Substituent Effects in Linear Organogermanium Catenates

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The trigermanes $EtOCH_2CH_2Ge(R_2)Ge(Ph_2)Ge(R_2)CH_2CH_2OEt$ (R = Et, Bu, Ph) and $Ph_3GeGe(Bu_2)Ge(Ph_2)CH_2CH_2OEt$ as well as the two tetragermanes $Ph_3GeGe(Bu_2)Ge(Ph_2)Ge(R_2)CH_2CH_2OEt$ (R = Et, Bu) have been prepared and characterized. The absorption and electrochemical attributes of these species, along with the butylated oligogermane series $Ph_3Ge(GeBu_2)_nCH_2CH_2OEt$ ($n = 1-3$) and the digermanes Ph_3GeGeR_3 (R = Et, Bu, Pr^i, Ph), have been investigated using UV/visible spectroscopy and cyclic voltammetry. In general, the position of the absorption maximum shifts to lower energy and the oxidation potential decreases with increasing chain length. Variation of the organic substituents at germanium was also found to have a measurable effect on these spectral and electrochemical features. The experimental results were correlated with the energies of the HOMO and LUMO in these molecules, which were determined by density functional theory (DFT) calculations.

Introduction

The development of molecular wires having tunable properties and size is of significant interest in the areas of molecular electronics and nanotechnology.[1–4] Most attention has centered on the investigation of purely organic systems such as linear oligo- or polyphenylenes, oligothiophenes, and π-stacked systems where the extent of π conjugation controls the efficacy of electronic communication.[5–8] A variety of transition-metal-containing systems have also been explored for this purpose, from discrete self-assembled moieties and complexes connected via π-conjugated spacers[9–13] to covalent assemblies of multimetallic complexes.[14–17] The possibility of using catenated compounds of the heavier group 14 elements has also been investigated, and wires based on arrays of Si, Ge, or Sn centers might be expected to have interesting properties and could be used as electronic models for enhancing the understanding of one-dimensional semiconducting nanowires of these elements.

As has been addressed with silicon[18–28] and tin[29–46] oligomers and polymers, as well as in some sporadic reports on the related germanium congeners,[47–52] the optical and electronic properties of these compounds are intimately related to their structure. The

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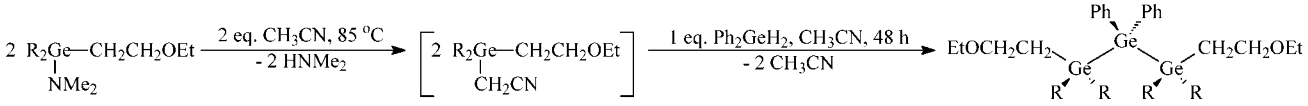
Scheme 1



1a: R = Et, 72 %
1b: R = Bu^n, 83 %
1c: R = Ph, 92 %

electronic properties of linear chains of R_2E units (E = Si, Ge, Sn) have been suggested to arise from σ conjugation of sp^3 hybrid orbitals.[53–55] Therefore, one can "coarse-tune" the electronic properties of these molecules by changing the number of bonded group 14 atoms in the backbone of the molecule. For example, the absorbance maximum (λ_{max}) in a series of perethylated germanes $Et(GeEt_2)_nEt$ ($n = 2-6$) undergoes a red shift with increasing chain length, varying from 202 nm for the digermane to 258 nm for the hexagermane.[56] Similarly, in the series $Me(GeMe_2)_nMe$ ($n = 2-6$) the absorption maximum varies from 194 nm for the dimer ($n = 2$) to 255 nm for the hexamer ($n = 6$), and the oxidation potential for the series was also shown to decrease with increasing Ge−Ge chain length, from 1.28 V for the dimer to 0.53 V for the hexamer.[47] For the same series of permethylated oligomers the ionization potential was also shown to decrease in energy with increasing chain length.[48]

Several issues have hindered widespread investigation into these compounds as viable candidates for molecular wires, particularly in the case of the germanium-containing species. Although several methods have been reported for the preparation of oligogermanes,[56–77] a viable synthetic methodology has not yet been fully established to give full control over all possible substitution patterns at the germanium atoms. Furthermore, the impact of the organic supporting ligands on the electronic properties of these catenates has not yet been fully addressed. For instance, it is highly desirable to understand how the variation of the organic substituents affects the fine-tuning of the electronic and electrochemical behavior properties of these systems.

We have recently demonstrated that the hydrogermolysis reaction involving an α-germyl nitrile and a germanium hydride (eq 1), where the R_3GeCH_2CN species is generated in situ from the amide R_3GeNMe_2 and CH_3CN, is a versatile synthetic route to oligogermanes which allows control over both the length of the Ge−Ge backbone and the peripheral organic substituents.[50–52] This method can be used for the synthesis of a wide variety of oligogermanes in good to excellent yields, thus permitting a detailed survey of their properties. We now wish to expound on our previous findings concerning the synthesis of these systems and describe our findings on the impact of the variation of the composition of these molecules on their optical and electronic attributes by considering a combination of experimental data and density functional calculations.

$$R_3GeNMe_2 \xrightarrow[-HNMe_2]{CH_3CN,\ 85°C} R_3GeCH_2CN \xrightarrow{R'_3GeH,\ CH_3CN,\ 85°C} R_3Ge{-}GeR'_3 + CH_3CN \quad (1)$$

Results and Discussion

Syntheses. The synthetic method used for the preparation of various oligogermanes is collected in Schemes 1 and 2, where the hydrogermolysis reaction serves as the key step for the construction of the Ge−Ge backbone in each case. We have previously demonstrated that the use of acetonitrile as the solvent is essential for the success of the Ge−Ge bond forming reaction,

