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Synthesis, Characterization and Electronic Properties of *trans*-[4-(Alkoxycarbonyl)phenyl]porphyrin-[Ru^{II}(bpy)₃]₂ Complexes or Boron–Dipyrrin Conjugates as Panchromatic Sensitizers for DSSCs

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Two porphyrin-based dyes were synthesized that incorporate two additional chromophores to absorb in a wider UV/Vis region. In the first dye, a porphyrin ring is linked through an amide bond to two $[Ru(bpy)_3]^{2+}$ units, forming a symmetric $[Ru(bpy)_3]$ -porphyrin- $[Ru(bpy)_3]$ {Por(COOH)₂[Ru(bpy)₃]₂} system. The second porphyrin is *trans* substituted through a triple bond to the *meso* position with two boron dipyrrin

Introduction

In recent years dye-sensitized solar cells (DSSCs) have attracted great attention due to their relatively low production cost and high power conversion efficiencies.^[1-4] At present, ruthenium polypyridyl complexes^[2,5-20] and several organic dyes are extensively used as sensitizers for DSSCs, achieving high efficiencies.^[21-38] Among all the organic dyes used, porphyrins are one of the most widely studied because of their strong Soret (400-450 nm) and moderate Q bands (550-600 nm) and their appropriate LUMO and HOMO energy levels.^[39–45] Moreover, porphyrins can be easily modified by peripheral substitution or inner metal complexation, and this can alter their optical, electrochemical and photophysical properties. It is well-known that one of the most important requirements to attain highly efficient solar energy is broad light absorption capability of the dye. Attachment of various chromophores to the porphyrin periphery will increase the ability of the dye to absorb over a wide range of the UV/Vis region. A few examples have been reported in which mixtures of different dyes have been

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(BDP) molecules $\{Por(COOH)_2(BDP)_2\}$. Both porphyrins bear two carboxylic groups capable of binding onto a TiO₂ surface, with potential applications in dye-sensitized solar cells (DSSCs). The title dyes were characterized by means of ¹H and ¹³C NMR spectroscopy, elemental analysis, MALDI-TOF, UV/Vis absorption and emission studies.

loaded onto the semiconductor surface, giving satisfactory results in several cases.^[46–50] In this work, molecules such as polypyridine-ruthenium(II) complexes and BDP were attached to a porphyrin to build dyes with a wider absorption range. First, complexes such as $[Ru(bpy)_3]^{2+}$ and its derivatives can be attached to the porphyrin periphery. This suitable "auxiliary" ligand displays an absorption maximum within the 400–500 nm region as well as excellent photophysical and redox properties. Therefore, a chromophore bearing a porphyrin and a ruthenium(II) tris-bipyridine complex could constitute a good candidate for DSSC applications because their complementary absorption spectra can provide an extended absorption range.

A plethora of articles have been published on porphyrins and $[Ru(bpy)_3]$ complexes, allowing the exploitation of their supramolecular properties particularly for applications in catalysis, artificial photosynthesis, and molecular devices.^[51–65] These types of triads (or larger architectures) continue to be very interesting due to their ability to act as efficient sensitizers for energy- and electron-transfer. This type of ruthenium-porphyrin dyes have been reported as sensitizers for DSSCs.^[13]

Secondly, BDP molecules as highly absorbing antenna chromophores can be attached to the porphyrin ring. Moreover, BDP dyes combine a high fluorescence quantum yield, a relatively long lifetime, a suitable excited state energy, and excellent photostability.^[66–68] There are examples reported in the literature in which porphyrin and BDP molecules (covalently attached or not to the porphyrin) have been used for DSSC applications.^[47,69–71]



Herein, we present the synthesis and full characterization of symmetric [Ru(bpy)₃]-porphyrin-[Ru(bpy)₃] {Por(COOH)₂-[Ru(bpy)₃]₂} and BDP-porphyrin-BDP {Por(COOH)₂-(BDP)₂}, which are A_2B_2 type systems. In the first case, two suitably modified [Ru(bpy)₃]²⁺ units are anchored on opposite sides of a tetraphenyl-substituted porphyrin through two amide bonds, whereas each of the remaining two porphyrinic phenyl substituents carry a carboxylic group capable of immobilizing the system onto TiO₂ substrate. In the second system, two BDP molecules are attached at the *meso* position of the porphyrin through a triple bond.

Results and Discussion

Synthesis

$Por(COOH)_2[Ru(bpy)_3]_2$

The synthesis of all compounds related to the preparation of chromophore $Por(COOH)_2[Ru(bpy)_3]_2$ is shown in Scheme 1. Bis-amino-substituted $Por(COOMe)_2(NH_2)_2$ was prepared in three steps. First, *meso-*(4-nitrophenyl)dipyrromethane (DipNO₂) was synthesized in high yield by acidcatalyzed condensation of 4-nitrobenzaldehyde and pyrrole, according to the literature.^[72] The bis-nitro-substituted Por-(COOMe)₂(NO₂)₂ was prepared by condensation of 4-(methoxycarbonyl)benzaldehyde with DipNO₂ in a ratio of 1:1, in the presence of trifluoroacetic acid (TFA), followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), as described in the literature (Scheme 1).^[73] Reduction of the nitro groups was first carried out in concentrated aqueous HCl with SnCl₂ by a known procedure.^[74] The amino-substituted Por(COOMe)₂(NH₂)₂ was purified by column chromatography on silica gel but this gave a low yield. Further investigation (column chromatography, Maldi-Tof mass spectrometry) revealed that another two byproducts, the mono-hydrolyzed substitute and the di-hydrolyzed compounds, had been formed due to the acidic conditions of the reaction. To avoid the hydrolysis of the ester groups at the meso position of the porphyrin, a catalytic hydrogenation in tetrahydrofuran (THF) was used, which afforded the desired Por(COOMe)₂(NH₂)₂ in 95% yield.^[75] Por(COOMe)₂(NH₂)₂ was further treated with an excess of 4'-methyl-2,2'-bipyridine-4-carbonyl chloride in THF in the presence of Et₃N to form porphyrin-bipyridine ligand Por(COOMe)₂(bpy)₂. This derivative could not be purified by column chromatography or recrystallization from the excess of 4'-methyl-[2,2'-bipyridine]-4-carboxylic acid (BpyCOOH) and was used without any further purifi-



Scheme 1. Synthesis of Por(COOH)₂[Ru(bpy)₃]₂.



