The first example of photochemical reduction of nitrite into nitrogen monoxide by a dinuclear Ru(II)–Cu(II) complex and photoinduced intramolecular electron transfer reaction between Ru(II) and Cu(II) moieties†

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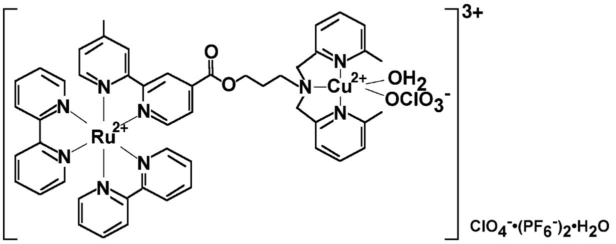
The photochemical reduction of nitrite to NO by the dinuclear Ru(II)–Cu(II) complex ([Ru(bpy)$_2$(Mebpy-COOC$_3$H$_6$)Me$_2$bpaCu(H$_2$O)(ClO$_4$)](ClO$_4$)·(PF$_6$)$_2$·(H$_2$O) was observed in the absence of sacrificial electron donor reagents in CH$_2$Cl$_2$. The reaction rate of the photoreduction of nitrite depended upon the concentration of the excited Ru(II) moiety in the complex. The photoinduced intramolecular electron transfer rate constants between the Ru(II) and Cu(II) moieties (*Ru(II)–Cu(II) → Ru(III)–Cu(I) and Ru(III)–Cu(I) → Ru(II)–Cu(II)) in the dinuclear complex were calculated to be 2.3 × 10^9 and 8.3 × 10^7 s^{-1}, respectively, by laser flash photolysis.

Copper-containing nitrite reductase (CuNIR) plays a key role in biological denitrification,[1] which is the dissimilatory reduction of nitrate (NO_3^-) or nitrite (NO_2^-) usually leading to the production of dinitrogen by prokaryotic organisms, and an environmentally important process for the inorganic nitrogen cycle. CuNIR, which catalyses the reduction of nitrite to nitrogen monoxide ($NO_2^- + e^- + 2H^+ \rightarrow NO + H_2O$), has two kinds of Cu centres per subunit. Type 1 Cu accepts an electron from an external electron carrier, and type 2 Cu, which accepts an electron from the reduced type 1 Cu site, is the reduction centre of NO_2^-. The type 2 Cu site shows a distorted tetrahedral geometry and is ligated by three His imidazolyls and a water molecule. The coordinated water to the type 2 Cu is displaced by the substrate (NO_2^-). Subsequently, the reduction of nitrite to NO proceeds with an attack of protons on the nitrite bound to the Cu site and a concomitant electron transfer reaction from the type 1 Cu.[2] Several model complexes of the type 2 Cu site, which is the CuNIR active site, have been reported.[3,4] Recently, we reported that [CuMe$_2$bpa(ClO$_4$)](ClO$_4$) (Me$_2$bpa = bis(6-methyl-2-pyridylmethyl)amine) catalyses the reduction of nitrite with acid to produce NO effectively.[4] The coordination modes of the nitrite ligands in CuMe$_2$bpa complexes depends on the oxidation state of the copper ion; thus the nitrite is coordinated to Cu(II) through two oxygen atoms (*O*,*O*′-coordination mode) and to Cu(I) through one nitrogen atom (*N*-coordination mode). We have also reported the photochemical reduction of nitrite to NO catalysed by the CuMe$_2$bpa complex with a photosensitiser[5] [Ru^{2+}(bpy)$_3$]Cl$_2$ in H$_2$O.[6] In this paper, we present the first example of the photochemical reduction of nitrite to nitrogen monoxide by the dinuclear Ru(II)–Cu(II) complex (Ru–Cu = [Ru(bpy)$_2$(Mebpy-COOC$_3$H$_6$)Me$_2$bpaCu(H$_2$O)(ClO$_4$)](ClO$_4$)·(PF$_6$)$_2$·H$_2$O, Chart 1) in the absence of sacrificial electron donor reagents in CH$_2$Cl$_2$. The photoinduced intramolecular electron transfer reaction between the Ru(II) and Cu(II) moieties in the Ru–Cu complex was also investigated by laser flash photolysis.



