

*Supplementary Information*

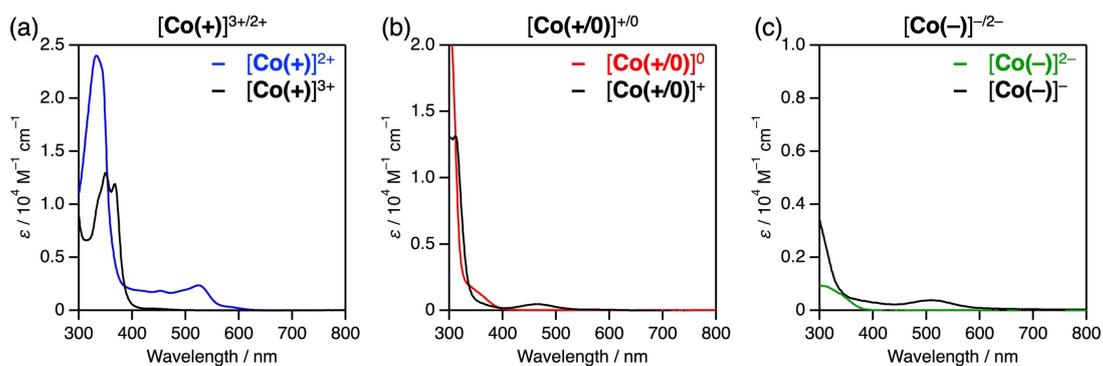
**Active control of forward/backward charge transfer in Z-scheme water splitting: manipulating electrostatic affinity/repulsion between photocatalyst surface and electron mediator**

