Ag(I) induced H-type and Pd(II) induced J-type phthalocyanines to enhance PDT applications: synthesis, optical behaviors, photochemical/photophysical properties, and DFT studies.

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Content of supplementary materials

1. Photophysical and Photochemical Parameters

1.1. Fluorescence quantum yields

The fluorescence quantum yield (Φ_F) of the synthesized zinc phthalocyanines (**2** and **5**) was determined with the comparative method using the following equation in DMSO at room temperature **(1) [1, 2].**

$$\Phi_F = \Phi_F(Std) \; \frac{F. A_{Std}. n^2}{F_{Std} A. n_{Std}^2} \qquad (1)$$

In this equation, Φ_F is the quantum yield of the compound **(1)**, Φ_F (Std) is the quantum yield of the reference compound, F and F_{Std} are the areas under the fluorescence emission curves of the non-peripheral substituted zinc phthalocyanines **(2** and **5)** and unsubstituted zinc phthalocyanine as a standard, respectively. The absorbance of the reference and sample compounds is A_{Std} and A. n^2 and n_{Std}^2 are the refractive indices of solvents used for the samples and standard compounds. The quantum yield of the reference compound (unsubstituted zinc phthalocyanine) was used as $\Phi_F = 0.20$, according to the literature **[3].**

1.2. Singlet oxygen quantum yields

The singlet oxygen quantum yields of non-peripheral substituted zinc phthalocyanines (**2** and **5**) were determined in the air by using the following equation in DMSO at room temperature. In equation (2), zinc phthalocyanines as a reference and DPBF as a chemical quencher were used.

$$\Phi_{\Delta} = \Phi_{\Delta}^{Std} \frac{R \,.\, I_{abs}^{Std}}{R^{Std} \,.\, I_{abs}} \tag{2}$$

In this equation, Φ_{Δ}^{Std} is the singlet oxygen quantum yield of the reference sample. According to the literature, the singlet oxygen quantum yield of the reference compound (unsubstituted zinc phthalocyanines) was used as / = 0.67 in DMSO. **[3]**. R and R_{Std} are the photobleaching rates of DPBF in the presence of non-peripheral substituted zinc phthalocyanines (**2** and **5**) and unsubstituted zinc phthalocyanines as a reference. I_{abs} and I_{abs}^{Std} are light absorption rates in the presence of the zinc phthalocyanine and unsubstituted zinc phthalocyanines are used as a reference. The solutions containing DPBF were prepared in a dark environment, and the degradation of DPBF at 417 nm was monitored after each 5s irradiation **[4, 5]**. The absorption band of DPBF at 417 nm was reduced after light irradiation **[5]**.

1.3. Photodegradation quantum yields

The photodegradation quantum yield of synthesized zinc phthalocyanine derivatives was determined by using the following equation (3);

$$\Phi_d = \frac{(C_0 - C_t) \,.\, V \,.\, N_A}{I_{abs} \,.\, S \,.\, t} \tag{3}$$

In this equation, C_0 is the concentration of zinc phthalocyanine derivatives before the irradiation, and C_t is the concentration after the irradiation. V is the reaction volume, N_A is Avogadro's constant, S is the irradiated cell area, "t" is the irradiation time, I_{abs} is the overlap integral of the radiation source light intensity and the absorption of the samples **[5]**.

