Supplementary Information

of

A Redox Active Columnar Metallomesogen and Its Cyclic Voltammetric Responses

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1. Experimental Section

1-1. Synthesis

Chemicals 4,4'-Ditridecyl-2,2'-dipyridyl (C13bpy) was synthesized by the literature methods.¹ Diisopropylamine, 2-octyl-1-dodecanol, and 4,4'-dimethyl-2,2'-dipyridyl were purchased from Aldrich Chemical. Catechol (CatH₂) was purchased from Wako Pure Chemical Industries Ltd.. *N*-bromosuccinimide was purchased from Nacalai Tesque, Inc.. Potassium tetrachloroplatinate(II) was purchased from Furuya Metal Co., Ltd.. All of the solvents for the synthesis and the measurements were distilled by standard methods under a dinitrogen atmosphere. All synthetic operations were performed under a dinitrogen atmosphere using Schlenk line techniques.

1-Bromo-2-octyldodecane 2-octyl-1-dodecanol (59.3 g, 199 mmol) and triphenylphosphine (106.2 g, 405 mmol) were dissolved in dichloromethane (130 ml) and cooled to 273 K. To the mixture *N*-bromosuccinimide (54.5 g, 306 mmol) was added slowly, then stirred at room temperature for 24 hours. After evaporation of solvents in vacuo the products were dissolved in hexane. Purification by column chromatography (silica gel, hexane, $R_f = 0.6$) yielded 1-Bromo-2-octyldodecane as a colorless oil. Yield 68.0 g (197 mmol, 98%). FAB-MS: m/z: 361 [M+1]⁺. ¹H-NMR (CDCl₃, 500 MHz): d = 3.45 (d, 2H, J = 5.0 Hz), 1.59 (m, 1H), 1.4-1.2 (m, 32H), 0.88 (t, 6H, J = 7.0 Hz). Calc. for C₂₀H₄₁Br: C, 66.46; H, 11.43. Found: C, 66.21; H, 11.49.

4,4'-Di(3-octyltridecyl)-2,2'-dipyridyl (C8,10bpy) An anhydrous 300 ml THF solution of diisopropylamine (12.6 ml, 90.0 mmol) was added to a 500 ml three-neck flask containing 4,4'-dimethyl-2,2'-dipyridyl (8.29 g, 45.0 mmol). The resulting mixture was cooled to 273 K, then 1.58 M *n*-butyllithium in hexane (54.9 ml, 90.0 mmol) was added. The pale yellow solution obtained after 30 min was slowly combined with a THF (10 ml) solution of 1-Bromo-2-octyldodecane (32.5 g, 90.0 mmol). On addition a dark reddish brown solution was produced. After further stirring at 273 K for 2 hours, the mixture was stirred for a week at 293 K. The reaction was quenched by adding methanol (200 ml) and the product was poured into water (200 ml). The organic material extracted with diethyl ether (2 x 100 ml), washed with water, dried with MgSO₄ and concentrated under reduced pressure. After

recrystallization from dichloromethane at 183 K, the hexane solution was treated with activated carbons, then purification by column chromatography (silica gel, n-hexane/ethylacetate (20/1), $R_f = 0.5$) yielded a colorless oil. Yield 17.5 g (23.4 mmol, 52%). FAB-MS: m/z: 745 [M⁺]. ¹H-NMR (CD₂Cl₂, 500 MHz): d = 8.52 (d, 2H, J = 5.0 Hz), 8.29 (d, 2H, J = 2.0 Hz), 7.14 (dd, 2H, J = 5.0, 2.0 Hz), 2.68 (m, 4H), 1.64 (m, 4H), 1.4-1.2 (m, 66H), 0.89 (t, 12H, J = 7.0 Hz). Calc. for C₅₂H₉₂N₂: C, 83.80; H, 12.44. Found: C, 83.72; H, 12.64.

