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A Robust Precious Metal-free Dye-sensitized Photoanode for Water Oxidation: Nanosecond Long Excited State Lifetime via a Prussian Blue Analogue

T. Gamze Ulusoy Ghobadi, Amir Ghobadi, Muhammed Buyuktemiz, Elif Akhuseyin Yildiz, Dilara Berna Yildiz, H. Gul Yagioglu*, Yavuz Dede*, Ekmel Ozbay*, Ferdi Karadas*

Abstract: The realization of a precious metal-free and robust photoanode for water oxidation has been one of the bottle-necks for dye-sensitized photoelectrochemical cells (DS-PECs). Here, we establish a simple synthetic strategy affording a heterogeneous, precious metal-free, dye-sensitized photoelectrode for water oxidation, which incorporates a Prussian blue structure for the sensitization of TiO₂ and water oxidation catalysis. Our approach involves the use of a Fe(CN)₆³⁻ bridging group not only as a cyanide precursor for the formation of a Prussian blue-type structure but also as an electron shuttle between an organic chromophore and the catalytic center. The photoanode retains its structural integrity and photoelectrochemical activity for at least 2 hours. The resulting hetero-functional Prussian blue modified TiO₂ electrode demonstrates a low-cost and easy-to-construct photoanode, which exhibits favorable electron transfers with a remarkable excited state lifetime in the order of nanoseconds and an extended light absorption capacity of up to 500 nm. The crucial role of cobalt and iron sites on the charge separation process was investigated with transient absorption studies. Our results suggest that our facile molecular dyad strategy where a covalent linkage will ensure the CoO₂ particles on the semiconductor surface in addition to the catalytic site is made of Ir or Ru based metalated complexes, which violates the motivation for building an entirely precious metal-free dye-sensitized photoanode. The only example of an entirely precious metal-free water oxidizing dye-sensitized photoanode, Kirner et al. proposed an organic chromophore sensitized SnO₂ photoanode with a photocurrent, which decayed from ~40 to 20 μA/cm² over 5 min. Later, this photoactive chromophore is coupled with a bulk cobalt oxide (CoO₂) WOC layer, in which the catalytic oxide layer also serves as a protective layer for the chromophore during the photocatalytic process. The system, however, suffered from electron-hole recombination due to the inevitable growth of the CoO₂ particles on the semiconductor surface in addition to the organic dye layer and, consequently, resulted in a dramatic decrease in the photocurrent. This deficiency can be mitigated via molecular dyad strategy where a covalent linkage will ensure close proximity between the chromophore and WOC and this, in turn, will promote fast and efficient carrier dynamics. It is, therefore, evident that a new chemistry toolbox is necessary for the proper coordination of chromophore and WOC in a three-dimensional bulk system. Beside metal oxide WOCs, cyanide-based extended networks, so-called Prussian blue (PB)