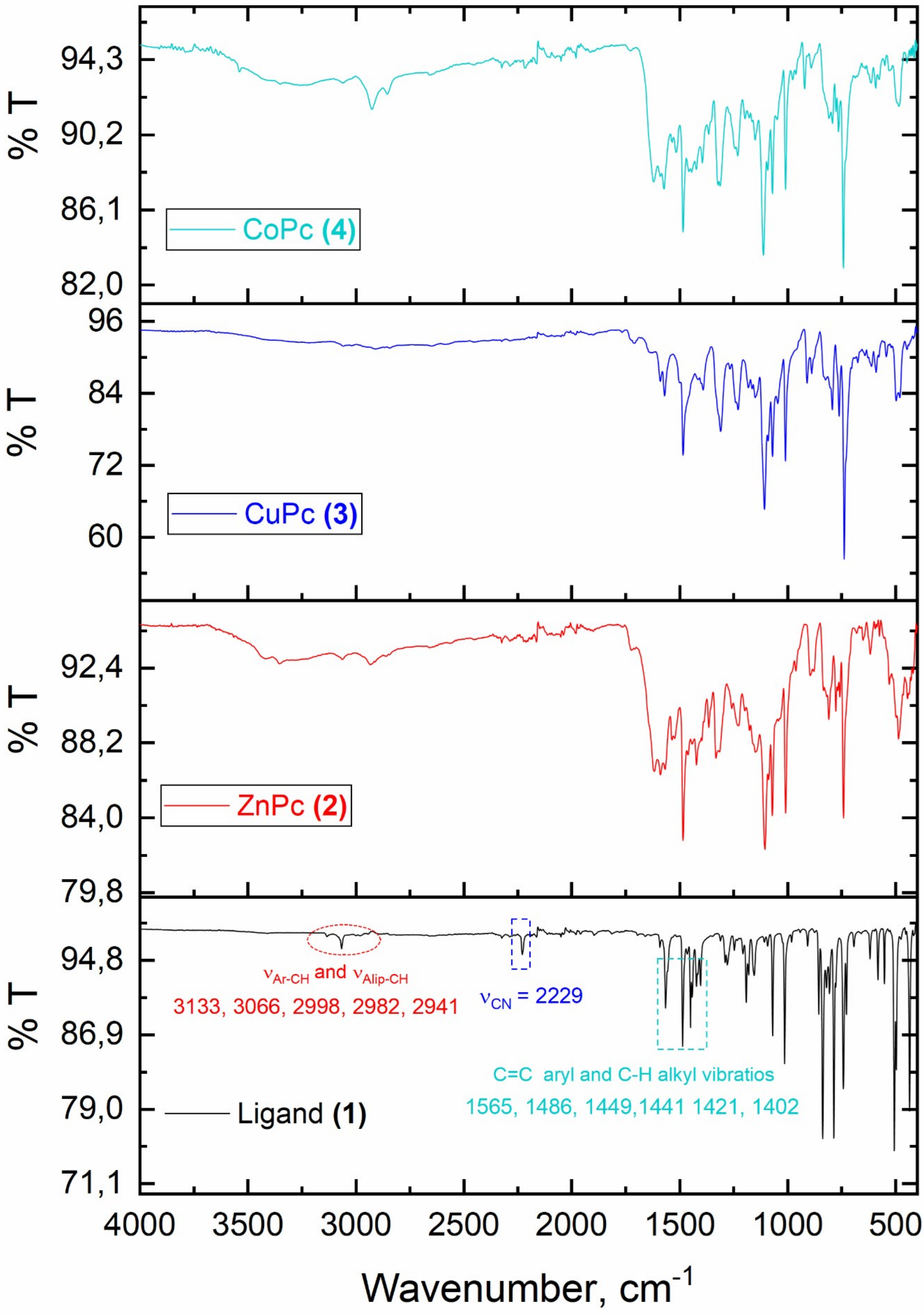

Fig. S1 FTIR spectra of compound **(1)** and its metallophthalocyanine derivatives [ZnPc**(2)**, CuPc**(3)**, and CoPc**(4)**].

