Towards enhancing light harvesting – subphthalocyanines as electron acceptors

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SUPPORTING INFORMATION

General Remarks:

IR spectra were recorded on a Bruker Vector 22 spectrophotometer. LSI-MS and HRMS spectra were determined on a VG AutoSpec instrument. MALDI-TOF MS were recorded with a Bruker Reflex III spectrometer. NMR spectra were recorded with a BRUKER AC-300 instrument and a BRUKER DRX-500 instrument. Elemental analyses were performed with a Perkin-Elmer 2400 apparatus. Column chromatographies were carried out on silica gel Merck-60 (230-400 mesh, 60 Å), and TLC on aluminum sheets precoated with silica gel 60 F_{254} (E. Merck). Chemicals were purchased from Aldrich Chemical Co. and used as received without further purification.

The Electrospray analysis were performed on a mass spectrometer with quadrupole analyzer coupled with an HPLC apparatus from Agilent (model 1100). The samples were introduced every 30 min by Flow injection analysis using the automatic injector from the HPLC with an acetone flow of 20 μl/min. The instrument parameters were the following: ionization type: electrospray positive mode, fragmenter: 30 V, Mass range: 100-3000 umas, drying gas flow(N_2): 5L/min, nebulizer pressure: 25 psi, drying gas temperature: 30 °C, capillary voltage: 4500 V, mobile phase: acetone, flow: 20 μl/min.

UV/Vis spectra were recorded with a Hewlett-Packard 8453 and Varian Cary 5000 UV-VIS-NIR instruments. The fluorescence experiments were carried out using a Horiba Jobin Yvon Fluoromax 3P and Horiba Jobin Yvon Fluorolog-3 spectrometer. The quantum yields were determined using cresyl violet in methanol (QY = 0.54) as standards. The fluorescence-lifetime measurements were performed by time correlated single photon counting (TCSPC) by using a FluoroLog-3 spectrometer.

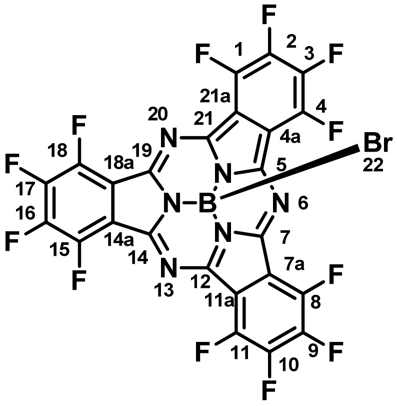
Femtosecond transient absorption studies were performed with 775 and 387 nm laser pulses (1 kHz, 150 fs pulse width, 200 nJ) from an amplified Ti/sapphire laser system (Model CPA 2101, Clark-MXR Inc. – output 775 nm).

Molecular geometries were optimized with HyperChem (version 8.0.4) using AM1 semiempirical method. Molecular orbitals were generated with the ChemBio 3D (version 12.0) software using extended Hückel method.

Electrochemical measurements were performed at room temperature in a Bioanalytical Systems BASCV-50W potentiostat with a three electrode configuration cell, containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as supporting electrolyte. A glassy carbon electrode (3 mm) was used as working electrode, a platinum mesh separated from the solution by a Vycor tip was used as counter electrode and $Ag/AgNO_3$ as the reference electrodes. Prior to each voltammetric measurement, the cell was degassed. The solvent, THF (5 mL), which was distillated and also degassed, was then transferred into the cell. The electrochemical measurements were performed using a concentration of approximately 0.5 mM of the corresponding compound, and ferrocene was added as an internal reference. The scan rate was 100 mV/s.

Supplementary data for:

COMPOUND 5



Compound 5:

In a 25-ml two-necked round-bottomed flask, equipped with a condenser, magnetic stirrer and rubber seal, dry tetrafluorophthalonitrile (800 mg, 4 mmol) was dissolved in chlorobenzene (1.1 ml) and was stirred at room temperature under argon atmosphere for five minutes. BBr_3 (4 mmol, 1 M solution in dichloromethane) was added and after five minutes THF (5 μl) was added. Solution was heated at 60 ºC for one hour. The reaction mixture was cooled down to room temperature, the solvent was evaporated and the resulting dark pink solid was further purified by precipitation from MeOH, washed with hexane and dried under vacuum, yielding 857 mg of subphthalocyanine **5** as a dark pink solid.[1] Yield: 93%. Mp > 250ºC. ^{19}F-NMR (470 MHz, $CDCl_3$): δ (ppm) = -135.3 (AA´BB´ system; F-1, F-4, F-8, F-11, F-15, F-18), -145.9 (AA´BB´ system; F-2, F-3, F-9, F10, F-16, F-17). ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ (ppm) = 146.5 (C-5, C-7, C-12, C-14, C-19, C-21), 144.3-143.7 (C-F), 140.6-139.6 (C-F), 115.3-114.5 (C-4a, C-7a, C-11a, C-14a, C-18a, C-21a). MS (LSI-MS, *m*-NBA): *m/z* = 690 $[M]^+$ (35%). HRLSI-MS ($C_{24}F_6N_6BBr$) $[M]^+$: Calculated: 689.9269. Found: 689.9290. UV-vis ($CHCl_3$): λ_{max} (nm) (log ε (dm^3 mol^{-1} cm^{-1})) = 575 (4.5), 523 (sh), 499 (sh), 300 (4.2). FT-IR (KBr), ν (cm^{-1}): 1534, 1480, 1423, 1288, 1260, 1174, 1119, 1026, 881, 741, 634 (B-Br).

