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Noncovalent dyads of lanthanide nitride cluster fullerenes $Ln_3N@C_{80}$ and bisphthalocyanines $LnPc_2$: A DFT Study

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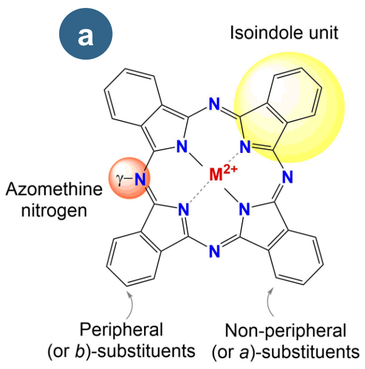
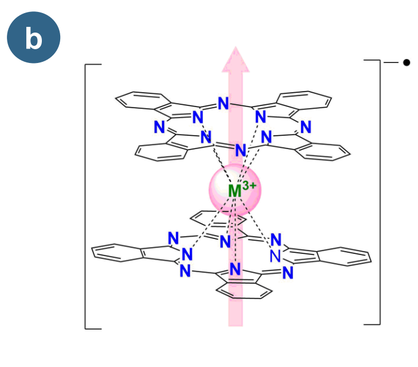
Background

Phthalocyanines (Pcs)



MPc (M = 3*d* metal transition)



MPc_2 (M = rare earth elements, including Y and lanthanides); Ln = lanthanides.

Single molecule magnets (SMMs)
Application: Spintronic devices

Fig.1. Structure of (**a**) monophthalocyanines and (**b**) bisphthalocyanine. [1]

Carbon nanomaterials + MPc_2

Noncovalent interactions between $LnPc_2$ and carbon nanotubes as well as graphene (with defects), have been investigated using density functional theory (DFT). The most relevant conclusion from the published studies is that the interaction of $GdPc_2$ with zigzag CNTs [2] and graphene with 5665 defects [3] leads **to changes in spin orientation compared to the isolated components.**

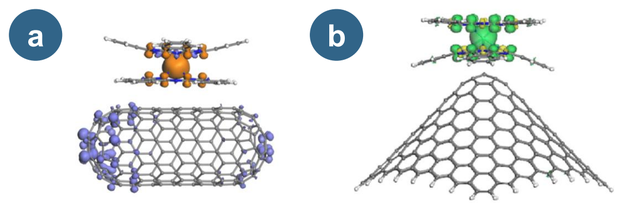
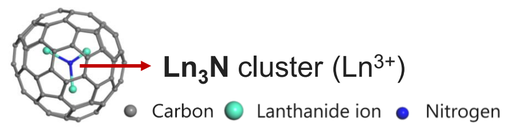


Fig.2. Spin density plots for (**a**) $GdPc_2$+SWCNTs and **(b)** $GdPc_2$+G-5665 (Isosurfaces at 0.01 a.u.). [2,3]

a) Violet and orange lobes represent spin-up and spin-down electrons.
b) Green and yellow lobes represent spin-up and spin-down electrons

Nitride cluster fullerene ($Ln_3N@C_{80}$; NCFs)

What changes occurs in HOMO, LUMO, and spin density distribution of $LnPc_2$ (Ln = La, Ce, Gd, Lu) upon interaction with $Ln_3N@C_{80}$, compared to the isolated $LnPc_2$ systems?



Aim

- To analyze the geometric and electronic property changes of $LnPc_2$ upon noncovalent interaction with $Ln_3N@C_{80}$ using DFT.

Computational method

accelrys MATERIALS STUDIO Module DMol3

DFT

Functional: general gradient approximation (**GGA**) functional by Perdew-Burke-Ernzerhof (**PBE**) in combination with a long-range dispersion correction by Grimme (**PBE- D)**.

Different basis sets (DN, DND, DNP) were tested; structures were selected based on agreement with XRD data. DN was used to simulate the dyads.