Scheme 2. Synthesis of reference compound AnilbpyRu(bpy)2.

cation. By heating the mixture of [Ru(bpy)₂Cl₂] and Por-(COOMe)₂(bpy)₂ to reflux in acetic acid, according to a literature method,^[55] complex Por(COOMe)₂[Ru(bpy)₃]₂ was obtained in 52% yield. Finally, the latter complex was hydrolyzed in a mixture of THF/MeOH/aq. KOH at room temperature and then neutralized with hydrochloric acid solution to afford the corresponding porphyrin-[Ru^{II}-(bpy)₃]₂ complex Por(COOH)₂[Ru(bpy)₃]₂ in almost quantitative yield. The aniline-[Ru^{II}(bpy)₃]₂ complex Anilbpy-Ru(bpy)₂ that was used as a reference compound was synthesized in two steps as shown in Scheme 2. Coupling of 4methyl-2,2'-bipyridinyl-4-carbonyl chloride with aniline afforded the aniline-bipyridine ligand Anilbpy and subsequent heating to reflux with Ru(bpy)₂Cl₂ in a mixture of MeOH/acetic acid, afforded the aniline-[Ru^{II}(bpy)₃] complex AnilbpyRu(bpy)₂ in 82% yield.

Por(COOH)₂(BDP)₂

The synthesis of chromophore $Por(COOH)_2(BDP)_2$ is shown in Scheme 3. $Por(COOMe)_2Br_2$ was prepared in excellent yield following the a literature procedure.^[76] Basic hydrolysis of the latter resulted in formation of $Por(COOH)_2$ - Br_2 in high yield. Subsequent Sonogashira coupling with BDP-ethynyl, which was synthesized according to the literature,^[77] afford the desired $Por(COOH)_2(BDP)_2$.

Photophysical Properties

$Por(COOMe)_2[Ru(bpy)_3]_2$

The absorption spectrum of the $[Ru(bpy)_3]$ -porphyrin conjugate Por(COOMe)₂[Ru(bpy)₃]₂ is essentially the sum of those of its constituent chromophores, as can be seen





in Figure 1. The peak at 288 nm corresponds to the 1π - π^* transition of the 2,2'-bipyridyl (bpy) ligands of the Ru chromophores, whereas the intense absorption at 418 nm is due to the porphyrin Soret band. The metal-to-ligand charge transfer (MLCT) manifold of the ruthenium units appear as a shoulder on the low energy side (ca. 460 nm) of the Soret band, whereas the four Q bands of the free-base porphyrin chromophore are found at 513, 549, 590 and 644 nm. Detailed comparison of the absorption spectrum of Por(COOMe)₂[Ru(bpy)₃]₂ with those of the model compounds Por(COOMe)₂(NH₂)₂ and AnilbpyRu(bpy)₂ reveals only modest shifts in the porphyrin Q bands (ca. 5 nm), indicating that the two chromophores constituting Por-(COOMe)₂[Ru(bpy)₃]₂ interact only weakly in the ground state.



Figure 1. The UV/Vis absorption spectra of Por(COOMe)₂-(NH₂)₂, Por(COOMe)₂[Ru(bpy)₃]₂, and AnilbpyRu(bpy)₂ in CH₃CN at 298 \pm 3 K.

The room temperature emission spectrum of Por-(COOMe)₂[Ru(bpy)₃]₂ upon excitation at 461 nm (thus exciting predominantly the [Ru(bpy)₃] chromophores) is depicted in Figure 2 (a), revealing the characteristic emission features of the porphyrin chromophore without any apparent Ru-based emission features. The excitation spectra of Por(COOMe)₂[Ru(bpy)₃]₂ monitored at the two porphyrin emission peaks at 650 and 730 nm (Figure 3) match well to the absorption spectrum of the porphyrin chromophore and show a weak bipyridyl ${}^{1}\pi$ - π * feature at ca. 288 nm and no apparent ¹MLCT Ru(bpy)₃-based absorption features, indicating that ¹MLCT to porphyrin energy transfer is not operational when the $[Ru(bpy)_3]$ chromophore in Por- $(COOMe)_2[Ru(bpy)_3]_2$ is excited and that the emission observed upon excitation of Por(COOMe)₂[Ru(bpy)₃]₂ at 461 nm is solely due to excitation of the porphyrin chromophore. The fact that the phosphorescence from the [Ru- $(bpy)_{3}$ units is not apparent in the emission spectrum of Por(COOMe)₂[Ru(bpy)₃]₂ in Figure 2 (a) can potentially be attributed to the inherently strong fluorescence of the porphyrin unit, which masks the $[Ru(bpy)_3]$ emission features, as can be witnessed by the emission spectrum of reference compound AnilbpyRu(bpy)₂ in Figure 2 (a). However, when $Por(COOMe)_2[Ru(bpy)_3]_2$ is excited at 288 nm in MeCN at room temperature and in a rigid EtOH/MeOH (4:1) matrix at 77 K, dual emission due to both chromophores is clearly observed (Figure 2, b). Especially in the case of the 77 K emission spectrum, the $[Ru(bipy)_3]$ -based ³MLCT, phosphorescence becomes more apparent due to its matrix and temperature-induced blueshift and enhancement.



