



SUPPORTING INFORMATION (SI)

Research Article

Peripherally tetra 1,2,4-triazole substituted novel phthalocyanines: synthesis, characterization, electrochemical and spectroelectrochemical properties

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1. Experimental

1.1. Materials and equipment

2-((E)-{[3-(4-methylphenyl)-5-phenyl-4H-1,2,4-triazol-4-yl]imino}methyl)phenol **1** [1] and 4-nitrophthalonitrile **2** [2] were prepared according to literature. All solvents were dried and purified as described by Perrin and Armarego. ¹H-NMR, ¹³C-NMR spectra were recorded on a Varian XL-200 NMR spectrophotometer in CDCl₃, and chemical shifts were reported (δ) relative to Me₄Si as internal standard. IR spectra were recorded on a Perkin–Elmer Spectrum one FT-IR spectrometer. The MS spectra were measured with a Micromass Quattro LC/ULTIMA LC- MS/MS spectrometer equipped with chloroform–methanol as solvent. UV–Vis spectra were recorded by means of a Unicam UV2-100 spectrophotometer, using 1 cm pathlength cuvettes at room temperature.

1.2 Electrochemical and in situ spectroelectrochemical measurements

The cyclic voltammetry (CV) and square wave voltammetry (SWV) measurements were carried out with Gamry Reference 600 potentiostat/galvanostat utilizing a three-electrode configuration at 25 °C. The working electrode was a Pt disc with a surface area of 0.071 cm². A Pt wire served as the counter electrode. Saturated calomel electrode (SCE) was employed as the reference electrode and separated from the bulk of the solution by a double bridge. Electrochemical grade TBAP in extra pure dichloromethane (DCM) was employed as the supporting electrolyte at a concentration of 0.10 mol dm⁻³. Ferrocene was used as universal indicator and ΔE_p's of ferrocene were changed from 60 to 110 mV with increasing scan rates from 0.010 to 1.00 Vs⁻¹ in our system.

UV-Vis absorption spectra and chromaticity diagrams were measured with a OceanOptics QE65000 diode array spectrophotometer. *In situ* spectroelectrochemical measurements were carried out by utilizing a three-electrode configuration of thin-layer quartz thin-layer spectroelectrochemical cell at 25 °C. The working electrode was a Pt tulle. A Pt wire counter electrode separated by a glass bridge and a SCE reference electrode separated from the bulk of the solution by a double bridge were used. *In situ* electrocolorimetric measurements, under potentiostatic control, were obtained using an OceanOptics QE65000 diode array spectrophotometer at color measurement mode by utilizing a three-electrode configuration of thin-layer quartz spectroelectrochemical cell. The standard illuminant A with 2 degree observer at constant temperature in a light booth designed to exclude external light was used. Prior to each set of measurements, background color coordinates (x, y and z values) were taken at open-circuit, using the electrolyte solution without the complexes under study. During the measurements, readings were taken as a function of time under kinetic control, however, only the color coordinates at the beginning and final of each redox processes were reported.

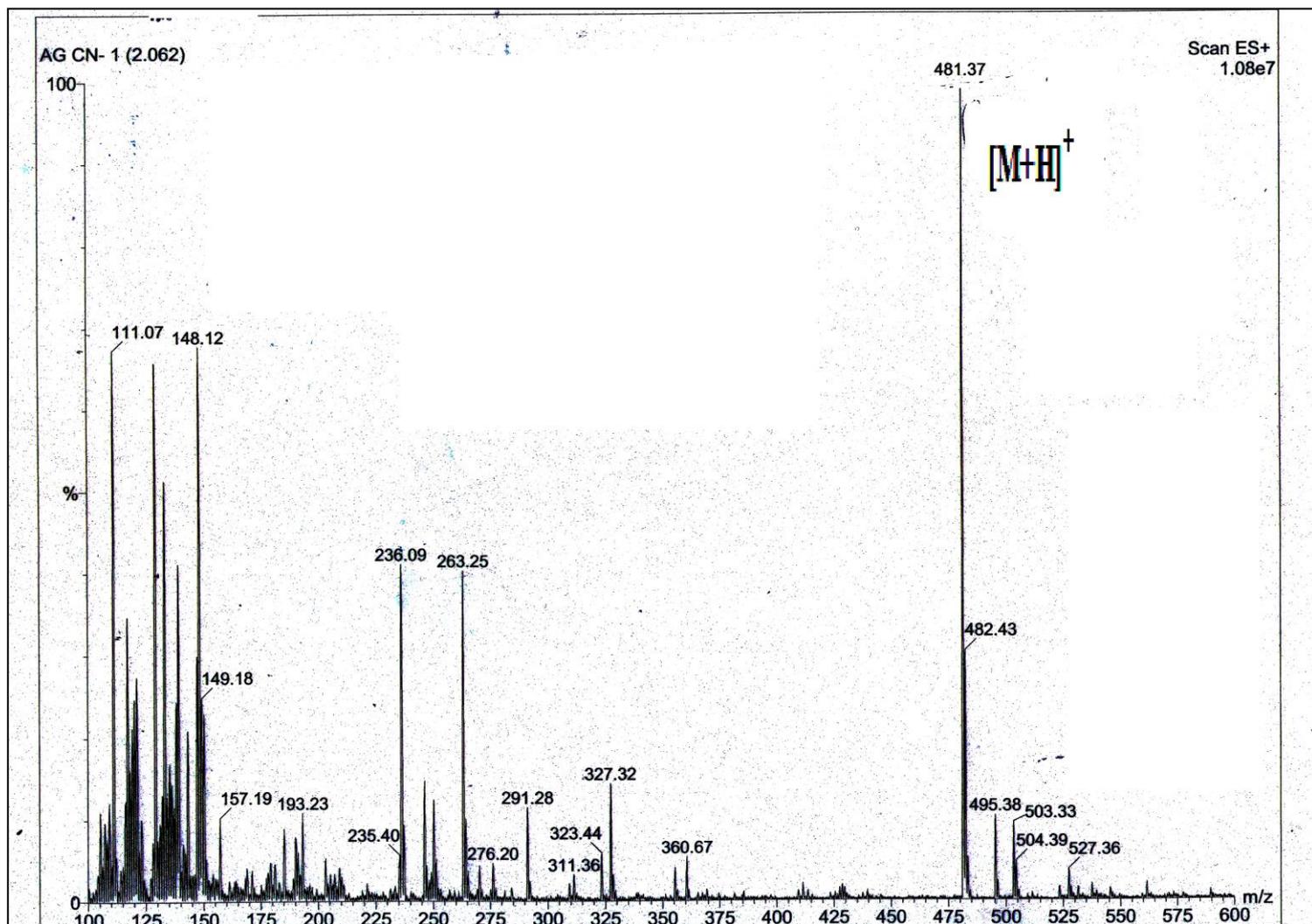


Figure S1. The MS spectrum of compound 3.

