Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

Enzyme Immobilization in Ru(N^N)$_3$-modified Covalent Oganic Framework for Photoenzymatic Cascade Catalysis

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Section 1. Materials and methods

1.1 General

All starting materials, reagents and solvents were purchased from commercial sources and used without further purification.

1.2 Instrumentation

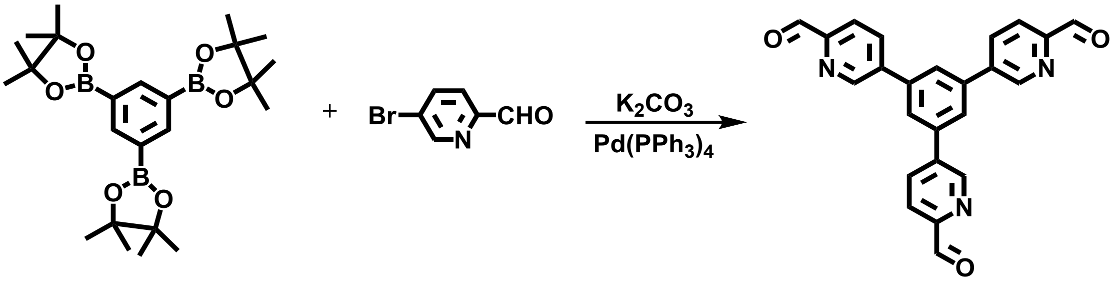
^{1}H nuclear magnetic resonance (^{1}H NMR) was recorded on Bruker 400M NMR spectrometer. Fourier transformed infrared spectra were recorded as KBr pellets using a Nicolet IS 10 spectrometer (FT-IR: Thermo Fisher, USA). Powder X-ray diffraction was recorded on a D8 Advance X-ray diffraction meter (PXRD: Bruker, German), using CuKα radiation over a 2θ range from 5^o to 90^o at a scanning rate of 5°/min. An inductively coupled plasma (ICP) spectrophotometer (Varian, 725-ES) was used to quantify the content of Ru and Rh in the COFs. The N_2 adsorption-desorption isotherms were recorded at 77 K by using a BelSorp Max (Ankersmid b.v., Netherlands) surface area and porosity analyzer. Before the adsorption measurement, the samples (200 mg) were activated at 120 °C under vacuum ($< 10^{-3}$ torr) for 12 h. X-ray photoelectron spectroscopy measurement was carried out using PHI5000 Versaprobe III spectrometer (XPS: ULVAC-PHI, Japan) using an Al Kα source. The scanning electron microscope was carried out on an JSM-7500F apparatus (SEM: JEOL, Japan) equipped with a field emission gun. The ultraviolet-visible diffuse reflectance spectra were recorded on a Nicolet Evolution 500 Spectrophotometer (UV-Vis DRS: Thermo Fisher Scientific, USA ThermoFisher) with BaSO4 as reflectance standard from 200 to 900 nm. The electrochemical measurements were performed in 1.0 M Na_2SO_4 aqueous solution using a typical three electrode cell (equipped with a plane quartz window in front), with a Pt wire counter electrode, and an Ag/AgCl reference electrode. The curve was recorded via an electrochemical workstation (CHI 660D, Shanghai, China). Photoluminescence spectra (PL) were obtained using Spectrofluorometer FS5, and all samples were tested with solid powders. The emission spectrum was collected with excitation of 550 nm through a 3.5 nm scan slit and emission range from 570 to 800 nm. Zeta potential was tested in phosphoric acid buffer solution (pH 7.0) to determine the charges around the COFs and *Re*ADH, using laser doppler microelectrophoresis (Zetasizer, Nano-ZS, Malvern, UK). A ZEISS LSM 800 with Airyscan instrument was used to verify the FITC-labelled *Re*ADH were encapsulated into Ru/Rh-COF. The FITC- labelled *Re*ADH@Ru/Rh-COF was exposed under 488 nm, and the emission wavelength was 525 nm. The products were identified by GC-MS (Column: SH-Rxi-5SilMS; GC procedure: inlet temperature 200 °C, temperature procedure 50 °C up to 200°C at 10 °C/min; MS procedure: ion source temperature 200 °C, interface temperature 240°C, detector voltage 0.2 kV; Acquisition mode: Scan, scan range m/z: 25-400) and GC (Chiral column: CycloSil-B; vaporizer temperature 200 °C, detector temperature 200 °C, column oven temperature 50 °C up to 200 °C at 0.5 °C/min or 0.3 °C/min, split ratio 29:1). HPLC analysis was carried out using an Agilent 1260 II HPLC system coupled with UV/Vis set to 254 nm. The columns used were Chiralpak IC® by Daicel. Hexane and isopropanol (98:2) were used as an isocratic mobile phase with 1.0 mL/min flow rate.

1.3 Structure simulations

Structural modeling of I-COF was generated using the Accelrys Materials Studio software package. The lattice model was geometry optimized using the Forcite module. Pawley refinement was applied to define the lattice parameters.

Section 2. Experimental section

2.1 Synthesis of (1,3,5-tris(4′,4″,4‴-formylpyridine)benzene) (TFPB)



A mixture of 1,3,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (456 mg, 1.0 mmol), 5-bromo-2-pyridinecarboxaldehyde (0.93 mg, 5.0 mmol), K_2CO_3 (2 g, 15 mmol), $Pd(PPh_3)_4$ (346.7 mg, 0.30 mmol) in anhydrous DMF (60 mL) was degassed and stirred under N_2 atmosphere at 100 ºC for 72 h. The solvent was removed under reduced pressure and the solid residue triturated with water, collected by filtration and washed with water (3×), hot methanol (2×) and hot CH_2Cl_2 (2×). The resulting product was redissolved in hot $CHCl_3$, the insoluble materials filtered off and diethyl ether added to the filtrate to precipitate out pure product TFPB as a pale yellow solid. The ^1H NMR spectrum of TFPB was shown in Figure S1.

2.2 Synthesis of I-COF

I-COF was synthesized using a reported protocol.[2,3] TFPB (11.8 mg, 0.03 mmol), 4,4′-diamino-*p*-terphenyl (DAT) (11.7 mg, 0.045 mmol), aqueous acetate acid solution

(6 M, 0.10 mL), 1,4-dioxane (0.60 mL), and mesitylene (0.03 mL) were added to a Pyrex tube and mixed thoroughly by ultrasonic. The tube was flashed frozen in a liquid N_2 bath, flame sealed under a vacuum, and placed in a 120 °C oven for 5 d. After that, the solid was collected, washed with DMF and THF. Finally, the materials were dried at 80 °C under reduced pressure to give yellow colored I-COF in an isolated yield of ~83%.

2.3 Synthesis of Q-COF

Q-COF was prepared by the single-step reaction of I-COF with phenylacetylene.[4,5] I-COF (23.5 mg), phenylacetylene (20.4 mg, 0.2 mmol), $BF_3 \cdot OEt_2$ (13 μL, 0.1 mmol), and tetrachloro-1,4-benzoquinone (24.6 mg, 0.1 mmol) were dissolved in toluene (3 mL) in a Pyrex tube. The tube was flashed frozen in a bath of liquid N_2, flam-sealed, and subsequently subjected to an oven at 110 °C for 48 h. The resulting precipitates were isolated via centrifugation, washed thrice with THF, and dried under vacuum overnight at 100 °C to yield Q-COF as a power.

2.4 Preparation of dichlorobis (2,2′-bipyridine) ruthenium (II) ($Ru(bpy)_2Cl_2$)

A mixture of $RuCl_3 \cdot 3H_2O$ (0.400 g, 1.91 mmol), 2,2′-bipyridine (0.506 g, 3.82 mmol), and LiCl (0.0054 g, 0.128 mmol) was refluxed in DMF (5 mL) in a round-bottom flask for 12 h under argon. After cooling to room temperature, acetone (25 mL) was added and the solid was filtered, washed with hexane and diethyl ether, and dried under vacuum to give red-black solid. The ^1H NMR spectrum of $Ru(bpy)_2Cl_2$ was shown in Figure S2.

