Macropolyhedral syn-B\textsubscript{18}H\textsubscript{22}, the “Forgotten” Isomer

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Cite This: https://doi.org/10.1021/jacs.3c05530

INTRODUCTION

As the search for new and unusual molecules and materials in various fields intensifies, boron hydrides emerge as fascinating candidates with properties substantially different from those of organic molecules. Among the boron hydrides, the structural motif of the deltahedron is the most common. A prominent position belongs to the isocarborane due to the exceptional stability and geometry of the \([\text{B}_{12}\text{H}_{12}]^{2-}\) dianion and its heteroatomic analogues, e.g., the 12-vertex carbaborane \([\text{C}_{2}\text{B}_{10}\text{H}_{12}]^{2-}\). Most boron hydride molecules with a number of boron atoms fewer than 12 take the form of a simple convex deltahedron or its open fragment, and they can thus be viewed as analogues of cyclic hydrocarbons. For boron hydrides with more than 12 skeletal atoms, the structures of the so-called macropolyhedral boranes are formed by the fusion of two or more polyhedra or polyhedral fragments, analogous to polycyclic hydrocarbons. Two of the largest known macropolyhedral boranes are the isomeric docosahydrooctadecaboranes \(\text{B}_{31}\text{H}_{42}\). They exhibit a unique molecular structure with two open faces and six acidic bridging hydrogen atoms (\(\mu\text{-HBB}\)). Their structural and chemical properties, together with their interaction with light, make \(\text{B}_{18}\text{H}_{22}\) a promising candidate for a wide range of applications, from energy storage, semiconductor doping, to nano- and optoelectronic devices. The molecular structure of \(\text{B}_{18}\text{H}_{22}\) can be viewed as two decaborane molecules condensed together, with each subcluster sharing atoms \(B(5)\) and \(B(6)\) in the decaborane numbering system, in common (Figure 1B,C). The isomer syn-\(\text{B}_{18}\text{H}_{22}\) on which this study focuses is a much less-studied (“forgotten”) system compared to its anti-\(\text{B}_{18}\text{H}_{22}\) isomer, and it has a 2-fold symmetry axis due to the fusion of two \{B10\} units sharing the \(B(5)\) and \(B(6)\) edge so that \(B(5)\equiv B(5')\) and \(B(6)\equiv B(6')\) (Figure 1B); in the anti-\(\text{B}_{18}\text{H}_{22}\) isomer, \(B(5)\equiv B(6')\) and \(B(6)\equiv B(5')\), which results in the inversion symmetry (Figure 1C). What has stimulated most of the recent interest in anti-\(\text{B}_{18}\text{H}_{22}\) and its substituted derivatives has mainly been their luminescence properties. Our interest in the “forgotten”, nonluminescent isomer, syn-\(\text{B}_{18}\text{H}_{22}\), has been stimulated mainly by its unique geometry and size with respect to its use as constituents of purely borane, carbon-free self-assembled monolayers and its further use toward 2-dimensional membranes with thickness below 1 nm and with a 3D-aromatic...
character, as well as capping ligands of atomically precise metal nanoclusters, a newly emerging class of materials with adjustable geometry, size, and properties.\textsuperscript{40,41}

Previously, we reported the thiol derivatives of decaborane (nido-B\textsubscript{10}H\textsubscript{14}), specifically [1-HS-nido-B\textsubscript{10}H\textsubscript{13}], [2-HS-nido-B\textsubscript{10}H\textsubscript{13}], and [1,2-(HS)\textsubscript{2}-nido-B\textsubscript{10}H\textsubscript{12}] as reactive building blocks for self-assembled monolayers (SAMs).\textsuperscript{32,43} Although the macropolyhedral cluster anti-B\textsubscript{18}H\textsubscript{22} has been extensively explored over the last decade, for various applications including lasers\textsuperscript{4} and semiconductor dopants,\textsuperscript{4,16,19} the syn-B\textsubscript{18}H\textsubscript{22} isomer has remained relatively unexplored, perhaps due to its supposed lack of luminescence. For numerous reasons mentioned foregoing, we have synthesized three new monothiol-substituted derivatives: [1-HS-syn-B\textsubscript{18}H\textsubscript{17}], [3-HS-syn-B\textsubscript{18}H\textsubscript{17}], and [4-HS-syn-B\textsubscript{18}H\textsubscript{17}]\textsuperscript{4}. We have found interesting interactions in the supramolecular structures, observed the changes in the molecular structure caused by substitution at different vertices, and, surprisingly and interestingly, observed luminescence not only in the novel thiol derivatives but also in the parent syn-B\textsubscript{18}H\textsubscript{22} molecule, which, until now, has been presented in various reports\textsuperscript{7,26} as the nonluminescent isomer of anti-B\textsubscript{18}H\textsubscript{22}. Also, we have observed that substitution affects its photophysical properties extensively. The syn-B\textsubscript{18}H\textsubscript{22} cluster functionalization thus promises new directions for novel materials with a range of properties and uses.

