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Supplementary information
for
Light induced nitric oxide release from physiologically stable porous coordination polymers

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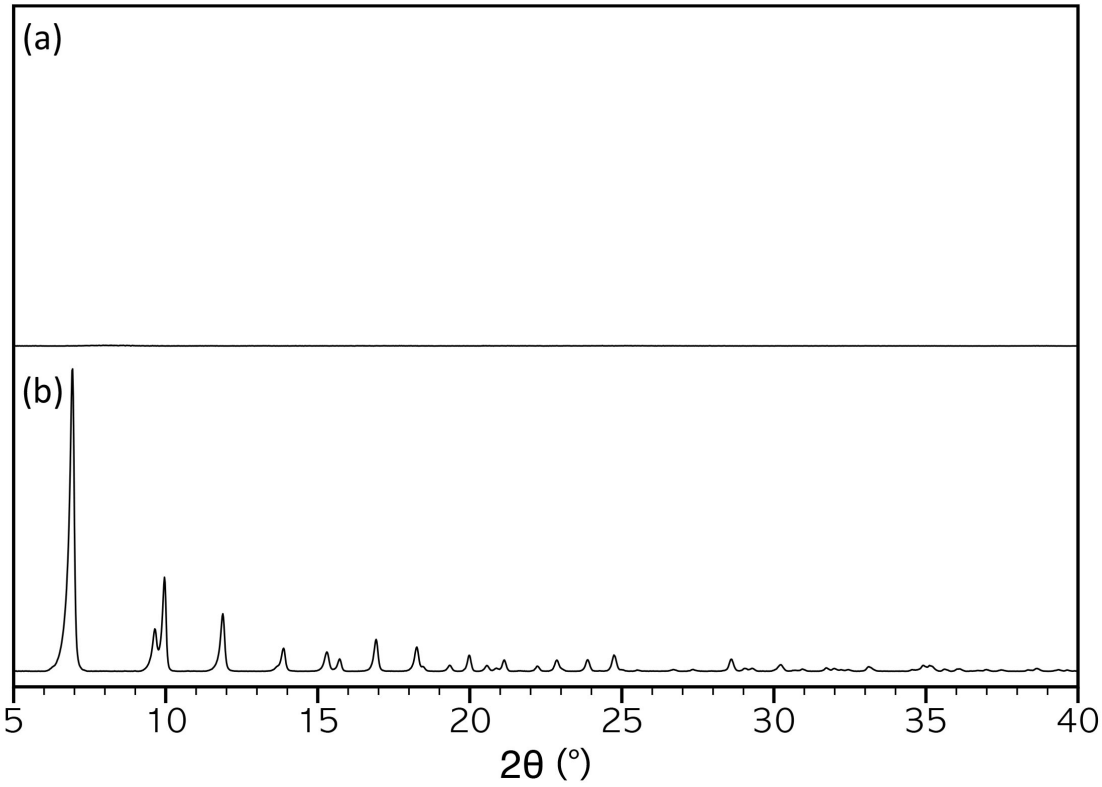

Fig. S1 PXRD patterns of powders, which are synthesized with metal precusor and MeNNO-H_2bdc. (a) Amorphous powder was obtained with $Ti(iOPr)_4$ and (b) isostructural framework of CAU-1 was obtained with $AlCl_3 \cdot 6H_2O$

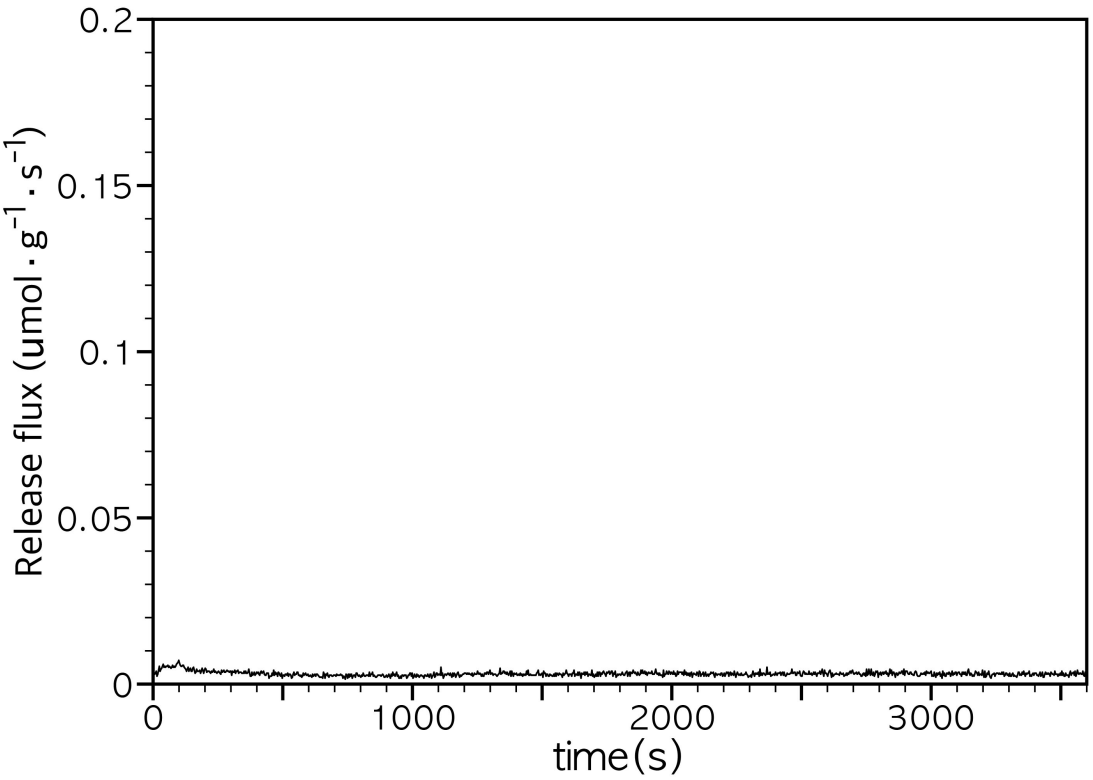

Fig. S2 The result of NO releasing experiment using the powder, which was synthesized with $AlCl_3 \cdot 6H_2O$ and MeNNO-H_2bdc. Only background level of NO concentration was detected under the UV irradiation.

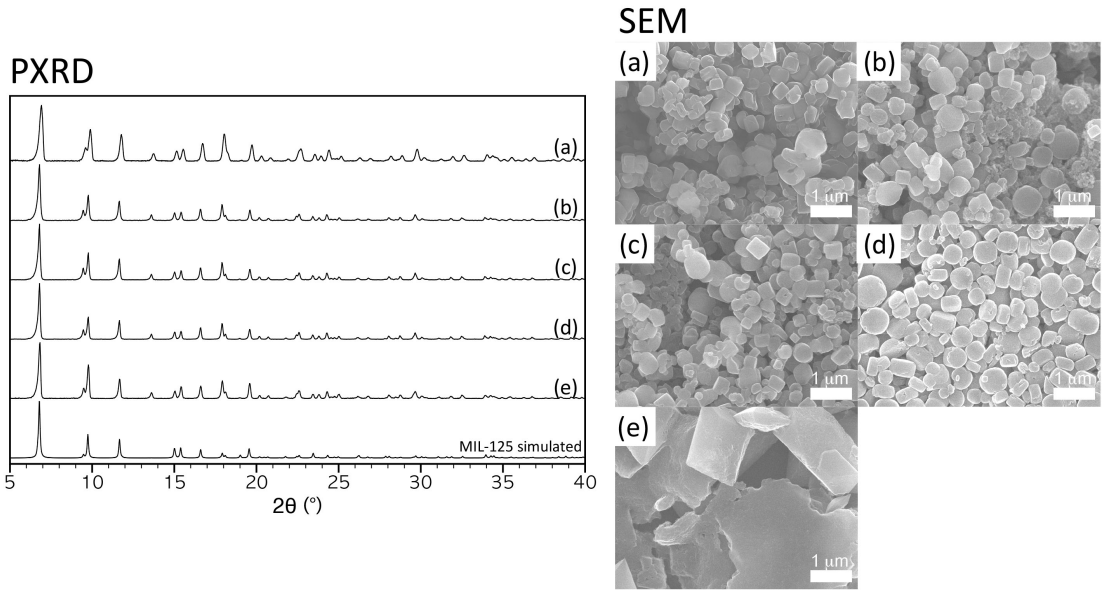

Fig. S3 PXRD patterns and SEM images of preNOF-11, which are synthesized with (a) 0 equiv., (b) 5 equiv., (c) 10 equiv., (d) 20 equiv. and (e) 40 equiv. of modulator (acetic acid).

