

Supporting Information

for

Dynamic Interconversion of Amorphous Microparticles and Crystalline Rods in Salen-based Homochiral Infinite Coordination Polymers**

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[**] CAM acknowledges the ARO, ONR and NSF for support of this work. He is also grateful for a NIH Director's Pioneer Award.

General Methods and Instrument Details

Solvents and all other chemicals were obtained from commercial sources and used as received unless otherwise noted. Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc. and used as received. ^1H NMR spectra were recorded on a Varian Mercury 300 MHz FT-NMR spectrometer and referenced relative to residual proton resonances in pyridine- d_5 and DMSO- d_6 . All chemical shifts are reported in ppm. Matrix assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF) were recorded on a Perseptive Biosystems Voyager Pro DE. Elemental analyses were performed by Quantitative Technologies Inc. Whitehouse, NJ. All scanning electron microscopy (SEM) images and energy dispersive X-ray (EDX) spectra were obtained using a Hitachi S-4500 cFEG SEM (Electron Probe Instruments Center (EPIC), NUANCE, Northwestern University) equipped with an Oxford Instruments EDS system. All optical and fluorescence microscopy images were obtained using a Zeiss Axiovert 100A inverted optical/fluorescence microscope (Thomwood, NY) equipped with a Penguin 600CL digital camera (HQ FITC/Bopidy/Fluo3/Dio/EGFP filter sets was used for green emission). Particle sizes and size distributions in solution were measured with a Zetasizer Nano-ZS.

Salen(Ni) Monomer H₂-1a. The ligand precursor **LP 1a** (40 mg, 59.3 μmol) and $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (15 mg, 60.3 μmol) were combined with pyridine (10 mL) and stirred for 6 h at room temperature (Scheme S1). The solvent was removed under reduced pressure, after which the precipitate was washed with methanol (3 x 10 mL). The product was isolated by filtration and dried under vacuum (42 mg, 97%). ¹H NMR ($\text{DMSO}-d_6$): δ 1.37 (br s, 11H, $-\text{C}(\text{CH}_3)_3$, $-\text{CH}_2-$), 1.78 (br s, 2H, $-\text{CH}_2-$), 3.14 (br s, 1H, $-\text{CH}-$), 7.48 (s, 1H, Ar-*H*), 7.68 (d, 2H, Ar-*H*), 7.76 (s, 1H, Ar-*H*), 7.84 (s, 1H, $-\text{CH}=\text{N}-$), 7.93 (d, 2H, Ar-*H*), 12.84 (br s, 1H, $-\text{CO}_2\text{H}$). IR (KBr pellet, cm^{-1}): 574 (w), 757 (w), 767 (w), 852 (w), 1173 (w), 1229 (w), 1273 (w), 1327 (w), 1341 (w), 1395 (w), 1424 (w), 1534 (w), 1599 (s), 1620 (m), 1683 (m), 2946 (w). MS (MALDI-TOF, m/z) = 730.54 (Calcd. for $\text{C}_{42}\text{H}_{44}\text{N}_2\text{O}_6\text{Ni}$ = 730.26). Elemental analysis for $\text{C}_{42}\text{H}_{44}\text{N}_2\text{O}_6\text{Ni} \cdot \text{H}_2\text{O}$ Calcd.: C, 67.30; H, 6.19; N, 3.74. Found: C, 67.00; H, 5.80; N, 3.83.

