Two new imine-linked covalent organic frameworks with flexibility, porosity, crystallinity, for high iodine uptake

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Materials

N-butanol (n-BuOH), ortho dichlorobenzene (o-DCB), N, N-dimethylformamide (DMF), acetone, tetrahydrofuran, and other chemicals were purchased from TCI and J&K Scientific company.

Methods

The infrared spectra were recorded from 600 to 3500 cm-1 on an IRTracer-100 spectrometer. Powder X-ray diffraction data were performed on a XRD (Empyrean DY01610) diffractometer by depositing powder on glass substrate, from 2θ = 3.0° to 35° with 0.02°. Field emission scanning electron microscopy and energy dispersive spectroscopy for elemental mapping were recorded on S-4800 and JEOL JSM-6700 microscope. Thermogravimetric analysis (TGA) was performed on a DTG-60 thermal analyzer with the heating at a rate of 10 °C min-1 from room temperature to 800 °C under nitrogen atmosphere. The sorption isotherm for N2 were measured at 77 K with a JW-BK 132F analyzer. The transmission electron microscopy (TEM) images were obtained on JEM-2100 transmission electron microscopy. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 XPS system.

Synthesis of NI-COF-1

The 4,4',4''-((1,3,5-triazine-2,4,6-triyl)tris(oxy))trianiline (40.2, 0.10 mmol), 1,3,5-triformylbenzene (16.2 mg, 0.1 mmol), o-DCB (0.4 mL), n-BuOH (1.2 mL), and acetic acid (6 M, 0.2 mL) were added into a Pyrex tube (10 mL). The tube was then flash frozen at 77 K and degassed by three freeze-pump-thaw cycles. The tube was sealed off and then heated at 120 °C for 3 d. After cooling down to room temperature, the sample was filtered and washed by DMF, and acetone. The sample was Soxhleted by THF for 12 h and dried in vacuum at 60 °C for 12 h to a white-yellow powder (Yield: 88%).

Synthesis of NI-COF-2

The 4,4',4''-((1,3,5-triazine-2,4,6-triyl)tris(oxy))trianiline. (40.2, 0.10 mmol), 1,3,5-tris(p-formylphenyl)benzene (39.0 mg, 0.10 mmol), o-DCB (0.6 mL), n-BuOH (1.0 mL), and acetic acid (6 M, 0.2 mL) were added into a Pyrex tube (10 mL). The tube was then flash frozen at 77 K and degassed by three freeze-pump-thaw cycles. The tube was sealed off and then heated at 120 °C for 3 d. After cooling down to room temperature, the sample was filtered and washed by DMF, and acetone. The sample was Soxhleted by THF for 12 h and dried in vacuum at 60 °C for 12 h to a white-yellow powder (Yield: 90%).

Iodine vapor uptake experiment

Three open vials (5 mL) with COFs samples were placed in a large vial (70 mL) containing iodine, which was s sealed and kept at 350 K. The first vail kept COFs samples (10 mg) and the second tube was selected to accommodate excess iodine. The vials were cooled down to room temperature by the selected time. The small vial containing the COFs samples and blank

vial were recorded. One vial was used only once. Each experiment was repeated for three times and the final results was collected via the average value. The COFs@iodine samples were added into EtOH (30 mL) and stirred for 3 h under room temperature. The COFs samples were collected by filtration and washed with EtOH for several times. The operation was repeated for five times until there was colourless solution. The regenerated COFs samples were collected and dried under vacuum for the next experiment.

