Supporting information for

A Squaraine-Phthalocyanine Ensemble: Towards Panchromatic Materials in Solar Cells

Fabio Silvestri,[a,b,d] **Ismael López-Duarte,**[a] **Wolfgang Seitz,**[c] **Luca Beverina,**[b] **M. Victoria Martínez-Díaz,**[a] **Tobin J. Marks,***[d] **Dirk M. Guldi,***[c] **Giorgio A. Pagani,***[b] **and Tomás Torres***[a]

[a]*Universidad Autonoma de Madrid, Departamento de Quimica Organica,Cantoblanco, 28049 Madrid, Spain. E-mail:* tomas.torres@uam.es

[b]*University of Milano-Bicocca, Department of Materials Science,20215, Milan, Italy ; E-mail:* giorgio.pagani@mater.unimib.it

[c]*Department of Chemistry and Pharmacy & Interdisciplinary Center for Molecular Materials, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen, Germany, E-mail:* dirk.guldi@chemie.uni-erlangen.de

[d]*Department of Chemistry and the Materials Research Center, Northwestern University, Evanston, Illinois, 6020, USA E-mail :* t-marks@northwestern.edu

General. NMR spectra were recorded using a Bruker AC-300 instrument. UV/Vis spectra were recorded with a Hewlett-Packard 8453 instrument. MALDI-TOF MS and HRMS spectra were recorded with a Bruker Reflex III spectrometer. The Electrospray analyses were performed on a mass spectrometer with quadrupole analyzer coupled with an HPLC apparatus from Agilent (model 1100). Column chromatographies were carried out on silica gel Merck-60 (230-400 mesh, 60 Å) and TLC was performed on aluminum sheets precoated with silica gel 60 F254 (E. Merck). Chemicals were purchased from Aldrich Chemical Co. and used as received without further purification. Alkylation of pyrrole 2-carbaldehyde was made modifying the previously reported preparative.[1]

Synthesis of Sq-PEP. A suspension of squaric acid (0.252 g, 2.21 mmol), pyridine (0.320 g, 4.03 mmol) and **PEP** (1.5 g, 4.43 mmol) in a 1:1 toluene/BuOH mixture (40 ml) was refluxed in a Dean-Stark apparatus for 3 h. The resulting deep green solution was chilled at 0°C overnight. Solvent was eliminated and the solid was purified by column chromatography (silica gel, CH_2Cl_2/AcOEt, 1:1) and then by gel permeation chromatography (BioBeads, THF) yielding 35% of a green solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ, ppm 8.65 (d, $J = 6$ Hz, 4H), 7.90 (d, $J = 4$ Hz, 2H), 7.36 (d, $J = 6$ Hz, 4H), 7.25 and 7.15 (AB system $J = 16$ Hz, 4H), 6.96 (d, $J = 4.7$ Hz, 2H), 4.02 (m, 4H), 1.75 (m, 36H), 1.39-1.26 (m, 18H), 0.79 (t, 6H). HR MALDI-TOF MS (dithranol): *m/z*: 755.5225 $[M + H]^+$, calcd for $C_{50}H_{66}N_4O_2$: 754.5186. UV-Vis ($CHCl_3$, λ_{max}, logε) 680 (5.2).

Synthesis of Pc-Sq-Pc. A solution of bis(pyridyl) derivative **Sq-PEP** (30 mg, 0.039 mmol) and **Ru(CO)Pc** (85 mg, 0,098 mmol) in chloroform (10 ml) was heated with stirring at 60 ºC for 4 h. The solvent was removed and the residue subjected to gel exclusion chromatography (Bio-Beads SX-1, CH_2Cl_2). The first eluted fraction was collected and the solvent rotary evaporated. The solid was suspended in hexanes, filtered, and washed with hexanes and methanol yielding a dark-violet blue solid (50%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ, ppm 9.40 (d, $J = 8.0$ Hz, 8H, Pc), 9.3-9.2 (m, 8H, Pc), 8.13 (d, *J* = 8.0 Hz, Pc), 7.44 (d, *J* = 4.7 Hz, 2H, pyrrol), 6.30 (d, 4.7 Hz, pyrrol), 6.03 and 5.85 (AB system, *J* = 16 Hz, C=C), 5.27 (d, *J* = 6 Hz, 4H, Py), 4.22 (m, 4H, CH_2N), 1.96 (d, *J* = 6 Hz, 4H, Py), 1.7 (m, 36H, *t*-Bu), 1.3-0.7 (m, 46H). ESI (methanol + 1% TFA): *m/z* = 864.299 - 870.299, $[C_{49}H_{49}N_8ORu]^+$, 755.5175 $[C_{50}H_{67}N_4O_2]^+$. UV-Vis ($CHCl_3$, λ_{max}, $\log\varepsilon$) 700 (5.2), 651 (5.5), 589 (4.9), 301 (5.3).