2.5 Synthesis of Ru-COF

Q-COF (100 mg) and a certain amount of Ru(bpy)$_2$Cl$_2$ was added together into a 25 mL flask under nitrogen atmosphere. After addition of dry DMF (10 mL), the mixture was shaken at 120 °C for 12 h. The theoretically required amount of all bipyridines to react with Ru(bpy)$_2$Cl$_2$ was defined as 100%. The resulting solid was isolated by centrifugation and washed with DMF and THF, then dried at 80 °C under vacuum for 12 h to yield Ru-COF. The added concentration of Ru(bpy)$_2$Cl$_2$ after optimization was 30%.

2.6 Evaluation of photocatalytic thiol-ene reaction

To 3 mL phosphate buffer (pH 7.4) was added Ru-COF (1.0 mg mL^{-1}), 1-propanethiol (1.0 mM) and 1-penten-3-one (1.0 mM). After incubating for 1 h in darkness, the solution was illuminated by Xe lamp ($\lambda \geq 420$ nm, 300 W) for a certain time under N$_2$ atmosphere. At different time intervals, aliquots were taken to monitor the progress of the reaction. The 1-(propylthio)pentan-3-one were detected by GC-MS) and GC.

2.7 Synthesis of Ru/Rh-COF

10 mg Ru-COF was added to a suspension of a certain amount of dichloro(pentamethylcyclopentadienyl)rhodium (III) dimer ([Rh(Cp*)Cl$_2$]$_2$) (X% of theoretical adsorption capacity) in 10 mL methanol. The saturated theoretical loading of RhCp* was considered to be 100% (all of the bipyridine units in the framework participate in the coordination). After ultrasonic dispersion of the above systems containing different contents of RhCp* (3%, 6%, 12%, and 24%) were put on the shaker for 24 h. The solid was filtered and washed with deionized water and dried in vacuum at 60 °C overnight to afford the samples.

2.8 Photocatalytic NADH regeneration

For NADH regeneration, Ru/Rh-COF (3 mg), NAD^+ (1 mM), TEOA (300 μL) was added in 2.7 mL of phosphate buffer (10 mM, pH 7.0). The reaction vial was initially allowed to equilibrate in the dark for 30 min, followed by xenon lamp illumination ($\lambda \geq 420$ nm, 300W) at room temperature. The concentration of NADH was determined by measuring the absorbance at 340 nm using the UV-vis spectrophotometer. The NADH concentration in the solution was calculated by the regression equation shown in Figure S3, and then the yield was calculated. The cycle experiment was carried out under the same conditions. The Ru/Rh-COF was reused with methanol washing and fresh NAD^+ and TEOA were added every time. Additionally, to determine the specificity of NADH regeneration, the insoluble photocatalyst was removed from the reaction solution by filtration after the NADH regeneration reaction was completed. Then, enzyme and substrate were added and reacted. The concentration of any NADH derivatives in the solution before and after reaction was monitored by the UV-vis spectrophotometer at 340 nm.

2.9 Expression and purification of *Re*ADH

The gene of the NADH-dependent alcohol dehydrogenase (*Re*ADH) from *Rhodococcus erythropolis* (AAN73270.1) was synthesized and cloned into pET22b plasmid (SynbioB Inc., Tianjin, China). The plasmid was transformed into *E. coli* BL21(DE3). Single colonies were incubated in 5 mL LB medium containing antibiotics (100 μg/mL ampicillin) at 37 °C overnight. The overnight culture was inoculated into 500 mL LB medium containing antibiotics (100 μg/mL ampicillin) and cultured for

2.5-3.0 h at 37 °C. Isopropyl β-D-1-thiogalactopyranoside at a final concentration of 0.1 mM was added and induced at 16 °C on a rotary shaker for 16-20 h, while the cell optical density at 600 nm of cultures reached 0.6-0.8.

After incubation, the cells were collected by centrifugation at 4 °C and 8000 rpm for 15 min and resuspended by adding buffer A (20 mM Tris-HCl, 300 mM NaCl, pH 7.0). Then, the cells were lysed using a cell crusher; lysates were cleared of cell debris by centrifugation at 4 °C and 13000 rpm for 30 min and purified using a Ni-NTA column (GenScript, Nanjing, China). The proteins were eluted following the increasing gradient of imidazole from 10 mM to 250 mM and collected into different tubes. Based on the SDS-PAGE, the collected eluate was concentrated by ultrafiltration and then stored in the refrigerator.

2.10 Immobilization of *Re*ADH

To adsorb *Re*ADH for immobilization, 3 mg I-COF, Q-COF, Ru-COF or Ru/Rh-COF was activated with phosphate buffer (10 mM, pH 7.0), and then the activated COF was directly added into 1.0 mg/mL *Re*ADH phosphate buffer (10 mM, pH 7.0). The supernatants were determined at different time points by measuring the absorbance at 280 nm using the UV-vis spectrophotometer.

2.11 Evaluation of photoenzyme cascade catalytic performance

To 3 mL phosphate buffer (10 mM, pH 7.0) was added integrated photocatalysts (1.0 mg mL^{-1}), NAD^{+} (1.0 mM), TEOA (10 w/V%), thiol (1.0 mM) and α,β-unsaturated ketone (1.0 mM). After incubating for 1 h in darkness, the solution was illuminated by Xe lamp ($\lambda \geq 420$ nm, 300 W) for a certain time under N_2 atmosphere at room temperature. At different time intervals, aliquots were taken to monitor the progress of the reaction. The ketone and alcohol were detected by GC, GC-MS, or HPLC.

Section 3. Figures and Tables

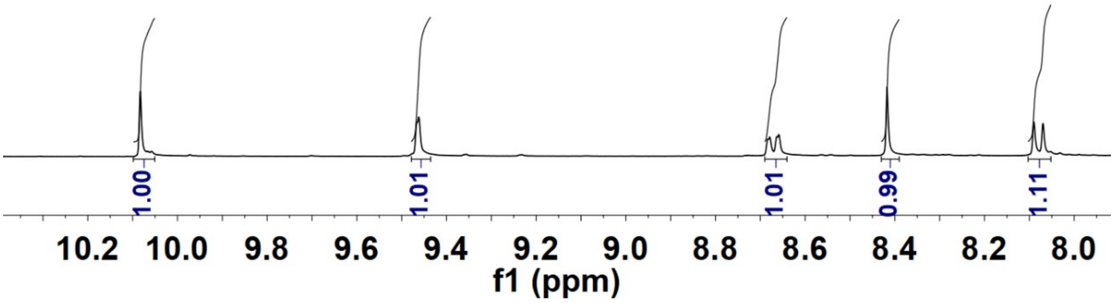


Figure S1. ^{1}H NMR (400 MHz) spectrum of TFPB in DMSO-d6 at room temperature.

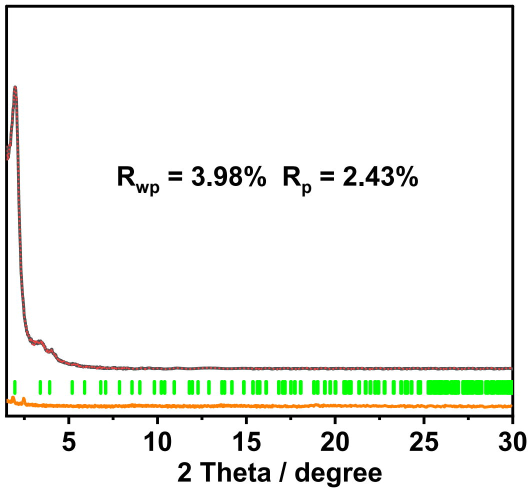


Figure S2. PXRD pattern of I-COF: the experimental (red circle) and Pawley refined (black line) profiles, the Bragg positions (green) and the refinement differences (orange).

