Electronic Supplementary Information for Dalton Transactions

Supporting Information

Microwave-assisted synthesis and complexation of luminescent cyanobipyridyl-zinc(II) bis(thiolate) complexes with intrinsic and ancillary photophysical tunability

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CONTENTS.

General Procedures.

Commercially available reagents were used without further purification; solvents were dried by standard procedures. Light petroleum refers to the fraction with bp 40-60 °C. Flash chromatography was carried out using Merck Kieselgel 60 H silica or Matrex silica 60. Analytical thin layer chromatography was carried out using aluminium-backed plates coated with Merck Kieselgel 60 GF_{254} that were visualised under UV light (at 254 and/or 360 nm). Microwave irradiation experiments were performed in a sealed tube using a self-tunable CEM Discover® focused monomodal microwave synthesizer at the given temperature by varying the irradiation power (initial power given in parentheses) and monitoring temperature through the instrument's in-built IR sensor. Infra-red (IR) spectra were recorded in the range 4000-600 cm^{-1} using KBr disks or between NaCl plates and are reported in cm^{-1}. Nuclear magnetic resonance (NMR) spectra were recorded in

$CDCl_3$ at 25 °C unless stated otherwise and were reported in ppm; *J* values were recorded in Hz and multiplicities were expressed by the usual conventions. Low-resolution mass spectra (MS) were determined using electrospray ionization (ES) unless otherwise stated. *In vacuo* refers to evaporation at reduced pressure using a rotary evaporator and diaphragm pump, followed by the removal of trace volatiles using a vacuum (oil) pump.

Experimental Procedure for Synthesis of 3-(4-Bromophenyl)-1-(2-pyridyl)prop-2-yn-1-ol.[1]

A *n*-butyllithium (11.20 mmol, 1 equiv) in hexanes (2.5 M) was added to an anhydrous solution of 1-bromo-4-ethynylbenzene (2.09 g, 11.20 mmol) in THF (60 mL) at -78 °C under a nitrogen atmosphere. After the mixture was stirred for 1 h, 2-pyridinecarboxaldehyde (11.20 mmol, 1 equiv) was added, and the temperature was maintained at -78 °C under nitrogen overnight. After the reaction was completed, the mixture was poured over ice (10 g) and partitioned between saturated ammonium chloride solution (30 mL) and diethyl ether (30 mL). The aqueous layer was further extracted with diethyl ether (2 × 25 mL), and the combined ethereal extracts were washed sequentially with water (50 mL) and brine (50 mL), dried ($MgSO_4$) evaporated *in vacuo*. Purification by flash chromatography on silica gel, eluting with hexane–light petroleum (1:6), gave the *title compound* (2.61 g, 80%) as a clear oil (Found: MH^+, 287.9940. $C_{14}H_{11}{}^{79}BrNO$ $[MH^+]$ requires 287.9946); ν_{max} (KBr) 3598, 2986, 2208, 1632, 1600, 1260, 814, 760; λ_{max} ($CHCl_3$)/nm 326 (log ε 4.20), 232 (log ε 4.72); δ_H (400 MHz; $CDCl_3$) 8.60 (1H, d, *J* 6.4, 6'-H), 8.10 (1H, m, 4'-H), 7.80 (1H, d, *J* 8.0, 3'-H), 7.70 (2H, d, *J* 8.8, 3'',5''-H), 7.32 (1H, m, 5'-H), 6.78 (2H, d, *J* 8.8, 2'',6''-H), 5.50 (1H, s, 1-H), 2.56 (1H, br s, OH); δ_C (100 MHz; $CDCl_3$) 160.6 (C), 150.7 (C), 138.2 (CH), 136.5 (CH), 133.3 (CH), 126.1 (CH), 124.8 (C), 122.7 (C), 122.9 (CH), 86.5 (C), 88.4 (C), 66.9 (CH); *m/z* 289 (MH^+, 97%), 287 (MH^+, 100).

Experimental Procedure for Microwave-Assisted Synthesis of 2-Methyl-4-(4-bromophenyl)-6-(2-pyridyl)nicotinonitrile (1a).[2]

A solution of 3-aminocrotononitrile (0.57 mmol, 1 equiv), 3-(4-bromophenyl)-1-(2-pyridyl)prop-2-yn-1-ol (0.30 mL, 1.14 mmol) and barium manganate (1.70 mmol, 3 equiv) in ethanol–acetic acid (5:1) (5.0 mL) was irradiated at 170 °C at an initial power of 150 W (which was moderated to maintain constant temperature) in a sealed Pyrex® vessel for 15 min in a self-tuned single-mode CEM Discover® microwave synthesizer. The mixture was cooled rapidly to room temperature, by passing compressed air through the microwave cavity for 5 min, and then filtered through Celite®. The filtrate was poured into water (15 mL) and extracted with ethyl acetate (8 mL). The aqueous layer was further extracted with ethyl acetate (8 mL) and the organic extracts were combined, washed sequentially with saturated aqueous sodium hydrogen

