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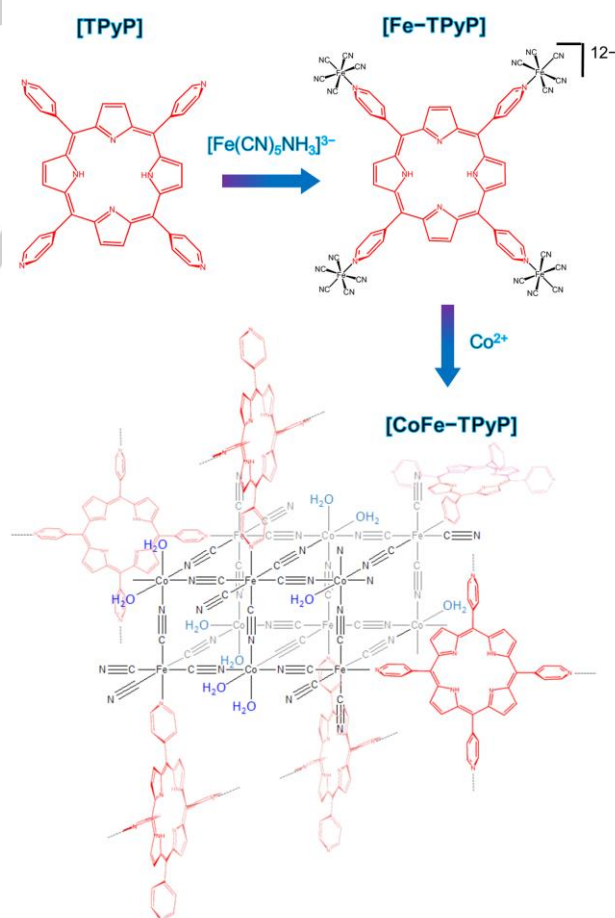
# A Noble-Metal-Free Heterogeneous Photosensitizer–Relay–Catalyst Triad Catalyzes Water Oxidation under Visible Light

T. Gamze Ulusoy Ghobadi, Elif Akhuseyin Yildiz, Muhammed Buyuktemiz, Sina Sadigh Akbari, Derya Topkaya, Ümit İsci, Yavuz Dede\*, H. Gul Yaglioglu\*, Ferdi Karadas\*

**Abstract:** An entirely earth abundant chromophore-relay-water oxidation catalyst triad system, which is robust and efficient at neutral pH, is presented. The synthesis involves the coordination of a porphyrin derivative to a bridging  $\text{Fe}(\text{CN})_5$  group, which is then reacted with Co ions to prepare a covalently linked chromophore-Prussian blue analogue assembly. Light driven water oxidation studies in the presence of an electron scavenger indicate that the triad is active and it maintains a steady activity for at least 3 hours. Transient absorption experiments and computational studies reveal that the  $\text{Fe}(\text{CN})_5$  group is more than a linker as it takes part in electron-transfer and co-operates with porphyrin in the charge separation process.

Artificial photosynthesis, which harnesses sunlight to split water, is a chemical transformation of utmost interest.<sup>[1]</sup> Several innovative photoelectrochemical cells for water splitting have been proposed since the pioneering work by Fujishima and Honda.<sup>[2,3]</sup> Of these, dye-sensitized photoelectrochemical cells (DS-PECs) utilize covalently coordinated chromophore-water oxidation catalyst (WOC) dyad assemblies<sup>[4–6]</sup> in an effort to mimic natural photosynthesis. This approach has further been expanded by integrating suitable donor and acceptor units to prepare molecular triads, tetrads, and pentads for efficient charge separation.<sup>[7–9]</sup> Molecular ruthenium complexes (as photosensitizers and/or WOCs) remain the most widely used despite their high cost and easy decomposition under photocatalytic conditions.<sup>[10–19]</sup> Although the use of robust heterogeneous assemblies such as oxides could be a promising solution to improve stability, the lack of complete control on the coordination of metal ions in oxide chemistry does not allow the preparation of oxide-based dyads.<sup>[20]</sup> On the other hand, many

