Electronic Supplementary Information for:

Photo-induced Electron Transfer in a Diamino-substituted Ru(bpy)$_3$[PF$_6$]$_2$ Complex and Its Application as Triplet Photosensitizer for Nitric Oxide (NO)-Activated Triplet-Triplet Annihilation Upconversion

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1.0 Synthesis of Ru-1 and Ru-2

Scheme S1. Synthesis of Ru-1 and Ru-2

\[ \text{Key: (a) acetic anhydride, Fuming nitric acid, 1.5 h. Yield: 81%; (b) } \text{NaOH, ethanol, 60 °C, 1 h. Yield: 49%; (c) } \text{LiCl, DMF, 160 °C, 8 h. Yield: 42%; (d) methanol, reflux, 8 h. Yield: 83%; (e) NaH, dry CH}_3\text{CN, r.t. Yield: 95%; (f) hydrazine hydrate, Pd/C, ethanol, reflux, 2 h. Yield: 96%; (g) } \text{NaNO}_2, 2 \text{ M HCl, 0 °C, 2 h. Yield: 69%}. \]

Synthesis of Compound 2

2: The compound 1 and compound 2 was synthesized according to the literature report.\(^1\) Compound 2: (Yield: 49.0 %). mp 149.2–150.4 °C. \(^1\)H NMR (400 MHz, CDCl)\(_3\): \( \delta 7.57 \text{ (d, 1H, } J = 4.0 \text{ Hz), 7.04 (m, 1H), 6.76 (d, 1H, } J = 12.0 \text{ Hz), 5.81 (s, 2H), 4.98 (s, 1H). MALDI-HRMS: calcd ([C}_6\text{H}_6\text{N}_2\text{O}_3]^+), m/z = 154.0378, found m/z = 154.0379. \)
Synthesis of Compound 2

Yield: 41.6%. \(^1\)H NMR (400 MHz, DMSO-d6): \(\delta\) (ppm) 9.98 (d, 2H, \(J = 5.0\) Hz), 8.64 (d, 2H, \(J = 10.0\) Hz), 8.49 (d, 2H, \(J = 10.0\) Hz), 8.07–8.04 (m, 2H), 7.76 (t, 2H, \(J = 5.0\) Hz), 7.69–7.65 (m, 2H), 7.51 (d, 2H, \(J = 5.0\) Hz), 7.11–7.09 (m, 2H). ESI-MS (m/z): calcd ([C\(_{20}\)H\(_{16}\)N\(_4\)Cl\(_2\)Ru + Na] \(^+\)), m/z = 506.9693, found m/z = 506.9702.

Synthesis of Compound 4

Yield: 83%. \(^1\)H NMR (400 MHz, CD\(_3\)CN): \(\delta\) 8.58 (d, 1H, \(J = 4.0\) Hz), 8.51–8.48 (m, 5H), 8.09–8.03 (m, 5H), 7.78–7.70 (m, 5H), 7.65 (d, 1H, \(J = 4.0\) Hz), 7.44–7.39 (m, 6H); ESI-MS (m/z): calcd ([M – 2PF\(_6\)]\(^2+\)), m/z = 302.0358, found m/z = 302.0365.

Synthesis of Compound 5

Yield: 95%. \(^1\)H NMR (400 MHz, CD\(_3\)CN): \(\delta\) 8.51–8.47 (m, 4H), 8.41 (d, 1H, \(J = 12.0\) Hz), 8.09–7.97 (m, 6H), 7.90 (d, 1H, \(J = 4.0\) Hz), 7.83 (d, 1H, \(J = 4.0\) Hz), 7.76–7.71 (m, 4H), 7.50–7.35 (m, 6H), 7.28–7.25 (m, 1H), 7.11 (d, 1H, \(J = 8.0\) Hz), 6.93–6.91 (m, 1H), 6.65 (s, 2H); ESI-MS (m/z): calcd ([M – 2PF\(_6\)]\(^2+\)), m/z = 361.0664, found m/z = 361.0657.

Synthesis of Ru-1

Yield: 95.7%. \(^1\)H NMR (400 MHz, CD\(_3\)CN): \(\delta\) 8.50–8.46 (m, 4H), 8.37 (d, 1H, \(J = 8.0\) Hz), 8.08–7.99 (m, 6H), 7.83 (d, 1H, \(J = 4.0\) Hz), 7.76–7.70 (m, 4H), 7.43–7.35 (m, 6H), 6.82–6.80 (m, 1H), 6.69 (d, 1H, \(J = 8.0\) Hz), 6.43 (d, 1H, \(J = 4.0\) Hz), 6.34–6.32 (m, 1H), 3.92 (br, 4H); ESI-MS (m/z): calcd ([M – PF\(_6\)]\(^+\)), m/z = 837.1228, found m/z = 837.1242.

