

**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 dipyrromethane (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, 4H, J = 4.7 Hz), 9.12 (d, 4H, 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^-)).

(5,15-Dipyridyl-10,20-bis(pentafluorophenyl))porphyrinato tin(IV) dihydroxide [$L^2-Sn(OH)_2$].

(5,15-Dipyridyl-10,20-bis(pentafluorophenyl))porphyrin (200 mg, 0.25 mmol) was dissolved in pyridine (20 ml). Tin chloride dihydrate (300 mg, 1.33 mmol) was added, and the solution was refluxed for 4h. During refluxing, flask was covered by aluminum foil to prevent light. After removal of solvent in vacuo, the product was purified by running through a short column of basic alumina eluted with 5 vol% MeOH in CH_2Cl_2 to obtain a purple solid (149 mg, 76% yield). 1H NMR (CD_3OD): 9.21 (d, 4H, $J = 4.8$ Hz), 9.17 (d, 4H, $J = 4.8$ Hz), 9.15 (d, 4H, $J = 5.8$ Hz), 8.28 (d, 4H, $J = 5.8$ Hz). MALDI-ToF MS: m/z 930.8 (Calcd m/z 931.0 for M^+ (w/out OH^-)).

General procedure for the synthesis of $[Zn_2(L^1-M^1)(L^2-M^2)]_n$ (M^1M^2 -RPM).

A solid mixture of L^1-2H (11.8 mg, 0.015 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (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 Zn_2H -RPM, $ZnCo$ -RPM and $ZnSn$ -RPM.

Zn_2H -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 $Zn(NO_3)_2 \cdot 6H_2O$. 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 $Zn(NO_3)_2 \cdot 6H_2O$ (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 $L^2\text{-Sn(OH)}_2$ (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 Zn_2H (non-ground sample)

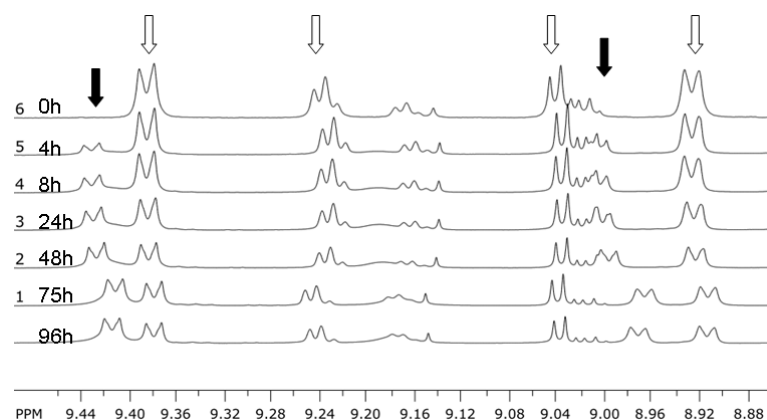


Figure S1 ^1H NMR spectra of linker exchanged samples (non-ground, dissolved into DMSO-d^6 with slight HCl).

Blank arrows: Zn-dipy , Filled arrows: 2H-dipy

b) ZnZn to ZnH_2 (ground sample)

^1H NMR spectra (dissolved into DMSO-d^6 with slight HCl). Blank arrows: Zn-dipy , Filled arrows: 2H-dipy

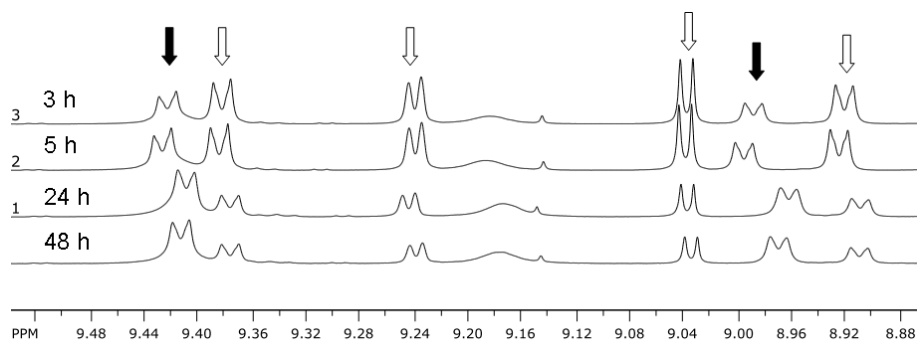
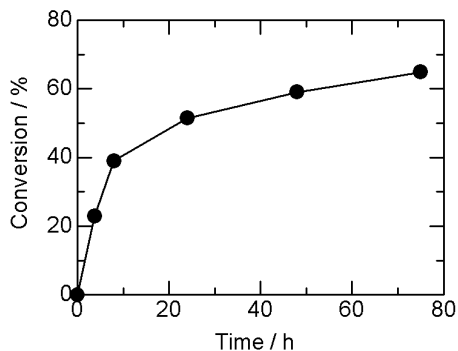


Figure S2 ^1H NMR spectra of linker exchanged samples (ground, dissolved into DMSO-d^6 with slight HCl).

