

Supporting Information

Transistor properties of salen-type metal complexes

Kyohei Koyama, Kodai Iijima, Dongho Yoo, and Takehiko Mori

Synthesis

All commercial chemicals and solvents were used without further purification. The data of Nuclear Magnetic Resonance spectrum (NMR) and Mass spectrum (MS) were obtained with a JEOL JNM-AL300 spectrometer and a JEOL JMS-Q1050GC mass spectrometer, respectively.

H₂(salen)²⁸ To a 20 mL methanol solution of ethylenediamine monohydrate (10 mmol, 0.78 g) was dropwise added salicylaldehyde (20 mmol, 2.44 g), and stirred for 3 h. The yellow precipitate was filtered, washed with methanol, and dried in vacuo to give the product (2.01 g, yield 75%). EI-MS *m/z*: 268 [M]⁺; ¹H NMR (CDCl₃): δ 13.19 (s, 2H), 8.36 (s, 2H), 7.32-7.22 (m, 4H), 6.95-6.86 (m, 4H), 3.95 (t, 4H).

Cu(salen)¹⁵⁻¹⁹ To a 15 mL ethanol solution of H₂(salen) (3 mmol, 0.80 g) in Ar was added copper acetate monohydrate (3 mmol, 0.54 g) dissolved in 20 mL methanol, and stirred for 3 h. The green solid was filtered, washed with methanol, and dried in vacuo. Recrystallization from dichloromethane/ethanol afforded green crystals (0.73 g, 74%). EI-MS *m/z*: 329 [M]⁺.

Ni(salen)¹⁵⁻¹⁹ To a 15 mL ethanol solution of H₂(salen) (3 mmol, 0.80 g) in Ar was added nickel acetate tetrahydrate (3 mmol, 0.74 g) dissolved in 15 mL methanol, and stirred for 4 h. The red solid was filtered, washed with methanol, and dried in vacuo. Recrystallization from dichloromethane/ethanol afforded red crystals (0.80 g, 83%). EI-MS *m/z*: 324 [M]⁺; ¹H NMR (CDCl₃): δ 7.49 (s, 2H), 7.23-7.12 (m, 2H), 7.05 (t, 4H), 6.53 (t, 2H), 3.44 (t, 4H).

Pd(salen)²⁰⁻²¹ To a 10 mL methanol solution of H₂(salen) (1 mmol, 0.27 g) was added palladium chloride (1 mmol, 0.17 g) dissolved in 10 mL methanol, and refluxed for 4 h. The white yellow solid was filtered, washed with methanol, and dried in vacuo. Recrystallization from chloroform gave yellow crystals (0.17 g, 46%). EI-MS *m/z*: 372 [M]⁺.

Co(salen)¹⁵ To a 10 mL ethanol solution of H₂(salen) (1 mmol, 0.27 g) was added cobalt chloride hexahydrate (1 mmol, 0.24 g) dissolved in 10 mL methanol, and refluxed for 2 h. The black solid was filtered, washed with methanol, and dried in vacuo. Recrystallization from methanol afforded brown crystals (0.10 g, 31%). EI-MS *m/z*: 325 [M]⁺.

H₂(salpn)²² To a 10 mL ethanol solution of propylenediamine (5 mmol, 0.78 g) was dropwise added salicylaldehyde (10 mmol, 1.23 g), and refluxed for 15 h. The yellow liquid was evaporated in vacuo. The yellow to orange solid was washed with methanol, and dried in vacuo to give the product (0.91 g, yield 65%). EI-MS *m/z*: 282 [M]⁺.

Cu(salpn)²² To a warm 5 mL ethanol solution of H₂(salen) (2 mmol, 0.56 g) containing 2 mL 25% aqueous ammonia was added copper acetate monohydrate (2 mmol, 0.40 g) dissolved in 5 mL warm water, and stirred for 2 h. The green solid was filtered, washed with ethanol, and dried in vacuo. Recrystallization from dichloromethane/ethanol afforded green crystals (0.50 g, 72%). EI-MS *m/z*: 343 [M]⁺.

