Strongly Coupled Cyclometalated Ruthenium Triarylamine Chromophores as Sensitizers for DSSCs


Abstract: A series of anchor-functionalized cyclometalated bis(tridentate) ruthenium(II) triarylamine hybrids \([\text{Ru(dpbb-X)(tctpy)}^2]^{2-}\) \((2a)\)
and \([\text{Ru(dbp-X)(tctpy)}^2]^{2-}\) \((2c)\) was synthesized and characterized. All complexes show broad absorption bands in the range of 300–700 nm with a maximum at about 545 nm. Methyl esters \([\text{Ru(Me}_{3}-\text{tricarboxylic acid)](\text{dbpy})\}(2a)^{2-}\) and \([\text{Ru}^3\text{N}(4-C_4,4'-\text{dimethyl-biphenylamine})(\text{tctpy})\](2b)^{2-}\) were oxidized to the strongly coupled mixed-valent species \([1a]^{2+} - [1c]^{2+}\) and the Ru^3(amine) complexes \([1a]^{3+} - [1c]^{3+}\) at comparably low oxidation potentials. Theoretical calculations suggest an increasing spin delocalization between the metal center and the triarylamine unit in the order \([1a]^{2+} < [1b]^{2+} < [1c]^{2+}\).

Solar cells were prepared with the saponified complexes \((2a)^{2-}\) and \((2c)^{2-}\) and the reference dye N719 as sensitizers using the \(I_1 / I_3\) couple and \([\text{Co(bpy)}_3]^{3+/2+}\) and \([\text{Co}^2(\text{dppd})]^{1+/2+}\) couples as \([\text{BiC}_nF_{2n}]^-\) salts as electrolytes (bpy = 2,2'-bipyridine; dppd = N,N'-dimethyl-N,N'-dipyridin-2-yl-pyridine-2,6-diamine). Cells with \((2c)^{2-}\) and \(I_1 / I_3\) electrolyte perform similarly to cells with N719. In the presence of cobalt electrolytes, all efficiencies are reduced, yet under these conditions \((2c)^{2-}\) outperforms N719.

Introduction

Pioneered by O’Regan and Grätzel in 1991,[1] the dye-sensitized solar cell (DSSC) has emerged as a promising light-to-energy conversion device.[2,3] Its setup has been optimized and standardized over the past 25 years. Typically, its central component is a molecular dye that is absorbed onto a mesoporous wide-bandgap semiconductor electrode, such as TiO_2 or ZnO.[3,4]

Upon excitation by visible light, electrons are injected from the excited state of the dye into the conduction band of the semiconductor. The oxidized dye is then regenerated by an electrochemical mediator, which transports the positive charge to the counter electrode. The major advantages of dye sensitized solar cells over conventional silicon-based or inorganic thin film solar cells are lower costs and their modular architecture allowing for systematic optimization of all components (semiconductor, sensitizer, electrolyte) individually.[3-5]

Tremendous efforts have been put particularly into the development of new molecular dyes to optimize cell performance. An ideal sensitizer should be thermally and photochemically stable under working conditions, should rapidly inject electrons into the conduction band of the semiconductor after excitation and, most importantly, should efficiently absorb light between 400 and 900 nm. Among others, polypyridine complexes of iron,[6,7] copper,[8-9] platinum,[10,11] iridium,[12,13] and rhenium[14] as well as polyaromatic and conjugated organic compounds,[15,16] porphyrins,[17-19] and quantum dots[20] have proven suitable for sensitization. Particularly, polypyridine complexes of ruthenium and osmium have emerged as a promising class of sensitizers due to their suitable photophysical properties.[21-26] The visible range of the electromagnetic spectrum of these complexes is dominated by characteristic metal-to-ligand charge transfer (MLCT) absorptions.[25-27] In these transitions, metal orbitals of the \(t_{2g}\) set serve as electron donors, while the polypyridine \(\pi^*\) orbitals function as electron acceptors.

The most prominent and well-established sensitizers are the complexes \([\text{nBu}_2\text{N}]_2[\text{Ru}^2(\text{Hdcbbpy})_2][\text{NCS}]_2\)\). N719 \((\text{H}_2\text{dcbbpy} = 2,2',6',2''-\text{terpyridine-4,4',4''-tricarboxylic acid})[22]\) reaching power conversion efficiencies (PCE, \(\eta\)) of 10–11% under full air mass 1.5 (AM 1.5) irradiation. In these complexes, the carboxy...
groups serve as anchors to the TiO$_2$ surface while the [NCS]$^-$ ligands are responsible for an efficient charge transfer from the redox mediator onto the dye after charge injection (dye regeneration). However, a major drawback of complexes containing monodentate ligands is their high lability towards [NCS]$^-$ substitution in photoexcited or oxidized states hampering long-term application in photovoltaic devices.

Recently, bi- and tridentate cyclometalating ligands emerged as viable and more robust alternatives for the labile [NCS]$^-$ ligands. In 2007, van Koten and co-workers reported the successful sensitization of TiO$_2$ by bis(tridentate) [Ru(pbpy)$_2$(tpy)]$^+$ complexes (tpy = 2,2′,6,2′-terpyridine, Hpbpy = 6-phenyl-2,2′-bipyridine). Shortly thereafter, Grätzel and co-workers published a dye with record-breaking characteristics [Ru(H$_2$dcbbpy)$_2$(ppy-F$_2$)]$^+$ ($\eta > 10\%$) based on a tris(bidentate) cyclometalating motif (Hppy-F$_2$ = 2-(2,4-difluorophenyl)pyridine). Since then, much work has been dedicated towards the development of new cyclometalated ruthenium dyes both in the field of tris(bidentate) and bis(tridentate) complex architectures. These studies indeed reveal several key benefits of the cyclometalating motif. The introduction of a Ru-C $\sigma$ bond in the coordination environment reduces the local symmetry around the metal center. This yields a broad absorption band in the visible range resulting from multiple closely-lying MLCT transitions involving both the polypyridine and cyclometalating ligands as electron acceptors. Additionally, cyclometalation substantially increases the energy of the polypyridine-centered lowest unoccupied molecular orbital (LUMO) compared to non-cyclometalated counterparts. This should potentially accelerate charge injection into the TiO$_2$ conduction band. The highest occupied molecular orbital (HOMO) on the other side typically extends over the metal center and the anionic part of the cyclometalating ligand. This should facilitate dye regeneration after charge injection. Furthermore, the high $\sigma$-donating strength destabilizes the inherently photochemically reactive metal-centered ($^{1}$MC) excited states. The electron donating or withdrawing character of the cyclometalating ligands are easily tuned by further substitution (for example $\left[A^X{\text{Me}}\right]^-$, Scheme 1) including hole-transport facilities ($X=\text{amines}$). Indeed, several approaches have been developed to incorporate electron donors into the dye structure to rapidly detract the positive charge remaining on the sensitizer after electron injection away from the semiconductor surface. Attaching the reversible triphenylamine radical cation/triphenylamine redox couple (TPA $^{\text{+/0}}$) proved particularly successful in conjunction with several porphyrin dyes, for example, YD2-o-C8, yielding solar cells with $\eta > 12\%$. Berlinguette and co-workers demonstrated that the overall cell performance can benefit from a TPA unit linked to a [Ru(pbpy)(tpy)]$^+$ complex via a thiophene spacer. This architecture yields cell efficiencies of up to 8.0% (Scheme 1, $\left[B^X\right]^-$, $\left[C^X\right]^-$). Through clever dye design and adjustment of relative oxidation potentials of Ru$^{II}$ and TPA $^{\text{+/0}}$ an efficient transfer of the electron hole from the ruthenium center to the TPA unit is achieved after charge injection. This retards parasitic electron recombination processes with oxidized dyes in the DSSC. The mixed-valent complexes $\left[B^X\right]^+$ are valence-localized and assigned to Robin–Day class II with measurable electronic coupling between the metal center and the TPA unit. Recently, Zhong and co-workers presented a structurally related series of complexes combining bis(tridentate) cyclometalated ruthenium complexes with TPA units (Scheme 1, $\left[A^X{\text{Me}}\right]^-$/$\left[A^X{\text{Me}}\right]^+$) lacking the thiophene unit. The mixed-valent state $\left[A^X{\text{Me}}\right]^+$ is valence-delocalized (Robin–Day class III) between the metal center and the amine moiety as evidenced by the shape and bandwidth of the near infrared absorption band and by density functional theoretical calculations. The parent complex $\left[A^X\right]^+$ lacking the amine substituent ($X=\text{H}$) has been reported recently as well.