Salen(Ni) Monomer H₂-1b. The metallo-salen ligand **H₂-1b** was synthesized according to the method of **H₂-1a** using ligand precursor **LP 1b** (40 mg, 59.3 μmol) and $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (15 mg, 60.3 μmol) in pyridine (41 mg, 95%). ¹H NMR ($\text{DMSO}-d_6$): δ 1.33 (br s, 11H, $-\text{C}(\text{CH}_3)_3$, $-\text{CH}_2-$), 1.78 (br s, 2H, $-\text{CH}_2-$), 3.15 (br s, 1H, $-\text{CH}-$), 7.44-7.50 (m, 3H, Ar-*H*), 7.72 (s, 1H, Ar-*H*), 7.79 (s, 1H, $-\text{CH}=\text{N}-$), 7.88 (s, 1H, Ar-*H*), 8.11 (s, 1H, Ar-*H*), 13.04 (br s, 1H, $-\text{CO}_2\text{H}$). IR (KBr pellet, cm^{-1}): 578 (w), 687 (w), 758 (w), 786 (w), 1171 (w), 1264 (w), 1326 (w), 1343 (m), 1397 (w), 1427 (m), 1536 (w), 1584 (w), 1612 (s), 1620 (s), 1692 (m), 2946 (w). MS (MALDI-TOF, m/z) = 730.91 (Calcd. for $\text{C}_{42}\text{H}_{44}\text{N}_2\text{O}_6\text{Ni}$ = 730.26). Elemental analysis for $\text{C}_{42}\text{H}_{44}\text{N}_2\text{O}_6\text{Ni} \cdot \text{H}_2\text{O}$ Calcd.: C, 67.30; H, 6.19; N, 3.74. Found: C, 67.23; H, 5.80; N, 3.76.

Microparticle 2a. A precursor solution was prepared by mixing the corresponding salen ligand (26 mg, 38.5 μmol) and $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (20 mg, 80.3 μmol) in pyridine (10 mL). Diethyl ether was allowed to slowly diffuse into the precursor solution over 2 days. Particle products were isolated and subsequently washed with toluene via centrifugation and redispersion cycles. Each successive supernatant was decanted and replaced with fresh toluene (28 mg, ~ 90 %). The microparticle **2a** can

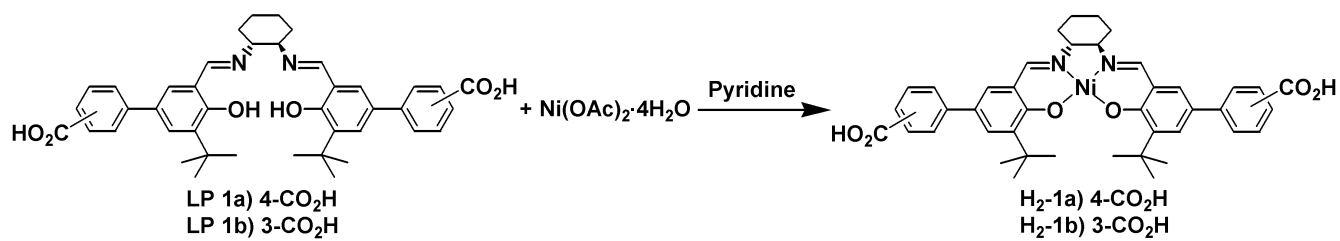
be synthesized using metallated salen precursor **1a** (10 mg, 13.6 μmol) and one equivalent of $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (3.5 mg, 14.0 μmol) in pyridine with a similar yield (9 mg, $\sim 84\%$, Scheme S2). Anal. Calcd. for $\text{Ni}(\mathbf{1a})(\text{Pyridine})$: C, 65.09; H, 5.46; N, 4.85. Found: C, 62.11; H, 5.56; N, 4.85. IR (KBr pellet, cm^{-1}): 572 (w), 699 (w), 769 (w), 787 (m), 1172 (m), 1343 (m), 1392 (s), 1437 (m), 1447 (m), 1531 (m), 1602 (vs), 1619 (s), 2945 (w). There are inherent difficulties in formulating the exact number of pyridine and other guest molecules in the particles due to the possibility of exchange with other molecules during washing and centrifugation steps.

