

1 Title

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3 Stimuli-Responsive Optical Materials Based on Hypervalent

4 Antimony-Containing Conjugated Molecules

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17 reaction

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19 Abstract

20 Stimuli-responsive materials have been applied for sensor devices because they can transform and amplify various
21 target stimuli into observable signals. Much effort has been devoted to exploring effective molecular designs for obtaining
22 stimuli-responsive behaviors by taking advantage of unique optoelectronic properties of π -conjugated molecules involving
23 various elements. This study focuses on the modulation of the electronic state of the π -conjugated scaffolds by the oxidation
24 number change of the hypervalent antimony. We demonstrate that the strength of the intramolecular interaction between
25 hypervalent antimony and the π -conjugated framework can be tuned with ligand structure, substituent effect, and oxidation
26 number shifts of hypervalent antimony. In particular, the color changes represented by hypsochromic and bathochromic
27 wavelength shifts of optical bands were achieved by the oxidative reaction of hypervalent antimony in the solid state.
28 Significantly, the direction of the color changes can be confidently predicted by quantum chemical calculations. Our
29 findings, based on the electronic interaction between π -conjugated scaffolds and hypervalent main-group elements, provide
30 logical design strategies for advanced stimuli-responsive materials.

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1 Introduction

2 π -Conjugated compounds are widely used for organic light-emitting diodes (OLEDs)^[1–3] and organic photovoltaics
3 (OPVs)^[4–7] because of their superior optical and electronic properties. In recent years, based on the environmental
4 responsiveness of π -conjugated molecules, the applications for sensing materials have also become popular.^[8–10] Stimuli-
5 responsiveness refers to the ability of a material to change its properties in reaction to an external stimulus and then return
6 to its original state once the stimulus is removed. In particular, the concept of irreversible stimuli-responsiveness expands on
7 this idea and can lead to the development of new functional materials, such as those exhibiting stimulus hysteresis.^[11–13]
8 Therefore, there is an increasing demand for developing new mechanisms of stimuli-responsiveness. The incorporation of
9 heteroatoms into the π -conjugated systems is one of the promising strategies for introducing the sensing ability to
10 optoelectronic molecules. By employing the unique reactivity of heteroatoms, such as Lewis acidity^[14–17] and oxidation
11 number shifts through redox reactions^[17–20], intriguing stimuli-responsiveness has been accomplished.^[21] There is still much
12 room to explore further functions in combination with π -conjugated scaffolds and heteroatoms.

13 We have explored the potential of hypervalent states to offer further functionality to the π -conjugated frameworks.^[22,23]
14 Hypervalent states are defined as electronic states where valence electrons of main-group elements formally exceed the
15 octet rule.^[24–26] We prepared the stimuli-responsive π -conjugated systems involving the hypervalent tin^[27–30] and bismuth^[31]
16 atoms. These hypervalent compounds exhibit intramolecular interactions between their elements and π -conjugated scaffolds
17 and form a hypervalent state. We observed stimuli-responsiveness, which was based on shifts in coordination numbers and
18 transformations of different hypervalent states. This behavior arises from the Lewis acid-base interactions between
19 hypervalent elements and Lewis bases, leading to observable color changes. In these reactions, the oxidation numbers of the
20 hypervalent elements remain constant. Therefore, it is presumable that more diverse stimuli-responsiveness and,
21 subsequently, optical property changes can be expected by inducing the oxidation number shift after the coordination. Thus,
22 we set the next goal to induce the oxidation number shift at the hypervalent element and to apply these shifts to dynamic
23 controls for optical and electronic properties of π -conjugated systems.

24 Since antimony can exist in a hypervalent state with two different stable oxidation states, Sb(III) and Sb(V),^[32–36] the
25 antimony-based molecular design is a promising strategy for fulfilling the above purpose. Furthermore, hypervalent states
26 can be regarded as reaction intermediates in heavy main-group elements, and various reactions, such as hypervalent
27 antimony interacting with metal atoms, have been studied because of their high reactivity.^[37–41] These physical properties
28 and reactivity suggest that a hypervalent antimony atom could serve as a starting point for control of the electronic state in

the π -conjugated systems. In other words, hypervalent antimony is expected to play a role as a switch module for regulating the optical and electronic properties of the π -conjugated system.

Herein, we report hypervalent antimony compounds with π -conjugated frameworks and the differences in the electronic effects on π -conjugated systems originating from oxidation number shifts. As the π -conjugated ligand which is capable of forming electronic communications with hypervalent elements, we used azobenzene derivatives.^[27,31,42] Consequently, we found that the electronic states of the π -conjugated scaffold can be tuned depending on the oxidation number and substituents in the hypervalent antimony compounds (Figure 1a). Additionally, by applying the conventionally known oxidation of antimony^[43–45], we realized the reaction between antimony and *o*-chloranil even in the solid state, resulting in a color change by mechanical stimuli (Figure 1b). Conventional mechanochromic materials show color changes derived from the crystalline–amorphous transition. Meanwhile, chromic behaviors in our system can be expressed in the amorphous state, suggesting that wider applicability as stimuli-responsive materials should be obtained. Furthermore, by manipulating the substituent in the π -conjugated scaffolds, we were able to control the direction of color change between hypsochromic and bathochromic wavelength shifts. In particular, from reaction reagents and products, it is possible to predict the direction of color change through quantum chemical calculations. We demonstrate here a unique approach for logically designing stimuli-responsive optical materials based on the electronic effects and reactivity of hypervalent antimony in the π -conjugated system.

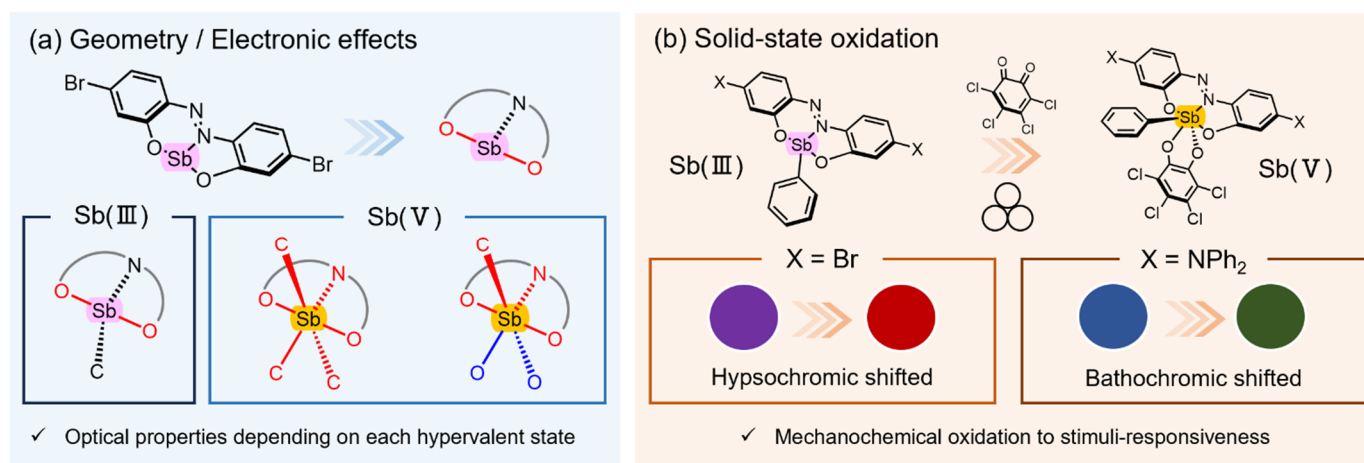


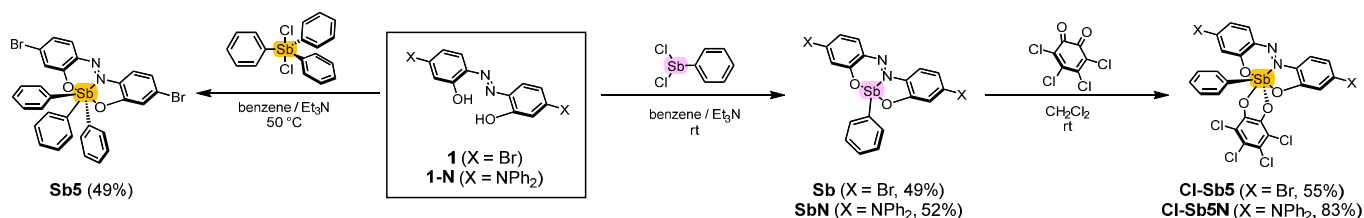
Figure 1. Design of hypervalent antimony compounds. (a) Evaluation of the geometry and electronic effects in different oxidation numbers of antimony. (b) The color changes using the solid-state oxidation reaction. Inset colors represent the actual color of each compound.

Results and Discussion

Synthesis and characterization

The hypervalent antimony compounds, **Sb** and **Sb5**, were synthesized by the reaction of azobenzene ligand **1** and antimony reagents, as illustrated in Scheme 1. The bromine groups in **1** play a crucial role in enhancing crystallinity. According to the previous study, monophenyl antimony dichloride (PhSbCl_2) was prepared by comproportionating triphenyl antimony and antimony trichloride in a 1:2 molar ratio.^[46] The ligand **1** and PhSbCl_2 were subjected to basic conditions, and **Sb** was obtained as a brown solid in 50% isolated yield. Additionally, **Sb5** was synthesized by the reaction with **1** and triphenyl antimony dichloride under basic conditions. The residue was reprecipitated to afford **Sb5** as an orange powder in 49% isolated yield. In the solid state, **Sb** shows high stability, whereas degradation occurred in solution. In contrast, **Sb5** is stable both in solid and solution states under ambient conditions. According to the previous research, it implies that **Sb** might be reacted with oxygen.^[40] Because the hypervalent compound with the diphenylamine group as a donor unit showed excellent optical properties in the previous study,^[47] we synthesized **SbN** via the reaction with **1-N** and PhSbCl_2 (52% isolated yield). For testing the reactivity of antimony(III) with an oxidizer and characterizing resulting compounds, we conducted oxidation of **Sb** and **SbN** with the *o*-quinone derivative (Scheme 1). Similar to the results in the previous research,^[45] we obtained **Cl-Sb5** and **Cl-Sb5N** in 55 and 83% isolated yields through the oxidative addition of *o*-chloranil with **Sb** and **SbN**, respectively. The structures of all new compounds were confirmed by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, high-resolution mass spectroscopy, and elemental analysis. From these data, we concluded that all materials had expected structures and enough purity to evaluate optical properties. These data and detailed synthetic procedures are shown in the Supporting Information.

Scheme 1. Synthesis of hypervalent antimony(III) and (V) compounds with the azobenzene tridentate ligands



Electronic structures of hypervalent antimony compounds

The molecular structures of each compound were elucidated by the single-crystal X-ray structure analysis (Figures 2 and S1–S3 and Tables S1–S3). The hypervalent state can be classified as *N*–*X*–*L* (*N* is the formally assigned electrons, *X* is

the element, and L is the number of ligands coordinated to the central atom). As we expected, depending on the oxidation number, **Sb** derived from 10–Sb–4 adopts a distorted pseudo trigonal bipyramidal geometry, while **Sb5** and **Cl-Sb5** adopt an octahedral geometry derived from 12–Sb–6. In addition, **Sb** was found to form dimer structures by filling the coordination site because of the Lewis acidity of antimony (Figure S1). To gain insight into the electronic structure of hypervalent antimony, we focused on the bond distance between the antimony and the nitrogen atom of azobenzene. The Sb–N bond distances were 2.251(7) Å for **Sb**, 2.320(2) Å for **Sb5**, and 2.165(6) Å for **Cl-Sb5**. These data suggest that the magnitude of intramolecular interactions between antimony and nitrogen is different in each compound. To be precise, the strength of the intramolecular interaction is weaker in the order of **Cl-Sb5**, **Sb**, and **Sb5**. This result also correlated with the bond distances and the natural bond orbital (NBO) analysis with density functional theory (DFT) calculations (Figure S4). The Sb–N interaction was estimated by the NBO analysis with the second-order perturbation energy ($E(2)$), which means the interaction between their orbitals.^[48] The values of $E(2)$ were calculated to be 92.51 kcal/mol for **Sb**, < 0.50 kcal/mol for **Sb5**, and 94.38 kcal/mol for **Cl-Sb5**. As mentioned above, the structural differences result from differences in the geometry of hypervalent states because of different oxidation numbers.

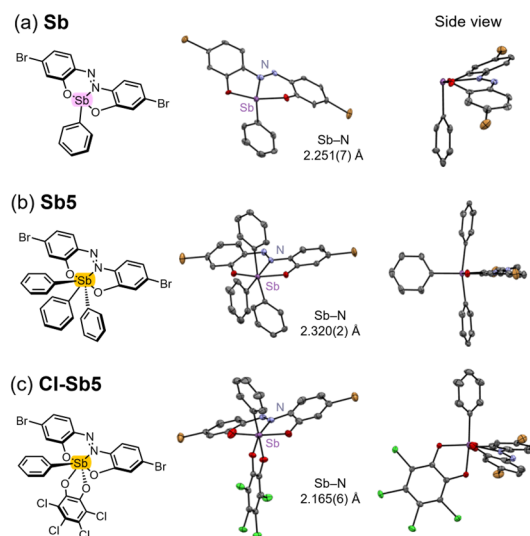


Figure 2. ORTEP drawings of (a) **Sb**, (b) **Sb5**, and (c) **Cl-Sb5** (50% probability for thermal ellipsoids). Hydrogen, solvents, and disordered atoms are omitted to clarify. All crystallographic data are shown in the Supporting Information.

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15 Electronic properties of hypervalent antimony compounds

To investigate the electronic state for each compound, UV–vis absorption of **Az**, **Sb**, **Sb5**, and **Cl-Sb5** were measured (Figure 3a and Table S4). Compared to **Az** which is the model compound, the distinct absorption bands in the longer wavelength region appeared in the spectra of **Sb**, **Sb5**, and **Cl-Sb5** (**Az**: $\lambda_{\text{abs,max}} = 380$ nm, **Sb**: $\lambda_{\text{abs,max}} = 567$ nm, **Sb5**: $\lambda_{\text{abs,max}}$

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1 = 502 nm, and **Cl-Sb5**: $\lambda_{\text{abs,max}} = 529$ nm). In **Sb**, the absorption spectrum altered with time even in inert N₂ atmosphere
2 (Figure S5). This indicates that the compound should be decomposed during the measurement. As for photoluminescence
3 (PL), although **Sb** was not able to be evaluated due to low stability, **Sb5** showed luminescence in solution ($\lambda_{\text{PL,max}} = 600$ nm,
4 absolute PL quantum yield (QY) = 1.3%) and solid ($\lambda_{\text{PL,max}} = 600$ nm, QY = 1.1%) (Figure S6). The low quantum yield of
5 **Sb5** might be induced due to the vibrations of the molecular framework, the deactivation of excitation energy to a dark state,
6 the heavy atom effect of antimony, and so on. It is also assumed that the steric hindrance of three phenyl groups in **Sb5**
7 could contribute to avoiding aggregation-caused quenching (ACQ). Emission from **Cl-Sb5** was under the detectable level
8 (Table S4). The data from the DFT calculations support that only **Cl-Sb5** did not emit because the molecular orbitals (MOs)
9 were separated between the catechol and azobenzene moieties (Figure 3b and Tables S5–S8).

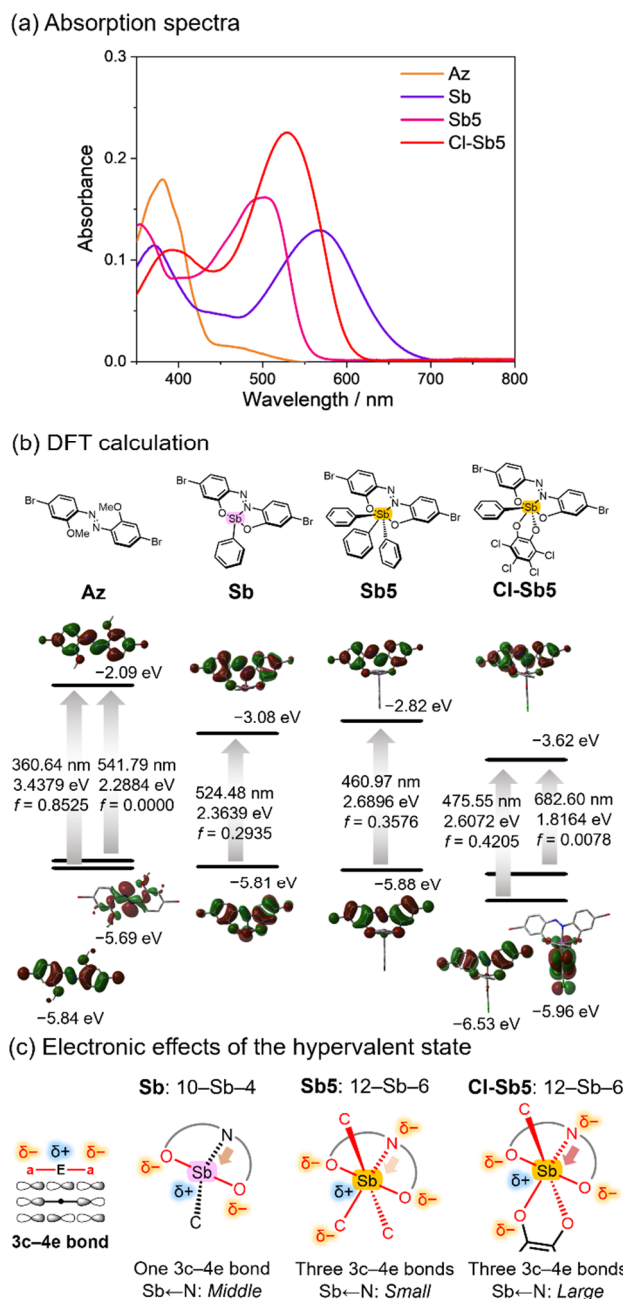


Figure 3. (a) UV-vis absorption spectra of **Az**, **Sb**, **Sb5**, and **Cl-Sb5** in toluene (1.0×10^{-5} M, only **Sb** measured under inert conditions). (b) Calculation results of **Az**, **Sb**, **Sb5**, and **Cl-Sb5**. Kohn-Sham orbitals (isovalue=0.02) and energy diagrams from HOMO-1 to LUMO for **Az**, oscillator strength (f), transition energy of S_0 to S_1 transition from the optimized ground state. (c) Schematic illustrations of the electronic effects of the hypervalent state of each compound.

