

Electronic Supplementary Information:

Photoelectrochemical cells with a pyridine-anchored organic dye photoanode for efficient H₂ generation by water reduction

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Materials and Measurements

Phenylboronic acid, pyridylboronic acid, bis(4-bromophenyl)amine, cesium carbonate, sodium tert-butoxide, tris(tert-butyl)phosphine (10% in toluene), tetrakis(triphenylphosphine)-palladium(0) and tris(dibenzylideneacetone)dipalladium(0) were purchased from Inno-chem and used without further purification. Di(*p*-pyrid-4-ylphenyl)amine was prepared according to the literature method.¹ All solvents in the synthesis are reagent grade. The ¹H NMR and ¹³C NMR spectra were recorded with a 400 MHz Bruker Avance spectrometer. Steady state absorptions were recorded by using a Perkin-Elmer Lambda 750 UV/VIS/NIR spectrophotometer. Hydrogen evolution was detected by gas chromatography (GC7900) using high-purity argon as carrier gas. Photocurrent measurements were taken using a CHI 660D potentiostat under an atmosphere of nitrogen. Potentials are referenced to a Ag/AgCl electrode in saturated aqueous KCl without compensation for the liquid junction potential.

Synthesis and characterization

APyr: A mixture of 1-bromopyrene (28 mg, 0.1 mmol), di(*p*-pyrid-4-ylphenyl)amine (48 mg, 0.15 mmol), tris(dibenzylideneacetone)dipalladium(0) (18.3 mg, 0.02 mmol), tris(tert-butyl)phosphine (3.3 mg, 0.015 mmol) and sodium tert-butoxide (48 mg, 0.5 mmol) in 10 mL dry toluene was bubbled with nitrogen for 15 min, followed by refluxing at 120 °C for 1 day. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was subjected to column chromatography on silica gel (eluent: dichloromethane/methanol, 100/1) to afford 23.5 mg of **APyr** as a yellow solid in 45% yield. ¹H NMR (400 MHz, chloroform-*d*): δ 8.61 (d, *J* = 5.8 Hz, 4H), 8.23 (dd, *J* = 7.8, 4.6 Hz, 2H), 8.18 – 8.07 (m, 4H), 8.02 (dd, *J* = 14.4, 8.4 Hz, 2H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 4H), 7.46 (d, *J* = 6.0 Hz, 4H), 7.22 (d, *J* = 8.6 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃): δ 150.24, 148.94, 147.48, 139.51, 131.38, 131.23, 130.99, 130.26, 128.54, 128.39, 127.67, 127.63, 127.16, 126.45, 126.41, 126.14, 125.62, 125.45, 124.77, 122.75, 122.26, 120.88. MALDI-HRMS for C₃₈H₂₅N₃: calcd 523.2043; found: 523.2042.

DAPyr: A mixture of 1,6-dibromopyrene (72 mg, 0.20 mmol), di(*p*-pyrid-4-ylphenyl)amine (194 mg, 0.60 mmol), tris(dibenzylideneacetone)dipalladium(0) (16.5 mg, 0.018 mmol), tris(tert-butyl)phosphine (13 mg, 0.060 mmol) and sodium tert-butoxide (91 mg, 1.0 mmol) in 25 mL

dry toluene was bubbled with nitrogen for 10 min, followed by refluxing at 120 °C for 2 days. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was subjected to column chromatography on silica gel (eluent: dichloromethane/methanol/ammonia, 100/2/0.2) to afford 93 mg of **DAPyr** as a yellow solid in 55% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.21 (d, *J* = 8.6 Hz, 8H), 7.46 (d, *J* = 6.0 Hz, 8H), 7.55 (d, *J* = 8.6 Hz, 8H), 7.91 (d, *J* = 8.1 Hz, 2H), 8.01 (d, *J* = 9.3 Hz, 2H), 8.16-8.21 (m, overlapped, 4H), 8.62 (d, *J* = 6.0 Hz, 8H). ¹³C NMR (100 MHz, chloroform-*d*): δ 120.89, 122.36, 123.03, 126.52, 126.62, 127.94, 128.23, 128.48, 130.01, 131.59, 140.16, 147.41, 148.88, 150.28. MALDI-HRMS for C₆₀H₄₀N₆: calcd 844.3309; found: 844.3314.

TAPyr: A mixture of 1,3,6,8-tetrabromopyrene (26 mg, 0.05 mmol), di(*p*-pyrid-4-yl-phenyl)amine (113 mg, 0.35 mmol), tris(dibenzylideneacetone)dipalladium(0) (9.16 mg, 0.01 mmol), tris(*tert*-butyl)phosphine (3.0 mg, 0.015 mmol) and sodium *tert*-butoxide (24 mg, 0.25 mmol) in dry toluene (15 mL) was bubbled with nitrogen for 15 min and heated at 120 °C for 3 days. After cooling, the solvent was removed under reduced pressure. The residue was subjected to column chromatography on silica gel (eluent: dichloromethane/methanol/ammonia, 100/4/0.3) to afford 35 mg of **TAPyr** as a yellow solid in 47% yield. ¹H NMR (400 MHz, chloroform-*d*): δ 8.58 (d, *J* = 6.2 Hz, 16H), 8.09 (s, 4H), 7.80 (s, 2H), 7.51 (d, *J* = 8.7 Hz, 16H), 7.40 (d, *J* = 6.2 Hz, 16H), 7.17 (d, *J* = 8.7 Hz, 16H). ¹³C NMR (101 MHz, chloroform-*d*): δ 150.08, 148.44, 147.29, 141.51, 131.96, 130.55, 128.46, 128.00, 127.68, 123.74, 122.35, 120.84, 120.84. MALDI-HRMS for C₁₀₄H₇₀N₁₂: calcd 1486.5841; found: 1486.5840.