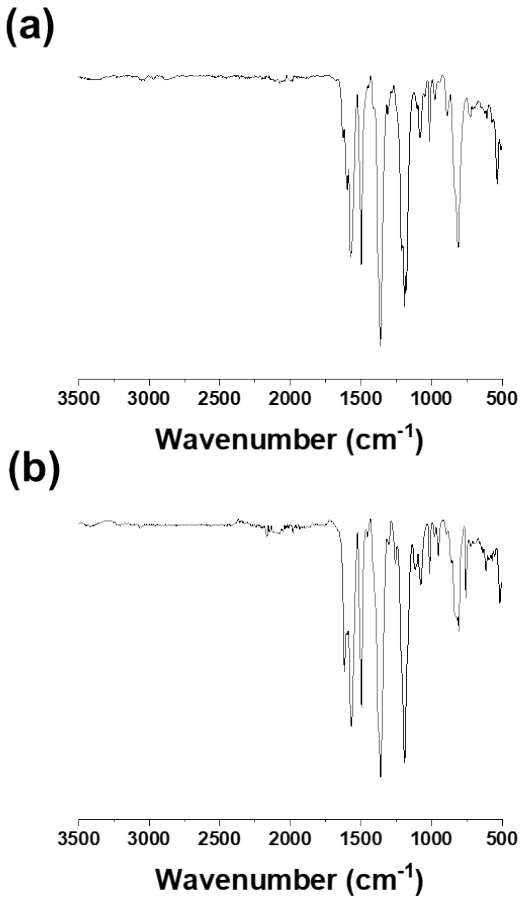

Fig. S1. FT IR spectra of (a) NI-COF-1 and (b) NI-COF-2.

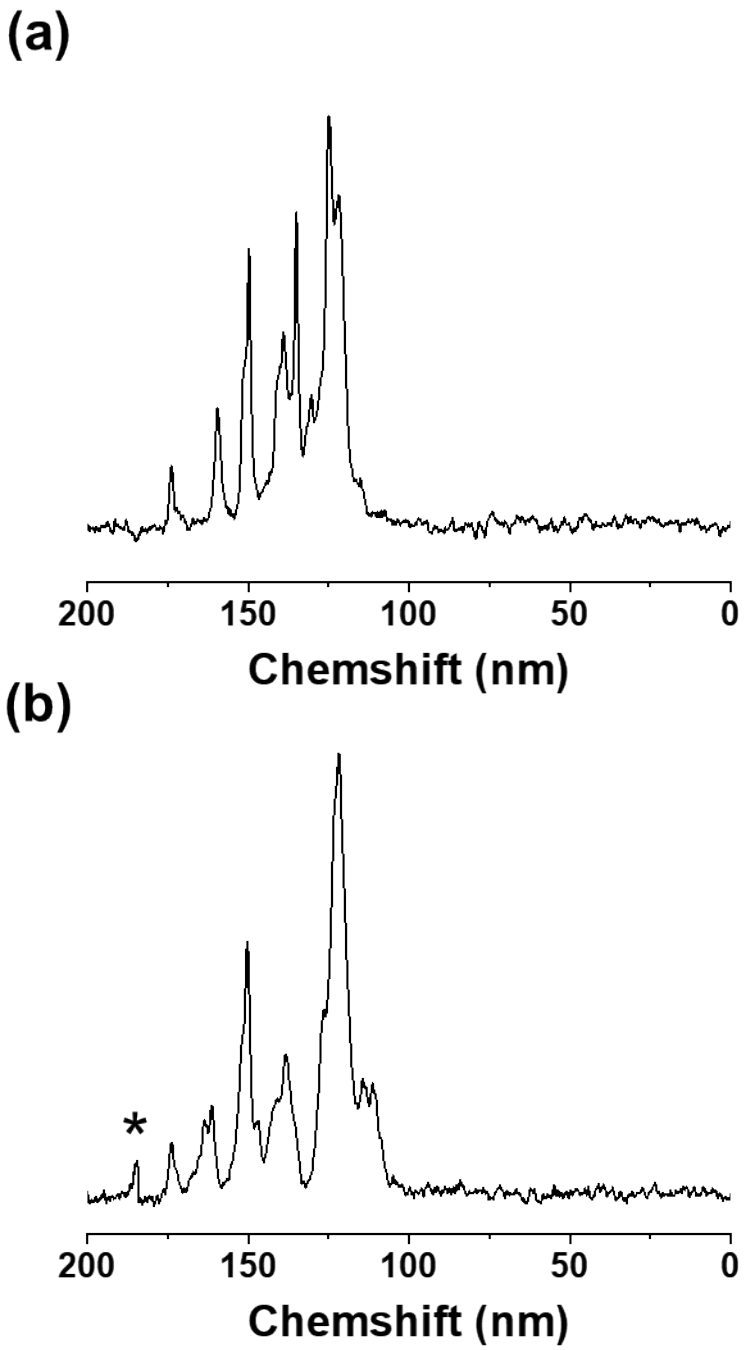

Fig. S2. ^{13} CNMR spectra of a) NI-COF-1 and (b) NI-COF-2.