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[1] a) Morse, G. E.; Helander, M. G.; Maka, J. F.; Lu, Z.-H.; Bender, T. P. *Appl. Mater. Interfaces* **2010**, *2*, 1934-1944; b) Sharman, W. M.; van Lier, J. E. *Bioconjugate Chem.* **2005**, *16*, 1166.

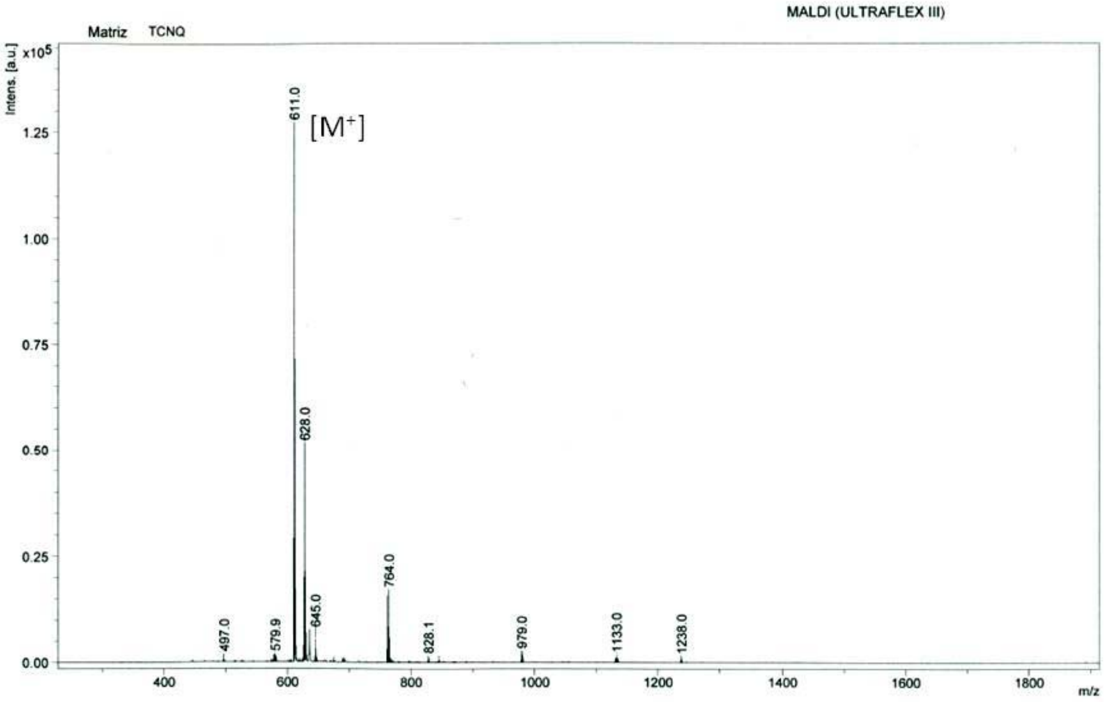


Figure S1: MS (MALDI TOF, TCNQ) of SubPc **5**.

