Angewandte
International Edition Chemie

DOI: 10.1002/anie.201108963

Electron Transfer

Carboxyethynyl Anchoring Ligands: A Means to Improving the Efficiency of Phthalocyanine-Sensitized Solar Cells**

Maria-Eleni Ragoussi, Juan-José Cid, Jun-Ho Yum, Gema de la Torre, Davide Di Censo, Michael Grätzel, Mohammad K. Nazeeruddin,* and Tomás Torres**

Dye-sensitized solar cells (DSSCs)[1] can be considered realistic, low-cost alternatives to conventional silicon-based photovoltaic devices. Typically, these cells are composed of nanocrystalline TiO_2 deposited onto a transparent conducting glass substrate, which is covered with a molecular sensitizer endowed with an appropriate anchoring group. Energy conversion efficiencies up to 11.4% have been achieved using Ru^{II}/polypyridyl complexes as molecular sensitizers.[2] Nonetheless, Ru^{II}/polypyridyl complexes lack strong absorption in the red or near-infrared region, where the solar flux of photons is still significant, thus limiting the realization of more efficient devices. In the search for ideal ruthenium-free sensitizers, dyes with large π-conjugated systems such as porphyrins[3,4] and phthalocyanines[4,5] which are suitable for efficient electron-transfer processes, are receiving considerable attention. Porphyrins, in particular, have been successfully used in DSSCs[6] and, very recently, Grätzel, Diau, and Yeh et al. reported a DSSC with an incorporated porphyrin dye having a cell performance that achieves the figure of merit for the state-of-the-art devices.[7]

Phthalocyanine (Pc) derivatives are also suitable sensitizers for DSSCs because of their intense and tunable absorption in the red or near-infrared region, transparency over a large portion of the visible spectrum, and extraordinary robustness.[8] However, the efficiency values of Pc-based DSSCs are in general below those of devices made from their porphyrin relatives.[4,5] Their relatively poor performance is a consequence of the general tendency of Pcs to form molecular aggregates on the surface of the titanium dioxide nanocrystals; the aggregates result from the more π-extended aromatic surface. Even so, overall efficiencies of 3.5% at 1 sun have been reported by us when employing highly soluble carboxy functionalized $Zn^{II}Pc$ derivatives, such as **TT1**, which show low tendency towards aggregation.[9] Moreover, Mori et al. recently confirmed that the presence of bulky substituents is fundamental for completely suppressing aggregation and, therefore achieved high energy conversion efficiencies. The carboxy functionalized $Zn^{II}Pc$ substituted at the periphery with six 2,6-diphenylphenoxy groups achieved up to a 4.6% efficiency.[10]

Recent studies on Pcs for DSSC applications reported by us have focused on understanding the relationship between the structure and function in terms of the spacer located between the aromatic core and the anchoring carboxy group in a series of $Zn^{II}Pcs$.[11] An important finding is that the carboxy (or other) anchoring group needs to be electronically connected to the $Zn^{II}Pc$ to facilitate the charge transfer from the LUMO of the dye to the Ti 3d orbital. Rigid π-conjugated bridges and, in particular, vinyl-type conjugated spacers, have proven to be very effective groups for connecting the Pc π system to the carboxylic anchoring group.[12] In this regard carboxyethynyl groups emerge as ideal candidates for optimal coupling and directionality in the linking of the $Zn^{II}Pc$ to TiO_2.

With all these previous structure–property relationships in mind, we developed the synthesis of a series of $Zn^{II}Pcs$ bearing carbon–carbon triple bonds (Figure 1) to serve as

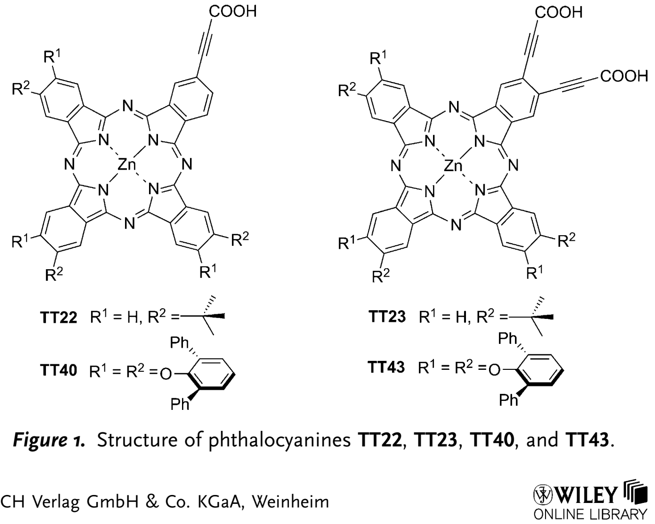

Figure 1. Structure of phthalocyanines **TT22**, **TT23**, **TT40**, and **TT43**.