Boron hydrides as functional molecules, going beyond alkanethiol derivatives, and macropolyhedral borane derivatives assembled on metal or other substrate surfaces have not been investigated yet. Keeping all of this in mind, we delved into the world of macropolyhedral boron hydrides, explored the H functionalization of syn-octadecaborane, and investigated the impact of these modifications on its physical and chemical properties, together with the first preliminary view of these molecules as building blocks of carbon-free SAMs on a flat metal surface.

\section{RESULTS AND DISCUSSION}

Three thiol isomers of the octadecaborane cluster [1-HS-syn-B\textsubscript{18}H\textsubscript{17}]\textsuperscript{1} (two polymorphic structures labeled as PM1a and PM1b), [3-HS-syn-B\textsubscript{18}H\textsubscript{17}]\textsuperscript{3}, and [4-HS-syn-B\textsubscript{18}H\textsubscript{17}]\textsuperscript{4} (two polymorphs labeled PM4a and PM4b) were synthesized directly from syn-B\textsubscript{18}H\textsubscript{22} by heating it with sulfur in the presence of anhydrous aluminum trichloride for 6 h at 125 °C under an Ar atmosphere. The crude product contained a mixture of monothiolated isomers and unreacted syn-B\textsubscript{18}H\textsubscript{22}, and these were all separated using standard chromatography on a silica gel column with diethyl ether as the eluent. The separated products were crystalline, with many single crystals suitable for X-ray diffraction. Three isomers were structurally resolved by X-ray diffraction (Figure 2), with two of the isomers found to be in two polymorphic structures. All of these results gave us a very good possibility to look at the effect of substitution on the parent syn-B\textsubscript{18}H\textsubscript{22} molecular structure as well as to investigate the molecular packing of these isomers in order to set a basis for further investigation toward the origin of their luminescent properties.
Molecular Structure, the Effect of a Substituent. All of the three isomers 1, 3, and 4 were prepared in quantities ranging from a few tens to hundreds of milligrams. Isomer 4 was dominating the crude product, but chromatography and crystallization from diethyl ether yielded many well-developed single crystals of all three and two of them in two polymorphic forms. Crystallization experiments from diethyl ether yielded all three isomers pure, and they were further characterized using $^1$H and $^{11}$B NMR, MS, IR, and X-ray studies. Computational analysis of the electrostatic potential map suggests that the thiol (HS-) group might substitute positions B1, B2, B3, and B4 of the syn-B$_{18}$H$_{32}$ cluster due to the relatively high negative charge localization in that part of the molecule (Figure 1D). Conformational analysis and mutual comparison of the respective energies of all four isomers and their most stable conformers also do not show significant differences, and isomer 3-HS-syn-B$_{18}$H$_{32}$ seems to be even more stable than isomer 4-HS-syn-B$_{18}$H$_{32}$ (Figure 3). Experimentally, we have found that thiol substitution follows the order B4 > B1 ≈ B3, and, interestingly, we have not observed the 2-HS-syn-B$_{18}$H$_{32}$ isomer.

The molecular composition of the thiol derivatives was confirmed by the positive ion mode ESI-MS analysis. The monocationic species with the mass value centered at $m/z$ 248.3152 was identified as HS-B$_{18}$H$_{31}$, while the $m/z$ value at 216.3422 corresponds to B$_{18}$H$_{31}$, which can be attributed to the loss of an HS fragment (Figure S28). The introduction of a thiol (HS-) group to B$_{18}$H$_{32}$ breaks the twofold symmetry as manifested in its $^{11}$B-$^1$H NMR spectra by the splitting of the peaks that had intensity 2 in the parent compound. The resonance of the substituted boron atom is easily identifiable in comparison to the decoupled $^{11}$B-$^1$H spectrum with the simple coupled $^{11}$B one as a third singlet in addition to the peaks of boron vertices 5 and 6. The thiol group causes a deshielding of the substituted atom and moves its peak around 10 ppm downfield; the effect of the substitution on other boron atoms is weaker and more complex (Figure 4). Unsurprisingly, the NMR signals of the atoms of the unsubstituted subunit (numbers with prime) are, in general, less affected than those of the substituted subunit (labeled by simple numbers), often observed at positions almost unchanged from the parent borane. One remarkable exception is position 2, which is very little affected by the substitution in all our compounds, where in 3 the peak of 2′ is shifted upfield more than that of position 2. The calculation of the NMR spectra at the DFT level (Table S2) reproduces well only the most prominent features of the spectra, often failing to capture the more sophisticated ones, and several times even the relative positions of the peak of an atom of the substituted subunit (n) with respect to its symmetry counterpart from the unsubstituted subunit (n′) differ between the calculation and the experiment (Figures S11, S17, and S24). Additionally, FT-IR spectroscopy corroborates the structure of isomers 1, 3, and 4 (Figure S29). A strong band at ~2560 cm$^{-1}$ can be attributed to the terminal B–H and SH stretching vibrations. Another strong band at about 1490 cm$^{-1}$ is characteristic of the bridging $\mu$-BHB vibrations.

