

Calix[4]arene-based molecular photosensitizers for sustainable hydrogen production and other solar applications

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This review collects the most representative literature reports on the use of calix[4]arene-based molecules as components, namely photosensitizer dyes, in solar devices, including photovoltaics (dye-sensitized solar cells, DSSC), hydrogen photocatalytic and photoelectrochemical generation from water and sunlight, and CO₂ photoreduction. Calix[4]arenes are versatile and easily obtainable scaffolds to be integrated with solar device molecular components either as electron-donor groups in π -conjugated dyes or as host-guest moieties to favor intermolecular interactions. Their beneficial role has been exploited to enhance photovoltaic, hydrogen production, and CO₂ reduction performance, paving the way to a new class of molecular active components for next generation solar devices.

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Introduction

In the urgent search for sustainable energy production, sunlight is a very promising energy source that can be

exploited to produce both electricity and the so-called ‘solar fuels’ using different devices for different applications [1–4]. In particular, photovoltaic panels can provide electricity, while photocatalysis (PC) and photoelectrochemical cells (PEC) are valuable techniques to directly produce, under sunlight irradiation, ‘green’ hydrogen from water via water splitting or carbon-based fuels and chemicals via CO₂ reduction [5–8]. A mandatory requirement for these devices is their ability to absorb as many photons as possible in order to trigger the subsequent catalyzed processes. Therefore, a material able to efficiently absorb solar radiation, in particular, across the visible range, is compulsory. A straightforward solution to efficiently extend the absorption to the visible range is to use a semiconductor (SC) sensitized by a proper molecular sensitizer. Typically, TiO₂ is the most common choice as SC, and a variety of organic and organometallic molecular sensitizers have been proposed in the last years, offering wide visible absorption and potentially low-cost for the final device [9]. Such approach is used in Dye-Sensitized Solar Cells (DSSC) [10], dye-sensitized PC (DS-PC) [11,12] and dye-sensitized PEC (DS-PEC) [13,14]. Metal-free organic dyes have attracted much attention thanks to their easily tailorable structure that allows a better fitting of the solar spectrum, low toxicity, absence of expensive rare elements, and easy synthesis with high batch-to-batch reproducibility and potential for scale-up. One of the most common approaches is the use of donor–acceptor molecules (D– π –A), composed by a donor electron-rich part (D) connected by a π -conjugated bridge to an acceptor electron-poor moiety (A), which also embeds an anchoring group needed to covalently bind the dye to SC surface. Multibranched or multifunctional structures can be prepared to increase light-harvesting properties and/or strengthen bonding to the TiO₂ surface. Very interestingly, in the last years, calix[4]arene-based sensitizers have been investigated for solar devices. Calix[4]arenes are versatile phenol-formaldehyde macrocycles easily obtainable in high yields from inexpensive starting materials and easily functionalizable on the phenol OH groups and on the aromatic positions para-to the OHs. By introducing on the OH groups alkyl groups larger than ethyl, the calix[4]arene scaffold can be blocked in one of four

different conformations (*cone*, *partial cone*, *1,2-* and *1,3-alternate*) identified by the reciprocal orientation of the aromatic rings [15]. In the *cone* structure, the four rings are *sin* oriented and slightly tilted outward, defining a truncated cone shape endowed with a permanent cavity. Thanks to the combination of the aromatic cavity with the possibility of attaching additional binding sites on both rims, calix[4]arenes have been extensively exploited in the field of Supramolecular Chemistry as receptors for cations, anions, neutral molecules, or as building blocks for the preparation of functional self-assembled architectures [16]. However, despite their success, their scope is hardly limited to the field of molecular recognition. Indeed, the ease of introduction of up to eight moieties in well-defined positions and orientations makes the calixarene macrocycle an ideal molecular scaffold to obtain complex systems with specific properties [17]. In particular, the functionalization of the calix[4]arene with multiple copies of the same or different dyes allowed the synthesis of multichromophoric systems for the study of energy/charge transfer phenomena [18–20], fluorescent sensors [21], OLEDs [22] and fluorescent smart materials [23], as well as metal-free organic sensitizers in solar technologies [11,24]. For this last purpose, calix[4]arene-based molecules offer several advantages. First of all, the calix[4]arene *cone* conformation could hinder detrimental dye aggregation, which leads to excited state self-quenching, and thus, lower photocurrents and amounts of generated products. Typically, two or more light-harvesting molecular units are connected to the calix[4]arene cone, thus offering higher molar extinction coefficients for the multidyed integrated system without decreasing dye loading, and usually a more efficient electron transfer from the dye to the SC due to preferred geometry with respect to the SC surface. Each sensitizing unit has its own anchoring group, so a stronger bond to the surface is expected. Finally, calix[4]arenes are highly photostable and thermostable that is crucial for DS-PC, DS-PEC, and DSSC. Calix[4]arene derivatives are also being deeply investigated in conjunction with titanium-oxo clusters, with good results in their stabilization (this type of cluster is easily hydrolyzed) and in widening their absorption spectrum to the visible region [25]. In 2015, Both M.J. Blesa et al. and C.-Y. Su et al. first reported different calix[4]arene-based molecules for energy application. The former used it as a scaffold [26] and the latter as the donor part of a multibranching D- π -A dye [27]. In 2016, a monolayer of calix[4]arenes derivatives was also successfully exploited to suppress charge recombination and minimize back electron transfer between N-719 dye and the CB of TiO₂ [28].

