

Supplementary Information

Porphyrin-based imine gels for enhanced visible-light photocatalytic
hydrogen production

Peisen Liao, Ya Hu, Ziwei Liang, Jianyong Zhang, Hao Yang, Lan-Qi He, Ye-Xiang
Tong, Jun-Min Liu, Liuping Chen, and Cheng-Yong Su*

*Sun Yat-Sen University, MOE Laboratory of Bioinorganic and Synthetic Chemistry,
Lehn Institute of Functional Materials, Guangzhou 510275, China. *E-mail:
zhjyong@mail.sysu.edu.cn*

Experimental

Analytical grade solvents were purchased from Damao Chemical Reagent Factory (Tianjin, China), analytical grade reagents were obtained from Aladdin (Shanghai, China), and PdCl₂ (99%) was purchased from HWRK Chem. Co., LTO (Beijing, China). Chemicals and solvents obtained from commercial sources were used as received without further purification unless otherwise stated. The free-base porphyrin H₂TAPP was synthesized¹ and subsequently metallated with metal salts (PdCl₂ and SnCl₂·2H₂O) to yield PdTAPP and SnTAPP according to the literature procedure.² 1,3,5-tris-(4-formyl-phenyl)triazine (TFPT) was synthesized as reported previously.³ Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) analysis was performed using either a Quanta 400F SEM equipped with an INCA energy dispersive X-ray spectrometer or an ultra-high resolution SU8010 FE-SEM. Prior to SEM measurements, gel samples were dispersed in EtOH with the aid of sonication, and then deposited on a silicon plate. Transmission electron microscopy (TEM) investigations were carried out on a FEI Tecnai G2 Spirit 120 kV or 200 kV TEM system. To prepare a sample for TEM measurement, wet gel was dispersed in EtOH using sonication method, and then mounted on a carbon coated copper grid. Gas adsorption measurements were carried out using a Quantachrome Autosorb-iQ2 analyzer. Prior to an adsorption measurement, aerogel was typically degassed at 100 °C for 10 h to remove solvent molecules within the network. The absorption spectra were observed with a Shimadzu UV-3600 spectrometer. Powder X-ray diffraction (XRD) was recorded on a Rigaku Smart Lab diffractometer (Bragg-Brentano geometry, Cu-Kα1 radiation, $\lambda = 1.54056 \text{ \AA}$). Cross-polarization magic-angle-spinning (CP/MAS) ¹³C NMR spectroscopy was performed on a Bruker Ascend 300 MHz spectrometer (MAS probe with 4 mm outside diameter, zirconia rotors). Photoluminescent spectra were measured on a Shimadzu RF-5301 fluorescence spectrophotometer and time-resolved emission decay behaviours were obtained using a FluoroLog-TCSPC spectrometer from HORIBA instruments.

Gel Preparation: Typical procedure: A solution of 1,3,5-tris-(4-formyl-phenyl)triazine

(TFPT) (15.7 mg, 0.04 mmol) in DMSO (0.5 mL) was added into a solution of PdTAPP (23.4 mg, 0.03 mmol) in DMSO (0.5 mL), and then HOAc (30 μL , 3 mol L⁻¹ in DMSO) was added whilst stirring. Heating the precursor solution at 80 °C accelerated the gelation to give an opaque brownish black gel within 0.5 h.

For drying by subcritical CO₂(l),⁴ the wet gel was subjected to solvent exchange with EtOH (5 mL \times 3). The gel was then placed in a high-pressure Soxhlet stainless-steel autoclave extractor (0.75 L). The solvent in the wet gel was extracted with liquid CO₂ (ca. 270 g) for 24 h, and the extraction temperature was kept at 35.0 °C (pressure 5.9 MPa). After the extractor was depressurized slowly at room temperature over ca. 2–3 h, PdTAPP-TFPT aerogel was obtained (25.4 mg, 69%).

SnTAPP-TFPT aerogel (25.7 mg, 71%) and H₂TAPP-TFPT aerogel (25.0 mg, 74%) were prepared following similar procedures.

Electrochemical measurement: Electrochemical measurements were performed using a CHI-760e electrochemical workstation (CH Instruments, China). The electrochemical cell used is equipped with three electrodes including a Pt mesh counter-electrode, an Ag/AgCl reference electrode (3 mol L⁻¹ KCl) and a fluorin-doped tin oxide (FTO) glass functionalized with porphyrin gels as a working electrode. KH₂PO₄ aqueous solutions (0.1 mol L⁻¹) were used as the electrolyte medium for the electrochemical measurements.

The PdTAPP-TFPT gel film was prepared by drop deposition of a premixed DMSO solution containing both PdTAPP and TFPT. Firstly, PdTAPP (0.03 mmol, 23.7 mg) and TFPT (15.7 mg, 0.04 mmol) were dissolved in 500 μL of DMSO, respectively. Secondly, the PdTAPP/DMSO solution (4 μL) and the TFPT/DMSO solution (4 μL) were mixed thoroughly with the aid of ultrasonication. For the sample measured in the electrochemical experiments, a drop of the solution mixture (2 μL) was deposited onto a 1 \times 1 cm² area at one end of a FTO substrate to produce a PdTAPP-TFPT gel film. Gelation was observed to occur in 2 min. After standing at ambient conditions

for 24 h, the sample underwent two solvent exchange processes including one with DMSO for 72 h, and then the other with water for 24 h.

In a similar protocol, the H₂TAPP-TFPT gel film was also prepared by the drop deposition of a premixed solution of H₂TAPP and TFPT dissolved in DMSO.

All the solutions for the gel formation were confined within the area where the FTO glass was in contact with electrolytic solutions (1×1 cm²).

Photocatalytic hydrogen production: The photocatalytic hydrogen production system was Per-fect Light Lab Solar-IIIAG and H₂ measurement was performed on Agilent Technologies 78. The photocatalytic hydrogen evolution by water splitting was performed in a glass reaction cell with quartz cover connected to a closed gas circulation which was swept by high purity N₂ before illumination.⁵ Pt was loaded onto the gels by the in situ photodeposition method. PdTAPP-TFPT wet gel (25 mg based on gelator) was dispersed in water (10 mL) with the aid of ultrasonication for 5 min. H₂PtCl₆ (300 μL, 10 mmol L⁻¹) and H₂O (90 mL) was added into the dispersion. After full illumination with a 300 W Xe lamp for 30 min, Pt@PdTAPP-TFPT wet gel was obtained. For long-time hydrogen evolution experiments, Pt@PdTAPP-TFPT wet gel (25 mg) was suspended in water (100 mL) and dispersed in an ultrasonic bath for 10 min. And then sodium ascorbate (700 mg) as sacrificial electron donor was added (pH = 7.0). Then the suspension was exposed to a 300 W Xe lamp equipped with a 420 nm cut-off filter to remove UV light. The power densities of the light going through all the bandpass filters and finally illuminating on the flask are 1255 W m⁻², measured by a radiometer (FZ-A, Beijing Normal University photoelectric instrument factory). The reaction solution was stirred continuously and kept at 298 K by a circulation of cooling water. The amount of hydrogen evolved was determined with online gas chromatography.

Determination of quantum yield: The irradiation was conducted with an incident LED

light (Zolix, MLED4, $\lambda = 450 \text{ nm}$, 100 mW cm^{-2} , irradiation area 0.8 cm^2) at $25 \text{ }^\circ\text{C}$. The total number of incident photons was measured by a standard method using a potassium ferrioxalate ($\text{K}_3[\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]$) actinometer. The photon flux was determined to be $1083 \text{ } \mu\text{mol h}^{-1}$. The generated gas samples were analyzed by an Agilent 7820A gas chromatography equipped with a thermal conductivity detector (TCD) and a TDX-01 packed column. The oven temperature was held constant at $60 \text{ }^\circ\text{C}$, and the inlet and detector temperature were set at $80 \text{ }^\circ\text{C}$ and $200 \text{ }^\circ\text{C}$, respectively.

