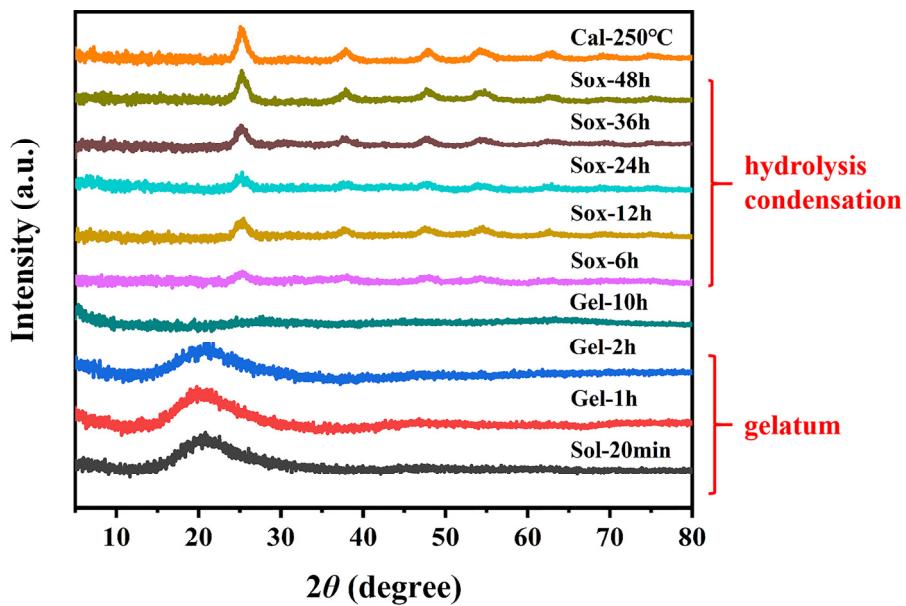
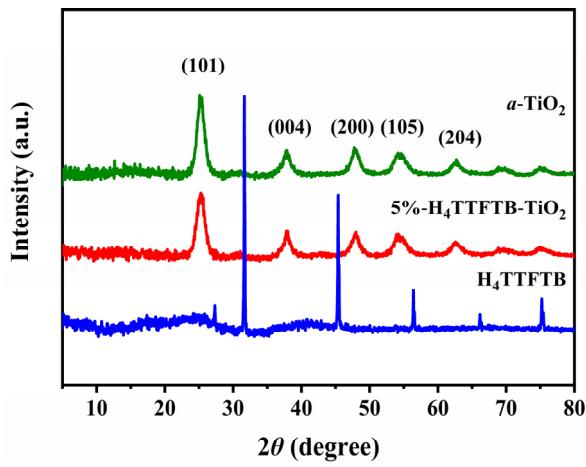


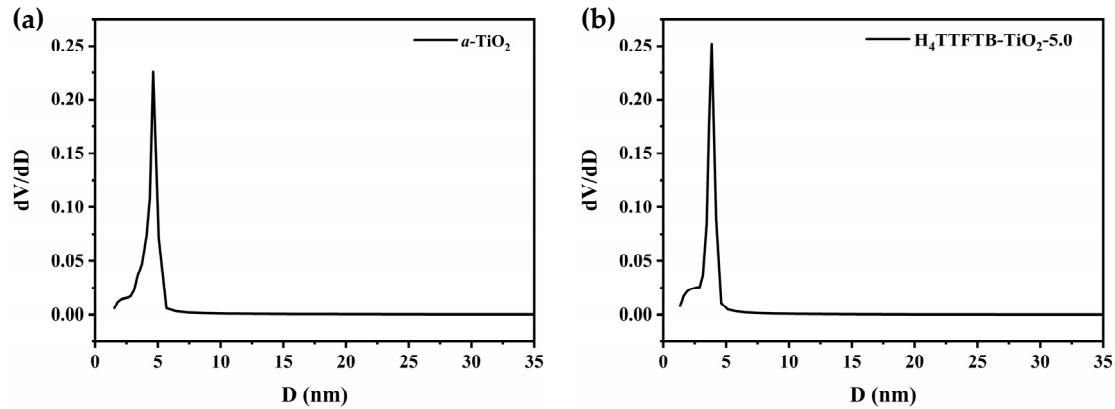
**Figure S1.** (a) The structure of H<sub>4</sub>TTFTB, (b) illustration of the fabrication of the H<sub>4</sub>TTFTB-TiO<sub>2</sub>.