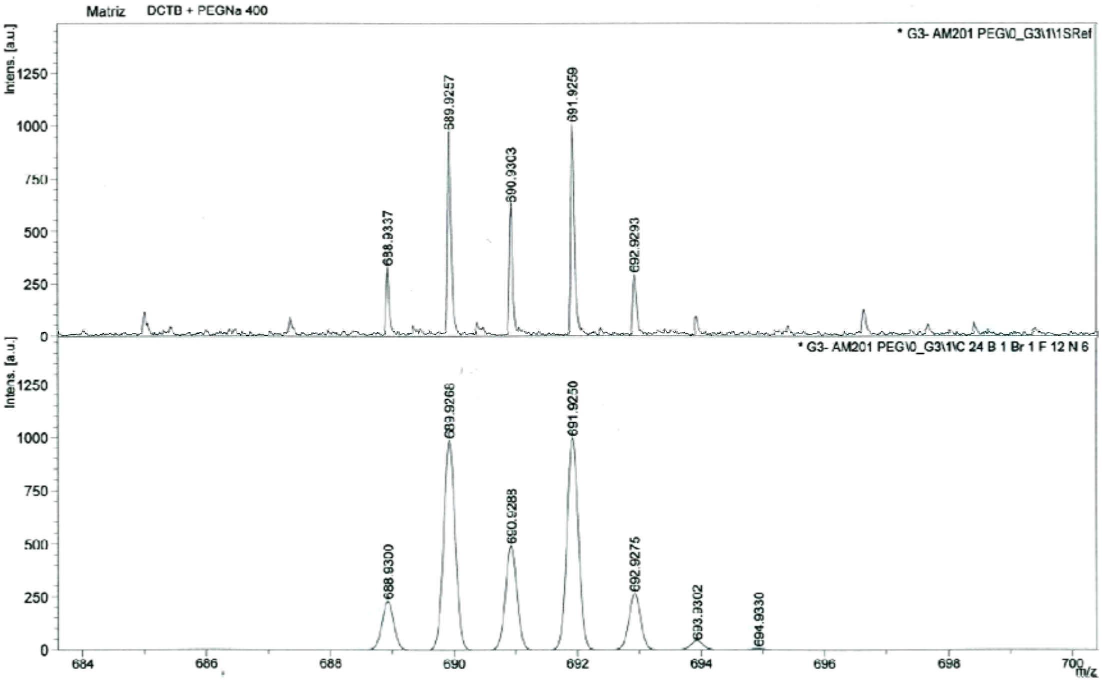


Figure S2: HRLSI-MS of SubPc **5** showing the experimental isotopic pattern compared to the theoretical one.

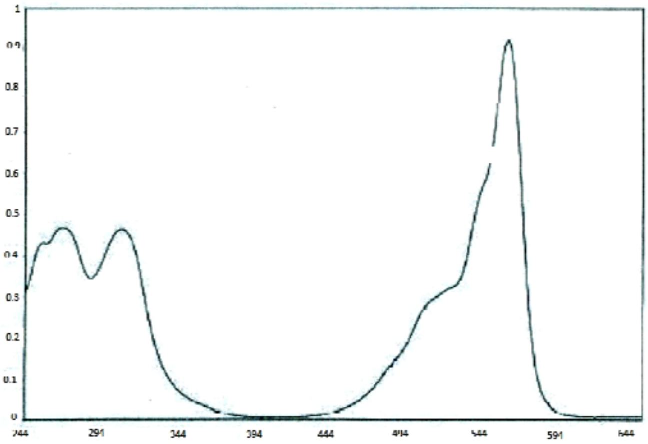
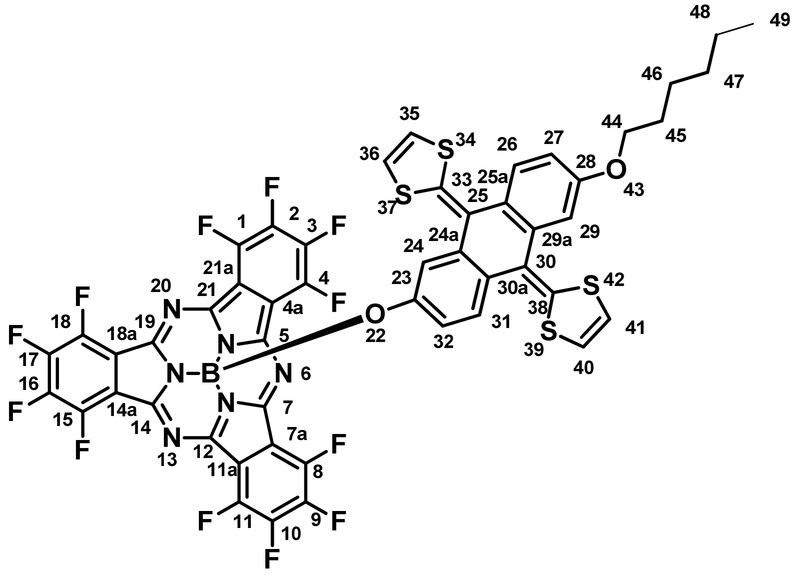


Figure S3: UV-Vis of SubPc **5** in chloroform.

Supplementary data for:

COMPOUND 1



Compound 1:

In a 25-ml round-bottomed flask, equipped with a condenser and a magnetic stirrer, ex-TTF **3** (75 mg, 0.15 mmol) and bromosubphthalocyanine **5** (35 mg, 0.05 mmol) were heated at 90ºC in toluene (1 ml) for 7h. The reaction mixture was cooled down to room temperature, the solvent was evaporated and the solid residue was purified by column chromatography on silica gel using hexane / ethyl acetate (10 : 1) as eluent. SubPc-exTTF **1** was obtained as a purple solid; 15 mg, yield 27%. Mp > 250ºC. ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.41 (d, J_o = 8.6 Hz, 1H, H-26), 7.12 (d, J_o = 8.4 Hz, 1H, H-31), 7.09 (d, J_m = 2.5 Hz, 1H, H-29), 6.71 (dd, J_o = 8.6 Hz, J_m = 2.5 Hz, 1H, H-27), 6.26 (m, 4H, H-35, H-36, H-40, H-41), 5.78 (d, J_m = 3.0 Hz, 1H, H-24), 5.21 (dd, J_o = 8.4 Hz, J_m = 3.0 Hz, 1H, H-32), 3.95 (m, 2H, H-44), 1.76 (m, 2H, H-45), 1.44 (m, 2H, H-46), 1.32 (m, 4H, H-47, H-48), 0.89 (m, 3H, H-49). MS (MALDI, DCTB) m/z = 1106.1 $[M]^+$. HRMS MS ($C_{50}H_{23}BN_6O_2S_4F_{12}$): Calculated: 1106.0670, Found: 1106.0644. UV-vis ($CHCl_3$): λ_{max} (nm) (log ε ($dm^3\ mol^{-1}\ cm^{-1}$)) = 568 (4,9), 561 (sh), 511 (sh), 422 (4,5). Anal. Calcd for $C_{50}H_{23}BN_6O_2S_4F_{12}$: C 54.26, H 2.09, N 7.59. Found: C 54.58, H 2.22, N 7.21%.

