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Synthesis and Electron Transfer Studies of Ruthenium–Terpyridine-Based Dyads Attached to Nanostructured TiO_2

Henriette Wolpher,[†] Subrata Sinha,[‡] Jingxi Pan,[‡,§] Anh Johansson,[†] Maria J. Lundqvist,[||] Petter Persson,[||] Reiner Lomoth,[⊥] Jonas Bergquist,[#] Licheng Sun,[†,▽] Villy Sundström,[‡] Björn Åkermark,*[,†] and Tomás Polívka*[,‡,◆]

Department of Organic Chemistry, Stockholm University, S-106 91 Stockholm, Sweden, Department of Chemical Physics, Lund University, P.O. Box 124, S-22100 Lund, Sweden, Department of Quantum Chemistry, Uppsala University, Box 518, S-751 20 Uppsala, Sweden, Department of Physical Chemistry, Uppsala University, Box 579, S-751 23 Uppsala, Sweden, and Department of Analytical Chemistry, Uppsala University, Box 599, SE-751 24 Uppsala, Sweden

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A series of bis(terpyridine)Ru^{II} complexes have been prepared, where one of the terpyridines is functionalized in the 4′-position by a phosphonic or carboxylic acid group for attachment to TiO_2. The other is functionalized, also in the 4′-position, by a potential electron donor. In complexes **1a**, **3a**, and **4a**,**b**, this donor is tyrosine or hydrogen-bonded tyrosine, while in **2a** it is carotenoic amide. The synthesis and photophysical properties of the complexes are discussed. On irradiation with visible light, the formation of a long-lived charge-separated state was anticipated, via primary electron ejection into the TiO_2, followed by secondary electron transfer from the donor to the photogenerated Ru^{III}. However, such a charge-separated state could be observed with certainty only with complex **2a**. To explain the result, quantum chemical calculations were performed on the different types of complexes.

Introduction

Much research effort has aimed at understanding light-induced charge separation in natural or artificial molecular systems and designing model systems that are capable of converting light into chemical or electrical energy. Efficient dye-sensitized solar cells have been developed based on ruthenium−polypyridine complexes attached to nanocrystalline films of TiO_2.[1−7] Besides other factors, the light-to-electricity conversion yield of the photovoltaic systems depends on the efficiency of the charge separation at sensitizer (S)−semiconductor interfaces, and a long-lived charge-separated state is necessary for dye-sensitized solar cells to get a good photovoltaic performance. Accordingly, the performance of a photovoltaic cell is limited by electron−sensitizer recombination ($S^+|(e^-)TiO_2 \rightarrow S|TiO_2$). One way to influence the charge recombination rate is to introduce an electron donor covalently linked to the sensitizer. By replacement of the simple sensitizer with molecular dyads, based on Ru−polypyridine complexes linked to phenothiazine or triarylamine, long-lived photoinduced charge separation has been obtained.[8−12] For several years, we have studied

* To whom correspondence should be addressed. E-mail: bjorn.akermark@organ.su.se (B.Å.).
[†] Department of Organic Chemistry, Stockholm University.
[‡] Department of Chemical Physics, Lund University.
[§] Current address: State Key Laboratory of Fine Chemicals, Dalian University of Technology, 116012 Dalian, China.
[||] Department of Quantum Chemistry, Uppsala University.
[⊥] Department of Physical Chemistry, Uppsala University.
[#] Department of Analytical Chemistry, Uppsala University.
[▽] Current address: KTH Chemistry, Organic Chemistry, Royal Institute of Technology, 100 44 Stockholm, Sweden.
[◆] Current address: Institute of Physical Biology, University of South Bohemia, CZ-373 33 Nove Hrady, Czech Republic.

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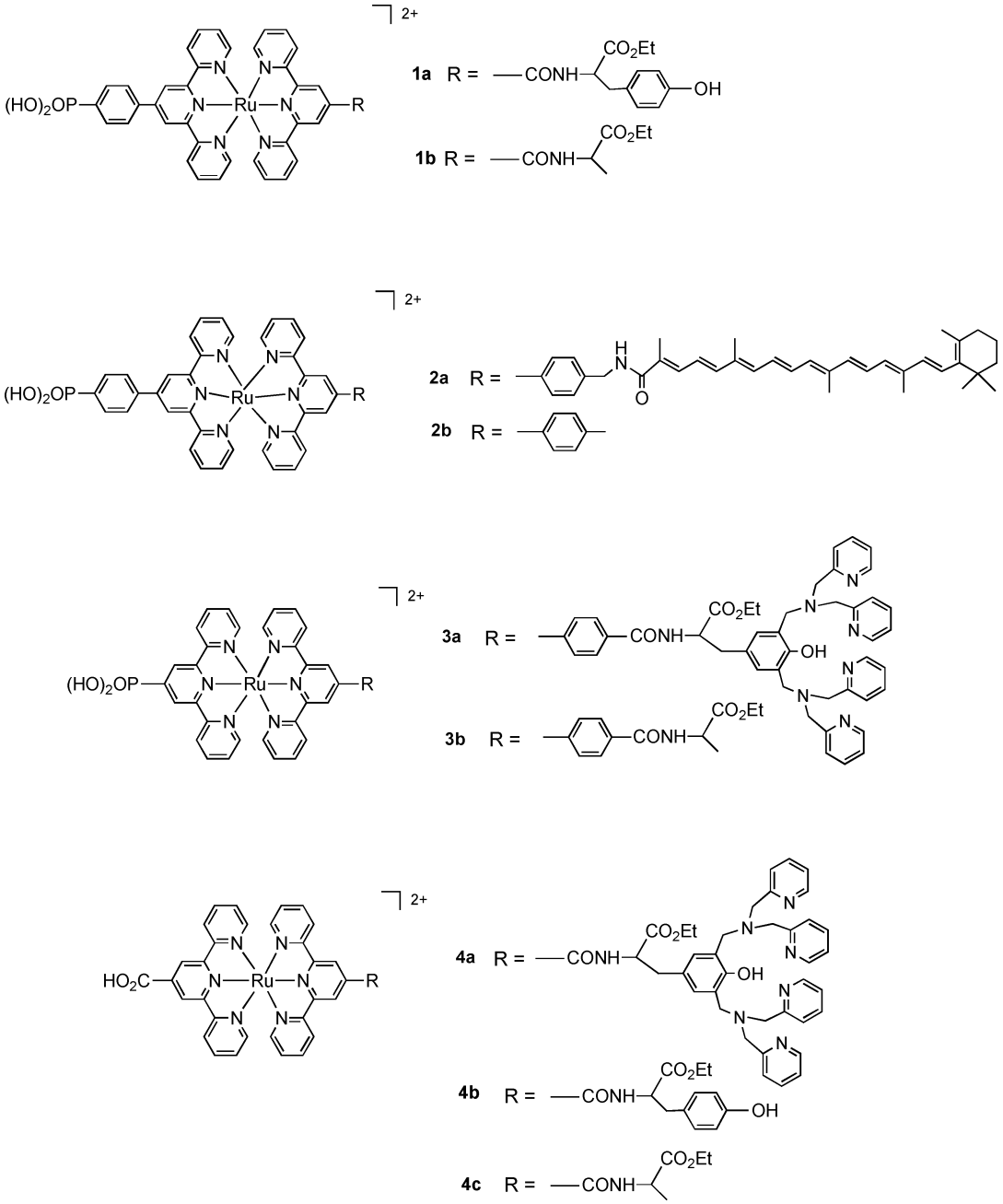
Chart 1



donor−sensitizer systems where the sensitizer is a Ru^{II} tris-(bipyridine) ($Ru(bpy)_3$) complex and the primary donor is a phenol such as covalently linked tyrosine (tyr).[13,14] In the presence of an external acceptor, these systems are capable of transferring an electron from the excited sensitizer to the acceptor, generating Ru^{III}. This is then rereduced to Ru^{II} by intramolecular electron transfer from the phenol. Attached to TiO_2, such a tyrosine−$Ru(bpy)_3$ dyad formed a charge-separated state in which tyrosine acted as electron donor to the photooxidized Ru^{III} mimicking the electron transfer from Tyr_z to P680 in photosystem II (PSII) in nature.[14] This type of system is interesting not only for preparation of photovoltaic cells but also for further development of dyads containing electron donors that can take part in photoinduced oxidative catalysis such as water oxidation.

When one is working with Ru−polypyridine-based dyads linked to an acceptor (in this case TiO_2), terpyridine (tpy) ligands should be preferred due to the favorable geometry of the complex formed. In the $Ru(bpy)_3$ type complexes several isomers can potentially be formed, in some of which the donor and the acceptor are close in space. By contrast, the link to TiO_2 and the donor (tyrosine) can be placed in

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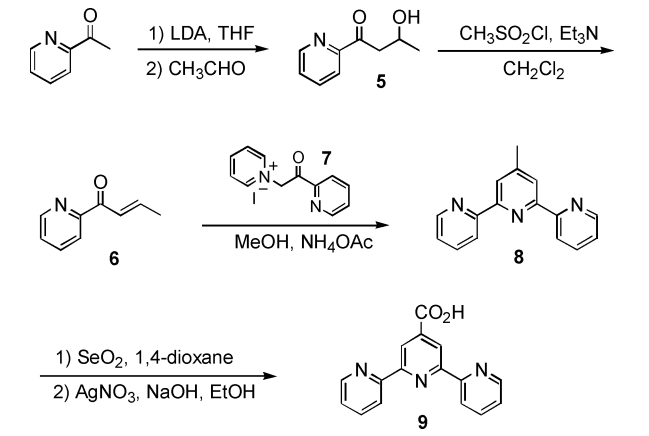
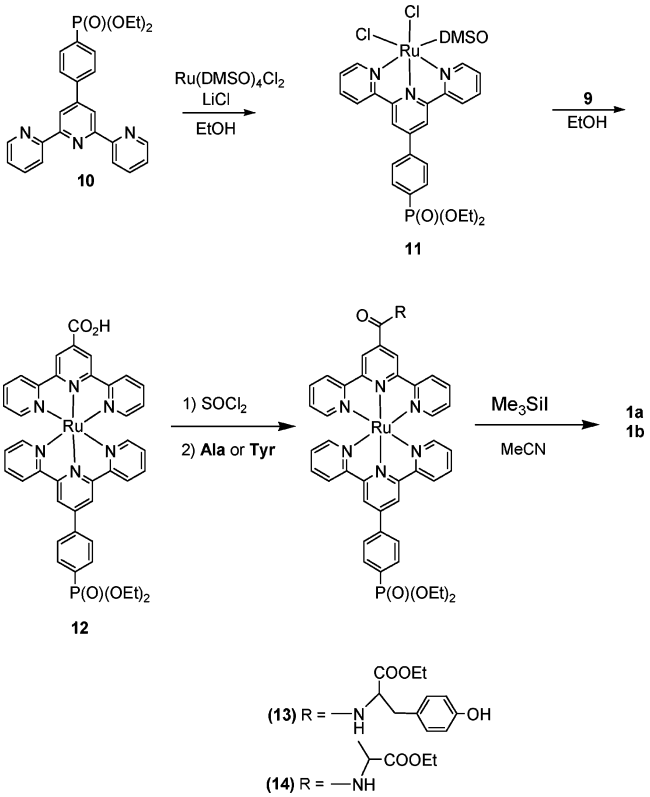
Scheme 1



Scheme 2



linear arrangement in $Ru(tpy)_2$ complexes, with maximal spatial separation of the donor and the acceptor. A drawback of using $Ru(tpy)_2$ is its much shorter excited-state lifetime of ~250 ps[15] as compared with ~1 μs lifetime of $Ru(bpy)_3$,[16] but chromophore is known to efficiently inject electrons into TiO_2.[12]

To study the properties of a terpyridine analog to the Tyr-$Ru(bpy)_3$ dyad, we initially synthesized complex **1a** (Chart 1; Schemes 1 and 2) on the basis of $Ru(tpy)_2$, using tyrosine as electron donor. In complex **1a,** one of the two tpy ligands carries a phosphonate group, while the second tpy ligand is linked to tyrosine−ethyl ester via an amide bond. The reference complex **1b** (Scheme 2), where alanine (Ala) has replaced tyrosine, was also prepared. We also prepared the related complex **2a** (Chart 1 and Scheme 3), where the sensitizer is linked to a carotenoid, as well as the reference complex **2b** (Chart 1 and Scheme 4). The phosphonate group was chosen as anchoring group because it has been shown to bind more strongly to TiO_2 than carboxylate, which is more commonly used.[5,6,17,18]