In contrast to reported dyes $\left[B^X\right]^+$, featuring a valence-isomeric description of the $\left[B^X\right]^+$ state (Robin–Day class II), potential DSSC sensitizers $\left[A^X{\text{Me}}\right]^+$ with $X=\text{amine}$ that provide a means of detracting the electron hole away from the semiconductor surface in a resonant fashion ($\left[A^X{\text{Me}}\right]^+$; Robin–Day class III) have not yet been reported. Saponifying the three methyl esters of $\left[A^X{\text{Me}}\right]^+$ type complexes should provide suitable sensitizers $\left[A^X{\text{Me}}\right]^+$ with a class III mixed-valent state. Herein, we present a series of three complexes of the general structure $\left[nBu_N\left[Ru(dpbb-X)(tctpy)\right]\right]$ (Hdpb-X = 5-substituted 1,3-di-(2-pyridyl)benzene) with different amine substituents $X$ of increasing electron withdrawing power, namely $N,N$-bis-[4-methoxyphenyl]amine ($X=N(4$-$C{\text{H}}_2{\text{OMe}})_2$), $nBu_N[2a]$, $nB
amine (X = N(C6H5)2); [nBu4N][2b]) and carbazole (X = N-carbazolyl; [nBu4N][2c]). We will discuss how the substituents at the dpb ligand affect the valence-delocalization in the mixed-valent state [2++] and to what extent such delocalization is beneficial for the application of such sensitizers in DSSCs.

As outer-sphere cobalt-based electrolytes67–69 should deliver higher open-circuit voltages \( V_{oc} \) due to their more positive redox potential as compared to the standard triiodide/iodide couple and as they perform extremely well in conjunction with TPA-appended porphyrin dyes (YD2-o-C8) as well as with other potent TPA-appended dyes (Y123, D35), we study the TPA-appended ruthenium(II) dyes [nBu4N][2a]–[nBu4N][2c] with cobalt-based electrolytes in addition to the commonly used triiodide/iodide couple. Specifically, we employ the [Co(bpy)3]3+/2+ and [Co(ddpd)2]3+/2+ redox mediators (bpy = 2,2′-bipyridine, ddpd = N,N′-dimethyl-3,3′-dipyridyl-2-yl-pyridine-2,6-diamine,90 Scheme 1).91–93 The DSSCs are studied by incident photon-to-current conversion efficiency measurements, by current-voltage characteristics under AM 1.5 irradiation and in the dark as well as by electron lifetime measurements.

Results and Discussion

Synthesis and characterization of chromophores

The 5-substituted 1,3-di-(2-pyridyl)benzene ligands L4 (R = N(4-ClC6H4)2), L5 (R = N(C6H5)2) and L6 (R = N-carbazolyl) were synthesized starting from the previously reported 1-bromo-3,5-di-(2-pyridyl)benzene under Buchwald–Hartwig cross-coupling reaction conditions similar to a method we,[48] as well Zhong and co-workers employed previously.94 In the present study, the dimeric palladium(II) precatalyst bis(μ-mesylate)bis(2′-aminoarylphosphanyl-kN-phenyl-kC) palladium(II) ([Pd]295 was used along with the phosphane ligand 2-dicyclohexylphosphanyl-2′,6′-disopropoxybiphenyl96 to provide a catalytically competent catalyst that afforded the ligands in yields of 82–98%. The identity of L4 was confirmed by comparison of its \(^1^H\) NMR spectrum with that reported before.62,63a The purity and integrity of the new ligands Lb and Lc were ascertained by \(^1^H\) and \(^13^C\) NMR spectroscopy, mass spectrometry, and elemental analyses (Experimental Section; Supporting Information, Figures S1–S4).

The heteroleptic ester-substituted [Ru(dpbb(tpyl])\(^+\) complexes [1a]–[1c]\(^+\) were prepared according to a previously employed synthetic method starting from RuCl3(Me3ptcpty) (Scheme 2).

The two-step procedure includes chloride abstraction with silver tetrafluoroborate followed by complexation with the respective dipyridylbenzene ligand Lg–Lh under reducing conditions in n-butanol. Similar to observations made by Zhong and co-workers,62,63a we were not able to isolate the complexes [1a]–[1c]\(^+\) with high purity. Despite the reducing conditions during their synthesis, the substantial amount of the open-shell Ru\(^+\) complexes [1a]2–[1c]\(^2+\) were obtained, as evidenced from ESI mass spectra and the NMR silence of all three compounds (paramagnetic broadening).62,63a Additionally, the isolated products are black in solution and in the solid state instead of the dark purple color typically observed for [Ru(dpbb(tpyl])\(^+\) complexes, suggesting the presence of a second colored species. Yet, cyclic voltammograms confirm the purity of the synthesized complexes by absence of redox waves in the range of \(-3.0 \) and \(1.5 \) V other than the five expected reversible waves,62,63a namely for the [1]3+/2+, [1]1+/0, [1]3+/2+, and [1]1+/0 couples (Figure 1, Supporting Information, Figure S5).

Subsequent saponification of the three methyl ester groups of [1a]–[1c]\(^+\) in aqueous solution using [nBu4N][OH] as base and hydrazine as reductant yielded the corresponding carboxylates as tetrabutylammonium salts [nBu4N][2a]–[nBu4N][2c]. This method affords the fully deprotonated complexes [2a]\(^2+\) – [2c]\(^2+\), in contrast to Berlinguette’s procedure,38 which yields the complexes in their neutral zwitterionic form with two protonated carboxy groups. Owing to the high solubility of the
tetra-butylammonium salts \([\text{Bu}_4\text{N}]_2\)[2a]–\([\text{Bu}_4\text{N}]_2\)[2c] in organic solvents, the products are isolated straightforwardly by extraction of the aqueous phase with dichloromethane. Co-extracted \([\text{Bu}_4\text{N}][\text{PF}_6]\) was removed by subsequent dissolution of the raw products in acetonitrile and addition of a diethyl ether/hexanes mixture that precipitates the desired complexes. The integrity of \([\text{Bu}_4\text{N}]_2[\text{a}]-[\text{Bu}_4\text{N}]_2[\text{b}]-[\text{c}][\text{PF}_6]^-\) was confirmed by \(^1\)H NMR and \(^{13}\)C NMR spectra as well as by ESI\(^+\) and ESI\(^-\) mass spectra (Supporting Information, Figures S6–S19). All NMR spectra lack paramagnetic shifts or broadening, substantiating the absence of Ru\(^{3+}\) in the pristine samples. The \(^1\)H NMR spectra confirm the presence of two equivalents of \([\text{Bu}_4\text{N}]_2\) cations per complex anion in all three cases corroborating the stoichiometry of the salt. IR spectra as KBr disk of the complexes \([\text{Bu}_4\text{N}]_2[\text{a}]-[\text{Bu}_4\text{N}]_2[\text{b}]-[\text{c}][\text{PF}_6]^-\) lack the characteristic vibrations of \([\text{PF}_6]^-\) ions at 843 cm\(^{-1}\) (asym. stretch) and 588 cm\(^{-1}\) (sym. stretch) and 588 cm\(^{-1}\) (def.) present in the parent complexes \([\text{a}][\text{PF}_6]-[\text{b}][\text{PF}_6]\) underlining the quantitative \([\text{PF}_6]^-\) removal (Supporting Information, Figure S20). Additionally, \(^{19}\)F NMR spectra of \([\text{Bu}_4\text{N}]_2[\text{a}]-[\text{c}][\text{PF}_6]^-\) confirm the absence of \([\text{PF}_6]^-\). Under the acidic and ionizing conditions of the ESI\(^+\) mass spectrometry technique, the complexes are observed in their fully protonated form as monocations \([\text{a}]+[\text{PF}_6]^-\) with Ru\(^3+\) or Ru\(^4+\) centers (Supporting Information, Figure S18). The ESI\(^+\) mass spectra (Supporting Information, Figure S19) show mass peaks at the expected \(m/z\) values for the dianions \([\text{a}]^-[\text{PF}_6]^-\) and anions \([\text{a}]^-[\text{PF}_6]^-\) with typical rhenium-isotope patterns. Furthermore, several \(m/z\) peaks of decarboxylated complexes are found for all three complexes \([\text{Bu}_4\text{N}]_2[\text{a}]-[\text{Bu}_4\text{N}]_2[\text{b}]-[\text{c}][\text{PF}_6]^-\), confirming the presence of carboxylate substituents. The carboxylate groups are also evident from the characteristic IR CO stretching vibrations around 1617 cm\(^{-1}\) (Supporting Information, Figure S20).