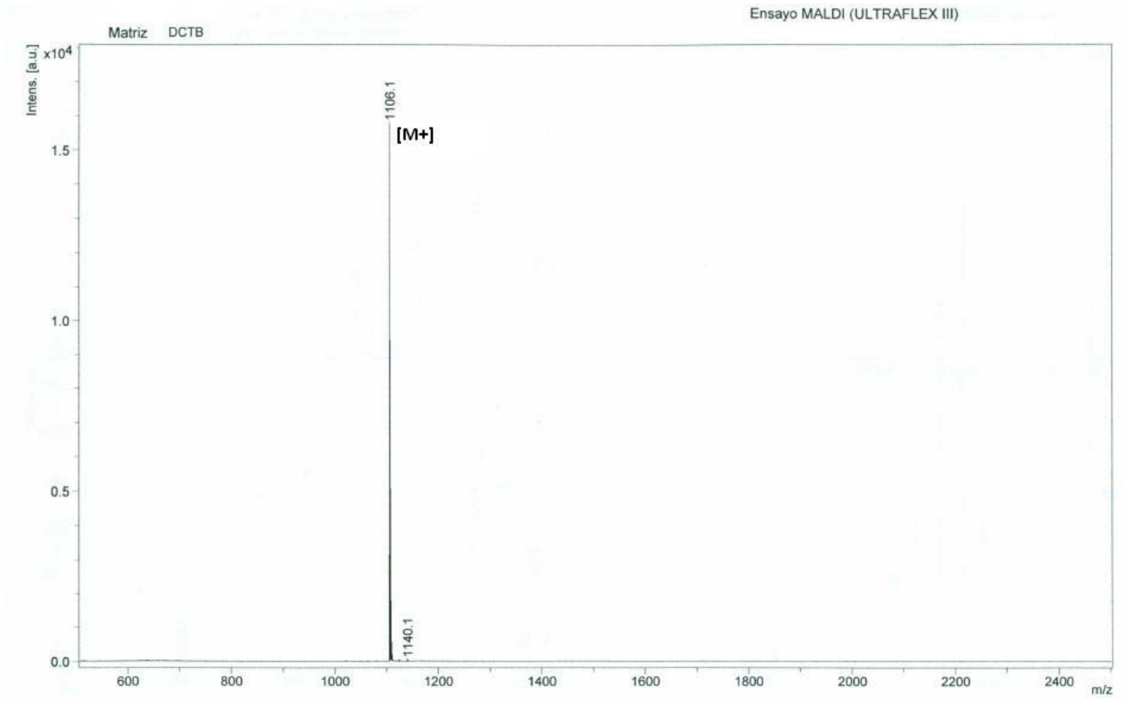


Figure S4: MS (MALDI TOF, DCTB) of SubPc-exTTF **1**.

