

Supplementary Materials
for
Hydrogen Evolution Reaction, Electrochemical Reduction of CO₂ and Oxidative
Photodegradation of Organic Dyes Catalyzed by
Co(II) trimethoxy-*meso*-arylporphyrin

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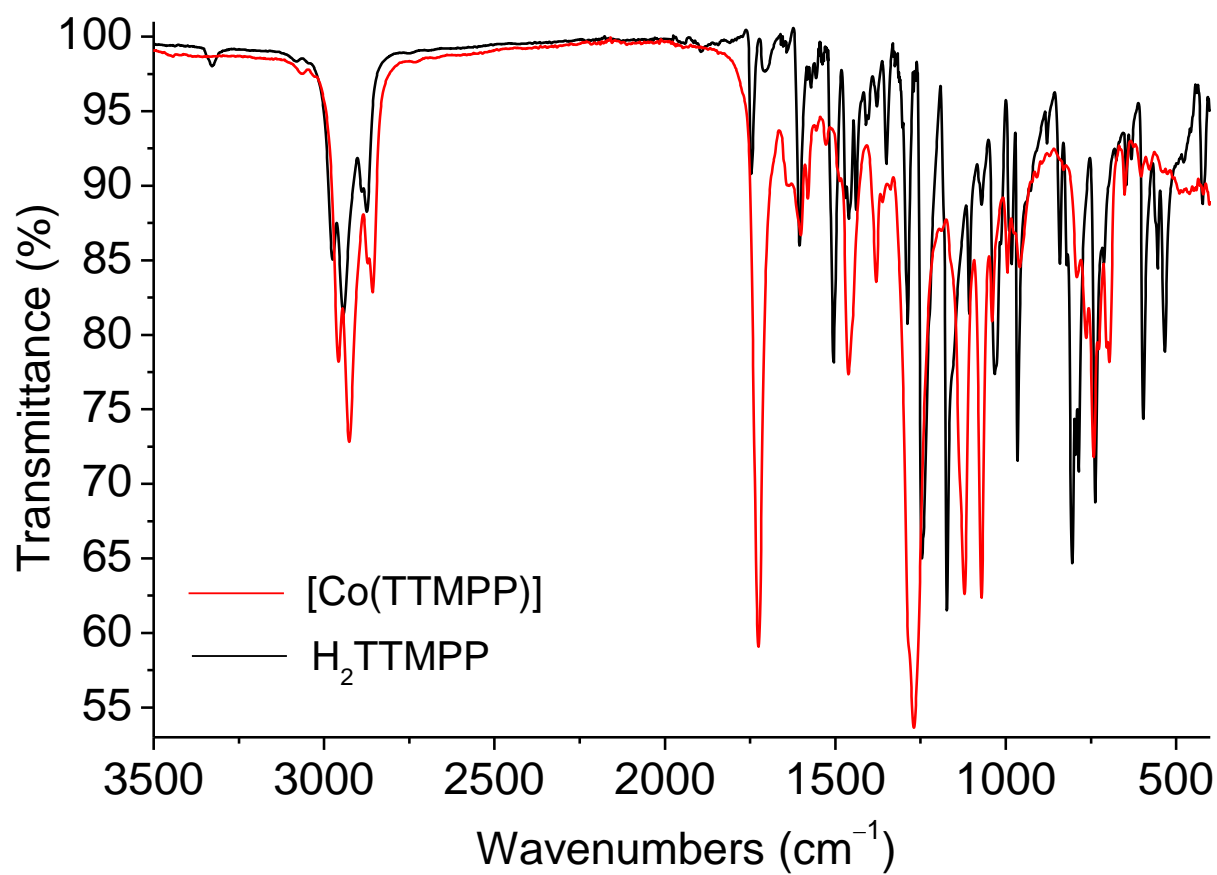


Figure S1. FT-IR spectra of powder samples of H_2TTMPP and $[\text{Co}(\text{TTMPP})]$.