BHJ OPV device fabrication and Thin Film Characterization. Devices were fabricated by spin-coating a blend of **Pc-Sq-Pc/PCBM** in different ratio, sandwiched between a transparent anode and a cathode. The anode consisted of glass substrates pre-coated with indium tin oxide (ITO), modified by spin-coating polyethylenedioxythiophene/ polystyrenesulphonate (PEDOT/PSS) layer, and the cathode consisted of LiF (0.12 nm) capped with Al (150 nm). The rates used were 0.1 Å/s for LiF (Acros, 99.98%) and 2 Å/s for Al (Sigma-Aldrich, 99.999%), with a chamber pressure of $1.1\text{x}10^{-6}$ Torr. Before device fabrication, the ITO-coated (150 nm) glass substrates were cleaned by ultrasonic treatment in detergent, deionized water and soap, deionized water, isopropyl alcohol, methanol and acetone sequentially and finally in a UV-ozone cleaner for 30 minutes under ambient atmosphere. A thin layer (30 nm) of PEDOT/PSS (Baytron P VP A1 4083) was spin-coated to modify the ITO surface. After baking at 150 °C for 15 minutes, the active layer was obtained by spin-coating the blends at 3000 rpm for 60 seconds by chloroform. Contact areas were cleaned with dry toluene and a cotton swab; the thickness of film was measured with profilometry (Tencor, P10). The best devices were obtained spin coating a solution of 8mg/ml. Atomic force microscopic (AFM) images were obtained using a JEOL-5200 Scanning Probe Microscope with silicon cantilevers in the tapping mode, using WinSPM Software.

BHJ OPV I-V characterization. Device evaluation was performed at 298K using a Class A Spectra-Nova Technologies solar cell analyzer having a xenon lamp that simulates AM1.5G light from 400 – 1100 nm. The instrument was calibrated with a monocrystalline Si diode fitted with a

KG3 filter to bring spectral mismatch to unity. The calibration standard was calibrated by the National Renewable Energy Laboratory (NREL). Four-point contacts were made to the substrate with Ag paste and copper alligator clips. Individual devices were isolated by a mask during testing to avoid current collection from adjacent devices and edge effects.

