Supporting Information for

Responsive Ruthenium Complex Probe for Phosphorescence and Time-
Gated Luminescence Detection of Bisulfite

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Lucia, QLD 4072, Australia

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1. General information

Reagents and instruments

4-Bromo-1,10-phenanthroline\(^1\) and \(\text{cis-Ru(bpy)}\text{Cl}_2\cdot2\text{H}_2\text{O}\)\(^{2-3}\) were synthesized following literature methods. 2,4-Dinitroaniline and phenol were purchased from Aladdin (China). Wine sample was purchased from local supermarket in Dalian, China. Unless otherwise stated, all the reagents used in experiments were obtained from commercial sources. The solvents and reagents are analytical grade from commercial suppliers, and were used directly without further purification. Deionized water was used throughout.

\(^1\)H NMR and \(^{13}\)C NMR spectra were acquired on a Bruker Avance NMR spectrometer (500 MHz for \(^1\)H and 100 MHz for \(^{13}\)C). Mass spectra of the compounds were determined on a LTQ Orbitrap XL mass spectrometer and an Agilent 6224 mass spectrometer. Elemental analysis was performed on a Vario-EL analyser. UV-visible absorption spectra were recorded on a Perkin-Elmer Lambda 35 UV-vis spectrometer (1.0 cm quartz cell) at 25 °C. Phosphorescence (0 ns delay time) and time-gated luminescence (TGL, 100 ns delay time) spectra were recorded using an Edinburgh FS5 spectrometer with excitation and emission slits of 3 nm (1.0 cm quartz cell) at 25 °C.

Theoretical calculation

The theoretical computation was conducted by using the Gaussian 09 package of programs.\(^4\) The molecular structures of Ru-azo and Ru-SO3 at ground-states and excited states were firstly optimized using the density functional theory (DFT).\(^5\) Based on these optimized molecular structures, the related excited-state calculations were then conducted by the time-dependent DFT (TD-DFT) method. The Beck’s three-parameter hybrid functional with the Lee-Yang-Parr correlation functional (B3LYP)\(^6\) was used throughout. The LanL2DZ basis set\(^7\) was used for Ru atoms in both complexes, whereas 6-311*G(d, p) basis set\(^8\) was applied to hydrogen, carbon, nitrogen, sulphur and oxygen atoms. The polarized continuum model (PCM)\(^9\) was employed for the solvent effects (water) in optimization, absorbance and emission calculations.
2. Synthesis and characterization of Ru(II) complexes

Scheme S1. Reaction pathway for the synthesis of 4-((2,4-dinitrophenyl)diazenyl)phenol.

Fig. S1. 'H NMR spectrum of 4-((2,4-dinitrophenyl)diazenyl)phenol in CDCl₃.
Fig. S2. ESI-MS of 4-((2,4-dinitrophenyl)diazenyl)phenol in CHCl₃.

Fig. S3. ¹H NMR spectrum of [Ru(bpy)₂(Br-phen)](PF₆)₂ in CD₃CN.
Fig. S4. ESI-MS of [Ru(bpy)$_2$(Br-phen)](PF$_6$)$_2$ in CH$_3$CN.

Fig. S5. $^1$H NMR spectrum of Ru-azo in CD$_3$CN.
**Fig. S6.** $^{13}$C NMR spectrum of Ru-azo in CD$_3$CN.

**Fig. S7.** ESI-MS of Ru-azo in CH$_3$CN.
Fig. S8. HRMS of Ru-azo in the presence of bisulfite.

Fig. S9. Job plot analysis of the reaction between Ru-azo and HSO$_3^-$ in PBS (25 mM, pH = 7.4). Total concentration of Ru-azo and HSO$_3^-$ was at a constant at 10 μM. (λ$_{ex}$ = 466 nm, λ$_{em}$ = 635 nm).
**Fig. S10.** Emission decay trace of Ru-azo in 25 mM PBS buffer of pH 7.4.
3. Theoretical computations

**Fig. S11.** Emission decay trace of **Ru-SO3** in 25 mM PBS buffer of pH 7.4.

**Fig. S12.** Molecular structure of **Ru-azo** (A) and optimized molecular geometries of **Ru-azo** in the ground state (S₀) (B) and first triplet state (T₁) (C) obtained from DFT calculations at B3LYP/6-311+G(d, p)//LANL2DZ level of theory.
Table S1. Cartesian coordinates of **Ru-azo** in the ground state (S<sub>0</sub>) and excited state (T<sub>1</sub>).

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Fig. S13. Molecular structure of Ru-SO₃ (A) and optimized molecular geometries of Ru-SO₃ in the ground state (S₀) (B) and first triplet state (T₁) (C) obtained from DFT calculations at B3LYP/6-311+G(d, p)//LANL2DZ level of theory.

Table S2. Cartesian coordinates of Ru-SO₃ in the ground state (S₀) and excited state (T₁).

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S-13
Fig. S14. Representative frontier molecular orbital distributions of Ru-azo and their corresponding energies at ground state \( (S_0) \) optimized geometries (isodensity contour = 0.02 a.u.).
Fig. S15. Representative frontier molecular orbital distributions of Ru-SO3 and their corresponding energies at ground state (S₀) optimized geometries (isodensity contour = 0.02 a.u.).

Table S3. Absorptions of Ru-azo and Ru-SO3 in aqueous solution from the calculation conducted by TDDFT//B3LYP//6-311+G(d, p), based on the optimized molecular geometries in the ground state.

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*only the selected low-lying excited states are presented. *oscillator strength. *only the main configurations are presented. *contributions over 10% are presented. IL’CT: intraligand charge transfer; ET: electron transfer (L: bpy; L’: azo-phen or SO3-phen).
**Fig. S16.** Representative frontier molecular orbital distributions of Ru-azo and their corresponding energies at excited state ($T_1$) optimized geometries (isodensity contour = 0.02 a.u.).

**Fig. S17.** Representative frontier molecular orbital distributions of Ru-SO3 and their corresponding energies at excited state ($T_1$) optimized geometries (isodensity contour = 0.02 a.u.).
4. Supplementary phosphorescence and TGL detection results

**Fig. S18.** Time-dependent phosphorescence response ($\lambda_{ex} = 466$ nm, $\lambda_{em} = 635$ nm) of Ru-azo (10 $\mu$M) to the addition of bisulfite (500 $\mu$M).

**Fig. S19.** Effects of pH on the phosphorescence intensity ($\lambda_{ex} = 466$ nm, $\lambda_{em} = 635$ nm) of Ru-azo (10 $\mu$M) in the absence and presence of bisulfite (500 $\mu$M).
Fig. S20. Correlation between the phosphorescence intensity and bisulfite concentration after Ru-azo (10 μM) was reacted with different concentrations of bisulfite in 25 mM PBS buffer of pH 7.4.

\[
y = 133.5 + 3.943x \\
R^2 = 0.992
\]

Fig. S21. Phosphorescence (A, 0 ns delay) and TGL (B, 100 ns delay) emission spectra (λ_{ex} = 450 nm) of Ru-azo (10 μM), 50-fold diluted wine, and Ru-azo (10 μM) in 50-fold diluted wine before and after addition of bisulfite (5.0 μM).

5. Reference


