Electronic Supplementary Information for

Development of singlet oxygen-responsive phosphorescent ruthenium(II) complexes

Zhiqiang Ye,* Bo Song, Yuejiao Yin, Run Zhang, Jingli Yuan*

State Key Laboratory of Fine Chemicals, School of Chemistry, Dalian University of Technology, Dalian 116024, China

*Corresponding authors. Tel/Fax: +86-411-84986041. E-mail addresses: yezq@dlut.edu.cn (Z.Y.); jingliyuan@aliyun.com (J.Y.).

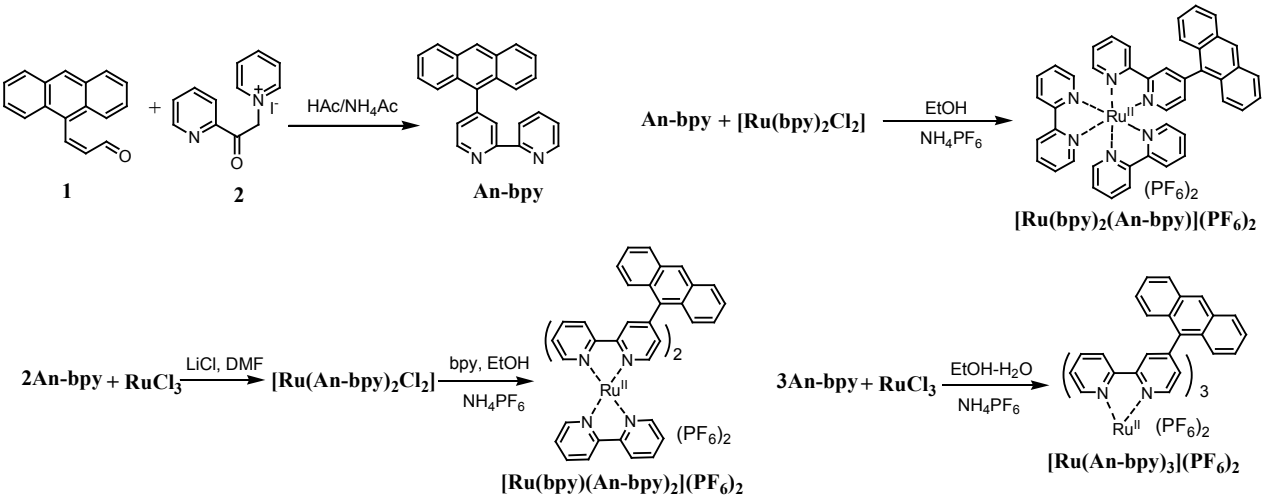
Experimental Details

Materials and physical measurements. $RuCl_3 \cdot 3H_2O$ and anthracene-9-carboxaldehyde were purchased from Acros Organics (Belgium). cis-Ru(II)$(bpy)_2Cl_2 \cdot 2H_2O$, and the compound **1** and **2** used for the synthesis of An-bpy were synthesized according to the literature methods.[S1-S3] The reactive oxygen/nitrogen species (ROS/RNS) including $^1O_2$, H_2O_2, ClO^-, $^{\cdot}OH$, NO, $ONOO^-$ and $O^{2-\cdot}$ were prepared using the previous methods.[S4] Unless otherwise stated, all chemical materials were purchased from commercial sources and used without further purification.

^1H NMR spectra were recorded on a Bruker Avance spectrometer (400 MHz). MS spectra were measured on a Q-TOF Micro MS spectrometer. Absorption spectra were measured on a Perkin-Elmer Lambda 35 UV-vis spectrometer. Elemental analysis was carried out on a Vario-EL

analyser. Phosphorescence spectra were measured on a Perkin-Elmer LS 50B luminescence spectrometer with excitation and emission slits of 10 nm.

Syntheses of the Ru(II) Complexes. The reaction pathway for the synthesis of $[Ru(bpy)_{3-n}(An\text{-}bpy)_n](PF_6)_2$ (n = 1, 2, 3) is shown in Scheme S1.



Scheme S1. Reaction pathway for the synthesis of $[Ru(bpy)_{3-n}(An\text{-}bpy)_n](PF_6)_2$ (n = 1, 2, 3).

