

## Chiral Tetranuclear Copper(II) Complexes: Syntheses, Optical and Magnetic Properties

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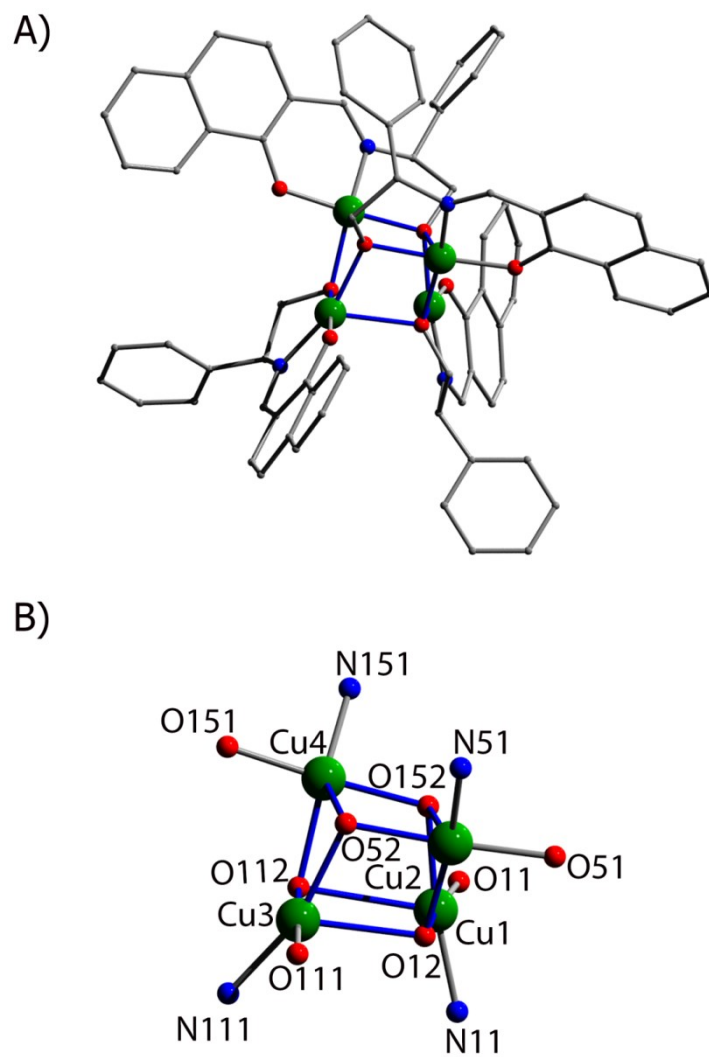
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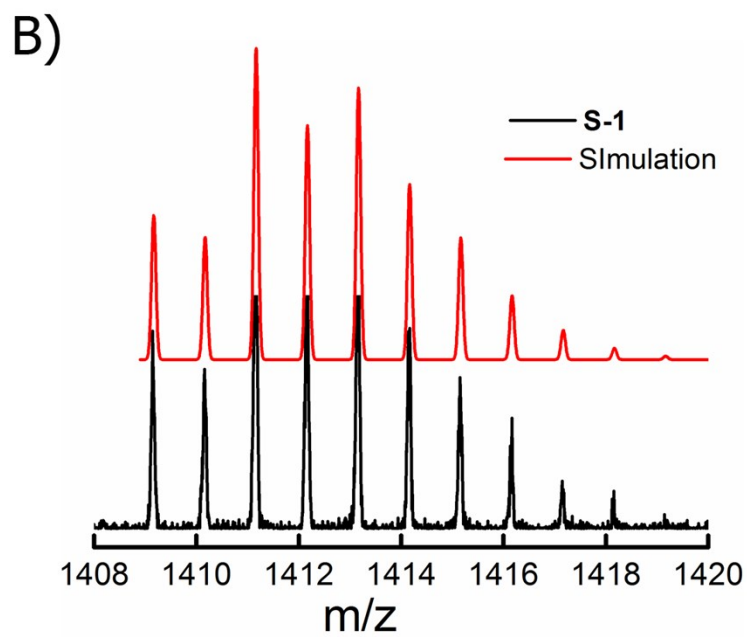
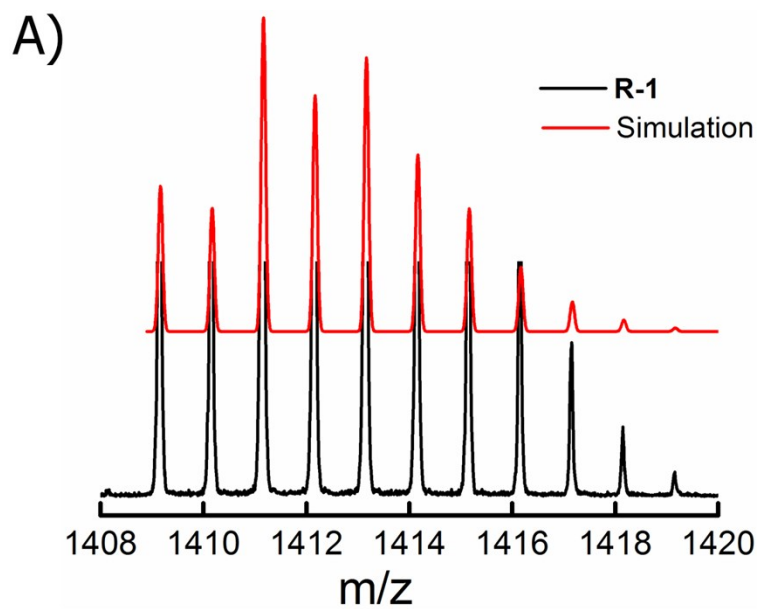
**Figure S1.** A) Ball and stick representation of crystal structure of **S-1**. Hydrogen atoms were removed for clarity B) The metal core found in **S-1**. The same labelling scheme is followed in panel A as in panel B. Colour code: Green = Cu, Red = O, Blue = N, grey = C.