Quantum yield (Φ) was calculated according to the following equation:

$$\Phi = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\% = \frac{\text{number of evolved H}_2 \text{ molecules} \times 2}{\text{number of incident photons}} \times 100\%$$

$0.75 \text{ } \mu\text{mol}$, $0.65 \text{ } \mu\text{mol}$ and $0.09 \text{ } \mu\text{mol}$ of H_2 were produced within 24 h for 0.03 mmol (based on TAPP) of Pt@PdTAPP-TFPT, Pt@H₂TAPP-TFPT and Pt@SnTAPP-TFPT, respectively. The calculated quantum yields for Pt@PdTAPP-TFPT, Pt@H₂TAPP-TFPT and Pt@SnTAPP-TFPT are 0.0029%, 0.0025%, 0.00034%, respectively.

References

- 1 A. Bettelheim, B. A. White, S. A. Raybuck and R. W. Murray, *Inorg. Chem.*, 1987, **26**, 1009–1017.
- 2 L. Zeng, P. Liao, H. Liu, L. Liu, Z. Liang, J. Zhang, L. Chen and C.-Y. Su, *J. Mater. Chem. A*, 2016, **4**, 8328-8336.
- 3 S. Li, H. Huang, S. Yu and X. Li, *Chin. J. Chem.*, 2006, **24**, 1225-1229.
- 4 S. Xiang, L. Li, J. Zhang, X. Tan, H. Cui, J. Shi, Y. Hu, L. Chen, C.-Y. Su and S. L. James, *J. Mater. Chem.*, 2012, **22**, 1862-1867.
- 5 Y. Chen, L. Tan, J. Liu, S. Qin, Z. Xie, J. Huang, Y. Xu, L. Xiao and C.-Y. Su, *Appl. Catal. B Environ.*, 2017, **206**, 426-433.

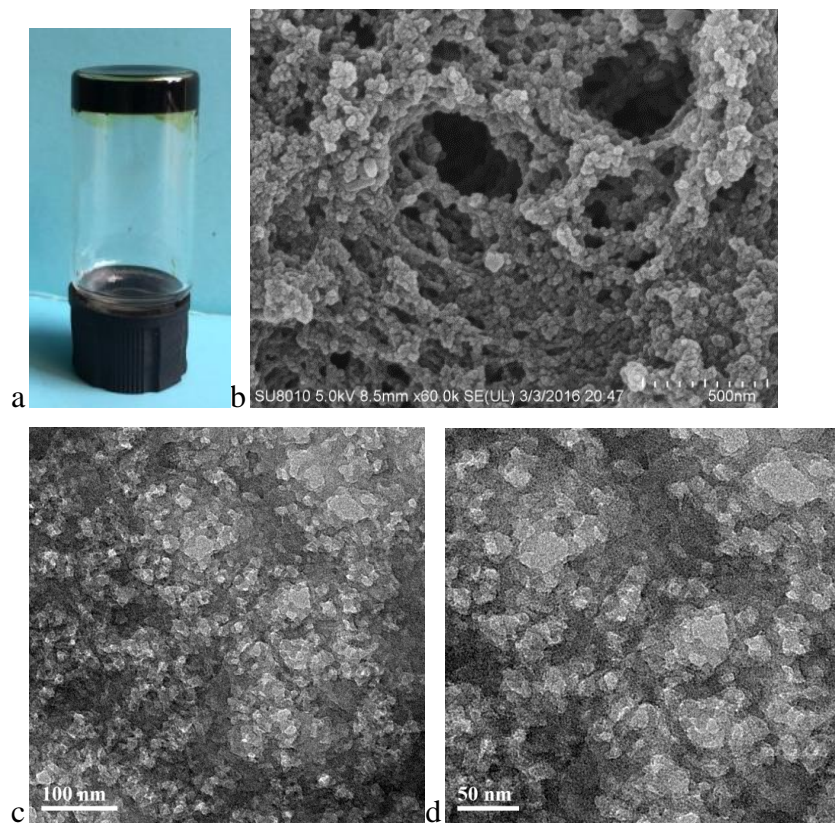


Fig. S1 (a) Photographic, (b) SEM and (c,d) TEM images of H₂TAPP-TFPT wet gel (bars represent 500,100 and 50 nm, respectively, for SEM and TEM).

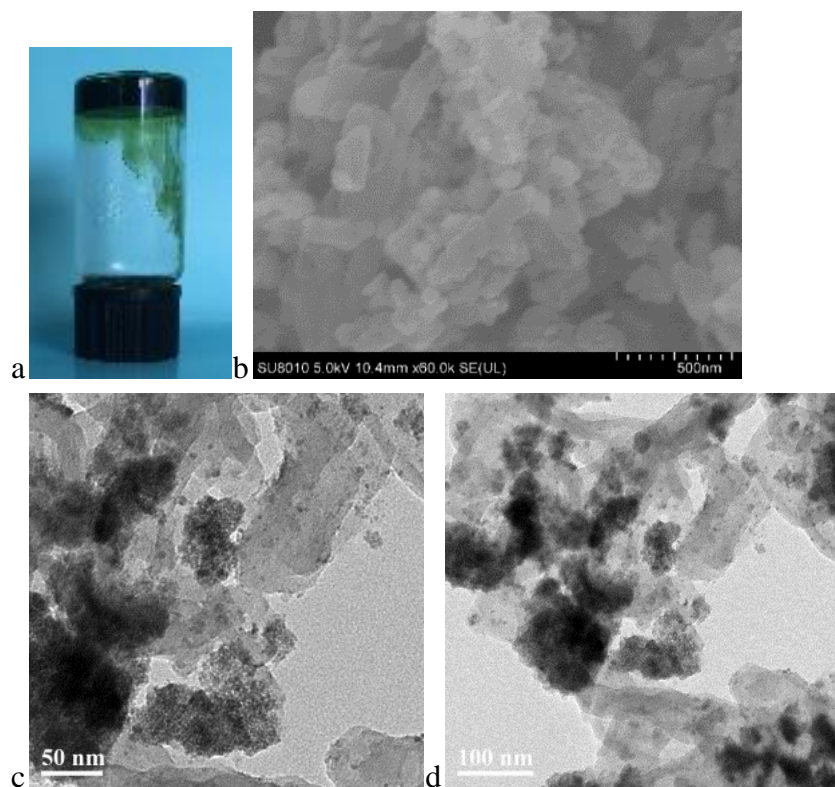


Fig. S2 (a) Photographic, (b) SEM and (c,d) TEM images of the SnTAPP-TFPT wet gel (bars represent 500,100 and 50 nm, respectively, for SEM and TEM).

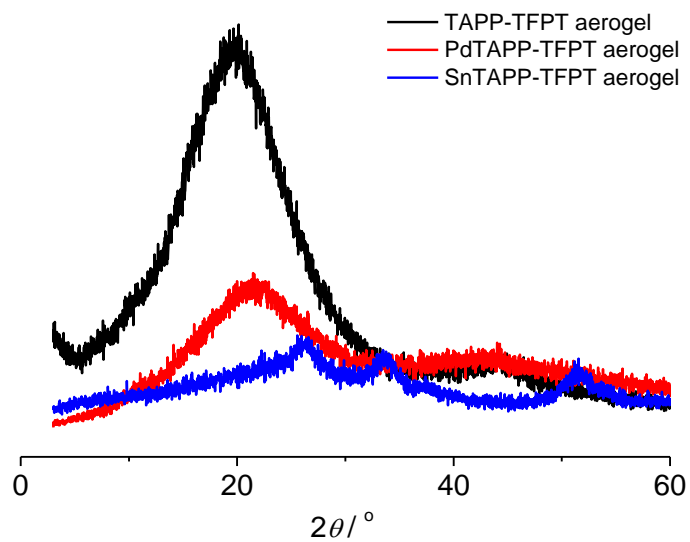


Fig. S3 PXRD patterns of the a) PdTAPP-TFPT b) H_2 TAPP-TFPT and c) SnTAPP-TFPT aerogels.

