## **Supporting Information for**

## A Ruthenium(II) arene complex showing emission enhancement and photocleavage activity towards DNA from singlet and triplet excited states respectively

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Figure S1. Plot of the fluorescence intensity of 1 (20  $\mu$ M) as a function of the concentration of CT-DNA (0-220  $\mu$ M).



**Figure S2.** (a) Absorption spectra of **3** (25  $\mu$ M) in PBS buffer (pH 7.4) in the presence of varied concentrations of CT-DNA. (b) Plot of ( $\varepsilon_a - \varepsilon_f$ )/( $\varepsilon_b - \varepsilon_f$ ) as a function of CT-DNA concentration. (C<sub>t</sub> = 25  $\mu$ M, in PBS buffer, pH7.4)



**Figure S3.** (a) Fluorescence quenching of EB (5  $\mu$ M) bound to CT-DNA (10  $\mu$ M) by **1.** (b) Plot of I/ I<sub>0</sub> of EB bound to CT-DNA as a function of the concentration of **1** ([EB] = 5  $\mu$ M, [DNA] = 10  $\mu$ M, in PBS buffer, pH7.4).



**Figure S4.** (a) Fluorescence quenching of EB (5  $\mu$ M) bound to CT-DNA (10  $\mu$ M) by **2.** (b) Plot of I/ I<sub>0</sub> of EB bound to CT-DNA as a function of the concentration of **2** ([EB] = 5  $\mu$ M, [DNA] = 10  $\mu$ M, in PBS buffer, pH7.4).



**Figure S5.** (a) Fluorescence quenching of EB (5  $\mu$ M) bound to CT-DNA (10  $\mu$ M) by **3.** (b) Plot of I/ I<sub>0</sub> of EB bound to CT-DNA as a function of the concentration of **3** ([EB] = 5  $\mu$ M, [DNA] = 10  $\mu$ M, in PBS buffer, pH7.4).



**Figure S6.** Agarose gel electrophoresis pattern of the photocleaved supercoiled pBR322 DNA (31  $\mu$ M in base pair) by **1**, **3** or **4** (30  $\mu$ M) upon irradiation (> 420 nm) for 20 min in Tris-CH<sub>3</sub>COOH/EDTA buffer (pH = 7.4). Lane 1, DNA alone; lane 2, DNA + **1** (light); lane 3, DNA + **1** (dark); lane 4, DNA + **3** (light); lane 5, DNA + **3** (dark); lane 6, DNA + **4** (light); lane 7, DNA + **4** (dark). Form I, II and III denote supercoiled circular, nicked circular and linear form, respectively.



**Figure S7.** Confocal micrographs of the double-stained A549 cells with Hoechst 34580 and **1** (each 5  $\mu$  M incubated for 3 h). (a) Hoechst 34580 fluorescence image upon excitation at 408 nm. (b) **1** fluorescence image upon excitation at 408 nm. (c) Overlay of the former two fluorescence images.