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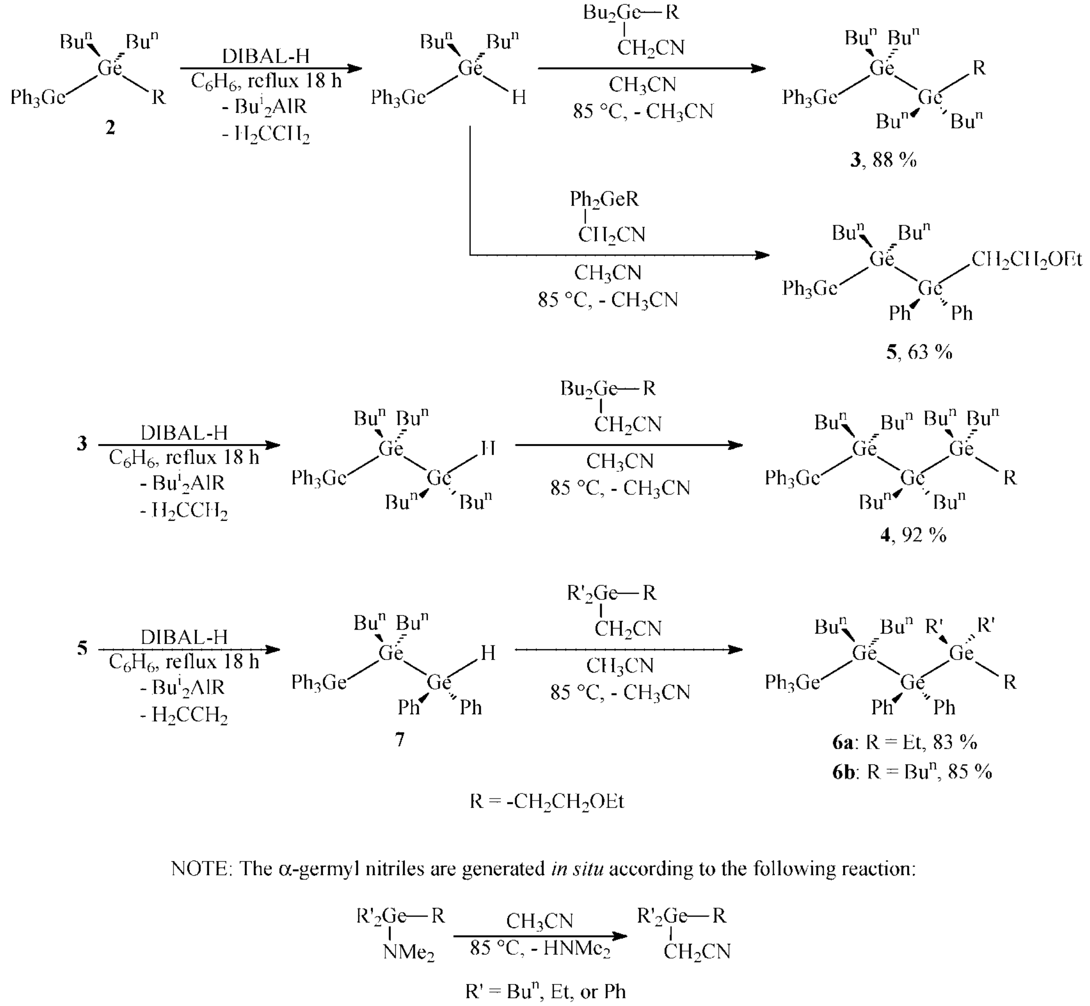
Scheme 2



as the germanium amides react with this solvent to furnish α-germyl nitriles which are the active species in hydrogermolysis reactions and react with the germanium hydrides to generate Ge−Ge bonds.[50–52] The α-germyl nitriles have been described to contain a labile Ge−C bond,[78,79] although this assumption was based on the reactivity of Et_3GeCH_2CN.[78] We have recently demonstrated that the lability of the Ge−C bond in these species depends on the steric and electronic attributes of the other organic substituents bound to germanium.[51]

Unlike most other preparative routes that have been previously described, our synthetic method allows for the stepwise preparation of oligogermanes, where the organic substituents attached to the germanium center can be systematically varied. We have used this method to prepare the three trigermanes **1a**−**c** in excellent yields starting from Ph_2GeH_2 and the three synthons $R_2Ge(NMe_2)CH_2CH_2OEt$ (R = Et, Bu^n, Ph)[50] (Scheme 1). The ethyl-substituted derivative **1a** is volatile, and care must be taken when distilling the crude product under vacuum to remove excess Ph_2GeH_2. The synthesis of the digermane **2** was previously reported, and compound **2** was employed for the preparation of the trigermane **3** and the tetragermane **4** in good to excellent yields (Scheme 2).[50] The trigermane **5** was also prepared from **2**, and compound **5** was subsequently used for the preparation of the two tetragermanes **6a**,**b** (Scheme 2). The intermediate hydrides generated by the reactions of the oligomers with diisobutylaluminum hydride (DIBAL-H) were neither isolated nor purified but, rather, were treated in crude form with the germanium amides in CH_3CN solution in order to provide the desired products **5** and **6** in high yields. All Ge−Ge bond forming reactions proceed by initial conversion of the germanium amides to α-germyl nitriles by reaction with the CH_3CN solvent.

The reaction of $Ph_3GeGePh_2CH_2CH_2OEt$ with DIBAL-H was previously found to be unsuccessful,[50] but the ethoxyethyl group of **5** can readily be cleaved by DIBAL-H to furnish the intermediate trigermane hydride **7**, which was subsequently converted to the tetragermanes **6a**,**b**. The difference in reactivity of $Ph_3GeGePh_2CH_2CH_2OEt$ and **5** therefore appears to be electronic rather than steric in nature, since compound **5** contains electron-donating *n*-butyl groups located between the two phenyl-substituted Ge centers. The oligogermanes prepared in these investigations have been characterized by NMR (^1H and ^{13}C) spectroscopy, elemental (C, H) analyses, cyclic voltammetry, and UV−visible spectroscopy. All of these materials are soluble in typical organic solvents and are viscous oils which are air- and moisture-sensitive.

Computational Studies. In order to facilitate the discussion of the electronic properties of the oligogermanes, it is useful to examine the results of computational studies performed on a comprehensive set of 51 derivatives ranging from digermanes to octagermanes that are either known or hypothetical compounds (see the Supporting Information). In these studies, all

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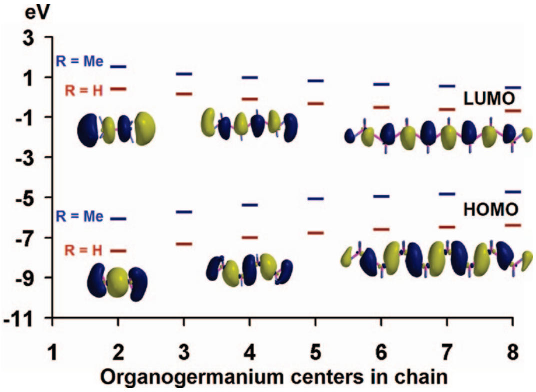


Figure 1. Relative energies (eV) of frontier orbitals for $R_3Ge(GeR_2)_nGeR_3$ ($n = 0-6$): (red lines) R = H; (blue lines) R = Me. The orbital plots for $n = 0$, 2, 6 are also shown.

compounds were subject to semiempirical quantum mechanical PM3-geometry optimization prior to single-point density functional calculations (DFT) using the B3LYP/6-31G* basis set. Higher level calculations on several derivatives were also explored (ab initio HF/3-21G geometry optimization followed by DFT B3LYP/6-311G**), which gave identical trends but were significantly more computationally expensive (in some cases, prohibitively). Therefore, only the results of the smaller, but complete, set using the B3LYP/6-31G* basis will be addressed, as these are also in qualitative agreement with the experimental absorbance and voltammetry investigations. Selected frontier orbitals (HOMO and LUMO) are shown for some parent oligogermanes in Figure 1, along with the calculated energies of the orbitals for $R_3Ge(GeR_2)_nGeR_3$ ($n = 0-6$; R = H, Me) derivatives.

