

A Redox Asymmetric, Cyclometalated Ruthenium Dimer: Toward Upconversion Dyes in Dye-Sensitized TiO₂ Solar Cells^{\perp}

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We have prepared the dinuclear ruthenium complexes $[(R_3-tpy)Ru(N^{C^{N}}-tpy)Ru(tpy)]^{3+}$ (R = H $([5a]^{3+})$, CO₂Me $([6a]^{3+})$, N^C(H)^N-tpy = 4'-(3,5-dipyridylphenyl)-2,2':6',2''-terpyridine, tpy = 2,2':6',2''-terpyridine) and $[(R_3-tpy)Ru(N'^C^N'-tpy)Ru(tpy)]^{3+}$ (R = H $([5b]^{3+})$, CO₂Me $([6b]^{3+})$, $N'^{C}(H)^{N'-tpy} = 4'-(3,5-di(4-tert-butylpyridyl)phenyl)-2,2':6',2''-terpyridine)$ in a stepwise manner. The directional nature of the bridging ligand, which is potentially cyclometalating on one side, induces large redox asymmetry in the resulting dinuclear complexes. One-electron oxidation gives rise to a strong metal-to-metal charge transfer transition from the $[Ru(tpy_2)]^{2+}$ moiety to the cycloruthenated group, centered at 1034 nm for $[6b]^{4+}$. The localized nature of the oxidation processes, the shape of the NIR band, and TD-DFT calculations allow assignment of these systems to localized Robin-Day class II. Exclusive substitution of the terminal tpy ligand on the cyclometalated ruthenium with acid moieties allows selective attachment of the dye to a semiconductor surface, whereby a possible two-step upconversion path is created in dye-sensitized solar cells for the utilization of low-energy photons.

Introduction

Solar energy is the most abundant renewable energy source available to mankind. In fact, the resource base represented by terrestrial irradiation exceeds by far that of all other renewable energy sources combined.^{1,2} Semiconductor solar cells offer high conversion efficiencies and long-term stability, but the need for high-purity materials renders them expensive.³ In 1991, Grätzel and co-workers showed that widebandgap semiconductors can be sensitized to visible light and that cheap and efficient solar cells can be obtained in this way.⁴ With these dye-sensitized solar cells (DSSCs) energy power conversion efficiencies (η_{sun}) up to 11% have been reached.^{5,6} The crux of DSSCs is light absorption by a

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sensitizer molecule and the following charge injection into the conduction band of a semiconductor, usually anatase TiO₂, Figure 1. Several different sensitizers have been prepared and tested such as organic molecules,^{7,8} porphyrins,⁹ phthalo-cyanines,^{10,11} and transition metal complexes.^{12–15} Among these sensitizers, polypyridine complexes of ruthenium have displayed superior properties. The most well-known pigments

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Figure 1. Operational scheme for DSSC (left) and upconversion scheme employed (right). Please note that the photoelectrochemical experiments described later utilize an HTM material that possesses an energy level that is actually above the ground state of D1.

are the N719 dye $[Ru(NCS)_2(dcbpy)_2]$ (dcbpy = 4,4'dicarboxy-2,2'-bipyridine)¹² and the black dye [Ru(NCS)₃- $(tctpy)]^{-}(tctpy = 4,4',4''-tricarboxy-2,2':6',2''-terpyridine).^{13}$ Amphiphilic analogues of these dyes have been prepared in order to decrease sensitivity toward water-induced decomposition by forming a shielding hydrophobic layer. Extension of the conjugated system on the peripheral bpy ligand is used to increase the extinction coefficient of the dye, and this allows for the use of thinner, more efficient layers. The ideal sensitizer for a single layer cell should absorb all light below 920 nm and convert it into electricity with unit efficiency. Photons that do not possess sufficient energy to bridge this threshold will not contribute to the current, resulting in a low theoretical maximum efficiency. In multilayered semiconductor stacked cells, low-energy photons are used to increase the voltage, but matching of the current from the individual layers is necessary. Using this approach power conversion efficiencies as high as 40% have been reached upon concentration of the solar light.³ We propose a similar way to utilize low-energy photons in DSSCs, Figure 1.¹⁶ The setup consists of two dye moieties, one of which is attached to the TiO₂ surface. Upon excitation of this primary dye, it injects an electron into the TiO₂ CB, replicating a standard sensitizer. This is rather similar to antennae or donor-acceptor systems that have been utilized earlier, in which the excitation energy is transferred to the titania surface, where the actual charge injection takes place, a principle that has been utilized since the early days of sensitized solar cells.4,17-24 However, this dye, D1, is not regenerated by electron transfer from the electrolyte, as is common practice. Instead it is regenerated by optical electron transfer from a second dye moiety, D2, which is in turn regenerated from the electrolyte.

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Intervalence charge transfer (IVCT) transitions are known to occur in symmetric bimetallic complexes upon partial oxidation and are observed at very long wavelengths.^{25–27} When the bimetallic complex possesses redox asymmetry between the metal moieties, the IVCT band is shifted to higher energy, corresponding to the difference in oxidation potential, which makes this type of transition very interesting for regenerating the primary dye. Sufficient electronic communication has to be ensured by covalently linking the individual dye moieties. However, electronic coupling should not be so strong that the redox centers lose their individuality and form a Robin–Day class III delocalized system.^{28–30}

Cyclometalation is an excellent tool to destabilize the ground state of a complex as a result of the strong σ -donation by a formally anionic carbon atom.^{31–36} The initial oxidation potential can be significantly negatively shifted without dramatically changing the overall geometry of the system. In a bimetallic complex cyclometalation of only one metal center will result in the necessary redox asymmetry in the system. Moreover, we have already demonstrated that properly designed cyclometalated ruthenium complexes are efficient and stable sensitizers for DSSC.³⁷ More recently also others have shown that other cyclometalated ruthenium complexes are efficient sensitizers indeed.^{38,39}

We have prepared a redox asymmetric, dinuclear ruthenium compound with a bridging ligand that is N,C,N'cyclometalated to one ruthenium center and N,N',N''-coordinated to the second ruthenium center. The bridging ligand N^C(H)^N-tpy (4'-(3,5-dipyridylphenyl)-2,2':6',2''-terpyridine) is reported in the literature, and the redox symmetric complexes support sufficient electronic communication to observe a well-defined IVCT transition at 2360 nm.^{40–42}

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These systems are defined as Robin-Day class II,²⁸ since electronic communication is present but the system is well described using localized states. We have prepared the complexes $[(R_3-tpy)Ru(N^{\wedge}C^{\wedge}N-tpy)Ru(tpy)]^{3+}$ ($\mathbf{R} = H([\mathbf{5a}]^{3+})$, $CO_2Me([6a]^{3+})$ and its t-Bu-substituted analogue $[(R_3-tpy) Ru(N'^{C}N'-tpy)Ru(tpy)]^{3+}(N'^{C}(H)^{N'}-tpy) = 4'-(3,5$ di(4-*tert*-butylpyridyl)phenyl)-2,2':6',2''-terpyridine), R =H ($[5b]^{3+}$), CO₂Me ($[6b]^{3+}$)) in a stepwise manner. The new t-Bu-substituted ligand aids tremendously in raising the solubility of the resulting complexes, which is otherwise problematic at best. A number of experimental techniques are used to analyze the electronic properties of these complexes, which are supported by TD-DFT calculations. The individual electron transfer processes necessary for the upconversion scheme to be exerted are demonstrated. Selective introduction of anchoring groups on the cyclometalated moiety allows grafting of the complexes to a semiconductor surface in a well-defined manner. After deprotection of the esters in $[6b]^{3+}$ to free carboxylates in [8b] the complex can be incorporated in an operational dye-sensitized solar cell.

Results

Synthesis. The bridging ligands **3aH** and **3bH** were prepared as outlined in Scheme 1. Starting from 3,5-dibromobenzaldehyde using a two-step Kröhnke⁴³-type condensation reaction, **1** could be obtained in 75% overall yield.