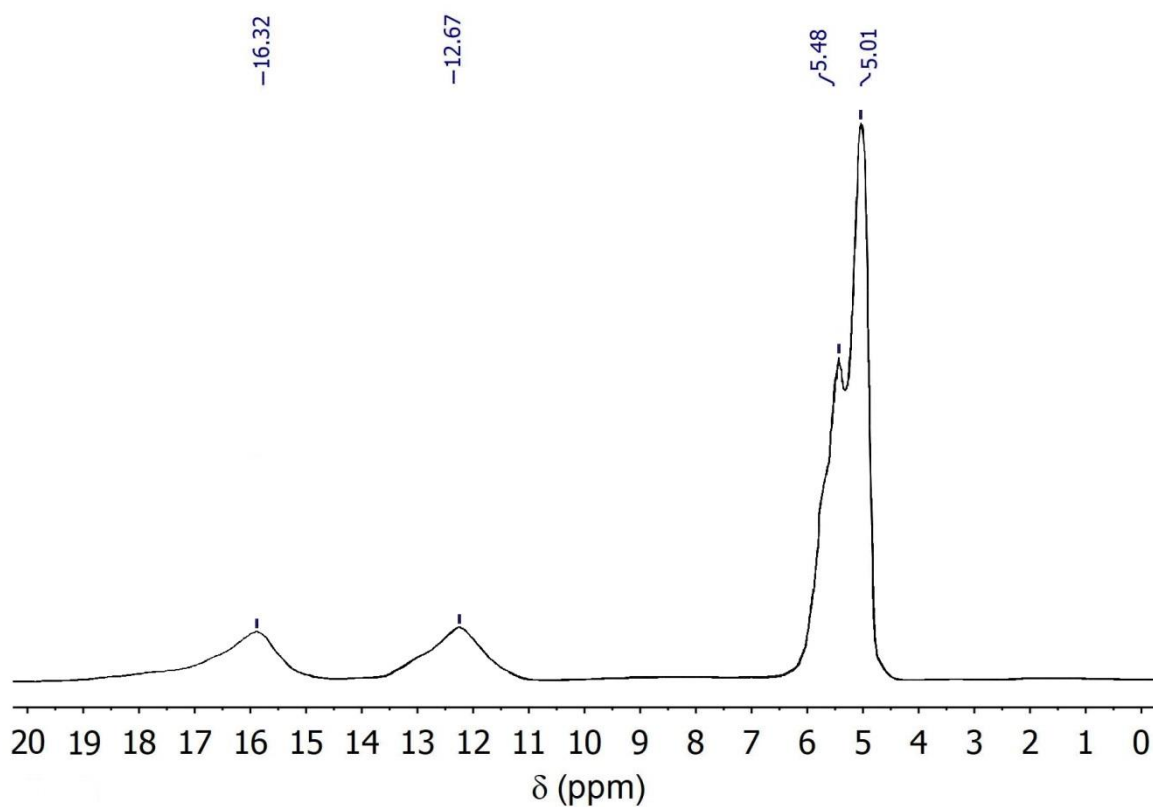


Figure S2. 500 MHz ^1H NMR spectrum of $[\text{Co}(\text{TTMPP})]$ in CDCl_3 .