carbonate solution (10 mL) and brine (10 mL), dried (Na_2SO_4) and evaporated *in vacuo*. Purification by flash chromatography on silica gel, eluting with EtOAc–light petroleum (1:6), gave the *title compound* **1a** (0.17 g, 87%) as colourless crystals, mp 296–298 °C (EtOH) (Found: MH^+, 350.2124. $C_{18}H_{13}{}^{79}BrN_3$ [MH^+] requires 350.0215); ν_{max} (KBr) 2988, 2206, 1630, 1600, 816, 760; λ_{max} ($CHCl_3$)/nm 310 (log ε 4.26), 226 (log ε 4.64); δ_H (400 MHz; $CDCl_3$) 8.68 (1H, d, *J* 6.4, 6'-H), 8.52 (1H, d, *J* 8.0, 3'-H), 8.40 (1H, s, 5-H), 7.87 (1H, m, 4'-H), 7.72 (2H, d, *J* 8.8, 3'',5''-H), 7.34 (1H, m, 5'-H), 6.80 (2H, d, *J* 8.8, 2'',6''-H), 2.98 (3H, s, 2-Me); δ_C (100 MHz; $CDCl_3$) 164.2 (C), 160.0 (C), 159.6 (C), 156.2 (C), 154.6 (C), 150.2 (CH), 138.8 (CH), 130.8 (C), 128.4 (CH), 127.9 (CH), 124.0 (CH), 120.8 (CH), 119.6 (CH), 118.0 (CH), 104.8 (CN), 26.4 (CH_3); *m/z* 352 (MH^+, 97%), 350 (MH^+, 100).

Experimental Procedure for Microwave-Assisted Suzuki-Miyaura Reaction: Synthesis of 2-Methyl-4-(4-biphenyl)-6-(2-pyridyl)nicotinonitrile (3a).[3]

A solution of 2-methyl-4-(4-bromophenyl)-6-(2-pyridyl)nicotinonitrile **1a** (0.57 mmol, 2 equiv) in DMSO (3 mL) was added to a suspension of $Pd(PPh_3)_4$ (0.029 mmol, 10 mol%) in DMSO (1 mL). The mixture was stirred for 5 min while degassing with nitrogen in a pressure-rated Pyrex® reaction tube (10 mL). To this solution was added phenylboronic acid (0.29 mmol, 1 equiv) and Na_2CO_3 (0.86 mmol, 3 equiv) in DMSO (2 mL) and then the mixture was stirred for a further 5 min under nitrogen. The reaction tube was sealed and irradiated at 150 °C, at an initial power of 150 W, in a self-tuned single-mode CEM Discover® Focused Synthesizer for 30 min. The mixture was cooled rapidly to room temperature, by passing compressed air through the microwave cavity for 5 min, and then filtered through Celite®. The filtrate was poured into water (15 mL) and extracted with acetonitrile (15 mL). The aqueous layer was further extracted with acetonitrile (15 mL) and the organic extracts were combined, washed sequentially with water (10 mL) and brine (10 mL), dried (Na_2SO_4) and evaporated *in vacuo*. Purification by flash chromatography on silica gel, eluting with acetonitrile–acetone (1:1), gave the *title compound* **3a** (0.18 g, 90%) as colourless crystals, mp 198–200 °C (EtOH) (Found: MH^+, 348.1419. $C_{24}H_{18}N_3$ [MH^+] requires 348.1422); ν_{max} (KBr) 2989, 2208, 1630, 1558, 816; λ_{max} ($CHCl_3$)/nm 328 (log ε 4.06), 285 (log ε 4.20); δ_H (400 MHz; $CDCl_3$) 8.66 (1H, d, *J* 6.4, 6'-H), 8.18 (1H, d, *J* 7.9, 3'-H), 8.15 (1H, s, 5-H), 7.85 (1H, m, 4'-H), 7.70 (2H, d, *J* 8.8, 2'',6''-H), 7.32 (1H, m, 5'-H), 7.40 (3H), 7.30 (2H, m, 2''',6'''-H), 6.72 (2H, d, *J* 8.8, 3'',5''-H), 2.94 (3H, s, 2-Me); δ_C (100 MHz; $CDCl_3$) 162.2 (C), 159.6 (C), 155.6 (C), 154.6 (C), 149.6 (CH), 137.2 (CH), 137.0 (C), 136.8 (C), 136.4 (C), 129.3 (CH×2), 128.4 (CH×2), 127.9 (CH×2), 127.6 (CH×2), 127.5 (CH), 124.2 (CH), 120.8 (CH), 118.7 (CH), 110.2 (C), 103.8 (CN), 26.2 (CH_3); *m/z* 348 (MH^+, 100%).