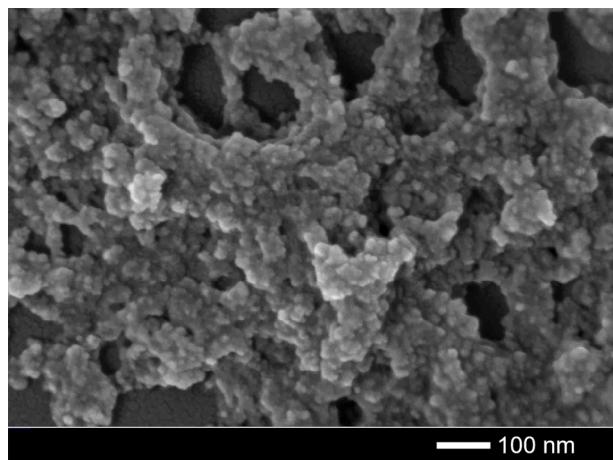
**Figure S2.** The XRD patterns of the intermediate products at different reaction times.



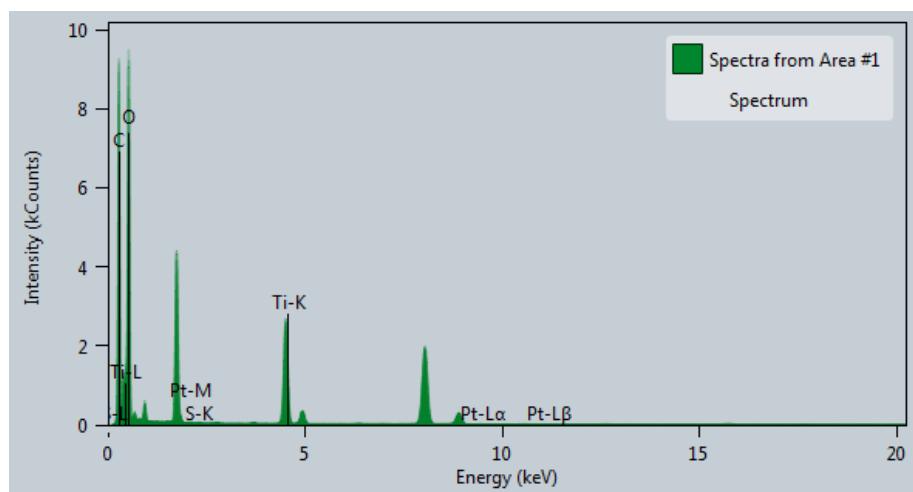
**Figure S3.** The XRD patterns of the  $\alpha$ -TiO<sub>2</sub>, H<sub>4</sub>TTFTB and H<sub>4</sub>TTFTB-TiO<sub>2</sub>-5.0.



