Supplementary Material (ESI) for Chemical Communications

Supporting Information

A Metal-Complex-Tolerant CuAAC 'Click' Protocol Exemplified Through the Preparation of Homo- and Mixed-Metal-Coordinated [2]Rotaxanes

Diego González Cabrera, Bryan D. Koivisto and David A. Leigh*

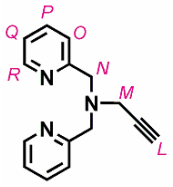
School of Chemistry, University of Edinburgh, The King's Buildings, West Mains Road, Edinburgh EH9 3JJ, UK.
Fax: +44 131 650 6453; Tel: +44 131 650 4721; E-mail: David.Leigh@ed.ac.uk

General Experimental Procedures

Prior to use, isophthaloyl dichloride was purified by recrystallization from hexane; p-xylylenediamine was purified by distillation under reduced pressure; triethylamine was dried by distillation over calcium hydride, then stored over 4 Å molecular sieves. Chloroform ($CHCl_3$) and tetrahydrofuran (THF) solvents were analytical grade, without stabilizer; dry acetonitrile, chloroform, dichloromethane, *N*,*N*-dimethylformamide (DMF), methanol, tetrahydrofuran and toluene were obtained by passing these solvents through activated alumina columns on a PureSolvTM solvent purification system (Innovative Technologies, Inc., MA). Unless stated otherwise, all other reagents were purchased from commercial sources and used without further purification. Saturated Na_4EDTA solutions were approximately 4.0 M. Column chromatography was carried out using Kiesegel C60 (Fisher Scientific) as the stationary phase. Preparative thin-layer chromatography (TLC) was performed on glass-backed plates pre-coated with silica 60 F254 adsorbent (20 cm × 20 cm, with concentration zone, 0.25 mm thick, Fluka) and analytical TLC was performed on aluminium-backed sheets pre-coated with silica 60 F254 adsorbent (0.25 mm thick, Merck, Germany) and visualized under UV light. Size exclusion chromatography was performed using Toyopearl HW-405 (Tosoh, Japan) with methanol/chloroform in a

1:1 v/v ratio as the eluent. ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz on a Bruker AV 400 instrument. Spectra were recorded at ambient temperature, unless otherwise stated. Chemical shifts (δ) are reported in parts per million from low to high field and referenced to residual solvent. Standard abbreviations indicating multiplicity are used as follows: br s = broad, d = doublet, m = multiplet, q = quartet, quint. = quintet, s = singlet, t = triplet. In many cases [D_7]-*N*,*N*-dimethylformamide was used as a solvent and the ^{1}H was referenced to 2.935 ppm for the downfield methyl signal. ^{13}C was reference to the amide carbon triplet at 163.15. Fast atom bombardment (FAB) and electron impact (EI) mass spectrometry was carried out by the services at the University of Edinburgh.

_N_,_N_-bis(pyridin-2-ylmethyl)prop-2-yn-1-amine (1)

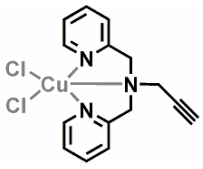


To a stirred solution of bis(2-picolyl)amine (BPA) (3.0 g, 15.0 mmol) in toluene (150 mL) were added propargyl bromide (80% in toluene) (2.0 mL, 15.3 mmol) and triethylamine (2.2 mL, 15.3 mmol). The reaction was heated to reflux for 24 h during which time a solid precipitated. The reaction mixture was filtered, concentrated under reduced pressure, and purified using column chromatography on silica gel using dichloromethane/acetonitrile/NH_4OH (aq) in a 5:5:0.1 v/v ratio as eluent. Yield 2.6 g (73%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (d, J = 4.8 Hz, 2H, H_R), 7.62 (dt, J = 7.7 Hz and J = 1.8 Hz, 2H, H_P), 7.47 (d, J = 7.8 Hz, 2H, H_O), 7.12 (ddd, J = 7.3 Hz, J = 5.0 Hz and J = 1.0 Hz, 2H, H_Q), 3.88 (s, 4H, H_N), 3.38 (d, J = 2.3 Hz, 2H, H_M), 2.27 (t, J = 2.4 Hz, 1H, H_L); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.7, 149.2, 136.6, 123.2, 122.2, 78.3, 73.7, 59.4, 42.6; HRMS (FAB, 3-NOBA matrix): m/z = 238.1348 [$(M+H)^+$] (anal. calcd for $C_{15}H_{16}N_3^+$: m/z = 238.1339).

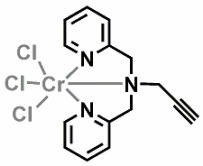
General Procedure for the formation of [1MX_n]

To a solution of **1** (1.0 g, 4.2 mmol) in methanol (10 mL) was added a saturated solution of the metal chloride salt (1.1 eq) in methanol. The reaction mixture was

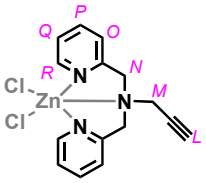
stirred for 1 h during which time a solid precipitated. The precipitate was collected under filtration and the resulting solid dried in air.