cyanide-based assemblies have been prepared previously via a building block approach, similar to the preparation of dyads.<sup>[21]</sup> Different perspectives of cobalt based Prussian blue analogues (PBAs) as WOCs have recently been explored by us and other researchers.<sup>[22–31]</sup> PBAs consist of earth-abundant elements, perform at relatively low overpotentials ( $<500$  mV for a current density of  $1 \text{ mA cm}^{-2}$ ), exhibit exceptional stabilities in a wide pH range (from 1 to 13), and can operate even with molecular chromophores for light-driven catalysis.<sup>[32]</sup> Recently, we employed a pentacyanoferrate complex rather than a hexacyanometal precursor to prepare an amorphous PBA with enhanced electrocatalytic activity.<sup>[25]</sup> The aforementioned study and many others reveal that the ammino group of  $[\text{Fe}(\text{CN})_5(\text{NH}_3)]^{3-}$  complex can be substituted with pyridyl containing organic moieties via a straightforward synthesis.<sup>[33,34]</sup> Moreover, our preliminary results suggesting that  $[\text{Fe}(\text{CN})_5]$  could facilitate the electron transfer between the chromophore and the catalyst encouraged us to use it for the development of a molecular sensitizer-heterogeneous catalyst system. For this purpose, a symmetrically substituted porphyrin derivative, 5,10,15,20-tetra(4-pyridyl)-21*H*,23*H*-porphyrin [TPyP], was selected as the chromophore since it can be produced in bulk scale, it has a high molar absorption coefficient in the visible region, and it contains available pyridyl groups for coordination to pentacyanoiron(II) group.



**Scheme 1.** General synthetic scheme and molecular structures of [TPyP], [Fe-TPyP], and [CoFe-TPyP].

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The aminopentacyanoferrate complex,  $[\text{Fe}(\text{CN})_5\text{NH}_3]^{3-}$  (Figure S1), was first reacted with [TPyP] to prepare  $[\text{Fe-TPyP}]$ , which was then reacted with  $\text{Co}^{2+}$  ions to prepare the triad,  $[\text{CoFe-TPyP}]$  (Scheme 1). An assembly, in which a molecular chromophore is coordinated to a heterogeneous cyanide-based catalyst, was prepared with this synthetic route. The synthetic pathway adopts a molecular bottom-up approach similar to the ones previously reported for chromophore-catalyst assemblies,<sup>[7-19]</sup> while it differs significantly from those by the formation of a heterogeneous assembly in the final step.

The H-NMR spectrum of  $[\text{Fe-TPyP}]$  exhibits the characteristic chemical shifts of [TPyP], which indicates that the porphyrin ring is still intact and each pyridyl group is coordinated to iron sites (Figure S2). Infrared studies also confirm the complexation and the formation of a Prussian blue network (Figure S3). XPS spectra of N1s and Fe2p bands (Figures S4-S6 and Table S1) are also in good agreement with the expected structures.<sup>[35]</sup> The corresponding SEM-EDX elemental mapping reveals the homogenous distribution of the elemental species (Figures S7 and S8) in  $[\text{Fe-TPyP}]$  and  $[\text{CoFe-TPyP}]$ . The energy dispersive X-ray spectroscopy (EDS) of  $[\text{CoFe-TPyP}]$  (Figure S9) also reveals a stoichiometric ratio of 3:2 (Co:Fe), which is in line with the expected formula based on charge balance.

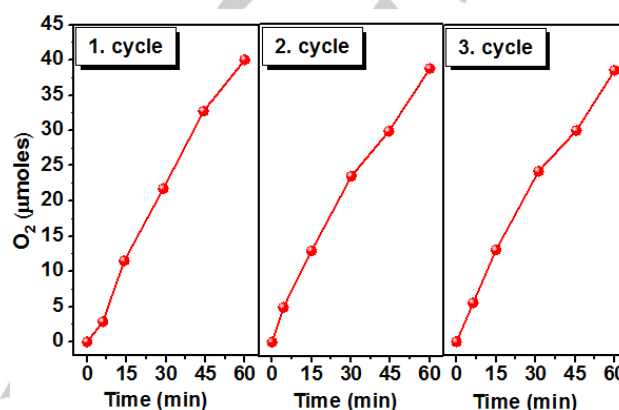
For comparison,  $[\text{ZnFe-TPyP}]$  was also prepared and characterized with infrared, XPS, and SEM studies (Figures S10 and S11). The cyclic voltammogram (CV) of  $[\text{CoFe-TPyP}]$  modified FTO electrode exhibits an irreversible peak at high anodic potentials corresponding to catalytic water oxidation process. This feature is absent in the CV of  $[\text{ZnFe-TPyP}]$  modified FTO electrode, which indicates that water is oxidized only at cobalt sites (Figure S12).

Characterization studies and unique coordination mode of cyanide ligand suggest the presence of random sized PB structures with limited dimensionalities due to surrounding molecular porphyrin rings in  $[\text{CoFe-TPyP}]$  (Note that the compound has an amorphous nature, see Figure S13). The coordination of each Fe site to a porphyrin macrocycle reduces the dimensionality of PB structures significantly, which in return yields cobalt sites coordinated to at least one  $\text{H}_2\text{O}$  molecule that is essential for water oxidation.