The complexes **3a**,**b** (Chart 1 and Scheme 5), where the phosphonate group is directly attached to the terpyridine ligand, were also synthesized, as well as the complexes **4a**−**c**, which have a carboxylate binding group in place of the phosphonate (Chart 1 and Scheme 6). Finally, density functional theory (DFT) calculations have been performed to determine the characteristics of the lowest unoccupied molecular orbital (LUMO) for a number of different Ru-$(tpy)_2$ complexes.[19−24]

Results and Discussion

Synthesis. The complexes **1a**,**b** were prepared according to Scheme 2. The two terpyridine ligands **9** and **10** were consecutively added to $Ru(DMSO)_4Cl_2$[25] in ethanol solution to give complex **12**. This complex was then converted to the acid chloride and allowed to react with the ethyl esters of tyrosine and alanine, respectively. Selective hydrolysis of the phosphonate esters then gave the phosphonic acids **1a**,**b**. The ligand **10** was prepared according to a literature procedure,[7] while the ligand **9** was synthesized by two different routes. The first route goes via the methylterpyridine **8**, Scheme 1. It involves the enone **6** as intermediate. The initial attempts to prepare this directly by condensation of acetylpyridine and acetaldehyde gave intractable mixtures as product. However, by preparation of the enolate of 2-acetylpyridine by treatment with LDA, followed by addition to acetaldehyde at low temperature, the aldole **5** could be obtained in a decent yield. Dehydration gave the enone **6**, which was then allowed to react with pyridacylpyridinium iodide (**7**) and ammonium acetate according to the Kröhnke procedure[26,27] to give 4′-methyl-2,2′:6′,2″-terpyridine (**8**). Oxidation gave the terpyridine carboxylic acid **9**. The second method used was oxidation of 4′-(2-furyl)-2,2′:6′,2″-terpyridine[28] to the corresponding acid using potassium perman-

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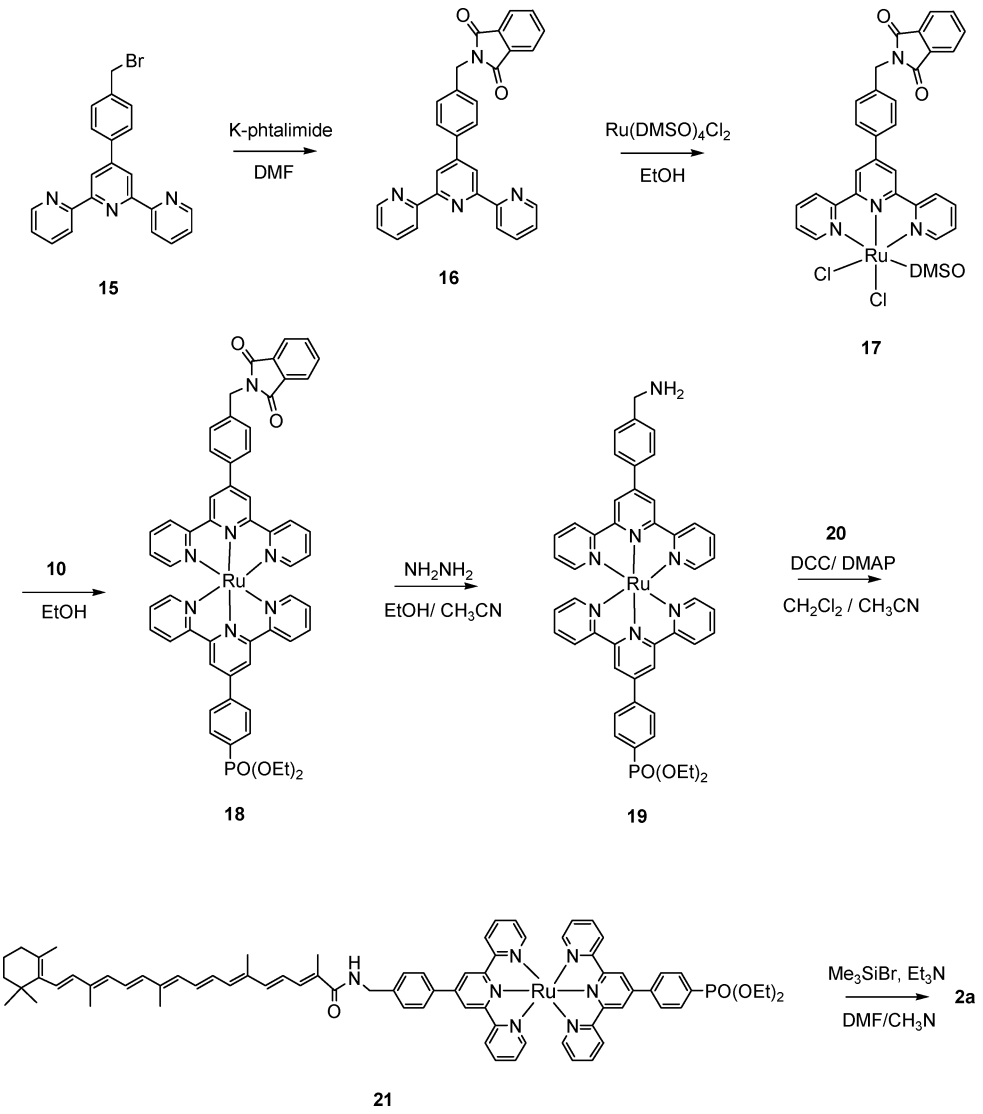
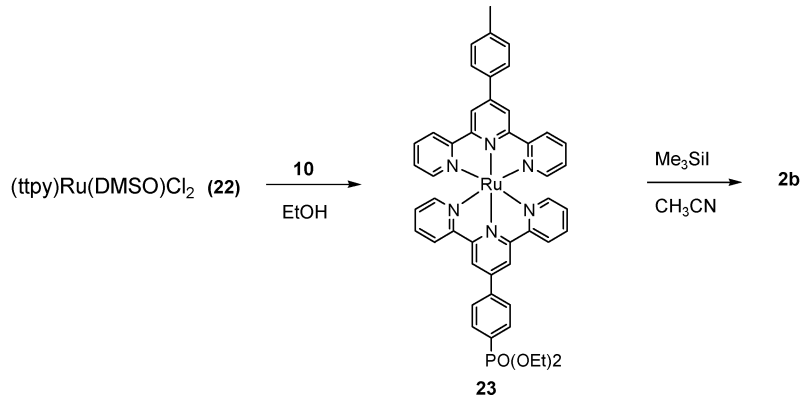
Scheme 3



Scheme 4



ganate.[29] By this route compound **9** is formed in three steps. Several other procedures for the preparation of **8** and **9** can be found in the literature.[30−34] The synthesis of complex **2a** is presented in Scheme 3. To prepare an amine-functionalized terpyridine ligand, ((bromomethyl)phenyl)terpyridine (**15**) was allowed to react with phtalimide to give the protected

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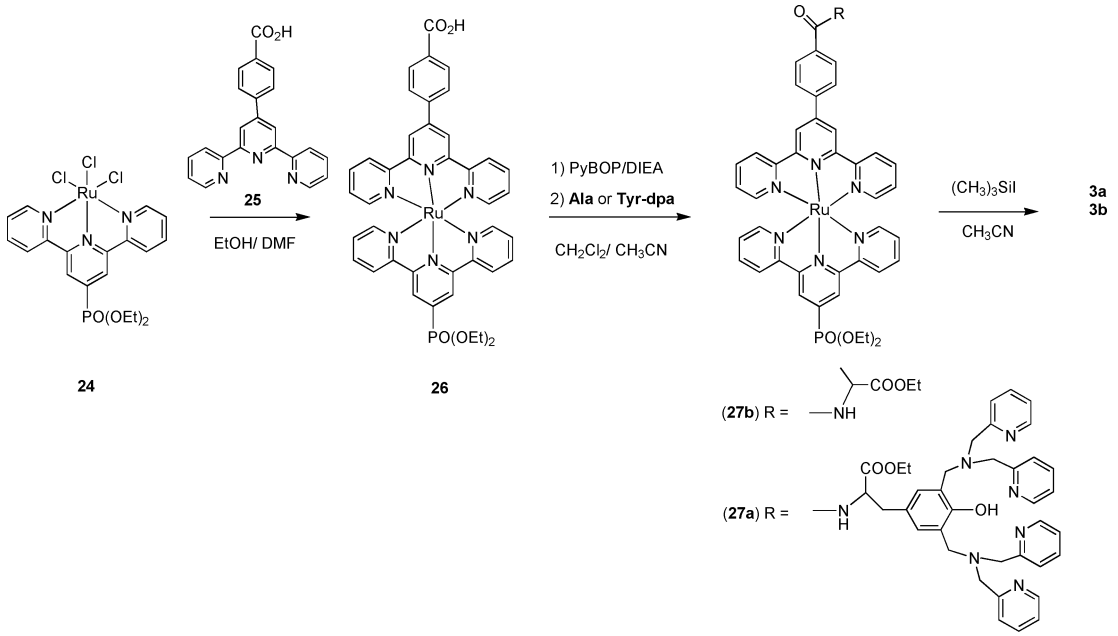
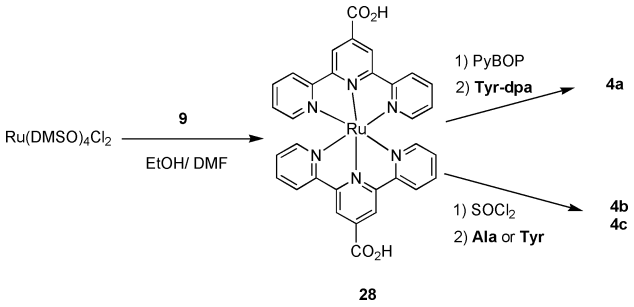
Scheme 5



Scheme 6



amine **16**. The reaction between $Ru(DMSO)_4Cl_2$[25] and **16** in EtOH gave the mono(terpyridyl)ruthenium complex **17**. Further reaction with the phosphonated terpyridine **10**[7] gave complex **18**. Deprotection with hydazine hydrate gave complex **19** with a free amino group that could subsequently be linked to all-*trans*-8′-apo-β-carotenoic acid (**20**),[35] to give complex **21**. The hydrolysis of the phosphonate ester groups in **21** was performed using trimethylsilyl bromide in the presence of triethylamine, giving the target complex **2a**. In this last reaction, the more reactive trimethylsilyl iodide reagent could not be used, since it turned out to react with the carotenoid moiety. The reference complex **2b** was prepared by refluxing $Ru(tpy)(DMSO)Cl_2$ (**22**) and the phosphonated terpyridine **10** in EtOH giving complex **23**, followed by hydrolysis of the phosphonate ester groups using trimethylsilyl iodide.

In the preparation of **3a**,**b** (Scheme 5), Ru(4′-PO_3Et_2-terpyridine)Cl_3 (**24)** and ligand **25** were refluxed in EtOH giving the bis(terpyridine) complex **26**. This was then linked to alanine ethyl ester (**Ala**) or hydrogen-bonded tyrosine (**Tyr-dpa**)[36] using (benzotriazol-1-yloxy)tris(pyrrolidino)-phosphonium hexafluorophosphate (PyBop) as coupling reagent, in the presence of diisopropylethylamine (DIEA). Hydrolysis of the phosphonate ester groups was accomplished by using trimethylsilyl iodide.

The preparation of the carboxylic acid functionalized ruthenium complexes **4a**−**c** is shown in Scheme 6. Coordination of 2 equiv of ligand **9** to the ruthenium(II) precursor $Ru(DMSO)_4Cl_2$ gave the bis(terpyridine) complex **28**. Reacting the acid chloride of **28** with 1 equiv of hydrogen-bonded tyrosine (**Tyr-dpa**), tyrosine-ethyl ester (**Tyr**), or alanine-ethyl ester (**Ala**) afforded complexes **4a**−**c**.

Photophysics of the Complexes 1a,b. The steady-state absorption spectra of **1a**,**b** on TiO_2 films are shown in Figure 1. Both spectra are nearly identical with those measured for the free molecules in methanol solution. They exhibit the characteristic MLCT band of ruthenium complexes[16] centered at 487 nm, without any appreciable splitting or red shift. This shows that the attachment to the TiO_2 surface via the phosphonate group has negligible effect on the spectroscopic properties of the $Ru(tpy)_2$ chromophore.

