

Supplementary Information

A highly active Cu-Freudenbergite/TiO₂ heterojunction for solar-driven hydrogen evolution and 5-hydroxymethylfurfural oxidation

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Table S1. Rietveld Refinement of bare Cu-FDT photocatalyst

CIF	COD entry	Space Group Symbol	Space Group No	Lattice
Freudenbergite	9011187	C12/m1	12	Monoclinic

Atom (Occupancy)	Wyckoff	x	y	z
Na (1)	a	0.0	0.0	0.0
Ti (0.73) Cu (0.27)	i	0.297590	0.0	0.710600
Ti (0.73) Cu (0.27)	i	0.397740	0.0	0.302300
O (1)	i	0.372500	0.0	0.995800
O (1)	i	0.236600	0.0	0.346500
O (1)	i	0.134900	0.0	0.709400
O (1)	i	0.441200	0.0	0.633300

Fit Statistics			
Rwp ^a	Rexp ^b	χ^2	GoF ^d
4.81	1.02	22.23	4.7157

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Cell parameters			
a (nm)	b (nm)	c (nm)	beta
1.2245 (1)	0.38209 (4)	0.64920 (8)	107.68 (1)

^aWeighted Profile R factor: Indication of the agreement between the observed and calculated diffraction patterns

^bExpected R factor: Indication of the quality of the experimental results