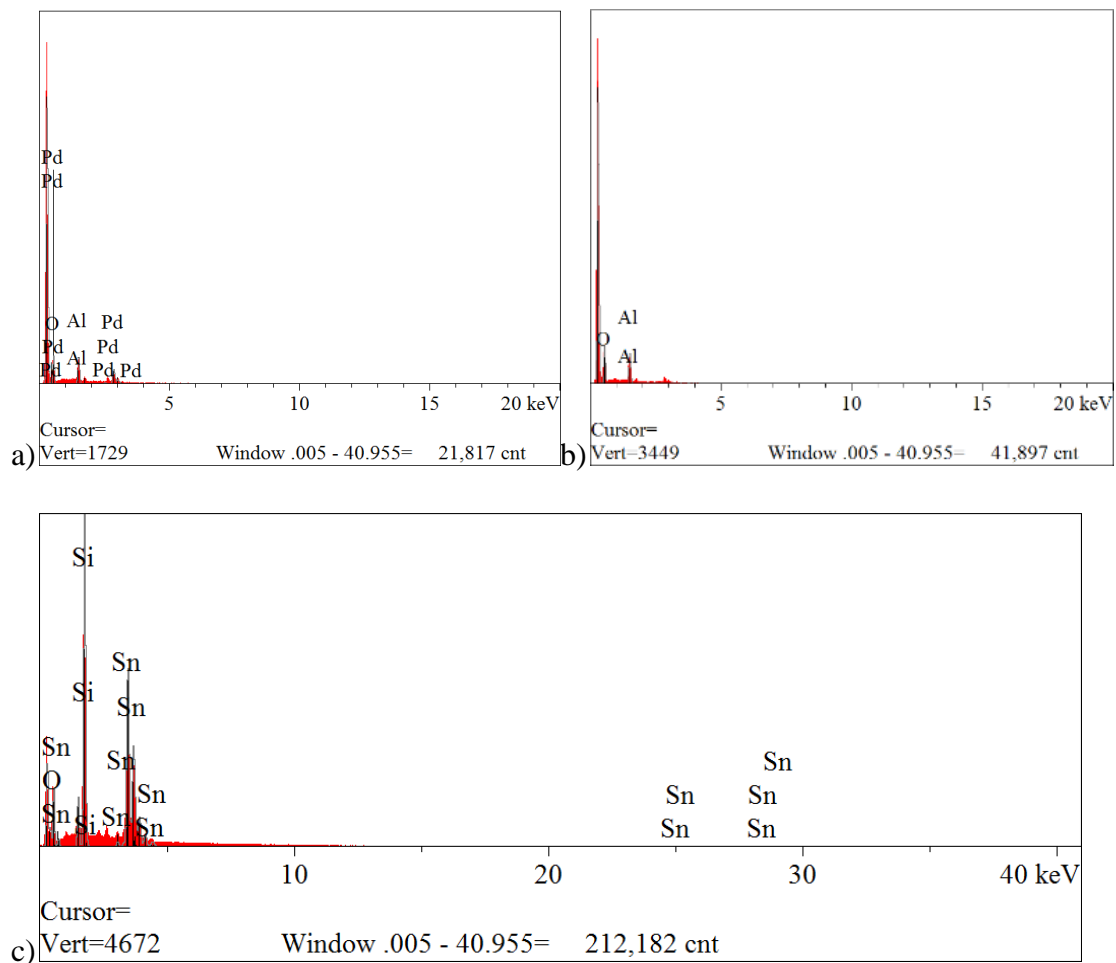


Fig. S4 Energy dispersive X-ray spectra of a) PdTAPP-TFPT (Quantitative values/atom%: Pd 1.065, C 78.148, and O 18.987), b) H₂TAPP-TFPT (Quantitative values/atom%: C74.312, O 23.912) and c) SnTAPP-TFPT (Quantitative values/atom%: Sn 16.040, C 50.361, and O 28.512). Al element was detected due to aluminum foil.

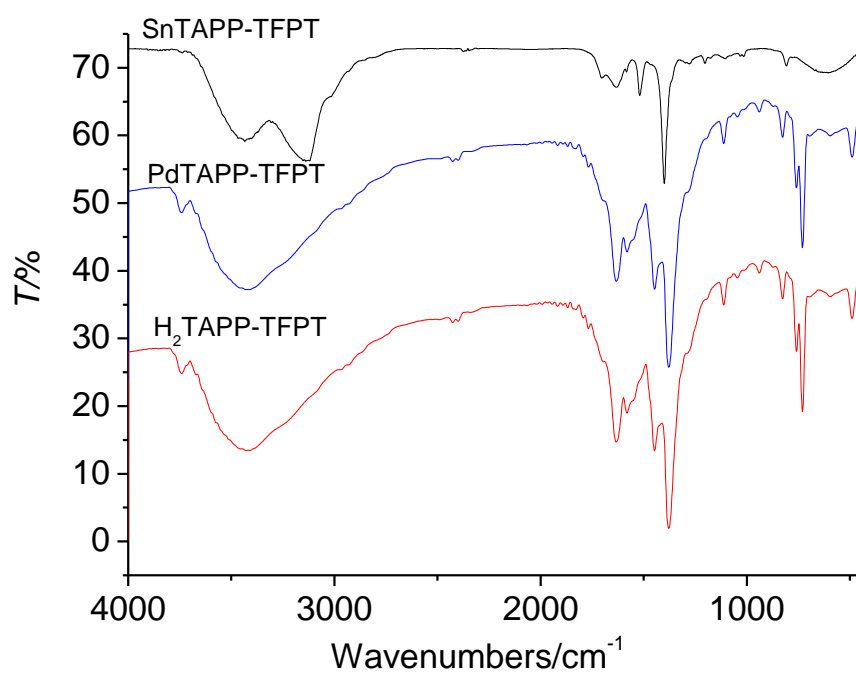


Fig. S5 FT-IR spectra of PdTAPP-TFPT, H₂TAPP-TFPT and SnTAPP-TFPT aerogels.

