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A new Ru,Ru,Pt supramolecular architecture for photocatalytic H₂ production†

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A new polyazine-bridged RuRuPt trimetallic supramolecular architecture emulates the photophysical properties of the previously reported Ru₂RuPt tetrametallic architecture that exhibits photo-induced charge separation. The RuRuPt complexes are more robust H₂O reduction photocatalysts with enhanced stability compared to the Ru₂RuPt tetrametallic analogues.

Solar-to-chemical energy conversion is an important topic in the quest for clean and renewable energy.^{1–5} Converting H₂O to H₂ fuel by harvesting solar energy is a complicated multi-electron process that involves bond breaking and formation.^{1,6–8} Ru(II)-polyazine complexes, such as the prototypical [Ru(bpy)₃]²⁺ (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.^{9–12} Molecular photocatalysts provide a means for analysing and understanding the complicated processes involved in H₂O reduction.¹³

Supramolecular complexes,¹⁴ individual components each possessing their own function assembled into systems that perform a complex task, are an important class of molecular photocatalysts for H₂ production from H₂O. Several supramolecular photocatalysts featuring a Ru-polyazine LA coupled to a reactive metal (RM) such as Co,¹⁵ Rh,^{16–21} Pd,^{22–24} and Pt,^{25–29} are reported. The photocatalytic activity of a series of Ru,Pt bimetallic complexes, [(bpy)₂Ru{phenNHCO(Rbpy)}PtCl₂]²⁺ (phen = 1,10-phenanthroline, R = –COOH, –COOEt, or –CH₃) 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.^{25,27} 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 [(^tBu₂bpy)₂Ru(tpphz)PtX₂]²⁺ (^tBu₂bpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine; tpphz = tetrapyrido-[3,2-*a*:2',3'-*c*:3'',2''-*h*:2''',3'''-*j*]phenazine; X = Cl[–] or I[–]) produces H₂ from H₂O with 7 TON when X = Cl[–], while a 40 fold increase in TON and enhanced stability is achieved when X = I[–].³⁰ It was recently discovered that the active catalyst of the Pd^{II}Cl₂ analogue, [(^tBu₂bpy)₂Ru(tpphz)PdCl₂]²⁺, is colloidal Pd,³¹ corroborating results of a previously reported Ru,Pd photocatalyst.³²

The supramolecular architecture [(TL)₂Ru(dpp)]₂Ru(BL)PtCl₂]⁶⁺ (Ru₂RuPt; TL = phen or Ph₂phen = 4,7-diphenyl-1,10-phenanthroline; BL = dpp = 2,3-bis(2-pyridyl)pyrazine or dpq = 2,3-bis(2-pyridyl)quinoxaline) is active in photocatalytic H₂ production from H₂O 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.^{33,34} 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) π → π* and metal-to-ligand charge transfer (MLCT) transitions in the UV and visible regions, respectively.

Reported herein is the new trimetallic supramolecular architecture [(Ph₂phen)₂Ru(dpp)Ru(bpy)(BL)PtCl₂]⁴⁺ (labelled RuRuPt; BL = dpp or dpq) designed to provide analogous redox, spectroscopic, photophysical, and photocatalytic properties compared to the Ru₂RuPt tetrametallic complexes. Reducing the number of (Ph₂phen)₂Ru^{II}(dpp) LA units from two to one simplifies the molecular architecture and provides more active photocatalysts for H₂O reduction compared to the Ru₂RuPt analogues. Fig. 1 depicts the structures of the new RuRuPt trimetallic complexes, [(Ph₂phen)₂Ru(dpp)Ru(bpy)(dpp)PtCl₂]⁴⁺ (**RuRudppPt**) and [(Ph₂phen)₂Ru(dpp)Ru(bpy)(dpq)PtCl₂]⁴⁺ (**RuRudpqPt**), and the previously reported Ru₂RuPt tetrametallic complexes (**Ru₂RudppPt** and **Ru₂RudpqPt**). The synthesis, redox and

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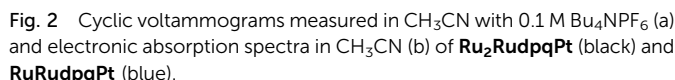
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spectroscopic properties, and photocatalytic activity towards H₂O reduction of this new architecture are discussed below.