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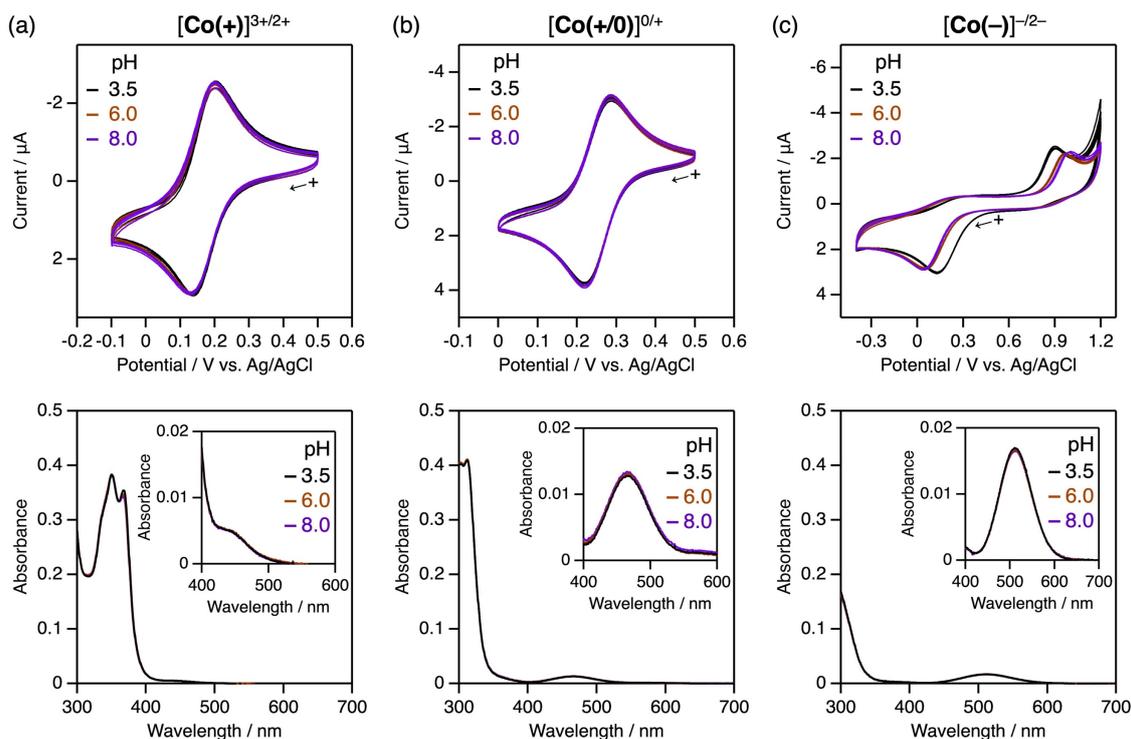
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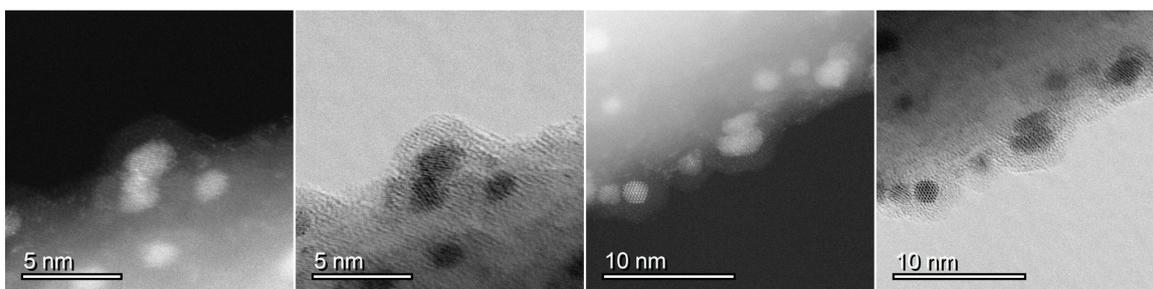
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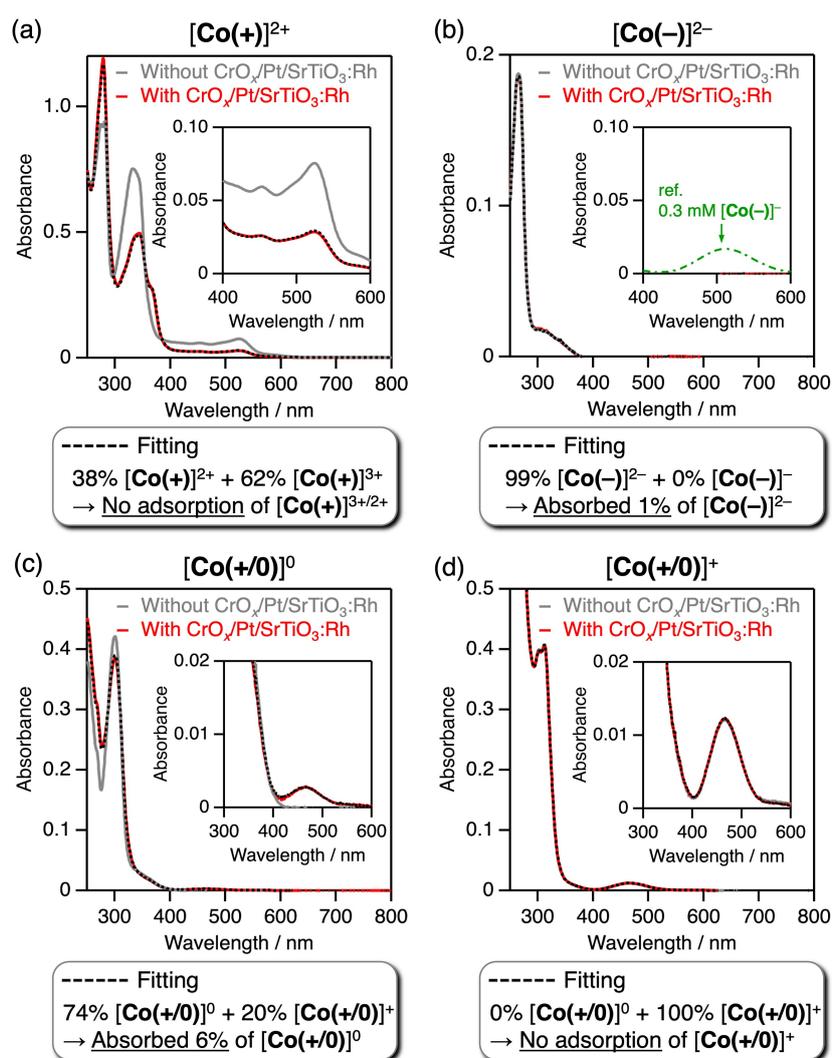
**Fig. S1** UV-vis absorption spectra of (a)  $[\text{Co}(+)]^{3+/2+}$ , (b)  $[\text{Co}(+0)]^{+/0}$ , and (c)  $[\text{Co}(-)]^{-2-}$  in an aqueous solution.



