Supporting Information

Linear Bilateral Extended 2,2′:6′,2″-Terpyridine Ligands, Their Coordination Complexes and Heterometallic Supramolecular Networks

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1. General

All reagents and solvents used for reactions were reagent grade and used without further purification unless otherwise noted. Anhydrous THF and toluene was supplied from an Mbraun solvent purification system. PdCl$_2$(PPh$_3$)$_2$ was prepared according to the reported protocol.$^1$ Analytical thin-layer chromatography was performed with Macherey–Nagel POLYGRAM SIL N-HR/UV254 or ALOX N/UV254. Flash silica gel column chromatography was performed with Merck silica gel 60 (particle size 0.040–0.063 mm). Flash alumina column chromatography was performed with deactivated (5% water) Fluka alumina (particle size 0.05–0.15 mm, pH 7.0±0.5). Melting points were recorded on a Büchi B-540 melting point apparatus. For characterization purposes, proton nuclear magnetic resonance ($^1$H-NMR) spectra were all recorded on Bruker instruments (AV-300 and ARX-300 at 300 MHz, AV2-400 at 400 MHz, and AV-500 at 500 MHz). Chemical shifts are reported in ppm relative to CHCl$_3$ (δ 7.26), CD$_2$Cl$_2$ (δ 5.31), CD$_3$CN (δ 1.94) or DMSO-d$_6$ (2.50). Multiplicity and shape are indicated by one or more of the following abbreviations: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); td (triplet of doublets); m (multiplet); br (broad). Carbon-13 nuclear magnetic resonance ($^{13}$C- NMR) spectra were recorded on Bruker instruments (ARX-300 at 75 MHz, AV2-400 at 100 MHz, and AV-500 at 125 MHz). Chemical shifts are reported relative to CDCl$_3$ (δ 77.2), CD$_2$Cl$_2$ (δ 53.8), CD$_3$CN (δ 1.3) or DMSO-d$_6$ (δ 39.5). Infrared spectroscopic data were recorded on NaCl plates as thin films, as KBr pellets or neat sample on a Perkin Elmer Spectrum One (PE) or Jasco FT/IR-4100 spectrophotometer. The intensities are given as follows: s = strong, m = medium, and w = weak. An Agilent 8453 UV/Vis spectrophotometer was used to record all UV/Vis spectra. Emission spectra and lifetimes (ns) were recorded on an Edinburgh Instruments FLS920 spectrometer. Solid-state quantum yields were measured using an integrating sphere accessory for FLS920 spectrometer. X-ray structures were carried out by the Laboratorium für Computerchemie und Röntgenstrukturanalyse of the Institute of Organic Chemistry of the University of Zurich using a Nonius KappaCCD diffractometer with MoKα radiation (λ = 0.71037 Å).

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2. Experimental Procedures

2.1. Synthesis of 4,4”-Diiodo-5,5”-bis(methoxymethoxy)-2,2’:6’,2”-terpyridine (14)

2-Bromo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (8)

To a solution of 2,5-dibromopyridine (7) (22.46 g, 94.80 mmol) in Et₂O (800 mL) was added dropwise a solution of n-BuLi (2.50 M in hexane, 39.80 mL, 99.50 mmol) at −78 °C under N₂ atmosphere. After addition, the mixture was stirred at −78 °C for 3 h, then a solution of 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15.88 g, 100.5 mmol) in Et₂O (20 mL) was introduced dropwise to the reaction mixture at −78 °C. The reaction was gradually warmed up to room temperature and stirred for 12 h, then the solvent was removed under reduced pressure. The residue was dissolved in 10% NaOH solution (200 mL) and washed with CH₂Cl₂ (100 mL × 2). The organic layers were discarded and the aqueous phase was acidified carefully to pH 1–2 with 32% HCl, then extracted with CH₂Cl₂ (200 mL × 3). The combined organic extracts were dried over MgSO₄, filtered and concentrated reduced pressure to afford boronic ester 8 (23.66 g, 83%) as a pale white solid.

Mp 94–95.5 °C (lit. mp 94 °C)².

¹H NMR (400 MHz, CDCl₃, δ): 8.67 (dd, J = 0.7, 2.0 Hz, 1H), 7.87 (dd, J = 2.0, 7.9 Hz, 1H), 7.47 (dd, J = 0.7, 7.9 Hz, 1H), 1.34 (s, 12H).

¹³C NMR (100 MHz, CDCl₃, δ): 156.1 (d), 145.6 (s), 144.5 (d), 127.7 (d), 84.6 (s), 25.0 (q) C-Bpin was not observed in ¹³C NMR due to line broadening of the short relaxation time and the quadrupole moment of ¹¹B (I = 3/2).

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IR (film on NaCl, cm\(^{-1}\)): 2978\(m\), 1578\(s\), 1546\(m\), 1455\(m\), 1385\(vs\), 1357\(vs\), 1142\(m\), 1103\(s\), 1015\(m\), 857\(m\), 823\(m\), 742\(m\), 662\(m\).

MS (ESI) \(m/z\): 284.1 ([M + H\(^+\)]; 306.1 ([M + Na\(^+\)]).

HRMS (ESI) \(m/z\): [M + Na\(^+\)] calcd for C\(_{11}\)H\(_{15}\)NO\(_2\)BrBNa: 306.0291; found: 306.0284.
2,6-Bis(trimethylstannyl)pyridine (10)

To a suspension of fresh finely chopped sodium (32.3 g, 1.40 mol, 7.38 eq) in anhydrous DME (200 mL) a solution of Me₃SnCl (94.5 g, 0.474 mol, 2.50 eq) in anhydrous DME (100 mL) was slowly added at –15 °C under N₂ atmosphere. After stirring for 3 h at –15 °C, the pistachio green suspension of NaSnMe₃ in DME was introduced in 30 min., via a cannula, to a solution of 2,6-dichloropyridine (9) (28.07 g, 0.1897 mol, 1.00 eq) in anhydrous DME (200 mL) at –15 °C under N₂ atmosphere. The dark brown reaction mixture was stirred at –15 °C for 1 h, then gradually warmed up to room temperature and stirred for 18 h. The solvent was removed under reduced pressure, and the residue was treated with Et₂O (350 mL). The insoluble inorganic salts were filtered off through a plug of Celite (3 cm) and the cake was washed with Et₂O (300 mL). The combined filtrates were concentrated under reduced pressure to afford the crude product as dark brown oil. The crude residue was purified by vacuum distillation (0.05 mbar, 80-82 °C) to give 2,6-bis(trimethylstannyl)pyridine (10) (64.39 g, 84%) as colorless oil.³⁴

¹H NMR (400 MHz, CD₂Cl₂, δ): 7.38-7.25 (m, 3H), 0.30 (s, with Sn satellites, ²J_HSn = 55.8/53.4 Hz, 18H).

¹³C NMR (75 MHz, CD₂Cl₂, δ): 174.4 (s), 131.5 (d), 130.3 (d), -9.7 (q, with Sn satellites, ¹J_CSn = 346.9/331.6 Hz).

To a degassed mixture of boronic ester 8 (99.6 g, 342 mmol, 2.15 eq) and Pd(PPh$_3$)$_4$ (8.97 g, 7.76 mmol, 4.87 mol%) in toluene (600 mL) a solution of bisstannyl pyridine 10 (64.5 g, 159 mmol, 1.00 eq) in degassed toluene (250 mL) was added under N$_2$ atmosphere.
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The reaction mixture was heated to reflux for 24 h. The mixture was cooled to 5 °C and the resulting precipitate was collected by filtration. The solid was dissolved in CH₂Cl₂ (600 mL) and washed with 10% aqueous KF solution (500 mL x 2). The aqueous phases were extracted with CH₂Cl₂ (200 ml x 2). The combined organic phases were dried over MgSO₄, filtered and concentrated under reduced pressure to give diboronic ester 11 (42.26 g, 56%) as an off-white solid.

Mp 259.5–260.5 °C (lit. mp 251 °C).²

¹H NMR (400 MHz, CDCl₃, δ): 9.03 (dd, J = 0.9, 1.7 Hz, 2H), 8.59 (dd, J = 0.9, 7.9 Hz, 2H), 8.51 (d, J = 7.8 Hz, 2H), 8.23 (dd, J = 1.7, 7.9 Hz, 2H), 7.96 (t, J = 7.8 Hz, 1H), 1.39 (s, 24H).

¹³C NMR (125 MHz, CDCl₃, δ): 158.3 (s) 155.6 (s), 155.2 (d), 143.3 (d), 138.0 (d), 121.9 (d), 120.4 (d), 84.3 (s), 25.0 (q) C-Bpin was not observed in ¹³C NMR due to line broadening of the short relaxation time and the quadrupole moment of ¹¹B (I = 3/2).

IR (film on NaCl, cm⁻¹): 2977m, 1593s, 1547m, 1359vs, 1316m, 1142m, 1107m, 1022m, 857m, 820m, 765m, 666m.

MS (ESI) m/z: 486.3 ([M + H]⁺); 508.3 ([M + Na]⁺).

HRMS (ESI) m/z: [M + Na]⁺ calcd for C₂₇H₃₃N₃O₄B₂Na: 508.2567; found: 508.2561.
To a solution of diboronic ester 11 (42.16 g, 86.89 mmol, 1.00 eq) in THF (1.5 L) an aqueous solution of NaOH (6.0 M, 41.7 mL, 260 mmol, 3.00 eq) was added. After stirring the mixture for 10 min at room temperature, white precipitate formed. Then, to the resulting suspension an aqueous solution of H₂O₂ (30%, 23.6 mL, 226 mmol, 2.60 eq)
was added dropwise in ~ 10 min by cooling the mixture with ice-water bath. The reaction mixture was allowed to stir at room temperature for 18 h and quenched with 10% \( \text{Na}_2\text{S}_2\text{O}_3 \) aqueous solution (250 mL). After complete removal of volatile organic solvents under reduced pressure, the aqueous layer was acidified with 10% HCl to pH 6–7. The resulting yellow precipitate was filtered, washed with H\(_2\)O (400 mL) and dried under high vacuum at 40 °C for 24 h to afford the dihydroxy terpyridine \( \text{12} \) (22.19 g, 96%) as a yellowish orange solid.\(^5\,6\)

Mp 153–154 °C.

\(^1\text{H} \) NMR (500 MHz; DMSO-\(d_6 \), \( \delta \)): 10.26 (s, 2H), 8.45 (d, \( J = 8.6 \) Hz, 2H), 8.25 (d, \( J = 2.7 \) Hz, 2H), 8.20 (d, \( J = 7.8 \) Hz, 2H), 7.95 (t, \( J = 7.8 \) Hz, 1H), 7.34 (dd, \( J = 8.6, 2.8 \) Hz, 2H).

\(^{13}\text{C} \) NMR (125 MHz, DMSO-\(d_6 \), \( \delta \)): 154.8 (s), 154.4 (s), 146.6 (s), 137.9 (d), 137.4 (d), 122.9 (d), 121.5 (d), 118.4 (d).

IR (film on NaCl, cm\(^{-1} \)): 3093\( br \), 1705\( m \), 1565\( s \), 1537\( s \), 1490\( m \), 1440\( vs \), 1361\( m \), 1283\( s \), 1221\( m \), 853\( m \), 807\( m \).

MS (ESI) \( m/z \): 288.1 ([M + Na]\(^+ \)).

HRMS (ESI) \( m/z \): [M + Na]\(^+ \) calcd for C\(_{15}\)H\(_{11}\)N\(_3\)O\(_2\)Na: 288.0749; found: 288.0746.

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Supporting Information

5,5''-Bis(methoxymethoxy)-2,2':6',2''-terpyridine (13)

To a suspension of NaH (60% in oil, 3.80 g, 99.1 mmol, 3.00 eq) in anhydrous THF (120 mL) was added dropwise a solution of dihydroxy terpyridine 12 (8.76 g, 33.0 mmol, 1.00 eq) in DMF (40 mL) at 0 °C under N₂ atmosphere. After addition, the mixture was allowed to warm up and stirred at room temperature for 30 min, then cooled down to 0 °C.
°C. To this mixture was added slowly a freshly prepared solution of MOMCl in MeOAc, obtained as described in the literature from ZnBr₂ (3.9 mg, 1.8 mmol, 0.018 mol%) catalyzed reaction of AcCl (8.21 mL, 115.6 mmol, 3.50 eq) and (MeO)₂CH₂ (10.23 mL, 115.6 mmol, 3.50 eq)⁷, at 0 °C under N₂ atmosphere. The reaction mixture was then warmed up to room temperature and stirred for 12 h. After slowly quenched with H₂O (200 mL) at 0 °C, the mixture was extracted with CH₂Cl₂ (200 mL × 3). The combined organic layers were dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was treated with hexane and collected by filtration. The residue was filtered through a short pad of silica gel eluating with hexane/EtOAc/MeOH (25:25:1) to afford terpyridine 13 (11.2 g, 96%) as a white solid.

Mp 75.5–76.5 °C.

¹H NMR (500 MHz, CDCl₃, δ): 8.53 (dd, J = 8.8, 0.6 Hz, 2H), 8.47 (dd, J = 2.9, 0.6 Hz, 2H), 8.31 (d, J = 7.8 Hz, 2H), 7.88 (t, J = 7.8 Hz, 1H), 7.51 (dd, J = 8.7, 2.9 Hz, 2H), 5.26 (s, 4H), 3.52 (s, 6H).

¹³C NMR (125 MHz, CDCl₃, δ): 155.1 (s), 154.0 (s), 150.3 (s), 138.7 (d), 137.8 (d), 123.7 (d), 121.8 (d), 119.9 (d), 94.8 (t), 56.4 (q).

IR (film on NaCl, cm⁻¹): 2951w, 2908w, 1562s, 1486m, 1448m, 1283m, 1207m, 1154m, 1141m, 1077m, 961vs, 933m, 808s, 753m, 636m.

MS (ESI) m/z: 376.2 ([M + Na]⁺).


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4,4’-Diiodo-5,5’-bis(methoxymethoxy)-2,2’:6’2”-terpyridine (14)

To a mixture of terpyridine 13 (1.10 g, 3.12 mmol, 1.00 eq) and TMEDA (0.94 mL, 6.24 mmol, 2.00 eq) in THF (70 mL) was added dropwise a solution of n-BuLi (2.50 M in hexane, 2.74 mL, 6.85 mmol, 2.20 eq) at −78 °C under N₂ atmosphere. The resulting deep

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A blue mixture was allowed to stir at −78 °C for 1 h. To the mixture a solution of I₂ (1.74 g, 6.86 mmol, 2.20 eq) in THF (10 mL) was added dropwise in 20 min at −78 °C. The reaction mixture was allowed to warm to room temperature, stirred for 18 h and quenched with aqueous Na₂S₂O₃ (10%, 50 mL). The organic layer was separated and the aqueous phase was extracted with CH₂Cl₂ (100 mL × 3). The combined organic layers were washed with brine and dried over MgSO₄, filtered and evaporated under reduced pressure. The residue was suspended in EtOH (60 mL), heated to reflux and allowed to cool to room temperature. The resulting solid was collected by filtration and washed with EtOH (8 mL × 2) to give diiodo terpyridine 14 (0.94 g, 50%) as an off-white solid.

Mp 212–213 °C.

¹H NMR (500 MHz, CDCl₃, δ): 8.98 (s, 2H), 8.38 (s, 2H), 8.32 (d, J = 7.8 Hz, 2H), 7.89 (t, J = 7.8 Hz, 1H), 5.36 (s, 4H), 3.58 (s, 6H).

¹³C NMR (125 MHz, CDCl₃, δ): 154.0 (s), 153.7 (s), 150.8 (s), 138.1 (d), 135.8 (d), 132.2 (d), 120.8 (d), 99.5 (s), 95.7 (t), 56.9 (q).

IR (film on NaCl, cm⁻¹): 2946w, 2905w, 1563m, 1480s, 1443s, 1351m, 1301m, 1265s, 1238m, 1202m, 1160s, 1037m, 985vs, 899m, 821m.

MS (ESI) m/z: 627.9 ([M + Na]⁺).

HRMS (ESI) m/z: [M + Na]⁺ calcd for C₁₉H₁₇N₃O₄I₂Na: 627.9206; found: 627.9203.
2.2. Synthesis of Acetylenes 18, 22a and 22b

2-Iodo-5-methoxy-1,3-dimethylbenzene (16)

To a solution of 2-bromo-5-methoxy-1,3-dimethylbenzene (15) (1.00 g, 4.64 mmol, 1.00 eq) in anhydrous THF (15 mL) a solution of n-BuLi (2.50 M in hexane, 1.95 mL, 4.87
mmol, 1.05 eq) was added dropwise under N₂ atmosphere at -78 °C over 10 min. The resulting white suspension was stirred for 30 min. at -78 °C, then a solution of iodine (1.29 g, 5.10 mmol, 1.10 eq) in anhydrous THF was added dropwise at -78 °C over 15 min. The reaction mixture was allowed to warm up to room temperature and stirred overnight. The solvent was evaporated under reduced pressure and the residue was dissolved in CH₂Cl₂ (50 mL), washed with 10% Na₂S₂O₃ aqueous solution (50 mL), water and brine. The organic phase was dried over MgSO₄, filtered and evaporated under reduced pressure. The residue was purified by silica gel column chromatography with hexane/ethyl acetate (99:1) to give 2-iodo-5-methoxy-1,3-dimethylbenzene (16)⁸ (0.98 g, 81%) as a yellow oil.

¹H NMR (300 MHz, CDCl₃, δ): 6.67 (s, 2H), 3.77 (s, 3H), 2.45 (s, 6H).

¹³C NMR (75 MHz, CDCl₃, δ): 159.3 (s), 143.0 (s), 113.0 (d), 97.2 (s), 55.4 (q), 29.9 (q).

IR (film on NaCl, cm⁻¹): 2996w, 2952m, 2836m, 1586s, 1464s, 1402w, 1377w, 1317s, 1275w, 1195m, 1163s, 1075m, 1030w, 1005m, 933w, 853m, 833m, 690w, 609w.

HRMS (EI) m/z: [M]⁺ calcd for C₉H₁₁O₁I: 261.9854; found: 261.9854.

[(4-Methoxy-2,6-dimethylphenyl)ethynyl]trimethylsilane (17)

To a degassed mixture of 2-iodo-5-methoxy-1,3-dimethylbenzene (16) (2.00 g, 7.63 mmol, 1.00 eq), Pd(PPh₃)₂Cl₂ (267 mg, 0.380 mmol, 5 mol%) and CuI (145 mg, 0.760 mmol, 10 mol%) in toluene (40 mL) and triethylamine (20 mL) was added a solution of trimethylsilylacetylene (1.52 mL, 10.7 mmol, 1.40 eq) in toluene (20 mL) and triethylamine (20 mL) at 80 °C. The reaction mixture was heated to reflux for 18 h, allowed to cool to room temperature and diluted with CH₂Cl₂ (100 mL). The mixture was washed with 10% aqueous NH₄OH, water and brine. The organic phase was dried over MgSO₄, filtered and evaporated under reduced pressure. The residue was purified by silica gel column chromatography with hexane/ethyl acetate (50:1) to give [(4-methoxy-2,6-dimethylphenyl)ethynyl]trimethylsilane (17) (1.68 g, 95%) as a pale yellow oil.

¹H NMR (300 MHz, CDCl₃, δ): 6.57 (s, 2H), 3.77 (s, 3H), 2.41 (s, 6H), 0.25 (s, 9H).

¹³C NMR (75 MHz, CDCl₃, δ): 159.2 (s), 142.6 (s), 115.6 (s), 112.4 (d), 103.1 (s), 101.0 (s), 55.3 (q), 21.4 (q), 0.4 (q).