Introduction

Dye-sensitization is at the heart of several photochemical applications including solar cells, energy harvesting devices, and photoelectrochemical cells. Recently, this concept has been ingeniously adapted to oxidize water, forming the foundation of dye-sensitized photoelectrolysis systems (DS-PECs)[1–3]. A DS-PEC architecture consists of a water oxidation catalyst (WOC) coupled to a dye-sensitized metal oxide semiconductor with a large band gap. Two main strategies have been employed so far to improve the rate of the catalytic four-electron water oxidation reaction and to reduce the back electron transfer in DS-PECs: i) connecting the chromophore and the catalyst with appropriate bridging groups forming a dyad[4–12] and ii) introducing secondary electron donor and acceptor groups forming a triad[13] tetrad[14] and so on[15]. Along this path, the use of organic sensitizers has been found to be a promising design strategy for the replacement of Ru-based assemblies[22]. Aromatic macrocycles such as porphyrin and phthalocyanine derivatives have been the most commonly utilized sensitizers among organic based DS-PECs[23–26]. The short excited state lifetime and short hole diffusion length of these dyes, however, generally limit their photocurrent to a value well below 100 μA/cm², which decays rapidly with a nominal half-life of a couple-to-ten of minutes, limiting their long-term stability for practical usage. Moreover, in all of these organic systems, the catalytic site is made of Ir or Ru based metalated complexes, which violates the motivation for building an entirely precious metal-free photoanode system. In this respect, the use of bulk systems can be considered as a viable approach not only to introduce earth-abundant earth-abundant units to the field but also to improve the stability of such multi-component photoelectrodes. As the only example of an entirely precious metal-free water oxidizing dye-sensitized photoanode, Kirner et al. proposed an organic chromophore sensitized SnO₂ photoanode with a photocurrent, which decayed from ~40 to 20 μA/cm² over 5 min. Later, this photoactive chromophore is coupled with a bulk cobalt oxide (CoO₂) WOC layer, in which the catalytic oxide layer also serves as a protective layer for the chromophore during the photocatalytic process. The system, however, suffered from electron-hole recombination due to the inevitable growth of the CoO₂ particles on the semiconductor surface in addition to the organic dye layer and, consequently, resulted in a dramatic decrease in the photocurrent. This deficiency can be mitigated via molecular dyad strategy where a covalent linkage will ensure close proximity between the chromophore and WOC and this, in turn, will promote fast and efficient carrier dynamics. It is, therefore, evident that a new chemistry toolbox is necessary for the proper coordination of chromophore and WOC in a three-dimensional bulk system. Beside metal oxide WOCs, cyanide-based extended networks, so-called Prussian blue (PB)
analogues (PBAs) have also attracted vigorous attention as potential non-oxide heterogeneous WOCs due to their diversity, entirely earth-abundant components, and exceptional stabilities in a wide pH range (from 1 to 13).\textsuperscript{[29–43]} In photoconversion applications, PBAs are essentially used as WOCs for efficient extraction of photogenerated holes of a semiconductor photoanode. We have recently demonstrated that a pentacyanoferrate complex can be used as a bridging group to incorporate an organic chromophore to a PBA structure, thereby forming a robust three-dimensional triad assembly for the light-driven water oxidation process.\textsuperscript{[29]}

Herein, we move a step forward and employ this synthetic methodology to build a robust precious-metal free dye-sensitized photoanode for water oxidation. The synthesis involves the straightforward coordination of pentacyanoferrate group to a pyridyl containing organic chromophore followed by reaction with cobalt ions to build a hetero trifunctional PBA in situ on a rutile TiO\textsubscript{2} nanowire (NW) electrode. The rutile phase has been preferred to anatase since the recombination kinetics for a rutile phase TiO\textsubscript{2} is an order of magnitude slower compared to the latter.\textsuperscript{[44]} Several different pyridyl containing organic ligands including positively charged nitrogen bearing ones were screened with quantum chemical calculations prior to synthesis. Guided by computational studies, the targeted organic chromophore, in this study, is Janus green B ([JG]) which has a broad absorption response with an upper edge in the near-infrared (NIR) regime. The sensitization ability of JG coordinated PB assembly and the role of each of the components in the electron transfer mechanism and charge separation is discussed based on...
photoelectrochemical measurements, transient absorption studies, and quantum chemical calculations.

**Results and Discussion**

**Design of the Photoelectrode.** Guided by our previous findings, we kept the [Fe(CN)₃]⁺ fragment and active Co site unchanged and screened various organic ligands (R) featuring a pyridyl group (Figure 1a). A combination of up to date quantum chemical simulations showed that, in line with our previous results,[29,43,45] the critical LUMO is on the Co–O fragment (Figure 1a) for the active Co oxo/oxyl species. Moreover, the inclusion of a formal positive charge on the ligand by virtue of quaternized pyridyl salts resulted in a more electrophilic LUMO. This was a hint to exploit ligands, possessing quaternized N atoms, on Fe in order to facilitate the nucleophilic attack of water at the Co–O center. The ground and excited state calculations on the model H₂O–Co–NC–Fe–R system (Figure 1a) is further put for PBA electrode (Figure S1-7). Table S1 lists the LUMO of some of the pristine NWs, TiO₂ NWs and the cofactors. A phenazine-based dye, Janus green B, satisfies these conditions with its available pyridyl nitrogen site and quaternized nitrogen group. Moreover, it exhibits a superior optical response with several absorptions in the visible and NIR regions and possesses several amine groups that can be used to enhance the interaction between the chromophore and TiO₂ surface.