### Photophysical and electrochemical behavior

The absorption and emission spectra of the complexes \([\text{Bu}_4\text{N}]_2[\text{a}]-[\text{Bu}_4\text{N}]_2[\text{b}]-[\text{c}][\text{PF}_6]^-\) are depicted in Figure 2 and data are summarized in Table 1 (Supporting Information, Figure S21). In the spectral range between 300 and 800 nm all dyes exhibit very similar absorption features. The absorption maximum around 536–549 nm is accompanied by three additional bands around 500, 425, and 375 nm. These bands characteristic for cyclometalated [Ru(dpdb)(tpy)]\(^{+}\) complexes arise from metal-to-ligand charge transfer excitations involving both ligands as electron-accepting sites (\(\delta_{\text{nu}}-\pi_{\text{tpy}}^*\) and \(\delta_{\text{nu}}-\pi_{\text{dpdb}}^*\)). Owing to the low local symmetry around the metal center, the number of absorption bands is larger than for the more symmetric systems containing all-nitrogen donor ligands such as [Ru(tpy)]\(^{3+}\), or [Ru(dpdb)(tpy)]\(^{2+}\), for example. The lower symmetry yields substantially broadened absorption spectra and a more efficient light harvesting throughout the visible range of the electromagnetic spectrum.

The tris(carboxylate) complexes \([\text{Bu}_4\text{N}]_2[\text{a}]-[\text{Bu}_4\text{N}]_2[\text{b}]-[\text{c}][\text{PF}_6]^-\) are very weakly emissive at room temperature (Figure 2, Table 1) with quantum yields below \(5\times10^{-4}\). The wavelength of the emission maximum is shifted hypsochromically in the order \([\text{Bu}_4\text{N}]_2[\text{b}]-[\text{c}][\text{PF}_6]^-\) from 817 to 744 nm. On the one hand, this trend is due to a more pronounced vibrational progression in \([\text{Bu}_4\text{N}]_2[\text{a}]-[\text{Bu}_4\text{N}]_2[\text{b}]-[\text{c}][\text{PF}_6]^-\) than in \([\text{Bu}_4\text{N}]_2[\text{b}]-[\text{c}][\text{PF}_6]^-\) similar to that observed for other [Ru(dpdb)(tpy)]\(^{+}\) complexes with a strong push–pull substitution. On the other hand, the energy of the emissive MLCT state increases with decreasing donor strength of the amine substituent, as this lowers the energy of the metal orbitals involved in the emission process while essentially maintaining the tctpy-centered LUMO energy (Figure 3; Supporting Information, Figure S22).

Cyclovoltammetric studies of the ester-substituted complexes \([\text{a}][\text{PF}_6]-[\text{c}][\text{PF}_6]^-\) reveal multiple reversible redox processes (Figure 1, Table 1, Supporting Information, Figure S5).

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**Table 1.** Optical and electrochemical data of \([\text{a}][\text{PF}_6]-[\text{c}][\text{PF}_6]^-\) and \([\text{Bu}_4\text{N}]_2[\text{a}]-[\text{Bu}_4\text{N}]_2[\text{b}]-[\text{c}][\text{PF}_6]^-\).

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<th>UV/Vis (CH(<em>3)CN) (\lambda</em>{\text{max}}/\text{nm} (\times10^2 \text{ M}^{-1} \text{ cm}^{-1}))</th>
<th>Emission (CH(<em>3)CN) (\lambda</em>{\text{em}}/\text{nm} (\times10^3 \text{ M}^{-1} \text{ cm}^{-1}))</th>
<th>Cyclic voltammetry E/V vs. FcH/FcH(^+)</th>
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<tr>
<td>([\text{a}][\text{PF}_6]^-)</td>
<td>323 (29), 339 (26), 420 (16), 507 (13), 583 (10)</td>
<td>(\ldots)</td>
<td>(-1.87, -1.52, -0.05, +0.31)</td>
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<tr>
<td>([\text{b}][\text{PF}_6]^-)</td>
<td>(\ldots)</td>
<td>(-1.85, -1.49, +0.09, +0.49)</td>
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<tr>
<td>([\text{c}][\text{PF}_6]^-)</td>
<td>(\ldots)</td>
<td>(-1.83, -1.47, +0.34, +0.88)</td>
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<tr>
<td>([\text{a}][\text{PF}_6]^-)</td>
<td>549 (15.4), 503 (12.1), 424 (9.7), 379 (11.3), 528 (22.7)</td>
<td>817 (549)(^{1\text{c}})</td>
<td>(-2.52, -2.09, -0.21, +0.46)</td>
</tr>
<tr>
<td>([\text{a}][\text{PF}_6]^-)</td>
<td>578 (15.4), 501 (12.1), 425 (9.3), 374 (10.4), 525 (23.2), 328 (29.1), 283 (63.2)</td>
<td>791 (543)(^{1\text{c}})</td>
<td>(-2.54, -2.10, -0.15, +0.46)</td>
</tr>
<tr>
<td>([\text{a}][\text{PF}_6]^-)</td>
<td>536 (13.9), 499 (12.5), 426 (9.1), 373 (10.0), 328 (29.1), 283 (63.2)</td>
<td>744 (536)(^{1\text{c}})</td>
<td>(-2.51, -2.07, -0.06, +0.34)</td>
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[a] From Ref. [63a]. [b] No optical data measured due to the presence of Ru\(^{3+}\) species. [c] Quantum yield < \(5\times10^{-4}\). [d] No second oxidation potential was obtained due to precipitation of the neutral dye on the electrode surface.
The complexes are oxidized at quite low potentials to the mixed-valent counterparts $[1]^{2+}$ (−0.05 to 0.34 V vs. FcH/FcH$^+\)). A second oxidation step occurs at higher potentials yielding the Ru(amine) complexes $[1]^{3+}$ (0.31 to 0.88 V vs. FcH/FcH$^+\)). The trend of the first and second oxidation potentials towards higher values in the order N(4-C$_6$H$_4$OCH$_3$)$_2$ < N(C$_6$H$_5$)$_2$ < N-carbazole is in agreement with the decreasing +1 effect of the respective amine substituent X. Additionally, the unpaired electron of the mixed-valent compounds $[1]^{2+}$ is substantially delocalized between the metal center and the triarylamine fragment via the 1,4-phenylene bridge.$^{62,63a}$ The electron donor strength of the dpb substituent$^{62,63a}$ strongly affects degree of delocalization as evidenced by DFT calculations (Figure 3b). Mulliken spin density analysis of $[1a]^{2+}$ indicates a balanced spin population of 0.26 and 0.25 at ruthenium and the amine nitrogen atom, respectively, while for $[1b]^{2+}$, values of 0.43 (Ru) and 0.20 (N) are obtained. In $[1c]^{2+}$, the spin density is further shifted towards the ruthenium atom with spin populations of 0.63 (Ru) and 0.07 (N). Thus, the degree of delocalization is reduced in this series from an essentially delocalized Robin–Day class III system in $[1a]^{2+}$ to a strongly coupled class II compound in $[1c]^{2+}$. As a consequence, the resonance stabilization within complex $[1a]^{2+}$ is the largest, yielding the most pronounced negative shift of the first oxidation potential followed by complexes $[1b]^{2+}$ and $[1c]^{2+}$.$^{61,63a}$ Additionally, two reversible reduction waves are observed for the ester-substituted complexes $[1a][PF_6]^-–[1c][PF_6]^-$. As these reductions are tpy-centered$^{53b,46,48a,63a,87,88}$ their potentials are essentially independent from the substitution pattern at the dpb-X ligand with the first reduction occurring at −1.5 V and the second at −1.85 V vs. FcH/FcH$^+\) for all three complexes.

