Supplementary Information

Electron paramagnetic resonance and photoluminescence study on local structure of Gd^{3+} ions in Gd:CaF_2 crystals.

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Fitting Code

```
%fitting code for NCF
clear,clf;
clc
B = 9.27400899e-21;      %Bohr magneton J*G^-1
 h = 6.62606876;          %Planck's constant
%% **********************************
% This part generates the matrix for the spin operators.
S = 7/2;                 %electron spin number
I = 0;                   %nuclear spin number
dim = 2*S+1;             %size of the Hamiltonian matrix
for s1 = 0:(2*S)
for i1 = 1:(1+2*I)
for s2 = 0:(2*S)
for i2 = 1:(1+2*I)
      S1 = -(s1 - S);  I1 = -(i1 - (I + 1));
      S2 = -(s2 - S);  I2 = -(i2 - (I + 1));

      a = i2 + (s2*(2*I+1));      b = i1 + (s1*(2*I+1));

      if (I1 == I2) & (S2 == S1 + 1)
            Sp(a,b) = sqrt(S*(S+1) - S1*(S1+1));
      else
            Sp(a,b) = 0;
      end

      if (I1 == I2) & (S2 == S1 - 1)
            Sm(a,b) = sqrt(S*(S+1) - S1*(S1-1));
      else
            Sm(a,b) = 0;
      end

      if (I1 == I2) & (S2 == S1)
            Sz(a,b) = S1;
      else
            Sz(a,b) = 0;
      end


end
end
end
end
```

```
Sx = (Sp + Sm)/2     ;
Sy = i*(Sp - Sm)/2;
Sz;
%% ********************************************************************
% initial input for the spin Hamiltonian parameters
g = 1.99;      % principle values of g;

n1 = 6;      % angle between the cutting surface and the actual crystal face;
n2 = 0; %bc
n3 = -2; %ac
m1 = -1; %ab
m2 = 5;
m3 = 1;

B4 = -2.31; % principle values of B4, B6;
B6 = -0.0004;

S = eye(8)*(7/2);    % spin vectors;

%*********************************
p = [g B4 n1 n2 n3 m1 m2 m3 B6];      % cubic
% p = [g B2_0 B4_0 B4 B6_0 B6];      % tetragonal
% p = [g B2_0 B4_0 B4 B6_0 B6 B6_3];      % T

%% define data in ab, bc    and ca planes, respectively: Experimental
data*****************************************
%% ab plane
ab1l_w=[2611    2716    3029    3442    3745    3777    0    3101    2744    2574];
ab2l_s=[2975    3033    3226    3500    3716    3740    0    3274    3050    2955];
ab3l_w=[3092    3163    3351    3545    3658    3668    0    3387    3182    3067];
ab4c_s=[3552    3568    3593    3576    3529    3521    3550    3590    3571    3546];
ab3r_w=[4031    3979    3810    0    3420    3402    0    3769    3964    4049];
ab2r_s=[4109    4030    3810    0    3443    3431    0    3769    4009    4137];
ab1r_w=[4498    4364    3982    0    3273    3247    3481    3902    4329    4544];

%% bc plane
bc1l_w=[2550    2706    3063    3481    3745    3725    3427    3027    2711    2608];
bc2l_s=[2932    3022    3245    0    3716    3699    3487    3218    3024    2965];
bc3l_w=[3041    3151    3358    0    3644    3638    0    3342    3155    3084];
bc4c_s=[3528    3552    3571    3543    3502    3508    3557    3576    3553    3537];
bc3r_w=[4039    3958    0    0    3392    3405    0    0    3955    4008];
bc2r_s=[4130    4008    3767    0    3425    3431    0    3785    4003    4083];
bc1r_w=[4543    4338    3910    0    3244    3261    0    3948    4331    4464];
```

```
%% ac plane
ac1l_w=[2551 2633 2939 3349 3674 3738 3498 3090 2727 2553];
ac2l_s=[2932 2979 3166 3441 3674 3716 0 3264 3035 2933 ];
ac3l_w=[3042 3102 3290 3491 3616 3636 0 3371 3165 3043];
ac4c_s=[3528 3541 3568 3553 3505 3493 3539 3569 3554 3528];
ac3r_w=[4038 3995 3836 3610 3428 3394 0 3753 3947 4038];
ac2r_s=[4129 4064 3846 3610 3463 3439 0 3753 3994 4129];
ac1r_w=[4542 4433 4050 3610 3306 3255 3468 3881 4312 4541];

H =
[ab1l_w,ab2l_s,ab3l_w,ab4c_s,ab3r_w,ab2r_s,ab1r_w,ac1l_w,ac2l_s,ac3l_w,ac4c_s,ac3r_w,ac2r_s,ac1
r_w,bc1l_w,bc2l_s,bc3l_w,bc4c_s,bc3r_w,bc2r_s,bc1r_w];

length(H)


%Euler angles of ba, ca, cb plane
a_ba = [0 0 0 0 0 0 0 0 0 0]+n1;
a_cb = [0 10 20 30 40 50 60 70 80 90]+n2;
a_ca = [0 10 20 30 40 50 60 70 80 90]+n3;
alpha1 = [a_ba a_ba a_ba a_ba a_ba a_ba a_ba a_ca a_ca a_ca a_ca a_ca a_ca a_ca a_cb a_cb a_cb
a_cb a_cb a_cb a_cb];

b_ba = [0 10 20 30 40 50 60 70 80 90]+m1;
b_cb = [0 0 0 0 0 0 0 0 0 0]+m2;
b_ca = [0 0 0 0 0 0 0 0 0 0]+m3;
beta1 =    [b_ba b_ba b_ba b_ba b_ba b_ba b_ba b_ca b_ca b_ca b_ca b_ca b_ca b_ca b_cb b_cb b_cb
b_cb b_cb b_cb b_cb];

%%%;

s1_1=1*ones(1,length(ab1l_w));
s1_2=1*ones(1,length(ab2l_s));
s1_3=1*ones(1,length(ab3l_w));
s1_4=1*ones(1,length(ab4c_s));
s1_5=1*ones(1,length(ab3r_w));
s1_6=1*ones(1,length(ab2r_s));
s1_7=1*ones(1,length(ab1r_w));


s2_1=1*ones(1,length(ac1l_w));
s2_2=1*ones(1,length(ac2l_s));
s2_3=1*ones(1,length(ac3l_w));
s2_4=1*ones(1,length(ac4c_s));
```

```
s2_5=1*ones(1,length(ac3r_w));
s2_6=1*ones(1,length(ac2r_s));
s2_7=1*ones(1,length(ac1r_w));

s3_1=1*ones(1,length(bc1l_w));
s3_2=1*ones(1,length(bc2l_s));
s3_3=1*ones(1,length(bc3l_w));
s3_4=1*ones(1,length(bc4c_s));
s3_5=1*ones(1,length(bc3r_w));
s3_6=1*ones(1,length(bc2r_s));
s3_7=1*ones(1,length(bc1r_w));

site1 =    [s1_1 s1_2 s1_3 s1_4 s1_5 s1_6 s1_7];
site2 =    [s2_1 s2_2 s2_3 s2_4 s2_5 s2_6 s2_7];
site3 =    [s3_1 s3_2 s3_3 s3_4 s3_5 s3_6 s3_7];

site = [site1 site2 site3] ;
freqq1 = 1000*9.8646*ones(1,length(site1)); %in Mhz ab
freqq2 = 1000*9.8619*ones(1,length(site2)); %in Mhz ac
freqq3 = 1000*9.8603*ones(1,length(site2)); %in Mhz bc
freqq = [freqq1 freqq2 freqq3];

alpha = alpha1*pi/180;
beta = beta1*pi/180;
points = length(H);
sitenumber=length(site);
alphanumber=length(alpha);
betanumber=length(beta);
freqqnumber=length(freqq);

dddd=0;
%%
for k = 1:points
    if H(k)> 1
        dddd=dddd+1;
    end
end
dddd % The total effective experimental data