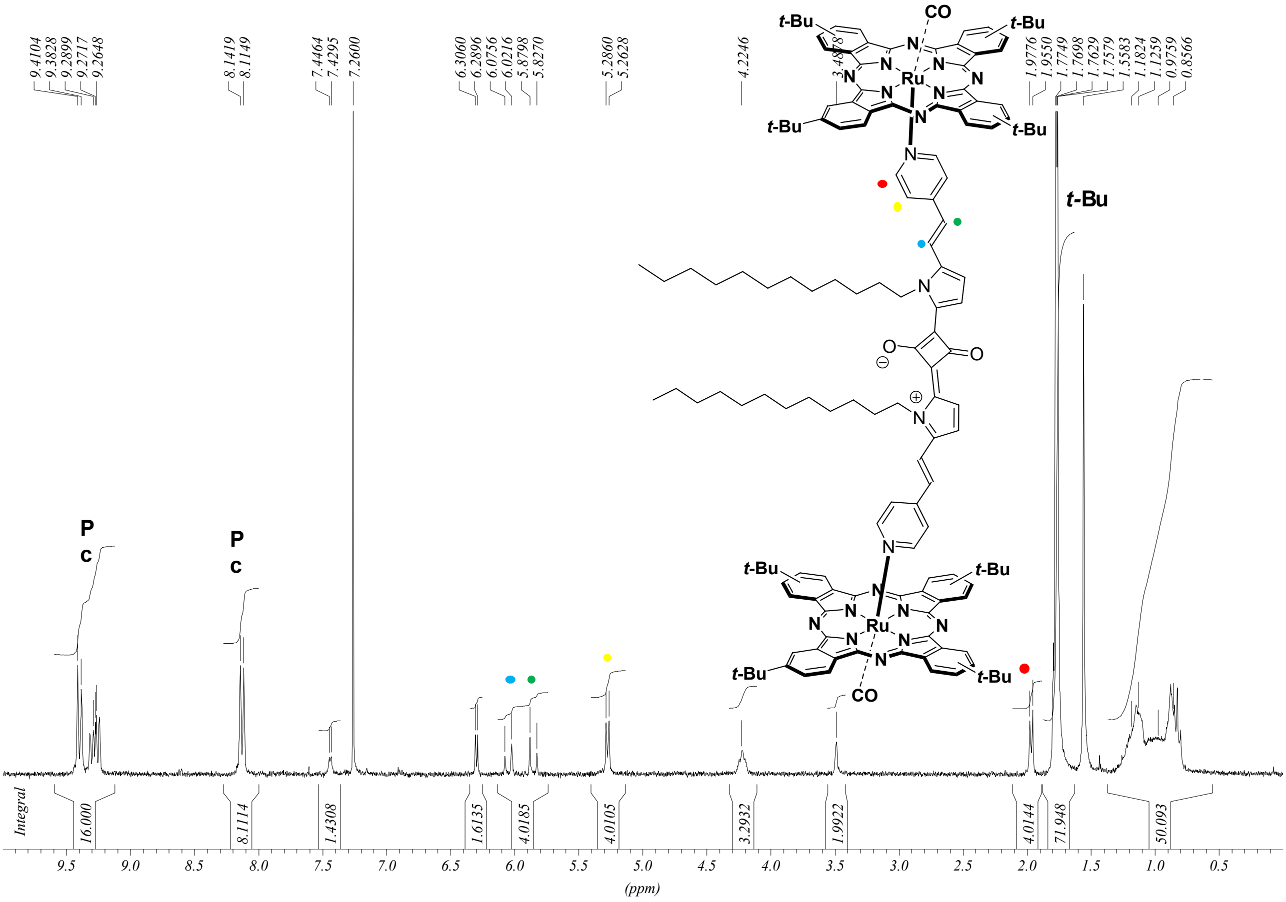

Figure S1. ^{1}H NMR of **Pc-Sq-Pc** in $CDCl_3$.

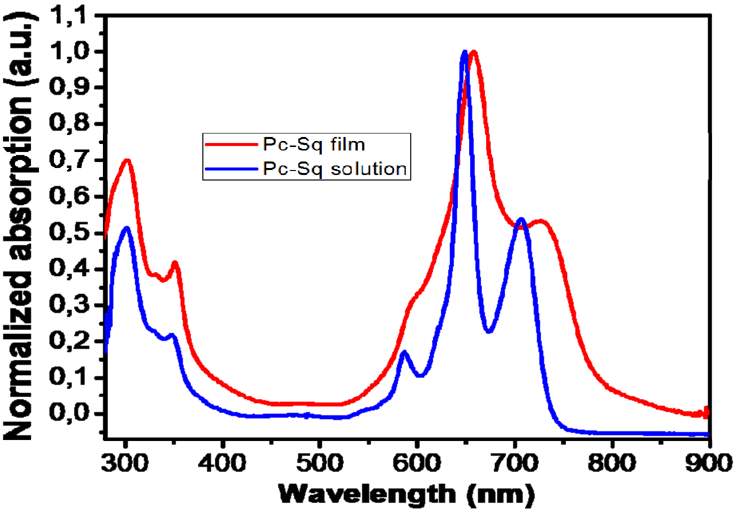

Figure S2. Normalized optical absorption spectra of **Pc-Sq-Pc** ensemble: in $CHCl_3$ solution (blue line) and films from $CHCl_3$ (red line).

