



# Dissociation and reconstruction of double-decker bis(phthalocyaninato) terbium(III) complex (TbPc<sub>2</sub>) on Pd(001): A theoretical investigation



Heng Liu, Yujie Hu, Hao Wang, Bo Jiang, Xuechun Xu, Yingxiang Cai\*

Department of Physics, NanChang University, Jiangxi, Nanchang 330031, PR China

## ARTICLE INFO

### Article history:

Received 6 June 2016

Received in revised form

6 September 2016

Accepted 7 September 2016

Available online 13 September 2016

### Keywords:

Density functional theory

Molecule dissociation

Charge transfer

Surface reconstruction

## ABSTRACT

The study of molecule dissociation is helpful to disclose the nature of chemical bonds and to extend molecular functions. The double-decker bis(phthalocyaninato) terbium(III) complex (TbPc<sub>2</sub>) is a promising single-molecule magnet (SMM) which exhibits potential applications in spin-devices. In this study, we investigate the dissociation and reconstruction of TbPc<sub>2</sub> on Pd(001) surface. The results show that a single TbPc<sub>2</sub> adsorbed on Pd(001) tends to split into Pc/Pd(001)+TbPc. However, the TbPc/Pd(001)+Pc might also be observed in an experimental study due to only a slight difference in their dissociation energy. The TbPc<sub>2</sub> molecules on Pd(001) will form a (5 × 3) reconstruction which is different from the (3 × 4) reconstruction of PbPc on Pd(001). If the TbPc<sub>2</sub> molecules with (5 × 3) reconstruction is dissociated, this reconstruction will be inherited by its daughter molecules due to strong molecule–substrate interaction. In addition, nudged elastic band (NEB) calculation shows that Tb-down is the stable state of TbPc/Pd(001) and Tb-up is a metastable state. The transition between two states might be utilized to realize TbPc's switch or storage functions.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

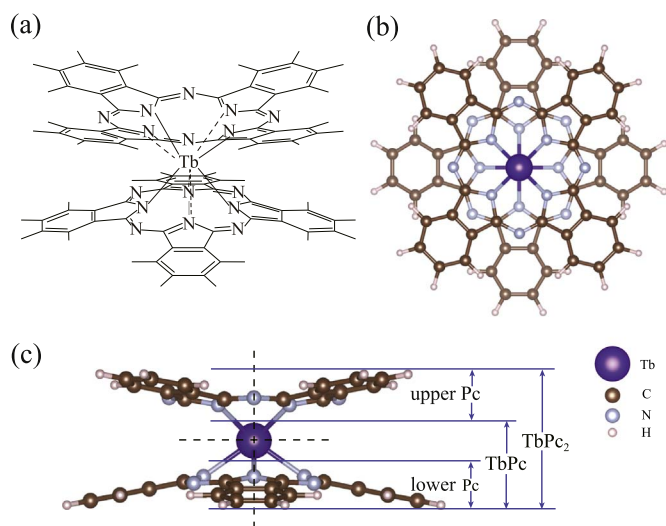
Molecule dissociation is a general process in which molecules or complexes split into simpler constituents or atoms under external stimuli. After dissociation, many properties, such as magnetism [1,2] and electron transport [3], might be changed. Molecule dissociation can be viewed as the reversible process of molecule formation [4]. Many experimental techniques, such as thermal decomposition [3,5], laser flash photolysis [6–8] and tunneling electron excitation [1,9,10] have been used to dissociate molecules. With respect to the thermal decomposition, Katoh et al. have discovered the coexistence of LnPc (Ln = Tb<sup>3+</sup>, Dy<sup>3+</sup> and Y<sup>3+</sup>) and LnPc<sub>2</sub> by evaporating LnPc<sub>2</sub> at 600 K [3]. Zhang et al. have investigated the surface adsorption of single-decker dysprosium phthalocyanine (DyPc) obtained by thermal decomposition of DyPc<sub>2</sub> [5]. As for photoinduced dissociation, Wanat et al. have achieved the dissociation of diatomic NO photolabilisation from nitrosyl complexes [6]. Saracini et al. have realized a direct O<sub>2</sub> photorelease from Cu(II)-superoxide compounds [7]. Doane et al. have cleaved the Si–C bond in axial Si–Phthalocyanines by means of light-triggered photolysis [8]. Using tunneling electron injection technique, the dissociation has been achieved for both diatomic and polyatomic molecules, such as O<sub>2</sub> [9,11], H<sub>2</sub>S [12], B<sub>10</sub>H<sub>14</sub> [13],

iodobenzene (C<sub>6</sub>H<sub>5</sub>I) [10,14] and porphyrin molecule [15]. Selective bond breaking has also been performed on metalloporphyrins and phthalocyanines [1,16–19]. Kim et al. have realized selective dissociation of diatomic NO from NO–Co–porphyrin complexes and disclosed its dissociation mechanisms [16]. Zhao et al. have realized the dehydrogenations of single CoPc on Au(111) [1]. Stróżecka has demonstrated the change of the spin state in MnPc by selective dissociation of diatomic Co from the Co–MnPc complex [19]. All these studies have shown that chemical bonds can be broken using scanning tunneling microscopy (STM) technique. Among the three methods mentioned above, using STM technique can effectively control molecule dissociation at the single molecule level and disclose its dissociation mechanism which might be hidden in the photo- or thermal-induced dissociation.

