Gold(I) bridged dimeric and trimeric heterometallic {Cr_7Ni}-based Qubit systems and their characterization

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Electronic Supplementary Information (ESI)

Data Collection. X-Ray data for compounds **2**, **3**, **6**, **4** and **5** were collected at a temperature of 100 K using a Rigaku Supernova with Mo-Kα radiation equipped with a Eos CCd detector, a Bruker X8 prospector with Cu-Kα radiation equipped with CCD detector and a Rigaku FR-X with Cu-Kα radiation equipped with a HypixHE6000 detector. All instruments were equipped with an Oxford Cryosystems nitrogen flow gas system. Data were measured using APEX2 and CrysAlisPro suite of programs. X-ray data for compound **7** were collected using synchrotron X-ray radiation (λ = 0.6808 Å) at beamline I19 in Diamond Light Source.[S1] Data were measured using GDA suit of programs.

Crystal structure determinations and refinements. X-Ray data were processed and reduced using CrysAlisPro suite of programmes. Absorption correction was performed using empirical methods (SCALE3 ABSPACK) based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles.[S2] The crystal structure was solved and refined against all F^2 values using the SHELXL and Olex 2 suite of programmes.[S3] Despite the highly intense X-ray source, crystals of **7** present a diffraction limit of 1.4 Å.

All atoms in crystal structures **2**, **3**, **6**, **4** and **5** were refined anisotropically with the exception of the hydrogens atoms and some solvent molecules. In the crystal structure **7**, only the metals atoms and central ligand were refined anisotropically in order to keep the highest data/parameters ratio. Hydrogen atoms were placed in the calculated idealized positions. The pivalate ligands were found disordered and modelled over two positions. The C-C atomic distances were restrained using SADI (same distance) and DFIX (distance fix) Shelxl commands. The atomic displacement parameters (adp) of the pivalate ligands have been restrained using similar Ueq (SIMU) and rigid bond (RIGU) SHELX restraints.

Compounds **5** and **7** present large voids filled with featureless electron density; three different pockets with 100, 151 and 84 electrons were found in **7** which could correspond to 2.5, 4 and 2 molecules of DCM. Five different pockets with 165, 175, 55 146 and 60 electrons in **7**, which could correspond with 7.5, 8, 2.5, 6.5 and 3 molecules of acetonitrile.

A large number of A and B alerts were found, especially for structure **7** , due to the crystal poor resolution obtained. Unfortunately, this resolution is common in large molecules with large intermolecular spaces filled with disordered solvent molecules.

CCDC 1499587-1499590 and 2052037-2052038 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

S1. Nowell H, Barnett SA, Christensen KE, Teat SJ, Allan DR. *J Synchrotron Radiat.*,**2012,** *19*, 435-441.

S2. (a) G. M. Sheldrick, *SADABS*, empirical absorption correction program based upon the method of Blessing. (b) L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, An empirical correction for absorption anisotropy *J. Appl. Cryst.* **2015**, *48*. (c) R. H. Blessing, An empirical correction for absorption anisotropy, *Acta Crystallogr.* **1995**, *A51*, 33-38.

S3. a) Sheldrick. G. M. Crystal structure refinement with SHELXL, *Acta Crystallogr.*, **2015**, *C71*, 3-8; b**)** O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst.., **2009,** *42*, 339–341

Table S1. Crystallographic information for **2**, **3**, **6**, **4**, **5** and **7**