Photocatalytic  $\text{O}_2$  evolution profile of  $[\text{CoFe-TPyP}]$  in the presence of a sacrificial electron acceptor ( $\text{K}_2\text{S}_2\text{O}_8$ ) reveals a steady increase during a 1 h experiment (Figure 1). The curve yields a turnover frequency of  $3.2 \times 10^{-4} \text{ sec}^{-1}$  ( $1.2 \text{ h}^{-1}$ ), which is similar to the one obtained with PBAs in the presence of a  $\text{Ru}(\text{bpy})_3^{2+}/\text{S}_2\text{O}_8^{2-}$  system and much higher than the one obtained when [TPyP] was mixed with a cobalthexacyanoferrate (Figure S14).<sup>[32]</sup> Similar profile was obtained for three cycles of the same batch, which indicates that  $[\text{CoFe-TPyP}]$  is stable during photocatalytic water oxidation process. This is also confirmed with comprehensive characterization studies performed on the post-catalytic powder sample (Figures S15-S17). Overall, photocatalytic tests confirm that porphyrin and PB structures collaborate for light-assisted water oxidation catalysis, which could be due to an efficient pathway for electron transfer between the chromophore and the catalytic cobalt sites. This mechanism has been investigated by computational and femtosecond transient absorption (TA) studies.

Previously, we have explored the electronic structure details of similar Co sites used as WOCs and have shown that it is critical to oxidize the Co site and increase its electrophilicity in order to enhance the nucleophilic attack of water.<sup>[26,36]</sup> The reactivity parameters in the current study suggest a similar Co centered O–O bond formation under photocatalytic conditions. Moreover,  $[\text{Fe-TPyP}]$  moiety in the  $[\text{CoFe-TPyP}]$  system is presumably the

photochemically active species and the role of the Co centers is similar to what we have previously reported.<sup>[26,36]</sup> We therefore studied the electronic structure and excitation characteristics of  $[\text{CoFe-TPyP}]$  and  $[\text{Fe-TPyP}]$  with Density Functional Theory (DFT). For simplicity we discuss the excitation motif of  $[\text{Fe-TPyP}]$  below and emphasize that  $[\text{CoFe-TPyP}]$  computations yield exactly the same results (Figures S18 and S19). Due to the complexity in reliable computation of the electronic structures of multiple high spin Co centers, electron transfer dynamics of  $[\text{CoFe-TPyP}]$  were studied with TA spectra.



**Figure 1.** Photocatalytic oxygen evolution by  $[\text{CoFe-TPyP}]$  (10 mg) and  $\text{K}_2\text{S}_2\text{O}_8$  (20 mM) in pH 7, 50mM phosphate buffer solution. Same batch was used in each cycle.

The ground state of  $[\text{Fe-TPyP}]$  is found to be a closed shell singlet (Table S2) with four electronically identical Fe centers having low spin configurations (Table S3) as expected for Fe in strong ligand environment. From the frontier orbitals HOMO is comprised of Fe- $d$  and porphyrin- $\pi$  orbitals. Two other high lying occupied orbitals involved in the excitation are of porphyrin  $\pi$  and Fe- $d +$  porphyrin- $\pi$  in character (Figures 2 and S19). These three molecular orbitals (MOs) delocalized on the porphyrin ring and Fe center are the domain for the excitation.

The two lowest lying unoccupied MOs, both of porphyrin- $\pi^*$  character, are the degenerate pair of LUMO and LUMO+1. The calculated excitation motif suggests that an electron hosted in a hybrid Fe- $d +$  porphyrin- $\pi$  orbital is transferred to porphyrin based  $\pi^*$  orbital upon irradiation. Thus,  $\text{Fe}(\text{CN})_5$  fragment is partly oxidized during the excitation and an internal charge transfer state with one unpaired electron on Fe and one on the porphyrin is accessed. Such an excited state of charge transfer nature can easily hop to the triplet surface (within only 0.1 eV, Tables S4 and S5) and live long enough to further oxidize the Co-centers. Excitations and proton coupled electron transfer events studied for the  $[\text{CoFe-TPyP}]$  shed light on the nature of the intermediates (Figures S20 and S21). Comparison with the  $[\text{ZnFe-TPyP}]$  system (Figure S22) reveal that the Zn center does not possess the key electronic structure (Table S6) to carry the O–O bond formation.<sup>1</sup> The effect of cobalt sites on the electron transfer is supported by the transient absorption studies (*vide infra*).

