Supporting Information

# Rings and threads as linkers in metal-organic frameworks and poly-rotaxanes

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## 1. General Experimental Section

**$[NH_2Pr_2][Cr_7NiF_8(O_2CCMe_3)_{16}]$ (1)**, was prepared by the method given in Larsen et al, *Angew. Chem. Int. Ed*., **2003**, 42, 101-105 using $[2NiCO_3.3Ni(OH)_2.4H_2O]$ as the source of Ni(II) instead of the compound $[Ni_2(O_2CMe_3)_4(HO_2CCMe_3)_4]$ used in the original method and the reaction time was for 24h at 160°C.

**$[Cu_2(O_2CCMe_3)_4(HO_2CCMe_3)_4]$** was obtained by a procedure identical to the method given for $[Ni_2(O_2CMe_3)_4(HO_2CCMe_3)]$ in Chaboussant *et al* Dalton Trans., **2004** , 2758 – 2766 using basic copper carbonate instead of the nickel hydroxide.

All the other reagents and solvents were commercially available and used as received..

Column chromatography was carried out using Silica 60A (particle size 35-70 μm, Fisher, UK) as the stationary phase, and TLC was performed on precoated silica gel plates (0.25 mm thick, 60 $F_{254}$, Merck, Germany). ESI mass spectrometry was carried out by the services at the University of Manchester.

Microanalysis was performed by the Microanalysis department in the School of Chemistry, Universoty of Manchester. Carbon, nitrogen and hydrogen analysis was performed using a Flash 200 elemental analyser. Metal analysis was performed by Thermo iCap 6300 Inductively Coupled Pleasma Optical Emission Spectroscopy (ICP-OES)

## 2. Synthesis and Experimental Section

### 2.1 Synthesis of $[NH_2{}^nPr_2][Cr_7NiF_8(O_2CCMe_3)_{14}(O_2C_5H_4N)_2]$ (2)

Compound **1** (15.0g 6.54 mmol), iso-nicotinic acid (2.48g 19.5 mmol) and *n*-propanol (300 mL) were refluxed for 24h with constant stirring. The resulting solution was cooled to room temperature and filtered. The solvent from the filtrate was removed under reduced pressure and the residue was washed with a large quantity of acetonitrile. The residue was then dissolved in diethyl ether (~ 300 ml). The obtained solution was filtered and the diethyl ether was removed by distillation leaving a solid which was dissolved in pentane (~ 200 ml). The pentane extract was filtered and evaporated to dryness giving a green solid which still was a mixture of products. Further purification of **2** was performed by column chromatography on 40-63 μm mesh silica gel (BDH). First toluene was used as solvent, which allowed un-reacted **1** to be eluted, leaving the products of the reaction at the top of the column. Thereafter a mixture of petroleum ether:ethyl acetate elution was used. Firstly, a 10:1 mixture was used eluting a large single band of mono-substituted product. The solvent ratio was then gradually worked up to a 5:1 mixture, eluting a second fainter band **2 (**0.63g, 0.27mmol, 4.13% ES-MS *m/z*: +2337 $[M+H]^+$, +2359 $[M+Na]^+$ Elemental anal. calculated (%) for $C_{88}H_{150}N_3O_{32}F_8Cr_7Ni$: C 45.23, H 6.47, N 1.80, Cr 15.57, Ni 2.51; Found: C 45.96, H 6.77, N 1.62, Cr 15.46, Ni 2.38). The solvent ratio was then worked up to 1:1, eluting a third band, **3** (0.54g, 0.23mmol, 3.52% *m/z*: +2337 $[M+H]^+$, +2359 $[M+Na]^+$ Elemental anal. calculated (%) for $C_{88}H_{150}N_3O_{32}F_8Cr_7Ni$: C 45.23, H 6.47, N 1.80; Found: C 45.62, H 6.58, N 1.79). For both products solvent was removed by distillation and each were recrystallised by slow evaporation of diethyl ether and acetonitrile

### 2.2 Synthesis of $\{-2-[Cu(NO_3)_2(THF)]-\}_\infty$ (4)

Cu(NO3)2 · 2.5H2O (0.0132 g, 0.057 mmol) was added to a warm solution of **2** (0.107 g, 0.046 mmol) in acetone (10 ml) and the solution was refluxed for 10 mins, after which a green precipitate formed. The reaction was allowed to cool to room temperature and left covered for 24 hrs. The precipitate was collected by filtration, washed with acetone, extracted with THF and recrystallised from slow evaporation of THF/toluene. Dark green crystals (including suitable for X-ray structure study) were collected by filtration and washed with toluene. Yield: 0.114 g (0.044 mmol, 95.4% based on **2**) Elemental anal. calculated (%) for $C_{92}H_{158}Cr_7CuF_8N_5NiO_{39}$: C 42.55, H 6.13, N 2.69; Found: C 42.82, H 5.96, N 3.12)

### 2.3 Synthesis of {-2-$[Cu_2(O_2CCMe_3)_4]\}_\infty$ (5)

$[Cu_2(O_2CCMe_3)_4(HO_2CCMe_3)_4]$ (0.0402g 0.0428 mmol) was added to a warm solution of **2** (0.1 g, 0.0428 mmol) in toluene (20 ml) and the solution was stirred for 10 mins, after which a precipitate formed. This was collected by filtration, extracted in diethyl ether and recrystallised from slow evaporation of THF/toluene. Dark green crystals (including suitable for X-ray structure study) were collected by filtration and washed with toluene. Yield: 0.118g, (0.422mmol, 98.6% yield based on **2** Elemental anal. calculated (%) for $C_{88}H_{150}N_3O_{32}F_8Cr_7Ni$: C 45.22, H 6.54, N 1.46; Found: C 45.27, H 6.50, N 1.72)

### 2.4 Synthesis of {-3-$[Cu(NO_3)_4]$-3-$[Cu(NO_3)]$-$(3)_2$-$[Cu(NO_3)]$-$\}_\infty$ (6)

Cu(NO3)2 · 2.5H2O (0.013g, 0.056 mmol) was added to a warm solution of **2** (0.124 g, 0.053 mmol) in acetone (20 ml) and the solution was stirred for 10 mins, after which a precipitate formed. This was collected by filtration, extracted in diethyl ether and recrystallised from slow evaporation of diethyl ether/acetonitrile. Dark green crystals (including suitable for X-ray structure study) were collected by filtration and washed with acetone. Yield: (0.132g, 93.5% based on **2**.) Elemental anal. calculated (%) for $C_{376}\ H_{600}\ Cr_{28}\ Cu_3\ F_{32}\ N_{30}\ Ni_4\ O_{148}$: C41.69, H5.96, N2.76; Found: C41.70, H5.66, N3.02)

### 2.5 Synthesis of thread N,N'-bis(pyridin-4-ylmethyl)decane-1,10-diamine (T1)

1,10- diaminiodecane (1.40 g, 7.9 mmol) and methanol (30 mL) were heated to reflux, to which 4-pyridinecarboxaldehyde (1.41 mL, 15 mmol) in methanol (30 mL) were added and refluxed for a further three hours. The solution was then cooled to room temperature, to which excess $NaBH_4$ was added and left to stir overnight. Deionised water (30 mL) was added and the solution was extracted using chloroform (25 mL x 4), dried with magnesium sulfate and solvents removed giving a syrupy residue. A white solid was obtained upon recrystallisation from $CHCl_3$/Pentane.

Yield: 1.704 g (66.2 %). ES-MS *m/z*: +327 $[M+H]^+$. $^1$H NMR (400 MHz, 293 K, $CDCl_3$): δ= 1.2 (s, 8H), 1.4 (m, 4H), 2.5 (t, 4H), 3.8 (s, 4H), 7.2 (d, 4H), 8.5 (d, 4H).

### 2.6 Synthesis of $\{(H_2T1)[Cr_7NiF_8(O_2C^tBu)_{16}]_2\}$ (7)

Pivalic acid (20.0 g, 195.83 mmol), $CrF_3.4H_2O$ (3.0 g, 16.57 mmol), $Ni_2(\mu\text{-}OH_2)(O_2CCMe_3)_4(HO_2CCMe_3)_4$ (1.0 g, 1.038 mmol) and thread **T1** (0.5 g, 1.14 mmol) were heated to 150 °C with stirring for 24 h in open Teflon flask. The reaction mixture was then cooled to room temperature and acetonitrile (30 mL) was added. The solid was then filtered, washed with acetonitrile, dried in air and extracted in diethyl ether/THF. The solid obtained was purified using column chromatography on silica gel (toluene followed by a gradient elution of 10:1 toluene: EtOAc followed by diethyl ether as eluent).

