Supplementary Material for Dalton Transactions

Electronic Supporting Information

Photophysical study of a family of $[Ru(phen)_2(Me_ndpq)]^{2+}$ complexes in different solvents and DNA: a specific water effect promoted by methyl substitution

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Table S1. Photophysical properties of $[Ru(phen)_2(dpq)]^{2+}$, **1**, in a range of solvents

	DMSO	MeCN	MeOH	EtOH	pH 7 tris buffer
$\lambda_{max\ abs}$ (nm)	450	447	446	446	448
$\varepsilon^{\lambda max}$ ($M^{-1}cm^{-1}$)	19500	19300	19100	19200	16100
$\lambda_{max\ em}$ (nm)	617	604	602	599	609
ϕ_{aer} [a]	0.038	0.012	0.019	0.016	0.019
τ_{aer} (ns)	423	155	167	170	250
ϕ_{deg} [a]	0.126	0.064	0.061	0.043	0.024
τ_{deg} (ns)	1360	760	602	351	335
$k_q[O_2]$ (M^{-1} s^{-1})[b]	3.5×10^9	2.7×10^9	2.1×10^9	1.4×10^9	3.5×10^9
k_r (s^{-1})	9.3×10^4	7.2×10^4	1.0×10^5	1.2×10^5	7.1×10^4
k_{nr} (s^{-1})	6.4×10^5	1.2×10^6	1.6×10^6	2.7×10^6	3.0×10^6

[a]Relative quantum yields compared to $[Ru(bpy)_3]^{2+}$, $\phi = 0.042$ in degassed aqueous solution and 0.028 in aerated aqueous solution. [b]k_q (O_2) evaluated using Stern-Volmer eq. $\tau_0/\tau = 1 + k_q\tau_0[O_2]$. Errors: $\lambda_{max.}$ abs ± 2 nm, ε ± 10 %, $\lambda_{max.}$ em ± 2 nm, ϕ_{em} ± 0.005, τ ± 10 %, k_q (O_2) ± 2×10^8 $M^{-1}s^{-1}$, k_r and k_{nr} ± 30%.

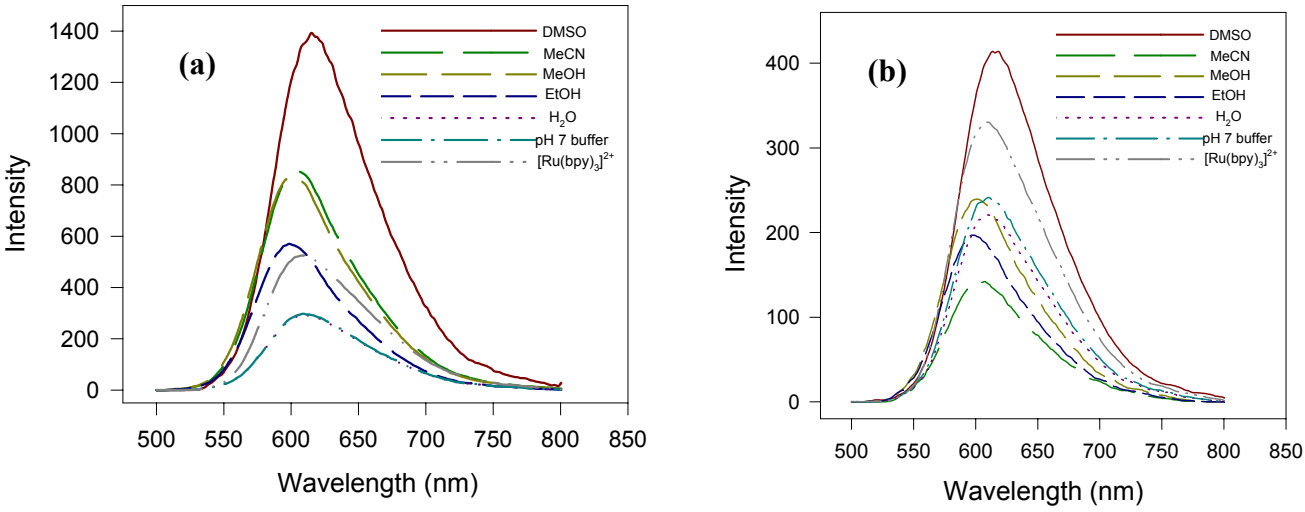

Figure S1. Emission spectra of **1** in degassed **(a)** and aerated **(b)** solutions. (Excitation at λ_{max} abs of the MLCT band)

