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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 a crystal **3** forms wide channels, in which the solvated nonpolar *n*-hexane molecule is present. The NMR (^1H, ^{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 by the electron withdrawing groups (at the terminal position, such as in **3**, or within the compound, such as in **5**), on the physical properties was also studied.

1. Introduction

Recently, a significant 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, so the widening of the spectrum of catenated organogermanes is an actual synthetic task. 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 have only been superficially investigated.

The directed synthesis of compounds bearing a Ge-Ge bond could be achieved in two main ways. In the first group of methods, a nucleophilic lithium (or potassium) 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 Dräger [7], Castel [8], Marschner [9] et al. The main drawback of these 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 uncontrolled processes due to partial substitution of organic groups at Ge atom [10] or destruction of Ge-Ge bond [11] (Scheme 1, reaction

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☆ This article is dedicated to Prof. Irina P. Beletskaya in recognition of her merits in the field of the chemistry of organoelement compounds.

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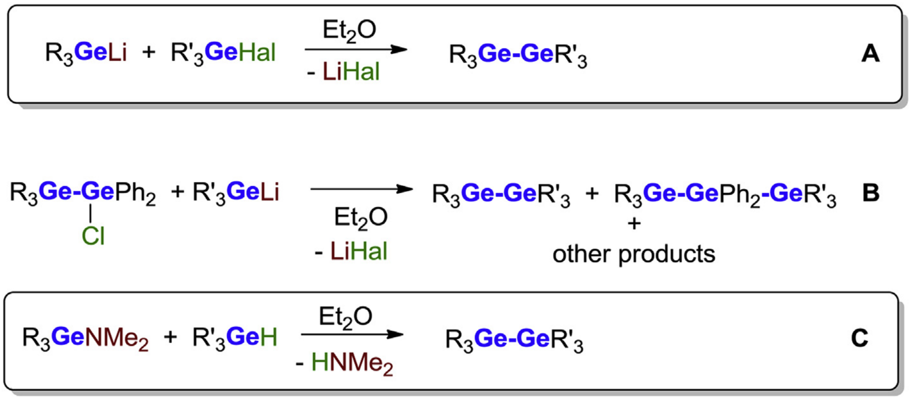


Scheme 1. General methods for creation the Ge-Ge bond.

B). The latest side reaction is very typical for aromatic derivatives.

A second way to prepare Ge-Ge building blocks is to react the free germane with a germylamide under prolonged heating conditions (hydrogermolysis reaction) (Scheme 1, reaction C). This reaction was initially developed for the synthesis of oligogermanes by Weinert et al. [12]. The main drawback of this method is 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 the corresponding vicinal diamides, $Me_2NGePh_2GePh_2NMe_2$ [14] or $Et_2NGeMe_2GeMe_2NEt_2$ [15], and branched monoamides, $[Ph_3Ge]_3GeNMe_2$ [16], are known and are sufficiently stable to be used under hydrogermolysis conditions, there is no data in the literature on using linear catenated germylmonoamides 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 strongly 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 destabilizes the HOMO [17] 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 [18]. Therefore, the introduction of substituents with different electronic properties (electron donating and withdrawing) within the oligogermane molecule in various places (to the terminal positions or within of the molecule) is expected to change its properties significantly.

In continuation of our works on molecular oligogermanes [1,2,10,13,19] we are reporting on the synthesis and on the investigations of the properties of novel donor-acceptor compounds, **3** and **4**. Their structure (NMR, XRD), optical (UV/vis absorbance, luminescence emission) and electrochemical properties were studied in detail. Furthermore, germanium amides **1** and **2**, useful for the further application in organometallic chemistry of Ge are also reported.

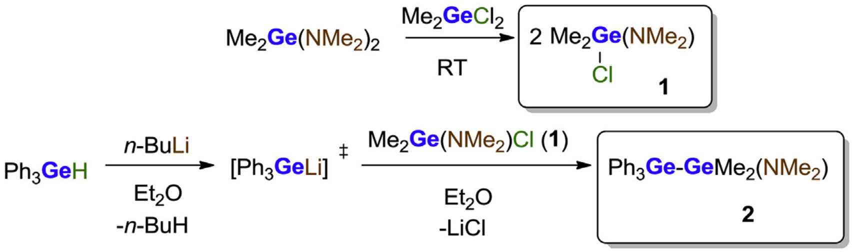
2. Results and discussion

2.1. Synthesis

Hydrogermolysis 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). Corresponding germylamides may be regarded as key initial compounds in these reactions. Usually, for the synthesis of germylamides, the direct reaction between R_3GeHal and $LiNMe_2$ has been used earlier [10,20]. In this work a novel method for the synthesis of linear oligogermyl amide **2**, $Ph_3GeGeMe_2NMe_2$, was elaborated by indirect way under creation of Ge-Ge bond. For this purpose compound **1**, $Me_2Ge(Cl)NMe_2$, was obtained on the first stage (Scheme 2).

