

## Supporting Information to

# Mechanical ordering of pigment crystallites in oil binder: Can EPR reveal the gesture of an artist?

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### 1. Derivation of Equation (7)

The Wigner matrix elements  $D_{00}^{(l)}(\Omega)$  in Eq. 6 can be expressed as (Eq. 12 in Hentschel et al., 1978):

$$D_{00}^{(l)}(\Omega) = \sum_{n=-l}^l D_{0n}^{(l)}(\Omega') D_{0n}^{*(l)}(\Omega_0) \quad (S1)$$

Then Eq. 4 becomes:

$$S(B, \Omega_0) = \sum_{l=0}^{\infty} p_{l00} \left\{ \sum_{n=-l}^l \left[ D_{0n}^{*(l)}(\Omega_0) \int_{\Omega'} D_{0n}^{(l)}(\Omega') \omega(\Omega') f(B - B_r(\Omega')) d\Omega' \right] \right\} \quad (S2)$$

where the integration over  $\Omega$  is replaced by an integration over  $\Omega'$  since a set of orientations  $(\Omega, \Omega_0)$  determines an orientation  $\Omega$  in a bi-univocal way. In the above equation:

$$\int_{\Omega'} D_{0n}^{(l)}(\Omega') f(B - B_r(\Omega')) d\Omega' = \int_{\varphi=0}^{2\pi} d\varphi \int_{\theta=0}^{\pi} \omega(\theta) f(B - B_r(\theta)) \sin \theta d\theta \int_{\psi=0}^{2\pi} D_{0n}^{(l)}(\varphi, \theta, \psi) d\psi \quad (S3)$$

From the property:

$$\int_{\psi=0}^{2\pi} D_{0n}^{(l)}(\varphi, \theta, \psi) d\psi = \begin{cases} 0 & \text{if } n \neq 0 \\ 2\pi D_{00}^{(l)}(0, \theta, 0) & \text{if } n = 0 \end{cases} \quad (S4)$$

we get:

$$S(B, \Omega_0) = 2\pi \sum_{l=0}^{\infty} p_l D_{00}^{*(l)}(\Omega_0) \int_{\theta=0}^{\pi} D_{00}^{(l)}(0, \theta, 0) \omega(\theta) f(B - B_r(\theta)) \sin \theta d\theta \quad (S5)$$

and since  $D_{00}^{*(l)}(\Omega_0) = P_l(\cos \beta_0)$  and  $D_{00}^{(l)}(0, \theta, 0) = P_l(\cos \theta)$ , we finally get Eq. 7:

$$S(B, \Omega_0) = S(B, \beta_0) = \sum_{l=0}^{\infty} p_l P_l(\cos \beta_0) \int_{\theta=0}^{\pi} \omega(\theta) f(B - B_r(\theta)) P_l(\cos \theta) \sin \theta d\theta \quad (S6)$$

after dropping the irrelevant  $2\pi$  factor.

## 2. Numerical calculation of the coefficients $p_l$ from experimental EPR spectra

For practical implementation, the discrete summation over  $l$  in Eq. S7 must be truncated to a finite order  $l_{max}$ . In addition, EPR spectra are recorded for a finite discrete set of  $m$  field values  $(B_i)_{i=1,\dots,m}$ . For a specific orientation  $\beta_{0,k}$  ( $k = 1, \dots, n$ ) in a set of  $n$  different orientations of the sample in the laboratory frame, we then define a matrix  $G(\beta_{0,k})$  with elements:

$$G_{ij}(\beta_{0,k}) = P_{2(j-1)}(\cos \beta_{0,k}) \int_{\theta=0}^{\pi} \omega(\theta) f(B_i - B_r(\theta)) P_{2(j-1)}(\cos \theta) d \cos \theta \quad (S7)$$

with  $j = \frac{l}{2} + 1$ , which runs from 1 to  $N = \frac{l_{max}}{2} + 1$  by step of 1 when  $l$  runs from 0 to  $l_{max}$  by step of 2, since  $l$  is even. In practice, the integral in Eq. S7 is replaced by a discrete summation and a Voigt line shape is used for  $f(B_i - B_r(\theta))$ . The theoretical EPR spectrum at orientation  $\beta_{0,k}$  is then expressed as an  $m$ -line column vector:

$$S_k^{th} = G(\beta_{0,k}) \begin{pmatrix} p_0 \\ \vdots \\ p_{l_{max}} \end{pmatrix} \quad (S8)$$

