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π -Stacking attraction vs. electrostatic repulsion: competing supramolecular interactions in a tpphz-bridged Ru(II)/Au(III) complex†

Dieter Sorsche,^a Markus Schaub,^a Frank W. Heinemann,^b Johannes Habermehl,^a Susanne Kuhri,^c Dirk Guldi,^d Julien Guthmüller^e and Sven Rau^{*a}

The synthesis and characterization of a mixed metal ruthenium(II)/gold(III) complex bridged by tetrapyridophenazine (tpphz) are described. It is isostructural and isoelectronic to the well-known photocatalysts with palladium(II) or platinum(II). Concentration dependent ¹H-NMR spectroscopy and XRD studies show that the electrostatic repulsion between the gold(III) moieties exceeds the attractive π -stacking interaction. Theoretical calculations based on the new structural data confirm an increased positive charge on the bridging ligand as well as significantly altered orbital symmetry as compared to the previously investigated palladium(II) complex. This is the first example of a tpphz ruthenium(II) complex where π -stacking is completely inhibited. The detailed investigation of the solid-state structure showed for the first time in bi-metallic tpphz bridged complexes no significant torsion within the bridging ligand itself. Although catalytic performance for proton reduction by gold(III) is naturally not observed, its photochemical decomposition in colloidal gold particles could be shown by TEM and DLS.

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Introduction

Recent studies on the photocatalytic hydrogen evolution using photochemical molecular devices (PMD) based on tpphz-bridged dinuclear ruthenium/d⁸ metal catalysts (tpphz = tetrapyrido[3,2-*a*:2',3'-*c*:3'',2''-*h*:2''',3'''-*f*]phenazine) have shown that π -stacking interactions between the large aromatic scaffold of the bridge significantly influence the catalytic activity.^{1–3} Tackling this issue, it was shown that the activity of a tpphz-bridged ruthenium/palladium catalyst could be enhanced by the addition of an electron-rich organic π -system, *i.e.* pyrene or anthracene, as they build π -stacked assemblies with the catalyst complex and therefore inhibit dimerization.^{4,5} In this study, a

solid-state structure of the [(tbbpy)₂Ru(tpphz)PdCl₂]²⁺ catalyst with a polyoxometallate (POM) as the counter-ion has been reported. A bending of the tpphz towards the POM indicated that electrostatic interactions between the positively charged ruthenium(II) and palladium(II) centers and the four-fold anionic cluster play a significant role in the intermolecular assembly. However, theoretical calculations on the electron transfer processes during catalysis were based on a planar model of the dinuclear PMD.^{3,6,7} Therefore, it was highly desirable to obtain further model structures. Generally, replacing the catalyst metal by gold(III) adds an additional charge to the system while retaining the coordination environment and, hence, provides an isostructural and isoelectronic model complex with respect to the literature known photocatalysts (Scheme 1). Square-planar phenanthroline gold(III) complexes have been shown to be potent intercalators in DNA, which in combination with the chromophore gives rise to potential applications in photodynamic therapy.^{8–12} The heterodinuclear complex containing a photoreductive ruthenium chromophore and gold(III) can be further envisaged as a precursor for the formation of gold(0) particles or clusters by visible light.

Results and discussion

Synthesis

Bis(4,4'-di-*tert*-butyl-2,2'-bipyridine- κ^2N^1,N^1') ruthenium(2+) [(tetrapyrido[3,2-*a*:2',3'-*c*:3'',2''-*h*:2''',3'''-*f*]phenazine- κ^4N^4,κ^5N^5) hexa-

^aInstitute for Inorganic Chemistry I, Ulm University, Albert-Einstein-Allee 11, D-89081 Ulm, Germany. E-mail: sven.rau@uni-ulm.de

^bInstitute of Inorganic and General Chemistry, Egerlandstr. 1, D-91058 Erlangen, Germany

^cInstitute of Energy and Climate Research, Electrochemical Process Engineering (IEK-3), Wilhelm-Johnen-Straße, D-52428 Jülich, Germany

^dFriedrich-Alexander-Universität Erlangen/Nürnberg, Department Chemie und Pharmazie, Lehrstuhl für Physikalische Chemie I, Egerlandstraße 3, D-91058 Erlangen, Germany

^eFaculty of Applied Physics and Mathematics, Gdansk University of Technology, Narutowicza 11/12, 80-233 Gdansk, Poland

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Scheme 1 Introduction of gold(III) into a dinuclear tpphz bridged ruthenium(II) model photocatalyst, introducing an additional positive charge; letters and numbers refer to the assignment of ^1H -NMR signals.