Table S2. Photophysical properties of $[Ru(phen)_2(Medpq)]^{2+}$, **2**, in a range of solvents

	DMSO	MeCN	MeOH	EtOH	pH 7 tris buffer
$\lambda_{max\ abs}$ (nm)	452	447	446	446	448
$\varepsilon^{\lambda max}$ ($M^{-1}cm^{-1}$)	19400	19300	19200	19500	16200
$\lambda_{max\ Em}$ (nm)	613	598	599	597	608
ϕ_{aer} [a]	0.040	0.012	0.011	0.013	0.035
τ_{aer} (ns)	390	140	150	147	465
ϕ_{deg} [a]	0.122	0.052	0.054	0.024	0.063
τ_{deg} (ns)	1267	603	482	270	803
$k_q[O_2]$ (M^{-1} s^{-1})[b]	3.9×10^9	2.9×10^9	2.2×10^9	1.5×10^9	3.1×10^9
k_r (s^{-1})	9.6×10^4	8.5×10^4	1.1×10^5	8.9×10^4	7.9×10^4
k_{nr} (s^{-1})	6.9×10^5	1.6×10^6	2.0×10^6	3.6×10^6	1.2×10^6

[a]Relative quantum yields compared to $[Ru(bpy)_3]^{2+}$, $\phi = 0.042$ in degassed aqueous solution and 0.028 in aerated aqueous solution. [b] k_q (O_2) evaluated using Stern-Volmer eq. $\tau_0/\tau = 1 + k_q\tau_0[O_2]$. Errors: $\lambda_{max.}$ abs ± 2 nm, ε ± 10 %, $\lambda_{max.}$ em ± 2 nm, ϕ_{em} ± 0.005, τ ± 10 %, k_q (O_2) ± 2×10^8 $M^{-1}s^{-1}$, k_r and k_{nr} ± 30%.

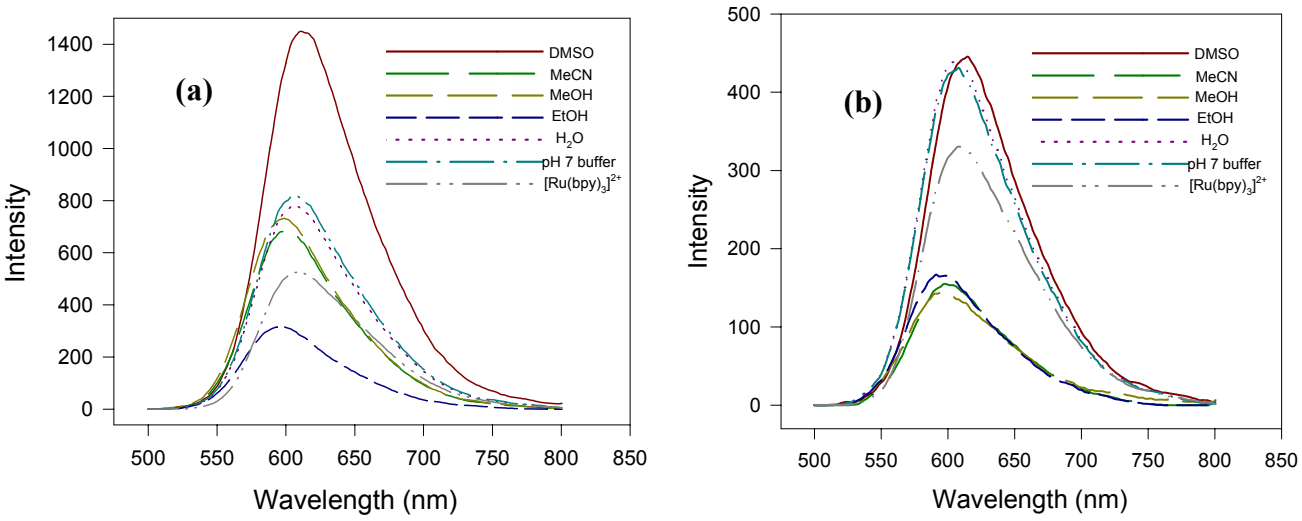

Figure S2. Emission spectra of **2** in degassed **(a)** and aerated **(b)** solutions. (Excitation at λ_{max} abs of the MLCT band)