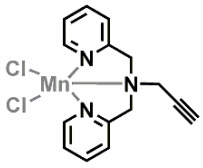
***N*,*N*-bis(pyridin-2-ylmethyl)prop-2-yn-1-amine copper (II) dichloride [1**$CuCl_2$**] -** *$CuCl_2 \cdot 2H_2O$;* green-blue solid, yield 1.5 g (95%); mp 143 °C (decomp); FT-IR (KBr): 3249 (m, *C-*H_{alkyne}), 2106 (m, *C-*C_{alkyne}), cm^{-1}; λ_{max} (CH_2Cl_2:MeOH [1:1]) ($\varepsilon(M^{-1}cm^{-1})$): 707 nm ($1.65\times10^2$); HRMS (FAB, 3-NOBA matrix): *m/z* = 335.0248 $[(M\text{-}Cl)^+]$ (anal. calcd for $C_{15}H_{15}ClCuN_3^+$: *m/z* = 335.0251).



***N*,*N*-bis(pyridin-2-ylmethyl)prop-2-yn-1-amine chromium (III) trichloride [1**$CrCl_3$**] -** *$CrCl_3(THF)_3$*; green solid, yield 1.6 g (95%); mp 255 °C (decomp); FT-IR (KBr): 3272 (m, *C-*H_{alkyne}), 2119 (m, *C-*C_{alkyne}), cm^{-1}; λ_{max} (CH_2Cl_2:MeOH [1:1]) ($\varepsilon(M^{-1}cm^{-1})$): 454 nm ($1.90\times10^2$), 622 nm ($1.25\times10^2$); HRMS (FAB, 3-NOBA matrix): *m/z* = 393.9859 $[M^+]$ (anal. calcd for $C_{15}H_{15}Cl_3CrN_3^+$: *m/z* = 393.9737).

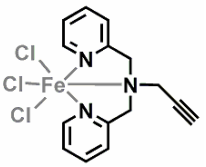


***N*,*N*-bis(pyridin-2-ylmethyl)prop-2-yn-1-amine zinc (II) dichloride [1**$ZnCl_2$**] -** *$ZnCl_2 \cdot Et_2O$;* cream white solid, yield 1.4 g (88%); mp 210 °C (decomp); ^{1}H NMR (400 MHz, [D_7]*N*,*N*-dimethylformamide): δ = 9.16 (d, *J* = 4.2 Hz, 2H, H_R), 8.20 (t, *J* = 7.4 Hz, 2H, H_P), 7.78 (d, *J* = 8 Hz, 2H, H_O), 7.75 (t, 2H, H_Q), 4.32 (br s, 4H, H_N), 3.54 (s, 2H, H_M), 3.50 (s, 1H, H_L); ^{13}C NMR (100 MHz, [D_7]*N*,*N*-dimethylformamide): δ = 155.5, 150.1, 141.8, 125.7, 125.6, 78.6, 77.2, 56.6, 43.1; LRMS (ESI-MS, MeOH): *m/z* = 336 $[(M\text{-}Cl)^+]$.

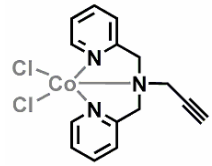


***N*,*N*-bis(pyridin-2-ylmethyl)prop-2-yn-1-amine manganese (II) dichloride [1**$CuCl_2$**] -** *$MnCl_2 \cdot 4H_2O$;* cream solid, yield 1.3 g (83%); mp 251 °C; (decomp) FT-IR (KBr): 3242 (m, *C-*H_{alkyne}), 2110 (m, *C-*C_{alkyne}), cm^{-1}; λ_{max} (CH_2Cl_2:MeOH [1:1]) ($\varepsilon(M^{-1}cm^{-1})$): no absorptions in the visible spectrum; HRMS (FAB, 3-NOBA matrix): *m/z* = 327.0302 $[(M\text{-}Cl)^+]$ (anal. calcd for $C_{15}H_{15}Cl_3MnN_3^+$: *m/z* = 327.0335).

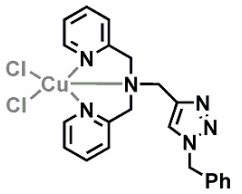
***N*,*N*-bis(pyridin-2-ylmethyl)prop-2-yn-1-amine iron (III) trichloride [1**$FeCl_3$**]** - *$FeCl_3 \cdot 6H_2O$*; yellow solid, yield 1.5 g (91%); mp 162 °C (decomp); FT-IR (KBr): 3270 (m, *C*-H_{alkyne}), 2117 (m, *C*-C_{alkyne}) cm^{-1}; λ_{max} (CH_2Cl_2:MeOH [1:1]) ($\varepsilon(M^{-1}cm^{-1})$): 384 nm ($8.40\times10^2$); LRMS (ESI-MS, MeOH): *m/z* = 363 $[(M\text{-}Cl)^+]$.



***N*,*N*-bis(pyridin-2-ylmethyl)prop-2-yn-1-amine cobalt (II) dichloride [1**$CoCl_2$**]** - *$CoCl_2 \cdot 6H_2O$;* yield 1.4 g (86%); mp 234 °C (decomp); FT-IR (KBr): 3240 (m, *C*-H_{alkyne}), 2113 (m, *C*-C_{alkyne}) cm^{-1}; λ_{max} (CH_2Cl_2:MeOH [1:1]) ($\varepsilon(M^{-1}cm^{-1})$): 548 nm ($1.40\times10^2$), 628 nm ($1.00\times10^2$); HRMS (FAB, 3-NOBA matrix): *m/z* = 331.0292 $[(M\text{-}Cl)^+]$ (anal. calcd for $C_{15}H_{15}Cl_3MnN_3^+$: *m/z* = 331.0287).