Figure 2. The emission spectra of isoabsorbing (A = 0.1) solutions (a) Por(COOMe)₂[Ru(bpy)₃]₂ ($\lambda_{ex} = 461 \text{ nm}$) and AnilbpyRu(bpy) ₂ ($\lambda_{ex} = 461 \text{ nm}$) in CH₃CN at 298 ± 3 K and (b) Por(COOMe)₂-[Ru(bpy)₃]₂ in CH₃CN at 298 ± 3 K ($\lambda_{ex} = 288 \text{ nm}$) and in EtOH/ MeOH (4:1) matrix at 77 K ($\lambda_{ex} = 288 \text{ nm}$).



Figure 3. The excitation spectra of $Por(COOMe)_2[Ru(bpy)_3]_2$ in CH_3CN at 298 ± 3 K monitoring at 650 and 730 nm.

Time-resolved fluorescence measurements (Figure 4) in MeCN at room temperature and 400 nm pulsed excitation show that Por(COOMe)₂[Ru(bpy)₃]₂ exhibits a dual exponential decay with lifetimes of ca. 7 and 207 ns. The short lifetime corresponds to the fluorescence of the porphyrin chromophore in Por(COOMe)₂[Ru(bpy)₃]₂, whereas the long lifetime is attributed to [Ru(bpy)₃] phosphorescence. The fact that the [Ru(bpy)₃] lifetime of Por(COOMe)₂-



the [Ru(bpy)₃] donors and the porphyrin acceptor.^[80,81] This observation was also corroborated by our DFT investigation, which reveals poor electronic delocalization between the central porphyrin and the terminal [Ru(bpy)₃] units.

Por(COOH)₂(BDP)₂

The electronic absorption spectra of BDP-ethynyl and Por(COOH)₂(BDP)₂ are presented in Figure 5. All absorption spectra were measured in tetrahydrofuran. The absorption spectrum of triad Por(COOH)₂(BDP)₂ clearly shows a combination of absorption features from its two constituent chromophores. The intense peak at 502 nm corresponds to the lowest energy π - π * transitions of the BDP chromophores,^[82] whereas the strong Soret band at 451 nm and the moderate Q bands at 601 and 654 nm are typical porphyrin absorption features. The porphyrin-based bands of Por-(COOH)₂(BDP)₂ are red-shifted by ca. 30 nm compared to those of zinc tetraphenylporphyrin,^[83] reflecting extended π -conjugation. This observation is consistent with other reports in the literature on ethylene-substituted porphyrins.^[47,84,85]



Figure 5. The UV/Vis absorption spectra of BDP-ethynyl and $Por(COOH)_2(BDP)_2$ in THF at 298 ± 3 K.

The emission spectra of BDP-ethynyl and Por(COOH)2- $(BDP)_2$ in tetrahydrofuran solutions at room temperature are shown in Figure 6; selected emission data are listed in Table 1. BDP-ethynyl shows the typical bright fluorescence of BDP at 515 nm when excited at 490 nm. In trimer Por-(COOH)₂(BDP)₂, irradiation at 490 nm, corresponding to selective excitation of the two BDP units, results in emission from the Zn-porphyrin chromophore at 662 nm, as well as residual fluorescence from the two BDP groups at 517 nm. BDP emission is strongly quenched, as shown in Figure 6, in which the fluorescence spectra of isoabsorbing solutions of BDP-ethynyl and Por(COOH)₂(BDP)₂ are compared. The excitation spectrum of Por(COOH)₂(BDP)₂, monitoring at the fluorescence of the porphyrin moiety at 680 nm, reveals a pronounced BDP absorption feature at 503 nm (Figure 7). This is a clear indication of photoinduced energy transfer from the ${}^{1}\pi - \pi^{*}$ excited state of the BDP chromophore to the lower lying singlet excited state of the porphyrin unit, leading to sensitized fluorescence from the latter.

interact appreciably in the excited state and formation of the [Ru(bipy)₃]-based ¹MLCT is *not* followed by energy transfer to the porphyrin $\pi^{-\pi^{*}}$ excited states but instead rapid intersystem crossing occurs with almost unit efficiency followed by phosphorescence from the ³MLCT excited state. This is consistent with the results of other studies on supramolecular assemblies of Ru complexes and porphyrins,^[62,78] which have shown a lack of energy transfer from the ³MLCT excited state of a ruthenium polypyridyl chromophore to a porphyrin ${}^{1}\pi$ - π * excited state at room temperature, likely because of the spin-forbidden nature of such a transition. In addition, the energies of the [Ru-(bipy)₃] ³MLCT and porphyrin ${}^{1}\pi$ - π * excited states are estimated at 16556 and 15432 cm⁻¹, respectively, from the emission spectra at 77 K (Figure 2, b). Thus, the gradient for [Ru(bipy)₃] ³MLCT to porphyrin ${}^{1}\pi$ - π * energy transfer in $Por(COOMe)_2[Ru(bpy)_3]_2$ ($E_{Rubipy} - E_{Por}$) is estimated at ca. 1120 cm⁻¹. This gradient is quite low given the fact that a gradient higher than 1500 cm⁻¹ is needed to prevent thermal back-energy-transfer in donor-acceptor systems.^[79] Therefore, the spin-forbidden nature of a triplet-to-singlet transition combined with a poor energy gradient can account for the observed lack of quenching of the [Ru-(bipy)₃] ³MLCT emission in Por(COOMe)₂[Ru(bpy)₃]₂. However, we would expect the ³MLCT excited state of the $[Ru(bpy)_3]$ chromophores of Por(COOMe)₂ $[Ru(bpy)_3]_2$ to be quenched by the porphyrin first triplet excited state, as has been observed in related bichromophoric systems.^[62] In Por(COOMe)₂[Ru(bpy)₃]₂, phosphorescence from the $[Ru(bpy)_3]$ units is not appreciably quenched, either at room temperature or at 77 K, which is probably due to the relatively large distance between them and the central porphyrin {the average distance between Ru atoms and the center of the porphyrin is ca. 16 Å as estimated from the DFT optimized structure of Por(COOMe)₂[Ru(bpy)₃]₂, see below} and the lack of electronic communication between

