

## Supporting information

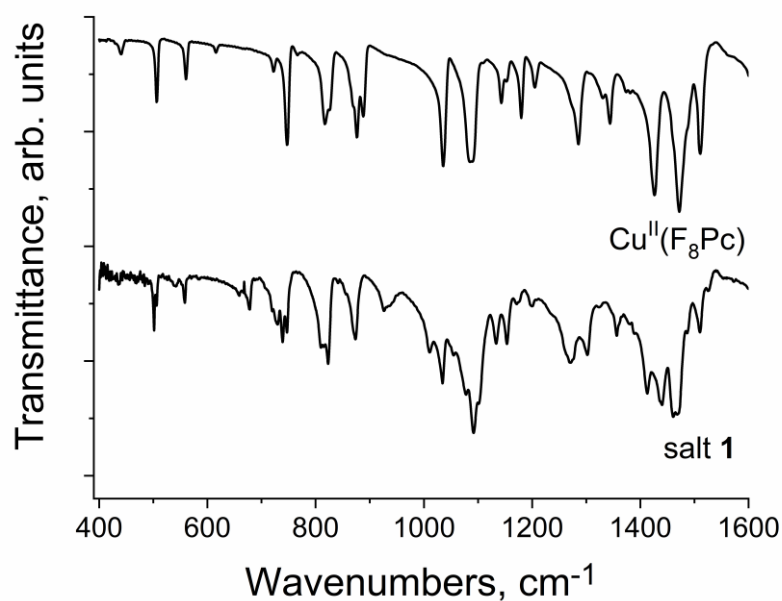
### IR- spectra

**Table S1.** IR spectra of starting  $\text{Cu}^{\text{II}}(\text{F}_x\text{Pc})$  ( $x = 8, 16$ ) and salts **1** and **2**