With the exceptions noted below for aryl derivatives, the main features of the corresponding frontier orbitals for the substituted oligogermanes mirror those for the simple $H_3Ge(GeR_2)_nGeH_3$ ($n = 0-6$) series in that the HOMO is σ bonding while the LUMO is σ^* antibonding in nature. As will be elaborated on, the relatively low symmetry of the oligogermanes (giving rise to a large number of molecular orbitals of the same symmetry) combined with the close energy separation of the valence 4s and 4p orbitals on germanium results in extensive mixing. Of the compounds studied, the homoleptic digermanes Ge_2R_6 can be differentiated from the higher oligomers by symmetry considerations. For instance, the Ge_2R_6 series has idealized D_{3d} symmetry which renders one 4p orbital on each germanium atom (p_z, along the internuclear C_3 axis) available for σ-bonding interactions and a pair of degenerate 4p orbitals per germanium ($p_{x,y}$ orthogonal to the C_3 axis) available for π-bonding interactions. In contrast, for the homoleptic $R_3Ge(GeR_2)_nGeR_3$ ($n = 1-6$) series, the highest symmetry is C_{2v} for odd values of n and C_{2h} for even values of n. In this manner, only one 4p orbital which is orthogonal to the plane of the molecule participates in π-bonding interactions, while the other two 4p orbitals participate in σ-bonding interactions (*vide infra*).

The main contributions to the frontier orbitals (HOMO and LUMO) for a representative series of oligogermanes $H_3Ge(GeR_2)_nGeH_3$ ($n = 0-3$) are summarized in Table 1. The HOMO of Ge_2H_6 is a mainly germanium-based σ orbital with only 10% bonding contribution from an A_{1g} hydrogen group orbital, where the germanium component is comprised mainly (96%) of two out-of-phase Ge $4p_z$ orbitals mixed with a small amount (4%) of two in-phase Ge 4s orbitals (bottom left, Table 1). The LUMO of Ge_2H_6 is a germanium-based σ^* orbital (only 1% bonding contribution from the A_{2u} hydrogen group orbital) where the germanium component is constructed from a mixture of mainly (68%) two out-of-phase 4s orbitals mixed with a significant contribution (32%) of two in-phase Ge $4p_z$ orbitals (top left, Table 1).

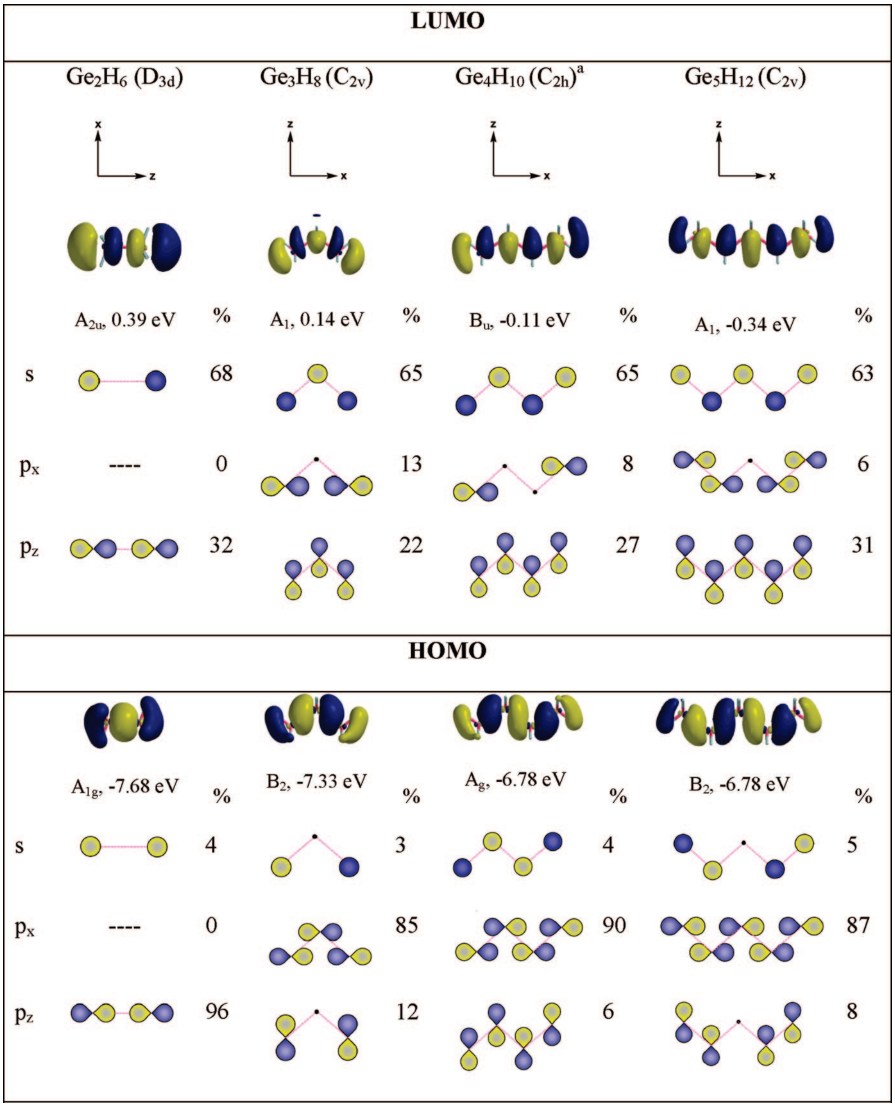
For the higher oligogermanes of the form Ge_nH_{2n+2}, the HOMO is germanium-based and is comprised mainly (85−91%) of a molecular orbital composed of out-of-phase $4p_x$ (see Table 1 for coordinate system) atomic orbitals. These are mixed with 5−12% of a molecular orbital comprised of partly out-of-phase in-plane $4p_z$ atomic orbitals (see Table 1 for coordinate system) that have one node in the *yz* plane and also with 2−5% of a molecular orbital containing n 4s atomic orbitals that are partly "out of phase" with $n - 2$ nodes. The LUMO of the higher oligogermanes, Ge_nH_{2n+2}, is also a mixture of three components. In this case the major component (ca. 65%) is a molecular orbital comprised of out-of-phase 4s atomic orbitals mixed with 22−30% of a molecular orbital constructed form in-phase $4p_z$ atomic orbitals. The smallest component (6−13%) of the LUMO is a set of partly out-of-phase $4p_x$ orbitals (x directed along the internuclear axis) that has $n - 1$ nodes. To a first approximation, with the smallest component of mixing being ignored, the HOMO is essentially out-of-phase $4p_x$ in character while the LUMO represents an in-phase combination of sp hybrid orbitals.

