EnhancementofNear-infraredEmissionBasedonHypervalentGermanium(IV)-Fused Azobenzene Compounds with Electron-donating Groups

Masayuki Gon, Misao Yaegashi, Kazuo Tanaka*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

E-mail: tanaka@poly.synchem.kyoto-u.ac.jp



Kazuo Tanaka

Kazuo Tanaka received his Ph.D. degree in 2004 from Kyoto University, and worked in Stanford University, USA, Kyoto University, and RIKEN as a postdoctoral fellow. In 2007, he has moved to the Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, and in 2018, he was promoted to Professor. His research projects especially focus on design of new functional materials relating optics and nanotechnology based on the heteroatom-containing conjugated polymers and organic-inorganic polymer hybrids.

Abstract

NIR-light emitting materials are significant for the source of NIR-light technology. Previously, we have found that hypervalent germanium-fused azobenzene (GAz) compounds showed NIR emissions despite the small π -conjugated systems owing to trigonal bipyramidal geometry with three-center four-electron (3c-4e) bonds. Herein, we succeed in enhancing properties luminescence by their introduction of electron-donating groups. It is revealed that the frontier molecular orbitals of the π -conjugated systems with the hypervalent bonds can be varied depending on the type of substituents. As a result, the GAz compound with diphenylamine groups shows efficient NIR emission at room temperature ($\lambda_{PL} = 761$ nm and $\Phi_{PL} = 0.07$) and at 77 K ($\lambda_{PL} =$ 749 nm and $\Phi_{PL} = 0.20$). Furthermore, the data from theoretical calculations can support the experimental results and provide additional information on the producibility of the hypervalent compounds. Our findings afford strategies to expand the library of the fine-tunable NIR-luminescent materials involving heteroatoms.

Keywords: Germanium, Hypervalent compound, Near-infrared emission

1. Introduction

The NIR-luminescent materials have still attracted attention for realizing next generation technology, such as security sensors, bio-imaging probes, and optical communications owing to unique physical properties of NIR light, such as invisibility to human eyes, good biotissue permeability, and low light scattering property.1 Because of versatility, designability, and intense luminescence properties, π -conjugated organic molecules are regarded as a suitable platform for creating NIR-light emitting materials.² Although a largely expanded π -surface having a narrow energy gap is necessary to provide NIR emission, it often restricts diversity of a chemical modification to tune the optical properties and solubility. Thus, construction of small π -conjugated scaffolds showing NIR emission is strongly required.

Introduction of heteroatoms into carbon-based π -conjugated backbones to create "element-blocks",³ which are defined as a functional unit composed of heteroatoms, is effective for controlling energy levels of the frontier molecular orbitals (FMOs).⁴ We have recently proposed that the replacement of the structural carbon with nitrogen at "the

isolated FMOs" in which only one of the FMOs is located on the skeletal carbon in π -conjugated systems can selectively lower the energy level of the highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO).5 From this standpoint, azobenzene (Ph-N=N-Ph) is the effective example having the low-lying LUMO followed by the narrow energy gap created by the nitrogen substitution at the isolated LUMO in the azomethine structure.⁶ One the other hand, azobenzene is also famous for a non-luminescent skeleton due to fast internal conversion accompanied by cis-trans photoisomerization and its forbidden HOMO-LUMO $(n-\pi^*)$ transition.⁷ It has been proposed that heteroatom coordination to nitrogen to form ring-fused structure can suppress the photoisomerization and convert the HOMO-LUMO transition into allowed π - π * transition.⁸ This means azobenzene can be used as a stable π -conjugated scaffold with the narrow energy gaps.

developed heteroatom-fused Recently, we have azobenzene structures with tridentate ligands to create stable NIR-luminescent materials.9 For instance, it has been disclosed that low LUMO energy levels of boron-fused azobenzene (BAz) complexes can be used as a strong acceptor, and the resulted donor-acceptor π -conjugated system provided highly efficient NIR emission.¹⁰ More recently, further narrower energy gaps have been accomplished by using hypervalent bonds¹¹ with heavy group 14 elements such as tin¹² and germanium¹³ and heavy group 15 elements such as bismuth¹⁴. The asymmetric chemical bonds composed of the sp^2 hybrid orbital at equatorial positions and the three-center four-electron (3c-4e) bond at apical positions contributed to simultaneous increase in HOMO and decrease in LUMO energy levels. In particular, the germanium-fused azobenzene (GAz) compounds showed narrower energy gap with NIR emission than tin-fused azobenzene (TAz) ones because the trigonality of GAz ones was larger than those of TAz ones due to their atom sizes.¹² Although most germanium compounds were constructed by the bidentate ligands¹⁵ and some hypervalent germanium compounds were also reported16, we expect that our molecular design is suitable for creating NIR-light emitting materials and can bring out further potentials of germanium.

We have found that the absolute photoluminescence quantum efficiency (Φ_{PL}) of the GAz compound was improved by preparing the π -conjugated polymer, meanwhile those of the small GAz compounds were still not high.¹² Herein, we report the substitution effects of the GAz compounds. We found that introduction of electron-donating groups can effectively

Scheme 1. Synthesis of Ge-fused azobenzene compounds, GAzPh-Br, GAzPh-tBu, GAzPh-Th, and GAzPh-NPh2 with a name of substitution positions, and structure of GAziPr-Br.



enhance the optical properties, such as a molar extinction coefficient (ε), the Φ_{PL} even with bathochromic-shifted absorption and emission wavelengths in the NIR region. Finally, the π -conjugated systems with hypervalent bonds can be used as versatile and compact units with narrow energy gaps. According to the mechanistic studies and theoretical calculations, the roles of substituents are illustrated.

2. Results and Discussion 2.1 Synthesis

The synthetic procedures of GAz compounds are shown in Scheme 1. To evaluate substituent effects, we designed the series of 4,4'-modified compounds having bromine groups for extending π -conjugated system through lone pairs, *tert*-butyl groups as a weak electron-donor through hyperconjugation, thienyl groups as a planar electron-donating aromatic ring, and diphenylamine groups as a strong electron-donor. First, the four types of azobenzene tridentate ligands were synthesized. LAz-Br was prepared according to our previous literature.^{10a} LAz-tBu was obtained from 3-tert-butylphenol (1) in 5 steps in 12% total isolated yield. The less-hindered hydroxy group at the ortho position in 1 was selectively nitrated to yield 2. The hydroxy group in 2 was protected by methylation with dimethyl sulfate under basic condition. Subsequently, the nitro group was reduced to an amine group with iron powder in the presence of ammonium chloride to afford 4. Next, oxidative coupling reaction with manganese dioxide was carried out to convert an amine group into an azo group. Finally, the methyl groups were quantitatively removed by boron tribromide to gain LAz-tBu. Thienyl and diphenylamine groups in LAz-Th and LAz-NPh2 were introduced into 6 with palladium-catalyzed cross-coupling reactions, respectively. Then, similarly to the previous method, the methyl groups were eliminated by BBr3 to afford LAz-Th and LAz-NPh2. Hypervalent GAz compounds (GAzPh-Br, GAzPh-tBu, GAzPh-Th, and GAzPh-NPh2) were obtained from the condensation reaction with each corresponding tridentate ligand and commercially available diphenyldichlorogermane in the presence of triethylamine to trap generated hydrogen chloride. To obtain information on the substituent effect at germanium, we provided the structure and spectroscopic data of the GAz compound with isopropyl groups (GAziPr-Br) according to our previous report.13 All the synthesized compounds were characterized by ¹H and ¹³C{¹H} NMR spectroscopy and high-resolution mass spectrometry (HRMS) (the data are shown in the Supporting Information). According to these characterization data, we concluded that the products should have the designed structures and enough purity for further analyses.

