

Supplementary Materials: Effect of Porphyrin Molecular Structure on Water Splitting Activity of a KTaO_3 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, CDCl_3); 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, CDCl_3); 158.97, 135.60, 134.49, 119.81, 112.72, 69.83, 22.85, 10.74, MS (MALDI) $[\text{M}+\text{H}]^+$ 846.4

5,10,15,20-tetrakis(4-(hexyloxy)phenyl)porphyrin (precursor compound of Dye 4)

Following the general procedure gave a purple solid (218 mg, 42%). δH (400MHz, CDCl_3); 8.86 (s, 8H), 8.10 (d, $J = 8.52$ Hz, 8H), 7.27-7.25 (overlapped with CHCl_3 , 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, CDCl_3); 158.96, 135.60, 134.49, 119.81, 112.70, 68.33, 31.74, 29.49, 25.93, 22.72, 14.13; MS (MALDI) $[\text{M}+\text{H}]^+$ 1014.6

5,10,15,20-tetrakis(4-(dodecyloxy)phenyl)porphyrin (precursor compound of Dye 5)

Following the general procedure gave a purple solid (498 mg, 71%). δH (400MHz, CDCl_3); 8.86 (s, 8H), 8.10 (d, $J = 8.56$ Hz, 8H), 7.28-7.25 (overlapped with CHCl_3 , 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, CDCl_3); 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) $[\text{M}+\text{H}]^+$ 1350.9

5,10,15,20-tetrakis(4-(hexadecyloxy)phenyl)porphyrin (precursor compound of Dye 6)

Following the general procedure gave a purple solid (563 mg, 69%). δH (400MHz, CDCl_3); 8.86 (s, 8H), 8.10 (d, $J = 8.56$ Hz, 8H), 7.28-7.26 (overlapped with CHCl_3 , 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, CDCl_3); 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) $[\text{M}+\text{H}]^+$ 1575.2

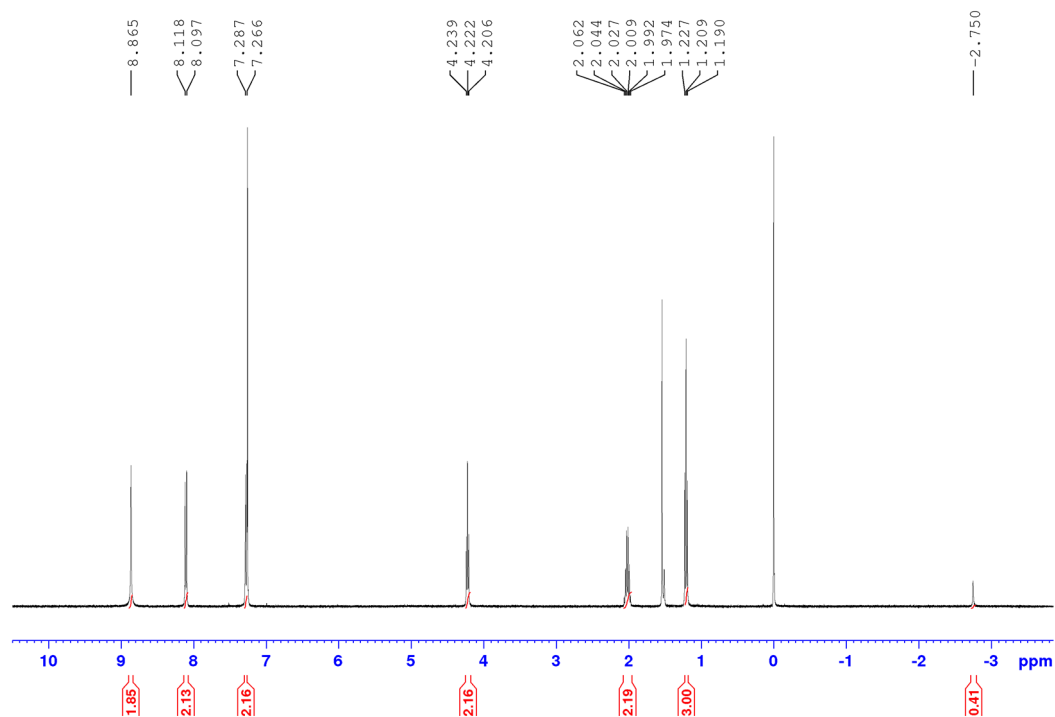


Figure S1. ^1H NMR spectrum of 5,10,15,20-tetrakis(4-propoxyphenyl)porphyrin (precursor compound of Dye 3, CDCl_3 , 400MHz)