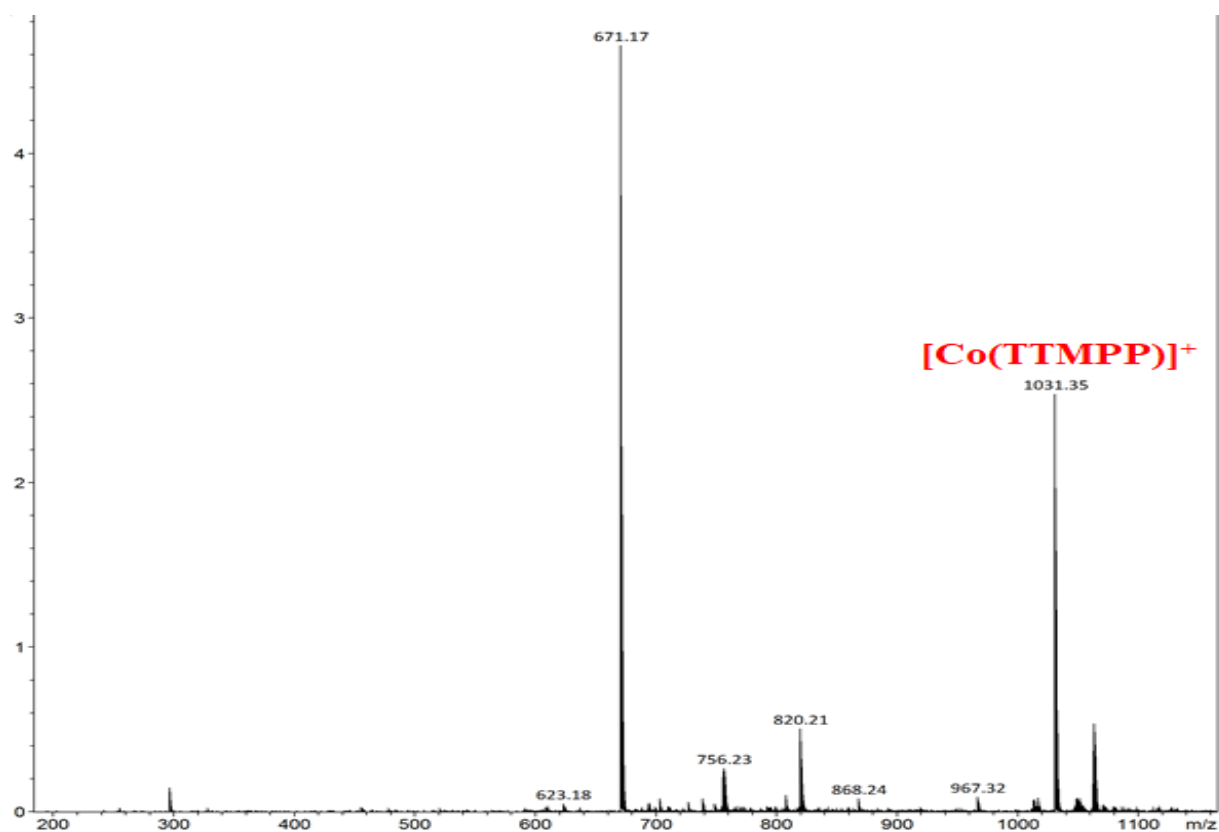


Figure S3. ESI-MS(+) of $[\text{Co}(\text{TTMPP})]$. Marked in red is the mol peak for $[\text{M}]^+$ at 1031.35 (calc. 1031.29) m/z .

