Subtle Changes to Peripheral Ligands Enable High Turnover Numbers for Photocatalytic Hydrogen Generation with Supramolecular Photocatalysts

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Supporting Information

ABSTRACT: The photocatalytic generation of hydrogen (H₂) from protons by two cyclometalated ruthenium–platinum polypyridyl complexes, [Ru(bpy)₂(2,5-bpp)PtS]²⁺ (1) and [Ru(dceb)₂(2,5-bpp)PtS]²⁺ (2) [where bpy = 2,2'-bipyridine, 2,5-bpp = 2,2',5,2'-terpyridine, dceb = 4,4'-di(carboxyethyl)bipyridine, and S = solvent], is reported. Turnover numbers (TONs) for H₂ generation were increased by nearly an order of magnitude by the introduction of carboxyethyl ester units, i.e., from 80 for 1P to 650 for 2P after 6 h of irradiation, with an early turnover frequency (TOF) increasing from 15 to 200 h⁻¹. The TON and TOF values for 2P are among the highest reported to date for supramolecular photocatalysts. The increase correlates with stabilization of the excited states localized on the peripheral ligands of the light-harvesting RuII center.

INTRODUCTION

Anthropogenic climate change and an inexorable rise in energy demands are key global challenges, where the hydrogen (H₂) economy is expected to play a key role. Clean, economic, and sustainable approaches to producing H₂ from abundant, renewable energy resources are central to the development of the H₂ economy. A promising method for localized H₂ production is the direct conversion of solar energy to fuel. Intramolecular photocatalytic systems that combine a light-harvesting unit, a bridging ligand, and a catalytic center offer considerable opportunities, and many bimetallic systems have been reported based on combinations such as Ru–Re, Re–Co, Ru–Pt, Os–Rh, Ru–Rh, Pt–Co, and Ir–Rh.¹ In particular, systems where RuII-based photosensitizers are bound covalently to PtII or PdII catalysts have received extensive attention.²–⁶ Mononuclear and homodinuclear cyclometalated platinum complexes have been described as catalysts for H₂ generation,⁷,⁸ however, the corresponding heterodinuclear Ru–Pt complexes have yet to be investigated.

Here, we report the first heterodinuclear cyclometalated Ru–Pt systems (1/1P and 2/2P, Figure 1) capable of photocatalytic H₂ generation in the presence of triethylamine (TEA). The 2,2',5,2”-terpyridine (2,5-bpp) bridging ligand enables simultaneous N^N and N^C binding modes for (bpy)₃RuII type (where bpy = 2,2'-bipyridine) photosensitizers and PtII-based catalytic centers (Figure 1). We show that turnover numbers (TONs) of 650 over 6 h can be achieved with compound 2P, which, to the best of our knowledge, is the highest catalytic activity achieved to date for dinuclear polypyridyl-based Ru–Pt photocatalysts. Furthermore, we demonstrate that the photocatalytic properties of these assemblies are highly dependent on the nature of the peripheral ligands, i.e., bpy versus 4,4'-di(carboxyethyl)bipyridine (dceb). The data obtained are compared with those reported for the analogous PdII complex (see Table 1).⁹ The paradigm in this field with regard to photocatalyst design is that the bridging ligand should act as an energy/electron reservoir and hence host the lowest-lying excited states. However, it has recently been suggested that this approach may be problematic. If the bridging ligand is to act as a reservoir, transfer of the second electron needed to produce H₂ may be impeded.¹⁰ In addition, recent photophysical studies¹¹ of compound 5 show that, after photoexcitation, most of the electron density resides on the

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increase in the TON values obtained upon the introduction of would be expected to limit electronic coupling with the catalytic (DMSO)2Cl2] (1.50 g, 3.6 mmol) and KI (1.50 g, 9.0 mmol) were Table 1. UV/Vis Absorption and Emission Maxima in Figure 1. Structures of compounds discussed. (a) Proposed structures of pentanuclear compounds 1P and 2P in the solid state. (b) Structures 1 and 2, formed in situ upon dissolution, and 5 and 6. Compound 1 was also isolated. TONs after 6 h and (*) 18 h. S = solvent. For photocatalytic conditions, see Figure 4. peripheral ligands and that the triplet metal-to-ligand charge-transfer (MLCT) states involving the bridging ligand lie higher in energy than those of the peripheral ligands. This difference would be expected to limit electronic coupling with the catalytic center and reduce the overall efficiency. However, the dramatic increase in the TON values obtained upon the introduction of 4,4'-di(carboxyethyl) groups on the peripheral ligands would suggest that better matching of the relative energies of the peripheral and bridging ligands improves the catalytic performance of the photocatalysts.