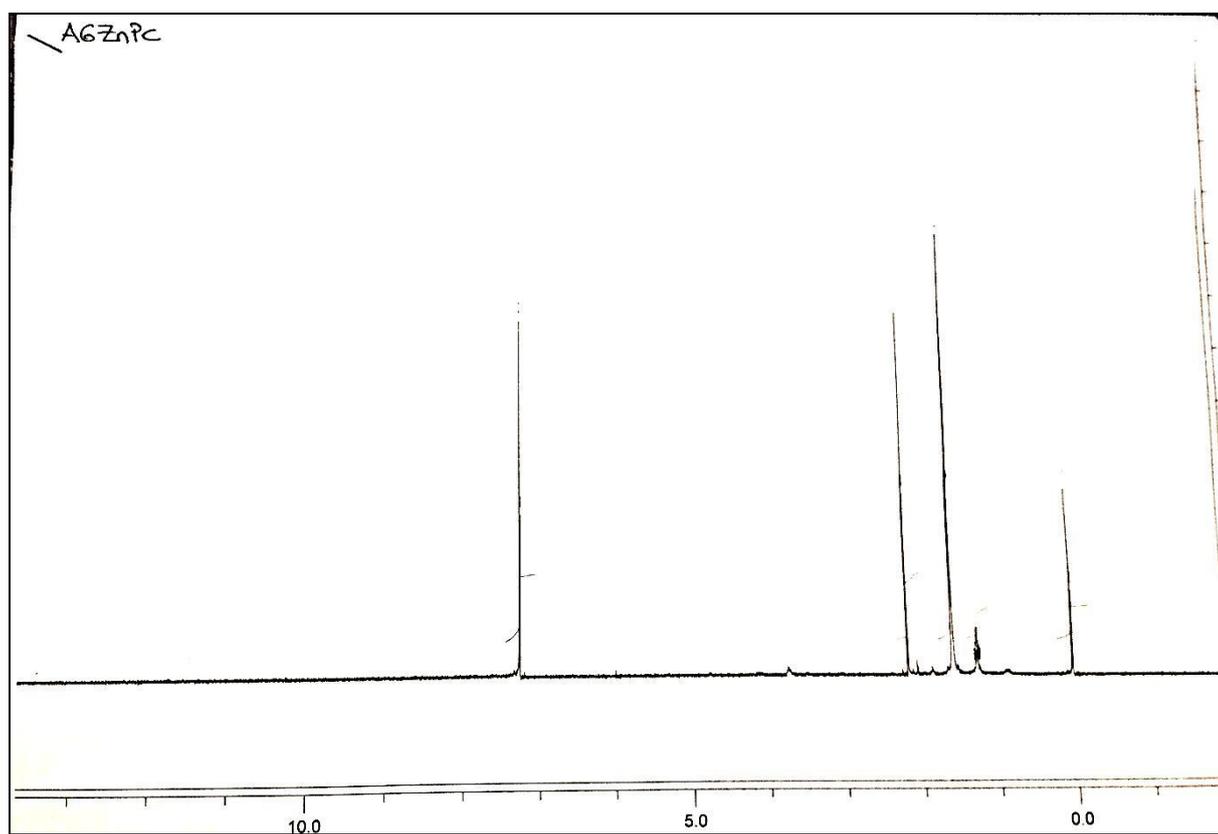
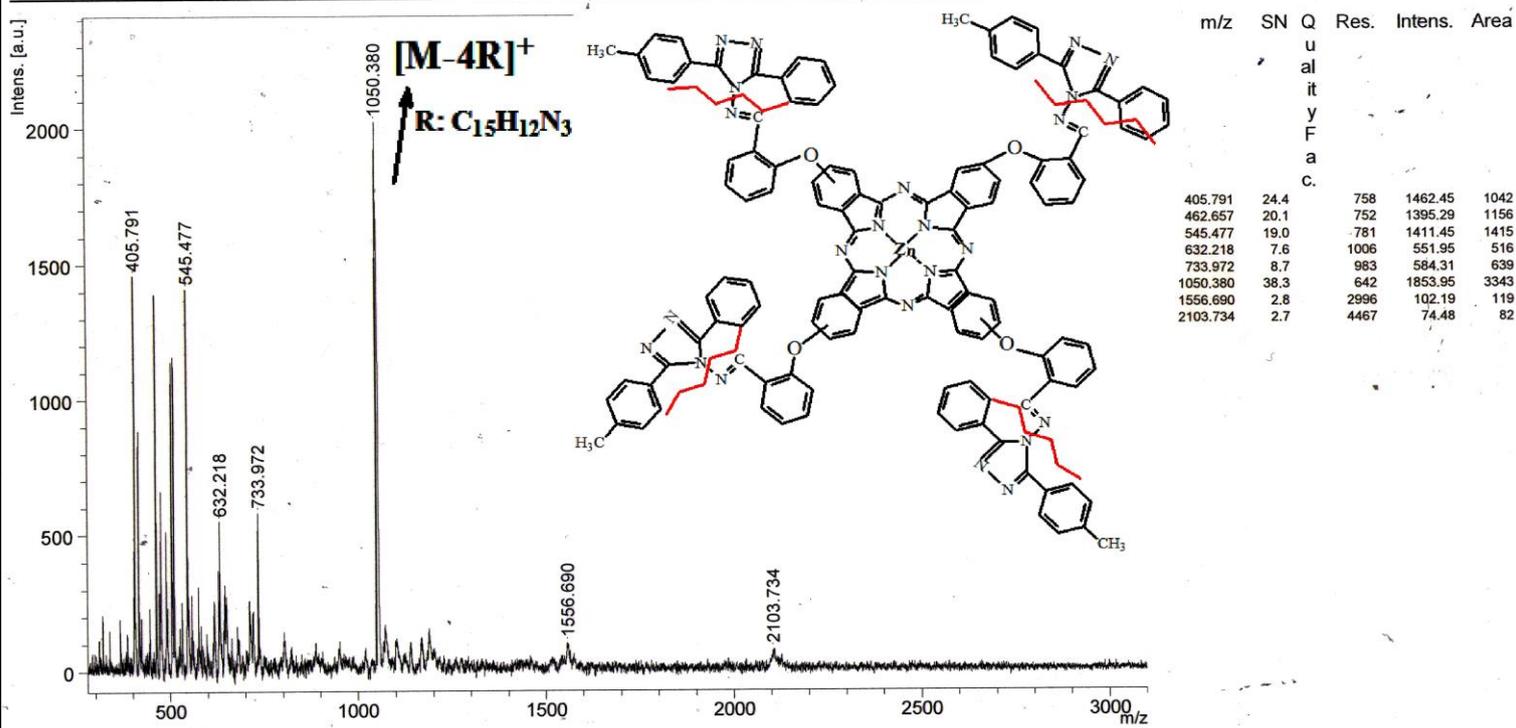


