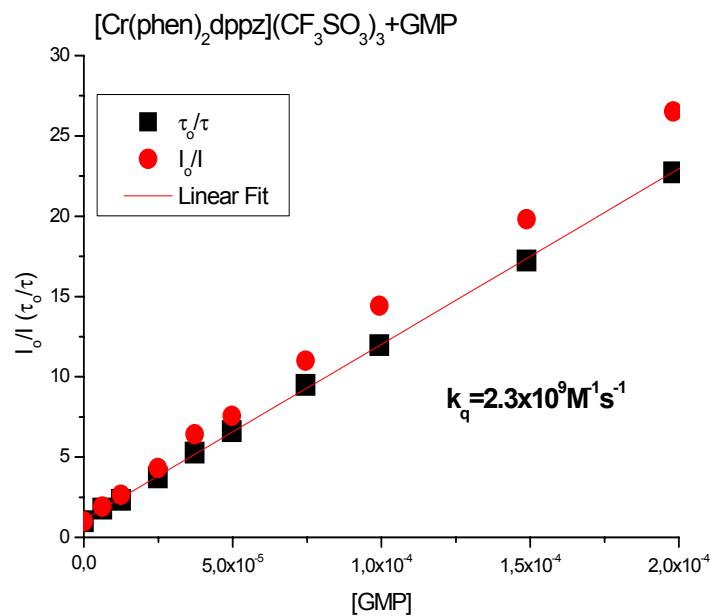


Fig. S4. Steady state and lifetime Stern Volmer plot for emission quenching (at 730 nm) of an air saturated 100mM phosphate buffer (pH = 7.4) solution of $[\text{Cr}(\text{phen})_2(\text{dppz})(\text{CF}_3\text{SO}_3)_3$ (61 μM) in the presence of increasing concentration of GMP.

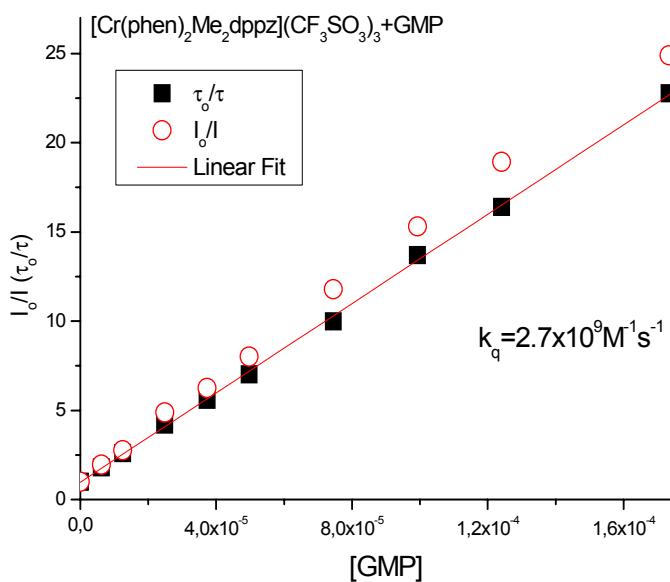


Fig. S5. Steady state and lifetime Stern Volmer plot for emission quenching (at 730 nm) of an air saturated 100 mM phosphate buffer (pH = 7.4) solution of $[\text{Cr}(\text{phen})_2(\text{Me}_2\text{dppz})](\text{CF}_3\text{SO}_3)_3$ (45 μM) in the presence of increasing concentration of GMP.

