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Photoinduced Ligand Transformation in a Ruthenium Polypyridophenazine Complex

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Irradiation of a ruthenium polypyridyl complex in the presence of oxygen leads to the oxidation of a benzodipyridophenazine ligand to a quinone. The corresponding tetraazatetrapyridopentacene complex is not oxidized under the same conditions.

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Introduction

Polypyridophenazine-type complexes of ruthenium have recently gained considerable interest due to their capability to mediate directional photoinduced electron transfer between metal centres[1] and their application as luminescent DNA sensors and cleavage agents.[2] The redox properties of the central phenazine moiety are important for these applications.[3] For example the redox activity of dipyridophenazine has recently been employed for photochemical reduction of the central pyrazine moiety to dihydropyrazine in various alcohols.[4] The capacity of the dinuclear ruthenium complexes of 9,11,20,22-tetraazatetrapyrido[3,2-*a*:2′,3′-*c*:3′′,2′′-l:2′′′,3′′′-*n*]pentacene (tatpp) and its related quinone 9,11,20,22-tetraazatetrapyrido[3,2-*a*:2′,3′-*c*:3′′,2′′-l:2′′′,3′′′-*n*]pentacene-10,21-quinone (tatpq) derivative to reversibly store up to four electrons using directional photoelectron transfer has been reported.[5] The investigation of related ligand systems, tetrapyridophenazine, has recently let to a report on the light driven catalytic production of hydrogen using a heterodinuclear ruthenium palladium complex.[6]

In this contribution, we report on the photochemical reaction between a mononuclear complex of benzodipyrido[3,2-*a*:2′,3′-*c*]phenazine (bdppz) and oxygen. The reactivity of a homodinuclear ruthenium tatpp complex is also investigated. Both ligand structures contain an extended aromatic system with an integrated phenazine motif. The results reported are not only of interest from a synthetic and photochemical perspective but also with respect to the stability of such complexes towards O_2. This is illustrated by the very different behavior observed for the two compounds studied.

Results and Discussion

The potential oxygen sensitivity for this type of compounds was first observed during the synthesis of complex **1** (Figure 1). When bdppz and [Ru-bis(4,4′-di-*tert*-butyl-2,2′-bipyridine)Cl_2], $(tbbpy)_2RuCl_2$,[7] are reacted under aerobic conditions two different compounds were obtained (Figure 1). HPLC studies showed the disappearance of the initially formed peak for **1**, (retention time of 12.9 min) with a simultaneous formation of a signal for **2** observed at 16.4 min (see Supporting Information).

A more detailed investigation of this phenomenon showed the oxidation reaction to be photoinduced with conversion of **1** to complex **2**. Ultimately, **2** could be obtained in 95% yield upon irradiation of **1** with light of 470 ± 15 nm [chosen to overlap with the Ru(dπ)–L(pπ) ^{1}MLCT transition] in acetonitrile solution for 48 h in the presence of O_2 (see Supporting Information). No reaction is observed under anaerobic conditions or in the absence of light. Complex **1** can be obtained in pure form simply by carrying out the ligand-substitution reaction under anaerobic conditions (see experimental details).

Complex **2** shows a NMR spectrum very similar to that of **1** exhibiting only small shifts for the bdppz and tbbpy based signals. The most prominent difference being the absence of the signal for H4 in **2**, which appears at δ =

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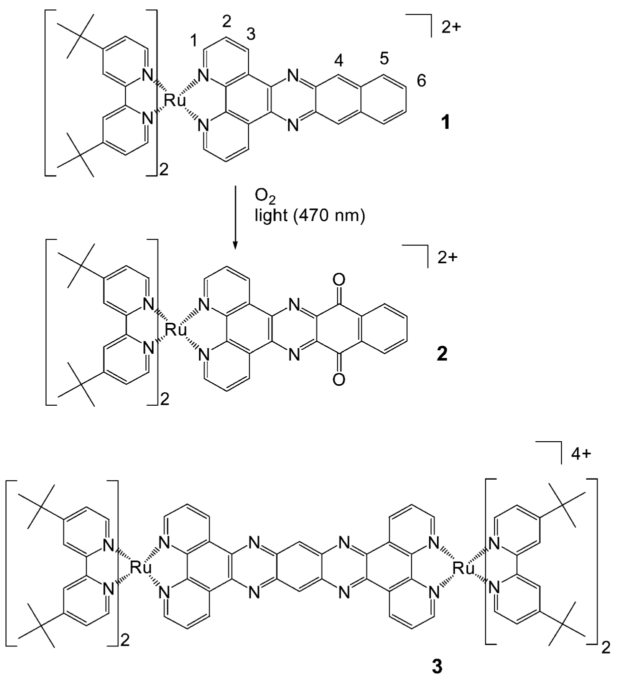

Figure 1. Novel light-driven synthetic route to a quinone-containing dipyridophenazine-type complex and the dinuclear tatpp complex for comparison.

