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Accessory Publication

Unusual Terpyridines as Ligands for Novel Light-Emitting Ir(III) Complexes: Synthesis and Characterisation

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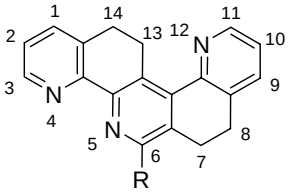
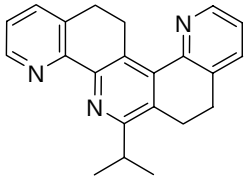
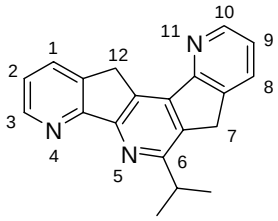
General procedure for the synthesis of S-shaped teryridines 3: A suspension of 5,6,7,8-tetrahydroquinolinone **1a** (900 mg, 6.0 mmol), ammonium acetate (1.24 g, 16.1 mmol) and the respective iminium salt **2** (3 mmol) in dry $CHCl_3$ (35 mL) was heated at reflux for 16 h. The reaction mixture was cooled to room temperature and water (20 mL) was added. The solution was then extracted with CH_2Cl_2 (4 × 30 mL). The combined organic layers were washed neutral with water (2 × 20 mL) and dried over $MgSO_4$. After removal of the solvent, the crude product was purified by chromatography on Al_2O_3.[1]







3a: R = Phenyl
3b: R = 3-Br-Phenyl
3c: R = 4-MeO-Phenyl
3d: R = 4-NEt_2-Phenyl
3e: R = 3-NO_2-Phenyl
3f: R = 2-Naphthyl

3g **3h**

7,8,13,14-Tetrahydro-6-phenylchino[8,7-k][1,8]phenanthroline (3a): Prepared from **1a** (900 mg, 6.0 mmol) and *N*-(benzylidene)morpholinium chloride **2a** (630 mg, 3.0 mmol). Yield: 490 mg (45%), yellow crystals, after chromatography on Al_2O_3 (CH_2Cl_2/acetone, 10:1), m.p. 280–281°C. IR (KBr) ν = 3050, 2960, 2930, 2890, 2830, 1570, 1530, 1435, 1385, 1090, 905, 785 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$, 25°C, TMS) δ = 2.80 (m_c, 2H, 7-*H*), 2.92 (m_c, 4H, 8,14-*H*), 3.66 (m_c, 2H, 13-*H*), 7.20–7.25 (m, 2H, 2,10-*H*), 7.36–7.48 (m, 3H, 3',4',5'-*H*), 7.56–7.63 (m, 4H, 1,9,2',6'-*H*), 8.64 (dd, ^3J = 4.8 Hz, ^4J = 1.7 Hz, 1H, 3-*H*), 8.72 ppm (dd, ^3J = 4.8 Hz, ^4J = 1.6 Hz, 1H, 11-*H*); ^{13}C NMR (50 MHz, $CDCl_3$, 25°C, TMS) δ = 25.9 (t), 26.5 (t), 27.9 (t), 28.8 (t), 123 (d), 123.2 (d), 127.9 (d), 128.0 (d), 129.7 (d), 131.0 (s), 132.1 (s), 134.0 (s), 135.0 (d), 135.2 (d), 135.3 (s), 140.5 (s), 140.6 (s), 147.1 (d), 148.9 (d), 151.1 (s), 152.4 (s), 152.8 (s), 156.4 ppm (s); MS (70 eV, EI): *m/z* (%): 361 (60) [M^+], 360 (100), 359 (17), 358 (33), 356 (11), 344 (13), 255 (13), 180 (5), 179 (18), 178 (17); elemental analysis: calcd (%) for $C_{25}H_{19}N_3$ (361.4): C 83.08, H 5.30, N 11.63; found C 82.96, H 5.37, N 11.67.[2]

