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Noble-metal-free BODIPY-cobaloxime photocatalysts for visible-light-driven hydrogen production†

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In this study a series of supramolecular BODIPY-cobaloxime systems Co-Bn (n = 1-4): [{Co(dmgH)2Cl}4,4-difluoro-8-(4-pyridyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-indacene] (Co-B1), [{Co(dmgH)2Cl}4,4-difluoro-8-(4-pyridyl)-1,3,5,7-tetramethyl-2,6-diodo-4-bora-3a,4a-diaza-indacene] (Co-B2), [{Co(dmgH)2Cl}4,4-difluoro-8-(3-pyridyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-indacene] (Co-B3), and [{Co(dmgH)2Cl}4,4-difluoro-8-(3-pyridyl)-1,3,5,7-tetramethyl-2,6-diodo-4-bora-3a,4a-diaza-indacene] (Co-B4) (BODIPY = boron dipyrromethene, dmgH = dimethylglyoxime) have been synthesized by replacing one axial chlorine of cobaloxime moieties with the pyridine residues of BODIPYs, and structural characterization. Absorption spectra show that the optical properties of the BODIPY-cobaloximes are essentially the sum of their constituent components, indicating weak interactions between the cobaloxime units and BODIPY chromophores in the ground state, if any, electronic communications may take place through the intramolecular electron transfer across their orthogonal structures. The possibility of intramolecular electron transfer is further supported by the results of the density functional theory (DFT) calculations at UB3LYP/LANL2DZ levels on Co-B2· and Co-B4·, which show that the highest occupied molecular orbitals (HOMOs) possess predominantly BODIPY character, while the lowest unoccupied molecular orbitals (LUMOs) are located on the cobalt centers. The HOMO→LUMO transition is an electron-transfer process (BODIPY· radical anions→cobaloxime fragment). In view of the possible occurrence of electron transfer, these noble-metal-free BODIPY-cobaloximes are studied as single-component homogeneous photocatalysts for H2 generation in aqueous media. Under optimized conditions, the 2,6-diodo BODIPY-sensitized cobaloxime Co-B4 that contains a meta-pyridyl at the 8-position of BODIPY presents excellent H2 photoproduction catalytic activity with 85 turnover number (TON), which is comparable to that of its analogue Co-B2 that has a para-pyridyl substitution attached onto 2,6-diodo BODIPY (TON = 82), but both of noniodinated BODIPY-sensitizer cobaloximes (Co-B1, Co-B3) result in a complete lack of activity under the same experimental conditions. These results show that the presence of heavy atoms in the core of BODIPY is essential for the catalytic process and regenerative quenching pathways (namely, the intramolecular electron transfers from BODIPY· species to the cobalt centers) for these photocatalytically active systems of Co-Bn (n = 2 and 4) are thermodynamically feasible for the hydrogen-evolving reaction.

1. Introduction

Photocatalytic hydrogen evolution from water splitting is regarded as a holy grail of science, being one route to a no-fossil fuel and a potential source of clean and renewable energy to meet the rising global energy.1 Generally, photoreduction of water into H2 under visible-light irradiation includes heterogeneous and homogeneous catalytic systems. The development of heterogeneous catalytic systems using semiconductor-based photocatalysts for hydrogen production has been investigated during last three decades.2 Homogeneous photocatalysts, however, have experienced considerable growth in sense that their chemical and photochemical properties can be understood and tuned on the molecular level. Currently, homogeneous catalytic systems for the proton reduction to molecular hydrogen comprise multiple-component and single-component systems. A catalytic multiple-component system usually contains a photosensitizer, an electron mediator and a proton reduction catalyst in the presence of a sacrificial electron donor. Nevertheless, these systems still need to be improved because many interfacial interactions could affect the photoinduced electron transfer reactions. In contrast with these multi-component systems, development of single-component photocatalysts in which the photosensitizer is chemically coupled to the hydrogen-evolving catalyst through a bridging ligand to generate integrated molecular or supramolecular systems, would benefit since the more desirable electron transfer processes may be achieved by precise tuning of the physical properties and orientation of the molecular components.3,4 In recent years, a number of single-component
supramolecular photocatalysts have been designed and reported to be active for photochemical H\textsubscript{2} production. These systems include Ru-Pt complexes,\textsuperscript{5} Ru-Pd complexes,\textsuperscript{6} Ru-Rh complexes\textsuperscript{7} and Ir-Co complexes.\textsuperscript{8} However, molecular components of these reported systems usually require expensive and unsustainable noble metals as the catalysts or photosensitizers. Completely noble-metal-free molecular devices for water splitting with relatively effective catalysts overall turnover numbers (TONs) for hydrogen formation were still limited.\textsuperscript{9}

On the other hand, compared with noble-metal ruthenium, iridium and platinum complexes, a wide variety of organic dyes such as xanthene dyes (Eosin Y and Rose Bengal) and rhodamine dyes as photosensitizers have displayed high efficiencies of photocatalytic hydrogen production from water in the homogeneous multiple-component systems.\textsuperscript{10} Besides, another conjugated organic molecule boron-dipyromethene (BODIPY) is targeted as more tunable photosensitizer due to their outstanding optical properties such as high absorption coefficients, excellent chemical and photochemical stability, high solubility and weak nonradiative decay of the excited state.\textsuperscript{11} Additionally, ease of functionalization of BODIPY makes it possible to fine-tune the energy levels of the S\textsubscript{1} and T\textsubscript{1} excited state by attaching heavy atoms directly onto the chromophore. As pointed out by earlier studies, the presence of heavy atoms facilitates intersystem crossing (ISC) and thus production of a long-lived triplet state.

According to the changes observed in the aromatic region of 1\textsuperscript{H} NMR spectra with all NMR signals undergoing an upfield shift. These BODIPY-sensitized cobaloximes in the solid state can be stored in the dark for a long time without decomposition.