3,5-Dibromobenzaldehyde was first converted to a chalcone by aldol condensation with acetylpyridine, which was then reacted with 1-(2-oxo-2-(pvridin-2-vl)ethvl)pvridinium iodide in the presence of NH4OAc as nitrogen source to form the central pyridine ring. The resulting dibromide was reacted with stannane 2a, and the desired ligand was obtained in 89% yield and ultimately prepared on a multigram scale. The presence of copper⁴⁴ or lithium salts⁴⁵ in this catalyzed C-C coupling reaction is beneficial, since they compete with palladium for coordination to the product, which is a good ligand for platinum group metals and inhibits the catalyst. For the preparation of the t-Bu-substituted bridging ligand the same methodology was adopted, using stannane 2b in the final step. Stannane 2b was prepared directly from 4-tert-butylpyridine by selective lithiation using n-BuLi/LiDMAE aggregate⁴⁶ instead of first introducing a bromine atom at the 2 position.⁴⁷

The bimetallic complexes were prepared in a two-step procedure, Scheme 2. By reacting ligand **3aH** with [RuCl₃-(tpy)] the monometallic complex [**4aH**]²⁺ was obtained. Additional species were also synthesized, including the compound in which the bridging ligand is coordinated in a cyclometalated fashion, [**7a**]⁺. The desired compound [**4aH**]²⁺ could be isolated by sequential column chromatography on SiO₂ and Al₂O₃ in 19% yield. Reaction of [**4aH**]²⁺ with another equivalent of [RuCl₃(tpy)] or [RuCl₃((CO₂Me)₃tpy)] allows the preparation of the cyclometalated compounds [**5a**]³⁺ and [**6a**]³⁺, respectively. Increased yields of [**6a**]³⁺ could be obtained using μ -wave-assisted heating. Reaction of the substituted ligand **3bH** is more selective and allows the isolation of the

Scheme 1. Synthesis and NMR Numbering Scheme of Free Ligands 3aH and 3bH^a



^a Conditions: (i) 2-acetylpyridine, NaOH, MeOH, room temperature,
 1 h, (ii) 1-(2-oxo-2-(pyridin-2-yl)ethyl)pyridinium iodide, NH4OAc,
 MeOH, reflux, 20 h, (iii) *N*,*N*-dimethylethanolamine, *n*-BuLi, SnClBu₃,
 hexane, -70 °C, (iv) LiCl, [Pd(PPh₃)4], toluene, reflux, 24 h.

monometallic complex $[4bH]^{2+}$ in 56% yield. Using μ -waveassisted heating, cyclometalated $[5b]^{3+}$ could be prepared by reaction of $[4bH]^{2+}$ with $[RuCl_3(tpy)]$ in ethylene glycol. The ester-substituted $[6b]^{3+}$ was prepared using μ -wave irradiation in MeOH at 97 °C in a closed vessel. Deprotection of the ester functionalities in $[6a]^{3+}$ and $[6b]^{3+}$ to the free deprotonated acids [8a] and [8b] (see Scheme 2), respectively, could be performed by heating a solution of the complex in MeCN solution in the presence of H₂O and using NEt₃ as base.

Electrochemical Data. The half-wave oxidation and reduction potentials in MeCN solution as determined by cyclic voltammetry (CV) for the complexes are summarized in Table 1. For the more soluble *t*-Bu-substituted complexes, $[4bH]^{2+}$, $[5b]^{3+}$, and $[6b]^{3+}$, it was also possible to determine the respective electrode potentials in CH₂Cl₂. For the monometallic complexes a single metal-based⁴⁸ oxidation is present, while for the bimetallic complexes two distinct waves are observed. Cyclometalation shifts the oxidation potential by about 0.7 V to less positive values. The oxidation process corresponding to the [Ru(tpy)₂]²⁺ moiety is rather constant throughout the series. The redox asymmetry, as defined by $\Delta E_{1/2}(ox) = E_{1/2}(ox2) - E_{1/2}(ox1)$, is slightly solvent dependent.

Electronic Absorption Spectroscopy. The UV-vis absorption spectra of complexes in this study are depicted in Figure 2 and summarized in Table 2.

Polypyridine complexes of ruthenium are characterized by strong ligand-centered (LC) $\pi - \pi^*$ transitions in the UV region and moderately intense metal-to-ligand charge transfer (MLCT) absorptions in the visible light region.^{48–51}

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^{*a*}Conditions: (i) [RuCl₃(tpy)], AgBF₄, MeOH, reflux, 20 h, (ii) [RuCl₃(tpy)], *N*-methylmorpholine, ethylene glycol, μ-wave, 150 °C, 30 min or [RuCl₃((CO₂Me)₃tpy)], *N*-methylmorpholine, MeOH, μ-wave, closed vessel, 97 °C, 30 min, (iii) NEt₃, MeCN, H₂O, 70 °C, 40 h.

Table 1. Electrochemical Data^{*a*} for $[4aH]^{2+}$, $[4bH]^{2+}$, $[7a]^+$, $[5a]^{3+}$, $[5b]^{3+}$, $[6a]^{3+}$, and $[6b]^{3+}$

	$E_{1/2}$ (V) ($\Delta E_{\rm p}$ (mV))					
cation	$R{u'}^{II}/R{u'}^{III}$	$Ru^{\rm II}/Ru^{\rm III}$	$L/L^{\bullet-}$	$L^{\prime}/L^{\prime \bullet -}$	$\frac{\Delta E_{1/2}(0\mathbf{X})}{(\mathbf{V})^b}$	
[4aH] ²⁺		0.88 (59)	-1.65(66)	-1.93(100)		
[4bH] ²⁺		0.88(64)	-1.63(60)	-1.88(73)		
		$0.93(68)^{c}$	$-1.61(70)^{c}$			
[7a] ⁺		0.16(59)	-1.91(73)			
$[5a]^{3+}$	0.89(69)	0.20(63)	-1.67(58)	$-1.91(86)^d$	690	
$[5b]^{3+}$	0.89(89)	0.17 (59)	-1.67(60)	$-1.93(95)^{e}$	710	
	$0.92(93)^{c}$	$0.12(64)^c$	$-1.67(75)^{c}$		800	
$[6a]^{3+f}$	0.90(65)	0.37 (58)	-1.48(68)	-1.68(50)	530	
$[6b]^{3+g}$	0.90(61)	0.34 (59)	-1.48(58)	-1.61(55)	560	
	$0.93(80)^{c}$	$0.32(59)^c$	$-1.56(63)^{c}$	$-1.69(63)^{c}$	610	

^{*a*} Data collected in MeCN with [*n*-Bu₄N]PF₆ as supporting electrolyte at 100 mV/s; potentials reported vs ferrocene/ferrocenium (Fc/Fc⁺) used as internal reference. ^{*b*} Redox asymmetry, separation between the two successive Ru^{II}/Ru^{III} couples ($\Delta E_{1/2}(ox) = E_{1/2}(ox1) - E_{1/2}(ox2)$). ^{*c*} Data collected in CH₂Cl₂. ^{*d*} Product adsorbs on electrode surface. ^{*e*} Two overlapping one-electron processes. ^{*f*} Two overlapping one-electron processes observed at -1.89 (210) V. ^{*g*} Two overlapping one-electron processes observed at -1.83 V (140 mV).

The different tpy and N^CN groups result in the presence of many overlapping LC absorptions in the UV. The mononuclear complex $[4aH]^{2+}$ displays visible MLCT features very similar to those observed for $[Ru(tpy)_2]^{2+}$.⁵² As is commonly observed for cycloruthenated complexes, the visible absorption features of the mononuclear, cyclometalated complex $[7a]^+$ are red-shifted, broadened, and slightly decreased in molar absorption coefficient compared to the



Figure 2. Electronic absorption spectra of $[4aH]^{2+}$ (dotted, black), $[4bH]^{2+}$ (dotted, red), $[7a]^+$ (dash dot, black), $[5a]^{3+}$ (dash, black), $[5b]^{3+}$ (dash, red), $[6a]^{3+}$ (solid, black), $[6b]^{3+}$ (solid, red) in MeCN.

non-cyclometalated analogues.^{36,53-55} The absorption spectra of the dinuclear, cyclometalated complexes $[5a]^{3+}$ and $[6a]^{3+}$ are clearly not a superimposition of the spectra of the mononuclear units. Obviously, many different transitions are involved in the visible absorption feature. An especially large increase in absorption is observed at the low-energy side of the MLCT band. These low-energy features are most likely assigned to transitions from the cyclometalated ruthenium center to the terminal tpy ligand. Introduction of the

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Table 2. Electronic Absorption Data for [4aH]²⁺, [4bH]²⁺, [7a]⁺, [5a]³⁺, [5b]³⁺, [6a]³⁺, and [6b]³⁺

complex	$ \begin{array}{l} \lambda_{\max} \ (\text{nm}) \ \text{in MeCN} \\ (\varepsilon \ (10^3 \ \text{M}^{-1} \ \text{cm}^{-1})) \end{array} $	$\begin{array}{l} \lambda_{\max} \ (nm) \ in \ CH_2Cl_2 \\ (\varepsilon \ (10^3 \ M^{-1} \ cm^{-1})) \end{array}$
[4aH] ²⁺	482 (19.5), 307 (67.3), 281 (82 6), 241 (69 9)	484, 309, 283, 242 ^{<i>a</i>}
[4bH] ²⁺	482 (23.7), 308 (75.3), 282 (70.1), 240 (59.8)	483 (24.1), 309 (79.4), 283 (69 0), 275 (70 0)
$[7a]^{2+}$	540 (sh), 502(15.7), 379 (19.2), 278 (72.3), 241 (63.6)	590 (sh), 544 (sh), 505, 377, 281 ^a
[5a] ³⁺	540 (35.6), 481(sh), 350 (sh), 309 (99.5), 280 (76.8), 235 (68.9)	554, 523 (sh), 485 (sh), 309, 282, 235 ^a
$[5b]^{3+}$	545 (39.8), 500 (sh), 350 (sh), 309 (107.1), 278 (83.4), 233 (sh)	560 (sh), 528 (34.2), 310 (11.3), 282 (89.9)
[6a] ³⁺	768 (sh), 570 (sh), 511 (35.4), 423 (22.8), 308 (82.5), 295 (84.6).	805(sh), 655 (sh), 585 (sh), 517, 427, 309, 296. ^a
[6b] ³⁺	779 (sh), 575 (sh), 515 (39.3), 424 (sh), 308 (92.0), 295 (92.1), 210 (115.4)	813 (sh), 670 (sh), 589 (sh), 522 (34.4), 491 (sh), 436 (31.7), 309 (99.6), 297 (100.0)

 $^{a}\varepsilon$ was not determined due to low solubility in CH₂Cl₂.

