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New Arylene–Germylene–Vinylene Compounds: Stereoselective Synthesis, Characterization, and Photophysical Properties

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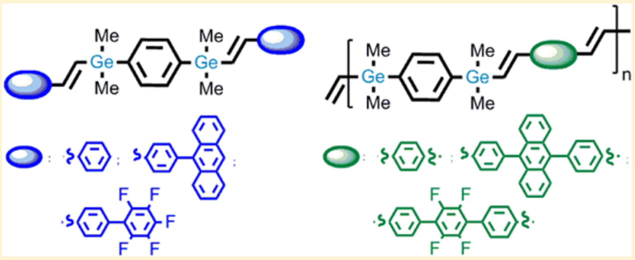
Supporting Information

ABSTRACT: The stereoselective route toward new molecular and macromolecular compounds containing arylene–germylene–vinylene units is described. The reagents for germylative coupling reaction were 1,4-bis(dimethylvinylgermyl)benzene (**1**) and vinyl- and divinylarenes with ruthenium complexes (**2a**, **2b**) as catalysts. NMR characterization of all isolated products, results of MS and elemental analysis for molecular compounds (**3**–**5**), and GPC for oligomers (**6**–**8**) are presented. Absorption and luminescence properties of the synthesized compounds are discussed and compared with those of model chromophores.



■ INTRODUCTION

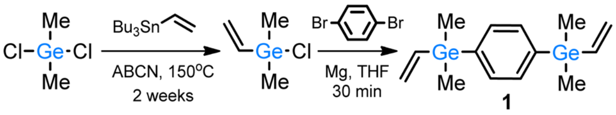
Organogermanium compounds have not gained widespread attention due to the rarity and high price of germanium as well as the commercially limited availability of starting materials: halogermanes. Nonetheless, their chemistry is well developed, and interest in these compounds has increased due to their interesting properties and low toxicity (a potential alternative to organostannanes).[1,2] Organogermanium derivatives containing π-conjugated systems have also been found to be attractive precursors of optoelectronic materials.[3]

Among the many synthetic approaches, catalytic transformations mediated by transition metal complexes are the most important procedures leading to alkenylgermanes. Hydrogermylation of alkynes is probably the most recognizable method for the preparation of substituted vinylgermanes, and, depending on the properties of applied reagents, this can result in *E*, *Z*, or *gem* products.[4] Dehydrogenative germylation of olefins with hydrogermanes[5] and germylative coupling (germylation with vinylgermanes)[6] have also been reported as convenient routes to obtain functionalized alkenylgermanes. The mechanism of the germylative coupling reaction has already been established, and it shows wide possibilities for its further application in organometallic synthesis. Therefore, we employed the above-mentioned process, as well as our previous experience with silicon compounds,[7] in the synthesis of molecular and macromolecular organogermanium derivatives containing arylene–germylene–vinylene units with high stereoselectivity. Spectroscopic absorption and luminescence properties have been characterized.

■ RESULTS AND DISCUSSION

Monomer Synthesis. 1,4-Bis(dimethylvinylgermyl)benzene (**1**) was obtained in the two-step synthesis shown in Scheme 1.

Scheme 1. Preparation of the Monomer 1



ABCN = 1,1'-Azobis(cyclohexanecarbonitrile)

Preparation of chlorodimethylvinylgermane requires a two-week reaction time, and the conditions applied permitted minimization of byproduct formation and at the same time simplification of the isolation procedure.[8] A one-pot procedure employing the Grignard reaction was used to prepare monomer **1**. The Grignard reagent was generated "*in situ*" from the presence of 1,4-dibromobenzene and Mg in tetrahydrofuran (THF) in the presence of a 10% excess of chlorodimethylvinylgermane in less than 1 h in good yield (85%). The crucial point was the rapid initiation of the reaction after addition of all reagents. The mixture was heated at the beginning to start up the process. It was observed that when the reaction was left to initiate itself, byproducts were obtained more frequently, and the yield of the expected product was drastically lowered (≤30%). The monomer was purified according to the

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procedure presented in the Experimental Section and kept under an inert atmosphere for further use.

Catalytic Studies. Based on our previous experience with vinylsilanes[7] as well as earlier reports for simple vinylgermane coupling,[6] two catalysts were chosen for the preliminary experiments: $RuHCl(CO)(PCy_3)_2$ (**2a**) and $RuHCl(CO)(PPh_3)_3$ (**2b**). A germylative coupling reaction of the monomer (**1**) and styrene was used as a model reaction to optimize general conditions. Because of the low *m*/*z* of the expected product, we used GC-MS spectra to control the reaction and identify the reagents. The starting conditions included an open system with argon flow, toluene as a solvent (1 mol·dm^{-3}), stoichiometric ratio of reagents, 2−5 mol % of catalysts, and temperature in the range 80−110 °C. Although the reactivity of vinylgermanes was expected to be a little lower than that of analogous vinylsilyl derivatives, it was surprising to obtain little or no conversion at temperatures below 120 °C. Neither the addition of styrene in excess nor an increase in the catalyst content (10 mol %) changed the outcome. The reaction heating conditions were changed from a dynamic system under argon to a closed system. The Rotaflo Schlenk vacuum was used to withstand the increasing pressure of toluene vapors, the reaction mixture was heated for 24 h at 120 °C, and a change in the color was observed: the usual yellow solution turned deep red.

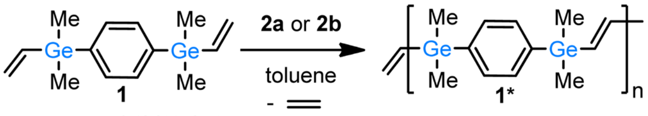
GC-MS analyses did not show the expected product, but a small amount (5%) of monocoupling was observed. The temperature was increased to 140 °C, resulting in a 99% conversion to the expected product. Table 1 shows representative results for different reaction conditions. The temperature of the process was high, but it was still possible to obtain the expected product using the stoichiometric ratio of reagents. Radical polymerization was prevented by using diluted solutions (0.1 mol·dm^{-3}). Although only cross-coupling was observed, germylative coupling of 1,4-bis(dimethylvinyl)germane itself was possible as well. Scheme 2 shows homocoupling of monomer **1**. It was proven that only 50% of substrate was consumed after 24 h. The results were promising for further experiments in which co-oligomers A-B-A-B were expected to be obtained. This is possible only if cross-coupling is more favorable than coupling of the monomer with itself under the given reaction conditions.