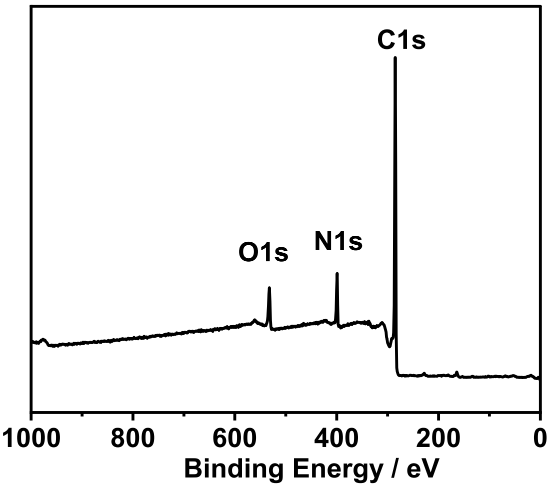


Figure S3. XPS survey data of I-COF.

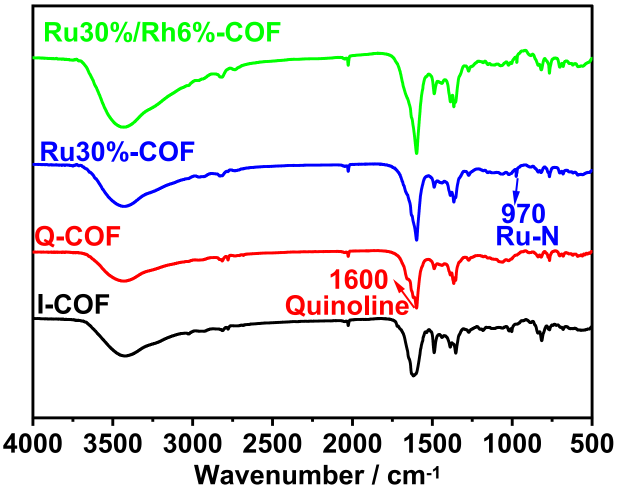


Figure S4. FT-IR spectra of I-COF, Q-COF, Ru30%-COF, and Ru30%/Rh6%-COF.

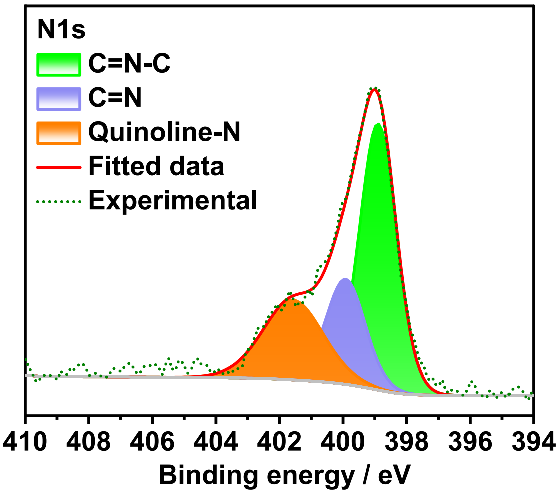


Fig. S5. Deconvoluted N1s XPS spectrum for the Q-COF.

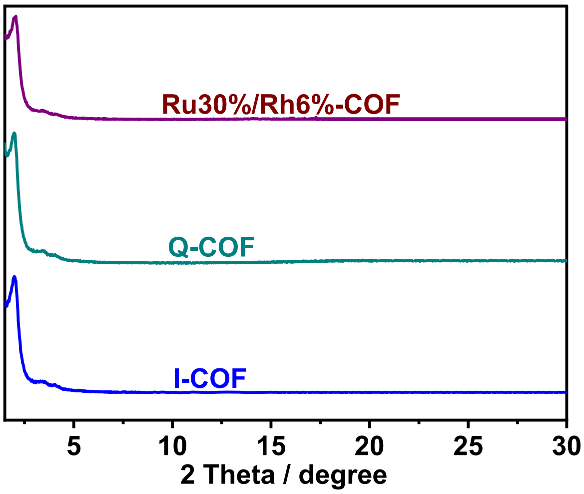


Fig. S6. PXRD patterns of I-COF, Q-COF, and Ru30%/Rh6%-COF.

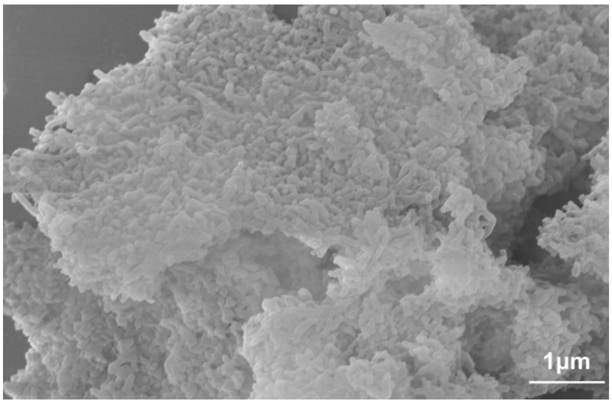


Figure S7. SEM image of Q-COF.

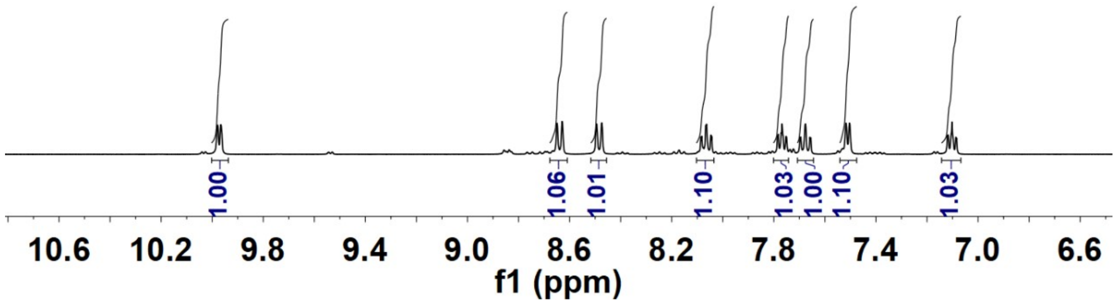


Figure S8. ^1H NMR (400 MHz) spectrum of $Ru(bpy)_2Cl_2$

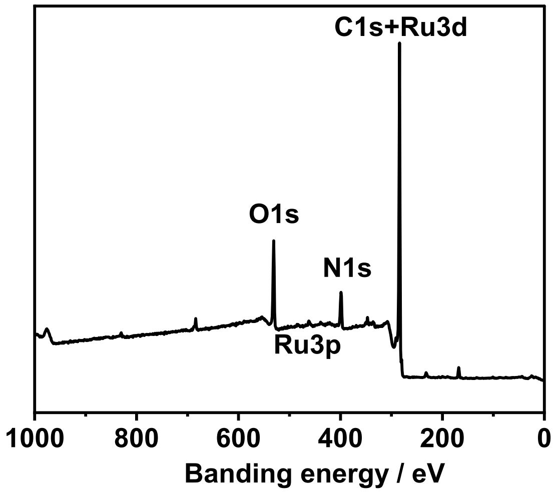


Figure S9. XPS survey data of Ru30%-COF.

