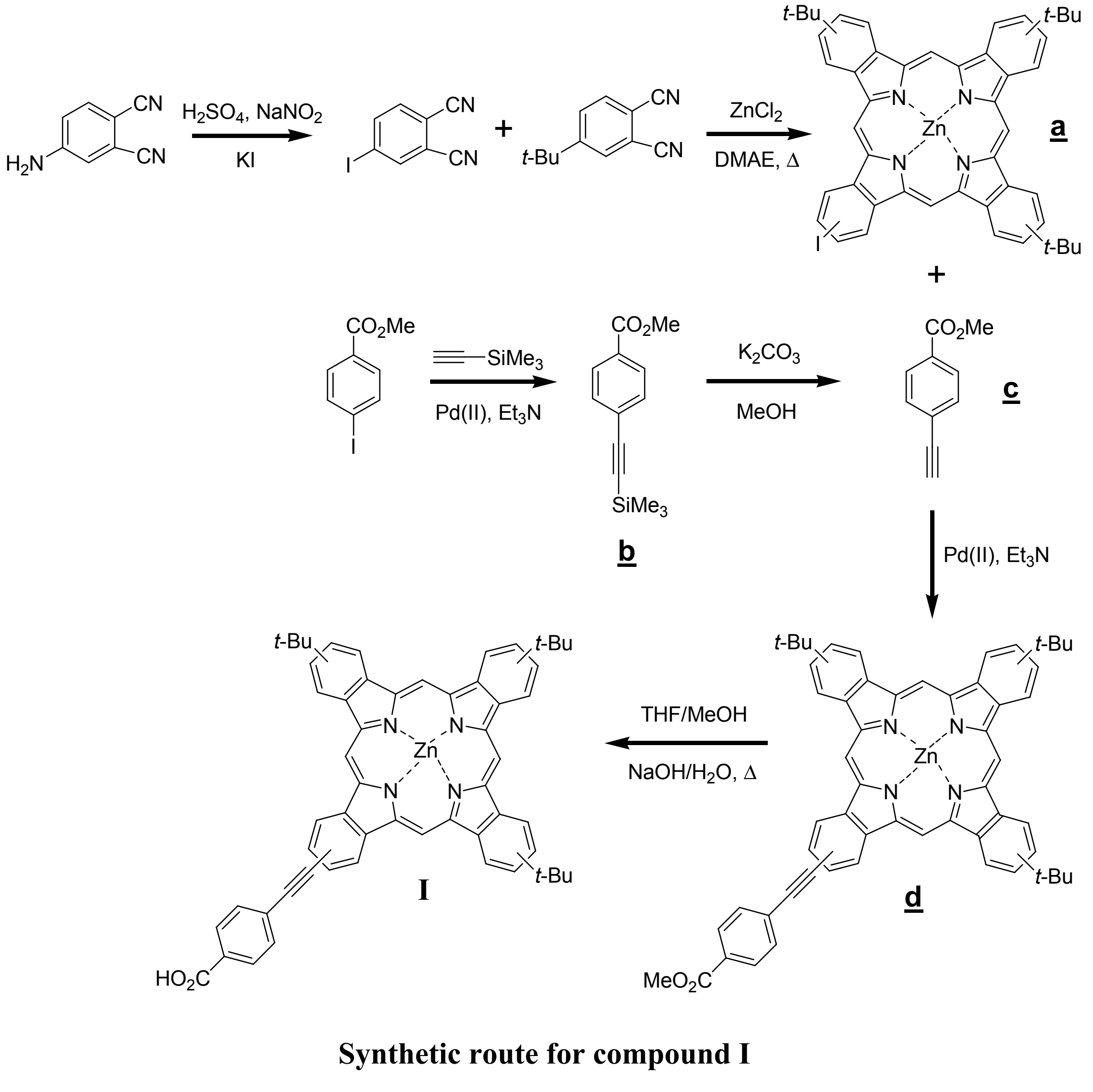
Supporting Information

Synthesis of a novel unsymmetrical Zn(II) Phthalocyanine bearing a phenyl ethynyl moiety as efficient sensitizer for dye-sensitized solar cells

Gloria Zanotti,[b] Nicola Angelini[a], Anna Maria Paoletti[a], Giovanna Pennesi[a], Gentilina Rossi[a], Aldo Amore Bonapasta[a], Giuseppe Mattioli[a], Aldo Di Carlo[b], Thomas M. Brown[b], Angelo Lembo[b], Andrea Reale[b] .