Table 1. Germylative Cross-Coupling Conditions[a]

molar ratio[b]	molarity [mol/L]	*T* [°C]	conversion of [ViGe][c] [%]
1:4:0.05	1	80	0
1:4:0.05	0.5	100	0
1:4:0.05	0.125	120	5
1:4:0.05	0.125	140	>99
1:2: 0.02	0.125	140	>99

[a] Toluene, Ar, closed system, 24 h. [b] [ViGe]:[Styrene]:[RuH]. [c] GC-MS.

Scheme 2. Germylative Coupling of 1,4-Bis(dimethylvinylgermyl)benzene



2a $[RuHCl(CO)(PCy_3)_2]$
2b $[RuHCl(CO)(PPh_3)_3]$
1* Mixture of **1** and short oligomers

Applying the same conditions as chosen for cross-coupling of the monomer **1** and styrene, two other molecular germanium derivatives were synthesized (**4** and **5**; see Scheme 3). Products **4** and **5** were isolated according to the procedures described in the Experimental Section and characterized via ^1H NMR and ^{13}C NMR spectra.

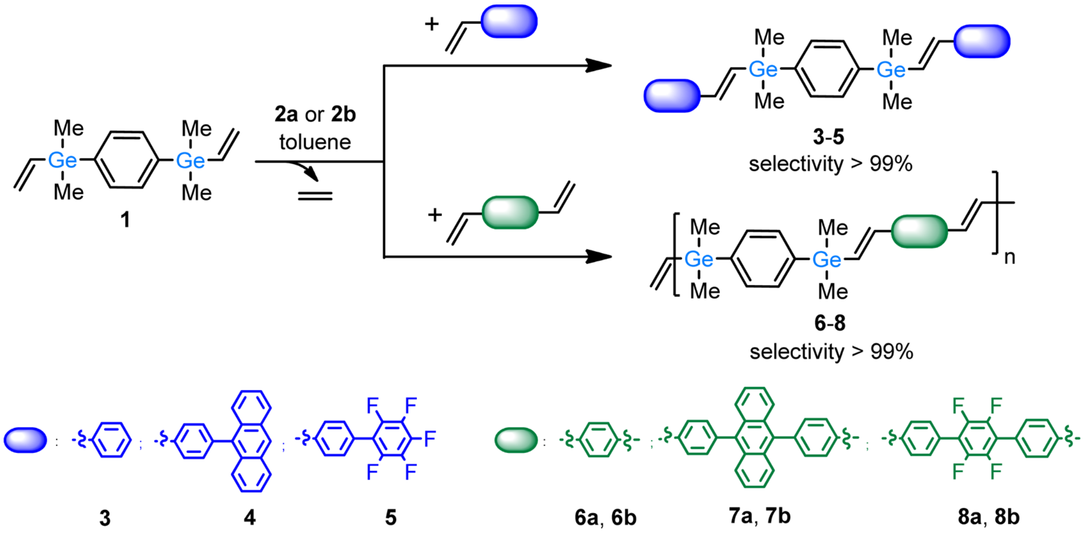
Characterization and Properties of Products. Figure 1 shows ^1H NMR spectra of the monomer **1**, 1,4-divinylbenzene, and compounds **3** and **6** with the presence of signals characteristic of *trans* isomers. No traces of homocoupling were observed. Using terminal vinyl groups seen on NMR spectra, the numbers of mers from integration were described; compound **6** had 6 mers that were confirmed by GPC. According to the literature,[5] there is a high possibility of obtaining mixtures of mono- and dicoupling products in the presence of divinyl derivatives; however, we proved the possibility of coupling both of the terminal vinyl groups and obtaining one product selectively. 1,4-Divinylbenzene, 1,4-bis[(4-vinylphenyl)-2,3,5,6-tetrafluoro]benzene, and 9,10-bis(4-vinylphenyl)anthracene were used. We expected to obtain oligomers instead of polymers, which would be convenient for photophysical analyses. Figure 2 shows the results of GPC analysis of the obtained oligomers. An increase in the reaction time did not significantly change the length of the chain and results in higher values of polydispersity index (PDI).

Table 2 presents GPC analyses for oligomers obtained via 3- and 5-day germylative coupling reactions. All oligomers were analyzed by the thermogravimetric method. A similar correlation in their thermal stability was expected based on almost the same number of mers between products of 3- and 5-day syntheses. Table 3 and Figure 3 show that no significant differences were noted between oligomers from particular groups. Oligomers **6**−**8** lost 1% of mass in the temperature range 189−242 °C. The final transition ends below 550 °C, regardless of the chromophore in the structure. At the beginning of mass loss, oligomer **7** shows higher thermal stability than **6** and **8**, but ultimately all oligomers show similar residues of samples: 32−39% (at 800 °C).

Absorption and emission properties of compounds **3**−**8** were examined (see Table 4, Figure 4). Due to the presence of 9-(4-vinylphenyl)anthracene chromophore, compound **4** shows the highest fluorescence efficiency (φ_{FL} = 0.49) and the longest fluorescence lifetime (3.3 ns) from among molecular compounds **3**−**5**. Compounds **3** and **5** show very weak fluorescence, as expected. The absorption and emission properties of **3** were found to be almost identical to those of its silicon-based analogue **S1**.[9] Likewise, oligomers **6** and **S3** displayed similar photophysical behavior relative to each other. The presence of germanium and silicon in these compounds introduced a large, 20 nm red shift in absorption and emission spectra of both of the compounds relative to the DVB chromophore. Silicon shifted the spectra to the longer wavelengths than germanium. Both germanium- and silicon-based analogues exhibited very similar absorption and emission properties, i.e., similar molar absorption coefficients, quantum yields, and fluorescence lifetimes.