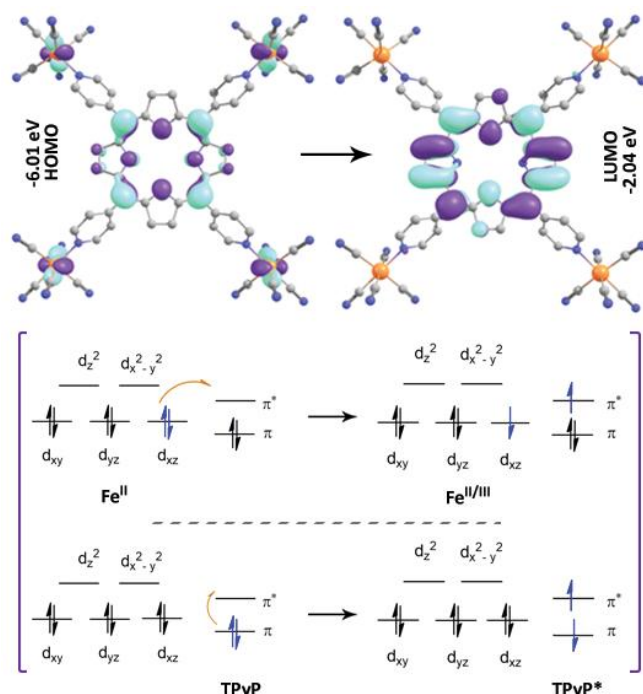
Quantum chemical calculations thus suggest that i) Fe-centers are involved in donating electrons and porphyrin is an electron acceptor. ii) This internal charge transfer repositions the electrons in two distinct fragments of the system and decreases the likelihood of charge recombination, thereby allowing the excited state to live long enough and to undergo other important

<sup>1</sup> A detailed computational study about the electronic structure of the intermediates and their transformations will be reported as a subsequent work.



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electronic changes. iii) The electron transfer yields an MLCT state. iv) The internally oxidized Fe-centers act as holes to further oxidize Co-sites – an essential feature for O–O bond formation at the Co-site as shown previously.<sup>[26]</sup> These results are also verified by steady state absorption (SSA), fluorescence (FL), and transient absorption (TA) measurements.

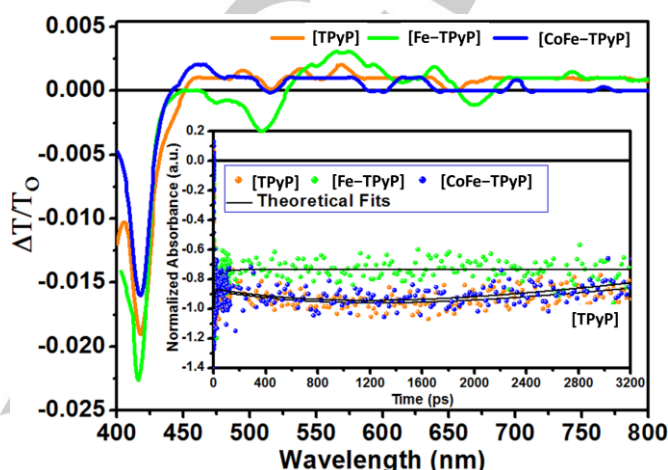


**Figure 2.** TD-DFT excitation behavior for [Fe-TPyP] at UB3LYP/def2-TZV level of theory. A hybrid Fe-d + porphyrin- $\pi \rightarrow$  porphyrin- $\pi^*$  state is generated.

SSA graphs of the investigated compounds show typical characteristic of porphyrins as shown in Figure S23.<sup>[37]</sup> FL measurements are given in Figures S24 and S25.

TA spectra for [TPyP], [Fe-TPyP], and [CoFe-TPyP] at zero time delay and decay traces of the bleach signals at 424 nm probe wavelength are given in Figure 3 along with the proposed electron transfer mechanism (Scheme 2). [TPyP] shows typical features including a characteristic ground state bleaching and a stimulated emission around 420 nm, Q bands bleaching around 520 and 650 nm, and  $T_1-T_n$  absorption around 440 nm developing by intersystem crossing (ISC) process after 48 ps time delay (Figures S26 and S27). Although TA measurement of [Fe-TPyP] is similar to that of [TPyP], it shows enhanced bleaching of Q bands as well as  $T_1-T_n$  absorption band (Figures S28 and S29).<sup>[38]</sup> These data show the electron transfer from Fe-center to porphyrin as supported by the TD-DFT calculations (Figures 2 and S30). On the other hand, decay trace of 430 nm bleach signal for [Fe-TPyP] exhibits a longer lifetime (from pumped state to ground state) than that of [TPyP], which is required for efficient photocatalytic process (Table S7 and Figure S31). In the case of