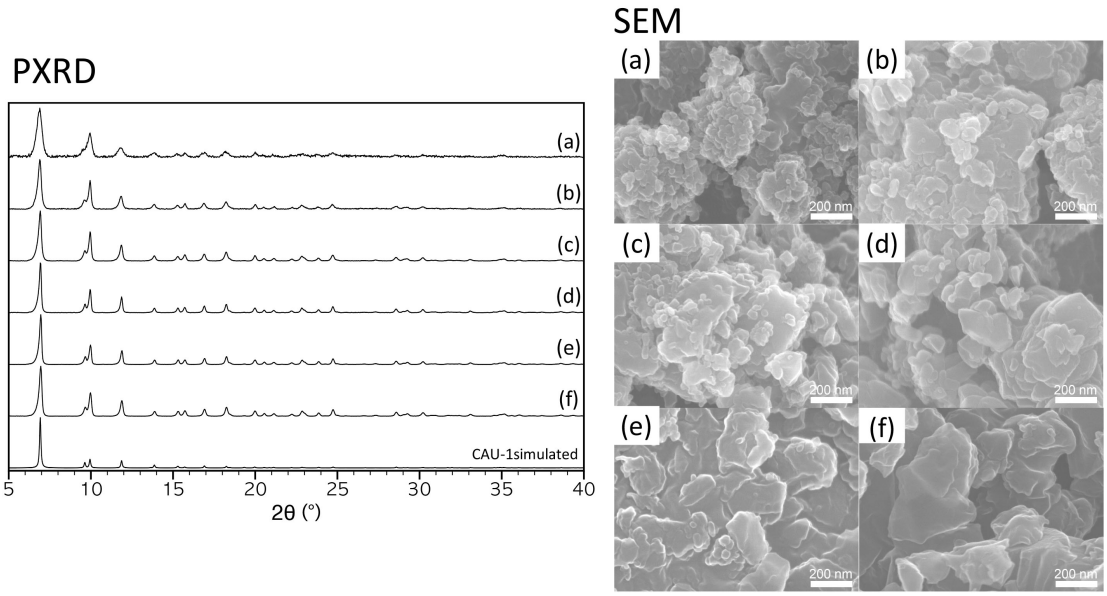

Fig. S4 PXRD patterns and SEM images of preNOF-12, which are synthesized with (a) 0 equiv., (b) 10 equiv., (c) 20 equiv., (d) 40 equiv., (e) 60 equiv. and (f) 80 equiv. of modulator (acetic acid).

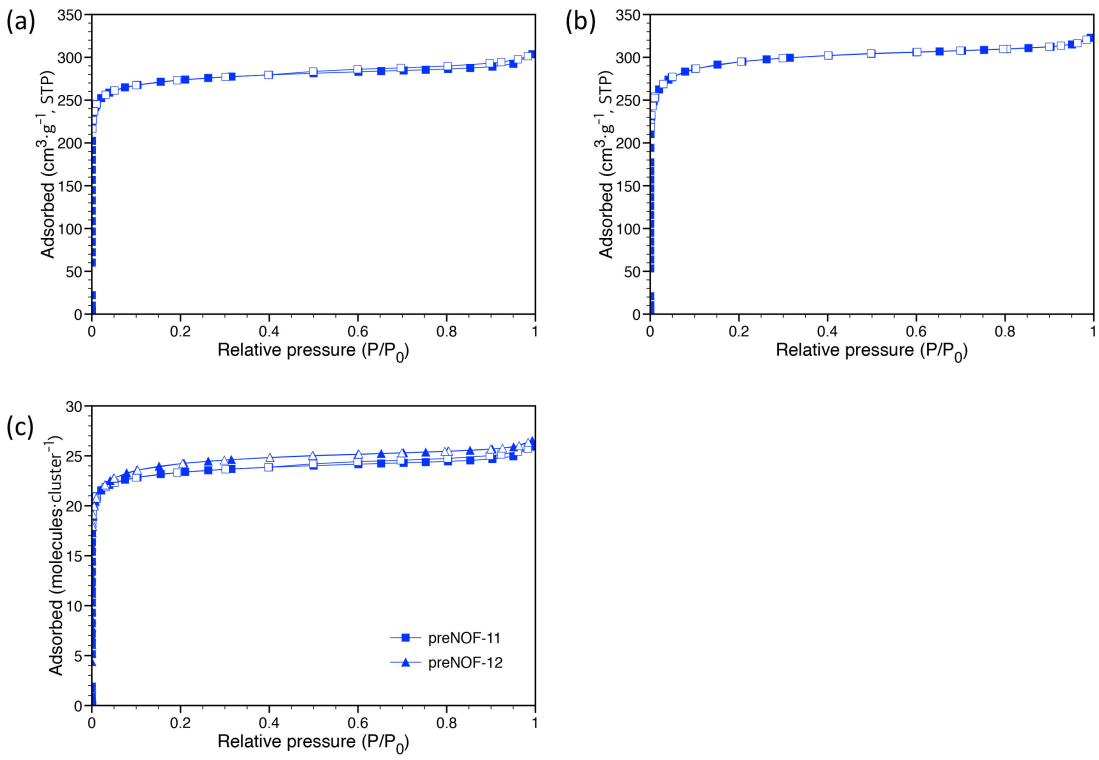

Fig. S5 Nitrogen gas adsorption isotherms of (a) preNOF-11 and (b) preNOF-12 at 77K. (c) Adsorbed amount is normalized to molecules·cluster^{-1} (cluster : $[Ti_8O_8(OH)_4(MeNH\text{-}bdc)_6]$ for preNOF-11 and $[Al_8(OMe)_8(OH)_4(MeNH\text{-}bdc)_6]$ for preNOF-12).