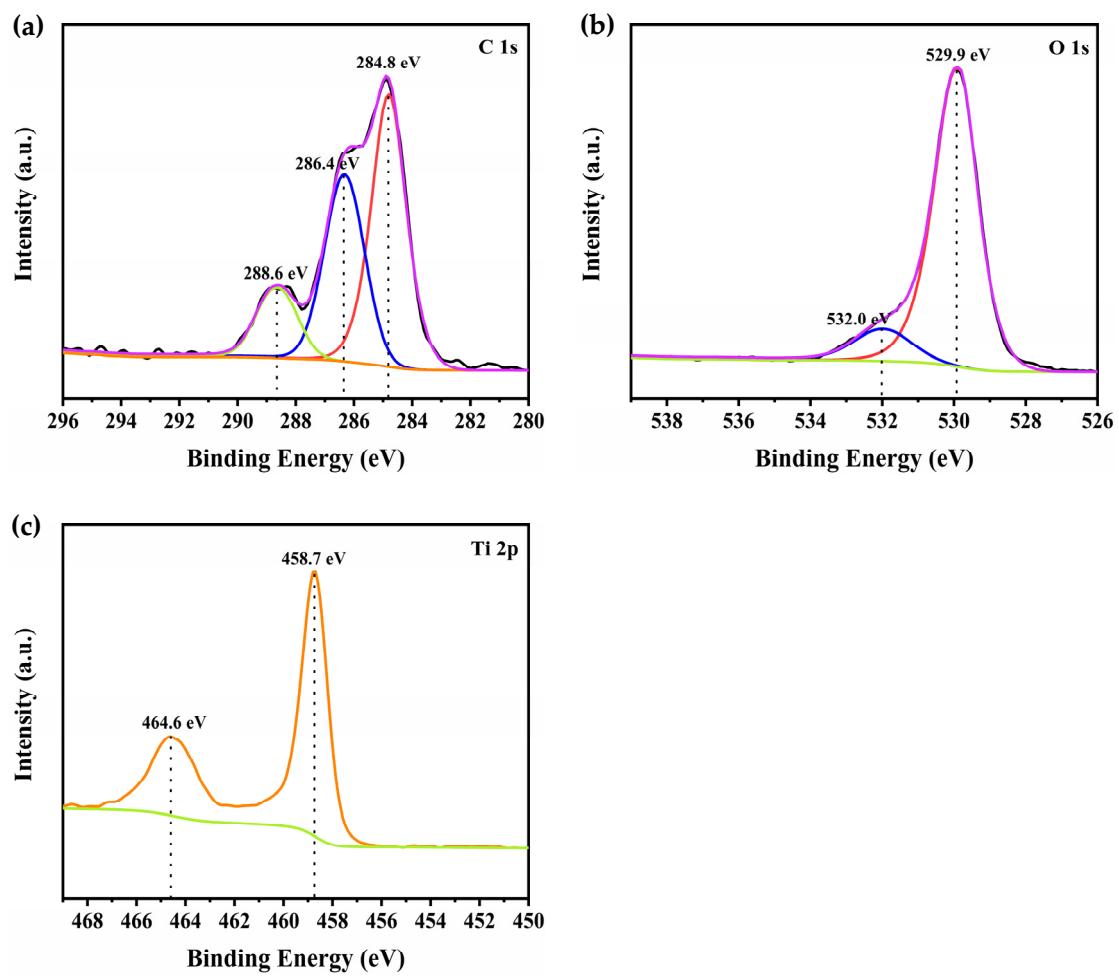
**Figure S4.** The pore size distributions of (a)  $\alpha$ -TiO<sub>2</sub>, (b) H<sub>4</sub>TTFTB-TiO<sub>2</sub>-5.0.