Table 3. Low-Energy Bands for $[5a]^{4+}$, $[5b]^{4+}$, $[6a]^{4+}$, and $[6b]^{4+}$ upon Chemical Oxidation in MeCN

	$\lambda_{\max}(\exp)$ (nm) (i	calc $\lambda'_{ m max} (m cm^{-1})^a$ $\Delta \tilde{v}_{1/2, m calc} (m cm^{-1})^b$	
	$(\Delta \tilde{\nu}_{1/2} \ (\mathrm{cm}^{-1})) \ (\varepsilon$		
	MeCN	CH_2Cl_2	MeCN
[5a] ⁴⁺	956 (10 460) (4174) (5 0)	945 (10 582) (41 55)	4895
$[5b]^{4+}$	939 (10 650) (5097) (6.2)	904 (11 062) (4260) (5.3)	4925 3365
[6a] ⁴⁺	1057 (9461) (3828) (6.3)	1061 (9425) (3955)	5185 3450
[6b] ⁴⁺	1034 (9671) (4000) (7.2)	1014 (9862) (4405) (6.4)	5155 3440

^{*a*}Calculated using $\lambda'_{max} = \lambda_{max} + \Delta E_{1/2, ox}$. ^{*b*}Calculated using the Hush formula using the reduced value for the absorption maxima; see main text.

t-Bu moiety results in a small bathochromic shift as it further destabilizes the metal center by electron donation. Additionally, the *t*-Bu moiety seems to have a small hyperchromic effect. The electronic spectrum of fully protonated $[H_38b]Cl_3$ in DMSO in the presence of an excess of HCl closely resembles that of $[6b]^{2+}$, while the shape of the visible features is distinctively changed when [8b] is fully deprotonated by an excess of NaOH (Figure 4).

Near-Infrared Spectra. The near-infrared (NIR) spectra of the singly oxidized dinuclear complexes $[5a]^{4+}$, $[5b]^{4+}$, $[6a]^{4+}$, and $[6b]^{4+}$ were recorded in MeCN and CH₂Cl₂, Table 3. Oxidation was performed by titration with a concentrated solution of (NH₄)₂[Ce(NO₃)₆] in MeCN or SbCl₅ in CH₂Cl₂, and the original spectrum was fully regenerated upon addition of an excess of ferrocene. Representative results obtained for [6b]⁴⁺ are depicted in Figure 3. Upon oxidation, the MLCT features are partly diminished and a broad band arises in the NIR. One-electron oxidation of the symmetric complexes $[(Ru(tpy))_2(\mu-tpy-tpy)]^{4+}$ and $[(Ru(tpy))_2(\mu-tpy-tpy)]^{4+}$ $N^{C}N^{N-N^{C}N}]^{2+}$ into the mixed valence state resulted in the observation of an IVCT transition at 1580 and 1936 nm, respectively.⁴² For symmetric, weakly coupled, class II mixed valence systems the bandwidth of the NIR IVCT transition can be predicted from the Hush formula ($\Delta v_{1/2}$ = $(16RT\ln 2(\lambda_{max}))^{1/2}$, R = 0.695 cm⁻¹ K⁻¹, T = 298 K (e.g., for $[5a]^{4+}$; $\Delta \nu_{1/2} = (16 \times 0.695 \times 298 \times 0.693 \times 4895)^{1/2} = 3355$ cm⁻¹)).²⁷ In the case of the nonmetalated [(Ru(tpy))₂(μ tpy-tpy)]4+ the bandwidth is well predicted by the Hush



Figure 3. UV-vis-NIR spectra recorded during chemical oxidation of $[6b]^{3+}$ to $[6b]^{4+}$ in MeCN (red to blue). The absorptions of $[5a]^{4+}$ predicted by TD-DFT *in vacuo* are given as black bars.

formula, and it is thus considered a Robin–Day class II system.²⁸ On the other hand, the band for bis-cyclometalated $[(Ru(tpy))_2(\mu-N^{C^N}-N^{C^N})]^{2+}$ is rather narrow and, moreover, solvent independent, and the system can be considered borderline class II–III.^{25–27} To an approximation the Hush formula can be extended to asymmetric systems, where the Gaussian-shaped band is shifted by the redox asymmetry and is centered at λ'_{max} ($\lambda'_{max} = \lambda_{max} + \Delta E_{1/2}(ox)$).²⁵ Using $\Delta E_{1/2}(ox)$ obtained from CV in the appropriate solvent as an upper limit, the theoretical bandwidths can be derived, Table 3. Compared to the reported λ_{max} for the symmetric compounds, λ'_{max} is consequently calculated at decreased energy, indicating that $\Delta E_{1/2}(ox)$ is overestimated from CV data. Data collected in CH₂Cl₂ are also represented in Table 3, with all low-energy bands showing solvatochromism.

Being very much aware of the severe limitations of TD-DFT in these systems, we utilized it nonetheless as an indicative tool for the nature of the IVCT transition in $[5a]^{4+}$. A complete listing of the applied methodology, electronic transitions, energy levels, isovalue plots,⁵⁶ and Mulliken

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population analysis⁵⁷ of the frontier molecular orbitals can be found in the Supporting Information. In $[5a]^{3+}$ the three highest occupied molecular orbitals (HOMOs) are associated with the cyclometalated ruthenium, while HOMO-4, HOMO-5, and HOMO-6 are associated with the all-N-coordinated metal. The lowest unoccupied spin orbital (LUSO) is localized on the cyclometalated ruthenium in $[5a]^{4+}$. The highest occupied spin orbitals (HOSOs) are localized on the second ruthenium center. A strong transition is predicted for $[5a]^{4+}$ at 1060 nm (f = 0.173) assigned to β -HOMO-1 $\rightarrow \beta$ -LUMO, Figure 3.

Photoelectrochemical Experiments. A solid-state dye-sensitized solar cell was constructed using the soluble [H₂8b]Cl₂ precipitated from DMSO solution as sensitizer and 2.2'-7.7'tetrakis(N,N-bis(4-methoxyphenyl)amino)-9,9'-spirobifluorene (spiro-MeOTAD) as solid hole-conducting material.58,59 It has to be noted that the exact degree of protonation of [8b] is unknown, as HCl slowly escapes from the dry solid (the degree of protonation can be judged from NMR spectroscopy but changes over time as the compound is dried). Under sunlight simulated by a LumiLED lightsource (mismatch 15-20%) the cell reached a power conversion efficiency of 1.37% with open circuit voltage $V_{oc} = 724 \text{ mV}$, short circuit current $I_{sc} = 2.6$ mA, and fill factor ff = 0.73. The incident photon-to-current conversion efficiency (IPCE) spectrum of this cell was measured using a 300 W Xe lamp with 10 nm step width (Figure 4).

Discussion

Synthesis. Ligand **3aH** has been previously reported, but was prepared on a 25 mg scale with 2% overall yield, using a pyridine condensation and Negishi cross-coupling methodology.⁴² The methodology applied here allows easy preparation of the bridging ligands on a multigram scale. Furthermore, it allows for easy functionalization of the ligand. Introduction of the *t*-Bu moieties increases the solubility of the ligands and corresponding complexes. As a result **3bH** is soluble in common organic solvents, while **3aH** is soluble only in halogenated solvents but sparingly in other solvents.

Reaction of 3aH with [RuCl₃(tpy)] is only slightly selective toward the N, N', N''-coordinating side. As a result, a mixture of several complexes was obtained, but the desired product $[4aH]^{2+}$ could be isolated by repeated column chromatography. Reaction with **3bH** is more selective, probably as a result of the decreased reactivity of the potentially cyclometalating moiety by steric interference, electronic effects on the coordinating nitrogen, or changed acidity of the C-H bond. The bimetallic compounds could be obtained by reaction of the monometallic complexes with the appropriate ruthenium precursor. Fast and effective reactions could be achieved using μ -wave-assisted heating in a closed vessel. Whereas the unsubstituted $[5a]^{3+}$ is rather insoluble in MeCN and its ${}^{13}C$ NMR spectrum could be obtained only in DMSO- d_6 , the *t*-Bu- and ester-substituted $[6b]^{3+}$ are highly soluble in MeCN, acetone, and CH_2Cl_2 . Deprotection of $[6a]^{3+}$ resulted in the formation of a dark solid that is insoluble in common organic solvents. After deprotection of the ester moieties in $[6b]^{3+}$ to



Figure 4. Photocurrent action spectrum of $[H_28b](Cl)_2$ in a solidstate DSSC (squares). Normalized absorption spectra of $[H_x8b]^{x+}$ in DMSO in the presence of NaOH (black) or HCl (red).

the free carboxylates, the resulting complex, i.e., **[8b]**, is soluble in MeOH and DMSO, especially upon addition of two additional equivalents of aqueous HCl. Its identity and purity could be confirmed using ¹H and ¹³C NMR spectroscopy.

