Novel methoxyphenylthio substituted phthalocyanines; Synthesis, characterization, proton-transfer and acid-sensing properties

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1. Experimental

1.1. Materials and equipment for synthesis

In this study, novel 4-methoxyphenylthio and 2,4,6-trimethoxyphenylthio tetra-substituted metal free Pcs were synthesized. Although 4-methoxythiophenol was purchased from Alfa Aesar, 2,4,6-trimethoxythiophenol was synthesized using appropriate starting compounds[1] with a little change. All used chemicals were of reagent grade quality. 4-Methoxythiophenol, $NaOCH_3$, 1,8- diazabicyclo-[5.4.0]undec-7-ene (DBU) and solvents were used as supplied commercially (Alfa Aesar, Fluka, Merck) and most of them were used as received, very few of that were dried by using molecular sieve (3Å) if necessary. 4-Methoxyphenylthio and 2,4,6-trimethoxyphenylthio substituted phthalonitrile compounds were synthesized nucleophilic aromatic substitution reaction [2] and purified with column chromatography on silica gel 60. Silica gel for column chromatography was also purchased from Merck Millipore. The solvents were purified, dried and stored over molecular sieves (3Å). All reactions were carried out under dry nitrogen atmosphere unless otherwise noted. The purity of the products was tested in each step by thin layer chromatography (Silicagel F-254 coated TLC plate). Melting points of the Pc complexes were found to be higher than 350 °C. FT-IR Spectra and electronic spectra were recorded on a Shimadzu FTIR-8300 (ATR) and a Shimadzu UV–1601 spectrophotometer, respectively. The Instrumental Analysis Laboratory of TUBITAK–Ankara performed elemental analyses. Mass spectra were acquired on a Microflex III MALDI-TOF mass spectrometer (Bruker Daltonics, Germany) equipped with a nitrogen UV–Laser operating at 337 nm in reflectron mode with average of 50 shots.

2,4,6-trimethoxythiophenol [1]

2,4,6-trimethoxybenzene (6.73, 40 mmol) was dissolved by dry toluene (20 mL) in a three-necked flask equipped with N_2 gas, $CaCl_2$ tube and septum for adding other chemical with a syringe. n-Butyllithium in toluene (25 mL, 40 mmol) was added at 0 °C followed by the addition of a catalytic amount of N,N,N',N'-tetramethylethylenediamine (0.5 mL, 3.35 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 1 h to give an orange suspension, to which was added dropwise a solution of elemental crystaline sulfur (1.155 g, 36 mmol) in dry toluene (60 mL, mild heating was needed to solubilize the sulfur in toluene). The reaction mixture was stirred at room temperature for 6 h and subsequently quenched by the addition of water (50 mL). The aqueous layer was acidified with 1 M aqueous hydrochloric acid (40 mL), extracted with CH_2Cl_2 (3 × 25 mL), washed with water (3 × 25 mL), brine (25 mL). Organic phase was dried by $MgSO_4$ and concentrated under reduced pressure. It was purified by column chromatography using Silica Gel 60 and Hexane/$CHCl_3$ -3/1 as mobile phase. Yield: %46 (3,68 g); MP: 55-56 °C; Solubility: $CHCl_3$, CH_2Cl_2, Acetone, MeOH, THF, DMF, DMSO. FT-IR (ν_{max}/(cm^{-1}): 675, 734, 802, 914, 945, 1025, 1083, 1115(Ar-O-CH_3), 1152, 1205, 1226, 1327, 1401, 1444, 1576(C=C), 2540 (Ar-SH), 2832(Alph-H), 2938(Alph-H), 2996(Alph-H), 3054(Ar-H). ^{1}H-NMR ($CDCl_3$-400 MHz), (δ, ppm): 3,76 (s, SH), 3,77 (s, 9H), 6,08 (s, 2H).

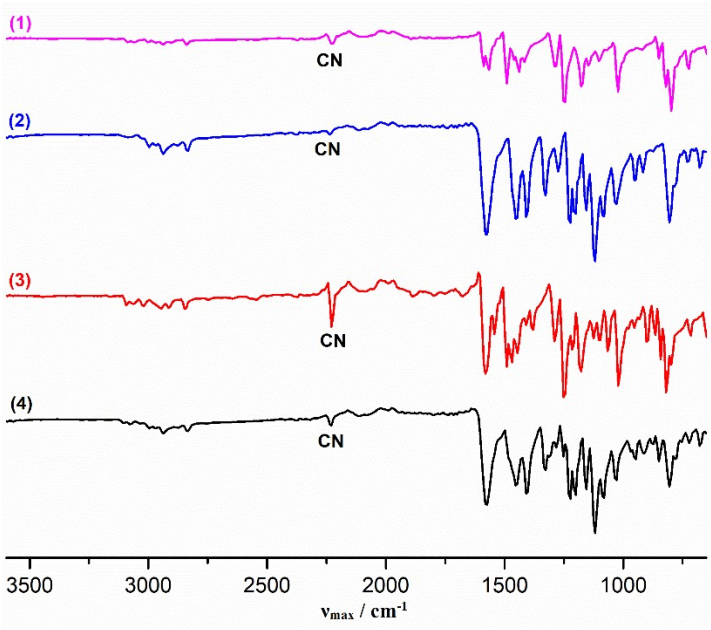

Figure S1. FT-IR Spectrums of starting compounds (**1**-**4**)

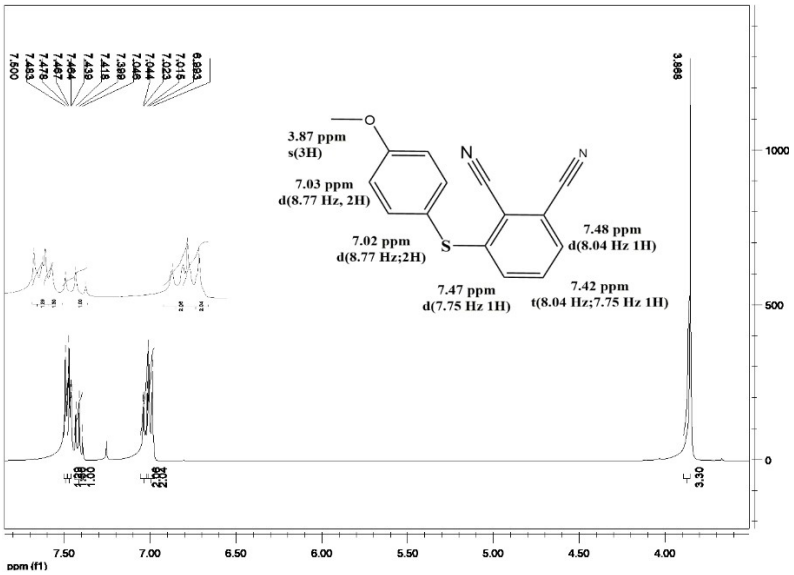

Figure S2. ^{1}H-NMR Spectrum of 3-((4-Methoxyphenyl)thio)phthalonitrile (**1**)

