

SUPPORTING INFORMATION

Solar Light-Driven Hydrogen Evolution by co-catalyst-free SubPhthalocyanine-sensitized Photocatalysts

Şifa Doğan,^{a#} Buket Güntay,^{b#} Perihan Kübra Demircioğlu,^a Yigit Osman Akyıldız,^b Hasan Aydın,^c Emre Aslan,^{*b}
Mustafa Can,^c Imren Hatay Patir^{d*} and Mine Ince^{a*}

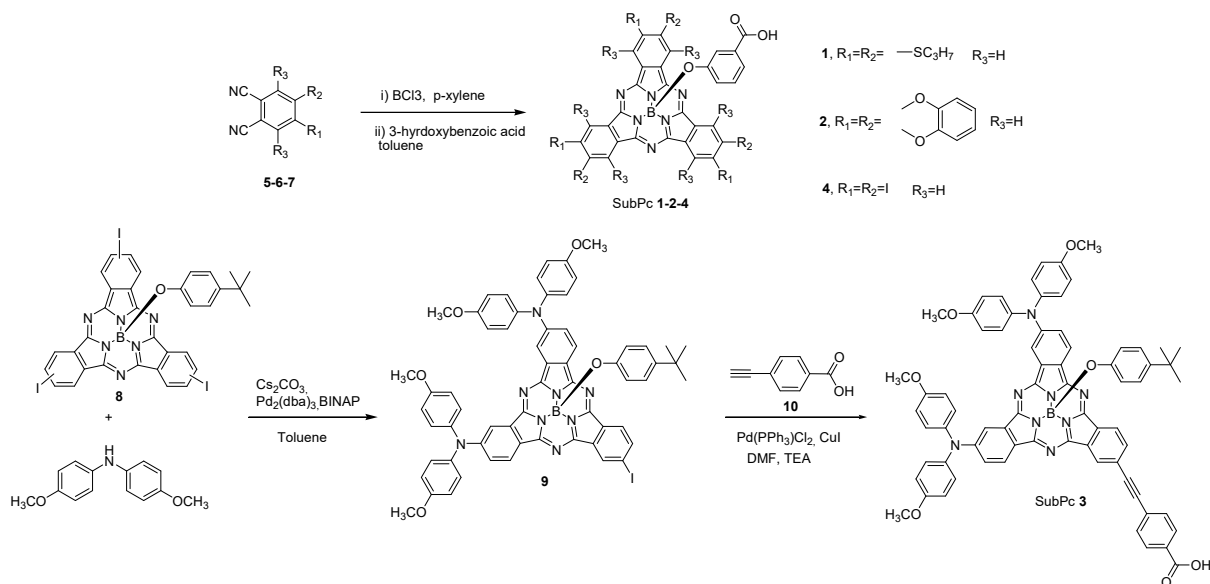
^aDepartment Natural and Mathematical Sciences Sciences, Faculty of Engineering, Tarsus University, 33400, Tarsus, Turkey.

^bDepartment of Biochemistry, Selcuk University, 42250, Konya, Turkey

^cDepartment of Engineering Sciences, Faculty of Engineering and Architecture, Izmir Katip Celebi University, Cigli, 35620, Izmir, Turkey

^dDepartment of Biotechnology, Selcuk University, 42250, Konya, Turkey.

Synthesis of SubPc-1-4



Scheme S1. Synthesis of SubPc 1-4.

Synthesis of SubPc derivatives:

4,5-bis(propylthiol) phthalonitrile (**5**), dibenzo[*b,e*][1,4]dioxin-2,3-dicarbonitrile phthalonitrile (**6**), 4-iodophthalonitrile (**7**) and 4-ethynylbenzoic acid (**10**) were successfully synthesized according to previously published procedures.²⁰⁻²⁴

General procedure for the synthesis of SubPc derivatives 1, 2 and 4:

BCl_3 (1 M solution in *p*-xylene) (1eq.) was added to the corresponding phthalonitriles, 4,5-bis(propylthiol) phthalonitrile (**5**) for SubPc **1**, dibenzo[*b,e*][1,4]dioxin-2,3-dicarbonitrile phthalonitrile (**6**) for SubPc **2** and 4-iodophthalonitrile (**7**) for SubPc **4** (1eq.) under an argon atmosphere. The reaction mixture was stirred at reflux for 3 h. After cooling down to room temperature the crude mixture was dissolved in dry toluene (10 mL) and 3-hydroxybenzoic acid (4eq.) was added in one portion. The mixture was stirred at reflux till the starting material was complete (checked by TLC). The solvent was evaporated in *vacuo* and the solid was purified by column chromatography on silica gel DCM/MeOH (10:1) to give desired SubPc **1-2-4**.

3'-Hydroxybenzoic acid [(2,3, 9,10,16,17) hexapropylthiol subphthalocyanine] boron (III) (SubPc 1):

SubPc **1** was obtained in **45%** yield as a purple solid.

$^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ (ppm) : 8.63 (s, 6H), 7.40 (d, $J=4$, 1H), 6.88 (t, $J=8$, 1H), 6.20-6.14 (brs, 1H), 5.73-5.70 (m, 1H), 3.29-3.09 (m, 12H), 1.91-1.76 (m, 12H), 0.92-0.78 (m, 18H).

IR (ATR): ν , cm^{-1} : 3060, 2964, 2918, 2864, 2361, 1995, 1935, 1864, 1716, 1686, 1606, 1558, 1462, 1436, 1385, 1360, 1320, 1272, 1254, 1176, 1134, 1092, 1039, 960, 936, 886, 768, 543, 418.

Uv-Vis (CHCl_3): λ_{max} , nm ($\log \epsilon$): 591 (4.88), 533 (4.38), 362 (4.50).

MALDI; MS (MALDI, DHB): $m/z = 977.18$ $[\text{M}+\text{H}]^+$.