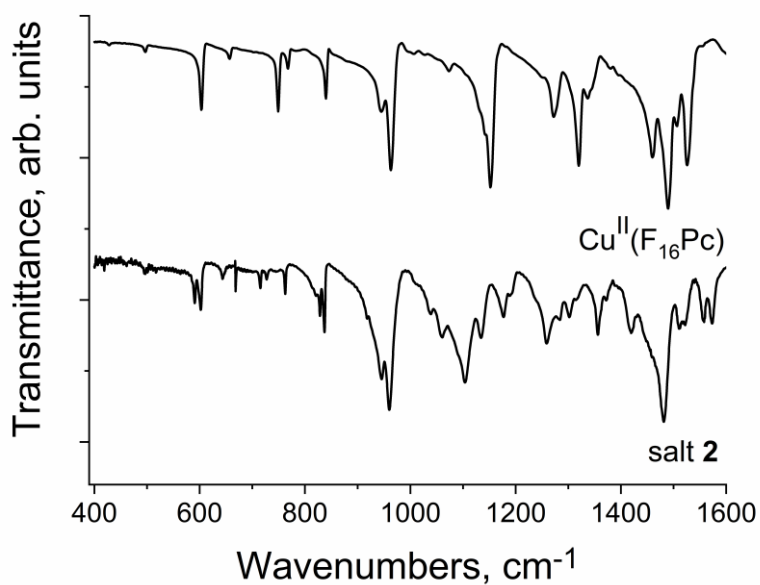
| Components                                   | Cryptand | $\text{Cu}^{\text{II}}(\text{F}_8\text{Pc})$ | $\{\text{cryptand}(\text{Na}^+)\}$<br>$[\text{Cu}^{\text{II}}(\text{F}_8\text{Pc})^{\bullet 3-}]^-$<br>$\cdot 2\text{C}_6\text{H}_4\text{Cl}_2$ ( <b>1</b> ) | $\text{Cu}^{\text{II}}(\text{F}_{16}\text{Pc})$ | $\{\text{cryptand}(\text{Na}^+)\}_2$<br>$[\text{Cu}^{\text{II}}(\text{F}_{16}\text{Pc})^{4-}]^{2-}$<br>$\cdot \text{C}_6\text{H}_{14}$ ( <b>2</b> ) |
|----------------------------------------------|----------|----------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------|
| $\text{Cu}^{\text{II}}(\text{F}_x\text{Pc})$ |          | 441w                                         | -                                                                                                                                                            | 497w                                            | -                                                                                                                                                   |
|                                              |          | 506m                                         | 502m                                                                                                                                                         | 603m                                            | 602m                                                                                                                                                |
|                                              |          | 560m                                         | 558w                                                                                                                                                         | 657w                                            | -                                                                                                                                                   |
|                                              |          | 617w                                         | -                                                                                                                                                            | 750m                                            | -                                                                                                                                                   |
|                                              |          | 722w                                         | -                                                                                                                                                            | 768w                                            | 763w                                                                                                                                                |
|                                              |          | 748s                                         | 739m*                                                                                                                                                        | 840m                                            | 837m                                                                                                                                                |
|                                              |          | 818m                                         | 823s                                                                                                                                                         | 964s                                            | 960s                                                                                                                                                |
|                                              |          | 877s                                         | 874m                                                                                                                                                         | 1074w                                           | -                                                                                                                                                   |
|                                              |          | 1036s                                        | 1035s*                                                                                                                                                       | 1153s                                           | -                                                                                                                                                   |
|                                              |          | 1085s                                        | 1092s*                                                                                                                                                       | 1273m                                           | -                                                                                                                                                   |
|                                              |          | 1144w                                        | 1153m                                                                                                                                                        | 1321s                                           | -                                                                                                                                                   |
|                                              |          | 1180m                                        | -                                                                                                                                                            | 1337m                                           | -                                                                                                                                                   |
|                                              |          | 1205w                                        | 1200w                                                                                                                                                        | 1459s                                           | -                                                                                                                                                   |
|                                              |          | 1286s                                        | -                                                                                                                                                            | 1490s                                           | 1482s*                                                                                                                                              |
|                                              |          | 1344m                                        | -                                                                                                                                                            | 1526s                                           | -                                                                                                                                                   |
|                                              |          | 1426s                                        | -                                                                                                                                                            | 1618w                                           | -                                                                                                                                                   |
|                                              |          | 1472s                                        | -                                                                                                                                                            | 1638w                                           | 1645w                                                                                                                                               |
|                                              |          | 1511m                                        | 1510m                                                                                                                                                        |                                                 |                                                                                                                                                     |
|                                              |          | 1621m                                        | 1616w                                                                                                                                                        |                                                 |                                                                                                                                                     |
| Cryptand( $\text{Na}$ ) <sup>+</sup>         | 476w     |                                              | -                                                                                                                                                            |                                                 | -                                                                                                                                                   |
|                                              | 528w     |                                              | -                                                                                                                                                            |                                                 | -                                                                                                                                                   |
|                                              | 581w     |                                              | -                                                                                                                                                            |                                                 | -                                                                                                                                                   |
|                                              | 735m     |                                              | 739m*                                                                                                                                                        |                                                 | 727w                                                                                                                                                |
|                                              | 922m     |                                              | 926m                                                                                                                                                         |                                                 | -                                                                                                                                                   |
|                                              | 1038w    |                                              | 1035s*                                                                                                                                                       |                                                 | -                                                                                                                                                   |
|                                              | 1071m    |                                              | -                                                                                                                                                            |                                                 | 1061m                                                                                                                                               |
|                                              | 1100s    |                                              | 1092s*                                                                                                                                                       |                                                 | 1103s                                                                                                                                               |
|                                              | 1127s    |                                              | 1134m                                                                                                                                                        |                                                 | 1134m                                                                                                                                               |
|                                              | 1213w    |                                              | -                                                                                                                                                            |                                                 | -                                                                                                                                                   |
|                                              | 1295m    |                                              | 1302m                                                                                                                                                        |                                                 | 1302m                                                                                                                                               |
|                                              | 1329m    |                                              | -                                                                                                                                                            |                                                 | -                                                                                                                                                   |
|                                              | 1360s    |                                              | 1357m                                                                                                                                                        |                                                 | 1356m                                                                                                                                               |
|                                              | 1446m    |                                              | 1441s                                                                                                                                                        |                                                 | -                                                                                                                                                   |
|                                              | 1462m    |                                              | 1461s*                                                                                                                                                       |                                                 | -                                                                                                                                                   |
|                                              | 1490w    |                                              | -                                                                                                                                                            |                                                 | 1482s*                                                                                                                                              |
|                                              | 2790w    |                                              | -                                                                                                                                                            |                                                 | -                                                                                                                                                   |
| Solvent                                      | 2877w    |                                              | 2870w                                                                                                                                                        |                                                 | 2872m*                                                                                                                                              |
|                                              | 2943w    |                                              | -                                                                                                                                                            |                                                 | -                                                                                                                                                   |
|                                              |          |                                              | $\text{C}_6\text{H}_4\text{Cl}_2$                                                                                                                            |                                                 | $\text{C}_6\text{H}_{14}$                                                                                                                           |
|                                              |          |                                              | 659w                                                                                                                                                         |                                                 | 659w                                                                                                                                                |
|                                              |          |                                              | -                                                                                                                                                            |                                                 | -                                                                                                                                                   |
|                                              |          |                                              | 1035s*                                                                                                                                                       |                                                 | -                                                                                                                                                   |
|                                              |          |                                              | -                                                                                                                                                            |                                                 | -                                                                                                                                                   |
|                                              |          |                                              | 1461s*                                                                                                                                                       |                                                 | -                                                                                                                                                   |

