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## A new Ru,Ru,Pt supramolecular architecture for photocatalytic $H_2$ production<sup> $\dagger$ </sup>

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A new polyazine-bridged RuRuPt trimetallic supramolecular architecture emulates the photophysical properties of the previously reported Ru<sub>2</sub>RuPt tetrametallic architecture that exhibits photoinduced charge separation. The RuRuPt complexes are more robust H<sub>2</sub>O reduction photocatalysts with enhanced stability compared to the Ru<sub>2</sub>RuPt tetrametallic analogues.

Solar-to-chemical energy conversion is an important topic in the quest for clean and renewable energy.<sup>1–5</sup> Converting H<sub>2</sub>O to H<sub>2</sub> fuel by harvesting solar energy is a complicated multi-electron process that involves bond breaking and formation.<sup>1,6–8</sup> Ru( $\pi$ )–polyazine complexes, such as the prototypical [Ru(bpy)<sub>3</sub>]<sup>2+</sup> (bpy = 2,2'-bipyridine), are attractive light absorbers (LA) for harnessing solar energy due to their broad UV and visible light absorption and long-lived, strongly reducing/oxidizing excited states.<sup>9–12</sup> Molecular photocatalysts provide a means for analysing and understanding the complicated processes involved in H<sub>2</sub>O reduction.<sup>13</sup>

Supramolecular complexes,<sup>14</sup> individual components each possessing their own function assembled into systems that perform a complex task, are an important class of molecular photocatalysts for H<sub>2</sub> production from H<sub>2</sub>O. Several supramolecular photocatalysts featuring a Ru–polyazine LA coupled to a reactive metal (RM) such as Co,<sup>15</sup> Rh,<sup>16–21</sup> Pd,<sup>22–24</sup> and Pt,<sup>25–29</sup> are reported. The photocatalytic activity of a series of Ru,Pt bimetallic complexes, [(bpy)<sub>2</sub>Ru{phenNHCO(Rbpy)}PtCl<sub>2</sub>]<sup>2+</sup> (phen = 1,10-phenanthroline, R = -COOH, -COOEt, or -CH<sub>3</sub>) depends on the nature of R. The charge separated (CS) excited state is most stabilized in the -COOH complex, providing the greatest activity in aqueous solution with 5 TON in 10 h.<sup>25,27</sup> Dimerization of this architecture through the R-bpy unit doubles the efficiency by enhancing Pt–Pt dimerization for proton coupled electron transfer. A Ru,Pt bimetallic system  $[({}^{t}Bu_{2}bpy)_{2}Ru(tpphz)PtX_{2}]^{2+}$   $({}^{t}Bu_{2}bpy = 4,4'-di-$ *tert*-butyl-2,2'-bipyridine; tpphz = tetrapyrido-<math>[3,2-a:2',3'-c:3'',2''-h:2''',3'''-j]phenazine; X = Cl<sup>-</sup> or I<sup>-</sup>) produces H<sub>2</sub> from H<sub>2</sub>O with 7 TON when X = Cl<sup>-</sup>, while a 40 fold increase in TON and enhanced stability is achieved when X = I<sup>-</sup>.<sup>30</sup> It was recently discovered that the active catalyst of the Pd<sup>II</sup>Cl<sub>2</sub> analogue,  $[({}^{t}Bu_{2}bpy)_{2}Ru(tpphz)PdCl_{2}]^{2+}$ , is colloidal Pd,<sup>31</sup> corroborating results of a previously reported Ru,Pd photocatalyst.<sup>32</sup>