Synthesis of Ru-2

Yield: 69.0%. \(^1\)H NMR (400 MHz, CD\(_3\)CN): \(\delta\) 8.53–8.49 (m, 4H), 8.38 (d, 1H, \(J = 8.0\) Hz), 8.10–7.99 (m, 7H), 7.87 (d, 1H, \(J = 4.0\) Hz), 7.78–7.73 (m, 5H), 7.54 (d, 1H, \(J = 8.0\) Hz), 7.48–7.37 (m, 5H), 7.32–7.29 (m, 1H), 6.67–6.94 (m, 1H); ESI-MS (m/z): calcd ([M– 2PF\(_6\)]\(^2+\)), m/z = 351.5691, found m/z = 351.5679.

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2.0 NMR and HR-MS spectra

**Fig. S1** $^1$H NMR of compound 2 (400 MHz, CDCl$_3$).

**Fig. S2** TOF EI MS of compound 2.
Fig. S3 $^1$H NMR of compound 3 (400 MHz, DMSO-d$_6$).

Fig. S4 MALDI-HRMS of compound 3.
Fig. S5 $^1$H NMR of compound 4 (400 MHz, CD$_3$CN).

Fig. S6 MALDI-HRMS of compound 4.
Fig. S7 $^1$H NMR of compound 5 (400 MHz, CD$_3$CN).

Fig. S8 MALDI-HRMS of compound 5.
**Fig. S9** $^1$H NMR of Ru-1 (400 MHz, CD$_3$CN).

**Fig. S10** MALDI-HRMS of Ru-1.
Fig. S11 $^1$H NMR of Ru-2 (400 MHz, CD$_3$CN).

Fig. S12 MALDI-HRMS of Ru-2.
3.0 Changes of phosphorescence spectra of Ru-1 upon the addition of NO

**Fig. S13** Changes of phosphorescence spectra of Ru-1 upon the addition of NO (saturated solution in CH₃CN). \( c = 1.0 \times 10^{-5} \text{M} \), \( \lambda_{\text{ex}} = 445 \text{nm} \), In deaerated CH₃CN, 20 °C.

4.0 Phosphorescence emission spectra of Ru-1 and Ru-2 in different deaerated solvents

**Fig. S14** Phosphorescence emission spectra of Ru-1 (a) and Ru-2 (b) in different deaerated solvents. \( \lambda_{\text{ex}} = 445 \text{nm} \), 20 °C, optically matched solution was used (\( A = 0.14 \)).
5.0 Emission spectra and the decay trace of Ru-1 and Ru-2 at 77 K

Fig. S15 (a) Normalized emission spectra of Ru-1 and Ru-2 at 77 K (in deaerated EtOH–MeOH, 4: 1, v/ v) and 298 K (in deaerated CH$_3$CN); (b) The lifetime of Ru-1 and Ru-2 at 77 K in deaerated EtOH–MeOH (4: 1, v/ v). $c = 1.0 \times 10^{-5}$ M, $\lambda_{ex} = 405$ nm, $\lambda_{em} = 585$ nm.

6.0 Transient absorption spectra of Ru-1 with a high concentration

Fig. S16 Transient absorption spectra of Ru-1. $c$ [Ru-1] = $1.0 \times 10^{-4}$ M. In deaerated CH$_3$CN. $\lambda_{ex} = 445$ nm, 20 °C.
7.0 Nanosecond transient absorption spectra of Ru-1, Ru-2 and Ru(bpy)$_3$

![Fig. S17](image_url) Transient absorption spectra of the complexes. (a) Ru-1 and (b) Decay curves of Ru-1 at 450 nm; (c) Decay curves of Ru-1 at 610 nm; (d) Ru-2 and (e) Decay curves of Ru-2 at 450 nm; (f) Decay curves of Ru-2 at 610 nm; (g) Ru(bpy)$_3$Cl$_2$; (h) Decay curves of Ru(bpy)$_3$Cl$_2$ at 450 nm; (i) Decay curves of Ru(bpy)$_3$Cl$_2$ at 610 nm. c [Complexes] = 1.0 × 10$^{-5}$ M. In deaerated CH$_3$CN. $\lambda_{ex} = 445$ nm, 20 ºC.
8.0 Femtosecond Transient absorption spectra of Ru-2 and Ru(bpy)$_3$ 

