

Electronic Supplementary Information (ESI)

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

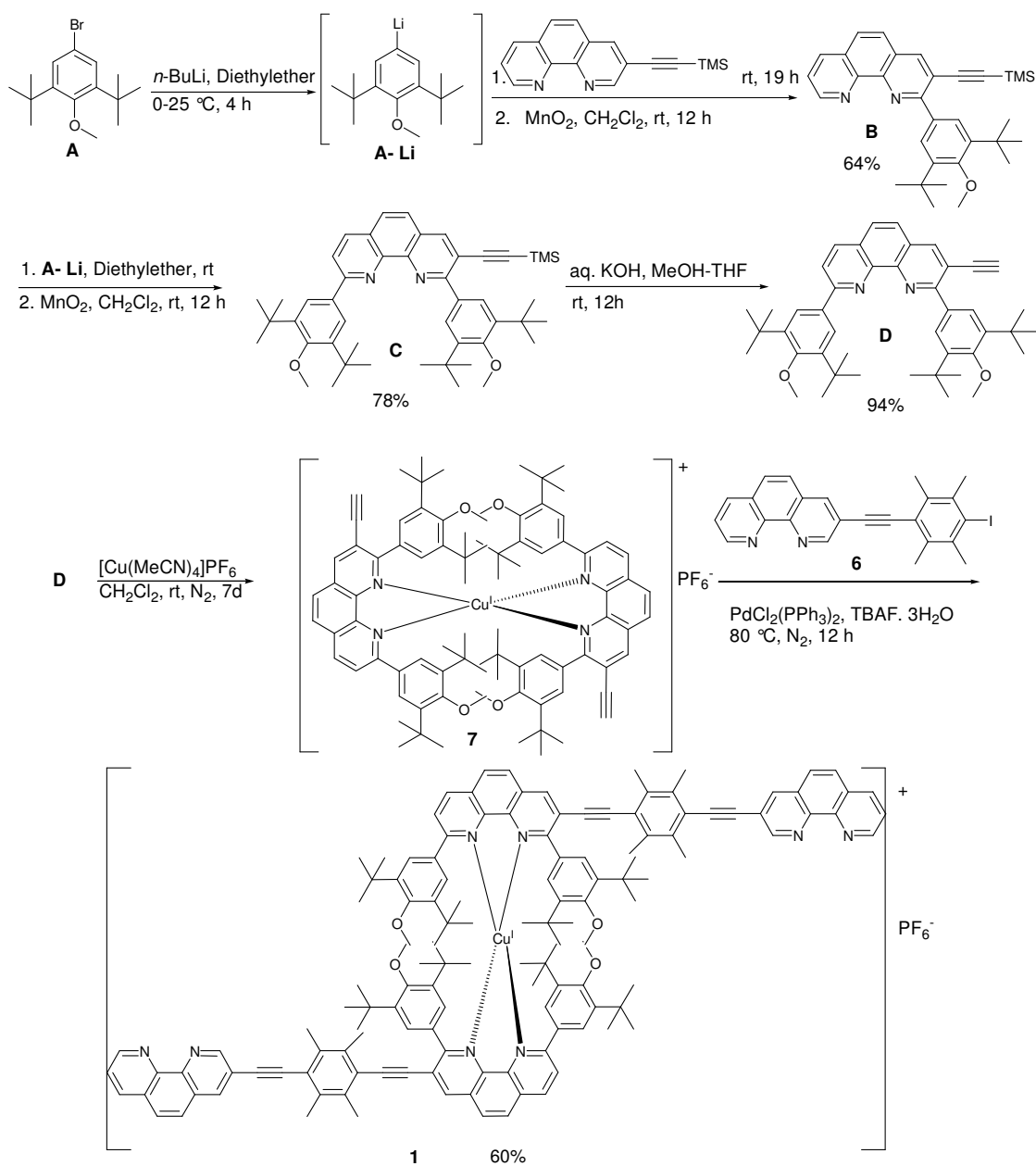
Michael Schmittel, Kingsuk Mahata*

*Center of Micro and Nanochemistry and Engineering, Organische Chemie I, Universität
Siegen, Adolf-Reichwein-Str. 2, D-57068 Siegen, Germany,*

E-mail: schmittel@chemie.uni-siegen.de

Fax: (+49) 271-740-3270

Synthesis



Scheme S1. Synthesis of angular molecule **1**.

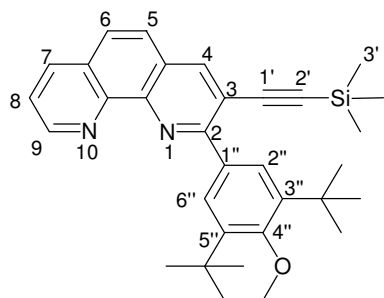
All reagents were commercially available and used without further purification. The solvents were dried with appropriate desiccants and distilled prior to use. Thin-layer chromatography (TLC) was performed using TLC plates from Merck (silica gel 60 F₂₅₄). Silica gel 60 was used for column chromatography. ¹H NMR and ¹³C 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 procedure¹

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

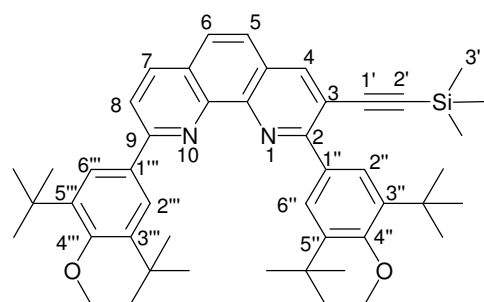
(**B**)



Yield 64%; mp 107 °C; ¹H NMR (400 MHz, CD₂Cl₂) δ 0.23 (s, 9 H, 3'-H), 1.53 (s, 18 H, *t*-Bu), 3.78 (s, 3 H, methoxy), 7.63 (dd, ³*J* = 8.0 Hz, ³*J* = 4.3 Hz, 1 H, 8-H), 7.78 (d, ³*J* = 8.8 Hz, 1 H, 6-H), 7.80 (d, ³*J* = 8.8 Hz, 1 H, 5-H), 7.91 (s, 2 H, 2''-, 6''-H), 8.26 (dd, ³*J* = 8.0 Hz, ⁴*J* = 1.6 Hz, 1 H, 7-H), 8.48 (s, 1 H, 4-H), 9.14 (dd, ³*J* = 4.3 Hz, ⁴*J* = 1.6 Hz, 1 H, 9-H); ¹³C NMR (100 MHz, CD₂Cl₂) δ 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) ν 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 C₃₂H₃₈N₂O₂Si · H₂O: 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**)