Experimental Procedure for Microwave-Assisted Cu-Mediated *N*-Arylation: Synthesis of 2-Methyl-4-[4-(diphenylamino)phenyl]-6-(2-pyridyl)nicotinonitrile (3b).[4]

A solution of 2-methyl-4-(4-bromophenyl)-6-(2-pyridyl)nicotinonitrile **1a** (0.57 mmol, 2 equiv) in toluene (3 mL) was added to a stirred solution of diphenylamine (1.13 mmol, 2 equiv), Cu(neocup)(PPh_3)Br[4] (10 mol%) and potassium-*tert*-butoxide (0.85 mmol, 1.5 equiv) in toluene (3 mL) in a pressure-rated Pyrex® reaction tube (10 mL). The vessel was sealed and irradiated at 120 °C, at an initial power of 150 W, in a self-tuned single mode CEM Discover® Focused Synthesiser for 1 h. The mixture was then cooled rapidly to room temperature, by passing compressed air through the microwave cavity for 5 min, and then filtered through Celite®. The filtrate was poured into water (15 mL) and extracted with diethyl ether (15 mL). The aqueous layer was further extracted with ether (15 mL) and the ethereal extracts were combined, dried (Na_2SO_4) and evaporated *in vacuo*. Purification by flash chromatography on silica gel, eluting with ethyl acetate–light petroleum (1:6), gave the *title compound* **3b** (0.22 g, 88%) as green crystals, mp 268–270 °C (EtOH) (Found: MH^+, 439.1838. $C_{30}H_{23}N_4$ [MH^+] requires 439.1844); ν_{max} (KBr) 2986, 2206, 1628, 1556, 814; λ_{max} ($CHCl_3$)/nm 393 (log ε 4.52), 302 (log ε 4.70); δ_H (400 MHz; $CDCl_3$) 8.72 (1H, d, *J* 6.4, 6'-H), 8.54 (1H, d, *J* 7.9, 3'-H), 8.44 (1H, s, 5-H), 7.88 (1H, m, 4'-H), 7.62 (2H, d, *J* 8.8, 2'',6''-H), 7.40 (1H, m, 5'-H), 7.35 (6H), 7.20 (2H, d, *J* 8.8, 3'',5''-H), 7.18 (4H, m), 2.92 (3H, s, 2-Me); δ_C (100 MHz; $CDCl_3$) 161.2 (C), 159.8 (C), 155.6 (C), 154.6 (C), 149.5 (CH), 141.7 (C), 141.2 (C×2), 137.2 (CH), 132.6 (C), 129.9 (CH×4), 128.5 (CH×2), 124.4 (CH), 123.4 (CH×2), 123.2 (CH×2), 122.7 (CH×4), 120.8 (CH), 118.9 (CH), 117.2 (C), 102.6 (CN), 26.0 (CH_3); *m/z* 439 (MH^+, 100%).

Experimental Procedure for Microwave-Assisted Complexation: Synthesis of Cyanobipyridyl-Zn^{II}-bis(thiolate) Complexes 4.[5]

Thiophenol (0.8 mmol, 2 equiv) was added dropwise to a vigorously stirred solution of zinc acetate dihydrate (0.4 mmol, 1 equiv) in hot EtOH (3 mL) in a pressure-rated Pyrex® tube (10 mL). After stirring for 5 min, a solution of 2-methyl-4-(4-biphenyl)-6-(2-pyridyl)nicotinonitrile (**3a**) (0.4 mmol, 1 equiv) in ethanol (3 mL) was added dropwise. After another 5 min of vigorous stirring, a SiC passive heating element (*Anton Paar Ltd.*) was added to the vessel, which was sealed and irradiated at 120 °C, at an initial power of 150 W, in a self-tuned single-mode CEM Discover® Focused Synthesizer for 10 min. The mixture was then cooled rapidly to room temperature, by passing compressed air through the microwave cavity for 5 min, and then filtered through a sinter funnel. The crude sample was collected and washed thoroughly with EtOH (10 mL) and diethyl ether (10 mL). Purification by recrystallization (CH_2Cl_2–Et_2O) gave the *title compound* **4a** (0.24 g, 94%).

2-Methyl-3-cyano-4-(4-biphenyl)-6-(2-pyridyl)pyridyl-Zn^{II}-bis(benzenethiolate) (4a) (0.24 g, 94%) was prepared according to the given procedure using thiophenol (0.08 mL, 0.8 mmol) and 2-methyl-4-(4-biphenyl)-6-(2-pyridyl)nicotinonitrile (**3a**) (0.4 mmol, 1 equiv) and was obtained as bright yellow crystals, mp 220–222 °C (Found: M^+, 629.0926. $C_{36}H_{28}N_3S_2Zn$ [M^+] requires 629.0938); ν_{max} (KBr) 2990, 2209, 1630, 1556, 1250, 818; λ_{max} ($CHCl_3$)/nm 390 (log ε 4.03), 325 (log ε 4.37); δ_H (400 MHz; $CDCl_3$) 8.86 (1H, d, *J* 6.4, 6'-H), 8.38 (1H, d, *J* 7.9, 3'-H), 8.36 (1H, s, 5-H), 8.09 (1H, m, 4'-H), 7.88 (2H, d, *J* 8.8, 2'',6''-H), 7.78 (3H), 7.69 (2H, m, 2''',6'''-H), 7.52 (6H), 7.40 (4H, m), 6.92 (1H, m, 5'-H), 6.88 (2H, d, *J* 8.8, 3'',5''-H), 3.29 (3H, s, 2-Me); δ_C (100 MHz; $CDCl_3$) 164.8 (C), 161.6 (C), 158.6 (C), 154.4 (C), 145.2 (CH), 137.4 (CH), 137.0 (C), 136.8 (C), 136.4 (C), 132.5 (C×2), 129.4 (CH×4), 129.2 (CH×2), 129.0 (CH×4), 128.4 (CH×2), 127.9 (CH×2), 127.6 (CH×2), 127.4 (CH), 125.6 (CH×2), 124.2 (CH), 120.8 (CH), 118.7 (CH), 117.0 (C), 108.2 (CN), 28.4 (CH_3); *m/z* 629 (M^+, 100%).