IR (film on NaCl, cm⁻¹): 3000w, 2959s, 2840w, 2147s, 1606s, 1575w, 1481m, 1470m, 1377w, 1321s, 1284w, 1250m, 1222m, 1194m, 1152s, 1064m, 943w, 862s, 786w, 760m, 698w, 625w.

HRMS (ESI) m/z: [M + H⁺] calcd for C₁₄H₂₁OSi: 233.13562; found: 233.13522.
To a solution of [(4-methoxy-2,6-dimethylphenyl)ethynyl]trimethylsilane (17) (1.31 g, 5.64 mmol, 1.00 eq) in methanol (140 mL) KF (3.27 g, 56.4 mmol, 10.0 eq) was added. The reaction mixture was heated to 40 °C for 18 h (followed by GC/MS). After
evaporation of solvent under reduced pressure, the residue was filtered through a pad of Celite eluting with diethyl ether (100 mL). The filtrate was evaporated under reduced pressure and the crude product was purified by silica gel column chromatography with hexane/ethyl acetate (95:5) to give 2-ethynyl-5-methoxy-1,3-dimethylbenzene\(^9\)\(^,\)\(^10\) (18) as a white waxy solid (0.866 g, 96%).

Mp 42–44 °C.

\(^1\)H NMR (300 MHz, CDCl\(_3\), δ): 6.59 (s, 2H), 3.78 (s, 3H), 3.42 (s, 1H), 2.43 (s, 6H).

\(^13\)C NMR (75 MHz, CDCl\(_3\), δ): 159.3 (s) 142.8 (s), 114.5 (s), 112.5 (d), 83.9 (d), 81.5 (s), 55.3 (q), 21.4 (q).

IR (film on NaCl, cm\(^{-1}\)): 3310s, 3290s, 3001w, 2957m, 2919m, 2840w, 2144w, 2097m, 1606s, 1582m, 1481m, 1470m, 1443m, 1377w, 1320s, 1206m, 1196m, 1147s, 1062m, 858m, 840m, 725w, 680w.

HRMS (ESI) \(m/z\): [M + H]\(^+\) calcd for C\(_{11}\)H\(_{13}\)O: 161.09609; found: 161.09607.

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Supporting Information

5-Bromo-5’-(4-methoxy-2,6-dimethylphenyl)-2,2’-bipyridine (20a)

To a solution of 2-bromo-5-(4-methoxy-2,6-dimethylphenyl)pyridine (19a)¹¹ (7.20 g, 24.6 mmol, 1.00 eq) in anhydrous THF (150 mL) a solution of n-BuLi (2.50 M in hexane, 10.8 mL, 27.1 mmol, 1.10 eq) was added dropwise under N₂ at -78 °C over 15 min. The reaction mixture was allowed to stir for 1 h at -78 °C and then a solution of dry ZnCl₂ (3.70 g, 27.1 mmol, 1.10 eq) in anhydrous THF (50 mL) was added via cannula. Upon warming to room temperature, the resulting aryl zincate solution was cannulated into a solution of 2,5-dibromopyridine (7) (6.13 g, 25.9 mmol, 1.05 eq.) and Pd(PPh₃)₄ (427 mg, 0.370 mmol, 1.5 mol%) in anhydrous THF (100 mL). The reaction mixture was heated to reflux for 18 h and allowed to cool to room temperature. The resulting white precipitate was filtered off, washed with THF, and dried under reduced pressure. The dry precipitate was then suspended in a mixture of CH₂Cl₂ and a basic aqueous solution EDTA (basified using an aqueous solution of NaHCO₃) and stirred until all precipitate dissolve. The organic phase was separated, washed with water and brine, dried over MgSO₄, and evaporated under reduced pressure to give 5-bromo-5’-(4-methoxy-2,6-dimethylphenyl)-2,2’-bipyridine (20a) (2.84 g, 31%) as a white solid.

Mp 132–134 °C.

¹H NMR (400 MHz, CDCl₃, δ): 8.74 (d, J = 2.1 Hz, 1H) 8.47 (s, 1H), 8.44 (d, J = 8.1 Hz, 1H), 8.36 (d, J = 8.5 Hz, 1H), 7.96 (dd, J = 8.5, 2.3 Hz, 1H), 7.63 (dd, J = 8.1, 2.1 Hz, 1H), 6.71 (s, 2H), 3.83 (s, 3H), 2.06 (s, 6H).

¹³C NMR (100 MHz, CDCl₃, δ): 159.1 (s), 154.7 (s), 153.6 (s), 150.4 (d), 150.2 (d), 139.6 (d), 138.6 (d), 137.9 (s), 137.2 (s), 130.3 (s), 122.4 (d), 121.2 (s), 120.8 (d), 113.2 (d), 55.3 (q), 21.3 (q).

IR (film on NaCl, cm\(^{-1}\)): 2954\textit{w}, 2836\textit{w}, 1607\textit{m}, 1539\textit{vs}, 1453\textit{vs}, 1359\textit{w}, 1318\textit{s}, 1275\textit{w}, 1193\textit{w}, 1155\textit{s}, 1092\textit{w}, 1075\textit{w}, 1056\textit{w}, 1005\textit{m}, 837\textit{m}, 738\textit{w}.

HRMS (ESI) \textit{m/z}: [M + H]\textsuperscript{+} calcd for C\textsubscript{19}H\textsubscript{18}BrN\textsubscript{2}O: 369.05970; found: 369.05953.
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5-Ethynyl-5’-(4-methoxy-2,6-dimethylphenyl)-2,2’-bipyridine (22a)

![Chemical Structure of 22a](image)

To a mixture of 5-bromo-5’-(4-methoxy-2,6-dimethylphenyl)-2,2’-bipyridine (20a) (2.79 g, 7.56 mmol, 1.00 eq), CuI (72 mg, 0.38 mmol, 5 mol%) and PdCl$_2$(PPh$_3$)$_2$ (0.530 g, 0.756 mmol, 10 mol%) in degassed Et$_3$N (150 mL) was added trimethylsilylacetylene (2.12 mL, 15.1 mmol, 2.00 eq) under N$_2$ atmosphere at 80 °C. The reaction mixture was heated to reflux for 19 h, allowed to cool to room temperature and evaporated to dryness under reduced pressure. The residue was redissolved in CH$_2$Cl$_2$ (100 mL), washed with 10% aqueous NH$_4$OH, water and brine. The organic phase was dried over MgSO$_4$, filtered and evaporated under reduced pressure. The crude residue was dissolved in MeOH (100 mL), and to the resulting mixture KF (1.32 g, 22.8 mmol, 3.00 eq) was added. The reaction mixture was stirred at room temperature for 18 h. The solvent was evaporated under reduced pressure, and the residue was filtered through a pad of Celite eluting with CH$_2$Cl$_2$ (100 mL). After evaporation of solvent, the crude product was purified by silica gel column chromatography with hexane/ethyl acetate (3:1) to give 5-ethynyl-5’-(4-methoxy-2,6-dimethylphenyl)-2,2’-bipyridine (22a) (1.72 g, 72%) as an off-white solid.

Mp 137.5–138.5 °C.

$^1$H NMR (500 MHz, CDCl$_3$, δ): 8.80 (dd, $J = 2.1$, 0.8 Hz, 1H), 8.49 (dd, $J = 2.2$, 0.8 Hz, 1H), 8.47 (dd, $J = 8.1$, 0.8 Hz, 1H), 8.43 (dd, $J = 8.2$, 0.8 Hz, 1H), 7.92 (dd, $J = 8.2$, 2.1 Hz, 1H), 7.64 (dd, $J = 8.1$, 2.2 Hz, 1H), 6.71 (s, 2H), 3.84 (s, 3H), 3.30 (s, 1H), 2.08 (s, 6H).

$^{13}$C NMR (125 MHz, CDCl$_3$, δ): 159.1 (s), 155.5 (s), 153.8 (s), 152.4 (d), 150.3 (d), 140.1 (d), 138.5 (d), 137.9 (s), 137.2 (s), 130.3 (s), 121.2 (d), 120.3 (d), 119.1 (s), 113.1 (d), 81.4 (d), 80.9 (s), 55.3 (q), 21.4 (q).
Supporting Information

IR (film on NaCl, cm⁻¹): 3287m, 2955w, 2836w, 2105vw, 1605m, 1589m, 1461vs, 1318s, 1192m, 1155s, 1074m, 1056m, 844m, 746m.

Supporting Information

5-Ethynyl-6’-(4-methoxy-2,6-dimethylphenyl)-2,2’-bipyridine (22b)

To a mixture of 5-bromo-6’-(4-methoxy-2,6-dimethylphenyl)-2,2’-bipyridine (20b)\(^\text{12}\) (7.00 g, 19.0 mmol, 1.00 eq), CuI (0.181 g, 0.948 mmol, 5 mol%) and PdCl\(_2\)(PPh\(_3\))\(_2\) (1.33 g, 1.89 mmol, 10 mol%) in degassed Et\(_3\)N (150 mL) was added trimethylsilylacetylene (5.33 mL, 38.0 mmol) under N\(_2\) atmosphere at 80 °C. The reaction mixture was heated to reflux for 18 h, allowed to cool to room temperature and evaporated to dryness under reduced pressure. The residue was redissolved in CH\(_2\)Cl\(_2\) (200 mL), washed with aqueous 10% NH\(_4\)OH, water and brine. The organic phase was dried over MgSO\(_4\), filtered and evaporated under reduced pressure. The crude residue was dissolved in MeOH (250 mL), and to the resulting mixture KF (3.50 g, 22.8 mmol, 3.23 eq) was added. The reaction mixture was stirred at room temperature for 18 h. The solvent was evaporated under reduced pressure, and the residue was filtered through a pad of Celite eluting with CH\(_2\)Cl\(_2\) (250 mL). After evaporation of solvent, the crude product was purified by silica gel

column chromatography with hexane/ethyl acetate (3:1) to give 5-ethynyl-6′-(4-methoxy-2,6-dimethylphenyl)-2,2′-bipyridine (22b) (4.65 g, 78%) as an off-white solid.

Mp 123.5–125 °C.

$^1$H NMR (400 MHz, CDCl$_3$, δ): 8.78 (dd, $J = 2.1$, 0.8 Hz, 1H) 8.43 (dd, $J = 8.2$, 0.8 Hz, 1H), 8.37 (dd, $J = 7.6$, 1.0 Hz, 1H), 7.87 (t, $J = 7.6$ Hz, 1H), 7.84 (dd, $J = 8.2$, 2.1 Hz, 1H), 7.24 (dd, $J = 7.6$, 1.1 Hz, 1H), 6.70 (s, 2H), 3.84 (s, 3H), 3.28 (s, 1H), 2.11 (s, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$, δ): 159.3 (s), 159.1 (s), 155.8 (s), 155.2 (s), 152.2 (d), 140.0 (d), 137.6 (s), 137.2 (d), 133.6 (s), 125.6 (d), 120.8 (d), 119.2 (d), 119.1 (s), 113.2 (d), 81.3 (d), 80.9 (s), 55.3 (q), 20.9 (q).

IR (film on NaCl, cm$^{-1}$): 3288m, 2954w, 2836w, 2105w, 1606m, 1585m, 1450s, 1321m, 1192m, 1157vs, 1070m, 858m, 819m, 751m.

MS (ESI) $m/z$: 337.2 ([M + Na]$^+$). HRMS (ESI) $m/z$: [M + Na]$^+$ calcd for C$_{21}$H$_{18}$N$_2$ONa: 337.1317; found: 337.1315.
Supporting Information
2.3. Synthesis of 23a-h, 24a-c and 26a,b by Sonogashira Coupling Reaction

5,5”-Bis(methoxymethoxy)-4,4”-bis(phenylethynyl)-2,2’:6’,2”-terpyridine (23a)

To a mixture of diiodoterpyridine 14 (300 mg, 0.496 mmol, 1.00 eq), CuI (9.4 mg, 0.050 mmol, 10 mol%) and PdCl$_2$(PPh$_3$)$_2$ (17.4 mg, 0.0248 mmol, 5 mol%) in degassed THF/Et$_3$N (10 mL/10 mL) was added ethynylbenzene (0.126 mL, 1.24 mmol, 2.50 eq) under N$_2$ atmosphere at 80 °C. The reaction mixture was heated to reflux for 20 h, allowed to cool to room temperature and evaporated to dryness under reduced pressure. The residue was redissolved in CH$_2$Cl$_2$ (30 mL), washed with 10% aqueous NH$_4$OH, water and brine. The organic phase was dried over MgSO$_4$, filtered and evaporated under reduces pressure. The residue was purified by neutral alumina (Brockman III) column chromatography with hexane/ethyl acetate (3:1) to give 5,5”-bis(methoxymethoxy)-4,4”-bis(phenylethynyl)-2,2’:6’,2”-terpyridine (23a) (261 mg, 95 %) as an off-white solid.

Mp 149–151 °C.

$^1$H NMR (400 MHz, CDCl$_3$, δ): 8.72 (s, 2H), 8.60 (s, 2H), 8.36 (d, $J$ = 7.8 Hz, 2H), 7.92 (t, $J$ = 7.8 Hz, 1H), 7.63 (dd, $J$ = 7.6, 1.7 Hz, 4H), 7.41-7.34 (m, 6H), 5.40 (s, 4H), 3.61 (s, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$, δ): 154.8 (s), 153.6 (s), 150.3 (s), 137.9 (d), 137.5 (d), 132.0 (d), 129.1 (d), 128.5 (d), 124.6 (d), 122.7 (s), 120.3 (d), 97.7 (s), 95.9 (t), 83.9 (s), 56.7 (q).

IR (film on NaCl, cm$^{-1}$): 2957w, 2906w, 2219w, 1600w, 1573m, 1544w, 1494m, 1484s, 1457m, 1379m, 1308w, 1268m, 1232w, 1200m, 1155s, 1077m, 982s, 921w, 823w, 757m, 690w.
Supporting Information

MS (ESI) m/z: 554.3 ([M + H]^+); HRMS (ESI) m/z: [M+Na]^+ calcd for C_{35}H_{27}N_{3}NaO_{4}: 576.18938; found: 576.18905.
4,4”-Bis(1-octynyl-1-yl)-5,5”-bis(methoxymethoxy)-2,2’:6’,2”-terpyridine (23b)

To a mixture of diiodoterpyridine 14 (300 mg, 0.496 mmol, 1.00 eq), Cul (9.4 mg, 0.050 mmol, 10 mol%) and PdCl$_2$(PPh$_3$)$_2$ (17.4 mg, 0.0248 mmol, 5 mol%) in degassed THF/Et$_3$N (10 mL/10 mL) was added 1-octyne (0.182 mL, 1.24 mmol, 2.50 eq) under N$_2$ atmosphere at 80 °C. The reaction mixture was heated to reflux for 20 h, allowed to cool to room temperature and evaporated to dryness under reduced pressure. The residue was redisolved in CH$_2$Cl$_2$ (30 mL), washed with 10% aqueous NH$_4$OH, water and brine. The organic phase was dried over MgSO$_4$, filtered and evaporated under reduces pressure. The residue was purified by neutral alumina (Brockman III) column chromatography with hexane/ethyl acetate (3:1) to give 4,4”-bis(1-octynyl-1-yl)-5,5”-bis(methoxymethoxy)-2,2’:6’,2”-terpyridine (23b) (261 mg, 92 %) as an off-white solid.

Mp 73–74 °C.

$^1$H NMR (400 MHz, CDCl$_3$, δ): 8.54 (s, 2H), 8.52 (s, 2H), 8.31 (d, $J = 7.8$ Hz, 2H), 7.88 (t, $J = 7.8$ Hz, 1H), 5.34 (s, 4H), 3.57 (s, 6H), 2.54 (t, $J = 7.1$ Hz, 4H), 1.69 (quintet, $J = 7.4$ Hz, 4H), 1.51 (quintet, $J = 7.0$ Hz, 4H), 1.39-1.31 (m, 8H), 0.91 (t, $J = 6.8$ Hz, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$, δ): 154.8 (s), 153.8 (s), 150.3 (s), 137.8 (d), 137.4 (d), 124.8 (d), 123.5 (s), 120.3 (d), 99.9 (s), 95.8 (t), 75.2 (s), 56.6 (q), 31.4 (t), 28.7 (t), 28.6 (t), 22.7 (t), 20.0 (t), 14.2 (q).

IR (film on NaCl, cm$^{-1}$): 2931s, 2955s, 2857m, 2235w, 1576m, 1543w, 1485s, 1456s, 1376m, 1278m, 1193m, 1154s, 1082m, 984s, 924w, 823w.

MS (ESI) $m/z$: 570.5 ([M + H$^+$]). HRMS (ESI) $m/z$: [M+Na]$^+$ calcd for C$_{35}$H$_{43}$N$_3$NaO$_4$: 592.31458; found: 592.31377.
4,4’-Diethynyl-5,5’-bis(methoxymethoxy)-2,2’:6’,2”-terpyridine (23c)

To a mixture of diiodoterpyridine 14 (908 mg, 1.50 mmol, 1.00 eq), PdCl₂(PPh₃)₂ (53 mg, 0.075 mmol, 5 mol%) and Cul (18 mg, 0.15 mmol, 10 mol%) in degassed THF/Et₃N (35 mL/30 mL) was added trimethylsilylacetylene (1.1 mL, 7.5 mmol, 5.0 eq) under N₂ atmosphere. The reaction mixture was heated to 80 °C for 4.5 h, filtered through Celite and the filter was washed with CH₂Cl₂ (150 ml). The filtrate was washed with 10%
aqueous NH$_4$OH, water and brine. The organic phase was dried over MgSO$_4$, filtered and evaporated under reduces pressure. The crude residue was dissolved in CH$_2$Cl$_2$/MeOH (40 mL/40 mL) and to the resulting mixture KF (348.6 mg, 6.00 mmol) was added. The reaction mixture was stirred at room temperature for 18 h. After evaporation of solvents, the residue was treated with CH$_2$Cl$_2$ (100 mL) and filtered through a Celite plug (1 cm). The cake was washed with CH$_2$Cl$_2$ (100 mL) and the combined organic phase was concentrated in vacuo. The residue was purified by neutral alumina (Brockman III) column chromatography with hexane/ethyl acetate (3:1) to give 4,4”-diethynyl-5,5”-bis(methoxymethoxy)-2,2’:6’,2”-terpyridine (23e) (516 mg, 86%) as a white solid.

Mp 167.5–169 °C.

$^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 8.64 (s, 2H), 8.60 (s, 2H), 8.33 (d, $J = 7.8$ Hz, 2H), 7.90 (t, $J = 7.8$ Hz, 1H), 5.38 (s, 4H), 3.58 (s, 6H), 3.55 (s, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$, $\delta$): 154.6 (s), 154.2 (s), 150.1 (s), 138.0 (d), 137.1 (d), 125.1 (d), 121.2 (s), 120.4 (d), 95.6 (t), 85.6 (s), 78.1 (d), 56.7 (q).

IR (film on NaCl, cm$^{-1}$): 3179m, 2966w, 2939w, 2909w, 2105m, 1570m, 1488m, 1457m, 1369m, 1271m, 1204m, 1157m, 1079m, 979vs, 921m, 824m, 614m.

5,5’-Bis(methoxymethoxy)-4,4’-bis[2-(pyridine-4-yl)ethynyl]-2,2’:6’,2”-terpyridine (23d)

A mixture of bis-ethynyl terpyridine 23c (401 mg, 1.00 mmol, 1.00 eq), 4-iodopyridine (25) (431 mg, 2.10 mmol, 2.10 eq), PdCl₂(PPh₃)₂ (70.2 mg, 0.100 mmol, 10 mol%) and CuI (38.2 mg, 0.200 mmol, 20 mol%) in degassed THF/ Et₃N (20 mL/20 mL) was heated
to 80 °C for 20 h under N₂ atmosphere. After evaporation of solvents, the residue was redissolved in CH₂Cl₂ (100 mL), washed with 10% aqueous NH₄OH, water and brine. The organic phase was dried over MgSO₄, filtered and evaporated under reduces pressure. The crude product was purified by silica gel column chromatography with CH₂Cl₂/MeOH (gradient 99:1 to 9:1) to give 5,5”-bis(methoxymethoxy)-4,4”-bis[2-(pyridine-4-yl)ethynyl]-2,2’:6’,2”-terpyridine (23d) (489 mg, 88%) as a white solid.

