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

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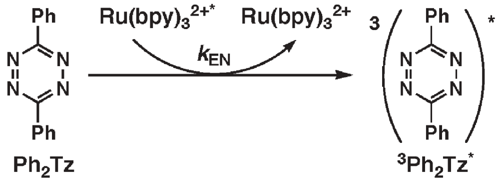
Received (in Cambridge, UK) 15th September 2005, Accepted 22nd November 2005
First published as an Advance Article on the web 20th December 2005
DOI: 10.1039/b513110c

An efficient energy transfer from $Ru(bpy)_3{}^{2+}$* (bpy = 2,2′-bipyridine, * denotes the excited state) to tetrazines occurs to yield the triplet excited states of tetrazines, which have much longer lifetimes and higher oxidizing ability as compared with those of $Ru(bpy)_3{}^{2+}$*.

1,2,4,5-Tetrazines are electron-deficient 4π compounds containing an N=N double bond, which have been extensively utilized in Diels–Alder reactions with inverse electron demanding for synthesis of a variety of valuable compounds.[1–4] Tetrazines have also been used as electron acceptors in thermal electron-transfer reactions because of the electron-deficient character.[5] The oxidizing ability of tetrazines is expected to be enhanced significantly by photoexcitation. However, the lifetime of the singlet excited state is too short ($\tau_S < 500$ ps), to be utilized in any useful photochemical reaction.[6–8] In addition, the direct photoexcitation of tetrazines affords no triplet excited state.[9] On the other hand, $Ru(bpy)_3{}^{2+}$ has proven to be the most versatile photosensitizer amongst a number of photosensitizers, because the strongly emitting excited state is produced by visible light irradiation with unitary efficiency with a relatively long excited state lifetime ($\tau = 0.85$ μs).[10–12] However, the oxidizing ability of $Ru(bpy)_3{}^{2+}$* ($E_{red}{}^* = 0.77$ V *vs.* SCE) has been limited to be rather low because of the low reduction potential of the ground state ($E_{red} = -1.35$ V *vs.* SCE) and the low excitation energy (2.12 eV).[11]

We report herein that the triplet excited state of 3,6-diphenyl-1,2,4,5-tetrazine ($^3Ph_2Tz$*) is efficiently formed by photosensitization with $Ru(bpy)_3{}^{2+}$ in deaerated acetonitrile (MeCN) and that the lifetime ($\tau = 28.4$ μs) and the oxidizing ability ($E_{red}{}^* = 1.09$ V *vs.* SCE) are much improved as compared with those of $Ru(bpy)_3{}^{2+}$*.

No transient absorption spectrum is observed by the laser excitation of Ph_2Tz at 355 nm in deaerated MeCN. When $Ru(bpy)_3{}^{2+}$ is added to an MeCN solution of Ph_2Tz, however, the laser excitation at 450 nm results in formation of $^3Ph_2Tz$* by energy transfer from $Ru(bpy)_3{}^{2+}$* to Ph_2Tz [eqn (1)] as shown in Fig. 1.[13,14] The decay at 363 nm due to $Ru(bpy)_3{}^{2+}$* coincides with the rise in a new absorption band at $\lambda_{max} = 535$ nm ($\varepsilon = 3.5 \times 10^3$ mol^{-1} dm^3 cm^{-1}).[15] This is exemplified in the inset of Fig. 1. The absorption band at 535 nm is efficiently quenched by small concentrations of O_2 to produce singlet oxygen as shown in Fig. 2a.[16] The formation singlet oxygen ($^1\Delta_g$) was confirmed by observation of the phosphorescence at 1270 nm of an aerated CD_3CN solution of $Ru(bpy)_3{}^{2+}$ (4.6×10^{-5} mol dm^{-3}) containing Ph_2Tz (9.6×10^{-4} mol dm^{-3}); see ESI, S3†.[17] Thus, the new absorption band at 535 nm in Fig. 1 is definitely assigned due to $^3Ph_2Tz$*.