2-Methyl-3-cyano-4-(4-biphenyl)-6-(2-pyridyl)pyridyl-Zn^{II}-bis(4-methoxybenzenethiolate) (4b) (0.28 g, 96%) was prepared according to the given procedure using 4-methoxythiophenol (0.10 mL, 0.8 mmol) and 2-methyl-4-(4-biphenyl)-6-(2-pyridyl)nicotinonitrile (**3a**) (0.4 mmol, 1 equiv) and was obtained as deep yellow crystals, mp 230–232 °C (Found: M^+, 689.1134. $C_{38}H_{32}N_3O_2S_2Zn$ [M^+] requires 689.1149); ν_{max} (KBr) 2994, 2208, 1628, 1554, 1252, 1200, 816; λ_{max} ($CHCl_3$)/nm 392 (log ε 3.96), 322 (log ε 4.40); δ_H (400 MHz; $CDCl_3$) 8.84 (1H, d, *J* 6.4, 6'-H), 8.36 (1H, d, *J* 7.9, 3'-H), 8.30 (1H, s, 5-H), 8.04 (1H, m, 4'-H), 7.86 (2H, d, *J* 8.8, 2'',6''-H), 7.76 (4H, d, *J* 8.9), 7.70 (3H), 7.64 (2H, m), 7.20 (4H, d, *J* 8.9), 6.90 (1H, m, 3'-H), 6.86 (2H, d, *J* 8.8, 3'',5''-H), 3.86 (6H, s, 2×OMe), 3.26 (3H, s, 2-Me); δ_C (100 MHz; $CDCl_3$) 162.6 (C), 161.4 (C), 157.5 (C×2), 157.0 (C), 154.4 (C), 145.0 (CH), 137.2 (CH), 137.0 (C), 136.8 (C), 136.5 (C), 130.4 (CH×4), 129.3 (CH×2), 128.4 (CH×2), 127.9 (CH×2), 127.6 (CH×2), 127.2 (CH), 124.8 (C×2), 124.2 (CH), 120.8 (CH), 118.7 (CH), 114.6 (CH×4), 110.2 (C), 108.0 (CN), 58.9 (CH_3×2), 27.6 (CH_3); *m/z* 689 (M^+, 100%).

2-Methyl-3-cyano-4-(4-biphenyl)-6-(2-pyridyl)pyridyl-Zn^{II}-bis(2-naphthalenethiolate) (4c) (0.28 g, 96%) was prepared according to the given procedure using 2-naphthalenethiol (0.13 g, 0.8 mmol) and 2-methyl-4-(4-biphenyl)-6-(2-pyridyl)nicotinonitrile (**3a**) (0.4 mmol, 1 equiv) and was obtained as light yellow crystals, mp 238–240 °C (Found: M^+, 729.1169. $C_{44}H_{32}N_3S_2Zn$ [M^+] requires 729.1251); ν_{max} (KBr) 2990, 2210, 1626, 1556, 1250, 816; λ_{max} ($CHCl_3$)/nm 388 (log ε 4.06), 328 (log ε 4.32); δ_H (400 MHz; $CDCl_3$) 8.86 (1H, d, *J* 6.4, 6'-H), 8.38 (1H, d, *J* 7.9, 3'-H), 8.34 (1H, s, 5-H), 8.06 (1H, m, 4'-H), 7.88 (2H, d, *J* 8.8, 2'',6''-H), 7.78 (2H, s, 1-NapH), 7.70 (3H), 7.62 (2H, m, 2''',6'''-H), 7.58 (2H, d, *J* 8.6, 4-NapH), 7.46 (4H, 5,8-NapH), 7.32 (2H, d, *J* 8.6, 3-NapH), 7.16 (4H, 6,7-NapH), 6.96 (1H, m, 3'-H), 6.89 (2H, d, *J* 8.8, 3'',5''-H), 3.32 (3H, s, 2-Me); δ_C (100 MHz; $CDCl_3$) 163.4 (C), 161.8 (C), 157.6 (C), 154.6 (C), 145.0 (CH), 137.4 (CH),

137.0 (C), 136.9 (C), 136.6 (C), 134.1 (C×2), 131.6 (CH×2), 130.6 (C×2), 129.9 (C×2), 129.3 (CH×2), 128.4 (CH×2), 128.2 (CH×2), 128.0 (CH×4), 127.6 (CH×2), 127.4 (CH×2), 127.0 (CH), 126.6 (CH×2), 126.2 (CH×4), 124.2 (CH), 120.8 (CH), 118.7 (CH), 117.0 (C), 108.4 (CN), 28.8 (CH_3); *m/z* 729 (M^+, 100%).