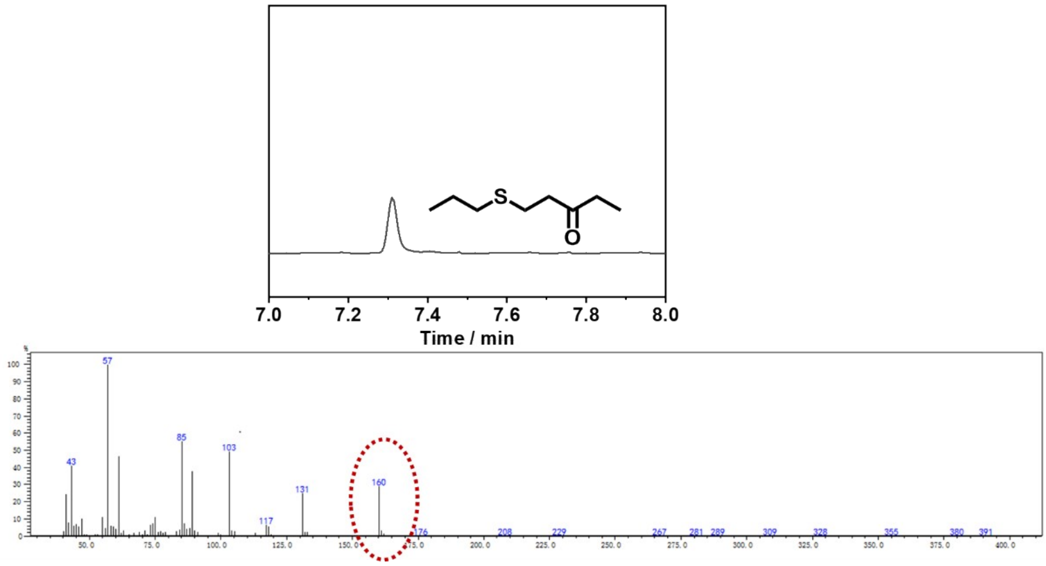


Figure S10. GC-MS result of 1-(propylthio)pentan-3-one product.

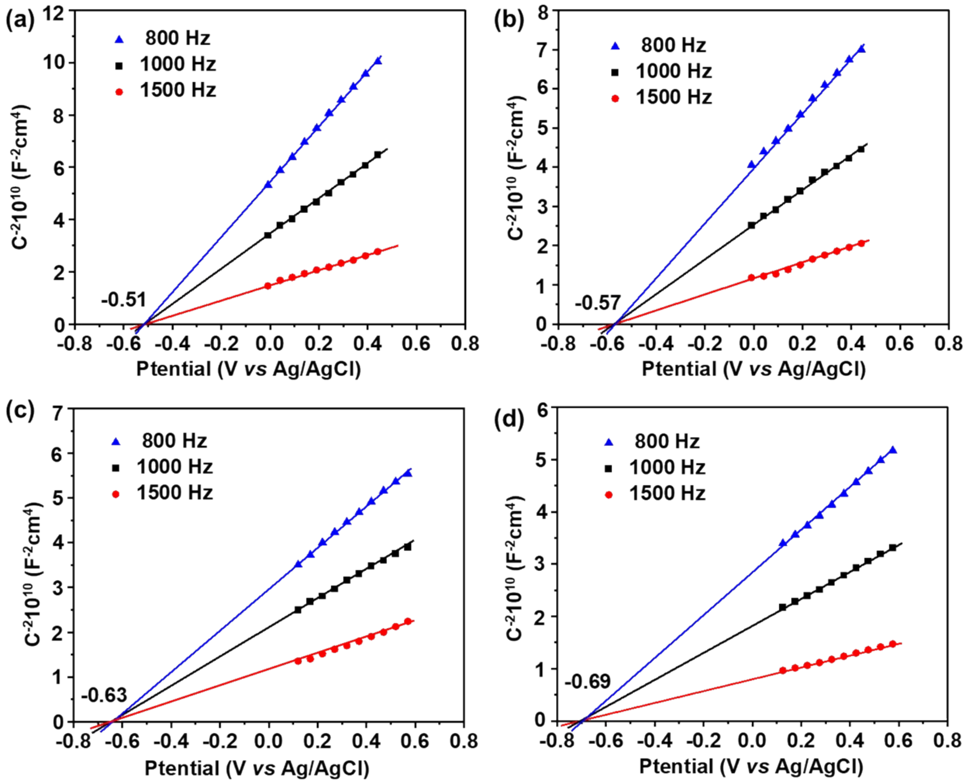


Figure S11. Mott-Schottky plots of I-COF, Q-COF, Ru30%-COF, and Ru30%/Rh6%-COF.

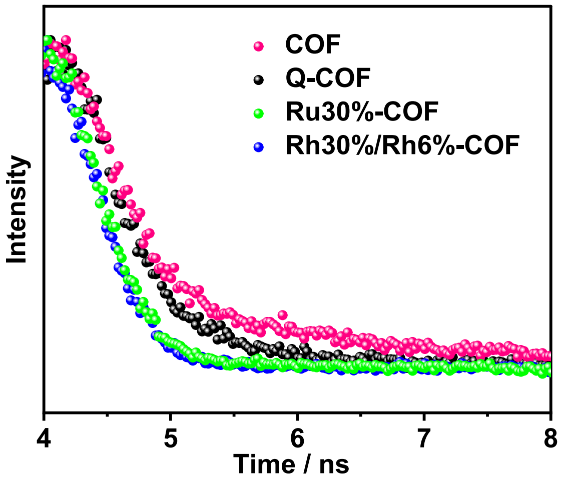
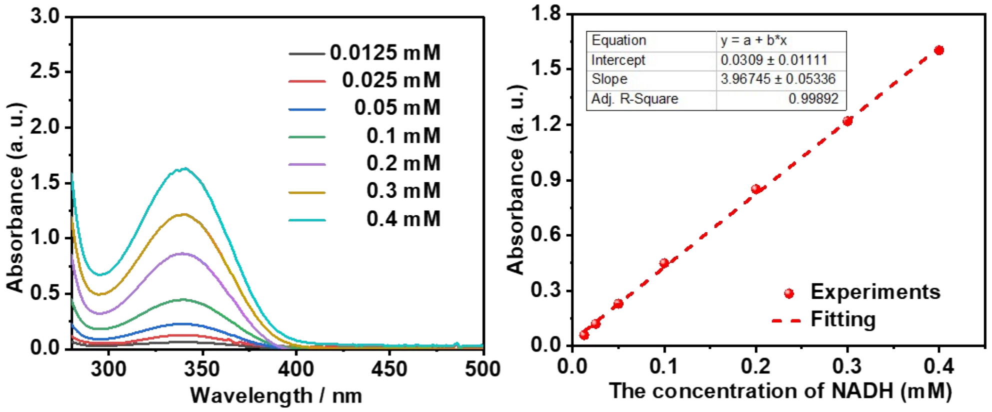


Figure S12. TRPL spectra of I-COF, Q-COF, Ru-COF, and Ru30%/Rh6%-COF.



Equation	y = a + b*x
Intercept	0.0309 ± 0.01111
Slope	3.96745 ± 0.05336
Adj. R-Square	0.99892

Figure S13. UV-vis spectra of NADH with known concentrations for preparing standard curve.

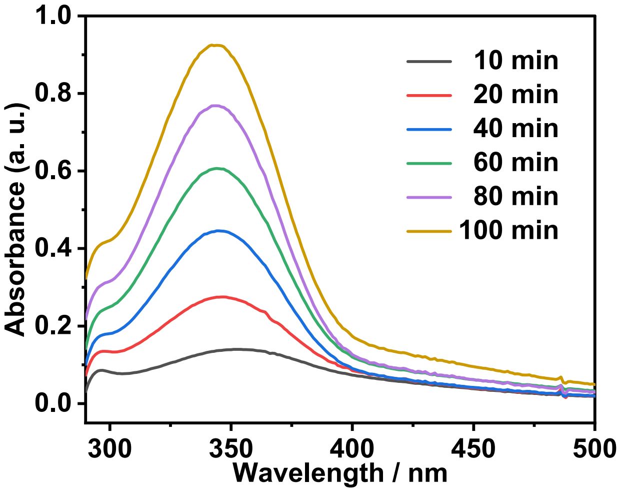


Figure S14. UV-Vis absorbance spectra changes of NADH during the photo regeneration process: Ru30%/Rh6%-COF.

