Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Photoelectrochemical water oxidation improved by pyridine N-oxide as a mimic of Tyrosine Z in photosystem II

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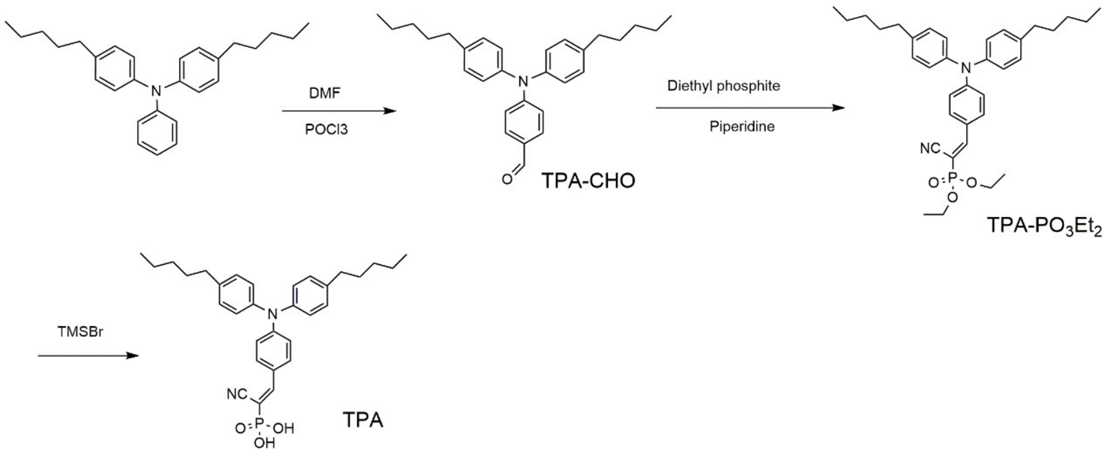
Materials

All synthetic reactions were carried out under N_2 atmosphere with standard Schlenk techniques. The solvents were dried and purified prior to use. Catalyst **2** was prepared according to the literature procedures.[1] All other chemicals are commercially available. High purity water (18.2 MΩ·cm) supplied by a Milli-Q system (Millipore, Direct-Q 3 UV) was used in all experiments. FTO substrates were purchased from Dalian Heptachroma SolarTech Co., Ltd. (thickness of *ca.* 2.2 mm, transmittance > 90%, resistance < 15 Ω cm^{-2}). Before using, the FTO substrates were ultrasonically cleaned in deionized water, ethanol and acetone, respectively.

Characterization

^1H NMR spectra were collected at 298 K using a Bruker Avance NEO 600M NMR Spectroscopy instrument. Electrospray ionization mass spectra were recorded on a LTQ Orbitrap XL Micromass spectrometer (Thermo Scientific, USA). Electrochemical measurements were taken with a CHI 760E electrochemical potentiostat (Shanghai Chenhua, China). Scanning electron microscopy (SEM) of the electrodes were conducted with a Hitachi SU8220 instrument with an accelerating voltage of 5.0 kV.

Synthesis

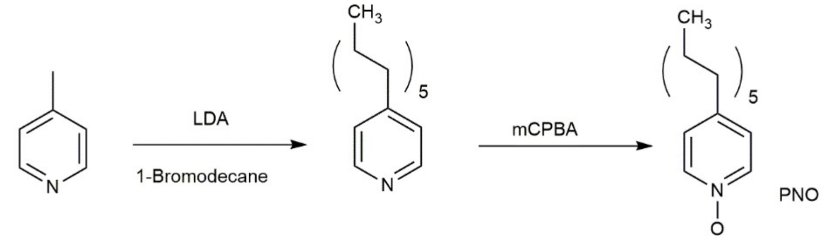


4-(bis(4-pentylphenyl)amino)benzaldehyde (TPA-CHO): To a solution of 4-pentyl-*N*-(4-pentylphenyl)-*N*-phenylaniline (15.4 g, 40 mmol) in 100 ml of DMF 4.73 mL (50.98 mmol) of phosphorus oxychloride were added dropwise at 0 °C. Subsequently, the reaction mixture was heated to 95 °C and stirred for 24 hours. The reaction mixture was poured into ice water, neutralized with NaOH and extracted with methylene chloride. The organic phase was removed, washed with water and dried over sodium sulfate. The crude product obtained after concentration to dryness was purified by chromatography on silica gel chromatography with acetone/hexanes (1:25 V/V) to collect TPA-CHO yellow oil, yield 7.9g, 48%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.77 (s, 1H), 7.75 – 7.54 (m, 2H), 7.14 (d, 4H), 7.11 – 7.05 (m, 4H), 6.94 (d, 2H), 2.63 – 2.52 (m, 4H), 1.69 – 1.56 (m, 4H), 1.44 – 1.31 (m, 8H), 0.91 (t, 6H). HRMS (ESI, *m/z*): $[M+H]^+$ calcd for $C_{29}H_{36}NO$, 414.2791; found, 414.2795. $[M+Na]^+$ calcd for $C_{29}H_{35}NONa$, 436.2611; found, 436.2612.

Diethyl (2-(4-(bis(4-pentylphenyl)amino)phenyl)-1-cyanovinyl)-phosphonate (TPA-PO$_3$Et$_2$): A mixture of 4-(bis(4-pentylphenyl)amino)benzaldehyde (TPA-CHO) (4.13g, 10 mmol), 2.13g of Diethyl (cyanomethyl)phosphonate (1.2 equiv.), and piperidine (3mL, 30 mmol) were heated with stirring in dry toluene (200 mL) for 16 h at 100 °C under N_2 atmosphere. After cooling to room temperature, water was added, and the organic phase was successively washed with 1 M HCl (2×) and saturated NaCl

(2×). The organic phase was dried with $MgSO_4$, and volatiles were removed by rotary evaporation. The residue was purified by silica gel chromatography with dichloromethane-methanol (20:1, V: V) as the eluent. Complex TPA-PO_3Et_2 was obtained as a yellow solid. Yield: 4.1 g, 72%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.79 (d, 2H), 7.15 (d, 4H), 7.10 – 7.05 (m, 4H), 6.90 (t, 2H), 4.25 – 4.12 (m, 4H), 2.61 – 2.54 (m, 4H), 1.62 (dq, 4H), 1.39 (t, 6H), 1.37 – 1.30 (m, 8H), 0.91 (t, 6H). HRMS (ESI, *m/z*): $[M+H]^+$ calcd for $C_{35}H_{46}N_2O_3P$, 573.3241; found, 573.3240. $[M+Na]^+$ calcd for $C_{35}H_{45}N_2O_3PNa$, 595.3060; found, 595.3056.

(2-(4-(bis(4-pentylphenyl)amino)phenyl)-1-cyanovinyl)phosphonic acid (TPA): A mixture of TPA-PO_3Et_2 (2.86g, 5 mmol) and 6.5mL of TMSBr was stirred in dry methylene chloride (100 mL) for 20 h at room temperature under N_2 atmosphere. Then 5mL of methanol was added and continued stirring for 4 hours. Volatiles were removed by rotary evaporation and the solid was washed with water and ethyl ether to obtain TPA as an orange solid in quantitative yield. ^{1}H NMR (600 MHz, CD_3OD_SPE) δ 7.77 (d, 2H), 7.71 (d, 1H), 7.19 (d, 4H), 7.07 (d, 4H), 6.88 (d, 2H), 2.63-2.58 (m, 4H), 1.63 (dt, 4H), 1.38 – 1.33 (m, 8H), 0.91 (t, 6H). HRMS (ESI, *m/z*): $[M-H]^-$ calcd for $C_{31}H_{36}N_2O_3P$, 515.2469; found, 515.2466.



4-undecylpyridine: 4-picoline (2 mL, 20 mmol) was dissolved in 50 mL of dry THF and the solution was cooled to -78 ° C, then 10 mL of 2 M LDA solution (20 mmol) was added to the reaction mixture. The reaction was stirred for 1 hour under N_2 atmosphere at -78° C, then a solution of 1-Bromodecane (4.42 g 20 mmol) in 20 mL of THF is added dropwise within 15 min. The resulting solution was warmed to room temperature and stirred for 5 hours. Water was added to the reaction and was extracted with DCM. The organic layer was washed with saturated NH_4Cl, followed by saturated NaCl and dried with Na_2SO_4, and volatiles were removed by rotary evaporation. The residue was purified by silica gel chromatography with EtOAc/hexanes (1:5 V/V). Complex 4-undecylpyridine was obtained as a yellow oil. Yield: 3.3 g (70%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.48 (d, 2H), 7.15 (d, 2H), 2.63 (t, 2H), 1.66 – 1.59 (m, 2H), 1.33 – 1.24 (m, 16H), 0.88 (t, 3H). ESI-MS: m/z = 234.18 $[M + H]^+$ (calcd: 234.21).