Figure S2. The ^1H -NMR spectrum of the ZnPc



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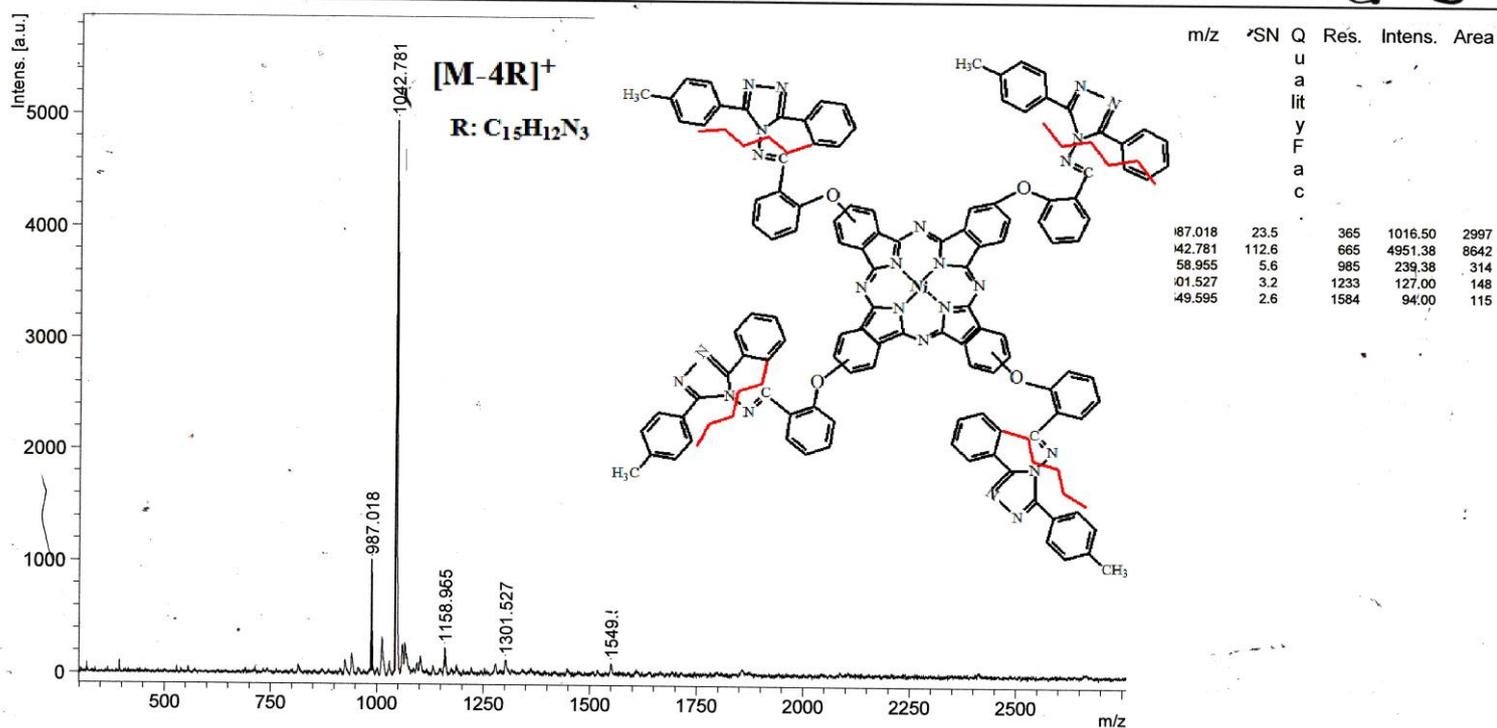
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Figure S3. The MALDI-MS spectrum of Zinc phthalocyanine 5.