2-Methyl-3-cyano-4-[4-(diphenylamino)phenyl]-6-(2-pyridyl)pyridyl-Zn^{II}-bis(benzenethiolate) (4d) (0.28 g, 96%) was prepared according to the given procedure using thiophenol (0.08 mL, 0.8 mmol) and 2-methyl-4-[4-(diphenylamino)phenyl]-6-(2-pyridyl)nicotinonitrile (**3b**) (0.4 mmol, 1 equiv) and was obtained as bright red crystals, mp 236–238 °C (Found: M^+, 720.1328. $C_{42}H_{33}N_4S_2Zn$ [M^+] requires 720.1360); ν_{max} (KBr) 2988, 2204, 1628, 1556, 1252, 816; λ_{max} ($CHCl_3$)/nm 486 (log ε 3.86), 392 (log ε 4.18); δ_H (400 MHz; $CDCl_3$) 8.86 (1H, d, *J* 6.4, 6'-H), 8.26 (1H, d, *J* 7.9, 3'-H), 8.20 (1H, m, 4'-H), 8.01 (1H, s, 5-H), 7.79 (1H, m, 5'-H), 7.61 (2H, d, *J* 8.8, 2'',6''-H), 7.53 (6H), 7.46 (4H, m), 7.38 (6H), 7.20 (4H, m), 6.89 (2H, d, *J* 8.8, 3'',5''-H), 3.24 (3H, s, 2-Me); δ_C (100 MHz; $CDCl_3$) 163.9 (C), 161.4 (C), 157.2 (C), 154.6 (C), 145.0 (CH), 141.5 (C), 141.0 (C×2), 137.2 (CH), 132.6 (C×2), 132.2 (C), 129.7 (CH×4), 129.4 (CH×4), 129.1 (CH×4), 128.3 (CH×2), 125.6 (CH×2), 124.2 (CH), 123.2 (CH×2), 123.0 (CH×2), 122.7 (CH×4), 120.6 (CH), 118.4 (CH), 116.0 (C), 103.6 (CN), 28.0 (CH_3); *m/z* 720 (M^+, 100%).

2-Methyl-3-cyano-4-[4-(diphenylamino)phenyl]-6-(2-pyridyl)pyridyl-Zn^{II}-bis(4-methoxybenzenethiolate) (4e) (0.30 g, 96%) was prepared according to the given procedure using 4-methoxythiophenol (0.10 mL, 0.8 mmol) and 2-methyl-4-[4-(diphenylamino)phenyl]-6-(2-pyridyl)nicotinonitrile (**3b**) (0.4 mmol, 1 equiv) and was obtained as deep red crystals, mp 248–250 °C (Found: M^+, 780.1560. $C_{44}H_{37}N_4O_2S_2Zn$ [M^+] requires 780.1571); ν_{max} (KBr) 2989, 2206, 1629, 1558, 1254, 1202, 818; λ_{max} ($CHCl_3$)/nm 490 (log ε 3.78), 390 (log ε 4.20); δ_H (400 MHz; $CDCl_3$) 8.84 (1H, d, *J* 6.4, 6'-H), 8.24 (1H, d, *J* 7.9, 3'-H), 8.19 (1H, m, 4'-H), 8.00 (1H, s, 5-H), 7.77 (1H, m, 5'-H), 7.60 (2H, d, *J* 8.8, 2'',6''-H), 7.48 (4H, d, *J* 8.9), 7.36 (6H), 7.18 (4H, m), 6.96 (4H, d, *J* 8.9), 6.84 (2H, d, *J* 8.8, 3'',5''-H), 3.84 (6H, s, 2×OMe), 3.22 (3H, s, 2-Me); δ_C (100 MHz; $CDCl_3$) 162.4 (C), 161.4 (C), 157.5 (C×2), 157.0 (C), 152.4 (C), 144.0 (CH), 141.2 (C), 140.8 (C×2), 137.2 (CH), 132.4 (C), 130.2 (CH×4), 129.5 (CH×4), 128.0 (CH×2), 124.8 (C×2), 124.0 (CH), 123.2 (CH×2), 123.0 (CH×2), 122.5 (CH×4), 120.6 (CH), 118.5 (CH), 117.0 (C), 114.4 (CH×4), 102.8 (CN), 58.0 (CH_3×2), 27.6 (CH_3); *m/z* 780 (M^+, 100%).