Yield=1.232 g (22.8 %). ES-MS *m/z*: + 2393 $[M/2+Na]^+$. Elemental analysis calculated (%) for $C_{182}H_{322}N_4O_{64}F_{16}Cr_{14}Ni_2$: C 46.10, H 6.89, N 1.18, Cr 15.35, Ni 2.48; Found: C 46.30, H 6.99, N 1.14, Cr 15.01, Ni 2.44.

### 2.7 Synthesis of $\{\text{-}7\text{-}[Cu_2(O_2CCMe_3)_4]\}_\infty$ 8

$[Cu_2(O_2CCMe_3)_4(HO_2CCMe_3)_4]$ (0.077 g, 0.105 mmol) and **7** (0.5 g, 0.105 mmol) were dissolved separately in THF before combined, toluene added and left for recrystallisation.

Yield = 0.456g (84.2%). Elemental analysis calculated (%) for $C_{202}H_{358}N_4O_{72}F_{16}Cr_{14}Ni_2$: C 46.01, H 6.88, N 1.06, Cr 13.80, Ni 2.23, Cu 2.41; Found: C 46.32, H 7.18, N 1.09, Cr 13.82, Ni 2.25, Cu 2.44.

### 2.8 Synthesis of {[Cu(Hfacec)$_2$($H_2O$)]-7-[Cu(Hfacec)$_2$($H_2O$)]} (9)

**5b**: Cu(Hfacec)$_2$($H_2O$)$_2$ (0.0492 g, 0.105 mmol). and **7** (0.5 g, 0.105 mmol) were dissolved separately in THF before being combined and left for evaporation.

Elemental analysis calculated (%) for: C 42.58, H 5.80, N 0.98, Cr 12.77, Ni 2.06; Found: C 42.91, H 6.08, N 0.99, Cr 12.59, Ni 2.02.

### 2.9 Synthesis of [{$PyCH_2CH_2NH(CH_2)_{10}NHCH_2CH_2Py$} (T2)

1,10-decanedial was prepared according the literature[i]. 4(2-ethylamino)-pyridine (1.4 mL, 11.76 mmol) in toluene (10 mL) was added drop wise to a solution of 1,10-decanedial (1g, 5.8 mmol) in Toluene (50 mL) and stirred at room temperature for 12 hrs under a nitrogen atmosphere. The solvent was concentrated $NaBH_4$ in methanol (40 mL) was added and reaction mixture stirred overnight at under a nitrogen atmosphere. The reaction was quenched with water and the solvent removed under reduced pressure. The solid was extracted with chloroform, washed several times with water, dried over anhydrous magnesium sulphate and evaporated. A yellow oil was obtained**.**

Yield (1.46 g, 65%). ES-MS: m/z = 383 $[M+H]^+$. $^1H$ NMR (500 MHz, 293K, $CDCl_3$): $\delta$ = 1.1-1.4 (m, 16H), 2.5(t, 4H), 2.74 (t, 4H), 2.85 (t, 4H), 7.05(d, 4H), 8.40(d, 4H).

### 2.10 Synthesis of [{$H_2$T2}{$Cr_7NiF_8(O_2CCMe_3)_{16}$}$_2$] (10)

Pivalic acid (20.0 g, 195.83 mmol), $CrF_3.4H_2O$ (3.31 g, 18.28 mmol), $Ni_2(m\text{-}OH_2)(O_2CCMe_3)_4(HO_2CCMe_3)_4$ (1.35 g, 1.4 mmol) and thread **T2** (0.5 g, 1.38 mmol) were heated to 150 °C with stirring for 24 h in open Teflon flask. The reaction mixture was then cooled to room temperature and acetonitrile (30 mL) was added. The solid was then filtered, washed with acetonitrile, dried in air and extracted in hot THF. This was purified by column chromatography on silica gel (elution of EtOAc followed by $Et_2O$ and then THF as eluent) and recrystallised from toluene.

Elemental analysis calculated (%) for $C_{184}H_{328}N_4O_{64}F_{16}Cr_{14}Ni_2$: C 46.33, H 6.93, N 1.17, Cr 15.26, Ni 2.46; Found: C 46.32, H 6.97, N 1.20, Cr 15.33, Ni 2.42.

### 2.11 Synthesis of [-10-{Cu(Hfacec)$_2$}]$_\infty$ (11)

Cu(Hfacec)$_2$ (0.010 g, 0.02 mmol) and **9** (0.1 g, 0.02 mmol) were dissolved separately in THF before combined, toluene was added and the mixture was refluxed during 5 minutes and left to room temperature for recrystallisation. Dark green crystals suitable for X-ray structure study were collected. Elemental analysis calculated (%) for $C_{194}H_{330}Cr_{14}CuF_{28}N_4Ni_2O_{68}$: C 44.40, H 6.33, N 1.06, Cr 13.87, Ni 2.24; Found: C 44.72, H 6.29, N 1.05, Cr 13.77, Ni 2.23.

# 3. X-Ray Crystallography

## 3.1 X-Ray Crystallographic Data for axial-axial {$Cr_7Ni(^inic)_2$} (2)

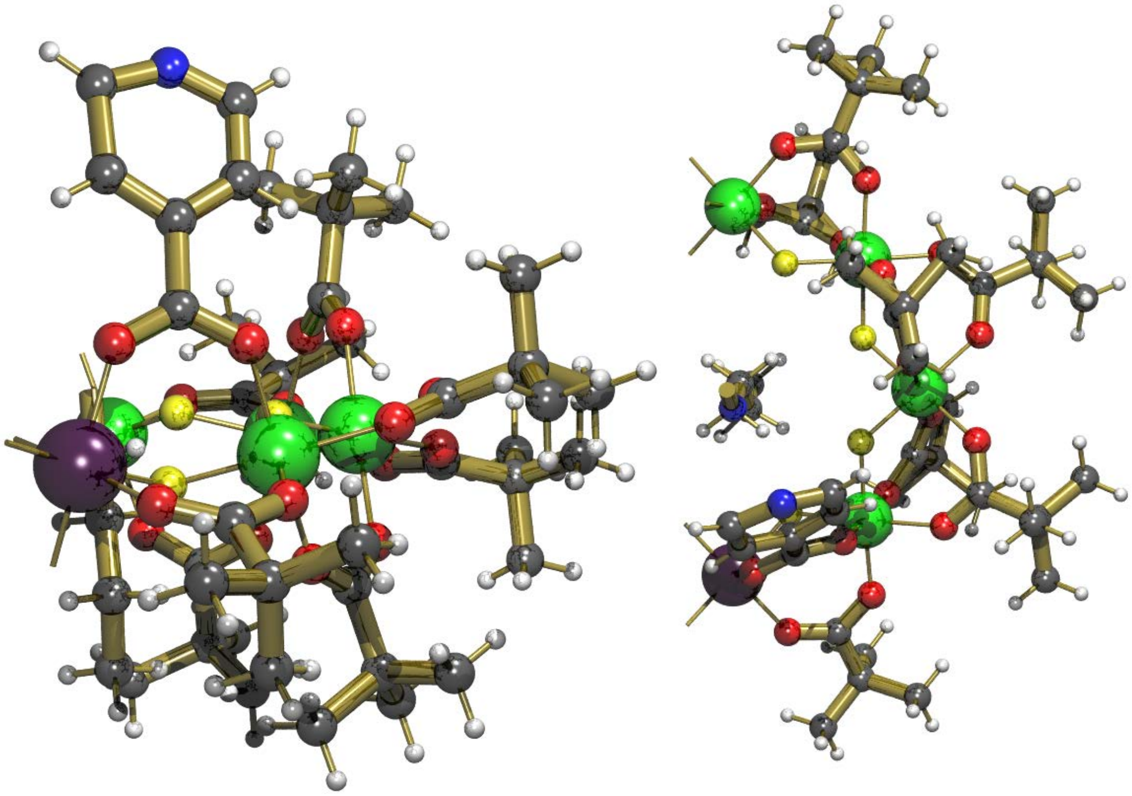

**Figure S1:** Graphical representation of the X-ray crystal structure of axial-axial {$Cr_7Ni(^inic)_2$} **2**
Colours: Cr = green, Ni = violet, O = red, F = yellow, N = blue, C = grey, H = white