Identification code	**2**	**3**	**6**
Empirical formula	$C_{100}H_{165}Cr_7F_8NNiO_{32}P$	$C_{100}H_{165}AuClCr_7F_8NNiO_{32}P$	$C_{102}H_{167}AuCl_2Cr_7F_8N_2NiO_{32}PS$
Formula weight	2499.00	2731.42	2838.97
Temperature/K	150.02(10)	150.0	100
Crystal system	monoclinic	monoclinic	monoclinic
Space group	C2/c	$P2_1/c$	I2/a
a/Å	47.1357(15)	25.2554(5)	33.774(7)
b/Å	16.5185(5)	16.5156(4)	16.524(3)
c/Å	33.9008(8)	32.7311(7)	50.211(10)
α/°	90	90	90
β/°	92.227(3)	90.9080(19)	96.43(3)
γ/°	90	90	90
Volume/Å^3	26375.5(13)	13650.7(5)	27845(10)
Z	8	4	8
ρ_{calc}g/cm^3	1.259	1.329	1.354
μ/mm^{-1}	0.781	1.844	7.5712
F(000)	10488.0	5628.0	11688.0
Crystal size/mm^3	0.23 × 0.2 × 0.15	0.2 × 0.2 × 0.1	0.3 × 0.1 × 0.05
Radiation	Mo Kα (λ = 0.71073)	MoKα (λ = 0.71073)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.538 to 50.7	1.612 to 52.878	5.661 to 130.1626
Index ranges	$-54 \leq h \leq 56, -19 \leq k \leq 15, -40 \leq l \leq 38$	$-30 \leq h \leq 26, -20 \leq k \leq 18, -40 \leq l \leq 33$	$-28 \leq h \leq 28, -13 \leq k \leq 13, -41 \leq l \leq 41$
Reflections collected	57939	100180	26636
Independent reflections	24079 [R_{int} = 0.0706, R_{sigma} = 0.1393]	26586 [R_{int} = 0.0989, R_{sigma} = 0.1089]	23624 [R_{int} = 0.1459, R_{sigma} = 0.1386]
Data/restraints/parameters	24079/6279/1772	26586/3474/1361	23624/3578/1467
Goodness-of-fit on F^2	1.029	1.031	0.895
Final R indexes [I>=2σ (I)]	R_1 = 0.0979, wR_2 = 0.2245	R_1 = 0.1123, wR_2 = 0.3133	R_1 = 0.1237, wR_2 = 0.2954
Final R indexes [all data]	R_1 = 0.2080, wR_2 = 0.2910	R_1 = 0.1918, wR_2 = 0.3563	R_1 = 0.2469, wR_2 = 0.3662
Largest diff. peak/hole / e Å^{-3}	1.51/-1.38	1.77/-2.21	2.41/-1.62

Identification code	**4**	**5**	**7**
Empirical formula	$C_{200}H_{330}AuClCr_{14}F_{16}N_2Ni_2O_{64}P_2$	$C_{302}H_{499}AuCl_5Cr_{21}F_{24}N_3Ni_3O_{96}P_3$	$C_{303}H_{495}Au_3Cr_{24}F_{24}N_6O_{96}P_3S_3$
Formula weight	5230.42	7899.27	8242.01
Temperature/K	100	100.01(10)	100.0
Crystal system	monoclinic	triclinic	triclinic
Space group	C2/c	P-1	P-1
a/Å	47.273(10)	16.3361(3)	16.831(3)
b/Å	16.388(3)	34.1374(4)	29.996(6)
c/Å	33.769(7)	41.1846(4)	45.326(9)
α/°	90	104.8540(10)	76.93(3)
β/°	93.46(3)	96.8760(10)	88.56(3)
γ/°	90	102.7770(10)	86.70(3)
Volume/Å^3	26113(9)	21267.7(5)	22251(8)
Z	4	2	2
ρ_{calc}g/cm^3	1.330	1.234	1.230
μ/mm^{-1}	1.359	6.023	1.640
F(000)	10872.0	8226.0	8490.0
Crystal size/mm^3	0.2 × 0.2 × 0.1	0.55 × 0.52 × 0.5	0.05 × 0.05 × 0.02
Radiation	MoKα (λ = 0.71073)	Cu Kα (λ = 1.54184)	MoKα (λ = 06808)

2Θ range for data collection/°	1.726 to 52.516	4.52 to 152.524	3.246 to 29.408
Index ranges	$-58 \le h \le 58, -18 \le k \le 17, -40 \le l \le 41$	$-20 \le h \le 20, -42 \le k \le 42, -51 \le l \le 45$	$-14 \le h \le 10, -24 \le k \le 24, 37 \le l \le -37$
Reflections collected	60899	257368	13382
Independent reflections	24379 [R_{int} = 0.2067, R_{sigma} = 0.2412]	85430 [R_{int} = 0.0747, R_{sigma} = 0.0801]	13382 [R_{int} = 14.59, R_{sigma} = 0.1538]
Data/restraints/parameters	24379/2765/1397	85430/4675/5233	13382/16719/2029
Goodness-of-fit on F^2	0.985	1.037	1.223
Final R indexes [I>=2σ (I)]	R_1 = 0.1309, wR_2 = 0.3266	R_1 = 0.0910, wR_2 = 0.2417	R_1 = 0.1409, wR_2 = 0.3586
Final R indexes [all data]	R_1 = 0.2555, wR_2 = 0.3945	R_1 = 0.1115, wR_2 = 0.2585	R_1 = 0.1967, wR_2 = 0.3868
Largest diff. peak/hole / e $Å^{-3}$	1.65/-3.56	2.88/-4.58	1.22/-0.82