fluoridophosphate], $[(\text{tbbpy})_2\text{Ru}(\text{tpphz})](\text{PF}_6)_2$ (abbr. **[Ru]** tpphz = tetrapyrido[3,2-*a*:2',3'-*c*:3'',2''-*h*:2''',3'''-*f*]phenazine, tbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine), was synthesized according to the literature.³ The dinuclear complex bis(4,4'-di-*tert*-butyl-2,2'-bipyridine- $\kappa^2\text{N}^1, \text{N}^1$)ruthenium(2+) [μ -(tetrapyrido[3,2-*a*:2',3'-*c*:3'',2''-*h*:2''',3'''-*f*]phenazine- $\kappa\text{N}^4, \kappa\text{N}^5: \kappa\text{N}^{13}, \kappa\text{N}^{14}$)]dichlorido gold(3+) hexafluoridophosphate, $[(\text{tbbpy})_2\text{Ru}(\text{tpphz})\text{AuCl}_2](\text{PF}_6)_3$ **[RuAu]**, was synthesized in a one-pot biphasic synthesis similar to that reported for the respective platinum(II) complex $[(\text{tbbpy})_2\text{Ru}(\text{tpphz})\text{PtCl}_2](\text{PF}_6)_2$.⁶ Tetrachloroauric(III) acid trihydrate was used as a water-soluble gold precursor, while **[Ru]** was dissolved in dichloromethane. A five-fold excess of ammonium hexafluoridophosphate was added and the product complex precipitated from the mixture after one day of stirring at room temperature. Literature procedures suggested the synthesis of gold(III) complexes using elevated temperatures.^{13–15} We therefore wish to report that all attempts to synthesize **[RuAu]** at elevated temperatures led to the formation of colloidal gold. The formation of the target dinuclear complex has been confirmed by ESI-MS spectrometry and NMR-spectroscopy as will be discussed in detail below.

Concentration dependent NMR studies

As shown in recent reports, the strong formation of π -stacked dimers from **[Ru]** and its dinuclear complexes can be observed *via* concentration dependent ^1H -NMR spectroscopy. An identification value I (eqn (1)) has been defined with respect to characteristic shifts of tpphz and tbbpy signals in order to be able to identify the monomeric complex independently of its concentration.⁵

$$I = (\delta\text{Hc} - \delta\text{H6}) \cdot (\delta\text{Hc}' - \delta\text{a}') \quad (1)$$

The ^1H -NMR spectrum of **[RuAu]** clearly shows the formation of a new species with an identification value of $I(\text{[RuAu]}) = -1.29$, as compared to the mononuclear complex with $I(\text{[Ru]}) = 1.42$ (Fig. 1). The negative value reflects the strong shift of signal Ha' beyond Hc' in the low-field regime. The ^1H -NMR spectrum is extended towards the downfield region by three distinct doublets. The two signals below

Fig. 1 ^1H -NMR spectra of **[Ru]** (top) and **[RuAu]** (below) in MeCN-d_3 ; a strong shift of signals a', c, and c' shows the formation of the dinuclear complex.

10 ppm were assigned to protons c', *i.e.* the proton in the *para* position to the gold(III) center, and c that is in the *para* position to ruthenium. The signal below $\delta = 10.5$ ppm was identified as a', *i.e.* the proton adjacent to the gold(III) center. The latter shift accounts for the negative sign of the identification value in contrast to **[Ru]**. Its counterpart adjacent to the ruthenium(II) core is found to be far more downfield shifted, at about $\delta = 8.6$ ppm due to shielding by electron density of the aromatic ring system of *tert*-butylbipyridine. Remarkably, a series of ^1H -NMR spectra at concentrations from 6.2×10^{-4} M to 1.5×10^{-2} M showed virtually no shifts of signals in contrast to the previously reported complexes, *i.e.* **[Ru]**, **[RuPd]**, and **[RuPt]**, showing that for the first time, π -stacking is completely inhibited even in concentrated solutions (Fig. S1†). This difference can be understood from the calculated electrostatic potential (ESP) maps (Fig. 2 and S7†), which show a significant increase of the ESP values going from **[Ru]**, **[RuPd]**, **[RuPt]** to **[RuAu]**. Indeed, the ESP values obtained for **[RuAu]** are positive over the whole isodensity surface, leading to a strong electrostatic repulsion between tpphz ligands, which hinders the formation of π -stacked dimers. For comparison, concentration dependent ^1H -NMR measurements have been performed with **[Ru]** as well. It shows that the protons c, c', and especially a' are the signals that are most sensitive to dimerization. Accordingly, the strong shift of these signals upon coordination to gold(III) may be caused by the inhibition of π -stacking, apart from the electron withdrawing effect of the metal center.