**Table S1.** Crystallographic parameters for complex **S-1**

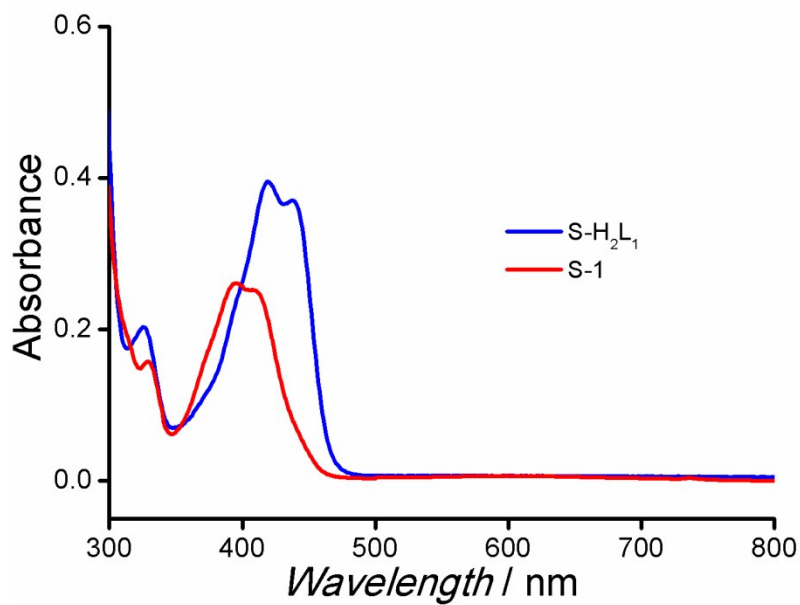
Formula	$C_{153}H_{126}N_8O_{20}Cl_2$
Size [mm]	$0.19 \times 0.08 \times 0.05$
System	Monoclinic
Space group	$C2$
$a$ [Å]	21.674(6)
$b$ [Å]	13.050(4)
$c$ [Å]	23.581(6)
$\alpha$ [°]	90
$\beta$ [°]	90
$\gamma$ [°]	90
$V$ [Å <sup>3</sup> ]	6670(3)
$Z$	2
$\rho_{\text{calcd}}$ [g/cm <sup>3</sup> ]	1.482
$2\theta_{\text{max}}$	49.41
radiation	Mo $K_{\alpha}$
$\lambda$ [Å]	0.7107
$T$ [K]	100
reflns	24051
Ind. reflns	9615
reflns with $I > 2\sigma(I)$	4344
$R1$	0.0881
$wR2$	0.2096