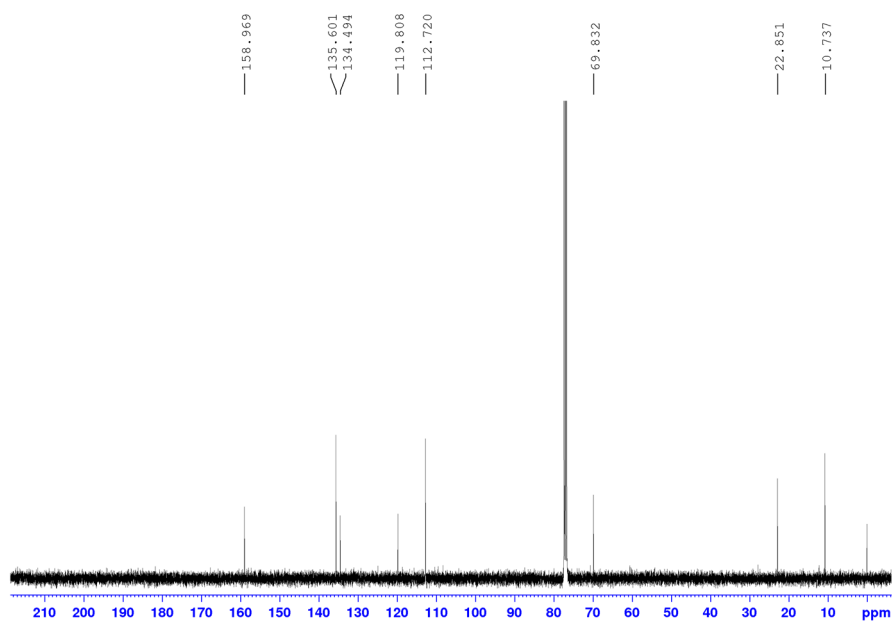


Figure S2. ^{13}C -NMR spectrum of 5,10,15,20-tetrakis(4-propoxyphenyl)porphyrin (precursor compound of Dye 3, CDCl_3 , 100MHz)

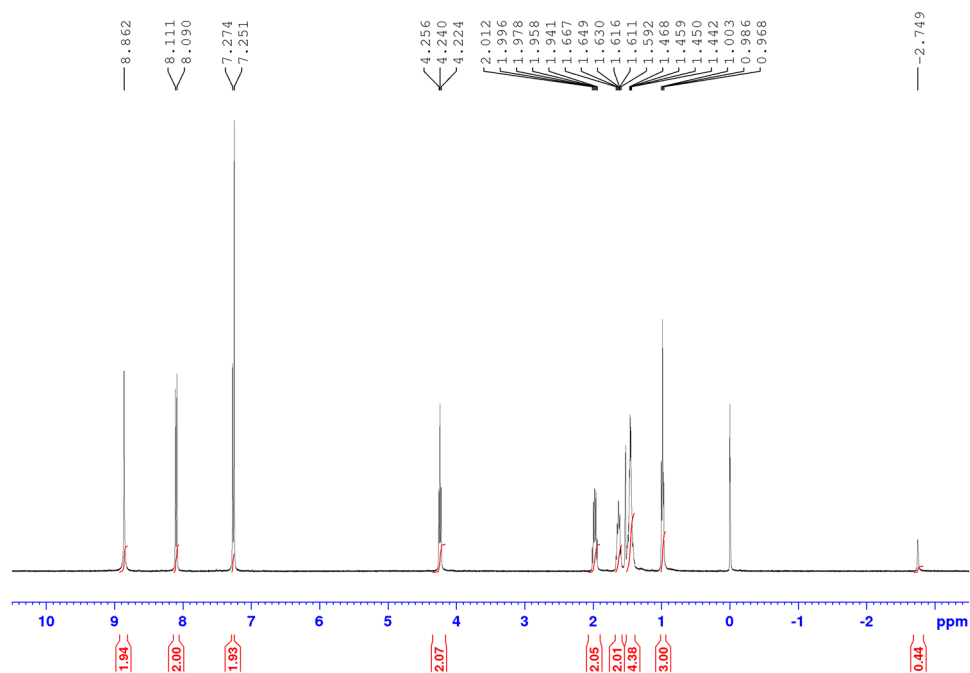


Figure S3. ^1H -NMR spectrum of 5,10,15,20-tetrakis(4-(hexyloxy)phenyl)porphyrin (precursor compound of Dye 4, CDCl_3 , 400MHz)

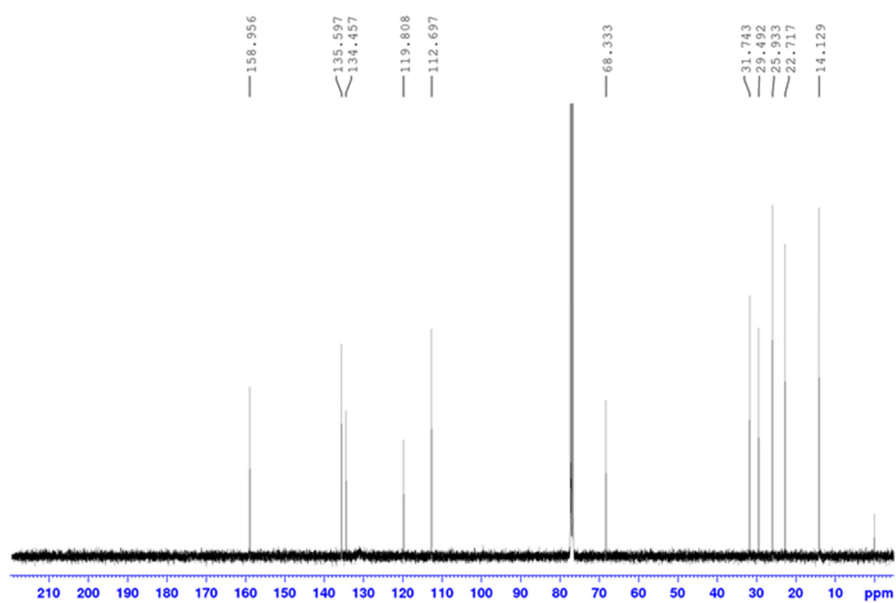


Figure S4. ^{13}C -NMR spectrum of 5,10,15,20-tetrakis(4-(hexyloxy)phenyl)porphyrin (precursor compound of Dye 4, CDCl_3 , 100MHz).