2.2 Crystal structure

Figure 1 shows the ORTEP drawings of GAz derivatives obtained from the analysis with single crystal X-ray diffraction (SC-XRD). The structures except for **GAzPh-tBu** are disordered and the major ones are shown here.^{12a,13} Detail crystallographic data are listed in Figures S1–S4 and Tables S1–S4. Additionally, information on the selected bond lengths, angles and dihedral angles is listed in Table S5. Accordingly, it was found that all synthesized GAz derivatives had five-coordinated germanium centers with distorted trigonal bipyramidal geometry due to their tight tridentate ligands (Figure 1). These data indicate that hypervalent germanium should be realized with the ligands. The similar distorted structures were also observed in previous works on the



Figure 1. ORTEP drawings of (A) GAzPh-Br, GAzPh-tBu, GAzPh-Th, and GAzPh-NPh2 (50% probability for thermal ellipsoids). The minor structures of GAzPh-Br, GAzPh-Th, and GAzPh-NPh2 and hydrogen atoms are omitted to clarify. Detail crystallographic data are shown in the Supplementary Information.

halogenated GAz compounds including GAziPr-Br13 and the TAz ones.^{12,17} The bond lengths of the GAz derivatives between N(1) and N(2) were 1.27~1.30 Å, indicating that a nitrogen double bond should be formed between these nitrogen atoms.18 The phenyl groups at germanium shorten the N(1)-Ge(1) bond lengths (2.02~2.07 Å) compared to the isopropyl groups (2.11 Å). It should be emphasized that the strong coordination bonds should be formed because the bond lengths are between the covalent ($\Sigma r_{cov}(N, Ge)$ 1.92 Å)¹⁹ and van der Waals radii ($\Sigma r_{vdW}(N, Ge)$ 3.66 Å)²⁰. Furthermore, the average bond lengths of O(1)-Ge(1) and O(2)-Ge(2) were 1.92~1.94 Å. Since these values were longer than covalent radii $(\Sigma r_{cov}(O, Ge) 1.84 \text{ Å})$ ¹⁹ the bond type can be categorized as a 3c-4e bond.¹⁴ In GAzPh-Th and GAzPh-NPh2, the differences of their bond lengths were large due to the disordered structures. The angles of O(1)-Ge(1)-O(2) and sums of angles between equatorial atoms were 165.8° and 358.6° for GAziPr-Br, 167.2° and 359.1° for GAzPh-Br, 164.9° and 360.0° for GAzPh-tBu, 161.7° and 359.0° for GAzPh-Th and 163.2° and 358.6° for GAzPh-NPh2, indicating that the structures are categorized as distorted trigonal bipyramidal geometry.12a,13 values The absolute of dihedral angles of C(1)–N(1)–N(2)–C(7) were 179.6° for GAziPr-Br, 177.8° for GAzPh-Br, 176.2° for GAzPh-tBu, 176.5° for GAzPh-Th and 172.9° for GAzPh-NPh2, implying that the π -conjugated system of azobenzene had highly planar structures and bulky substituents partially distorted the planarity. Although GAziPr-Br and GAzPh-Br had no major structural differences, the bulky and electron-donating isopropyl groups seemed to produce a slight variation. From these data, we confirmed that the five-coordinated hypervalent GAz compounds with distorted trigonal bipyramidal geometry can be obtained regardless of the substituents.

2.3 Optical Properties

We initially performed UV–vis absorption measurements in CHCl₃ (1.0×10^{-5} M) to investigate electronic properties of the GAz derivatives in the ground state (Figure 2 and Table 1). All the GAz derivatives showed strong absorption bands in the visible to NIR region (500~750 nm) (Figure 2A). Especially, by introducing electron-donating units, the maximum absorption wavelength (λ_{abs}) was shifted to the longer wavelength region. It is implied that hypervalent germanium might work as an electron-acceptor. Moreover, by changing the substituents at germanium from the phenyl group to isopropyl one, λ_{abs} was shifted to the long wavelength region. These tendencies will be discussed later with the calculation data. From these results, it



Figure 2. (A) UV–vis absorption and (B) PL spectra at room temperature in CHCl₃ $(1.0 \times 10^{-5} \text{ M})$ (C) at 77 K in 2Me-THF $(1.0 \times 10^{-5} \text{ M})$ of **GAzPh-Br**, **GAzPh-tBu**, **GAzPh-Th**, and **GAzPh-NPh2**, excited at wavelengths of absorption maxima.

can be said that the electronic properties of the π -conjugated system in the ground state can be modulated by the substituents not only in the ligand but also at germanium.

Next, photoluminescence (PL) properties followed by electronic structures in the excited state were investigated (Figure 2 and Table 1). It should be noted that all the GAz derivatives exhibited NIR emission (Figure 2B), and the $\Phi_{\rm PL}$ was enhanced to be 0.07 (GAzPh-NPh2) with diphenylamine groups. In particular, increases in their ε , bathochromic shifts of λ_{abs} and decreases in the Stokes shift (v) were observed by introducing strong electron-donating groups, such as thienyl (GAzPh-Th) and diphenylamine groups (GAzPh-NPh2). These data mean that the electron-donating substituents and extension of π -conjugation can induce favorable effects for NIR emission, such as narrowing the energy gap between FMOs, enhancing transition probability and suppressing structural relaxation. The solvent effects evaluated by Lippert-Mataga plots proved that the GAz derivatives formed moderate donor-acceptor interactions and the strongest effect was observed in GAzPh-NPh2 (Figure S5). Therefore, the optical properties were originated from their intramolecular charge transfer (ICT) states. All the GAz derivatives showed larger Φ_{PL} at 77 K in 2-methyl tetrahydrofuran (2Me-THF) where molecular motions should be frozen (Figure 2C). It is suggested that molecular motions should play a critical role in emission annihilation. Indeed, the λ_{abs} of GAzPh-tBu was similar to GAzPh-Br, whereas GAzPh-tBu show weak emission. It is probably because rotation of tert-butyl groups could promote the non-radiative deactivation. Comparing to emission properties between GAzPh-Br and GAziPr-Br, larger Stokes shift was observed from GAzPh-Br. The rotation of nonconjugated phenyl rings might promote structural relaxation in the excited state.

To gather deeper information on emission mechanisms, kinetic parameters, such as a radiative rate constant (k_r) and a non-radiative rate constant (k_{nr}), were calculated from the PL lifetime measurements (Figure S6). All the GAz derivatives showed relatively large k_{nr} (~10⁹ s⁻¹) in solution, while the values of Φ_{PL} were dramatically enhanced corresponding to the decreases in those of k_{nr} (~10⁸ s⁻¹) at 77 K. These data

Table 1. Spectroscopic data of GAz derivatives.

	Temp.	λ_{abs} /nm (ε /M ⁻¹ cm ⁻¹)	$\lambda_{\mathrm{PL}}{}^{b}/\mathrm{nm}$	<i>v^c</i> /cm ⁻¹	${{{{\varPhi}}_{{ m{PL}}}}^{b,d}}$	$ au_{\mathrm{av}}{}^{b,e}/\mathrm{ns}$	$k r^{f} / 10^{8} s^{-1}$	$k_{ m nr}^f / 10^8 \ { m s}^{-1}$
GAziPr-Br ^h	r.t. ^a	587 (22,000)	712	3000	0.04	0.59	0.71	16
	77 K ^g	i	679	i	0.16	1.8	0.89	4.7
GA7Ph-Br	r.t. ^a	570 (21,500)	715	3600	0.03	0.37	0.81	26
-	77 K ^g	<i>i</i>	684	i	0.24	2.7	0.90	2.9
GA7Ph-tRu	r.t. ^a	572 (15,800)	726	3700	< 0.01	i	_i	_i
	77 K ^g	_i	683	i	0.10	1.4	0.72	6.5
GAzPh-Th	r.t. ^a	614 (40,200)	728	2600	0.04	0.46	0.87	21
	77 K ^g	<i>i</i>	699	i	0.24	1.7	1.4	4.4
GAzPh-NPh2	r.t. ^a	649 (53,000)	761	2300	0.07	0.59	1.2	16
	77 K ^g	i	749	i	0.20	0.88	2.3	9.1

^{*a*} In CHCl₃ (1.0×10⁻⁵ M). ^{*b*} Excited at λ_{abs} . ^{*c*} Stokes shift (ν) = 1/(λ_{abs} ×10⁻⁷) – 1/(λ_{PL} ×10⁻⁷). ^{*d*} Determined as an absolute value. ^{*e*} PL lifetime monitored at λ_{PL} , excited at 532 nm. ^{*f*} $k_r = \Phi_{PL}/\tau_{av}$, $k_{nr} = (1 - \Phi_{PL})/\tau_{av}$, $\tau_{av} = \Sigma \alpha_i \tau_i$. α : relative amplitude (see Supporting Information). ^{*g*} In 2Me-THF (1.0×10⁻⁵ M). ^{*h*} From ref. 12. ^{*i*} Not detected.