9.07 ppm in **1**. The mass spectroscopic data show an increase in mass from (*m*/*z*) 1115 to 1145 for the $[M - PF_6]^+$ peak, corresponding to the loss of two hydrogen atoms and the addition of two oxygen atoms. The complexes display similar absorption spectra in the visible, with maxima around 444 nm which are ^{1}MLCT in nature. Two transitions in the UV region of **1** at 389 and 412 nm are absent in the spectrum of **2**. The aromatic system is destroyed due to the presence of the quinone moiety and therefore the amount of electronic transitions is reduced. Thus the fine structure in the absorption spectra of **1** is lost in the spectra of **2**. Complex **1** displays a weak emission peak at 625 nm in deaerated acetonitrile whereas no emission could be observed for **2**.

The structure for **2** was confirmed by a single-crystal X-ray analysis as shown in Figure 2. The bond lengths [Ru–N 2.046(5)–2.064(6) Å] and angles [N–Ru–N 78.8(2)°–79.5(2)°] around the ruthenium core are within experimental error identical with values reported for other similar compounds.[9] The distances of 1.225(9) Å between C14–O2 and C21–O1 clearly indicate that a quinone moiety has been formed. In contrast to other known ruthenium complexes of oligopyridophenazines, the dpbqz ligand in **2** displays a rather twisted conformation with a deviation from planarity of 14° which is significant.

While some earlier works with related ruthenium complexes mention this kind of photooxidation process, no products were ever isolated.[10,11] To the best of our knowledge, this is the first time that such a product has been isolated in good yield and the structure was confirmed by X-ray crystallography.

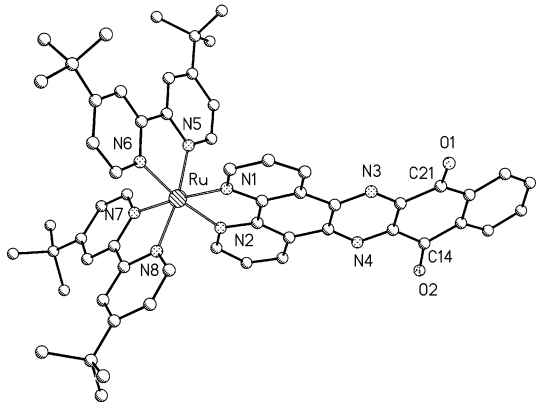

Figure 2. Solid-state molecular structure of the ruthenium complex **2** containing dipyrido[3,2-*a*:2′,3′-*c*]benzo[3,4]phenazine-11,16-quinone, dpbqz.[8]

We postulate that the oxidation process involves singlet oxygen which is created by triplet sensitisation from the excited ruthenium ^{3}MLCT state. It is known from literature that polypyridylruthenium complexes are able to create singlet oxygen which can be used in organic transformations which can also be exploited for the preparative catalytic oxidation of citronellol.[12–15]

In an attempt to prepare the free dpbqz ligand using intermolecular photoinduced process, bdppz was mixed with the tris(2,2′-bipyridine)ruthenium(II) cation under aerobic conditions in acetonitrile and illuminated as with **1** for 48 h. The oxidation of the bdppz ligand is observed but the yield is much more modest (approximately 15% conversion).

This high yield photochemical route to **2** and consequently to dpbqz is fortuitous as the only prior synthetic route to dpbqz ligand, to the best of our knowledge, requires a 5-step reaction sequence from 2,3-diamino-1,4-naphthoquinone chlorohydrate and has an overall yield of less than 40%.[16]

Surprisingly, the photooxidation is not observed in the related complex **3** (Figure 1). Illumination of **3** in acetonitrile under aerobic conditions does not lead to any observable oxidation of the central tatpp ligand structure. Even prolonged irradiation over 72 h did not result in the formation of detectable amounts of the corresponding oxidation product $[(tbbpy)_2Ru(tatpq)Ru(tbbpy)_2](PF_6)_4$. It should be noted that peroxy disulfate oxidation of **3** and related bpy and phen analogues quantitatively yields the quinone (tatpq) products.[17] This result shows that structurally similar polypyridyl ligands can have dramatically different photochemical reactivity and stability towards O_2.