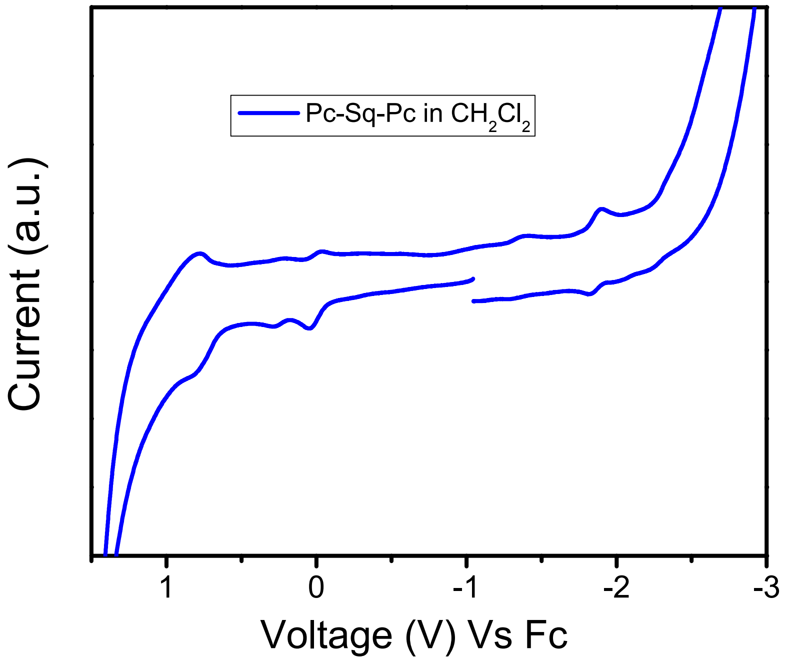

Figure S3. CV curves of **Pc-Sq-Pc** in 0.1 M $Bu_4N^+PF_6^-$ solution in CH_2Cl_2 at a scan rate of 100 mV/s.

Compd	$E_{½}(1)$ [mV]	$E_{½}(2)$ [mV]	E_{gap}^{opt}	E^{red} [V]
Pc-Sq-Pc	0.02	0.82	1.8	-1.84
Sq-PEP				-1.19[1]
RuPcCOPy	0.09	0.88		-1.69

Table S1. Half-Wave Potentials ($E_{1/2}$ vs Fc/Fc^+), Energy gap and reduction potentials of **Pc-Sq-Pc**, **Sq-PEP** and **RuPcCOPy**.

