Supporting Information for

Photophysical and Computational Insights into Ag(I) Complexation of Porphyrinic Covalent Cages Equipped with Triazoles Incorporating Linkers

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Additional spectroscopic data:

- **2H-S-2H**

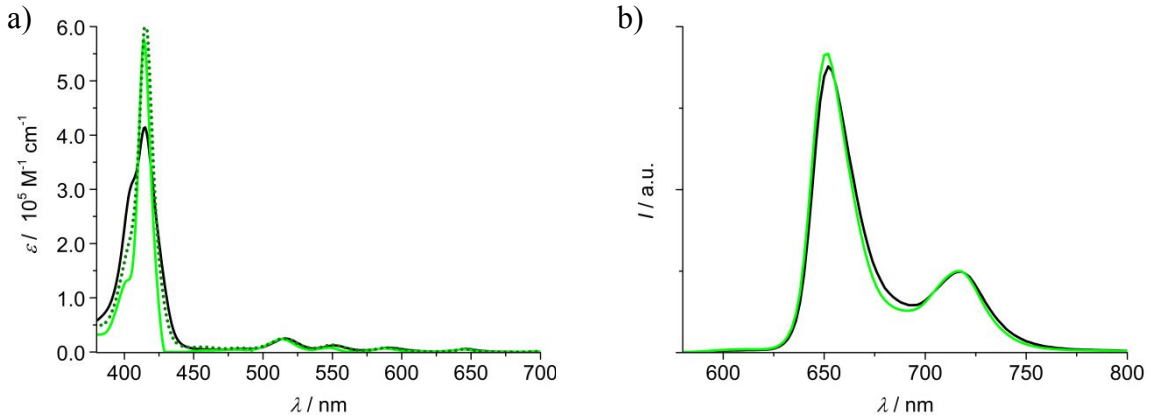

Figure S1. a) Experimental absorption spectrum of **2H-S-2H** (black, imposed in the fitting) and fitted absorption spectrum of the complex [(**2H-S-2H**)Ag_4]$^{4+}$ (green) in DCM/MeOH (9:1). The experimental absorption spectrum registered at the end of the titration is also reported for comparison purposes (olive dotted). b) Fitted emission spectra of **2H-S-2H** (black) and [(**2H-S-2H**)Ag_4]$^{4+}$ (green). The fittings were performed with the software Reactlab Equilibria by using a 1:4 (cage:Ag^+) binding model and Ag^+ as a non-absorbing and non-emissive species.

- **2H-L-2H**

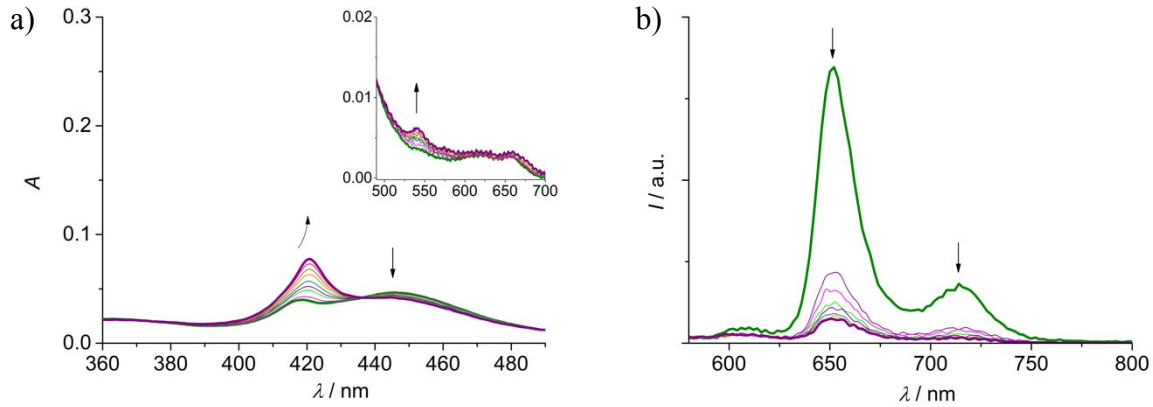

Figure S2. Absorption (a) and uncorrected emission (b) spectra (λ_{exc} = 434 nm, isosbestic point) of DCM/MeOH (9:1) solutions containing **2H-L-2H** (5.6×10^{-7} M) and increasing amounts of Ag(OTf) (30-400 equivalents). Inset of (a): amplification of the Q-bands region (490-700 nm). In (b) the y-axis scale is amplified by a factor 3 with respect to the scale of Figure 3b.