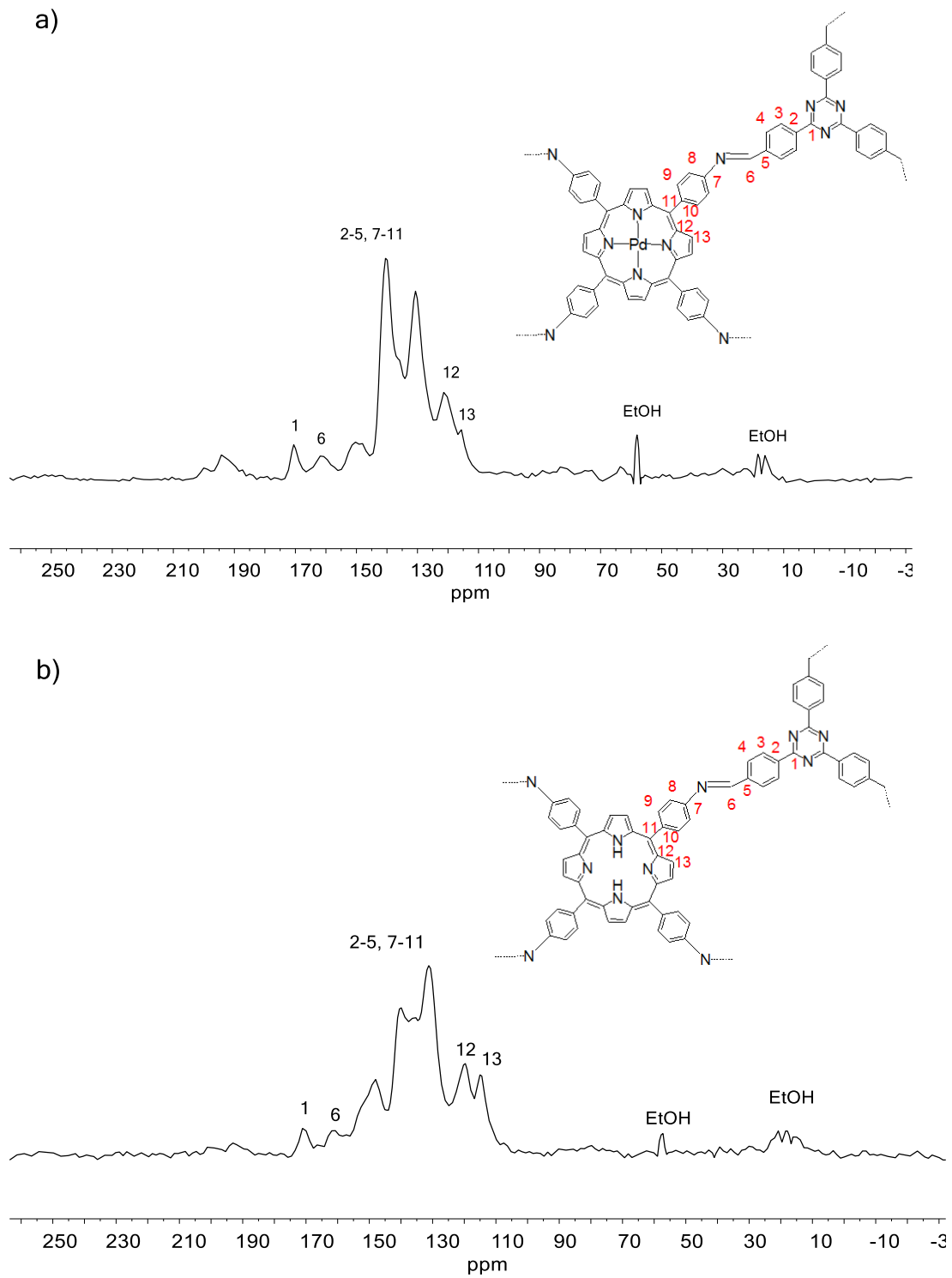


Fig. S6 Cross-polarization magic-angle-spinning (CP/MAS) ^{13}C NMR spectra of a) PdTAPP-TFPT and b) $\text{H}_2\text{TAPP-TFPT}$ aerogels.

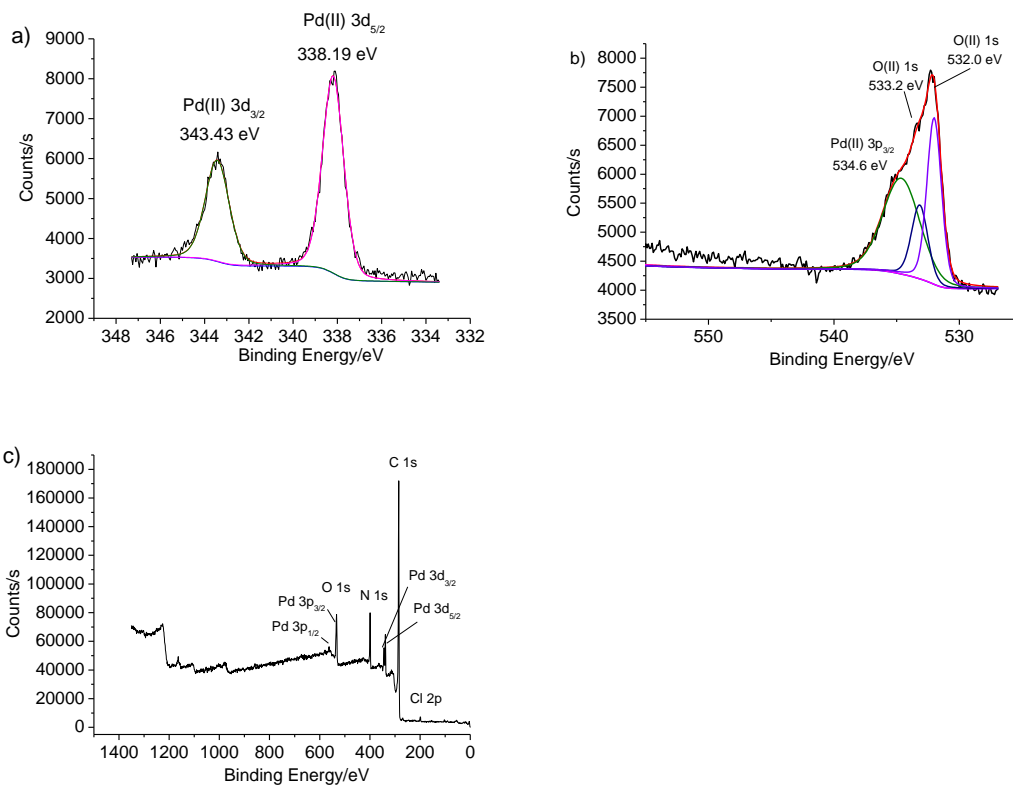


Fig. S7 a) XPS Pd 3d, b) O1s, and c) survey spectra of PdTAPP-TFPT aerogel.

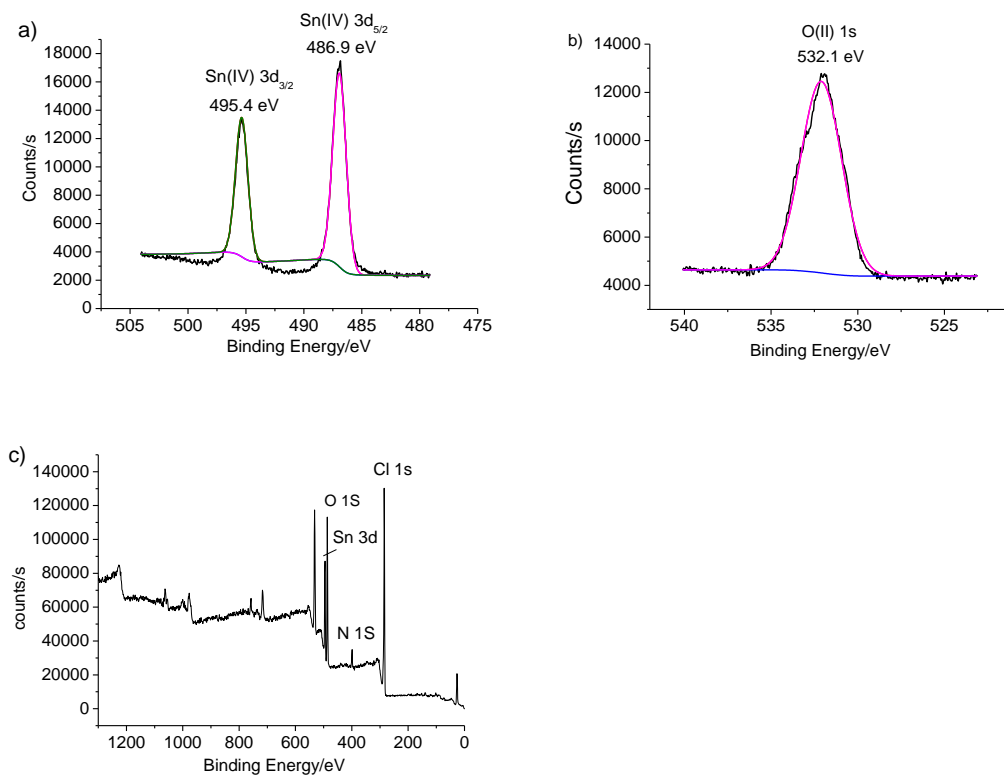


Fig. S8 a) XPS Sn 3d, b) O 1s, and c) survey spectra of SnTAPP-TFPT aerogel.

