

Electronic Supplementary Information

Chirality of self-assembled achiral porphyrins induced by chiral Zn(II) Schiff-base complexes and maintained after spontaneous dissociation of the template: a new case of chiral memory

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Experimental procedures

Materials and General Procedures. H₂T₄ and CuTPPS4 porphyrins were purchased from Mid-Century. Aqueous solutions were prepared dissolving the solid porphyrins in ultrapure water obtained from Elga Purelab Flex system by Veolia; then their concentration was checked by spectrophotometric methods using the followed molar extinction coefficients: $\epsilon_{423} = 224000 \text{ M}^{-1}\text{cm}^{-1}$ for H₂T₄ and $\epsilon_{412} = 416000 \text{ M}^{-1}\text{cm}^{-1}$ for CuTPPS4. Stock solutions of ZnL₂-S and ZnL₂-R complexes were prepared dissolving the solid in DMSO. For the kinetic experiment, in order to obtain a K values, a first order equation ($\ln_{\text{Abs}} = -kt + \ln_{\text{Abs}^0}$) was used.

Physical Measurements. Elemental analyses were performed on a Carlo Erba 1106 elemental analyzer. Solution ¹H NMR experiments were carried out on a Varian Unity Inova 500 MHz spectrometer. CD and UV measurements were carried out with a spectropolarimeter JASCO J-710 and a spectrophotometer JASCO V-530, respectively. Dynamic light scattering measurements were performed with Horiba LB-550 analyzer.

Synthesis of sodium 5-formyl-4-hydroxy-2-methoxybenzenesulfonate. The ligand was prepared as previously reported.¹ ¹H NMR (500 MHz, DMSO-d₆, TMS): $\delta = 3.81$ (s, 3H; OCH₃), 6.51 (s, 1H; ArH), 8.01 (s, 1H; ArH), 10.00 (s, 1H; CHO).

Synthesis of the Schiff base ligand HL-R. A solution of sodium 5-formyl-4-hydroxy-2-methoxybenzenesulfonate (0.250 g, 1.00 mmol) and (*R*)-(+)- α -methylbenzylamine (0.122 g, 1.00 mmol) in methanol (8.00 mL) was heated at reflux with stirring under a nitrogen atmosphere for 1 h. After cooling, the yellow product obtained was filtered, washed with methanol and dried under vacuum at 80 °C (yield: 40%). C₁₆H₁₆NNaO₅S (357.36): calcd C, 53.78; H, 4.51; N, 3.92; S, 8.97; found C, 53.65; H, 4.47; N, 3.88; S, 8.88; ¹H NMR (500 MHz, DMSO-d₆, TMS) δ : 1.54 (d, J = 6.5 Hz, 3H, CH₃), 3.74 (s, 3H, OCH₃), 4.68 (q, J = 6.5 Hz, 1H, CH-N), 6.29 (s, 1H, ArH); 7.26-7.38 (m, 5H, ArH); 7.69 (s, 1H, ArH), 8.54 (s, 1H, CH=N).

Synthesis of the Zn^{II} Schiff base complex ZnL₂-R. A solution of the Schiff base HL-R ligand (0.179 g; 0.500 mmol) and Zn(OAc)₂·2H₂O (0.055 g, 0.25 mmol) in DMSO (3.00 mL) was heated at reflux with stirring under a nitrogen atmosphere for 3 h. After cooling, the pale yellow product obtained was filtered, washed with diethyl ether and dried under vacuum at 120 °C (yield: 70%). C₃₂H₃₀N₂Na₂O₁₀S₂Zn (778.10): calcd C, 49.40; H, 3.89; N, 3.60; S, 8.24; found C, 49.24; H, 3.82; N, 3.55; S, 8.15; ¹H NMR (500 MHz, DMSO-d₆) δ : 1.35 (d, J = 7.0 Hz, 6H, CH₃), 3.73 (s, 6H, OCH₃), 4.52 (q, J = 7.0 Hz, 2H, CH-N), 6.08 (s, 2H, ArH), 7.13-7.36 (m, 10 H, ArH), 7.54 (s, 2H, ArH), 8.31 (s, 2H, CH=N).

References

- 1 D. F. Evans and D. A. Jakubovic, *Dalton Trans.*, 1988, DOI: 10.1039/DT9880002927, 2927-2933.