**EXPERIMENTAL SECTION**

Materials. 4,4'-Di(carboxyethyl)-2,2'-bipyridine, cis-[Ru(bpy)2Cl2], 2H2O, cis-[Pt(DMSO)Cl2], and [Ru(bpy)(2,5-bpp)](PF6)2 (3) were prepared using literature methods. Solvents obtained were used without further purification.

cis-[Pt(DMSO)Cl2] (DMSO = Dimethyl Sulfoxide), cis-[Pt(DMSO)2Cl2] (1.50 g, 3.6 mmol) and KI (1.50 g, 9.0 mmol) were dissolved in 20 mL of DMSO and stirred for 1.5 h at 50–60 °C. After cooling to room temperature, 100 mL of water (H2O) was added, and the mixture was allowed to stand at room temperature for 2 h. The orange solid resulting was collected through vacuum filtration, washed with H2O, ethanol (EtOH), and diethyl ether (Et2O), and finally dried in vacuo. Yield: 86% (1.85 g, 3.11 mmol). MW: 605.16 g/mol. cis-[Ru(dceb)2Cl2]/0.5H2O, RuCl3·3H2O (303 mg, 1.16 mmol) was dissolved in 30 mL of EtOH and heated at reflux for 30 min. 44'-di(carboxyethyl)-2,2'-bipyridine (696 mg, 2.32 mmol) was added slowly over 45 min, and the reaction mixture was heated at reflux under N2 for a further 24 h. After cooling, EtOH was removed in vacuo, and the green product was washed with Et2O and collected by filtration. Yield: 81% (726 mg, 0.94 mmol). 1H NMR (400 MHz, DMSO-d6): δ 10.11 (d, J = 5.9 Hz, 2H, H-d), 9.14 (d, J = 1.3 Hz, 2H, H-2, H-4), 8.95 (d, J = 1.5 Hz, 2H, H-a), 8.27 (d, J = 5.9 and 1.7 Hz, 2H, H-c), 7.77 (d, J = 6.1 Hz, 2H, H-d′), 7.49 (d, J = 6.0 and 1.8 Hz, 2H, H-c′), 4.53 (q, J = 7.0 Hz, 4H, OCH2), 4.36 (q, J = 7.1 Hz, 4H, OCH2), 1.45 (t, J = 7.1 Hz, 6H, OCH2CH2). Elem anal. Calcd for C32H33Cl2N4O8.5Ru: C, 49.18; H, 2.58; N, 7.37. Found: C, 49.2; H, 2.4; N, 6.6.

[cis-[Ru(dceb)2Cl2]], Cl]-0.5H2O (487 mg, 0.631 mmol) dissolved in 12 mL of EtOH was added dropwise to a solution of 2.2':5',2'-terpyridine (147 mg, 0.631 mmol) in 9 mL of EtOH–H2O (3:1). The reaction mixture was heated at reflux for 10 h. Subsequently, the mixture was cooled to room temperature, and EtOH was removed in vacuo. The product was precipitated by the addition of aqueous NH4PF6, recovered by filtration, and washed with H2O and Et2O. The product was recrystallized from acetone–water (3:1). For further purification, the compound was stirred in cold EtOH and filtered repeatedly, affording a brown/redish solid. Yield: 42% (337 mg, 0.236 mmol). MW: 1278.93 g/mol. 1H NMR (400 MHz, acetone): δ 9.41–9.30 (m, 4H, 4'H-a), 8.96 (d, J = 8.3 Hz, 1H, H-3), 8.93 (d, J = 8.0 Hz, 1H, H-3'), 8.86 (dd, J = 8.6 and 1.9 Hz, 1H, H-4), 8.60 (d, J = 1.5 Hz, 1H, H-6), 8.54–8.52 (m, 1H, H-6'), 8.51 (d, J = 5.9 Hz, 1H, H-4), 8.46 (d, J = 5.8 Hz, 1H, H-3), 8.38 (dd, J = 5.6 and 3.1 Hz, 2H, 2H-d), 8.30 (td, J = 8.0, 1.4 Hz, 1H, H-6), 8.05–8.74 (m, 4H, 4'H-c, H-4', 7.98–7.93 (m, 2H, H-4', H-3'), 7.64–7.58 (m, 1H, H-3'), 7.64–7.11 (dd, J = 6.1, 4.8, and 2.7 Hz, 1H, H-3), 4.52–4.41 (m, 8H, OCH2), 1.42–1.34 (m, 12H, OCH2CH2). Elem anal. Calcd for C32H33Cl2N4O8.5Ru: C, 47.72; H, 3.72; N, 7.77. Found: C, 45.0; H, 3.3; N, 7.5.

