Electronic Supplementary Material (ESI) for Photochemical and Photobiological Science

Electronic Supporting Information (ESI)

Excited State Dependent Electron Transfer of Re-dppz Intercalator in DNA: A Time-resolved UV-Visible and IR Absorption Investigation into the Photophysics of *fac*-[Re(CO)$_3$(dppz-F$_2$)(py)]$^+$ Bound to Either [poly(dA-dT)]$_2$ or [poly(dG-dC)]$_2$

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Estimation of Binding Constants

The intrinsic binding constants, K_b, for the complex bound to [poly(dGdC)]$_2$ and [poly(dAdT)]$_2$ were determined by adding aliquots of the polynucleotide to a buffered solution (50 mM phosphate, pH 7) of known concentration of rhenium and employing using the method described by Yam et al.[1] using the following equation:

$$D/\Delta\varepsilon_{ap} = (D/\Delta\varepsilon) + (\Delta\varepsilon K_b)^{-1}$$

where:

- D is the concentration of the polynucleotide in base pairs, determined spectrophotometrically using molar (phosphate) absorption coefficients of ε_{254} = 8400 dm^3 mol^{-1} cm^{-1} [2] for [poly(dGdC)]$_2$ and ε_{262} = 6600 dm^3 mol^{-1} cm^{-1} for [poly(dAdT)]$_2$ [3]
- $\Delta\varepsilon_{ap} = (\varepsilon_a - \varepsilon_f)$, where ε_a is the apparent molar absorption coefficient, obtained from $A_{observed}$/[Re], and ε_f is the molar absorption coefficient of the free complex
- $\Delta\varepsilon = (\varepsilon_b - \varepsilon_f)$, where ε_b is the molar absorption coefficient of the fully-bound complex

A linear fit of a plot of $D/\Delta\varepsilon_{ap}$ vs D therefore yields a slope, $1/\Delta\varepsilon$ and y intercept, $(\Delta\varepsilon K_b)^{-1}$ respectively, the ratio of which gives the intrinsic binding constant, K_b.

1. Yam, V. W. W., Lo, K. K. W., Cheung, K. K., and Kong, R. Y. C., *J. Chem. Soc., Dalton Trans*., **1997**, 2067.
2. Wells, R. D. et al., *J. Mol. Biol.*, **1970**, *54*, 465.
3. Inman, R. B. et al., *J. Mol. Biol*., **1962**, *5*, 172.

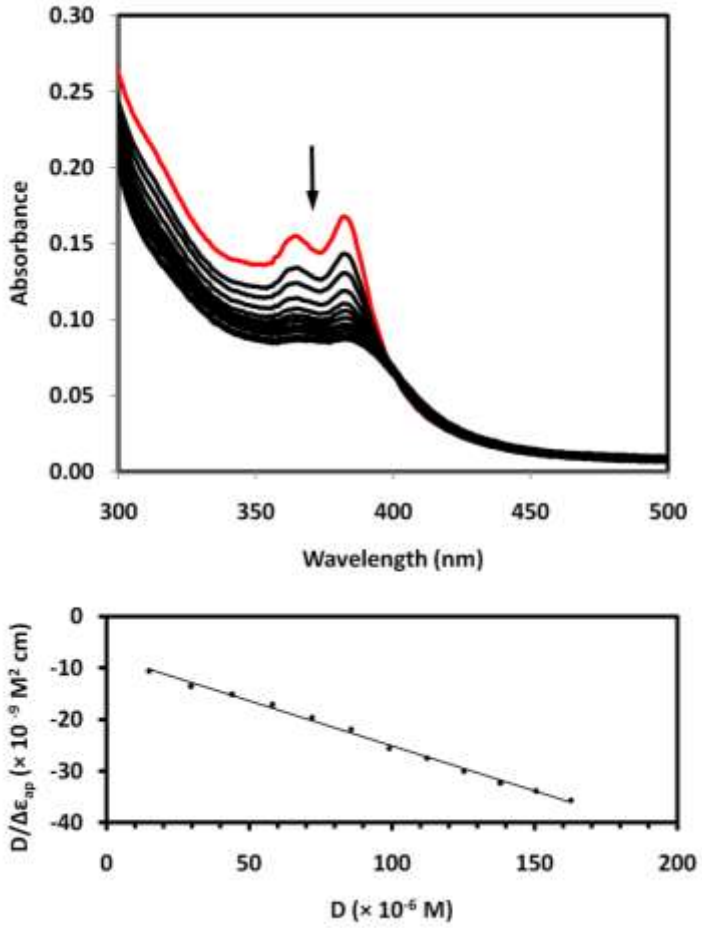

Figure S1. UV/vis absorption spectra of *fac*-$[Re(CO)_3(dppz\text{-}F_2)(py)]^+$ recorded at room temperature in buffered D_2O solution (red trace, 1.51 x 10^{-5}M) and in the presence of increasing concentrations (black traces) of $[poly(dA\text{-}dT)]_2$, up to [nucleotide]:[Re] ≈ 12:1. Also shown is the plot of $D/\Delta\varepsilon_{ap}$ vs. D for this experiment.