[PtCl₂(C8,10bpy)] Neat C8,10bpy (2.08 g, 2.79 mmol) was added to a 150 ml aqueous solution of K₂PtCl₄ (1.16 g, 2.79 mmol) containing 1 M HCl(aq.) (11.2 ml, 11.2 mmol). The mixture was heated at 368 K for 41 hours to afford a yellow oil. The oil was extracted by chloroform (100 mL), then washed with water. Purification by column chromatography (silica gel, dichloromethane, $R_f = 0.8$) yielded yellow solid after evaporation. Yield 2.50 g (2.48 mmol, 89%). FAB-MS: m/z: 1010.7 [M+1]⁺. ¹H-NMR (CD₂Cl₂, 500 MHz): d = 9.43 (d, 2H, J = 6.0 Hz), 7.81 (d, 2H, J = 1.5 Hz), 7.36 (dd, 2H, J = 6.0, 1.5 Hz), 2.76 (m, 4H), 1.68 (m, 4H), 1.40-1.24 (m, 66H), 0.88 (t, 12H, J = 6.0 Hz). Calcd. for C52H92Cl2N2Pt : C, 61.76; H, 9.17; N, 2.77. Found: C, 61.90; H, 9.25; N, 2.72.

[Pt(Cat)(C8,10bpy)] (1) A 45.9 ml *N*,*N*-dimethylacetamide and a 15.3 ml MeOH were added to mixture of CatH₂ (114 mg, 1.04 mmol), NaOH (124 mg, 3.11 mmol), and [PtCl₂(C8,10bpy)] (1.05 g, 1.04 mmol). The mixture was heated at 358 K for a day, affording a deep violet solution. The solution was evaporated to dryness in vacuo, and washed with MeOH. The product was dissolved in 10 ml CH₂Cl₂ and filtered. Recrystallization from CH₂Cl₂/MeOH at 253 K afforded a violet precipitates. Removal of solvent by filtration yielded a violet oil. Yield 682 mg (0.65 mmol, 62%). FAB-MS: *m/z* : 1047 [M⁺]. ¹H-NMR (CD₂Cl₂, 500 MHz): *d* = 9.05 (d, 2H, *J* = 5.5 Hz), 7.67 (d, 2H, *J* = 1.5 Hz), 7.32 (dd, 2H, *J* = 5.5, 1.5 Hz), 6.60 (dd, 2H, *J* = 6.0, 3.0 Hz), 6.34 (dd, 2H, *J* = 6.0, 3.0 Hz), 2.71 (m, 4H), 1.67 (m, 4H), 1.40-1.24 (m, 66H), 0.88 (t, 12H, *J* = 9.0 Hz). Calcd. for C58H96N2O2Pt : C, 66.44; H, 9.23; N, 2.67. Found : C, 66.10; H, 9.06; N, 2.80.

[PtCl₂(C13bpy)] Neat C13bpy (830 mg, 1.59 mmol) was added to a 78 ml aqueous solution of K_2 PtCl₄ (663 mg, 1.60 mmol) containing 2.3 M HCl(aq.) (3.75 ml, 8.75 mmol). The yellow solid was obtained after refluxing the suspension for 35 hours. The solid was filtered

and washed with H₂O, MeOH, and Et₂O, then dried in vacuo. Yield 1.05 g (1.32 mmol, 83.6%). FAB-MS: m/z: 786 [M⁺]. ¹H-NMR (CD₂Cl₂, 500 MHz): d = 9.52 (d, 2H, J = 6.0 Hz), 7.78 (d, 2H, J = 2.0 Hz), 7.40 (dd, 2H, J = 6.0, 2.0 Hz), 2.77 (t, 4H, J = 7.5 Hz), 1.73 (m, 4H), 1.40-1.24 (m, 40H), 0.88 (t, 6H, J = 7.0 Hz). Calcd. for C36H60Cl2N2Pt : C, 54.95; H, 7.69; N, 3.56. Found: C, 55.20; H, 7.77; N, 3.52.