Single-crystal X-ray diffraction (SC-XRD) investigation of all five thiol isomers/polymorphs of HS-syn-B$_{18}$H$_{32}$, structures 1 (PM1a and PM1b), 3, and 4 (PM4a and PM4b), reveal the positions of all of the heavier elements (B and S) in the compound. After refining the heavier atoms anisotropically, the remaining electron-density map reveals all of the hydrogen atoms in the cluster. After isotropic hydrogen atom refinement, the maximum electron-density peak for the thiol hydrogen atoms was near the sulfur atom; however, the final refinement was done with a riding model. Both the [1-HS-syn-B$_{18}$H$_{32}$]$_1$ and [4-HS-syn-B$_{18}$H$_{32}$]$_4$ 4 isomers were found to exist in two polymorphic structures PM1a, PM1b and PM4a, PM4b, respectively. Although the 18-vertex cage structure of the parent syn-B$_{18}$H$_{32}$ remains intact after thiolation, a more detailed comparative analysis of the interatomic distances and angles of all six single-crystal structures, 1 (PM1a, PM1b), 3, and 4 (PM4a, PM4b), and the parent syn-B$_{18}$H$_{32}$ demonstrates that the presence of the thiol substituent produces an obvious effect on the clusters’ geometry (see Table 1). This effect is difficult to spot if we look at a local vertex to adjacent vertex distances in close proximity to the substitution. However, as shown in Figure 5, we here selected geometrical parameters that cover the accumulation of small changes across the whole molecules, such as the d(B$_{18}$H$_{32}$) distance, or related angles that reflect the changes in mutual orientation of the two 10-vertex subclusters, and we can thus demonstrate and evaluate the substituents’ effect on the molecular structure. The substitution at position 3 of syn-B$_{18}$H$_{32}$ has a significant effect on isomer 3-HS-syn-B$_{18}$H$_{32}$.

The distances between the respective centroids, $c_1$–$c_2$, as well as between the vertices from opposite ends of the molecule, B(9)–B(9′), increased compared to the parent syn-B$_{18}$H$_{32}$. Intramolecular angles $\alpha$ and $\beta$, specified in Figure 5, also showed expansion as the direct consequence of the substitution (for detail, see Figure S35), causing a change in the cage geometry.
which may be disadvantageous for the stability of the cluster and responsible for the lower yields of isomers 1 and 3 compared to that of isomer 4 (Table 1). All of the above changes in distance between centroid \( c_1 \rightarrow c_2 \), intracage \( B(9) \rightarrow B(9') \), and intracage angle \( \alpha \) and \( \beta \) are due to the accumulation of small changes in the \( B \rightarrow B \) bond length of the cage (for more detail, see Table S5).

**Table 1.** Selected Centroid Distance [Å] \( (c_1$: Centroid of 10 B Atoms Representing One Subcluster of the \( \text{syn-B}_{18} \text{H}_{22} \) Cage, \( c_2$: Centroid of 10 B Atoms of Another Fused Borane Cage), Intracage \( d(B_9 \cdots B_9') \) Bond Distance [Å], and Bond Angle for \( \text{[1-\text{HS-syn-B}_{18} \text{H}_{21}]} \) 1 (PM1a and PM1b), \( \text{[3-\text{HS-syn-B}_{18} \text{H}_{21}]} \) 3, and \( \text{[4-\text{HS-syn-B}_{18} \text{H}_{21}]} \) 4 (PM4a and PM4b) with Comparison Data of \( \text{syn-B}_{18} \text{H}_{22} \)