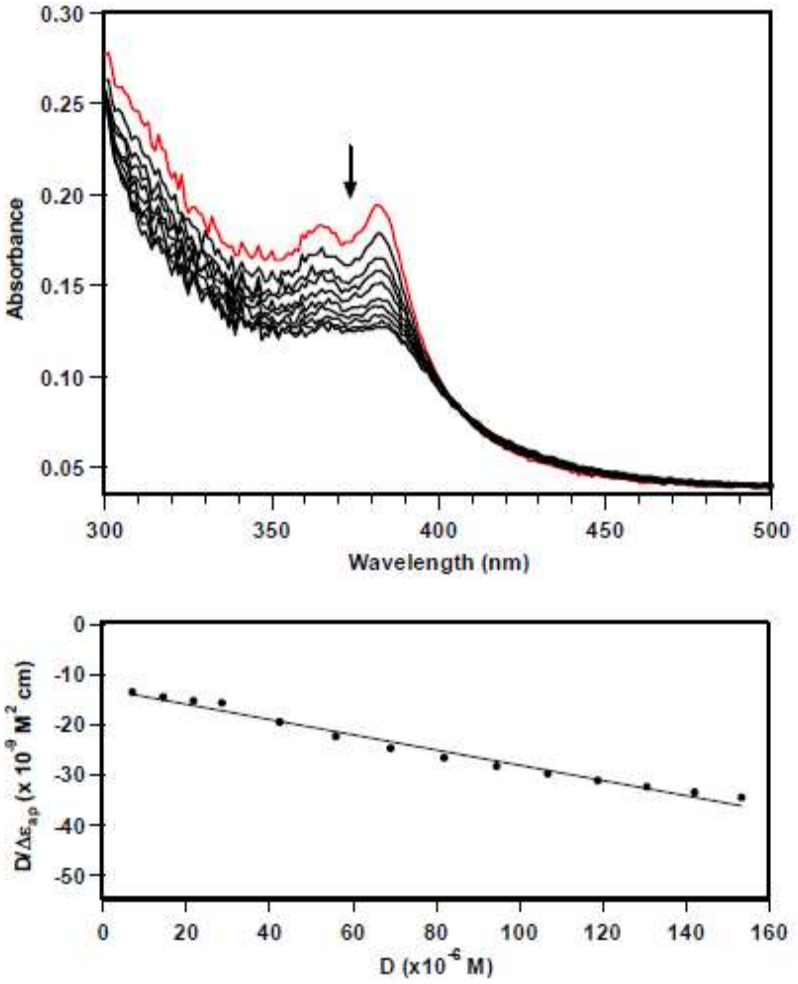

Figure S2. UV/vis absorption spectra of *fac*-$[Re(CO)_3(dppz\text{-}F_2)(py)]^+$ recorded at room temperature in buffered D_2O solution (red trace, 1.44 x 10^{-5}M) and in the presence of increasing concentrations (black traces) of $[poly(dG\text{-}dC)]_2$, up to [nucleotide]:[Re] ≈ 12:1. Also shown is the plot of $D/\Delta\varepsilon_{ap}$ vs. D for this experiment.

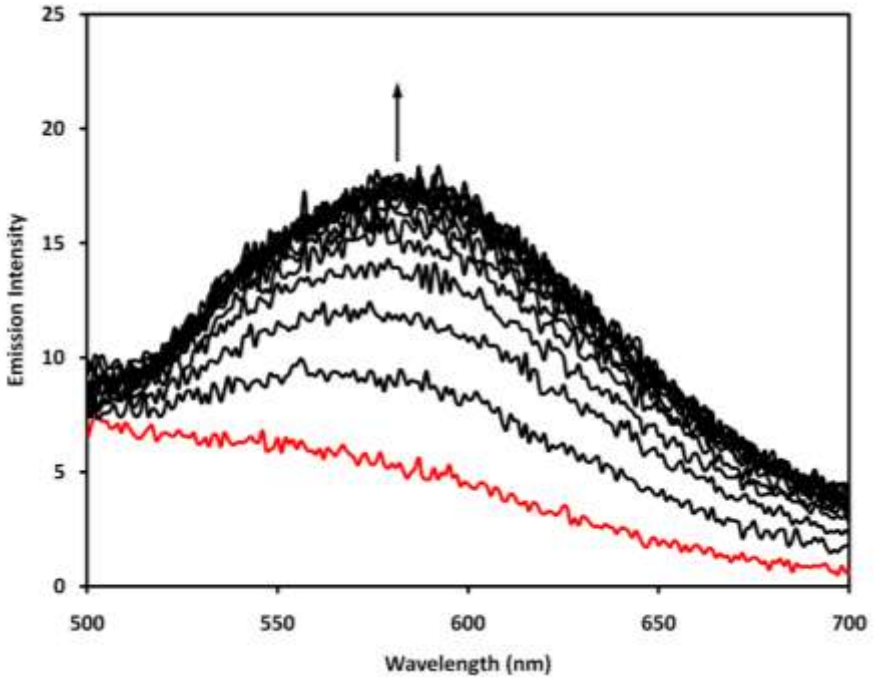

Figure S3. Steady state emission spectra of *fac*-$[Re(CO)_3(dppz\text{-}F_2)(py)]^+$ (λ_{ex} = 365 nm) recorded at room temperature in buffered D_2O solution (1.51×10^{-5} M, red trace) and in the presence of increasing concentrations (black traces) of $[poly(dA\text{-}dT)]_2$, up to [nucleotide]:[Re] ≈ 12:1. Spectra are corrected for background (10 mM phosphate buffer in D_2O).