In this paper, the use of calix[4]arene-based molecules as photosensitizers for DSSC, DS-PC, and DS-PEC will be reviewed, focusing attention on the most interesting

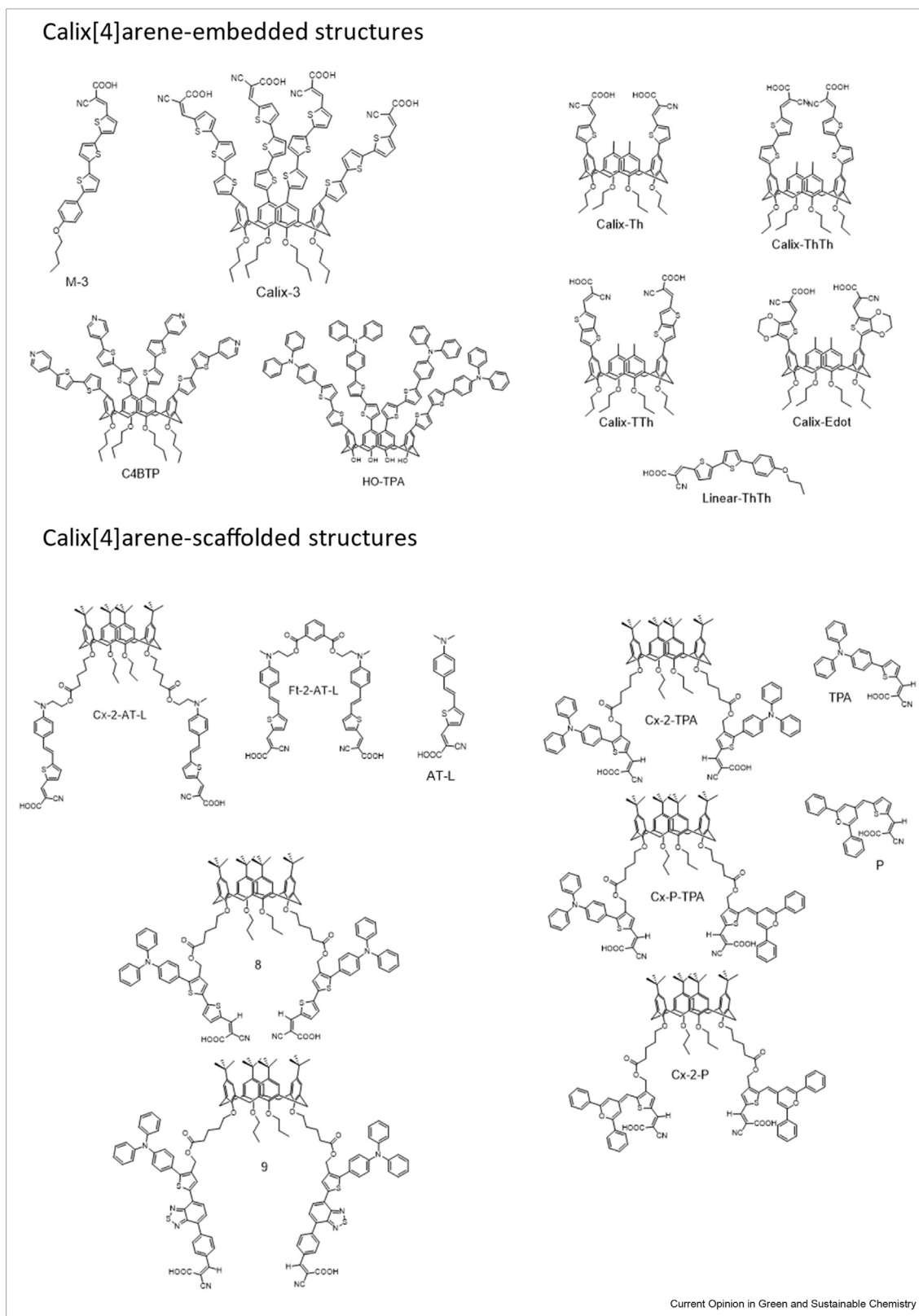
results reported in the literature in the last four years. More precisely, we will distinguish two types of calix[4]arene-based sensitizers: (a) calix[4]arene-embedded structures, where the calix[4]arene moiety is part of the D- π -A framework, and (b) calix[4]arene-scaffolded structures, where the calix[4]arene moiety acts as an external (covalently bonded) scaffold of D- π -A units. The calix[4]arene-based systems herein described are depicted in Figure 1.