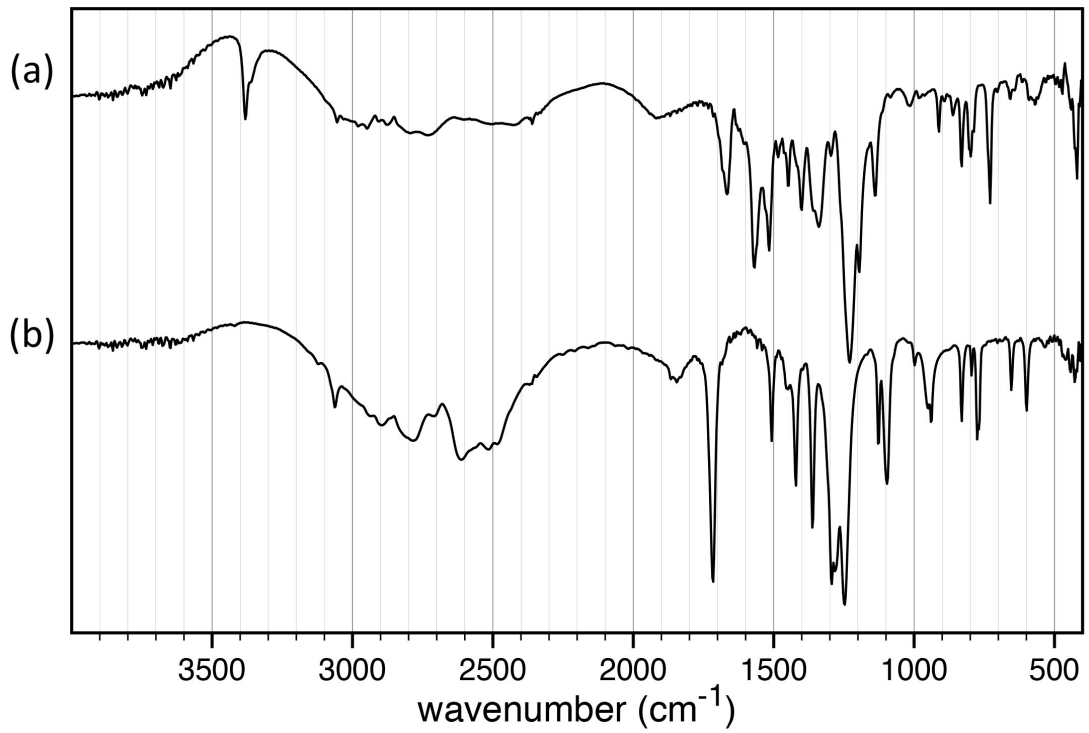

Fig. S6 IR spectra of (a) MeNH-H_2bdc and (b) MeNNO-H_2bdc. The novel adsorption band at 2190 cm^{-1}, which was observed in spectra of NOFs was not observed from spectra of MeNNO-H_2bdc.

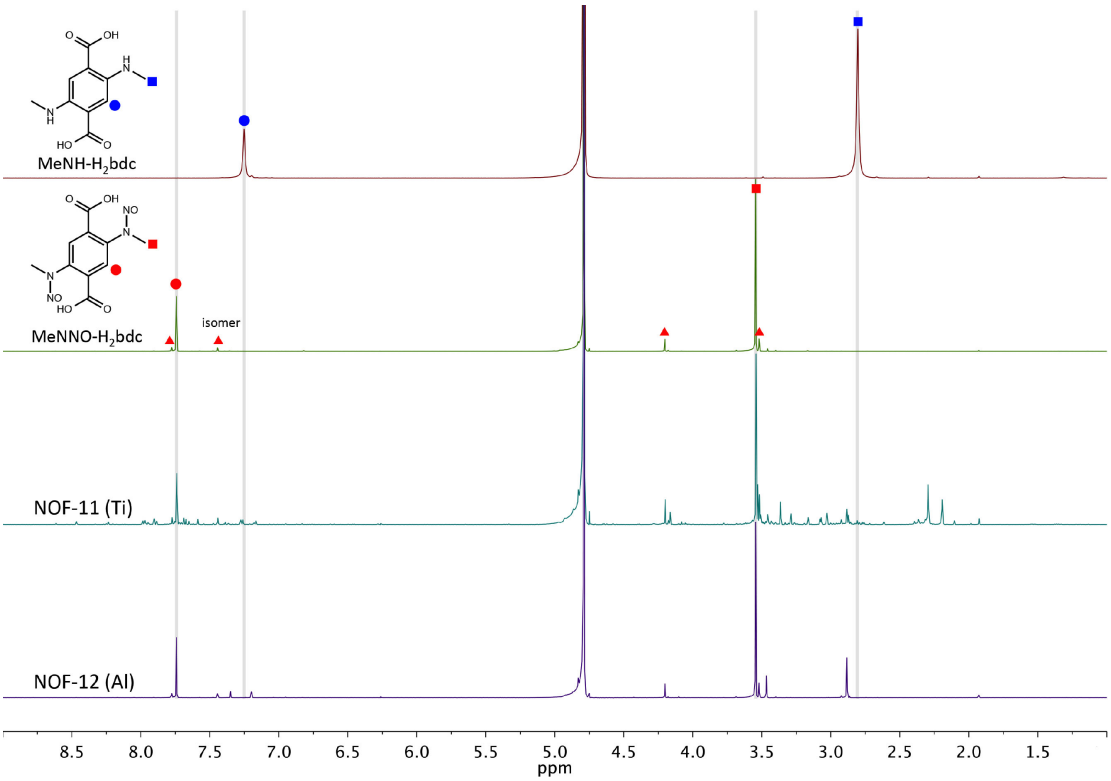

Fig. S7 NMR spectra of MeNH-H_2bdc, MeNNO-H_2bdc, digested NOF-11 and digested NOF-12.

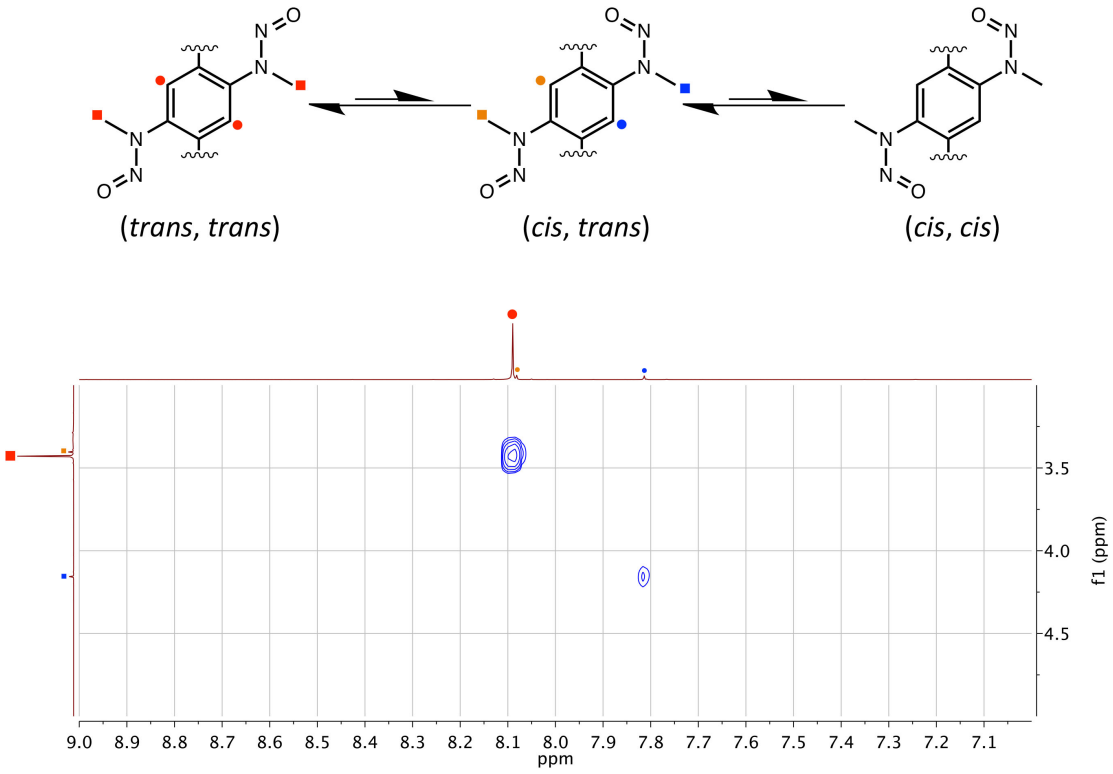

Fig. S8 ^{1}H-^{1}H NOESY spectrum of MeNNO-H_2bdc in DMSO-d_6. The correlation signal between chemical shift 3.43 and 8.09 ppm can be assigned either *trans-trans* or *cis-cis*. Previous study reported that *cis* from of *N*-nitrosamine is less stable than trans from. Therefore, this signal is most likely assigned as *trans-trans* MeNNO-H_2bdc. The correlation signal between chemical shift 4.16 and 7.81 ppm is assigned as *cis* form of *trans-cis* MeNNO-H_2bdc. Although it is overlapped with *trans-trans* signal, the signal of *trans* form of *trans-cis* MeNNO-H_2bdc also observed.