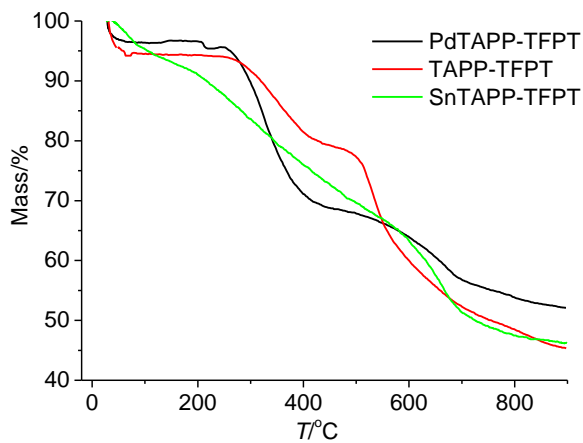


Fig. S9 TG curves of a) PdTAPP-TFPT b) H₂TAPP-TFPT c) SnTAPP-TFPT aerogels under N₂ atmosphere.

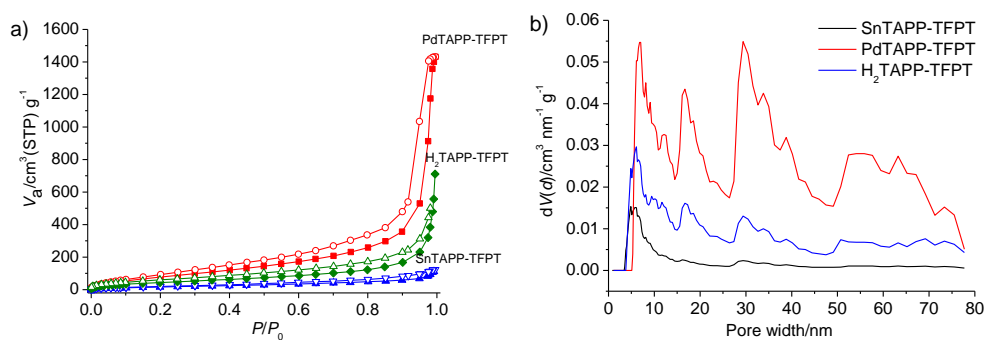


Fig. S10 a) N₂ adsorption (closed symbols) /desorption (open symbols) isotherms at 77 K, and b) NL-DFT pore size distributions (model: N₂ at 77 K on silica, cylinder pore, NLDET adsorption branch model) of PdTAPP-TFPT, H₂TAPP-TFPT and SnTAPP-TFPT aerogels.

Table S1 Porosity properties of PdTAPP-TFPT, H₂TAPP-TFPT and SnTAPP-TFPT aerogels.

Aerogel	$S_{\text{BET}}^{\text{a)}}$ /m ² g ⁻¹	$V_{\text{t}}^{\text{b)}}$ /cm ³ g ⁻¹	$V_{\text{micro}}^{\text{c)}}$ /cm ³ g ⁻¹	$V_{\text{meso}}^{\text{d)}}$ /cm ³ g ⁻¹
PdTAPP-TFPT	343	2.21	0	2.215
H ₂ TAPP-TFPT	180	1.10	0.033	1.074
SnTAPP-TFPT	61	0.19	0.010	0.183

a) S_{BET} is the BET specific surface area in the units of m² g⁻¹. b) V_{t} is the total specific pore volume. c) V_{micro} is the specific micropore volume calculated using the SF method. d) V_{meso} is the specific mesopore volume calculated using the BJH method.

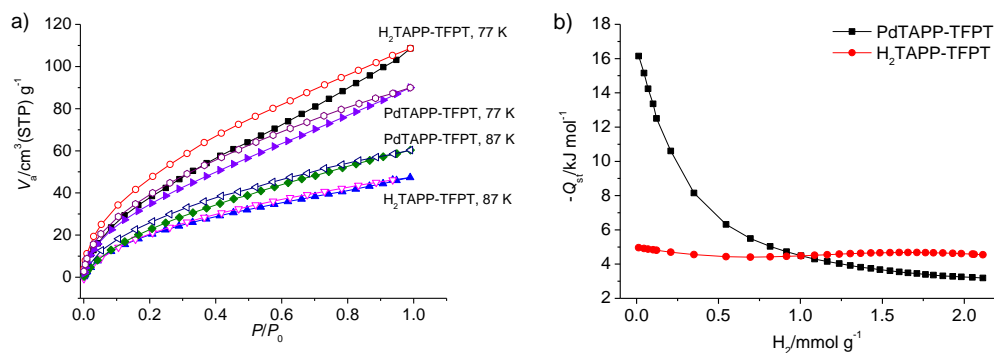


Fig. S11 a) H₂ adsorption (closed symbols)/desorption (open symbols) isotherms for PdTAPP-TFPT and H₂TAPP-TFPT aerogel at 77 and 87 K, and b) isosteric heats of adsorption (Q_{st}) as a function of gas loading, estimated from low pressure isotherms at 273 and 298 K by applying the virial equation.

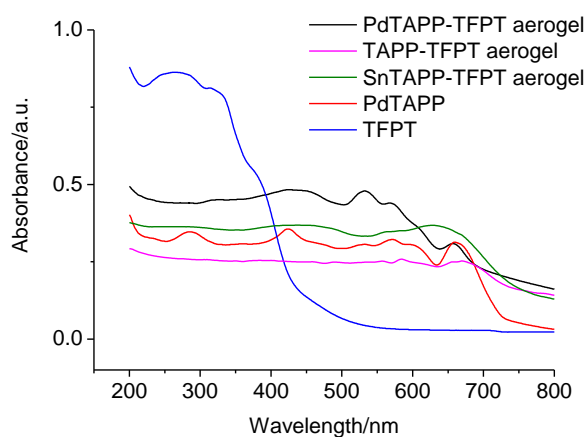


Fig. S12 Solid-state diffuse reflectance UV/Vis spectra of PdTAPP-TFPT, H₂TAPP-TFPT, SnTAPP-TFPT aerogels, PdTAPP and TFPT.