The best estimates of the unknown coefficients  $(p_0, \dots, p_{l_{max}})$  are obtained by minimizing:

$$L^2 = \sum_{k=1}^n \|S_k^{exp} - S_k^{th}\|^2 \quad (S9)$$

which represents the squared distance between all theoretical spectra  $S_k^{th}$  and experimental spectra  $S_k^{exp}$ , with respect to the variations of the coefficients  $p_l$ . The best estimates are then given by:

$$\begin{pmatrix} p_0 \\ \vdots \\ p_{l_{max}} \end{pmatrix} = \left( \sum_{k=1}^n G(\beta_{0,k})^T G(\beta_{0,k}) \right)^{-1} \left( \sum_{k=1}^n G(\beta_{0,k})^T S_k^{exp} \right) \quad (S10)$$

where the upper script  $T$  denotes the transposed matrix.

### 3. Matlab script for the calculation of the orientation probability density

```
clear;

[B_exp_angle, spc_exp, Params]=eprload('Experimental spectrum file name');

% B_exp_angle: cell containing the experimental magnetic field values and
the rotation angles
% spc_exp: experimental EPR spectra at different orientations
% Params : cell containing the EPR acquisition settings
% eprload : Function in Easyspin allowing the loading of EPR spectra in
Bruker format

B_exp_angle{1,1}=B_exp_angle{1,1}/10; % G to mT conversion of magnetic
fields

size_Bexp=size(B_exp_angle{1,1});
index_point_B250=find(B_exp_angle{1,1}>=250); % indices of all points such
as field >= 250 mT
index_point_B400=find(B_exp_angle{1,1}>=400);%indices of all points such as
field >= 400 mT

% Restriction of the experimental spectra to 250 mT < field <400 mT
Bmax=B_exp_angle{1,1}(index_point_B400(1));
Bmin=B_exp_angle{1,1}(index_point_B250(1));
B_sweep= Bmax-Bmin; % magnetic field interval width

length_spc_exp=size(spc_exp);
for i=1:length_spc_exp(2)
    spc_exp(:,i)=spc_exp(:,i)-spc_exp(index_point_B400(1),i); %base line
set to 0
end

    %PLOT THE SUPERPOSED SPECTRA SET
