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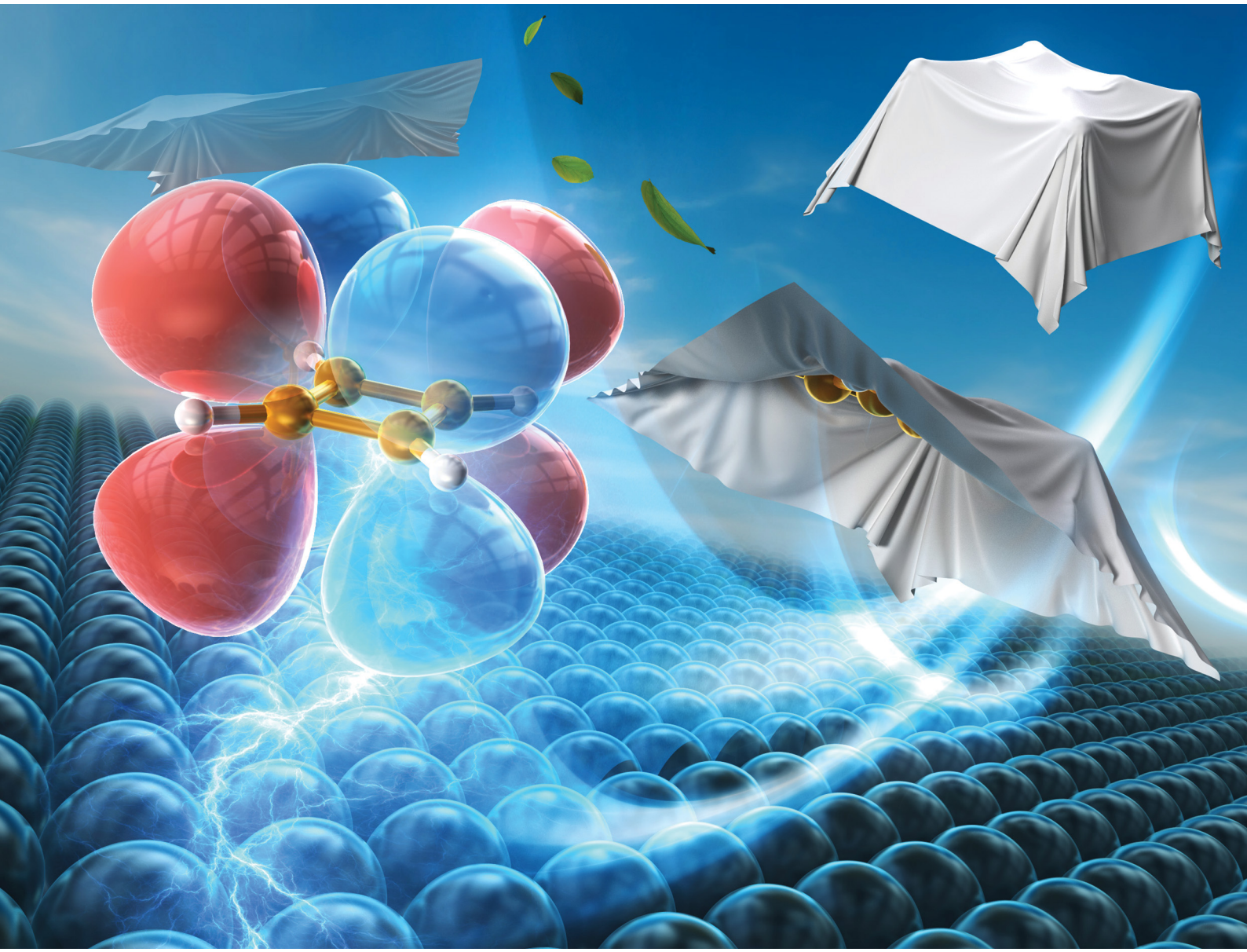

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Unveiled open-shell nature of an antiaromatic molecule by surface–molecule interaction: a concept suggestion by spin-projected density functional theory†

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Research on the physical properties of antiaromatic molecules lags behind that of aromatic molecules, despite their unique electronic structures. We propose to control the electronic states of antiaromatic molecules through surface adsorption. Ferro/antiferromagnetism can be induced by surface adsorption on cyclobutadiene, a nonmagnetic molecule in the gas phase.

