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

Co1: R = H  
Co2: R = -C(CH₃)₃
Figure S2. Contact angle measurements of (a) BiVO$_4$, (b) Co$_1$/BiVO$_4$ and (c) Co$_2$/BiVO$_4$.

Figure S3. XPS spectra of the Co 2p region of Co$_1$/BiVO$_4$ and Co$_2$/BiVO$_4$. 
Figure S4. UV-Vis spectra of BiVO₄, Co1/BiVO₄ and Co2/BiVO₄.

Figure S5. Applied bias photon-to-current efficiencies (ABPE) of (a) Co1/BiVO₄ and (b) Co2/BiVO₄ in comparison with the bare BiVO₄.
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) BiVO$_4$, (b) Co1/BiVO$_4$, (c) Co2/BiVO$_4$ under AM 1.5G simulated sunlight with and without 0.5 M Na$_2$SO$_3$.

Figure S8. The relative charge separation efficiencies of Co1/BiVO$_4$ and Co2/BiVO$_4$ in comparison with the bare BiVO$_4$. 
Figure S9. Charge transfer efficiencies of different anodes extracted from IMPS analysis.

Figure S10. J–V curves of Co1/BiVO₄ after soaking in different solutions overnight.
Figure S11. Oxygen and hydrogen evolution curves of (a) BiVO₄, (b) Co₁/BiVO₄ and (c) Co₂/BiVO₄ at 1.23V vs RHE.
Figure S12. J–V curves of (a) BiVO$_4$ and Co(OAc)$_2$·4H$_2$O/BiVO$_4$ electrodes, (b) BiVO$_4$ and salophen/BiVO$_4$ under AM 1.5G simulated sunlight.
Figure S13. J–V curves of Co1/BiVO$_4$ 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 BiVO$_4$ (black), Co$^{2+}$/BiVO$_4$ (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/BiVO₄ before and after 3 h PEC measurement.