Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

SUPPLEMENTARY INFORMATION

Supramolecular Organic-Inorganic Domains integrating Fullerene-based acceptors with Polyoxometalate-bis-Pyrene Tweezers for Organic Photovoltaic applications.

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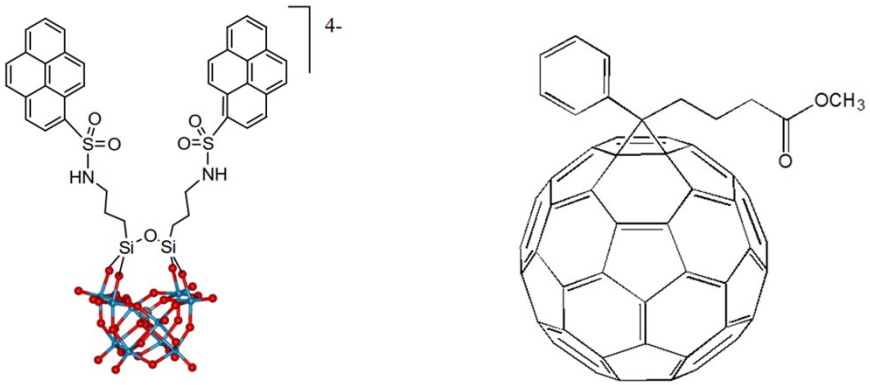

a) **b)**

Figure 1S. Chemical structure of a) divacant Keggin-type decatungstosilicate bisfunctionalized with pyrene and b) Phenyl-C61-butyric acid methyl ester (PCBM) used to form the supramolecular adduct.

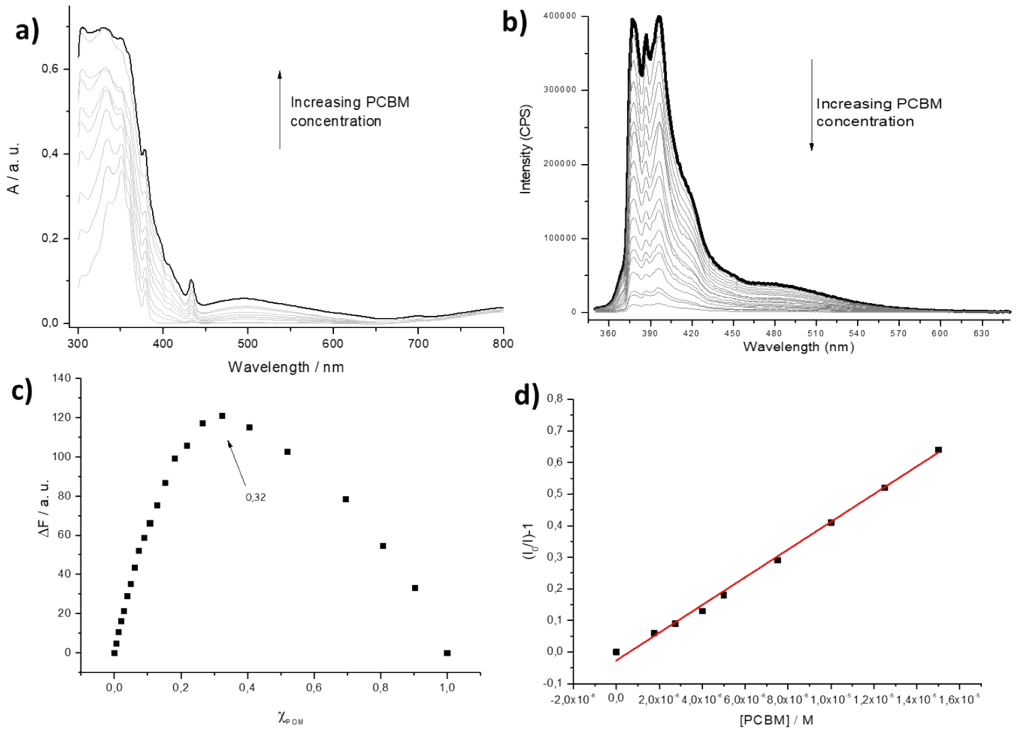

Figure 2S. Influence of PCBM (dissolved in o-DCB, $5x10^{-3}$ M) added 4 µL at each step on a) absorption and b) fluorescence spectra of pyrPOM (10 µM in DMF) solution. c) Job's plot for pyrPOM and PCBM in DMF/o-DCB at room temperature. d) Fluorimetric Stern–Volmer graph (λ_{ex} = 350 nm; λ_{em} = 397 nm) .