Germanium-based polymer **7**, containing the 9,10-bis(4-vinylphenyl)anthracene chromophore, displayed absorption properties nearly identical to those of the **S5** chromophore itself. Similarly, the presence of germanium did not significantly affect the emission properties. The red shift observed in the

Scheme 3. Germylative Cross-Coupling of 1,4-Bis(dimethylvinylgermyl)benzene and Olefins



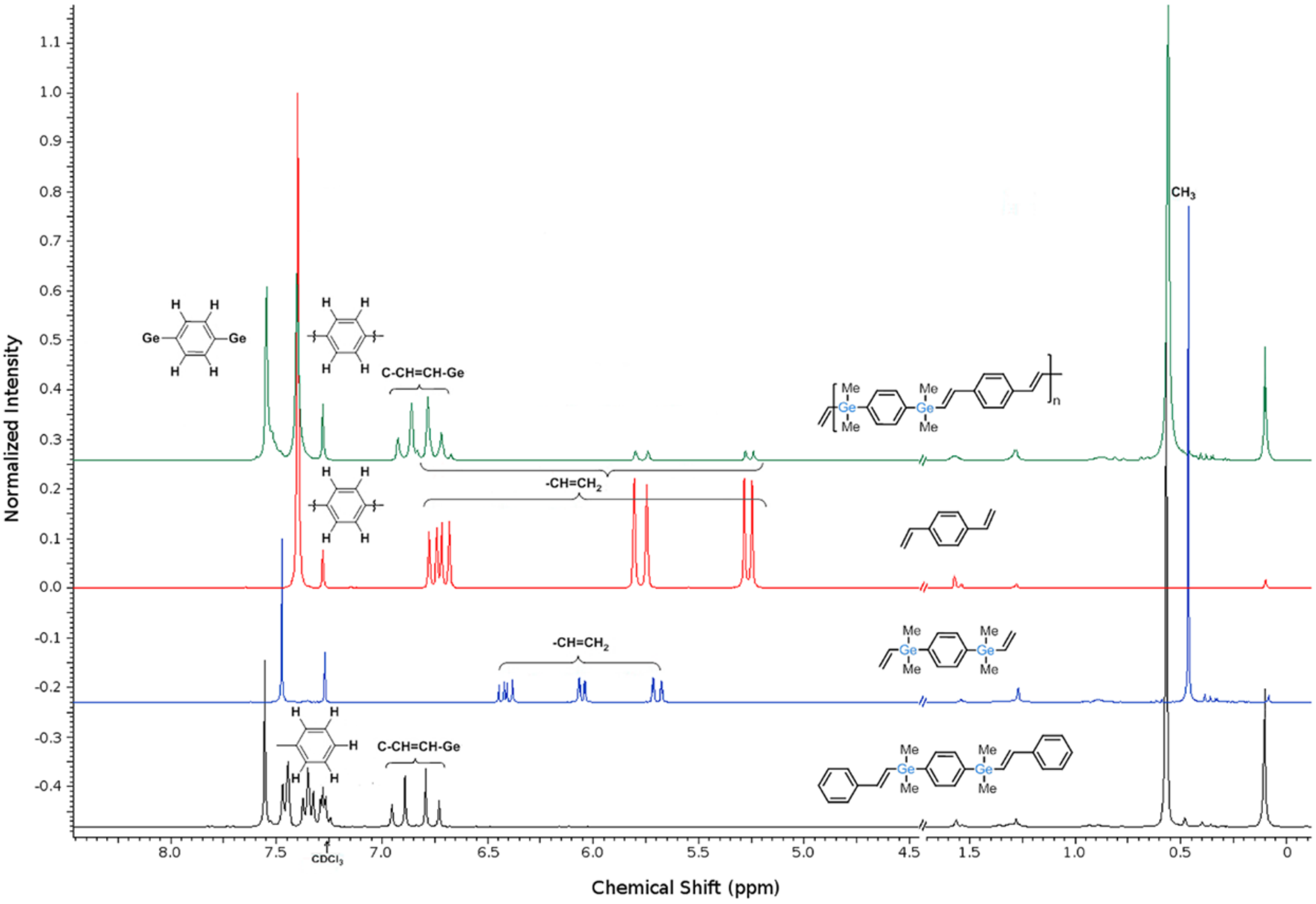


Figure 1. ^{1}H NMR spectra of 1,4-bis(dimethylvilnylgermyl)benzene, 1,4-divinylbenzene, **3**, and **6** in $CDCl_3$.

emission of the polymer was rather small (8 nm). The fluorescence efficiency and lifetimes are only slightly lower than those of the olefin **S5**.

The absorption spectra of 1,4-bis(4-vinylphenyl)benzene (**S7**), 1,4-bis[(4-vinylphenyl)-2,3,5,6-tetrafluoro]benzene (**S8**), and **8** exhibited one maximum characterized by similar values of their molar absorption coefficients. The first of these absorbed with a maximum at 312 nm. The introduction of four fluorine atoms shifted the absorption spectrum by 23 nm toward the blue. The absorption spectrum of oligomer **8** was 9 nm shifted to longer wavelengths compared to that of the chromophore. This observation is consistent with the general tendency of germanium to lower the transition energy. Similar behavior was observed for the emission spectra. The blue shift (referenced **S7**) was larger for **S8** (20 nm) than for **8** (3 nm). Only the **S7** fluorescence spectrum had vibronic structure, whereas the

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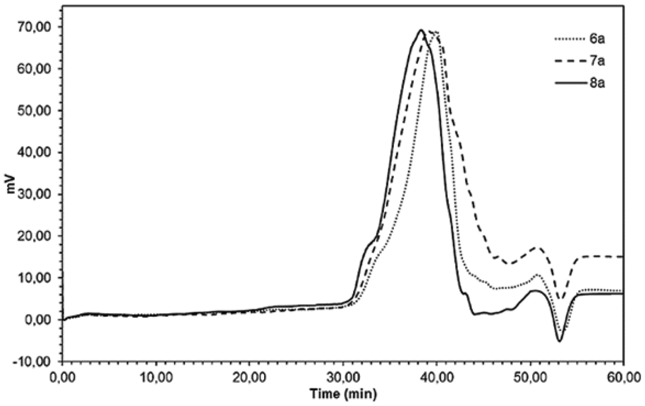

Figure 2. GPC chromatogram of **6a**−**8a**.