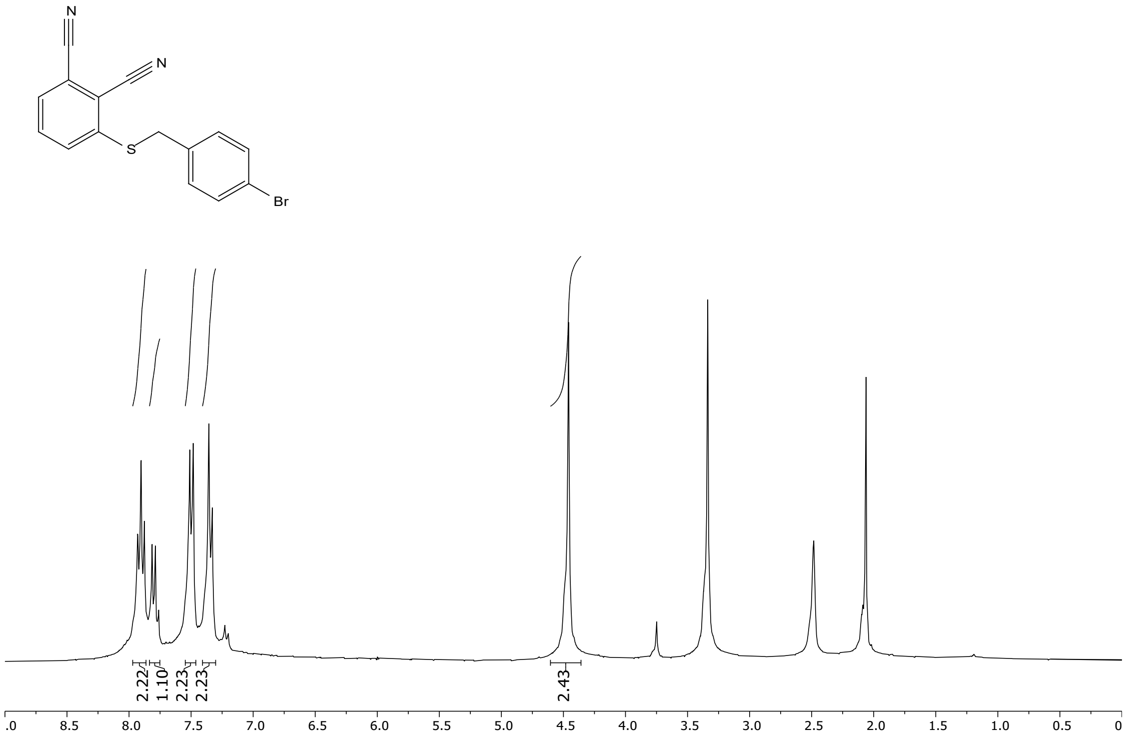

Fig. S2 ^{1}H-NMR spectra of compound **(1)**

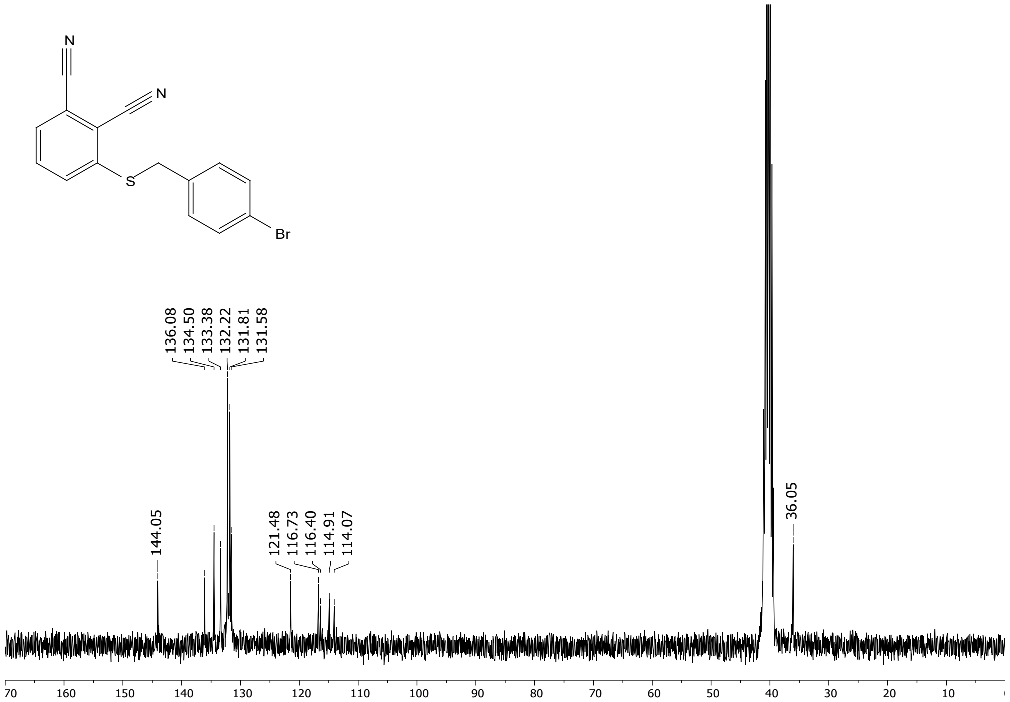

Fig. S3 ^{13}C-NMR spectra of compound **(1)**

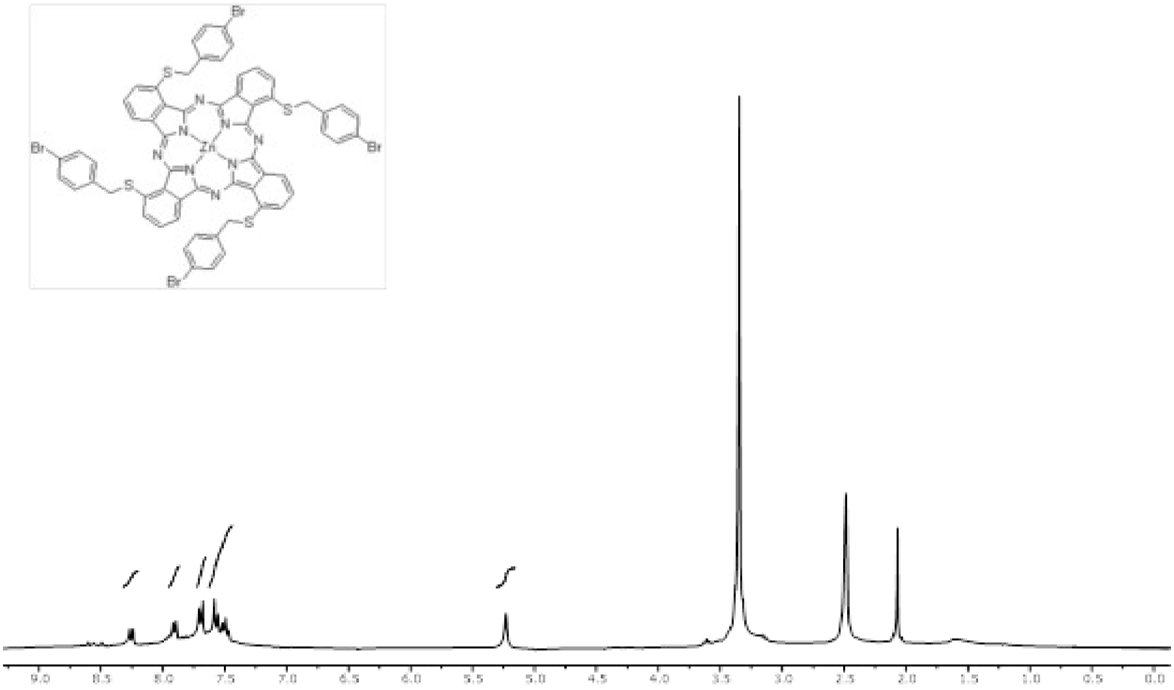

Fig. S4 ^{1}H-NMR spectra of ZnPc **(2)**.

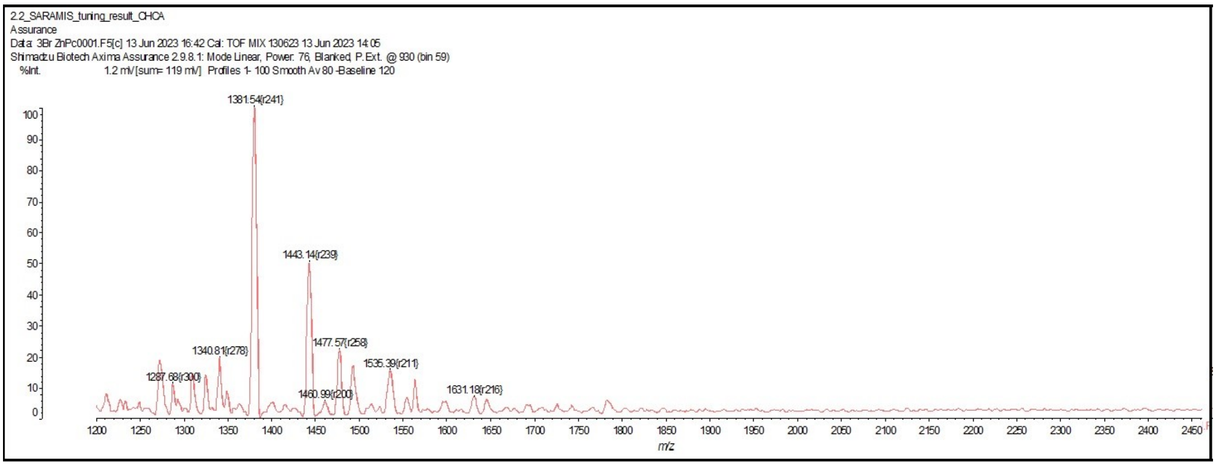

Fig. S5 MALDI-TOF spectrum of ZnPc**(2)**.

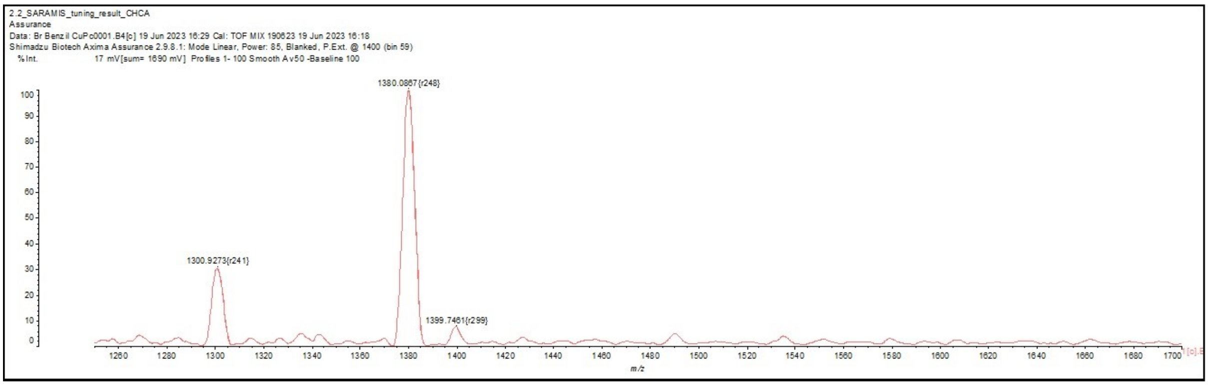

Fig. S6 MALDI-TOF spectrum of CuPc**(3)**.