### 3.1.1 Table S1: Crystal data and structure refinement for 2

| Formula | $C_{88}H_{150}Cr_7F_8N_3Ni_1O_{32}$ |
|---|---|
| $M$ | 2336.82 |
| Crystal system | Hexagonal |
| Space group | *P6(5) 2 2* |
| $a$ / Å | 16.6211 (3) |
| $c$ / Å | 77.743 (3) |
| $U$ / Å$^3$ | 18599.9 (8) |
| T / K | 150 |
| $Z$ | 6 |
| $\rho$ / gcm$^{-1}$ | 1.251 |
| Shape and color | Block, Green |
| size (mm) | 0.10 × 0.08 × 0.02 |
| λ / Å | 0.6933 |
| μ / mm $^{-1}$ | 0.81 |
| Unique data | 14772 |
| Absorption correction | multi-scan |
| transmission max/min | 0.923/0.984 |
| unique data [$F_o > 4$□$F_o$)] | 11971 |
| parameters/restraints | 629/0 |
| $R1$, $wR2$[a] | 0.074, 0.211 |
| weighting scheme[b] [$w^{-1}$] | $1/[\sigma^2(F_o^2) + (0.1073P)^2 + 22.9845P]$ |
| goodness of fit | 1.04 |
| largest residuals [e Å$^{-3}$] | 0.54, −0.54 |
| Flack Parameter | 0.11 (4) |

[a] $R1$ based on observed data, $wR2$ on all unique data.

[b] $P = 1/3[\max(F_o^2,0) + 2F_c^2]$

The crystal contains solvent accessible voids (234Å$^3$). However, the location of discrete solvent molecules could not be determined.

## 3.2 X-Ray Crystallographic Data for axial-equatorial {$Cr_7Ni(^inic)_2$} (3)

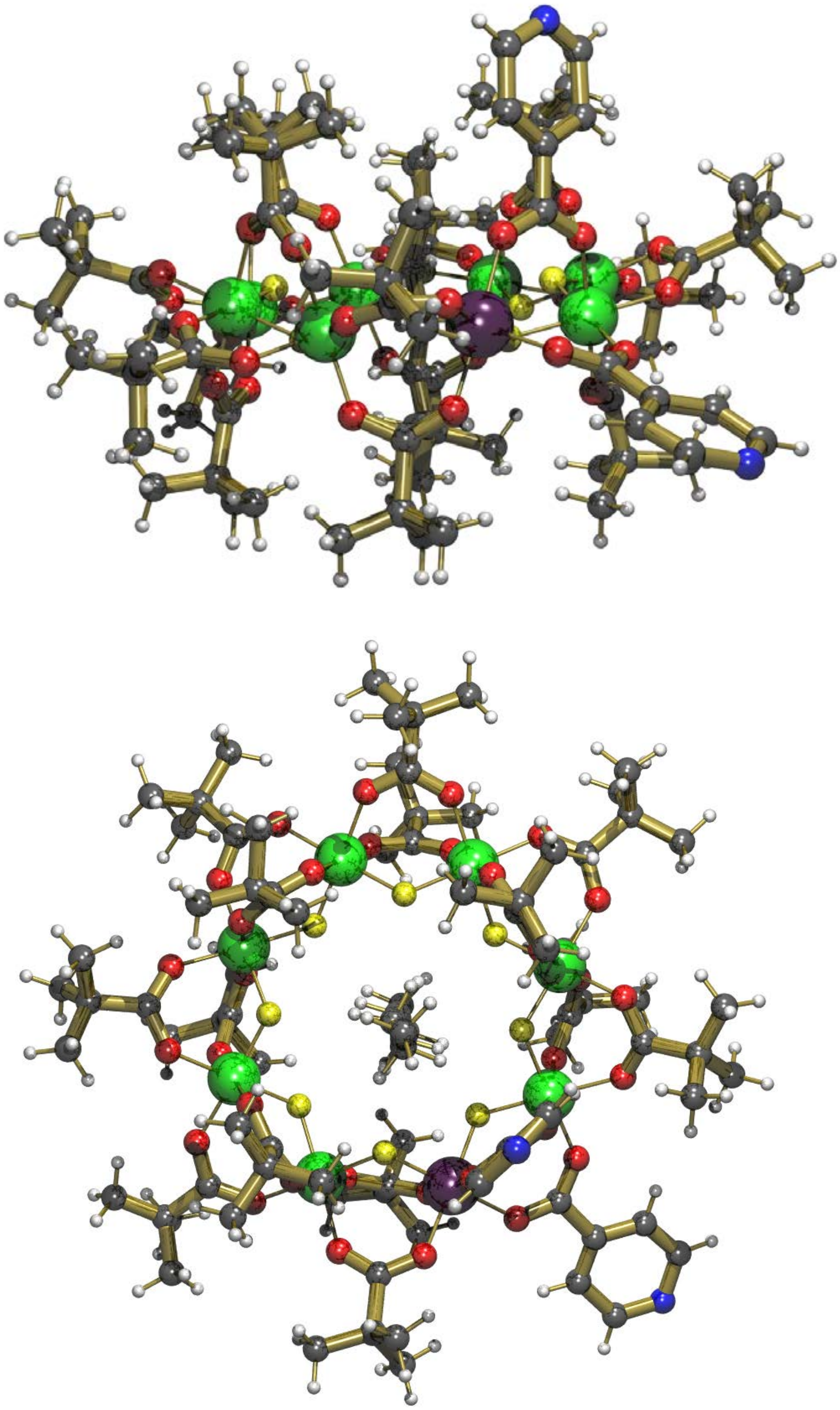

**Figure S2:** Graphical representation of the X-ray crystal structure of axial-equatorial {$Cr_7Ni(^inic)_2$} **3**
Colours: Cr = green, Ni = violet, O = red, F = yellow, N = blue, C = grey, H = white

### 3.2.1 Table S2: Crystal data and structure refinement for 3

| Formula | $C_{88}H_{150}Cr_7F_8N_3Ni_1O_{32}$ |
|---|---|
| $M$ | 2336.81 |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ |
| $a$ / Å | 25.1317 (7) |
| $b$ / Å | 16.6128 (4) |
| $c$ / Å | 30.9750 (9) |
| $\beta$ / ° | 109.473 (2) |
| $U$ / Å$^3$ | 12192.6 (6) |
| T / K | 100 |
| $Z$ | 4 |
| $\rho$ / g cm$^{-1}$ | 1.273 |
| Shape and color | Needle, Green |
| size (mm) | 0.35 × 0.08 × 0.05 |
| $\lambda$ / Å | 0.7749 |
| $\mu$ / mm$^{-1}$ | 1.05 |
| Unique data | 14064 |
| Absorption correction | multi-scan |
| transmission max/min | 0.762, 0.960 |
| unique data [$F_o > 4\sigma F_o$)] | 10505 |
| parameters/restraints | 1253, 2049 |
| $R1$, $wR2$[a] | 0.092, 0.327 |
| weighting scheme[b] [$w^{-1}$] | $1/[\sigma^2(F_o^2) + (0.2P)^2]$ |
| goodness of fit | 1.371 |
| largest residuals [e Å$^{-3}$] | 1.00, −0.68 |

[a] $R1$ based on observed data, $wR2$ on all unique data.

[b] $P = 1/3[\max(F_o^2,0) + 2F_c^2]$

The crystal contains solvent accessible voids (301Å$^3$). However, the location of discrete solvent molecules could not be determined. Due to the degree of disorder of the $^t$butyl groups in the crystal structure a large number of restraints were applied. SADI restraints were applied to the bonds of one of the $^t$butyl groups and SAME was applied to the remaining $^t$butyl groups to generate an average idealised geometry for all. SIMU and DELU restraints were also applied to C, N, and O atoms to improve the thermal ellipsoids.