**Synthesis and Characterization.** Here, an organic chromophore coordinated PB structure was obtained with a straightforward two-step synthetic route. First, the ammino ligand of [Fe(CN)₅(NH₃)] (Fe–NH₃) complex was substituted with a pyridyl containing molecular organic chromophore, [JG] in our case. Then, the [JG] coordinated pentacyanorhodin(III) complex, [Fe–JG] was reacted with Co³⁺ ions to afford a chromophore–PB (Co–Fe–JG) assembly (Scheme S1). For the preparation of a [Co–Fe–JG] modified TiO₂ electrode, an in situ procedure was adopted. The interaction between the semiconductor surface and [Co–Fe–JG].

Hydrothermally grown rutile TiO₂ NWs on FTO coated glass was soaked in a solution containing [Fe–JG] overnight, forming the dye-sensitized TiO₂ electrode. This resulting electrode is reacted with Co³⁺ ions to obtain PB assembled dye-sensitized TiO₂ working electrode (TiO₂[Co–Fe–JG]) (see the chemical structures of photosensitizer-catalyst assembly and the in situ construction on TiO₂ NWs in Figures 1b,c). The Co sites are coordinated to single/multiple Fe linkers to form an interconnected bulky layer covering the photosensitizer organic molecules. The electrode preparation process is summarized in Scheme S2. A reference electrode was prepared by the sequential dip-coating of a regular CoFe PBA on TiO₂ NWs (TiO₂[CoFe]). Four dip-coating steps are carried out for PBA layer. The optical images of these thin film TiO₂ NWs, TiO₂[CoFe], and TiO₂[Co–Fe–JG] are displayed in Figure S8a. Top and cross-sectional scanning electron microscopy (SEM) images of the TiO₂[Co–Fe–JG] photoanode indicate that TiO₂ NWs (with a ~1.5 μm length and a ~100 nm diameter) retain their morphology after [Co–Fe–JG] coating (Figure 1d). Transmission electron microscopy-energy dispersive X-ray spectroscopy (TEM-EDS) line scan analysis was performed in the vicinity of the NW surface to investigate the content of the coating (Figure 1e). The obtained TEM image and TEM-EDS analysis results confirm the formation of an ultrathin [CoFe] assembly with a thickness of around 20 nm on the surface of NW. The infrared spectra (ATR-FTIR) of [JG], [Fe–JG], and [Co–Fe–JG] exhibit similar features in the 1000-1600 cm⁻¹ range confirming the presence of JG in the PB structure. [Fe–H₂] exhibits a sharp CN peak at 2031 cm⁻¹, which shifts to a higher wavenumber for [Fe–JG] (~2058 cm⁻¹).[29] The blue shift is evident for not only the coordination of JG to an iron complex but also the donor-acceptor interaction between the iron site and JG, which plays a critical role in efficient electron transfer. The cyanide stretch exhibits a further shift (~2090 cm⁻¹) for [Co–Fe–JG] due to Fe–CN–Co coordination of JG. Thus, the JG coordination is, in essence, evident by the conformational change of a PB structure (Figure 1f).