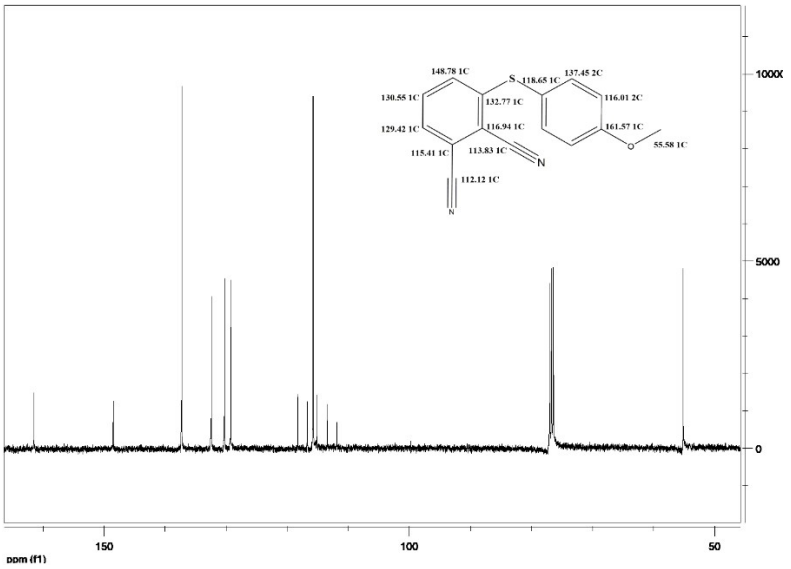

Figure S3. ^{13}C-NMR Spectrum of 3-((4-Methoxyphenyl)thio)phthalonitrile (**1**)

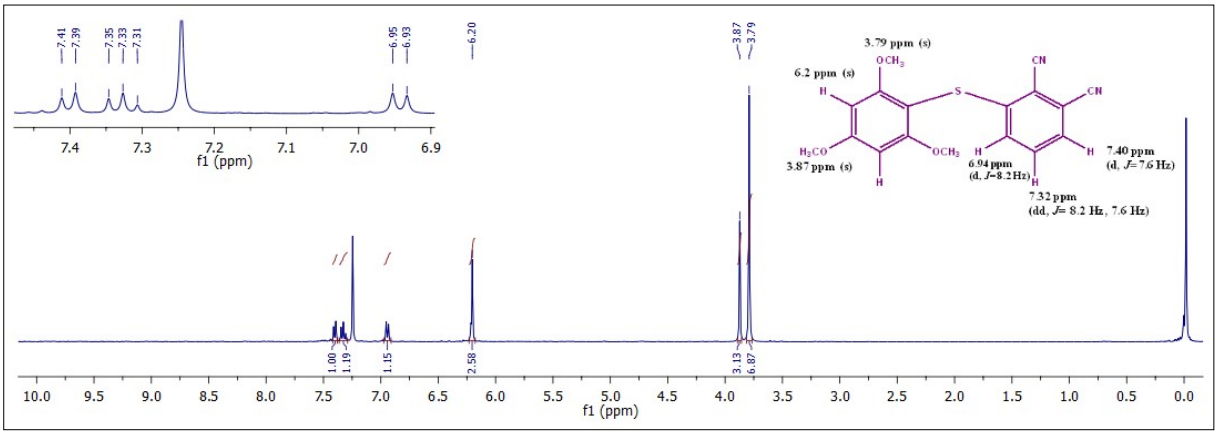

Figure S4. ^{1}H-NMR Spectrum of 3-((2,4,6-trimethoxyphenyl)thio)phthalonitrile (**2**)

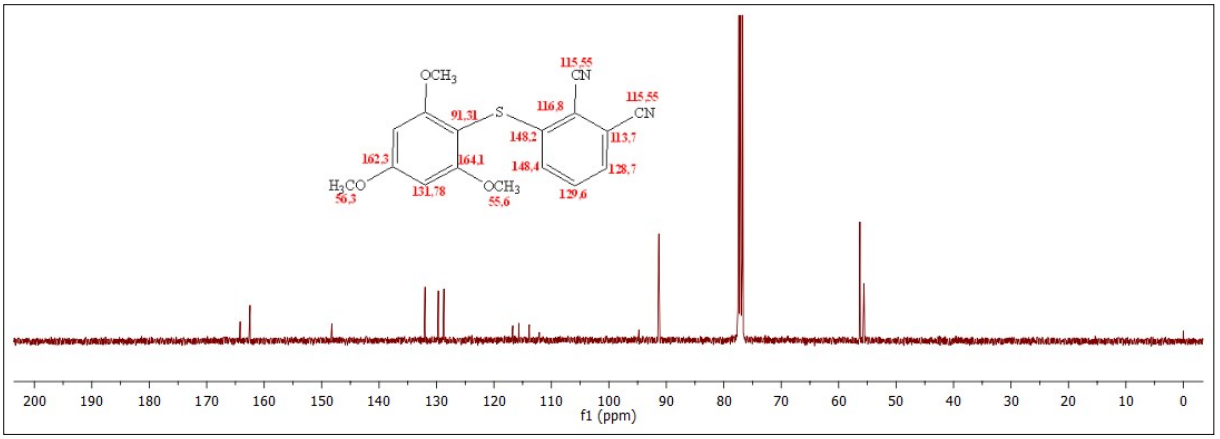

Figure S5. ^{13}C-NMR Spectrum of 3-((2,4,6-trimethoxyphenyl)thio)phthalonitrile (**2**)

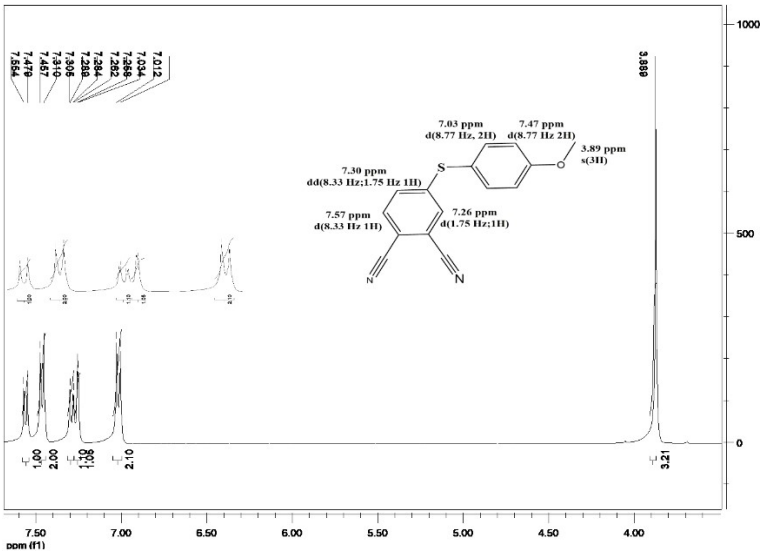

Figure S6. ^{1}H-NMR Spectrum of 4-((4-trimethoxyphenyl)thio)phthalonitrile (**3**)

