# **Supporting Information**

## Halogenated earth abundant metalloporphyrins as photostable sensitizers for visible-light-driven water oxidation in neutral phosphate buffer solution

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### **Experimental Details**

**Electrochemical measurements:** The electrochemical measurements were performed with a potentiostat/galvanostat MacLab model ML160 controlled by NOVA software (version 1.8 for Windows) using a conventional single-compartment three-electrode cell with a platinum working electrode, a silver wire as reference electrode, and a platinum wire as counter electrode. All measurements in deaerated dichloromethane were carried out with freshly distilled solvent with a solute concentration of ca. 1.0 mM in the presence of tetrabutylammonium hexafluorophosphate, NBu<sub>4</sub>PF<sub>6</sub> (0.1 M) as supporting electrolyte and a scan rate of 100 mVs<sup>-1</sup> cyclic voltammetry. Ferrocene was added at the end of the experiment as internal standard for calibrating redox potentials. The ferrocene/ferrocenium redox couple (Fc/Fc<sup>+</sup>) with half-wave potential  $E_{1/2}$  is equivalent to 0.690 V vs NHE in dichloromethane. For the aqueous cyclic voltammetry (scan rate 100 mV s<sup>-1</sup>) and differential pulse voltammetry (scan rate 5 mV s<sup>-1</sup>) measurements, a three-electrode cell setup was used with glassy carbon working electrode, Pt wire counter electrode and Ag/AgCl, 3 M KCl reference electrode. The electrolyte was a 0.2 M, KH<sub>2</sub>PO<sub>4</sub>/K<sub>2</sub>HPO<sub>4</sub> (pH 7.0) buffer solution.

**Photophysical measurements:** UV/Vis absorption spectra were measured on a HP/Agilent 8453 UV-Vis spectrophotometer using 10 mm path-length quartz cuvettes at room temperature.

Room temperature emission spectra were measured on a Spex Fluorolog 3 spectrometer, equipped with double grating monochromators in the excitation and emission channels. The excitation light source was a 450 W Xe lamp and the detector a Peltier cooled R636-10 (Hamamatsu) photomultiplier tube. All sample solutions were degassed by argon purging for ca.10 mins.

Triplet state lifetimes were determined by means of nanosecond time-resolved absorption spectroscopy using an EKSPLA NT342B laser system in which the third harmonic of a Nd:YAG laser system was used to pump an OPO ( $\lambda_{ex} = 540$  nm, pulse width ~5 ns, 2 mJ per pulse). The setup has been described in more detail in ref. S1.

Time-resolved emission measurements were performed on a picosecond single photon counting

setup. The excitation wavelength of 500 nm was generated by frequency doubling of the output of a tunable Ti:sapphire laser (Chameleon Ultra, Coherent). The repetition rate is decreased to 8 MHz using a pulse picker (Pulse Select, APE). After second harmonic generation (SHG), a dichroic mirror is used to separate the doubled light which is directed to the sample. Fundamental light is guided via a delay line to a fast photodiode (PD) and used as a reference pulse. The emission is collected with magic angle (54.7°) polarization and focused onto a red sensitive multichannel plate photomultiplier tube (Hamamatsu R3809U-51) through a single-grating monochromator (Oriel Cornerstone 260). Although the excitation source produces sub-picosecond pulses, the electronics and the detector cause a broadening of the signal and are the limiting factor of the time resolution. The overall instrument response function (IRF) is ~20 ps (FWHM) measured from a dilute scattering solution (Ludox) at the excitation wavelength.

**Light-driven oxygen evolution measurements:** the oxygen evolution was analyzed by means of a Clark-type oxygen electrode (Hansatech Instruments, DW2/2 unit with an S1 electrode) in liquid phase. A 120 W halogen lamp was used as the excitation light source. The reaction vessel was cooled with flowing water adjusted to T = 20 °C. The signal was calibrated using air saturated aqueous solutions ( $[O_2] = 276.3 \mu M$ , T = 20 °C) and N<sub>2</sub>-purged solutions ( $[O_2] \approx 0$ ). Before each measurement, the photocatalytic solutions were also purged with N<sub>2</sub> to provide an oxygen-free solution. In order to confirm the oxygen generation coming from light driven water oxidation, the illumination starts after ~2 minutes of flat zero  $[O_2]$  signal in dark. The turnover number (TON) of oxygen generation was determined by the ratio of the mole number of O<sub>2</sub> related to mole number of catalyst at a given time. The maximum turnover frequency (TOF<sub>max</sub>) was determined at the steepest slope of the oxygen evolution curve.

