

Supporting Information

Structure dependent activation of Co molecular catalyst through photoinduced electron transfer from CdTe quantum dot

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S1 Synthesis

All reagents and solvents (HPLC grade) were purchased from Sigma–Aldrich Co., Tokyo Industry Co., or VWR International. The solvents used were dried following the standard procedure and the commercial reagents were used without further purification. The solvents for the reactions were dried as per the standard procedure and the reagents were used as received without further purification. Pyrrole was distilled at atmospheric pressure under argon and CHCl_3 (reagent grade with 0.5 % ethanol as a stabilizer) were subjected to simple distillation from K_2CO_3 . Monitoring of the reactions was performed by thin-layer chromatography (TLC) using aluminum sheets precoated with silica gel 60 F254 or neutral Al_2O_3 60 F254 (Merck). The purification and isolation of the products were performed by preparative TLC (either Al_2O_3 or silica gel) or column chromatography on silica gel 60 (mesh size 40–63 μm) or silica gel 100 (mesh size 63–200 μm).

S1.1 Synthesis of CoPp

We followed the reaction scheme shown in Figure S1 to synthesize the CoPp.

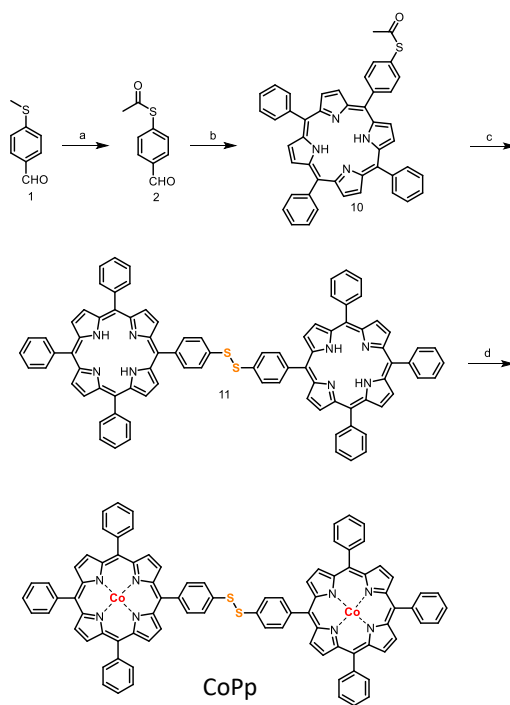


Figure S1 Synthesis scheme of CoPp. (a) 2-methyl-2-propanethiolate, acetyl chloride, DMF, 150°C , 4 h; (b) (i) pyrrole, benzaldehyde, $\text{BF}_3\text{Et}_2\text{O}$, CHCl_3 , RT, 2 h and (ii) DDQ, CDCl_3 , RT, 1 h; (c) NaBH_4 , THF/MeOH, RT, 18 h; (d) $\text{Co}(\text{OAc})_2$, $\text{CHCl}_3/\text{MeOH}$, 55°C , 4 h.

S1.2 Synthesis of CoPm

We followed the scheme shown in Figure S2 to synthesize the CoPm.

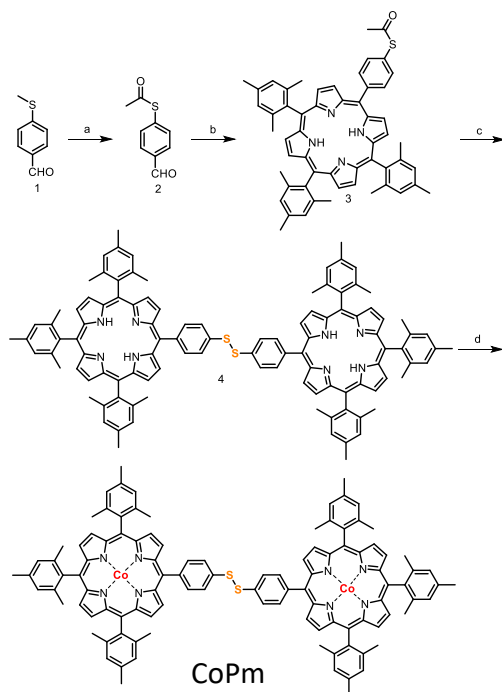


Figure S2 Synthesis of CoPm. (a) 2-methyl-2-propanethiolate, acetyl chloride, DMF, 150 °C, 4 h; (b) (i) pyrrole, mesitaldehyde, $\text{BF}_3\text{Et}_2\text{O}$, CHCl_3 , RT, 2 h and (ii) DDQ, CDCl_3 , RT, 1 h; (c) NaBH_4 , THF/MeOH, RT, 3 h; (d) $\text{Co}(\text{OAc})_2$, $\text{CHCl}_3/\text{MeOH}$, reflux, 24 h.

S1.3 Synthesis of compound 2 in Figure S1



Figure S3 Synthesis of Compound-2.

Compound 2 was synthesized by following the method shown in Figure S3. A 2-neck 100 mL round bottom flask was charged with sodium 2-methyl-2-propanethiolate (1.47 g; 13.14 mmol) and 15 mL of anhydrous DMF (15 mL) was added. To this solution, 4-methylthiobenzaldehyde (compound-1) (1.0 g; 6.57 mmol) was injected via a syringe with vigorous stirring. The solution was stirred at 150 °C for 4 h under argon. The obtained dark brown solution was cooled in an ice bath and acetyl chloride (2.3 mL; 31.5 mmol) was slowly injected under Ar with uniform stirring. After 45 min, the resulting suspension

was poured into 400 mL of water and extracted with EtOAc. The organic layer was washed with brine and dried over MgSO₄. After evaporation of the solvent under reduced pressure, the crude product was purified by flash column chromatography (hexane:EtOAc 10:2 v/v) to yield compound-2 (400 mg, 34 %) as a white solid.

S1.4 Synthesis of Compound Por-SAc-p

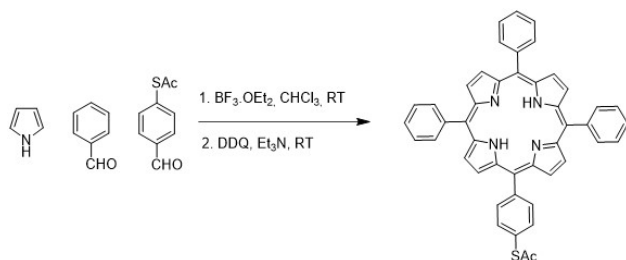


Figure S4 Synthesis scheme of Por-SAc-p

To a CHCl₃ solution (500 mL) of pyrrole (0.41 mL, 5.96 mmol), benzaldehyde (474.54 mg, 4.47 mmol) and S-(4-formylphenyl) ethanethioate (2) (268.6 mg, 1.49 mmol) were added and stirred under dark (reaction scheme in Figure S4). After degassing the solution with Ar for 30 min, BF₃·Et₂O (0.37 mL, 2.98 mmol) was added, and the mixture was stirred for 1.5 h at RT. DDQ (845.8 mg, 3.73 mmol) was added to the reaction mixture and the solution was stirred for 1 h at RT. After mixing with 1 mL Et₃N, the reaction mixture was passed through a short silica column and eluted with DCM. After removing the solvent under reduced pressure, the crude product was purified by silica gel column chromatography using Hexane/CH₂Cl₂ 1:3 (v/v) as eluent. The second fraction was collected and evaporated. Compound 10 (Por-SAc-p) was obtained as purple solid (100 mg) in 10% yield. ¹H NMR (in Figure-S6) (CDCl₃, 500 MHz) δ: 8.86 (d, J = 6.8 Hz, 8H), 8.31 – 8.18 (m, 8H), 7.78 (m, 11H), 2.61 (s, 3H), -2.80 (s, 2H). ¹³C NMR (in Figure-S7) (CDCl₃, 126 MHz,) δ: 194.10, 161.60, 143.43, 142.89, 142.15, 137.15, 135.31, 134.65, 132.58, 128.87, 127.85, 126.80, 124.26, 120.38, 120.02, 118.76, 106.95, 77.36, 77.11, 76.85, 51.35, 31.69, 30.59, 21.43, 0.09, -4.59. HR-Mass (ESI): m/z = 689.2359 (Calcd.

for $C_{46}H_{32}N_4OS$ $[M+H]^+$: 689.2369).

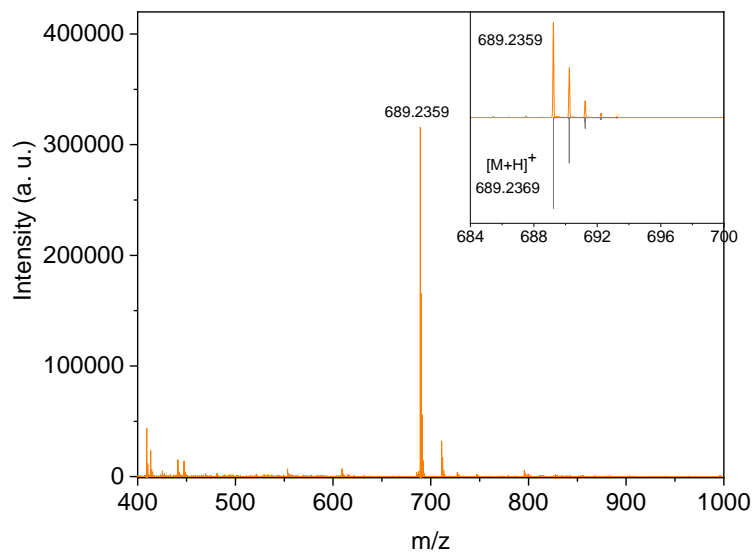


Figure S5 HR mass of Por-SAc-p.