%*****This begins the least squares analysis portion of the program*****

scale = 10;
new_sum = 1000000000;
while scale > 0.00001
      diff = 2;
```

```
scale = scale/10;
while diff > 0.00001      %*****program loops until parameters stop changing


   for k= 1:9         %*****loops through the parameters
            if (k==9)
                  old_sum = new_sum;
             end
             if k < 9
                  delta = 0.001*scale;
            else
            delta = 0.00001*scale;
            end

            sum1 = sum_NCF_2(site, alpha, B, p, H, freqq, beta, points, Sm, Sp, Sx,Sy,Sz,B4,B6);
             p(k) = p(k) + delta;
             sum2 = sum_NCF_2(site, alpha, B, p, H, freqq, beta, points, Sm, Sp, Sx,Sy,Sz,B4,B6);
             p(k) = p(k) - 2*delta;
             sum3 = sum_NCF_2(site, alpha, B, p, H, freqq, beta, points, Sm, Sp, Sx,Sy,Sz,B4,B6);

      if (sum1 < sum2) & (sum1 < sum3)
                  p(k) = p(k) + delta;
                  sum = sum1;
             elseif (sum2 < sum1) & (sum2 < sum3)
                  p(k) = p(k) + 2*delta;
                  sum = sum2;
             else
                  sum = sum3;
             end

       if (k==9)
            new_sum = sum;
            old_sum;
                  diff = abs(old_sum - new_sum);
       end
   end
      dev = (sqrt(sum/210))/2.8;       %****gives standard deviation in Gauss

      pp=p;

   pp;
      scale
     dev
end
```

```
end
pp


% Subroutine for EPR angular dependence fitting of center in NCF
function sum = sum_NCF_2(site, alpha, B, p, H, freqq, beta, points, Sm, Sp, Sx,Sy,Sz,B4,B6)
sum = 0;
S = 7/2;

   T_G = eye(3);      % no theta, phi, psi

for k =1:210      % all experimental data
    if H(k)==0000.00 %
        else
          RM = [cos(alpha(k)) -sin(alpha(k))*sin(beta(k)) sin(alpha(k))*cos(beta(k)); 0 cos(beta(k))
sin(beta(k)); -sin(alpha(k)) -cos(alpha(k))*sin(beta(k)) cos(alpha(k))*cos(beta(k))];

    %% Magnetic magnetically inequivalent points
         if site(k) == 1
            Mod = [1 0 0; 0 1 0; 0 0 1];
         end
         if site(k) == 2
            Mod = [1 0 0; 0 -1 0; 0 0 -1];
         end
        if site(k) == 3
            Mod = [-1 0 0; 0 1 0; 0 0 -1];
        end
        if site(k) == 4
            Mod = [-1 0 0; 0 -1 0; 0 0 1];
        end
        if site(k) == 5
            Mod = [0 1 0; 0 0 1; 1 0 0];
        end
        if site(k)== 6
            Mod = [0 1 0; 0 0 -1 ; -1 0 0];
        end
        if site(k) == 7
            Mod = [0 -1 0;0 0 -1 ; -1 0 0];
        end
        if site(k) == 8
            Mod = [0 -1 0; 0 0 -1;1 0 0 ];
        end
        if site(k) == 9
            Mod = [0 0 1; 1 0 0;0 1 0 ];
        end
```

```
if site(k) == 10
    Mod = [0 0 1; -1 0 0;0 -1 0 ];
end
if site(k) == 11
    Mod = [0 0 -1; 1 0 0;0 -1 0 ];
end
if site(k) == 12
    Mod = [0 0 -1; -1 0 0;0 1 0 ];
end
if site(k) == 13
    Mod = [0 -1 0; -1 0 0;0 0 -1 ];
end
if site(k) == 14
    Mod = [0 -1 0; 1 0 0;0 0 1 ];
end
if site(k) == 15
    Mod = [0 1 0; -1 0 0;0 0 1 ];
end
if site(k) == 16
    Mod = [0 1 0; 1 0 0;0 0 -1 ];
end
if site(k) == 17
    Mod = [-1 0 0; 0 0 -1;0 -1 0 ];
end
if site(k) == 18
    Mod = [-1 0 0; 0 0 1;0 1 0 ];
end
if site(k) == 19
    Mod = [1 0 0; 0 0 -1;0 1 0 ];
end
if site(k) == 20
    Mod = [1 0 0; 0 0 1;0 -1 0 ];
end
if site(k) == 21
    Mod = [0 0 -1; 0 -1 0;-1 0 0 ];
end
if site(k) == 22
    Mod = [0 0 -1; 0 1 0;1 0 0 ];
end
if site(k) == 23
    Mod = [0 0 1; 0 -1 0;1 0 0 ];
end
if site(k) == 24
    Mod = [0 0 1; 0 1 0;-1 0 0 ];
```

```
        end

g=[p(1) 0 0 ; 0 p(1) 0 ; 0 0 p(1)];
gg=T_G'*g*T_G;
S = eye(8)*(7/2);

RM=Mod*RM;
mag=[0 0 H(k)] ;
mag=(RM*(mag'))';

%% Stevens operators
O4_0 = 35*Sz^4-30*S*(S+eye(8))*Sz^2+25*Sz^2-6*S*(S+eye(8))+3*S^2*(S+eye(8))^2;
O4_4 = 0.5*(Sp^4+Sm^4);
O6_0 = 231*Sz^6-315*S*(S+eye(8))*Sz^4+735*Sz^4+105*S^2*(S+eye(8))^2*Sz^2-
525*S*(S+eye(8))*Sz^2+294*Sz^2-5*S^3*(S+eye(8))^3+40*S^2*(S+eye(8))^2-60*S*(S+eye(8));
O6_4 = 0.25*((11*Sz^2-S*(S+eye(8))-eye(8)*38)*(Sp^4+Sm^4)+(Sp^4+Sm^4)*(11*Sz^2-
S*(S+eye(8))-eye(8)*38));

H_EZ = 1000*B*(
Sx*(gg(1,1)*mag(1)+gg(1,2)*mag(2)+gg(1,3)*mag(3))+Sy*(gg(2,1)*mag(1)+gg(2,2)*mag(2)+gg(2,3)
*mag(3))+Sz*(gg(3,1)*mag(1)+gg(3,2)*mag(2)+gg(3,3)*mag(3)))/(6.62e-18); %/ Electron_Zeeman
term UNit is Mhz

H_ZFS = B4*(O4_0+5*O4_4) + B6*(O6_0-21*O6_4);      % cubic
Hamiltonian=H_EZ+H_ZFS;
level=sort(real(eig(Hamiltonian)));

if k<11
    freq(k)=abs(level(2)-level(1));
    elseif k<21
    freq(k)=abs(level(6)-level(5));
    elseif k<31
    freq(k)=abs(level(7)-level(6));
    elseif k<41
    freq(k)=abs(level(5)-level(4));
    elseif k<51
    freq(k)=abs(level(3)-level(2));
    elseif k<61
    freq(k)=abs(level(4)-level(3));
    elseif k<71
    freq(k)=abs(level(8)-level(7)); %ba



    elseif k<81
```

```
    freq(k)=abs(level(2)-level(1));
    elseif k<91
    freq(k)=abs(level(6)-level(5));
    elseif k<101
    freq(k)=abs(level(7)-level(6));
    elseif k<111
    freq(k)=abs(level(5)-level(4));
    elseif k<121
    freq(k)=abs(level(3)-level(2));
    elseif k<131
    freq(k)=abs(level(4)-level(3));
    elseif k<141
    freq(k)=abs(level(8)-level(7)); %ca

    elseif k<151
    freq(k)=abs(level(2)-level(1));
    elseif k<161
    freq(k)=abs(level(6)-level(5));
    elseif k<171
    freq(k)=abs(level(7)-level(6));
    elseif k<181
    freq(k)=abs(level(5)-level(4));
    elseif k<191
    freq(k)=abs(level(3)-level(2));
    elseif k<201
    freq(k)=abs(level(4)-level(3));
else
    freq(k)=abs(level(8)-level(7)); %cb
end



        deltaf(k) = (freq(k)-freqq(k))^2;
        sum = sum + deltaf(k);