#### Synthesis of metalloporphyrins and water oxidation catalyst

The products were identified by <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectroscopy (Bruker AMX 400) and field desorption mass spectrometry (FD-MS), carried out on an AccuTOF GC v 4g, JMS-T100GCV mass spectrometer equipped with FD Emitter with an emitter voltage of 10 kV. Infra-red spectra were recorded on a Bruker IR spectrometer model  $\alpha$ -Platinum ATR using neat solid samples.



Scheme S1. Synthetic routes to porphyins and halogenated porphyins.

- (1) 5,10,15,20-Tetrakis(4-methoxycarbonylphenyl)porphyrin (H<sub>2</sub>-TCMePP).
- (2) Cu(II)-5,10,15,20-tetrakis(4-methoxycarbonylphenyl)porphyrin (Cu-TCMePP)
- (3) Ni(II)-5,10,15,20-tetrakis(4-methoxycarbonylphenyl)porphyrin (Ni-TCMePP)
- (4) Cu(II)-5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (Cu-TCPP)
- (5) Ni(II)-5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (Ni-TCPP)

The synthesis procedures of these compounds followed the method in ref. S2.

The synthesis procedures of halogenated (metallo-)porphyrins followed the methods in ref. S2 and S3.

# (6) 7,8,17,18-tetra-β-chloro-5,10,15,20-tetrakis(4-methoxycarbonylphenyl)porphyrin (H<sub>2</sub> TCITCMePP)

The synthesis of H<sub>2</sub>-TCITCMePP was performed according to the method in ref. S3.

A mixture of  $H_2$ -TCMePP (600 mg, 0.70 mmol) and 5.4 equiv of N-chlorosuccinimide (510 mg, 3.83 mmol) in 1,1,2,2-tetrachloroethane (120 mL) was heated to 100 °C for 18 h under N<sub>2</sub> atmosphere. The solution was cooled and the reaction mixture was concentrated under reduced pressure. The black product was precipitated by addition of methanol (100 mL). The precipitate was filtered and washed with methanol. The resultant residue was dissolved in chloroform and purified by column chromatography on silica gel with chloroform. The collecting product in chloroform solution was concentrated under reduced pressure. The product was recrystallized by slow addition of methanol to the concentrated chloroform solution to afford H<sub>2</sub>-TCITCMePP (551 mg, 79 %

yield) as a dark-purple powder. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) = 8.81 (s, 4H), 8.44 (d, 8H, J = 8 Hz), 8.27 (d, 8H, J = 8 Hz), 4.11 (s, 12H). FD-MS (10 kV): m/z calcd 984.1101 for C<sub>52</sub>H<sub>34</sub>Cl<sub>4</sub>N<sub>4</sub>O<sub>8</sub>, found 984.1113. FTIR: 2944 (w), 1719 (s), 1604 (m), 1537 (m), 1398 (m), 1269 (s), 1106 (m), 1014 (s), 997 (m), 865 (s), 762(s), 714 (m) cm<sup>-1</sup>.

### (7) Cu(II)-7,8,17,18-tetra-β-chloro-5,10,15,20-tetrakis(4-methoxycarbonylphenyl)porphyrin (Cu-TCITCMePP)

A mixture of H<sub>2</sub>-TCITCMePP (400 mg, 0.41 mmol) and excess copper(II) acetate (296 mg, 1.62 mmol) in DMF (120 mL) was heated to 140 °C for 4 h under N<sub>2</sub> atmosphere. The solution was cooled and the reaction mixture was concentrated under reduced pressure. The product was precipitated by addition of methanol (100 mL). The precipitate was filtered and washed with methanol. The resultant residue was dissolved in chloroform and purified by column chromatography (silica gel, chloroform) to afford **Cu-TCITCMePP** (405 mg, 95 % yield). FD-MS (10 kV): m/z calcd 1045.0241 for  $C_{52}H_{32}Cl_4CuN_4O_8$ , found 1045.0572. FTIR: 2994 (w), 1720 (s), 1606 (m), 1434 (m), 1401 (m), 1270 (s), 1174 (m), 1098 (m), 1059 (m), 1010 (s), 866 (m), 761 (s), 711 (m) cm<sup>-1</sup>.

