Supporting Information

Effect of the Diamagnetic Single Crystalline Host on the Angular Resolved Electron Nuclear Double Resonance Experiments: Case of Paramagnetic $[^{n}Bu_4N]_2[Cu(opba)]$ Embedded in Diamagnetic $[^{n}Bu_4N]_2[Ni(opba)]$

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1. Optimized structures of considered systems

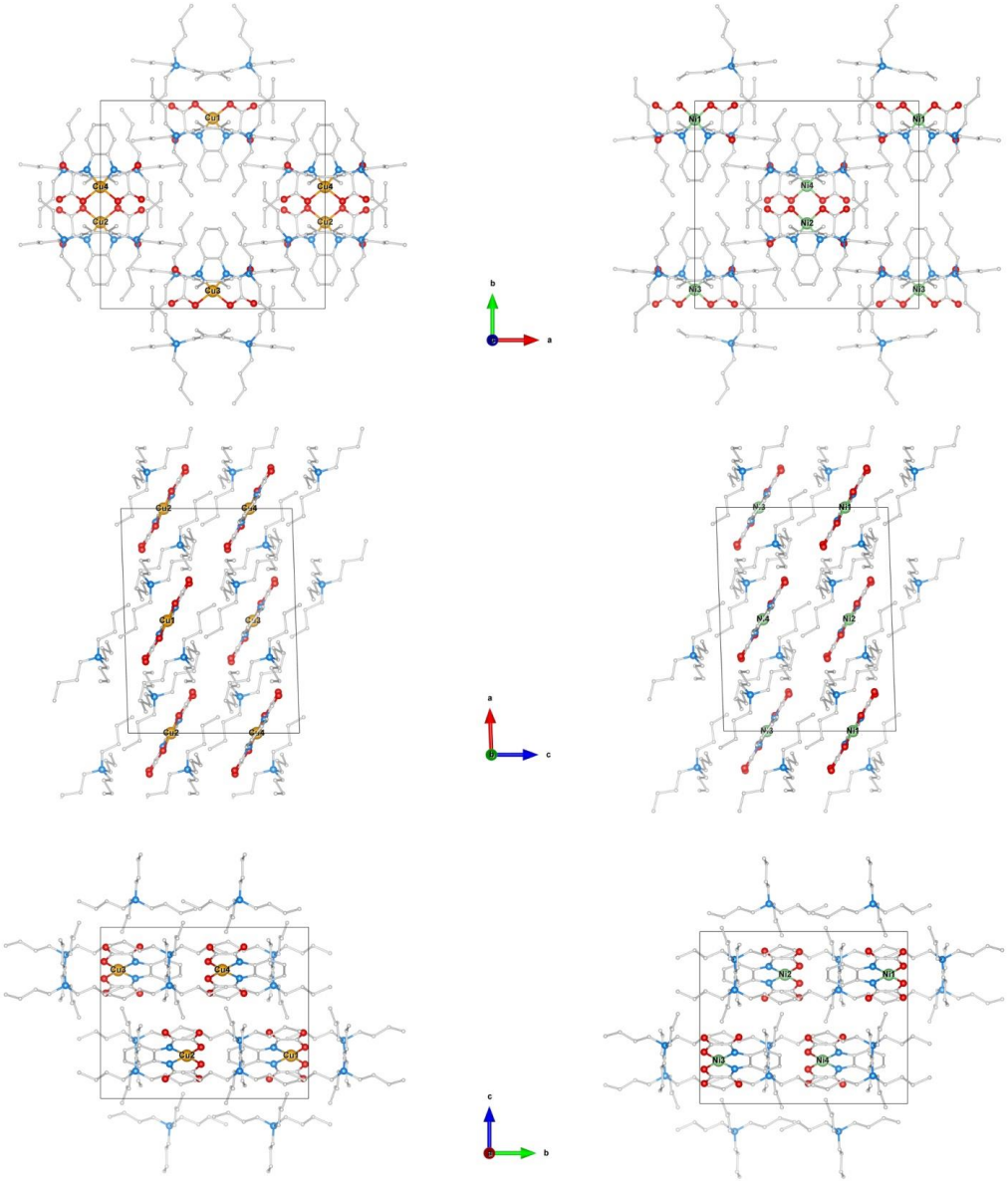


Figure S1. *a*- *b*-, and *c*- projections of VASP optimized paramagnetic $[^{n}Bu_4N]_2[Cu(opba)]$ diamagnetic $[^{n}Bu_4N]_2[Ni(opba)]$ polymorphs.