Electrochemical Data. It has already been put forward that care has to be taken in using localized descriptions of molecular orbitals and transitions in cyclometalated complexes,⁶⁰⁻⁶³ because orbitals formally associated with the metal center may have a significant component on the cyclometalated ligand and vice versa. However, the HOMOs are still well described as metal-based, and for ease of discussion we will continue to use terms associated with localized descriptions. The extra electron density at the ruthenium nucleus from the strong σ -donation of the anionic carbon places the oxidation potential of $[7a]^+$ at 700 mV less positive values than that of $[4aH]^{2+}$, similar to the negative shifts for the oxidation potential of other cyclometalated ruthenium complexes.^{36,53-55} Introduction of the t-Bu and CO₂Me moieties shifts the oxidation potential of the ruthenium center negatively and positively, respectively, in line with the respective Hammett⁶⁴ parameters $\sigma_p = -0.20$ and 0.45. Several reduction processes are observed that are assigned to successive reduction of the different tpy ligands in the complexes. In the dinuclear complexes $[5a]^{3+}$ - $[6b]^{3+}$ two successive and electrochemically reversible one-electron oxidation waves are observed, which are assigned to the stepwise oxidation of the two metal centers.

In symmetric, dinuclear metal complexes, splitting of the individual oxidation waves is usually taken as an indication

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of metal-metal interaction, although other effects may play a non-negligible role.^{65–67} In [{Ru(ttpy)}₂(μ -tpy-tpy)]⁴⁺ and $[{Ru(ttpy)}_2(\mu - N^{C^{N}}N - N^{C^{N}}N)]^{2+}$ (ttpy = 4'-tolyl-2.2':6'.2''-terpyridine) the separation between the two oxidation waves is 70 and 170 mV, respectively, and the IVCT band is indeed much stronger in the latter.^{41,42,68} Delocalization of the metal states over the cyclometalated bridging ligand increases the electronic communication between the metal centers. In unsymmetric complexes, the redox asymmetry ($\Delta E_{1/2}(ox)$) hampers direct determination of the interaction-induced splitting between the respective redox waves. The difference between the two waves in $[5a]^{3+}$ is smaller than the difference observed between the oxidation potentials of $[4aH]^{2+}$ and $[7a]^+$. This is a result of the positive shift of the oxidation potential of the cyclometalated ruthenium moiety upon coordination of the tpy moiety on the bridging ligand.

Near-Infrared Spectra. Upon one-electron oxidation of the bimetallic complexes $[5a]^{3+}$ - $[6b]^{3+}$, the MLCT feature is partly diminished, with the remaining MLCT band very akin to the band observed for the mononuclear complexes $[4aH]^{2+}$ and $[4bH]^{2+}$. This corresponds with an initial anodic step localized on the cyclometalated ruthenium center. The new low-energy transition is assigned IVCT character. It has to be noted that the term IVCT is strictly speaking not applicable to unsymmetric systems, where the diabatic states are of different energy. But we will continue to use the term for ease of discussion. As a result of the redox asymmetry, the IVCT bands are observed at increased energy compared to that observed for the redox symmetric analogues. The redox asymmetry $\Delta E_{1/2}(ox)$ as obtained from CV data can be used to estimate the theoretical bandwidth with the Hush formula. All observed bandwidths are larger than the calculated values, which indicates localized Robin-Day class II behavior.²⁸ The IVCT NIR band is therefore expected to possess significant charge transfer character, which should result in strong solvent dependence of the energy of this excitation. Indeed, the low-energy absorption feature is solvatochromic. However, the energy shift of this transition can also be ascribed to the dependence of $\Delta E_{1/2}(ox)$ on the solvent.

Extreme care has to be taken in using DFT for extended binuclear systems, as DFT often results in artificial overestimation of delocalization.^{69–71} The energy of CT excitations can be strongly underestimated by TD-DFT, especially for weakly interacting systems.⁷¹ Additionally, spurious charge transfer states might be present. Indeed, for [**5a**]³⁺ two strong excitations are predicted around 680 nm, viz., at lower energy than the main experimental MLCT features. These transitions are assigned large CT character from the cyclometalated ruthenium to the tpy moiety of the bridging ligand, which is unlikely to be a transition of high intensity. However, even with the tendency of DFT toward delocalization, the metal levels are localized on the individual ruthenium centers. *In silico* one-electron oxidation results in a LUSO associated with the cyclometalated ruthenium center and HOSOs associated with the second metal center. These results corroborate metal-based initial and secondary oxidation processes. The predicted strong NIR transition for the one-electron-oxidized $[5a]^{4+}$ at 1060 nm is assigned metal-to-metal charge transfer character with some involvement of the bridging ligand. For all the uncertainty involved in applying TD-DFT in this fashion, this excitation supports the experimental assignment of the absorption as an unsymmetric class II IVCT transition.

Photoelectrochemical Experiments. A simple DSSC was constructed to investigate some of the sensitizing properties of the dinuclear dye [8b]. With the dye complex attached to the TiO₂ surface, many individual processes can occur. Upon absorption of the first photon, either dye moiety D1 or D2 is excited, eqs 1 and 2, respectively. D1 represents the cyclometalated moiety of [8b], D2 the $[Ru(tpy)_2]^{2+}$ moiety, and HTM the hole transfer medium. As dye moiety D1 is directly attached to the TiO₂ surface, electron injection into the TiO₂ conduction band (CB) from its excited state is fast, eq 3. Direct electron injection from the second dye moiety D2 can also occur, reaction 4. It has previously been demonstrated that in a $[{RuCl(dcbpy)_2}BL{OsCl(bpy)_2}]^{2+}$ (dcbpy = 4,4'dicarboxyl-2,2'-bipyridine, BL = 1,2-bis(4-pyridyl)ethane) direct electron transfer from the osmium moiety to the TiO₂ conduction band occurred, eq 4, mediated by the flexible BL that allows proximity to the surface.¹⁸ Direct electron transfer is unlikely to occur in [8b], as the D2 moiety is remote from the surface and, moreover, efficient energy transfer can occur to the D1 moiety, eq 5. After excitation transfer, the dye moiety D1 can inject an electron into the TiO_2 CB.

 $TiO_2-D1-D2-HTM + h\nu \rightarrow TiO_2-D1^*-D2-HTM \quad (1)$

 $TiO_2-D1-D2-HTM + h\nu \rightarrow TiO_2-D1-D2*-HTM \qquad (2)$

 $TiO_2-D1^*-D2-HTM \rightarrow TiO_2(e^-)-D1^+-D2-HTM \qquad (3)$

$$TiO_2-D1-D2^*-HTM \rightarrow TiO_2(e^-)-D1-D2^+-HTM \qquad (4)$$

 $TiO_2-D1-D2^*-HTM \rightarrow TiO_2-D1^*-D2-HTM \qquad (5)$

The thus formed TiO₂(e⁻)-D1⁺-D2-HTM can undergo several processes. Depending on the redox level of the HTM, D1 can be directly regenerated, eq 6. Spiro-MeOTAD was used as hole-conductor material, as with its oxidation potential of $E_{1/2}(\text{ox1}) = 0.11 \text{ V}$ and $E_{1/2}(\text{ox2}) = 0.23 \text{ V}$ in CH₂Cl₂⁷² only a small driving force is present for regeneration of the primary dye $[6b]^{2+}$ with $E_{1/2}(\text{ox1}) = 0.32$ V vs Fc/ Fc^+ , which should thus be slow. Additionally to the small driving force, the D1 moiety is shielded from the solid-state HTM by D2, further slowing direct regeneration according to eq 6. However, in the current setup direct regeneration cannot be excluded as the main transfer pathway to regenerate D1. Future investigations will focus on alternative HTM materials that could utilize the potential increase in open circuit voltage as well as time-resolved data that could clarify the time-scale of each of these processes.

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As demonstrated by the solution experiments, when D1 is oxidized, the MLCT features of the D2 moiety remain and this group can absorb another photon to form the excited state $TiO_2(e^-)-D1^+-D2^*-HTM$. Excited-state electron transfer can now occur, as D2* is a stronger reductant than both D1 and D2, thus forming $TiO_2(e^-)-D1-D2^+-HTM$, eq 7. Perhaps a more interesting process is the direct regeneration of D1 by optical electron transfer from D2, eq 8, which corresponds to the metal-to-metal charge transfer transition that was demonstrated in solution and occurs around 1000 nm (i.e., at energies below the threshold assumed for conventional sensitizers).

$$TiO_2(e^-)-D1^+-D2-HTM \rightarrow TiO_2(e^-)-D1-D2-HTM^+$$
(6)

$$TiO_{2}(e^{-})-D1^{+}-D2^{-} HTM + h\nu \rightarrow TiO_{2}(e^{-})-D1^{+}-D2^{*}$$
$$- HTM \rightarrow TiO_{2}(e^{-})-D1-D2^{+}- HTM$$
(7)

$$TiO_2(e^-)-D1^+-D2^- HTM + h\nu$$

$$\rightarrow TiO_2(e^-)-D1-D2^+ - HTM \qquad (8)$$

The TiO₂(e⁻)-D1-D2⁺-HTM state can either be regenerated by the electrolyte according to eq 9 or can relax back to the TiO₂(e⁻)-D1⁺-D2-HTM state, eq 10. Additionally, back electron transfer from the TiO₂ CB to either the D1⁺ or D2⁺ cation or to the HTM itself (eqs 11–13) can occur, which is generally a slow process, especially when the distance between the surface and the cation is increased.

