

## **Electronic supplementary information**

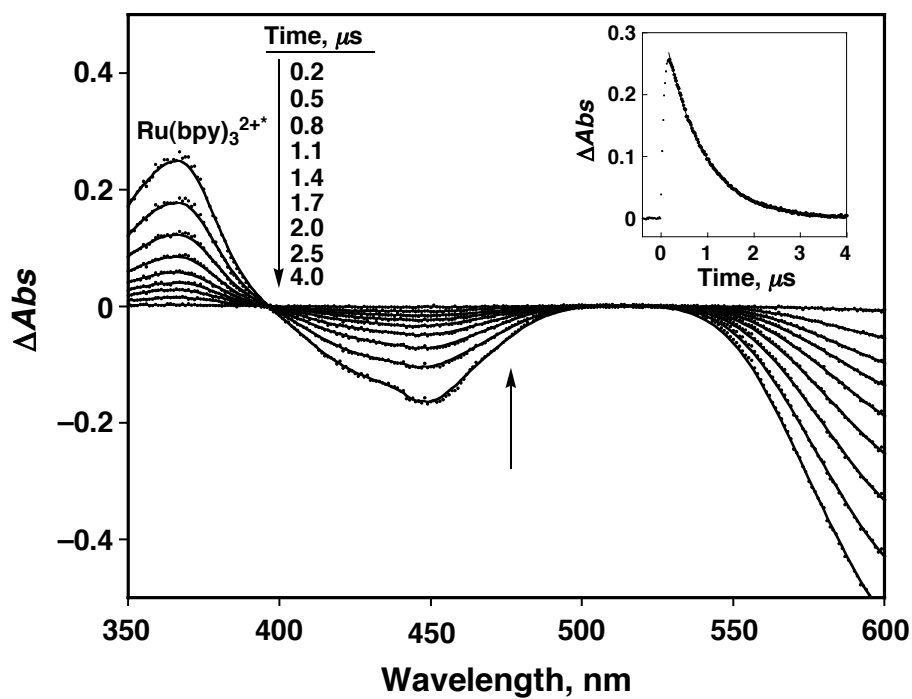
### **Remarkable oxidizing ability of triplet excited states of tetrazines produced by photosensitization with $\text{Ru}(\text{bpy})_3^{2+}$**

Junpei Yuasa and Shunichi Fukuzumi\*

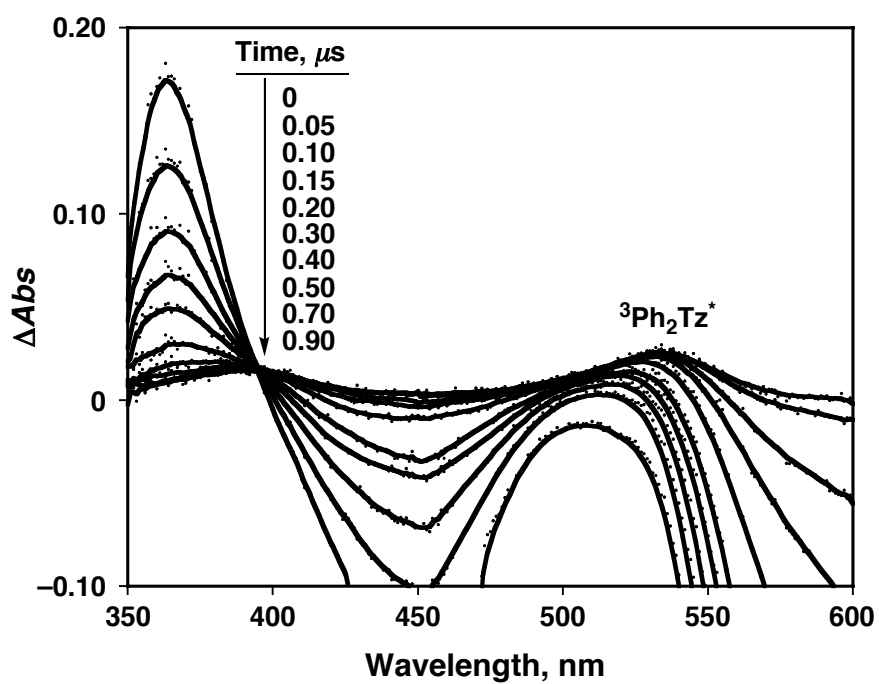
*Department of Material and Life Science, Division of Advanced Science and  
Biotechnology, Graduate School of Engineering, Osaka University, SORST, Japan  
Science and Technology Agency (JST), Suita, Osaka 565-0871, Japan*

\* To whom correspondence should be addressed.