Applications in electricity photogeneration: Dye-sensitized solar cells (DSSC)

In the last four years, Prof. Blesa's group published other three sets of sensitizers where calix[4]arenes were used as scaffolds [29–31]. All these dyes were based on *p*-*tert*-butyl-calix[4]arene that should hinder aggregation between D- π -A portions of the dye. In the first work, the investigated sensitizers consisted of a donor group based on triphenylamine (TPA) and/or 4H-pyranilidene (P) moieties, a thiophene ring as a heteroaromatic π -conjugated spacer, and a cyanoacetic acid as acceptor group [29]. The comparison among these molecules aimed to verify if a wider solar spectrum absorption (as in Cx-P-TPA, bearing the two different donor groups) would correspond to a higher DSSC efficiency. The presence of the P group offered higher values of both short-circuit current density (J_{sc}) and Fill Factor (FF), ensuring a higher efficiency for Cx-P-TPA and Cx-2-P with respect to Cx-2-TPA. The addition of a co-adsorbent like chenodeoxycholic acid (CDCA) worsened the performance of calixarene-based dyes, likely due to limited adsorption of sensitizer on the TiO₂ surface. The best results were obtained by Cx-2-P cells that showed the highest J_{sc} , and Incident photon-to-current efficiency (IPCE) measurements showed the widest absorption in the visible region, with a 50% efficiency from 400 to 700 nm. Electron lifetimes calculated from electrochemical impedance spectroscopy (EIS) measurements suggested that the calix[4]arene scaffold reduced the recombination process on the TiO₂ surface, thus increasing the V_{oc} .

Cx-2-TPA was then further functionalized, changing π -spacers: from the thiophene (Cx-2-TPA) to a bi-thiophene (8) and to a benzothiazole coupled to a phenyl ring (9) to extend the range of the absorption spectrum [30]. The best efficiency was recorded by cells sensitized with 9, notwithstanding the lower dye-loading, and IPCE curves confirmed the broadest spectrum for this dye, absorbing up to 650 nm. A further increase in J_{sc} , and thus in the efficiency, was observed when increasing TiO₂-layer-thickness from 6 to 13 μ m. EIS measurements revealed that the trend of electron lifetimes was Cx-2-TPA > 9 > 8, suggesting a more efficient hindering of the recombination processes on the TiO₂ surface in the devices based on Cx-2-TPA. All these cells proved to be very stable over

Figure 1



Calix[4]arene-based structures described in this review.

time, with a 98–100% retention of the starting values after a 500-h-long light soaking.

Most lately, Blesa et al. decided to test a different arrangement of the calix[4]arene moiety in the dye, connecting the scaffold to the D part of the D– π –A units rather than the π -bridge [31]. An *N,N*-dialkylaniline was used as an electron donor and thiophene as a π -spacer. The flexible calix[4]arene scaffold (**Cx-2-AT-L**) was also compared to a rigid isophthalic acid one (**Ft-2-AT-L**) and to the linear dye (**AT-L**). Also, in this case, two different TiO₂ thicknesses were tested, and the best results were recorded when using the thicker 13 μ m-layer, thanks to a higher dye-loading, leading to a 6.3% best efficiency value for **Cx-2-AT-L**. IPCE spectra showed a broad absorption up to 700 nm, reflecting the high recorded J_{sc} . The 1000-h long-term stability test highlighted the superior stability of **Cx-2-AT-L** sensitized cells that still retained 100% of the efficiency at the end of the experiment (Figure 2). Charge recombination resistance (R_{rec}) at the TiO₂/dye/electrolyte interface measured by EIS decreased in the order of **Cx-2-AT-L** > **Ft-2-AT-L** > **AT-L**. This suggested that the use of calix[4]arene as a scaffold could inhibit the injected electron recombination with the redox couple, forming a kind of blocking layer between TiO₂ and the electrolyte.