Ru-Cu:
[Ru(bpy)$_2$(Mebpy-COOC$_3$H$_6$)Me$_2$bpaCu(H$_2$O)(ClO$_4$)](ClO$_4$)•(PF$_6$)$_2$•H$_2$O

Chart 1

The synthesis of Ru–Cu is described in the ESI.† The absorption spectrum of Ru–Cu in CH$_2$Cl$_2$ (Fig. S1†) displays two bands at 458 (ε = 17 000 M^{-1} cm^{-1}) and 686 nm (ε = 160 M^{-1} cm^{-1}) in the visible region, which are characteristic of MLCT of bpy coordinated to the Ru(II) ion and d–d transition of the Cu(II) complex, respectively. The emission spectrum of Ru–Cu in acetonitrile (Fig. S2†) displays an emission band at 647 nm, which originates from the lowest MLCT state of predominantly triplet character.[7] The wavelength maximum is red-shifted by 24 nm and the emission intensity is one third lower than that of the corresponding Ru–Zn complex ([Ru(bpy)$_2$(Mebpy-COOC$_3$H$_6$)Me$_2$bpaZnCl$_2$](PF$_6$)$_2$·H$_2$O). The spectroscopic data show that the Cu(II) moiety partially quenches the excited state of Ru(II) in Ru–Cu. The redox potentials for Ru^{3+}/Ru^{2+} and Cu^{2+}/Cu^{1+} couples of Ru–Cu in CH$_2$Cl$_2$ with 0.1 M [N(nC$_4$H$_9$)$_4$]ClO$_4$ as the supporting electrolyte were observed at 928 mV and 86 mV *vs.* Ag/AgNO$_3$, respectively. The difference in $E_{1/2}$ values (0.84 eV) is the driving force (ΔG°) for the intramolecular electron transfer in Ru–Cu.

Photochemical NO production from deaerated CH$_2$Cl$_2$ solution including 100 μM Ru–Cu, 15 mM [(Ph$_3$P)$_2$N]NO$_2$, and 6 mM trifluoroacetic acid was observed at 28 °C under irradiation

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† Electronic supplementary information (ESI) available: Synthesis of Ru–Cu, NMR spectra of L, Ru–Cu and Ru–Zn, absorption spectrum of Ru–Cu, emission spectra of Ru–Cu and Ru–Zn, transient absorption spectra of Ru–Cu and Ru–Zn, time profiles of Ru(II) ground and excited states and Ru(III) absorptions in Ru–Cu and Ru–Zn, EPR spectrum of NO-Fe(DTCS)$_2$ and calibration curve of [NO] *vs.* EPR peak height. See DOI: 10.1039/b907484h

with 460 nm light (power = 3.0 mW cm^{-1}) and the continuous flow of Ar (1 ml/min), where the vent gas was passed into the aqueous solution including 2.5 mM $FeCl_3$ and 12.5 mM *N*-(dithiocarboxy)sarcosine (DTCS) at 5 °C. The NO generated in the reaction vessel was transported to the $Fe(DTCS)_3$ solution by carrier Ar gas and reacted with $Fe(DTCS)_3$ to produce NO-$Fe(DTCS)_2$ immediately.[8] The distinct triplet EPR spectrum (g = 2.040 and A^N = 1.27 mT), which is identified as the NO-$Fe(DTCS)_2$ complex, of the NO trapping solution is observed at room temperature (Fig. S3†). The yield of NO generated was estimated based on the calibration curve of the amount of NO *vs.* the peak height of the EPR spectrum (Fig. S4†). As shown in Fig. 1, the linear generation of NO from the Ru–Cu solution including nitrite and acid under visible light irradiation within 30 min was observed, while the NO formation did not occur when Ru–Zn was employed instead of Ru–Cu. Therefore, the nitrite reduction site must be the Cu(II) moiety in Ru–Cu.