Microparticle 2b. Microparticle **2b** was synthesized according to the method of **2a** using **LP 1b** (20 mg, 29.6 μmol) and $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (15 mg, 60.3 μmol) in pyridine/ether (14 mg, $\sim 60\%$). The microparticle **2b** can be synthesized using metallated salen precursor **1b** (10 mg, 13.6 μmol) and one equivalent of $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (3.5 mg, 14.0 μmol) in pyridine with similar yield (7 mg, $\sim 65\%$). Anal. Calcd. for $\text{Ni}(\mathbf{1b})(\text{Pyridine})$: C, 65.09; H, 5.46; N, 4.85. Found: C, 62.62; H, 5.42; N, 4.67. IR (KBr pellet, cm^{-1}): 577 (w), 685 (w), 696 (w), 771 (w), 1342 (w), 1389 (s), 1404 (m), 1423 (m), 1447 (w), 1535 (s), 1612 (vs), 1620 (vs), 2945 (w). There are inherent difficulties in formulating the exact number of pyridine and other guest molecules in the particles due to the possibility of exchange with other molecules during the washing and centrifugation steps.

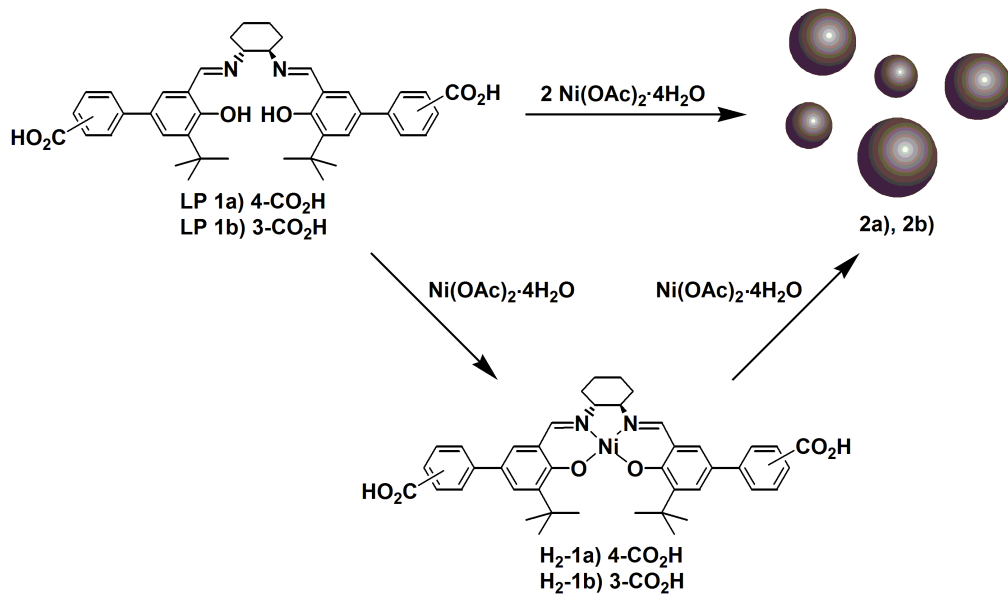
Crystalline rod 3a. Microparticle **2a** (15 mg) was immersed in MeOH and agitated vigorously by vortex mixing for 1 h at room temperature. Yellow precipitate was isolated and dried *in vacuo* (14 mg). Anal. Calcd. for $\text{Ni}(\mathbf{1b})(\text{Pyridine})_2(\text{MeOH})_8$: C, 59.92; H, 7.04; N, 4.66. Found: C, 60.35; H, 6.73; N, 4.16. IR (KBr pellet, cm^{-1}): 578 (w), 770 (w), 787 (w), 1172 (w), 1344 (w), 1392 (s), 1439 (m), 1531 (m), 1602 (vs), 2946 (w). Alternatively, single crystals were grown from a pyridine solution of precursors with methanol: IR (KBr pellet, cm^{-1}): 575 (w), 700 (w), 769 (w), 787 (w), 1172 (w), 1343 (w), 1392 (vs), 1439 (m), 1531 (m), 1603 (vs), 2945 (w).

Crystalline rod 3b. Crystalline **3b** was synthesized according to the method of **3a** using particle **2b** in quantitative yield. Anal. Calcd. for Ni(**1b**)(Pyridine)₂(MeOH)₆: C, 60.08; H, 6.75; N, 3.97. Found: C, 60.85; H, 6.59; N, 3.55. IR (KBr pellet, cm⁻¹): 577 (w), 687 (w), 771 (w), 787 (w), 1174 (w), 1326 (w), 1343 (s), 1390 (s), 1425 (s), 1536 (s), 1613 (vs), 1619 (vs), 2945 (w).