In the DFT calculation data, we also focused on the energy level of the lowest unoccupied molecular orbital (LUMO) of the compounds to evaluate the electronic effects of hypervalent antimony against the azobenzene moiety (Tables S4–S7). It was found that the LUMO energy levels of the compounds differed depending on the situation of hypervalent antimony, compared to that of **Az**. As observed in Figure 3b, the degree of decrease in LUMO follows the following order, **Cl-Sb5** > **Sb** > **Sb5** (**Cl-Sb5**: -3.62 eV, **Sb**: -3.08 eV, and **Sb5**: -2.82 eV). This tendency in the LUMO energy level is corresponded with the order in the Sb–N bonding distance as mentioned above. With these results, the electronic state of hypervalent

antimony can be interpreted based on the three-center, four-electron (3c-4e) bond polarized in the apical position shown in the hypervalent state (Figure 3c). In general, one 3c-4e bond is formed in the trigonal bipyramidal geometry in the hypervalent state, while three 3c-4e bonds are approximately constructed in the octahedral geometry.^[25] Therefore, we confirmed the existence of the related MOs of 3c-4e bonds by the DFT calculations (Figures S7–S13). By comparing **Sb** and **Sb5**, it was clarified that **Sb5** forms 3c-4e bonds on C–Sb–N as well as O–Sb–O. The 3c-4e bond is a polarized bond known to localize negative charge in the apical position. Therefore, we can expect the Sb–N bond to be weakened in **Sb5** due to the presence of the 3c-4e bond in C–Sb–N. In fact, NBO calculations also reveal that the $E(2)$ of donor–acceptor interaction in Sb–N is smaller in **Sb5** (Figure S4). Thus, although the pentavalent antimony is generally more acidic, the degree of reduction of the LUMO energy level in the pentavalent antimony is less than that in the trivalent antimony because the polarization effect of the 3c-4e bond weakens the Lewis donor–acceptor interaction between antimony and nitrogen. In **Sb5** and **Cl-Sb5**, both form three 3c-4e bonds. On the other hand, focusing on the difference in substituents, **Cl-Sb5** has the electron-withdrawing group derived from *o*-chloranil, which should enhance the Lewis acidity of antimony by the inductive effect of chloral substituents. Therefore, by comparing **Sb5** and **Cl-Sb5**, we confirmed that the stronger intramolecular interaction in **Cl-Sb5** stabilized the LUMO energy level compared to that in **Sb5**. From these results, it is possible to interpret the difference in the electronic structure of π -conjugated systems based on the oxidation number of hypervalent antimony and the effect of substituents. These results also represent that the electronic states of π -conjugated systems can be modulated by the oxidation number shifts at the hypervalent antimony.

Incorporation of donor units to hypervalent antimony compounds

Next, the influence of electron-donating diphenylamine groups on the hypervalent antimony compounds was evaluated. It is noted that the changes in the absorption spectrum of **SbN** were hardly observed in solution, while the changes probably due to decomposition in that of **Sb** were detected in Figure S1. It might be due to decomposition in that of **Sb**. This implied that the electron-donating diphenylamine groups could improve the stability of the hypervalent antimony compounds. The absorption and PL spectra of **SbN** and **Cl-Sb5N** were subsequently measured in toluene (Figure 4a). The absorption wavelengths of **SbN** and **Cl-Sb5N** were bathochromically shifted to the longer wavelength region compared to those of **Sb** and **Cl-Sb5**, respectively (**SbN**: $\lambda_{\text{abs, max}} = 640$ nm, and **Cl-Sb5N**: $\lambda_{\text{abs, max}} = 664$ nm). In addition, **SbN** and **Cl-Sb5N** exhibited intense emission in the near-infrared region (**SbN**: $\lambda_{\text{PL, max}} = 753$ nm, QY = 4.6% and **Cl-Sb5N**: $\lambda_{\text{PL, max}} = 777$ nm, QY = 5.3%). Particularly, in contrast to **Cl-Sb5**, **Cl-Sb5N** exhibited luminescence. In the solid state, the PL spectra were

detectable (**SbN**: $\lambda_{\text{PL, max}} = 799 \text{ nm}$, $\text{QY} = 0.2\%$ and **Cl-Sb5N**: $\lambda_{\text{PL, max}} = 876 \text{ nm}$, $\text{QY} = 0.1\%$), although ACQ occurred (Figure S14). From these results, it is concluded that the electronic states and the related optical properties strongly depend on the oxidation numbers and substituents, and the color change of the materials can be inducible by the oxidation reaction at the hypervalent antimony.

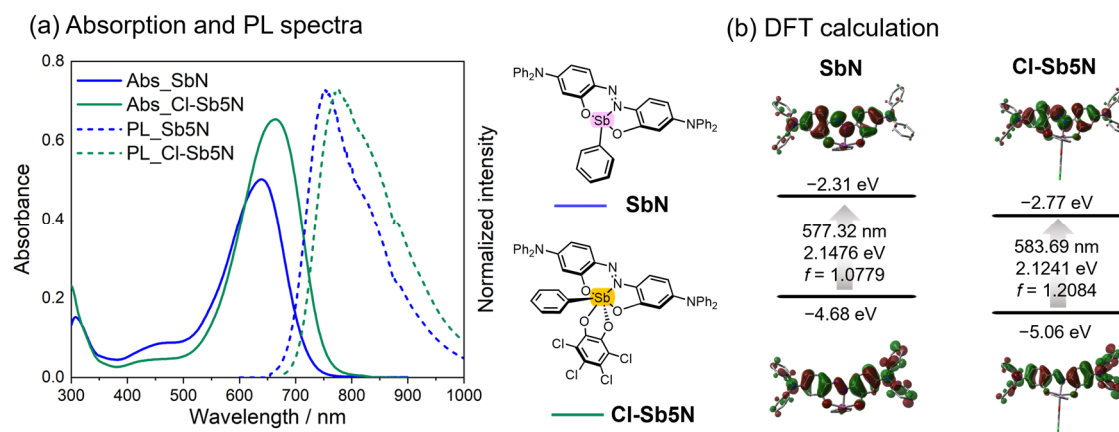


Figure 4. (a) UV-vis absorption and PL spectra of **SbN** and **Cl-Sb5N** in toluene ($1.0 \times 10^{-5} \text{ M}$, only **SbN** measured under inert conditions). (b) Calculation results of **SbN** and **Cl-Sb5N**. Kohn-Sham orbitals (isovalue=0.02) and energy diagrams from HOMO to LUMO, oscillator strength (f), transition energy of S_0 to S_1 transition from the optimized ground state.

The effects of introducing donor substituents were supported by a DFT calculation. The MOs for **SbN** and **Cl-Sb5N** from DFT calculations are shown in Figure 4b and Tables S9 and S10. In both cases, it was found that the energy levels of the highest occupied molecular orbital (HOMO) and LUMO increase with the introduction of donor substituents (HOMO: -4.68 eV and LUMO: -2.31 eV in **SbN** and HOMO: -5.06 eV and LUMO: -2.77 eV in **Cl-Sb5N**). Interestingly, the π -orbital derived from the azobenzene moiety in HOMO-4 of **Cl-Sb5** was changed to HOMO of **Cl-Sb5N**. Consequently, the HOMO-LUMO transition become allowed, which led to the appearance of luminescent properties. Evaluation of the HOMO and LUMO energy levels showed that the energy gap of **Cl-Sb5N** is narrower than that in **SbN**. This fact is corresponded to the experimental data that the absorption spectrum of **Cl-Sb5N** was bathochromically shifted compared to that of **SbN**. In **SbN** derivatives, the diphenylamine groups act as the donor units, and the azobenzene moiety serves as the acceptor unit. As a result, a Donor-Acceptor-Donor (D-A-D) structure can be formed within the π -conjugated framework. In this configuration, the HOMO of the entire molecule is primarily influenced by the donor unit, whereas LUMO is primarily determined by the acceptor unit. In the current molecule, the HOMO remains relatively unchanged since the diphenylamine groups dominate, while the oxidation at the electron-accepting azobenzene moiety by *o*-chloranil should significantly lower the LUMO level. This reduction is responsible for achieving a narrow energy gap followed by bathochromic shift. This result is opposite to the hypsochromic wavelength shift in **Cl-Sb5** caused by the oxidation of **Sb**.

From these data, it can be said that by introducing substituents, different directions of the absorption spectral shift after the oxidation are inducible. This result suggests that different color changes with hypsochromic and bathochromic wavelength shifts can be achieved in the same oxidation reaction by dynamically changing the oxidation number of the hypervalent antimony.

Mechanochemical reaction to stimuli-responsiveness

Finally, we attempted to realize the color change in the amorphous state by oxidation of antimony in the solid state. As shown above, the absorption spectral changes with both hypsochromic and bathochromic wavelength shifts were inducible by selecting the substituents through the same oxidation reaction of antimony. Therefore, we aimed to achieve the absorption spectral shifts of **Sb** and **SbN** in different directions using the solid-state oxidation mechanism (Figure 5a). First, each compound was dispersed in sea sand (5 wt%) and subjected to the ball mill for 30 minutes to realize completely homogeneous dispersion states. The diffuse reflection spectra (5 wt% dispersed in BaSO₄) with the samples are shown in Figures 5b and 5c (**Sb**: $\lambda_{\text{abs,max}} = 578$ nm, and **SbN**: $\lambda_{\text{abs,max}} = 630$ nm). After the milling treatment, an equivalent amount of *o*-chloranil was added to the homogeneously dispersed compounds (**Sb** and **SbN**) and milled by ball mill for 60 minutes. Then, the spectra of the reaction products and the pure model compounds (**Cl-Sb5** and **Cl-Sb5N**) were compared. Consequently, the absorption spectra of both **Sb** and **SbN** were changed by the reaction, and those of the reaction products were in good agreement with the pure model compounds (**Sb** + *o*-chloranil: $\lambda_{\text{abs,max}} = 532$ nm, and **SbN** + *o*-chloranil: $\lambda_{\text{abs,max}} = 669$ nm, **Cl-Sb5** (model): $\lambda_{\text{abs,max}} = 538$ nm, and **Cl-Sb5N** (model): $\lambda_{\text{abs,max}} = 667$ nm). These data indicate that the oxidation reaction proceeds in the solid state through the mechanochemical process. The changes in color tone in the photographs may be derived from baseline changes caused by sea sand used as a dispersant. However, we were able to confirm that the peaks of **Sb** and *o*-chloranil disappeared. Furthermore, the spectral changes observed in the solid state were similar to those detected in the solution, where the hypsochromic and bathochromic wavelength shifts in **Sb** and **SbN** were monitored, respectively. Additionally, these reactions can also occur by grinding on a glass slide (Figure S15). Since conventional mechanochromic behaviors are induced by molecular environmental changes caused by crystalline–amorphous phase transition, the fabrication of the initial crystalline state is essential. Due to the difficulty in fabricating the film materials with desired behaviors and the intrinsic fragility of crystalline samples, the application of conventional substances as a sensing material is still limited. Because our materials can also be used in an amorphous state, a variety of applications have been proposed, including spray coatings that allow visualization of contact history. Thus, we can say that

the combination of hypervalent antimony and π -conjugated scaffold provides a valid molecular design strategy for practical color-changeable materials.

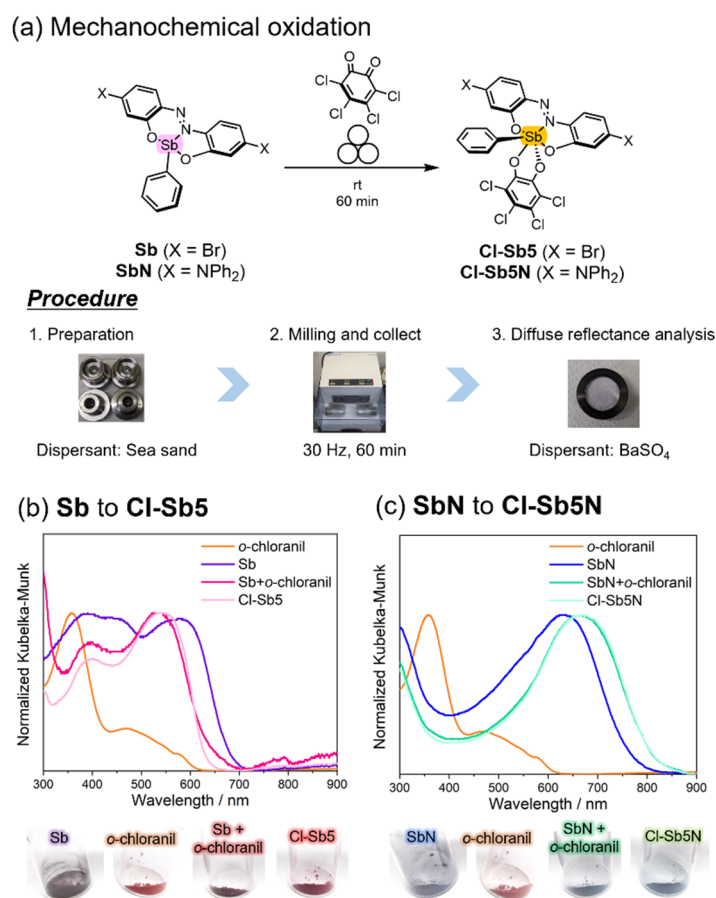


Figure 5. (a) Synthetic scheme of mechanochemical oxidation from Sb(III) to Sb(V). Normalized UV-vis diffuse spectra of (b) **Sb** and (c) **SbN** in the mechanochemical oxidation reaction with *o*-chloranil. The pictures show the sample color changes of **Sb** and **SbN** to **Cl-Sb5** and **Cl-Sb5N**, respectively.

Conclusion

We synthesized hypervalent antimony compounds with varying oxidation numbers and substituents and studied their impact on the electronic properties of π -conjugated systems. From optical measurements and theoretical calculations, it was revealed that hypervalent antimony can significantly alter the electronic properties of π -conjugated scaffolds. Additionally, we achieved stimuli-responsiveness to take advantage of the reactivity of hypervalent antimony, resulting in the predictable color change by the mechanochemical oxidation reaction. By the combination with the reducing reactions, further diverse responses might be inducible. Thus, it can be said that the redox reaction of main-group elements could be a versatile tool for designing advanced stimuli-responsive materials. This combination of hypervalent antimony and the π -conjugated system should be a novel molecular design strategy for creating functional optical materials originating from hypervalent states.

Supporting information

Experimental details “Antimony_SI.pdf”.

Acknowledgment

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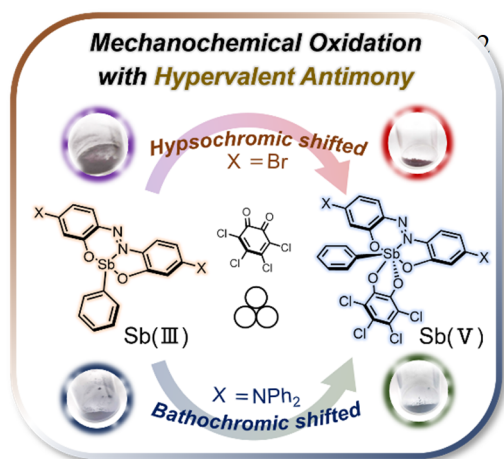
Accession Codes

CCDC 2387699 for **Sb**, 2387700 for **Sb5**, and 2387701 for **Cl-Sb5** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033

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8

Stimuli-responsive materials are realized by π -conjugated molecules containing hypervalent antimony. This allows for the control of electronic states and the mechanical stimuli-responsiveness through oxidation reactions. The strength of the intramolecular interaction between hypervalent antimony and the π -conjugated framework can be tuned based on its geometry, substituents, and oxidation numbers. Our findings suggest that hypervalent states are versatile for designing stimuli-responsive materials.