### 3.3 X-Ray Crystallographic Data for polymer 4

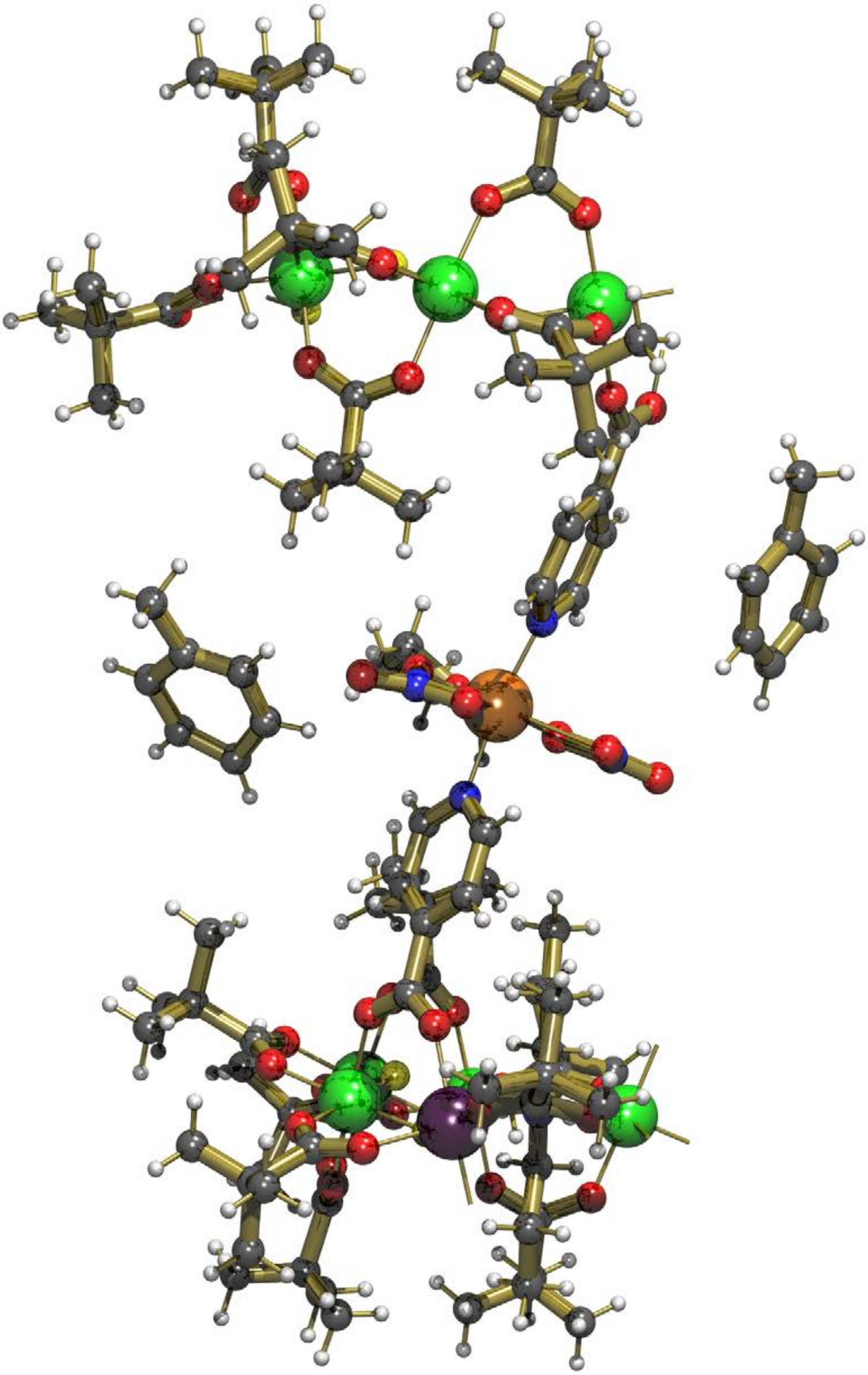

**Figure S3:** Graphical representation of the asymmetric unit of {-2-[Cu($NO_3$)$_2$(THF)-}$_\infty$ (**4**)
Colours: Cr = green, Ni = violet, O = red, F = yellow, N = blue, C = grey, H = white

### 3.3.1 Table S3: Crystal data and structure refinement for 4

| | |
|---|---|
| Formula | $C_{205}H_{340}Cr_{14}Cu_2F_{16}N_{10}Ni_2O_{78}$ |
| $M$ | 5469.37 |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ |
| $a$ / Å | 16.9352(6) |
| $b$ / Å | 29.4007(11) |
| $c$ / Å | 29.4140(13) |
| $\beta$ / ° | 90.834(3) |
| $U$ / Å$^3$ | 14643.9(10) |
| T / K | T = 100 K |
| $Z$ | 2 |
| $\rho$ / g cm$^{-1}$ | 1.240 |
| Shape and color | Plate, Green |
| size (mm) | 0.27 × 0.18 × 0.05 |
| $\lambda$ / Å | 0.7749 |
| $\mu$ / mm$^{-1}$ | 0.843 |
| Unique data | 14064 |
| unique data [$F_o > 4\sigma F_o$)] | 8195 |
| parameters/restraints | 1506, 1927 |
| $R1$, $wR2$[a] | 0.106, 0.253 |
| weighting scheme[b] [$w^{-1}$] | $1/[\sigma^2(F_o^2) + (0.0843P)^2 + 161.9089P]$ |
| goodness of fit | 1.107 |
| largest residuals [e Å$^{-3}$] | 0.95, −0.49 |

[a] $R1$ based on observed data, $wR2$ on all unique data.

[b] $P = 1/3[\max(F_o^2,0) + 2F_c^2]$

The crystal contains solvent accessible voids (573 Å$^3$), even though the location of some discrete solvent molecules could be determined. Due to the degree of disorder of the $^t$butyl groups in the crystal structure a large number of restraints were applied. SADI restraints were applied to the bonds of one of the $^t$butyl groups and SAME was applied to the remaining $^t$butyl groups to generate an average idealised geometry for all. SIMU and DELU restraints were also applied to C, N and O atoms to improve the thermal ellipsoids.