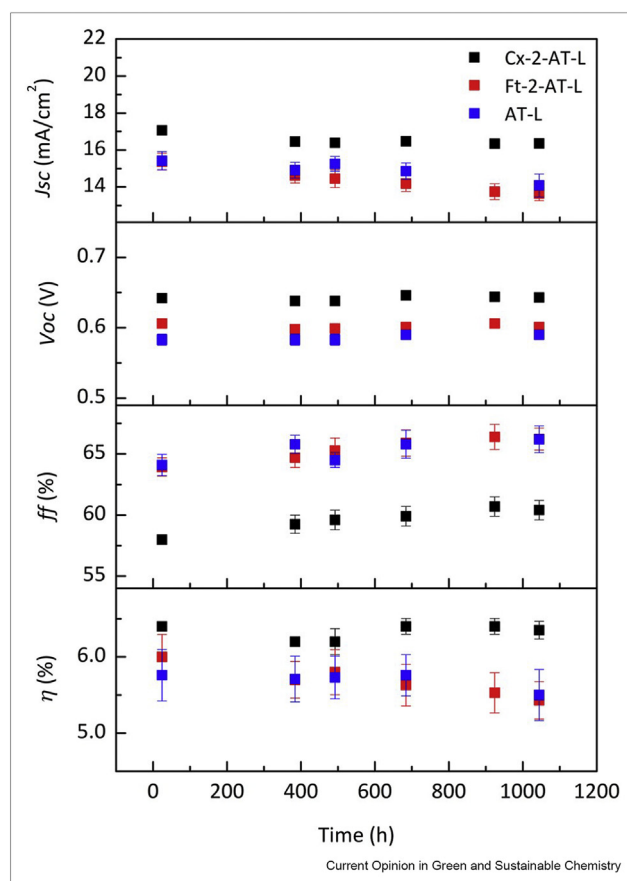
Applications in ‘green’ hydrogen photogeneration from water and sunlight: DS-PC and DS-PEC

Besides DSSCs, much attention has been devoted in the last years to organic sensitizers for photocatalytic applications. It must be underlined that, when presenting photocatalytic H₂ production results, the direct comparison of H₂ production rates does not provide a reliable assessment about the performance of various photocatalysts, considering that the experimental conditions adopted in different works can significantly differ (in terms of reactor geometry, light power, amount of catalyst, type and concentration of the sacrificial agent, etc.). Therefore, photocatalytic performance can be assessed only by comparing other parameters such as apparent quantum yield (AQY), which takes into account the number of photons actually absorbed in the experiments [6].

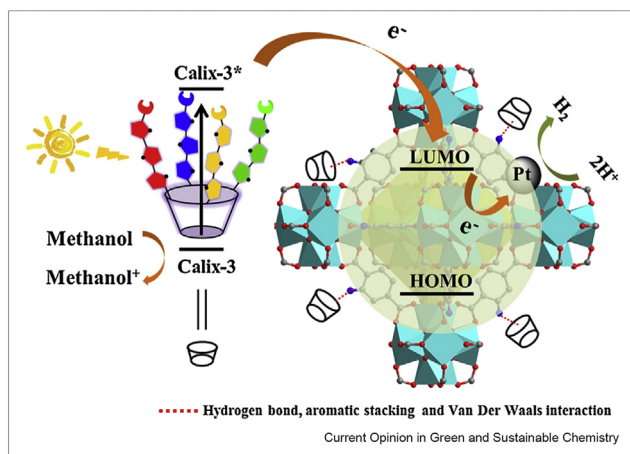
Regarding the use of calix[4]arenes as sensitizers, the group of C.-Y. Su has been working on calix[4]arenes derivatives for photocatalytic water splitting, and lately, CO₂ reduction for several years up to now. In 2017, the molecule **Calix-3**, previously reported for DSSC, was used as a sensitizer for a Zr-containing metal-organic framework (MOF) embedded with Pt particles (Pt@UiO-66-NH₂), Figure 3 [32]. It consisted of a cone-calix[4]arene dye with four D– π –A units, so it could offer a good light-harvesting, and with four

