Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Field supported slow magnetic relaxation in quasi-one-dimensional copper(II) complex with a pentaheterocyclic triphenodioxazine

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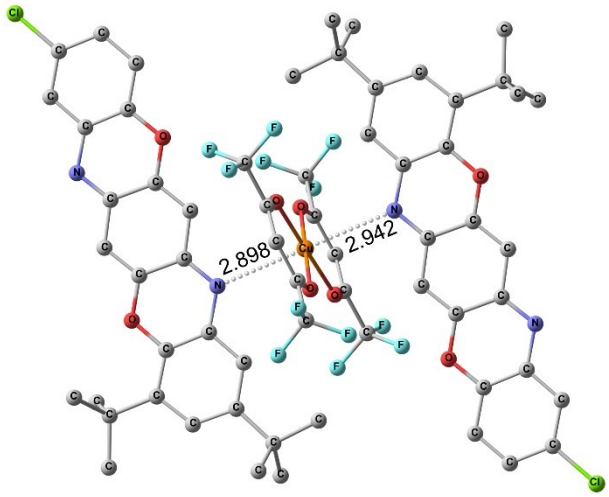


Fig. S1. Geometry characteristics of monomeric fragment of coordination polymer **I** calculated by the DFT (B3LYP/6-311++G(g,p)) method. Bond lengths are given in Å, hydrogen atoms are omitted for clarity.

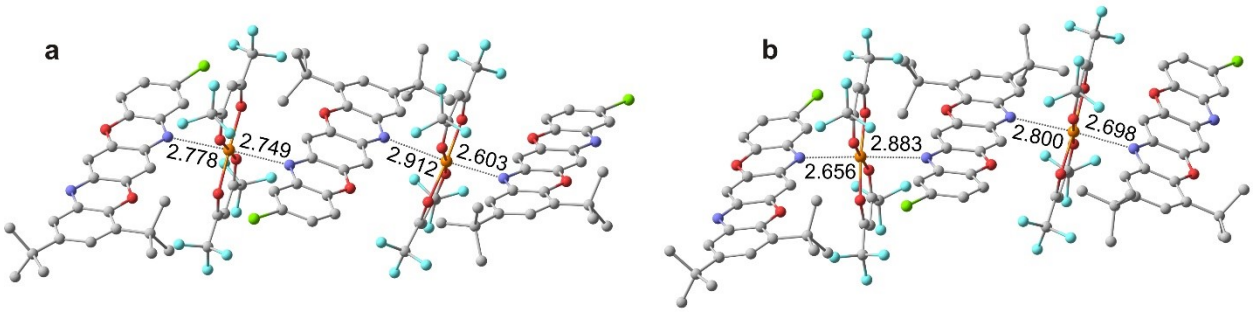


Fig. S2. Optimized geometries of dimer fragments of **I** calculated at B3LYP/Def2-SVP level. Bond lengths are given in Å, hydrogen atoms are omitted for clarity.

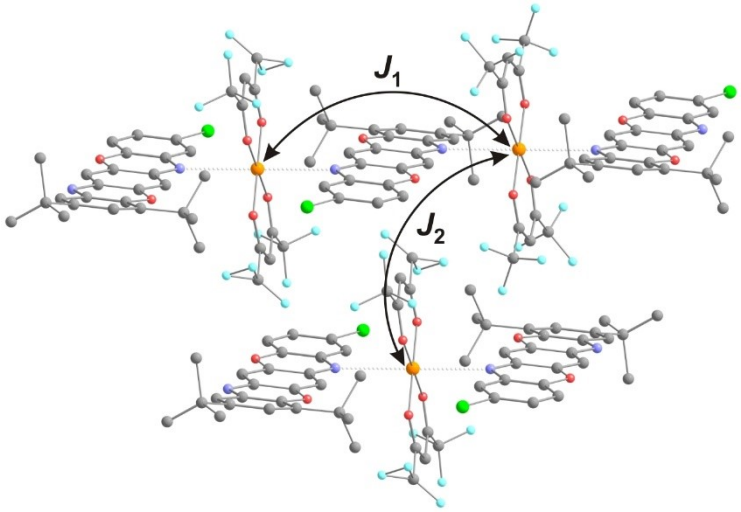


Fig. S3. Possible Cu-Cu exchange coupling channels in **I**.