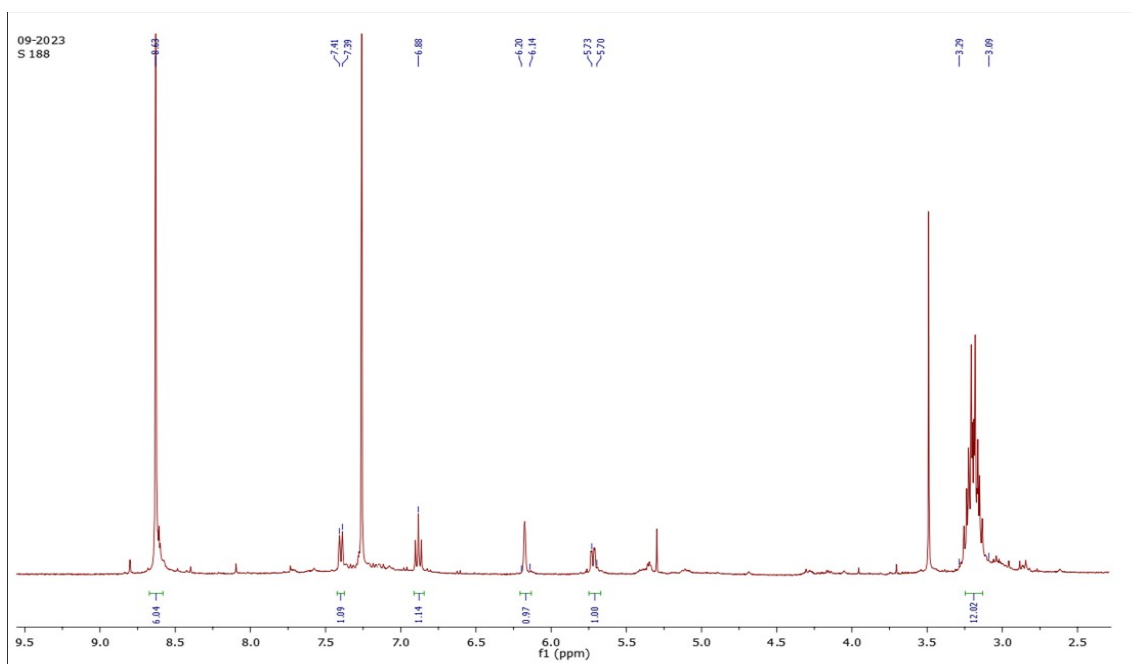


Figure S1. $^1\text{H-NMR}$ spectrum (CDCl_3) of SubPc 1.

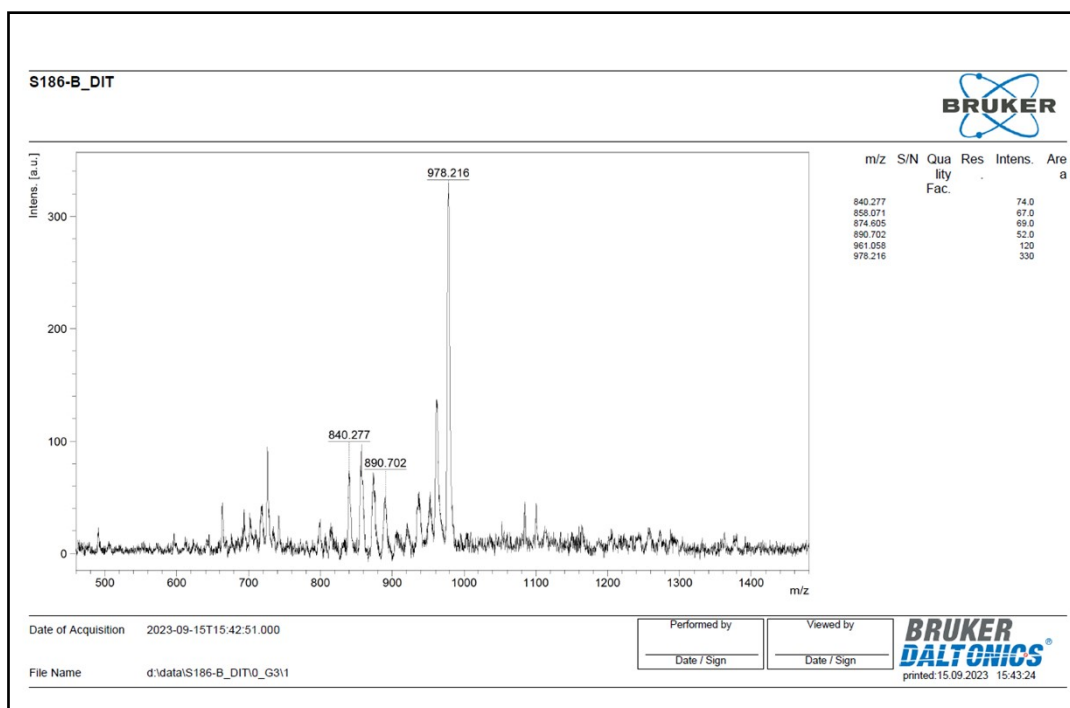


Figure S2. MALDI-TOF spectrum of SubPc 1.

3'-Hydroxybenzoic acid [(2,3, 9,10,16,17-tri(benzo[1,4] dioxine) subphthalocyanine) boron (III) (SubPc 2):

SubPc 2 was obtained in **31%** yield as a purple solid.

^1H NMR (CDCl_3 , 400 MHz): δ (ppm) : 8.10 (s, 6H), 7.55-7.45 (m, 2H), 7.03-6.81 (m, 12H), 5.90-5.69 (m, 1H), 5.42-5.30 (m, 1H).

IR (ATR): ν , cm^{-1} : 3064, 2918, 2852, 2320, 2041, 1687, 1605, 1638, 1610, 1562, 1434, 1377, 1276, 1164, 1139, 1044, 878, 788, 757, 705, 586, 485.

Uv-Vis (CHCl_3): λ_{max} , nm ($\log \epsilon$): 568 (4.99), 528 (4.53), 377 (4.66).

MALDI; MS (MALDI, DHB): $m/z = 850.16$ $[\text{M}]^+$.