Solid-state aggregation

Although no π -aggregation was observed in solution in terms of concentration dependent ^1H -NMR signal shifts, π -stacking still had to be considered to occur at higher concentrations, *i.e.* ultimately in the solid state. In the single crystal X-ray structure of **[RuPd]** we reported recently that stacked dimers of the complex cation were formed despite steric and electrostatic repulsion between the tris(bipyridine) ruthenium(II) and dichlorido bipyridine palladium(II) moieties. However, in this

Fig. 2 ESP maps of [RuPd] and [RuAu]. A value of 0.0004 a.u. is taken for the isodensity surface. The red color indicates a negative potential (min. value: -0.05 a.u.) and the blue color indicates a positive potential (max. value: 0.28 a.u.).

study crystals could only be obtained using a highly charged POM anion, which caused an unexpected bending of the tp-phz bridging ligand. Single-crystals of [RuAu] were grown from a solution of the hexafluoridophosphate salt and the respective solid-state structures were elucidated. It is well known in the literature that gold(III) complexes undergo decomposition when stored in solution for longer time periods as is the case under the conditions of a crystallization process. Therefore, many solid-state structures have been reported, which exhibit tetrachlorido aurate(III) or dichlorido aurate(I) as alternative counter-ions of gold(III) complexes.^{16–20} We obtained two different structures: one containing PF₆ as well as the aurate(III) AuCl₄ and aurate(I) AuCl₂ as the counter-ions (structure A) and the other solely containing the disordered aurates in a 1.5 : 1.5 stoichiometry with respect to the [RuAu] cation (structure B).[‡] We have reproduced these findings with the reference compound dichlorido-1,10-phenanthroline gold(III) chloride (ESI, Fig. S2[†]). In the herein reported structures, for the first time, π -stacking between the two tp-phz moieties appeared to be completely inhibited. Instead, a couple of short contact packing effects are observed between tp-phz and the planar or linear aurate(I)/(III) anions (Fig. 3).

Therefore, the strong impact of electrostatic repulsion between the positively charged dichlorido-1,10-phenanthroline gold(III) fragments together with the electrostatic attraction towards the auric anions promotes an arrangement that, in contrast to any solid-state structure of tp-phz complexes known

Fig. 3 Solid-state structures of [RuAu][‡] (ball-and-stick depiction, hydrogen atoms, solvent molecules, and counter-ions which are not included in the columnar arrangement of the cationic complexes are omitted for clarity); top: structure A, [(tpbpy)₂Ru(tp-phz)Au(Cl)₂](AuCl₄)_{1.5}(AuCl₂)(PF₆)_{0.5}·tBuOMe·MeCN (AuCl₄ adjacent to the tbbpy ligands grown from (AuCl₄)_{0.5}); bottom: structure B, [(tpbpy)₂Ru(tp-phz)Au(Cl)₂](AuCl₄)_{1.5}(AuCl₂)_{1.5}·Et₂O.

so far, avoids π -stacking between the polyaromatic ligands. Although auriphilic interactions between the tp-phz coordinated gold(III) center and anionic aurates were not observed in the reported structures, the PF₆ anion was found to be sandwiched between two gold(III) moieties, thus bringing the two respective gold centers within a minimum Au–Au distance of $8.1909(5)$ Å (Fig. 4). The intramolecular distance between the ruthenium(II) and the gold(III) center is $12.7392(6)$ Å (A) or $12.688(1)$ Å (B) (Table 1).

The latter value being slightly smaller refers to the fact that the tp-phz bridging ligand appears to be slightly bent out of plane (Fig. 5). This bending was characterized by an angle of 8.15° between two calculated mean planes of the phenanthroline-M (M = Ru, Au) chelating coordination spheres (Fig. 5

Fig. 4 Packing of [RuAu][‡] structure A; electrostatic interactions are emphasized through the location of one PF₆ anion in between two dichlorido phenanthroline gold(III) fragments.

[‡] Refinement data for crystal structures: [RuAu], structure A CCDC 1452865, $R_1 = 5.69\%$ $wR_2 = 13.99\%$; structure B, CCDC 1452866, $R_1 = 3.84\%$, $wR_2 = 8.05\%$.