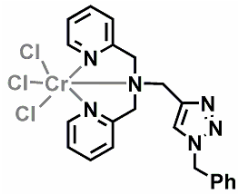


***N*-((1-benzyl-1H-1,2,3-triazol-4-yl)methyl)(pyridin-2-yl)-*N*-(pyridin-2-ylmethyl)-methanamine copper (II) dichloride [2**$CuCl_2$**]**



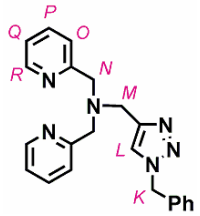
To a solution of benzyl azide (50 mg, 0.38 mmol), [**1**$CuCl_2$] (154 mg, 0.41 mmol) and *N*,*N*-disopropylethylamine (0.07 mL, 0.38 mmol) in dichloromethane/methanol in a 9:1 v/v ratio (10 mL) was added $Cu(CH_3CN)_4PF_6$ (21 mg, 0.06 mmol). The resulting mixture was stirred for 12 h. The reaction mixture was concentrated under reduced pressure. To the residue was added acetone (5 mL) and the resulting suspension collected under filtration and the resulting solid washed with acetone (5 mL). Yield 171 mg (90%); mp 133 °C (decomp); FT-IR (KBr): 3112 (m, *C*-$H_{triazole}$), 1611 (s, *C*=$C_{triazole}$) cm^{-1}; λ_{max} (CH_2Cl_2:MeOH [1:1]) ($\varepsilon(M^{-1}cm^{-1})$): 713 nm ($1.70\times10^2$); HRMS (FAB, 3-NOBA matrix): *m/z* = 468.0894 $[(M\text{-}Cl)^+]$ (anal. calcd for $C_{22}H_{22}ClCuN_6^+$: *m/z* = 468.0890).

_N_-((1-benzyl-1H-1,2,3-triazol-4-yl)methyl)(pyridin-2-yl)-_N_-(pyridin-2-ylmethyl)-methanamine chromium (III) trichloride [2$CrCl_3$**]**



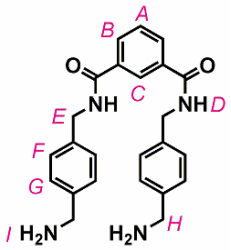
The synthesis of [**2**$CrCl_3$] was similar to that described for [**2**$CuCl_2$] except that [**1**$CrCl_3$] (210 mg, 0.41 mmol) was used. The reaction mixture was concentrated under reduced pressure. To the residue was added acetone (5 mL) and the resulting suspension collected under filtration and the resulting solid washed with acetone (5 mL). Yield 189 mg (95%); mp 211 °C (decomp); FT-IR (KBr): 3114 (m, *C-H*$_{triazole}$), 1610 (s, *C*=*C*$_{triazole}$) cm^{-1}; λ_{max} (CH_2Cl_2:MeOH [1:1]) ($\varepsilon(M^{-1}cm^{-1})$): 451 nm ($1.85\times10^2$), 620 nm ($1.20\times10^2$); HRMS (FAB, 3-NOBA matrix): *m/z* = 492.0683 [(M-Cl)$^+$] (anal. calcd for $C_{22}H_{22}Cl_2CrN_6^+$: *m/z* = 492.0688).

_N_-((1-benzyl-1H-1,2,3-triazol-4-yl)methyl)(pyridin-2-yl)-_N_-(pyridin-2-ylmethyl)methanamine (2)



A solution of [**2**$CuCl_2$] (100 mg, 0.20 mmol) in $CHCl_3$/isopropanol in a 3:1 v/v ratio (25mL) was washed with saturated aqueous Na_4EDTA (3 x 10 mL) and saturated aqueous sodium chloride (2 x 10 mL), dried ($MgSO_4$) and concentrated under reduced pressure to give a yellow oil. Yield 64 mg (87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (d, *J* = 4.1 Hz, 2H, H_R), 7.62 (dt, *J* = 7.7 Hz and *J* = 1.8 Hz, 2H, H_P), 7.52 (d, *J* = 7.8 Hz, 2H, H_O), 7.50 (s, 1H, H_L), 7.37-7.21 (m, 5H, H_{Ph}), 7.12 (ddd, *J* = 7.3 Hz, *J* = 5.0 Hz, and *J* = 1.0 Hz, 2H, H_Q), 3.85 (s, 2H, H_M), 3.82 (s, 4H, H_N); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2, 149.0, 144.7, 136.4, 134.8, 129.0, 128.6, 127.9, 123.2, 122.9, 122.2, 59.6, 54.0, 48.6; HRMS (FAB, 3-NOBA matrix): *m/z* = 371.1984 [(M+H)$^+$] (anal. calcd for $C_{22}H_{33}N_6^+$: *m/z* = 371.1984).