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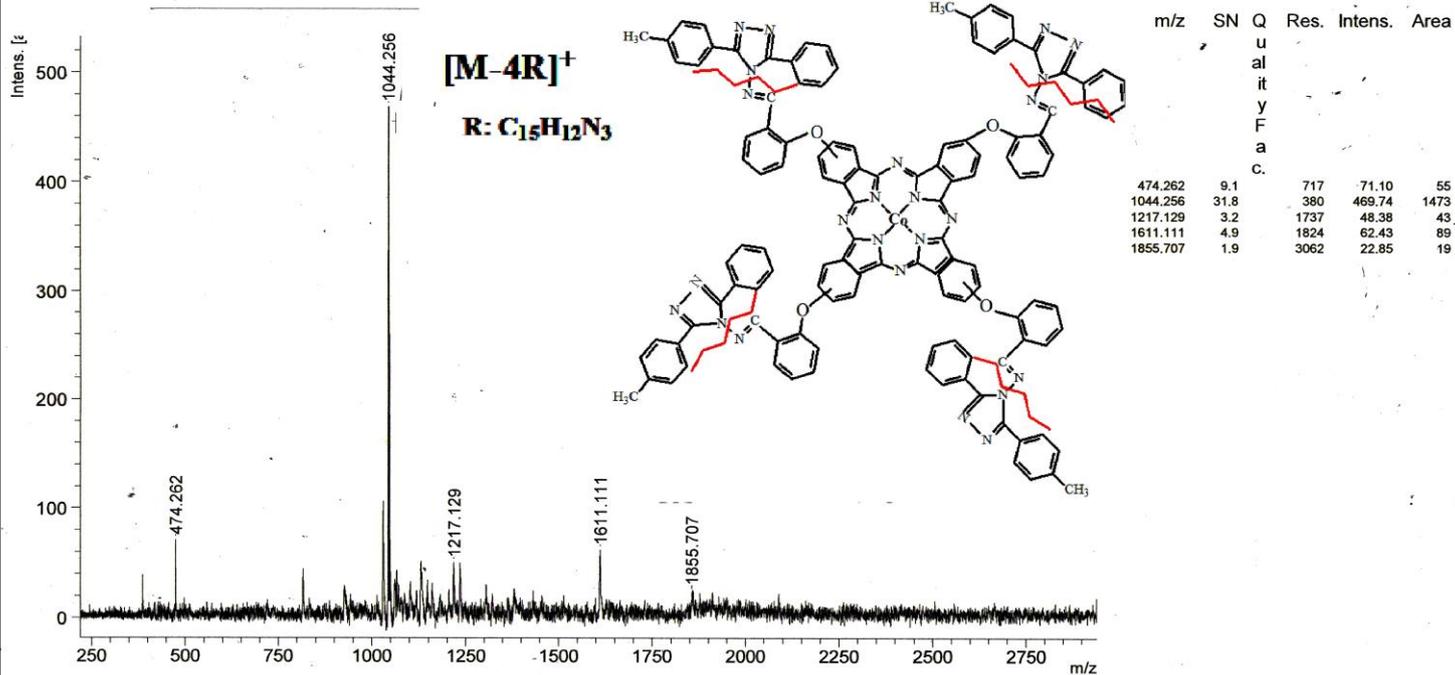
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Figure S4. The MALDI-MS spectrum of Nickel phthalocyanine 7.



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Figure S5. The MALDI-MS spectrum of Cobalt phthalocyanine 8.

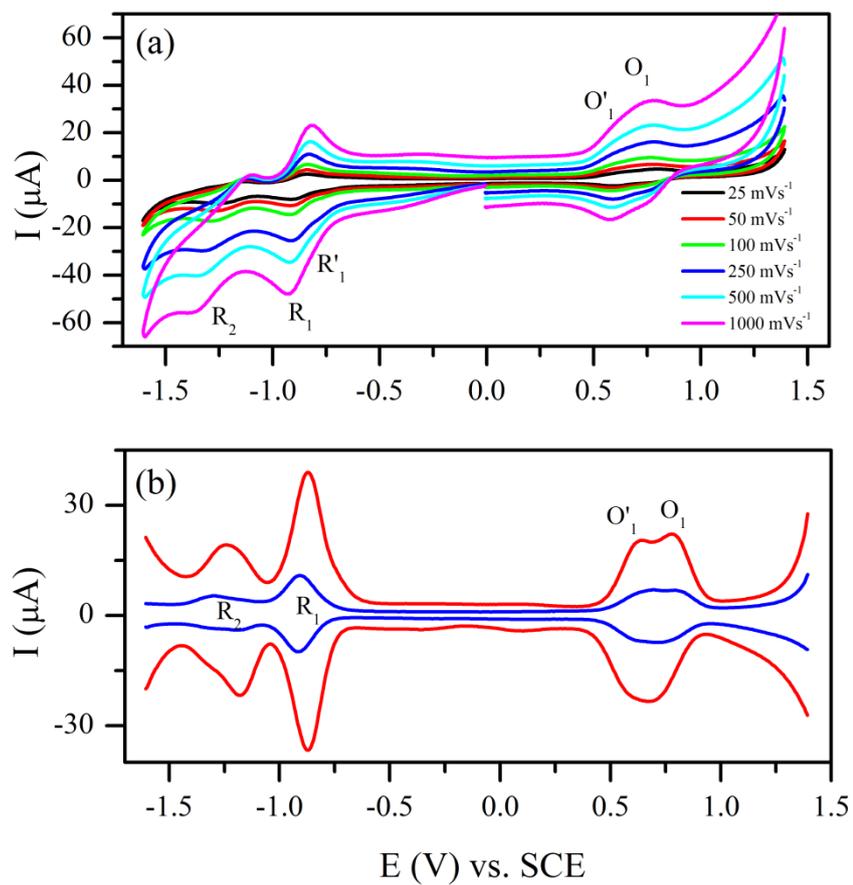


Figure S6. (a) CVs of **ZnPc** at various scan rates and (b) SWVs of **ZnPc** recorded with two different concentrations ($5 \times 10^{-4} \text{ mol dm}^{-3}$ and $10 \times 10^{-4} \text{ mol dm}^{-3}$) at 0.100 Vs^{-1} scan rate on a Pt working electrode in DCM/TBAP.

