Linker Engineering of Iron-Based MOFs for Efficient Visible-Light-Driven Water Oxidation Reaction

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Table of content

Synthesis and characterization of MOFs ................................................................................................3
MIL-88-4H...........................................................................................................................................3
MIL-88-4F...........................................................................................................................................4
MIL-88-4CH$_3$......................................................................................................................................5
MIL-88-2CH$_3$...................................................................................................................................6
MIL-88-2OH......................................................................................................................................7
MIL-88-NH$_2$.....................................................................................................................................8
MIL-88-OH.......................................................................................................................................9
MIL-88-NO$_2$...................................................................................................................................10
MIL-88-Br........................................................................................................................................11
XPS analysis......................................................................................................................................12
XRD patterns before and after WOR .................................................................................................13
Synthesis and characterization of MOFs

MIL-88-4H

**Synthesis** (The material here is called MIL-88-4H-as, “as” for as-synthesized): FeCl₃·6H₂O (1 mmol; 270 mg) and terephthalic acid (1 mmol; 166 mg) were dissolved into DMF (5 mL) and 2M NaOH (0.4 mL). The mixture was transposed into a Teflon lined autoclave and heated for 12 hours at 373 K. After cooling down until room temperature, the powder was centrifuged and washed with acetone then water.

**Activation** (MIL-88-4H): The powder was dispersed into 20 mL of MeOH and stirred for 16 hours. The material was centrifuged and washed with MeOH until the supernatant became colorless. Finally, the MOF was dried at 353 K under air before being collected.

**Characterization:**

![Figure S1](image-url)

**Figure S1.** (a) Powder XRD patterns of as synthesized (red) and activated (black) forms of MIL-88-4H, (b) N₂ adsorption-desorption isotherms of activated MIL-88-4H, (c) IR spectra of MIL-88-4H (black) and linker (red) at room temperature, the yellow part represents the Fe₃O vibrational peak, (d) SEM image of MIL-88-4H
MIL-88-4F

Synthesis (MIL-88-4F-as): FeCl$_3$·6H$_2$O (1 mmol; 270 mg) and tetrafluoroterephthalic acid (1 mmol; 238 mg) were dissolved into distilled water (10 mL). The mixture was transposed into a Teflon lined autoclave and heated for 12 hours at 358 K. After cooling down until room temperature, the powder was centrifugated and washed with acetone then water.

Activation (MIL-88-4F): The powder was dispersed into 20 mL of distilled water and stirred for 3 hours. The material was centrifugated and washed with H$_2$O until the supernatant became colorless. Finally, the MOF was dried at 353 K under air before being collected.

Characterization:

![Figure S2](image)

**Figure S2**. (a) Powder XRD patterns of as synthesized (red) and activated (black) forms of MIL-88-4F, (b) N$_2$ adsorption-desorption isotherms of activated MIL-88-4F, (c) IR spectra of MIL-88-4F (black) and linker (red) at room temperature, the yellow part represents the Fe$_3$O vibrational peak, (d) SEM image of MIL-88-4F
MIL-88-4CH₃

*Synthesis* (MIL-88-4CH₃-as): FeCl₃·6H₂O (1 mmol; 270 mg) and tetramethylterephthalic acid (1 mmol; 222 mg) were dissolved into DMF (5 mL). The mixture was transposed into a Teflon lined autoclave and heated for 16 hours at 373 K. After cooling down until room temperature, the powder was centrifugated and washed with acetone then water.

*Activation* (MIL-88-4CH₃): The powder was dispersed in 10 mL of distilled water and stirred for 16 hours. The material was centrifugated and washed with H₂O until the supernatant became colorless. Finally, the MOF was dried at 353 K under air before being collected.

*Characterization:*

![Figure S3](image)

**Figure S3.** (a) Powder XRD patterns of as synthesized (red) and activated (black) forms of MIL-88-4CH₃, (b) N₂ adsorption-desorption isotherms of activated MIL-88-4CH₃, (c) IR spectra of MIL-88-4CH₃ (black) and linker (red) at room temperature, the yellow part represents the Fe₃O vibrational peak, (d) SEM image of MIL-88-4CH₃
MIL-88-2CH₃

*Synthesis* (MIL-88-2CH₃-as): Fe(ClO₄)₃·nH₂O (1 mmol; 354 mg) and 2,5-dimethylterephthalic acid (1 mmol; 194 mg) were dissolved into MeOH (5 mL). The mixture was transposed into a Teflon lined autoclave and heated for 72 hours at 373 K. After cooling down until room temperature, the powder was centrifuged and washed with acetone then water.

*Activation* (MIL-88-2CH₃): The powder was dispersed into 20 mL of MeOH and stirred for 16 hours. The material was centrifuged and washed with MeOH until the supernatant became colorless. Finally, the MOF was dried at 353 K under air before being collected.

*Characterization:*

![Figure S4](image)

**Figure S4.** (a) Powder XRD patterns of as synthesized (red) and activated (black) forms of MIL-88-2CH₃, (b) N₂ adsorption-desorption isotherms of activated MIL-88-2CH₃, (c) IR spectra of MIL-88-4H (black) and linker (red) at room temperature, the yellow part represents the Fe₃O vibrational peak, (d) SEM image of MIL-88-2CH₃
MIL-88-2OH

Synthesis (MIL-88-2OH-as): Fe(ClO4)3·nH2O (1 mmol; 354 mg) and 2,5-dihydroxyterephthalic acid (1 mmol; 198 mg) were dissolved into DMF (5 mL). The mixture was transposed into a Teflon lined autoclave and heated for 12 hours at 353 K. After cooling down until room temperature, the powder was centrifugated and washed with acetone then water.