Table 2. Electrochemical data of GAz derivatives.

GAziPr-Br ^{<i>a</i>} +0.85 -1.10	-5.65	-3.70
GAzPh-Br +0.93 -0.97	-5.73	-3.83
GAzPh-tBu +0.70 -1.19	-5.50	-3.61
GAzPh-Th +0.65 -1.05	-5.45	-3.75
GAzPh-NPh2 +0.10 -1.31	-4.90	-3.49

^{*a*} From ref. 12. ^{*b*} E_{HOMO} /eV = -4.8 - $E_{\text{onset}}^{\text{ox}}$ /V, E_{LUMO} /eV = -4.8 - $E_{\text{onset}}^{\text{red}}$ /V.

correspond to the speculation that structural relaxation in the excited state should be crucially responsible for emission annihilation. The largest k_r was obtained from **GAzPh-NPh2** (~10⁸ s⁻¹) of the other compounds (~10⁷ s⁻¹). The Stokes shift of **GAzPh-NPh2** was smaller than those of others, and therefore structural relaxation in the excited state should be suppressed. Consequently, the radiation channel can be opened.

2.4 Cyclic Voltammetry

To estimate energy diagrams, we calculated the FMO energy levels with cyclic voltammetry (CV). The HOMO and LUMO energy levels (E_{HOMO} and E_{LUMO}) were estimated from the onset potentials of oxidation and reduction (E_{onset}^{ox} and E_{onset}^{red}) curves in voltammograms, respectively (Figure S7 and Table 2).²¹ It was found that the electron-donating groups drastically increased E_{HOMOS} , and extension of π -conjugation also had a potential to decrease E_{LUMOS} . By these effects, the narrow energy gaps of **GAzPh-Th** and **GAzPh-NPh2** should be realized. Owing to the strongest electron-donating ability of diphenylamine groups among the other substituents, the largest increase in E_{HOMO} could be induced. It was revealed that the hypsochromic shift of λ_{abs} in **GAzPh-Br** should be attributed to larger decrease in the E_{LUMO} than in the E_{HOMO} . On the other hand, *tert*-butyl groups in **GAzPh-tBu** equally increased both E_{HOMO} and E_{LUMO} from **GAzPh-Br**, and as a result those energy gaps were almost the same. Compared with **GAzPh-Br** and **GAziPr-Br**, the phenyl groups reduced both E_{HOMO} and E_{LUMO} . Correspondingly, it is because the electron-donating ability of phenyl groups was weaker than that of isopropyl groups. Those results suggest that substituent effects can be observed not only in the ligand but also at germanium.

2.5 Theoretical calculation

density functional theory Finally, (DFT) and time-dependent (TD)-DFT calculations were executed to obtain further insight of optical properties of the GAz derivatives (Figures 3 and S11-S13). Similarly to the results of SC-XRD analysis, the optimized structures of the GAz derivatives had the distorted trigonal bipyramidal geometry (Figure 3A). The HOMOs and LUMOs were delocalized throughout the π -conjugated systems of azobenzene including the substituents at 4,4' positions. The tendency of the energy levels of FMOs (Figure 3B) and the $S_0 \rightarrow S_1$ ($\pi - \pi^*$) transition energy (Figure 3C) showed good agreements with the experimental results. The contribution of 3c-4e bonds in hypervalent compounds can be visualized by theoretical calculation.^{12-14,22} In the GAz derivatives, the related MOs were found in the list of MOs obtained from the calculation (Figures S8A-S12A). For instance, the bonding, non-bonding, and anti-bonding orbitals in the 3c-4e bond of GAzPh-Br were assigned to be HOMO-14, HOMO-7, and LUMO+19, respectively (Figure S9A). Therefore, it can be said that the GAz derivatives should show the features of hypervalent compounds originating from the asymmetric chemical bonds composed of sp^2 hybrid orbitals and 3c-4e bonds around germanium. In addition, a natural bond orbital (NBO) calculation provided information on the strength of donor-acceptor interaction between an NBO donor and an acceptor as the second-order perturbation stabilization energy (E⁽²⁾) (Figures S8B-S12B).^{12-14,23}



Figure 3. Calculation results of GAz derivatives. (A) Selected Kohn–Sham orbitals (isovalue = 0.02). (B) Energy diagrams of HOMO (H) and LUMO (L). (C) Oscillator strength (*f*), transition energy of $S_0 \rightarrow S_1$ (H \rightarrow L) transition from the optimized ground state. Calculation details are shown in the Supplemental Information.

the Regarding interaction around germanium, the $LP(O1) \rightarrow LP^*(Ge1)$ ($E^{(2)}$ = 81.83 kcal mol⁻¹) and $LP(O2) \rightarrow LP^*(Ge1)$ ($E^{(2)} = 79.64$ kcal mol⁻¹) in GAzPh-Br were stronger than those in **GAzPh-iPr** ($E^{(2)} = 77.57$ and 73.44 kcal mol⁻¹, respectively), whereas the LP(N1) \rightarrow LP*(Ge1) was almost the same ($E^{(2)} = 106.05$ kcal mol⁻¹ for **GAzPh-Br** and 107.34 kcal mol⁻¹ for **GAziPr-Br**). Moreover, the electron-donating groups can tend to reinforce the $LP(N1) \rightarrow LP^*(Ge1)$ ($E^{(2)}$ = 115.25 kcal mol^{-1} for GAzPh-NPh2). These results suggest that both phenyl groups at germanium and introduction of electron-donating groups increase the structural stability. Thus, the hypervalent GAz derivatives can be generated. Furthermore, the average NBO energy levels of one of the LP(O1)s and LP(O2)s which contribute to construct HOMOs and LUMOs are high (Figure S13).12,13 Therefore, the electron-donating ability of oxygen atoms should be enhanced by the 3c-4e bond.

3. Conclusion

We synthesized the series of hypervalent germanium compounds and investigated the substitution effects. Introduction of electron-donating groups can provide not only the bathochromic-shifted absorption and emission spectra but also enhancement of the luminescent properties. All the GAz compounds showed emission in the NIR region at room temperature and significantly enhanced emission at 77 K. In particular, the phenyl groups at germanium induced the shorter λ_{abs} and the larger structural relaxation in the excited state than the isopropyl ones, however the Φ_{PL} of **GAzPh-Br** was higher than that of **GAziPr-Br** at 77 K. This means the substituents at germanium also critically affect the optical properties in the NIR region. The CV revealed that the substitution at germanium or 4,4' positions affected the HOMO and LUMO energy levels. Theoretical calculations also suggest that these electronic perturbations to the π -conjugated systems are applicable for the modulation of the optical properties. In other words, the electronic properties of the π -conjugated systems and the hypervalent bonds can be synergistically controlled by the substituent effect based on preprogrammed molecular designs. Additionally, the NBO analysis provided information on stability of the hypervalent compounds and existence and contribution of 3c-4e bonds. We expect that our findings could contribute to extending the possibility of the molecular design with various heteroatom-containing π -conjugated systems.

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The authors declare no conflicts of interest

Supporting Information

Details of synthetic procedures and characterization, single crystal X-ray structure analysis (Figures S1–S4, Tables S1–S4), solvent effects evaluated by Lippert Mataga-plots (Figure S5), selected bond lengths, angles, and torsion angles (Table S5), PL lifetime decay curves (Figure S6), cyclic voltammograms (Figure S7), computational details for theoretical calculation (Figures S8–S13 and Table S6). This

material is available on https://doi.org/10.1246/bcsj.xxxxxx.

