Supporting Information
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Supporting Information

for

New Ditopic Ligands Containing 2,2’:6’,2”’-Terpyridine and a Rigid U-/S-Shaped Terpyridine

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Experimental Section

Instrumentation: Meltig points were determined in open capillaries on a Büchi SMP-20 apparatus and were not corrected. IR spectroscopy was performed on a Nicolet 510 P FT-IR spectrometer. $^1$H and $^{13}$C NMR spectra were recorded in deuterated solvents on a Bruker AVANCE 500 MHz instrument at 298 K and chemical shifts are reported im ppm downfield to TMS as reference. Electron-ionization (EI) mass spectrometry was carried out on a Finnigan MAT Magnum TM GC/MS system. Fast-atom-bombardment (FAB) mass spectrometry was performed on a Finnigan MAT 8230 apparatus using m-nitrobenzyl alcohol as matrix. Elemental analyses were obtained on a Perkin-Elmer 240 analyser for CHNS-O. Die UV/vis absorption and photoluminescence spectra were measured on a Perkin-Elmer Lambda-16 spectrophotometer and Quanta Master 2000-4 fluorescence spectrometer (Photon Technology Industry), respectively. For both techniques concentrations of $10^{-6}$ M in CH$_2$Cl$_2$ (1 cm cuvettes) were used.

General Methods: All reagents were purchased from commercial sources and used without further purification unless specified. Solvents were dried and distilled according to standard procedures and stored under argon. All reactions were performed under an atmosphere of argon unless specified. Chromatographic separations were performed on silica gel 60 (Merck, 0.040–0.063) or aluminium oxide (neutral, Macherey & Nagel, 0.063–0.200 mm). 2,2′:6′,2″-Terpyridines 1 and 7 as well as 5,6,7,8-tetrahydroquinolin-8-one were synthesized following a previously published method.

Bismorpholino-(4′-(4-formylphenyl)-[2,2′:6′,2″]-terpyridyl)-methane (2)

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A suspension of 4′-(4-formylphenyl)-[2,2′:6′,2″]-terpyridine (1, 1.78 g, 5.3 mmol) in morpholine (20 mL) was stirred for 12 h at room temperature. The residual morpholine was evaporated and the crude product was recrystallized from ethanol to yield 2 (2.1 g, 81%) as a pale brown amorphous solid. Mp 92.3 °C. \(^1\)H NMR (CDCl\(_3\), 500 MHz, ppm): \(\delta\) 2.85–2.89 (m, 8H), 3.65–3.69 (m, 9H), 7.31–7.37 (m, 4H), 7.83–7.91 (m, 4H), 8.63–8.69 (m, 2H), 8.70–8.75 (m, 4H). Anal. calcd. for C\(_{30}\)H\(_{31}\)N\(_5\)O\(_2\): C 73.00, H 6.33, N 14.19; found: C 72.74, H 6.12, N 13.88.

**N-(4′-(4-Formylphenyl)-[2,2′:6′,2″]-terpyridylene)-morpholinium chloride (3)**

A acetylchloride (0.5 mL) was added slowly under argon to a suspension of 2 in dry diethyl ether (20 mL) at 0 ºC. The reaction mixture was kept at room temperature for 12 h and the obtained brown iminium salt (3) was filtered off, washed rapidly with dry diethyl ether (5 mL) and dried in vacuo (yield: 820 mg, 87%). \(^1\)H NMR (CDCl\(_3\), 500 MHz, ppm): \(\delta\) 3.05–3.09 (m, 4H), 3.83–3.88 (m, 4H), 7.32–7.39 (m, 4H), 7.85–7.92 (m, 4H), 8.65–8.69 (m, 2H), 8.72–8.75 (m, 4H). Due to the low solubility in organic solvents and the hygroscopic nature no further characterization was carried out.