2-Methyl-3-cyano-4-[4-(diphenylamino)phenyl]-6-(2-pyridyl)pyridyl-Zn^{II}-bis(2-naphthalenethiolate) (4f) (0.32 g, 98%) was prepared according to the given procedure using 2-naphthalenethiol (0.13 g, 0.8 mmol) and 2-methyl-4-[4-(diphenylamino)phenyl]-6-(2-pyridyl)nicotinonitrile (**3b**) (0.4 mmol, 1 equiv) and was obtained as light red crystals, mp 256–258

°C (Found: M^+, 820.1588. $C_{50}H_{37}N_4S_2Zn$ [M^+] requires 820.1673); ν_{max} (KBr) 2994, 2208, 1630, 1559, 1254, 820; λ_{max} ($CHCl_3$)/nm 484 (log ε 3.90), 394 (log ε 4.14); δ_H (400 MHz; $CDCl_3$) 8.89 (1H, d, *J* 6.4, 6'-H), 8.26 (1H, d, *J* 7.9, 3'-H), 8.23 (1H, m, 4'-H), 8.12 (1H, s, 5-H), 7.84 (1H, m, 5'-H), 7.59 (2H, d, *J* 8.8, 2'',6''-H), 7.44 (2H, s, 1-NapH), 7.34 (6H), 7.24 (2H, d, *J* 8.60, 4-NapH), 7.16 (4H, m), 7.12 (4H, 5,8-NapH), 6.88 (2H, d, *J* 8.60, 3-NapH), 6.80 (2H, d, *J* 8.8, 3'',5''-H), 6.72 (4H, 6,7-NapH), 3.26 (3H, s, 2-Me); δ_C (100 MHz; $CDCl_3$) 164.8 (C), 163.6 (C), 159.4 (C), 157.4 (C), 147.0 (CH), 143.5 (C), 143.0 (C×2), 140.2 (CH), 137.1 (C×2), 135.4 (C), 134.5 (CH×2), 133.6 (C×2), 132.9 (C×2), 130.7 (CH×4), 129.4 (CH×2), 128.6 (CH×2), 128.2 (CH×4), 127.6 (CH×2), 127.0 (CH×4), 126.2 (CH), 124.2 (CH×2), 123.8 (CH×2), 123.4 (CH×4), 121.8 (CH), 119.7 (CH), 118.0 (C), 104.2 (CN), 28.6 (CH_3); *m/z* 820 (M^+, 100%).

Experimental Procedure for Microwave-Assisted Complexation: Synthesis of Zn^{II}-bis{3-cyano-4-[4-(diphenylamino)phenyl]-6-(2-pyridyl)pyridyl} Perchlorate Complex (5).[6]

A solution of zinc perchlorate hexahydrate (0.2 mmol, 1 equiv) in hot dichloromethane (3 mL) was added dropwise to a solution of 2-methyl-4-[4-(diphenylamino)phenyl]-6-(2-pyridyl)nicotinonitrile (**3b**) (0.4 mmol, 2 equiv) in hot dichloromethane (3 mL) in a pressure-rated Pyrex® tube (10 mL). After 5 min of vigorous stirring, a SiC passive heating element (*Anton Paar Ltd.*) was added to the vessel, which was sealed and irradiated at 120 °C, at an initial power of 150 W, in a self-tuned single-mode CEM Discover® Focused Synthesiser for 10 min. The mixture was then cooled rapidly to room temperature, by passing compressed air through the microwave cavity for 5 min, and filtered through a sinter funnel. The filtrate was concentrated *in vacuo* to *ca*. 3 mL, and diethyl ether (3 mL) was added to give the *title compound* **5** (0.22 g, 96%) as bright orange crystals, mp 296–298 °C (Found: M^+, 1138.1940. $C_{60}H_{45}Cl_2N_8O_8Zn$ [M^+] requires 1138.1951); ν_{max} (KBr) 2988, 2208, 1630, 1556, 816; λ_{max} ($CHCl_3$)/nm 450 (log ε 4.16), 302 (log ε 4.51); δ_H (400 MHz; $CDCl_3$) 8.90 (2H, d, *J* 6.4, 2×6'-H), 8.74 (2H, d, *J* 7.9, 2×3'-H), 8.66 (2H, s, 2×5-H), 8.02 (2H, m, 2×4'-H), 7.88 (4H, d, *J* 8.8, 2×2'',6''-H), 7.66 (2H, m, 2×5'-H), 7.56 (12H), 7.40 (4H, d, *J* 8.8, 2×3'',5''-H), 7.36 (8H, m), 3.28 (6H, s, 2×2-Me); δ_C (100 MHz; $CDCl_3$) 162.8 (C×2), 161.6 (C×2), 157.6 (C×2), 155.6 (C×2), 150.5 (CH×2), 143.8 (C×2), 143.4 (C×4), 139.2 (CH×2), 134.6 (C×2), 131.9 (CH×8), 130.5 (CH×4), 126.4 (CH×2), 124.4 (CH×4), 124.0 (CH×4), 123.7 (CH×8), 122.8 (CH×2), 119.9 (CH×2), 118.0 (C×2), 103.8 (CN×2), 28.8 (CH_3×2); *m/z* 1138 (M^+, 100%).