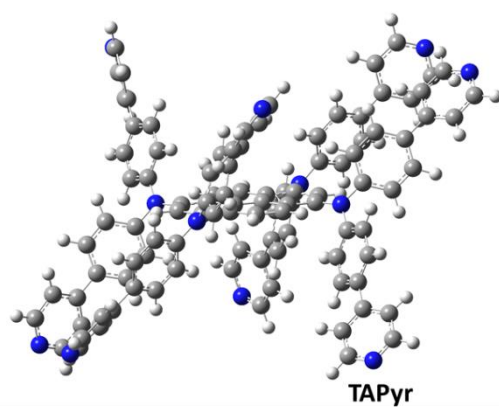
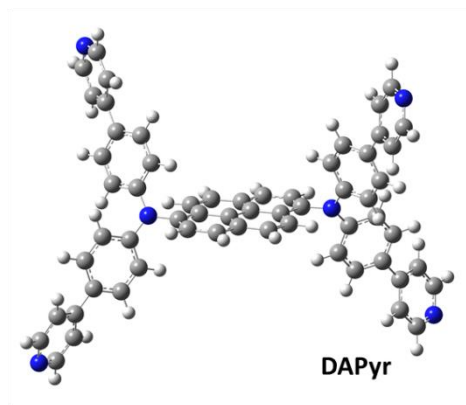
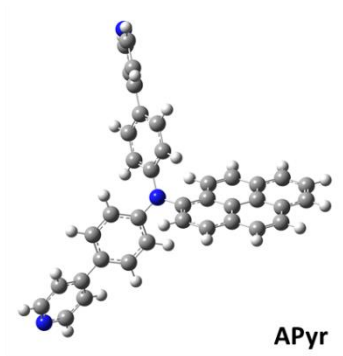


Figure S1. DFT-optimized structures of dye molecules (b3lyp/6-31g*).

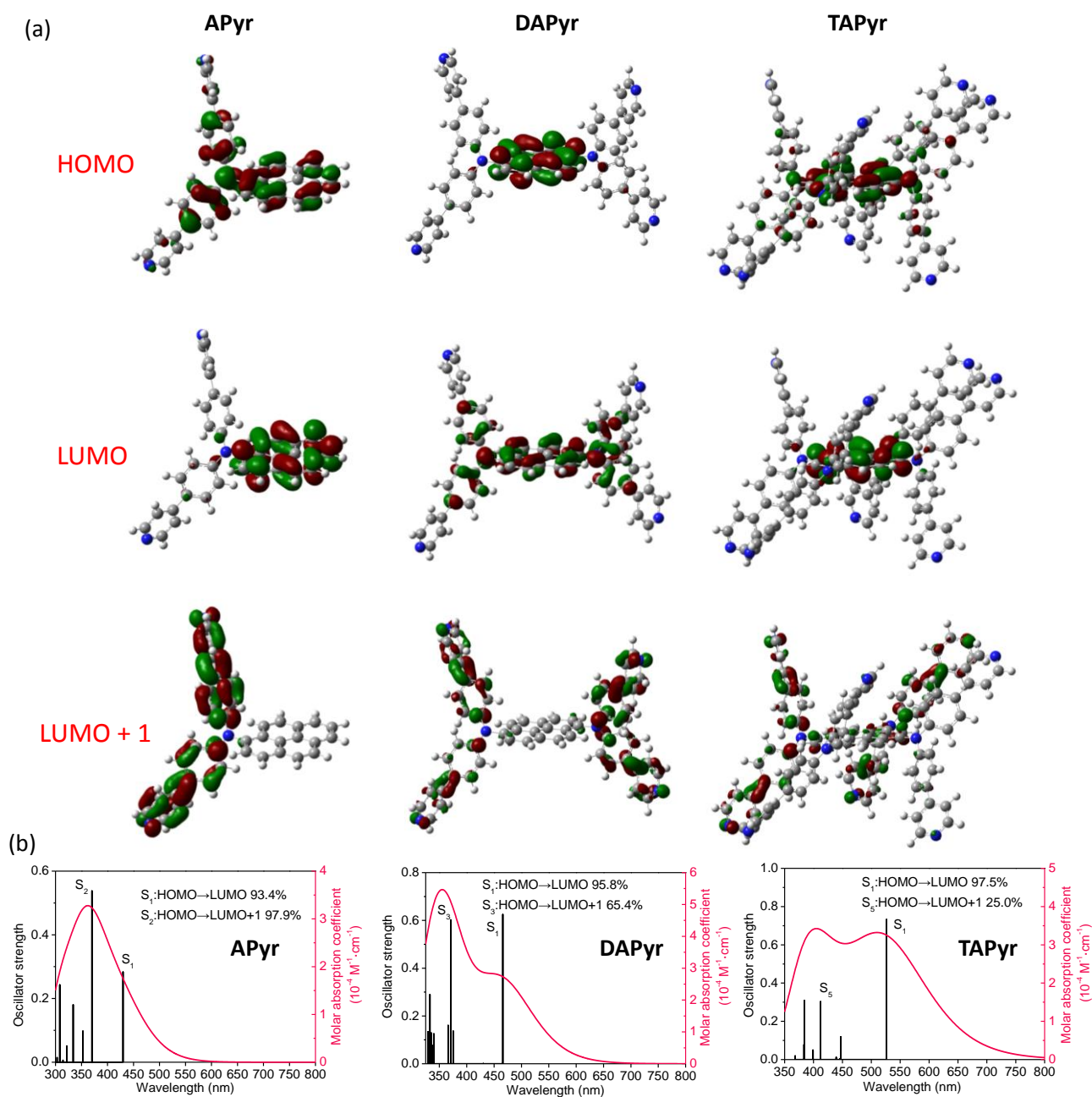


Figure S2. (a) DFT calculated HOMO and LUMO and (b) TD-DFT calculated excitations of the dye molecules (on the level of b3lyp/6-31g*, isovalue=0.03). HOMO = highest occupied molecular orbital; LUMO = lowest unoccupied molecular orbital.