7,8,13,14-Tetrahydro-6-(3'-bromophenyl)chino[8,7-k][1,8]phenanthroline (3b): Prepared from **1a** (900 mg, 6.0 mmol) and *N*-(3-brombenzylidene)morpholinium chloride **2b** (870 mg, 3.0 mmol). Yield: 955 mg (72%), yellow solid, after chromatography on Al_2O_3 (CH_2Cl_2/hexanes, 2:1), m.p. 100°C. IR (KBr) ν = 3042, 2945, 3038, 2842, 1589, 1536, 1444, 1384, 1254, 1091, 781 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$, 25°C, TMS) δ = 2.91 (m_c, 6H, 7,8,14-*H*), 3.66 (m_c, 2H, 13-*H*), 7.27–7.40 (m, 3H, 1,2,10-*H*), 7.54–7.67 (m, 4H, 4',5',6',9-*H*), 7.84 (m, 1H, 2'-*H*), 8.60–8.65 ppm (m, 2H, 3,11-*H*); ^{13}C NMR (50 MHz, $CDCl_3$, 25°C, TMS) δ = 25.7 (t), 26.3 (t), 28.1 (t), 28.4 (t), 122.5 (s), 123.9 (d), 124.1 (d), 128.6 (d), 130.0 (d), 131.5 (d), 131.8 (s), 133.0 (d), 134.8 (s), 135.9 (s), 136.0 (d), 136.2 (d), 141.2 (s), 142.7 (s), 147.5 (d), 148.5 (d), 151.2 (s),

[1] D. Sielemann, A. Winter, U. Flörke, N. Risch, *Org. Biomol. Chem.* **2004**, *2*, 863.
[2] R. Keuper, N. Risch, U. Flörke, H.-J. Haupt, *Liebigs Ann. Org. Bioorg. Chem.* **1996**, *5*, 705.

152.1 (s), 152.6 (s), 155.2 ppm (s); MS (70 ev, EI): *m/z* (%): 441 (64) [M(^{81}Br)$^+$], 440 (100), 439 (65) [M(^{79}Br)$^+$], 438 (99), 360 (10), 356 (18), 282 (7), 255 (16), 220 (12), 179 (13); elemental analysis: calcd (%) for $C_{25}H_{18}BrN_3$ (440.3): C 69.19, H 4.12, N 9.54; found: C 69.25, H 4.17, N, 9.61.[3]

7,8,13,14-Tetrahydro-6-(4'-methoxyphenyl)chino[8,7-k][1,8]phenanthroline (3c): Prepared from **1a** (900 mg, 6.0 mmol) and *N*-(4-methoxybenzylidene)morpholinium chloride **2c** (725 mg, 3.0 mmol). Yield: 704 mg (60%), yellow crystals, after chromatography on Al_2O_3 (CH_2Cl_2/acetone, 10:1), m.p. 232–234°C. IR (KBr) ν = 3010, 2960, 2940, 2860, 1610, 1510, 1430, 1390, 1240, 1175, 1020, 835, 780 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$, 25°C, TMS) δ = 2.79 (m_c, 2H, 7-*H*), 2.89–2.95 (m, 4H, 8,14-*H*), 3.65 (m_c, 2H, 13-*H*), 3.86 (s, 3H, OC*H*$_3$), 6.97 (m_c, 2H, 3',5'-*H*), 7.16–7.26 (m, 2H, 2,10-*H*), 7.54–7.62 (m, 4H, 1,9,2',6'-*H*), 8.63 (dd, ^3J = 4.8 Hz, ^4J = 1.7 Hz, 1H, 3-*H*), 8.72 ppm (dd, ^3J = 4.8 Hz, ^4J = 1.7 Hz, 1H, 11-*H*); ^{13}C NMR (50 MHz, $CDCl_3$, 25°C, TMS) δ = 25.9 (t), 26.6 (t), 28.0 (t), 28.8 (t), 55.4 (q), 113.4 (d), 122.9 (d), 123.0 (d), 130.6 (s), 131.0 (d), 132.0 (s), 133.4 (s), 134.0 (s), 135.0 (s), 135.1 (s), 135.3 (s), 140.5 (s), 147.1 (d), 149.0 (d), 151.1 (s), 152.6 (s), 152.9 (s), 156.1 (s), 159.5 ppm (s); MS (70 eV, EI): *m/z* (%): 391 (82) [M$^+$], 390 (100), 388 (12), 347 (10), 346 (21), 344 (11), 255 (10), 195 (14), 194 (15), 172 (14); elemental analysis: calcd (%) for $C_{26}H_{21}N_3O$ (391.5): C 79.77, H 5.41, N 10.73; found: C 79.86, H 5.52, N 10.57.[2]