Deprotection and deprotonation of the ester functionalities, however, shifts the first and second reduction potentials by 600 mV towards more negative values (Figure 1, Table 1; Supporting Information, Figure S5). This is consistent with the substantial increase of negative charge density on the tctpy$^-$ ligand in $[2]^{2-}$ and corroborates the tpy centered reduction. The oxidation waves shift to lower potentials as well, but to a lesser extent. This is mainly due to the fact, that the metal orbital involved with the oxidation process is orthogonal to the tpy ligand. However, a trend of the potential shifts is observed. While the first oxidation wave of $[2a]^{2-}$ occurs 160 mV below that of $[1a]^{2+}$, the first oxidation potentials of $[2c]^{2-}$ and $[1c]^{2+}$ differ by 400 mV. Consequently, the first oxidation potentials of complexes $[2a]^{2-}–[2c]^{2-}$ only differ by 150 mV as opposed to a difference of 390 mV between the esters $[1a]^{2+}–[1c]^{2+}$ . This can be understood on the basis of the Mulliken spin populations of the metal center and the amine nitrogen atom in the mixed-valent anions $[2a]^{2-}–[2c]^{2-}$ . These amount to 0.49 (Ru)/0.17 (N) in $[2a]^{2-}$, 0.57 (Ru)/0.13 (N) in $[2b]^{2-}$, and 0.74 (Ru)/0.03 (N) in $[2c]^{2-}$ . Apparently, the charge delocalization over the triarylamine fragment is significantly reduced and the spin densities of the mixed-valent anions $[2]^{2-}$ are more valence-localized at the electron-rich metal center than their ester counterparts. Consequently, the resonance stabilization of the mixed-valent species $[2]^{2-}$ is not as pronounced as that of $[1]^{2+}$ resulting in similar oxidation potentials for all three complexes. The strongest impact of deprotection and deprotonation is observed for $[2c]^{2-}$ , since its spin density is basically metal-centered. Accordingly, oxidation occurs in the closest proximity to the negatively charged tctpy$^-$ ligand and is facilitated to the largest extent in the dye series $[2]^{2-}$.

Increasing the potential beyond 0.15 V vs FcH/FcH$^+\) results in a multitude of irreversible redox waves. We ascribe this to the deposition of the neutral Ru(amine) complexes $[2]^0$ on the platinum electrode surface, which impeded an unambiguous determination of the second oxidation potentials.

Combining all electrochemical and spectroscopic data of the dyes $[1a]^{2+}–[1c]^{2+}$ and $[2a]^{2-}–[2c]^{2-}$ with the redox data of the electrolytes $I_1/II_1$, $3^{2+}/2^+$, and $4^{3+}/2^+$ and the conduction band edge of TiO$_2$ yields the redox potential diagram depicted in Figure 4. Cyclic voltammetry of the dyes (see above) highlighted the strong dependence of the ground state oxidation potentials of the dyes from the degree of protonation of the carboxylic acids of the tpy ligand. For the setup of the DSSCs, the tris(carboxylate) dyes $[2a]^{2-}–[2c]^{2-}$ were employed. Yet, under the given experimental conditions, partial protonation from water at the TiO$_2$ surface is conceivable. Additionally, the coadsorbent chenoxyxchokylic acid (CDCA), as an organic acid, will modify the degree of protonation of the sensitiser. Hence, Figure 4 depicts redox potential ranges instead of distinct values for the redox potentials of the ruthenium dyes. An analogous range of ground state potentials is applied for N719 owing to the conceivable variation of the protonation state.$^{28}$ In a similar manner, the excited state 1MLCT and 3MLCT redox potentials span ranges.

It is apparent from Figure 4 that, similar to the reference dye N719, all cyclometalated dyes are thermodynamically capable of injecting an electron from both excited states into the conduction band of TiO$_2$. Regeneration of the oxidized dyes by
the employed electrolytes on the other hand is not generally possible. While the carbazol-substituted ruthenium(III) complex \([2\text{c}]^-\) is potentially regenerated by iodide even if the diiodide radical anion is formed as an intermediate,\(^{[69,90]}\) this is not the case for the diarylamine-substituted dyes \([2\text{a}]^-\) and \([2\text{b}]^-\) in this simplified consideration of standard redox potentials. Hence, in a DSSC \([2\text{c}]^-\) is expected to outperform \([2\text{a}]^-\) and \([2\text{b}]^-\). DSSC performances of all cyclometalated dyes in conjunction with the standard triiodide/iodide electrolyte and cobalt electrolytes will be discussed in the next section.

Solar cell performance

Dye-sensitized solar cells were prepared from the carboxylate substituted dyes \([\text{nBuN}]_2[2\text{a}]^-–[\text{nBuN}]_2[2\text{c}]^-\) and the benchmark dye N719. The coadsorbent CDCA was employed to protect the TiO\(_2\) surface in several setups. Three different liquid electrolytes were utilized, namely the standard triiodide/iodide couple and two cobalt-based redox mediators.\(^{[67–69,82,83]}\) The cobalt(III/II) complexes \([\text{Co(bpy)}]^{3+/2+}\) and \([\text{Co(ddpdh)}]^{3+/2+}\) were prepared according to literature procedures.\(^{[74,76,82,91]}\) Counter ion exchange was accomplished using \(\text{Li[B(C_6F_5)]_n}\) giving the cobalt salts \([\text{Co(bpy)}]_n[\text{B(C_6F_5)]_n}\) and \([\text{Co(ddpdh)}]_n[\text{B(C_6F_5)]_n}\). NMR and mass spectrometric data confirm their compositions (Supporting Information, Figure S23–S31). The redox potential of \([4\text{a}]^{1+/0+}\) (\(E_{\text{oc}} = 0.52 \text{ V vs. NHE}\)) is intermediate of the \(I^-/I^-\) (\(E_{\text{i}} = 0.32 \pm 0.03 \text{ V vs. NHE}\)) and the \([3\text{a}]^{1+/0+}\) (\(E_{\text{i}} = 0.65 \text{ V vs. NHE}\)) couples (Figure 4).

The incident photon-to-current conversion efficiency (IPCE, Figure 5) depends on several individual key steps, namely light-harvesting, electron injection, dye regeneration, and charge collection.\(^{[87]}\) The extinction coefficients around the MLCT maxima of \([\text{nBuN}]_2[2\text{a}]^-–[\text{nBuN}]_2[2\text{c}]^-\) (Figure 2, Experimental Section) are close to that of N719 \((\lambda = 535 \text{ (14700), 395 (14300}\ \mu\text{m}^{-1}\text{cm}^{-1})}\) nm.\(^{[88]}\) The achieved dye loadings of \([\text{nBuN}]_2[2\text{a}]^-–[\text{nBuN}]_2[2\text{c}]^-\) are consistently somewhat higher than that found with N719 (Experimental Section). Hence, we assume that the light-harvesting efficiencies of \([\text{nBuN}]_2[2\text{a}]^-–[\text{nBuN}]_2[2\text{c}]^-\) in the cells prepared are in the same range as that of the reference dye N719.

Concerning the injection efficiency, all dyes feature \(^1\text{MLCT}\) and \(^3\text{MLCT}\) levels well above the Fermi level of TiO\(_2\) (Figure 4). Hence, electron injection from the excited sensitizers should be feasible and fast for all dyes.\(^{[87]}\) We assume rather similar injection efficiencies for all dyes.\(^{[87]}\) Hence, the differences in DSSC performance in terms of power conversion efficiency \(\eta\) should predominantly relate to the dye regeneration efficiency, the charge collection efficiency (recombination losses) and the open-circuit voltage \(V_{\text{OC}}\).

According to the electrochemical data of the dyes and the redox mediators, the Ru\(^{3+}\) complex \([2\text{a}]^-\) cannot be efficiently regenerated by the bipyridine cobalt(II) complex \([3\text{a}]^{2+}\), while \([2\text{a}]^-\) cannot be regenerated by both cobalt(II) complexes \([3\text{b}]^{2+}\) and \([4\text{b}]^{2+}\) (Figure 4). For all other dye/redox mediator combinations, dye regeneration is thermodynamically possible. In the electrolyte series, the highest driving force for dye re-

Figure 4. Diagram of the ground-state (‘GS’) and excited-state (‘MLCT’ and ‘MLCT’) redox potentials of \([1\text{a}]^-/2\text{a}^2-, [1\text{b}]^-/2\text{b}^2-, [1\text{c}]^-/2\text{c}^2-, \) and N719, the conduction band edge of TiO\(_2\), and the redox potentials of the electrolytes.