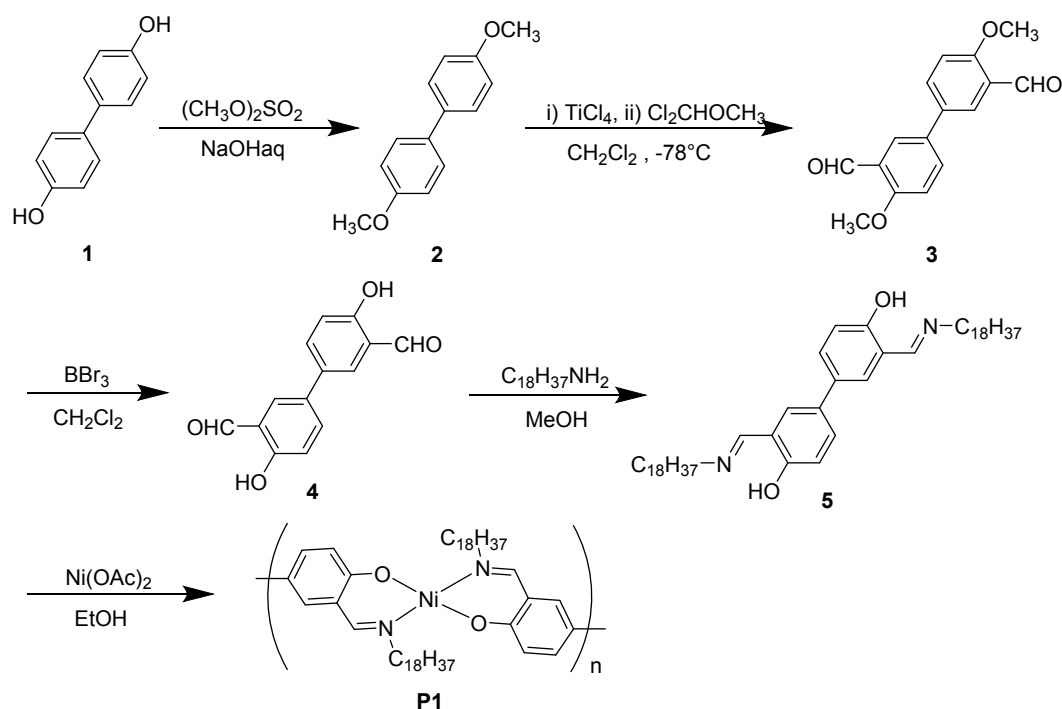
Ni(salpn)²² To a warm 5 mL ethanol solution of H₂(salen) (1.8 mmol, 0.50 g) containing 2 mL 25% aqueous ammonia was added nickel acetate tetrahydrate (1.8 mmol, 0.45 g) dissolved in 5 mL warm water, and stirred for 2 h. The green solid was filtered, and dried in vacuo. Recrystallization from dichloromethane/ethanol afforded green crystals (0.18 g, 30%). EI-MS *m/z*: 338 [M]⁺.

H₂(salcyh)²³⁻²⁶ To a 10 mL methanol solution of *trans*-cyclohexanediamine (10 mmol, 1.24 g) was added salicylaldehyde (5 mmol, 1.24 g), and stirred for 3 h. The yellow solid was filtered. Recrystallization from methanol afforded a yellow solids (1.00 g, yield 62%). EI-MS *m/z*: 322 [M]⁺.

Cu(salcyh)²³ To a warm 5 mL methanol solution of H₂(salcyh) (0.5 mmol, 0.16 g) was added copper acetate monohydrate (0.5 mmol, 0.10 g) dissolved in 6 mL methanol, and stirred for 2 h. The violet solid was filtered, washed with ethanol, and dried in vacuo to afford a violet solid (0.15 g, 78%). EI-MS *m/z*: 383 [M]⁺.

Ni(salcyh)^{24,26} To a warm 10 mL ethanol solution of H₂(salcyh) (1 mmol, 0.32 g) was added nickel acetate tetrahydrate (1 mmol, 0.25 g), and stirred for 2 h. The orange solid was filtered, washed with ethanol, and dried in vacuo to afford an orange solid (0.31 g, 82%). EI-MS *m/z*: 379 [M]⁺.

