Supplementary Materials: Effect of Porphyrin Molecular Structure on Water Splitting Activity of a KTaO₃ Photocatalyst

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1H- and 13C-NMR data of precursor compounds of Dye 3-6.

5,10,15,20-tetrakis(4-propoxyphenyl)porphyrin (precursor compound of Dye 3)
Following the general procedure gave a purple solid (265 mg, 61%). δH (400MHz, CDCl3): 8.87 (s, 8H), 8.11 (d, J = 8.48 Hz, 8H), 7.28 (d, J = 8.56 Hz, 8H), 4.22 (dd, J = 13.04, 13.04 Hz, 8H), 2.04 (ddd, J = 28.04, 28.04, 7.04 Hz, 8H), 1.21 (t, J = 14.84 Hz, 12H), -2.75 (s, 2H); δC (100 MHz, CDCl3): 158.97, 135.60, 134.49, 119.81, 112.72, 69.83, 22.85, 10.74, MS (MALDI) [M+H]+ 846.4

5,10,15,20-tetrakis(4-hexyloxyphenyl)porphyrin (precursor compound of Dye 4)
Following the general procedure gave a purple solid (218 mg, 42%). δH (400MHz, CDCl3): 8.86 (s, 8H), 8.10 (d, J = 8.52 Hz, 8H), 7.27-7.25 (overlapped with CHCl3, 8H), 4.24 (dd, J = 12.96, 12.96 Hz, 8H), 1.98 (ddd, J = 21.84, 21.84, 6.68 Hz, 8H), 1.66-1.59 (m, 12H), 1.47-1.43 (m, 12H), 0.99 (t, J = 13.92 Hz, 12H), -2.75 (s, 2H); δC (100 MHz, CDCl3): 158.96, 135.60, 134.49, 119.81, 112.70, 68.33, 31.74, 29.49, 25.93, 22.72, 14.13; MS (MALDI) [M+H]+ 1014.6

5,10,15,20-tetrakis(4-dodecyloxyphenyl)porphyrin (precursor compound of Dye 5)
Following the general procedure gave a purple solid (498 mg, 71%). δH (400MHz, CDCl3): 8.86 (s, 8H), 8.10 (d, J = 8.56 Hz, 8H), 7.28-7.25 (overlapped with CHCl3, 8H), 4.25 (dd, J = 12.96, 12.96 Hz, 8H), 1.98 (ddd, J = 21.28, 21.28, 6.48 Hz, 8H), 1.66-1.58 (m, 12H), 1.50-1.27 (m, 12H), 0.88 (t, J = 13.68 Hz, 12H), -2.75 (s, 2H); δC (100 MHz, CDCl3): 158.97, 135.60, 134.47, 119.81, 112.71, 68.36, 31.96, 29.74, 29.69, 29.56, 29.54, 29.40, 26.36, 22.73, 14.15; MS (MALDI) [M+H]+ 1350.9

5,10,15,20-tetrakis(4-hexadecyloxyphenyl)porphyrin (precursor compound of Dye 6)
Following the general procedure gave a purple solid (563 mg, 69%). δH (400MHz, CDCl3): 8.86 (s, 8H), 8.10 (d, J = 8.56 Hz, 8H), 7.28-7.26 (overlapped with CHCl3, 8H), 4.25 (dd, J = 12.96, 12.96 Hz, 8H), 1.98 (ddd, J = 21.28, 21.28, 6.48 Hz, 8H), 1.66-1.58 (m, 12H), 1.50-1.27 (m, 12H), 0.88 (t, J = 13.68 Hz, 12H), -2.75 (s, 2H); δC (100 MHz, CDCl3): 158.98, 135.60, 134.47, 119.81, 112.71, 68.36, 31.94, 29.74, 29.69, 29.56, 29.54, 29.38, 26.27, 22.70, 14.13; MS (MALDI) [M+H]+ 1575.2
**Figure S1.** $^1$HNMR spectrum of 5,10,15,20-tetrakis(4-propoxyphenyl)porphyrin (precursor compound of Dye 3, CDCl$_3$, 400MHz)