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[*] Dr. M.-E. Ragoussi, Dr. J.-J. Cid, Dr. G. de la Torre, Prof. T. Torres
Universidad Autónoma de Madrid, Departamento de Química Orgánica, Cantoblanco, 28049 Madrid (Spain)
E-mail: tomas.torres@uam.es
Dr. J.-H. Yum, Dr. D. Di Censo, Prof. M. Grätzel, Dr. M. K. Nazeeruddin
Laboratory for Photonics and Interfaces, Institute of Chemical Sciences and Engineering, School of Basic Sciences
Swiss Federal Institute of Technology, 1015 Lausanne (Switzerland)
E-mail: michael.graetzel@epfl.ch
mdkhaja.nazeeruddin@epfl.ch
Prof. T. Torres
IMDEA Nanociencia, Facultad de Ciencias
Cantoblanco, 28049 Madrid (Spain)

[**] This work has been supported by the Spanish MICINN and MEC (CTQ2011-24187/BQU and CONSOLIDER INGENIO 2010, CSD2007-00010 Nanociencia Molecular, PLE2009-0070), and the Comunidad de Madrid (MADRISOLAR-2, S2009/PPQ/1533). M.K.N. thanks the World Class University program, Photovoltaic Materials, Department of Material Chemistry, Korea University, Chungnam, 339-700, Korea, funded by the Ministry of Education, Science and Technology through the National Research Foundation of Korea (No. R31-2008- 000-10035-0).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201108963.

spacers between the conjugated core and the anchoring COOH group. These nonflexible spacers having an extended electronic delocalization may keep the Zn^{II}Pc core perpendicularly arranged and close enough to the TiO_2 surface. Therefore, Zn^{II}Pcs with one (i.e., **TT22** and **TT40**) or two carboxyethynyl groups (i.e., **TT23** and **TT43**) were synthesized and studied as sensitizers in DSSCs[13] to establish if the presence of two anchoring moieties in the dye is beneficial in terms of efficiency. Concerning the peripheral substitution of these unsymmetrically substituted Zn^{II}Pc derivatives, we introduced either three surrounding *tert*-butyl groups (i.e., **TT22** and **TT23**) or six diphenylphenoxy groups (i.e., **TT40** and **TT43**) to determine if the influence of peripheral substitution is paramount for achieving high efficiencies in compounds having similar anchoring moieties. In particular, we report herein that when using **TT40** as a sensitizer we obtained record efficiency values of 5.5% and 6.1% under 100 and 9.5 mW cm^{-2} intensities of standard AM 1.5, respectively.

The carboxyethynyl phthalocyanines **TT22**, **TT23**, **TT40**, and **TT43** were synthesized by means of two consecutive oxidation steps from the corresponding hydroxypropargyl derivatives: the reaction with the periodinane derivative IBX in DMSO afforded the corresponding formylethynyl derivatives, which were isolated and treated with $NaClO_2$ in water in the presence of sulfamic acid to yield the target compounds (see the Supporting Information). The synthesis of the corresponding mono- and bis(hydroxypropargyl) precursors were carried out by either a single or double Sonogashira coupling between a propargylic alcohol and the corresponding mono- or diiodo Pc derivatives, respectively.[14]

All final compounds and their corresponding intermediates were fully characterized by spectroscopic techniques. The effectiveness of peripheral substituents in suppressing Pc aggregation was confirmed by ^{1}H NMR spectroscopy. The spectra of carboxyethynyl phthalocyanines in [D_8]THF show well-resolved signals in the aromatic region, especially in the case of **TT40** and **TT43** (see Figure S1 in the Supporting Information). Please note that **TT22** and **TT23** are obtained as a mixture of regioisomers.