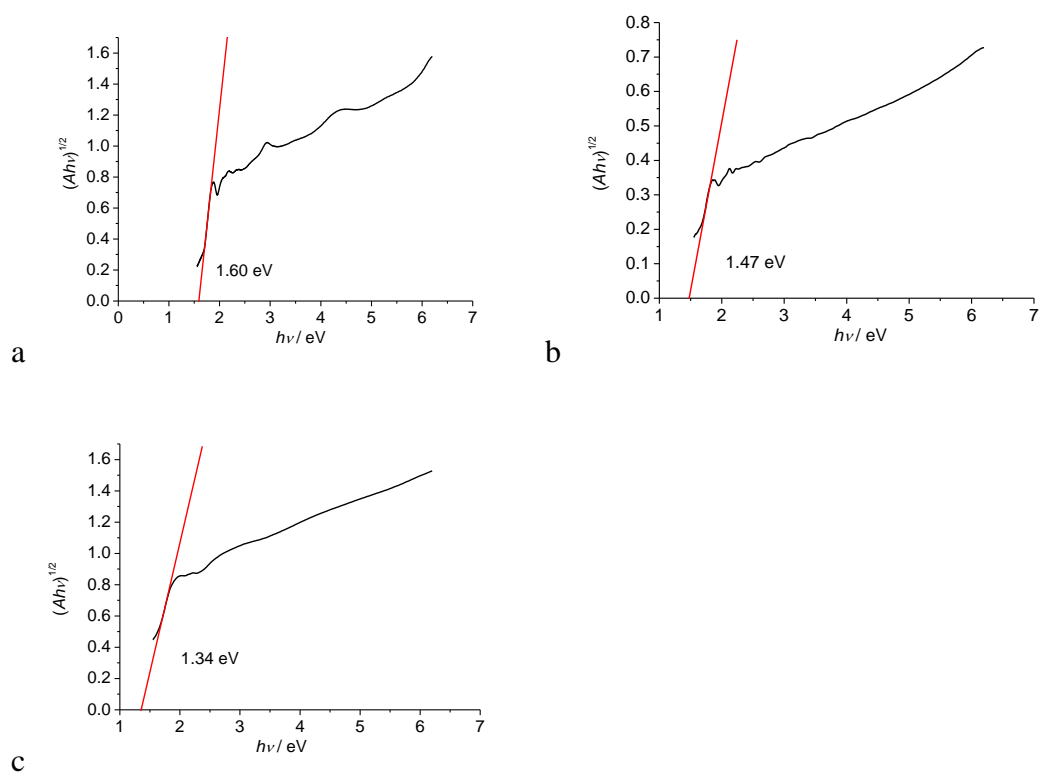


Fig. S13 Tauc plots of a) PdTAPP-TFPT, b) H₂TAPP-TFPT, c) SnTAPP-TFPT.

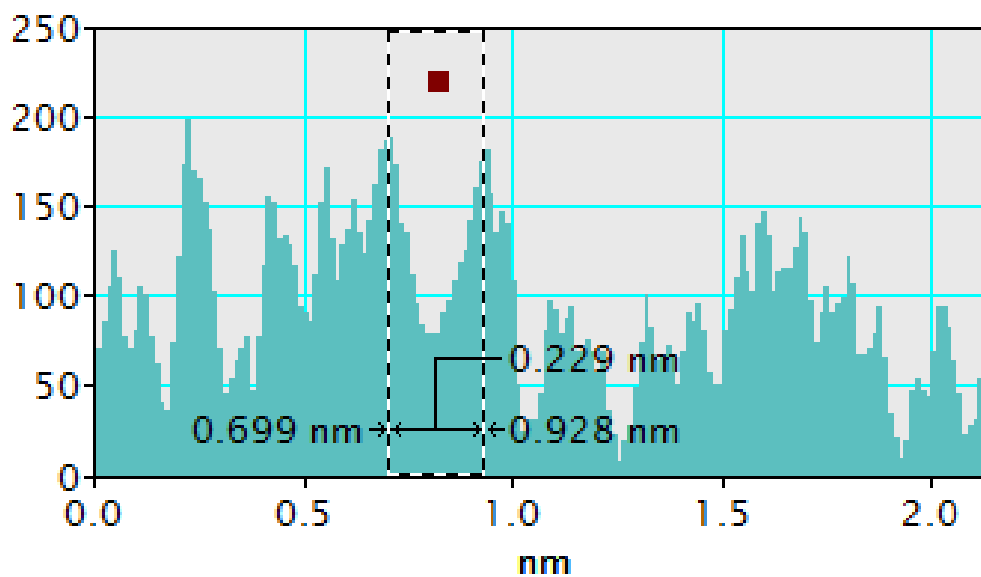


Fig. S14 TEM profile of calibration of Pt@PdTAPP-TFPT (fresh).

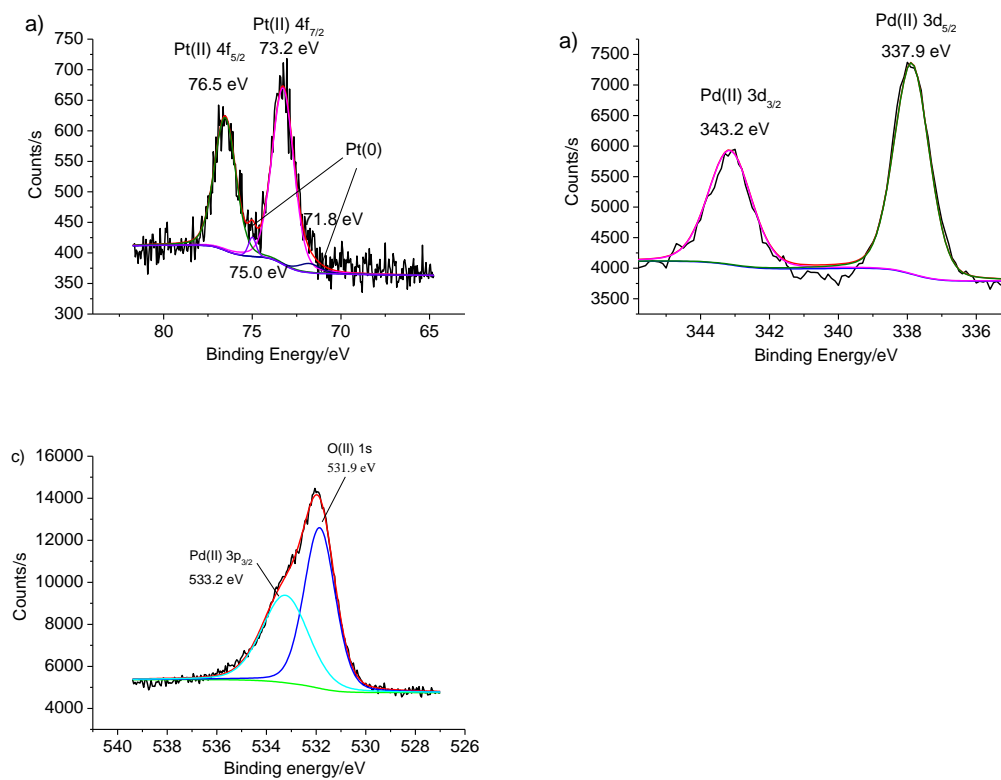


Fig. S15 a) XPS Pt 4f, b) Pd 3d, and c) O 1s spectra of Pt@PdTAPP-TFPT.

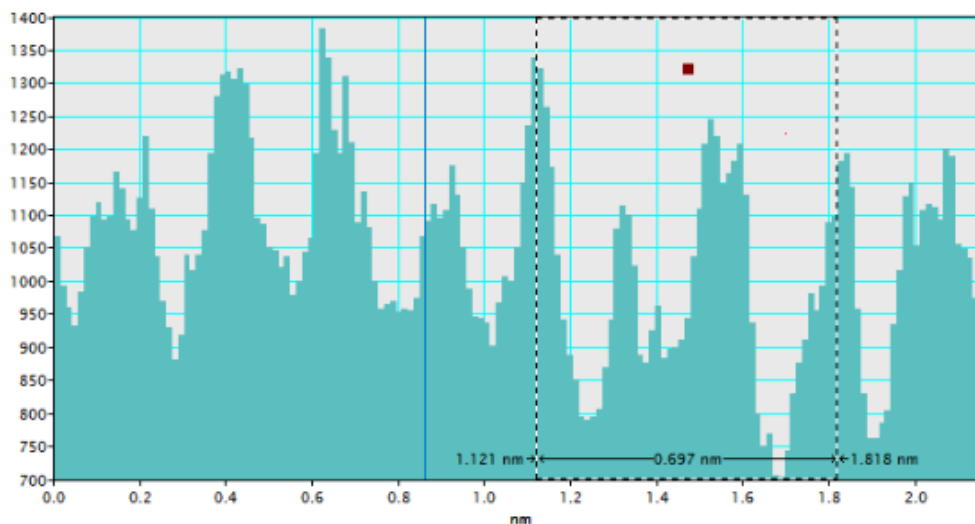


Fig. S16 TEM Profile of calibration of Pt@PdTAPP-TFPT (recycle after 4 runs).