Table 1 Selected bond lengths and angles in the solid-state structures of [RuAu]

	Structure A	Structure B
$d(\text{N-Ru})^{a,b}$	2.0635 Å	2.058 Å
$d(\text{N-Au})^b$	2.0435 Å	2.0445 Å
$d(\text{Au-Cl})^b$	2.2485 Å	2.248 Å
$d(\text{Ru-Au})$	12.7392(6) Å	12.688(1) Å
$\angle(\text{N-Ru-N})^a$	79.3(2)°	79.5(3)°
$\angle(\text{N-Au-N})^a$	81.5(2)°	81.0(3)°
$\angle(\text{Cl-Au-Cl})$	89.76(7)°	89.0(1)°
MPLA ^c	0.0470 Å	0.0811 Å

^a N = ligating nitrogen atoms of tpphz. ^b Average of all measured values. ^c Mean deviation of tpphz from its calculated mean plane.

Fig. 5 Top: Bending of [RuAu]₂ structure B; the bridging ligand appears to be slightly bent due to packing effects (angle calculated between the phenanthroline metal coordination spheres, red lines), thus shortening the Ru(II)-Au(III) distance to 12.688(1) Å (dashed blue line), as compared to structure A; bottom: a comparison of the planarity of [RuAu] structures A and B with [RuPd] from ref. 11.

top). In structure A, no such bending was observed and therefore it has been ascribed to packing effects. The mean deviation of the bridging ligand from its mean plane calculated from the position of all 30 non-H atoms is 0.0470 Å (structure A) or 0.0811 (structure B), which represents a smaller deviation as compared to the recently published ruthenium/palladium structure, where the respective value was determined to be 0.1023 Å. This is in agreement with both the theoretical calculations on the optimization of this class of complexes with a planar tpphz moiety as well as the observed bending as a

result of electrostatic interactions with a highly charged POM anion in the crystal packing. The coordination polyhedra of both ruthenium (2.047(5) Å < Ru-N < 2.081(4) Å; 77.82° < N-Ru-N < 79.5°) and gold (2.031(4) < Au-N < 2.056 (6); 2.245(3) < Au-Cl < 2.251(3); 81.0(3) < N-Au-N < 81.4(2); 89.0(1) < Cl-Au-Cl < 89.76(7)) are in agreement with literature-known bipyridine or phenanthroline complexes (with respect to structures deposited in the CCDC database). Accordingly, the tpphz bridging ligand provides two separate coordination spheres for both metal centers which do not seem to influence each other by means of electrostatic repulsion or electronic coupling.

Photophysical characterization

The photophysical properties of [RuAu] were investigated via steady state UV/Vis and emission spectroscopy in acetonitrile solution. The ligand-centered absorption bands corresponding to the bipyridine ligands are virtually unaltered with respect to [Ru]. The characteristic absorption bands referring to tpphz π - π and n - π transitions are bathochromically shifted (see Table 2). For [RuPt], in contrast, a characteristic loss of the structured tpphz-centered π - π and n - π absorption features between 350 nm and 400 nm has been reported.

In this regard, the absorption features of [RuAu] compare rather well with [RuPd] as the aforementioned features are retained and shifted slightly hypsochromically. The MLCT absorption maximum of the dinuclear complex appears at $\lambda_{\text{max}}([\text{RuAu}]) = 446$ nm with a molar extinction coefficient of $\epsilon_{\text{max}}(446) = 19\,000$ L mol⁻¹ cm⁻¹ (± 1000 L mol⁻¹ cm⁻¹). The ³MLCT emission of [Ru] appears to be quenched upon the coordination of gold(III). Emission spectra initially showed a weak luminescence in acetonitrile solution. Measurements in very dilute solutions (approximately below 10⁻⁶ M) eventually revealed decomposition of [RuAu] and hence luminescence from the mononuclear complex [Ru], which is supported by the respective excitation spectra. Upon measuring in the non-coordinating solvent dichloromethane, no luminescence from [RuAu] has been observed.

Theoretical calculations support the almost identical absorption spectra obtained for [Ru] and [RuAu] (Fig. S8†). Indeed, the MLCT band is dominated by transitions to the tbbpy ligands and to the phenanthroline (phen) part of the tpphz ligand. However, the electronic structure of [RuAu] presents also some differences in comparison with [Ru], [RuPd]²¹

Table 2 Photophysical features of [Ru] and [RuAu]

	Absorption ^a λ_{max} [nm] (ϵ [L mol ⁻¹ cm ⁻¹])	Emission ^a λ_{max} [nm] (Φ)
[Ru]	283, 362, 382, 440 (20 000) ^b	638 (0.74%) ^c
[RuAu]	283, 356, 375, 446 (19 000)	(n.l.) ^d 638 (from [Ru] due to decomp.) ^c

^a Measured in acetonitrile. ^b From ref. 4. ^c Determined in aerated acetonitrile with [Ru(bpy)]²⁺ as in ref. 23 and 24. ^d Measured in dichloromethane.

