Supplementary information

for

Light induced nitric oxide release from physiologically stable
porous coordination polymers

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Contents

• PXRD patterns of directly synthesized frameworks using MeNNO-H$_2$bdc  ------------------ S1
• Result of NO releasing experiment of directly synthesized
  Al frameworks using MeNNO-H$_2$bdc  ---------------------------------------------------- S2
• PXRD patterns and SEM images of preNOF-11  --------------------------------------------- S3
• PXRD patterns and SEM images of preNOF-12  --------------------------------------------- S4
• Nitrogen gas adsorption isotherms of preNOFs  --------------------------------------------- S5
• IR spectra of MeNH-H$_2$bdc and MeNNO-H$_2$bdc  --------------------------------------------- S6
• NMR spectra of digested NOFs  ------------------------------------------------------------- S7
• $^1$H-1H NOESY spectrum of MeNNO-H2bdc  ------------------------------------------------ S8
• NMR spectra of NOF-11 with various digestion methods  -------------------------------------- S9
• NMR spectra of digested preNOFs  ----------------------------------------------------------- S10
• PXRD patterns of preNOFs and NOFs after soaking in aqueous medias  ---------------------- S11
• IR spectra of preNOFs and NOFs after soaking in PBS  -------------------------------------- S12
• Total amount of release NO from NOFs  ------------------------------------------------------ S13
• Diffuse reflectance spectra spectra of frameworks  ------------------------------------------- S14
• NO releasing properties of NOFs depending on wavelength  ---------------------------------- S15
• Light intensity of xenon lamp depending on power (%)  -------------------------------------- S16
• Nitrogen sorption isotherm of preNOF (w/o modulator)  -------------------------------------- S17
• IR spectra of NOF-11 depending irradiation time  -------------------------------------------- S18
• FWHM of preNOFs  -------------------------------------------------------------------------- S19
• FWHM of preNOFs and NOFs after soaking in aqueous medias  -------------------------------- S20
• The calculation of conversion ratio from MeNH-bdc to MeNNO-bdc
  in the frameworks by TG data  -------------------------------------------------------------- S21
Fig. S1 PXRD patterns of powders, which are synthesized with metal precursor and MeNNO-H₂bdc. (a) Amorphous powder was obtained with Ti(iOPr)₄ and (b) isostructural framework of CAU-1 was obtained with AlCl₃·6H₂O
Fig. S2 The result of NO releasing experiment using the powder, which was synthesized with AlCl$_3$·6H$_2$O and MeNNO-H$_2$bdc. 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 : [Ti₈O₆(OH)₄(MeNH-bdc)₆] for preNOF-11 and [Al₈(OMe)₈(OH)₄(MeNH-bdc)₆] for preNOF-12).
Fig. S6 IR spectra of (a) MeNH-H$_2$bdc and (b) MeNNO-H$_2$bdc. The novel adsorption band at 2190 cm$^{-1}$, which was observed in spectra of NOFs was not observed from spectra of MeNNO-H$_2$bdc.
Fig. S7 NMR spectra of MeNH-H$_2$bdc, MeNNO-H$_2$bdc, digested NOF-11 and digested NOF-12.
Fig. S8 $^1$H-$^1$H NOESY spectrum of MeNNO-H$_2$bdc 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 form of N-nitrosamine is less stable than trans from. Therefore, this signal is most likely assigned as trans-trans MeNNO-H$_2$bdc. The correlation signal between chemical shift 4.16 and 7.81 ppm is assigned as cis form of trans-cis MeNNO-H$_2$bdc. Although it is overlapped with trans-trans signal, the signal of trans form of trans-cis MeNNO-H$_2$bdc 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$_2$O 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$_2$O solution was mixed. Then, 0.5 mL of D$_2$O 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$_2$O 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$_2$ bdc. 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$_2$ bdc 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.
<table>
<thead>
<tr>
<th>Equiv. of modulator</th>
<th>FWHM (°)</th>
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<tbody>
<tr>
<td></td>
<td>preNOF-11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.251</td>
<td></td>
<td>0.389</td>
</tr>
<tr>
<td>5</td>
<td>0.1546</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>0.1438</td>
<td></td>
<td>0.2572</td>
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<tr>
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<td>0.1415</td>
<td></td>
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<td>40</td>
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<td></td>
<td>0.1567</td>
</tr>
<tr>
<td>60</td>
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<td></td>
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<tr>
<td>80</td>
<td>-</td>
<td></td>
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**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.
<table>
<thead>
<tr>
<th></th>
<th>preNOF-11</th>
<th>preNOF-12</th>
<th>NOF-11</th>
<th>NOF-12</th>
</tr>
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<tbody>
<tr>
<td>as-synthesis</td>
<td>0.1415</td>
<td>0.1567</td>
<td>0.1593</td>
<td>0.2119</td>
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<tr>
<td>water, stirred, 24 h</td>
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<td>0.1803</td>
<td>0.1635</td>
<td>0.2109</td>
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<tr>
<td>PBS, stirred, 24 h</td>
<td>-</td>
<td>0.1683</td>
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<td>0.1633</td>
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<tr>
<td>cell culture medium,</td>
<td>-</td>
<td>0.1658</td>
<td>0.1289</td>
<td>0.1828</td>
</tr>
<tr>
<td>stirred, 24 h</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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</table>

**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 the following equation:

\[
\text{weight loss } Y = \frac{12x \cdot M_{NO}}{M_{\text{cluster}} + 6x \cdot M_{MeN\text{O-bdc}} + 6(1 - x) \cdot M_{MeNH\text{-bd}}}
\]

\[
= \frac{12x \cdot M_{NO}}{M_{\text{cluster}} + 6M_{MeNH\text{-bd}} + 6x \cdot (M_{MeN\text{O-bdc}} - M_{MeNH\text{-bd}})}
\]

\[
= \frac{12x \cdot M_{NO}}{M_{\text{preNOF}} + 6x \cdot (M_{MeN\text{O-bdc}} - M_{MeNH\text{-bd}})}
\]

where \( M_{NO}, M_{\text{cluster}}, M_{MeNH\text{-bd}}, M_{MeN\text{O-bdc}} \) and \( M_{\text{NOF}} \) are molecule weight of NO, metal cluster ((Ti₈O₈(OH)₄) for NOF-11 and (Al₈(OMe)₈(OH)₄) for NOF-12), MeNH-bdc, MeNNO-bdc and preNOF ((Ti₈O₈(OH)₄(MeNH-bdc)₆) for NOF-11 and (Al₈(OMe)₈(OH)₄(MeNH-bdc)₆) for NOF-12), respectively.

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

\[
\text{conversion ratio } x = \frac{Y \cdot M_{\text{NOF}}}{12M_{NO} - 6Y \cdot (M_{MeN\text{O-bdc}} - M_{MeNH\text{-bd}})}
\]