Table 2. GPC Results[a]

polymer	M_n [g·mol^{-1}]	M_w [g·mol^{-1}]	PDI	DP$_n$	time [days]
6a	2275	4027	1.77	6	3
6b	2863	5679	1.99	7	5
7a	2343	4461	1.90	3	3
7b	2875	5150	1.90	4	5
8a	2681	4160	1.55	4	3
8b	3128	5431	1.70	5	5

[a] PDI = M_w/M_n; DP$_n$ = number-average degree of polymerization; polystyrene Shodex standards calibration curve in a range from 1.31 × 10^3 to 3.64 × 10^6 Da; THF.

Table 3. Thermal Properties of Oligomers after 3- and 5-Day Synthesis (Heating Rate of 10°C·min^{-1})

	temperature loss [°C]			
oligomer	1%	5%	10%	residue at 800 °C [%]
6a	201	264	295	39
6b	232	290	339	37
7a	189	313	373	35
7b	228	334	387	38
8a	242	297	333	32
8b	232	292	338	37

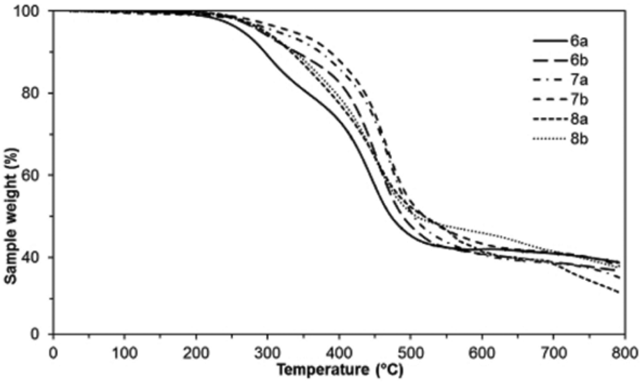

Figure 3. Thermal properties of copolymers **6**−**8**.

emissions of **S8** and **8** were structureless. The lack of vibronic structure in the fluorinated compounds results from their different sequence congestion compared to **S7**. All of the compounds displyed large emission efficiencies and rather short fluorescence lifetimes (below 1 ns). The fluorescence quantum yields and fluorescence lifetimes decreased in the order **S7** > **S8** > **8**.

■ CONCLUSIONS

New arylene−vinylene−germylene derivatives with strictly defined structure were successfully synthesized via germylative coupling condensation. All products obtained were isolated and fully characterized via NMR. The molecular compounds were subjected to GC-MS and elemental analyses. Oligomers were characterized via GPC, and their thermal stability was discussed. Photophysical properties of the synthesized compounds were described. The emission properties of chromophores were not significantly affected by the presence of germanium. Moreover, the similarity of compounds **3** and **6** to their silicon analogues was described.

■ EXPERIMENTAL SECTION

1. Materials. The chemical reagents were obtained from the following sources: hexane, pentane, toluene, diethyl ether, tetrahydrofuran (THF), and acetone were purchased from Fluka, $CDCl_3$ was from Dr Glaser A. G. Basel, tetrakis(triphenylphosphine)palladium(0), 1,4-dibromobenzene, terephtalic aldehyde, methyltriphenylphosphonium bromide, 4-vinylphenylboronic acid, bromopentafluorobenzene, 1,4-dibromotetrafluorobenzene, 9-bromoanthracene, 9,10-dibromoanthracene, potassium *tert*-butoxate, styrene, 1,2-dibromoethane, ethanol, methanol, magnesium sulfate, calcium hydride, sodium hydride, and potassium hydroxide were from Aldrich, and chlorodimethylvinylsilane was from Gelest. The solvents were distilled (tetrahydrofuran, toluene, and diethyl ether from sodium and hexane from calcium hydride) under argon and stored over type 4 Å molecular sieves. Dichloromethane (DCM) used for photophysical measurements was of spectroscopic grade from Merck and was used as received. 1,4-Divinylbenzene was dried and degassed, and chlorodimethyl vinylsilane was purified by "bulb-to-bulb" distillation and stored under argon. All the syntheses of monomers and macromolecular compounds and catalytic tests were carried out under an inert argon atmosphere. 2,3,4,5,6-Pentafluoro-4′-vinylbiphenyl, 9-(4-vinylphenyl)-anthracene, 1,4-bis[(4-vinylphenyl)-2,3,5,6-tetrafluoro]benzene (**S8**), and 9,10-bis(4-vinylphenyl)anthracene (**S5**) were synthesized according to an already known procedure,[10] except for the catalyst, which was replaced with commercially available tetrakis(triphenylphosphine)-palladium(0). Ruthenium complexes [RuHCl(CO)(PCy$_3$)$_2$] (**2a**) and [RuHCl(CO)(PPh$_3$)$_3$] (**2b**) were also prepared according to the literature procedure.[11,12]

2. General Methods. ^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz), and ^{29}Si NMR (60 MHz) spectra were recorded on a Varian XL 300 MHz spectrometer in $CDCl_3$ solution. Chemical shifts are reported in δ (ppm) with reference to the residue solvent ($CDCl_3$) peak for ^{1}H and ^{13}C and to TMS for ^{29}Si. Gas chromatographic (GC) analyses were performed on a Varian Star 3400CX with a DB-5 fused silica capillary column (30 m × 0.15 nm) and TCD. Mass spectra of the organic and organometallic molecular products were obtained by GC-MS analysis (Varian Saturn 2100T, equipped with a BD-5 capillary column (30 m) and an ion trap detector). Gel permeation chromatography (GPC) analyses were performed using a Waters 2414 RI detector and a set of three serially connected 7.8 × 300 mm columns (Waters Styragel HR1, HR2, and HR4; THF; flow rate 0.80 mL/min; temperature 20 °C; injection volume 10 μL). The number-average molecular weight (M_n), weight-average molecular weight (M_w), and PDI were determined by polystyrene standard calibration curves. Thin-layer chromatography (TLC) was performed on plates coated with 250 mm thick silica gel (Aldrich and Merck), and column chromatography was conducted with silica gel 60 (70e 230 mesh, Fluka). A TA Instruments TGA Q50 analyzer was used to investigate the thermal stability of the samples. The measurements were conducted in a nitrogen flow of 60 mL·min^{-1} from ambient temperature to 800 °C at a heating rate of 10 °C·min^{-1}. Measurement of the elemental composition of the samples was performed on a Flash