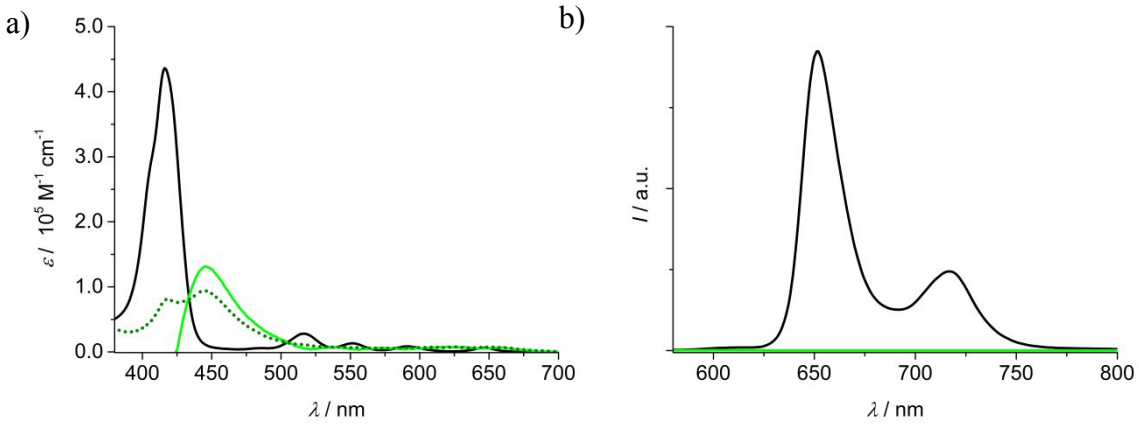

Figure S3. a) Experimental absorption spectrum of **2H-L-2H** (black, imposed in the fitting) and fitted absorption spectrum of the complex [(**2H-L-2H**)Ag_2]$^{4+}$ (green) in DCM/MeOH (9:1). The experimental absorption spectrum registered at the end of the first step (30 equiv.) of the titration is also reported for comparison purposes (olive dotted). b) Fitted emission spectra of **2H-L-2H** (black) and [(**2H-L-2H**)Ag_2]$^{4+}$ (green). The fitting was performed with the software Reactlab Equilibria by using a 1:2 (cage:Ag^+) binding model and Ag^+ as a non-absorbing and non-emissive species.

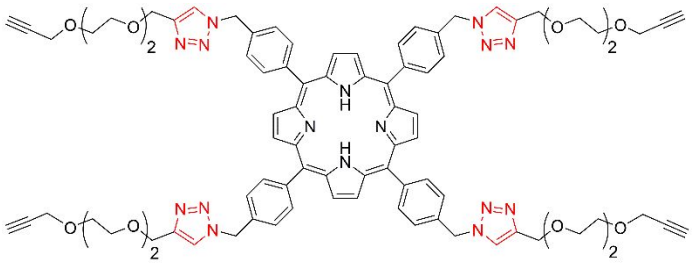

Chart S1. Structure of model **2H-alkyne**.