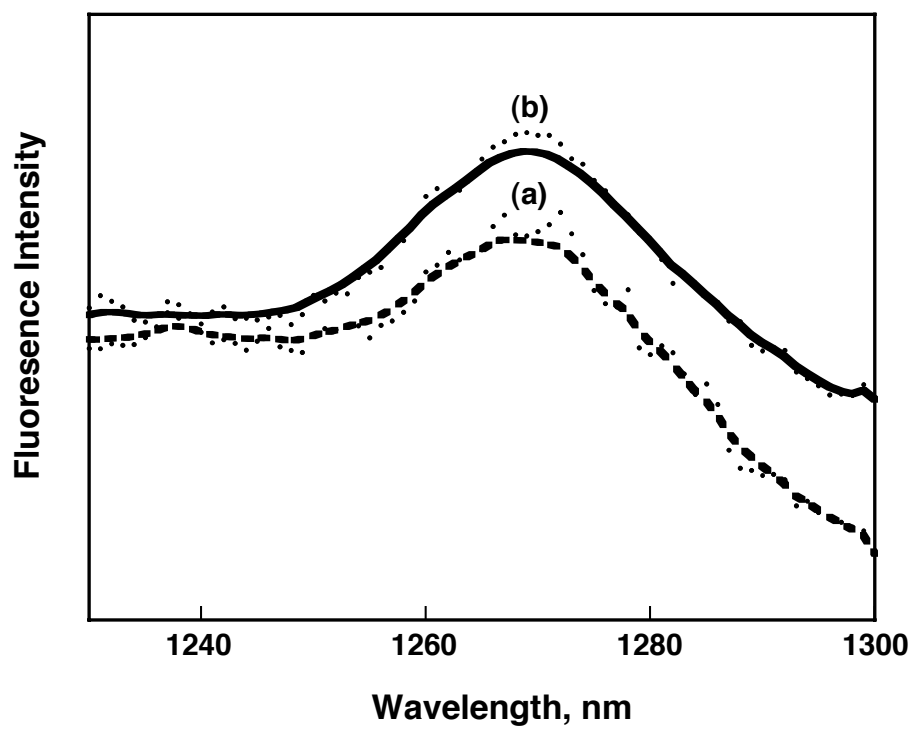
E-mail: fukuzumi@chem.eng.osaka-u.ac.jp



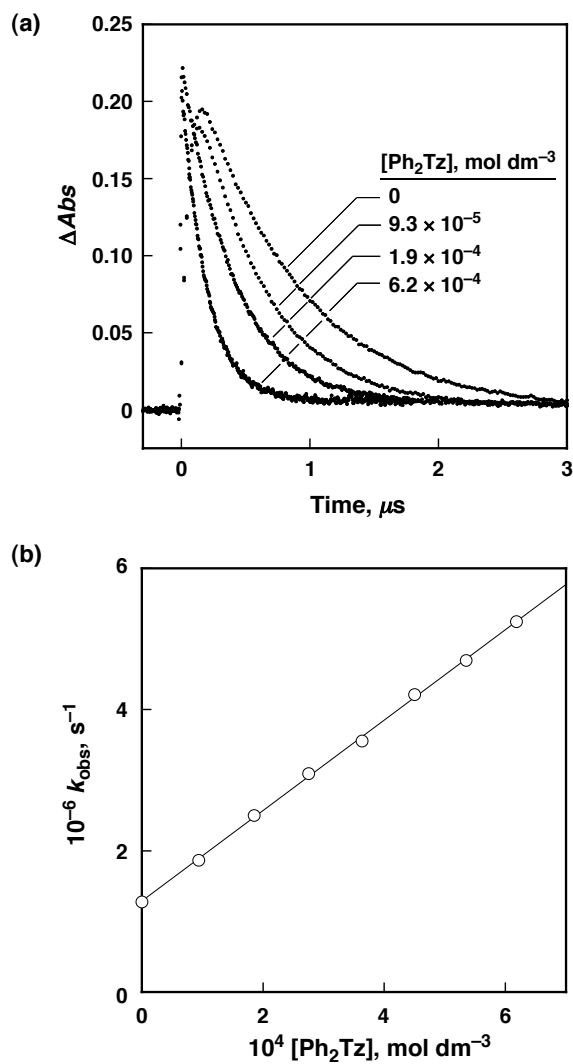
**Fig. S1** Transient absorption spectra observed by laser flash photolysis of a deaerated MeCN solution of Ru(bpy)<sub>3</sub><sup>2+</sup> ( $4.6 \times 10^{-5}$  mol dm<sup>-3</sup> at 0.2 – 4.0  $\mu s$  after laser excitation at  $\lambda = 450$  nm at 298 K. Inset: Decay of the absorbance at 363 nm.



