Molecular Dye-Sensitized Photocatalysis with Metal-Organic Framework and Metal Oxide Colloids for Fuel Production

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Abstract: Colloidal dye-sensitized photocatalysis is a promising route toward efficient solar fuel production by merging properties of catalysis, support, light absorption, and electron mediation in one. Metal-organic frameworks (MOFs) are host materials with modular building principles allowing scaffold property tailoring. Herein, we combine these two fields and compare porous Zr-based MOFs UiO-66-NH₂(Zr) and UiO-66(Zr) to monoclinic ZrO₂ as model colloid hosts with co-immobilized molecular carbon dioxide reduction photocatalyst fac-ReBr(CO)₂(4,4′-dcbpy) (dcbpy = dicarboxy-2,2′-bipyridine) and photosensitizer Ru(bpy)₃(5,5′-dcbpy)Cl₂ (bpy = 2,2′-bipyridine). These host-guest systems demonstrate selective CO₂-to-CO reduction in acetonitrile in presence of an electron donor under visible light irradiation, with turnover numbers (TONs) increasing from ZrO₂, to UiO-66, and to UiO-66-NH₂ in turn. This is attributed to MOF hosts facilitating electron hopping and enhanced CO₂ uptake due to their innate porosity. Both of these phenomena are pronounced for UiO-66-NH₂(Zr), yielding TONs of 450 which are 2.5 times higher than under MOF-free homogeneous conditions, highlighting synergistic effects between supramolecular photosystem components in dye-sensitized MOFs.

Keywords: dye-sensitized; metal-organic frameworks; metal oxides; host-guest photosystems; molecular catalysis; fuel production; artificial photosystems

1. Introduction

Solar fuel production has emerged as a pertinent possibility on route to address growing energy challenges and shift fossil fuel dependency toward sustainable sources [1]. It aptly merges solar energy harvesting with subsequent energy conversion to form value-adding products [2]. At this cross-section, molecular coordination complexes can play a key role as discrete nature-mimicking photosystems combining light sensitizing and chemical reactivity [3]. Previous advances include molecular catalyst and dye engineering to improve catalytic parameters such as activity and selectivity on the one hand, as well as light harvesting and antenna effects on the other [4,5]. Additionally, immobilizing such species to host materials can yield beneficial sustained performance, with dye-sensitized photocatalysis (DSP) emerging as a selected approach with distinct advantages [6,7]. Specifically, this methodology bridges the fields of molecular (photo)catalysis and material chemistry by coupling a catalyst and a dye via co-anchoring onto a semiconductor particle—effectively employing the latter as a solid-state electron mediator and a scaffold [6]. While this working principle has been studied for several host particle compounds in colloidal DSP [8,9], applying metal-organic frameworks (MOFs) as the matrix component can provide similar benefits and is an area with burgeoning interest [10–13]. MOFs combine metal-based nodes with organic multilopic linkers to form porous coordination polymers, thus unlocking adjustable chemical properties, topologies, porosities, and molecular complex hosting capabilities [14]. Particularly regarding dye-sensitization possibilities, MOFs can substantially influence guest photophysics through approaches such as confinement effects as well as scaffold-directed photochromicity [15]. However, their organic/inorganic building principle can result in limited stability or conductivity [16]. This presents the question how...
dye-sensitized MOFs (DSMs) directly compare to their commonly used metal oxide-based particle counterparts in colloidal solar fuel production.

We devised a conceptual side-by-side model comparison of CO$_2$ reducing DSP and DSM systems based on ZrO$_2$ nanoparticles alongside the UiO-66(Zr) MOF composed of Zr$_6$O$_4$(OH)$_4$ nodes, simulating the oxide support (Figure 1a,b) [17].