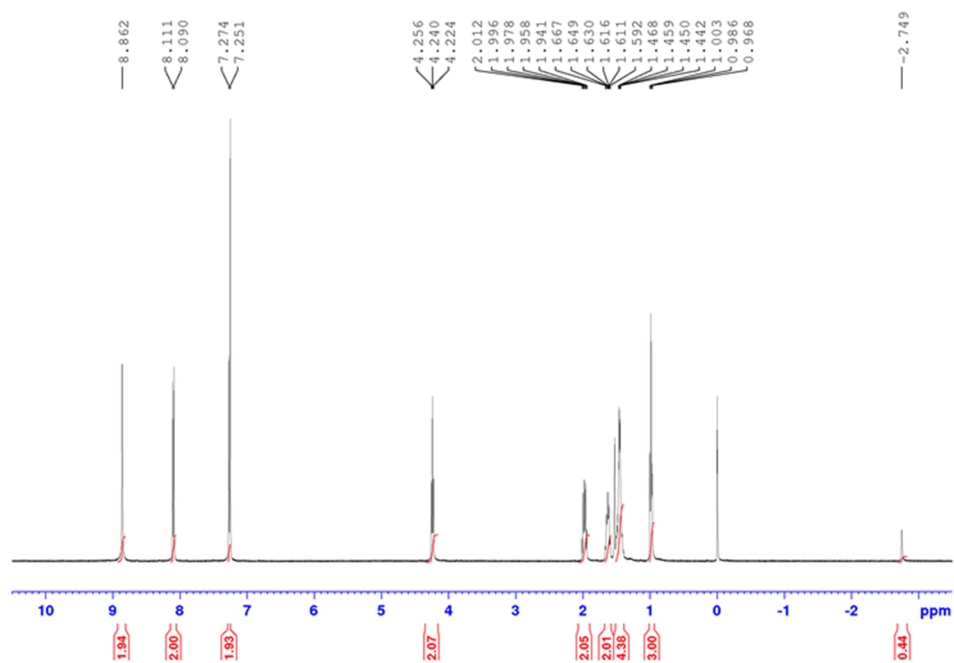


Figure S5. ¹H-NMR spectrum of 5,10,15,20-tetrakis(4-(dodecyloxy)phenyl)porphyrin (precursor compound of Dye 5, CDCl₃, 400MHz).

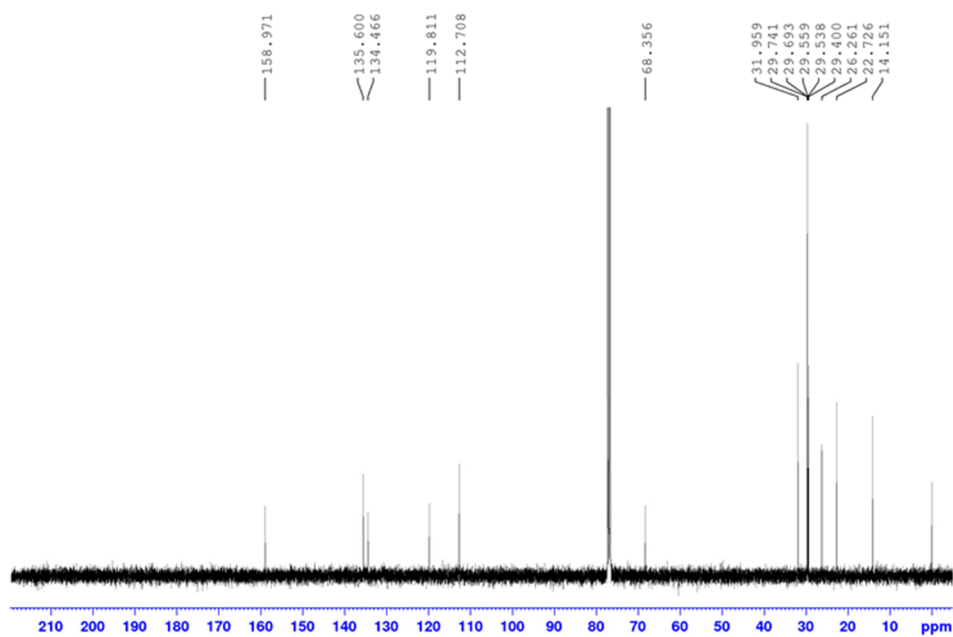


Figure S6. ¹³C-NMR spectrum of 5,10,15,20-tetrakis(4-(dodecyloxy)phenyl)porphyrin (precursor compound of Dye 5, CDCl₃, 100MHz).