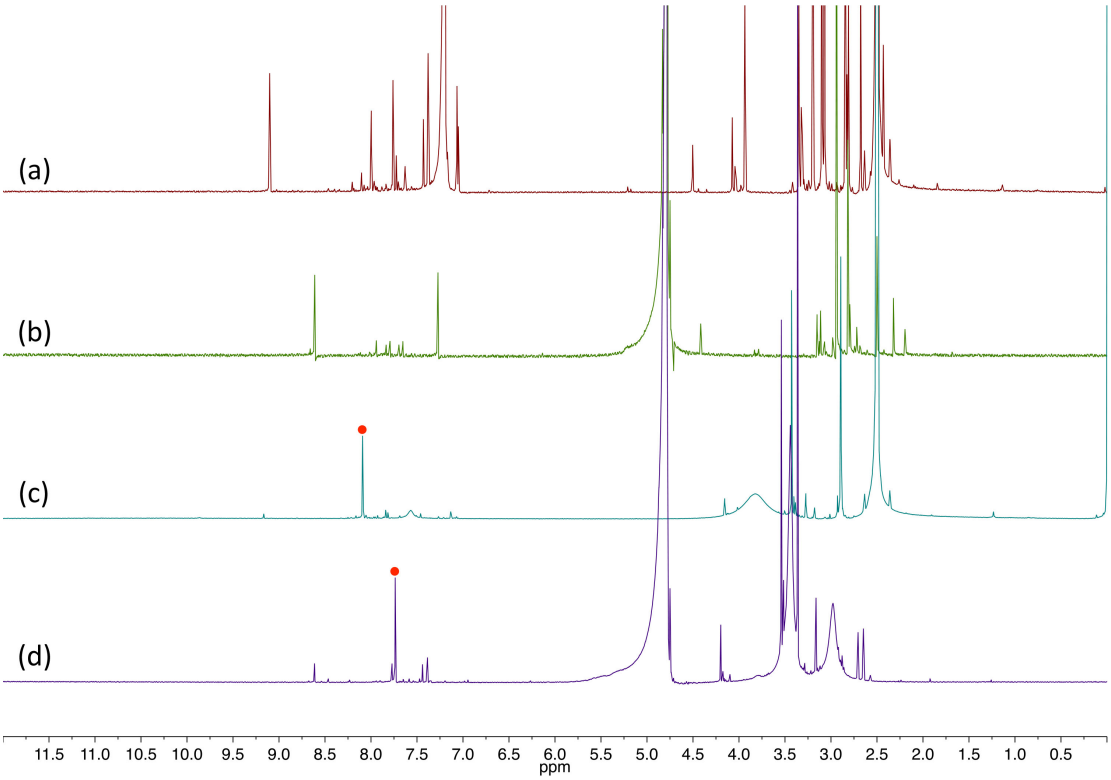

Fig. S9 NMR spectra of NOF-11 that digested in various conditions. Each spectrum was measured with following digestion methods.

(a) 2 mg of NOF-11 and 50 ml of DCl/D_2O solution was mixed. Then, 0.5 mL of DMSO-d_6 was added into mixture. The clear mixture was used for NMR experiment.

(b) 2 mg of NOF-11 and 50 ml of DCl/D_2O solution was mixed. Then, 0.5 mL of D_2O was added into mixture. Appeared precipitation was separated by centrifugation.

(c) The precipitation, which was separated from (b) was dissolved into 0.5 mL of DMSO-d_6.

(d) 2 mg of NOF-11, 2 mg of ethylenediaminetetraacetic acid tetrasodium salt hydrate and 0.5 mL of D_2O was mixed. Before the NMR measurement, appeared precipitation was separated by centrifugation.

The peaks with ● mark can be assigned as protons of phenyl group of MeNNO-bdc.

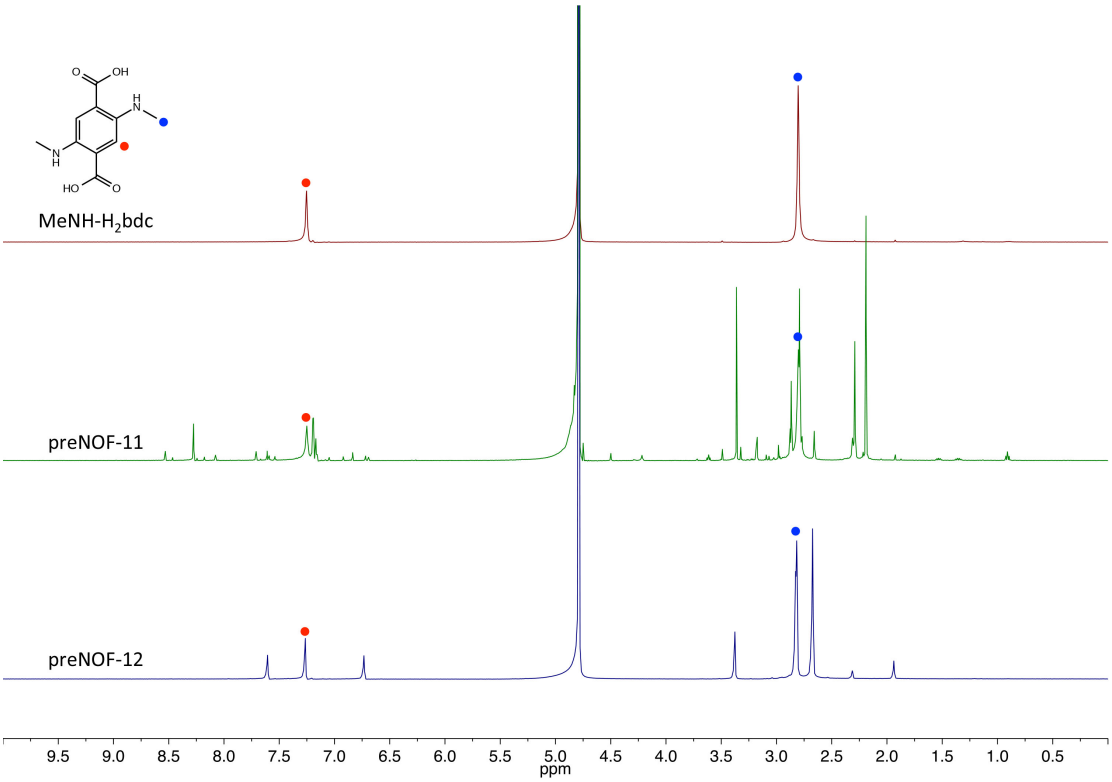

Fig. S10 NMR spectra of digested preNOF-11 and preNOF-12. The peaks with ● and ● marks can be assigned as peaks of MeNH-bdc.