Synthesis



Synthetic route for compound I

(**a**) 9(10),16(17),23(24)-Tri-*tert*-butyl-2-iodophthalocyaninatozinc(II) was synthesized as previously described[8] and characterized by NMR; ^{1}H NMR (300 MHz, rt, Acetone d$_6$): δ= 8.22-7.16 (m, 12H, aromatic), 1.35 (s, 27H), $C_{44}H_{39}N_8ZnI\cdot C_4H_8O_2$(dioxane)(959.67) calcd. C60.02, H 4.93, N 11.67; found C 59.75, H 5.23, N 11.56.

(**b**) 4-(trimethylsilyl)ethynylmethylbenzoate: 700 mg (2.7 mmol) of 4-iodomethylbenzoate and 0.44 ml (3.2 mmol) of trimethylsilylacetylene were dissolved in 10 ml of Et_3N in argon atmosphere. Then 37.7 mg (0.053 mmol) of bis(triphenylphosphine)palladium(II)dicloride and 5.1 mg (0.027 mmol) of CuI were added and the mixture was stirred for 4 hours at room temperature. It was then concentrated

to remove the solvent. After purification with column chromatography on silica gel using hexane-toluene 3:2 as eluent, 600 mg of desired product were obtained. (yield 97%).
^{1}H NMR (300 MHz, rt, $CDCl_3$):δ= 7.97 (d, J = 8.7 Hz, 2H aromatic) 7.49 (d, J = 8.7 Hz, 2H aromatic), 3.91 (s, 3H, CH_3), 0.26 (s, 9H, $Si(CH_3)_3$); IR (nujol, cm^{-1} 2160 C≡C, 1732 C=O)

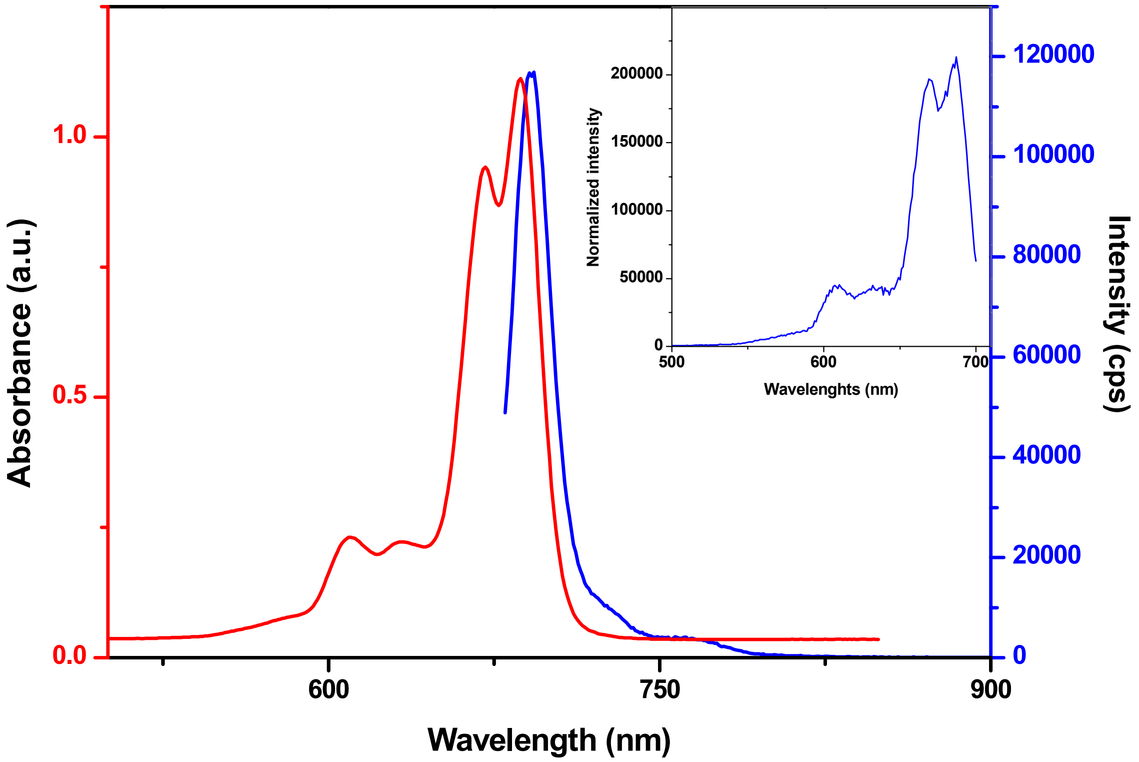
(**c**) 4-ethynylmethylbenzoate: 600 mg of 4-(trimethylsilyl)ethynylmethylbenzoate (2.58 mmol) were dissolved in 12 ml of methanol and then 156 mg of anhydrous K_2CO_3 were added. The mixture was stirred under argon atmosphere at room temperature for 3 hours and then diluted with dichloromethane and washed 3 times with water. The aqueous phase was extracted with dichloromethane and the organic phase dried over Na_2SO_4 and concentrated to afford 346 mg of product, which was used without any purification, (yield 84%).^{1}H NMR (300 MHz, rt, $CDCl_3$): δ= 7.99 (d, J = 9.1 Hz, 2H aromatic) 7.54 (d, J = 9.1 Hz, 2H aromatic), 3.92 (s, 3H, CH_3), 3.22 (s, 1H, ≡CH); IR (nujol cm^{-1}, 2102 C≡C, 1700 C=O)