Mp 174–175 °C dec.

¹H NMR (500 MHz, CDCl₃, δ): 8.68 (d, J = 0.6 Hz, 2H), 8.66-8.64 (m, 6H), 8.36 (d, J = 7.8 Hz, 2H), 7.94 (t, J = 7.8 Hz, 1H), 7.47-7.46 (m, 4H), 5.40 (s, 4H), 3.60 (s, 6H).

¹³C NMR (125 MHz, CDCl₃, δ): 154.5 (s), 153.6 (s), 150.1 (s), 149.8 (d), 137.8 (d), 137.1 (d), 130.6 (s), 125.6 (d), 124.3 (d), 120.9 (s), 120.4 (d), 95.5 (t), 94.1 (s), 88.0 (s), 56.6 (q).

IR (film on NaCl, cm⁻¹): 2957w, 2831w, 2219w, 1591s, 1483m, 1456m, 1379m, 1309m, 1269m, 1201m, 1154s, 1076m, 974vs, 902m, 819s, 753w.

5,5''-Bis(methoxymethoxy)-4,4''-bis[2-(pyridine-3-yl)ethynyl]-2,2':6',2''-terpyridine (23e)

A mixture of diiodoterpyridine 14 (242 mg, 0.400 mmol, 1.00 eq), 3-ethynlpyridine (981 mg, 3.12 mmol, 7.80 eq), PdCl$_2$(PPh$_3$)$_2$ (14 mg, 0.040 mmol, 5 mol%) and Cul (7.6 mg, 0.080 mmol, 10 mol%) in degassed THF/Et$_3$N (40 mL/40 mL) was heated to 80 °C
Supporting Information

for 20 h under N₂ atmosphere. After evaporation of solvents, the residue was redissolved in CH₂Cl₂ (200 mL), washed with 10% NH₄OH aqueous solution, water and brine. The organic phase was dried over MgSO₄, filtered and evaporated under reduces pressure. The crude product was purified by silica gel column chromatography with CH₂Cl₂/MeOH (gradient 99:1 to 9:1) to give 5,5”-bis(methoxymethoxy)-4,4”-bis[2-(pyridine-3-yl)ethynyl]-2,2’:6’,2”-terpyridine (23e) (189 mg, 85%) as a white solid.

Mp 164–165 °C dec.

¹H NMR (400 MHz, CDCl₃, δ): 8.86 (d, J = 1.2 Hz, 2H), 8.69 (s, 2H), 8.63 (s, 2H), 8.61 (ddd, J = 4.9, 1.6 Hz, 2H), 8.36 (d, J = 7.8 Hz, 2H), 7.93 (t, J = 7.9 Hz, 1H), 7.90 (dt, J = 7.9, 1.9 Hz, 2H), 7.34 (ddd, J = 7.9, 4.9, 0.7 Hz, 2H), 5.40 (s, 4H), 3.60 (s, 6H).

¹³C NMR (125 MHz, CDCl₃, δ): 154.7 (s), 153.7 (s), 152.4 (d), 150.2 (s), 149.3 (d), 139.0 (d), 138.0 (d), 137.2 (d), 124.5 (d), 123.4 (d), 121.7 (s), 120.6 (d), 119.9 (s), 95.7 (t), 94.0 (s), 87.0 (s), 56.8 (q).

IR (film on NaCl, cm⁻¹): 2958w, 2831w, 2220w, 1570.8m, 1545.9w, 1486.0s, 1456.5m, 1408.9w, 1378m, 1308w, 1268w, 1234w, 1200m, 1155s, 1076m, 976vs, 923w, 821w, 703w.

HRMS (ESI) m/z: [M + H]⁺ calcd for C₃₃H₂₆N₅O₄: 556.19793; found: 556.19697.
Supporting Information

4-Iodo-4’- {2-[5’-(4-methoxy-2,6-dimethylphenyl)-2,2’-bipyridin-5-yl|ethynyl]-5,5”-bis(methoxymethoxy)-2,2’:6’,2”-terpyridine (24a)

A mixture of diiodoterpyridine 14 (450 mg, 0.744 mmol, 1.00 eq), 5-ethynyl-5’-(4-methoxy-2,6-dimethylphenyl)-2,2’-bipyridine (22a) (245 mg, 0.781 mmol, 1.05 eq ), PdCl₂(PPh₃)₂ (26 mg, 0.037 mmol, 5 mol%) and CuI (14 mg, 0.074 mmol, 10 mol%) in degassed THF/Et₃N (15 mL/15 mL) was heated to 80 °C for 6 h under N₂ atmosphere. The reaction mixture was diluted with CH₂Cl₂ (50 mL), washed with 10% aqueous NH₄OH, water and brine. The organic phase was dried over MgSO₄, filtered and evaporated under reduces pressure. The crude residue was separated by silica gel column chromatography with hexane/ethyl acetate (3:1) to give monosubstituted 24a (225 mg, 40%), disubstituted 23f (132 mg, 18%) and recovered starting diiodoterpyridine 14 (110 mg, 24%).

Yellowish amorphous solid, Mp 108–110 °C.

¹H NMR (400 MHz, CDCl₃, δ): 9.04 (s, 1H), 8.95 (d, J = 1.3 Hz, 1H), 8.69 (s, 1H), 8.64 (s, 1H), 8.52 (d, J = 8.2 Hz, 2H), 8.51 (s, 1H), 8.39 (s, 1H), 8.37 (dd, J = 7.9, 0.8 Hz, 2H), 8.34 (dd, J = 7.8, 0.8 Hz, 1H), 8.08 (dd, J = 8.2, 2.1 Hz, 1H), 7.92 (t, J = 7.8 Hz, 1H), 7.66 (dd, J = 7.9, 2.2 Hz, 1H), 6.72 (s, 2H), 5.43 (s, 2H), 5.36 (s, 2H), 3.84 (s, 3H), 3.63 (s, 3H), 3.58 (s, 3H), 2.08 (s, 6H).

¹³C NMR (100 MHz, CDCl₃, δ): 159.2 (s), 155.6 (s), 154.8 (s), 154.0 (s), 153.7 (s), 153.7 (s), 152.2 (d), 150.9 (s), 150.3 (d), 150.2 (s), 139.9 (d), 138.7 (d), 138.0 (d), 137.9 (s), 137.4 (d), 137.3 (s), 135.8 (d), 132.2 (d), 130.3 (s), 124.5 (d), 121.9 (s), 121.3 (d), 120.7 (d), 120.6 (d), 120.4 (d), 119.7 (s), 113.2 (d), 99.5 (s), 95.8 (t), 95.7 (t), 94.5 (s), 87.9 (s), 56.9 (q), 56.8 (q), 55.4 (q), 21.4 (q).
Supporting Information

IR (film on NaCl, cm\(^{-1}\)): 2956w, 2832w, 2220w, 1606w, 1569m, 1540m, 1482m, 1463s, 1451s, 1354w, 1317m, 1267m, 1235s, 1200m, 1155vs, 1084m, 976s, 922w, 845w, 821w, 733m.

MS (ESI) m/z: 792.3 ([M + H]\(^+\)); HRMS (ESI) m/z: [M]\(^+\) calcd for C\(_{40}\)H\(_{34}\)N\(_5\)O\(_5\): 792.16707; found: 792.16774.
### Supporting Information

4,4”-Bis{2-[5’-(4-methoxy-2,6-dimethylphenyl)-2,2’-bipyridin-5-yl]ethynyl}-5,5”-bis(methoxymethoxy)-2,2’:6’,2”-terpyridine (23f)

![Chemical Structure Image]

A mixture of diiodoterpyridine 14 (908 mg, 1.50 mmol, 1.00 eq), 5-ethynyl-5’-(4-methoxy-2,6-dimethylphenyl)-2,2’-bipyridine (22a) (981 mg, 3.12 mmol, 2.08 eq), PdCl$_2$(PPh$_3$)$_2$ (53 mg, 0.075 mmol, 5 mol%) and CuI (29 mg, 0.15 mmol, 10 mol%) in degassed THF/Et$_3$N (30 mL/30 mL) was heated to 80 °C for 20 h under N$_2$ atmosphere. The reaction mixture was diluted with CH$_2$Cl$_2$ (150 mL), washed with 10% aqueous NH$_4$OH, water and brine. The organic phase was dried over MgSO$_4$, filtered and evaporated under reduces pressure. The crude residue was separated by silica gel column chromatography with hexane/ethyl acetate (2:1) to give 4,4”-bis{2-[5’-(4-methoxy-2,6-dimethylphenyl)-2,2’-bipyridin-5-yl]ethynyl}-5,5”-bis(methoxymethoxy)-2,2’:6’,2”-terpyridine (23f) (1.325 g, 90%) as a white solid. Single crystals suitable for X-ray diffraction analysis were obtained from a mixture of hexane/ethyl acetate.

White crystalline solid, Mp 237–238.5 °C dec.

$^1$H NMR (400 MHz, CDCl$_3$, δ): 8.95 (d, $J = 2.1$ Hz, 2H), 8.74 (s, 2H), 8.65 (s, 2H), 8.54 (d, $J = 8.2$ Hz, 2H), 8.53 (d, $J = 8.1$ Hz, 2H), 8.47 (d, $J = 2.2$ Hz, 2H), 8.38 (d, $J = 7.8$ Hz, 2H), 8.08 (dd, $J = 2.1$, 8.2 Hz, 2H), 7.94 (t, $J = 7.8$ Hz, 1H), 7.61 (dd, $J = 2.2$, 8.1 Hz, 2H), 6.69 (s, 4H), 5.44 (s, 4H), 3.84 (s, 6H), 3.64 (s, 6H), 2.02 (s, 12H).

$^{13}$C NMR (125 MHz, CDCl$_3$, δ): 159.1 (s), 155.7 (s), 154.9 (s), 153.8 (s), 153.7 (s), 152.1 (d), 150.4 (s), 150.3 (d), 139.9 (d), 138.6 (d), 138.0 (d), 137.9 (s), 137.5 (d), 137.2 (s), 130.3 (s), 124.4 (d), 121.9 (s), 121.4 (d), 120.6 (d), 120.5 (d), 119.6 (s), 113.1 (d), 95.8 (t), 94.6 (s), 87.8 (s), 56.8 (q), 55.3 (q), 21.3 (q).
Supporting Information

IR (film on NaCl, cm⁻¹): 2955w, 2833w, 2215vw, 1606m, 1573m, 1482m, 1461vs, 1378m, 1316m, 1268m, 1195m, 1155vs, 1075m, 976m, 843m, 746m.

MS (ESI) m/z: 1000.7 ([M + Na]⁺); HRMS (ESI) m/z: [M + Na]⁺ calcd for C₆₁H₅₁N₇O₆Na: 1000.3799; found: 1000.3798.
A mixture of diiodoterpyridine 14 (450 mg, 0.744 mmol, 1.00 eq), 5-ethynyl-6’-(4-methoxy-2,6-dimethylphenyl)-2,2’-bipyridine (22b) (245 mg, 0.781 mmol, 1.05 eq), PdCl$_2$(PPh$_3$)$_2$ (26 mg, 0.037 mmol, 5 mol%) and CuI (14 mg, 0.074 mmol, 10 mol%) in degassed THF/Et$_3$N (15 mL/15 mL) was heated to 80 °C for 6 h under N$_2$ atmosphere. The reaction mixture was diluted with CH$_2$Cl$_2$ (50 mL), washed with 10% aqueous NH$_4$OH, water and brine. The organic phase was dried over MgSO$_4$, filtered and evaporated under reduces pressure. The crude residue was separated by silica gel column chromatography with hexane/ethyl acetate (3:1) to give monosubstituted 24b (230 mg, 39%), disubstituted 23g (126 mg, 17%) and recovered starting diiodoterpyridine 14 (100 mg, 22%).

White crystalline solid, Mp 166–169 °C.

$^1$H NMR (400 MHz, CDCl$_3$, δ): 9.04 (s, 1H), 8.93 (dd, $J = 2.0$, 0.6 Hz, 1H), 8.68 (s, 1H), 8.63 (s, 1H), 8.51 (dd, $J = 8.3$, 0.6 Hz, 1H), 8.41 (dd, $J = 7.9$, 0.9 Hz, 1H), 8.39 (s, 1H), 8.37 (dd, $J = 7.8$, 0.8 Hz, 1H), 8.34 (dd, $J = 7.8$, 0.9 Hz, 1H), 8.00 (dd, $J = 8.3$, 2.0 Hz, 1H), 7.92 (t, $J = 7.9$ Hz, 1H), 7.89 (t, $J = 7.8$ Hz, 1H), 7.26 (dd, $J = 7.9$, 0.9 Hz, 1H), 6.71 (s, 2H), 5.42 (s, 2H), 5.36 (s, 2H), 3.84 (s, 3H), 3.62 (s, 3H), 3.58 (s, 3H), 2.13 (s, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$, δ): 159.4 (s), 159.1 (s), 156.0 (s), 155.2 (s), 154.7 (s), 154.0 (s), 153.7 (s), 152.0 (d), 150.9 (s), 150.2 (s), 139.8 (d), 138.1 (d), 137.7 (s), 137.4 (d), 137.2 (d), 135.8 (d), 133.6 (s), 132.2 (d), 125.7 (d), 124.6 (d), 122.1 (s), 121.0 (d), 120.8
Supporting Information

(d), 120.6 (d), 119.6 (s), 119.4 (d), 113.3 (d), 99.6 (s), 95.9 (t), 95.7 (t), 94.8 (s), 87.7 (s), 56.9 (q), 56.8 (q), 55.4 (q), 20.9 (q).

IR (film on NaCl, cm\(^{-1}\)): 2957\(\text{w}\), 2831\(\text{w}\), 2221\(\text{vw}\), 1607\(\text{m}\), 1568\(\text{m}\), 1482\(\text{m}\), 1451\(\text{s}\), 1387\(\text{w}\), 1312\(\text{m}\), 1266\(\text{m}\), 1236\(\text{w}\), 1200\(\text{m}\), 1156\(\text{vs}\), 1084\(\text{m}\), 976\(\text{s}\), 908\(\text{m}\), 820\(\text{m}\), 732\(\text{m}\).

HRMS (ESI) \(m/z\): [M + H]\(^+\) calced for C\(_{40}\)H\(_{35}\)IN\(_5\)O\(_5\): 792.16774; found: 792.16789.

\(4,4''\)-bis\{2\'-[6'-\(\text{4-methoxy-2,6-dimethylphenyl}\)-2,2'-bipyridin-5-yl\]ethynyl\}-5,5''-bis\(\text{methoxymethoxy}\)-2,2':6',2''-terpyridine (23g)

White crystalline solid, Mp 248–249.5 °C dec.

\(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 8.92 (d, \(J = 2.1\) Hz, 2H), 8.69 (s, 2H), 8.64 (s, 2H), 8.48 (d, \(J = 8.3\) Hz, 2H), 8.38 (d, \(J = 7.9\) Hz, 2H), 8.36 (d, \(J = 7.8\) Hz, 2H), 7.98 (dd, \(J = 8.3, 2.1\) Hz, 2H), 7.94 (t, \(J = 7.9\) Hz, 1H), 7.82 (t, \(J = 7.8\) Hz, 2H), 7.22 (d, \(J = 7.6\) Hz, 2H), 6.69 (s, 4H), 5.42 (s, 4H), 3.83 (s, 6H), 3.62 (s, 6H), 2.10 (s, 12H).

\(^{13}\)C NMR (125 MHz, CDCl\(_3\), \(\delta\)): 159.3 (s), 159.1 (s), 156.0 (s), 155.3 (s), 155.0 (s), 153.8 (s), 152.0 (d), 150.5 (s), 139.6 (d), 138.0 (d), 137.8 (s), 137.5 (d), 137.2 (d), 133.6 (s), 125.6 (d), 124.4 (d), 122.0 (s), 120.9 (d), 120.6 (d), 119.6 (s), 119.4 (d), 113.2 (d), 95.9 (t), 94.8 (s), 87.6 (s), 56.8 (q), 55.3 (q), 20.9 (q).

IR (film on NaCl, cm\(^{-1}\)): 2955\(\text{w}\), 2831\(\text{w}\), 2215\(\text{vw}\), 1606\(\text{m}\), 1567\(\text{m}\), 1490\(\text{m}\), 1452\(\text{s}\), 1378\(\text{m}\), 1311\(\text{m}\), 1266\(\text{m}\), 1195\(\text{m}\), 1156\(\text{vs}\), 1072\(\text{m}\), 976\(\text{m}\), 819\(\text{m}\), 752\(\text{w}\).

MS (ESI) \(m/z\): 1000.5 ([M + Na\(^+\)]. HRMS (ESI) \(m/z\): [M + Na\(^+\)] calced for C\(_{61}\)H\(_{51}\)N\(_7\)O\(_6\)Na: 1000.3799; found: 1000.3803.
To a mixture of diiodoterepyridine 14 (450 mg, 0.744 mmol, 1.00 eq), CuI (14 mg, 0.074 mmol, 10 mol%) and Pd(PPh₃)₃Cl₂ (26 mg, 0.037 mmol, 5 mol%) in anhydrous THF (15 mL) was added a solution of 2-ethynyl-5-methoxy-1,3-dimethylbenzene (18) (125 mg,
Supporting Information

0.781 mmol, 1.05 eq) in degassed Et₃N (15 mL) under N₂ atmosphere at 80 °C. The reaction mixture was heated to reflux for 15 h, allowed to cool to room temperature and diluted with CH₂Cl₂ (100 mL). The mixture was washed with 10% aqueous NH₄OH, water and brine. The organic phase was dried over MgSO₄, filtered and evaporated under reduced pressure. The residue was purified by silica gel column chromatography with hexane/ethyl acetate/MTBE (2:2:1) to give monosubstituted 24c (179 mg, 38%), disubstituted 23h (81 mg, 15%) and recovered starting diiodoterpyridine 14 (126 mg, 28%).

4-iodo-4’’-[2-(4-methoxy-2,6-dimethylphenyl)-ethynyl]-5,5’’-bis(methoxymethox)-2,2’’;6’’,2’’’’-terpyridine (24c)

White solid, Mp 146.5–147.5 °C.

¹H NMR (400 MHz, CDCl₃, δ): 9.06 (s, 1H), 8.65 (s, 1H), 8.55 (s, 1H), 8.37 (s, 1H), 8.35 (d, J = 7.8 Hz, 1H), 8.31 (d, J = 7.8 Hz, 1H), 7.90 (t, J = 7.8 Hz, 1H), 6.67 (s, 2H), 5.39 (s, 2H), 5.35 (s, 2H), 3.82 (s, 3H), 3.58 (s, 3H), 3.57 (s, 3H), 2.60 (s, 6H).

¹³C NMR (100 MHz, CDCl₃, δ): 160.0 (s), 154.7 (s), 153.8 (s), 153.7 (s), 153.2 (s), 150.9 (s), 150.0 (s), 142.9 (s), 138.1 (d), 137.1 (s), 135.8 (d), 132.4 (d), 124.2 (d), 123.7 (s), 120.4 (d), 114.9 (s), 112.8 (d), 99.4 (s), 96.5 (s), 95.7 (t), 95.6 (t), 90.8 (s), 56.8 (q), 56.7 (q), 55.3 (q), 21.5 (q).