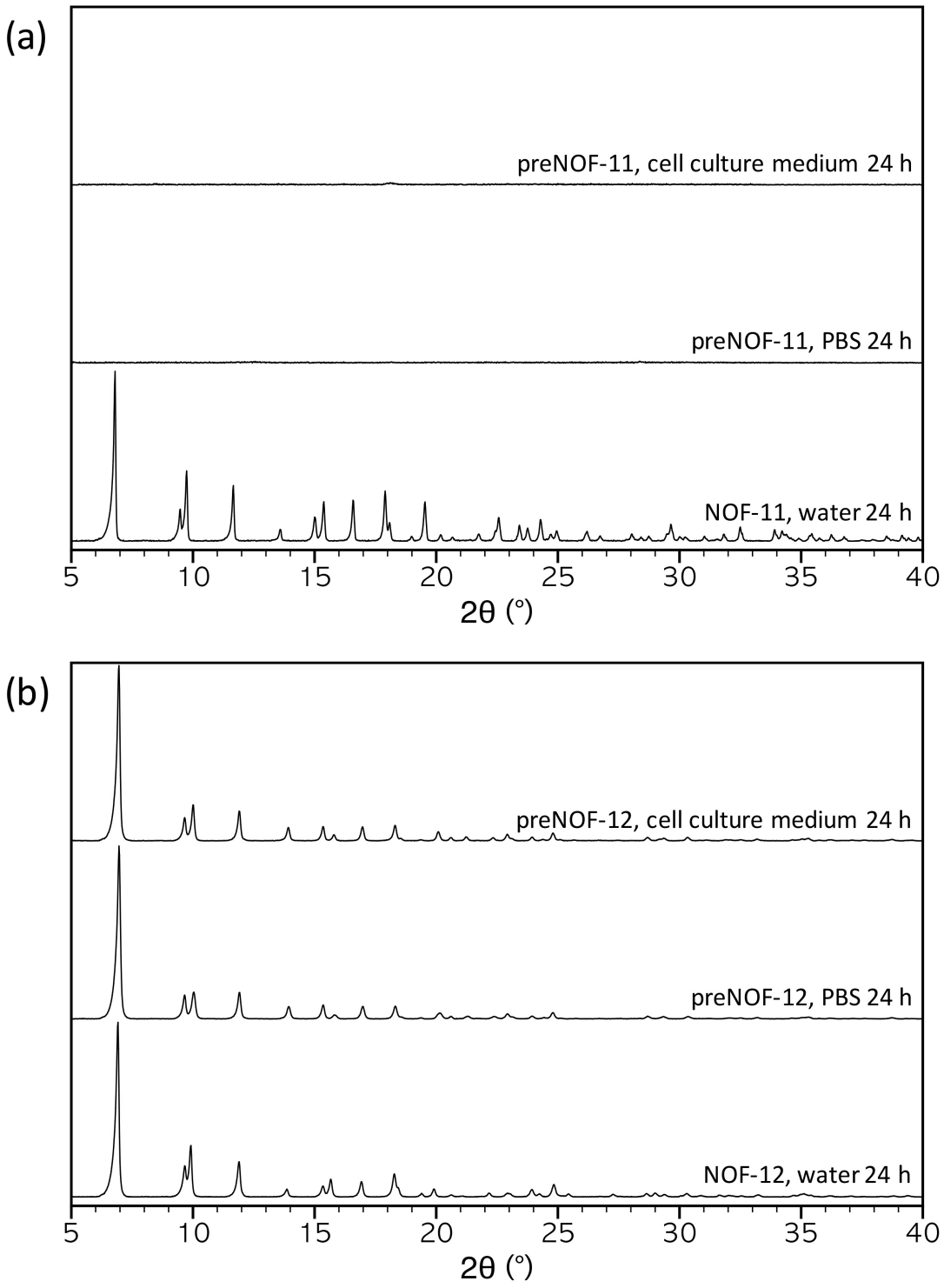

Fig. S11 PXRD patterns of (a) titanium and (b) aluminium frameworks after soaking in aqueous medias.

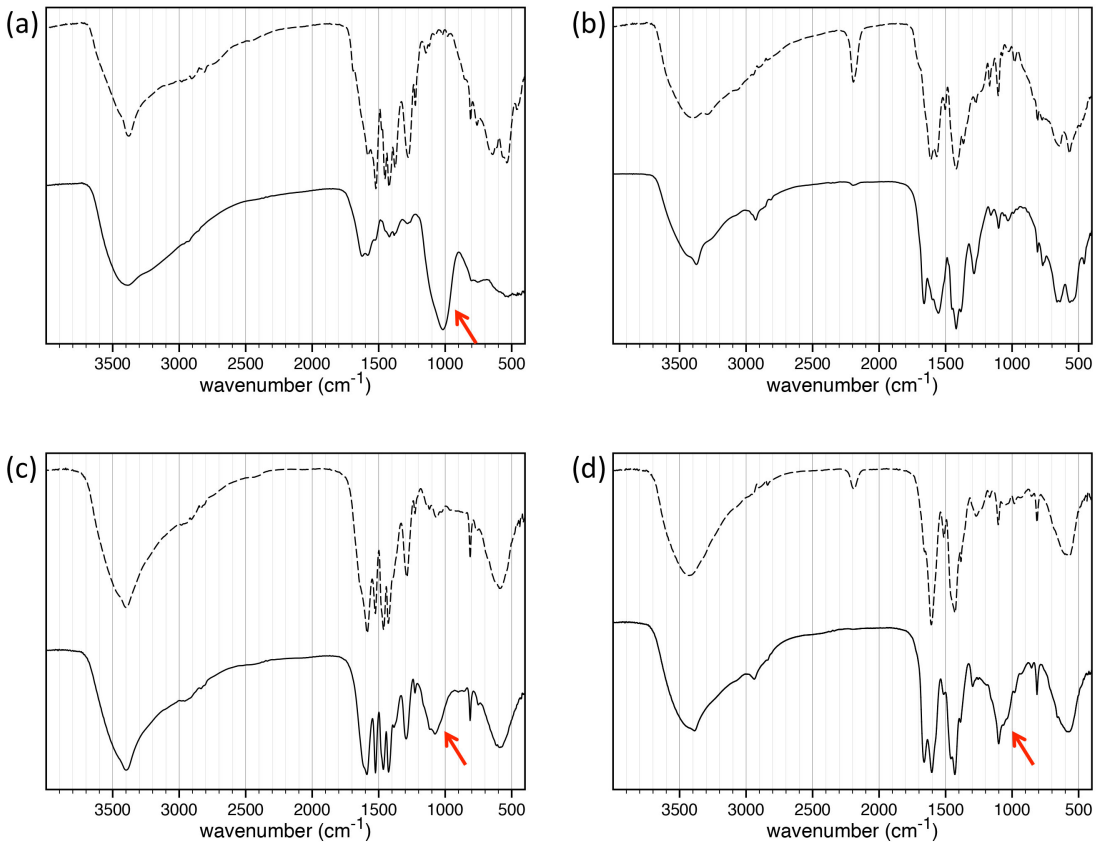

Fig. S12 IR spectra of (a) preNOF-11, (b) NOF-11, (c) preNOF-12 and (d) NOF-12 after PBS soaking. The spectra of samples before soaking and after soaking are presented in dashed line and solid line, respectively. Red arrow indicates adsorption band of phosphate.