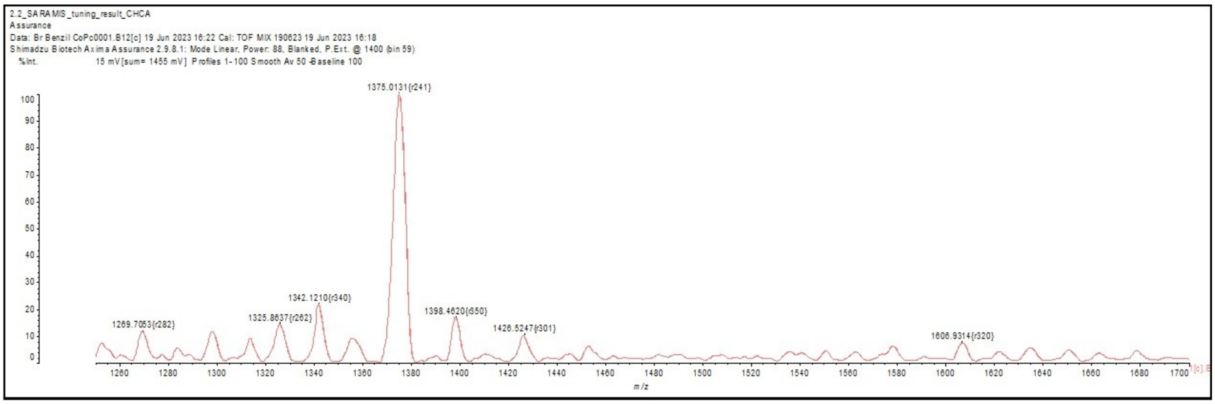

Fig. S7 MALDI-TOF spectrum of CoPc**(4)**.

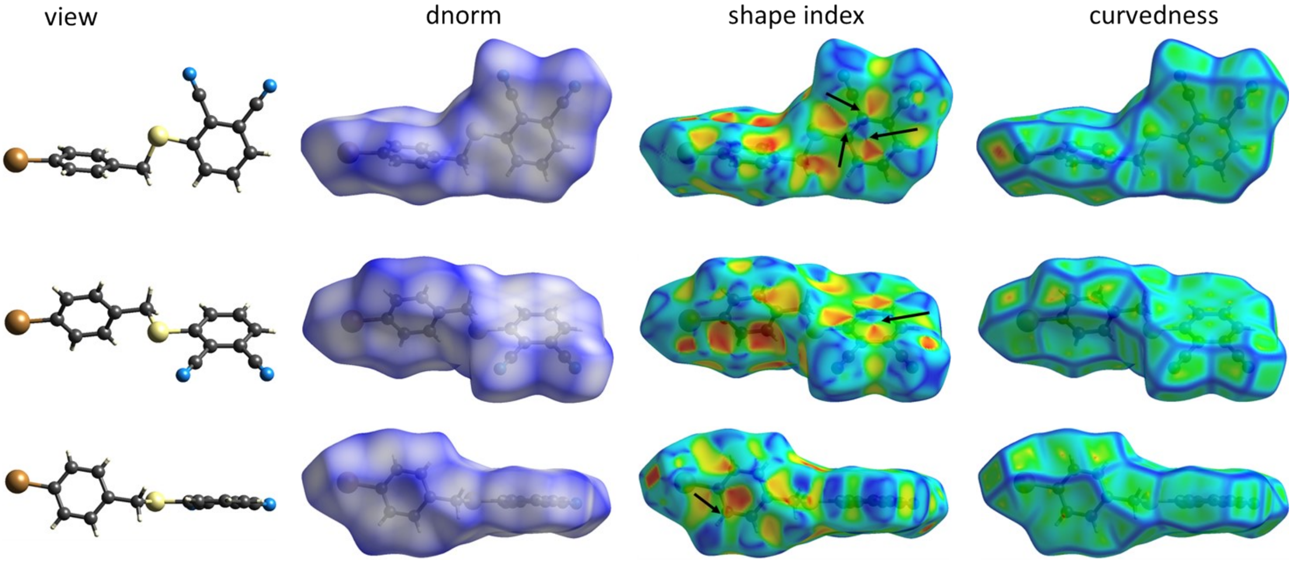

Fig. S8. Three different views for the molecular structure of compound (x). Intermolecular interactions (dnorm), Cg···Cg (π···π) interactions (shape index), and relatively flat surfaces (curvedness) are all represented by Hirshfeld surfaces.

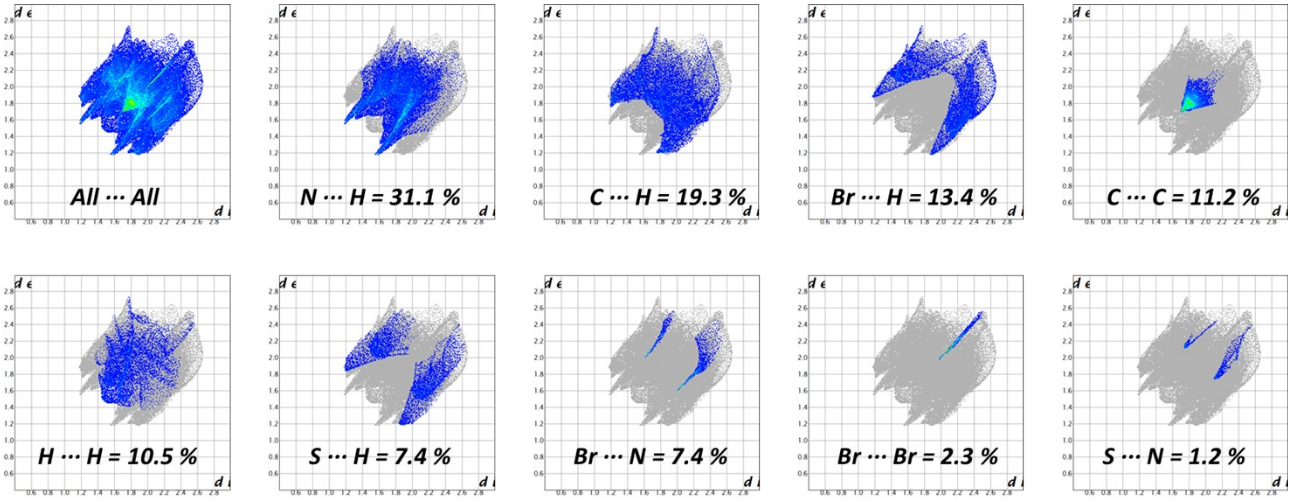

Fig. S9. The 2D fingerprint plot for the asymmetric unit.