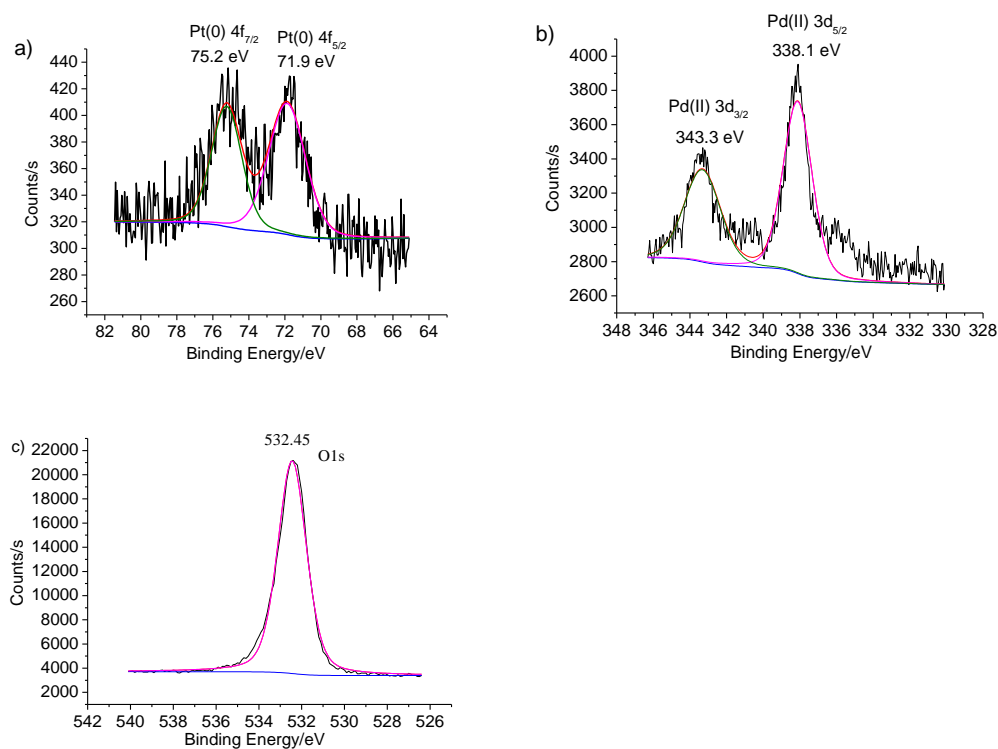


Fig. S17 a) XPS Pt 4f, b) Pd 3d, and c) O 1s spectra of Pt@PdTAPP-TFPT (recycled after 4 runs). Compared with that of fresh Pt@PdTAPP-TFPT, the Pd 3p photoelectric peak was masked by the O 1s arising from the reduction of Pt(II) into Pt(0).

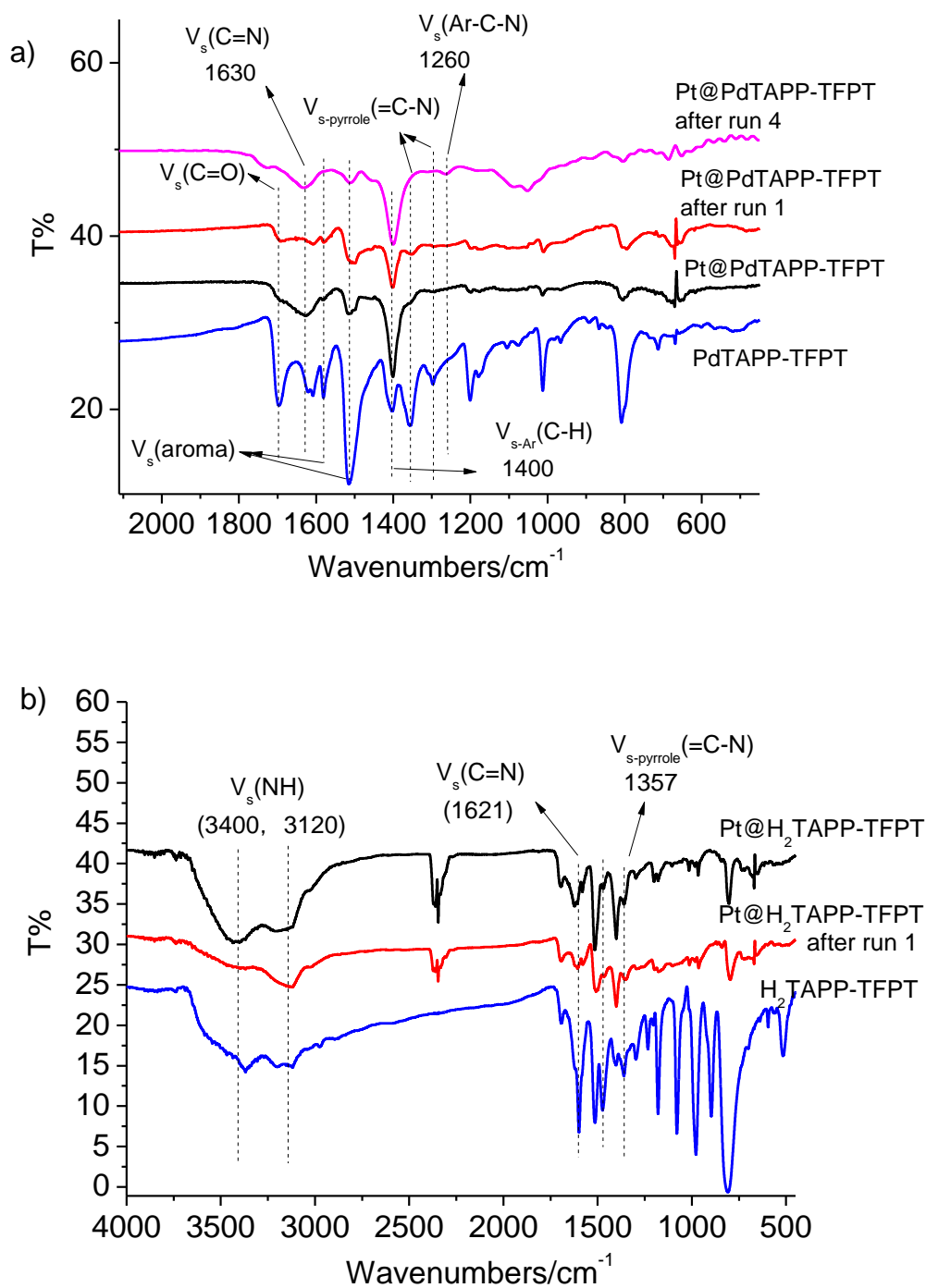


Fig. S18 FT-IR spectra of a) Pt@PdTAPP-TFPT fresh, Pt@PdTAPP-TFPT after run 1, Pt@PdTAPP-TFPT after run 4, and PdTAPP-TFPT, b) Pt@H₂TAPP-TFPT, Pt@H₂TAPP-TFPT after run 1, and H₂TAPP-TFPT. The spectra are vertically offset for clarity.