X-ray Crystallography. A red column crystal of **3a** having approximate dimensions of 0.250 x 0.224 x 0.070 mm was mounted using oil (Infinitec V8512) on a glass fiber. All measurements were made on a CCD area detector with graphite monochromated Mo K α ($\lambda=0.71073$ Å) radiation on a Bruker SMART-1000 diffractometer. The raw data collected were processed to produce conventional intensity data by the program SAINT. The intensity data were corrected for Lorentz and polarization effects. Absorption correction was also applied using the SADABS empirical method. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The ½ occupied pyridine solvent molecules were fixed in idealized rings. Hydrogen atoms were included in idealized positions, but not refined. The final cycle of full-matrix least-squares refinement on F² was based on 22126 reflections and 1313 variable parameters and converged (largest parameter shift was 0.021 times its esd) with unweighted and weighted agreement factors. Selected X-ray crystallographic data of **3a**: C_{57.5}H_{69.5}N_{4.5}Ni₂O₉, Trilinic, space group *P1* (no. 1), $a = 13.3754(12)$ Å, $b = 15.3953(14)$ Å, $c = 15.7098(15)$ Å, $\alpha = 70.609(2)^\circ$, $\beta = 70.501(2)^\circ$, $\gamma = 67.214(2)^\circ$, $V = 2733.9(4)$ Å³, $Z = 2$, $T = 153(2)$ K, $2\theta_{\max} = 57.7^\circ$, MoK α ($\lambda = 0.71073$ Å), $R_1 = 0.0762$ ($I > 2\sigma(I)$), $wR_2 = 0.2447$ (all data), and GOF on F² = 1.028 for 1313 parameters and 22126 unique reflections.



Scheme S1. Synthesis of metallo-salen ligand **H₂-1a** and **H₂-1b**.



Scheme S2. Direct and stepwise synthesis of ICP particles **2a** and **2b**.

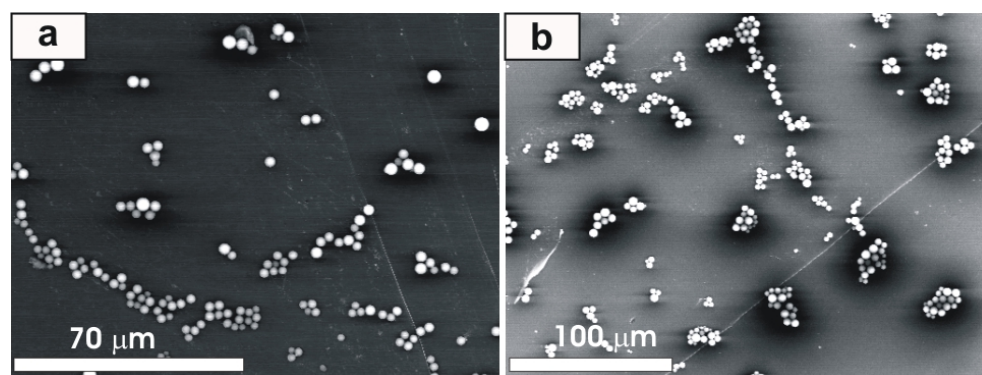


Figure S1. SEM images of ICP particles in large area for: (a) **2a** and (b) **2b**.

