Electronic Supplementary Information (ESI)

Clean formation and dynamic exchange reactions of a supramolecular equilateral triangle that is both heterometallic and heteroleptic

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Synthesis

Scheme S1. Synthesis of angular molecule 1.

All reagents were commercially available and used without further purification. The solvents were dried with appropriate desiccants and distilled prior to use. Thin-layer chromatography (TLC) was performed using TLC plates from Merck (silica gel 60 F_{254}). Silica gel 60 was used for column chromatography. $^1$H NMR and $^{13}$C NMR were recorded on Bruker Avance 400 MHz spectrometer using the deuterated solvent as the lock and residual solvent as the internal reference. The numbering of the carbon atoms of the molecular formulae shown in the experimental section is only used for the assignments of the NMR signal and is not in
accordance with the IUPAC nomenclature rules. Electrospray ionisation mass spectra (ESI-MS) were recorded using a Thermo-Quest LCQ Deca. Differential pulse voltammetry (DPV) was measured on a Parstat 2273 in dry acetonitrile.

Phenanthrolines B, C and D were prepared according to known procedure\(^1\)

2-(3,5-Di-tert-butyl-4-methoxyphenyl)-3-trimethylsilanylethynyl-[1,10]phenanthroline (B)

Yield 64%; mp 107 °C; \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 0.23 (s, 9 H, 3'-H), 1.53 (s, 18 H, t-Bu), 3.78 (s, 3 H, methoxy), 7.63 (dd, \(J = 8.0\) Hz, \(J = 4.3\) Hz, 1 H, 8-H), 7.78 (d, \(J = 8.8\) Hz, 1 H, 6-H), 7.80 (d, \(J = 8.8\) Hz, 1 H, 5-H), 7.91 (s, 2 H, 2''-, 6''-H), 8.26 (dd, \(J = 8.0\) Hz, \(J = 1.6\) Hz, 1 H, 7-H), 8.48 (s, 1 H, 4-H), 9.14 (dd, \(J = 4.3\) Hz, \(J = 1.6\) Hz, 1 H, 9-H); \(^{13}\)C NMR (100 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 0.2, 32.5, 36.5, 65.1, 101.5, 103.8, 118.1, 123.7, 126.1, 126.9, 127.4, 128.6, 130.0, 134.9, 136.5, 142.5, 143.6, 145.2, 146.7, 150.9, 160.4, 161.1; IR (KBr) \(\nu\) 2958, 2921, 2869, 2147, 1618, 1583, 1545, 1489, 1467, 1441, 1397, 1363, 1299, 1261, 1250, 1221, 1175, 1116, 1078, 1011, 916, 890, 854, 844, 774, 760, 738, 699, 637; ESI-MS \(m/z\) (%): 495.3 (100), [M + H]\(^+\). Anal. Calcd for C\(_{32}\)H\(_{38}\)N\(_2\)OSiH\(_2\)O: C, 74.96; H, 7.86; N, 5.46. Found: C, 74.83; H 7.70; N, 5.22.

2,9-Bis-(3,5-di-tert-butyl-4-methoxyphenyl)-3-trimethylsilanylethynyl-[1,10]phenanthroline (C)

Yield 78%; mp 120 °C; \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 0.23 (s, 9 H, 3'-H), 1.52 (s, 18 H, t-Bu), 1.53 (s, 18 H, 3''-, 5''- t-Bu), 1.53 (s, 18 H, 3''-, 5''- t-Bu), 3.74 (s, 3 H, 4'''-methoxy), 3.76 (s, 3 H, 4'''-methoxy), 7.75 (d, \(J = 8.7\) Hz, 1 H, 6-H), 7.82 (d, \(J = 8.7\) Hz, 1 H, 5-H), 7.95 (s, 2 H, 2'''-, 6'''-H), 8.04 (d, \(J = 8.4\) Hz, 1 H, 8-H), 8.09 (s, 2 H, 2'''-, 6'''-H), 8.29 (d, \(J = 8.4\) Hz, 1 H, 7-H), 8.49 (s, 1 H, 4-H); \(^{13}\)C NMR (100 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 0.2, 32.6, 32.7, 36.4, 36.5, 65.0, 65.1, 101.2, 104.2, 118.0, 121.5, 125.6, 126.8, 127.3 (2C), 128.7, 128.8, 134.9, 135.0, 137.2, 142.8, 143.5, 144.6, 145.4, 146.5, 158.8, 160.3, 161.1, 161.7; IR (KBr) \(\nu\) 2959, 2915, 2866, 2149, 1618, 1603, 1584, 1533, 1501, 1459, 1416, 1391, 1359, 1319, 1251, 1225, 1176, 1116, 1078, 1011, 915, 891, 865, 844, 760, 697,
2,9-Bis-(3,5-di-tert-butyl-4-methoxyphenyl)-3-ethynyl-[1,10]phenanthroline (D)