^dGoodness of Fit: Statistical parameter for the quality of the fit

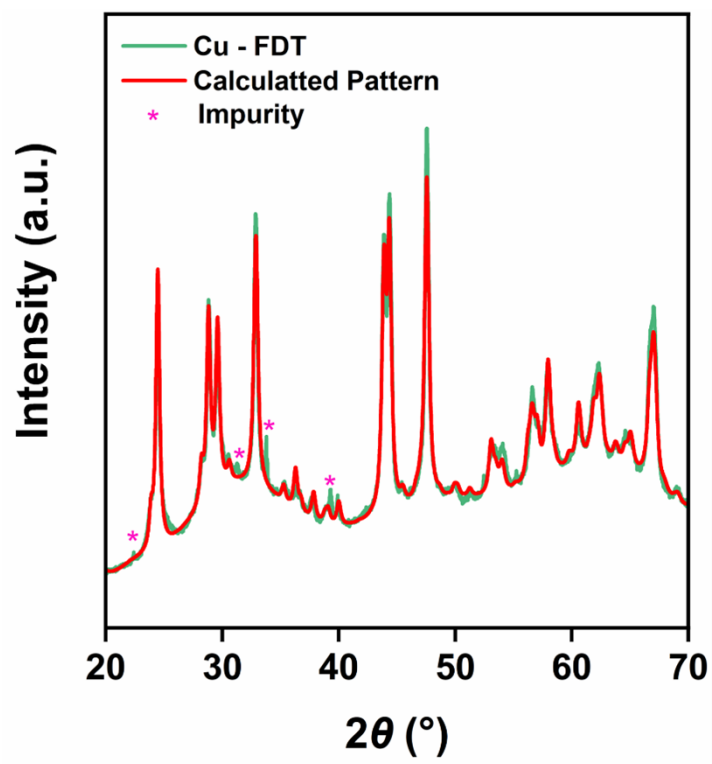


Figure S1: Fitted pattern from 20° - 70° 2θ for the compound Cu-FDT

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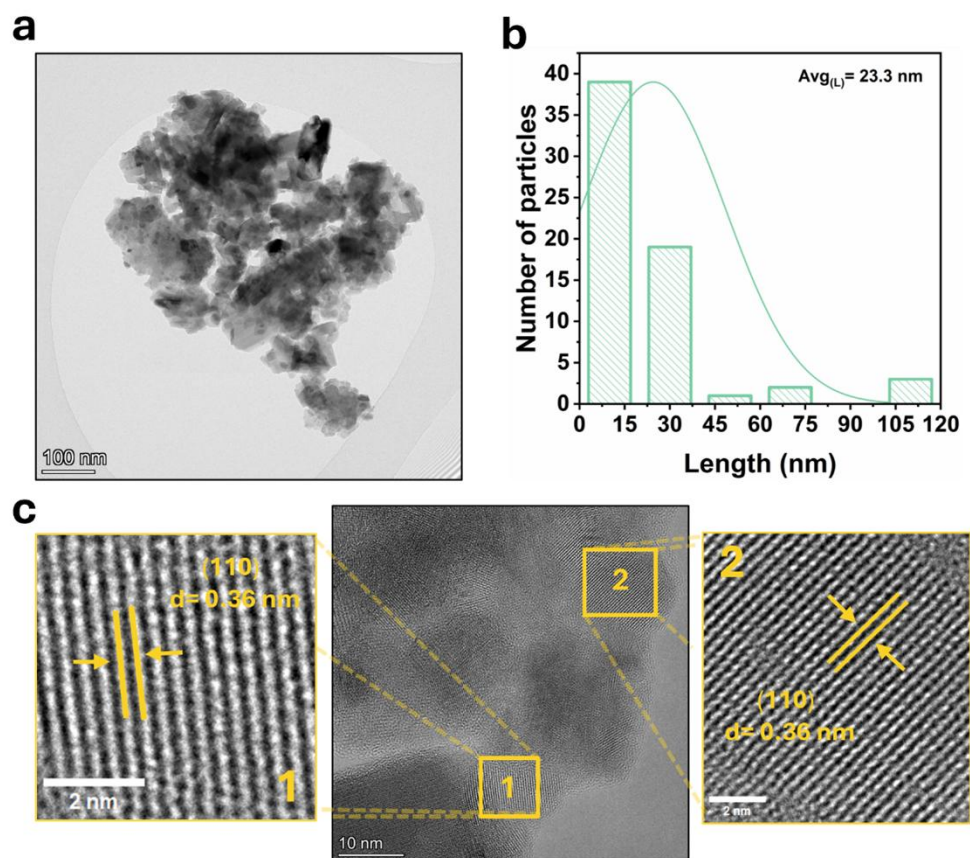


Figure S2. **a)** TEM image of Cu-FDT, **b)** particle size distribution as calculated after measuring 80 individual particles from **(a)**, **c 1, 2)** d-spacings of the marked regions

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Table S2. Elemental composition of Cu-FDT through TEM-EDS (RAW data below)

Z	Element	Family	Atomic Fraction (%)	Atomic Error (%)	Mass Fraction (%)	Mass Error (%)	Fit Error (%)
8	O	K	63.8	2.97	40.49	3.31	0.02
11	Na	K	10.46	1.93	9.56	1.89	1.30
22	Ti	K	24.67	3.18	46.93	4.31	0.14
29	Cu	K	1.20	0.18	3.02	0.49	0.16

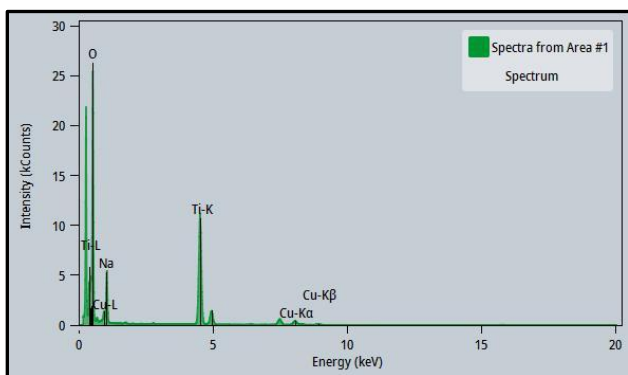


Table S3. Elemental composition of Cu-FDT through XPS

Ti2p		C1s			Atomic concentration (%)				
Ti ⁴⁺ (%)	Ti ³⁺ (%)	C-C (%)	C-O (%)	COOH (%)	Ti	Cu	Na	O	C
87.5	12.5	36	19	45	12.2	0.4	9.6	49.2	28.6