### 3.4 X-Ray Crystallographic Data for polymer 5

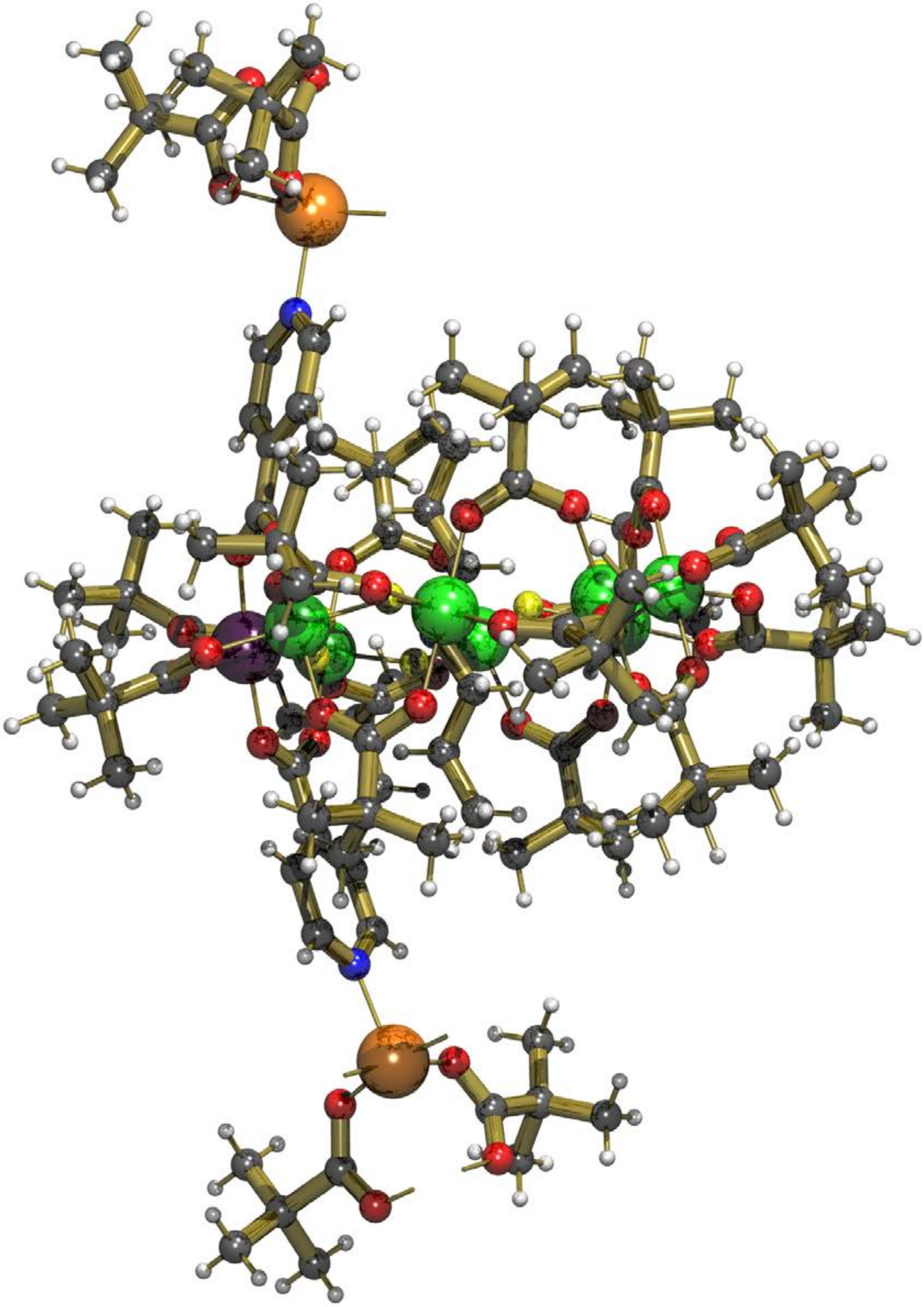

**Figure S4:** The asymmetric unit of the X-ray crystal structure of polymer **5**
Colours: Cr = green, Ni = violet, O = red, F = yellow, N = blue, C = grey, 50% probability thermal ellipsoids.

### 3.4.1 Table S4: Crystal data and structure refinement for polymer 5

| | |
|---|---|
| Formula | $C_{108}H_{184}Cr_7Cu_2F_8N_3NiO_{40}$ |
| M | 2866.38 |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ |
| a / Å | 30.6539 (11) |
| b / Å | 16.5114 (5) |
| c / Å | 35.9700 (11) |
| β / ° | 111.244 (2) |
| U / Å3 | 16968.6 (10) |
| T / K | 150 |
| Z | 4 |
| ρ / g cm–1 | 1.122 |
| Shape and color | Needle, green |
| size (mm) | 0.2 × 0.08 × 0.03 |
| λ / Å | 0.7749 |
| μ / mm-1 | 0.842 |
| Unique data | 11622 |
| Absorption correction | multi-scan |
| transmission max/min | 0.8496/0.9752 |
| unique data [Fo > 4sFo)] | 8137 |
| parameters/restraints | 1522/3009 |
| R1, wR2[b] | 0.119, 0.372 |
| weighting scheme[c] [w-1] | [σ2(Fo2) + (0.2P)2] |
| goodness of fit | 1.53 |
| largest residuals [e Å-3] | 1.16, −0.95 |

[a] *R*1 based on observed data, *wR*2 on all unique data.

[b] $P = 1/3[\max(F_o^2,0) + 2F_c^2]$

The crystal contains solvent accessible voids (1800Å$^3$). However, the location of discrete solvent molecules could not be determined. Due to the degree of disorder of the $^t$butyl groups in the crystal structure a large number of restraints were applied. SADI restraints were applied to the bonds of one of the $^t$butyl groups and SAME was applied to the remaining $^t$butyl groups to generate an average idealised geometry for all. SIMU and DELU restraints were also applied to C N and O atoms to improve the thermal ellipsoids.

### 3.5 X-Ray Crystallographic Data for polymer 6

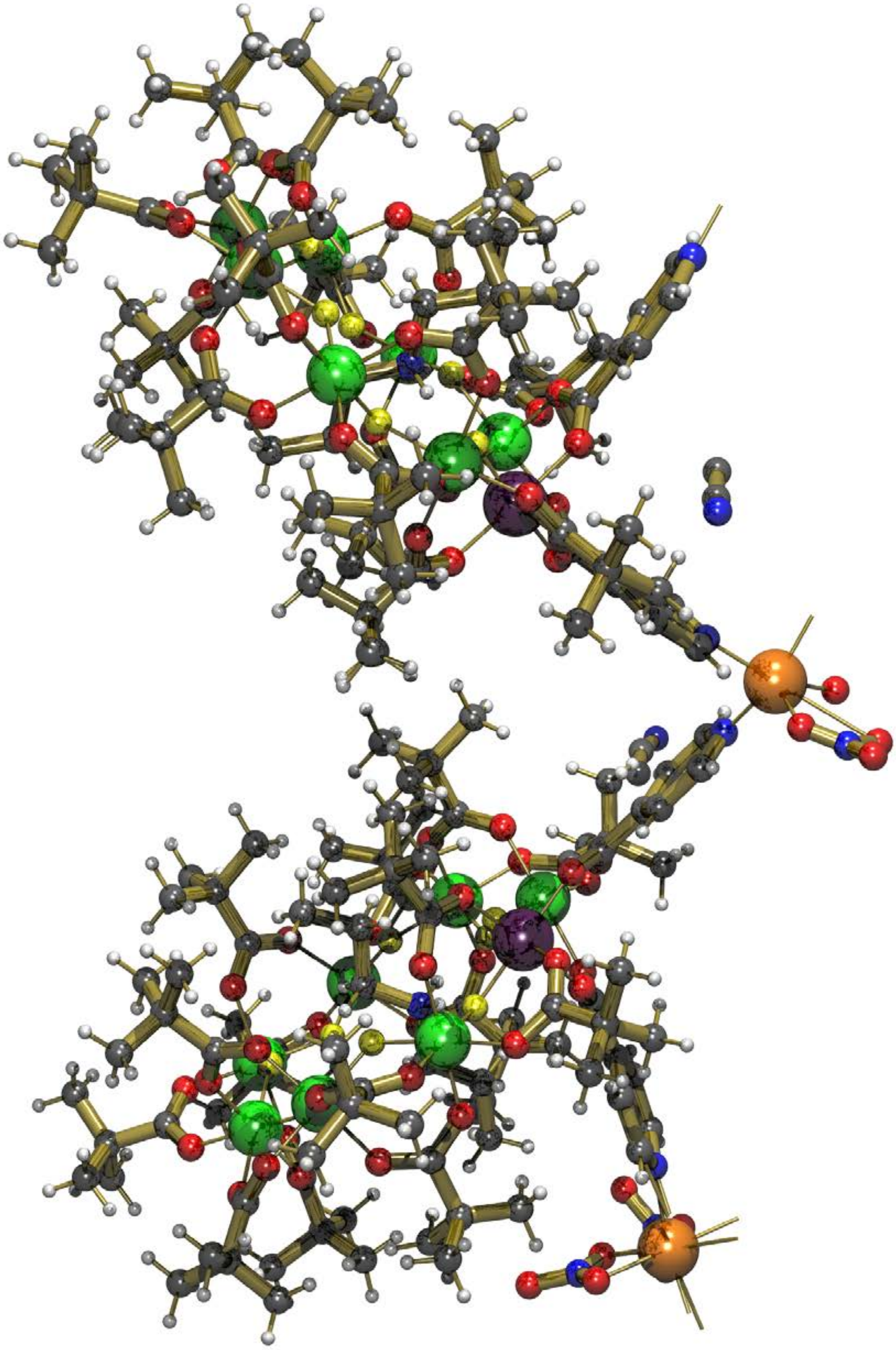

**Figure S5:** The asymmetric unit of the X-ray crystal structure of polymer **6**
Colours: Cr = green, Ni = violet, Cu = orange, O = red, F = yellow, N = blue, C = grey, H = white

### 3.5.1 Table S5: Crystal data and structure refinement for polymer 6

| | |
|---|---|
| Formula | $C_{376}H_{600}Cr_{28}Cu_{3}F_{32}N_{30}Ni_{4}O_{148}$ |
| M | 10398.15 |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| a / Å | 16.1810 (4) |
| b / Å | 28.3116 (6) |
| c / Å | 33.5398 (7) |
| α / ° | 96.992 (2) |
| β / ° | 102.583 (2) |
| γ / ° | 93.852 (2) |
| U / $Å^3$ | 14814.6 (6) |
| T / K | 100 |
| Z | 1 |
| ρ / g $cm^{-1}$ | 1.166 |
| Shape and color | Plate, green |
| size (mm) | 0.34 × 0.17 × 0.03 |
| λ / Å | 0.6889 |
| μ / $mm^{-1}$ | 0.8 |
| Unique data | 56300 |
| Absorption correction | multi-scan |
| transmission max/min | 0.64755/1 |
| unique data [Fo > 4sFo)] | 42353 |
| parameters/restraints | 2722/6586 |
| R1, wR2[a] | 0.100, 0.343 |
| weighting scheme[b] [w-1] | [σ2(Fo2) + (0.2P)2] |
| goodness of fit | 1.321 |
| largest residuals [e Å-3] | 1.97, -1.22 |

[a] $R1$ based on observed data, $wR2$ on all unique data.