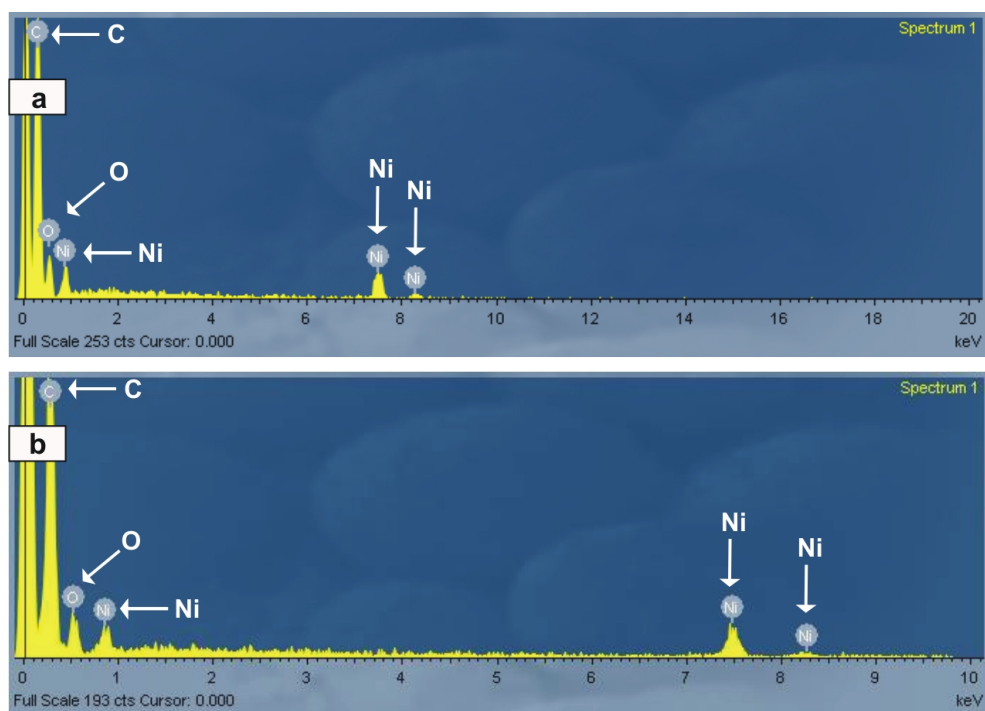


Figure S2. EDX spectra of ICP particles for: (a) **2a** and (b) **2b**.