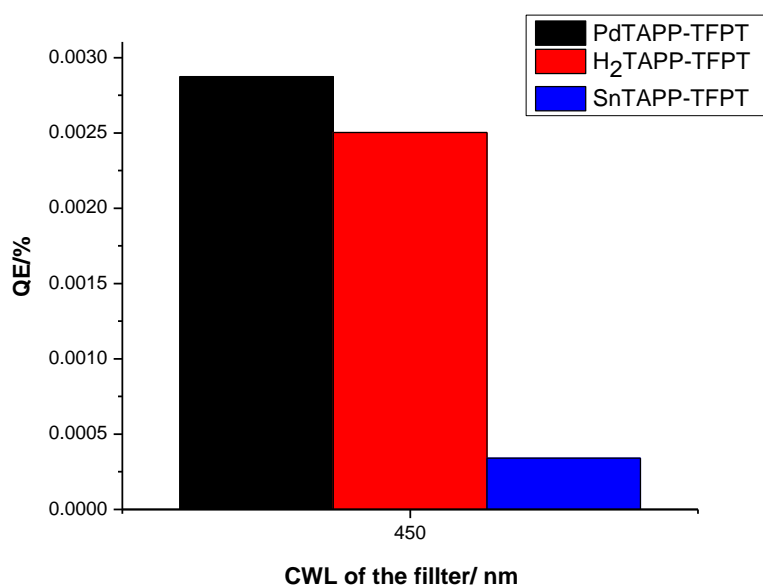


Fig. S19 Quantum yields measured with band-pass filter with central wavelengths (CWLs) at 450 nm.

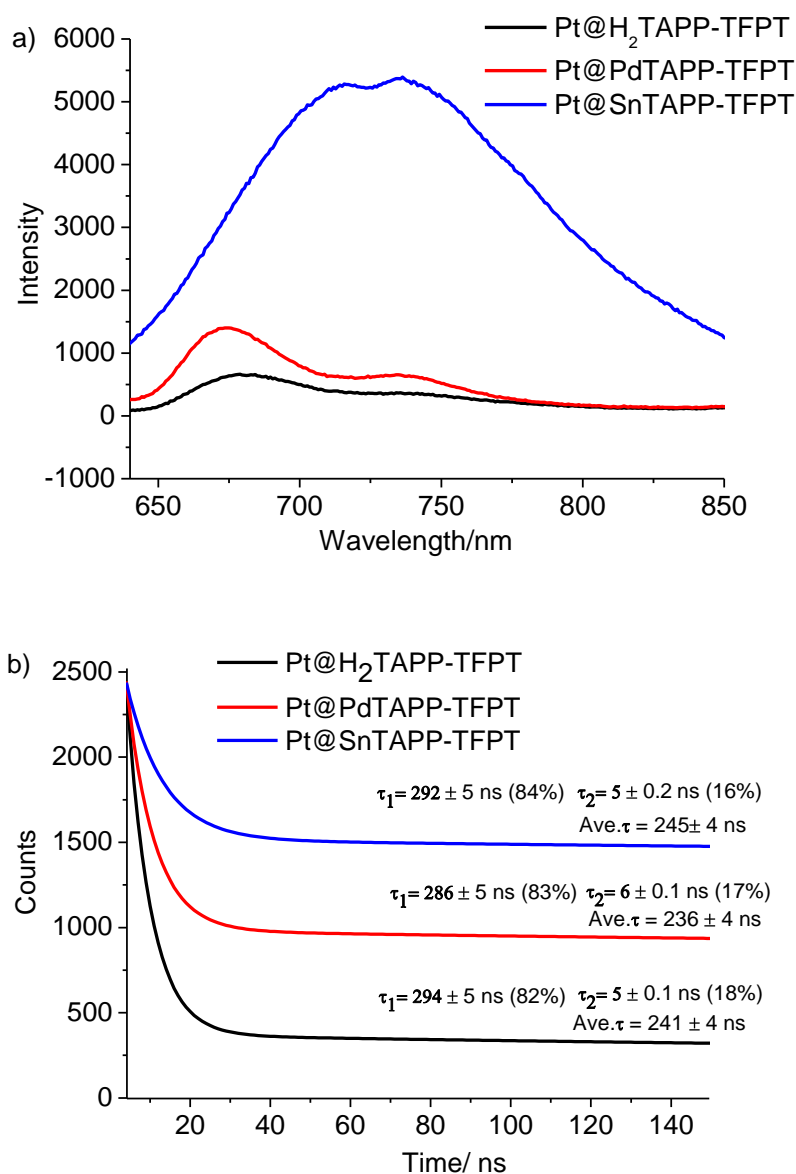


Fig. S20 a) Photoluminescent spectra of Pt@H₂TAPP-TFPT wet gel, Pt@PdTAPP-TFPT wet gel and Pt@SnTAPP-TFPT wet gel under an excitation wavelength of 365 nm, and b) time-resolved photoluminescent decay profiles after pulsed excitation at $\lambda = 680$ nm for Pt@H₂TAPP-TFPT, Pt@PdTAPP-TFPT and Pt@SnTAPP-TFPT wet gel.

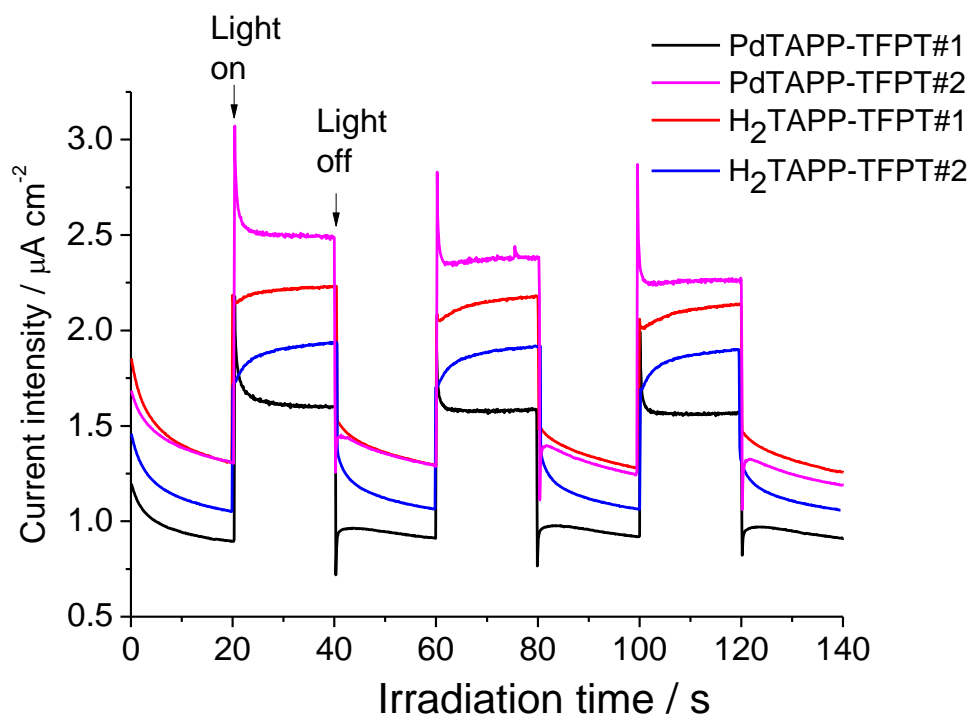


Fig. S21 Photocurrent time ($I-t$) curves of PdTAPP-TFPT and H₂TAPP-TFPT wet gel working electrodes tested with light under chronoamperometric conditions at 1.0 V vs. Ag/AgCl in 0.1 M KH₂PO₄ aqueous solution (pH = 7.0) (two parallel tests each).