The experimental details are described as follows.

Synthesis of An-bpy. After a solution of compound **2** (10.4 g, 30 mmol) and ammonium acetate (28 g) in 100 mL of acetic acid was refluxed for 0.5 h, compound **1** (6.0 g, 30 mmol) was slowly added within 1.5 h. The reaction mixture was refluxed for 16 h, then cooled to room temperature. The pH of the mixture was adjusted to ~7 with 15% NaOH, and then the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The organic phase was dried with Na_2SO_4 and evaporated. After purification by silica gel column chromatography with CH_2Cl_2/CH_3OH (100:1, v/v) as eluent, An-bpy was obtained as a brown solid (1.0 g, 10% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (m, 3H), 7.51 (m, 3H), 7.63 (d, *J* = 8.8 Hz, 2 H), 7.94 (m, 1H), 8.09 (d, *J* = 8.4 Hz, 2 H), 8.57 (s, 1 H), 8.61 (s, 1 H), 8.65 (d, *J* = 6.8 Hz, 2 H), 8.96 (d, *J* = 4.8 Hz, 1 H). MS (*m*/*z*): 333.0 ($[M+H]^+$).

Synthesis of $[Ru(bpy)_2(An\text{-}bpy)](PF_6)_2$. A mixture of An-bpy (170 mg, 0.5 mmol) and *cis*-Ru(II)$(bpy)_2Cl_2 \cdot 2H_2O$ (240 mg, 0.5 mmol) in 50 mL of ethanol was refluxed for 8 h. After the solvent was evaporated, the residue was purified by silica gel column chromatography using CH_3CN-H_2O-KNO_3 (sat.) (100:10:1, v/v/v) as eluent. A fraction containing the target product was collected, and the solvent was evaporated. The resulting solid was dissolved in 5.0 mL of ethanol-water (1:1), and then a solution of NH_4PF_6 (2 mM) was added dropwise to give a red precipitate. The product was filtered, washed with small amount of water, and dried. Complex $[Ru(bpy)_2(An\text{-}bpy)](PF_6)_2$ was obtained (360 mg, 70% yield). ^{1}H NMR (400 MHz, CD_3CN): δ = 7.37 (m, 5H), 7.48 (m, 6H), 7.77 (m, 5H), 7.89 (d, *J* = 8.0 Hz, 1 H), 7.96 (d, *J* = 8.0 Hz, 1 H), 8.02 (m, 1H), 8.09 (m, 3H), 8.18 (m, 3H), 8.45 (d, *J* = 8.0 Hz, 1 H), 8.55 (m, 4H), 8.65 (s, 1H), 8.75 (s, 1H). MS (*m/z*): 891.1 ($[M-PF_6]^+$), 373.1 ($[M-2PF_6]^{2+}$). Elemental analysis (%) calcd. for $C_{44}H_{32}F_{12}N_6P_2Ru$: C 51.02, H 3.11, N 8.11; found: C 50.89, H 3.28, N, 8.07.

Synthesis of $[Ru(An\text{-}bpy)_2Cl_2]$. After An-bpy (390 mg, 1.17 mmol) and LiCl (150 mg, 3.48 mmol) were added into 4 mL of DMF containing $RuCl_3 \cdot 3H_2O$ (120 mg, 0.58 mmol), the mixture was refluxed for 8 h under an argon atmosphere. The solution was cooled to room temperature, then 20 mL acetone was added, and the reaction mixture was stored at -20 °C overnight. The precipitate was filtered, washed with water (3 × 10 mL) and ethyl ether (2 × 10 mL), and dried. The obtained product was directly used for the synthesis of $[Ru(bpy)(An\text{-}bpy)_2](PF_6)_2$ without further purification.