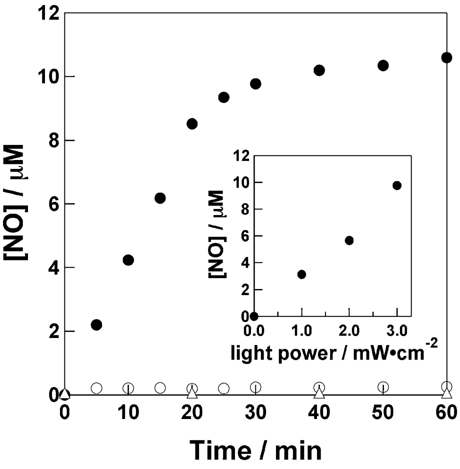

Fig. 1 NO generated upon photolysis (λ = 460 nm, light power: 3.0 mW cm^{-1}) of 100 µM Ru–Cu (●), 100 µM Ru–Zn (○) and 100 µM $[CuMe_2bpa(ClO_4)](ClO_4)$ (△) in deaerated CH_2Cl_2 solution including 15 mM $[(Ph_3P)_2N]NO_2$ and 6 mM trifluoroacetic acid at 28 °C under Ar atmosphere. Inset: plots of generated NO concentration *vs.* light power upon photolysis of 100 µM Ru–Cu in deaerated CH_2Cl_2 solution including 15 mM $[(Ph_3P)_2N]NO_2$ and 6 mM trifluoroacetic acid at 28 °C under Ar atmosphere for 30 min.

A plausible mechanism of the photoreduction of nitrite to NO may be written as follows:

$$Ru^{2+}–Cu^{2+} + h\nu \rightarrow Ru^{2+*}–Cu^{2+} \quad (1)$$

$$Ru^{2+*}–Cu^{2+} \rightarrow Ru^{3+}–Cu^{1+} \quad (2)$$

$$Ru^{3+}–Cu^{1+} + NO_2^- + 2H^+ \rightarrow Ru^{3+}–Cu^{2+} + NO + H_2O \quad (3)$$

$$Ru^{3+}–Cu^{2+} + X(e.g.\ CH_2Cl_2) \rightarrow Ru^{2+}–Cu^{2+} + X^{\bullet}(e.g.\ Cl^{\bullet}) \quad (4)$$

As the yield of NO generated was proportional to the light power (inset of Fig. 1), the photoreduction of the nitrite reaction rate should be dependant upon the concentration of the excited Ru(II) moiety in the complex. Eqn (2) is the intermolecular electron transfer step. The Cu moiety accepts an electron from the excited Ru(II) moiety, and the reduction of nitrite to NO proceeds with an attack of protons on the nitrite bound to the reduced Cu moiety in Ru–Cu (eqn (3)). It is interesting to note that the photoreduction of nitrite to NO proceeds until the amount of NO generated is equal to *ca.* 10% of Ru–Cu despite the lack of addition of any sacrificial reductants, such as EDTA. As the absorption spectrum of the Ru–Cu solution after the photochemical reaction was very similar to that before the reaction, the $Ru^{3+}–Cu^{2+}$ species could not be confirmed. The $Ru^{3+}–Cu^{2+}$ species may react with some compounds (such as CH_2Cl_2) in the system and return to the $Ru^{2+}–Cu^{2+}$ species (eqn (4)), although we could not clarify what the compound which reacts with the $Ru^{3+}–Cu^{2+}$ species is. The NO generation was not observed when H_2O or CH_3CN was employed instead of CH_2Cl_2. We speculate that the organic solvent (CH_2Cl_2) may play the role of sacrificial reductant in this system. In the $Rubpy_3$ and $CuMe_2bpa$ unconjugated system in H_2O,[6] the addition of a sacrificial reductant (KSeCN) is essential for the catalytic reduction of nitrite to nitrogen oxide.

Transient absorption spectra of Ru–Cu and Ru–Zn were observed by nanosecond laser flash photolysis (λ_{ex} = 532 nm, fwhm 4 ns) in deaerated CH_3CN at 298 K (Fig. S5 and S6†). The recovery of the Ru(II) ground state bleach at 460 nm and the decay curves of absorption at 370 nm due to the excited Ru(II) moiety are a mirror image in Ru–Zn, with both the recovery and decay having lifetimes of 1.2 µs (Fig. S7†). Both the time profiles of the Ru(II) ground state absorption at 460 nm and the ^{3}MLCT state absorption of the Ru(II) moiety at 370 nm in Ru–Cu show bi-exponential curves (Fig. S8†). As the lifetime (1.1 µs) of the slow component is almost the same as those obtained for Ru–Zn, the component is assigned to the emission process of the Ru(II) moiety in Ru–Cu. The fast components with lifetimes of 5.1 and 7.9 ns at 370 and 460 nm, respectively, are suggested to be due to the intramolecular electron transfer from the excited Ru(II) to Cu(II) moieties in Ru–Cu because another spectral change at 503 nm due to the Ru(III) moiety was observed in the transient absorption spectra of Ru–Cu (Fig. S8†).[5] Unfortunately, the reduction of the Cu(II) moiety could not be observed because of the very small extinction coefficient for the Cu(II) moiety, and there is no absorption band for the Cu(I) complex in the visible region. To determine the detailed lifetime of the fast component, the transient absorption spectra of Ru–Cu and Ru–Zn were observed by subpicosecond laser flash photolysis (λ_{ex} = 400 nm, fwhm *ca.* 300 fs) in deaerated CH_3CN at 298 K (Fig. 2). The spectral change at 503 nm was clearly observed for Ru–Cu, but not for Ru–Zn. Time profiles of absorbance at 503 nm due to the Ru(III) moiety in Ru–Cu are shown in Fig. 3. From the results of the transient absorption spectra of Ru–Cu, the rate constant of the intramolecular electron

