Supplemental Material

Enabling visible-light water photooxidation by coordinative incorporation of Co(II/III) cocatalytic sites into organic-inorganic hybrids: Quantum-chemical modeling and photoelectrochemical performance

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Table S1. Selected structural parameters of Co and Zn complexes models

$d_{\text{Co(II)}-\text{N}}^{\text{a}}, \text{\AA}$	2.11; 2.66; 2.15; 2.23
$d_{\text{Co(II)}-\text{O}}^{\text{a}}, \text{\AA}$	2.20 (water); 2.06 (Ti–O)
$d_{\text{Co(III)}-\text{N}}^{\text{b}}, \text{\AA}$	1.89; 3.00; 1.85; 2.29
$d_{\text{Co(III)}-\text{O}}^{\text{b}}, \text{\AA}$	1.99 (water); 1.82 (Ti–O)
$d_{\text{Co(III)}-\text{N}}^{\text{c}}, \text{\AA}$	2.22; 2.29; 2.09; 2.22
$d_{\text{Co(III)}-\text{O}}^{\text{c}}, \text{\AA}$	2.06 (water); 1.91 (Ti–O)
$d_{\text{Zn(II)}-\text{N}}, \text{\AA}$	2.25; 2.50; 2.17; 2.17
$d_{\text{Zn(II)}-\text{O}}, \text{\AA}$	2.05 (water); 2.00 (Ti–O)

^a quartet state^b singlet state^c quintet state**Calculated energies of the systems**E(**Ti5M1CoAq**³⁺, quintet) = -9007.830283904 EhE(**Ti5M1CoAq**³⁺, triplet) = -9007.826449840 EhE(**Ti5M1CoAq**³⁺, singlet) = -9007.828701558 EhE(**Ti5M1CoAq**²⁺, quartet) = -9008.262095169 EhE(**Ti5M1CoAq**²⁺, doublet) = -9008.244627742 EhE(**Ti5M1CoAq6**³⁺, singlet) = -9389.882363752 EhE(**Ti5M1CoAq6**³⁺, quintet) = -9389.876757409 EhE(**Ti5M1CoAq6**²⁺, quartet) = -9390.281059421 EhE(**Ti5M1**) = -7549.702785877 EhE([Co(H₂O)₆]²⁺, quartet) = -1840.400973475 EhE([Co(H₂O)₆]³⁺, singlet) = -1839.771526632 EhE([Co(en)₃]²⁺, quartet) = -1953.287109999 EhE([Co(en)₃]³⁺, singlet) = -1952.830864812 Eh

E(en) = -190.358371785 Eh

E(H₂O) = -76.380428035 Eh

(a)

(b)

(c)

(d)

(e)

(f)

(g)

(h)

(i)

Figure S1. DFT-optimized (PBE/def2-TZVPP) geometries of the models. (a) **Ti5M1** (side view); (b) **Ti5M1** (top view); (c) **Ti5M1CoAq²⁺** (side view); (d) **Ti5M1CoAq²⁺** (top view); (e) **Ti5M1CoAq^{5²⁺}**; (f) **Ti5M1CoAq^{5²⁺}**; (g) **Ti5M1CoAq³⁺** (side view); (h) **Ti5M1CoAq³⁺** (top view); (i) **Ti5M1CoAq³⁺**_r (after reaction).