Magnetic interaction at the metalorganic molecule–substrate interface: Insights from first-principles calculations

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Thanks and collaboration

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Christian Wäckerlin
Nirmalya Ballav
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SLS - Villigen (CH)
Armin Kleibert
Frithjof Nolting

SN Bose - Calcutta (India)
Tanusri Saha-Dasgupta

Uni Duisburg (DE)
Heiko Wende

FU - Berlin (DE)
Felix Hermanns
Matthias Bernien
Wolfgang Kuch

TU - Kaiserslautern (DE)
Steffan Lach
Martin Aeschlimann
Christiane Ziegler
Aim: control of spin for switchable molecular devices

Outline

- On-surface magnetochemistry
  
  *Chemical off and on spin-switching of spin-bearing porphyrins*

- Exchange coupling of porphyrins on graphene

- Tuning of spin-polarized interface state for spin pol. e-injection

**Metalloporphyrins & Metallophthalocyanines**
Computational DFT methodology

- **VASP**, full potential code, with GGA (PBE) and GGA+$U$
  400-600 plane wave cut-off; *full* structural optimization of molecule;
  initially simplification of end groups, $U\sim2$-8 eV, $J=1$ eV

Molecules on surfaces: up to 3 atomic surface layers, $2\times2\times2$ k-points,
with/out full geometrical relaxation, $\sim200$ atoms for porphyrins, over
250 for Pc. With or without *Van der Waals interaction* (Grimme D2).

- Gaussian03/09, with hybrid-density functionals
  B3LYP: hybrid of 20% HF exchange & Becke-Lee-Yang-Parr exc-
corr. functional; full optimization of the molecular structure, 6-
311G(d,p) up to about 160 atoms for gas-phase molecules
Benchmarking molecular spin states

Many metalloporphyrins have experimentally a *high-spin state* (Hund’s rule)

BUT common DFT functionals (LSDA, GGA) predict *low or interm. S.*

Example: Cl-ligated FeP (FePCl)

<table>
<thead>
<tr>
<th>Method</th>
<th>GGA+U (4 eV)</th>
<th>GGA+U (6 eV)</th>
<th>B3LYP *</th>
<th>UB3LYP</th>
<th>CASTP2 *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spin S</td>
<td>3/2</td>
<td>5/2</td>
<td>3/2</td>
<td>5/2</td>
<td>5/2</td>
</tr>
</tbody>
</table>

GGA: $S=3/2$


Transition to high spin state for $U \approx 5$ eV

Discovery of induced magnetic order in porphyrins


**Induced** ferromagnetic order in (paramagnetic) MnTPPCl on Co at room temperature!
Ferromagnetic coupling of Fe porphyrins to Ni/Co surface

Induced magnetic order & ferromagnetic coupling (Fe-OEP)

*Indirect* exchange-coupling of Fe & Co mediated through N atoms stabilizes FM ordering on Fe

Wende et al., Nature Mater. 6, 516 (2007)
Chemically assisted spin-switching

In nature:
O₂ bonding to heme:
\[ S = 2 \Rightarrow S = 0 \]

Reversible *double* spin-crossover reaction


In synthetic molecular layers:


Showed reversible switching
Are on-surface magnetochemical effects the same as those known from gas-phase coordination chemistry?
Studied systems - on-surface magnetochemistry

Exp. & computational investigation of several systems

Coordination chem. in gas phase:  On-surface coord. chemistry:

\[
\begin{align*}
\text{CoP S}=1/2 & & \text{NO (-1/2)} & & \text{S}=0 & & \text{CoTPP/Ni} & \Rightarrow & \text{same} \\
\text{FeP S}=1 & & \text{S}=1/2 & & \text{FeTPPP/Ni} & \Rightarrow & \text{different} \\
\text{MnP S}=5/2 & & \text{NH}_3 (S=0) & & \text{S}=0 & & \text{MnTPP/Co} & \Rightarrow & \text{different} \\
\text{MnPc S}=3/2 & & \text{S}=3/2 & & \text{MnPc/Co} & \Rightarrow & \text{different}
\end{align*}
\]

Novel on-surface magnetochemical effects *beyond* gas-phase coordination chemistry

(due to the weak interaction with surface, => *surface spin-trans effect*)
XMCD observations

Spin on => off  Spin high => low  Spin FM => AFM  IM spin => high

What is the microscopic explanation?

CoP ± NO on Ni – What happens?

S~1/2

CoP/Ni (0.71 μB)  

S~0

NO-CoP/Ni (0.04 μB)  

CoP (d^7)

DFT+U calculations:

CoP S~1/2 on surface and FM coupled to Ni surface due to hybridization of d_{z^2};
d_{z^2} becomes quenched through binding with NO
Unusual case MnP/Co+NO – Reverses mag. coupling

Interplay of several processes leads to AFM coupling: charge transfer, CEF effect with NO binding, switching to low spin.
FeP on Ni initially is high spin $S \approx 2$, with NO the Fe spin state is first reduced to $S=1$ (large $\Delta z \approx 0.58\text{Å}$).
MnPc/Co + NH$_3$: change in spin & exch. strength

Innocent ligand NH$_3$ (S=0) induces on-surface spin-switch of MnPc to higher spin (S≥2); changes $\Delta z \approx 0.4\text{Å}$ and exchange coupling.
Chemical “off-to-on-switching” of spin?

Ni(II)P on Co with NH₃ (S=0)

\[ d_{x^2-y^2}, \quad d_{z^2} \]

\[ d_{x^2-y^2}, \quad d_{z^2} \]

With spin-trans effect

S=0 \quad \xrightarrow{\text{off-to-on-switching}} \quad S=1
Experimental verification - reversible switching

Thermal de-sorption

NiTPP

Intensity / arbitrary units

Photon energy / eV

Co L₃ & L₂

Experimental verification - reversible switching

circ+ XAS  circ- XAS  circ+ XAS  circ- XAS

"off"  "on"  "off"  "on"

5  10  15

NMCD background

XAS background

5  10  15

850  860  870

850  860  870

850  860  870

850  860  870

850  860  870

Ni L₃ & L₂

Backgrounds:

95

5  10  15

850  860  870

850  860  870

850  860  870

850  860  870

850  860  870

5  10  15

850  860  870
Selective spin-switching in a supramolecular layer

NH$_3$ binds to MnPc, switches its spin

FeF$_{16}$Pc  MnPc

c(2x2) O-reconstructed Co(001) - AFM coupling to Co
Spin-switching in a supramolecular layer

FeF$_{16}$Pc  MnPc

Full NH$_3$ coverage
Important issue for spin-pol. electron injection

Overcoming conductance mismatch at FM/OSC interfaces

No conductance mismatch for interface state
Consider a typical case: CuPc on Co(001)

Free CuPc molecule: $S=1/2$

CuPc chemis. on Co: $S \sim 0$

Bridge position

GGA+U ($U=4$ eV, $J=1$ eV)

Charge density

$\Rightarrow$ Small charge transfer to Cu $\sim d^{10}$
DFT+U predicts spin-polarized interface state below $E_F$ for CuPc chemisorbed on Co.
SP-PES show a spin-polarized interface state just below $E_F$ (only for submono-layer)

*Not seen* for FePc, CoPc

To conclude ...

- Novel on-surface magnetochemical effects, distinct from gas phase
- Spin-switching chem. CuPc on Co (and physisorbed MnP-Co) predicted
- First observation of spin-polarized *interface state* in CuPc on Co
- Sensitive dependence of interface state on 3d-metal species
- AFM super-exchange type coupling through graphene