Results and discussion

1 Optimization of isolated bisphthalocyanines and nitride cluster fullerenes

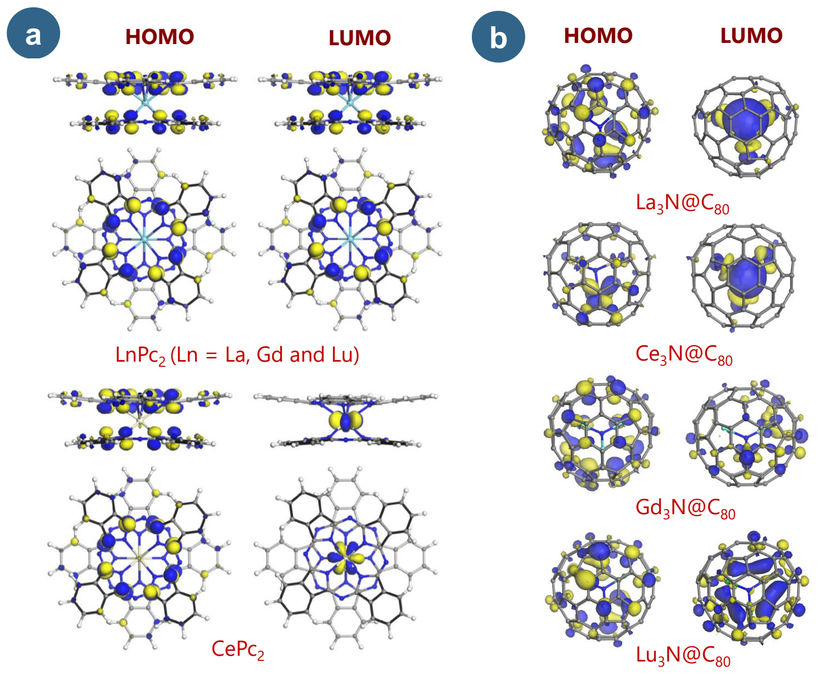


Fig. 3. Frontier orbital distribution (HOMO and LUMO; isosurfaces at 0.03 a.u.) for isolated (a) bisphthalocyanine and (b) $Ln_3N@C_{80}$.

Table 1. HOMO-LUMO gap energies (in eV) for isolated components $Ln_3N@C_{80}$ and $LnPc_2$.

System	E_{gap} (eV)
$La_3N@C_{80}$	1.371
$Ce_3N@C_{80}$	0.862
$Gd_3N@C_{80}$	1.457
$Lu_3N@C_{80}$	1.528
$LaPc_2$	0.131
$CePc_2$	0.196
$GdPc_2$	0.130
$LuPc_2$	0.137

2 $LnPc_2$ + $La_3N@C_{80}$ dyads

Structural characteristics

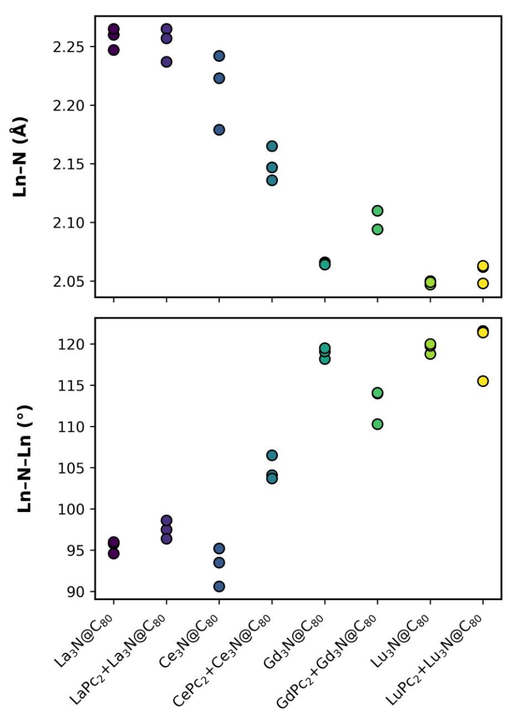


Fig. 4. Comparison of the Ln-N bond lengths (Å; top) and Ln-N-Ln angles (°; bottom) in the isolated lanthanide nitride cluster $Ln_3N@C_{80}$ (Ln = La, Ce, Gd, and Lu) and in the noncovalent $LnPc_2$ + $Ln_3N@C_{80}$ dyads.

The changes in spin density distribution are evident in the dyads containing Ce and Gd atoms, contrary to their La and Lu-derived counterparts.The interaction of $Ce_3N@C_{80}$ and $Gd_3N@C_{80}$ with $CePc_2$ and $GdPc_2$, respectively, causes redistribution of the spin density, with changes in the orientation of spin-up and spin-down electrons in the encapsulated Ce_3N and Gd_3N clusters.