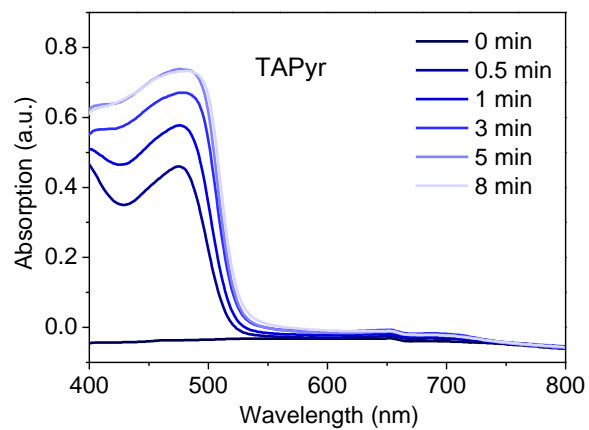
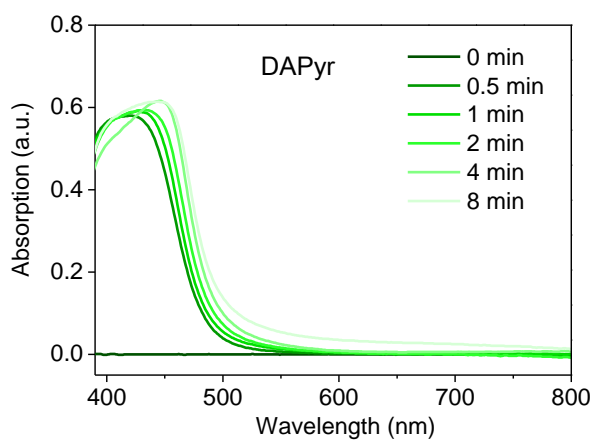
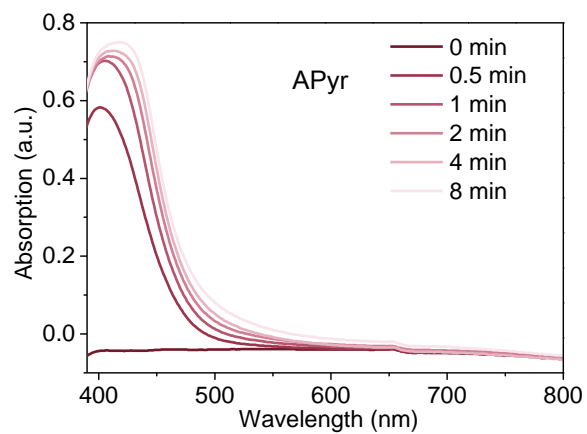


Figure S3. Absorption spectra of the FTO/TiO₂/dyes versus immersion time in dyes/DCM solutions.

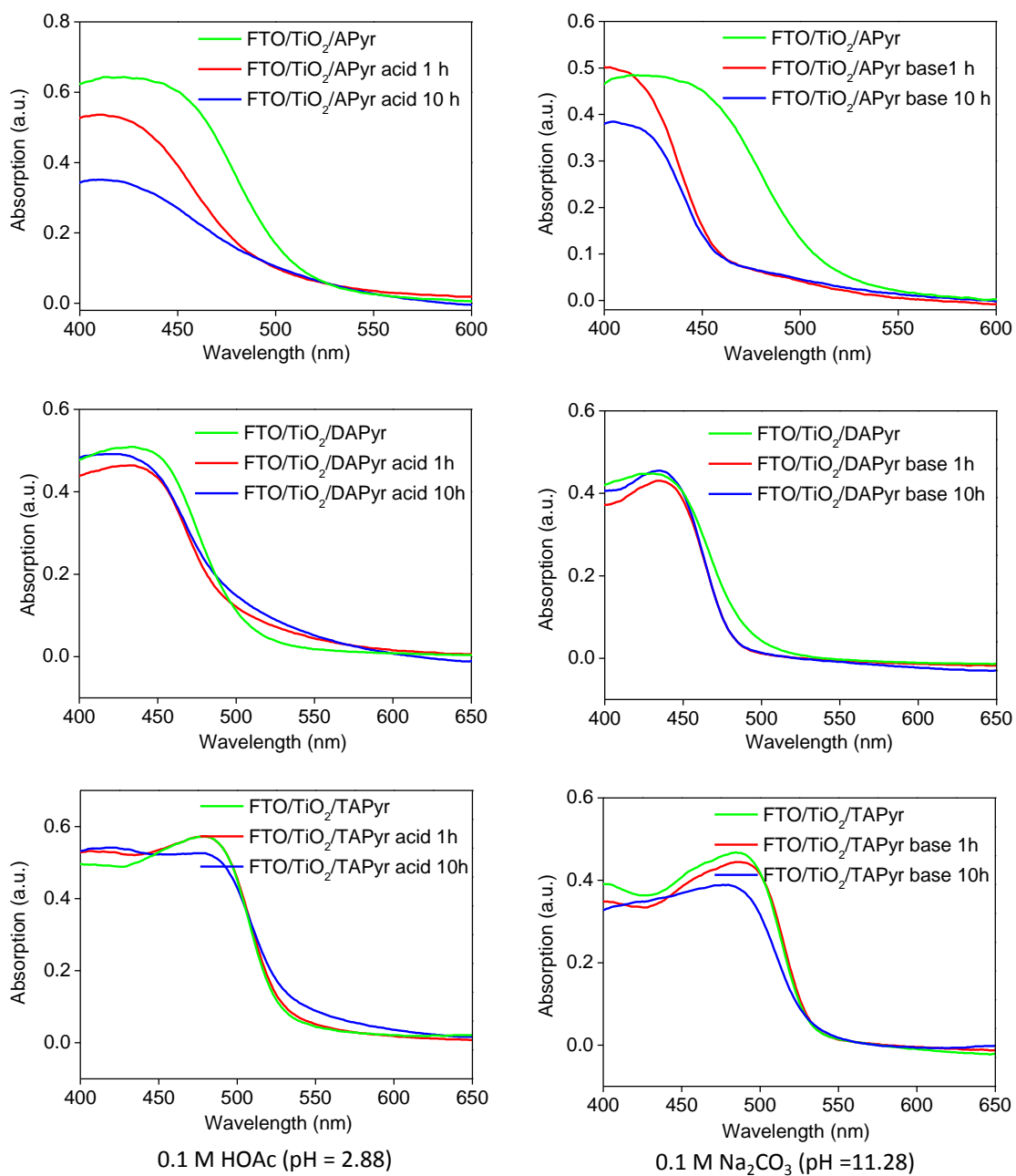


Figure S4. Absorption spectra of the FTO/TiO₂/dye electrodes after the electrodes were immersed in 0.1 M HOAc or 0.1 M Na₂CO₃ solution for 10 hours.