Stimuli-Responsive Optical Materials Based on Hypervalent Antimony-Containing Conjugated Molecules

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General

^1H , $^{13}\text{C}\{^1\text{H}\}$, and ^{119}Sn NMR spectra were recorded on JEOL ECZ400 instruments at 400, 100, and 149 MHz, respectively. High-resolution $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on an ECZ600R instrument at 150 MHz. Samples were analyzed in CD_2Cl_2 , THF- d_8 , and DMSO- d_6 . The chemical shift values were expressed relative to Me_4Si for ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR as an internal standard in CDCl_3 , DMSO for ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR as an internal standard in DMSO- d_6 , and Me_4Sn for ^{119}Sn NMR as an external standard. High-resolution mass (HRMS) spectrometry was performed at the Technical Support Office (Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University), and the HRMS spectra were obtained on a Thermo Fisher Scientific EXACTIVE spectrometer for electrospray ionization (ESI). UV-vis absorption and diffuse reflectance UV-vis absorption spectra were recorded on a SHIMADZU UV-3600i Plus spectrophotometer, and the samples were analyzed at room temperature. The Kubelka-Munk equation was applied for diffuse reflective spectra. Fluorescence emission spectra were recorded on a HORIBA Scientific Fluorolog-3 spectrofluorometer, and samples were analyzed at room temperature with PMT P928 (250~810 nm) and DSS-IGA (810~1550 nm) as detectors. Absolute photoluminescence (PL) quantum efficiency (Φ_{PL}) was recorded on a Hamamatsu Photonics Quantaaurus-QY Plus C13534-01 equipped with infrared measurement unit C13684-01 using an integrating sphere. Elemental analyses were performed at the Microanalytical Center of Kyoto University. X-ray crystallographic analysis was carried out by Rigaku Saturn 724+ with MicroMax-007HF CCD diffractometer with Varimax Mo optics using graphite-monochromated $\text{MoK}\alpha$ radiation. A symmetry-related absorption correction was carried out by using the program REQAB.^[1] The structures were solved with SHELXT 2018/2^[2,3] and refined on F^2 with SHELXL 2018/3^[3-5] on YadokariXG.^[6] The program ORTEP3^[7] and Mercury-4.2.0 were used to generate the X-ray structural diagram. All mechanochemical reactions were carried out using grinding vessels in a Retsch MM400 mill. Both jars (1.5 mL) and balls (5 mm) are made of stainless steel.

Materials

Commercially available compounds used without purification:

Antimony trichloride (Nacalai Tesque, Inc.)

Triphenyl antimony (Tokyo Chemical Industry Co, Ltd.)

Triphenyl antimony dichloride (Tokyo Chemical Industry Co, Ltd.)

o-Chloranil (Tokyo Chemical Industry Co, Ltd.)

Commercially available solvents:

The solvents listed below were used without purification.

MeCN (Wako Pure Chemical Corporation)

CH₂Cl₂ (deoxidized grade, Wako Pure Chemical Corporation)

Benzene (deoxidized grade, Wako Pure Chemical Corporation)

Tetrahydrofuran (THF, Wako Pure Chemical Corporation) and triethylamine (Et₃N, Kanto Chemical Co., Inc.) were purified using a two-column solid-state purification system (Glasscontour System, Joerg Meyer, Irvine, CA).

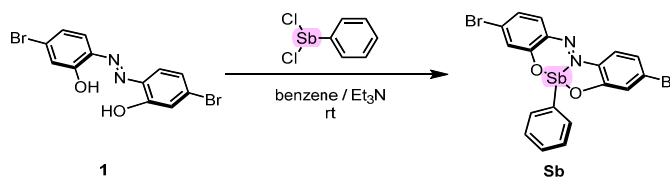
Compounds prepared as described in the literature:

1 ^[8]

1-N ^[9]

Synthetic procedures and characterization

Synthesis of **Sb**

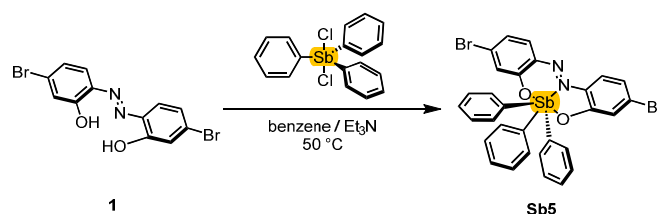


In the glove box filled with inert argon gas, triphenyl antimony (1 equiv.) and antimony trichloride (2 equiv.) were placed in the flask and stirred and disproportionated for 3 days. After producing monophenyl antimony dichloride (PhSbCl_2 , 0.229 g, 0.850 mmol, 1 equiv.) as liquid, it was placed in the two-neck round bottom flask. Also, **1** was placed in the two-neck round flask and filled the nitrogen gas with the Schlenk technique. After adding tetrahydrofuran (THF, 32 mL) and triethylamine (Et_3N , 8 mL), the solution of **1** (0.316 g, 0.850 mmol, 1 equiv.) was added to the solution of PhSbCl_2 and stirred for 16 h. The reaction mixture was filtrated and washed with anhydrous THF and removed the solvent by evaporation. The residue was recrystallized from THF (good solvent) / acetonitrile (poor solvent) and afforded **Sb** (0.243 g, 0.427 mmol, 50%) as a brown crystal.

Characterization:

^1H NMR ($\text{THF}-d_8$, 600 MHz) δ 7.71–7.69 (m, 2H), 7.52 (d, $J = 8.8$ Hz, 1H), 7.31–7.28 (m, 3H), 7.24–7.21 (m, 1H), 7.17 (d, $J = 2.0$ Hz, 1H), 7.08 (d, $J = 2.1$ Hz, 1H), 6.91 (dd, $J = 8.7, 2.1$ Hz, 1H), 6.88 (dd, $J = 8.8, 2.0$ Hz, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{THF}-d_8$, 151 MHz) 165.3, 159.2, 152.9, 137.5, 137.0, 136.5, 134.1, 133.0, 130.6, 129.4, 129.3, 126.8, 124.1, 122.7, 122.2, 119.8 ppm; HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{11}\text{Br}_2\text{N}_2\text{O}_2\text{SbCl}$ $[\text{M}+\text{Cl}]^+$: 600.7919, found: 600.7925. Elemental analysis; calcd. for $\text{C}_{18}\text{H}_{11}\text{SbBr}_2\text{N}_2\text{O}_2$: H 1.95 C 38.01 N 4.92, found H 1.89, C 37.99, N 5.01.

Synthesis of **Sb5**



Triphenyl antimony dichloride (0.228 g, 0.538 mmol, 1 equiv.) was placed in the two-neck round bottom flask. After degassing and filling the nitrogen gas three times, benzene (10 mL) was added to the flask. Next, **1** was placed in the two-neck flask and filled with nitrogen gas by the Schlenk technique. After adding benzene (10 mL) and Et₃N (2 mL), the solution of **1** was added to the solution of triphenyl antimony dichloride and stirred for 3 h at 50 °C. The reaction mixture was filtered, and evaporated the solvents. The residue was dissolved in dichloromethane and reprecipitated by adding hexane. The solid **Sb5** (0.190 g, 0.263 mmol, 49%) was collected by filtration as an orange powder.

Characterization:

¹H NMR (CD₂Cl₂, 600 MHz,) 7.60–7.58 (m, 4H), 7.49–7.42 (m, 3H), 7.37–7.33 (m, 4H), 7.29–7.23 (m, 7H), 7.20 (d, *J* = 2.1 Hz, 1H), 7.03 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.90 (dd, *J* = 8.8, 2.1 Hz, 1H) ppm; ¹³C{¹H} NMR (CD₂Cl₂, 151 MHz) δ 161.6, 156.2, 149.5, 143.1, 138.4, 137.0, 135.4, 134.9, 133.3, 131.2, 130.0, 129.9, 129.8, 129.1, 129.0, 127.3, 124.2, 123.5, 123.3, 118.1 ppm; HRMS (ESI) calcd. for C₃₀H₂₁Br₂N₂O₂Sb [M][−] : 719.9013, found: 719.9013. Elemental analysis; calcd. for C₃₀H₂₁SbBr₂N₂O₂: H 2.93 C 49.83 N 3.87, found H 2.93, C 49.97, N 4.07.

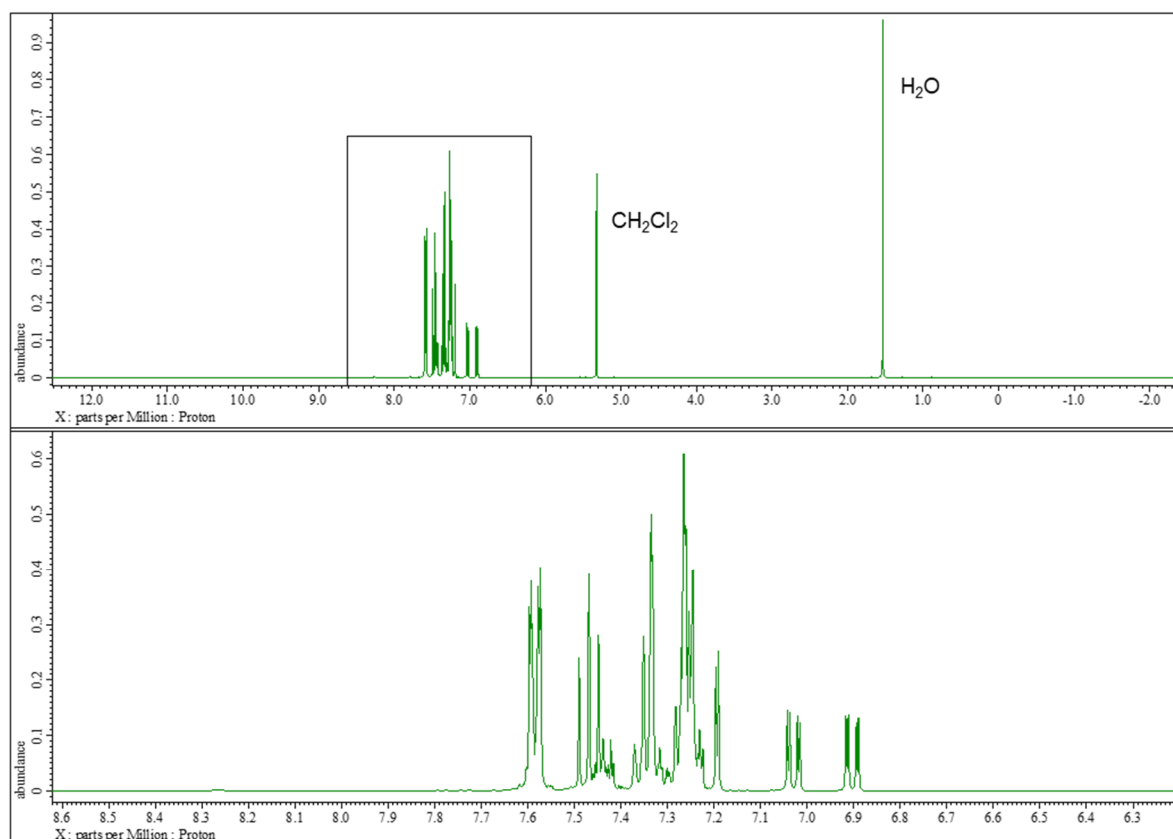


Chart S3. ^1H NMR spectrum of **Sb5** in CD_2Cl_2 at 600 MHz.

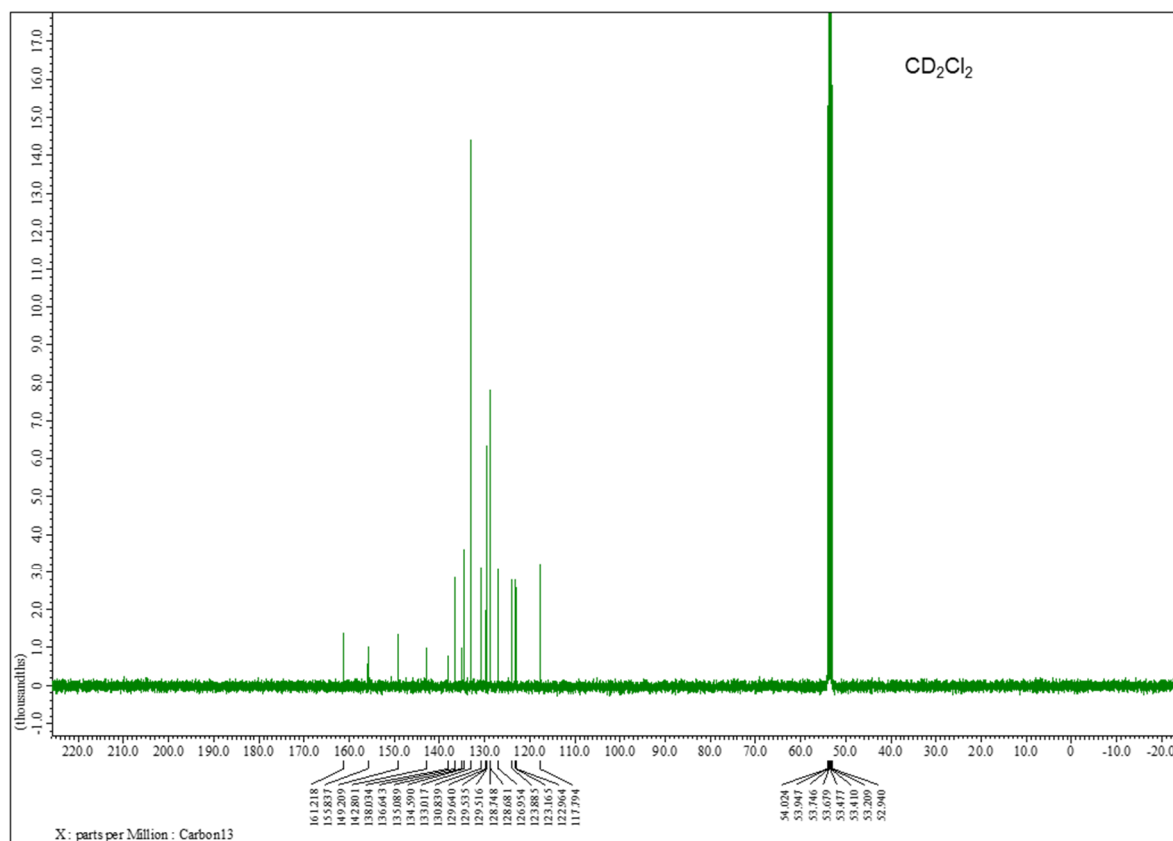
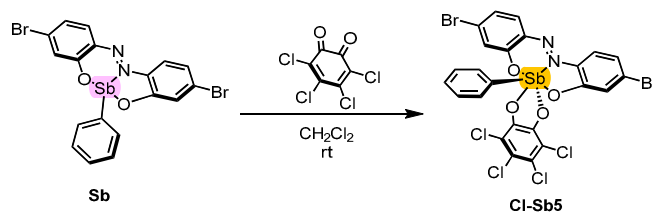


Chart S4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **Sb5** in CD_2Cl_2 at 151 MHz.

Synthesis of **Cl-Sb5**



Sb (0.140 g, 0.246 mmol, 1 equiv.) was placed in the two-neck round bottom flask. After degassing and filling the nitrogen gas three times, CH₂Cl₂ (20 mL) was added to the flask. Next, *o*-chloranil (0.0666 g, 0.271 mmol, 1.1 equiv.) was added to the solution of **Sb** and stirred for 30 minutes at room temperature. The reaction mixture was evaporated by a rotary evaporator. The residue was dissolved in dichloromethane and reprecipitated by adding acetonitrile (MeCN) and washed with hexane. The solid **Cl-Sb5** (0.110 g, 0.135 mmol, 55%) was washed by MeCN and collected by filtration as a red powder.

Characterization:

¹H NMR (CD₂Cl₂, 600 MHz,) δ 7.82–7.78 (m, 3H), 7.71 (d, J = 8.8 Hz, 1H), 7.60–7.57 (m, 1H), 7.55–7.52 (m, 2H), 7.32 (dd, J = 8.8, 2.1 Hz, 1H) 7.26 (dd, J = 8.8, 2.1 Hz, 1H), 7.18 (dd, J = 8.9, 2.0 Hz, 2H) ppm; ¹³C{¹H} NMR (CD₂Cl₂, 151 MHz) δ 157.1, 155.8, 143.9, 143.7, 139.6, 137.2, 136.3, 135.4, 133.5, 133.3, 133.1, 131.7, 130.6, 126.5, 126.5, 125.7, 123.2, 122.9, 122.0, 118.9, 118.2, 117.4 ppm; HRMS (ESI) calcd. for C₂₄H₁₁Br₂N₂O₄SbNa [M+Na]⁺: 832.6770, found: 832.6777. Elemental analysis; calcd. for C₂₄H₁₁SbBr₂N₂O₄: H 1.36 C 35.38 N 3.44, found H 1.53, C 35.48, N 3.52.