[cis-[Ru(bpy)2(2,5-bpp)](PF6)2]·H2O (4·2H2O). cis-[Ru(bpy)(2,5-bpp)](PF6)2 (cis-[Ru(bpy)2Cl2], Cl)], 0.5H2O (487 mg, 0.631 mmol) dissolved in 12 mL of EtOH was added dropwise to a solution of 2.2':5',2'-terpyridine (147 mg, 0.631 mmol) in 9 mL of EtOH–H2O (3:1). The reaction mixture was heated at reflux for 10 h. Subsequently, the mixture was cooled to room temperature, and EtOH was removed in vacuo. The product was precipitated by the addition of aqueous NH4PF6, recovered by filtration, and washed with H2O and Et2O. The product was recrystallized from acetone–water (3:1). For further purification, the compound was stirred in cold EtOH and filtered repeatedly, affording a brown/redish solid. Yield: 42% (337 mg, 0.236 mmol). MW: 1278.93 g/mol. 1H NMR (400 MHz, acetone): δ 9.41–9.30 (m, 4H, 4'H-a), 8.96 (d, J = 8.3 Hz, 1H, H-3), 8.93 (d, J = 8.0 Hz, 1H, H-3'), 8.86 (dd, J = 8.6 and 1.9 Hz, 1H, H-4), 8.60 (d, J = 1.5 Hz, 1H, H-6), 8.54–8.52 (m, 1H, H-6'), 8.51 (d, J = 5.9 Hz, 1H, H-4), 8.46 (d, J = 5.8 Hz, 1H, H-3), 8.38 (dd, J = 5.6 and 3.1 Hz, 2H, 2H-d), 8.30 (td, J = 8.0, 1.4 Hz, 1H, H-6), 8.05–8.74 (m, 4H, 4'H-c, H-4', 7.98–7.93 (m, 2H, H-4', H-3'), 7.64–7.58 (m, 1H, H-3'), 7.64–7.11 (dd, J = 6.1, 4.8, and 2.7 Hz, 1H, H-3), 4.52–4.41 (m, 8H, OCH2), 1.42–1.34 (m, 12H, OCH2CH2). Elem anal. Calcd for C32H33Cl2N4O8.5Ru: C, 47.72; H, 3.72; N, 7.77. Found: C, 45.0; H, 3.3; N, 7.5.
by filtration. The red solid was then washed with H2O and EtO. Yield (based on the formation of a pentanuclear structure): 90% (136 mg, 0.087 mmol). †1H NMR (400 MHz, DMSO-d6): δ 9.75 (d, J = 5.4 Hz, 1H, H-6), 9.20 (s, 1H, H-3), 8.80–8.92 (m, 4H, 4H-a), 7.92 (d, J = 8.2 Hz, 1H, H3), 7.81 (t, J = 8.4 Hz, 1H, H-4), 7.74 (d, J = 5.8 Hz, 2H, H-d, H-4), 7.57 (t, J = 6.9 Hz, 1H, H-d), 7.45–7.55 (m, 4H, H-6, H-d, 2H-c), 7.35–7.42 (m, 3H, 2H-c, H-d), 7.28 (d, J = 5.6 Hz, 1H, H-6), 7.17 (d, J = 8.3 Hz, 2H, H-5, H-3), 7.11–7.03 (m, 1H, H5), 3.95–4.05 (m, 8H, OCH2C6H4), 0.95–0.87 (m, 12H, OCH2CH3). Elem anal. Calcld for pentanuclear structure C60H48Ni2Pt3O16P3PtRu2C: C, 51.89; H, 2.39; N, 5.4. Found: C, 51.88; H, 2.17; N, 5.45. Compound 2 is obtained in situ upon dissolution in acetonitrile.