[Pt(Cat)(C13bpy)] A 8.4 ml MeOH solution of NaOH (1.25 mmol) was added to a 22.5 ml MeOH solution of CatH₂ (68.6 mg, 0.62 mmol) to give a light yellowish-green solution. The solution was combined with a 22.5 ml MeOH suspension of $[PtCl_2(C13bpy)]$ (225 mg, 0.38 mmol), and refluxed for a day, affording a deep red solution. The red solid obtained after evaporation was washed with H₂O until the filtrate becomes colorless. Then, the solid was washed with MeOH and dried in vacuo. Recrystallization from CH₂Cl₂/*n*-hexane gave violet platet crystals. Yield 196 mg (0.24 mmol, 63%). FAB-MS: *m*/*z* : 823 [M⁺]. ¹H-NMR (CDCl₃, 500 MHz): *d* = 9.18 (d, 2H, *J* = 6.0 Hz), 7.64 (s, 2H), 7.29 (d, 2H, *J* = 6.0 Hz), 6.81 (dd, 2H, *J* = 6.0, 3.0 Hz), 6.47 (dd, 2H, *J* = 6.0, 3.0 Hz), 2.72 (t, 4H, *J* = 7.5 Hz), 1.72 (m, 4H), 1.40-1.24 (m, 40H), 0.86 (t, 6H, *J* = 9.0 Hz). Calc. for C42H64N2O2Pt: C, 61.22; H, 7.83; N, 3.40. Found: C, 61.25; H, 7.73; N, 3.38.

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1-2. Physical Measurements

¹H-NMR spectroscopy was performed using a JEOL A-500 spectrometer. Mass spectra were recorded using a JEOL JMS-HX110A mass spectrometer. Elemental analyses were carried out on a Flash EA 112 series, Thermo Finnigan instrument. Differential scanning calorimetry measurements were performed on a METTLER DSC822e. Electrochemical measurements were carried out with an ALS model 650A electrochemical analyzer. A standard three-electrode system (a glassy carbon working electrode, platinum-wire counter electrode, and Ag/Ag⁺/CH₃CN electrode as reference) was used for CV studies in solution. Liquid crystalline 1 was spin-coated (4000 rpm, 30 sec) from 100 µl of a 10 mM toluene solution on an indium tin oxide electrode purchased from Sanyo Vacuum Industries Co. Ltd. (5.7 Ω/\Box , A = 2.4 cm²) or a fluorine-doped tin oxide electrode purchased from Asahi Glass Fabritech Co., Ltd. (10 Ω/\Box , $A = 2.4 \text{ cm}^2$). An experimental setup for visualized direct electrochemical measurement was obtained by combining with a Pt counter electrode and Ag/Ag⁺ reference electrode within a handmade electrochemical cell. Microphotographs were taken by a Olympus BX51 polarizing microscope equipped with DP70 digital camera. The samples were cooled and heated on a Linkam THM600 hot stage programmable temperature controller. Variable temperature X-ray powder diffraction measurements were carried out with Cu Ka radiation equipped with a Rigaku RINT-2000 diffractometer using Al sample pans. The AFM image was taken with a NANOSCALE hybrid microscope VN-8000 series (Keyence) in a tapping mode.



Figure S1. DSC curves of [Pt(Cat)(C8,10bpy)] (1) at a scan rate of 5 K/min (second heating scan after holding temperature at 0 °C for 5 hours in the first cooling scan).



Figure S2. Temperature dependent XRPD patterns of [Pt(Cat)(C8,10bpy)] (1) (second heating scan after holding temperature at 0 °C for 5 hours in the first cooling scan).



Figure S3. Polarized microscope images of [Pt(Cat)(C8,10bpy)] (1) taken at a) 210 °C (IL), b) 185 °C (Col_{ho}), c) 30 °C (Col_{ho}), d) -30 °C (X), and e) -70 °C (G_X) under crossed polarizers (the first cooling process at 5K/min).



Figure S4. An atomic force microscopy image of a spin-coated film on an ITO electrode. The film is very flat and has a thickness of 50 nm (a part of the film was removed using hexane before the AFM measurement to expose the bare ITO surface. This procedure formed edges with thick thickness.).