### (8) Ni(II)-7,8,17,18-tetra-β-chloro-5,10,15,20-tetrakis(4-methoxycarbonylphenyl)porphyrin (Ni-TCITCMePP)

A mixture of **H<sub>2</sub>-TCITCMePP** (400 mg, 0.41 mmol) and excess nickel(II) acetate tetrahydrate (405 mg, 1.62 mmol) in DMF (120 mL) was heated to 140 °C for 4 h under N<sub>2</sub> atmosphere. The solution was cooled and then the reaction mixture was concentrated under reduced pressure. The product was precipitated by addition of methanol (100 mL). The precipitate was filtered and washed with methanol. The resultant residue was dissolved in chloroform and purified by column chromatography (silica gel, chloroform) to afford **Ni-TCITCMePP** (390 mg, 92 % yield) as red powder. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) = 8.52 (s, 4H), 8.29 (d, 8H, J = 8 Hz), 7.90 (d, 8H, J = 8 Hz), 4.04 (s, 12H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) = 168.4, 145.0, 141.7, 135.1, 132.1, 130.2, 128.3, 120.8, 51.6; FD-MS (10 kV): m/z calcd 1040.0298 for C<sub>52</sub>H<sub>32</sub>Cl<sub>4</sub>Ni N<sub>4</sub>O<sub>8</sub>, found 1040.0305. FTIR: 2949 (w), 1720 (s), 1606 (m), 1565 (m), 1511 (m), 1443 (m), 1401 (m), 1271 (s), 1099 (m), 1064 (m), 1014 (s), 821 (s), 741 (m), 714 (m) cm<sup>-1</sup>.

# (9) Cu(II)-7,8,17,18-tetra-β-chloro-5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (Cu-TCITCPP)

To a well-stirred mixture of **Cu-TCITCMePP** (350 mg, 0.34 mmol) in 5 % MeOH solution in THF (80 mL) powdered KOH (751 mg, 13.4 mmol) was added. The mixture was stirred at r.t. for 4 h, and then several drops of water were added to dissolve the precipitate formed. The solution was stirred for 1h and then THF was removed by rotary evaporation. The homogeneous solution was acidified with 1M HCl until no further precipitate was observed. The precipitated was collected by

filtration, washed with water and dried in vacuum at 50 °C overnight. The red powder of **Cu-TCITCPP** was obtained (280 mg, 85 % yield). FD-MS (10 kV): m/z calcd 988.9615 for  $C_{48}H_{24}Cl_4CuN_4O_8$ , found 987.9547 [M–H]<sup>-</sup>. FTIR: 2968 (w), 1696 (s), 1692 (m), 1606 (s), 1531 (w), 1511 (m), 1403 (s), 1273 (s), 1175 (m), 1059 (s), 1010 (s), 792 (s), 764 (s) cm<sup>-1</sup>.

# (10) Ni(II)-7,8,17,18-tetra-β-chloro-5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (Ni-TCITCPP)

To a well-stirred mixture of **Ni-TCITCMePP** (350 mg, 0.34 mmol) in 5 % MeOH solution in THF (80 mL) KOH (754 mg, 13.4 mmol) was added. The mixture was stirred at r.t. for 4 h, and then several drops of water were added to dissolve the precipitate formed. The solution was stirred for 1h and then THF was removed by rotary evaporation. The homogeneous solution was acidified with 1M HCl until no further precipitate was observed. The precipitated was collected by filtration, washed with water and dried in vacuum oven at 50 °C overnight. The red-brown powder of **Ni-TCITCPP** was obtained (296 mg, 87 % yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) = 8.64 (s, 4H), 8.30 (d, 8H, J = 8 Hz), 8.03 (d, 8H, J = 8 Hz). FD-MS (10 kV): m/z calcd 983.9672 for C<sub>48</sub>H<sub>24</sub>Cl<sub>4</sub>N<sub>4</sub>NiO<sub>8</sub>, found 982.9599 [M–H]<sup>-</sup>. FTIR: 2958 (w), 1692 (s), 1606 (s), 1566 (m), 1404 (s), 1309 (s), 1239 (s), 1174 (s), 1097 (m), 1064 (s), 1015 (s), 867 (m), 833 (m), 788 (s), 739 (m) cm<sup>-1</sup>.

#### Co<sub>4</sub>O<sub>4</sub> cubane complex; Co<sub>4</sub>O<sub>4</sub>(OAc)<sub>4</sub>(py)<sub>4</sub>

The synthesis procedure followed the method of ref. S4.



**Figure S1.** Emission spectra of metalloporphyrins upon 540 nm excitation (deoxygenated by Ar purging) at room temperature (21°C). (a) Cu-TCMePP, Cu-TCITCMePP in dichloromethane. (b) Cu-TCPP, and Cu-TCITCPP in phosphate buffer (0.1 M, pH 7.0). For the corresponding Niporphyrins no emission was detected.



