Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Co-based Metal-organic Framework for Photocatalytic Hydrogen Generation

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EXPERIMENTAL SECTION

Chemicals. Cobalt(II) chloride hexahydrate ($CoCl_2·6H_2O$, 95.0%) was purchased from Ajax Finechem, Australia. methanol (MeOH, ≥ 99.9%) and sodium hydroxide (NaOH) were procured by Sigma Aldrich, United states, respectively. Nickel(II) chloride hexahydrate ($NiCl_2·6H_2O$, 96.0%) was purchased from Daejung, Korea. 1,2,4-triazole (Tz, >99.0%), fluorescein (Fl**,** 98.0%), tris(2,2′-bipyridyl) dichlororuthenium(II) hexahydrate ($[Ru(bpy)_3]Cl_2·6\,H_2O$, 98.0%), and triethylamine (TEA, >99.0%) were procured from Tokyo Chemical Industry, Japan. All chemicals were used as received without further purification.

Material preparation. Co-Tz was synthesized at 180 °C under microwave irradiation at 300 W. 1,290.0 mg (5.4 mmol) $CoCl_2·6H_2O$ and 5.0 mL of DI water were mixed in 35 mL microwave vials. The solution of 800.0 mg (11.6 mmol) of 1,2,4-triazole and 5.0 mL of DI water was then added to the metal solution. The synthesis of mixed-metal Co/Ni-Tz was carried out following the abovementioned method except that two metal salts, 642.4 mg (2.70 mmol) of $CoCl_2·6H_2O$ and 641.8 mg (2.70 mmol) of $NiCl_2·6H_2O$ were used. The reactant mixtures were sealed and placed in a microwave oven (CEM Discovery). The mixtures were heated at 180 ˚C at 20 min in the microwave reactor. After cooling down to room temperature, the resulting products were collected by centrifugation and then washed with fresh DI water thrice to remove the remaining unreacted organic linkers. Then, the samples were dried under vacuum overnight at 40 ˚C

Material Characterization. The crystal phase and the crystallinity of synthesized samples were examined by using powder XRD analysis (Cu Kα radiation (λ = 1.54 Å), Bruker, New D8). The optical property and energy level were carried out by Ultraviolet-visible spectrometer (UV/Vis/NIR Lambda 1050 instrument, PerkinElmer, USA) and ultraviolet photoelectron spectrometer (UPS, RIKEN KEIKI, AC-2, USA). The morphology and particle size were analyzed using a field-emission scanning electron microscope (FE-SEM, JEOL, JSM-7610F) and a transmission electron microscope (TEM, JEOL, JEMARM200F, operated at 200 kV). For SEM sample preparation, the powders were attached on carbon tape and coated with Pt (20 sec sputtering at 10 mA under vacuum) to increase the electrical conductivity. Elemental distributions were derived by a scanning transmission electron microscopic (STEM) mode equipped with an energy dispersive X-ray spectroscopy (EDS) and a scanning electron microscope with an energy dispersive X-ray spectrometer (SEM/EDS). Agilent Technology 700 Series inductively coupled plasma optical emission spectrometer (ICP-OES) was used to analyze the composition of metal ions. Additionally, X-ray absorption near edge structure (XANES) analyses of Co K-edge and Ni K-edge were performed at beamline BL1.1W: Multiple X-ray Techniques Beamline, Synchrotron Light Research Institute, Thailand. The measurement was conducted at ambient temperature and pressure by simultaneously measuring the samples together with the Co and Ni foils as standard references for an in-line alignment of the energy shift during the synchrotron-operating time. The obtained data were analyzed using ATHENA software.[1]

Photocatalysis. 17 mg of FI or 32 mg of $[Ru(bpy)_3]Cl_2·6\ H_2O$, 3.75 mL of TEA, and 25 mL of DI water (H_2O) were homogeneously mixed in the closed system of 50 mL round-bottom flask. Then 10 mg of Co-Tz or Co/Ni-Tz was added in the mixture. Stopper and paraffin were used to close the flask. The solution was further degassed by N_2 gas for 2 h. After that, the prepared one was irradiated under solar simulator 100 W Xe lamp (AM 1.5G) at 4 cm. The sampling H_2 was performed at 0, 0.5, 1, 2, 3, and 4 hours by gas chromatography (SHIMAZU GC-2010 Plus) with a barrier discharge ionization detector (BID) and a SH-Rt-5 Å molecular column (⌀ 0.53 mm x 30 m) analyzed under helium.