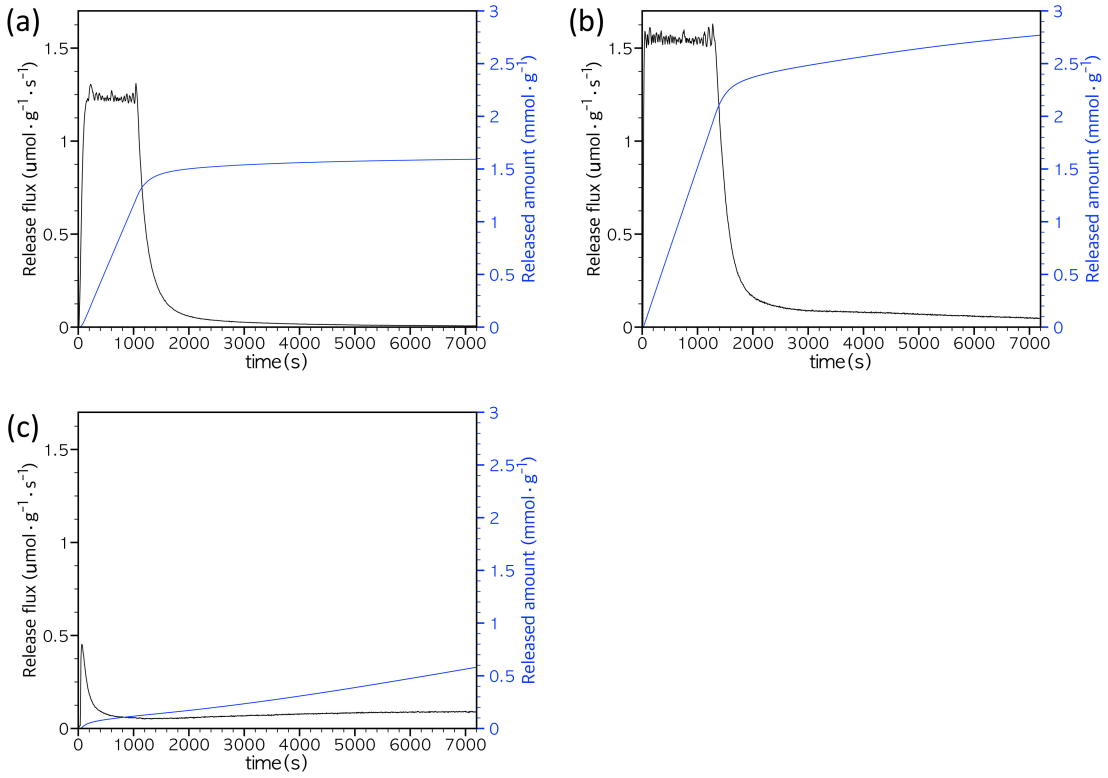

Fig. S13 NO releasing properties of (a) NOF-11, (b) NOF-12 and (c) MeNNO-H_2bdc. Light power was gradually increased from 10 to 100% to keep constant release speed for NOF-11 and NOF-12. The NO releasing property of MeNNO-H_2bdc was recorded under the 100% of light power for 2 h.

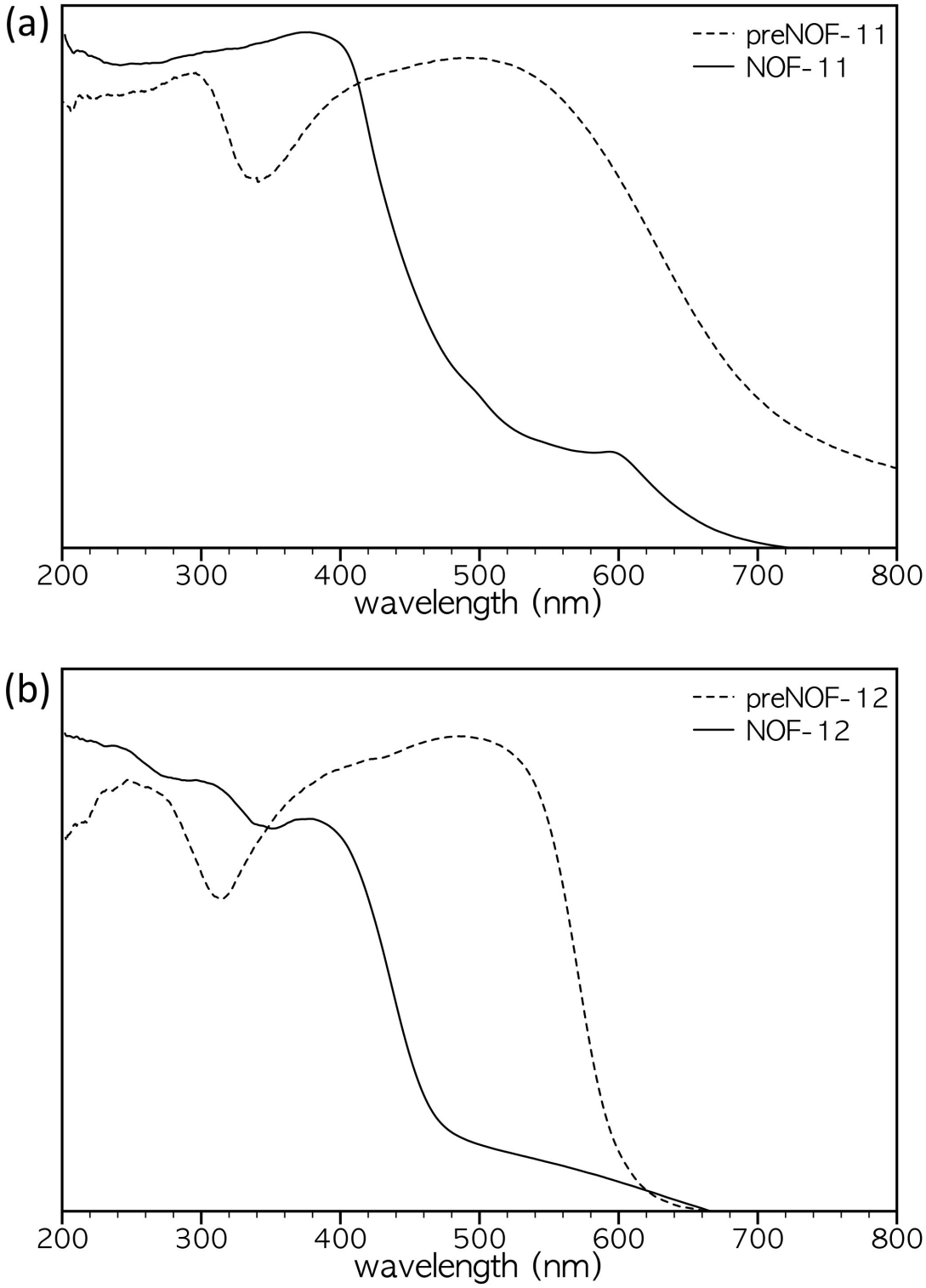

Fig. S14 Diffuse reflectance spectra of (a) titanium and (b) aluminium frameworks.