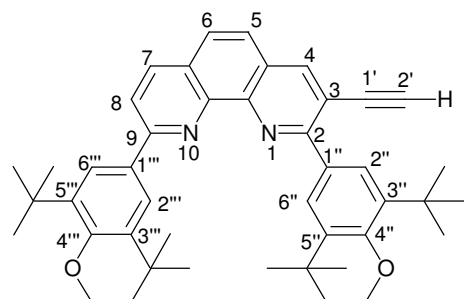


Yield 78%; mp 120 °C; ¹H NMR (400 MHz, CD₂Cl₂): δ 0.23 (s, 9 H, 3'-H), 1.52 (s, 18 H, 3''-, 5''- *t*-Bu), 1.53 (s, 18 H, 3''-, 5''- *t*-Bu), 3.74 (s, 3 H, 4''-methoxy), 3.76 (s, 3 H, 4''-methoxy), 7.75 (d, ³*J* = 8.7 Hz, 1 H, 6-H), 7.82 (d, ³*J* = 8.7 Hz, 1 H, 5-H), 7.95 (s, 2 H, 2''-, 6''-H), 8.04 (d, ³*J* = 8.4 Hz, 1 H,

8-H), 8.09 (s, 2 H, 2''-, 6''-H), 8.29 (d, ³*J* = 8.4 Hz, 1 H, 7-H), 8.49 (s, 1 H, 4-H); ¹³C NMR (100 MHz, CD₂Cl₂) δ 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) ν 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,

641; ESI-MS m/z (%) 713.5 (100), $[M + H]^+$. Anal. Calcd for $C_{47}H_{60}N_2O_2Si$: C, 79.16; H, 8.48; N, 3.93. Found: C, 79.15; H, 8.90; N, 3.50.

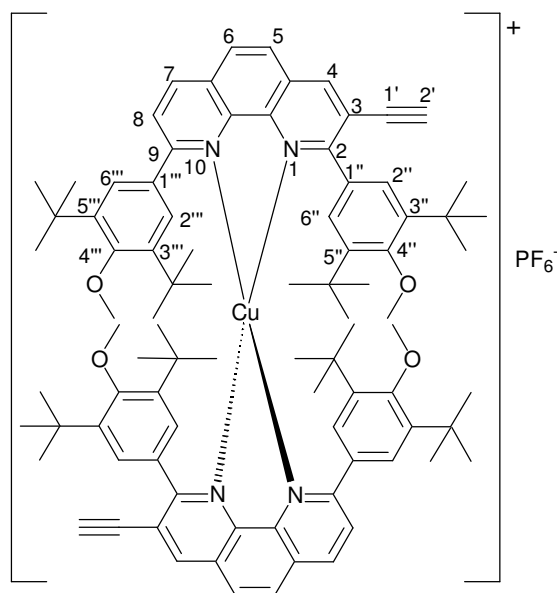
2,9-Bis-(3,5-di-*tert*-butyl-4-methoxyphenyl)-3-ethynyl-[1,10]phenanthroline (**D**)



Yield 94%; mp 212 °C; 1H NMR (400 MHz, CD_2Cl_2): δ 1.53 (s, 18 H, 3'''-, 5'''-*t*-Bu), 1.54 (s, 18 H, [3''-, 5''-*t*-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'''-, 6'''-H), 8.06 (d, $^3J = 8.4$ Hz, 1 H, 8-H), 8.11 (s, 2 H, 2''-, 6''-H), 8.30 (d, $^3J = 8.4$ Hz, 1 H, 7-H), 8.52 (s, 1 H, 4-H); ^{13}C NMR (100 MHz, CD_2Cl_2)

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 $C_{44}H_{52}N_2O_2$: C, 82.46; H, 8.18; N, 4.37. Found: C, 82.84; H, 8.53; N, 3.88.

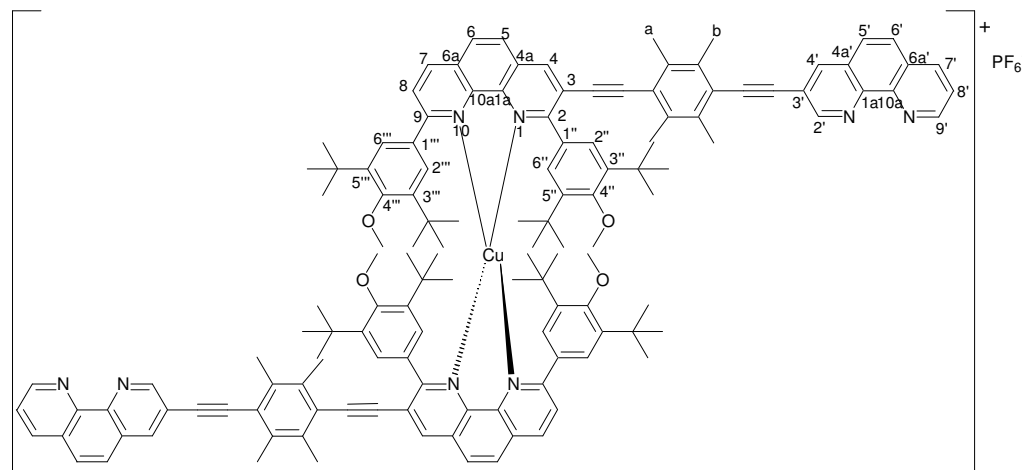
Compound 7



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. $[Cu(MeCN)_4]PF_6$ (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 (SiO_2 , DCM: EtOAc, 9:1). Yield 99%; mp > 300 °C; 1H NMR (400 MHz, CD_2Cl_2): δ 0.90 (s, 36 H, 3'''-, 5'''-*t*-Bu), 0.96 (s, 36 H, 3''-, 5''-*t*-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'''-, 6'''-H) 7.52 (s, 4 H, 2''-, 6''-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); ^{13}C NMR (100 MHz, CD_2Cl_2) 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 $C_{88}H_{104}CuF_6N_4O_4P \cdot EtOAc$: C, 70.01; H, 7.15; N, 3.55. Found: C, 70.20; H, 7.00; N, 3.63.