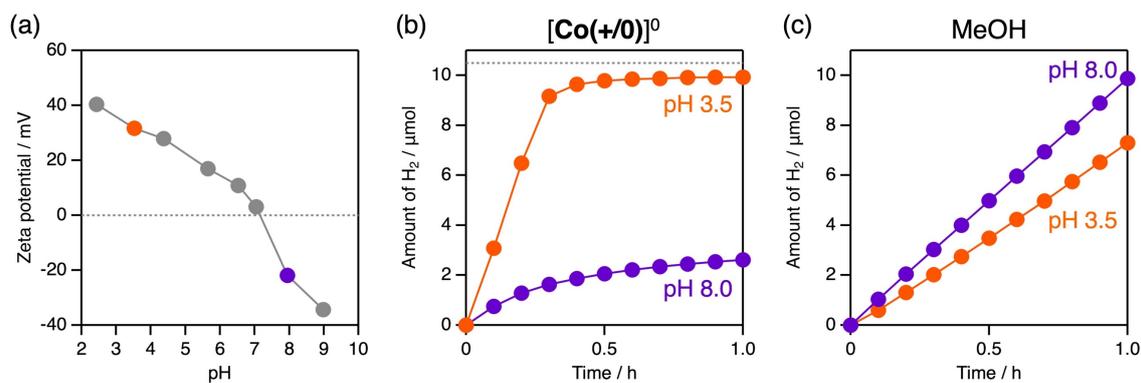
**Fig. S2** pH dependence (at 3.5, 6.0, or 8.0 adjusted with HCl or NaOH) of cyclic voltammograms (5 cycles;  $0.1 \text{ V s}^{-1}$ ) and UV-vis absorption spectra of (a)  $[\text{Co}(+)]^{3+/2+}$ , (b)  $[\text{Co}(+0)]^{+/0}$ , and (c)  $[\text{Co}(-)]^{-2-}$  ( $0.3 \text{ mM}$  each) in  $0.1 \text{ M NaCl}$  aqueous solution.



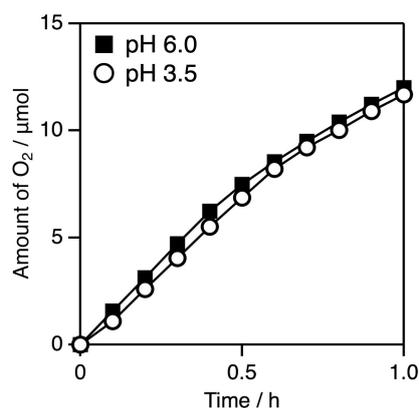
**Fig. S3** TEM images of  $\text{CrO}_x/\text{Pt}/\text{SrTiO}_3:\text{Rh}$ .