**Figure S2.** C$^{13}$NMR spectrum of 5,10,15,20-tetrakis(4-propoxyphenyl)porphyrin (precursor compound of Dye 3, CDCl$_3$, 100MHz)
Figure S3. $^1$H-NMR spectrum of 5,10,15,20-tetrakis(4-(hexyloxy)phenyl)porphyrin (precursor compound of Dye 4, CDCl$_3$, 400MHz)

Figure S4. $^{13}$C-NMR spectrum of 5,10,15,20-tetrakis(4-(hexyloxy)phenyl)porphyrin (precursor compound of Dye 4, CDCl$_3$, 100MHz).
Figure S5. H-NMR spectrum of 5,10,15,20-tetrakis(4-(dodecyloxy)phenyl)porphyrin (precursor compound of Dye 5, CDCl₃, 400MHz).

Figure S6. C13-NMR spectrum of 5,10,15,20-tetrakis(4-(dodecyloxy)phenyl)porphyrin (precursor compound of Dye 5, CDCl₃, 100MHz).
**Figure S7.** $^1$H-NMR spectrum of 5,10,15,20-tetrakis(4-(hexadecyloxy)phenyl) porphyrin (precursor compound of Dye 6, CDCl$_3$, 400MHz)

**Figure S8.** $^{13}$C-NMR spectrum of 5,10,15,20-tetrakis(4-(hexadecyloxy)phenyl) porphyrin (precursor compound of Dye 6, CDCl$_3$, 100MHz)
Figure S9. CSI-MS spectra of Dye 1-6.

CSI-MS spectrum data of Dye 2-6.

5,10,15,20-tetrakis(4-methoxyphenyl)porphyrin-chromium chloride complexes (Dye 2), MS (CSI) [M+H]+: 820.08

5,10,15,20-tetrakis(4-propoxyphenyl)porphyrin-chromium chloride complexes (Dye 3), MS (CSI) [M+H]+: 932.3

5,10,15,20-tetrakis(4-(hexyloxy)phenyl)porphyrin-chromium chloride complexes (Dye 4), MS (CSI) [M+H]+: 1100.5

5,10,15,20-tetrakis(4-(dodecyloxy)phenyl)porphyrin-chromium chloride complexes (Dye 5), MS (CSI) [M+H]+: 1436.9

5,10,15,20-tetrakis(4-(hexadecyloxy)phenyl)porphyrin-chromium chloride complexes (Dye 6), MS (CSI) [M+H]+: 1661.1
Figure S10. Cyclic voltammograms of (a) Dye 1, (b) Dye 2, (c) Dye 3, (d) Dye 4, (e) Dye 5, and (f) Dye 6. Conditions: Scan rate is 100 mV/s, solvent is de-oxygenated CH2Cl2 that containing 0.1M tetrabutylammonium perchlorate, 22 °C.

Figure S11. Particle size distribution of KTa(Zr)O3 measured by a laser diffraction particle size analyser. Average particle size: 0.77 μm.
**Figure S12.** TEM image of KTa(Zr)O3.

**Figure S13.** UV-vis spectrum of KTa(Zr)O3.
Figure S14. Time course of water splitting on Pt-loaded KTa(Zr)O₃ modified with (a) Dye 1, (b) Dye 3, (c) Dye 4, (d) Dye 5, and (e) Dye 6.
**Figure S15.** UV-vis absorption spectra of Dye 2 remained on KTa(Zr)O₃ before (red) and after (blue) the photocatalytic reaction for 15 h.

**Figure S16.** Gas formation rates of water splitting on Pt/Dye 2/KTa(Zr)O₃ during 5 h. The values are the average formation rates and standard deviates of hydrogen and oxygen gases in four times reactions.

**Figure S17.** XRD pattern of KTa(Zr)O₃. All diffraction peaks were assigned to KTaO₃ (JCPDS 38-1470) and shifted to lower angle side because of the substitution of Zr⁴⁺ ion to Ta⁵⁺ site.
**Figure S18.** Schematic image of a closed-circulation type glass reactor.

**Figure S19.** Spectrum of 300 W Xe lamp used in this study.

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