<table>
<thead>
<tr>
<th>isomers/PMs</th>
<th>( d(c_1 \cdots c_2) )</th>
<th>( d(B_9 \cdots B_9') )</th>
<th>( \alpha(B_{10}B_{10'}) )</th>
<th>( \beta(B_{10}B_{10'}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{syn-B}<em>{18} \text{H}</em>{22} )</td>
<td>3.332</td>
<td>6.343</td>
<td>126.02</td>
<td>125.97</td>
</tr>
<tr>
<td>1-\text{HS-syn-B}<em>{18} \text{H}</em>{21} ) (PM1a)</td>
<td>3.342</td>
<td>6.370</td>
<td>129.53</td>
<td>128.52</td>
</tr>
<tr>
<td>1-\text{HS-syn-B}<em>{18} \text{H}</em>{21} ) (PM1b)</td>
<td>3.334</td>
<td>6.348</td>
<td>127.85</td>
<td>126.78</td>
</tr>
<tr>
<td>3-\text{HS-syn-B}<em>{18} \text{H}</em>{21} )</td>
<td>3.452</td>
<td>6.383</td>
<td>130.18</td>
<td>128.96</td>
</tr>
<tr>
<td>4-\text{HS-syn-B}<em>{18} \text{H}</em>{21} ) (PM4a)</td>
<td>3.330</td>
<td>6.345</td>
<td>128.44</td>
<td>128.20</td>
</tr>
<tr>
<td>4-\text{HS-syn-B}<em>{18} \text{H}</em>{21} ) (PM4b)</td>
<td>3.330</td>
<td>6.356</td>
<td>127.94</td>
<td>127.57</td>
</tr>
</tbody>
</table>

**Figure 4.** Experimentally decoupled \( ^{11}\text{B} \{(\^1\text{H}) \) NMR spectra of \( \text{syn-B}_{18} \text{H}_{22} \) and \( \text{HS-syn-B}_{18} \text{H}_{21} \) isomers.

**Figure 5.** Schematic illustration of selected distances and bond angles of \( \text{syn-B}_{18} \text{H}_{22} \) and its thiol derivatives.

**Supramolecular Structure.** The successful X-ray diffraction analysis of five different single crystals provided sufficient data for the investigation of intermolecular interactions. In all of the synthesized thiol isomers, the respective sulfur atoms bear high electron densities and show interactions with the acidic bridging hydrogen atoms, \( \mu\text{-BHB} \), which manifest their presence by strong bands at about 1490 cm\(^{-1}\) in the IR spectra. In addition to their acidic nature, i.e., the bridging hydrogen atom bearing a relatively high positive charge, it was interesting to see the supramolecular structures and how this interaction influences the orientation of the clusters. **Figure 6** shows four out of five of the analyzed structures, and in all of them, the -\( S(\text{H}) \cdots \mu\text{-BHB} \) interaction dominates the packing forces.
single-crystal supramolecular structure of isomer 3-HS-syn-B\textsubscript{18}H\textsubscript{21}, this interaction leads to a pair of molecules directly connected by two such interactions. The sulfur atom of the substituted subcluster shows an interaction with the bridging hydrogen atoms of the unsubstituted subcluster of another molecule. This isomer was found only in one polymorphic form.

In comparison, the most preferred isomer 4-HS-syn-B\textsubscript{18}H\textsubscript{21} exhibits a similar interaction in which the sulfur atom of one molecule interacts with the bridging hydrogen atoms of another molecule to form a zigzag chain or, in a second polymorph of this isomer, the sulfur atom shows an interaction with the bridging hydrogen atoms of two other molecules, leading to a fork-like arrangement. Both supramolecular structures are easy to distinguish. The last isomer, 1-HS-syn-B\textsubscript{18}H\textsubscript{21}, shows two very similar polymorphic structures in which the sulfur atom also interacts with the bridging hydrogen atoms of two other molecules in such a way that it resembles wooden logs. The existence of different polymorphic structures can therefore be rationalized as a result of this specific interaction, -S(H)···μBHB, between sulfur and some of the six similar bridging hydrogen atoms per molecule of each isomer. In addition to influencing the packing of molecules in their respective SC supramolecular structures, this interaction also explains the difference between the parent syn-B\textsubscript{18}H\textsubscript{22} and all three thiolated isomers in the differential thermal analysis (Figure S30). While the parent syn-B\textsubscript{18}H\textsubscript{22} shows complete loss of mass due to sublimation, all three thiol isomers sublime off at slightly higher temperature and only partly, 20–40%. The remaining 60–80% of the starting material turns into highly involatile blackish material. The lower volatility of the thiolated isomers compared to syn-B\textsubscript{18}H\textsubscript{22} can be attributed particularly to this -S(H)···μBHB interaction. One related issue is the HS-hydrogen atom and its orientation, as the hydrogen is not directly involved in this structure-determining interaction between the sulfur of the HS group and the bridging hydrogen, μ-BHB, and is left to either exhibit a weak interaction with terminal BH vertices or be left to free conformation, which corresponds to computationally optimized minima.