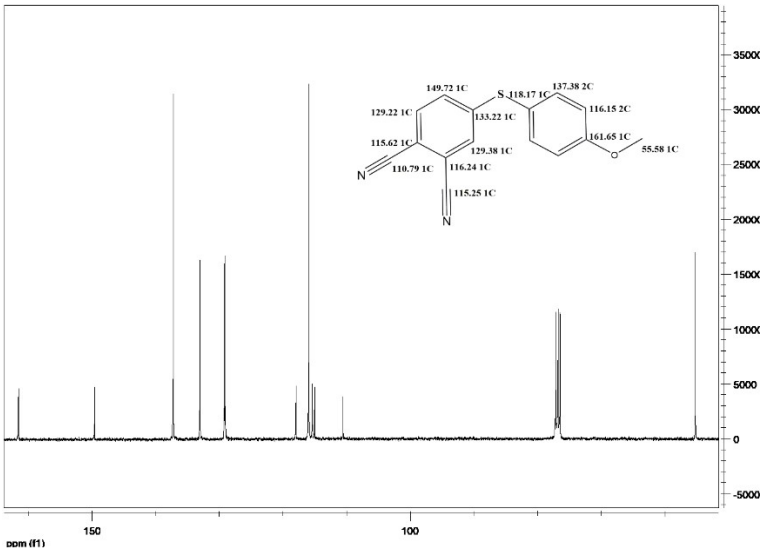

Figure S7. ^{13}C-NMR Spectrum of 4-((4-trimethoxyphenyl)thio)phthalonitrile (**3**)

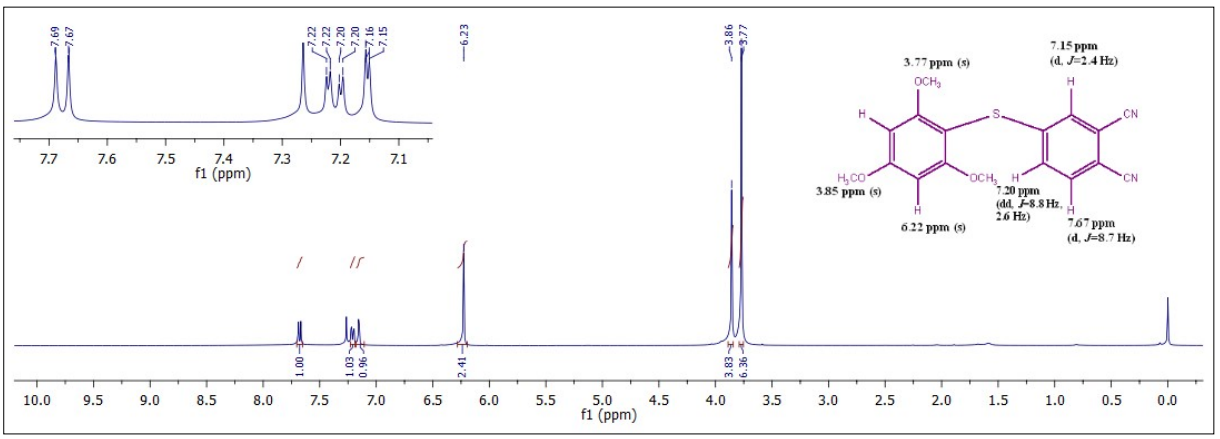

Figure S8. ^{1}H-NMR Spectrum of 4-((2,4,6-trimethoxyphenyl)thio)phthalonitrile (**4**)

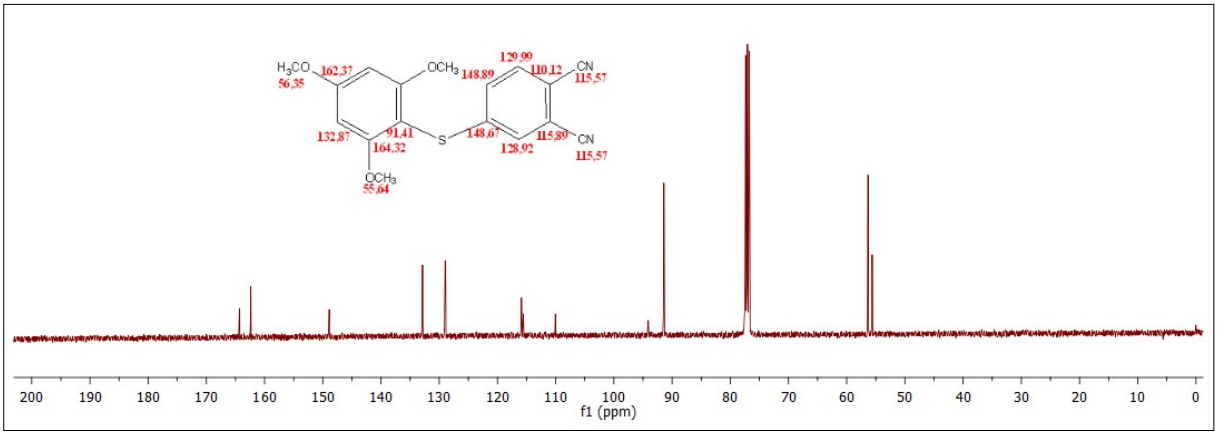

Figure S9. ^{13}C-NMR Spectrum of 4-((2,4,6-trimethoxyphenyl)thio)phthalonitrile (**4**)