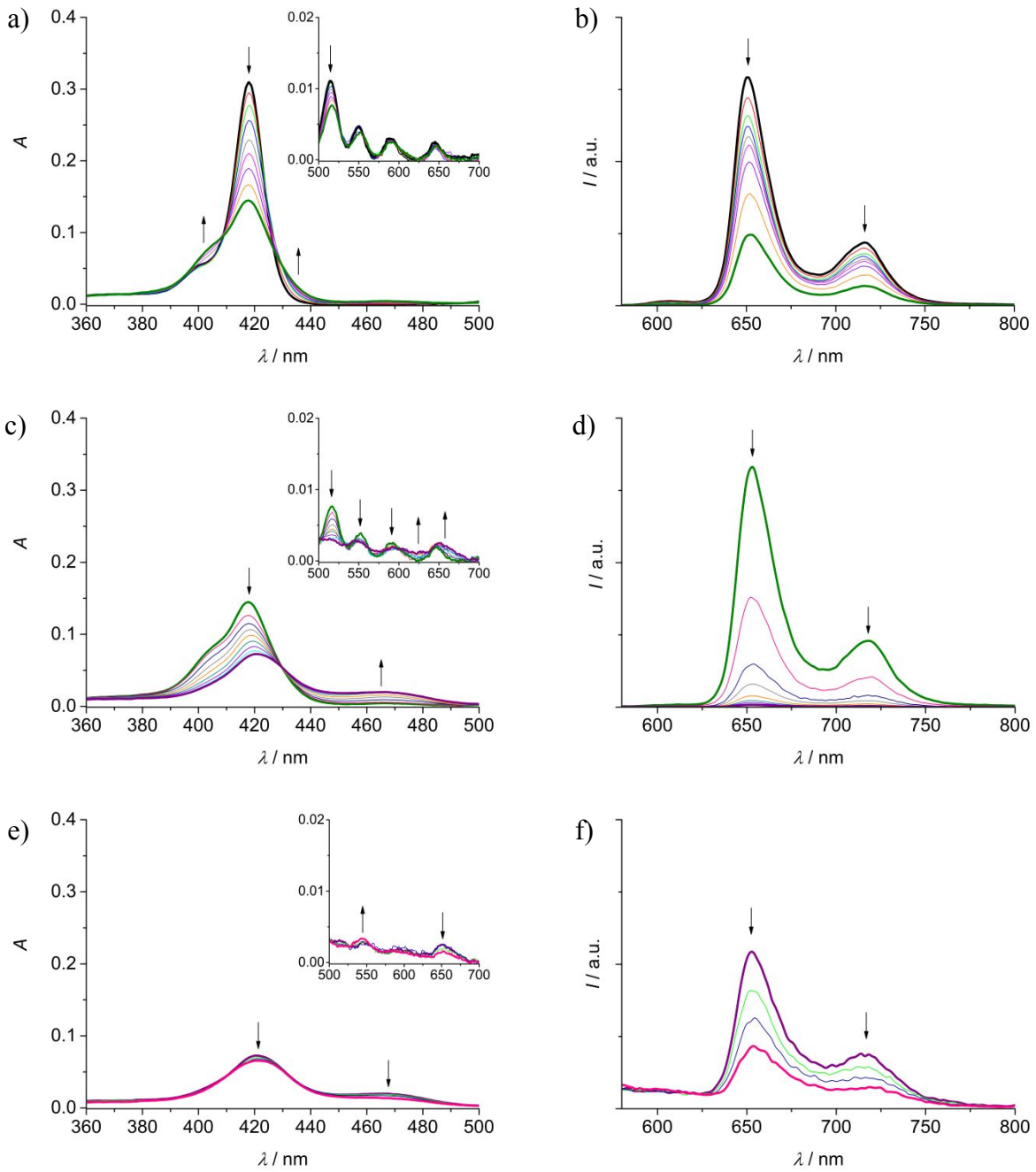

Figure S4. Absorption and uncorrected emission spectra of DCM/MeOH (9:1) solutions containing **2H-alkyne** (1.2×10^{-6} M) and increasing amounts of Ag(OTf): (a-b) 0-9 equivalents, λ_{exc} = 428 nm, isosbestic point; (c-d) 9-30 equivalents, λ_{exc} = 430 nm, isosbestic point; (e-f) 30-250 equivalents, λ_{exc} = 430 nm, isoabsorbing point. In (f) the y-axis scale is amplified by a factor 15 with respect to the scale of (d). Insets of (a,c,e): amplification of the Q-bands region (500-700 nm).