7,8,13,14-Tetrahydro-6-(4'-diethylaminophenyl)chino[8,7-k][1,8]phenanthroline (3d): Prepared from **1a** (900 mg, 6.0 mmol) and *N*-(4-diethylaminobenzylidene)morpholinium perchlorate **2d** (910 mg, 3.0 mmol). Yield: 440 mg (34%), yellow solid, after chromatography on Al_2O_3 (CH_2Cl_2/acetone, 10:1), m.p. 221–223°C. IR (KBr) ν = 3035, 2961, 2844, 1607, 1515, 1439, 1405, 1321, 1253, 1115, 1067, 832, 777 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$, 25°C, TMS) δ = 1.03 (t, ^3J = 6.9 Hz, 6H, CH_2CH_3), 2.57 (m_c, 2H, 7-*H*), 2.72 (m_c, 2H, 8-*H*), 2.83 (m_c, 2H, 14-*H*), 2.95–3.23 (m, 4H, CH_2CH_3,13-*H*), 3.47 (q, ^3J = 7.0 Hz, 2H, CH_2CH_3), 6.61 (m_c, 2H, 3',5'-*H*), 7.04 (m_c, 2H, 2,10-*H*), 7.40 (m_c, 4H, 1,9,2',6'-*H*), 8.42 (m_c, 1H, 3-*H*), 8.51 ppm (m_c, 1H, 11-*H*); ^{13}C NMR (50 MHz, $CDCl_3$, 25°C, TMS) δ = 12.0 (q), 25.1 (t), 26.3 (t), 27.3 (t), 28.2 (t), 43.9 (t), 110.7 (d), 122.4 (d), 122.6 (d), 126.9 (s), 129.2 (s), 130.3 (d), 131.4 (s), 133.6 (s), 134.6 (d), 134.8 (d), 134.9 (s), 139.9 (s), 146.3 (d), 147.0 (s), 147.7 (d), 150.0 (s), 151.9 (s), 152.3 (s), 156.0 ppm (s); MS (70 eV, EI): *m/z* (%): 432 (50) [M$^+$], 404 (100), 361 (55), 299 (21), 285 (31), 255 (17); elemental analysis: calcd (%) for $C_{29}H_{28}N_4$ (432.6): C 80.52, H 6.52, N 12.95; found: C 80.40, H 6.39, N 13.11.[2]