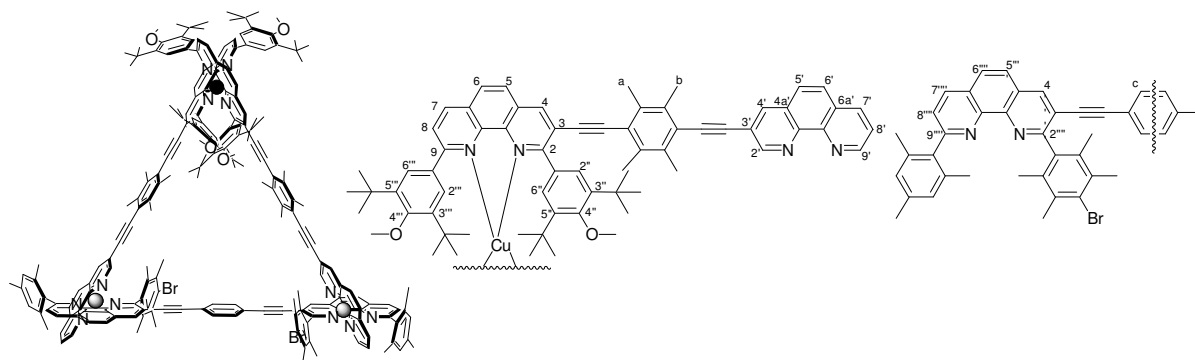
Angular Molecule 1



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·3H₂O (0.48 g, 1.5 mmol) and PdCl₂(PPh₃)₂ (14 mg, 20 μ mol) were combined in a 25 mL side-armed test tube under N₂ atmosphere. The solid mixture was stirred at 80 °C for 12 h. Then it was cooled, dissolved with dichloromethane (50 mL) and washed successively with aqueous KOH (50 mL) and water (50 mL). After drying over Na₂SO₄ the organic solvent was removed under reduced pressure. The crude product was purified using column chromatography (SiO₂). 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; ¹H NMR (400 MHz, CD₂Cl₂): 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*J* = 8.1 Hz, ³*J* = 4.3 Hz, 2 H, 8'-H), 7.80 (d, ³*J* = 8.8 Hz, 2 H, 6'-H), 7.87 (d, ³*J* = 8.8 Hz, 2 H, 5'-H), 7.93 (d, ³*J* = 8.8 Hz, 2 H, 6-H), 7.94 (d, ³*J* = 8.5 Hz, 2 H, 8-H), 8.03 (d, ³*J* = 8.8 Hz, 2 H, 5-H), 8.29 (dd, ³*J* = 8.1 Hz, ⁴*J* = 1.7 Hz, 2 H, 7'-H), 8.40 (d, ⁴*J* = 2.0 Hz 2 H, 4'-H), 8.43 (d, ³*J* = 8.5 Hz, 2 H, 7-H), 8.61 (s, 2 H, 4-H), 9.14 (dd, ³*J* = 4.3 Hz, ⁴*J* = 1.7 Hz, 2 H, 9'-H), 9.21 (d, ⁴*J* = 2.0 Hz, 2 H, 2'-H); ¹³C NMR (100 MHz, CD₂Cl₂) 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 $C_{136}H_{140}CuF_6N_8O_4P \cdot 2CH_2Cl_2$: C, 71.17; H, 6.23; N, 4.81. Found: C, 71.59; H, 6.34; N, 4.89.

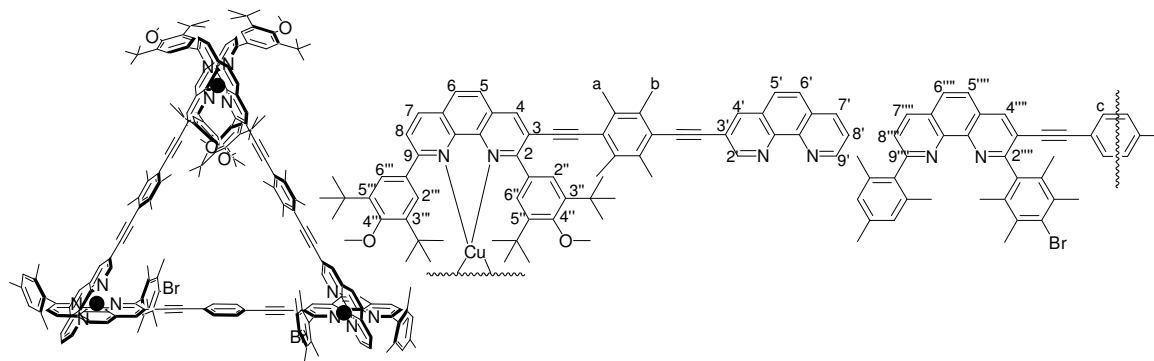
Heterometallic Triangle T_1



Bisphenanthroline **2a** (4.25 mg, 3.73 μ mol) was loaded into a NMR tube and was dissolved in CD_2Cl_2 (0.15 mL). $AgPF_6$ (1.89 mg, 7.46 μ mol), 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 μ mol) was added to the mixture furnishing a yellowish-black solution. T_1 was received in quantitative yield. mp > 300 $^\circ C$; 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); ^{13}C 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 $C_{208}H_{200}Ag_2Br_2CuF_{18}N_{12}O_4P_3 \cdot 4CH_2Cl_2$: C, 61.42; H, 5.06; N, 4.05. Found: C, 61.21; H, 5.32; N, 3.94.

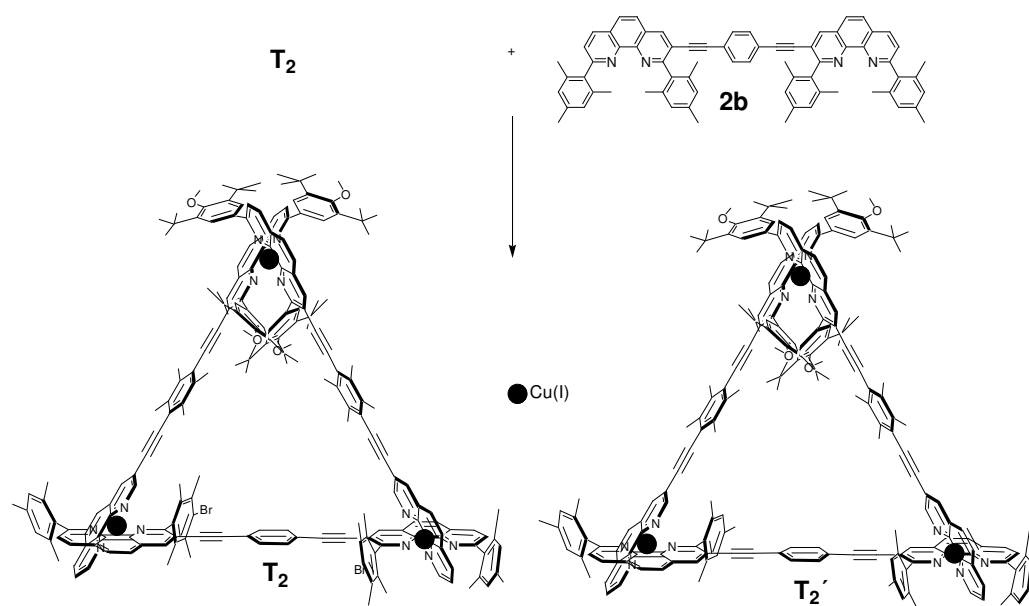
Homometallic Triangle T_2



Bisphenanthroline **2a** (4.01 mg, 3.51 μ mol) and $Cu(MeCN)_4PF_6$ (2.62 mg, 7.03 μ mol) were put into a NMR tube and were dissolved with CD_2Cl_2 furnishing a yellow solution. After addition of **1** (7.59 mg, 3.51 μ mol) a color change to dark red occurred. T_2 was received in quantitative yield. mp > 300 $^{\circ}C$; 1H NMR (400 MHz, CD_2Cl_2): δ 0.62 (s, 18 H, [3'' or 5'']-*t*-Bu), 0.88 (s, 36 H, 3''', 5'''-*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''', 6'''-H), 7.55 (s, 2 H, [2'' or 6'']-H), 7.76 (dd, $^3J = 8.0$ Hz, $^3J = 4.4$ Hz, 2 H, 8'-H), 7.88-7.95 (m, 10 H, 5'-, 6-, 6'-, 8-, 8''''-H), 8.02 (d, $^3J = 8.8$ Hz, 2 H, 5-H), 8.21 (d, $^3J = 8.8$ Hz, 2 H, 6''''-H), 8.27 (d, $^3J = 8.8$ Hz, 2 H, 5''''-H), 8.41 (d, $^3J = 8.4$ Hz, 2 H, 7-H), 8.46 (d, $^3J = 8.0$ 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, $^3J = 8.0$ Hz, 2 H, 7''''-H), 8.82 (s, 2 H, 4''''-H); ^{13}C NMR (100 MHz, CD_2Cl_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) ν 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 $C_{208}H_{200}Br_2Cu_3F_{18}N_{12}O_4P_3 \cdot 4CH_2Cl_2$: C, 62.76; H, 5.17; N, 4.14. Found: C, 62.63; H, 5.43; N, 4.14.