N^1,N^3-bis(4-(aminomethyl)benzyl)isophthalamide (5)



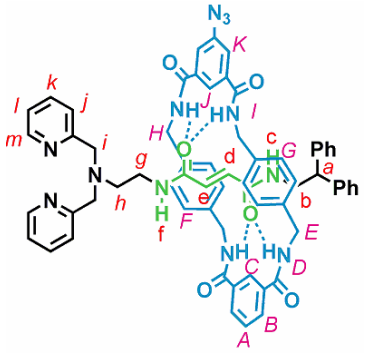
To a suspension of [4-({3-[4-(tert-butoxycarbonylamino-methyl)-benzylcarbamoyl]-benzoylamino}-methyl)-benzyl]-carbamic acid tert-butyl ester (**6**) (4.2 g, 6.94 mmol) in $CHCl_3$ (150 mL) was added trifluoroacetic acid (5.2 mL, 69.41 mmol). The pale yellow solution was stirred vigorously for 12 h. The reaction mixture was concentrated under pressure to give a pale yellow solid. The resulting powder was stirred with Amberlyst A-21 resin in a dichoromethane/methanol 1:1 v/v ratio (150 mL) for 1 h. The solvent was removed under pressure to yield a hygroscopic powder 2.8 g, (100%); ^{1}H NMR (400 MHz, [D_6]dimethylsulfoxide): δ = 9.31 (t, *J* = 6.8 Hz, 2H, H_D), 8.44 (s, 1H, H_C), 8.06 (dd, *J* = 7.8 Hz and *J* = 1.4 Hz, 2H, H_B), 7.58 (t, *J* = 7.7 Hz, 1H, H_A), 7.40 (d, *J* = 8.0 Hz, 4H, H_F), 7.36 (d, *J* = 8.0 Hz, 4H, H_G), 5.40 (br s, 4H, H_I), 4.50 (d, *J* = 5.1 Hz, 4H, H_E), 3.95 (s, 4H, H_H); ^{13}C NMR (100 MHz, [D_7]*N*,*N*-dimethylformamide): δ = 167.0, 141.2, 135.7, 133.7, 130.9, 129.9, 128.6, 127.2, 43.7, 43.6; HRMS (FAB, 3-NOBA matrix): *m/z* = 403.2134 [$(M+H)^+$] (anal. calcd for $C_{24}H_{27}N_4O_2^+$: *m/z* = 403.2134).

[4-({3-[4-(tert-Butoxycarbonylamino-methyl)-benzylcarbamoyl]-benzoylamino}-methyl)-benzyl]-carbamic acid tert-butyl ester (6)

1-(*N*-Boc-aminomethyl)-4-(aminomethyl)benzene (5.0 g, 21.2 mmol) and triethylamine (7.4 mL, 53.1 mmol) in $CHCl_3$ (150 mL) were cooled to 0 ^{o}C. Isophthaloyl chloride (2.2 g, 10.6 mmol) was dissolved in $CHCl_3$ (75mL) and added to the reaction mixture dropwise over 1 h. The reaction mixture was allowed to warm

to room temperature and was stirred for a further 12 h during which time a solid precipitated. The precipitate was collected under filtration and the resulting solid washed with diethyl ether. Yield 5.2 g (81%); mp 188-190 °C; ^{1}H NMR (400 MHz, [D$_6$]dimethylsulfoxide): δ = 9.17 (t, *J* = 6.0 Hz, 2H, H$_D$), 8.42 (s, 1H, H$_C$), 8.03 (dd, *J* = 7.7 Hz and *J* = 1.7 Hz, 2H, H$_B$), 7.57 (t, *J* = 7.7 Hz, 1H, H$_A$), 7.38 (t, *J* = 6.0 Hz, 2H, H$_I$), 7.28 (d, *J* = 8.1 Hz, 4H, H$_F$), 7.19 (d, *J* = 8.1 Hz, 4H, H$_G$), 4.47 (d, *J* = 6.0 Hz, 4H, H$_E$), 4.10 (d, *J* = 6.0 Hz, 4H, H$_H$), 1.39 (s, 18H, H$_{Boc}$); ^{13}C NMR (100 MHz, [D$_6$]dimethylsulfoxide): δ = 165.8, 155.8, 137.9, 134.6, 129.9, 128.4, 127.2, 126.9, 126.3, 77.7, 43.1, 42.5, 28.2; HRMS (FAB, 3-NOBA matrix): *m/z* = 603.3178 [(M+H)$^+$] (anal. calcd for $C_{34}H_{43}N_4O_6^+$: *m/z* = 603.3183).

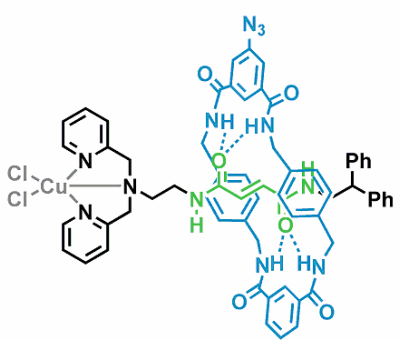
([2](azido-1,7,14,20-Tetraaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetrabenzocyclohexacosane)-(*N*^{1}-(2-(bis(pyridine-2-ylmethyl)amino)ethyl)-*N*^{4}-(2,2-diphenylethyl)fumaramide) rotaxane (7)



To a suspension of **4** (0.3 g, 0.58 mmol), **5** (2.8 g, 6.93 mmol) and triethylamine (2.4 mL, 17.3 mmol) in $CHCl_3$ (200mL) was added a solution of 5-azidoisophthaloyl chloride (1.7 g, 6.93 mmol) in $CHCl_3$ (50 mL) *via* motor-driven syringe pump over a period of 4-6 h. The reaction mixture was stirred for a further 12 h. The resulting precipitate was filtered over celite and the solution washed with saturated aqueous sodium hydrogen carbonate (3 x 20 mL) and saturated aqueous sodium chloride (2 x 20 mL), dried ($MgSO_4$) and concentrated under reduced pressure. The remaining residue was subjected to column chromatography on silica gel using dichloromethane/methanol/NH_4OH (aq) in a 9.6:0.4:0.01 v/v ratio as eluent to yield [2]rotaxane. Yield 0.3 g (52%); mp 196 °C (decomp); ^{1}H NMR (400 MHz, [D$_7$]*N*,*N*-dimethylformamide): δ = 8.95 (t, *J* = 5.5 Hz, 1H, H$_c$), 8.79 (t, *J* = 5.5 Hz, 1H, H$_f$), 8.77 (s, 1H, H$_C$), 8.59 (s, 1H, H$_J$), 8.49 (d, *J* = 5.8 Hz, 2H, H$_m$), 8.18 (dd, *J* = 7.7 Hz and *J* = 1.5 Hz, 2H, H$_B$), 8.12 (t, *J* = 5.5 Hz, 2H, H$_I$), 8.07 (t, *J* = 5.0 Hz, 2H, H$_D$), 7.80