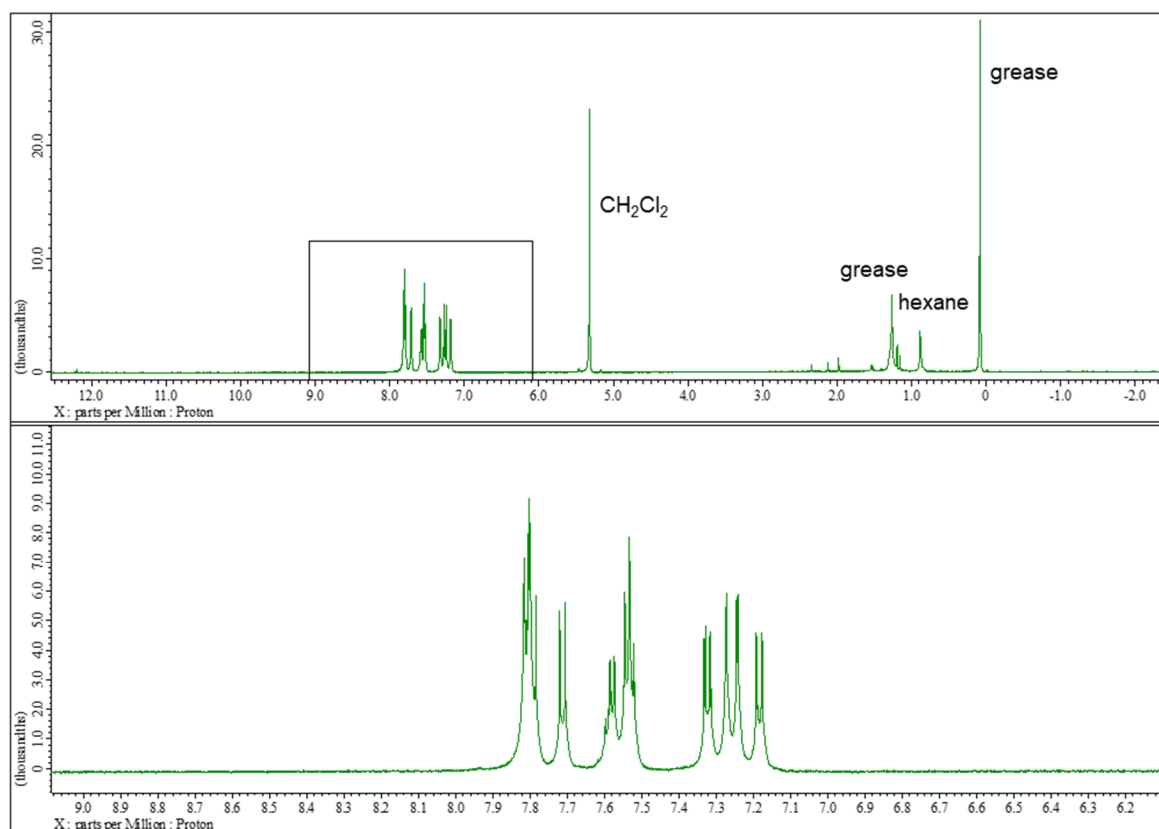


Chart S5. ^1H NMR spectrum of **Cl-Sb5** in CD_2Cl_2 at 600 MHz.

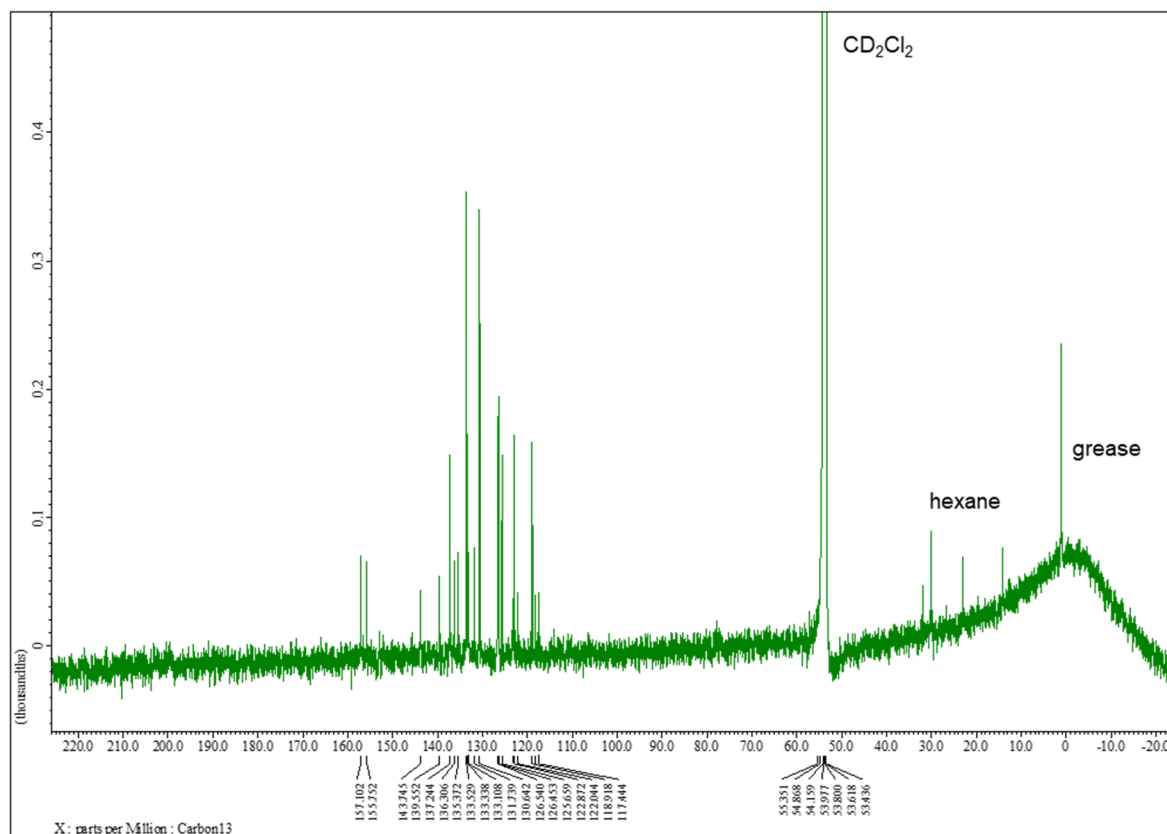
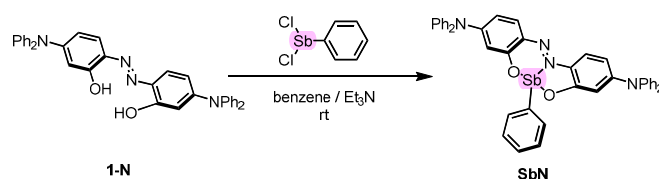


Chart S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **Cl-Sb5** in CD_2Cl_2 at 151 MHz.

Synthesis of **SbN**



In the glove box filled with inert argon gas, triphenyl antimony (1 equiv.) and antimony trichloride (2 equiv.) were placed in the flask and stirred and disproportionated for 3 days. After producing monophenyl antimony dichloride (PhSbCl_2 , 0.148 g, 0.547 mmol, 1 equiv.) as liquid, it was placed in the two-neck round bottom flask. Also, **1-N** was placed in the two-neck round flask and filled the nitrogen gas with the Schlenk technique. After adding benzene (40 mL) and triethylamine (Et_3N , 10 mL), the solution of **1-N** (0.300 g, 0.547 mmol, 1 equiv.) was added to the solution of PhSbCl_2 and stirred for 5 h. The reaction mixture was filtrated and washed with benzene and removed the solvent by evaporation. The residue was recrystallized from CH_2Cl_2 (good solvent) / acetonitrile (poor solvent) and afforded **SbN** (0.213 g, 0.285 mmol, 52%) as a brown crystal.

Characterization:

^1H NMR ($\text{DMSO}-d_6$, 400 MHz) δ 7.57–7.55 (m, 2H), 7.47–7.43 (m, 4H), 7.39–7.34 (m, 7H), 7.30–7.07 (m, 14H), 6.28 (dd, $J = 9.1, 2.3$ Hz, 1H), 6.20 (d, $J = 2.3$ Hz, 1H), 6.16 (dd, $J = 9.0, 2.2$ Hz, 1H), 5.93 (d, $J = 2.3$ Hz, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{DMSO}-d_6$, 101 MHz) δ 162.5, 158.5, 154.4, 153.0, 151.0, 146.4, 144.9, 135.3, 133.1, 132.5, 132.2, 129.9, 129.7, 129.3, 128.4, 127.0, 126.1, 125.6, 124.3, 117.7, 111.9, 110.4, 109.5, 107.9 ppm; HRMS (ESI) calcd. for $\text{C}_{42}\text{H}_{31}\text{N}_2\text{O}_2\text{SbNa}$ $[\text{M}+\text{Na}]^+$: 767.1377, found: 767.1377.

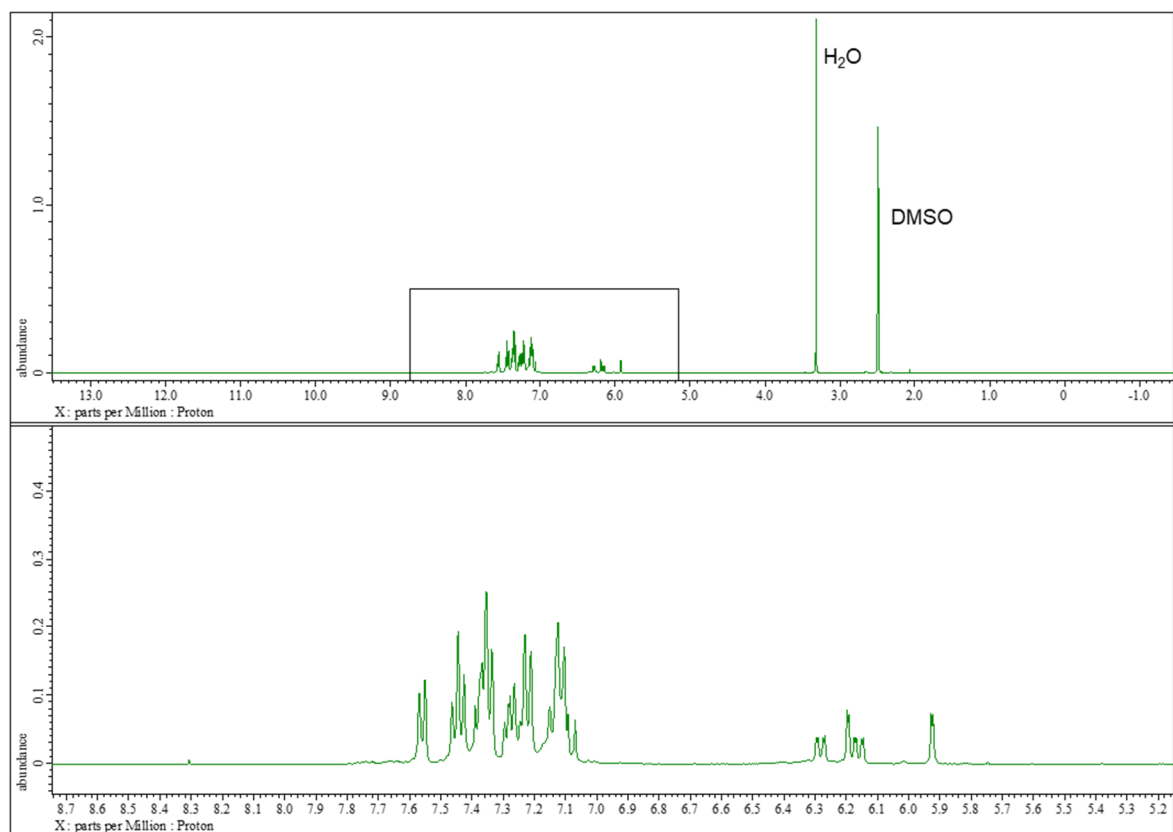


Chart S7. ^1H NMR spectrum of **SbN** in $\text{DMSO-}d_6$ at 400 MHz.

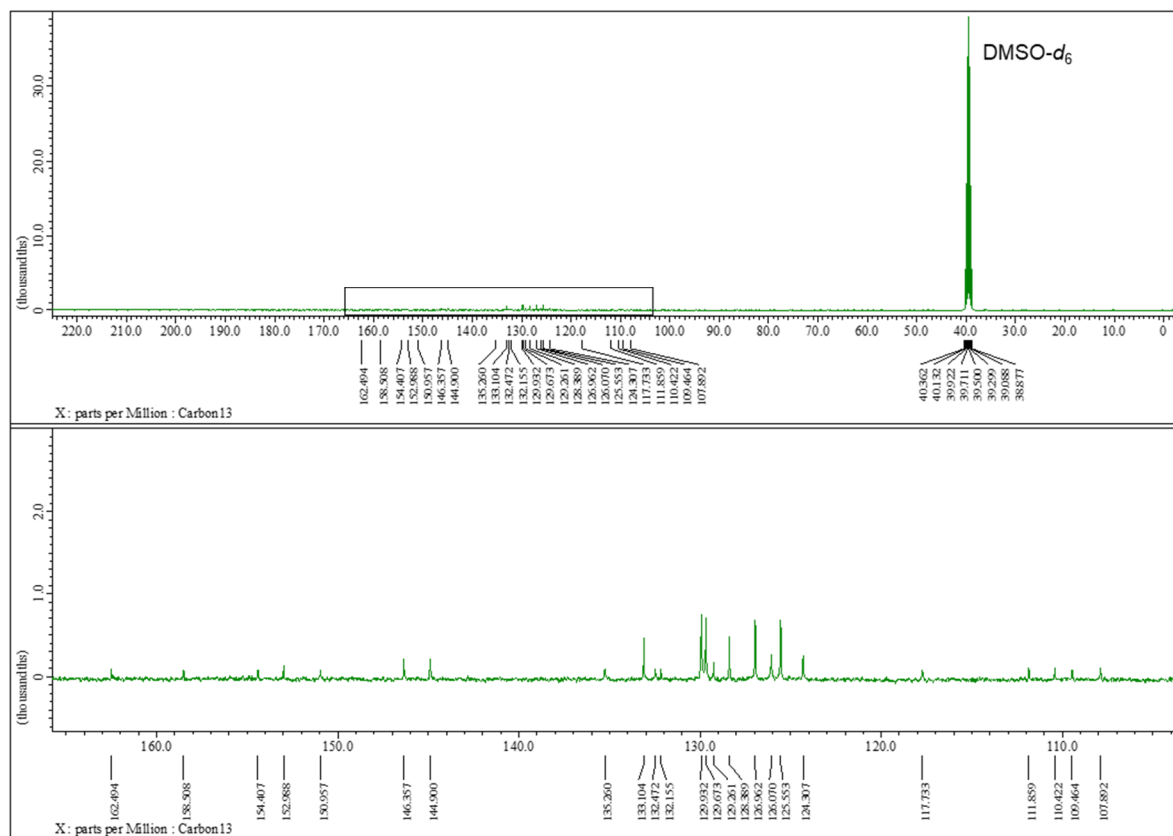
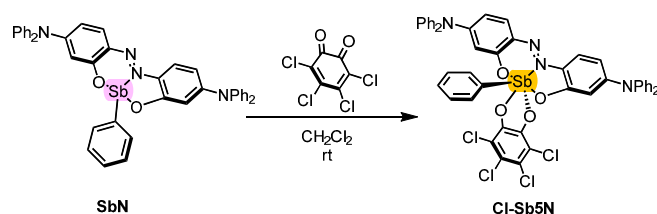


Chart S8. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **SbN** in $\text{DMSO-}d_6$ at 100 MHz.

Synthesis of **Cl-Sb5N**



SbN (0.0500 g, 0.0671 mmol, 1 equiv.) was placed in the two-neck round bottom flask. After degassing and filling the nitrogen gas three times, CH_2Cl_2 (5 mL) was added to the flask. Next, *o*-chloranil (0.0181 g, 0.0738 mmol, 1.1 equiv.) was added to the solution of **SbN** and stirred for 30 minutes at room temperature. The reaction mixture was evaporated by a rotary evaporator. The residue was dissolved in dichloromethane and reprecipitated by adding acetonitrile (MeCN). The solid **Cl-Sb5N** (0.0550 g, 0.0555 mmol, 83%) was washed by MeCN and collected by filtration as a blue powder.

Characterization:

^1H NMR (CDCl_3 , 400 MHz) δ 7.75 (m, 2H), 7.60–7.12 (m, 25H), 6.55–6.50 (m, 2H), 6.36 (d, $J = 2.3$ Hz, 1H), 6.18 (d, $J = 2.3$ Hz, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz) δ 158.0, 156.2, 155.5, 152.8, 146.3, 144.7, 144.6, 144.1, 141.4, 136.8, 133.3, 132.4, 132.3, 130.3, 130.1, 130.0, 127.8, 127.7, 127.4, 126.9, 125.6, 122.4, 121.1, 117.8, 117.2, 117.0, 114.3, 113.3, 108.0, 107.0 ppm; HRMS (ESI) calcd. for $\text{C}_{48}\text{H}_{31}\text{N}_4\text{O}_4\text{SbNa}$ $[\text{M}+\text{Na}]^+$: 1011.0030, found: 1011.0027.