Ligand Exchange Study

Ligand exchange study was carried out according to Scheme S3. To a solution of T_2 in dichloromethane (72 μ 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**.



Scheme S3. Ligand exchange study.

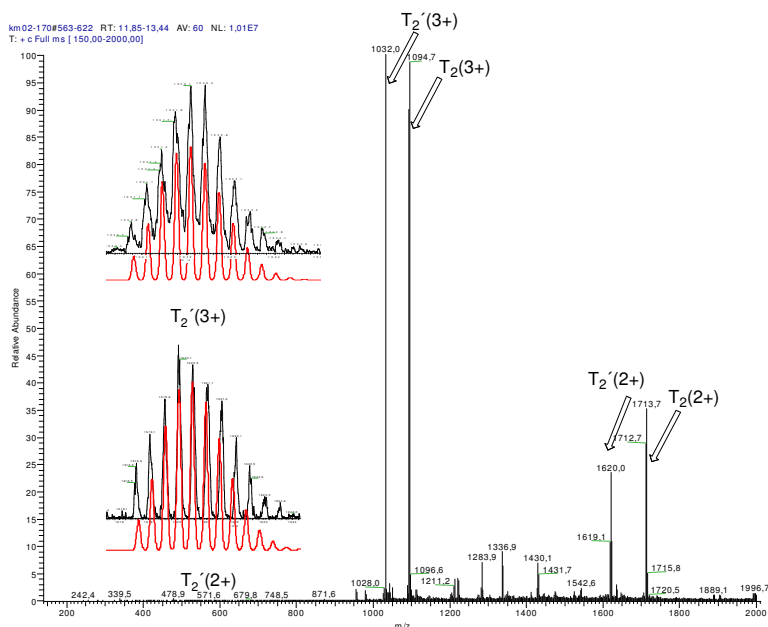


Figure S2. ESI-MS of a solution of T_2 in DCM after addition of **2b** (1.0 eq. with respect to T_2). Time after mixing until the ESI-MS was recorded: 5 min. Only signals of the mixture of the homometallic triangles T_2 and T_2' were detected. Experimental isotopic distributions (black lines) for the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