In flash photolysis experiments, when **1a**,**b** were dissolved in methanol and excited at 532 nm, no long-lived transients were observed, which is expected since the excited state of $Ru(tpy)_2$ has a subnanosecond lifetime.[6] By contrast, irradiation of **1a**−TiO_2 and **1b**−TiO_2 gave rise to a strong bleaching centered at 490 nm, accompanied by two positive absorption bands at around 410 and 515 nm (Figure 2), which all recover by a multiexponential process. It is known that bleaching of ground-state absorption due to electron injection in TiO_2 is ultrafast (time scale fs−ps),[37−41] while recovery by recom-

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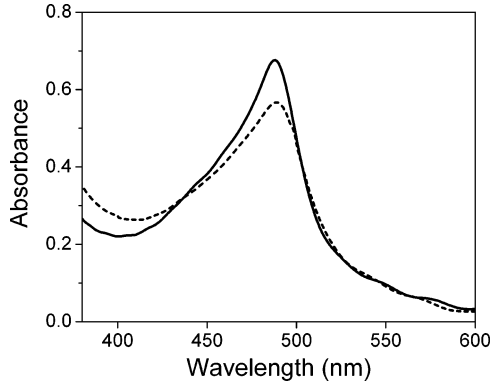

Figure 1. Steady-state absorption spectra of **1a**−TiO_2 (dotted line) and **1b**−TiO_2 (solid line) in methanol.

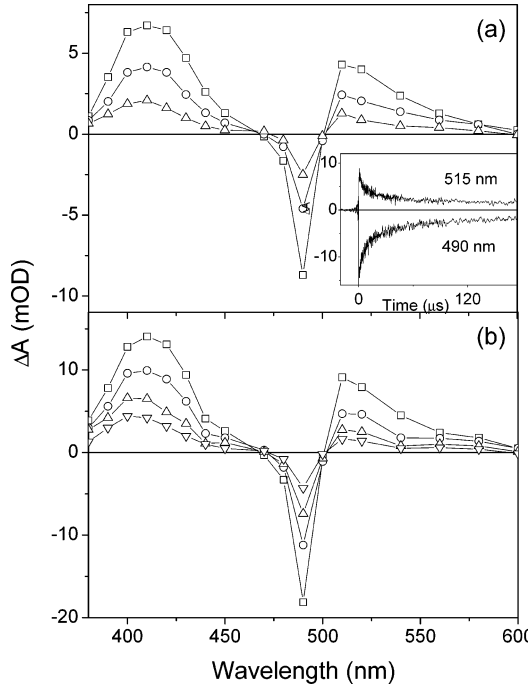

Figure 2. Transient absorption spectra recorded after excitation at 532 nm of the dye-sensitized films in methanol: (a) **1b**−TiO_2, recorded at 2 μs (squares), 20 μs (circles), 180 μs (triangles); (b) **1a**−TiO_2, recorded at 2 μs (squares), 10 μs (circles), 50 μs (triangles), 180 μs (down triangles). The inset shows kinetics at 515 and 490 nm, respectively.

bination of the injected electrons with the oxidized dye is multiexponential, taking place with rates ranging from μs to ms.[42−45] Performing a three-exponential fit of the recovery of the bleached **1b**−TiO_2 system, we obtained the lifetimes (amplitudes in parentheses) 4 μs (44%), 210 μs (40%), and >1 ms (16%). The **1a**−TiO_2 system behaved in a similar way. It must be noted, however, that we have not been able to detect formation of the oxidized form of **1a** or **1b**, because the 410 and 515 nm bands are not due to the oxidized Ru(tpy)$_2$ chromophore (see, e.g., Figure 8 below showing spectroelectrochemistry on a similar complex). Nevertheless, it seems probable that the recovery process, which we have observed, is the result of recombination between the oxidized sensitizer and injected electrons, because we have successfully observed an electron transfer to the oxidized Ru(tpy)$_2$ from a secondary donor (see below the complex **2a**). With comparison of the dynamics of the complexes **1a**,**b** shown in Figure 2, however, there is no conclusive evidence for secondary electron transfer from the tyrosine in **1b**. This is in contrast to the behavior of bipyridine type Ru complexes,[46−48] and the reason could be that the redox potential of Ru^{III}−terpyridine complexes is too low for efficient oxidation of tyrosine (cf. Table 1).

Table 1. Electrochemical Data in Acetonitrile Solution

	$E_{1/2}$/V vs $Fc^{+/0}$			
compd	*[$Ru^{III/II}$LL′]$^{3+/2+}$	[$Ru^{II/III}$LL′]$^{3+/2+}$	carotenoid	φ-$OH^{+/0}$
1a	∼−1.2[a]	0.92		>0.9
1b	∼−1.2[a]	0.92		
2a	∼−1.2[a]	0.92	0.5[b]	
3a	∼−1.2[a]	0.91		0.52[c]
3b	∼−1.2[a]	0.91		
4a	∼−1.2[a]	0.91		0.52[c]
Ru^{II}(bpy)$_3$	−1.15[d]	0.89[d]		
Ru^{II}(ttpy)$_2$	−1.24[d]	0.91[d]		

[a] Calculated with E_{0-0} = 2.1 eV. [b] Reference 64. [c] First oxidation peak assigned to H-bonded phenol. Non-H-bonded phenol is oxidized at E > 0.9 V. [d] Reference 61.

Photophysics of Complex 2a. It seemed possible that, by the use of an efficient secondary donor, both injection and secondary electron transfer could be observed. We therefore synthesized complex **2a** in which a carotenoid, all-*trans*-8′-apo-β-carotenoic acid, is attached to the Ru(tpy)$_2$ chromophore. Since carotenoids are excellent electron donors[49] and oxidized carotenoids have a strong distinct absorption band in the 800−1000 nm region,[50,51] reduction of Ru^{III}(tpy)$_2$ by secondary electron transfer from the carotenoid moiety should be easy to follow. To minimize direct excitation of the carotenoid moiety, which has a strong absorption in the 400−500 nm region,[52] we excited the complex **2a** at 520 nm corresponding to the red tail of the Ru(tpy)$_2$ chromophore, where the carotenoid has a negligible absorption. In solution, excitation of **2a** produced transient absorption spectra consistent with formation of the carotenoid triplet state, most likely via triplet−triplet energy transfer from the Ru(tpy)$_2$ moiety (data not shown). However, in **2a**−

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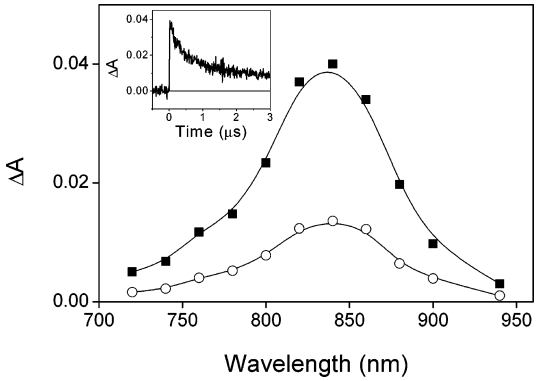

Figure 3. Transient absorption spectra at 0.1 μs (full symbols) and 2 μs (open symbols) obtained after 520 nm excitation of **2a**−TiO_2. The inset shows kinetics measured at 840 nm for **2a**−TiO_2 (λ_{Exc} = 520 nm).

TiO_2 no carotenoid triplet was observed. Instead, a new transient absorption centered at 840 nm appeared in less than 10 ns (Figure 3). The position of this band matches exactly the spectrum of the all-*trans*-8′-apo-β-carotenal radical observed earlier.[41] Thus, we assign the 840 nm band to the carotenoid radical. Since no carotenoid radical was observed for the complex **2a** in solution, we can safely conclude that it is formed as a result of a sequential electron transfer according to the following scheme: (1) Excited $Ru(tpy)_2$ injects an electron into the conduction band of TiO_2. (2) Oxidized $Ru(tpy)_2$ is reduced by the secondary electron transfer from the carotenoid, forming a charge-separated state between the carotenoid and TiO_2. (3) Recombination of charges between carotenoid and TiO_2 occurs on the time scale of a few μs (Figure 3).

Finally, transient absorption measurements in the fs−ps time domain (data not shown) show that both complexes **1a** and **2a** suffer from low efficiency of the initial electron injection from the excited $Ru(tpy)_2$ moiety into the conduction band of TiO_2. This was somewhat unexpected, since it has earlier been demonstrated that terpyridine complexes with phosphonate as linking group can be quite efficient dyes in solar cells, as judged from IPCE values.[5,6,53] Therefore, we have performed quantum chemical calculations to find origin of the low efficiency of the electron injection.

Calculations. It is reasonable to assume that the long-wavelength transitions in all the complexes involve excitation of Ru 4d electrons to tpy π*, as in the parent $Ru^{II}(tpy)_2$, where the highest few occupied and the lowest few unoccupied orbitals consist of Ru 4d and tpy π* orbitals, respectively. The electronic transitions involving these orbitals give rise to the characteristic MLCT absorption bands around 500 nm. The efficiency of subsequent excited-state electron transfer into the TiO_2 conduction band depends on the spatial overlap of the LUMO with TiO_2 orbitals and on LUMO energy relative to the conduction band. It thus seems reasonable that efficient electron injection is favored if the LUMO is localized on the tpy ligand with the substituents that bind to the surface. When using the (4-phosphonatophenyl)tpy ligand as in complexes **1a** and **2a**, it has been shown

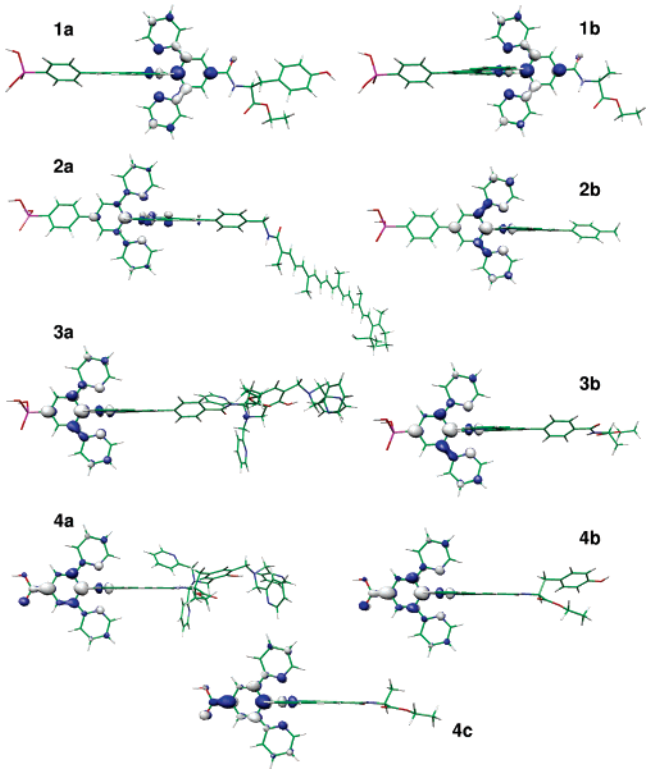

Figure 4. Calculated lowest unoccupied molecular orbital (LUMO) of complexes **1a**−**4c**.

that the injection efficiency of the dye as measured by the maximum IPCE is strongly dependent on the remote ligand.[53]

To study this, we have used the B3LYP/LANL2DZ approach, which like other DFT/LANL2DZ combinations, has been used successfully to describe the geometrical, electronic, and spectroscopic properties of related organometallic systems.[19−23] We have also recently shown that such calculations can be extended to Ru dyes bound to TiO_2 nanocrystals.[24]

Here the DFT calculations on complexes **1a**,**b** showed that the LUMO is located on the remote terpyridine (tpy) ligand (Figure 4). This is probably not an effect of the amide group of **1a**,**b** since we obtain the same LUMO when the remote ligand is unsubstituted terpyridine.

By contrast, the LUMO of both complexes **2a**,**b** is located on the tpy that is connected to the TiO_2 (Figure 4), which suggests a more favorable interaction than in **1a**,**b**. Despite this, the electron injection from these complexes is also inefficient. Intuitively, one would think that the phenyl spacer could work, by conjugation to the tpy ring, as a mediator in the excited electron transfer. However, as seen in Figure 4, the phenyl does not contribute to the LUMO of complexes **1** and **2** because it is rotated out of the tpy plane, according to our calculations by ca. 30°. In contradiction, Jing et al.[53] report efficient injection with a complex which, although the other ligands are different from those in our complexes, has the 4′-(4-phosphonatophenyl)tpy ligand.

Because of the indications that the linking phenyl group reduces the interfacial electronic coupling, we also calculated the electronic structure of a series of complexes in which the anchoring group is directly attached to the tpy ligand.