2. Result and discussion

2.1. Synthesis

para-pyridyl substituted BODIPY derivatives of B1-B2 were prepared according to published procedures,\textsuperscript{15} and the method was modified and used to synthesize meta-pyridyl substituted BODIPYs of B3-B4 in this study. Starting from B1-B4, the corresponding photocatalysts Co-Bn (n = 1-4) were synthesized in a straightforward manner by the reaction of a 1:1 ratio of cobaloxime precursor Co(dmgH)(dmgH)Cl\textsubscript{2} and the corresponding pyridyl-functionalized BODIPYs (B1-B4) in the presence of TEA in a mixture of methanol and dichloromethane at room temperature, as shown in Scheme 1. A more detailed description of the synthesis and the analytical characterization is given in the Experimental Section. The desired products were precipitated and isolated by filtration. Axial coordination of BODIPY units (B1-B4) to the Co(dmgH)(dmgH)Cl\textsubscript{2} was characterized by the changes observed in the aromatic region of the 1\textsuperscript{H} NMR spectra with all NMR signals undergoing an upfield shift. These BODIPY-sensitized cobaloximes in the solid state can be stored in the dark for a long time without decomposition.

2.2. Solid-state structure analysis

Well-formed X-ray-quality single crystals of pyridine-substituted BODIPY derivatives (B1-B3) except B4 were obtained by slow evaporation of their CH\textsubscript{2}Cl\textsubscript{2} solution. As shown in Figure 1, the single crystal X-ray diffractions reveal there are two isomers of both B1 and B3 in their respective asymmetric unit cells, while the asymmetric unit of B2 only
contains one independent molecule. The crystallographic details are shown in Table S1(ESI†). As expected, in each BODIPY unit, the central six-membered ring lies coplanar with the two adjacent five-membered rings. The rms deviation from planarity is 0.012 Å for B1 (the average of 0.010 and 0.014 Å in two molecules), 0.0 Å for B2, and 0.012 Å for B3 (the average of 0.010 and 0.014 Å in two molecules), respectively, indicating the nearly planar degree of C6BN2 frame for B1-B3. The dihedral angle between the meso-pyridine and BODIPY moiety is 84.3º in B1 (the average of 87.45 and 81.15º in two molecules) and 82.77º in 3 (the average of 83.40 and 82.14º in two molecules), indicating an almost perpendicular configuration between the meso-pyridine and BODIPY moiety for B1 and B3. In contrast, the meso-pyridine ring is completely orthogonal to the indacene plane with dihedral angle of 90º in B2.

Figure 1. ORTEP diagram of pyridine-substituted BODIPY derivatives B1 (a), B2 (b) and B3 (c). Symmetry code: (i) –x, y, –z+1/2. Thermal ellipsoids drawn at the 50% probability level. H atoms omitted for clarity.

Figure 2. (a) Solid-state molecular structures of Co-B2 (left) found in the unit cell of Co-B2·2CH3CN and Co-B3 (right). Symmetry code: (i) –x, y, –z+1/2. Thermal ellipsoids displaying 50% probability level. Solvent molecules and hydrogen atoms (except bridging hydrogen atoms of the cobaloxime macrocycle) are omitted for clarity. (b) Crystal packing of Co-B3 when viewed in the [001] direction.

Structural characterization and the stereochemistry of BODIPY-cobaloxime complexes (Co-B1, Co-B2, and Co-B3) except Co-B4 were further confirmed through X-ray crystallography (Figure 2). The crystallographic data are given in Table S2 (ESI†). In Co-B1 and Co-B2, the refined structure reveals a six-coordinate Co(III) ion that is ligated by two coplanar dimethylglyoximate ligands and trans chloride and pyridine ligands. The observed axial Co-Npyridine distances of 1.952 Å in Co-B1, and 1.955 Å in Co-B2 agree closely with those of in other Co(III) cobaloximate complexes, such as Co(dmguH)pyCl with a Co-Npyridine distance of 1.959 Å.16

A crystallographic study on the molecular device Co-B3 suggested that Co-B3 crystallized in the C2/m space group, which contemplates a mirror plane bisecting the BODIPY and cobaloxime (Figure 2a). Co-B3 shows the expected distorted octahedral coordination geometry with a meta-pyridyl and a chloride ligand in the axial location and a pair of dmgH ligands joined in the equatorial plane through intramolecular hydrogen bonds between the oxime oxygen atoms [O1···O1i, 2.486(3) Å; O2···O2i, 2.472(3) Å]. The average Co-Nimine and Co-Npyridine bond distances in Co-B3 are 1.897 and 1.958 Å, respectively, and do not significantly differ from those found in Co-B1 or Co-B2. The most interesting features of the crystal structure are revealed by the analysis of the packing diagram. Firstly, two adjacent molecules pack via weak B···π and π···π interactions to generate a molecular dimer. Secondly, the neighboring dimers are involved in additional nonclassic H-bonds (Cmethyl···H···Cl) interactions generating a two-dimensional (2D) sheet structure (Figure 2b). When 2D networks are viewed in the [001] direction, it is revealed that these interactions lead to the formation of rhombic channels. The rhombic channels of ca. ~11.4 × 6.2 Å contain no guest solvent molecules. The amount of void space encapsulated the network is 912.5 Å³, i.e., 25% of the unit cell volume.

2.3. Photophysical properties and electrochemical studies

Figure 3. Absorbance and emission spectra of BODIPY dyes: (a) B1, (b) B2, (c) B3, and (d) B4. c = 1.0 × 10⁻⁷ M in CH3CN, at room temperature.

A series of BODIPY derivatives (B1-B4) were characterized via UV-vis absorption and fluorescence spectroscopy in various solvents with increasing polarity from toluene to methanol, and photophysical parameters are gathered in Table 1. It should be
noteworthy that some photophysical data for B2 in dichloromethane and acetonitrile is previously reported. As shown in Figure 3, B1 and B3 share a similar absorption and emission profile with high extinction coefficients ($\varepsilon = 79700$ for B1 and 78200 for B3) and high quantum efficiency of fluorescence ($\Phi_{fl} = 0.82$ for B1 and 0.76 for B3), irrespective of para- or meta-pyridyl substitution. It is noteworthy that the previously measured $\Phi_{fl}$ for B1 in CH$_2$CI$_2$ is only 0.30. However, both we and S. Banfi have determined the $\Phi_{fl}$ of B1 in CH$_2$CN is ~0.70-0.80. Upon iodination of two pyrrole 2,6-positions, both the absorption and emission maxima of B2 and B4 shift to lower energy. The absorption coefficients of bisiodo-BODIPYs B2 and B4 are comparable to those of nonhalogenated BODIPYs B1 and B3; however the $\Phi_{fl}$ of both B2 and B4 sharply decreases to 0.01-0.02 in CH$_2$CN. Significant decrease of $\Phi_{fl}$ is an indication of an efficient intersystem crossing efficiency ($\Phi_{isc}$) from the lowest singlet excited state ($S_1$) to one of the other triplet states except the lowest one ($T_1$), which has been accelerated by the internal heavy-atom effect.

