Spin tuning of electron-doped metal-phthalocyanine layers

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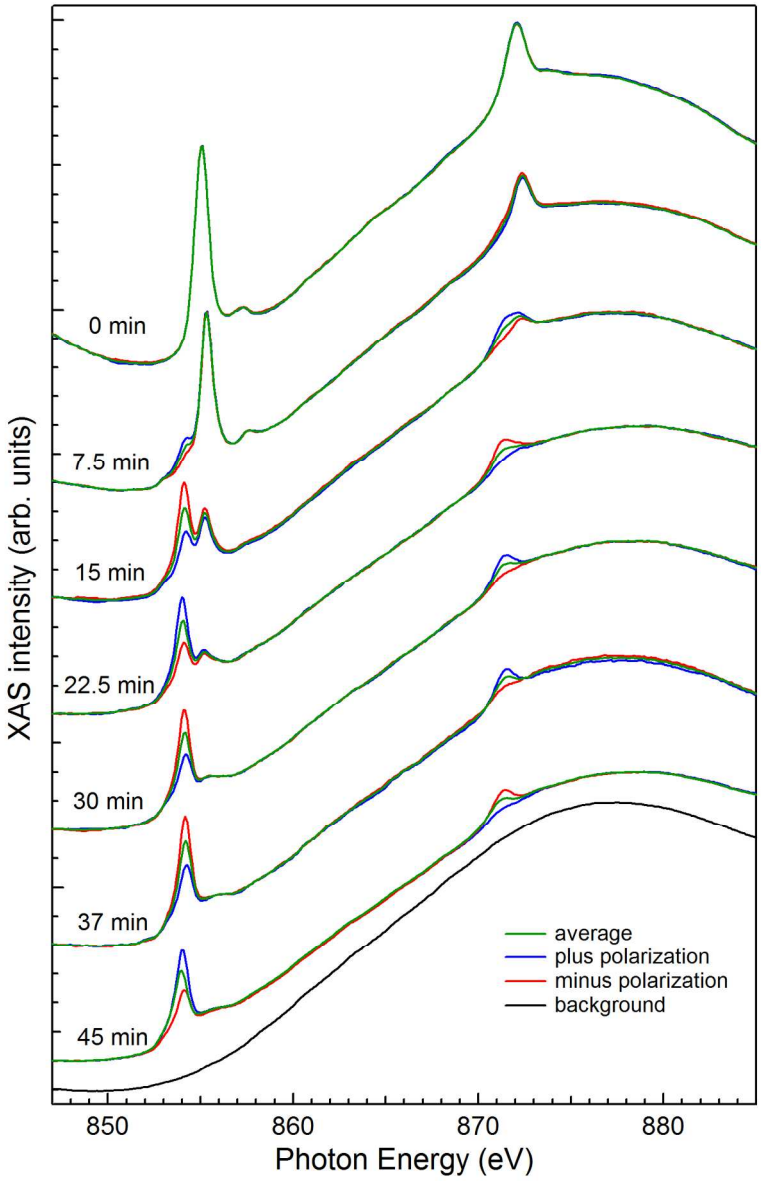

Figure S1. Evolution of NiPc XAS (normal incidence) with subsequent Li atom deposition. Exposure time is indicated for each series of circular polarized spectra.

Details of the multiplet calculations

The final state crystal field parameters were scaled according to the ratio of the $\langle r^n \rangle$ expectation values as obtained by Cowan's code, see below.

The first table for each system presents the orbital occupation by calculating the weight of the single electron orbitals in the many-electron wavefunction. (Definition: xxx_d = down spin; xxx_u = up spin; x2y2, xz, z2, yz, xy denote the symmetry of the d-orbital)

The magnetic moments in the second table show their z-projection normal to the surface apart from $\langle LS \rangle = \langle \mathbf{L} \cdot \mathbf{S} \rangle$ which is the isotropic value.

The behavior of the wavefunction under the indicated symmetry operations is presented in the third table. z > -z and y > -y are reflections with respect to the xy-plane and xz-plane, respectively, with the z-axis being the fourfold symmetry axis. C4 corresponds to a 90° rotation around the fourfold axis. After the operation the wavefunction is projected back onto itself and the resulting value is noted in the table. The two values for the C4 rotation give the real and imaginary part of the projection, respectively. Note that only the spatial part of the wavefunction was transformed under the symmetry operations. From these values the (approximate) symmetry of the total wavefunction is derived. Non-integer values come from strong mixing of states with different orbital symmetry by the spin-orbit coupling.

