Donor-Acceptor Molecular Oligogermanes: Novel Properties and Structural Aspects

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Abstract: The linear oligogermyl amide **2**, $Ph_3GeGeMe_2NMe_2$, was obtained by reacting Ph_3GeLi with **1**, $Me_2Ge(Cl)NMe_2$. The amide **2** was used for the synthesis of molecular oligogermanes **3**, $Ph_3GeGeMe_2Ge(C_6F_5)_3$, and **4**, $[Ph_3GeGeMe_2]_2Ge(C_6F_5)_2$, containing electron donor (Me, Ph) and acceptor (C_6F_5) groups, by using a hydrogermolysis reaction in *n*-hexane. The molecular structures of **3** and **4** were studied by XRD. It was shown that, in its crystal form, **3** forms wide channels, in which the solvated nonpolar *n*-hexane molecule is present. The NMR (^{1}H, ^{13}C and ^{19}F), optical (UV/vis absorption, luminescence) and electrochemical (cyclic voltammetry) properties of both compounds were also studied. The impact of the substitution type (at the end of the compound, such as in **3,** or within the compound, such as in **5,** on the physical properties was also studied.
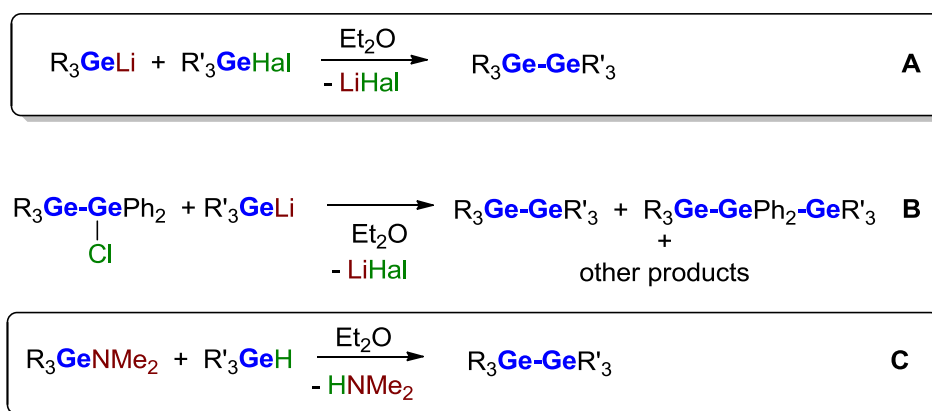
Keywords: oligogermane, main group metal chemistry, element – element bond, donor, acceptor, luminescence, X-ray diffraction analysis

1. Introduction

Recently, a recent interest has risen for the study of molecular catenated derivatives of Group 14 elements. This phenomenon is driven not only by a pure academic interest [1], but also by the need for seeking for new useful properties for those compounds [2]. In these compounds

the bonding electrons on HOMO orbitals (mainly sp^3 hybridized) are delocalized along the M-M chain, this phenomenon is known as σ-conjugation between the M atoms. This makes catenated compounds (saturated compounds) analogous to alkenes in which special useful properties (intensive UV/vis absorbance, luminescence, electrochemical properties, non-linear properties, conductivity *etc.*) are observed. Among all catenated compounds, Si [3] and Sn [4] derivatives have been intensively investigated. Surprisingly,the Ge derivatives [5] have been rarely investigated. This might be explained by the synthetic challenge that those compounds represent.. The main challenge in the chemistry of oligogermanes is to be able to prepare a specific structure for a specific application. Therefore, it is crucial to study the impact of the structure of the oligogermane on its physical properties.. Furthermore, several polymeric germanes [6] are known, but their precise "structure – property" relationships are established have only been superficially investigated.

The synthesis of compounds bearing a Ge-Ge bond could be achieved in two main ways. In the first group of methods, a nucleophilic lithium germyl reagent is reacted with an electrophilic germane (Scheme 1, reaction A). The most significant contribution to development of this method for the preparation of Ge derivatives was made by Draeger [7], Castel [8], Marschner [9] *et al.*. The main drawback of this reactions lies in the fact that the Ge-Ge bond is sensitive to strong nucleophiles (i.e. organolithium compounds) and very often, such reaction, leads to anuncontrolled processes due to partial substitution of organic groups at Ge atom [10] or destruction of Ge-Ge bond [11] (Scheme 1, reaction B). The latest side reaction is very typical for aromatic derivatives.

$$R_3GeLi + R'_3GeHal \xrightarrow[- LiHal]{Et_2O} R_3Ge\text{-}GeR'_3 \qquad \textbf{A}$$

$$R_3Ge\text{-}GePh_2(Cl) + R'_3GeLi \xrightarrow[- LiHal]{Et_2O} R_3Ge\text{-}GeR'_3 + R_3Ge\text{-}GePh_2\text{-}GeR'_3 + \text{other products} \qquad \textbf{B}$$

$$R_3GeNMe_2 + R'_3GeH \xrightarrow[- HNMe_2]{Et_2O} R_3Ge\text{-}GeR'_3 \qquad \textbf{C}$$

Scheme 1. General methods for creation the Ge-Ge bond.

A second way to prepare Ge-Ge building blocks is to react ta free germane with a germylamide under prolonged heating conditions (hydrogermolysis reaction) (Scheme 1, reaction C). This reaction was initially developped for the synthesis of oligogermanes by Weinert *et al.* [12]. The main drawback of this method are the harsh conditions that are required as well as the sensitivity of the reaction to the steric volumes of the substituents. Furthermore, this method has been limited by the compatibility of some of the initial reagents. For instance, it is impossible to use geminal polyamides, $R_2Ge[NMe_2]_2$, to construct the Ge-Ge bond [13]. Although

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the corresponding vicinal diamides, $Me_2NGePh_2GePh_2NMe_2$ [14], and branched monoamides, $[Ph_3Ge]_3GeNMe_2$ [15], are known and are sufficiently stable to be used under hydrogermolysis conditions, there is no data in the literature on using linear catenated germylmonoamide and their application in Ge-Ge bond formation. It could be expected that the synthesis of such compounds using strong nucleophiles like $LiNMe_2$ would destroy the Ge-Ge bond analogously to the case stated above (Scheme 1, B). This is why the synthesis of oligogemyl monoamide may be regarded as interesting challenge.

It was previously established that the physical properties of the oligogermanes highly depend on the nature of the substituent, on their geometrical volume, on the number of Ge atoms in the chain and on the overall conformation of the molecule. Thus, the introduction of donating groups destabilize the HOMO [16] level, whereas the presence of withdrawing groups resulted in a stabilization of the LUMO [10, 13], by improving the σ-conjugation. The same effect is observed when the Ge chain is elongated. The presence of voluminous groups on the Ge resulted in an elongation of Ge-Ge bond length. The effective conjugation is observed on the *trans*-coplanar configuration of Ge atoms in the chain [17].. Therefore, the introduction of substituents with different electronic properties (electron donating and withdrawing) within the oligogermane molecule is expected to change its properties significantly.

In continuation of our works on molecular oligogermanes [1-2, 10, 13, 18] we are reporting on the synthesis and on the investigations of the properties of novel donor-acceptor compounds, **2** and **3**. Their structure (NMR, XRD), optical (UV/vis absorbance, emission) and electrochemical properties were studied in detail.

