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Scheme 1. Synthesis routes of the salophen ligands and Co(salophen) complexes.



Figure S1. XRD pattern of BiVO₄ photoelectode.



Figure S2. Contact angle measurements of (a) $BiVO_4$, (b) $Co1/BiVO_4$ and (c) $Co2/BiVO_4$.



Figure S3. XPS spectra of the Co 2p region of Co1/BiVO₄ and Co2/BiVO₄.



Figure S4. UV-Vis spectra of BiVO₄, Co1/BiVO₄ and Co2/BiVO₄.



Figure S5. Applied bias photon-tocurrent efficiencies (ABPE) of (a) $Co1/BiVO_4$ and (b) $Co2/BiVO_4$ in comparison with the bare $BiVO_4$.



Figure S6. Incident photon-to-current efficiencies (IPCE) of (a) $Co1/BiVO_4$ and (b) $Co2/BiVO_4$ in comparison with the bare $BiVO_4$ at 1.23 V vs. RHE.



Figure S7. J–V curves of (a) BiVO₄, (b) Co1/BiVO₄, (c) Co2/BiVO₄ under AM 1.5G simulated sunlight with and without 0.5 M Na₂SO₃.



Figure S8. The relative charge separation efficiencies of Co1/BiVO₄ and Co2/BiVO₄ in comparison with the bare BiVO₄.



Figure S9. Charge transfer efficiencies of different anodes extracted from IMPS analysis.



Figure S10. J–V curves of $Co1/BiVO_4$ after soaking in different solutions overnight.



Figure S11. Oxygen and hydrogen evolution curves of (a) $BiVO_4$, (b) $Co1/BiVO_4$ and (c) $Co2/BiVO_4$ at 1.23V vs RHE.



Figure S12. J–V curves of (a) BiVO₄ and Co(OAc)₂·4H₂O/BiVO₄ electrodes, (b) BiVO₄ and salophen/BiVO₄ under AM 1.5G simulated sunlight.



Figure S13. J–V curves of Co1/BiVO₄ in 0.1 M phosphate buffer solution with and without a certain amount of bpy under AM 1.5G simulated sunlight irradiation.



Figure S14. I-t curves of BiVO₄ (black), Co²⁺/BiVO₄ (red) at 1.23 V vs. RHE.



Figure S15. UV-Vis spectra of Co1 in solution before and after 3 h irradiation



Figure S16. SEM image of Co1/BiVO₄ after 3 h PEC measurement.



Figure S17. Raman spectra of $Co1/BiVO_4$ before and after 3 h PEC measurement.