[b] $P = 1/3[\max(F_o^2,0) + 2F_c^2]$

The crystal contains solvent accessible voids (1286.6 $Å^3$), even though the location of some discrete solvent molecules could be determined. Due to the degree of disorder of the $^{t}$butyl groups in the crystal structure a large number of restraints were applied. SADI restraints were applied to the bonds of one of the $^{t}$butyl groups and SAME was applied to the remaining $^{t}$butyl groups to generate an average idealised geometry for all. SIMU and DELU restraints were also applied to C, N and O atoms to improve the thermal ellipsoids.

### 3.6 X-Ray Crystallographic Data for [3]-rotaxane 7

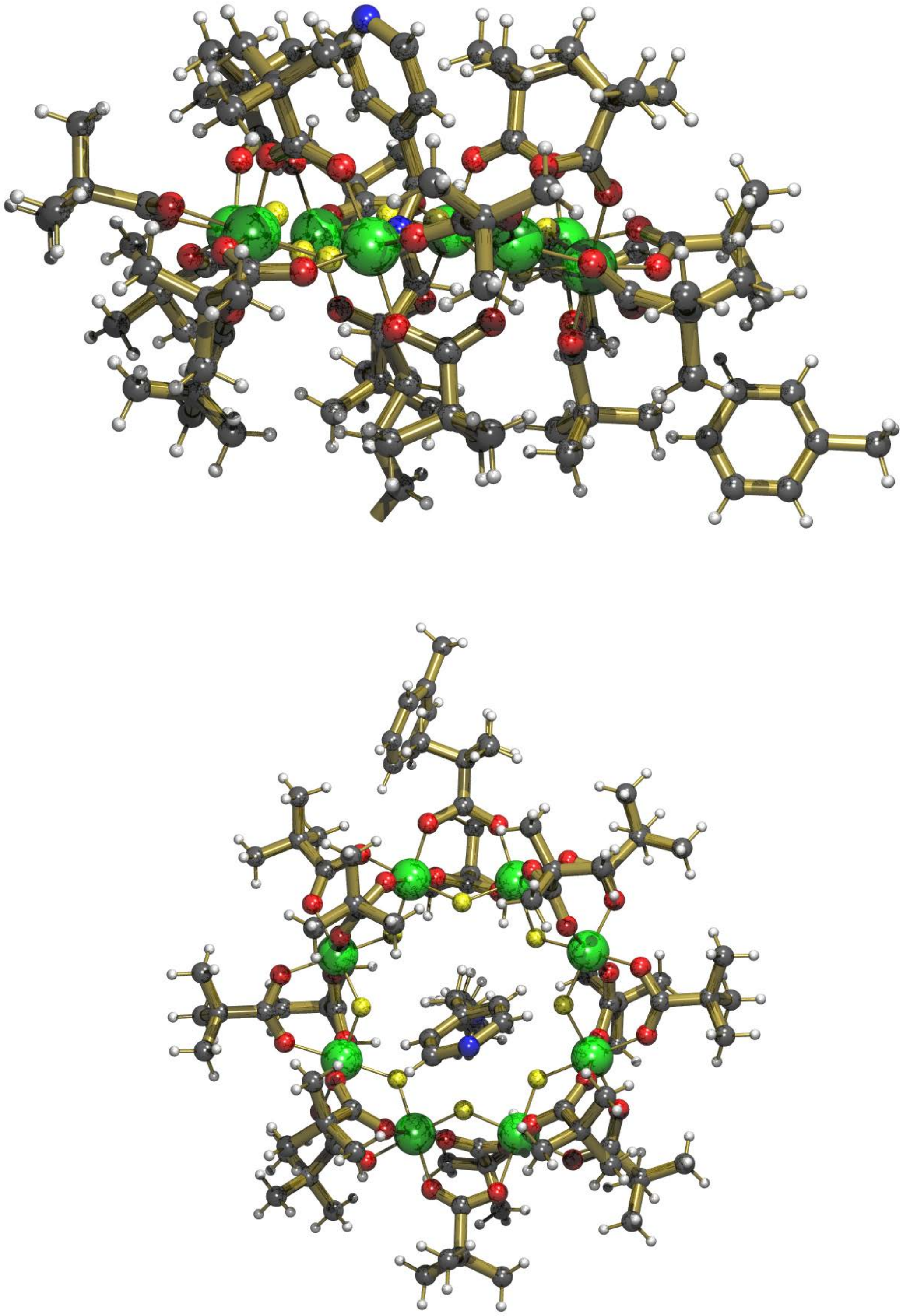

**Figure S6:** Graphical representation of the asymmetric unit of [3]-rotaxane **7**
Colours: Cr = green, Ni = violet, O = red, F = yellow, N = blue, C = grey, H = white

### 3.6.1 Table S6: Crystal data and structure refinement for [3]-rotaxane 7

| | |
|---|---|
| Formula | $C_{98}H_{170}Cr_7F_8N_2NiO_{32}$ |
| M | 2467.49 |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ |
| a / Å | 21.2560 (13) |
| b / Å | 29.816 (3) |
| c / Å | 23.074 (2) |
| β / ° | 98.865 (2) |
| U / $Å^3$ | 14449 (2) |
| T / K | 100 |
| Z | 4 |
| ρ / g $cm^{-1}$ | 1.134 |
| Shape and color | Block, green |
| size (mm) | 0.5 × 0.5 × 0.3 |
| λ / Å | 0.71073 |
| μ / $mm^{-1}$ | 0.71 |
| Unique data | 13896 |
| unique data [Fo > 4sFo)] | 6842 |
| parameters/restraints | 1310/2952 |
| R1, wR2[a] | 0.200, 0.535 |
| weighting scheme[b] [w-1] | [σ2(Fo2) + (0.2P)2] |
| goodness of fit | 1.85 |
| largest residuals [e Å-3] | 1.31, -0.66 |

[a] *R*1 based on observed data, *wR*2 on all unique data.

[b] $P = 1/3[\max(F_o^2,0) + 2F_c^2]$

The crystal contains solvent accessible voids (726 $Å^3$), even though the location of some discrete solvent molecules could be determined. Due to the degree of disorder of the $^t$butyl groups in the crystal structure a large number of restraints were applied. SADI restraints were applied to the bonds of one of the $^t$butyl groups and SAME was applied to the remaining $^t$butyl groups to generate an average idealised geometry for all. SIMU and DELU restraints were also applied to C, N and O atoms to improve the thermal ellipsoids.