Spectra

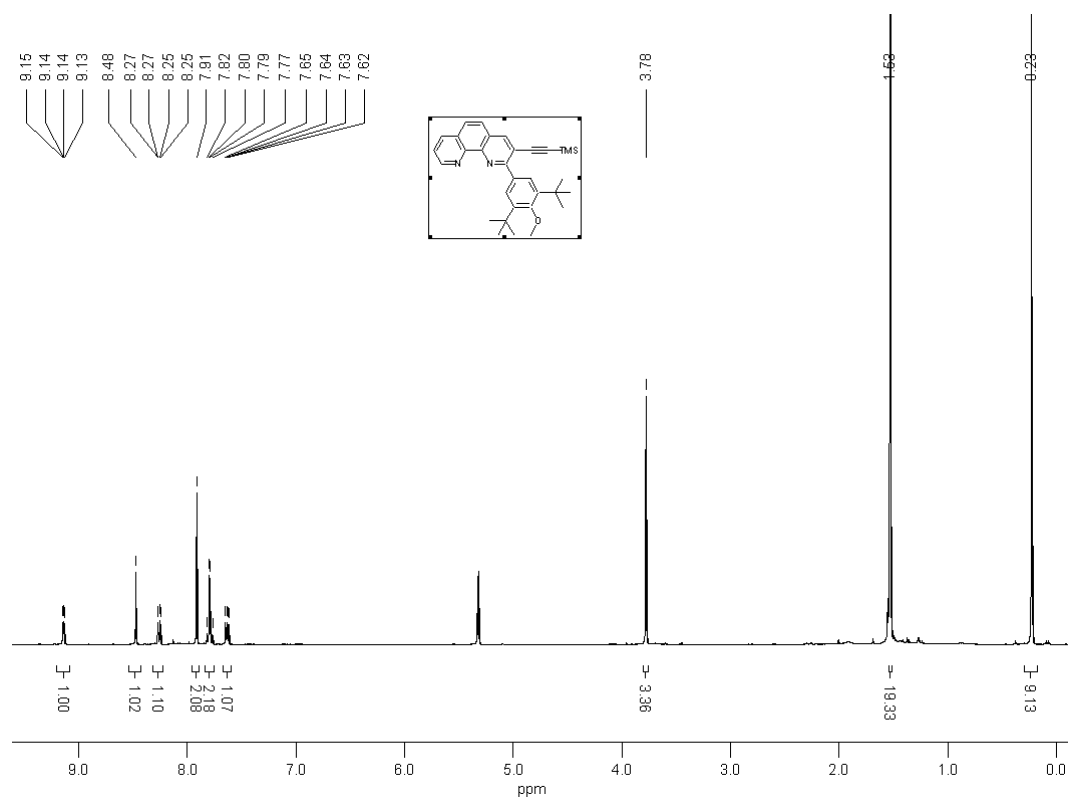


Figure S3. ^1H NMR spectrum of B

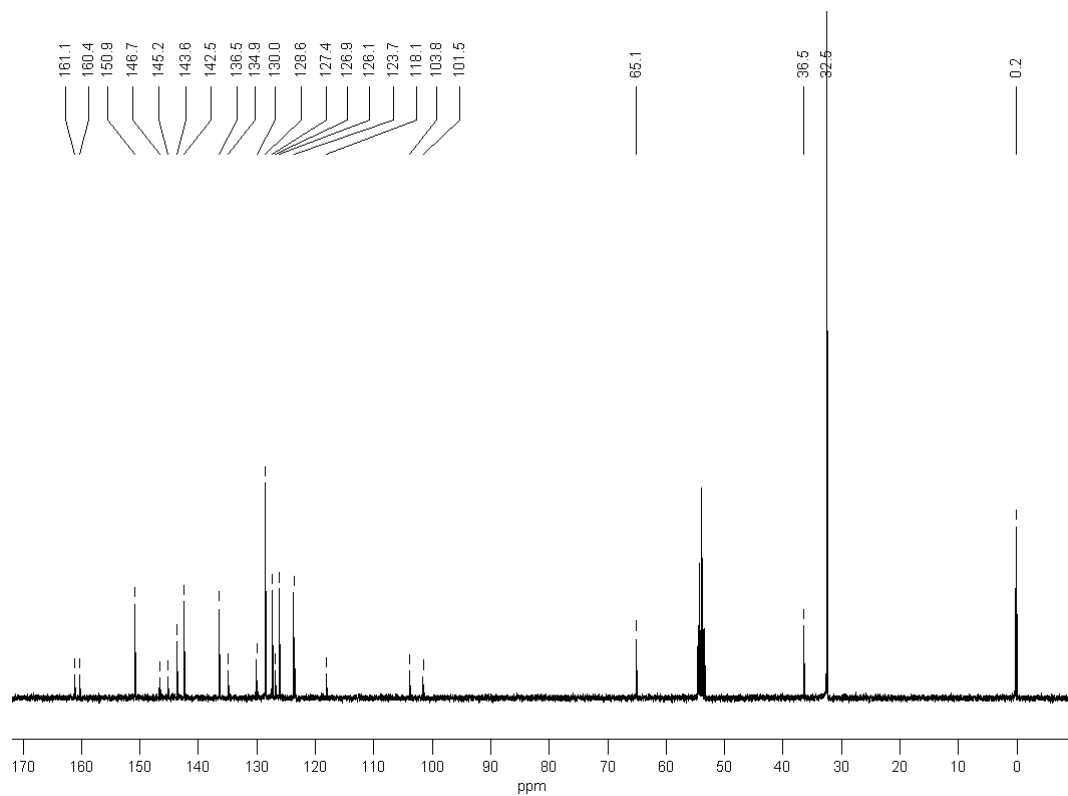


Figure S4. ^{13}C NMR spectrum of B

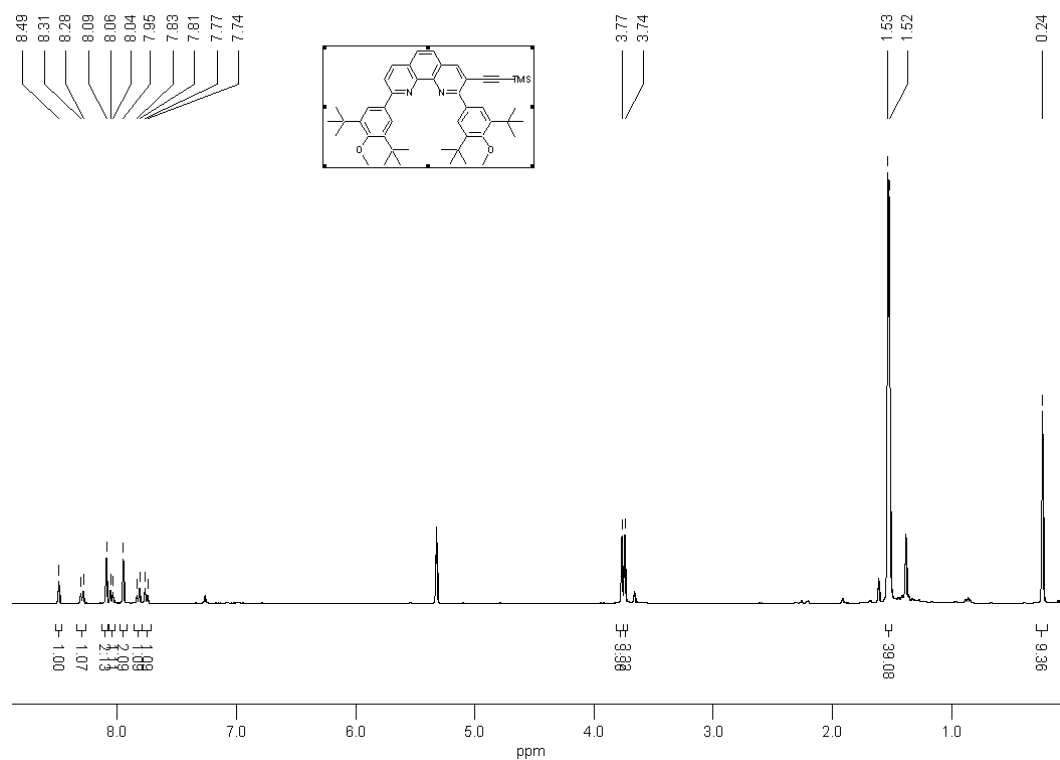


Figure S5. ^1H NMR spectrum of C

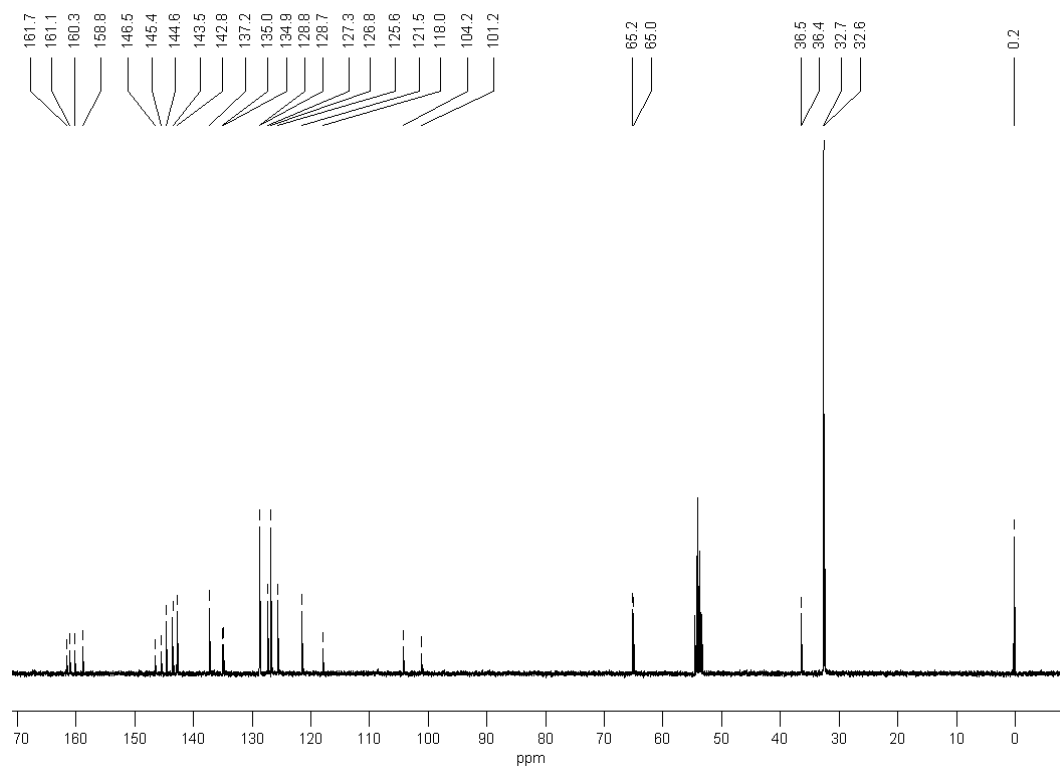


Figure S6. ^{13}C NMR spectrum of C