Figure 5. Photocurrent action spectra of cells with \([\text{nBuN}]_2[2\text{a}]^-,[\text{nBuN}]_2[2\text{b}]^-,[\text{nBuN}]_2[2\text{c}]^-\), and N719. a) \(I^-/I^-\) redox mediator with/without CDCA (—/••••••••) b) \([3\text{a}]^{1+/0+}\) (—••••••••••••) and \([4\text{a}]^{1+/0+}\) (—••••••••••••) electrolytes.
generation and hence the highest regeneration rate based on Marcus theory (Marcus normal region) is achieved with the \( I_1^-/I^- \) couple (although the \( I_2^-/I^- \) couple with a higher potential is more suitable for the dye regeneration; Figure 4).\(^{[39,40]} \) As the regeneration rate furthermore depends on the concentration of the reduced mediator,\(^{[47]} \) the regeneration rate should decrease in the series \( I_1^- \) (0.550 m), \( I_2^- \) (0.165 m) and \( I_3^- \) (0.080 m). All of these factors strongly favor the \( I_1^-/I^- \) couple over cobalt-based couples.

Electron recombination with oxidized dyes (driving forces around 1.0–1.5 eV)\(^{[42]} \) (Figure 4) is reported to occur in the Marcus inverted region. However, the rates better correlate with the inverse distance of the positive charge in the dye and the TiO\(_2\) surface instead of the driving force.\(^{[47]} \) In oxidized N719 the positive charge is delocalized between Ru and the [NCS\(_{\text{2}}\)] ligands. In \( [\text{1a}]^2^-/\text{1c}^2^- \) the positive charge is efficiently delocalized onto the amine substituents of the dpb ligands (Robin–Day class III/class I behavior, see above). This is visualized in the DFT-calculated singly occupied molecular orbitals and corresponding spin densities of \( [\text{1a}]^2^-/\text{1c}^2^- \) spreading over the metal center and the amine substituent (see Figure 3). In this respect, amine substituted sensitizers should be somewhat advantageous as compared to N719. On the other hand, electron recombination with oxidized dyes depends on the lifetime of the oxidized dye and hence on its regeneration efficiency in the specific cell. Dye regeneration is very efficient for SCN-based ruthenium dyes and iodide, but often slowed down with other dye/electrolyte combinations for various reasons (lower electrolyte concentration, lower driving force, smaller electronic coupling, inner/outer sphere electron transfer).\(^{[47–49]} \) Considering the slower dye regeneration using \( [\text{2a}]^2^-/\text{2c}^2^- \) sensitizers or cobalt redox mediators, the better performance of cells with the N719/\( I_1^-/I^- \) combination is quite expected (Figure 5a, Tables 2, Table 3). Interestingly, a lower electrolyte concentration decreases the efficiency of the N719 cell to 5.8\% but improves the efficiency of the cell with the \( [\text{nBuN}_3]_2 \text{c} \) sensitizer to 3.3\% (Table 2). Obviously, the effects of electrolyte concentration on dye regeneration and electron recombination kinetics differs for both dyes. This shows that the standard electrolyte concentration is optimized for N719, but the optimum electrolyte concentration needs to be determined for each dye individually. However, this is beyond the scope of this study.

Electron regeneration of conduction band electrons with the oxidized mediator (\( I_1^-/\text{3}^+ \), \( \text{4}^+ \)) is a complex function of the driving force (Marcus normal or inverted region), the electronic coupling, and the presence of surface protection.\(^{[48]} \) Recombination kinetics with \( I_1^- \) is slow,\(^{[49]} \) yet all cells with \( [\text{2}]^2^-/I_1^-/I^- \) combinations profit from the presence of CDCA as a surface protecting agent and show higher short-circuit current densities (Table 2, Figure 5a, Figure 6a). With the \( I_1^-/I^- \) couple, the dark current for \( [\text{2a}]^2^-/\text{2c}^2^- \) sensitizers is higher than that of N719 (Figure 6b). However this observation reverses for the cobalt-based electrolytes (Figure 7b). Obviously, cells with the tridentate cyclometalated complexes \( [\text{2b}]^2^- \) and \( [\text{2c}]^2^- \) cope with the cobalt-based electrolytes, but the cell performance with N719 dyes and cobalt-based electrolytes is severely reduced. The poor performance of N719 in combination with cobalt-based electrolytes can be traced back to the higher dark current densities and consequently a strongly diminished short-circuit current density (Figure 6b, 7b; Table 1 and Table 2). As a working hypothesis, the N719 dye better shields TiO\(_2\) from \( I_1^- \), but \( [\text{2b}]^2^- \) and \( [\text{2c}]^2^- \) better shield TiO\(_2\) from cobalt-based electrolytes. This effect is certainly related to molecular structure, packing density (cf. dye loadings, Table 4) and protonation state of the dyes.\(^{[48]} \)

Comparing the influence of the two cobalt-based electrolytes on the dark current densities of the N719 and \( [\text{2c}]^2^- \) dyes, the bpy-based electrolyte \( [\text{3}]^1^-/\text{2}^- \) shows the lower dark current density (Figure 7b). For cobalt-based electrolytes with potentials above about 0.55 V vs. NHE, recombination with electrons in the conduction band should be in the Marcus inverted region.\(^{[46]} \) In accordance with this reported limiting value, recombination with \( [\text{3}]^+ \) is hampered as compared to

### Table 2. Photovoltaic data of cells using the \( I_1^-/I^- \) redox mediator with and without CDCA under AM1.5 light conditions (the data correspond to averaged values of several cells).

<table>
<thead>
<tr>
<th>Dye</th>
<th>CDCA</th>
<th>( V_{OC} ) [V]</th>
<th>( J_{SC} ) [mAcm(^{-2})]</th>
<th>FF [%]</th>
<th>( \eta ) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( [\text{nBuN}_3]_2 )</td>
<td>0.50</td>
<td>1.77</td>
<td>63</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>( [\text{nBuN}_3]_2 )</td>
<td>+</td>
<td>0.54</td>
<td>3.37</td>
<td>67</td>
<td>1.2</td>
</tr>
<tr>
<td>( [\text{nBuN}_3]_2 )</td>
<td>-</td>
<td>0.59</td>
<td>5.47</td>
<td>73</td>
<td>2.4</td>
</tr>
<tr>
<td>( [\text{nBuN}_3]_2 )</td>
<td>+</td>
<td>0.57</td>
<td>5.06</td>
<td>72</td>
<td>2.1</td>
</tr>
<tr>
<td>( [\text{nBuN}_3]_2 )</td>
<td>+</td>
<td>0.59</td>
<td>5.58</td>
<td>74</td>
<td>2.5</td>
</tr>
<tr>
<td>( [\text{nBuN}_3]_2 )</td>
<td>+</td>
<td>0.70</td>
<td>6.74</td>
<td>70</td>
<td>3.3</td>
</tr>
<tr>
<td>N719</td>
<td>+</td>
<td>2.74</td>
<td>13.4</td>
<td>75</td>
<td>7.3</td>
</tr>
<tr>
<td>N719</td>
<td>+</td>
<td>0.78</td>
<td>1.07</td>
<td>68</td>
<td>5.8</td>
</tr>
<tr>
<td>( [\text{A}]^+ )</td>
<td>+</td>
<td>0.55</td>
<td>8.22</td>
<td>69</td>
<td>3.1</td>
</tr>
<tr>
<td>( [\text{B}]^+ )</td>
<td>+</td>
<td>0.54</td>
<td>8.49</td>
<td>73</td>
<td>3.4</td>
</tr>
<tr>
<td>( [\text{C}]^+ )</td>
<td>+</td>
<td>0.69</td>
<td>11.61</td>
<td>73</td>
<td>5.8</td>
</tr>
</tbody>
</table>

[a] Guanidinium thiocyanate was employed additionally in the electrolyte solution. [b] The electrolyte concentration was reduced to 0.100 m 1-methyl-3-propylimidazolium iodide and 0.020 m iodine in CH\(_3\)CN.
accounting for the lower dark current.

For both low-spin cobalt(III) complexes [3]^{3+/2+} and [4]^{3+/2+} recombination with an electron initially yields low-spin cobalt(II) complexes corresponding to a metastable low-spin state which then undergoes spin crossover to the high spin state.\(^\text{83, 95}\) This effect might account for the favorable dark current densities of the cobalt-based electrolytes compared to the \(I_1^-/I^-\) couple for [2b]\(^{2+}\) and [2c]\(^{2+}\) (Figure 6b).\(^\text{7b}\).

Electron lifetimes were determined by the photovoltage response to a small amplitude light modulation as a function of the quasi Fermi level of \(\text{TiO}_2\) (Figure 8). All responses are linear in the semi-logarithmic plot, suggesting that recombination depends exponentially on the potential without participation of surface states.\(^\text{96}\) As suggested above, CDCA retards recombination with [4]^{3+/2+} accounting for the lower dark current density.