\* - bands are coincided

w – weak, m –middle and s – strong intensity

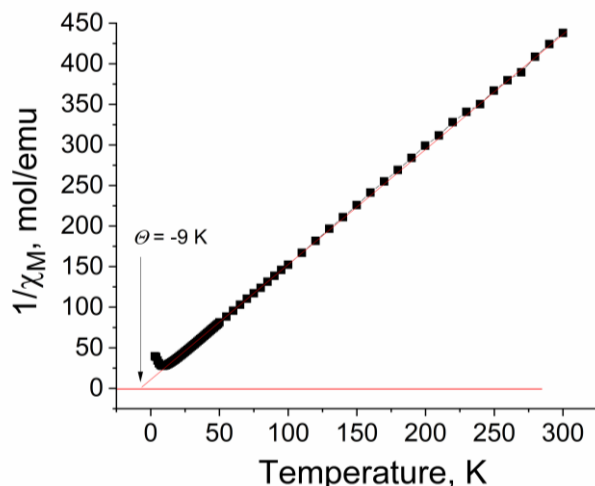


**Figure S1.** IR spectra of starting neutral  $\text{Cu}^{\text{II}}(\text{F}_8\text{Pc})$  and salts  $\{\text{cryptand}(\text{Na}^+)\}_2[\text{Cu}^{\text{II}}(\text{F}_8\text{Pc})^{3\bullet-}] \cdot 2\text{C}_6\text{H}_4\text{Cl}_2$  (**1**) in KBr pellets prepared in anaerobic condition.



**Figure S2.** IR spectra of starting neutral  $\text{Cu}^{\text{II}}(\text{F}_{16}\text{Pc})$  and salts  $\{\text{cryptand}(\text{Na}^+)\}_2[\text{Cu}^{\text{II}}(\text{F}_{16}\text{Pc})^{4-}]^{2-} \cdot \text{C}_6\text{H}_{14}$  (**2**) in KBr pellets prepared in anaerobic condition.

## Magnetic measurements



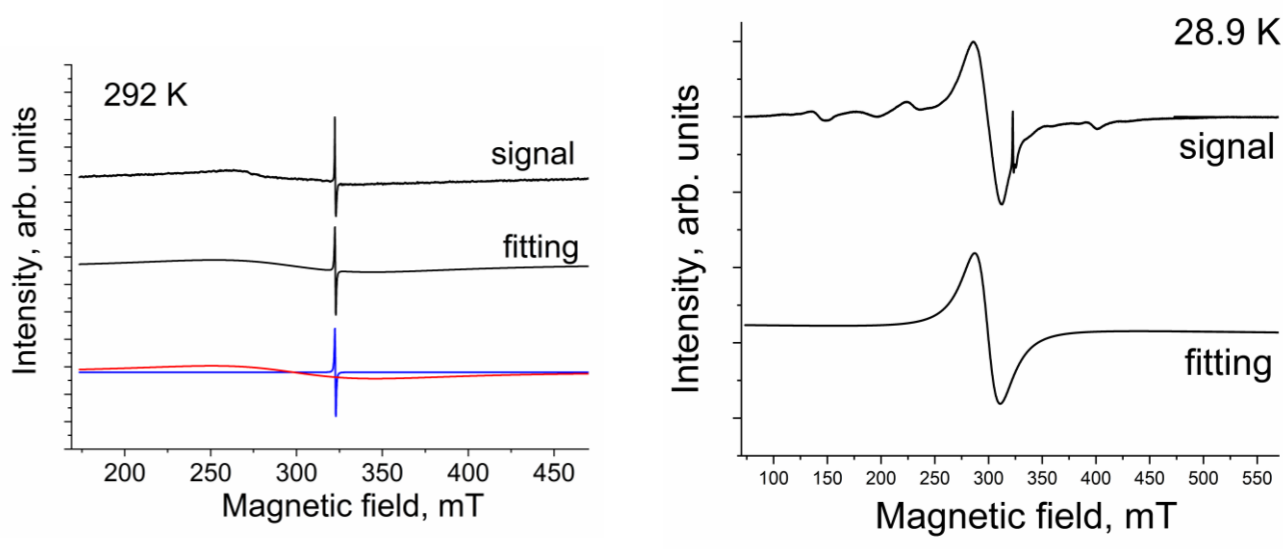
**Figure S3.** Temperature dependence of reciprocal molar magnetic susceptibility (b) for salt **1**.