**Luminescence Properties.** Borane compounds possess fascinating photophysical properties such as stimulated emission, thermochromism, or singlet oxygen photosensitization.\cite{7,25,28,33,34,36,51} We were therefore tempted to investigate the photophysical properties of the prepared borane compounds. In contrast to the remarkable fluorescence efficiency of anti-B\textsubscript{16}H\textsubscript{22} in hexane (\(\phi_L \sim 1\)), its syn-B\textsubscript{18}H\textsubscript{21} isomer has been reported to be nonemissive in solution.\cite{29} However, our measurement of the as-received powder of syn-B\textsubscript{18}H\textsubscript{22}, precursor to the thiolated boranes, showed an intense fluorescence in the
solid state with a maximum at 385 nm, a quantum yield of 0.17, and an amplitude average lifetime of 0.4 ns (Figure 7 and Table 2). Interestingly, the recrystallization of syn-B$_{18}$H$_{22}$ from a diethyl ether/hexane mixture provided homoostructural single crystals that displayed fluorescence with a maximum at 420 nm, a quantum yield of 0.20, and an amplitude average lifetime of 1.6 ns (Figure 7 and Table 2). For both samples, the excitation spectra were characterized by broad absorption bands in the UV-A region (Figure 7A). Thus, syn-B$_{18}$H$_{22}$ displays aggregation-induced fluorescence, and its photophysical parameters are microstructure-dependent. For comparison, solid anti-B$_{18}$H$_{22}$, recrystallized from a diethyl ether/hexane mixture, displayed a fluorescence band with maximum at 420 nm, an emission quantum yield of 0.78, and a lifetime of 6.5 ns, significantly higher than for syn-B$_{18}$H$_{22}$ (Figure S33 and Table 2).

Single crystals of the thiolated boranes were measured on a single-crystal X-ray diffractometer to ensure their crystallographic purity, and they were then used for photophysical characterizations, the results of which are summarized in Table 3. Upon excitation at 380 nm, single crystals of 1, 3, and 4 displayed broad luminescence bands in the green/yellow region, with the respective maxima at 582, 535, and 570 nm (Figure 8). Interestingly, isomer 1 possessed a shoulder near its main emission band located in the blue region, which might be caused by additional emissive excited states. The excitation spectra recorded at the maximum of emission revealed broad absorption bands in the UV-A region (Figure 8A). Analysis of the luminescence decay kinetics recorded at the emission maximum evidenced amplitude average lifetimes of 14, 8.8, and 40 µs for isomers 1, 3, and 4, respectively (Figure 8B). Thus, the thiolation of syn-B$_{18}$H$_{22}$ causes a bathochromic shift of the emission maximum and a decrease in luminescence efficiency. In addition, it leads to a switch from fluorescence to phosphorescence due to an increased intersystem crossing from singlet excited to triplet excited states, as already reported for iodinated or thiolated anti-B$_{18}$H$_{22}$ (Figure 8).

\[ \text{Table 2. Photophysical Properties of syn-B}_{18}\text{H}_{22} \text{ and anti-B}_{18}\text{H}_{22} \text{ in the Solid State at Room Temperature} \]

<table>
<thead>
<tr>
<th>sample</th>
<th>( \lambda_{\text{em}} ) (nm)</th>
<th>( \phi )</th>
<th>( \tau_L ) (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>syn-B$<em>{18}$H$</em>{22}$</td>
<td>385</td>
<td>0.17</td>
<td>0.4</td>
</tr>
<tr>
<td>syn-B$<em>{18}$H$</em>{22}^{c}$</td>
<td>420</td>
<td>0.20</td>
<td>1.6</td>
</tr>
<tr>
<td>anti-B$<em>{18}$H$</em>{22}$</td>
<td>420</td>
<td>0.78</td>
<td>6.5</td>
</tr>
</tbody>
</table>

\( ^{a} \lambda_{\text{em}} \), luminescence maximum; \( \lambda_{\text{exc}} = 340 \text{ nm} \); \( ^{b} \tau_{\text{L}} \), amplitude average lifetime; \( \lambda_{\text{exc}} = 402 \text{ nm} \) measured at 420 nm; \( \Phi_{L} \), luminescence quantum yields \( \lambda_{\text{exc}} = 340 \text{ nm} \), experimental error of \( \Phi_{L} \) is ±0.01. \( ^{c} \)As-received. \( ^{d} \)Recrystallized diethyl ether/hexane mixture.

\[ \text{Table 3. Photophysical Properties of Crystals of the Thiolated Boranes at Room Temperature} \]

<table>
<thead>
<tr>
<th>sample</th>
<th>( \lambda_{\text{L}} ) (nm)</th>
<th>( \phi_{L} )</th>
<th>( \tau_{L} ) (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-HS-syn-B$<em>{18}$H$</em>{22}$</td>
<td>582, 465$^{b}$</td>
<td>0.06</td>
<td>40</td>
</tr>
<tr>
<td>3-HS-syn-B$<em>{18}$H$</em>{22}$</td>
<td>535</td>
<td>0.06</td>
<td>40</td>
</tr>
<tr>
<td>4-HS-syn-B$<em>{18}$H$</em>{22}$</td>
<td>490</td>
<td>0.02</td>
<td>2.2</td>
</tr>
</tbody>
</table>