For both low-spin cobalt(III) complexes [3]^{3+/2+} and [4]^{3+/2+} recombination with an electron initially yields low-spin cobalt(II) complexes corresponding to a metastable low-spin state which then undergoes spin crossover to the high spin state.\(^\text{83, 95}\) This effect might account for the favorable dark current densities of the cobalt-based electrolytes compared to the \(I_1^-/I^-\) couple for [2b]\(^{2+}\) and [2c]\(^{2+}\) (Figure 6b).\(^\text{7b}\).

Electron lifetimes were determined by the photovoltage response to a small amplitude light modulation as a function of the quasi Fermi level of \(\text{TiO}_2\) (Figure 8). All responses are linear in the semi-logarithmic plot, suggesting that recombination depends exponentially on the potential without participation of surface states.\(^\text{96}\) As suggested above, CDCA retards recombination with the iodine shuttle and increases the lifetime (Figure 8a). \(\text{N719}\) displays the highest lifetime with the \(I_1^-/I^-\) couple but performs poorly with the cobalt-based electrolytes (Figure 8). The slow dye regeneration kinetics of the cobalt-based electrolytes allowing for recombination with the oxidized dyes easily accounts for this observation. Slightly faster dye regeneration and/or better surface shielding with the dye/electrolyte combination [2c]\(^{2+}\)/[3]^{3+/2+} yields a higher electron lifetime (Figure 8b).

Finally, the open-circuit voltages \(V_{\text{OC}}\) should increase in the electrolyte series \(I_1^-/I^-<[3]^{3+/2+}<[4]^{3+/2+}\) according to the electrochemical data (Figure 4). Indeed, \(V_{\text{OC}}\) of the cobalt electrolytes is somewhat larger than that of the \(I_1^-/I^-\) couple for [2a]\(^{2+}\), [2b]\(^{2+}\), and [2c]\(^{2+}\) dyes, although the effect is less pronounced than expected from the redox potentials (Figure 4).

Overall, the combination of cobalt-based electrolytes with TPA-appended dyes, especially [2c]\(^{2+}\) outperforms the standard dye \(\text{N719}\) with cobalt-based electrolytes. The absolute performance of \(\text{N719}\) and the \(I_1^-/I^-\) couple with optimized concentration is still unrivaled with the systems under study.

**Conclusion**

The bis(tridentate) cycometalated ruthenium complexes [1a]\([\text{PF}_6^-]_2\)-[1c]\([\text{PF}_6^-]\) as well as their saponified counterparts [nBu\(_4\)]\(_2\)[2a]-[nBu\(_4\)]\(_2\)[2c] were synthesized and characterized.
surpassed however ($\eta = 5.8\%$ under the same conditions). Compared to the triiodide/iodide cells, the efficiencies of the cells containing cobalt electrolytes are smaller by about a factor of three despite larger open-circuit voltages. We attribute this to the substantially slowed dye regeneration by the cobalt electrolytes which results in reduced short-circuit currents. In the presence of cobalt electrolytes, however, the cyclometalated dye with the carbazole substituent ($[2c]$$^{2+}$ ($\eta = 1.4\%$) surpasses the thiocyanato-based dye N719 ($\eta = 1.1\%$). This once again underlines the exceptional suitability of the triiodide/iodide electrolyte for thiocyanate-based sensitizers. We aim to dedicate further work to the understanding of the opposing trends of overall cell performances with the cobalt and iodide based electrolytes.

**Experimental Section**

Chemicals were obtained from commercial suppliers (Acros, Sigma-Aldrich, Solaronix SA, Wakó, TCI, Boulder Scientific) and used without further purification. Air- or moisture-sensitive reactions were performed in dried glassware in an inert gas atmosphere (argon, quality 4.6). Acetonitrile was refluxed over CaH$_2$ and distilled under argon prior to use. Toluene was refluxed over sodium and distilled under argon prior to use. The ligands trimethyl-2,2$'$,6$'$,2$''$-terpyridine-4,4$'$,4$''$-tricarboxylate Me$_6$tcptpy$^{[22]}$ 1-bromo-3,5-dil(2-pyridyl)benzene$^{[20]}$ ddpdp$^{[23]}$ as well as the ruthenium(III) complex RuCl$_3$(Me$_6$tcptpy)$^{[24]}$ and the palladium precursor [Pd]$^{[24]}$ were synthesized according to previously reported procedures. IR spectra were recorded on a Varian Excalibur Series 3100 FTIR spectrometer using KBr disks. IR absorption band intensities are classified as strong (s), medium (m), weak (w), and shoulder (sh). UV/Vis spectra were recorded on a Varian Cary 5000 spectrometer in 1 cm cuvettes. Emission spectra were recorded on a Varian Cary Eclipse spectrometer. Quantum yields were determined by comparing the areas under the emission spectra on an energy scale recorded for solutions of the samples and a reference with matching absorbances ($\Phi$([Ru(bipy)$_3$Cl$_2$]) = 0.094 in deaerated MeCN.$^{[25]}$ Experimental uncertainty is estimated to be 15%. ESI$^-$ and high-resolution ESI$^-$ mass spectra were recorded on a Micromass QToF Ultima API mass spectrometer with analyte solutions in acetonitrile. FD mass spectra were recorded on a Thermo Fisher DFS mass spectrometer with a LIFDI upgrade. Elemental analyses were performed by the microanalytical laboratory of the chemical institutes of the University of Mainz. NMR spectra were obtained with a Bruker Avance II 400 spectrometer at 400.31 (H), 100.66 (C), 376.67 (F) at 25 $°$C. Chemical shifts $\delta$ (ppm) are reported with respect to residual solvent signals as internal standards (H, $^{15}$C); CD$_3$CN $\delta$(H) = 1.94 ppm, $\delta$(C) = 1.32 and 118.26 ppm.$^{[26]}$ CD$_3$Cl $\delta$(H) = 5.32 ppm, $\delta$(C) = 53.84 ppm.$^{[27]}$ $\delta$(F: $\delta$ = 0 ppm). Electrochemical experiments were performed with a BioLogic SP-50 voltammetric analyzer at a sample concentration of 10$^{-3}$ m using platinum wire working and counter electrodes and a 0.01 m Ag/AgNO$_3$ reference electrode. Measurements were carried out at a scan rate of 100 mVs$^{-1}$ for cyclic voltammetry experiments and at 10 mVs$^{-1}$ for square-wave voltammetry experiments using 0.1 m [NiBu$_3$][PF$_6$] as supporting electrolyte in acetonitrile. Potentials are given relative to the ferrocene/ferrocenium couple (0.40 V vs. SCE, $E_{Fc/Fc} = 0.09 \pm 0.5$ mV under the given conditions.$^{[27]}$ Current–voltage characteristics of the DSSCs were measured with a Keithley Model 2400 source meter and a solar simulator with a 300 W Xenon arc-lamp (Newport) under 1 sun illumination using mass spectrometry, UV/Vis and emission spectroscopy, and electrochemical methods. Oxidation of $[2a]$$^{2-}$–$[2c]$$^{3+}$ yields strongly coupled mixed valent species $[2a]$$^{-}$–$[2c]$$^{-}$ with substantial charge delocalization between the metal center and the triarylamine fragment as evidenced from TD-DFT calculations.$^{[18,63]}$ Yet, the degree of this delocalization is reduced in the saponified complexes $[2a]$$^{-}$–$[2c]$$^{-}$ as compared to the corresponding esters $[1a]$$^{2-}$–$[1c]$$^{2+}$ due to an increased charge density at the metal center. Concomitantly, all redox potentials shift to substantially lower values. Charge delocalization should be beneficial for applications in dye-sensitized solar cells as it hampers undesired recombination processes. However, the low redox potentials, which result from the large resonance stabilization, poses a challenge in the selection of a suitable redox electrolyte for efficient dye regeneration. As a consequence, dye $[2c]$$^{2+}$ with the highest oxidation potential yields the best cell performance of the cyclometalated complexes in this study in conjunction with triiodide/iodide ($\eta = 3.3\%$). The reference dye N719/triiodide/iodide combination remains useful but unsuccessful: $\eta = 5.8\%$. Cyclic voltammetry experiments with $[2b]$$^{2+}$ and $[2c]$$^{2+}$ using a $\mu$A electrooxidator at the I$_3$/I$_2$ couple ($\eta = 1.1\%$) surpasses the thiocyanato-based dye N719 ($\eta = 1.1\%$). This once again underlines the exceptional suitability of the triiodide/iodide electrolyte for thiocyanate-based sensitizers. We aim to dedicate further work to the understanding of the opposing trends of overall cell performances with the cobalt and iodide based electrolytes.