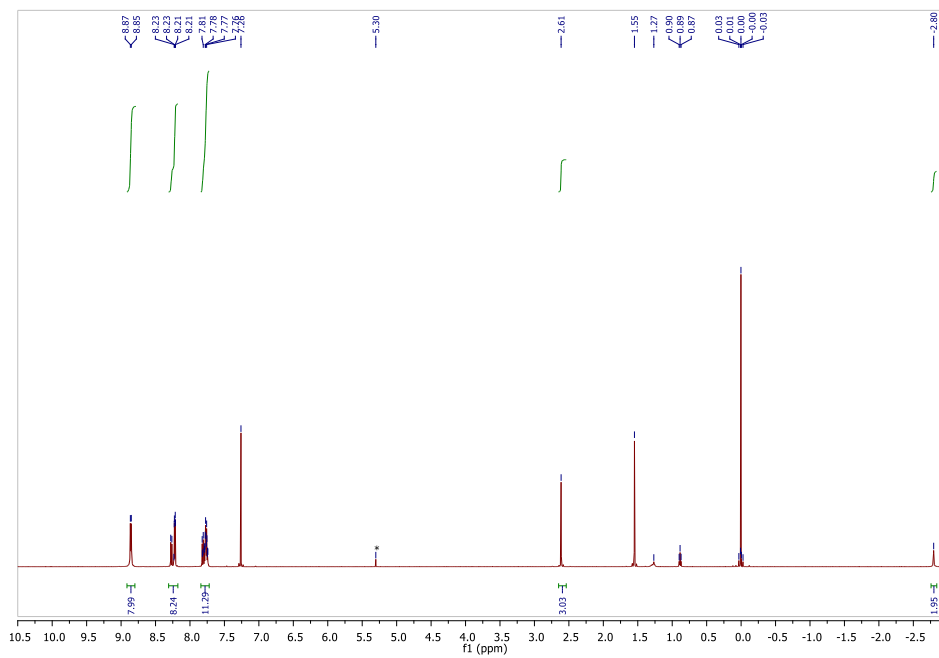


Figure S6 1H NMR of Por-SAc-p.

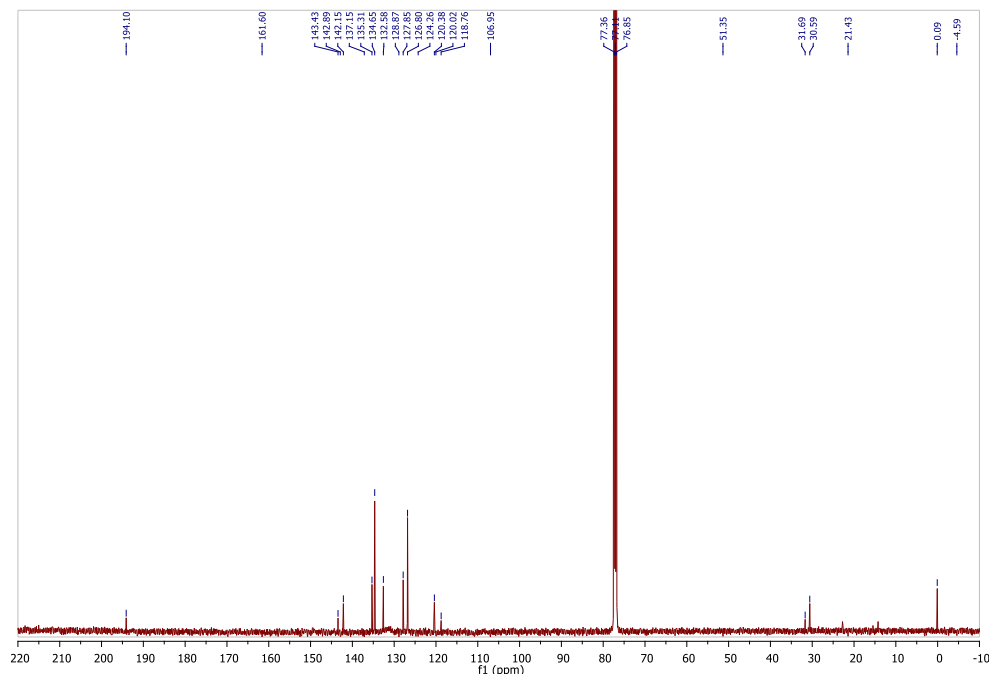


Figure S7 ^{13}C NMR of Por-SAc-p.

S1.5 Synthesis of Por-SAc-m

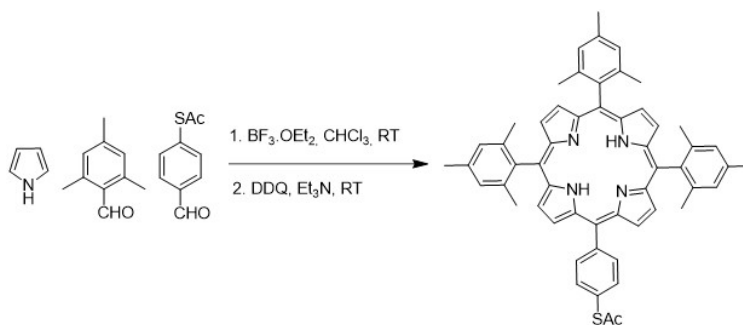


Figure S8 Synthesis of Por-SAc-m

Por-SAc-m was synthesized by following the method in literature [1] as shown in Figure S8. To a CHCl_3 solution (500 mL) of pyrrole (0.42 mL, 5.96 mmol), mesitaldehyde (662.7 mg, 4.47 mmol) and S-(4-formylphenyl) ethanethioate (compound-2) (268.6 mg, 1.49 mmol) were added and stirred under dark. After degassing the solution with Ar for 30 min, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.37 mL, 2.98 mmol) was added, and the mixture was stirred for 2 h at room temperature (RT). 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (845.8 mg,

3.73 mmol) was added to the reaction mixture and the solution was stirred for 1 h at RT. After mixing with 1 mL Et₃N, the reaction mixture was passed through a short silica column and eluted with DCM. After removing the solvent under reduced pressure, the crude product was purified by silica gel column chromatography using hexane/CH₂Cl₂ 3:1 (v/v) as eluent. The second fraction was collected and evaporated. Por-SAc-m was obtained as purple solid (150 mg) in 12% yield. ¹H NMR (in Figure S9) (CDCl₃, 500 MHz) δ: 8.79 (d, J = 4.6 Hz, 2H), 8.71 – 8.58 (m, 6H), 8.25 (d, J = 8.1 Hz, 2H), 7.79 (d, J = 7.8 Hz, 2H), 7.28 (m, 6H), 2.67 – 2.57 (m, 12 H), 1.85 (d, J = 4.2 Hz, 18H), -2.58 (s, 2H). ¹³C NMR (in Figure S10) (CDCl₃, 126 MHz) δ: 139.50, 137.80, 135.18, 132.54, 127.85, 77.36, 77.11, 76.85, 21.74. HR-Mass (in Figure S11) (ESI): m/z 815.3759 (Calcd. for C₅₅H₅₀N₄OS [M+H]⁺: 815.3778)

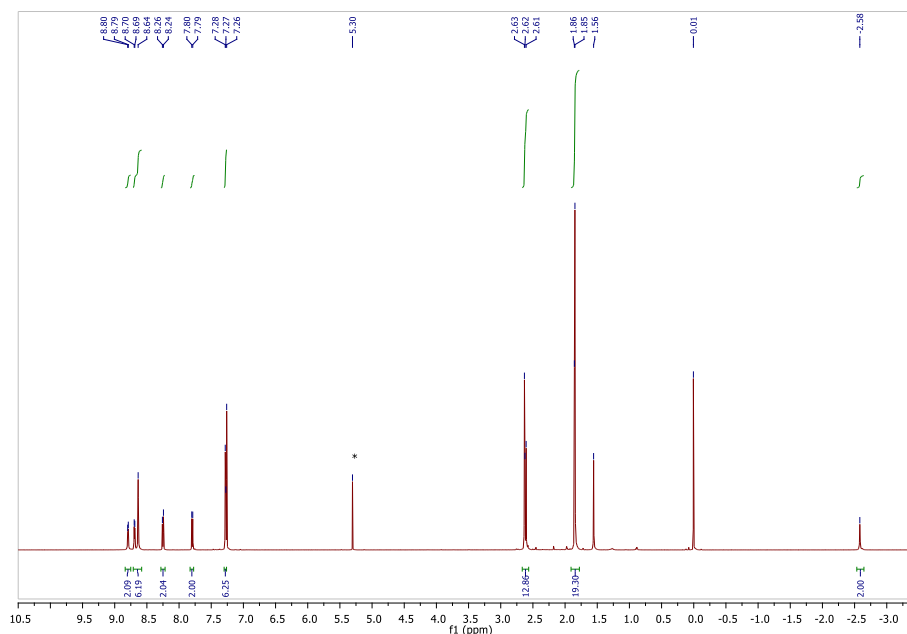


Figure S9 ¹H NMR of Por-SAc-m.