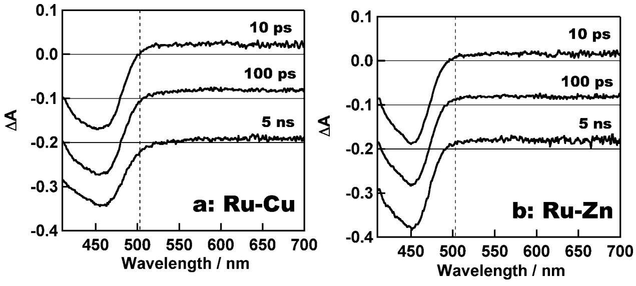

Fig. 2 Transient absorption spectra after excitation of Ru–Cu (a) and Ru–Zn (b) at 400 nm (FWHM *ca.* 300 fs) in deaerated CH_3CN at 298 K. Sample concentration is 60 µM.

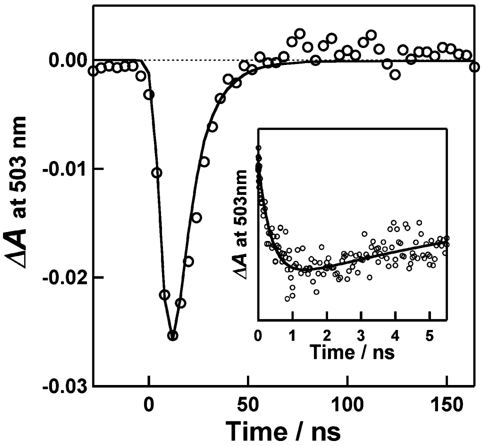

Fig. 3 Time profile of the absorbance at 503 nm due to the Ru(III) state by laser flash photolysis (λ_{ex} = 532 nm, FWHM 4 ns) of a deaerated CH$_3$CN solution of Ru–Cu (60 μM) at 298 K. Inset: time profile of the absorbance at 503 nm due to the Ru(III) state by laser flash photolysis (λ_{ex} = 400 nm, FWHM *ca.* 300 fs) of a deaerated CH$_3$CN solution of Ru–Cu (60 μM) at 298 K.

transfer from the excited Ru(II) to Cu(II) moieties (*Ru(II)–Cu(II) → Ru(III)–Cu(I)) in Ru–Cu and the back electron transfer rate constant (Ru(III)–Cu(I) → Ru(II)–Cu(II)) were calculated to be 2.3×10^9 and 8.3×10^7 s^{-1}, respectively. The latter value is somewhat larger than the reported intramolecular electron transfer rate (1.1×10^7 s^{-1}) from Mn(II) to photooxidised Ru(III) moieties in a Ru(II)–Mn(II) complex ($\Delta G^\circ = 0.59$ eV).[7]

Conclusions

This is the first example of the photoreduction of nitrite to NO by a binuclear complex in the absence of any sacrificial electron donor reagents in CH$_2$Cl$_2$, and the photoinduced intramolecular electron transfer reaction from the Ru(II) to Cu(II) moieties in the binuclear Ru(II)–Cu(II) complex. The reaction rate of the photoreduction of nitrite should be dependent on the concentration of the excited Ru(II) moiety in the complex. The intramolecular electron transfer reaction rate was estimated to be ~2×10^9 s^{-1} by laser flash photolysis. The photoreduction of nitrite to NO proceeded until the amount of NO generated was equal to about 10% of the dinuclear complex despite the lack of any sacrificial reductants.

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