$$\text{TiO}_2(e^-)-\text{D1}-\text{D2}^+-\text{HTM} \rightarrow \text{TiO}_2(e^-)-\text{D1}-\text{D2}-\text{HTM}^+$$
 (9)

$$TiO_2(e^-)-D1-D2^+-HTM \rightarrow TiO_2(e^-)-D1^+-D2-HTM$$
 (10)

$$\text{TiO}_2(\text{e}^-)$$
-D1⁺-D2–HTM \rightarrow TiO₂-D1-D2–HTM (11)

 $TiO_2(e^-)-D1-D2^+-HTM \rightarrow TiO_2-D1-D2-HTM$ (12)

$$TiO_2(e^-)-D1-D2-HTM^+ \rightarrow TiO_2-D1-D2-HTM$$
 (13)

It should be noted that the IPCE curve is measured monochromatically and is sensitive only to photons of sufficient energy to produce current. In this aspect, no IPCE is expected for the low-energy absorption feature, as no pathway is available in which photons of this energy inject electrons, and photons of higher energy are essential to produce current. Also in efficiency measurements, no upconversion process would be measurable, as no wavelengthdependent information is available. Direct regeneration of D1 by the electrolyte according to eq 6 is probably a slow process, resulting in low efficiency. Thus, no direct evidence is available that the two-photon process as proposed in Figure 1 is operational in the cell. However, the individual processes that are necessary for such a scheme have been demonstrated in a single bimetallic cyclometalated complex. Additional tests that allow, for instance, time-resolved observation of the stepwise processes are necessary. Also IPCE determination under bias illumination (in the presence of photons of sufficiently low energy) would be instrumental in the analysis. Obviously, tuning of the electronic interaction between the metal centers and the respective oxidation potentials can be achieved by modification of the bridging and peripheral ligands in the dinuclear complex. Such adaptations can have a tremendous influence on the rate or intensity of the absorption associated with the individual processes. For instance, decreasing the electronic coupling will decrease the intensity of the NIR band associated with eq 8, but will also decrease the rate of eq 10, viz., the corresponding back electron transfer. Tuning of these levels, as well as further decreasing the position of the HTM level, is necessary to use the low-energy photons in this fashion to increase the open circuit voltage in dye-sensitized solar cells.

Conclusion

We have prepared a series of redox asymmetric diruthenium complexes using the monocyclometalating bridging ligand $N^{C}(H)^{N-tpy}$ and its *t*-Bu-substituted analogue. The *t*-Bu moieties ensure higher solubility of the ligand and the corresponding complexes and increase the selectivity of formation of the mononuclear nonmetalated complex. Subsequent cyclometalation could be performed by direct C-H activation in methanol using μ -wave-assisted heating. The bimetallic complexes undergo reversible metal localized first and second oxidation processes. Cyclometalation induces strong redox asymmetry by positively shifting the electrode potential of the oxidation of the affected ruthenium center. The visible electronic absorption spectra are dominated by strong MLCT features, resulting from the presence of many different transitions. One-electron oxidation into the mixed valence state diminishes the visible absorption band, while the MLCT features of the nonmetalated moiety are preserved. Additionally, a strong NIR absorption band arises that is associated with a metal-to-metal charge transfer transition. The localized nature of the oxidation processes, the shape of the NIR band, and TD-DFT calculations allow assignment of these systems as Robin-Day class II. Initial tests in a solid-state DSSC indicate that the proposed twophoton process could be operational, but no direct evidence was obtained and additional tests are necessary. As it stands, the asymmetric dinuclear ruthenium compound described here represents the first model for a sensitizer for an upconversion scheme in DSSCs that could greatly increase the maximum theoretical efficiency of these solar cells.

Experimental Section

General Procedures. All air-sensitive reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Absolute solvents were dried over appropriate drying agents and distilled before use. All other solvents and reagents were purchased and used as received. Microwave reactions have been carried out in an Ethos Sel microwave solvent extraction labstation using closed pressure vessels. The temperature was controlled via a reference vessel containing the same amount of solvent but no reactants. ¹H and ${}^{13}C{}^{1}H{}$ NMR spectra were recorded at 298 K on a Varian 300 MHz Inova spectrometer and on a Varian 400 MHz NMR system. NMR spectra were referenced to the solvent residual signal.⁷³ Spectral assignments were based on chemical shift and integral considerations as well as COSY and NOESY two-dimensional experiments. Elemental analyses were carried out by Kolbe Mikroanalytisches Laboratorium (Mülheim an der Ruhr, Germany). 1-(2-Oxo-2(pyridin-2-yl)ethyl)pyridinium iodide,⁷⁴

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Electronic Spectroscopic Measurements and Electrochemical Experiments. Solution UV-vis spectra were recorded on a Cary 50 Scan UV-vis spectrophotometer or on a Cary 5 UVvis-NIR spectrophotometer. Chemical oxidation of samples was performed by titration with freshly prepared concentrated solutions of [Ce(NO₃)₆](NH₄)₂ in MeCN or SbCl₅ in CH₂Cl₂. Cyclic voltammograms were recorded in a single compartment cell under a dry nitrogen atmosphere. The cell was equipped with a Pt microdisk working electrode, a Pt wire auxiliary electrode, and a Ag/AgCl wire pseudoreference electrode. The working electrode was polished with alumina nanopowder between scans. The potential control was achieved with a PAR model 263A potentiostat. All redox potentials are reported against the ferrocene-ferrocenium (Fc/Fc⁺) redox couple used as an internal standard.^{77,78} All electrochemical samples were 10^{-1} M in [n-Bu₄N]PF₆ as the supporting electrolyte in MeCN distilled over $KMnO_4$ and Na_2CO_3 or in CH_2Cl_2 distilled over CaH_2 .

DFT Calculations. DFT calculations were performed at the DZ Dunning^{79,80} level of theory for carbon, nitrogen, and hydrogen and using the Stuttgart RSC 1997 ECP relativistic core potential⁸¹ for ruthenium using the B3LYP functional. Geometries were optimized using the Gamess UK⁸² program package. Subsequent TD-DFT calculations were run on the optimized geometry at the same level of theory using the Gaussian version 03 program package.⁸³ Isovalue plots of the frontier molecular orbitals were made using MOLDEN.⁵⁶

Syntheses. (*E*)-3-(3,5-Dibromophenyl)-1-(pyridin-2-yl)prop-2-en-1-one. A solution of 3,5-dibromobenzaldehyde (9.4 g, 36 mmol) and 2-acetylpyridine (4.0 mL, 36 mmol) in MeOH (400 mL) was treated with an aqueous NaOH solution (4 M, 13 mL, 42 mmol), and the resulting mixture stirred at room temperature for 1 h. The suspension was filtered, and the product isolated with CH₂Cl₂ (100 mL), washed with H₂O (100 mL), dried over MgSO₄, and evaporated *in vacuo*. The product was obtained as a white solid (10.4 g, 80%). ¹H NMR (400 MHz, CDCl₃): δ 8.75 (d, 1H, ³J = 4.8 Hz, Ar'⁶H), 8.27 (d, 1H, ³J = 16.0 Hz, CH), 8.17 (d, 1H, ³J = 8.0 Hz, Ar'³H), 7.88 (dd, 1H, ³J = 8.0 Hz, ³J = 7.6, Ar'⁴H), 7.76 (d, 2H, ⁴ = 1.6, Ar²H), 7.72 (d, 1H, ³J = 16 Hz,

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4'-(3,5-Dibromophenyl)-2,2':6',2"-terpyridine, 1. A suspension of (E)-3-(3,5-dibromophenyl)-1-(pyridin-2-yl)prop-2-en-1-one (10.4 g, 28 mmol), 1-(2-oxo-2(pyridin-2-yl)ethyl)pyridinium iodide (14.6 g, 45 mmol), and NH₄OAc (29.7 g, 385 mmol) in MeOH (400 mL) was heated under reflux for 20 h. The mixture was diluted with H₂O (200 mL) and filtered. The product was isolated with CH₂Cl₂, washed with aqueous NaOH (0.2 M, 100 mL), dried over MgSO₄, filtered, and evaporated in vacuo, yielding the product as a white solid (12.3 g, 94%). ¹H NMR $(400 \text{ MHz}, \text{CDCl}_3)$: $\delta 8.72 (d, 2H, {}^3J = 4.8 \text{ Hz}, \text{F6}), 8.65 (d, 2H, 32)$ ${}^{3}J = 8.0$ Hz, F3), 8.62 (s, 2H, E3,5), 7.96 (s, 2H, D2,6), 7.89 (dd, 2H, ${}^{3}J = 8.0$ Hz, ${}^{3}J = 7.6$ Hz, F4), 7.74 (s, 1H, D4), 7.37 (dd, 2H, ${}^{3}J = 7.6 \text{ Hz}, {}^{3}J = 4.8 \text{ Hz}, \text{ F5}.$ ${}^{13}\text{C} \text{ NMR} (100 \text{ MHz}, \text{CDCl}_3): \delta$ 156.4, 155.9, 149.3, 147.8, 142.3, 137.3, 134.6, 129.4, 124.4, 123.8, 121.7, 118.9. Anal. Calcd for C₂₁H₁₃Br₂N₃: C, 53.99; H, 2.80; N, 8.99. Found: C, 54.10; H, 2.86; N, 9.05.