## 3.7 X-Ray Crystallographic Data for poly-[3]-rotaxane 8

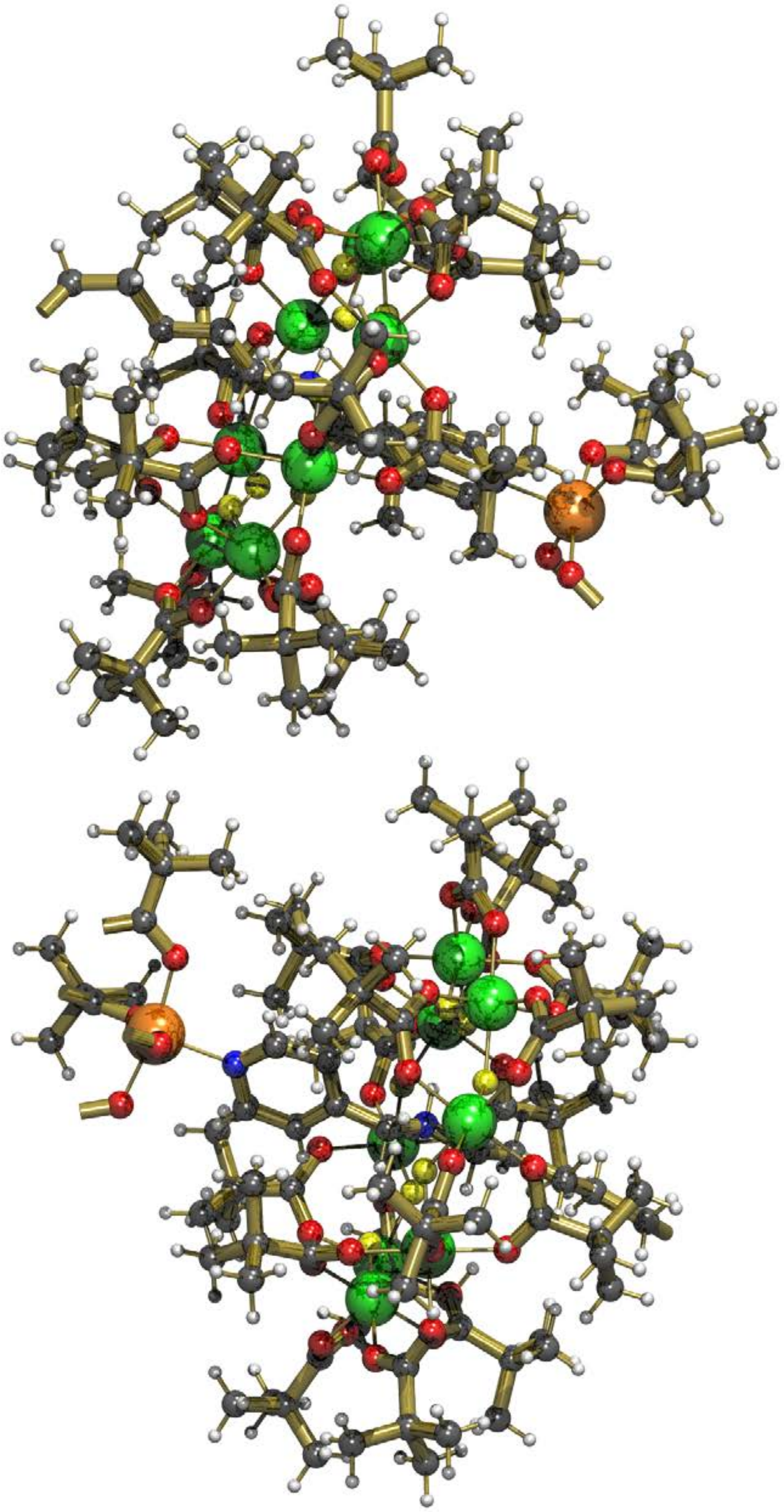

**Figure S7.** Graphical representation of the asymmetric unit of poly-[3]-rotaxane **8**
Colours: Cr = green, Ni = violet, Cu = orange, O = red, F = yellow, N = blue, C = grey, H = white

### 3.7.1 Table S7: Crystal data and structure refinement for poly-[3]-rotaxane 8

| | |
|---|---|
| Formula | $C_{101}H_{180}Cr_8CuF_8N_2O_{36}$ |
| M | 2630.03 |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| a / Å | 16.1810 (4) |
| b / Å | 28.3116 (6) |
| c / Å | 33.5398 (7) |
| α / ° | 70.065(10) |
| β / ° | 87.592 (10) |
| γ / ° | 81.189 (10) |
| U / Å$^3$ | 14384 (3) |
| T / K | 100 |
| Z | 4 |
| ρ / g cm$^{-1}$ | 1.214 |
| Shape and color | Plate, green |
| size (mm) | 0.8 × 0.6 × 0.1 |
| λ / Å | 0.6889 |
| μ / mm$^{-1}$ | 0.78 |
| Unique data | 36265 |
| Absorption correction | multi-scan |
| unique data [Fo > 4sFo)] | 18056 |
| parameters/restraints | 2846/5078 |
| R1, wR2[a] | 0.123, 0.336 |
| weighting scheme[b] [w-1] | $1/[\sigma^2(F_o^2) + (0.1257P)^2 + 81.2233P]$ |
| goodness of fit | 1.08 |
| largest residuals [e Å-3] | 0.82, -0.54 |

[a] *R*1 based on observed data, *wR*2 on all unique data.

[b] $P = 1/3[\max(F_o^2,0) + 2F_c^2]$

The crystal contains solvent accessible voids (442Å$^3$). However, the location of discrete solvent molecules could not be determined. Due to the degree of disorder of the $^t$butyl groups in the crystal structure a large number of restraints were applied. SADI restraints were applied to the bonds of one of the $^t$butyl groups and SAME was applied to the remaining $^t$butyl groups to generate an average idealised geometry for all. SIMU and DELU restraints were also applied to C N and O atoms to improve the thermal ellipsoids.

### 3.8 X-Ray Crystallographic Data for [3]-rotaxane 9

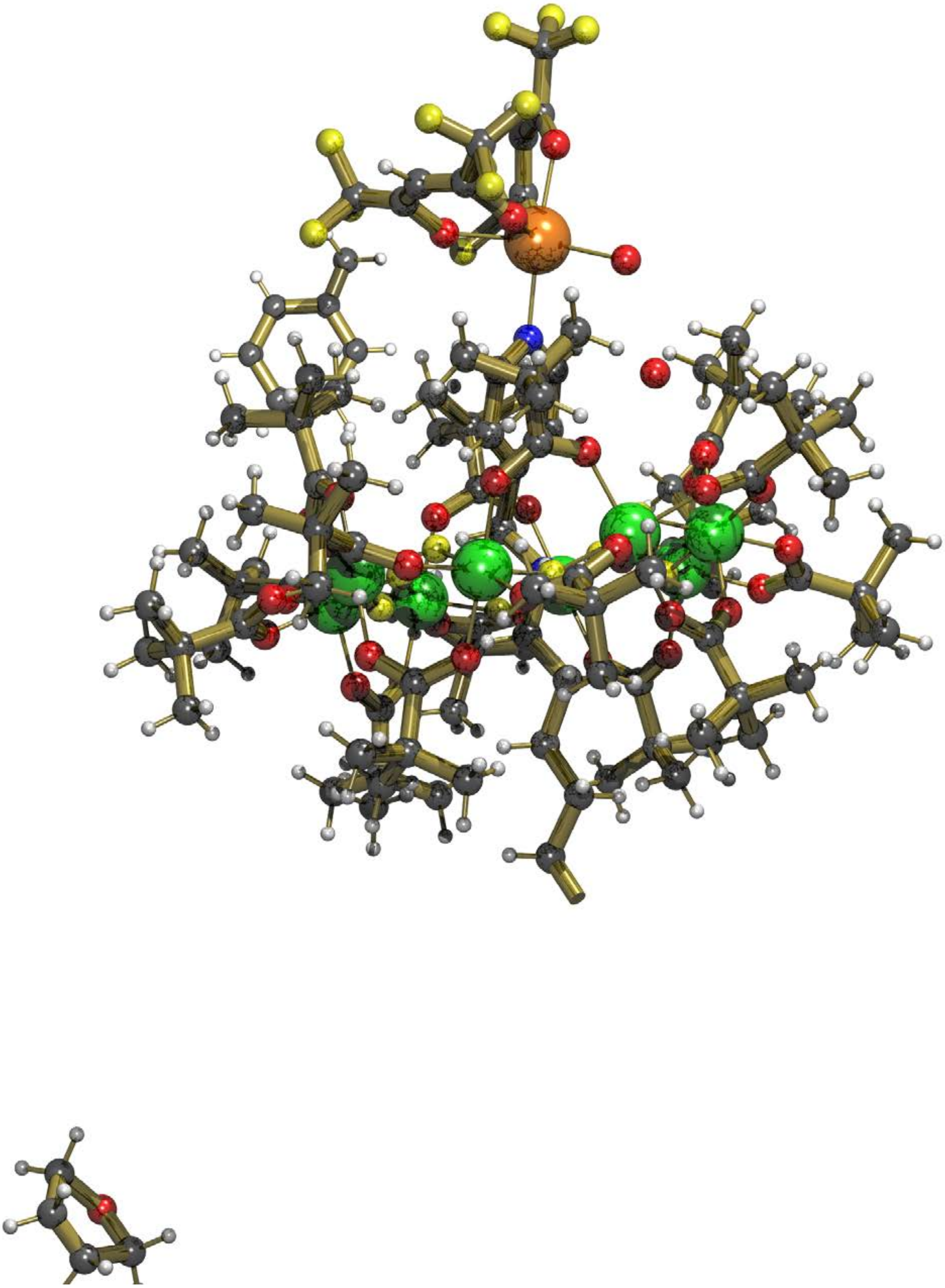

**Figure S8.** Graphical representation of the asymmetric unit of [3]-rotaxane (**9**)
Colours: Cr = green, Ni = violet, Cu = orange, O = red, F = yellow, N = blue, C = grey, H = white