anchoring points, strong interaction with the MOF, and high stability. The performances of this dye were also compared to those of the linear analog, namely **M-3**. After optimizing the Pt loading, different dye loadings were investigated, and the best performance was obtained from the sample with an intermediate dye concentration, 200 ppm, with apparent quantum yields determined to be 2.3% at 420 nm and 1.8% at 450 nm. Further increase of the dye loading resulted in a lower hydrogen production activity, ascribed to a loss of light harvesting and reduced effective electron transport. Also, the linear **M-3** dye was tested, both with the same dye loading of **Calix-3** (200 ppm) or with a 4-fold dye loading (800 ppm), which should correspond to the same number of light-harvesting units. In both cases, the catalytic activity of **M-3** was lower than **Calix-3**, suggesting that the latter sensitizer had not only a better light-harvesting ability but also an improved effective electron transfer between the dye and the MOF.

Figure 2



Temporal evolution of photovoltaic parameters of devices prepared with dyes **AT-L**, **Cx-2-AT-L**, and **Ft-2-AT-L**. Reprinted from Dyes and Pigments, 182, I. Duerto et al., Difunctionalized dyes for DSSCs based on two different scaffolds: p-tert-butylcalix[4]arene or isophthalic acid, 108530. Copyright (2020), with permission from Elsevier.

Figure 3

Proposed mechanism of photocatalytic H₂ production over Calix-3 sensitized Pt@UiO-66-NH₂ under visible light irradiation. Reprinted from Applied Catalysis B: Environmental, 206, Y.-F. Chen et al., Calix[4] arene-based dye-sensitized Pt@UiO-66-NH₂ metal-organic framework for efficient visible-light photocatalytic hydrogen production, 426–433, Copyright (2017), with permission from Elsevier.

The same dye was then reported as the sensitizer of a robust hybrid material, covalently linked to TiO₂ (**Calix-3-TiO₂**), synthesized with a facile sol-gel method [33]. Besides the advantages offered by **Calix-3**, this hybrid material could also count on micro/mesoporous structures, large surface areas, and abundant active sites for the reactions, thus enhancing light harvesting through multireflection in the pores. With an optimized 7.5 wt% dye-doping amount, the system reached an AQY of 2.89 at 450 nm. Pt/**Calix-3-TiO₂** was also very stable in long-term cycling compared to the corresponding dye-sensitized system, with a Turnover Number (TON) of 16,927 after a 50-h-long test.

In the same year, C.-Y. Su et al. published another calix[4] arene-based hybrid material with a different dye, **HO-TPA**, where the calix[4] arene moiety was used as an acceptor portion of the molecule, in combination with a triphenylamine group as a donor and an oligothiophene as a spacer [34]. This material was tested both for water splitting (with Pt nanoparticles) and for CO₂ reduction to CO (with **ReP** co-catalyst [35]). With an optimized 5 wt% dye-doping, **HO-TPA-TiO₂** showed a hydrogen generation rate of 3.7 mmol g⁻¹ h⁻¹, almost twice larger than that of the analogous dye-sensitized TiO₂ system. The gas production was very stable over time (TON = 8120 after 75 h). When using the Re catalyst, the hybrid **ReP/HO-TPA-TiO₂** was tested for CO evolution, with a TON of 300 after 25 h, a better result than the analogous dye-sensitized system, suggesting a robust coordination linkage between the organic and inorganic components of the hybrid system. For improving the photocatalytic

activity, another test was carried out adding triethanolamine (TEOA), which allows CO₂ trapping to Re(I) complexes. In this way, a remarkable TON of 534 after 26 h was recorded, with a corresponding Turnover Frequency (TOF) of 20.5 h⁻¹, which is the highest value so far reported for hybrid catalytic systems.