7,8,13,14-Tetrahydro-6-(3'-nitrophenyl)chino[8,7-k][1,8]phenanthroline (3e): Prepared from **1a** (900 mg, 6.0 mmol) and *N*-(3-nitrobenzylidene)morpholinium chloride **2e** (770 mg, 3.0 mmol). Yield: 869 mg (71%), orange crsystals, after chromatography on Al_2O_3 (CH_2Cl_2/acetone, 3:1), m.p. 241°C. IR (KBr) ν = 3073, 2957, 2889, 2840, 1578, 1526, 1441, 1387, 1345, 1262, 1219, 1169, 1098, 1022, 905, 799, 782, 743, 702 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$, 25°C, TMS) δ = 2.57 (m_c, 6H, 7,8,14-*H*), 3.60 (m_c, 2H, 13-*H*), 7.16 (m_c, 2H, 2,10-*H*), 7.53 (m_c, 3H, 1,9,4'-*H*), 7.88 (m_c, 1H, 6'-*H*), 8.16 (m_c, 1H, 5'-*H*), 8.44 (s, 1H, 2'-*H*), 8.55 (m_c, 1H, 3-*H*), 8.63 ppm (m_c, 1H, 11-*H*); ^{13}C NMR (50 MHz, $CDCl_3$, 25°C, TMS) δ = 26.5 (t), 26.8 (t), 28.1 (t), 29.0 (t), 123.2 (d), 123.7 (d), 123.9 (d), 125.1 (d), 129.5 (d), 132.5 (s), 134.5 (s), 135.4 (s), 135.6 (d), 135.7 (d), 136.3 (d), 141.4 (s), 142.6 (s), 147.7 (d), 148.5 (s), 149.3 (d), 152.1 (s), 152.4 (s), 152.7 (s), 154.0 ppm (s); MS (70 eV, EI): *m/z* (%): 406 (68) [M$^+$], 405 (100), 375 (32), 360 (37), 282 (5), 255 (10), 202 (5), 179 (22); elemental analysis: calcd (%) for $C_{25}H_{18}N_4O_2$ (438.4): C 73.88, H 4.46, N 13.78; found: C 73.92, H 4.34, N 13.89.[2]

7,8,13,14-Tetrahydro-6-(2'-naphthyl)chino[8,7-k][1,8]phenanthroline (3f): Prepared from **1a** (900 mg, 6.0 mmol) and *N*-(2-naphthylidene)morpholinium chloride **2f** (790 mg, 3.0 mmol). Yield: 965 mg (79%), yellow crystals, after chromatography on Al_2O_3 (CH_2Cl_2/methanol, 4:1), m.p. 239°C. IR (KBr) ν = 3058, 2942, 2015, 1700, 1641, 1576, 1541, 1435, 1394, 1250, 1194, 1094, 911, 864, 824, 770, 758, 662 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$, 25°C, TMS) δ = 2.80 (m_c, 2H, 7-*H*), 2.94 (m_c, 4H, 8,14-*H*), 3.71 (m_c, 2H, 13-*H*), 7.22 (m_c, 2H, 2,10-*H*), 7.52 (m_c, 4H), 7.77 (m_c, 1H), 7.90 (m_c, 3H), 8.11 (s, 1H, 1'-*H*), 8.67 (dd, ^3J = 4.7 Hz, ^4J = 1.6 Hz, 1H, 3-*H*), 8.73 ppm (dd, ^3J = 4.8 Hz, ^4J = 1.6 Hz, 1H, 11-*H*); ^{13}C NMR (50 MHz, $CDCl_3$, 25°C, TMS) δ = 26.4 (t), 27.0 (t), 28.3 (t), 29.1 (/t), 123.4 (d), 123.5 (d), 126.4 (d), 126.5 (d), 127.8 (d), 127.9 (d), 128.0 (d), 128.7 (d), 129.2 (d), 131.5 (s), 132.8 (s), 133.4 (s), 133.7 (s), 134.4 (s), 135.4 (d), 135.5 (d), 135.6 (s), 138.5 (s), 141.0 (s), 147.5 (d), 149.2 (d), 151.6 (s), 152.8 (s), 153.2 (s), 156.7 ppm (s); MS (70 eV, EI): *m/z* (%): 411 (22) [M$^+$], 410 (100), 360 (22), 308 (17), 260 (41), 182 (21); elemental analysis: calcd (%) for $C_{29}H_{21}N_3$ (411.5): C 84.65, H 5.14, N 10.21; found: C 84.72, H 5.03, N 10.25.[2]

7,8,13,14-Tetrahydro-6-*iso*-propyl-chino[8,7-k][1,8]phenanthroline (3g): Prepared from **1a** (900 mg, 6.0 mmol) and *N*,*N*-dimethyl*iso*butylidene iminium perchlorate **2g** (680 mg, 3.0 mmol). Yield: 707 mg (72%), yellow needles, after chromatography on Al_2O_3 (CH_2Cl_2/methanol, 50:1), m.p. 206°C. IR (KBr) ν = 3050,

[3] D. Sielemann, A. Winter, N. Risch, *Heterocycles* **2005**, *65*, 1663.