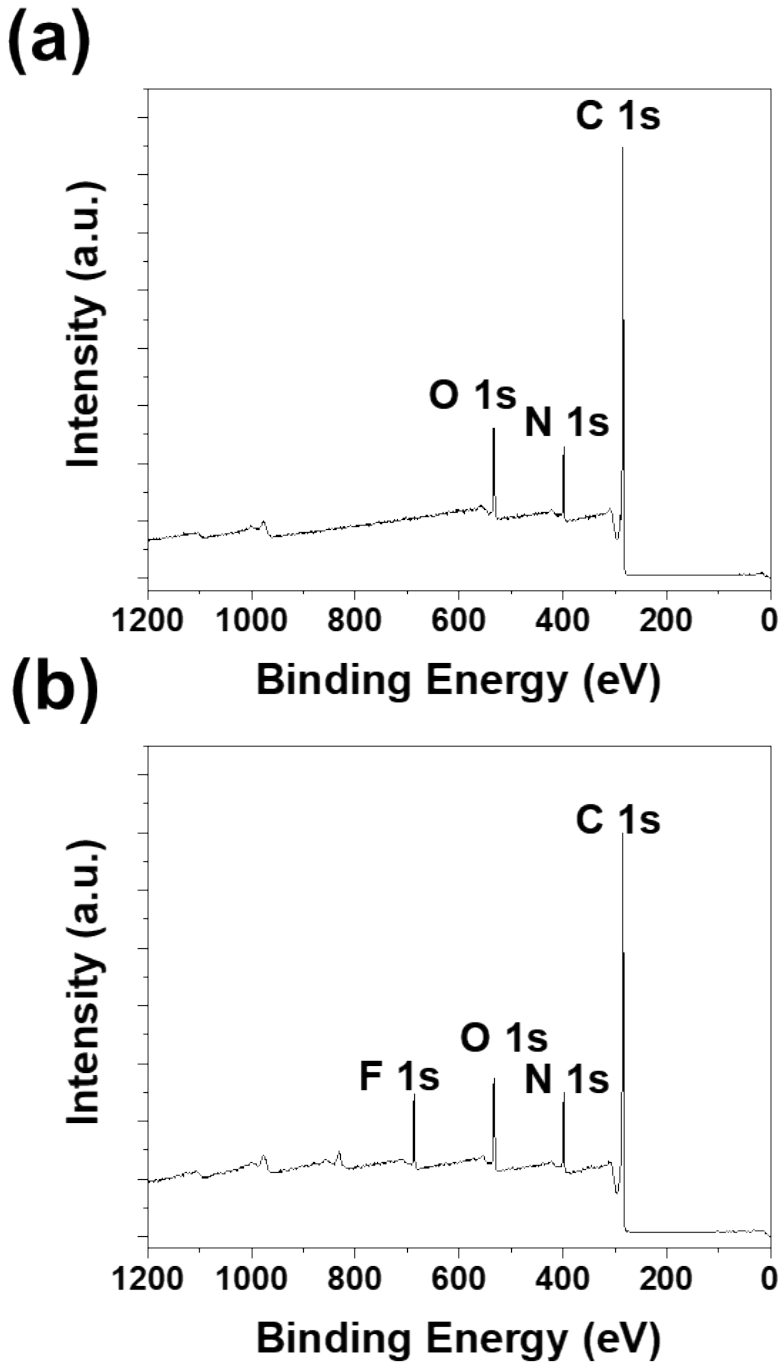

Fig. S3. XPS spectra of (a) NI-COF-1 and (b) NI-COF-2.

