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Multibranched calix[4]arene based sensitizers for efficient photocatalytic hydrogen production

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Dedicated to Professor Franco Cozzi on the occasion of his 70th birthday.

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Abstract: In the field of direct production of hydrogen from solar energy and water, photocatalytic methods hold a great potential especially when metal-free molecular components are preferred. In this work, we have developed a new class of calix[4]arene-based molecular photosensitizers to be used as antenna systems in the photocatalytic production of hydrogen. The structure of the dyes has a typical donor-π-acceptor molecular architecture where a calix[4]arene scaffold is used as an embedded donor. The new materials have been fully characterized in their optical, electrochemical and photocatalytic properties. The properties conferred by the calix[4]arene donor afforded twice larger performances compared to the corresponding linear system though showing similar quantitative optical properties. The new molecular design paves the way to a new strategy for photocatalytic hydrogen production where the calix[4]arene scaffold can afford more efficient systems, and can offer the potential for host-guest supramolecular effects.

To favour the transition from fossil fuels to renewable energies, a new paradigm in energy production must be developed.[1] Solar energy can be easily used to produce electricity and the emerging technologies of electricity storage are growing to satisfy the increasing demands.[2] Among them, a way to satisfy the needs of solar energy storage is the direct conversion of solar radiation into valuable chemicals and fuels through water splitting or carbon dioxide reduction.[3] One of the most investigated methods to convert sunlight into chemicals is the photocatalytic approach.[3a, 3c, 4]

In a photocatalytic process, a semiconductor (SC, e.g. TiO_2) absorbs light and transfer the excited electron from its conduction band (CB) to the catalyst (ie.g. Pt) where the production of solar chemicals actually happens.[5] Critical requirements for a proper SC are absorption of a large portion of the visible light, correct alignment of energy levels with respect to those of the catalyst, and stability under working condition.[6] While the last two conditions are easily satisfied by a large number of SCs, the light absorption is always a tough compromise.[7] The easiest way to modify the absorption spectrum of a SC is its sensitization to the visible portion of sunlight using an organometallic or an organic dye-sensitizer.[8] The energetic requirements in dye-sensitized photocatalysis (DS-PC) are similar to those of dye-sensitized solar cells (DSSCs). Indeed, many DSSC sensitizers can be successfully used in DS-PC as well. One of the detrimental losses of charges occurring in the photoactivated process is the recombination taking place on or close to the SC surface (dye-dye, dye-SC, dye-medium).[8a, 8b] In the last years, many researchers have investigated several types of sensitizers improving photocatalytic performances through molecular engineering which in turn optimizes light harvesting, stability, and surface interaction.[8b, 8d, 9] A common method to reduce intermolecular dye-dye recombination is the use of passive co-adsorbents but their presence also limits the dye-loading on the surface and, thus, the overall light harvesting capacity of the sensitized material. The use of specific molecular geometries given by proper building blocks can be also successfully exploited.

Calix[4]arenes are synthetic macrocycles widely exploited not only as hosts[10] but also as scaffolds for the construction of functional molecular[11] or supramolecular complex structures.[12] Both their rims can be easily functionalized and their conformation can be locked in the cone structure by the introduction of alkyl chains larger than ethyl. Moreover, the functionalities anchored at the upper rim of a cone calix[4]arene are oriented in the same direction and kept at a distance dictated by the geometry of the scaffold. Recently, the use of calix[4]arene based dyes in DSSC[13] and in DS-PC have been reported with encouraging results.[14]