The supramolecular architecture  $[{(TL)_2Ru(dpp)}_2Ru(BL)PtCl_2]^{6+}$ ( $Ru_2RuPt$ ;  $TL = phen or Ph_2phen = 4,7-diphenyl-1,10-phenanthro$ line; BL = dpp = 2,3-bis(2-pyridyl)pyrazine or dpq = 2,3-bis(2-pyridyl)quinoxaline) is active in photocatalytic  $H_2$  production from  $H_2O$ by virtue of photoinduced charge separation in which the HOMO is localized on the terminal Ru and the LUMO is localized on BL coordinated to the Pt RM.<sup>33,34</sup> The catalytic efficiency of this architecture is strongly influenced by the nature of BL; the complexes with BL = dpq display greatly enhanced catalysis compared to their BL = dpp counterparts owing to the stabilized LUMO and enhanced driving force for intramolecular electron transfer toward the reactive Pt centre. Spectroscopic analysis of these complexes is difficult due to the presence of multiple overlapping, strongly absorbing intraligand (IL)  $\pi \to \pi^*$  and metal-to-ligand charge transfer (MLCT) transitions in the UV and visible regions, respectively.

Reported herein is the new trimetallic supramolecular architecture  $[(Ph_2phen)_2Ru(dpp)Ru(bpy)(BL)PtCl_2]^{4+}$  (labelled RuRuPt; BL = dpp or dpq) designed to provide analogous redox, spectroscopic, photophysical, and photocatalytic properties compared to the Ru\_2RuPt tetrametallic complexes. Reducing the number of  $(Ph_2phen)_2Ru^{II}(dpp)$  LA units from two to one simplifies the molecular architecture and provides more active photocatalysts for H<sub>2</sub>O reduction compared to the Ru\_2RuPt analogues. Fig. 1 depicts the structures of the new RuRuPt trimetallic complexes,  $[(Ph_2phen)_2Ru(dpp)Ru(bpy)(dpp)PtCl_2]^{4+}$  (**RuRudppPt**) and  $[(Ph_2phen)_2Ru(dpp)Ru(bpy)(dpq)PtCl_2]^{4+}$  (**RuRudpqPt**), and the previously reported Ru\_2RuPt tetrametallic complexes (**Ru\_2RudppPt** and **Ru\_2RudpqPt**). The synthesis, redox and

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Fig. 1 Structural representations of the RuRuPt and Ru<sub>2</sub>RuPt complexes.

spectroscopic properties, and photocatalytic activity towards  $H_2O$  reduction of this new architecture are discussed below.

The RuRuPt complexes were assembled using a six step building block process. Synthetic details are provided in ESI.<sup>†</sup> The synthetic approach to these structurally complicated supramolecules required initial assembly of the bimetallic complex  $[(Ph_2phen)_2Ru(dpp)RuCl_2(bpy)](PF_6)_2$  by coupling  $[(Ph_2phen)_2.$  $Ru(dpp)](PF_6)_2^{35}$  and  $[(bpy)RuCl_2(DMSO)_2]^{36}$  monometallic precursors. This complex was reacted with either dpp or dpq to provide an open coordination site to extend the molecular architecture, thereby generating bimetallics of the design  $[(Ph_2phen)_2Ru(dpp)Ru(bpy)(BL)](PF_6)_4$ . The RuRuPt trimetallics,  $[(Ph_2phen)_2Ru(dpp)Ru(bpy)(BL)PtCl_2](PF_6)_4$  (**RuRudppPt** and **RuRudpqPt**), were prepared upon reacting the BL-containing bimetallic with *cis*-[PtCl\_2(DMSO)\_2]. ESI-MS data is consistent with the desired product for each complex.

