Electronic Supplementary Information

for

Solvent-Directed Conformational Variation of Co(II)/(III) Complexes with a Diiminopyridine Ligand

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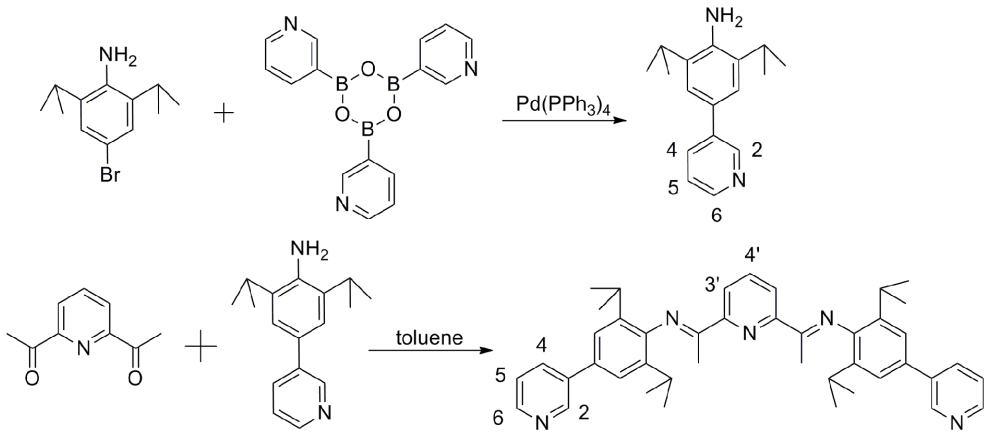
S1. Experimental Section

S1.1 General Procedures.

All chemicals were of analytical reagent grade. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. Manipulations of air sensitive materials were carried out under an atmosphere of nitrogen. 2,6-Diisopropyl-4-bromoaniline[1] and 3-pyridylboroxin[2] were prepared by literature methods. 2,6-Diisopropyl-4-(3-pyridyl)aniline[3] was prepared by using the Suzuki coupling as described below. The ligand L was prepared by the condensation reactions according to literature methods for related compounds.



Scheme S1. The synthetic procedure for the ligand L.

S1.2 Synthesis of 2,6-diisopropyl-4-(3-pyridyl)aniline

A mixture of 2.56 g (10 mmol) of 2,6-diisopropyl-4-bromoaniline, 1.30 g (4 mmol) of 3-pyridylboroxin, 1.15 g (1.00 mmol) of $Pd(PPh_3)_4$, 1.56 g (5 mmol) of tetrabutylammonium bromide, and 3.22 g of KOH powder in 50 mL of anhydrous THF was refluxed with stirring for 24 h under nitrogen. It was then extracted with CH_2Cl_2, dried over $MgSO_4$ and evaporated. The product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate eluent. Crystallization from hexane gave colorless prism crystals in 56% yield. M.p.: 116–117 °C. ESI-MS: *m*/*z* 255.1 ($[M+H]^+$). IR (KBr, cm^{-1}): 3496, 2958, 1642 (ν_{NH2}), 1463,1440, 1319, 1266, 1022, 885, 802, 708 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, ppm): 8.83 (d, 1H, *J* = 2.0 Hz, H2), 8.51 (d, 1H, *J* = 4.8 Hz, H6), 7.85 (d, 1H, *J* = 4.0, 8.0 Hz, H4), 7.32 (dd, 1H, *J* = 4.8, 8.0 Hz, H5), 7.27 (s, 2H, Ar-H), 3.74 (s, 2H, NH_2), 2.98 (m, 2H, *J* = 6.8 Hz, CH), 1.34 (d, 12H, *J* = 6.8 Hz, CH_3). ^{13}C NMR: (100 MHz, $CDCl_3$, ppm) : 148.0, 147.3, 140.7, 137.6, 133.7, 133.0, 127.7, 123.4, 121.8, 28.1, 22.4.

S1.3 Synthesis of 2,6-bis(1-(2,6-diisopropyl-4-(pyridin-3-yl)phenylimino)ethyl)pyridine (L)