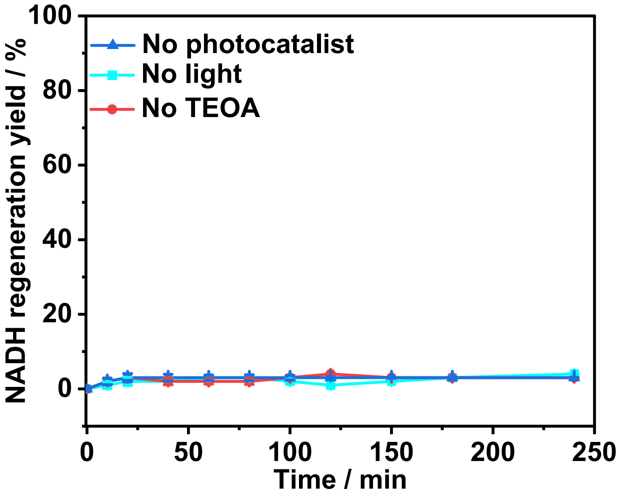


Figure S15. Effects of photocatalyst, light, and TEOA on the photo-regeneration yield of NADH.

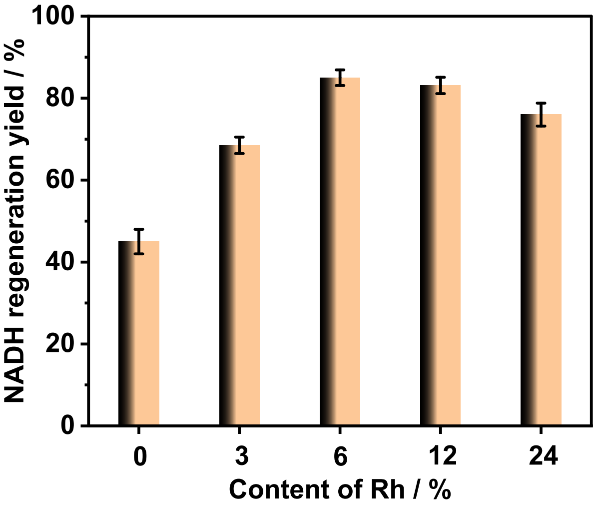


Figure S16. Effects of Rh contents on the photo-regeneration yield of NADH in 2.5 h.

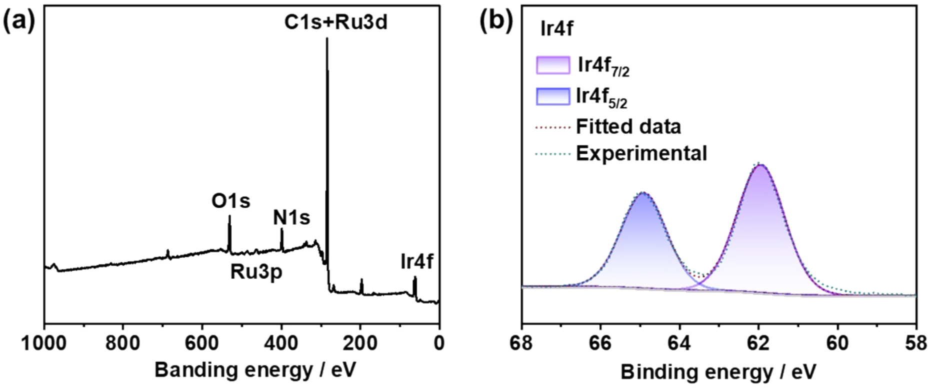


Figure S17. (a) XPS survey data of Ru30%/Ir6%-COF. (b) Ir4f deconvoluted XPS spectra of Ru30%/Ir6%-COF.

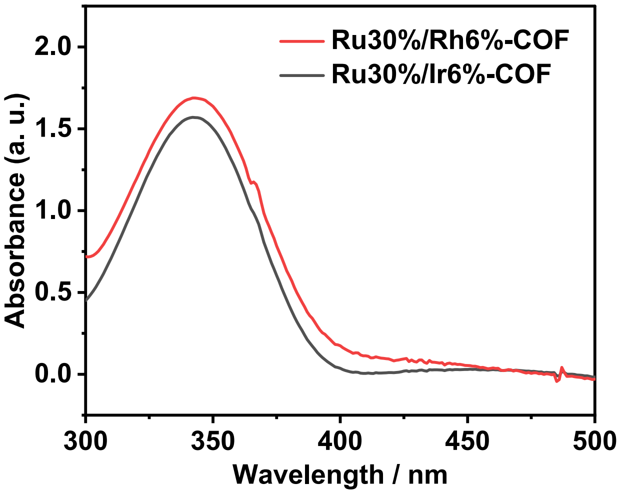


Figure S18. UV-Vis absorption spectra of photocatalytic NADH regeneration by the Ru30%/Rh6%-COF and Ru30%Ir6%-COF.

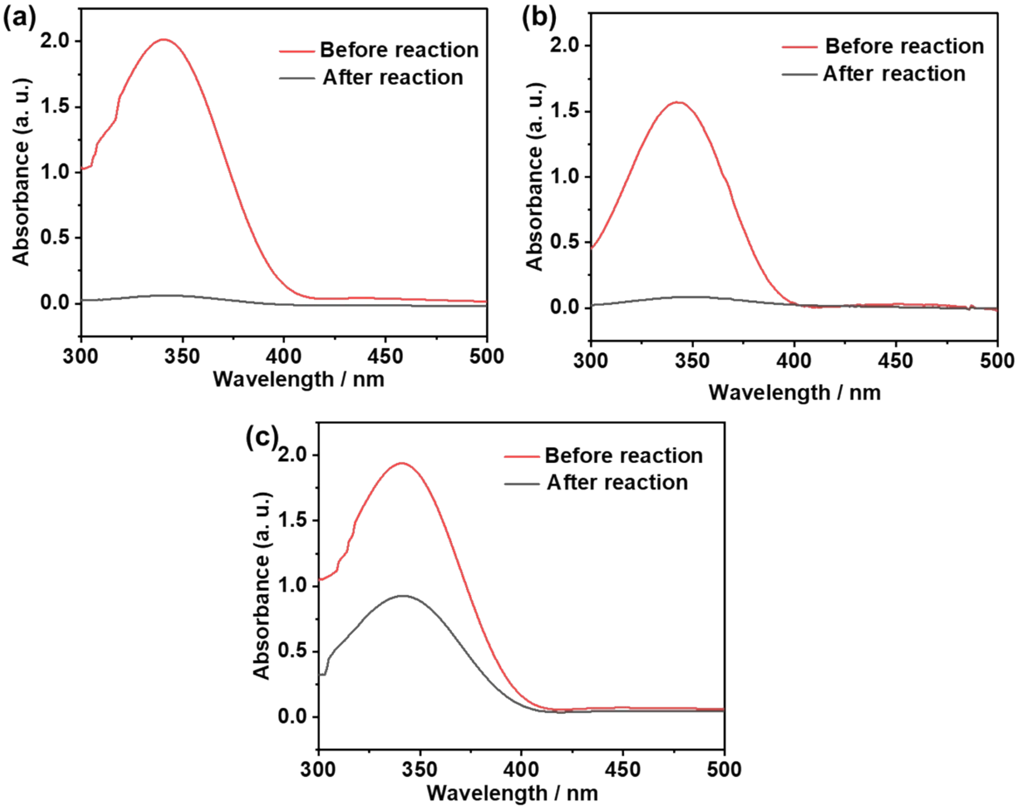


Figure S19. UV-Vis absorption spectra of photocatalytic NADH regeneration by the (a) Ru30%/Rh6%-COF, (b) Ru30%/Ir6%-COF and (c) Ru30%-COF (Before reaction, red line), and UV-Vis absorption spectra of the solution after catalyzed by enzyme with substrate (After reaction, black line).