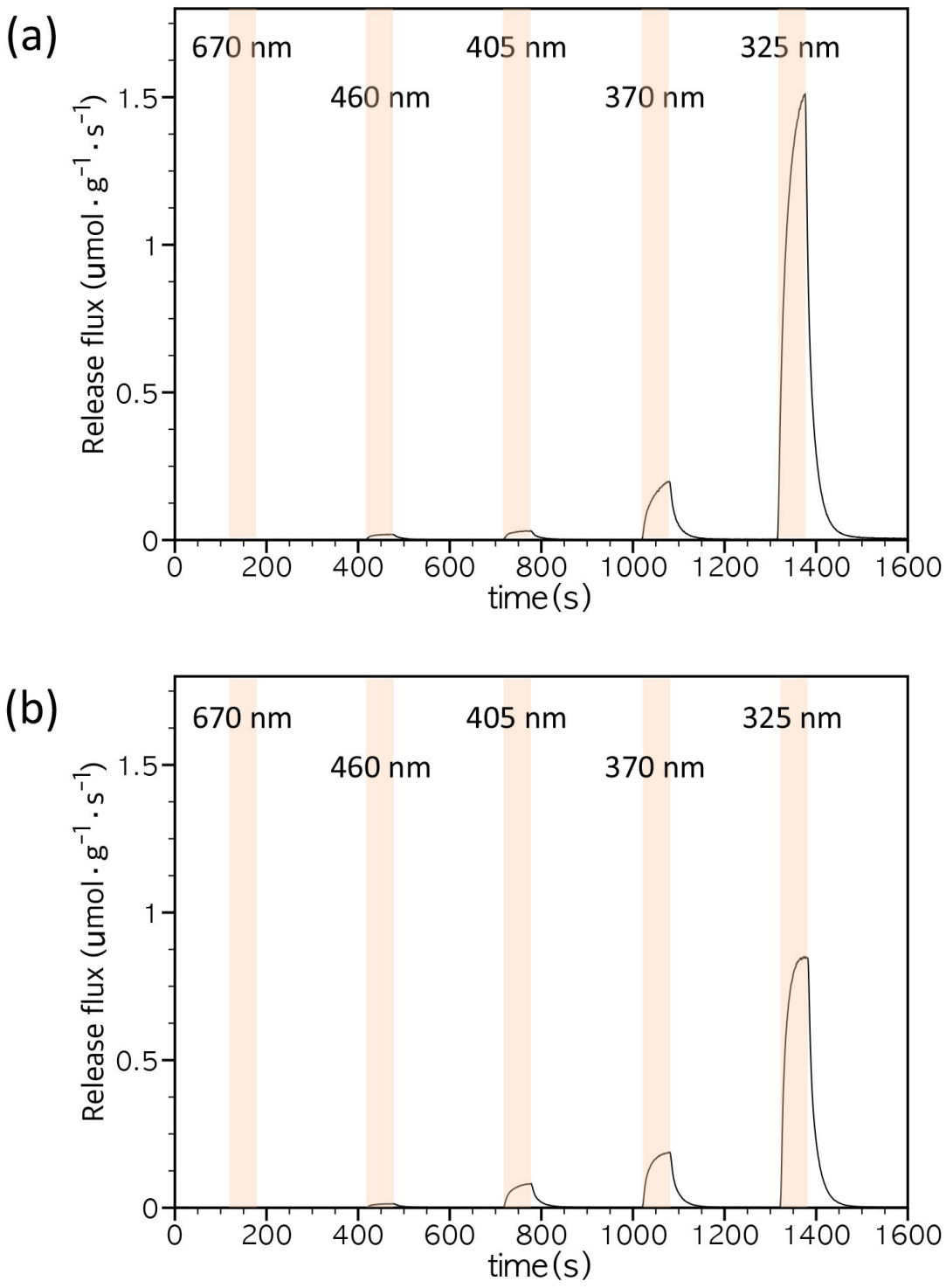

Fig. S15 NO releasing properties of (a) NOF-11 and (b) NOF-12 depending on wavelength. NO releasing properties were recorded under the 30% of light power irradiation with 670, 460, 405, 370 and 325 nm of bandpass filters (± 5 nm).

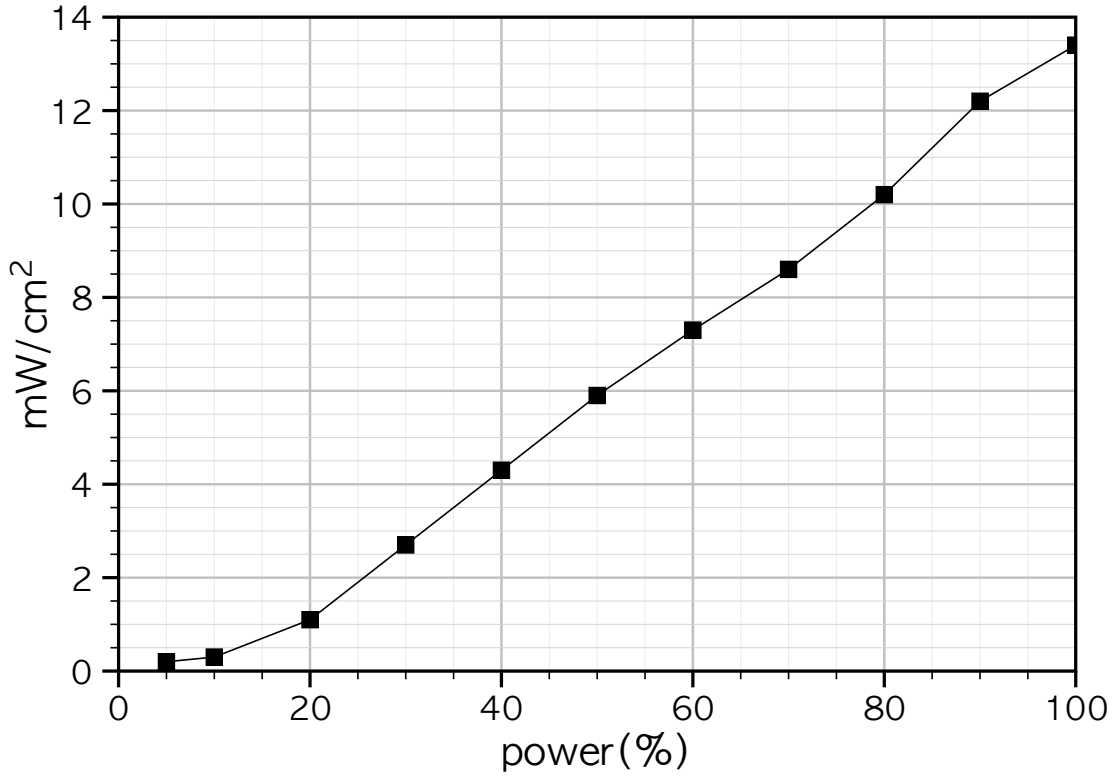

Fig. S16 Light intensity of Xenon lamp depending on light power. Intensity was measured using Digital UV Intensity Meter UIT-201 (USHIO) equipped with UVD-365PD detector.