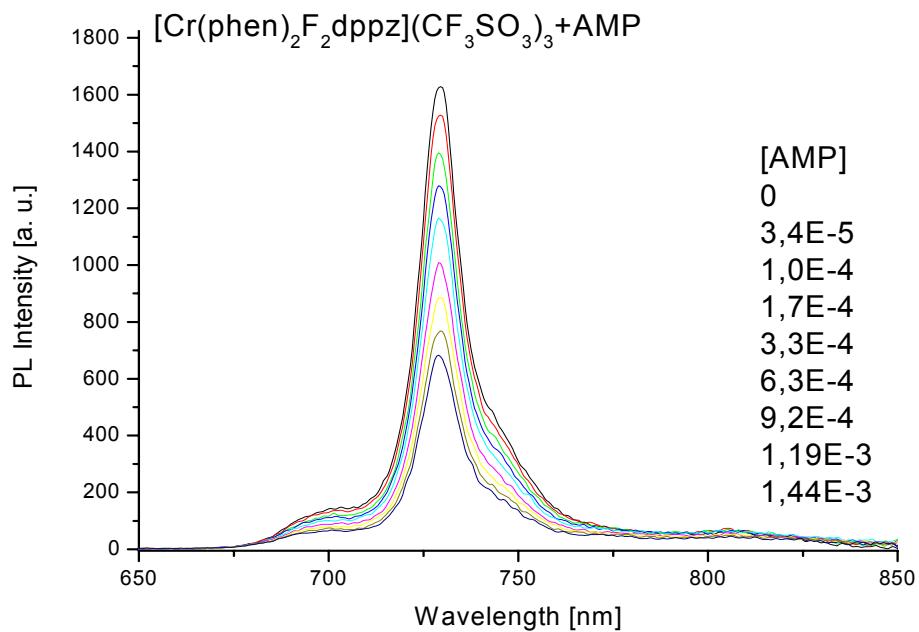


Fig. S6. Emission quenching of 100 mM phosphate buffer solution (pH 7.4) of $[\text{Cr}(\text{phen})_2(\text{F}_2\text{dppz})](\text{CF}_3\text{SO}_3)_3$ (36 μM) in the presence of increasing concentration of AMP.

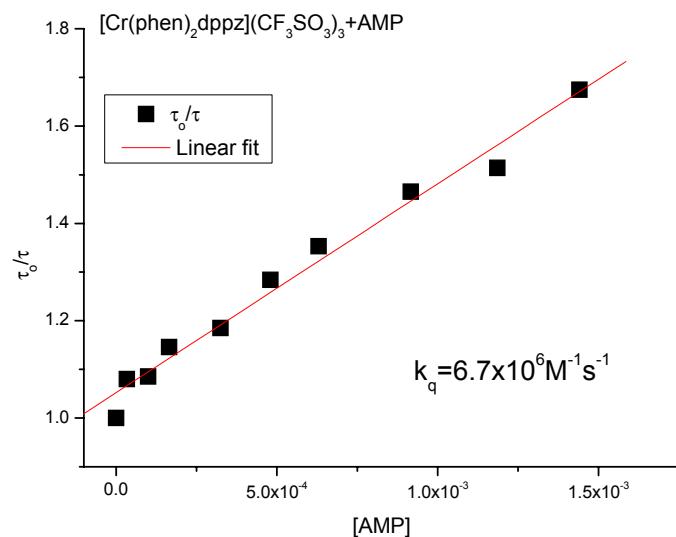


Fig. S7 Linear fit analysis of lifetime Stern Volmer plot for emission quenching (at 730 nm) of an air saturated 100 mM phosphate buffer solution (pH = 7.4) of [Cr(phen)₂(dppz)](CF₃SO₃)₃ (16 μM) in the presence of increasing concentration of AMP.