Respective orientation of $\{Cr_7Ni\}$ rings in 4 and 5

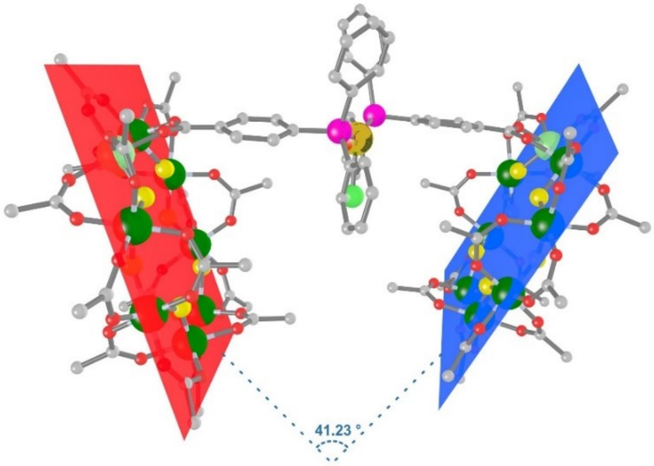

Figure S1: Diagram showing relative orientations of the two $\{Cr_7Ni\}$ rings in **4**. Hydrogen atoms, methyl groups and ammonium cation omitted for clarity.

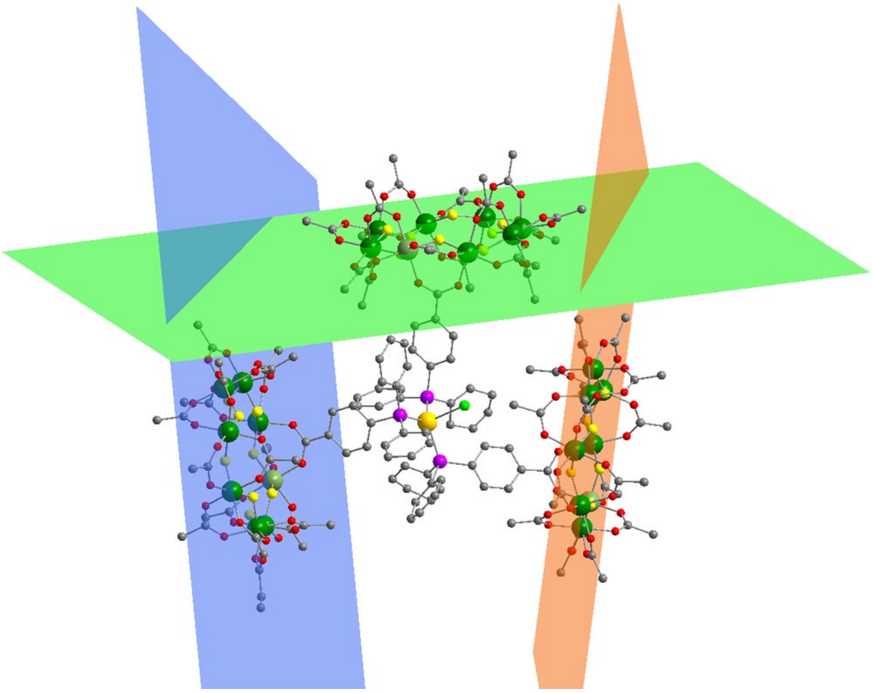

Figure S2: Diagram showing relative orientations of the three $\{Cr_7Ni\}$ rings in **5.** Hydrogen atoms, methyl groups and ammonium cation omitted for clarity. Dihedral angles between Plane-1(green) – Plane-2(orange) and Plane-1(green) – Plane-3(blue) is 81.7° whereas Plane-2(orange) and Plane-3(blue) make an angle of 17.4°.