Conclusions

The observed photochemical reactivity of **1** but not **3** towards oxygen has potentially important implications for the application of ruthenium complexes in a number of photocatalytic processes. The identification of the photo product **2** in the presence of starting material **1** is compli-

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cated by the very similar NMR and UV/Vis spectra. This may have severe consequences in photocatalytic experiments carried out with this type of compounds under aerobic conditions. Complexes such as **3** have been shown to undergo photochemically driven multi-electron reduction and are quantitatively reoxidized by O_2.[5a] The bdppz ligand in **1** has a similar potential but due to its O_2 sensitivity, an irreversible oxidation process takes place. Such dramatically different sensitivities show that the photoreactivity of such ligands when coordinated to ruthenium moieties has to be investigated in more detail. As ruthenium polypyridyl complexes are frequently employed as sensitizers in a number of photocatalytic water-splitting schemes, an understanding of their reactivity towards water and O_2 is often essential.[18] We also note that the facile transformation of **1** to **2** under mild conditions is of significant interest from the synthetic point of view. Further investigations of the photochemical and photophysical properties of **1**, **2** and **3** and the mechanism of the oxidation of **1** to **2** are in progress.

Experimental Section

[Ru(tbbpy)$_2$(bdppz)](PF$_6$)$_2$ (1): All manipulations were done under an atmosphere of argon to prevent oxidation by oxygen at all times. $Ru(tbbpy)_2Cl_2$ (0.28 g, 0.4 mmol) and bdppz (0.17 g, 0.5 mmol) are suspended in a degassed mixture of ethanol/water (80 mL/20 mL) and heated to reflux for 24 h. Ethanol is removed by distillation and water (20 mL) is added. The solution is filtered through Celite to remove excess of ligand. The residue is washed three times with 10 mL of degassed water. To the combined solutions NH_4PF_6 is added. The resulting red precipitate is collected on a frit, washed with diethyl ether and dried in vacuo. Yield 0.34 g (68%). $C_{58}H_{60}F_{12}N_8P_2Ru\cdot 1.5H_2O$ (1287.16): calcd. C 54.12, H 4.93, N 8.71; found C 53.89, H 4.86, N 8.69. MS (ESI in methanol): *m*/*z* (%) = 485 (50) $[(M - 2PF_6)/2]^{2+}$, 1115 (30) $[M - PF_6]^+$, 2375 (10) $[2M - PF_6]^+$. ^{1}H NMR (200 MHz, [D$_3$]MeCN): δ = 9.60 (dd, *J* = 1.4 and 8.2 Hz, 2 H), 9.07 (s, 2 H), 8.53 (d, *J* = 1.8 Hz, 2 H), 8.50 (d, *J* = 1.8 Hz, 2 H), 8.33 (m, 2 H), 8.11 (dd, *J* = 1.4 and 5.4 Hz, 2 H), 7.87 (dd, *J* = 5.4 and 8.2 Hz, 2 H), 7.72 (m, 2 H), 7.69 (d, *J* = 6.0 Hz, 2 H), 7.65 (d, *J* = 6.0 Hz, 2 H), 7.48 (dd, *J* = 1.8 and 6.0 Hz, 2 H), 7.27 (dd, *J* = 1.8 and 6.0 Hz, 2 H), 1.45 (s, 18 H), 1.36 (s, 18 H) ppm. ^{13}C NMR (100 MHz, [D$_3$]MeCN): δ = 30.4, 30.5, 36.3, 36.4, 122.6, 122.7, 125.6, 125.7, 128.5, 129.0, 129.1, 129.5, 131.9, 134.1, 136.0, 139.4, 141.6, 152.1, 152.4, 154.5, 157.9, 158.0, 163.7, 163.8 ppm.

[Ru(tbbpy)$_2$(dpbqz)](PF$_6$)$_2$ (2): A solution of **1** (0.127 g, 0.1 mmol) in 30 mL of acetonitrile/water (3:1) was illuminated with LED light (470 nm ±15 nm) for 48 h under aerobic conditions. On evaporation of acetonitrile a red crystalline solid is formed which is collected, washed with a small amount of ethanol and diethyl ether and dried on air. Yield 0.124 g (96%). $C_{58}H_{58}F_{12}N_8O_2P_2Ru$ (1290.12): calcd. C 53.99, H 4.53, N 8.69; found C 54.08, H 4.74, N 8.12. MS (ESI in methanol): *m*/*z* (%) = 500 (10) $[(M - 2PF_6)/2]^{2+}$, 999 (5) $[M - 2PF_6 - H]^+$, 1145 (100) $[M - PF_6]^+$. IR (KBr): = ν(C=O) 1691 (s) cm^{-1}. ^{1}H NMR (400 MHz, [D$_3$]MeCN): δ = 9.62 (d, *J* = 8.4 Hz, 2 H), 8.53 (d, *J* = 2.0 Hz, 2 H), 8.49 (d, *J* = 2.0 Hz, 2 H), 8.45 (m, 2 H), 8.25 (d, *J* = 5.2 Hz, 2 H), 8.03 (m, 2 H), 7.96 (dd, *J* = 5.2 and 8.4 Hz, 2 H), 7.69 (d, *J* = 6.0 Hz, 2 H), 7.57 (d, *J* = 6.0 Hz, 2 H), 7.48 (dd, *J* = 2.0 and 6.0 Hz, 2 H), 7.23 (dd, *J* = 2.0 and 6.0 Hz, 2 H), 1.45 (s, 18 H), 1.35 (s, 18 H) ppm. ^{13}C NMR (50 MHz, [D$_3$]MeCN): δ = 30.4, 30.5, 36.3, 36.4, 122.6, 122.7, 125.5, 125.7, 128.6, 130.8, 134.8, 136.6, 143.4, 146.3, 152.0, 152.1, 152.5, 155.7, 157.8, 158.0, 163.8, 163.9, 181.7 ppm.

