Synthesis, characterization and molecular recognition of bis-platinum terpyridine dimer

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Supporting information

Experimental

General Procedures. ¹H NMR spectra were recorded on a Bruker ARX400 (400 MHz), Bruker AVANCE AV400 (400 MHz) or a Bruker AVANCE AV600 (600 MHz) spectrometer. ¹³C NMR spectra were recorded on a Bruker ARX400 (100 MHz) spectrometer. Chemical shifts (δ) are given in ppm relative to internal tetramethylsilane and coupling constants are reported in Hertz (Hz). Nominal mass spectra (*m*/*z*) under the conditions of electrospray ionization were recorded on an Applied Biosystems Qstar/Pulsar *i*. Elemental analyses were performed at Chemical Analysis Center, University of Tsukuba. Melting points were obtained using a Yanaco melting point apparatus and are uncorrected.

Materials. All reagents, obtained from WAKO Pure Chemical Industries, Ltd., TCI Tokyo Chemical Industry Co., Ltd., Nacalai Tesque, Inc. suppliers were used directly as supplied.

3-(3-bromophenyl)pyridine 2



3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine¹ (9.32 g, 45.40 mmol), 1,3dibromobenzene (21.44 g, 2.0 eq) and tetrakis(triphenylphosphine)palladium (2.62 g, 0.05 eq) were placed in 500 ml flask. Dioxane (250 ml) degassed *via* three freezepump-thaw cycles and potassium carbonate (15.70 g, 2.5 eq) were added, and the resulting mixture was then stirred at 80 °C for 2 days. The mixture was poured into water and extracted with chloroform (4x150 ml). The combined organic layers were dried with anhydrous MgSO₄. Solvents were removed and the reaction was purified by column chromatography (CHCl₃:MeOH – 5:0.05) on silica gel to afford **2** as colorless oil (5.97 g, 56%). Found: C, 56.62; H, 3.62; N, 6.06. Calc. for C₁₁H₈BrN: C 56.44, H 3.44, N 5,98%; $\delta_{\rm H}$ (300 MHz, CDCl₃) 7.29-7.36 (2H, m), 7.46-7.52 (2H, m), 7.68-7.69 (1H, t, *J* 1.8 Hz), 7.79-7.81 (1H, dt, *J* 2.1, 8.1 Hz), 8.59-8.61 (1H, dd, *J* 1.8, 5.1 Hz), 8.79 (1H, d, *J* 2.4 Hz); $\delta_{\rm C}$ (100 MHz, CDCl₃) 123.15, 123.58, 125.71, 130.11, 130.54, 131.02, 134.29, 135.13, 139.85, 148.12, 149.01; *m/z* (ESI-MS+) 233.97 [*M* + H]⁺.

3-[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]pyridine 3



3-(3-Bromophenyl)pyridine (5.97 g, 25.50 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'bi-1,3,2-dioxaborolane (6.50)1 eq), [1,1'g, bis(diphenylphosphino)ferrocene]dichloropalladium(II) "Pd(dppf)Cl₂" (0.62 g, 0.03 eq) and 1,1'-bis(diphenylphosphino)ferrocene (0.42 g, 0.03 eq) were placed in 100 ml flask. Dioxane (80 ml) degassed via three freeze-pump-thaw cycles and potassium acetate (7.50 g, 3 eq) were added, and the resulting mixture was then stirred at 80 $^{\circ}$ C for 4 days. The mixture was poured into water and extracted with chloroform (4x50 ml). The combined organic layers were dried with anhydrous MgSO₄. Solvents were removed and the reaction was purified by column chromatography (CHCl₃) on silica gel to afford **3** as colorless solid (6.74 g, 94%). M.p. 95-97 °C. Found: C, 72.02; H, 7.25; N, 4.81. Calc. for $C_{17}H_{20}BNO_2 \cdot 1/5H_2O$: C, 71.70; H, 7.22; N, 4.91%; $\delta_{\rm H}$ (300 MHz, CDCl₃) 1.3 (12H, s), 7.33-7.31 (1H, dd, J 4.9, 7.2 Hz), 7.43-7.48 (1H, t, J 7.5 Hz), 7.63-7.66 (1H, dt, J 1.5, 7.5 Hz), 7.81-7.90 (2H, m), 7.99 (1H, s), 8.64-8.55 (1H, dd, *J* 1.5, 4.8 Hz), 8.84 (1H, d, *J* 2.4 Hz); δ_C (100 MHz, CDCl₃) 24.85, 83.99, 123.52, 128.46, 129.89, 133.48, 134.47, 134.58, 136.67, 137.11, 148.21; *m/z* (ESI-MS+) $282.16 [M + H]^+$, $304.14 [M + Na]^+$.