4-undecylpyridine-N-oxide (PNO): A solution containing 4-undecylpyridine (2.5 g 10 mmol) in 50 mL of $CHCl_3$ was cooled to 0 ° C, and meta-chloroperbenzoic acid (1.7 g 10 mmol) in 50mL of $CHCl_3$ was added. The temperature was maintained at 0 ° C for 1 hour. Then 0.17 g of additional meta-chloroperbenzoic acid was added and solution was warmed to room temperature and stirred under N_2 atmosphere overnight. The reaction mixture was filtered through a column of basic alumina, eluted with $CHCl_3$ to given 2.0g (81%) of a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d,2H), 7.10 (s, 2H), 2.60 (t, 2H), 1.61 (dd, 2H), 1.35 – 1.21 (m, 16H), 0.88 (t, 3H). ESI-MS: m/z = 25.26 $[M + H]^+$ (calcd: 250.21).

$Ru(bda)(4\text{-undecylpyridine})_2$ (1): A 40 mL methanol solution containing $Ru(bda)(DMSO)_2Cl_2$[2] (500 mg, 1.0 mmol) and 4-undecylpyridine (700 mg, 3.0 mmol) was refluxed for 6 h under N_2 atmosphere. The solvent was removed under reduced pressure, the residue was purified by silica gel chromatography with dichloromethane-methanol (20:1, V:V) as the eluent. Complex **1** was obtained as a dark red solid. Yield: 560 mg (70%). 1H NMR (600 MHz, CD3OD) δ 8.58 (d, 2H), 8.03 (d, 2H), 7.87 (t, 2H), 7.66 (d, 4H), 7.04 (d, 4H), 2.55-2.47 (m, 4H), 1.50 (dd, 4H), 1.23 (s, 32H), 0.87 (t, 6H). HRMS (ESI, *m/z*): $[M+H]^+$ calcd for $C_{44}H_{61}N_4O_4Ru$, 811.3731; found, 811.3738.

$Ru(tda)(4\text{-undecylpyridine})_2$ (3): A 40 mL methanol solution containing $Ru(tda)(dmso)(O_2H)$[3] (500 mg, 1.0 mmol) and 4-undecylpyridine (700 mg, 3.0 mmol) was refluxed for 16 h under N_2 atmosphere. The solvent was removed under reduced pressure, the residue was purified by silica gel chromatography with dichloromethane-methanol (50:1 to 1:1, V:V) as the eluent. Complex **3** was obtained as a dark red solid. Yield: 260 mg (30%).^{1}H NMR (600 MHz, CD_3OD) δ 8.58 (d, 2H), 8.47 (d, 2H), 8.13 (s, 2H), 8.06 – 7.97 (m, 3H), 7.92 (s, 4H), 6.89 (d, 4H), 2.41 (t, 4H), 1.38 (d, 4H), 1.20 (d, 32H), 0.87 (t, 6H). HRMS (ESI, *m/z*): $[M+H]^+$ calcd for $C_{49}H_{64}N_5O_4Ru$, 888.3996; found, 888.4000.

Fabrication of photoanodes. TiO_2 films were prepared according to previously published methods.[2] First, FTO supported TiO_2 films were sensitized by soaking the slides in a methanol solution of TPA (1 mM) for 2 h, the sensitized electrodes (TiO_2|TPA) were dried in dark at room temperature after rinsing by methanol. Next, the TiO_2|TPA|PNO, TiO_2|TPA|PMMA and TiO_2|TPA|Nafion films were fabricated by drop-casting PNO, PMMA or Nafion solution on TPA-sensitized TiO_2 films, respectively. In a typical experiment, PNO was dissolved in DCM with a concentration of 25 mg mL^{-1} as a stock solution. The TiO_2|TPA|PNO film was obtained by drop-casting 20 μL of the above stock solution on the surface of TiO_2|TPA film with an active area of 1 cm × 1 cm, the resulting electrode was allowed to dry by solvent evaporation. For TiO_2|TPA|PMMA and TiO_2|TPA|Nafion, identical procedure was used for electrode fabrication except that the stock solution was made by dissolving PMMA or Nafion in DCM at a concentration of 10 mg mL^{-1}. Herein, a lower concentration was chosen to optimize the thickness of polymer coating layers towards the best PEC performance.

The final integrated photoanode TiO_2|TPA|PNO|Cat was obtained by drop-casting a 10 μL methanol solution of catalyst **1**, **2** or **3** (5 mM) on the surface of TiO_2|TPA|PNO, which was followed by drying at ambient conditions. The catalyst loading was 5×10^{-8} mol cm^{-2}. TiO_2|TPA|PMMA|**1** and TiO_2|TPA|Nafion|**1** films were prepared by the same method.

Photoelectrochemical measurements. All photoelectrochemical measurements were carried out at room temperature by using a CHI 760E electrochemical workstation (Shanghai Chenhua Instrument Co., LTD). The photoelectrochemical performance was operated in a typical three-electrode cell with the photoanode as the working electrode, a platinum wire as the counter electrode, and saturated Ag/AgCl (0.194 V *vs* NHE) as the reference electrode. The simulated sunlight was obtained by passing light from a 300W Xenon arc lamp (Perfect light Technology Co., Ltd.) equipped with a 400 nm filter, the power intensity of the incident light was calibrated to 100 mW cm^{-2} using a THORLABS S401C power meter. The photocurrent-time curves were recorded after 100 s of photolysis to eliminate the charging currents.

Determination of the loading of TPA on TiO_2 film. First, the molar absorption coefficient of TPA was determined in a methanol/water (V: V = 5:1) solution of sodium hydroxide (NaOH). The TPA dye-sensitized TiO_2 film (area: $1cm^2$) was then placed in 5 mL of the above alkali solution for 1 h. During this period of time, the dye absorbed on the surface of TiO_2 was desorbed and dissolved in the solution, followed by diluting the solution to a volume of 10 mL. The UV-visible absorption spectrum of the solution was measured and the coverage of the dye on the surface of TiO_2 film was estimated based on Lambert-Beer law.

Incident photon to current efficiency (IPCE). IPCE was measured using a 300 W Xenon arc lamp equipped with a monochromator. The photocurrent density (J_{light}) and dark current density (J_{dark}) of photoanode were measured at an applied potential of 0.4 V *vs* NHE with a controlled active area (0.5×0.5 cm^2). The light intensity (P_λ) at each wavelength (λ) was determined with a THORLABS S120VC power meter. The IPCE value was calculated with the following equation:

$$IPCE(\%) = \frac{1240 \times (J_{light} - J_{dark})}{\lambda \times P_\lambda} \times 100\%$$

Determination of Faradaic efficiency. The PEC reaction with TiO_2|TPA|PNO|**1** as the working electrode was operated at a constant bias of 0.4 V *vs* NHE in an air-tight sealed PEC cell under simulated sunlight illumination (> 400 nm ,100 mW cm^{-2}). The O_2 evolution was analyzed by a Shimadzu GC-2014 instrument equipped with a thermal conductivity detector (CBM-20A). To quantify the evolved O_2, a 5Å molecular sieve column was used as the stationary phase and Ar gas was employed as the mobile phase. The oven temperature was 70°C, the temperatures for both injection port and thermal conductivity detector were set to 110°C. Argon was used as the carrier gas at a flow rate of 4 mL min^{-1}. Before the experiment, the electrolyte of PEC cell was thoroughly degassed by Argon. After the PEC reaction for 1 h, 500 µL of the gas sample taken from the headspace of the sealed cell was injected into the gas chromatograph. Finally, the passed charge of 1.9 C was measured by potentiostat, GC analysis revealed that 4.0 µmol of O_2 was evolved. A Faradaic efficiency was determined to be 82% based on the equation:

$$\eta(\%) = \frac{96485 \times n_{O_2} \times 4}{Q} \times 100\%$$

Using the same method, after the PEC reaction with TiO_2|TPA |**1** as the working electrode for 1 h, the passed charge of 0.66 C was measured by potentiostat, GC analysis revealed that 1.26 μmol of O_2 was evolved. A Faradaic efficiency was determined to be 75%.

Open-circuit photovoltage decays (OCVD). For the open-circuit photovoltage decay measurements, the photoelectrochemical cell was illuminated for 6s by a white LED with a 400 nm cutoff filter (100 mW cm^{-2}) to reach a steady voltage. The illumination was turned off with a Zahner electrochemical workstation (CIMPS-2) controller. The OCVD was also recorded by the electrochemical workstation. The decay analysis refers only to values measured after full darkness.

Spectroelectrochemical measurements. Spectroelectrochemical measurements were carried out with an Agilent-8453 UV−vis spectrophotometer by inserting TiO_2|TPA|PMMA, TiO_2|TPA|Nafion, TiO_2|TPA and TiO_2|TPA|PNO thin films at a 45° angle into a standard 10 mm path length cuvette containing a pH 7, 0.1 M phosphate buffer. The applied bias voltage was controlled by a CHI 660E electrochemical workstation with the measured film as the working electrode, an Ag/AgCl reference electrode and a platinum counter electrode. In a typical experiment, the absorption changes at 700 nm were monitored at a constant potential of 1.2V *vs* NHE for 5 min, followed by polarized at 0 V *vs* NHE for 1 min.

