"Nindigo": Synthesis, coordination chemistry, and properties of indigo diimines as functional bridging ligands

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Supporting Information

Experimental Details

General Considerations

All reactions and manipulations were carried out under an argon atmosphere using standard Schlenk or glovebox techniques unless stated otherwise. Solvents were dried and distilled under argon prior to use. Indigo (95%) was used as received from commercial sources. The aniline derivatives were purified prior to use (aniline(99%), 2.6-dimethylaniline (98%), and 2,6-diisopropylaniline (>90%) by distillation; p-toluidine (99%) by sublimation) and DABCO (99%) was also sublimed prior to use. NMR spectra were recorded at room temperature on either 300 MHz or 500MHz instruments. UV-Vis spectra were recorded on a Perkin Elmer Lambda 1050 instrument in CH_2Cl_2. Cyclic voltammetry experiments were performed with a Bioanalytical Systems CV50 voltammetric analyzer. Typical electrochemical cells consisted of a three-electrode setup including a glassy carbon working electrode, platinum counter electrode, and silver quasi-reference electrode. Experiments were run at scan rates of 100 or 250 mV/s. Acetonitrile solutions of analyte (~1 mM) and electrolyte (0.1 M $Bu_4N^+BF_4^-$) were referenced against an internal standard (~1 mM Fc). Mass spectra were recorded on a Q-TOF II instrument using electrospray ionization source in the positive mode. Elemental analyses were carried out by Canadian Microanalytical Services Ltd., Vancouver, BC.

Synthesis of indigo-N,N′-diphenyldiimine (3a): Aniline (0.60 mL, 6.6 mmol) was added to a bromobenzene (40mL) solution of DABCO (2.1g, 19 mmol) under argon, forming a pale orange solution. $TiCl_4$ (4.8 mL, 1.0 M in toluene, 4.8 mmol) was added dropwise via syringe, immediately generating a white vapour and turning the solution brown with a light green precipitate. Once the fuming subsided, indigo (550 mg, 2.1 mmol) was added. The dark green mixture was heated to reflux overnight and then cooled and evaporated to dryness. The remaining residue was dissolved in acetone (200 mL) and filtered. The dark blue filtrate was evaporated and the residue was dissolved in CH_2Cl_2, washed with water (2 x 200 mL), dried over anhydrous Na_2SO_4, filtered, and condensed. The crude residue was recrystallized from CH_2Cl_2/hexanes to give **3a** as a dark purple solid. Yield 616 mg (71 %). IR (KBr): 3370, 3059, 1612, 1566, 1547. ^1H NMR (300 MHz, CD_2Cl_2): δ 9.95 (s, 2H), 7.44 (t, *J* = 7.8, 4H), 7.28-7.18 (m, 10H), 6.95 (d, *J* = 7.9, 2H), 6.78 (m, 2H). ^{13}C NMR (125.8 MHz, CD_2Cl_2): δ 152.8, 150.4, 147.7, 135.4, 131.2, 129.9, 125.4, 124.6, 121.5, 120.0, 119.4, 115.8. HRMS, *m/z*: calcd for $(M+H)^+$ $C_{28}H_{21}N_4$ 413.1766; found 413.1751.

Synthesis of indigo-N,N′bis(p-tolyl)diimine (3b): A solution of $TiCl_4$ (1 M in toluene, 53.49 mmol, 53.49 mL) was added dropwise to a stirred bromobenzene (250 mL) solution containing DABCO (24 g, 214 mmol) and *p*-toluidine (9.55 g, 89.2 mmol). After the addition of $TiCl_4$ was complete, solid indigo (9.55 g, 35.7 mmol) was added and the reaction was heated to reflux for 24 hours. The reaction mixture was filtered hot, allowed to cool, and washed with ether until the filtrate was colorless. The combined filtrates were evaporated the crude product was washed with water resulting in 14.56g of a dark powder. The crude product was recrystallized from *n*-butanol to give 10.5 g (70%) of **3b** as a dark blue powder. ^1H NMR (CD_2Cl_2): $\delta = 2.41$ (s, 6H, CH_3), 6.77 (m, 2H), 6.98 (t, 1H, $J = 0.93$ Hz), 7.01 (t, 1H, $J = 0.96$ Hz), 7.09 (2H, t, $J = 0.95$Hz), 7.11 (2H, t, $J = 0.95$ Hz), 7.26 (m, 8H), 9.93 (s, 2H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 20.9$ (CH_3), 115.4, 118.9 (${}^{Q}C$), 120.0, 120.9, 124.9, 129.9, 124.9, 130.6, 134.2 (${}^{Q}C$), 144.4 (${}^{Q}C$), 151.1 ppm. HRMS, *m/z*: calcd for $[M+H]^+$ $C_{30}H_{35}N_4$ 441.2079; found 441.2068.