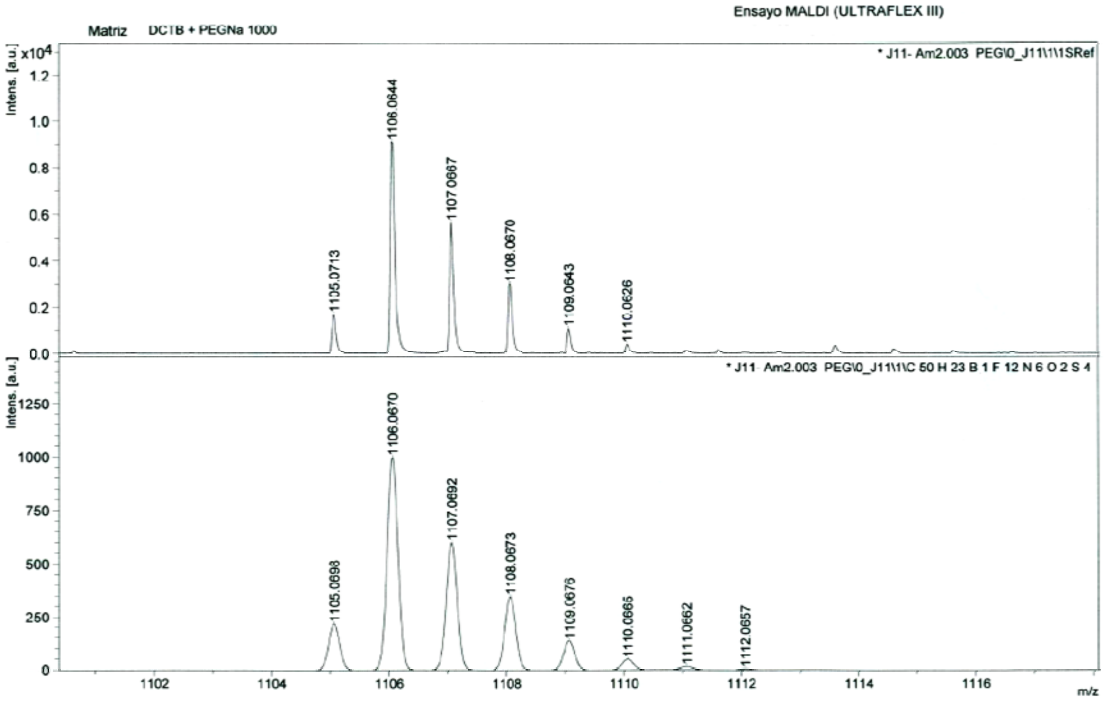


Figure S5: HRLSI-MS of SubPc-exTTF **1** showing the experimental isotopic pattern compared to the theoretical one.

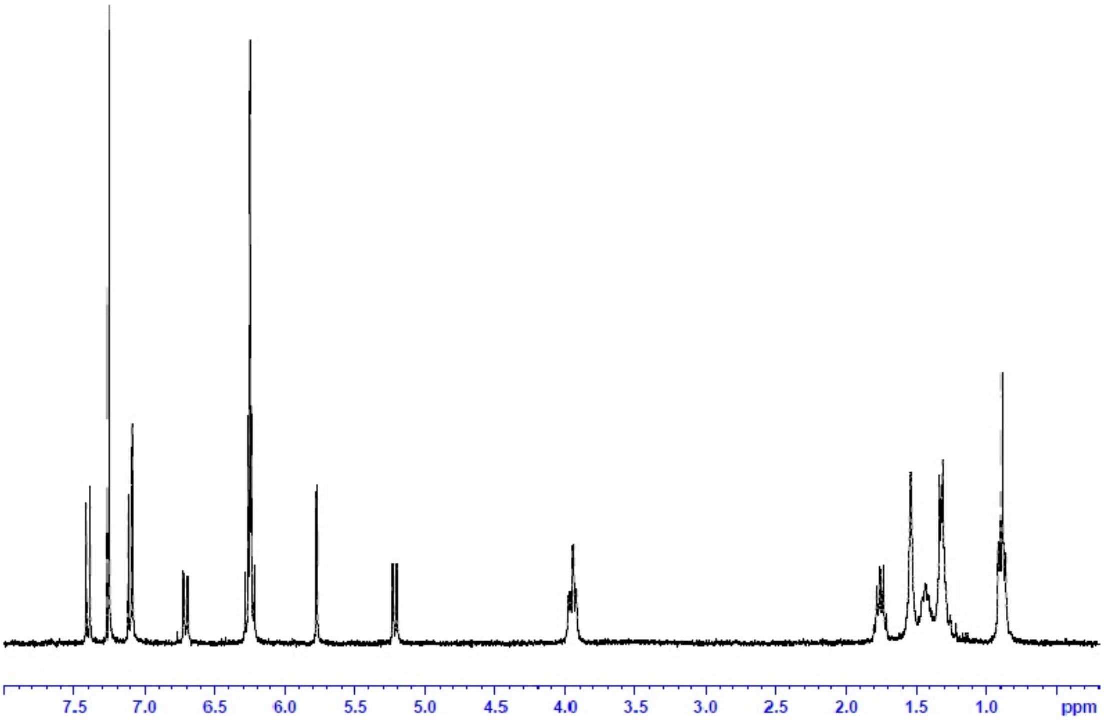
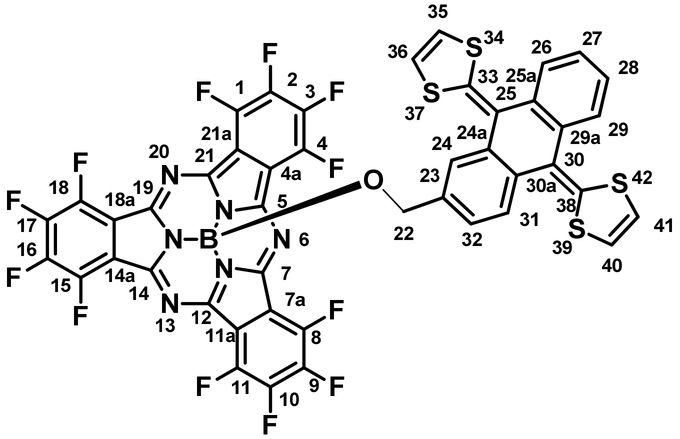


Figure S6: ^{1}H NMR of SubPc-exTTF **1**.

