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Radicals

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Persistent Antimony- and Bismuth-Centered Radicals in Solution**

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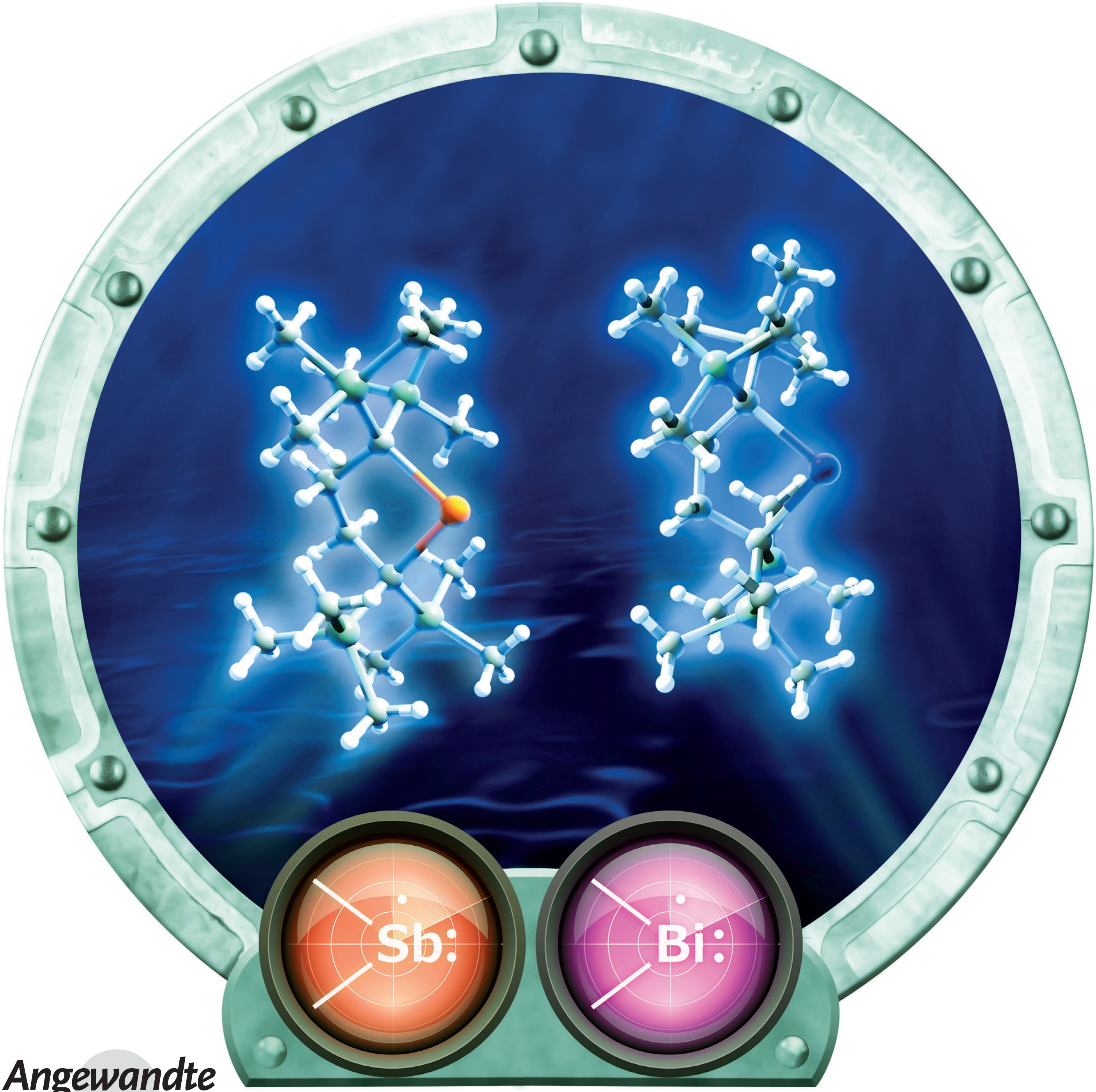

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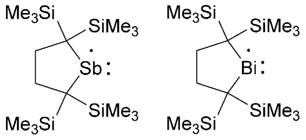
Abstract: *Stibinyl and bismuthinyl radicals are recognized as representative intermediates of antimony and bismuth compounds, but still elusive in the condensed phase. We successfully synthesized persistent stibinyl and bismuthinyl radicals in solution by facile dissociation of the corresponding dimers with bulky substituents. We characterized the radicals by NMR and UV/Vis spectroscopy and estimated the thermodynamic parameters for the dissociation equilibria. The radicals show n→p (HOMO→SOMO) transition bands at 497 nm (stibinyl) and 543 nm (bismuthinyl) in 3-methylpentane and react with a stable nitroxyl radical to give the cross-radical coupling products in good yields.*