UV/Vis spectral data demonstrate the consistently low aggregation of these carboxyphthalocyanines in THF solution (Figure 2). Absorption spectra of **TT22**, **TT23**, **TT40**, and **TT43** show split Q bands ranging from $\lambda = 670$ to 715 nm. Notably, the grafting of two carboxyethynyl groups onto the Pc molecule (i.e., **TT23** and **TT43**) causes a larger splitting and redshift of the Q bands. In particular, **TT43** shows the most redshifted and split of the Q bands of the series.

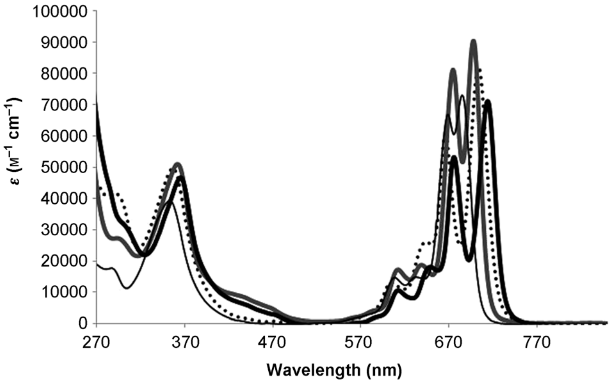

Figure 2. UV/Vis spectra in THF ($c = 1.2 \times 10^{-5}$ M) of **TT22** (thin black line), **TT23** (dotted line), **TT40** (thick gray line), and **TT43** (thick black line).

Table 1: *J–V* characteristics plotted as wavelength of DSSCs sensitized by **TT22**, **TT23**, **TT40**, and **TT43**.

Dye	I_0 [mW cm^{-2}]	J_{sc} [mA cm^{-2}]	V_{oc} [mV]	*FF*[a]	η [%][b]
TT22[c]	9.5	0.70	564	0.78	3.26
	100	7.01	610	0.73	3.13
TT23[d]	9.5	0.35	455	0.75	1.24
	100	3.70	520	0.73	1.40
TT40[e]	9.5	1.31	585	0.76	6.13
	100	12.3	638	0.70	5.50
TT43[f]	9.5	0.85	521	0.76	3.54
	100	8.77	584	0.71	3.63

[a] Fill factor. [b] Overall efficiency η is derived from $J_{sc} V_{oc} FF/I_0$. [c] TiO_2: ≈9 + 5 μm, 0.1 mM **TT22** solution with 20 mM CDCA. [d] TiO_2: ≈6 + 6 μm, 0.1 mM **TT23** solution with 20 mM CDCA. [e] TiO_2: ≈6 + 5 μm, 0.05 mM **TT40** solution. [f] TiO_2: ≈6 + 5 μm, 0.05 mM **TT43** solution.

The characteristics of the photovoltaic device were measured under standard global AM 1.5 simulated solar conditions and are summarized in Table 1. The impact of the lack of aggregation of the macrocycles on the TiO_2 surface may be inferred from the comparison of the efficiencies of **TT22** and **TT40**. In general, either a low dye concentration or the presence of a coadsorbent is essential for reducing the molecular aggregation, thus leading to a higher efficiency.[15] At full sun, using **TT22** as a sensitizer with a JH34 electrolyte we observed a short-circuit photocurrent density (J_{sc}) of 7.01 mA cm^{-2}, an open-circuit voltage (V_{oc}) of 610 mV, and a fill factor (*FF*) of 0.73, thus corresponding to an overall power conversion efficiency (PCE, η) of 3.13%. In this case, a thicker TiO_2 film was required to optimize the PCE, because using a film that was 5.7 + 5 μm thick (i.e., as used with other Pc sensitizers studied in this work) gave a PCE value of 2.93% as a result of a $J_{sc} = 6.73$ mA cm^{-2}. The presence of chenodeoxycholic acid (CDCA) in the **TT22** solution was essential for achieving the above-mentioned performance. Indeed, a **TT22**-based device without CDCA attained only 61% of the efficiency of the device prepared in the presence of CDCA, primarily because of a loss in photocurrent. However, a **TT40**-sensitized solar cell in the absence of CDCA yielded a PCE of 5.5% and 6.1% under 100 (1 sun irradiation) and 9.5 mW cm^{-2}, respectively (Table 1 and Figure 3). The higher efficiency of the **TT40**-based molecular photovoltaic devices is attributed to the reduced molecular aggregates on the surface of the TiO_2. Additional evidence confirming the non-aggregating nature of **TT40** is that no change in the incident photon-to-current efficiency (IPCE) and the photovoltaic characteristics was observed even with a solution having 0.4 mM dye concentration (see Figure S2 and Table S1 in the Supporting Information). In addition, absorption spectra on TiO_2 films showed that the actual dye loading on the TiO_2 surface is independent of the