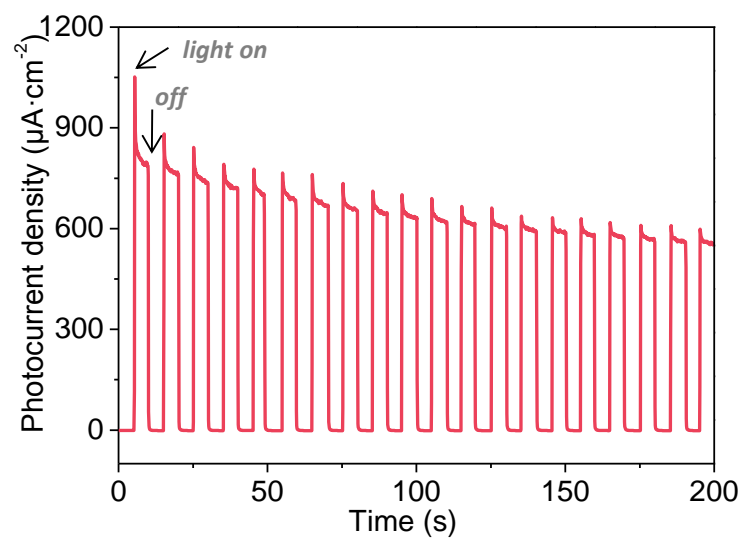


Figure S5. Photocurrent density of FTO/TiO₂/DAPyr versus different initial bias.

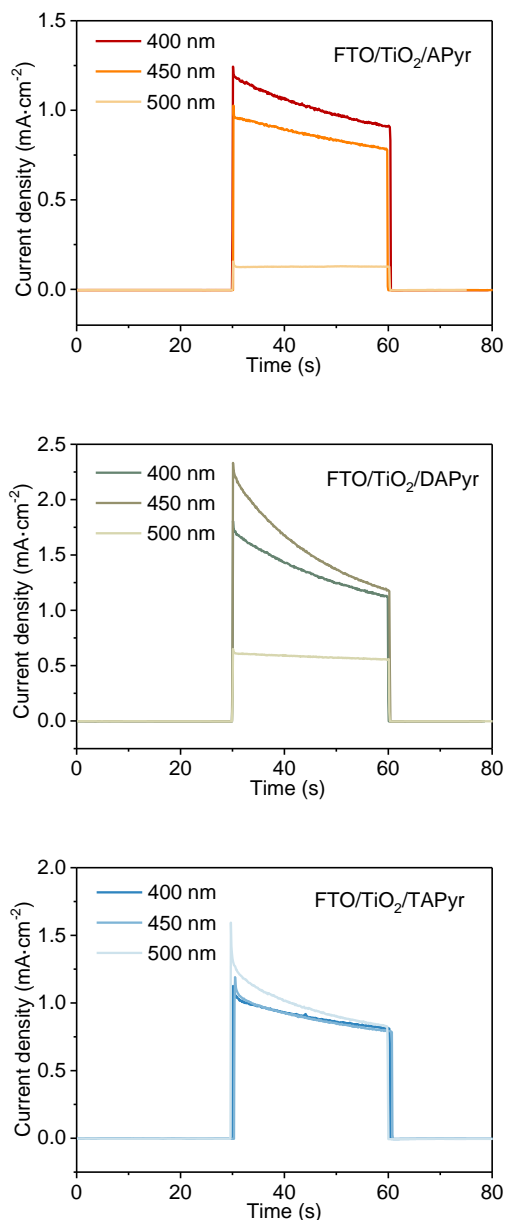


Figure S6. The photocurrent generated in the PECs under monochromatic light with wavelengths of 400, 450, and 500 nm.

$$\text{IPCE}\% = \frac{1240 (\text{V} \times \text{nm}) \times J(\text{photocurrent})(\text{mA}/\text{cm}^2)}{\text{Wavelength}(\text{nm}) \times I(\text{photo power})(\text{mW}/\text{cm}^2)} \times 100\%$$

J is the steady-state photocurrent density and I is the incident power density at each wavelength.

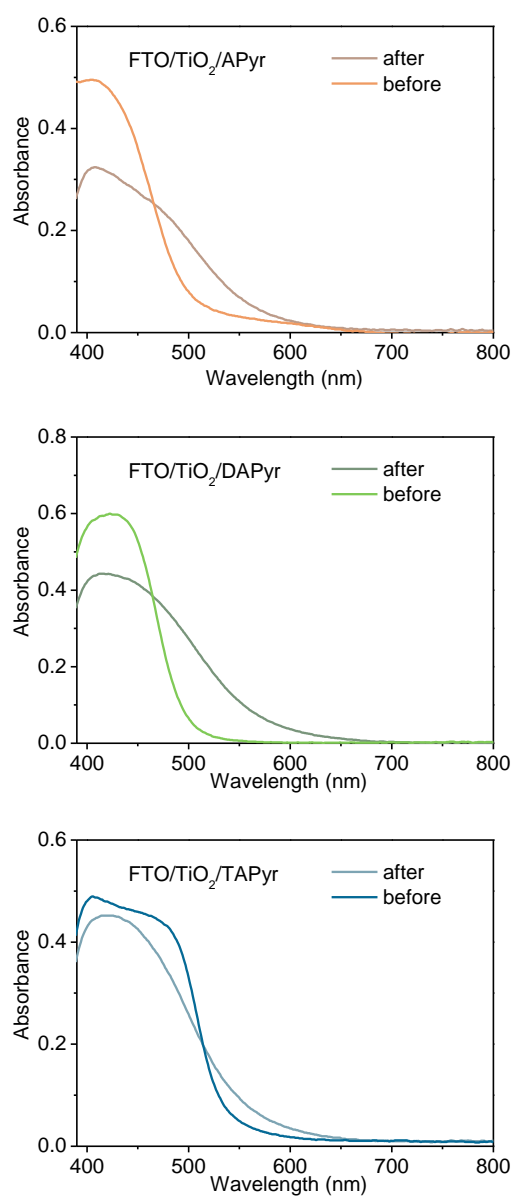


Figure S7. Absorption spectra of the electrodes before and after irradiation for 30 min (1.1 W/cm^2).