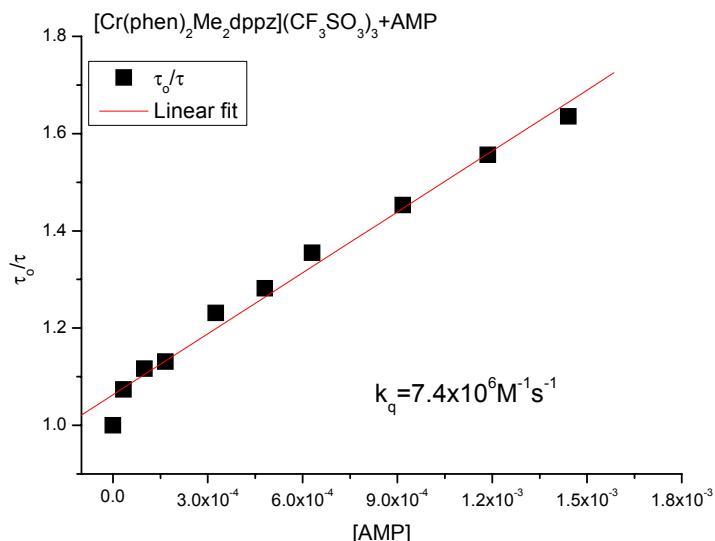


Fig. S8. Linear fit analysis of lifetime Stern Volmer plot for emission quenching (at 730 nm) of an air saturated 100 mM phosphate buffer solution (pH = 7.4) of [Cr(phen)₂(Me₂dppz)](CF₃SO₃)₃ (39 μM) in the presence of increasing concentration of AMP.

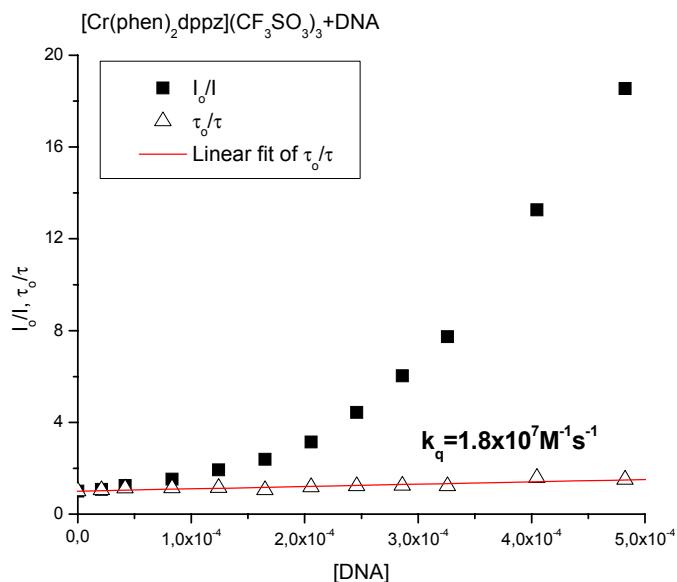


Fig. S9. Steady state and lifetime Stern Volmer plot for emission quenching (at 730 nm) of an air saturated 100 mM phosphate buffer (pH = 7.4) solution of [Cr(phen)₂(dppz)](CF₃SO₃)₃ (65 μM) in the presence of increasing concentration of CT-DNA.

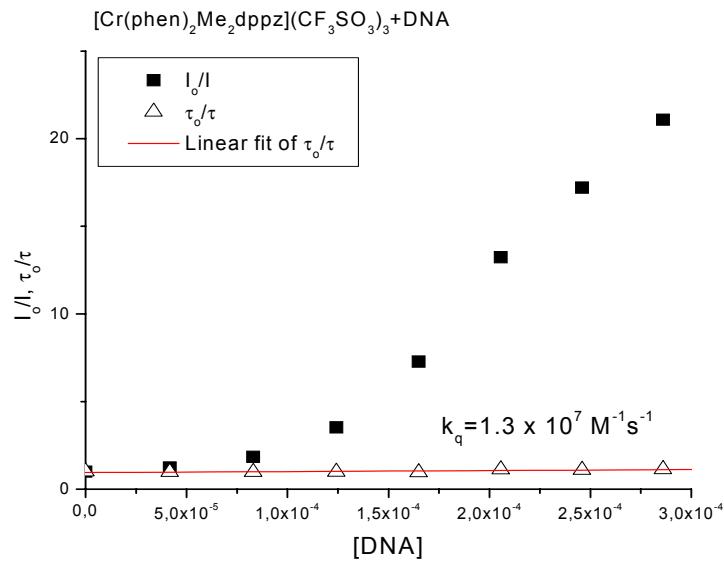


Fig. S10. Steady state and lifetime Stern Volmer plot for emission quenching (at 730 nm) of an air saturated 100 mM phosphate buffer (pH = 7.4) solution of [Cr(phen)₂(Me₂dppz)](CF₃SO₃)₃ (42 μM) in the presence of increasing concentration of CT-DNA.