Compound **1** is known, but has not been fully characterized yet [21]. The known procedure for its synthesis is a reaction between gaseous Me_2NH with Me_2GeCl_2, what 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 materials ($Me_2Ge(NMe_2)_2$, Me_2GeCl_2).

Compound **2** is novel one; it was prepared by reaction of



Scheme 2. Synthetic strategy for the synthesis of catenated germanium amides.

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Ph_3GeLi, 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_3GeH is detailed in the experimental information also (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.

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 (^1H, ^{13}C, ^{19}F) and their composition was established on the basis of elemental analysis. In general, ^1H and ^{13}C NMR spectra for both compounds are very similar.

The ^{19}F NMR spectra of **3** and **4** show three signals (*ortho-*, *para-* and *metha-*) with integral intensities of 2:1:2, what indicates the free rotation of C_6F_5 rings and their identity. Due to spin-spin coupling all these signals are appeared as multiplets. The compounds bearing terminal C_6F_5 group ($Ph_3GeGe(C_6F_5)_3$, (p-Tol)$_3$Ge-Ge(C_6F_5)$_3$ [10] and **3**, $Ph_3GeGeMe_2Ge(C_6F_5)_3$) have multiplet signals centered at −124, −149, −159 ppm; this means that the nature of the donating group and quantity of Ge atoms in the chain insignificantly impacts on the ^{19}F NMR spectra. At the same time, derivatives bearing median C_6F_5 ([(p-Tol)$_3$Ge]$_2$Ge(C_6F_5)$_2$ [10] and **4**, $[Ph_3GeGeMe_2]_2Ge(C_6F_5)_2$) have the signals of the corresponding related groups centered at −119/-121, −153/-152, −161/-159 ppm, which differ from the case of terminal C_6F_5 derivatives, stated above. It means that the substitution on the oligogermanes by withdrawing groups (terminal 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 and 2; Supporting Information, Table S1, Fig. S1).

Until today only 12 linear molecular trigermanes have been studied by XRD (for details see Ref. [13]), where Ge-Ge bond length and Ge-Ge-Ge angle vary within 2.413–2.622 Å and 110.4–125.0°, respectively, depending on the steric size and on the electronic nature of the substituents located at Ge atoms.

In **3** the presence at Ge atoms groups straightly different on their electronic properties (Ph *vs.* C_6F_5) has a very limited impact 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_6F_5)$_3$ (2.4652(11) Å) [10], containing terminal 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** (increasing of σ-conjugation).

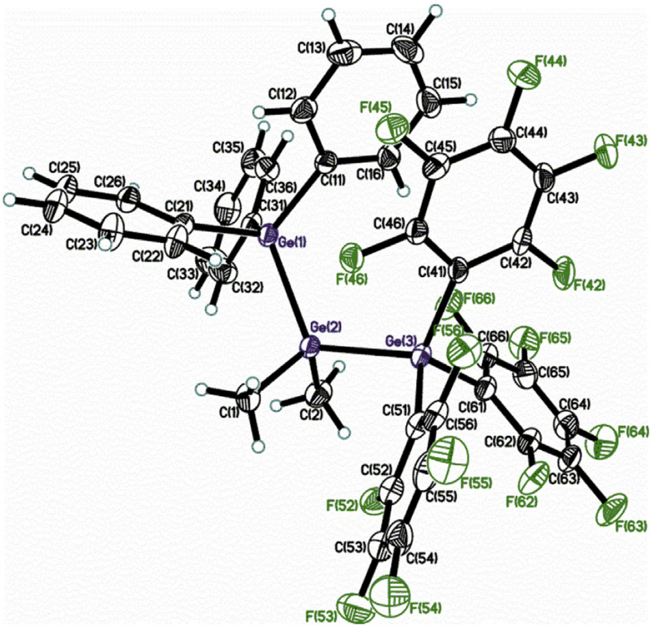
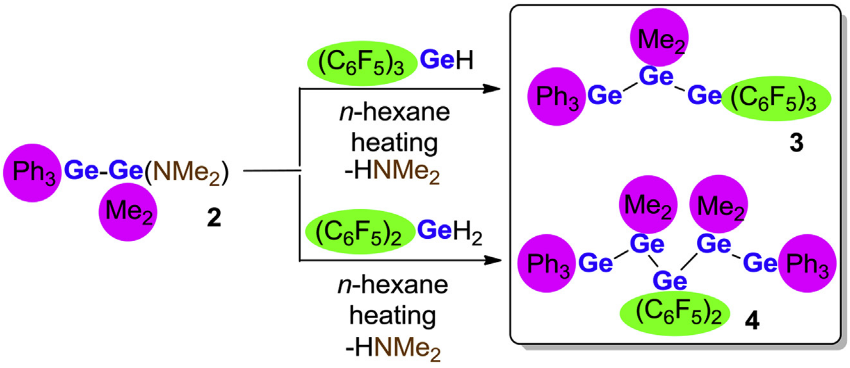


Fig. 1. Molecular structure of compound **3**. Solvate molecule of *n*-hexane was not shown. Displacement ellipsoids are shown at 50% probability level. Selected bond lengths (Å) and bond angles (deg): Ge(1)-Ge(2) 2.4475(4), Ge(2)-Ge(3) 2.4522(4), Ge(1)-C_{av} 1.950(2), Ge(2)-C_{av} 1.958(3), Ge(3)-C_{av} 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), C-Ge(3)-C_{av} 107.30(10).