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Supporting Information

Enhancement of Near-infrared Emission Based on Hypervalent Germanium(IV)-Fused Azobenzene Compounds with Electron-donating Groups

Masayuki Gon, Misao Yaegashi, Kazuo Tanaka*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

E-mail: tanaka@poly.synchem.kyoto-u.ac.jp

Key words: germanium; azobenzene; hypervalent bond; trigonal bipyramidal geometry; near-infrared emission

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General

¹H and ¹³C{¹H} NMR spectra were recorded on JEOL AL400 and ECZ400 instruments at 400 and 100 MHz, respectively. High-resolution ${}^{13}C{}^{1}H$ NMR spectra were recorded on JEOL ECZ500R and ECZ600R instruments at 125 and 150 MHz, respectively. Samples were analyzed in CDCl₃ and DMSO- d_6 . The chemical shifts were expressed relative to Me₄Si (TMS) for ¹H and ¹³C NMR as an internal standard in CDCl₃. Analytical thin layer chromatography (TLC) was performed with silica gel 60 Merck F254 plates. Column chromatography was performed with Wakogel® C-300 silica gel. High-resolution mass (HRMS) spectrometry was performed at the Technical Support Office (Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University), and the HRMS spectra were obtained on a Thermo Fisher Scientific EXACTIVE spectrometer for electrospray ionization (ESI) and a Thermo Fisher Scientific EXACTIVE spectrometer for atmospheric pressure chemical ionization (APCI). UV-vis spectra were recorded on a SHIMADZU UV-3600 spectrophotometer, and samples were analyzed at room temperature. HORIBA JOBIN YVON Fluorolog-3 and Oxford Optistat DN2 were used for PL spectra at room temperature and 77 K. An absolute photoluminescence quantum efficiency (Φ_{PL}) was recorded on a Hamamatsu Photonics Quantaurus-QY Plus C13534-01. The PL lifetime measurement was performed on a Horiba FluoreCube spectrofluorometer system; excitation was carried out using visible diode lasers (NanoLED 532 nm). Cyclic voltammetry (CV) was conducted on a BASALS-Electrochemical-Analyzer Model 600D with a grassy carbon working electrode, a Pt counter electrode, an Ag/AgCl reference electrode, and the ferrocene/ferrocenium (Fc/Fc⁺) external reference at a scan rate of 0.1 V s⁻¹. X-ray crystallographic analysis was carried out by Rigaku Saturn 724+ with MicroMax-007HF CCD diffractometer with Varimax Mo optics using graphite-monochromated MoKa radiation. A symmetry-related absorption correction was carried out by using the program ABSCOR.1 The analysis was carried out with Yadokari-XG.² The program ORTEP3³ and Mercury-4.2.0 were used to generate the X-ray structural diagram.

Materials

Commercially available compounds used without purification: Diphenyldichlorogermane (Ph2GeCl2) (Tokyo Chemical Industry Co, Ltd.) 3-tert-Butylphenol (Tokyo Chemical Industry Co, Ltd.) Nitric acid (HNO₃) (69 wt%, 1.42 g cm⁻³) (FUJIFILM Wako Pure Chemical Corporation) Potassium carbonate (K₂CO₃) (FUJIFILM Wako Pure Chemical Corporation) Dimethyl sulfate (FUJIFILM Wako Pure Chemical Corporation) Ammonium chloride (NH₄Cl) (FUJIFILM Wako Pure Chemical Corporation) Iron (Fe), powder (FUJIFILM Wako Pure Chemical Corporation) Manganese(IV) Oxide, Powder (MnO₂) (FUJIFILM Wako Pure Chemical Corporation) Boron tribromide (17% in CH₂Cl₂, ca. 1 M) (BBr₃ in CH₂Cl₂) (Tokyo Chemical Industry Co, Ltd.) 2-Thiopheneboronic acid (Tokyo Chemical Industry Co, Ltd.) Pd₂(dba)₃ (dba = dibenzylideneacetone) (Tokyo Chemical Industry Co, Ltd.) 2-Dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos) (FUJIFILM Wako Pure Chemical Corporation) Cesium carbonate (CsCO₃) (FUJIFILM Wako Pure Chemical Corporation) Diphenylamine (Tokyo Chemical Industry Co, Ltd.) Tri-tert-butylphosphine tetrafluoroborate ('Bu₃P·HBF₄) (FUJIFILM Wako Pure Chemical Corporation)

Sodium tert-butoxide ('BuONa) (FUJIFILM Wako Pure Chemical Corporation)

Commercially available solvents:

MeOH, toluene, CHCl₃, CH₂Cl₂, acetone, hexane, ethyl acetate, acetonitrile, EtOH, AcOH were purchased from FUJIFILM Wako Pure Chemical Corporation and used without purification.

H₂O was purified by a water purifier (WEX3NUV, Yamato Scientific co., Ltd.).

THF (FUJIFILM Wako Pure Chemical Corporation) and Et_3N (Kanto Chemical Co., Inc.) were purified by passage through solvent purification columns under N_2 pressure.⁴

Compounds prepared as described in the literatures:

4,4'-Dibromo-2,2'-dihydroxyazobenzene (LAz-Br)⁵

Synthetic procedures and characterization

Synthesis of GAzPh-Br



Diphenyldichlorogermane (1.43 g cm⁻³, 66.0 μ L, 0.317 mmol, 2.0 equiv.) and then Et₃N (88.3 μ L, 0.634 mmol, 4.0 equiv.) were added to the solution of **LAz-Br** (60.0 mg, 0.158 mmol, 1.0 equiv.) in THF (20 mL). The reaction mixture was stirred at room temperature for 7 h under N₂ atmosphere, and then filtered to remove the precipitated salt. The product was purified by recrystallization from mixed solvent of hexane (poor solvent) and chloroform (good solvent) to afford **GAzPh-Br** (76.0 mg, 0.127 mmol, 80%) as a black solid.

¹H NMR (CDCl₃, 400 MHz) δ 7.93–7.90 (m, 4H), 7.52 (d, J = 8.7 Hz, 1H), 7.41–7.38 (m, 7H), 7.30–7.20 (br, 2H), 7.01 (d, J = 8.8 Hz, 1H), 6.90 (d, J = 8.2 Hz, 1H) ppm. ¹³C{¹H} NMR (CDCl₃, 150 MHz) δ 161.3, 160.0, 138.0, 135.3, 135.0, 134.9, 134.2, 133.8, 130.6, 129.6, 128.5, 125.7, 123.4, 122.3, 121.2, 118.2 ppm. HRMS (ESI) calcd. for C₂₄H₁₆Br₂GeN₂O₂ [M]⁻: 595.8784, found: 595.8789.



Chart S1. ¹H NMR spectrum of GAzPh-Br in CDCl₃, 400 MHz.



Chart S2. ¹³C{¹H} NMR spectrum of GAzPh-Br in CDCl₃, 150 MHz.

Synthesis of 2 (5-(tert-butyl)-2-nitrophenol)



Nitric acid (69 wt%, 1.42 g cm⁻³, 3.13 mL, 48.7 mmol, 1.00 equiv.) in acetic acid (20 ml) was slowly dropwised to the solution of 3-*tert*-butylphenol (**1**) (10.0 g, 66.6 mmol, 1.37 equiv.) at 0 °C. The reaction mixture was stirred at 0 °C for 1.5 h. The solution was washed with water, and organic layer was extracted with ethyl acetate. The organic layer was dried over MgSO₄. After filtration, volatile materials were removed by evaporation under reduced pressure. The product was purified by column chromatography on SiO₂ (hexane/ethyl acetate = 9/1 v/v as an eluent). Further purification was carried out by Kugelrohr distillation at 140 °C under reduced pressure to afford pure **2** (2.70 g, 13.8 mmol, 32%) as a yellow liquid.

 $R_{\rm f} = 0.60$ (hexane/ethyl acetate = 9/1 v/v). ¹H NMR (CDCl₃, 400 MHz) δ 10.61 (s, 1H), 8.02 (d, J = 8.9 Hz, 1H), 7.13 (d, J = 2.1 Hz, 1H), 7.01 (dd, J = 8.9, 1.8 Hz, 1H), 1.33 (s, 9H) ppm. ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 162.6, 155.0, 131.3, 124.6, 118.2, 116.3 35.6, 30.7 ppm. HRMS (ESI) calcd. for C₁₀H₁₂NO₃ [M–H]⁻: 194.0823, found: 194.0822.



Chart S3. ¹H NMR spectrum of 2 in CDCl₃, 400 MHz.



Chart S4. ¹³C{¹H} NMR spectrum of 2 in CDCl₃, 100 MHz.



Synthesis of 4 (4-(*tert*-butyl)-2-methoxyaniline) via 3 (4-(*tert*-butyl)-2-methoxy-1-nitrobenzene)

In a 100 ml round bottom tow-neck flask, **2** (2.70 g, 13.8 mmol, 1.0 equiv.) and potassium carbonate (3.82 g, 27.7 mmol, 2.0 equiv.) were dissolved in acetone (25 ml) at 0 °C. Dimethyl sulfate (1.33 g cm⁻³, 5.25 mL, 55.3 mmol, 4.0 equiv.) was added and the mixture was stirred at reflux temperature for 2.5 h. Upon cooling to ambient temperature, the reaction mixture was quenched by water. The organic layer was extracted by chloroform and washed by water. The organic layer was dried over MgSO₄. After filtration, volatile materials were removed by evaporation under reduced pressure to afford crude **3** (2.80 g) as a yellow liquid. The crude product was used as such without further purification.