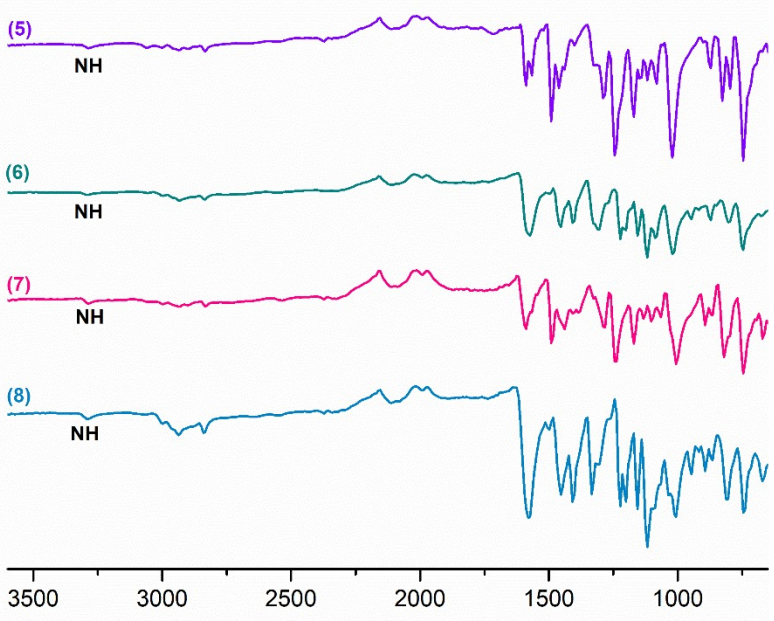

Figure S10. FT-IR Spectrums of metal free Pcs (**5**-**8**)

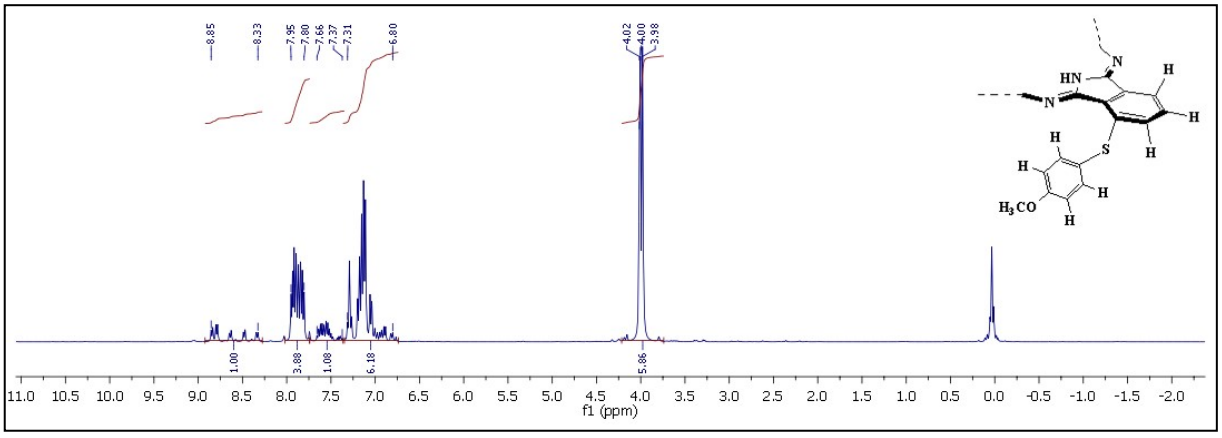

Figure S11. ^{1}H-NMR Spectrum of 1(4),8(11),15(18),22(25)-Tetrakis((4-methoxyphenyl)thio)phthalocyanine (**5**)

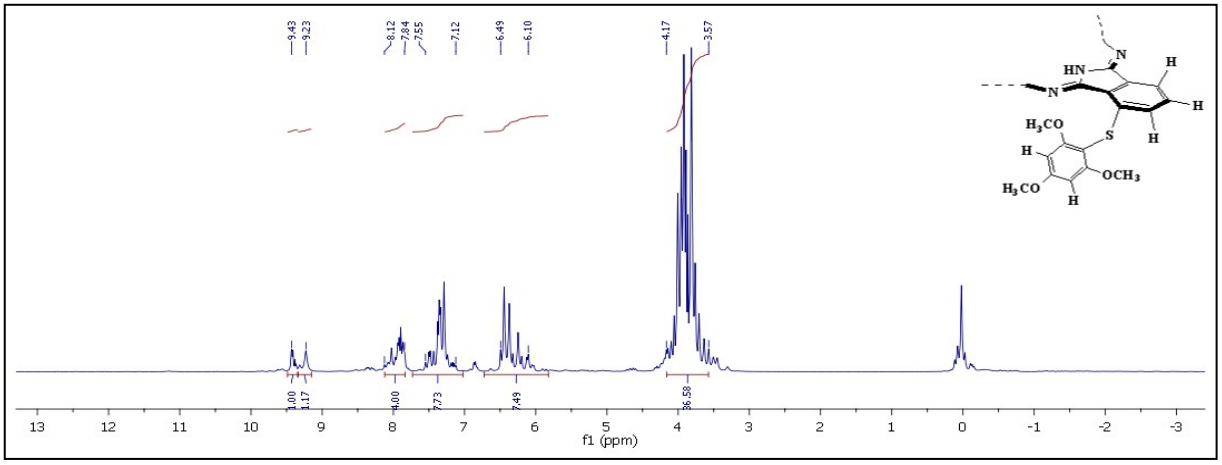

Figure S12. ^{1}H-NMR Spectrum of 1(4),8(11),15(18),22(25)-Tetrakis((2,4,6-trimethoxyphenyl)thio)phthalocyanine (**6**)

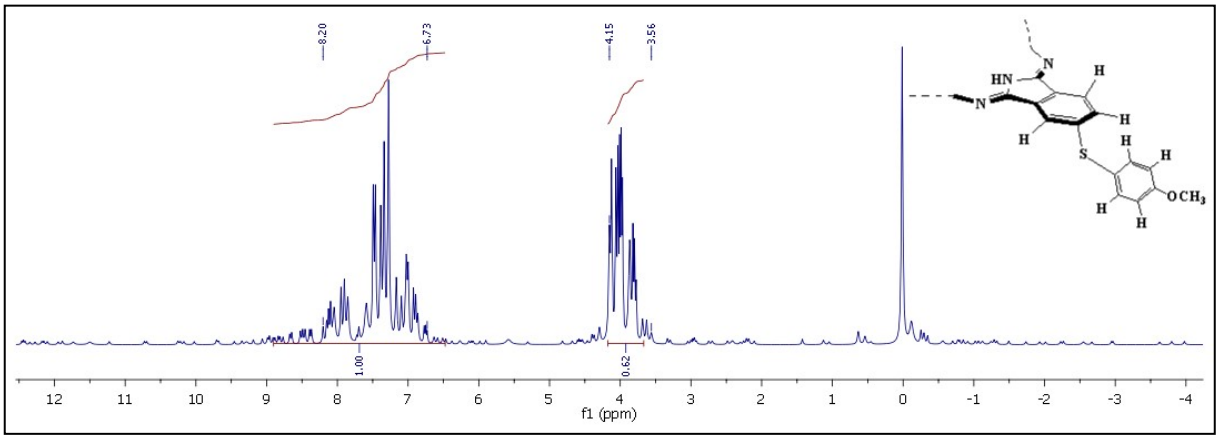

Figure S13. ^{1}H-NMR Spectrum of 2(3),9(10),16(17),23(24)-Tetrakis((4-methoxyphenyl)thio)phthalocyanine (**7**)