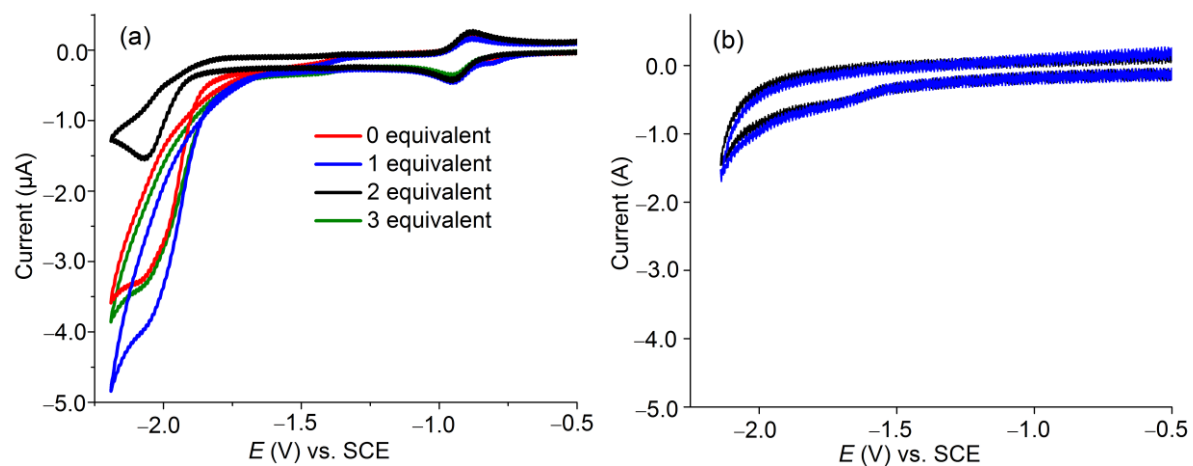


Figure S4. (a): CVs of $[\text{Co}(\text{TTMPP})]$ (1 mM) in the absence (black trace) or in the presence of 1 to 3 eq. TFA in DMF at 250 mV s^{-1} under an Ar atmosphere. (b): Blank test without catalyst (b).

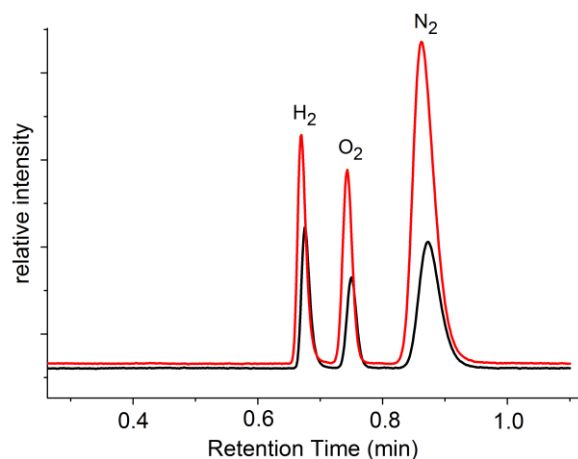


Figure S5. GC trace of evolved H_2 gas from controlled potential electrolysis (CPE) of $[\text{Co}(\text{TTMPP})]$ in $0.1 \text{ M } n\text{-Bu}_4\text{NBF}_4/\text{DMF}$ under an Ar atmosphere with: (red) 3 eq. TFA and (black) with 3 eq. HNEt_3^+ .