3-[2,6-bis(pyridin-2-yl)pyridin-4-yl]phenyl trifluoromethanesulfonate 4



To a pyridine solution (20 ml) of 4'-(3-hydroxyphenyl)-2,2':6',2"-terpyridine² (2.78 g, 8.54 mmol) was slowly added trifluoromethanesulfonic anhydride (2.89 g, 1.2 eq) at 0 °C. The resulting mixture was stirred at 0 °C for 5 min and warmed to room temperature with stirring for 1 h. The resulting mixture was poured into water and extracted with dichloromethane (4x60 ml). The dichloromethane extract was washed with brine (1x60 ml) and dried over MgSO₄. Solvents were removed and the reaction was purified by column chromatography (CHCl₃) on alumina to afford **4** as colorless solid (2.73 g, 70%). M.p. 117-119 °C. Found: C, 57.61; H, 3.15; N, 9.21. Calc. for C₂₂H₁₄F₃N₃O₃S: C, 57.77; H, 3.08; N, 9.19%; $\delta_{\rm H}$ (400 MHz, CDCl₃) 7.33-7.37 (3H, m), 7.55-7.59 (1H, t, *J* 8.2 Hz), 7.74-7.75 (1H, t, *J* 2.2 Hz), 7.84-7.89 (3H, m), 8.63-8.65 (2H, dd, *J* 0.8, 8.0 Hz), 8.67 (2H, s), 8.71-8.72 (2H, dt, *J* 1.1, 5.2 Hz); $\delta_{\rm C}$ (100 MHz, CDCl₃) 118.75, 120.21, 121.34, 121.47, 124.02, 127.35, 130.74, 136.89, 141.43, 148.05, 149.15, 150.03, 155.73, 156.24. *m/z* (ESI-MS+) 458.07 [*M* + H]⁺.

2,6-bis(pyridin-2-yl)-4-{3-[3-(pyridin-3-yl)phenyl]phenyl}pyridine 5



3-[2,6-Bis(pyridin-2-yl)pyridin-4-yl]phenyl trifluoromethanesulfonate (2.73 g, 5.87 mmol), 3-[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]pyridine (2.00 g, 1.2 eq), [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) "Pd(dppf)Cl₂" (0.15 g, 0.03 eq) and 1,1'-bis(diphenylphosphino)ferrocene "dppf" (0.10 g, 0.03 eq) were

placed in 100 ml flask. Dioxane (60 ml) degassed via three freeze-pump-thaw cycles and potassium carbonate (2.03 g, 2.5 eq) were added, and the resulting mixture was then stirred at 80 °C for 2 days. The mixture was poured into water and extracted with chloroform (4x50 ml). The combined organic layers were dried with anhydrous MgSO₄. Solvents were removed and the reaction was purified by column chromatography (CHCl₃:MeOH:Et₃N - 25:0.3:0.1) on silica gel to afford 5 as white solid (0.91 g, 33%). Mp 195.0-196.0 °C. Found: C, 83.01; H, 5.08; N, 11.98. Calc. for C₃₂H₂₂N₄: C, 83.09; H, 4.79; N, 12.11%; δ_H (400 MHz; DMSO-*d*₆) 7.56-7.51 (3H, m, H^{A5, E5}), 7.67 (1H, t, *J* 7.7, H^{D5}), 7.73 (1H, t, *J* 7.7, H^{C5}), 7.79 (1H, d, *J* 7.8, H^{D4}), 7.88 (1H, d, J 7.8, H^{D6}), 7.95 (2H, m, H^{C4, C6}), 8.06 (2H, td, J 7.8, 1.7, H^{A4}), 8.14 (1H, s, H^{D2}), 8.23 (1H, dt, J 8.0, 2.0, H^{E6}), 8.26 (1H, s, H^{C2}), 8.61 (1H, dd, J 4.8, 1.4, H^{E4}), 8.69 (2H, d, J 7.8, H^{A3}), 8.77 (2H, d, J 4.6, H^{A6}), 8.79 (2H, s, H^{B3, B5}), 9.05 (1H, d, J 2.3, H^{E2}); δ_C (100 MHz, CDCl₃) 119.49, 121.83, 124.00, 124.32, 126.68, 126.73, 126.80, 127.16, 127.67, 128.36, 129.92, 130.01, 135.01, 136.99, 137.34, 138.94, 139.78, 142.10, 142.29, 148.89, 149.08, 149.57, 150.70, 156.42, 156.60; m/z (ESI-MS+) 463.17 $[M + H]^+$, 485.15 $[M + Na]^+$, 947.35 $[2M + Na]^+$.