†1H NMR spectra were obtained on a Bruker Advance 400 NMR spectrometer in acetone-d6, acetonitrile-d3, or DMSO-d6 with either trimethylsilylane (TMS) or residual solvent peaks as the reference. The free induction decay profiles were processed using a MestReNova. Spin multiplicities are indicated with the abbreviations s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of a doublet), and m (multiplet) and coupling constants, J, in hertz. CHN analyses were carried out using an Exador Analytical CE440 analyzer by the Microanalytical Department, University College Dublin. Elemental analyses for Ru and Pt were recorded using a Optima 8300 inductively coupled plasma atomic emission spectroscopy (ICP-OES) system with analyses for Ru and Pt were recorded using a Optima 8300, a PerkinElmer FL WinLab, with an optical density of ca. 0.2 for all PMT detector, interfaced with an Elonex PC466 employing TCSPC). A NanoLED-460 laser source (462 nm, 1.3 ns pulse duration) was used to excite the samples at repetition rates of 100 kHz that two dinuclear RuPt compounds are formed. In the pentanuclear species show the same1H NMR spectra, this indicates that in solvent the pentanuclear species show the same1H NMR spectra, this indicates that in

The nature of the Pt species released at this disproportionation is at present unclear, but in acetonitrile, the formation of a species such as cis-[Pt(CH3CN)2] is most likely. The formation of the pentanuclear complexes, dinuclear species with the structure [Ru(N^N)2(2,5-bpp)PtI(S)]2+ are formed as shown in Figure 1 and are in agreement with the structure observed for compound 3.† The most notable change in the †1H NMR spectra upon cyclometalation of 3 and 4 with the Pt catalyst is a shift downfield of the two signals assigned to H5 and H3 of the 2,5-bpp ligand due to deshielding by PtII (see Figures S5 and S6). 1H NMR spectra for numbering of protons (see Figures S2–S7). These techniques indicate only the presence of dinuclear species with the overall formula [Ru(N^N)2(2,5-bpp)PtI(S)]2+(PF6)2, where S = solvent, and signals indicative of pentanuclear compounds are not observed. This suggests that, upon dissolution of the pentanuclear complexes, dinuclear species with the structure [Ru(N^N)2(2,5-bpp)PtI(S)]2+ are formed as shown in Figure 1 and are in agreement with the structure observed for compound 3.†

The nature of the Pt species released at this disproportionation is at present unclear, but in acetonitrile, the formation of a species such as cis-[Pt(CH3CN)2] is most likely. The potential effect of this species on the photocatalytic effect is discussed below. The UV/vis absorption and emission spectra of 1P, 2P, 3, and 4 (Figure 2 and Table 1) are typical of ruthenium(II) polypyridyl complexes. The transitions in the UV spectra are assigned to π−π* transitions of the polypyridyl ligands, with the band at 330–370 nm assigned to the 2,5-bpp ligand and the vials are cooled by cooling fans from the side, in order to keep the catalytic solutions at room temperature. After irradiation, the amount of H2 produced was measured by means of GC after 0, 1, 2, 4, 6, 18, and 24 h and an average of three samples was taken for calculating the TON and TOF values. H2 evolution was determined by headspace GC using a Bruker Scion gas chromatograph/mass spectrometer, with thermal conductivity (column, molecular sieve 5A, 75 m × 0.53 mm i.d.; oven temperature 70 °C; flow rate 22.5 mL/min; detector temperature 200 °C) with argon as the carrier gas.
transitions at $\lambda > 350$ nm to singlet-state MLCT ($1^\text{MLCT}$) transitions (vide infra). The bathochromic shift of the $\pi-\pi^*$ transitions at 300 nm upon the introduction of ester moieties (i.e., in 2P and 4) reflects the stabilization provided by these electron-withdrawing moieties. The visible absorption spectra of 1P and 2P are generally similar to those of the mononuclear complexes 3 and 4, respectively, indicating that orthometalation by PtII has a minor influence on the electronic structure of the RuII moiety. Complexation to PtII results in ca. a 15 nm bathochromic shift in the emission maxima and a decrease in the emission decay lifetimes in both cases. The absorption and emission data (Figure 2) show that the changes in the shape and position of the $1^\text{MLCT}$ absorption bands upon the introduction of ester moieties are relatively minor and that there is little change in the molar absorptivities of 1P and 2P at the wavelength of irradiation for photocatalysis (470 nm). Therefore, the improved photocatalytic efficiency is not related to the increased molar absorptivity in the case of 2P. Although, 2P, 3, and 4 show wavelength-independent monoeponential emission decay kinetics (Table 1), 1P decays biexponentially (136 and 659 ns), albeit with no wavelength dependence (Table S2), as previously observed for the analogous Ru–Pd complex 5 ([Ru(bpy)$_2$(2,5-bpp)PdCH$_2$CN]$_2^+$), for which the faster process was assigned to relaxation from a 2,5-bpp-ligand-localized $3^\text{MLCT}$ state. The monoexponential decay observed for 2P indicates that its excited-state dynamics differ from those of 1P.