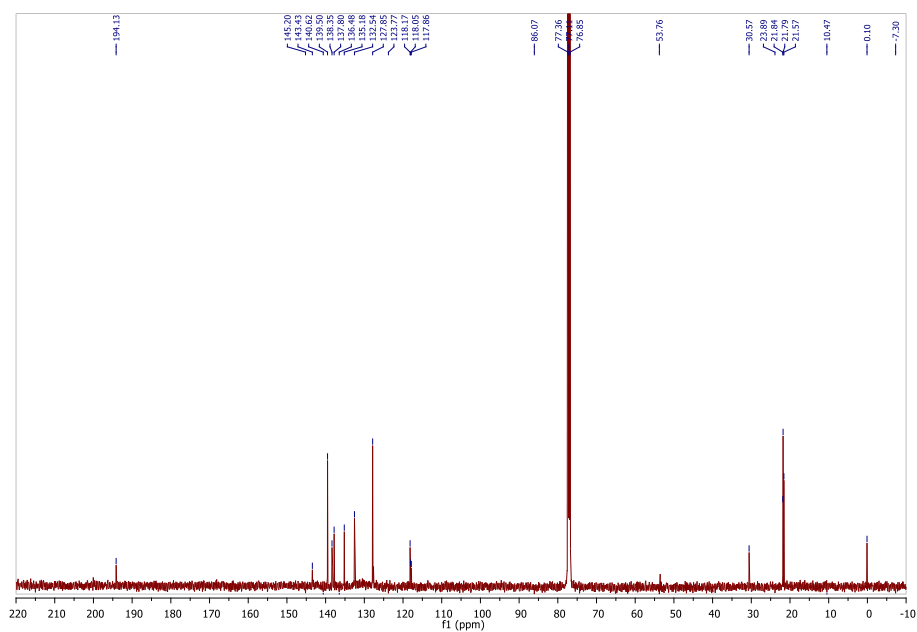


Figure S10 ^{13}C NMR of Por-SAc-m.

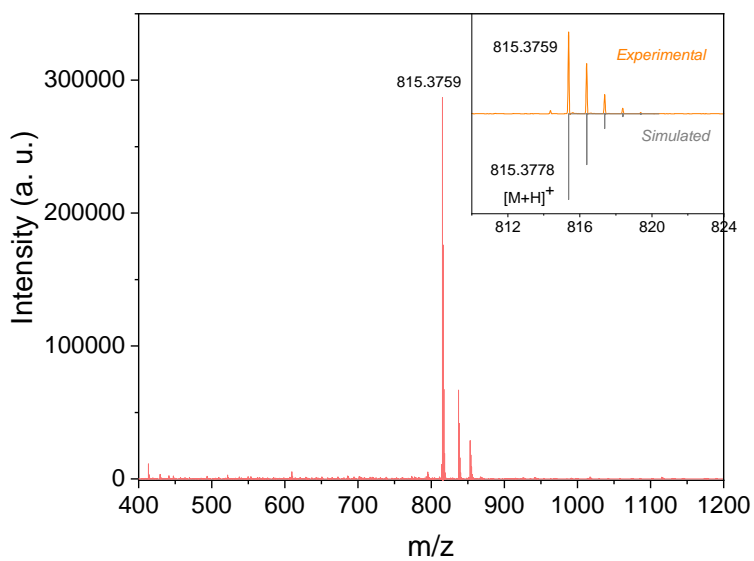


Figure S11 HR-Mass (ESI) of Por-SAc-m.

S1.6 Synthesis of (Por-S)2-p

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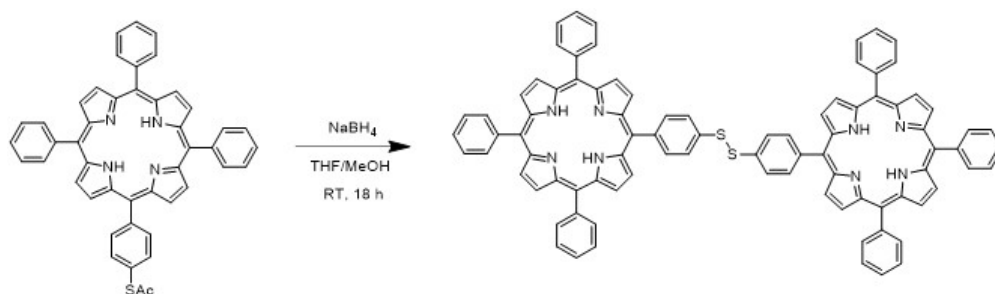


Figure S12 Synthesis of (Por-S)₂-p

Por-SAc-p (30.0 mg, 0.044 mmol) and NaBH₄ (24.7 mg, 0.65 mmol) was charged to a 25 mL round bottom flask and flushed with Ar for 10 min (reaction scheme in Figure S12). 10 mL of dry THF and 3 mL dry MeOH was injected in the flask and stirred the solution for 1.5 h under Ar at RT. The solution was further stirred under air for overnight. After confirming the reaction completion by TLC analysis, the solvent was evaporated under reduced pressure. The crude product was purified by silica chromatography by using hexanes/CH₂Cl₂ 1:1 (v/v) as eluent. Yield = 17 mg (60%): ¹H NMR (in Figure S14) (CDCl₃, 500 MHz) δ: 8.94 – 8.77 (m, 8H), 8.28 (d, J = 8.2 Hz, 2H), 8.19 (dd, J = 11.5, 5.1 Hz, 6H), 8.09 (d, J = 8.2 Hz, 2H), 7.80 – 7.67 (m, 9H), -2.79 (s, 2H). ¹³C NMR (in Figure S15) (CDCl₃, 126 MHz) δ: 142.14, 141.50, 138.88, 136.99, 135.40, 134.64, 127.82, 126.78, 125.91, 121.05, 120.43, 120.36, 118.99, 80.24, 77.36, 77.11, 76.85, 44.98, 31.69, 23.31, 22.76, 19.69, 14.24, 0.44, 0.10. HR-Mass (ESI): m/z = 1291.4270 (Calcd. for C₈₈H₅₈N₈S₂ [M+H]⁺: 1291.4298).

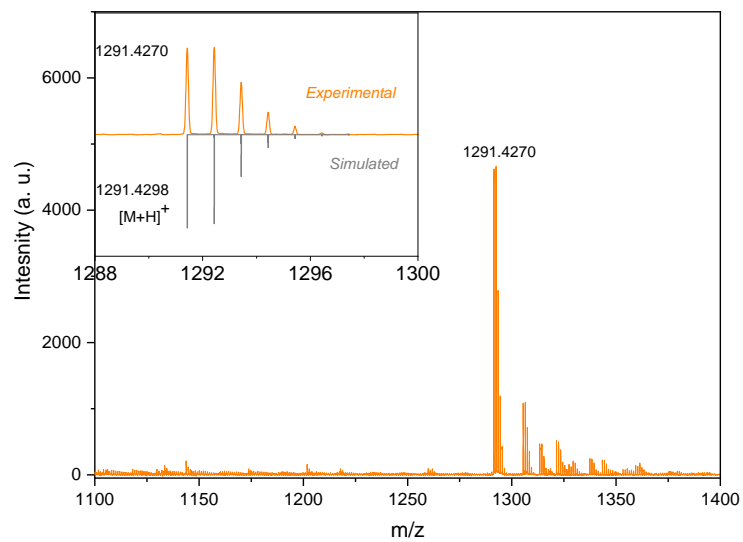


Figure S13 HR mass of (Por-S)2-p.

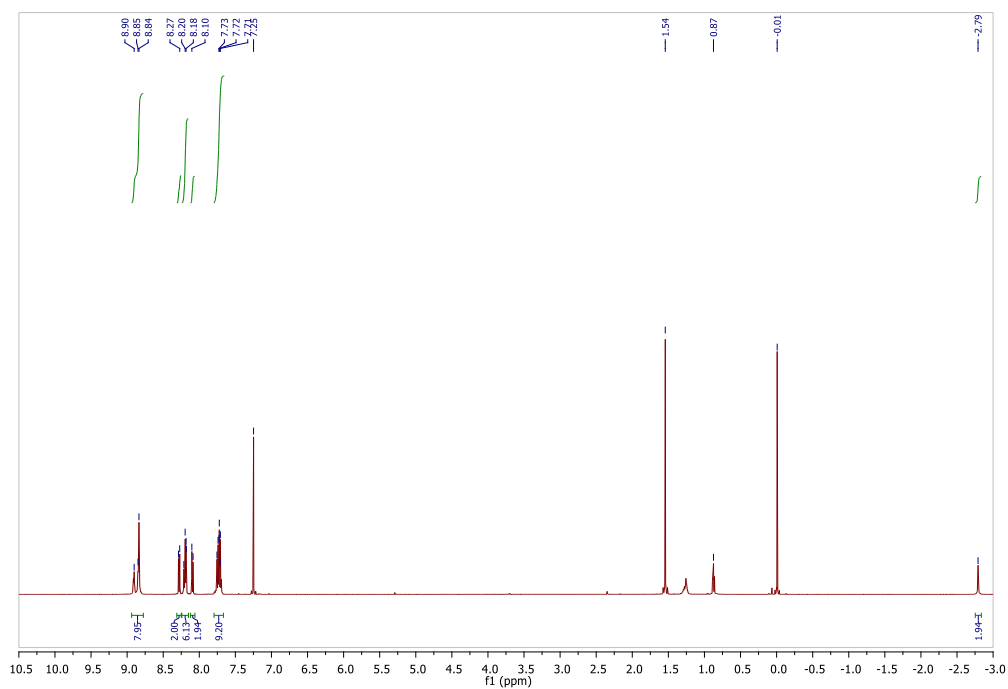


Figure S14 ^1H NMR of (Por-S)2-p.