**Table S2.** CShM parameters for the co-ordination geometries of the complexes **R-1**

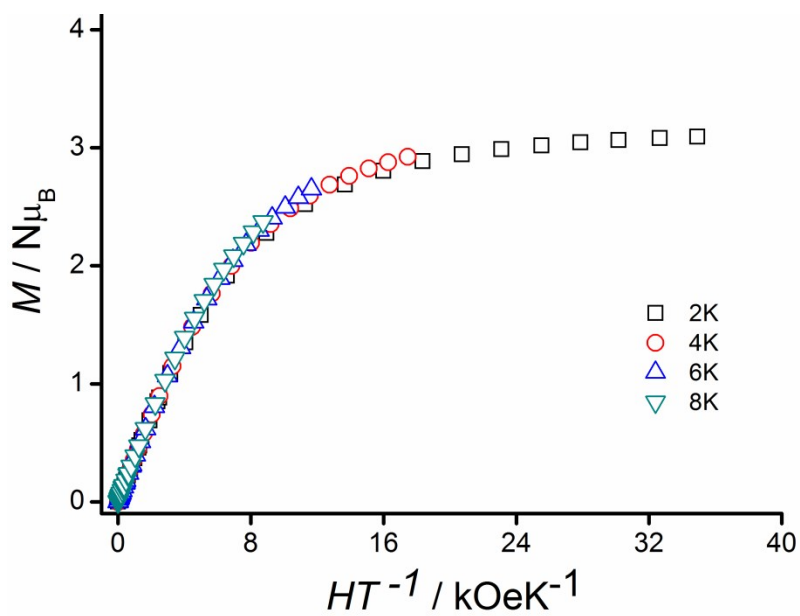
Metal Site	Pentagon/PP- $5/D_{3h}$	Vacant octahedron/vOC- $5/C_{4v}$	Trigonal bipyramid/TBPY- $5/D_{3h}$	Square pyramid/SPY- $5/C_{4v}$	Johnson trigonal bipyramid (J12)/ JTBPY- $5/D_{3h}$
Cu1	20.869	5.276	9.380	4.369	12.448
Cu2	24.470	3.733	5.692	3.506	8.737
Cu3	25.352	6.218	4.442	5.481	7.698
Cu4	23.812	3.602	6.028	3.324	9.243



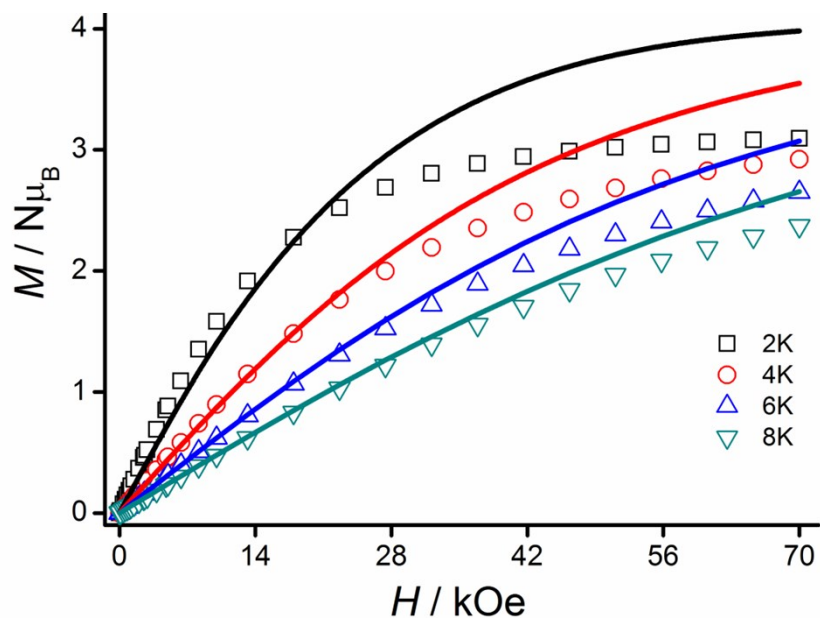
**Figure S2.** ESI-MS spectrum of **R-1** and **S-1** recorded in DMF solution (black trace) and the simulation of its isotopic distribution pattern (red trace).