Metal complexes were sublimed under a pressure of 10⁻⁴ Pa before the device fabrication.



Scheme S1. Synthesis route of **P1**.

P1

4,4'-Dihydroxy-[1,1'-biphenyl]-3,3'-dicarbaldehyde (**4**) was prepared from 4,4'-

dihydroxybiphenyl (**1**).^{29,S1}

4,4'-Dihydroxy-[1,1'-biphenyl]-3,3'-dicarbaldehyde (**4**, 0.6 mmol, 0.15 g) was added to octadecylamine (1.2 mmol, 0.33 g) dissolved in 20 mL methanol in Ar. The mixture was refluxed for 2 h. After cooled to room temperature, filtration and recrystallization from hexane gave a yellow solid of 3,3'-bis((E)-(octadecylimino)methyl)-[1,1'-biphenyl]-4,4'-diol (**5**, 0.25 g, 56 %). MALDI-TOF MS ($M_w = 745.23$): $m/z = 745.14$ [M^+].

5 (0.18 g, 0.25 mmol) dissolved in 6 ml dry ethanol was added to nickel (II) acetate tetrahydrate (0.1 g, 0.25 mmol) in 6 ml hot ethanol in Ar. The mixture was stirred overnight at 75 °C. The solution slowly changed from yellow to green and a solid appeared. A green sparingly soluble solid was collected by filtration. MALDI-TOF MS consists of a series of peaks with the interval of 800 ($M_w = 799.85$) starting from the monomer ($M_w = 1541.01$): $m/z = 1541.05$ [M^+].

Cyclic Voltammetry (CV) and ultraviolet-visible spectroscopy (UV-Vis)

Redox potentials were measured by cyclic voltammetry (CV) on an ALS model 701E electrochemical analyzer (Figs. 1 and S1) using DMF, chloroform, acetonitrile, and trichloroethane as a solvent and 0.1 M tetrabutylammonium hexafluorophosphate as an electrolyte. The working electrode was glassy carbon, and the counter electrode was platinum. Ag in a 0.1 M AgNO₃ solution was used as a reference electrode, and scanned at 100 mV s⁻¹. The HOMO levels were estimated by assuming the reference energy level of ferrocene/ferrocenium (Fc/Fc⁺: $E^{1/2} = +0.195$ V vs. Ag/AgNO₃ measured under the identical conditions) to be 4.8 eV from the vacuum level (Table 1).

UV-Vis spectra were collected on a Shimadzu UV1800 Spectrophotometer in DMF, chloroform, acetonitrile, trichloroethane, and Cu(salen) thin film (Figs. 1 and S1). Thin film was fabricated by vacuum deposition same as device fabrication. The optical gaps were estimated from the absorption edges (Table 1). The LUMO levels were evaluated from the HOMO levels by adding the optical gaps.

Table S1. Solvents used in the CV and UV-Vis measurements.

solvent	substances
DMF	Cu(salen), Ni(salen), Pd(salen)
chloroform	Co(salen), Cu(salcyh), Ni(salcyh)
acetonitrile	Cu(salpn), Ni(salpn)
trichloroethane	P1

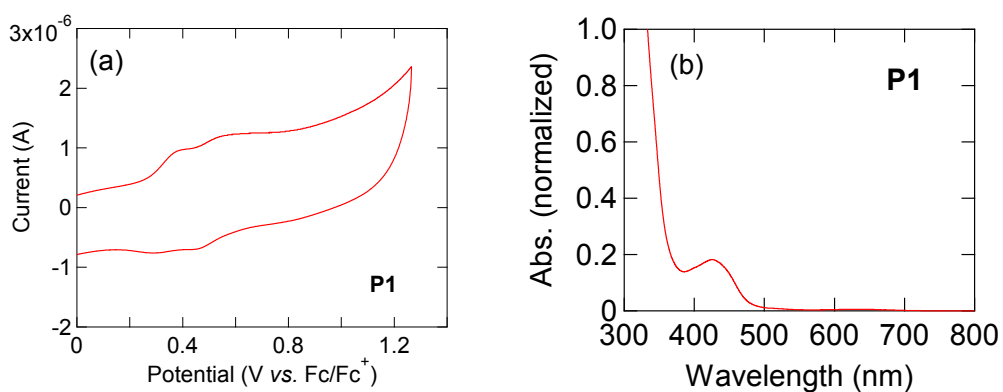


Fig. S1. (a) Cyclic voltammograms, and (b) absorption spectrum of of **P1**.