        deltaff(k)=(freq(k)-freqq(k))/freqq(k);

end
end
```

```
%fitting code for 1GCF
clear,clf;
clc
B = 9.27400899e-21;      %Bohr magneton J*G^-1
 h = 6.62606876;          %Planck's constant
%% **********************************
% This part generates the matrix for the spin operators.
S = 7/2;                 %electron spin number
I = 0;                   %nuclear spin number
dim = 2*S+1;             %size of the Hamiltonian matrix
for s1 = 0:(2*S)
for i1 = 1:(1+2*I)
for s2 = 0:(2*S)
for i2 = 1:(1+2*I)
      S1 = -(s1 - S);  I1 = -(i1 - (I + 1));
      S2 = -(s2 - S);  I2 = -(i2 - (I + 1));

      a = i2 + (s2*(2*I+1));      b = i1 + (s1*(2*I+1));

      if (I1 == I2) & (S2 == S1 + 1)
            Sp(a,b) = sqrt(S*(S+1) - S1*(S1+1));
      else
            Sp(a,b) = 0;
      end

      if (I1 == I2) & (S2 == S1 - 1)
            Sm(a,b) = sqrt(S*(S+1) - S1*(S1-1));
      else
            Sm(a,b) = 0;
      end

      if (I1 == I2) & (S2 == S1)
            Sz(a,b) = S1;
      else
            Sz(a,b) = 0;
      end


end
end
end
end

Sx = (Sp + Sm)/2     ;
```

```
Sy = i*(Sp - Sm)/2;
Sz;
%% ********************************************************************
% initial input for the spin Hamiltonian parameters
g = 1.99;      % principle values of g;
n1 = 0;      % angle between the cutting surface and the actual crystal face;
n2 = 4;
n3 = 0;
m1 = 3;
m2 = 0;
m3 = 1;


% principle values of zero-field splitting parameters ;
B4 = -2.3;
B6 = 0.001;
S = eye(8)*(7/2);    % spin vectors;

%*********************************
p = [g B4 n1 n2 n3 m1 m2 m3 B6];      % cubic
%% define d ata in ab, bc    and ca planes, respectively: Experimental
data*******************************************

%% ab plane
ab1l_w=[2577 2777 3152 0 0 0 3300 2893 2613 2567];
ab2l_s=[2950 3066 3307 3576 3730 3654 3410 3139 2970 2944];
ab3l_w=[3063 3199 3405 0 3644 3614 3472 3267 3088 3055];
ab4c_s=[3536 3563 3571 0 3494 3514 3561 3570 3541 3533];
ab3r_w=[4031 3936 3721 3527 3438 3478 3640 0 4012 4035];
ab2r_s=[4114 3963 3721 0 3393 3452 3640 3875 4086 4121];
ab1r_w=[4516 4258 3820 3430 3249 3337 0 4113 4467 4528];

%% ac plane
ac1l_w=[2587 2801 3179 0 0 0 3273 2862 2601 2571];
ac2l_s=[2955 3080 3324 3589 3732 3635 3390 3120 2963 2945];
ac3l_w=[3070 3213 3417 0 3645 3610 3459 3250 3080 3058];
ac4c_s=[3536 3565 3571 0 3494 3517 3563 3568 3539 3534];
ac3r_w=[4023 3920 3705 3512 3433 3486 3654 3894 4017 4032];
ac2r_s=[4104 3943 3705 0 3389 0 3654 3894 4094 4118];
ac1r_w=[4500 4224 3791 3402 3243 3354 0 4149 4482 4523];

%% bc plane
bc1l_w=[2549 2687 3029 3445 0 0 3427 3011 2684 2563];
bc2l_s=[2933 3012 3225 0 3707 3700 0 3214 3011 2941];
```

```
bc3l_w=[3041 3139 3340 0 3633 3631 0 3333 3138 3052];
bc4c_s=[3529 3551 3572 3549 3500 3502 3559 3573 3551 3532];
bc3r_w=[4043 3972 3791 0 3447 3449 0 3800 3977 4035];
bc2r_s=[4134 4026 3791 0 3410 3417 0 3800 4028 4123];
bc1r_w=[4551 4368 3954 0 3272 3279 0 3974 4371 4531];

H =
[ab1l_w,ab2l_s,ab3l_w,ab4c_s,ab3r_w,ab2r_s,ab1r_w,ac1l_w,ac2l_s,ac3l_w,ac4c_s,ac3r_w,ac2r_s,ac1
r_w,bc1l_w,bc2l_s,bc3l_w,bc4c_s,bc3r_w,bc2r_s,bc1r_w];

length(H)


%Euler angles of ba, ca, cb plane
a_ba = [0 0 0 0 0 0 0 0 0 0]+n1;
a_ca = [0 10 20 30 40 50 60 70 80 90]+n2;
a_cb = [0 10 20 30 40 50 60 70 80 90]+n3;
alpha1 = [a_ba a_ba a_ba a_ba a_ba a_ba a_ba a_ca a_ca a_ca a_ca a_ca a_ca a_ca a_cb a_cb a_cb
a_cb a_cb a_cb a_cb];

b_ba = [0 10 20 30 40 50 60 70 80 90]+m1;
b_ca = [0 0 0 0 0 0 0 0 0 0]+m2;
b_cb = [0 0 0 0 0 0 0 0 0 0]+m3;
beta1 =    [b_ba b_ba b_ba b_ba b_ba b_ba b_ba b_ca b_ca b_ca b_ca b_ca b_ca b_ca b_cb b_cb b_cb
b_cb b_cb b_cb b_cb];

%%%;

s1_1=1*ones(1,length(ab1l_w));
s1_2=1*ones(1,length(ab2l_s));
s1_3=1*ones(1,length(ab3l_w));
s1_4=1*ones(1,length(ab4c_s));
s1_5=1*ones(1,length(ab3r_w));
s1_6=1*ones(1,length(ab2r_s));
s1_7=1*ones(1,length(ab1r_w));


s2_1=1*ones(1,length(ac1l_w));
s2_2=1*ones(1,length(ac2l_s));
s2_3=1*ones(1,length(ac3l_w));
s2_4=1*ones(1,length(ac4c_s));
s2_5=1*ones(1,length(ac3r_w));
s2_6=1*ones(1,length(ac2r_s));
s2_7=1*ones(1,length(ac1r_w));
```

```
s3_1=1*ones(1,length(bc1l_w));
s3_2=1*ones(1,length(bc2l_s));
s3_3=1*ones(1,length(bc3l_w));
s3_4=1*ones(1,length(bc4c_s));
s3_5=1*ones(1,length(bc3r_w));
s3_6=1*ones(1,length(bc2r_s));
s3_7=1*ones(1,length(bc1r_w));

site1 =    [s1_1 s1_2 s1_3 s1_4 s1_5 s1_6 s1_7];
site2 =    [s2_1 s2_2 s2_3 s2_4 s2_5 s2_6 s2_7];
site3 =    [s3_1 s3_2 s3_3 s3_4 s3_5 s3_6 s3_7];

site = [site1 site2 site3] ;
%site = site1;

freqq_ab = [9.8712      9.8712      9.8711      9.8710      9.8708      9.8707      9.8705      9.8704
9.8702      9.8702];
freqq_ac = [9.8690      9.8691      9.8691      9.8692      9.8693      9.8693      9.8693      9.8693
9.8692      9.8691];
freqq_bc = [9.8676      9.8675      9.8674      9.8673      9.8673      9.8671      9.8672      9.8674
9.8675      9.8676];

freqq1 = 1000*[freqq_ab freqq_ab freqq_ab freqq_ab freqq_ab freqq_ab freqq_ab];
freqq2 = 1000*[freqq_ac freqq_ac freqq_ac freqq_ac freqq_ac freqq_ac freqq_ac];
freqq3 = 1000*[freqq_bc freqq_bc freqq_bc freqq_bc freqq_bc freqq_bc freqq_bc];
freqq = [freqq1 freqq2 freqq3];

alpha = alpha1*pi/180;
beta = beta1*pi/180;
points = length(H);
sitenumber=length(site);
alphanumber=length(alpha);
betanumber=length(beta);
freqqnumber=length(freqq);

dddd=0;
%%
for k = 1:points
        dddd=dddd+1;
    end
end
dddd % The total effective experimental data
%*****This begins the least squares analysis portion of the program*****
```

```
scale = 10;
new_sum = 1000000000;
while scale > 0.00001
      diff = 2;
      scale = scale/10;
