Electronic Supplementary Information for:

Heteropolymetallic copper(II)-gold(III) dithiocarbamate catenanes *via* magic ring synthesis

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Synthetic Procedures

Copper(II) dithiocarbamate macrocycles

The appropriate diamine compound was dissolved in MeCN (50 ml) and Et_3N (2 eq.) and CS_2 (2 eq.) were added. The mixture was then stirred for 10 min at room temperature and copper(II) acetate hexahydrate (1 eq.) was added. The resulting mixture was stirred at room temperature overnight and the resulting precipitate was collected by filtration. The residue was subsequently washed with MeCN (50 ml) followed by MeOH (50 ml) and finally diethyl ether (50 ml) to give the corresponding products.

(1): A black crystalline solid (1.1 g 51% yield) was collected. MS (ESI positive ion, CH_2Cl_2/MeOH): *m/z* 924 $[M]^+$. Anal. calcd. for $C_{36}H_{52}N_4S_8Cu_2$: C, 46.77; H, 5.67; N, 6.06. Found: C, 46.72; H, 5.65; N, 6.08.

(2): A brown solid (0.20 g, 25% yield) was collected. MS (ESI positive ion, CH_2Cl_2/MeOH): *m/z* 1024 $[M]^+$. Anal. calcd. for $C_{44}H_{56}N_4S_8Cu_2$: C, 51.58; H, 5.51; N, 5.47. Found: C, 52.11; H, 5.63; N, 5.46.

(3): A brown solid (0.55 g, 33% yield) was collected. MS (ESI positive ion, CH_2Cl_2/MeOH): *m/z* 1076 $[M]^+$. Anal. calcd. for $C_{48}H_{60}N_4S_8Cu_2$: C, 53.55; H, 5.62; N, 5.20. Found: C, 53.44; H, 5.61; N, 5.36.

(4) A brown solid (0.60 g, 36% yield) was collected. MS (ESI positive ion, CH_2Cl_2/MeOH): *m/z* 1076 $[M]^+$. Anal. calcd. for $C_{48}H_{60}N_4S_8Cu_2$: C, 53.55; H, 5.62; N, 5.20. Found: C, 54.98; H, 5.83; N, 5.21.

(5) A brown solid (0.50 g, 32% yield) was collected. MS (ESI positive ion, CH_2Cl_2/MeOH): *m/z* 1045 $[M]^+$. Anal. calcd. for $C_{40}H_{60}N_4O_4S_8Cu_2$: C, 45.95; H, 5.88; N, 5.36. Found: C, 45.60; H, 6.18; N, 5.36.

Transmetallation of copper(II) to gold(III) dtc macrocycles

The appropriate copper(II) dtc macrocycle (0.1 g, 1 eq.) was dissolved in CH_2Cl_2 (50 ml) and MeCN (20 ml) was added. Sodium tetrachloroaurate (0.09g, 2.1 eq.) in MeCN (5 ml) was then added to the solution and the reaction mixture stirred at room temperature overnight. The solvent was removed under vacuum and the resultant residue redissolved in DMF (2 ml). Any insoluble solid was removed by filtration, then a saturated solution of ammonium tetrafluoroborate was added to the filtrate to give a yellow precipitate. The precipitate was collected by filtration and washed with water (10 ml) followed by methanol (10 ml) and diethyl ether (10 ml) and dried to give the product.

(6): A yellow solid (0.20 g, 80% yield) was collected. ^{1}H NMR (300MHz, DMSO) δ = 7.43 (m, 8H, ArH), 5.10 (s, 8H, $ArCH_2$), 3.71 (t, *J*=7.8, 8H, $N\underline{CH_2}CH_2$), 1.60 (m, 8H, $NCH_2C\underline{H_2}$), 1.27 (m, 8H, $C\underline{H_2}CH_3$), 0.86 (m, 12H, CH_3). MS (ESI positive ion, MeCN): *m/z* 595 $[M]^{2+}$. Anal. calcd. for $C_{36}H_{52}N_4S_8Au_2.2BF_4$: C, 31.68; H, 3.84; N, 4.10. Found: C, 31.62; H, 3.75; N, 4.05.

(7): A yellow solid (0.10 g, 60% yield) was collected. ^{1}H NMR (300MHz, DMSO) δ = 8.06 (d, *J*=8.5, 4H, ArH), 8.03 (s, 4H, ArH), 8.56 (d, *J*=8.5, 4H, ArH), 5.24 (s, 8H, $ArCH_2$), 3.77 (t, *J*=7.5, 8H, $NC\underline{H_2}CH_2$), 1.63 (m, 8H, $NCH_2C\underline{H_2}$), 1.28 (m, 8H, $C\underline{H_2}CH_3$), 0.82 (t, *J*=7.0, 12H, CH_3). ^{13}C NMR (75.43MHz, DMSO) δ = 190.2 (CS_2), 132.5, 130.6, 128.9, 127.9, 126.7 (ArC), 54.6, 52.1, 28.3, 19.3 (CH_2), 13.4 (CH_3). MS (ESI positive ion, MeCN): *m/z* 645 $[M]^{2+}$. Anal. calcd. for $C_{44}H_{56}N_4S_8Au_2.2AuCl_4$: C, 26.84; H, 2.87; N, 2.85. Found: C, 28.68; H, 2.80; N, 3.02.