Table S1. The exchange spin coupling parameters (J, cm^{-1}) calculated by the DFT method.

Approximation	*J1	J2	J3
B3LYP/def2-SVP	0.42	0.21	0.42
B3LYP/def2-TZVP	-0.01	-0.01	-0.01
TPSSh/def2-TZVP	0.18	0.09	0.18

*Formulas for the calculation J1-J3.

$J1 = -(E_{HS}-E_{BS}])/S_{max}^2$), [1].

$J2 = -(E_{HS}-E_{BS})/(S_{max}*(S_{max}+1))$, [2].

$J3 = -(E_{HS}-E_{BS})/(\langle S^2\rangle_{HS} - \langle S^2\rangle_{BS}))$, [3].

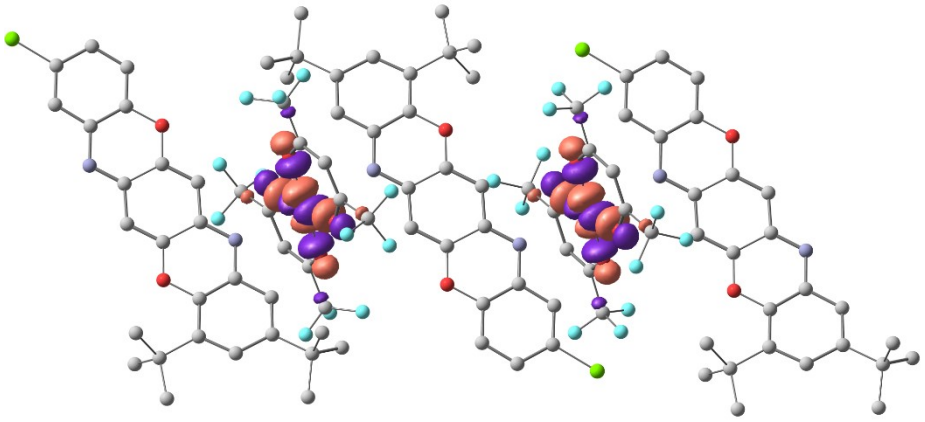


Fig. S4. Single-occupied natural (magnetic) orbital in dimer fragment of **I**.