In this manuscript we present the study of a series of new multibranched calix[4]arene based dyes in DS-PC hydrogen production. The new donor-π-acceptor (D-π-A) dyes are depicted in **Figure 1** and have been designed using a calix[4]arene scaffold as both a donor and templating moiety. The D-π-A structure, and corresponding optical and electronic properties, have been tuned upon varying the π-spacer. The common cyanoacrylic acid has been selected as the acceptor/anchoring group. The peculiar structure of the donor scaffold has been exploited to design a bis-dye sensitizer where the two D-π-A branches are not connected through a π-conjugated link. The photocatalytic activities of the calix[4]arene dyes have been tested and the linear dye, corresponding to the best performing calix[4]arene system, was taken as a reference, showing that the use of the calix[4]arene scaffold induced a significant enhancement of the PC performances.
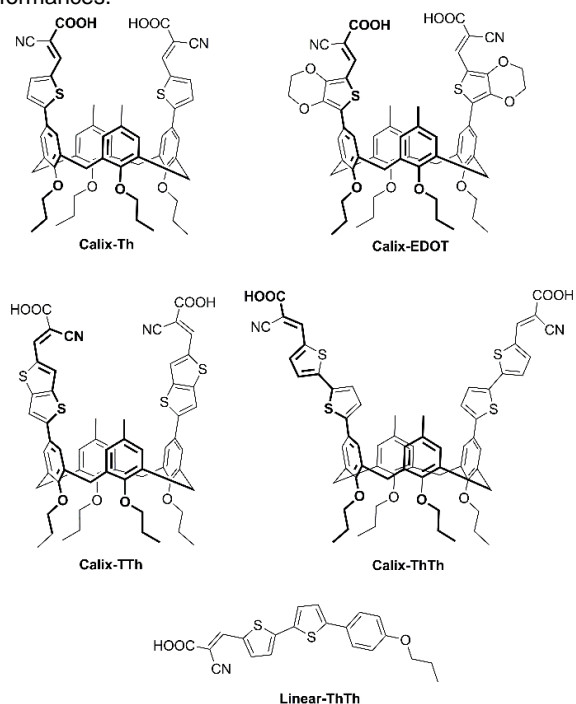

Figure 1. Calix[4]arene-based dyes and corresponding linear reference investigated in this work.

The calixarene derivatives have been synthesized according to a modification of the procedure previously reported in the literature and depicted in Scheme S1 and Scheme S2 in Supporting Information.[13b] 5,17-diformyl-25,27-dipropoxycalix[4]arene[15] has been submitted to Clemmensen reduction to obtain the corresponding 5,17-dimethyl-25,27-dipropoxycalix[4]arene. After alkylation reaction with iodopropane and subsequent bromination with NBS, the 5,17-bromo-11,23-dimethyl-25,26,27,28-tetrapropoxycalix[4]arene (**Calix-Br**) has been obtained. The **Calix-Br** has been submitted to a Suzuky-Miyaura coupling with the corresponding boronic derivatives. The commercially available functionalized π-spacers were used to synthesize the precursors aldehydes in good yield for **Calix-Th** and **Calix-ThTh**. In the case of **Calix-TTh**, the dibromocalixarene was first submitted to the Suzuky-Miyaura coupling with 4,4,5,5-tetramethyl-2-(thieno[3,2-*b*]thiophen-2-yl)-1,3,2-dioxaborolane,[16] and the product submitted to a Vilsmeier-Haak reaction to afford the intermediate aldehyde. Finally, in the case of **Calix-EDOT** the dibromocalixarene was first borylated by reaction with 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) and the boron derivative subsequently submitted to the Suzuky-Miyaura coupling with 7-bromo-2,3-dihydrothieno[3,4-*b*][1,4]dioxine-5-carbaldehyde. All of the precursor aldehydes have been submitted in the last step to a Knoevenagel condensation with cyanoacetic acid using piperidine as a base.

The molecules were characterized by FT-IR spectroscopy (see Supporting Information). The optical characterization of the calix[4]arene based dyes was performed in 10^{-5} M DMSO solutions. The absorption spectra normalized to the molar extinction coefficient are shown in **Figure 2** (top) and the light harvesting efficiency (LHE) of the Dye/TiO$_2$/Pt on thin films in **Figure 2** (bottom). All of the dyes showed an intense absorption band in the visible region attributed to the intramolecular donor to acceptor charge-transfer transition. As expected, the introduction of more extended thiophene-based π-spacers resulted to substantial bathochromic and hyperchromic effects, hence allowing a more efficient photon harvesting.
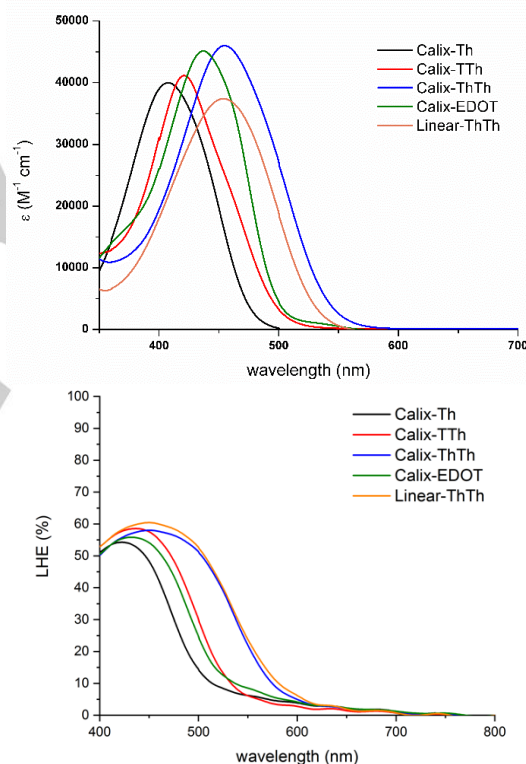
Figure 2. Top: UV-Vis spectra in 10^{-5} DMSO solution of the investigated sensitizers. Bottom: LHE of the investigated dyes absorbed on a 3-μm thick transparent TiO$_2$+Pt film.