Stability test. To mimic the solvent system of the photocatalytic performance test, an aqueous solution pH=9 was prepared by dissolving NaOH in DI water. Afterward, 20 mg of Co-Tz was soaked in 10 ml of the solution under stirring for 1 day at room temperature. The resulting product and supernatant were separated by centrifugation. The collected Co-Tz powder was washed with copious amount of DI water to remove the remaining NaOH. Then, the sample was dried under vacuum overnight at 40 ˚C prior to PXRD analysis. To probe the possible leaching of Co^{2+} ions from Co-Tz, the obtained supernatant was analyzed using UV-Vis spectroscopy. Noted that the standard solution of Co^{2+} ion was prepared by dissolving $CoCl_2 \cdot 6H_2O$ in aqueous NaOH solution (pH=9).

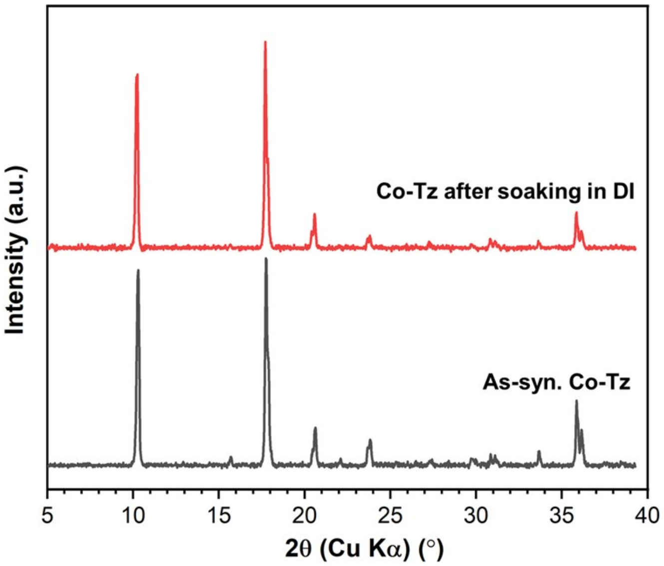

Figure S1. PXRD pattern of Co-Tz after soaking in H_2O for 1 day as compared to that of as-synthesized one.

