Solvent-Assisted Linker Exchange (SALE) and Post-Assembly Metallation in Porphyrinic Metal-Organic Framework Materials

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I. Materials. Meso-Tetra(4-carboxyphenyl)porphine was obtained by Frontier Scientific and used as received. TMSN₃ was obtained by Aldrich and used as received. Solvents were obtained from Sigma-Aldrich and used as received. All deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received.

II. Characterization and instrumental procedures.

NMR and ICP-OES measurements were performed in the IMSERC facility at Northwestern University, which is supported by NSF (CHE-9871268), the State of Illinois, and Northwestern University. SEM measurements were taken in the Electron Probe Instrumentation Center (EPIC) in a NUANCE facility at Northwestern University.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was conducted on a Varian ICP-OES spectrometer that is equipped to cover the spectral range from 175 to 785 nm. Samples (1-2 mg) were digested in 3:1 v/v conc. H₂SO₄:H₂O₂ (30 wt% in H₂O), and heated at 120 °C until the solution became clear and colorless and no further vapor was produced. An aliquot of this acidic solution was diluted to 1 vol% with deionized H₂O.

Powder X-ray diffraction patterns for capillary-encapsulated samples were obtained at room temperature with a Bruker MX IμS microsource (CuKα radiation) and ApexII CCD detector. Samples were mounted in capillaries with supernatant liquid; capillaries were sealed with wax and placed on goniometer heads for mounting on the diffractometer. The PXRD data were collected with an area detector as rotation frames over 180° in φ at 2θ values of 12°, 24°, and 36° and exposed for 10 minutes for each frame. At a distance of 150mm, the detector area covers 24° in 2θ. Overlapping sections of data were matched and the resulting pattern integrated using the Bruker APEX2 Phase ID program. Powder pattern data were treated for amorphous background scatter and unit cell indexing was performed with the Bruker Topas program.

III. Syntheses.

(5,15-Dipyridyl-10,20-bis(pentafluorophenyl))porphyrin [L₂-H₂].

In a 500-mL round-bottom flask equipped with a water-cooled reflux condenser, and a magnetic stir bar were combined 5-pentafluorophenyl dipyrrromethane (3.12 g, 10 mmol), 4-pyridine carboxaldehyde (1.07 g, 10 mmol), and propionic acid (200 mL). The solution was refluxed for 2 hours, and then cooled to room temperature. The solvent was reduced in vacuo and methanol was slowly added. Filtration and rinsing with methanol gave a purple solid which was recrystallized in CH₂Cl₂/MeOH (1:4 v/v) to give product (625 mg, 16 % yield). ¹H NMR (CDCl₃): 9.49 (s, 4 H), 9.13 (m, 8 H), 8.45 (d, 4 H), -2.95 (s, 2 H). MS (MALDI-TOF): m/z 797.6 (Calcd m/z 797.2 for M-H⁺).

(5,15-Dipyridyl-10,20-bis(pentafluorophenyl))porphyrinato aluminum(III) hydroxide [L₂-Al(OH)].

(5,15-Dipyridyl-10,20-bis(pentafluorophenyl))porphyrin (500 mg, 0.63 mmol) was dissolved in dry methylene chloride (20 ml). Trimethylaluminum (0.5 mL of a 2M solution in toluene) was added, and the solution was stirred overnight at room temperature before being quenched with methanol. After removal of solvent, the product was purified by running through a short column of neutral alumina (Brockmann I) eluted with 5 vol% MeOH in CH₂Cl₂ to obtain a purple solid (436 mg, 82% yield). ¹H NMR (CD₃OD): 9.22 (d, 4 H, J = 4.7 Hz), 9.12 (d, 4 H, J = 4.8 Hz),
9.05 (d, 4H, $J = 5.6$ Hz), 8.39 (d, 4H, $J = 5.8$ Hz). MALDI-ToF MS: m/z 820.9 (Calcd m/z 821.1 for $M^+$ (w/out OH-)).

**General procedure for the synthesis of [Zn$_2$(L$_1$-M$^1$)(L$_2$-M$^2$)]$_n$ (M$^1$M$^2$-RPM).**

A solid mixture of L$_1$-2H (11.8 mg, 0.015 mmol) and Zn(NO$_3$)$_2$•6H$_2$O (17.8 mg, 0.06 mmol) was dissolved in DMF (2 mL) in a 2-dram screw-cap vial. The vial was capped and placed in an oven at 80 °C for 2 h. While the solution was warm, solid L$_2$-2H (11.9 mg, 0.015 mmol) and a mixture of 0.03M HNO$_3$ in EtOH (2 ml) were added. The vial was then recapped and the resulting suspension was heated in an oven at 80 °C for 20 h. After cooling to room temperature, the solvent was decanted and replaced with fresh DMF. The mixture was gently swirled and allowed to settle before the solution was decanted. If the decanted solution was colored, additional fresh DMF was added and the swirling-settling-decanting process was repeated until the DMF became clear. The remaining purple crystals were then stored in DMF until ready for use. TGA revealed the amount of solvent by weight in the crystals and this was taken into account to calculate the yield. Yield = 75%.

**IV. De Novo attempts on the syntheses of Zn2H-RPM, ZnCo-RPM and ZnSn-RPM.**

**Zn2H-RPM**

Briefly, we examined the reaction rate for the Zn metalation to L$_2$-2H in DMF at 80°C, and we found that Zn metalation is complete within 1h. Thus, we concluded that it is impossible to keep unmetalated porphyrin during the solvothermal synthesis. We had tried to make RPM with free base porphyrin units by changing the amount of Zn(NO$_3$)$_2$•6H$_2$O. However, we did not obtain any RPM with free base porphyrin using this method.