The relative energies of the HOMO and LUMO vary in the expected manner according to chain length, the Ge−Ge distances which are guided by the steric bulk of substituents and by the inductive effects of peripheral groups bound to the oligogermane core. Thus, the HOMO energy increases (becomes destabilized) as the proportion of electron-rich R_2Ge^{II} centers increases relative to the terminal R_3Ge^{III} centers. Electron-donating groups bound to germanium destabilize the HOMO by making the chain more electron rich, as exemplified by comparing the relative energies of the HOMO in $R_3Ge(GeR_2)_nGeR_3$ ($n = 0-6$; R = H versus R = Me) in Figure 1. Similarly, the energy of the HOMO increases along the series Me < Et < Pr^n < Bu^n due to the inductive effects of replacing C−H with C−alkyl groups.

With increasing chain length, the LUMO becomes stabilized via conjugation, as expected from the σ^* character. As found for the HOMO, the substitution of electron-donating substituents destabilizes the LUMO via inductive effects, as indicated by a comparison of the CH_3 versus H groups in Figure 1. It is also noteworthy that for the new compounds described here replacing a germanium−alkyl group with the CH_2CH_2OEt group has only a very small stabilizing effect on the energies of the frontier orbitals, an exception being the replacement of the CH_3 group with the CH_2CH_2OEt group, where the inductive (destabilizing) effects become important.

Phenyl substitution has a significant impact on the frontier orbitals of oligogermanes, since the phenyl group both is a better σ donor than either methyl groups or hydrogens and is sufficiently bulky to increase the Ge−Ge bond distance. Therefore, this substitution is expected to significantly raise the energy of the HOMO; however, conjugation with the phenyl group orbitals partially offsets the expected destabilization. Furthermore, the LUMO and next-higher virtual orbitals of the aryl-substituted oligogermanes, which consist of two group orbitals per phenyl ring, are almost exclusively composed of linear combinations of phenyl-based π^* orbitals rather than being germanium-based σ^*, as these are in-phase sp hybrid orbitals which are higher in energy. Thus, the variation in LUMO energy is very small throughout the series of aryl-substituted oligogermanes.

Table 1. Summary of LUMO and HOMO Composition from DFT Calculations



	Ge_2H_6 (D_{3d})	%	Ge_3H_8 (C_{2v})	%	Ge_4H_{10} (C_{2h})[a]	%	Ge_5H_{12} (C_{2v})	%
LUMO								
	A_{2u}, 0.39 eV		A_1, 0.14 eV		B_u, -0.11 eV		A_1, -0.34 eV	
s		68		65		65		63
p_x	----	0		13		8		6
p_z		32		22		27		31
HOMO								
	A_{1g}, -7.68 eV		B_2, -7.33 eV		A_g, -6.78 eV		B_2, -6.78 eV	
s		4		3		4		5
p_x	----	0		85		90		87
p_z		96		12		6		8

[a] Nonstandard coordinate system employed for simplicity (*x*, *y* normally in molecular plane).

As expected, the HOMO−LUMO energy gap in oligogermanes can be coarsely tuned by varying the degree of catenation, with longer chains giving rise to smaller energy gaps. Changing the nature of substituents bound to the oligogermane core changes the relative energy of the HOMO to a greater extent than the energy of the LUMO and therefore provides a simple means for fine-tuning the HOMO−LUMO energy gap of these compounds. Both of these conclusions were also observed experimentally, as described below.

Absorption and Electrochemical Characteristics. Cyclic voltammograms for the various oligogermanes were obtained in CH_3CN solution using 1.0 M $[Bu_4N][PF_6]$ as the supporting electrolyte. Irreversible oxidation waves were observed in all cases, as exemplified for the $Ph_3Ge(GeBu_2)_nGeBu_2CH_2CH_2OEt$ (**2**, $n = 0$; **3**, $n = 1$; **4**, $n = 2$) series shown in Figure 2. The reported values for the oxidations found in Table 2 are for the anodic waves, as the expected cathodic return waves were absent, and are average values of four independent measurements which were generally reproducible with errors of less than ±30 mV. The irreversibility of the oxidation waves is in accord with previous findings of electrochemical measurements on permethyloligogermanes.[47,49] Chain contraction of oligogermanes has also been reported to occur via germylene extrusion

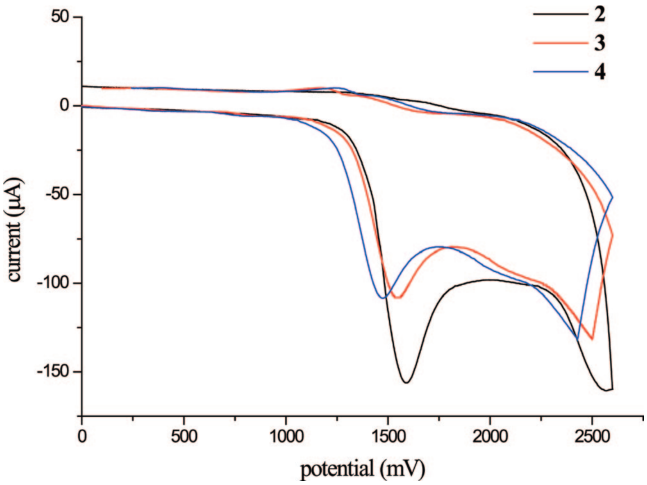


Figure 2. Cyclic voltammograms for CH_3CN solutions of $Ph_3Ge(GeBu_2)_nGeBu_2CH_2CH_2OEt$ obtained at 150 mV/s using $(^nBu_4N)(PF_6)$ as the supporting electrolyte: (black line) $n = 0$ (**2**); (red line) $n = 1$ (**3**); (blue line) $n = 2$ (**4**).

Table 2. Absorption, Electrochemical Data, and Calculated HOMO/LUMO Energy Levels (B3LYP/6-31G*) for Oligogermanes 1−6 and 8 (R = CH_2CH_2OEt)

compd	formula	λ_{max} (nm)	E_{ox} (mV)	HOMO	LUMO
1a	$REt_2GeGePh_2GeEt_2R$	243	1577 ± 22	−5.23	−0.19
1b	$RBu_2GeGePh_2GeBu_2R$	243	1500 ± 18	−5.18	−0.10
1c	$RPh_2GeGePh_2GePh_2R$	247	1609 ± 24	−5.49	−0.52
2	$Ph_3GeGeBu_2R$	224	1590 ± 19	−5.45	−0.36
3	$Ph_3Ge(GeBu_2)_2R$	232	1546 ± 16	−5.41	−0.37
4	$Ph_3Ge(GeBu_2)_3R$	245	1474 ± 21	−5.20	−0.38
5	$Ph_3GeGeBu_2GePh_2R$	232	1525 ± 26	−5.43	−0.35
6a	$Ph_3GeGeBu_2GePh_2GeEt_2R$	248	1483 ± 17	−5.22	−0.38
6b	$Ph_3GeGeBu_2GePh_2GeBu_2R$	248	1462 ± 19	−5.19	−0.38
8a	$Ph_3GeGePh_3$	240	1576 ± 13	−5.45	−0.66
8b	$Pr^i{}_3GeGePh_3$	235	1635 ± 12	−5.56	−0.30
8c	$Et_3GeGePh_3$	231	1587 ± 17	−5.46	−0.35
8d	$Bu_3GeGePh_3$	232	1588 ± 11	−5.38	−0.34

and heterolytic Ge−Ge bond cleavage,[80] and similar reactions may be responsible for the irreversible processes in the compounds described here. Regardless, the relative oxidation potentials of the series of oligogermanes measured in these studies parallel the results found from the DFT calculations, in that the oxidation potential decreases with an increasing proportion of R_2Ge centers along the oligogermane backbone. Thus, the oxidation potentials of the series **2**−**4** decrease on traversing from the digermane (1589 mV) to the trigermane (1546 mV) and to the tetragermane (1474 mV).