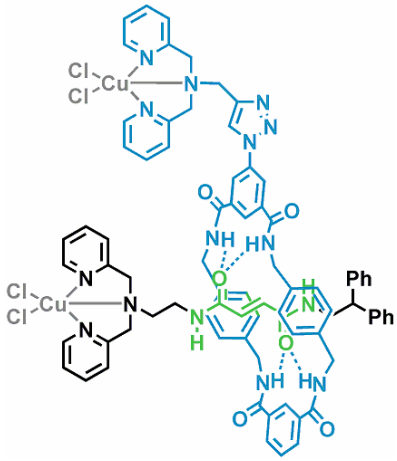
(d , J = 1.2 Hz, 2H, H_K), 7.74 (t, J = 7.7 Hz, 1H, H_A), 7.72 (dt, J = 7.7 Hz and J = 1.8 Hz, 2H, H_k), 7.52 (d, J = 7.8 Hz, 2H, H_j), 7.37-7.31 (m, 10H, H_{Ph}), 7.26-7.20 (m, 2H, H_l), 7.02 (s, 8H, H_F & H_G), 5.94 (s, 2H, H_d & H_e), 4.47-4.37 (m, 8H, H_E & H_H), 4.26 (t, J = 7.8Hz, 1H, H_a), 3.93 (dd, J = 7.8 Hz and J = 2.3 Hz, 2H, H_b), 3.82 (s, 4H, H_i), 3.37 (dd, J = 14.0 Hz and J = 6.0 Hz, 2H, H_g), 2.69 (t, J = 7.7 Hz, 2H, H_h); ^{13}C NMR (100 MHz, [D_7]*N*,*N*-dimethylformamide): δ = 167.1, 166.8, 166.7, 165.7, 150.0, 143.9, 142.2, 138.4, 138.0, 137.5, 137.4, 135.5, 132.0, 131.1, 131.0, 130.1, 130.1, 129.7, 129.2, 129.1, 127.7, 125.8, 124.0, 123.2, 122.4, 122.1, 60.8, 53.5, 51.5, 45.1, 44.6, 44.5, 38.8; HRMS (FAB, 3-NOBA matrix): *m/z* = 1093.4814 [$(M+H)^+$] (anal. calcd for $C_{64}H_{61}N_{12}O_6^+$: *m/z* = 1093.4837).

([2](azido-1,7,14,20-Tetraaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetrabenzocyclohexacosane)-(N^1-(2-(bis(pyridine-2-ylmethyl)amino)ethyl)-N^4-(2,2-diphenylethyl)fumaramide) copper (II) dichloride rotaxane [**7**(*thread*-$CuCl_2$)]



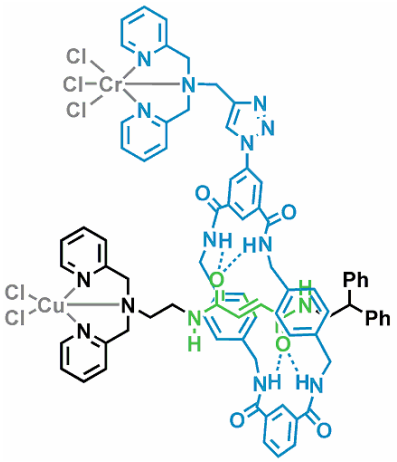
To a solution of rotaxane **7** (200 mg, 0.18 mmol) in methanol (20 mL) was added a saturated solution of $CuCl_2 \cdot 2H_2O$ (34 mg, 0.20 mmol) in methanol (1 mL). The reaction mixture was stirred for 1h during which time a solid precipitated. The precipitate was collected under filtration and the resulting solid washed with methanol. Yield 213 mg (95%); mp 213 ^{o}C (decomp); FT-IR (KBr): 3443 (br s, *N*-H_{amide}), 3307 (br s, *N*-H_{amide}), 2115 (s, $N{=}N_{azide}$) cm^{-1}; λ_{max} (CH_2Cl_2:MeOH [1:1]) (ε($M^{-1}cm^{-1}$)): 708 nm (1.60×10^2); HRMS (FAB, 3-NOBA matrix): *m/z* = 1190.3710 [$(M-Cl)^+$] (anal. calcd for $C_{64}H_{60}ClCuN_{12}O_6^+$: *m/z* = 1190.3743).

