

Supplementary Information

Assembly of Iron-Based Complex into Metal-Organic Framework: A Space Confinement Strategy for Isolation of Mono-Iron Complex from Dimerization

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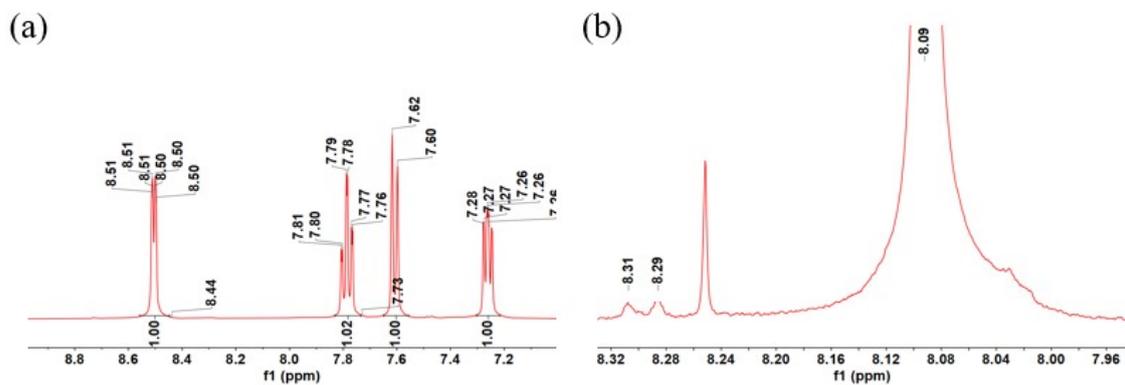


Figure S1. ¹H NMR spectra for (a)TPA and (b)TPA@UiO-66 (after fully digestion).

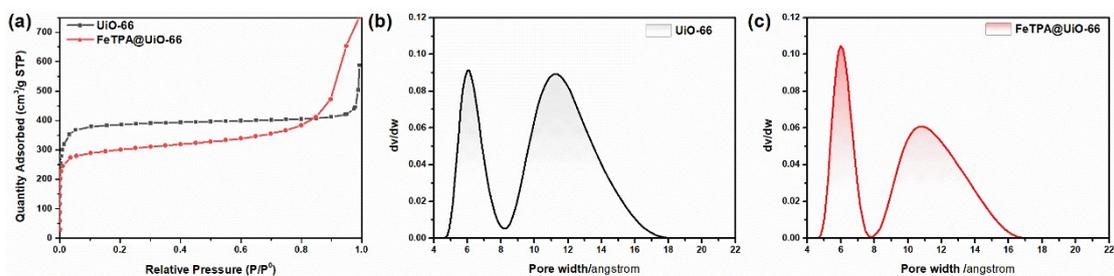


Figure S2 (a) N₂ adsorption isotherms of UiO-66 and FeTPA@UiO-66; pore width analysis of UiO-66 (b) and FeTPA@UiO-66 (c).

Table S1 Comparison of surface area, pore volume, and pore width

| | UiO-66 | FeTPA@UiO-66 |
|------------------|---------------------------|--|
| BET surface area | 1234 m ² /g | 993 m ² /g |
| Pore volume | 0.6173 cm ³ /g | 0.5055 cm ³ /g |
| Pore width | 6.2 Å, 11.5 Å | 6.2 Å, 11.5 Å (40% lower in intensity) |

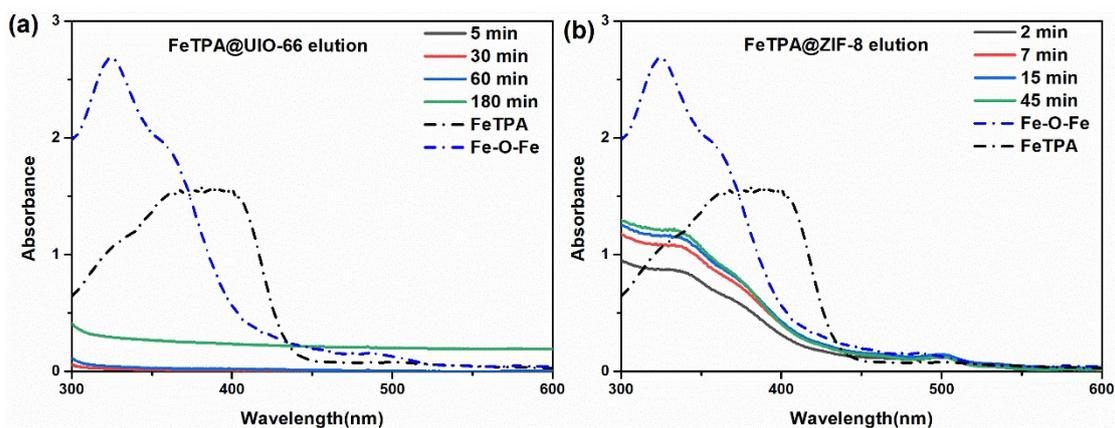


Figure S3 *in-situ* elution measurements of FeTPA@UiO-66 and FeTPA@ZIF-8 monitoring by UV-Vis spectroscopy.