**Figure S2.** Nanosecond transient absorption spectra of Cu(II)-TCMePP (50  $\mu$ M) in deaerated CH<sub>2</sub>Cl<sub>2</sub>. Time steps between successive spectra 5 ns. The time trace (inset) is monitored at a triplet-triplet absorption band ranging from 430 to 460 nm and the transient absorption as function of time fitted with a mono-exponential decay function.



**Figure S3.** (a) Nanosecond transient absorption spectra of Cu(II)-TCPP in deaerated phosphate buffer (0.1 M, pH 7.0). Time steps between successive spectra 1 ns. (b) The time trace is monitored at the triplet-triplet absorption band ranging from 394 to 428 nm and the transient absorption as function of time fitted with a bi-exponential decay function for the range from 12 to 26 ns. Decay times of 14 ns (minor) and 1.2 ns (major component) are obtained.



**Figure S4.** Nanosecond transient absorption kinetics (a) Cu(II)-TCITCMePP in deaerated  $CH_2Cl_2$ . (b) Cu(II)-TCITCPP, (c) Ni(II)-TCPP and (d) Ni(II)-TCITCPP in deaerated phosphate buffer (0.1 M, pH 7.0). Herein, the transient absorption spectra only show the decay from maximum intensity in steps of 2 ns.



**Figure S5.** Time resolved emission of (a) Cu(II)-TCMePP, (b) Cu(II)-TCITCMePP in deaerated CH<sub>2</sub>Cl<sub>2</sub>, (c) Cu(II)-TCPP and (d) Cu(II)-TCITCPP in deaerated phosphate buffer (0.1 M, pH 7.0). Excitation at 500 nm ( $\sim$  20 ps FWHM).

Compd.	$\tau_1$ (ns)	A <sub>1</sub>	$\tau_2$ (ns)	A <sub>2</sub>	$\tau_3(ns)$	A <sub>3</sub>	$\lambda_{(det)}(nm)$
(a) Cu(II)-TCMePP	28	0.39	1.5	0.35	0.04	0.26	800
(b) Cu(II)-TCITCMePP	0.94	0.30	0.40	0.70			700
(c) Cu(II)-TCPP	12	0.35	0.26	0.65			850
(d) Cu(II)-TCITCPP	0.80	0.24	0.05	0.76			850

**Table S1.** Emission lifetimes  $\tau$  and amplitudes A from the multi-exponential fitting of the time resolved emission data in Figure S5.  $\lambda_{(det)}$  is the detection wavelength.



**Figure S6.** Emission spectra of Cu(II)-TCITCPP ( $1.0 \times 10^{-4}$  M) with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> upon 540 nm excitation in deaerated phosphate buffer (0.1 M, pH 7.0).



**Figure S7.** Cyclic voltammograms (CV) for 1 mM of (a) Cu-TCPP, (b) Cu-TCITCPP, (c) Ni-TCPP, (d) Ni-TCITCPP in the  $KH_2PO_4/K_2HPO_4$  (0.2 M, pH 7.0) electrolyte aqueous solution.



**Figure S8.** Differential pulse voltammograms (DPV) for 1 mM of (a) Cu-TCPP, (b) Cu-TCITCPP, (c) Ni-TCPP, (d) Ni-TCITCPP in the  $KH_2PO_4/K_2HPO_4$  (0.2 M, pH 7.0) electrolyte aqueous solution.



**Figure S9.** Cyclic voltammograms of water-oxidation catalysts of  $Co(NO_3)_2$  (2 mM) and electrolyte background (black curves) in 0.2 M KPi. Herein, the potential was measured against Ag/AgCl reference and E(NHE) = E(Ag/AgCl) + 0.197 V.



**Figure S10.** UV-vis spectra and photographs taken before and after illumination of photocatalytic solutions of (a) Cu(II)-TCPP with Co(NO<sub>3</sub>)<sub>2</sub> at pH 7.0; (b) Cu(II)-TCITCPP with Co(NO<sub>3</sub>)<sub>2</sub> at pH 7.0; (c) Ni(II)-TCPP with Co<sub>4</sub>O<sub>4</sub>-cubane at pH 7.0; (d) Ni(II)-TCITCPP with Co<sub>4</sub>O<sub>4</sub>-cubane at pH 7.0. All solutions are diluted by a factor of 100 for measuring the spectra in a 1 cm path length cell.



**Figure S11.** (a) UV-Vis spectra and (b) solar irradiance photon flux AM1.5G (black) plotted with photon absorption rate for 2  $\mu$ M solution of Cu(II)-TCITCMePP (blue), Ni(II)-TCITCMePP (magenta), Pt(II)-TCMePP (yellow), Ru(bpy)<sub>3</sub><sup>2+</sup> (red), chlorophyll *a* (green) in a 1-cm path length cell.

#### References

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