Yield 94%; mp 212 °C; 1H NMR (400 MHz, CDCl2): δ 1.53 (s, 18 H, 3‴-‴′′-‴′′-‴-Bu), 1.54 (s, 18 H, 3‴-‴′′-‴-Bu), 3.45 (s, 1 H, 2′-H), 3.75 (s, 3 H, 4‴-methoxy), 3.77 (s, 3 H, 4″-methoxy), 7.76 (d, 3J = 8.7 Hz, 1 H, 6-H), 7.83 (d, 3J = 8.7 Hz, 1 H, 5-H), 8.01 (s, 2 H, 2″-‴′′-‴′′-‴-H), 8.06 (d, 3J = 8.4 Hz, 1 H, 8-H), 8.11 (s, 2 H, 2‴′-‴′-‴′′-‴-H), 8.30 (d, 3J = 8.4 Hz, 1 H, 7-H), 8.52 (s, 1 H, 4-H); 13C NMR (100 MHz, CDCl2) δ 32.5, 32.6, 36.4, 36.5, 65.0 (2C), 83.0, 83.5, 116.9, 121.6, 125.6, 126.8, 127.2, 127.4, 128.7, 129.1, 134.6, 134.9, 137.2, 142.7, 143.6, 144.6, 145.8, 146.5, 158.8, 160.6, 161.1, 161.7; IR (KBr) ν 3304, 2960, 2925, 2864, 1618, 1603, 1586, 1534, 1500, 1459, 1416, 1391, 1360, 1317, 1262, 1224, 1116, 1011, 891, 843, 648; ESI-MS m/z (%) 641.5 (100), [M + H]+. Anal. Calcd for C44H52N2O2Si: C, 82.46; H, 8.18; N, 4.37. Found: C, 82.84; H, 8.53; N, 3.88.

Compound 7

Compound D (0.50 g, 0.78 mmol) was dissolved in dry dichloromethane (25 mL) in a 50 mL two-necked round-bottomed flask under nitrogen. [Cu(MeCN)4]PF6 (0.15 mg, 0.39 mmol) was added to the solution and the mixture was stirred at room temperature for 7 days. Then the solvent was removed under reduced pressure to afford a blackish solid. Small traces of the free ligand were separated off using column chromatography (SiO2, DCM: EtOAc, 9:1). Yield 99%; mp > 300 °C; 1H NMR (400 MHz, CDCl2): δ 0.90 (s, 36 H, 3‴-‴′′-‴′′-‴-Bu), 0.96 (s, 36 H, 3‴-‴′′-‴′′-‴-Bu), 3.11 (s, 6 H, 4‴-‴′′-‴-methoxy), 3.21 (s, 6 H, 4″-‴′′-‴-methoxy), 3.46 (s, 2 H, ethynyl-H), 7.48 (s, 4 H, 2″-‴′′-‴′′-‴′′-‴-H) 7.52 (s, 4 H, 2‴′-‴′′-‴′′-‴′′-‴-H), 7.91 (d, 3J = 8.9 Hz, 2 H, 6-H), 7.91 (d, 3J = 8.6 Hz, 2 H, 8-H), 8.01 (d, 3J = 8.9 Hz, 2 H, 5-H), 8.39 (d, 3J = 8.6 Hz, 2 H, 7-H), 8.60 (s, 2 H, 4-H); 13C NMR (100 MHz, CDCl2) δ 31.6, 32.0,
36.0, 36.2, 64.9, 65.5, 81.2, 86.3, 121.4, 126.3, 126.4, 126.9, 128.0, 128.2, 128.5, 129.6, 132.3, 133.4, 137.2, 142.3, 143.1, 143.5, 144.1, 144.3, 158.1, 158.9, 161.5, 162.8; IR (KBr) ν 3308, 3279, 2963, 2871, 1620, 1580, 1543, 1501, 1458, 1406, 1392, 1360, 1319, 1256, 1223, 1113, 1004, 921, 842, 648; ESI-MS m/z (%) 1344.7 (100), [M]+. Anal. Calcd for C_{88}H_{104}CuF_{6}N_{4}O_{4}P·EtOAc: C, 70.01; H, 7.15; N, 3.55. Found: C, 70.20; H, 7.00; N, 3.63.

