Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

for

Heteroleptic bis(dipyrrinato)copper(II) and nickel(II) complexes

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1. General experimental procedures

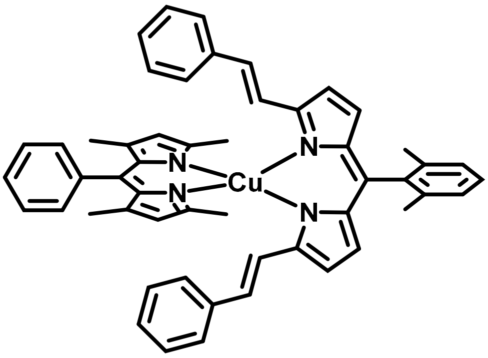
All commercially available chemicals were purchased and used without further purification unless otherwise noted. Preparative gel permeation liquid chromatography (GPC) was performed by LC-918 with JAIGEL 1H and 2H column (Japan Analytical Industry) using chloroform as the mobile phase. ^{1}H NMR and ^{13}C NMR data were collected in $CDCl_3$ on a Bruker US500 spectrometer. Tetramethylsilane ($\delta_H = 0.00$) was used as an internal standard for the ^{1}H NMR spectrum, and $CDCl_3$ ($\delta_C = 77.00$) was used as an internal standard for the ^{13}C NMR spectrum, respectively. High resolution mass spectroscopy was performed on JEOL JMS-700MStation mass spectrometer (HRFAB-MS). UV-visible absorption spectra were recorded on a JASCO V-570 spectrometer. Fluorescence spectra were collected with a HITACHI F-4500 spectrometer. X-ray diffraction data were collected at 93 K on a Rigaku Saturn724 (Varimax dual) diffractometer with multi-layer mirror monochromated MoKα radiation ($\lambda = 0.71075$ Å) using Crystal Clear (Rigaku) or at 173 K on a Rigaku Saturn724 diffractometer with graphite monochromated MoKα radiation ($\lambda = 0.71070$ Å) using Crystal Clear (Rigaku). The structures were solved by means of the direct method using SIR92[S1] and refined by the full-matrix least-squares using SHELXL97.[S2] CCDC 1047911 (for **3**) and 1047912 (for **4**) contain the supplementary crystallographic data for this paper. These data may be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Cyclic voltammetry and chronocoulometry were performed by ALS 650DT electrochemical analyzer. For each measurement, an Ag^+/Ag reference electrode (0.01 M $AgClO_4$ and Bu_4NClO_4/acetonitrile) and a Pt wire counter electrode were implemented in order to establish a three-electrode system. The cell was filled with dichloromethane solution of each sample (0.5 mM) and Bu_4NClO_4 (0.1 M) as an electrolyte. The cell was sealed, and was deoxygenized by Ar bubbling for more than 5 min prior to a measurement.

2. Synthesis

2.1 Dipyrrin ligands

The two ligands for the complexes, **1** and **2**, were obtained following the reported methods.[S3]

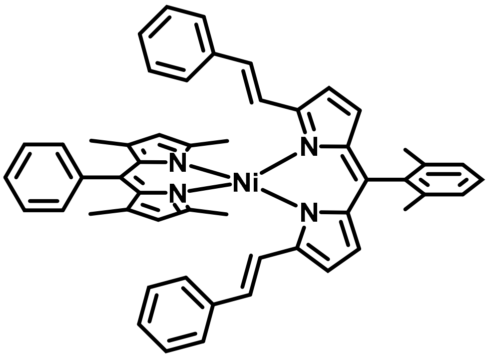
2.1 Copper complex 3



To a MeOH (5 mL) solution of $Cu(OAc)_2$ (25 mg, 0.14 mmol),was added a $CHCl_3$ (20 mL) solution of **1** (56 mg, 0.20 mmol) and **2** (91 mg, 0.20 mmol). After stirring the reaction mixture overnight at room temperature, the solvent was evaporated and the residue was purified by GPC to give complex **3** (16 mg, 15 %) as a brown solid.

HRFAB-MS: 789.2991 $[M]^+$, calcd. for : $C_{52}H_{46}N_4Cu^+$: 789.3018.