Table 1 Photophysical parameters of B1-B4 in different solvents.

<table>
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<tr>
<th>BODIPY</th>
<th>solvent</th>
<th>$\lambda_{max}$ (nm)</th>
<th>$\varepsilon$ (M$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{em}$ (nm)</th>
<th>$\Phi_{fl}$ (%)</th>
<th>$\tau$ (ns)</th>
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<td>65600</td>
<td>559</td>
<td>0.02</td>
<td>f</td>
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</table>

$\lambda_{max}$ (nm): absorption wavelength (at the maximum intensity). $\varepsilon$ (M$^{-1}$ cm$^{-1}$): extinction coefficient. $\lambda_{em}$ (nm): emission wavelength (at the maximum intensity). $\Phi_{fl}$ (%): the fluorescence quantum yields of B1 and B3 were estimated with 1,3,5,7-tetramethyl-8-phenyl-BODIPY as a standard ($\Phi_{fl} = 0.72$ in tetrahydrofuran); the fluorescence quantum yields of B2 and B4 were estimated with Rhodamine B (0.49 in ethanol). $\tau$ (ns): fluorescence lifetimes. Not determined.

The frontier molecular orbital (FMO) diagrams were also generated for the BODIPYs (B1-B4) from the optimized geometries. Time-dependent density functional theory (TDDFT) calculations in combination with the 6-31+G(d) basis set and a solvation model for acetonitrile were performed to determine the transitions involved in the lowest energy states. The parameters for the optimized geometries and full list of excited states are included in the Electronic Supplementary Information. Both B1 and B3 possess a highest occupied molecular orbital (HOMO) that is of BODIPY π character and a lowest unoccupied molecular orbital (LUMO) that is a BODIPY-based $\pi^*$ orbital. The TDDFT calculation shows a lowest energy singlet transition of HOMO→LUMO character with a high oscillator strength of 0.58 and energy of 2.86 eV. Although the energy of the predicted BODIPY-based transition is much higher than that of the observed experimental values, TDDFT calculations are known to overestimate the excitation energy of BODIPY chromophores. The B2 and B4 were hypothesized to enable the formation of the triplet excited state by ISC as iodine atoms are introduced into the cores of BODIPYs. The HOMO($\pi$)-LUMO($\pi^*$) transition corresponds to the first singlet excitation as assigned by TDDFT, which is observed in other BODIPY derivatives. In each iodinated BODIPY, the nature of the HOMO and LUMO is unchanged upon iodination (see ESI†). The computed similarity between these FMO orbitals indicates that, apart from its influence on the rate of ISC, iodination exerts negligible change on the electronic structures of the BODIPYs.

The optical properties of these BODIPY-sensitized cobaloximes Co-Bn (n = 1-4) were examined by electronic absorption spectroscopy at room temperature (Figure S1 of ESI†). Figure 4 shows the absorption spectra of these complexes as well as the reference Co(dmgH)$_2$pyCl and reagent Co(dmgH)(dmgH)$_2$Cl$_2$ in CH$_2$CN. These studied complexes exhibit a combination of absorption features from their specific subunits of BODIPYs and cobaloximes, indicating they absorb light efficiently throughout the ultraviolet and visible regions. The visible region is dominated by intense peak more than 500 nm, which corresponds to the 0-0 vibrational band of the S$_0$→S$_1$ (π→π*) transition localized on the BODIPY chromophore. Complexation of BODIPYs with cobaloxime leads to a bathochromic shift of the BODIPY absorption maxima of 5 nm. Two strong high-energy absorption bands at ~230 and ~255 nm were assignable to spin-allowed intraligand (π→π*) transitions of the dmgH ligand from cobaloxime. It can be noted that the absorption spectra of these complexes are largely superpositions of their individual subunits: this indicates that the interactions between the cobaloxime and BODIPY chromophores in the ground state are weak and complexation of the BODIPY to the cobaloxime causes minimal perturbation of its optical properties, so that these complexes can be regarded as supramolecular systems.

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The steady-state fluorescence studies were further carried out on these supramolecular systems (Figure S2 of ESI†). Attachment of the cobaloximes is accompanied by a substantial decrease in fluorescence from the BODIPY chromophore due to intramolecular energy or electron transfer across the orthogonal structure. Since we will observe photocatalytic hydrogen production for these supramolecular systems, these observations supported the hypothesis that the quenching of BODIPY-based fluorescence was due to the intramolecular electron-transfer processes in which the cobaloxime serves as an acceptor.

The electrochemical activity of the BODIPY dyes B1-B4 and the above-prepared complexes Co-Bn (n = 1-4) was determined by cyclic voltammetry in dichloromethane using tetrabutylammonium hexafluorophosphate (TBAP) as a supporting electrolyte, and the results are gathered in Table 2. BODIPYs with two iodo atoms on the β-positions (B2 and B4) have more positive reduction and oxidation potentials than noniodinating BODIPYs (B1 and B3), which is consistent with previously reported results (Table 2). The oxidation and reduction potentials of para-pyridyl attached at the 8-position of BODIPY are similar to and meta-pyridyl substituted BODIPYs, demonstrating that the position of meso-pyridyl substitutions has little electron effect on the redox activity of the central BODIPY core. This tendency is consistent with the aforementioned results by optical analysis. When pyridyl-functionalization BODIPYs are bound to the cobaloximes, the redox potentials were found to occur at more positive values. The catalytically relevant CoIII/CoII redox couple is of special interest for hydrogen evolution, and can be assigned, together with the reference complex Co(dmgH)pyCl for comparison. In the noniodinated BODIPY-cobaloximes Co-B1 and Co-B3, the CoIII/CoII redox couple is slightly reduced, by 0.06 V (Co-B1) and 0.05 V (Co-B3). However, for the iodinated complexes, the potential of the CoIII/CoII redox couple is significantly reduced, by 0.22 V (Co-B2) and 0.26 V (Co-B4), when compared to the reference Co(dmgH)pyCl. Through these comparisons, it was clear that this substantial reduction in the potential of the CoIII/CoII redox couple for Co-B2 and Co-B4 is a favourable step toward photogeneration of hydrogen.