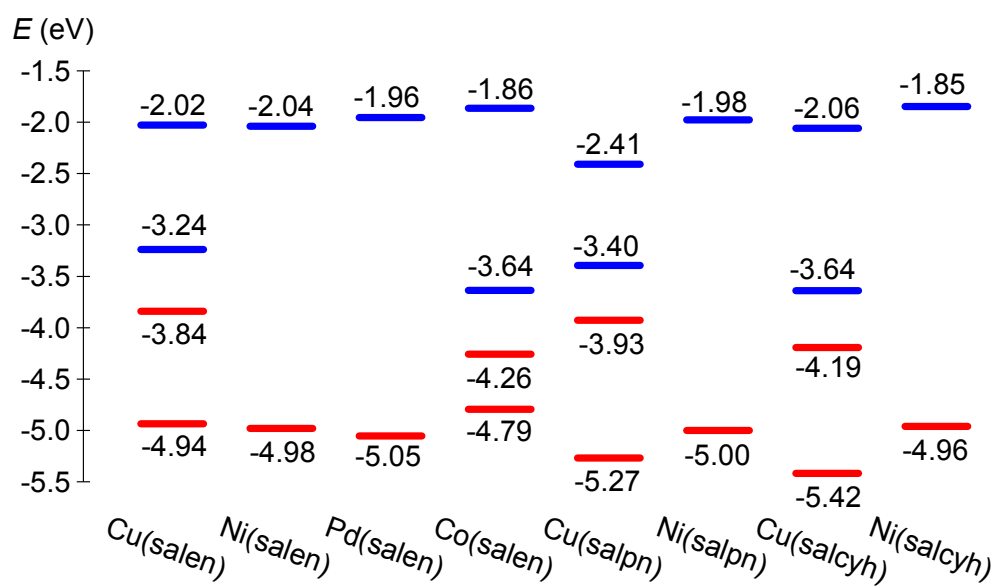


Fig. S2. Calculated energy levels of the complex dimers.

Device fabrication and thin-film properties

The transistors were prepared by using a commercially available heavily doped *n*-type Si wafer with 300 nm SiO₂ insulator ($\epsilon = 3.9$ and the capacitance of 11.5 nF cm⁻²) as a gate.^{S2} A passivation layer of TTC was evaporated ($\epsilon = 2.5$ and 20 nm thickness with the capacitance of 106 nF cm⁻²),⁷ and the resulting overall capacitance of the gate dielectric was 10.4 nF cm⁻². Then the metal complexes (50 nm) were vacuum evaporated at a rate of 1.0 Å s⁻¹ under a pressure of 10⁻³ Pa. Gold source and drain (S/D) electrodes were evaporated through a shadow mask ($L/W = 100/1000$ μm) at a pressure of 10⁻³ Pa to accomplish the bottom-gate top-contact transistors. Transistor characteristics were measured with a Keithley 4200 semiconductor parameter analyzer under vacuum. The mobility values were evaluated from the transconductance in the saturated region. The average values were average for at least four devices. The output characteristics are shown in Fig. S3.