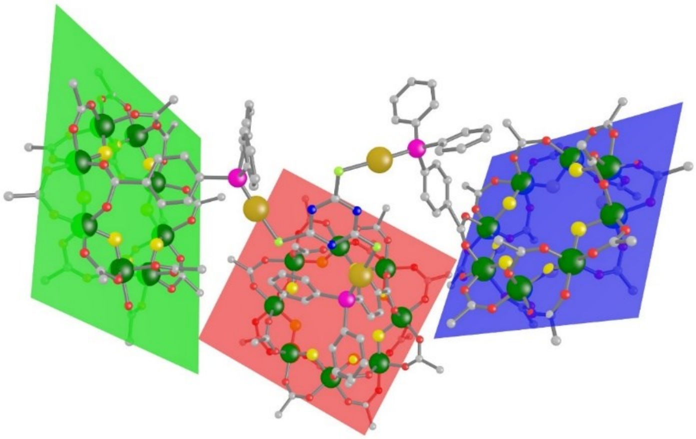

Figure S3: Diagram showing relative orientations of the three {Cr_7Ni} rings in **7**. Hydrogen atoms, methyl groups and ammonium cation omitted for clarity.

Disordered binding conformations in 3

Shown below are the two distinct binding conformations for gold in compound **3**. P-Au-Cl bond in the major conformation, with a crystallographic occupancy of 89.67 %, is found to be nearly linear 176.30 (2)°. The minor conformation has a crystallographic occupancy of 10.33 %. It is distinctly bent with a P-Au-Cl angle of 156.40 (18) °.

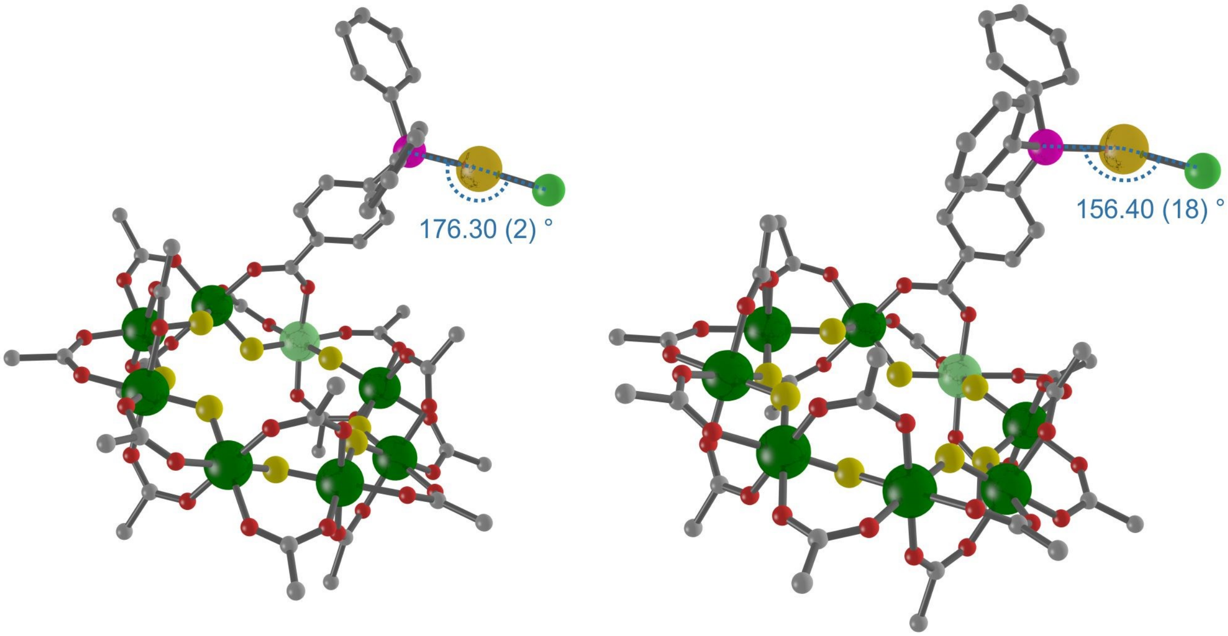

Figure S4: Single crystal X-ray structure of **3** showing the two different P-Au-Cl conformations. Colours – Cr (green), Ni (pale green), Au (gold), F (yellow), O (red), P (purple), C (grey), Cl (grass green). Hydrogen atoms, methyl groups and ammonium cation omitted for clarity.