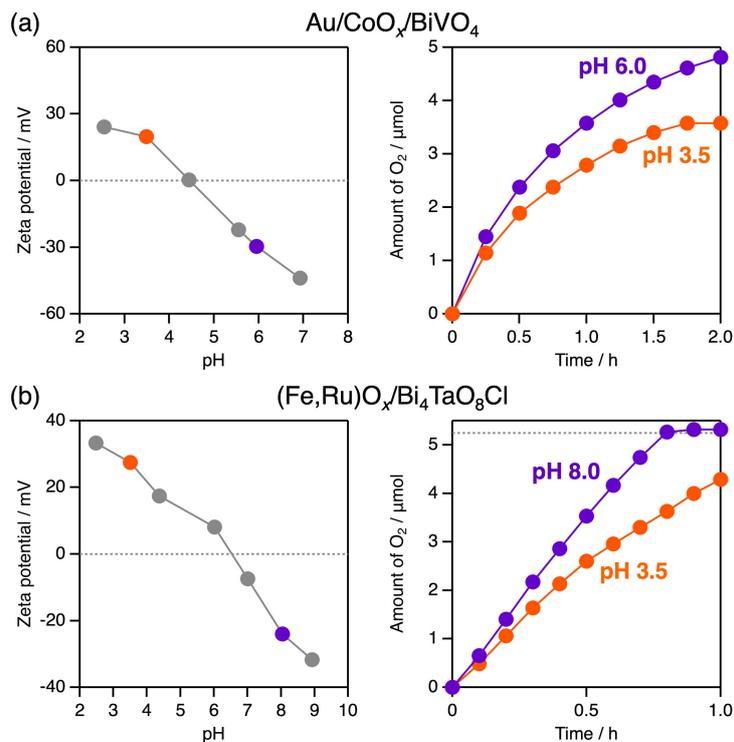
**Fig. S4** UV-vis absorption spectra of (a)  $[\text{Co}(+)]^{2+}$ , (b)  $[\text{Co}(-)]^{2-}$ , (c)  $[\text{Co}(+/0)]^0$ , and  $[\text{Co}(+/0)]^+$  adsorbed by  $\text{CrO}_x/\text{Pt}/\text{SrTiO}_3:\text{Rh}$  (pH 3.5 adjusted with HCl).



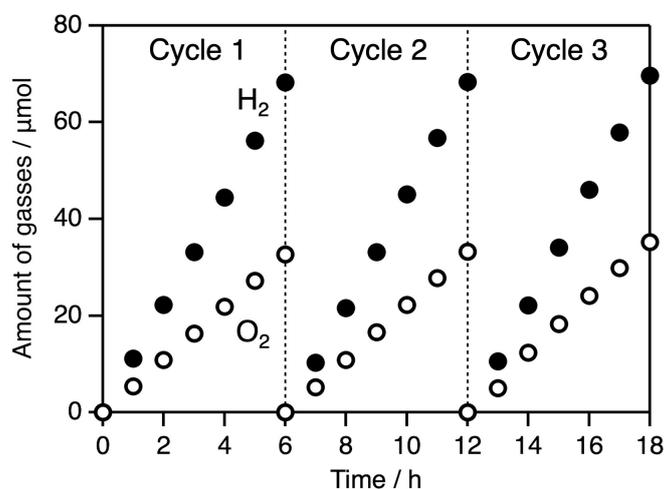
**Fig. S5** (a) pH-dependency of zeta potentials and time courses of H<sub>2</sub> evolution using CrO<sub>x</sub>/Pt/ZrO<sub>2</sub>/TaON (10 mg) in an aqueous solution containing (b) 0.3 mM [Co(+0)]<sup>0</sup> or (c) 10 vol% MeOH aq. (70 mL) as an electron donor at pH 3.5 or pH 8.0 (adjusted with HCl or NaOH) under visible-light irradiation ( $\lambda = 430$  nm).



**Fig. S6** Time courses of O<sub>2</sub> evolution using PtO<sub>x</sub>/WO<sub>3</sub> (35 mg) in an aqueous solution (70 mL) containing AgNO<sub>3</sub> (4 mM) as a sacrificial electron acceptor at pH 3.5 or 6.0 (adjusted with HNO<sub>3</sub> or NaOH) under visible-light irradiation ( $\lambda = 430$  nm).



**Fig. S7** pH-dependency of zeta potentials and time courses of O<sub>2</sub> evolution using (a) Au/CoO<sub>x</sub>/BiVO<sub>4</sub> and (b) (Fe,Ru)O<sub>x</sub>/Bi<sub>4</sub>TaO<sub>8</sub>Cl (each 35 mg) in an aqueous solution (70 mL) containing 0.3 mM [Co(+0)]<sup>+</sup> as an electron acceptor at various pH (adjusted with HCl or NaOH) under visible-light irradiation ( $\lambda = 430$  nm). Note: when using (Fe,Ru)O<sub>x</sub>/Bi<sub>4</sub>TaO<sub>8</sub>Cl, the light intensity was set to 45 mW cm<sup>-2</sup>.