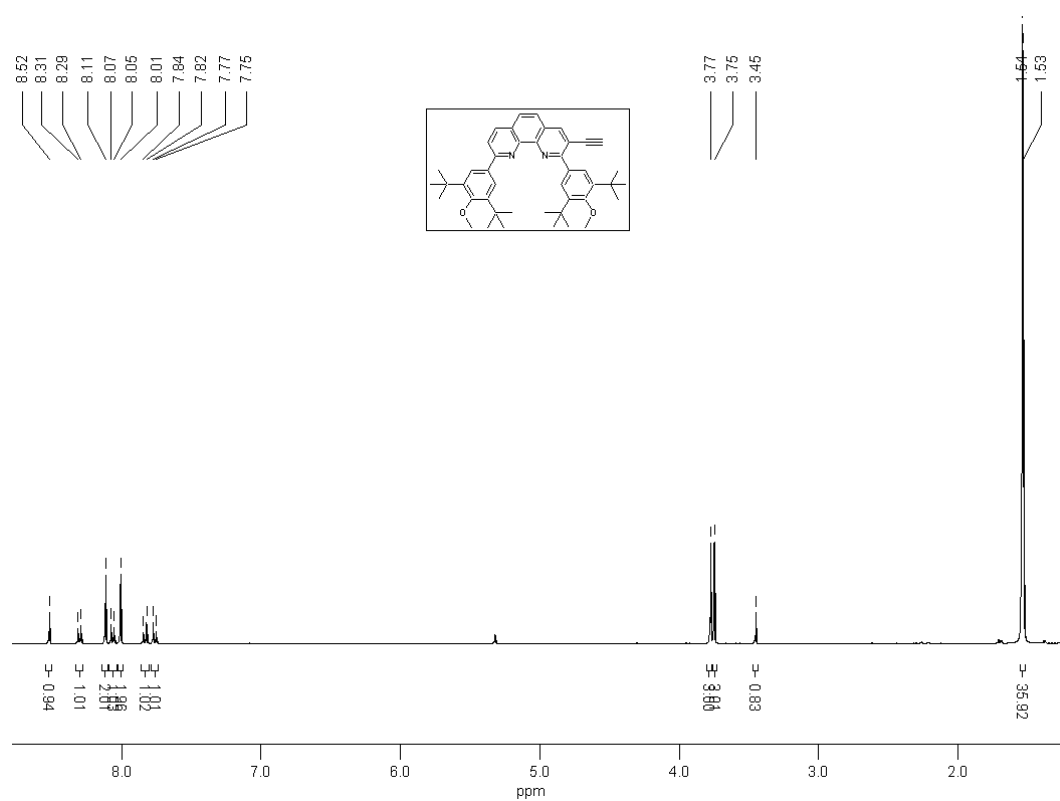


Figure S7. ¹H NMR spectrum of **D**

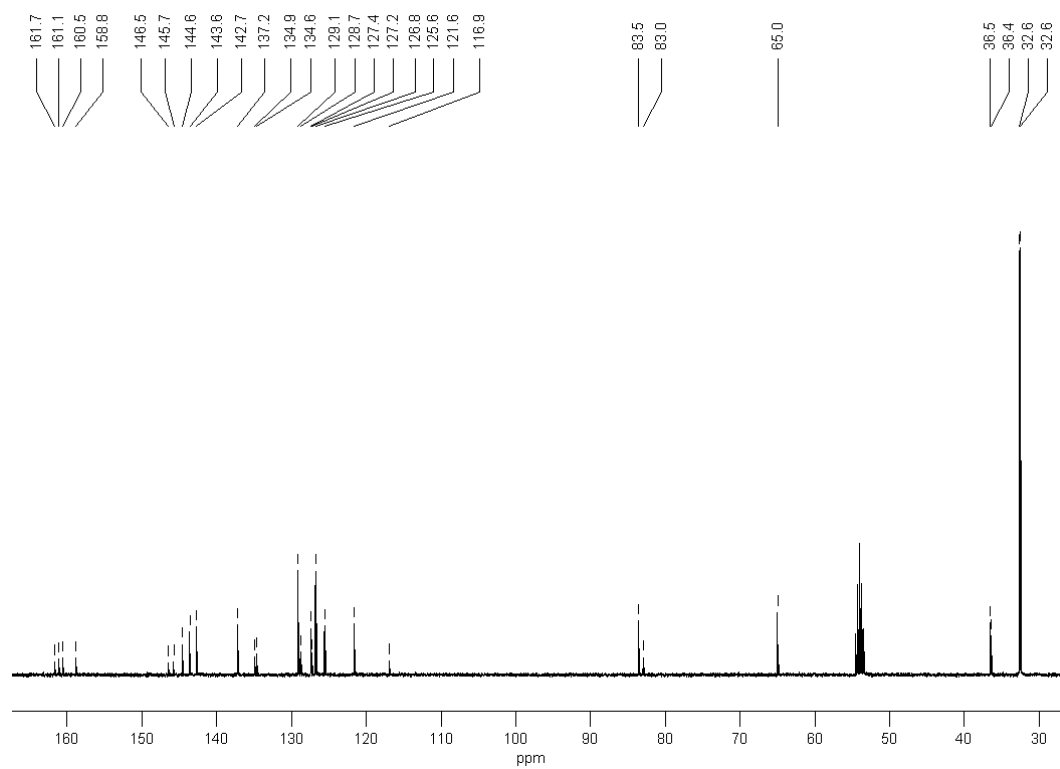


Figure S8. ¹³C NMR spectrum of **D**

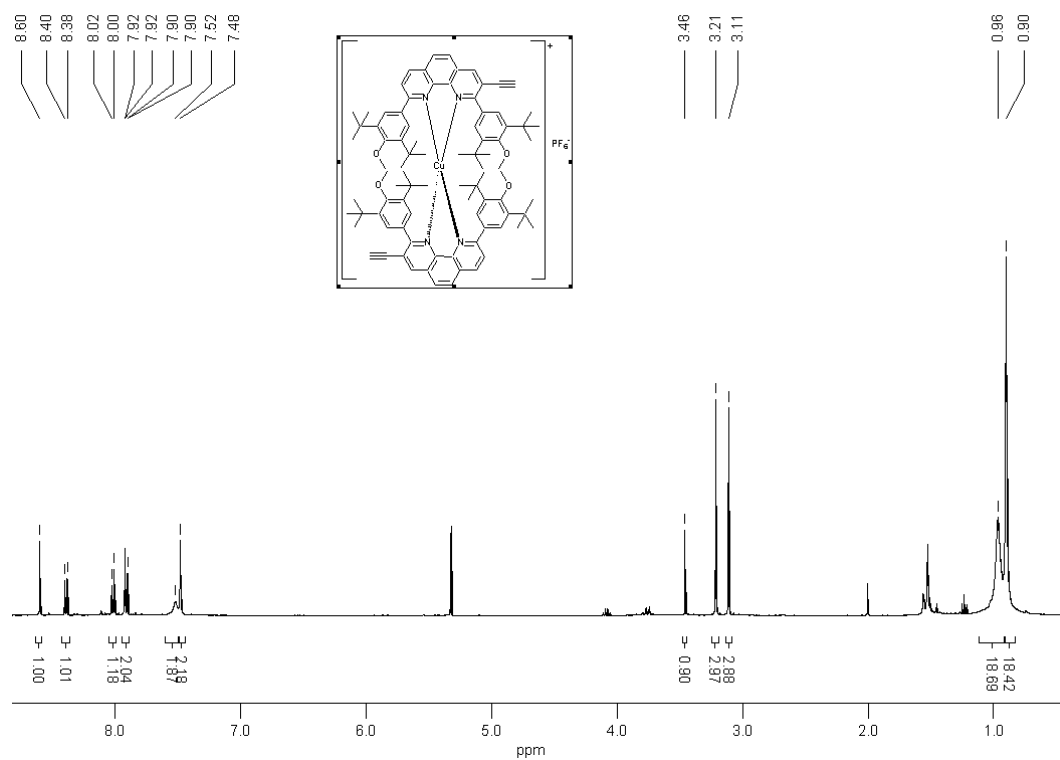


Figure S9. ^1H NMR spectrum of **7**

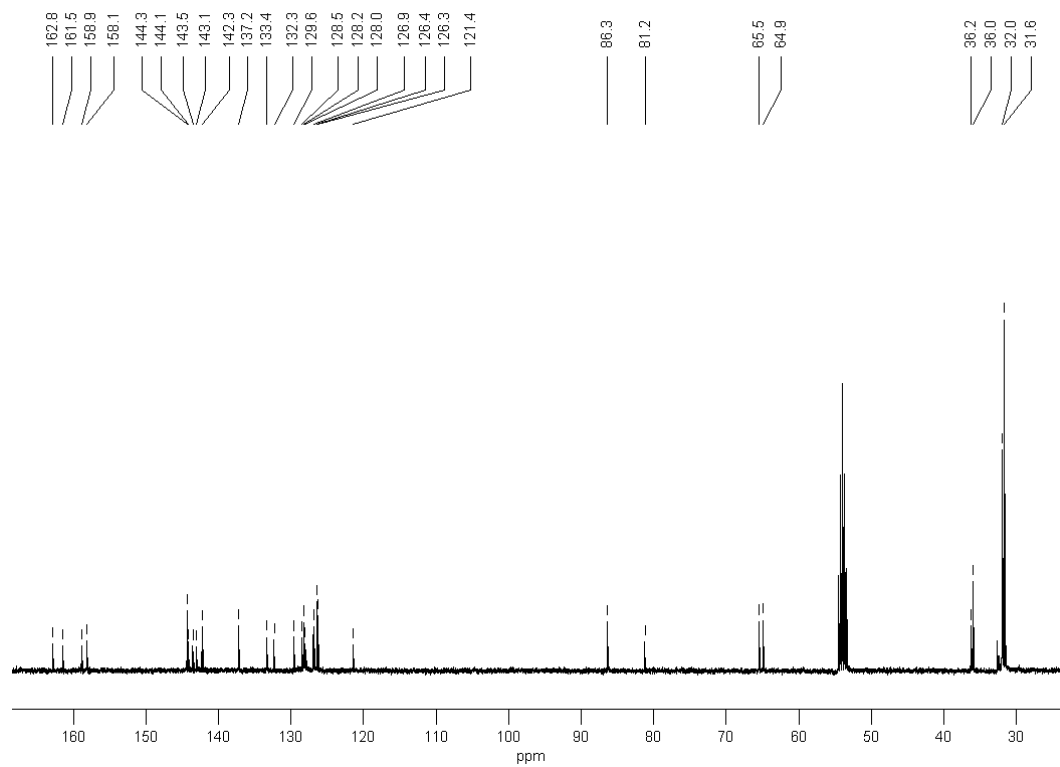


Figure S10. ^{13}C NMR spectrum of **7**

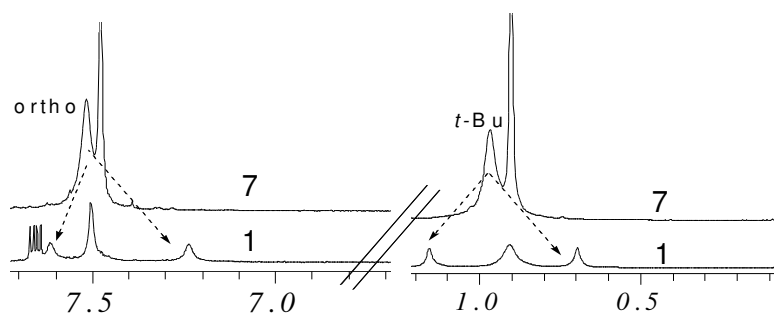


Figure S13. Part of the ^1H NMR spectrum of complexes **7** and **1**. Due to steric effects of the duryl group, *ortho*-protons and *tert*-butyl protons of the aromatic substituent at the 2-position of the phenanthroline split into two different sets in **1**.