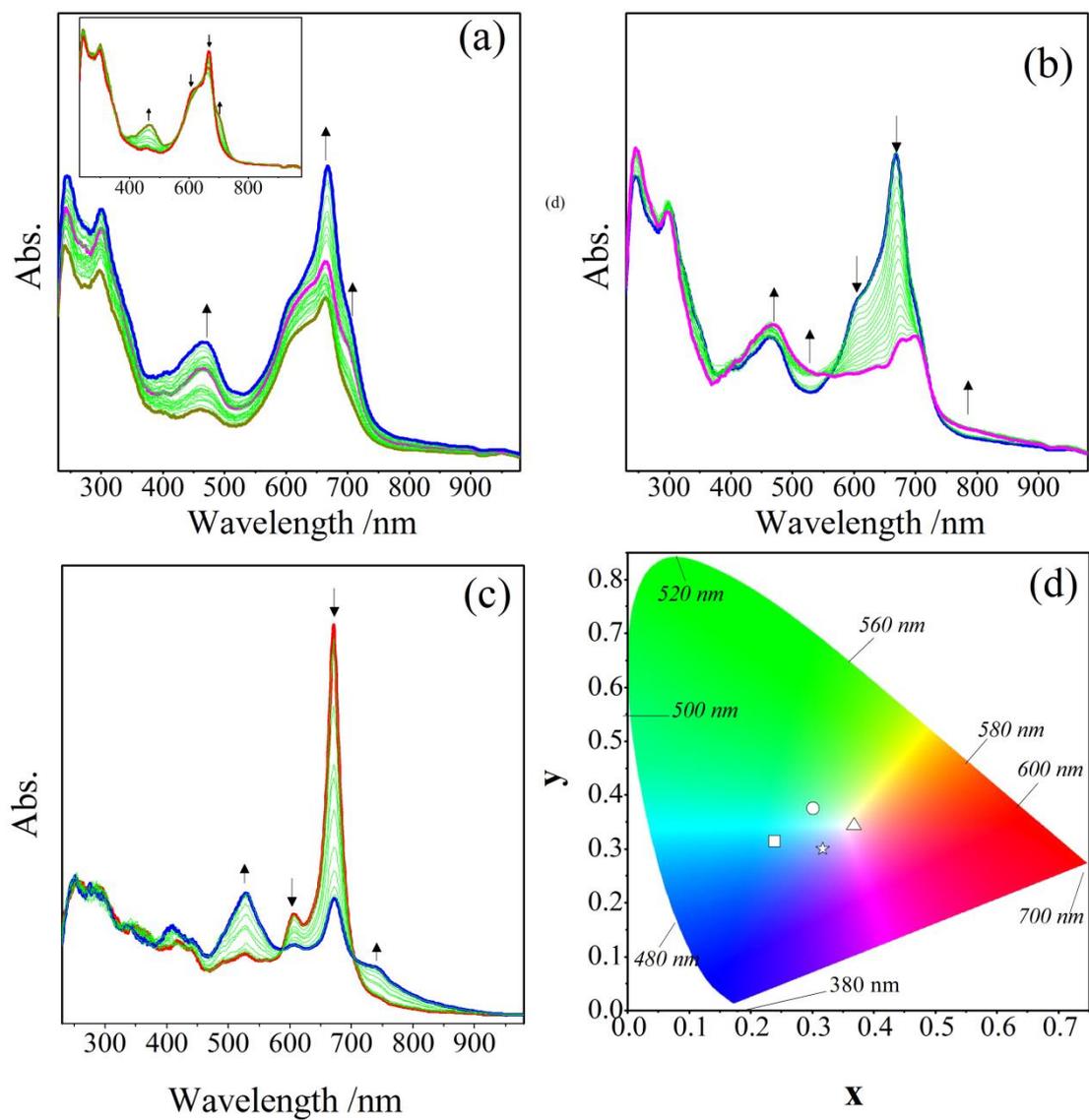


Figure S7. In-situ UV-Vis spectral changes of CoPc in DCM/TBAP. **a)** $E_{app} = -0.70$ V. **b)** $E_{app} = -1.40$ V. **c)** $E_{app} = 0.80$ V. **d)** Chromaticity diagram (each symbol represents the color of electro-generated species; \square : $[Co^{II}Pc^{-2}]$, \circ : $[Co^IPc^{-2}]^{-1}$, \triangle : $[Co^IPc^{-3}]^{-2}$, \star : $[Co^{II}Pc^{-1}]^{+1}$).

