Cite this: Chem. Commun., 2012, 48, 5680-5682

COMMUNICATION

1,4-Benzene-bridged covalent hybrid of triarylamine and cyclometalated ruthenium: a new type of organic-inorganic mixed-valent system[†]

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Received 10th March 2012, Accepted 20th April 2012 DOI: 10.1039/c2cc32471g

A 1,4-benzene-bridged covalent hybrid of triarylamine and cyclometalated ruthenium 1^{2+} was isolated as a bench-stable open-shell substance. The free spin in this complex is mainly associated with the triarylamine unit, as indicated by EPR and DFT calculations and electrochemical analysis. It exhibits an intense intervalence-charge-transfer transition around 1050 nm that is not present in 1^+ and 1^{3+} .

Open-shell compounds with a general formula of $[M_1$ -bridge- $M_2]^{n\pm}$ have attracted considerable attention since the pioneering work of Creutz and Taube on mixed-valent (MV) chemistry.¹ The interest arises from their implications in a wide range of fields such as molecular electronics, optoelectronics, and artificial photosynthesis.² In most reported examples, $M_1 = M_2$ and they stand for either a purely organic³ or organometallic/inorganic redox center.⁴ Only a few studies have been devoted to those with redox/energetically asymmetric centers.⁵ MV systems with strong electronic coupling provide a simple means to absorb light in the near infrared (NIR, 750-3000 nm),⁶ which is of great importance in many military and civilian uses.⁷ In particular, those exhibiting distinct redox-switchable NIR absorptions are of paramount interest as intelligent materials.8 However, NIR materials with high stability, low redox-switching potentials, and strong molar absorptivities are still in great demand. We present in this communication a covalent hybrid $\mathbf{1}^{n+}$ (n = 1-3, Fig. 1) of triarylamine and cyclometalated ruthenium.9 It should be noted that both redox species exhibit chemically reversible redox processes (N/N $^{\bullet\,+}$ and Ru $^{\rm II/III}$) at appreciably low potentials. Upon one-electron oxidation, 1,4-benzene-bridged bistriarylamine¹⁰ and biscyclometalated ruthenium¹¹ have previously been reported to generate fully delocalized systems with strong NIR absorptions. As will be presented in this communication, open-shell compound 1^{2+} was isolated as a bench-stable material and it displays an

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Fig. 1 Hybrids of triarylamine and ruthenium. Counter-anions are PF_6^- .

intense intervalence-charge-transfer transition that is not present in 1^+ and 1^{3+} .

Details for the preparation of 1 are provided in the ESI.[†] On the basis of known procedures for the synthesis of cyclometalated ruthenium complexes,⁹ the reaction of Ru(tpy)Cl₃ and 1-(di-p-anisylamino)-3,5-di(2-pyridyl)benzene in the presence of AgOTf followed by anion exchange with KPF₆ was carried out. To our surprise, the only isolated product was the openshell complex $\mathbf{1}^{2+}$ instead of the expected $\mathbf{1}^+$ with one counteranion. Although we failed to obtain a single crystal of this complex for X-ray analysis at this stage, the identity of 1^{2+} has been fully proved. The polarity (as judged by thin layer chromatography) and microanalysis of 1^{2+} agree well with the presence of two counter-anions. No distinct ¹H NMR spectrum of 1^{2+} could be recorded, which indicates that it is a paramagnetic substance. More importantly, it displays a singlet electron paramagnetic resonance signal at g = 2.0348at room temperature (Fig. 2). The density functional theory (DFT)-calculated spin density plot of 1^{2+} is shown in Fig. 2 (see details in the ESI[†]), which suggests that the triarylamine unit provides a major contribution to the free spin in 1^{2+} .

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[†] Electronic supplementary information (ESI) available: Synthesis and characterization and computational results of **1** and **2**. See DOI: 10.1039/c2cc32471g



Fig. 2 EPR signal (left) and calculated spin density (right) of 1^{2+} .