NiPc, d^8

```
Crystal Field Parameters [eV]
initial state     10Dq = 2.5000, Ds = 0.8000, Dt = 0.2000
final state       10Dq = 1.9922, Ds = 0.7114, Dt = 0.1594
Slater-Condon parameters scaled by 0.70

  #    x2y2_d x2y2_u xz_d   xz_u   z2_d   z2_u   yz_d   yz_u   xy_d   xy_u
  1    0.025  0.025  0.994  0.994  0.992  0.992  0.994  0.994  0.995  0.995

  #      <L>     2<S>    <T>     <LS>     E        Etot
  1      0.000   0.000   0.000  -0.295   0.00000  -4.45376

  #   z > -z   y > -y         C4       state  energy
  1    0.996    0.985    0.998 -0.000   A1g   0.000     -4.4538
```

Li+NiPc, d^9

```
Crystal Field Parameters [eV]
initial state     10Dq = 1.0000, Ds = 0.2800, Dt = 0.2000
final state       10Dq = 0.7664, Ds = 0.2447, Dt = 0.1533
Slater-Condon parameters scaled by 0.70

  #    x2y2_d x2y2_u xz_d   xz_u   z2_d   z2_u   yz_d   yz_u   xy_d   xy_u
  1    1.000  0.008  0.998  1.000  1.000  1.000  0.998  1.000  1.000  0.995
  2    0.008  1.000  1.000  0.998  1.000  1.000  1.000  0.998  0.995  1.000

  #      <L>     2<S>    <T>     <LS>     E        Etot
  1      0.275   0.993   0.252  -0.219   0.00000  -0.96834
  2     -0.275  -0.993  -0.252  -0.219   0.00000  -0.96834

  #   z > -z   y > -y         C4       state  energy
  1    0.993    0.987   -0.996 -0.004   B1g   0.000     -0.9683
  2    0.993    0.987   -0.996  0.004   B1g   0.000     -0.9683
```

FePc, d^6

```
Crystal Field Parameters [eV]
initial state     10Dq = 2.3000, Ds = 0.5900, Dt = 0.1440
final state       10Dq = 1.7674, Ds = 0.5151, Dt = 0.1107
Slater-Condon parameters scaled by 0.60

  #    x2y2_d x2y2_u xz_d   xz_u   z2_d   z2_u   yz_d   yz_u   xy_d   xy_u
  1    0.022  0.022  0.974  0.974  0.509  0.509  0.974  0.974  0.522  0.522
  2    0.021  0.023  0.982  0.974  0.996  0.015  0.982  0.974  0.997  0.036
  3    0.023  0.021  0.974  0.982  0.015  0.996  0.974  0.982  0.036  0.997

  #      <L>       2<S>    <T>     <LS>     E        Etot
  1      0.000   0.000   0.000  -0.707   0.00000  -4.26005
  2     -0.082   1.956  -0.021  -0.509   0.00523  -4.25482
  3      0.082  -1.956   0.021  -0.509   0.00523  -4.25482

  #   z > -z   y > -y         C4       state  energy
  1    0.908   -0.953   -0.954  0.000   B2g   0.000     -4.2600
  2    0.947   -0.973   -0.973 -0.022   B2g   0.005     -4.2548
  3    0.947   -0.973   -0.973  0.022   B2g   0.005     -4.2548
```

Li+FePc, d^7

```
Crystal Field Parameters [eV]
initial state     10Dq = 1.0000, Ds = 0.0480, Dt = 0.0380
final state       10Dq = 0.7289, Ds = 0.0408, Dt = 0.0277
Slater-Condon parameters scaled by 0.90

  #    x2y2_d x2y2_u xz_d   xz_u   z2_d   z2_u   yz_d   yz_u   xy_d   xy_u
  1    0.865  0.162  0.942  0.603  0.872  0.215  0.942  0.603  0.951  0.845
  2    0.162  0.865  0.603  0.942  0.215  0.872  0.603  0.942  0.845  0.951
  3    0.519  0.500  0.767  0.745  0.545  0.554  0.767  0.745  0.924  0.934
  4    0.500  0.519  0.745  0.767  0.554  0.545  0.745  0.767  0.934  0.924
  5    0.702  0.316  0.839  0.710  0.745  0.364  0.839  0.710  0.963  0.812
  6    0.316  0.702  0.710  0.839  0.364  0.745  0.710  0.839  0.812  0.963
  7    0.984  0.020  0.993  0.507  0.985  0.141  0.993  0.507  0.994  0.876
  8    0.020  0.984  0.507  0.993  0.141  0.985  0.507  0.993  0.876  0.994

  #      <L>     2<S>    <T>     <LS>     E        Etot
  1      0.811   2.145  -0.027  -1.188   0.00000  -2.79876
  2     -0.810  -2.145   0.027  -1.188   0.00000  -2.79876
  3      0.571   0.045   0.024  -0.605   0.02187  -2.77689
  4     -0.571  -0.045  -0.024  -0.605   0.02187  -2.77689
  5     -0.869   1.177  -0.036  -0.560   0.03307  -2.76569
  6      0.869  -1.177   0.036  -0.560   0.03307  -2.76569
  7     -0.932   2.898  -0.077   0.269   0.06170  -2.73706
  8      0.932  -2.898   0.077   0.269   0.06170  -2.73706

  #   z > -z   y > -y         C4       state  energy
  1   -0.771   -0.113    0.113 -0.574   Eg    0.000     -2.7988
  2   -0.771   -0.113    0.113  0.574   Eg    0.000     -2.7988
  3   -0.921   -0.039    0.031 -0.515   Eg    0.022     -2.7769
  4   -0.921   -0.039    0.031  0.515   Eg    0.022     -2.7769
  5   -0.719   -0.139    0.123  0.825   Eg    0.033     -2.7657
  6   -0.719   -0.139    0.123 -0.825   Eg    0.033     -2.7657
  7   -0.977   -0.009    0.000  0.960   Eg    0.062     -2.7371
  8   -0.977   -0.009    0.000 -0.960   Eg    0.062     -2.7371
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MnPc, d^5