Electrochemical analysis of the RuRuPt complexes and their bimetallic precursors indicates orbital energetics that are similar to the analogous Ru₂RuPt 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[†]). Fig. 2a highlights the similarities between the cyclic voltammograms of **RuRudppqPt** and **Ru₂RudppqPt**. The new RuRuPt complexes possess the same spatially separated HOMO and LUMO that was reported in the Ru₂RuPt complexes and is necessary for photoinduced charge separation.^{33,34,37} The first oxidation process at 1.54–1.57 V vs. Ag/AgCl is assigned the terminal Ru^{II/III} oxidation in all four Pt-containing complexes. This couple for **Ru₂RudppPt** and **Ru₂RudppqPt** has approximately twice the peak current of **RuRudppPt** and **RuRudppqPt**, 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 **RuRudppqPt**, respectively, and this trend is consistent with dpq's stabilized π* orbitals compared to those of dpv. The BL^{0/-} potentials are quite similar to those of the corresponding tetrametallic complexes (-0.33 V and -0.02 V for **Ru₂RudppPt** and **Ru₂RudppqPt**, respectively). This supports the validity of the RuRuPt complexes as analogues for the Ru₂RuPt complexes.



The emissive nature of the RuRuPt complexes provides a convenient probe into the excited state dynamics that are similar to those observed for the Ru₂RuPt complexes. A simplified state diagram for **RuRu₂dppqPt** is pictured in Fig. S3 and emission spectroscopy data is presented in Table S3 and Fig. S4 and S5 (ESI[†]). Emission is observed from the terminal Ru → dpp ³MLCT excited state in each case. The two [(Ph₂phen)₂Ru(dpp)Ru(bpy)(BL)](PF₆)₄ bimetallic complexes emit at 762 nm with τ = 120 ns and ϕ^{em} = 1.5 × 10⁻³. These homobimetallics serve as photophysical models to study charge separation in the

Pt-containing complexes. Coordination of *cis*-PtCl₂ results in quenched emission ($\Phi^{\text{em}} = 1.1 \times 10^{-3}$ and 5.2×10^{-4} 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(π^*) orbitals and enables intramolecular electron transfer to populate a low-lying, non-emissive charge separated (^3CS) state. As observed in the Ru₂RuPt complexes, the degree of emission quenching and charge separation is strongly dependent on the nature of BL.^{34,37} The emissive $^3\text{MLCT}$ state is populated with 98% and 43% efficiency for **RuRudppPt** and **RuRudpqPt** with $\lambda^{\text{exc}} = 540$ nm (equations in ESI†). These efficiencies are close to the analogous Ru₂RuPt complexes (99% and 51% for **Ru₂RudppPt** and **Ru₂RudpqPt**, respectively).³⁴ Less efficient emissive state population results from more efficient population of the ^3CS state. The degree by which Φ^{em} and τ of the $^3\text{MLCT}$ state are quenched varies substantially due to population of the ^3CS from both the emissive $^3\text{MLCT}$ state and a higher-energy $^3\text{MLCT}$ state, as discussed previously.^{34,37} The agreement in photophysical properties of the Ru₂RuPt 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 H₂ production from H₂O compared to their Ru₂RuPt analogues. Table 1 features the amount of H₂ produced and turnover number (TON = moles of H₂ produced/moles of catalyst) for **RuRudppPt** and **RuRudpqPt** as well as for the previously reported **Ru₂RudppPt** and **Ru₂RudpqPt** following 470 nm irradiation (flux = 2.3×10^{19} photons per min) for 20 hours in RT CH₃CN with 50 μM metal complex, 0.62 M H₂O, 1.5 M DMA sacrificial electron donor, and 110 μM [DMAH⁺][SO₃CF₃[−]]. 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 H₂ production vs. time for **RuRudpqPt** and **Ru₂RudpqPt** is provided in Fig. 3, and the plot for the dpp analogues are provided in Fig. S6 (ESI†). **RuRudpqPt** is the most active catalyst in this series, producing 52 ± 4 μmol of H₂ in 20 hours and undergoing 230 ± 20 TON (quantum yield of H₂ production, $\Phi = 1.1 \times 10^{-3}$). The enhancement in photocatalytic activity within the trimetallic series of **RuRudpqPt** and **RuRudppPt** (29 ± 2 μmol of H₂, 130 ± 9 TON, $\Phi = 6.2 \times 10^{-4}$) is related to the enhanced ^3CS state population in the BL = dpq complex and agrees with the trend observed in the analogous Ru₂RuPt complexes.³⁴ For each BL, the H₂ production