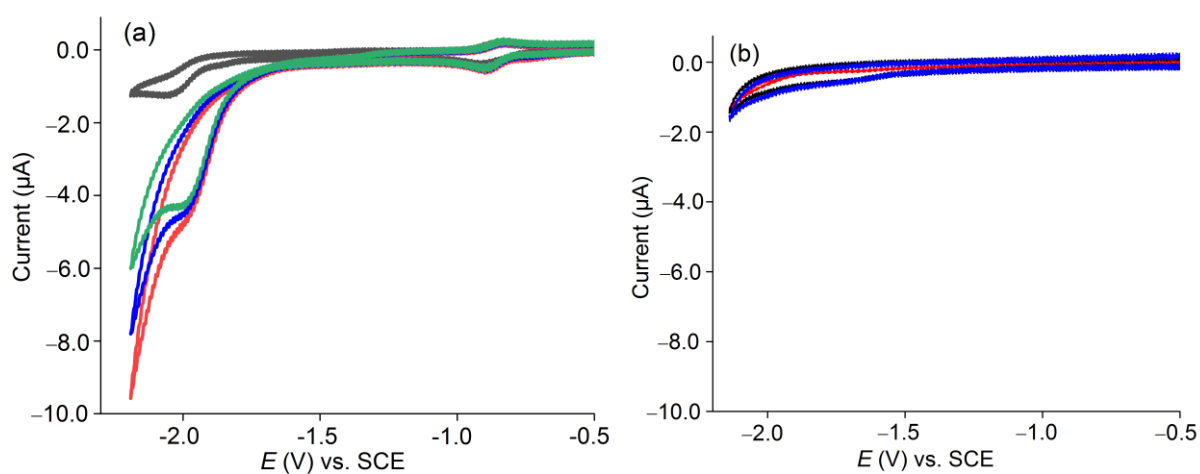


Figure S6. (a): CVs of 1 mM solutions of $[\text{Co}(\text{TTMPP})]$ in $0.1 \text{ M } n\text{-Bu}_4\text{NBF}_4/\text{DMF}$ in the absence of TFE (black: in Ar, green: in CO_2) and in the presence of 1 mM of TFE (blue: in Ar, red: in CO_2). (b) Blank test in the presence of 1 mM of TFE (blue: in Ar, red: in CO_2) without catalyst.

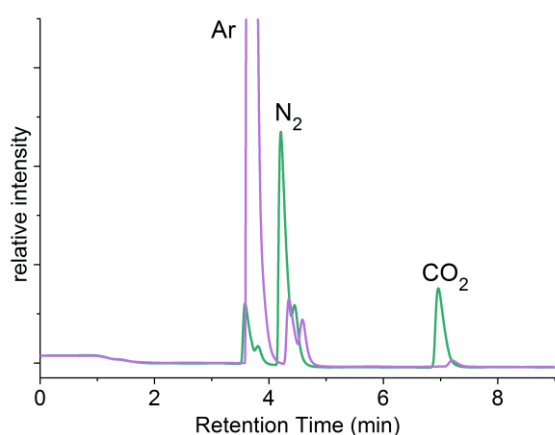


Figure S7. GC trace of evolved hydrogen and CO_2 gas from controlled potential electrolysis (CPE) of $[\text{Co}(\text{TTMPP})]$ in $0.1 \text{ M } n\text{-Bu}_4\text{NBF}_4/\text{DMF}$ under a CO_2 atmosphere with: (purple) 3 eq. PhOH and (green) with 3 eq. TFE.

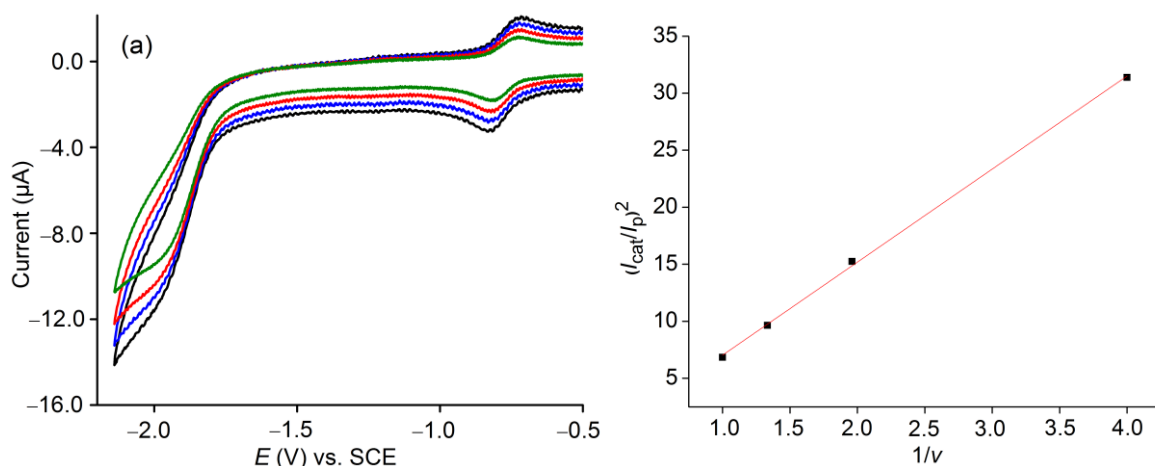


Figure S8. (a): CVs of [Co(TTMPP)] in CO₂-saturated DMF with 0.1 M *n*-Bu₄NBF₄ and 1 eq. TFE, scan rate varying from 250 to 1000 mV·s⁻¹. (b): Plots of $(I_{\text{cat}}/I_p)^2$ values against $1/v$. The catalytic rate constant with 1 eq. TFE was calculated from the slope using equation 3 (see manuscript text).