**Figure 8.** a) Electron recombination lifetimes (r) of cells with [nBu$_4$N]$_2$[2a], [nBu$_4$N]$_2$[2b], [nBu$_4$N]$_2$[2c], and N719 using a: the 1,1'-redox mediator with/without CDCA (c$^-$c) and b) using the (1)$^{1+/2-}$ (c$^-$c) and (4)$^{1+/2+}$ (c$^-$c) redox mediators.
(AM 1.5, 100 mW cm$^{-2}$). A light shading mask, placed on the residu-
al area of the front side of the FTO substrate (except for the 0.16 cm$^2$ TiO$_2$ active area), was employed to prevent overestima-
tion of the power conversion efficiency. The quantum efficiencies of the DSSCs were measured by incident photon-to-current con-
version efficiency (IPCE) measurements (PV Measurements, Inc.). UV/Vis spectra of the dye loading solutions were collected on a Jasco V-670 UV/Vis spectrometer. The electron lifetimes were ob-
tained by intensity modulated photovoltage spectroscopy (IMVS) under open-circuit conditions as a function of light intensity using a controlled intensity modulated photo spectroscopy (CIMPS) system (Zahner).

Density functional theory calculations: DFT calculations were car-
ried out using the ORCA program package (version 3.0.2)[109] Tight convergence criteria were chosen for all calculations (Keywords TightSCF and TightOpt). All calculations employ the resolution of
niveau. The ZORA keyword automatically invokes relativistically
adjusted basis sets.[107] To account for solvent effects a conductor-
like screening model (COSMO) modelling acetoni lone was used in all calculations.[108] Explicit counterions and/or solvent molecules were not taken into account in all cases.

Synthesis of N,N-bis-(4-methoxyphenyl)-3,5-di(2-pyridyl)aniliane (dpbH-N(4-C$_8$H$_7$O$_2$)Me)$_2$: 2-Dicyclohexylphosphino-phosphano-2,6-diisopropoxybiphenyl (12 mg, 0.026 mmol, 0.04 equiv) and the precatalyst [Pd$_2$(8 mg, 0.01 mmol, 0.02 equiv) were suspended in dry toluene (10 mL) and stirred for 10 min followed by the addition of 1-bromo-3,5-
di(2-pyridyl)benzene (200 mg, 0.643 mmol, 1 equiv), barbaco (161 mg, 0.964 mmol, 1.50 equiv), sodium tert-butoxide (93 mg, 0.968 mmol, 1.51 equiv), and further dry toluene (40 mL). The re-
sulting mixture was refluxed for 12 h. After cooling to room tem-
perature, the solvent was removed under reduced pressure and the brown residue was purified by column chromatography on silica gel (eluent: dichloromethane/ethyl acetate 20:1) yielding $L^a$ as slightly yellow solid. Yield: 212 mg (0.556 mmol, 98%). Anal. calc. for C$_{36}$H$_{29}$N$_2$O: C 82.96, H 4.53, N 10.34; found: C 82.73, H 4.96, N 10.34.

Synthesis of [Ru(L)$_3$](Me$_2$tcyp)][PF$_6$] [1a][PF$_6$]: RuCl$_2$(Me$_2$tcyp) (222 mg, 0.361 mmol, 1 equiv) and AgBF$_4$ (204 mg, 1.05 mmol, 2.9 equiv) were dissolved in dry acetonitrile (15 mL) and refluxed in the dark for 3 h. After cooling to room temperature, the mixture was refluxed for 3 h and stirred for 10 min followed by the addition of 1-bromo-3,5-
di(2-pyridyl)benzene (200 mg, 0.643 mmol, 1 equiv), sodium tert-butoxide (93 mg, 0.968 mmol, 1.51 equiv), and further dry toluene (40 mL). The resulting mixture was refluxed for 12 h. After cooling to room temperature, the solvent was removed under reduced pressure and the brown residue was purified by column chromatography on silica gel (eluent: dichloromethane/ethyl acetate 10:1–7:1), yielding $L^a$ as slightly yellow solid. Yield: 212 mg (0.556 mmol, 86%). NMR and mass spectrometric data agree with reported values.[109]

Synthesis of N,N-di-piphenyl-3,5-di(2-pyridyl)aniliane (dpbH-NPh)$_2$: 2-Dicyclohexylphosphino-phosphano-2,6-diisopropoxybiphenyl (12 mg, 0.026 mmol, 0.04 equiv) and the precatalyst [Pd$_2$(8 mg, 0.01 mmol, 0.02 equiv) were suspended in dry toluene (10 mL) and stirred for 10 min followed by the addition of 1-bromo-3,5-di(2-pyridyl)benzene (200 mg, 0.643 mmol, 1 equiv), diphenylamine (163 mg, 0.964 mmol, 1.50 equiv), sodium tert-butoxide (93 mg, 0.968 mmol, 1.51 equiv) and further dry toluene (40 mL). The resulting mixture was refluxed for 12 h. After cooling to room temperature, the solvent was removed under reduced pressure and the brown residue was purified by column chromatography on silica gel (eluent: dichloromethane/ethyl acetate 10:1) yielding $L^b$ as slightly yellow solid. Yield: 222 mg (0.556 mmol, 86%). Anal. calc. for C$_{36}$H$_{29}$N$_2$O: C 82.96, H 4.53, N 10.34; found: C 82.73, H 4.96, N 10.34.

Synthesis of 1-(N-carbazolyl)-3,5-di(2-pyridyl)benzene (dpbH-N-
carbazole) L$_1$: 2-Dicyclohexylphosphino-phosphano-2,6-diisopropoxybiphenyl (12 mg, 0.026 mmol, 0.04 equiv) and the precatalyst [Pd$_2$(7 mg, 0.009 mmol, 0.01 equiv) were suspended in dry toluene (10 mL) and stirred for 10 min followed by the addition of 1-bromo-
di(2-pyridyl)benzene (200 mg, 0.643 mmol, 1 equiv), barbaco (161 mg, 0.964 mmol, 1.50 equiv), sodium tert-butoxide (93 mg, 0.968 mmol, 1.51 equiv), and further dry toluene (40 mL). The re-
sulting mixture was refluxed for 12 h. After cooling to room tem-
perature, the solvent was removed under reduced pressure and the brown residue was purified by column chromatography on silica gel (eluent: dichloromethane/ethyl acetate 20:1) yielding $L^b$ as slightly yellow solid. Yield: 251 mg (0.556 mmol, 98%). Anal. calc. for C$_{36}$H$_{29}$N$_2$O: C 82.97, H 4.33, N 10.34; found: C 82.96, H 4.96, N 10.34.

Synthesis of [Ru(L)$_3$](Me$_2$tcyp)][PF$_6$] [1a][PF$_6$]: RuCl$_2$(Me$_2$tcyp) (222 mg, 0.361 mmol, 1 equiv) and AgBF$_4$ (204 mg, 1.05 mmol, 2.9 equiv) were dissolved in dry acetonitrile (15 mL) and refluxed in the dark for 3 h. After cooling to room temperature, the mixture was filtered through a syringe filter (0.2 μm) and the solvent re-
moved under reduced pressure. The dark residue was dissolved in deaerated n-butanol (20 mL) and $L^b$ (200 mg, 0.435 mmol, 1.2 equiv) was added. The mixture was refluxed for 13 h followed by removal of the solvent under reduced pressure. The raw prod-
uct was redissolved in MeCN (5 mL) and triturated by addition of a solution of [Ni(H$_2$)[PF$_6$] (177 mg, 0.083 mmol, 3 equiv) in H$_2$O (2 mL). The black precipitate was filtered off and washed with diethyl ether and hexanes. After purification via column chromatography on silica gel (eluent: chloroform/methanol 1:1–7:1), [1a][PF$_6$] was obtained as black powder. Yield: 364 mg (0.327 mmol, 91%). MS(ESI): m/z (%) = 697.1 (100) [1a]$^+$. Traces of the paramagnetic Ru$^{III}$ complex [1a][PF$_6$] broaden all NMR resonances of [1a][PF$_6$] due to the presence of a fast self-exchange reaction.[62,63]
The black precipitate was filtered off and washed with diethyl ether and hexanes. After purification via column chromatography on silica gel (eluents: chloroform/methanol 1.0:−0.7), [1]PF₆ was obtained as black powder. Yield: 389 mg (0.370 mmol, 86%).