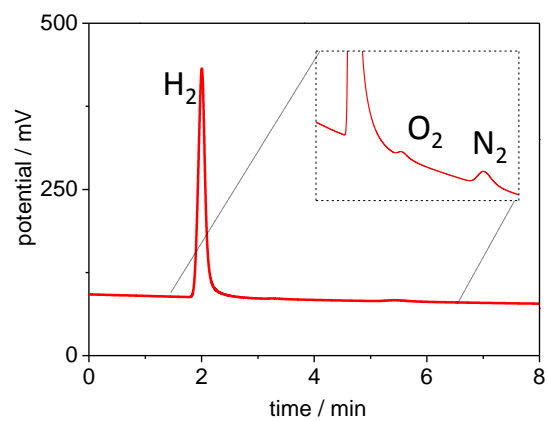


Figure S8. Gas chromatograms analysis to the gas collected at the Pt counter electrode of a representative PEC with FTO/TiO₂/**TAPyr** photoanode.

Table S1. Parameters of DSPECs with different dyes^a

dye	APyr	DAPyr	TAPyr
$Q/\mu\text{C}$	1325248	2666559	3571825
$n(\text{e}^-)/\mu\text{mol}$	13.74	27.64	37.02
$V(\text{H}_2)/\mu\text{L}$	167	330	442
$n(\text{H}_2)/\mu\text{mol}$	6.80	13.40	17.95
Faraday efficiency	99%	97%	97%

^aThe Faraday efficiency (FE) is calculated by the following equation: $\text{FE} = 100\% \times n(\text{H}_2) (\mu\text{mol}) \times 2 \times 96485 (\text{C} \cdot \text{mol}^{-1}) / Q (\mu\text{C})$. The photoanode has an area of $1 \times 1 \text{ cm}^2$.

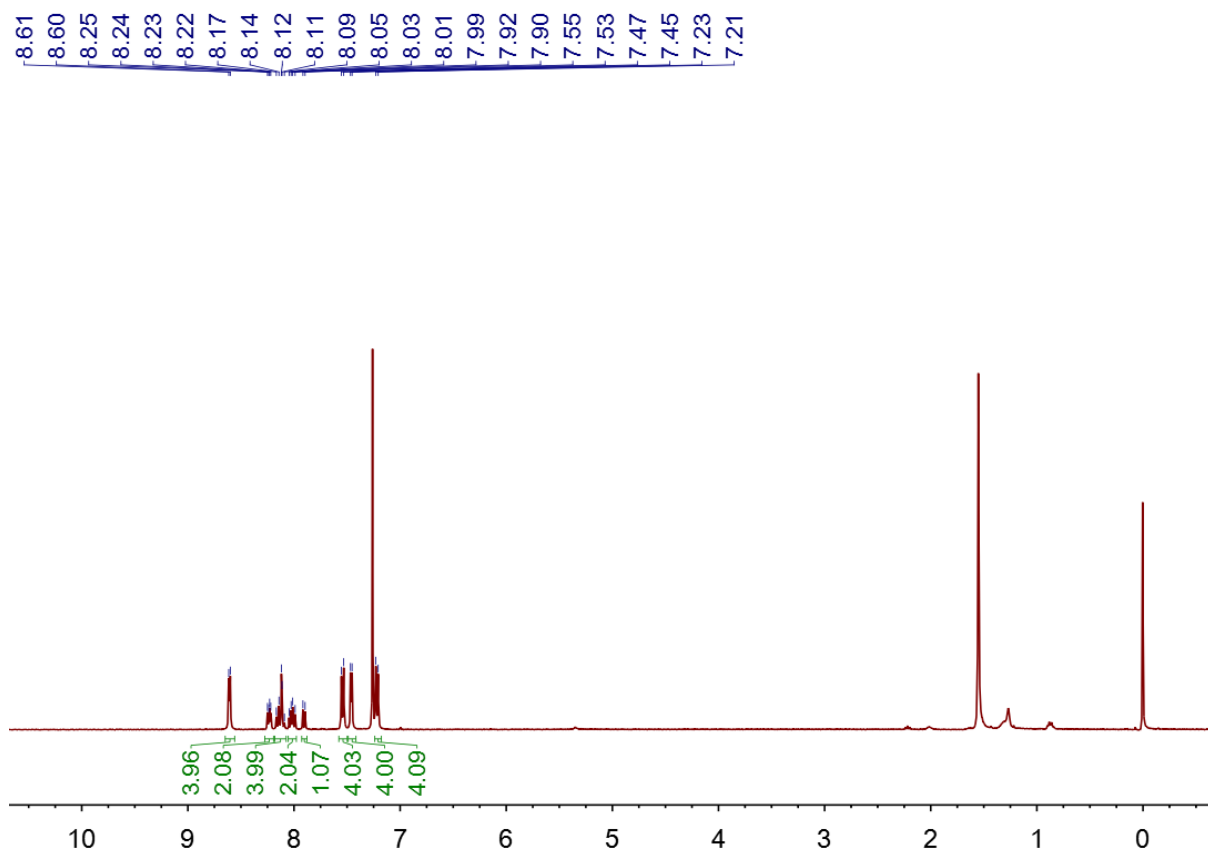


Figure S9. ^1H NMR spectrum of APyr in chloroform- d .