      while diff > 0.00001      %*****program loops until parameters stop changing


        for k= 1:9        %*****loops through the parameters
              if (k==1)
                    old_sum = new_sum;
               end
               if k < 9
                    delta = 0.001*scale;
              else
              delta = 0.00001*scale;
              end

              sum1 = sum_GCF_3plane(site, alpha, B, p, H, freqq, beta, points, Sm, Sp,
Sx,Sy,Sz,B4,B6);
               p(k) = p(k) + delta;
               sum2 = sum_GCF_3plane(site, alpha, B, p, H, freqq, beta, points, Sm, Sp,
Sx,Sy,Sz,B4,B6);
               p(k) = p(k) - 2*delta;
               sum3 = sum_GCF_3plane(site, alpha, B, p, H, freqq, beta, points, Sm, Sp,
Sx,Sy,Sz,B4,B6);

          if (sum1 < sum2) & (sum1 < sum3)
                    p(k) = p(k) + delta;
                    sum = sum1;
               elseif (sum2 < sum1) & (sum2 < sum3)
                    p(k) = p(k) + 2*delta;
                    sum = sum2;
               else
                    sum = sum3;
               end

           if (k==9)
              new_sum = sum;
              old_sum;
                    diff = abs(old_sum - new_sum);
           end
        end
```

```
            dev = (sqrt(sum/210))/2.8;       %****gives standard deviation in Gauss

            pp=p;
           pp;
            scale
           dev
      end
end
pp

%Subroutine for EPR angular dependence fitting ofcenter in 1GCF
function sum = sum_GCF_3plane(site, alpha, B, p, H, freqq, beta, points, Sm, Sp, Sx,Sy,Sz,B4,B6)

sum = 0;
S = 7/2;

   T_G = eye(3);     % no theta, phi, psi

for k =1:210      % all experimental data
    if H(k)==0000.00 %
        else
          RM = [cos(alpha(k)) -sin(alpha(k))*sin(beta(k)) sin(alpha(k))*cos(beta(k)); 0 cos(beta(k))
sin(beta(k)); -sin(alpha(k)) -cos(alpha(k))*sin(beta(k)) cos(alpha(k))*cos(beta(k))];

    %% Magnetic magnetically inequivalent points
         if site(k) == 1
            Mod = [1 0 0; 0 1 0; 0 0 1];
         end
         if site(k) == 2
            Mod = [1 0 0; 0 -1 0; 0 0 -1];
         end
        if site(k) == 3
            Mod = [-1 0 0; 0 1 0; 0 0 -1];
        end
        if site(k) == 4
            Mod = [-1 0 0; 0 -1 0; 0 0 1];
        end
        if site(k) == 5
            Mod = [0 1 0; 0 0 1; 1 0 0];
        end
        if site(k)== 6
            Mod = [0 1 0; 0 0 -1 ; -1 0 0];
        end
        if site(k) == 7
```

```
    Mod = [0 -1 0;0 0 -1 ; -1 0 0];
end
if site(k) == 8
    Mod = [0 -1 0; 0 0 -1;1 0 0 ];
end
if site(k) == 9
    Mod = [0 0 1; 1 0 0;0 1 0 ];
end
if site(k) == 10
    Mod = [0 0 1; -1 0 0;0 -1 0 ];
end
if site(k) == 11
    Mod = [0 0 -1; 1 0 0;0 -1 0 ];
end
if site(k) == 12
    Mod = [0 0 -1; -1 0 0;0 1 0 ];
end
if site(k) == 13
    Mod = [0 -1 0; -1 0 0;0 0 -1 ];
end
if site(k) == 14
    Mod = [0 -1 0; 1 0 0;0 0 1 ];
end
if site(k) == 15
    Mod = [0 1 0; -1 0 0;0 0 1 ];
end
if site(k) == 16
    Mod = [0 1 0; 1 0 0;0 0 -1 ];
end
if site(k) == 17
    Mod = [-1 0 0; 0 0 -1;0 -1 0 ];
end
if site(k) == 18
    Mod = [-1 0 0; 0 0 1;0 1 0 ];
end
if site(k) == 19
    Mod = [1 0 0; 0 0 -1;0 1 0 ];
end
if site(k) == 20
    Mod = [1 0 0; 0 0 1;0 -1 0 ];
end
if site(k) == 21
    Mod = [0 0 -1; 0 -1 0;-1 0 0 ];
end
```

```
        if site(k) == 22
            Mod = [0 0 -1; 0 1 0;1 0 0 ];
        end
        if site(k) == 23
            Mod = [0 0 1; 0 -1 0;1 0 0 ];
        end
        if site(k) == 24
            Mod = [0 0 1; 0 1 0;-1 0 0 ];
        end


g=[p(1) 0 0 ; 0 p(1) 0 ; 0 0 p(1)];
gg=T_G'*g*T_G;
S = eye(8)*(7/2);

RM=Mod*RM;
mag=[0 0 H(k)] ;
mag=(RM*(mag'))';

%% Stevens operators
O4_0 = 35*Sz^4-30*S*(S+eye(8))*Sz^2+25*Sz^2-6*S*(S+eye(8))+3*S^2*(S+eye(8))^2;
O4_4 = 0.5*(Sp^4+Sm^4);
O6_0 = 231*Sz^6-315*S*(S+eye(8))*Sz^4+735*Sz^4+105*S^2*(S+eye(8))^2*Sz^2-
525*S*(S+eye(8))*Sz^2+294*Sz^2-5*S^3*(S+eye(8))^3+40*S^2*(S+eye(8))^2-60*S*(S+eye(8));
O6_4 = 0.25*((11*Sz^2-S*(S+eye(8))-eye(8)*38)*(Sp^4+Sm^4)+(Sp^4+Sm^4)*(11*Sz^2-
S*(S+eye(8))-eye(8)*38));

H_EZ = 1000*B*(
Sx*(gg(1,1)*mag(1)+gg(1,2)*mag(2)+gg(1,3)*mag(3))+Sy*(gg(2,1)*mag(1)+gg(2,2)*mag(2)+gg(2,3)
*mag(3))+Sz*(gg(3,1)*mag(1)+gg(3,2)*mag(2)+gg(3,3)*mag(3)))/(6.62e-18); %/Electron_Zeeman
term UNit is Mhz

H_ZFS = B4*(O4_0+5*O4_4) + B6*(O6_0-21*O6_4);      % cubic

Hamiltonian=H_EZ+H_ZFS;
level=sort(real(eig(Hamiltonian)));

if k<11
    freq(k)=abs(level(2)-level(1));
    elseif k<21
    freq(k)=abs(level(6)-level(5));
    elseif k<31
    freq(k)=abs(level(7)-level(6));
    elseif k<41
```

```
    freq(k)=abs(level(5)-level(4));
    elseif k<51
    freq(k)=abs(level(3)-level(2));
    elseif k<61
    freq(k)=abs(level(4)-level(3));
    elseif k<71
    freq(k)=abs(level(8)-level(7)); %ba


    elseif k<81
    freq(k)=abs(level(2)-level(1));
    elseif k<91
    freq(k)=abs(level(6)-level(5));
    elseif k<101
    freq(k)=abs(level(7)-level(6));
    elseif k<111
    freq(k)=abs(level(5)-level(4));
    elseif k<121
    freq(k)=abs(level(3)-level(2));
    elseif k<131
    freq(k)=abs(level(4)-level(3));
    elseif k<141
    freq(k)=abs(level(8)-level(7)); %ca

    elseif k<151
    freq(k)=abs(level(2)-level(1));
    elseif k<161
    freq(k)=abs(level(6)-level(5));
    elseif k<171
    freq(k)=abs(level(7)-level(6));
    elseif k<181
    freq(k)=abs(level(5)-level(4));
    elseif k<191
    freq(k)=abs(level(3)-level(2));
    elseif k<201
    freq(k)=abs(level(4)-level(3));
else
    freq(k)=abs(level(8)-level(7)); %cb
end


        deltaf(k) = (freq(k)-freqq(k))^2;
        sum = sum + deltaf(k);
        deltaff(k)=(freq(k)-freqq(k))/freqq(k);
```

```
end
end
```