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_6F_5)$_2$ [10], containing median disposition of withdrawing groups in the molecule. The Ge-Ge(C_6F_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



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

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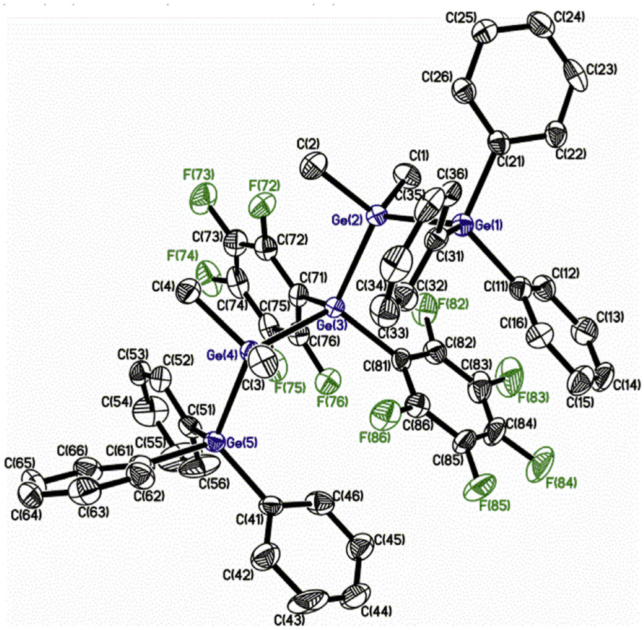

Fig. 2. Molecular structure of compound **4**. Displacement ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ge(1)-Ge(2) 2.4441(8), Ge(2)-Ge(3) 2.4333(8), Ge(3)-Ge(4) 2.4352(7), Ge(4)-Ge(5) 2.4320(8), Ge(1)-C_{av} 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(81)-Ge(3)-C(71) 105.6(2), C(4)-Ge(4)-C(3) 105.0(2), C-Ge(5)-C_{av} 108.7(2).

(115.780(14) *vs.* 124.10(3)°); this shows the effect of the substitution (terminal or median) on the oligogermanium chain.

The geometry of Ge atoms may be described as a slightly distorted tetrahedron, where the largest deviation from the ideal tetrahedral was observed for the central Ge(2) atom. All phenyl rings exhibit a propeller-like conformation. The opposite phenyl ring C11 > C16 and C_6F_5 group C41 > C46 are almost coplanar with dihedral angle equal to 2.6°. They form short intramolecular π..π stacking interaction with Ph_{cent} … C45 separation 3.28 Å. 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 of **3** the solvated molecules of *n*-hexane are located in wide channels propagated along *a*-axis (Fig. S1, Supporting Information). Surprisingly, the molecule of *n*-hexane is fully ordered and exhibit low ADP's for all carbon atoms. There are no short intermolecular contacts between adjacent *n*-hexane molecules. However, any attempts to remove the *n*-hexane molecule from the channels (by applying the high vacuum over 24 h or even mild heating) were unsuccessful according to XRD; all characteristics of the crystal remain unchangeable. Therefore, donor-acceptor oligogermanes may form crystals suitable to fix inert molecules in a fashion similar to MOFs.

Crystals of molecular oligogermanes containing solvated molecules are known, but only with molecules of solvated benzene or toluene ($Ph_3G_3GePh_3{*}2C_6H_6$ [22], (p-Tol)$_3$GeGe(Tol-p)$_3{*}C_6H_6$ [23], (p-Tol)$_3$GeGePh$_3{*}C_6H_6$, [(p-Tol)$_3$Ge]$_2$GePh$_2{*}$PhMe, [(p-Tol)$_3$Ge]$_2$-Ge(Tol-p)$_2{*}$PhMe [24], $Ge_4Ph_{10}{*}2C_6H_6$ [25]).

To the best of our knowledge there are only 3 linear pentagermanes with known molecular solid state structures, Ph[GePh$_2$]$_5$Ph (at 295 K: d(Ge-Ge)$_{av}$ 2.460(4) Å and Ge-Ge-Ge$_{av}$ 115.6(2)°; at 100 K: d(Ge-Ge)$_{av}$ 2.4502(6) Å and Ge-Ge-Ge$_{av}$ 115.52(2)° [11a,26]), ($Me_3Ge)_3GeGeMe_2Ge(GeMe_3)_3$ (d(Ge-Ge)$_{av}$ 2.4425(9) Å 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) Å and Ge-Ge-Ge$_{av}$ 117.01(3)°) [27].