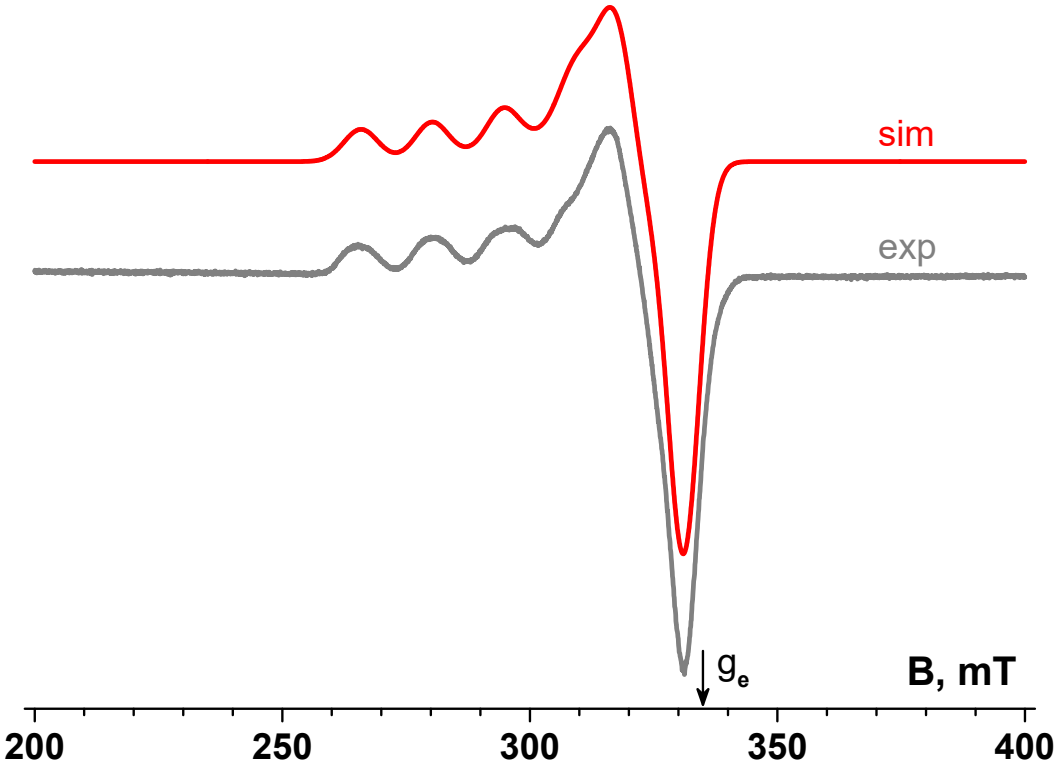


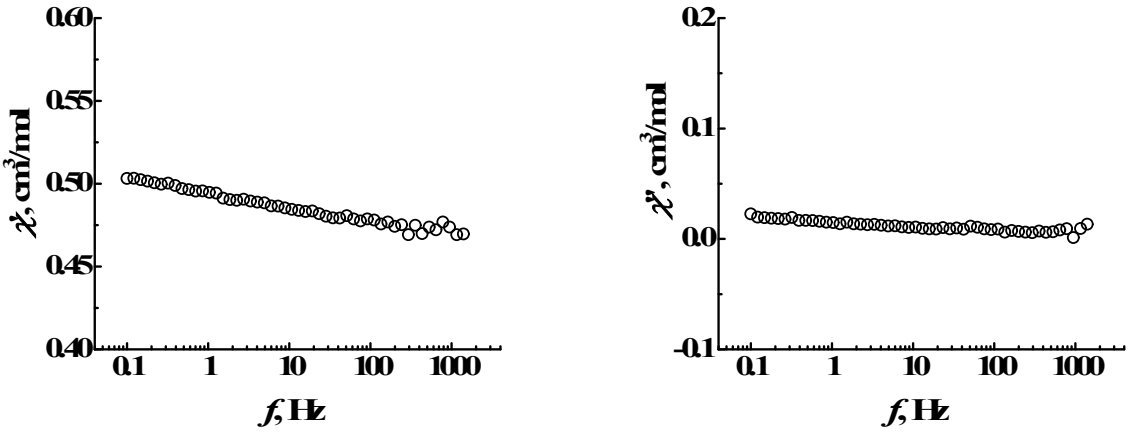
Fig. S5. Solid state EPR spectra for **I** (gray line) collected at 7 K and simulated EPR spectra for S=1/2, $g_{\perp}$ = 2.0639, $g_{\parallel}$ = 2.3332, A(^{65}Cu) = [84.5; 84.5; 459] MHz (red line), linewidth 6.6 G. Microwave frequency 9.385423 GHz

Table S2. The DFT calculated principle values of g-tensor for monomeric fragment of **I**.

	g-Tensor		
Level of theory	x	y	z
B3LYP def2-SVP	2.055	2.057	2.179
B3LYP def2-TZVP	2.057	2.058	2.190
TPSSH def2-SVP/QZVPP*	2.046	2.047	2.149
TPSSH def2-TZVP/QZVPP*	2.046	2.047	2.147
ZORA TPSSH def2-SVP/QZVPP*	2.047	2.048	2.152

ZORA TPSSH def2-TZVP/QZVPP*	2.047	2.048	2.150
ZORA D3 TPSSH def2-SVP/QZVPP*	2.047	2.048	2.152
D3 TPSSH def2- TZVP/QZVPP*	2.049	2.050	2.157

* QZVPP basis set was used for copper atom



(a) (b)

Fig. S6. Frequency dependence of the in-phase χ' (a), out-of-phase χ'' (b) AC susceptibility χ_M at temperature T = 2K and H_{DC}=0 Oe.