EPR Measurements:

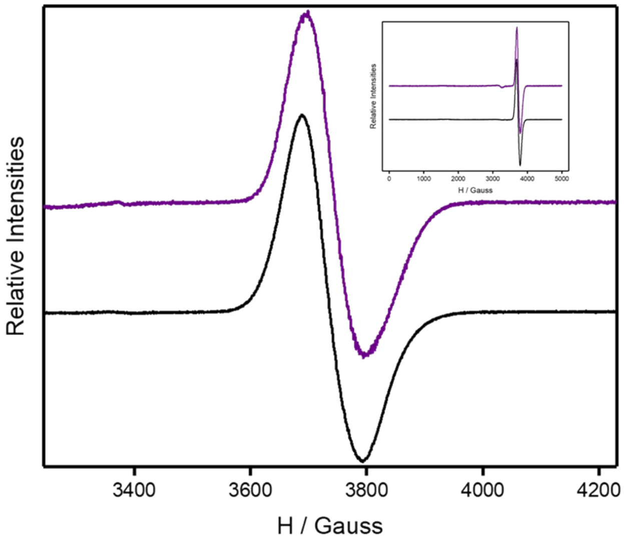

Figure S5: X-Band (c.a. ~9.5 GHz) CW EPR spectra for **4**, at 5 K of powder (black) and a 3 mM solution (purple). Insert; a full field sweep of the samples.

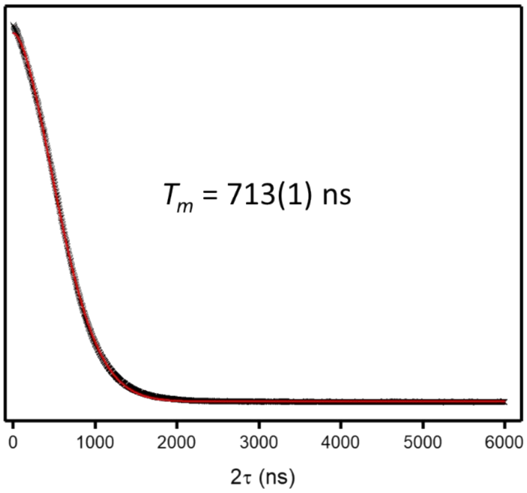

Figure S6: Phase memory times (T_m) plot for **4** using Q-Band (ca. 34 GHz) featured at B_0 = 13701 Gauss at 3 K. Experimental measurements using 20 and 40 ns for π/2 and π pulses respectively (back), echo decay fit to an exponential decay with the form $I(2\tau) = I(2\tau_0)\exp(-2\tau/T_m)$, (red).

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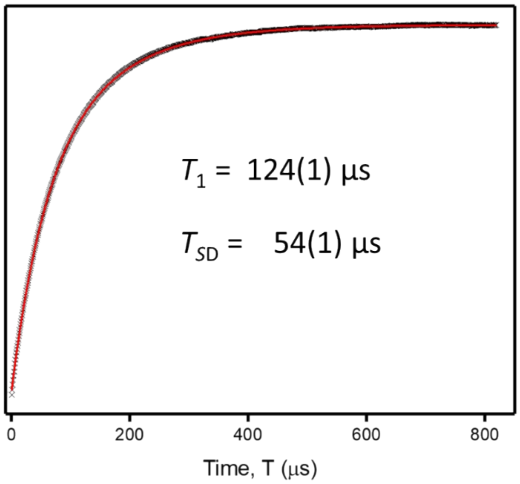

Figure S7: Spin lattice relaxation (T_1) measurements of **4**, Q-Band (ca. 34 GHz), 0.2 mM solution sample in dry and degassed toluene at 3 K; featured at B_0 = 13701 Gauss. Using 20 and 40 ns for π/2 and π pulses respectively with *T* = 500 ns. Experimental trace (black crosses), echo decay fit to an exponential decay with the form $I(T) = I(T_0)\exp(-T/T_1) + I(T_0)\exp(-T/T_{SD})$, (solid red line).