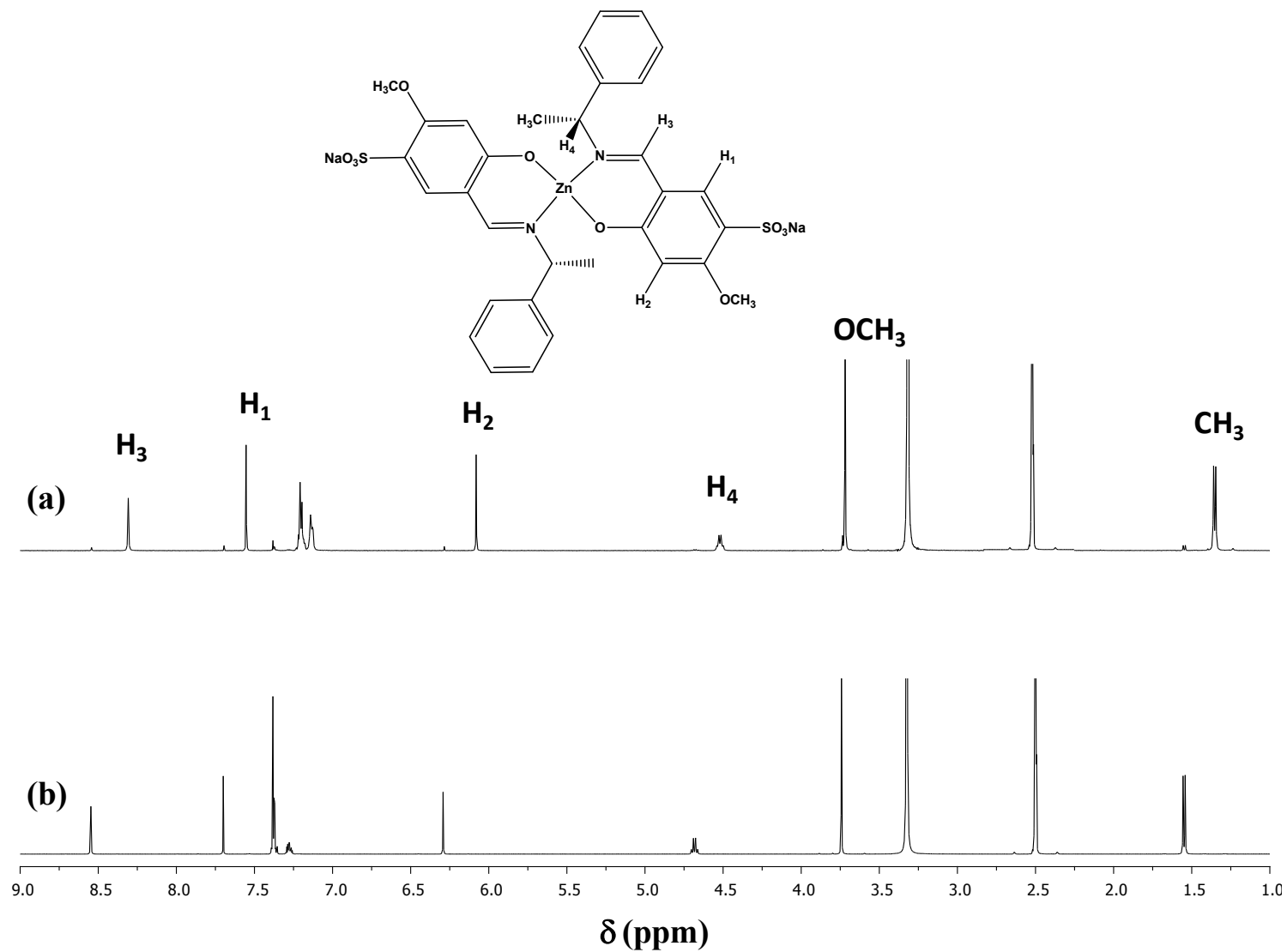


Figure S1. ¹H NMR spectra of ZnL₂-R (a) and HL-R (b) in DMSO-d₆ solution ($\approx 1 \times 10^{-3}$ M). Identical ¹H NMR spectra are recorded for the HL-S and ZnL₂-S enantiomers.

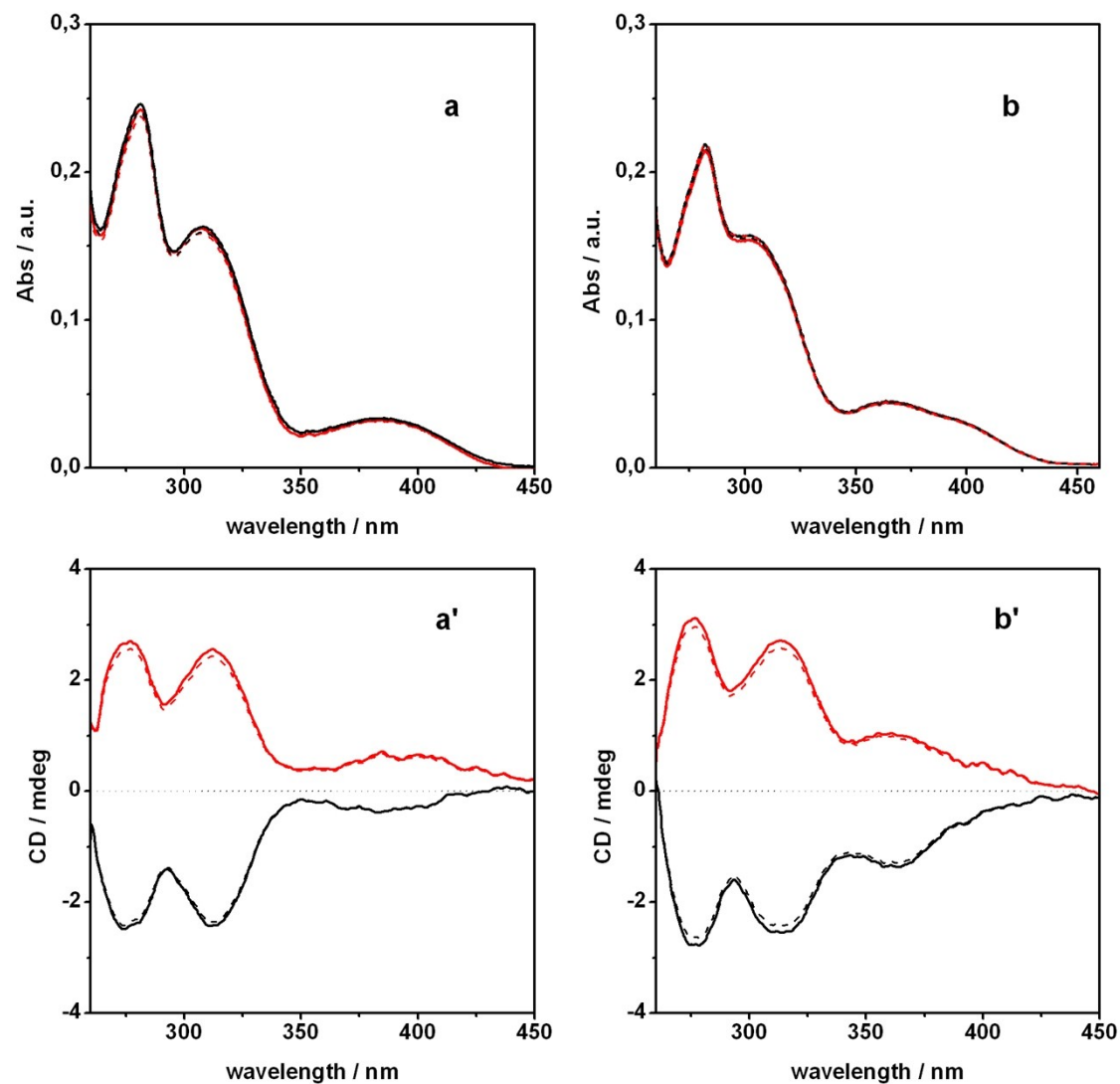


Figure S2. UV (a, b) and CD (a', b') spectra of HL-R (black curve), HL-S (red curve) 20 μM (left) and $\text{ZnL}_2\text{-R}$ (black curve), $\text{ZnL}_2\text{-S}$ (red curve) 10 μM (right) in DMSO solution, recorded as dissolved in solution ($t = 0$; solid curves) and after one year (dashed curves).