2960, 2940, 2840, 1575, 1540, 1440, 1410, 1400, 1360, 1250, 1210, 1190, 1110, 1090, 920, 905, 820, 785, 660, 635 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$, 25°C, TMS) δ = 1.46 (d, 6H, ^3J = 6.9 Hz, $CH(CH_3)_2$), 2.85 (m_c, 2H, 14-*H*), 2.92 (m_c, 4H, 7,8-*H*), 3.47 (sept, 1H, ^3J = 6.9 Hz, $CH(CH_3)_2$), 3.55 (m_c, 2H, 13-*H*), 7.18–7.23 (m, 2H, 2,10-*H*), 7.55 (dd, 1H, ^3J = 7.6 Hz, ^4J = 1.7 Hz, 9-*H*), 7.61 (dd, 1H, ^3J = 7.6 Hz, ^4J = 1.7 Hz, 1-*H*), 8.59 (dd, 1H, ^3J = 4.8 Hz, ^4J = 1.7 Hz, 3-*H*), 8.75 ppm (dd, 1H, ^3J = 4.8 Hz, ^4J = 1.7 Hz, 11-*H*); ^{13}C NMR (50 MHz, $CDCl_3$, 25°C, TMS) δ = 21.8 (q), 24.0 (t), 26.0 (t), 28.1 (t), 28.5 (t), 32.6 (d), 122.7 (d), 129 (s), 131.3 (s), 134.1 (s), 134.8 (d), 134.9 (s), 135.0 (d), 139.8 (s), 147.0 (d), 148.9 (d), 150.5 (s), 153.0 (s), 161.5 ppm (s). MS (70 eV, EI): *m/z* (%): 327 (70) [M^+], 326 (100), 312 (23), 310 (16), 298 (8), 290 (8), 284 (9), 282 (8), 155 (19), 154 (8); elemental analysis: calcd (%) for $C_{22}H_{21}N_3$ (327.4): C 80.70, H 6.47, N 12.83; found: C 80.44, H 6.54, N 12.70.[2]

6-*Iso*-propyl-7,12-dihydro-4,5,11-triazaindeno[1,2-a]fluorene (3h): Prepared from 5,6-dihydro-7*H*-1-pyrinden-7-one **1b** (1.60 g, 12.0 mmol) and *N*,*N*-dimethylisobutylidene iminium perchlorate **2g** (1.20 g, 6.0 mmol). Yield: 862 mg (48%), brown solid, after chromatography on Al_2O_3 (CH_2Cl_2/acetone, 4:1), m.p. 215°C. IR (KBr) ν = 3050, 2962, 2870, 1566, 1472, 1397, 1341, 1273, 1184, 1169, 1092, 930, 770, 779, 723 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$, 25°C, TMS) δ = 1.53 (d, ^3J = 6.7 Hz, 6H, CH_3), 3.46 (m_c, 1H, $CH(CH_3)_2$), 4.02 (s, 2H, CH_2), 4.30 (s, 2H, CH_2), 7.31 (m_c, 2H), 7.93 (m_c, 2H), 8.75 ppm (m_c, 2H); ^{13}C NMR (50 MHz, $CDCl_3$, 25°C, TMS) δ = 22.2 (q), 31.9 (t), 33.9 (d), 34.0 (t), 1226.6 (d), 123.0 (d), 129.6 (s), 133.2 (d), 133.4 (d), 134.7 (s), 138.5 (s), 138.6 (s), 149.5 (d), 149.6 (d), 158.6 (s), 159.7 (s), 159.9 (s), 163.7 ppm (s); MS (70 EV, EI): *m/z* (%): 299 (82) [M^+], 284 (100), 271 (80), 256 (30), 229 (12), 150 (5), 142 (12) [M^{2+}], 128 (7); elemental analysis: calcd (%) for $C_{20}H_{17}N_3$ (299.4): C 80.24, H 5.72, N 14.04; found: C 80.16, H 5.75, N 14.09.[2]