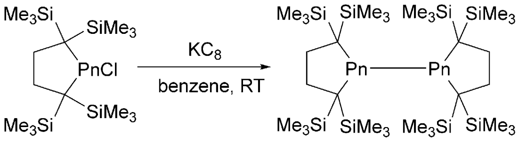
Neutral dicoordinate antimony- and bismuth-centered radicals ($R_2Sb^{\bullet}$ = stibinyl and $R_2Bi^{\bullet}$ = bismuthinyl), generated by the homolytic cleavage of the weak Pn−R bond in R_3Pn (Pn = Sb, Bi), are recognized as intermediates of antimony and bismuth compounds in organic synthesis, polymerization processes, and organometallic chemical vapor deposition processes.[1–4] Stibinyl and bismuthinyl radicals were proposed as intermediates in the reactions of distibines and dibismuthines (R_2Pn-PnR_2) with various reagents and in their disproportionation reactions.[5–8] The parent $H_2Sb^{\bullet}$ and $H_2Bi^{\bullet}$ were observed in Ar or Ne matrices at 3–35 K by IR spectroscopy.[9] However, in sharp contrast to the extensive study of various persistent/stable phosphinyl and arsinyl radicals,[10–12] stibinyl and bismuthinyl radicals in a condensed phase remain elusive to date. Herein, we report the spectroscopic observation of stibinyl and bismuthinyl radicals **1** and **2** in solution (Figure 1). These radicals were generated through the dissociation of distibine **5** and dibismuthine **6**, both of which bear the bulky bidentate alkyl group 1,1,4,4-tetrakis(trimethylsilyl)butane-1,4-diyl (abbreviated as R^{H}_2 hereafter).[13,14]



$R^{H}_2Sb^{\bullet}$ (**1**) $R^{H}_2Bi^{\bullet}$ (**2**)

Figure 1. Radicals of heavy pnictogens with bulky dialkyl substituents.

The reduction of chlorostibine **3** with one equivalent of potassium graphite in benzene at room temperature for two days gave an orange-red crystalline solid of distibine **5** in 34 % yield [Eq. (1)]. Similarly, dibismuthine **6** was obtained from chlorobismuthine **4** as a purple crystalline solid in 47 % yield. The structures of **5** and **6** were determined by NMR spectroscopy, elemental analysis, and X-ray structural analysis.[15] Compounds **5** and **6** are sensitive to air, ambient light, and moisture.



(1)

3 (Pn = Sb) **5** (Pn = Sb, 34%)

4 (Pn = Bi) **6** (Pn = Bi, 47%)

The molecular structures of **5** and **6** in the solid state were determined by X-ray analysis (Figure 2). The most striking feature of the structures of **5** and **6** is an exceptionally long pnictogen−pnictogen distance. The Sb−Sb distance of

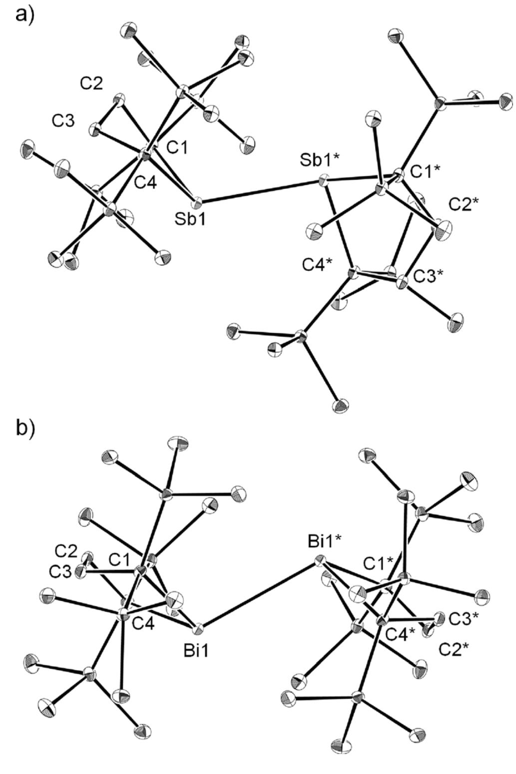


Figure 2. Molecular structures of a) distibine **5** and b) dibismuthine **6**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] of **5**: Sb1–Sb1* 3.0297(4), C1–Sb1 2.2527(19), C4–Sb1 2.2520(18); C1-Sb1-C4 86.93(7), C1-Sb1-Sb1* 100.11(5), C4-Sb1-Sb1* 125.19(5). Selected bond lengths [Å] and angles [°] of **6**: Bi1–Bi1* 3.1821(3), C1-Bi1 2.371(3), C4-Bi1 2.370(3); C1-Bi1-C4 84.74(9), C1-Bi1-Bi1* 116.33(6), C4-Bi1-Bi1* 103.19(7).