(1)

The second-order rate constant (k_{EN}) of energy transfer from $Ru(bpy)_3{}^{2+}$* to Ph_2Tz is determined as 6.4×10^9 mol^{-1} dm^3 s^{-1} by the linear plot of the pseudo-first-order rate constant of the decay of $Ru(bpy)_3{}^{2+}$* *vs.* concentration of Ph_2Tz (see ESI, S4†). The k_{EN} value of energy transfer from $^3Ph_2Tz$* to O_2 is also determined as 1.1×10^9 mol^{-1} dm^3 s^{-1} from the linear plot of the pseudo-first-order rate constant of the decay of $^3Ph_2Tz$* (k_{obs}) *vs.* concentration of O_2 (Fig. 2b). In the absence of O_2, $^3Ph_2Tz$* decays through both first-order and second-order processes, which

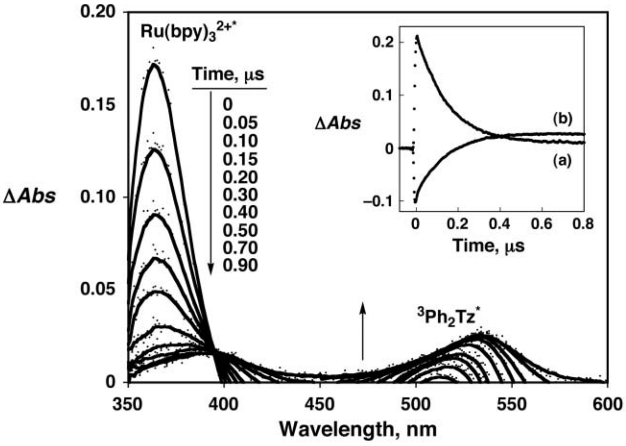


Fig. 1 Transient absorption spectra observed by laser flash photolysis of a deaerated MeCN solution of $Ru(bpy)_3{}^{2+}$ (4.6×10^{-5} mol dm^{-3}) and Ph_2Tz (9.6×10^{-4} mol dm^{-3}) at 0–0.9 μs after laser excitation at λ = 450 nm at 298 K. Inset: (a) Decay of the absorbance at 363 nm and (b) rise of the absorbance at 535 nm.

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† Electronic supplementary information (ESI) available: Transient absorption spectrum of $Ru(bpy)_3{}^{2+}$* alone, transient absorption spectrum of $^3Ph_2Tz$* including the bleaching part, the phosphorescence spectrum of singlet oxygen, plot of the pseudo-first-order rate constant of the decay of $Ru(bpy)_3{}^{2+}$* *vs.* concentration of Ph_2Tz, the decay dynamics of T–T absorption due to $^3Ph_2Tz$* using different laser intensities, transient absorption spectra of triplet excited states of other tetrazines [3,6-bis(2-chlorophenyl)-1,2,4,5-tetrazine and 3,6-di-2-pyridyl-1,2,4,5-tetrazine], and plots of $(\Delta G^{\neq}/F) - E_{ox}$ *vs.* $(\Delta G^{\neq}/F)^{-1}$. See DOI: 10.1039/b513110c

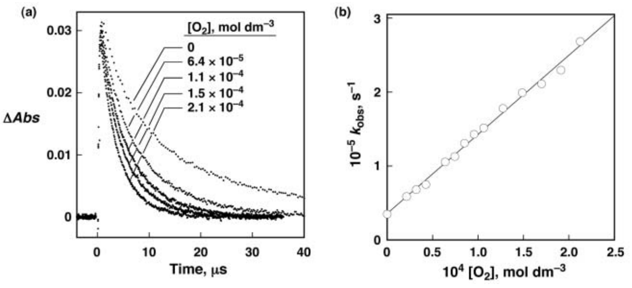
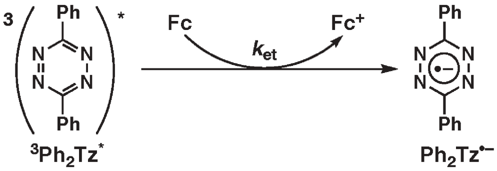


Fig. 2 (a) Decay dynamics of T–T absorption change at 535 nm observed by laser-flash photolysis of an MeCN solution of $Ru(bpy)_3^{2+}$ (4.6×10^{-5} mol dm^{-3}) and Ph_2Tz (9.6×10^{-4} mol dm^{-3}) in the presence of O_2 (0 mol dm^{-3}, 6.4×10^{-5} mol dm^{-3}, 1.1×10^{-4} mol dm^{-3}, 1.5×10^{-4} mol dm^{-3}, and 2.1×10^{-4} mol dm^{-3}) at 298 K. (b) Plot of k_{obs} *vs.* [O_2].