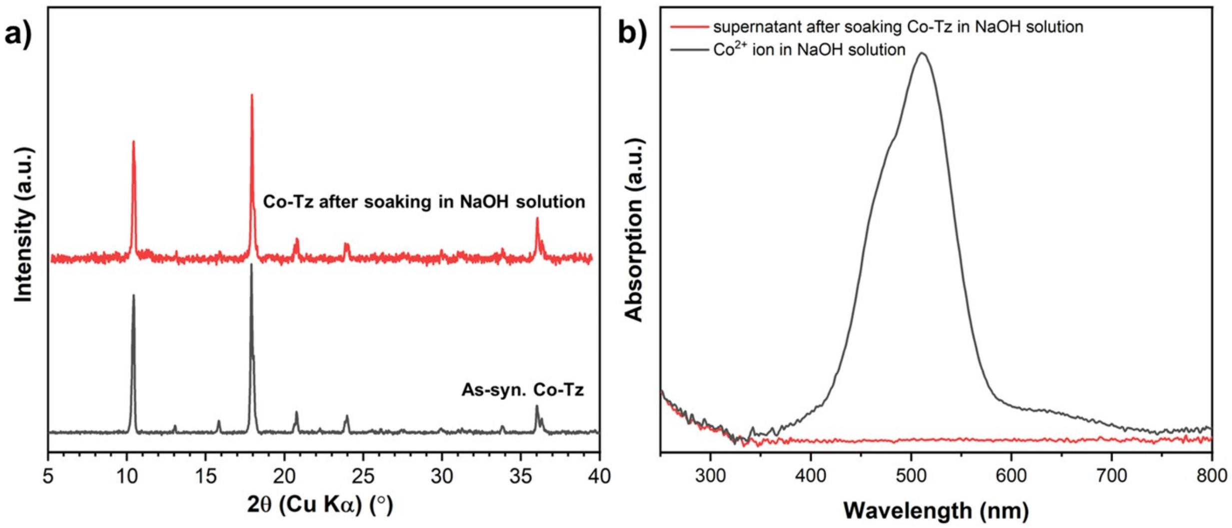

Figure S2. (a) PXRD patterns of Co-Tz after soaking in NaOH solution (aq.) (pH = 9) for 1 day and the as-synthesized one. (b) UV-Vis absorption spectra of the supernatant after soaking Co-Tz in aqueous NaOH solution (pH=9) for 1 day as compared to the standard solution of Co^{2+} ion.

: PXRD results of the Co-Tz immersed in NaOH pH=9 demonstrated the maintained crystalline nature of the framework. This well agreed with the indiscernible amount of Co^{2+} ion leaching into the supernatant probed by UV-Vis spectroscopy compared to the standard solution of Co^{2+} ion in NaOH solution (pH = 9) (Figure S2(b)). The results strongly affirm the superior stability of material in basic solution.

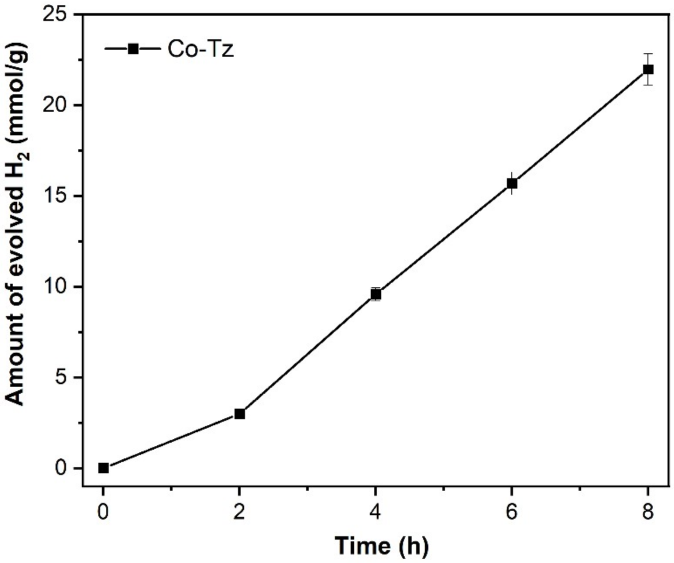

Figure S3. Photocatalytic H_2 evolution performance from Co-Tz up to 8 h.

: A constant increase of produced hydrogen was still obtained without losing its reactivity up to 8 h, highlighting the superior catalytic stability of Co-Tz towards the photocatalytic hydrogen production.