Supplementary data for:

COMPOUND 2



In a 25-ml round-bottomed flask, equipped with a condenser and a magnetic stirrer, ex-TTF **4** (59 mg, 0.15 mmol), bromosubphthalocyanine **5** (35 mg, 0.05 mmol) and pyridine (6μl, 0.05 mmol) were heated at 90ºC in toluene (1 ml) for 2h. The reaction mixture was cooled down to room temperature, the solvent was evaporated and the solid residue was purified by column chromatography on silica gel using hexane / ethyl acetate (10 : 1) as eluent. Dyad **2** was obtained as a purple solid; 23 mg, yield 43%. Mp > 250ºC. ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.62 (m, 2H, H-26, H-29), 7.45 (m, 1H, H-31), 7.33 (m, 2H, H-27, H-28), 6.69 (m, 1H, H-24), 6.40 (m, 1H, H-32), 6.29 (m, 4H, H-35, H-36, H-40, H-41), 2.17 (m, 2H, H-22). ^{19}F-NMR (470 MHz, $CDCl_3$): δ (ppm) = -135.9 (AA´BB´ system; F-1, F-4, F-8, F-11, F-15, F-18), -146.5 (AA´BB´ system; F-2, F-3, F-9, F10, F-16, F-17). ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ (ppm) = 146.8 (C-5, C-7, C-12, C-14, C-19, C-21), 144.9-143.1 (C-F), 141.5-140.9 (C-F), 140.3 (C-22), 138.6 (C-25a, C-29a), 135.3 (C-24a), 134.8 (C-30a), 125.9 (C-35, C-36, C-40, C-41), 125.2 (C-25, C-30), 124.9 (C-27, C-28), 124.5 (C-31), 123.6 (C-26, C-29), 117.2 (C-32), 117.1 (C-24), 115.5-115.1 (C-4a, C-7a, C-11a, C-14a, C-18a, C-21a), 65.4 (C-17). MS (MALDI, DCTB) *m/z* = 1020.0 $[M]^+$. HRMS MS ($C_{45}H_{13}BN_6OS_4F_{12}$): Calculated: 1019.9937, Found: 1019.9958. UV-vis ($CHCl_3$): λ_{max} (nm) (log ε (dm^3 mol^{-1} cm^{-1})) = 573 (4,8), 553 (sh), 524 (sh), 492 (sh), 436 (4,2).

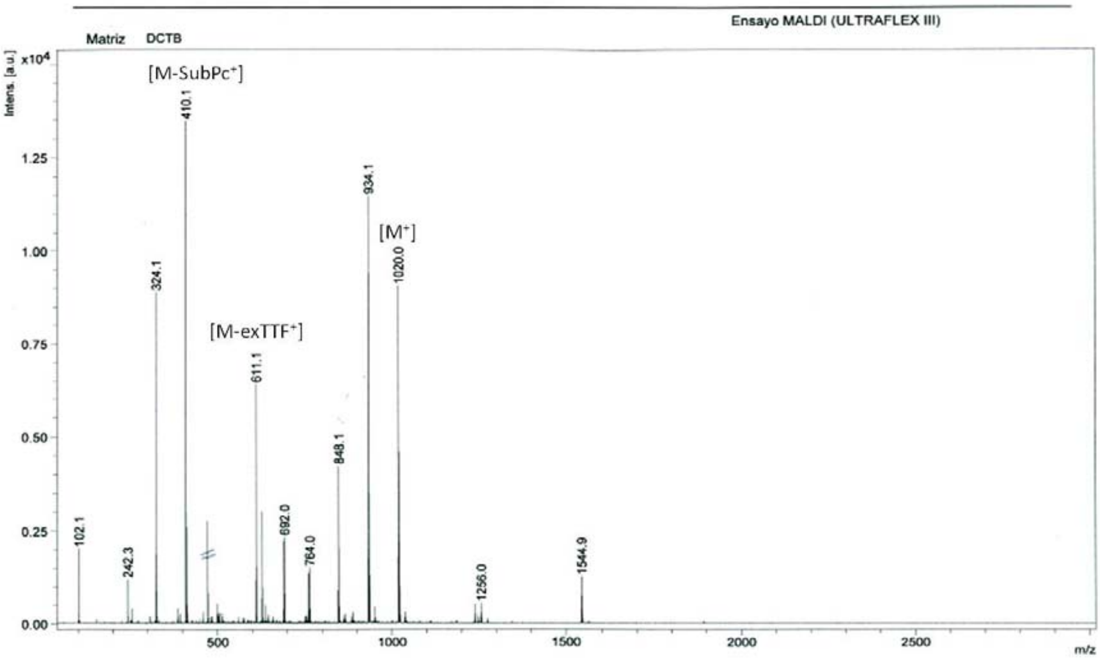


Figure S7: MS (MALDI TOF, DCTB) of SubPc-exTTF **2**.