Photophysical Analyses.

General Measurements.

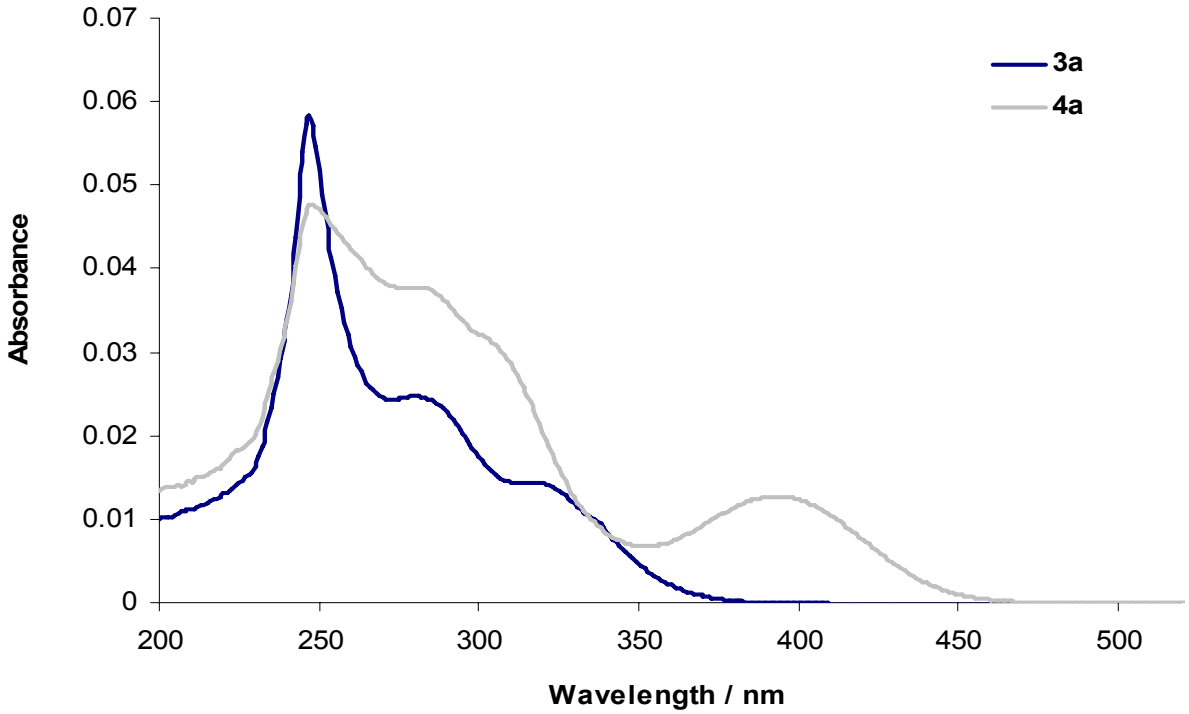
Electronic absorption spectra were measured upon 1.0×10^{-6} mol L^{-1} solutions in aerated chloroform, methanol, acetonitrile and DMSO for selected compounds at room temperature from 200 to 600 nm on a Varian Cary 500 Scan UV-vis NIR spectrophotometer using Cary WinUV Scan Application software, estimated errors are ±1 nm for λ_{max} and ±5% for ε. Steady-state luminescence analyses were processed using the same 1.0×10^{-6} mol L^{-1} solutions as for the absorption measurements. A Perkin-Elmer Luminescence Spectrometer LS55 with FL Winlab v. 4.00.02 software was used over the range 300-800 nm. Radiative lifetimes were measured using a JobinYvon-Horiba Fluorolog spectrometer fitted with a JY TBX picosecond photodetection module. Aerated solution samples for luminescence lifetime decays were irradiated using a pulsed NanoLED configured for 330 nm or 400 nm output and emission detected at emission maxima. Data sets were obtained using the JY-Horiba FluorHub single photon counting module and lifetimes determined using the provided decay analysis software package, v6.1. Fluorescence quantum yields, Φ_f, were measured in various solvents using 1.0×10^{-6} mol L^{-1} fluorescein in 0.1 mol L^{-1} NaOH as the reference standard ($\Phi_{std} = 0.79$).[7] Each was diluted with the appropriate solvent until the absorbance [λ_{max}(LLCT)] at 385-495 nm was eventually calibrated between 0.05 and 0.01.[8] The fluorescence spectra were then recorded with excitation wavelengths between 320-490 nm. The peak was integrated using Microsoft Excel. This process was repeated three times at different optical densities. The integrated intensity was plotted against the absorbance of each sample. The slopes of the resulting lines were calculated using Microsoft Excel. The quantum yield was then determined by the following equation, taking into account the respective refractive indices: [9]

$$\phi_{sample} = \phi_{std} \frac{(Slope_{sample})}{(Slope_{std})} \frac{(\eta^2_{sample})}{(\eta^2_{std})}$$

All solutions used for the spectroscopic analysis (i.e. λ_{abs}, λ_{em}, τ_f & Φ_f) were freshly prepared before each measurement.