**Figure S5.** The SEM of H<sub>4</sub>TTFTB-TiO<sub>2</sub>-5.0.

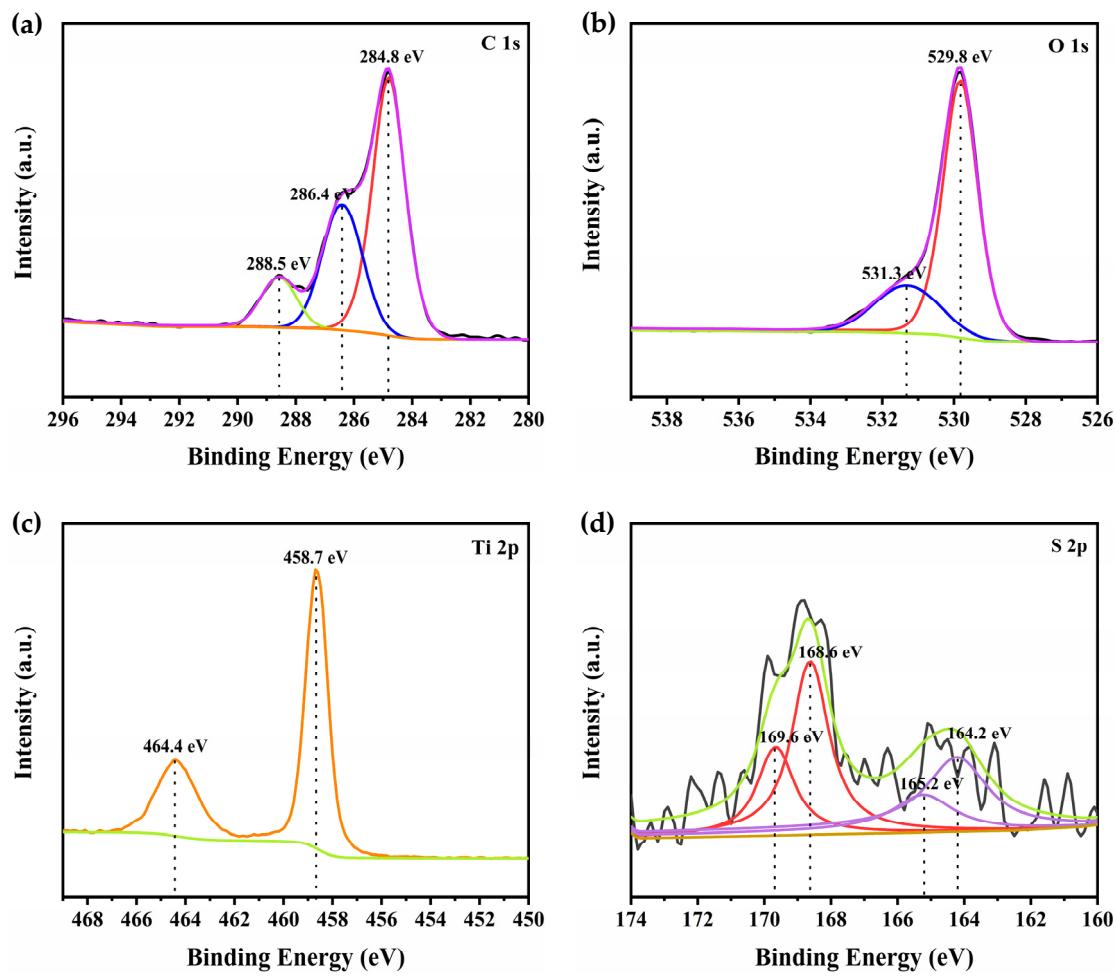


**Figure S6.** EDX of the Pt@H<sub>4</sub>TTFTB-TiO<sub>2</sub>-5.0.

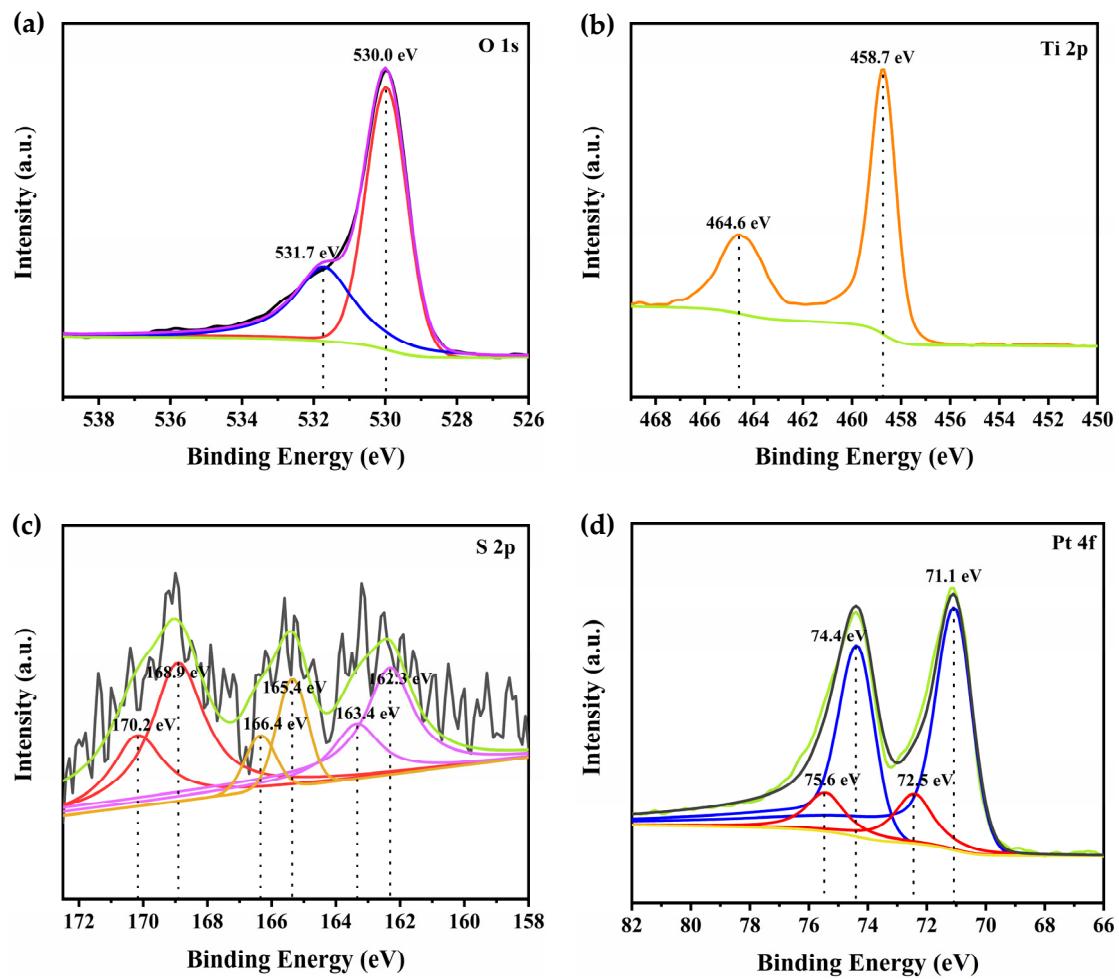