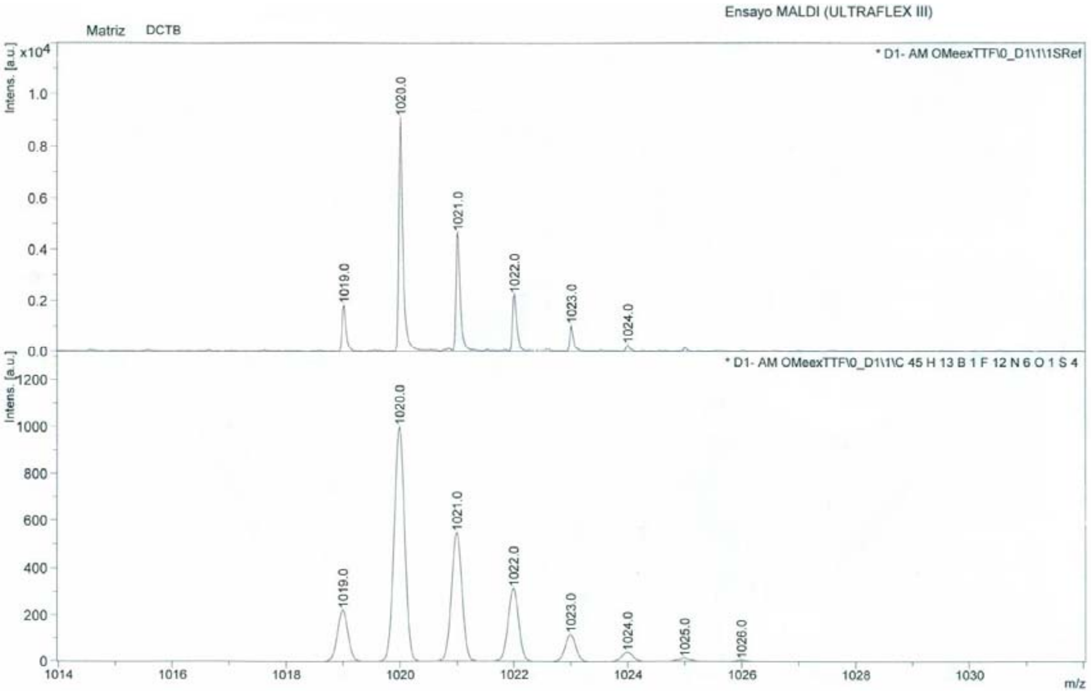


Figure S8: HRLSI-MS of SubPc-exTTF **2** showing the experimental isotopic pattern compared to the theoretical one.

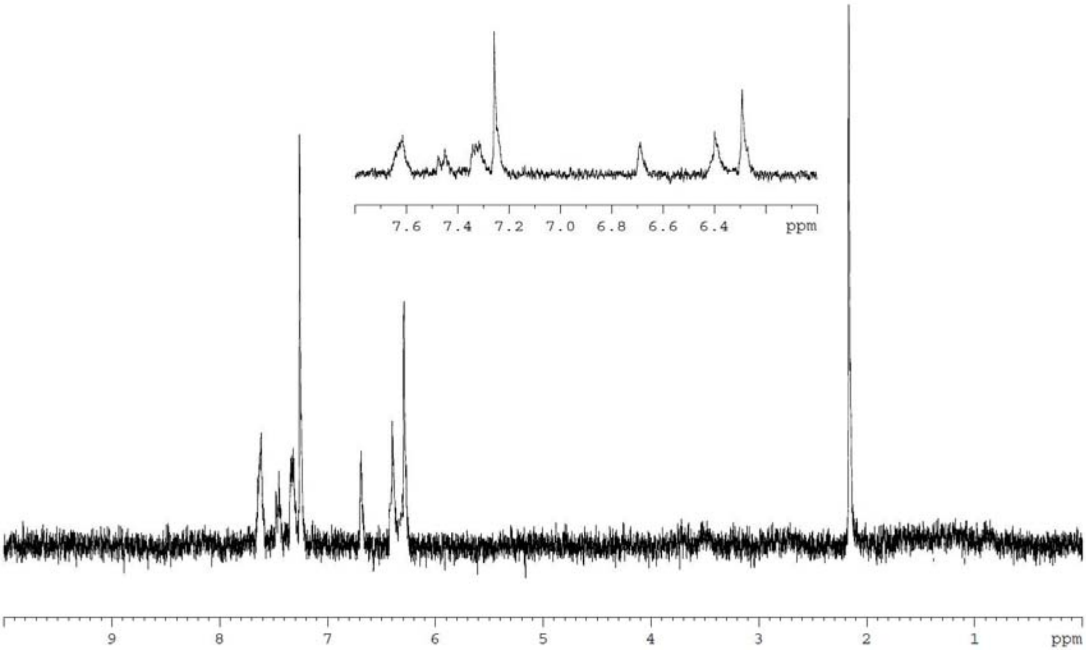


Figure S9: ^{1}H NMR of SubPc-exTTF **2**.