Activation (MIL-88-2OH): The powder was dispersed into 20 mL of MeOH and stirred for 16. The material was centrifugated and washed with MeOH until the supernatant became colorless. Finally, the MOF was dried at 353 K under air before being collected.

Characterization:

Figure S5. (a) Powder XRD patterns of as synthesized (red) and activated (black) forms of MIL-88-2OH, (b) N2 adsorption-desorption isotherms of activated MIL-88-2OH, (c) IR spectra of MIL-88-2OH (black) and linker (red) at room temperature, the yellow part represents the Fe3O vibrational peak, (d) SEM image of MIL-88-2OH
MIL-88-NH$_2$

**Synthesis** (MIL-88-NH$_2$-as): FeCl$_3$·6H$_2$O (1 mmol; 270 mg) and 2-aminoterephthalic acid (1 mmol; 181 mg) were dissolved into MeOH (15 mL). The mixture was transposed into a Teflon lined autoclave and heated for 24 hours at 373 K. After cooling down until room temperature, the powder was centrifugated and washed with acetone then water.

**Activation** (MIL-88-NH$_2$): The powder was dispersed into 20 mL of MeOH and stirred for 16 hours. The material was centrifugated and washed with MeOH until the supernatant became colorless. Finally, the MOF was dried at 353 K under air before being collected.

**Characterization:**

![Figure S6](image)

**Figure S6.** (a) Powder XRD patterns of as synthesized (red) and activated (black) forms of MIL-88-NH$_2$, (b) N$_2$ adsorption-desorption isotherms of activated MIL-88-NH$_2$, (c) IR spectra of MIL-88-NH$_2$ (black) and linker (red) at room temperature, the yellow part represents the Fe$_3$O vibrational peak, (d) SEM image of MIL-88-NH$_2$
MIL-88-OH

Synthesis (MIL-88-OH-as): Fe(ClO$_4$)$_3$·nH$_2$O (1 mmol; 354 mg) and 2-hydroxyterephthalic acid (1 mmol; 182 mg) were dissolved into distilled water (10 mL). The mixture was transposed into a Teflon lined autoclave and heated for 12 hours at 373 K. After cooling down until room temperature, the powder was centrifugated and washed with acetone then water.

Activation (MIL-88-OH): The powder was dispersed into 20 mL of distilled water and stirred for 16 hours. The material was centrifugated and washed with H$_2$O until the supernatant became colorless. Finally, the MOF was dried at 353 K under air before being collected.

Characterization:

![Figure S7](image_url)

**Figure S7.** (a) Powder XRD patterns of as synthesized (red) and activated (black) forms of MIL-88-OH, (b) N$_2$ adsorption-desorption isotherms of activated MIL-88-OH, (c) IR spectra of MIL-88-OH (black) and linker (red) at room temperature, the yellow part represents the Fe$_3$O vibrational peak, (d) SEM image of MIL-88-OH
MIL-88-NO₂

**Synthesis** (MIL-88-NO₂-as): The synthetic method used was the one reported by R.E Morris but in a smaller scale. Typically, FeCl₃·6H₂O (1 mmol; 270 mg) and nitroterephthalic acid (1 mmol; 211 mg) were dissolved into distilled water (5 mL). The mixture was transposed into a Teflon lined autoclave and heated for 12 hours at 373 K. After cooling down until room temperature, the powder was centrifuged and washed with acetone then water.

**Activation** (MIL-88-NO₂): The powder was dispersed into 10 mL of EtOH and stirred for 16 hours. The material was centrifuged and washed with EtOH until the supernatant became colorless. Finally, the MOF was dried at 353 K under air before being collected.

**Characterization:**

*Figure S8.* (a) Powder XRD patterns of as synthesized (red) and activated (black) forms of MIL-88-NO₂, (b) N₂ adsorption-desorption isotherms of activated MIL-88-NO₂, (c) IR spectra of MIL-88-NO₂ (black) and linker (red) at room temperature, the yellow part represents the Fe₃O vibrational peak, (d) SEM image of MIL-88-NO₂
MIL-88-Br

Synthesis (MIL-88-Br-as): FeCl$_3$·6H$_2$O (1 mmol; 270 mg) and 2-bromoterephthalic acid (1 mmol; 245 mg) were dissolved into DMF (5 mL). The mixture was transposed into a Teflon lined autoclave and heated for 12 hours at 373 K. After cooling down until room temperature, the powder was centrifugated and washed with acetone then water.

Activation (MIL-88-Br-as): The powder was dispersed into 20 mL of DMF and stirred for 16 hours. The material was centrifugated and washed with DMF until the supernatant became colorless. Finally, the MOF was dried at 353 K under air before being collected.

Characterization:

Figure S9. (a) Powder XRD patterns of as synthesized (red) and activated (black) forms of MIL-88-Br, (b) N$_2$ adsorption-desorption isotherms of activated MIL-88-Br, (c) IR spectra of MIL-88-Br (black) and linker (red) at room temperature, the yellow part represents the Fe$_3$O vibrational peak, (d) SEM image of MIL-88-Br
Figure S10. XPS spectra of Fe2p for (a) MIL-88-4H, (b) MIL-88-4F, (c) MIL-88-4CH₃, (d) MIL-88-2CH₃, (e) MIL-88-2OH, (f) MIL-88-NH₂, (g) MIL-88-OH, (h) MIL-88-NO₂, (i) MIL-88-Br

The peaks at 712 and 726 eV are attributed respectively to Fe³⁺ Fe₂p³/₂ and Fe₂p₁/₂
XRD patterns before and after WOR

Figure S11. PXRD patterns before (top curve, black) and after (bottom curve, red) Water Oxidation Reaction of (a) MIL-88-4H and (b) MIL-88-4F