Stevens Operators

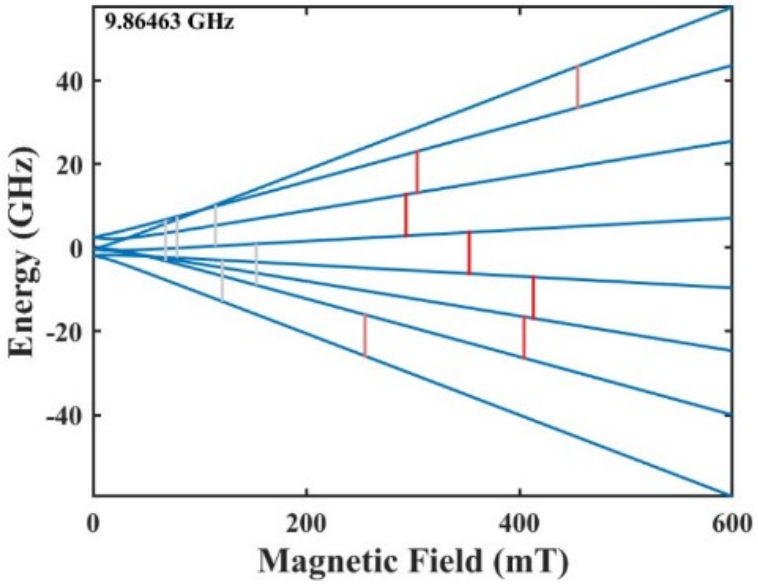
The Stevens operators are used to express higher order spin-Hamiltonian terms. The fourth- and sixth-order Stevens operators used in this work are as follows:

$$O_4^0 = 35S_z^4 - \{30S(S+1) - 25\}S_z^2 - 6S(S+1) + 3S^2(S+1)^2$$

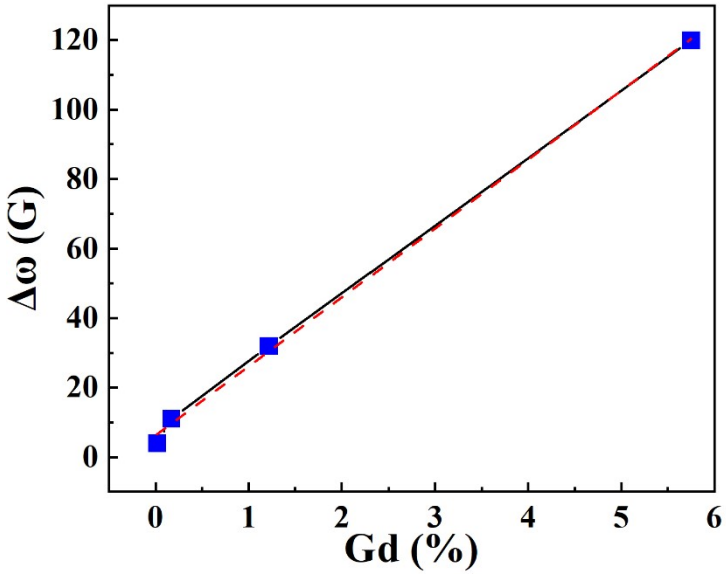
$$O_4^4 = \frac{1}{2}(S_+^4 + S_-^4)$$

$$O_6^0 = 231S_z^6 - 105\{3S(S+1) - 7\}S_z^4 + \{105S^2(S+1)^2 - 525S(S+1) + 294\}S_z^2$$
$$S^3(S+1)^3 + 40S^2(S+1)^2 - 60S(S+1)$$

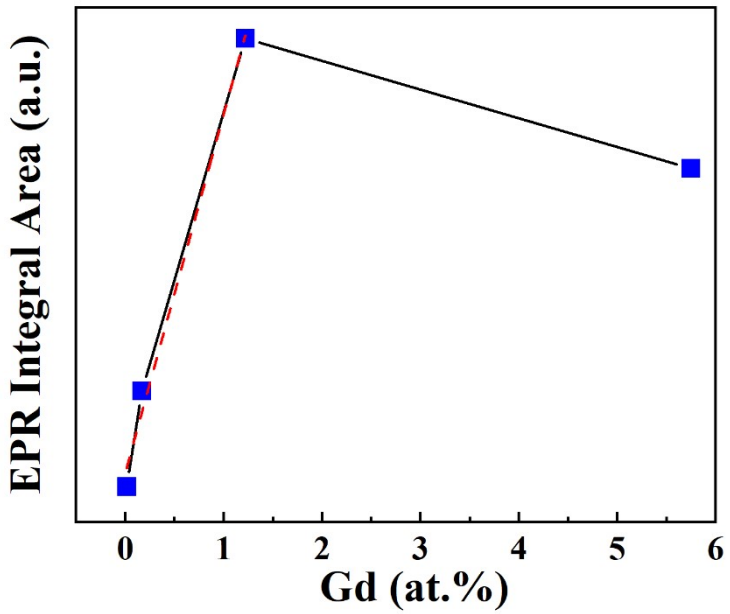
$$O_6^4 = \frac{1}{4}\{(11S_z^2 - S(S+1) - 38)(S_+^4 + S_-^4) + (S_+^4 + S_-^4)(11S_z^2 - S(S+1) - 38)\}$$