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3.0297(4) Å in **5** is considerably longer than those of other reported distibines (2.835(1)–2.9194(6) Å).[6] No intermolecular interactions between antimony atoms were found in **5**; the closest intermolecular Sb···Sb distance was 8.292 Å, which is far longer than the sum of van der Waals (vdW) radii of two Sb atoms (4.12 Å).[16] The C4-Sb-Sb* angle of 125.19(5)° is unusually large compared to the C1-Sb-Sb* angle of 100.11(5)° and the angles in the R_3Sb species. In compound **6**, similar structural characteristics were observed; the Bi–Bi distance of 3.1821(3) Å is long in comparison with the reported Bi–Bi bond lengths of dibismuthines without additional intramolecular coordination (2.9902(5)–3.087(3) Å)[7] The smallest intermolecular distance between the bismuth atoms of **6** is 7.861 Å, which is far from the sum of the vdW radii of two bismuth atoms (4.14 Å).[16] These structural characteristics suggest that **5** and **6** are weakly bound dimers of radicals **1** and **2**, respectively.[17]

The NMR spectra of **5** and **6** in solution showed a unique temperature-dependent behavior. The ^{1}H NMR spectrum of **5** in [D$_8$]toluene at 193 K exhibits a set of the signals resulting from the Me_3Si protons at 0.34 and 0.41, and a set of signals resulting from the methylene protons at 1.74 and 2.32 ppm (Figure 3b). With an increase in the measurement temperature, a dramatic broadening and low-field shift of the signals were observed, and at 298 K a broad signal was present at 16.80 ppm (Figure 3a). As the phosphinyl radical $R^{H}_{2}P^{\bullet}$[13] shows similarly broadened and down-field-shifted ^{1}H NMR resonances as a result of a paramagnetic shift at various temperatures (Figures S6 and S7 in the Supporting Information), the observed signals at 298 K can be assigned to paramagnetically shifted trimethylsilyl protons of the stibinyl radical **1**. In the case of dibismuthine **6**, a similar temperature dependence was observed in the ^{1}H NMR spectrum (Figure S11). These spectral changes are reversible, thus indicating an equilibrium between $R^{H}_{2}Pn^{\bullet}$ radicals (Pn = Sb, Bi) and the corresponding dimers, as shown in Equation (2).

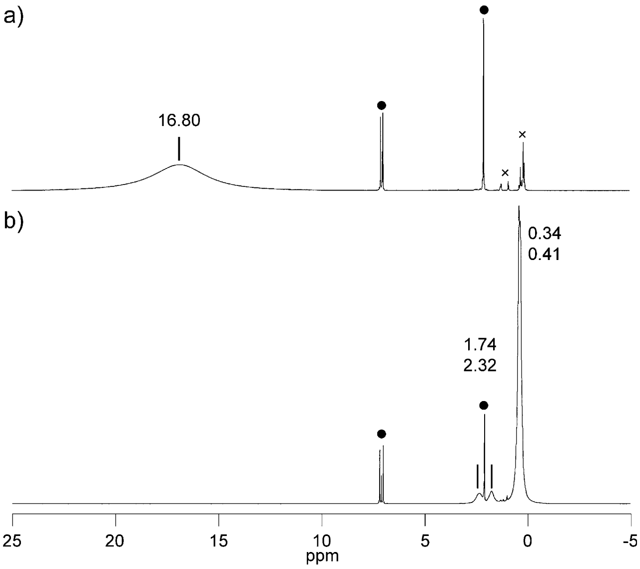


Figure 3. ^{1}H NMR spectra of compound **5** (a) at 298 K (almost only **1**) and (b) at 193 K (almost only **5**) in [D$_8$]toluene. ●: C_7D_7H, ×: hexane and unidentified impurities.

$$R^{H}_{2}Pn{-}PnR^{H}_{2} \rightleftharpoons 2\ R^{H}_{2}Pn^{\bullet} \qquad (2)$$

Pn = Sb (**5**), Bi (**6**) Pn = Sb (**1**), Bi (**2**)