Blank arrows: Zn-dipy , Filled arrows: 2H-dipy

c) ZnZn to ZnAl (non-ground sample)



ICP-OES result

3.5h Al : Zn = 0.23 : 3.77

8h Al : Zn = 0.39 : 3.61

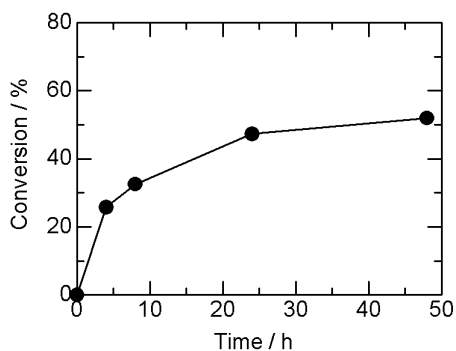
24h Al : Zn = 0.51 : 3.49

48h Al : Zn = 0.59 : 3.41

75h Al : Zn = 0.65 : 3.35

Figure S3 Time dependence of linker exchange reaction evaluated by ICP-OES result.

d) ZnZn to ZnSn (non-ground sample)



ICP-OES result

4h Sn : Zn = 0.26:3.74

8h Sn : Zn = 0.33:3.67

24h Sn : Zn = 0.47:3.53

48h Sn : Zn = 0.52:3.48

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

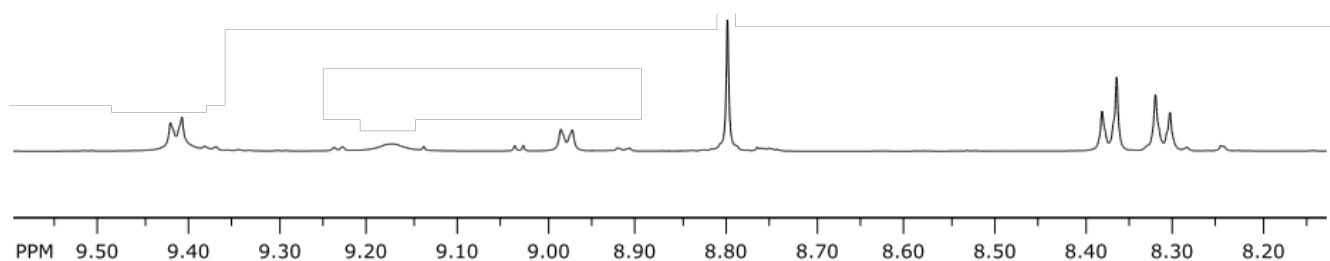


Figure S5 ¹H NMR spectrum of ZnH₂-RPM prepared by repeating SALE processes three times. (dissolved into DMSO-d₆ with slight HCl)

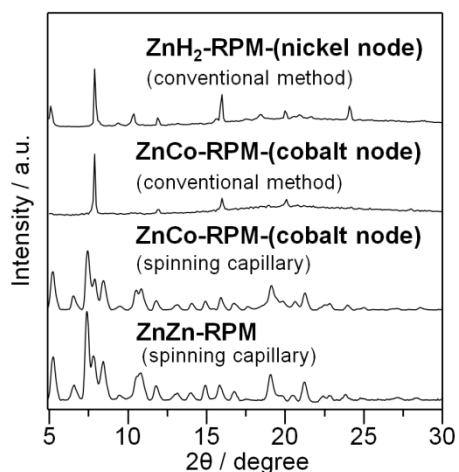


Figure S6 PXRD of Zn₂H-RPM-(nickel node), ZnCo-RPM-(cobalt node), and ZnZn-RPM

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).