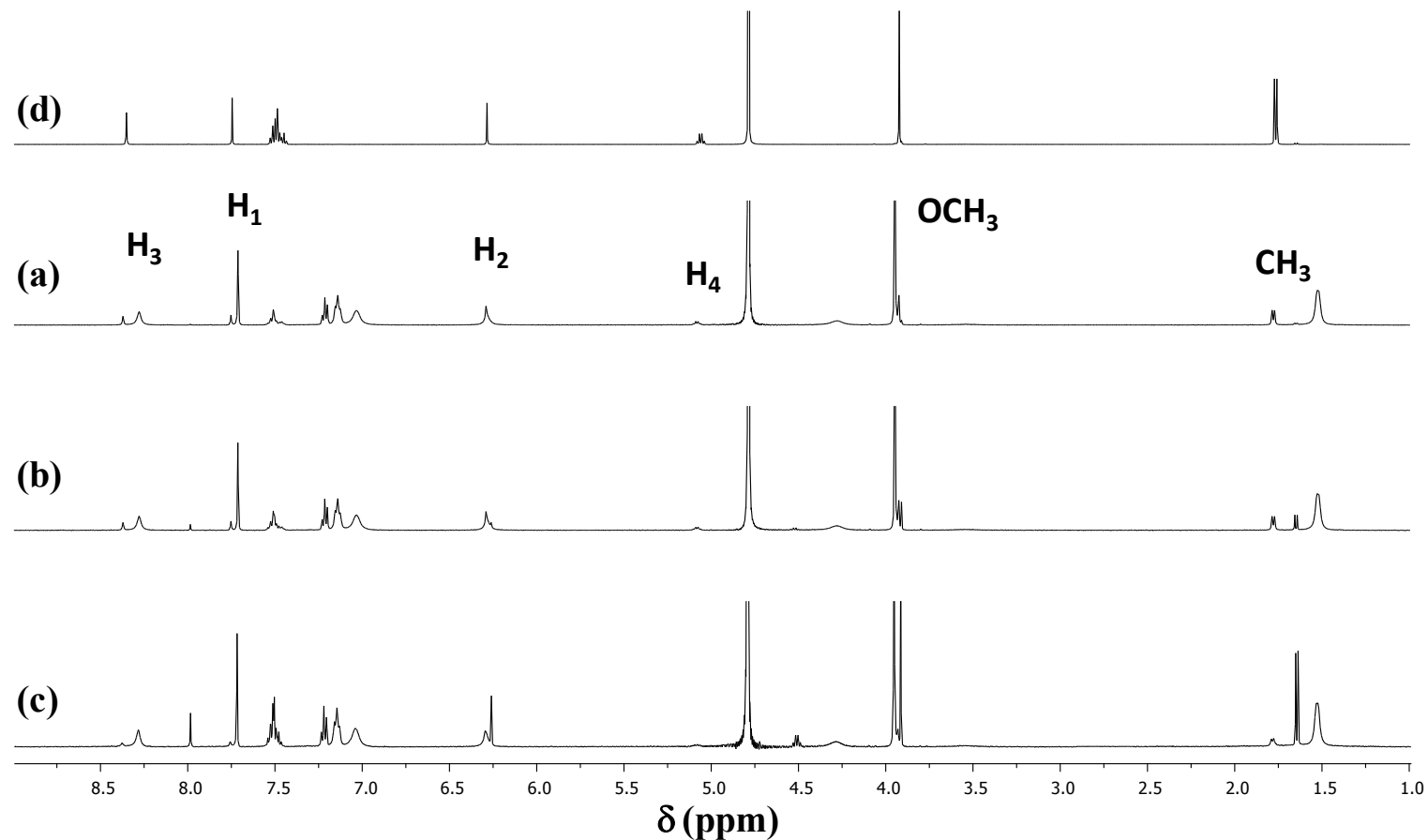


Figure S3. ^1H NMR spectra of $\text{ZnL}_2\text{-R}$ in D_2O ($\approx 1 \times 10^{-3}$ M): recorded as-dissolved in solution **(a)**; recorded after 40 min **(b)**; recorded after 24 hours **(c)**. The ^1H NMR spectrum of the HL-R ligand as dissolved in D_2O ($\approx 1 \times 10^{-3}$ M) is reported for comparison **(d)**. The ^1H NMR spectrum of the as-dissolved $\text{ZnL}_2\text{-R}$ indicates a partial demetallation of the complex with formation of the free Schiff-base ligand. The new signals in the spectra recorded after 40 min and 24 hours are related to the hydrolysis of the ligand with formation of the starting aldehyde and amine (see Figure S4). Moreover, the formation of a white solid precipitate, characterized as $\text{Zn}(\text{OH})_2$, is observed after 24 hour standing.