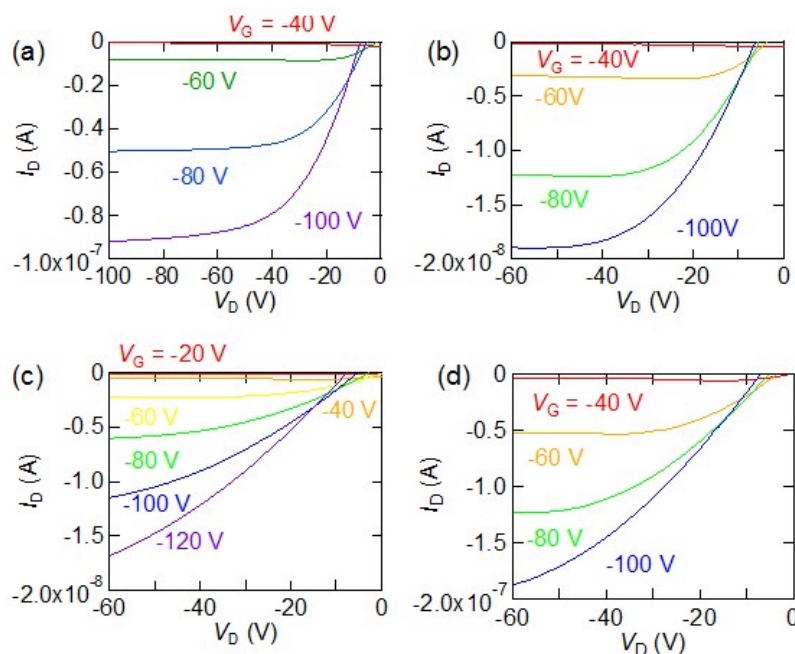


Fig. S3. Output characteristics of (a) Cu(salen), (b) Pd(salen), (c) Co(salen), and (d) Ni(salcyh).

Estimation of transfer integrals

Molecular orbital calculations in the B3LYP* level with TZP basis set were performed using the the Amsterdam Density Functional (ADF) program.³¹ The molecular orbitals were very similar to the results of the AM1 calculations.³⁹ In order to calculate the transfer integrals, the frozen orbital approximation was adopted, where the molecular orbitals were extracted and used to calculate the intermolecular transfers to the bridge orbitals.⁴⁰

Thin film properties

The X-ray diffraction (XRD) patterns were taken by using a Philips X'Pert-Pro-MRD with CuK α radiation ($\lambda = 1.540598 \text{ \AA}$).

Atomic force microscopy (AFM) images were taken by an SII scanning probe microscope system SPI3800N and SPA-300 by using a Si₃N₄ cantilever in air (Fig. S4).

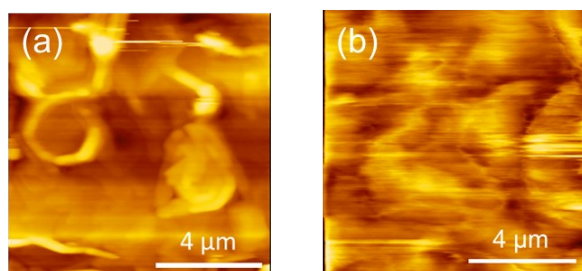


Fig. S4. Atomic force microscopy (AFM) images of (a) Pd(salen), and (b) Co(salen).