IR (film on NaCl, cm⁻¹): 2956w, 2838w, 2208w, 1605m, 1581m, 1569m, 1539m, 1482s, 1453s, 1354w, 1321s, 1287m, 1269m, 1236w, 1199m, 1156vs, 1083m, 979s, 820m, 738w.

HRMS (ESI) m/z: [M + H]⁺ calcd for C₃₀H₂₉IN₃O₅: 638.11464; found: 638.11406.

4,4’’-bis[2-(4-methoxy-2,6-dimethylphenyl)-ethynyl]-5,5’’-bis(methoxymethoxy)-2,2’’;6’’,2’’’’-terpyridine (23h)
White solid, Mp 181.5–182.5 °C.

$^1$H NMR (400 MHz, CDCl₃, δ): 8.65 (s, 2H), 8.57 (s, 2H), 8.38 (d, $J = 7.9$ Hz, 2H), 7.94 (t, $J = 7.9$ Hz, 1H), 6.62 (s, 4H), 5.39 (s, 4H), 3.82 (s, 6H), 3.58 (s, 6H), 2.53 (s, 12H).

$^{13}$C NMR (100 MHz, CDCl₃, δ): 159.9 (s), 154.7 (s), 153.3 (s), 150.1 (s), 142.9 (s), 138.1 (d), 136.9 (d), 124.2 (d), 123.8 (s), 120.5 (d), 115.0 (s), 112.7 (d), 96.6 (s), 95.6 (t), 90.7 (s), 56.7 (q), 55.3 (q), 21.4 (q).

IR (film on NaCl, cm⁻¹): 2954w, 2839w, 2206m, 1605m, 1575s, 1539w, 1485m, 1456m, 1377m, 1321s, 1287m, 1266w, 1196m, 1158vs, 1121w, 1076m, 1059w, 985s, 922w 822m, 732w.

Supporting Information

4-{2-[5’-(4-Methoxy-2,6-dimethylphenyl)-2,2’-bipyridin-5-yl]ethynyl}-4”-[2-(4-methoxy-2,6-dimethylphenyl)-ethynyl]-5,5”-bis(methoxymethoxy)-2,2’:6’,2”-terpyridine (26a)

To a mixture of iodoterpyridine 14 (257 mg, 0.325 mmol, 1.00 eq), Pd(PPh₃)₂Cl₂ (11.4 mg, 0.016 mmol, 5 mol%) and CuI (6.2 mg, 0.032 mmol, 10 mol%) in degassed THF/Et₃N (3 mL/3 mL) was added a solution of 2-ethyl-5-methoxy-1,3-dimethylbenzene (18) (57 mg, 0.36 mmol, 1.1 eq) in degassed THF/Et₃N (3 mL/3 mL) under N₂ atmosphere at 75 °C. The reaction mixture was heated to reflux for 20 h, allowed to cool to room temperature and diluted with CH₂Cl₂ (25 mL). The mixture was washed with 10% NH₄OH aqueous solution, water and brine. The organic phase was dried over MgSO₄, filtered and evaporated under reduces pressure. The residue was purified by neutral alumina (Brockman III) column chromatography with hexane/ethyl acetate (3:1) to give desired product 26a (232 mg, 87%) as an off-white solid. Single crystals suitable for X-ray diffraction analysis were obtained from slow evaporation of CDCl₃ solution.
Supporting Information

Mp 177–178.5 °C.

$^1$H NMR (400 MHz, CDCl$_3$, δ): 8.92 (s, 1H), 8.75 (s, 1H), 8.69 (s, 1H), 8.64 (s, 1H), 8.57 (s, 1H), 8.55-8.51 (m, 3H), 8.37 (d, $J = 7.8$ Hz, 2H), 8.04 (d, $J = 8.2$ Hz, 1H), 7.93 (t, $J = 7.8$ Hz, 1H), 7.67 (d, $J = 8.1$ Hz, 1H), 6.73 (s, 2H), 6.61 (s, 2H), 5.43 (s, 2H), 5.39 (s, 2H), 3.84 (s, 3H), 3.75 (s, 3H), 3.63 (s, 3H), 3.58 (s, 3H), 2.56 (s, 6H), 2.09 (s, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$, δ): 159.9 (s), 159.2 (s), 155.6 (s), 154.9 (s), 154.6 (s), 153.8 (s), 153.6 (s), 153.2 (s), 152.1 (d), 150.4 (d), 150.3 (s), 150.2 (s), 142.8 (s), 139.8 (d), 138.6 (d), 138.0 (d), 137.9 (s), 137.4 (d), 137.3 (d), 137.1 (s), 130.3 (s), 124.7 (d), 124.1 (d), 123.6 (s), 121.8 (s), 121.3 (d), 120.4 (d), 120.4 (d), 120.2 (d), 119.7 (s), 114.9 (s), 113.2 (d), 112.8 (d), 112.7 (s), 96.5 (s), 95.8 (t), 95.5 (t), 94.2 (s), 90.8 (s), 87.9 (s), 56.8 (q), 56.7 (q), 55.4 (q), 55.3 (q), 21.5 (q), 21.4 (q).

IR (film on NaCl, cm$^{-1}$): 2957$m$, 2837$m$, 2208$w$, 1606$m$, 1575$s$, 1539$w$, 1486$s$, 1463$s$, 1456$s$, 1378$m$, 1320$s$, 1270$m$, 1231$w$, 1196$m$, 1157$s$, 1076$m$, 1057$w$, 982$s$, 924$m$, 907$m$, 845$m$, 822$m$, 734$m$.

HRMS (ESI) m/z: [M + H]$^+$ calcd for C$_{51}$H$_{46}$N$_5$O$_6$: 824.34426; found: 824.34373.
4-{2-[6’-(4-Methoxy-2,6-dimethylphenyl)-2,2’-bipyridin-5-yl]ethyl}yl-4”-[2-(4-methoxy-2,6-dimethylphenyl)ethyl]yl-5,5”-bis(methoxymethoxy)-2,2’:6’,2”-terpyridine (26b)

To a mixture of iodoterpyridine 14 (131 mg, 0.165 mmol, 1.00 eq), Pd(PPh₃)₂Cl₂ (5.8 mg, 0.0083 mmol, 5 mol%) and CuI (3.2 mg, 0.017 mmol, 10 mol%) in degassed THF/Et₃N (2.5 mL/2.5 mL) was added a solution of 2-ethynyl-5-methoxy-1,3-dimethylbenzene (18) (34 mg, 0.22 mmol, 1.3 eq) in degassed THF/Et₃N (2.5 mL/2.5 mL) under N₂ atmosphere at 75 °C. The reaction mixture was heated to reflux for 17 h, allowed to cool to room temperature and diluted with CH₂Cl₂ (15 mL). The mixture was washed with 10% NH₄OH aqueous solution, water and brine. The organic phase was dried over MgSO₄, filtered and evaporated under reduces pressure. The residue was purified by neutral alumina (Brockman III) column chromatography with hexane/ethyl acetate (3:1) to give desired product 26b (107 mg, 79%) as a white solid.

Mp 164–166 °C.
Supporting Information

$^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 8.91 (s, 1H), 8.73 (s, 1H), 8.68 (s, 1H), 8.63 (s, 1H), 8.57 (s, 1H), 8.50 (d, $J = 8.2$ Hz, 1H), 8.43 (d, $J = 8.2$ Hz, 1H), 8.37 (d, $J = 7.7$ Hz, 1H), 7.99-7.87 (m, 3H), 7.29-7.25 (d, $J = 7.1$ Hz, 1H), 6.72 (s, 2H), 6.59 (s, 2H), 5.42 (s, 2H), 5.39 (s, 2H), 3.85 (s, 3H), 3.71 (s, 2H), 3.62 (s, 3H), 3.58 (s, 3H), 2.56 (s, 6H), 2.14 (s, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$, $\delta$): 159.9 (s), 159.3 (s), 159.1 (s), 155.9 (s), 155.2 (s), 154.7 (s), 154.6 (s), 153.6 (s), 153.2 (s), 152.0 (d), 150.3 (s), 150.1 (s), 142.8 (s), 139.5 (d), 138.1 (s), 138.0 (d), 137.6 (s), 137.4 (d), 137.2 (d), 136.9 (d), 133.6 (s), 125.7 (d), 124.6 (d), 124.1 (d), 123.6 (s), 121.9 (s), 120.8 (d), 120.4 (d), 120.3 (d), 119.6 (s), 119.3 (d), 114.8 (s), 113.2 (d), 112.8 (d), 96.6 (s), 95.8 (t), 95.5 (t), 94.3 (s), 90.7 (s), 87.7 (s), 56.8 (q), 56.6 (q), 55.3 (q), 55.2 (q), 21.4 (q), 20.9 (q).

IR (film on NaCl, cm$^{-1}$): 2956m, 2837w, 2207w, 1605m, 1575s, 1546w, 1485m, 1455s, 1377m, 1321s, 1268m, 1233w, 1196m, 1157vs, 1075m, 982s, 925w, 821m, 737w.

HRMS (ESI) m/z: [M + H]$^+$ calcd for C$_{51}$H$_{46}$N$_5$O$_6$: 824.34426; found: 824.34402.
2.4. Synthesis of Ligands L1-L6

2,6-Bis[2-(phenyl)furo[2,3-c]pyridin-5-yl]pyridine (L1)

To a solution of 5,5”-bis(methoxymethoxy)-4,4”-bis(phenylethynyl)-2,2’:6’,2”-terpyridine (23a) (217 mg, 0.391 mmol, 1.00 eq) in DMF (10 mL) was added 32% aq. HCl (0.19 mL, 2.0 mmol, 5.0 eq). The reaction mixture was heated to 80 °C for 2 h, then Cs₂CO₃ (5.47 g, 16.8 mmol, 43.0 eq) was added portion-wise. The resulting mixture was heated to 90 °C for 48 h. Evaporation of DMF resulted in residue that was treated with water (100 ml) and the mixture was extracted with CH₂Cl₂ (100 mL × 4). The combined organic fractions were washed with water and brine, dried over MgSO₄, filtered and evaporated under reduced pressure. The resulting solid was treated with hexane (20 ml), collected by filtration and washed with Et₂O (10 ml) to give desired ligand L1 (168 mg, 92%) as an off-white solid. Single crystals suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of Et₂O into a CH₂Cl₂ solution of L1.

Mp 294–295 °C dec.
Supporting Information

$^1$H NMR (400 MHz, CDCl$_3$, δ): 9.02 (s, 2H), 8.98 (s, 2H), 8.48 (d, $J = 7.8$ Hz, 2H), 7.98 (t, $J = 7.8$ Hz, 1H), 7.97-7.95 (m, 4H), 7.54-7.45 (m, 6H), 7.23 (s, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$, δ): 160.2 (s), 155.3 (s), 152.4 (s), 149.8 (s), 138.2 (d), 137.3 (s), 132.2 (d), 130.2 (d), 129.4 (s), 129.2 (d), 125.9 (d), 120.8 (d), 113.8 (d), 101.2 (d).

IR (KBr, cm$^{-1}$): 2919w, 1606w, 1586m, 1567m, 1448vs, 1424w, 1399m, 1306w, 1154w, 1019w, 913w, 903w, 894m, 894m, 821m, 767s, 756w, 691m.

HRMS (ESI) m/z: [M + Na]$^+$ calcd for C$_{31}$H$_{19}$N$_3$NaO$_2$: 488.13695; found: 488.13659.
To a solution of 4,4”-bis(1-octynyl-1-yl)-5,5”-bis(methoxymethoxy)-2,2’:6’,2”-terpyridine (23b) (244 mg, 0.429 mmol, 1.00 eq) in DMF (10 mL) was added 32% aq. HCl (0.21 mL, 2.0 mmol, 5.0 eq). The reaction mixture was heated to 80 °C for 2 h, then Cs₂CO₃ (5.99 g, 18.4 mmol, 43 eq) was added portion-wise. The reaction mixture was heated to 90 °C for 48 h. Evaporation of DMF resulted in residue that was treated with water (100 ml) and the mixture was extracted with CH₂Cl₂ (50 mL × 3). The combined organic fractions were washed with water and brine, dried over MgSO₄, filtered and evaporated under reduced pressure. The crude product was purified by neutral alumina (Brockman III) column chromatography with hexane/ethyl acetate (3:1) to give desired ligand L2 (196 mg, 95%) as a white solid.

Mp 86–87 °C.
Supporting Information

$^1$H NMR (400 MHz, CDCl$_3$, δ): 8.82 (s, 2H), 8.78 (s, 2H), 8.40 (d, $J = 7.8$ Hz, 2H), 7.91 (t, $J = 7.8$ Hz, 1H), 6.52 (s, 2H), 2.82 (t, $J = 7.6$ Hz, 4H), 1.78 (quintet, $J = 7.5$ Hz, 4H), 1.43-1.31 (m, 12H), 0.92-0.88 (m, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$, δ): 164.3 (s), 155.8 (s), 152.5 (s), 149.9 (s), 137.8 (d), 136.9 (s), 131.8 (d), 120.4 (d), 113.2 (d), 102.2 (d), 31.6 (t), 29.0 (t), 28.7 (t), 27.5 (t), 22.7 (t), 14.2 (q).

IR (film on NaCl, cm$^{-1}$): 2933s, 2859m, 1595s, 1567s, 1455s, 1424m, 1399m, 1304s, 1285m, 1149m, 1072w, 1035w, 949w, 933w, 915m, 897m, 823s, 793w, 744w, 734w, 660m.

HRMS (ESI) m/z: [M + H]$^+$ calcd for C$_{31}$H$_{36}$N$_3$O$_2$: 482.28020; found: 482.28030.
Supporting Information

2,6-Bis[2-(pyridin-4-yl)furo[2,3-c]pyridin-5-yl]pyridine (L3)

To a solution of 5,5”-bis(methoxymethoxy)-4,4”-bis[2-(pyridin-4-yl)ethynyl]-2,2’:6’,2”-terpyridine (23d) (117 mg, 0.211 mmol, 1.00 eq) in DMF (6 mL) was added 32% aq. HCl (0.10 mL, 3.2 mmol, 5.0 eq). The reaction mixture was heated to 80 °C for 2 h, then Cs₂CO₃ (2.94 g, 9.05 mmol, 43.0 eq) was added portion-wise. The reaction mixture was heated to 90 °C for 72 h. Evaporation of DMF resulted in residue that was treated with water (40 ml). The resulting precipitate was collected by filtration, washed with pentane (15 ml) and Et₂O (15 ml) to give desired ligand L3 (88 mg, 90%) as an off-white solid.

Mp 335–336 °C dec.

¹H NMR (500 MHz, CDCl₃, δ): 9.04 (s, 2H), 8.95 (d, J = 0.8 Hz, 2H), 8.79 (dd, J = 4.5, 1.6 Hz, 4H), 8.48 (d, J = 7.8 Hz, 2H), 7.99 (t, J = 7.8 Hz, 1H), 7.81 (dd, J = 4.5, 1.6 Hz, 4H), 7.40 (d, J = 0.5 Hz, 2H).

¹³C NMR (125 MHz, CDCl₃, δ): 156.7 (s), 155.6 (s), 152.7 (s), 150.8 (d), 150.7 (s), 138.2 (d), 136.6 (s), 136.0 (s), 133.3 (d), 120.9 (d), 119.5 (d), 113.9 (d), 104.5 (d).
Supporting Information

IR (KBr, cm⁻¹): 3038w, 2919w, 2853w, 1635w, 1604m, 1568s, 1448s, 1401s, 13101w, 1296w, 1223w, 1210w, 1156w, 1037w, 993w, 916w, 905m, 895w, 821vs, 810w, 742w, 690w, 650w.

MS (ESI) m/z: 468.2 ([M + H]⁺); 490.2 ([M + Na]⁺); HRMS (ESI) m/z: [M + Na]⁺ calcd for C₂₉H₁₇N₅NaO₂: 490.12745; found: 490.12704.
Supporting Information

2-(4-Methoxy-2,6-dimethylphenyl)-5-(6-{2-[5’-(4-methoxy-2,6-dimethylphenyl)-2,2’-bipyridin-5-yl]furo[2,3-c]pyridin-5-yl}pyridin-2-yl)furo[2,3-c]pyridine (L4)

To a solution of terpyridine 26a (231 mg, 0.281 mmol, 1.00 eq) in DMF (10 mL) was added 32% aq. HCl (0.58 mL, 5.9 mmol, 21 eq). The reaction mixture was heated to 80 °C for 5 h, then Cs₂CO₃ (3.93 g, 12.1 mmol, 43 eq) was added portion-wise. The reaction mixture was heated to 90 °C for 76 h. Evaporation of DMF resulted in residue that was treated with water (50 ml) and the mixture was extracted with CH₂Cl₂ (15 mL × 4). The combined organic fractions were washed with water and brine, dried over MgSO₄, filtered and evaporated under reduced pressure. The crude product was purified by neutral alumina (Brockman III) column chromatography with hexane/CH₂Cl₂/MeOH (50:50:1) to give desired product L4 (200 mg, 97%) as a white solid. Single crystals suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of Et₂O into a CH₂Cl₂ solution of L4.

Mp 304–305 °C dec.

1H NMR (500 MHz, CDCl₃, δ): 9.28 (d, J = 2.3 Hz, 1H), 9.03 (s, 1H), 9.01 (s, 1H), 8.97 (s, 1H), 8.94 (s, 1H), 8.62 (d, J = 8.3 Hz, 1H), 8.56 (d, J = 8.3 Hz, 1H), 8.53 (d, J = 2.2 Hz, 1H), 8.49 (d, J = 7.8 Hz, 1H), 8.48 (d, J = 7.8 Hz, 1H), 8.37 (dd, J = 8.3, 2.3 Hz, 1H), 7.99 (t, J = 7.8 Hz, 1H), 7.68 (dd, J = 8.0, 2.2 Hz, 1H), 7.35 (s, 1H), 6.84 (s, 1H), 6.73 (s, 2H), 6.73 (s, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 2.29 (s, 6H), 2.09 (s, 6H).

13C NMR (125 MHz, CDCl₃, δ): 160.5 (s), 159.8 (s), 159.1 (s), 156.9 (s), 156.8 (s), 155.7 (s), 155.6 (s), 153.7 (s), 152.7 (s), 152.4 (s), 150.6 (s), 150.4 (d), 149.8 (s), 146.7 (d), 140.3 (s), 138.6 (d), 138.1 (d), 138.0 (s), 137.3 (s), 136.8 (s), 136.5 (s), 133.7 (d), 132.8 (d), 132.3 (d), 130.3 (s), 125.4 (s), 122.1 (s), 121.3 (d), 121.1 (d), 120.7 (d), 120.6 (d), 113.7 (d), 113.6 (d), 113.3 (d), 113.1 (d), 106.5 (d), 102.7 (d), 55.4 (q), 55.3 (q), 21.4 (q), 21.0 (q).
Supporting Information

IR (KBr, cm⁻¹): 2923w, 1607s, 1570m, 1447s, 1460s, 1402m, 1319m, 1193w, 1154vs, 1063w, 1012w, 826w, 653w.

HRMS (ESI) m/z: [M + H]⁺ calcd for C₄₇H₃₇N₅O₄: 736.29183; found: 736.29141.
Supporting Information

2-(4-Methoxy-2,6-dimethylphenyl)-5-(6-[[6’-(4-methoxy-2,6-dimethylphenyl)-2,2’-bipyridin-5-yl]furo[2,3-c]pyridin-5-yl]pyridin-2-yl)furo[2,3-c]pyridine (L5)

To a solution of terpyridine 26b (51.6 mg, 0.0604 mmol, 1.00 eq) in DMF (2 mL) was added 32% aq. HCl (0.069 mL, 0.22 mmol, 21 eq). The reaction mixture was heated to 80 °C for 4 h, then Cs$_2$CO$_3$ (844 mg, 2.60 mmol, 43.0 eq) was added portion-wise. The reaction mixture was heated to 90 °C for 48 h. Evaporation of DMF resulted in residue that was treated with water (20 ml) and the mixture was extracted with CH$_2$Cl$_2$ (15 mL × 4). The combined organic fractions were washed with water and brine, dried over MgSO$_4$, filtered and evaporated under reduced pressure. The crude product was purified by neutral alumina (Brockman III) column chromatography with hexane/CH$_2$Cl$_2$/MeOH (50:50:1) to give desired product L5 (43.3 mg, 94%) as a white solid.