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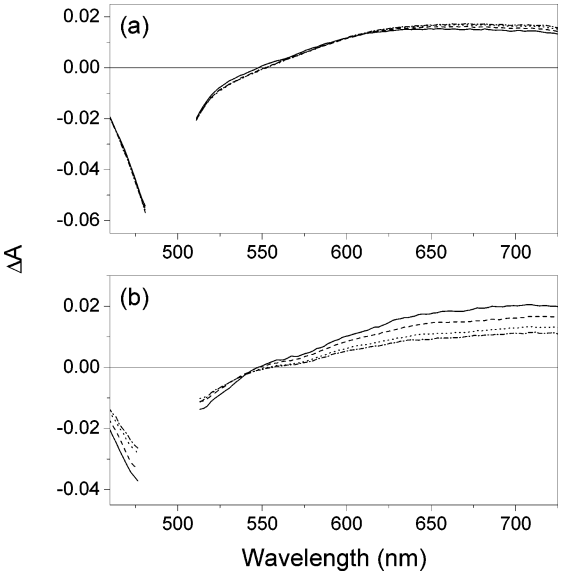

Figure 5. Transient absorption spectra of (a) **4b** in ACN solution at 0.4 ps (solid line), 2.5 ps (dashed line), 10 ps (dotted line), and 200 ps (dash dotted line) and (b) **4b**−TiO_2 at 0.25 ps (solid line), 10 ps (dashed line), 100 ps (dotted line), and 300 ps (dash dotted line). Excitation is at 490 nm.

The resulting LUMOs of the complexes **3a,b** and **4**−**c** are shown in Figure 4. In **3a**,**b**, the LUMO is located largely on the tpy ligand connected to the anchoring phosphonyl group. This is in fact true also for the complexes **4a**−**c**, where the carboxyl anchor is directly attached to the tpy ligand but where also the other tpy ligand has a carbonyl substituent. According to our calculations, the injection into TiO_2 from complexes **3** and **4**, in which the chromophore is directly connected to the anchor, should be more efficient than from complexes **1**, which contain an intervening phenyl group.

Photophysics of Complexes 3a,b and 4a−**c.** All measurements on these complexes were carried out in acetonitrile (ACN) instead of methanol because of solubility problems. As for the complexes **1**, the absorption spectra of the complexes exhibit the characteristic MLCT band located around 490 nm, regardless of whether the complex is in solution or attached to TiO_2 film (data not shown), demonstrating that the attachment group, carboxylate or phosphonate, has no effect on the spectroscopic properties of the $Ru(tpy)_2$ chromophore (Figure 1).

Transient absorption spectra measured in the fs−ps time domain are similar for all complexes. The transient spectra recorded after 490 nm excitation of the complex **4b** in solution and attached to the TiO_2 film are shown in Figure 5. In solution, the transient absorption spectrum consists of a ground-state bleaching of the $Ru(tpy)_2$ chromophore (<540 nm) and broad, structureless excited-state absorption extending beyond 730 nm. It is obvious that these spectral features are present regardless of whether the complex is in solution or attached to the TiO_2 film, but attachment clearly changes excited-state dynamics.

To explore the attachment-induced changes further, we have recorded the transient absorption kinetics of complexes **4b**,**c** and **3b** at 465 nm and 600−675 nm, which corresponds to the bleaching and excited-state absorption signals, respectively. For these complexes in solution and adsorbed on TiO_2,

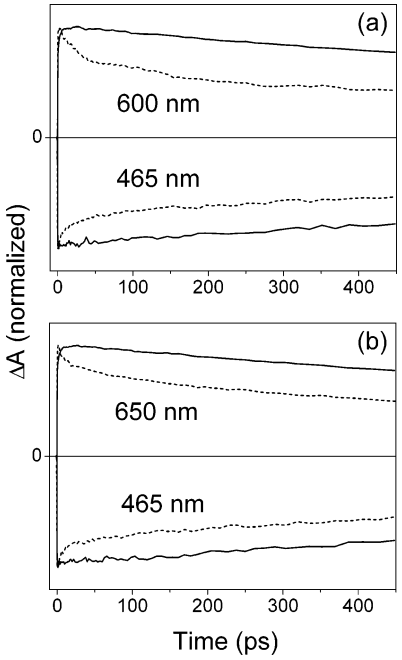

Figure 6. Transient absorption kinetics (λ_{Exc} = 490 nm) of (a) **3b** and (b) **4c** in ACN solution (solid lines) and on TiO_2 film (dashed lines) showing decay of excited-state absorption (top) and ground-state bleaching recovery (bottom).

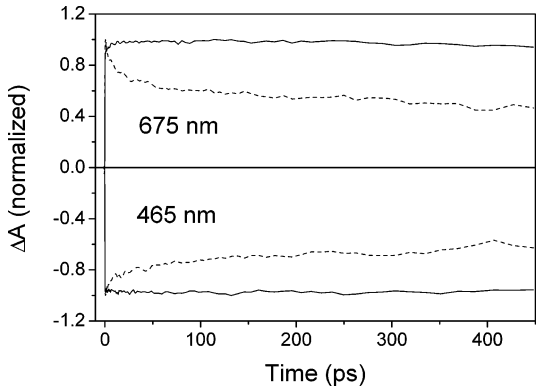

Figure 7. Transient absorption kinetics of **4b** in ACN solution (solid lines) and **4b**-sensitized TiO_2 film in ACN (dashed lines) measured at 675 nm (top) and 465 nm (bottom). Excitation is at 490 nm.

the kinetics after 490 nm excitation are shown in Figures 6a,b and 7, respectively. In solution the decay of the excited-state absorption and recovery of ground-state bleaching are slow (>500 ps, Figures 6 and 7, solid lines). This means that, perhaps due to the presence of substituted ligands, the lifetime is significantly longer than the ∼250 ps expected for $Ru(tpy)_2$.[15]

When the complexes were attached to TiO_2 film, additional decay occurring on a time scale of a few picoseconds was observed (Figures 6 and 7, dotted lines). Since recovery of the ground state, measured at 465 nm, and decay of the excited-state absorption, measured at ∼600 nm, occur with the same rate, the process corresponds to a quenching of the excited $Ru(tpy)_2$ chromophore. This quenching, however, is not due to electron injection, because the oxidized $Ru(tpy)_2$, which must be formed during electron injection, has no absorption bands in this spectral region (Figure 8). Instead, this process, whose nature is not clear, forms the ground-

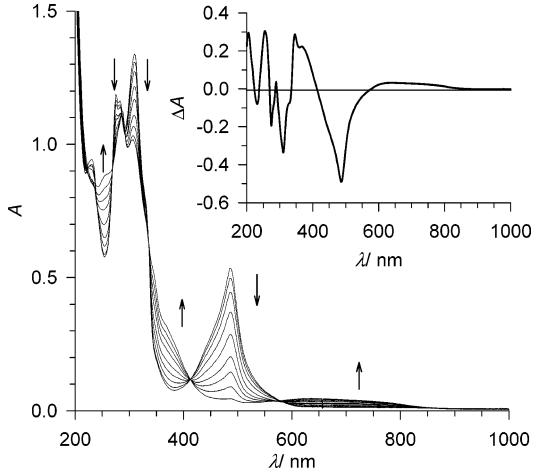

Figure 8. Spectroelectrochemical changes ($l = 1$ mm) upon oxidation of **4b** (~0.3 mM) at 1.10 V vs ferrocene/ferrocenium in acetonitrile solution with 0.1 M $[(n\text{-}C_4H_9)_4N][PF_6]$ as supporting electrolyte. Inset: difference spectrum.

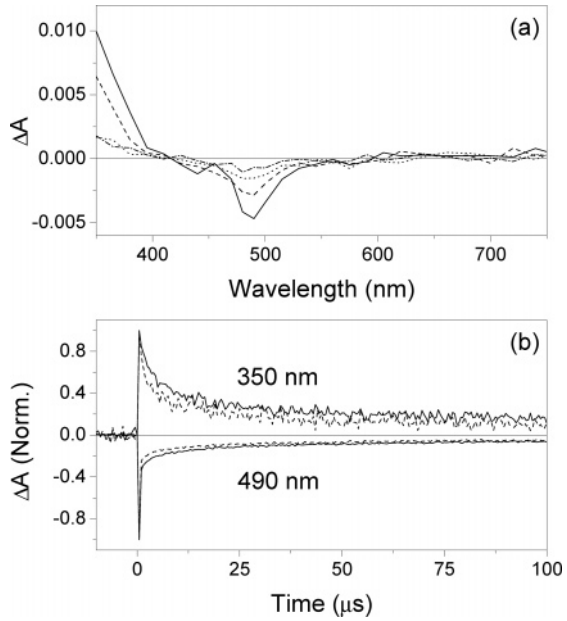

Figure 9. Transient absorption spectra of **4b**−TiO_2 measured at 2 μs (solid line), 10 μs (dashed line), 50 μs (dotted line), and 150 μs (dash dotted line). (b) Kinetics of **4c**−TiO_2 (solid lines) and **4b**−TiO_2 (dashed lines) recorded at 350 nm (top) and 490 nm (bottom). Excitation is at 460 nm.

state $Ru(tpy)_2$. Perhaps it may correspond to a small fraction of molecules, which, following the fast electron injection, undergo also a rapid recombination, leading to a formation of a ground state $Ru(tpy)_2$ within a few picoseconds. Although we are unable to conclusively explain the origin of the rapid process, nanosecond flash photolysis measurements gave strong indications of electron injection. Excitation of the **4b**−TiO_2 system by nanosecond pulses gave rise to a transient absorption spectrum consisting of a bleaching at 490 nm and a positive band below 400 nm (Figure 9a). These features can be attributed to the oxidized $Ru(tpy)_2$ (see Figure 8), which is formed during the laser pulse and recombines with the electrons in TiO_2 on the microsecond time scale. Thus, some electron injection indeed occurs. The kinetics of both spectral bands (Figure 9b) reflect the dynamics of back electron transfer. The recovery kinetics at 490 nm

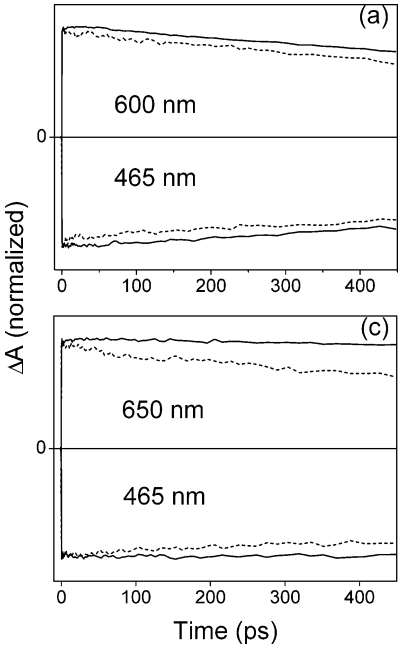

Figure 10. Transient absorption kinetics ($\lambda_{Exc} = 490$ nm) of (a) **3a** and (b) **4a**.

exhibits a multiexponential decay with three time constants of 0.22, 9.5, and 130 μs. Since the time constants are considerably greater for complexes **1a**,**b** (see above), back electron transfer is faster for complex **4b** than for complex **1a**. This could be a result of shorter distance between the $Ru(tpy)_2$ chromophore and TiO_2 surface in the complex **4b**. In Figure 9b, the microsecond kinetics of the complex **4b** are compared with the reference complex **4c**, lacking the tyrosine moiety. Similar to the complexes **1a**,**b** (Figure 2), the decay at 350 nm (as well as the recovery at 490 nm) is slightly faster for the complex **4b** than for **4c**, but the difference is too small to unambiguously assign this effect to secondary electron transfer from tyrosine to the oxidized $Ru(tpy)_2$ moiety. Thus, although the change of the attachment group in the complex **4b** appears to improve electron injection, the evidence for secondary electron transfer is not conclusive. One reason is most certainly that the oxidation potential for tyrosine is too high for efficient oxidation by $Ru^{III}(tpy)_2$ (Table 1). However, by introduction of hydrogen-bonding substituents on tyrosine, the oxidation potential can be decreased, leading to efficient secondary electron transfer.[36] We therefore also prepared the complexes **3a** and **4a**. Absorption spectra of these complexes are again similar to those of the complexes **1a**,**b**, and the femtosecond transient absorption spectra exhibit the same features as shown for **4b** (Figure 5). In contrast to complexes **3b** and **4b**,**c**, the kinetics of the decay of the excited states of the complexes **3a** and **4a** were not appreciably changed on going from solution to TiO_2 film (Figure 10a,b). The reason is not clear but could be related to the bulky dpa arms on one tpy. In addition, there was no indication of electron transfer from the dpa arms to Ru^{III}.