\( ^{a} \lambda_{\text{em}} \), luminescence maximum; \( \lambda_{\text{exc}} = 380 \text{ nm} \); \( ^{b} \tau_{\text{L}} \), amplitude average lifetime; \( \lambda_{\text{exc}} = 380 \text{ nm} \) measured at the maximum of emission; \( \Phi_{L} \), luminescence quantum yields \( \lambda_{\text{exc}} = 380 \text{ nm} \), experimental error of \( \Phi_{L} \) is ±0.01. \( ^{c} \)Shoulder. *After grinding.

\[ \text{Figure 8. Normalized emission spectra (plain lines) of single crystals of 1, 3, and 4 excited at 380 nm in the air atmosphere; normalized excitation spectra (dashed lines) recorded at the maximum of emission (A). Phosphorescence decay kinetics of single crystals of 1, 3, and 4 in the air atmosphere, excited at 380 nm, recorded at the maximum of emission (B).} \]
peculiar behaviors, which may further deepen the interest in this class of photoactive compounds.

**Self-Assembled Monolayers on Silver Surfaces, XPS Analysis.** Self-assembled monolayers (SAMs) of the isomer [4-HS-syn-B_{18}H_{21}] 4 on silver substrates were prepared by vapor deposition in ultra-high vacuum (UHV). The successful formation of these carbon-free SAMs was investigated using X-ray photoelectron spectroscopy (XPS). Figure 10A shows the high-resolution S 2p spectrum consisting of a main doublet (orange) with the binding energy (BE) of the S 2p_{3/2} and S 2p_{1/2} components at 161.3 and 162.5 eV, respectively, due to the formation of thiolates. The signal is accompanied by another doublet at the BE values of S 2p_{3/2} and S 2p_{1/2} at 162.9 and 164.1 eV, respectively (red). The formation of this additional sulfur signal can be attributed to the partial formation of disulfides during the self-assembly or to the presence of some physisorbed thiol molecules integrated into the monolayer via hydrogen bridge bonds. Both signals are shifted by ~0.5 eV to lower BE values in comparison to the published values for boron-bound thiolates (typical values of S 2p_{1/2} at about 161.7 eV) and disulfides, or thiols, with the typical values of S 2p_{1/2} electrons at 163.0 eV.\(^{53,54}\) This indicates higher electron density on sulfur in [4-HS-syn-B_{18}H_{21}] 4, as also evidenced by the value of the HS\(^{1}\)H NMR chemical shift at about 1.4 ppm and indirectly also from the above-reported short-contact interactions with the acidic bridging hydrogen atoms.

In the B 1s spectrum, the main component (green) is found at a BE value of 189.1 eV with the full width at half-maximum of 1.5 eV, which corresponds to B–S bonds in the cluster (Figure 10B). This peak is accompanied by a shoulder at a BE of 190.2 eV (dark green), which we assign to the boron atom attached directly to sulfur in the B–S bonds. At 192.6 eV, a broad low-intensity peak due to aromatic shake-ups is visible. No other XP signals, with the exception of the metallic Ag substrate, were detected (see Figure S34) in the samples. Especially the absence of carbon and oxygen confirms the formation of high-quality, carbon-free SAM on the silver surface. The thickness was calculated to be 7 ± 2 Å and the B/S ratio to 19 ± 1:1, matching very well to the molecular structure and nominal stoichiometry of the isomer [4-HS-syn-B_{18}H_{21}] 4. Figure 11 further shows the steric requirements (both lateral and longitudinal) of all three synthesized isomers and shows the theoretically enabled range in the subnanometer thickness of the respective SAMs.

**CONCLUSIONS**

We have investigated the syn-B_{18}H_{22} isomer, the “forgotten” isomer of the long-established B_{18}H_{12} molecule.\(^{12,15,24}\) The more intensely studied anti-B_{18}H_{12} isomer has been recently recognized for its lasing properties.\(^{7,26}\) Several previous studies\(^{7,26}\) stated that the syn-isomer is nonluminescent, and thus comparatively little attention has been paid to it over the last decade compared to anti-B_{18}H_{12} boron hydride. In this study, we have demonstrated that not only does the parent compound have luminescence properties in its crystalline form but also that the HS-substituted isomers, (1-HS-syn-B_{18}H_{12}) 1, (3-HS-syn-B_{18}H_{12}) 3, and (4-HS-syn-B_{18}H_{12}) 4, show luminescence both in their crystalline form and in solution. Within our systematic investigation of the HS-derivatives of syn-B_{18}H_{22}, we have aimed to use this molecule to reach our goal for the preparation of carbon-free self-assembled monolayers. Additionally, we have focused on monothiolated isomers of syn-B_{18}H_{22} as constituents that enable us to adjust SAM thicknesses below 1 nm, depending on which vertex bears the HS group. In total, we have prepared five new crystal structures, as two of the isomers, isomers 1-HS-syn-B_{18}H_{12} and 4-HS-syn-B_{18}H_{12}, were found to exist as two polymorphs. The packing of the molecules in the respective supramolecular structures of all of the isomers was commonly found to exhibit -S(H)...μBH- interactions, and these give rise to the existence of different crystal polymorphs. We have also observed the substituent effect on the structure in comparison with the parent syn-B_{18}H_{22} molecule. Changes of interboron distances adjacent to the substituent are too subtle to be
apparent, but they become more obvious when we measure the effect on geometrical parameters effectively encompassing the whole molecule, as a whole, i.e., on the distance between the centroids of the two subclusters of syn-\( \text{HS-B} \text{H}_{12} \text{H}_{22} \), or on the distance between vertices from the opposite ends of the molecule, such as \( B(9) - B(9') \). Such substituent metrics have also been estimated in terms of the overall cluster volume, and it is anticipated that \( \text{syn-B} \text{H}_{12} \text{H}_{22} \) with other substituents should also modify the photophysical properties. This study lays a solid foundation for further work in this direction.