**5,6,8,9-Tetrahydro-7-(4′-[2,2′:6′,2″]-terpyridyl)-phenolchino[8,7-b][1,10]phenanthroline (4)**

A solution of 5,6,7,8-tetrahydroquinolin-8-one\(^2\) (333 mg, 2.26 mmol) and ammonium acetate (177 mg, 2.3 mmol) in dry DMSO (10 mL) was heated for 5 min at 85 ºC. In a second flask, a suspension of 5,6,7,8-tetrahydroquinolin-8-one (333 mg, 2.26 mmol) and 3 (1.00 g, 2.25 mmol) in dry DMSO (10 mL) was heated until a clear solution was formed. Subsequently,
this solution was added to the first flask and the reaction mixture was heated under nitrogen for 16 h at 150 ºC. After cooling to room temperature, water (40 mL) was added and the mixture was extracted with CH₂Cl₂ (3 × 25 mL). The combined organic layers were washed with water (4 × 20 mL) and dried over MgSO₄. After removal of the solvent, the crude product was purified by column chromatography (Al₂O₃, CH₂Cl₂/MeOH 50:1), followed by precipitation into diethyl ether to yield 4 as a brown powder (370 mg, 28%). Mp 115.4 ºC. IR (KBr, cm⁻¹): ν(combiningtildeaccent) 3427, 3051, 2920, 2846, 2361, 2338, 1582, 1560, 1542, 1467, 1437, 1409, 1387, 1265, 1218, 1037, 989, 792, 735, 657, 617. ¹H NMR (CDCl₃, 500 MHz, ppm): δ 2.76 (m, 4H), 2.90 (m, 4H), 7.23 (dd, ³J = 7.5 Hz, ³J = 4.7 Hz, 2H), 7.32–7.38 (m, 4H), 7.55 (d, ³J = 7.5 Hz, 2H), 7.83–7.92 (m, 2H), 8.03 (d, ³J = 8.3 Hz, 2H), 8.65–8.74 (m, 8H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 25.3, 27.4, 118.9, 121.4, 123.6, 124.0, 127.9, 129.2, 132.3, 133.4, 135.7, 126.9, 137.7, 138.5, 147.3, 148.6, 149.8, 149.7, 150.3, 152.1, 156.1, 156.2. EI-MS (70 eV): m/z (%) 362 (10), 361 (26), 360 (29), 308 (21), 284 (56), 283 (56), 282 (100), 255 (8), 229 (6), 179 (7), 78 (6). Anal. calcd. for C₄₀H₂₈N₆: C 81.06, H 4.76, N 14.18; found: C 81.23, H 5.02, N 14.41.

5,6,8,9-Tetrahydro-7-(4'-benzyloxy-phenyl)chino[8,7-b][1,10]phenanthroline (5)

A modification of a previously reported protocol³ was used: A solution of 5,6,7,8-tetrahydroquinolin-8-one² (930 mg, 6.29 mmol) and ammonium acetate (530 mg, 6.90 mmol) in dry DMSO (20 mL) was heated for 10 min at 85 ºC. In a second flask, a suspension of 5,6,7,8-tetrahydroquinolin-8-one (930 mg, 6.29 mmol) and N-(4'-benzyloxybenzylidene)-morpholinium chloride (2.00 g, 6.29 mmol) in dry DMSO (15 mL) was heated until a clear solution was formed. Subsequently, this solution was added to the first flask and the reaction mixture was heated under nitrogen for 16 h at 120 ºC. After cooling to room temperature, water (40 mL) was added and the mixture was extracted with CH₂Cl₂ (3 × 25 mL). The combined organic layers were washed with water (4 × 20 mL) and dried over MgSO₄. After removal of the solvent, the crude product was purified by column chromatography (Al₂O₃, CH₂Cl₂/MeOH 100:1), followed by precipitation into diethyl ether to yield 5 as a colorless