(**d**) 9(10),16(17),23(24)-Tri-*tert*-butyl-2-[ethynyl-(4-carboxymethyl)phenyl]phthalocyaninatozinc(II)
In argon atmosphere, 73 mg of a (0.084 mmol) were dissolved in 2 ml of Et_3N and then 16 mg of c (0.1 mmol), 1.2 mg of $(PPh_3)_2PdCl_2$ (0.00168 mmol) and 0.16 mg of CuI (0.00084 mmol) were added. The mixture was stirred for 5 hours in argon atmosphere and then it was concentrated to afford 137 mg of crude product. After purification with column chromatography using hexane-dioxane 9:1 and 4:1 as eluents, the desired product was obtained as a green solid. (75 mg, 99% yield). ^{1}H NMR (300 MHz, rt, THF d_8): δ= 9.42-8.86 (m, 8H, ring), 8.30-8.11 (m, 6H, phthalocyanine macrocycle and benzoic ring), 7.93-7.87 (m, 2H, benzoic ring), 3.94 (s, 3H, CH_3), 1.87 (s, 27H, $C(CH_3)_3$)
IR (KBr cm^{-1}, 2206 C≡C,),UV-Vis (THF, nm): 671, 686; ISI/MS (m/z) [$M+H^+$] 903.2-909.2 ; elemental analysis: $C_{54}H_{46}N_8O_2Zn{\cdot}2C_4H_8O_2$(dioxane) (1060.39), calcd. C 70.16, H 6.08, N 10.56; found C 70.20, H 6.15, N 10.01.

(**I**) 9(10),16(17),23(24)-Tri-*tert*-butyl-2-[ethynyl-(4-carboxy)phenyl]phthalocyaninatozinc(II)
20 mg of ester (0.022 mmol) were dissolved in 5 ml of a 1:1 THF-methanol solution and after the addiction of 190 mg of NaOH dissolved in 5 ml of H_2O the resultant mixture was refluxed under stirring until the TLC showed the complete disappearance of the reagent. Then it was concentrated to eliminate THF and methanol and the resulting aqueous phase was acidified to allow the precipitation of the product which was collected by filtration and washed several times with water. The resulting 19 mg of crude were purified by column chromatography using silica gel as stationary phase and 4:1 hexane-dioxane and 1:1 chloroform-methanol as mobile phases and the blue-greenish solid obtained was washed several times with water and methanol. (13 mg, yield 66.5%); ^{1}H NMR (300 MHz, rt, THF d_8): δ= 9.86-7.67 (m, 16H, aromatics), 1.67 (s, 27H, $C(CH_3)_3$)
IR (nujol cm^{-1}, 2203 C≡C)
UV-Vis (THF, nm): 671, 685

Optical characterization

UV-vis spectra of solution (~10^{-4}M) were recorded on a Perkin-Elmer Lambda 950 UV-vis-NIR spetrophotometer. Fluorescence spectra (~10^{-6}M) were recorded on a Jobin-Yvon Spectrofluorometer Fluorolog 3-22.