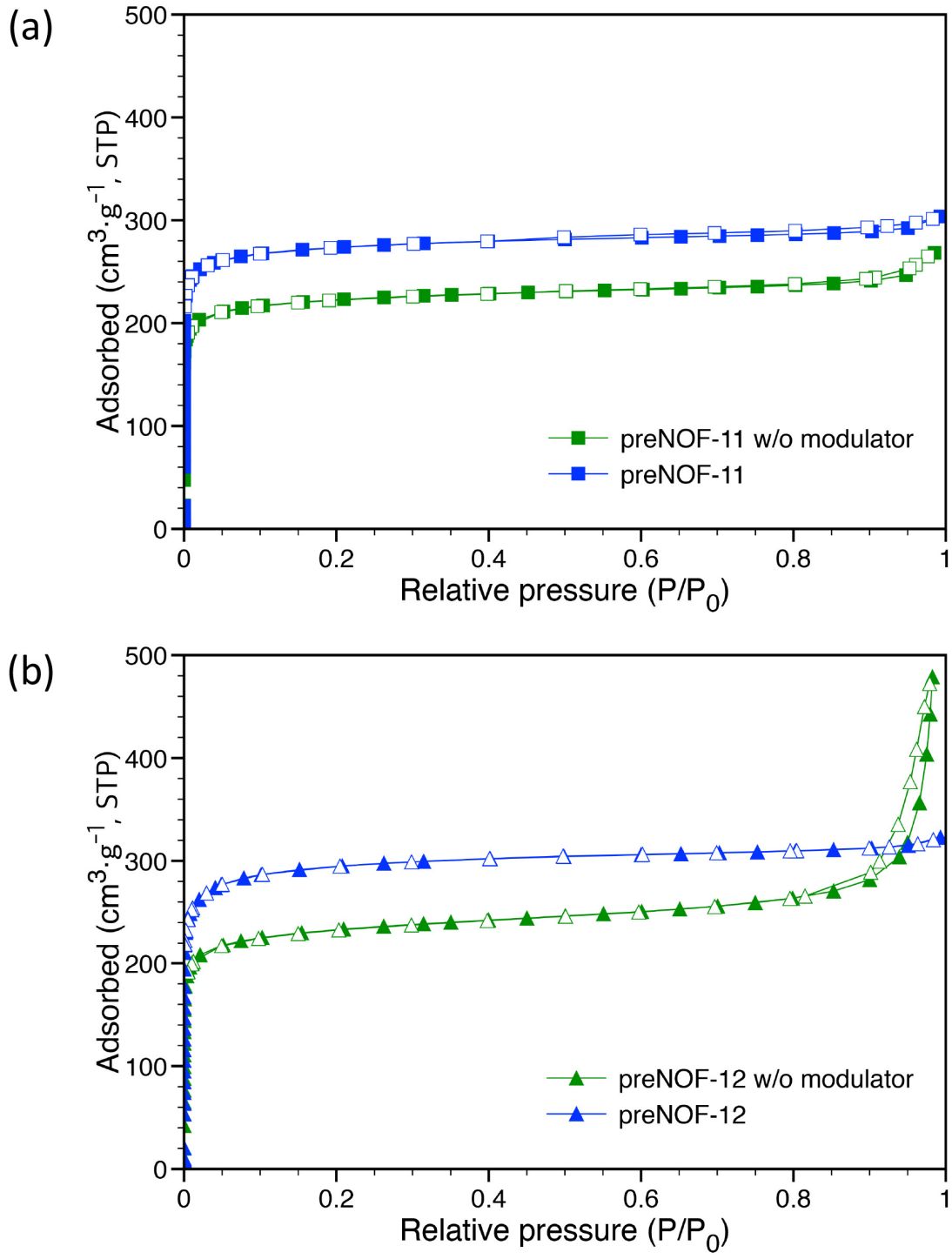

Fig. S17 The difference of nitrogen sorption isotherm between preNOFs, which were synthesized without modulator and with modulator. (a) preNOF-11 and (b)preNOF-12

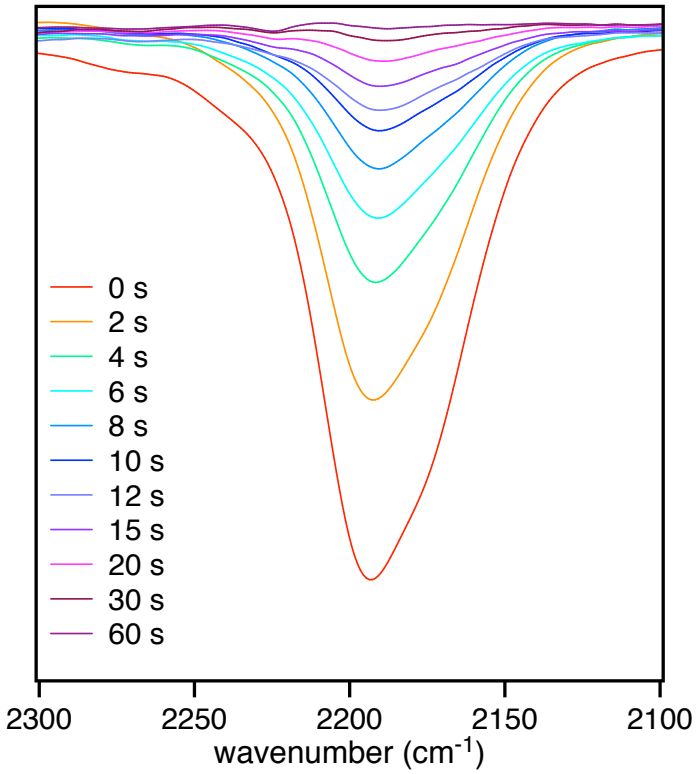

Fig. S18 IR spectra of NOF-11 depending on UV-vis irradiation time. KBr pellet of NOF-11 was irradiated under the UV-vis light. The adsorption band on 2189 cm^{-1} was gradually decreased by irradiation

Equiv. of modulator	FWHM (°)	
	preNOF-11	preNOF-12
0	0.251	0.389
5	0.1546	-
10	0.1438	0.2572
20	0.1415	0.2223
40	0.1555	0.1567
60	-	0.1724
80	-	0.2015

Table S1 FWHM (full width at half maximum) of the Bragg peak at the lowest angle of as-synthesized preNOF-11 and preNOF-12 samples using various equivalent of modulator.

	FWHM (°)			
	preNOF-11	preNOF-12	NOF-11	NOF-12
as-synthesis	0.1415	0.1567	0.1593	0.2119
water, stirred, 24 h	0.1753	0.1803	0.1635	0.2109
PBS, stirred, 24 h	-	0.1683	0.1386	0.1633
cell culture medium, stirred, 24 h	-	0.1658	0.1289	0.1828

Table S2 FWHM (full width at half maximum) of the Bragg peak at the lowest angle of preNOFs and NOFs after soaking in water, PBS and cell culture medium.

The calculation of conversion ratio from MeNH-bdc to MeNNO-bdc in the frameworks by TG result.

The conversion ratio (x) of MeNH-bdc to MeNNO-bdc in the frameworks was calculated by result of TG

The weight loss (Y) corresponding to nitroso functionality from NOF is given by following equation :

$$weigth\ loss\ Y = \frac{12x \cdot M_{NO}}{M_{cluster} + 6x \cdot M_{MeNO-bdc} + 6(1-x) \cdot M_{MeNH-bdc}}$$

$$= \frac{12x \cdot M_{NO}}{M_{cluster} + 6M_{MeNH-bdc} + 6x \cdot (M_{MeNO-bdc} - M_{MeNH-bdc})}$$

$$= \frac{12x \cdot M_{NO}}{M_{preNOF} + 6x \cdot (M_{MeNO-bdc} - M_{MeNH-bdc})}$$

where M_{NO}, $M_{cluster}$, $M_{\text{MeNH-bdc}}$, $M_{MeNNO\text{-}bdc}$ and M_{NOF} are molecule weight of NO, metal cluster ($(Ti_8O_8(OH)_4)$ for NOF-11 and $(Al_8(OMe)_8(OH)_4)$ for NOF-12), MeNH-bdc, MeNNO-bdc and preNOF ($(Ti_8O_8(OH)_4(\text{MeNH-bdc})_6)$for NOF-11 and $(Al_8(OMe)_8(OH)_4(\text{MeNH-bdc})_6)$ for NOF-12), respectively.

Thus, the conversion ratio x is expressed as following equation.

$$conversion\ raito\ x = \frac{Y \cdot M_{NOF}}{12M_{NO} - 6Y \cdot (M_{MeNNO-bdc} - M_{MeNH-bdc})}$$