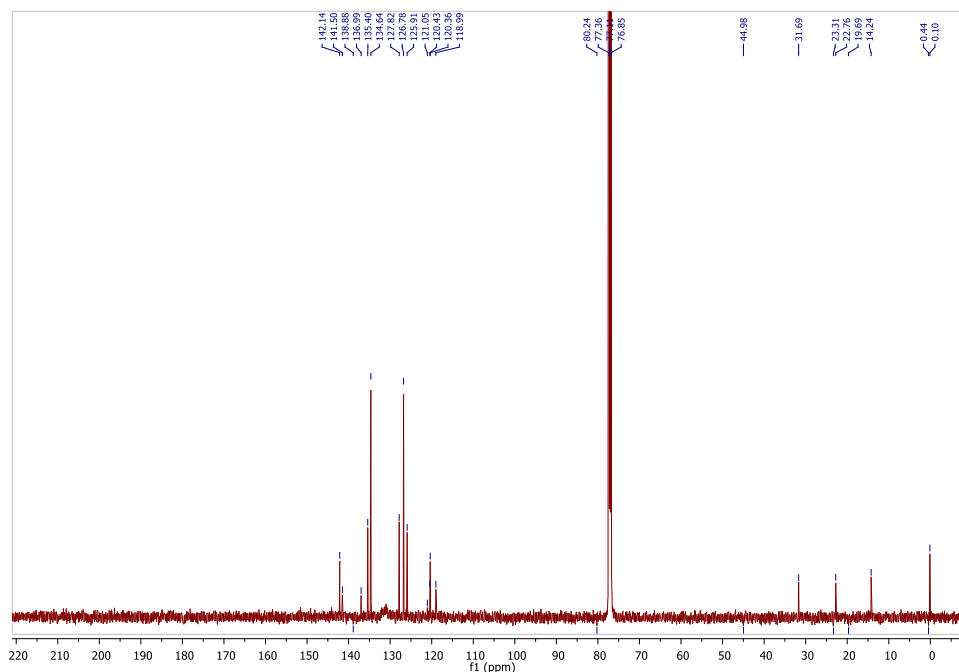


Figure S15 ^{13}C NMR of (Por-S)2-p.

S1.7 Synthesis of (Por-S)2-m

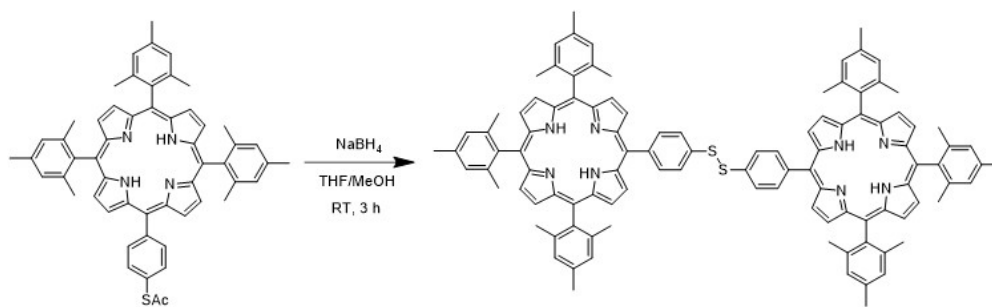


Figure S16 Synthesis of (Por-S)2-m

We followed reaction scheme in Figure S16 to synthesis (Por-S)2-m. Por-SAc-m (20 mg, 0.025 mmol) and NaBH_4 (9.3 mg, 0.25 mmol) was charged to a 25 mL two-necked round bottom flask and flushed with Ar for 10 min. 10 mL of dry THF and 3 mL dry MeOH was injected the flask, and stirred the solution for 3 h under Ar at RT. After confirming the reaction completion by TLC analysis, the solvent was evaporated under reduced pressure. The crude product was purified by silica chromatography by using hexanes/ CH_2Cl_2 1:1

(v/v) as eluent. Yield = 11 mg (57%): ^1H NMR (in Figure S18) (CDCl_3 , 500 MHz) δ : 8.84 (s, 2H), 8.74 – 8.57 (m, 6H), 8.31 – 8.23 (m, 2H), 8.08 (d, $J = 8.0$ Hz, 2H), 7.27 (d, $J = 7.6$ Hz, 6H), 2.61 (d, $J = 11.1$ Hz, 9H), 1.85 (d, $J = 10.0$ Hz, 18H), -2.56 (s, 2H). ^{13}C NMR (in Figure S19) (CDCl_3 , 126 MHz) δ : 139.48, 138.35, 137.77, 135.24, 127.83, 125.95, 118.27 – 117.84, 77.37, 77.11, 76.86, 31.70, 22.77, 21.82, 21.56, 0.11. . HR-Mass (ESI): $m/z = 1543.7198$ (Calcd. for $\text{C}_{106}\text{H}_{94}\text{N}_8\text{S}_2$ $[\text{M}+\text{H}]^+$: 1543.7121).

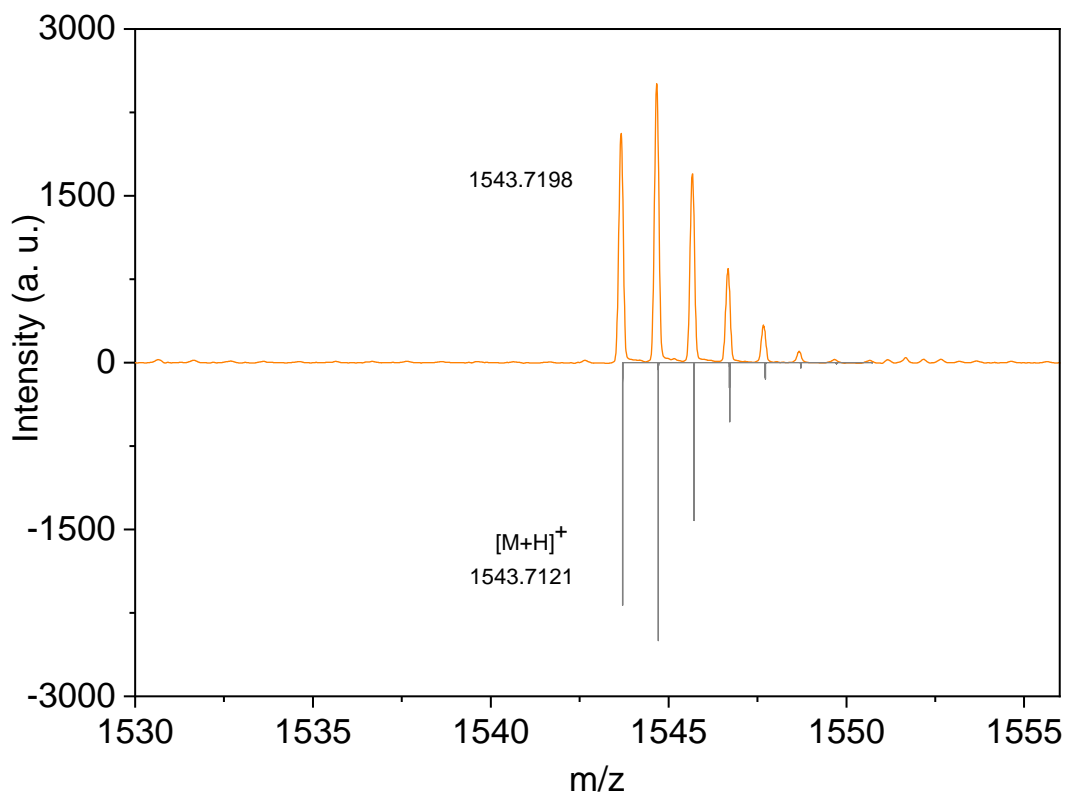


Figure S17 HR-Mass (ESI) of (Por-S)₂-m.

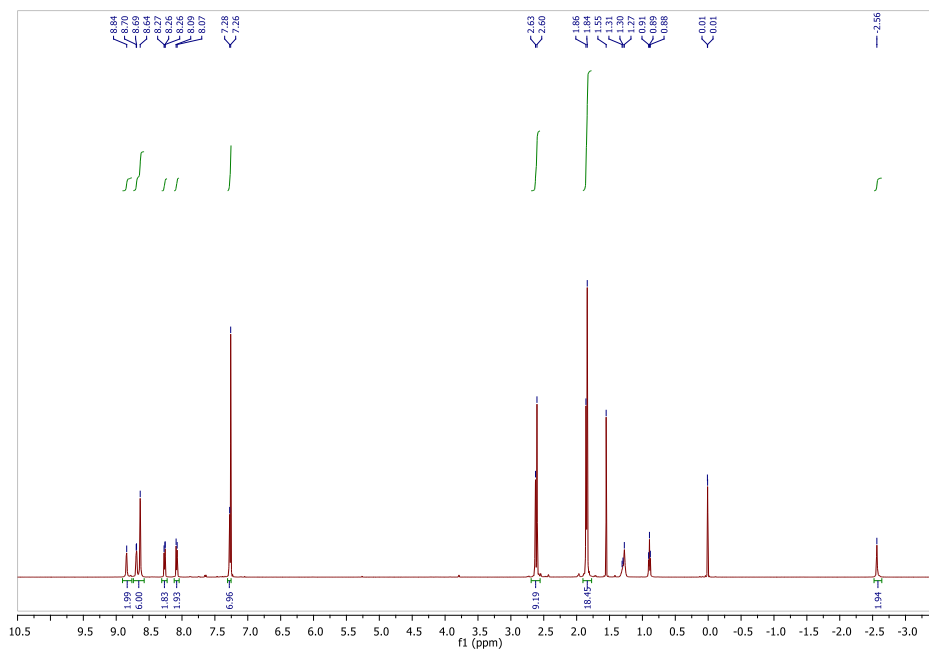


Figure S18 ^1H NMR of (Por-S) $_2$ -m.