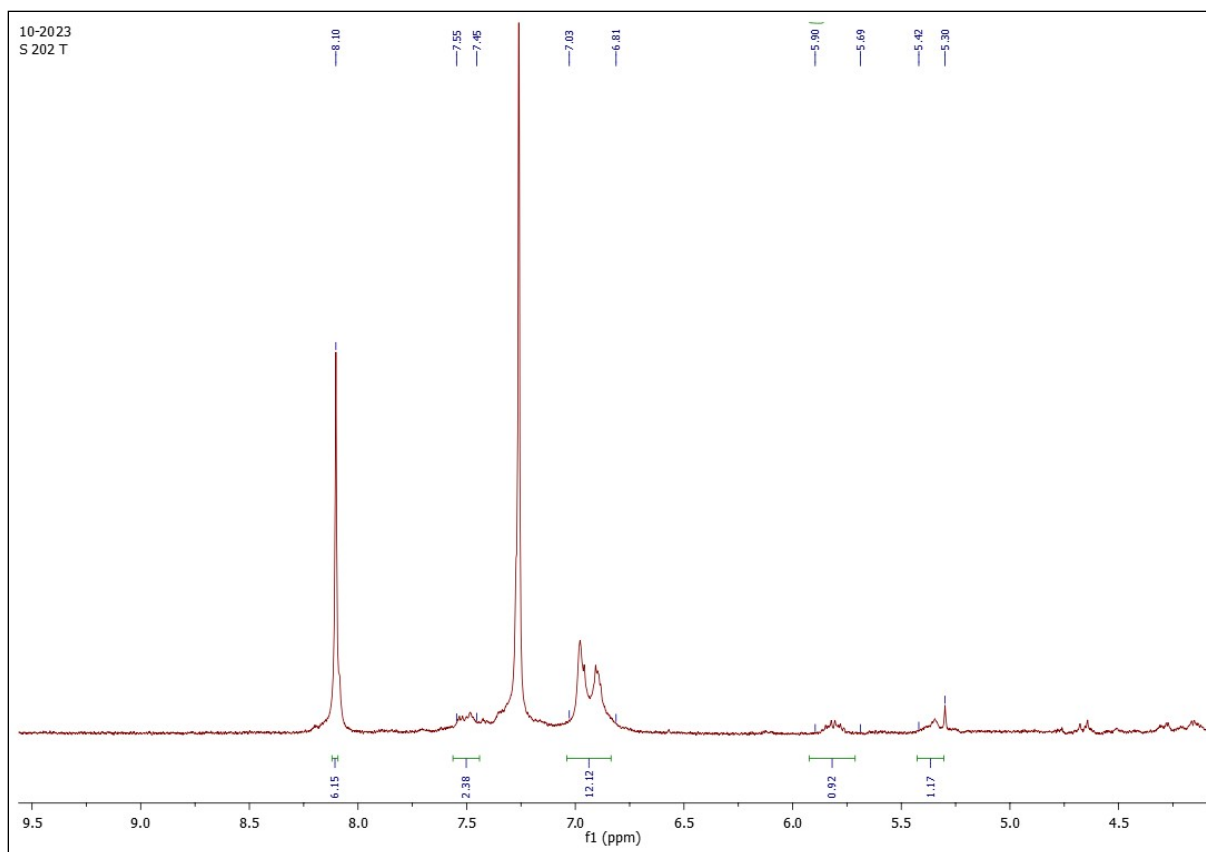


Figure S3. $^1\text{H-NMR}$ spectrum (CDCl_3) of SubPc **2**.

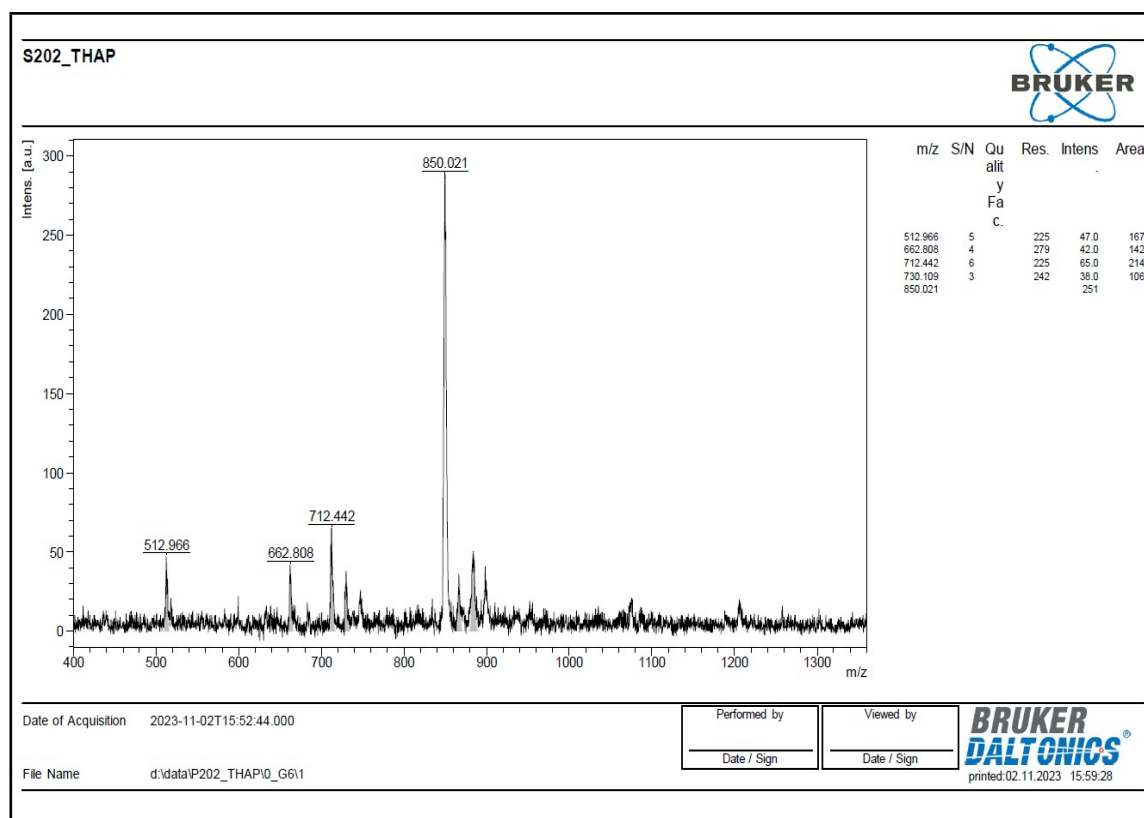


Figure S4. MALDI-TOF spectrum of SubPc **2**.

4'-tert-butylphenol [(2(3),9(10),16(17)-triiodo subphthalocyanine) boron (III) (SubPc 8)

4-iodophthalonitrile (**7**) (650 mg 2.55 mmol) and in a 1M solution of BCl₃ in *p*-xylene (2.5 ml, 2.5 mmol), was stirred at 135 °C for 3 h under argon atmosphere. After cooling to room temperature, the solvent was evaporated to dryness. Dry toluene (4ml) and 4-*tert*-butylphenol (1.5 gr, 10.23 mmol) were added to the crude mixture and stirring was continued at 110 °C for 3 h. The solvent was removed by vacuum distillation and the solid was washed with a mixture of methanol/water (4:1). The compound was purified by column chromatography on silica gel DCM/Hexane (5:1) as eluent to give SubPc **8** (140 mg, 0.14 mmol) in 36 % yield.

¹H-NMR (CDCl₃, 400 MHz,): δ (ppm) : 9.19 (s, 3H), 8.54 (d, *J*=8, 3H), 8.20 (d, *J*=8, 3H), 6.75 (d, *J*=8, 2H), 5.25 (d, *J*=8, 2H), 1.08 (s, 9H).