Fig. S18 (a) Observed fs-TA spectra from 340 to 750 nm at various time delays from $\tau = 0.2$ (red) to $\tau = 2700$ ps (blue), and pre time zero $\tau = -0.2$ ps (black) for a ca. 120 M solution of (Ru-2) in CH$_3$CN solution using $\lambda_{ex} = 470$ nm. (b) Corresponding kinetic plots and global fit of observed fs-TA signals from $\tau = 0.2$ to $\tau = 2700$ ps in 10 nm wavelength increments from 340 nm (red) to 750 nm (blue). NB: data between 450-490 nm was excluded due to the presence of scattered laser excitation, and note the change to log scale from $\tau > 10$ ps on the x-axis. (c) Deconvolution of globally fitted kinetic data into Decay Associated Difference Spectra (DADS).
Fig. S19 (a) Observed fs-TA spectra from 340 to 750 nm at various time delays from $\tau = 0.2$ (red) to $\tau = 2700$ ps (blue), and pre time zero $\tau = -0.2$ ps (black) for a ca. 160 M solution of [Ru(bpy)$_3$]$^{2+}$ in CH$_3$CN solution using $\lambda_{ex} = 470$ nm. (b) Corresponding kinetic plots and global fit of observed fs-TA signals from $\tau = 0.2$ to $\tau = 2700$ ps in 10 nm wavelength increments from 340 nm (red) to 750 nm (blue). NB: data between 450-490 nm was excluded due to the presence of scattered laser excitation, and note the change to log scale from $\tau > 10$ ps on the x-axis. (c) Deconvolution of globally fitted kinetic data into Decay Associated Difference Spectra (DADS). (d) Expansion of fs-TA data showing blue shift of 370 nm ESA feature over first 5 ps due to vibrational cooling of rapidly formed $^3$MLCT excited state (see text).
9.0 Changes of emission intensity of DPA upon the addition of NO

![Graph showing changes in emission intensity of DPA upon the addition of NO](image)

**Fig. S20** Changes of emission spectrum of DPA upon the addition of NO (saturated solution in CH$_3$CN). $c = 1.0 \times 10^{-5}$ M, $\lambda_{ex} = 350$ nm, In CH$_3$CN, 20 °C.

10.0 Changes of emission intensity of Ru-1 and Ru-2 upon the addition of NO

![Graph showing changes in emission intensity of Ru-1 and Ru-2 upon the addition of NO](image)

**Fig. S21** Changes of emission spectrum of Ru-2 (a) and [Ru(bpy)$_3$]Cl$_2$ (b) upon the addition of NO (saturated solution in CH$_3$CN). $c = 1.0 \times 10^{-5}$ M, $\lambda_{ex} = 445$ nm, In deaerated CH$_3$CN, 20 °C.
11.0 HPLC analysis of the complexes Ru-1, Ru-2 and the reaction mixture of Ru-1 + NO

![HPLC analysis](image)

**Fig. S22** HPLC analysis of the complexes Ru-1, Ru-2 and the reaction mixture of Ru-1 + NO. Line A: pure Ru-1 solution (1 × 10⁻³ M); Line B: pure Ru-2 solution (1 × 10⁻³ M); Line C: the reaction mixture of Ru-1 + NO (NO saturated solution) (1 × 10⁻³ M).

12.0 The TTA upconversion of Ru-1 and Ru-2 upon the addition of NO

![Upconversion](image)

**Fig. S23** The upconversion intensity of Ru(bpy)₃Cl₂ and Ru-2 upon the addition of NO (saturated solution in CH₃CN or pure NO gas). (a) Purging of the solution with pure NO gas for 10 second, c(DPA) = 2.0 × 10⁻⁴ M; (b) NO saturated solution in CH₃CN was added, c(DPA) = 4.0 × 10⁻⁴ M. c(Sensitizers) = 2.0 × 10⁻⁵ M. λₑx = 473 nm (4.8 mW). In deaerated CH₃CN, 20 °C.
Fig. S24 Upconverted fluorescence intensity upon the addition of NO (NaNO₂ + HCl solution). (a) Ru-1 as photosensitizer, the detail procedure was that: different equivalent of NaNO₂ + HCl solution was added into Ru-1 solution (in CH₃CN) at 0 °C for 10 min, then remove the solvent and dissolve the mixture in fresh CH₃CN for the TTA upconversion measurement; (b) the upconversion intensity of Ru-2, Ru-1 and Ru-1 in the presence of NO (NaNO₂ + HCl solution). λₑₓ = 473 nm (laser power: 4.8 mW). c(sensitizers) = 2.0 × 10⁻⁵ M, c(DPA) = 4.0 × 10⁻⁴ M, in deaerated CH₃CN, 20 °C.