In conclusion, although efficient secondary electron transfer is only observed with certainty with a carotenoid donor, phenolic donors can probably also function provided they

have sufficiently low redox potentials. Carboxylate and phosphonate attachment groups are essentially equally efficient in electron injection, but it seems necessary that these groups are attached directly to the terpyridine ligands.

Experimental Section

TiO_2 Film Preparation. TiO_2 paste (average particle size ~13 nm) was purchased from Solaronix SA. To obtain a mesoporous film of uniform thickness, we used Scotch tape as framer and a glass rod to spread a drop of viscous TiO_2 suspension onto a 76 × 26 × 1 mm^3 microscope glass slip. After removal of the tape and drying in air at room temperature for about 2 h, it was sintered at 420−440 °C for 30 min to form a transparent TiO_2 film. The thickness of the film was measured to be about 3 μm by both interference pattern in the steady-state absorption spectrum and by a profilometer. Dye sensitization of the TiO_2 film was carried out by soaking the still hot (80 °C) film in a ~1 mM methanol or ACN solution and incubated at room temperature for about 24 h. After the sensitization procedure, the film was rinsed with solvent several times to wash off the nonattached dye, covered with solvent and another microscope glass slip, and finally sealed. All the dye-sensitized films were freshly prepared and kept in the dark before all measurements.

Spectroscopy. Steady-state absorption measurements were made on a Jasco-V-530 spectrophotometer. Nanosecond−microsecond transient absorption measurements were carried out on a laser flash photolysis setup described elsewhere.[54] Briefly, the excitation pulse at 532 nm (3 mJ/pulse, 7 ns fwhm) was obtained from a Quanta-Ray 230 Nd:YAG laser. For other wavelengths, the excitation light (1 mJ/pulse, 7 ns fwhm) was generated by a Quanta-Ray MOPO pumped by a 355 nm output of Quanta-Ray 230 Nd:YAG laser. The probe light was provided by a 75 W Xe arc lamp and was collinear with the excitation beam. After passing through the sample, the probe light was spectrally filtered using two monochromators and finally detected by a Hamamatsu R928 photomultiplier tube. To prevent degradation of the dye due to laser light irradiation, samples in solution were measured in a 1 cm quartz cell with stirring by a magnetic stirrer and samples on TiO_2 film were kept moving during measurements by using an X−Y translation stage.

Femtosecond transient absorption measurements were carried out on an amplified titanium−saphire laser system (Spectra Physics), with tunable pulses obtained from an optical parametric amplifier. The amplified titanium−saphire laser system was operated at a repetition rate of 1 kHz, producing ~120 fs pulses with an average output power of ~1 W and a central wavelength of 800 nm. The amplified pulses were divided into two paths: one to pump an optical parametric amplifier (TOPAS, Light Conversion) for the generation of excitation pulses centered at 490 nm and the other to produce white-light continuum probe pulses in a 0.5 cm sapphire plate. To prevent sample degradation, the excitation pulses were attenuated to an energy of ~50 nJ/pulse by using neutral density filters. The mutual polarization of pump and probe beams was set to magic angle (54.7°). Steady-state absorption spectra were measured before and after fs transient absorption measurements to ensure that no permanent photochemical changes occurred over the duration of the experiment.

Electrochemistry. Cyclic voltammetry was carried out in a three-compartment cell by using a glassy-carbon disk working electrode, a platinum wire as the counter electrode, and a Ag/Ag^+ (10 mM $AgNO_3$ in CH_3CN) reference electrode. The experiments were carried out in dry ACN with 0.1 M tetrabutyl ammonium hexafluorophosphate.

Mass spectrometry experiments were done on a BioAPEX-94e superconducting 9.4 T Fourier transform ion cyclotron resonance mass spectrometer (Bruker Daltronics, Billerica, MA) (ESI-FTICR MS).

Computational Details. Density functional theory (DFT) calculations were employed to investigate the electronic structures of the substituted $Ru^{II}(tpy)_2$ complexes. Geometry optimizations as well as calculations of relevant molecular orbitals were performed using the B3LYP functional[55,56] together with the LANL2DZ basis set.[57,58] The geometries of the complexes **1a**,**b**, **2b**, **3b**, and **4b**,**c** were obtained by full geometry optimization. Due to the many degrees of freedom, the geometries of complexes **2a**, **3a**, and **4a** were obtained by a partial optimization scheme that reduced the computational time. The fully optimized templates (**2b**, **3b**, and **4b**) were merged with the separately optimized flexible donors (R of **2a**, **3a**, and **4a** in Chart 1), and the electronic structure of the assembled complex was then calculated. All calculations were performed using the Gaussian03 program.[59]

Synthesis. General Methods. Acetaldehyde was treated with $NaHCO_3$ and distilled from $MgSO_4$. Tetrahydrofuran (THF) was distilled over Na and benzophenone. Dimethylformamide (DMF) and diisopropylamine were distilled from CaH_2 and stored over molecular sieves and NaOH pellets, respectively. Dry CH_2Cl_2 was distilled from CaH_2 prior to use. All other reagents and solvents were purchased as reagent grade and used without further purification. NMR spectra were recorded on a Varian (300 MHz or 400 MHz) spectrometer. Compounds **10**,[7] **7**,[60] **20**,[35] **Tyr-dpa**,[36] Ru(ttpy)-$(DMSO)Cl_2$,[61] and $Ru(DMSO)_4Cl_2$[25] were prepared according to literature procedures.

3-Hydroxy-1-pyridin-2-ylbutan-1-one (5). 2-Acetylpyridine (7.5 mL, 0.067 mol) was added dropwise to a solution of LDA [prepared from diisopropylamine (14.5 mL, 0.10 mol) and *n*-BuLi (2.1 M, 47 mL, 0.10 mol) in 100 mL of THF] cooled at −15 °C. The resulting solution was stirred at −15 °C for 2 h. Acetaldehyde (7.5 mL, 0.13 mol) was added dropwise and the reaction mixture stirred for 0.5 h. A saturated solution of NH_4Cl (75 mL) was added.

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The organic phase was collected, and the aqueous phase extracted with 40 mL of Et_2O. The organic phases were combined and dried over Na_2SO_4, and the solvent was evaporated. The crude product was purified on a column of silica gel and eluted with EtOAc−pentane (2:3). Condensation products from acetaldehyde eluted first and then unreacted 2-acetylpyridine, followed by the desired product **5** (6.6 g, 60%). ^{1}H NMR ($CDCl_3$): $\delta = 1.31$ (d, $J = 6.2$ Hz, 3H), 3.21−3.27 (m, 1H, PyCOCH_2−), 3.41−3.46 (m, 1H, PyCOCH_2−), 3.80 (d, $J = 3.3$ Hz, 1H, −CHO*H*), 4.33−4.40 (m, 1H, −C*H*OH), 7.48−7.52 (m, 1H, Py-*H*), 7.84−7.89 (m, 1H, Py-*H*), 8.05−8.08 (m, 1H, Py-*H*), 8.67−8.69 (m, 1H, Py-*H*).

1-Pyridin-2-ylbut-2-en-1-one (6). 5 (2.0 g, 0.012 mol) was dissolved in dry CH_2Cl_2 (50 mL), and the solution was cooled to −30 °C. Et_3N (5.1 mL, 0.036 mol) was added, and then methanesulfonyl chloride (1.1 mL, 0.014 mol) was added dropwise. The solution was allowed to reach ambient temperature over night. The dark solution was filtered through Celite, which was washed with CH_2Cl_2. Evaporation of solvent and purification on a column of silica gel eluting with EtOAc−pentane (1:1) afforded 1.4 g (79%) of product **6**. ^{1}H NMR ($CDCl_3$): $\delta = 2.03$ (dd, $J = 7.0$, 1.5 Hz, 3H, −C=CHCH_3), 7.25 (dq, $J = 15$, 7.0 Hz, 1H, −C=C*H*CH$_3$), 7.45 (ddd, $J = 7.7$, 4.8, 1.1 Hz, 1 H, Py-*H*), 7.60 (dq, $J = 15$, 1.5 Hz, 1H, −C*H*=CHCH$_3$), 7.84 (dt, $J = 7.7$, 1.8 Hz, 1H, Py-*H*), 8.10−8.13 (m, 1H, Py-*H*), 8.69−8.71 (m, 1H, Py-*H*).

4′-Methyl-2,2′:6′,2″-terpyridine (8). A mixture of the pyridyl−enone **6** (1.3 g, 8.8 mmol), 2-pyridacylpyridinium iodide (**7**)[60] (2.87 g, 8.8 mmol), and ammonium acetate (14 g, 180 mmol) in methanol (20 mL) was refluxed for 6 h. The solvent was evaporated, and water was added (50 mL). The solution was extracted with CH_2Cl_2 (3 × 30 mL). The solvent was evaporated, and the crude product was recrystallized from cold EtOH−H_2O (1:1). Yield: 1.1 g (50%). ^{1}H NMR ($CDCl_3$): $\delta = 2.53$ (s, 3H, PyCH_3), 7.26−7.34 (m, 2H, Py-*H*), 7.83−7.87 (m, 2H, Py-*H*), 8.29 (s, 2H, Py-*H*), 8.60−8.63 (m, 2H, Py-*H*), 8.69−8.71 (m, 2H, Py-*H*).

2,2′:6′,2″-Terpyridine-4′-carboxylic Acid (9). Method A. The oxidation was performed according to a modified procedure described by McCafferty et al.[62] Methylterpyridine **7** (0.20 g, 0.81 mmol) and selenium dioxide (0.31 g, 2.8 mmol) in 5 mL of dioxane were refluxed for 24 h. The solution was filtered through Celite, which was washed with warm ethanol. The solvent was removed under reduced pressure, and the resulting solid was suspended in ethanol (5 mL). A solution of silver nitrate (0.15 g, 0.89 mmol in 1 mL water) and 3 mL of NaOH (1 M) was added. The black suspension was stirred at room temperature for 16 h. The black silver oxide was removed by filtration and the solid washed with NaOH (1 M). Ethanol was removed under reduced pressure, and the pH of the resulting solution was adjusted to pH 4−5 with HCl (2 M). The solid was collected by filtration and washed with water and dried to yield 0.15 g (66%) of the acid. ^{1}H NMR (DMSO-d_6): $\delta = 7.51$−7.55 (m, 2H, Py-*H*), 8.03 (dt, $J = 7.7$, 1.8 Hz, 2H, Py-*H*), 8.64 (dd, $J = 8.1$, 1.1 Hz, 2H, Py-*H*), 8.74−8.76 (m, 2H, Py-*H*), 8.85 (s, 2H, Py-*H*).

2,2′:6′,2″-Terpyridine-4′-carboxylic Acid (9). Method B. To a solution of 4′-(2-furyl)-2,2′:6′,2″-terpyridine[28] (1.6 g, 5.3 mmol) in pyridine (60 mL) and H_2O (30 mL) was added $KMnO_4$ (4 g, 25 mmol) in small portions. The reaction was stirred for 24 h, and the remaining $KMnO_4$ was reduced by adding $Na_2S_2O_3$ in H_2O until the violet color disappeared. The solution was made basic by addition of NaOH (2 M), and the MnO_2 formed was filtered off and washed with MeOH. The filtrate was evaporated, and the resulting solid dissolved in NaOH (pH ∼ 10). The pH of the resulting solution was adjusted to pH 4−5 with HCl (2 M). The solid was collected by filtration and washed with water and dried to yield 1.15 g (78%) of the acid. For NMR, see method A.

Complex 11. A suspension of Ru(DMSO)$_4$Cl$_2$[25] (1.3 g, 2.7 mmol), **10** (0.50 g, 1.1 mmol), and LiCl (0.20 g, 4.7 mmol) in ethanol (100 mL) was refluxed for 1.5 h under nitrogen atmosphere. The solvent was evaporated, and the crude product was purified on a column of aluminum oxide. The product was eluted with MeCN−EtOH (100:0 to 95:5). A brown band was collected, and solvent was evaporated. The resulting solid was suspended in 50 mL of acetone−diethyl ether (2:1) and filtered to give 0.66 g (79%) of the monoterpyridyl complex. ^{1}H NMR (DMSO-d_6): $\delta = 1.27$ (t, $J = 7.0$ Hz, 6H, −POCH$_2$CH_3), 4.06−4.10 (m. 4H, −POCH_2-CH$_3$), 7.79−7.82 (m, 2H, Py-*H*), 7.91−7.96 (m, 2H, Ph-*H*), 8.18 (dt, $J = 7.7$, 1.5 Hz, 2H, Py-*H*), 8.30−8.33 (m, 2H, Ph-*H*), 8.79 (d, 7.7 Hz, 2H, Py-*H*), 8.93 (s, 2H, Py-*H*), 9.01−9.03 (m, 2H, Py-*H*).