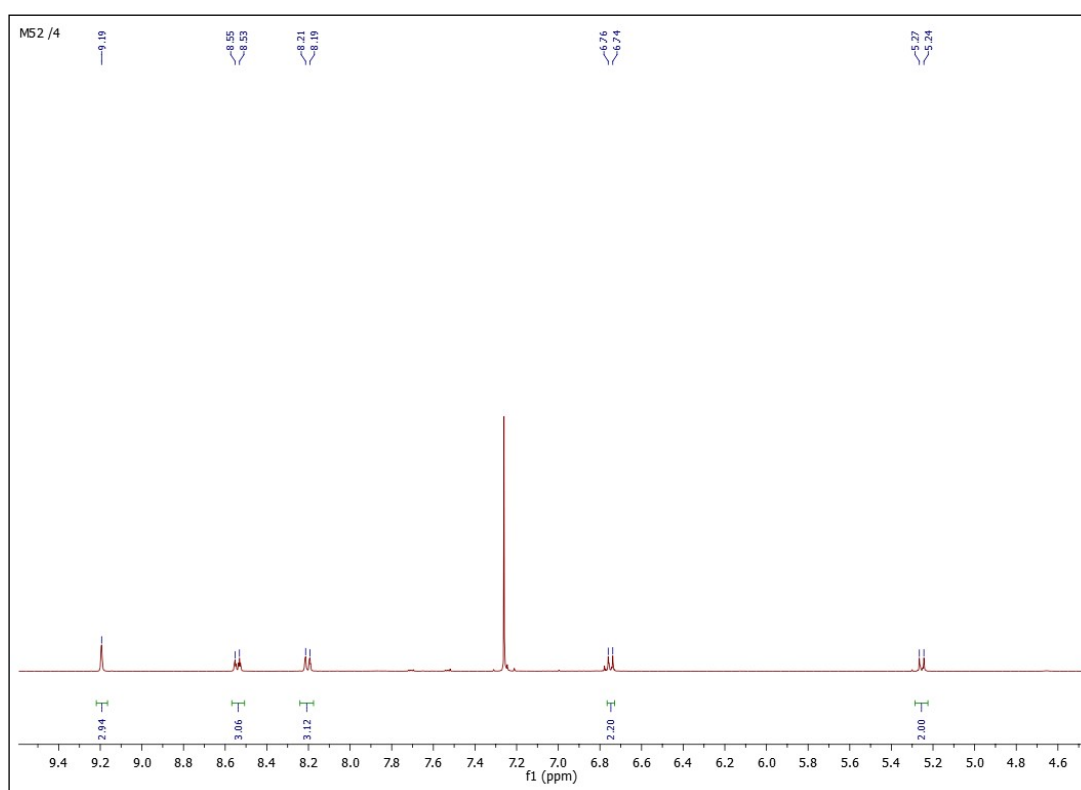


Figure S5. ¹H-NMR spectrum (CDCl₃) of SubPc-8.

4'-tert-butylphenol [(2-iodo-9(10),16(17)- di (4'-methoxydiphenylamine) subphthalocyanine) boron (III) (SubPc 9)

SubPc **8** (140 mg 0.15 mmol), bis(4-methoxyphenyl)amin (105 mg 0.45 mmol), Pd₂(dba)₃ (14 mg 0.015 mmol), BINAP (10 mg 0.015 mmol) and Cs₂CO₃ (214 mg 0.6 mmol) was dissolved in dry toluene (10 mL) was stirred 100 °C for 4 h under argon atmosphere. The solvent was removed by vacuum distillation and the solid was washed with a mixture of methanol/water (4:1). The compound was purified by column

chromatography on silica gel Hexane/THF (2:1) as eluent to give SubPc **9** 30 mg, 0.026 mmol) in 53 % yield.

$^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ (ppm) : 9.16-9.08 (m, 1H), 8.53-8.41 (m, 3H), 8.24-8.10 (m, 3H), 7.45-7.33 (m, 3H), 7.22-7.10 (m, 8H), 7.0-6.84 (m, 8H), 6.75 (d, $J=8$, 2H), 5.38-5.25 (m, 2H), 3.85 (brs, 12H), 1.26 (s, 9H).

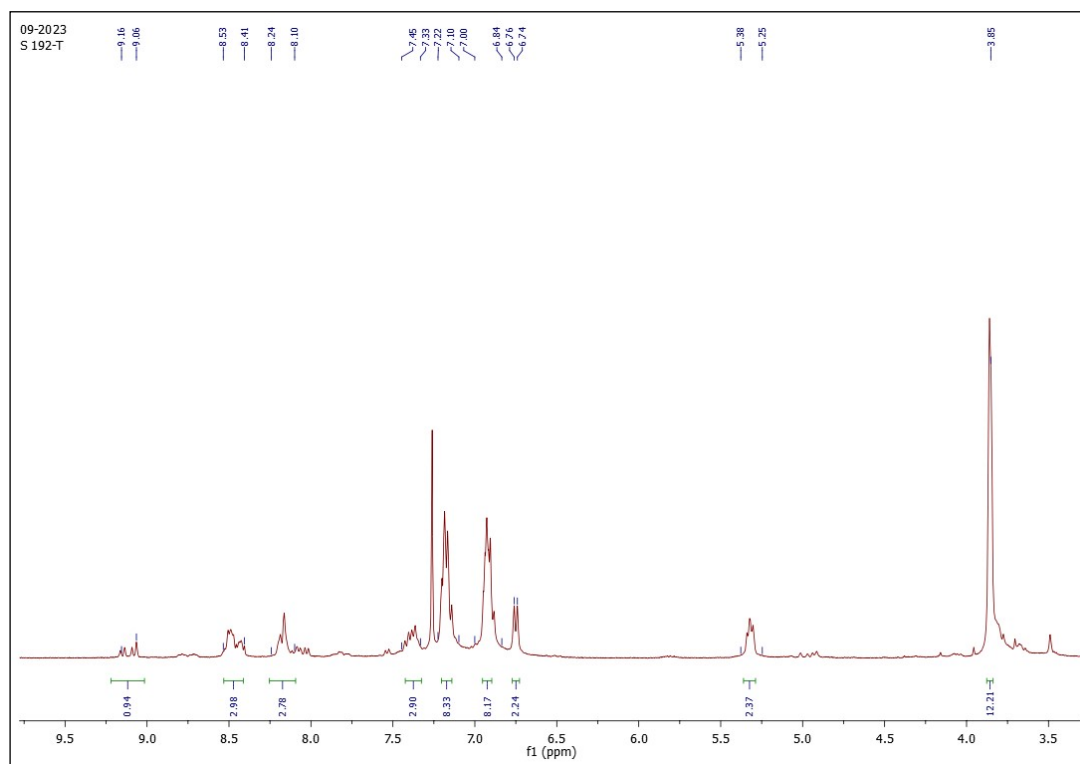


Figure S6. $^1\text{H-NMR}$ spectrum (CDCl_3) of SubPc-**9**.