    %{
figure;
hold on
for j=1:2:19
    plot(B_exp_angle{1,1}, spc_exp(:,j))
end
hold off
    %}

Sys.S=1/2; % Electron spin of Cu2+
Sys.g=[2.055 2.34]; % [g_perpendicular g_parallel] g-factors for Cu2+

Param.mwFreq = Params.MWFQ/10^9;% Experimental microwave frequency
Param.Range = [Bmin Bmax];% Magnetic field range

[phi,theta,weight]= sphgrid('Dinhf',100); % Set of orientations of the
magnetic field in the molecular frame for a magnetic system with axial
symmetry

Param.CrystalOrientation = transpose([phi; theta; weight]);
```

```
[pos, amp, wid, trans]= resfields(Sys, Param); % resfields : Easyspin
function to compute the resonance fields (pos) and transition probabilities
(amp)
```

```
% Calculation of the EPR spectra
```

```
nb_trans= size(pos); % number of calculated EPR transitions
nb_orientations=size(theta); % number of field orientations in the
molecular frame
beta0=B_exp_angle{1,2}*pi/180; % conversion of angles in radian
max_spectre=19; % number of spectra at different sample orientations

max_order=16; % highest order of the Legendre polynomials in the expansion
of the probability density P(beta)
```

```
A_l=[];
for l=0:2:max_order
    sum=0;
    for i=1:nb_trans(1)
        for k=1:nb_orientations(2)
            w_i_thetak=amp(i,k);
            P_l_thetak= legendreP(l,cos(theta(k)));

            B_res_i_k=pos(i,k);
            if isnan(B_res_i_k)==0
                fwhmGL=[0
8.6+sqrt(6.1^2*cos(theta(k))^2+3.4^2*sin(theta(k))^2)]; % width at half
maximum for gaussian and lorentzian component of the EPR line shape
                f_B_Bres_i_k=
voigtian(B_exp_angle{1,1}(index_point_B250(1):index_point_B400(1)),
B_res_i_k, fwhmGL,1);
                sum= sum + P_l_thetak* w_i_thetak * f_B_Bres_i_k *
weight(1,k);
            end
        end