**Figure S3.** Electronic spectra recorded for  $2 \times 10^{-5}$  M and  $1 \times 10^{-4}$  M concentrated solutions of ligand  $S-H_2L_1$  and complex  $S-1$  in the DMF solvent respectively.



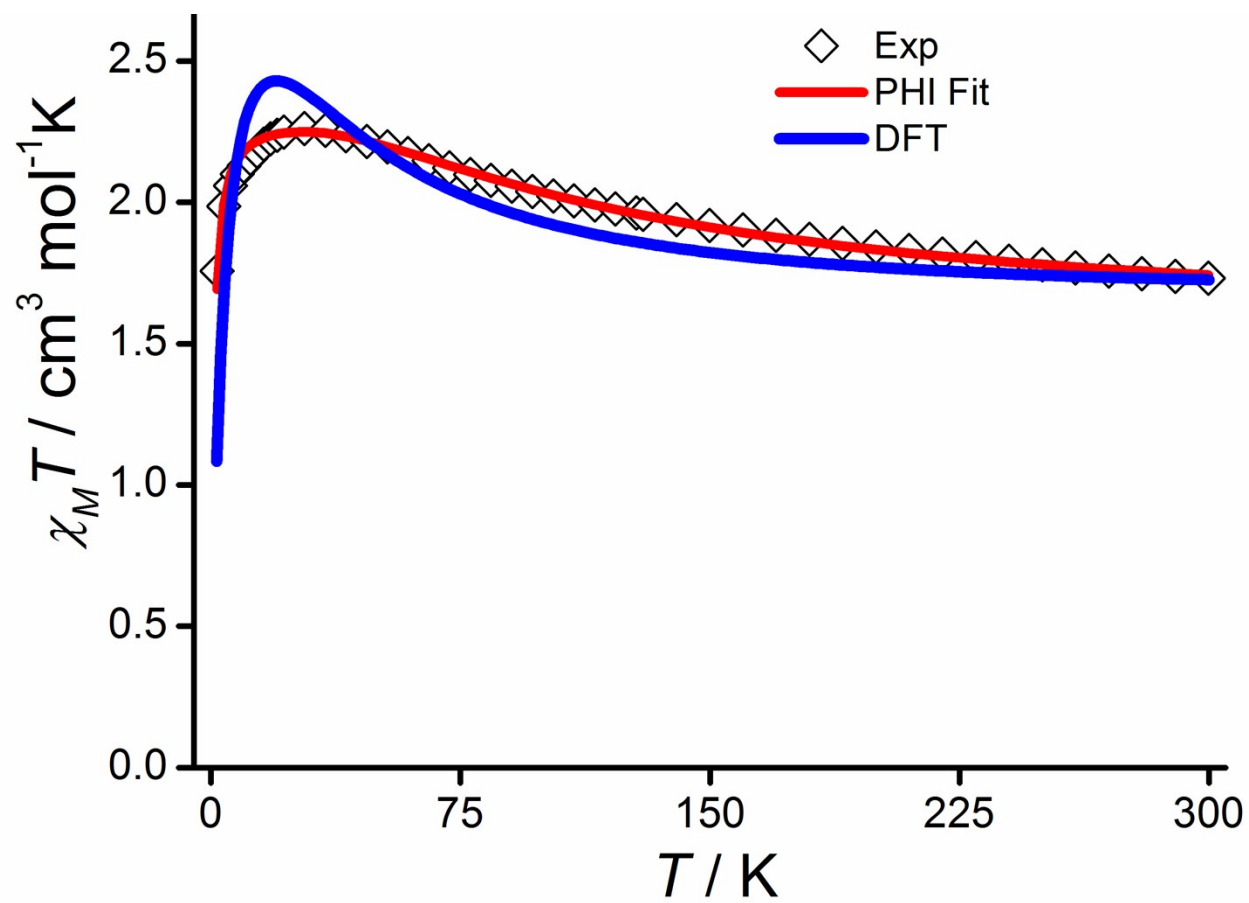
**Figure S4.** Reduced magnetization curves for  $R-1$ .