A solution of 2,6-diisopropyl-4-(3-pyridyl)aniline (1.02 g, 4.0 mmol), 2,6-diacetylpyridine (0.33 g, 2.0 mmol), and *p*-toluenesulfonic acid (0.02 g) in toluene (20 mL) was refluxed for 3 days with azeotropic removal of water using a Dean-Stark trap. Then the reaction mixture was cooled to room temperature, and the solvent was removed in vacuo. The crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate. L was obtained as a yellow powder in 80% yield. M.p.: 308–309 °C. Anal. Calc for $C_{43}H_{49}N_5$: C, 81.22; H, 7.77; N, 11.01%. Found: C, 81.01; H, 7.56; N, 11.21%. ESI-MS: *m*/*z* 319.0 ($[M+2H]^{2+}$), 636.9 ($[M+H]^+$). IR (KBr, cm^{-1}): 2961, 2928, 2868, 1642 ($\nu_{C=N}$), 1571, 1456, 1431, 1365, 1183, 1116, 1076, 1020, 881, 824, 800 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, ppm): 8.91 (d, 2H, *J* = 1.6 Hz, H2), 8.58 (dd, 2H, *J* = 1.6, 3.2 Hz, H6), 8.53 (d, 2H, *J* = 8.0 Hz, H3′), 7.98 (t, 1H, *J* = 8.0 Hz, H4′), 7.94 (dt, 2H, *J* = 2.0, 3.6 Hz, H4), 7.40 (s, 4H, Ar-*H*), 7.36–7.38 (m, 2H, H5), 2.84 (m, 4H, *J* = 5.2 Hz, *CH*Me_2), 2.35 (s, 6H, N=C*Me*), 1.23 (t, 24H, *J* = 5.2 Hz, CH*Me*$_2$). ^{13}C NMR: (100 MHz, $CDCl_3$, ppm) : 167.2, 155.1, 148.3, 147.8, 146.7, 137.3, 137.0, 136.7, 134.0, 133.0, 123.4, 122.4, 122.0, 28.5, 23.2, 22.8, 17.3.

S2. PXRD patterns of compounds **1a, 1b, 2,** and **3**

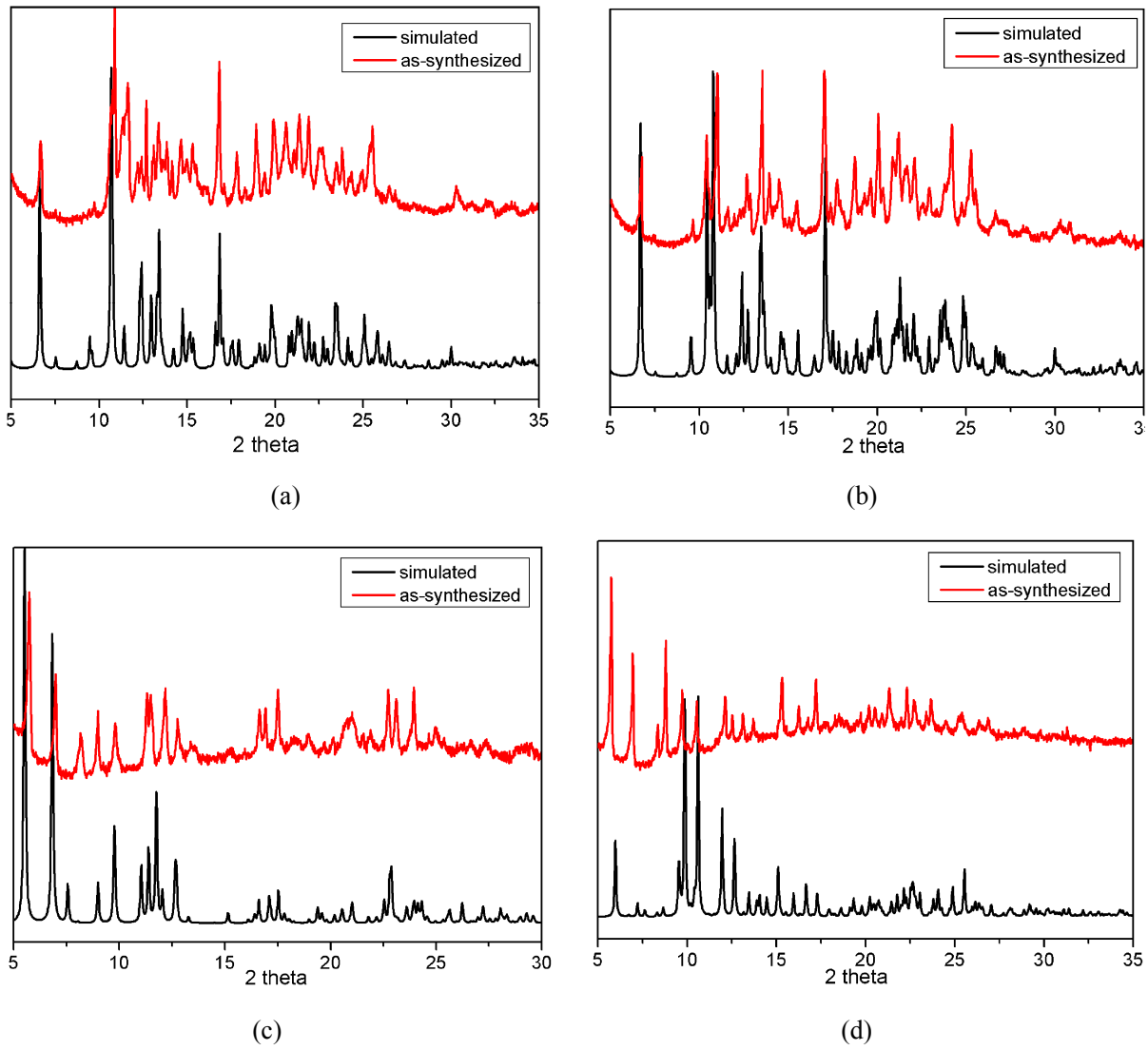


Figure S2. Powder X-ray diffraction patterns of the compounds: as-synthesized (red) and simulated from the single-crystal diffraction data (black). (a) **1a**; (b) **1b**; (c) **2**; (d) **3**.