Mp 300–301 °C dec.

$^1$H NMR (400 MHz, CDCl$_3$, δ): 9.23 (s, 1H), 8.99 (s, 1H), 8.94 (s, 1H), 8.93 (s, 2H), 8.59 (d, $J = 8.3$ Hz, 1H), 8.47 (s, 1H), 8.47-8.41 (m, 2H), 8.24 (d, $J = 8.4$ Hz, 1H), 7.96 (t, $J = 7.8$ Hz, 1H), 7.89 (t, $J = 7.7$ Hz, 1H), 7.28-7.26 (m, 2H), 6.82 (s, 1H), 6.72 (s, 4H), 3.85 (s, 3H), 3.85 (s, 3H), 2.28 (s, 6H), 2.14 (s, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$, δ): 160.5 (s), 159.4 (s), 159.1 (s), 157.2 (s), 156.9 (s), 156.0 (s), 155.6 (s), 155.2 (s), 152.7 (s), 152.5 (s), 150.7 (s), 150.2 (s), 146.5 (d), 140.3 (s), 137.9 (d), 137.7 (s), 137.2 (d), 136.5 (s), 136.4 (s), 136.3 (s), 133.6 (s), 133.5 (d), 132.8 (d), 132.5 (d), 125.7 (d), 125.4 (s), 122.3 (s), 121.5 (d), 120.7 (d), 120.5 (d), 119.2 (d), 113.6 (d), 113.5 (d), 113.3 (d), 113.2 (d), 106.4 (d), 102.5 (d), 55.4 (q), 55.3 (q), 21.0 (q), 20.9 (q).

IR (KBr, cm$^{-1}$): 2925w, 1606s, 1568m, 1448vs, 1401w, 1319m, 1195w, 1154s, 1071w, 821w, 651w.
HRMS (ESI) $m/z$: [M + H]$^+$ calcd for C$_{47}$H$_{37}$N$_5$O$_4$: 736.29183; found: 736.29186.

2,6-Bis{2-[5'-(4-methoxy-2,6-dimethylphenyl)-2,2'-bipyridin-5-yl]furo[2,3-c]pyridin-5-yl}pyridine (L6)

To a solution of terpyridine 23f (185 mg, 0.190 mmol, 1.00 eq) in DMF (10 mL) was added 32% aq. HCl (0.19 mL, 1.9 mmol, 10 eq). The reaction mixture was heated to 80
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°C for 4 h, then Cs$_2$CO$_3$ (926 mg, 2.84 mmol, 15.0 eq) was added portion-wise. The reaction mixture was heated to 90 °C for 72 h. Evaporation of DMF resulted in residue that was treated with water (20 ml) and the mixture was extracted with CH$_2$Cl$_2$ (20 mL × 4). The combined organic fractions were washed with water and brine, dried over MgSO$_4$, filtered and evaporated under reduced pressure. The crude product was treated with acetone and collected by filtration to give desired product L6 (123 mg, 73%) as a yellow solid.

Mp >330 °C dec.

$^1$H NMR (400 MHz, CDCl$_3$, δ): 9.26 (dd, J = 2.2, 0.7 Hz, 2H), 9.00 (s, 2H), 8.93 (s, 2H), 8.61 (dd, J = 8.3, 0.7 Hz, 2H), 8.55 (dd, J = 8.0, 0.8 Hz, 2H), 8.53 (dd, J = 2.2, 0.8 Hz, 2H), 8.46 (d, J = 7.8 Hz, 2H), 8.34 (dd, J = 8.3, 2.2 Hz, 2H), 7.97 (t, J = 7.8 Hz, 1H), 7.68 (dd, J = 8.0, 2.2 Hz, 2H), 7.32 (s, 2H), 6.73 (s, 4H), 3.85 (s, 6H), 2.09 (s, 12H).

$^{13}$C NMR (125 MHz, CDCl$_3$, δ): 159.2 (s), 156.9 (s), 156.8 (s), 155.6 (s), 153.7 (s), 152.7 (s), 150.6 (s), 150.4 (d), 146.7 (d), 138.6 (d), 138.1 (d), 138.0 (s), 137.3 (s), 136.4 (s), 133.7 (d) 132.9 (d), 130.3 (s), 125.4 (s), 121.2 (d), 121.1 (d), 120.7 (d), 113.6 (d), 113.1 (d), 102.6 (d), 55.3 (q), 21.4 (q).

IR (film on NaCl, cm$^{-1}$): 2921w, 1605s, 1570m, 1460vs, 1448s, 1316m, 1274w, 1193w, 1155vs, 1078w, 1061w, 1012w, 998w, 905w, 844w, 820m, 733w, 648w.

HRMS (ESI) m/z: [M + 2H]$^{2+}$ calcld for C$_{57}$H$_{45}$N$_7$O$_4$: 445.67610; found: 445.67560.
2.5. Preparation of Zn\(^{2+}\), Fe\(^{2+}\) and Ru\(^{2+}\) Complexes of Ligands L1-L6

\[
\text{Zn}[2,6\text{-bis}(2\text{-phenylfuro}[2,3\text{-c}][\text{pyridin-5-yl}]\text{pyridine})\text{-2PF}_6] (\text{[L1Zn][PF}_6\text{]})
\]

To a solution of ligand L1 (25.0 mg, 0.0537 mmol, 1.00 eq) in THF (12 mL) a solution of Zn(OTf)\(_2\) (9.78 mg, 0.0264 mmol, 0.50 eq) in MeOH (2.2 mL) was added dropwise in 5 minutes at room temperature. The reaction mixture was stirred for 18 h at room temperature. To the mixture saturated aq. KPF\(_6\) was added and the resulting yellow precipitate was filtered over Celite, washed with water, Et\(_2\)O, hexane and redissolved with acetonitrile. The solvent was evaporated to give desired Zn complex ([L1Zn][PF\(_6\)]\(_2\)) (32.3 mg, 94%) as a yellow solid. Single crystals suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of Et\(_2\)O into an acetonitrile solution of ([L1Zn][PF\(_6\)]\(_2\)).

Mp >370 °C dec.

\(^1\text{H NMR}\) (500 MHz, CD\(_3\)CN, δ): 8.84 (s, 2H), 8.81-8.76 (m, 3H), 8.02 (s, 2H), 7.87-7.82 (m, 4H), 7.48-7.44 (m, 6H), 7.37 (s, 2H).

\(^{13}\text{C NMR}\) (125 MHz, CD\(_3\)CN, δ): 163.7 (s), 153.5 (s), 151.0 (s), 144.9 (d), 142.5 (s), 140.4 (s), 132.1 (d), 131.7 (d), 129.9 (d), 128.6 (s), 126.6 (d), 123.0 (d), 116.3 (d), 102.0 (d).

\(\text{IR (KBr, cm}^{-1}\): 3116w, 3065w, 1616\text{m}, 1583w, 1478w, 1454s, 1425w, 1324\text{m}, 1177w, 1021w, 959w, 842vs, 767w, 687w, 558s.

HRMS (ESI) \(m/z\) [M]\(^{2+}\) calcd for C\(_{62}\)H\(_{38}\)N\(_6\)O\(_4\)Zn: 497.11175; found: 497.11197.
Fe[2,6-bis(2-phenylfuro[2,3-c]pyridin-5-yl)pyridine]-2PF$_6$ ([L$_1$Fe][PF$_6$]$_2$)

To a solution of ligand L$_1$ (25.0 mg, 0.0537 mmol, 1.00 eq) in THF (12 mL) a solution of Fe(BF$_4$)$_2$·6H$_2$O (9.06 mg, 0.0269 mmol, 0.500 eq) in water (2.2 mL) was added dropwise in 5 minutes at room temperature. The dark purple reaction mixture was stirred for 18 h at
room temperature. To the mixture saturated aq. KPF₆ was added and the resulting dark purple precipitate was filtered over Celite, washed with water, Et₂O, hexane and redissolved with acetonitrile. The solvent was evaporated to give desired Fe complex [L₁²Fe][PF₆]₂ (30.8 mg, 90 %) as a dark purple solid. Single crystals suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of Et₂O into an acetonitrile solution of [L₁²Fe][PF₆]₂.

Mp >370 °C dec.

¹H NMR (500 MHz, CD₃CN, δ): 8.96 (d, J = 8.1 Hz, 2H), 8.80 (t, J = 8.1 Hz, 1H), 8.78 (s, 2H), 7.78-7.75 (m, 4H), 7.45-7.41 (m, 6H), 7.34 (s, 2H), 7.24 (s, 2H).

¹³C NMR (125 MHz, CD₃CN, δ): 162.52 (s) 161.1 (s), 152.6 (s), 151.6 (s), 138.8 (d), 138.5 (s), 136.7 (d), 131.5 (d), 129.6 (d), 128.2 (s), 126.4 (d), 122.6 (d), 116.9 (d), 101.7 (d).

IR (KBr, cm⁻¹): 3116w, 3086w, 1622m, 1585w, 1564w, 1459s, 1449s, 1320m, 1278w, 1252w, 1174w, 1020w, 841vs, 766m, 746w, 687m, 558s.

HRMS (ESI) m/z: [M]²⁺ calcd for C₆₂H₃₈N₆O₄Fe: 493.11473; found: 493.11390.
A suspension of ligand L1 (25.0 mg, 0.0537 mmol, 1.00 eq) and Ru(DMSO)₄Cl₂ (13.0 mg, 0.0269 mmol, 0.500 eq) in ethylene glycol (15 ml) was heated to 120 °C for 18 h. The reaction mixture was allowed to cool to room temperature and a saturated aq. KPF₆
solution was added. The resulting red precipitate was filtered over Celite, washed with water, Et₂O, hexane and redissolved with acetonitrile. The solvent was evaporated and the residue was purified by silica gel column chromatography with acetonitrile/H₂O/aq. KPF₆ (97:3:0.3), reprecipitated with a saturated aq. KPF₆ solution and collected by filtration. The red solid was washed with water and Et₂O to give desired complex [L₁₂Ru][PF₆]₂ (32.5 mg, 92%) as a dark red solid. Single crystals suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of Et₂O into an acetonitrile solution of [L₁₂Ru][PF₆]₂.

Mp >350 °C dec.

¹H NMR (500 MHz, CD₃CN, δ): 8.82 (s, 2H), 8.80 (d, J = 8.2 Hz, 2H), 8.50 (t, J = 8.2 Hz, 1H), 7.83-7.80 (m, 4H), 7.68 (s, 2H), 7.48-7.46 (m, 6H), 7.34 (s, 2H).

¹³C NMR (125 MHz, CD₃CN, δ): 163.1 (s), 156.8 (s), 152.9 (s), 152.8 (s), 137.9 (s), 137.0 (d), 136.8 (d), 131.9 (d), 130.2 (d), 128.9 (s), 126.9 (d), 123.2 (d), 117.9 (d), 102.4 (d).

IR (KBr, cm⁻¹): 3116w, 3069w, 1621m, 1585w, 1567w, 1485w, 1459s, 1447s, 1385w, 1313w, 1278w, 1176w, 1020w, 842vs, 767w, 687w, 558s.

HRMS (ESI) m/z: [M]²⁺ calcd for C₆₂H₃₈N₆O₄Ru: 516.10018; found: 516.09979.
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Zn[2,6-bis(2-hexylfuro[2,3-c]pyridin-5-yl)pyridine]-PF$_6$ ([L$_2$Zn][PF$_6$]$_2$)

To a solution of ligand L$_2$ (15.0 mg, 0.0311 mmol, 1.00 eq) in THF (3 mL) a solution of Zn(OTf)$_2$ (5.66 mg, 0.0156 mmol, 0.500 eq) in MeOH (1.3 mL) was added dropwise in 5 minutes at room temperature. The reaction mixture was stirred for 18 h at room
temperature. To the mixture saturated aq. KPF$_6$ was added and the resulting yellow precipitate was filtered over Celite, washed with water, Et$_2$O, hexane and redissolved with acetonitrile. The solvent was evaporated to give desired Zn complex ([L$_2$Zn][PF$_6$]$_2$) (17.8 mg, 87%) as a yellow solid. Recrystallization by slow vapor diffusion of Et$_2$O into a CH$_2$Cl$_2$ solution of ([L$_2$Zn][PF$_6$]$_2$) gives yellow needles.

Mp 257–258 °C dec.

$^1$H NMR (500 MHz, CD$_2$Cl$_2$, δ): 8.75-8.71 (m, 3H), 8.68 (s, 2H), 7.75 (s, 2H), 6.70 (s, 2H), 2.74 (t, $J = 7.6$ Hz, 4H), 1.64 (quintet, $J = 7.4$ Hz, 4H), 1.29-1.20 (m, 12H), 0.81 (t, $J = 6.8$ Hz, 6H).

$^{13}$C NMR (125 MHz, CD$_2$Cl$_2$, δ): 169.46 (s), 153.2 (s), 150.6 (s), 144.9 (d), 141.5 (s), 140.3 (s), 130.7 (d), 122.3 (d), 115.5 (d), 103.2 (d), 31.6 (t), 29.0 (t), 28.9 (t), 27.4 (t), 22.7 (t), 14.1 (q).

IR (film on NaCl, cm$^{-1}$): 3125w, 2931m, 2859w, 1620w, 1587m, 1485w, 1456s, 1429w, 1324s, 1257w, 1182w, 1158w, 959w, 900w, 841vs, 740w, 665w, 558m.

HRMS (ESI) m/z: [M]$^{2+}$ calcd for C$_{62}$H$_{70}$N$_6$O$_4$Zn: 513.23695; found: 513.23769.
To a solution of ligand $\text{L}_2$ (15.0 mg, 0.0311 mmol, 1.00 eq) in THF (3 mL) a solution of Fe(BF$_4$)$_2$·6H$_2$O (5.26 mg, 0.0156 mmol, 0.500 eq) in water (1.3 mL) was added dropwise in 5 minutes at room temperature. The dark purple reaction mixture was stirred for 18 h at
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room temperature. To the mixture saturated aq. KPF$_6$ was added and the resulting dark purple precipitate was filtered over Celite, washed with water, Et$_2$O, hexane and redissolved with acetonitrile. The solvent was evaporated to give desired Fe complex [L$_2$Fe][PF$_6$]$_2$ (18.4 mg, 90 %) as a dark purple solid. Recrystallization by slow vapor diffusion of Et$_2$O into a CH$_2$Cl$_2$ solution of [L$_2$Fe][PF$_6$]$_2$ gives dark purple blocks.

Mp 299–300 °C dec.

$^1$H NMR (500 MHz, CD$_2$Cl$_2$, δ): 8.87 (d, $J$ = 7.9 Hz, 2H) 8.74 (t, $J$ = 8.0 Hz, 1H), 8.64 (s, 2H), 7.11 (s, 2H), 6.61 (s, 2H), 2.68 (t, $J$ = 7.6 Hz, 4H), 1.62-1.52 (m, 4H), 1.27-1.17 (m, 12H), 0.80 (t, $J$ = 6.9 Hz, 6H).

$^{13}$C NMR (125 MHz, CD$_2$Cl$_2$, δ): 168.3 (s), 161.1 (s), 152.6 (s), 150.8 (s), 138.6 (s), 138.5 (d), 135.5 (d), 122.0 (d), 116.4 (d), 103.1 (d), 31.6 (t), 28.9 (t), 28.6 (t), 27.4 (t), 22.7 (t), 14.0 (q).

IR (film on NaCl, cm$^{-1}$): 3123w, 2931m, 2860w, 1624w, 1585m, 1456s, 1320m, 1259w, 1157w, 904w, 841vs, 749w, 674w, 558m.

HRMS (ESI) m/z: [M]$^{2+}$ calcd for C$_{62}$H$_{70}$FeN$_6$O$_4$: 509.23993; found: 509.23943.
A suspension of ligand L2 (25.0 mg, 0.0519 mmol, 1.00 eq) and Ru(DMSO)₄Cl₂ (12.6 mg, 0.0260 mmol, 0.500 eq) in ethylene glycol (15 ml) was heated to 120 °C for 18 h.
The reaction mixture was allowed to cool to room temperature and a saturated aq. KPF$_6$ solution was added. The resulting red precipitate was filtered over Celite, washed with water, Et$_2$O, hexane and redissolved with acetonitrile. The solvent was evaporated to give desired Ru complex ([L$_2$Ru][PF$_6$]$_2$) (34.8 mg, 99%) as a dark red solid.

Mp >320 °C dec.

$^1$H NMR (500 MHz, CD$_2$Cl$_2$, $\delta$): 8.68 (d, $J = 8.2$ Hz, 2H) 8.63 (s, 2H), 8.45 (t, $J = 8.2$ Hz, 1H), 7.38 (s, 2H), 6.64 (d, $J = 0.7$ Hz, 2H), 2.70 (t, $J = 7.5$ Hz, 4H), 1.59 (quintet, $J = 7.5$ Hz, 4H), 1.28-1.18 (m, 12H), 0.80 (t, $J = 6.9$ Hz, 6H).

$^{13}$C NMR (125 MHz, CD$_2$Cl$_2$, $\delta$): 168.6 (s), 156.1 (s), 152.4 (s), 151.2 (s), 137.6 (s), 136.5 (d), 135.0 (d), 122.1 (d), 117.0 (d), 103.1 (d), 31.6 (t), 28.9 (t), 28.7 (t), 27.4 (t), 22.7 (t), 14.1 (q).

IR (film on NaCl, cm$^{-1}$): 3125 w, 2931 m, 2859 w, 1623 w, 1584 m, 1493 w, 1455 s, 1314 m, 1259 w, 1156 w, 903 w, 840 vs, 740 w, 557 m.

HRMS (ESI) m/z: [M]$^{2+}$ calcd for C$_{62}$H$_{70}$RuN$_6$O$_4$: 532.22539; found: 532.22467.
Zn[2,6-bis(2-(pyridin-4-yl)furo[2,3-c]pyridin-5-yl)pyridine]-PF$_6$ ([L3$_2$Zn][PF$_6$]$_2$)

To a solution of ligand L3 (12.0 mg, 0.0257 mmol, 1.00 eq) in THF (12 mL) a solution of Zn(OTf)$_2$ (4.67 mg, 0.0156 mmol, 0.500 eq) in MeOH (1.1 mL) was added dropwise in 5 minutes at room temperature. The reaction mixture was stirred for 48 h at room temperature. To the mixture saturated aq. KPF$_6$ was added and the resulting yellow precipitate was filtered over Celite, washed with water, Et$_2$O, hexane and redissolved with acetonitrile. The solvent was evaporated to give desired Zn complex [L3$_2$Zn][PF$_6$]$_2$ (15.5 mg, 94%) as a yellow solid. Recrystallization by slow vapor diffusion of Et$_2$O into an acetonitrile solution of [L3$_2$Zn][PF$_6$]$_2$ gives yellow block.

Mp >350 °C dec.

$^1$H NMR (500 MHz, CD$_3$CN, δ) 8.93 (d, $J = 0.9$ Hz, 2H), 8.85-8.83 (m, 2H), 8.80-8.76 (m, 1H), 8.69-8.68 (m, 4H), 8.12 (d, $J = 0.8$ Hz, 2H), 7.73-7.71 (m, 4H), 7.63 (d, $J = 0.7$ Hz, 2H).
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$^{13}$C NMR (125 MHz, CD$_3$CN, $\delta$): 161.1 (s), 154.0 (s), 151.8 (d), 151.2 (s), 145.2 (d), 143.2 (s), 139.9 (s), 136.0 (s), 133.5 (d), 123.6 (d), 120.5 (d), 117.3 (d), 105.7 (d).