Compound **4** crystallizes in a triclinic P-1 (Z = 2) space group and the main molecule occupies general positions. All four Ge-Ge bonds have slightly different lengths, where the longest and shortest ones are observed for the same terminal groups (Ge(1)-Ge(2) and Ge(4)-Ge(5), respectively); the average value is 2.4362(8) Å. This value is the smallest among known 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 the terminal substitution in **3**. Really, 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 Ph[GePh$_2$]$_5$Ph, the Ge-Ge bond length in the center 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) [26], but in **4** this effect is negligible, what may be explained by the presence of methyl groups instead of phenyl groups.

In **4**, only four Ge atoms (Ge2, Ge3, Ge4 and Ge5) lie in the same plane within 0.006 Å, while Ge(1) deviates from this plane by 2.217 Å. Interestingly, the same situation has been observed earlier for aryl pentagermane Ph[GePh$_2$]$_5$Ph [11a,26]. Referring to the crystal structures for longer oligogermanes, namely (i-Pr)$_3$Ge[GePh$_2$]$_4$Ge(i-Pr)$_3$ [14,28], it is possible to state that for higher catenated Ge derivatives (more than 4 atoms in the chain) the terminal atoms are bended slightly from the plane formed by the central atoms. Furthermore, in **4** contrary to Ph[GePh$_2$]$_5$Ph, 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 noticeable deviation of bond angles from the typical tetrahedral values 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$_3$GeGe(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 oligogermanes **3** and **4** were investigated in details.

The UV/vis absorbance of **3** and **4** is shown below (Fig. 3). 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. For the comparison purposes the data for the related tetragermanes are also given.

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 impacts on the energy level and disposition of these orbitals. Introduction of aryl groups moves the LUMO toward the Ar

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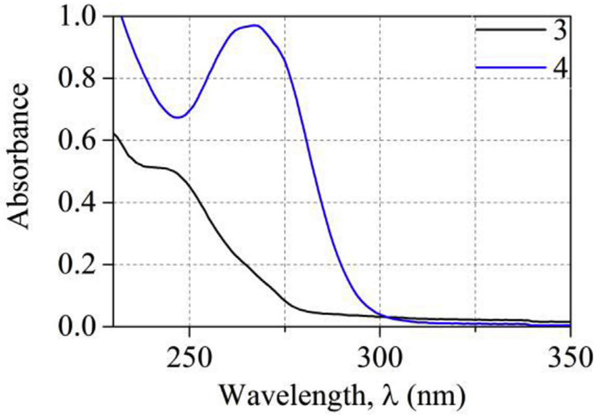

Fig. 3. UV/visible absorption spectra for compounds **3** and **4** (CH_2Cl_2, room temperature).

substituent, making the transitions to LUMO-1 *etc.* more preferable. In general, elongation of the Ge chain resulted to bathochromic shift.

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_6F_5 groups at the terminal (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 stabilization. Furthermore, modification of substituent on the median part of the molecule leads to a stronger bathochromic shift in comparison with the terminal 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 increasing of extinction coefficient also.

The luminescence properties of the compounds **3** and **4** in solid state and in solution were also studied (Fig. 4). The compounds show broad luminescence in both states. To the best of our knowledge, 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).

In the solid state an emission of **3** and **4** is red shifted than in solution, what 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%.

It should be noted, that simple elongation of the Ge chain has no significant impact on the expected red shift of the luminescence. Apparently, the coplanar *trans*-disposition of the Ge atoms in the chain plays a critical role for efficiency of the luminescence (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. Apparently, the appearance of luminescent properties in these compounds is explained by the high level of conjugation as between Ge atoms and between Ge atoms and organic (electron donor or electron acceptor, aryl or alkyl) substituent, what resulted to "rigidity" of the whole molecule. In this case such "rigidity" should give the luminescence and therefore excludes the possibility of full or partial non-radiative excitation energy waste by the thermal irradiation (vibration and rotation of molecule's parts). Furthermore, changing the nature of the substituents (for example, to electron withdrawing) may result to the stabilization of the charge separated forms in excited states (intramolecular charge transfer), what also effect on luminescence. Further investigation in this field will be performed in the near future.

Table 1
UV/vis absorption data for carbon substituted tri-, tetra- and pentagermanes.