Angular Molecule 1

3-(4-Iodo-2,3,5,6-tetramethyl-phenylethynyl)-[1,10]phenanthroline (0.11 mg, 0.23 mmol), 7 (0.15 g, 0.10 mmol), TBAF.3H_{2}O (0.48 g, 1.5 mmol) and PdCl_{2}(PPh_{3})_{2} (14 mg, 20 µmol) were combined in a 25 mL side-armed test tube under N\textsubscript{2} atmosphere. The solid mixture was stirred at 80 °C for 12 h. Then it was cooled, dissolved with dichloromethane (50 mL) and washed w successively ith aqueous KOH (50 mL) and water (50 mL). After drying over Na_{2}SO\textsubscript{4} the organic solvent was removed under reduced pressure. The crude product was purified using column chromatography (SiO\textsubscript{2}). First separation was run using a 1:1 mixture of dichloromethane and ethyl acetate as eluent. Finally the target compound was obtained using 1:10 mixture of methanol and dichloromethane. Yield 60%; mp > 300 °C; \textsuperscript{1}H NMR (400 MHz, CD\textsubscript{2}Cl\textsubscript{2}): δ 0.70 (s, 18 H, [3'' or 5'']-t-Bu), 0.91 (s, 36 H, 3''', 5'''-t-Bu) 1.16 (s, 18 H, [3'' or 5'']-t-Bu), 1.99 (s, 12 H, a-H), 2.47 (s, 12 H, b-H), 3.06 (s, 6 H, 4'''-methoxy), 3.22 (s, 6 H, 4'''-methoxy), 7.23 (s, 2 H, [2'' or 6'']-H), 7.50 (s, 4 H, 2'''''- 6'''''-H), 7.61 (s, 2 H, [2'' or 6'']-H), 7.65 (dd, 3\textsuperscript{J} = 8.1 Hz, 3\textsuperscript{J} = 4.3 Hz, 2 H, 8'-H), 7.80 (d, 3\textsuperscript{J} = 8.8 Hz, 2 H, 6'-H), 7.87 (d, 3\textsuperscript{J} = 8.8 Hz, 2 H, 5'-H), 7.93 (d, 3\textsuperscript{J} = 8.8 Hz, 2 H, 6-H), 7.94 (d, 3\textsuperscript{J} = 8.5 Hz, 2 H, 8-H), 8.03 (d, 3\textsuperscript{J} = 8.8 Hz, 2 H, 5-H), 8.29 (dd, 3\textsuperscript{J} = 8.1 Hz, 4\textsuperscript{J} =1.7 Hz, 2 H, 7'-H), 8.40 (d, 4\textsuperscript{J} = 2.0 Hz 2 H, 4'-H), 8.43(d, 3\textsuperscript{J} = 8.5 Hz, 2 H, 7-H), 8.61 (s, 2 H, 4-H), 9.14 (dd, 3\textsuperscript{J} = 4.3 Hz, 4\textsuperscript{J} = 1.7 Hz, 2 H, 9'-H), 9.21 (d, 4\textsuperscript{J} = 2.0 Hz, 2 H, 2'-'H); \textsuperscript{13}C NMR (100 MHz, CD\textsubscript{2}Cl\textsubscript{2}) δ 18.1, 18.7, 31.6, 31.8, 32.3, 36.0, 36.3, 65.0, 65.8, 92.8, 95.5, 96.2, 97.2, 120.2, 123.1, 123.7, 123.8,
124.1, 126.2, 126.5 (2C), 126.6, 127.0, 128.0, 128.1, 128.5, 128.6, 128.8, 129.3, 129.7, 132.4, 133.5, 133.6, 136.4, 136.6, 136.7, 137.2, 138.2, 139.5, 142.2, 143.0, 144.3, 145.4, 146.6, 151.0, 152.1, 158.3, 159.7, 161.1, 163.1; IR (KBr) ν 3411, 2960, 2920, 2868, 2202, 1617, 1579, 1541, 1502, 1447, 1421, 1408, 1391, 1360, 1255, 1222, 1113, 1003, 909, 848, 733; ESI-MS m/z (%) 2012.8 (100), [M]+. Anal. Calcd for C_{138}H_{140}CuF_6N_8O_4P .2CH_2Cl_2: C, 71.17; H, 6.23; N, 4.81. Found: C, 71.59; H, 6.34; N, 4.89.