- **Zn-S-2H**

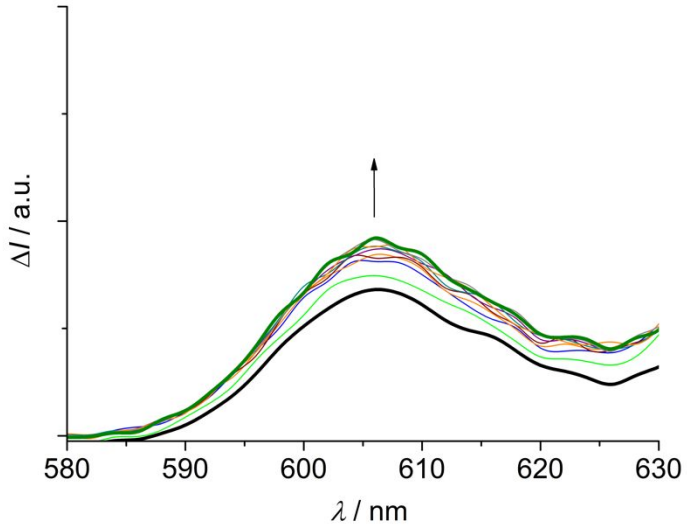

Figure S5. Emission spectra (λ_{exc} = 415.5 nm) of DCM/MeOH (9:1) solutions containing **Zn-S-2H** (5.5×10^{-7} M) and increasing amounts of AgOTf (0-40 equivalents). The spectra are expressed as differential intensity, calculated by subtracting, from the spectrum of the cage at each point of the titration, an emission spectrum of **2H-S-2H** normalized at 712 nm.

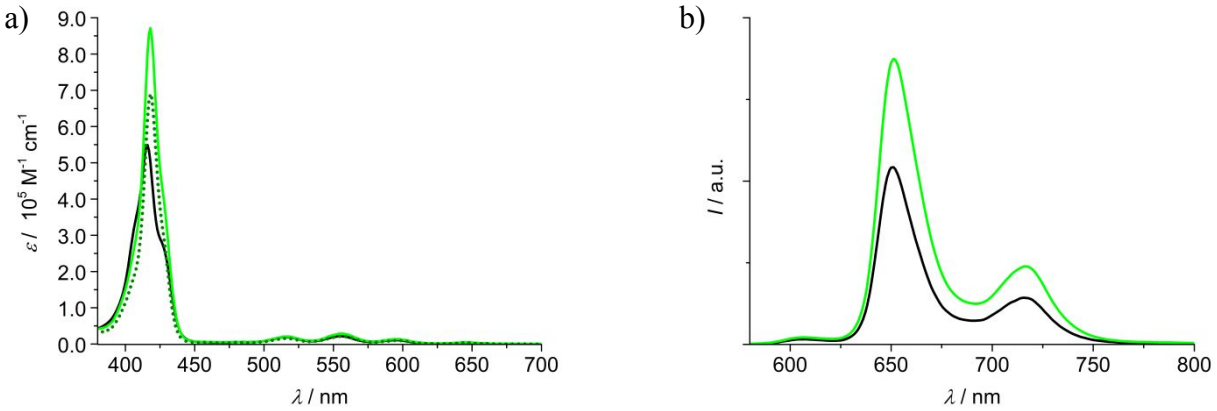

Figure S6. a) Experimental absorption spectrum of **Zn-S-2H** (black, imposed in the fitting) and fitted absorption spectrum of the complex [(**Zn-S-2H**)Ag_4]$^{4+}$ (green) in DCM/MeOH (9:1). The experimental absorption spectrum registered at the end of the titration is also reported for comparison purposes (olive dotted). b) Fitted emission spectra of **Zn-S-2H** (black) and [(**Zn-S-2H**)Ag_4]$^{4+}$ (green). The fittings were performed with the software Reactlab Equilibria by using a 1:4 (cage:Ag^+) binding model and Ag^+ as a non-absorbing and non-emissive species.