(4-tert-Butylpyridin-2-yl)tributylstannane, 2b. A solution of N,N-dimethylethanolamine (9.0 mL, 90 mmol) in hexane (200 mL) was treated with *n*-BuLi (1.6 M in hexane, 112.5 mL, 180 mmol) at 0 °C. The mixture was stirred for 20 min, 4-tertbutylpyridine (8.8 mL, 60 mmol) was added, and the mixture was stirred for 1 h. After cooling to $-70 \,^{\circ}\text{C}$, SnCl(*n*-Bu)₃ (90%) pure, 37 mL, 120 mmol) was added, and the mixture was allowed to warm to room temperature and stirred for 2 h. The reaction was quenched with aqueous NH₄Cl, the phases were separated, and the aqueous phase was extracted with Et₂O (100 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated in vacuo, yielding the product (48 g, 188%, Sn(n-Bu)₄ present as impurity) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 8.62 (d, 1H, ³J = 5.2 Hz, Ar⁶H), 7.37 (s, 1H, $Ar^{3}H$), 7.10 (d, 1H, ${}^{3}J = 5.2$ Hz, $Ar^{5}H$), 0.70–1.60 (m, 36H, n-Bu + t-Bu).

4'-(3,5-Di(2-pyridinyl)phenyl)-2,2':6',2''-terpyridine, 3aH. A suspension of 1 (3.6 g, 7.7 mmol), tributyl-2-pyridylstannane (17.5 g, 31 mmol), LiCl (3.1 g, 74 mmol), and Pd(PPh₃)₄ (0.5 g, 0.4 mmol) in toluene (80 mL) was degassed and heated under reflux for 24 h. An aqueous solution of KF was added, the resulting mixture was filtered over Celite, and the solids were washed with CH₂Cl₂. The combined organic fractions were dried over K_2CO_3 , and concentrated *in vacuo*. The product was purified by washing with pentane $(3 \times 50 \text{ mL})$ and toluene (30 mL), yielding the product as a white solid (3.16 g, 89%). ¹H NMR (400 MHz, CDCl₃): δ 8.97 (s, 2H, E3,5), 8.77–8.83 (m, 5H, D4 + C3 + C6), 8.63 (s, 2H, D2,6), 8.02 (d, 2H, ${}^{3}J = 8.0$ Hz, F3), 7.94 (dd, 2H, ${}^{3}J = 8.0$ Hz, ${}^{3}J = 7.6$ Hz, C4), 7.86 (dd, 2H, ${}^{3}J = 8.0$ Hz, ${}^{3}J =$ 7.6 Hz, F4), 7.39–7.43 (m, 4H, C5 + F6), 7.33 (d, 2H, ${}^{3}J$ = 7.6 Hz, ${}^{3}J$ = 5.2 Hz, F5). 13 C NMR (100 MHz, CDCl₃): δ 157.0, 156.4, 156.1, 150.6, 149.9, 149.2, 140.9, 140.1, 137.2, 137.1, 126.8, 126.5, 124.1, 122.8, 121.7, 121.4, 119.6.

4'-(3,5-Di(4-*tert*-butylpyridin-2-yl)phenyl)-2,2':6',2''-terpyridine, 3bH. A suspension of 1 (5.0 g, 11 mmol), 2b (40.6 g, 30 mmol, Sn(*n*Bu)₄ present), LiCl (5.4 g, 127 mmol), and Pd(PPh₃)₄ (0.9 g, 0.8 mmol) in degassed toluene (100 mL) was heated under reflux for 3 days. After cooling to room temperature, an aqueous solution of KF (20 mL) was added, the mixture was filtered, the phases were separated, and the aqueous phase was extracted with CH₂Cl₂ (100 mL) and concentrated *in vacuo*. The product was purified by column chromatography on SiO₂ (hexane/ethyl acetate, 9:1) and Al₂O₃ (hexane/ethyl acetate, 9:1), yielding the product as a white solid (1.4 g, 23%). ¹H NMR (400 MHz, C₆D₆): δ 9.30 (s, 2H, E3,5), 9.28 (s, 1H, D4), 8.88 (s, 2H, D2,6), 8.68 (d, 2H, ³J = 8.0 Hz, F3), 8.59 (d, 2H, ³J = 5.2 Hz, C6), 8.52 (d, 2H, ³J = 5.2 Hz, F6), 7.91 (s, 2H, C3), 7.34 (dd, 2H, ³J = 8.0 Hz, ³J = 7.6 Hz, F4), 6.85 (d, 2H, ³J = 5.2 Hz, C5), 6.77 (dd, 2H, ³J = 7.6 Hz, ³J = 5.2 Hz, F5), 1.05 (s, 18H, *t*-Bu). ¹³C NMR (100 MHz, C₆D₆): δ 160.3, 157.3, 156.6, 156.4, 150.8, 150.0, 149.3, 141.7, 140.4, 136.3, 126.9, 126.7, 123.5, 121.2, 119.8, 119.6, 117.6, 34.5, 30.3. Anal. Calcd for $C_{39}H_{37}N_5$: C, 81.36; H, 6.48; N, 12.16. Found: C, 81.25; H, 6.43; N, 12.18.

 $[Ru(3aH)(tpy)](PF_6)_2$, $[4aH](PF_6)_2$. A suspension of $[RuCl_3-$ (tpy)] (164 mg, 0.37 mmol) and AgBF₄ (275 mg, 1.41 mmol) in acetone (50 mL) was heated under reflux for 2 h. After filtration over Celite, the solvent was removed in vacuo. The mauve solid was dissolved in EtOH (150 mL), a solution of 3aH (174 mg, 0.37 mmol) in CH₂Cl₂ (40 mL) was added, and the solution was heated under reflux for 2 h. The product was precipitated by addition of an aqueous KPF₆ solution. The product was purified by column chromatography on SiO₂ (MeCN/aqueous 0.5 M NaNO₃, 9:1, v/v) and on Al₂O₃ (MeCN:/toluene, 1:1, v/v), during which $[7a]^+$ was isolated as a side product. The product was precipitated from MeCN with ethyl acetate, yielding the product as an orange solid (76 mg, 19%). ¹H NMR (400 MHz, CD₃CN): δ 9.15 (s, 2H, E3,5), 9.05 (s, 1H, D4), 8.91 (s, 2H, D2,6), 8.79 (d, 2H, ${}^{3}J = 8.0$ Hz, H3,5), 8.77 (br, 2H, C6), 8.68 (d, 2H, ${}^{3}J = 8.0$ Hz, F3), 8.53 (d, 2H, ${}^{3}J = 8.0$ Hz, G3), 8.45 (t, 1H, ${}^{3}J = 8.0$ Hz, G3), 8.45 (t, 1H, J = 8.0 Hz, H4), 8.27 (d, 2H, ${}^{3}J = 8.0$ Hz, C3), 8.02 (dd, 2H, ${}^{3}J = 8.0$ Hz, ${}^{3}J = 6.0$ Hz, C4), 7.94–7.98 (m, 4H, F4+G4), 7.53 $(d, 2H, {}^{3}J = 5.2 \text{ Hz}, G6), 7.46 (dd, 2H, {}^{3}J = 6.0 \text{ Hz}, {}^{3}J = 4.4 \text{ Hz},$ C6), 7.3 (d, 2H, ${}^{3}J = 6.2$ Hz, F6), 7.19–5.25 (m, 4H, F5+G5). ¹³C NMR (100 MHz, CD₃CN): δ 159.2, 159.1, 156.7, 156.5, 156.4, 153.5, 153.4, 150.8, 149.1, 142.5, 139.2, 139.1, 139.0, 138.4, 136.8, 128.5, 128.4, 127.8, 127.6, 125.9, 125.4, 124.7, 124.3, 123.0, 121.9. Anal. Calcd for C₄₆H₃₂F₁₂N₈P₂Ru: C, 50.79; H, 2.97; N, 10.30. Found: C, 50.71; H, 2.91; N, 10.29.

[**Ru(3a)(tpy)**](**PF**₆), [**7a**](**PF**₆). ¹H NMR (400 MHz, acetone-*d*₆): δ 9.15 (s, 2H, E3,5), 9.04 (d, 2H, ³*J* = 8.0 Hz, A3,5), 8.93 (s, 2H, D3,5), 8.87 (d, 2H, ³*J* = 8.0 Hz, F3), 8.84 (d, 2H, ³*J* = 4.8 Hz, F6), 8.71 (d, 2H, ³*J* = 8.0 Hz, B3), 8.57 (d, 2H, ³*J* = 8.0 Hz, C3), 8.43 (t, 1H, ³*J* = 8.0 Hz, A4), 8.09 (dd, 2H, ³*J* = 8.0 Hz, ³*J* = 7.6 Hz, F4), 7.85 (dd, 2H, ³ = 7.6 Hz, ³*J* = 7.6 Hz, B4), 7.76 (dd, 2H, ³*J* = 7.6 Hz, ³*J* = 6.4 Hz, C4), 7.56 (dd, 2H, ³*J* = 7.6 Hz, ³*J* = 4.8 Hz, F5), 7.37 (d, 2H, ³*J* = 7.2 Hz, B6), 7.28 (d, 2H, ³*J* = 6.8 Hz, C6), 7.15 (dd, 2H, ³*J* = 7.6 Hz, ³*J* = 68 Hz, B5), 6.82 (dd, 2H, ³*J* = 7.2 Hz, ³*J* = 6.4 Hz, C5). ¹³C NMR (100 MHz, CD₃CN): δ 225.8, 169.4, 160.0, 157.2, 157.1, 155.4, 153.7, 152.9, 152.8, 150.3, 143.8, 138.2, 136.6, 136.2, 133.3, 131.5, 127.3, 125.2, 124.5, 123.3, 123.1, 122.8, 122.1, 120.9, 119.4.