Complex 12. Complexes **11** (0.23 g, 0.33 mmol) and **8** (0.1 g, 0.36 mmol) were refluxed in ethanol (40 mL) and DMF (6 mL) for 14 h. The solvent was evaporated and the crude product purified by column chromatography (silica gel, eluent $CH_3CN-H_2O-KNO_3$(sat.), 60:40:10). Fractions containing product were collected, and the solvent was removed. The resulting solid was dissolved in a small amount of CH_3CN-H_2O (1:1), and a saturated solution of NH_4PF_6 was added. Addition of HCl (0.5 M) gave a red precipitate that was filtered out, washed with diluted HCl, and dried to give 0.16 g (43%) of **12**. ^{1}H NMR (CD_3CN): $\delta = 1.38$ (t, 6H, −POCH$_2$CH_3), 4.18−4.25 (m. 4H, −POCH_2CH$_3$), 7.18−7.24 (m, 4H, Py−*H*), 7.37 (d, 2H, Py-*H*), 7.45 (d. 2H, Py-*H*), 7.95−8.02 (m, 4 H, Ph-*H*), 8.12−8.2 (m, 2H, Py-*H*), 8.32−8.36 (m, 2H, Py-*H*), 8.65 (dd, 4H, Py-*H*), 9.04 (s, 2H, Py-*H*), 9.12 (s, 2H, Py-*H*).

Complex 13. The complex **12** (40 mg, 36 μmol) was suspended in thionyl chloride (4 mL) and refluxed under nitrogen for 3 h. The excess of thionyl chloride was evaporated. A solution of tyrosine ethyl ester hydrochloride (10 mg, 41 μmol) in 3 mL of MeCN and 0.1 mL triethylamine was immediately added. This solution was stirred at room temperature for 16 h. The crude product was purified on a column of silica gel using MeCN−H_2O−KNO_3-(sat.) (91:5:1) as eluent. The solvent was evaporated, and the complex was redissolved in a minimum amount of MeOH and precipitated with a saturated solution of KPF_6. The red precipitate was collected by filtration, washed with water, and dried to give 0.030 g (64%) of product. ESI-FTICR MS (*m*/*e*): singly charged peak at 1160.2, $[M - PF6]^+$, calcd 1160.2; doubly charged peak at 507.6, $[M - 2PF6]^{2+}$, calcd 507.6. ^{1}H NMR (CD_3CN): $\delta = 1.32$ (t, 3H, −OCH$_2$CH_3), 1.40 (t, 6H, −POCH$_2$CH_3), 3.22−3.40 (m, 2H, −CHCH_2Ph), 4.17−4.31 (m, 6H, −POCH_2CH$_3$−OCH_2-CH$_3$), 5.0−5.07 (q, 1H, −*CH*CH$_2$Ph), 6.84 (d, 2H, Ph-*H*) 6.92 (s, 1H, −Ph−*OH*) 7.17−7.27 (m, 4H, Ph-*H*), 7.30 (d, 2H, Py-*H*), 7.38 (d, 2H, Py-*H*), 7.47 (d, 2H, Py-*H*), 7.95−8.02 (m, 4H, Ph-*H*), 8.06 (d, 1H, −*NH*−), 8.12−8.18 (m, 2H, Py-*H*), 8.32−8.36 (m, 2H, Py-*H*), 8.62−8.67 (m, 4H, Py-*H*), 9.04 (s, 2H, Py-*H*), 9.08 (s, 2H, Py-*H*). Anal. Found: C, 47.64; H, 3.89; N, 7.40. Calcd: C, 47.86; H, 3.71; N, 7.51.

Complex 14. This complex was prepared in the same way as **13**. The complex **12** (66 mg, 59 μmol) was suspended in thionyl chloride (4 mL) and refluxed under nitrogen for 3 h. Excess of thionyl chloride was evaporated. A solution of alanine ethyl ester hydrochloride (11 mg, 72 μmol) in 3 mL of MeCN and 0.1 mL triethylamine was immediately added. This solution was stirred at room temperature for 16 h. The crude product was purified on a

(62) McCafferty, D. G.; Bishop, B. M.; Wall, C. G.; Hughes, S. G.; Mecklenberg, S. L.; Meyer, T. J.; Erickson, B. W. *Tetrahedron* **1995**, 1093.

column of silica gel using MeCN−H_2O−KNO_3(sat.) (91:5:1) as eluent. The solvent was evaporated, and the complex was redissolved in a minimum amount of MeOH and precipitated with a saturated solution of KPF_6. The red precipitate was collected by filtration, washed with water, and dried to give 0.045 g (63%) of product. ESI-FTICR MS (*m*/*e*): singly charged peak at 1068.2, [M − PF6]$^+$, calcd 1068.2. ^{1}H NMR (CD_3CN): δ = 1.33−1.42 (m, 9H, −OCH$_2$*CH$_3$*−POCH$_2$C*H$_3$*), 1.69 (d, 3H, −CH*CH$_3$*), 4.15−4.32 (m, 6H, −O*CH$_2$*CH$_3$−PO*CH$_2$*CH$_3$), 4.76−4.84 (m, 1H, −*CH*−CH$_3$), 7.16−7.26 (m, 4H, Py-*H*) 7.37 (d, 2H, Py-*H*), 7.47 (d, 2H, Py-*H*), 7.95−8.02 (m, 4H, Ph-*H*), 8.08 (d, 1H, −*NH*−), 8.12−8.19 (m, 2H, Py-*H*), 8.32−8.36 (m, 2H, Py-*H*), 8.63−8.67 (m, 4H, Py-*H*), 9.05 (s, 2H, Py-*H*), 9.13 (s, 2H, Py-*H*). Anal. Found: C, 45.65; H, 4.56; N, 7.90. Calcd: C, 45.55; H, 3.66; N, 8.08.

Complex 1a. Complex **13** (30 mg, 23μmol) was dissolved in 3 mL of dry CH_3CN under argon. The solution was cooled to 0 °C, and 0.4 mL of Si(CH$_3$)$_3$I (2.8 mmol) was added slowly under stirring. After 2 h, 4 mL of MeOH was added and the solution was left at room temperature for 3 h. A saturated NH_4PF_6 water solution was added and the red precipitate filtered off and washed with water to give pure product 25 mg (87%). ESI-FTICR MS (*m*/*e*): doubly charged peak at 479.62, [M − 2PF6]$^{2+}$, calcd 479.59. ^{1}H NMR (CD_3CN): δ = 1.32 (t, 3H, −OCH$_2$*CH$_3$*), 3.22−3.40 (m, 2H, −CH*CH$_2$*Ph), 4.28 (q, 2H, −O*CH$_2$*CH$_3$), 5.0−5.07 (m, 1H, −*CH*CH$_2$Ph), 6.84 (d, 2H, Ph-*H*) 7.17−7.27 (m, 4H, Py-*H*), 7.30 (d, 2H, Ph-*H*), 7.38 (d, 2H, Py-*H*), 7.47 (d, 2H, Py-*H*), 7.95−8.05 (m, 5H, Ph-*H*, −N*H*−), 8.18−8.24 (m, 2H, Py-*H*), 8.32−8.36 (m, 2H, Py-*H*), 8.63−8.70 (m, 4H, Py-*H*), 9.04 (s, 2H, Py-*H*), 9.09 (s, 2H, Py-*H*).

Complex 1b. Complex **14** (22 mg, 18μmol) was dissolved in 3 mL of dry CH_3CN under argon. The solution was cooled to 0 °C, and 0.3 mL of $SiMe_3I$ (2.1 mmol) was added slowly under stirring. After 2 h 4 mL of MeOH was added and the solution was left in room temperature for 3 h. A saturated NH_4PF_6 water solution was added and the red precipitate filtered off and washed with water to give 18 mg (86%) of pure product. ESI-FTICR MS (*m*/*e*): doubly charged peak at 433.60, [M − 2PF6]$^{2+}$, calcd 433.58. ^{1}H NMR (CD_3CN): δ = 1.36 (t, 3H, −OCH$_2$*CH$_3$*), 1.69 (d, 3H, −CH*CH$_3$*), 4.29 (q, 2H, −O*CH$_2$*CH$_3$), 4.76−4.84 (m, 1H, −*CH*CH$_3$), 7.16−7.24 (m, 4H, Py-*H*) 7.37 (d, 2H, Py-*H*), 7.50 (d, 2H, Py-*H*), 7.94−99 (m, 4H, Ph-*H*), 8.1 (1H, −N*H*−), 8.20−8.24 (m, 2H, Ph-*H*), 8.26−8.31 (m, 2H, Py-*H*), 8.65−8.70 (m, 4H, Py-*H*), 9.16 (s, 2H, Py-*H*), 9.13 (s, 2H, Py-*H*).

Ligand 16. A suspension of **15** (4.0 g, 10 mmol) and potassium phtalimide (3.3 g, 18 mmol) in dry dimethylformamide (100 mL) was heated under argon at 80 °C for 3 h. The solution was cooled to room temperature, diluted with $CHCl_3$ (100 mL), and filtered. The white precipitate was washed with $CHCl_3$. The combined filtrate was washed with water (100 mL), and the aqueous phase was extracted with $CHCl_3$ (2 × 50 mL). The combined organic phase was washed with 100 mL of NaOH (0.1 M) and water (2 × 100 mL). The solvent was evaporated until a white solid started to precipitate. Et_2O was added to get complete precipitation. The solid was collected by filtration, washed with Et_2O, and dried to give 4.5 g (96%) of the product. ^{1}H NMR ($CDCl_3$): δ = 4.92 (s, 2H, PhtC*H$_2$*Ph−), 7.32−7.36 (m, 2H, Py-*H*), 7.57 (d, *J* = 8.2 Hz, 2H, Ph-*H*), 7.69−7.73 (m, 2H, Py-H), 7.84−7.88 (m, 6H, Ph-*H* and Pht-*H*), 8.62−8.65 (m, 2H, Py-*H*), 8.68−8.72 (m, 4H, Py-*H*).

Complex 17. Ru(DMSO)$_4$Cl$_2$ (0.21 g, 0.43 mmol) was dissolved in EtOH (40 mL) at 85 °C under argon atmosphere. Ligand **16** (0.17 g, 0.36 mmol) was added, and the solution was heated at reflux for 1 h while a precipitate was formed. The reaction mixture was cooled to room temperature, and the product filtered off, washed with EtOH, and dried under vacuum to give **17** (0.17 g, 66%). ^{1}H NMR (DMSO-d_6): δ = 3.58 (s, 6H, −C*H$_3$*), 4.91 (s, 2H, −C*H$_2$*−), 7.52 (t, 2H, Py-*H*), 7.59 (d, 2H, Ph-*H*), 7.84−7.93 (m, 4H, Pht-*H*), 7.99 (t, 2H, Py-*H*), 8.15 (d, 2H, Ph-*H*), 8.75 (d, 2H, Py-*H*), 8.94 (s, 2H, Py-*H*), 9.34 (d, 2H, Py-*H*).

Complex 18. Complex **17** (0.17 g, 0.24 mmol) and **10** (0.11 g, 0.25 mmol) were refluxed in EtOH (40 mL) for 1.5 h under argon atmosphere. The solvent was removed and the residue chromatographed on silica gel (eluent: CH_3CN−H_2O− KNO_3(sat.), 90:7:2). Fractions containing product were combined, and the solvent was removed. The remaining solid was dissolved in a small amount of CH_3CN−H_2O (2:1), and an excess of NH_4PF_6 in water was added. The formed precipitate was filtered off, washed with H_2O, and dried under vacuum to give **18** (0.25 g, 81%). ^{1}H NMR (CD_3CN): δ = 1.39 (t, 6H, −C*H$_3$*), 4.17−4.25 (m, 4H, −C*H$_2$*−), 5.03 (s, 2H, −C*H$_2$*−), 7.19−7.23 (m, 4H, Py-*H*), 7.43−7.47 (m, 4H, Py-*H*), 7.78 (d, 2H, Ph-*H*), 7.84−7.98 (m, 8H, Py-*H*, Pht-*H*), 8.12−8.20 (m, 4H, Ph-*H*), 8.32−8.37 (m, 2H, Ph-*H*), 8.62−8.67 (m, 4H, Py-*H*), 9.02 (s, 2H, Py-*H*), 9.05 (s, 2H, Py-*H*).