In 2020, J.-M. Liu et al. reported another hybrid material based on a different calix[4] arene-based dye **C4BTP** [36]. The main innovation is represented by replacing the traditional anchoring group, the carboxylic acid, with a pyridyl group, avoiding ester hydrolysis in an aqueous environment. **C4BTP** featured a tetrabutyoxy-calix[4] arene moiety as a donor, four linked bithiophene as π -spacers, and four 4-pyridyl end-groups as acceptors. With a sol-gel synthesis, the hybrid **C4BTP-TiO₂** material was prepared and then used with Pt nanoparticles for H₂ generation and with **ReP** catalyst for CO₂ reduction. Also, in this case, the H₂ evolution rate was much higher for the hybrid system than for the dye-sensitized analog. A TON of 12,981 after 50 h was recorded. When using Re as a catalyst, a TON of 112 after 25 h for selective CO production was obtained.

Finally, very recently, our group published a series of calix[4] arene-based sensitizers where the calix[4] arene moiety acted as a donor group in two D- π -A branches. The cyanoacrylic acid was chosen as an acceptor/anchoring group while different thiophene-based π -spacers were investigated [37]. The dyes were absorbed on a Pt-functionalized TiO₂ nanopowder and tested in a photocatalytic setup. The optical properties, as well as the hydrogen generation efficiency, were similar for all of the dyes, except for **Calix-ThTh**, for which an AQY of 0.138% under irradiation around 450 nm was recorded. The larger hydrogen evolution rates with respect to that of its linear counterpart **Linear-ThTh** was explained based on host-guest interaction between the calix[4] arene ring and the protonated TEOA. The gas generation photocatalytic activity was higher as the π -conjugated spacer length increased, indeed **Calix-ThTh**, the dye with the longest π -spacer, offering the best performance, followed by **Calix-TTh**, while shortest **Calix-Th** and **Calix-EDOT** performed worse. Therefore, we concluded that a longer spacer resulted in a more efficient interaction between the sacrificial electron donor (SED) and the dye since there is more space between the macrocycle and the Pt/TiO₂ surface to accommodate the SED.

Calix[4] arenes have been recently tested also in DS-PEC devices. A first example has been published by Yildiz et al., who proposed a thiol/carboxylic acid functionalized SH-calix[4] arene-COOH as a coating for a gold electrode photoanode and then sensitized by a cyanine dye attached to IrO₂ nanoparticles as a catalyst [38]. The conjugated structure of the calix[4] arene unit

served as a suitable matrix for electrons to reach the electrode, avoiding charge recombination.

Most recently, J.-M. Liu et al. used the previously described **Calix-3**, together with other two dyes (**Calix-1** and **Calix-2**), to sensitize a TiO₂ photoanode [39], in combination with a well-known water oxidation catalyst (WOC) Ru(bda) (pic)₂ [40] loaded on a Nafion membrane over the photoelectrode. Chronoamperometry (CA) and IPCE measurements showed the trend: WOC/**Calix-3**/TiO₂ > WOC/**Calix-2**/TiO₂ > WOC/**Calix-1**/TiO₂, with **Calix-3** giving an initial photocurrent density of ca. 300 μA/cm² and an IPCE max value of ca. 9.0% at 365 nm. Oxygen generation ability was evaluated by measuring the Faradaic efficiency (FE) with the collector-generator technique [41] (FE = 82%). The superior performance of **Calix-3** could be attributed to its better light-harvesting ability, best intramolecular charge transfer property, and to its highest oxidation potential that allowed a better WOC activation.

Conclusions

In conclusion, calix[4]arene-based molecular dyes are a promising class of photosensitizers for solar applications, in particular DSSC, hydrogen photogeneration, and CO₂ reduction. The calix[4]arene scaffold introduces additional relevant features such as unconventional donor groups in donor–acceptor dyes and host properties to be exploited for ancillary functions. In this review, we have seen that the introduction of the calix[4]arene is useful to induce beneficial effects for improved photovoltaic efficiencies, hydrogen production, and CO₂ reduction. We think that the judicious use of calix[4]arene-based molecular photosensitizers can play an important role, in particular with reference to the interfacial relationships between the different components of the device, thus favoring intermolecular interactions and charge transfer and, eventually, device performance.

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Authors contributions

Chiara Liliana Boldrini: Writing - Review & Editing, **Norberto Manfredi:** Writing - Review & Editing, **Tiziano Montini:** Writing - Review & Editing, **Laura Baldini:** Conceptualization, Writing - Review & Editing, **Alessandro Abboto:** Conceptualization, Writing - Review & Editing, **Paolo Fornasiero:** Conceptualization, Writing - Review & Editing

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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