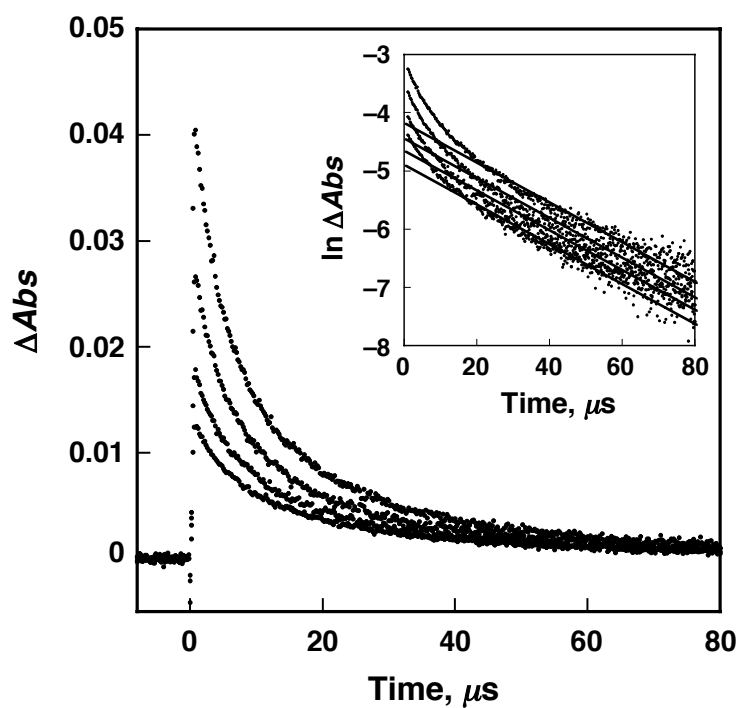
**Fig. S2** Transient absorption spectra observed by laser flash photolysis of a deaerated MeCN solution of  $\text{Ru}(\text{bpy})_3^{2+}$  ( $4.6 \times 10^{-5} \text{ mol dm}^{-3}$ ) and  $\text{Ph}_2\text{Tz}$  ( $9.6 \times 10^{-4} \text{ mol dm}^{-3}$ ) at 0 – 0.9  $\mu\text{s}$  after laser excitation at  $\lambda = 450 \text{ nm}$  at 298 K.



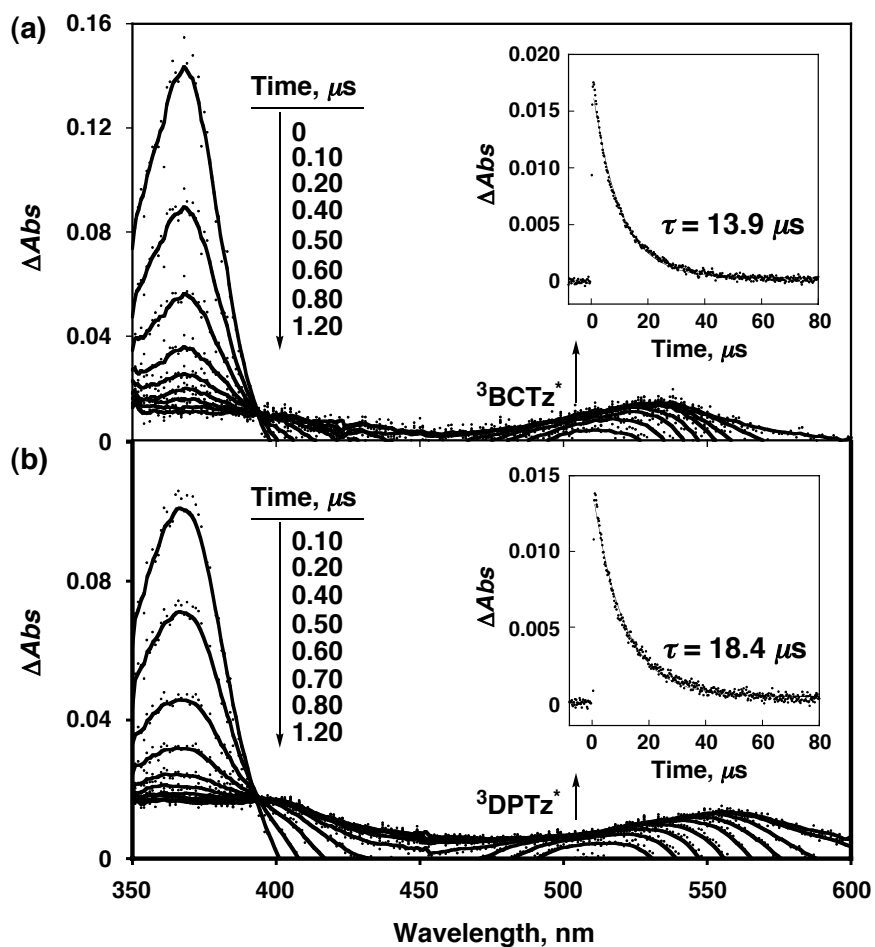
**Fig. S3** Phosphorescence spectra of  $^1\text{O}_2^*$  produced by excitation of  $\text{Ru}(\text{bpy})_3^{2+}$  ( $4.6 \times 10^{-5} \text{ mol dm}^{-3}$ ) at  $\lambda = 450 \text{ nm}$  (a) in the absence and (b) in the presence of  $\text{Ph}_2\text{Tz}$  ( $9.6 \times 10^{-4} \text{ mol dm}^{-3}$ ) in deaerated  $\text{CD}_3\text{CN}$  at 298 K.