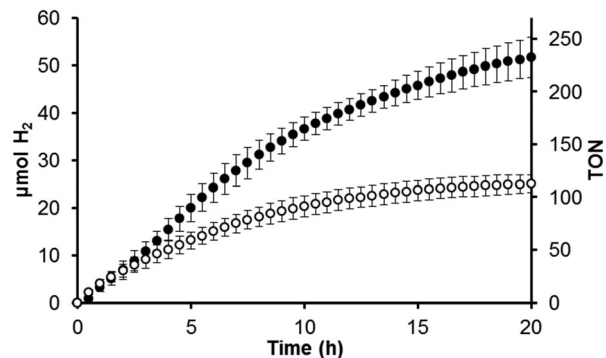


Fig. 3 Photocatalytic H₂ production with **RuRudppPt** (black circles) and **Ru₂RudpqPt** (white circles) with 50 μM catalyst in spectral grade CH₃CN, 0.62 M H₂O, 1.5 M DMA, and 110 μM [DMAH⁺][SO₃CF₃[−]]. Solutions were irradiated with $\lambda = 470 \pm 10$ nm.

of the RuRuPt complex is greater than the Ru₂RuPt analogue (shown in Fig. 3 for the BL = dpq 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*-PtCl₂ site, whereas the presence of two bulky (Ph₂phen)₂Ru^{II}(dpp) units in the Ru₂RuPt 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 **Ru₂RudppPt** and **RuRudppPt** architectures are provided in Fig. S7 (ESI†). The RuRuPt and Ru₂RuPt complexes are expected to exist in up to 16 and 32 isomers, respectively, as a result of *A* and *A* 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(II)-polyazine LA and a *cis*-PtCl₂ 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 Ru₂RuPt 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 ^3CS state in competition with population of the emissive $^3\text{MLCT}$ state, with BL = dpq affording a complex with a more efficiently populated ^3CS state compared to the BL = dpp analogue. The enhanced charge separation in **RuRudppPt** is important in providing an active and stable catalyst for H₂ production from H₂O (52 μmol of H₂ and 230 TON in 20 h) while **RuRudppPt** is less active (29 μmol of H₂ and 130 TON in 20 h). Both of these complexes are superior to their Ru₂RuPt analogues, possibly due to steric factors provided by the bulky (Ph₂phen)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.

Table 1 Photocatalytic H₂ production data for RuRuPt and Ru₂RuPt supramolecular complexes^a

Complex	$\mu\text{mol H}_2$	TON ^b	$\Phi^c \times 10^4$
Ru₂RudppPt	7.1 ± 3.2	32 ± 14	1.6 ± 0.7
Ru₂RudpqPt	25 ± 1	110 ± 6	5.5 ± 0.3
RuRudppPt	29 ± 2	130 ± 9	6.2 ± 0.4
RuRudpqPt	52 ± 4	230 ± 20	11 ± 1

^a 50 μM catalyst in spectral grade CH₃CN, 0.62 M H₂O, 1.5 M DMA, 110 μM [DMAH⁺][SO₃CF₃[−]], $\lambda_{\text{irr}} = 470 \pm 10$ nm (flux = 2.3×10^{19} photons per min). Values represent H₂ production after 20 h photolysis. ^b TON = moles of H₂ produced/moles of catalyst. ^c Quantum yield of H₂ production.



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