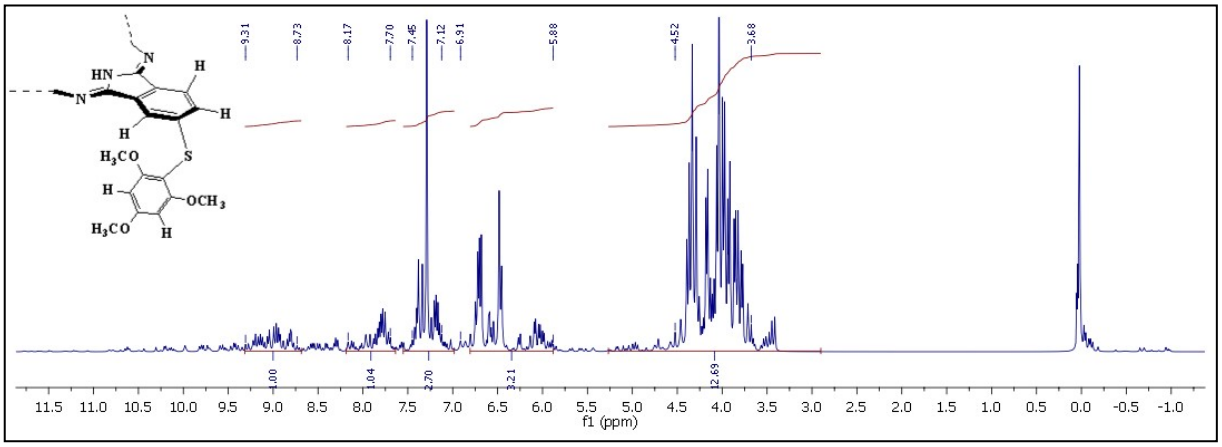

Figure S14. ^{1}H-NMR Spectrum of 2(3),9(10),16(17),23(24)-Tetrakis((2,4,6-trimethoxyphenyl)thio)phthalocyanine (**8**)

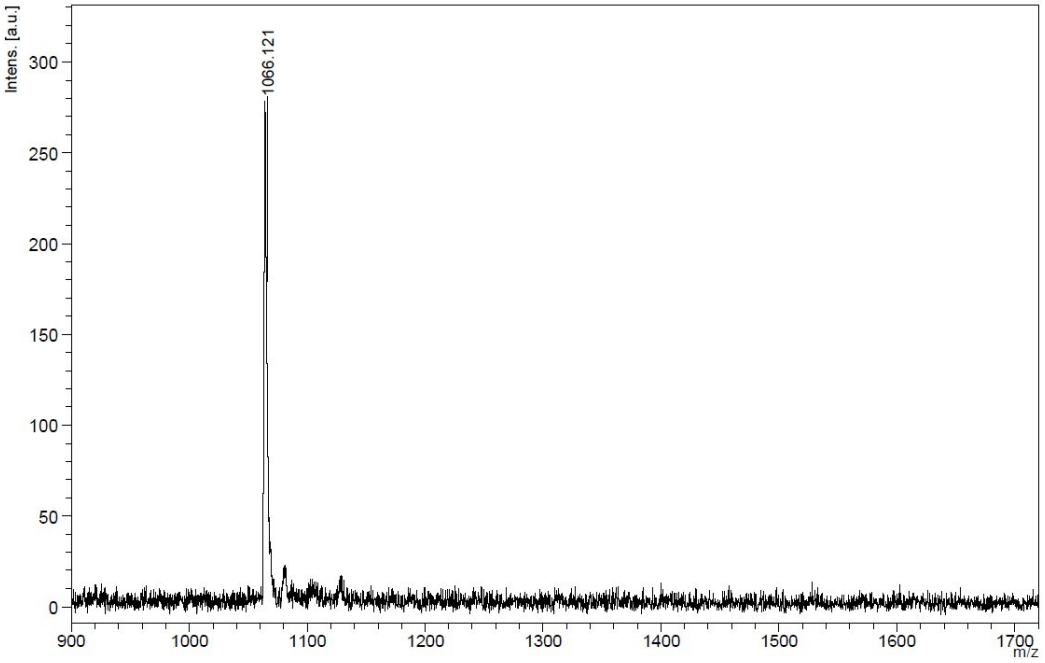

Figure S15. MALDI-TOF-MS Spectrum for 1(4),8(11),15(18),22(25)- Tetrakis((4-methoxyphenyl)thio)phthalocyanine (**5**)

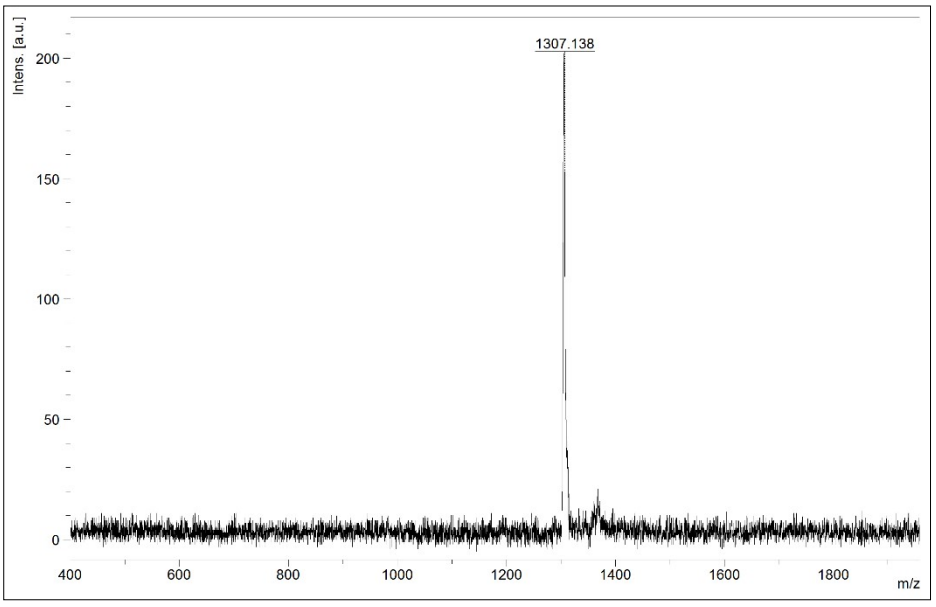

Figure S16. MALDI-TOF-MS Spectrum for 1(4),8(11),15(18),22(25)-Tetrakis((2,4,6-trimethoxyphenyl)thio)phthalocyanine (**6**).