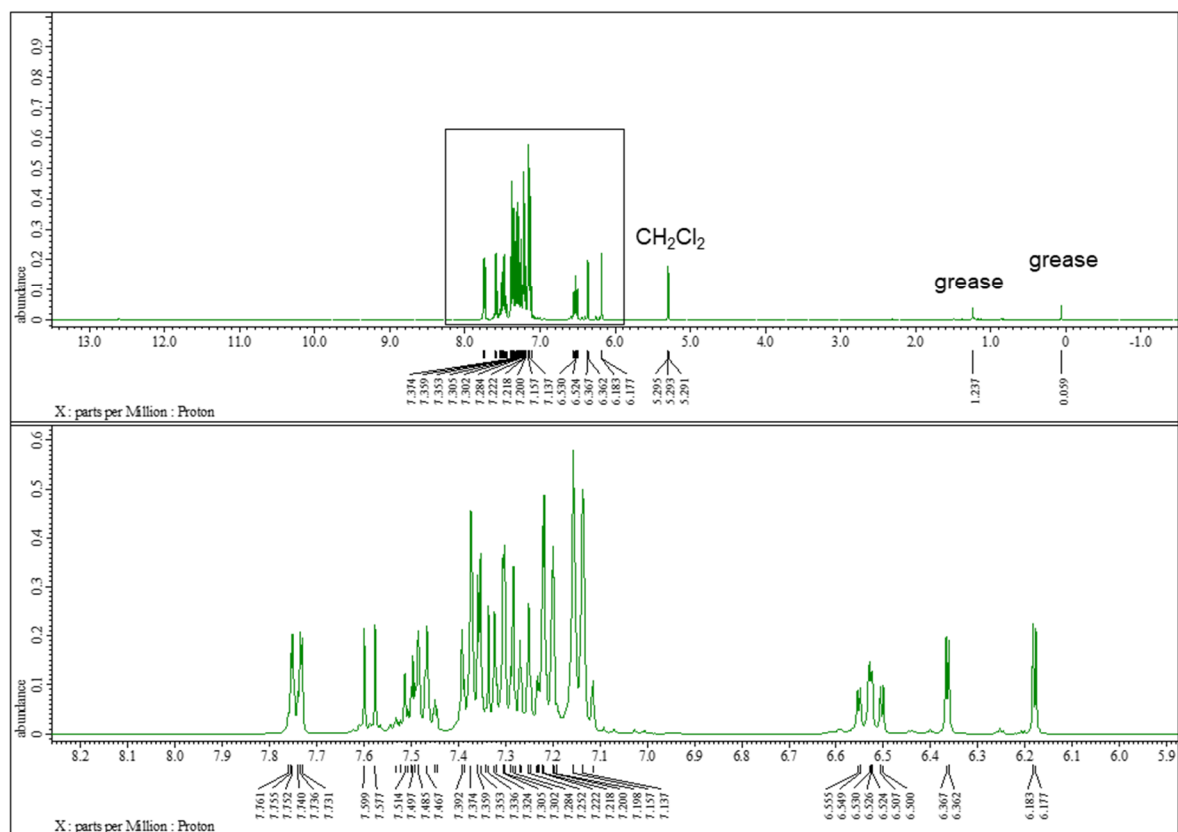


Chart S9. ¹H NMR spectrum of Cl-Sb5N in CD₂Cl₂ at 400 MHz.

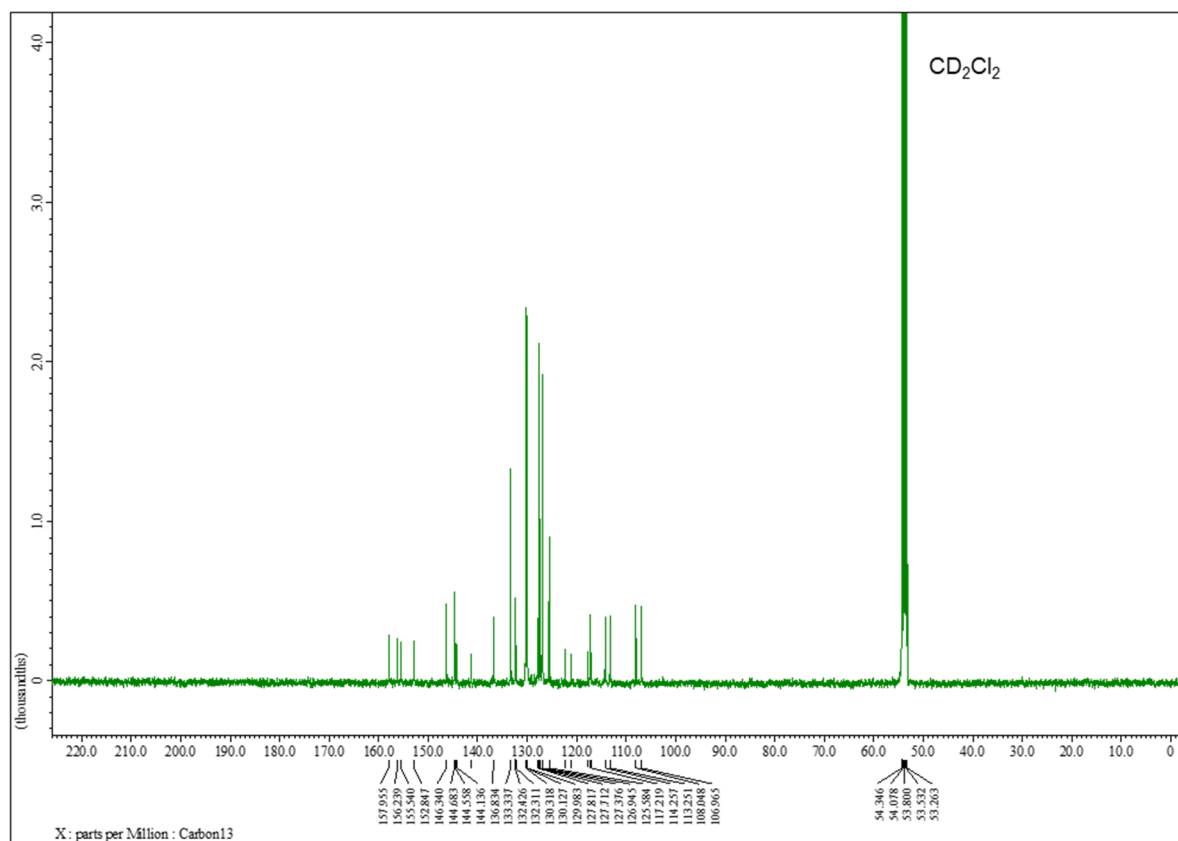


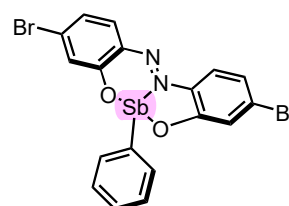
Chart S10. ¹³C{¹H} NMR spectrum of Cl-Sb5N in CD₂Cl₂ at 100 MHz.

Single crystal X-ray structure analysis of Sb

Intensity data were collected on a Rigaku Saturn 724+ with MicroMax-007HF CCD diffractometer with Varimax Mo optics using graphite-monochromated MoK α radiation. The structures were solved and refined by full-matrix least-squares procedures based on F² (SHELXL-2018/3).^[7]

Table S1. Crystallographic data of **Sb**

Empirical formula	C18 H11 Sb Br2 N2 O2
Formula weight	568.86
Temperature (K)	143
Wavelength (Å)	0.71075
Crystal system, space group	Triclinic, <i>P</i> -1
Unit cell dimensions (Å)	a = 9.051(11) b = 9.804(11) c = 10.586(11)
Unit cell dimensions (°)	α = 97.841(10) β = 94.663(15) γ = 108.59(3)
Volume (Å ³)	874.2(17)
Z, calculated density (g cm ⁻³)	2, 2.161
Absorption coefficient	6.163
F(000)	540
Crystal size (mm)	0.11×0.10×0.03
θ range for data collection (°)	3.0-27.5
Limiting indices	-11≤h≤11, -12≤k≤12, -13≤l≤10
Reflections collected (unique)	7122/2725, [R(int)=0.0760]
Completeness to theta	0.952
Max. and min. transmission	1.000, 0.708
Goodness-of-fit on <i>F</i> ²	0.792
Final R indices [<i>I</i> > 2σ(<i>I</i>)] ^[a]	<i>R</i> ₁ = 0.0467, w <i>R</i> ₂ = 0.0971
R indices (all data)	<i>R</i> ₁ = 0.0607 w <i>R</i> ₂ = 0.0989



CCDC # 2387699

[a] $R_1 = \Sigma(|F_0| - |F_c|) / \Sigma|F_0|$, $wR_2 = [\Sigma w(F_0^2 - F_c^2)^2 / \Sigma w(F_0^2)^2]^{1/2}$, $w = 1 / [\sigma^2(F_0^2) + (ap)^2 + bp]$, where $p = [\max(F_0^2, 0) + 2F_c^2] / 3$.

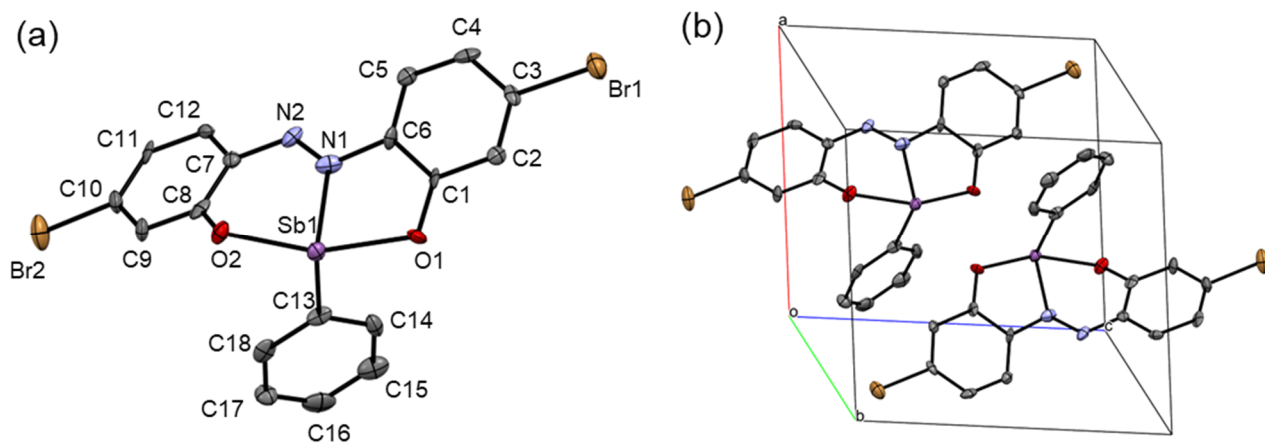
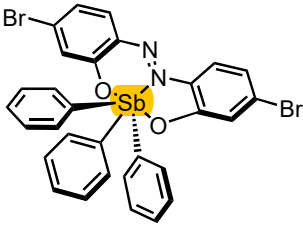


Figure S1. (a) ORTEP drawings and (b) packing diagrams of **Sb**. Thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms are omitted for clarity.

Single crystal X-ray structure analysis of Sb5

Intensity data were collected on a Rigaku Saturn 724+ with MicroMax-007HF CCD diffractometer with Varimax Mo optics using graphite-monochromated MoK α radiation. The structures were solved and refined by full-matrix least-squares procedures based on F² (SHELXL-2018/3).^[7]

Table S2. Crystallographic data of **Sb5**

Empirical formula	C30 H21 Sb Br2 N2 O2	
Formula weight	723.06	
Temperature (K)	143	
Wavelength (Å)	0.71075	CCDC # 2387700
Crystal system, space group	Monoclinic, C 2/c	
Unit cell dimensions (Å)	a = 25.149(8) b = 9.583(3) c = 21.986(7)	
Unit cell dimensions (°)	α = 90 β = 97.832(5) γ = 90	
Volume (Å³)	5249(3)	
Z, calculated density (g cm⁻³)	8, 1.830	
Absorption coefficient	4.127	
F(000)	2816	
Crystal size (mm)	0.11×0.10×0.02	
θ range for data collection (°)	3.0–27.5	
Limiting indices	$-32 \leq h \leq 32$, $-12 \leq k \leq 11$, $-28 \leq l \leq 22$	
Reflections collected (unique)	20708/8019, [R(int)=0.0527]	
Completeness to theta	0.994	
Max. and min. transmission	1.000, 0.845	
Goodness-of-fit on F^2	0.954	
Final R indices [$I > 2\sigma(I)$]^[a]	$R_1 = 0.0334$, $wR_2 = 0.0588$	
R indices (all data)	$R_1 = 0.0459$, $wR_2 = 0.0632$	

[a] $R_1 = \Sigma(|F_0| - |F_c|) / \Sigma|F_0|$, $wR_2 = [\Sigma w(F_0^2 - F_c^2)^2 / \Sigma w(F_0^2)^2]^{1/2}$, $w = 1 / [\sigma^2(F_0^2) + (ap)^2 + bp]$, where $p = [\max(F_0^2, 0) + 2F_c^2] / 3$.

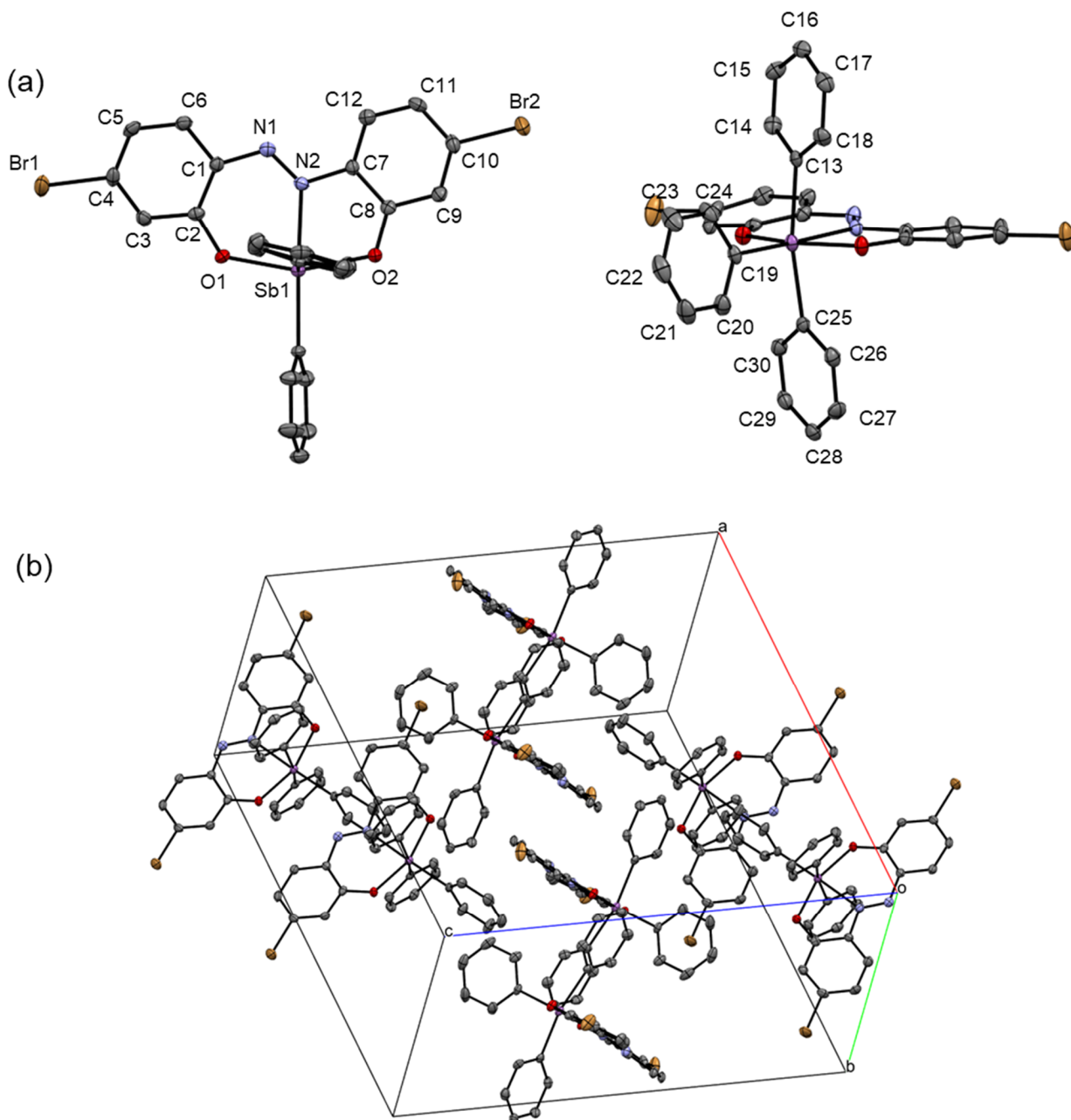
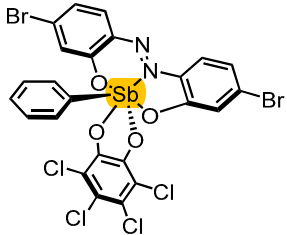


Figure S2. (a) ORTEP drawings and (b) packing diagrams of **Sb5**. Thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms are omitted for clarity.