rR spectra of 1/1P, 2P, and 4 were recorded at $\lambda_{exc} = 355$ nm (Figure S8), 457 nm (Figure S9), and 473 nm (Figure 3).

Resonance enhancement of Raman scattering is observed only for modes of the chromophoric moiety, which facilitates assignment of the $1^\text{MLCT}$ and $\pi-\pi^*$ absorption bands (see Table 1 for major bands). The spectra of 3$^{11}$ and 4 are almost identical with that of [Ru(bpy)$_3$]$^{2+}$ except for shoulders on either side of the band at 1489 cm$^{-1}$ and an increase in the relative intensity of the band at 1606 cm$^{-1}$ indicating that 2,5-bpp-based $1^\text{MLCT}$ absorption bands, in addition to bpy-based $1^\text{MLCT}$ transitions, are present. In the case of 4, additional bands related to the ester moiety are observed also. Hence, the transitions at 473 nm are assigned primarily but not exclusively to $1^\text{MLCT}$ ($\pi_{bpy}^* \leftarrow \pi_t$) transitions. For 1/1P and 2P, additional bands are observed at 1290, 1476, 1504, 1594, and 1606 cm$^{-1}$, as observed earlier for the related PdII analogue 5, indicating that excitation at 473 nm is resonant with $1^\text{MLCT}$ ($\pi_{bpy}^* \leftarrow \pi_t$) transitions also. Hence, rR spectroscopy indicates that excitation at 457 and 473 nm leads to the initial population of both bpy- and bridging-ligand-based $1^\text{MLCT}$ states for 1P to 4, albeit with varying relative contributions and with a decrease, compared with 1P, in the contributions from the bridging ligand on the long-wavelength side of the spectrum of 2P. Raman spectroscopy at $\lambda_{exc} = 355$ nm shows enhancement of primarily 2,5-bpp features for both the mono- and heterobimetallic complexes (Figure S8), with a substantial change observed upon coordination of PtII, as expected.

Photocatalytic studies were performed on the isolated pentamer and penta/dinuclear assemblies, in addition to intermolecular photolysis using compounds 3 and 4 together with cis-[Pt(CH$_2$CN)$_2$I$_2$]. The H$_2$ generation capacity of 1, 1P, and 2P was studied for up to 18 h of irradiation in triplicate. Typical examples of H$_2$ gas generation over the first 6 h are shown in Figure 4 (Table 1; see the figure legend for the experimental conditions). The photocatalytic activity of compound 1P, with a TON of 99 after 6 h (100 after 18 h), is similar to that observed for 5$^5$ (Figure 4) and indicates that for the bpy analogue the replacement of a Pd center with the
Pt-based catalytic center does not improve the catalytic behavior. However, the introduction of carboxyethyl moieties on the peripheral ligands of 2P results in almost an order of magnitude increase in activity to 650 after 6 h (720 over 18 h). In addition, TOFs of up to 200 h⁻¹ are observed in the early stage of the catalytic reaction. A number of control experiments were also carried out. Irradiation of compounds 3, 4, cis-[Pt(CH₃CN)₂I₂], or TEA individually using the same experimental conditions did not produce H₂. Upon irradiation of equimolar mixtures of the photosensitizer and the catalytic center using cis-[Pt(CH₃CN)₂I₂] as the catalyst, TON values of 69 and 88 were obtained for compounds 3 and 4, respectively, after 6 h (see Table 1). During these intermolecular experiments, colloid formation was observed. In the preformed heterobimetallic complexes, a small quantity of colloid formation was observed for the pentanuclear complex 1P.