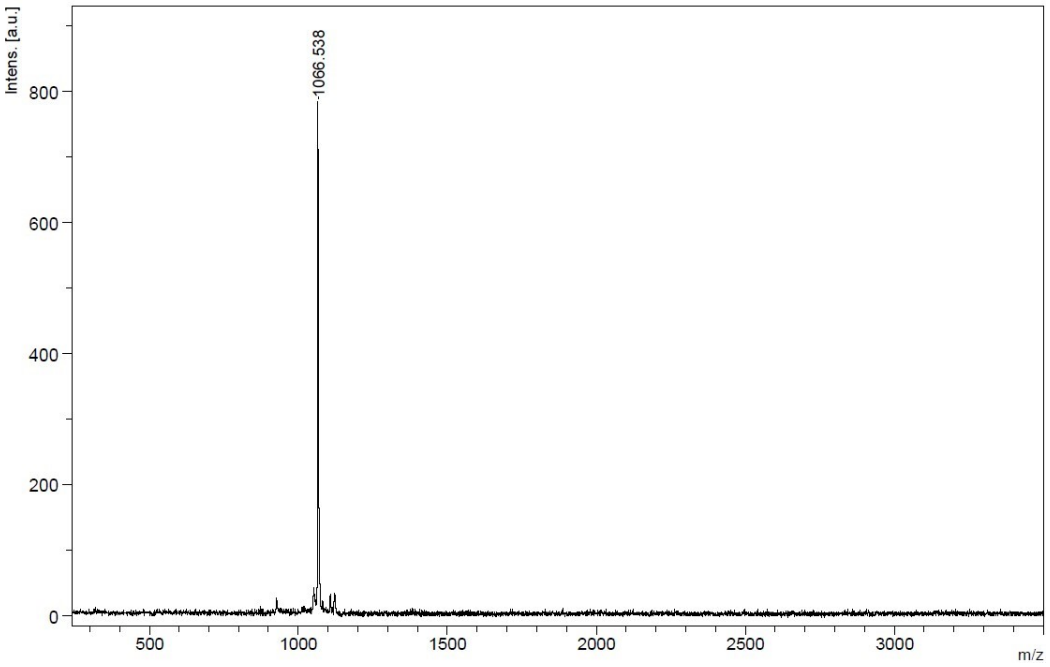

Figure S17. MALDI-TOF-MS Spectrum for 2(3),9(10),16(17),23(24)-Tetrakis((4-methoxyphenyl)thio)phthalocyanine (**7**).

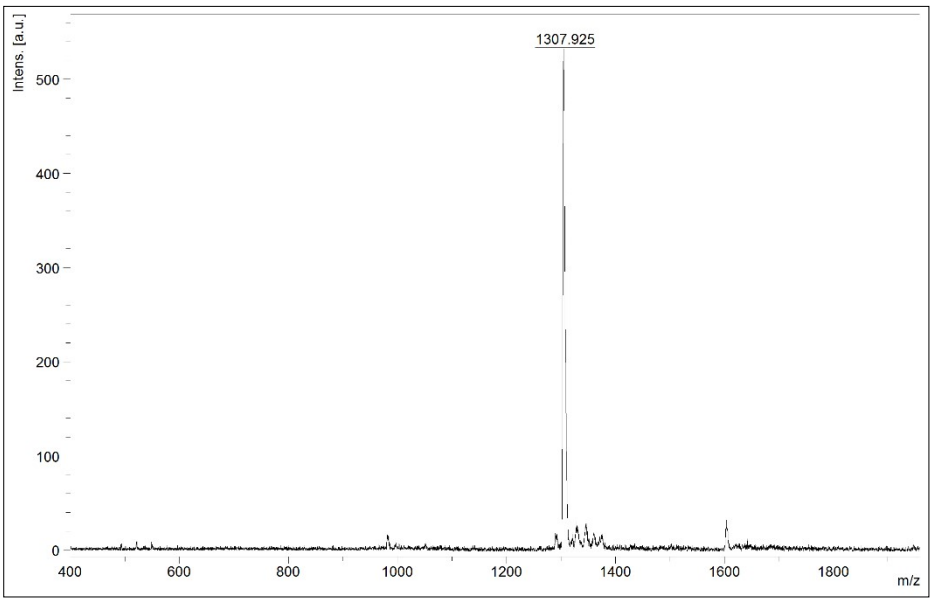

Figure S18. MALDI-TOF-MS Spectrum for 2(3),9(10),16(17),23(24)-Tetrakis((2,4,6-trimethoxyphenyl)thio)phthalocyanine (**8**).

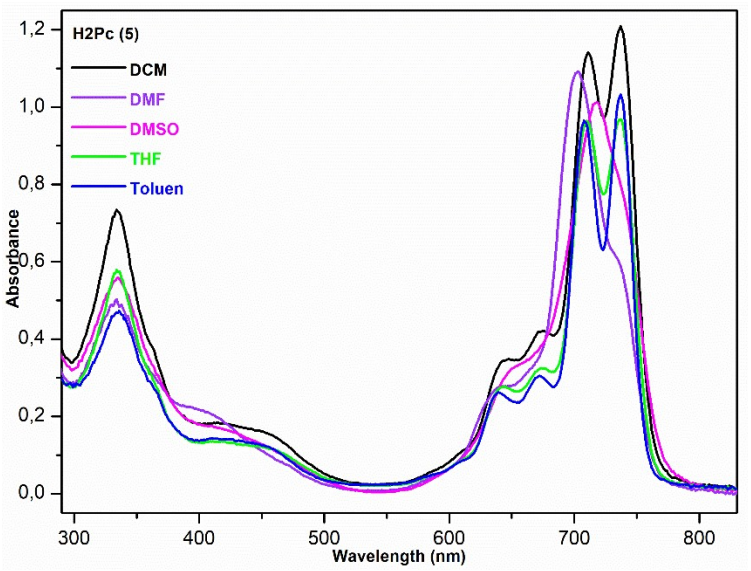

Figure S19. UV-*Vis* Spectra of 1(4),8(11),15(18),22(25)-Tetrakis((4-methoxyphenyl)thio)phthalocyanine(**5**) in various solvents at 1.10^{-5} M.