4-*tert*-butylphenol [2-(4-ethynylbenzoic acid)-9(10),16(17)-di-methoxydiphenylamine - subphthalocyanine] boron (III) (SubPc 3)

A mixture of monoiodo SubPc derivative (30 mg, 0.026 mmol) (**9**), $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$ (1.8 mg, 0.0026 mmol) and CuI (catalytic amount) 6:1 mixture of dry DMF/TEA was stirred under argon and subsequently 4-ethynylbenzoic acid (**10**) (7.8 mg, 0.053 mmol) was added. The reaction was then stirred at room temperature for additional 2 h. The mixture was evaporated. The resulting solid was purified by silica column chromatography with the mobile phase of dichloromethane/MeOH (10:0.5). SubPc **3** was obtained (0.010 mmol, 12 mg) as a purple solid. Yield 41 %.

$^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ (ppm) : 9.01-8.91 (dd, $J=8, 12$, 1H), 8.72-8.56 (m, 1H), 8.51-8.33 (m, 2H), 8.10-8.02 (m, 4H), 7.93-7.78 (m, 1H), 7.68-7.37 (m, 2H), 7.37-7.25 (m, 2H), 7.14-7.07 (m, 8H), 6.87-6.81 (m, 8H), 6.69 (d, $J=8$, 2H), 5.31-5.25 (m, 2H), 3.82-3.69 (m, 12H), 1.01 (s, 9H).

IR (ATR): ν , cm^{-1} : 3045, 2654, 2916, 2846, 2124, 1989, 1917, 1769, 1682, 1596, 1534, 1426, 1346, 1265, 1224, 1226, 1172, 1105, 1034, 1014, 892, 822, 738, 641, 550.

Uv-Vis (CHCl₃): λ_{max}, nm (log ε): 618 (4.56), 571 (4.34), 463 (4.17), 358 (4.39).

MS (MALDI-TOF) m/z: calculated for C₇₁H₅₅BN₈O₇: 1143.06; found 1443.06 [M]⁺.

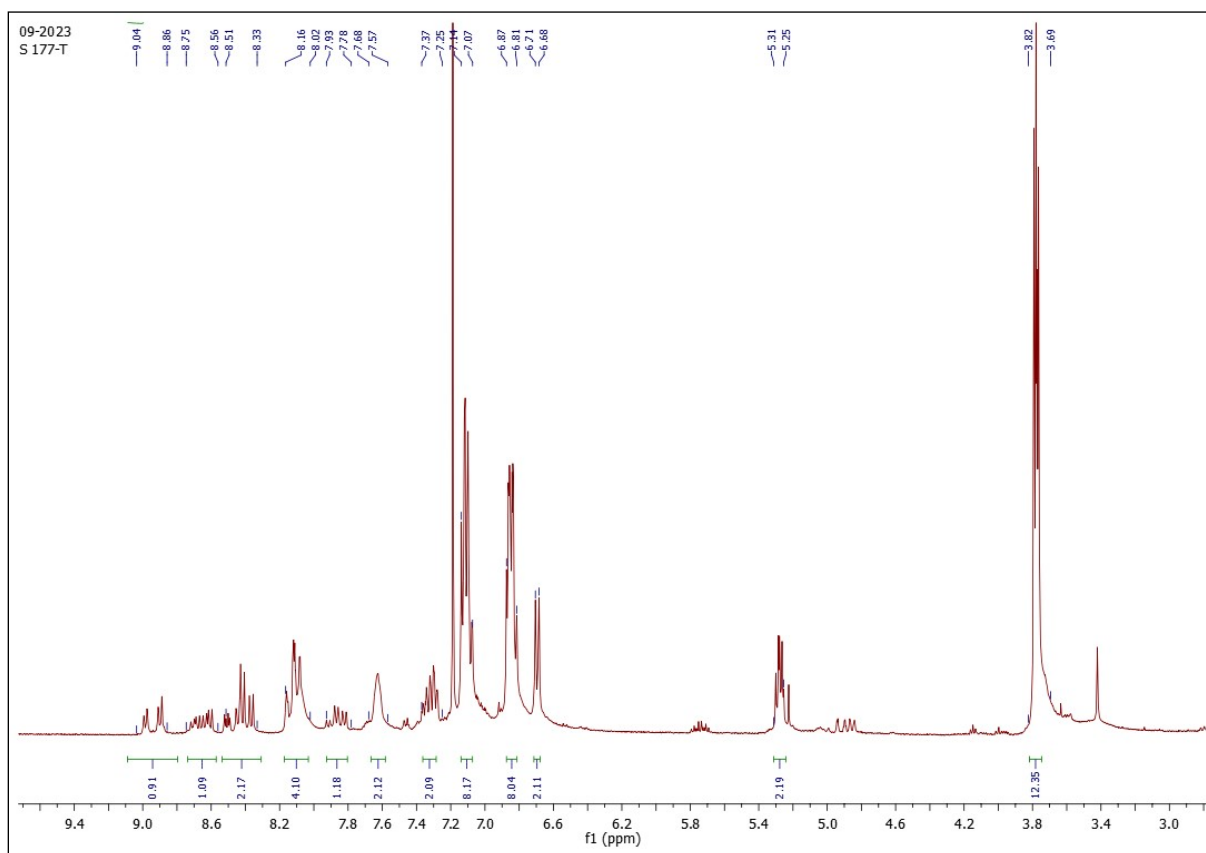


Figure S7. ¹H-NMR spectrum (CDCl₃) of SubPc-3.