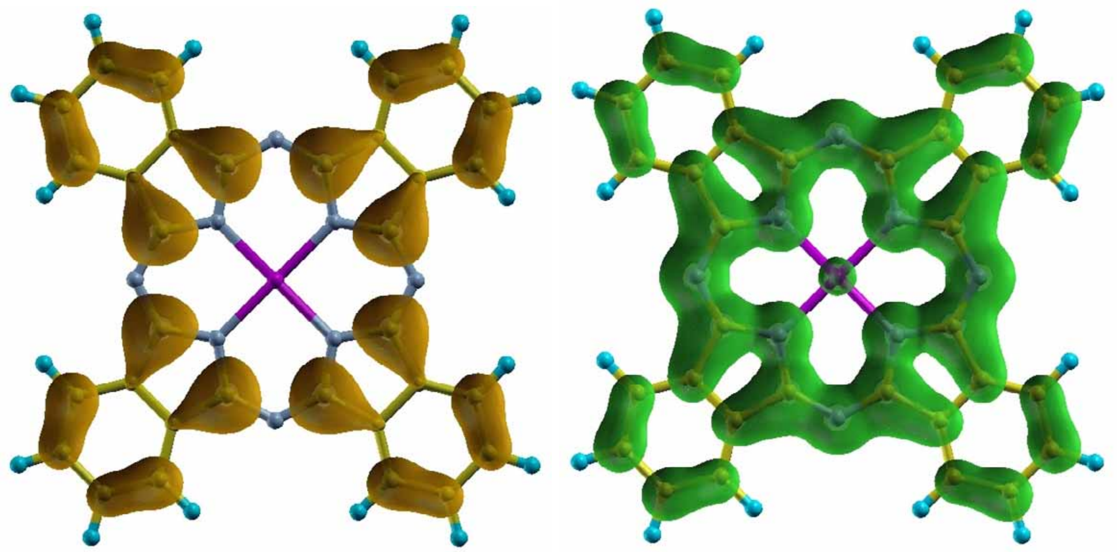
UV-vis absorption (red) and steady-state fluorescence emission (blue) (λ_{exc} = 670 nm) spectra of **I** in THF solution, in the inset fluorescence excitation spectrum (λ_{em}= 710 nm).

Electrochemical measurements

Cyclic voltammograms were recorded at 25 °C with a computer aided system (AMEL INSTRUMENTS 2059 potentiostat/galvanostat, 568 function generator) in a conventional three electrodes cell, a platinum disk was used as working electrode together with a platinum wire as auxiliary electrode. The reference electrode was Ag/$AgNO_3$(0.01M) in distilled acetonitrile (E_0 vs SCE = 0.298 V). The samples solutions were about 10^{-4} M in distilled anhydrous THF and tetra(*n*-butyl)ammonium tetrafluoroborate (TBATFB, 0.1 M) was used as supporting electrolyte. The solutions were previously purged for 10 minutes with nitrogen and all measurements were performed in inert atmosphere.

Theoretical methods.

The structure and the electronic properties of the ZnPc molecule have been investigated by using *ab initio* Density Functional Theory methods in the generalized gradient approximation (GGA) and a supercell approach.[1] Total energies have been calculated by using ultrasoft pseudopotentials,[2] plane-wave basis sets, and the PBE gradient corrected exchange-correlation functional.[3] Satisfactorily converged results have been achieved by using cutoffs of 30 Ry on the plane waves and of 240 Ry on the electronic density as well as the Γ point for the **k**-point sampling of the Brillouin zone. Geometry optimization procedures have been performed by fully relaxing the positions of all of the atoms in a large (60 a.u. edge) cubic supercell as well as by applying a Makov-Payne correction to the total energy, in order to minimize the occurrence of spurious interactions between periodically repeated images. The electronic properties have been investigated by analyzing the electronic eigenvalues and eigenfunctions calculated at the Γ point. The electronic eigenvalues could be affected, in principle, by two limits of the DFT-GGA methods: i) a wrong ordering of the frontier molecular orbitals, due to a self-interaction error inducing a bad description of the strongly localized *d* orbitals of the central metal,[4] and ii) the well known GGA limit leading to too small values of the molecule HOMO-LUMO gap. However, the former limit does not affect the results achieved for the investigated metallo-organic molecules carrying a Zn atom, whose fully occupied *d* shell is quite deeply embedded in the region of the occupied ligand orbitals[5]. The frontier HOMO-LUMO belong indeed to the Pc macrocycle and are not affected by the *d* orbitals of the central atom. Regarding the latter limit, the GGA error on the energy gaps, our HOMO-LUMO gap (1.42 eV) reasonably compares with the experimental values (1.7-1.9 eV). The HOMO and LUMO eigenfunctions have been used to calculate the $|\psi|^2$ isosurfaces reported in Fig. 2 of the paper. Similar isosurfaces are plotted in the following figure for the HOMO and LUMO $|\psi|^2$ estimated in the case of the unsubstituted ZnPc.