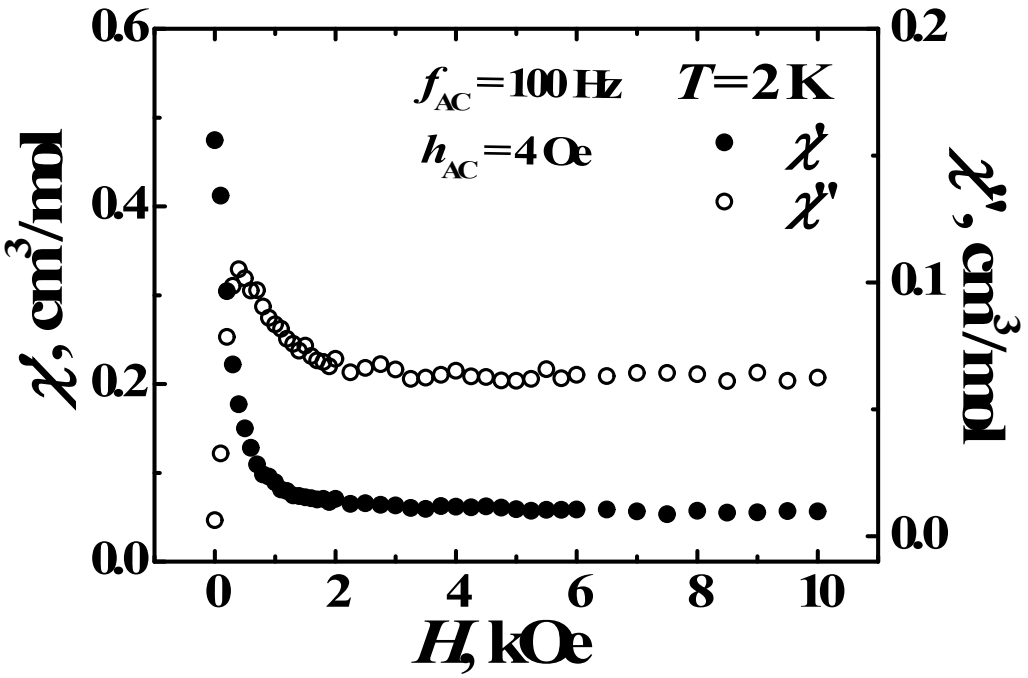
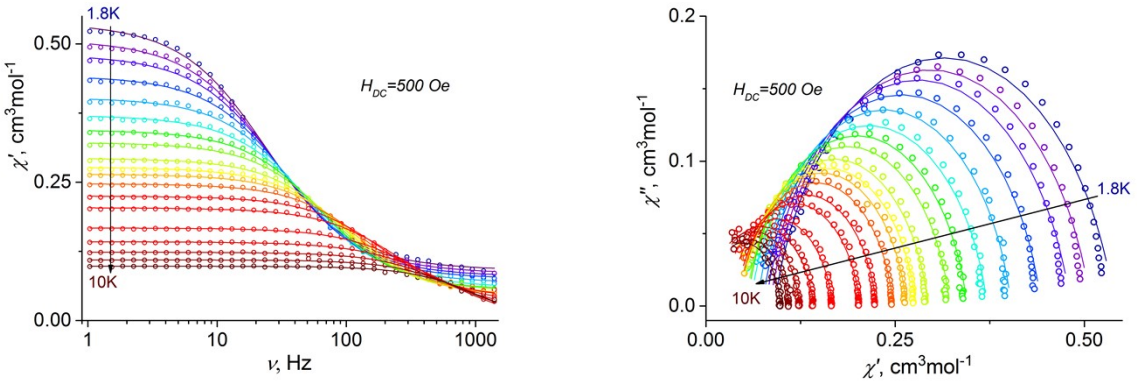


Fig. S7. Field dependence of the in-phase χ' and out-of-phase χ'' AC susceptibility χ_M at temperature T = 2K and frequency f_{AC} = 100 Hz. The maximum on the out-of-phase χ'' AC susceptibility is at H_{DC} ~ 500 Oe.



(a) ***(b)***

Fig. S8. Frequency dependence of the in-phase χ' (a) AC susceptibility χ_M and Cole-Cole diagrams (b) at different temperatures and H_{DC}=*500 Oe* for **I** (points – experiment, lines – fit by generalized Debye model).