In a 100 mL round bottom flask, **3** (2.80 g, 13.4 mmol, 1.0 equiv.) and NH₄Cl (3.58 g, 66.9 mmol, 5.0 equiv.) were dissolved in ethanol (30 mL) and H₂O (10 mL) at 80 °C. Fe powder (3.74 g, 66.9 mmol, 5.0 equiv.) was added and the mixture was stirred at 80 °C for 4 h. Upon cooling to ambient temperature, the reaction mixture was filtered through celite to remove Fe powder. The solution was washed with sat. NaHCO₃, water and brine. The organic layer was extracted with ethyl acetate and dried with MgSO₄. After filtration, volatile materials were removed by evaporation under reduced pressure, the product was purified by column chromatography on SiO₂ (hexane/ethyl acetate = 9/1 v/v as an eluent) and reprecipitated from chloroform and hexane to afford **4** (1.39 g, 7.75 mmol, 56% for two steps) as a white solid.

 $R_{\rm f} = 0.21.$ ¹H NMR (CDCl₃, 400 MHz) δ 6.84 (d, J = 2.0 Hz, 1H), 6.81 (dd, J = 8.0, 2.1 Hz, 1H), 6.66 (d, J = 8.0 Hz, 1H), 3.86 (s, 3H), 3.68 (s, 2H), 1.29 (s, 9H) ppm. ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 147.0, 141.9, 133.6, 117.6, 114.7, 108.2, 55.5, 34.3, 31.6 ppm. HRMS (ESI) calcd. for C₁₁H₁₈NO [M+H]⁺: 180.1383, found: 180.1382.



Chart S5. ¹H NMR spectrum of 4 in CDCl₃, 400 MHz.



Chart S6. ¹³C{¹H} NMR spectrum of 4 in CDCl₃, 100 MHz.





4 (1.38 g, 7.70 mmol, 1.0 equiv.) and toluene (30 mL) were added to 100 mL round bottom flask. After warming to 70 °C, MnO_2 (2.68 g, 30.8 mmol, 5.0 equiv.) was added and stirred for 22 h. Upon cooling to ambient temperature, the reaction mixture was filtered through celite and silica. Volatile materials were removed by evaporation under reduced pressure, the product was purified by recrystallization from mixed solvent of methanol (poor solvent) and chloroform (good solvent) and washed with methanol to afford **5** (890 mg, 2.51 mmol, 65%) as a brown solid.

¹H NMR (CDCl₃, 400 MHz) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.06 (d, *J* = 1.7 Hz, 2H), 7.02 (d, *J* = 8.4 and 1.9 Hz, 2H), 4.02 (s, 6H), 1.35 (s, 18H) ppm. ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 156.6, 155.9, 141.2, 118.2, 117.0, 110.1, 56.7, 35.3, 31.2 ppm. HRMS (ESI) calcd. for C₂₂H₃₀N₂O₂Na [M+Na]⁺: 377.2199, found: 377.2199.



Chart S8. ¹³C{¹H} NMR spectrum of 5 in CDCl₃, 100 MHz.





5 (780 mg, 2.20 mmol, 1.0 equiv.) and CH_2Cl_2 (60 mL) were added to 100 mL round bottom two neck flask equipped with a rubber septum. After degassing and filling Ar three times, the mixture was cooled to -78 °C, and then boron tribromide (1 M in CH_2Cl_2 , 5.50 mL, 5.50 mmol, 2.5 equiv.) was added. The reaction mixture was stirred at ambient temperature for 7 h. The reaction was quenched by methanol, and volatile materials were removed by evaporation under reduced pressure, the product was purified by recrystallization from mixed solvent of methanol (poor solvent) and chloroform (good solvent) and washed with methanol to afford LAz-tBu (718 mg, 2.20 mmol, quant.) as an orange solid.

¹H NMR (CDCl₃, 400 MHz) δ 12.30 (s, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.08 (dd, J = 2.0 and 8.5 Hz, 2H), 7.04 (d, J = 2.0 Hz, 2H), 1.35 (s, 18H) ppm. ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 157.4, 152.6, 133.2, 130.5, 117.9, 115.5, 35.3, 31.0 ppm. HRMS (ESI): [M–H][–] Calcd., 327.2067; Found, 327.2067.



Chart S9. ¹H NMR spectrum of LAz-tBu in CDCl₃, 400 MHz.



Chart S10. ¹³C{¹H} NMR spectrum of LAz-tBu in CDCl₃, 100 MHz.

Synthesis of GAzPh-tBu



Diphenyldichlorogermane (1.43 g cm⁻³, 63.8 μ L, 0.306 mmol, 2.0 equiv.) and then Et₃N (0.0854 mL, 0.613 mmol, 4.0 equiv.) were added to the solution of **LAz-tBu** (50.0 mg, 0.153 mmol, 1.0 equiv.) in toluene (20 mL). The reaction mixture was stirred at 60 °C for 6 h under nitrogen atmosphere, and then filtered to remove salt. The product was purified by recrystallization from hexane to afford **GAzPh-tBu** (20.0 mg, 0.0363 mmol, 24%) as a black solid.

¹H NMR (CDCl₃, 400 MHz) δ 7.97–7.94 (m, 4H), 7.60 (d, J = 8.7 Hz, 1H), 7.45 (d, J = 8.6 Hz, 1H), 7.39–7.36 (m, 6H), 7.02 (d, J = 2.0 Hz, 1H), 6.96 (d, J = 1.8 Hz, 1H), 6.92 (dd, J = 2.0, 8.6 Hz, 1H), 6.82 (dd, J = 1.7, 8.6 Hz, 1H), 1.34 (s, 9H), 1.33 (s, 9H) ppm. ¹³C{¹H} NMR (CDCl₃, 150 MHz) δ 162.3, 160.5, 159.9, 158.6, 139.4, 135.0, 134.5, 133.4, 132.8, 130.1, 128.3, 118.9, 117.7, 116.7, 116.3, 114.5, 35.7, 35.4, 31.0, 30.7 ppm. HRMS (ESI) calcd. for C₃₂H₃₄GeN₂O₂Na [M+Na]⁺: 575.1727, found, 575.1724.



Chart S11. ¹H NMR spectrum of GAzPh-tBu in CDCl₃, 400 MHz.



Chart S12. ¹³C{¹H} NMR spectrum of GAzPh-tBu in CDCl₃, 150 MHz.



Synthesis of 7 ((*E*)-1,2-bis(2-methoxy-4-(thiophen-2-yl)phenyl)diazene)

In the 200 ml round bottom two-neck flask, **6** (400 mg, 1.00 mmol, 1.0 equiv.) and 2-thiopheneboronic acid (269 mg, 2.10 mmol, 2.1 equiv.), cesium carbonate (3.26 g, 10.0 mmol, 10 equiv.), $Pd_2(dba)_3$ (2.75 mg, 0.00300 mmol, 0.0030 equiv.), SPhos (4.93 mg, 0.0120 mmol, 0.012 equiv.) were dissolved in the solvent mixture of toluene (25 mL) and degassed water (25 mL). The reaction mixture was stirred at 90 °C for 15 h under nitrogen atmosphere. Upon cooling to ambient temperature, the reaction mixture was washed with water and brine. The organic layer was separated, dried with MgSO₄. After filtration, volatile materials were removed by evaporation under reduced pressure. The product was purified by column chromatography on SiO₂ (hexane/ethyl acetate = 4/1 v/v as an eluent). Further purification was carried out by recrystallization from mixed solvent of methanol (poor solvent) and chloroform (good solvent), and the collected product was washed by methanol to afford **7** (230 mg, 0.566 mmol, 57%) as a red solid.