```
Crystal Field Parameters [eV]
initial state     10Dq = 4.0000, Ds = 0.7000, Dt = 0.5200
final state       10Dq = 2.9895, Ds = 0.6040, Dt = 0.3886
Slater-Condon parameters scaled by 0.60

  #    x2y2_d x2y2_u xz_d   xz_u   z2_d   z2_u   yz_d   yz_u   xy_d   xy_u
  1    0.006  0.004  0.995  0.001  0.996  0.994  0.995  0.001  1.000  0.007
  2    0.004  0.006  0.001  0.995  0.994  0.996  0.001  0.995  0.007  1.000
  3    0.005  0.004  0.665  0.334  0.995  0.995  0.665  0.334  0.668  0.334
  4    0.004  0.005  0.334  0.665  0.995  0.995  0.334  0.665  0.334  0.668

  #      <L>      2<S>    <T>    <LS>    E         Etot
  1     -0.046   2.984  -0.065  -0.212   0.00000  -6.11343
  2      0.046  -2.984   0.065  -0.212   0.00000  -6.11343
  3     -0.015   0.996  -0.018  -0.148   0.00112  -6.11231
  4      0.015  -0.996   0.018  -0.148   0.00112  -6.11231

  #    z > -z   y > -y        C4       state  energy
  1    0.984    0.992   -0.992 -0.008   B1g   0.000     -6.1134
  2    0.984    0.992   -0.992  0.008   B1g   0.000     -6.1134
  3    0.995    0.997   -0.997 -0.002   B1g   0.001     -6.1123
  4    0.995    0.997   -0.997  0.002   B1g   0.001     -6.1123
```

Li+MnPc, d^5

```
Crystal Field Parameters [eV]
initial state     10Dq = 1.0000, Ds = -.0200, Dt = 0.0900
final state       10Dq = 0.7474, Ds = -.0173, Dt = 0.0673
Slater-Condon parameters scaled by 0.85

  #    x2y2_d x2y2_u xz_d   xz_u   z2_d   z2_u   yz_d   yz_u   xy_d   xy_u
  1    0.600  0.400  0.600  0.400  0.600  0.400  0.600  0.400  0.600  0.400
  2    0.400  0.600  0.400  0.600  0.400  0.600  0.400  0.600  0.400  0.600
  3    0.800  0.200  0.800  0.200  0.800  0.200  0.800  0.200  0.800  0.200
  4    0.200  0.800  0.200  0.800  0.200  0.800  0.200  0.800  0.200  0.800
  5    1.000  0.000  1.000  0.000  1.000  0.000  1.000  0.000  1.000  0.000
  6    0.000  1.000  0.000  1.000  0.000  1.000  0.000  1.000  0.000  1.000

  #      <L>     2<S>    <T>     <LS>     E        Etot
  1      0.000   1.000   0.000  -0.109   0.00000  -5.64455
  2      0.000  -1.000   0.000  -0.109   0.00000  -5.64455
  3      0.000   2.999   0.000  -0.107   0.00002  -5.64453
  4      0.000  -2.999   0.000  -0.107   0.00002  -5.64453
  5      0.001   4.999  -0.001  -0.105   0.00007  -5.64448
  6     -0.001  -4.999   0.001  -0.105   0.00007  -5.64448

  #   z > -z   y > -y         C4       state  energy
  1    1.000    0.999    1.000  0.000   A1g   0.000     -5.6446
  2    1.000    0.999    1.000  0.000   A1g   0.000     -5.6446
  3    0.999    0.999    1.000  0.000   A1g   0.000     -5.6445
  4    0.999    0.999    1.000  0.000   A1g   0.000     -5.6445
  5    0.999    0.999    0.999  0.001   A1g   0.000     -5.6445
  6    0.999    0.999    0.999 -0.001   A1g   0.000     -5.6445
```