    end
    A_l=[A_l, transpose(2*pi*sum)];
end
```

```
G={};
sum_GS=0;
sum_GG=0;
for num_spectrum=1:max_spectre
    G_beta = [];
    for l=0:2:max_order
        P_l_beta=legendreP(l,cos(beta0(num_spectrum)));
        G_beta= [G_beta,P_l_beta*A_l(:,l/2+1)];
    end
    G{end+1}=G_beta;
    sum_GS = sum_GS + transpose(G_beta) *
spc_exp(index_point_B250:index_point_B400,num_spectrum) ;
    sum_GG= sum_GG +transpose(G_beta)*G_beta;
end
```

```
p_matrix= inv(sum_GG)*sum_GS;
```

```
% Plot of experimental and calculated spectra
```

```

for num_spectrum_reconstitute=1:1:max_spectre
    spc_th= G{1,num_spectrum_reconstitute}* p_matrix; % Calculates the
theoretical EPR spectrum

    figure;

plot(B_exp_angle{1,1}(index_point_B250(1):index_point_B400(1)),transpose(sp
c_th),B_exp_angle{1,1}(index_point_B250(1):index_point_B400(1)),spc_exp(ind
ex_point_B250:index_point_B400,num_spectrum_reconstitute));

end

% Plot of the probability density

betas=linspace(0,pi,480);
distrib_beta_i=[];
distrib_deconv=[];
for beta=betas
    legendres=[];
    for l=0:2:max_order
        legendres = [legendres, legendreP(l,cos(beta))];
    end
    proba_beta_i = legendres*p_matrix;
    distrib_beta_i=[distrib_beta_i, proba_beta_i];
end

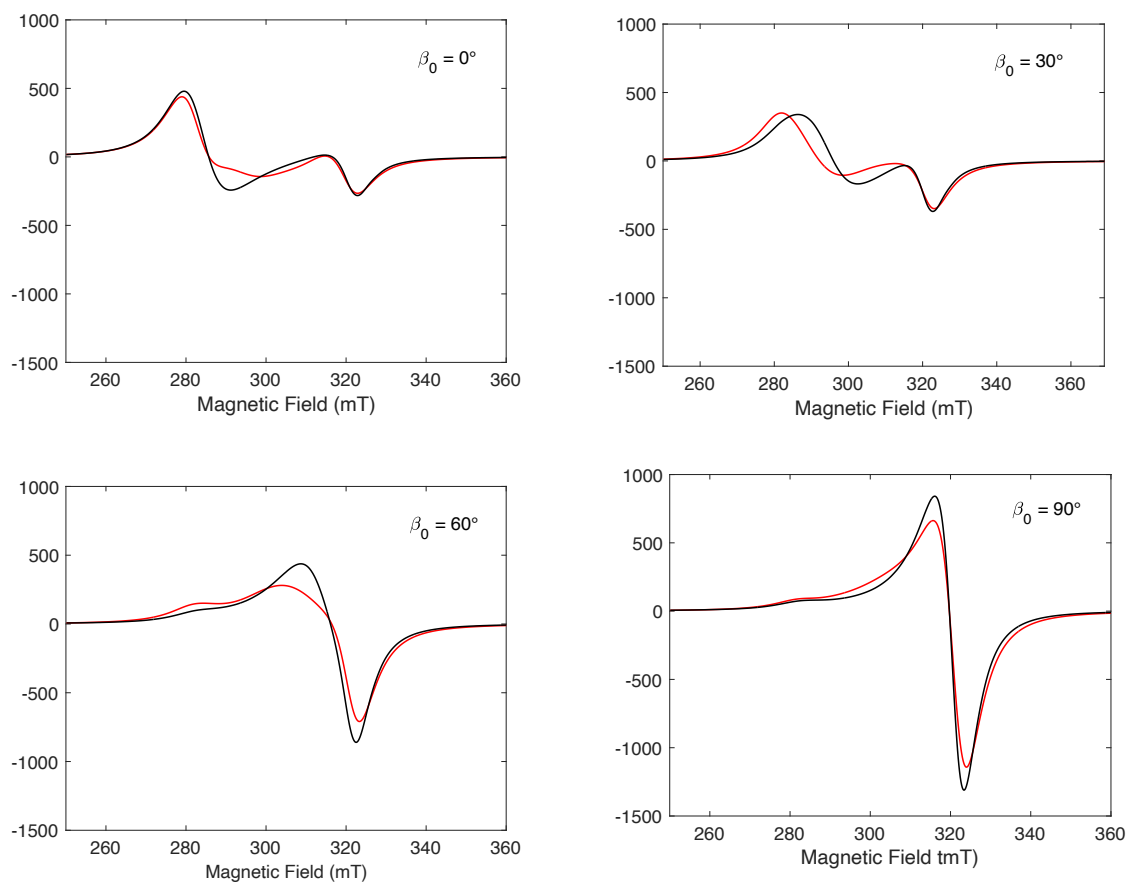
distrib_beta_i_norm=distrib_beta_i/trapz(betas,4*pi*pi*distrib_beta_i.*sin(
betas)); % normalisation of the probability density

p_matrix=p_matrix/trapz(betas,4*pi*pi*distrib_beta_i.*sin(betas));%
normalisation of the p_l coefficients

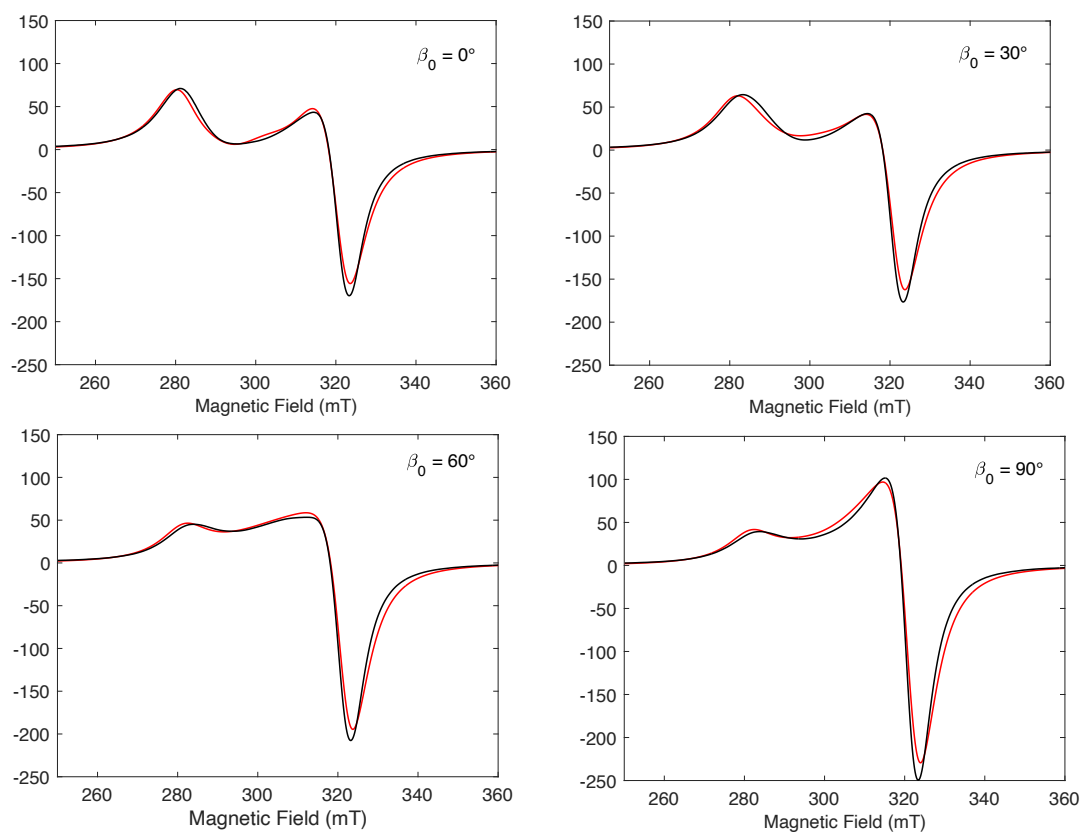
figure;
polarplot([betas,betas+pi], [distrib_beta_i_norm,distrib_beta_i_norm])%
plot in polar coordinate the orientation probability density
hold on
polarplot([betas,betas+pi], 1/(8*pi*pi)*ones(2*size(betas)))% plots the
isotropic probability density