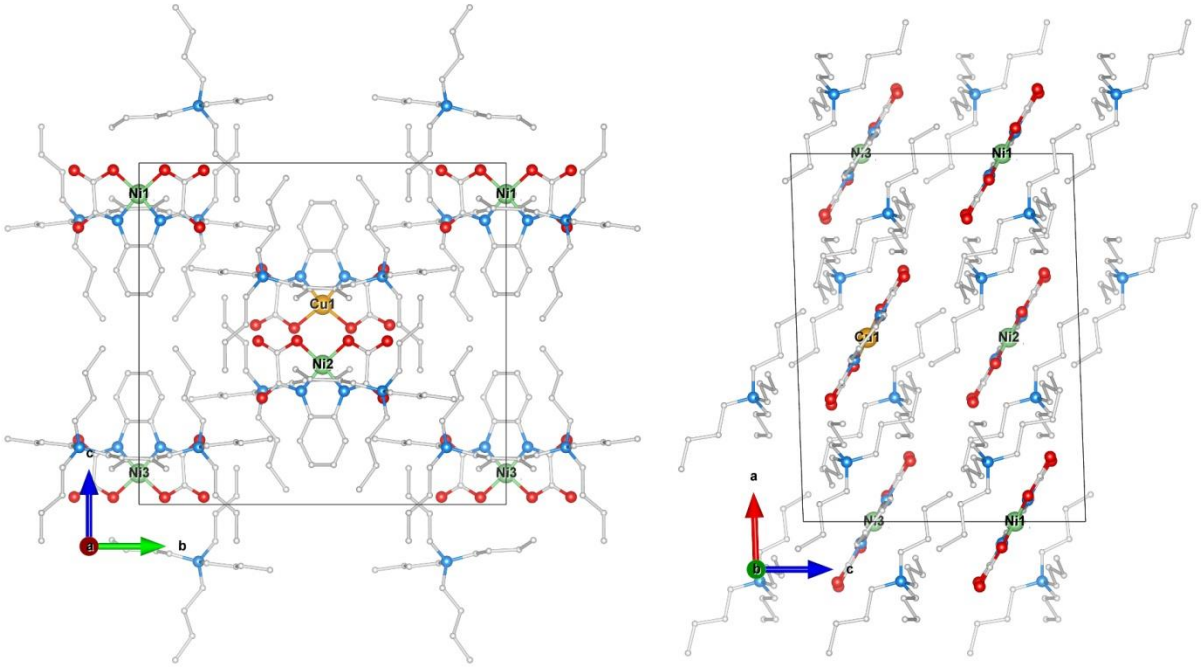


Figure S2. *a*-, *b*- projection of VASP optimized mixed (MIX) system $[^{n}Bu_4N]_2[Cu(opba)]$ in $[^{n}Bu_4N]_2[Ni(opba)]$ matrix.

2. VASP and Orca scripts

Examples of employed theoretical scripts in VASP and ORCA modeling:

a) $[^{n}Bu_4N]_2[Cu(opba)]$ VASP optimization script:

```
PREC = Normal                  ! standard precision
ENCUT = 600                    ! cutoff
ISMEAR = 0 ; SIGMA = 0.1
IBRION = 1                     ! optimization
NSW = 3000                     ! # of steps
IVDW=11                        ! DFT-D3 by Grimme
ISPIN = 2                      ! spin polarized
MAGMOM = 512*0.0000 4*1.0000 ! starting spin
EDIFFG = -0.005                ! optimization criteria
ALGO = F                       ! RMMDIIS method
LREAL=Auto
```