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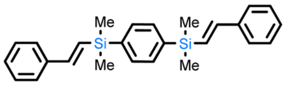
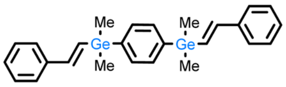
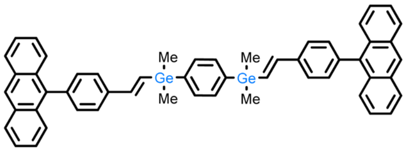
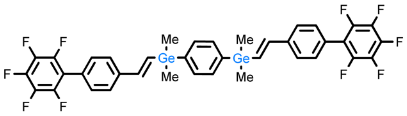
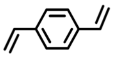
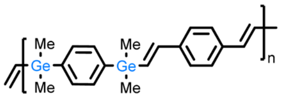
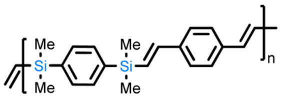
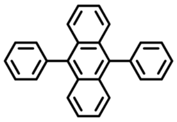
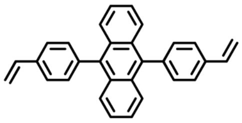
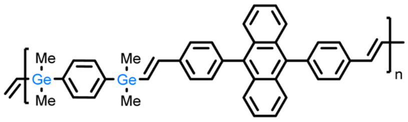
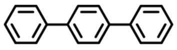
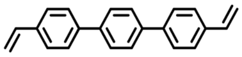
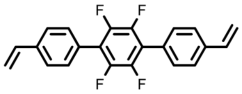
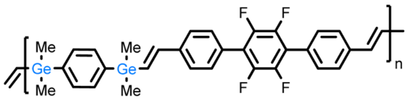
Table 4. Absorption and Emission Properties of Compounds 3−8 (in CH_2Cl_2 as Solvent)

	structure	$\lambda_{Abs,\,max}$ [nm]	$\varepsilon(\lambda)$ [$dm^3 \cdot mol^{-1} \cdot cm^{-1}$]	$\lambda_{FL,\,max}$ [nm]	φ_{fl}	τ_{FL} [ns]	E(S1) [$kJ \cdot mol^{-1}$] (λ_{0-0})
S1		261	46 700	---	---	---	---
3		259	42 000	--- [a)]	< 0.01	---	---
4		349 367 387	10 900 16 900 15 600	412 430[b)]	0.49	3.3	301 (397 nm)
5		278	38 600	354[c)]	< 0.01	---	---
S2		280	n.d.	333[d)]	0.12	1.5	386 (310 nm)
6		298	22 900	349[d)]	0.030	< 600 ps	368 (325 nm)
S3		301	27 900	354[d)]	0.032	< 600 ps	365 (328 nm)
S4		395 374 356 261	n.d.	412 432[b)]	0.91	7.69	298 (401 nm)
S5		396 376 358 262	11 100 11 400 7 100 86 900	428[b)]	0.52	3.52	292 (409 nm)
7		398 377 259 263	10 800 11 500 7 400 98 300	436[b)]	0.45	2.7 (~ 70%) 5.6 (~ 30%)	290 (412 nm)
S6		n.d.	n.d.	n.d.	0.93	950 ps	
S7		312	44 900	363 380[d)]	0.83	870 ps	346 (346 nm)
S8		289	42 800	360[d)]	0.79	790 ps	364 (329 nm)
8		298	43 800	377[d)]	0.57	640 ps	353 (339 nm)

[a] λ_{exc} = 260 nm. [b] λ_{exc} = 360 nm. [c] λ_{exc} = 280 nm. [d] λ_{exc} = 300 nm.

2000 elemental analyzer. Absorption spectra were recorded using a Cary 100 UV−vis spectrophotometer (at room temperature, RT). Fluorescence spectra were measured on a PerkinElmer LS-50B spectrofluorimeter (RT) and were corrected for nonlinear PMT response. Both absorption and emission spectra were recorded for argon-saturated solutions using 1 cm × 1 cm rectangular cells.

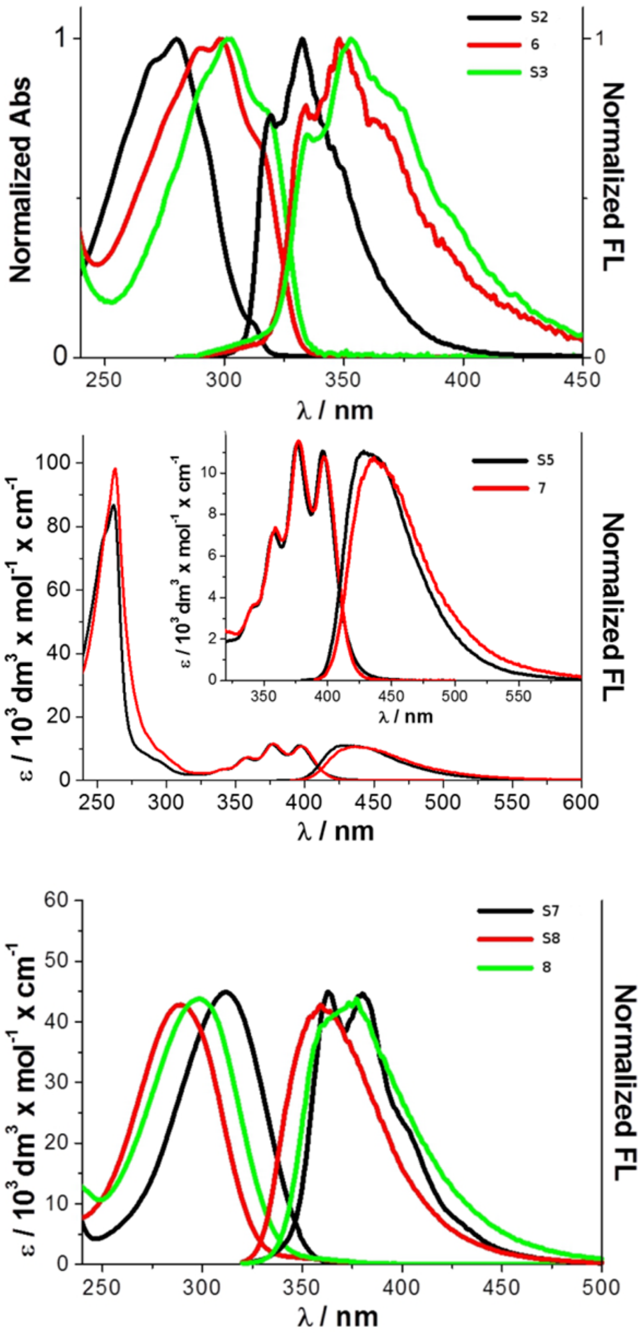
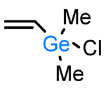


Figure 4. Absorption and emission spectra of **6**−**8** in comparison to standards (in CH_2Cl_2).