**Figure 1.** Schematic overview of the studied hosts and molecular complexes. (a) Representation of the porous MOF hosts UiO-66-NH$_2$(Zr) (66-NH$_2$) and UiO-66(Zr) (66), as well as monoclinic ZrO$_2$ nanoparticles. Chemical structures of the molecular photocatalyst fac-ReBr(CO)$_3$(4,4′-dcbpy) (1) and the [Ru(bpy)$_2$(5,5′-dcbpy)]Cl$_2$ photosensitizer (2). (b) Anchoring interactions between the molecular species 1 and 2 to 66, 66-NH$_2$ and ZrO$_2$, respectively.

UiO-66 is well-studied due to its versatility and chemical stability [18]. Additionally, a few reports showed UiO-66(Zr)’s applicability in DSM using Pt nanoparticles for H$_2$ evolution [19,20]. Functional group implementation through linker variation offers further advantages [18]. For example, UiO-66-NH$_2$(Zr), constructed from 2-aminoterephthalic acid linkers, allows improved gas and molecular guest adsorption capabilities, as well as as shifts the optical absorption through amine group incorporation [10,21]. Due to its small pore apertures and diameters, molecular species are typically loaded onto the MOFs’ surface [10,22]. ZrO$_2$ has also been previously applied as a support for DSP primarily enabling so-called “on particle” electronic communication between PS and catalyst due to the high energy level of the conduction band [3,23].

We selected a molecular CO$_2$ reduction catalyst (CRC) fac-ReBr(CO)$_3$(4,4′-dcbpy) (dcbpy = dicarboxy-2,2′-bipyridine) (1) and the photosensitizer [Ru(bpy)$_2$(5,5′-dcbpy)]Cl$_2$ (bpy = 2,2′-bipyridine) (2) as a benchmark photosystem (Figure 1a). These have been studied together under homogeneous conditions in the presence of a sacrificial electron donor (SED) [10,24,25], as well as in DSP upon anchoring to semiconductor supports such...
as TiO$_2$, SiO$_2$, and SrTiO$_3$, as well as to MOFs, often delivering moderate photoactivity with turnover numbers (TONs) in the range of 10–600 [10,11,26–29].

Ligands with carboxylic acid groups were chosen to enable outer surface anchoring to MOF nodes, free amines for UiO-66-NH$_2$(Zr), as well as to ZrO$_2$ surface hydroxyl groups (Figure 1b) [11,12,30]. This approach has previously yielded stable host-guest colloidal assemblies, allowing for photoinduced electron transfers from the SED to the sensitizing units and subsequently to vicinal catalysts for CO$_2$ reduction [10–13,30]. Herein, we report the synthesis, thorough characterization, and photocatalytic CO$_2$ reduction performance of DSM UiO-66-NH$_2$(Zr) and UiO-66(Zr), in direct comparison to DSP with their metal oxide counterpart ZrO$_2$. This revealed key working principles and considerations for selecting suitable hosts in solar DSP and DSM.

2. Materials and Methods

A detailed overview on analysis methods, step-by-step synthesis routes, and characterization techniques is available to the reader in the Supplementary Material (SM). The most relevant material syntheses are described here.

fac-ReBr(CO)$_3$(4,4’-dcbpy) (1)

The synthesis was conducted according to a modified literature procedure [25]. ReBr(CO)$_5$ (0.30 g, 0.74 mmol, 1.0 eq.) was dissolved in ethylene glycol dimethyl ether (20 mL) in an argon atmosphere. 4,4’-dicarboxyl-2,2’-bipyridine (0.18 g, 0.74 mmol, 1.0 eq.) was added to the solution and stirred at 90 °C overnight. After cooling, the solvent was removed in vacuo and the residue was dissolved in minimal amounts of ethylene glycol dimethyl ether and added to hexane (100 mL) at 0 °C. The solid was then isolated via centrifugation and dried to afford the product, matching literature characterizations [25].