As shown in the experimental part, both the pentanuclear (1P) and dinuclear (1) forms were isolated. The latter was obtained by dissolving the pentanuclear compound in acetonitrile. The dinuclear species (1P) shows CHN analysis and ¹H NMR spectroscopic data that are in agreement with those of [Ru(bpy)₂(2,5-bpp)PtI₂][PF₆]₂, i.e., a monoplatinum complex.

Photocatalytic studies for both 1P and 1 were carried out to estimate any potential effect that the “free Pt” generated in situ may have on photocatalysis. The data obtained show that, for the pentanuclear precursor complex, a TON of 99 is obtained, while for the dinuclear analogue, a value of 80 is obtained. As outlined above, intermolecular studies using equimolar amounts of the precursor 3 and cis-[Pt(CH₃CN)₂I₂] show TONs of 69. Hence, the mononuclear Pt species released upon dissolution of 1P does not appear to contribute significantly to H₂ generation.

The influence of the ester groups on the photocatalytic H₂ generation capacity of the supramolecular assemblies presented here are consistent with the findings reported for the related complexes [Ru(bpy)₂(2,5-dpp)PdCl₂]⁺ [where 2,5-dpp = 2,5-bis(pyrid-2-yl)pyrazine], which did not produce H₂, and [Ru(2,3-cyclobutanedione)₂PdCl₂]⁺ (6; see Figure 1b), which showed a TON value of 400 after 18 h. Hence, H₂ generation increases considerably by the introduction of ester moieties on the peripheral ligands. The results show that, apart from manipulation of the bridging ligands and the catalytic center, changes in the peripheral ligands can also greatly improve the photocatalytic efficiency of photocatalysts. UV/vis absorption and emission spectroscopy indicate that the introduction of the carboxyethyl substituent lowers the energy of the MLCT states located on the peripheral ligand, and hence one could anticipate that this would decrease the catalytic activity because this energy may now be lower than that of the bridging ligand. However, the opposite is observed. The exact cause of the 7-fold increase (after 18 h) in TON upon the introduction of the ester groups is at present unclear. Spectroscopic data as well as emission lifetime studies suggest that 1P and 2P have distinctly different photophysical properties, and the study of these properties will be the focus of future efforts.

**CONCLUSION**

In the wider field of photocatalytic solar fuel production by supramolecular assemblies, the best approach to optimization of the interaction between the photosensitizer and catalytic center with regard to the overall photocatalytic activity is still a matter of debate. At present, for assemblies designed for H₂ generation, bridging ligands that allow for weak-to-medium interaction between these two components have emerged as the most active. However, in the area of CO₂ reduction, the use of bridging ligands that provide little or no through-bond interaction between the photosensitizer and catalytic center appears to be the better approach. This difference reflects the complexity of the overall two-electron reduction processes and highlights the experimental challenge faced in disentangling the several distinct elementary steps that the overall reactions involve. Unfortunately, detailed kinetic studies on supramolecular assemblies of this type are at present not available. More detailed photophysical studies are needed to allow for a detailed discussion on what processes are dominant, ranging from coupling between the various orbitals to the influence of a possible back-reaction. Also the issue of reductive versus oxidative quenching needs to be considered. In the design of photocatalytic assemblies for H₂ generation, considerable attention has been devoted to the choice of the various components present in the supramolecular systems, such as the bridging ligand, the catalytic center, and the nature of the photosensitizer. Efforts have been directed toward balancing the overall efficiency of photoinduced intramolecular electron transfer between the light-harvesting unit and catalytic center and in maintaining a sufficiently long-lived excited state to allow for reduction of the light-harvesting unit by the terminal reductant.

In this contribution, a significant improvement in the efficiency of light-driven H₂ generation by intramolecular photocatalysts is reported in terms of both TON and TOF, which are, to the best of our knowledge, among the highest catalytic activities reported for intramolecular Ru-based supramolecular assemblies. Most importantly, it is shown here that the peripheral ligands of the light-harvesting unit can have as dramatic an influence on the catalytic efficiency as the bridging unit or catalytic center and that further studies are needed in this area.

**ASSOCIATED CONTENT**

Supporting Information

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Additional ¹H NMR, PL, and MS data (PDF)
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Notes
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