Synthesis of $[Ru(bpy)(An\text{-}bpy)_2](PF_6)_2$. A mixture of $[Ru(An\text{-}bpy)_2Cl_2]$ (148 mg, 0.18 mmol) and bpy (27.6 mg, 0.18 mmol) in 30 mL of ethanol was refluxed for 8 h. After the solvent was evaporated, the residue was purified by silica gel column chromatography using CH_3CN-H_2O-KNO_3 (sat.) (100:10:1, v/v/v) as eluent. A fraction containing the target product was

collected, and the solvent was evaporated. The resulting solid was dissolved in 5.0 mL of ethanol-water (1:1), and then a solution of NH_4PF_6 (2 mM) was added dropwise to give a red precipitate. The product was filtered, washed with small amount of water, and dried. Complex $[Ru(bpy)(An\text{-}bpy)_2](PF_6)_2$ was obtained (105 mg, 60% yield). ^1H NMR (400 MHz, CD_3CN): δ = 7.39 (m, 7H), 7.53 (m, 6H), 7.61 (m, 4H), 7.88 (m, 4H), 8.01 (m, 4H), 8.15 (m, 7H), 8.46 (m, 2H), 8.61 (m, 2H), 8.73 (m, 3H), 8.77 (s, 1H). MS (m/z): 1067.1 ($[M-PF_6]^+$), 461.1 ($[M-2PF_6]^{2+}$). Elemental analysis (%) calcd. for $C_{58}H_{40}F_{12}N_6P_2Ru\cdot H_2O$: C 56.64, H 3.44, N 6.83; found: C 57.01, H 3.74, N, 6.45.

Synthesis of $[Ru(An\text{-}bpy)_3](PF_6)_2$. A solution of An-bpy (81 mg, 0.24 mmol) in 20 mL ethanol was added into 4 mL of water containing $RuCl_3\cdot 3H_2O$ (17 mg, 0.08mmol). After the solution was refluxed for 24 h under an argon atmosphere, the solvent was evaporated, and the residue was purified by silica gel column chromatography using CH_3CN-H_2O-KNO_3 (sat.) (80:10:1, v/v/v) as eluent. A fraction containing the target product was collected, and the solvent was evaporated. The resulting solid was dissolved in 5.0 mL of ethanol-water (1:1), and then a solution of NH_4PF_6 (2 mM) was added dropwise to give a red precipitate. The product was filtered, washed with small amount of water, and dried. Complex $[Ru(An\text{-}bpy)_3](PF_6)_2$ was obtained (85 mg, 75% yield). ^1H NMR (400 MHz, CD_3CN): δ = 7.36 (m, 3H), 7.49 (m, 3H), 7.54 (m, 18H), 7.73 (d, J = 4.0 Hz, 3H), 8.11 (m, 3H), 8.18 (m, 9H), 8.54 (m, 3H), 8.79 (d, J = 12.0 Hz, 6H). MS (m/z): 1243.2 ($[M-PF_6]^+$), 549.1 ($[M-2PF_6]^{2+}$). Elemental analysis (%) calcd. for $C_{72}H_{48}F_{12}N_6P_2Ru\cdot 2H_2O$: C 60.72, H 3.68, N 5.90; found: C 61.13, H 4.12, N, 5.62.

Reaction of $[Ru(bpy)_{3-n}(An\text{-}bpy)_n](PF_6)_2$ with $^1O_2$. All the experiments were carried out in 0.1 M carbonate buffer of pH 10.5 using Na_2MoO_4-H_2O_2 system as a $^1O_2$ source.[S4] After various concentrations of H_2O_2 were added into the buffer containing $[Ru(bpy)_{3-n}(An\text{-}bpy)_n]^{2+}$ (n = 1, 2, 3)

(10 μM) and Na_2MoO_4 (1.0 mM), respectively, the solutions were stirred for 3 h at room temperature, and then their phosphorescence spectra were measured on the Perkin-Elmer LS 50B luminescence spectrometer.