Photolysis of $H_2{}^{18}O$ and $^{18}O_2$ Detection by GC-MS. The PEC reaction with TiO_2|TPA|PNO|1 as the working electrode was operated at a constant bias of 0.4 V *vs* NHE in an air-tight sealed PEC cell under illumination (> 400 nm ,100 mW cm^{-2}). Before the experiment, the electrolyte of PEC cell was thoroughly degassed by Argon. ^{18}O-labeled water ($H_2{}^{18}O$, 97 atom%) was used as 0.1 M NaF solution for the photolysis experiments. GC-MS spectra were collected on Agilent 7000B Triple Quadrupole GC/MS. Agilent J&W HP-PLOT/Q+PT (length: 30 m, diameter: 0.32 mm, film 20μm) was used as the stationary phase, and He gas was employed as the mobile phase. The He flow rate was 1.0 mL min^{-1}, and the column temperature was 40 °C. The mass spectra were obtained with m/z values from 10 to 120. Aliquots (500 µL) of gas from the air-tight sealed PEC cell before and after the measurements were delivered to the GC-MS system using an Agilent SampleLock syringe to qualitatively analyze the evolved gases.

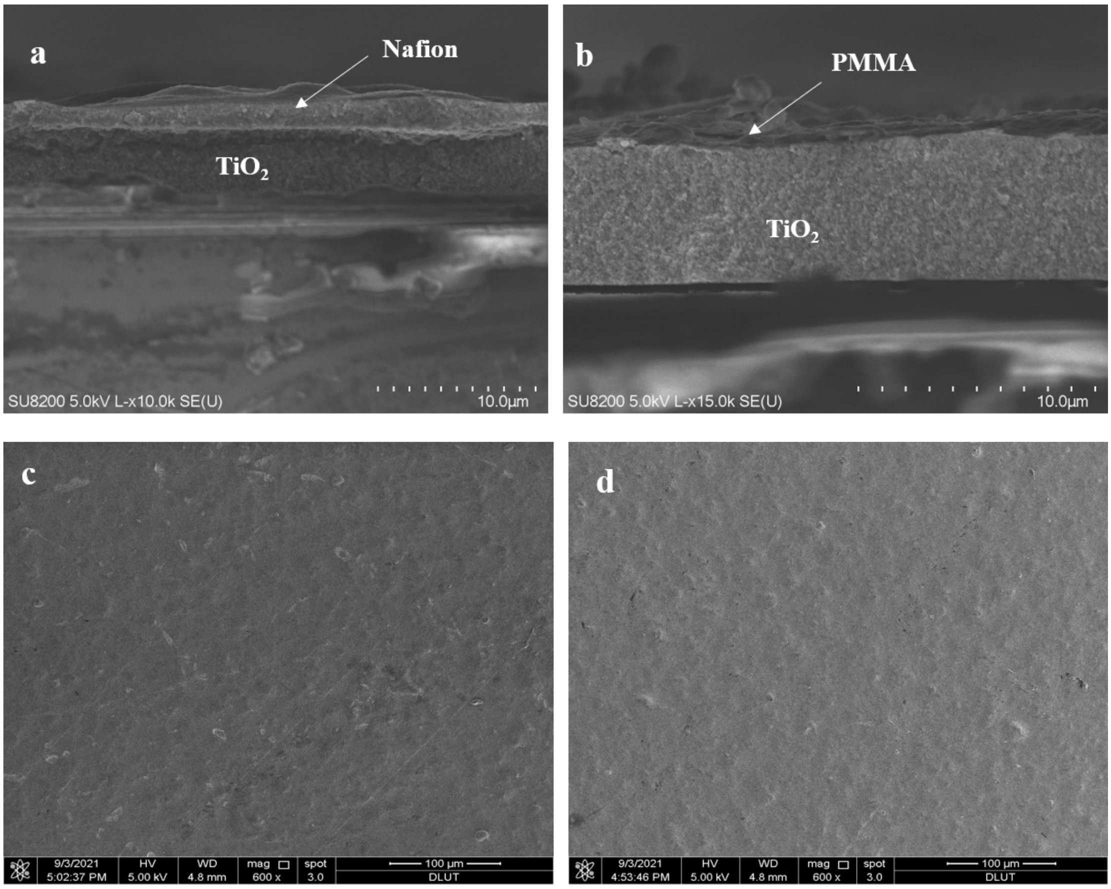


Figure S1. Cross-sectional SEM images of (a) TiO_2|TPA|Nafion and (b) TiO_2|TPA|PMMA. Top view SEM images of (c) TiO_2|TPA|Nafion and (d) TiO_2|TPA|PMMA.

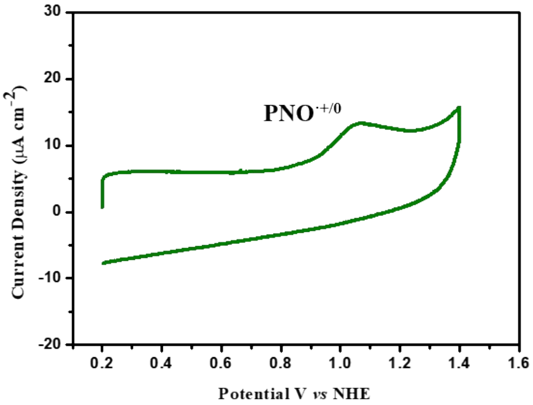


Figure S2. Cyclic voltammogram for PNO on *nano*ITO at pH 7 in 0.1 M phosphate buffer with a scan rate of 20 mVs^{-1}.

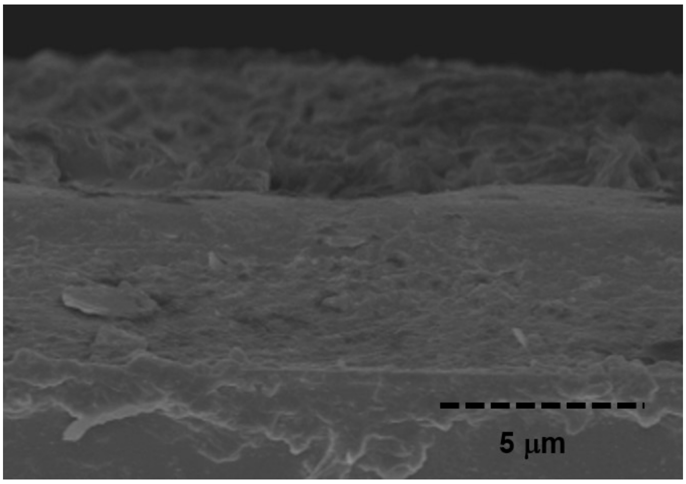


Figure S3. Cross-sectional SEM image of TiO_2|TPA|PNO|**1**.

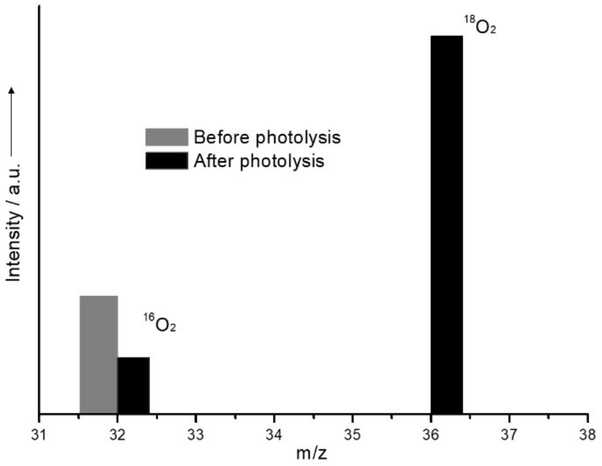


Figure S4. GC-MS of aliquot of gas from the air-tight sealed PEC cell before (gray) and after (black) 30min of photolysis of 97 atom% $H_2{}^{18}O$ containing 0.1 M NaF. The amplitude was normalized to the N_2 intensity.

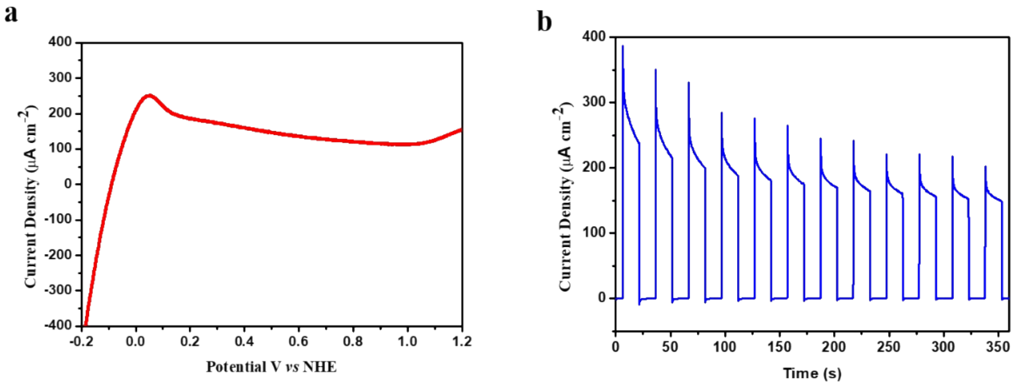


Figure S5. (a) Linear sweep voltammogram for TiO_2|TPA|Nafion|**1** under illumination above 400 nm at 100 mW cm^{-2} in pH =7 0.1 M phosphate buffer containing 0.4 M $NaClO_4$. (b) Current density-time trace over 15 s dark-light cycles for TiO_2|TPA|Nafion|**1** at a constant bias of 0.4 V *vs* NHE under the identical conditions used in (a).