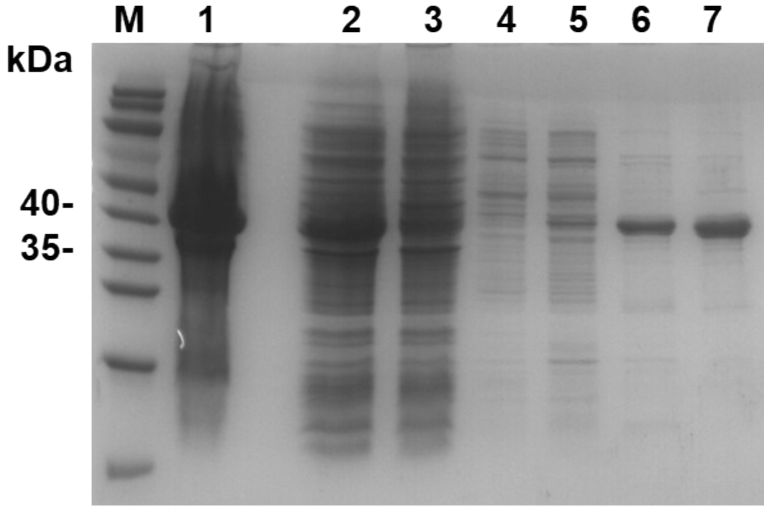


Figure S20. The SDS-PAGE of purified *Re*ADH. Lane M: protein molecular weight marker; Lanes 1-3: supernatant, precipitate, and flowthrough; Lanes 4-7: 10, 50, 100, and 250 mM imidazole-eluted protein. (The imidazole-eluted protein of lanes 6 and 7 were desalted and concentrated for use in this study.)

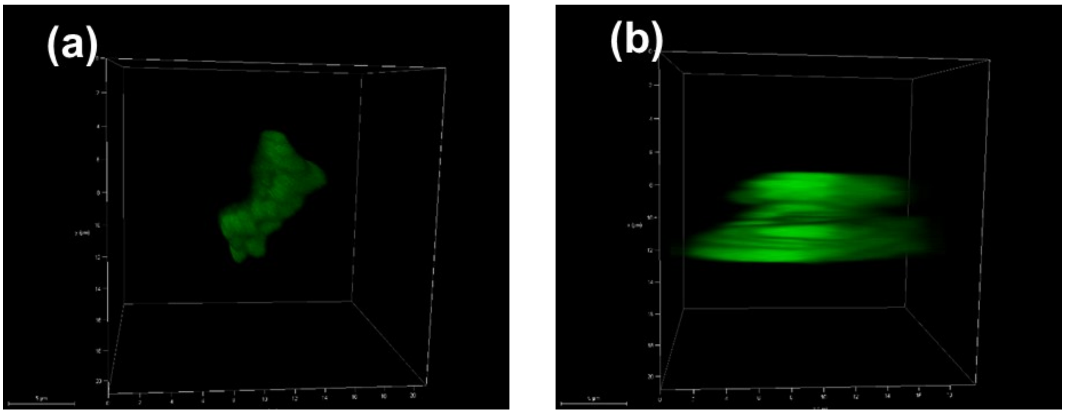


Figure S21. (a) The 3D top view CLSM image of FITC-labelled *Re*ADH@Ru30%/Rh6%-COF. (b) The 3D side view CLSM image of the FITC-labelled *Re*ADH@Ru30%/Rh6%-COF.

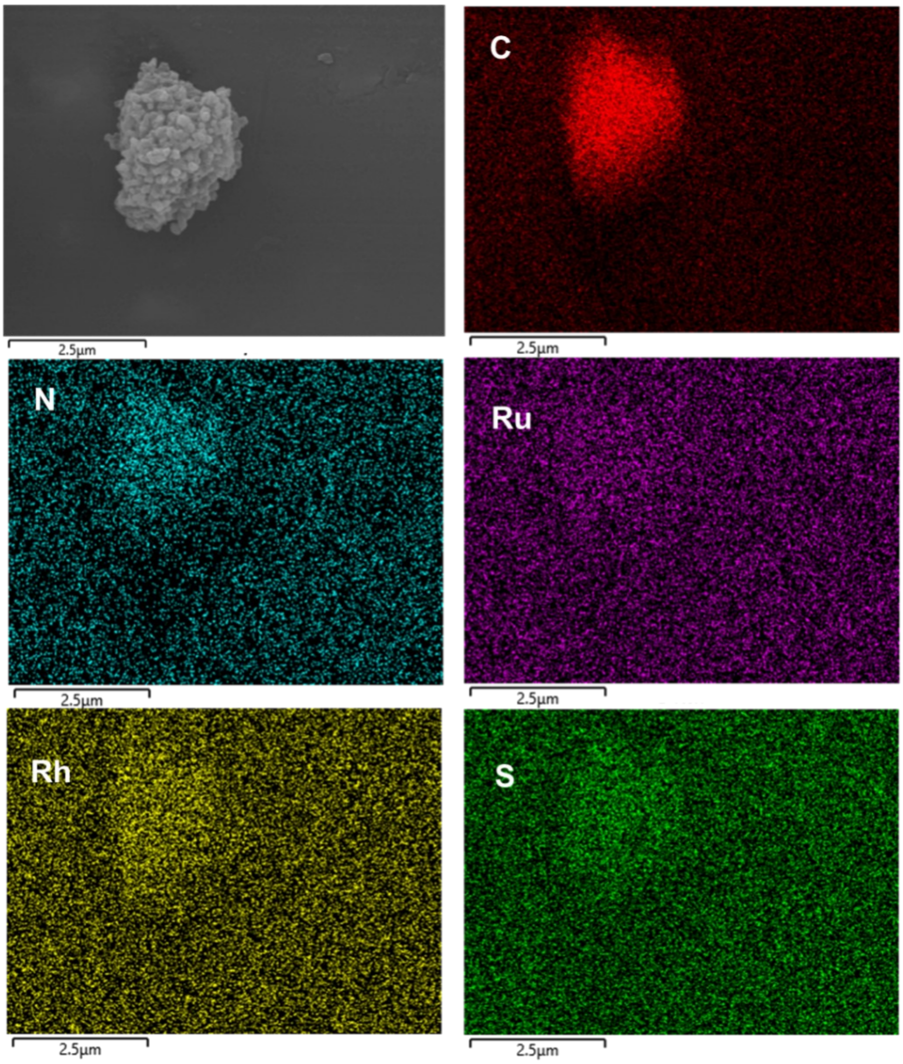


Figure S22. Mapping of the elements (C, N, Ru, Rh and S) in *Re*ADH@Ru/Rh-COF from EDX analysis.

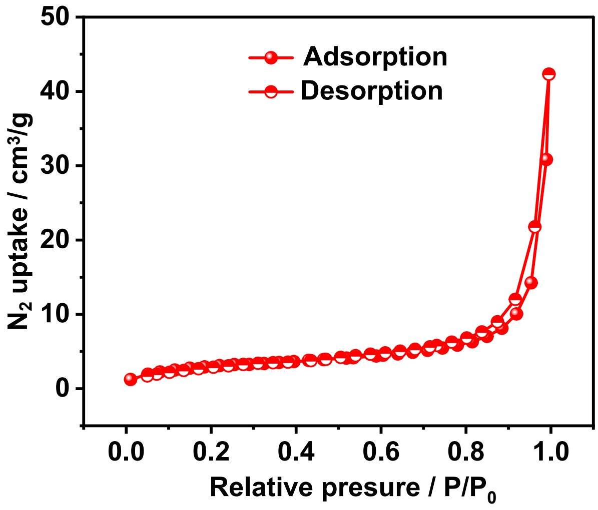


Figure S23. N_2 adsorption isotherm of the *Re*ADH@Ru30%/Rh6%-COF at 77 K.