[Ru(3bH)(tpy)](PF₆)₂, [4bH](PF₆)₂. A suspension of [RuCl₃-(tpy)] (105 mg, 0.24 mmol), **3bH** (75 mg, 0.12 mmol), and AgBF₄ (160 mg, 0.82 mmol) in MeOH (40 mL) was heated under reflux for 20 h. After cooling, the orange solution was filtered over Celite, and the product was precipitated by addition of aqueous KPF₆ and removal of the MeOH in vacuo. The product was purified by column chromatography on SiO₂ (MeCN/aqueous 0.5 M NaNO_3 , 9:1, v/v) and on Al₂O₃ (MeCN/toluene, 1:1, v/v), yielding the product as an orange solid (81 mg, 56%). ¹H NMR (400 MHz, CD₃CN): δ 9.06 (s, 2H, E3,5), 8.98 (t, 1H, ⁴J = 1.6 Hz, D4), 8.91 (d, 2H, ⁴J = 1.6 Hz, D2,6), 8.80 (d, 2H, ³J = 8.0 Hz, H3,5), 8.50-8.58 (m, 6H, F3+C6+G3), 8.46 (t, 1H, ³J = 8.0 Hz, H4), 8.22 (d, 2H, ${}^{4}J = 1.6$ Hz, C3), 7.98 (dd, 2H, ${}^{3}J = 8.0$ Hz, ${}^{3}J = 8.0$ Hz, F4), 7.90 (dd, 2H, ${}^{3}J = 8.0$ Hz, ${}^{3}J = 7.6$ Hz, G4), 7.65 (d, 2H, ${}^{3}J = 5.6$ Hz, F6), 7.38–7.44 (m, 4H, C5+G6), 7.29 (dd, 2H, ${}^{3}J = 8.0$ Hz, ${}^{3}J = 5.6$ Hz, F5), 7.20 (dd, 2H, ${}^{3}J = 7.6$ Hz, ${}^{3}J = 5.6$ Hz, G5), 1.44 (s, 18H, *t*-Bu). 13 C NMR (100 MHz, CD₃CN): δ 162.5, 159.1, 159.1, 156.9, 156.4, 156.3, 153.5, 153.5, 150.7, 149.2, 142.4, 139.2, 139.1, 139.0, 136.8, 128.5, 128.4, 128.0, 127.9, 125.4, 125.4, 124.7, 123.1, 121.4, 119.0, 35.8, 30.8. Anal. Calcd for C54H48F12N8P2Ru: C, 54.05; H, 4.03; N, 9.34. Found: C, 54.00; H, 4.10; N, 9.29.

 $[Ru_2(\mu-3a)(tpy)_2](PF_6)_2$, $[5a](PF_6)_3$. A mixture of $[RuCl_3(tpy)]$ (143 mg, 0.32 mmol) and AgBF₄ (211 mg, 1.08 mmol) in acetone (30 mL) was heated under reflux for 2 h. The mixture was filtered over Celite, and the solvent was removed *in vacuo*. The mauve solid was dissolved in *n*-BuOH (20 mL), and **3aH** (50 mg, 0.11 mmol) was added. The mixture was heated under reflux for 20 h. The solvent was removed *in vacuo*, and the dark solid was

dissolved in MeCN (50 mL) and precipitated by addition of aqueous KPF₆ and removal of MeCN. The product was purified by column chromatography on SiO₂ (MeCN/aqueous 0.5 M NaNO₃, 9:1, v/v), yielding the product as a dark purple solid (98 mg, 58%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.76 (s, 2H, E3,5), $\begin{array}{l} \text{m}_{23}, \text{s}, \text{o}, \text{o}) & \text{m}_{11}, \text{m}_{11}, \text{c}(\text{tot} \text{m}_{11}, \text{p}_{13}, \text{m}_{16}, \text{o}), \text{o}, \text{$ ${}^{3}J = 8.0$ Hz, B3), 8.55 (t, 1H, ${}^{3}J = 8.0$ Hz, H4), 8.45 (t, 1H, ${}^{3}J =$ 8.0 Hz, A4), 8.13 (dd, 2H, ${}^{3}J = 8.0$ Hz, ${}^{3}J = 7.6$ Hz, F4), 8.06 $(dd, 2H, {}^{3}J = 8.0 Hz, {}^{3}J = 7.6 Hz, G4), 7.82-7.90 (m, 4H, B4 +$ C4), 7.63 (d, 2H, ${}^{3}J = 5.6$ Hz, G6), 7.49 (d, 2H, ${}^{3}J = 5.2$ Hz, F6), 7.30–7.38 (m, 4H, B6 + C6), 7.10–7.20 (m, 6H, B5 + F5 + G5), 6.90 (dd, 2H, ${}^{3}J$ = 7.6 Hz, ${}^{3}J$ = 5.2 Hz, C5). 13 C NMR (100 MHz, dmso-*d*₆): δ 228.6, 168.4, 159.4, 159.0, 158.7, 155.7, 155.6, 154.3, 153.0, 152.8, 152.7, 152.4, 149.8, 143.5, 138.8, 138.7, 136.4, 136.3, 133.9, 128.5, 128.4, 128.2, 127.4, 125.3, 125.2, 124.8, 124.7, 123.5, 123.3, 122.8, 121.0, 120.9. One additional resonance could not be resolved.

 $[Ru_2(\mu-3b)(tpy)_2](PF_6)_2$, $[5b](PF_6)_3$. A mixture of $[4bH](PF_6)_2$ (33 mg, 0.025 mmol) and [RuCl₃(tpy)] (29 mg, 0.066 mmol) was suspended in ethylene glycol (25 mL) and heated to 150 °C for 30 min using μ -wave radiation in a closed vessel. The product was precipitated by addition of aqueous KPF₆, filtered, and collected with MeCN. The product was purified by column chromatography on SiO₂ (MeCN/aqueous 0.5 M NaNO₃, 9:1, v/v) and recrystallized from MeCN and H₂O, yielding the product as a purple solid (28 mg, 67%). ¹H NMR (400 MHz, CD₃CN),: δ 9.44 (s, 2H, E3,5), 9.12 (s, 2H, D3,5), 8.88 (d, 2H, ${}^{3}J = 8.0$ Hz, F3), 8.83 (d, 2H, ${}^{3}J = 8.0$ Hz, A3,5), 8.82 (d, 2H, ${}^{3}J = 8.0$ Hz, H3,5), 8.57 (d, 2H, ${}^{3}J = 8.0$ Hz, G3), 8.55 (d, 2H, ${}^{4}J = 1.2$ Hz, C3), 8.51 (d, 2H, ${}^{4}J = 1.2$ Hz, B3), 8.47 (t, 1H, ${}^{3}J =$ 8.0 Hz, H4), 8.35 (t, 1H, ${}^{3}J = 8.0$ Hz, A4), 8.06 (dd, 2H, ${}^{3}J = 8.0$ Hz, ${}^{3}J = 8.0$ Hz, F4), 8.00 (dd, 2H, ${}^{3}J = 8.0$ Hz, ${}^{3}J = 8.0$ Hz, G4), 7.79 (dd, 2H, ${}^{3}J = 8.0$ Hz, ${}^{3}J = 7.6$ Hz, B4), 7.60 (d, 2H, ${}^{3}J = 4.8$ Hz, G6), 7.44 (d, 2H, ${}^{3}J = 5.6$ Hz, F6), 7.23–7.30 (m, 6H, B6+G5+F5), 7.06 (d, 2H, ${}^{3}J = 6.8$ Hz, C6), 7.05 (dd, 2H, ${}^{3}J = 7.6$ Hz, ${}^{3}J = 5.6$ Hz, B5), 6.85 (dd, 2H, ${}^{3}J = 6.8$ Hz, ${}^{4}J = 6.8$ Hz, ${}^{$ 1.2 Hz, C5), 1.38 (s, 18H, t-Bu). ¹³C NMR (100 MHz, CD₃CN): δ 228.7, 168.9, 161.4, 160.0, 159.5, 159.2, 156.5, 156.3, 155.0, 153.5, 153.5, 153.2, 152.3, 151.3, 148.7, 143.0, 139.1, 139.0, 136.7, 136.4, 133.6, 129.5, 128.6, 128.4, 127.3, 125.6, 125.5, 124.7, 123.5, 123.2, 122.1, 120.7, 118.4, 35.8, 30.7. Anal. Calcd for C₆₉H₅₈F₁₈N₁₁O₆P₃Ru₂·2H₂O: C, 48.34; H, 3.65; N, 8.99. Found: C, 48.78; H, 3.75; N, 8.62.