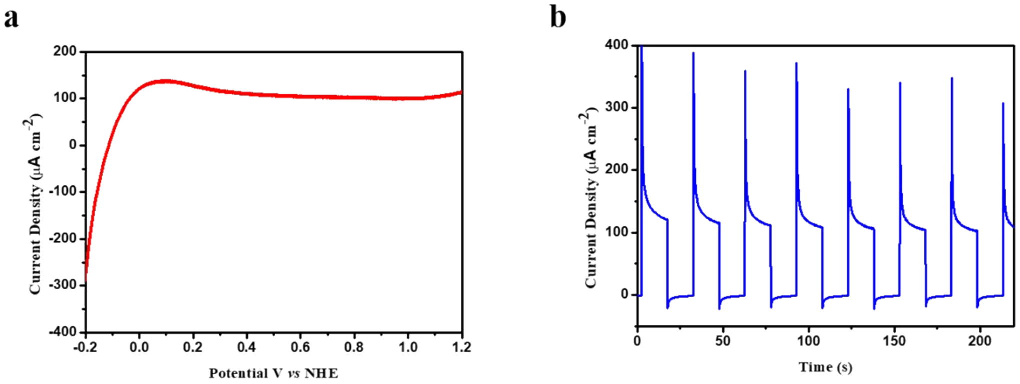


Figure S6. (a) Linear sweep voltammograms for TiO_2|TPA|PMMA|**1** under illumination above 400 nm at 100 mW cm^{-2} in pH =7, 0.1 M phosphate buffer containing 0.4 M $NaClO_4$. (b) Current density-time traces over 15s dark−light cycles for TiO_2|TPA|PMMA|**1** at a constant bias of 0.4 V *vs* NHE under the identical conditions used in (a).

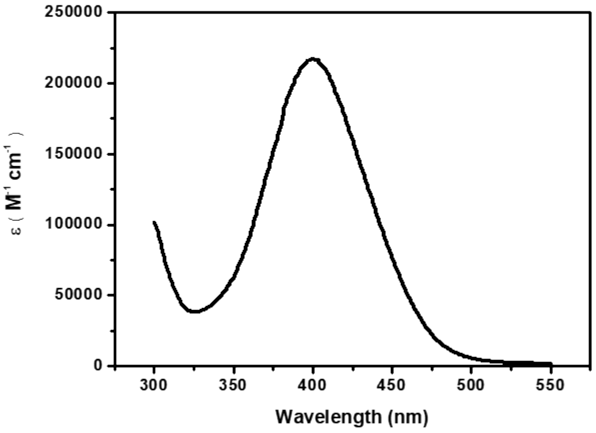


Figure S7. UV-vis absorption of the TPA dye in CH_2Cl_2.

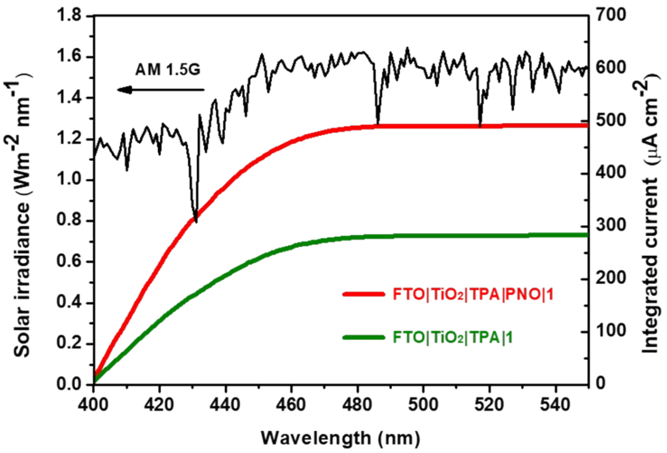


Figure S8. Solar irradiance of AM 1.5G (ASTM G173-03) and calculated photocurrent of TiO_2|TPA|PNO|**1** and TiO_2|TPA|PNO|**1** electrodes by integrating IPCE at 0.4 V *vs* NHE over the photon flux of AM 1.5G.

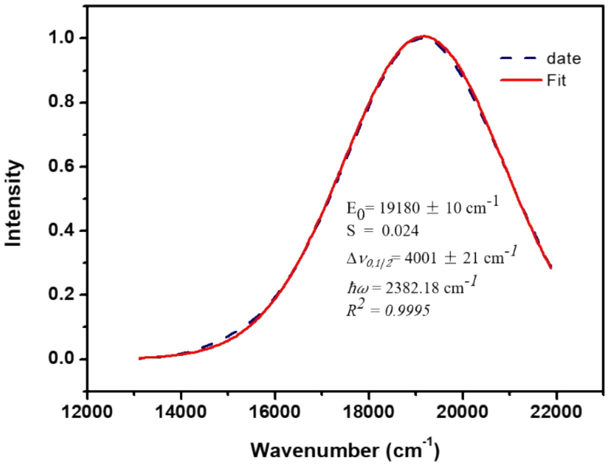


Figure S9. Emission spectra of TPA sensitized TiO_2 film immersed in pH 7 phosphate buffer and fitting thereof. Emission spectra of TiO_2|TPA were first converted to intensity units of quanta per second with the x-axis expressed as wavenumbers and then fitted using a single-mode Franck-Condon analysis as the following equation:

$$I(\tilde{\nu}) = \sum_{\nu=0}^{10}\left\{\left(\frac{E_0 - \nu\hbar\omega}{E_0}\right)^3\left(S^{\nu}\right) \times exp\left[-4ln(2)\left(\frac{\tilde{\nu} - E_0 + \nu\hbar\omega}{\Delta\tilde{\nu}_{0,1/2}}\right)^2\right]\right\}$$

In this equation, $\hbar\omega$ is the quantum vibrational energy spacing of the single acceptor mode of medium frequency, E_0 is the free-energy difference between the ground and lowest-energy excited-states, $\Delta\tilde{\nu}_{0,1/2}$ is the full-width-at-half-maximum of the gaussian-broadened 0-0 vibronic component. *S* is the Huang-Rhys factor. The value of $\hbar\omega$ was obtained by previously described method.[4] The fitting was performed in MATLAB (version R2018a) with 11 vibrational levels included in the summation.

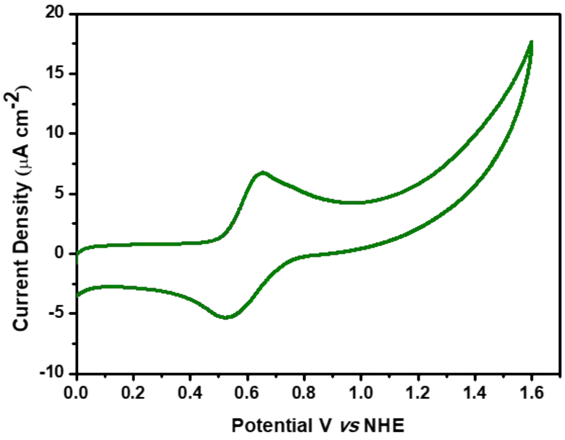


Figure S10. Cyclic voltammogram for **1** loaded on *nano*ITO at pH = 7 in 0.1 M phosphate buffer with 0.4 M $NaClO_4$, scan rate 20 mV s^{-1}.

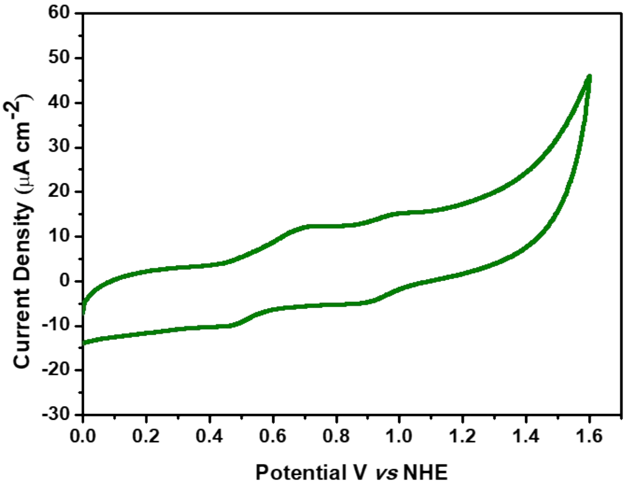


Figure S11. Cyclic voltammogram for catalyst **3** (1 mM) in the mixed CH_3CN/H_2O (v/v = 1 : 2) solution. Working electrode = glassy carbon electrode, scan rate =20 mV s^{-1}.