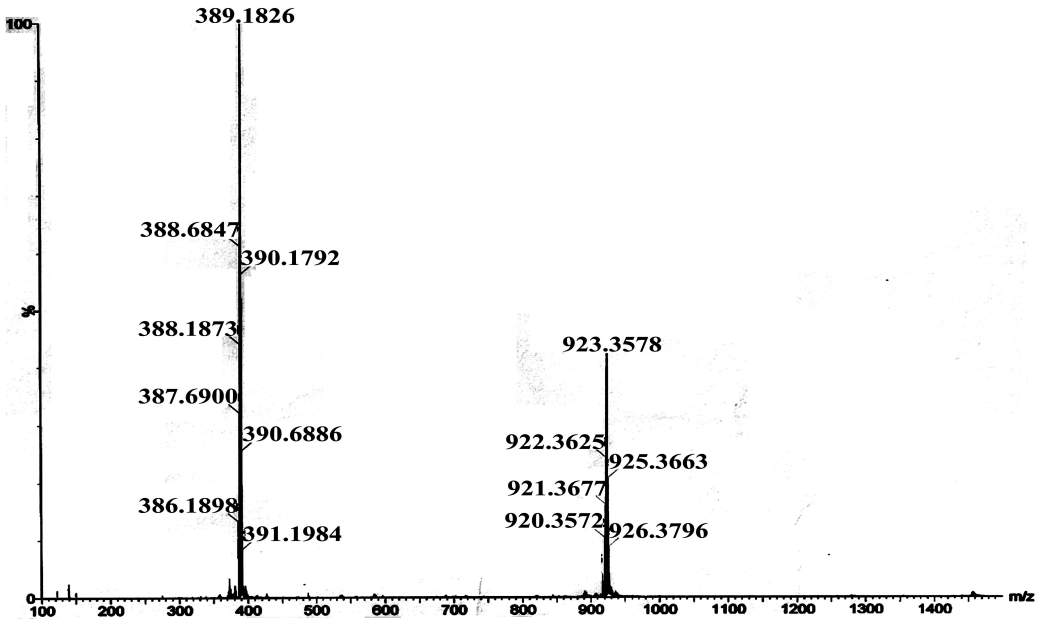


Figure S1. TOF-MS spectrum of the product of $[Ru(bpy)_2(An\text{-}bpy)](PF_6)_2$ reacted with $^1O_2$.

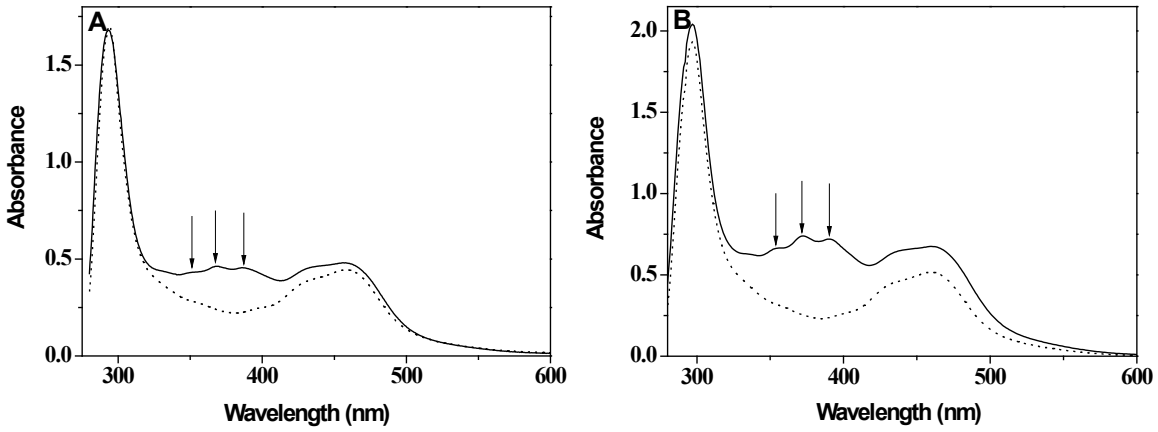


Figure S2. UV-vis absorption spectra of $[Ru(bpy)(An\text{-}bpy)_2](PF_6)_2$ (A, solid line), $[(An\text{-}bpy)_3](PF_6)_2$ (B, solid line), and their corresponding endoperoxides (dot lines) in 0.1 M carbonate buffer of pH 10.5.