2. Results and Discussion

2.1. Synthesis

0Hydrogermolysis is a best way for the synthesis of donor-acceptor oligogermanes as it was reported earlier [10], since it leads to high yield of the desired compound, only gaseous byproducts and by almost absence of hardly separated impurities (especially in comparison with lithium reagents) usually, for the synthesis of germyl amides, the direct reaction between R_3GeHal and $LiNMe_2$ has been used earlier [10, 19]. In this work a novel method for the synthesis of oligogermyl amide **2**, $Ph_3GeGeMe_2NMe_2$, is reported.. Compound **1**, $Me_2Ge(Cl)NMe_2$, was obtained using a previously reported methodology (Scheme 1).
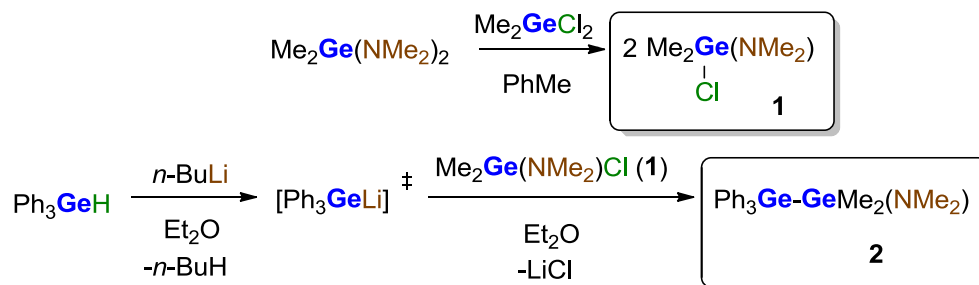
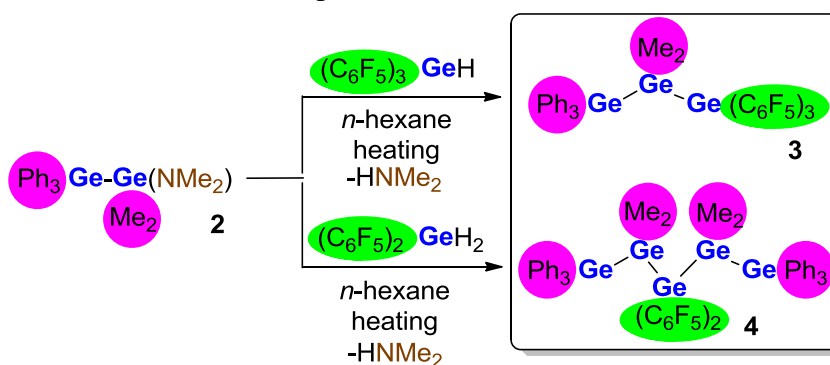**Scheme 2.** Synthetic strategy for the synthesis of catenated germanium amides.

Compound **1** is known, but has not been fully characterized yet [20]. The known procedures for its synthesis reaction between gaseous Me_2NH with Me_2GeCl_2) is very specific and not widely suitable for the laboratory synthesis. Thus, in this work, an optimal detailed

procedure for the synthesis of **1** was elaborated using simple conditions and readily available starting material (Me$_2$Ge(NMe$_2$)$_2$), Me$_2$GeCl$_2$).

Compound **2** is novel one; it was prepared by reaction Ph$_3$GeLi, generated *in situ,* with **1**. To the best of our knowledge, **2** is the first example of linear oligogermyl amide. The improved procedure for the synthesis of Ph$_3$GeH is detailed in the experimental information (for details, see Experimental part).

Both compounds **1** and **2** are soluble in common organic solvents and are highly moisture sensitive.

For the synthesis of compounds **3** and **4** the hydrogermolysis reaction was used (Scheme 3). This reactions were performed in *n*-hexane, much to our surprise, using MeCN [12] as a solvent revealed to be unsuccessful in this case and resulted only in the formation of an inseparable mixture of unidentified compounds.


Scheme 3. Synthetic strategy for the synthesis of catenated germanium amides.

Compounds **3** and **4** were isolated as white air- and moisture stable powders in high yields (78 and 84 %, respectively). The structure of these compounds in solution was confirmed by multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{19}F) and their composition was established on the basis of elemental analysis. In general, ^{1}H and ^{13}C NMR spectra for both compounds are very similar. The ^{19}F NMR spectra show three signals (*ortho-*, *para-* and *metha-*) with integral intensities of 2:1:2, what indicates the free rotation of C$_6$F$_5$ rings. The compounds bearing an end C$_6$F$_5$ group (Ph$_3$GeGe(C$_6$F$_5$)$_3$, (*p*-Tol)$_3$GeGe(C$_6$F$_5$)$_3$ [10] and **3**) have multiplet signals centered at -124, -149, -159 ppm, which means that the nature of the donating group and quantity of Ge atoms in the chain insignificantly impacts on the NMR spectra. At the same time, derivatives bearing median C$_6$F$_5$ ([(*p*-Tol)$_3$Ge]$_2$Ge(C$_6$F$_5$)$_2$ [10] and **4**) have signals at -119/-121, -153/-152, -161/-159 ppm, which differ from the first case. It means that the substitution on the oligogermanes by withdrawing groups (end- or median in the chain) change the electronic structure of the whole molecule. The change of nature of donor groups (tolyl *vs.* phenyl) or amount of Ge atoms in the chain showed to be less dramatic.

2.2. Molecular structure

The molecular structures of compounds **3** and **4** in the solid state were investigated by single crystal X-ray diffraction analysis (Figs. 1, 3; Supporting Information, Table S1).
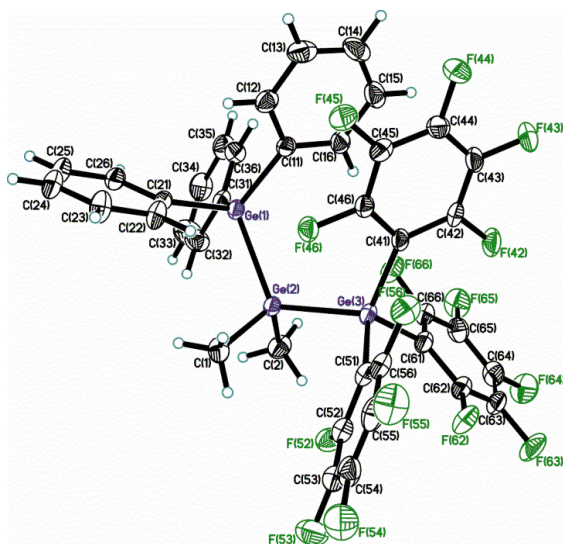
Fig. 1. Molecular structure of compound **3**. Solvate molecule of *n*-hexane was not shown. Displacement ellipsoids are shown at 50% probability level. Selected bond lengths (Å) and bond angles (deg): Ge(1)-Ge(2) 2.4475(4), Ge(2)-Ge(3) 2.4522(4), Ge(1)-C_{av} 1.950(2), Ge(2)-C_{av} 1.958(3), Ge(3)-C_{av} 1.969(2); Ge(1)-Ge(2)-Ge(3) 115.780(14), C-Ge(1)-C_{av} 107.84(10), Ge(2)-Ge(1)-C_{av} 110.04(7), C(2)-Ge(2)-C(1) 107.99(12), Ge(1)-Ge(2)-C_{av} 118.18(8), Ge(3)-Ge(2)-C_{av} 105.08(8), C-Ge(3)-C_{av} 107.30(10), C-Ge(3)-Ge(2)$_{av}$ 111.54(7).