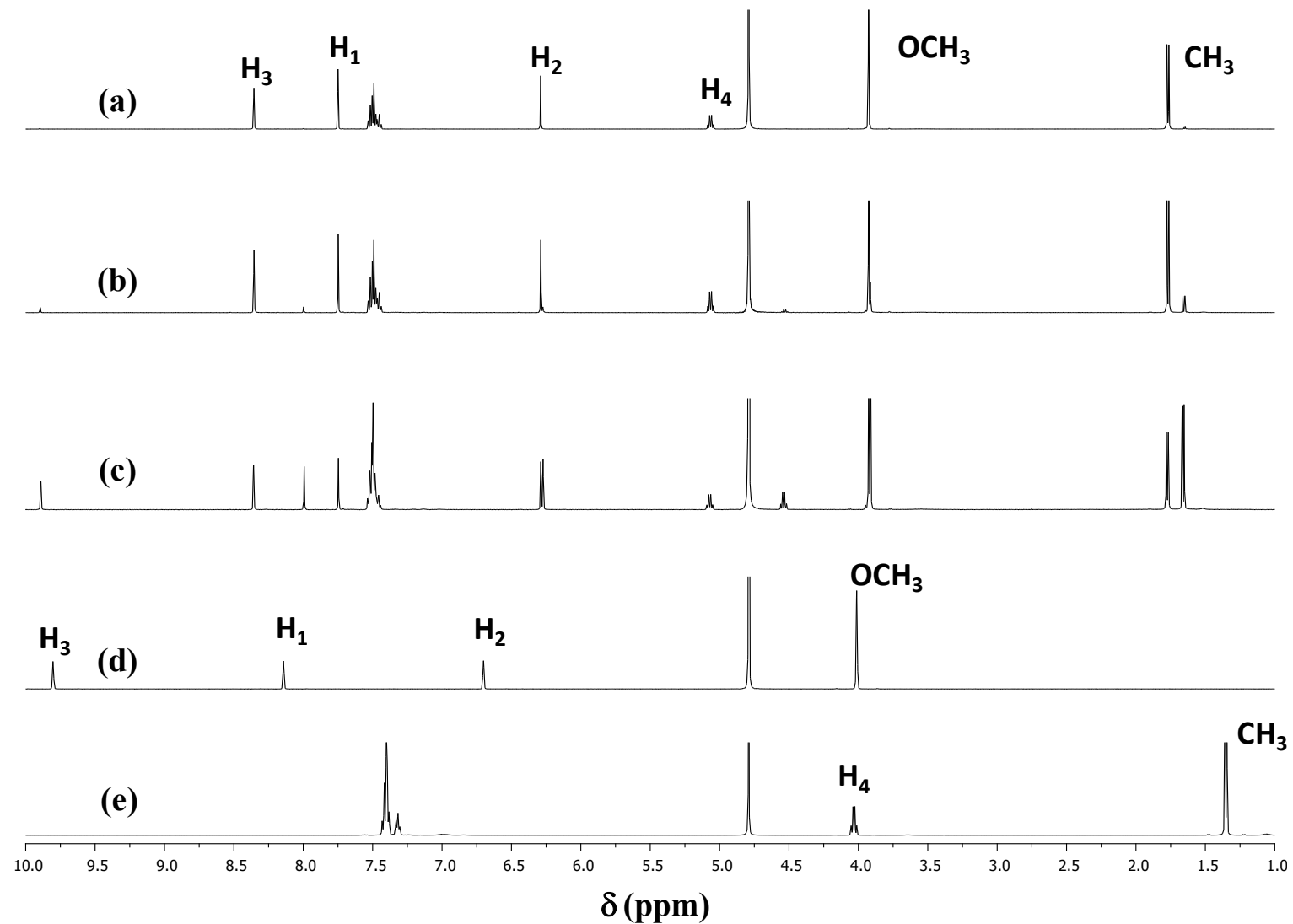


Figure S4. ^1H NMR spectra of HL-R in D_2O ($\approx 1 \times 10^{-3}$ M): recorded as-dissolved in solution (a); recorded after 40 min (b); recorded after 24 hours (c). The ^1H NMR spectra of the starting aldehyde (d) and amine (e) in D_2O are reported for comparison.