Synthesis of indigo-N,N′bis(2,6-dimethylphenyl)diimine (3c):

Dimethylaniline (5.78 g, 47.66 mmol), indigo (5.0 g, 19.06 mmol) and DABCO (12.83 g, 114.39 mmol) were combined in bromobenzene (150 mL). The mixture was stirred under argon and heated to approximately 80°C. $TiCl_4$ (1M in toluene, 28.6 mL, 28.6 mmol) was added slowly and the mixture stirred at reflux for 24 hours.

The mixture was then filtered hot and the solids washed with diethyl ether until the washings lost their purple colour. The solvent was removed in vacuo and the crude product was washed with water and dried. Recrytallization n-butanol gave 6.64 g (74.7 %) of **3c** as a purple powder. ^1H NMR (CD_2Cl_2): $\delta = 2.17$ (s, 12H), 6.43 (s, 1H), 6.46 (s, 1H), 6.60 (td, 2H, $J = 8$Hz & 0.93 Hz), 7.09 (m, 4H), 7.18 (m, 4H), 7.235 (td, 2H, $J = 8$Hz & 0.93 Hz) ppm. $^{13}C\{^1H\}$ NMR (500 MHz, CD_2Cl_2, 293K): $\delta = 18.5$ (CH_3), 113.5, 119.5 (${}^{Q}C$), 120.7, 124.8 , 125.0, 128.6 (${}^{Q}C$), 128.8, 132.2, 147.7 (${}^{Q}C$), 149.3 (${}^{Q}C$), 158.4 (${}^{Q}C$) . HRMS, *m/z*: calcd for $[M+H]^+$ $C_{32}H_{29}N_4$ 469.2392; found 469.2364.

Synthesis of indigo-N,N′bis(2,6-diisopropylphenyl)diimine (3d): A 1M toluene solution of $TiCl_4$ (34.3 mL, 34.3 mmol) was added dropwise to a stirred bromobenzene (225 mL) solution containing DABCO (15.39g, 137.2 mmol) and 2,6- diisopropylaniline (5.33 g, 57.18 mmol) at 70 °C. Indigo (6.0 g, 22.87 mmol) was then added and the reaction mixture heated to reflux for 24 hours. The reaction mixture was filtered hot, allowed to cool, and washed with ether until the washings were colorless. The combined filtrates were evaporated and the crude product was washed with water and recrystallized from *n*-butanol to give 3.10 g (23.4 %) of **3d** as a purple powder. ^1H NMR (CD_2Cl_2): $\delta = 1.03$ (d, 12H, $J = 6.9$ Hz), 1.22 (d, 12H, $J = 6.9$ Hz), 3.11 (septet, 4H, $J = 6.9$ Hz), 6.37 (t, 1H, $J = 0.93$ Hz), 6.40 (t, 1H, $J = 0.93$ Hz), 6.57 (td, 2H, $J = 7.6$Hz & 1 Hz), 7.06 (t, 1H, $J = 0.93$ Hz), 7.08 (t, 1H, $J = 0.93$ Hz), 7.22 (td, 2H, $J = 7.7$ Hz & 1 Hz), 7.28 (s, 6H), 9.92 (s, 2H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 23.6$ (CH_3), 24.1 (CH_3), 29.0 (CH), 113.5, 119.3 (${}^{Q}C$), 120.2, 124.0, 125.7 (${}^{Q}C$), 125.8, 128.5 (${}^{Q}C$), 132.1, 139.2 (${}^{Q}C$), 145.5 (${}^{Q}C$), 150.2 (${}^{Q}C$), 159.1 (${}^{Q}C$) HRMS, *m/z*: calcd for $[M+H]^+$ $C_{40}H_{45}N_4$ 581.3644; found 581.3618. Anal. Calcd. For $C_{40}H_{44}N_4$ C 82.72, H 7.68, N 9.40%; found C 82.72, H 7.64 , N 9.65 %.