[Ru(bpy)₃]₂ coincides within experimental error with that of the reference compound AnilbpyRu(bpy)₂ (255 ns), shows

that the ³MLCT phosphorescence of Por(COOMe)₂-

 $[Ru(bpy)_3]_2$ is not appreciably quenched. Therefore, the

photophysical data of Por(COOMe)₂[Ru(bpy)₃]₂ show that,

at room temperature, the constituent chromophores do not



Figure 4. Decay of Por(COOMe)₂[Ru(bpy)₃]₂ (black line), fit (red line), $\tau_1 = 7$ ns (due to the porphyrin moiety), $\tau_2 = 207$ ns due to the [Ru(bpy)₃] moiety.



	Absorption $\lambda_{\max} \text{ [nm]} (\varepsilon / M^{-1} \text{ cm}^{-1})$	Emission λ _{max} [nm] 298 K	Ф 298 К	τ [ns] 298 K	λ _{max} [nm] 77 K
Por(COOMe) ₂ [Ru(bpy) ₃] ₂	288 (113.4), 418 (224.2), 457 (30.9), 513 (15.4), 549 (8.6), 589 (3.9), 645 (3.1)	653	4.2 ^[a]	7, 207 ^[c]	604, 648, 710
AnilbpyRu(bpy) ₂ BDP-ethynyl	287 (74.4), 456 (16.1) 502 (89.8)	640 515	$1.4^{[a]}$	255 2.1	600 511
Por(COOH) ₂ (BDP) ₂	451 (492.6), 502 (176.9), 601 (20.7), 654 (88.2)	517, 662	7.1 ^[b]	1.4, ^[d] 2.3 ^[e]	511, 661, 727

Table 1. Summary of spectroscopic data for Por(COOMe)₂[Ru(bpy)₃]₂, AnilbpyRu(bpy)₂, BDP-ethynyl, and Por(COOH)₂(BDP)₂.

[a] Quantum yields were measured by using $[Ru(bpy)_3]Cl_2$ in H₂O as standard. [b] Quantum yields were measured by using ZnTPP in THF as standard. [c] Using a ±40 nm interference filter centered at 600 nm to monitor porphyrin fluorescence. [d] Using a ±40 nm interference filter centered at 670 nm to monitor porphyrin fluorescence. [e] Using a ±40 nm interference filter centered at 500 nm to monitor BDP residual fluorescence.



Figure 6. Room temperature fluorescence spectra of isoabsorbing (A = 0.1) THF solutions of BDP-ethynyl and Por(COOH)₂-(BDP)₂ exciting at 480 nm (BDP chromophore).



Figure 7. The excitation spectrum of $Por(COOH)_2(BDP)_2$ in THF at 298 \pm 3 K monitoring at 680 nm.

Electrochemistry

$Por(COOMe)_2[Ru(bpy)_3]_2$

The redox potentials for Por(COOMe)₂[Ru(bpy)₃]₂ and reference compound AnilbpyRu(bpy)₂ are summarized in Table 2; representative cyclic voltammograms are shown in Figure S10. The cyclic voltammogram for Por(COOMe)₂-[Ru(bpy)₃]₂ and AnilbpyRu(bpy)₂ was recorded in acetonitrile and 0.1 M TBAPF₆. The oxidation part of the cyclic voltammogram exhibited one reversible one-electron process peak at $E_{1/2} = 0.91$ V vs. Fc/Fc⁺ assigned to the metalbased oxidation (Ru²⁺/Ru³⁺) couple, compared to reference compound AnilbpyRu(bpy)₂. The irreversible peak at $E_{1/2}$ = 0.64 V vs. Fc/Fc⁺ is assigned to the oxidation of the porphyrin unit. Our DFT calculations on Por(COOMe)₂[Ru-(bpy)₃]₂ shows that the HOMO is dominated by porphyrinbased orbitals, thus supporting the experimentally observed first porphyrin-based oxidation. However, contrary to the DFT results, the second oxidation was found to be [Ru-(bpy)₃]-based. This is probably because of the change of composition of the frontier orbitals due to solvent effect under the experimental conditions.^[86,87] The reduction side of Por(COOMe)₂[Ru(bpy)₃]₂ is dominated by irreversible reduction peaks that could not be assigned.

Por(COOH)₂(BDP)₂

The redox behavior of $Por(COOH)_2(BDP)_2$ and its reference compound BDP-ethynyl was studied by cyclic and square wave voltammetry in tetrahydrofuran solutions, with tetrabutylammonium hexafluorophosphate [(TBA)PF₆] as the supporting electrolyte, using ferrocene as an internal

Table 2. Redox data reported vs. Fc/Fc^+ in acetonitrile or tetrahydrofuran using tetrabutylammonium hexafluorophosphate 0.1 M as supporting electrolyte.