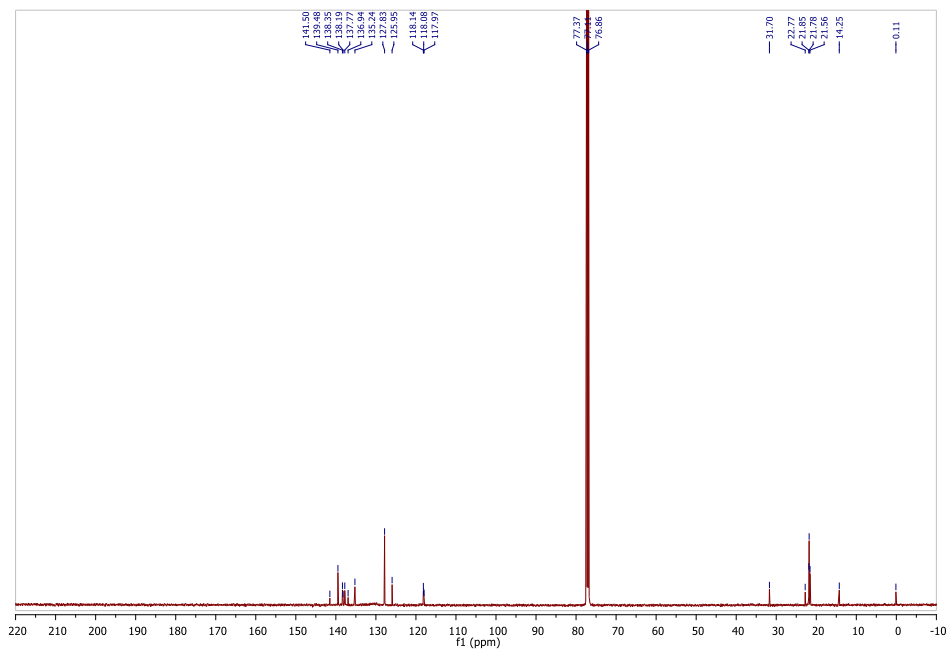


Figure S19 ^{13}C NMR of (Por-S) $_2$ -m.

S1.8 Synthesis of CoPp

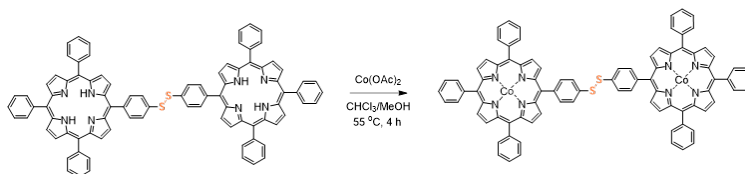


Figure S20 Synthesis of CoPp.

A 25 mL round bottom flask was charged with compound 11 (8 mg, 0.012 mmol) and Co(OAc)_2 (15.3 mg, 0.087 mmol) and flushed with Ar for 10 min. 10 mL of dry CHCl_3 and 3 mL dry MeOH was injected the flask, and heated at $55\text{ }^\circ\text{C}$ under Ar (reaction scheme in Figure S20). After 4 h, orange precipitates were formed, and the TLC indicated the disappearance of starting material. The reaction mixture was brought to RT and mixed with 10 mL MeOH. The precipitate was separated by filtration and the orange solid was washed with excess of MeOH. Yield = 5 mg (57%): NMR (in Figure S22) (500 MHz, benzene- d_6) δ : 16.43, 16.13, 13.54, 13.00, 12.06, 11.01, 9.59, 9.37, 9.12, 8.76. HR-Mass (ESI): $m/z = 1404.2570$ (Calcd. for $\text{C}_{88}\text{H}_{54}\text{Co}_2\text{N}_8\text{S}_2$ $[\text{M}]^+$: 1404.2571).

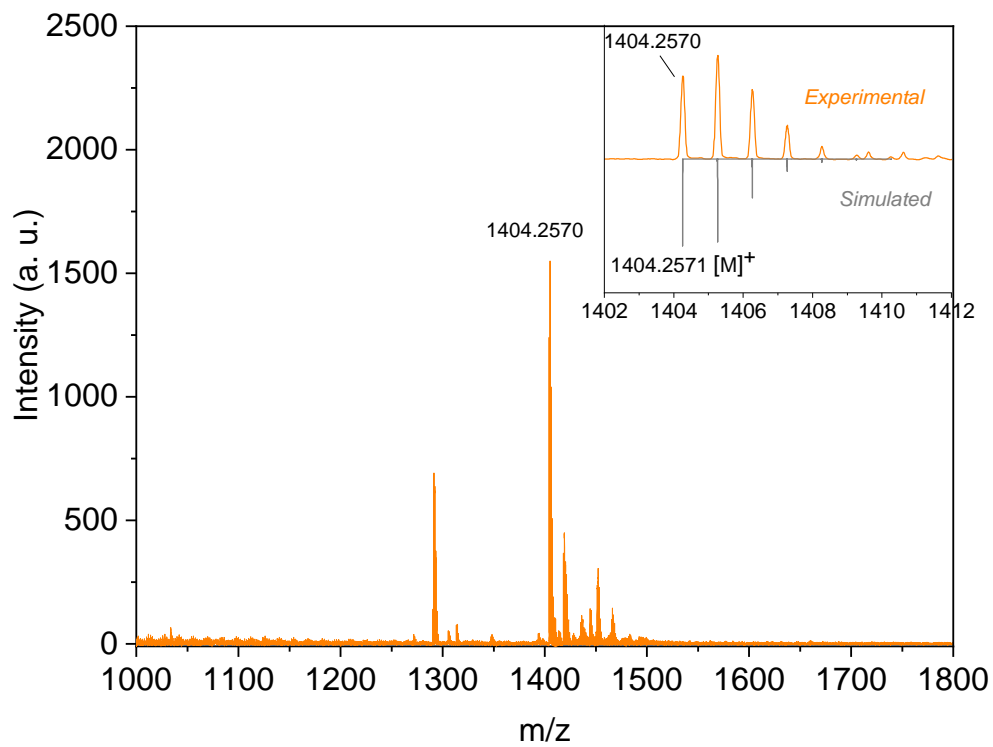


Figure S21 HR mass of CoPp.

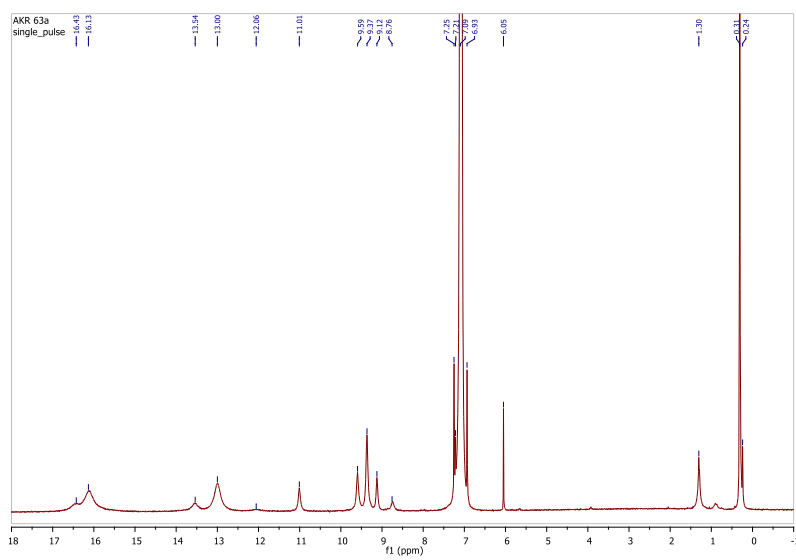


Figure S22 ¹H NMR of CoPp.

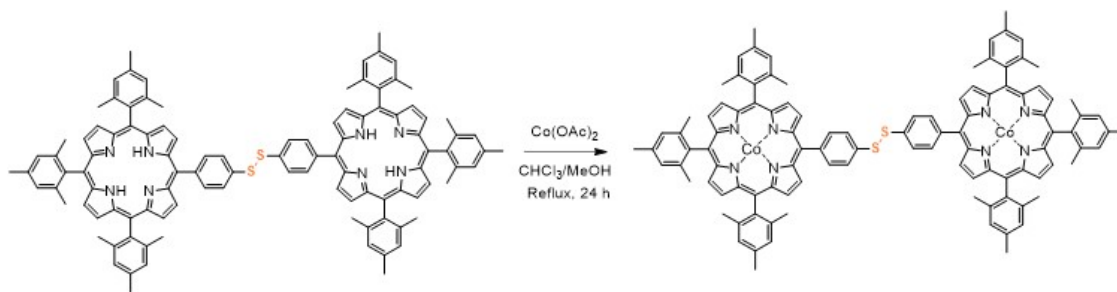


Figure S23 Synthesis of CoPm

S1.9 Synthesis of CoPm

A 25 mL two-necked round bottom flask was charged with compound (Por-S)2-m (12 mg, 0.015 mmol) and $\text{Co}(\text{OAc})_2$ (22.0 mg, 0.12 mmol) and flushed with Ar for 10 min. 14 mL of dry CHCl_3 and 4 mL dry MeOH was injected the flask, and refluxed the purple solution for 24 h under Ar (scheme in Figure S23). The orange solution was brought to RT and removed the solvents under reduced pressure. The crude product was purified by silica chromatography by using hexanes/ CH_2Cl_2 1:1 (v/v) as eluent to afford the orange solid. Yield = 8 mg (61 %): NMR (500 MHz, CDCl_3) (in Figure S25) δ : 15.68, 15.53, 15.21, 13.06, 10.81, 9.13, 3.89, 3.79, 3.53, 3.23. HR-Mass (ESI): $m/z = 1656.5395$ (Calcd. for $\text{C}_{106}\text{H}_{90}\text{Co}_2\text{N}_8\text{S}_2$ $[\text{M}]^+$: 1656.5388).