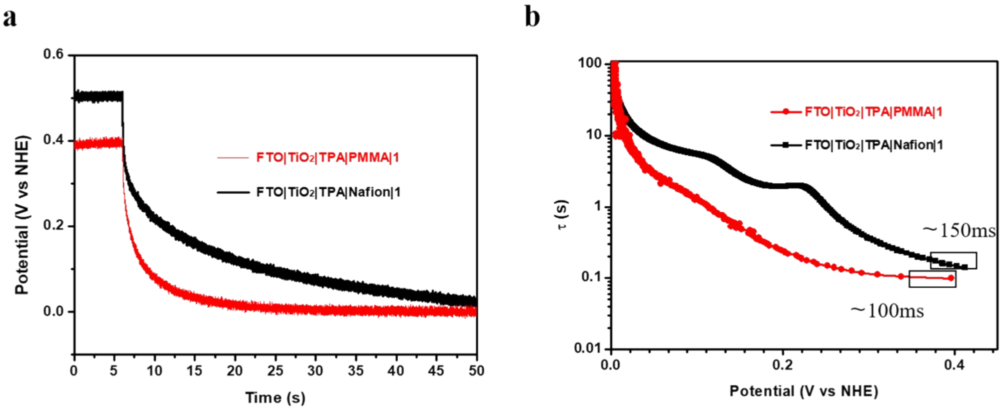


Figure S12. (a) Open-circuit voltage decays for the electrodes TiO$_2$|TPA|PMMA|**1** (red) and TiO$_2$|TPA|Nafion|**1** electrodes (black). (b) Electron lifetime derived from Equation 7 plotted as a function of V_{oc} at the transient when illumination (> 400nm, 100 mW cm^{-2}) was removed under the open-circuit condition. The results were obtained in 0.1 M phosphate buffer solution at pH 7.

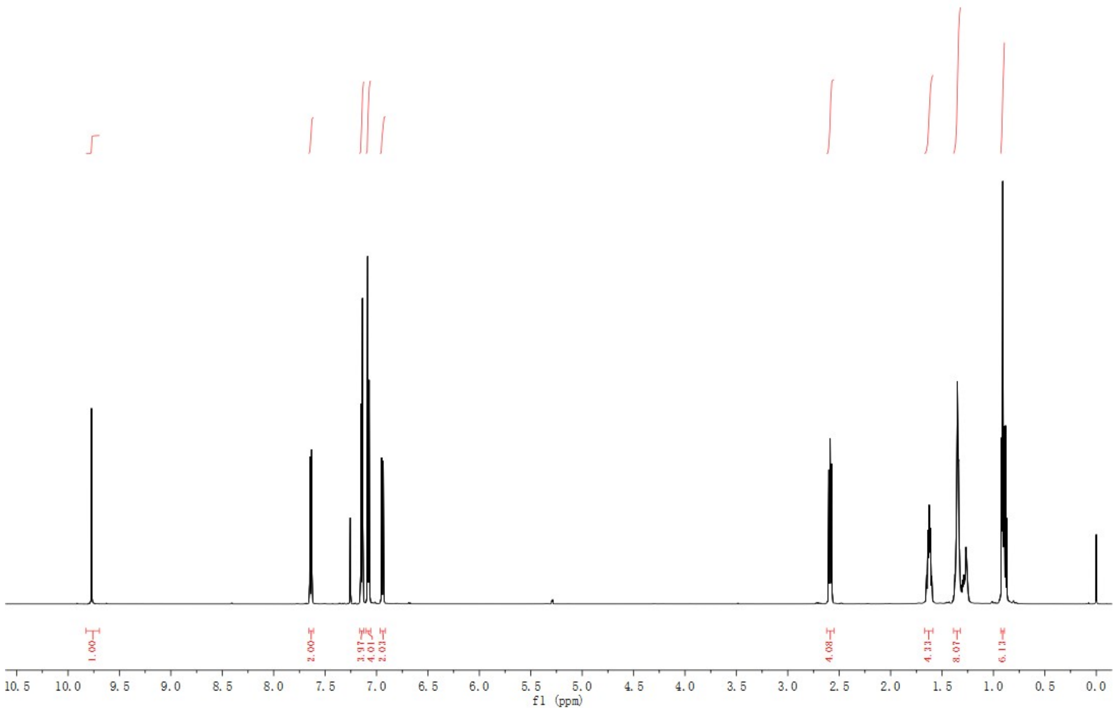


Figure S13. ^1H NMR spectrum of complex TPA-CHO in $CDCl_3$.

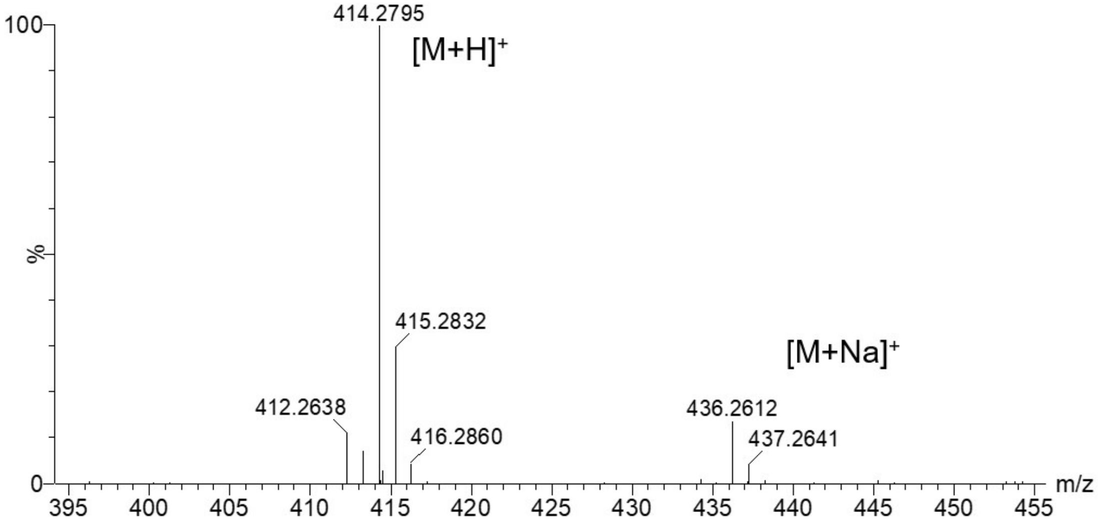


Figure S14.HRMS spectrum of complex TPA-CHO in CH_3OH.

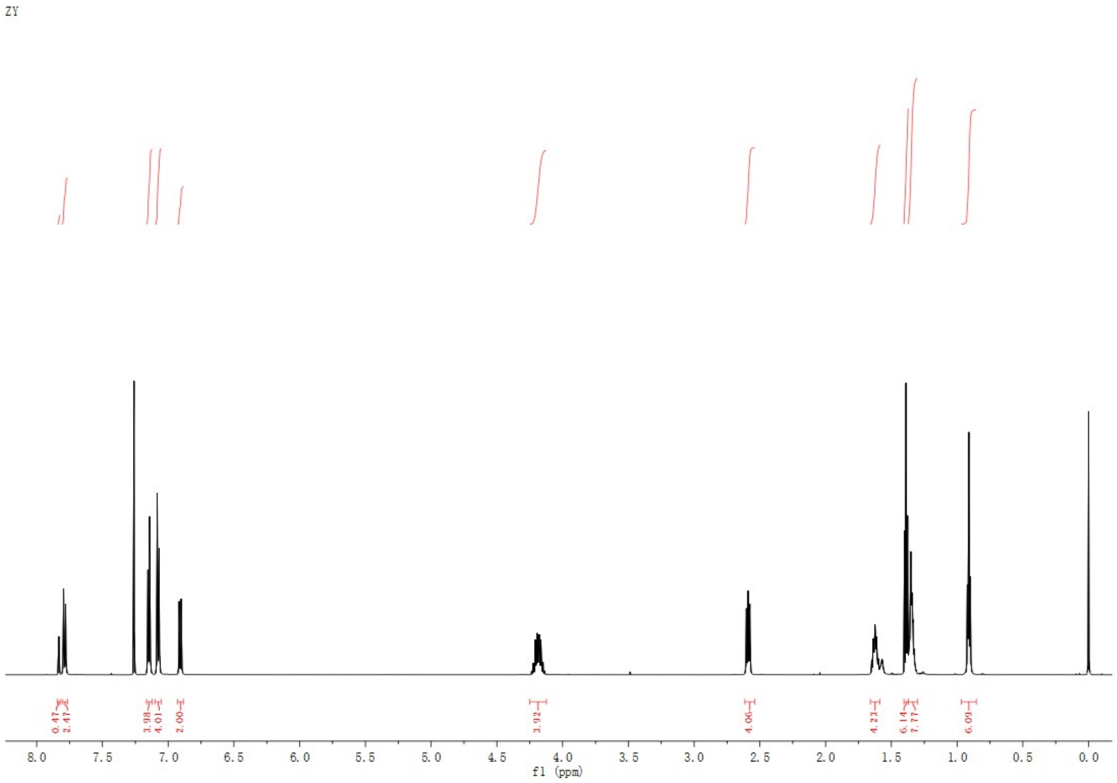


Figure S15. ^{1}H NMR spectrum of complex TPA-PO$_3$Et$_2$ in CDCl$_3$.