	$E_{1/2}^{\text{Ox1}}$ [V] $(\Delta E_{\text{p}}$ [V]) ^[a]	$E_{1/2}^{\text{Ox2}}$ [V]	$E_{1/2}^{\text{Red1}}$ [V]	$E_{1/2}^{\operatorname{Red2}}$ [V]
AnilbpyRu(bpy) ₂	0.90 (0.06)	1.53 ^[b]	-1.77 (0.07)	-1.98 (0.07)
$Por(COOMe)_2[Ru(bpy)_3]_2$	0.64 ^[b]	0.91 (0.07)	$-1.46^{[b]}$	$-2.03^{[b]}$
BDP-ethynyl ^[c]	0.82		-1.67	
Por(COOH) ₂ (BDP) ₂ ^[c]	0.50	0.82	-1.56	-1.66

[a] The anodic-cathodic peak separations are given in parenthesis. [b] Irreversible process. [c] Square wave voltammetry was used to calculate all redox potentials.



standard. The redox data are summarized in Table 2, and representative square wave voltammograms are shown in Figure S11. BDP-ethynyl showed a reversible oxidation at 0.82 V vs. Fc/Fc⁺ due to formation of the BDP cationic radical and a reversible reduction at -1.67 V vs. Fc/Fc⁺, which is consistent with similar reported BDP derivatives.^[82] For Por(COOH)₂(BDP)₂, it was not possible to estimate the redox potentals from cyclic voltammetry because all the waves were irreversible, so square wave voltammetry was used to estimate these values. During the anodic scan an oxidation at 0.50 V vs. Fc/Fc⁺ attributed to the oxidation of the porphyrin ring was observed. This value is consistent with literature reports of porphyrins with ethynyl substituents at the meso position.[84] A second anodic peak was observed at 0.82 V vs. Fc/Fc⁺, which is assigned to oxidation of BDP units. Compound Por(COOH)2(BDP)2 also shows two irreversible reduction peaks: the first (-1.56 V vs. Fc/ Fc⁺) corresponds to porphyrin-based reduction and the second (-1.66 V vs. Fc/Fc⁺) to simultaneous reduction of the BDP molecules.

DFT Results

To obtain further insight into the electron distribution of the frontier molecular orbitals (FMOs), we carried out quantum chemical calculations on Por(COOMe)₂[Ru-(bpy)₃]₂ using density functional theory (DFT). The geometry-optimized structure of Por(COOMe)₂[Ru(bpy)₃]₂ revealed two trans oriented terminal [Ru(bpy)₃] units on both sides of the central porphyrin ring (Figure 8). The electron density map of the selected FMOs and their energy level diagram (gas- and solution-phase) are shown in Figures 9 and 10 and Figure S15. In the case of Por(COOMe)₂[Ru-(bpy)₃]₂, the electronic densities of HOMO and HOMO-1 are mainly distributed on the porphyrin ring and could be characterized as porphyrin π -orbitals. No contribution from Ruthenium d-orbitals was observed in the frontier side HOMO orbitals (HOMO to HOMO-3). On the other hand, LUMO and LUMO+1 exhibit atomic contributions localized over the π^* -orbitals of the bpy ligand moiety of the terminal [Ru(bpy)₃] units. A minor contribution from Ru dorbitals along with bpy ligand contributions was observed in LUMO+2. In this regard, it is important to mention that for a dye in DSSC applications, the LUMO density should localize over the anchoring group to allow successful electron injection into the TiO₂ conduction band.^[87,88] However, contrary to our expectation, the LUMO electron density of Por(COOMe)₂[Ru(bpy)₃]₂ is primarily localized on the terminal bpy ligand moiety, rather than on the caboxy ester group of the porphyrin. Additionally, very weak delocalization of electronic density was observed between the central porphyrin and the two terminal [Ru(bpy)₃] units, suggesting weak electronic communication between the two. This observation also suggests poor electron injection efficiency from the anchoring carboxy group to the TiO₂ semiconductor, which is also reflected in the experimentally observed low efficiency (0.27%) of the dye Por(COOH)₂[Ru-(bpy)₃]₂.



Figure 8. Gas-phase DFT optimized structure of Por(COOMe)₂-[Ru(bpy)₃]₂ (cyan: Ru; blue: N; red: O; grey: C; off-white: H).

Solar Cell Measurements

The photocurrent J-V curves measured at three different light intensities are shown in Figures S12–S14 (see Supporting Information). The photovoltaic performance parameters are listed in Table S3. The results confirm the activity of the porphyrin complexes in the DSSCs, however, the performance of the cells sensitized with Por(COOH)₂[Ru-(bpy)₃]₂ was low (less than 0.3%). This finding is in accordance with our DFT results. Moreover, in the case of dibromo dye Por(COOH)₂Br₂, which was used as a reference compound, the efficiency was measured to be 1.31% greater than that for the bis-BDP dye Por(COOH)₂(BDP)₂ (0.58%).



Figure 9. Frontier molecular orbitals (gas-phase DFT) of Por(COOMe)₂[Ru(bpy)₃]₂ (cyan: Ru; blue: N; red: O; grey: C; off-white: H).



Figure 10. Energy landscape of frontier MOs of $Por(COOMe)_2$ -[Ru(bpy)₃]₂ (gas-phase DFT). Energy values are given in eV.

Conclusions

Triad chromophores containing porphyrin and tris-bipyridyl-ruthenium derivatives as well as porphyrin and BDP molecules are reported and fully characterized. The photophysical data complete this study and describe the "communication" between the two different entities in both cases. In the case of Por(COOMe)₂[Ru(bpy)₃]₂, photophysical studies show weak interactions between the central porphyrin and the side $[Ru(bpy)_3]$ units in the ground state, which is consistent with the DFT calculations. The efficiency in DSSC is very poor and the design of the triad is actually under reinvestigation by a new synthetic approach in our laboratory. In the case of the BDP-porphyrin-BDP chromophore Por(COOH)₂(BDP)₂, photophysical studies show an interaction between the BDP moieties and the central Zn porphyrin in the excited state. The photovoltaic properties of this dye are, however, very poor, with an efficiency of about 0.6%.