Single crystal X-ray structure analysis of Cl-Sb5

Intensity data were collected on a Rigaku Saturn 724+ with MicroMax-007HF CCD diffractometer with Varimax Mo optics using graphite-monochromated MoK α radiation. The structures were solved and refined by full-matrix least-squares procedures based on F² (SHELXL-2018/3).^[7]

Table S3. Crystallographic data of Cl-Sb5

Empirical formula	C24 H11 Sb1 Br2 N2 O4 Cl4	
Formula weight	814.72	
Temperature (K)	143	
Wavelength (Å)	0.71075	
Crystal system, space group	Triclinic, <i>P</i> -1	CCDC # 2387701
Unit cell dimensions (Å)	<i>a</i> = 10.480(3) <i>b</i> = 11.605(4) <i>c</i> = 13.184(4)	
Unit cell dimensions (°)	α = 93.187(3) β = 102.989(4) γ = 106.132(5)	
Volume (Å³)	1488.9(8)	
Z, calculated density (g cm⁻³)	2, 1.817	
Absorption coefficient	4.001	
F(000)	780	
Crystal size (mm)	0.09×0.05×0.02	
θ range for data collection (°)	3.2–27.5	
Limiting indices	–13 ≤ <i>h</i> ≤ 13, –14 ≤ <i>k</i> ≤ 15, –16 ≤ <i>l</i> ≤ 17	
Reflections collected (unique)	12108/6523, [R(int)=0.0387]	
Completeness to theta	0.955	
Max. and min. transmission	1.000, 0.854	
Goodness-of-fit on <i>F</i>²	0.949	
Final R indices [<i>I</i> > 2σ(<i>I</i>)]^[a]	<i>R</i> ₁ = 0.0379, <i>wR</i> ₂ = 0.0682	
R indices (all data)	<i>R</i> ₁ = 0.0504, <i>wR</i> ₂ = 0.0722	

[a] $R_1 = \Sigma(|F_0| - |F_c|) / \Sigma|F_0|$, $wR_2 = [\Sigma w(F^2_0 - F^2_c) / \Sigma w(F^2_0)]^{1/2}$, $w = 1 / [\sigma^2(F^2_0) + (ap)^2 + bp]$, where $p = [\max(F^2_0, 0) + 2F^2_c] / 3$.

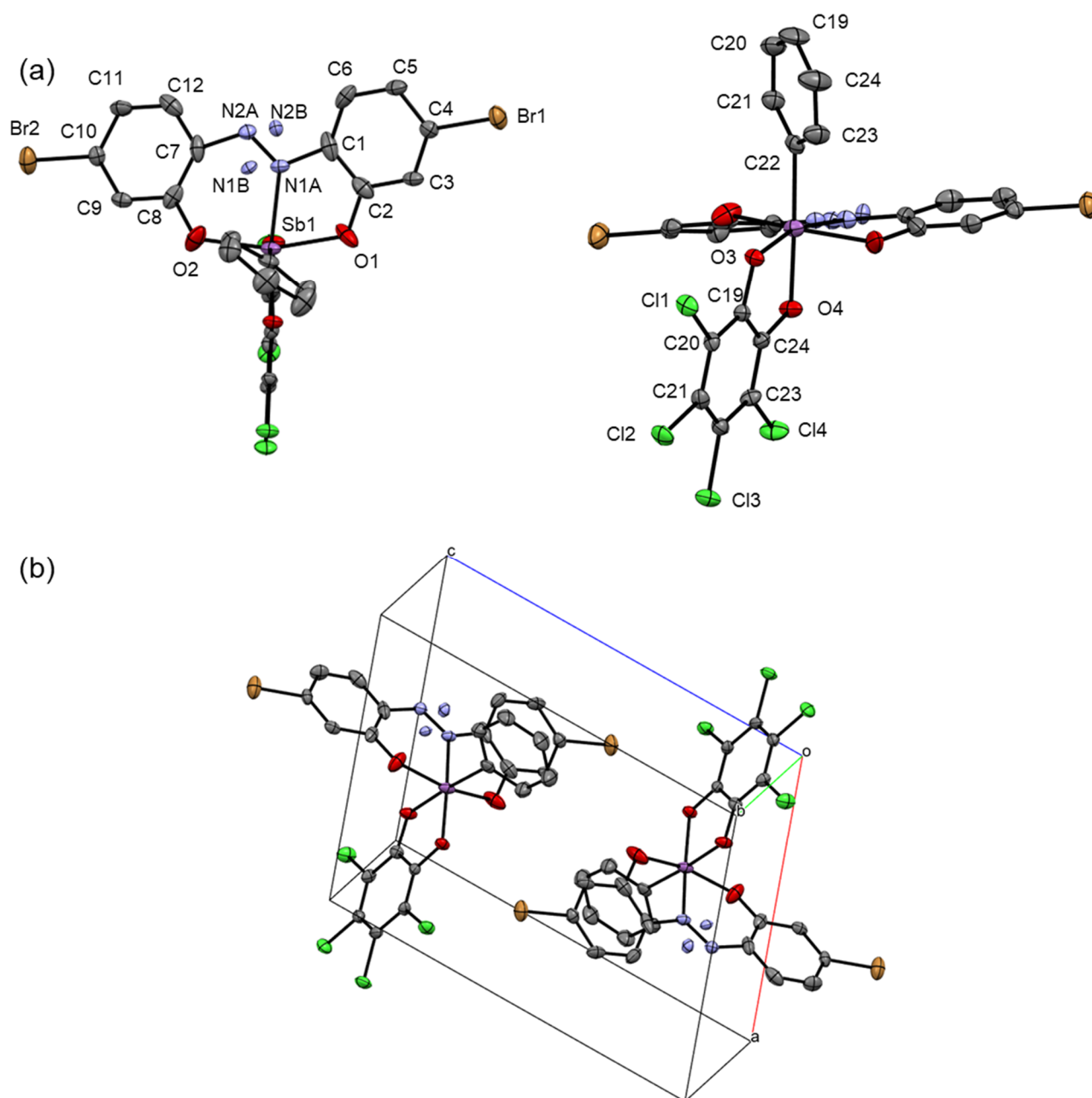


Figure S3. (a) ORTEP drawings and (b) packing diagrams of **Cl-Sb5**. Thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms are omitted for clarity.

Computational details for theoretical calculation

The Gaussian 16 program^[10] package was used for computation. We optimized the structures of the azobenzene, **Az**, **Sb**, **Sb5**, **Cl-Sb5**, **SbN**, and **Cl-Sb5N** in the ground S_0 states and calculated their molecular orbitals. The DFT was applied to optimize the structures in the S_0 states at B3LYP/6-31G(d) level for C, H, N, O, Cl and LanL2DZ for Br and Sb levels. We calculated the energy of the S_0 - S_1 transition with optimized geometries in the S_0 states by time-dependent (TD) DFT at B3LYP/6-31G(d) level for C, H, N, O, Cl and LanL2DZ for Br and Sb levels. Natural bond orbital (NBO) calculation was carried out by DFT at TD-B3LYP/6-31G(d) level for C, H, N, O, Cl and LanL2DZ for Br and Sb levels.

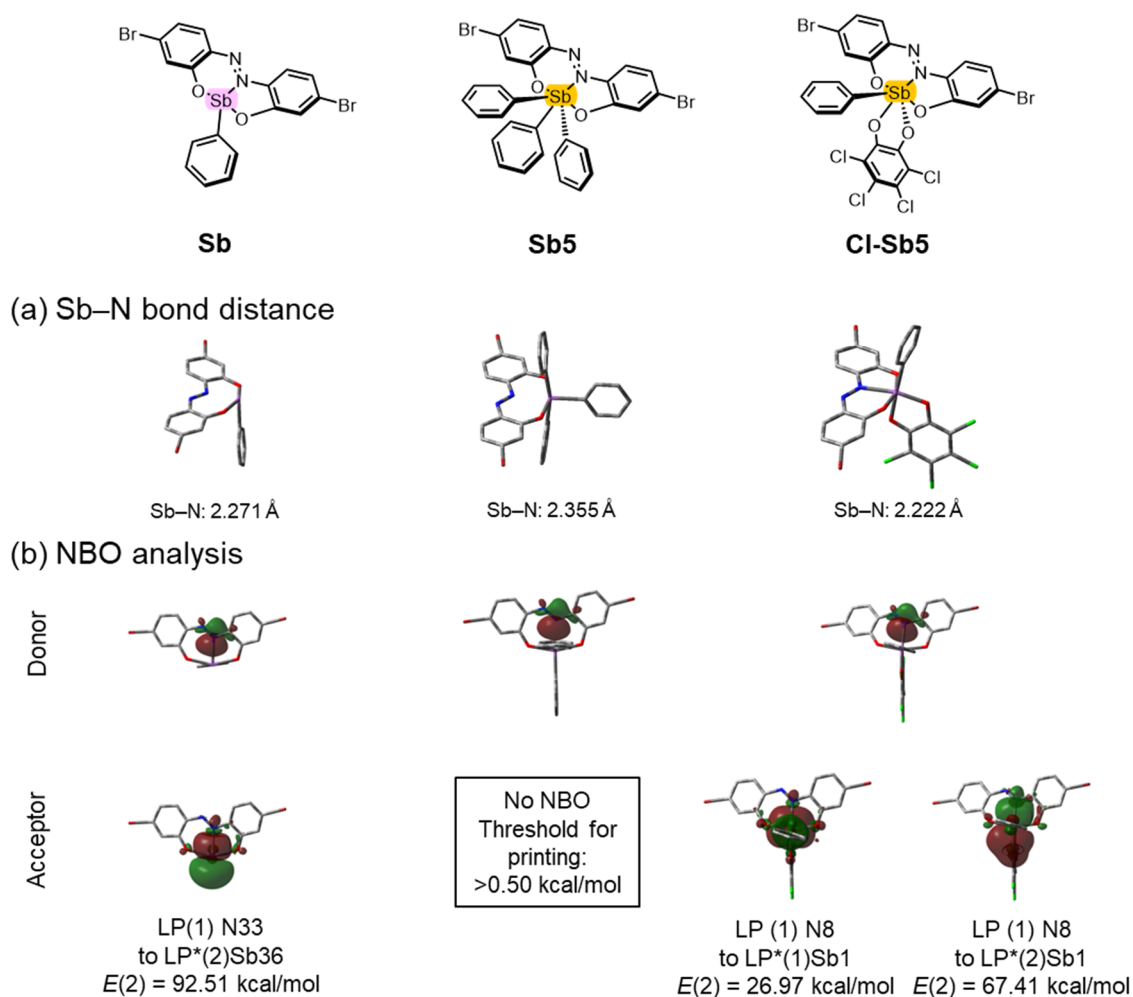


Figure S4. (a) Optimized structure of **Sb**, **Sb5**, and **Cl-Sb5**. (b) NBO plots showing the donor–acceptor interaction between a vacant p(Sb) orbital with a filled p(N) orbital (isovalue = 0.02) in **Sb**, **Sb5**, and **Cl-Sb5**. In **Sb5**, acceptor orbital derived from antimony was not observed because of weak interaction between antimony and nitrogen atom.

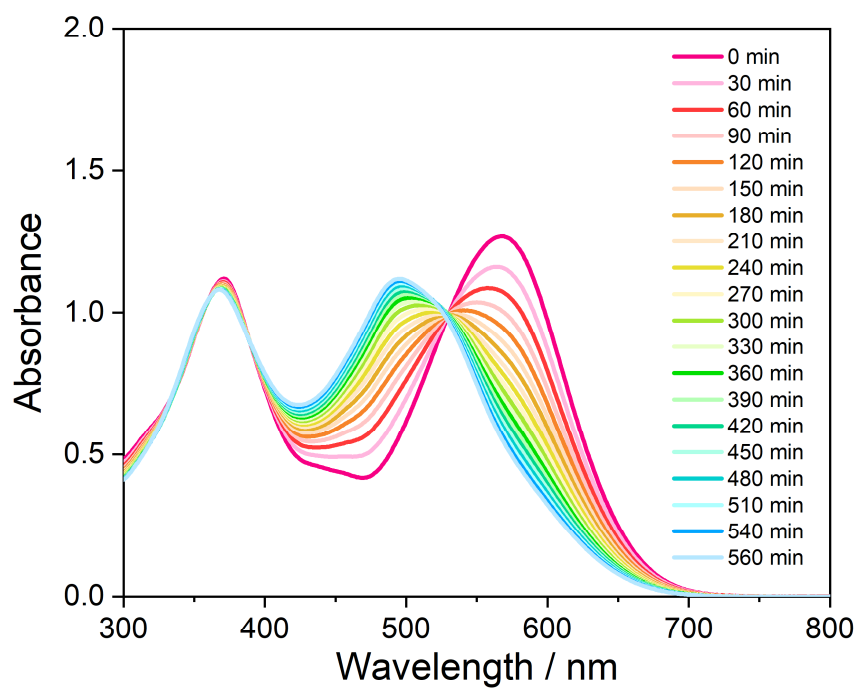


Figure S5. Time-dependent UV-vis absorption spectra of **Sb** (1.0×10^{-5} M in toluene under inert conditions).

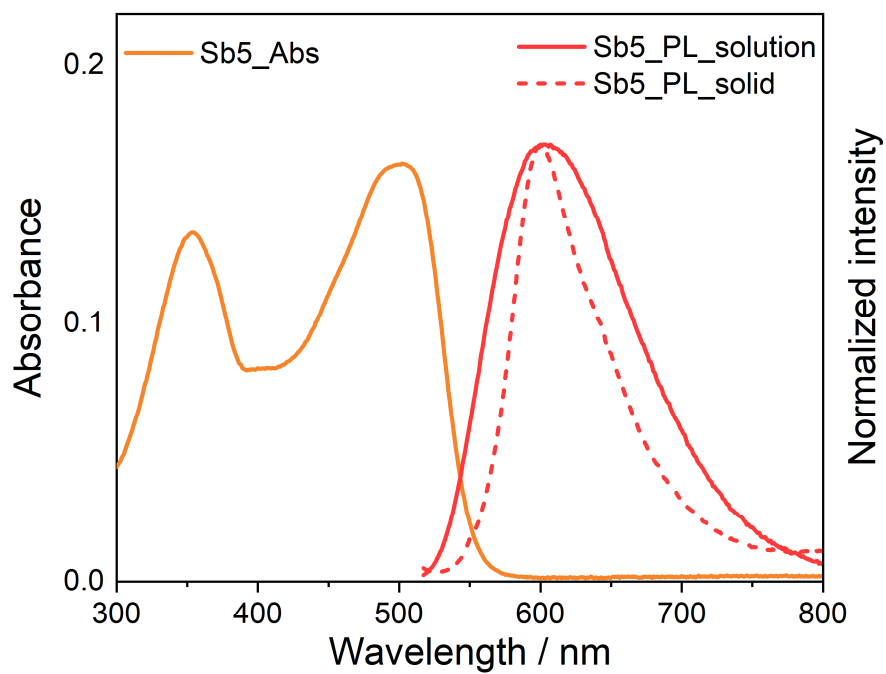
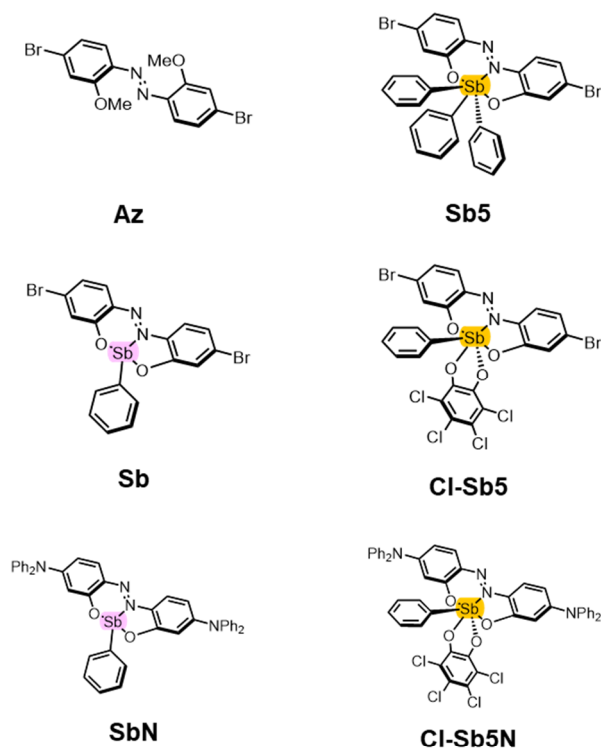


Figure S6. UV-vis absorption and PL spectra of **Sb5** (1.0×10^{-5} M in toluene and PL in solid state).

Table S4. Optical properties of the hypervalent antimony compounds^a



	$\lambda_{\text{abs, max}} / \text{nm}$	$\lambda_{\text{PL, max}} / \text{nm}$	QY / %
Az	380	---	---
Sb	567	---	---
Sb5	502	600	1.3
Cl-Sb5	529	---	---
SbN	640	753	4.6
Cl-Sb5N	664	777	5.3

^aIn toluene (1.0×10^{-5} M). Absolute FL quantum yield, excited at absorption maxima for each compound. **Sb** and **SbN** were measured under the N_2 atmosphere.