Heterometallic Triangle T_1

Bisphenanthroline 2a (4.25 mg, 3.73 µmol) was loaded into a NMR tube and was dissolved in CD_2Cl_2 (0.15 mL). AgPF_6 (1.89 mg, 7.46 µmol), dissolved in CD_3CN (0.45 mL), was added to the bisphenanthroline solution leading to a light yellow hue. Finally, 1 (8.05 mg, 3.73 µmol) was added to the mixture furnishing a yellowish-black solution. T_1 was received in quantitative yield. mp > 300 °C; ^1H NMR (400 MHz, CD_3CN/CD_2Cl_2, 3:1): δ 0.59 (s, 18 H, [3'' or 5'']-t-Bu), 0.86 (s, 36 H, 3''', 5'''-t-Bu), 1.19 (s, 18 H, [3'' or 5'']-t-Bu), 1.25-2.03 (m, 54 H, methyl, a-H), 2.39 (s, 12 H, b-H), 3.00 (s, 6 H, 4'''-methoxy), 3.20 (s, 6 H, 4'''-methoxy), 6.21-6.48 (m, 4 H, mes-H), 6.96 (s, 4 H, c-H), 7.16 (s, 2 H, [2'' or 6'']-H), 7.50 (s, 4 H, 2''', 6'''-H), 7.56 (s, 2 H, [2'' or 6'']-H), 7.80 (dd, ^3J = 8.0 Hz, ^3J = 4.4 Hz, 2 H, 8'''-H), 7.95-8.07 (m, 12 H, 5-, 5'-, 6-, 6'-, 8'', 8''''-H), 8.19 (d, ^3J = 8.8 Hz, 2 H, 6''''-H), 8.26 (d, ^3J = 8.8 Hz, 2 H, 5''''-H), 8.47 (d, ^3J = 8.4 Hz, 2 H, 7-H), 8.53-8.82 (m, 14 H, 2', 4-, 4', 4''', 7', 7''', 9'-H); ^13C NMR (100 MHz, CD_3CN/CD_2Cl_2, 3:1): δ 18.0, 18.5, 18.8, 20.3, 20.6 (2C), 31.4, 31.6, 32.3, 35.9, 36.2, 65.2, 66.1, 88.4, 94.5, 95.1, 96.0, 96.1, 96.5, 121.2, 121.5, 123.1 (2C), 123.3, 123.9, 125.3, 126.2, 126.8, 126.9 (2C), 127.0, 127.6, 128.1, 128.3, 128.5, 128.6 (2C), 128.9, 129.0 (2C), 129.3, 129.7, 130.1, 132.1, 132.2, 133.6, 133.7, 134.2, 135.9, 136.8, 137.0, 137.9, 138.7, 138.8 (2C), 139.1, 139.4, 139.9, 140.3, 140.4 (2C), 141.0 (2C), 141.3, 142.2, 142.4, 142.5, 144.2 (2C), 144.3, 151.4, 151.7, 157.9, 159.4, 161.0, 161.6, 162.3, 163.3; IR (KBr) ν 3427, 2957, 2920, 2868, 2203, 1617, 1580, 1544, 1503, 1449, 1426, 1408, 1390, 1361, 1297, 1256, 1222, 1113, 1004, 911, 843, 727, 557; ESI-MS m/z (%) 1123.4
(100), [M – 3PF$_6$]$^{3+}$, 1757.5 (10), [M – 2PF$_6$]$^{2+}$. Anal. Calcd for C$_{208}$H$_{200}$Ag$_2$Br$_2$CuF$_{18}$N$_{12}$O$_4$P$_3$·4CH$_2$Cl$_2$: C, 61.42; H, 5.06; N, 4.05. Found: C, 61.21; H, 5.32; N, 3.94.