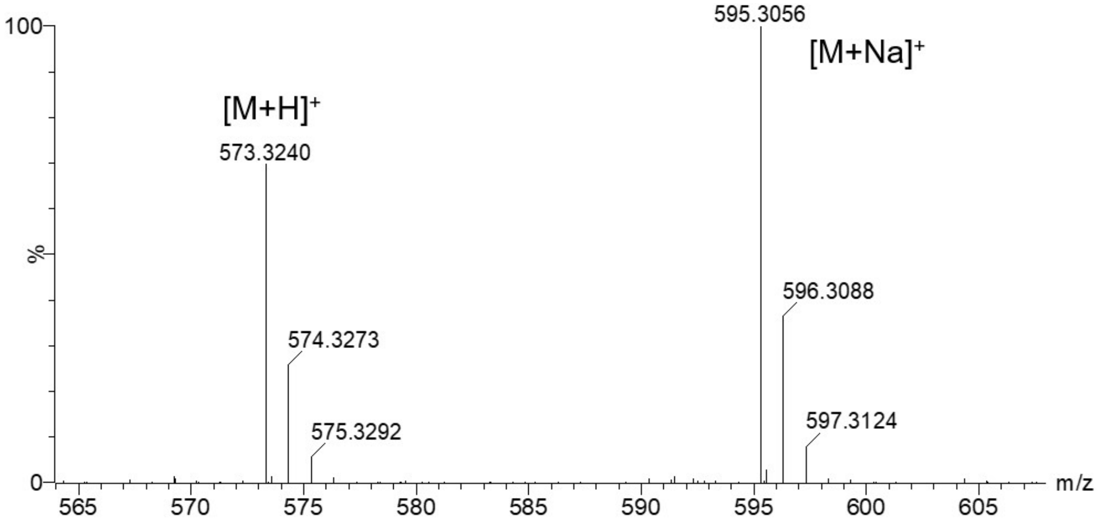


Figure S16. HRMS spectrum of complex TPA-PO$_3$Et$_2$ in CH$_3$OH.

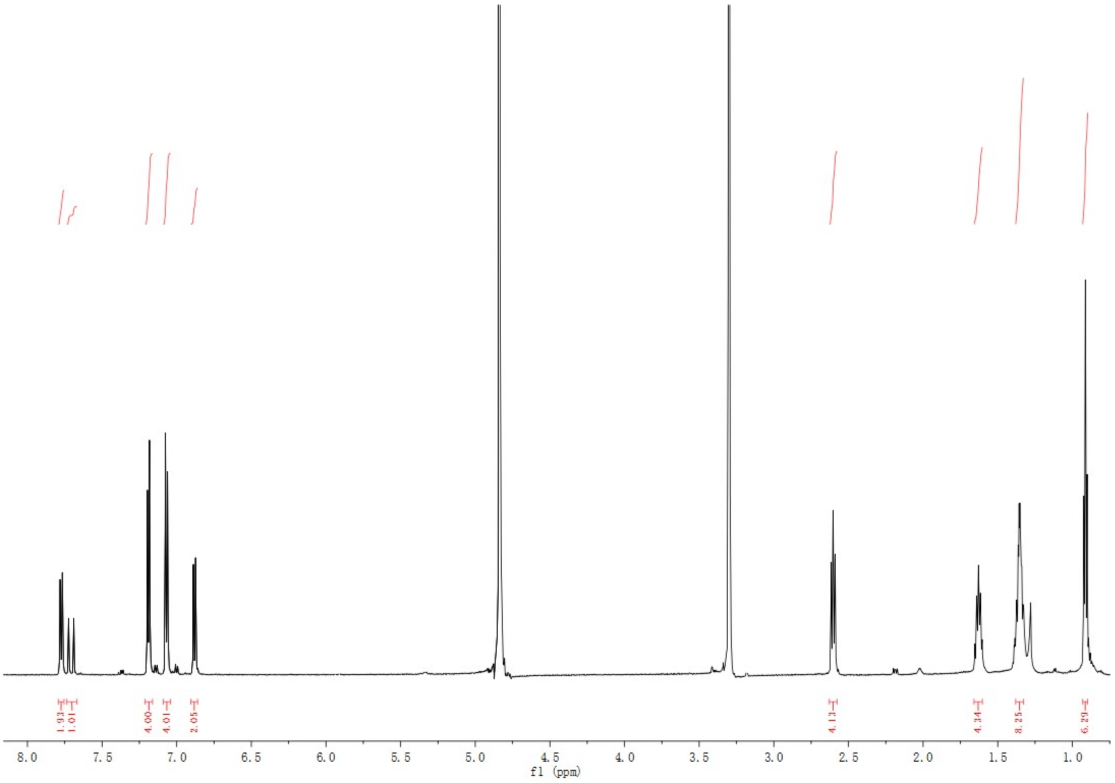


Figure S17. ^1H NMR spectrum of complex TPA in CD_3OD.

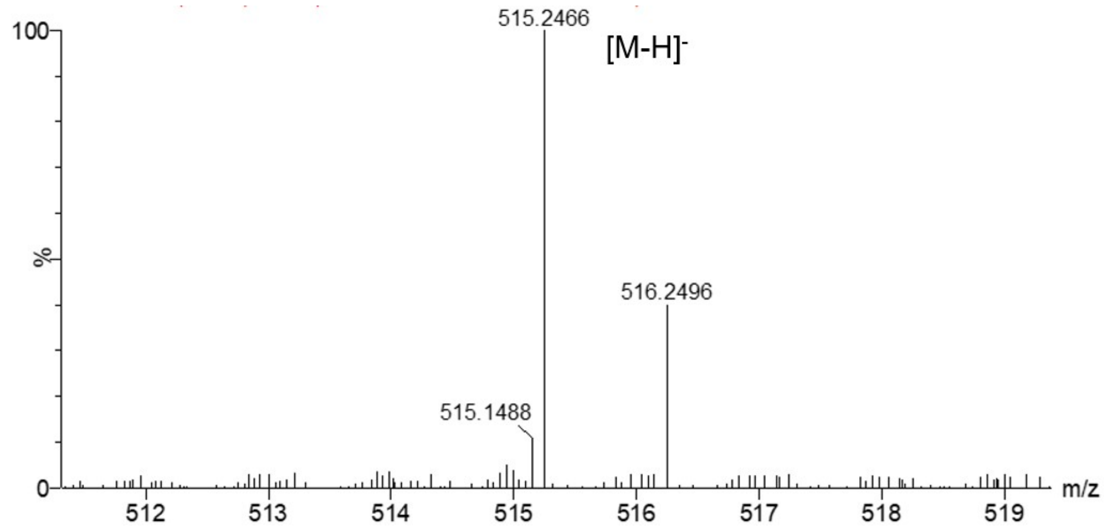


Figure S18. HRMS spectrum of complex TPA in CH_3OH.

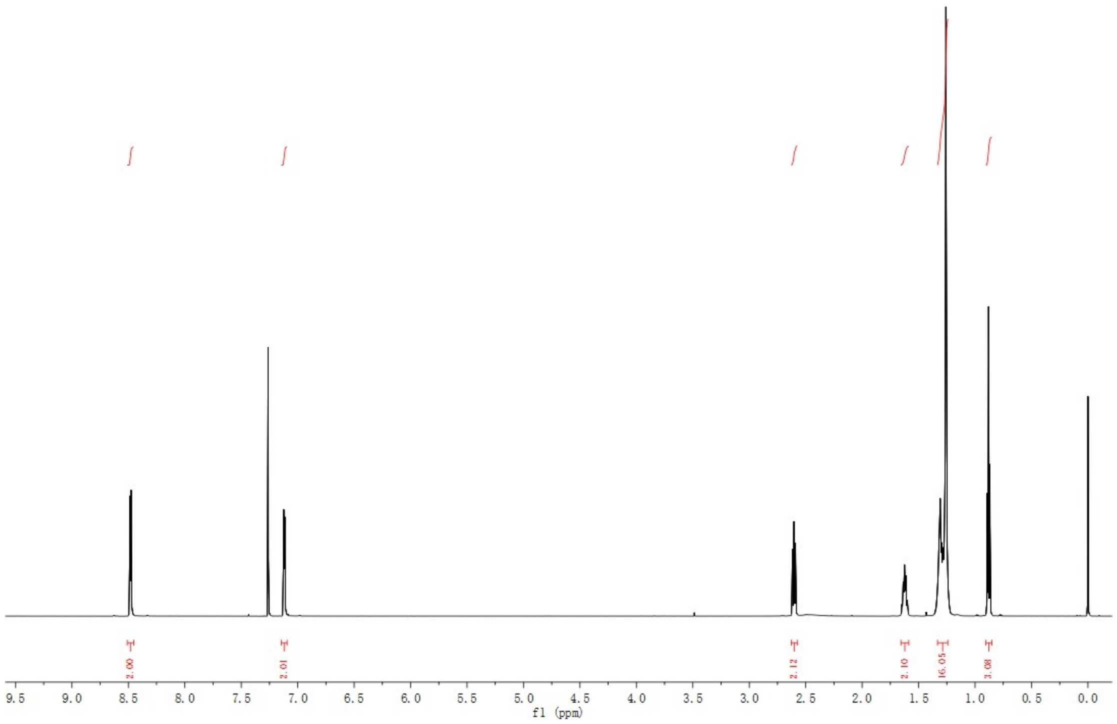


Figure S19. ^{1}H NMR spectrum of complex 4-undecylpyridine in $CDCl_3$.