**Photoelectrochemical (PEC) Measurements.** The PEC water oxidation measurements were performed with a three-electrode cell using TiO₂, TiO₂[CoFe], and TiO₂[Co–Fe–JG] as working electrodes (see cell configuration in Figure 2a). The linear sweep voltammetry (LSV) was employed to study the photocurrent at 0.23 V vs. RHE under visible light illumination, demonstrating a current density of approx. 0.20% to have a better qualitative comparison, the photoresponse raised from TiO₂/[Co–Fe–JG] is even poorer for JG for TiO₂/[CoFe] due to the current density in the absence of light (dark condition) at low overpotentials. At high potentials, above ~1.6 V RHE, the current density of TiO₂[Co–Fe–JG] increases due to the electrocatalytic water oxidation process at the cobalt sites. This feature is, however, less prominent for TiO₂[Co–Fe–JG] due to the presence of the insulating JG units, which indicates that TiO₂[Co–Fe–JG] serves as a direct acceptor. The photocurrent density of TiO₂[Co–Fe–JG] is the highest reaching a photocurrent density of 551 μA/cm² at 1.23 V RHE (Figure S13a). A similar trend was observed with amorphous biofilm-to-current efficiency (ABE) plots (Figure S13b). At 0.65 V RHE, TiO₂[Co–Fe–JG] electrode shows an ABP of approximately 0.20%. To have a better qualitative comparison, the photoresponse raised from TiO₂ has been suppressed using a 420 nm cut-off filter. LSV profiles, under visible light illumination, demonstrate a current density of approx. 60 μA/cm² at 1.23 V RHE for TiO₂[Co–Fe–JG] electrode (Figure 2b). The bare TiO₂ reveals a photocurrent density of 27 μA/cm² at the same voltage (originated from the tail absorption of the NW design). The photocurrent response is even poorer for JG sensitized TiO₂ (TiO₂[Co–JG]), without PBA, as explained in detail in supplementary information, Figures S14a,b. Since the filter has not completely suppressed the TiO₂ activity, it is essential to scrutinize whether this response arises from the dye absorber layer or from the
catalyst-induced enhancement of the TiO₂ host. To answer this question, sequential dip-coating steps were carried out to maximize the PBA loading. As illustrated in Figures S15, the highest light-dark current difference was achieved after four dipping steps. Larger steps do not significantly enhance the photocurrent but rather increase the dark activity. Moreover, TiO₂[CoFe-JG] electrode exhibits lower dark current densities and a higher onset overpotential compared to those of TiO₂[CoFe]. Finally, the electrochemically active surface areas (ECSAs) for TiO₂[CoFe] and TiO₂[CoFe-JG] have been measured experimentally, as explained in supplementary information, Figures S16a-c. The ECSA for TiO₂[CoFe] was found to be higher than that for TiO₂[CoFe-JG], which can be attributed to the insulating nature of dye molecules that reduces the active sites on TiO₂ surface. These observations suggest that the relatively photocurrent enhancement of TiO₂[CoFe-JG] cannot be explained by an increase in the surface concentration of catalytically active sites. Further evidence on the effect of chromophore to the activity enhancement of the photoanode will be provided in the next sections.

To test the long-term stability of the photoanode, transient photocurrent measurement by the chronocoulometry (CA) technique is conducted on TiO₂[CoFe-JG] over a total period of two hours (made of 4 independent time-slots) at 1.23 V vs. RHE with regular time intervals while leaving the electrodes in the electrolyte solution. A gradual decrease in the photocurrent density is observed initially, followed by a consistent stable value (around 50 µA/cm²) at each step. (Figure 2c). This near constant photocurrent of TiO₂[CoFe-JG] (unlike TiO₂[CoFe]) as depicted in Figure S14a) confirms the stability of [CoFe-JG] assembly. XPS studies, performed on TiO₂[CoFe-JG] after long-term CA, also rule out the decomposition of PBA structure to metal oxides (Figures S12,b,d). A similar electrolysis experiment at 1.23 V (vs. RHE electrode at pH 7) was performed with a gas-tight cell and the amount of O₂ produced was recorded with the gas chromatography technique yielding a Faradaic efficiency of approximately 83% (as explained in Figure S17), indicating that the photocurrent response is mainly originating from the water oxidation process. Short-term CA for a duration of 300 seconds is a consecutive on-off cycles has also been plotted in Figure S18a. Moreover, TEM-EDS line scan analysis was performed on TiO₂[CoFe-JG] after CA measurements, shown in Figure S18b. The elemental analysis in this figure confirms the existence of [CoFe] PB structure on the surface of TiO₂ NWs, which confirms the morphological stability of the photoanode. It is noteworthy that the lack of long-term stability is one of the main limiting factors in molecular Ru and organic based dyads systems. Moreover, [JG] belongs to a family of phenazine-based chromophores, which are known to easily decompose under photocatalytic conditions. Therefore, the unprecedented stability of the photoelectrode implies that this methodology can be employed for a variety of organic chromophores even with low photostabilities. It can also be inferred that the PB network could play a crucial role in the stabilization of the organic chromophore, which is in good agreement with our previous study on a molecular Ru coordinated PBA. LSV measurements under light conditions (with and without filter) were also carried out under an O₂ scavenging electrolyte, which is known as a hole scavenger (hₐ), in order to scrutinize the interfacial processes in terms of...
charge transfer efficiency, $\eta_{CT}$. The photocurrent has been significantly improved in a $h_v$ environment (Figures S19a-c) in the case of 1 sun solar irradiation (unfiltered case). There is, however, a small difference between PBS and $h_v$ electrolyte responses for the LSV results, upon filtering the TiO$_2$ response. The extracted data shows a near unity $n_{CT}$ maxima (where the dye response is dominant, $\lambda >420$ nm), while this efficiency is limited to values below 0.8 for unfiltered cases (where the TiO$_2$ response is dominant) (Figure S19d). Therefore, from the perspective of interfacial charge transfer dynamics, the TiO$_2$/[CoFe-JG] electrode exhibits quite efficient charge transfer dynamics.