Table S3. Photophysical properties of $[Ru(phen)_2(Me_2dpq)]^{2+}$, **3,** in a range of solvents

	DMSO	MeCN	MeOH	EtOH	pH 7 tris buffer
$\lambda_{max\ abs}$ (nm)	452	447	446	447	448
$\varepsilon^{\lambda max}$ ($M^{-1}cm^{-1}$)	19200	19000	19400	19200	15400
$\lambda_{max\ Em}$ (nm)	610	597	593	592	605
ϕ_{aer} [a]	0.042	0.011	0.014	0.010	0.041
τ_{aer} (ns)	376	122	137	141	545
ϕ_{deg} [a]	0.117	0.047	0.040	0.019	0.080
τ_{deg} (ns)	1199	544	425	270	1078
$k_q[O_2]$ (M^{-1} s^{-1})[b]	4.0×10^9	3.3×10^9	2.4×10^9	1.6×10^9	3.1×10^9
k_r (s^{-1})	9.8×10^4	8.6×10^4	9.4×10^4	7.0×10^4	7.4×10^4
k_{nr} (s^{-1})	7.4×10^5	1.8×10^6	2.3×10^6	3.4×10^6	8.5×10^5

[a] Relative quantum yields compared to $[Ru(bpy)_3]^{2+}$, $\phi = 0.042$ in degassed aqueous solution and 0.028 in aerated aqueous solution. [b] k_q (O_2) evaluated using Stern-Volmer eq. $\tau_0/\tau = 1 + k_q\tau_0[O_2]$. Errors: $\lambda_{max.}$ abs ± 2 nm, ε ± 10 %, $\lambda_{max.}$ em ± 2 nm, ϕ_{em} ± 0.005, τ ± 10 %, k_q (O_2) ± 2×10^8 $M^{-1}s^{-1}$, k_r and k_{nr} ± 30%.

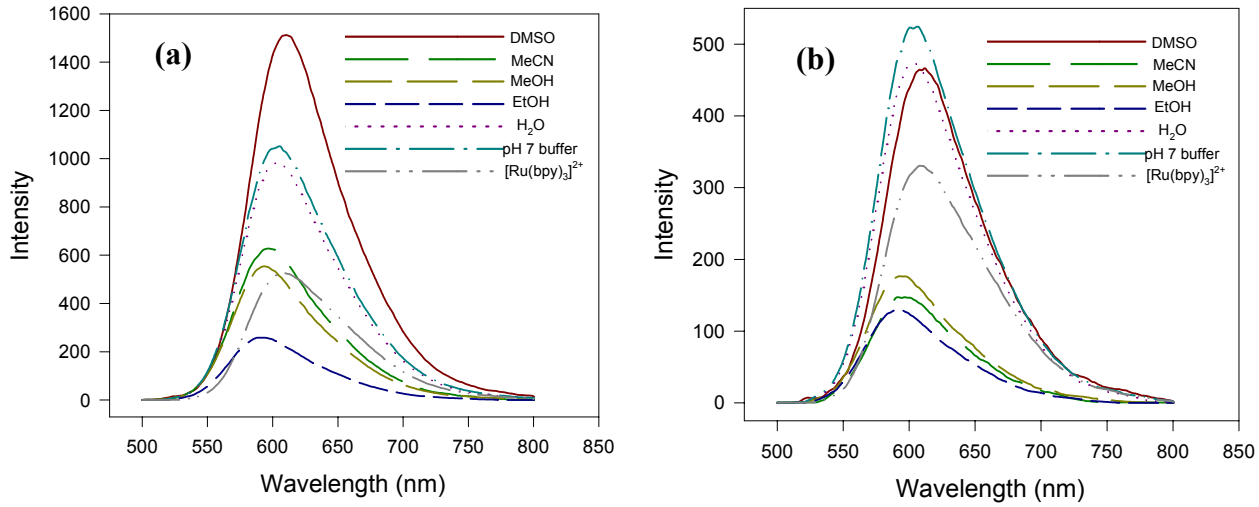

Figure S3. Emission spectra of **3** in degassed **(a)** and aerated **(b)** solutions. (Excitation at λ_{max} abs of the MLCT band)