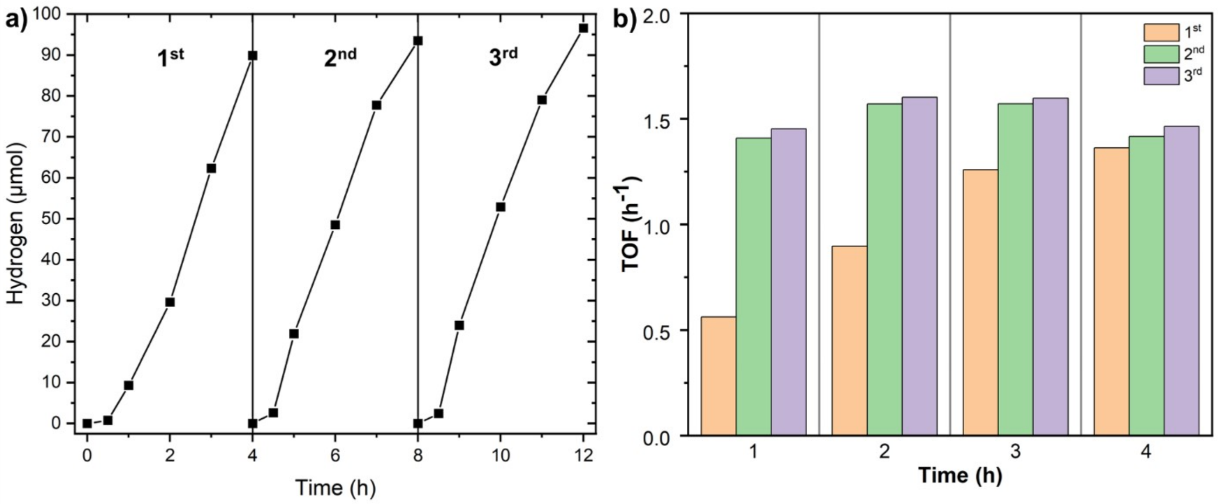

Figure S4. (a) Photocatalytic H_2 evolution performance and (b) TOF plot of recycling tests on Co-Tz with re-addition of 17 mg Fl and 3.75 ml TEA in 25 ml H_2O.

: The catalytic performances of the reused Co-Tz for 2nd and 3rd runs showed the only a negligible increase in accumulated amount of H_2 at 4 h as compared to that of the 1st run. Noting that H_2 production at the initial stage up to 3 h for the reused runs was improved. Suggested by the catalyst activation process in our previous study,[4] the enhanced catalytic performance at initial stage of the successive runs can be attributed by the complete catalyst activation after the 1st run by the de-coordination of Cl^- ion and photocatalytic activation. It was clearly discernible for the turnover frequency (TOF) of the fresh Co-Tz sample that gradually increased for the initial stage up to 4 h while the activated one produced the similar TOF since the initial stage for the 2nd and 3rd runs (Figure S4 (b)). The same trend was also observed while the reaction was prolonged up to 8 h as shown in Figure S3.

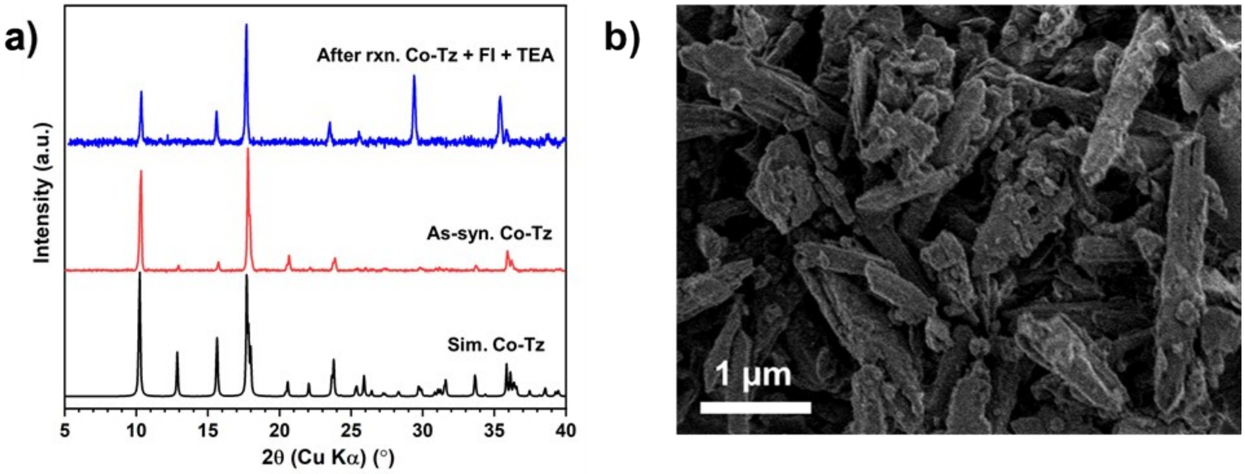

Figure S5. (a) PXRD patterns and (b) FE-SEM images of Co-Tz after reaction (10 mg catalyst, 17 mg FI, 3.75 mL TEA, 25 mL H_2O).