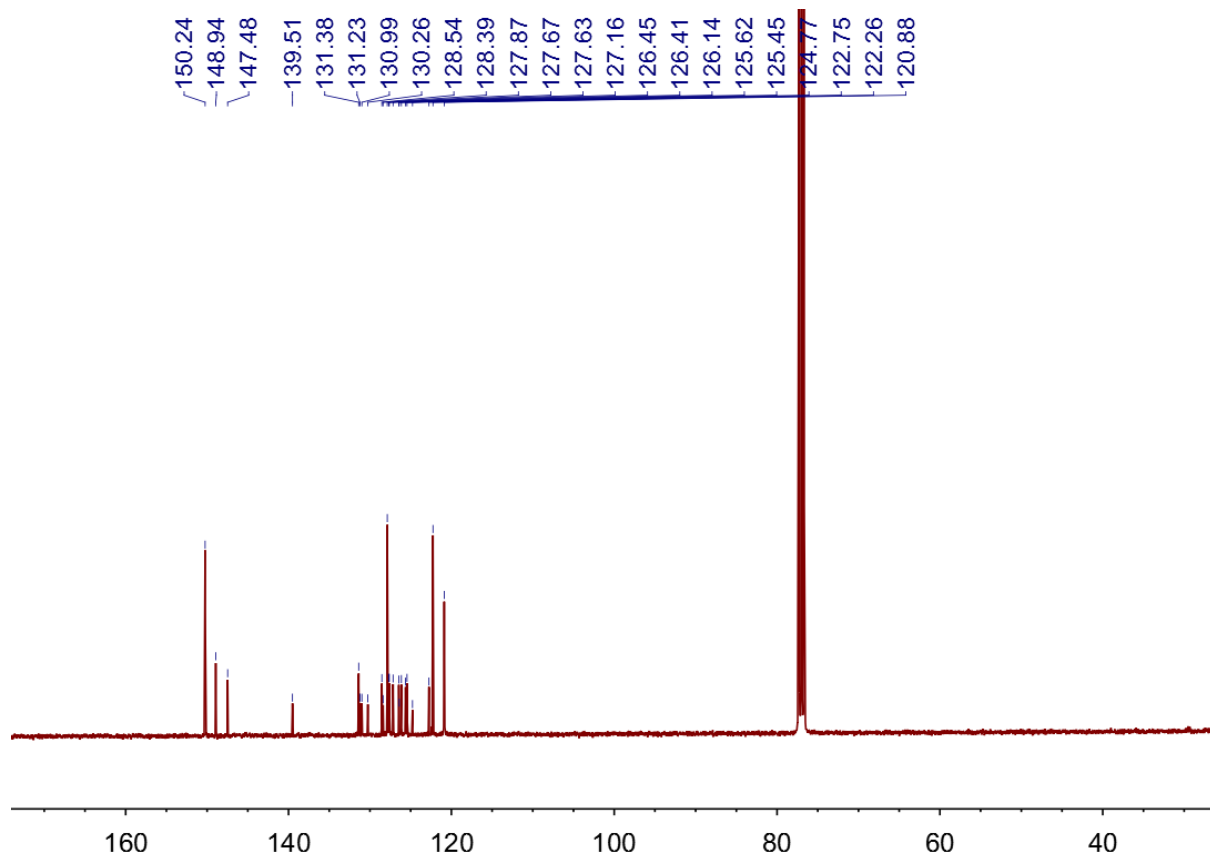


Figure S10. ^{13}C NMR spectrum of APyr in chloroform-*d*.