$^1$H NMR (400 MHz, 300 K, CD$_3$CN): $\delta$ (ppm) = 9.20 (d, $^3$J = 5.7 Hz, 2H), 8.95 (s, 2H), 8.06 (d, $^3$J = 5.7 Hz, 2H); ATR-IR (Re(CO)$_3$) = 1870, 1915 and 2021 cm$^{-1}$

Ru(bpy)$_2$(5,5’-dcbpy)Cl$_2$·6H$_2$O (2)

The synthesis was performed following a literature known procedure [31]. 5,5’-dicarboxyl-2,2’-bipyridine (0.064 g, 0.260 mmol, 1.27 eq.) and Ru(bpy)$_2$Cl$_2$ (0.10 g, 0.21 mmol, 1.00 eq.) were dissolved in ethanol/water (15 mL, 1/1 v/v) and refluxed for 25 h in an Ar atmosphere. After cooling, the solvent was removed in vacuo. The resulting powder was dissolved in water, filtered, and the filtrate was evaporated to give the crystalline product (0.120 mg, 0.143 mmol, 70% yield), matching literature characterizations [31].

$^1$H NMR (400 MHz, 300 K, DMSO-d$_6$): $\delta$ (ppm) = 8.87 (m, 4H), 8.80 (d, $^3$J = 8.3 Hz, 2H), 8.37 (d, $^3$J = 8.1 Hz, 2H), 8.19 (m, 4H), 8.00 (s, 2H), 7.79 (d, $^3$J = 5.6 Hz, 2H), 7.77 (d, $^3$J = 5.6 Hz, 2H), 7.58 (t, $^3$J = 6.5 Hz, 2H), 7.53 (t, $^3$J = 6.5 Hz, 2H)

UiO-66-NH$_2$(Zr)

The synthesis was modified from a literature procedure [32]. 2-aminoterephthalic acid (0.186 g, 1.03 mmol, 1.00 eq.) and ZrCl$_4$ (0.240 g, 1.03 mmol, 1.00 eq.) were dissolved in anhydrous N,N-dimethylformamide (DMF, 60 mL). To the mixture deionized water (0.19 mL) was added. The mixture was stirred at r.t. for 10 min and then transferred to a 100 mL Teflon liner before heating at 120 °C for 24 h to yield a yellow solid. The latter was isolated by centrifugation, washed with DMF (3×) and methanol (3×), immersed in methanol for 2 days with solvent exchange (2×), and dried at 80 °C in vacuo to yield UiO-66-NH$_2$(Zr) (0.244 g).

UiO-66(Zr)

The synthesis was modified from a literature procedure [33]. ZrCl$_4$ (0.100 g, 0.43 mmol) was dissolved in DMF (25 mL) in a Teflon autoclave by sonication. Then terephthalic acid (71.3 mg, 0.43 mmol) and distilled water (0.033 mL, 1.71 mmol) were added to the solution. The solution was heated for 24 h at 120 °C. After cooling, the MOF nanoparticles were isolated by centrifugation washed with DMF (3×) and methanol (3×), immersed in methanol for 2 days with solvent exchange (2×), and dried at 80 °C in vacuo to yield UiO-66(Zr) (0.112 g).
ZrO$_2$
Zirconium oxide nanoparticles (99.9%, 50 nm, monoclinic, nanopowder, 100 g) were purchased from GetNanoMaterials®.

**Molecular Complex Immobilization**
In a typical experiment, a 0.09 mM solution of 1 in acetonitrile (MeCN) and a 0.05 mM solution of 2 in MeCN (quantities for both varied according to the desired ratio, see SI, Table S1) were added simultaneously to the respective pristine host powder (10.0 mg). The supernatant was removed after 24 h, and the resulting powder was washed with pure MeCN ($3 \times 20$ mL). Then the powder was dried at 80 °C overnight.