```

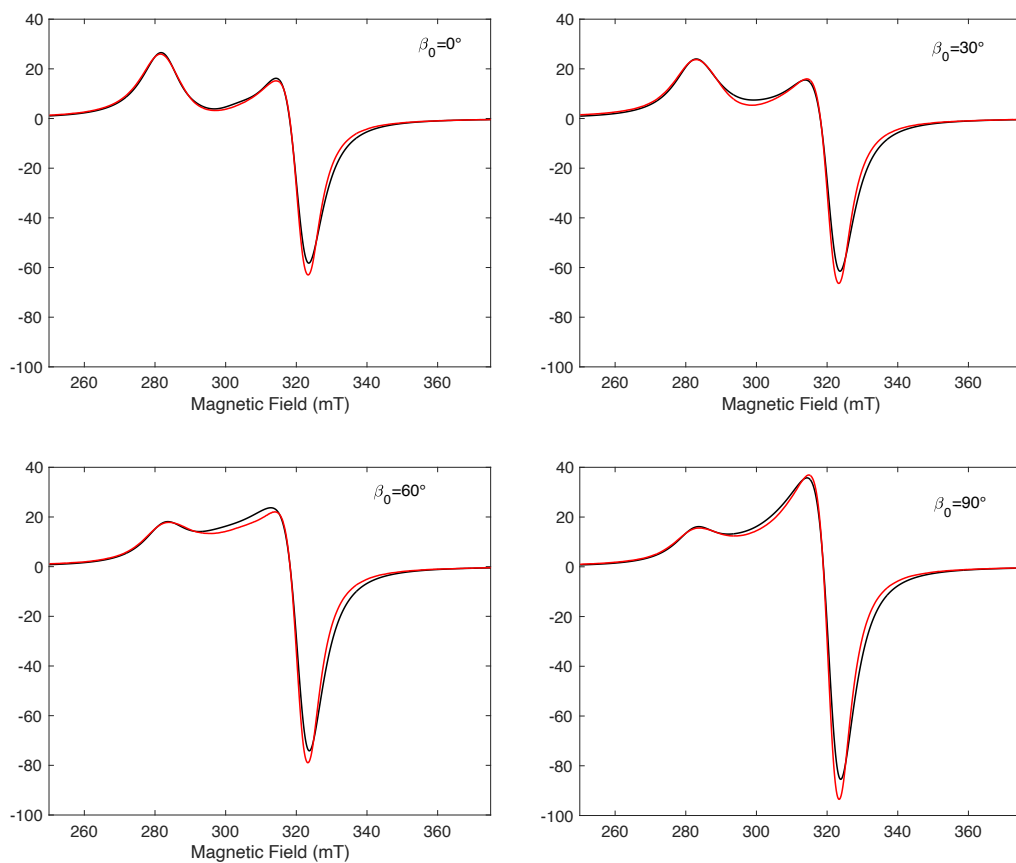
### 3. Experimental and calculated EPR spectra



**Figure S1.** Experimental (red) and calculated (black) EPR spectra of microcrystals of cuprorivaite magnetically oriented in fluid oil for different orientations of the measuring field with respect to the sample Z-axis, upon rotation about the Y-axis.