Fluorescence lifetimes were measured on a time-resolved spectrofluorimeter operating on a nanosecond scale with the detection system based on the single photon counting technique (fluorescence lifetime spectrofluorimeter FluoTime 300 from PicoQuant, equipped with 255, 300, and 375 nm diodes as its excitation sources).

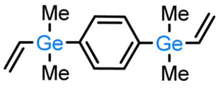
3. Syntheses of Organogermanium Compounds. *3.1. Chlorodimethylvinylgermane.* Chlorodimethylvinylgermane was synthe-



sized according to the literature.[8] A 100 mL high-pressure Schlenk vessel connected to a gas and vacuum line was charged under argon with tributylvinylstannane (15 mL, 51.32 mmol), dichlorodimethylgermane (3.36 mL, 28.8 mmol), and 1,1′-azobis(cyclohexanecarbonitrile) (1.76 g, 7.2 mmol). The mixture was frozen in a liquid nitrogen bath and subjected to freeze−pump−thaw cycling. After the mixture was warmed to RT, it was heated in an oil bath for 2 weeks at 150 °C. After the reaction was complete, the mixture was cooled to RT and transferred to a 50 mL round-bottom flask. Careful trap-to-trap distillation gave 3.6 g (75% yield) of chlorodimethylvinylgermane.

^{1}H NMR ($CDCl_3$, δ, ppm): 0.48 (s, 3H, CH_3), 5.98 (m, 3H, $-CH{=}CH_2$). ^{13}C NMR ($CDCl_3$, δ, ppm): 3.00 (CH_3), 132.50 ($={CH}-Ge$), 137.00 ($={CH_2}$). MS: *m*/*z* (rel intensity) 166 (1), 151 (100), 131 (20), 139 (22). Anal. Calcd (%) for C_4H_9ClGe: C, 29.08, H, 5.49. Found: C, 29.12, H, 5.56.

*3.2. 1,4-Bis(dimethylvinylgermyl)benzene (**1**).* A solution of 1,4-dibromobenzene (0.300 g, 1.7 mmol) in 10 mL of THF was added to

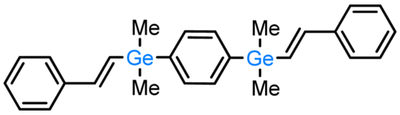


a suspension of Mg (0.09 g, 3.3 mmol, magnesium surface was activated by the use of 1,2-dibromoethane, 0.1 mL) and chlorodimethylvinylgermane (0.495 g, 3 mmol) in 10 mL of THF (the mixture was warmed). After the addition was completed, the reaction mixture was refluxed and the reaction progress was controlled by GC analysis. After the full conversion of 1,4-dibromobenzene, the mixture was cooled to RT and the solvent was evaporated. The crude product was extracted with hexane/water solvents. The organic layer was dried under magnesium sulfate and filtered off. The solvent was evaporated, and the residue was separated on a silica gel column (hexane, R_f = 0.45). The product was obtained as a colorless liquid (yield 75%). ^{1}H NMR ($CDCl_3$, δ, ppm): 0.46 (s, 12H, $-CH_3$), 5.69 (dd, 2H, J_{HH} = 20.1, 3.0 Hz, $-CH{=}CH_2$), 6.05 (d, 2H, J_{HH} = 13.5, 3.1 Hz, $-CH{=}CH_2$), 6.77 (dd, 2H, J_{HH} = 13.4, 20.1 Hz, $-CH{=}CH_2$), 7.47 (s, 4H, $-C_6H_4-$). ^{13}C NMR ($CDCl_3$, δ, ppm): −3.5 ($-CH_3$), 130.9 ($-CH{=}CH_2$), 133 ($-C_6H_4-$), 138.6 (C_i), 140.79 ($-CH{=}CH_2$). MS (EI): *m*/*z* (rel intensity, %) ($M^{+\bullet}$) 335 (1), 321 (68), 295 (13), 279 (7), 265 (4), 251 (5), 235 (4), 219 (14), 207 (100), 191 (13), 177 (15), 165 (18), 151 (27), 127 (17), 105 (15), 89 (21), 74 (6), 51 (5). Anal. Calcd (%) for $C_{14}H_{22}Ge_2$: C, 50.10; H, 6.61. Found: C, 50.18 ; H, 6.64.

4. General Procedure for Catalytic Examination. In a typical test, the syntheses were carried out in dried and evacuated (vacuum/argon) 5 mL glass ampules equipped with a magnetic stirring bar, under an argon atmosphere. Ruthenium catalyst and olefins were dissolved in dried and degassed toluene. Then, 1,4-bis(dimethylvinylgermyl)benzene was added. The ampule was heated for 24 h at 80, 100, 120, and 140 °C. Concentrations of solutions ranged from 0.125 to 1 mol·dm^{-3}, 1,4-bis(dimethylvinylgermyl)benzene and olefin were added in the molar ratio [ViGe]:[olefin] = 1:2, the catalyst content was 1−2% mol (per germane). The progress of germylative coupling was monitored by GC-MS or ^{1}H NMR analyses (oligomers).

