Self-Assembly of a Bis-Porphyrinic Supramolecular Rectangle Using Two Orthogonal Binding Strategies

Ravuri S. K. Kishore, Venkateshwarlu Kalsani, and Michael Schmittel

Supporting Information

Synthesis of Cu(I) complexes.

**Complex 3:** To equimolar amounts of 1 and [Cu(CH$_3$CN)$_4$]PF$_6$ in dichloromethane was added one equivalent of anhydrous [1,10]-phenanthroline. The resulting solution showed an instantaneous change in color to deep red. The complex, obtained in quantitative yield, was isolated without any further purification and was found to be 3.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): δ= 8.95 (s, 1 H, 4-H), 8.72 (d, $J = 7.8$ Hz, 1 H, 7-H), 8.72 (d, $J = 4.6$ Hz, 2 H, pyrrol-H1), 8.68 (d, $J = 4.8$ Hz, 2 H, pyrrol-H3), 8.67 (d, $J = 4.8$ Hz, 2 H, pyrrol-H4), 8.66 (d, $J = 4.6$ Hz, 2 H, pyrrol-H2), 8.52 (dd, $^3J = 4.6$ Hz, $^4J = 1.3$ Hz, 2 H, 2',-9'-H), 8.44 (dd, $^3J = 8.1$ Hz, $^4J = 1.5$ Hz, 2 H, 4',-7'-H), 8.27 (d, $J = 9.1$ Hz, 1 H, 5-H ), 8.24 (d, $J = 9.1$ Hz, 1 H, 6-H), 8.08 (d, $J = 8.2$ Hz, 2 H, Ar-Ha, -Ha'), 7.92 (s, 2 H, 5', 6'-H), 7.91 (d, $J = 7.8$ Hz, 1 H, 8-H), 8.27 (dd, $^3J = 8.0$ Hz, $^4J = 4.8$ Hz, 2 H, 3',-8'-H), 7.44 (d, $J = 8.2$ Hz, 2 H, Ar-Hb, -Hb'), 7.26 (s, 6 H, por-mes), 6.02 (s, 2 H, 3''',-5'''-H), 2.59 (s, 12 H, 7''-, 10''-, 7'''-, 9'''-H), 1.81 (s, 18 H, por-mes-Me), 1.78 (s, 9 H, por-mes-Me), 1.64 (s, 6 H, 8''-, 9''-H), 1.54 (s, 3 H, 8'''-H).

$^{13}$C NMR (100MHz, CD$_2$Cl$_2$): δ= 160.5, 159.0, 149.4, 149.2, 149.2, 148.9, 147.2, 144.4, 143.4, 142.4, 141.8, 139.0, 138.9, 138.5, 137.3, 136.9, 135.9, 134.2, 132.8, 131.8, 131.0, 130.4, 130.1, 129.1, 128.3, 127.8, 127.3, 127.1, 126.6, 126.4, 125.8, 124.2, 122.3, 120.0, 118.1, 117.9, 97.0, 85.3, 21.1, 20.7, 19.6, 19.5 (2), 19.4 (2), 17.7.

ESI-MS m/z (%): 1579.6 (100) [M]$^+$. 

Elemental analysis calcld(%) for C$_{98}$H$_{81}$BrCuF$_{6}$N$_{8}$PZn: C 68.25, H 4.73, N 6.50; found: C 68.77, H 4.68, N 6.56.
Complex 5a/6a: To equimolar amounts of 1 and [Cu(CH₂CN)₄]PF₆ in dichloromethane was added one equivalent of 4. The resulting solution showed an instantaneous change in color to deep red. The complex was isolated without any further purification and was found to be 5a, obtained in quantitative yield.