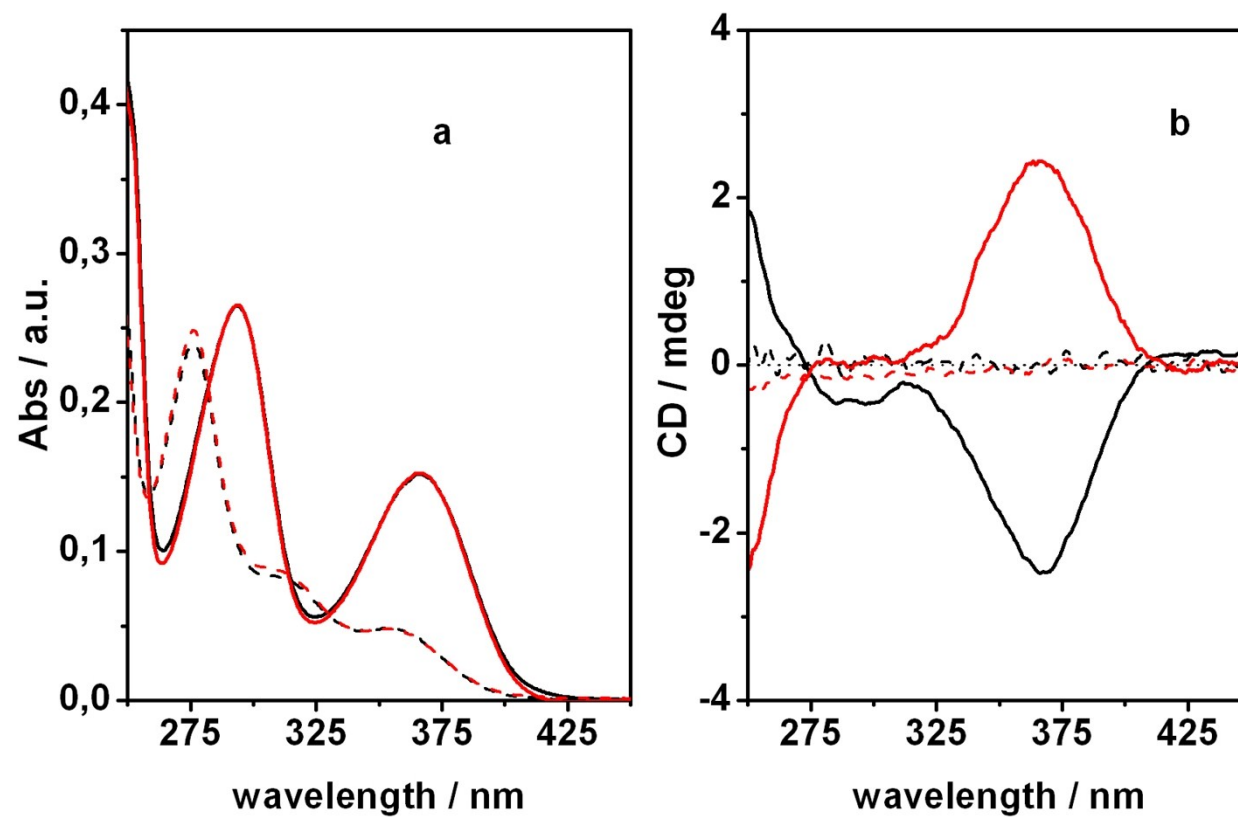


Figure S5. UV (a) and CD (b) spectra of HL-R (black curve), HL-S (red curve) 20 μ M in aqueous solution, recorded as dissolved in solution ($t = 0$ solid curves) and after 24 hours (dashed curves).

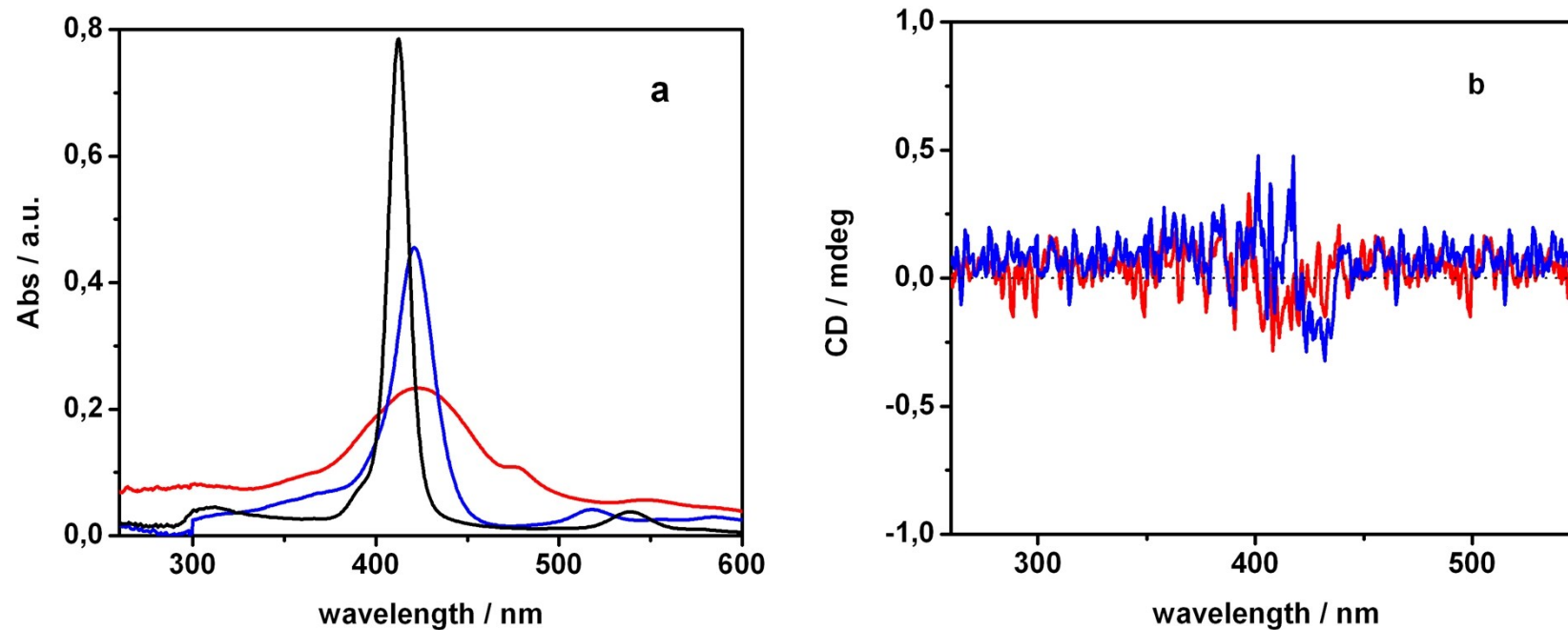


Figure S6. UV (a) spectra of an aqueous solution prepared mixing of a 2 μM solution of H₂T4 and a 2 μM solution of CuTPPS4 (red curve). UV spectra of independent solutions of H₂T4 2 μM (blue curve) and CuTPPS4 2 μM (black curve) are reported for comparison. CD (b) spectra of an aqueous solution 2 μM of H₂T4 and 2 μM of CuTPPS4 (red curve) and after the further addition of an equimolar concentration of porphyrins (blue curve).