The hidden material properties of antiaromatic molecules have attracted considerable attention for a long time. These molecules have not only closed-shell structures but also open-shell singlet and triplet structures in near-energy ranges, and their multiple configurations impart unique properties.[1–8] However, the diradical states (open-singlet/triplet) are excited states, and the molecules are generally unstable. Therefore, research on the physical properties of antiaromatic molecules lags behind that of aromatic molecules, and despite the unique electronic structures revealed by fundamental research,[1–8] their applications in materials and devices remain challenging.

Recently, the synthesis of unstable molecules on surfaces has been reported.[9–17] Although the detailed mechanism of the on-surface synthesis is still unclear, theoretical calculations have shown that interactions with solid surfaces, even at physisorption distances, can change the resonance structure of the diradical molecules and their open-shell nature.[18–20] In addition, interactions with magnetic metals, such as Ni, cause magnetic changes in the metal–molecular interfaces and single-molecule magnetisms.[21,22] Composites with solids are important in the device deployment of molecules; hence, the effect of solid–molecule interactions on electronic states should be investigated. Previous studies[14–20] on diradical molecules have shown that unstable diradical states are stabilised on the surface, and their molecular functions would be effectively utilised by combining them with solids.

Based on these previous studies, we hypothesised that the ground states of antiaromatic molecules can be altered by surface adsorption. Previous studies on diradical molecules[17,18] have focused on the conditions and mechanisms by which isolated ferro/antiferromagnetic molecules are stabilised on the surface, particularly whether the function of the open-shell electrons can be retained. By contrast, this study presents a new concept: the induction of an open-shell nature and its functions in closed-shell molecules by a solid surface.

Here, our proposal is introduced. Fig. 1(a) shows the frontier orbitals (ϕ_1, ϕ_2, ϕ_3, ϕ_4) of cyclobutadiene (CB), a typical antiaromatic molecule. The ground state of CB is a closed singlet with D_{2h} symmetry in the gas phase owing to the distortion by the pseudo Jahn–Teller effect,[23] as illustrated on the left side of Fig. 1(b). Therefore, the D_{4h}-symmetric structure with an open-singlet state (right side of Fig. 1(b)) is at a saddle point for singlet states in the gas phase (upper side of Fig. 1(c)). The energy gap between the open-singlet and triplet states is small, and CB shows exotic magnetic properties based on a diradicaloid.[2–4] To this end, the electronic and geometric structures of CB are affected by the contributions of not only ϕ_2 and ϕ_3 but also ϕ_4.[4,23,24] Hence, decreasing the energy gap between the π and π* orbitals would stabilise the diradical states (Fig. 1(b)). Model calculations of s-electron diradicals have revealed that the covalent interactions between atoms are weakened by orbital correlations with the surface, and the model molecules with closed-singlets in the gas phase become open-singlets on surfaces[19,20] (schematic view: Fig. 1(d)).

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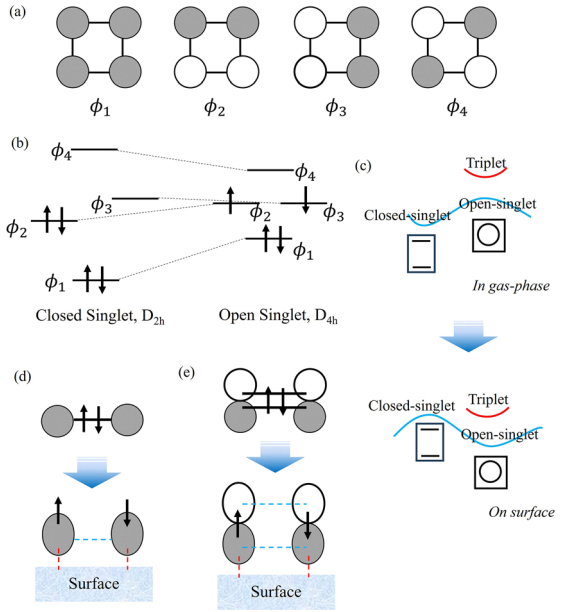

Fig. 1 (a) π orbitals of CB. (b) Schematic comparison of π orbitals of closed- and open-singlet states. (c) Schematic view of the energy potential change by CB–surface interaction. (d) Schematic view of the surface stabilisation mechanism of the open-singlet state of s-electron diradicals. (e) Inspired mechanism of stabilisation of the open singlet state of CB on the Ni surface.