solid (700 mg, 24%). Mp 270–272 °C. \(^1\)H NMR (CDCl\(_3\), 500 MHz, ppm): \(\delta\) 2.68–2.75 (m, 4H), 2.80–2.87 (m, 4H), 5.13 (s, 2H), 7.11 (d, \(^2J\ = 9.0\) Hz, 4H), 7.19 (dd, \(^3J\ = 7.5\) Hz, \(^3J\ = 5.0\) Hz, 2H), 7.35 (m, 1H), 7.39–7.44 (m, 2H), 7.45–7.53 (m, 4H), 8.71 (d, \(^3J\ = 5.0\) Hz, 2H). \(^{13}\)C NMR (CDCl\(_3\), 125 MHz, ppm): \(\delta\) 25.4, 27.5, 70.2, 115.1, 123.4, 124.4, 127.5, 128.1, 129.9, 132.8, 133.3, 135.5, 136.8, 152.3, 158.6.

5,6,8,9-Tetrahydro-7-(4′-hydroxyphenyl)[8,7-b][1,10]phenanthroline hydrochloride (6)

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\text{HO-} \begin{array}{c}
\text{N} \\
\text{N} \\
\text{xHCl}
\end{array}
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A mixture of U-shaped terpyridine 5 (860 mg, 1.84 mmol) and diluted HCl (4 M, 20 mL) was heated under reflux for 12 h.\(^4\) After cooling the reaction mixture was stored in the freezer for 24 h. The yellow precipitate was filtered off, washed with cold water (10 mL) as well as diethyl ether (10 mL) and dried at 40 °C in vacuo to yield 6 as a mixture of \textit{mono}- and \textit{bis}-

hydrochloride salts (310 mg, 41%). Mp >280 °C. IR (KBr, cm\(^{-1}\)): \(\tilde{\nu}\) 3450, 3002, 2875, 1605, 1530, 1476, 1473, 1396, 1295, 1224, 1206, 855, 769, 743. \(^1\)H NMR (D\(_2\)O, 500 MHz, ppm): \(\delta\) 2.49–2.82 (m, 4H), 2.84–3.23 (m, 4H), 6.76 (d, \(^3J\ = 8.5\) Hz, 2H), 6.99 (d, \(^3J\ = 8.5\) Hz, 2H), 7.85 (dd, \(^3J\ = 7.5\) Hz, \(^3J\ = 5.8\) Hz, 2H), 8.36 (dd, \(^3J\ = 7.5\) Hz, \(^4J\ = 1.2\) Hz, 2H), 8.67 (d, \(^3J\ = 5.8\) Hz, \(^4J\ = 1.2\) Hz, 2H). \(^{13}\)C NMR (D\(_2\)O, 125 MHz, ppm): \(\delta\) 23.9, 25.0, 115.8, 126.3, 127.1, 130.3, 137.8, 139.6, 142.2, 144.2, 146.6, 156.2. EI-MS (70 eV): \(m/z\) (%) 377 (100), 374 (30), 282 (11), 221 (13), 188 (13), 147 (18), 123 (18), 73 (38); 36 (92).

5,6,8,9-Tetrahydro-7-(4′-(methylphenyl)-[2,2′:6′,2″]-terpyridyloxy)phenylchino[8,7-b][1,10]phenanthroline (8)

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\begin{array}{c}
\text{N} \\
\text{N} \\
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\text{N} \\
\text{N}
\end{array}
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To a suspension of 6 (200 mg, 0.44 mmol) and K\(_2\)CO\(_3\) (500 mg) in dry DMF (20 mL) was added 7\(^\dagger\) (187 mg, 0.44 mmol) and stirring at 60 °C under argon is continued for 2 h. The