$[Ge]_n$	compound	λ, nm	ε*10^4, M^{-1} cm^{-1}	solvent	reference
trigermanes	$[Ph_3Ge]_2GeMe_2$	245	2.8	cyclohexane	[8]
	$[Ph_3Ge]_2GeMePh$	250	3.6	cyclohexane	[8]
	$[Ph_3Ge]_2GeEt_2$	247	2.7	cyclohexane	[8]
	$Ph[GeEt_2]_3Ph$	241	2.0	cyclohexane	[8]
	$[Ph_3Ge]_2GePh_2$	250	2.6	cyclohexane	[8]
		249	3.2	CH_2Cl_2	[25]
	$[Me_3Ge]_2GeMe_2$	218	0.9	cyclohexane	[29]
	$[(p\text{-Tol})_3Ge]_2GeMe_2$	251	4.0	CH_2Cl_2	[2]
	$[(p\text{-Tol})_3Ge]_2GePh_2$	251	n.g.[a]	CH_2Cl_2	[24]
	$[(p\text{-Tol})_3Ge]_2Ge(p\text{-Tol})_2$	253	n.g.[a]	CH_2Cl_2	[24]
	$[(i\text{-Pr})_3Ge]_2GePh_2$	242	2.1	CH_2Cl_2	[27]
	$[(p\text{-Tol})_3Ge]_2Ge(C_6F_5)_2$	258	1.4	CH_2Cl_2	[10]
	$[(p\text{-}F_3CC_6H_4)_3Ge]_2Ge(C_6F_5)_2$	264	2.4	CH_2Cl_2	[13]
	$Ph_3GeGeMe_2Ge(C_6F_5)_3$ (**3**)	246	2.1	CH_2Cl_2	this work
tetragermanes	$Ph[GeEt_2]_4Ph$	248	2.7	cyclohexane	[8]
	$Ph_3Ge[GeEt_2]_2GePh_3$	256	4.0	cyclohexane	[8]
	$Ph[GePh_2]_4Ph$	282	3.1	CH_2Cl_2	[25]
	$Me[GeMe_2]_4Me$	233	1.6	cyclohexane	[29]
	$[(p\text{-Tol})_3GeGePh_2]_2$	285	n.g.[a]	CH_2Cl_2	[24]
	$[(i\text{-Pr})_3GeGePh_2]_2$	273	4.6	CH_2Cl_2	[27]
pentagermanes	$Ph[GeEt_2]_5Ph$	256	3.2	cyclohexane	[8]
	$Ph_3Ge[GeEt_2]_3GePh_3$	269	3.9	cyclohexane	[8]
	$Me_3Ge[GeMe_2]_3GeMe_3$	246	2.1	cyclohexane	[29]
	$Ph_3Ge[GePh_2]_3GePh_3$	293	6.3	CH_2Cl_2	[11a]
		295	4.5	CH_2Cl_2	[26]
	$[(i\text{-Pr})_3GeGePh_2]_2GePh_2$	300	5.7	CH_2Cl_2	[27]
	$[Ph_3GeGeMe_2]_2Ge(C_6F_5)_2$ (**4**)	267	4.5	CH_2Cl_2	this work

[a] Not given.

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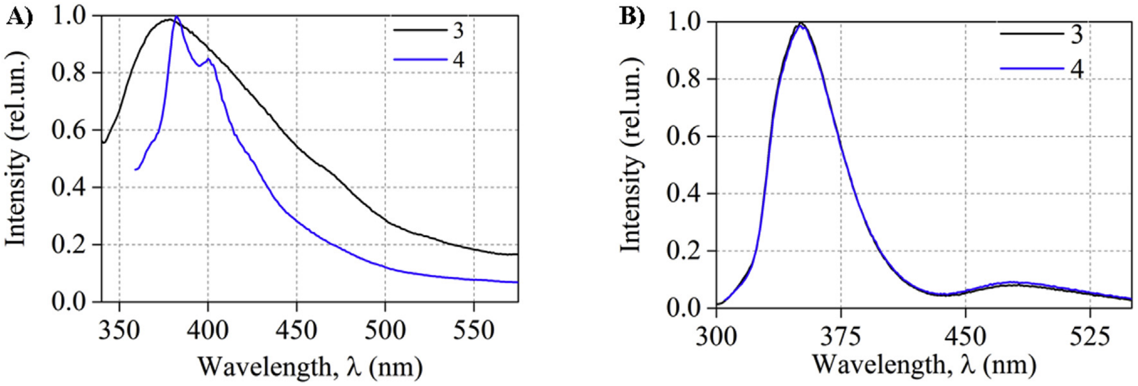

Fig. 4. Luminescence emission spectra for **3** and **4** at room temperature: A) in the solid state; B) in the solution (CH_2Cl_2).

Table 2
Luminescence emission data for the catenated germanium compounds.

type	compound	solid state	solution[a]			reference
		λ_{em}, nm[b]	λ_{em} (nm)	Stokes shift, nm	Φ_f (%)[c]	
polymer	$[(Me_3SiOC_6H_4\text{-}p)MeGe]_n$	367 (film)	369 (332, THF)	39	n.g.[d]	[30]
molecular	$(p\text{-Tol})_3GeGeMe_3$	357, 373, 393 (300)	286 (270)	54	3.27	[19c]
	$[(p\text{-Tol})_3Ge]_2GeMe_2$	438 (380)	338 (285)	87	1.85	[2]
	$Ph_3Ge\text{-}Ge(C_6F_5)_3$	373 (270)	377 (265)	151	12.50	[2]
	$[(p\text{-}F_3CC_6H_4)_3Ge]_2Ge(C_6F_5)_2$	476 (320)	376 (290)	112	12.36	[13]
	$(i\text{-}Pr)_3Ge[GePh_2]_4Ge(i\text{-}Pr)_3$	n.g.[d]	370 (312)	60	n.g.[d]	[14]
	$(i\text{-}Pr)_3Ge[GePh_2]_3Ge(i\text{-}Pr)_3$	n.g.[d]	380 (302)	80	n.g.[d]	[27]
	$Ph_3GeGeMe_2Ge(C_6F_5)_3$ (**3**)	379 (325) 373 (270)	351 (290)	107	5.45	this work
	$[Ph_3GeGeMe_2]_2Ge(C_6F_5)_2$ (**4**)	382 (345) 400 (345)	350 (295)	84	2.11	this work

[a] Spectra were recorded in CH_2Cl_2 (unless otherwise noted); excitation wavelength, λ_{ex}, in parentheses.
[b] Excitation wavelength, λ_{ex}, in parentheses.
[c] Quantum yield.
[d] Not given.