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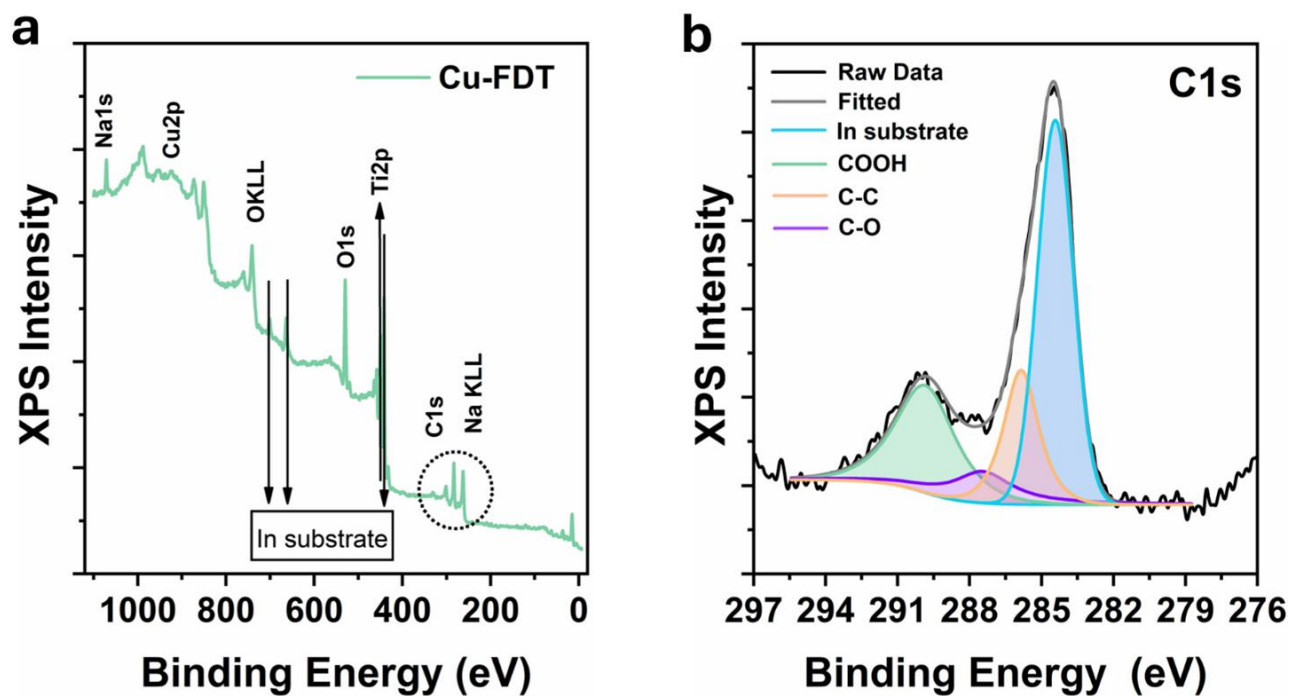


Figure S3. a) XPS survey scan of Cu-FDT and b) Fitted XPS C1s spectra for the Cu-FDT photocatalyst.

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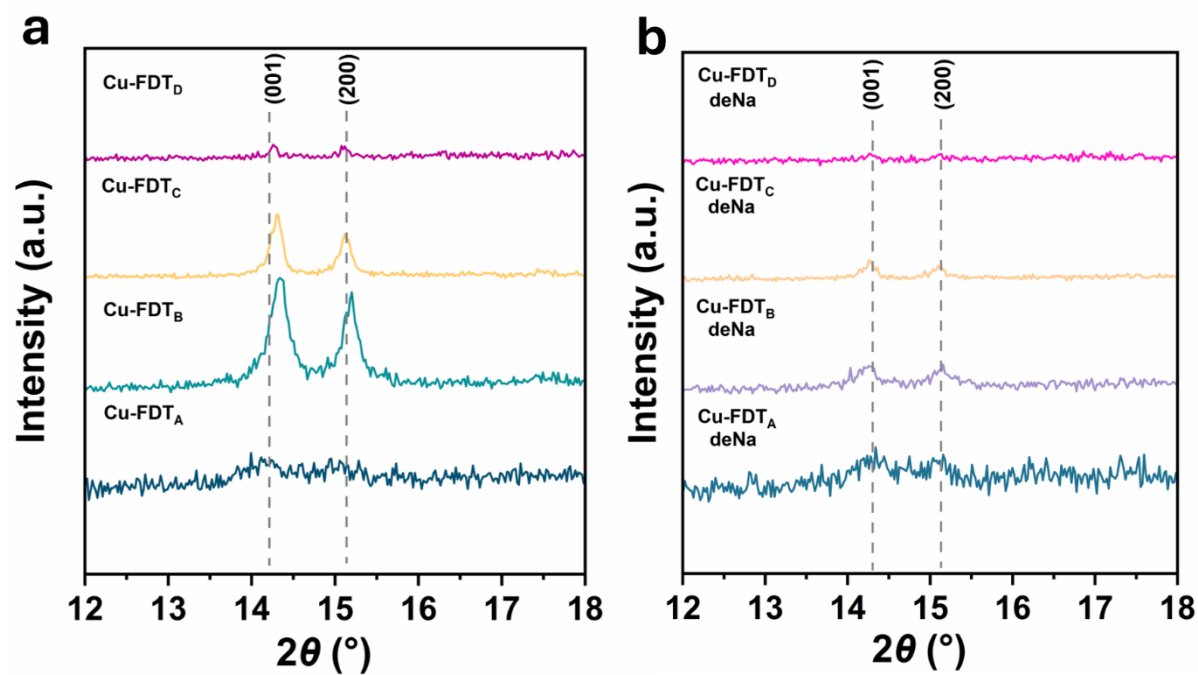