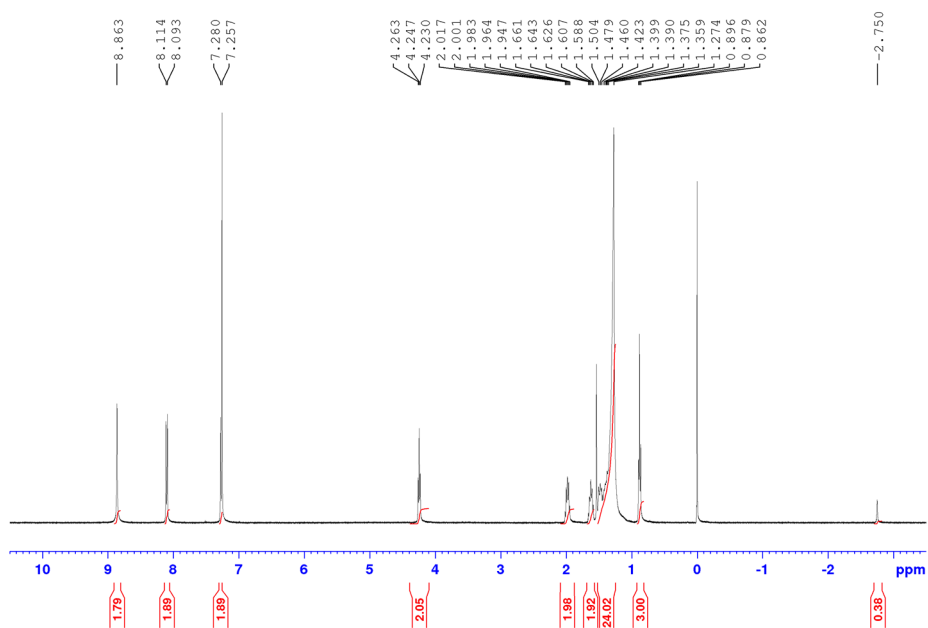


Figure S7. ^1H -NMR spectrum of 5,10,15,20-tetrakis(4-(hexadecyloxy)phenyl) porphyrin (precursor compound of Dye 6, CDCl_3 , 400MHz)

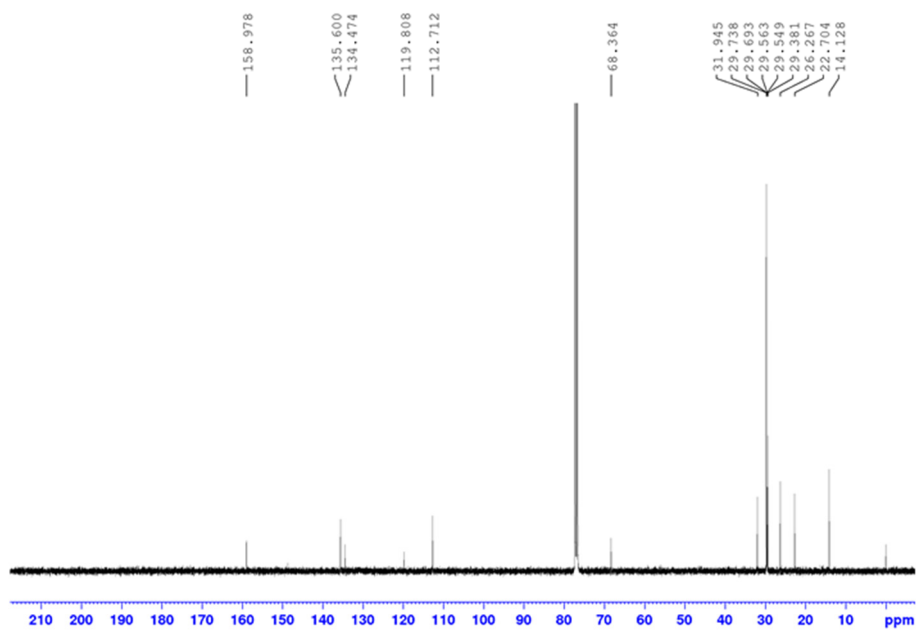


Figure S8. ^{13}C -NMR spectrum of 5,10,15,20-tetrakis(4-(hexadecyloxy)phenyl) porphyrin (precursor compound of Dye 6, CDCl_3 , 100MHz)