Up todayonly 12 linear molecular trigermanes have been studied by XRD (for details see [13]), where Ge-Ge bond length and Ge-Ge-Ge angle vary between 2.413-2.6223 Å and 110.4-125.00°, respectively, depending on the steric size and on the electronic nature of the substituents located at Ge atoms. Compound **3** crystallizes in the P-1 space group (Z = 2). The presence of a phenyl or a pentafluorophenyl group has a very limited impact on the on the length of Ge-Ge bond (2.4475(4) *vs.* 2.4522(4) Å), where the longer bond is typical for Ge containing electron withdrawing groups. At the same time the average Ge-Ge bond length in **3** is 2.4499(4) Å, what is somewhat longer than what would could be expected for aryl sterically non-hindered groups (2.429(1) Å in $Ph_3GeGeMe_2GePh_3$ [11b]). Furthermore, *d*(Ge(2)-Ge(3)) is shorter than in related donor-acceptor digermanes $Ph_3GeGe(C_6F_5)_3$ (2.4623(4) Å) and (*p*-Tol)$_3$GeGe(C$_6$F$_5$)$_3$ (2.4652(11) Å) [10], containing end substitution by perfluorophenyl groups. This could be explained by the decrease of the steric volume of the substituents (Me *vs.* Ph or Tol) and by the elongation of the Ge chain in **3**.

It is interesting to compare the structural parameters of **3** with the ones of the donor-acceptor trigermane [(*p*-Tol)$_3$Ge]$_2$Ge(C$_6$F$_5$)$_2$ [10], containing median disposition of withdrawing groups in the molecule. The Ge-Ge(C$_6$F$_5$) bond lengths (2.4522(4) *vs.* 2.459(5) Å) and central C-Ge-C angle (C(2)-Ge(2)-C(1) 107.99(12) *vs.* 108.0(2)°) are very similar, but Ge-Ge-Ge angle differs significantly(115.780(14) *vs.* 124.10(3)°), this shows the effect of the substitution (end or median) on the oligogermanium chain.

The geometry of Ge atoms may be described as a distorted tetrahedron, where the largest deviation from the ideal tetrahedral was observed for the central Ge(2) atom. In a crystal, the planes of one of the aromatic groups lie almost in parallel planes due to the electron stacking. The Ge-C bond length is slightly longer in the perfluorophenyl derivative possibly due to an increase of the steric volume. All phenyl rings are in propeller-like conformation in relation to

the corresponding Ge-Ge bonds (Ge$_{Me}$-Ge$_{Ar}$-C-C torsions are 42.81, 50.45° for Ph and 51.78, 54.19° for C$_6$F$_5$), wherein the rings in stacking are deviated more significantly (59.88 and 50.82, correspondingly). Furthermore, all substituents are in *syn*-conformation along the Ge-Ge bonds (*syn-syn* conformation; the average torsion along Ge(2)-Ge(1) is 1.38 and along Ge(2)-Ge(3) is 10.96).

In the crystal **3** the solvated molecule of *n*-hexane is observed within wide channels formed by 3D packing (Fig. 2). There are no intermolecular contacts or interactions between the molecule of *n*-hexane and **3**. The molecule of *n*-hexane is fully ordered and any vibrations may be observed only in a low extent. Moreover, any attempts to remove the *n*-hexane molecule from the channels (by applying the high vacuum over 24 h or even by using a mild heating) were unsuccessful according to XRD,all characteristics of the crystal remained unchanged.. Therefore, donor-acceptor oligogermanes may form crystals suitable to fix inert moleculesin a fashion similar to MOFs.
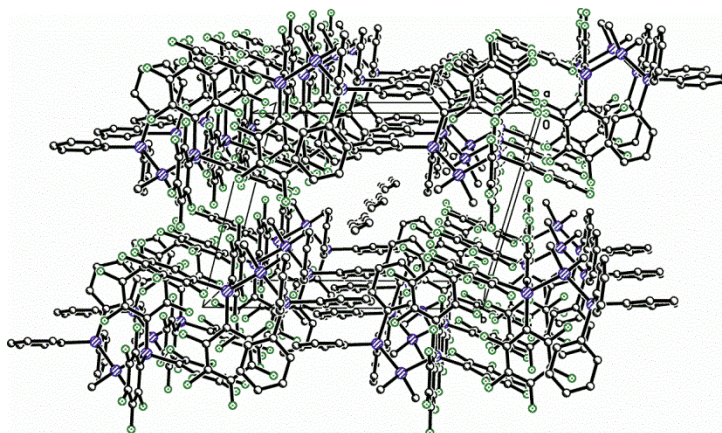
Fig. 2. Disposition of solvated molecule of *n*-hexane in the 3D structure of **3**.

Crystals of molecular oligogermanes containing solvated molecules are known, but only with molecules of solvated benzene or toluene (Ph$_3$G$_3$GePh$_3$*2C$_6$H$_6$ [21], (*p*-Tol)$_3$GeGe(Tol-*p*)$_3$*C$_6$H$_6$ [22], (*p*-Tol)$_3$Ge-Ph$_3$*C$_6$H$_6$, [(*p*-Tol)$_3$Ge]$_2$GePh$_2$*PhMe, [(*p*-Tol)$_3$Ge]$_2$Ge(Tol-*p*)$_2$*PhMe [23], Ge$_4$Ph$_{10}$*2C$_6$H$_6$ [24]).

To the best of our knowledge there are only 3 linear pentagermanes with known molecular solid state structure, Ge$_5$Ph$_{12}$ (at 295 K: d(Ge-Ge)$_{av}$ 2.460(4) and Ge-Ge-Ge$_{av}$ 115.6(2)°; at 100 K: d(Ge-Ge)$_{av}$ 2.4502(6) and Ge-Ge-Ge$_{av}$ 115.52(2)° [11a, 25]), (Me$_3$Ge)$_3$GeGeMe$_2$Ge(GeMe$_3$)$_3$ (d(Ge-Ge)$_{av}$ 2.4425(9) and Ge-Ge-Ge$_{av}$ 111.68(4)°) [9b] and (*i*-Pr)$_3$Ge[GePh$_2$]$_3$Ge(*i*-Pr)$_3$ (d(Ge-Ge)$_{av}$ 2.4710(8) and Ge-Ge-Ge$_{av}$ 117.01(3)°) [26].
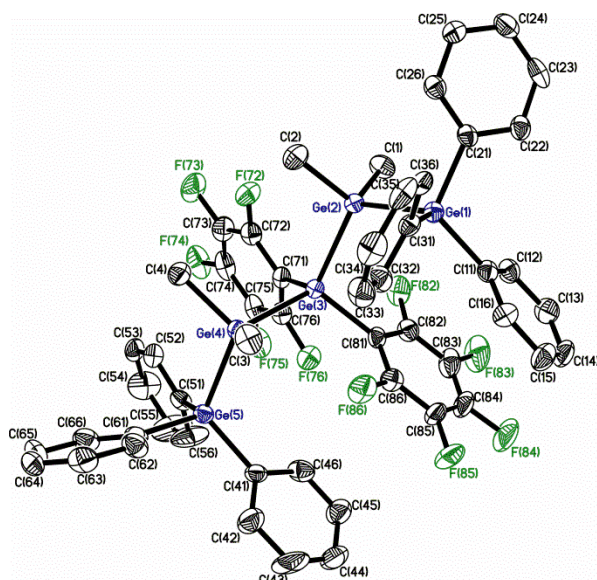
Fig. 3. Molecular structure of compound **4**. Displacement ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ge(1)-Ge(2) 2.4441(8), Ge(2)-Ge(3) 2.4333(8), Ge(3)-Ge(4) 2.4352(7), Ge(4)-Ge(5) 2.4320(8), Ge(1)-C_{av} 1.953(5), Ge(2)-C_{av} 1.960(5), Ge(3)-C_{av} 1.987(5), Ge(4)-C_{av}1.956(5), Ge(5)-C_{av} 1.954(5); Ge(3)-Ge(2)-Ge(1) 115.50(3), Ge(2)-Ge(3)-Ge(4) 117.65(3), Ge(5)-Ge(4)-Ge(3) 115.04(3), C(31)-Ge(1)-Ge(2) 112.41(15), C(11)-Ge(1)-Ge(2) 114.45(15), C(21)-Ge(1)-Ge(2) 99.73(15), C(2)-Ge(2)-C(1) 110.2(2), C-Ge(2)-Ge(3)$_{av}$ 108.06(17), C-Ge(2)-Ge(1)$_{av}$107.49(17), C(81)-Ge(3)-C(71) 105.6(2), C-Ge(3)-Ge(2)$_{av}$ 108.63(15), C(81)-Ge(3)-Ge(4) 115.65(15), C(71)-Ge(3)-Ge(4) 100.09(14), C(4)-Ge(4)-C(3) 105.0(2), C-Ge(4)-Ge(5)$_{av}$ 109.61(17), C(4)-Ge(4)-Ge(3) 103.54(16), C(3)-Ge(4)-Ge(3) 113.06(17), C-Ge(5)-C_{av} 108.7(2), C-Ge(5)-Ge(4)$_{av}$ 110.09(15).