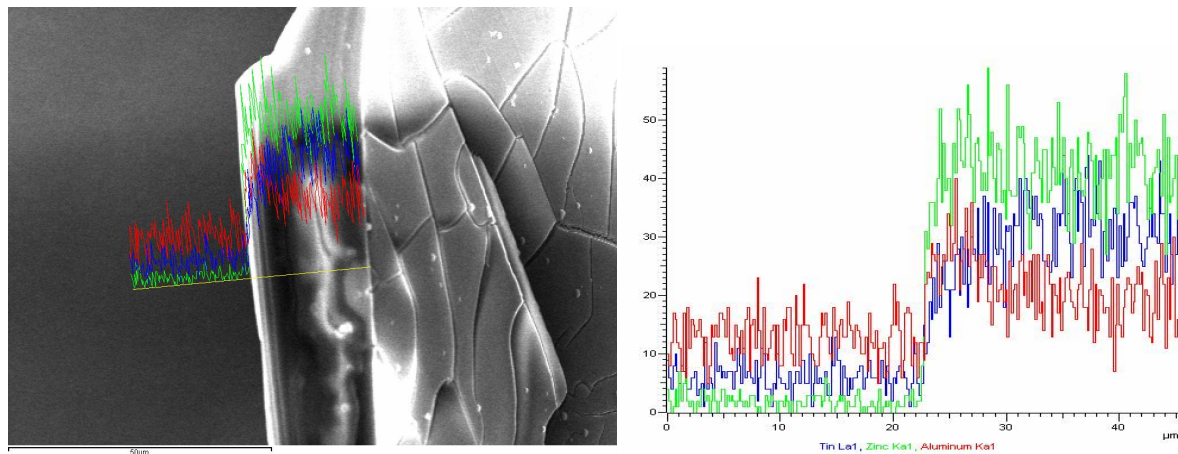


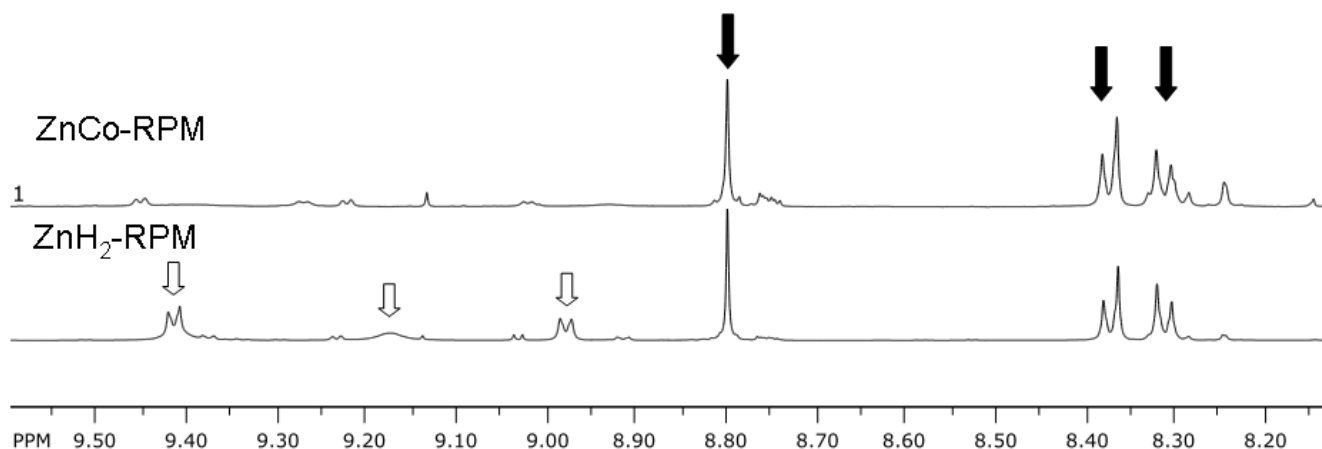
Figure S7 SEM image and associated EDS concentration profiles of ZnSn-RPM sample after SALE

V. Post-synthetic metalation:

a) Post-synthetic metalation with CoCl_2

$\text{Zn}_2\text{H-RPM}$ (5mg, ca. $1 \mu\text{mol}^*$) was suspended into DMF (1 ml) in a 2-dram screw-cap vial. To the suspension, CoCl_2 (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: $\text{Co}/\text{Zn} = 3:1.1$.

*Formula weight of $\text{Zn}_2\text{H-RPM}$ including solvent molecules was estimated to be approximately 4000 by considering the formula of the framework ($\text{C}_{90}\text{H}_{42}\text{F}_{10}\text{N}_{10}\text{O}_8\text{Zn}_3$; FW= 1777.51) and TGA data of isostructural $\text{ZnZn-RPM}^{\text{S1}}$ (60% of the total weight belongs to the solvent molecules)



$\text{Zn}:\text{Co}$ 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 $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$

$\text{Zn}_2\text{H-RPM}$ (5mg, ca. $1 \mu\text{mol}$) was suspended into DMF (1 ml) in a 2-dram screw-cap vial. To the suspension, $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$ (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: $\text{Ni}/\text{Zn} = 2:1.0$

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

S1 O. K. Farha, A. M. Shultz, A. A. Sarjeant, S. T. Nguyen and J. T. Hupp, *Journal of the American Chemical Society*, 2011, **133**, 5652-5655.