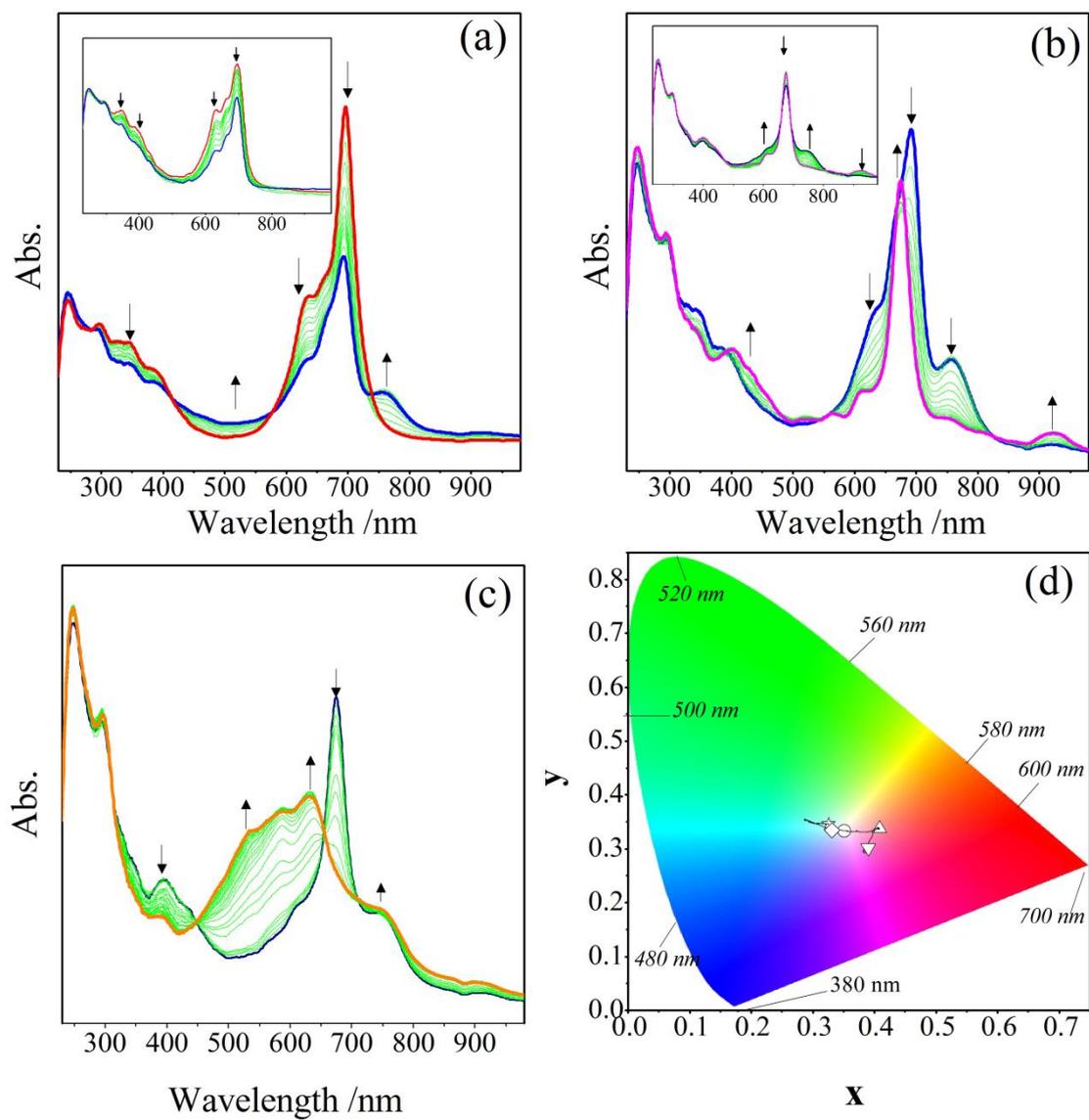


Figure S8. In-situ UV-Vis spectral changes of **TiOPc** in DCM/TBAP. **a)** $E_{app} = -0.60$ V (inset: $E_{app} = 1.00$ V). **b)** $E_{app} = -0.80$ V (inset: $E_{app} = -0.95$ V). **c)** $E_{app} = -1.20$ V. **d)** Chromaticity diagram (each symbol represents the color of electro-generated species; \square : $[\text{Ti}^{\text{IV}}\text{OPc}^{-2}]$, \diamond : $[\text{Ti}^{\text{IV}}\text{OPc}^{-3}]^{-1}$; \circ : $[\text{Ti}^{\text{III}}\text{OPc}^{-3}]^{-2}$; \triangle : $[\text{Ti}^{\text{III}}\text{OPc}^{-4}]^{-3}$; ∇ : $[\text{Ti}^{\text{II}}\text{OPc}^{-4}]^{-4}$; \star : $[\text{Ti}^{\text{IV}}\text{OPc}^{-1}]^{+1}$).

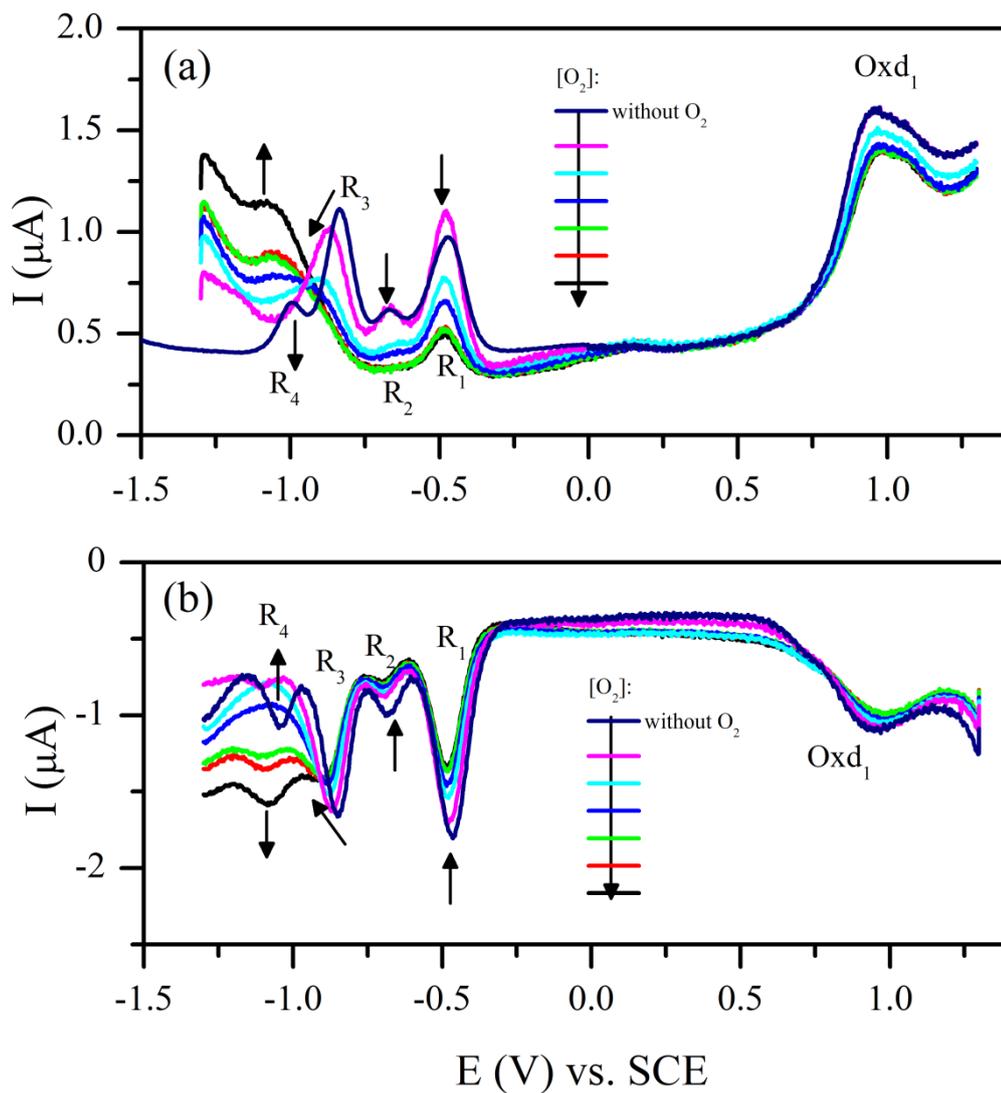


Figure S9. SWV responses of TiOPc recorded gas at 0.100 Vs⁻¹ scan rate on a Pt working electrode in DCM/TBAP which is gradually bubbled with O₂.