The increased measurement temperature also resulted in an increased pseudocontact shift of tetramethylsilane (reference compound) in the solution of **5** and **6**, thus also suggesting that the dissociation of **5** and **6** to the corresponding radicals is more favorable at higher temperatures.[18] The thermodynamic parameters for the dissociation of distibine **5** to stibinyl radical **1** ($\Delta H_{\mathrm{Sb}} = 54.3 \pm 0.3\ \mathrm{kJ\,mol^{-1}}$, $\Delta S_{\mathrm{Sb}} = 191.9 \pm 1.3\ \mathrm{J\,mol^{-1}K^{-1}}$) were estimated by using equilibrium constants that were determined by employing Evans' method[19,20] at various temperatures. The positive sign of ΔH_{Sb} and the large, positive value of ΔS_{Sb} are reasonable for the dissociation process of **5**. Similarly, thermodynamic parameters for the dissociation of dibismuthine **6** to bismuthinyl radical **2** ($\Delta H_{\mathrm{Bi}} = 54.5 \pm 0.7\ \mathrm{kJ\,mol^{-1}}$, $\Delta S_{\mathrm{Bi}} = 155.8 \pm 2.4\ \mathrm{J\,mol^{-1}K^{-1}}$) were estimated. The values of ΔH_{Sb} and ΔH_{Bi} are considerably smaller than those of the theoretically predicted dissociation energies of the Sb–Sb and Bi–Bi bonds in tetrasilyl-substituted distibine and dibismuthine, respectively (155.8 and 141.3 kJ mol^{-1}).[7g] The equilibrium constants at 298 K for the dissociation of distibine **5** to **1** is 10^2 times larger than that of **6** to **2** ($K^{298}_{\mathrm{Sb}} = 3.16\ \mathrm{mol\,L^{-1}}$, $K^{298}_{\mathrm{Bi}} = 3.78 \times 10^{-2}\ \mathrm{mol\,L^{-1}}$). A higher steric repulsion between the R^{H}_{2} ligands as a result of shorter C–Sb and Sb–Sb bonds in distibine **5** may be the reason for the larger dissociation equilibrium constant of **5**. Based on the obtained equilibrium constants, distibine **5** and dibismuthine **6** dissociate almost completely (> 99%) into radicals **1** and **2**, respectively, in solution ($1.0 \times 10^{-3}\ \mathrm{mol\,L^{-1}}$ for **5** and $1.0 \times 10^{-5}\ \mathrm{mol\,L^{-1}}$ for **6**) at 298 K.

In 3-methylpentane (3-MP), compounds **5** and **6** displayed a reversible thermochromism (Figures 4 and S5), while no thermochromic behavior was observed for $R^{H}_{2}P^{\bullet}$ in 3-MP (Figure S3).[21] The UV/Vis spectrum of **5** at 298 K showed a weak and broad absorption band at 497 nm, accompanied by a shoulder at 385 nm, while a set of intense absorption bands at 440 and 380 nm appeared at 183 K (Figure 4).[22] Time-dependent (TD) DFT calculations of the optimized structures of **1** ($\mathbf{1}_{\mathrm{opt}}$)[23] showed transitions at 468 and 332 nm (superimposed as solid bars into Figure 4), which reproduce the experimental spectrum at 298 K. Judging from the TD-DFT calculations and NMR spectra, the absorption bands at 497 nm and 385 nm can be assigned to the n(Sb)→5p(Sb) (HOMO→SOMO) and σ(C-Sb)→5p(Sb) (HOMO-1→SOMO) transitions, respectively, of stibinyl radical **1**. As an electron transition of the optimized structure of **5** ($\mathbf{5}_{\mathrm{opt}}$)[23] was calculated to appear at 430 nm with a large oscillator strength (superimposed as an open bar into Figure 4), one of the two intense absorptions at 183 K can be assigned to the σ(Sb-Sb)→σ*(Sb-Sb) transition of distibine **5**.[24] A similar reversible thermochromism was observed for a solution of dibismuthine **6** in 3-MP. An absorption band at 543 nm appeared at 298 K, while intense absorption bands at 504, 385, 344 nm appeared at 183 K (see Figure S5 in the Supporting

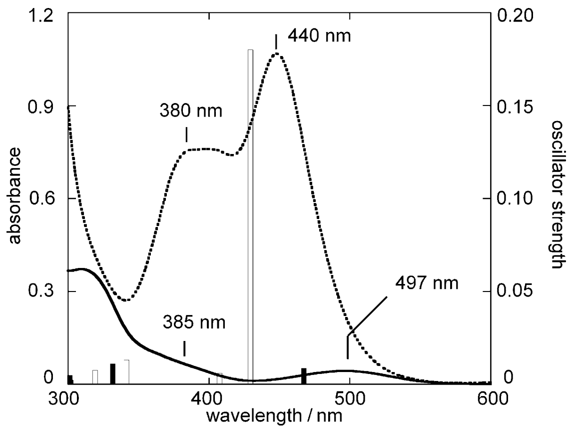
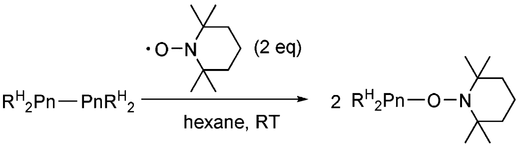