**Figure S7.** X-ray photoelectron spectra of  $\alpha$ -TiO<sub>2</sub>: (a) C 1s; (b) O 1s and (c) Ti 2p.

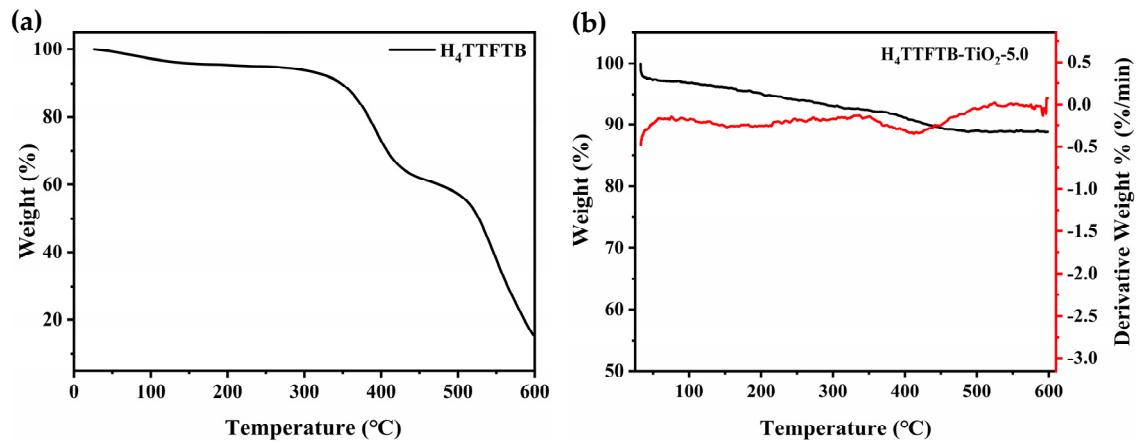
Atomic ratio of Ti : O = 35% : 65%  $\approx$  1 : 2.