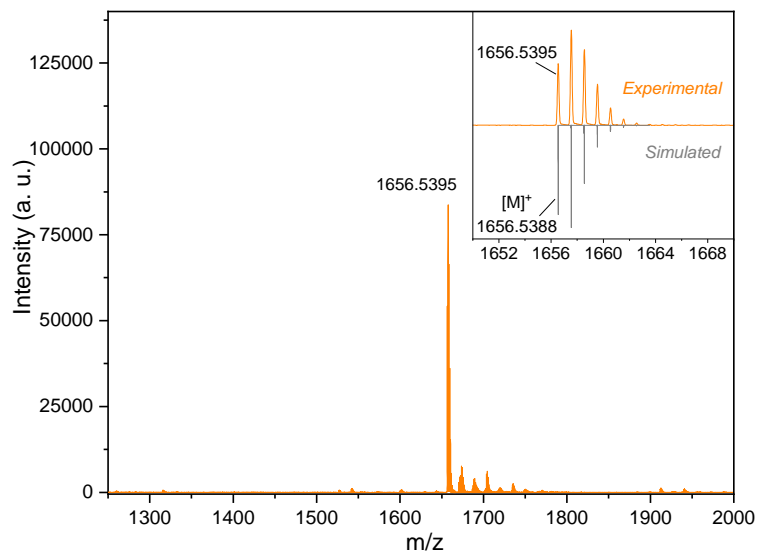


Figure S24 HR-Mass (ESI) of CoPm.

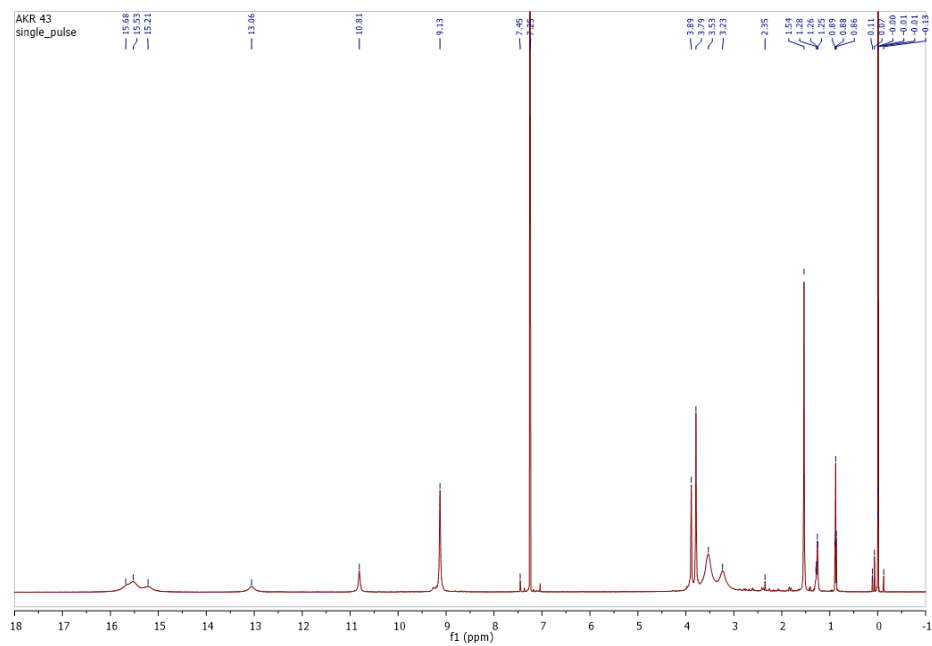


Figure S25 ¹H NMR of CoPm.

S2 TEM measurement

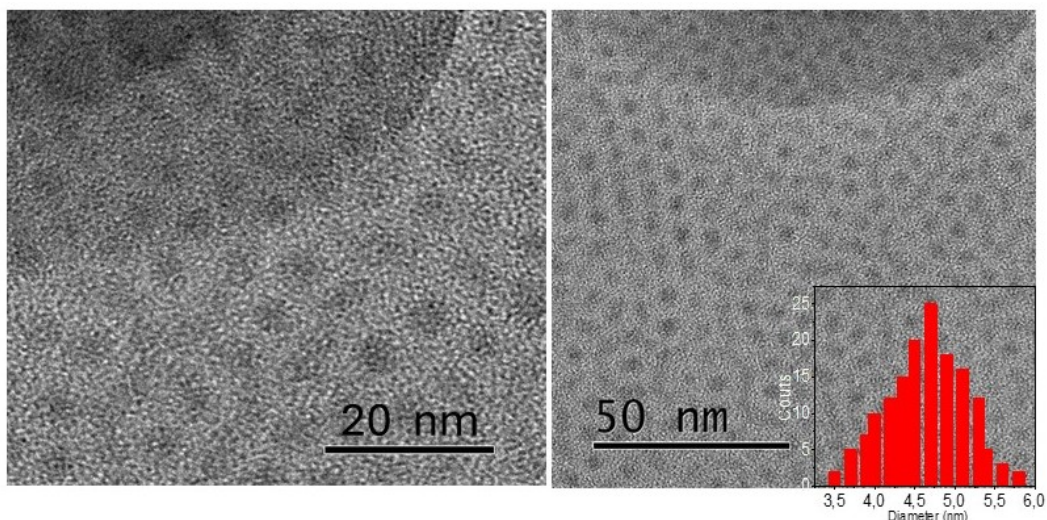


Figure S26 TEM of synthesized CQD. In inset: Histogram for the size distribution. The zinc blende morphology with an average size $4.7 (\pm 0.5)$ nm.

S3 CQD and (Por-S)₂-p (DPor) interaction

To test the photophysical interaction between CQD and DPor we have performed the steady-state absorption study as shown in Figure S27. The Soret band is not changed at all in presence of CQD.

S4 CoPp and oleic acid (OA)

To test the protonation of CoPp in the presence of oleic acid, we measured the steady-state absorption of CoP in presence of OA, as shown in Figure S28.

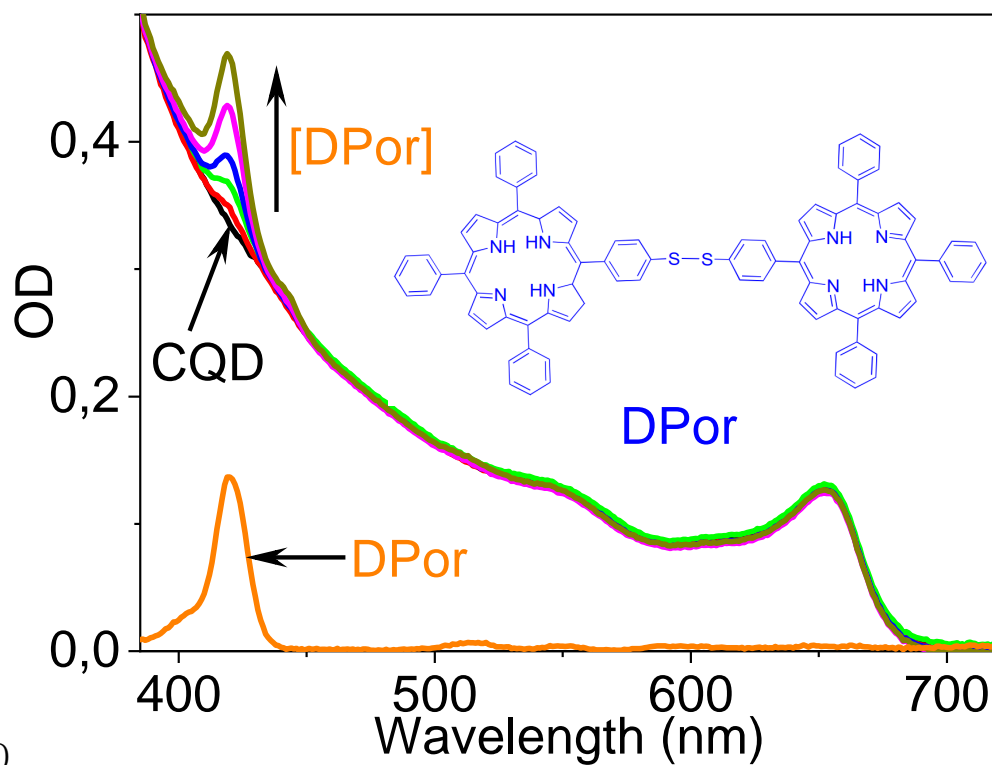


Figure S27 (a) Absorbance spectra of CQD, DPor, and mixture of CQD and different concentrations (0.30, 0.6, 1.2, 2, 3 μM) of DPor in chloroform solvent.