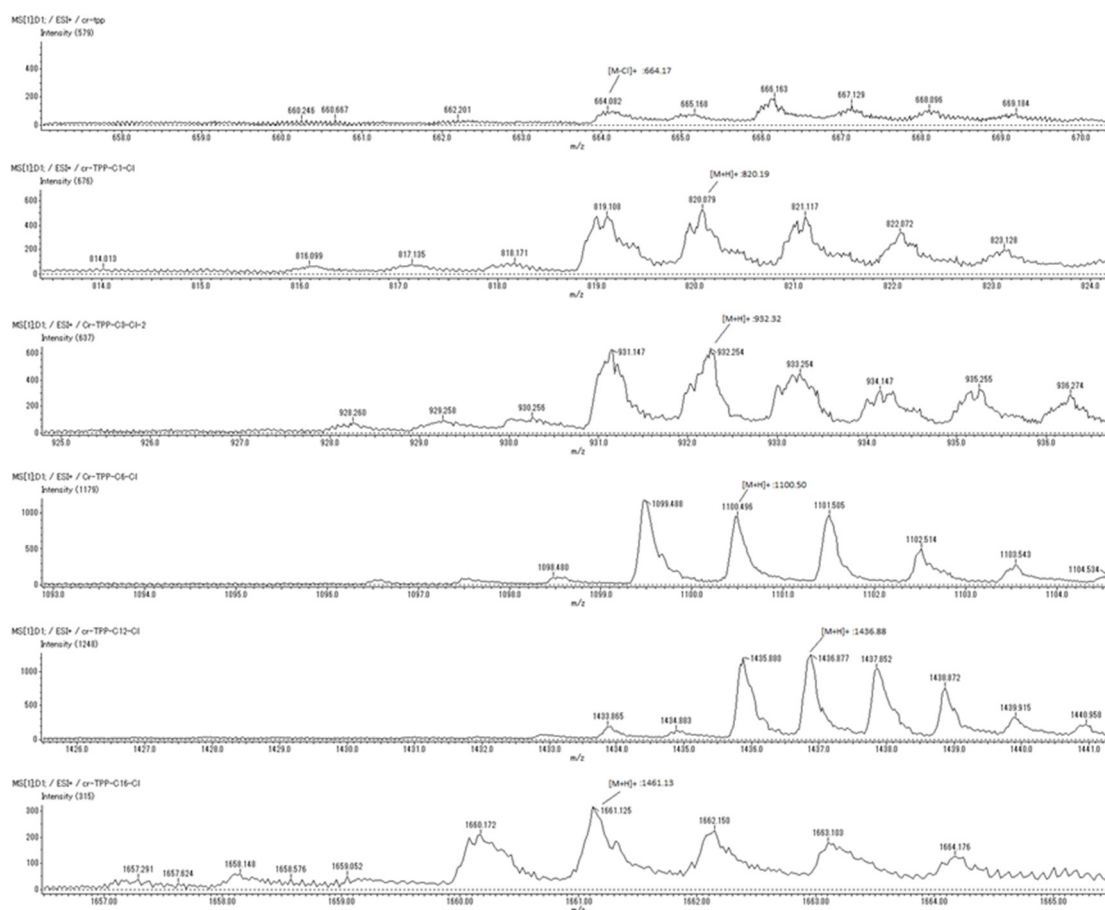


Figure S9. CSI-MS spectra of Dye 1-6.

CSI-MS spectrum data of Dye 2-6.

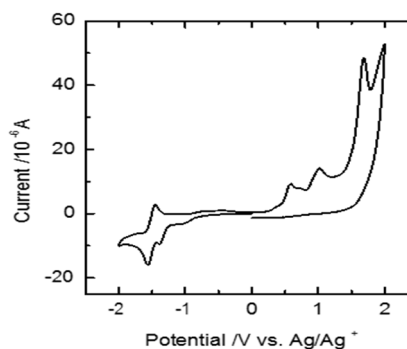
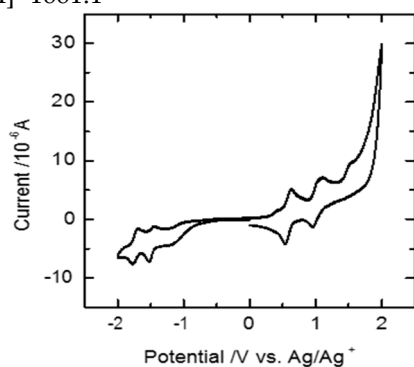
5,10,15,20-tetrakis(4-methoxyphenyl)porphyrin-chromium chloride complexes (Dye 2), MS (CSI) $[M+H]^+$ 820.08

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



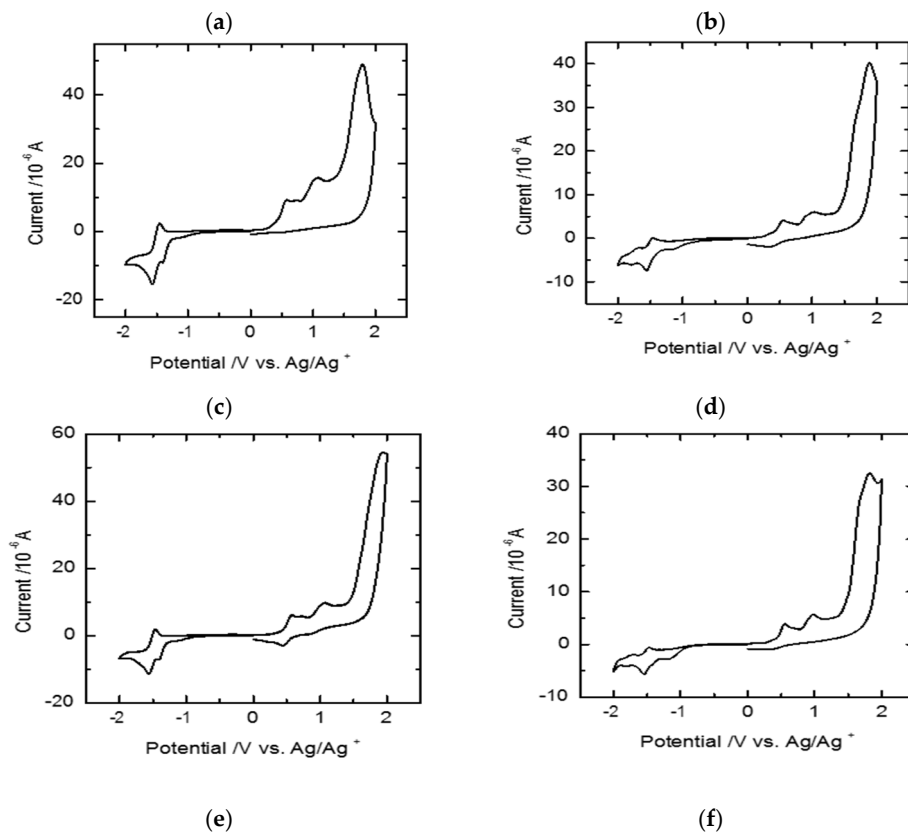


Figure S10. Cyclic voltammograms of (a) Dye 1, (b) Dye 2, (c) Dye 3, (d) Dye 4, (e) Dye 5, and (f) Dye 6. Conditions: Scan rate is 100 mV/s, solvent is de-oxygenated CH_2Cl_2 that containing 0.1M tetrabutylammonium perchlorate, 22 °C.