**Homometallic Triangle T$_2$**

Bisphenanthroline 2a (4.01 mg, 3.51 µmol) and Cu(MeCN)$_4$PF$_6$ (2.62 mg, 7.03 µmol) were put into a NMR tube and were dissolved with CD$_2$Cl$_2$ furnishing a yellow solution. After addition of 1 (7.59 mg, 3.51 µmol) a color change to dark red occurred. T$_2$ was received in quantitative yield. mp > 300 °C; $^1$H NMR (400 MHz, CD$_2$Cl$_2$): δ 0.62 (s, 18 H, [3’’ or 5’’]-t-Bu), 0.88 (s, 36 H, 3’’’-t-Bu) 1.20 (s, 18 H, [3’’ or 5’’]-t-Bu), 1.26-1.88 (m, 42 H, methyl), 1.95 (s, 12 H, a-H), 2.38 (s, 12 H, b-H), 3.01 (s, 6 H, 4’’’-methoxy), 3.21 (s, 6 H, 4’’-methoxy), 5.77-6.24 (m, 4 H, mes-H), 6.93 (s, 4 H, c-H), 7.15 (s, 2 H, [2’’ or 6’’]-H), 7.48 (s, 4 H, 2’’’-H), 7.55 (s, 2 H, [2’’ or 6’’]-H), 7.76 (dd, $^3$J = 8.0 Hz, $^3$J = 4.4 Hz, 2 H, 8’-H), 7.88-7.95 (m, 10 H, 5’’, 6’, 6’’, 8’, 8’’’-H), 8.02 (d, $^3$J = 8.8 Hz, 2 H, 5’-H), 8.21 (d, $^3$J = 8.8 Hz, 2 H, 6’’-H), 8.27 (d, $^3$J = 8.8 Hz, 2 H, 5’’’-H), 8.46 (d, $^3$J = 8.0 Hz, 2 H, 7’-H), 8.50-8.55 (m, 6 H, 2’-, 4’, 9’-H), 8.63 (s, 2 H, 4-H), 8.72 (d, $^3$J = 8.0 Hz, 2 H, 7’’-H), 8.82 (s, 2 H, 4’’’-H); $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$): δ 18.2, 18.5, 18.7, 18.9, 20.1, 20.3, 20.6 (2C), 20.8, 31.5, 31.8, 32.4, 36.0, 36.2, 65.1, 65.9, 87.8, 94.5, 95.2, 95.8, 96.8, 97.0, 122.1, 122.7, 123.0, 123.1, 123.5, 123.9, 125.4, 126.1, 126.5, 126.6, 126.8, 127.1, 127.4, 127.6 (2C), 128.0, 128.1, 128.2, 128.3, 128.6, 128.7, 128.9, 129.2, 129.3, 129.5, 132.0, 132.2, 132.3, 133.0, 133.4, 133.5 (2C), 134.2, 135.0, 135.4, 136.7, 136.8, 137.0, 137.2, 137.9 (2C), 138.1, 138.4, 139.4, 139.7, 141.6, 142.2, 142.5, 143.0, 143.1, 144.2, 144.3 (2C), 148.6, 149.4, 158.2, 159.7, 160.0, 160.9, 161.3, 163.3; IR (KBr) v 3428, 2957, 2921, 2867, 2203, 1618, 1578, 1547, 1502, 1449, 1426, 1409, 1390, 1361, 1295, 1256, 1222, 1113, 1004, 912, 842, 723, 557; ESI-MS m/z (%) 1094.1 (100), [M – 3PF$_6$]$^{3+}$, 1713.5 (10), [M – 2PF$_6$]$^{2+}$. Anal. Calcd for C$_{208}$H$_{200}$Br$_2$Cu$_3$F$_{18}$N$_{12}$O$_4$P$_3$·4CH$_2$Cl$_2$: C, 62.76; H, 5.17; N, 4.14. Found: C, 62.63; H, 5.43; N, 4.14.
Metal Exchange Study