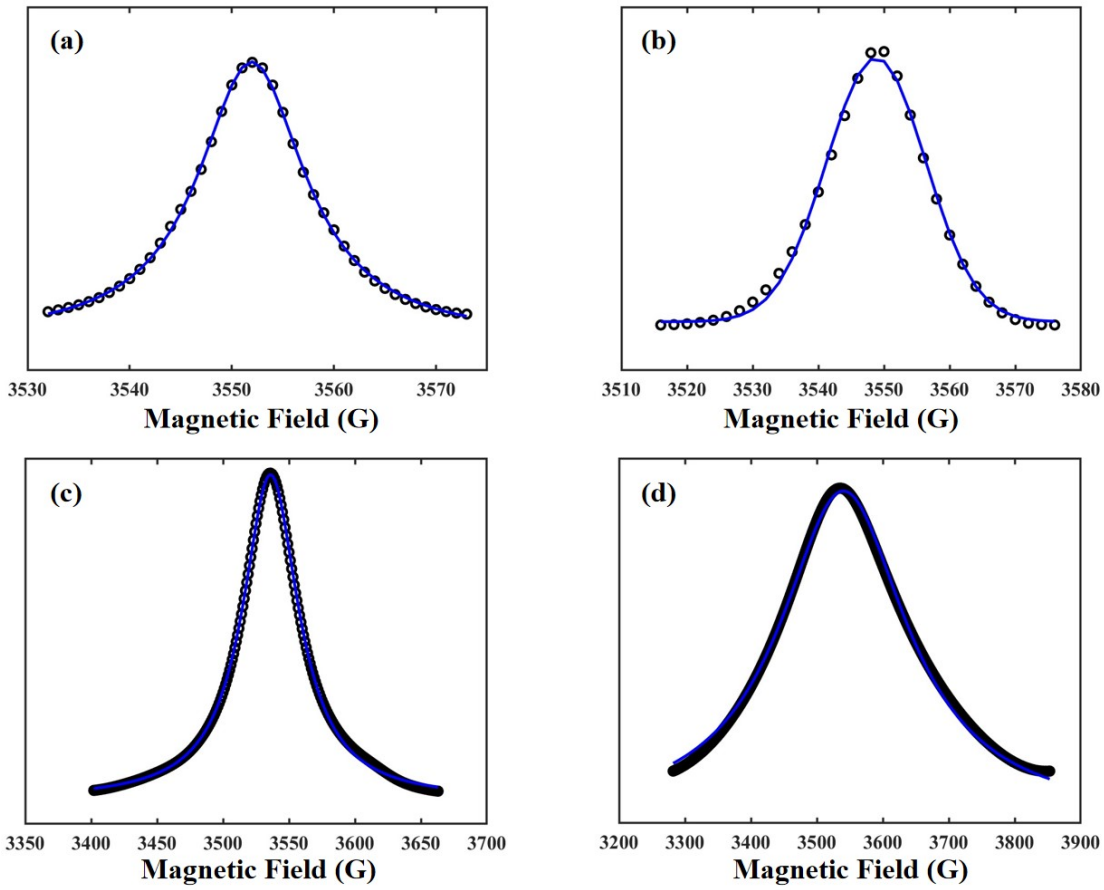
Supplementary Fig. 1 Calculated energy levels of the Cubic Gd^{3+} center in CaF_2 as a function of the magnetic field for the B//c axis. The red line segments indicate the EPR lines from the low field to the high field, which are sequentially caused by the M_S = (-7/2→-5/2), M_S = (3/2→1/2), M_S = (5/2→3/2), M_S = (1/2→-1/2), M_S = (-5/2→-3/2), M_S = (-3/2→-1/2) and M_S = (7/2→5/2) transitions are induced. The gray line segment indicates that although the light quantum carrying energy satisfies the resonance condition E = hv, the spin angular momentum carried is not equal to +1, which cannot make the change in the electron spin magnetic quantum number $|\Delta M_S|$ = 1, i.e., it does not satisfy the selection rule, and the transitions cannot occur.



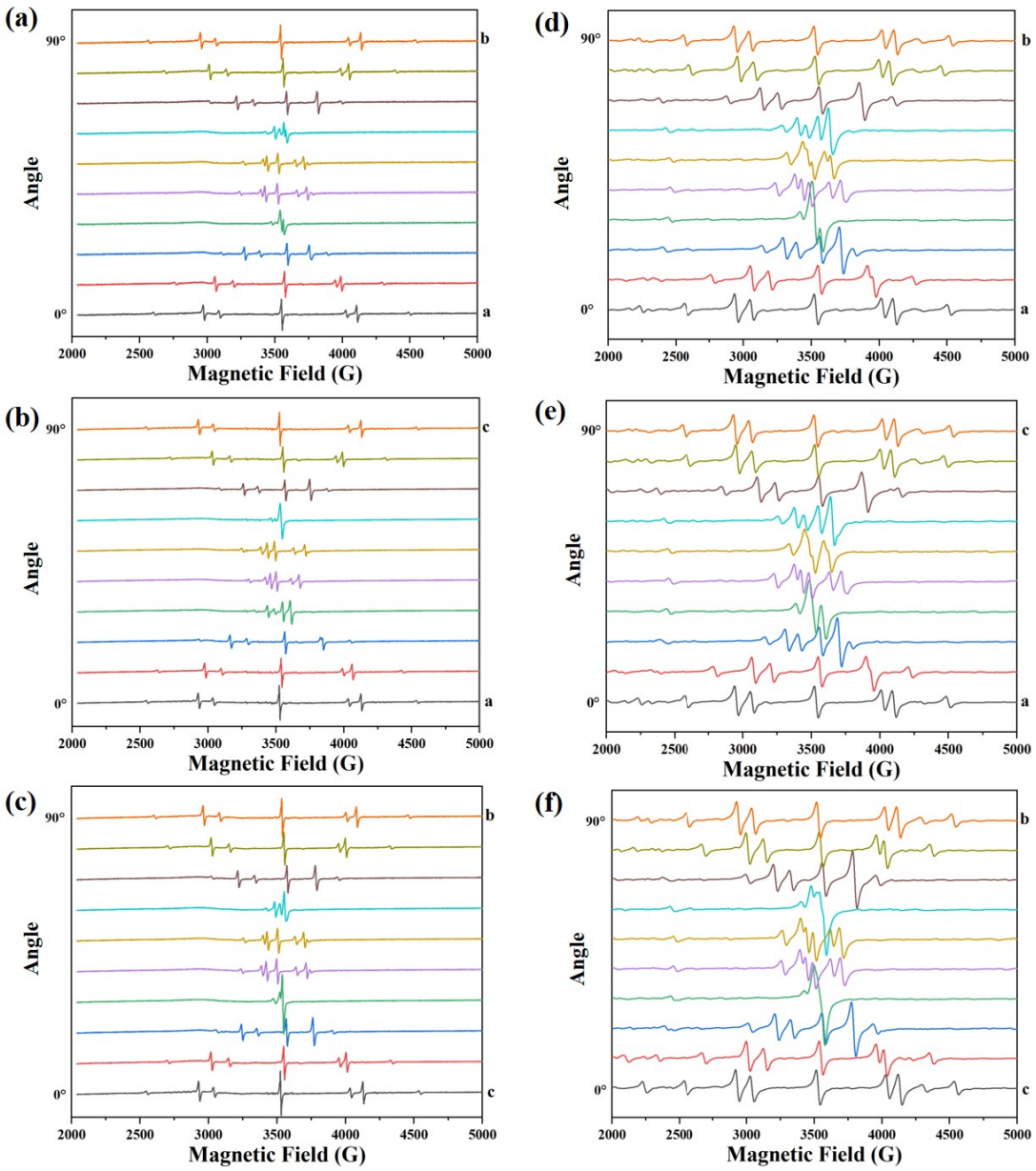
Supplementary Fig. 2 | Gd doping concentration and peak-to-peak width of the center EPR line. The four points are linearly related, $R^2 = 0.99873$.