### 3. Results

#### 3.1. Catalyst, Dye, and Host Characterization

The CRC 1 showed two characteristic UV-Vis absorption bands in MeCN, namely a $\pi$-$\pi^*$ transition at 310 nm as well as a metal to ligand charge transfer (MLCT) transition at 415 nm (molar absorption coefficient $\varepsilon = \sim 1100$ dm$^3$ mol$^{-1}$ cm$^{-1}$, Figure S1) with a reduction potential $E(1/1^{-})$ of $-0.94$ V vs saturated calomel electrode ($V_{SCE}$) [24,34]. The molecular dye 2 displayed two predominant UV-Vis bands in MeCN, a $\pi$-$\pi^*$ transition at 288 nm and also a $^1$MLCT at 450 nm ($\varepsilon = \sim 15000$ dm$^3$ mol$^{-1}$ cm$^{-1}$), allowing for strong visible light absorption (Figure S1). The latter yields the triplet excited state $^{3}$Ru(bpy)$_2$(5,5′-dcbpy)* with an excited state reduction potential $E(^32^*/2^{-})$ of 1.07 $V_{SCE}$, enabling reductive quenching from a variety of sacrificial electron donors (SEDs) [35,36]. With $E(2/2^{-}) \approx -1$ $V_{SCE}$, electron transfer from 2 to 1 is thermodynamically allowed in solution [37]. Besides, SED oxidation from the photoexcited CRC can also proceed to directly drive CO$_2$ reduction with $E(^12^*/1^{-}) = 1.26$ $V_{SCE}$ [36,38]. The synthesized MOFs, UiO-66(Zr) ($66$) and amine-modified UiO-66-NH$_2$(Zr) ($66$-$NH_2$), illustrated powder X-ray diffraction (PXRD) reflexes in close agreement with simulated patterns from single crystal structures. This was also the case for zirconium oxide monoclinic nanoparticles (ZrO$_2$), highlighting crystallinity for all host systems (Figure 2a). $N_2$ gas adsorption experiments revealed UiO’s characteristic permanent porosity, giving Brunauer-Emmett-Teller (BET) areas of $960 \pm 4$ ($66$-$NH_2$), $965 \pm 3$ ($66$), $12 \pm 1$ (ZrO$_2$) m$^2$ g$^{-1}$ (Figure S2). This striking discrepancy highlights the MOFs’ porosity compared to an inorganic bulk material. Particle imaging occurred with scanning electron microscopy (SEM), showing uniform topology and morphology within each sample (Figure 2b and Figures S3–S5). Importantly, analyzing particle sizes with histograms from SEM images gave average diameters of $55.2 \pm 9.1$ ($66$-$NH_2$), $48.6 \pm 7.0$ ($66$), and $48.8 \pm 6.2$ nm (ZrO$_2$) (Figure 2c). Such closely matching values enable studying intrinsic dye-sensitized host effects unbiased by size-induced discrepancies. The latter has been shown to have significant implications in heterogeneous colloidal catalysts [39], including MOF-based reactions [13,39], with smaller particles favoring reactant transport, increasing accessible active sites, and providing larger surface-to-volume ratio [39]. Further, particles in the $\sim 50$ nm size range are ideal as agglomeration was found to typically occur for pristine MOFs with $<50$ nm [39,40].

$66$-$NH_2$ was isolated as a light-yellow powder, 66 and ZrO$_2$ as white powders, and their corresponding solid-state UV-Vis spectra showed no light absorption at wavelengths above 440 nm in all cases (Figure 3a). Applying the Tauc formula for pristine hosts yielded direct optical bandgaps of 2.86 ($66$-$NH_2$), 3.78 ($66$), and 5.19 eV (ZrO$_2$), in-line with previously reported values, and suggesting exclusive dye excitation upon irradiation at higher wavelengths after dye sensitization (Figure S6) [21,41–43].
3.2. Host-Guest Photosystem Assembly

Following the pristine host characterization, we sensitized the materials with photocatalyst 1 and dye 2. This was achieved by soaking from a corresponding MeCN solution. The respective pristine host (10.0 mg in all cases) was immersed in a solution of 1 (and 2) in MeCN (quantities in Table S1) for 24 h, then washed with pure MeCN and dried. Molecular species are expected to load specifically at the surface for all materials, as the MOF pore sizes, channels, and windows (8.0 Å) are substantially smaller than both molecular diameters (1: 12.0 Å; 2: 14.5 Å) [10]. Surface anchoring was monitored via supernatant UV-Vis
spectroscopy, showing an absorption decay over time for all hosts, with stable values reached after 24 h (Figure S7). While 66-NH$_2$ and 66 provided comparable spectra, ZrO$_2$ samples illustrated a smaller absorption decrease, suggesting a lower loading per mass of host. Further, measuring the washing solution after 8 h revealed no absorption in all cases, indicating no leaching and stable complex anchoring to the host surfaces (Figure S7).