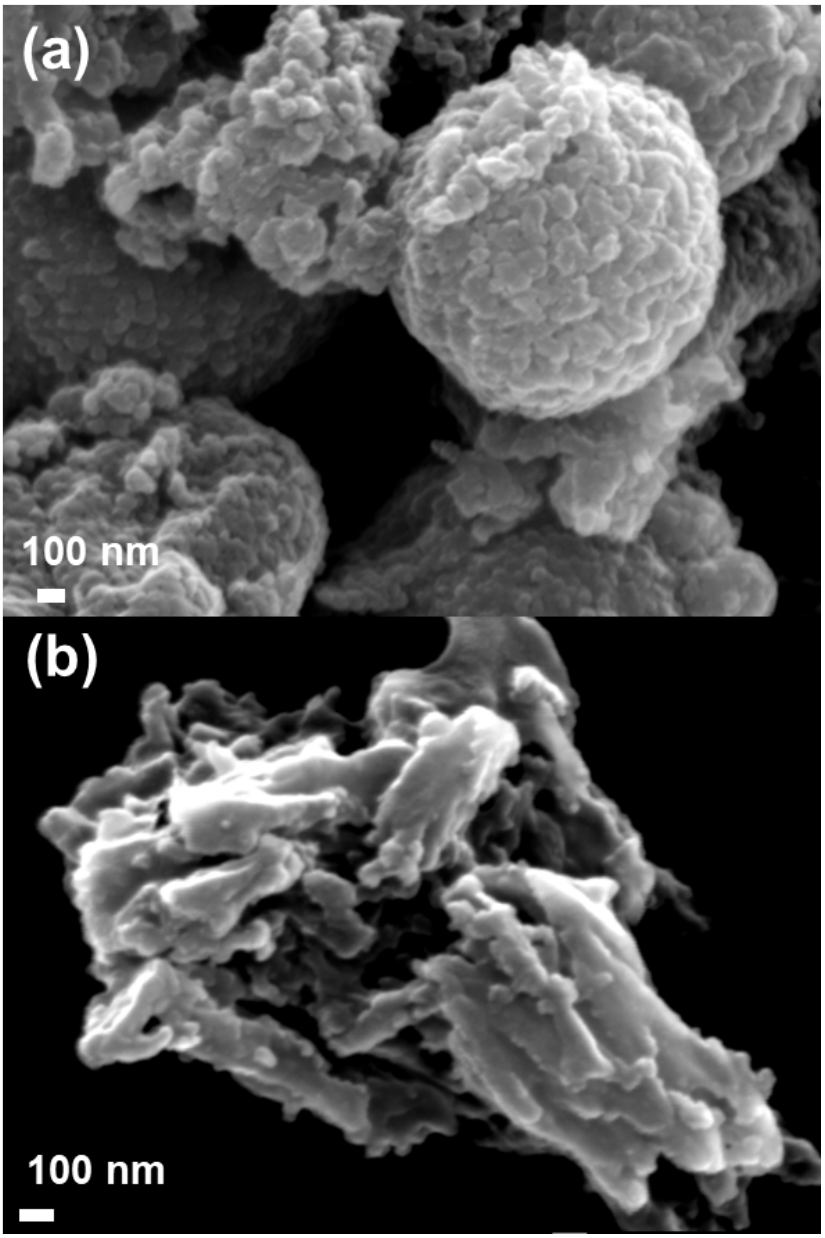

Fig. S4. FE SEM images of (a) NI-COF-1 and (b) NI-COF-2.