Electrochemical analysis of the RuRuPt complexes and their bimetallic precursors indicates orbital energetics that are similar to the analogous Ru<sub>2</sub>RuPt tetrametallic complexes and their trimetallic precursors. Square wave voltammograms are provided in Fig. S1 and the data and assignments are given in Table S1 (ESI<sup>†</sup>). Fig. 2a highlights the similarities between the cyclic voltammograms of RuRudpqPt and Ru<sub>2</sub>RudpqPt. The new RuRuPt complexes possess the same spatially separated HOMO and LUMO that was reported in the Ru<sub>2</sub>RuPt complexes and is necessary for photoinduced charge separation.<sup>33,34,37</sup> The first oxidation process at 1.54-1.57 V vs. Ag/AgCl is assigned the terminal Ru<sup>II/III</sup> oxidation in all four Pt-containing complexes. This couple for Ru<sub>2</sub>RudppPt and Ru<sub>2</sub>RudpqPt has approximately twice the peak current of RuRudppPt and RuRudpqPt, consistent with the number of terminal Ru centres (two and one, respectively). The first reduction is assigned as  $BL^{0/-}$ ; this reduction occurs at -0.39 V and -0.08 V for RuRudppPt and RuRudpqPt, respectively, and this trend is consistent with dpq's stabilized  $\pi^*$ orbitals compared to those of dpp. The BL<sup>0/-</sup> potentials are quite similar to those of the corresponding tetrametallic complexes (-0.33 V and -0.02 V for Ru<sub>2</sub>RudppPt and Ru<sub>2</sub>RudpqPt, respectively). This supports the validity of the RuRuPt complexes as analogues for the Ru<sub>2</sub>RuPt complexes.



Fig. 2 Cyclic voltammograms measured in CH<sub>3</sub>CN with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> (a) and electronic absorption spectra in CH<sub>3</sub>CN (b) of  $Ru_2RudpqPt$  (black) and RuRudpqPt (blue).

The electronic absorption spectrum for each of the RuRuPt complexes is similar to the Ru<sub>2</sub>RuPt analogue while exhibiting a decrease in the molar absorptivity throughout the UV and visible regions due to the absence of a strongly absorbing  $(Ph_2phen)_2Ru^{II}(dpp)$  unit. This is shown in Fig. 2b and Fig. S2 and Table S2 (ESI<sup>†</sup>). Similar to related Ru(II)-polyazine complexes, the UV and visible regions are dominated by IL and MLCT transitions, respectively, with transitions involving dpp or dpq red-shifted compared to Ph2phen transitions. The broad, lowest energy absorption band for RuRudpqPt is centred at 543 nm  $(\varepsilon = 22\,000 \text{ M}^{-1} \text{ cm}^{-1})$  with contributions from Ru  $\rightarrow$  dpp and Ru  $\rightarrow$  dpg <sup>1</sup>MLCT transitions. The lowest energy band for **Ru<sub>2</sub>RudpqPt** is centred at 550 nm with  $\varepsilon = 31\,000 \text{ M}^{-1} \text{ cm}^{-1}$ due to additional central Ru  $\rightarrow$  dpp and terminal Ru  $\rightarrow$  dpp <sup>1</sup>MLCT transitions. Similar trends are observed in comparing RuRudppPt with Ru<sub>2</sub>RudppPt (Table S2, ESI<sup>†</sup>). The RuRuPt architecture maintains the broad light absorption that covers the entire visible region which is desirable in solar energy conversion, while decreasing the number of possible transitions to allow for further studies such as transient absorption spectroscopy.

The emissive nature of the RuRuPt complexes provides a convenient probe into the excited state dynamics that are similar to those observed for the Ru<sub>2</sub>RuPt complexes. A simplified state diagram for **RuRudpqPt** is pictured in Fig. S3 and emission spectroscopy data is presented in Table S3 and Fig. S4 and S5 (ESI<sup>†</sup>). Emission is observed from the terminal Ru  $\rightarrow$  dpp <sup>3</sup>MLCT excited state in each case. The two [(Ph<sub>2</sub>phen)<sub>2</sub>. Ru(dpp)Ru(bpy)(BL)](PF<sub>6</sub>)<sub>4</sub> bimetallic complexes emit at 762 nm with  $\tau = 120$  ns and  $\Phi^{em} = 1.5 \times 10^{-3}$ . These homobimetallics serve as photophysical models to study charge separation in the