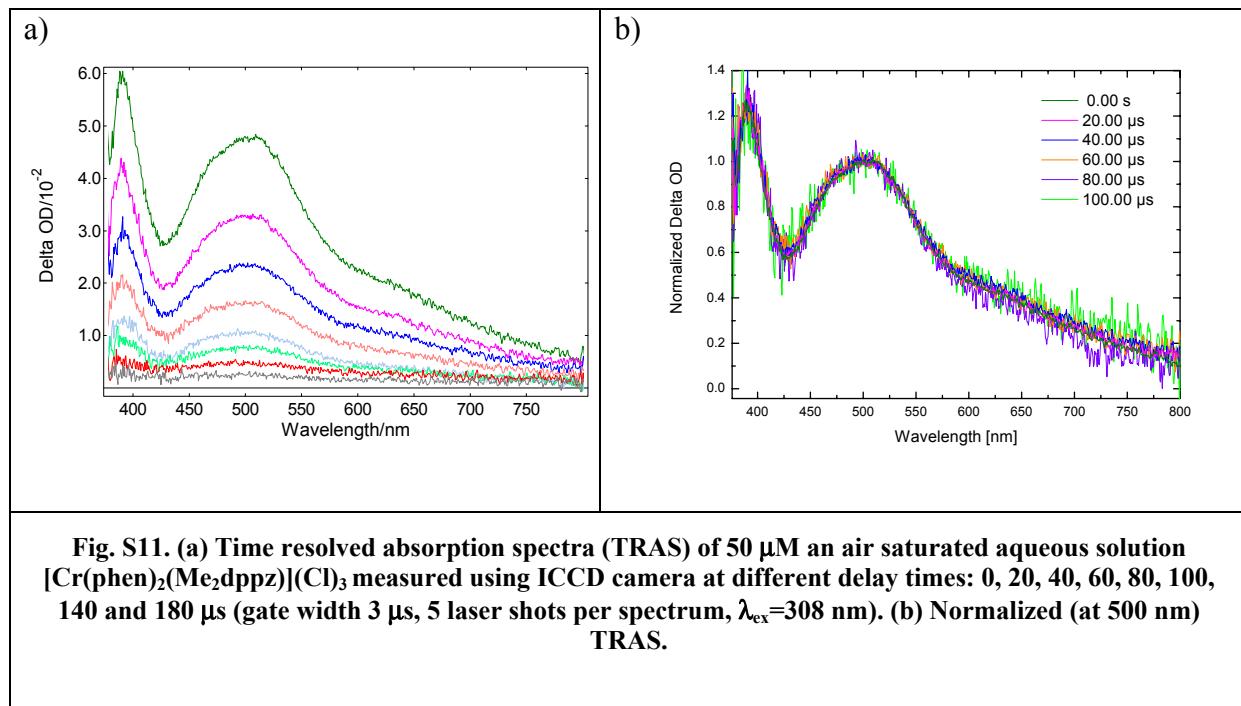


Fig. S11. (a) Time resolved absorption spectra (TRAS) of 50 μM an air saturated aqueous solution $[\text{Cr}(\text{phen})_2(\text{Me}_2\text{dppz})](\text{Cl})_3$ measured using ICCD camera at different delay times: 0, 20, 40, 60, 80, 100, 140 and 180 μs (gate width 3 μs , 5 laser shots per spectrum, $\lambda_{\text{ex}}=308 \text{ nm}$). (b) Normalized (at 500 nm) TRAS.