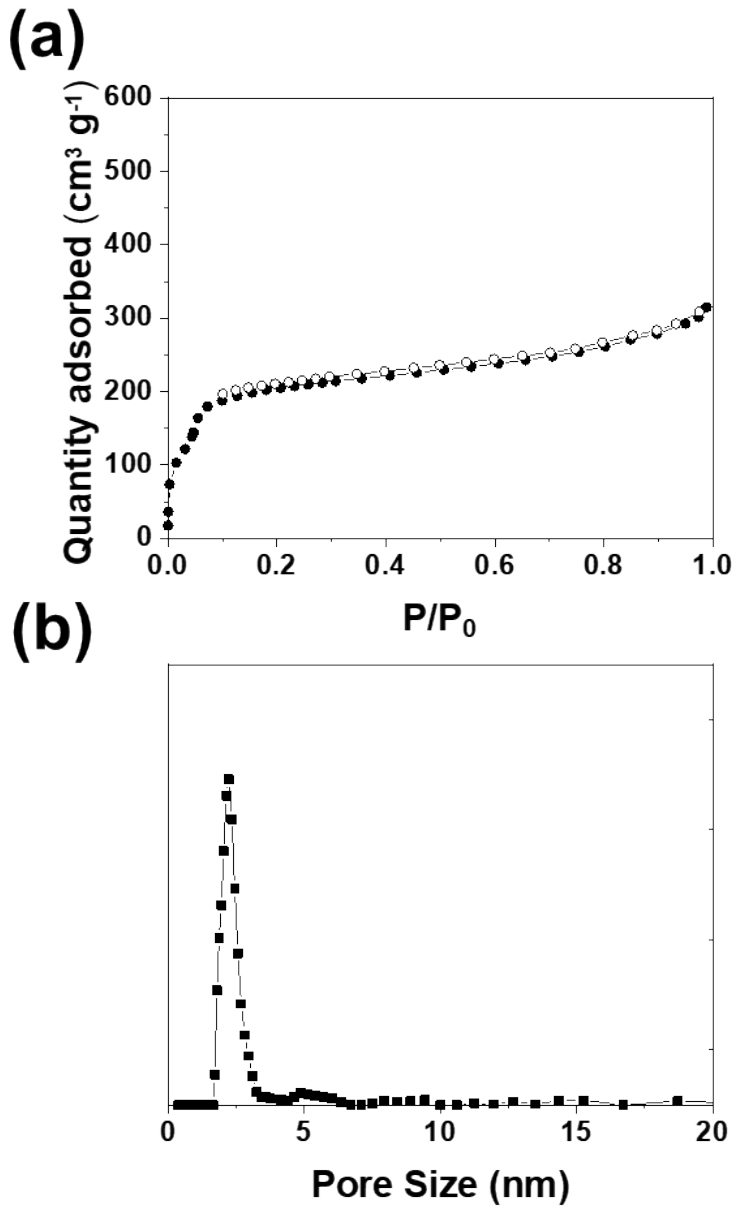

Fig. S5. Nitrogen adsorption-desorption isotherms of (a) NI-COF-1 measured at 77K (●: adsorption, ○: desorption). Pore size distribution of (b) NI-COF-1.

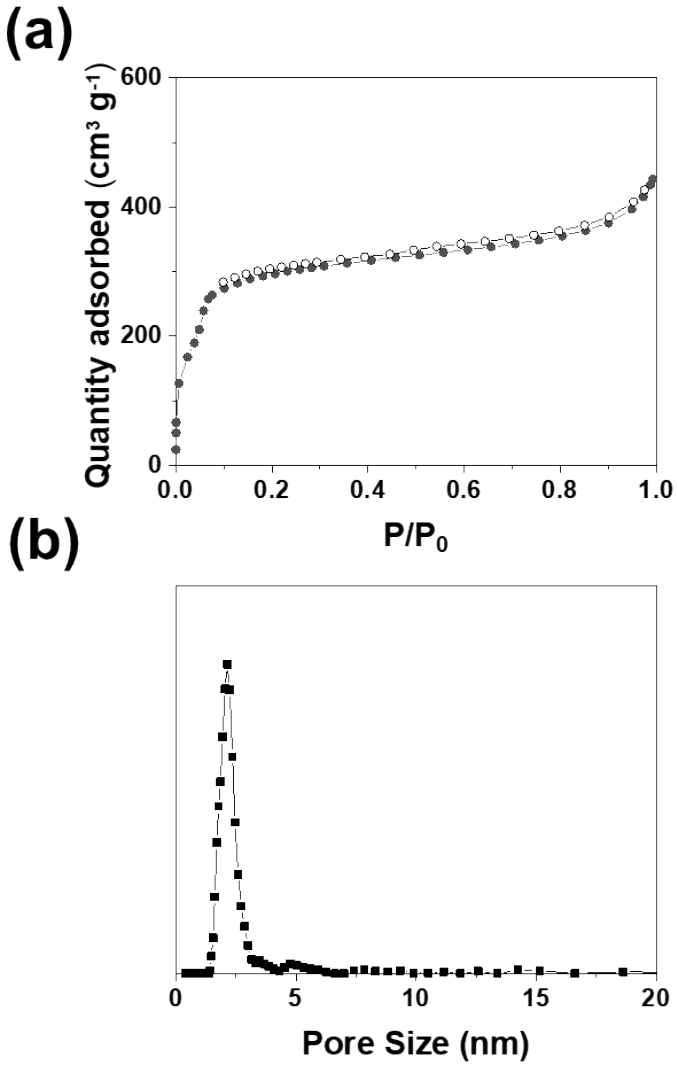

Fig. S6. Nitrogen adsorption-desorption isotherms of (a) NI-COF-2 measured at 77K (●: adsorption, ○: desorption). Pore size distribution of (b) NI-COF-2