The molar absorptivities range from 40000 (**Calix-Th**) to 46000 M^{-1} cm^{-1} (**Calix-ThTh**), to be compared with the value of **Linear-ThTh** (37400 M^{-1} cm^{-1}). Therefore, the molar absorptivities of the calixarene dye resulted in much less than a two-fold increase compared to that of the corresponding linear dyes, as one would expect from the presence of two dye units. In the case of **Calix-EDOT**, the presence of the alkoxy auxochrome groups on the thiophene core red-shifted the absorption maximum by more than 30 nm compared to the **Calix-Th** with no substitution on the

thiophene ring. Optical bandgaps were calculated by means of the Tauc plots and listed in **Table 1** together with their main optical parameters.[17]

To better compare the different light harvesting capability of the sensitizers, the oscillator strengths were determined and collected in Table 1.[18] As already suggested from the molar extinction coefficients at the absorption peaks, it is evident that the absorption quantitative capacity in the calixarene dyes and the reference linear system are indeed very similar. In particular, the oscillator strength of **Calix-ThTh** (f = 11.4 D) is only 1.1 times larger than that of the corresponding linear dye **Linear-ThTh** (f = 10.1 D). The LHE of the sensitizers adsorbed on Pt/TiO$_2$ film showed similar values for most of the investigated compounds with an absorption in the spectral range below 550 nm except for **Calix-ThTh** and **Linear-ThTh,** where LHE extends up to 600 nm with a peak of 60% at 455 nm. It is worth noting that the LHE for the two adsorbed sensitizers is very similar, thus confirming the optical properties in solution.

The electrochemical characterization is summarized in Figure S1 and Figure S2 (Supporting Information) and **Table 1**. Cyclic voltammetry profiles showed an irreversible oxidation behaviour for all the investigated dyes. For this reason, Differential Pulsed Voltammetry (DPV) was used. DPV was able to isolate the different electrochemical processes and was used to determine oxidation potential and allows to calculate the HOMO energy levels from the current peak. The LUMO levels have been derived from electrochemical HOMO values and optical bandgaps. A sensitizer to be used in photocatalytic hydrogen production should present a LUMO energy higher than that of the TiO$_2$ CB and a HOMO energy lower than the SED oxidation potential.[8b,19] Even though the HOMO energy levels are quite similar for most of the dyes (~ -6 eV), the different bandgaps determine their LUMO energies and, accordingly, affect the electron injection capabilities to the Pt/TiO$_2$ system. In particular, the LUMO energy of all the dyes is very close to CB of TiO$_2$ (-4.0 eV). A schematic of the energy levels is depicted in Figure S3 (Supporting information).

Table 1. Optical and electrochemical parameters of investigated sensitizers in solution

Dye[a]	λ_{max} (nm)	ε (M^{-1} cm^{-1})	f [b] (D)	E_{gap}^{opt} (eV)	V_{ox} (V vs Fc) ± 10 mV	HOMO^c (eV) ± 0.05 eV	LUMO^c (eV) ± 0.05 eV
Linear-ThTh	454	37400 ± 500	10.1	2.2	0.78	-6.01	-3.81
Calix-Th	405	40000 ± 500	9.1	2.4	0.96	-6.19	-3.79
Calix-TTh	421	41200 ± 500	10.5	2.1	0.82	-6.05	-3.95
Calix-ThTh	455	46000 ± 1400	11.4	2.2	0.71	-5.94	-3.74
Calix-EDOT	437	45100 ± 350	10.3	2.1	0.81	-6.04	-3.94

[a] In DMSO. [b] Oscillator strength measured in the 300–800 nm range. [c] Vacuum potential = Fc/Fc$^+$ + 5.23 V.