([2]({1H-1,2,3-triazol-4-yl-*N*,*N*-bis(pyridine-2-yl methyl)methanamine copper (II) dichloride}-1,7,14,20-tetraaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetrabenzocyclohexacosane)-(N^1-(2-(bis(pyridine-2-ylmethyl)amino)ethyl)-N^4-(2,2-diphenylethyl)fumaramide) copper (II) dichloride rotaxane [**3**(*mac*-$CuCl_2$)(*thread*-$CuCl_2$)]



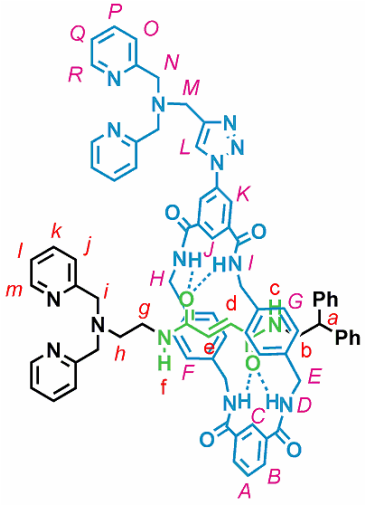
To a solution of [**7**(*thread*-$CuCl_2$)] (100 mg, 0.08 mmol), [**1**$CuCl_2$] (36 mg, 0.10 mmol) and *N*,*N*-disopropylethylamine (0.01 mL, 0.08 mmol) in dichloromethane/methanol in a 9:1 v/v ratio (10 mL) was added $Cu(CH_3CN)_4PF_6$ (5 mg, 0.01 mmol). The resulting mixture was stirred for 12 h. The reaction mixture was concentrated under reduced pressure. To the residue was added acetone (10 mL) and the precipitate collected under filtration and the resulting solid washed with acetone (5 mL). Yield 104 mg (80%); mp 210 °C (decomp); FT-IR (KBr): 3290 (br s, *N*-H_{amide}) cm^{-1}; λ_{max} (CH_2Cl_2:MeOH [1:1]) ($\varepsilon(M^{-1}cm^{-1})$): 713 nm ($3.50\times10^2$); HRMS (FAB, 3-NOBA matrix): *m/z* = 1560.1284 [$(M\text{-}Cl)^+$] (anal. calcd for $C_{79}H_{75}Cl_3Cu_2N_{15}O_6^+$: *m/z* = 1560.3682).

([2]({1H-1,2,3-triazol-4-yl-*N*,*N*-bis(pyridine-2-yl-methyl)methanamine chromium (III) trichloride}-1,7,14,20-Tetraaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetrabenzocyclohexacosane)-(*N*^{1}-(2-(bis(pyridine-2-ylmethyl)amino)ethyl)-*N*^{4}-(2,2-diphenylethyl)fumaramide) copper (II) dichloride rotaxane [**3**(*mac*-$CrCl_3$)(*thread*-$CuCl_2$)]



To a solution of [**7**(*thread*-$CuCl_2$)] (100 mg, 0.08 mmol), [**1**$CrCl_3$] (39 mg, 0.10 mmol) and *N*,*N*-disopropylethylamine (0.01 mL, 0.08 mmol) in dichloromethane/methanol in a 9:1 v/v ratio (10 mL) was added $Cu(CH_3CN)_4PF_6$ (5 mg, 0.01 mmol). The resulting mixture was stirred for 12 h. The reaction mixture was concentrated under reduced pressure. To the residue was added acetone (10 mL), the precipitate collected under filtration, and the resulting solid washed with acetone (5 mL). Yield 106 mg (82%); mp 220 °C (decomp); FT-IR (KBr): 3272 (br s, *N*-H_{amide}), 2115 (s, $N{=}N_{azide}$) cm^{-1}; λ_{max} (CH_2Cl_2:MeOH [1:1]) ($\varepsilon(M^{-1}cm^{-1})$): 449 nm ($2.20\times10^2$), 625 nm ($1.25\times10^2$), 724 nm ($1.70\times10^2$); HRMS (FAB, 3-NOBA matrix): *m/z* = 1584.8869 $[(M\text{-}Cl)^+]$ (anal. calcd for $C_{79}H_{75}Cl_4CrCuN_{15}O_6^+$: *m/z* = 1584.3480).

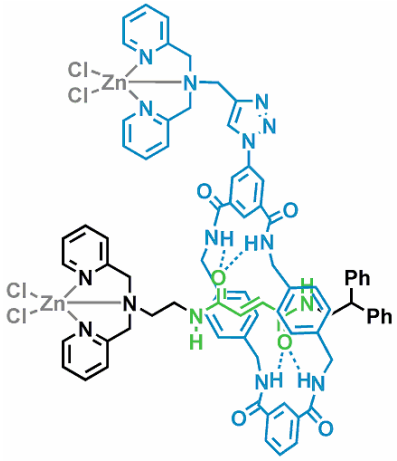
([2]({1H-1,2,3-triazol-4-yl-*N*,*N*-bis(pyridine-2-yl-methyl)methanamine}-1,7,14,20-Tetraaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetrabenzocyclohexacosane)-(N^1-(2-(bis(pyridine-2-ylmethyl)amino)ethyl)-N^4-(2,2-diphenylethyl)fumaramide)rotaxane (3)