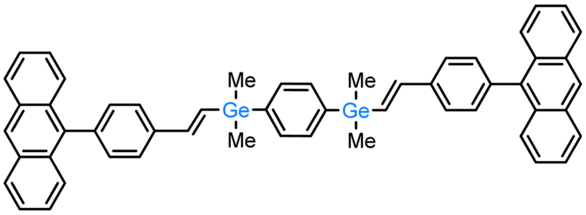
5. General Procedure for Germylative Coupling Condensation. All the reagents and solvents were dried and deoxygenated. The syntheses were carried out under argon using standard Schlenk techniques. $[RuHClCO(PCy_3)_2]$ was used as a catalyst. A mixture of reagents was placed in a 25 mL glass reactor equipped with a magnetic stirring bar and heated for 24 h (molecular products) or 72 h (oligomers) at 140 °C. The concentration of the solutions was 0.125 mol·dm^{-3}; monomers and olefins were added in the molar ratio [monomer]:[olefin] = 1:2.5 (for molecular products) and 1:1 (for macromolecular products); the catalyst loading was 2% mol (per monomer). After the reaction was complete, the solvent was evaporated under a vacuum. The molecular products were purified on a silica gel column (hexane/CH_2Cl_2 = 1:1). The oligomers were dissolved in THF and purified by repeated precipitation from methanol, filtered, and dried. Yields ranged from 83% to 95% for molecular derivatives and 65−77% for macromolecular compounds.

6. Analytical Data of Isolated Products. *6.1. 1,4-Bis{((E)-2-phenylethenyl)dimethylgermyl}benzene (**3**).* ^{1}H NMR ($CDCl_3$, δ,

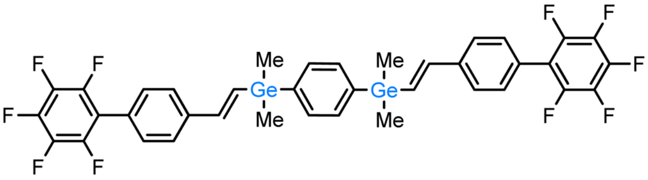


ppm): 0.57 (s, 12H, −C*H*$_3$), 6.76 (d, 2H, J_{HH} = 18.8, Ge−CH=C*H*-C<), 6.92 (d, 2H, J_{HH} = 18.8, Ge−C*H*=CH−C<), 7.28 (t, 2H, *p*-C_6H_5), 7.35 (t, 4H, *m*-C_6H_5), 7.46 (t, 4H, *o*-C_6H_5), 7.56 (s, 4H, Ge−C_6H_4−Ge). ^{13}C NMR ($CDCl_3$, δ, ppm): −3.07 (CH_3), 126.36 (Ge−CH=CH−C<), 127.95 (*p*-C from C_6H_5), 128.52 (*m*-C from C_6H_5), 128.55 (*o*-C from C_6H_5), 133.15 (CH from Ge−C_6H_4−Ge), 138.02 (C_i), 141.02 (C_i), 143.70 (Ge−CH=CH−C<). MS (EI): *m*/*z* (rel intensity, %) ($M^{+\bullet}$) 488 (6), 471 (31), 369 (44), 283 (49), 267 (21), 206 (69), 191 (100), 179 (48), 165 (33), 147 (46), 117 (34), 105 (93), 87 (77), 73 (39). Anal. Calcd (%) for $C_{26}H_{30}Ge_2$: C, 64.02; H, 6.20. Found: C, 64.09 ; H, 6.26.

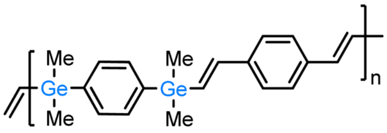
*6.2. 1,4-Bis(((E)-4-(anthracen-9-yl)styryl)dimethylgermyl)benzene (**4**).* ^{1}H NMR ($CDCl_3$, δ, ppm): 0.63 (s, 12H, −C*H*$_3$), 6.93 (d, 2H, J_{HH} = 18.9, Ge−CH=C*H*-C<), 7.09 (d, 2H, J_{HH} = 18.9, Ge−C*H*=CH−C<), 7.32−7.48 (m, 12H, H_3 from −C_6H_4−, H_2 and H_3 from −$C_{14}H_9$), 7.63 (s, 4H, Ge−C_6H_5−Ge), 7.66−7.70 (m, 8H, H_2 from −C_6H_4− and H_1 from −$C_{14}H_9$), 8.05 (d, 4H, J_{HH} = 8.4, H_4 from −$C_{14}H_9$), 8.50 (s, 2H, H_{10} from −$C_{14}H_9$). ^{13}C NMR ($CDCl_3$, δ, ppm): −3.02 (CH_3), 125.10, 125.35, 126.34 (Ge−CH=CH−C<), 126.76, 128.33, 128.41, 130.13 (CH from −C_6H_4−), 130.17, 131.32, 131.53, 133.21 (CH from Ge−C_6H_4−Ge), 136.67, 136.71, 137.19 (C_i), 138.49 (C_i), 143.40 (Ge−CH=CH−C<). MS (EI): *m*/*z* (rel intensity, %) ($M^{+\bullet}$) 840 (5), 739 (2), 723 (2), 634 (24), 459 (13), 367 (37), 352 (23), 280 (100), 251 (38), 209 (10), 181 (38), 165 (19), 151 (20), 126 (13), 105 (44), 89 (22). Anal. Calcd (%) for $C_{54}H_{46}Ge_2$: C, 77.19; H, 5.52. Found: C, 77.15; H, 5.57.



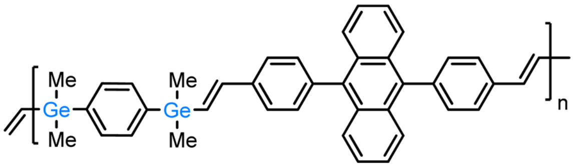
*6.3. 1,4-Bis(dimethyl((E)-2-(2′,3′,4′,5′,6′-pentafluoro-[1,1′-biphenyl]-4-yl)vinyl)germyl)benzene (**5**).* ^{1}H NMR ($CDCl_3$, δ, ppm): 0.58 (s, 12H, −C*H*$_3$), 6.89 (d, 2H, J_{HH} = 18.8, Ge−CH=C*H*−C<), 6.91 (d, 2H, J_{HH} = 19.0, Ge−C*H*=CH−C<), 7.40 (d, 4H, −C_6H_4−), 7.55 (m, 8H, −C_6H_4− and Ge−C_6H_4−Ge). ^{13}C NMR ($CDCl_3$, without −C_6F_5, δ, ppm): −3.16 (CH_3), 126.54 (Ge−CH=CH−C<), 130.33 (CH from −C_6H_4−), 130.79 (C_i), 133.14 (CH from Ge−C_6H_4−Ge), 138.83 (C_i), 140.80 (C_i), 142.64 (Ge−CH=CH-C<). MS (EI): *m*/*z* (rel intensity, %) ($M^{+\bullet}$) 820 (1), 805 (3), 703 (10), 614 (8), 537 (6), 474 (4), 449 (93), 431 (10), 419 (7), 396 (7), 373 (74), 357 (67), 345 (7). 317 (11), 270 (14), 204 (100), 181 (22), 151 (27), 127 (12), 115 (10), 105 (80), 87 (30), 73 (6). Anal. Calcd (%) for $C_{38}H_{28}F_{10}Ge_2$: C, 55.67; H, 3.44. Found: C, 55.61; H, 3.48.