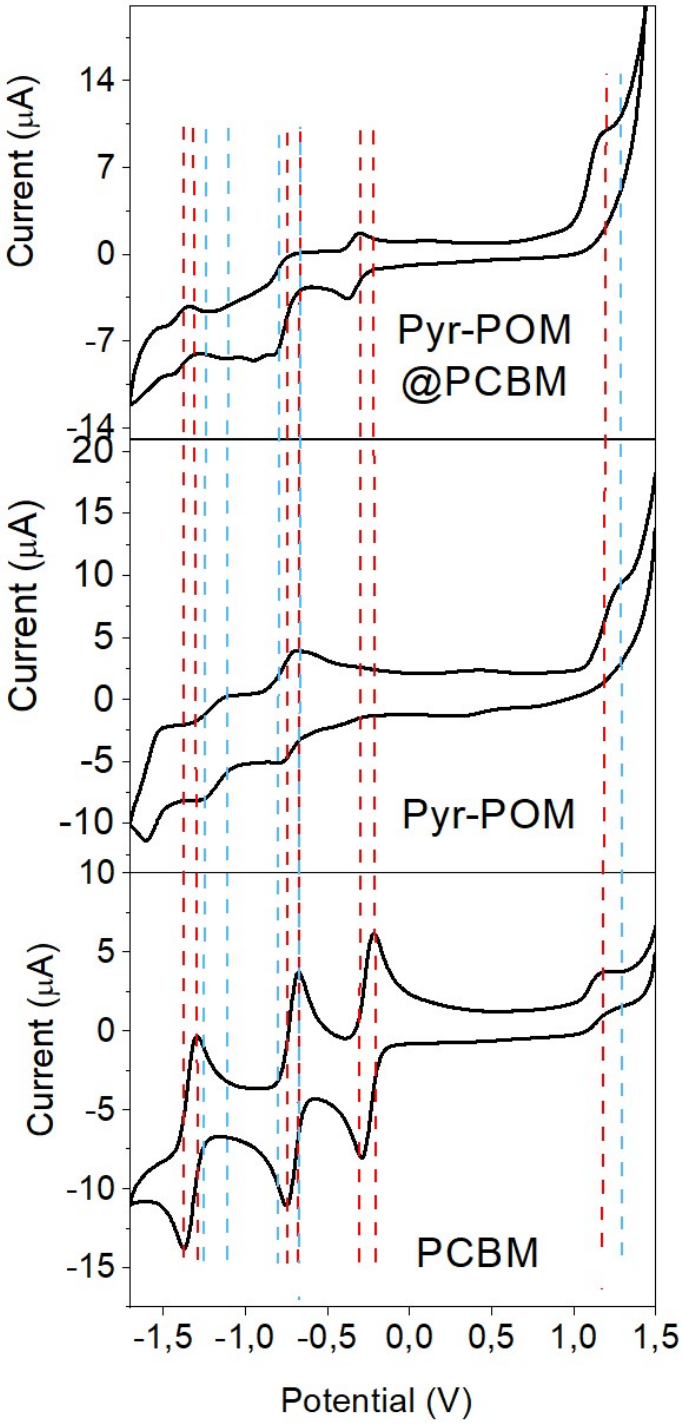

Figure S3. Cyclic voltammograms of pyrPOM@PCBM (1:2) (pyrPOM 0.5 mM), compared with those of pyrPOM (0.5 mM) and PCBM (1 mM) in degassed DMF solution containing TBAP 0.10 M, at a scan rate of 50 mV s^{-1}. While the irreversible oxidation wave of pyrPOM@PCBM (with anodic peak potential E_{pa}= +1.19 V vs Ag/Ag^{+}) appears as the overlap of POM-linked pyrene band (E_{pa}= +1.27 V vs Ag/Ag^{+}) and PCBM oxidation band (E_{pa}= +1.18 V vs Ag/Ag^{+}), the reduction waves of the two building blocks are strongly modified upon assembly of the two components: the characteristic pattern given by the three reversible reduction bands of PCBM (red dashed lines, with half-wave potentials $E_{1/2}$=-0.246; -0.709; -1.330 V vs. Ag/Ag^{+}) become much

less defined, being the first reduction band of PCMB shifted towards more negative potentials ($E_{1/2}$=-0.336 V vs Ag/Ag^{+}) and the other bands mixed with those of pyrPOM (light blue dashed lines).