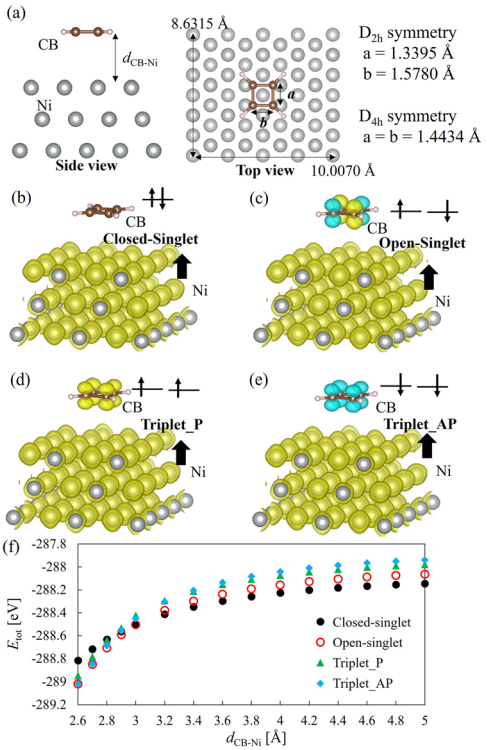

Fig. 2 (a) Calculated models verifying our hypothesis. Spin density distributions of (b) closed-singlet, (c) open-singlet, (d) triplet_P, and (e) triplet_AP states. Yellow and blue represent the distributions of major and minor spins, respectively. The threshold is 0.015 e^- $Bohr^{-3}$. The arrows represent their schematic spin configurations. (f) Total energy (E_{tot}) dependence on the distance between CB and Ni (d_{CB-Ni}).

Hence, a weak orbital correlation between antiaromatic molecules and solid surfaces will weaken the C–C bond and stabilise the open-singlet state (Fig. 1(e)). Then, the energy potential for CB on the surface will differ from that in the gas phase (Fig. 1(c)), and the hidden open-shell nature of CB will be unveiled.

Using Ni(111) as the magnetic surface and CB as the antiaromatic molecule, we investigated this hypothesis by spin-projected density functional theory (DFT).[25–27] The geometry of CB was optimised at each symmetry in the gas phase, and a CB/Ni model with varying CB–Ni distances (d_{CB-Ni}) was calculated. The calculated model is shown in Fig. 2(a). In this study, the four main electronic states of the CB/Ni(111) complex were identified. In the closed-singlet state (Fig. 2(b)), CB has D_{2h} symmetry, and all electrons are paired; in the open-singlet state (Fig. 2(c)), CB has two unpaired electrons coupled in antiparallel; in the triplet_P state (Fig. 2(d)), the two unpaired electrons in CB couple in parallel, with spins parallel to those of Ni metal; and in the triplet_AP (Fig. 2(e)), the unpaired electrons in CB couple in parallel, antiparallel to those of Ni metal. The open-shell states (Fig. 2(c–e)) have D_{4h} symmetry in CB.

To analyse the open-shell nature of the CB/Ni(111) systems, multi-referenced approaches should be adopted; however, these approaches incur high computational costs. Therefore, we have developed a spin-projected DFT/plane-wave method[25–27] with some approximations (see ESI,† Notes). In this method, broken-symmetry (BS) electronic states are optimised *via* self-consistent field calculations, and the contamination of higher-order spin states is corrected using spin-projection. Hence, we refer to the BS singlet energy as that of the open-singlet state. Owing to the self-interaction error in DFT, the spin states could not be distinguished below d_{CB-Ni} = 2.6 Å (see Fig. S1–S4, ESI†); hence, we discuss the results in 2.6 < d_{CB-Ni} < 5.0 Å.