$^1$H NMR (400 MHz, CD₂Cl₂): $\delta$ = 8.91 (s, 2 H, 4-H), 8.70 (d, $J = 8.2$ Hz, 2 H, 7-H), 8.68 (d, $J = 4.6$ Hz, 4 H, pyrrol-H1), 8.65 (d, $J = 4.8$ Hz, 4 H, pyrrol-H3), 8.62 (s, 8 H, pyrrol-H2, H4), 8.49 (dd, $^3J = 4.5$ Hz, $^4J = 1.2$ Hz, 2 H, 9'-H), 8.42 (dd, $^3J = 8.9$ Hz, $^4J = 1.2$ Hz, 2 H, 7'-H), 8.28 (br s, 4 H, 5', 6'-H), 8.23 (d, $J = 9.1$ Hz, 2 H, 5-H), 8.22 (d, $J = 9.1$ Hz, 2 H, 6-H), 8.09 (d, $J = 7.9$ Hz, 4 H, Ar-Ha, -Ha'), 7.88 (dd, $^3J = 8.7$ Hz, $^3J = 4.1$ Hz, 2 H, 8'-H), 7.88 (d, $^3J = 4.5$ Hz, 2 H, 2'-H), 7.76 (d, $^2J = 8.9$ Hz, 2 H, 4'-H), 7.75 (dd, $^3J = 8.1$ Hz, $^4J = 4.8$ Hz, 2 H, 8'-H), 7.44 (d, $J = 7.4$ Hz, 4 H, Ar-Hb, -Hb'), 7.26 (s, 12 H, por-mes), 7.07 (br s, 2 H, 3''-H), 6.12 (br s, 2 H, 5''-H), 6.02 (s, 2 H, 3'''-H), 5.87 (s, 2 H, 5'''-H), 2.59 (s, 18 H, por-mes-Me), 1.80 (s, 18 H, por-mes-Me), 1.79 (s, 18 H, por-mes-Me), 1.69 (s, 6 H, 7''-H), 1.68 (s, 6 H, 9''-H), 1.64 (s, 6 H, 7'''-H), 1.56 (s, 6 H, 8''-H), 1.55 (s, 6 H, 10''-H), 1.48 (s, 6 H, 8'''-H), 1.44 (s, 6 H, 9'''-H)

$^{13}$C NMR (100 MHz, CD₂Cl₂): $\delta$ = 161.4, 159.9, 150.4, 150.2, 150.1, 149.8, 149.4, 148.6, 145.5, 144.3, 142.8, 142.7, 142.2, 140.0, 139.9, 139.8, 139.6, 139.5, 139.4, 139.1, 138.4, 138.1, 137.9, 137.8, 137.1, 135.2, 135.1, 134.0, 133.6, 132.9, 132.6, 131.9, 131.5, 131.3, 130.9, 130.0, 129.7, 129.2, 128.7, 128.4, 128.3 (2), 128.1, 127.7, 127.5, 127.3, 126.9, 126.8, 125.6, 125.2, 123.3, 120.9, 120.1, 119.0, 118.7, 98.1, 91.6, 89.7, 86.1, 22.1(2), 21.7, 20.6, 20.4, 20.3, 18.8, 18.6.

ESI-MS m/z (%): 1680 (100) [M]$^+$.