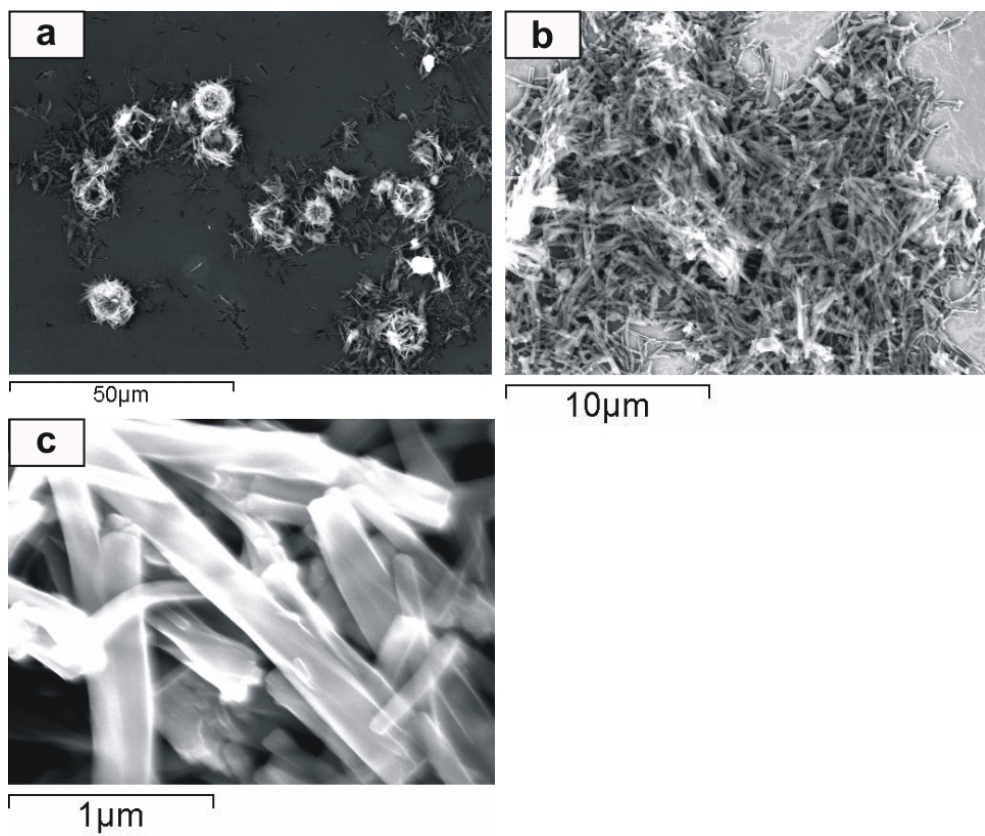


Figure S3. SEM images of crystalline rods for: (a) **3a**, (b) **3b** (large area) and (c) **3b** (zoom).

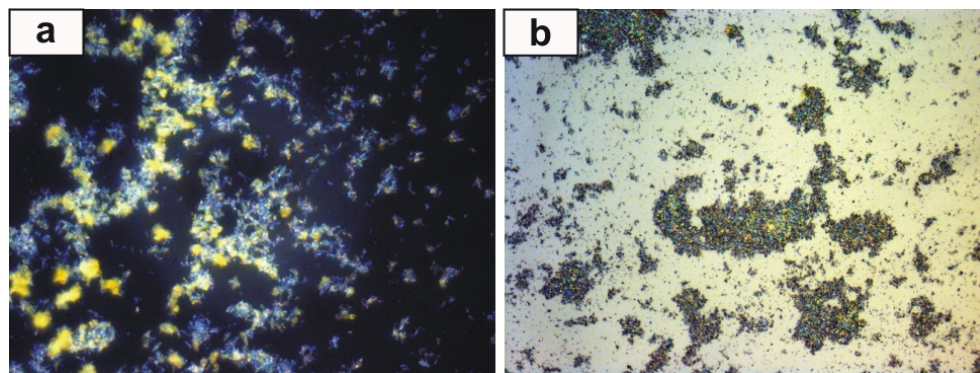


Figure S4. OM images of crystalline rods of (a) **3a** and (b) **3b**.

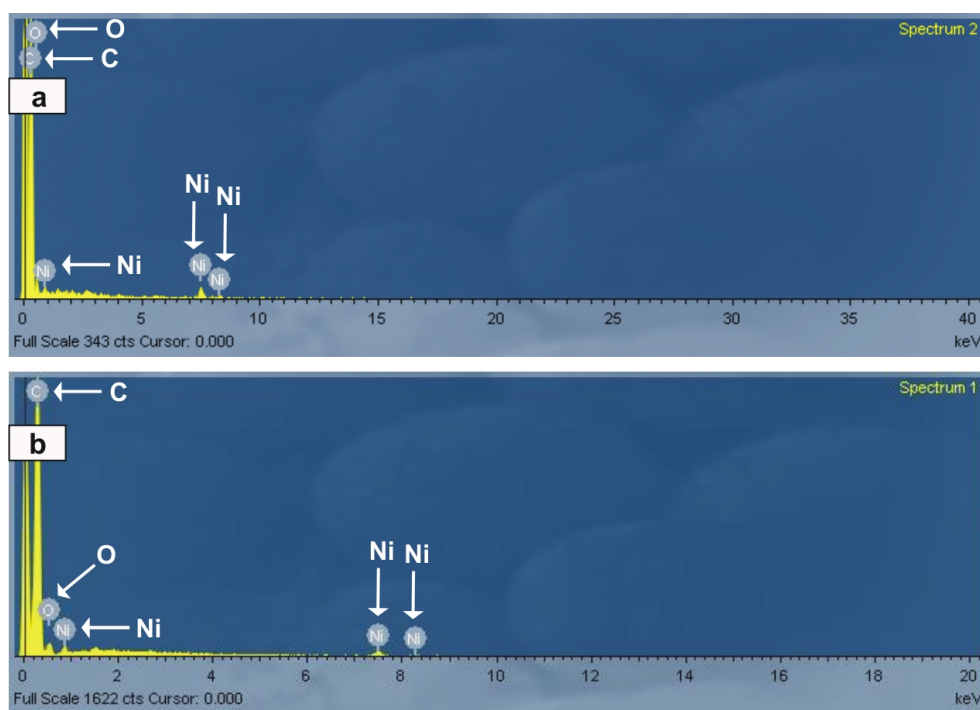


Figure S5. EDX spectra of crystalline rods for: (a) **3a** and (b) **3b**.