**EXPERIMENTAL SECTION**

**General Procedure and Instrumentation.** All of the experiments were performed under an inert (argon, Ar) atmosphere using the standard Schlenk-line vacuum technique. Prior to use, all of the solvents were dried with sodium-benzophenone ketyl and distilled under an Ar atmosphere. Chloroform-\( d \) was purchased from ACROS Organic Chemicals. Starting \( \text{HS-B} \text{H}_{12} \text{H}_{22} \) was purchased from Katchem s.r.o., Czech Republic, and used as received. Other chemicals, such as anhydrous aluminum trichloride and sulfur, were dried with sodium-benzophenone ketyl and distilled under an Ar atmosphere using the standard Schlenk-line vacuum technique. Prior to use, all of the solvents were dried with sodium-benzophenone ketyl and distilled under an Ar atmosphere overnight. The reaction mixture was then left to cool to the B2 \( \text{−axis} \) > B1 (15.0 ppm) > B10 \( \text{−axis} \) > B1 (10.9 ppm) > B10 \( \text{−axis} \) > B1 (9.6 ppm) > B10 (8.3 ppm, according to the B10−B5 cross peak 8.6 ppm) > B6 (8.3 ppm, according to the B6−B2, B2’ cross peak 8.3 ppm) > B9 (3.3 ppm) > B1′ (2.0 ppm) > B9 (1.0 ppm) > B8 (0.0 ppm) > B8’ (−2.0 ppm) > B7 (−3.8 ppm) > B7 (−14.3 ppm) > B7 (−16.6 ppm) > B2 (−28.1 ppm, according to the B2−B1 and B2–B3 cross peaks: 28.0 ppm on the \( x \)-axis, −27.9 on the \( y \)-axis) > B2′ (−28.1 ppm, according to the B2′−B3’ and B1′−B2’ cross peaks: −28.4 ppm on the \( x \)-axis, −28.3 on the \( y \)-axis) > B4 (−37.2 ppm) > B4’ (−40.6 ppm).

**Crystal Data for PM1a.** Empirical formula = \( \text{B}_4 \text{H}_2 \text{S}_5 \) \( \text{M}_2 \) (288, \( m / z \) calculated for \( \text{HS-B} \text{H}_{12} \text{H}_{22} \) monocationic species: 248.3148 experimentally found 248.3152).

| NMR for [1-HS-syn-B3H42]- 1, \( ^{11} \text{B} \{ ^{1} \text{H} \} \) NMR (192.6 MHz, 295 K, CDCl3): B3 (16.7 ppm) > B3’ (15.0 ppm) > B1 (10.9 ppm) > B10 (9.6 ppm) > B10 (8.3 ppm, according to the B10−B5 cross peak 8.6 ppm) > B6 (8.3 ppm, according to the B6−B2, B2’ cross peak 8.3 ppm) > B9 (3.3 ppm) > B1’ (2.0 ppm) > B9 (1.0 ppm) > B8 (0.0 ppm) > B8’ (−2.0 ppm) > B7 (−3.8 ppm) > B7 (−14.3 ppm) > B7 (−16.6 ppm) > B2 (−28.1 ppm, according to the B2−B1 and B2–B3 cross peaks: 28.0 ppm on the \( x \)-axis, −27.9 on the \( y \)-axis) > B2′ (−28.1 ppm, according to the B2′−B3’ and B1′−B2’ cross peaks: −28.4 ppm on the \( x \)-axis, −28.3 on the \( y \)-axis) > B4 (−37.2 ppm) > B4’ (−40.6 ppm). |
NMR for [3-HS-syn-B$_2$H$_3$]$_3$. 1.$^3$B$^1$H NMR (192.6 MHz, 295 K, CDCl$_3$): B$_3$ (21.4 ppm) > B$'$ (13.5 ppm) > B$_10$ (10.3 ppm) > B'0 (9.7 ppm) > B$_6$ (6.6 ppm) > B$_1$ (4.4 ppm) > B$_9$ (3.7 ppm) > B'1 (2.7 ppm) > B$_9$ (0.8 ppm) > B'8 (−0.2 ppm according to COSY) > B$_5$ (−2.2 ppm) > B$_8$ (−3.2 ppm) > B$_7$ (−15.4 ppm) > B$_7$ (−16.8 ppm) > B$_5$ (−28.6 ppm) > B$_2$ (−29.4 ppm) > B$_4$ (−38.5 ppm) > B$_4$ (−39.4 ppm).