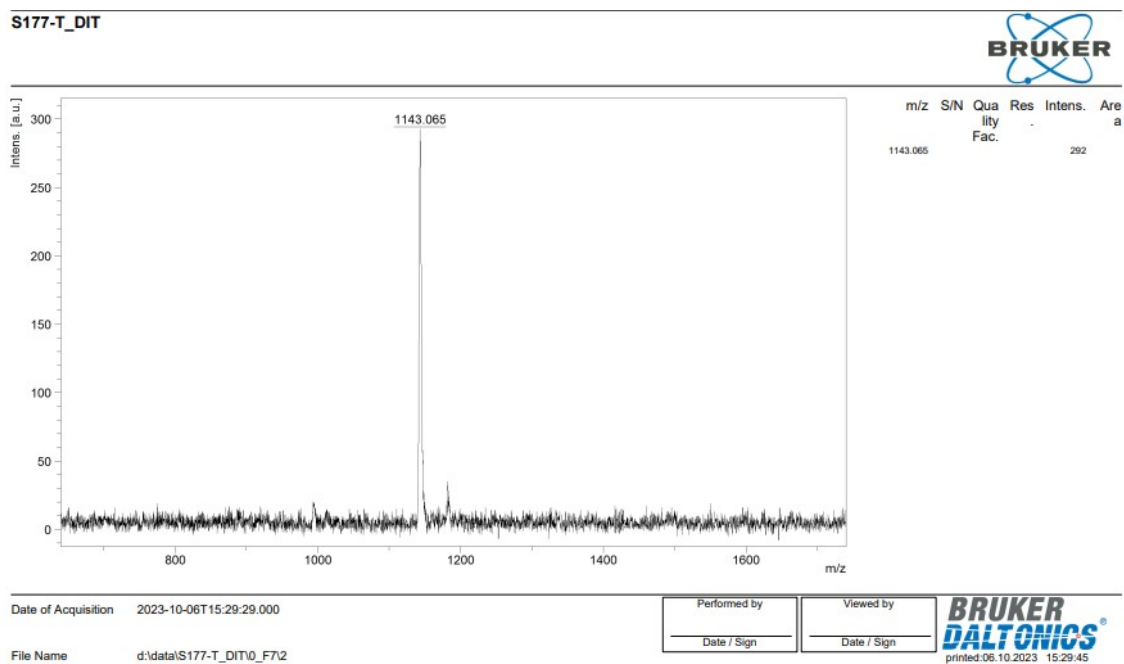


Figure S8. MALDI-TOF spectrum of SubPc-3.

3'-hydroxybenzoic acid [(2(3), 9(10),16(17)-triiodo subphthalocyanine)] boron (III) (SubPc 4)

SubPc **4** was obtained in **60%** yield as a purple solid.

$^1\text{H-NMR}$ (CDCl_3 , 400 MHz,): 9.18 (s, 3H), 8.58-8.49 (d, $J=8$, 3H), 8.24-8.12 (d, $J=8$, 3H), 7.43-7.34 (d, $J=8$, 1H), 6.93-6.82 (m, 1H), 6.13 (s, 1H), 5.63-5.51 (m, 1H).

IR (ATR): ν , cm^{-1} : 3052, 2956, 2916, 2846, 2364, 1944, 1870, 1770, 1697, 1598, 1492, 1456, 1414, 1358, 1258, 1176, 1096, 1069, 1048, 960, 798, 740, 705, 608, 486.

Uv-Vis (CHCl_3): λ_{max} , nm (log ϵ): 569 (4.69), 519 (4.14), 319 (4.31).

MALDI; MS (MALDI, DHB): m/z = calculated for $\text{C}_{31}\text{H}_{14}\text{BI}_3\text{N}_6\text{O}_3$: 910.006, found: 910.82 $[\text{M}]^+$

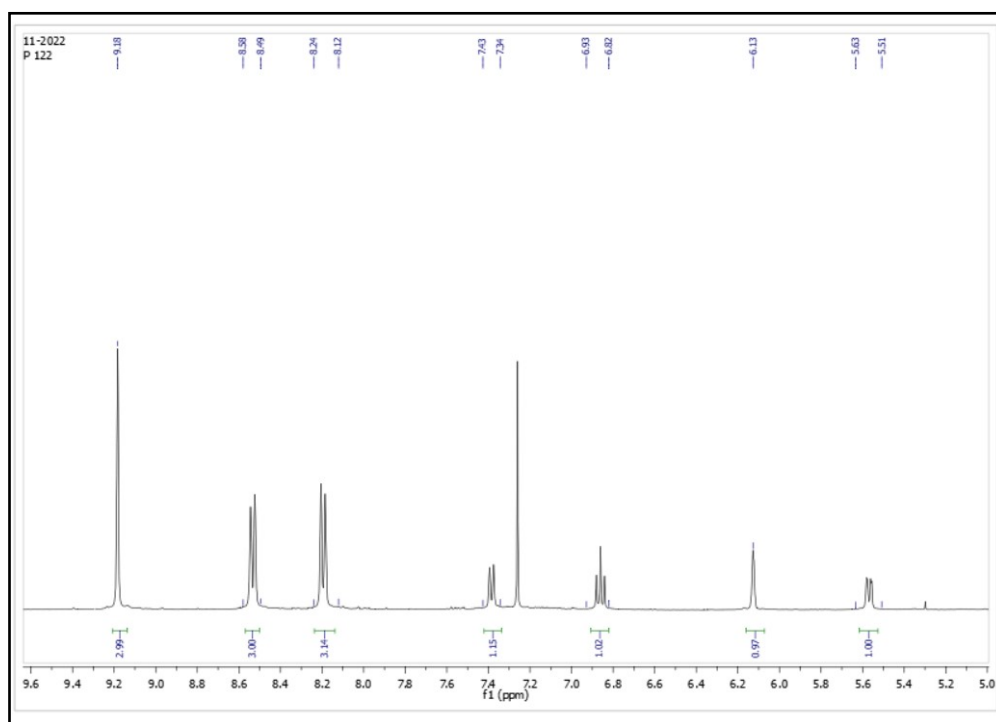


Figure S9. $^1\text{H-NMR}$ spectrum (CDCl_3) of SubPc-4.