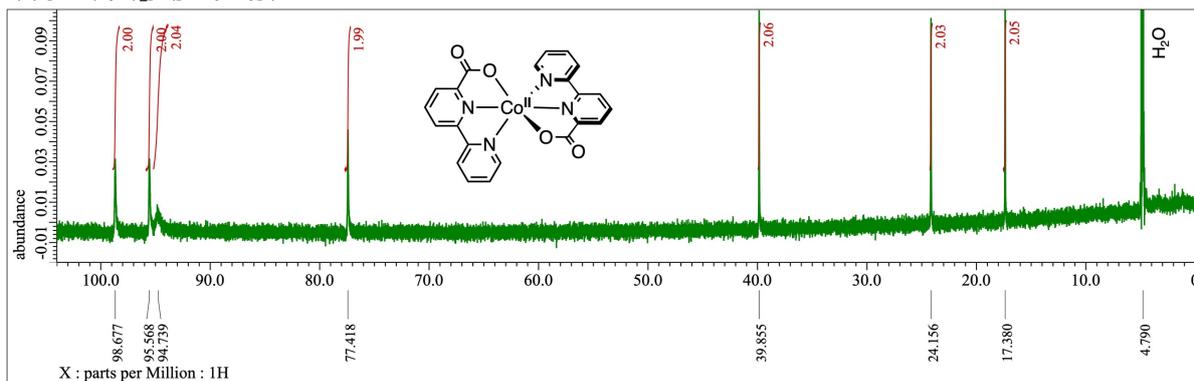
**Fig. S8** Time courses of H<sub>2</sub> and O<sub>2</sub> evolution through Z-scheme water splitting in an aqueous solution (70 mL) containing 0.3 mM [Co(+0)]<sup>+</sup> as an electron mediator using CrO<sub>x</sub>/Pt/SrTiO<sub>3</sub>:Rh and PtO<sub>x</sub>/WO<sub>3</sub> (70 mg each) under visible-light irradiation ( $\lambda = 430$  nm). The pH of the solution was adjusted to 3.5 by HCl.