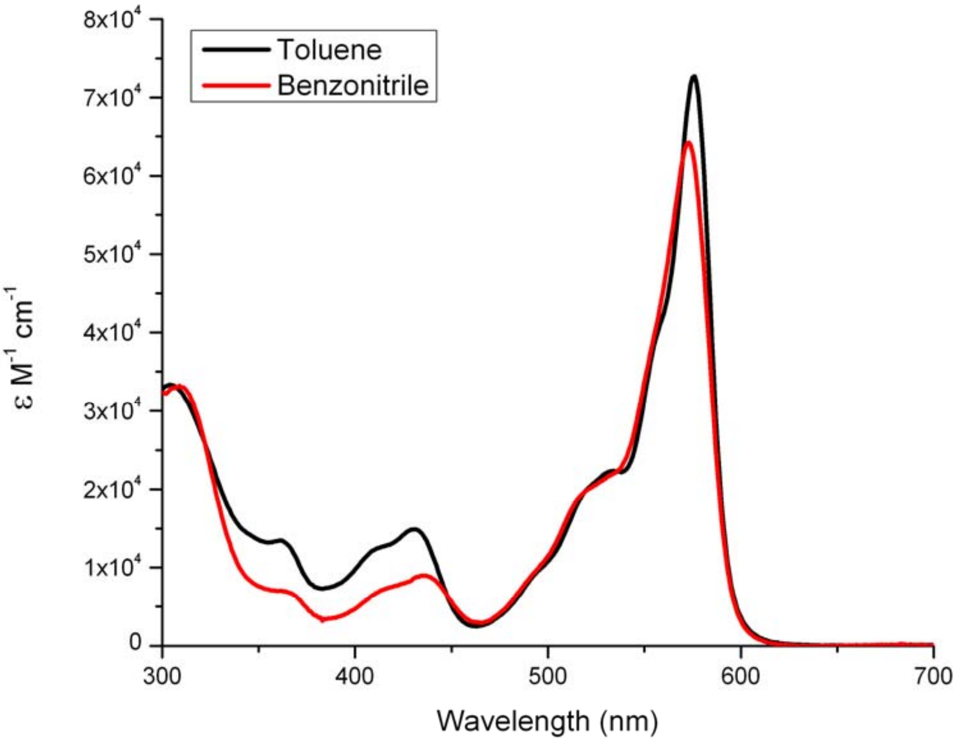
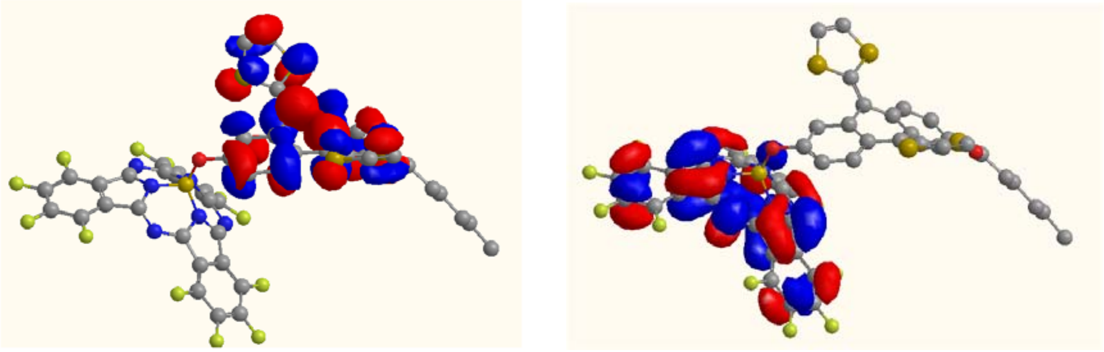


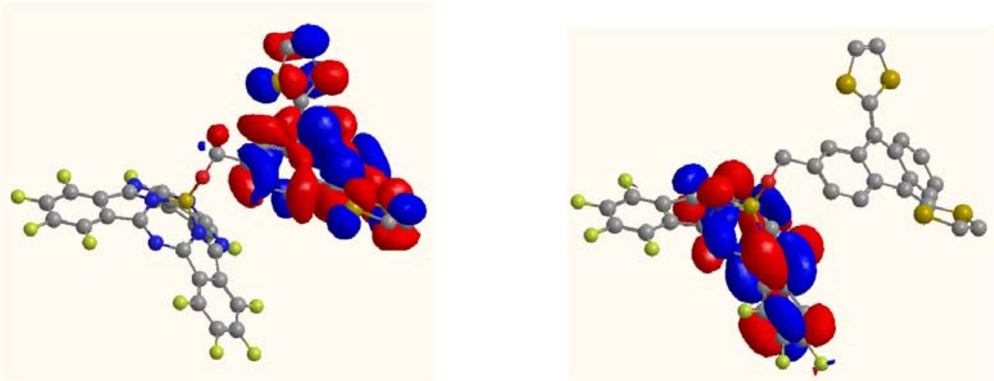
Figure S10: Absorption spectra of SubPc-exTTF **2** in toluene and benzonitrile.

Molecular geometries optimizations.



HOMO of **1**

LUMO of **1**



HOMO of **2**

LUMO of **2**

Figure S11. HOMO-LUMO representations of s 1 and 2. Note the different electronic density distributions. In both compounds, the HOMO is located over the exTTF moeity (electron donor) while the LUMO is distributed over the SubPc (electron accepetor), supporting the observed electron transfer from the exTTF to the SubPc.