 $R_{\rm f} = 0.33$ (hexane/ethyl acetate = 4/1 v/v). ¹H NMR (CD₂Cl₂, 400 MHz) δ 7.73 (d, J = 8.0 Hz, 2H), 7.42 (dd, J = 3.6, 1.2 Hz, 2H), 7.35 (dd, J = 5.1, 1.1 Hz, 2H), 7.29–7.26 (m, 4H), 7.12 (dd, J = 5.1, 3.7 Hz, 2H), 4.10 (s, 6H) ppm. ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 157.3, 143.7, 142.2, 138.2, 128.3, 125.9, 124.2, 118.6, 118.1, 109.9, 56.6 ppm. HRMS (ESI) calcd. for C₂₂H₁₈N₂O₂S₂Na [M+Na]⁺: 429.0700, found: 429.0702.



Chart S13. ¹H NMR spectrum of 7 in CDCl₃, 400 MHz.



Chart S14. ¹³C{¹H} NMR spectrum of 7 in CDCl₃, 100 MHz.



Synthesis of LAz-Th ((*E*)-6,6'-(diazene-1,2-diyl)bis(3-(thiophen-2-yl)phenol))

7 (200 mg, 0.492 mmol, 1.0 equiv.) and CH_2Cl_2 (10 mL)were added to 100 mL round bottom two neck flask equipped with a rubber septum. After degassing and filling Ar three times, the mixture was cooled to -78 °C, and then boron tribromide (1 M in CH_2Cl_2 , 1.23 mL, 1.23 mmol, 2.5 equiv.) was added slowly. The reaction mixture was stirred at ambient temperature for 5 h under nitrogen atmosphere. The reaction was quenched by methanol, and volatile materials were removed by evaporation under reduced pressure. The product was purified by recrystallization from mixed solvent of methanol (poor solvent) and chloroform (good solvent). The collected product was washed with methanol to afford LAz-Th (160 mg, 0.423 mmol, 86%) as a red solid.

¹H NMR (DMSO- d_6 , 400 MHz) δ 11.90 (s, 2H), 7.88 (d, J = 8.4 Hz, 2H), 7.67–7.66 (m, 4H), 7.36–7.32 (m, 4H), 7.19 (dd, J = 5.0, 3.7 Hz, 2H) ppm. ¹³C{¹H} NMR (DMSO- d_6 , 400 MHz) δ 154.5, 142.2, 137.9, 137.1, 128.9, 127.5, 125.5, 123.9, 117.2, 113.8 ppm. HRMS (APCI) calcd. for $C_{20}H_{15}N_2O_2S_2$ [M+H]⁺: 379.0569, found: 379.0570.



Chart S15. ¹H NMR spectrum of LAz-Th in DMSO-*d*₆, 400 MHz.



Chart S16. ¹³C{¹H} NMR spectrum of **LAz-Th** in DMSO-*d*₆, 100 MHz.

Synthesis of GAzPh-Th



Diphenyldichlorogermane (1.43 g cm⁻³, 55.0 μ L, 0.264 mmol, 2.0 equiv.) and then Et₃N (73.7 μ L, 0.528 mmol, 4.0 equiv.) were added to the solution of **LAz-Th** (50.0 mg, 0.132 mmol, 1.0 equiv.) in toluene (20 mL). The reaction mixture was stirred at 60 °C for 6 h under nitrogen atmosphere, and then filtered to remove salt. the product was purified by recrystallization from acetone to afford **GAzPh-Th** (58.0 mg, 0.0961 mmol, 73%) as a black solid.

¹H NMR (CDCl₃, 400 MHz) δ 8.01–7.98 (m, 4H), 7.70 (d, J = 8.6 Hz, 1H), 7.56 (d, J = 3.7 Hz, 1H), 7.53 (d, J = 8.5 Hz, 1H), 7.45 (d, J = 5.1 Hz, 1H), 7.43 (d, J = 3.6 Hz, 1H), 7.40–7.38 (m, 6H), 7.36 (d, J = 5.1Hz, 1H), 7.28 (dd, J = 11.2, 1.8 Hz, 2H), 7.19 (dd, J = 1.8, 8.4 Hz, 1H), 7.16 (dd, J = 4.0, 4.9 Hz, 1H), 7.11 (dd, J = 5.1, 3.9 Hz, 1H), 7.08 (dd, J = 8.4, 1.8 Hz, 1H) ppm. ¹³C{¹H} NMR (CDCl₃, 125 MHz) δ 160.8, 160.5, 143.9, 142.9, 142.8, 139.0, 139.0, 136.0, 135.0, 134.6, 130.3, 129.1, 128.7, 128.4, 128.3, 128.0, 126.3, 126.2, 124.4, 118.0, 117.5, 117.5, 117.0, 113.9 ppm. HRMS (ESI) calcd for C₃₂H₂₂GeN₂O₂S₂Na [M+Na]⁺: 627.0227, found: 627.0229.



Chart S17. ¹H NMR spectrum of GAzPh-Th in CDCl₃ at 400 MHz.



Chart S18. ${}^{13}C{}^{1}H$ NMR spectrum of GAzPh-Th in CDCl₃ at 125 MHz.



Synthesis of 8 ((E)-4,4'-(diazene-1,2-diyl)bis(3-methoxy-N,N-diphenylaniline))

6 (1.20 g, 3.00 mmol, 1.0 equiv.) and diphenylamine (1.02 g, 6.00 mmol, 2.0 equiv.), tri-*tert*-butylphosphine tetrafluoroborate (131 mg, 0.500 mmol, 0.15 equiv.), $Pd_2(dba)_3$ (68.6 mg, 0.0750 mmol, 0.025 equiv.), *tert*-BuONa (0.865 g, 9.00 mmol, 3.0 equiv.), toluene (35 mL) were added to 100 mL round bottom flask. The reaction mixture was stirred at 100 °C for 6.5 h under argon atmosphere. Upon cooling to ambient temperature, the reaction mixture was washed with water and brine. The organic layer was extracted with chloroform, and then dried over Na₂SO₄. After filtration, volatile materials were removed by evaporation under reduced pressure. The product was purified by column chromatography on SiO₂ (dichloromethane as an eluent) and then recrystallization from mixed solvent of methanol (poor solvent) and chloroform (good solvent). The collected product was washed with methanol to afford **8** (1.70 g, 2.95 mmol, 98%) as an orange solid.

 $R_{\rm f} = 0.83$ (dichloromethane). ¹H NMR (CDCl₃, 400 MHz) δ 7.57 (d, J = 8.8 Hz, 2H), 7.32–7.27 (m, 8H), 7.17–7.14 (m, 8H), 7.11–7.06 (m, 4H), 6.66 (d, J = 2.2 Hz, 2H), 6.62 (dd, J = 8.9, 2.3 Hz, 2H), 3.80 (s, 6H) ppm. ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 157.6, 151.1, 147.0, 138.4, 129.3, 125.3, 123.8, 118.1, 114.9, 105.9, 56.3 ppm. HRMS (ESI) calcd. for C₃₈H₃₂N₄O₂Na: [M+Na]⁺: 577.2598, found, 577.2576.



Chart S19. ¹H NMR spectrum of 8 in CDCl₃, 400 MHz.



Chart S20. ¹³C{¹H} NMR spectrum of 8 in CDCl₃, 100 MHz.



Synthesis of LAz-NPh2 ((E)-6,6'-(diazene-1,2-diyl)bis(3-(diphenylamino)phenol))

8 (1.70 g, 2.95 mmol, 1.0 equiv.) and CH₂Cl₂ (140 mL) were added to 500 mL round bottom two neck flask equipped with a rubber septum. After cooling to -78 °C, boron tribromide (1 M in CH₂Cl₂, 11.8 mL, 11.8 mmol, 4.0 equiv.) was added. The reaction mixture was stirred at ambient temperature for 13 h under argon atmosphere. The reaction was quenched by methanol, and volatile materials were removed by evaporation under reduced pressure. The product was purified by recrystallization from mixed solvent of methanol (poor solvent) and chloroform (good solvent). The collected product was washed with methanol to afford LAz-NPh2 (850 mg, 1.55 mmol, 53%) as a black solid.

¹H NMR (CDCl₃, 400 MHz) δ 12.74 (s, 2H), 7.36–7.30 (m, 10H), 7.20–7.12 (m, 12H), 6.58 (dd, J = 8.7, 2.2 Hz, 2H), 6.49 (d, J = 2.4 Hz, 2H) ppm. ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 154.6, 151.0, 146.3, 130.8, 130.2, 129.6, 126.3, 124.8, 112.7, 108.1 ppm. HRMS (ESI): [M–H][–] Calcd., 549.2285; Found, 549.2274.