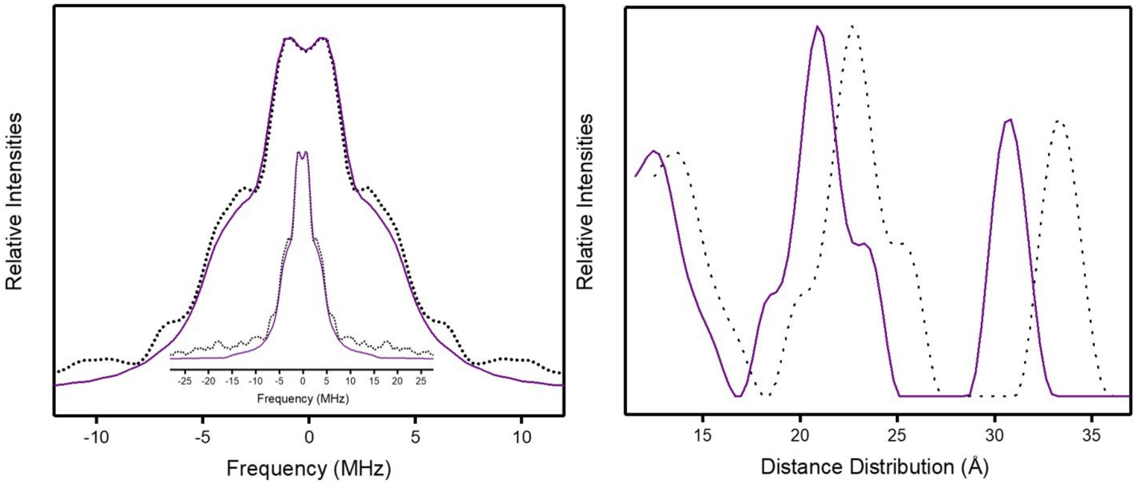

Figure S8: On the left Pake pattern from Fourier transformation of dipolar evolution (black) and fitted data (purple), and on the right distance distribution with default *g* values (black) shown with corrected *g* values (purple).

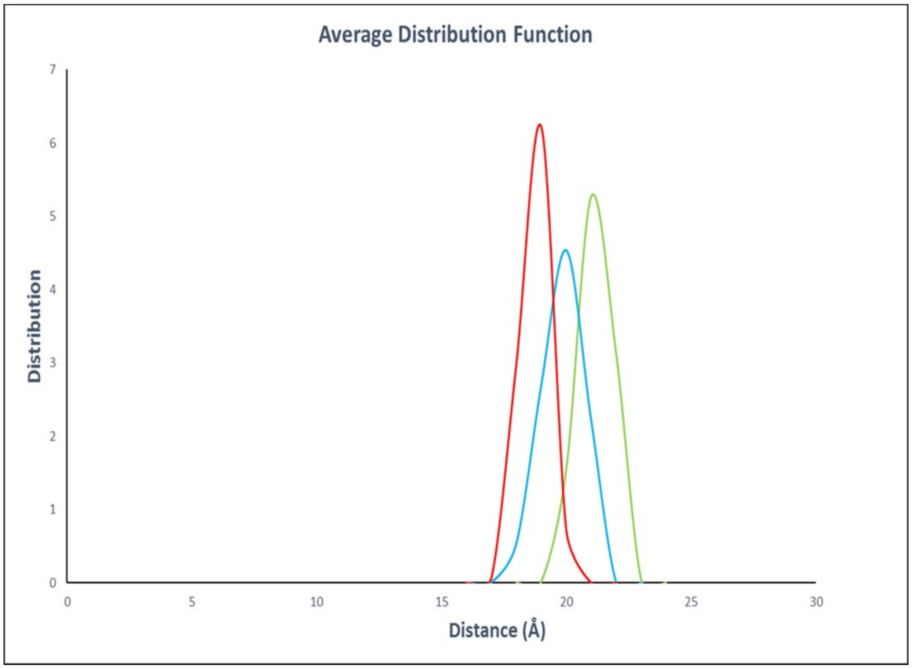

Figure S9: The average distance distribution function of the two metal rings for Rotaxane **4-A**, **4-B** (Blue) and **4-C** (Green).