Average maximum molecular surface loadings of ~58, ~58, and ~32 nmol mg$^{-1}$ were obtained for 66-NH$_2$, 66 and ZrO$_2$-based assemblies, respectively, from inductively coupled plasma mass spectrometry (ICP-MS) measurements for Ru and Re content (see SM). The lower loading for ZrO$_2$-based assembly is in-line with the reduced absorption decay in the sensitizing solution compared to MOFs (Figure S7) and is rationalized by the higher crystal density of monoclinic zirconium oxide compared to porous UiO samples. Calculating surface areas and maximum coverages from SEM particle sizes (Figure 2b,c) with DFT-optimized 1 and 2 gave values close to experimental ICP-MS results (SM, pages S4–S5), supporting that maximum surface coverage is attained by immobilization from solution. Exact metal contents further allowed molecular loading and photosensitizer to catalyst ratio calculations (R, Equation (1), Tables S1–S4). For each host in turn, assemblies with an R value of 0.5 and 2.1 were synthesized (Tables S1–S4), i.e., a sample with double the molar catalyst quantity compared to the dye, and vice versa.

$$R = \frac{n(2)}{n(1)} = \frac{n(\text{Ru per mg host})}{n(\text{Re per mg host})} \quad (1)$$

1-loaded, as well as 1- and 2-loaded assemblies, denoted as Re-Host and ReRu-host, respectively, were analyzed by PXRD, dynamic light scattering (DLS), attenuated total reflectance infrared (ATR-IR) spectroscopy, and solid-state UV-Vis spectroscopy to further assess the impact of molecular anchoring.

PXRD data of the functionalized hosts (R = 0.5) showed matching reflex positions as pristine hosts, suggesting retained sample crystallinity after the anchoring process (Figure 2a). Importantly, DLS distributions revealed comparable hydrodynamic diameters of pristine and loaded hosts (~158, ~201, and ~284 nm for 66-NH$_2$, 66 and ZrO$_2$-based samples), highlighting that MOFs and nanoparticles do not agglomerate in MeCN solution and during molecular complex immobilization (Figure S8). The received hydrodynamic diameters are larger than actual particle diameters determined by SEM (Figure 2b,c) due to the hydration shell additionally detected in DLS measurements.

Solid-state UV-Vis spectroscopy of complex-containing samples displayed additional bands between 250 and 600 nm not present in pristine host spectra, matching 1 and 2 (Figure 3a). Further, ATR-IR spectra for all 1-loaded assemblies showed additional bands at 1917 and 2025 cm$^{-1}$, which are characteristic of the Re(CO)$_3$ moiety (Figure 3b). These support retained molecular catalyst integrity upon anchoring [11,44].

Finally, N$_2$ gas adsorption experiments were conducted to evaluate the porosity of the dye-sensitized MOF samples (Figure S2). ReRu-66-NH$_2$(R 2.1) and ReRu-66(R 2.1) demonstrated a significant reduction in uptake in respect to their pristine counterparts, however, with a non-zero BET area of 338 ± 1 and 360 ± 1 m$^2$ g$^{-1}$, respectively. This is in-line with previous studies, which showed that surface-anchored molecules of this size partially block outer MOF pores [10]. As for ZrO$_2$, ReRu-ZrO$_2$(R 2.1) illustrated negligible nitrogen adsorption.