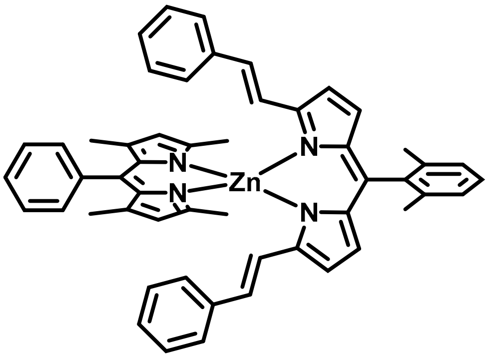
2.1 Nickel complex 4



To a MeOH (5 mL) solution of $Ni(OAc)_2\cdot 4H_2O$ (35 mg, 0.14 mmol), was added a $CHCl_3$ (20 mL) solution of **1** (56 mg, 0.20 mmol) and **2** (91 mg, 0.20 mmol). After stirring the reaction mixture overnight at room temperature, the solvent was evaporated and the residue was purified by GPC to give complex **4** (44 mg, 40 %) as a brown solid.

HRFAB-MS: 784.3070 $[M]^+$, calcd. for : $C_{52}H_{46}N_4Ni^+$: 784.3076.

2.3 Zinc complex 5



To a MeOH (5 mL) solution of $Zn(OAc)_2$ (25 mg, 0.14 mmol), was added a $CHCl_3$ (20 mL) solution of **1** (55 mg, 0.20 mmol) and **2** (91 mg, 0.20 mmol). After stirring the reaction mixture overnight at room temperature, the solvent was evaporated and the residue was purified by GPC to give complex **5** (48 mg, 44 %) as a brown solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ= 7.53–7.54 (m, 3H), 7.44–7.46 (m, 2H), 7.20–7.28 (m, 11H), 7.14 (d, J = 7.6 Hz, 2H), 7.03 (d, J = 16 Hz, 2H), 6.95(d, J = 16 Hz, 2H), 6.76 (d, J = 4.4 Hz, 2H), 6.52 (d, J = 4.1 Hz, 2H), 5.96 (s, 2H), 2.20 (s, 6H), 2.01 (s, 6H), 1.39 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.78, 157.07, 144.95, 144.54, 141.68, 140.80, 140.25, 138.50, 137.37, 136.96, 135.62, 132.05, 131.27, 129.86, 128.71, 128.55, 128.35, 127.81, 127.61, 126.90, 126.82, 122.76, 121.02, 115.06, 19.82, 16.19, 15.51; HRFAB-MS: 790.3032 $[M]^+$, calcd. for : $C_{52}H_{46}N_4Zn^+$: 790.3014.

3. X-ray Crystallographic data

3.1 Copper complex 3

Table S1. Crystallographic data for **3**

Empirical Formula	$C_{52}H_{46}CuN_4$
Formula Weight / g mol^{-1}	790.51
Temperature / K	93
λ / Å	0.71075
Crystal System	triclinic
Space Group	P-1
a / Å	8.024(3)
b / Å	12.015(5)
c / Å	21.266(9)
α / °	87.690(9)
β / °	89.191(9)
γ / °	88.2546(10)
V / Å^3	2047(2)
Z	2
d_{calcd} / g cm^{-3}	1.282
μ (MoKα) / cm^{-1}	5.749
F (000)	830.00
Crystal size / mm^3	0.350×0.050×0.050
Theta range for data collection	3.00 to 27.50 °
Index ranges	-10<=h<=10, -15<=k<=15, -18<=l<=27
Reflections collected	16535
Independent reflections	8976 (R_{int} = 0.0564)
Data completeness	95.3 %
Max. and min. transmission	0.692 and 0.972
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8976 / 0 / 514
[a] Goodness-of-Fit on F^2	1.000
[b] R_1 [$I > 2.00\sigma(I)$]	0.0623
[c] wR_2 (all reflections)	0.2049
Largest diff. peak and hole / eÅ^{-3}	0.84 and -1.01

[a] GOF = $[\Sigma(w(Fo^2 - Fc^2)^2/\Sigma(Nr - Np)^2]$. [b] $R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$ ($I > 2\ \sigma\ (I)$).

[c] $wR_2 = [\Sigma(w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$ ($I > 2\ \sigma(I)$).