IR (KBr, cm$^{-1}$): 2921 w, 1611 m, 1582 w, 1599 w, 1452 m, 1414 w, 1384 w, 1325 m, 1179 w, 1046 w, 835 vs, 690 w, 558 s.

HRMS (ESI) $m/z$: [M]$^{2+}$ calcd for C$_{58}$H$_{34}$N$_{10}$O$_4$Zn: 499.10225; found: 499.10186.
Fe[2,6-bis(2-(pyridin-4-yl)furo[2,3-c]pyridin-5-yl)pyridine]-PF₆ ([L₃Fe][PF₆]₂)

To a suspension of ligand L₃ (100 mg, 0.214 mmol, 1.00 eq) in a mixture of THF (21 mL) and MeCN (2 mL) under N₂ atmosphere a solution of Fe(BF₄)₂·6H₂O (36.1 mg, 0.107 mmol, 0.500 eq) in water (9 mL) was added dropwise in 5 minutes at room temperature. The dark purple reaction mixture was stirred for 18 h at room temperature. To the mixture saturated aq. KPF₆ was added and the resulting dark purple precipitate was filtered over Celite, washed with water, Et₂O, hexane and redissolved with acetonitrile. The solvent was evaporated to give a dark purple solid. Recrystallization by slow vapor diffusion of Et₂O into an acetonitrile solution of crude product afforded dark purple blocks of [L₃Fe][PF₆]₂ that were collected by filtration (0.109 mg, 80%).

Mp >350 °C dec.

¹H NMR (500 MHz, CD₃CN, δ): 8.99 (d, J = 8.1 Hz, 2H), 8.86 (s, 2H), 8.81 (t, J = 8.1 Hz, 1H), 8.64 (d, J = 5.8 Hz, 4H), 7.64 (d, J = 6.0 Hz, 4H), 7.53 (s, 2H), 7.47 (s, 2H).

¹³C NMR (125 MHz, CD₃CN, δ): 161.5 (s), 159.8 (s), 153.2 (s), 152.6 (s), 151.7 (d), 139.3 (d), 138.6 (d), 138.1 (s), 135.8 (s), 123.5 (d), 120.3 (d), 117.9 (d), 105.6 (d).

IR (KBr, cm⁻¹): 2923w, 1611m, 1577w, 1455m, 1414w, 1384w, 1321w, 1174w, 1043w, 844vs, 690w, 558m.

HRMS (ESI) m/z: [M]²⁺ calcd for C₅₈H₄₆N₁₀O₄Fe: 495.10522; found: 495.10475.
A suspension of ligand L3 (12.0 mg, 0.0257 mmol, 1.00 eq) and Ru(DMSO)$_4$Cl$_2$ (6.22 mg, 0.0129 mmol, 0.500 eq) in ethylene glycol (10 ml) was heated to 120 °C for 18 h.
The reaction mixture was allowed to cool to room temperature and a saturated aq. KPF$_6$ solution was added. The resulting red precipitate was filtered over Celite, washed with water, Et$_2$O, hexane and redissolved with acetonitrile. The solvent was evaporated to give desired Ru complex [L$_3$Ru][PF$_6$]$_2$ (16.7 mg, 98%) as a dark red solid. Recrystallization by slow vapor diffusion of Et$_2$O into an acetonitrile solution of [L$_3$Ru][PF$_6$]$_2$ gives dark red blocks.

Mp >350 °C dec.

$^1$H NMR (400 MHz, CD$_3$CN, δ): 8.88 (d, $J = 0.7$ Hz, 2H), 8.82 (d, $J = 8.2$ Hz, 2H), 8.68-8.66 (m, 4H), 8.53 (t, $J = 8.2$ Hz, 1H), 7.76 (s, 2H), 7.68-7.67 (m, 4H), 7.57 (d, $J = 0.7$ Hz, 2H).

$^{13}$C NMR (125 MHz, CD$_3$CN, δ): 160.1 (s), 156.7 (s), 153.1 (s), 153.0 (s), 151.6 (d), 138.0 (d), 137.2 (s), 137.2 (d), 136.0 (s), 123.5 (d), 120.4 (d), 118.6 (d), 105.8 (d).

IR (KBr, cm$^{-1}$): 2922w, 1609m, 1576w, 1455s, 1414w, 1313w, 1177w, 1042w, 990w, 845vs, 690w, 558w.

HRMS (ESI) m/z: [M]$^{2+}$ calcd for C$_{58}$H$_{34}$N$_{10}$O$_4$Ru: 518.09061; found: 518.09079.
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([L4$_2$Zn][PF$_6$]$_2$)

![Chemical structure image]

To a solution of ligand L4 (24.0 mg, 0.0326 mmol, 1.00 eq) in THF (6 mL) a solution of Zn(OTf)$_2$ (5.93 mg, 0.0163 mmol, 0.500 eq) in MeOH (2 mL) was added dropwise in 5 minutes at room temperature. The reaction mixture was stirred for 18 h at room temperature. To the mixture saturated aq. KPF$_6$ was added and the resulting yellow precipitate was filtered over Celite, washed with water, Et$_2$O, hexane and redissolved with acetonitrile. The solvent was evaporated to give desired Zn complex [L4$_2$Zn][PF$_6$]$_2$ (29.3 mg, 98%) as a yellow solid. Recrystallization by slow vapor diffusion of Et$_2$O into an acetonitrile solution of [L4$_2$Zn][PF$_6$]$_2$ gives yellow precipitate.

Mp 286–289 °C dec.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$, δ): 9.12 (d, $J = 1.6$ Hz, 2H), 8.88 (d, $J = 0.5$ Hz, 2H), 8.85-8.78 (m, 8H), 8.55 (d, $J = 8.5$ Hz, 2H), 8.48 (d, $J = 8.1$ Hz, 2H), 8.43 (d, $J = 1.4$ Hz, 2H), 8.23 (dd, $J = 8.4$, 2.3 Hz, 2H), 8.01 (s, 2H), 7.97 (s, 2H), 7.61 (dd, $J = 8.1$, 2.2 Hz, 2H), 7.45 (d, $J = 0.5$ Hz, 2H), 6.96 (d, $J = 0.7$ Hz, 2H), 6.68 (s, 4H), 6.62 (s, 4H), 3.79 (s, 6H), 3.76 (s, 6H), 2.08 (s, 12H), 2.01 (s, 12H).

$^{13}$C NMR (100 MHz, CD$_2$Cl$_2$, δ): 164.4 (s), 161.4 (s), 161.3 (s), 159.4 (s), 158.3 (s), 153.5 (s), 153.5 (s), 153.3 (s), 150.8 (s), 150.7 (d), 150.6 (s), 147.2 (d), 145.2 (d), 142.3 (s), 141.7 (s), 140.5 (s), 140.1 (s), 140.1 (s), 138.8 (d), 138.1 (s), 137.9 (s), 134.5 (d), 131.7 (d), 131.5 (d), 130.5 (s), 124.1 (s), 122.8 (d), 122.7 (d), 121.4 (d), 121.2 (d), 120.7 (s), 116.4 (d), 116.1 (d), 113.7 (d), 113.3 (d), 107.5 (d), 103.0 (d), 55.6 (q), 55.5 (q), 21.3 (q), 20.9 (q).
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IR (film on NaCl, cm$^{-1}$): 2919w, 1603s, 1455vs, 1321s, 1283w, 1193w, 1155m, 1063w, 959w, 842vs, 558w.

HRMS (ESI) m/z: [M]$^{2+}$ calcd for C$_{94}$H$_{74}$N$_{10}$O$_{8}$Zn: 767.24858; found: 767.24808.
Supporting Information

Fe[2-(4-methoxy-2,6-dimethylphenyl)-5-(6-{2-[5’-(4-methoxy-2,6-dimethylphenyl)-2,2’-bipyridin-5-yl]furo[2,3-c]pyridin-5-yl}pyridin-2-yl)furo[2,3-c]pyridine]_2-2PF_6 ([L_4Fe][PF_6]_2)

To a solution of ligand L_4 (24.0 mg, 0.0326 mmol, 1.00 eq) in THF (6 mL) a solution of Fe(BF_4)_2·6H_2O (5.50 mg, 0.0163 mmol, 0.500 eq) in water (2 mL) was added dropwise in 5 minutes at room temperature. The dark purple reaction mixture was stirred for 48 h at room temperature. To the mixture saturated aq. KPF_6 was added and the resulting dark purple precipitate was filtered over Celite, washed with water, Et_2O, hexane and redissolved with acetonitrile. The solvent was evaporated to give desired Fe complex [L_4Fe][PF_6]_2 (28.3 mg, 97%) as a dark purple solid. Recrystallization by slow vapor diffusion of Et_2O into an acetonitrile solution of [L_4Fe][PF_6]_2 gives dark purple blocks.

Mp >330 °C dec.

^1^H NMR (400 MHz, CD_2Cl_2, δ): 9.06 (d, J = 1.6 Hz, 2H), 9.01-8.98 (m, 4H), 8.87-8.78 (m, 6H), 8.52 (d, J = 8.4 Hz, 2H), 8.45 (d, J = 8.1 Hz, 2H), 8.42 (d, J = 1.6 Hz, 2H), 8.17 (dd, J = 8.4, 2.0 Hz, 2H), 7.60 (dd, J = 8.1, 2.0 Hz, 2H), 7.39 (s, 2H), 7.37 (s, 2H), 7.32 (s, 2H), 6.87 (s, 2H), 6.68 (s, 4H), 6.60 (s, 4H), 3.79 (s, 6H), 3.75 (s, 6H), 2.02 (s, 12H), 2.01 (s, 12H).

^1^C NMR (100 MHz, CD_2Cl_2, δ): 163.3 (s), 161.7 (s), 161.3 (s), 161.2 (s), 161.0 (s), 160.4 (s), 159.4 (s), 158.2 (s), 153.4 (s), 152.9 (s), 152.7 (s), 151.7 (s), 151.0 (s), 150.7 (d), 147.2 (d), 140.5 (s), 139.1 (d), 138.8 (d), 138.4 (s), 138.1 (s), 137.9 (s), 136.6 (d), 136.2 (d), 134.4 (d), 130.5 (s), 123.9 (s), 122.5 (d), 122.5 (d), 121.4 (d), 121.2 (d), 120.4 (s), 117.1 (d), 116.9 (d), 113.7 (d), 113.3 (d), 107.3 (d), 102.8 (d), 55.6 (q), 55.5 (q), 21.3 (q), 20.8 (q).

S-84
IR (film on NaCl, cm⁻¹): 2919w, 1603s, 1455vs, 1318s, 1281w, 1193w, 1154s, 1063w, 841vs, 558w.

HRMS (ESI) m/z: [M]²⁺ calcd for C₉₄H₇₄N₁₀O₈Fe: 763.25153; found: 763.25054.
Ru[4-iodo-6’-(2-(4-methoxy-2,6-dimethylphenyl)furo[2,3-c]pyridin-5-yl)-2,2’-bipyridin-5-ol]2·2PF6 (28)

A suspension of 4-iodo-4”-[2-(4-methoxy-2,6-dimethylphenyl)-ethynyl]-5,5”-bis(methoxymethoxy)-2,2’:6’,2”-terpyridine (24c) (148 mg, 0.232 mmol, 1.00 eq) and Ru(DMSO)4Cl2 (56.3 mg, 0.116 mmol, 0.500 eq) in ethanol (44 ml) was heated to reflux for 72 h. The reaction mixture was allowed to cool to room temperature and a saturated aq. KPF6 solution was added. The resulting red precipitate was filtered over Celite, washed with water, Et2O, hexane and redissolved with acetonitrile. The solvent was evaporated to give Ru complex 28 (171 mg, crude yield 99%) as a dark red solid that was used without further purification in the subsequent reaction.

Mp >350 °C dec.

1H NMR (500 MHz, CD3CN, δ): 8.71 (br. s, 1H), 8.68 (br. s, 1H), 8.57-8.47 (m, 2H), 8.29-8.21 (m, 1H), 7.29 (br. s, 1H), 6.92 (s, 1H), 6.68 (br. s, 2H), 6.44 (br. s, 1H), 3.76 (s, 3H), 2.02 (s, 6H).

13C NMR (125 MHz, CD3CN, δ): 162.0 (s), 160.9 (s), 155.4 (s), 154.3 (s), 151.9 (s), 151.4 (s), 140.2 (s), 138.0 (d), 136.4 (s), 135.5 (d), 134.0 (d), 121.8 (d), 120.5 (d), 116.6 (d), 113.2 (d), 106.8 (d), 55.0 (q), 19.7 (q).

IR (film on NaCl, cm⁻¹): 3647 w, 3584 w, 3440 br, 3086 w, 2922 w, 2844 w, 2194 w, 1604 m, 1575 w, 1455 vs, 1381 w, 1318 s, 1193 w, 1154 m, 1068 w, 842 vs, 738 w, 623 w, 558 m.

A mixture of a crude complex 28 (130 mg, 0.0873 mmol, 1.00 eq), 5-ethynyl-5′-(4-methoxy-2,6-dimethylphenyl)-2,2′-bipyridine (22a) (56.2 mg, 0.179 mmol, 2.05 eq), PdCl$_2$(PPh$_3$)$_2$ (3.1 mg, 0.0044 mmol, 5 mol%) and CuI (1.7 mg, 0.0087 mmol, 10 mol%) in degassed DMF/Et$_3$N (20 mL/12 mL) was heated to 90 °C for 24 h under N$_2$ atmosphere. The reaction mixture was allowed to cool to room temperature and the solvent was evaporated under reduced pressure. The residue was redissolved in CH$_2$Cl$_2$, washed with 10% NH$_4$OH aqueous solution, water and brine. The organic phase was dried over MgSO$_4$, filtered and evaporated under reduces pressure. The crude residue was purified by silica gel column chromatography with acetonitrile/CH$_2$Cl$_2$/H$_2$O/aq. KPF$_6$ (140:100:8:3). The first red band was collected and the solvent was evaporated under reduced pressure. The residue was redissolved in CH$_2$Cl$_2$ and filtered through a pad of
Celite. The filtrate was evaporated under reduced pressure to give desired Ru complex [L4Ru][PF6]2 (70 mg, 43% from 24c over 2 steps) as a dark red solid.

Mp >350 °C dec.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$, δ): 9.09 (d, $J = 1.1$ Hz, 2H), 8.85-8.79 (m, 8H), 8.57-8.53 (m, 4H), 8.47 (d, $J = 8.1$ Hz, 2H), 8.43 (s, 2H), 8.19 (dd, $J = 8.4, 2.1$ Hz, 2H), 7.65 (s, 2H), 7.61 (dd, $J = 8.2, 2.0$ Hz, 3H), 7.58 (s, 2H), 7.41 (s, 2H), 7.91 (s, 2H), 6.91 (s, 2H), 6.68 (s, 4H), 6.61 (s, 4H), 3.79 (s, 6H), 3.76 (s, 6H), 2.05 (s, 12H), 2.01 (s, 12H).

$^{13}$C NMR (100 MHz, CD$_2$Cl$_2$, δ): 163.6 (s), 161.4 (s), 160.7 (s), 159.4 (s), 158.2 (s), 156.2 (s), 156.1 (s), 153.5 (s), 152.7 (s), 152.5 (s), 152.1 (s), 151.4 (s), 150.7 (s), 147.1 (d), 140.5 (s), 138.8 (d), 138.1 (s), 137.9 (s), 137.5 (s), 136.9 (d), 136.0 (d), 135.7 (d), 134.4 (d), 130.5 (s), 124.0 (s), 122.7 (d), 122.6 (d), 121.4 (d), 121.2 (d), 120.5 (s), 117.8 (d), 117.5 (d), 113.7 (d), 113.3 (d), 107.4 (d), 102.9 (d), 55.6 (q), 55.5 (q), 21.3 (q), 20.9 (q).

IR (film on NaCl, cm$^{-1}$): 2920w, 1603s, 1456vs, 1315s, 1278w, 1192w, 1154s, 1062w, 999w, 841vs, 557m.

HRMS (ESI) m/z: [M]$^{2+}$ calcd for C$_{94}$H$_{74}$N$_{10}$O$_8$Ru: 786.23642; found: 786.23519.
Supporting Information

Zn[2-(4-methoxy-2,6-dimethylphenyl)-5-(6-‘2-[6’-(4-methoxy-2,6-dimethylphenyl)-
([L52Zn][PF6]2)

To a solution of ligand L5 (5.08 mg, 0.00690 mmol, 1.00 eq) in THF (1 mL) a solution of
Zn(OTf)2 (1.25 mg, 0.00345 mmol, 0.500 eq) in water (0.4 mL) was added dropwise in 1
minutes at room temperature. The reaction mixture was stirred for 6 h at room
temperature. To the mixture saturated aq. KPF6 was added and the resulting yellow
precipitate was filtered over Celite, washed with water, Et2O, hexane and redissolved
with acetonitrile. The solvent was evaporated to give desired Zn complex [L52Zn][PF6]2
(6.23 mg, 99%) as a yellow solid. Recrystallization by slow vapor diffusion of Et2O into
an acetonitrile solution of [L52Zn][PF6]2 gives yellow precipitate.

Mp 270–272 °C dec.

1H NMR (400 MHz, CD2Cl2, δ): 9.11 (s, 2H), 8.84-8.79 (m, 10H), 8.49 (d, J = 8.6 Hz,
2H), 8.37 (d, J = 7.5 Hz, 2H), 8.15 (dd, J = 8.4, 2.2 Hz, 2H), 7.98 (s, 2H), 7.95 (s, 2H),
7.87 (t, J = 7.8 Hz, 3H), 7.42 (s, 2H), 7.26 (dd, J = 7.7, 0.6 Hz, 2H), 6.95 (s, 2H), 6.66 (s,
4H), 6.62 (s, 4H), 3.80 (s, 6H), 3.76 (s, 5H), 2.08 (s, 12H), 2.04 (s, 12H).

13C NMR (125 MHz, CD2Cl2, δ): 164.3 (s), 161.4 (s), 161.2 (s), 159.6 (s), 159.3 (s),
158.4 (s), 154.9 (s), 153.4 (s), 153.2 (s), 150.7 (s), 150.5 (s), 147.0 (d), 145.1 (d), 142.1
(s), 141.6 (s), 140.4 (s), 140.0 (s), 140.0 (s), 137.8 (s), 137.6 (d), 134.3 (d), 133.6 (s),
131.6 (d), 131.4 (d), 126.3 (d), 124.1 (s), 122.7 (d), 122.6 (d), 121.4 (d), 120.6 (s), 119.5
(d), 116.3 (d), 116.0 (d), 113.6 (d), 113.2 (d), 107.4 (d), 102.8 (d), 55.5 (q), 55.5 (q), 20.8
(q), 20.7 (q).
Supporting Information

IR (film on NaCl, cm\(^{-1}\)): 2921\(w\), 1603\(s\), 1582\(m\), 1454\(vs\), 1322\(s\), 1284\(w\), 1193\(w\), 1155\(m\), 1070\(w\), 841\(vs\), 558\(w\).