3.3. Photocatalytic Experiments

The assemblies’ light driven catalytic activity was studied to investigate host material and dye sensitization effects. Standard colloidal heterogeneous conditions were host-guest samples (~1 mg) in MeCN (4 mL) and 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole (BIH, 340 mg, 1.5 mmol) or triethanolamine (TEOA, 0.2 mL, 1.5 mmol) as the SED. Such a significant excess of SED-to-photocatalyst (molar ratio > 25,000) was chosen to ensure that the electron supply is not limiting. BIH has been shown to give increased catalytic activity and stability compared to TEOA in homogeneous and heterogeneous photosystems [11,38,45]. The resulting sus-
pension was first saturated with CO$_2$ ([CO$_2$] $\approx$ 0.28 mol L$^{-1}$ for MeCN) [46], and then vigorously stirred under irradiation at 450 nm (Blue LED LXZ1 PR01 at 5.1 W). The potential evolution of H$_2$ and CO was analyzed via micro gas chromatography (GC) via reaction headspace sampling.

As a benchmark, homogeneous samples with pure catalyst, as well as dye and catalyst (ratio 2.0), were examined with both SEDs. For TEOA-based experiments, a solution of 0.5 µmol pure 1 showed selective CO formation under irradiation that plateaued after 15 min reaching 11.2 ± 0.3 TONs per Re catalyst (Table S5, TON calculation in SM). Additionally, 0.5 µmol 1 with 1.0 µmol of 2 resulted in a longer activity of 1.5 h before deactivation, while affording similar TONs as the PS-free experiments (Table S5). A comparable trend with higher absolute performances was observed with BIH as the SED, with 0.5 µmol pure 1 reaching TONs of 173 ± 7 over 3 h, and 0.5 µmol 1 with 1.0 µmol 2 yielding 182 ± 15 over 10 h. Next, 1-loaded colloids were investigated. All three host materials showed limited activity with TONs below 5 and 100 for TEAO and BIH, respectively (Table S5). Subsequently, ReRu-host hybrid systems were examined (Figure 4a,b, Table S5). In all cases, the detected activity increased from ReRu-ZrO$_2$, to ReRu-66, and finally to ReRu-66-NH$_2$ samples. When using BIH all host-guest systems reached significantly higher TONs than under homogeneous conditions whereas TEOA afforded similar or lower activities. Additionally, higher TONs compared to R = 0.5 samples were obtained with R = 2.1 with the highest activity (TON = 450 ± 15; BIH) reached for ReRu-66-NH$_2$(R = 2.1).

Control experiments performed without irradiation or a SED yielded no detectable product formation under homogeneous conditions as well as colloidal photocatalysis (Table S5). Furthermore, CO$_2$ was confirmed as the sole source of CO as $^{13}$C-labelled CO$_2$ produced only $^{13}$CO (Figure S9). Both experiments highlight the central role of each photosystem constituent in selective CO$_2$ photoreduction.

The effectiveness of incident photon conversion to CO was determined with apparent quantum efficiency (AQE, Equation (2)) measurements under the best-performing conditions (BIH and R = 2.1) with details on formulas and measurements provided in the SM (Figure S10, Tables S6 and S7). AQEs of 2.2 ± 0.2% (ReRu-ZrO$_2$(R 2.1)), 6.1 ± 0.2%
(ReRu-66(R 2.1)), and 8.0 ± 0.2% (ReRu-66-NH₂(R 2.1)) were obtained after the first 3.5 h of irradiation before decreasing reaction rates were observed, followed by deactivation.

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\text{AQE} \, \% = \frac{\text{Moles of CO generated per unit of time}}{\text{Number of incident photons per unit of time}} \cdot \left(\frac{\text{Number of required electrons}}{100}\right) \tag{2}
\]

4. Discussion

The obtained homogeneous photocatalysis data matches previous studies with pure 1 showing modest activity and fast deactivation with TEOA, illustrating its instability under photocatalytic conditions [47]. Upon adding 2, the apparent CO evolution rate decreases, while not yielding effective electron transfers to the catalyst, apparent from unchanged TONs. This is ascribed to a too large mean distance between the photosystem components, as shown previously where higher dye concentrations or multinuclear complexes were required [4]. BIH was the more effective electron source as it quenches the excited state 32* more efficiently and detrimental TEOA radicals limit molecular dye/catalyst stability [11,45,47].