ynthesis of μ-[indigo-*N,N′*-diphenyldiimine)] bis (palladium hexafluoroacetylacetonate) 4a:A solution of Pd(hfac)$_2$ (360 mg, 0.69 mmol) was added by syringe to a solution of **3a** (95 mg, 0.23 mmol) in THF (25 mL), producing a dark green solution. The mixture was stirred at room temperature for 30 minutes. After removal of the solvent, the remaining residue was washed with hexanes. Dark green needles of **4a** were grown from the slow evaporation of dichloromethane/hexanes. Yield 145 mg (60 %). IR (KBr): 3063, 2961, 2927, 1629, 1508, 1444, 1110, 739, 691. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.49 – 7.42 (m, 6H), 7.31 – 7.23 (m, 4H), 7.19 – 7.06 (m, 4H), 6.32 (t, J = 7.4, 2H), 6.18 (s, 2H), 5.69 (d, J = 8.1, 2H). ^{13}C NMR (125.8 MHz, CD_2Cl_2): δ 175.6 (q, J = 35.9), 174.8 (q, J = 35.8), 158.4, 156.1, 146.3, 133.3, 133.1, 129.9, 128.0, 126.5, 126.4, 121.0, 119.2, 117.3 (q, J = 284.5), 116.7 (q, J = 284.9), 116.7, 92.8. ^{19}F NMR (282.4 MHz, CD_2Cl_2): δ -74.5, -75.2.

Synthesis of μ-[indigo-*N,N′*-bis(p-tolyl diimine)] bis (palladium hexafluoroacetylacetonate) 4b: 100 mg of **3b** (0.22mmol) and 360 mg Pd(hfac)$_2$ (0.66 mmol) were individually dissolved in THF giving a deep blue and a clear yellow solution, respectively. On mixing the two solutions a dark green solution was produced. This mixture was stirred vigorously for 30 min at room temperature and then the solution was evaporated to dryness. The solid residue was washed with hexanes and the remaining dark green solid was recrystallized from dichloromethane/ hexanes giving 159 mg (68%) of **4b** as dark green crystals. UV-Vis (CH_2Cl_2): ^{1}H NMR (acetone d$_6$) δ 7.32 (d, 8.2 Hz, 2H), 7.28 - 7.66 (m, 8H), 7.14 (t, 7.4 Hz, 2H), 6.36 (t, 7.7 Hz, 2H), 6.32 (s, 2H), 5.81 (d, 8.1 Hz, 2H), 2.41 ppm (s, 6H). Anal. Calcd For $C_{40}H_{25}F_{12}N_4O_4Pd_2$: C: 45.09, H: 2.27, N: 5.26. Found C: 44.59, H: 2.25, N: 5.26.

Figure S1. Concentration dependent UV-visible spectra of **3a** in CH_2Cl_2.