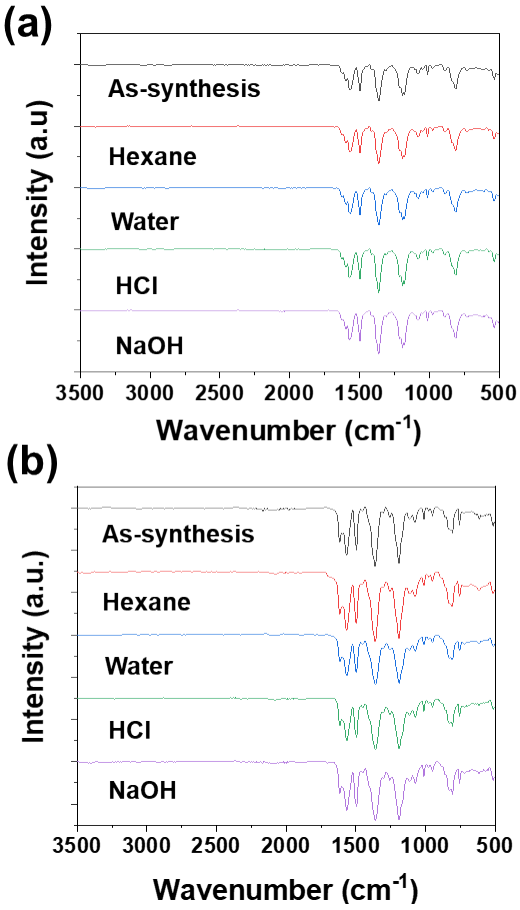

Fig. S7. FT IR spectra of (a) NI-COF-1 and (b) NI-COF-2 under different conditions.

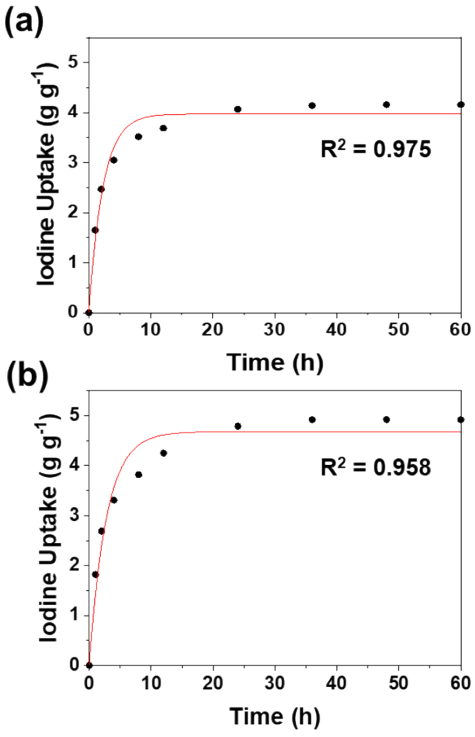

Fig. S8. The pseudo-first-order kinetic model of (a) NI-COF-1 and (b) NI-COF-2.

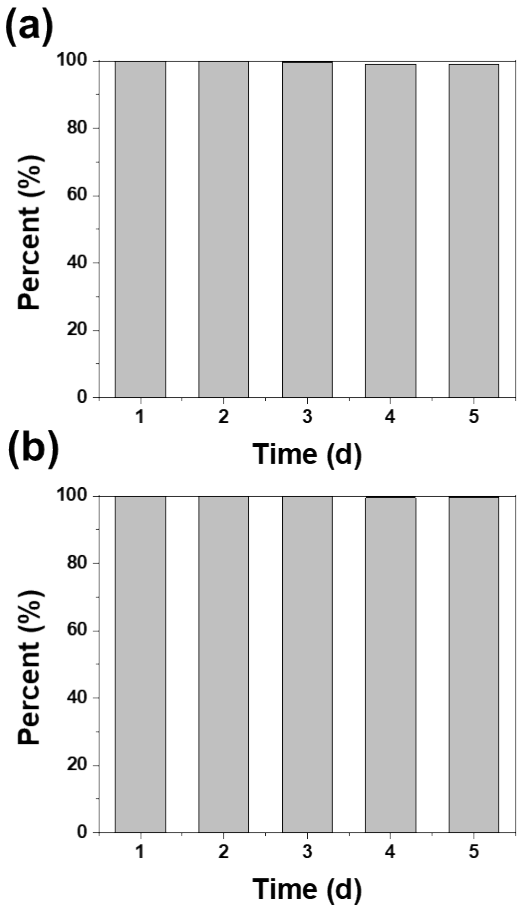

Fig. S9. Retention ability of (c) NI-COF-1 and (d) NI-COF-2.