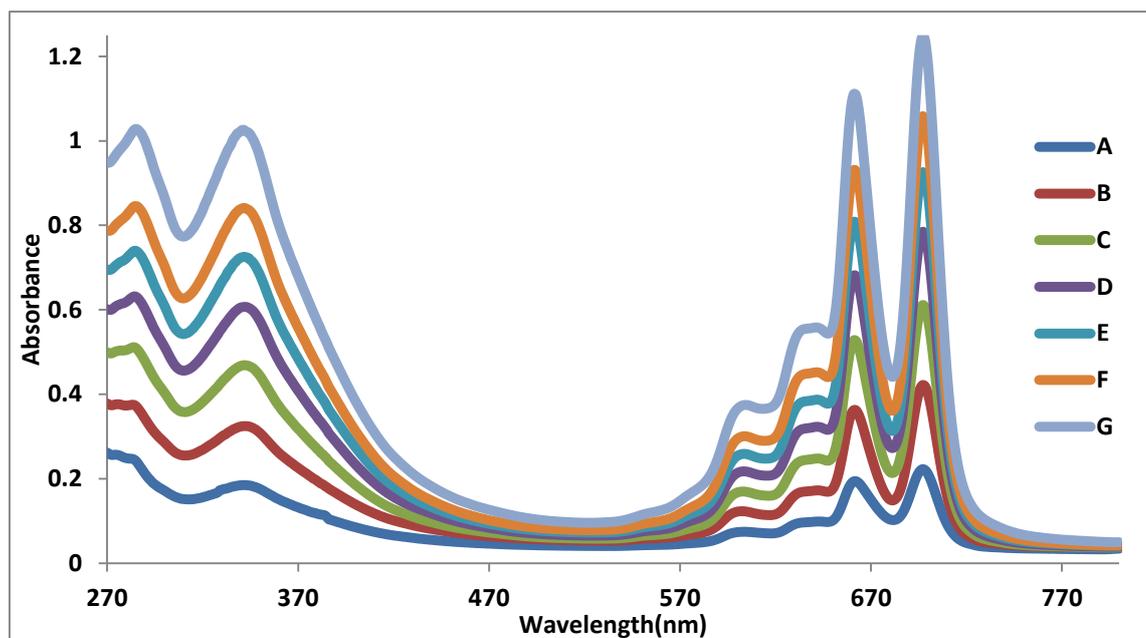


Figure S10a. Absorption spectra of the compound **4** in CHCl_3 at different concentrations: A; 2×10^{-6} , B; 4×10^{-6} , C; 6.0×10^{-6} , D; 8×10^{-6} , E; 10×10^{-6} , F; 12×10^{-6} , G; $14 \times 10^{-6} \text{ mol dm}^{-3}$.

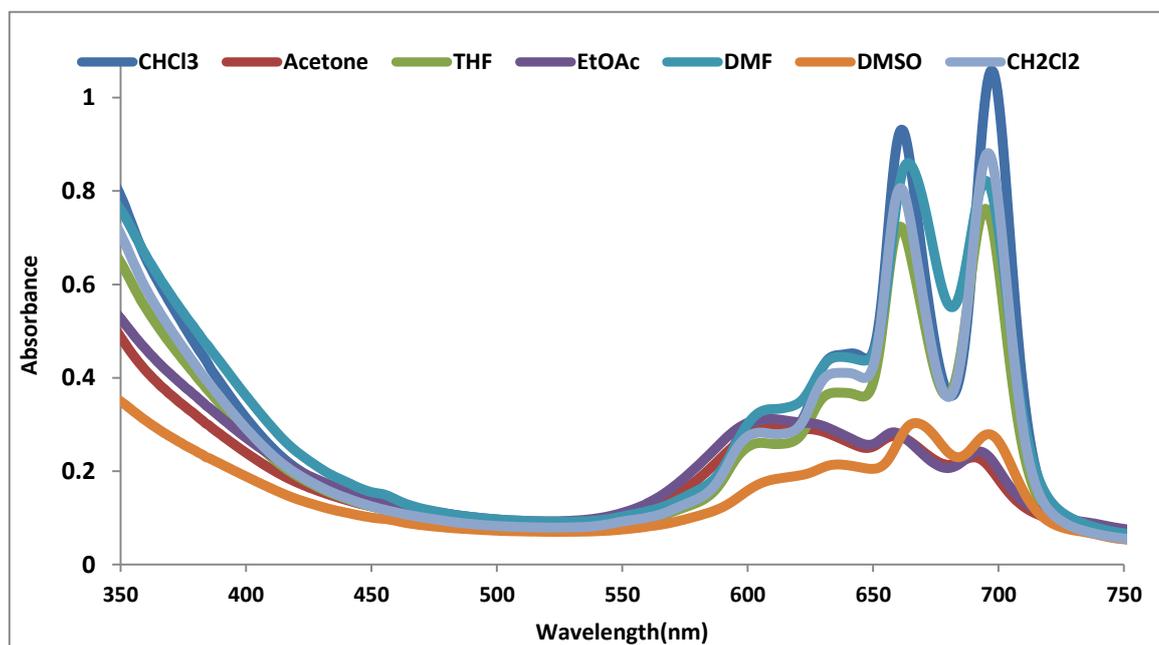


Figure S10b. Absorption spectra of the compound **4** in different solvents. Concentration = $12 \times 10^{-5} \text{ mol dm}^{-3}$.

