Supporting Information

for

Role of Cobalt(III) Cationic Complexes in the Self-assembling Process of a Water Soluble Porphyrin

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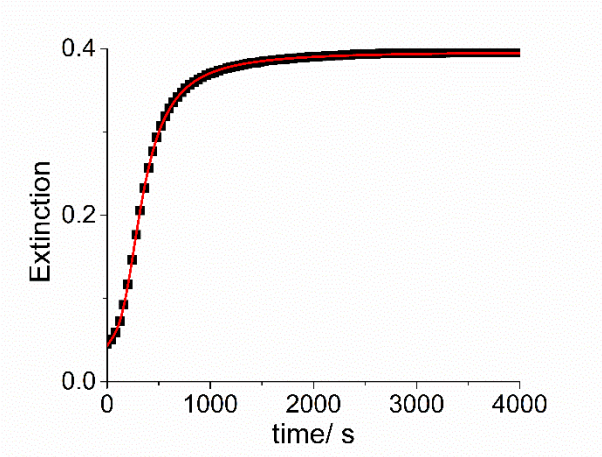


Figure S1. Typical extinction time trace for the formation of J-aggregates of H_2TPPS_4 at pH = 2 upon addition of $[Co(phen)_3]^{3+}$ (Experimental conditions: $[H_2TPPS_4]$ = 3 μM; [HCl] = 0.01 M, $[Co(phen)_3^{3+}]$ = 200 μM, T = 298 K). The solid line represents the best-fitted curve to the experimental data according eq. 1.

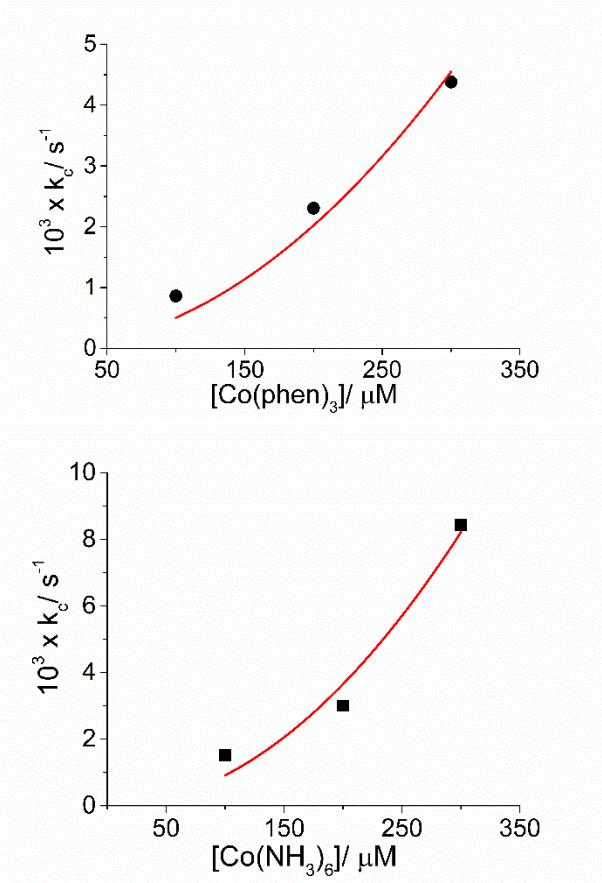
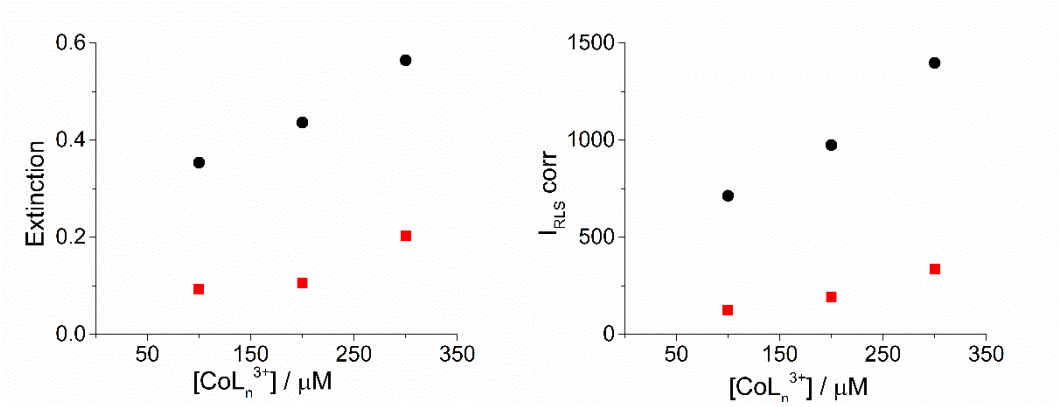
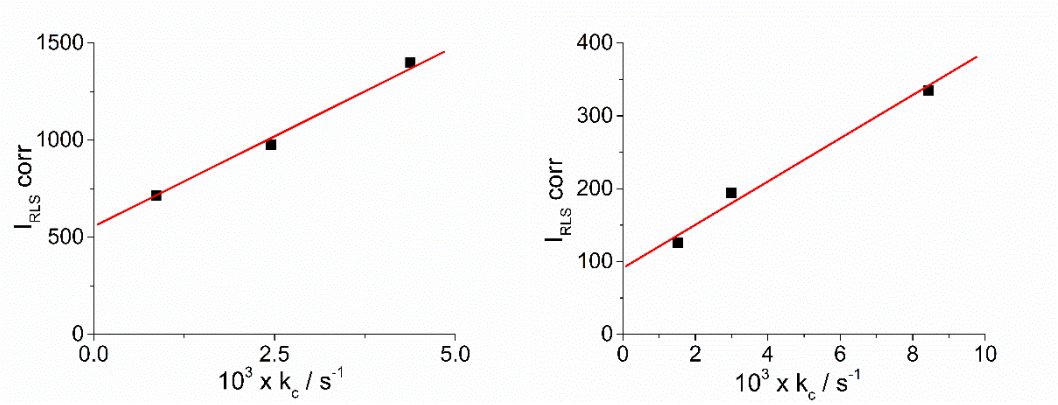