Comparing homogeneous results with 1 to heterogeneous 1-loaded colloids reveals a drop in performance for the latter independent of the SED. Similar performance decreases have been previously observed upon immobilizing fac-[ReCl(CO)₃(bpy)]-derivatives on SiO₂ or TiO₂ for photocatalysis and were assigned to reaction environment change and mass transport limitations [29,48]. This motivates dye-sensitization to drive efficient electron transfers to the catalyst units.

Upon providing surface proximity for 1 and 2, exergonic electron transfers from the photosensitizer to the catalyst can occur (relying on statistical molecular distribution), allowing rapid CO₂ reduction and improved performance [10,34]. This working principle highlights the advantages of using dye-sensitized materials, as pure host-photocatalyst assemblies result in activity decreases. For all ReRu-host systems, an increased dye-to-catalyst ratio R yielded higher TONs as excess dye increases the probability of each CO₂ reduction catalyst being in proximity to a photosensitizer [11]. Distinct differences were recorded between the three anchoring materials, with the performance increasing from ReRu-ZrO₂ (TON ~331, R = 2.1, BIH), to ReRu-66 (~395), to ReRu-66-NH₂ (~450) (Figure 4a,b). As all pristine host materials are photosilent at the irradiation wavelength of 450 nm, exhibit similar particle size, and bear similar dye-to-catalyst ratios, this activity trend does not stem from a discrepancy between direct host light absorption (Figures 2c, 3a, 4a,b and S6).

To gain more insights into the difference in the catalytic performance, we examined the reduction and oxidation potentials of the ground and excited molecule states, as well as the Zr-based materials’ conduction band energy levels. Reductive quenching, i.e., photoreduction of the PS from the SED followed by electron transfer to the CRC, is the main electron pathway in DSP systems with non-conducting hosts. As the scaffolds’ conduction band (CB) edges were previously evaluated at −3.3 eV (66-NH₂, −0.9 V SCE) [49], −3.1 eV (66, −1.1 V SCE) [50], and −2.1 eV (ZrO₂, −2.1 V SCE) [51], the triplet state 32* (−3.1 eV, −1.1 V SCE) is potentially able to inject electrons into the CB of 66-NH₂ through oxidative quenching, followed by regeneration from the SED. This could enable the MOF to act as a solid-state electron mediator, allowing electron hopping to distant catalyst units as E(1/1−) = −3.3 eV (−0.9 V SCE; Figure 5a,c). Electron hopping in MOFs is a topic of ongoing interest featuring reports of tailor-made MOFs with intrinsic conduction mechanisms and photoinduced electron injection by a Ru dye into a UiO material [52–54]. Although less thermodynamically favored, a similar electron cascade should also be possible with 66-based DSM especially as Ru dyes have been reported to perform electron injection from unrelaxed states [55]. The difference in band positions between 66-NH₂ and 66 has been assigned to the amine-functionalized linkers, effecting a change of the sp² bonding in the aromatic carbon ring [56]. In contrast, oxidative quenching is prevented for ZrO₂-based DSP due to the high CB energy value (Figure 5a). This implies that the reductive quenching...
cascade is the sole viable electron cascade for catalysis, potentially limiting the final activity of the system in comparison to MOF-based systems [23].

Figure 5. Proposed photocatalysis working principle showing advantages of dye-sensitized MOFs over ZrO$_2$. (a) Electrochemical potential representation of TEOA, BIH, the dye 2, and the catalyst 1 to produce an efficient directional electron transfer. Conduction bands of 66-NH$_2$, 66, and ZrO$_2$, allowing for electron hopping for MOFs. Values given in V referenced to SCE and eV referenced to the vacuum level [49–51]. (b) CO$_2$ adsorption isotherms at 298 K for ReRu-66-NH$_2$(R 2.1), ReRu-66(R 2.1), and ReRu-ZrO$_2$(R 2.1). (c) Schematic representation of dye- and catalyst-sensitized 66-NH$_2$ under photocatalytic conditions, yielding increased performance due to electron hopping, intrinsic porosity-based CO$_2$ uptake, and interactions between polar linker NH$_2$ groups and CO$_2$.