Synthesis of controlling sample FeTPA@ZIF-8: ZIF-8 was prepared according the reported method. FeTPA@ZIF-8: was obtained by dispersing ZIF-8 in saturated FeTPA solution in acetonitrile for 2 hours), in which most of FeTPA complex should be attached on the surface of ZIF-8 because of that the window diameter is too small to accommodate FeTPA. The obtained FeTPA@ZIF-8 was washed with ultrapure water and acetonitrile.

Experimental details for elution test: the synthesized the hybrid FeTPA@UiO-66 and FeTPA@ZIF-8 were dispersed in acetonitrile, the upper supernate was monitoring by UV-vis spectroscopy.

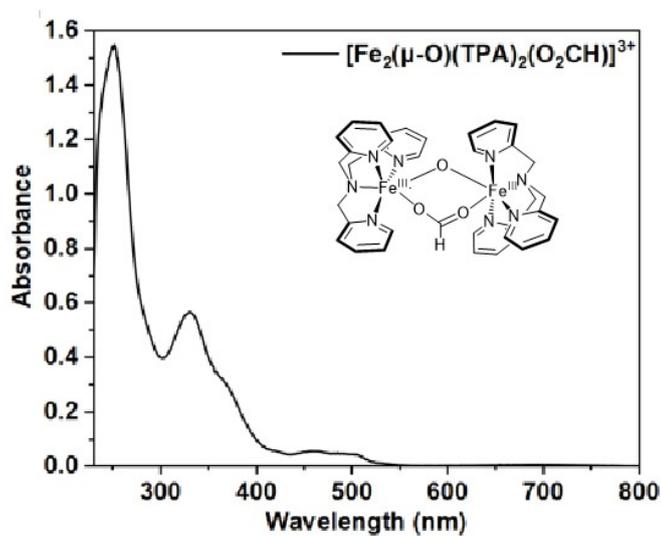


Figure S4. UV-Vis absorption spectrum of di-nuclear iron complex $[\text{Fe}^{\text{III}}_2(\mu\text{-O})(\text{TPA})_2(\text{O}_2\text{CH})](\text{OTf})_3$; inset is the chemical structure of $[\text{Fe}^{\text{III}}_2(\mu\text{-O})(\text{TPA})_2(\text{O}_2\text{CH})]^{3+}$.

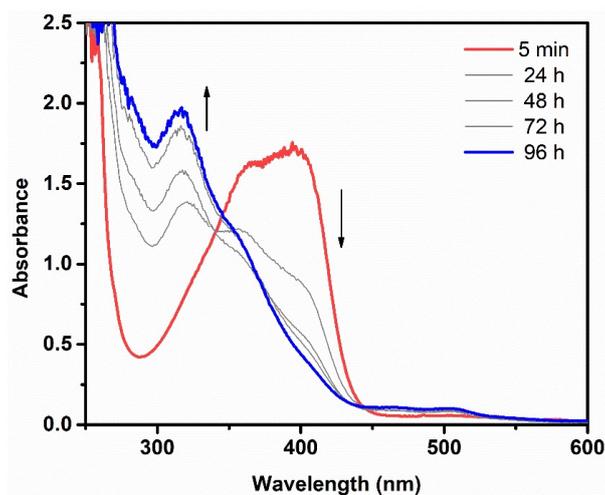


Figure S5. UV-Vis absorption spectrum monitoring of FeTPA (0.25 M/L) in acetonitrile, the spectra was taken by 125 times dilution each time.