2{[Pt(5)][BF₄]₂} 1



To a suspension of diiodo(cycloocta-1,5-diene)platinum (0.35 g, 0.63 mmol) in acetone (5 ml) was added silver tetrafluoroborate (0.26 g, 2.1 eq). The resulting mixture was stirred at room temperature until a colorless solution was obtained (~10 min). The AgI precipitate was then removed by filtration. The solution was added to a 2,6-bis(pyridin-2-yl)-4-{3-[3-(pyridin-3-yl)phenyl]phenyl}pyridine (158.60 mg, 0.34 mmol) in acetonitrile (70 ml) and chloroform (5 ml). The reaction mixture was stirred at room temperature for 7 days. The solution was concentrated to small volume,

acetone (50 ml) was added and the resulting yellow precipitate was filtered off, washed with acetone and vacuum dried to afford bis-platinum complex **1** (282.00 mg, 99%) as yellow microcrystalline yellow solid. M.p. above 300 °C. Found: C, 42.19; H, 3.09; N, 6.58. Calc. for C₆₄H₄₄B₄F₁₆N₈Pt₂(8H₂O): C, 42.55; H, 3.35; N, 6.20%; $\delta_{\rm H}$ (400 MHz, DMSO- d_6) 7.88-7.78 (8H, m, H^{A5, C5, D5}), 8.03 (2H, d, *J* 8.0, H^{D6}), 8.07 (2H, d, *J* 7.8, H^{C4}), 8.14-8.11 (8H, m, H^{A6, D4, E5}), 8.22-8.17 (4H, m, H^{C6, D2}), 8.46-8.42 (6H, m, H^{A4, C2}), 8.75 (4H, d, *J* 8.2, H^{A3}), 8.86 (2H, d, *J* 8.4, H^{E6}), 8.96 (4H, s, H^{B3, B5}), 9.23 (2H, d, *J* 5.5, H^{E4}), 9.91 (2H, s, H^{E2}); $\delta_{\rm C}$ (100 MHz, DMSO- d_6) 120.99, 125.03, 125.43, 125.89, 126.12, 126.70, 127.40, 128.31, 128.80, 129.18, 129.42, 133.70, 134.98, 138.00, 138.19, 138.97, 139.88, 141.89, 149.79, 150.21, 150.72, 153.55, 153.79, 156.67; *m/z* (ESI-MS+) 328.56 [*M* – 4BF₄]⁴⁺, 349.06 [1/2(*M* – 4BF₄) + CH₃CN]²⁺, 467.09 [*M* – 3BF₄]³⁺, 693.08 [1/2(*M* – 4BF₄) + CI]⁺.



Figure S1. ¹H COSY spectrum of 5 (DMSO- d_6 , 25 °C, [5] = 4 mM, 400 MHz).

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Figure S2. ¹H NOESY spectrum of **5** (DMSO- d_6 , 25 °C, [**5**] = 4 mM, 400 MHz).



Figure S3. ¹H COSY spectrum of 1 (DMSO- d_6 , 25 °C, [1] = 4 mM, 400 MHz).



Figure S4. ¹H NOESY spectrum of **1** (DMSO- d_6 , 25 °C, [**1**] = 4 mM, 400 MHz).



Figure S5. Illustration of the intermolecular NOE cross peaks observed in the adduct formed by the dimer 1 and naphthalene-2,6-diol.

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Figure S6. Partial ¹H NOESY spectrum of a 1:1 solution of **1** and naphthalene-2,6-diol (DMSO- d_6 , 25 °C, [**1**] = 2 mM, 400 MHz).



Figure S7. ESI-MS spectrum (positive mode) of **1** in MeOH/CHCl₃. Inset shows isotopic distribution and the calculated isotopic distribution for the $[1 - 4BF_4]^{4+}$ ion.



Figure S8. Representative ¹H NMR spectra of the NMR titration experiment performed by titrating **1** with naphthalene-2,6-diol at 25 °C, A) [**1**] = 2 mM, B) [naphthalene-2,6-diol] = 2 mM; all spectra recorded in DMSO- d_6 , black squares represent H_c proton (see assignment in Scheme 1).



Figure S9. Binding isotherm observed upon titration of 1 with naphthalene-2,6-diol.



Figure S10. The electronic absorption spectra of 1 by the addition of naphthalene-2,6-diol (DMSO, 25 °C, [1] = 0.5 mM).



Figure S11. Job's plot of 1 and naphthalene-2,6-diol indicating a 1:1 stoichiometry (DMSO, 25 °C, [1] + [G] = 2 mM).

References

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