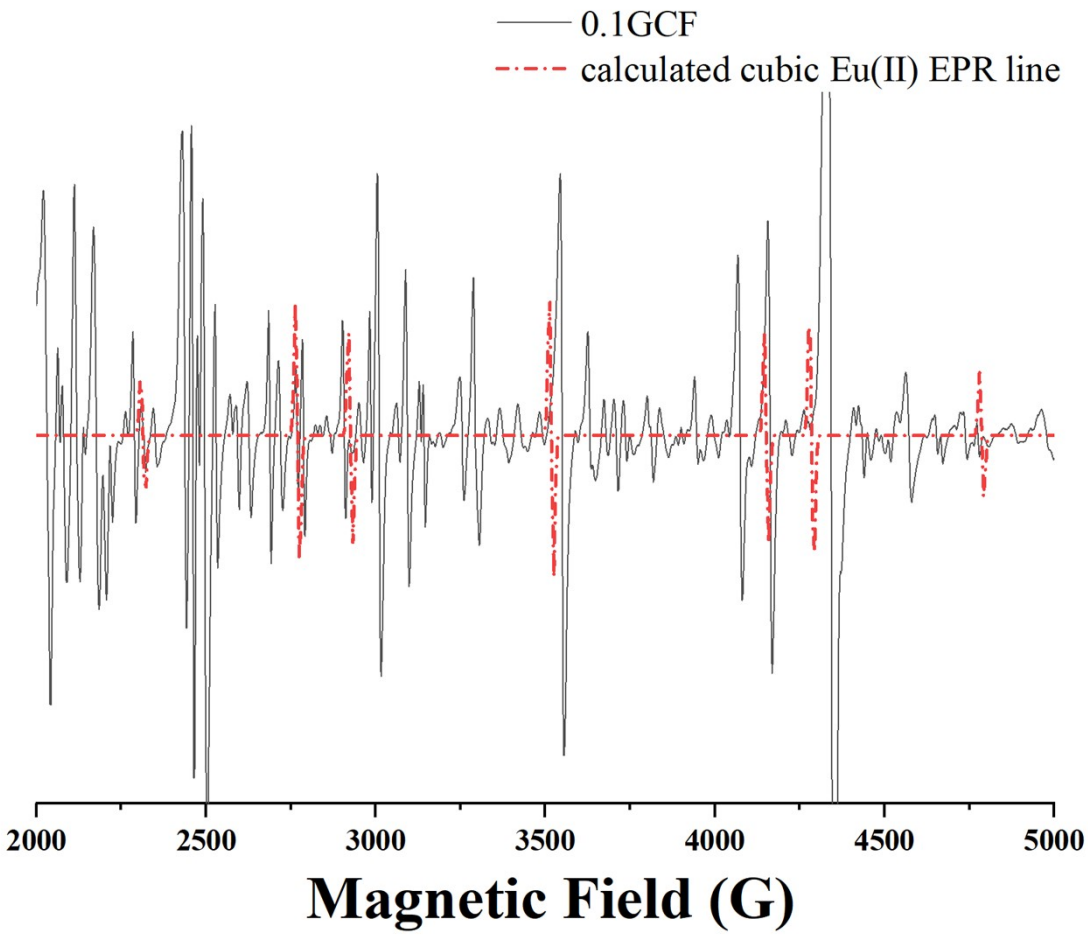
Supplementary Fig. 3 | Gd doping concentration and EPR integral area. The first three points were fitted with a linear relationship, $R^2 = 0.99273$.



Supplementary Fig. 4 | Fitting of the center EPR absorption peak. (a) NCF, Lorentzian, $R^2 = 0.9995$; **(b)** 01GCF, Gaussian, $R^2 = 0.9970$; **(c)** 1GCF, Lorentzian, $R^2 = 0.9993$; **(d)** 5GCF, Lorentzian, $R^2 = 0.9971$. The black hollow circles represent the experimental test points, and the blue lines are the fitting results.



Supplementary Fig. 5 | Full EPR spectra of NCF and 1GCF. The magnetic field lying in the **(a)** a-b plane, **(b)** a-c plane and **(c)** b-c plane of NCF, and **(d)** a-b plane, **(e)** a-c plane and **(f)** b-c plane of 1GCF.



Supplementary Fig. 6 | EPR spectra of 0.1GCF and calculated cubic Eu(Ⅱ) EPR line.

Supplementary Table 1 | The geometry-optimized coordinates obtained from the calculation. R = 5.44 Å, b-c plane.

Angle(degree)	0	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	160	170	180
|-7/2>->|-5/2> (G)	2425	2559	2912	3337	3631	3632	3338	2912	2559	2424	2559	2912	3338	3632	3631	3337	2912	2559	2425
	2664	2786	3114	3515	3795	3796	3516	3114	2786	2663	2786	3114	3516	3796	3795	3515	3114	2786	2664
|1/2>->|3/2> (G)	2825	2902	3119	3406	3617	3617	3406	3119	2902	2825	2902	3119	3406	3617	3617	3406	3119	2902	2825
	3033	3105	3308	3580	3782	3782	3580	3308	3105	3033	3105	3308	3580	3782	3782	3580	3308	3105	3033
|3/2>->|5/2> (G)	2936	3032	3241	3438	3547	3547	3438	3241	3032	2936	3032	3241	3438	3547	3547	3438	3241	3032	2936
	3137	3227	3423	3611	3715	3715	3611	3423	3227	3137	3227	3423	3611	3715	3715	3611	3423	3227	3137
|1/2>->|-1/2> (G)	3442	3463	3486	3460	3412	3412	3460	3486	3463	3442	3463	3486	3460	3412	3412	3460	3486	3463	3442
	3614	3635	3656	3632	3586	3586	3632	3656	3635	3614	3635	3656	3632	3586	3586	3632	3656	3635	3614
|-5/2>->|-3/2> (G)	3970	3901	3716	3484	3319	3319	3484	3716	3901	3970	3901	3716	3484	3319	3319	3484	3716	3901	3970
	4120	4054	3877	3654	3497	3497	3654	3877	4054	4120	4054	3877	3654	3497	3497	3654	3877	4054	4120
|-3/2>->|-1/2> (G)	4062	3960	3723	3493	3364	3364	3493	3723	3960	4062	3960	3723	3493	3364	3364	3493	3723	3960	4062
	4209	4111	3883	3663	3540	3540	3663	3883	4111	4209	4111	3883	3663	3540	3540	3663	3883	4111	4209
|5/2>->|7/2> (G)	4486	4313	3893	3451	3183	3183	3451	3893	4313	4486	4313	3893	3451	3183	3183	3451	3893	4313	4486
	4621	4452	4046	3623	3369	3369	3623	4046	4452	4621	4452	4046	3623	3369	3369	3623	4046	4452	4621

Supplementary Table 2 | The geometry-optimized coordinates obtained from the calculation. R = 5.44 Å, a-c plane.