**Table S1** List of HEPs, OEPs, and electron mediators used for water splitting by a Z-scheme driven by visible light.

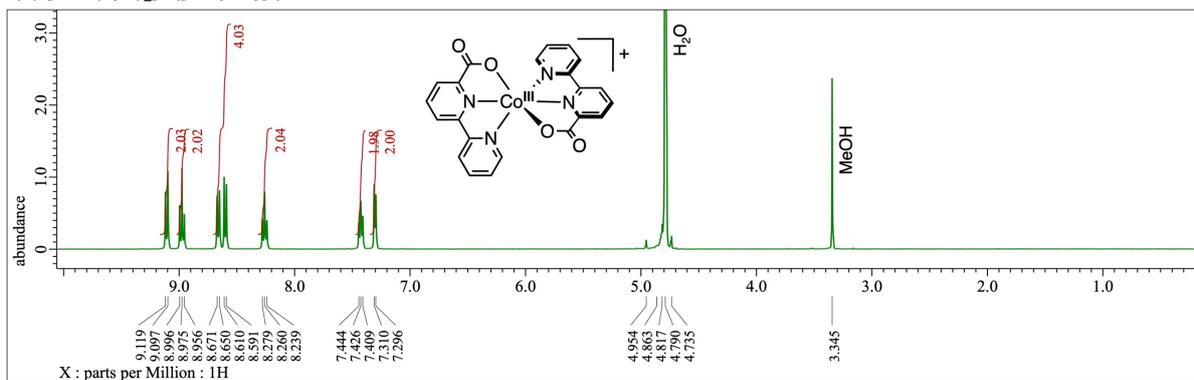
| HEP   | OEP                                       | Electron mediator<br>(concentration)   | AQE              | ref<br>(year)             |
|---|---|--|------------------|---------------------------|
| Pt/SrTiO <sub>3</sub> :Rh                   | WO <sub>3</sub>                           | Fe <sup>3+</sup> /Fe <sup>2+</sup><br>(2 mM)   | 0.5%<br>(420 nm) | S1<br>(2004)              |
| Pt/SrTiO <sub>3</sub> :Rh                   | WO <sub>3</sub>                           | Fe <sup>3+</sup> /Fe <sup>2+</sup><br>(10 mM)  | —                | S2<br>(2009) <sup>a</sup> |
| Au/SrTiO <sub>3</sub> :Rh                   | WO <sub>3</sub>                           | Fe <sup>3+</sup> /Fe <sup>2+</sup><br>(2 mM)   | —                | S3<br>(2008)              |
| Ru/SrTiO <sub>3</sub> :Rh                   | WO <sub>3</sub>                           | Fe <sup>3+</sup> /Fe <sup>2+</sup><br>(2 mM)   | —                | S3<br>(2008)              |
| Ru/SrTiO <sub>3</sub> :Rh                   | WO <sub>3</sub>                           | Fe <sup>3+</sup> /Fe <sup>2+</sup><br>(5 mM)   | —                | S4<br>(2017)              |
| Ru/SrTiO <sub>3</sub> :Rh                   | WO <sub>3</sub>                           | [Co(bpy) <sub>3</sub> ] <sup>3+/2+</sup><br>(1 mM)                                       | —                | S5<br>(2013)              |
| Ru/SrTiO <sub>3</sub> :Rh                   | WO <sub>3</sub>                           | [Co(phen) <sub>3</sub> ] <sup>3+/2+</sup><br>(1 mM)                                      | —                | S5<br>(2013)              |
| Pt/SrTiO <sub>3</sub> :Cr,Ta                | Pt/WO <sub>3</sub>                        | IO <sub>3</sub> <sup>-</sup> /I <sup>-</sup><br>(5 mM)                                   | 1%<br>(420 nm)   | S6<br>(2005)              |
| Pt/SrTiO <sub>3</sub> :Cr,Ta                | PtO <sub>x</sub> /H-Cs-WO <sub>3</sub>    | IO <sub>3</sub> <sup>-</sup> /I <sup>-</sup><br>(5 mM)                                   | 1.5%<br>(420 nm) | S7<br>(2013)              |
| CrO <sub>x</sub> /Pt/SrTiO <sub>3</sub> :Rh | PtO <sub>x</sub> /WO <sub>3</sub>         | IO <sub>3</sub> <sup>-</sup> /I <sup>-</sup><br>(0.1 mM/5 mM)                            | —                | S8<br>(2025) <sup>a</sup> |
| Ru/SrTiO <sub>3</sub> :Rh                   | PtO <sub>x</sub> /WO <sub>3</sub>         | [SiW <sub>11</sub> O <sub>39</sub> Mn(H <sub>2</sub> O)] <sup>5-/6-</sup><br>(1 mM/1 mM) | —                | S9<br>(2016)              |
| Ru/SrTiO <sub>3</sub> :Rh                   | PtO <sub>x</sub> /WO <sub>3</sub>         | [SiVW <sub>11</sub> O <sub>40</sub> ] <sup>5-/6-</sup><br>(0.05 mM)                      | 1.6%<br>(405 nm) | S10<br>(2022)             |
| Ru/SrTiO <sub>3</sub> :Rh                   | Fe-H-Cs-WO <sub>3</sub>                   | VO <sub>2</sub> <sup>+</sup> /VO <sup>2+</sup><br>(2 mM)                                 | —                | S11<br>(2017)             |
| Ru/SrTiO <sub>3</sub> :Rh                   | Fe-H-Cs-WO <sub>3</sub>                   | [Fe(CN) <sub>6</sub> ] <sup>3-/4-</sup><br>(0.5 mM)                                      | —                | S12<br>(2019)             |
| CrO <sub>x</sub> /Pt/SrTiO <sub>3</sub> :Rh | PtO <sub>x</sub> /Fe-H-Cs-WO <sub>3</sub> | [Co(bpc) <sub>2</sub> ] <sup>+0</sup><br>(0.3 mM)  | 2.0%<br>(405 nm) | <b><i>This work</i></b>   |

<sup>a</sup> Separate evolution of H<sub>2</sub> and O<sub>2</sub> in a two-compartment cell.