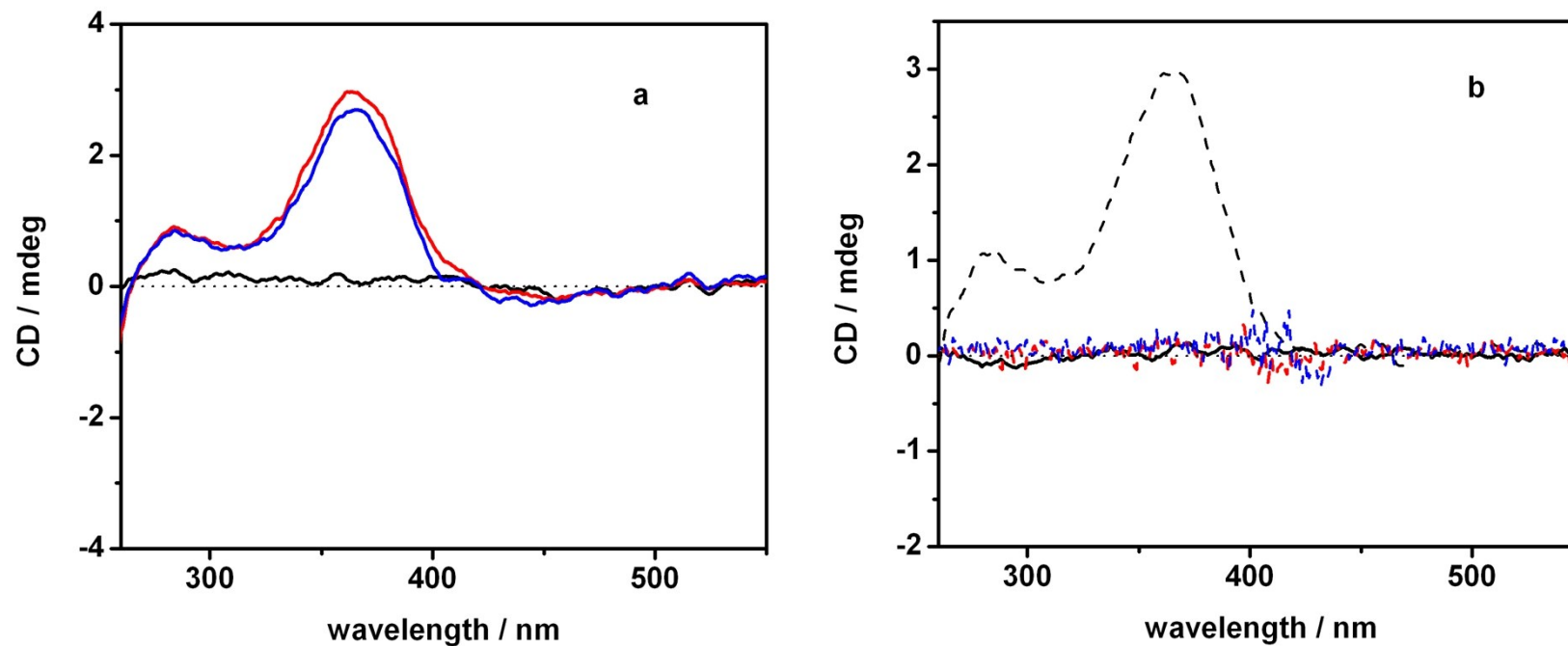


Figure S7. (a) CD spectra of an aqueous solution 4 μM of $\text{H}_2\text{T4}$ and 4 μM of CuTPPS4 before (black curve) and after the addition of $\text{ZnL}_2\text{-S}$ 10 μM (red curve) and after further addition of an equimolar concentration of porphyrins (blue curve). (b) CD spectra of $\text{ZnL}_2\text{-S}$ 10 μM as dissolved in aqueous solutions (dashed black curve) and after 24 h (solid black curve). CD spectra of this solution after the addition of $\text{H}_2\text{T4}$ (2 μM) and CuTPPS4 (2 μM) (red curve) and after the further addition of an equimolar concentration of porphyrins (blue curve).

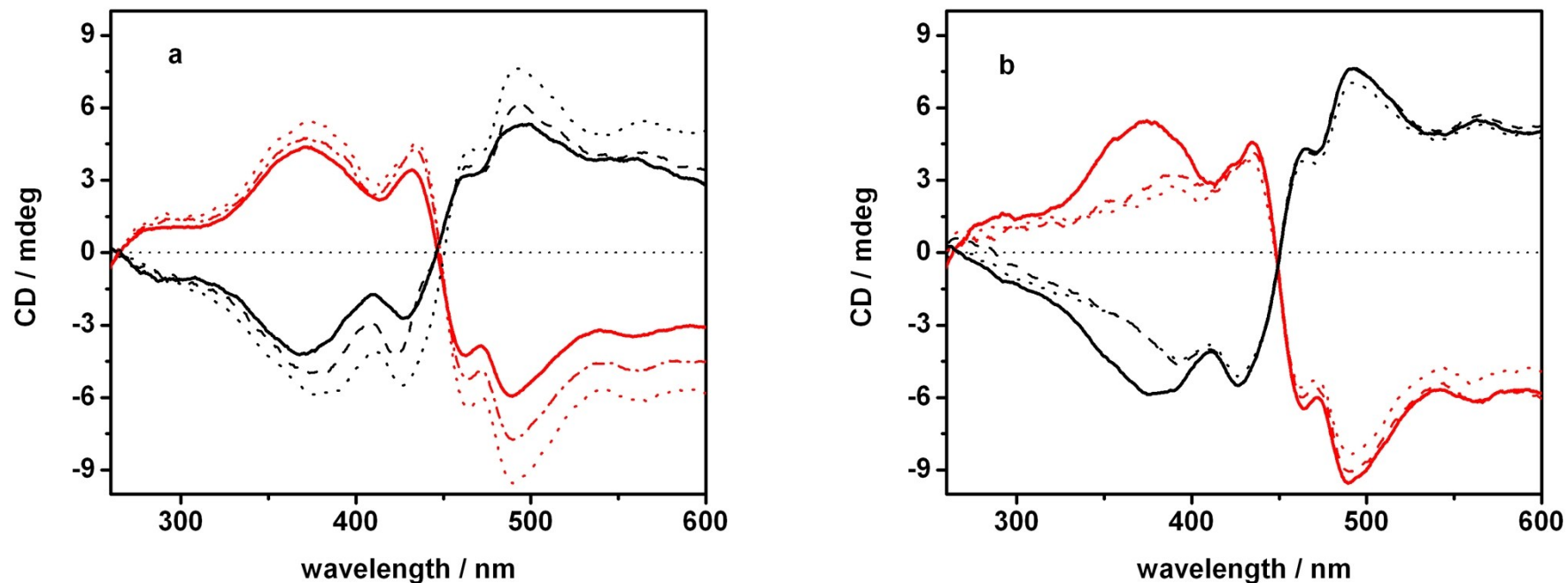


Figure S8. (a) CD spectra of aqueous solution of porphyrin hetero-aggregates (4 μM of $\text{H}_2\text{T4}$ and 4 μM of CuTPPS4) in the presence of ZnL_2 (10 μM) -*R* (black curves) and -*S* (red curves) enantiomer, before (solid curves) and after further addition of other $\text{H}_2\text{T4}$ and of CuTPPS4 (2 μM dashed curves and 4 μM dotted curves). The total concentration of each porphyrin is 10 μM . (b) CD spectra of the latter solution incubated for 24h (dashed curves) and after one month (dotted curves).