Chart S21. ¹H NMR spectrum of LAz-NPh2 in CDCl₃, 400 MHz.



Chart S22. ¹³C{¹H} NMR spectrum of LAz-NPh2 in CDCl₃, 100 MHz.

Synthesis of GAzPh-NPh2



Diphenyldichlorogermane (1.43 g cm⁻³, 22.8 μ L, 0.109 mmol, 2.0 equiv.) and then Et₃N (30.5 μ L, 0.219 mmol, 4.0 equiv.) were added to the solution of **LAz-NPh2** (30.0 mg, 0.0547 mmol, 1.0 equiv.) in THF (20 mL). The reaction mixture was stirred at ambient temperature for 18 h under nitrogen atmosphere, and then filtered to remove salt. the product was purified by recrystallization from mixed solvent of hexane (poor solvent) and chloroform (good solvent) to afford **GAzPh-NPh2** (20.0 mg, 0.0259 mmol, 47%) as a black solid.

¹H NMR (CDCl₃, 400 MHz) δ 7.90–7.88 (m, 4H), 7.45 (d, J = 8.9 Hz, 1H), 7.40–7.38 (m, 4H), 7.36–7.33 (m, 6H), 7.31–7.27 (m, 4H), 7.24–7.22 (m, 6H), 7.19 (d, J = 7.43 Hz, 1H), 7.18–7.16 (m, 4H), 7.10–7.07 (m, 2H), 6.52 (d, J = 2.4 Hz, 1H), 6.41 (dd, J = 2.3, 9.0 Hz, 1H), 6.40 (dd, J = 2.5, 9.1 Hz, 1H), 6.34 (d, J = 2.5 Hz, 1H) ppm. ¹³C{¹H} NMR (CDCl₃, 150 MHz) δ 161.8, 160.1, 155.2, 151.8, 147.0, 145.4, 139.9, 135.0, 134.5, 132.4, 130.3, 129.8, 129.7, 129.4, 128.1, 127.1, 126.0, 125.9, 124.0, 116.6, 112.9, 112.5, 108.3, 108.0 ppm. HRMS (ESI) calcd. for C₄₈H₃₆GeN₄O₂ [M]⁺: 774.2045, found: 774.2056.



Chart S23. ¹H NMR spectrum of LAz-NPh2 in CDCl₃, 400 MHz.



Chart S24. ¹³C{¹H} NMR spectrum of LAz-NPh2 in CDCl₃, 150 MHz.

Single crystal X-ray structure analysis of GAzPh-Br

Intensity data were collected on a Rigaku Saturn 724+ with MicroMax-007HF CCD diffractometer with Varimax Mo optics using graphite-monochromated MoK α radiation. The structures were solved and refined by full-matrix least-squares procedures based on F^2 (SHELXL-2018/3).⁶

Empirical formula	$C_{24}H_{16}Br_2GeN_2O_2$	
Formula weight	596.80	N. N.
Temperature (K)	143(2)	Br O-Ge. Br
Wavelength (Å)	0.71075	Ph Ph
Crystal system, space group	Monoclinic, C2/c	CCDC # 2262761
Unit cell dimensions (Å)	a=18.822(7)	
	b=17.197(5)	
	c=7.113(2)	
Unit cell dimensions (°)	a=90	
	β =111.168(5)	
	<i>γ</i> =90	
Volume (Å ³)	2147.0(12)	
Z, calculated density (g cm ⁻³)	4, 1.846	
Absorption coefficient	5.174	
F(000)	1168.0	
Crystal size (mm)	0.16×0.04×0.01	
θ range for data collection (°)	3.1-27.5	
Limiting indices	–24≤ <i>h</i> ≤21, –22≤ <i>k</i> ≤22, –8≤ <i>l</i> ≤8	
Reflections collected (unique)	8617/3185 [<i>R</i> (int)=0.0526]	
Completeness to theta	0.979	
Max. and min. transmission	1.000, 0.742	
Goodness-of-fit on F^2	1.066	
Final R indices $[I > 2\sigma(I)]^{[a]}$	$R_1 = 0.0579, wR_2 = 0.1198$	
R indices (all data)	$R_1 = 0.0781, wR_2 = 0.1292$	

Table S1. Crystallographic data of GAzPh-Br



Figure S1. (A) ORTEP drawings and (B) packing diagrams of **GAzPh-Br**. Thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms are omitted for clarity.

Single crystal X-ray structure analysis of GAzPh-tBu

Intensity data were collected on a Rigaku Saturn 724+ with MicroMax-007HF CCD diffractometer with Varimax Mo optics using graphite-monochromated MoK α radiation. The structures were solved and refined by full-matrix least-squares procedures based on F^2 (SHELXL-2018/3).⁶

Empirical formula	$C_{32}H_{34}GeN_2O_2$	
Formula weight	551.20	
Temperature (K)	143(2)	
Wavelength (Å)	0.71075	Ph Ph
Crystal system, space group	Monoclinic, $P2_1/c$	CCDC # 2262762
Unit cell dimensions (Å)	a=16.796(5)	
	b=17.846(6)	
	c=9.223(3)	
Unit cell dimensions (°)	a=90	
	$\beta = 97.727(4)$	
	<i>γ</i> =90	
Volume (Å ³)	2739.4(15)	
Z, calculated density (g cm ⁻³)	4, 1.336	
Absorption coefficient	1.150	
F(000)	1152	
Crystal size (mm)	0.13×0.09×0.02	
θ range for data collection (°)	3.2-27.5	
Limiting indices	–19≤ <i>h</i> ≤21, –23≤ <i>k</i> ≤23, –11≤ <i>l</i> ≤11	
Reflections collected (unique)	21823/8213 [<i>R</i> (int)=0.0521]	
Completeness to theta	0.995	
Max. and min. transmission	1.000, 0.829	
Goodness-of-fit on F^2	1.073	
Final R indices $[I > 2\sigma(I)]^{[a]}$	$R_1 = 0.0450, wR_2 = 0.0947$	
R indices (all data)	$R_1 = 0.0587, wR_2 = 0.1018$	

Table S2. Crystallographic data of GAzPh-tBu



Figure S2. (A) ORTEP drawings and (B) packing diagrams of **GAzPh-tBu**. Thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms are omitted for clarity.

Single crystal X-ray structure analysis of GAzPh-Th

Intensity data were collected on a Rigaku Saturn 724+ with MicroMax-007HF CCD diffractometer with Varimax Mo optics using graphite-monochromated MoK α radiation. The structures were solved and refined by full-matrix least-squares procedures based on F^2 (SHELXL-2018/3).⁶

Empirical formula	$C_{32}H_{22}GeN_2O_2S_2$	
Formula weight	603.22	
Temperature (K)	143(2)	-S O'Ge
Wavelength (Å)	0.71075	Ph Ph
Crystal system, space group	Triclinic, <i>P</i> –1	CCDC # 2262763
Unit cell dimensions (Å)	a=8.3373(19)	
	b=12.371(3)	
	c=13.956(4)	
Unit cell dimensions (°)	<i>α</i> =109.840(4)	
	$\beta = 101.691(2)$	
	<i>γ</i> =98.259(2)	
Volume (Å ³)	1290.2(6)	
Z, calculated density (g cm ⁻³)	2, 1.553	
Absorption coefficient	1.384	
F(000)	616.0	
Crystal size (mm)	0.16×0.12×0.12	
θ range for data collection (°)	3.2-27.5	
Limiting indices	-10≤ <i>h</i> ≤10, -15≤ <i>k</i> ≤15, -16≤ <i>l</i> ≤18	
Reflections collected (unique)	10224/4360 [<i>R</i> (int)=0.0226]	
Completeness to theta	0.950	
Max. and min. transmission	1.000, 0.898	
Goodness-of-fit on F^2	1.052	
Final R indices $[I > 2\sigma(I)]^{[a]}$	$R_1 = 0.0369, wR_2 = 0.1036$	
R indices (all data)	$R_1 = 0.0444, wR_2 = 0.1077$	

Table S3. Crystallographic data of GAzPh-Th



Figure S3. (A) ORTEP drawings and (B) packing diagrams of **GAzPh-Th**. Thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms are omitted for clarity.