13.0 The changes of phosphorescence intensity of the photosensitizers upon the addition of DPA

Fig. S25. (a), (b) and (c) the changes of phosphorescence intensity upon the addition of DPA, c(DPA) = 1.0 × 10⁻² M, c(Photosensitizers) = 1.0 × 10⁻⁵ M, λₑₓ = 445 nm in CH₃CN, 20 °C.
The bimolecular quenching efficiency \( f_Q \) was also studied. Stern-Volmer quenching constants were calculated as \( K_{SV} = 3.36 \times 10^3 \text{ M}^{-1} \) for **Ru-1**. The bimolecular quenching constant was calculated as \( k_q = K_{SV}/\tau_0 = 4.95 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \), where \( \tau_0 \) is the triplet state lifetime of the triplet energy donor (737.6 ns). In order to study the quenching efficiency, which is given by \( f_Q = k_q/k_0 \), where \( k_0 \) is the diffusion-controlled bimolecular quenching rating constants, we used the Smoluchowski equation,

\[
 k_0 = 4\pi RND / 1000 = \frac{4\pi N}{1000} \left( R_f + R_q \right) \left( D_f + D_q \right)
\]

(Eq. 3)

where \( D \) is the sum of the diffusion coefficients of the energy donor \( (D_f) \) and quencher \( (D_q) \), \( N \) is Avogadro’s number and \( R \) is the collision radius obtained as the sum of the molecule radii of the energy donor \( (R_f) \) and the quencher \( (R_q) \). Diffusion coefficients can be obtained from Stokes-Einstein equation:

\[
 D = kT/6\pi\eta R
\]

(Eq. 4)

where \( k \) is Boltzmann’s constant, \( \eta \) is the solvent viscosity and \( R \) is the molecule radius.

### 14.0 Decay curves of Ru-1 in aerated CH\(_3\)CN

![Decay curves of Ru-1](image)

**Fig. S26** Decay curves of **Ru-1** at 460 nm after pulsed laser excitation in aerated CH\(_3\)CN. \( c [\text{Ru-1}] = 1.0 \times 10^{-5} \text{ M}, \lambda_{ex} = 445 \text{ nm.} \)
15.0 Calculation of triplet state quantum yield

Table S1. The Parameter Related to Calculate the Triplet State Quantum Yields.\footnote{[a]}

<table>
<thead>
<tr>
<th></th>
<th>(\varepsilon)^{b}</th>
<th>(\Delta A)^{c}</th>
<th>(\Phi_T)(%)^{d}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru-1</td>
<td>1.36</td>
<td>– 0.0017</td>
<td>22.2 ± 5</td>
</tr>
<tr>
<td>Ru-2</td>
<td>1.36</td>
<td>– 0.0065</td>
<td>85.5 ± 5</td>
</tr>
<tr>
<td>Ru(bpy)(_3)Cl(_2)</td>
<td>1.26</td>
<td>– 0.0071</td>
<td>100.0</td>
</tr>
</tbody>
</table>

\([a]\) In deaerated CH\(_3\)CN, \([b]\) Molar absorption coefficient. \(\varepsilon: 10^4\) M\(^{-1}\) cm\(^{-1}\). \([c]\) The O.D. value of the triplet transient difference absorption spectrum at 450 nm. \([d]\) The triplet state quantum yield.

16.0 Cyclic voltammogram of Ru-1, Ru-2 and Ru(bpy)\(_3\)Cl\(_2\) in deaerated CH\(_3\)CN

Fig. S27. Cyclic voltammogram of Ru-1, Ru-2 and Ru(bpy)\(_3\)Cl\(_2\) in deaerated CH\(_3\)CN containing 0.10 M Bu\(_4\)NPF\(_6\) as supporting electrode and with Ag/AgNO\(_3\) reference electrode. Scan rates: 0.1 V/s, three cycles. Ferrocene (Fc) was used as internal reference, 20 °C.

Rehm-Weller equation (Eqs. 1 and 2.),\textsuperscript{63,64}

\[
\Delta G_{CS} = \varepsilon [E_{OX} - E_{RED}] - E_{00} + \Delta G_S
\]  \hspace{1cm} \text{(Eq. 1)}
\[
\Delta G_S = -\frac{e^2}{4\pi\varepsilon_0 e R_{CC}} - \frac{e^2}{8\pi\varepsilon_0} \left( \frac{1}{R_D} + \frac{1}{R_A} \right) \left( \frac{1}{\varepsilon_{REF}} - \frac{1}{\varepsilon_S} \right)
\]  
(Eq. 2)

where \( \Delta G_S \) is the static Coulombic energy, which is described by Eq. 2, \( e \) is the electronic charge, \( E_{OX} \) is the half-wave potential for mono-electron oxidation of the electron-donor unit and \( E_{RED} \) is the half-wave potential for one-electron reduction of the electron-acceptor unit.

17.0 Simplified Jablonski diagram illustrating the photophysical processes

**Scheme S2.** Simplified Jablonski Diagram Illustrating the Photophysical Processes Involved in the NO-switched TTA Upconversion, (a) Ru-1 as Photosensitizer, (b) Ru-2 as Photosensitizer. 

\[ \text{The component at the excited state was designated with red color. The number of the superscript designated either the singlet or the triplet excited state. CH}_3\text{CN as the solvent.} \]