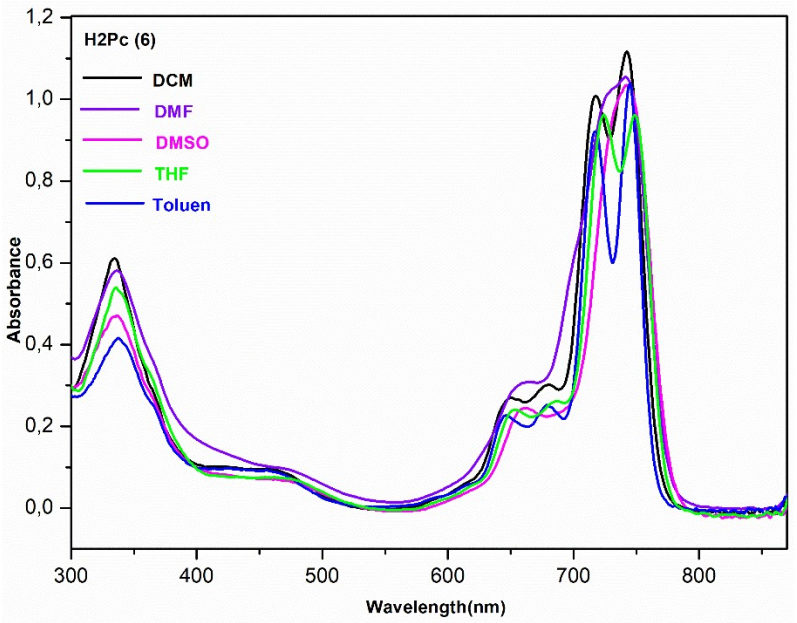

Figure S20. UV-*Vis* Spectra of 1(4),8(11),15(18),22(25)-Tetrakis((2,4,6-trimethoxyphenyl)thio)phthalocyanine(**6**) in various solvents at 1.10^{-5} M.

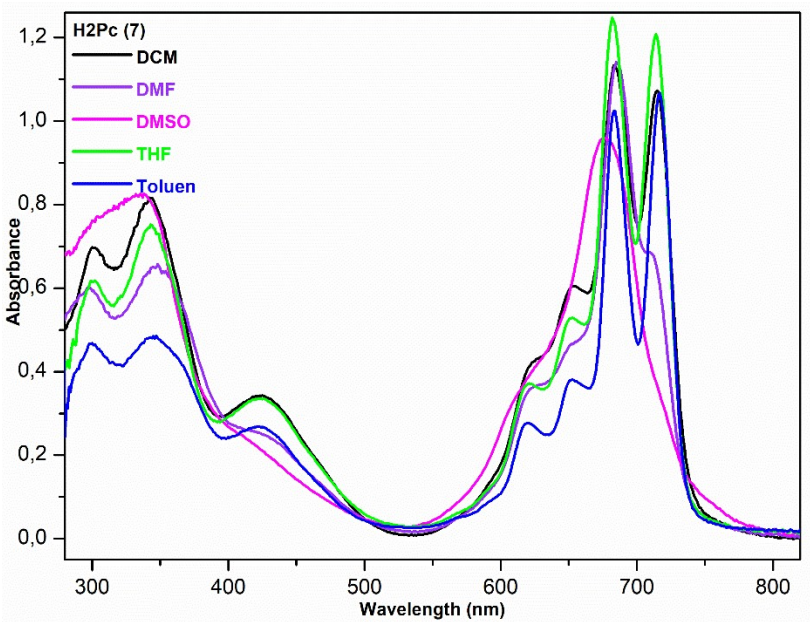

Figure S21. UV-*Vis* Spectra of 2(3),9(10),16(17),23(24)-tetrakis((4-methoxyphenyl)thio)phthalocyanine (**7**) in various solvents at 1.10^{-5} M.

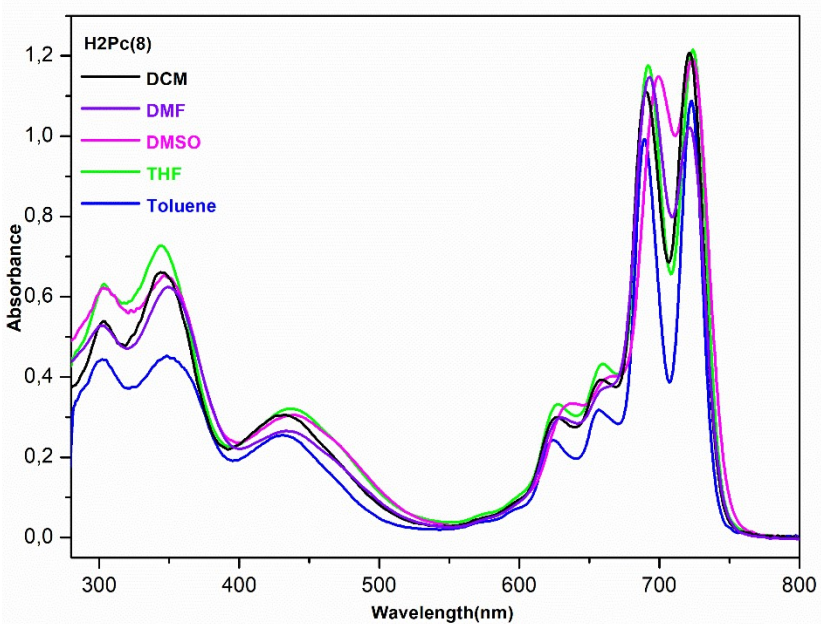

Figure S22. UV-*Vis* Spectra of 2(3),9(10),16(17),23(24)-Tetrakis((2,4,6-trimethoxyphenyl)thio)phthalocyanine(**8**) in various solvents at 1.10^{-5} M.

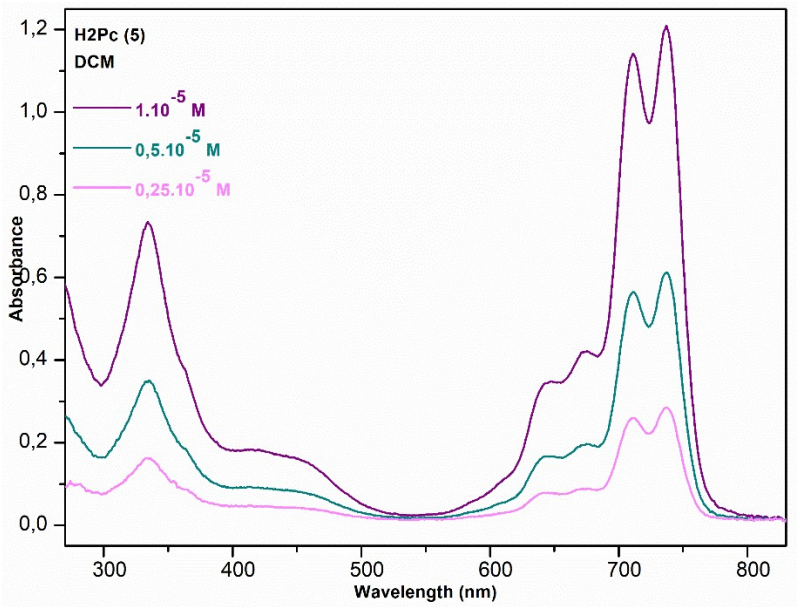

Figure S23. UV-*Vis* Spectra for 1(4),8(11),15(18),22(25)-Tetrakis((4-methoxyphenyl)thio)phthalocyanine (**5**) in DCM at different concentrations.