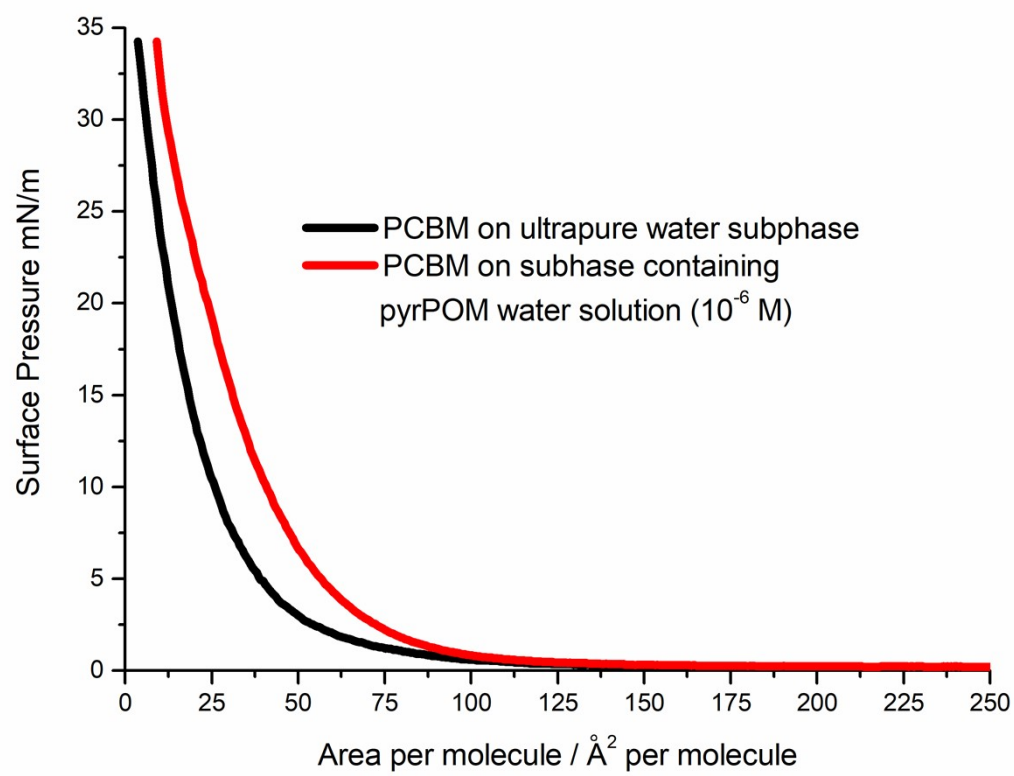

Figure 4S. Langmuir curves surface pressure *vs* area per molecule recorded for PCBM chloroform solution (10^{-3} M) spread on ultrapure water subphase (black line) and for PCBM chloroform solution (10^{-3} M) spread on subphase containing pyrPOM solution (10^{-6} M). An evident shift towards higher area per molecule values is observed when pyrPOM is dissolved in the subphase.