[(tbbpy)$_2$Ru(tatpp)Ru(tbbpy)$_2$](PF$_6$)$_2$ (3): A suspension of tatpp (0.120 g, 0.247 mmol) in 120 mL of ethanol and 120 mL of water was sonicated for 1 min and then $Ru(tbbpy)_2Cl_2$ (0.350 g, 0.494 mmol) and 2.5 mL concentrated HCl were added. The resulting mixture was heated in a microwave oven at 315 W for 5 h during which the solution was observed to vigorously reflux. The reaction mixture was then cooled to room temp. and filtered through a pad of Celite. The resulting filtrate was then concentrated by rotary evaporation to approximately 50% of the original volume, during which a small precipitate forms (most likely starting material). This solid was removed by filtration. An aqueous NH_4PF_6 solution (50 mg/mL) was then added to the filtrate, which caused the product to precipitate. The product was then filtered, washed with H_2O, and dried under vacuum at 60 °C. The crude product was purified by metathesis (interchanging PF_6^- and Cl^-) as it is sensitive to decomposition on silica or alumina. The dried hexafluorophosphate salt was dissolved in a minimal amount of acetone and the chloride salt precipitated by dropwise addition of an acetone solution of tetra-*n*-butylammonium chloride (50 mg/mL). Once the precipitate has formed, it was isolated by filtration, washed with 2–3 mL of acetone and dried under vacuum at 60 °C. The chloride salt was then dissolved in H_2O and dropwise addition of an aqueous NH_4PF_6 solution (50 mg/mL) resulted in precipitation of the PF_6^- salt. The solid was isolated by filtration, washed with 2–3 mL of water and dried under vacuum at 60 °C. Yield 0.219 g (38%). $C_{102}H_{110}F_{24}N_{16}P_4Ru_2\cdot 2H_2O$ (2378.13): calcd. C 51.51, H 4.83, N 9.42; found C 51.48, H 4.77, N 9.08 . ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 9.83 (d, *J* = 8.1 Hz, 4 H), 9.68 (s, 2 H), 8.95 (s, 4 H), 8.93 (s, 4 H), 8.51 (d, *J* = 4.8 Hz, 4 H), 8.11 (dd, J_1 = 8.1, J_2 = 5.4 Hz, 4 H), 8.04 (d, *J* = 6.3 Hz, 4 H), 7.99 (d, *J* = 5.7 Hz, 4 H), 7.65 (d, *J* = 5.7 Hz, 4 H), 7.47 (d, *J* = 6.0 Hz, 4 H), 1.44 (s, 36 H), 1.36 (s, 36 H) ppm. ^{13}C NMR (500 MHz, [D$_3$]MeCN): δ = 162.99, 162.85, 157.12, 156.89, 154.34, 152.14, 151.62, 151.15, 143.07, 141.44, 133.72, 130.92, 130.56, 127.97, 124.86, 124.67, 121.77, 121.70, 35.49, 35.39, 29.64, 29.55 ppm.

Dipyrido[3,2-*a*:2′,3′-*c*]benzo[3,4]phenazine-11,16-quinone (dpbqz): A suspension of bdppz (33 mg, 0.1 mmol) and [Ru(bpy)$_3$](PF$_6$)$_2$ (86 mg, 0.1 mmol) in 30 mL of acetonitrile was illuminated with LED light (470 nm ±15 nm) (home-made LED device identical to that mentioned in ref.[6] was used) for 48 h under aerobic conditions. The volume is reduced to 10 mL and the solid material is filtered off, washed with acetonitrile, ether and dried. ^{1}H NMR analysis in deuterated chloroform/trifluoric acid shows a ratio of 17:3 for bdppz to dpbqz.

Supporting Information (see also the footnote on the first page of this article): HPLC data, Crystal data for **2**, absorption and emission data, NMR assignments.

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