Fig. 6 UV/Vis absorption features of [Ru] and [RuAu] in acetonitrile solution, showing a slight hypsochromic shift of the absorbance features upon coordination to gold(III).

and [RuPt].⁶ This concerns the LUMO orbital in particular, which is predominantly centered on the gold(III) moiety in [RuAu] in contrast to the palladium(II) and platinum(II) analogues. This result is in agreement with the loss of emission in terms of a non-luminescent ³MM'CT lowest excited state (Tables S5 and S6†). Additionally, in [RuPd] and [RuPt] the tp-phz orbitals appear to be symmetrically distributed between the two metal ions, whereas in [RuAu] the orbital symmetry appears to be broken. That is, tp-phz-centered orbitals are predominantly localized on either phenanthroline fragment with the lowest energy MLCT state involving orbitals of the gold(III) center, rather than symmetrically distributed across the bridging ligand between the two metal centers (*cf.* ESI, Table S5†). These changes can be related to the additional positive charge on the phenanthroline AuCl₂ system in [RuAu], leading to very different coordination sites. The characteristically strong emission of [Ru] is almost completely quenched upon binding of the second metal center, that is, by about 80% (Fig. 6). These changes upon binding of the second metal center are in good agreement with the changes reported for the analogous dinuclear palladium(II) and platinum(II) complexes.^{3,6,22} To this end, electrochemical measurements were dominated by irreversible reduction processes, which did not allow for a more detailed characterization.

Photochemical decomposition

Gold(III) is not known to catalyze hydrogen formation from protons due to its own positive redox potential. However, under catalytic conditions, a small amount, namely 2.4 equivalent of hydrogen with respect to the photocatalyst (turnover-number (TON)), was detected upon irradiation for 24 hours. This process was accompanied by the formation of gold particles as observed *via* dynamic light scattering (DLS) as well as transmission electron microscopy (TEM). According to DLS, particles with a size of 312 ± 142 nm were detected in solution, whereas particles not larger than 100 nm were observed *via* TEM (see the ESI†). The formation of colloidal gold particles raises the question of the catalytic mechanism, the elucidation of which is rather complex and remains, in this case, subject to further research.⁶

Conclusion

With the synthesis and detailed structural characterization of the new dinuclear tp-phz-bridged complex [RuAu] we have provided evidence for electrostatics as another intermolecular force influencing the aggregation of photochemical molecular devices. The results show that the dominant interaction of tp-phz-bridged complexes *via* π -stacking as reported in several previous publications is overcompensated by electrostatic repulsion of an additional positive charge on the d⁸ metal center. The two solid-state structures presented in this work reveal an almost ideal planar structure of the bridging tp-phz unit depending on the packing and interaction with the counter-ions. The planar arrangement is in agreement with theoretical calculations on related PMD systems, while the packing effects suggest principal flexibility. Calculations based on the reported structures further support the increased overall charge on the bridging ligand and suggest a significant alteration of the tp-phz-centered molecular orbitals in the M²⁺/M³⁺ system as compared to previously reported M²⁺/M²⁺ complexes. In general, the susceptibility towards electrostatic interactions, which was already hinted in our previously reported structure, emphasizes the importance of this supra-molecular force for further optimization of these photocatalysts. Under catalytic conditions, a TON of 2.4 for hydrogen was determined, accompanied by the formation of gold nanoparticles, which were characterized *via* DLS and TEM and remain the subject of further investigations. As a final remark, this paper is, to the best of our knowledge, the first report of a dinuclear complex where a photoredox active tris(bipyridine) ruthenium(II) chromophore is linked to a strongly oxidative gold(III) unit through an organic bridge, pointing out the paramount importance and beauty of the seemingly simple tp-phz scaffold as a unique bridging ligand.

Experimental part

General materials and procedures

All chemicals used in this work were commercially available and used without further purification. If not further described, all solvents used were commercially available and of either analytical or technical quality. The latter were redistilled through a rotary evaporator prior to use. Dry dichloromethane was purified using a two-column solid-state purification system (Glasscontour System, Irvine, CA) and transferred to the reaction flask without exposure to air. Air-sensitive syntheses were carried out under argon. Deuterated solvents were purchased from Acros Organics®. ¹H-NMR spectra were recorded on JEOL 270 and 400 MHz instruments operating at respective frequencies of 269.714 and 400.178 MHz with a probe temperature of 23 °C. Chemical shifts were reported relative to the peak for SiMe₄ using ¹H (residual) chemical shifts of the solvent as a secondary standard and are reported in ppm. For the characterization of the spin multiplicities, the following abbreviations were used: s (singlet), d (doublet),