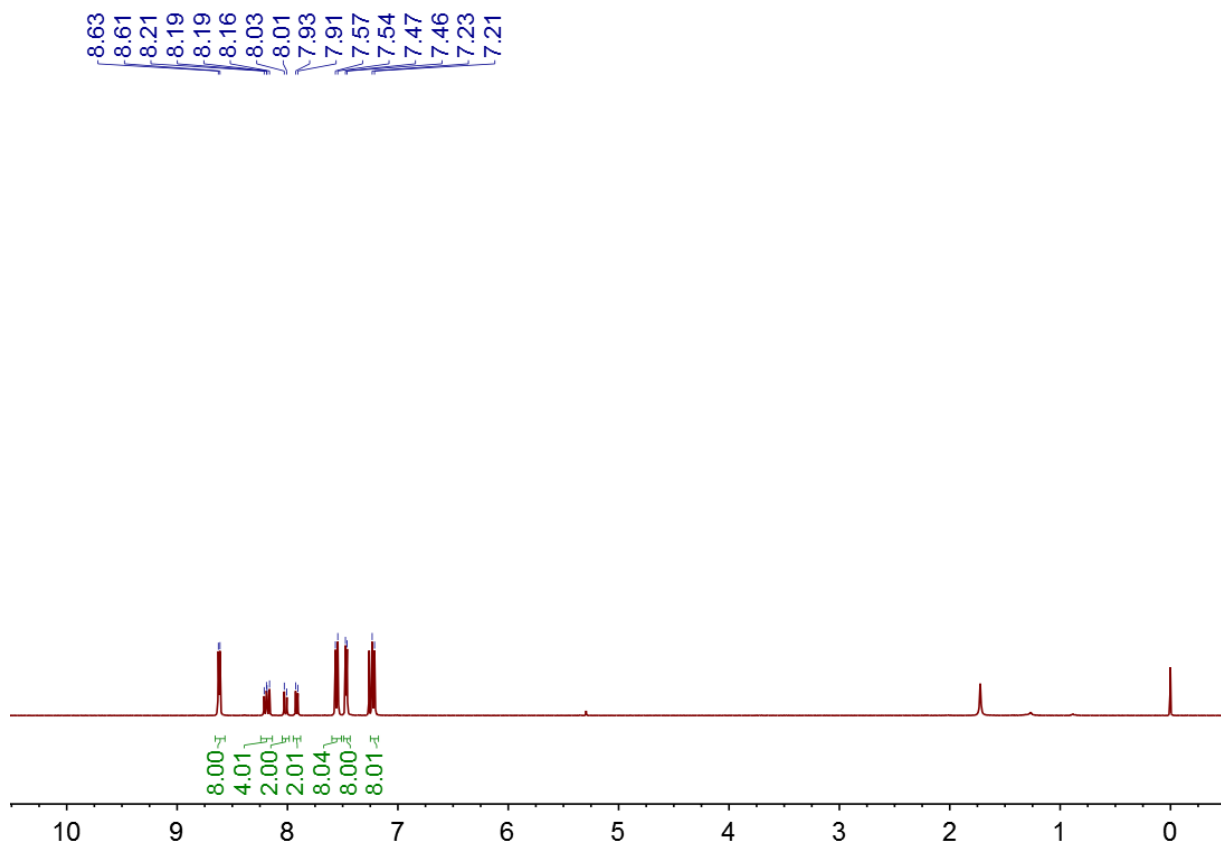


Figure S11. ^1H NMR spectrum of **DAPyr** in chloroform-*d*.

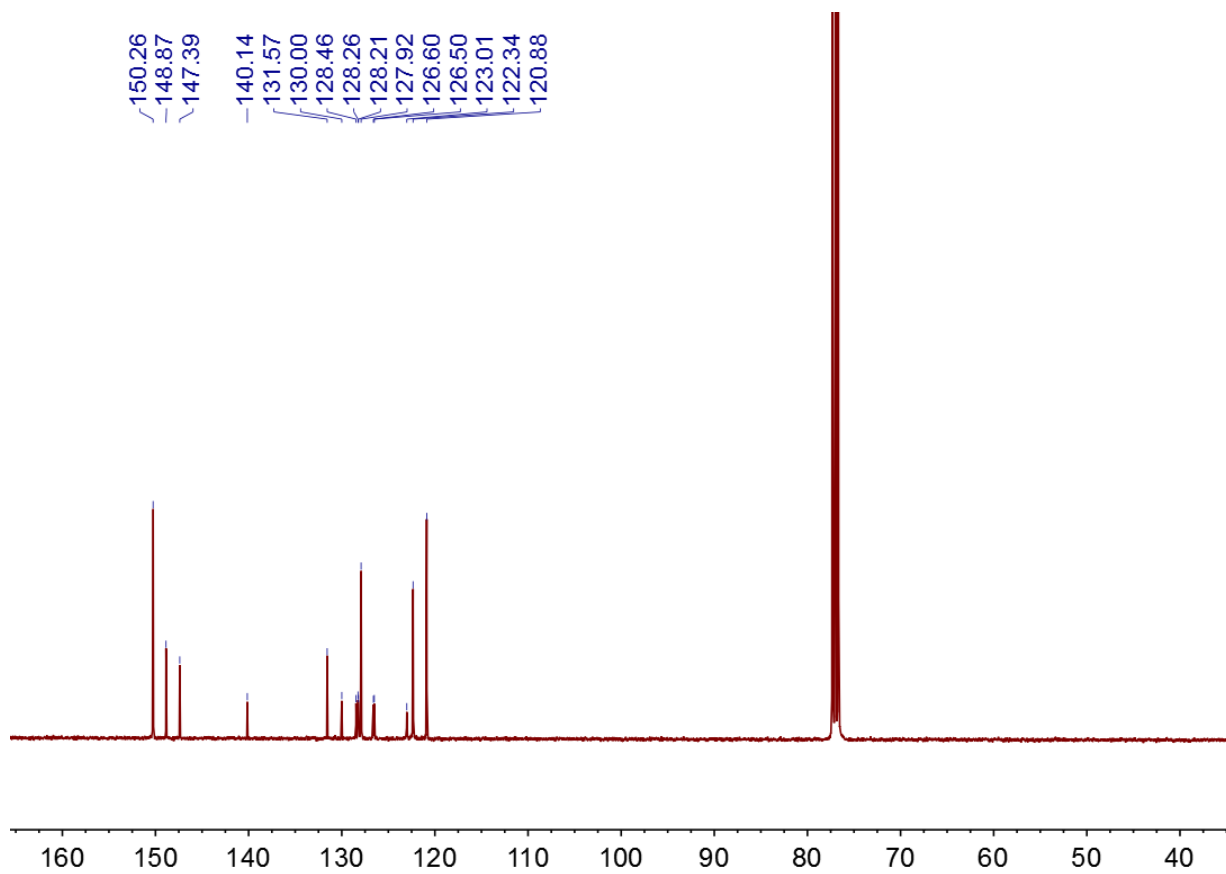


Figure S12. ^{13}C NMR spectrum of **DAPyr** in chloroform-*d*.