Pt-containing complexes. Coordination of cis-PtCl<sub>2</sub> results in quenched emission ( $\Phi^{\rm em}$  = 1.1  $\times$  10<sup>-3</sup> and 5.2  $\times$  10<sup>-4</sup> for BL = dpp and dpq, respectively) and shortened excited state lifetimes ( $\tau$  = 90 and 100 ns when BL = dpp and dpq, respectively) as the Pt unit stabilizes the  $BL(\pi^*)$  orbitals and enables intramolecular electron transfer to populate a low-lying, non-emissive charge separated (<sup>3</sup>CS) state. As observed in the Ru<sub>2</sub>RuPt complexes, the degree of emission quenching and charge separation is strongly dependent on the nature of BL.<sup>34,37</sup> The emissive <sup>3</sup>MLCT state is populated with 98% and 43% efficiency for RuRudppPt and **RuRudpqPt** with  $\lambda^{\text{exc}} = 540$  nm (equations in ESI<sup>†</sup>). These efficiencies are close to the analogous Ru<sub>2</sub>RuPt complexes (99% and 51% for Ru<sub>2</sub>RudppPt and Ru<sub>2</sub>RudpqPt, respectively).<sup>34</sup> Less efficient emissive state population results from more efficient population of the <sup>3</sup>CS state. The degree by which  $\Phi^{em}$  and  $\tau$  of the <sup>3</sup>MLCT state are quenched varies substantially due to population of the <sup>3</sup>CS from both the emissive <sup>3</sup>MLCT state and a higherenergy <sup>3</sup>MLCT state, as discussed previously.<sup>34,37</sup> The agreement in photophysical properties of the Ru<sub>2</sub>RuPt and RuRuPt complexes further demonstrates the suitability of the new architecture as analogues to the tetrametallic complexes.

The RuRuPt complexes exhibit remarkably enhanced photocatalytic activity and stability towards H<sub>2</sub> production from H<sub>2</sub>O compared to their Ru<sub>2</sub>RuPt analogues. Table 1 features the amount of H<sub>2</sub> produced and turnover number (TON = moles of H<sub>2</sub> produced/moles of catalyst) for RuRudppPt and RuRudpqPt as well as for the previously reported Ru<sub>2</sub>RudppPt and Ru<sub>2</sub>RudpqPt following 470 nm irradiation (flux =  $2.3 \times 10^{19}$  photons per min) for 20 hours in RT CH<sub>3</sub>CN with 50 µM metal complex, 0.62 M H<sub>2</sub>O, 1.5 M DMA sacrificial electron donor, and 110 µM  $[DMAH^+][SO_3CF_3^-]$ . The volume of the solution and the headspace are 4.5 mL and 15.3 mL, respectively. The reported values are the average of three experiments. To highlight the greater activity of the new architecture, a plot of H<sub>2</sub> production vs. time for RuRudpqPt and Ru<sub>2</sub>RudpqPt is provided in Fig. 3, and the plot for the dpp analogues are provided in Fig. S6 (ESI<sup>†</sup>). RuRudpqPt is the most active catalyst in this series, producing  $52\pm4~\mu mol$  of  $H_2$  in 20 hours and undergoing 230  $\pm$  20 TON (quantum yield of H<sub>2</sub> production,  $\Phi = 1.1 \times 10^{-3}$ ). The enhancement in photocatalytic activity within the trimetallic series of **RuRudpqPt** and **RuRudppPt** (29  $\pm$  2  $\mu$ mol of H<sub>2</sub>, 130  $\pm$  9 TON,  $\Phi = 6.2 \times 10^{-4}$ ) is related to the enhanced <sup>3</sup>CS state population in the BL = dpq complex and agrees with the trend observed in the analogous Ru<sub>2</sub>RuPt complexes.<sup>34</sup> For each BL, the H<sub>2</sub> production

Table 1 Photocatalytic  $H_2$  production data for RuRuPt and Ru<sub>2</sub>RuPt supramolecular complexes<sup>*a*</sup>

Complex	$\mu$ mol H $_2$	$\mathrm{TON}^b$	$arPhi^c imes 10^4$
Ru <sub>2</sub> RudppPt	$7.1\pm3.2$	$32\pm14$	$1.6\pm0.7$
Ru <sub>2</sub> RudpqPt	$25\pm1$	$110\pm 6$	$5.5\pm0.3$
RuRudppPt	$29\pm2$	$130\pm9$	$6.2\pm0.4$
RuRudpqPt	$52\pm4$	$230\pm20$	$11\pm1$