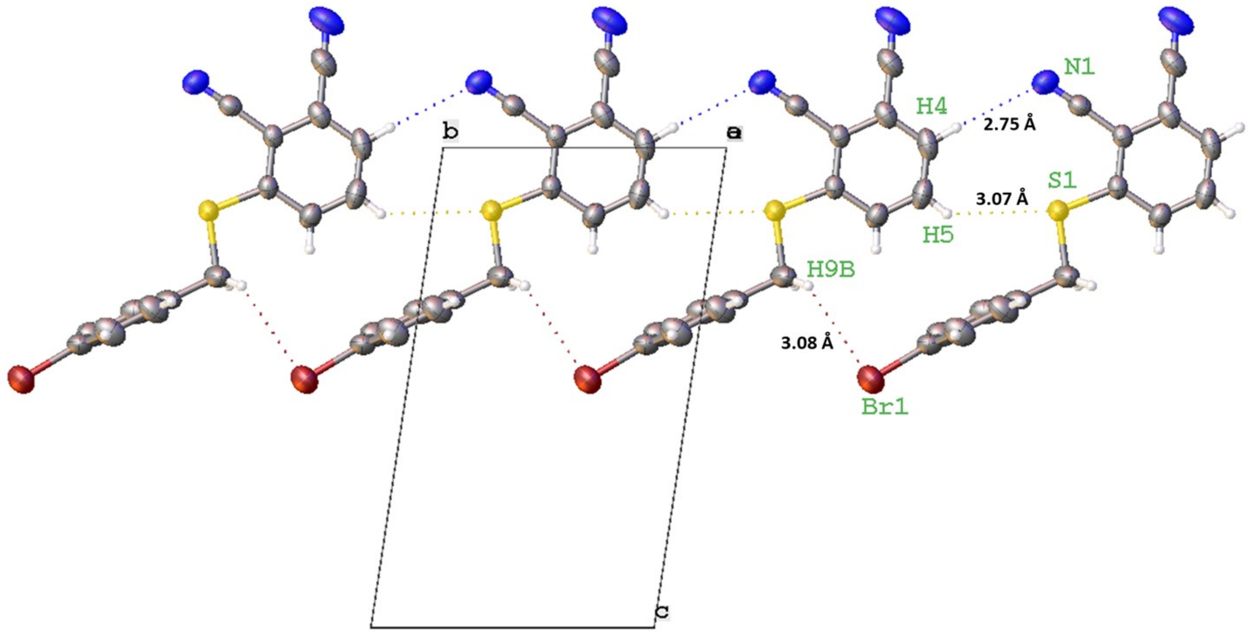

Fig. S10. Possible N···H, Br···H, and S···H interactions that show key and lock matching.

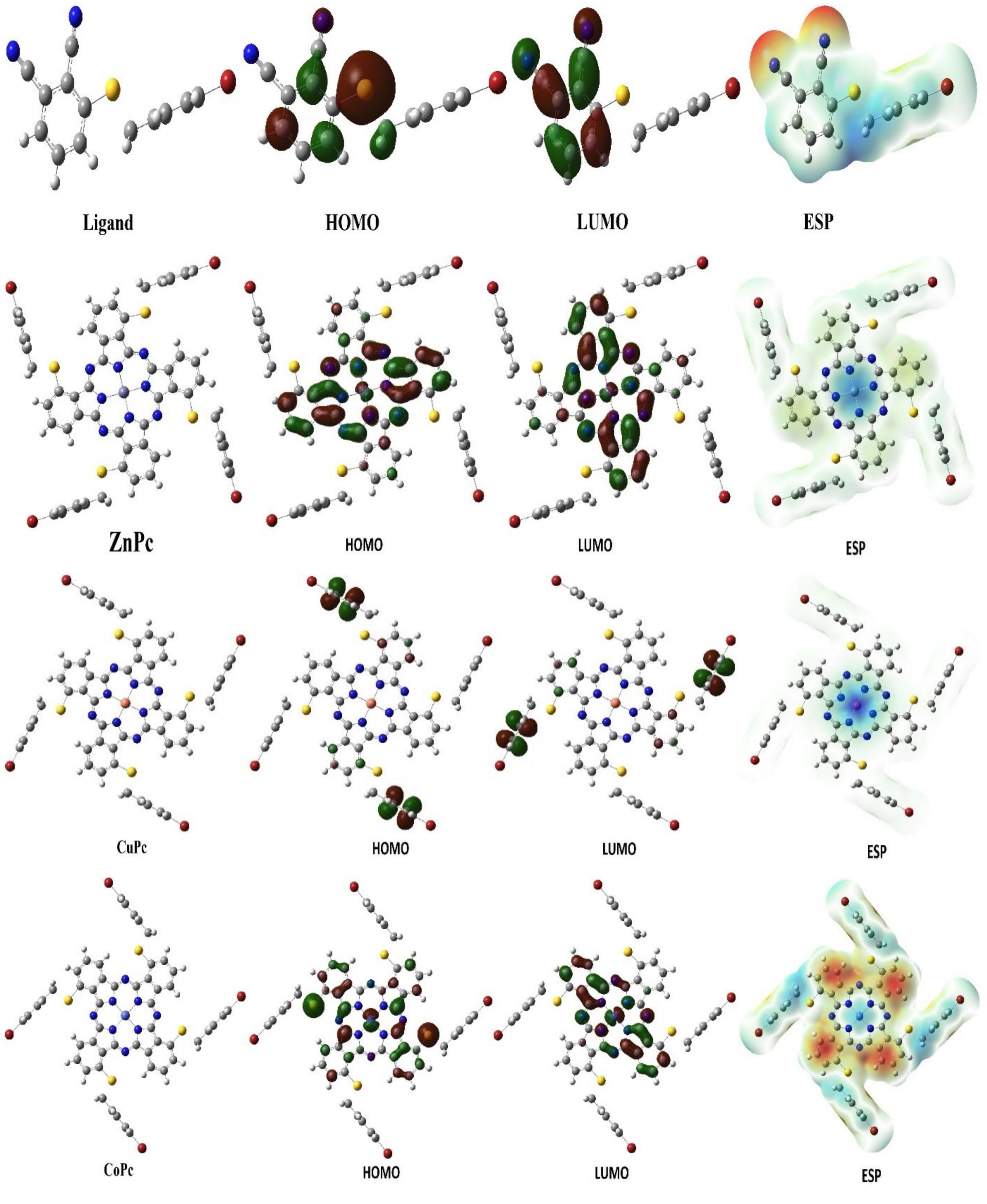

Fig. S11. Representations of optimized structure, HOMO, LUMO, and ESP of ligand **(1)** and its phthalocyanines **(2-4)**.