Synthesis of [Ru(L₃bpy)][PF₆] (263 mg, 0.429 mmol, 1 equiv) and AgBF₄ (243 mg, 1.2 mmol, 2.9 equiv) were dissolved in dry acetonitrile (15 mL) and refluxed in the dark for 3 h. After cooling to room temperature, the mixture was filtered through a syringe filter (0.2 µm) and the solvent removed under reduced pressure. The residue was dissolved in deaerated n-butanol (20 mL) and L⁻ (206 mg, 0.516 mmol, 1.2 equiv) was added. The mixture was refluxed for 13 h followed by removal of the solvent under reduced pressure. The raw product was redissolved in MeCN (5 mL) and triturated by addition of a solution of [NH₄][PF₆] (210 mg, 1.29 mmol, 3 equiv) in H₂O (2 mL). The black precipitate was filtered off and washed with diethyl ether and hexanes. After purification via column chromatography on silica gel (eluents: chloroform/methanol 1.0:−0.7), [1]PF₆ was obtained as black powder. Yield: 389 mg (0.370 mmol, 86%).

Synthesis of [Ru(L₃bpy)][PF₆] (263 mg, 0.429 mmol, 1 equiv) and AgBF₄ (243 mg, 1.2 mmol, 2.9 equiv) were dissolved in dry acetonitrile (15 mL) and refluxed in the dark for 3 h. After cooling to room temperature, the mixture was filtered through a syringe filter (0.2 µm) and the solvent removed under reduced pressure. The residue was dissolved in deaerated n-butanol (20 mL) and L² (206 mg, 0.516 mmol, 1.2 equiv) was added. The mixture was refluxed for 13 h followed by removal of the solvent under reduced pressure. The raw product was redissolved in MeCN (5 mL) and triturated by addition of a solution of [NH₄][PF₆] (204 mg, 1.25 mmol, 3 equiv) in H₂O (2 mL). The black precipitate was filtered off and washed with diethyl ether and hexanes. After purification via column chromatography on silica gel (eluents: chloroform/methanol 1.0:−0.7), [1]PF₆ was obtained as black powder. Yield: 385 mg (0.366 mmol, 88%).

Full Paper


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Synthesis of [Co(ddpd)][B(C6F5)4]: [Co(ddpd)]+[B(C6F5)4]− (2.94 g, 4.20 mol, 1.0 equiv) was dissolved in CH3CN (100 mL) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (1.43 g, 6.30 mmol, 1.5 equiv) was added. The solution was stirred for 5 h at room temperature. Li[B(C6F5)4]·Et2O (12.8 g, 16.8 mol, 4.0 equiv) was added and the mixture was diluted with water (200 mL). The precipitate was filtered off, washed with water (200 mL), and dried under reduced pressure to give a slight orange crystalline solid (7.65 g, 2.98 mmol, 71%). 1H NMR (CD3CN): δ [ppm] = 8.71 (d, 1H, JH-H = 7.8 Hz), 8.49 (pt, 1H, JH-H = 7.7 Hz), 7.96 (pt, 1H, JH-H = 6.5 Hz), 7.31 (d, 1H, JH-H = 5.5 Hz). 13C NMR (CD3CN): δ [ppm] = −133.04 (bs, 2F), −164.22 (pt, 1F, JF-F = 19.7 Hz), −166.65 (bs, 2F). MS(ESI)+: m/z (%) = 185.6 (7) [Co(ddpd)]+; 1206.2 (100) [Co(ddpd)+B(C6F5)4−]; 21493.1 (17) [3 × [Co(ddpd)+B(C6F5)4−]]; 3092.44 (19 [4 × [Co(ddpd)+B(C6F5)4−]]; 6 × [B(C6F5)4−]). HR-MS(ESI)+, m/z: Calcd. for C12H48N2B4CoF4N4: 1205.1204; found: 1205.1224.

Synthesis of [Co(dddp)][B(C6F5)4]: [Co(dddp)]+[B(C6F5)4]− (2.34 g, 3.83 mmol, 1.0 equiv) was dissolved in CH3CN (100 mL) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (1.30 g, 5.75 mmol, 1.5 equiv) was added. The solution was stirred for 5 h at room temperature. Li[B(C6F5)4]·Et2O (11.6 g, 15.3 mmol, 4.0 equiv) was added and the mixture was diluted with water (200 mL). The precipitate was filtered off, washed with water (200 mL), and dried under reduced pressure to give a pinkish powder (8.32 g, 3.06 mmol, 86%). 1H NMR (CD3CN): δ [ppm] = 8.33 (pt, 1H, JH-H = 8.1 Hz), 8.13 (pt, 2H, JH-H = 7.8 Hz), 7.38–7.43 (m, 4H), 7.01 pt, 2H, JH-H = 6.7 Hz), 6.90 (d, 2H, JH-H = 5.7 Hz), 3.12 (s, 6H). 13C NMR (CD3CN): δ [ppm] = −134.07 (s), −164.22 (pt), −168.68 (pt). The 1H NMR data match reported values of [Co(dddp)][B(C6F5)4]−: m/z (%) = 175.1 (10) [Co(dddp)]+; 181.4 (10) [Co(dddp)+B(C6F5)4−] + F−; 291.2 (12) [dddp]+. 320.6 (56) [Co(dddp)+B(C6F5)4−]; 320.2.8 (8) [Co(dddp)+B(C6F5)4−]; 1999.2 (100) [Co(dddp)+2 × [B(C6F5)4−]); 2535.5 (10), 2669.6 (20) [5 × (Co(dddp)+B(C6F5)4−)]; 2892.8 (7) [4 × (Co(dddp)+B(C6F5)4−)]; 3071.4 (12), 3339.4 (19) [3 × (Co(dddp)+B(C6F5)4−)]; 7 × [B(C6F5)4−]). HR-MS(ESI)+, m/z: Calcd. for Cs2H48N2B4CoF4N4: 1989.1847; found: 1999.1809.

TiO2 electrode preparation: Fluorine-doped tin oxide (FTO) glass plates (Pilkington-TEC8) were cleaned using a ultrasonic bath with 2 vol% of Helmanex in deionized water and ethanol. A doctor-bladed layer of 35 nm TiO2 particles (PST-35 NR, CICC) was used as photoelectrode. A 8 μm thick transparent film and an additional 4 μm scattering TiO2 film (PST-400C, CICC, particle size ca. 400 nm) were coated on the top of the conducting glass electrode. The TiO2 electrodes were heated to 450 °C for 30 min, treated with a 0.5 mm TCI solution in deionized water for 20 min at 70 °C, followed by an annealing process for 30 min at 450 °C. Following the heat treatment, these electrodes were immersed into the sensitizer/CdCA solutions (2.95 × 10−1 m of [nBu4N][2a], 3.01 × 10−6 m of [nBu4N][2b], 3.01 × 10−4 m of [nBu4N][2c]), and 3.11 × 10−6 m of N719 solution (CH3CN/BuOH) (1:1, volume ratio) with or without 5.99 × 10−10 m CdCA (Dysol) and kept at room temperature for 6 h, 16 h or 24 h, respectively. The TiO2 electrodes were rinsed with CH3CN and dried.

Electrolyte solutions: The triiodide/iodide electrolyte solutions were prepared from 1-methyl-3-propylimidazolium iodide (0.600 M) and iodine (0.050 M) in CH3CN. The Co(ii) electrolytes were employed as 0.035/0.165 M and 0.020/0.080 M CH3CN solutions of [3]+/[3]=2 and [4]+/[4]=2, respectively. Owing to the employed relative concentrations the redox potentials shift to lower values by 0.061, 0.039, and 0.036 V for 1/1’, 2/2’, 3/3’, and 4/4’, respectively. The absolute concentrations of the redox couples are 0.6, 0.2 and 1.0 M for 1/1’, 2/2’, 3/3’, and 4/4’, respectively. 4-tet-Butylpyridine (0.8 M) and lithium perchlorate (0.1 M) were used in all cells.

Counter electrode preparation: The Pt electrode was prepared by spin-coating of 10 μm H2PtCl6 (Sigma-Aldrich) in 2-propanol and then sintered at 450 °C for 30 min. The cells were sealed using 60 μm Surlyn. The electrolyte solutions were introduced through holes on the counter electrode.

Dye loading: TiO2/FTO electrodes were immersed in a 0.1 M KOH H2O/CH3CN 1:1 solution for at least 5 min. From the UV/Vis absorption spectra of the resulting dye solutions, the concentrations of the attached dyes were calculated (Table 4).

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