Compound **4** crystallizes in a triclinic P-1 (Z = 2) space group, without any symmetry element. All four Ge-Ge bonds have slightly different lengths, where the longest and shortest ones are observed for the same groups at the ends of the molecule (Ge(1)-Ge(2) and Ge(4)-Ge(5), respectively); the average value is 2.4362(8) Å. This bond length is shorter than the one known for other pentagermanes. This fact is explained by the electronic effects, due to a median substitution by electron withdrawing groups in the catenated Ge chain of **4**. This effect is significant and different from in the end substitution in **3**. Introduction of an electron withdrawing groups in the central part of the molecule results in a decrease of the Ge-Ge bond lengths.

As it was stated earlier for linear Ge_5Ph_{12}, the Ge-Ge bond length in the centre of the molecule is slightly longer than at the ends due to steric reasons (2.4359(6) and 2.4397(6) for end and 2.4549(6) and 2.47001(6) for central) [25], but in **4** this difference is almost negligeable. This could bebe explained by the presence of methyl groups instead of phenyl groups.

In **4,** only four Ge atoms lie in one plane, while Ge(1) remains outside of this plane. Interestingly, the same situation has been observed earlier for aryl pentagermane Ge_5Ph_{12} [11a, 25]. Refering to the crystal structures for longer oligogermanes, namely (*i*-Pr)$_3$Ge[GePh$_2$]$_4$Ge(*i*-Pr)$_3$ [14, 27], it is possible to state that for higher catenated Ge derivatives (more than 4 atoms in the

chain) the end atoms are canted from the plane formed by the central atoms. Furthermore, in **4** in contrary from $Ge_5Ph_{12,}$ the Ge-Ge bond with Ge(1) atom out of plane is the longest one.

Comparing structural data for **3** and **4** it is evident that that the conjugation between the Ge atoms decreases the Ge-Ge bond length (Ge_{Me}-Ge_{Ph} 2.4475(4) *vs.* 2.4320(8) Å). The values of the Ge-Ge-Ge angles in **3** and **4** (115.780(14) and average 116.06(3)°) are very similar.

In **4,** the deviation of bond angles from the typical tetrahedral are observed (C(21)-Ge(1)-Ge(2) 99.73(15), C(71)-Ge(3)-Ge(4) 100.09(14), C(4)-Ge(4)-Ge(3) 103.54(16)), possibly due to packing effects or to intermolecular interactions.Aryl groups (donor phenyl and acceptor perfluorophenyl) lie in parallel planes due to possible stacking, similar what was observed previously in $Ph_3GeGe(C_6F_5)_3$ [10]. The phenyl groups are in propeller-like conformation in relation to Ge-Ge bond, and the substituents at neighboring Ge atoms are in *anti-syn* (Ge(1)-Ge(3)), *gauche-gauche* (Ge(2)-Ge(4)) and *anti-syn* (Ge(3)-Ge(5)) conformations (torsions C(21)-Ge(1)-Ge(2)-Ge(3) 161.37; Ge(1)-Ge(2)-Ge(3)-Ge(4) 89.80; Ge(2)-Ge(3)-Ge(4)-Ge(5) 179.37; Ge(3)-Ge(4)-Ge(5)-C(61) 176.18).

2.3. Optical properties

The optical properties (UV/vis absorbance and luminescence emission) of new donor-acceptor ologogermanes **3** and **4** were investigated in details.

The UV/vis absorbance of **3** and is shown below (Fig. 4). In literature, only 5 known pentagermanes and 10 trigermanes have been reported to have been studied by UV/vis spectroscopy. The previously reported data are summarized in Table 1.
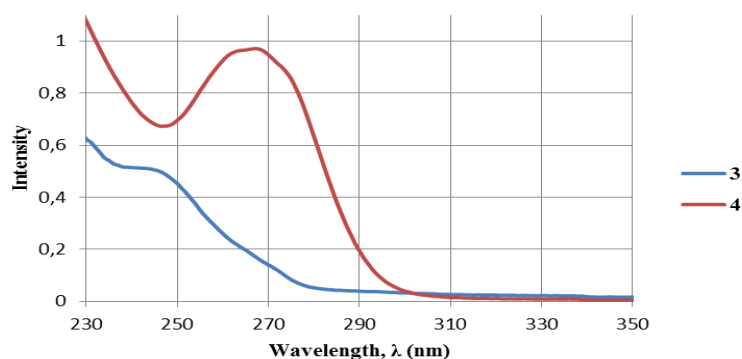
Fig. 4. UV/visible absorption spectra for compounds **3** and **4** (CH_2Cl_2, rt).

Table 1. UV/vis absotption data for tri- and pentagermanes.

compound	λ, nm	$\varepsilon *10^4$, M^{-1} cm^{-1}	solvent	reference
$Ph_3GeGeMe_2GePh_3$	245	2.8	cyclohexane	[8]
$Ph_3GeGeMePhGePh_3$	250	3.6	cyclohexane	[8]
$Ph_3GeGeEt_2GePh_3$	247	2.7	cyclohexane	[8]
$Ph[GeEt_2]_3Ph$	241	2.0	cyclohexane	[8]
$Ph_3GeGePh_2GePh_3$	250	2.6	cyclohexane	[8]
	249	3.2	CH_2Cl_2	[24]

Me$_3$GeGeMe$_2$GeMe$_3$	218	0.9	cyclohexane	[28]
[(p-Tol)$_3$Ge]$_2$GeMe$_2$	251	4.0	CH$_2$Cl$_2$	[2]
[(p-Tol)$_3$Ge]$_2$GePh$_2$	251		CH$_2$Cl$_2$	[23]
[(p-Tol)$_3$Ge]$_2$Ge(p-Tol)$_3$	253		CH$_2$Cl$_2$	[23]
(i-Pr)$_3$Ge[GePh$_2$]Ge(i-Pr)$_3$	242	2.1	CH$_2$Cl$_2$	[26]
[(p-Tol)$_3$Ge]$_2$Ge(C$_6$F$_5$)$_2$	258	1.4	CH$_2$Cl$_2$	[10]
(p-F$_3$CC$_6$H$_4$)$_3$Ge-Ge(C$_6$F$_5$)$_2$-Ge(C$_6$H$_4$CF$_3$-p)$_3$	264	2.4	CH$_2$Cl$_2$	[13]
Ph$_3$GeGeMe$_2$Ge(C$_6$F$_5$)$_3$ (**3**)	246	2.1	CH$_2$Cl$_2$	this work
Ph[GeEt$_2$]$_5$Ph	256	3.2	cyclohexane	[8]
Ph$_3$Ge[GeEt$_2$]$_3$GePh$_3$	269	3.9	cyclohexane	[8]
Me$_{12}$Ge$_5$	246	2.1	cyclohexane	[28]
Ph$_{12}$Ge$_5$	293	6.3	CH$_2$Cl$_2$	[11a]
	295	4.5	CH$_2$Cl$_2$	[25]
(i-Pr)$_3$Ge[GePh$_2$]$_3$Ge(i-Pr)$_3$	300	5.7	CH$_2$Cl$_2$	[26]
[Ph$_3$GeGeMe$_2$]$_2$Ge(C$_6$F$_5$)$_2$ (**4**)	267	4.5	CH$_2$Cl$_2$	this work

The main absorption in alkyl substituted oligogermanes is due to a σ-σ* transition where HOMO and LUMO are generally localized within the M-M bond [10], the nature of the substituent strongly impact on the energy level and disposition of these orbitals. Introduction of aryl groups moves the LUMO toward the Ar substituent, making the transitions to LUMO-1 *etc.* more preferable.