Crystal Data. Empirical formula = B$_9$H$_3$S$_3$. M$_r$ = 248.8, monoclinic, space group P2$_1$/c, a = 12.264(2) Å, b = 6.659(2) Å, c = 19.098(4) Å, $\beta$ = 90°, $\gamma$ = 107.06(3)°, $\rho$ = 1.538 mm$^{-1}$, F(000) = 512, R$_1$ = 0.0356, wR$_2$ = 0.0804, 2891 independent reflections and 238 parameters (for more details, see Table S10).

NMR for [4-HS-syn-B$_2$H$_3$]$_4$. 1.$^3$B$^1$H NMR (192.6 MHz, 295 K, CDCl$_3$): B$_4$ (14.9 ppm) > B$_3$ (13.8 ppm) > B$_10$ (10.3 ppm) > B'9 (9.1 ppm) > B$_6$ (8.1 ppm) > B$_1$ (3.0 ppm) > B$_9$ (2.6 ppm) > B'1 (2.0 ppm) > B ($1.2 ppm) > B'8 (−1.6 ppm) > B$_5$ (−3.4 ppm) > B$_7$ (−16.1 ppm) > B$_7$ (−16.2 ppm) > B$_2$ (−27.7 ppm) > B$_2$ (−28.1 ppm) > B$_4$ (−29.2 ppm) > B$_4$ (−39.8 ppm).

Crystal Data for PM4a. Empirical formula = B$_{18}$H$_3$S$_3$. M$_r$ = 248.8, orthorhombic, space group Pnca, a = 14.4249 (5) Å, b = 11.9778 (4) Å, c = 17.8595 (6) Å, $\alpha$ = 90°, $\beta$ = 90°, $\gamma$ = 90°, Z = 2085.74 (18) Å$^3$, Z = 8, $\rho_{\text{calc}}$ = 1.1072 g cm$^{-3}$, $\mu$ = 1.486 mm$^{-1}$, F(000) = 1024, R$_1$ = 0.0300, wR$_2$ = 0.0720, 2994 independent reflections and 238 parameters (for more details, see Table S11).

Computation. Quantum chemistry calculations were performed with the Gaussian 16 package. The geometries were optimized by means of the density functional theory with the long-range-corrected functional wB97XD from Head-Gordon and co-workers, which includes empirical dispersion, using Alldrich’s triple-zeta set with polarization functions def2-TZVPP. A series of optimizations were performed in internal coordinates with the torsion angle between the thiol hydrogen atom and a selected neighbor of the substituted boron (for 1 and 3, 6 for 2, and 1 for 4) kept fixed at values reflecting the pentagonal arrangement around the substituted boron: 36, 108, 180, 252, and 324° reflecting the pentagonal arrangement around the substituted boron: 36, 108, 180, 252, and 324° (hydrogen between two neighboring borons) as well as 0, 72, 144, 216, and 288° (hydrogen above a neighboring boron); then the angle was relaxed, and a full optimization to a local minimum was conducted without constraints. NMR shielding calculations of stoichiometry were performed with the software CasaXPS using the relative sensitivity factors of 1.68 (S 2p) and 0.49 (B 1s); the layer thickness was calculated using the Lambert−Beer equation. A mean free path of 27 Å was used for electrons that were released from the silver substrate and reached the detector through the SAM.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c05530.

Supporting information provides complete information on the NMR spectra (both experimental and computational), IR spectra, ESI mass spectra, results from thermal differential analysis, tables with structural data for all X-ray diffraction-determined isomers and polymorphs, analysis of supramolecular arrangement, more data on photophysical properties, X-ray photoelectron spectra of the respective SAM, and further computational data (PDF).

Optimized structure 1 (XYZ) Optimized structure 2 (XYZ) Optimized structure 3 (XYZ) Optimized structure 4 (XYZ) Optimized structure 5 (XYZ)

Accession Codes

CCDC 2262294, 2262296, 2262299, 2262306−2262308, 2265132, and 2265136 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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Notes

The authors declare no competing financial interest.

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