Table S3. Best fit parameters of the one-component Debye model for the Cole-Cole plot of complex **I** at H_{DC} =500 Oe

T, K	χ_S,cm^3 mol^{-1}	χ_T,cm^3 mol^{-1}	τ, s	α	R_1 [a]
1.8	0.090	0.540	0.679E-02	0.171	0.32E-02
1.9	0.084	0.509	0.604E-02	0.167	0.30E-02
2.0	0.079	0.482	0.537E-02	0.161	0.31E-02
2.2	0.074	0.443	0.451E-02	0.148	0.19E-02
2.4	0.068	0.403	0.366E-02	0.136	0.20E-02
2.6	0.059	0.372	0.299E-02	0.144	0.15E-02
2.8	0.054	0.345	0.253E-02	0.134	0.15E-02
3.0	0.052	0.322	0.217E-02	0.128	0.93E-03
3.3	0.046	0.293	0.173E-02	0.125	0.12E-02
3.5	0.045	0.277	0.153E-02	0.125	0.10E-02
3.7	0.042	0.265	0.133E-02	0.121	0.61E-03
4.0	0.043	0.247	0.113E-02	0.115	0.45E-03
4.5	0.039	0.225	0.867E-03	0.121	0.54E-03
5.0	0.031	0.204	0.655E-03	0.129	0.42E-03
6.0	0.020	0.167	0.441E-03	0.129	0.44E-03
7.0	0.005	0.142	0.291E-03	0.143	0.31E-03
8.0	0.001	0.123	0.237E-03	0.108	0.221E-03
9.0	0.004	0.110	0.202E-03	0.090	0.25E-03
10.0	0.000	0.098	0.163E-03	0.074	0.24E-03

[a] The mean residual sum of squares, $R_1 = \frac{1}{n}\sum_{i=1}^{n}\frac{(Y_{exp}-Y_{calc})^2}{Y_{exp}^{\ 2}}$

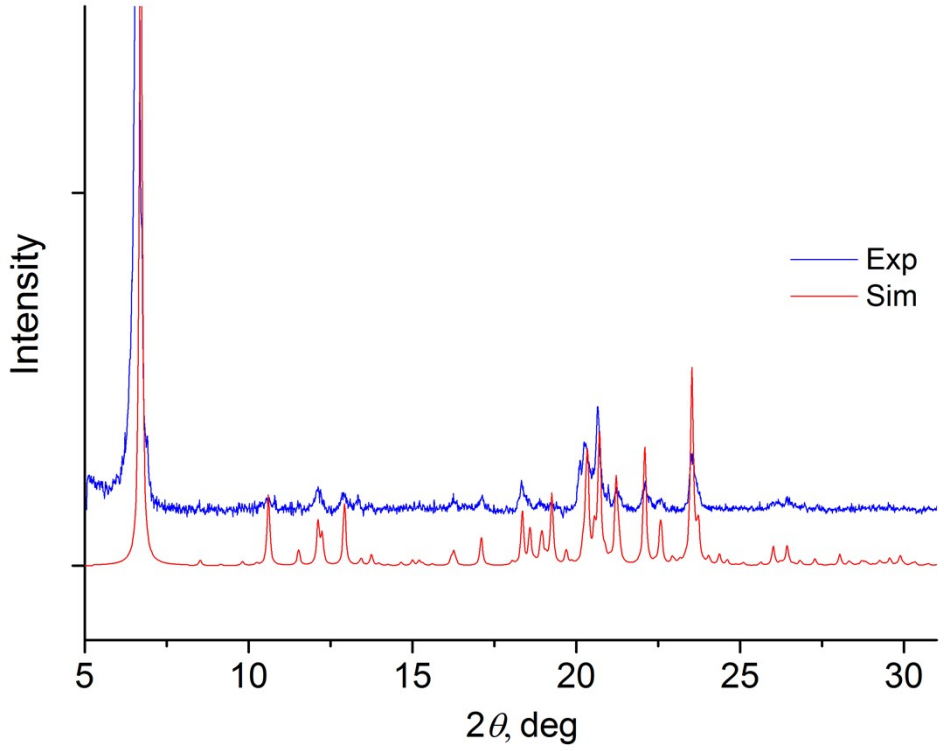


Fig. S9. Powder X-ray diffraction pattern of polycrystalline sample of complex **I**: experimental (blue), and calculated from single crystal data (red).

References

1. A. P. Ginsberg, *J. Am. Chem. Soc.*, 1980,**102**, 111-117.

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3. T. Soda, Y. Kitagawa, T. Onishi, Y. Takano, Y. Shigeta, H. Nagao, Y. Yoshioka, and K. Yamaguchi, *Chem. Phys. Lett.* 2000, **319**, 223-230.