Several other trends in the oxidation potentials of these systems are noteworthy. First, the observed oxidation potentials of the trigermanes **3** (1546 mV) and **5** (1525 mV) agree with the results predicted from the DFT calculations, that the presence of a phenyl substituent raises the relative energy of the HOMO compared to the presence of an alkyl substituent. Additionally, for the two tetragermanes **6a**,**b**, there is a small decrease in the oxidation potential with increasing inductive effects on exchanging ethyl substituents in **6a** (1483 mV) with the butyl groups of **6b** (1462 mV), which was also expected on the basis of the DFT calculations. Finally, for the four digermanes $R_3GeGePh_3$ investigated in this study, the oxidation potentials of **8a** (R = Ph), **8c** (R = Et), and **8d** (R = Bu) are all lower than that of **8b** (R = Pr^i). This result also agrees with the DFT calculations in that **8b** has the lowest lying HOMO in the series, which is presumably a steric consideration. Compound **8b** was calculated to have the longest Ge−Ge distance among the four digermanes (see the Supporting Information). This has also been observed experimentally, as the Ge−Ge distance in **8b** is 2.4637(7) Å[51] versus those for **8a** (2.437(2) Å),[67] **8c** (2.4253(7) Å),[50] and **8d** (2.4212(8) Å, average of two independent molecules).[50]

Absorption data for oligogermanes **1**−**6** and **8** are collected in Table 2, and UV/visible spectra for the three related series **1a**−**c**, **2**−**4**, and **8a**−**d** are shown in Figures 3–5, respectively. The absorption bands for the digermanes **8a**−**d** and the butylated series **3**−**5** are broad, and the absorbance maxima (λ_{max}) range from 221 to 245 nm. As expected on the basis of similar studies conducted for a series of permethylated[47] and perethylated[56] germanium oligomers as well as a related group of butylated tin species,[30] the position of the absorbance maximum among the oligomers **3**−**5** undergoes a red shift with increasing chain length. These findings agree with previous observations on related systems and with the magnitude of the HOMO/LUMO gap calculated by DFT (*vide supra*). The relative position of the LUMO remains approximately the same among the three molecules, but increasing the number of germanium atoms in the chain results in an overall destabilization of the energy of the HOMO, thus shifting the energy of the electronic transition to lower energy.

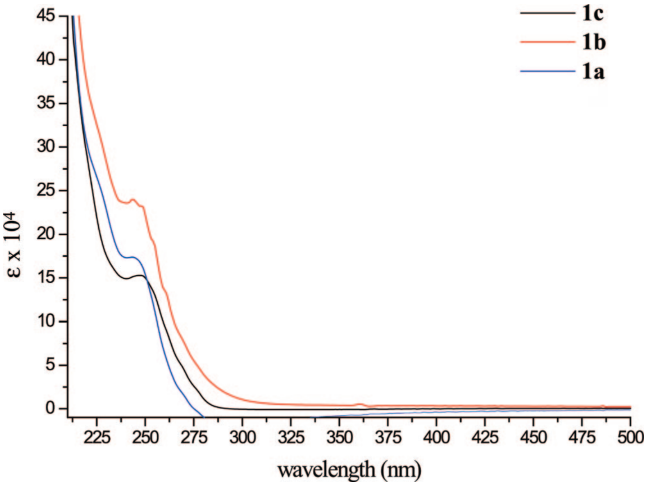


Figure 3. UV/visible spectra in CH_3CN solution: (black line) $EtOCH_2CH_2Ph_2GeGePh_2GePh_2CH_2CH_2OEt$ (**1c**); (red line) $EtOCH_2CH_2Et_2GeGePh_2GeEt_2CH_2CH_2OEt$ (**1b**); (blue line) $EtOCH_2CH_2Bu_2GeGePh_2GeBu_2CH_2CH_2OEt$ (**1a**).

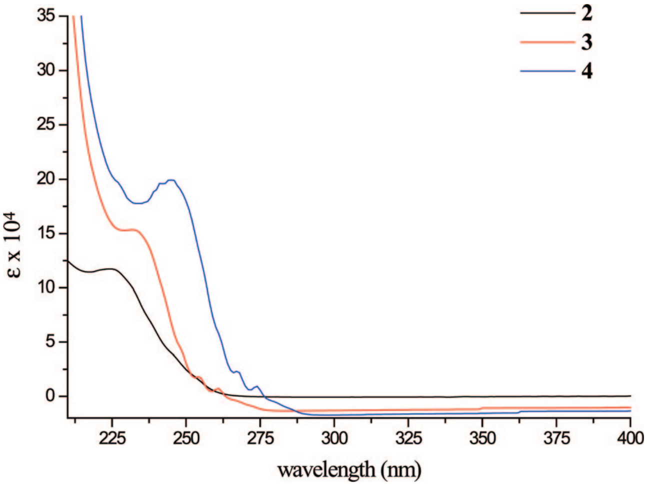


Figure 4. UV/visible spectra in CH_3CN solution: (black line) $Ph_3GeGeBu_2CH_2CH_2OEt$ (**2**); (red line) $Ph_3Ge(GeBu_2)_2CH_2CH_2OEt$ (**3**); (blue line) $Ph_3Ge(GeBu_2)_3CH_2CH_2OEt$ (**4**).

For the series of digermanes $R_3GeGePh_3$, the absorbance maximum of the phenyl-substituted derivative **8a** (R = Ph) is significantly red-shifted relative to the alkyl-substituted species **8b**−**d**. This trend parallels the results found from DFT calculations (see the Supporting Information) and can be attributed to the lower energy and greater number of low-lying virtual orbitals from the phenyl group substituents in **8a** relative to the alkyl-substituted derivatives **8b**−**d**. The three compounds **8b**−**d** all have similar absorption characteristics, as predicted from the DFT calculations, where the energetic differences between the frontier orbitals on traversing the series of these three compounds is negligible. Likewise, the series of trigermanes **1a**−**c** all have approximately the same HOMO/LUMO separation and their λ_{max} values fall into the narrow range of 243−247 nm. However, the absorbance bands **1a**−**c** are all significantly broader and tail off into the visible region when compared to those of compounds **1**, **4**−**6**, and **8**. This results in the trigermanes **1a**−**c** being slightly pale yellow while the remaining nine species are colorless.