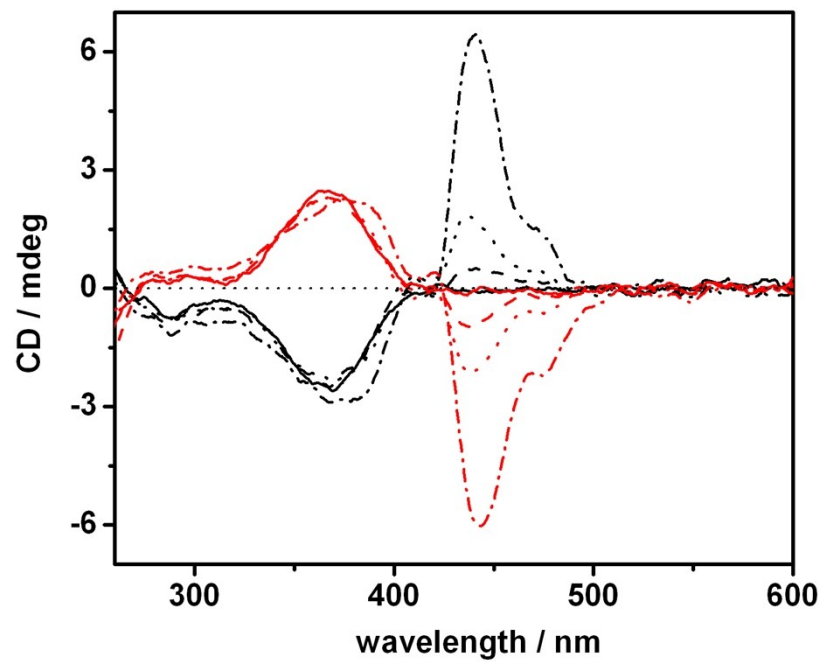


Figure S9. (a) CD spectra of an aqueous solution of porphyrin hetero-aggregates (4 μM of H_2T_4 and 4 μM of CuTPPS) in the presence of $\text{HL}_2\text{-R}$ (black curves) and $-S$ (red curves) enantiomer (20 μM), before (solid curves) and after the further addition of other H_2T_4 and of CuTPPS4 (2 μM dashed curves and 4 μM dotted curves). The total concentration of each porphyrin is 10 μM .

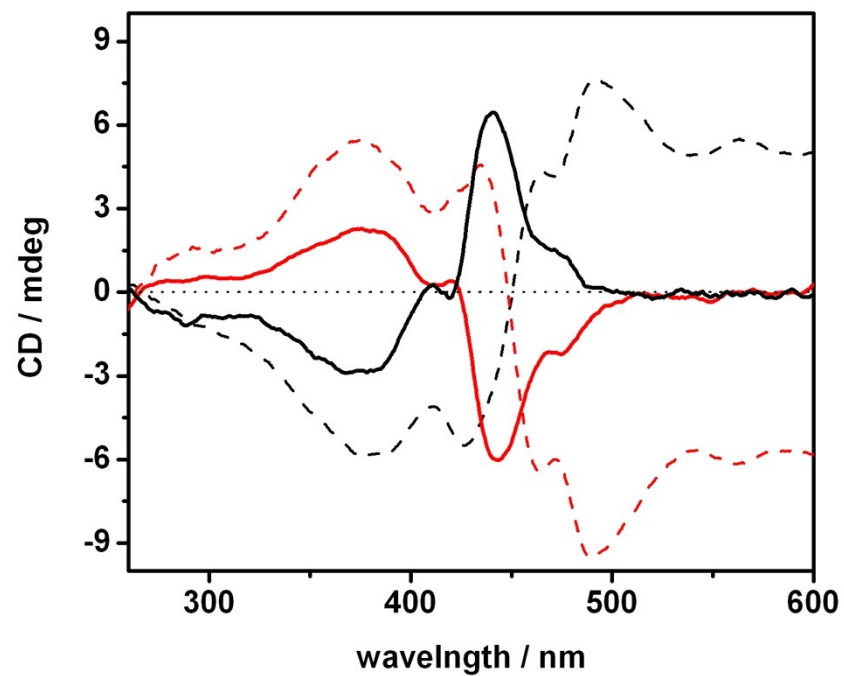


Figure S10. Comparison between CD spectra of an aqueous solution of porphyrin hetero-aggregates ($10 \mu\text{M}$ of $\text{H}_2\text{T4}$ and $10\mu\text{M}$ of CuTPPS4) in the presence of $\text{HL}_2\text{-R}$ (black curve) and -S (red curve) enantiomer ($20 \mu\text{M}$); and in the presence of $\text{ZnL}_2\text{-R}$ (dashed black curve) and -S (dashed red curve) enantiomer ($10 \mu\text{M}$).