t (triplet), q (quartet), dd (doublet of a doublet), and m (multiplet). Coupling constants J were reported in Hz. UV/Vis spectra were recorded on a single-beam Varian Cary 5000 spectrometer. Prior to measurements, the according solvents were probed as a reference. Fluorescence spectroscopy was performed on a Jasco FP-6200 spectrometer. Elemental analysis results were obtained from a EuroVektor EA 3000. Plate orange crystals of $[(\text{phen})\text{Au}(\text{Cl})_2](\text{AuCl}_4)[(\text{phen})\text{Au}(\text{Cl})_2](\text{AuCl}_2)$ and plate red crystals of $[(\text{tbbpy})_2\text{Ru}(\text{tpphz})\text{Au}(\text{Cl})_2](\text{AuCl}_2)1.5(\text{AuCl}_4)1.5\text{-Et}_2\text{O}$ were grown by layering the according solutions in acetonitrile with diethyl ether. The latter crystals were grown after addition of tetra(butyl)ammonium chloride (TBACl) to the ether phase. Suitable single crystals were embedded in protective perfluoropolyalkylether oil and transferred to the cold nitrogen gas stream of the diffractometer. Intensity data were collected at 100 K on a Bruker-Nonius Kappa CCD diffractometer using graphite monochromatized $\text{MoK}\alpha$ radiation. Data were corrected for Lorentz and polarization effects, and semi-empirical absorption corrections were performed on the basis of multiple scans using SADABS. All the structures were solved by direct methods and refined by full-matrix least-squares procedures on F_o^2 using SHELXTL NT 6.12.77. All non-hydrogen atoms were placed in positions of optimized geometry, and their isotropic displacement parameters were tied to those of the corresponding carrier atoms by a factor of either 1.2 or 1.5. Dark red prismatic crystals of $[(\text{tbbpy})_2\text{Ru}(\text{tpphz})\text{Au}(\text{Cl})_2](\text{AuCl}_4)_{1.5}(\text{AuCl}_2)(\text{PF}_6)_{0.5}\text{-}^t\text{BuOMe-MeCN}$ were embedded in protective perfluoropolyalkylether oil (Fomblin®) and measured at 180 K on a SuperNova (Dual Source) diffractometer equipped with an ATLAS detector from Agilent Technologies. The structures were refined by full-matrix least squares techniques against F_o^2 (SHELXL 2013).²⁵ Hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically. Dynamic light scattering was performed with a Delsa™ Nano C Particle Analyzer from Beckman Coulter. TEM measurements were performed using an EM900 from Carl Zeiss AG. Single drops of the solutions of the probed samples in water or acetonitrile/water/triethylamine were dripped on TEM grids which had been coated with a thin Formvar® layer prior to use. Photocatalytic hydrogen production experiments were carried out using home-built air-cooling apparatus for maintaining room temperature (22 °C) under constant irradiation of the sample. The acetonitrile used was dried over calcium hydride and triethylamine was dried over sodium before being freshly distilled under nitrogen. Samples for the irradiation experiments were prepared in GC vials (diameter = 13 mm, VWR) with a known headspace of 3 mL and a headpiece-solution ratio of 3:2. Furthermore the GC vials were charged under a nitrogen stream. After addition of 2 mL of dry triethylamine ($V = 0.55$ mL) and 10 vol% of degassed water ($V = 0.20$ mL) the final concentration of $[\text{RuAu}]$ or $[\text{RuPd}]$, respectively, in acetonitrile was 1.0×10^{-7} M. After illumination at 470 nm with a diode array for several hours, as described in the literature, 100 μL samples were drawn from the headspace and injected immediately into the GC apparatus. The hydro-

gen evolved was measured by headspace GC on a Varian CP3800 chromatograph, with a thermal conductivity detector and a CP7536 Plot Fused Silica 25 MX 0.32 MMID column (length 25 m, layer thickness 30 μm) with nitrogen as a carrier gas (purity 99.999%). The GC was calibrated by mixing different volumes of pure hydrogen with argon into a Schlenk vessel. The obtained signal (retention time for $\text{H}_2 = 0.9$ min) was plotted against the calibration curve and multiplied accordingly to obtain the total produced hydrogen content in the headspace.