HRMS (ESI) \(m/z\): [M\(^{2+}\)] calcd for C\(_{94}H_{74}N_{10}O_8\)Zn: 767.24858; found: 767.24783.
Supporting Information

Fe[2-(4-methoxy-2,6-dimethylphenyl)-5-(6-{2-[6'--(4-methoxy-2,6-dimethylphenyl)-2,2’-bipyridin-5-yl]furo[2,3-c|pyridin-5-yl|pyridin-2-yl]furo[2,3-c|pyridine]_2-2PF_6} ([L_5^2Fe][PF_6]_2)

To a solution of ligand L_5 (5.18 mg, 0.00704 mmol, 1.00 eq) in THF (3 mL) a solution of Fe(BF_4)_2⋅6H_2O (1.88 mg, 0.00352 mmol, 0.500 eq) in water (0.4 mL) was added dropwise in 1 minutes at room temperature. The dark purple reaction mixture was stirred for 6 h at room temperature. To the mixture saturated aq. KPF_6 was added and the resulting dark purple precipitate was filtered over Celite, washed with water, Et_2O, hexane and redissolved with acetonitrile. The solvent was evaporated to give desired Fe complex [L_5^2Fe][PF_6]_2 (5.11 mg, 80%) as a dark purple solid. Recrystallization by slow vapor diffusion of Et_2O into a acetonitrile solution of [L_5^2Fe][PF_6]_2 gives dark purple precipitate.

Mp >320 °C dec.

^1H NMR (500 MHz, CD_2Cl_2, δ): 9.05 (s, 2H), 8.99-8.92 (m, 4H), 8.85-8.74 (m, 6H), 8.47 (d, J = 7.6 Hz, 2H), 8.36 (d, J = 7.7 Hz, 2H), 8.10 (d, J = 7.5 Hz, 2H), 7.87 (t, J = 7.5 Hz, 2H), 7.35 (s, 2H), 7.33 (s, 2H), 7.30 (s, 2H), 7.25 (d, J = 7.6 Hz, 2H), 6.86 (s, 2H), 6.66 (s, 4H), 6.59 (s, 4H), 3.80 (s, 6H), 3.75 (s, 6H), 2.03 (s, 12H), 2.01 (s, 12H).

^13C NMR (125 MHz, CD_2Cl_2, δ): 163.2 (s), 161.3 (s), 161.1 (s), 160.9 (s), 160.3 (s), 159.6 (s), 159.3 (s), 158.4 (s), 154.9 (s), 152.8 (s), 152.6 (s), 151.5 (s), 150.9 (s), 147.0 (d), 140.4 (s), 139.0 (d), 138.2 (s), 137.8 (s), 137.6 (d), 136.5 (d), 136.1 (d), 134.2 (d), 133.6 (s), 126.3 (d), 123.9 (s), 122.4 (d), 122.4 (d), 121.4 (d), 120.3 (s), 119.5 (d), 117.0 (d), 116.8 (d), 113.6 (d), 113.2 (d), 107.2 (d), 102.7 (d), 55.5 (q), 55.5 (q), 20.8 (q), 20.7 (q).
Supporting Information

IR (film on NaCl, cm$^{-1}$): 2921w, 1604s, 1455vs, 1318s, 1282w, 1193w, 1155m, 1070w, 841vs, 558w.

HRMS (ESI) m/z: [M]$^{2+}$ calcd for C$_{94}$H$_{74}$FeN$_{10}$O$_8$: 763.25153; found: 763.25106.
A mixture of a crude complex 28 (15.7 mg, 0.0105 mmol, 1.00 eq), 5-ethynyl-6’-(4-methoxy-2,6-dimethylphenyl)-2,2’-bipyridine (22b) (6.79 mg, 0.0216 mmol, 2.05 eq), PdCl₂(PPh₃)₂ (0.37 mg, 0.00053 mmol, 5 mol%) and CuI (0.20 mg, 0.0011 mmol, 10 mol%) in degassed DMF/Et₃N (2 mL/2 mL) was heated to 90 °C for 39 h under N₂ atmosphere. The reaction mixture was allowed to cool to room temperature and the solvent was evaporated under reduced pressure. The residue was redissolved in CH₂Cl₂, washed with 10% NH₄OH aqueous solution, water and brine. The organic phase was dried over MgSO₄, filtered and evaporated under reduces pressure. The crude residue was purified by silica gel column chromatography with acetonitrile/CH₂Cl₂/H₂O/aq. KPF₆ (140:100:8:3). The first red band was collected and the solvent was evaporated under reduced pressure. The residue was redissolved in CH₂Cl₂ and filtered through a pad of Celite. The filtrate was evaporated under reduced pressure to give desired Ru complex [L₅Ru][PF₆]₂ (7.8 mg, 40% from 24c over 2 steps) as a dark red solid.

Mp >350 °C dec.

¹H NMR (400 MHz, CD₂Cl₂, δ): 9.07 (s, 2H), 8.81-8.74 (m, 8H), 8.53-8.44 (m, 4H), 8.36 (d, J = 7.5 Hz, 2H), 8.10 (d, J = 7.3 Hz, 2H), 7.86 (t, J = 7.8 Hz, 2H), 7.63 (s, 2H), 7.57 (s, 2H), 7.38 (s, 2H), 7.25 (d, J = 7.5 Hz, 2H), 6.91 (s, 2H), 6.67 (s, 4H), 6.60 (s, 4H), 3.81 (s, 6H), 3.75 (s, 6H), 2.04 (s, 12H), 2.03 (s, 12H).

¹³C NMR (125 MHz, CD₂Cl₂, δ): 163.5 (s), 161.2 (s), 160.5 (s), 159.5 (s), 159.4 (s), 158.1 (s), 156.1 (s), 155.9 (s), 154.7 (s), 152.6 (s), 152.4 (s), 152.0 (s), 151.3 (s), 147.0
Supporting Information

(d), 140.4 (s), 137.8 (d), 137.4 (s), 137.3 (s), 136.8 (d), 135.9 (d), 135.6 (d), 134.2 (d), 133.4 (s), 126.4 (d), 124.0 (s), 122.6 (d), 122.5 (d), 121.4 (d), 120.4 (s), 119.6 (d), 117.7 (d), 117.5 (d), 113.6 (d), 113.2 (d), 107.3 (d), 103.0 (d), 55.5 (q), 55.5 (q), 20.8 (q), 20.7 (q).

IR (film on NaCl, cm$^{-1}$): 2921 $w$, 1604 $s$, 1455 $vs$, 1313 $m$, 1291 $w$, 1193 $w$, 1156 $m$, 1070 $w$, 842 $vs$, 558 $w$.

HRMS (ESI) $m/z$: [M]$^{2+}$ calcd for C$_{94}$H$_{74}$N$_{10}$O$_{8}$Ru: 786.23642; found: 786.23652.
To a solution of ligand L6 (15.2 mg, 0.0171 mmol, 1.00 eq) in THF (12 mL) a solution of Zn(OTf)2 (3.10 mg, 0.00854 mmol, 0.500 eq) in water (1.4 mL) was added dropwise in 5 minutes at room temperature. The reaction mixture was stirred for 18 h at room temperature. To the mixture saturated aq. KPF6 was added and the resulting yellow precipitate was filtered over Celite, washed with water, Et2O, hexane and redissolved with acetonitrile. The solvent was evaporated to give desired Zn complex [L62Zn][PF6]2 (16.8 mg, 92%) as a yellow solid. Recrystallization by slow vapor diffusion of Et2O into an acetonitrile solution of [L62Ru][PF6]2 gives yellow precipitate.

Mp >350 °C dec.
Supporting Information

$^1$H NMR (400 MHz, CD$_2$Cl$_2$, $\delta$): 9.13 (s, 2H), 8.91-8.84 (m, 5H), 8.57 (d, $J = 8.5$ Hz, 2H), 8.48 (d, $J = 7.7$ Hz, 2H), 8.43 (s, 2H), 8.23 (d, $J = 8.5$ Hz, 2H), 8.05 (s, 2H), 7.62 (d, $J = 7.7$ Hz, 2H), 7.45 (s, 2H), 6.68 (s, 4H), 3.79 (s, 6H), 2.01 (s, 12H).

$^{13}$C NMR (125 MHz, CD$_2$Cl$_2$, $\delta$): 161.5 (s), 159.3 (s), 158.2 (s), 153.5 (s), 153.4 (s), 150.6 (d), 150.6 (s), 147.1 (d), 145.2 (d), 142.2 (s), 140.1 (s), 138.8 (d), 138.0 (s), 137.9 (s), 134.4 (d), 131.8 (d), 130.4 (s), 124.0 (s), 122.9 (d), 121.3 (d), 121.1 (d), 116.4 (d), 113.2 (d), 102.9 (d), 55.4 (q), 21.3 (q).

IR (film on NaCl, cm$^{-1}$): 2909w, 2841w, 1602m, 1454s, 1430w, 1322m, 1276w, 1192w, 1155m, 1062w, 1012w, 959w, 842vs, 747w, 558m.

HRMS (ESI) $m/z$: [M]$^{2+}$ calcd for C$_{114}$H$_{86}$ZnN$_{14}$O$_8$: 921.30168; found: 921.30007.
Fe[2,6-bis{2-[5’-(4-methoxy-2,6-dimethylphenyl)-2,2’-bipyridin-5-yl]furo[2,3-c]pyridin-5-yl]pyridine}-2PF₆ ([L₆Fe][PF₆]₂)

To a solution of ligand L₆ (15.0 mg, 0.0169 mmol, 1.00 eq) in THF (15 mL) a solution of Fe(BF₄)₂ ⋅ 6H₂O (2.84 mg, 0.00842 mmol, 0.500 eq) in water (1.1 mL) was added dropwise in 5 minutes at room temperature. The dark purple reaction mixture was stirred for 6 h at room temperature. To the mixture saturated aq. KPF₆ was added and the resulting dark purple precipitate was filtered over Celite, washed with water, Et₂O, hexane and redissolved with acetonitrile. The solvent was evaporated to give desired Fe complex [L₆Fe][PF₆]₂ (14.4 mg, 80%) as a dark purple solid. Recrystallization by slow vapor diffusion of Et₂O into an acetonitrile solution of [L₆Fe][PF₆]₂ gives dark purple precipitate.

Mp >350 °C dec.

¹H NMR (400 MHz, CD₂Cl₂, δ): 9.08-9.03 (m, 4H), 8.90 (t, J = 7.8 Hz, 1H), 8.86 (s, 2H), 8.52 (d, J = 8.5 Hz, 2H), 8.45 (d, J = 8.1 Hz, 2H), 8.41 (s, 2H), 8.17 (d, J = 8.5 Hz, 2H),
Supporting Information

7.60 (d, \( J = 8.1 \) Hz, 2H), 7.43 (s, 2H), 7.36 (s, 2H), 6.67 (s, 4H), 3.79 (s, 6H), 2.00 (s, 12H).

\(^{13}\)C NMR (100 MHz, CD\(_2\)Cl\(_2\), \( \delta \)): 161.0 (s), 160.5 (s), 159.4 (s), 158.2 (s), 153.4 (s), 152.9 (s), 151.6 (s), 150.7 (d), 147.2 (d), 139.2 (s), 138.8 (s), 138.4 (d), 138.1 (s), 137.9 (s), 136.7 (d), 134.4 (d), 130.5 (s), 123.9 (s), 122.8 (d), 121.4 (d), 121.2 (d), 117.2 (d), 113.3 (d), 102.8 (d), 55.5 (q), 21.3 (q).

IR (film on NaCl, cm\(^{-1}\)): 2914w, 2841w, 1601m, 1456s, 1318m, 1276w, 1192w, 1155m, 1062w, 1012w, 840v, 749w, 558m.

HRMS (ESI) \( m/z \): [M]\(^{2+}\) calcd for C\(_{114}\)H\(_{86}\)FeN\(_{14}\)O\(_8\): 917.80621; found: 917.80624.
Ru[5,5”-dihydroxy-4,4”-diiodo-2,2’:6’,2”-terpyridine]-2PF$_6$ (27)

A suspension of diiodoterpyridine 14 (333 mg, 0.550 mmol, 1.00 eq) and Ru(DMSO)$_4$Cl$_2$ (133 mg, 0.275 mmol, 0.500 eq) in ethylene glycol (60 ml) was heated to 120 °C for 48 h. To the hot reaction mixture a saturated aq. KPF$_6$ solution was added till the first precipitate forms. The mixture was allowed to cool to room temperature. After dilution with water, the resulting orange precipitate was collected by filtration, washed with water, Et$_2$O, ethanol and CH$_2$Cl$_2$. Drying under high vacuum resulted in desired Ru complex 27 (319 mg, crude yield 89%) as an orange solid, that is insoluble in water and common organic solvents and was used without further purification in the subsequent reaction.

Mp >350 °C dec.

IR (KBr, cm$^{-1}$): 3407br, 3077m, 2927m, 1573m, 1551m, 1509m, 1449vs, 1378m, 1299s, 1228w, 1170w, 1053w, 846s, 689w, 614w, 561m.
HRMS (ESI) m/z: [M]$^{2+}$ calcd for C$_{30}$H$_{14}$N$_6$O$_4$Ru calcd for: 568.8379; found: 567.82914.

Ru$_{2}$,6-bis{2-[5’-(4-methoxy-2,6-dimethylphenyl)-2,2’-bipyridin-5-yl]furo[2,3-c]pyridin-5-yl}pyridine-2PF$_6$ ([L$_6$Ru][PF$_6$]$_2$)

A mixture of crude 27 (40.0 mg, 0.0308 mmol, 1.00 eq), 5-ethynyl-5’-(4-methoxy-2,6-dimethylphenyl)-2,2’-bipyridine (22a) (40.7 mg, 0.129 mmol, 4.20 eq), PdCl$_2$(PPh$_3$)$_2$ (2.2 mg, 0.0031 mmol, 10 mol%) and CuI (1.2 mg, 0.0062 mmol, 20 mol%) in degassed DMF/DIPEA (7 mL/7 mL) was heated to 80 °C for 48 h under N$_2$ atmosphere. The reaction mixture was allowed to cool to room temperature and the solvent was evaporated under reduced pressure. The residue was treated with EtOAc, collected by filtration and purified by silica gel column chromatography with acetonitrile/CH$_2$Cl$_2$/H$_2$O/aq. KPF$_6$ (140:100:8:3). The first red band was collected and the solvent was evaporated under reduced pressure. The residue was redissolved in CH$_2$Cl$_2$ and filtered through a pad of Celite. The filtrate was evaporated under reduced pressure to give desired complex [L$_6$Ru][PF$_6$]$_2$ (36 mg, 48% from 14 over 2 steps) as a dark red solid.

Mp >350 °C dec.

$^1$H NMR (500 MHz, CD$_2$Cl$_2$, δ): 9.08 (d, J = 2.1 Hz, 2H), 8.94 (s, 2H), 8.93 (d, J = 9.8 Hz, 2H), 8.62 (t, J = 8.1 Hz, 1H), 8.53 (d, J = 8.5 Hz, 2H), 8.45 (d, J = 8.2 Hz, 2H), 8.41 (d, J = 1.7 Hz, 2H), 8.18 (dd, J = 8.4, 2.2 Hz, 2H), 7.69 (s, 2H), 7.61 (dd, J = 8.1, 2.1 Hz, 2H), 7.43 (s, 2H), 6.67 (s, 4H), 3.78 (s, 6H), 2.00 (s, 12H).

$^{13}$C NMR (125 MHz, CD$_2$Cl$_2$, δ): 160.8 (s), 159.4 (s), 158.2 (s), 156.0 (s), 153.4 (s), 152.7 (s), 152.0 (s), 150.7 (d), 147.1 (d), 138.8 (d), 138.1 (s), 137.9 (s), 137.5 (s), 137.1
Supporting Information

(d), 136.0 (d), 134.4 (d), 130.5 (s), 123.9 (s), 122.9 (d), 121.4 (d), 121.2 (d), 117.9 (d), 113.3 (d), 102.9 (d), 55.5 (q), 21.3 (q).

IR (film on NaCl, cm$^{-1}$): 2920 w, 2836 w, 1600 m, 1454 vs, 1383 w, 1315 m, 1276 w, 1192 w, 1155 m, 1061 w, 1011 w, 999 w, 841 vs, 558 m.

HRMS (ESI) m/z: [M]$^{2+}$ calcd for C$_{114}$H$_{86}$N$_{14}$O$_8$Ru: 940.28954; found: 940.28944.
3. **Heterometallic Supramolecular Networks** \([L_3\text{FeAg}]_n[PF_6]_{3n}\cdot6.5n\text{MeCN} (\text{L3FeAg})\) and \([L_3\text{FeCu(MeCN)}]_n[PF_6]_{3n}\cdot4.5n\text{MeCN} (\text{L3FeCu})\)

3.1. **Synthesis of 3D Heterometallic Supramolecular Network L3FeAg**

A solution of AgPF\(_6\) (0.91 mg, 2.0 eq, 0.0036 mmol) in ethanol (0.5 mL) was layered over a solution of \([L_3\text{Fe}]\)\([PF_6]_2\) (2.31 mg, 1.0 eq, 0.00180 mmol) in acetonitrile (0.5 mL). A small amount of cyclohexane (~0.05 ml) between the layers was used to slow down the diffusion process. In few days dark purple needle-like crystals formed which over 2 weeks transformed into dark purple blocks. A supernatant was removed with pipette and the crystals were washed with additional amount of EtOH (x2), then collected by filtration to give \([L_3\text{FeAg}]_n[PF_6]_{3n}\cdot6.5n\text{MeCN} (\text{L3FeAg})\) (1.94 mg, 70%). The crystals for the single crystal X-ray diffraction analysis where kept in the mother liquor to avoid solvent loss. Prior to data collection, the chosen crystal was embedded in a polyether oil.

The analytical sample for characterization was dried under vacuum at rt for 8 h:

\text{Mp > dec 250° C}

\(^1\text{H NMR (500 MHz, CD}_3\text{CN, }\delta)\): 8.99 (d, \(J = 8.2\) Hz, 4H), 8.87 (s, 4H), 8.81 (t, \(J = 8.2\) Hz, 2H), 8.66-8.64 (AA’BB’ spin system, 8H), 7.66-7.65 (AA’BB’ spin system, 4H), 7.54 (d, \(J = 0.9\) Hz, 4H), 7.48 (s, 4H).

\(^{13}\text{C NMR (125 MHz, CD}_3\text{CN, }\delta)\): 161.6, 159.8, 153.3, 152.6, 151.8, 139.4, 138.7, 138.2, 135.9, 123.5, 120.4, 118.0, 105.7.
FT-IR (neat, cm⁻¹): 3115 w, 3078 w, 3041 w, 1607 m, 1578 m, 1450 m, 1415 m, 1320 m, 1259 w, 1225 w, 1174 w, 1041 w, 918 w, 834 s, 808 s, 746 m, 689 m, 661 m, 555 m.

HRMS (ESI) (solvent MeCN) m/z: [Ag]⁺ calcd for Ag: 106.90454; found: 106.90489; [Ag+MeCN]⁺ calcd for C₂H₃AgN: 147.93131; found: 147.93109; [L₃Fe]²⁺ calcd for C₅₈H₃₄FeN₁₀O₄: 495.10522; found: 495.10546; ([L₃FeAg]ₙ[PF₆]₃n·6.5nMeCN disassociates in MeCN, but the observed [Ag]⁺ and [Ag+MeCN]⁺ species besides [L₃Fe]²⁺ in the mass spectrum support the presence of silver ions in the product).

3.2. Synthesis of 2D Heterometallic Supramolecular Network L₃FeCu

A solution of [L₃Fe][PF₆]₂ (4.75 mg, 1.0 eq, 0.00371 mmol) under N₂ in degassed acetonitrile (0.5 mL) was layered over a solution of [Cu(CH₃CN)₄]PF₆ (3.16 mg, 2.0 eq, 0.00742 mmol) in degassed EtOH (0.5 mL). A small amount of cyclohexane (~0.05 ml) between the layers was used to slow down the diffusion process. Over 3 weeks purple block like crystals formed. A supernatant was removed with pipette and the crystals were washed with additional amount of EtOH (x2), then collected by filtration to give [L₃FeCu(MeCN)]ₙ[PF₆]₃n·4.5nMeCN (L₃FeCu) (2.67 mg, 47%). The crystals for the single crystal X-ray diffraction analysis where kept in the mother liquor to avoid solvent loss. Prior to data collection, the chosen crystal was embedded in a polyether oil.