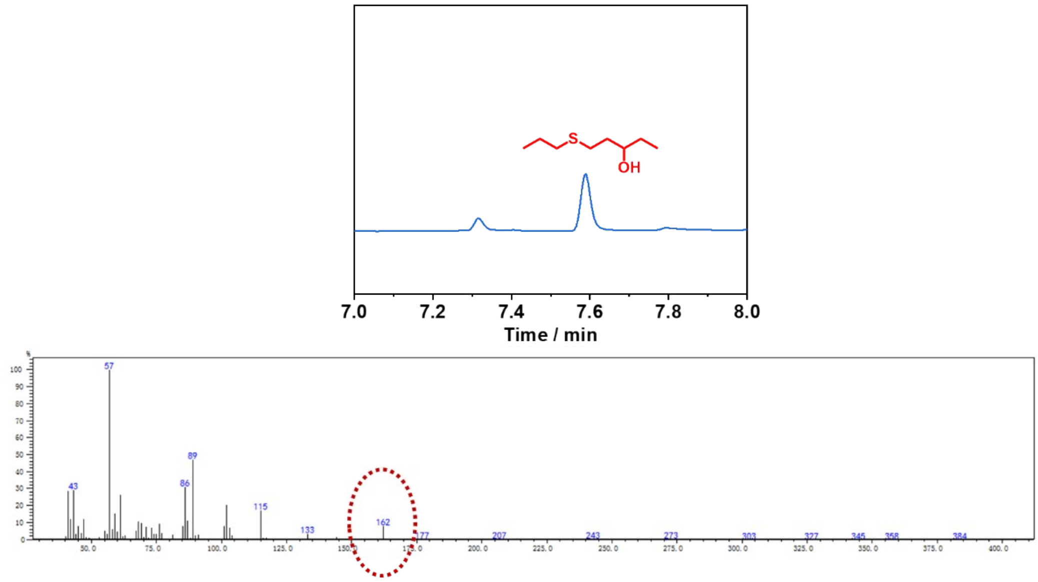


Figure S24. GC-MS result of 1-(propylthio)pentan-3-ol product.

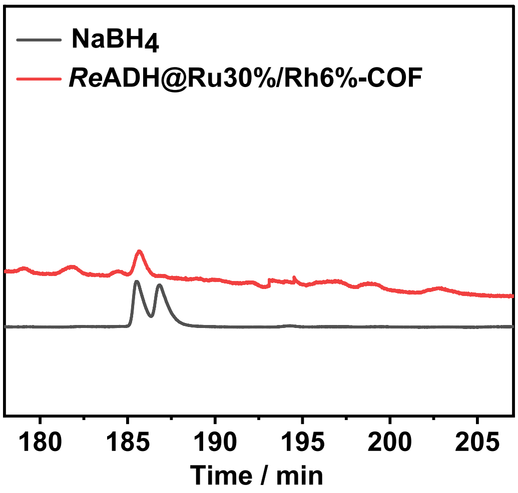


Figure S25. GC results of 1-(propylthio)pentan-3-ol reduced by *Re*ADH@Ru30%/Rh6%-COF and $NaBH_4$.

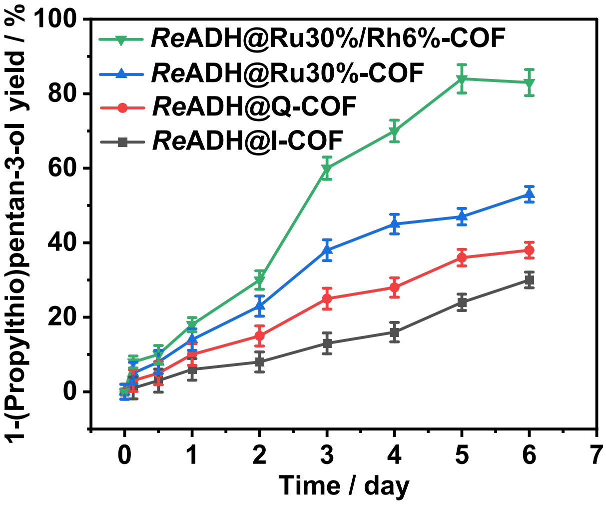


Figure S26. The yield of 1-(propylthio)pentan-3-ol as a function of reaction time with different integration systems.

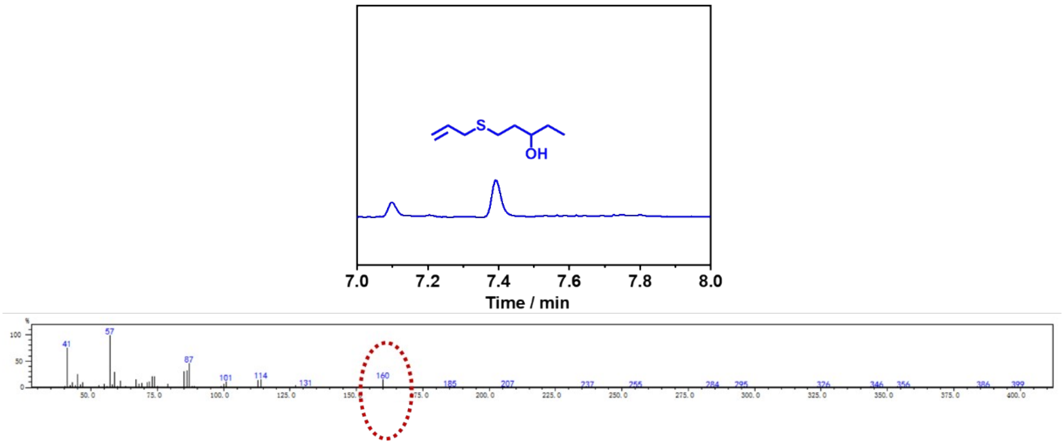


Figure S27. GC-MS result of 1-(allylthio)pentan-3-ol product.

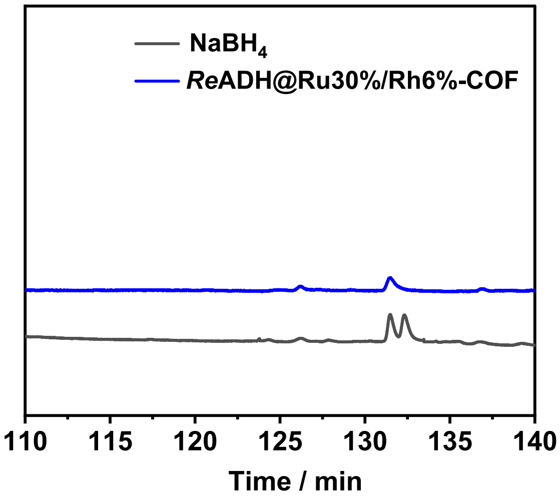


Figure S28. GC results of 1-(allylthio)pentan-3-ol reduced by *Re*ADH@Ru30%/Rh6%-COF and NaBH$_4$.

Table S1. Fractional atom coordinate of the I-COF unite cell.

Space group: P6				
unit cell parameters: a=b=51.9982Å, c=3.51923Å; α=β=90°, γ=120°				
Atom	Number	x	y	z
H	1	0.310614	0.699883	0
H	2	0.334055	0.73926	0
H	3	0.4456	0.784808	0
H	4	0.412674	0.728618	0
H	5	0.451462	0.83472	0
H	6	0.392832	0.87814	0
H	7	0.422837	0.934415	0
H	8	0.505394	0.930574	0
H	9	0.475429	0.874472	0
H	10	0.443742	0.473591	0
H	11	0.47007	0.443744	0
H	12	-0.69988	-0.38927	0
H	13	-0.73926	-0.40521	0
H	14	-0.78481	-0.33921	0
H	15	-0.72862	-0.31594	0
H	16	-0.83472	-0.38326	0
H	17	-0.87814	-0.48531	0
H	18	-0.93442	-0.51158	0
H	19	-0.93057	-0.42518	0
H	20	-0.87447	-0.39904	0
H	21	-0.47359	-0.02985	0
H	22	-0.44374	0.026326	0
H	23	0.389269	-0.31061	0
H	24	0.405205	-0.33406	0
H	25	0.339207	-0.4456	0
H	26	0.315944	-0.41267	0
H	27	0.383258	-0.45146	0
H	28	0.485308	-0.39283	0
H	29	0.511578	-0.42284	0
H	30	0.425181	-0.50539	0
H	31	0.399043	-0.47543	0
H	32	0.029849	-0.44374	0
H	33	-0.02633	-0.47007	0
H	34	-0.31061	-0.69988	0
H	35	-0.33406	-0.73926	0
H	36	-0.4456	-0.78481	0
H	37	-0.41267	-0.72862	0
H	38	-0.45146	-0.83472	0