The sensitized Pt/TiO$_2$ photocatalysts were tested for H$_2$ production under visible light irradiation (λ > 420 nm) from a triethanolamine (TEOA)/HCl aqueous buffer solution at pH = 7.0. The experiments have been performed adopting the same conditions previously optimized for di-branched organic dye based photocatalysts.[20] Measured H$_2$ productions vs the irradiation time are presented in Figure 3 while the H$_2$ production rates vs the irradiation time are shown in Figure S4 (Supporting Information). Turnover numbers (TON) and Light-to-Fuel Efficiency calculated after 2 and 15 h of irradiation (LFE$_2$ and LFE$_{15}$) are listed in Table 2.

All of the photocatalysts show an initial induction period (20 – 30 minutes) before the H$_2$ production is significant and detectable. This could be due to the need of activation of the photocatalysts and/or a sort of chromatographic effect within the dead volume of the photoreactor. After activation, the dye/Pt/TiO$_2$ materials showed a sharp increase in H$_2$ production rate during the initial 1 – 2 hours, followed by a progressive decrease, eventually reaching a plateau after 6 – 8 hours under irradiation (Figure S4, Supporting Information). The H$_2$ productions were similar for all of the photocatalysts, with the exception of **Calix-ThTh**, for which the H$_2$ production was significantly enhanced (Figure 3).

The performance in photocatalytic H$_2$ production are summarized in Table 2, presenting the data after 2 and 15 hours. The former set is representative of the activity of the materials close to the maximum H$_2$ production rate, while the latter one gives a picture of the overall performance of the samples during prolonged working conditions. Again, these data highlight the higher performance of the **Calix-ThTh** dye with respect to the other calix[4]arene-based dyes, showing both higher TON and Light-to-Fuel Efficiency values throughout the duration of the experiments. For this sample, it was also possible to measure an apparent quantum yield (AQY) of 0.138% under irradiation around 450 nm.
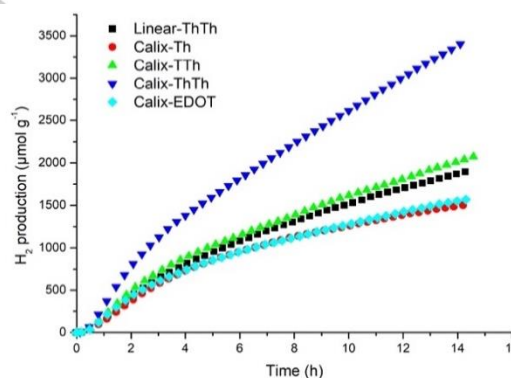
Figure 3. H$_2$ production measured from TEOA 10 % v/v solution at pH 7.0 using the dye/Pt/TiO$_2$ materials under irradiation with visible light (λ > 420 nm).

The comparison with the corresponding reference linear dye **Linear-ThTh** (ca. 275 μmol g^{-1} h^{-1}) shows that the peak production rate of the calixarene dye (ca. 525 μmol g^{-1} h^{-1}) is nearly twice larger! Very surprisingly, the superior photocatalytic activity does not arise from correspondingly larger optical properties (Table 1). Based on literature evidences,[21] and a possible rationale for the improved performance of the calixarene derivative with respect to the linear dye is the possibility of inducing host-guest interactions with protonated TEOA, thus favouring the charge transfer from the SED to the oxidized dye

upon photoexcitation of the latter. Accordingly, the relative activities of the calix[4]arene dyes follow the trend of the distances between the calixarene aromatic cavities and the COOH anchoring groups: **Calix-ThTh**, which bears the longest dyes, performs better than **Calix-TTh**, which in turns is more active than the shortest **Calix-Th** and **Calix-EDOT**. Considering that the interaction of protonated amines with the calix[4]arene is reported to take place through the cavity between the aromatic rings, the space between the macrocycle and the Pt/TiO$_2$ surface may be crucial for accommodating the SED. In this view, it seems reasonable to hypothesise that the longer is the spacer, the more efficient is the interaction between the dye and the SED, resulting in higher photocatalytic activity. Furthermore, this hypothesis is also supported by LHE measurements, which clearly show that the harvesting of the solar radiation is almost the same for **Calix-ThTh** and **Linear-ThTh**, thus emphasizing the importance of the different structural feature on the photocatalytic performance.