reaction mixture is poured into ice water (200 mL) and then extracted with CH$_2$Cl$_2$ (3 × 50 mL). The combined organic phases were washed with brine (50 mL) and dried over Na$_2$SO$_4$. After evaporation of the solvent, the crude product was purified by column chromatography (Al$_2$O$_3$, CH$_2$Cl$_2$/MeOH 100:1) to yield 8 as a brown solid (203 mg, 66%). Mp 181.5 °C. IR (KBr, cm$^{-1}$): ν 3444, 2918, 2846, 2359, 2336, 1579, 1560, 1543, 1507, 1457, 1387, 1239, 1220, 1172, 1114, 1016, 792, 737, 617. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): δ 2.70–2.76 (m, 4H), 2.85–2.91 (m, 4H), 5.23 (s, 2H), 7.13 (dd, $^3$J = 9.0 Hz, $^4$J = 1.2 Hz, 4H), 7.22 (dd, $^3$J = 7.3 Hz, $^4$J = 4.8 Hz, 2H), 7.35 (ddd, $^3$J = 7.5 Hz, $^4$J = 4.6 Hz, $^5$J = 1.2 Hz, 2H), 7.54 (dd, $^3$J = 7.5 Hz, $^4$J = 1.4 Hz, 2H), 7.62 (d, $^3$J = 8.3 Hz, 2H), 7.78 (ddd, $^3$J = 7.5 Hz, $^4$J = 1.7 Hz, 2H), 7.96 (d, $^3$J = 8.3 Hz, 2H), 8.68 (m, 4H). $^13$C NMR (CDCl$_3$, 125 MHz, ppm): δ 25.2, 27.3, 69.8, 115.3, 118.8, 121.4, 123.6, 123.9, 127.7, 127.9, 129.8, 133.0, 133.6, 135.9, 136.9, 137.7, 138.4, 148.4, 149.1, 149.8, 149.9, 152.1, 156.1, 156.2, 158.5. EI-MS (70 eV): m/z (%) 415 (4), 375 (37), 361 (25), 323 (25), 283 (75), 282 (100), 281 (75), 187 (19), 140 (22), 113 (11). Anal. calcd. for C$_{47}$H$_{34}$N$_6$O: C 80.78, H 4.90, N 12.03; found: C 81.10, H 4.97, N 12.27.

5,6,8,9-Tetrahydro-7-(4'-bromophenyl)[8,7-b][1,10]phenanthroline (9)

A solution of 5,6,7,8-tetrahydroquinolin-8-one (294 mg, 2.00 mmol) and ammonium acetate (158 mg, 2.05 mmol) in dry DMSO (15 mL) was heated at 85 °C for 10 min. Subsequently, a suspension of N-(4-bromobenzyliden)-morpholinium chloride (610 mg, 2.1 mmol) in dry DMSO (5 mL) and 5,6,7,8-tetrahydroquinolin-8-one (294 mg, 2.00 mmol) were added. After heating at 125 °C for 15 h the dark reaction mixture was hydrolyzed by the addition of water (50 mL). The crude product was obtained by extraction with CH$_2$Cl$_2$ (4 × 30 mL), drying over MgSO$_4$ and evaporation of the solvents. Purification by flash column chromatography on neutral Al$_2$O$_3$ using CH$_2$Cl$_2$ as eluent yielded 9 as a yellow powder (582 mg, 66%). Mp 291 °C. $^1$H NMR (CDCl$_3$, 500 MHz, ppm): δ 2.58–2.66 (m, 4H), 2.73–2.83 (m, 4H), 7.05 (m, 2H), 7.12 (dd, $^3$J = 7.5 Hz, $^4$J = 1.5 Hz, 2H), 7.44 (dd, $^3$J = 7.3 Hz, $^4$J = 1.6 Hz, 2H), 7.57 (d, $^3$J = 7.5 Hz, 2H), 8.69 (dd, $^3$J = 7.3 Hz, $^4$J = 1.6 Hz, 2H). $^{13}$C NMR (CDCl$_3$, 125 MHz, ppm): δ 25.2, 27.3, 69.8, 115.3, 118.8, 121.4, 123.6, 123.9, 127.7, 127.9, 129.8, 133.0, 133.6, 135.9, 136.9, 137.7, 138.4, 148.4, 149.1, 149.8, 149.9, 152.1, 156.1, 156.2, 158.5. EI-MS (70 eV): m/z (%) 415 (4), 375 (37), 361 (25), 323 (25), 283 (75), 282 (100), 281 (75), 187 (19), 140 (22), 113 (11). Anal. calcd. for C$_{47}$H$_{34}$N$_6$O: C 80.78, H 4.90, N 12.03; found: C 81.10, H 4.97, N 12.27.
ppm): δ 25.5, 27.4, 122.2, 123.2, 130.4, 131.9, 132.0, 132.9, 135.0, 136.1, 146.3, 149.1, 150.9, 152.2.5