Syntheses

Dichlorido-1,10-phenanthroline-gold(III) hexafluorophosphate $[(\text{phen})\text{Au}(\text{Cl})_2](\text{PF}_6)[(\text{phen})\text{AuCl}_2]\text{PF}_6$. A solution of 112 mg tetra(chlorido)auric acid $\text{HAuCl}_4\cdot\text{H}_2\text{O}$ (0.33 mmol), 1,10 phenanthroline and 200 mg ammonium hexafluorophosphate in 20 mL ethanol was boiled for 4 hours. The orange precipitate was filtered and washed with water and small portions of ethanol and diethyl ether. $^1\text{H-NMR}$ (400 MHz, CD_3CN): δ [ppm]: 8.33 (dd, 2H, $^3J_{\text{H,H}} = 5.7$ Hz, $^3J_{\text{H,H}} = 8.1$ Hz), 8.39 (s, 2H), 9.16 (d, 2H, $^3J_{\text{H,H}} = 8.1$ Hz), 9.68 (d, 2H, $^3J_{\text{H,H}} = 5.7$ Hz); EA: (calculated/experimental): C 24.30/24.15, N 4.72/4.64, H 1.36/1.24.

$[(\text{tbbpy})_2\text{Ru}(\text{tpphz})\text{Au}(\text{Cl})_2](\text{PF}_6)_3$. A solution of 50 mg $[(\text{tbbpy})_2\text{Ru}(\text{tpphz})](\text{PF}_6)_2$ (0.04 mmol) in 10 mL dichloromethane and a solution of 20 mg tetra(chlorido)auric acid $\text{HAuCl}_4\cdot\text{H}_2\text{O}$ (0.06 mmol) and 16 mg ammonium hexafluorophosphate NH_4PF_6 (0.10 mmol) in 10 mL were stirred together for 24 hours at room temperature. The orange precipitate was filtered and washed subsequently with small portions of ethanol, diethyl ether and dichloromethane. The orange solid was dissolved in acetonitrile and again precipitated from aqueous NH_4PF_6 solution. The solid was washed with water and ether and dried at $p = 10^{-2}$ mbar. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ [ppm]: 1.35 (s, 18H, ^tBu), 1.46 (s, 18H, ^tBu), 7.25 (dd, 2H, $^4J_{\text{H,H}} = 2.2$ Hz, $^3J_{\text{H,H}} = 5.9$ Hz, H5), 7.51 (dd, 2H, $^4J_{\text{H,H}} = 2.2$ Hz, $^3J_{\text{H,H}} = 6.0$ Hz, H5'), 7.61 (d, 2H, $^3J_{\text{H,H}} = 6.2$ Hz, H6), 7.71 (d, 2H, $^3J_{\text{H,H}} = 6.0$ Hz, H6'), 8.05 (dd, 2H, $^3J_{\text{H,H}} = 5.5$ Hz, $^3J_{\text{H,H}} = 8.1$ Hz, Hb), 8.29 (dd, 2H, $^4J_{\text{H,H}} = 1.4$ Hz, $^3J_{\text{H,H}} = 5.2$ Hz, Ha), 8.51 (d, 2H, $^4J_{\text{H,H}} = 1.7$ Hz, H3), 8.55 (d, 2H, $^4J_{\text{H,H}} = 2.0$ Hz, H3'), 8.63 (dd, 2H, $^3J_{\text{H,H}} = 5.9$ Hz, $^3J_{\text{H,H}} = 8.4$ Hz, Hb'), 9.90 (dd, 2H, $^4J_{\text{H,H}} = 1.1$ Hz, $^3J_{\text{H,H}} = 5.9$ Hz, Hc'), 9.96 (dd, 2H, $^4J_{\text{H,H}} = 1.3$ Hz, $^3J_{\text{H,H}} = 8.1$ Hz, Hc), 10.45 (dd, 2H, $^4J_{\text{H,H}} = 1.1$ Hz, $^3J_{\text{H,H}} = 8.3$ Hz, Ha'). UV/Vis (CH_3CN , $T = 298$ K): λ_{max} (ϵ [$\text{L mol}^{-1} \text{cm}^{-1}$]): 283 ($\pi\text{-}\pi^*$ tbbpy), 363 ($\pi\text{-}\pi^*$ tpphz), 382 ($n\text{-}\pi^*$ tpphz), 446 (MLCT) ($19\,000 \pm 1000$); MS (ESI, CH_3CN): m/z : 1361.4 $[\text{M} - 3(\text{PF}_6) + 2\text{Cl}]^+$, 1289.4 $[\text{M} - 3(\text{PF}_6)]^+$, 814.2 $[\text{M} - 3(\text{PF}_6) + \text{AuCl}_4]^{2+}$, 718.3 $[\text{M} - 2(\text{PF}_6)]^{2+}$, 663.3 $[\text{M} - 3(\text{PF}_6) + \text{Cl}]^{2+}$, 430.0 $[\text{M} - 3(\text{PF}_6)]^{3+}$.