 $[Ru_2(\mu-3a)((MeO_2C)_3-tpy)(tpy)](PF_6)_3, [6a](PF_6)_3$. A mixture of [4aH](PF₆)₂ (16.0 mg, 0.015 mmol) and [RuCl₃((MeO₂C)₃tpy)] (19 mg, 0.031 mmol) was suspended in MeOH (25 mL) and heated to 97 °C in a closed vessel for 30 min using μ -wave radiation. The product was precipitated by addition of aqueous KPF₆, filtered, and collected with MeCN. The product was purified by column chromatography on SiO₂ (MeCN/aqueous 0.5 M NaNO₃, 9:1, v/v) and recrystallized from MeCN with Et_2O , yielding the product as a purple solid (23 mg, 90%). ¹H NMR (400 MHz, CD₃CN): δ 9.50 (s, 2H, A3,5), 9.44 (s, 2H, E3,5), 9.16 (s, 2H, D3,5), 9.10 (s, 2H, B3), 8.89 (d, 2H, ${}^{3}J = 8.0$ Hz, F3), 8.82 (d, 2H, ${}^{3}J = 8.0$ Hz, H3,5), 8.59 (d, 2H, ${}^{3}J = 4.4$ Hz, G3), 8.57 (d, 2H, ${}^{3}J = 4.4$ Hz, C3), 8.47 (t, 1H, ${}^{3}J = 8.0$ Hz, H4), 8.05 (dd, 2H, ${}^{3}J = 7.6$ Hz, ${}^{3}J = 7.6$ Hz, F4), 7.99 (dd, 2H, ${}^{3}J = 7.6$ Hz, 3 7.2 Hz, C4), 7.54–7.60 (m, 6H, B5+B6+G6), 7.43 (d, 2H, ${}^{3}J =$ 6.0 Hz, F6), 7.23–7.29 (m, 4H, F5+G5), 7.04 (d, 2H, ${}^{3}J = 5.2$ Hz, C6), 6.78 (dd, 2H, ${}^{3}J = 7.6$ Hz, ${}^{3}J = 6.0$ Hz, C5), 4.25 (s, 3H, CO_2CH_3), 3.95 (s, 6H, CO_2CH_3). ¹³C NMR (100 MHz, CD₃CN): δ 224.7, 168.9, 166.2, 165.0, 160.6, 159.5, 159.2, 156.5, 155.8, 153.9, 153.6, 153.5, 153.4, 150.5, 143.9, 139.1, 137.8, 137.4, 136.6, 134.2, 130.8, 128.6, 128.4, 126.7, 125.6, 125.4, 124.7, 124.1, 123.9, 123.6, 123.5, 121.8, 121.6, 54.0, 53.8. Anal. Calcd for C₆₇H₄₈F₁₈N₁₁O₆P₃Ru₂: C, 46.24; H, 2.78; N, 8.85. Found: C, 45.20; H, 3.83; N, 8.88.

 $[Ru_2(\mu-3b)((MeO_2C)_3-tpy)(tpy)](PF_6)_3, [6b](PF_6)_3$. A mixture of [4bH](PF₆)₂ (57 mg, 0.047 mmol) and [RuCl₃(tpy)] (47 mg, 0.071 mmol) was suspended in MeOH (50 mL) and heated to 97 °C in a closed vessel for 30 min using μ -wave radiation. The product was precipitated by addition of aqueous KPF₆, filtered, and collected with MeCN. The product was purified by column chromatography on SiO₂ (MeCN/aqueous 0.5 M NaNO₃, 9:1, v/v) and recrystallized from MeCN with Et₂O, yielding the product as a purple solid (51 mg, 58%). ¹H NMR (400 MHz, CD₃CN): δ 9.50 (s, 2H, A3,5), 9.45 (s, 2H, E3,5), 9.15 (s, 2H, D3,5), 9.11 (s, 2H, B3), 8.89 (d, 2H, ³J = 4.4 Hz, F3), 8.83 (d, 2H, ³J = 4.4 Hz, F3), 8.58 (d, 2H, ³J = 4.4 Hz, G3), 8.55 (d, 2H, ³J = 4.4 Hz, C4), 8.48 (t, 1H, ³J = 4.4 Hz, H4), 8.06 (dd, 2H, ³J = 4.4 Hz, C4), 8.48 (t, 1H, ³J = 4.4 Hz, C4), 8.40 (dd, 2H, ³J = 4.4 Hz, C4), 8.48 (t, 1H, ³J = 4.4 Hz, C4), 8.40 (dd, 2H, ³J = 4.4 Hz, C4), 8.48 (t, 1H, ³J = 4.4 Hz, C4), 8.40 (dd, 2H, ³J = 4.4 Hz, C4), 8.48 (t, 1H, ³J = 4.4 Hz, C4), 8.40 (dd, 2H, ³J = 4.4 Hz, C4), 8.40 (dd, 2H, ³J = 4.4 Hz, C4), 8.41 (dd, 2H, ³J = 4.4 ${}^{3}J = 4.4 \text{ Hz}, {}^{3}J = 4.4 \text{ Hz}, \text{F4}), 8.00 (dd, 2H, {}^{3}J = 4.4 \text{ Hz}, {}^{3}J = 4.4 \text{ Hz}$ 4.4 Hz, G4), 7.56–7.61 (m, 6H, G6+B5+B6), 7.45 (d, 2H, ${}^{3}J =$ 4.4 Hz, F6), 7.24–7.30 (m, 4H, G5+F5), 6.89 (d, 2H, ${}^{3}J = 4.4$ Hz, G6), 6.79 (dd, 2H, ${}^{3}J = 4.4$ Hz, ${}^{3}J = 4.4$ Hz, C6), 4.25 (s, 3H, CO₂Me), 3.95 (s, 6H, CO₂Me), 1.35 (s, 18H, *t*-Bu). ${}^{13}C$ NMR (100 MHz, CD₃CN): δ 224.2, 168.5, 166.2, 165.0, 162.5, 160.6, 159.5, 159.2, 156.5, 156.4, 155.6, 153.8, 153.7, 153.3, 152.8, 150.8, 144.0, 139.1, 139.0, 137.3, 136.7, 133.7, 131.1, 128.6, 128.4, 126.6, 125.5, 125.4, 124.8, 124.0, 123.9, 123.6, 122.2, 120.9, 118.8, 53.9, 53.8, 35.9, 30.6. Anal. Calcd for C₇₅H₆₄F₁₈N₁₁O₆P₃Ru₂·7H₂O: C, 45.53; H, 3.97; N, 7.79. Found: C, 45.70; H, 4.24; N, 7.54.

[**Ru₂(\mu-3b)((⁻O₂C)₃-tpy)(tpy)], [8b].** A solution of [6b](PF₆)₃ (23 mg, 0,012 mg), H₂O (0.1 mL), and NEt₃ (0.1 mL) in MeCN (2 mL) was heated to 70 °C for 40 h. The resulting suspension was filtered, the solid was washed with acetone (1 mL), and the product was collected with MeOH. Concentration of the solution *in vacuo* yielded the product as a dark purple solid (13 mg, 78%). ¹H NMR (400 MHz, DMSO-*d*₆ in the presence of 2 equiv of aqueous HCl): δ 9.88 (s, 2H), 9.55 (s, 2H), 9.37 (s, 2H), 9.31

(d, 2H, ${}^{3}J = 8.0$ Hz), 9.16 (s, 2H), 9.11 (d, 2H, ${}^{3}J = 8.0$ Hz), 8.86 (d, 2H, ${}^{3}J = 8.0$ Hz), 8.69 (s, 2H), 8.53 (t, 1H, ${}^{3}J = 8.0$ Hz), 8.12 (dd, 2H, ${}^{3}J = 8.0$ Hz, ${}^{3}J = 7.6$ Hz), 8.06 (dd, 2H, ${}^{3}J = 8.0$ Hz, ${}^{3}J = 7.6$ Hz), 7.62 (d, 2H, ${}^{3}J = 5.2$ Hz), 7.58 (d, 2H, ${}^{3}J = 5.2$ Hz), 7.46 (d, 2H, ${}^{3}J = 5.6$ Hz), 7.30–7.40 (m, 6H), 6.93 (d, 2H, ${}^{3}J = 6.4$ Hz), 6.85 (d, 2H, ${}^{3}J = 6.4$ Hz), 1.28 (s, 18H). ${}^{13}C$ NMR (100 MHz, DMSO- d_6): δ 224.5, 167.3, 166.6, 165.3, 160.5, 159.2, 158.5, 158.1, 155.1, 155.0, 153.8, 152.3, 152.2, 152.0, 151.5, 149.9, 142.6, 140.9, 138.3, 135.9, 129.7, 128.0, 127.8, 126.2, 125.4, 124.8, 124.2, 123.6, 123.4, 122.9, 121.8, 120.2, 118.0, 35.1, 30.3. Two additional resonances could not be resolved.

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Supporting Information Available: Method description and results for DFT calculations on $[5a]^{3+}$ and $[5a]^{4+}$. This material is available free of charge via the Internet at http://pubs.acs.org.