Table 2 Electrochemical redox data for the BODIPY derivatives B1-B4 and BODIPY-cobaloximes Co-Bn (n = 1-4) as well as the reference Co(dmgH)pyCl.

<table>
<thead>
<tr>
<th>Compound</th>
<th>E1/2red, V</th>
<th>E1/2ox, V</th>
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<tbody>
<tr>
<td>B1</td>
<td>0.76</td>
<td>-1.58</td>
</tr>
<tr>
<td>B2</td>
<td>0.93</td>
<td>-1.34</td>
</tr>
<tr>
<td>B3</td>
<td>0.75</td>
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<tr>
<td>B4</td>
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<tr>
<td>Co-B4</td>
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<td>-0.75</td>
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</table>

4.2. Photocatalytic hydrogen evolution

To optimize H2 photocatalysis experiments for these BODIPY-cobaloximes, we initially used 2,6-diiodo BODIPY-sensitized cobaloxime Co-B4 as the model of photocatalyst with TEOA as sacrificial electron donor using a Xe lamp (300 W) with a cutoff filter (λ > 420 nm). No significant reaction is observed in the dark in the presence of the photocatalyst or without TEOA under light irradiation. We investigated the medium effects on photocatalytic hydrogen production of Co-B4. Among the solvents tested, CH3CN:HO, DMF:HO, THF:HO, CH3OH:HO, CH3CH2OH:HO (3:2, v/v), the best result for photoinduced H2 generation with Co-B4 (1.1×10⁻⁴ M) and TEOA (5%, v/v) was obtained in CH3CN:HO (3:2, v/v), with 9 TON of H2 evolution (Figure 5). The solvent dependence for hydrogen production from this system probably may be ascribed to many factors including solvent polarity, stabilization of reduction intermediates and Co(II/II) reduction potential necessary for hydrogen generation. The optimal ratio for CH3CN and water was further investigated. Changing the ratio of CH3CN:HO from 3:2 to 1:1 resulted in considerable decrease in H2 evolution to 2 TON. However, increasing the CH3CN/H2O ratio to 4:1 and then to 24:1, while keeping the catalyst concentration constant at 1.1×10⁻⁴ M, notably increases the activity of the catalyst, as indicated by consistently higher TON values. Indeed, the TON values as high as 19 and 74 have been, respectively, obtained and, these correspond to volumes of hydrogen of 4.6 and 18 mL. Similar effects of the ratios of CH3CN:HO on the photoinduced H2 production with the Pt6 PS/CoIII catalyst systems were previously reported by Eisenberg. The explanation for the apparent effect of the content of water may result from changes in the electrostatic properties of the medium and differences in the redox potentials as the CH3CN:HO ratio changes. Several other possible sacrificial electron donors such as triethylamine (TEA), ascorbate and EDTA were tried, but TEOA proved to be the most effective at hydrogen production under the same reaction conditions. The potential electron donors of TEA and ascorbate
only achieve TON 1 and 8, respectively, while EDTA resulted in no hydrogen production.

Figure 5. (a) Comparison of hydrogen production using different solvent:water (3:2, v/v) with 1.1×10\textsuperscript{-4} M Co-B4, TEOA (5%, v/v). (b) Comparison of hydrogen production using different ratios of CH\textsubscript{3}CN/H\textsubscript{2}O with 1.1×10\textsuperscript{-4} M Co-B4, TEOA (5%, v/v).

The hydrogen evolving performance of Co-B4 was found to be strongly dependent on pH, with results in terms of TONs peaking at the value of 8.5. As displayed in Figure 6, the TON based on complex Co-B4 was 85 (935 µmol) in a TEOA (5% v/v) and CH\textsubscript{3}CN/water (4:1) with pH = 8.5 after 5 h irradiation. The rate of H\textsubscript{2} production decreases sharply at both more acidic and more basic values. This strong dependence of the rate of H\textsubscript{2} evolution on pH has been observed in related photocatalytic systems.\textsuperscript{10-19} The pH-dependence is likely to arise from a balance between several factors playing together towards hydrogen generation: (i) the protonation of TEOA diminishing its ability to function as an electron donor with decreasing pH, (ii) the proton concentration and thermodynamic driving-force for water reduction (lower at basic pH than at acidic one), (iii) the formation of the cobalt hydride catalytic intermediate which is much more favored at acidic pH, and (iv) the presence of competition for protonation or metal coordination of BODIPY at more acidic medium.

Figure 6. (a) Influence of the pH on the photocatalytic H\textsubscript{2} evolution from a system comprising Co-B4 (1.1×10\textsuperscript{-4} M) and TEOA (5%, v/v) in CH\textsubscript{3}CN/H\textsubscript{2}O (4:1, v/v). (b) Comparison of hydrogen production using different BODIPY-cobaloximes Co-Bn (n = 1-4) with c = 1.1×10\textsuperscript{-4} M, TEOA (5%, v/v) in CH\textsubscript{3}CN/H\textsubscript{2}O (4:1, v/v) at pH 8.5.

To compare the efficiency of Co-B4 to those of Co-Bn (n = 1-3), these catalysts were tested under the same experimental conditions with 100 mL of CH\textsubscript{3}CN/H\textsubscript{2}O (4:1, v/v) containing 1.1×10\textsuperscript{-4} M Co-Bn (n = 1-4), TEOA (5%, v/v) combined in a 250 mL Pyrex flat-bottomed flask vigorously agitated with a magnetic stirrer. The pH of reaction system was kept at 8.5 with a 2.5 M HCl stock solution. Under these optimized conditions, as shown in Figure 6, the changes in the iodinated and noniodinated BODIPYs of Co-Bn (n = 1-4) result in quite different performances of H\textsubscript{2} generation. The H\textsubscript{2} evolution levels off after 5 h irradiation, with the turnovers of H\textsubscript{2} evolved up to 85 (935 umol) for Co-B4 under optimal conditions, while Co-B2 gave 82 turnovers (900 umol) of H\textsubscript{2} evolution in 5 h irradiation and no amount of H\textsubscript{2} production was detected by GC for Co-B1 and Co-B3. Compared with iodinated Co-B2 and Co-B4, noniodinated Co-B1 and Co-B3 lack any appreciable hydrogen evolution under the same reaction conditions due to the absence of internal heavy atom effect and long-lived photoexcited triplet state. In fact, previous studies have suggested that the heavy atom effect of the iodine substituents facilitates ISC to the longer-liver \( ^3\pi\pi^* \) excited state from which electron transfer occurred. The Co-B4 displays much higher photocatalytic efficiency than that reported for the photocatalyst composed of a Ru-based (TON = 14)\textsuperscript{20} or porphyrin chromophore (TON = 22) and the same Co\textsuperscript{lll} cobaloxime with a similar pyridyl coordination linkage.\textsuperscript{9} It should be noteworthy that the irradiation wavelength chosen substantially affects the hydrogen evolving efficiency. When we used purposely a 550±10 nm excitation (green monochromatic light) to ensure excitation near the absorption maxima of iodinated BODIPY, only 6 and 7 of TON was obtained for Co-B2 and Co-B4.