7,8,13,14-Tetrahydro-6-(4’-bromophenyl)chino[8,7-κ][1,8]phenanthroline (10)

A suspension of 5,6,7,8-tetrahydroquinolinol-8-one (883 mg, 6.0 mmol), ammonium acetate (1.24 g, 16.1 mmol) and the N-(4-brombenzyliden)-morpholinium chloride (871 mg, 3 mmol) in dry CHCl₃ (35 mL) was heated at reflux for 16 h. The reaction mixture was cooled to room temperature and water (20 mL) was added. The solution was then extracted with CH₂Cl₂ (4 × 30 mL). The combined organic layers were washed neutral with water (2 × 20 mL) and dried over MgSO₄. After removal of the solvent, the crude product was purified by column chromatography on Al₂O₃ using CH₂Cl₂/n-hexane (2:1 ratio) as eluent to yield 10 as a yellow solid (1.37 g, 52%). Mp 100 °C. ¹H NMR (500 MHz, CDCl₃, ppm) δ 2.85–2.97 (m, 6H), 3.66 (m, 2H), 7.27 (m, 2H), 7.51–7.65 (m, 6H), 8.63 (m, 2H). ¹³C NMR (125 MHz, CDCl₃, ppm) δ 25.7, 26.3, 28.1, 28.4, 122.5, 123.9, 124.1, 128.6, 130.0, 131.8, 133.0, 134.8, 135.9, 136.0, 136.2, 141.2, 142.7, 147.5, 148.5, 151.2, 152.1, 152.6, 155.2.5

4’-(4-Boronato-phenyl)-[2,2’:6,2’’]-terpyridine (11)

2-Acetylpyridine (931 mg, 7.68 mmol) was added to a stirred suspension of crushed NaOH (231 mg, 7.68 mmol) in PEG300 (10 mL) at 0 °C. After 10 min 4-formylphenyboronic acid (507 mg, 3.38 mmol) was added and stirring was continued at 0 °C for 2 h. Then concentrated aqueous NH₃ solution (10 mL) was added and the suspension stirred at room temperature for 4 h. The precipitate was isolated by vacuum filtration and washed with water (50 mL) and

cold methanol (10 mL) to yield 11 as an off-white powder (621 mg, 52%). $^1$H NMR (500 MHz, d$_6$-DMSO, ppm): δ 7.53 (dd, $^3$J = 5.1 Hz, $^4$J = 1.5 Hz, 2H), 7.90 (d, $^3$J = 8.0 Hz, 2H), 8.04 (d, $^3$J = 8.0 Hz, 2H), 8.07 (m, 2H), 8.71 (d, $^3$J = 8.0 Hz, 2H), 8.76 (s, 2H), 8.79 (d, $^3$J = 5.1 Hz, 2H). MALDI-TOF MS (dithranol): m/z 376.1 ([M+Na$^+$]), 354.1 ([M+H$^+$]).

**4-(5,6,8,9-Tetrahydroquino[8,7-b][1,10]phenanthrolin-7-yl)-4’-(2,2’:6’,2’’)-terpyridin-4’-yl)-biphenyl (12)**

![Chemical Structure](image)