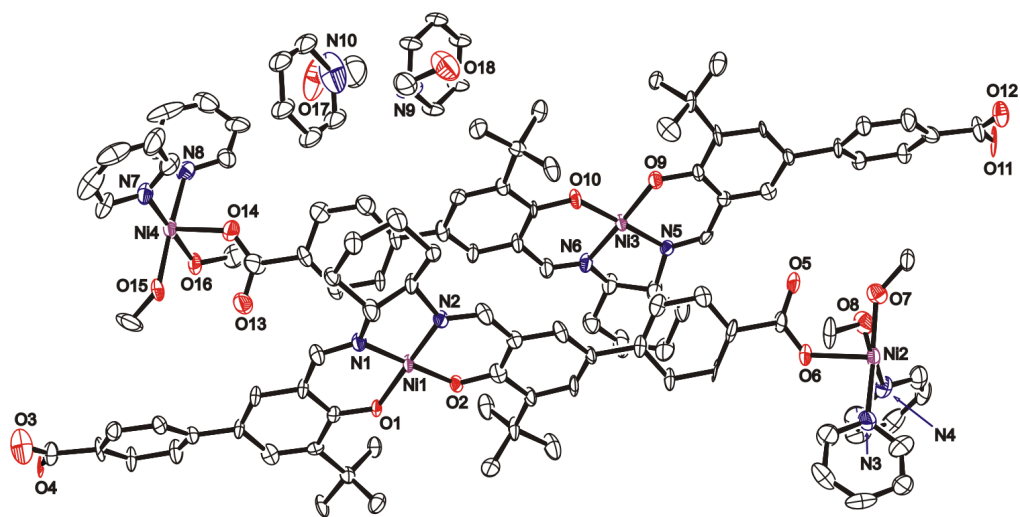


Figure S6. ORTEP diagram of asymmetric unit of crystalline ICP **3a** and selected labeling scheme with ellipsoid probability 50% (Hydrogen atoms have been omitted for clarity).

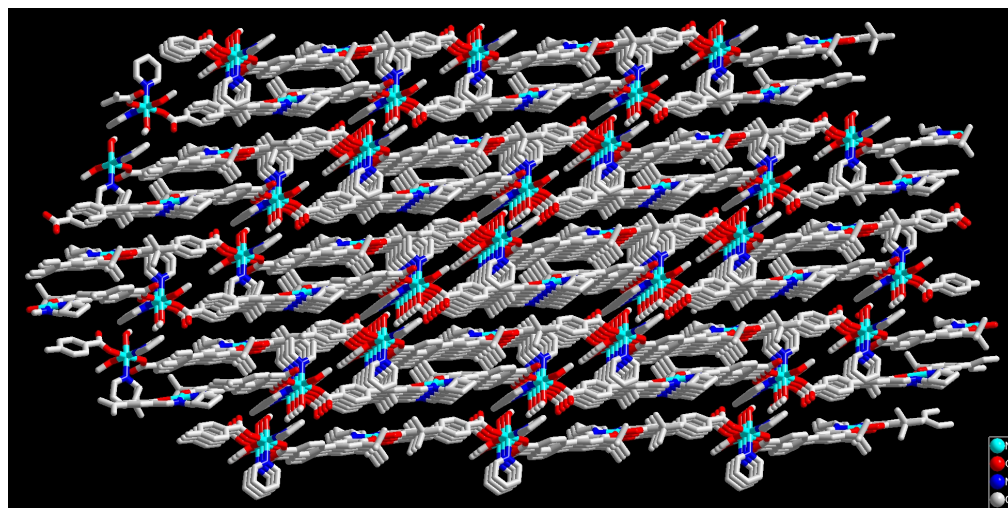


Figure S7. Stick representation of packing diagram of crystalline ICP **3a**. Hydrogen atoms and free pyridine and methanol molecules have been omitted for clarity.