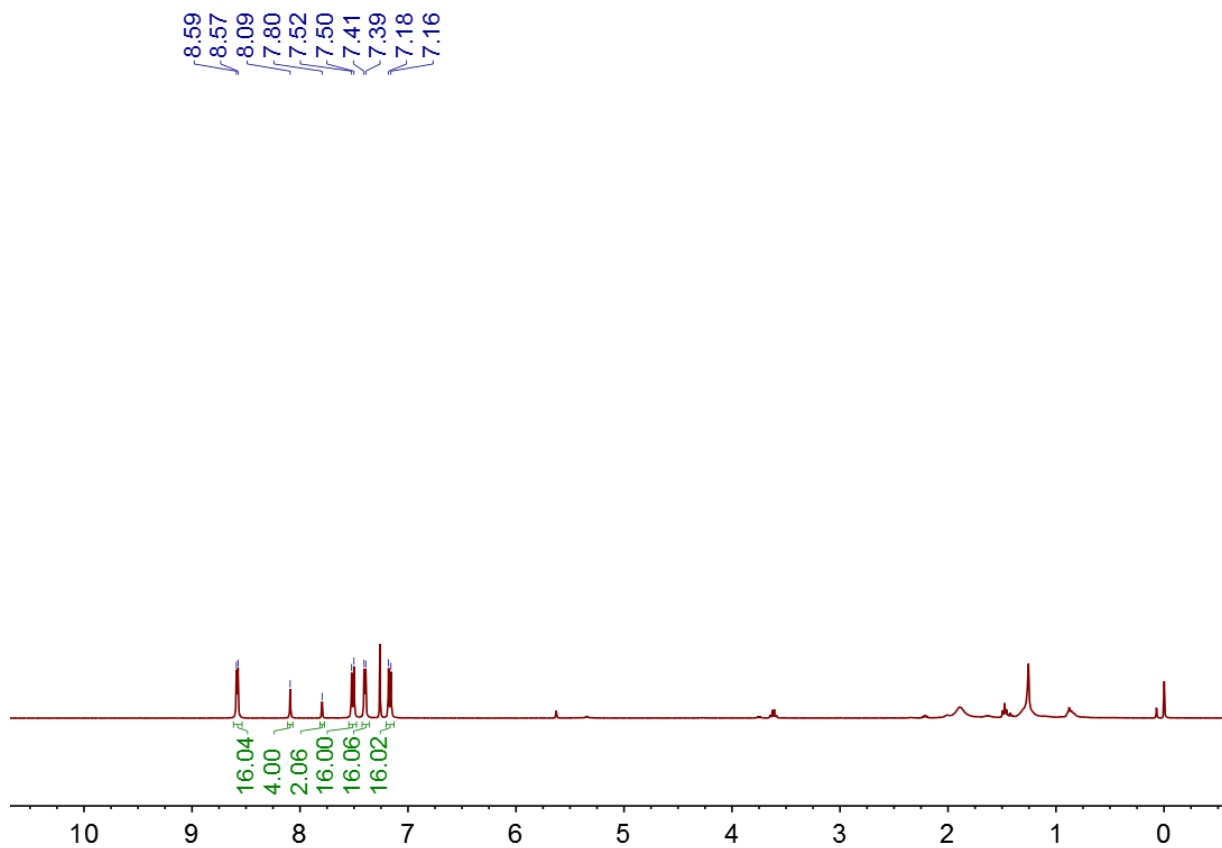


Figure S13. ^1H NMR spectrum of **TAPyr** in chloroform-*d*.

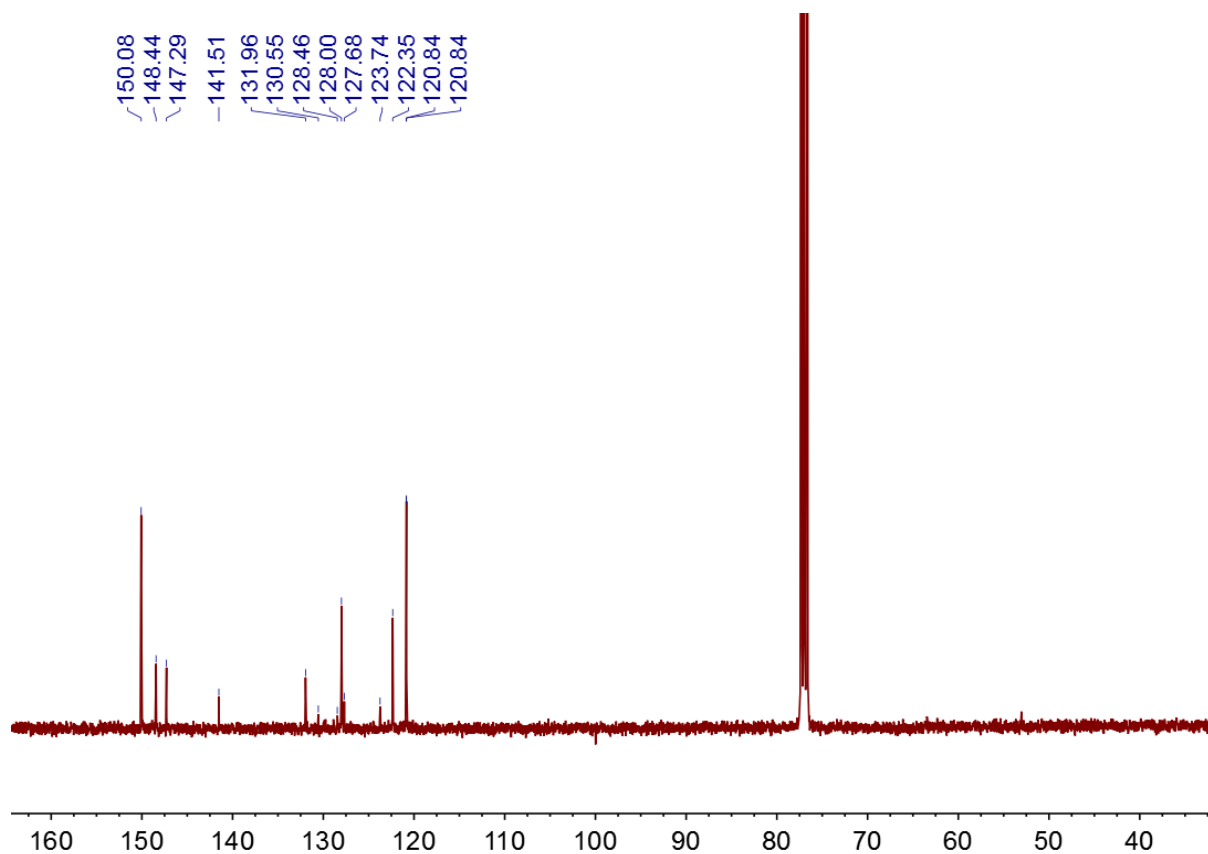


Figure S14. ^{13}C NMR spectrum of **TAPyr** in chloroform-*d* :

Reference:

1. J.-H. Tang, Z. Cai, D. Yan, K. Tang, J.-Y. Shao, C. Zhan, D. Wang, Y.-W. Zhong, L.-J. Wan and J. Yao, *J. Am. Chem. Soc.*, 2018, **140**, 12337-12340.