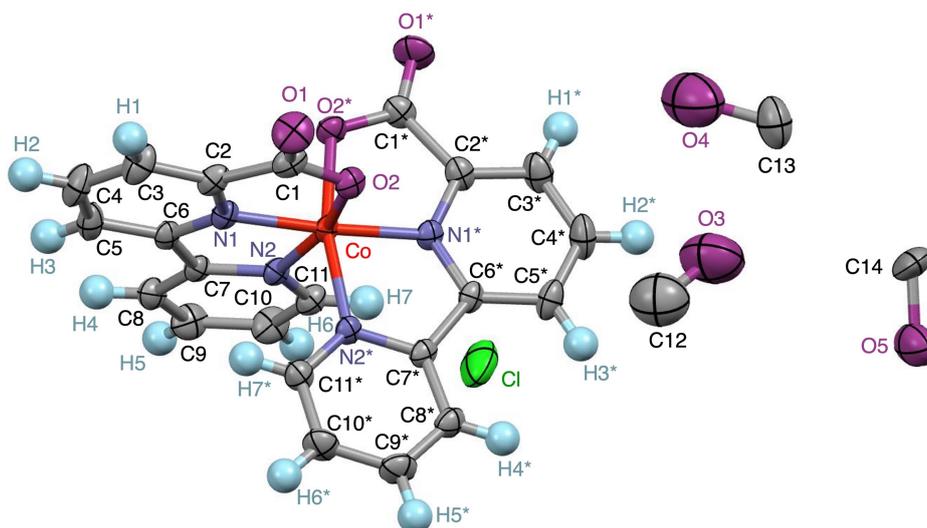
(a)  $[\text{Co}^{\text{II}}(\text{bpc})_2]^0$  ( $[\text{Co}(+/0)]^0$ )



(b)  $[\text{Co}^{\text{III}}(\text{bpc})_2]^+$  ( $[\text{Co}(+/0)]^+$ )



**Fig. S9**  $^1\text{H}$  NMR spectra of (a)  $[\text{Co}(+/0)]^0$  and (b)  $[\text{Co}(+/0)]^+$  in  $\text{D}_2\text{O}$  (400 MHz).