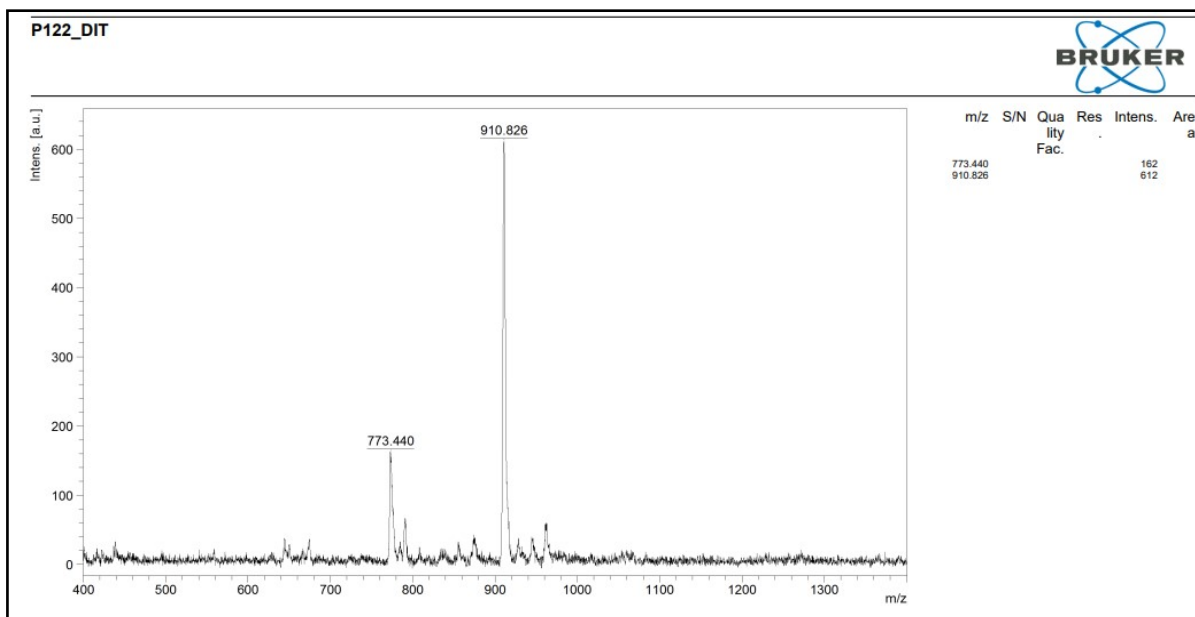
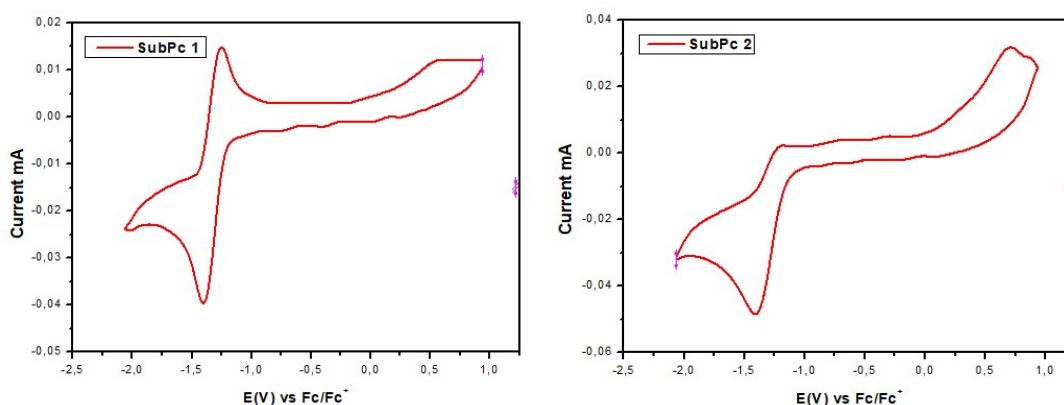


Figure S10. MALDI-TOF spectrum of SubPc 4.

Optical and electrochemical characterization of SubPcs sensitized TiO₂:

UV-*vis* spectra were recorded with an Analytic JENA S 600 UV-*vis* spectrophotometer. The electrochemical measurement of the SubPc sensitizer series (SubPc 1, SubPc 2, SubPc 3 and SubPc 4) was carried out by using an IviumStat electrochemical analyzer at room temperature. Tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte, a Pt wire as a counter electrode, glassy carbon as a working electrode, Ag/AgNO₃ as a reference electrode, and ferrocene/ferrocenium (Fc/Fc⁺) as an internal standard were used. All measurements were carried out in DMF solution with a scan rate of 100 mVs⁻¹.



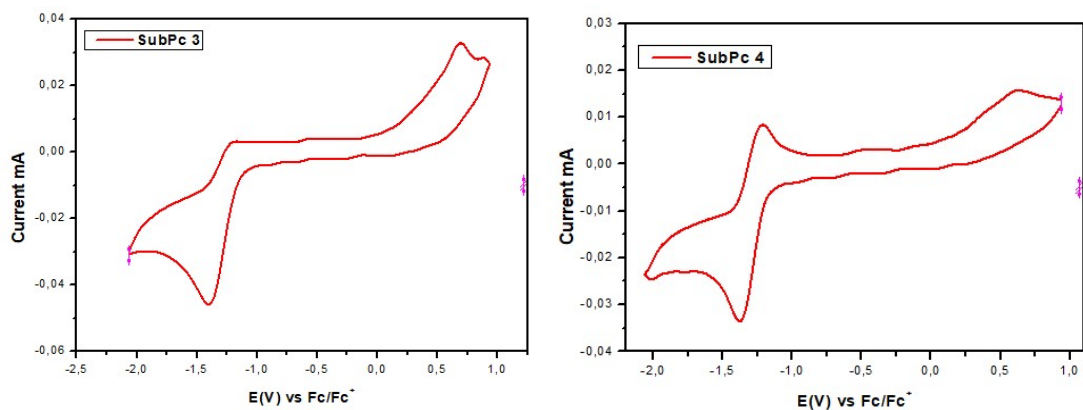


Figure S11. CV voltammograms of SubPc 1-4 with ferrocene.