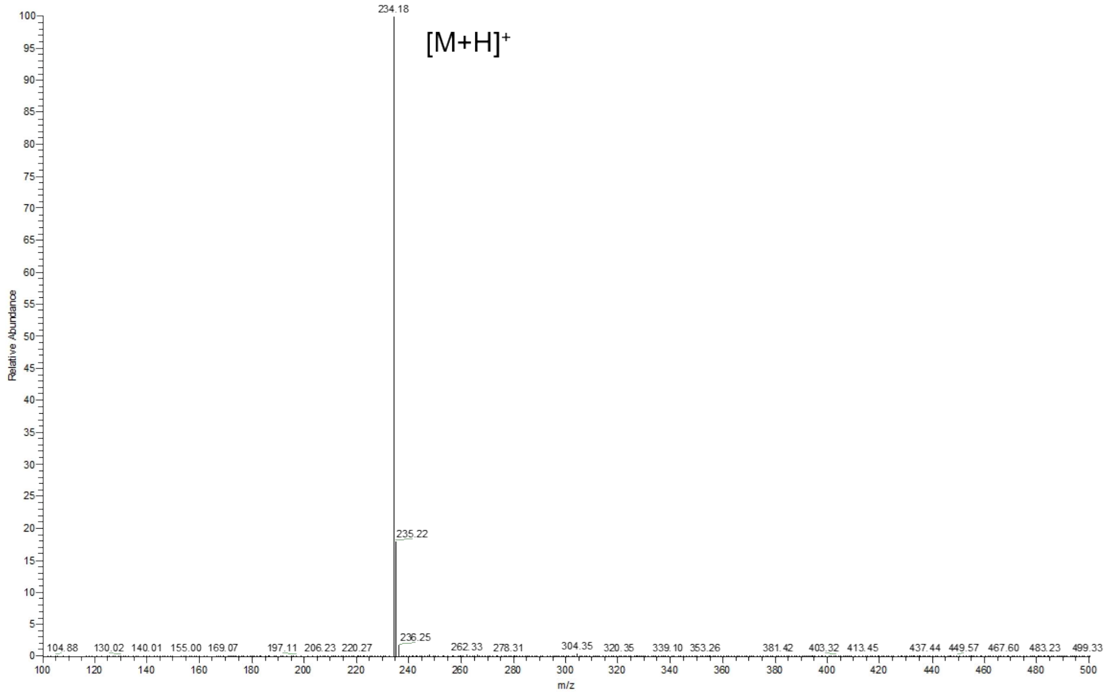


Figure S20. MS-ESI spectrum of complex 4-undecylpyridine in CH_3OH.

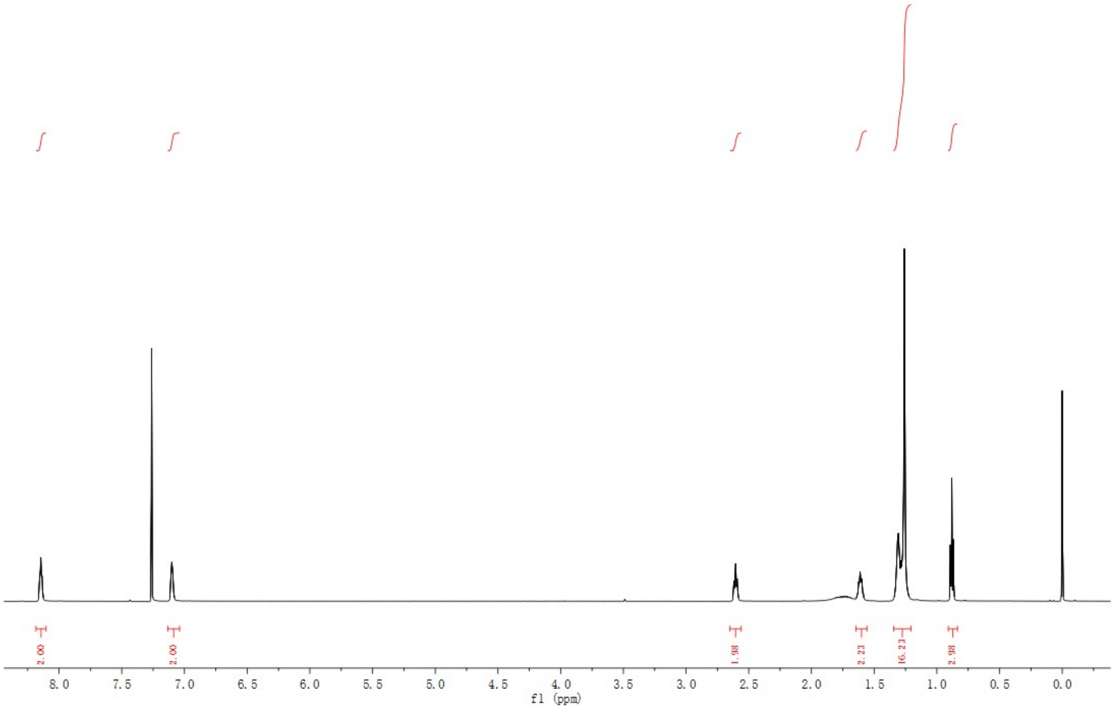


Figure S21. ^{1}H NMR spectrum of complex PNO in $CDCl_3$.

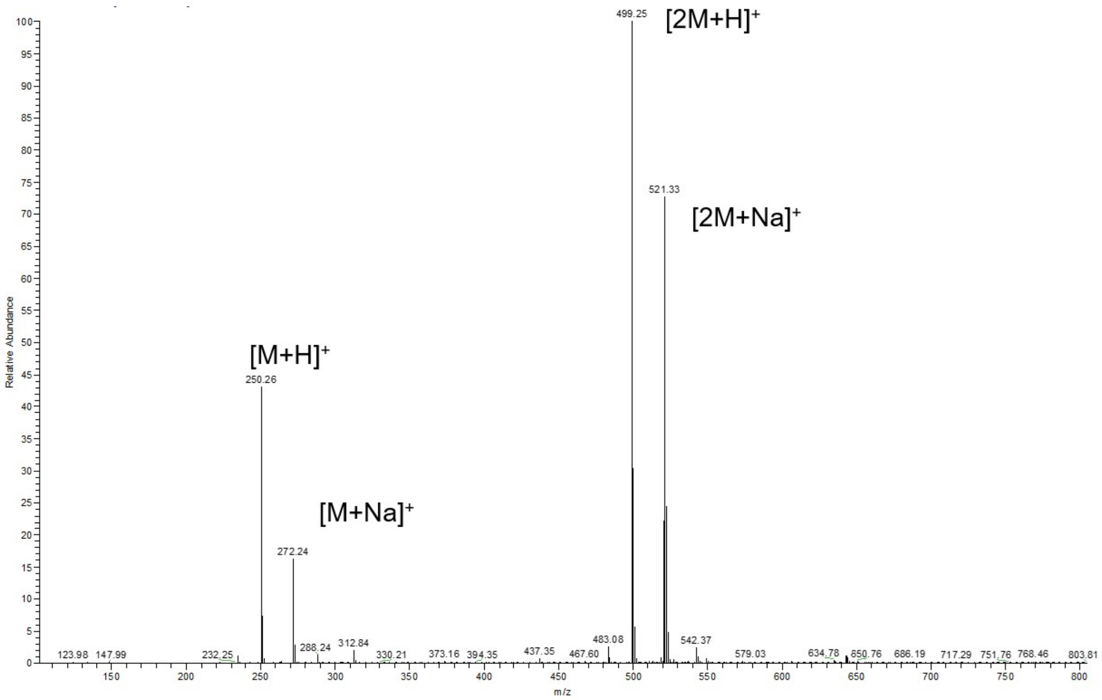


Figure S22. MS-ESI spectrum of complex PNO in CH_3OH.