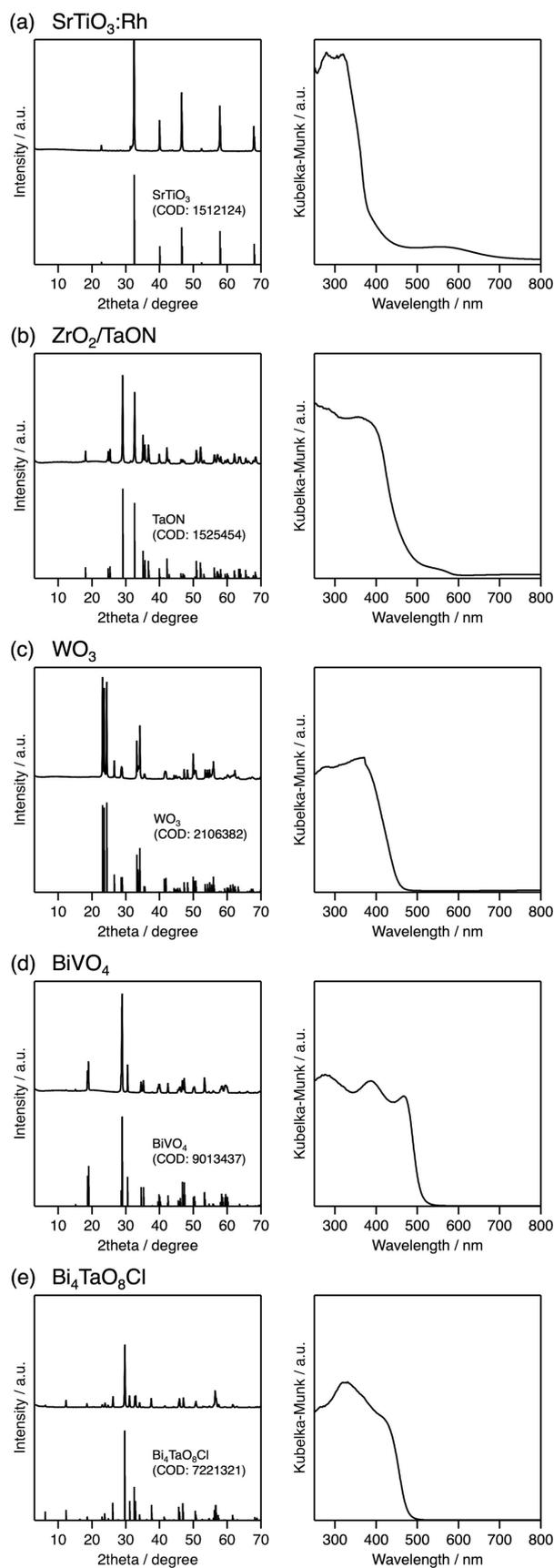


**Fig. S10** Molecular structure of  $[\text{Co}(+/0)]^+\text{Cl}^- \cdot 3\text{MeOH}$  with atomic displacement parameters for C (gray), N (blue), O (magenta), and Co (orange) set at 50% probability. Hydrogen atoms (light blue) are depicted as ball-and-stick models. Hydrogen atoms on the MeOH molecules are omitted for clarity. One  $\text{Cl}^-$  anion and three MeOH molecules exhibit positional disorder (occupancies 0.5/0.5), and only one disorder component is shown for clarity. The symbols \* denote pairs of crystallographically equivalent atoms related by symmetry operations (\* symmetry code:  $1-x, y, 1/2-z$ ).

**Table S2** Crystallographic data for  $[\text{Co}(+/0)]^+$ .

|   | $[\text{Co}(+/0)]^+\text{Cl}^- \cdot 3\text{MeOH}$   |
|---|--|
| Formula   | $\text{C}_{25}\text{H}_{26}\text{ClCoN}_4\text{O}_7$ |
| $F_w$   | 588.88   |
| Crystal size ( $\text{mm}^3$ )                    | $0.37 \times 0.09 \times 0.07$                       |
| Crystal system                                    | monoclinic   |
| Space group                                       | $\text{C}2/c$  |
| $a$ ( $\text{\AA}$ )                              | 17.2915(11)  |
| $b$ ( $\text{\AA}$ )                              | 13.2926(6)   |
| $c$ ( $\text{\AA}$ )                              | 14.2063(8)   |
| $\alpha$ ( $^\circ$ )                             | 90   |
| $\beta$ ( $^\circ$ )                              | 122.833(6)   |
| $\gamma$ ( $^\circ$ )                             | 90   |
| $V$ ( $\text{\AA}^3$ )                            | 2743.7(3)  |
| $T$ (K)   | 143  |
| $Z$   | 4  |
| $D_{\text{calcd}}$ ( $\text{g cm}^{-3}$ )         | 1.426  |
| $F(000)$  | 1216.0   |
| $\mu$ (Mo $\text{K}\alpha$ ) ( $\text{cm}^{-1}$ ) | 7.72   |
| Measured reflections                              | 10836  |
| Unique reflections                                | 3090   |
| Refined parameters                                | 209  |
| GOF on $F^2$                                      | 1.125  |
| $R_1^a$   | 0.0746   |
| $wR_2$ (all data) <sup>b</sup>                    | 0.2182   |

<sup>a</sup>  $R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$ . <sup>b</sup>  $wR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2]}{[\sum w(F_o^2)^2]}^{1/2}$ .



**Fig. S11** XRD patterns with reported simulations<sup>S13-17</sup> and diffuse reflectance spectra of (a)  $\text{SrTiO}_3\text{:Rh}$ , (b)  $\text{ZrO}_2/\text{TaON}$ , (c)  $\text{WO}_3$ , (d)  $\text{BiVO}_4$ , and (e)  $\text{Bi}_4\text{TaO}_8\text{Cl}$ .

## References

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