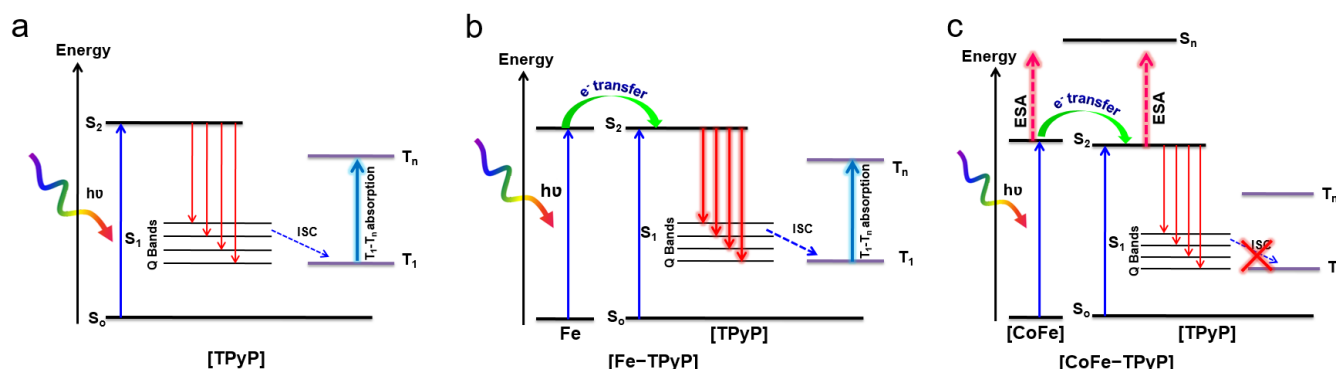
[CoFe-TPyP], excited state absorption with long lifetime around 430 nm appears at zero time delay suggesting that this is not a  $T_1-T_n$  absorption (Figures S32, S33 and Scheme 2).<sup>[39]</sup> This profile also implies that the deactivation pathway of [Fe-TPyP] excited state is altered with the presence of Co-sites due to further electron transfer, which yields a longer living [CoFe-TPyP] state. TA measurements, thus, conclude that the Co centers are internally oxidized with the assistance of Fe(CN)<sub>5</sub> group, hence the photocatalytic water oxidation utilizes the [Fe-TPyP] moiety as the photosensitizer and Co sites as the catalytic centers.



**Figure 3.** Transient absorption spectra at zero time delay and time evolution of the bleach signals at 424 nm wavelength for [TPyP], [Fe-TPyP], and [CoFe-TPyP] compounds.

In conclusion, an entirely earth abundant cyanide-based chromophore-relay-catalyst triad system for light driven water oxidation was reported for the first time by engaging cyanide chemistry with the dyad concept. The reported assembly is genuine due, not only to the simplicity of its synthesis but also to the bifunctionality of each of its components. Porphyrin fragment is both a chromophore and a capping ligand for reducing the dimensionality of PB structures, thus, increasing the number of active catalytic sites. Transient absorption measurements and computational studies show that [Fe(CN)<sub>5</sub>] moiety serves both as a robust linker and a relay group that facilitates the electron transfer from the catalyst to the chromophore. Co-sites are essential for catalytic water oxidation. They also play a critical role in the formation of a stable heterogeneous assembly. Overall, this proof-of-concept study indicates that cyanide-based systems could be the key element for the development of earth abundant, robust, and efficient dye-sensitized photoanodes. The modular and versatile Fe(CN)<sub>5</sub> chemistry is further explored in our labs by introducing other chromophores to generalize the concept of photocatalytic water oxidation with cyanide-based assemblies.

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**Scheme 2.** Schematic illustration of the energy diagram for (a) [TPyP], (b) [Fe-TPyP], and (c) [CoFe-TPyP] compounds.

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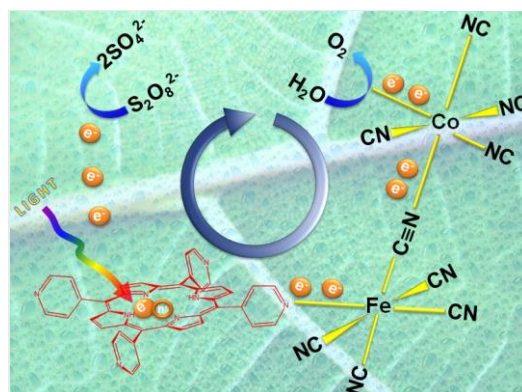
**Keywords:** water oxidation • Prussian blue • porphyrin • water splitting • triad • dye-sensitized

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