Figure 4. UV/Vis spectra of a solution of distibine **5** in 3-MP. Solid and dotted lines indicate absorptions at 298 K and 183 K, respectively. Open and solid vertical bars indicate calculated transitions of $\mathbf{5}_{opt}$ and $\mathbf{1}_{opt}$, respectively.

Information). The longest wavelength absorption band, observed at 504 nm at 183 K, is slightly red-shifted compared to that of silyl-substituted dibismuthine in toluene $[(t\text{Bu})\text{Ph}_2\text{Si}]_4\text{Bi}_2$ (465 nm).[7g] According to the discussion above, the absorption band at 543 nm (at 298 K) can be assigned to the n(Bi)→6p(Bi) (HOMO→SOMO) transition of the bismuthinyl radical **2**, and the bands observed at 183 K are due to those of dibismuthine **6**. To the best of our knowledge, this is the first observation and characterization of electronic transitions of stibinyl and bismuthinyl radicals by UV/Vis spectroscopy.

The reaction of **5** with two equivalent of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) in hexane afforded the corresponding radical coupling product **7** in 89% yield [Eq. (3)]. Dibismuthine **6** underwent a similar radical coupling reaction to form **8** in 88% yield. Compounds **7** and **8** were characterized by X-ray structural analysis (Figures S31 and S32). In contrast to **7**, compound **8** dissociates reversibly to **2** (and regenerates **6**) and TEMPO in solution [Eq. (4)].



(3)

5 (Pn = Sb)
6 (Pn = Bi)

7 (Pn = Sb, 89%)
8 (Pn = Bi, 88%)

$$\mathbf{8} \rightleftharpoons \mathbf{2} + \text{TEMPO} \qquad (4)$$

When analytically pure **8** was dissolved in C_6D_6, an EPR signal from the TEMPO radical was observed at room temperature. A weak Bi−O bond is responsible for the dissociation of **8**.[25]

The EPR spectrum of **1** (Figure S24) displayed a very broad (full width at half maximum = 24 mT) and weak signal with a large *g*-factor of 2.0669. The *g*-factor and shape of the signal of **1** resemble those of the distibene anion radical $[\text{Li(solvent)}_n]^+[\text{BbtSb=SbBbt}]^{-\cdot}$ (Bbt = 2,6-bis(trimethylsilyl)methyl-4-tris(trimethylsilyl)methylphenyl) reported by Tokitoh and Sasamori, which is only one example of reported antimony-centered radical ($g = 2.097$).[26] Despite our efforts to observe bismuthinyl radical **2** in solution, we did not detect an EPR signal between 298–114 K in common solvents,[27] which could be attributed to a very fast relaxation as a result of large spin-orbit coupling.[28]

In summary, we generated persistent stibinyl and bismuthinyl radicals from distibine **5** and dibismuthine **6**. Compounds **5** and **6** have extraordinarily long pnictogen−pnictogen bonds and dissociate reversibly into the corresponding pnictogen-centered radicals **1** and **2** in solution, evidenced by NMR and UV/Vis spectroscopy and theoretical studies. Cross-radical coupling reactions of **1** and **2** with TEMPO were also established.[29]

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Keywords: antimony · bismuth · dimerization · persistent radicals · pnictogens

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[15] Synthesis, characterization, and molecular structures (obtained by X-ray structural analysis) of compounds **3** – **8** are described in the Supporting Information. CCDC 999349 (**3**), 999348 (**4**), 999350 (**5**), 999347 (**6**), 999352 (**7**), 999351 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[18] Higher aggregation, such as that of **5** with **1**, may be ruled out because of the severe steric hindrance between the $R^{H}_{2}Pn$ units.

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[22] The UV/Vis spectra at various temperatures are shown in Figures S4 and S5 in Supporting Information.

[23] DFT calculations for geometry optimization and frequency analysis were carried out at the B3PW91/B1 level (B1 basis: SDD for Sb, 6-31G(d) for C, H, Si) and TD-DFT calculations of the optimized structures were performed at the B3PW91/B2 level (B2 basis: SDD for Sb and 6-311+G(d,p) for C, H, Si atoms). Theoretical details with full citation are given in the Supporting Information.

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