Figure S2. Plot of the rate constants k_c (s^{-1}) for the catalyzed growth of J-aggregates of H_2TPPS_4 at pH = 2 upon addition of $[Co(phen)_3]^{3+}$ (circles) and $[Co(NH_3)_6]^{3+}$ (solid squares). (Experimental conditions: $[H_2TPPS_4]$ = 3 µM; [HCl] = 0.01 M, T = 298 K). The solid lines represent the non-linear best-fits to the law $kc = kc' \times [CoL_n^{3+}]^2$ ($[Co(NH_3)_6]^{3+}$: $k_c'' = (9.13 \pm 0.66) \times 10^{-8}$ $s^{-1}\mu M^{-2}$, $R^2 = 0.9681$; $[Co(phen)_3]^{3+}$: $k_c'' = (5.05 \pm 0.35) \times 10^{-8}$ $s^{-1}\mu M^{-2}$, $R^2 = 0.9622$).



(a) **(b)**

Figure S3. Plot of (a) the extinction values and (b) the RLS intensity at maxima corrected for the extinction of the samples as function of $[Co(phen)_3]^{3+}$ (circles) and $[Co(NH_3)_6]^{3+}$ (solid squares) (Experimental conditions: $[H_2TPPS_4]$ = 3 μM; [HCl] = 0.01 M, T = 298 K).



(a) (b)

Figure S4. Plot of the RLS intensity at maxima corrected for the extinction of the samples as function of the corresponding rate constants k_c for the catalyzed growth of J-aggregates of H_2TPPS_4 at pH = 2 upon addition of a) $[Co(phen)_3]^{3+}$ and b) $[Co(NH_3)_6]^{3+}$. (Experimental conditions: $[H_2TPPS_4]$ = 3 μM; [HCl] = 0.01 M, $[CoL_n^{3+}]$= 100 μM, 200 μM an 300 μM, T = 298 K). The solid lines represent the linear best-fits to the equations: a) $I_{RLS}^{corr} = (527 \pm 47) + (1.95 \pm 0.16) \times 10^5 \times [Co(phen)_3]$ (R^2 = 0.9934); b) $I_{RLS}^{corr} = (93 \pm 18) + (2.90 \pm 0.35) \times 10^4 \times [Co(NH_3)_6]$.

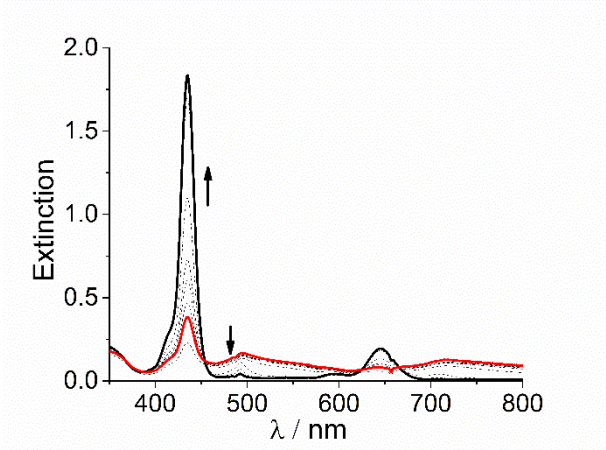


Figure S5. UV/Vis extinction spectral changes for the disassembling of J-aggregates of H_2TPPS_4 stabilized with $[Co(NH_3)_6]^{3+}$ at pH = 2 upon addition of PVS (Experimental conditions: $[H_2TPPS_4]$ = 3 μM; [HCl] = 0.01 M, $[Co(NH_3)_6]$ = 300 μM, [PVS] = 1 mM, T = 298 K, total scanning time 1800 s).