As photocatalysis proceeds in colloidal solution, the local CO$_2$ concentration available for catalyst centers could impact the final activity. Despite maximum molecular loading on the scaffolds’ surfaces, MOFs still provide a certain permanent porosity (Figure S2). To determine implications for photocatalysis, CO$_2$ gas adsorption experiments at room temperature were conducted with the three hosts (Figure 5b). As a non-porous crystalline solid, ReRu-ZrO$_2$ is not able to adsorb carbon dioxide within its structure and is therefore reliant on the diffusion of available CO$_2$ in solution. This differs for MOFs, as their intrinsic porosity could allow gas uptake when the reaction solution is saturated with CO$_2$ prior to irradiation. Noteworthy is that ReRu-66-NH$_2$(R 2.1) shows markedly higher uptake than ReRu-66(R 2.1), despite comparable N$_2$ adsorption isotherms (Figures 5b and S2). This has been previously observed and attributed to interactions/reactions between the polar linkers’ amine groups and carbon dioxide (Figure S6) [57,58].

Thus, 66-NH$_2$ provides an increased local CO$_2$ concentration available during the course of photocatalysis, thereby reducing diffusion limitations, as well as potentially activating CO$_2$ [59]. This is potentially shown by increased turnover frequencies (TOFs) from ZrO$_2$-based, to 66-based, to 66-NH$_2$-based assemblies (Figure S10). Such reactant-host-guest synergies are a unique benefit of DSM over conventional DSP (Figure 5c), yielding higher performances. This increase in efficiency is also apparent from obtained AQEs which improve from 2.2 ± 0.2% for ReRu-ZrO$_2$(R 2.1) to 8.0 ± 0.2% for ReRu-66-NH$_2$(R 2.1) under ideal conditions (Tables S6 and S7), allowing incident photons to be converted more
effectively to CO. The obtained performance and TONs for ReRu-66-NH$_2$ are comparable to state-of-the-art dye-sensitized semiconductors with Re-based molecular catalysts. For instance, dye-sensitized TiO$_2$ nanoparticles with ReCl(CO)$_3$(bpy)-derivatives reached maximum TONs between 165 and 570 in DMF with BIH, depending on irradiation conditions [26,27]. This system showed an AQE of 2.1% at 436 nm [27], and a recent report with organosilica nanotubes and anchored 1 and 2 yielded AQEs between 0.4% and 15.1% at 450 nm, depending on reaction conditions [60]. Accordingly, our results are well within this benchmark range for DSP with colloidal host-guest systems.

5. Conclusions

Herein we designed a model study to compare dye-sensitized metal oxides to metal-organic frameworks for colloidal photocatalytic CO$_2$ reduction. Thus, monoclinic ZrO$_2$ was evaluated against Zr-based MOFs 66 and 66-NH$_2$, all with surface co-immobilized molecular carbon dioxide reduction photocatalyst fac-ReBr(CO)$_3$(4,4′-dcbpy) and photosensitizer Ru(bpy)$_2$(5,5′-dcbpy)Cl$_2$. Photocatalytic CO$_2$-to-CO performance increased from ZrO$_2$, to UiO-66, and UiO-66-NH$_2$, respectively. While the former provides fixed proximity for the molecular photosystem constituents, the studied MOF scaffolds offer additional synergistic host properties. Particularly 66-NH$_2$ could enable host-mediated electron hopping, paired with uniquely increased CO$_2$ adsorption capacity from its permanent porosity and NH$_2$-CO$_2$ interaction. These combined phenomena enable an AQE of up to 8% for the studied DSM.

Overall, these findings highlight how DSM can combine multiple functionalities to drive photocatalysis and provide tunable material composites. Our results competitively position dye-sensitized MOFs as a hybrid material for efficient solar fuel production, which could be further exploited with alternative optimized components toward higher performance in the future.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/en14144260/s1: Detailed overview on all synthetic procedures, the analytical instrumentation and characterization methods, supporting calculations, as well as additional measurement data.

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