PHI [N. F. Chilton, R. P. Anderson, L. D. Turner, A. Soncini, K. S. Murray, J. Comput. Chem. 2013, 34, 1164-1175.] software allows one to model a magnetic system by means of an isotropic spin Hamiltonian (SH) accounting for various types fundamental interactions that could occur. In our case, however, parameters related to terms for spin-orbit (SO) coupling and crystal field (CF) interaction were not needed to be probed and the program presets for  $S = \frac{1}{2}$  radical and  $d^9$  Cu(II) were used. Therefore, with the two employed components of exchange coupling (EX) Zeeman effect (ZEE), SH splits into

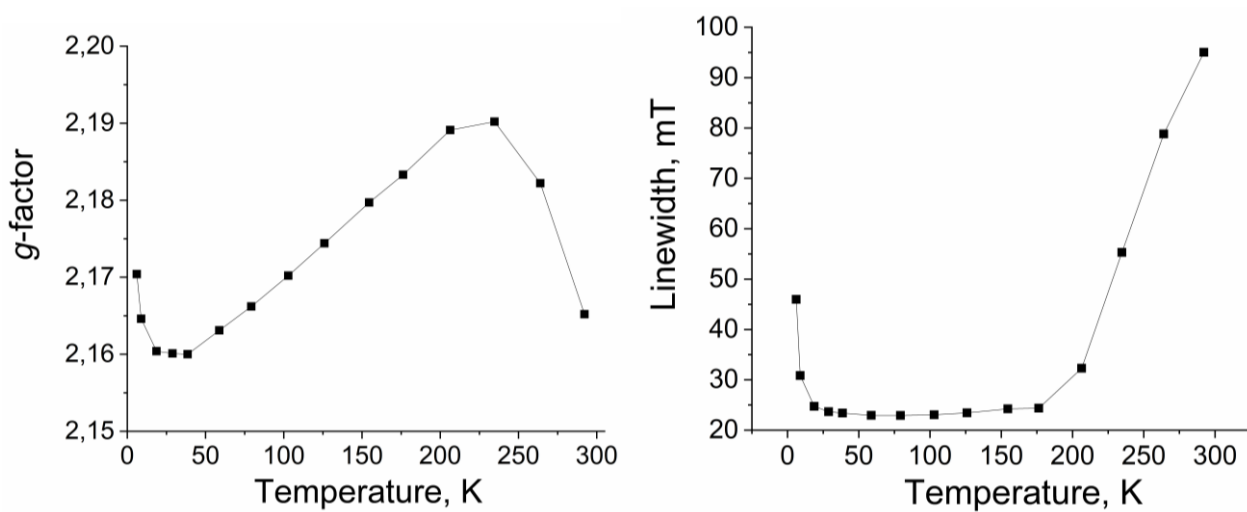
$$\hat{H} = \hat{H}_{EX} + \hat{H}_{ZEE},$$

$$\hat{H} = -2 \sum_{i \neq j}^{i,j} J_{ij} \cdot \vec{S}_i \cdot \vec{S}_j + \mu_B \sum_{i=1}^N \vec{S}_{i,j} \cdot g_{i,j} \cdot \vec{B},$$