To a stirred solution of 9 (252 mg, 0.57 mmol) and Pd(PPh$_3$)$_4$ (58 mg, 0.05 mmol) in toluene (7 mL) under an atmosphere of argon was added an aq. solution of Na$_2$CO$_3$ (2 M, 1 mL, 2 mmol) and 11 (194 mg, 0.55 mmol) in methanol (10 mL). The vigorously stirred mixture was refluxed for 16 h, then cooled, and partitioned between CH$_2$Cl$_2$ (20 mL) and aq. Na$_2$CO$_3$ (2 M, 20 mL) containing 1 mL of a conc. NH$_3$ solution. The organic layer was separated and the aqueous layer was extracted with CH$_2$Cl$_2$ (3 x 20 mL). The combined organic layers were dried over Na$_2$SO$_4$ and then concentrated to dryness. Flash column chromatography on neutral Al$_2$O$_3$ (CH$_2$Cl$_2$/MeOH, 50:1 ratio) yielded 12 as a brownish solid (188 mg, 51%). Mp >250 °C. IR (KBr, cm$^{-1}$): ν 3062, 3003, 2942, 2885, 2844, 1678, 1579, 1540, 1490, 1457, 1452, 1401, 1222, 1201, 1113, 1067, 1011, 847. $^1$H NMR (500 MHz, CDCl$_3$, ppm): δ 2.76 (m, 4H), 2.85 (m, 4H), 7.18 (m, 2H), 7.29 (d, $^3$J = 8.0 Hz, 2H), 7.34 (m, 4H), 7.50 (d, $^3$J = 7.2 Hz, 2H), 7.83 (m, 2H), 8.03 (m, 4H), 8.67 (d, $^3$J = 7.9 Hz, 2H), 8.72 (m, 4H), 8.80 (s, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$, ppm): δ 25.5, 27.4, 117.9, 118.1, 118.6, 121.4, 123.3, 123.9, 124.6, 127.3, 127.5, 127.6, 127.7, 127.8, 127.9, 129.2, 130.2, 135.3, 136.9, 137.1, 140.3, 142.4, 148.9, 149.1, 150.0, 152.3. FAB MS (m-nitrobenzyl alcohol): m/z (%) 669 (100, [M+H$^+$]), 436 (35), 384 (22), 361 (32), 310 (15). Anal. Calcd. for C$_{46}$H$_{32}$N$_6$: C 82.61, H 4.82, N 12.57; found: C 83.02, H 5.12, N 12.89.

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4-(7,8,13,14-Tetrahydroquino[8,7-k][1,8]phenanthroin-6-yl)-4’([2,2’:6’,2’’]-terpyridin-4’-yl)-biphenyl (13)

According to the synthesis of 12, S-shaped terpyridine 10 (185 mg, 0.42 mmol) and 11 (141 mg, 0.40 mmol) were reacted to yield 13 (165 mg, 62%) after rerecrystallization from methanol as brown powder. Mp >290 °C after. IR (KBr, cm⁻¹) ~ 3042, 2945, 3038, 2842, 1589, 1536, 1444, 1384, 1254, 1091, 781 cm⁻¹. ¹H NMR (500 MHz, CDCl₃, ppm): 2.81 (m, 2H), 2.93 (m, 2H), 2.99 (m, 2H), 3.66 (m, 2H), 7.17 (m, 4H), 7.35 (m, 2H), 7.67 (m, 2H), 7.74 (m, 2H), 7.79 (d, J = 8.0 Hz, 2H), 7.88 (m, 2H), 8.01 (d, J = 7.9 Hz, 2H), 8.38 (m, 1H), 8.69 (d, J = 7.2 Hz, 2H), 8.75 (m, 2H), 8.81 (m, 3H). ¹³C NMR (125 MHz, CDCl₃, ppm): 26.4, 26.9, 28.3, 29.2, 117.9, 118.7, 122.9, 123.6, 123.8, 126.2, 127.0, 127.9, 128.6, 128.9, 131.4, 132.9, 134.6, 135.7, 135.9, 137.5, 140.4, 140.8, 141.0, 141.2, 147.4, 148.6, 150.2, 150.9, 151.1, 152.4, 152.9, 153.2, 154.0, 156.7. FAB MS (m-nitrobenzyl alcohol): m/z (%) 668 (100, M⁺), 436 (27), 384 (30), 361 (19), 310 (21), 284 (31), 232 (11). Anal. Calcd. for C₄₆H₃₂N₆: C 82.61, H 4.82, N 12.57; found: C 82.46, H 4.55, N 12.13.