2.4. *Electrochemical behavior*

The redox properties of compounds **3** and **4** were studied by the mean of cyclic voltammetry (CV) (Fig. 5; Fig. S16, Supporting Information). The electrochemical data for known tri- and pentagermanes are shown in Table 3. The data for the related tetragermanes are also given for comparison.

The electrochemical data for the 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, which 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 [24]. In the case of oligogermanes containing aryl and alkyl groups the situation is less predictable (see Table 3). Furthermore, increasing the number of Ge atoms in the chain resulted in decrease of the oxidation potential due to reinforced σ-conjugation.

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 [29]. Elongation of the Ge chain in **3** in comparison with donor-acceptor digermane $Ph_3GeGe(C_6F_5)_3$ [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 destabilizes the HOMO even in the presence of electron withdrawing substituents. In general, introduction of alkyl or 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. It should be noted that for both **3** and **4** electrochemical processes are irreversible.

Although more electrochemical mechanistic investigations need 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 [32], 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 with the solvent or between each other. The presence of the reaction with the solvent was observed earlier by us [19c] and Weinert et al. [33]. The possibility of oxidation of cation-radical formed on the first stage is also may be regarded as doubtful. Nevertheless, it is impossible to

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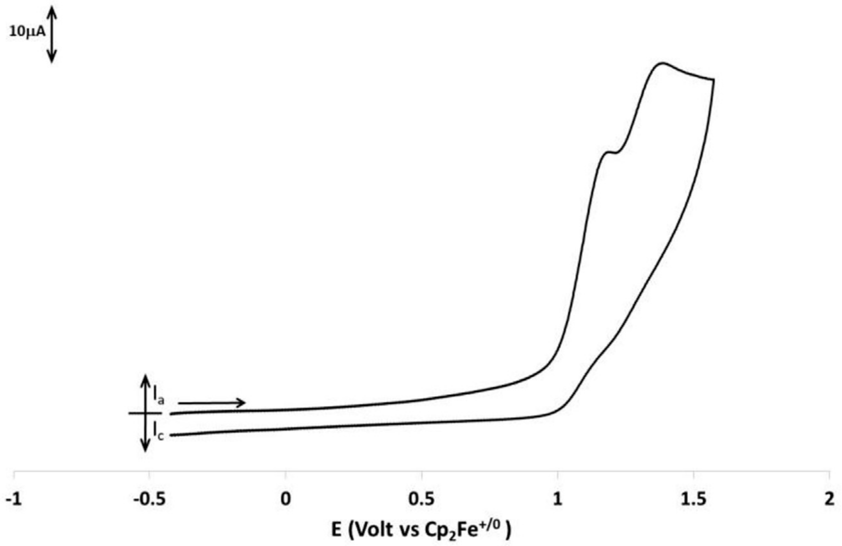

Fig. 5. Cyclic voltammogram of 1 mM $[Ph_3GeGeMe_2]_2Ge(C_6F_5)_2$ (**4**) in dichloromethane - $[NBu_4][PF_6]$ solution. Sweeping rate 200 mV/s at room temperature.

Table 3
Electrochemical data for carbon substituted tri-, tetra- and pentagermanes by CV.