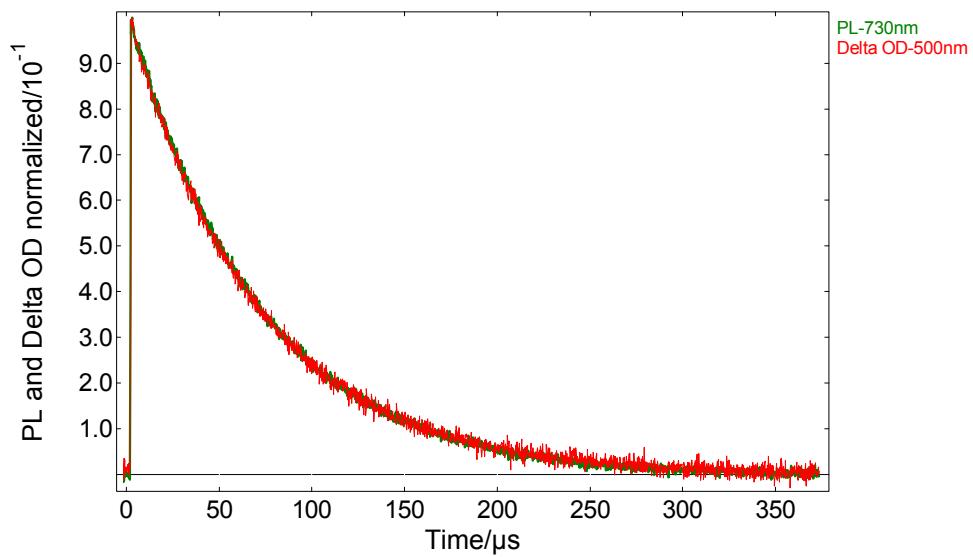


Fig. S12. Comparison of normalized kinetics of transient absorption band at 500 nm (red line) and phosphorescence at 730 nm (green line) of 50 μM aerated aqueous solution of $[\text{Cr}(\text{phen})_2(\text{Me}_2\text{dppz})](\text{Cl})_3$ ($\lambda_{\text{ex}}=308\text{nm}$). Note: both curves look almost identical.

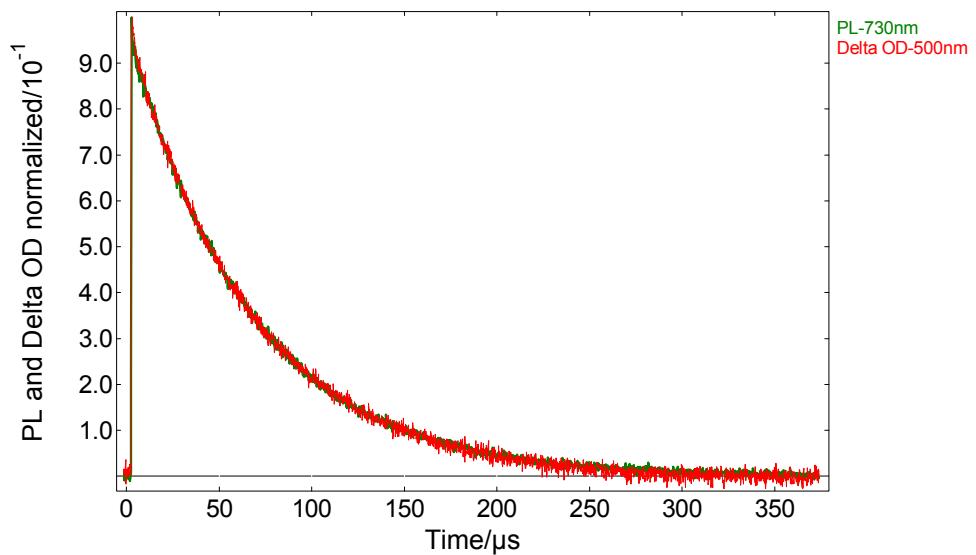


Fig. S13. Comparison of normalized kinetics of transient absorption band at 500 nm (green line) and phosphorescence at 730 nm (red line) of 50 μM aerated aqueous solution of $[\text{Cr}(\text{phen})_2(\text{dppz})](\text{Cl})_3$.