Figure S4. Evolution of the (001) and (200) crystal facets of Cu-FDT by increasing calcination temperature through the a) Cu-FDT_{A-D} and b) Cu-FDT_{A-D} deNa photocatalysts

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Table S4. Phase analysis and crystallite size for Cu-FDT, Cu-FDT_{A-D} and Cu-FDT_{A-D} deNa

Sample	Crystalline phases (%)				Crystallite size ^a (nm)	
	Cu-FDT	Anatase	Rutile	Na(Cu _{2.5} Ti _{0.5}) Ti ₄ O ₁₂	Cu-FDT (020)	Rutile (101)
Cu-FDT	98 (impurity 2%)	-	-	-	22.4 ± 0.2	-
Cu-FDT_A	65.5	34.5	-	-	10.3 ± 0.1	-
Cu-FDT_B	47.2	22.5	30.3	-	25.6 ± 0.3	73.11 ± 0.2
Cu-FDT_C	51.2	-	48.8	-	73.6 ± 0.2	110.6 ± 0.3
Cu-FDT_D	9.4	-	86.7	3.9	106.5 ± 0.2	131.4 ± 0.1
Cu-FDT_A deNa	64.9	35.1	-	-	9.3 ± 0.2	-
Cu-FDT_B deNa	27.1	39.4	33.5	-	20.3 ± 0.2	57.1 ± 0.2
Cu-FDT_C deNa	16.9	1.5	81.6	-	59.8 ± 0.3	105.2 ± 0.4
Cu-FDT_D deNa	17.2	-	79.9	10.2	65.7 ± 0.1	110.5 ± 0.5

^aCalculated from the FWHM of the (101) diffraction of anatase, employing the Scherrer equation, and assuming k: 0.89

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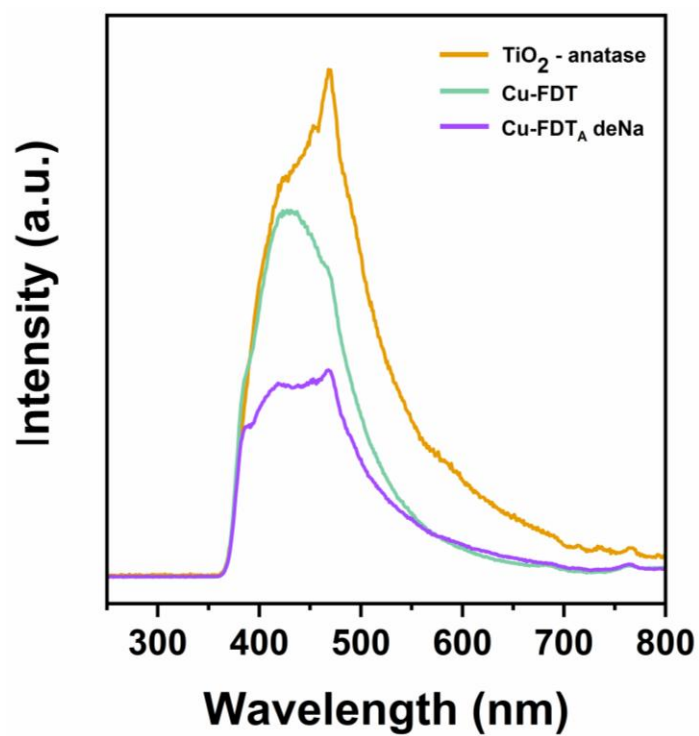


Figure S5 PL spectra of pristine TiO₂ – anatase, Cu-FDT_A, and Cu-FDT_A deNa using an excitation wavelength of 310 nm.