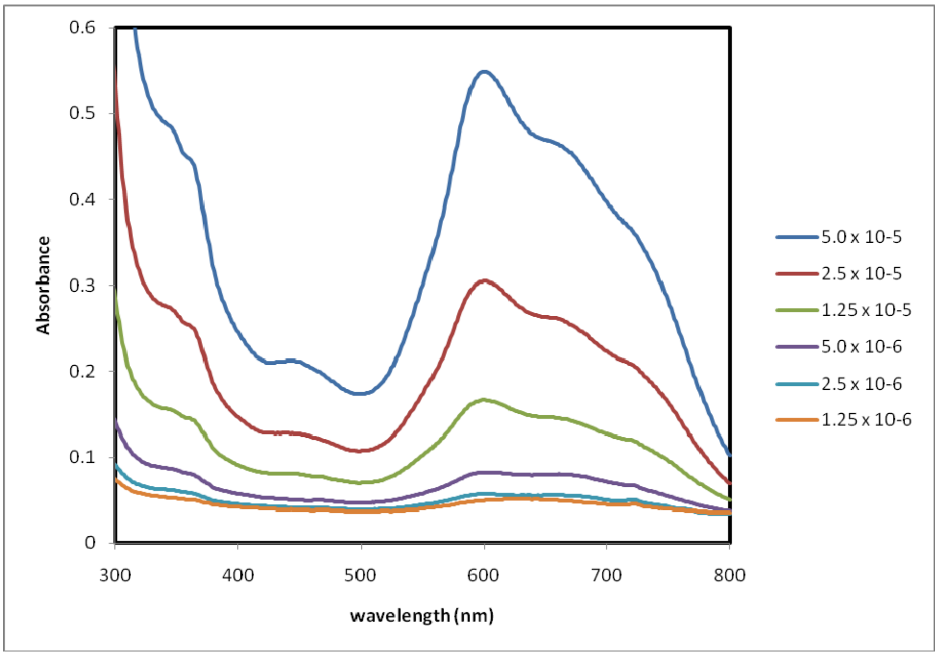

Figure S2. Concentration dependent UV-visible spectra of **3b** in CH_2Cl_2.

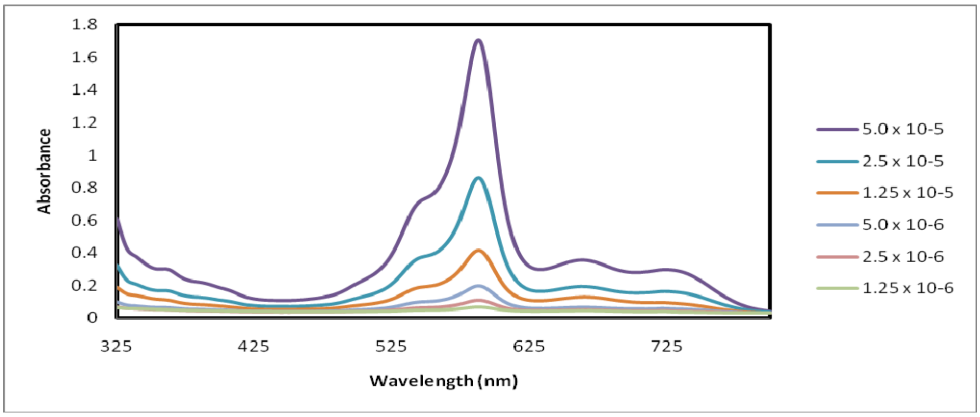

Figure S3. Concentration dependent UV-visible spectra of **3d** in CH_2Cl_2.

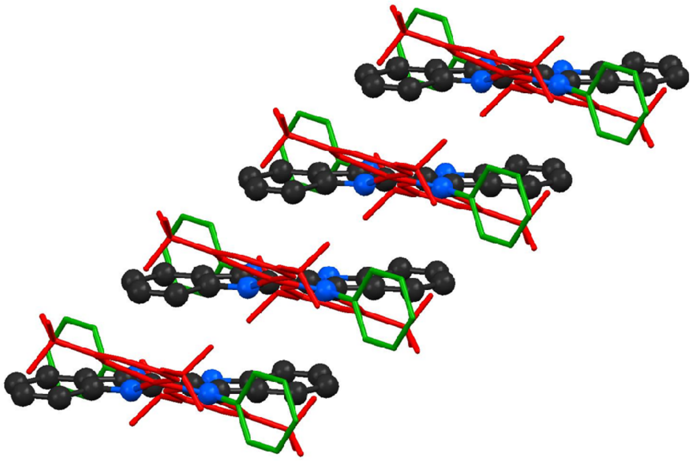

Figure S4. One-dimensional stacking of **4a**. The Pd(hfac) moeties are red and the imine-phenyl substituents are green.