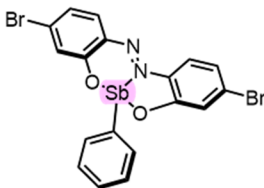
Table S5. Selected MOs and oscillator strengths (*f*) of selected transition bands of **Az**^a

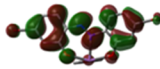
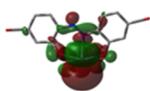
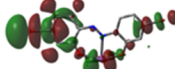
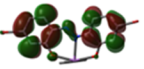
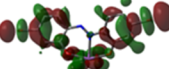
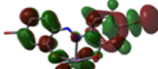
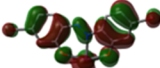
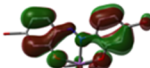
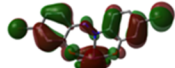
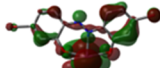
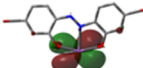
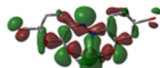
LUMO	LUMO+1	LUMO+2	LUMO+3	LUMO+4	LUMO+5
-2.09 eV	-0.32 eV	-0.30 eV	-0.17 eV	-0.15 eV	0.02 eV
HOMO	HOMO-1	HOMO-2	HOMO-3	HOMO-4	HOMO-5
-5.69 eV	-5.84 eV	-6.55 eV	-6.78 eV	-7.15 eV	-7.91 eV

Excited State	Excitation Energy / eV	Wavelength / nm	Oscillator Strength	Assignment (weight)
1	2.2884	541.79	0.0000	HOMO -> LUMO (0.70324)
2	3.4379	360.64	0.8525	HOMO-3 -> LUMO (0.12949) HOMO-1 -> LUMO (0.69399)
3	3.8785	319.67	0.0000	HOMO-2 -> LUMO (0.68447) HOMO-1 -> LUMO+5 (-0.10119)

^aObtained with DFT and TD-DFT calculations at TD-B3LYP/6-31G(d)//B3LYP/6-31G(d) level for C, H, N, O, and LanL2DZ for Br (isovalue=0.02).

Table S6. Selected MOs and oscillator strengths (*f*) of selected transition bands of **Sb^a**



	LUMO	LUMO+1	LUMO+2	LUMO+3	LUMO+4	LUMO+5
Side						
Top						
	-3.08 eV	-1.52 eV	-0.55 eV	-0.51 eV	-0.38 eV	-0.33 eV
	HOMO	HOMO-1	HOMO-2	HOMO-3	HOMO-4	HOMO-5
Side						
Top						
	-5.81 eV	-6.62 eV	-6.83 eV	-6.97 eV	-6.99 eV	-7.31 eV
Excited State	Excitation Energy / eV	Wavelength / nm	Oscillator Strength	Assignment (weight)		
1	2.3639	524.48	0.2935	HOMO-2 -> LUMO (0.13551) HOMO -> LUMO (0.69151)		
2	2.9747	416.79	0.0197	HOMO-1 -> LUMO (0.69513)		
3	3.0498	406.53	0.0005	HOMO-7 -> LUMO (-0.15174) HOMO-6 -> LUMO (-0.17668) HOMO-5 -> LUMO (0.59097) HOMO-3 -> LUMO (0.27890)		

^aObtained with DFT and TD-DFT calculations at TD-B3LYP/6-31G(d)//B3LYP/6-31G(d) level for C, H, N, O, and LanL2DZ for Br, Sb (isovalue=0.02).

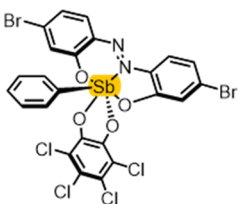
Table S7. Selected MOs and oscillator strengths (*f*) of selected transition bands of **Sb5^a**

	LUMO	LUMO+1	LUMO+2	LUMO+3	LUMO+4	LUMO+5
Side						
Top						
	-2.82 eV	-0.70 eV	-0.60 eV	-0.45 eV	-0.40 eV	-0.34 eV
	HOMO	HOMO-1	HOMO-2	HOMO-3	HOMO-4	HOMO-5
Side						
Top						
	-5.88 eV	-6.58 eV	-6.68 eV	-6.80 eV	-6.83 eV	-6.85 eV

Excited State	Excitation Energy / eV	Wavelength / nm	Oscillator Strength	Assignment (weight)
1	2.6896	460.97	0.3576	HOMO-3 -> LUMO (-0.13467) HOMO -> LUMO (0.69093)
2	2.7948	443.63	0.0023	HOMO-11 -> LUMO (0.19802) HOMO-2 -> LUMO (0.67341)
3	3.1815	389.70	0.0238	HOMO-1 -> LUMO (0.69706)

^aObtained with DFT and TD-DFT calculations at TD-B3LYP/6-31G(d)//B3LYP/6-31G(d) level for C, H, N, O, and LanL2DZ for Br, Sb (isovalue=0.02).

Table S8. Selected MOs and oscillator strengths (*f*) of selected transition bands of **Cl-Sb5^a**



	LUMO	LUMO+1	LUMO+2	LUMO+3	LUMO+4	LUMO+5
Side						
Top	 -3.62 eV	 -1.72 eV	 -1.15 eV	 -0.96 eV	 -0.82 eV	 -0.77 eV
	HOMO	HOMO-1	HOMO-2	HOMO-3	HOMO-4	HOMO-5
Side						
Top	 -5.96 eV	 -6.32 eV	 -6.53 eV	 -7.21 eV	 -7.37 eV	 -7.48 eV

Excited State	Excitation Energy / eV	Wavelength / nm	Oscillator Strength	Assignment (weight)
1	1.8164	682.60	0.0078	HOMO -> LUMO (0.70519)
2	2.2338	555.05	0.0009	HOMO-1 -> LUMO (0.70577)
3	2.6072	475.55	0.4205	HOMO-4 -> LUMO (-0.15786) HOMO-2 -> LUMO (0.67907)

^aObtained with DFT and TD-DFT calculations at TD-B3LYP/6-31G(d)//B3LYP/6-31G(d) level for C, H, N, O, Cl and LanL2DZ for Br, Sb (isovalue=0.02).

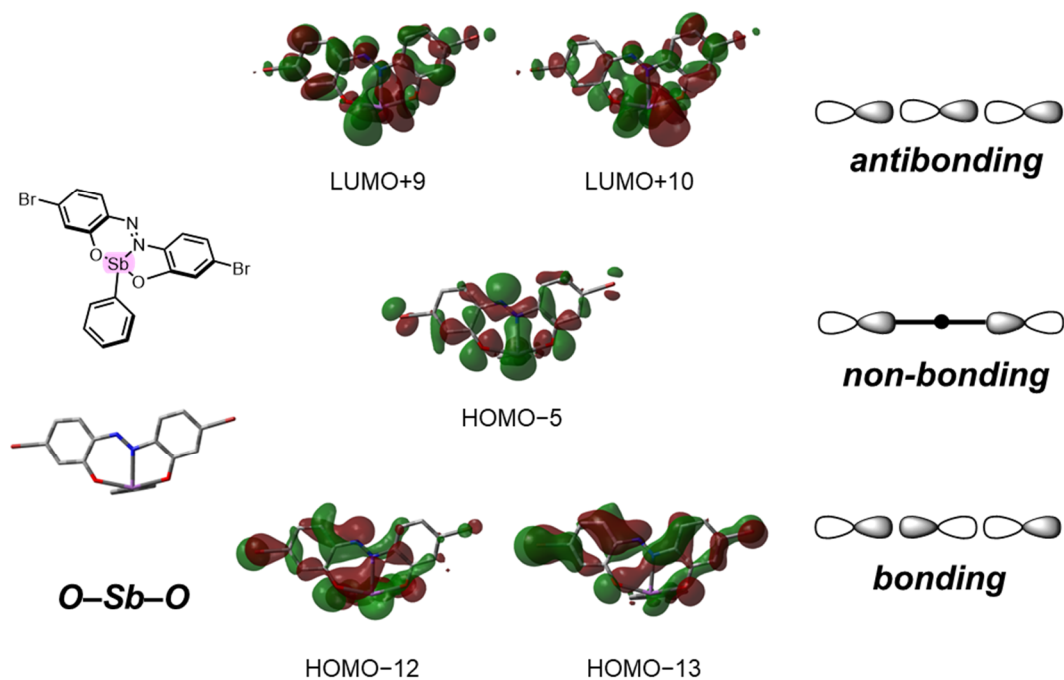


Figure S7. Bonding, non-bonding, and antibonding orbitals in the hypervalent O-Sb-O bond (3c-4e bond) of **Sb** obtained with DFT and TD-DFT calculations at the TD-B3LYP/6-31G(d)//B3LYP/6-31G(d) level for C, H, N, and O and LanL2DZ for Br and Sb (isovalue = 0.02).

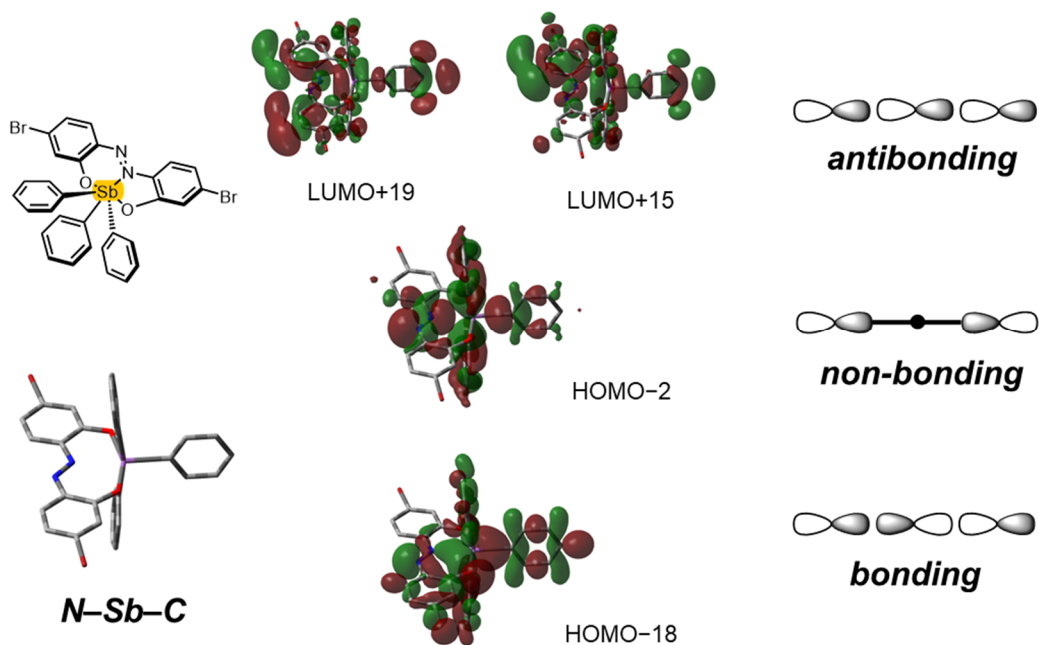


Figure S8. Bonding, non-bonding, and antibonding orbitals in the hypervalent N-Sb-C bond (3c-4e bond) of **Sb5** obtained with DFT and TD-DFT calculations at the TD-B3LYP/6-31G(d)//B3LYP/6-31G(d) level for C, H, N, and O and LanL2DZ for Br and Sb (isovalue = 0.02).

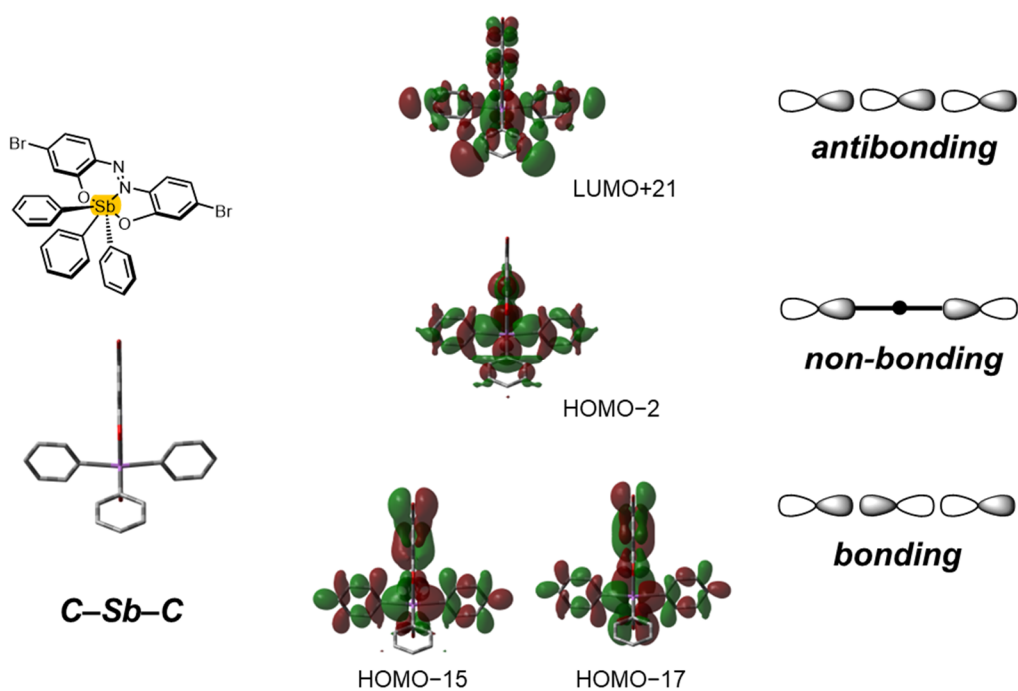


Figure S9. Bonding, non-bonding, and antibonding orbitals in the hypervalent C-Sb-C bond (3c-4e bond) of **Sb5** obtained with DFT and TD-DFT calculations at the TD-B3LYP/6-31G(d)//B3LYP/6-31G(d) level for C, H, N, and O and LanL2DZ for Br and Sb (isovalue = 0.02).

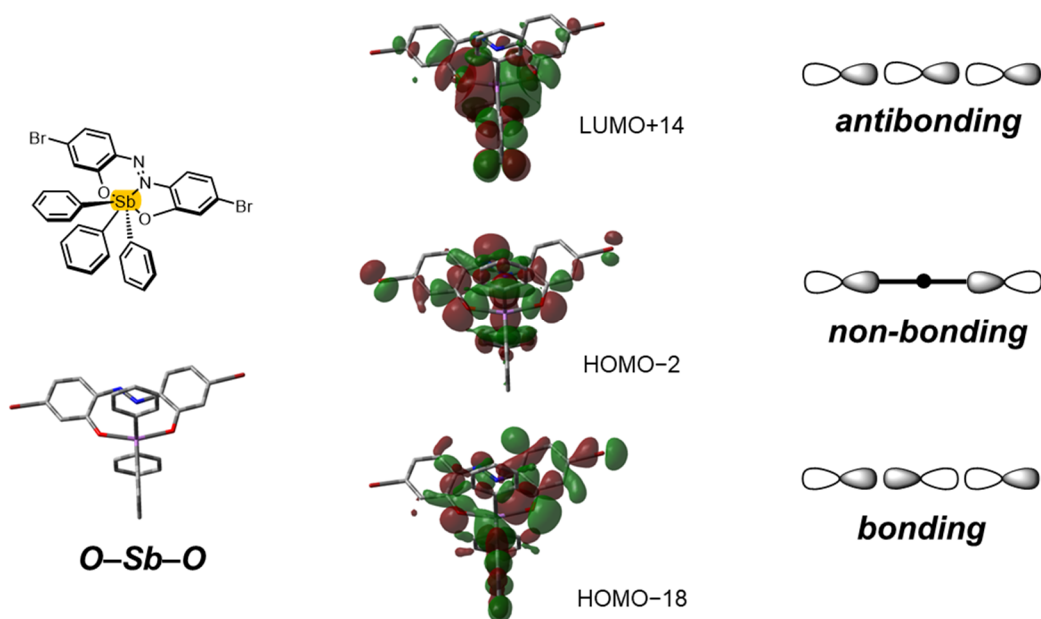


Figure S10. Bonding, non-bonding, and antibonding orbitals in the hypervalent O-Sb-O bond (3c-4e bond) of **Sb5** obtained with DFT and TD-DFT calculations at the TD-B3LYP/6-31G(d)//B3LYP/6-31G(d) level for C, H, N, and O and LanL2DZ for Br and Sb (isovalue = 0.02).

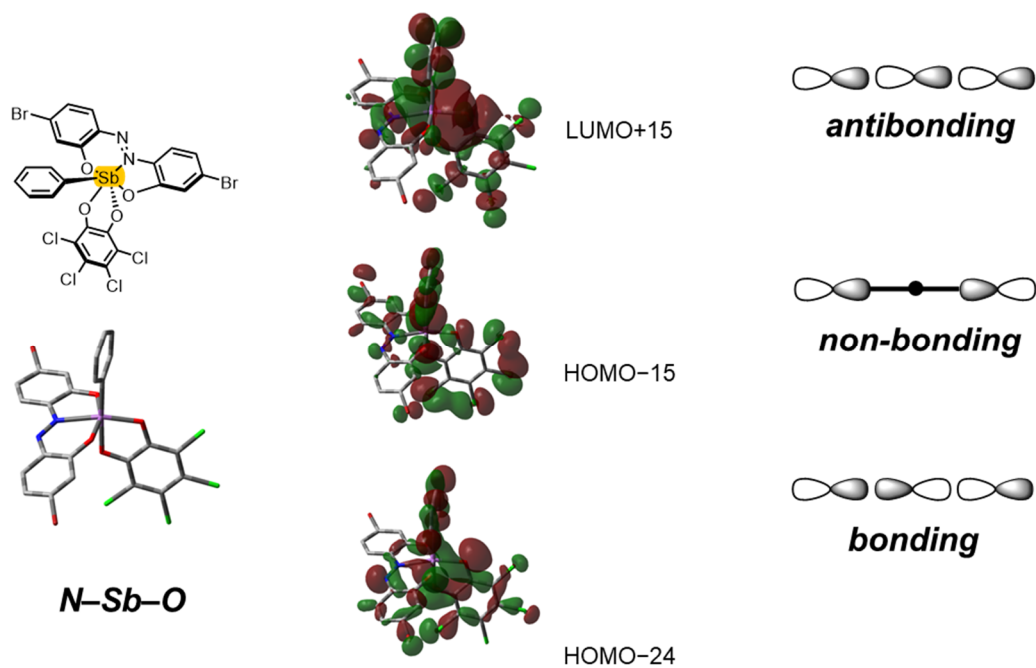


Figure S11. Bonding, non-bonding, and antibonding orbitals in the hypervalent N-Sb-O bond (3c-4e bond) of **Cl-Sb5** obtained with DFT and TD-DFT calculations at the TD-B3LYP/6-31G(d)//B3LYP/6-31G(d) level for C, H, N, O and Cl and LanL2DZ for Br and Sb (isovalue = 0.02).