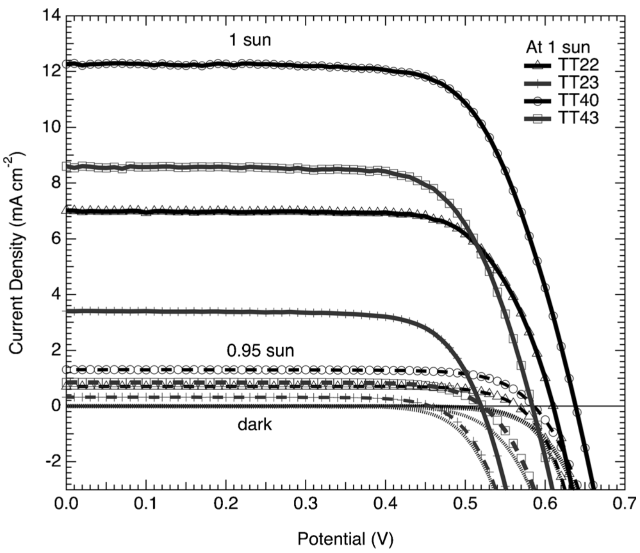

Figure 3. *J–V* characteristics of DSSCs sensitized by **TT22** (line with triangles), **TT23** (line with crosses), **TT40** (line with circles), and **TT43** (line with squares) when irradiated with simulated solar light at 9.5 (dash dotted line) and 100 (solid line with marker) mW cm^{-2}. Dotted lines show dark currents of all devices.

concentration (Figure S3). **TT40** on a double-layered TiO_2 film shows an IPCE greater than 85 % at $\lambda = 700$ nm (Figure 4), and is in agreement with the absorbance maximum on the UV/Vis spectrum of the molecule.

Despite being endowed with two conjugated anchoring groups, **TT23** and **TT43** sensitizers showed inferior photovoltaic performances compared to **TT22** and **TT40**, mainly because of a drop in the J_{sc} value caused by the lower LUMO of the sensitizers (see below the electrochemical characterization)

A rationalization of the different V_{oc} values for all sensitizers can be achieved from the electron injection lifetimes for the different sensitizers (see Figure S4 in the Supporting Information). Optimized **TT22** solar cells showed longer electron lifetimes than those of **TT40**, probably as a consequence of the addition of CDCA, a phenomenon that was demonstrated in previous work.[15a] Nonetheless, the highest V_{oc} value was achieved with **TT40**, and could be ascribed to a higher photoinduced charge density leading to a shift of the Fermi level of TiO_2. Meanwhile, electron lifetimes in **TT22** and **TT40** solar cells were longer than those of **TT23** and **TT43** cells. This result shows that dyes conjugated with single anchoring group have longer electron lifetimes than dyes having two anchoring groups. The dependence of the electron lifetime on the number of anchoring groups has been observed in our previous studies with **TT9**, (i.e., a Zn^{II}Pc endowed with two carboxylic acids), which exhibited a shorter lifetime, although it performed at a higher level than **TT1**.[16] The structures of both **TT1** and **TT9** are not shown herein. The relationship between the charge dynamics and the anchoring group is very interesting but not clear at this stage.