The analytical sample for characterization was dried under vacuum at rt for 6 h:

Mp > dec 300° C
Supporting Information

$^1$H NMR (400 MHz, CD$_3$CN, $\delta$): 8.99 (d, $J = 8.0$ Hz, 4H), 8.87 (s, 4H), 8.81 (t, $J = 7.99$ Hz, 2H), 8.66-8.64 (AA’BB’ spin system, 8H), 7.6-7.65 (AA’BB’ spin system, 8H), 7.54 (s, 4H), 7.48 (s, 4H), 1.96 (s, 12H, corresponds to 4 CH$_3$CN molecules).

$^{13}$C NMR (125 MHz, CD$_3$CN, $\delta$): 161.6, 159.8, 153.2, 152.6, 151.7, 139.4, 138.6, 138.1, 135.9, 123.5, 120.4, 117.9, 105.6.

FT-IR (neat, cm$^{-1}$): 3109w, 3047w, 1607m, 1570m, 1541w, 1450m, 1414m, 1318w, 1255w, 1178w, 1161w, 1042w, 988w, 962w, 917w, 837s, 740w, 690m, 655m, 556s.

HRMS (ESI) (solvent MeCN) m/z: [Cu+MeCN]$^+$ calcd for C$_2$H$_3$CuN: 103.95560; found: 106.90489; [Cu+2MeCN]$^+$ calcd for C$_4$H$_6$CuN$_2$: 144.98215; found: 144.98194. [L$_3$Fe+H]$^{3+}$ calcd for C$_{58}$H$_{35}$FeN$_{10}$O$_4$: 330.40526; found: 330.40590; [L$_3$Fe]$^{2+}$ calcd for C$_{58}$H$_{34}$FeN$_{10}$O$_4$: 495.10522; found: 495.10525; ([L$_3$FeCu(MeCN)]$_n$[PF$_6$]$_{3n}$·4.5nMeCN disassociates in MeCN, but the observed [Cu+MeCN]$^+$ and [Cu+2MeCN]$^+$ species besides [L$_3$Fe]$^{2+}$ species in the mass spectrum support the presence of copper ions in the product).
3.3. Supporting Spectra of [L3\textsubscript{2}FeAg\textsubscript{n}]\textsubscript{3n}[PF\textsubscript{6}]{3n} \cdot \text{6.5nMeCN (L3FeAg)} and [L3\textsubscript{2}FeCu(MeCN)]\textsubscript{n}[PF\textsubscript{6}]{3n} \cdot \text{4.5nMeCN (L3FeCu)}

Figure S1. \textsuperscript{1}H NMR (500 MHz, CD\textsubscript{3}CN) of the dried and dissolved crystals of L3FeAg.

Figure S2. \textsuperscript{13}C NMR (125 MHz, CD\textsubscript{3}CN) of the dried and dissolved crystals of L3FeAg.
Figure S3. $^1$H NMR (400 MHz, CD$_3$CN) of the dried and dissolved crystals of L$^3$FeCu.

Figure S4. $^{13}$C NMR (125 MHz, CD$_3$CN) of the dried and dissolved crystals of L$^3$FeCu.
**Supporting Information**

Figure S5. FT-IR spectra of L3FeAg (blue) and L3FeCu (green).

Figure S6. HRMS (ESI) of the L3FeCu crystals dissolved in acetonitrile.

Figure S7. HRMS (ESI) of the L3FeAg crystals dissolved in acetonitrile.
Supporting Information

Figure S8. UV-vis of L3FeAg crystals dissolved in acetonitrile (λ_max = 294 nm, log ε = 5.12 cm⁻¹mol⁻¹L).

Figure S9. UV-vis of L3FeCu crystals dissolved in acetonitrile (λ_max = 294 nm, log ε = 5.12 cm⁻¹mol⁻¹L).

UV-vis spectra of L3FeAg and L3FeCu for dissolved crystals in acetonitrile are shown in Figures S8 and S9. There is no observable difference in both absorption spectra and they are superimposable with the spectrum of [L3Fe(PF₆)₃] in acetonitrile. The spectra of dissolved L3FeAg and L3FeCu exhibit strong ligand centered absorptions with maxima at 294 nm and weaker absorptions at lower energy, which can be attributed to MLCT transitions. The polymeric structures observed in solid state disassociate in the acetonitrile solution. The mass spectra (HR-ESI) of L3FeAg and L3FeCu crystals in acetonitrile show only discrete species of [Ag]⁺, [Ag+MeCN]⁺ and [L3Fe]²⁺ for L3FeAg.
and, similarly, [Cu+MeCN]⁺, [Cu+2MeCN]⁺ and [L3Fe]²⁺ for L₃FeCu (Figure S6 and S7). However, this data supports that Ag(I) and Cu(I) species are present in both crystalline materials.

Crystallographic Data of L₃FeAg

<table>
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<tr>
<th>Crystallised from</th>
<th>MeCN / EtOH/Cyclohexane</th>
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<tbody>
<tr>
<td>Empirical formula</td>
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<td>Formula weight [g mol⁻¹]</td>
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<tr>
<td>Crystal system</td>
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<tr>
<td>Space group</td>
<td>P̅1 (#2)</td>
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<td>c [Å]</td>
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<tr>
<td>β [°]</td>
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<tr>
<td>γ [°]</td>
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<tr>
<td>V [Å³]</td>
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<td>F(000)</td>
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<td>R_int</td>
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<td>Parameters refined; restrains</td>
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<td>wR(F²) (all data)</td>
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Weights: \( w = \frac{2}{(\sigma^2(F_o^2) + (0.1380P)^2 + 8.9667P)} \) where \( P = (F_o^2 + 2F_c^2)/3 \)
Supporting Information

Goodness of fit 1.095
Final $\Delta_{\text{max}}/\sigma$ 0.002
$\Delta \rho \text{ (max; min)} \text{ [e Å}^{-3}\text{]}$ 5.42; -1.51
$\sigma(d_{\text{C-C}}) \text{ [Å]}$ 0.005 – 0.007

Figure S10. ORTEP drawing (50% probability) of a cation of L$_3$FeAg.
Figure S11. Unit cell of \textbf{L3FeAg}.

Figure S12. Ball and stick representations of the cationic network of \textbf{L3FeAg}. \textbf{A}. One layer viewed down the \textit{c} axis \textbf{B}. One layer viewed down [011]. \textbf{C}. One layer viewed down the \textit{b} axis. \textbf{D}. Three layers viewed down the \textit{b} axis.

\emph{Crystallographic Data of \textbf{L3FeCu}}

<table>
<thead>
<tr>
<th>Crystallised from</th>
<th>MeCN / EtOH/Chex</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>$C_{69}H_{50.5}CuF_{18}FeN_{15.5}O_{4}P_{3}$</td>
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</table>
Supporting Information

Formula weight [g mol\(^{-1}\)]  1715.03
Crystal colour, habit  dark purple, prism
Crystal dimensions [mm]  0.20 × 0.25 × 0.28
Temperature [K]  160(1)
Crystal system  triclinic

Space group  \(P\bar{T}\) (#2)
\(Z\)  2
Reflections for cell determination  20758
\(2\theta\) range for cell determination [°]  5–57
Unit cell parameters \(a\) [Å]  14.9414(2)
\(b\) [Å]  15.3956(2)
\(c\) [Å]  18.3235(2)
\(\alpha\) [°]  94.4451(12)
\(\beta\) [°]  91.6360(11)
\(\gamma\) [°]  113.0082(14)
\(V\) [Å\(^3\)]  3860.05(9)

\(F(000)\)  1734
\(D_x\) [g cm\(^{-3}\)]  1.475
\(\mu\)(Mo \(K\alpha\)) [mm\(^{-1}\)]  0.626
Scan type  \(\omega\)
\(2\theta_{\text{max}}\) [°]  56.7
Transmission factors (min; max)  0.820; 1.000
Total reflections measured  44801
Symmetry independent reflections  16211
\(R_{\text{int}}\)  0.033
Reflections with \(I > 2\sigma(I)\)  12223
Reflections used in refinement  16211
Parameters refined; restraints  1028; 1021
Final \(R(F)\) [\(I > 2\sigma(I)\) reflections]  0.0643
\(wR(F^2)\) (all data)  0.2069

Weights:  \(w = \left[ \sigma^2(F_o^2) + (0.1266P)^2 + 1.64P \right]^{-1}\) where \(P = (F_o^2 + 2F_c^2)/3\)
Goodness of fit  1.084
Final \(\Delta_{\text{max}}/\sigma\)  0.002
\(\Delta\rho\) (max; min) [e Å\(^{-3}\)]  1.01; -0.80
\(\sigma(d(C-C))\) [Å]  0.004 – 0.009
Figure S13. ORTEP drawing (50% probability) of a cation of L3FeCu.

Figure S14. Unit cell of L3FeCu. Color code: Fe, brown; Cu, purple; N, light blue; O, red; C, dark gray; P, orange; F, light green. Hydrogen atoms have been omitted for clarity.
Figure S14A. Ball and stick representation of the cationic network of L3FeCu. A. One layer viewed down the a axis. B. One layer viewed down the b axis. C. One layer viewed down the c axis. D. Three independent layers viewed down the c axis.
4. Photophysical Properties of Linear Bilateral Extended Terpyridines L1-L6 and their Zn(II), Fe(II) and Ru(II) Complexes.

The UV/Vis spectra (Table S1 and Figure S15) of the phenyl and 4-pyridyl substituted ligands L1 and L3 display absorption maximum at ~300 nm in dichloromethane, while the UV/Vis spectrum of the n-hexyl-substituted ligand L2 displays an absorption maximum at 239 nm and less pronounced transitions at ~300 nm. The introduction of bipyridyl groups in L4, L5, and L6 leads to a ~36 nm bathochromic shift in the absorption maxima. These absorptions can be attributed to π-π* transitions. The simple symmetric ligands L1 and L2 show structured emission bands with maxima at 341 and 338 nm, respectively, and show medium quantum yields (~0.30). The ligands L1 and L2 display relatively short fluorescence lifetimes (2.96 and 1.91 ns, respectively). The emission spectrum of 4-pyridyl derivative L3 is much less featured than those of L1 and L2. Its emission maximum, at 374 nm, also shows a bathochromic shift relative to L1 and L2. Its quantum yield (0.14) is also significantly lower; however, the fluorescence lifetime (4.47 ns) is slightly longer compared to L1 and L2.

The position of a manisyl group relative to the nitrogen atom strongly influences the emissive properties of bipy and terpy derivatives.\(^\text{13}\) This observation is true for the mixed L4, L5, and L6 ligands (Table S1 and Figure S15); when manisyl groups are placed at the β-position of the bipyridyl groups, as for L4 and L6, broad emission bands at ~435 nm and high quantum yields (~0.60) are observed, while α-substituted analogue L5 has structured emission band with maximum at 384 nm and relatively low quantum yield (0.19). The compounds L4, L5, and L6 display short lifetimes (1.53 ns, 2.58 ns, and 1.53 ns, respectively).

The solid-state (powder) emission spectra for ligands L1-L6 are broad and featureless. Ligands L1 and L3 exhibit significantly higher quantum yields in the solid state (Table S1) than in solution (an increase of 0.27 to 0.38 and an increase of 0.14 to 0.42,

respectively), as well as significantly red-shifted emission spectra (Δ110 nm and Δ143 nm, respectively).

Figure S15. Emission and absorption spectra of ligands L1-L6 in CH$_2$Cl$_2$ solution.

This suggests possible J-aggregate formation in the powder, with the fluorescence arising from exciton transitions. In contrast, the emission maximum of L2 in powder is red-shifted only by 12 nm compared to the solution emission maximum, and the quantum yield decreases from 0.30 to 0.11. The mixed ligand L5 shows a large bathochromic shift (Δ77 nm) but a lower quantum yield compared to that measured in solution. The solid-state quantum yields are decreased for the mixed ligands L4 and L6 as well, but emission maxima are less affected.

Table S1. Absorption and Emission Maxima, Molar Absorptivity Values (log ε), Quantum Yields (φ$_f$), and Lifetimes (τ$_f$) for Free Ligands L1-L6

<table>
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<tr>
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<th>UV/Vis$^a$</th>
<th>Fluorescence (solution)$^{13}$</th>
<th>(powder)$^c$</th>
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</thead>
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<tr>
<td></td>
<td>λ$_{abs}$ (nm)</td>
<td>log ε (log(cm$^{-1}$ mol$^{-1}$ L))</td>
<td>λ$_{em}$ (nm)</td>
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<tr>
<td>L1</td>
<td>261, 300, 318</td>
<td>4.74, 4.84, 4.68</td>
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<tr>
<td>L2</td>
<td>239, 287, 300</td>
<td>5.12, 4.55, 4.56</td>
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<tr>
<td>L3</td>
<td>270, 287, 300</td>
<td>4.76, 4.78, 4.82</td>
<td>300</td>
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<tr>
<td>L4</td>
<td>260, 338</td>
<td>4.60, 4.73</td>
<td>338</td>
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<tr>
<td>L5</td>
<td>258, 336</td>
<td>4.69, 4.71</td>
<td>336</td>
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<tr>
<td>L6</td>
<td>264, 338</td>
<td>4.60, 5.07</td>
<td>338</td>
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</table>

$^a$ All values were measured in CH$_2$Cl$_2$. Samples degassed with N$_2$. Maximum values for λ$_{abs}$, λ$_{em}$ and log ε are highlighted with bold. $^b$ PPO in cyclohexane (Φ$_f$ = 0.94) was used as the standard. $^{14}$ $^c$ All powder samples were measured with an integrating sphere.

The absorption spectra of zinc(II), iron(II), and ruthenium(II) complexes with L1-L6 (Table S2, Figures S16 and S17) display ligand centered (LC) transitions that are red-shifted by ~10-20 nm and of higher molar extinction coefficients relative to the parent ligands (Table S1). A sharp, intense band at ~330 nm appears for the metal complexes compared to the free ligands (Figures S16 and S17). Complexes with iron(II) and ruthenium(II) show characteristic lower energy bands from 360 to 600 nm and can be attributed to MLCT transitions.\textsuperscript{15}

Table S2. Absorption and Emission Maxima, Molar Absorptivity Values (log ε), Quantum Yields (φ\textsubscript{e}), and Lifetimes (τ\textsubscript{e}) for Metal Complexes [L\textsubscript{2}MI(PF\textsubscript{6})\textsubscript{2}]

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<tr>
<th>L</th>
<th>M</th>
<th>λ\textsubscript{abs} (nm)</th>
<th>log ε (log(cm\textsuperscript{-1} mol\textsuperscript{-1} L))</th>
<th>λ\textsubscript{ex} (nm)</th>
<th>λ\textsubscript{em} (nm)</th>
<th>Φ\textsubscript{e}</th>
<th>τ\textsubscript{e} (ns)</th>
<th>λ\textsubscript{em} (nm)</th>
<th>Φ\textsubscript{e}</th>
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<td>341</td>
<td>368</td>
<td>0.007\textsuperscript{b}</td>
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<td>-</td>
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<td>0.573\textsuperscript{c}</td>
<td>2.94</td>
<td>483</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>253, 346, 412, 533</td>
<td>4.96, 5.19, 4.43, 4.13</td>
<td>346</td>
<td>441</td>
<td>0.007\textsuperscript{d}</td>
<td>1.75</td>
<td>-</td>
<td>-</td>
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<tr>
<td>L5</td>
<td>Ru</td>
<td>252, 339, 388, 465</td>
<td>4.93, 5.12, 4.65, 4.32</td>
<td>339</td>
<td>443</td>
<td>0.001\textsuperscript{b}</td>
<td>2.89</td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
<td>Zn</td>
<td>248, 349</td>
<td>4.95, 5.17</td>
<td>349</td>
<td>497</td>
<td>0.097\textsuperscript{d}</td>
<td>3.34 (42%), 8.03 (58%)</td>
<td>-500</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>245, 345, 411, 534</td>
<td>4.81, 5.00, 4.25, 3.97</td>
<td>345</td>
<td>433</td>
<td>0.002\textsuperscript{d}</td>
<td>2.37 (75%), 7.60 (25%)</td>
<td>-</td>
<td>-</td>
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<tr>
<td>L6</td>
<td>Ru</td>
<td>260, 354, 396, 470</td>
<td>5.02, 5.33, 4.96, 4.54</td>
<td>354</td>
<td>449</td>
<td>0.009\textsuperscript{c}</td>
<td>2.18</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>260, 353</td>
<td>4.60, 5.07</td>
<td>353</td>
<td>494</td>
<td>0.577\textsuperscript{d}</td>
<td>2.06 (59%), 3.54 (41%)</td>
<td>501</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>263, 359, 430, 536</td>
<td>4.94, 5.35, 4.64, 4.21</td>
<td>359</td>
<td>452</td>
<td>0.004\textsuperscript{c}</td>
<td>2.25</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\textsuperscript{a} All values were measured in CH\textsubscript{2}Cl\textsubscript{2}. Samples degassed with N\textsubscript{2}. Maximum values for λ\textsubscript{abs}, λ\textsubscript{em} and log ε are highlighted with bold. \textsuperscript{b} PPO in cyclohexane (φ\textsubscript{e} = 0.94); \textsuperscript{c} DPA in cyclohexane (φ\textsubscript{e} = 1.00); \textsuperscript{d} POPOP in cyclohexane (φ\textsubscript{e} = 0.97) were used as the standard. \textsuperscript{14} e All powder samples were measured with an integrating sphere.

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Supporting Information

The MLCT bands of the iron(II) and ruthenium(II) complexes with $\text{L1-L6}$ are non-luminescent at room temperature. However, excitation at the LC bands shows weak but detectable fluorescence (Table S2), possibly arising from an intraligand charge transfer state (ILCT).\textsuperscript{16} The zinc(II) complexes exhibit a fluorescence comparable to that of parent ligands (Table S1 and S2), except the Zn(II) complex of $n$-hexyl-substituted $\text{L2}$. This complex has much higher quantum yield (0.63) than the free ligand (0.30).

The emission maxima of Zn(II), Fe(II), and Ru(II) complexes with $\text{L1, L2, and L4-L6}$ ligands are red-shifted relative to those of the free ligands (Figures S16 and S17). However, metal complexes of 4-pyridyl-substituted $\text{L3}$ show hypsochromic shift of emission maxima by $\sim$20 nm, with respect to that of free ligand (Figure S16c).

The fluorescence lifetimes of the $\text{L1-L4}$ metal complexes are in the range of 1.06 to 2.94 ns. The $\text{L5}$ complexes with Zn(II) and Fe(II), and $\text{L6}$ complex with Fe(II) display two lifetime values (Table S2).

The iron(II) and ruthenium(II) complexes of $\text{L1-L6}$ do not show any detectible luminescence in the solid state (powder). However, zinc(II) complexes are slightly emissive, with quantum yields ranging from 0.06 to 0.17, that are significantly lower than those in solution (Table S2). The only exception is zinc(II) complex of $\text{L3}$, which shows a slight increase in the quantum yield in the solid state compared to that in solution (from 0.11 to 0.16). This Zn(II) complex also exhibits a significant bathochromic shift ($\Delta 99$ nm) in the emission spectra of its powder compared to the solution.

Figure S16. Emission and absorption spectra of ligands L1, L2, L3 and their corresponding Zn$^{2+}$, Fe$^{2+}$, Ru$^{2+}$ complexes in CH$_2$Cl$_2$ solution.
Figure S17. Emission and absorption spectra of ligands L4, L5, L6 and their corresponding Zn²⁺, Fe²⁺, Ru²⁺ complexes in CH₂Cl₂ solution.