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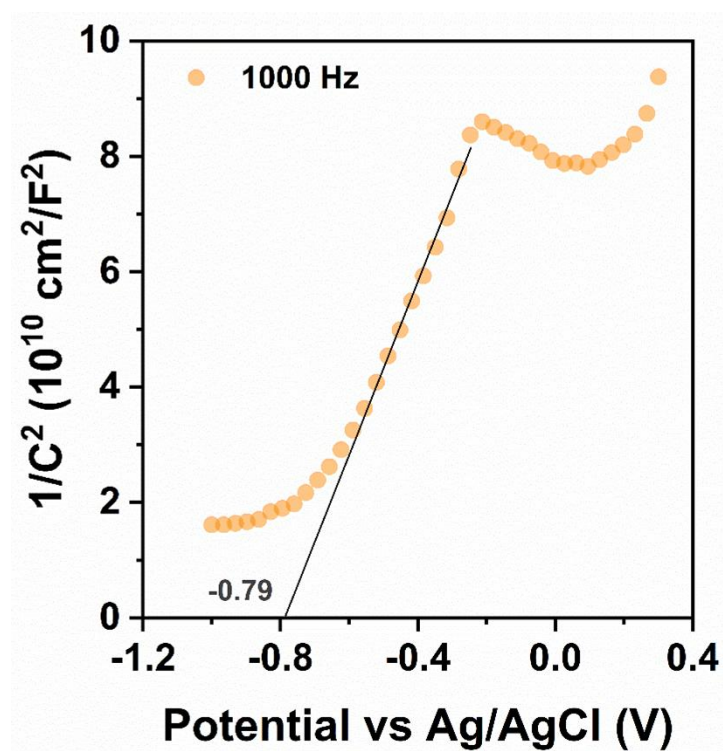


Figure S6 Mott-Schottky plot of TiO₂ anatase derived through the same experimental procedure without the addition of Cu precursor

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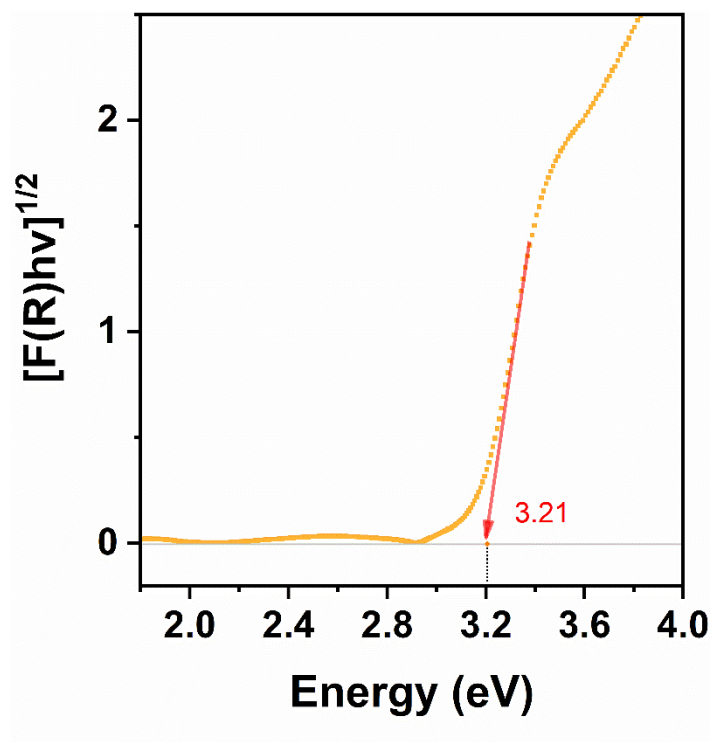