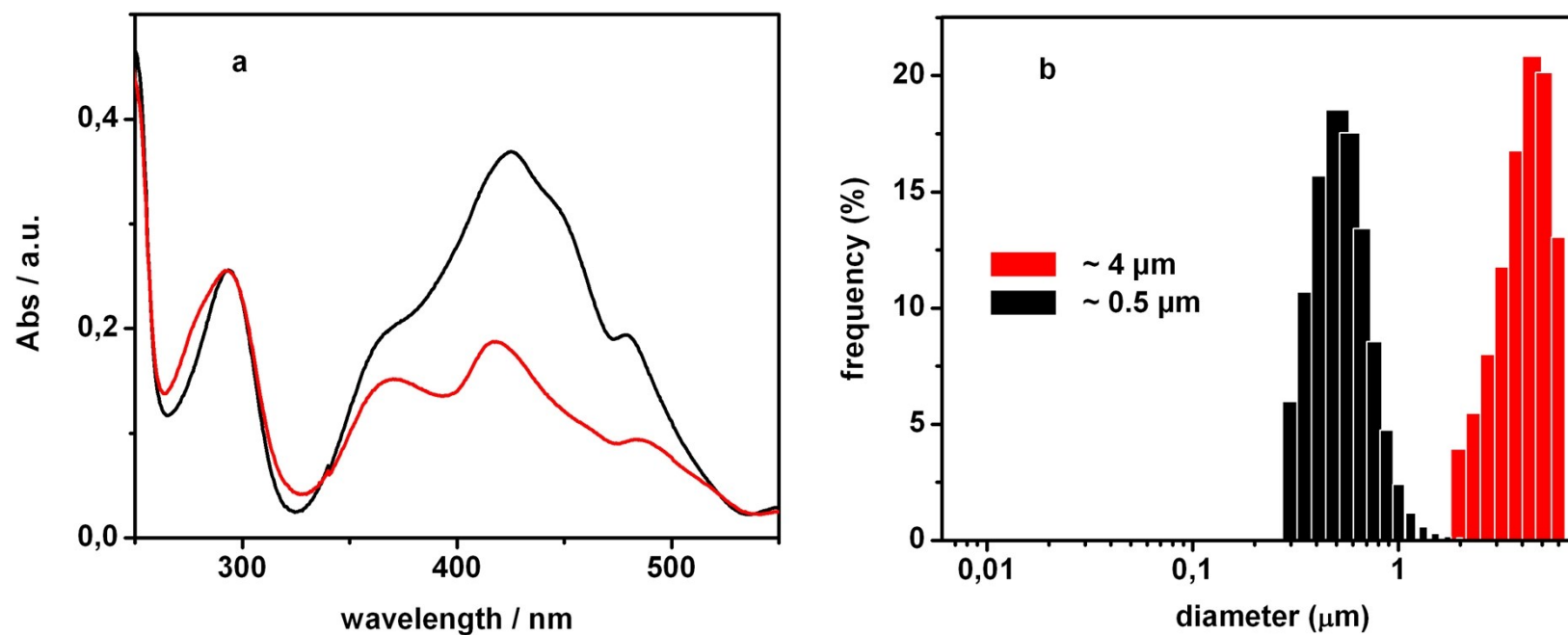


Figure S11. UV spectra (a) and DLS analysis (b) of porphyrin hetero-aggregates (10 μM of H_2T_4 and 10 μM of CuTPPS) templated onto ZnL2-S 10 μM (black curve and bars) and onto HL-S 20 μM (red curve and bars).

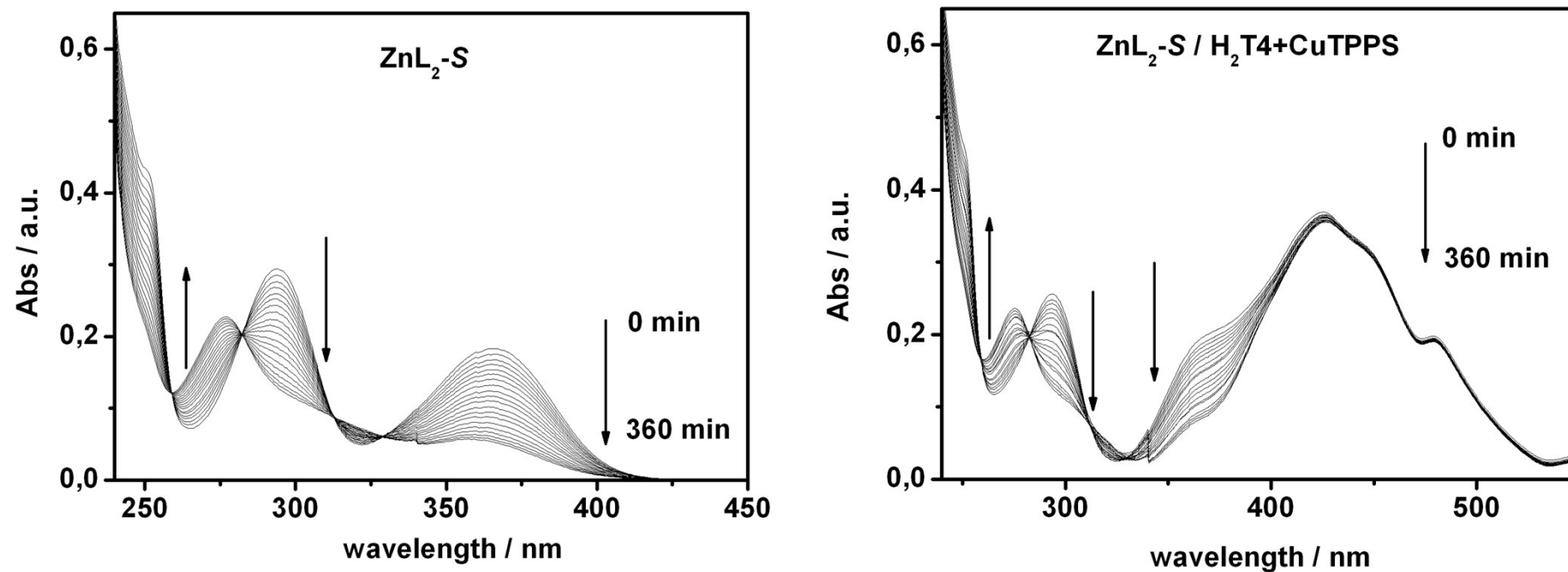


Figure S12. (left) UV spectra of an aqueous solution of ZnL₂-S 10 μ M from 0 to 360 minutes. (right) UV spectra of an aqueous solution of ZnL₂-S 10 μ M in the presence of porphyrin hetero-aggregates (10 μ M of H₂T₄ and 10 μ M of CuTPPS) from 0 to 360 minutes.