**Steady-State Absorption, Photoluminescence (PL), and Incident Photon-to-Current Conversion Efficiency (IPCE).**

The PL spectra of [JG] and [Fe-JG] reveal similar absorption trends with a peak at ~650 nm and a tail extending toward 800 nm. Figure 2d. The molar extinction coefficients for the dye were found to be in the order of $10^4$ M$^{-1}$ cm$^{-1}$, as shown in Figure S20. Once the cyanide groups of [Fe-JG] are coordinated to Co$^{2+}$ ions, a blue shift in the absorption peak (575 nm) is observed. A similar trend is observed for TiO$_2$ based electrodes. The only difference is the blue shift in peak position (585 nm for TiO$_2$/[Fe-JG], and ~540 nm for TiO$_2$/[CoFe-JG]), which is mainly due to higher refractive index of TiO$_2$ (compared to ethanol), see Figure S21. The PL spectra of the samples have been explored by an excitation at their main peak wavelength. While the [JG] and [Fe-JG] reveal a weak PL in the ~700–800 nm range, [CoFe-JG] represents a broad and strong response with a maximum at 615 nm. Therefore, it can be speculated that the PBA assembly tunes the energetic levels of the dye. While these absorption and PL results demonstrate a broad spectral response (covering visible and NIR regimes) and efficient absorption dynamics for [CoFe-JG], the corresponding photocurrent LSV response is rather low, see Figure 2b. Incident photon-to-current conversion efficiency (IPCE) is measured for all three photoanodes to interpret this unexpected low activity (Figure 2e). IPCE spectra exhibit a strong UV response for all electrodes. The profiles for bare TiO$_2$ and TiO$_2$/[CoFe] samples are similar, with a peak at 370 nm and an edge at 440 nm (the absorption tail of TiO$_2$). Therefore, the PBA assembly does not tailor the effective optical band gap of TiO$_2$ and it only facilitates interfacial charge transfer dynamics. However, a broad yet weak visible light response is probed for TiO$_2$/[JG] photoanode. It can be speculated that this weak response is derived from the [JG] chromophore. Nevertheless, this response shows an exponential decline as we go toward longer wavelengths and it becomes near zero at 490 nm. Therefore, a clear mismatch appears between the absorption and IPCE spectra ranges, which requires further exploration. To understand the reason behind the aforementioned discrepancy, the band alignment is extracted for [CoFe-JG] assembly by cyclic voltammetry (CV) measurements (Figure S22a,b and Table S9). The details of the band alignment extraction are given in the supplementary information. The optical band gap of TiO$_2$ NWs is estimated from Tauc plot, as shown in Figure S23. According to the extracted energy diagram, proper alignment is achieved between the TiO$_2$ valence band, HOMO of the dye, and water oxidation level. This matching, however, is not realized for the conduction band of TiO$_2$ and LUMO level of the photosensitizer, see Figure 2f, which limits the photoconversion efficiencies to wavelengths much smaller than the dye absorption edge. Another reason for the relatively low IPCE could be attributed to ultra-short excited state lifetime of the organic chromophore. This hypothesis is further interrogated by probing ultrafast carrier dynamics using femtosecond transient absorption measurements.

**Kinetic Analysis by Femtosecond Transient Absorption (TA) Spectroscopy.** TA measurements were performed for [JG], [Fe-JG], and [CoFe-JG] in EtOH to gain an insight into the ultrafast carrier dynamics of the photoanodes, which are explained in detail in the supplementary information section (Figures S24-S25, Table S10). In summary, the addition of Co WOC has significantly prolonged the ESA lifetime of [Fe-JG]. Therefore, it can be envisioned that electron injection probability from dye to the TiO$_2$ could be substantiated in the [CoFe-JG].

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**Figure 3. Transient absorption spectra of** (a) TiO$_2$/[JG], (b) TiO$_2$/[Fe-JG], and (c) TiO$_2$/[CoFe-JG] compounds at 400 nm (pump) excitation with different pump probe time delays. Decay dynamics for (d) GSB and (e) ESA signals. The pump pulse intensity for all these measurements is 9.95 GW/cm$^2$. 