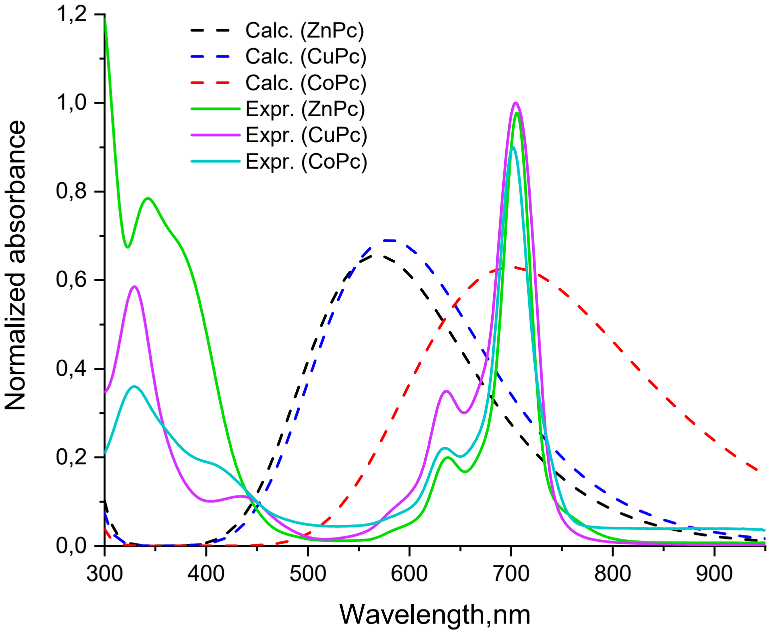

Fig. S12. Experimental and calculated UV-Vis spectra of ZnPc**(2)**, CuPc**(3)**, and CoPc**(4)**

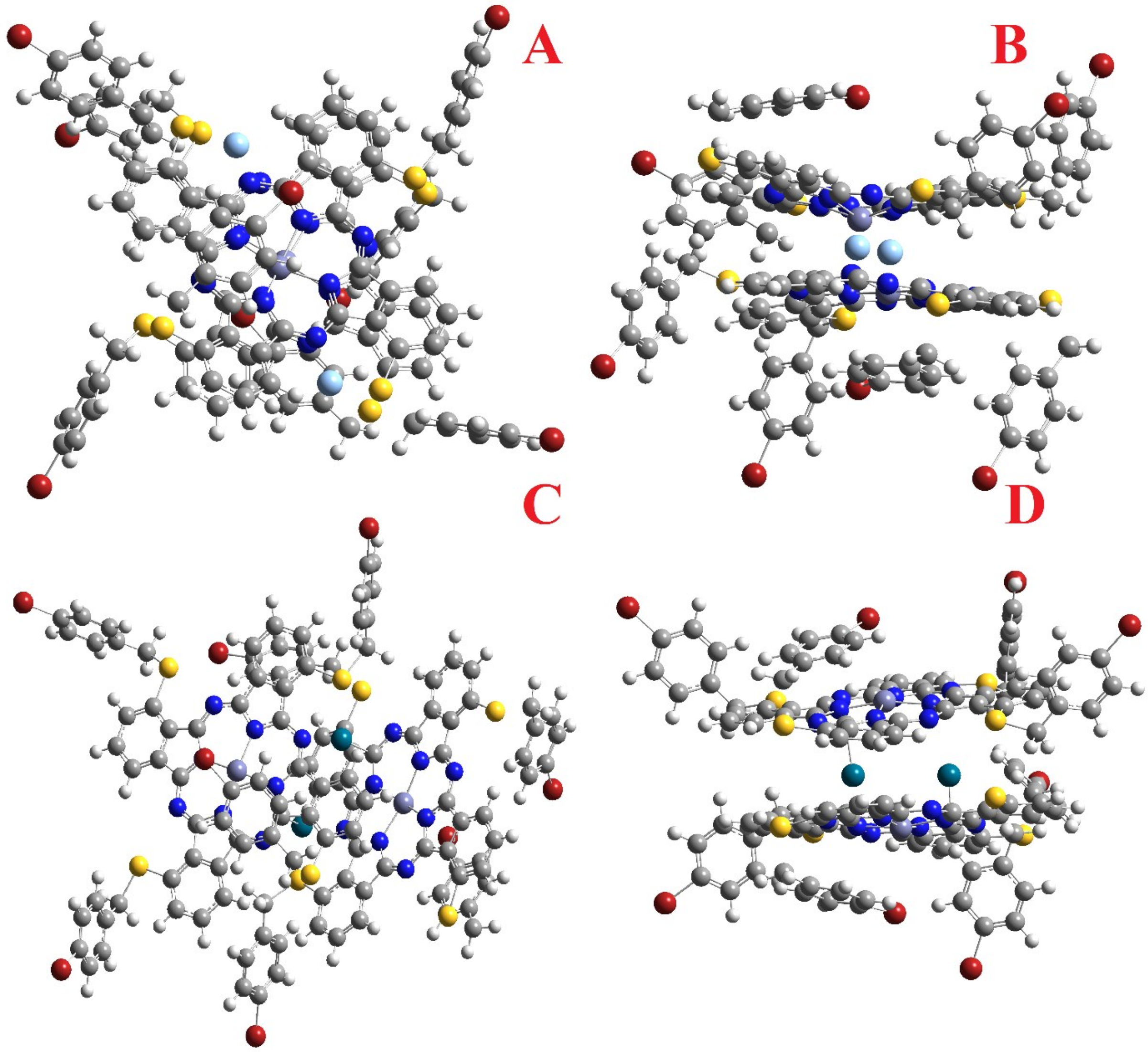

Fig. S13. Top and side views of the H- and J-aggregated forms of the ZnPc**(2)**.