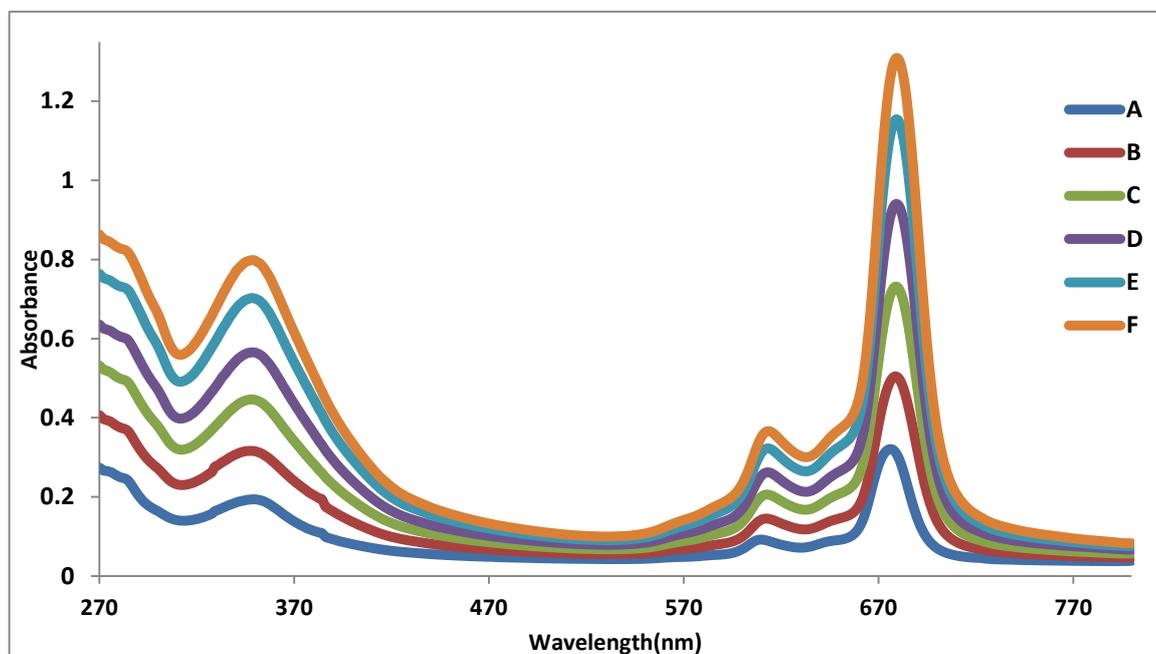


Figure S11a. Absorption spectra of the compound **5** in CHCl_3 at different concentrations: A; 2×10^{-6} , B; 4×10^{-6} , C; 6.0×10^{-6} , D; 8×10^{-6} , E; 10×10^{-6} , F; $12 \times 10^{-6} \text{ mol dm}^{-3}$.

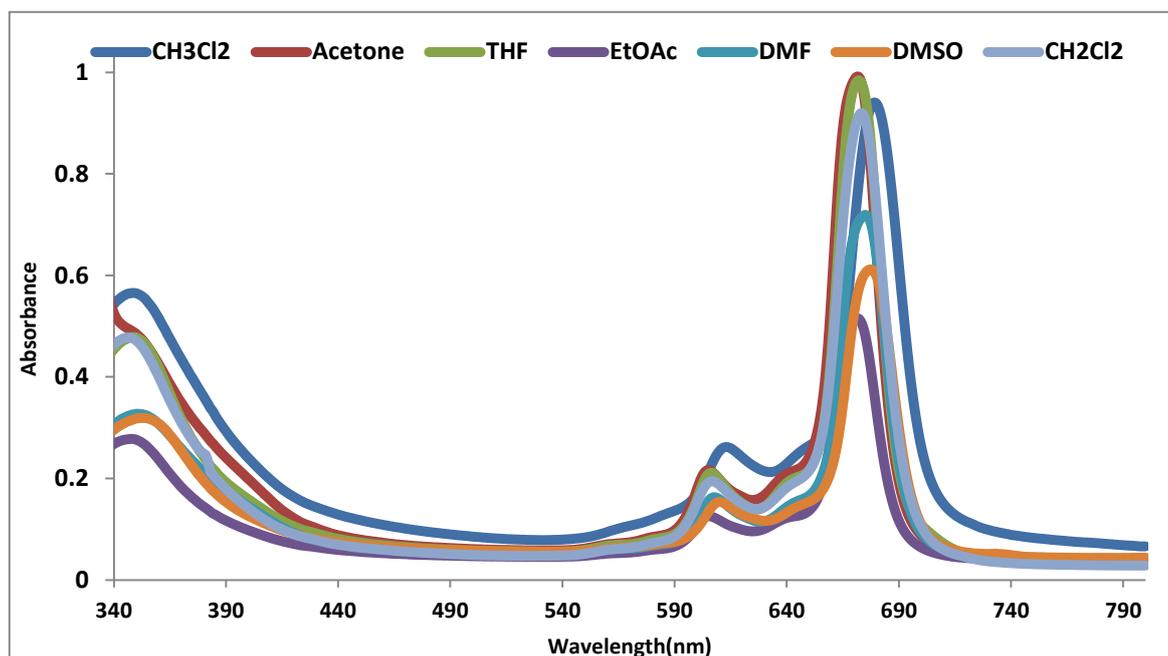


Figure S11b. Absorption spectra of the compound **5** in different solvents. Concentration = $8 \times 10^{-5} \text{ mol dm}^{-3}$.

References

- [1] Bekircan, O., Kahveci, B., Küçük, M., Synthesis and Anticancer Evaluation of Some New Unsymmetrical 3,5-Diaryl-4H-1,2,4-Triazole Derivatives, *Turk. J. Chem.* 2006, 30, 29-40.
- [2] Koca, A., Bayar, S., Dincer, H. A., Gonca, E., Voltammetric, in-situ spectroelectrochemical and in-situ electrochromic characterization of phthalocyanines, *Electrochim Acta*, 2009, 54, 2684-2692.