The double-decker bis(phthalocyaninato) terbium(III) complex (TbPc<sub>2</sub>, see Fig. 1) has attracted great interest because of its single-molecule magnets behavior [2,20–23]. And its spin functionality is retained in a single molecule, which makes it to be a promising candidate that is applied in spintronics and quantum computing [2,24–26]. Single double-decker TbPc<sub>2</sub> molecule has a sandwich-type geometry with a 45° angle between the upper and lower Pc molecule as shown in Fig. 1(a) and (b). Each daughter parts of TbPc<sub>2</sub> are labeled in Fig. 1(c). Although the thermal dissociation of TbPc<sub>2</sub> has been made by Katoh [3], the effective utilization of TbPc<sub>2</sub> or its daughter parts is difficult to achieve since this dissociation is uncontrolled. Both TbPc<sub>2</sub> and TbPc have been observed

\* Corresponding author.

E-mail address: [yingxiangcai@ncu.edu.cn](mailto:yingxiangcai@ncu.edu.cn) (Y. Cai).



**Fig. 1.** (a) Chemical structure of a single TbPc<sub>2</sub>. (b) Top view of TbPc<sub>2</sub>. The upper and lower Pc is emphasized by deep and semitransparent colors, respectively. The included angle between lower and upper Pc ligand is 45°. (c) The daughter parts of TbPc<sub>2</sub>. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

in experimental study. Large-scale highly ordered structures have not been formed on Au(111) due to the coexistence of TbPc<sub>2</sub> and TbPc. If the TbPc<sub>2</sub> is dissociated after adsorbing on solid surface, its dissociation can be more effectively controlled. In particular, if once ordered TbPc<sub>2</sub> formed on surface, its function can be well utilized. Therefore, more attention should be paid on the single molecule dissociation and surface reconstruction of TbPc<sub>2</sub>.

In this theoretical study, we firstly determine the adsorption geometry of TbPc<sub>2</sub> on Pd(001) and analyze its possible dissociation results. Secondly, the charge density difference (CDD) and charge transfer are evaluated in order to show how the TbPc<sub>2</sub> is dissociated. Thirdly, the surface reconstruction of TbPc<sub>2</sub> on Pd(001) is determined according to the adsorption energy per unit area. And the ordered structure after TbPc<sub>2</sub> dissociation is analyzed. Finally, we identify which one of Tb-up and Tb-down is the stable state of TbPc/Pd(001). The energy barrier from metastable state to stable state or the reversible transition is determined.

## 2. Theoretical methods

Our first-principles density functional theory (DFT) calculations are performed using the plane-wave-based VASP code [27–30]. The projector-augmented-wave (PAW) potentials are employed to describe the electron-ion interaction and the Perdew–Burke–Ernzerhof generalized gradient approximation (PBE-GGA) is adopted for exchange-correlation functional [31–33]. Throughout this study, a 400 eV kinetic energy cutoff for PBE-GGA is used to expand the wave functions into the plane-wave basis. Monkhorst–Pack scheme [34] is used for Brillouin-zone integration. In view of the large unit cell, the *k*-point mesh is 1 × 1 × 1 for a single TbPc<sub>2</sub> molecule adsorption and 2 × 2 × 1 for surface reconstructions. Our slab models consist of four Pd-layers and a vacuum region with the thickness of about 10 Å. In order to avoid the interaction between TbPc<sub>2</sub> molecules in neighboring unit cells, a (9 × 9) supercell is selected to simulate a single TbPc<sub>2</sub> adsorption, which ensures the shortest distance between two neighboring TbPc<sub>2</sub> not less than 10 Å. During structural relaxation, the topmost three Pd atomic layers are allowed to relax, nevertheless the bottom layer is fixed to the positions of bulk Pd. The convergence criterion is reached while the maximum Hellmann–Feynman force acting on each atom is less than 0.001 eV/Å. The adsorption energy