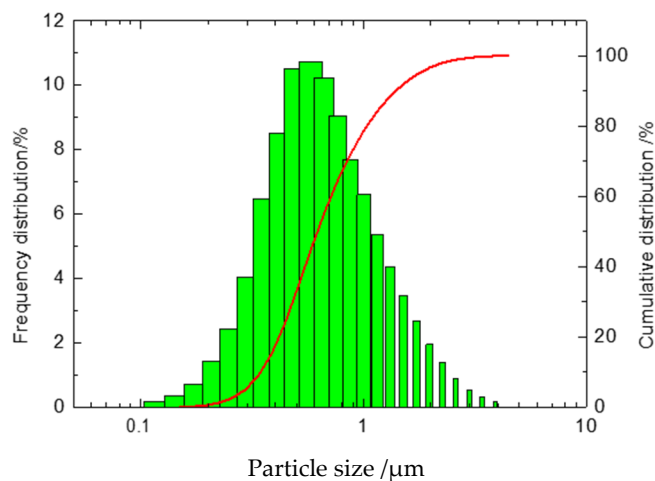


Figure S11. Particle size distribution of $\text{KTa}(\text{Zr})\text{O}_3$ measured by a laser diffraction particle size analyser. Average particle size: 0.77 μm .

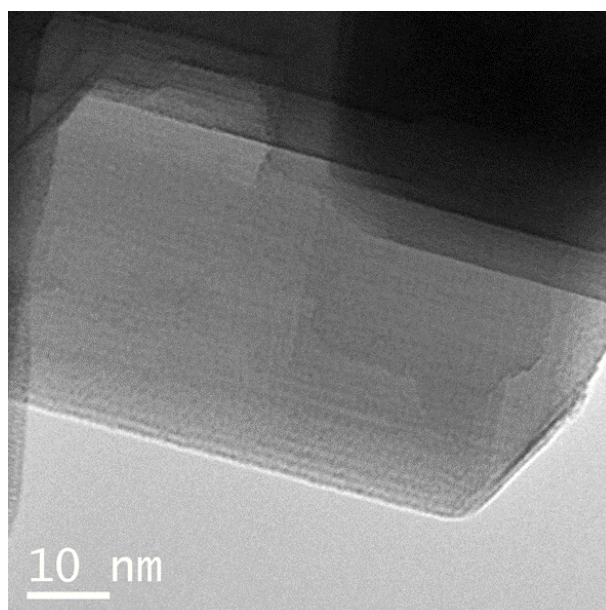


Figure S12. TEM image of KTa(Zr)O₃.