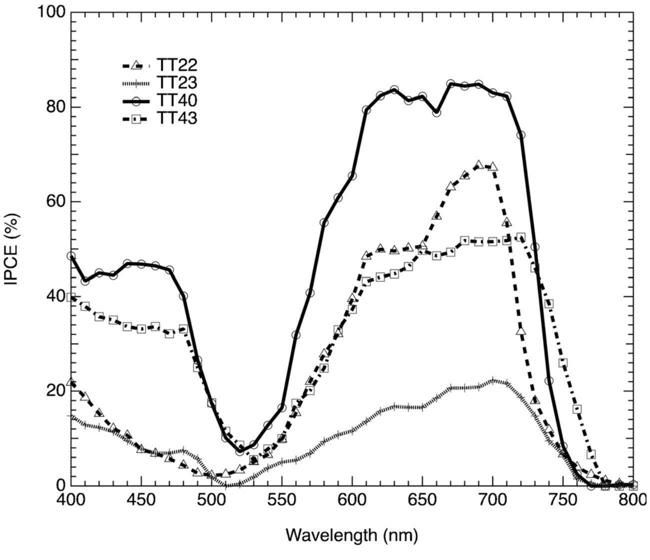

Figure 4. IPCEs of DSSCs sensitized by **TT22** (line with triangles), **TT23** (line with crosses), **TT40** (line with circles), and **TT43** (line with squares).

Electrochemical characterization of the dyes also supports the results with regard to the efficiencies obtained for the dye series. Electrochemical properties were characterized by differential pulse voltammetry (DPV) in *N,N′*-dimethylformamide (DMF) containing 0.1 M of tetrabutylammonium hexafluorophosphate ($TBAPF_6$; see Figure S5 and Table S2 in the Supporting Information). The reduction potentials of **TT23** and **TT43** are approximately 100 mV less negative than those of **TT22** and **TT40**, respectively, and are consistent with lower-energy LUMOs of the former derivatives. The reduction potential data are also in agreement with the UV/Vis spectral data. The lower-energy LUMOs of the **TT23** and **TT43** sensitizers, which contain two anchoring groups, result in a low efficiency for electron injection into TiO_2. It is noteworthy that **TT43**-based solar cells showed redshifted IPCEs (Figure 4), which is in agreement with the absorption spectra shown in Figure 2.

The most important contribution of this work is related to the benefits of the ethynyl moiety as a bridge for optimal electronic coupling between the Zn^{II}Pc and TiO_2. First, **TT22** showed PCEs similar to those previously reported for the **TT1** counterpart, which has solubilizing *tert*-butyl groups and a COOH group directly linked to the Zn^{II}Pc core. This fact points to the effectiveness of the alkynyl bridge as a connecting group. Secondly, and more significantly, **TT40** largely outperforms the 4.6 % efficiency previously reported by Mori et al.[10] for a Zn^{II}Pc substituted with diphenylphenoxy substituents and a phenyl bridge between the anchoring carboxy group and the macrocycle.

However, the presence of an additional anchoring group (i.e., in **TT23** and **TT43**) seems to be detrimental. A similar reduction in PCEs was observed on going from **TT22** to **TT23**, and from **TT40** to **TT43**; in both series, the introduction of an additional carboxyethynyl moiety reduces the efficiency of the molecular device by 55–60 %, mainly as a consequence of a strong reduction in the J_{SC} value. This drop is most likely ascribed to the low driving force for charge injection from the excited dyes into the TiO_2 conduction band.

Experimental Section

Solar cell fabrication and characterization: A TiO_2 film composed of ca. 6 μm (transparent layer) and ca. 5 μm (scattering layer) was prepared by screen-printing and treated with a 0.05 M titanium tetrachloride solution.[15a] The films were heated to 500 °C in air for 30 min before use, then dipped in either 0.1 mM **TT22** or **TT23** solutions in ethanol containing 20 mM 3α,7α-dihydroxy-5β-cholic acid (chenodeoxycholic acid, CDCA) for 5–6 h at room temperature. A quick rinse with acetonitrile was performed before fabrication of the solar cells using the procedure, testing conditions, and equipment previously reported.[17] The liquid electrolyte, JH34 consisted of 0.6 M 1,3-dimethylimidazolium iodide, 0.03 M iodine, 0.05 M LiI, 0.05 M guanidinium thiocyanate, and 0.25 M 4-*tert*-butylpyridine in 15/85 (v/v) mixture of valeronitrile and acetonitrile. For **TT40** or **TT43** based solar cells, the solutions with no CDCA were used and the other procedures were similar as for **TT22** and **TT23**.

Received: December 19, 2011

Keywords: conjugation · electron transfer · solar cells · synthetic methods · zinc

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