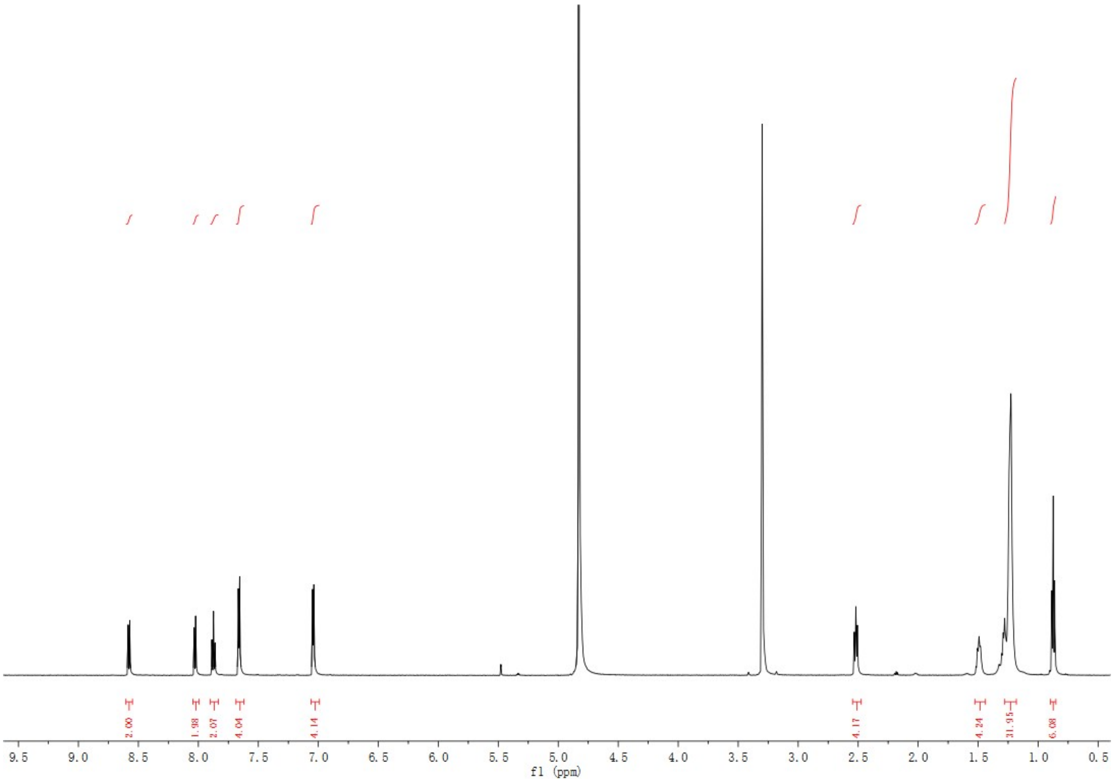


Figure S23. ^{1}H NMR spectrum of complex **1** in CD_3OD.

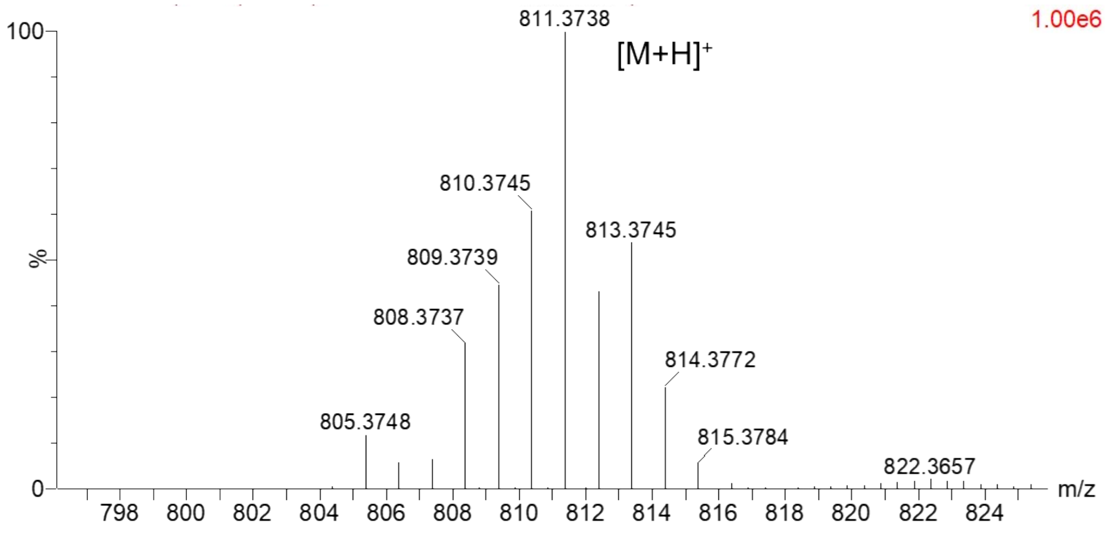


Figure S24. HRMS spectrum of complex **1** in CH_3OH.

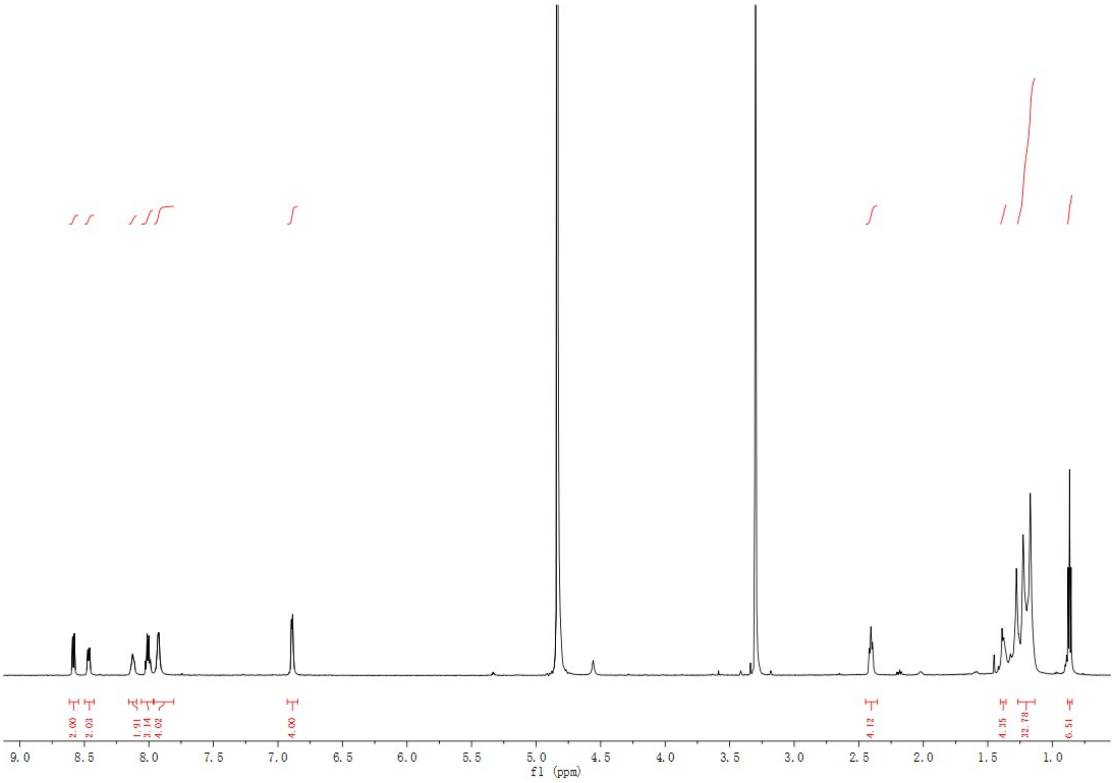


Figure S25. ^{1}H NMR spectrum of complex **3** in CD_3OD.

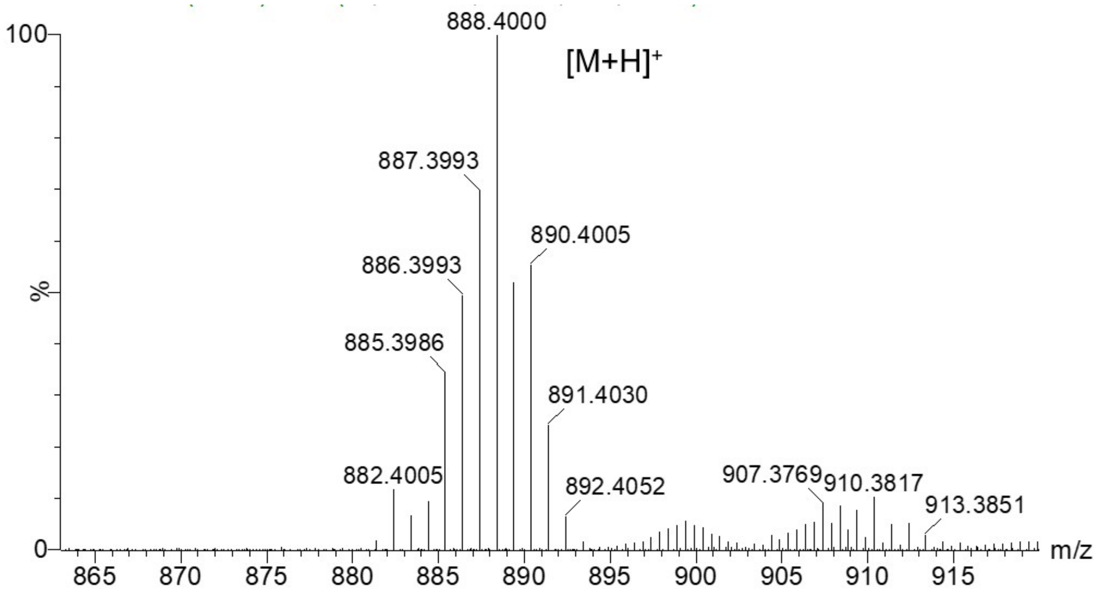


Figure S26. HRMS spectrum of complex **3** in CH_3OH.

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