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To gain insight on carrier dynamics in the ultimate photoanode, dye loaded TiO₂ NW samples were studied by TA analysis as well. The TA spectra have been collected for all three assemblies upon pumping at 400 nm. The choice of excitation pump wavelength has been justified in the supplementary information, (Figures S26-S27). All spectra were fitted by multi-exponential functions and the data is summarized in Table S11. For [JG] and [Fe-JG] on TiO₂ NWs, two main features, ground state bleaching (GBS) and excited state absorption (ESA), are identified clearly, as in the case of ethanolic solutions of [JG] and [Fe-JG] discussed above, see Figures 3a,b. In addition, a weak stimulated emission (STE) signal at 800 nm was observed with long delay times. Therefore, it can be deduced that excited states undergo ultrafast deactivation into the S₁ edge. CV results reveal that energies of S₁ edge and TiO₂ CB are improperly aligned and, thus, the injection abilities in TiO₂/[JG] and TiO₂/[Fe-JG] are hampered and ultrafast excited state lifetimes are observed. However, for TiO₂/[CoFe-JG], which was probed at several probe wavelengths, neither GSB nor STE signals were observed (see Figure 3c). TiO₂/[CoFe-JG] exhibits a broadband ESA signal. The decay dynamics of GSB and ESA signals are displayed in Figures 3d,e. The ESA signals for TiO₂/[JG] and TiO₂/[Fe-JG] decay to zero within the first 10 ps, while it shows a much longer lifetime for TiO₂/[CoFe-JG]. The time evolution of the ESA signal for TiO₂/[CoFe-JG] is probed at three different probe wavelengths; 500 nm, 600 nm, and 700 nm. Two ultrafast decay times of <100 fs and ~2–3 ps are deduced from the fitting parameters. Besides these two fast components, a long lifetime decay (in the order of 200 ps with an amplitude below 10%) are also present for TiO₂/[CoFe-JG], see Table S11. Moreover, the extracted decay rates for three probe wavelengths (of 500 nm, 600 nm, and 700 nm) are quite similar to each other, Table S11. Lack of the GSB signal, together with the above results, suggests that an efficient injection into TiO₂ NWs occurs in TiO₂/[CoFe-JG]. Equivalently, the assembly of Co catalyst has suppressed the deactivation pathway of the excited states.

Further insight into the critical electron transfer events is provided by quantum chemical calculations on the ground and excited states (Figure 4a, Tables S12-16, and Figures S28-36). Although a quantitative treatment of the photoanode is unrealistic, model systems provide valuable qualitative insight into the observed differences of [Fe-JG] and [CoFe-JG] systems as shown in Figure 4a-c. The modulation of the orbital levels upon the inclusion of Co to the system suggests that: (i) Ligand centered (LC) π → π* state is destabilized from 1.27 eV to 3.80 eV. Note also that the character of the excitation changes from phenezine → diazenylanilin to diazenylaniline → phenazine, (ii) the lowest metal to ligand charge transfer (MLCT) state changes character from Fe → JG to Co → JG, (iii) the energy of the lowest MLCT state shifts from 2.61 eV to 1.24 eV, and (iv) the Fe-based MLCT state of [Fe-JG] is also destabilized from 2.61 eV to 4.00 eV. Although we should not dwell on the calculated energies in the molecular orbital analysis the qualitative insight brought about is useful and suggests that, upon a mainly LC type of excitation, an electron transfer to the semi-conductor follows. Efficient charge separation is provided by the electron donating ability of Co sites given its properly aligned SOMO state with respect to the doubly occupied orbital on JG. The holes created on JG are transferred rapidly to the SOMO of cobalt, which leads to the activation of cobalt site for catalytic water oxidation. Thus, cobalt site emerges as both an electron donor group taking part in electron flow and water oxidation catalytic site. All of these theoretical results are in line with our transient absorption studies and characterizations.