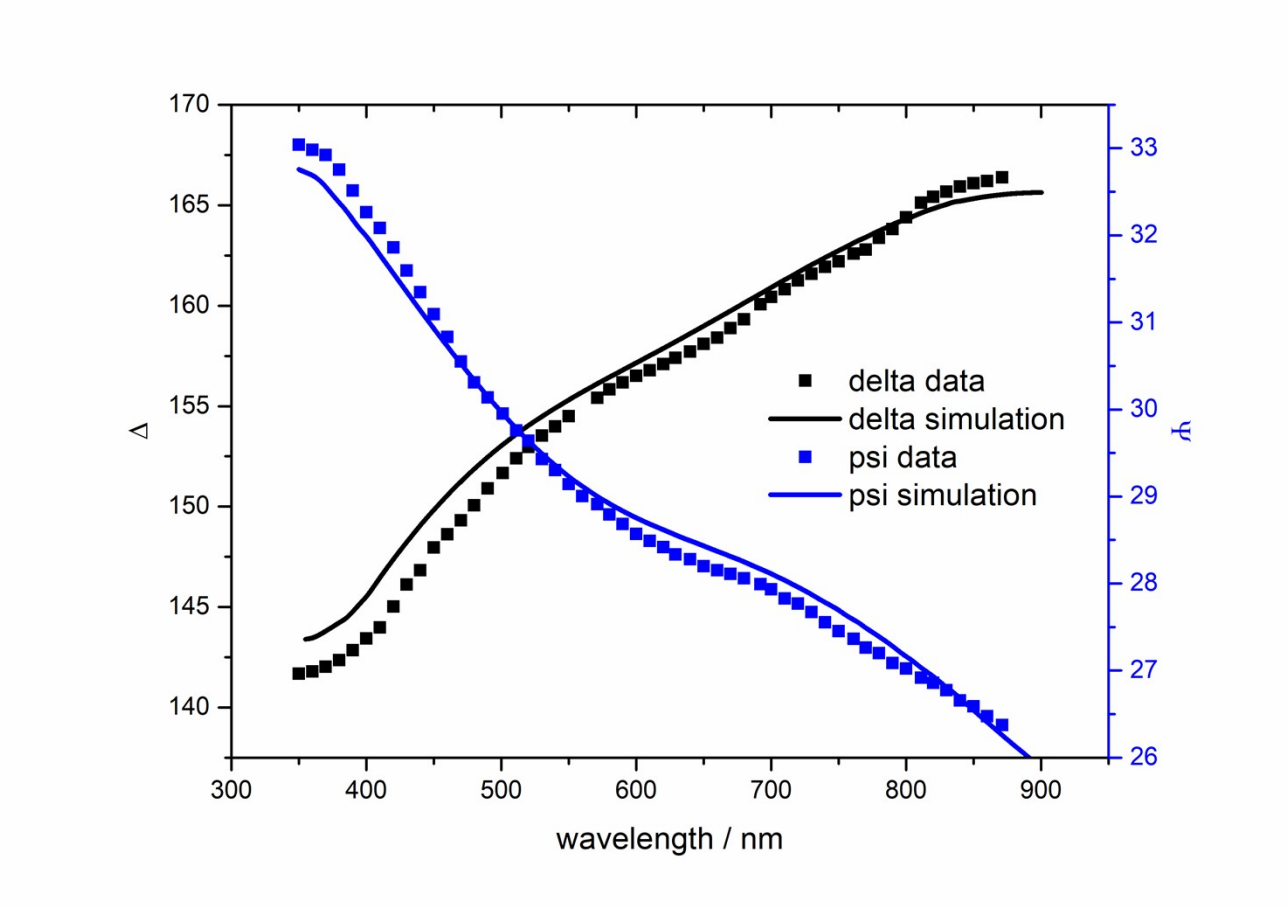

Figure 5S. Squared points represent the optical functions Δ and ψ of PCBM LS film (8 runs), continuous lines are the simulated curves obtained using two Lorentz oscillators as model. It was estimated that the thickness of 8 PCBM LS runs is 48.1±6.3 nm.