Figure 7. Frontier molecular orbitals of Co-B4\textsuperscript{+} obtained through DFT calculations (UB3LYP/LANL2DZ) since the anion has an unpaired electron. The alpha/beta molecular orbitals were all defined due to the negative charge on the open-shell system adopted. Both the HOMO orbitals of alpha (a) and beta (b) are exclusively localized on the BODIPY chromophores, while the LUMO orbitals of alpha (c) and beta (d) are located on the cobalt centers.

The redox potentials of Co-B2 and Co-B4 are adopted to evaluate the driving force of the intramolecular electron transfer reaction. According to the reduction potentials of Co-B2 and Co-B4, the ground-state redox potentials of B2 (\( E_{1/2}(B2/B2^+) = 1.02 \text{ V} \)) and B4 (\( E_{1/2}(B4/B4^+) = 1.02 \text{ V} \)) are the triplet excited state energies of \( B2^* \) (1.513 eV) and \( B4^* \) (1.514 eV) obtained from TDDFT calculations, the free energy \( \Delta G \) for formation of the Co\textsuperscript{0} species can be estimated according to the well-known Rehm-Weller equation (Table S4, ESI†).\textsuperscript{21} The calculated \( \Delta G \) suggests that the reduction process is exergonic, and intramolecular electron transfer from reduced Bn (n = 2 and 4)
species to the cobaloximes is thermodynamically feasible for Co-B2 and Co-B4, as estimated from the electrochemical and spectroscopic data.

For additional information on the location of the frontier molecular orbitals, we examined Co-B2$^-$ and Co-B4$^-$ by means of the density functional theory (DFT) methods on the UB3LYP/LANL2DZ level. Geometric parameters from the X-ray diffraction and analysis were used for the calculations. As expected, orthogonalization of the BODIPY moieties and cobaloximes results in the frontier molecular orbital residing on the individual units. Contributions to the HOMO distribution were mainly from the BODIPY chromophores, while the LUMO distributions were donated by all atomic orbitals in the centre of cobalt, as displayed in Figure 7. Therefore, the transition of HOMO→LUMO is a full electron-transfer process (from π-conjugated BODIPY→radical anion to cobaloxime fragment), which is in accordance with the experimental results.

Drawing on previous studies for the mechanisms of hydrogen evolution by cobaloxime catalysts,$^{10,12}$ and the results described above, it is postulated that the key step involves the generation of a catalytically active Co$^{3+}$ species. As shown in Scheme 2, there is one possible pathway for the generation of Co$^{3+}$ species with the quenching of the triplet BODIPY excited state (denoted $^3$BDP*): i.e., reductive quenching mechanism by electron transfer from TEOA, whereupon the BDP$^-$ species formed transfers an electron to Co$^{3+}$. The path produces the radical cation of TEOA$^+$, which decomposes through proton loss, electron transfer and hydrolysis to form glycolaldehyde and di(ethanol)amine along with transfer of a second proton and a second electron. The formed Co$^{3+}$ species further reacts with a proton to produce a postulated Co$^{3+}$-hydride, which releases molecular hydrogen via a homo- or heterolytic pathway.$^{22}$

**Scheme 2. Plausible mechanism for the formation of Co$^{3+}$ species. TEOA stands for triethanolamine and BDP for iodinated BODIPY's B2 and B4.**

**3. Conclusions**

In conclusion, we report four noble-metal-free supramolecular systems Co-Bn (n =1-4) with pyridine atoms of BODIPY moieties binding to the Co$^{3+}$ center of cobaloxime, and use them as single-component homogeneous photocatalysts for visible-light-driven H$_2$ evolution. Many factors including the medium, sacrificial electron donor, the ratio of solvent/water and pH in the reaction medium, irradiation wavelength are carefully investigated. Under optimized conditions (relative low photocatalyst concentration of 110 µmol L$^{-1}$, at weak basic pH ~8.5, CH$_3$CN/water ratio of 4:1, irradiation wavelength λ > 420 nm), the TONs of hydrogen evolution for iodinated Co-B2 and Co-B4 are 85 and 82, respectively, while the noniodinated Co-B1 and Co-B3 show no photocatalytic activity under the same reaction conditions. This study demonstrates unambiguously the beneficial effects for H$_2$ production of the use of such a photocatalyst in which the iodine heavy atoms are attached onto the BODIPY cores. This internal heavy atom effect stabilizes the system and enables the efficient formation of the long-lived triplet excited state photosensitizers by ISC, which is vital for the production of hydrogen. A reductive quenching pathway (namely, the intramolecular electron transfers from BDP$^-$ to the cobalt centers) in the photochemically driven step is possible for the hydrogen production, as evaluated by from the electrochemical and photophysical data as well as theoretical calculations. To our knowledge, the photoinduced H$_2$-evolving efficiency of Co-B4 up to 21 mL is the highest one ever reported for the absolutely precious-metal-free supramolecular photocatalysts.

**4. Experimental section**

**4.1. Chemicals and Instrumentation**

Reagents were purchased as reagent-grade and used without further purification unless otherwise stated. Solvents were dried by standard literature methods$^{23}$ before being distilled and stored under nitrogen over 3Å molecular sieves prior to use. All reactions were performed under a nitrogen atmosphere in oven-dried or flame-dried glassware unless otherwise stated and were monitored by TLC using 0.25 mm silica gel plates with UV indicator (60F-254).