Electronic properties

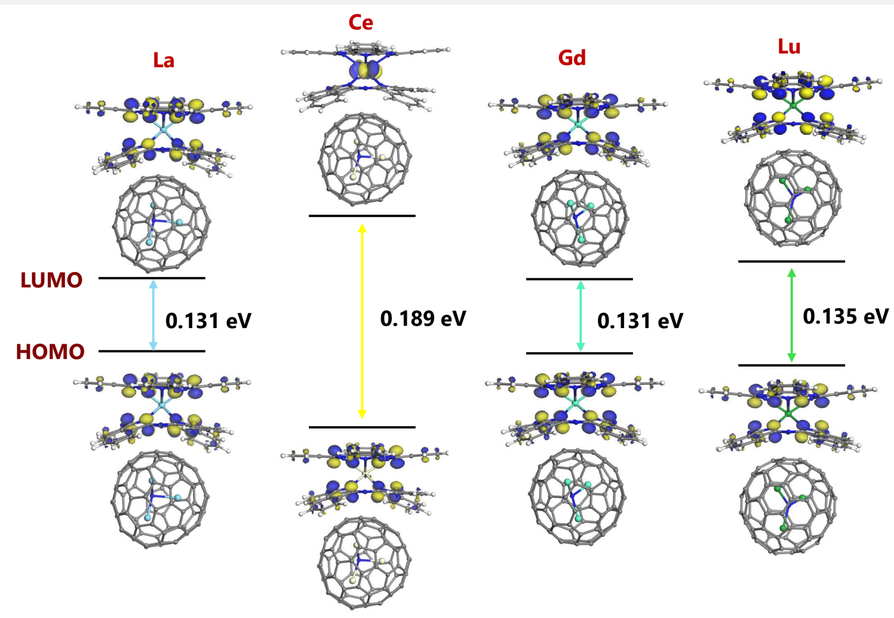


Fig. 5 HOMO and LUMO (isosurfaces at 0.03 a.u.) and gap energies for noncovalent $LnPc_2$ + $Ln_3N@C_{80}$ dyads.

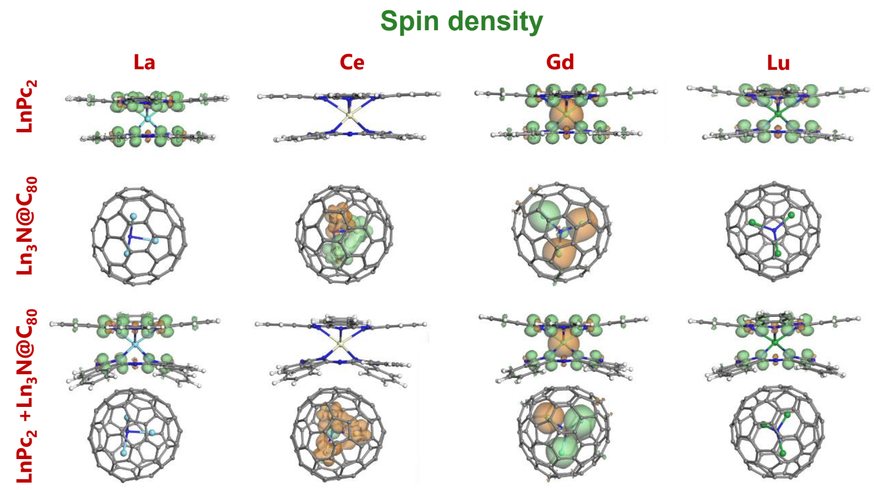


Fig. 6. Comparison of spin density patterns (isosurfaces at 0.01 a. u.) for isolated $LnPc_2$ and $Ln_3N@C_{80}$ molecules with those for their noncovalent dyads $LnPc_2$ + $Ln_3N@C_{80}$. The green and orange lobes correspond to spin-up and spin-down electrons, respectively.

Conclusions

- Using a smaller basis set (DN) proved effective for lanthanide species, with no convergence issue
- Noncovalent $LnPc_2$ + $Ln_3N@C_{80}$ interactions induce structural changes in the encapsulated Ln_3N cluster, favoring planar or pyramidal geometries.
- Energy gap values are closer to those of isolated bisphthalocyanines, indicating that the $LnPc_2$ component governs the reactivity of the dyad.

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