As far as the relative performance of the di-branched calix[4]arene dyes is concerned, the molecules with a single thiophene spacer showed the lowest activity, regardless of the presence of side substituents on the heteroaromatic rings, while a slightly higher activity was observed for the **Calix-TTh**. It must be underlined that, despite showing stable photocatalytic activities under comparable experimental conditions, the phenothiazine-based dyes showed lower H$_2$ production rates than the calix[4]arene-based dyes presented herein.[22] This difference could be related to the structure of the dye molecules, which likely affects the interaction with the sacrificial electron donor and/or the electronic dynamics upon dye excitation and electron injection to the CB of TiO$_2$. Notably, also the AQY of **Calix-ThTh** is significantly higher than the values previously observed for the phenothiazine-based dyes.[23]

Table 2. Summary of photocatalytic performance of the dye/Pt/TiO$_2$ materials in H$_2$ production from TEOA 10 % v/v solution at pH 7.0 under irradiation with visible light (λ > 420 nm).

Dye	After 2 hours			After 15 hours		
	H$_2$ amount (μmol g^{-1})	TON (μmol(H$_2$) μmol(dye)$^{-1}$)	LFE (%)	H$_2$ amount (μmol g^{-1})	TON (μmol(H$_2$) μmol(dye)$^{-1}$)	LFE (%)
Linear-ThTh	435	43.5	0.061	1870	187.0	0.024
Calix-Th	390	39.0	0.064	1502	150.2	0.015
Calix-TTh	535	53.5	0.071	2008	200.8	0.028
Calix-ThTh	810	81.0	0.103	3401	340.1	0.055
Calix-EDOT	448	44.8	0.053	1550	155.0	0.016

In conclusion, we have presented a study of the photocatalytic hydrogen generation of a new family of calix[4]arene-based donor-acceptor dyes acting as unconventional photosensitizers. The optical and electrochemical characterization was performed, in particular highlighting the fact that the molar absorptivities and oscillator strengths are similar to that of the linear dye, despite the presence of two chromophore units, as well as LHE. The photocatalytic study, in terms of generated gas amount, TON, and overall energy efficiency, demonstrated the superior activity of the calix[4]arene-based dyes. In particular, the photocatalytic efficiency of **Calix-ThTh** was almost twice larger than that of **Linear-ThTh**. Moreover, in general the calix[4]arene-based sensitizers were more efficient than phenothiazine-based dyes carrying the same spacers, despite the fact the latter represents a common donor unit for sensitizers in photocatalytic hydrogen generation.[8b, 9a] A deeper analysis of results in relation to the molecular structure of the sensitizers and similar data from the literature suggests that the higher efficiency of the calix[4]arene-based dyes may result from supramolecular interactions between the SED and the calix[4]arene scaffold. More detailed studies concerning the supramolecular interactions involving the calix[4]arene moiety are currently being actively studied in our laboratories and will be communicated in due course. We thus believe that this work paves the way to a new design strategy exploiting the calix[4]arene scaffold, even in terms of host-guest supramolecular chemistry, for novel efficient photocatalytic systems.

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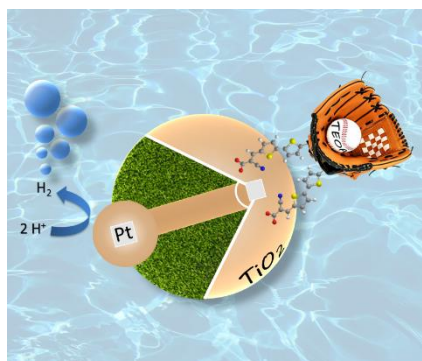
A new series of calix[4]arene-based push-pull dyes have been synthesized, fully characterized, and used in photocatalytic hydrogen production. Among the new dyes, the bithiophene-based π spacer derivative showed superior photoactivity. The incorporation of the calixarene aromatic donor unit into the dye structure provides hydrogen generation efficiencies that are twice as high as the corresponding linear analogue, although it exhibits similar quantitative light harvesting properties.