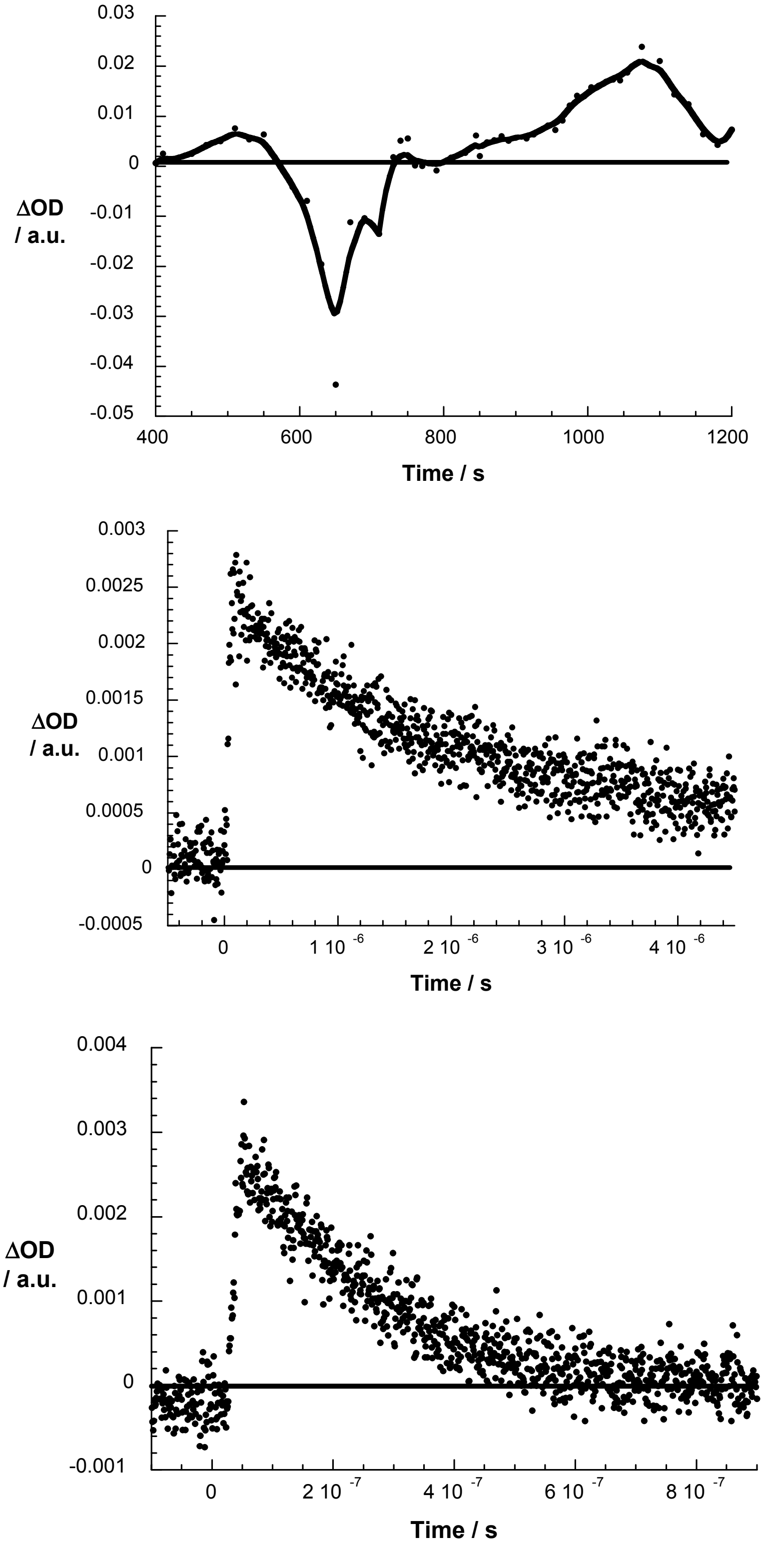

Figure S4. Upper part – differential absorption spectra (visible and near-infrared) obtained upon nanosecond flash photolysis (355 nm) of **Pc-Sq-Pc** in argon saturated toluene with a time delay of 50 ns at room temperature. Central part – time-absorption profiles of the radical ion pair state spectrum at 1050 nm, monitoring the charge recombination in oxygen free toluene. Lower part – time-absorption profiles of the radical ion pair state spectrum at 1050 nm, monitoring the charge recombination in oxygenated toluene.

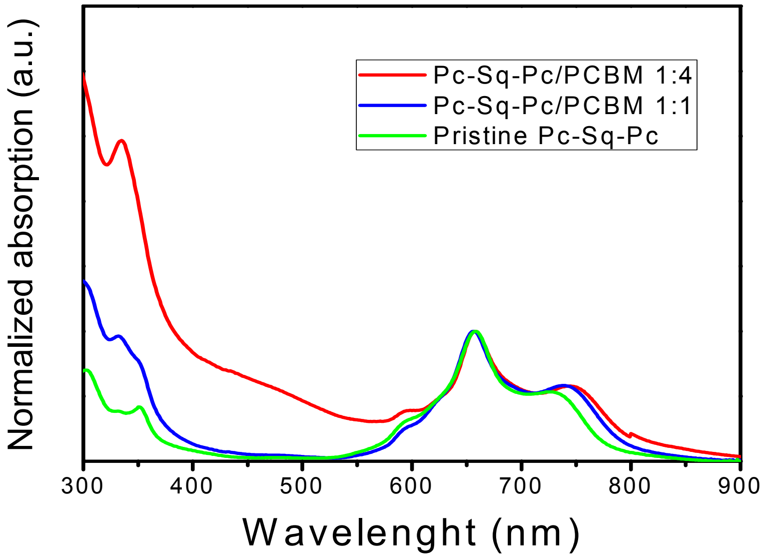

Figure S5. Absorption spectra for pristine **Pc-Sq-Pc** (green line), **Pc-Sq-Pc/PCBM** 1:1 wt/wt ratio (blue line) **and Pc-Sq-Pc/PCBM** 1:4 wt/wt ratio (blue line).