$^1$H and $^{13}$C NMR were obtained at room temperature using a Bruker PLUS 400 spectrometer with tetramethylsilane (TMS, 0.00 ppm) as an internal standard and CDCl$_3$ as solvent. Chemical shift multiplicities are reported as s = singlet, d = doublet, and br = broad singlet. Coupling constants (J) values are given in Hz. Mass spectrometry (MS) experiment was carried out in the positive ion mode on a Bruker Esquire HCT ion trap mass spectrometer (Billerica, MA) coupled with a homemade electrospray ionization (ESI) device. Parameters of the ESI source were optimized to enhance the signal intensity. The pressure of nebulizing nitrogen, the flow rate of desolvation gas, and the temperature of desolvation gas were set to 8 psi, 1L min$^{-1}$, and 250 ºC, respectively. Cyclic voltammetry experiments were carried out with a CHI 650E electrochemical analyzer using a three-electrode system at room temperature. The working electrode was 2 mm Pt with a Pt wire as auxiliary electrode and a 0.01M Ag/AgNO$_3$ solution reference electrode. All measurements were performed in freshly distilled and deoxygenated dichloromethane with a solute concentration of ca. 1.0 mM in the presence of 0.1 M tetrabutylammonium hexafluorophosphate (TBAP) as a supporting electrolyte. C, H,
and N microanalyses were carried out with a CE instruments EA 1110 analyzer.

4.2. Spectroscopic Measurements and Determination of Fluorescent Life and Quantum Yields

The solvents used for photophysical measurement were of spectroscopic grade and used without further purification. UV-vis spectra in solution were recorded on a UV-2100 (Shimadzu) spectrophotometer. Steady-state fluorescence spectroscopic studies in solution were performed on a Hitachi F-7000 spectrophotometer with a xenon arc lamp as light source. The slit width was set at 2.5 nm for excitation and 5.0 nm for emission. Fluorescence decay curves of the samples were measured with the time-correlated single-photon-counting (TCSPC) method on FLSP920 Lifespec-ps (Edinburgh) and the data were analyzed by Edinburgh software. The goodness of the fit of the decays as judged by reduced chi-squared (χ²) was measured with the time-correlated single-photon-counting data were analyzed by Edinburgh software. The goodness of the fit of the decays as judged by reduced chi-squared (χ²) was measured with the time-correlated single-photon-counting (TCSPC) method on FLSP920 Lifespec-ps (Edinburgh) and the data were analyzed by Edinburgh software. The goodness of the fit of the decays as judged by reduced chi-squared (χ²) was measured with the time-correlated single-photon-counting (TCSPC) method on FLSP920 Lifespec-ps (Edinburgh) and the data were analyzed by Edinburgh software.

Relative quantum efficiencies of fluorescence of BODIPY derivatives were obtained by comparing the area under the emission spectra of the reference and sample, as standards, respectively. Dilute solutions (0.01 < A < 0.05) were used to minimize the reabsorption effects. The following equation was used to calculate quantum yield:

\[ \Phi_{\text{sample}} = \Phi_{\text{standard}} \times \left( \frac{A_{\text{sample}}}{A_{\text{standard}}} \right) \times \left( \frac{n_{\text{sample}}}{n_{\text{standard}}} \right) \]

Where \( \Phi_{\text{sample}} \) and \( \Phi_{\text{standard}} \) are the emission quantum yields of the sample and the reference, respectively, \( A_{\text{sample}} \) and \( A_{\text{standard}} \) are the measured absorbances of the reference and sample at the excitation wavelength, respectively, \( n_{\text{sample}} \) and \( n_{\text{standard}} \) are the refractive indices of the solvents of the reference and sample, respectively. The \( \Phi_{\text{sample}} \) values reported in this work are the averages of multiple (generally three), fully independent measurements.

4.3. Synthetic Procedures

The syntheses of the starting BODIPY compounds B1 and B2 were achieved using literature methods15 and characterized by \(^1\)H NMR, \(^{13}\)C NMR and elemental analyses to determine their structures.

4,4-difluoro-8-(4-pyridyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (B1): In a flame-dried Schlenk flask, under nitrogen atmosphere, to a stirred solution of 2,4-dimethylpyrrole (0.41 mL, 4 mmol) and 3-pyridylcarbaldehyde (0.19 mL, 2 mmol) in anhydrous CHCl₃ (100 mL) were added trifluoroacetic acid (TFA, 0.15 mL). The solution was stirred overnight at room temperature in the dark until TLC indicated complete consumption of the aldehyde.

Dichlorodicyanobenzoquinone (DDQ, 681 mg, 3 mmol) were added and the mixture was stirred for an additional 2h. A large excess of triethylamine (9 mL) and BF₃·Et₂O (9 mL) was then added into the reaction mixture. After being stirred for 12 h at room temperature, it was diluted with water and extracted with CHCl₃. The organic layer was combined, dried over MgSO₄ and evaporated to dryness under vacuum. The crude product was purified by chromatography on a column packed with flash silica gel, using CHCl₃ as eluent, from which the desired product B1 was obtained as orange solid in 15.3% (155 mg). \(^1\)H NMR (CDCl₃, 400 MHz): δ (ppm) = 8.80 (d, J = 3.4 Hz, 2H), 7.34 (d, J = 2.6 Hz, 2H), 6.02 (s, 2H), 2.56 (s, 6H), 1.41 (s, 6H). \(^{13}\)C NMR (CDCl₃, 101 MHz): δ (ppm) = 156.44, 150.53, 143.60, 142.62, 137.60, 130.29, 123.31, 121.79, 14.57. Anal. Calcd for C₂₅H₁₃BF₃N₅: C, 66.49; H, 5.58; N, 12.92. Found: C, 66.42; H, 5.51; N, 12.85. ESI-MS m/z (C₁₉H₁₄BF₃N₃) calculated: 325.2, found 326.1 (M+H⁺), 348.1 (M+Na⁺).