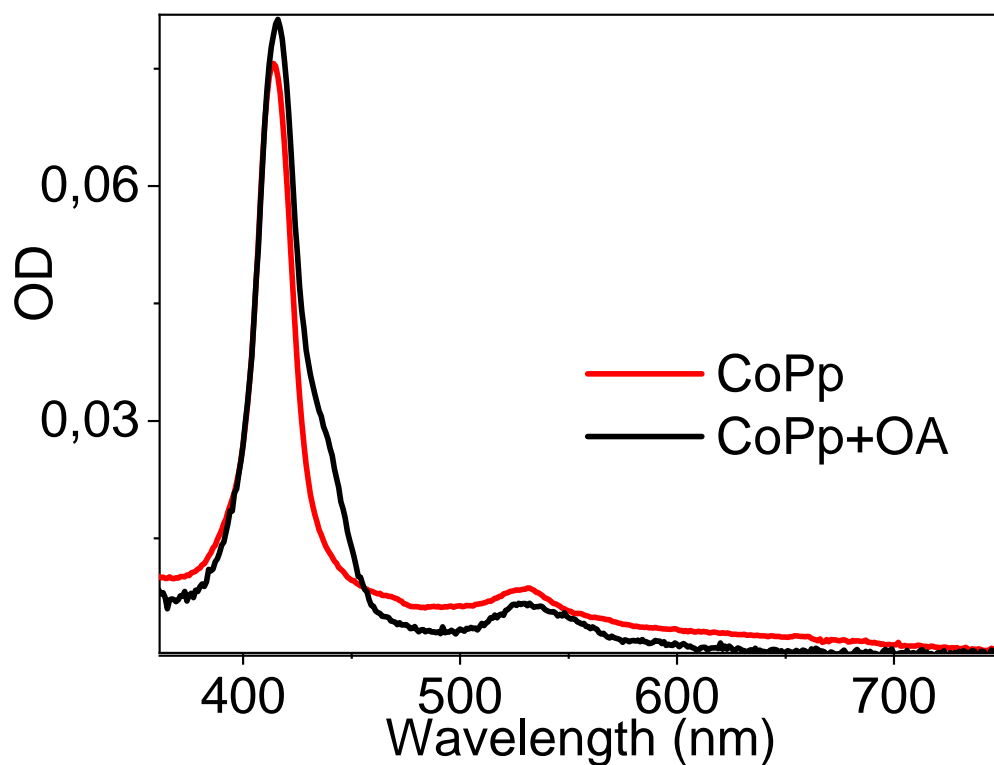


Figure S28 Absorbance spectra of CoPp presence and absence of OA.

S5 CoPp and Te-ToP

We performed the steady-state absorption of CoPp in the presence of Te-ToP to test the binding between Co and Te, as shown in Figure S29.

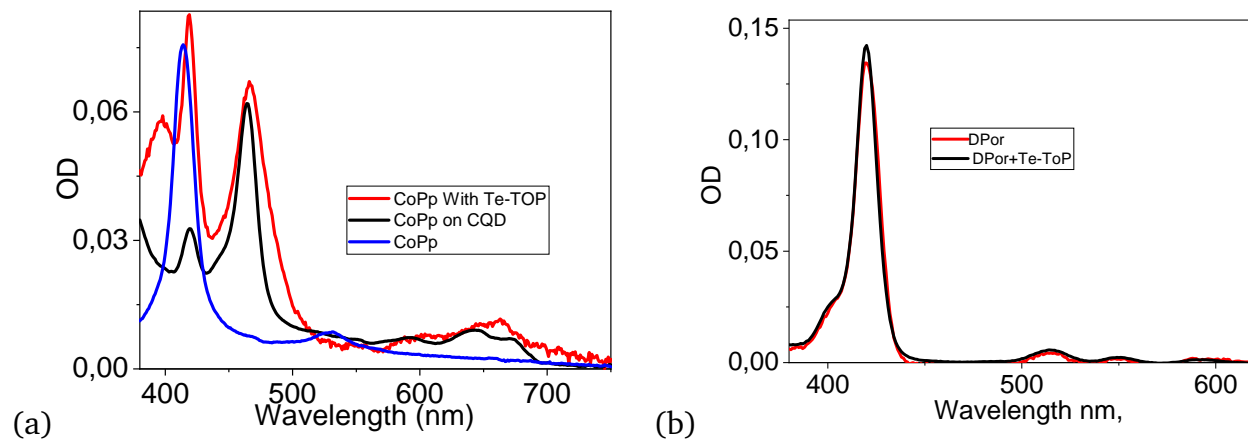


Figure S29 (a) Absorbance spectra of free CoPp, CoPp on CQD, and CoPp with Te-ToP. (b) Absorbance spectra of free DPor and DPor with Te-ToP. All are in chloroform solvent.

S6 High concentration measurement

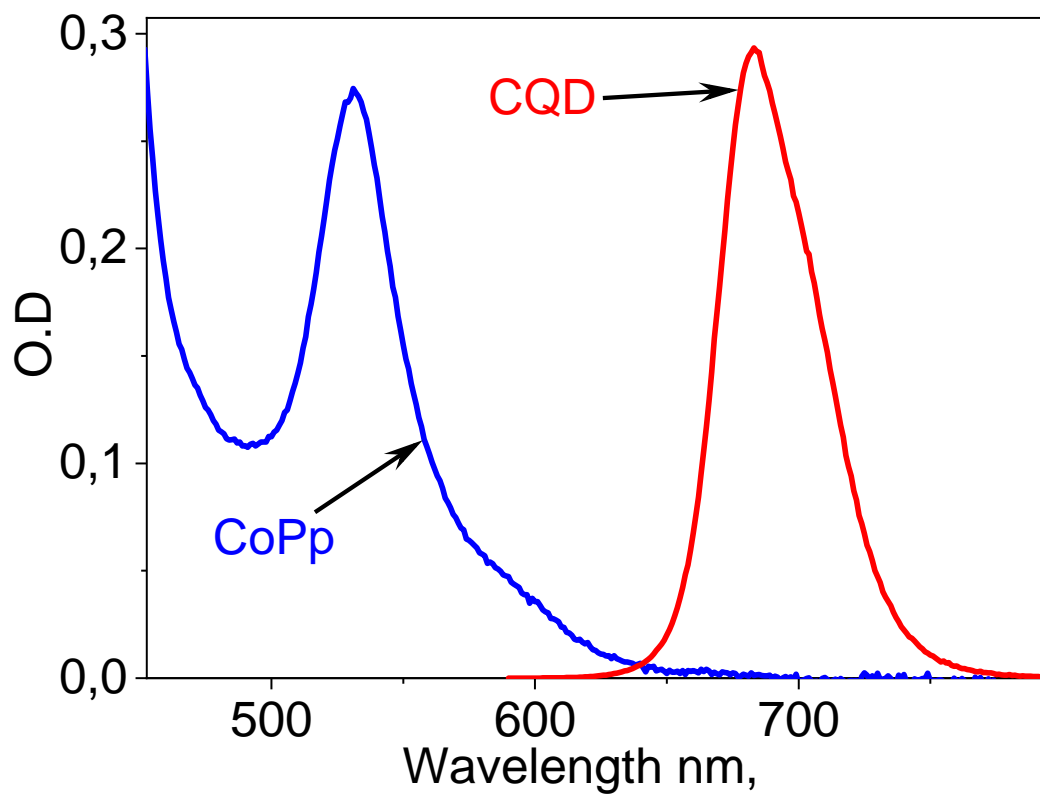


Figure S30 Absorbance spectrum of highly concentrated CoPp (60 μM) and emission spectrum of CQD. No overlap between absorbance spectrum of CoPp and emission spectrum of CQD.

S7 TCSPC measurement

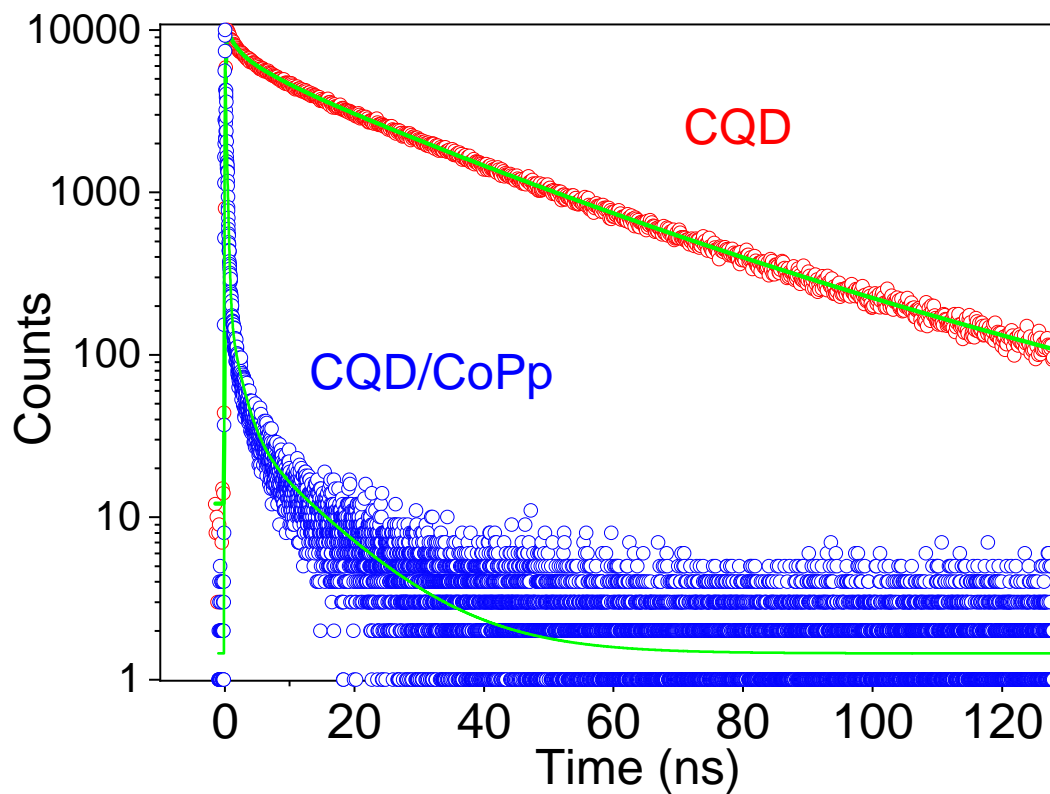


Figure S31 TCSPC of CQD and CQD/CoPp monitored at 680 nm following 405 nm excitation. The fitted components are 1.1ns (25 %) 4.5ns (64 %) and 25 ns(11 %) for CQD and 0.4ns (70 %), 2.2ns(25 %) and 10 ns(5%) for CQD/CoPp.

S8 Electrochemical measurement

The structure of mCoP and pCoP are shown in Figure S32, which are corresponding monomers of CoPm and CoPp, respectively.