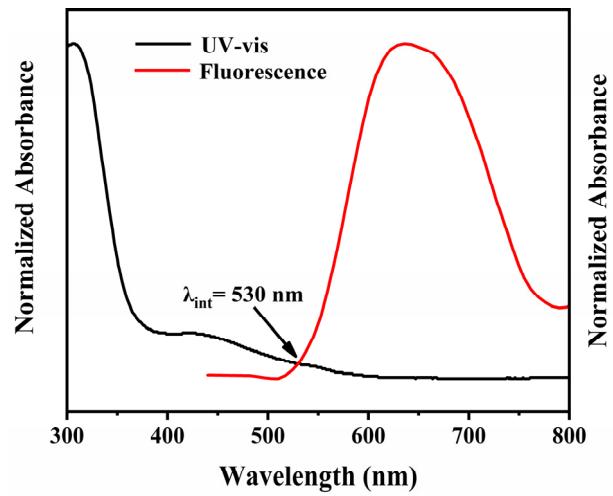
**Figure S8.** X-ray photoelectron spectra for of H<sub>4</sub>TTFTB-TiO<sub>2</sub>-5.0:(a) C 1s; (b) O 1s; (c) Ti 2p and (d) S 2p. Atomic ratio of Ti : O : C : S = 27% : 51% : 21% : 1.18%.



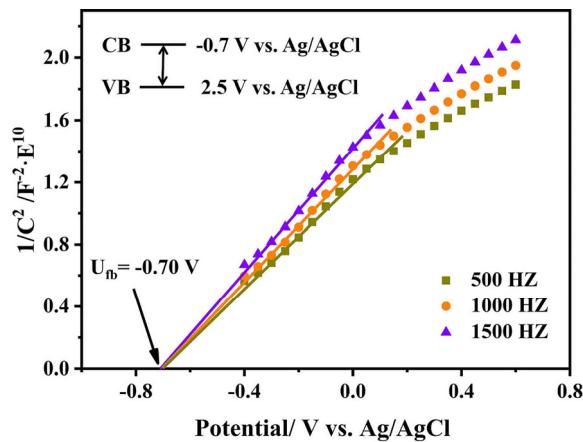
**Figure S9.** X-ray photoelectron spectra of of Pt@H<sub>4</sub>TTF-TB-TiO<sub>2</sub>-5.0: **(a)** O 1s; **(b)** Ti 2p; **(c)** S 2p and **(d)** Pt 4f.



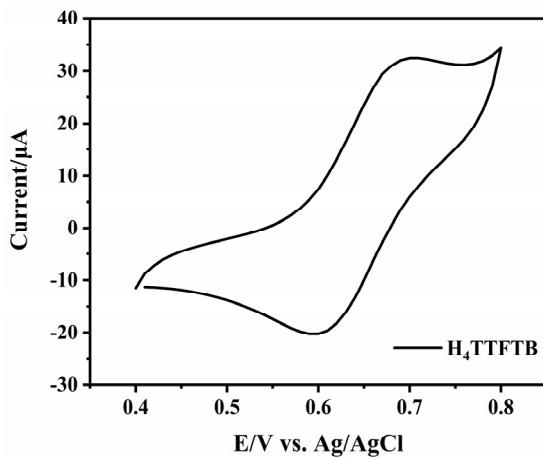
**Figure S10.** Thermogravimetry analysis of (a)  $\text{H}_4\text{TTFTB}$  compound, (b)  $\text{H}_4\text{TTFTB}-\text{TiO}_2\text{-}5.0$ .