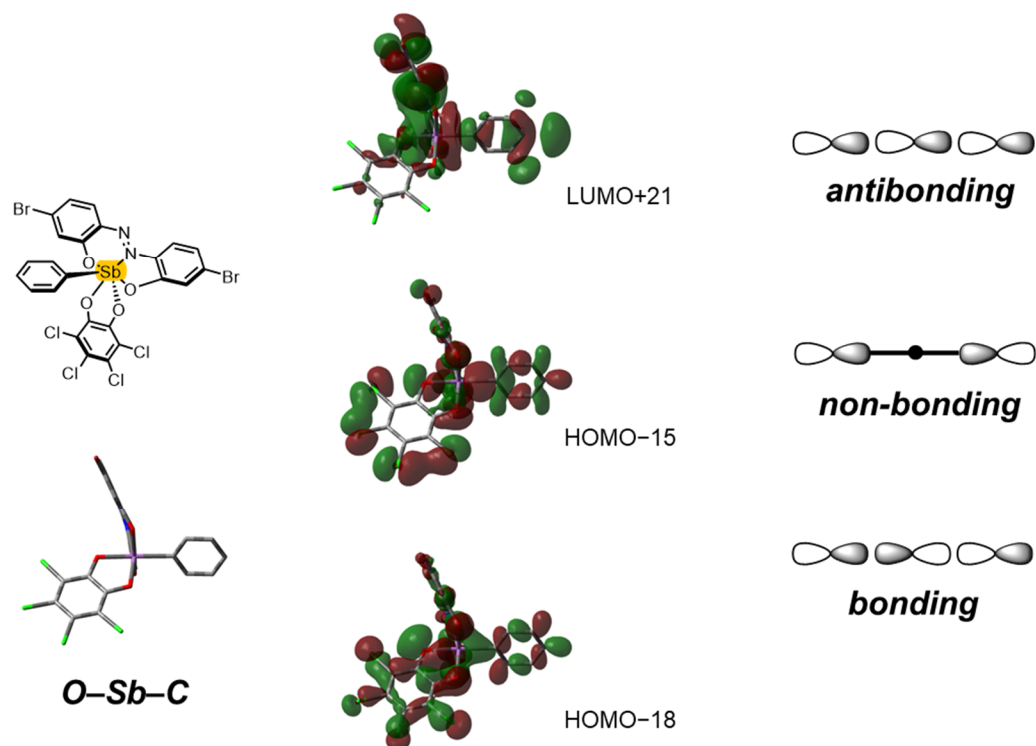


Figure S12. Bonding, non-bonding, and antibonding orbitals in the hypervalent O-Sb-C bond (3c-4e bond) of **Cl-Sb5** obtained with DFT and TD-DFT calculations at the TD-B3LYP/6-31G(d)//B3LYP/6-31G(d) level for C, H, N, O and Cl and LanL2DZ for Br and Sb (isovalue = 0.02).

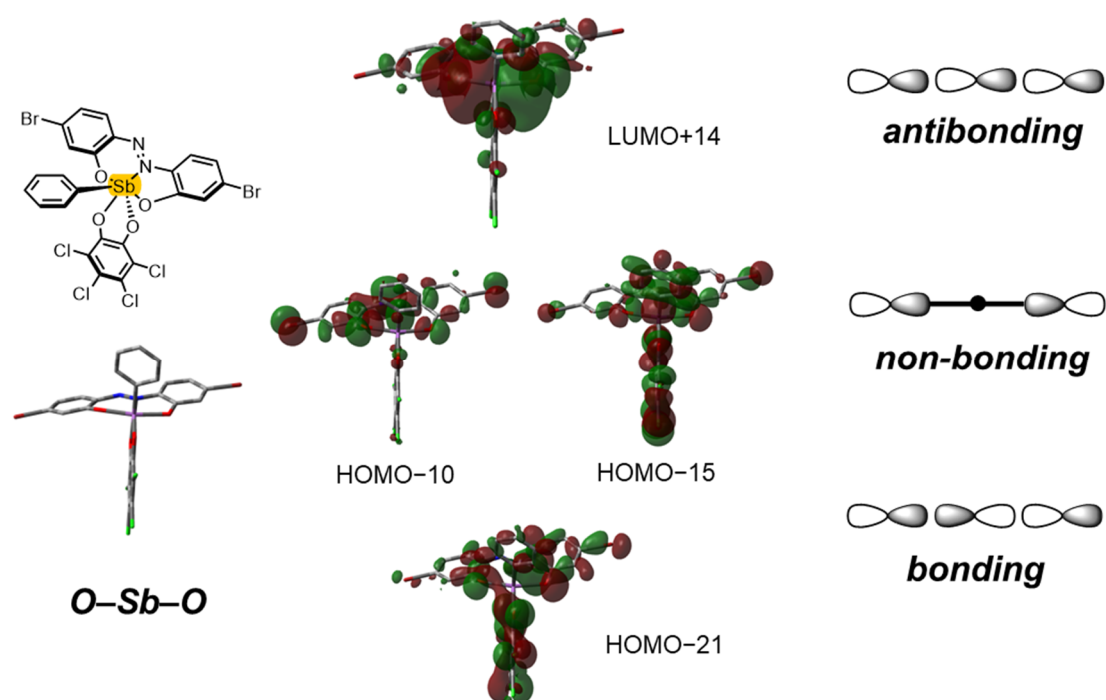


Figure S13. Bonding, non-bonding, and antibonding orbitals in the hypervalent O-Sb-O bond (3c-4e bond) of **Cl-Sb5** obtained with DFT and TD-DFT calculations at the TD-B3LYP/6-31G(d)//B3LYP/6-31G(d) level for C, H, N, O and Cl and LanL2DZ for Br and Sb (isovalue = 0.02).

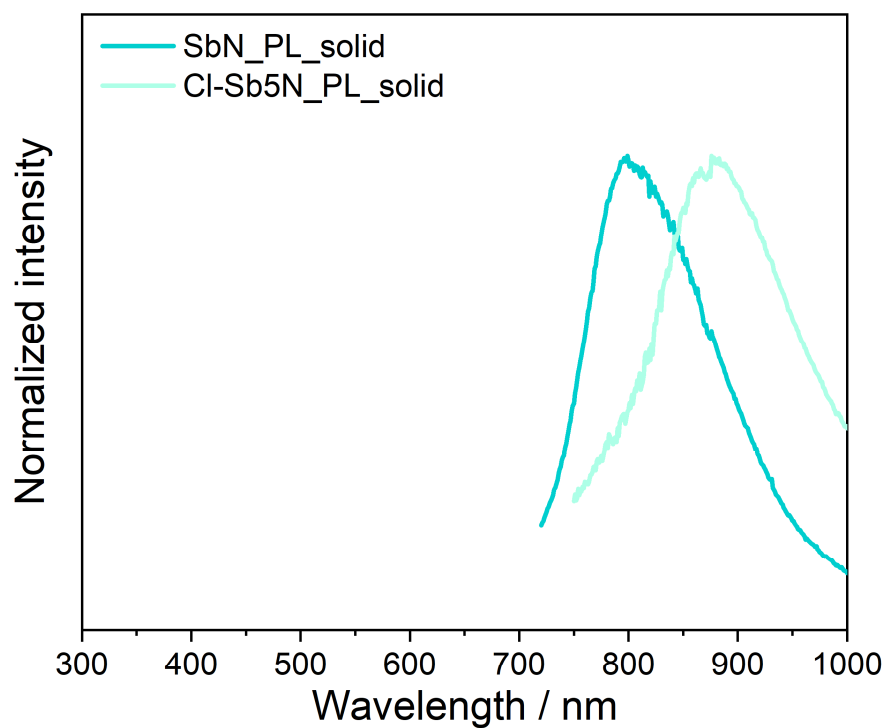


Figure S14. PL spectra of **SbN** and **Cl-Sb₅N** in solid state at room temperature with PMT P928 (250~810 nm) and DSS-IGA (810~1000 nm) as detectors.

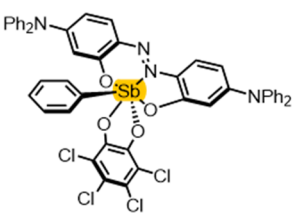
Table S9. Selected MOs and oscillator strengths (*f*) of selected transition bands of **SbN^a**

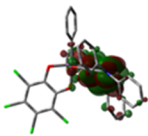
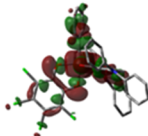
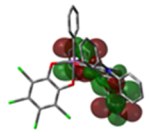
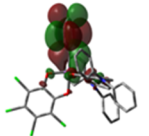
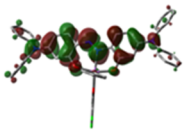
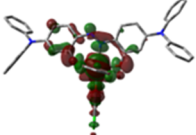
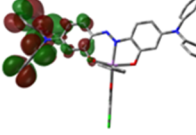
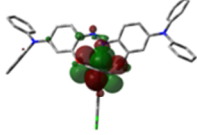
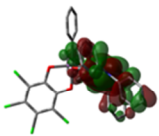
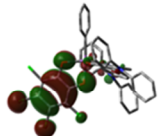
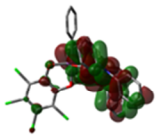
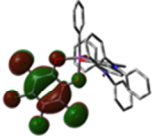
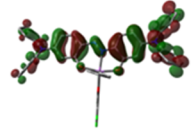
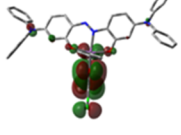
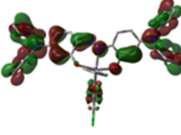
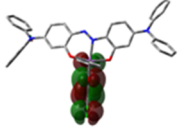
	LUMO	LUMO+1	LUMO+2	LUMO+3
Side				
Top				
	-2.31 eV	-0.89 eV	-0.53 eV	-0.41 eV
	HOMO	HOMO-1	HOMO-2	HOMO-3
Side				
Top				
	-4.68 eV	-5.34 eV	-5.59 eV	-5.98 eV

Excited State	Excitation Energy / eV	Wavelength / nm	Oscillator Strength	Assignment (weight)
1	2.1476	577.32	1.0779	HOMO -> LUMO (0.70403)
2	2.5917	478.40	0.0222	HOMO-2 -> LUMO (-0.28366) HOMO-1 -> LUMO (0.63834)
3	2.8436	436.01	0.1353	HOMO-3 -> LUMO (-0.22154) HOMO-2 -> LUMO (0.61248) HOMO-1 -> LUMO (0.25498)

^aObtained with DFT and TD-DFT calculations at TD-B3LYP/6-31G(d)//B3LYP/6-31G(d) level for C, H, N, O, and LanL2DZ for Br, Sb (isovalue=0.02).

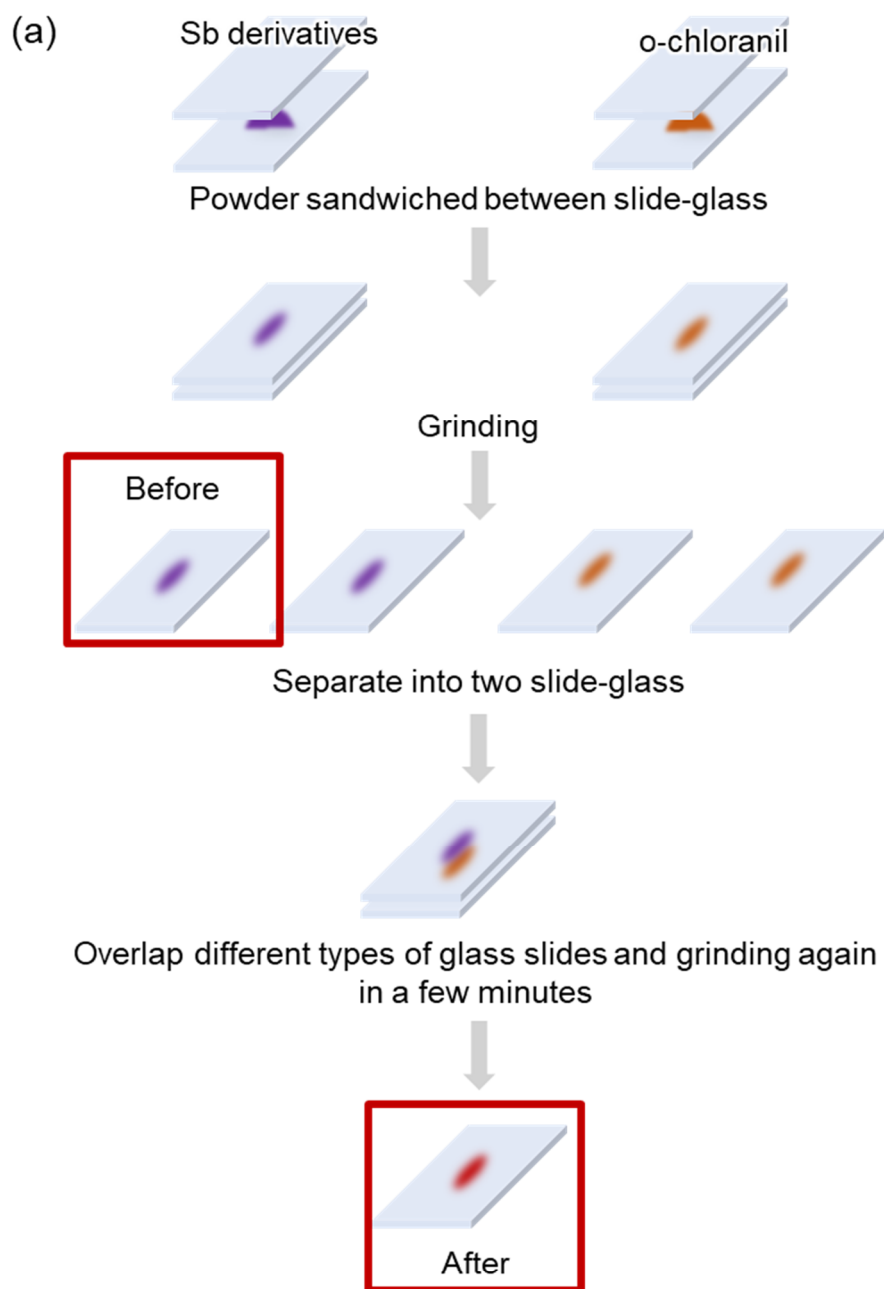
Table S10. Selected MOs and oscillator strengths (*f*) of selected transition bands of **Cl-Sb5N^a**



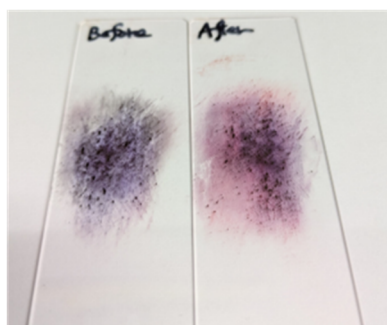
	LUMO	LUMO+1	LUMO+2	LUMO+3
Side				
Top	 -2.77 eV	 -1.03 eV	 -0.77 eV	 -0.65 eV
	HOMO	HOMO-1	HOMO-2	HOMO-3
Side				
Top	 -5.06 eV	 -5.51 eV	 -5.77 eV	 -5.95 eV

Excited State	Excitation Energy / eV	Wavelength / nm	Oscillator Strength	Assignment (weight)
1	2.1241	583.69	1.2084	HOMO -> LUMO (0.70314)
2	2.2291	556.20	0.0351	HOMO-1 -> LUMO (0.69916)
3	2.6946	460.12	0.0920	HOMO-4 -> LUMO (0.18256) HOMO-3 -> LUMO (-0.25405) HOMO-2-> LUMO (0.62106)

^aObtained with DFT and TD-DFT calculations at TD-B3LYP/6-31G(d)//B3LYP/6-31G(d) level for C, H, N, O, Cl and LanL2DZ for Br, Sb (isovalue=0.02).



(b)



(c)

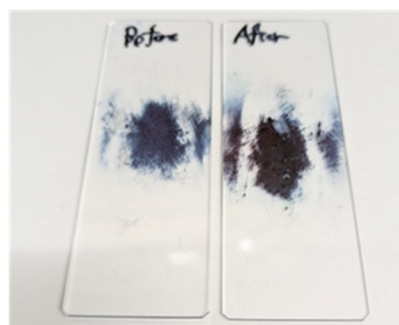


Figure S15. (a) Schematic illustration of grinding before and after Sb derivatives and *o*-chloranil. Photos of (b) **Sb** and (c) **SbN** before and after grinding with *o*-chloranil.

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