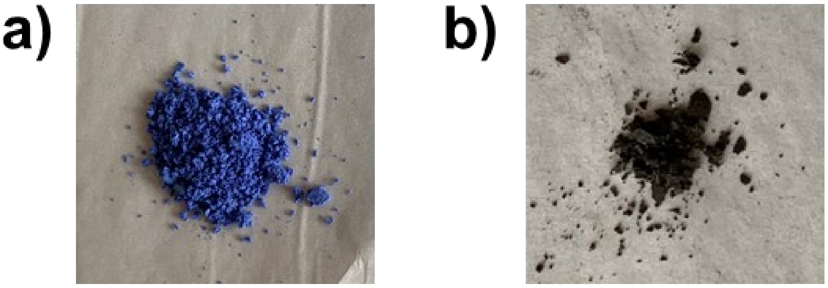

Figure S6. Photographs of (a) as-synthesized Co-Tz and (b) the sample after the reaction (10 mg catalyst, 17 mg FI, 3.75 mL TEA, 25 mL H_2O).

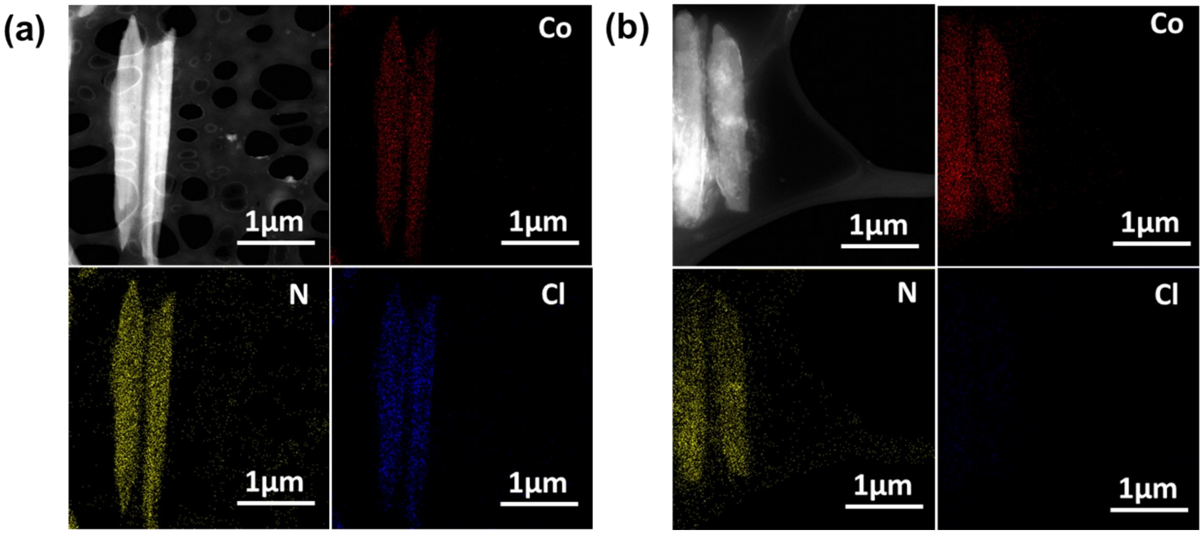

Figure S7. STEM/EDS elemental maps of Co-Tz (a) before and (b) after reaction (10 mg catalyst, 17 mg FI, 3.75 mL TEA, 25 mL H_2O).