Figure S5. a) A plot of the middle potentials, $E_{\rm mid}$, of the fiftieth scan in repetitive cycling experiments at 2 V/sec for a spin-coated **1** on an ITO electrode immersed in a DMSO solution containing different *n*-Bu₄NClO₄ concentrations (0.1, 0.33, and 1 M). A linear dependency of $E_{\rm mid}$ on the logarithm of the concentration of *n*-Bu₄NClO₄ was obtained by fitting with an equation, $E_{\rm mid}$ (V) = -0.018log[ClO₄⁻] + 0.056. b) A plot of the middle potentials, $E_{\rm mid}$, of the twentieth scan in repetitive cycling experiments at 2 V/sec for a spin-coated **1** on an FTO electrode immersed in DMSO solution containing different *n*-Bu₄NClO₄ concentrations (0.01, 0.1, and 1 M). A linear dependency of $E_{\rm mid}$ on the logarithm of the concentration of *n*-Bu₄NClO₄ concentrations (0.01, 0.1, and 1 M). A linear dependency of $E_{\rm mid}$ on the logarithm of the concentration of *n*-Bu₄NClO₄ was obtained by fitting with an equation, $E_{\rm mid}$ (V) = -0.036log[ClO₄⁻] + 0.040. The data indicated that the ClO₄⁻ anions insert to the layer of oxidized species.



Figure S6. a) A polarized microscope image and b) the CV of **1** immobilized on an FTO electrode using a drop casting method (500 mV/sec, DMSO, 0.1 M n-Bu₄NClO₄, N₂, 25 °C). c) A polarized microscope image under crossed polarizers and d) the CV of **1** immobilized on an FTO electrode using a gradual cooling method from the isotropic phase at 0.1 K/min (500 mV/sec, DMSO, 0.1 M n-Bu₄NClO₄, N₂, 25 °C).

8. X-ray crystallographic data of [Pt(Cat)(C13bpy)]



An ORTEP drawing and the selected bond distances and angles

Selected Bond Distances (Å)

Pt(1)–O(1)	1.992(3)	C(5)–C(6)	1.386(6)	C(15)–C(16)	1.385(5)
Pt(1)–O(2)	2.007(3)	C(1)–C(6)	1.408(7)	N(1)–C(7)	1.352(5)
Pt(1)–N(1)	1.992(4)	C(7)–C(8)	1.374(6)	N(1)–C(11)	1.346(6)
Pt(1)–N(2)	1.998(4)	C(8)–C(9)	1.369(5)	N(2)–C(12)	1.373(6)
O(1)–C(1)	1.361(5)	C(9)–C(10)	1.379(5)	N(2)–C(16)	1.341(5)
O(2)–C(6)	1.363(5)	C(10)–C(11)	1.382(6)		
C(1)–C(2)	1.391(6)	C(11)–C(12)	1.480(7)		
C(2)–C(3)	1.379(6)	C(12)–C(13)	1.385(5)		
C(3)–C(4)	1.397(6)	C(13)–C(14)	1.392(6)		
C(4)–C(5)	1.400(6)	C(14)–C(15)	1.384(5)		

Selected Angles (°)

O(1) - Pt(1) - O(2)	85.1(1)	O(1)-Pt(1)-N(1)	95.6(1)
O(1) - Pt(1) - N(2)	176.1(1)	O(2) - Pt(1) - N(1)	177.17(9)
O(2) - Pt(1) - N(2)	98.8(1)	N(1)-Pt(1)-N(2)	80.5(2)

The size of the mesogenic core, ca. 11 Å, was estimated from the above structure and the structures described in reference 5.

Crystallographic data:

1.425 g cm⁻³, Z = 2; $R_1 = 0.039$ ($I > 3\sigma(I)$), $R_w = 0.104$, GOF = 1.08. The single crystal structural analysis was performed on a Rigaku mercury diffractometer with a CCD two-dimensional detector with Mo $K\alpha$ radiation employing a graphite monochromator. The sizes of the unit cell was calculated from the reflections collected on the setting angles of seven frames by changing ω by 0.5° for each frame. Two different χ settings were used, and ω was changed by 0.5° per frame. Intensity data were collected in 720 frames (60 sec/image) with an ω scan width of 0.5°. Empirical absorption correction using the program REQABA¹ was performed. The structures were solved by SIR92.² The final cycles of the full-matrix least-squares refinements were based on the observed reflections $(I > 3\sigma(I))$. All of the calculations were performed using the teXsan crystallographic software package from Structure Corporation.³ CCDC-607227 contains the Molecular supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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