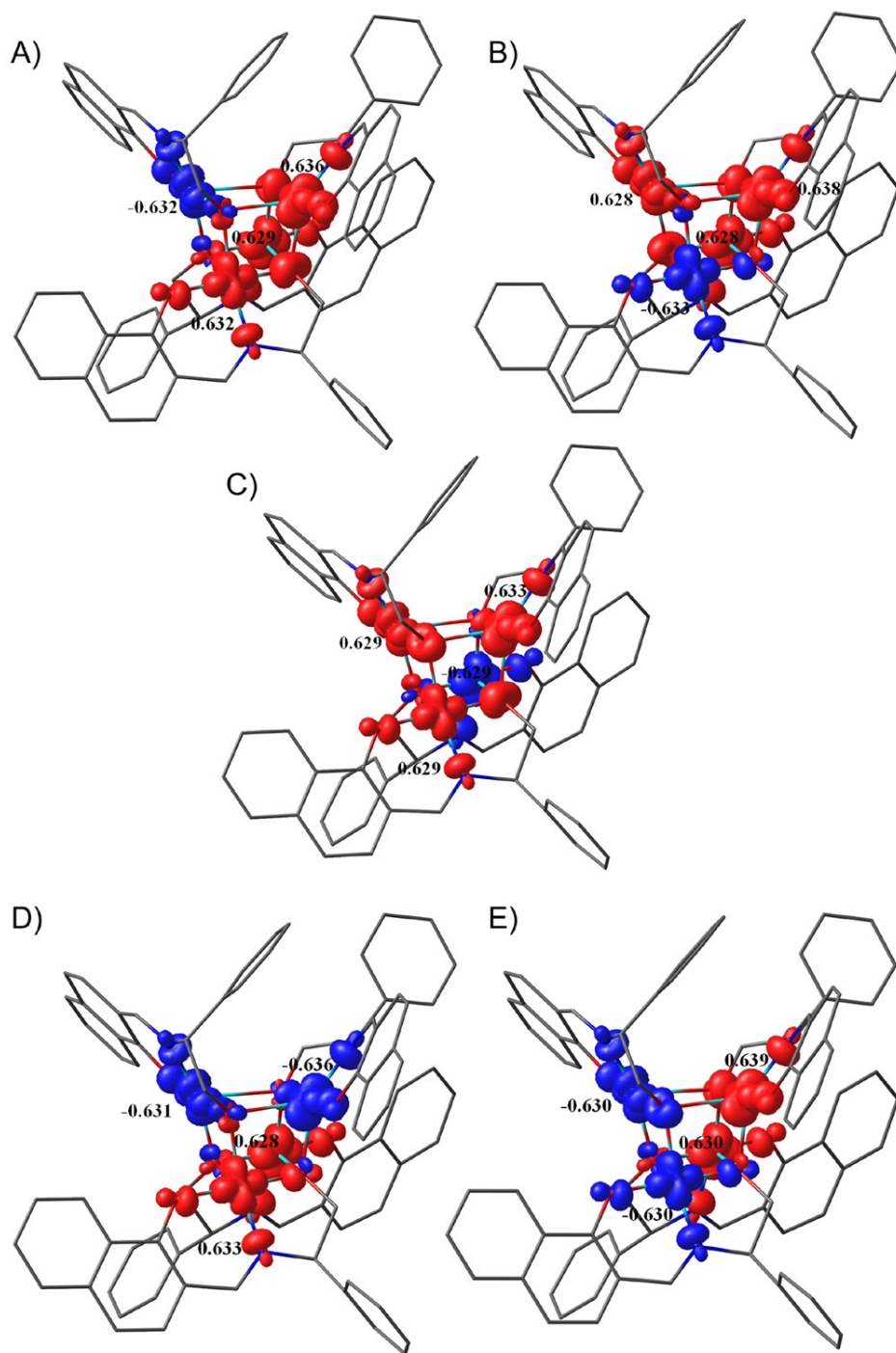
**Figure S5.** Result of simultaneous PHI fitting of magnetization data for **R-1**.