It should be kept in mind that a cyclometalated rutheniumdominated spin often exhibits a rhombic or axial EPR signal.¹¹

For comparison, cyclometalated complex 2^+ with an opposite Ru–C bond was prepared and studied. As will be presented below, complex 2^+ and a previously reported non-cyclometalated ruthenium complex ${}^{12} 3^{2+}$ containing a triarylamine motif exhibit significantly different electronic properties than 1. Besides, other transition metal complexes bearing a triarylamine ligand have been documented as well.¹³

The electronic properties of the above complexes were first studied by cyclic voltammetric (CV) analysis (Fig. 3). Complex 1^{2^+} exhibits two consecutive reversible couples at +0.27 and +0.68 V vs. Ag/AgCl. They are assigned to the N/N $^{\bullet+}$ and Ru^{II/III} processes, respectively. The DFT-optimized structure of 1^+ shows a triarylamine-dominated highest occupied molecular orbital (HOMO) and a much lower lying cyclometalated ruthenium-associated HOMO-1 (Fig. S1 and S2[†]), which are consistent with the above assignment. The remarkably low potential for the $N/N^{\bullet+}$ process in this complex is possibly caused by the electron delocalization and/or the inductive effect of the metal component. In contrast, the CV profile of complex 2^+ evidences two redox couples at +0.41 and +1.15 V vs. Ag/AgCl. The HOMO and HOMO-2 of 2^+ have major contributions from the cyclometalated ruthenium unit (Fig. S5 and S6[†]). The HOMO-1 has comparable contributions from the triarylamine and ruthenium motifs. A lower-lying HOMO-3 level is found to be mainly localized



Fig. 3 CV profiles of (a) 1^{2+} and (b) 2^+ in acetonitrile containing 0.1 M Bu₄NClO₄ as the supporting electrolyte at a scan rate of 100 mV s⁻¹. The working electrode was a glassy carbon, the counter electrode was a platinum wire, and the reference electrode was Ag/AgCl in aqueous NaCl.



Fig. 4 Vis/NIR absorption spectra of 1^{2+} in different solvents.

on the triarvlamine motif. This suggests that the couples at +0.41 and +1.15 V of 2^+ could be due to the Ru^{II/III} and $N/N^{\bullet+}$ processes, respectively. This assignment is reasonable but the order of these two processes is opposite to that for 1. The Ru^{II/III} redox potential for most cyclometalated monoruthenium complexes is in the range of +0.5 to +0.7 V vs. Ag/AgCl.⁹ The presence of the electron-donating amine group makes the oxidation of Ru^{II} in 2^+ easier. The N/N^{•+} process takes place at a relatively high potential due to the electronwithdrawing metal component. Oxidation of the amine unit in the non-cyclometalated complex 3^{2+} was previously found to occur at the same range of potential $(+0.98 \text{ V vs. Ag/AgCl})^{12}$ In addition to these events, both 1 and 2 exhibit a terpyridinebased reduction wave around -1.5 V and an irreversible wave at a higher potential, which is possibly due to the further oxidation of $N^{\bullet+}$ species.

The most interesting property of 1^{2+} is its absorption spectrum (Fig. 4 and 5). In addition to the metal-to-ligandcharge-transfer transitions (MLCT) in the visible region, it displays an intense absorption band in the NIR region ($\varepsilon_{max} = 2.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ in acetonitrile), which could be attributed to the intramolecular charge transfer transition from the metal to the amine radical cation center (Ru $\rightarrow N^{\bullet+}$ electronic transition). This is corroborated by the time-dependent DFT (TDDFT) computations of 1^{2+} , which suggest that its NIR absorptions are associated with the 187B \rightarrow 189B and



Fig. 5 Vis/NIR absorption spectral changes upon (a) one-electron reduction of 1^{2+} with stepwise addition of NH₂NH₂·H₂O in acetonitrile and (b, c) one-electron oxidation of 1^{2+} or 2^+ with stepwise addition of SbCl₅ in dichloromethane and (d) the second-electron oxidation of 2^+ with stepwise addition of SbCl₅.