correspond to the unimolecular decay to the ground state and the T–T annihilation, respectively. The first-order decay rate constant (k_T) and the second-order decay rate constant (k_{T-T}) were determined separately from the first-order and second-order plots as 3.5×10^4 s^{-1} and 2.0×10^{10} mol^{-1} dm^3 s^{-1}, respectively.[18] The lifetime of $^3Ph_2Tz^*$ is thereby determined as $\tau = 28.4$ μs, which is much longer than that of $Ru(bpy)_3^{2+*}$ (0.85 μs).[10–12]

When Ph_2Tz is replaced by 3,6-bis(2-chlorophenyl)-1,2,4,5-tetrazine and 3,6-di-2-pyridyl-1,2,4,5-tetrazine, the T–T absorption maxima (λ_{max}) are shifted to 530 nm and 555 nm with lifetimes of $\tau = 13.9$ μs and $\tau = 18.4$ μs, respectively (see ESI, S6†). It should be noted that no photochemical decomposition of the triplet excited state of 3,6-di-substituted tetrazines was observed in the energy-transfer reactions.[19]

In order to estimate the reduction potential (E_{red}*) of $^3Ph_2Tz^*$, the driving force dependence of the electron-transfer reduction of $^3Ph_2Tz^*$ was examined using a series of electron donors whose one-electron oxidation potentials are known (*vide infra*). For example, the triplet excited state of Ph_2Tz is quenched efficiently by electron transfer from ferrocene (Fc) to $^3Ph_2Tz^*$ [eqn (2)].



(2)

The decay of $^3Ph_2Tz^*$ becomes faster in the presence of Fc as shown in Fig. 3a. The second-order rate constant of electron transfer (k_{et}) is determined as 7.6×10^9 mol^{-1} dm^3 s^{-1} from the linear plot of the observed pseudo-first-order decay rate constant (k_{obs}) *vs.* concentration of Fc (Fig. 3b). Similarly the k_{et} values of electron transfer from a series of electron donors to $^3Ph_2Tz^*$ were determined and the k_{et} values are listed in Table 1 together with the one-electron oxidation potentials of electron donors (E_{ox}) employed in this work. The k_{et} value increases with decreasing E_{ox} value to reach a diffusion-limited value (2.0×10^{10} mol^{-1} dm^3 s^{-1}) as shown in Fig. 4 (●).[20] This is a typical feature of outer-sphere electron-transfer processes.[20] The dependence of the activation Gibbs energy of photoinduced electron transfer ($\Delta G^{\neq}$) on the Gibbs energy change of electron transfer (ΔG_{et}) has well been established as given by the Gibbs energy relationship [eqn (3)],[20] where $\Delta G_0^{\neq}$ is the intrinsic barrier that represents the activation Gibbs energy when the driving force of electron transfer is zero, *i.e.*, $\Delta G^{\neq} = \Delta G_0^{\neq}$ at $\Delta G_{et} = 0$.

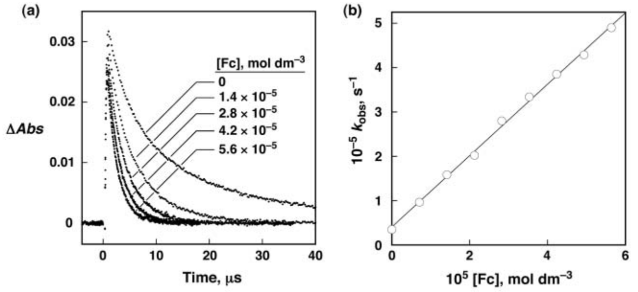


Fig. 3 (a) Decay dynamics of T–T absorption at 535 nm observed by laser-flash photolysis of a deaerated MeCN solution of $Ru(bpy)_3^{2+}$ (4.6×10^{-5} mol dm^{-3}) and Ph_2Tz (9.6×10^{-4} mol dm^{-3}) in the presence of Fc (0 mol dm^{-3}, 1.4×10^{-5} mol dm^{-3}, 2.8×10^{-5} mol dm^{-3}, 4.2×10^{-5} mol dm^{-3}, and 5.6×10^{-5} mol dm^{-3}) at 298 K. (b) Plot of k_{obs} *vs.* [Fc].

