Supporting Information

A New Os,Rh Bimetallic with O_2 Independent DNA Cleavage and DNA Photobinding with Red Therapeutic Light Excitation

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Table of Contents

Experimental Materials

Synthesis of [(bpy)$_2$Os(dpp)RhCl$_2$(phen)](PF$_6$)$_3$: The Os,Rh bimetallic complex [(bpy)$_2$Os(dpp)RhCl$_2$(phen)](PF$_6$)$_3$ was synthesized by reacting a Os monometallic synthon [(bpy)$_2$Os(dpp)](PF$_6$)$_2$ and Rh monochelate starting material K[Rh(phen)Cl$_4$]. [(bpy)$_2$Os(dpp)](PF$_6$)$_2$ and K[Rh(phen)Cl$_4$] were prepared as previously described.[1,2] The complex [(bpy)$_2$Os(dpp)](PF$_6$)$_2$ (0.10 g, 0.10 mmol) and K[Rh(phen)Cl$_4$] (0.060 g, 0.12 mmol) were heated to reflux under Ar in a 30 mL ethanol:H$_2$O v/v(1:1) solution for 75 min. The purple color mixture solution was cooled to RT; then, added into a saturated aqueous solution of NH$_4$PF$_6$ (30 mL) to induce the precipitation. The precipitate was collected by vacuum filtration and was dissolved in ca. 10 ml acetone, syringe filtered, reprecipitated in ca. 500 mL diethyl ether and collected by vacuum filtration. The precipitation was further purified by the recrystallization in ca. 200 mL absolute ethanol. The recrystallized product was collected by vacuum filtration, dissolved in ca. 10 ml acetone, precipitated in ca. 500 ml diethyl ether collected by vacuum filtration and dried under vacuum. Yield = 0.11 g, 0.075 mmol (75 %) ESI-MS: $[M-PF_6]^+$, m/z = 1381. Electrochemical, and spectroscopic data are summarized in Tables S1, and S2.

Electronic Absorption Spectroscopy. Electronic absorption spectra were collected using a Hewlett-Packard 8452A diode array spectrophotometer (2 nm resolution) in spectroscopic grade acetonitrile (Burdick and Jackson). Measurements were repeated three times on independently prepared solutions for calculation of molar absorptivity.

Electrochemistry. The cyclic voltammetry experiments were conducted with a Bioanalytical Systems (BAS) electrochemical analyzer with a three-electrode system, which has a platinum disk working electrode, a platinum wire auxiliary electrode and a Ag/AgCl reference electrode (0.209 V vs. NHE) which was calibrated against the $FeCp_2/FeCp_2^+$ redox couple in 0.1 M Bu_4NPF_6 CH_3CN.

DNA photobinding and photocleavage using gel shift electrophoresis assay: The DNA-metal complex solutions were prepared with 30.6 µM DNA and 6.1 µM metal complex, which results in a 5:1 BP (base pairs):MC (metal complex) ratio in 10 mM phosphate buffer (pH=7.4). The DNA-metal complex samples were deoxygenated using argon for 20 minutes prior to photolysis. Samples were blanketed with argon and photolyzed for 60, 120, 210, and 240 minutes using a 1000 W xenon arc lamp fitted with a water IR filter and a glass cut-on filter ($\lambda \geq$ 590 nm or 645 nm). A 0.8% w/w gel was made and placed in a model B1A stage (Owl Separation Systems) with 300 ml of 5X TB buffer (90 mM tris base, 90 mM boric acid). Each sample was prepared for loading by removing a 10 µl aliquot and adding 2 µl of loading dye. The samples were loaded into their respective wells. A potential of 1.04 V was applied through the gel for 1.5 h. Following electrophoresis, gels were stained in 0.5 µg/ml ethidium bromide for 1 h and washed using double deionized water for 0.5 h. The gels were visualized on a Fisher Biotech UV-transilluminator and images were captured using an Olympus SP-320 camera fitted with an ethidium bromide filter.

Table S1. Electrochemical Properties for Os Monometallic Complex and Os,Rh Bimetallic Complex and Related Os,Rh,Os Trimetallic Complex in RT CH_3CN

Complex [a]	$E_{1/2}$ (V)	Assignments
$[(bpy)_2Os(dpp)]^{2+}$ [b]	+0.94	$Os^{II/III}$
	−1.02	$dpp^{0/-}$
	−1.38	$bpy^{0/-}$
	−1.58	$bpy^{0/-}$
$[(bpy)_2Os(dpp)RhCl_2(phen)]^{3+}$	+1.20	$Os^{II/III}$
	−0.46[c]	$Rh^{III/II}$
	−0.75[c]	$Rh^{II/I}$
	−0.98	$dpp^{0/-}$
$[\{(bpy)_2Os(dpp)\}_2RhCl_2]^{5+}$ [d]	+1.21[e]	$Os^{II/III}$
	−0.39[c]	$Rh^{III/II/I}$
	−0.76	$dpp^{0/-}$
	−1.00	$dpp^{0/2-}$

[a] Measured against a Ag/AgCl reference electrode with a Pt disk working electrode and a Pt wire counter electrode in 0.1 M Bu_4PF_6 in acetonitrile at room temperature with bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, phen = 1,10-phenanthroline.
[b] Ref. 1.
[c] Reported E_p^c of irreversible process.
[d] Ref. 3.
[e] Two overlapping, one-electron reversible waves.

Table S2. Light Absorbing Properties of Os Monometallic Complex and Os,Rh Bimetallic Complex and Related Os,Rh,Os Trimetallic Complex in RT CH_3CN

Complex [a]	λ^{abs} (nm)	$\varepsilon \times 10^{-4}$ ($M^{-1}cm^{-1}$)	Assignment
$[(bpy)_2Os(dpp)]^{2+}$ [b]	290	6.7	bpy $\pi\to\pi^*$
	432	1.1	Os(dπ)→bpy(π^*) CT
	486	1.3	Os(dπ)→dpp(π^*) CT
$[(bpy)_2Os(dpp)RhCl_2(phen)]^{3+}$	284	7.0	bpy, phen $\pi\to\pi^*$
	413	1.0	Os(dπ)→bpy(π^*) CT
	521	1.8	Os(dπ)→dpp(π^*) CT
	750	0.29	Os(dπ)→dpp(π^*) CT ^{3}MLCT
$[\{(bpy)_2Os(dpp\}_2RhCl_2]^{5+}$	284	12	bpy $\pi\to\pi^*$
	412	2.2	Os(dπ)→bpy(π^*) CT
	534	3.6	Os(dπ)→dpp(π^*) CT
	798	0.61	Os(dπ)→dpp(π^*) CT ^{3}MLCT

[a] Measured in acetonitrile at room temperature, bpy = 2,2'-bipyridine, dpp = 2,3-bis(2-pyridyl)pyrazine, phen = 1,10-phenanthroline.
[b] Ref. 1.

References

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(3) Holder, A. A.; Swavey, S.; Brewer, K. J. *Inorg. Chem.* **2004**, *43*, 303.