A solution of [**3**(*mac*-$CuCl_2$)(*thread*-$CuCl_2$)] (125 mg, 0.08 mmol) in $CHCl_3$/isopropanol in a 3:1 v/v ratio (15 mL) was washed with saturated aqueous Na_4EDTA (3 x 10 mL) and saturated aqueous sodium chloride (2 x 10 mL), dried ($MgSO_4$) and concentrated under reduced pressure to give a yellow oil. The remaining residue was subjected to column chromatography on silica gel using dichloromethane/acetonitrile/NH_4OH (aq) in a 5:5:0.2 v/v ratio as eluent. Yield 75 mg (72 %). ^{1}H NMR (400 MHz, [D_7]*N*,*N*-dimethylformamide): δ = 9.25 (s, 1H, H_L), 8.95 (t, *J* = 5.2 Hz, 1H, H_c), 8.86 (s, 1H, H_J), 8.79 (t, *J* = 5.5Hz, 1H, H_f), 8.78 (s, 1H, H_C), 8.71 (s, 2H, H_K), 8.58 (d, *J* = 4.7 Hz, 2H, H_R), 8.48 (d, *J* = 4.1 Hz, 2H, H_m), 8.22 (s, 2H, H_I), 8.19 (dd, *J* = 7.7 Hz and *J* = 1.4 Hz, 2H, H_B), 8.08 (s, 2H, H_D), 7.87-7.80 (m, 2H, H_O & H_P), 7.75 (t, *J* = 7.7 Hz, 1H, H_A), 7.71 (dt, *J* = 7.7 Hz and *J* = 1.8 Hz, 2H, H_k), 7.51 (d , *J* = 7.7 Hz, 2H, H_j), 7.37-7.29 (m, 10H, H_Q & H_{Ph}), 7.23-7.19 (m, 4H, H_l & H_{Ph}), 7.05 (d, *J* = 9.0 Hz, 4H, H_G), 7.03 (d, *J* = 9.0 Hz, 4H, H_F), 5.97 (s, 2H, H_d & H_e), 4.52-4.40 (m, 8H, H_E & H_H), 4.26 (t, *J* = 7.8 Hz, 1H, H_a), 4.03 (s, 2H, H_M), 3.97 (s, 4H, H_N), 3.94 (t, *J* = 7.5 Hz, 2H, H_b), 3.83 (s, 4H, H_i), 3.40-3.37 (m, 2H, H_g), 2.71 (t, *J* = 6.7 Hz, 2H, H_h); ^{13}C NMR (100 MHz, [D_7]*N*,*N*-dimethylformamide): δ = 167.1, 166.9, 166.7, 165.6, 160.7, 160.4, 150.1, 150.0, 147.1, 143.9, 139.1, 138.4, 138.0, 137.6, 137.4 (x2), 135.5, 132.0, 131.1, 131.0, 130.1 (x2), 129.6 (x2), 129.2,

129.0, 127.7, 125.8, 125.4, 123.9 (x2), 123.2, 123.0, 60.8, 60.6, 53.5, 51.5, 49.8, 45.1, 44.7, 44.5, 38.8; HRMS (FAB, 3-NOBA matrix): *m/z* = 1330.6064 [$(M+H)^+$] (anal. calcd for $C_{79}H_{76}N_{15}O_6^+$: *m/z* = 1330.6103).

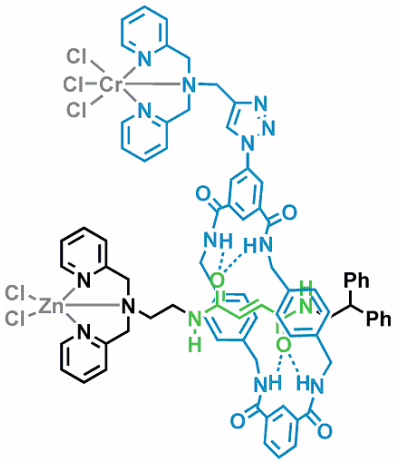
([2]({1H-1,2,3-triazol-4-yl-*N*,*N*-bis(pyridine-2-yl-methyl)methanamine-zinc (II) dichloride}-1,7,14,20-Tetraaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetrabenzocyclohexacosane)-(N^1-(2-(bis(pyridine-2-ylmethyl)amino)ethyl)-N^4-(2,2-diphenylethyl)fumaramide) zinc (II) dichloride rotaxane [3(***mac*-$ZnCl_2$)(*thread*-$ZnCl_2$)]



To a solution of rotaxane **3** (50 mg, 0.04 mmol) in methanol (5 mL) was added a saturated solution of $ZnCl_2$ (11 mg, 0.08 mmol) in methanol (1mL). The reaction was stirred for 1h during which time a solid precipitated. The precipitate was collected under filtration and the resulting solid washed with methanol (5 mL). Yield 59 mg (98 %); mp 235 ^oC (decomp); ^1H NMR (400 MHz, [D_7]*N*,*N*-dimethylformamide): δ = 9.25 (s, 1H, H_L), 9.19 (d, *J* = 4.8 Hz, 2H, H_R), 9.05 (d, *J* = 4.1 Hz, 2H, H_m), 8.92 (t, *J* = 5.2 Hz, 1H, H_c), 8.62 (t, *J* = 5.0 Hz, 1H, H_f), 8.78 (s, 1H, H_J), 8.68 (s, 2H, H_K), 8.65 (s, 1H, H_C), 8.23 (dt, *J* = 7.6 Hz and *J* = 1.4 Hz, 2H, H_P), 8.21 (dd, *J* = 7.7 Hz and *J* = 1.4 Hz, 2H, H_B), 8.06 (s, 2H, H_D), 7.92 (dt, *J* = 7.6 Hz and *J* = 1.4 Hz, 2H, H_k), 7.90 (t, *J* = 7.5 Hz, 2H, H_I), 7.81-7.75 (m, 5H, H_A, H_O & H_Q), 7.61 (t, *J* = 6.3 Hz, 2H, H_l), 7.52 (d, *J* = 7.7 Hz, 2H, H_j), 7.38-7.26 (m, 8H, H_{Ph}), 7.24-7.18 (m, 2H, H_{Ph}), 7.00 (d, *J* = 9.0 Hz, 4H, H_G), 6.98 (d, *J* = 9.0 Hz, 4H, H_F), 5.91 (d, *J* = 15.1 Hz, 1H, H_d), 5.79 (d, *J* = 15.1 Hz, 1H, H_e), 4.61-4.29 (m, 16H, H_E, H_H, H_i & H_N), 4.24 (t, *J* = 8.0 Hz, 1H, H_a), 4.11 (s, 2H, H_M), 3.93 (t, *J* = 5.0 Hz, 2H, H_b), 3.42-3.37 (m, 2H, H_g), 2.79-2.75 (m, 2H, H_h); ^{13}C NMR (100 MHz, [D_7]*N*,*N*-dimethylformamide): δ = 167.0,