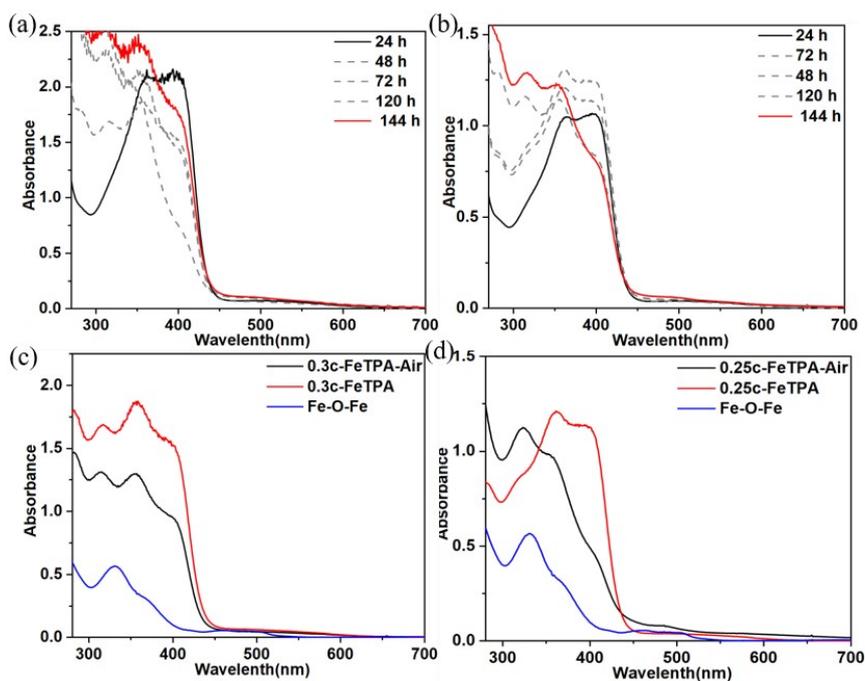


Figure S6. (a) The stability studies by UV-Vis spectroscopy of FeTPA in CH_3CN under N_2 atmosphere for 48 h, (a) $c = 83$ mmol/L (b) $c = 62$ mmol/L; Comparison between nitrogen protection and air atmosphere of FeTPA in CH_3CN after 48 h, (c) $c = 83$ mmol/L, (d) $c = 62$ mmol/L.

| catalyst | substrate | product | turnover number ^b |
|--------------|-------------|-----------------------|------------------------------|
| FeTPA | Methanol | methanal ^c | 5 |
| | Cyclohexane | cyclohexanol | 8 |
| FeTPA@UiO-66 | methanol | methanal ^c | 4.6 |
| | cyclohexane | cyclohexanol | 2 |
| UiO-66 | methanol | - | 0 |
| | cyclohexane | - | 0 |

a Reaction conditions: 1. 0.3 mL of a 70 mM H₂O₂ solution in CH₃CN was delivered by syringe pump over 1 h at 60 °C to a stirred 2.7 mL CH₃CN solution containing catalyst (0.7 mM FeTPA, 15 mg FeTPA@UiO-66 and 15 mg UiO-66) and 700 mM substrate. No products were observed in the absence of catalyst.

b Moles of product/moles of catalyst. Products listed were identified based on GC analysis or colorimetric titration and comparisons with standards.

c. The formation of formaldehyde was quantified as described in the literature (*Chem. Commun.*, 2017, 53, 12357-12360.).

The colorimetric reagent was prepared by dissolving NH₄OAc (15 g, 0.19 mol), acetic acid (0.3 mL, 5.4 mol) and pentane-2,4-dione (0.2 mL, 1.9 mol) in 100 mL water. 0.5 mL of reaction solution was diluted (0.5 mL reaction solution and 1.5 mL H₂O), then mixed with another 1 mL of colorimetric reagent. The standard samples were prepared with known concentrations (0.125, 0.25, 0.5, 1.0, and 2 mM) of formaldehyde solution with the same procedure (0.5 mL formaldehyde solution, 1.5 mL H₂O and 1 mL colorimetric solution). The 6 samples were monitored by UV-vis spectroscopy, until the increase of the absorbance at 412 nm of diacetyldihyrolutidine ceased. The concentration of formaldehyde was calculated from the calibration curve obtained from known concentrations of formaldehyde based on Lambert-Beer's law.

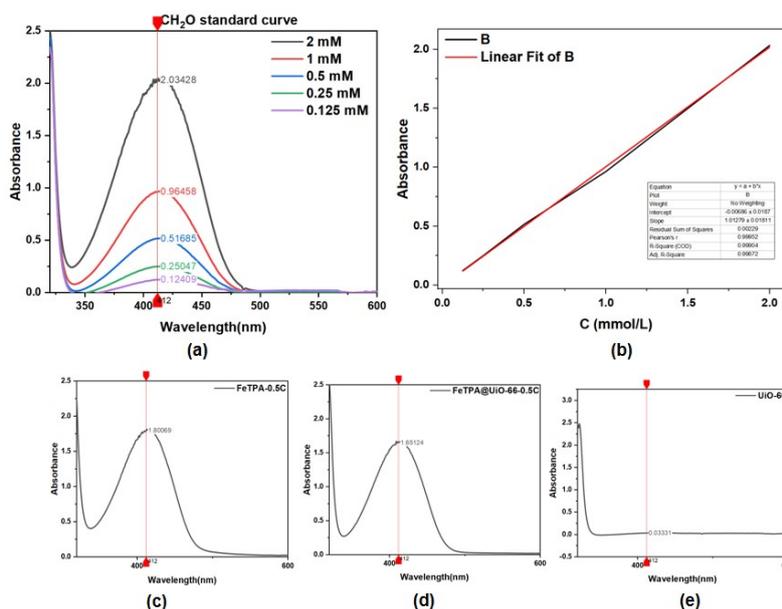


Figure S7 (a). Absorbance of standard sample; (b) the calibration curve according to the absorbance of the standard sample; (c) the absorbance of 0.5 C₀ sample obtained with FeTPA as catalyst; (d) the absorbance of 0.5 C₀ sample obtained with FeTPA@UiO-66 as catalyst; (e) the absorbance of the sample obtained with UiO-66 as catalyst.