*6.4. Poly[dimethylgermylene-1,4-phenylenedimethylgermylene-(E)-vinylene-1,4-phenylene-(E)-vinylene] (**6**).* ^{1}H NMR ($CDCl_3$, δ, ppm): 0.55 (s, 12H, −C*H*$_3$), 5.25 (d, traces, C−CH=C*H*$_2$), 5.76 (d, traces, C−CH=C*H*$_2$), 6.74 (d, traces, C−C*H*=CH$_2$), 6.74 (d, 2H, J_{HH} = 18.8, Ge−CH=C*H*−C<), 6.88 (d, 2H, J_{HH} = 18.8, Ge−C*H*=CH−C<), 7.39 (s, 4H, −C_6H_4−), 7.54 (s, 4H, Ge−C_6H_4−Ge). ^{13}C NMR ($CDCl_3$, δ, ppm): −3.08 (CH_3), 126.42 (Ge−CH=CH−C<), 126.55 (CH from C−C_6H_4−C), 128.65 (traces, −CH=CH_2), 132.94 (traces, −CH=CH_2), 133.14 (CH from Ge−C_6H_4−Ge), 137.59 (C_i), 140.99 (C_i), 143.23 (Ge−CH=CH−C<). GPC analysis (**6a**): M_w = 4027 [g·mol^{-1}], M_n = 2275 [g·mol^{-1}], PDI (M_w/M_n) = 1.77, *n* = 6. GPC analysis (**6b**): M_w = 5679 [g·mol^{-1}], M_n = 2863 [g·mol^{-1}], PDI(M_w/M_n) = 1.99, *n* = 7.

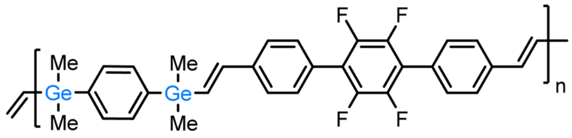


*6.5. Poly[dimethylgermylene-1,4-phenylenedimethylgermylene-(E)-vinylene-9,10-bis(4-phenyl)anthracenylene, (E)-vinylene] (**7**).*



^{1}H NMR ($CDCl_3$, δ, ppm): 0.65 (s, 12H, −C*H*$_3$), 5.39 (d, traces, C−CH=C*H*$_2$), 5.94 (d, traces, C−CH=C*H*$_2$), 6.91 (d, traces, C−C*H*=CH$_2$), 6.95 (d, 2H, J_{HH} = 18.8, Ge−CH=C*H*−C<), 7.11 (d, 2H, J_{HH} = 18.8, Ge−C*H*=CH−C<), 7.29−7.51 (m, 8H, H_3 from −C_6H_4− and H_2 from −$C_{14}H_8$), 7.65 (s, 4H, Ge−C_6H_5−Ge), 7.59−7.71 (m, 8H, H_2 from −C_6H_4− and H_1 from −$C_{14}H_8$) ^{13}C NMR ($CDCl_3$, δ, ppm): −3.06 (CH_3), 125.02, 126.37 (Ge−CH=CH−C<), 126.90, 129.78 (CH from C−C_6H_4−C), 131.55 (CH from C−C_6H_4−C), 133.11, 133.20 (CH from Ge−C_6H_4−Ge), 136.80, 137.17 (C_i), 138.74 (C_i), 143.38 (Ge−CH=CH−C<). GPC analysis (**7a**): M_w = 4461 [g·mol^{-1}], M_n = 2343 [g·mol^{-1}], PDI (M_w/M_n) = 1.90, *n* = 3. GPC analysis (**7b**): M_w = 5150 [g·mol^{-1}], M_n = 25875 [g·mol^{-1}], PDI(M_w/M_n) = 1.90, *n* = 4.

*6.6. Poly[dimethylgermylene-1,4-phenylenedimethylgermylene-(E)-vinylene-1,4-(2,3,5,6-tetrafluoro)bis(4′-phenyl)phenylene, (E)-vinylene] (**8**).* ^{1}H NMR ($CDCl_3$, δ, ppm): 0.59 (s, 12H, −C*H*$_3$), 5.37 (d, traces, C−CH=C*H*$_2$), 5.87 (d, traces, C−CH=C*H*$_2$), 6.77 (d, traces, C−C*H*=CH$_2$), 6.87 (d, 2H, J_{HH} = 18.8, Ge−CH=C*H*−C<), 6.97 (d, 2H, J_{HH} = 19.0, Ge−C*H*=CH−C<), 7.47 (m, 8H, −C_6H_4−), 7.57 (s, 4H, Ge−C_6H_4−Ge). ^{13}C NMR ($CDCl_3$, without C_6F_4 δ, ppm): −3.11 (CH_3), 126.41 (Ge−CH=CH−C<), 126.50 (CH from C−C_6H_4−C), 130.42 (CH from C−C_6H_4−C), 133.19 (CH from Ge−C_6H_4−Ge), 134.56 (C_i), 138.71 (C_i), 140.89 (C_i), 142.85 (Ge−CH=CH−C<). GPC analysis (**8a**): M_w = 4160 [g·mol^{-1}], M_n = 2681 [g·mol^{-1}], PDI(M_w/M_n) = 1.55, *n* = 4. GPC analysis (**8b**): M_w = 5431 [g·mol^{-1}], M_n = 3128 [g·mol^{-1}], PDI(M_w/M_n) = 1.70, *n* = 5.



■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00336.

Synthesis procedures for **S1** and **S2**; NMR spectra of new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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