Calix[4]arene-Based Sensitizers for Photo(electro)catalytic Hydrogen Production

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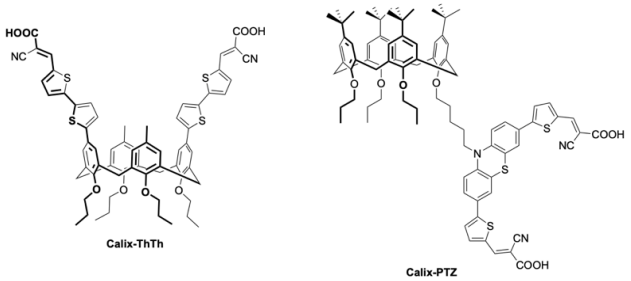
In the field of direct water splitting from solar energy, photocatalytic and photoelectrochemical methods hold great potential especially when metal-free molecular components are preferred.[1,2] The use of templating functionalities to exploit specific interaction has been attempted in few cases with the result of an improvement of the photo(electro)catalytic properties.[3,4] In this work, we have developed two classes of calix[4]arene-based molecular photosensitizers to be used as antenna systems in photocatalytic production of hydrogen and photoelectrochemical water oxidation. The structure of the first class of dyes shows the typical donor-π-acceptor molecular architecture where a calix[4]arene scaffold is used as an embedded donor. 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.[5] The second class of sensitizers uses the calix[4]arene structure as peripheral functionalization with the effect of coordinating the water oxidation catalyst in the solution. As a matter of fact, the device sensitized with the calix[4]arene functionalized dye showed an increased photocurrent in photoelectrochemical experiments. The new molecular design paves the way to a new strategy for photo(electro)catalytic water splitting where the calix[4]arene scaffold can afford more efficient systems offering the potential for host-guest supramolecular effects.



References

[1] Decavoli, C.; Boldrini, C. L.; Manfredi, N.; Abbotto, A. *Eur. J. Inorg. Chem.* **2020,** 978.

[2] Cecconi, B.; Manfredi, N.; Montini, T.; Fornasiero, P.; Abbotto, A. *Eur. J. Org. Chem.* **2016**, 5194.

[3] Manfredi, N.; Monai, M.; Montini, T.; Peri, F.; De Angelis, F.; Fornasiero, P.; Abbotto, A. *ACS Energy Lett.* **2017,** *3*, 85.

[4] Li, H.; Li, F.; Wang, Y.; Bai, L.; Yu, F.; Sun, L. *Chempluschem* **2016,** *81*, 1056.

[5] Manfredi, N.; Decavoli, C.; Boldrini, C. L.; Dolla, T. H.; Faroldi, F.; Sansone, F.; Montini, T.; Baldini, L.; Fornasiero, P.; Abbotto, A. *Eur. J. Org. Chem.* **2021,** 284.