UV-Vis & Luminescence Profiles.

Fig. 1 Solution UV-vis absorption spectra for complex **4a** (dark) and the corresponding free ligand **3a** (light) in chloroform.



Luminescence Profiles and Lifetime Decays.

Fig. 2 Normalised excitation spectra of complex **4f** in 10^{-6} M aerated chloroform at 298 K. λ_{em} = 524 nm (grey) and the free ligand **3b** λ_{em} = 612 nm (black).

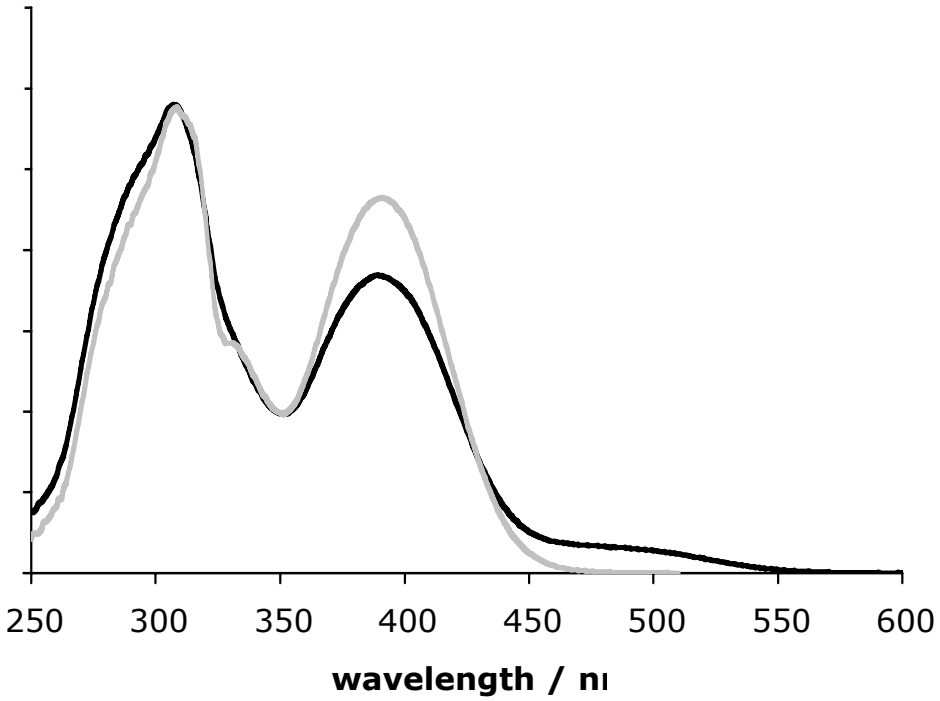
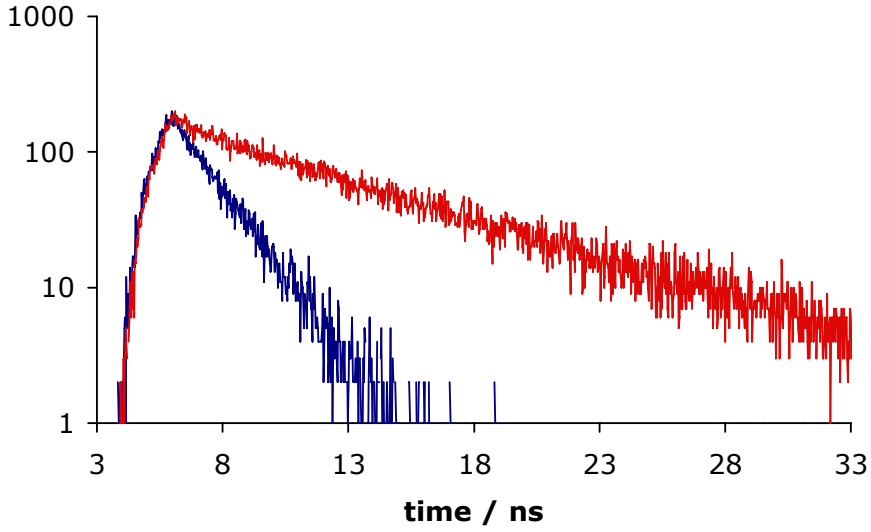


Fig. 3. Representative luminescence lifetime decay profiles for compound **4c** in chloroform. Red: 7.2 ns (λ_{em} = 512 nm**;** λ_{ex} = 459 nm). Blue: 1.6 ns (λ_{em} = 398 nm**;** λ_{ex} = 372 nm).



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