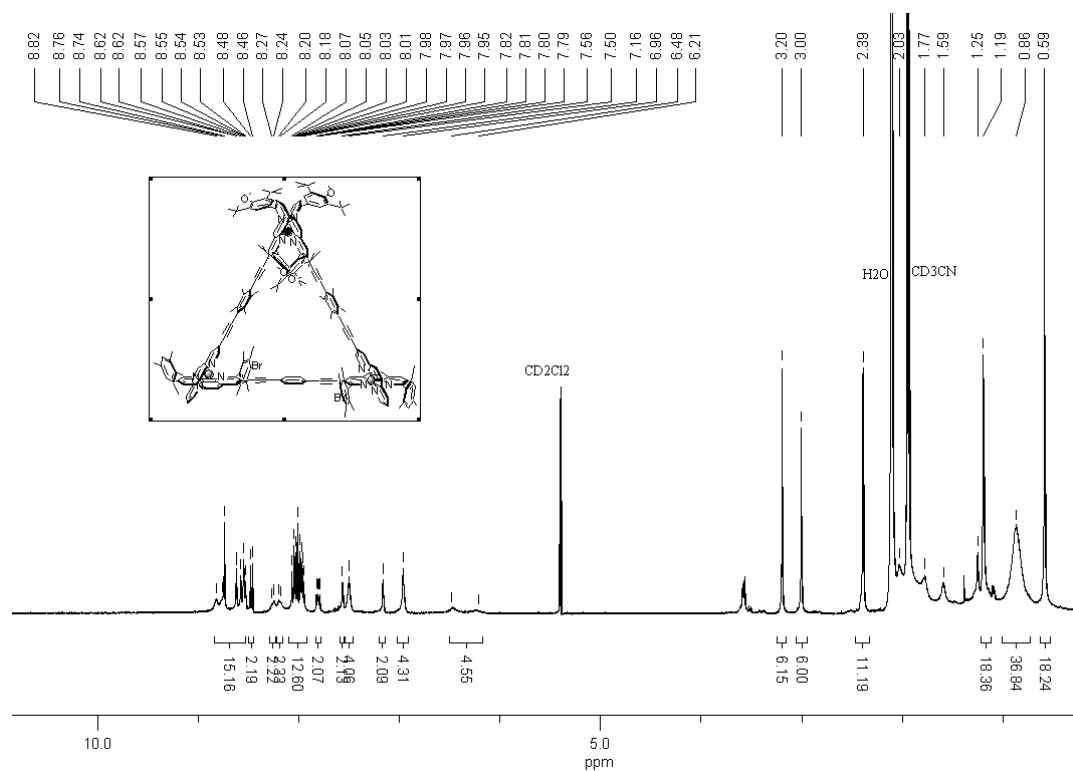


Figure S14. ^1H NMR spectrum of heterometallic triangle **T₁**

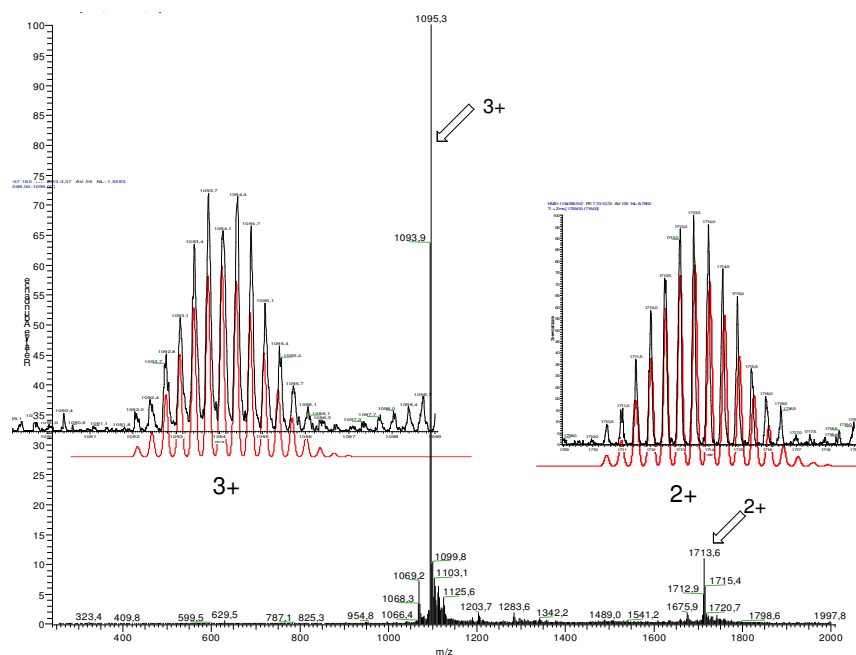


Figure S17. ESI-MS of homometallic triangle T_2 and the experimental isotopic distributions (black lines) for the 3+ and 2+ charged species along with their calculated ones (red lines).

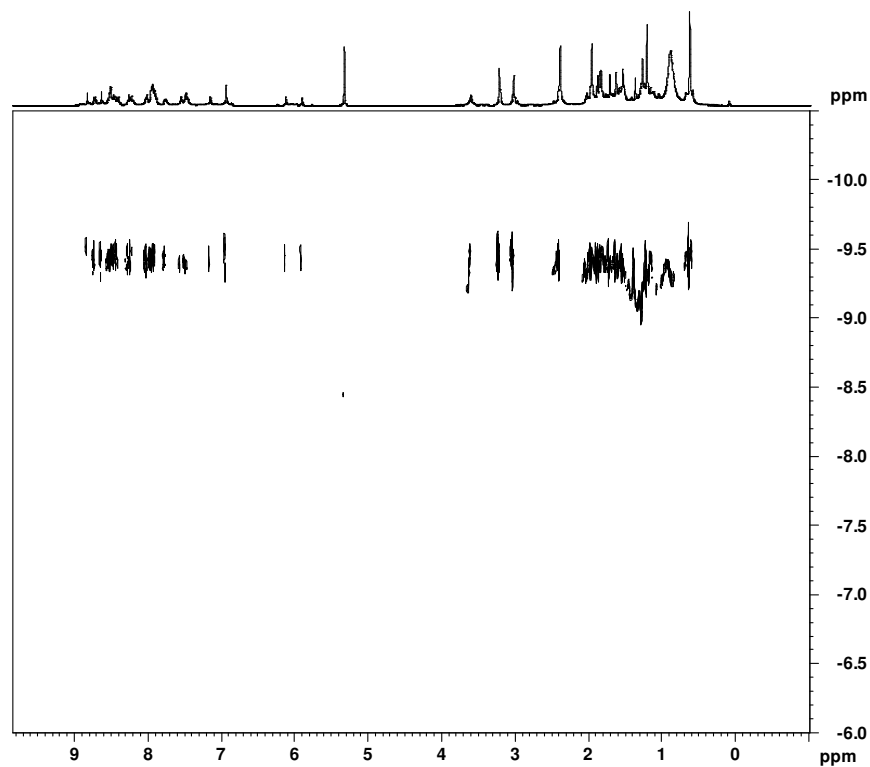


Figure S18. DOSY NMR of homometallic triangle T_2

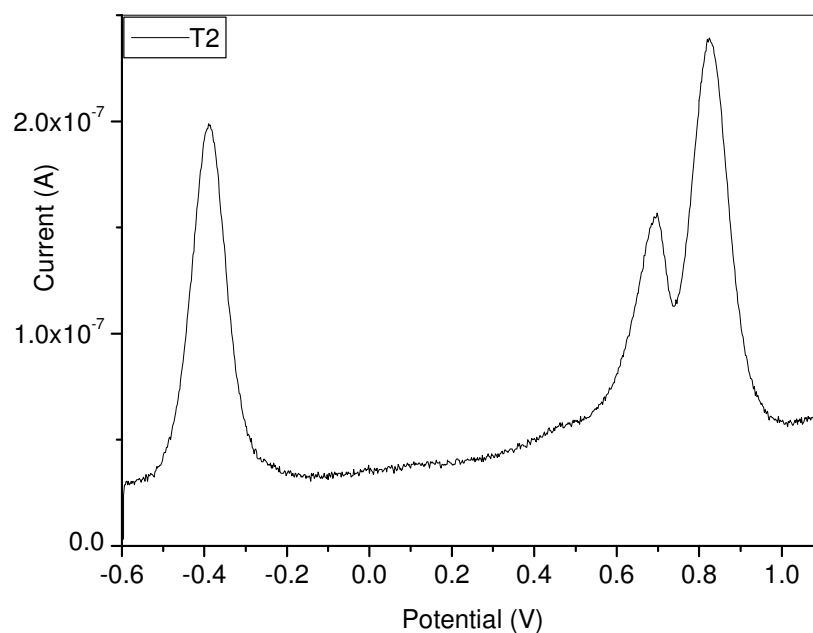


Figure S19. Differential pulse voltammetry (DPV) of homometallic triangle **T₂**. The experiment was carried out in acetonitrile with 0.1 M *n*Bu₄NPF₆ as electrolyte against a Ag wire as a quasi-reference electrode and 2,4,6-triphenylpyrylium tetrafluoroborate as internal standard (scan rate of 20 mVs⁻¹ and a pulse height of 2 mV).

References

- 1 V. Kalsani, M. Schmittl, A. Listorti, G. Accorsi and N. Armaroli, *Inorg. Chem.* 2006, **45**, 2061.