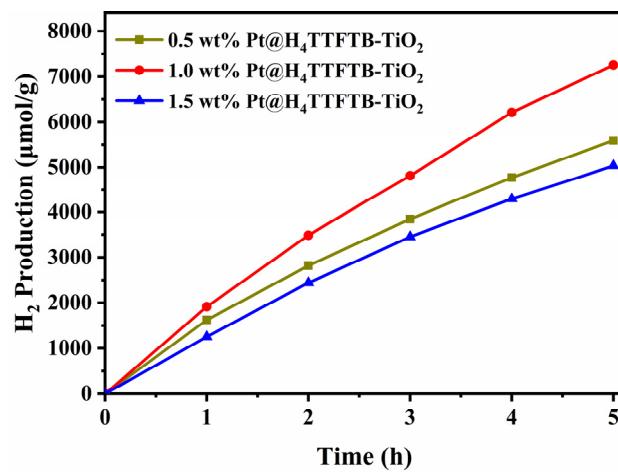
**Figure S11.** UV-vis absorption spectra and photoluminescence spectra of  $\text{H}_4\text{TTFTB}$  in DMF ( $E_{0-0} = 1240/\lambda_{\text{int}}$ ).



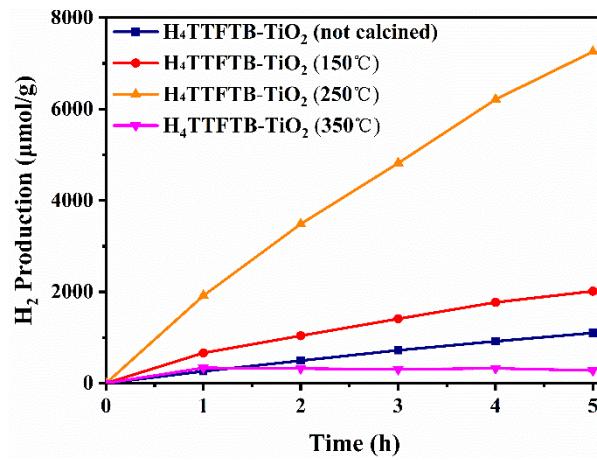
**Figure S12.** Mott-Schottky plot of  $\alpha$ -TiO<sub>2</sub> in 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution.



**Figure S13.** Cyclic voltammogram of H<sub>4</sub>TTFTB in 0.1 M TBAPF<sub>6</sub> of DMF solutions measured with a scan rate of 50 mV s<sup>-1</sup>.



**Figure S14.** Comparison of photocatalytic H<sub>2</sub> evolution of 5 hours of H<sub>4</sub>TTFTB-TiO<sub>2</sub>-5.0 hybrid material under different loads of Pt.



**Figure S15.** Comparison of photocatalytic H<sub>2</sub> evolution of H<sub>4</sub>TTFTB-TiO<sub>2</sub>-5.0 hybrid material under different calcined temperature loaded with 1.0 wt% Pt.

**Table. S1.** The amount of Pt NPs of Pt@H<sub>4</sub>TTFTB-TiO<sub>2</sub>.

Sample	Pt NPs Loading amount(wt%)
0.5 wt% Pt@H <sub>4</sub> TTFTB-TiO <sub>2</sub>	0.393
1.0 wt% Pt@H <sub>4</sub> TTFTB-TiO <sub>2</sub>	0.878
1.5 wt% Pt@H <sub>4</sub> TTFTB-TiO <sub>2</sub>	1.288

**Table. S2.** BET surface area, pore volume and pore size of  $\alpha$ -TiO<sub>2</sub>, H<sub>4</sub>TTFTB-TiO<sub>2</sub>-5.0 derived from 77 K N<sub>2</sub> sorption isotherm.