$[Ge]_n$	compound	E, V[a]	standard	conditions	reference
trigermanes	$[Me_3Ge]_2GeMe_2$[b]	0.93 (1.42)[c]	Fc^+/Fc	MeCN, 0.1 M TBAP	[29]
	$[(EtOCH_2CH_2)Et_2Ge]_2GePh_2$	1.577	Ag/AgCl	MeCN, 1.0 M $[Bu_4N][PF_6]$	[31]
	$[(EtOCH_2CH_2)Bu_2Ge]_2GePh_2$	1.500	Ag/AgCl	MeCN, 1.0 M $[Bu_4N][PF_6]$	[31]
	$[(EtOCH_2CH_2)Ph_2Ge]_2GePh_2$	1.609	Ag/AgCl	MeCN, 1.0 M $[Bu_4N][PF_6]$	[31]
	$Ph_3Ge[GeBu_2]_2(CH_2CH_2OEt)$	1.546	Ag/AgCl	MeCN, 1.0 M $[Bu_4N][PF_6]$	[31]
	$Ph_3GeGeBu_2GePh_2(CH_2CH_2OEt)$	1.525	Ag/AgCl	MeCN, 1.0 M $[Bu_4N][PF_6]$	[31]
	$[Ph_3Ge]_2GePh_2$	1.696, 2.052	Ag/AgCl	CH_2Cl_2, 0.1 M $[Bu_4N][PF_6]$	[24]
	$[(p\text{-Tol})_3Ge]_2GePh_2$	1.498, 1.860	Ag/AgCl	CH_2Cl_2, 0.1 M $[Bu_4N][PF_6]$	[24]
	$[(p\text{-Tol})_3Ge]_2Ge(p\text{-Tol})_2$	1.542, 1.865	Ag/AgCl	CH_2Cl_2, 0.1 M $[Bu_4N][PF_6]$	[24]
	$[(i\text{-Pr})_3Ge]_2GePh_2$	1.555	Ag/AgCl	CH_2Cl_2, 0.1 M $[Bu_4N][PF_6]$	[27]
	$[(n\text{-Bu})_3Ge]_2GePh_2$	1.540	Ag/AgCl	CH_2Cl_2, 0.1 M $[Bu_4N][PF_6]$	[17]
	$[(p\text{-}F_3CC_6H_4)_3Ge]_2Ge(C_6F_5)_2$	1.27 (1.76), 1.63 (2.12)	Fc^+/Fc	CH_2Cl_2, 0.05 M $[NBu_4][B(C_6F_5)_4]$	[13]
	$Ph_3GeGeMe_2Ge(C_6F_5)_3$ (**3**)	1.53 (2.02)	Fc^+/Fc	CH_2Cl_2, $[NBu_4][PF_6]$	this work
tetragermane	$[Me_3GeGeMe_2]_2$[d]	0.72 (1.21)[c]	Fc^+/Fc	MeCN, 0.1 M TBAP	[29]
	$[Ph_3GeGePh_2]_2$	1.644, 2.060, 2.450	Ag/AgCl	CH_2Cl_2, 0.1 M $[Bu_4N][PF_6]$	[24]
	$[(p\text{-Tol})_3GeGePh_2]_2$	1.398, 1.718, 2.242	Ag/AgCl	CH_2Cl_2, 0.1 M $[Bu_4N][PF_6]$	[24]
	$[(i\text{-Pr})_3GeGePh_2]_2$	1.525, 1.860, 2.055	Ag/AgCl	CH_2Cl_2, 0.1 M $[Bu_4N][PF_6]$	[27]
pentagermane	$[Me_3GeGeMe_2]_2GeMe_2$[e]	0.61 (1.10)[c]	Fc^+/Fc	MeCN, 0.1 M TBAP	[29]
	$[Ph_3GeGePh_2]_2GePh_2$	1.385, 1.605, 1.777, 1.998	Ag/AgCl	CH_2Cl_2, 0.1 M $[Bu_4N][PF_6]$	[26]
	$[(i\text{-Pr})_3GeGePh_2]_2GePh_2$	1.560, 1.695, 1.875, 2.095	Ag/AgCl	CH_2Cl_2, 0.1 M $[Bu_4N][PF_6]$	[27]
	$[Ph_3GeGeMe_2]_2Ge(C_6F_5)_2$ (**4**)	1.18 (1.67), 1.38 (1.87)	Fc^+/Fc	CH_2Cl_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 $E_{p/2} = -0.53$ V.
[e] Reduction process is also observed at $E_{p/2} = -0.48$ V.

completely rule out the presence of additional oxidations at higher potentials that would be located outside of the electrochemical window.

This mechanism may be applicable to the oxidation of alkyl substituted oligogermanes [29], [27]. Also, as it has been recently proven [33], an electrochemically generated cation R_3Ge^+ can be trapped with solvent (CCl_4) to give R_3GeCl using bulk electrolysis, what gives more support to the proposed mechanism shown in Scheme 4. 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. [24].

Therefore, it was established that the structure of oligogermanes (especially the nature of the substituents) strongly impacts on the oxidation potential, pathway and number of oxidation.

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 catenated germanes **3** and **4**. It has been experimentally shown that the physical properties of catenated germanes depend on the type of substitution by withdrawing groups. Median