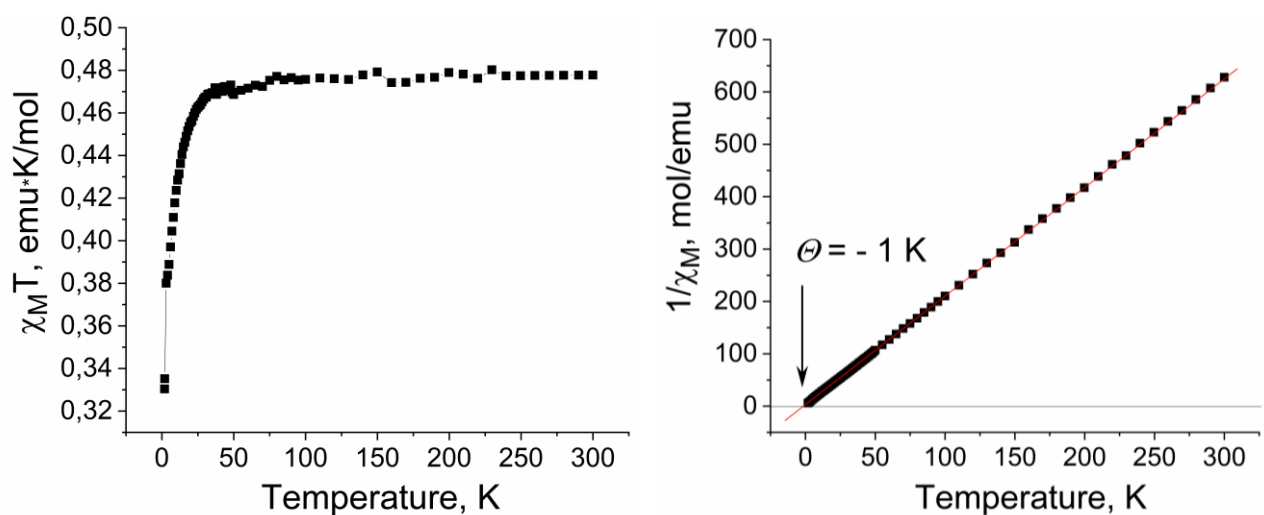
where for each general number  $N$  of pairs  $J_{ij}$  is the exchange constant between two magnetic centers  $i, j$  with g-factors  $g_{i,j}$  and spins  $S_{i,j}$ ;  $\vec{B}$  is the magnetic field vector;  $\mu_B$  is the Bohr magneton.



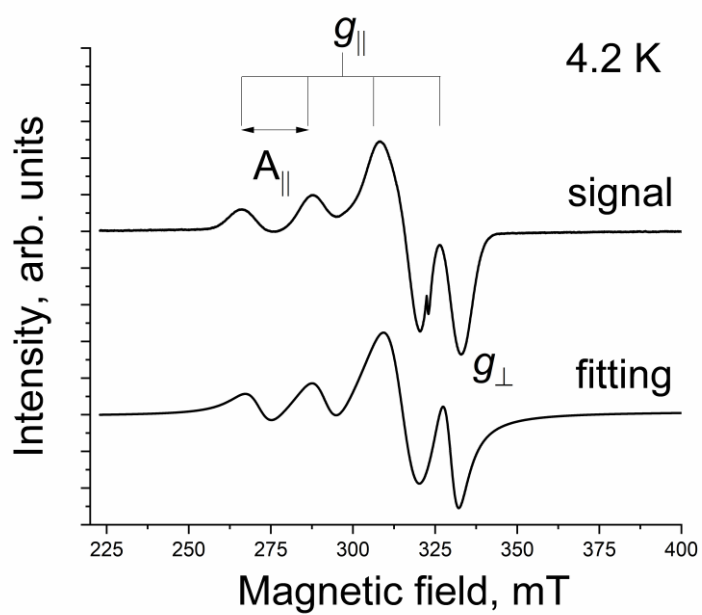
**Figure S4.** EPR spectra of polycrystalline **1** at 292 K and 28.9 K.



**Figure S5.** Temperature dependence of  $g$ -factor and linewidth of the main line manifested in the EPR spectra of salt **1**.



**Figure S6.** Temperature dependence of  $\chi_M T$  value and reciprocal molar magnetic susceptibility for salt 2.



**Figure S7.** EPR spectrum of polycrystalline 4 at 4.2 K.