**ZnCo-RPM**

L$_2$-Co was attempted by mixing L$_2$-2H and CoCl$_2$ in DMF. An insoluble black solid (due to self-aggregation) was obtained. The poor solubility of L$_2$-Co did not allow us to be able to grow ZnCo-RPM.

**ZnSn-RPM**

We attempted to make ZnSn-RPM by using the following procedure:

A solid mixture of L$_1$-2H (16 mg, 0.02 mmol) and Zn(NO$_3$)$_2$•6H$_2$O (17.8 mg, 0.06 mmol) was dissolved in DMF (4 mL) in a 2-dram screw-cap vial. The vial was capped and placed in an oven at 80 °C for 2 h. While the solution was
warm, solid $\text{L}^2\text{-Sn(OH)}_2$ (19 mg, 0.02 mmol) and a mixture of 0.03M HNO$_3$ in EtOH (4 ml) were added. The vial was then recapped and the resulting suspension was heated in an oven at 80 °C for 20 h. After cooling to room temperature, the solvent was decanted and replaced with fresh DMF. The mixture was gently swirled and allowed to settle before the solution was decanted and an amorphous black solids was obtained.

V. Linker exchange

a) Time dependence of linker exchange reaction: ZnZn to Zn2H (non-ground sample)

\[ \text{Figure S1} \] $^1$H NMR spectra of linker exchanged samples (non-ground, dissolved into DMSO-d$_6$ with slight HCl). Blank arrows: Zn-dipy, Filled arrows: 2H-dipy

b) ZnZn to ZnH$_2$ (ground sample)

$^1$H NMR spectra (dissolved into DMSO-d$_6$ with slight HCl). Blank arrows: Zn-dipy, Filled arrows: 2H-dipy

\[ \text{Figure S2} \] $^1$H NMR spectra of linker exchanged samples (ground, dissolved into DMSO-d$_6$ with slight HCl). Blank arrows: Zn-dipy, Filled arrows: 2H-dipy

c) ZnZn to ZnAl (non-ground sample)
**Figure S3** Time dependence of linker exchange reaction evaluated by ICP-OES result.

**Figure S4** Time dependence of linker exchange reaction evaluated by ICP-OES result.

**Figure S5** $^1$H NMR spectrum of ZnH2-RPM prepared by repeating SALE processes three times. (dissolved into DMSO-d$_6$ with slight HCl)
The spinning capillary method minimizes the effects of preferred orientation.

**SEM image and EDS concentration profile of cut ZnSn-RPM crystal**

The tin concentration profile for ZnSn-RPM was examined using energy dispersive X-ray spectroscopy (EDS, Hitachi S-4800-II).
V. Post-synthetic metalation:

a) Post-synthetic metalation with CoCl₂

ZnH₂-RPM (5mg, ca. 1 µmol*) was suspended into DMF (1 ml) in a 2-dram screw-cap vial. To the suspension, CoCl₂ (30mg, 0.23 mmol) was added and the vial was capped and placed in an oven at 80 °C for 24 h. After cooling to room temperature, the solvent was decanted and replaced with fresh DMF. The mixture was gently swirled and allowed to settle before the solution was decanted. The decanting-refilling process was repeated about 10 times during several days. ICP-OES analysis: Co/Zn = 3:1.1.

*Formula weight of Zn2H-RPM including solvent molecules was estimated to be approximately 4000 by considering the formula of the framework (C₉₀H₄₂F₁₀N₁₀O₈Zn₃: FW= 1777.51) and TGA data of isostructural ZnZn-RPM⁸¹ (60% of the total weight belongs to the solvent molecules)

Zn:Co ratio was nearly 3:1. Possibility of the partial replacement was excluded since we added large excess of Co salt. Thus, we can assume two possibilities: a) Zn of the paddlewheel and the porphyrin-tetraacid unit are replaced by Co, b) Zn of the paddlewheel and 2H of porphyrin-dipy units are replaced by Co. From the ¹H NMR spectra, the peaks from free based porphyrin-dipy were disappeared after metalation. This result indicates that free based porphyrin-dipy was metallated by Co II to form paramagnetic cobalt porphyrin-dipy. Thus we concluded that the paddlewheel and porphyrin-dipy units are replaced by Co during the post synthetic metalation process.

b) Post-synthetic metalation with NiCl₂·4H₂O

ZnH₂-RPM (5mg, ca. 1 µmol) was suspended into DMF (1 ml) in a 2-dram screw-cap vial. To the suspension, NiCl₂·4H₂O (30mg, 0.15 mmol) was added and the vial was capped and placed in an oven at 80 °C for 24 h. After cooling to room temperature, the solvent was decanted and replaced with fresh DMF. The mixture was gently swirled and allowed to settle before the solution was decanted. The decanting-refilling process was repeated about 10 times during several days. ICP-OES analysis: Ni/Zn =2:1.0
Zn:Ni ratio was nearly 2:1. The possibility of the partial replacement was excluded since we added large excess of Ni salt. Thus, we can assume two possibilities, a) paddlewheel is replaced by Ni, b) two porphyrin units are replaced by Ni. But latter possibility was excluded since Zn porphyrin-tetraacid is quite hard to replace by other metal ions under the reaction conditions.

References