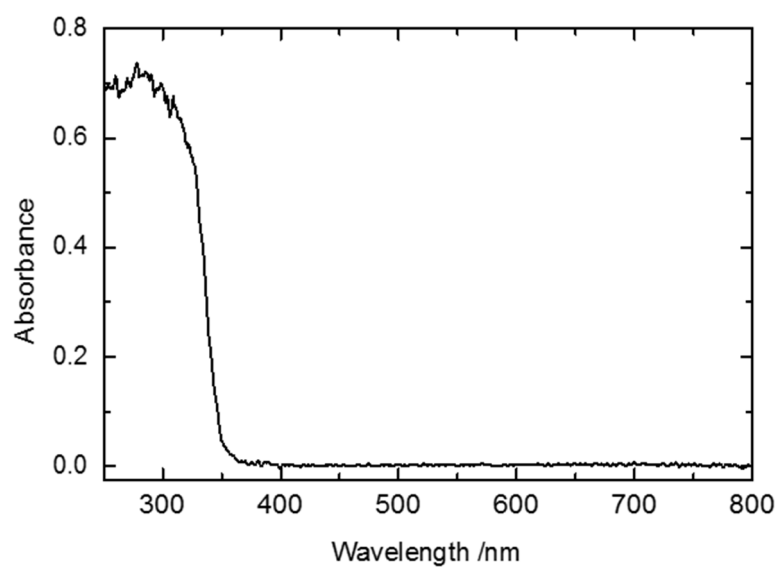


Figure S13. UV-vis spectrum of KTa(Zr)O

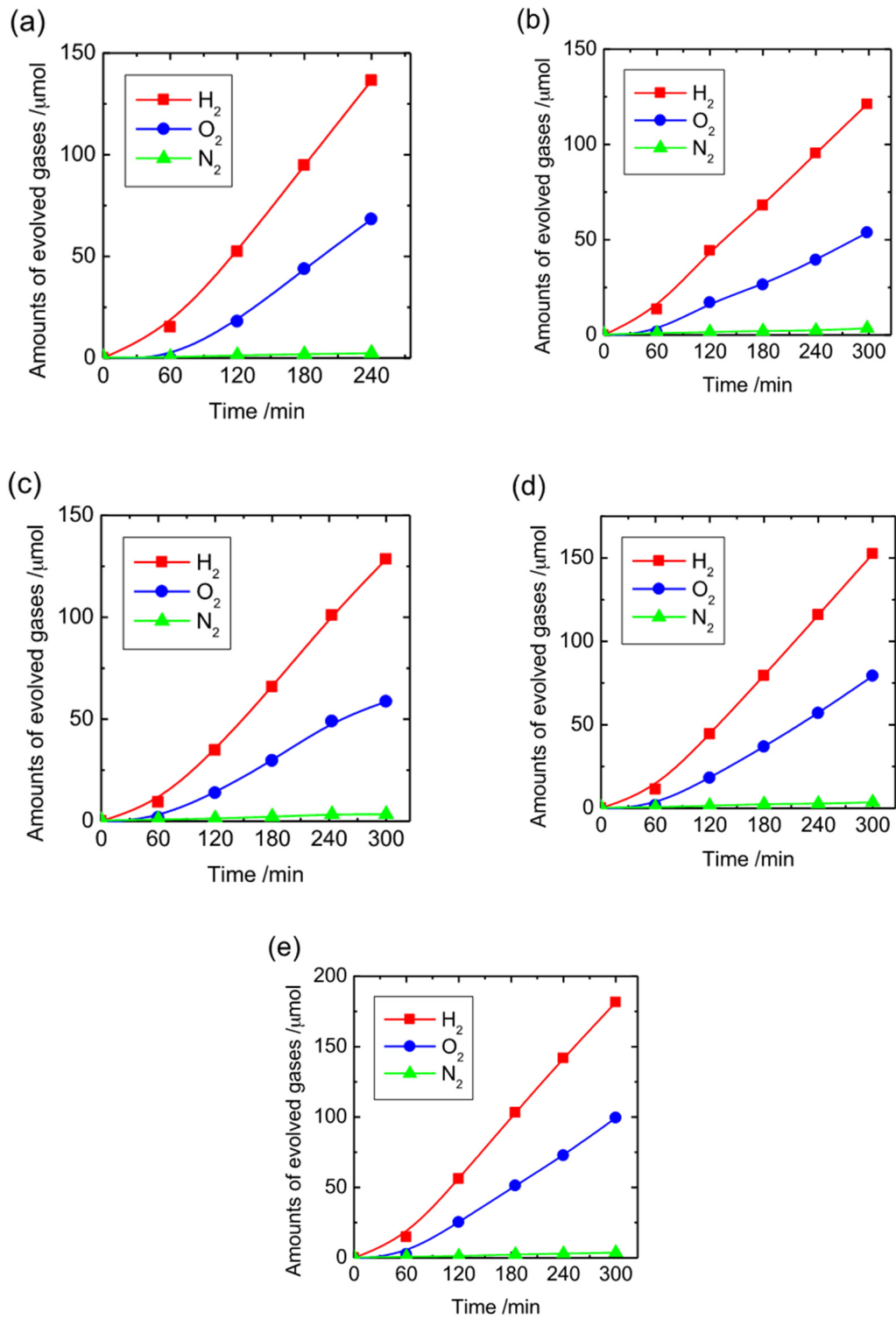


Figure S14. Time course of water splitting on Pt-loaded $\text{KTa}(\text{Zr})\text{O}_3$ modified with (a) Dye 1, (b) Dye 3, (c) Dye 4, (d) Dye 5, and (e) Dye 6.

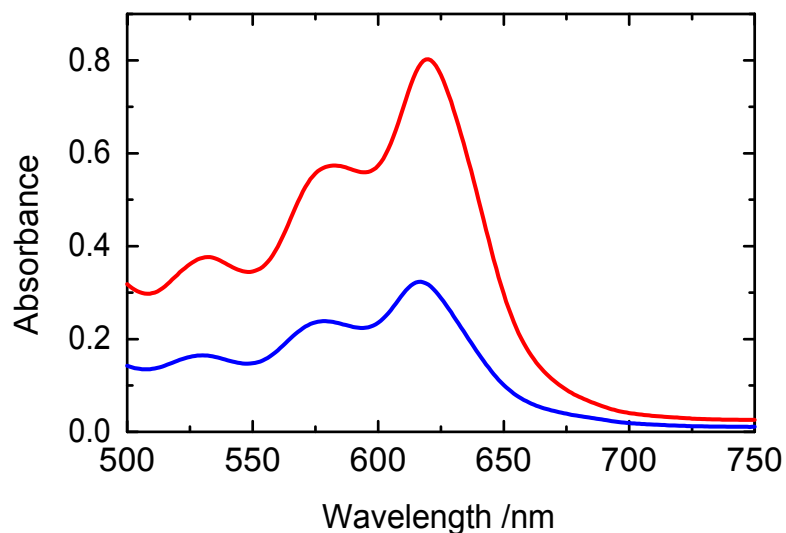


Figure S15. UV-vis absorption spectra of Dye 2 remained on KTa(Zr)O₃ before (red) and after (blue) the photocatalytic reaction for 15 h.