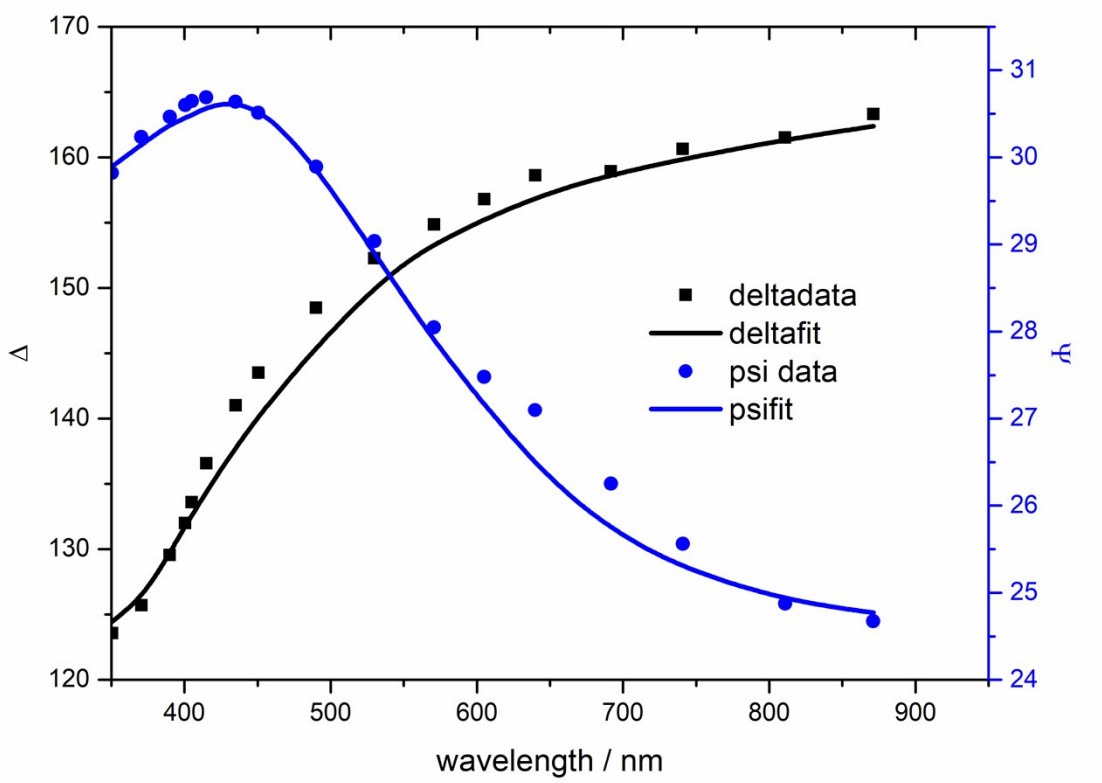

Figure 6S. Squared points represent the optical functions Δ and ψ of pyrPOM@PCBM LS film (8 runs), continuous lines are the simulated curves obtained using two Lorentz oscillators and a Drude equation as model. It was estimated that the thickness of 8 PCBM LS runs is 59.7±3.7 nm

In order to evaluate the **molar ratio** between pyrPOM and PCBM, two different EMAs (Effective Medium Approximations) have been used:

Maxwell-Garnett's approximation: $$\varepsilon_{eff} = \varepsilon_m \frac{2(1-\delta_i)\varepsilon_m + (1+2\delta_i)\varepsilon_i}{(2+\delta_i)\varepsilon_m + (1-\delta_i)\varepsilon_i}$$

Parameter	Best fit	+/-	unit
thickness	67,1	5,4	nm
fraction guest	0,29	0,02	ratio
RMSE	3,623		

PCBM:POM = 2,4:1

$$\delta_{POM}\frac{\varepsilon_{POM} - \varepsilon_{eff}}{\varepsilon_{POM} + (d-1)\varepsilon_{eff}} + \delta_{PCBM}\frac{\varepsilon_{PCMB} - \varepsilon_{eff}}{\varepsilon_{PCBM} + (d-1)\varepsilon_{eff}} = 0$$

Bruggeman's approximation:

Parameter	Best fit	+/-	unit
thickness	70,4	4,1	nm
fraction guest	0,32	0,02	ratio
RMSE	2,985		

PCBM:POM = 2,1:1

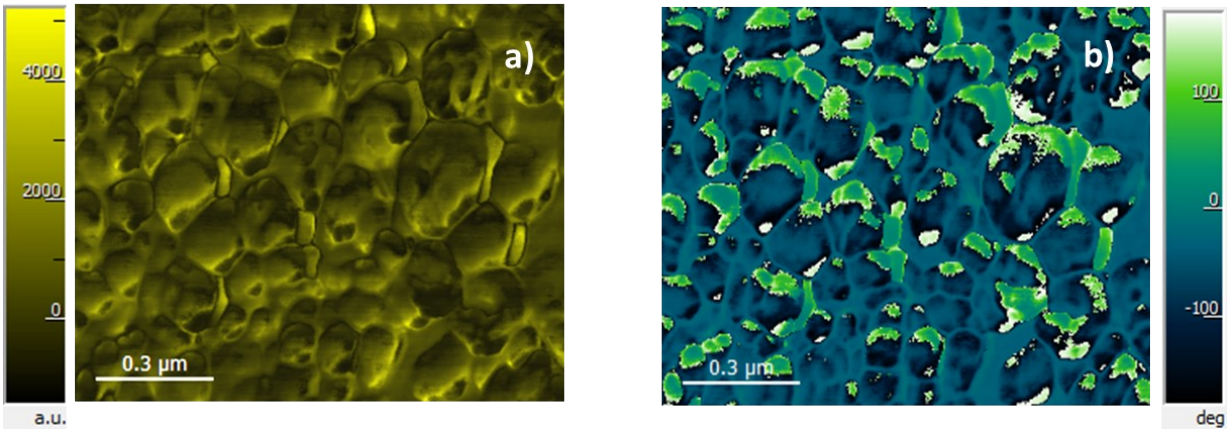

Figure 7S: PFM amplitude a) and phase b) of two LS runs of pyrPOM@PCBM film.