**Table S3:** Possible high spin and broken symmetry solutions performed on the R-1 complex along with their  $S^2$  values.

Spin state	Cu1	Cu2	Cu3	Cu4	$\langle S^2 \rangle$
HS	↑	↑	↑	↑	6.011
BS1	↑	↓	↑	↑	3.008
BS2	↑	↑	↓	↑	3.009
BS3	↑	↑	↑	↓	3.002
BS4	↓	↓	↑	↑	2.001
BS5	↑	↓	↓	↑	2.009



**Figure S6.** Simulation of magnetic susceptibility with DFT computed parameters for R-1.



**Figure S7.** B3LYP/TZV computed spin density plots of Cu<sub>4</sub>-cubane at different broken symmetry states (BS1-BS5) A-E respectively with an iso-surface value of 0.009 e/bohr<sup>3</sup>.



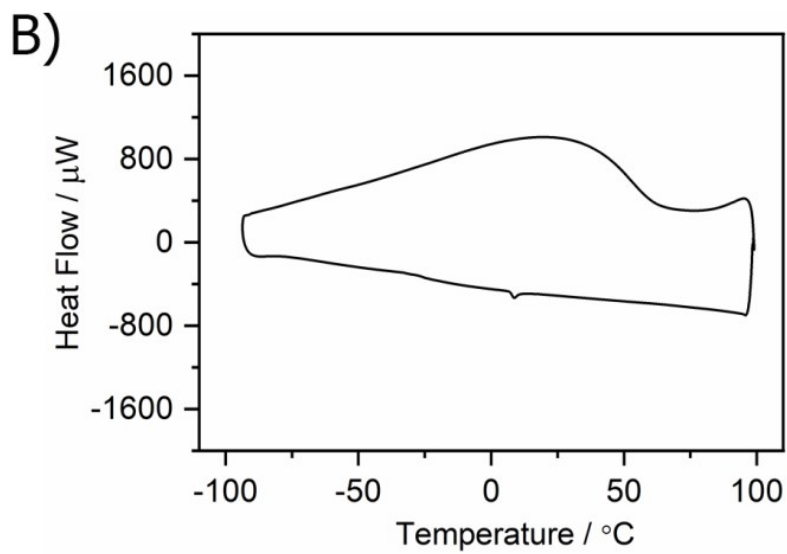