The calculated energies are shown in Fig. 2(f). The closed-singlet state was most stable when the chemical interaction with the surface was negligible (d_{CB-Ni} = 5.0 Å). At this distance, the triplet_P state is more stable than the triplet_AP state owing to the magnetic dipole–dipole interaction between CB and Ni (111). For all electronic states, the total energy decreased with decreasing d_{CB-Ni}, implying stabilisation between the CB and Ni(111). However, the gradients of the potential curves shown in Fig. 2(f) depend on the electronic state, where the gradient of the closed-singlet state is the lowest. Hence, as d_{CB-Ni} decreases, the energy difference between the closed-singlet state and other states with unpaired electrons decreases, leading to an inversion with the open-singlet state at d_{CB-Ni} = 2.9 Å. Furthermore, in the region of 2.6 < d_{CB-Ni} < 3.0 Å, the open-shell structures become dominant, as we hypothesised.

Fig. 2 illustrates that the D_{2h}-symmetric closed-shell singlet structure, which is stable in the gas phase, is converted into D_{4h}-symmetric open-shell electronic states (triplet and open singlets) by surface adsorption. Such D_{2h} → D_{4h} conversion has been theoretically predicted in closely stacked π-dimer structures of CB.[28–30] In the CB dimer, the two unpaired electrons occupying the singly occupied molecular orbitals interact with

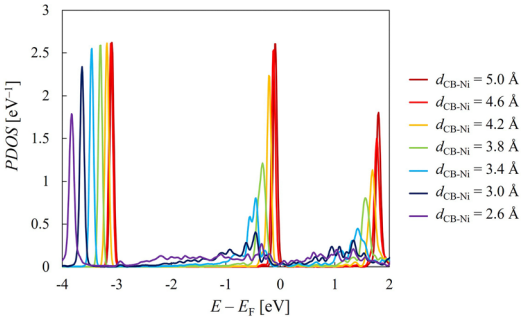

Fig. 3 Projected density of states (PDOS) of C atoms in open-singlet CB/Ni(111) with varying d_{CB-Ni} values. E_F is the Fermi energy, defined as the highest occupied band energy (the HOMO of CB in this study).

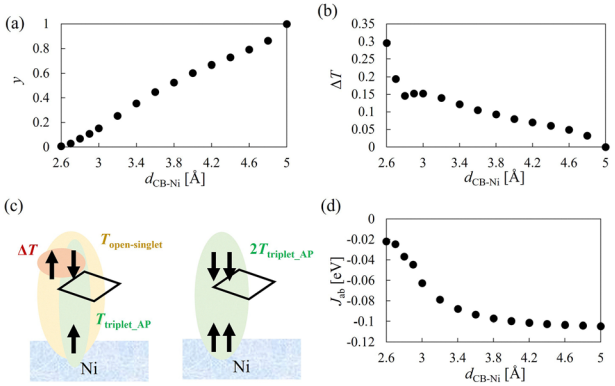

Fig. 4 Dependence of (a) y value and (b) effective bond order in CB (ΔT) on d_{CB-Ni} of the open-singlet state. (c) Schematic of the definition of ΔT; specific definitions of ΔT, $T_{open-singlet}$, and $T_{triplet\_AP}$ are shown in the ESI,† Note. (d) Dependence of effective magnetic coupling, J_{ab}, in CB on d_{CB-N}. The estimation scheme for J_{ab} is provided in the ESI,† Note.

the unpaired electrons in the other, and the CB dimer acquires aromaticity and is stabilised by the D_{4h} structure. Triplet states such as triplet_AP significantly stabilise with decreasing d_{CB-Ni} through the mechanism presented in the dimer models.[30] This quantum effect caused by orbital correlation is generally larger than classical magnetic dipole interactions; therefore, the triplet_AP state is more stable than the triplet_P state on the surface.

The results of the density of states (DOS) analysis are presented in Fig. 3 as a proof of the proposed stabilisation mechanism shown in Fig. 1(e). If the C p_z orbitals interact with the Ni d-band, the p_z-originating orbitals are stabilised by the orbital correlation with the surface band (red line in Fig. 1(e)), but are destabilised by the weakening C–C bond (HOMO shift shown in Fig. 1(b); blue line in Fig. 1(e)). The p_z-originating states are broadened by conflicting effects. As shown in Fig. 3, the HOMO peak of the closed-singlet model originating from the p_z orbital broadened under the influence of surface interactions. This result is proof of the mechanism shown in Fig. 1(e) and implies the importance of controlling the surface–molecule interactions.