S3. TGA curves of compounds **1a, 1b, 2,** and **3**

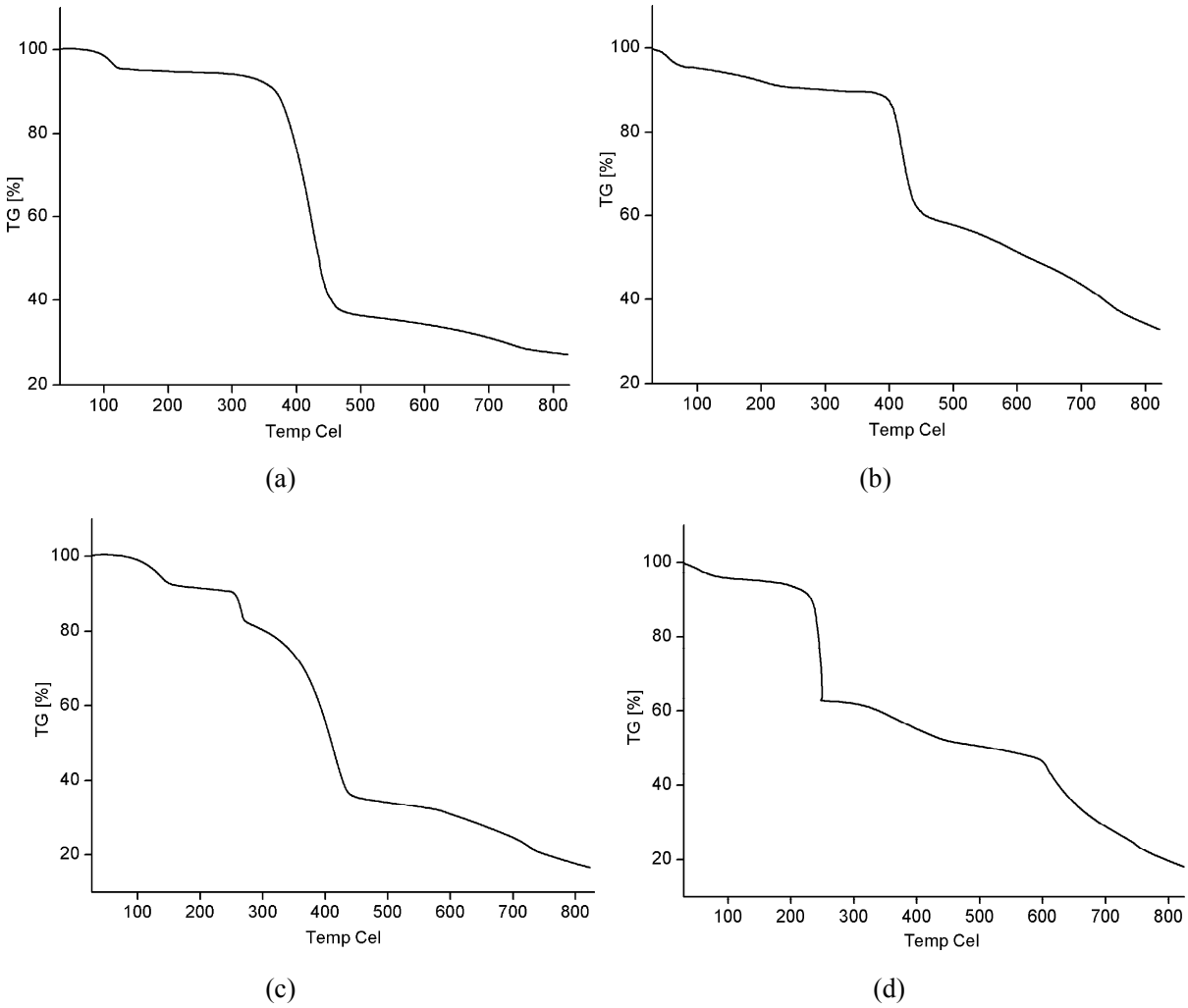


Figure S3. TGA curves of the compounds. (a) **1a**; (b) **1b**; (c) **2**; (d) **3**.

References

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