Supporting Information for

Fine control on the photochemical and photobiological properties of Ru(II) arene complexes

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Figure S1. Absorption spectra changes of 1 (25 µM) in PBS (pH = 7.4) after standing in the dark for 4 h at room temperature.

Figure S2. Absorption spectra changes of 2 (25 µM) in PBS (pH = 7.4) after standing in the dark for 4 h at room temperature.

Figure S3. Absorption spectra changes of 3 (25 µM) in PBS (pH = 7.4) after standing in the dark for 4 h at room temperature.
Figure S4. Absorption spectra changes of 4 (25 µM) in PBS (pH = 7.4) after standing in the dark for 4 h at room temperature.

Figure S5. Absorption spectra changes of 5 (25 µM) in PBS (pH = 7.4) after standing in the dark for 4 h at room temperature.

Figure S6. Absorption spectra changes of 6 (25 µM) in PBS (pH = 7.4) after standing in the dark for 4 h at room temperature.
Figure S7. Absorption (left) and fluorescence emission (right) spectra changes of 1 (25 μM) in PBS (pH = 7.4) upon irradiation with λ > 470 nm.

Figure S8. Absorption (left) and fluorescence emission (right) spectra changes of 2 (25 μM) in PBS (pH = 7.4) upon irradiation with λ > 470 nm.

Figure S9. Absorption (left) and fluorescence emission (right) spectra changes of 3 (25 μM) in PBS (pH = 7.4) upon irradiation with λ > 470 nm.
Figure S10. Absorption (left) and fluorescence emission (right) spectra changes of 4 (25 μM) in PBS (pH = 7.4) upon irradiation with $\lambda > 470$ nm.

Figure S11. Absorption (left) and fluorescence emission (right) spectra changes of 5 (25 μM) in PBS (pH = 7.4) upon irradiation with $\lambda > 470$ nm.

Figure S12. Absorption (left) and fluorescence emission (right) spectra changes of 6 (25 μM) in PBS (pH = 7.4) upon irradiation with $\lambda > 470$ nm.
Figure S13. $^1$H NMR spectra of 1 in CD$_3$COCD$_3$:D$_2$O (1:2) before and after irradiation ($\lambda > 400$ nm) for 12 h. The chemical shifts of the two protons (H$_a$ and H$_b$) on the central ring of benzoquinoxaline in the original complex are labeled by ▲.

Figure S14. $^1$H NMR spectra of 2 in CD$_3$COCD$_3$:D$_2$O (1:2) before and after irradiation ($\lambda > 400$ nm) for 12 h. The chemical shifts of the two protons (H$_a$ and H$_b$) on the central ring of benzoquinoxaline in the original complex are labeled by ▲.
Figure S15. EPR signals obtained upon irradiation of O$_2$-saturated CH$_3$CN solutions of TEMP and 1-6 with a 532 nm laser. The dark control means without irradiation.
**Figure S16.** Absorption spectra changes of 1-6 in air-saturated CH$_3$CN upon irradiation at 500 nm for 5 min.

**Figure S17.** Transient absorption spectra of dpb in Ar-saturated CH$_3$CN upon pulsed excitation at 355 nm.
Figure S18. Transient absorption spectra of [Ru(bpy)](dpb)]^{2+} in Ar-saturated CH_{3}CN upon pulsed excitation at 532 nm.

Figure S19. AMDA bleaching (at 405 nm) in the presence of 1-6 in PBS upon irradiation at 500 nm.

Figure S20. Agarose gel electrophoresis pattern of supercoiled pUC19 DNA (40 μg mL^(-1)) in PBS (pH = 7.4) in the dark in the presence of 1-6 (80 μM). Lane 1 and 8, supercoiled DNA alone; lane 2, DNA + 1; lane 3, DNA + 2; lane 4, DNA + 3; lane 5, DNA + 4; lane 6, DNA + 5; lane 7, DNA + 6.
Table S1. IC<sub>50</sub> values of 1-6 against A459 cells in the dark or under irradiation.

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