Complex 19. To a solution of **18** (0.25 g, 0.20 mmol) in EtOH (50 mL) and CH_3CN (10 mL) was added 0.2 mL of NH_2NH_2•*x*H_2O. The reaction mixture was left with stirring over night under argon atmosphere. The solvents were removed under reduced pressure, and the solid was dissolved in a small amount of CH_3CN−H_2O (2:1). Addition of excess NH_4PF_6 in water gave a precipitate that was filtered off, washed with water, and dried under vacuum to give **19** (0.19 g, 87%). ^{1}H NMR (CD_3CN): δ = 1.39 (t, 6H, −C*H$_3$*), 4.21 (m, 4H, −C*H$_2$*−), 4.35 (s, 2H, −C*H$_2$*−), 7.21 (t, 4H, Py-*H*), 7.45 (d, 4H, Py-*H*), 7.80 (d, 2H, Ph-*H*), 7.98 (t, 4H, Py-*H*), 8.12−8.19 (m, 2H, Ph-*H*), 8.29 (d, 2H, Ph-*H*), 8.32−8.37 (m, 2H, Ph-*H*), 8.67 (d, 4H, Py-*H*), 9.03 (s, 2H, Py-*H*), 9.06 (s, 2H, Py-*H*).

Complex 21. Complex **19** (91 mg, 0.08 mmol), carotenoid **20** (46 mg, 0.11 mmol), and DMAP (12 mg, 0.1 mmol) were dissolved in dry CH_2Cl_2 (8 mL) and CH_3CN (4 mL) under argon atmosphere, in the dark. After 15 min of stirring, DCC (33 mg, 0.16 mmol) dissolved in CH_2Cl_2 (1 mL) was added. The reaction mixture was left with stirring 13 h. The solvent was removed under reduced preassure and the resulting solid purified on silica column using CH_3CN−H_2O−KNO_3(sat.) (90:5:1) as eluent. Fractions containing product were combined, and the solvent was removed. The remaining solid was dissolved in a small amount of CH_3CN−H_2O (2:1), and an excess of NH_4PF_6 in water was added. The formed precipitate was filtered off, washed with H_2O, and dried under vacuum to give **21** (77 mg, 58%). ESI-FTICR MS (*m*/*e*): doubly charged peak at 649.80, [M − 2PF$_6$]$^{2+}$, calcd 649.75. ^{1}H NMR (CD_3CN): δ = 1.05 (s, 6H, Car−C*H$_3$*), 1.39 (t, 6H, −C*H$_3$*), 1.49−1.69 (m, 4H, Car−C*H$_2$*−), 1.73 (s, 3H, Car−C*H$_3$*), 2.02 (s, 3H, Car−C*H$_3$*), 2.04 (s, 3H, Car−C*H$_3$*), 2.07−2.13 (m, 8H, Car−C*H$_3$*, Car−C*H$_2$*−), 4.15−4.27 (m, 4H, −C*H$_2$*−CH$_3$), 4.64 (d, 2H, −C*H$_2$*−NH−), 6.13−6.47 (m, 6H, Car−C*H*−), 6.68−6.87 (m, 5H, Car−C*H*−),7.08−7.13 (m, 1H, Car−C*H*−), 7.18−7.25 (m, 4H, Py-*H*), 7.31 (t, 1H, −N*H*−), 7.42−7.49 (m, 4H, Py-*H*), 7.72 (d, 2H, Ph-*H*), 7.93−8.02 (m, 4H, Py-*H*), 8.12−8.20 (m, 4H, Ph-*H*), 8.35 (dd, 2H, Ph-*H*), 8.63−8.71 (m, 4H, Py-*H*), 9.03 (s, 2H, Py-*H*), 9.06 (s, 2H, Py-*H*).

Complex 2a. A solution of **21** (30 mg, 0.018 mmol) in DMF (2 mL), CH_3CN (3 mL), and Et_3N (0.1 mL) was cooled to 0 °C under argon. Me_3SiBr (0.1 mL, 0.77 mmol) was added, and the resulting mixture was allowed to reach room temperature, while left with stirring for 24 h in the dark. MeOH (degassed, 2 mL) was added and the stirring continued for 2 h. About 95% of the solvent was removed under reduced pressure, and Et_2O (2 mL) and CH_3CN (5 mL) were added. The precipitate formed was filtered off and washed

with Et_2O to give **2a** (14 mg, 51%). ^{1}H NMR (DMSO-d_6): δ = 1.01 (s, 6H, Car−CH_3), 1.40−1.61 (m, 4H, Car−CH_2−), 1.65 (s, 3H, Car−CH_3), 1.94−2.03 (m, 14H, Car−CH_3, Car−CH_2−), 4.58 (d, 2H, −CH_2−NH−), 6.18−6.49 (m, 6H, Car−CH−), 6.61−6.82 (m, 5H, Car−CH−),7.06−7.10 (m, 1H, Car−CH−), 7.23−7.29 (m, 4H, Py-*H*), 7.52−7.56 (m, 4H, Py-*H*), 7.62 (d, 2H, Ph-*H*), 7.93−8.10 (m, 6H, Py-*H*), 8.39 (d, 2H, Ph-*H*), 8.51 (dd, 2H, Ph-*H*), 8.61 (t, 1H, −N*H*−), 9.04−9.11 (m, 4H, Py-*H*), 9.43 (s, 2H, Py-*H*), 9.51 (s, 2H, Py-*H*).

Complex 23. Ru(tpy)(DMSO)Cl_2 (**22**) (0.30 g, 0.52 mmol) and **10** (0.24 g, 0.54 mmol) were refluxed in EtOH (60 mL) for 3 h under argon atmosphere. The solvent was removed and the residue chromatographed on silica gel (eluent: $CH_3CN-H_2O-KNO_3$ (sat.), 90:7:2). Fractions containing product were combined, and the solvent was removed. The remaining solid was dissolved in a small amount of CH_3CN, and an excess of NH_4PF_6 in acidic water was added. The formed precipitate was filtered off, washed with H_2O, and dried under vacuum to give **23** (0.360 g, 59%). ^{1}H NMR (CD_3CN): δ = 1.39 (t, 6H, −CH_3), 2.57 (s, 3H, −CH_3), 4.18−4.25 (m, 4H, −CH_2−CH_3), 7.18−7.24 (m, 4H, Py-*H*), 7.44 (d, 2H, Py-H), 7.47 (d, 2H, Py-*H*), 7.1 (d, 2H, Ph-*H*), 7.95−8.00 (m, 4H, Py-*H*), 8.13 (d, 2H, Ph-*H*), 8.17 (d, 2H, Ph-*H*), 8.34 (dd, 2H, Ph-*H*), 8.66−8.70 (m, 4H, Py-*H*), 9.02 (s, 2H, Py-*H*), 9.05 (s, 2H, Py-*H*).

Complex 2b. A solution of **23** (60 mg, 0.052 mmol) in dry CH_3CN (10 mL) was cooled under 0 °C argon atmosphere. Me_3SiI (0.1 mL, 0.7 mmol) was added, and the resulting mixture was allowed to reach room temperature, while left with stirring for 2 h in the dark. MeOH (degassed, 2 mL) was added and the stirring continued for 2 h. A saturated NH_4PF_6 water solution was added and the red precipitate filtered off and washed with water to give **2b** (47 mg, 83%). ESI-FTICR MS (*m*/*e*): singly charged peak at 813.18, [M − 2PF6, H^+]$^+$, calcd 813.13. ^{1}H NMR (DMSO-d_6): δ = 2.58 (s, 3H, −CH_3), 7.23−7.28 (m, 4H, Py-*H*), 7.52−7.60 (m, 6H, Py-*H*, Ph-*H*), 7.98−8.070 (m, 6H, Py-*H*, Ph-*H*), 8.36 (d, 2H, Ph-*H*), 8.47 (d, 2H, Ph-*H*), 9.07−9.13 (m, 4H, Py-*H*), 9.44 (s, 2H, Py-*H*), 9.50 (s, 2H, Py-*H*).

Ligand 25. To a solution of 4′-(*p*-(CO_2Me)Ph)-terpyridine[63] (0.84 g, 2.3 mmol) in methanol (20 mL) was added NaOH in water (1 M, 40 mL). The reaction was heated at 80 °C for 10 h while it became a clear solution. The solvent was removed under reduced pressure and the solid redissolved in water. The pH of the resulting solution was adjusted to pH 4−5 with HCl (2 M). The white precipitate was collected by filtration and washed with water and dried to give 0.76 g (93%) of the acid. ^{1}H NMR (DMSO-d_6): δ = 7.72 (t, 2H, Py-*H*), 8.1−8.71 (m, 4H, Ph-*H*), 8.24 (t, 2H, Py-*H*), 8.82−8.91 (m, 6H, Py-*H*).

Complex 26. A solution of **24**[5] (0.28 g, 0.49 mmol) and silver-(I) triflate (0.30 g, 1.2 mmol) in EtOH (40 mL) and DMF (10 mL) was heated at 60 °C for 20 min, to give a blue solution. Ligand **25** (0.173 g, 0.49 mmol) was added, and the resulting solution was heated at reflux under argon for 22 h. The red solution was filtered, and the solvent was removed under reduced pressure. The red solid was chromatographed on silica gel (eluent: $CH_3CN-H_2O-KNO_3$-(sat.), 80:15:5). Fractions containing product were combined, and the solvent was removed. The remaining solid was dissolved in a small amount of CH_3CN-H_2O (2:1), and an excess of NH_4PF_6 in water was added. The formed precipitate was filtered off, washed with H_2O, and dried under vacuum to give **26** (0.24 g, 44%). ^{1}H NMR (CD_3CN): δ = 1.53 (t, 6H, CH_2-CH_3), 4.43 (m, 4H, CH_2-CH_3), 7.18 (t, 2H, Py-*H*), 7.23 (t, 2H, Py-*H*), 7.36 (d, 2H, Py-*H*), 7.49 (d, 2H, Py-*H*), 7.95−8.02 (m, 4H, Py-*H*), 8.35 (d, 2H, Ph-*H*), 8.41 (d, 2H, Ph-*H*), 8.66−8.69 (m, 4H, Py-*H*), 8.98 (d, 2H, Py-*H*), 9.08 (s, 2H, Py-*H*).

Complex 27a. A solution of complex **26** (67 mg, 55 μmol), PyBOP (32 mg, 61 μmol), and DIEA (10.6 μL, 61 μmol) in 1 mL of dry CH_3CN and 2 mL of CH_2Cl_2 was left with stirring for 30 min under argon. Tyrosine ethyl ester−dpa (40 mg, 63 μmol) and DIEA (10.6 μL, 61 μmol) in 2 mL of CH_2Cl_2 was added, and the resulting solution was stirred under argon for 12 h. The solution was diluted with 50 mL of CH_2Cl_2 and washed with H_2O, the organic phase was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The red solid was chromatographed on silica gel (eluent gradient: $CH_3CN \rightarrow CH_3CN/H_2O/KNO_3$(sat.), 50:10:5). Fractions containing product were combined, and the solvent was removed. The remaining solid was taken up into CH_2Cl_2 by addition of $H_2O-NH_4PF_6$ and CH_2Cl_2. The organic phase was washed with water and dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give 71.7 mg (75%) of **27a**. ESI-FTICR MS (*m*/*e*): doubly charged peak at 718.77, [M − $2PF_6$]$^{2+}$, calcd 718.73; doubly charged peak at 791.76, [M − PF_6 + H^+]$^{2+}$, calcd 791.72. ^{1}H NMR (CD_3CN): δ = 1.22 (t, 3H, CH_2-CH_3), 1.53 (t, 6H, CH_2-CH_3), 3.08 (dd, 1H, tyr−CH_2−CH), 3.27 (dd, 1H, tyr−CH_2−CH), 4.14−4.21 (14H, CH_2-CH_3, Ph−CH_2−N, Py−CH_2−N), 4.44 (q, 4H, −CH_2-CH_3), 4.95 (q, 1H, tyr−CH−N), 7.17−7.27 (m, 6H, Py-*H*, tyr−Ph-*H*), 7.35−7.39 (m, 10H, Py-*H*), 7.48 (m, 3H, Py-*H*, −N*H*−), 7.78 (t, 4H, Py-*H*), 7.95−8.01 (m, 6H, Py-*H*, Ph-*H*), 8.14 (d, 2H, Ph-*H*), 8.57 (d, 4H, Py-*H*), 8.65−8.70 (m, 4H, Py-*H*), 8.97−9.01 (m, 4H, Py-*H*).