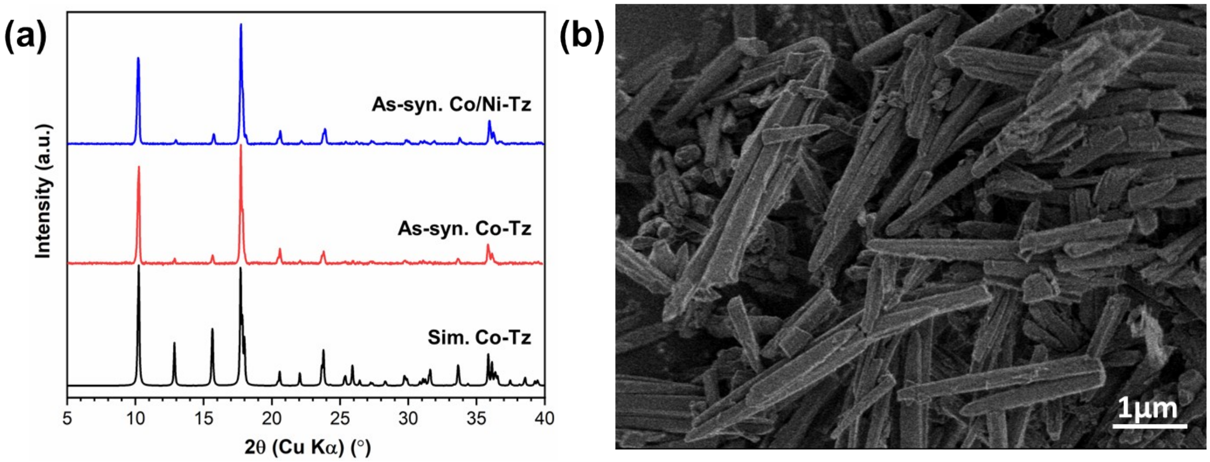

Figure S8. (a) PXRD patterns of as-synthesized Co-Tz and Co/Ni-Tz. (b) SEM image of Co/Ni-Tz.

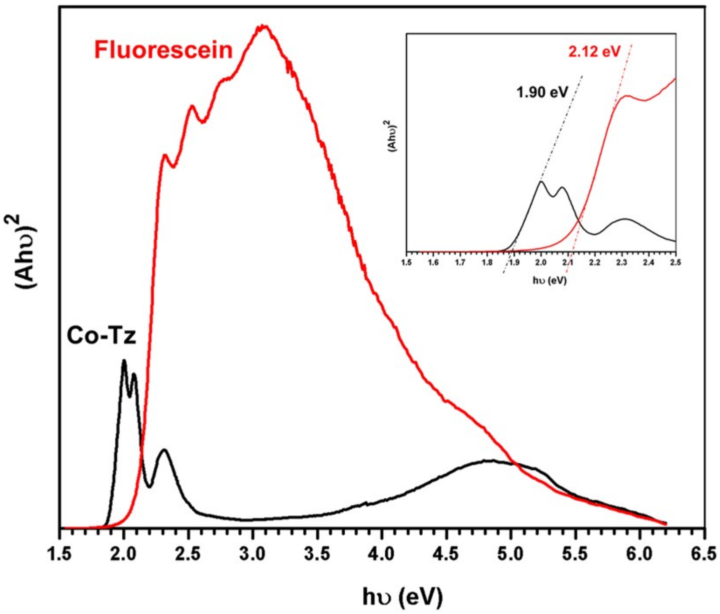

Figure S9. Tauc's plot for band gap energy determination of Co-Tz and fluorescein.

Table S1. Hydrogen production at 4h in various conditions.

Catalyst	Photosensitizer	Sacrificial agents	H_2(mmol/g) at 4h
Co-Tz (10 mg)	Fl (8.5 mg)	TEA (3.75 ml)	6.27
Co-Tz (10 mg)	Fl (34.0 mg)	TEA (3.75 ml)	4.35
Co-Tz (10 mg)	Fl (17.0 mg)	TEA (1.25 ml)	6.94
Co-Tz (5 mg)	Fl (17.0 mg)	TEA (3.75 ml)	3.98

Table S2. SEM/EDS elemental analysis of Co-Tz before and after catalytic reaction.