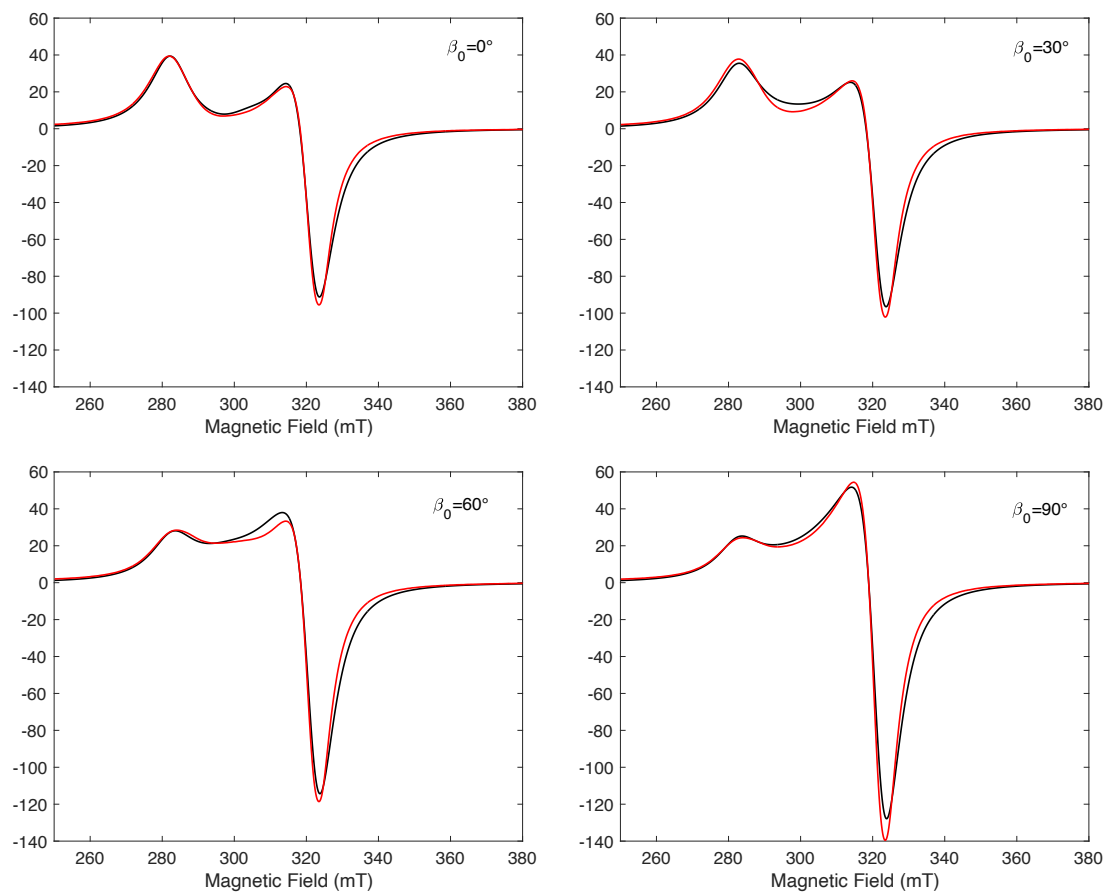


**Figure S2.** Experimental (red) and calculated (black) EPR spectra of microcrystals of cuprorivaite in a dried oil film deposited with an applicator for different orientations of the measuring field with respect to the sample Z-axis, upon rotation about the Y-axis.