4,4-difluoro-8-(4-pyridyl)-1,3,5,7-tetramethyl-2,6-diodo-4-bora-3a,4a-diaza-s-indacene (B2): To B1 (127.5 mg, 0.39 mmol) in 10 mL of CH₃OH was added iodine (198.9 mg, 0.78 mmol) and iodide acid (149.0 mg, 0.84 mmol). This mixture was left stirring at room temperature for 24 h, washed with an aqueous solution of sodium carbonate, and extracted by CH₂Cl₂. Organic layers were combined, dried over Na₂SO₄, and evaporated to dryness under vacuum. Purification was performed by column chromatography on silica gel using CH₂Cl₂ as eluent to obtain the desired product B2 as purple solid in 78% (176.4 mg).

H NMR (CDCl₃, 400 MHz): δ (ppm) = 8.88 (s, 2H), 7.52 (d, J = 9.8 Hz, 2H), 2.67 (s, 6H), 1.42 (s, 6H). \(^{13}\)C NMR (CDCl₃, 101 MHz): δ (ppm) = 158.06, 150.19, 144.71, 144.22, 136.62, 130.12, 123.57, 86.43, 17.31, 16.15. Anal. Calcd for C₂₅H₁₃BF₃I₃N₅: C, 37.47; H, 2.80; N, 7.28. Found: C, 37.60; H, 2.91; N, 7.41. ESI-MS m/z (C₁₉H₁₄BF₃I₃N₅) calculated: 577.0, found 576.1 (M+H⁺).

4,4-difluoro-8-(3-pyridyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (B3): In a flame-dried Schlenk flask, under nitrogen atmosphere, to a stirred solution of 2,4-dimethylpyrrole (0.41 mL, 4 mmol) and 3-pyridylcarbaldehyde (0.19 mL, 2 mmol) in anhydrous CH₂Cl₂ (100 mL) were added trifluoroacetic acid (TFA, 0.1 mL). The solution was stirred overnight at room temperature in the dark until TLC indicated complete consumption of the aldehyde. Dichlorodicyanobenzoquinone (DDQ, 454 mg, 2 mmol) were added and the mixture was stirred for an additional 2h. A large excess of triethylamine (6 mL) and BF₃·Et₂O (6 mL) was then added into the reaction mixture. After being stirred for 12 h at room temperature, it was diluted with water and extracted with CH₂Cl₂. The organic layer was combined, dried over MgSO₄, and evaporated to dryness under vacuum. The crude product was purified by chromatography on a column packed with flash silica gel, using CH₂Cl₂ as eluent, from which the desired product B1 was obtained as orange solid in 11.3% (76 mg). 1H NMR (CDCl₃, 400 MHz): δ (ppm) = 8.85 (d, J = 4.31, 1H); 8.59 (s, 1H), 7.70 (dd, J = 1.79, 1.57, 1H), 7.51 (dd, J = 4.92, 4.92, 1H), 6.00 (s, 2H), 2.57 (s, 6H), 1.38 (s, 6H). \(^{13}\)C NMR (CDCl₃, 101 MHz): δ (ppm) = 155.60, 149.68, 148.02, 142.70, 136.61, 136.82, 136.58, 131.56, 123.95, 121.86, 15.02, 14.65. Anal. Calcd for C₂₅H₁₃BF₃I₃N₅: C, 66.49; H, 5.58; N, 12.92. Found: C, 66.55; H, 5.48; N, 12.99. ESI-MS m/z (C₁₉H₁₄BF₃I₃N₅) calculated: 325.2, found 326.2 (M+H⁺).
4,4-difluoro-8-(3-pyridyl)-1,3,5,7-tetramethyl-2,6-diido-4-bora-3a,4a-diaza-s-indacene (B4): To B3 (114.3 mg, 0.35 mmol) in 10 mL of CH3OH was added iodine (184.4 mg, 0.72 mmol) and iodic acid (134.6 mg, 0.76 mmol). This mixture was left stirring at room temperature for 24 h, washed with an aqueous solution of sodium carbonate, and extracted by CH2Cl2. Organic layers were combined, dried over Na2SO4, and evaporated to dryness under vacuum. Purification was performed by column chromatography on silica gel using CH2Cl2 as eluent to obtain the desired product B4 as purple solid in 81.2% (164.7 mg). 1H NMR (CDCl3, 400 MHz): δ (ppm) = 8.84 (dd, J = 1.44, 1.54, 1H), 8.57 (d, J = 1.85, 1H), 7.67 (dd, J = 1.61, 1.55, 1H), 7.54 (m, J = 4.71, 1H), 2.67 (s, 6H), 1.42(s, 6H). 13C NMR (CDCl3, 400 MHz): δ (ppm) = 157.74, 150.62, 148.22, 144.93, 136.83, 135.91, 131.36, 131.20, 123.92, 86.28, 17.57, 16.11. Anal. Calc for C16H12BF2I2N2: C, 37.71, 150.62, 148.22, 144.93, 136.83, 135.91, 131.36, 131.20, 123.92, 86.28, 17.57, 16.11. Calculated: C, 37.71, 150.62, 148.22, 144.93, 136.83, 135.91, 131.36, 131.20, 123.92, 86.28, 17.57, 16.11. This journal is © The Royal Society of Chemistry [year].

BODIPY-cobaloxime complexes (Co-B1 and Co-B2). The reagent Co(dmgH)(dmgH)Cl2 and reference pyridine-cobaloxime Co(dmgH)2pyCl were prepared according to the literature methods.27,28

\[
[\text{Co(dmgH)Cl}] \{4,4\text{-difluoro-8-(4-pyridyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene}\} \ (\text{Co-B1})
\]

To a stirred solution of Co(dmgH)(dmgH)Cl2 (43.6 mg, 0.123 mmol) in anhydrous CH3OH (5 mL) was added triethylamine (Et3N, 16.9 μL, 0.12 mmol). The solution slowly turned into yellow-brown in color. B1 (39.2 mg, 0.12 mmol) in CH2Cl2 (3 mL) was then added. The reaction mixture was stirred for 3 h at room temperature. The formed microcrystalline purple precipitate was filtered off and washed with small amounts of ice cold CH3OH until the filtrate had no residual fluorescence under UV illumination. After drying under high vacuum, a dark purple product was obtained (yield 65.7 mg, 81.3%). 1H NMR (CDCl3, 400 MHz): δ (ppm) = 8.47 (d, J = 6.6 Hz, 2H), 7.29(s, 1H), 7.28 (s, 6H), 6.01 (s, 2H), 2.55 (s, 6H), 2.45 (s, 6H). 13C NMR (CDCl3, 101 MHz): δ (ppm) = 157.73, 152.49, 150.62, 148.22, 144.93, 136.83, 135.91, 131.36, 131.20, 123.92, 86.28, 17.57, 16.11. UV-Vis, λ\text{max} (nm): 233 nm (53900), 257 nm (50600), 361 nm (45600), 506 nm (42000), 250 nm (31300), 758 nm (60000).