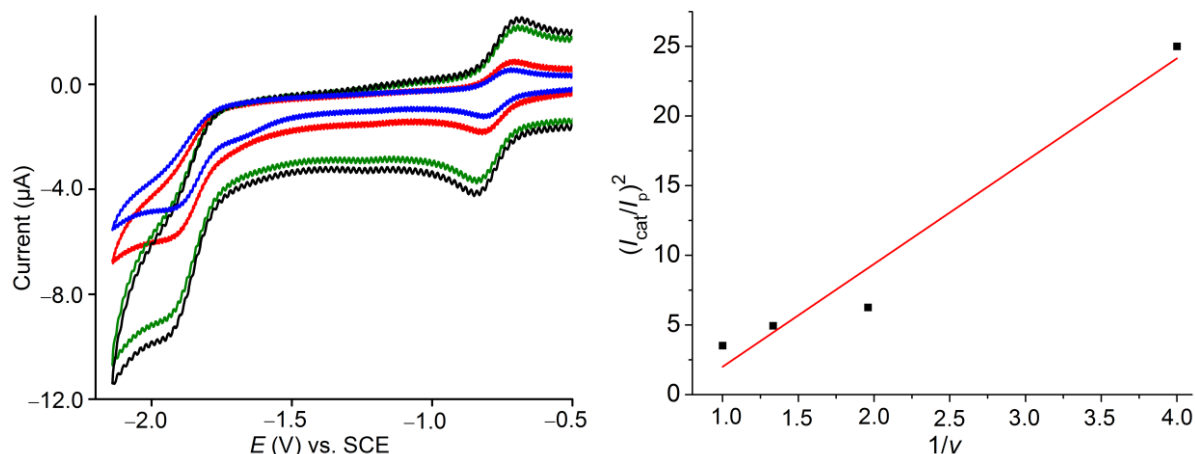


Figure S9. (a): CVs of [Co(TTMPP)] in CO₂-saturated DMF with 0.1 M *n*-Bu₄NBF₄ and 1 eq. PhOH, scan rate varying from 250 to 1000 mV·s⁻¹. (b): Plots of $(I_{\text{cat}}/I_p)^2$ values against $1/v$. The apparent catalytic rate constant of [Co(TTMPP)] with 1 eq. PhOH was calculated from the slope using equation 3 (see manuscript text).

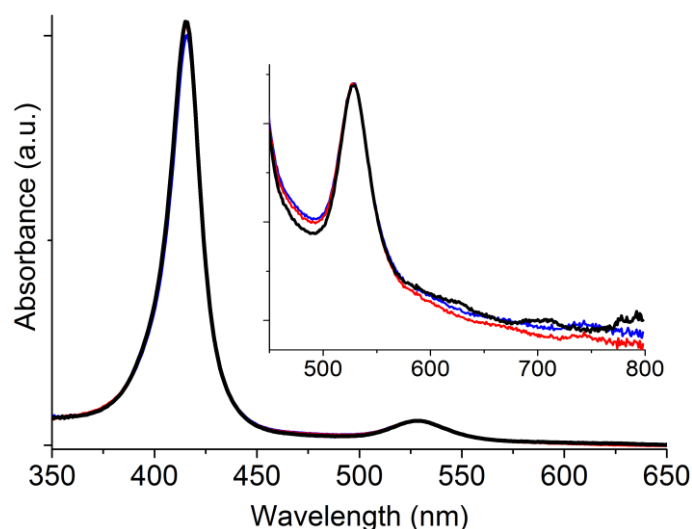


Figure S10. UV-vis absorption spectra of an aliquot of the solution of [Co(TTMPP)] in DMF before (black) and after a controlled-potential electrolysis, with 1 eq. PhOH (red) or with 1 eq. TFE (blue).