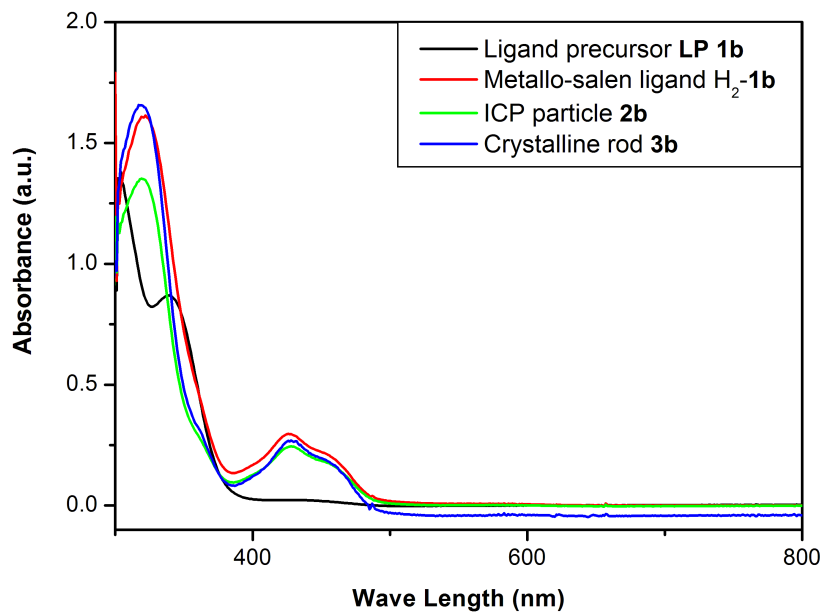


Figure S8. UV-Vis spectra of ligand precursor **LP 1b**, metallo-salen ligand **H₂-1b**, ICP particle **2b**, and crystalline rod **3b** in pyridine solution.

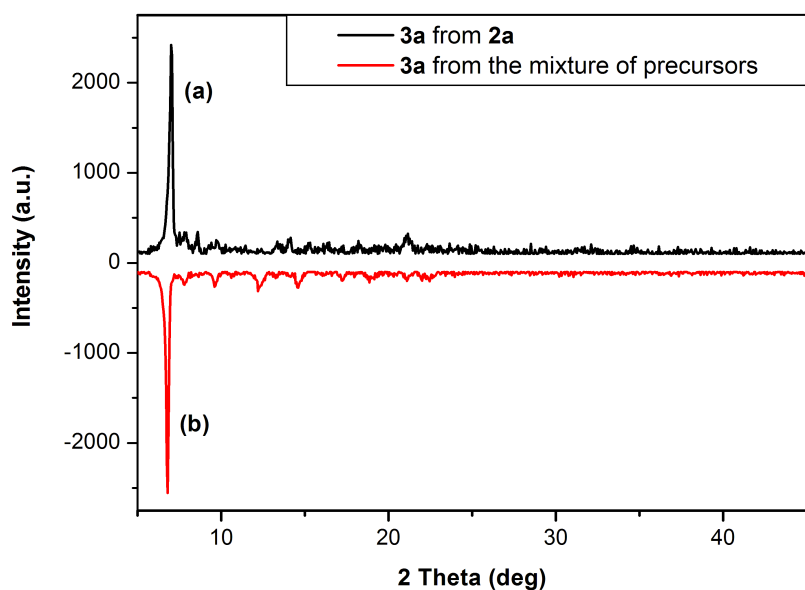


Figure S9. XRD spectra of crystalline complex **3a**: (a) crystalline rods transformed from the ICP particle **2a** and (b) single crystals grown from the mixture of precursors in pyridine/methanol solution.