<sup>*a*</sup> 50 μM catalyst in spectral grade CH<sub>3</sub>CN, 0.62 M H<sub>2</sub>O, 1.5 M DMA, 110 μM [DMAH<sup>+</sup>][SO<sub>3</sub>CF<sub>3</sub><sup>--</sup>],  $\lambda_{irr} = 470 \pm 10$  nm (flux = 2.3 × 10<sup>19</sup> photons per min). Values represent H<sub>2</sub> production after 20 h photolysis. <sup>*b*</sup> TON = moles of H<sub>2</sub> produced/moles of catalyst. <sup>*c*</sup> Quantum yield of H<sub>2</sub> production.



Fig. 3 Photocatalytic H<sub>2</sub> production with **RuRudpqPt** (black circles) and **Ru<sub>2</sub>RudpqPt** (white circles) with 50  $\mu$ M catalyst in spectral grade CH<sub>3</sub>CN, 0.62 M H<sub>2</sub>O, 1.5 M DMA, and 110  $\mu$ M [DMAH<sup>+</sup>][SO<sub>3</sub>CF<sub>3</sub><sup>-</sup>]. Solutions were irradiated with  $\lambda$  = 470  $\pm$  10 nm.

of the RuRuPt complex is greater than the Ru<sub>2</sub>RuPt analogue (shown in Fig. 3 for the BL = dpg analogues) despite the smaller molecule's less efficient absorption at 470 nm. The RuRuPt architecture is expected to provide less demanding steric bulk near the cis-PtCl<sub>2</sub> site, whereas the presence of two bulky (Ph<sub>2</sub>phen)<sub>2</sub>. Ru<sup>II</sup>(dpp) units in the Ru<sub>2</sub>RuPt architecture may hinder interactions between the substrate and the catalytic site. Three dimensional models highlighting the difference in sterics for different geometric isomers of the Ru<sub>2</sub>RudpqPt and RuRudpqPt architectures are provided in Fig. S7 (ESI<sup>+</sup>). The RuRuPt and Ru<sub>2</sub>RuPt complexes are expected to exist in up to 16 and 32 isomers, respectively, as a result of  $\Lambda$  and  $\Delta$  optical isomers as well as the AB chelating nature of the bridging ligands. The distribution of isomers in each sample is unknown; however, steric effects on reactivity, charge separation distance, and orbital overlap are expected to result from structural variations among isomers.

The new RuRuPt trimetallic supramolecular architecture features a Ru(n)-polyazine LA and a *cis*-PtCl<sub>2</sub> RM site with a spatially separated HOMO and LUMO that imparts unusual photophysical properties. This architecture provides redox and photophysical properties analogous to the previously reported Ru<sub>2</sub>RuPt architecture, demonstrating the ability to design supramolecular complexes with desired properties through knowledge of previously studied systems. The architecture features a terminal Ru-based HOMO and a remote BL-based LUMO which enables photoinduced charge separation. The nature of BL dictates the energy of the LUMO and largely impacts the population of the <sup>3</sup>CS state in competition with population of the emissive <sup>3</sup>MLCT state, with BL = dpq affording a complex with a more efficiently populated <sup>3</sup>CS state compared to the BL = dpp analogue. The enhanced charge separation in RuRudpqPt is important in providing an active and stable catalyst for H<sub>2</sub> production from H<sub>2</sub>O (52 µmol of H<sub>2</sub> and 230 TON in 20 h) while RuRudppPt is less active (29  $\mu$ mol of H<sub>2</sub> and 130 TON in 20 h). Both of these complexes are superior to their Ru<sub>2</sub>RuPt analogues, possibly due to steric factors provided by the bulky  $(Ph_2phen)_2Ru^{II}(dpp)$  units or a varied distribution of geometric isomers. Future studies include further probing the unusual excited state dynamics using transient absorption spectroscopy enabled by the less complicated spectroscopy by virtue of the absence of a strongly absorbing LA unit.

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