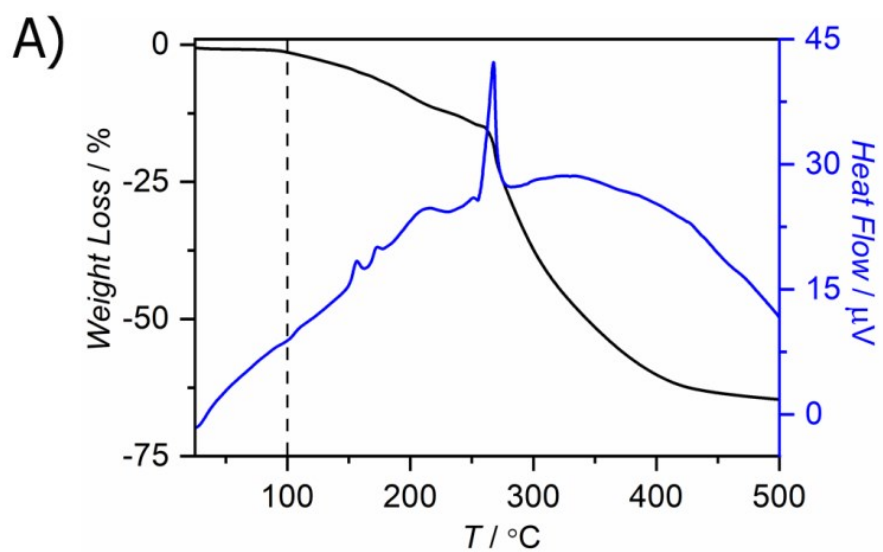
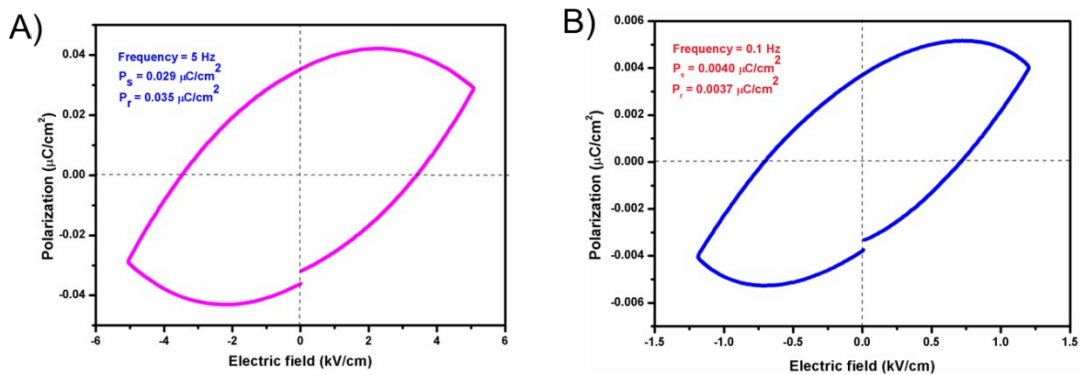
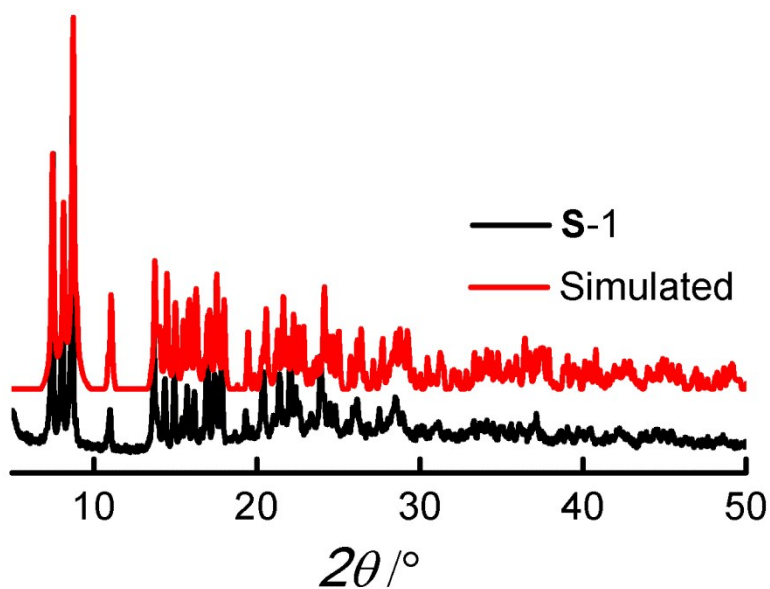


Figure S8. (A) TGA-DTA and (B) DSC data for **R-1**



**Figure S9.** Ferroelectric measurement on sample of complex **R-1**. (A) for single crystal and (B) for powder.



**Figure S10.** Comparison of PXRD profile of complex **S-1** (black trace) with its corresponding PXRD simulated for the crystal structure of **S-1** (red trace).