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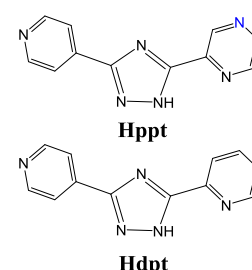
Adsorption of CO₂ into a Soft Porous Coordination Polymer: A Hybrid SCS-MP2:PBE-D3 Study

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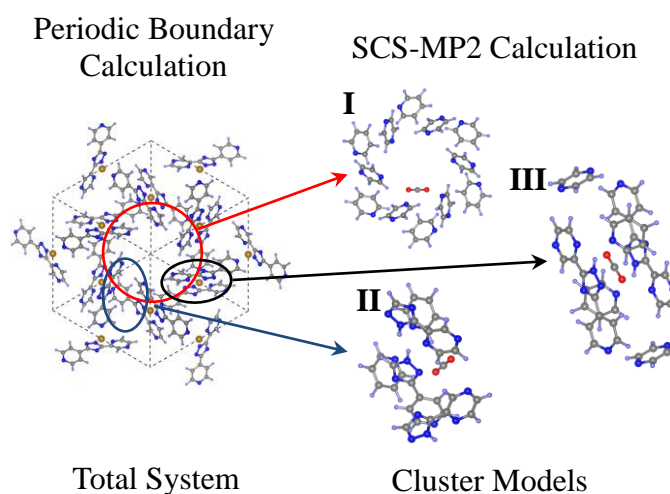
[Introduction] Soft porous coordination polymers (PCPs) have attracted continuous attention in recent years, because of their unique properties such as the gate-opening-type adsorption of gas species. However, little knowledge has been presented on the gate-opening mechanism. Very recently, a soft iron(II)-based PCP, [Fe(ppt)₂], (PCP-N) (Hppt = 3-(2-pyrazinyl)-5-(4-pyridyl)-1,2,4-triazole, Scheme 1), was synthesized and demonstrated to undergo gate-opening adsorption of N₂, C₂H₂ and CO₂, whereas its isostructural framework [Fe(dpt)₂], (PCP-C) (Hdpt = 3-(2-pyridyl)-5-(4-pyridyl)-1,2,4-triazole, Scheme 1) was found to undergo gas-adsorption without gate-opening.^[1] Theoretical studies on gas adsorption into these PCPs are of great importance to understand their different adsorption behaviour. However, it is challenging to estimate accurately the interaction energy between gas molecule and PCPs, because the post-HF calculation must be employed to incorporate dispersion interaction.

In this work, we theoretically investigated CO₂ adsorption into these two isostructural PCPs using a hybrid method combining DFT (PBE-D3) for periodic structure and SCS-MP2 for finite cluster model, to disclose the gate-opening mechanism and reasons for the difference in gate-opening behavior.

[Computational Methods] Geometrical optimization was carried out using PBE+D3 functional with periodic boundary condition as implemented in the VASP program. CO₂ binding energy was calculated with Eq (1).



Scheme 1. Structures of Hppt and Hdpt



Scheme 2. Computational Procedure

$$\begin{aligned} \text{BE}^{\text{SCS-MP2:PBE-D3}} = & \text{BE}^{\text{PBE-D3}} + \text{INT}^{\text{SCS-MP2}}(\text{H-G}) - \text{INT}^{\text{PBE-D3}}(\text{H-G}) \\ & + \text{INT}^{\text{SCS-MP2}}(\text{G-G}) - \text{INT}^{\text{PBE-D3}}(\text{G-G}) \end{aligned} \quad (1)$$

where $\text{BE}^{\text{PBE-D3}}$ is the binding energy calculated with the crystal structure, $\text{INT}^{\text{SCS-MP2}}(\text{H-G})$ and $\text{INT}^{\text{PBE-D3}}(\text{H-G})$ are interaction energies between CO_2 and cluster models (Scheme 2) calculated by SCS-MP2 and PBE-D3 methods, respectively, and $\text{INT}^{\text{SCS-MP2}}(\text{G-G})$ and $\text{INT}^{\text{PBE-D3}}(\text{G-G})$ are CO_2 - CO_2 interaction energies in CO_2 clusters.

[Results and Discussion] The calculated CO_2 binding energies for sites I, II, and III (Scheme 2) in PCP-N and PCP-C both decrease in the order $\text{I} > \text{III} > \text{II}$. These results indicate that CO_2 adsorption into PCP-N and PCP-C occurs first at the site I. The favorable adsorption at the site I arises from the smaller crystal deformation energy (ΔE_{def}) than those

for adsorption at the sites II and III (Table 1). PBE-D3 overestimates the CO_2 binding energy for the site I in PCP-N but the SCS-MP2:PBE-D3-calculated value agrees well with the experimental result ($-5.71 \text{ kcal mol}^{-1}$) at the initial adsorption stage. These

Table 1. Binding energies (in kcal mol^{-1}) of one CO_2 molecule with PCP-N at three sites.

PCP-N	I	II	III
$\text{BE}^{\text{PBE-D3}}$	-7.37	-2.94	-4.03
$\text{INT}^{\text{PBE-D3}}$	-7.72	-7.77	-8.58
ΔE_{def}	0.35	4.82	4.55
$\text{INT}^{\text{PBE-D3}}(\text{H-G})$	-7.34	-6.80	-6.95
$\text{INT}^{\text{SCS-MP2}}(\text{H-G})$	-5.37	-5.07	-6.08
$\text{BE}^{\text{SCS-MP2:PBE-D3}}$	-5.41	-1.21	-3.16
Exp.		-5.71^a	
PCP-C($\text{BE}^{\text{SCS-MP2:PBE-D3}}$)	-4.55	-2.00	-2.11

^a CO_2 adsorption energy at the initial stage.

results suggest that SCS-MP2 correction is of considerable importance to investigate correctly the adsorption behaviour of these PCPs. When the site I is fully occupied, subsequent CO_2 adsorption occurs at the sites II and III in different manner between PCP-N and PCP-C. The calculated binding energies (Table 2) indicate that CO_2 adsorption occurs at the sites II and III in PCP-N but does not in PCP-C after the full occupation of the site I. This difference arises from the smaller deformation energy of PCP-N than that of PCP-C. The binding energy for the site III in PCP-N increases with CO_2 loading, which corresponds to the gate-opening process. Details of the gate-opening mechanism will be discussed in the presentation.

Table 2. CO_2 binding energies with PCP-N and PCP-C at the sites II and III after the site I is fully occupied.

	PCP-N		PCP-C	
	II	III	II	III
$\text{BE}^{\text{PBE-D3}}$	-6.90	-6.29	-2.55	-1.42
ΔE_{def}	2.11	2.95	6.23	7.84
$\text{BE}^{\text{SCS-MP2:PBE-D3}}$	-4.77	-5.25	-0.27	-0.15

[1] Y. Ma, R. Matsuda, H. Sato, Y. Hijikata, L. Li, S. Kusaka, M. Foo, F. Xue, G. Akiyama, R. Yuan, S. Kitagawa, *J. Am. Chem. Soc.* **2015**, *137*, 15825-15832.