Table 1 shows that the change of the nature of the substituent in the central part of the molecule (insertion of aryl group) has a more significant red shift than when the groups at the end of the molecule are changed. Insertion of electron withdrawing C$_6$F$_5$ groups at the end (in **3**) or at median positions of Ge chain (in **4**) has an similar effect to what we reported before [10], i.e. weak bathochromic shift. Thus, in this case the degree of HOMO stabilization is less than the degree of LUMO destabilization. Furthermore, modification of substituent on the median part of the molecule leads to a stronger bathochromic shift in comparison with the end type.

When comparing the absorption of **3** with the one of **4** it is evident that the elongation of the Ge chain resulted in a bathochromic shift and in the coefficient of extinction also increased.

The luminescence properties of the compounds **3** and **4** in solid state and in solution have been also studied (Figs. 5, 6). The compounds show broad luminescence in both states. ItTothe best of our knowledge, in only few examples of investigation of catenated germanium compounds (including molecular and polymeric ones) as luminescent materials have been reported previously in the literature (see Table 2).

Table 2. Luminescence emission data for the catenated germanium compounds

type	compound	Solid state		Solution[a]			reference
		λ_{em}, nm[b]	Stokes shift, nm	λ_{em} (nm)	Stokes shift, nm	Φ_f (%)[c]	
polymer	$[(Me_3SiOC_6H_4$-$p)MeGe]_n$	367 (film)	35	369 (332, THF)	39	-	[29]
molecular	$(p$-Tol$)_3$GeGeMe$_3$	357, 373, 393 (300)	125, 141, 161	286 (270)	54	3.27	[18c]
	$(p$-Tol$)_3$GeGeMe$_2$Ge$(p$-Tol$)_3$	438 (380)	187	338 (285)	87	1.85	[2]
	Ph$_3$Ge-Ge(C$_6$F$_5$)$_3$	373 (270)	147	377 (265)	151	12.50	[2]
	$[(p$-F$_3$CC$_6$H$_4)_3$Ge]$_2$Ge(C$_6$F$_5$)$_2$	476 (320)	212	376 (290)	112	12.36	[13]
	$(i$-Pr$)_3$Ge[GePh$_2$]$_4$Ge$(i$-Pr$)_3$	-	-	370 (312)	60	-	[14]
	$(i$-Pr$)_3$Ge[GePh$_2$]$_3$Ge$(i$-Pr$)_3$	-	-	380 (302)	80	-	[26]
	Ph$_3$GeGeMe$_2$Ge(C$_6$F$_5$)$_3$ (**3**)	379 (325) 373 (270)	133 127	351 (290)	107	5.45	this work
	[Ph$_3$GeGeMe$_2$]$_2$Ge(C$_6$F$_5$)$_2$ (**4**)	382 (345) 400 (345)	115 133	350 (295)	84	2.11	this work

[a]Spectra were recorded in CH$_2$Cl$_2$, wavelength, λ_{ex}, in parentheses

[b]Excitation wavelength, λ_{ex}, in parentheses

[c]Quantum yield
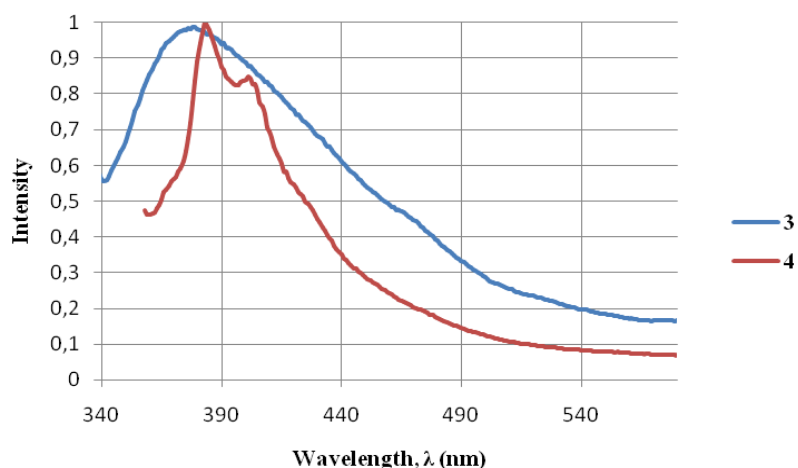
Fig. 5. Luminescence emission spectra for **3** and **4** in the solid state at room temperature.
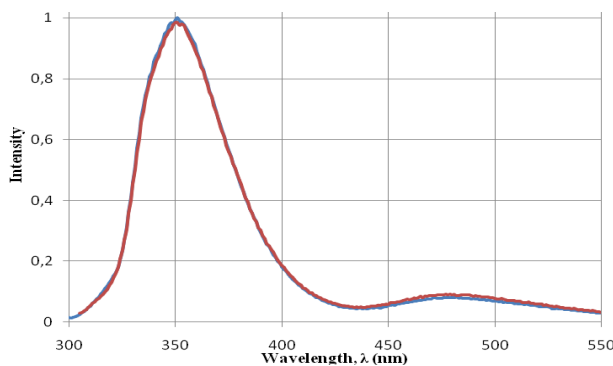
Fig. 6. Luminescence emission spectra for **3** and **4** in solution (CH$_2$Cl$_2$, room temperature).

In their solide state, **3** and **4** show an emission is shifted more toward the red than in solution, this may be explained by higher order in the condensed phase.

The spectra of **3** and **4** in solution are very similar due to common structural characteristics. In this case, the efficiency of the emission is low and the quantum yield is less than 6 %.

That simple elongation of the Ge chain has not significant impact on the expected red shift. Apparently, the coplanar *trans*-disposition of the Ge atoms in the chain plays a critical role for efficiency of the luminescence (high Stokes shift and quantum yield) as well as the electronic nature of the substituents, which strongly effect the HOMO/LUMO levels of the fundamental and excited states. Further investigation in this field will be performed in the near future.