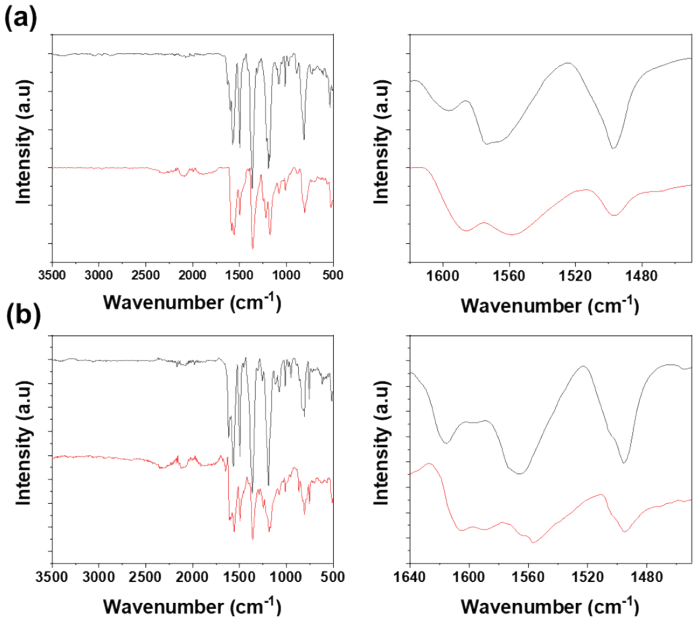

Fig. S10. FT IR spectra of (a) NI-COF-1 (black), NI-COF-1@iodine (red) and (b) NI-COF-2 (black), NI-COF-1@iodine (red).

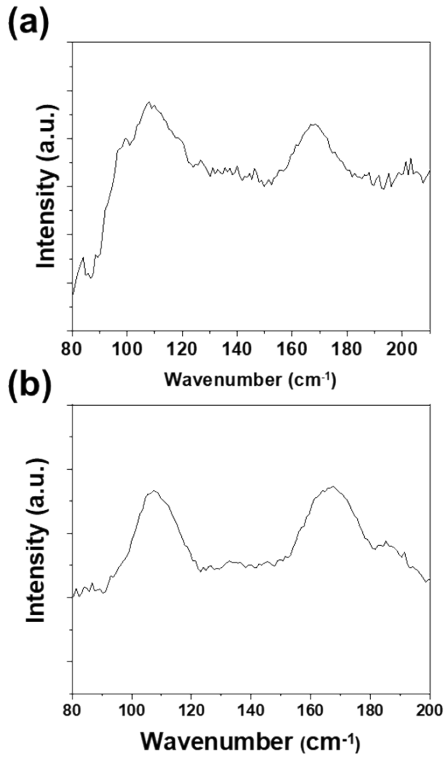

Fig. S11. Raman spectra of NI-COF-2@iodine.

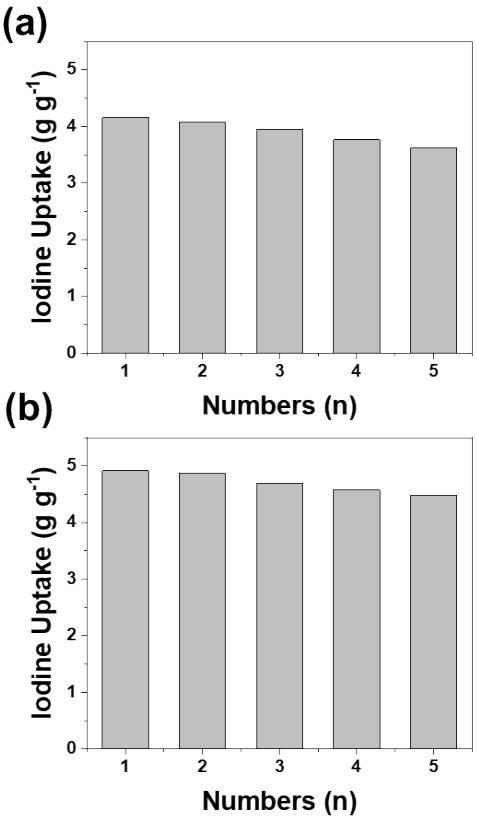

Fig. S12. Recycle performances of (a) NI-COF-1 and (b) NI-COF-2.

Table S1. Elemental analysis of NI-COFs.

		C (%)	H (%)	N (%)
NI-COF-1	Theoretical	78.03	4.09	11.38
	Observed	77.85	4.67	11.42
NI-COF-2	Theoretical	72.72	3.43	10.60
	Observed	72.35	3.98	9.98