Experimental Section

¹H NMR spectra were recorded with Bruker AMX-500 MHz and Bruker DPX-300 MHz spectrometers as solutions in deuterated solvents by using the solvent peak as the internal standard. UV/ Vis absorption spectra were measured with a Shimadzu UV-1700 spectrophotometer using 10 mm path-length cuvettes. The emission spectra were measured with a JASCO FP-6500 fluorescence spectrophotometer equipped with a red-sensitive WRE-343 photomultiplier tube (wavelength range 200–850 nm). Quantum yields were determined from corrected emission spectra following the standard methods^[89] using tris(bipyridine)ruthenium(II) dichloride [Ru-(bpy)₃Cl₂] ($\Phi = 0.042$ in water)^[90] or zinc *meso*-tetraphenylporphyrin (ZnTPP) ($\Phi = 0.03$ in toluene)^[91] as standards. Emission





lifetimes were determined by the time-correlated single-photon counting technique using an Edinburgh Instruments mini-tau lifetime spectrophotometer equipped with an EPL 405 pulsed diode laser at 406.0 nm with a pulse width of 71.52 ps and pulse periods of 2 ms and 50 ns and a high-speed red-sensitive photomultiplier tube (H5773–04) as detector. High-resolution mass spectra were obtained with a Bruker ultrafleXtreme MALDI-TOF/TOF spectrometer using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile as matrix. Dye-sensitized solar cells were prepared according to Grätzel and co-workers.^[92]

Computational Methods: Theoretical calculations on Por-(COOMe)₂[Ru(bpy)₃]₂ were performed by using the DFT method with GAUSSIAN $03^{[95]}$ program. All the structural optimizations were carried out in the gas phase by employing Becke three parameter exchange functional in conjunction with Lee–Yang–Parr correlation (B3LYP);^[96,97] 6-31G(d) basis sets was used for lighter atoms and LANL2DZ basis set was used for Ru atom. The global minimum of the optimized structures was confirmed by observation of no negative frequencies in the frequency calculation. Single point calculations of all the compounds were carried out by employing the geometry optimized coordinates. All the computed structures and orbitals were visualized by *ChemCraft* software (version 1.6).^[98]

5,15-Bis(4-methoxycarbonylphenyl)-10,20-bis(4-aminophenyl)-porphyrin [Por(COOMe)2(NH2)2]: To a solution of 5,15-bis(4-methoxycarbonylphenyl)-10,20-bis(4-nitrophenyl)porphyrin (300 mg, 0.37 mmol) in anhydrous THF (50 mL) and anhydrous Et₃N (280 μ L), was added Pd/C 10% (60 mg). The reaction mixture was stirred overnight, under a H₂ atmosphere, at room temperature. The solution was passed through Celite and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel (CH₂Cl₂/MeOH, 100:1.5) to obtain Por(COOMe)₂(NH₂)₂ as a purple solid (260 mg, 95%). ¹H NMR (500 MHz, CDCl₃): δ = 8.95 (d, J = 4.5 Hz, 4 H), 8.77 (d, J = 4.5 Hz, 4 H), 8.44 (d, J = 8.0 Hz, 4 H), 8.30 (d, J = 7.5 Hz, 4 H), 7.98 (d, J = 8.0 Hz, 4 H), 7.06 (d, J = 8.0 Hz, 4 H), 4.11 (s, 6 H), 4.05 (s br, 4 H), -2.75 (s, 2 H) ppm. UV/Vis (CH₂Cl₂): λ_{max} $(\varepsilon, \mathrm{mM}^{-1}\mathrm{cm}^{-1}) = 422 \ (291.8), \ 515 \ (16.6), \ 551 \ (6.0), \ 590 \ (5.3),$ 645 (3.3) nm. HRMS (MALDI-TOF): m/z calcd. for C₄₈H₃₇N₆O₄ 761.2876 $[M + H]^+$; found 761.2871. C₄₈H₃₆N₆O₄ (760.85): calcd. C 75.77, H 4.77, N 11.05; found C 75.82, H 4.75, N 11.41.

5,15-Bis(4-methoxycarbonylphenyl)-10,20-bis{4-[4'-methyl-(2,2'-bipyridine)-4-carboxamido]phenyl}porphyrin [Por(COOMe)₂(bpy)₂]: A mixture of 4'-methyl-[2,2'-bipyridine]-4-carboxylic acid (225 mg, 1.05 mmol) and SOCl₂ (15 mL) was heated to reflux for 2 h. The excess of SOCl₂ was distilled under reduced pressure and the acyl chloride product was dried in vacuo at 70 °C for 1 h. Anhydrous THF (30 mL) and anhydrous Et_3N (400 µL) were added and the mixture was stirred for 5 min. Por(COOMe)₂(NH₂)₂ (200 mg, 0.26 mmol) was added and the mixture was stirred at 60 °C overnight. After removing the solvent, CH₂Cl₂ (40 mL) was added and the mixture was washed with an aqueous solution of NaCl (2× 30 mL). The organic layer was dried with Na₂SO₄, filtered, and concentrated. The porphyrin–bipyridine ligand Por(COOMe) $_2(bpy)_2$ could not purified by column chromatography or recrystallization from the excess of the 4'-methyl-[2,2'-bipyridine]-4-carboxylic acid, and was used without any further purification.