Figure S7 Tauc plot of TiO₂ anatase for the determination of the E_g value

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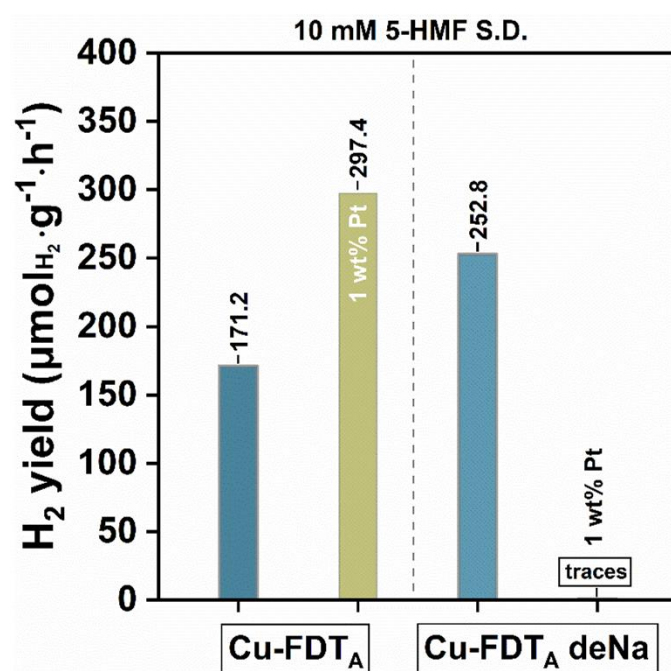


Figure S8. H₂ evolution rates through a 12 h time-course employing 10 mM 5-HMF as an electron donor

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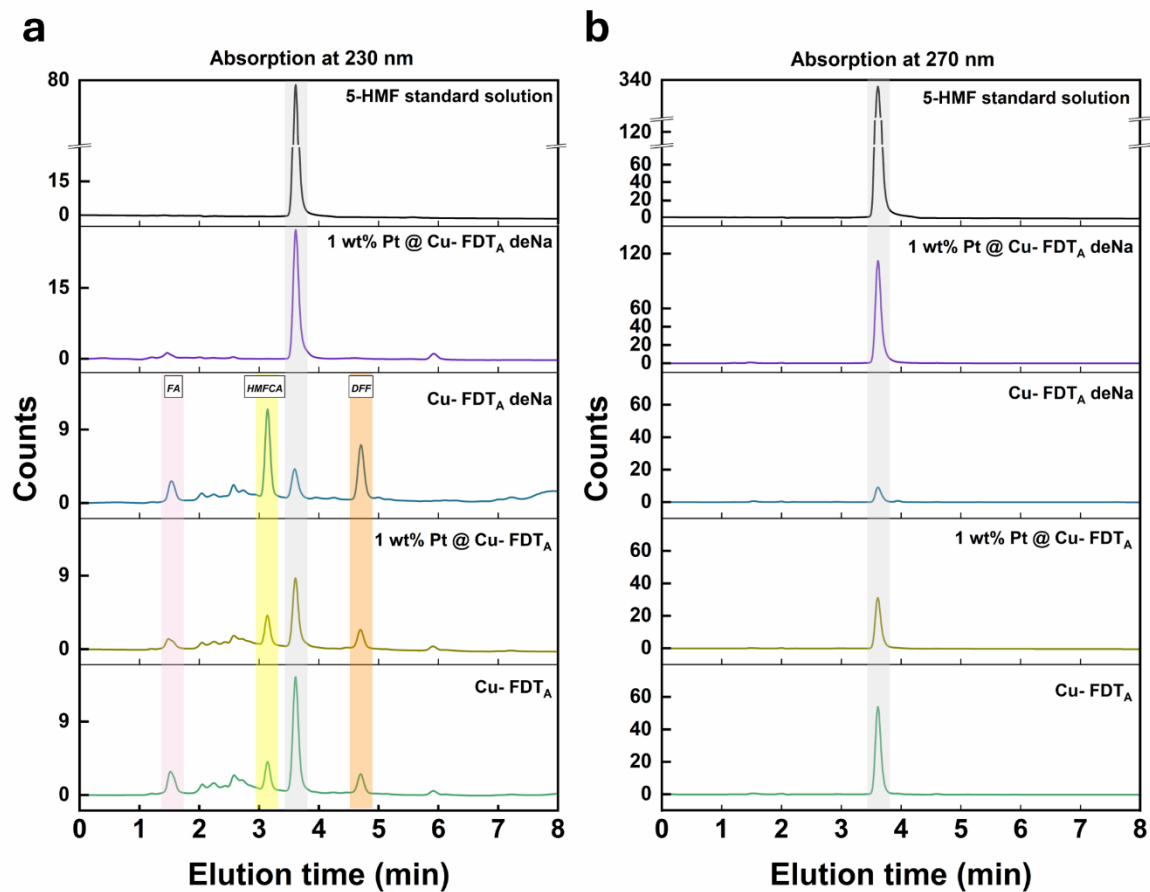


Figure S9. HPLC chromatographs of the reaction samples with 10 mM 5-HMF substrate after solar-light irradiation for 12 h.