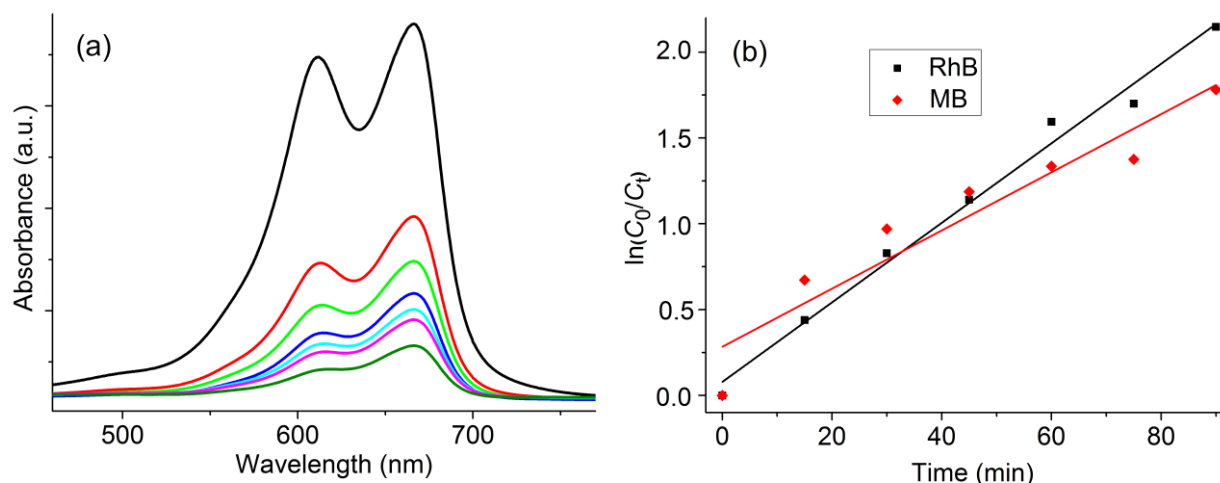


Figure S11. (a): Evolution of the absorbance of MB (over time (black (reference), red (15 min after addition of H₂O₂), green (30 min), blue (45 min), cyan (60 min), pink (75 min), olive (90 min) in H₂O at pH = 7 and 25 °C; 0.024 mmol [Co(TTMPP)], $C_{\text{dye}} = 0.05$ mmol, $C_{\text{H}_2\text{O}_2} = 0.06$ mmol. (b): Changes in $\ln(C_0/C_t)$ over time for both dyes.

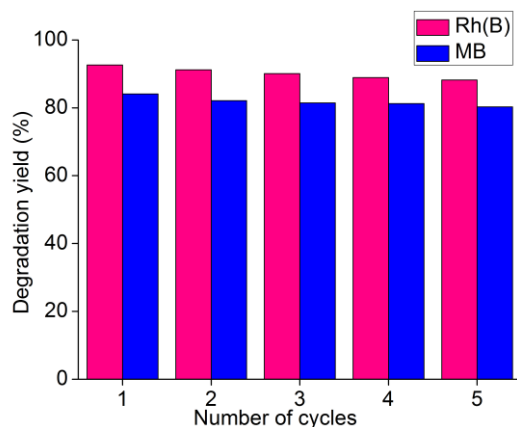


Figure S12. Consecutive runs in the photocatalytic of 0.05 mmol RhB or MB in the presence of 0.024 mmol [Co(TTMPP)] in H₂O at pH = 7 (right) and in the presence 0.06 mmol of H₂O₂. After each cycle the material was recovered and re-used (experimental details in the manuscript).