2.4. Electrochemical behavior

The redox properties of compounds **3** and **4** were studied by the mean of cyclic voltammetry (CV) (Fig. 7; Fig. S11, Supporting Information). The electrochemical data for known tri- and pentagermanes are shown in Table 3.
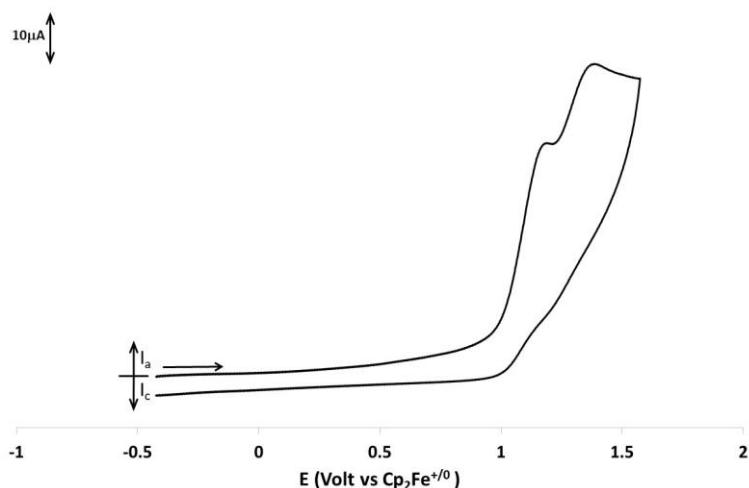
Fig. 7. Cyclic voltammogram of 1mM [Ph$_3$GeGeMe$_2$]Ge(C$_6$F$_5$)$_2$ (**4**) in dichloromethane - [NBu$_4$][PF$_6$] solution. Sweeping rate 200mV/s at room temperature.

Table 3. Electrochemical data for tri- and pentagermanes by CV.

compound	E, V[a]	standard	conditions	reference
Me$_3$GeGeMe$_2$GeMe$_3$[b]	0.93 (1.42)[c]	Fc$^+$/Fc	MeCN, 0.1 M TBAP	[28]
(EtOCH$_2$CH$_2$)Et$_2$GeGePh$_2$GeEt$_2$(CH$_2$CH$_2$OEt)	1.577	Ag/AgCl	MeCN, 1.0 M [Bu$_4$N][PF$_6$]	[30]
(EtOCH$_2$CH$_2$)Bu$_2$GeGePh$_2$GeBu$_2$(CH$_2$CH$_2$OEt)	1.500	Ag/AgCl	MeCN, 1.0 M [Bu$_4$N][PF$_6$]	[30]
(EtOCH$_2$CH$_2$)Ph$_2$GeGePh$_2$GePh$_2$(CH$_2$CH$_2$OEt)	1.609	Ag/AgCl	MeCN, 1.0 M [Bu$_4$N][PF$_6$]	[30]
Ph$_3$Ge[GeBu$_2$]$_2$(CH$_2$CH$_2$OEt)	1.546	Ag/AgCl	MeCN, 1.0 M [Bu$_4$N][PF$_6$]	[30]
Ph$_3$GeGeBu$_2$GePh$_2$(CH$_2$CH$_2$OEt)	1.525	Ag/AgCl	MeCN, 1.0 M [Bu$_4$N][PF$_6$]	[30]
Ph$_3$GeGePh$_2$GePh$_3$	1.696, 2.052	Ag/AgCl	CH$_2$Cl$_2$, 0.1 M [Bu$_4$N][PF$_6$]	[23]
[(*p*-Tol)$_3$Ge]$_2$GePh$_2$	1.498, 1.860	Ag/AgCl	CH$_2$Cl$_2$, 0.1 M [Bu$_4$N][PF$_6$]	[23]

[(p-Tol)$_3$Ge]$_2$Ge(p-Tol)$_3$	1.542, 1.865	Ag/AgCl	CH$_2$Cl$_2$, 0.1 M [Bu$_4$N][PF$_6$]	[23]
(i-Pr)$_3$Ge[GePh$_2$]Ge(i-Pr)$_3$	1.555	Ag/AgCl	CH$_2$Cl$_2$, 0.1 M [Bu$_4$N][PF$_6$]	[26]
(n-Bu)$_3$GeGePh$_2$Ge(n-Bu)$_3$	1.540	Ag/AgCl	CH$_2$Cl$_2$, 0.1 M [Bu$_4$N][PF$_6$]	[16]
(p-F$_3$CC$_6$H$_4$)$_3$Ge-Ge(C$_6$F$_5$)$_2$-Ge(C$_6$H$_4$CF$_3$-p)$_3$	1.27 (1.76), 1.63 (2.12)	Fc$^+$/Fc	CH$_2$Cl$_2$, 0.05 M [NBu$_4$][B(C$_6$F$_5$)$_4$]	[13]
Ph$_3$GeGeMe$_2$Ge(C$_6$F$_5$)$_3$ (3)	1.53 (2.02)	Fc$^+$/Fc	CH$_2$Cl$_2$, [NBu$_4$][PF$_6$]	this work
Me$_{12}$Ge$_5$^{d}	0.61 (1.10)^c	Fc$^+$/Fc	MeCN, 0.1 M TBAP	[28]
Ph$_3$Ge[GePh$_2$]$_3$GePh$_3$	1.385, 1.605, 1.777, 1.998	Ag/AgCl	CH$_2$Cl$_2$, 0.1 M [Bu$_4$N][PF$_6$]	[25]
(i-Pr)$_3$Ge[GePh$_2$]$_3$Ge(i-Pr)$_3$	1.560, 1.695, 1.875, 2.095	Ag/AgCl	CH$_2$Cl$_2$, 0.1 M [Bu$_4$N][PF$_6$]	[26]
[Ph$_3$GeGeMe$_2$]$_2$Ge(C$_6$F$_5$)$_2$ (4)	1.18 (1.67), 1.38 (1.87)	Fc$^+$/Fc	CH$_2$Cl$_2$, [NBu$_4$][PF$_6$]	this work

^{a} Values in relation to Ag/AgCl are given in the parentheses
^{b} Reduction process is also observed at E$_{p/2}$ = -0.56 V
^{c} Half peak potentials
^{d} Reduction process is also observed at E$_{p/2}$ = -0.48 V

The electrochemical data about oligogermanes containing alkyl and aryl groups are very rare, so this investigation makes a significant contribution to this field. As it was reported before, only one oxidation process is observed for fully alkylated oligogermanes. On contrary, in fully arylated oligogermanes, an electronic interaction between π- and σ-groups [10] is observed, what results in a stabilization of the HOMO and in a decrease of the oxidation potential. In this case Weinert *et al.* have previously established that aryl substituted oligogermanes with n Ge atoms in their chain, are characterized by n-1 irreversible oxidation processes [23]. In the case of oligogermanes containing aryl and alkyl groups the situation is less predictable (see Table 3).

Compound **3** showed only one oxidation at 1.53 V *vs.* Fc$^+$/Fc (2.02 V *vs.* Ag/AgCl). It is evident that if alkyl groups are present in oligogermanes, the oxidation potential will higher than for their aryl analogs and in this case it is possible to observe only one wave [28]. Elongation of the Ge chain in **3** in comparison with donor-acceptor digermane Ph$_3$GeGe(C$_6$F$_5$)$_3$ [2] decreases the first oxidation potential (1.53 *vs.* 1.62 V). Compound **4** has only two oxidation peaks at E$_{pa}$ = 1.18 and 1.38 V *vs.* Fc$^+$/Fc (1.67 and 1.87 V *vs.* Ag/AgCl). In this case, the elongation of the Ge chain significantly stabilizes the HOMO even in the presence of electron withdrawing substituents. In general, introduction of alkyl or of an electron withdrawing groups into the oligogermane chain stabilizes the HOMO of the oligogermane (as observed earlier for donor-acceptor and for oligogermanes fully substituted by acceptor groups [2, 13]) and hence increases the values of the oxidation potential.