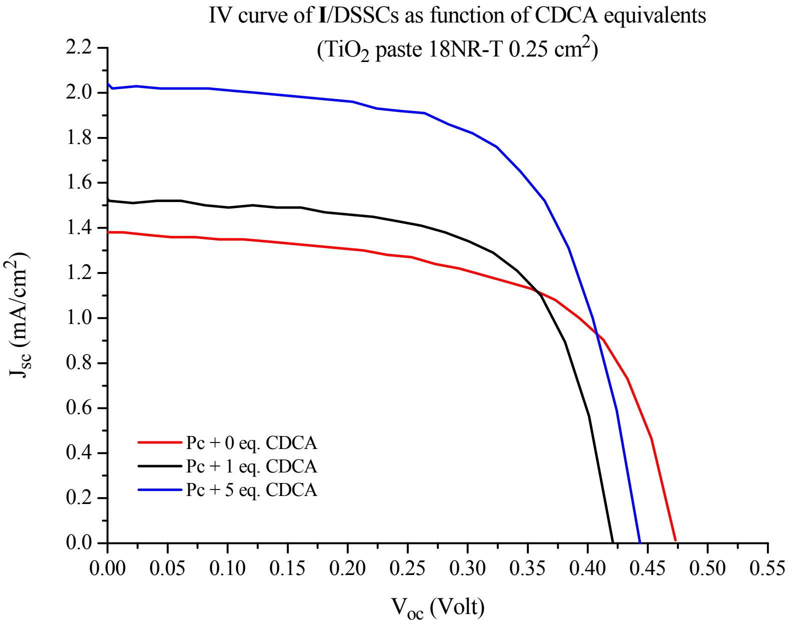


Electron density isosurfaces of the π HOMO (left) and of the doubly degenerate π^* LUMO (right) of the unsubstituted ZnPc molecule (isosurfaces are sampled at 0.0005 $e/a.u.^3$).

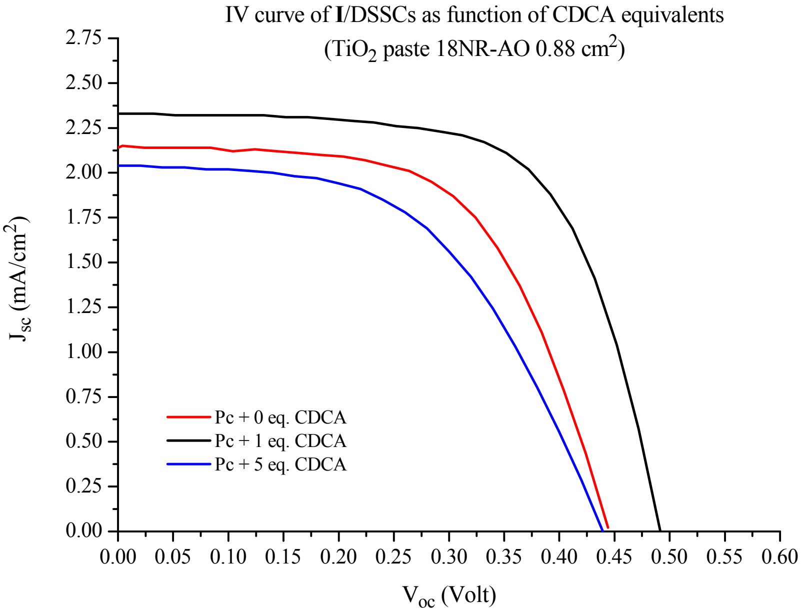
[1] Giannozzi, P.; et al. *J. Phys.: Condens. Matter*, 2009, **21**, 395502. http://www.quantum-espresso.org.
[2] D. Vanderbilt, *Phys. Rev. B*, 1990, **41**, 7892.
[3]J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
[4] N. Marom, O. Hod, G. E. Scuseria, and L. Kronik, *J. Chem. Phys.*, 2008, **128**, 164107.
[5] G. Mattioli *et al. Chem. Mater.*, 2009, **21**, 4555–4567.

DSSC fabrication.

Sensitization was carried out in 0.1mM EtOH solution of **I** at rt and different time depending on the Chenodeoxycholic Acid (CDCA) equivalents (16h for 0 and 1eqs, 48-72h for 5 and 10 eqs). Two different TiO_2 pastes were used: 18NR-T (transparent TiO_2 paste; 7 µm thickness, 0.25 cm^2 active area) and 18NR-AO (opaque TiO_2 paste; 14µm thickness, 0.88cm^2 active area) purchased by Dyesol. Electrolyte used was the I^{3-}/I^- based EL-HSE, while the platinum for the counter electrode was PT-1 catalyst, both purchased by Dyesol.



I-V curve of I/ DSSCs with 18NR-T (transparent) photoanode (active area: 0.25 cm^2, thickness 7µm)



I-V curve of I/DSSCs with 18NR-AO (opaque) photoanode (active area: 0.88 cm^2, thickness 14µm).