Complex 27b. A solution of complex **26** (60 mg, 54 μmol), PyBOP (29 mg, 56 μmol), and diisopropylethylamine (DIEA) (9.5 μL, 55 μmol) in 1 mL of dry CH_3CN and 2 mL of CH_2Cl_2 was left with stirring for 30 min under argon. L-Alanine ethyl ester hydrochloride (8.4 mg, 55 μmol) and DIEA (19 μL, 110 μmol) in 2 mL of CH_2Cl_2 was added, and the resulting solution was stirred under argon for 12 h. The solution was diluted with 50 mL of CH_2Cl_2 and washed with H_2O, the organic phase was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The red solid was chromatographed on silica gel (eluent gradient: $CH_3CN \rightarrow CH_3CN-H_2O-KNO_3$(sat.), 90:5:2). Fractions containing product were combined, and the solvent was removed. The remaining solid was taken up into CH_2Cl_2 by addition of $H_2O-NH_4PF_6$ and CH_2Cl_2. The organic phase was washed with water and dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give **27b** [50.4 mg (77%)]. ESI-FTICR MS (*m*/*e*): singly charged peak at 1068.23, [M − PF_6] $^+$, calcd 1068.18. ^{1}H NMR (CD_3CN): δ = 1.31 (t, 3H, CH_2-CH_3), 1.53 (t, 6H, CH_2-CH_3), 1.57 (d, 3H, CH−CH_3), 4.23 (q, 2H, −CH_2-CH_3) 4.43 (m, 4H, −CH_2-CH_3), 4.68 (qv, 1H, NH−CH−CH_3) 7.18 (t, 2H, Py-*H*), 7.24 (t, 2H, Py-*H*), 7.35 (d, 2H, Py-*H*), 7.49 (d, 2H, Py-*H*), 7.52 (d, 1H, −N*H*−), 7.94−8.01 (m, 4H, Py-*H*), 8.22 (d, 2H, Ph-*H*), 8.32 (d, 2H, Ph-*H*), 8.68 (d, 4H, Py-*H*), 8.98 (d, 2H, Py-*H*), 9.07 (s, 2H, Py-*H*).

Complex 3a. Complex **27a** (25 mg, 14 μmol) was dissolved in 3 mL of dry CH_3CN under argon. The solution was cooled to 0 °C, and 0.1 mL of $Si(CH_3)_3I$ (0.7 mmol) was added slowly under stirring. After 2 h 4 mL of MeOH was added and the solution was left at room temperature for 3 h. A saturated NH_4PF_6 water solution was added and the red precipitate filtered off and washed with water to give pure product 15.1 mg (64%). ESI-FTICR MS (*m*/*e*): doubly charged peak at 690.74, [M − $2PF_6$]$^{2+}$, calcd 690.70; doubly charged peak at 763.73, [M − PF_6 + H^+]$^{2+}$, calcd 763.69. ^{1}H NMR

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(CD_3CN): $\delta = 1.24$ (t, 3H, CH_2-CH_3), 3.05 (dd, 1H, tyr−CH_2−CH), 3.25 (dd, 1H, tyr−CH_2−CH), 4.11 (s, 4H, Ph−CH_2−N), 4.21 (q, 2H, CH_2-CH_3), 4.33 (s, 8H, Py−CH_2−N), 4.97 (q, 1H, tyr−CH−N), 7.17−7.21 (m, 6H, Py-*H*, tyr−Ph−*H*), 7.40 (d, 2H, Py-*H*), 7.45 (d, 2H, Py-*H*), 7.51−7.60 (m, 9H, Py-*H*, −N*H*−), 7.93 (t, 4H, Py-*H*), 8.01−8.06 (m, 6H, Py-*H*, Ph-*H*), 8.23 (d, 2H, Ph-*H*), 8.62−8.68 (m, 8H, Py-*H*), 8.98 (s, 2H, Py-*H*), 9.12 (d, 2H, Py-*H*).

Complex 3b. Complex **27b** (15 mg, 12 μmol) was dissolved in 2 mL of dry CH_3CN under argon. The solution was cooled to 0 °C, and 0.1 mL of $Si(CH_3)_3I$ (0.7 mmol) was added slowly under stirring. After 2 h 3 mL of MeOH was added and the solution was left with stirring in room temperature for 3 h. A saturated NH_4PF_6 water solution was added and the red precipitate filtered off and washed with water to give pure product 9.6 mg (69%). ESI-FTICR MS (*m*/*e*): single charged peak at 1012.17, $[M - PF_6]^+$, calcd 1012.12; doubly charged peak at 433.61, $[M - 2PF_6]^{2+}$, calcd 433.58; singly charged peak at 866.19, $[M - 2PF_6 - H^+]^+$, calcd 866.14. ^{1}H NMR (DMSO-d_6): $\delta = 1.23$ (t, 3H, CH_2-CH_3), 1.48 (d, 3H, CH−CH_3), 4.15 (q, 2H, $-CH_2-CH_3$), 4.55 (qv, 1H, NH−CH−CH_3), 7.24 (t, 2H, Py-*H*), 7.30 (t, 2H, Py-*H*), 7.42 (d, 2H, Py-*H*), 7.52 (d, 2H, Py-*H*), 7.97 (t, 2H, Py-*H*), 8.07 (t, 2H, Py-*H*), 8.25 (d, 2H, Ph-*H*), 8.57 (d, 2H, Ph-*H*), 8.91 (d, 2H, Py-*H*), 9.03 (d, 1H, −N*H*−), 9.11 (d, 2H, Py-*H*), 9.17 (d, 2H, P−Py-*H*), 9.53 (s, 2H, Py-*H*).

Complex 28. $Ru(DMSO)_4Cl_2$ (0.7 g, 1.44 mmol) and ligand **9** (0.8 g, 2.9 mmol) were refluxed in EtOH (60 mL) and DMF (10 mL) for 26 h. The solvent was removed and the residue chromatographed on silica gel eluent CH_3CN-H_2O- KNO_3(sat.) (60:30:10). Fractions containing product were combined, and the solvent was removed. The remaining solid was dissolved in a small amount of CH_3CN-H_2O (1:1), and an excess of NH_4PF_6 in water was added. The solution was acidified with HCl (1 M) until a precipitate formed. The product was filtered off, washed with H_2O, and dried under vacuum to give **28** (0.75 g, 55%). ^{1}H NMR (CD_3CN): $\delta =$ 7.20 (t, 4H), 7.38 (d, 4H), 7.87 (t, 4H), 8.68 (d, 4H), 9.27 (s, 4H).

Complex 4a. To a solution of complex **28** (85 mg, 90 μmol) and DIEA (15.6 μL, 90 μmol) in dry DMF (2 mL) was added PyBOP (47 mg, 89 μmol) in 1 mL of DMF. The solution was left with stirring for 30 min under argon. Tyrosine ethyl ester−dpa (56 mg, 89 μmol) and DIEA (30.8 μL, 178 μmol) in 1 mL of DMF was added, and the resulting solution was stirred under argon for 12 h. The solvent was removed under reduced pressure. The red solid was chromatographed three times on RP gel (eluent: $(CH_3)_2CO-H_2O-KNO_3$(sat.), 5:10:1). Fractions containing product were combined, and the solvent was removed. The remaining solid was dissolved in a small amount of CH_3CN-H_2O (1:1), and an excess of NH_4PF_6 in water was added. The resulting solution was acidified with HCl (1 M) to get quantitative precipitation. The product was filtered off, washed with H_2O, and dried under vacuum to give **4a** (15 mg, 11%). ESI-FTICR MS (*m*/*e*): singly charged peak at 1414.43, $[M - PF_6]^+$, calcd 1414.35; singly charged peak at 1560.41, $[M + H^+]^+$, calcd 1560.33. ^{1}H NMR (CD_3CN): $\delta = 1.18$ (t, 3H, CH_2-CH_3), 3.18−3.32 (m, tyr−CH_2−), 4.12 (s, 4H, Ph−CH_2−N), 4.17 (q, 2H, CH_2-CH_3), 4.33 (s, 8H, Py−CH_2−N), 4.98 (q, 1H, tyr−CH−NH), 7.16−7.22 (m, 6H, Py-*H*, Ph-*H*), 7.35 (t, 4H, Py-*H*), 7.51 (d, 4H, Py-*H*), 7.57 (t, 4H, Py-*H*), 7.94−8.04 (m, 9H, Py-*H*, CO−N*H*−CH), 8.56 (d, 2H, Py-*H*), 8.63 (d, 4H, Py-*H*), 8.68 (d, 2H, Py-*H*), 9.02 (s, 2H, Py-*H*), 9.24 (s, 2H, Py-*H*).

Complex 4b. Complex **28** (60 mg, 63 μmol) was suspended in thionyl chloride (5 mL) and refluxed for 3 h under argon. Excess thionyl chloride was evaporated and the resulting solid dissolved in dry DMF (3 mL). A solution of tyrosine ethyl ester hydrochloride (15.5 mg, 63 μmol) in dry acetonitrile (2 mL) and triethylamine (0.1 mL) was immediately added. The resulting mixture was heated at 90 °C for 2 h and left at 50 °C over night. The solvent was removed and the residue chromatographed on silica gel with eluent $CH_3CN-H_2O-KNO_3$(sat.), (80:12:4). Fractions containing product were combined, and the solvent was removed. The remaining solid was dissolved in a small amount of CH_3CN-H_2O (1:1), and an excess of NH_4PF_6 in water was added. The resulting solution was acidified with HCl (1 M) until a precipitate formed. The product was filtered off, washed with H_2O, and dried under vacuum to give **4b** (35 mg, 49%). ESI-FTICR MS (*m*/*e*): singly charged peak at 992.20, $[M - PF_6]^+$, calcd 992.13; singly charged peak at 846.21, $[M - 2PF_6, H^+]^+$, calcd 846.16. ^{1}H NMR (CD_3CN): $\delta = 1.31$ (t, 3H, $-CH_2-CH_3$), 3.22−3.40 (m, 2H, Tyr−CH_2), 4.26 (q, 2H, $-CH_2-CH_3$), 5.0−5.08 (m, 1H, Tyr−CH−), 6.84 (d, 2H, Ph-*H*), 7.09 (s, 1H, Ph−O*H*), 7.16−7.23 (m, 4H, Py-*H*), 7.29 (d, 2H, Ph-*H*), 7.37 (t, 4H, Py-*H*), 7.93−8.04 (m, 5H, Py-*H*, N−*H*), 8.61−8.69 (m, 4H, Py-*H*), 9.06 (s, 2H, Py-*H*), 9.24 (s, 2H, Py-*H*).

Complex 4c. Complex **28** (76 mg, 80 μmol) was suspended in thionyl chloride (5 mL) and refluxed for 3 h under argon. Excess thionyl chloride was evaporated and the resulting solid dissolved in dry DMF (3 mL). A solution of alanine ethyl ester hydrochloride (12.3 mg, 80 μmol) in dry acetonitrile (2 mL) and triethylamine (0.1 mL) was immediately added. The resulting mixture was heated at 90 °C for 2 h and left at 50 °C overnight. The solvent was removed and the residue chromatographed on silica gel eluent $CH_3CN-H_2O-KNO_3$(sat.) (80:12:4). Fractions containing product were combined, and the solvent was removed. The remaining solid was dissolved in a small amount of CH_3CN-H_2O (1:1), and an excess of NH_4PF_6 in water was added. The resulting solution was acidified with HCl (1 M) until a precipitate formed. The product was filtered off, washed with H_2O, and dried under vacuum to give **4c** (38 mg, 45%). ESI-FTICR MS (*m*/*e*): singly charged peak at 900.15, $[M - PF_6]^+$, calcd 900.11. ^{1}H NMR (CD_3CN): $\delta = 1.33$ (t, 3H, $-CH_2-CH_3$), 1.68 (d, 3H, Ala−CH−CH_3), 4.29 (q, 2H, $-CH_2-CH_3$), 4.78−4.85 (m, 1H, Ala−CH−CH_3), 7.17−7.24 (m, 4H, Py-*H*), 7.35−7.41 (m, 4H, Py-*H*), 7.93−8.01 (m, 4H, Py-*H*), 8.15 (d, 1H, N−*H*), 8.63−8.70 (m, 4H, Py-*H*), 9.17 (s, 2H, Py-*H*), 9.25 (s, 2H, Py-*H*).

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