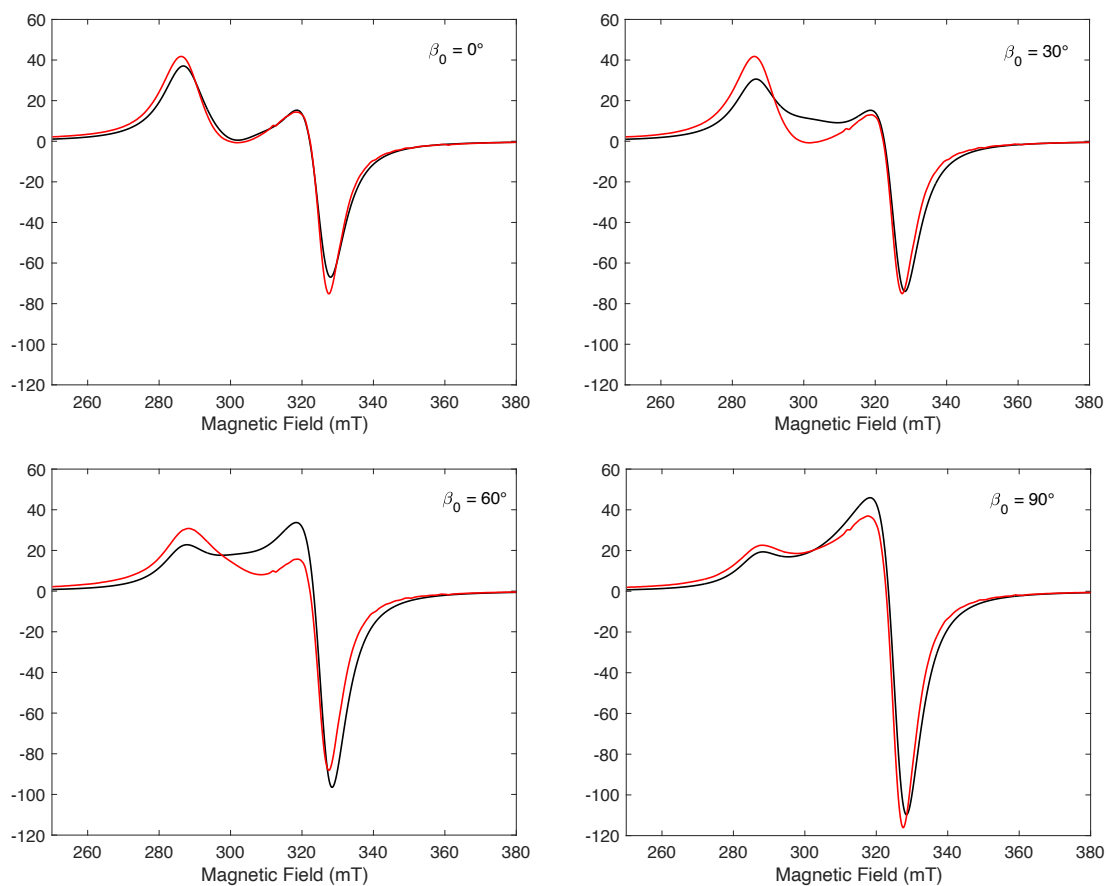


**Figure S3.** Experimental (red) and calculated (black) EPR spectra of microcrystals of cuprorivaite in a dried oil film deposited with paintbrush for different orientations of the measuring field with respect to the sample Z-axis, upon rotation about the Y-axis.





**Figure S4.** Experimental (red) and calculated (black) EPR spectra of microcrystals of cuprorivaite in a dried oil deposited as a droplet for different orientations of the measuring field with respect to the sample Z-axis, upon rotation about the Y-axis.



**Figure S5.** Experimental (red) and calculated (black) EPR spectra of microcrystals of cuprorivaite in a dried oil deposited by dabbing for different orientations of the measuring field with respect to the sample Z-axis, upon rotation about the Y-axis.