Elemental analysis calcd(%) for C₁₀₅H₈₄BrCuF₆N₉PZn*CH₃CN: C 68.85, H 4.70, N 7.50; found C 68.54, H 4.64, N 7.61;
**Complex 5b/6b:** To equimolar amounts of 1 and AgPF$_6$ in dichloromethane-acetonitrile (10:1) was added one equivalent of 4. The resulting solution showed an instantaneous darkening in color. The solvents were then removed and the solid was redissolved in dichloromethane. The complex was isolated without any further purification and was found to be 5b, obtained in quantitative yield.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ = 8.86 (s, 2 H, 4-H), 8.72-8.60 (m, 18 H, Pyrrol H, 7-H), 8.44 (br s, 4 H, 7'-4-H', J=4.5 Hz), 8.31 (s, 2 H, 2'-H), 8.25 (s, 2 H, 9'-H), 8.20 (d, $J$ = 9.1 Hz, 2 H, 5-H), 8.18 (d, $J$ = 9.1 Hz, 2 H, 6-H), 8.09 (d, $J$ = 7.9 Hz, 4 H, Ar-Ha, -Ha'), 7.99 (br s, 4 H, 5-', 6'-H), 7.79 (d, $^2$J = 4.5 Hz, 4 H, 8', 8-H), 7.37 (d, $J$ = 7.4 Hz, 4 H, Ar-Hb, -Hb'), 7.23 (s, 12 H, por-mes), 7.02 (br s, 4 H, 3''-H), 6.19 (s, 6 H, 3'''-H), 5.87 (s, 6 H, 5''', 5''-H), H), 2.53 (s, 18 H, por-mes-Me), 2.00 (s, 6 H, 7''-H), 1.92 (s, 6 H, 9''-H), 1.86 (s, 6 H, 7'''-H), 1.78 (s, 36 H, por-mes-Me), 1.66 (s, 6 H, 8''-H), 1.56 (s, 6 H, 10''-H), 1.32 (s, 6 H, 9''''-H), 1.23 (s, 6 H, 9'''-H)

$^{13}$C NMR (100MHz, CD$_2$Cl$_2$): $\delta$ = 162.7, 161.6, 151.4, 150.9, 150.4, 150.3, 150.2, 149.9, 149.7, 146.9, 146.8, 146.8, 145.9, 145.5, 145.5, 142.9, 142.1, 141.5, 141.3, 140.8, 140.7, 140.4, 140.1, 139.9, 139.6, 139.0, 138.9, 138.7, 137.9, 135.6, 135.3, 131.9, 131.6, 131.5, 131.4, 131.0, 130.5, 130.2, 130.0, 129.6, 128.9, 128.8, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 127.5, 127.0, 126.7, 125.2, 120.9, 119.0, 118.7, 117.3, 98.2, 98.1, 91.7, 90.0, 86.4, 22.1, 21.7, 20.8, 20.7, 20.6, 20.4, 19.1, 18.8.

**ESI-MS m/z (%):** 1724 (100) [M]+.

Elemental analysis calcd(%) for C$_{105}$H$_{84}$AgBrF$_6$N$_9$PZn·CH$_3$CN·0.5CH$_2$Cl$_2$: C 66.09, H 4.54, N 7.17, found: C 66.04, H 4.51, N 7.36

3-Pyridin-4-ylethynyl-[1,10]phenanthroline

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): 9.25 (s, 1 H, 2-H), 9.15 (s, 1 H, 9-H), 8.64 (dd, $^3$J=4.5 Hz, $^4$J=1.5 Hz, 2 H, 2', 6'-H), 8.45 (s, 1 H, 4-H), 8.29 (d, $J$=8.0 Hz, 1 H, 7-H), 7.88 (d, $J$=8.6 Hz, 1 H, 5-H), 7.82 (d, $J$=8.6 Hz, 1 H, 6-H), 7.67 (br. s, 1 H, 8-H), 7.48 (dd, $^3$J=4.5 Hz, $^4$J=1.5 Hz, 2 H, 3', 5'-H).

$^{13}$C NMR (100MHz, CD$_2$Cl$_2$): $\delta$=152.2, 150.9, 150.4, 146.3, 145.8, 139.1, 136.4, 130.9, 129.7, 128.1, 126.4, 125.9, 123.9, 118.7, 110.1, 91.0, 90.9.

**ESI-MS m/z (%):** 282.7 (100) [M+H]+
ESI-MS of 4.
ESI-MS of 3.
ESI-MS of 6a
ESI-MS of 6a and 5a in equilibrium.
ESI-MS of 6b
NMR of 4
Aromatic region of 6a

COSY of 6a
DOSY NMR

DOSY plot of 3

DOSY plot of 6a
DOSY plot of 6b