Although more electrochemical mechanistic investigations needs to be carried out, one possible mechanism for the oxidation of oligogermanes is depicted in Scheme 4. In this mechanism, the first oxidation occurs on the σ-bonding orbital between the M atoms[31], and the resulting highly unstable transient cation-radical decomposes rapidly. Among the two main pathways of decomposition, the extrusion of germylene with formation of a novel cation-radical or the rupture of Ge-Ge bond with formation of a cation and a radical [10], the latest one seems the more plausible.. The cation and radical formed would then further react. Nevertheless, it is

impossible to completely rule out the presence of additional oxidaitons at higher potentials that would be located outside of the electrochemical window.
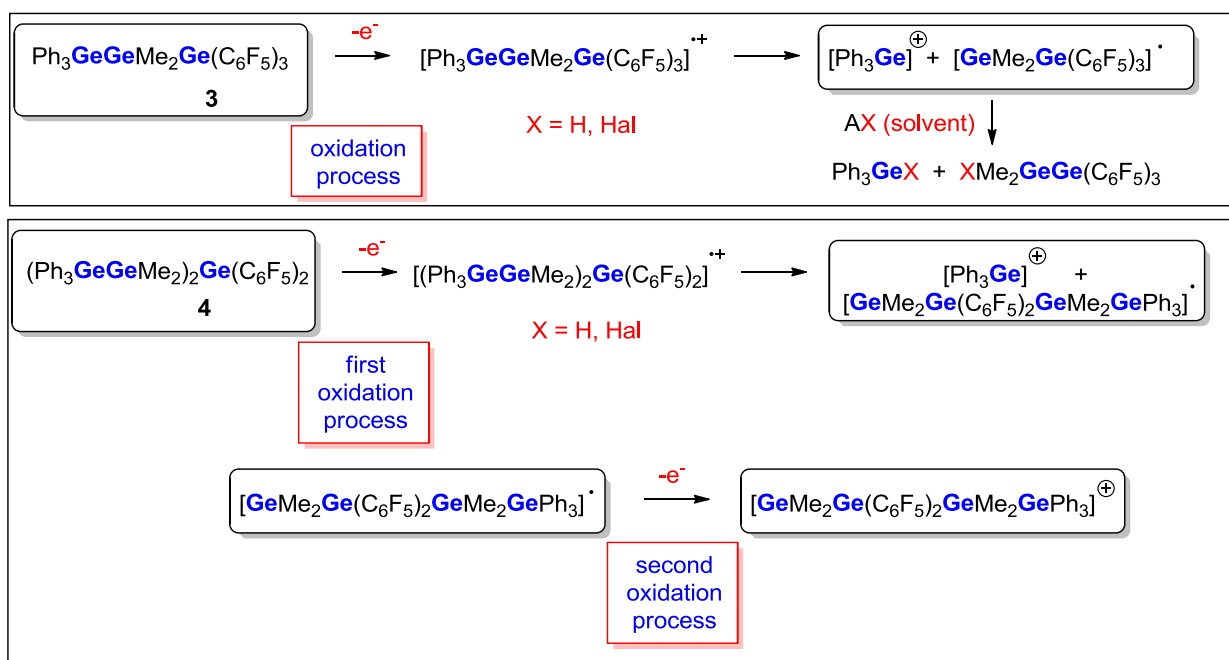
Scheme 4. Mechanism of irreversible oxidation of catenated germanes.

This mechanism may be applicable to the oxidation of alkyl substituted oligogermanes,.[28] [26] In the case of aryl substituted oligogermanes, the intermediate cation and radical should be sufficiently stable to form catenated derivative that could undergo subsequent oxidations as observed by Weinert *et al.* [23]

The structure of oligogermanes (especially the nature of the substituents) strongly impacts on the oxidation potential and pathway.

3.   Conclusions

Linear oligogermanium amide **2**, $Ph_3GeGeMe_2NMe_2$, was obtained and used in an hydrogermolysis reaction with $HGe(C_6F_5)_3$ and $H_2Ge(C_6F_5)_2$ by heating in *n*-hexane for the synthesis of the donor-acceptor germanes **3** and **4**. It has been experimentaly shown that the physical properties of catenated germanes depend on the type of substitution by withdrawing groups. Median insertion significantly has a greater effect than a substitution located at the end of the chain. The conformation of the molecule is determined by the intramolecular contacts between donor (phenyl) and acceptor (perfluorophenyl) groups, resulting in an eclipsed conformation along the Ge-Ge bonds. Nonpolar oligogermanes in a crystal could form wide channels in which organic molecules may be trapped. The number of oxidation waves in CV investigations strongly depends on the electronic nature of the substituent and on the number of Ge atoms within the molecule. As expected, electron withdrawing groups decrease the oxidation potential of the molecule, while longer Ge chain increases that potential. Oligogermanes have wide emission spectra, in solid state, their luminescence (Stokes shift) is snigificantly more shifted toward the red than when they are in solution.

4. Experimental Part

4.1. General Remarks

All reactions were carried out in protective atmosphere using standard Schlenk techniques. $GeCl_4$ (Aldrich) was distilled prior to use. *n*-BuLi (Aldrich) was used as supplied. Solvents were dried using standard procedures (ether was stored over KOH and then distilled over Na/benzophenone, *n*-hexane was distilled over Na).

^1H NMR (400.130 MHz), ^{13}C NMR (100.613 MHz) and ^{19}F (376.498 MHz) spectra were recorded on Bruker 400 or Agilent 400MR spectrometers at 298 K. Chemical shifts are given in ppm relative to internal reference Me_4Si (^1H and ^{13}C NMR spectra) or external reference $CFCl_3$ (^{19}F spectra). Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department of the Moscow State University using Heraeus Vario Elementar instrument. UV/visible spectra were recorded using a double-beam spectrophotometer Evolution 300 «Thermo Scientific» using a 1.00 cm cuvette.

Electrochemical measurements were carried out using an Autolab 302N potentiostat interfaced through Nova 2.0 software to a personal computer. Electrochemical measurements were performed in a glovebox under oxygen levels of less than 5 ppm using solvent that had been purified by passing through an alumina-based purification system. Diamond-polished glassy carbon electrodes of 3 mm diameter were employed for cyclic voltammetry (CV) scans. CV data were evaluated using standard diagnostic criteria for diffusion control and for chemical and electrochemical reversibility. The experimental reference electrode was a silver wire coated with anodically deposited silver chloride and separated from the working solution by a fine glass frit. The electrochemical potentials in this paper are referenced to ferrocene/ferrocenium couple, as recommended elsewhere.[38] The ferrocene potential was obtained by its addition to the analyte solution. At an appropriate time in the experiment.

Known compounds, Ph_3GeCl [18a], Me_2GeCl_2 [13], $Me_2Ge(NMe_2)_2$ [13], $(C_6F_5)_3GeH$ [10] and $(C_6F_5)_2GeH_2$ [10], were prepared according to published procedures. Improved protocols were used for the synthesis of Ph_3GeH.

4.2. Synthesis of Starting Materials

Synthesis of triphenylgermane. Improved procedure was applied [32]. At room temperature a solution of Ph_3GeCl (5.48 g, 16.10 mmol) in ether (40 ml) was added dropwise to the suspension of $LiAlH_4$ (0.79 g, 30.93 g) in ether (40 ml). The mixture obtained was refluxed for 3 h, then at room temperature 2 M H_2SO_4 (40 mL) was added dropwise, organic phase was separated, aqueous layer was extracted with ether (3 x 20 mL). Combined organic phases were dried over anhydrous Na_2SO_4, then solvent was removed under reduced pressure, and the residue was recrystallized from *n*-hexane. Ph_3GeH (4.21 g, 86 %) was isolated as a white powder, m.p. 42-43 °C, m.p. [32b] 42 °C. ^1H NMR (δ, ppm, $CDCl_3$): 7.61-7.57 (m, 6H, aromatic protons), 7.44-7.38 (m, 9H, aromatic protons), 5.77 (s, 1H, GeH). ^{13}C NMR (δ, ppm, $CDCl_3$): 135.68 (quaternary aromatic carbon), 135.18, 128.36 (*m*- and *o*-CH aromatic carbons), 129.14 (*p*-CH aromatic carbon). ^1H NMR (δ, ppm, C_6D_6): 7.54-7.49 (m, 6H, aromatic protons), 7.15-7.11 (m, 9H, aromatic protons), 5.85 (s, 1H, GeH). ^{13}C NMR (δ, ppm, C_6D_6): 135.83 (quaternary aromatic carbon), 135.50, 128.67 (*m*- and *o*-CH aromatic carbons), 129.37 (*p*-CH aromatic carbon).