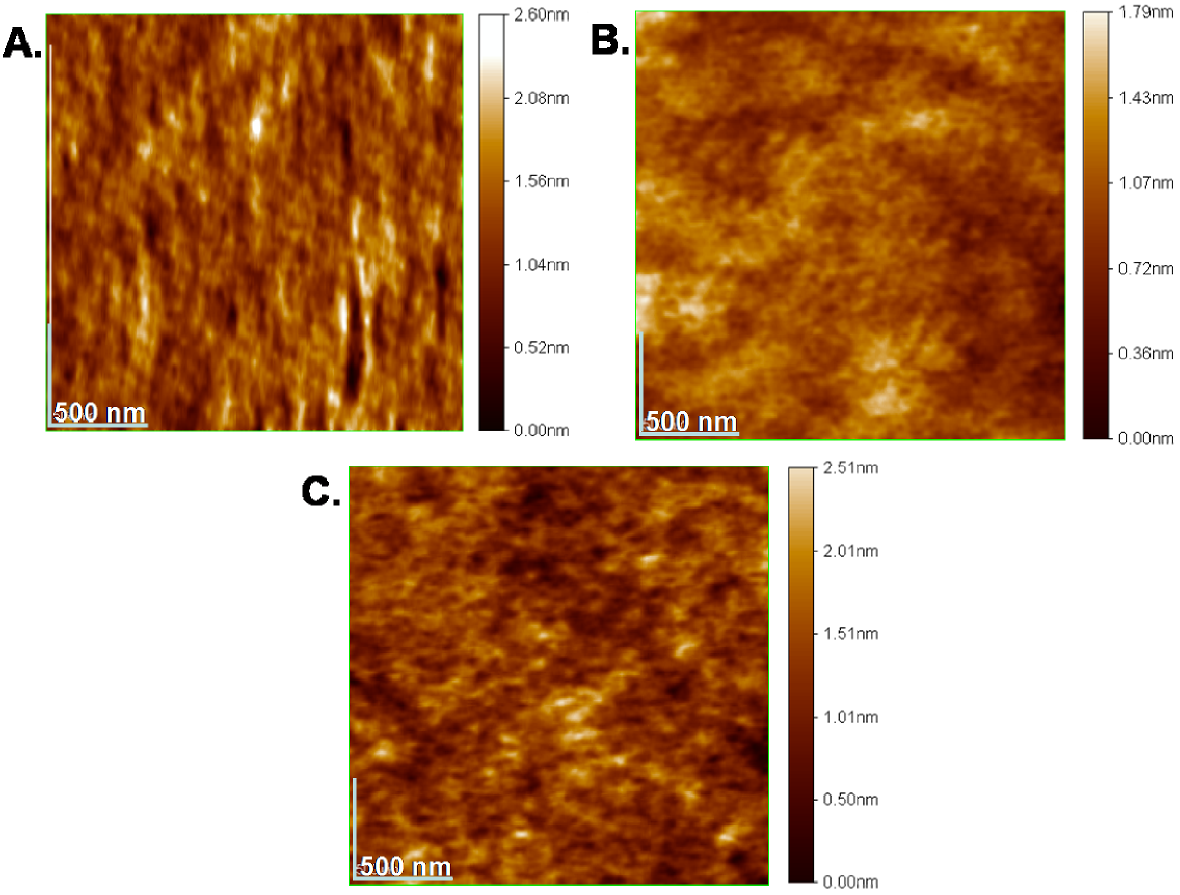

Figure S6. Tapping mode AFM imagines. **A.** Pristine **Pc-Sq-Pc** (δ_{RMS}= 0.296). **B. Pc-Sq-Pc/PCBM** 1:1 wt/wt ratio (δ_{RMS}= 0.329). **C. Pc-Sq-Pc/PCBM** 1:4 wt/wt ratio (δ_{RMS}= 0.351).

References

1 L. Beverina, M. Crippa, M. Landenna, R. Ruffo, P. Salice, F. Silvestri, S. Versari, A.Villa; L. Ciaffoni, C. Ferrante, S. Bradamante, C. M. Mari, R. Bozio, G. A. Pagani, *J. Am. Chem. Soc.,* 2008, **130**, 1894.

2 C.-C. Wu, J. C. Sturm, R. A. Register, J. Tian, E. P. Dana, M. E. Thompson, *IEEE Transaction on Electrons Devices*, 1997, **44**(8), 1269.