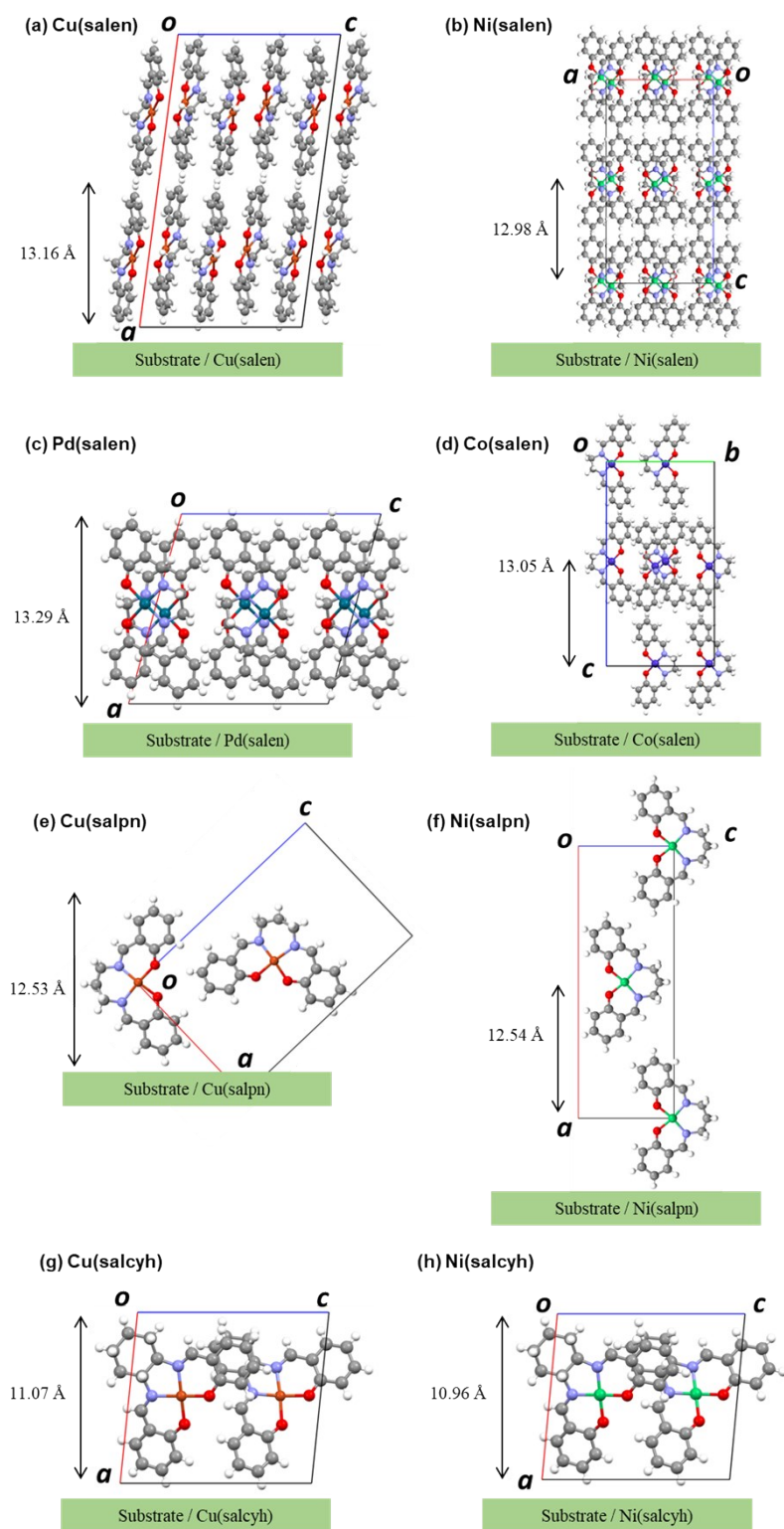


Fig. S5. Molecular arrangements of the complexes on the substrates.

Polymer

The conductivity was measured by placing a pellet of P1 (17.7 MPa, 30 s) on a plastic substrate. The pellet was connected to gold wires by carbon paste. The substrate was placed in iodine vapor when monitoring the conductivity. The conductivity was measured with a Keithley 4200 semiconductor parameter analyzer. The conductivity change during and after iodine doping is shown in Fig. S6.

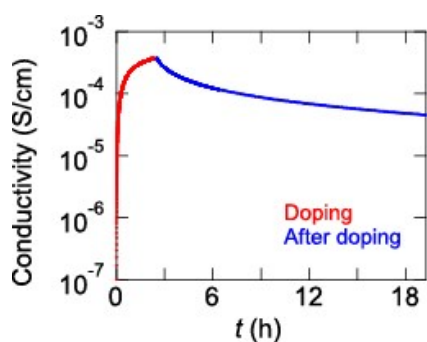


Fig. S6. Conductivity of **P1** during and after iodine doping.

References

- S1 P. Jagadesan, G. Eder and P. L. McGrier, *J. Mater. Chem. C*, 2017, **5**, 5676.
- S2 K.-J. Baeg, Y.-Y. Noh, J. Ghim, B. Lim and D.-Y. Kim, *Adv. Funct. Mater.*, 2008, **18**, 3678.