(*N*,*N*-Dimethylamino)chlorodimethylgermane, $Me_2Ge(NMe_2)Cl$ (1). At 0°C Me_2GeCl_2 (0.87 ml, 1.30 g, 7.50 mmol) was added slowly to the $Me_2Ge(NMe_2)_2$ (1.43 g, 7.50 mmol). Reaction mixture was stirred overnight, then all volatile materials were removed under

reduced pressure. Compound **1** (1.97 g, 72 %) was obtained as a colorless oil after distillation, b.p. 121 °C, b. p. 142 (1013 mbar) [20a], 114 [20b]. ^{1}H NMR (δ, ppm, C$_6$D$_6$): 2.41 (s, 6H, NMe$_2$), 0.43 (s, 6H, GeMe$_2$). 1H NMR specteum corresponds to literature data [20a]. ^{13}C NMR (δ, ppm, C$_6$D$_6$): 39.48 (NMe$_2$), 2.36 (GeMe$_2$).

Ph$_3$GeGeMe$_2$NMe$_2$ (2). *a) Synthesis of Ph$_3$GeLi:* At -78°C *n*-BuLi (6.00 ml, 2.5 M, 15.00 mmol) was added dropwise to the solution of Ph$_3$GeH (4.57 g, 15.00 mmol) in ether (60 ml). Then reaction mixture was heated slowly to room temperature and stirred for 3 h. The solution of Ph$_3$GeLi obtained *in situ* was used further without purification.

b) Synthesis of 2: At -78°C the solution of Ph$_3$GeLi in ether obtained as described above was added dropwise to the solution of compound **1** (2.73 g, 15 mmol) in ether (20 ml). Reaction mixture was slowly warmed to room temperature and stirred overnight. Then all volatile materials were removed under reduced pressure, dissolved in *n*-hexane and filtered. Compound **2** (5.54 g, 82 %) was obtained as a white low melting glass after evaporation. ^{1}H NMR (δ, ppm, C$_6$D$_6$): 7.67-7.61 (m, 6H, aromatic protons), 7.23-7.15 (m, 9H, aromatic protons), 2.51 (s, 6H, NMe$_2$), 0.48 (s, 6H, GeMe$_2$). ^{13}C NMR (δ, ppm, C$_6$D$_6$): 138.59 (quaternary aromatic carbon), 135.74, 128.70 (*m*- and *o*-CH aromatic carbons), 128.92 (*p*-CH aromatic carbon), 42.18 (NMe$_2$), -1.00 (GeMe$_2$). Anal. Calcd. for C$_{22}$H$_{27}$Ge$_2$N (M$_w$ 450.7365): C, 58.62; H, 6.04; N, 6.04. Found: C, 57.74; H, 5.73; N, 5.64.

4.3. Synthesis of Donor-Acceptor Oligogermanes

Ph$_3$GeGeMe$_2$Ge(C$_6$F$_5$)$_3$ (3). A mixture of compound **2** (0.44 g, 0.98 mmol) and (C$_6$F$_5$)$_3$GeH (0.56 g, 0.98 mmol) was dissolved in *n*-hexane (20 ml). The solution obtained was frozen in liquid nitrogen, evacuated in high vacuum and then slowly warmed to room temperatire (three times). The mixture was heated on oil bath at 100°C for 84 h. Then all volatile materials were removed under reduced pressure, the residue was extracted with CH$_2$Cl$_2$ (50 ml), evaporated and recrystallized from *n*-hexane. Compound **3** (0.75 g, 78%) was obtained as a white powder, m.p. 163-164 °C. ^{1}H NMR (δ, ppm, CDCl$_3$): 7.37-7.27 (m, 15H, aromatic protons), 0.78 (s, 6H, GeMe$_2$). ^{13}C NMR (δ, ppm, CDCl$_3$): 135.72 (quaternary aromatic carbon), 134.86, 128.33 (*m*- and *o*-CH aromatic carbons), 129.06 (*p*-CH aromatic carbon), -0.87 (GeMe$_2$). The signals of C$_6$F$_5$ in ^{13}C NMR spectra could not be obtained due to insufficient intensity of signals and nuclear coupling. ^{19}F NMR (δ, ppm, CDCl$_3$): -124.56 – (-124.73) (m, 2F), -149.48 – (-149.60) (m, 1F), -159.21 – (-159.33) (m, 2F). UV/visible absorption (CH$_2$Cl$_2$, λ_{max} in nm (ε in M^{-1} cm^{-1})): 246 (2.1 $\times$ 10^4). Anal. Calcd. for C$_{38}$H$_{21}$F$_{15}$Ge$_3$ (M$_w$ 980.4694): C, 46.55; H, 2.16. Found: C, 46.12; H, 1.88.

Crystals suitable for X-ray diffraction analysis were obtained from *n*-hexane at –30 °C.

[Ph$_3$GeGeMe$_2$]$_2$Ge(C$_6$F$_5$)$_2$ (4). The procedure is the similar used for the synthesis of **3** using two equivalents of compound **2**. Target compound **4** (0.55 g, 84 %) was obtained as a white powder after crystallization form *n*-hexane/toluene mixture, m.p. 206-207 °C. ^{1}H NMR (δ, ppm, CDCl$_3$): 7.34-7.31 (m, 6H, aromatic protons), 7.26-7.21 (m, 24H, aromatic protons), 0.71 (s, 12H, 2GeMe$_2$). ^{13}C NMR (δ, ppm, CDCl$_3$): 136.53 (quaternary aromatic carbon), 134.79, 128.13 (*m*- and *o*-CH aromatic carbons), 128.76 (*p*-CH aromatic carbon), -0.52 (GeMe$_2$). The signals of C$_6$F$_5$ in ^{13}C NMR spectra could not be obtained due to insufficient intensity of signals and nuclear coupling. ^{19}F NMR (δ, ppm, CDCl$_3$): -121.14 – (-121.23) (m, 2F), -152.29 – (-152.43) (m, 1F), -159.29 – (-159.45) (m, 2F). UV/visible absorption (CH$_2$Cl$_2$, λ_{max} in nm (ε in M$^-$

^{1} cm^{-1})): 267 (4.5 × 10^4). Anal. Calcd. for C$_{52}$H$_{42}$F$_{10}$Ge$_5$ (M$_w$ 1220.0739): C, 51.19; H, 3.47. Found: C, 51.06; H, 3.62.

Crystals suitable for X-ray diffraction analysis were obtained from saturated *n*-hexane/CH$_2$Cl$_2$ mixture at –30 °C.

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Highlights

-the first oligogermyl amide, $Ph_3GeGeMe_2NMe_2$, was synthesized

-novel tri- and pentagermanes donor-acceptor type were obtained and studied

-these compounds are luminescent and electrochemically active

-the physical properties of oligogermanes depend on median or end type of substitution

-unpolar oligogermanes, in a crystal, form cavities that could trap organic compounds

Graphical Abstract