(8): A yellow solid (0.11 g, 66% yield) was collected. ^{1}H NMR (300MHz, DMSO) δ = 7.73 (d, *J*=8.1, 4H, ArH), 7.67 (s, 4H, ArH), 7.56 (t, *J*=7.8, 4H, ArH), 7.43 (d, *J*=8.1, 4H, ArH), 5.14 (s, 8H, $ArCH_2$), 3.77 (t, *J*=7.2, 8H, $NC\underline{H_2}CH_2$), 1.64 (m, 8H, $NCH_2C\underline{H_2}$), 1.30 (m, 8H, $C\underline{H_2}CH_3$), 0.84 (t, *J*=7.5, 12H, CH_3). MS (ESI positive ion, MeCN): *m/z* 671 $[M]^{2+}$. Anal. calcd. for $C_{48}H_{60}N_4S_8Au_2.2BF_4$: C, 38.00; H, 3.99; N, 3.69. Found: C, 37.85; H, 3.95; N, 3.60.

(9) (R = butyl): A yellow solid (0.12 g, 72% yield) was collected. ^{1}H NMR (300MHz, DMSO) δ = 7.74 (d, *J*=8.1, 8H, ArH), 7.48 (d, *J*=8.1, 4H, ArH), 5.11 (8H, s, ArCH$_2$), 3.74 (t, *J*=7.8, 8H, NC$\underline{H_2}$CH$_2$), 1.65 (m, 8H, NCH$_2$C$\underline{H_2}$), 1.30 (m, 8H, C$\underline{H_2}$CH$_3$), 0.85 (t, *J*=7.5, 12H, CH$_3$). ^{13}C NMR (75.43MHz, DMSO) δ = 189.8 (CS$_2$), 139.7, 131.7, 129.4, 128.9, 127.8, 127.4 (ArC), 54.3, 52.0, 28.3, 19.4 (CH$_2$), 13.5 (CH$_3$). MS (ESI positive ion, MeCN): *m/z* 671 [M]$^{2+}$. Anal. calcd. for $C_{48}H_{60}N_4S_8Au_2.2BF_4$: C, 38.00; H, 3.99; N, 3.69. Found: C, 37.50; H, 3.82; N, 3.55.

(10) (R = butyl): A yellow solid (0.10 g, 60% yield) was collected. ^{1}H NMR (300MHz, DMSO) δ = 6.89 (s, 8H, ArH), 4.28 (t, *J*=4.5, 8H, -O$\underline{CH_2}$CH$_2$N-), 4.15 (t, *J*=4.5, 8H, -OCH$_2$$\underline{CH_2}$N-), 3.82 (t, *J*=7.8, 8H, NC$\underline{H_2}$CH$_2$), 1.68 (m, 8H, NCH$_2$C$\underline{H_2}$), 1.32 (m, 8H, C$\underline{H_2}$CH$_3$), 0.88 (t, *J*=7.5, 12H, CH$_3$). ^{13}C NMR (75.43MHz, DMSO) δ = 190.1 (CS$_2$), 152.1, 115.6 (ArC), 64.2, 51.8, 51.1, 28.3, 19.4 (CH$_2$), 13.5 (CH$_3$). MS (ESI positive ion, MeCN): *m/z* 655 [M]$^{2+}$. Anal. calcd. for $C_{40}H_{60}N_4O_4S_8Au_2.2BF_4$: C, 32.35; H, 4.07; N, 3.77. Found: C, 30.45; H, 3.80; N, 3.65.

Copper(II)-gold(III) dithiocarbamate [2]catenane (11)

A solution of copper(II) macrocycle **(2)** (50 mg, 1 eq.) in dichloromethane (25 ml) and a solution of gold(III) macrocycle **(7)** (96 mg, 1 eq.) in DMF (25 ml) were mixed together and stirred at room temperature for 2 h. The solvent volume was subsequently reduced to 5 ml *in vacuo*, then an aqueous saturated solution of ammonium tetrafluoroborate (5 ml) was added. The resulting precipitate was collected by filtration, washed with water (10 ml) and air-dried to give a brown powder (0.1 g, 84% yield).

MS (ESI positive ion, MeCN): *m/z* 1158 [M]$^{2+}$. Anal. calcd. for $C_{88}H_{112}N_8S_{16}Cu_2Au_2.2BF_4.4H_2O$: C, 41.26; H, 4.72; N, 4.37. Found: C, 41.12; H, 4.54; N, 4.04.

References

1. P. D. Beer, N. Berry, M. G. B. Drew, O. D. Fox, M. E. Padilla-Tosta and S. Patell, *Chem. Commun.*, 2001, 199.
2. N. G. Berry, M. D. Pratt, O. D. Fox and P. D. Beer, *Supramolecular Chemistry*, 2001, **13**, 677.

Conditions for cyclic voltammetric studies: Solvent = CH_2Cl_2/MeCN (1:1) with 0.1M $TBABF_4$ as the supporting electrolyte and Ag/$AgNO_3$ reference electrode, sample concentration $2x10^{-4}$M. Scan rate 10 mVs^{-1}, T= 293 K. Ferrocene reference: $E_{1/2}$ = 0.19 V and ΔE = 78 mV. Electrochemical potentials are quoted with errors of ± 10 mV.