Porphyrin-{NHCO-(bpy)-(CH₃)-Ru[(bpy)₂]}₂[PF₆]₄ {Por(COOMe)₂-[Ru(bpy)₃]₂]: A mixture of Por(COOMe)₂(bpy)₂ (150 mg, 0.13 mmol) and [Ru(bpy)₂Cl₂] (200 mg, 0.39 mmol) in acetic acid (50 mL) was heated to reflux under N₂ for 12 h. After removing the solvent, the product was purified by column chromatography on silica gel (CH₃CN/H₂O/KNO₃, 30:2:1). After removing the solvents, the residue dissolved in the minimum amount of water and NH₄PF₆ was added until a precipitate was formed. Filtration and washing with water and diethyl ether gave Por(COOMe)2[Ru- $(bpy)_{3}_{2}$ as a red-brown solid (174 mg, 52% over two steps). ¹H NMR [500 MHz, $(CD_3)_2CO$]: $\delta = 10.50$ (s br, 2 H), 9.42 (s, 2 H), 8.99 (s, 2 H), 8.90 (m, 8 H), 8.78 (m, 8 H), 8.43 (d, J = 7.0 Hz, 4 H), 8.37 (d, J = 7.0 Hz, 4 H), 8.29 (m, 6 H), 8.22–7.99 (m, 22 H), 7.91 (d, J = 5.5 Hz, 2 H), 7.58 (m, 8 H), 7.48 (d, J = 5.0 Hz, 2 H), 4.08 (s, 6 H), 2.63 (s, 6 H), -2.73 (s, 2 H) ppm. ¹³C NMR [75 MHz, $(CD_3)_2CO$]: $\delta = 167.4, 163.6, 159.2, 158.1, 157.2, 153.4, 152.8,$ 152.6, 151.9, 151.7, 147.5, 144.4, 139.5, 139.0, 138.8, 135.7, 135.4, 132.1, 130.8, 130.0, 128.9, 126.8, 126.4, 125.3, 123.0, 121.0, 120.1, 119.7, 52.7, 21.3 ppm. UV/Vis (CH₃CN): λ_{max} (ϵ , mm⁻¹ cm⁻¹) = 288 (113.4), 418 (224.2), 457 (30.9), 513 (15.4), 549 (8.6), 589 (3.9), 645 (3.1) nm. HRMS (MALDI-TOF): m/z calcd. for $C_{112}H_{85}F_{18}N_{18}O_6$ - P_3Ru_2 2416.3928 [M - PF_6^- +H]⁺; found 2416.3937. $C_{112}H_{84}F_{24}N_{18}O_6P_4Ru_2$ (2560.00): calcd. C 52.55, H 3.31, N 9.85; found C 52.59, H 3.36, N 9.88.

Carboxy-Porphyrin-{NHCO-(bpy)-(CH₃)-Ru[(bpy)₂]}₂[PF₆]₄ {Por-(COOH)₂[Ru(bpy)₃]₂}: A solution of Por(COOMe)₂[Ru(bpy)₃]₂ (30 mg, 0.011 mmol) in THF (5 mL), methanol (2 mL) and KOH (0.3 gr) in H₂O (2.5 mL) was stirred at room temperature overnight. The solution was evaporated to dryness and the precipitate was dissolved with water and an aqueous solution of HCl was added dropwise until pH 6. After distillation of the solvent and recrystallization (MeOH/H₂O), the product was obtained as a red-brown solid (27 mg, 95%). UV/Vis (DMSO): \lambda_{max} (\varepsilon, mM⁻¹ cm⁻¹): 292 (60.2), 423 (138.4), 461 (19.6), 516 (10.7), 554 (6.8), 590 (3.8), 647 (3.1) nm. HRMS (MALDI-TOF): *mlz* **calcd. for C₁₁₀H₈₁F₁₈N₁₈O₆P₃Ru₂ 2388.3615 [M – PF₆⁻ +H]⁺; found 2388.3622. C₁₁₀H₈₀F₂₄N₁₈O₆-P₄Ru₂ (2531.95): calcd. C 52.18, H 3.18, N 9.96; found C 52.15, H 3.12, N 9.98. ¹H and ¹³C NMR spectra could not be obtained due to solubility problems.**

4'-Methyl-N-phenyl-(2,2'-bipyridine)-4-carboxamide (Anilbpy): A mixture of 4'-methyl-[2,2'-bipyridine]-4-carboxylic acid (40 mg, 0.19 mmol) and SOCl₂ (2.3 mL) was heated to reflux for 2 h. The excess of SOCl₂ was distilled under reduced pressure and the acid chloride product was dried in vacuo at 70 °C for 1 h. Anhydrous THF (4.5 mL) and anhydrous Et₃N (55 µL) were added and the mixture was stirred for 5 min. Aniline (25 µL, 0.28 mmol) was added and the mixture was stirred at 60 °C overnight. After removing the solvent, CH₂Cl₂ (15 mL) was added and the mixture was washed with an aqueous solution of NaCl (2×15 mL). The organic layer was dried with Na₂SO₄, filtered, and concentrated. The residue was recrystallized (CH₂Cl₂ and hexane) to obtain a white solid (50 mg, 95%). ¹H NMR (500 MHz, CDCl₃): δ = 8.84 (m, 2 H), 8.55 (d, J = 5.0 Hz, 1 H), 8.45 (s br, 1 H), 8.32 (s, 1 H), 7.88 (dd, $J_1 = 5$, $J_2 = 1.5$ Hz, 1 H), 7.73 (d, J = 7.5 Hz, 2 H), 7.39 (t, J= 7.5 Hz, 2 H), 7.24 (d, J = 4.5 Hz, 1 H), 7.19 (t, J = 7.5 Hz, 1 H), 2.49 (s, 3 H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 163.7, 155.6, 154.4, 150.6, 150.3, 148.0, 143.3, 137.7, 129.3, 125.7, 125.2, 122.9, 122.6, 120.6, 117.9, 21.6 ppm. C₁₈H₁₅N₃O (289.34): calcd. C 74.72, H 5.23, N 14.52; found C 74.78, H 5.19, N 14.61.