( $E_a$ ) of TbPc<sub>2</sub> on metal(001) is given by  $E_a = E_M + E_{TbPc_2} - E_{TbPc_2/M}$ , where  $E_{TbPc_2/M}$  is the total energy of the TbPc<sub>2</sub>/metal(001) system at the equilibrium geometry.  $E_M$  and  $E_{TbPc_2}$  are the total energies of the clean metal substrate and of free TbPc<sub>2</sub> molecule, respectively. The adsorption energy per unit area ( $E_A$ ) is equal to  $E_a/A$ , where the  $A$  is the area of adsorption surface. While the van der Waals (vdW) interaction is taken into account, the BJ-damping DFT-D3 method [35,36] is used to evaluate the dispersion correction. Then, the total energy is given by  $E_{DFT-D3} = E_{DFT} + E_{disp}$ , where the  $E_{disp}$  is dispersion correction, the  $E_{DFT}$  is regular DFT energy and the  $E_{DFT-D3}$  is total energy with dispersion correction. The charge density difference (CDD) is evaluated by  $\Delta\rho = \rho_{TbPc_2/M} - \rho_M - \rho_{TbPc_2}$ , where  $\rho_{TbPc_2/M}$  is the total charge density of the metal(001) and TbPc<sub>2</sub> system, and  $\rho_M$  and  $\rho_{TbPc_2}$  are the unperturbed charge densities of the substrate and adsorbate fragments, respectively.

## 3. Results and discussion

Single double-decker TbPc<sub>2</sub> absorbed on Pd(001) surface keeps its original sandwich-type geometry and the center of TbPc<sub>2</sub> is located on the hollow site of Pd(001). The angle between the upper and lower Pc molecules is 45° just like a free TbPc<sub>2</sub>. The molecular orientation of the lower Pc is the same as that of PbPc on Pd(001). Both substrate and TbPc<sub>2</sub> are four-fold rotation symmetry and their point group is  $D_{4h}$ . The adsorption energy ( $E_a$ ) is up to 5.549 eV which shows that the TbPc<sub>2</sub> is chemically adsorbed on the Pd(001) surface. The strong chemical adsorption makes it possible to remove the upper part of TbPc<sub>2</sub> by means of external stimuli while the lower part of TbPc<sub>2</sub> still remains on the surface. The difficulty level of dissociation depends on the bond strength [10]. Among the four chemical bonds of C–C, C–N, C–H and N–Tb, the binding strength is the weakest for the longest N–Tb bond (2.452 Å). After adsorption, the molecule–substrate interaction will further weaken intramolecular bonds. [37] Therefore, TbPc<sub>2</sub> might split into TbPc and Pc if tunnelling current is applied on N–Tb bonds as shown in Fig. 2 (a). As for the dissociation of TbPc<sub>2</sub> on Pd(001), we should take into account whether the Tb atom remains on the surface or not. Two possible dissociation results are TbPc<sub>2</sub>/Pd(001) → TbPc + Pc/Pd(001) and TbPc<sub>2</sub>/Pd(001) → Pc + TbPc/Pd(001) as shown in Fig. 2(b) and (c). And the dissociation energy is 5.558 and 5.578 eV for the Pc/Pd(001) and TbPc/Pd(001), respectively. Tiny difference in the dissociation energy implies that two dissociation reactions might occur at the same time. In fact, our findings is consistent with the thermal dissociation of TbPc<sub>2</sub> [3]. The Pc is not found in experiments because it is very active. Before reaching Au(111) surface, the Pc has already been captured by the vacuum vessel.

Fig. 3 shows the CDD of Pc/Pd(001) and TbPc/Pd(001). It can be found from Fig. 3(a)–(d) that the charge transfer between the molecules and substrate mainly results from the carbon atoms of benzene groups and the first layer Pd atoms. Except for the marked region by red circle and three other equivalent positions, the CDD is almost the same for TbPc/Pd(001) and Pc/Pd(001). In the marked region, distinct charge transfer occurs around the N atom of Pc/Pd(001), but not charge transfer happens in the same region for TbPc/Pd(001). That explains why the dissociation energy of Pc/Pd(001) is a little lower than that of TbPc/Pd(001). We also evaluate the integrating CDD distribution along surface normal in order to quantitatively estimate the charge transfer. Similar method has been successfully utilized to determine the charge transfer of MPcs on Pt(001) [38] and C<sub>60</sub> on Au(111) or Ag(100) [39]. It should be noted that the quantity of charge transfer depends on the choice of integrated interval. In this study, we choose the inflexion of interface as the starting point of integrated interval as shown in Fig. 3(e). The charge gain is only 0.02e and 0.07e for Pc

Download English Version:

<https://daneshyari.com/en/article/5421283>

Download Persian Version:

<https://daneshyari.com/article/5421283>

[Daneshyari.com](https://daneshyari.com)