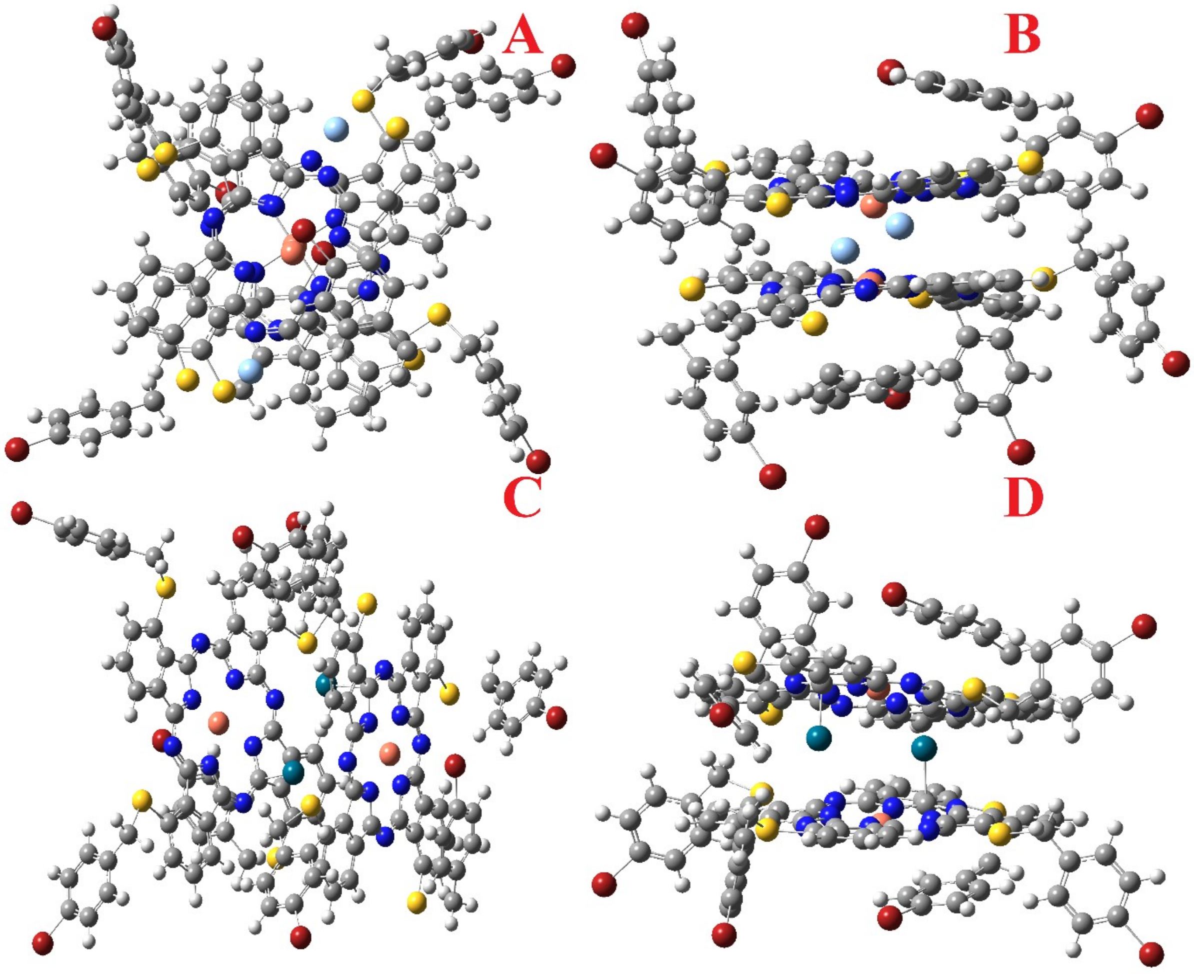

Fig. S14. Top and side views of the H- and J-aggregated forms of the CuPc**(3)**.