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Aniline-{NHCO-(bpy)-(CH₃)-Ru[(bpy)₂]}₂[PF₆]₂ [AnilbpyRu(bpy)₂]: A mixture of Anilbpy (20 mg, 0.07 mmol) and [Ru(bpy)₂Cl₂] (30 mg, 0.07 mmol) in a mixture of MeOH/acetic acid (5:1, 12 mL) was heated to reflux under N_2 for 5 h. After removing the solvent, the product was purified by column chromatography on silica gel (CH₃CN/H₂O/KNO₃, 30:2:1). After removing the solvents, the residue was dissolved in the minimum amount of water and NH₄PF₆ was added until a precipitate was formed. Filtration and washing with water and diethyl ether gave AnilbpyRu(bpy)₂ as an orange solid (57 mg, 82%). ¹H NMR (500 MHz, CD₃CN): δ = 9.06 (s br, 1 H), 8.87 (s, 1 H), 8.51 (dd, $J_1 = 8.0$, $J_2 = 2.0$ Hz, 4 H), 8.07 (m, 4 H), 7.91 (d, J = 6.0 Hz, 1 H), 7.76 (m, 7 H), 7.57 (d, J = 5.5 Hz, 1 H), 7.41 (m, 6 H), 7.29 (d, J = 5.5 Hz, 1 H), 7.22 (t, J = 7.5 Hz), 2.57 (s, 3 H) ppm. ¹³C NMR (75 MHz, CD₃CN): δ = 163.1, 159.0, 158.0, 157.8, 156.9, 153.4, 152.7, 152.5, 151.8, 151.7, 143.9, 138.9, 130.0, 129.7, 128.6, 126.5, 126.1, 125.7, 125.3, 122.8, 121.6, 21.2 ppm. UV/Vis (CH₃CN): λ_{max} (ϵ , mm⁻¹ cm⁻¹) = 287 (74.4), 456 (16.1) nm. HRMS (MALDI-TOF): m/z calcd. for $C_{38}H_{31}F_6N_7OPRu$ 848.1275 [M - PF₆-]⁺; found 848.1262. C₃₈H₃₁F₁₂N₇OP₂Ru (992.70): calcd. C 45.98, H 3.15, N 9.88; found C 45.92, H 3.17, N 9.91.

[5,15-Dibromo-10,20-bis(4-carboxyphenyl)porphyrinato]zinc [Por-(COOH)₂Br₂]: Por(COOMe)₂Br₂ (60 mg, 0.075 mmol) was dissolved in a solution of THF (18 mL), MeOH (8 mL) and H₂O (9 mL) and potassium hydroxide (0.9 g, 16 mmol) was added. The reaction mixture was stirred at room temperature overnight. After removing the organic solvents, an aqueous solution of HCl (1 N) was added dropwise until pH 6. A precipitate was formed, filtered, and washed with water to give a purple solid (56 mg, 97%). UV/ Vis (THF): λ_{max} (ϵ , mw⁻¹ cm⁻¹) = 430 (370.4), 565 (17.2), 605 (9.2) nm. HRMS (MALDI-TOF): *m*/*z* calcd. for C₃₄H₁₉Br₂N₄O₄Zn 768.9065 [M + H]⁺; found 768.9071. C₃₄H₁₈Br₂N₄O₄Zn (771.73): calcd. C 52.92, H 2.35, N 7.26; found C 52.87, H 2.28, N 7.31. ¹H and ¹³C NMR spectra could not be obtained due to solubility problems.

BDP-porphyrin-BDP [Por(COOH)₂(BDP)₂]: Por(COOH)₂Br₂ (50 mg, 0.06 mmol) was dissolved in anhydrous THF (5 mL) and anhydrous triethylamine (1.5 mL) was added. The solution was deoxygenated by bubbling Argon through it for 15 min, then tris-(dibenzylideneacetone)dipalladium(0) $[Pd_2(dba)_3]$ (15 mg. 0.02 mmol), triphenylphosphane (17 mg, 0.06 mmol), copper(I) iodide (6 mg, 0.03 mmol) and BDP-ethynyl (70 mg, 0.20 mmol) were added. The reaction mixture was stirred at 65 °C for 18 h and then the solvents were removed under reduced pressure. The desired compound was isolated by silica column chromatography (CH₂Cl₂/THF/MeOH, 100:10:1) to give Por(COOH)₂(BDP)₂ as a brown solid (64 mg, 78%). ¹H NMR (500 MHz, d_8 -THF): δ = 9.83 (d, J = 4.5 Hz, 4 H), 8.87 (d, J = 4.5 Hz, 4 H), 8.48 (d, J = 8.0 Hz, 4 H), 8.32 (d, J = 8.0 Hz, 4 H), 8.29 (d, J = 8.0 Hz, 4 H), 7.63 (d, J = 8.0 Hz, 4 H), 6.10 (s, 4 H), 2.48 (s, 12 H), 1.62 (s, 12 H) ppm. ¹³C NMR (75 MHz, [D₈]THF): δ = 167.6, 156.3, 152.8, 150.5, 147.8, 143.4, 142.8, 135.1, 132.9, 132.8, 132.0, 131.6, 131.2, 129.6, 128.6, 125.9, 122.7, 121.8, 101.7, 96.7, 95.0, 14.8, 14.4 ppm. UV/ Vis (THF): λ_{max} (ϵ , mm⁻¹ cm⁻¹) = 451 (492.6), 502 (176.9), 601 (20.7), 654 (88.2) nm. HRMS (MALDI-TOF): m/z calcd. for $C_{76}H_{55}B_2F_4N_8O_4Zn$ 1305.3760 [M + H]⁺; found 1305.3452. C₇₆H₅₄B₂F₄N₈O₄Zn (1306.31): calcd. C 69.88, H 4.17, N 8.58; found C 69.81, H 4.21, N 8.52.

Supporting Information (see footnote on the first page of this article): ¹H NMR and ¹³C NMR of Por(COOMe)₂(NH₂)₂, Por(COOMe)₂[Ru(bpy)₃]₂, Anilbpy, AnilbpyRu(bpy)₂, Por(COOH)₂-(BDP)₂; cyclic voltammograms of Por(COOMe)₂[Ru(bpy)₃]₂, An

ilbpyRu(bpy)₂; square wave voltammograms of BDP-ethynyl, Por-(COOH)₂(BDP)₂; current–voltage characteristics of Por(COOH)₂-[Ru(bpy)₃]₂, Por(COOH)₂Br₂, Por(COOH)₂(BDP)₂; photovoltaic performances of Por(COOH)₂[Ru(bpy)₃]₂, Por(COOH)₂Br₂, Por-(COOH)₂(BDP)₂.

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