Angle(degree)	0	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	160	170	180
|-7/2>->|-5/2> (G)	2425	2569	2948	3403	3693	3652	3316	2848	2458	2307	2458	2848	3316	3652	3693	3403	2948	2569	2425
	2664	2776	3079	3448	3732	3776	3538	3181	2892	2785	2892	3181	3538	3776	3732	3448	3079	2776	2664
|1/2>->|3/2> (G)	2825	2911	3152	3471	3679	3636	3384	3058	2812	2723	2812	3058	3384	3636	3679	3471	3152	2911	2825
	3033	3095	3275	3515	3719	3762	3602	3371	3198	3139	3198	3371	3602	3762	3719	3515	3275	3095	3033
|3/2>->|5/2> (G)	2936	3041	3272	3502	3611	3567	3416	3182	2945	2838	2945	3182	3416	3567	3611	3502	3272	3041	2936
	3137	3218	3391	3545	3651	3694	3632	3483	3317	3238	3317	3483	3632	3694	3651	3545	3391	3218	3137
|1/2>->|-1/2> (G)	3442	3471	3516	3524	3478	3433	3439	3431	3386	3357	3386	3431	3439	3433	3478	3524	3516	3471	3442
	3614	3627	3626	3567	3519	3565	3654	3712	3714	3701	3714	3712	3654	3565	3519	3567	3626	3627	3614
|-5/2>->|-3/2> (G)	3970	3909	3744	3548	3386	3340	3463	3665	3833	3896	3833	3665	3463	3340	3386	3548	3744	3909	3970
	4120	4048	3848	3590	3429	3476	3676	3929	4125	4196	4125	3929	3676	3476	3429	3590	3848	4048	4120
|-3/2>->|-1/2> (G)	4062	3966	3751	3556	3431	3385	3472	3672	3892	3989	3892	3672	3472	3385	3431	3556	3751	3966	4062
	4209	4104	3855	3599	3472	3519	3684	3936	4180	4284	4180	3936	3684	3519	3472	3599	3855	4104	4209
|5/2>->|7/2> (G)	4486	4320	3920	3515	3253	3205	3430	3844	4251	4420	4251	3844	3430	3205	3253	3515	3920	4320	4486
	4621	4446	4019	3558	3298	3346	3644	4096	4516	4686	4516	4096	3644	3346	3298	3558	4019	4446	4621

Supplementary Table 3 | The geometry-optimized coordinates obtained from the calculation. R = 7.7 Å, a-c plane.

Angle(degree)	0	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	160	170	180
|-7/2>->|-5/2> (G)	2505	2637	2986	3407	3703	3711	3424	3003	2657	2525	2657	3003	3424	3711	3703	3407	2986	2637	2505
	2589	2713	3044	3446	3725	3718	3432	3026	2693	2567	2693	3026	3432	3718	3725	3446	3044	2713	2589
|1/2>->|3/2> (G)	2894	2971	3187	3475	3689	3696	3490	3204	2989	2913	2989	3204	3490	3696	3689	3475	3187	2971	2894
	2968	3039	3243	3513	3711	3704	3498	3226	3021	2949	3021	3226	3498	3704	3711	3513	3243	3039	2968
|3/2>->|5/2> (G)	3003	3098	3306	3506	3621	3628	3521	3323	3115	3020	3115	3323	3521	3628	3621	3506	3306	3098	3003
	3073	3164	3359	3544	3643	3635	3529	3343	3146	3056	3146	3343	3529	3635	3643	3544	3359	3164	3073
|1/2>->|-1/2> (G)	3498	3521	3547	3528	3488	3496	3543	3562	3536	3514	3536	3562	3543	3496	3488	3528	3547	3521	3498
	3560	3579	3597	3566	3512	3504	3551	3581	3564	3544	3564	3581	3551	3504	3512	3566	3597	3579	3560
|-5/2>->|-3/2> (G)	4019	3954	3773	3551	3397	3405	3566	3788	3967	4032	3967	3788	3566	3405	3397	3551	3773	3954	4019
	4072	4005	3821	3589	3421	3413	3574	3806	3992	4059	3992	3806	3574	3413	3421	3589	3821	4005	4072
|-3/2>->|-1/2> (G)	4110	4011	3781	3560	3441	3449	3575	3795	4024	4123	4024	3795	3575	3449	3441	3560	3781	4011	4110
	4162	4062	3828	3598	3465	3457	3582	3813	4048	4149	4048	3813	3582	3457	3465	3598	3828	4062	4162
|5/2>->|7/2> (G)	4531	4360	3948	3519	3265	3273	3534	3961	4372	4542	4372	3961	3534	3273	3265	3519	3948	4360	4531
	4578	4406	3993	3557	3290	3281	3542	3979	4394	4565	4394	3979	3542	3281	3290	3557	3993	4406	4578

Supplementary Table 3 | The geometry-optimized coordinates obtained from the calculation. R = 7.7 Å, a-b plane.

Angle(degree)	0	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	160	170	180
|-7/2>->|-5/2> (G)	2525	2655	2997	3411	3700	3700	3412	2997	2655	2525	2655	2997	3412	3700	3700	3411	2997	2655	2525
	2567	2695	3033	3443	3729	3730	3443	3033	2695	2567	2695	3033	3443	3730	3729	3443	3033	2695	2567
|1/2>->|3/2> (G)	2913	2987	3198	3478	3685	3685	3478	3198	2987	2913	2987	3198	3478	3685	3685	3478	3198	2987	2913
	2949	3023	3232	3510	3715	3715	3510	3232	3023	2949	3023	3232	3510	3715	3715	3510	3232	3023	2949
|3/2>->|5/2> (G)	3020	3114	3317	3510	3617	3617	3510	3317	3114	3020	3114	3317	3510	3617	3617	3510	3317	3114	3020
	3056	3148	3349	3540	3647	3647	3540	3349	3148	3056	3148	3349	3540	3647	3647	3540	3349	3148	3056
|1/2>->|-1/2> (G)	3514	3535	3557	3532	3484	3484	3532	3557	3535	3514	3535	3557	3532	3484	3484	3532	3557	3535	3514
	3544	3565	3587	3562	3515	3515	3562	3587	3565	3544	3565	3587	3562	3515	3515	3562	3587	3565	3544
|-5/2>->|-3/2> (G)	4032	3966	3783	3555	3393	3393	3555	3783	3966	4032	3966	3783	3555	3393	3393	3555	3783	3966	4032
	4059	3993	3811	3585	3425	3425	3585	3811	3993	4059	3993	3811	3585	3425	3425	3585	3811	3993	4059
|-3/2>->|-1/2> (G)	4123	4022	3790	3564	3437	3437	3564	3790	4022	4123	4022	3790	3564	3437	3437	3564	3790	4022	4123
	4149	4049	3818	3594	3468	3468	3594	3818	4049	4149	4049	3818	3594	3468	3468	3594	3818	4049	4149
|5/2>->|7/2> (G)	4542	4371	3957	3523	3261	3261	3523	3957	4371	4542	4371	3957	3523	3261	3261	3523	3957	4371	4542
	4565	4396	3983	3553	3293	3293	3553	3983	4396	4565	4396	3983	3553	3293	3293	3553	3983	4396	4565