Sample	Surface area (m <sup>2</sup> /g)	Pore size (nm)	Pore volume (cm <sup>3</sup> /g)
$\alpha$ -TiO <sub>2</sub>	184.10	4.411	0.257
H <sub>4</sub> TTFTB-TiO <sub>2</sub> -5.0	212.65	3.630	0.239

**Table. S3.** Atmoic Fraction of Pt@H<sub>4</sub>TTFTB-TiO<sub>2</sub>.

Z	Element	Family	Atomic Fraction (%)	Atomic Error (%)	Mass Fraction (%)	Mass Error (%)	Fit Error (%)
6	C	K	58.16	7.63	43.36	3.48	2.79
8	O	K	34.35	8.16	34.12	7.29	0.55
16	S	K	0.01	0.00	0.02	0.01	14.70
22	Ti	K	7.46	1.38	22.16	3.38	0.04
78	Pt	L	0.03	0.00	0.34	0.05	2.28

**Table S4.** Comparison of H<sub>2</sub> evolution activity of TTF and TiO<sub>2</sub> photocatalytic systems.

Catalyst	Co-catalyst	Sacrificial agent	Solvent	Light source (nm)	H <sub>2</sub> Production rate (μ mol h <sup>-1</sup> g <sup>-1</sup> )	Ref
H <sub>4</sub> TTFTB-TiO <sub>2</sub>	Pt	TEOA	H <sub>2</sub> O	>400	1452	This work
Zn-TPY-TTF	Pt	TEA	H <sub>2</sub> O	>400	14727	[45]
G3T3	Pt	TEOA	H <sub>2</sub> O	>400	24560	[19]
DPPCN/TiO <sub>2</sub>	Pt	TEOA	H <sub>2</sub> O	>400	12080	[18]
DPPCA/TiO <sub>2</sub>	Pt	TEOA	H <sub>2</sub> O	>400	8400	[18]
MOC-16/TTF	Pd	TEOA	DMSO-H <sub>2</sub> O	>420	7344.9	[46]
Rh B-Co/TiO <sub>2</sub>	Co	-	water	>400	227.3	[47]
P42-TiO <sub>2</sub>	Pt	TEOA	H <sub>2</sub> O	>420	745.0	[48]
PI-OMe-TiO <sub>2</sub>	Pt	TEOA	H <sub>2</sub> O	>420	1190	[26]
3C/TiO <sub>2</sub>	Pt	TEOA	H <sub>2</sub> O	>420	247	[49]
ZnPc/TiO <sub>2</sub>	Pt	TEOA	H <sub>2</sub> O	>420	3448	[22]
CoPc/TiO <sub>2</sub>	Pt	TEOA	H <sub>2</sub> O	>420	3328	[22]
B-Car/TiO <sub>2</sub>	Pt	ascorbic acid	Water	>420	249	[50]
PAN-Pt@TiO <sub>2</sub>	Pt	thioglycolic acid	H <sub>2</sub> O	>420	61.8	[51]
Chl-3-TiO <sub>2</sub>	Pt	ascorbic acid	water	>400+>600	263.3	[52]
Eosin Y <sup>+</sup>	Ni(OH) <sub>2</sub>	TEOA	H <sub>2</sub> O	>420	1576	[53]
Ni(OH) <sub>2</sub> /TiO <sub>2</sub>						
MZ-341/TiO <sub>2</sub>	Cu <sub>2</sub> WS <sub>4</sub>	TEOA	water	>420	1406	[54]
1-P25	Pt	TEOA	water	>400	2364	[55]
FL@MOC-PC	Pd <sup>2+</sup>	TEOA	water	>420	2402	[56]