Crystal data for $[\text{RuAu}]$ (A). $\text{C}_{67}\text{H}_{75}\text{Au}_{3.5}\text{Cl}_{10}\text{F}_{30}\text{N}_{11}\text{O}_{0.5}\text{Ru}$, $M_r = 2267.81$ g mol^{-1} , dark red fragment, crystal size $0.1525 \times 0.0947 \times 0.0753$ mm³, triclinic, space group $P\bar{1}$, $a = 11.7043(3)$ Å, $b = 15.0514(4)$ Å, $c = 24.0777(4)$ Å, $\alpha = 78.063(2)^\circ$, $\beta = 79.898(2)^\circ$, $\gamma = 67.501(2)^\circ$, $V = 3812.28(17)$ Å³, $T = 180(2)$ K, $Z = 2$, $\rho_{\text{calcd.}} = 1.976$ Mg m⁻³, $\mu(\text{Mo-K}\alpha) = 7.323$ mm⁻¹, $F(000) = 2174$, altogether 43 402 reflexes up to $h(-14/12)$, $k(-18/18)$, $l(-30/28)$ measured in the range of $3.424^\circ \leq \theta \leq 26.372^\circ$, completeness

$\Theta_{\max} = 99.7\%$, 15 558 independent reflections, $R_{\text{int}} = 0.0362$, 12 551 reflections with $F_0 > 4\sigma(F_0)$, 929 parameters, 51 restraints, $R_{1\text{obs}} = 0.0381$, $wR_{2\text{obs}} = 0.0785$, $R_{1\text{all}} = 0.0542$, $wR_{2\text{all}} = 0.0855$, GOOF = 1.031, the largest difference peak and hole: 1.959/ – 1.309 e Å^{–3}. ISOR 0.100 and 0.010 were mainly used on disordered *tert*-butyl groups and two fluoride atoms. DFIX and DANG were used on acetonitrile which had further been left isotropic. CCDC 1452865 contains the supplementary crystallographic data for this paper.

Crystal data for [RuAu] (B). C₆₄H₇₀Au₄Cl₁₁N₁₀ORu, $M_r = 2274.20$ g mol^{–1}, red plate, crystal size 0.14 × 0.12 × 0.09 mm³, triclinic, space group $P\bar{1}$, $a = 11.2792(14)$ Å, $b = 15.2758(19)$ Å, $c = 23.259(3)$ Å, $\alpha = 78.519(2)^\circ$, $\beta = 78.669(2)^\circ$, $\gamma = 68.620(2)^\circ$, $V = 3623.2(8)$ Å³, $T = 100(2)$ K, $Z = 2$, $\rho_{\text{calcd.}} = 2.085$ Mg m^{–3}, $\mu(\text{Mo-K}\alpha) = 8.727$ mm^{–1}, $F(000) = 2158$, altogether 56 329 reflexes up to $h(-14/12)$, $k(-19/19)$, $l(-29/29)$ measured in the range of $2.36^\circ \leq \theta \leq 27.19^\circ$, completeness $\Theta_{\max} = 99.4\%$, 15 930 independent reflections, $R_{\text{int}} = 0.0541$, 12 441 reflections with $F_0 > 2\sigma(F_0)$, 921 parameters, 114 restraints, $R_{1\text{obs}} = 0.0569$, $wR_{2\text{obs}} = 0.1399$, $R_{1\text{all}} = 0.0786$, $wR_{2\text{all}} = 0.1544$, GOOF = 1.061, the largest difference peak and hole: 5.958/ – 7.342 e Å^{–3}. CCDC 1452866 contains the supplementary crystallographic data for this paper.

Theoretical part

To reduce the computational cost of the calculations without affecting the spectroscopic properties, the structures of the complexes were simplified by replacing the *tert*-butyl groups by methyl groups. The geometries and electrostatic potential maps of the singlet ground state were calculated by means of density functional theory (DFT) with the functional B3LYP. Harmonic vibrational frequencies were computed to confirm that the optimized structures correspond to minima on the potential energy surface. The 28-electron (60-electron) relativistic effective core potential MWB was used with its basis set for the ruthenium and palladium (platinum and gold) atoms. The 6-31G(d) basis set was employed for the ligands. The vertical excitation energies of the singlet excited states were obtained from time-dependent (TD) DFT calculations with the same functional, pseudopotential and basis set. The effects of the interaction with a solvent (acetonitrile, $\epsilon = 35.688$, $n = 1.344$) on the geometries and excitation energies were taken into account by the polarizable continuum model (PCM). A nonequilibrium procedure of solvation was used for the calculation of the excitation energies. All the computations were performed using Gaussian 09 (ref. 26).

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