Overall, the addition of cobalt ions changes the optical and electronic properties of the electrode. The lowest transition energy of [Fe-JG] belongs to π → π* LC state, which cannot inject its electrons to TiO₂ CB due to improper energy alignment.
Furthermore, the excited electrons of [JG] are self-quenched in an ultrafast fashion (within tens of ps) due to the undesirable intermolecular aggregations similar to most of the metal-free organic dyes. Therefore, an ultrafast deactivation of excited electrons into the LC state significantly limits the photoreponse of the phenazine-based dye, see Figure 4b. To increase the excited state lifetime of [JG], the aforementioned deactivation pathway should be eliminated, which is achieved by its conjugation to a PB structure. An in-depth computational and ultrafast transient analysis reveals an unprecedented modification in the electronic and optical properties of [JG] upon its covalent bonding to PB structure. In TiO$_2$[CoFe-JG], the energy of the LC state increases (relative to charge transfer states) due to strongly electron donating cobalt sites leading to a prolonged excited state lifetime (in the order of ns). The electron transfer depicted in Figure 4c also enhances the luminescence yield. The proposed PBA can, thus, be considered as a tri-functional assembly: i) a strong electron donating group, ii) a WOC, and iii) an assembly that modifies the energetic levels of the chromophore (its optical behavior).

**Conclusion**

In this work, we demonstrate a strategy and construct, for the first time, an entirely earth-abundant long-term durable dye-sensitized photoanode for water oxidation by utilizing a hetero-multifunctional cyanide-based chromophore-catalyst assembly. While the heterogeneous oxide-based synthetic route yields robust photoelectrodes, the molecular-based approach provides the complete control of the final structure of the photoanode, and hence relatively higher performances. On the other hand, cyanide chemistry offers the engagement of strengths of both of the aforementioned approaches. A computational study guided screening was performed to include the key structural elements into the selected chromophore, i.e. quaternized nitrogen atom, prior to synthesis. The synthesis involves the coordination of molecular organic chromophore to a pentacyanorhod(VI) group, which is completed by reacting with Co$^{3+}$ ions in situ on TiO$_2$ to obtain a robust heterogeneous photoelectrode. Unlike its superior optical response with an absorption edge in the NIR range, the pristine [JG] chromophore shows poor carrier dynamics with a ps excited state lifetime. The conducted TA analysis and quantum chemical calculations demonstrated that excited electrons undergo an ultrafast quenching into the lowest LUMO state with an energetically inadequate position for electron injection. However, the covalent connection of PBA moiety drastically changes the story (Figure 4d). Besides their primary function as catalytic water oxidation sites, the cobalt ions in PB structure serve as donor groups to feed the HOMO level of the dye. Overall, the holes are first transferred to Fe center invoking the Fe$^{2+}$ to Fe$^{3+}$ redox process and then to Co sites to activate them for the catalytic water oxidation process. The efficient charge transfer was achieved also as a result of desirable tuning of the LUMO level of the dye once it is connected to PB structure. Both iron and cobalt sites, hence the PB structure as a whole, serve as the electron donating group. The short cyanide bridging ligand (with a metal-to-metal distance of ca. 5 Å) plays a critical role in the electron donating ability of the catalytic cobalt sites since it provides fast electronic communication between metal ions and the organic chromophore. Thanks to this donation ability, a remarkably long excited state lifetime in the order of nanoseconds is recorded for the photoanode. Moreover, the DS-PEC cell design shows unprecedented stability for a phenazine-type chromophore, which is known to suffer from easy decomposition under photocatalytic conditions. The study marks the first successful attempt to utilizing a phenazine-type chromophore for a dye-sensitized photoanode. The most astonishing conclusion of this study is, thus, the robustness and scalability of the proposed strategy. This work provides an easy-to-employ recipe for the utilization of a variety of pyridyl containing organic chromophores for various photo-conversion devices including DSSCs and DS-PECs. Therefore, the method proposed herein paves the way for a new family of dye-sensitized photoactive devices that can utilize a variety of organic chromophores even with ultrafast charge separation lifetimes and low photostabilities. Realization of water oxidation photoanodes incorporating a variety of organic dyes with proper electronic band positions (LUMO of dye and conduction band of TiO$_2$), which utilizes the design principles demonstrated in this work, are under way in our laboratories.

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**Keywords:** water oxidation • Prussian blue • dye-sensitized • water splitting • photoelectrochemistry

**References**

Precious Metal-free Dye-sensitized Photoanode for Water Oxidation: Nanosecond Long Excited State Lifetime via a Prussian Blue Analogue

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