Metal exchange study with the heterometallic triangle $T_1$ was carried out according to Scheme S2. $[\text{Cu(MeCN)}_4]\text{PF}_6$ (1.0 eq. with respect to $\text{Ag}^+$ ions in $T_1$) in dichloromethane was added solution of heterometallic triangle $T_1$ in DCM-MeCN (0.745 mM) at room temperature. The resulting solution was checked by ESI-MS within 5 min after the addition of $\text{Cu}^+$. 

Scheme S2. Metal exchange reaction.

Figure S1. ESI-MS of a solution of $T_1$ in DCM-MeCN after addition of $[\text{Cu(MeCN)}_4]\text{PF}_6$ (1.0 eq. with respect to $\text{Ag}^+$ ions in $T_1$). Time after mixing until the ESI-MS was recorded: 5 min. Only signals of the homometallic triangle $T_2$ were detected.
Ligand Exchange Study

Ligand exchange study was carried out according to Scheme S3. To a solution of $T_2$ in dichloromethane (72 $\mu$M), solid bisphenanthroline $2b$ (1.0 eq. with regard to $T_2$) was added at room temperature. The resulting solution was checked by ESI-MS within 5 min after the addition of $2b$.

Figure S2. ESI-MS of a solution of $T_2$ in DCM after addition of $2b$ (1.0 eq. with respect to $T_2$). Time after mixing until the ESI-MS was recorded: 5 min. Only signals of the mixture of the homometallic triangles $T_2$ and $T_2'$ were detected. Experimental isotopic distributions (black lines) for the 3+ and 2+ charged species along with its calculated one (red lines) for $T_2'$ are depicted.
Spectra

Figure S3. $^1$H NMR spectrum of B

Figure S4. $^{13}$C NMR spectrum of B
Figure S5. $^1$H NMR spectrum of C

Figure S6. $^{13}$C NMR spectrum of C
Figure S7. $^1$H NMR spectrum of D

Figure S8. $^{13}$C NMR spectrum of D
Figure S9. $^1$H NMR spectrum of 7

Figure S10. $^{13}$C NMR spectrum of 7
Figure S11. $^1$H NMR spectrum of 1.

Figure S12. $^{13}$C NMR spectrum of 1.
Figure S13. Part of the $^1$H NMR spectrum of complexes 7 and 1. Due to steric effects of the duryl group, ortho-protons and tert-butyl protons of the aromatic substituent at the 2-position of the phenanthroline split into two different sets in 1.

Figure S14. $^1$H NMR spectrum of heterometallic triangle $T_1$
Figure S15. $^1$H NMR spectrum of homometallic triangle $T_2$.

Figure S16. Absorption spectra of heterometallic triangle $T_1$ and homometallic triangle $T_2$. 
Figure S17. ESI-MS of homometallic triangle $T_2$ and the experimental isotopic distributions (black lines) for the 3+ and 2+ charged species along with their calculated ones (red lines).

Figure S18. DOSY NMR of homometallic triangle $T_2$
**Figure S19.** Differential pulse voltammetry (DPV) of homometallic triangle T\(_2\). The experiment was carried out in acetonitrile with 0.1 M \(n\text{Bu}_4\text{NPF}_6\) as electrolyte against a Ag wire as a quasi-reference electrode and 2,4,6-triphenylpyrylium tetrafluoroborate as internal standard (scan rate of 20 mVs\(^{-1}\) and a pulse height of 2 mV).

**References**