Table 1 Oxidation potentials (E_{ox}) of various electron donors and rate constants (k_{et}) of photoinduced electron transfer from various electron donors to $^3PhTz^*$ in deaerated MeCN at 298 K

No.	Electron donor	E_{ox}/V *vs.* SCE	k_{et}/mol^{-1} dm^3 s^{-1}
1	Decamethylferrocene	−0.08	1.2×10^{10}
2	Dimethylferrocene	0.26	9.5×10^9
3	Ferrocene	0.37	7.6×10^9
4	*N*-Benzyl-1,4-dihydronicotinamide	0.57	3.6×10^9
5	4-Methyl-*N*,*N*-dimethylaniline	0.69	1.5×10^9
6	*N*,*N*-Dimethylaniline	0.78	6.4×10^8
7	4-Bromo-*N*,*N*-diemthylaniline	0.92	1.3×10^8
8	1,2,4-Trimethoxybenzene	1.12	6.3×10^6
9	1,4-Dimethoxybenzene	1.34	1.5×10^5

$$\Delta G^{\neq} = (\Delta G_{et}/2) + [(\Delta G_{et}/2)^2 + (\Delta G_0^{\neq})^2]^{1/2} \qquad (3)$$

On the other hand $\Delta G^{\neq}$ values are related to the rate constant of electron transfer (k_{et}) as given by eqn (4), where Z is the collision frequency that is taken as 1×10^{11} mol^{-1} dm^3 s^{-1}, F is the Faraday constant, and k_{diff} is the diffusion rate constant in MeCN (2.0×10^{10} mol^{-1} dm^3 s^{-1}).[20]

$$\Delta G^{\neq} = (2.3RT/F)\log[Z(k_{et}{}^{-1} - k_{diff}{}^{-1})] \qquad (4)$$

On the other hand, the ΔG_{et} values are obtained from the one-electron oxidation potential of donors (E_{ox}) and the one-electron reduction potential of the excited state of acceptors (E_{red}*) by using eqn (5).

$$\Delta G_{et} = F(E_{ox} - E_{red}{}^*) \qquad (5)$$

From eqn (3) and (5) a linear relation between $\Delta G^{\neq} - \Delta G_{et}$ and $(\Delta G^{\neq}/F)^{-1}$ is derived as shown in eqn (6). Thus, the unknown values of E_{red}* and $\Delta G_0^{\neq}$ can be determined from the intercept and slope of the plots of $(\Delta G^{\neq}/F) - E_{ox}$ *vs.* $(\Delta G^{\neq}/F)^{-1}$ by using eqn (6) (see ESI, S7†).

$$(\Delta G^{\neq}/F) - E_{ox} = -E_{red}{}^* + (\Delta G_0^{\neq}/F)^2/(\Delta G^{\neq}/F) \qquad (6)$$

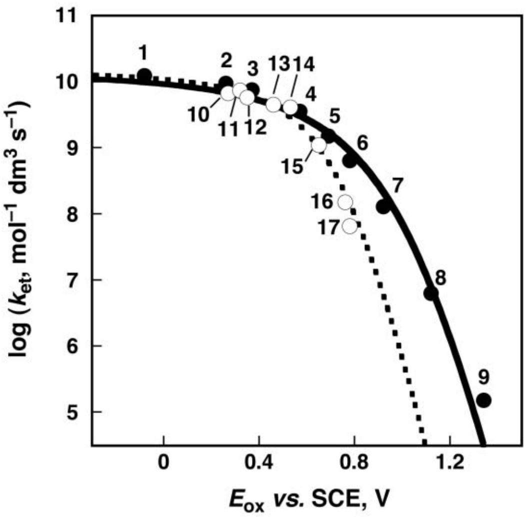


Fig. 4 Plots of log k_{et} *vs.* E_{ox} for photoinduced electron transfer from various electron donors to $^3Ph_2Tz^*$ (●) and $Ru(bpy)_3^{2+*}$ (○) in deaerated MeCN at 298 K. Numbers at closed circles (●) correspond to those in Table 1. Numbers at open circles (○) are taken from ref. 12 [10: 4-aminodiphenylamine, 11: *N,N,N′,N′*-tetramethylbenzidine, 12: *N,N′*-diphenyl-*p*-phenylenediamine, 13: benzidine, 14: phenothiazine, 15: 4-methyl-*N,N*-dimethylaniline, 16: *N,N*-diethylaniline, and 17: *N,N*-dimethylaniline].