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(80) Mochida, K.; Chiba, H.; Okano, M. *Chem. Lett.* **1991**, 109–112.

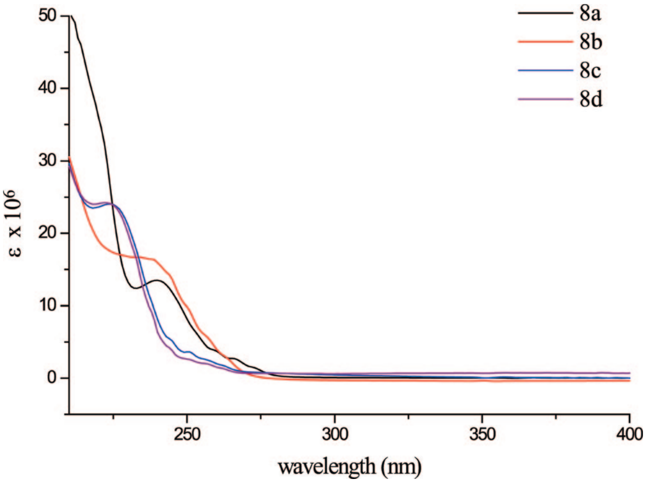

Figure 5. UV/visible spectra for in CH_3CN solution: (black line) $Ph_3GeGePh_3$ (**8a**); (red line) $Pr^i{}_3GeGePh_3$ (**8b**); (blue line) $Et_3GeGePh_3$ (**8c**); (purple line) $Bu_3GeGePh_3$ (**8d**).

Conclusions

The synthesis of oligogermanes with controllable nuclearity and organic substitution patterns has been described. Examination of the experimental electronic properties and the results of density functional calculations reveal that the HOMO in each of these molecules is a σ orbital resulting mainly from the out-of-phase linear combination of p orbitals on germanium, but with a small contribution from mixing of the 4s and the orthogonal 4p orbitals. For oligogermanes without phenyl substituents, the LUMO is σ^* in nature but is extensively mixed, mainly between the out-of-phase linear combination of 4s orbitals and the in-phase linear combination of $4p_z$ orbitals. The net result is that the LUMO can be adequately described as being due to an in-phase but spatially inverted linear combination of sp hybrid orbitals.

The HOMO/LUMO gap can be tuned in a predictable way by changing the length of the Ge−Ge chain in these compounds, as well as by altering the organic groups along the germanium−germanium backbone, where increasing the chain length is the most effective means for decreasing the HOMO/LUMO gap. Variation of the σ-donor abilities of the groups bound to germanium provides a means to more finely tune this energy difference, since the relative energy of the HOMO is more affected by such a change than that of the LUMO. For phenyl-substituted oligogermanes, the LUMO is derived from linear combinations of phenyl group π^* orbitals, rather than being germanium-based, which significantly alters the electronic properties of these compounds. However, the electronic tunability according to the findings of the aliphatic series is still preserved, as seen experimentally from UV/visible spectroscopic and electrochemical measurements. For consideration of the use of oligogermanes as viable candidates for molecular wires, it would be desirable to improve the air and electrochemical stability and, to this end, we are currently investigating new ligand systems that would promote reversibility by constraining Ge−Ge bond dissociation.

Experimental Section

General Considerations. All manipulations were carried out under an inert N_2 atmosphere using standard Schlenk, syringe, and glovebox techniques.[81] The compounds $R_2Ge(NMe_2)CH_2CH_2OEt$ (R = Et, Bu, Ph),[50] **2**−**4**,[50] **8a**,[51] **8b**,[51] **8c**,[50] and **8d**[50] were prepared by literature methods. The reagents DIBAL-H (1.0 M in hexanes) (Aldrich) and Ph_2GeH_2 (Gelest) were purchased from commercial sources and used without further purification. Solvents were purified using a Glass Contour Solvent Purification System. NMR spectra were recorded using a Varian Gemini 2000 spectrometer operating at 300.0 MHz (^1H) or 75.5 MHz (^{13}C) and were referenced to the C_6D_6 solvent. Cyclic voltammograms were obtained using a Bioanalytical Systems Epsilon Electrochemical Workstation with a glassy-carbon-disk working electrode, a platinum-wire counter electrode, and a Ag/AgCl reference electrode using 1.0 M $[Bu_4N]PF_6$ in CH_3CN as the supporting electrolyte. UV/visible spectra were obtained using a Hewlett-Packard Agilent UV/visible spectroscopy system. Elemental analyses were conducted by Desert Analytics or Midwest Microlabs.

Preparation of $EtOCH_2CH_2(GeEt_2)(GePh_2)(GeEt_2)CH_2CH_2OEt$ (1a). To a solution of $Et_2Ge(NMe_2)CH_2CH_2OEt$[50] (0.535 g, 2.16 mmol) in acetonitrile (20 mL) in a Schlenk tube was added Ph_2GeH_2 (0.250 g, 1.09 mmol) in acetonitrile (10 mL). The tube was sealed and heated in an oil bath at 85 °C for 48 h, after which time the volatiles were removed *in vacuo*. Residual Ph_2GeH_2 was removed by Kugelrohr distillation (110 °C, 0.05 Torr) to yield 0.498 g (72%) of **1a** as a thick colorless liquid. ^1H NMR (C_6D_6, 25 °C): δ 7.68 (d, J = 6.3 Hz, 4 H, *m*-H), 7.23−7.13 (m, 6 H, *p*- and *o*-H), 3.49 (t, J = 7.8 Hz, 4 H, $GeCH_2CH_2O-$), 3.24 (q, J = 7.2 Hz, 4 H, $-OCH_2CH_3$), 1.54 (t, J = 7.8 Hz, 4 H, $GeCH_2CH_2O-$), 1.15−1.06 ppm (m, 26 H, aliphatics). ^{13}C NMR (C_6D_6, 25 °C): δ 140.2 (*ipso*-C), 135.9 (*o*-C), 128.4 (*m*-C), 128.0 (*p*-C), 68.7 ($-OCH_2CH_3$), 65.6 ($-GeCH_2CH_2O-$), 15.8 ($-OCH_2CH_3$), 15.5 ($Ge(CH_2CH_3)_2$), 10.2 ($GeCH_2CH_2O-$), 7.4 ppm ($Ge(CH_2CH_3)_2$). UV/visible: λ_{max} 243 nm (v br, $\epsilon = 2.05 \times 10^4$ cm^{-1} M^{-1}). Anal. Calcd for $C_{28}H_{48}Ge_3O_2$: C, 53.01; H, 7.63. Found: C, 52.93; H, 7.25.