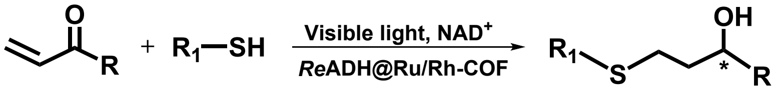
H	39	-0.39283	-0.87814	0
H	40	-0.42284	-0.93442	0
H	41	-0.50539	-0.93057	0
H	42	-0.47543	-0.87447	0
H	43	-0.44374	-0.47359	0
H	44	-0.47007	-0.44374	0
H	45	0.699883	0.389269	0
H	46	0.73926	0.405205	0
H	47	0.784808	0.339207	0
H	48	0.728618	0.315944	0
H	49	0.83472	0.383258	0
H	50	0.87814	0.485308	0
H	51	0.934415	0.511578	0
H	52	0.930574	0.425181	0
H	53	0.874472	0.399043	0
H	54	0.473591	0.029849	0
H	55	0.443744	-0.02633	0
H	56	-0.38927	0.310614	0
H	57	-0.40521	0.334055	0
H	58	-0.33921	0.4456	0
H	59	-0.31594	0.412674	0
H	60	-0.38326	0.451462	0
H	61	-0.48531	0.392832	0
H	62	-0.51158	0.422837	0
H	63	-0.42518	0.505394	0
H	64	-0.39904	0.475429	0
H	65	-0.02985	0.443742	0
H	66	0.026326	0.47007	0
C	1	0.320878	0.684975	0
C	2	0.302217	0.654069	0
C	3	0.371296	0.730456	0
C	4	0.359196	0.749259	0
C	5	0.407336	0.792031	0
C	6	0.420394	0.774232	0
C	7	0.402287	0.743418	0
C	8	0.426278	0.824356	0
C	9	0.440809	0.567557	0
C	10	0.418129	0.889932	0
C	11	0.434651	0.920932	0
C	12	0.465818	0.935786	0
C	13	0.480105	0.918935	0
C	14	0.463602	0.887943	0
C	15	0.485341	0.516685	0

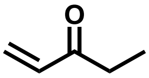
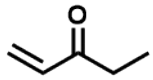
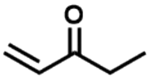
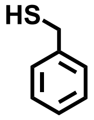
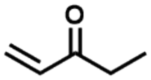
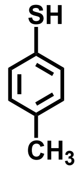
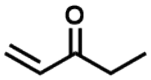
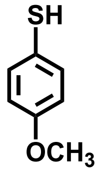
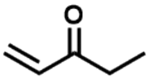
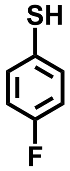
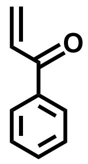
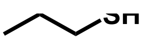
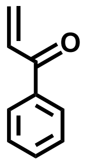
C	16	0.469044	0.485539	0
C	17	0.483537	0.469042	0
C	18	-0.68498	-0.3641	0
C	19	-0.65407	-0.35185	0
C	20	-0.73046	-0.35916	0
C	21	-0.74926	-0.39006	0
C	22	-0.79203	-0.3847	0
C	23	-0.77423	-0.35384	0
C	24	-0.74342	-0.34113	0
C	25	-0.82436	-0.39808	0
C	26	-0.56756	-0.12675	0
C	27	-0.88993	-0.4718	0
C	28	-0.92093	-0.48628	0
C	29	-0.93579	-0.46997	0
C	30	-0.91894	-0.43883	0
C	31	-0.88794	-0.42434	0
C	32	-0.51669	-0.03134	0
C	33	-0.48554	-0.0165	0
C	34	-0.46904	0.014495	0
C	35	0.364097	-0.32088	0
C	36	0.351852	-0.30222	0
C	37	0.35916	-0.3713	0
C	38	0.390063	-0.3592	0
C	39	0.384696	-0.40734	0
C	40	0.353838	-0.42039	0
C	41	0.341131	-0.40229	0
C	42	0.398078	-0.42628	0
C	43	0.126748	-0.44081	0
C	44	0.471803	-0.41813	0
C	45	0.486281	-0.43465	0
C	46	0.469968	-0.46582	0
C	47	0.43883	-0.48011	0
C	48	0.424341	-0.4636	0
C	49	0.031343	-0.48534	0
C	50	0.016495	-0.46904	0
C	51	-0.0145	-0.48354	0
C	52	-0.32088	-0.68498	0
C	53	-0.30222	-0.65407	0
C	54	-0.3713	-0.73046	0
C	55	-0.3592	-0.74926	0
C	56	-0.40734	-0.79203	0
C	57	-0.42039	-0.77423	0
C	58	-0.40229	-0.74342	0

C	59	-0.42628	-0.82436	0
C	60	-0.44081	-0.56756	0
C	61	-0.41813	-0.88993	0
C	62	-0.43465	-0.92093	0
C	63	-0.46582	-0.93579	0
C	64	-0.48011	-0.91894	0
C	65	-0.4636	-0.88794	0
C	66	-0.48534	-0.51669	0
C	67	-0.46904	-0.48554	0
C	68	-0.48354	-0.46904	0
C	69	0.684975	0.364097	0
C	70	0.654069	0.351852	0
C	71	0.730456	0.35916	0
C	72	0.749259	0.390063	0
C	73	0.792031	0.384696	0
C	74	0.774232	0.353838	0
C	75	0.743418	0.341131	0
C	76	0.824356	0.398078	0
C	77	0.567557	0.126748	0
C	78	0.889932	0.471803	0
C	79	0.920932	0.486281	0
C	80	0.935786	0.469968	0
C	81	0.918935	0.43883	0
C	82	0.887943	0.424341	0
C	83	0.516685	0.031343	0
C	84	0.485539	0.016495	0
C	85	0.469042	-0.0145	0
C	86	-0.3641	0.320878	0
C	87	-0.35185	0.302217	0
C	88	-0.35916	0.371296	0
C	89	-0.39006	0.359196	0
C	90	-0.3847	0.407336	0
C	91	-0.35384	0.420394	0
C	92	-0.34113	0.402287	0
C	93	-0.39808	0.426278	0
C	94	-0.12675	0.440809	0
C	95	-0.4718	0.418129	0
C	96	-0.48628	0.434651	0
C	97	-0.46997	0.465818	0
C	98	-0.43883	0.480105	0
C	99	-0.42434	0.463602	0
C	100	-0.03134	0.485341	0
C	101	-0.0165	0.469044	0

C	102	0.014495	0.483537	0
N	1	0.377219	0.779245	0
N	2	0.426654	0.585128	0
N	3	-0.77925	-0.40203	0
N	4	-0.58513	-0.15848	0
N	5	0.402026	-0.37722	0
N	6	0.158475	-0.42665	0
N	7	-0.37722	-0.77925	0
N	8	-0.42665	-0.58513	0
N	9	0.779245	0.402026	0
N	10	0.585128	0.158475	0
N	11	-0.40203	0.377219	0
N	12	-0.15848	0.426654	0

Table S2. One-pot photo-biocatalytic cascade.



Entry[a]	α,β-Unsaturated ketone	Thiol	Yield (%)[b]	*ee* (%)[b]
1			83	>99
2			78	>99
3			N.D.	N.D.
4			N.D.	N.D.
5			N.D.	N.D.
6			N.D.	N.D.
7			N.D.	N.D.
8			N.D.	N.D.

[a] Conditions: thiol (1.0 mM), α,β-unsaturated ketone (1.0 mM) NAD$^+$ (1.0 mM), TEOA (10 w/V%), and photocatalysts (1.0 mg mL^{-1}) in 3.0 mL phosphate buffer under N_2 atmosphere at room temperature. [b] GC, GC-MS or HPLC analysis.