188B → 189B excitations (Table S1 and Fig. S3[†]). This assignment is also supported by data shown below. The Ru → N^{•+} transition is only slightly solvent dependent both in terms of shape and energy (Fig. 4, 1084, 1050, 1066, and 1084 nm for CH₂Cl₂, CH₃CN, THF, and DMF, respectively). This suggests that the Ru–N coupling is very strong. The electronic coupling parameter H_{ab} in acetonitrile is roughly estimated to be 2760 cm⁻¹, according to the Hush formula¹⁴ $H_{ab} = 2.06 \times 10^{-2} (ε_{max}ν_{max}\Delta ν_{1/2})^{1/2}/(r_{ab})$, where r_{ab} is taken to be the DFT-calculated Ru–N distance (6.16 Å). However, this value is underestimated because the effective electron transfer distance is much smaller than the geometrical separation¹⁵ due to a charge delocalization and it can be taken only as a low limit of the actual value.

Fig. 5a and b show the vis/NIR spectral changes of 1^{2+} upon one-electron reduction or oxidation in acetonitrile or dichloromethane. When 1^{2+} was reduced to 1^+ by slowly adding 1 equiv. hydrazine hydrate, the Ru \rightarrow N^{•+} NIR transition decreased continuously until it disappeared. At the same time, a peak at 540 nm increased, which could be interpreted as the recovery of the ligand-to-ligand-chargetransfer (triarylamine \rightarrow pyridines, associated with the S₃ and S_6 excitations of 1^+ , Table S1[†]) transitions after N^{•+} was reduced back to a neutral amine. When 1^{2+} was oxidized to 1^{3+} by slowly adding one equivalent of SbCl₅, the $Ru \rightarrow N^{\bullet^+}$ NIR transition decreased as well. Interestingly, a very intense peak appeared at 714 nm, which arises from the electronic transition of the triarylamine radical cation (N^{\bullet^+}) itself. TDDFT results of 1^{3+} predict that this peak is mainly associated with its $187B \rightarrow 189B$ excitation with an admixture of the 182B \rightarrow 188B excitation (Table S1 and Fig. S4[†]). A similar peak at 810 nm was previously found for one-electron oxidized species of 3^{2+} .¹² It is clear from these results that the NIR band at 1050 nm is only observed in the form of 1^{2+} , but not 1^+ and 1^{3+} , which agrees with the nature of the $Ru \rightarrow N^{\bullet^+}$ transition.

As for complex 2^+ , it does not show any NIR absorption itself. However, upon transformation into 2^{2^+} by adding 1 equiv. SbCl₅, MLCT transitions of 2^+ at 520 nm decreased and a broad and shallow band between 600 and 1300 nm appeared (Fig. 5c, $\varepsilon_{max} = 2600 \text{ M}^{-1}\text{cm}^{-1}$). This band is ascribed to the ligand-to-metal-charge-transfer (LMCT) transition. More precisely, it is of the character of the N \rightarrow Ru^{III} excitation, as suggested by the TDDFT computations of 2^{2+} $(188B \rightarrow 189B \text{ excitation}, \text{ Table S1 and Fig. S7})$. Upon further addition of SbCl₅, the generated 2^{2+} was oxidized to 2^{3+} and an intense peak at 904 nm arising from the N^{•+} species showed up (Fig. 5d). TDDFT results indicate that this band is mainly associated with its $187B \rightarrow 188B$ excitation (Table S1 and Fig. S8[†]). These interpretations are consistent with the assignment of the electrochemical behaviors of 2^+ (Fig. 3b), where the Ru^{II/III} process proceeded before oxidation of the amine moiety.

In conclusion, we present in this contribution a new type of mixed-valent system consisting of mixed organic and inorganic asymmetric redox species. The covalent hybrid 1^{n+} of triaryl-amine and cyclometalated ruthenium displays two consecutive and widely separated redox couples at considerably low potentials and strong redox-switchable NIR absorptions.

These features will make them excellent candidates for NIR electrochromic devices.¹⁶ Work is under way to construct other [M-bridge- $N]^{n\pm}$ hybrid systems where a metal component and an organic amine unit are covalently connected by a conjugated bridge.

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