### 3.8.1 Table S8: Crystal data and structure refinement for [3]-rotaxane 9

| Formula | $C_{112}H_{184}Cr_7CuF_{20}N_2NiO_{39}$ |
|---|---|
| M | 3053.26 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| a / Å | 16.8905 (5) |
| b / Å | 26.6323 (9) |
| c / Å | 34.0471 (14) |
| β / ° | 95.733 (3) |
| U / Å$^3$ | 15238.9 (9) |
| T / K | 100 |
| Z | 4 |
| ρ / g cm$^{-1}$ | 1.329 |
| Shape and color | Block, green |
| size (mm) | 0.40 × 0.30 × 0.20 |
| λ / Å | 1.54178 |
| μ / mm$^{-1}$ | 5.12 |
| Unique data | 18004 |
| Absorption correction | multi-scan |
| transmission max/min | 0.309/1.000 |
| unique data [Fo > 4sFo)] | 12265 |
| parameters/restraints | 1627/3056 |
| R1, wR2[a] | 0.100, 0.252 |
| weighting scheme[b] [w-1] | $1/[\sigma^2(F_o^2) + (0.1029P)^2 + 411.8141P]$ |
| goodness of fit | 1.109 |
| largest residuals [e Å-3] | 1.58, -0.84 |

[a] *R*1 based on observed data, *wR*2 on all unique data.

[b] $P = 1/3[\max(F_o^2,0) + 2F_c^2]$

Due to the degree of disorder of the $^t$butyl groups in the crystal structure a large number of restraints were applied. SADI restraints were applied to the bonds of one of the $^t$butyl groups and SAME was applied to the remaining $^t$butyl groups to generate an average idealised geometry for all. SIMU and DELU restraints were applied to all C atoms and F atoms on H(facac) to improve the thermal ellipsoids. ISOR was also applied to F atoms on H(facac).

### 3.9 X-Ray Crystallographic Data for poly-[3]-rotaxane 11

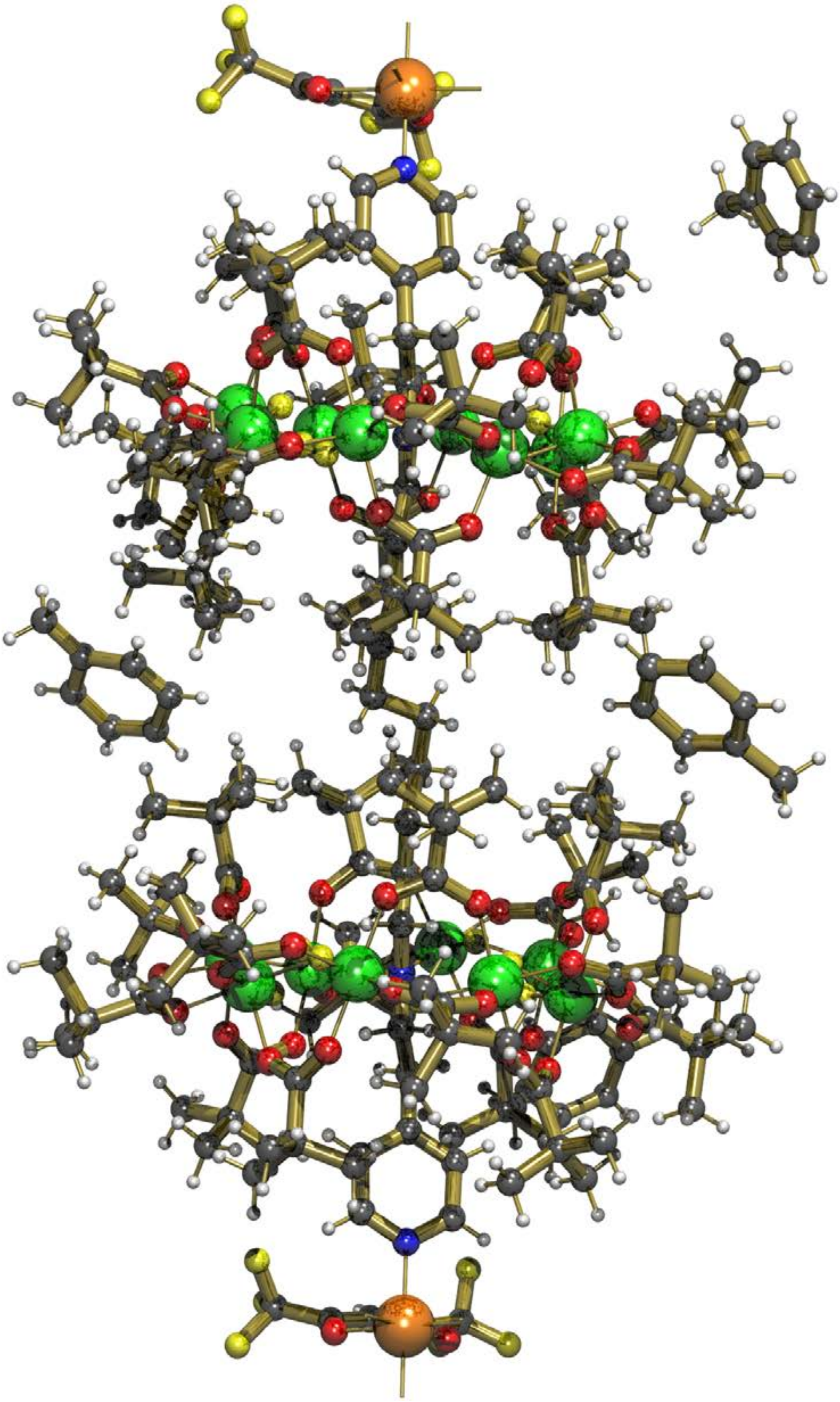

**Figure S9.** Graphical representation of the asymmetric unit of poly-[3]-rotaxane (**11**)
Colours: Cr = green, Ni = violet, Cu = orange, O = red, F = yellow, N = blue, C = grey, H = white

### 3.9.1 Table S9: Crystal data and structure refinement for poly-[3]-rotaxane 11

| | |
|---|---|
| Formula | $C_{222}H_{357}Cr_{14}CuF_{28}N_4Ni_2O_{68}$ |
| M | 5611.08 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| a / Å | 49.322 (2) |
| b / Å | 19.4560 (9) |
| c / Å | 30.1093 (15) |
| β / ° | 102.583 (2) |
| U / $Å^3$ | 28824 (2) |
| T / K | 100 |
| Z | 4 |
| ρ / g $cm^{-1}$ | 1.293 |
| Shape and color | Needle, green |
| size (mm) | 0.42 × 0.10 × 0.10 |
| λ / Å | 1.54178 |
| μ / $mm^{-1}$ | 5.12 |
| Unique data | 40453 |
| Absorption correction | multi-scan |
| transmission max/min | 0.363/0.752 |
| unique data [Fo > 4sFo)] | 24204 |
| parameters/restraints | 3188/1849 |
| R1, wR2[a] | 0.106, 0.291 |
| weighting scheme[b] [w-1] | $1/[\sigma^2(F_o^2) + (0.1029P)^2 + 411.8141P]$ |
| goodness of fit | 1.01 |
| largest residuals [e Å-3] | 1.81, -1.20 |

[a] *R*1 based on observed data, *wR*2 on all unique data.

[b] $P = 1/3[\max(F_o^2,0) + 2F_c^2]$

Due to the degree of disorder of the $^t$butyl groups in the crystal structure a large number of restraints were applied. SADI restraints were applied to the bonds of one of the $^t$butyl groups and SAME was applied to the remaining $^t$butyl groups to generate an average idealised geometry for all. SIMU and DELU restraints were also applied to C, N and O atoms to improve the thermal ellipsoids.

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[i] Loic Guillonneau, David Taddei and Christopher J. Moody. Org. Lett., 2008, 10 (20), pp 4505–4508