b) $[Cu(opba)]^{-2}$ Orca ***A***-, ***Q***- tensors modeling script:

```
! UKS PBE0 def2-TZVP SlowConv Grid7 NoFinalGrid VERYTIGHTSCF PRINTBASIS
%pal nprocs 48
  end
%cosmo epsilon 8.93
       refrac  1.424
       end
* xyz -2 2
C         2.572289856     -0.043527309      0.018908301
C         2.701731833     -1.601408694     -0.069541268
C         0.716228814      1.598922398      0.050540165
C         1.399235448      2.821679999      0.161833910
C         0.693728363      4.025505249      0.095864631
C        -2.572765115     -0.042833190     -0.018677221
C        -2.701074556     -1.600347928      0.069444448
C        -0.715813725      1.599218028     -0.050223476
C        -1.398503122      2.822007421     -0.161874083
C        -0.692753395      4.025732177     -0.096440887
H         2.480519080      2.802065734      0.277722960
H         1.232935724      4.970613372      0.181602388
H        -2.479803093      2.802603687     -0.277773307
H        -1.231657192      4.970792041     -0.182396181
N         1.287483355      0.328408916      0.022144363
N        -1.287286967      0.328615515     -0.021738381
O         3.591670214      0.686850331      0.086073750
O         1.580995758     -2.273061326     -0.125778994
O         3.828241850     -2.124112270     -0.087337844
O        -3.591247366      0.687566083     -0.085700397
O        -1.581578595     -2.272729158      0.125095997
O        -3.829444101     -2.123546177      0.087513075
Cu       -0.000168824     -1.103780758     -0.000011101
*
%basis
   newGTO N "EPR-III" end
   newGTO H "EPR-III" end
   newGTO Cu "CP(PPP)" end
end
%method
 ProgPlot "./orca_plot"
 IntAcc 9.0
end
%eprnmr
        nuclei = all Cu {aiso, adip, aorb, fgrad, rho}
        nuclei = all N  {aiso, adip, aorb, fgrad, rho}
        GTensor 1
        Ori 22
        PrintLevel 4
 end
%rel
      SOCType  3
      SOCFlags 1,3,3,1
end
```

3. Theoretical background for ENDOR modeling

Although in the main text we employed wildly used set of pre-scripted algorithms in EasySpin5.2 below we outline the minimal level of theory sufficient for ENDOR modeling within density matrix formalism.

ENDOR. Theoretical calculations were performed numerically within the framework of a formalism of the density matrix considering one electron and two nitrogen nuclei spins. In this

case, the transitions between the nitrogen sublevels are excited. The carrier frequency of the ENDOR pulse was selected specifically for the region of transitions between the nuclear sublevels of nitrogen, so we restricted ourselves to only these nuclei.

The initial density matrix was taken as an equilibrium one, i.e.

$\rho_0 = S_z$.

The hyperfine and quadrupole interactions were described as:

$$H_{int} = A_{(N1)zz}S_z I_{(N1)z} + A_{(N2)zz}S_z I_{(N2)z} + Q_{(N1)zz}I_{(N1)z}I_{(N1)z} + Q_{(N2)zz}I_{(N2)z}I_{(N2)z}$$

where A is the HFI tensor and Q is the quadrupole interaction tensor.

During the pulse, the spin Hamiltonian can be written as:

$H_p = (\gamma g_{eff} B_0 - \omega_0)S_z - \gamma_N B_0 I_{(N1)z} - \gamma_N B_0 I_{(N2)z} + \gamma g_{eff} B_1 S_x + H_{int}$.

Here the parameters were set as $B_1 \approx 10$ Gs; $t_{p1} = t_{p2} = t_{p4} = 8$ ns and $\omega_0 = 9682$ MHz.

The density matrix after the first microwave pulse reads:

$\rho_1 = e^{-i H_p t_{p1}} \rho_0 e^{i H_p t_{p1}}$.

The evolution period can be described by the spin Hamiltonian:

$H_0 = \gamma g_{eff} B_0 S_z - \gamma_N B_0 I_{(N1)z} - \gamma_N B_0 I_{(N2)z} + H_{int}$.