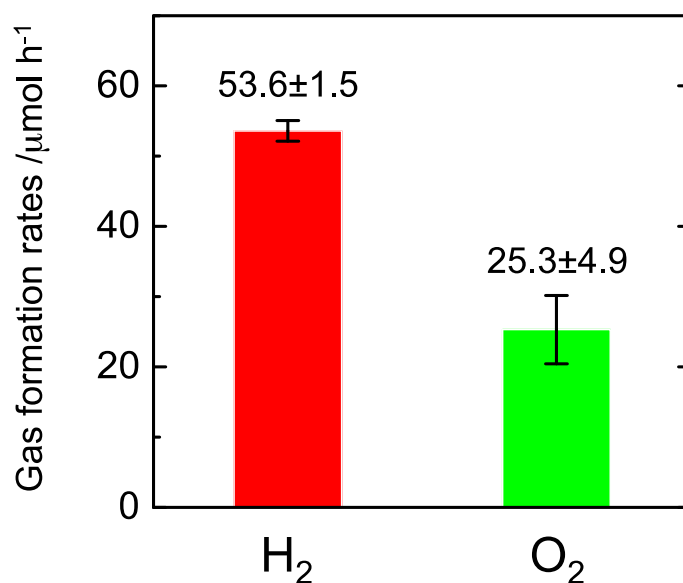


Figure S16. Gas formation rates of water splitting on Pt/Dye 2/KTa(Zr)O₃ during 5 h. The values are the average formation rates and standard deviates of hydrogen and oxygen gases in four times reactions.

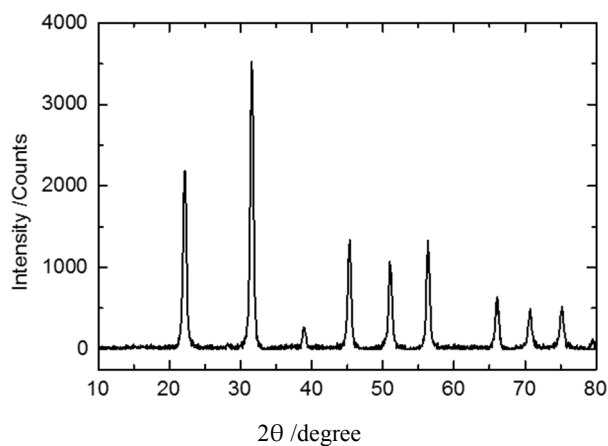


Figure S17. XRD pattern of KTa(Zr)O₃. All diffraction peaks were assigned to KTaO₃ (JCPDS 38-1470) and shifted to lower angle side because of the substitution of Zr⁴⁺ ion to Ta⁵⁺ site.

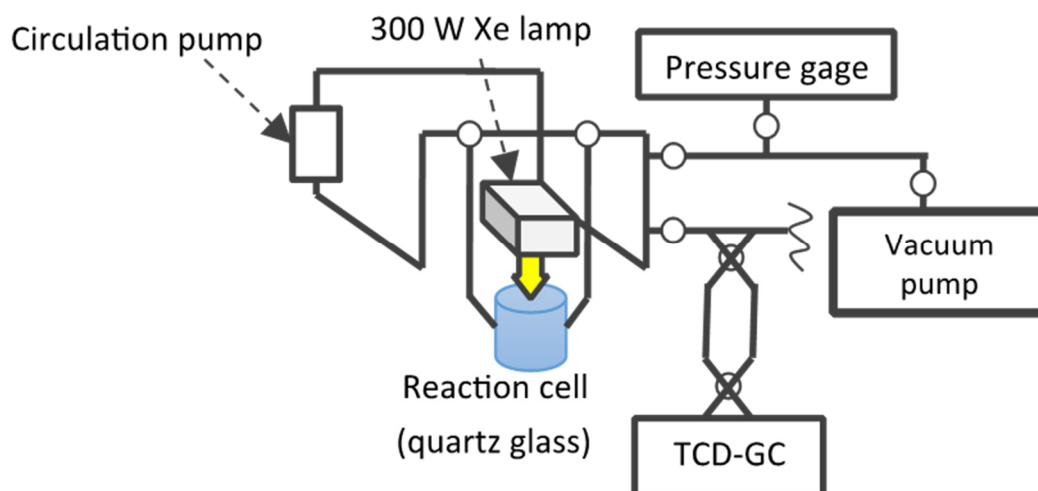


Figure S18. Schematic image of a closed-circulation type glass reactor.

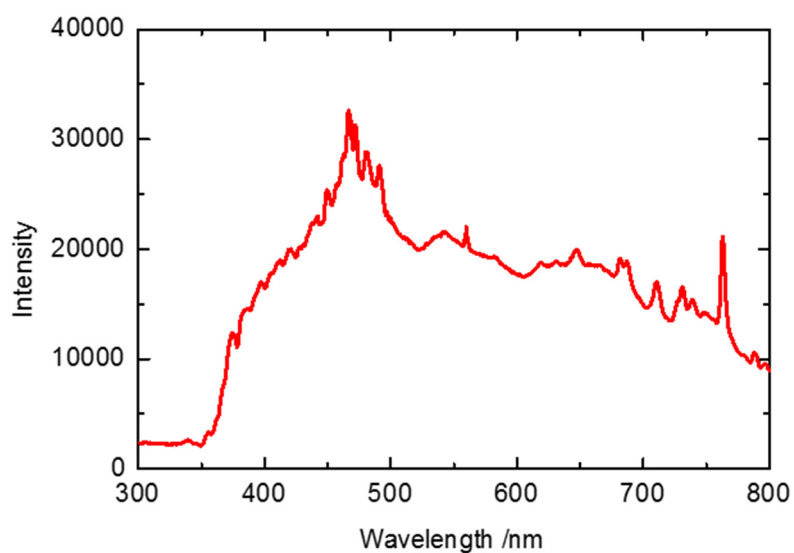


Figure S19. Spectrum of 300 W Xe lamp used in this study.

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