Table S1. Phosphorescence properties of $[Ru(bpy)_{3-n}(An\text{-}bpy)_n]^{2+}$ and $[Ru(bpy)_{3-n}(EP\text{-}An\text{-}bpy)_n]^{2+}$ (n = 1, 2, 3) in 0.1 M carbonate buffer of pH 10.5.

complex	$\lambda_{abs,max}$ (nm)	$\lambda_{em,max}$ (nm)	ϕ^a (%)	ε_{455nm} ($cm^{-1}M^{-1}$)
$[Ru(bpy)_2(An\text{-}bpy)]^{2+}$	455	627	0.31	1.44×10^4
$[Ru(bpy)_2(EP\text{-}An\text{-}bpy)]^{2+}$	455	627	2.30	1.32×10^4
$[Ru(bpy)(An\text{-}bpy)_2]^{2+}$	455	615	0.11	1.51×10^4
$[Ru(bpy)(EP\text{-}An\text{-}bpy)_2]^{2+}$	455	615	1.40	1.32×10^4
$[Ru(An\text{-}bpy)_3]^{2+}$	455	615	0.06	2.04×10^4
$[Ru(EP\text{-}An\text{-}bpy)_3]^{2+}$	455	615	1.70	1.55×10^4

[a]Phosphorescence quantum yield was measured by using $[Ru(bpy)_3]Cl_2$ (ϕ = 2.8%) as a standard.[S5]

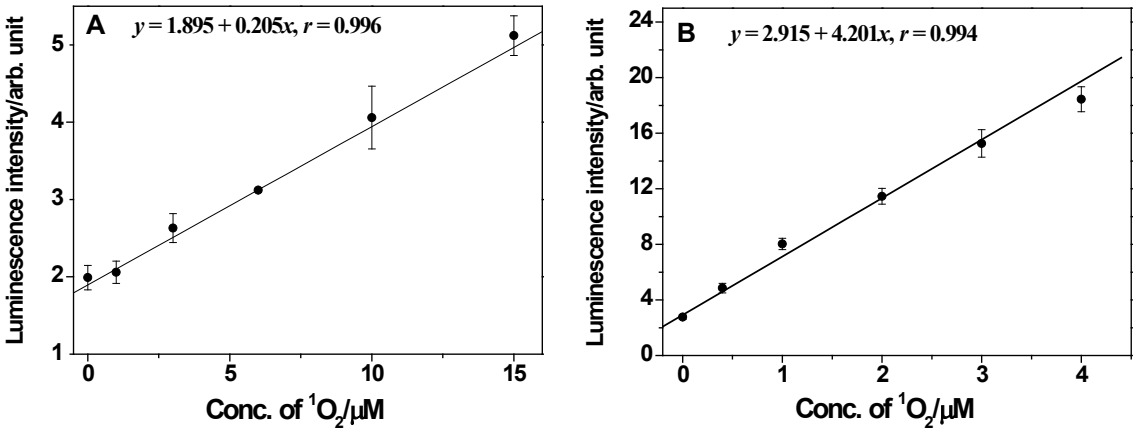


Figure S3. Calibration curves for the phosphorescence detection of $^1O_2$ by using $[Ru(bpy)(An\text{-}bpy)_2](PF_6)_2$ (A, 5.0 μM) and $[(An\text{-}bpy)_3](PF_6)_2$ (B, 5.0 μM) as probes, respectively.

References

(S1) M. E. Marmion and K. J. Takeuchi, *J. Am. Chem. Soc.* 1988, **110**, 1472.

(S2) L. A. MacManus-Spencer, D. E. Latch, K. M. Kroncke and K. McNeill, *Anal. Chem.,* 2005, **77**, 1200.

(S3) B. P. Sullivan, D. J. Salon and T. J. Meyer, *Inorg. Chem.,* 1978, **17**, 3334.

(S4) (a) B. Song, G. L. Wang and J. L. Yuan, *Chem. Commun*., 2005, 3553; (b) B. Song, G. L. Wang, M. Q. Tan and J. L. Yuan, *New J. Chem*., 2005, **29**, 1431; (c) B. Song, G. L. Wang, M. Q. Tan and J. L. Yuan, *J. Am. Chem. Soc*., 2006, **128**, 13442.

(S5) A. Juris and V. Balzani, *Coord. Chem. Rev*. 1988, **84**, 85.