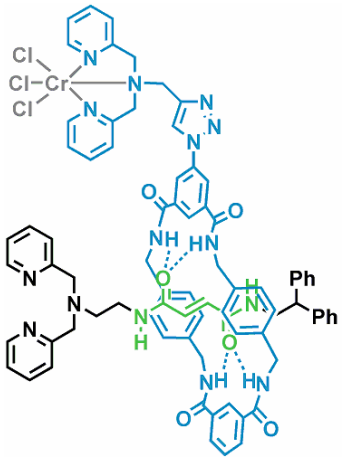
166.8, 166.6, 165.4, 156.0, 155.7, 149.9, 149.6, 143.9, 141.8, 141.4, 138.8, 138.4, 138.0, 137.4, 135.5, 132.0, 131.5, 130.4, 130.1, 130.0 (x2), 129.6 (x2), 129.0 (x2), 127.7, 125.9, 125.7, 125.6, 125.5, 125.0, 123.4, 57.2, 56.8, 51.8, 51.4, 47.8, 45.0, 44.5, 44.3, 44.2; HRMS (FAB, 3-NOBA matrix): *m/z* = 1562.4371 [(M-Cl)$^+$] (anal. calcd for $C_{79}H_{75}Cl_3N_{15}O_6Zn_2^+$: *m/z* = 1562.3673).

([2]({1H-1,2,3-triazol-4-yl-*N*,*N*-bis(pyridine-2-yl-methyl)methanamine-chromium (III) trichloride}-1,7,14,20-Tetraaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetrabenzocyclohexacosane)-(*N*^{1}-(2-(bis(pyridine-2-ylmethyl)amino)ethyl)-*N*^{4}-(2,2-diphenylethyl)fumaramide) zinc (II) dichloride [**3**(*mac*-$CrCl_3$)(*thread*-$ZnCl_2$)]



To a solution of rotaxane [**3**(*mac*-$CrCl_3$)] (65 mg, 0.04 mmol) in methanol (5 mL) was added a saturated solution of $ZnCl_2$ (7 mg, 0.05 mmol) in methanol (1 mL). The reaction was stirred for 1 h during which time a solid precipitated. The precipitate was collected under filtration and the resulting solid washed with methanol (5 mL). Yield 64 mg (90%); mp 246 ^oC (decomp); FT-IR (KBr): 3257 (br s, *N*-H_{amide}) cm^{-1}; λ_{max} (CH_2Cl_2:MeOH [1:1]) ($\varepsilon(M^{-1}cm^{-1})$): 448 nm ($1.90\times10^2$), 622 nm ($1.25\times10^2$); HRMS (FAB, 3-NOBA matrix): *m/z* = 1585.2985 [(M-Cl)$^+$] (anal. calcd for $C_{79}H_{75}Cl_4CrN_{15}O_6Zn^+$: *m/z* = 1585.3475).

([2]({1H-1,2,3-triazol-4-yl-*N*,*N*-bis(pyridine-2-yl-methyl)methanamine-chromium (III) trichloride}-1,7,14,20-Tetraaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetrabenzocyclohexacosane)-(*N*^{1}-(2-(bis(pyridine-2-ylmethyl)amino)ethyl)-*N*^{4}-(2,2-diphenylethyl)fumaramide) rotaxane [**3**(*mac*-$CrCl_3$)]



A solution of [**3**(*mac*-$CrCl_3$)(*thread*-$CuCl_2$)] (100 mg, 0.06 mmol) in $CHCl_3$/isopropanol in a 3:1 v/v ratio (15 mL) was washed with saturated aqueous Na_4EDTA (3 x 10 mL) and saturated aqueous sodium chloride (2 x 10 mL), dried ($MgSO_4$) and concentrated under reduced pressure to give a green solid. The product was subjected to column chromatography on silica gel using dichloromethane/acetonitrile/NH_4OH (aq) in a 5:5:0.1 v/v ratio as eluent. Yield 65 mg (71%); mp 211 ^oC (decomp); FT-IR (KBr): 3261 (br s, *N*-H_{amide}) cm^{-1}; λ_{max} (CH_2Cl_2:MeOH [1:1]) ($\varepsilon(M^{-1}cm^{-1})$): 449 nm ($2.10\times10^2$), 625 nm ($1.35\times10^2$); HRMS (FAB, 3-NOBA matrix): *m/z* = 1487.4586 [$(M+H)^+$] (anal. calcd for $C_{79}H_{76}Cl_3CrN_{15}O_6^+$: *m/z* = 1487.4574).