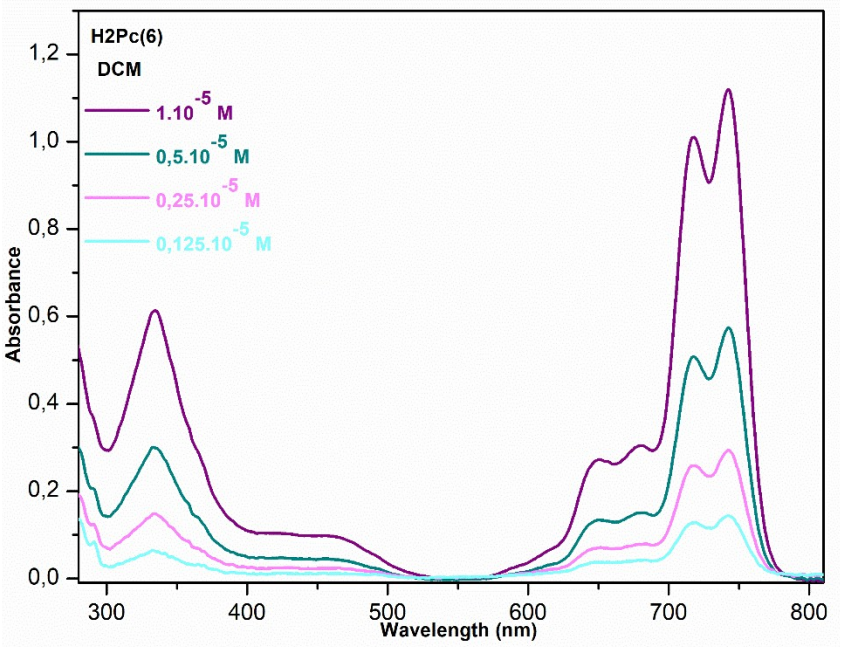

Figure S24. UV-*Vis* Spectra for 1(4),8(11),15(18),22(25)-Tetrakis((2,4,6-trimethoxyphenyl)thio)phthalocyanine (**6**) in DCM at different concentrations.

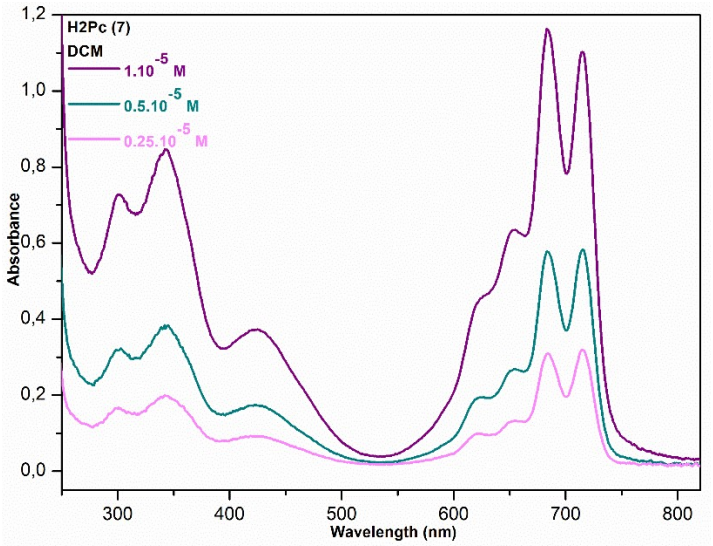

Figure S25. UV-*Vis* Spectra of 2(3),9(10),16(17),23(24)-Tetrakis((4-methoxyphenyl)thio)phthalocyanine(**7**) in DCM at different concentrations.

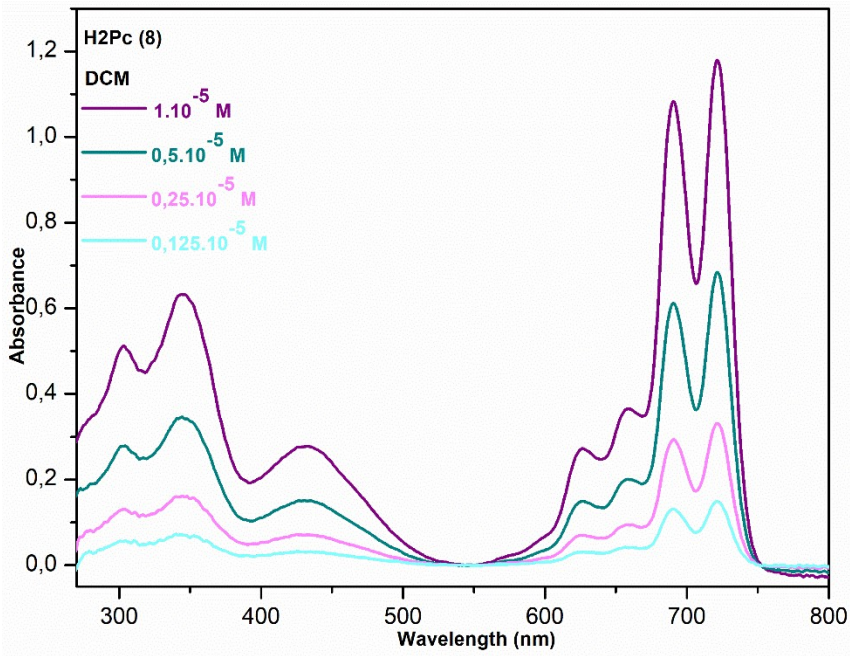

Figure S26. UV-*Vis* Spectra of 2(3),9(10),16(17),23(24)-Tetrakis((2,4,6-trimethoxyphenyl)thio)phthalocyanine(**8**) in DCM at different concentrations.

References

1. T. M. Postma, M. Giraud and F. Albericio, Trimethoxyphenylthio as a Highly Labile Replacement for tert-Butylthio Cysteine Protection in Fmoc Solid Phase Synthesis, *Organic Letters*, 2012, **14**, 5468-5471.
2. H. H. Mohamed, I. Hammami, S. Akhtar and T. E. Youssef, Highly efficient Cu-phthalocyanine-sensitized ZnO hollow spheres for photocatalytic and antimicrobial applications, *Composites Part B: Engineering*, 2019, **176**, 107314.