Sample	Resulting content (mol %)	
	Co	Cl
As-synthesized Co-Tz	73.00	27.00
Co-Tz after reaction	99.91	0.09

Table S3. SEM/EDS and ICP elemental analysis of as-synthesized Co/Ni-Tz.

Technique	Initial content (mol %)		Resulting content (mol %)	
	Co	Ni	Co	Ni
SEM/EDS	50.0	50.0	50.8	49.2
ICP			50.3	49.7

Table S4. Energy gaps and energy levels for Co-Tz, Co/Ni-Tz, and fluorescein.

Sample	Energy gap (eV)	HOMO level (eV)	LUMO level (eV)
Co-Tz	1.90	6.20	4.30
Co/Ni-Tz	1.89	6.20	4.31
Fluorescein	2.12	5.90	3.78

Table S5. Comparison of Co-Tz with Co- based MOF for photocatalysis reported in the literatures.

Sample	Photosensitizer	Solution system	Sacrificial agent	Light source	Turnover frequency (TOF)/h^{-1}	Reference
Co-Tz	Fluorescein	H_2O	TEA	100 W Xe lamp (AM 1.5G)	1.4[b]	This work
Co-ZIF-67	RuN_3[a]	CH_3CN and H_2O	TEOA	blue LED (405nm)	0.5	2
Co@MOF	NH_2-MIL-125	CH_3CN and H_2O	TEA	500 W Hg/Xe lamp (>408 nm)	0.8	3

[a](cis-diisothiocyanato-bis (2,2'-bipyridyl-4,4'-dicarboxylic acid) ruthenium(II)).

[b] The TOF calculation was based on the amount of catalyst in the reaction.

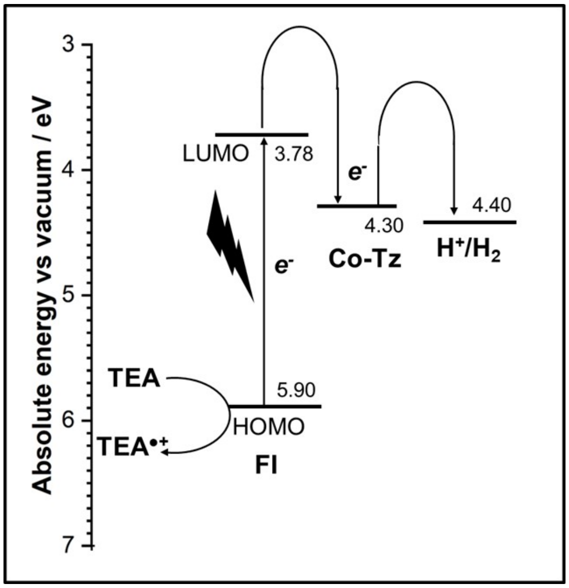

Figure S10. Schematic diagram of redox potentials of components of Co-Tz. TEA = Trimethylamine, FI = Fluorescein.

References.

1. B. Ravel, M. Newville, *J. Synchrotron Radiat.* 2005, **12**, 537-541.
2. S. Yang, B. Pattengale, E. L. Kovrigin, J. Huang, *ACS Energy Lett.*, 2017, **2**, 75-80.

3. M. A. Nasalevich, R. Becker, E. V. Ramos-Fernandez, S. Castellanos, S. L. Veber, M. V. Fedin, F. Kapteijn, J. N. H. Reek, J. I. van der Vlugt, J. Gascon, *Energy Environ. Sci.*, 2015, **8**, 364-375.

4. K. Adpakpang, L. Pukdeejorhor, L. Ngamwongwan, S. Suthirakun, S. Impeng, S. Wannapaiboon, P. Chakthranont, K. Faungnawakij, S. Bureekaew, *Chem. Commun*, 2022, DOI : 10.1039/D2CC02526D.