3.2 Nickel complex 4

Table S2. Crystallographic data for **4**

Empirical Formula	$C_{52}H_{46}NiN_4$
Formula Weight / g mol^{-1}	785.66
Temperature / K	173
λ / Å	0.71070
Crystal System	triclinic
Space Group	P-1
a / Å	8.0620(12)
b / Å	12.042(2)
c / Å	21.376(4)
α / °	87.391(3)
β / °	88.849(4)
γ / °	88.017(3)
V / Å^3	2071.4(6)
Z	2
d_{calcd} / g cm^{-3}	1.260
μ (MoKα) / cm^{-1}	5.094
F (000)	828.00
Crystal size / mm^3	0.100×0.300×0.500
Theta range for data collection	3.18 to 27.48 °
Index ranges	-9<=h<=10, -15<=k<=15, -26<=l<=27
Reflections collected	16143
Independent reflections	9013 (R_{int} = 0.0183)
Data completeness	94.6 %
Max. and min. transmission	0.833 and 0.950
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9013 / 0 / 520
[a] Goodness-of-Fit on F^2	1.038
[b] R_1 [$I > 2.00\sigma(I)$]	0.0379
[c] wR_2 (all reflections)	0.1018
Largest diff. peak and hole / eÅ^{-3}	0.35 and -0.37

[a] GOF = $[\Sigma(w(Fo^2 - Fc^2)^2/\Sigma(Nr - Np)^2]$. [b] $R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$ ($I > 2\sigma(I)$).

[c] $wR_2 = [\Sigma(w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$ ($I > 2\sigma(I)$).

4. Chronocoulometry

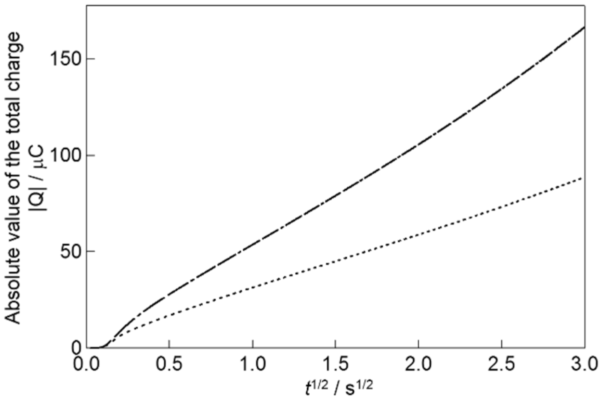


Fig. S1 $|Q|$-$t^{1/2}$ plots of the oxidation process (dashed dotted line) and the reduction process (dotted line) in the cyclic voltammogram of **4**.

Fig. S1† shows the $|Q|$-$t^{1/2}$ plots, where Q is the total charge and t is the elapsed time. Apart from the beginning of the polarization, where charging of the electric double layer plays a chief role, the $|Q|$-$t^{1/2}$ plot shows a linear relationship. Therefore, both the oxidation and reduction processes are diffusion-controlled. In this scenario, eq (1) may be applicable.[S4]

$$Q = 2nFACD\pi^{1/2}t^{1/2} \qquad (1)$$

where n is the number of electrons involved in the redox reaction, F is the Faraday constant, A is the electrode area, C is the concentration, and D is the diffusion coefficient of the analyte. All factors are common for the oxidation and reduction of **4** except for n; hence, the slope of the $|Q|$-$t^{1/2}$ plot is proportional to n. The slopes are 5.7×10^{-5} and 2.9×10^{-5} for oxidation and reduction, respectively, indicating a ratio of 2:1 for n.

5. References for ESI

S1 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.

S2 G. M. Sheldrick, *Acta Crystallogr. A.*, 2008, **64**, 112.

S3 (*a*) M. Tsuchiya, R. Sakamoto, S. Kusaka, Y. Kitagawa, M. Okumura and H. Nishihara, *Chem. Commun.*, 2014, **50**, 5881; (*b*) S. Telitel, J. Lalevée, N. Blanchard, T. Kavalli, M. Tehfe, S. Schweizer, F. Morlet-Savary, B. Graff and J. Fouassier, *Macromolecules*, 2012, **45**, 6864.

S4 A. J. Bard, L. R. Faulkner, in *Electrochemical Methods: Fundamentals and Applications*, ed. D. Harris, E. Swain, C. Robey and E. Aiello, Wiley, Hoboken, 2nd edn., 2000, ch. 5, pp. 210.