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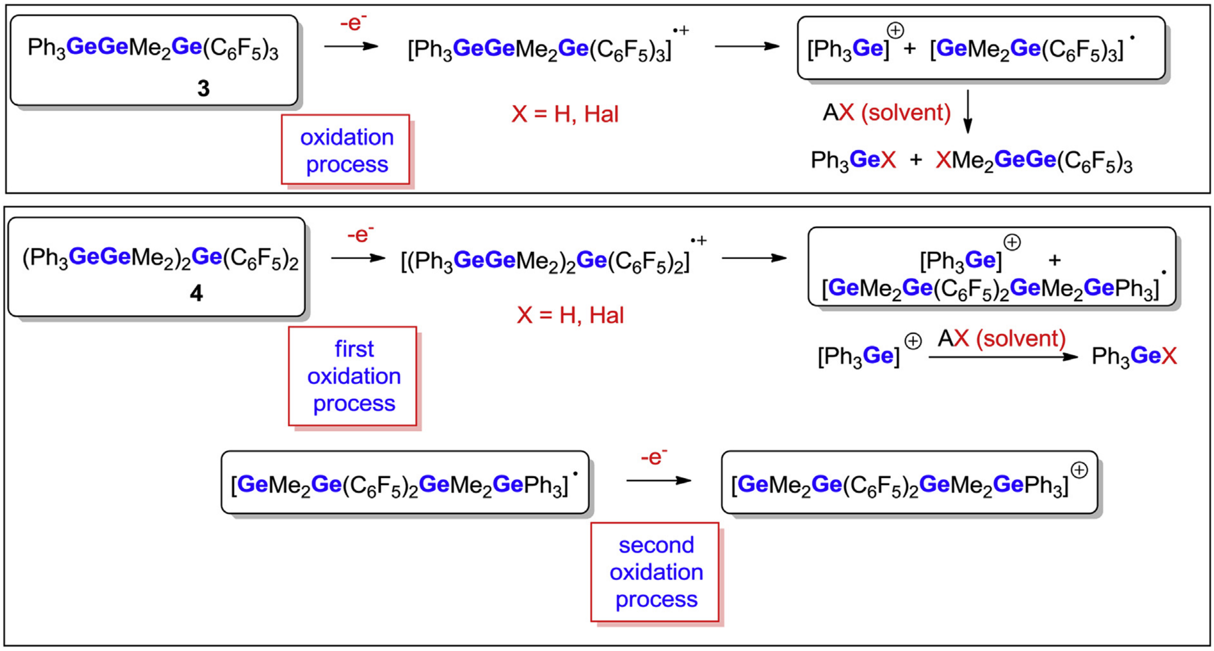

Scheme 4. Mechanism of irreversible oxidation of catenated germanes.

insertion has a greater effect than a substitution located at the terminal positions 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 this amount, while elongation of the Ge chain increases. Oligogermanes have wide emission spectra; in solid state, their luminescence is significantly red shifted 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), *n*-BuLi (Aldrich) were 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 400 MR 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). The signals of C_6F_5 in ^{13}C NMR spectra of **3** and **4** could not be obtained due to insufficient intensity of signals and nuclear coupling. 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. Fluorescence spectra at room temperature were recorded with Hitachi F-7000 luminescence spectrometer. The fluorescence quantum yields were measured using Rhodamine as reference.

Electrochemical measurements were carried out using an Autolab 302 N 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 [34]. The ferrocene potential was obtained by its addition to the analyte solution at an appropriate time in the experiment.

Known compounds, Ph_3GeCl [19a], 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

4.2.1. Synthesis of triphenylgermane, Ph_3GeH

Improved procedure was applied [35]. 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, 20.79 mmol) 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 × 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. [35b] 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).

4.2.2. *(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 at room temperature, 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) [21a], 114 [21b]. ^{1}H NMR (*δ*, ppm, C_6D_6): 2.41 (s, 6H, NMe_2), 0.43 (s, 6H, $GeMe_2$). ^{1}H NMR spectrum corresponds to literature data [21a]. ^{13}C NMR (*δ*, ppm, C_6D_6): 39.48 (NMe_2), 2.36 ($GeMe_2$).

4.2.3. *$Ph_3GeGeMe_2NMe_2$ (2)*

4.2.3.1. Synthesis of Ph_3GeLi. At −78 °C *n*-BuLi (6.00 ml, 2.5 M, 15.00 mmol) was added dropwise to the solution of Ph_3GeH (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_3GeLi obtained *in situ* was used further without purification.

*4.2.3.2. Synthesis of **2**.* At −78 °C the solution of Ph_3GeLi in ether obtained as described above was added dropwise to the solution of compound **1** (2.73 g, 15.00 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_6D_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_6D_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 $C_{22}H_{27}Ge_2N$ (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*

4.3.1. *$Ph_3GeGeMe_2Ge(C_6F_5)_3$ (**3**)*

A mixture of compound **2** (0.44 g, 0.98 mmol) and $(C_6F_5)_3GeH$ (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 temperature (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_2Cl_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 ($GeMe_2$). ^{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_2Cl_2, λ_{max} in nm (ε in M^{-1} cm^{-1})): 246 (2.1×10^4). 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.

4.3.2. *$[Ph_3GeGeMe_2]_2Ge(C_6F_5)_2$ (**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 ($GeMe_2$). ^{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_2Cl_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_2Cl_2 mixture at −30 °C.

4.4. *X-ray diffraction studies*

Intensity data for **3** and **4** were measured on a Bruker SMART APEX II diffractometer (graphite monochromatized Mo K*α* radiation, $\lambda = 0.71073$ Å) using *ω*-scan mode at 150 K. The structures were solved by direct methods and refined by full matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms [36]. In both structures all H atoms were placed in calculated positions and refined using a riding model. Details of X-ray experiments are given in Table S1 (for details, see Supporting Information).

Crystallographic data for **3** and **4** have been deposited at the Cambridge Crystallographic Data Center as supplementary publications (CCDC-1580741 and 1580742). The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jorganchem.2017.11.029.

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