Preparation of $EtOCH_2CH_2(GeBu_2)(GePh_2)(GeBu_2)CH_2CH_2OEt$ (1b). To a solution of $Bu_2Ge(NMe_2)CH_2CH_2OEt$[50] (1.505 g, 4.950 mmol) in acetonitrile (25 mL) in a Schlenk tube was added Ph_2GeH_2 (0.569 g, 2.49 mmol) in acetonitrile (10 mL). The tube was sealed and heated in an oil bath at 80 °C for 48 h, after which time the volatiles were removed *in vacuo*. Residual Ph_2GeH_2 was removed by Kugelrohr distillation to yield 1.535 g (83%) of **1b** as a thick pale yellow liquid. ^1H NMR (C_6D_6, 25 °C): δ 7.73 (d, J = 7.8 Hz, 4 H, *m*-H), 7.23−7.11 (m, 6 H, *p*- and *o*-H), 3.57 (t, J = 7.5 Hz, 4 H, $GeCH_2CH_2O-$), 3.28 (q, J = 7.2 Hz, 4 H, $-OCH_2CH_3$), 1.62 (t, J = 7.5 Hz, 4 H, $GeCH_2CH_2O-$), 1.48 (m, 8 H, $Ge(CH_2CH_2CH_2CH_3)_2$), 1.35 (pent, J = 6.8 Hz, 8 H, $Ge(CH_2CH_2CH_2CH_3)_2$), 1.25 (t, J = 7.5 Hz, 8 H, $Ge(CH_2CH_2CH_2CH_3)_2$), 1.13 (t, J = 7.5 Hz, 6 H, $-OCH_2CH_3$), 0.89 ppm (t, J = 6.8 Hz, 12 H, $Ge(CH_2CH_2CH_2CH_3)_2$). ^{13}C NMR (C_6D_6, 25 °C): δ 140.4 (*ipso*-C), 138.0 (*o*-C), 128.4 (*m*-C), 128.1 (*p*-C), 68.9 ($-OCH_2CH_3$), 65.7 ($-GeCH_2CH_2O-$), 28.8 ($-OCH_2CH_3$), 27.0 ($Ge(CH_2CH_2CH_2CH_3)_2$), 16.6 ($Ge(CH_2CH_2CH_2CH_3)_2$), 15.8 ($Ge(CH_2CH_2CH_2CH_3)_2$), 15.4 ($GeCH_2CH_2O-$), 13.8 ppm ($Ge(CH_2CH_2CH_2CH_3)_2$). UV/visible: λ_{max} 243 nm (v br, $\epsilon = 1.57 \times 10^4$ cm^{-1} M^{-1}). Anal. Calcd for $C_{36}H_{64}Ge_3O_2$: C, 57.91; H, 8.64. Found: C, 58.06; H, 8.78.

Preparation of $EtOCH_2CH_2(GePh_2)(GePh_2)(GePh_2)CH_2CH_2OEt$ (1c). To a solution of Ph_2GeH_2 (0.510 g, 2.23 mmol) in acetonitrile (15 mL) in a Schlenk tube was added $Ph_2Ge(NMe_2)CH_2CH_2OEt$[50] (1.52 g, 4.42 mmol) in acetonitrile (10 mL). The tube was sealed and heated in an oil bath at 85 °C for 48 h, after which time the volatiles were removed *in vacuo* to yield a thick viscous liquid, which was distilled in a Kugelrohr oven (140 °C, 0.05 Torr) to yield 1.681 g (92%) of **1c** as a white solid.

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[81] Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

^{1}H NMR (C_6D_6, 25 °C): δ 7.68−7.64 (m, 4 H, *m*-H), 7.49−7.45 (m, 8 H, *m*-H), 7.17 (m, 6 H, *p*- and *o*-H), 7.11−7.05 (m, 12 H, *p*- and *o*-H), 3.45 (t, J = 7.8 Hz, 4 H, $GeCH_2CH_2O-$), 3.02 (q, J = 6.9 Hz, 4 H, $-OCH_2CH_3$), 1.93 (t, J = 7.8 Hz, 4 H, $GeCH_2CH_2O-$), 0.95 ppm (t, J = 6.9 Hz, 6 H, $-OCH_2CH_3$). ^{13}C NMR (C_6D_6, 25 °C): δ 138.2 (ipso-C), 136.5 (*o*-C), 135.6 (*o*-C),139.0 (*ipso*-C), 128.8, 128.5, 128.4, 128.3 (*m*- and *p*-C), 68.0 ($-OCH_2CH_3$), 65.4 ($-GeCH_2CH_2O-$), 17.3 ($-OCH_2CH_3$), 15.3 ppm ($GeCH_2CH_2O-$). UV/visible: λ_{max} 247 nm (v br, $\epsilon = 1.98 \times 10^4$ cm^{-1} M^{-1}). Anal. Calcd for $C_{44}H_{48}Ge_3O_2$: C, 63.93; H, 5.85. Found: C, 63.51; H, 5.69.

Preparation of $Ph_3Ge(GeBu_2)(GePh_2)CH_2CH_2OEt$ (5). To a solution of $Ph_3Ge(GeBu_2)CH_2CH_2OEt$[50] (0.672 g, 1.19 mmol) in benzene (15 mL) was added a solution of 1.0 M DIBAL-H in hexane (1.31 mL, 1.31 mmol). The reaction mixture was refluxed under N_2 for 24 h, after which time the solvent was removed *in vacuo* to yield a viscous oil. The oil was dissolved in acetonitrile (20 mL), transferred to a Schlenk tube, and treated with a solution of $Ph_2Ge(NMe_2)CH_2CH_2OEt$[50] (0.409 g, 1.19 mmol) in acetonitrile (10 mL). The tube was sealed, and the reaction mixture was heated at 90 °C for 4 days. The volatiles were removed *in vacuo*, and the crude product mixture was washed through a 1 in. × 3 in. silica gel column using benzene (35 mL). The solvent was removed *in vacuo* to yield **5** (0.595 g, 63%) as a thick colorless oil. ^{1}H NMR (C_6D_6, 25 °C): δ 7.65−7.61 (m, 10 H, aromatics, *m*-H), 7.20−7.08 (m, 15 H, aromatics, *o*-H and *p*-H), 3.48 (t, J = 7.5 Hz, 2 H, $-CH_2CH_2O-$), 3.14 (q, J = 6.6 Hz, 2 H, $--OCH_2CH_3$), 1.53 (t, J = 7.5 Hz, 2 H, $-CH_2CH_2O-$), 1.39 (m, 4H, aliphatics), 1.15 (m, 8H, aliphatics), 0.77 (t, 3H, J = 6.6 Hz, $-OCH_2CH_3$), 0.76 ppm (t, J = 7.2 Hz, 6H, $-CH_2CH_2CH_2CH_3$). ^{13}C NMR (C_6D_6, 25 °C): δ 139.3 (*ipso*-C), 139.2 (*ipso*-C), 136.0 (*o*-C), 135.7 (*o*-C), 128.7, 128.5 (2 *m*- and 2 *p*-C), 68.8 ($-OCH_2CH_3$), 65.7 ($-GeCH_2CH_2O-$), 28.7 ($-OCH_2CH_3$), 26.8 ($-CH_2CH_2CH_2CH_3$), 14.0 ($-CH_2CH_2CH_2CH_3$), 13.8 ($-CH_2CH_2CH_2CH_3$), 10.4 ($GeCH_2CH_2O-$), 7.1 ppm ($-CH_2CH_2CH_2CH_3$). UV/visible: λ_{max} 232 nm (br, $\epsilon = 4.02 \times 10^4$ cm^{-1} M^{-1}). Anal. Calcd for $C_{42}H_{52}Ge_3O$: C, 63.80; H, 6.63. Found: C, 64.11; H, 7.15.