\[
[\text{Co(dmgH)Cl}] \{4,4\text{-difluoro-8-(3-pyridyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene}\} \ (\text{Co-B4})
\]

To a stirred solution of Co(dmgH)(dmgH)Cl2 (30 mg, 0.085 mmol) in anhydrous CH3OH (5 mL) was added triethylamine (Et3N, 11.4 μL, 0.081 mmol). The solution slowly turned into yellow-brown in color. B1 (47.3 mg, 0.085 mmol) in CH2Cl2 (3 mL) was then added. The reaction mixture was stirred for 3 h at room temperature. The formed microcrystalline purple precipitate was filtered off and washed with small amounts of ice cold CH3OH until the filtrate had no residual fluorescence under UV illumination. After drying under high vacuum, a dark purple product was obtained (yield 66.6 mg, 90.1%). 1H NMR (CDCl3, 400 MHz): δ (ppm) = 8.49 (d, J = 6.6 Hz, 2H), 2.62 (s, 6H), 2.46 (s, 6H), 1.71 (s, 6H). UV-Vis, λ\text{max} (nm, /L mol\text{-1} cm\text{-1}): (CH2CN): 231 nm (40000), 250 nm (27700), 389 nm (8110), 542 nm (54000).

4.4. Crystallization Experiments and X-ray Crystallography

Well-formed X-ray-quality crystals of B1, B2 and B3 were obtained by slow evaporation of their CH2Cl2 solution at room temperature. Suitable crystals of Co-B1 and Co-B2 were grown by slow evaporation of solutions in CH2Cl2/CH3CN 3:1, and Co-B3 were grown by the slow evaporation of a solution in toluene/DMF 1:1. Intensity data for these compounds were collected on a Rigaku R-AXIS RAPID Image Plate single-crystal diffractometer using graphite-monochromated Mo Kα radiation source (λ = 0.71073 Å). Single crystals of these compounds with appropriate dimensions were chosen under an optical microscope, coated in oil and mounted on a glass fiber for data collection. Absorption correction was applied by correction of symmetry-equivalent reflections using the ABSCOR program.29 All structures were solved by direct methods using SHELXS-9730 and refined by full-matrix least-squares on F2 using SHELXL-9731 via the program interface X-Seed.32 Non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to oxygen in Co-B1, Co-B2 and Co-B3 were located by difference Fourier maps and other hydrogen atoms were isotropically in a riding model with Uiso values 1.2-1.5 times
those of their parent atoms. All structures were examined using the Addsym subroutine PLATON\textsuperscript{35} to ensure that no additional symmetry could be applied to the models. Crystal structure views were obtained using Diamond v3.1.\textsuperscript{34} Details of the data collection conditions and the parameters of the refinement process are given in Table S1 and Table S2. Selected bond lengths and angles are listed in Table S3.

### 4.5. Water splitting reaction

The photocatalytic water splitting experiment was performed in a Pyrex top-irradiation reaction vessel connected to a glass closed gas circulation system (Labscale-IIHAG photocatalytic system, Beijing Perfectlight Co., Ltd., Figure S3). In a typical hydrogen production experiment, 1.1×10\textsuperscript{4} M solutions of the BODIPY-cobaloximes \textit{Co-Bn} (n = 1–4) were prepared in a mixture of acetonitrile-water 4:1 (v/v), containing 5 vol\% of triethanolamine (TEOA) at pH = 8.5. The obtained reactant solution was put into a 250 mL Pyrex flat-bottomed reaction vessel and vigorously stirred in the dark for 0.5 h. The reaction system was evacuated three times with half an hour each time to remove air completely prior to visible light illumination. The reaction solution was irradiated using an external light source comprising a 300 W Xe arc lamp (MICROSOLAR 300, Beijing Perfectlight Co., Ltd.) with an optical filter employed to cut off light with wavelengths below 420 nm. During the water photochemical reaction, the reaction mixture was mixed using a magnetic stirring bar and the temperature of the reactant solution was maintained at room temperature by a flow of cooling water. The amount of \textit{H\textsubscript{2}} gas produced in the reaction system was measured with a gas chromatograph (GC 7900, Shanghai Techcomp Instrument Ltd.) with a thermal conductivity detector (TCD), a 5 Å molecular sieve column (4 mm(OD) × 3 mm(ID) × 3 m), and with \textit{N\textsubscript{2}} as carrying gas. Each photocatalysis experiment was conducted three times with the reported \textit{μmol} hydrogen being the average of the trials. The amounts of hydrogen were quantified by external standard method, and the turnovers were calculated versus the amount of BODIPY-cobaloxime in the systems.

### 4.6. Computational Details

Theoretical calculations have been performed with the \textit{Gaussian 09} software package.\textsuperscript{35} The geometric parameters from X-ray diffraction analysis were used as the starting point for the geometry optimization when available. Geometries were optimized under the DFT level of theory using the hybrid functional B3LYP, which combines Becke’s 3-parameter exchange functional\textsuperscript{36} and Lee, Yang, and Parr’s correlation functional.\textsuperscript{37} The polarizable continuum model (PCM)\textsuperscript{38} of acetonitrile was used in all calculations. The BODIPY chromophores were optimized using the 6-31+G(d) basis set,\textsuperscript{39} excluding the iodinated compound, for which 3-21G\textsuperscript{40} was used for iodine while the 6-31+G(d) basis set was used for the remaining atoms. For the optimization of BODIPY-cobaloximes, LAN2DZ\textsuperscript{41} basis set on the Co atoms, 3-21G basis set on the iodine and 6-31+G(d) basis set for the rest were used. All geometries were deemed minima, as no negative frequencies were found. TDDFT\textsuperscript{42} was used to model the excitation energies. All molecular orbitals were visualized with the software \textit{GaussView} 5.0.

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Graphical Abstract

Four BODIPY-cobaloxime systems Co-Bn (n = 1-4) were studied as single-component homogeneous photocatalytic systems for H$_2$ generation in aqueous media.