After the first evolution period τ the density matrix can be defined as:

$\rho_2 = e^{-i H_0 \tau} \rho_1 e^{i H_0 \tau}$.

The density matrix after the action of the second $\pi / 2$ pulse takes the form:

$\rho_3 = e^{-i H_p t_{p2}} \rho_2 e^{i H_p t_{p2}}$.

Before and after the action of the second π / 2 pulse, we nullified the off-diagonal elements of the density matrix, leaving only the populations:

$\rho_{3(i,j)} = 0, i \neq j$.

The action of the ENDOR pulse (B1≈0.1 Gs; tp3 = 8 *ns*) can be described by the spin Hamiltonian:

$$H_{ENDOR} = -(\gamma_N B_0 - \omega)I_{(N1)z} - (\gamma_N B_0 - \omega)I_{(N2)z} + H_{int} + \gamma_N B_1 I_{(N1)x} + \gamma_N B_1 I_{(N2)x}.$$

The density matrix after the action of the ENDOR pulse reads:

$\rho_4 = e^{-i\,H_{ENDOR}\,t_{p3}}\rho_3 e^{i\,H_{ENDOR}\,t_{p3}}$.

Before and after the action of the ENDOR pulse, we again nullified the off-diagonal elements of the density matrix, leaving only populations.

$\rho_{4(i,j)} = 0, i \neq j.$

The density matrix after the action of the third π / 2 pulse takes the form:

$\rho_5 = e^{-i\,H_p\,t_{p4}}\rho_4 e^{i\,H_p\,t_{p4}}$.

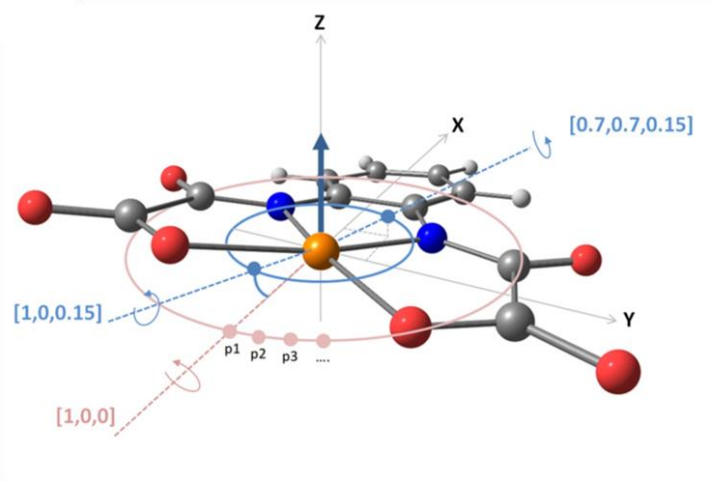
The density matrix after the second evolution during the time τ can be written as:

$$\rho = e^{-i\,H_0\tau}\rho_5 e^{i\,H_0\tau}$$

Finally, the signal was estimated from the amplitude of the echo signal as *Spur*[Sy.ρ], where ρ is the density matrix of the system at the time of the echo formation. The dependence of the ENDOR signal was constructed from the ENDOR of the ω pulse. The parameters for the simulation were the eigenvalues of the HFI tensors of two nitrogen ligands ($A_{N1\perp}$, $A_{N1\parallel}$, $A_{N1\perp}$, $A_{N1\parallel}$), and their rotation Euler angles (α, β) relative to the copper HFI tensor. Since we assumed the axial

symmetry of all the HFI tensors, we limited ourselves to two rotation angles for each HFI tensor of the nitrogen nuclei.

EasySpin modeling. The online version of ESI also contains the animations for angle resolved ESR/ENDOR spectra for different orientation rotation axis.



A1: rotation axis on the ping ring axes (ϕ_1, ϕ_2, ϕ_3 ...): **anim1_video.mp4**

A2: rotation axis on the blue ring: **anim2_video.mp4**

A3. rotation axis goes through the origin and a node of the Fibonacci Sphere with 120 nodes: **anim3_video.mp4**

S1. ES spectra evaluation while rotation axis on the ping ring axes: **anim4_video.mp4**