- **Zn-L-2H**

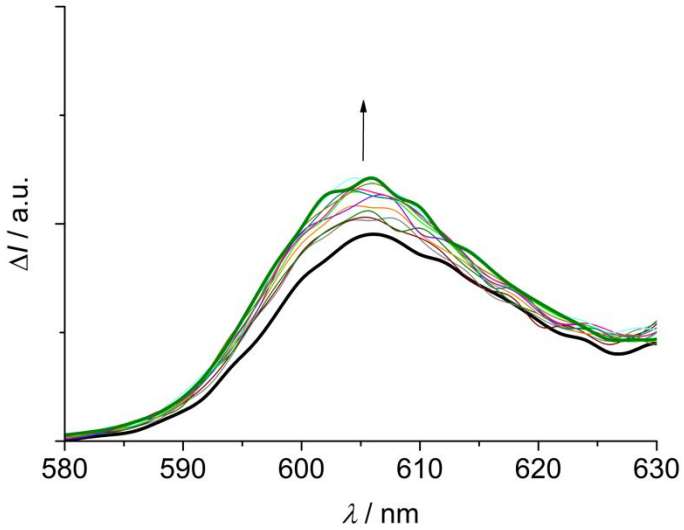

Figure S7. Emission spectra (λ_{exc} = 421 nm) of DCM/MeOH (9:1) solutions containing **Zn-L-2H** (6.5×10^{-7} M) and increasing amounts of AgOTf (0-40 equivalents). The spectra are expressed as differential intensity, calculated by subtracting, from the spectrum of the cage at each point of the titration, an emission spectrum of **2H-L-2H** normalized at 712 nm.

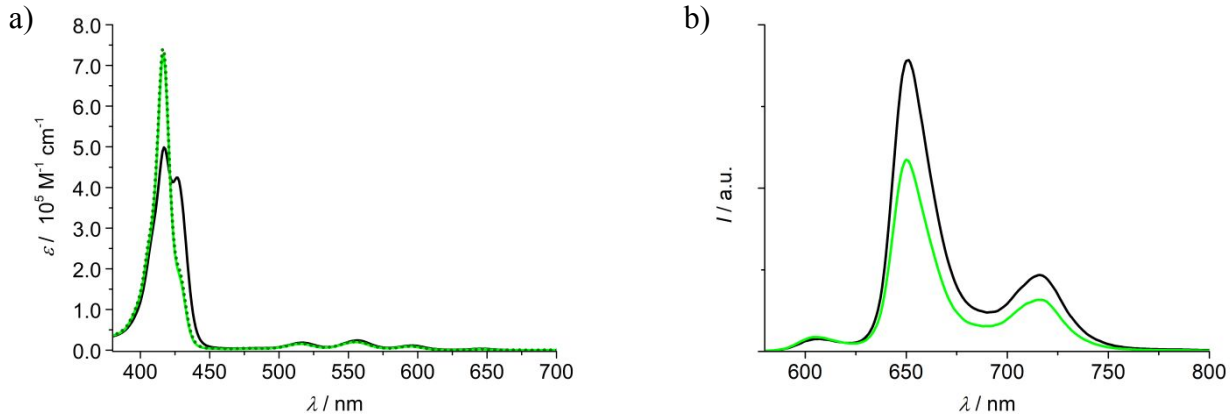

Figure S8. a) Experimental absorption spectrum of **Zn-L-2H** (black, imposed in the fitting) and fitted absorption spectrum of the complex [(**Zn-L-2H**)Ag_4]$^{4+}$ (green) in DCM/MeOH (9:1). The experimental absorption spectrum registered at the end of the titration is also reported for comparison purposes (olive dotted). b) Fitted emission spectra of **Zn-L-2H** (black) and [(**Zn-L-2H**)Ag_4]$^{4+}$ (green). The fittings were performed with the software Reactlab Equilibria by using a 1:4 (cage:Ag^+) binding model and Ag^+ as a non-absorbing and non-emissive species.