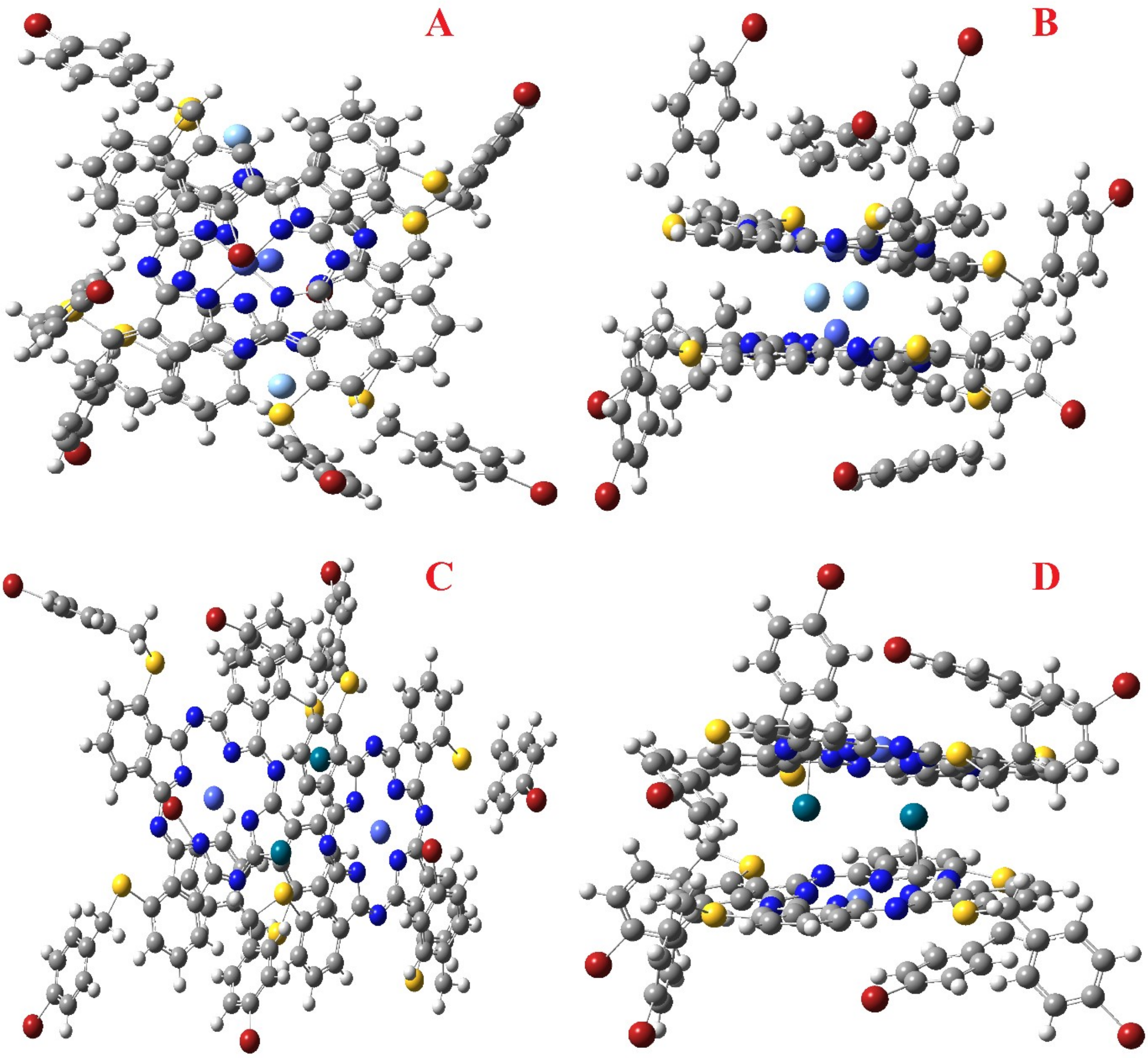

Fig. S15. Top and side views of the H- and J-aggregated forms of the CoPc**(4)**.

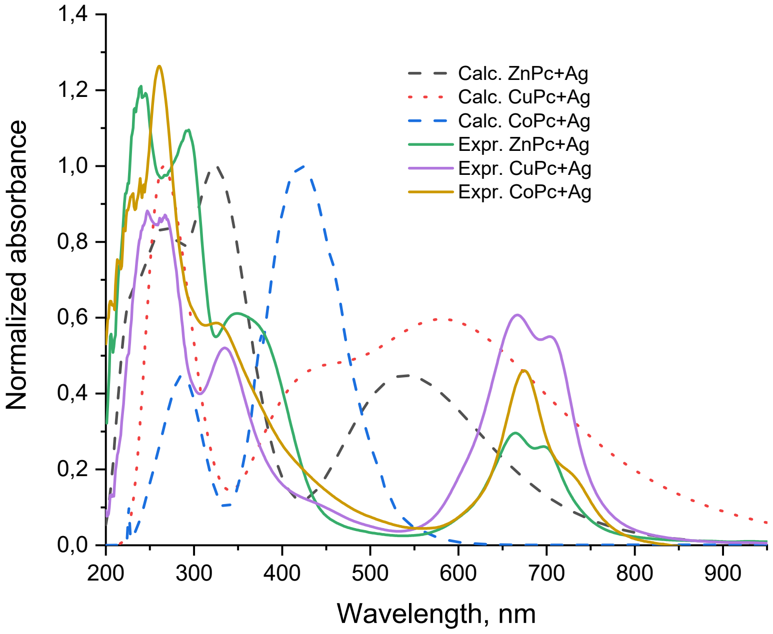

Fig. S16. Experimental and calculated UV-Vis spectra of ZnPc**(2)**, CuPc**(3)**, and CoPc**(4)** in the presence of Ag^+ ions induced to H-type aggregation formation.

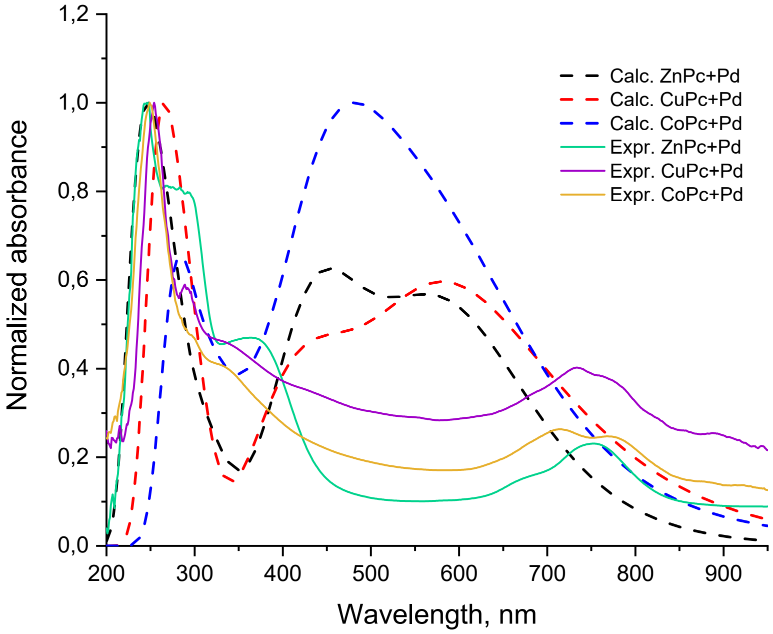

Fig. S17. Experimental and calculated UV-Vis spectra of ZnPc**(2)**, CuPc**(3)**, and CoPc**(4)** in the presence of Pd^{2+} ions induced J-type aggregation formation.

References

[1] S. Fery-Forgues, D. Lavabre, *J. Chem. Edu.*, 1999, 1260-1264.

[2] D. Maree, T. Nyokong, K. Suhling, D. Phillips, *J. Porphyrin Phthalocyanines*, 2002, **6**, 373-376.

[3] A. Ogunsipe, J.Y. Chen, T. Nyokong, *New J. Chem.*, 2004, **28**, 822-827.

[4] E. Kirbac, G.Y. Atmaca, A. Erdogmus, *Journal of Organometallic Chemistry*, 2014, **752**, 115-122.

[5] G. Yaşa, A. Erdoğmus, A.L. Uğur, M.K. Şener, U. Avciata, T. Nyokong, *J.Porphyr.Phthalocyanine*, 2012, **16**, 845-854.