For further discussion, we performed diradical analysis[25,31–33] based on spin-projected DFT/plane-wave.[27] The contribution of the two-electron excitations is called diradical character (y),[25] where a more prominent y weakens the C=C double bond in the closed-singlet to a greater extent.[33] The calculated y values are summarised in Fig. 4(a); these decrease monotonically with decreasing d_{CB-Ni}. This trend is similar to the diradical change in the 2H/Pt(111) model system.[24] As shown by the mechanism in Fig. 1(e), y would be amplified because the radical coupling within the molecule weakens as it approaches the surface. On the other hand, Fig. 1(e) also shows the mechanism the radicals used to interact with unsaturated bonds on the surface; when this interaction is strong, the molecule loses radicals, accompanied by a decrease in y. Hence, the balance between these mechanisms determines whether y decreases or increases upon surface adsorption. This balance depends on the combination of surfaces and molecules.[18–20] In the model system used in this study, the latter effect is dominant. The significant contribution of the CB–Ni interaction was confirmed by the DOS shown in Fig. 3. The peaks of the occupied orbitals shifted to lower energies with decreasing d_{CB-Ni}.

Next, we provide evidence that intramolecular radical coupling is weakened by surface interactions based on the results of effective bond order (T) analysis[27,32] for diradicals. The open-singlet state contained both intramolecular radical coupling and CB–Ni radical coupling, whereas triplet_AP exhibited only CB–Ni coupling. Hence, the change in intramolecular radical coupling can be discussed in terms of the difference in T values of triplet_AP and open-singlet states (ΔT in Fig. 4(c); details are provided in ESI,† Note). ΔT decreases at $d_{CB-Ni} < 3.0$ Å (Fig. 4(b)), where the open-shell states of CB become dominant. This is a direct result of the weakening of intramolecular radical coupling owing to surface–molecule interactions.

The ability to switch between two states (on and off) is important for device applications. Transitions between the on- and off-states of molecular materials generally exhibit large conformational changes and bond switching.[34] However, switching with large conformational changes results in low durability. The open-singlet and triplet states of CB have a D_{4h} structure; hence, these states may allow switching without large conformational changes. The effective magnetic exchange integral, J_{ab}, was estimated for the CB molecule by approximating the generalised spin-projection method[26] (see ESI,† Note for details). The calculated values are −0.104 eV at d_{CB-Ni} = 5.0 Å and −0.037 eV at d_{CB-Ni} = 2.8 Å; the absolute values decrease with surface adsorption (Fig. 4(d)). This result indicates that the surface interaction weakens the magnetic coupling of intramolecular radicals, making the open-singlet/triplet switch easier than that for isolated molecules.

The effect of surface adsorption on the electronic state of the antiaromatic molecule was investigated using the developed spin-projection with the DFT/plane-wave method. These results demonstrate the possibility of controlling the magnetism and stability of antiaromatic molecules *via* surface adsorption. Although surface adsorption is known to stabilise magnetic molecules,[14–16] in contrast to this, we can induce ferro/antiferromagnetism on CB, a nonmagnetic molecule in the gas phase, by surface adsorption. This closed-shell-to-open-shell

transition was caused by the quantum effect: orbital correlation. Molecules with weak diradical character, such as antiaromatic molecules, are suitable for inducing magnetism because they have small HOMO–LUMO gaps and sensitive correlations between their electronic and geometric structures. Our calculations demonstrate that this surface-adsorption effect has an optimum molecule–surface distance (Fig. S1–S4, ESI†); therefore, steric control of adsorption by substituents will be important for maximising the surface effect. The adsorption site will also be important because the key orbital is p_z in CB. Self-interaction and spin-contamination errors hinder discussions on vibration modes, which is important for the pseudo Jahn–Teller effect; hence, collaboration with experiments is needed. Although optimising computational methods, substituents, and surface structures is a future endeavour, controlling the electronic states of antiaromatic molecules *via* surfaces, as presented in this study, will open a new field of chemistry.

K. T., R. S., and R. K. conceived the study. K. T. performed the theoretical calculations and analysed the results with inputs from R. S. and R. K. The calculated results were discussed by K. T., R. S., and R. K., and Y. K. validated the results and discussion. K. T. wrote the original draft. All authors commented on the manuscript. K. T., R. K., and Y. K. received the funding.

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Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the ESI.†

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