Additional computational data:

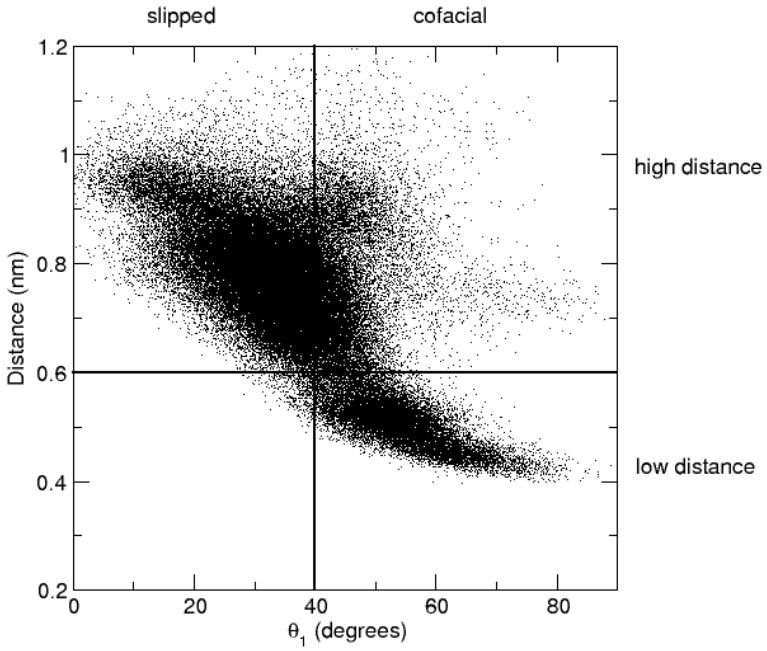

Figure S9. Bidimensional distribution of the distance between the centers of mass of the two porphyrin rings and θ1 in the MD simulation of **2H-S-2H**.

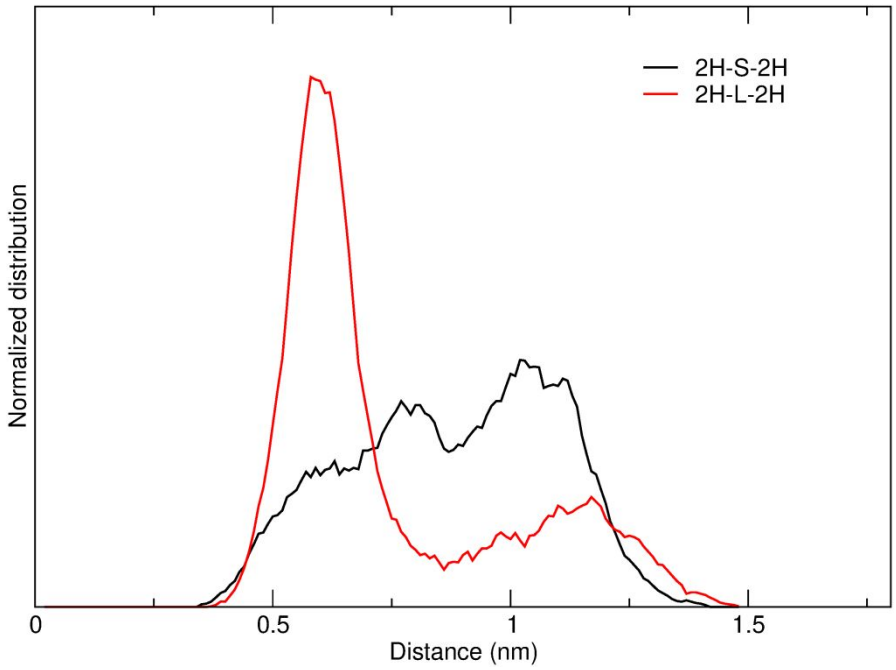

Figure S10. Normalized distribution of the distance between the two carbons connecting the phenyl and triazole rings of each linker in the MD simulations of **2H-S-2H** (black) and **2H-L-2H** (red). The curves are obtained by averaging the distributions of the distance obtained for each of the four linkers of the two cages.