The E_{red}* value and the $\Delta G_0^{\neq}$ value of $^3Ph_2Tz^*$ were determined as 1.09 V *vs.* SCE and 5.24 kcal mol^{-1}, respectively from the best fit line shown in Fig. 4. The plot of log k_{et} *vs.* E_{ox} for electron transfer from $Ru(bpy)_3^{2+*}$ to a similar series of electron donors is also shown in Fig. 4 (○) for comparison.[12] The plot of $Ru(bpy)_3^{2+*}$ is shifted to a negative direction (−0.32 eV) in accordance with the difference in the E_{red}* values between $Ru(bpy)_3^{2+*}$ (0.77 V *vs.* SCE)[11] and $^3Ph_2Tz^*$ (1.09 V *vs.* SCE). The excited state energy of $^3Ph_2Tz^*$ was determined as 2.00 eV from the subtraction of the E_{red} value of Ph_2Tz (−0.91 V *vs.* SCE)[5] from the E_{red}* value of $^3Ph_2Tz^*$.

In conclusion, efficient energy transfer form $Ru(bpy)_3^{2+*}$ to Ph_2Tz occurs to produce the triplet excited state ($^3Ph_2Tz^*$), which would otherwise be difficult to be generated. The much longer lifetime (τ = 28.4 μs) and the high oxidizing ability (E_{red}* = 1.09 V *vs.* SCE) of $^3Ph_2Tz^*$ as compared with those of $Ru(bpy)_3^{2+*}$ provide the promising prospects as newly available, strong and robust oxidants with long lifetimes in photoinduced electron-transfer reactions.

This work was partially supported by a Grant-in-Aid (Nos. 16205020 and 17550058) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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9 The phosphorescence can only be observed under specific conditions, such as in 1,2,4,5-tetrazine vapor,[6] or mixed crystal at low temperature.[7,8] In addition, unsubstituted 1,2,4,5-tetrazine is known to undergo efficient photochemical decomposition, breaking apart to $2HCN + N_2$[6–8].

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13 Transient absorption spectrum of $Ru(bpy)_3^{2+*}$ alone was measured by the laser excitation of a deaerated MeCN solution containing only $Ru(bpy)_3^{2+}$ at 450 nm. There was no absorption band at 450–600 nm. Thus, the observed transient absorption band at 450–600 nm can be definitely assigned to $^3Ph_2Tz^*$ (see ESI, S1)†.

14 The transient absorption spectra in Fig. 1 are cut at zero to emphasize the formation of $^3Ph_2Tz^*$. The spectra including the negative bleaching part are shown in ESI, S2†.

15 The extinction coefficient (ε) of the triplet absorption can be determined from the rise of absorption at 535 nm due to $^3Ph_2Tz^*$ and the decay of absorption at 363 nm due to $Ru(bpy)_3^{2+*}$, because the ε value of $Ru(bpy)_3^{2+*}$ has been reported previously; see: R. Bensasson, C. Salet and V. Balzani, *J. Am. Chem. Soc.*, 1976, **98**, 3722.

16 Oxygen also quenches the emission of $Ru(bpy)_3^{2+*}$; see: K. Kalyanasundaram, *Coord. Chem. Rev.*, 1982, **46**, 159. However the k_{EN} value of energy transfer from $^3Ph_2Tz^*$ to O_2 was not affected by the quenching of $Ru(bpy)_3^{2+*}$ with O_2, because the energy transfer form $Ru(bpy)_3^{2+*}$ to Ph_2Tz is much faster under the present experimental conditions.

17 The phosphorescence spectra were measured on a SPEX Fluorolog τ_3 fluorescence spectrophotometer. The solution was irradiated with monochromatized light (λ = 450 nm) from a xenon lamp and the phosphorescence spectra were measured. The phosphorescence intensity of $^1O_2$ becomes larger in the presence of Ph_2Tz, since $^3Ph_2Tz^*$ have much longer lifetimes compared with that of $Ru(bpy)_3^{2+*}$ (see ESI, S3)†.

18 The decay dynamics of T–T absorption change at 535 nm due to $^3Ph_2Tz^*$ has also been examined using different laser intensities in order to determine the unimolecular decay to the ground state accurately (see ESI, S5†).

19 No absorbance change was observed in a deaerated MeCN solution of $Ru(bpy)_3^{2+}$ (4.6×10^{-5} mol dm^{-3}) in the presence of Ph_2Tz (9.6×10^{-4} mol dm^{-3}) after 8000 times laser excitation at 450 nm (laser power: 8.6 mJ).

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