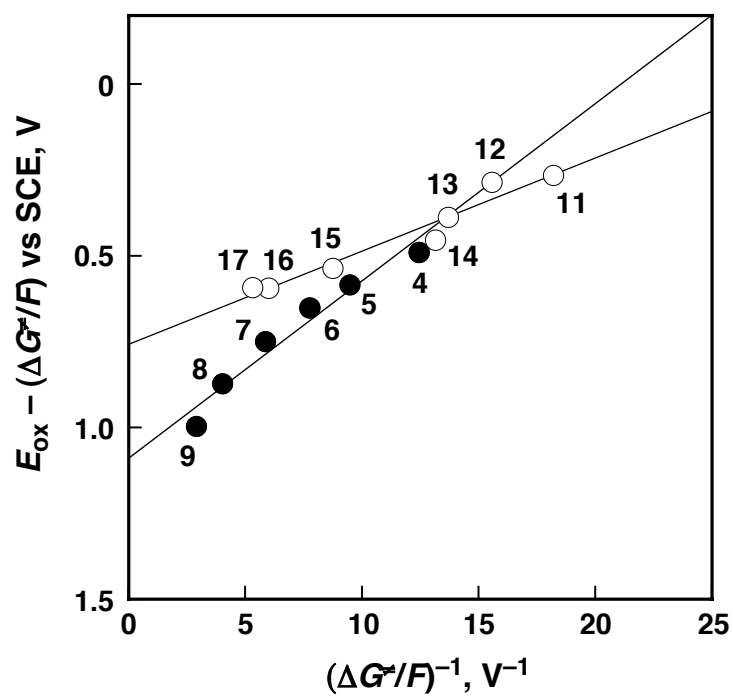
**Fig. S4** (a) Decay dynamics of  $Ru(bpy)_3^{2+}$  at 363 nm observed by laser-flash photolysis of a deaerated MeCN solution of  $Ru(bpy)_3^{2+}$  ( $4.6 \times 10^{-5} mol\ dm^{-3}$ ) in the presence of  $Ph_2Tz$  ( $0 mol\ dm^{-3}$ ,  $9.3 \times 10^{-5} mol\ dm^{-3}$ ,  $1.9 \times 10^{-4} mol\ dm^{-3}$ , and  $6.2 \times 10^{-4} mol\ dm^{-3}$ ) at 298 K. (b) Plot of  $k_{obs}$  vs.  $[Ph_2Tz]$ .



**Fig. S5** Decay dynamics of T-T absorption change at 535 nm observed by laser-flash photolysis of a deaerated MeCN solution of  $Ru(bpy)_3^{2+}$  ( $4.6 \times 10^{-5} \text{ mol dm}^{-3}$ ) and  $Ph_2Tz$  ( $9.6 \times 10^{-4} \text{ mol dm}^{-3}$ ) with different laser intensities (1.1 mJ, 1.8 mJ, 6.6 mJ, and 16.3 mJ) at 298 K. (b) First-order plots.



**Fig. S6** Transient absorption spectra by laser-flash photolysis of  $\text{Ru}(\text{bpy})_3^{2+}$  ( $4.6 \times 10^{-5}$  M) and (a) BCTz ( $9.6 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ), and (b) DPTz ( $9.6 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ), at 0 – 1.2 μs after laser excitation at  $\lambda = 450$  nm in deaerated MeCN at 298 K. Insets: decay time profiles of triplet excited states of tetrazines at (a) 530 nm and (b) 555 nm.



**Fig. S7** Plots of  $E_{\text{ox}} - (\Delta G^\circ/F)$  vs.  $(\Delta G^\circ/F)^{-1}$  in the photoinduced electron transfer from various electron donors to  $\text{Ru}(\text{bpy})_3^{2+*}$  (O) and  ${}^3\text{Ph}_2\text{Tz}^*$  (●) in deaerated MeCN at 298 K. Numbers refer to electron donors in Fig. 4.