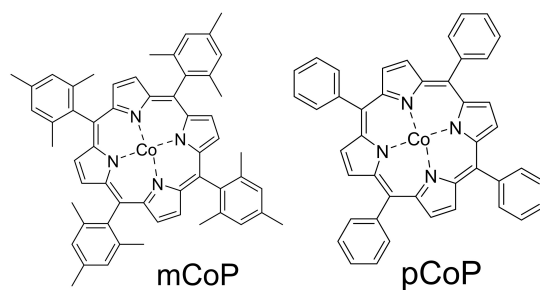


Figure S32 Structure of mCoP and pCoP.

The differential pulse voltammetry (DPV) was measured by Iviumstat and plots for all these molecules are shown in Figure S33.

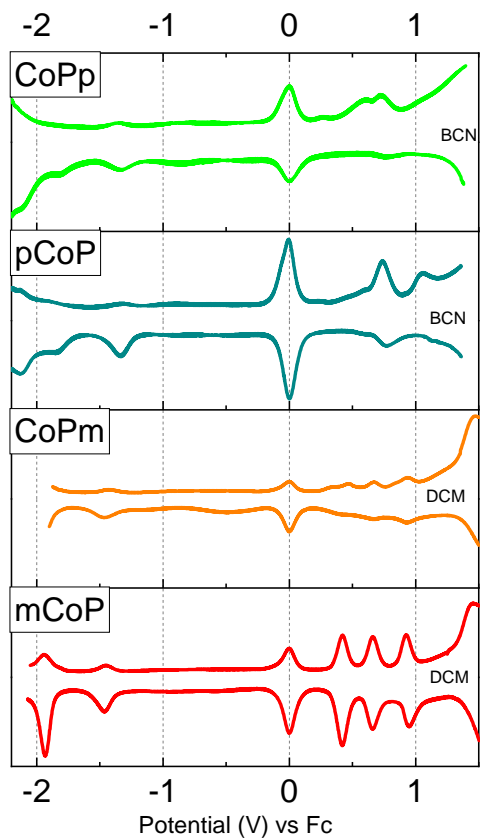


Figure S33 DPV of all porphyrines.

The HOMO/LUMO energies and relative position of the CB bottom are summarized in the main text.

S9 TA 2D-contour map

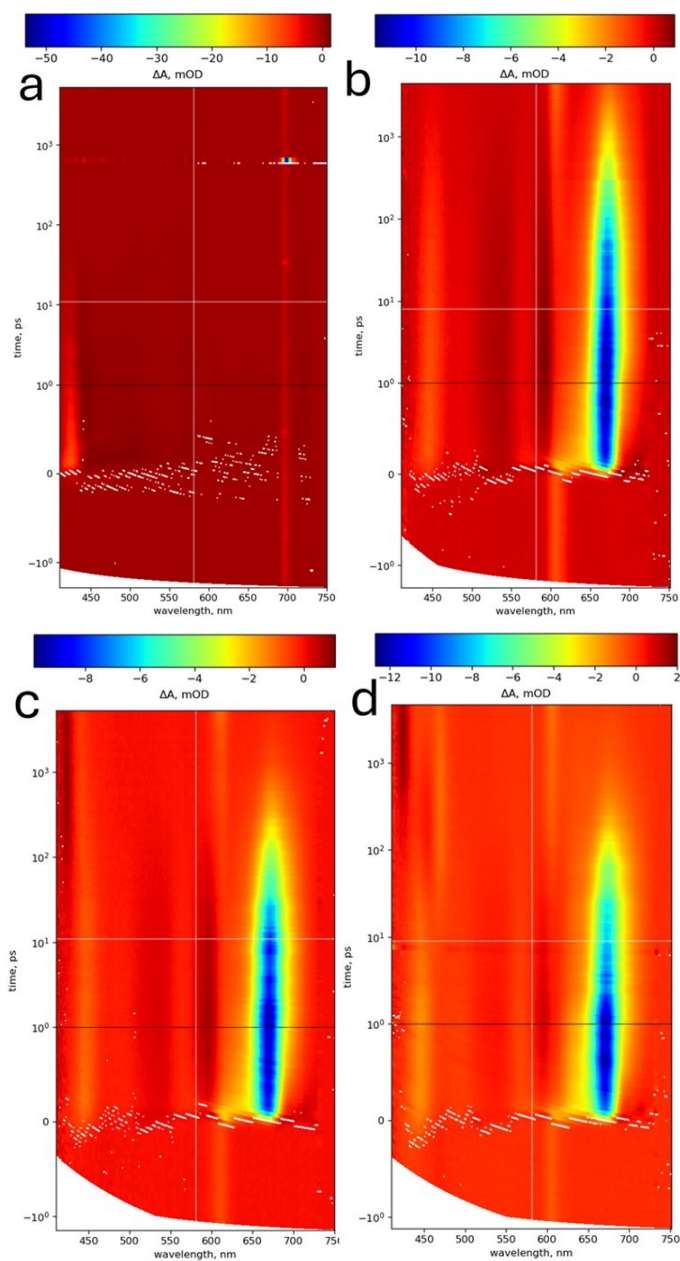


Figure S34 TA 2D contour map of (a) CoP (b) CQD, (c) CQD/CoPm and (d) CQD/CoPp.

S10 TA Fitting

The TA data were globally fitted to present the measured data as a sum of functions

$$F(t, \lambda) = \sum_{n=1}^N f_n(t) c_n(\lambda) \quad (\text{S1})$$

where, $f_n(t)$ are the decay functions which depend on the delay time t only, $c_n(\lambda)$ are the function which depends on the wavelength only and conventionally called decay associated spectra (DAS) and N is the number of functions. The aim of the fit is to get the model $F(t, \lambda)$ as close to the measured data $\Delta A(t, \lambda)$ as possible. In this study we have used exponential functions $\exp(-t/\tau_n)$ which each have individual time constants (τ_n), the decay function derived for the Poisson distribution of quenchers (see the following section), and a step function which is 0 at $t < 0$ and one otherwise. The latter presents the states with lifetime much longer than the measurement time scale (roughly 5 ns), or the state which to not decay within the measured time window.

S11 Poisson distribution and the population decay

The decay resulting from the Poisson distribution of quenchers on a photo-excited entity (e.g. quantum dot) follow the equation¹

$$\exp \left[-\frac{t}{\tau} - c_q \left(1 - \exp \frac{t}{\tau_q} \right) \right] \quad (\text{S2})$$

where τ is the natural or non-quenched lifetime, τ_q is the time constant of quenching by a single quencher, and c_q is the average number of quenchers per entity under study (a relative concentration of quenchers).

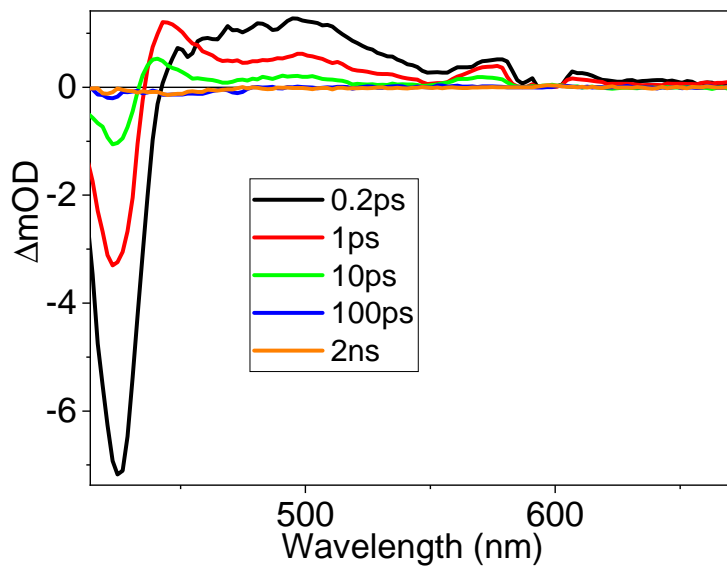


Figure S35 TA spectra of CoPm following 610 nm excitation in the chloroform.

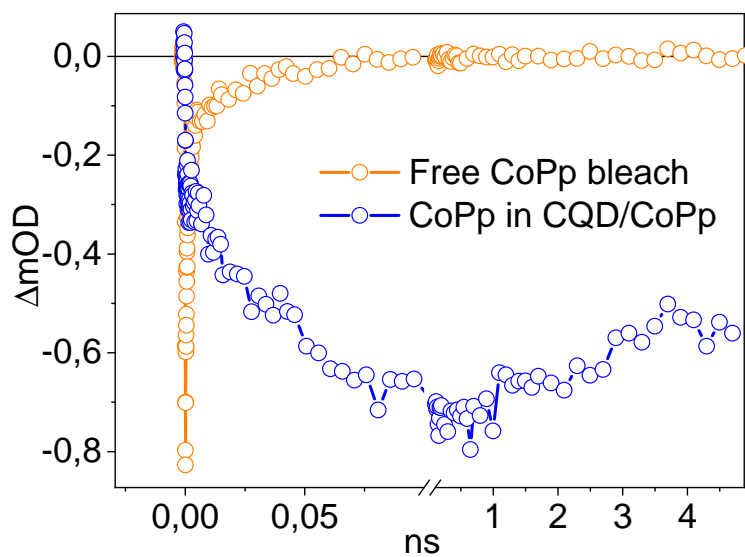


Figure S36 Spectral cuts of CoPp in free state at 425 nm and complexed form at 470 nm in the chloroform.

Notes and references

- (1) Tkachenko, N. V. Photoinduced Charge Separation in Semiconductor-Quantum-Dot/Organic-Molecule Hybrids. *ChemPhotoChem* **2018**, *2*, 112.