Preparation of $Ph_3Ge(GeBu_2)(GePh_2)(GeEt_2)CH_2CH_2OEt$ (6a). To a solution of $Ph_3Ge(GeBu_2)(GePh_2)CH_2CH_2OEt$ (**5**; 0.525 g, 0.664 mmol) in benzene (20 mL) was added a solution of 1.0 M DIBAL-H in hexane (0.75 mL, 0.75 mmol). The reaction mixture was refluxed under N_2 for 24 h, after which time the solvent was removed *in vacuo* to yield a thick opaque oil. The oil was dissolved in acetonitrile (25 mL), transferred to a Schlenk tube, and treated with a solution of $Et_2Ge(NMe_2)CH_2CH_2OEt$[50] (0.165 g, 0.666 mmol) in acetonitrile (15 mL). The tube was sealed, and the reaction mixture was heated at 90 °C for 48 h. The volatiles were removed *in vacuo*, and the crude product mixture was washed through a 1 in. × 3 in. silica gel column using benzene (50 mL). The solvent was removed *in vacuo* to yield **6a** (0.508 g, 83%) as a thick colorless oil. ^{1}H NMR (C_6D_6, 25 °C): δ 7.70−7.54 (m, 10 H, aromatics, *m*-H), 7.19−7.03 (m, 15 H, aromatics, *o*-H and *p*-H), 3.42 (t, J = 7.2 Hz, 2 H, $GeCH_2CH_2O-$), 3.09 (q, J = 6.8 Hz, 2 H, $-OCH_2CH_3$), 1.48 (t, J = 7.2 Hz, 2 H, $GeCH_2CH_2O-$), 1.44−1.28 (m, 4 H, aliphatics), 1.19−1.13 (m, 4 H, aliphatics), 1.09−0.98 (m, 14 H, aliphatics), 0.73 (t, J = 6.8 Hz, 3 H, $-OCH_2CH_3$), 0.71 ppm (t, J = 7.2 Hz, 6H, $Ge(CH_2CH_2CH_2CH_3)_2$). ^{13}C NMR (C_6D_6, 25 °C): δ 139.1 (*ipso*-C), 139.0 (*ipso*-C), 136.0 (*o*-C), 135.6 (*o*-C), 128.6, 128.5 (2 *m*- and 2 *p*-C), 68.7 ($-OCH_2CH_3$), 65.6 ($-GeCH_2CH_2O-$), 28.5 ($-OCH_2CH_3$), 26.6 ($Ge(CH_2CH_2CH_2CH_3)_2$), 14.0 ($Ge(CH_2CH_3)_2$), 13.7 ($Ge(CH_2CH_2CH_2CH_3)_2$), 10.3 ($Ge(CH_2CH_2CH_2CH_3)_2$), 8.6 ($GeCH_2CH_2O-$), 7.0 ($Ge(CH_2CH_2CH_2CH_3)_2$), 5.6 ppm ($Ge(CH_2CH_3)_2$). UV/visible: λ_{max} 248 nm (v br, $\epsilon = 2.97 \times 10^4$ cm^{-1} M^{-1}). Anal. Calcd for $C_{46}H_{62}Ge_4O$: C, 59.97; H, 6.78. Found: C, 60.10; H, 6.90.

Preparation of $Ph_3Ge(GeBu_2)(GePh_2)(GeBu_2)CH_2CH_2OEt$ (6b). To a solution of $Ph_3Ge(GeBu_2)(GePh_2)CH_2CH_2OEt$ (**5**; 0.211 g, 0.267 mmol) in benzene (10 mL) was added a solution of 1.0 M DIBAL-H in hexane (0.28 mL, 0.28 mmol). The reaction mixture was refluxed under N_2 for 24 h, after which time the solvent was removed *in vacuo* to yield a thick opaque oil. The oil was dissolved in acetonitrile (10 mL), transferred to a Schlenk tube, and treated with a solution of $Bu_2Ge(NMe_2)CH_2CH_2OEt$[50] (0.083 g, 0.27 mmol) in acetonitrile (10 mL). The tube was sealed and the reaction mixture was heated at 90 °C for 48 h. The volatiles were removed *in vacuo*, and the crude product mixture was washed through a 1 in. × 3 in. silica gel column using benzene (45 mL). The solvent was removed *in vacuo* to yield **6b** (0.224 g, 86%) as a thick pale yellow oil. ^{1}H NMR (C_6D_6, 25 °C): δ 7.60−7.56 (m, 10 H, *m*-H), 7.14−7.07 (m, 25 H, *o*- and *p*-H), 3.42 (t, J = 7.6 Hz, 2 H, $-CH_2CH_2O-$), 3.09 (q, J = 6.8 Hz, 2 H, $-OCH_2CH_3$), 1.48 (t, J = 6.8 Hz, 2 H, $GeCH_2CH_2O-$), 1.40−1.26 (m, 4 H, aliphatics), 1.21−0.97 (m, 13 H, aliphatics), 0.71 ppm (m, 12 H, $(GeCH_2CH_2CH_2CH_3)_4$). ^{13}C NMR (C_6D_6, 25 °C): δ 139.1 (*ipso*-C), 139.0 (*ipso*-C), 135.6 (*o*-C), 135.3 (*o*-C), 128.6 (2 *m*- and 2 *p*-C), 68.7 ($-OCH_2CH_3$), 65.6 ($-GeCH_2CH_2O-$), 28.6 ($-OCH_2CH_3$), 26.6 (2 $-CH_2CH_2CH_2CH_3$), 16.1 ($-CH_2CH_2CH_2CH_3$), 15.3 ($-CH_2CH_2CH_2CH_3$), 14.9 ($-CH_2CH_2CH_2CH_3$), 13.9 ($-CH_2CH_2CH_2CH_3$), 13.6 ($GeCH_2CH_2O-$), 10.2 ($GeCH_2CH_2CH_2CH_3$), 6.9 ppm ($GeCH_2CH_2CH_2CH_3$). Anal. Calcd for $C_{50}H_{70}Ge_4O$: C, 61.44; H, 7.22. Found: C, 64.41; H, 7.42.

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Supporting Information Available: Text giving computational details, tables giving calculated HOMO/LUMO energy levels, figures giving frontier orbital diagrams, and tables giving Cartesian (*xyz*) coordinates for compounds **1**−**6** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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