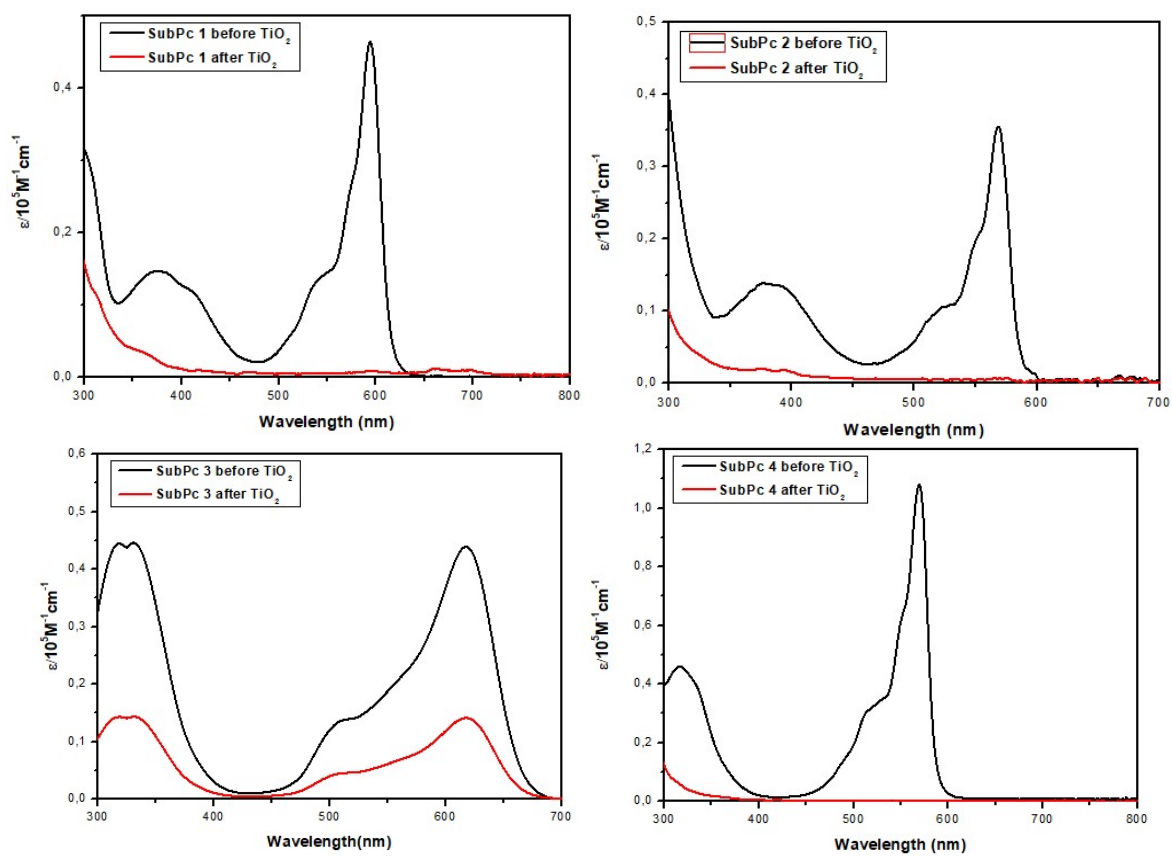


Figure S12. Absorption spectra of SubPc dye solutions ($1 \cdot 10^{-5}$ M, THF) before and after the addition of TiO_2 .

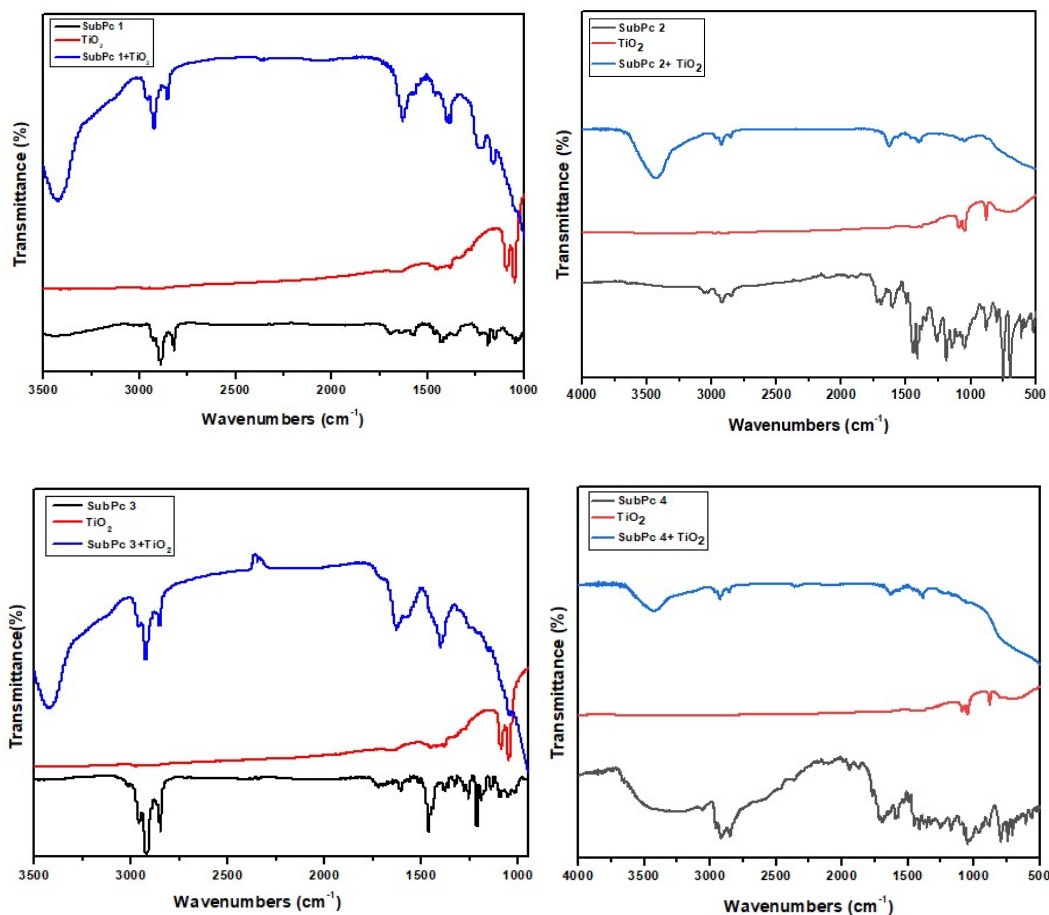


Figure S13. FT-IR spectra of SubPc dye solutions, SubPc-TiO₂ photocatalysts prepared with SubPc dye solutions prepared in 1.10⁻⁵ M THF, and TiO₂.

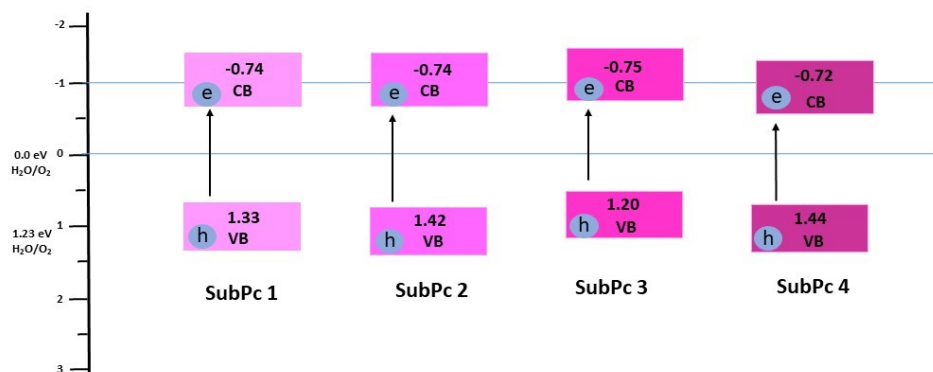


Figure S14. Schematically arranged energy band diagram of SubPc molecules.

Preparation of SubPc/TiO₂ samples

100 mg TiO₂ (Degussa P25) was mixed with 10 ml of SubPc solution (1.10⁻⁵ M in THF) under stirring overnight at dark, afterwards, the product was filtered washed with THF, and dried overnight under vacuum. For photoelectrochemical studies, the commercially available TiO₂ electrodes (Dyesol MS001630) were sintered at 500 °C for 30 min before they were dipped into the dye solution. Afterwards, TiO₂ electrodes were immersed into the SubPc solutions (1.10⁻⁵ M in THF) and kept at room temperature overnight.