Single crystal X-ray structure analysis of GAzPh-NPh2

Intensity data were collected on a Rigaku Saturn 724+ with MicroMax-007HF CCD diffractometer with Varimax Mo optics using graphite-monochromated MoK α radiation. The structures were solved and refined by full-matrix least-squares procedures based on F^2 (SHELXL-2018/3).⁶ Heavily disordered solvent molecules (CH₂Cl₂) were removed by using SQUEEZE procedure.⁷

Empirical formula	$C_{48}H_{36}GeN_4O_2$				
Formula weight	773.40				
Temperature (K)	143(2)				
Wavelength (Å)	0.71075				
Crystal system, space group	Triclinic, P-1				
Unit cell dimensions (Å)	a=12.226(4)				
	b=13.890(5) CCDC # 2262764				
	c=15.049(5)				
Unit cell dimensions (°)	<i>α</i> =100.892(2)				
	$\beta = 108.089(4)$				
	<i>γ</i> =114.347(3)				
Volume (Å ³)	2059.7(12)				
Z, calculated density (g cm ⁻³)	2, 1.247				
Absorption coefficient	0.786				
F(000)	800				
Crystal size (mm)	0.06×0.02×0.01				
θ range for data collection (°)	3.0-27.5				
Limiting indices	-15≤h≤14, -14≤k≤17, -19≤l≤19				
Reflections collected (unique)	16796/5168 [<i>R</i> (int)=0.0386]				
Completeness to theta	0.957				
Max. and min. transmission	1.000, 0.865				
Goodness-of-fit on F^2	0.992				
Final R indices $[I > 2\sigma(I)]^{[a]}$	$R_1 = 0.0523, wR_2 = 0.1095$				
R indices (all data)	$R_1 = 0.0824, wR_2 = 0.1248$				

Table S4. Crystallographic data of GAzPh-NPh	2
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Figure S4. (A) ORTEP drawings and (B) packing diagrams of **GAzPh-NPh2**. Thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms are omitted for clarity.

Selected bond lengths, angles, and torsion angles

Table S5. Selected bond lengths, angles, and torsion angles from single crystals of the GAz compounds.Since the structures of GAzPh-Th and GAzPh-NPh2 are disordered, the values of major structures arelisted.

	GAziPr-Br ^a	GAzPh-Br	GAzPh-tBu	GAzPh-Th	GAzPh-NPh2
Bond / Å					
Ge(1)-C(13)	1.949(3)	1.933	1.948(3)	1.938(3)	1.947(3)
Ge(1)-C(19)	1.943(3)	1.933	1.949(2)	1.933(2)	1.932(4)
Ge(1)-O(1)	1.967(3)	1.936	1.936(2)	2.045(6)	2.070(8)
Ge(1)-O(2)	1.965(3)	1.936	1.944(2)	1.819(4)	1.790(7)
Ge(1)-N(1)	2.107(5)	2.033	2.031(2)	2.074(3)	2.034(5)
N(1)-N(2)	1.270(8)	1.28(1)	1.278(3)	1.296(6)	1.303(7)
N(1)-C(1)	1.409(6)	1.542(9)	1.406(3)	1.40(1)	1.40(2)
N(2)-C(7)	1.509(7)	1.357(9)	1.379(3)	1.37(1)	1.37(2)
O(1)-C(2)	1.319(4)	1.306(6)	1.335(3)	1.31(1)	1.33(2)
O(2)–C(8)	1.312(5)	1.306(6)	1.312(3)	1.316(6)	1.34(1)
C(1)-C(2)	1.403(5)	1.399(8)	1.393(3)	1.416(9)	1.37(1)
C(7)-C(8)	1.402(6)	1.399(8)	1.411(3)	1.41(1)	1.41(2)
Angle / °					
C(13)-Ge(1)-C(19)	129.5(1)	123.3	123.9(1)	122.6(1)	118.1(1)
N(1)-Ge(1)-C(13)	112.9(2)	118.2	118.86(9)	126.7(1)	121.9(2)
N(1)-Ge(1)-C(19)	116.2(2)	117.6	117.24(9)	109.7(1)	118.6(2)
O(1)-Ge(1)-O(2)	165.8(1)	167.2	164.86(7)	161.7(2)	163.2(3)
N(1)-Ge(1)-O(1)	69.8(1)	74.0	80.45(7)	78.0(2)	76.5(3)
N(1)-Ge(1)-O(2)	96.2(2)	93.2	84.41(7)	87.3(2)	86.8(3)
Torsion Angle / $^{\circ}$					
C(1)-N(1)-N(2)-C(7)	-179.6(4)	177.8(6)	176.2(2)	176.8(6)	-178(1)

^{*a*} ref 8.

Solvent effects evaluated by Lippert-Mataga plots

$$v = [2(\mu_{e} - \mu_{g})^{2}/hca^{3}]\Delta f + v^{o}$$
$$\Delta f = [(\varepsilon - 1)/(2\varepsilon + 1)] - [(n^{2} - 1)/(2n^{2} + 1)]$$

- v : Stokes shift
- v^{o} : Stokes shift in the absence of solvent
- $\mu_{\rm e}$: dipole moments in the ground state
- $\mu_{\rm g}$: dipole moments in the excited state
- *a* : Onsager cavity radius
- Δf : orientation polarizability
- ε : solvent dielectric constant
- *n* : solvent refractive index



Figure S5. (A) UV–vis absorption (left) and PL spectra (right), (B) Lippert–Mataga plots and (C) spectroscopic data of GAz derivatives in the non-coordinating solvents (solvent/chloroform = 99/1 v/v, 1.0×10^{-5} M) at room temperature, excited at the wavelength of the absorption maxima. The non-coordinating solvents were used because coordinating solvents can interact with germanium center to construct six coordination, which should affect the optical properties of GAz derivatives.⁹



Figure S6. PL lifetime decay curves of GAz derivatives in CHCl₃ at room temperature and in 2Me-THF at 77 K, excited at 532 nm with a LED. Their emissions at the PL peak tops were monitored.

Cyclic voltammograms

Experimental values of HOMO and LUMO energy levels (E_{HOMO} and E_{LUMO} , respectively) were estimated by onset potentials of oxidation (E_{onset}^{ox}) and reduction (E_{onset}^{red}) peaks by a cyclic voltammetry, respectively (Figure S12 and Table S9) according to the literature with the equation of E_{HOMO} /eV = -4.8 – E_{onset}^{ox} /V and E_{LUMO} /eV = -4.8 – E_{onset}^{red} /V.¹⁰ Cyclic voltammograms of samples were recorded in CH₂Cl₂ (1.0×10⁻³ M) containing N*n*Bu₄PF₆ (0.10 M) using a glassy carbon (GC) working electrode, a Pt wire counter electrode, an Ag/AgCl reference electrode, and a Fc/Fc⁺ external standard at room temperature with a scan rate of 0.1 V s⁻¹.



Figure S7. Cyclic voltammograms of GAz derivatives in CH_2Cl_2 (1.0×10⁻³ M).

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Computational details for theoretical calculation

The Gaussian 16 program package¹¹ was used for computation. We optimized the structures of the **GAziPr-Br**, **GAzPh-Br**, **GAzPh-tBu**, **GAzPh-Th**, and **GAzPh-NPh2** in the ground S₀ states and calculated their molecular orbitals. The density functional theory (DFT) was applied for the optimization of the structures in the S₀ states at B3LYP/6-311G(d,p) level. We calculated the energy of the S₀ \rightarrow S₁ transitions with optimized geometries in the S₀ by TD-DFT at B3LYP/6-311G(d,p) level. Natural bond orbital (NBO) calculation was carried out by DFT at B3LYP/6-311G(d,p) level.

	Energy band gap	Wavelength	Oscillator Strength	Assignment (Weight)
	/ eV	/ nm		
GAziPr-Br	2.2904	541.32	0.3461	HOMO \rightarrow LUMO (0.69487)
				HOMO-2 \rightarrow LUMO (0.12883)
GAzPh-Br	2.3907	518.60	0.3707	HOMO \rightarrow LUMO (0.69269)
				HOMO-2 \rightarrow LUMO (0.10847)
GAzPh-tBu	2.3745	522.15	0.3542	HOMO \rightarrow LUMO (0.69524)
				HOMO-2 \rightarrow LUMO (-0.13400)
GAzPh-Th	2.2076	561.62	0.8156	HOMO \rightarrow LUMO (0.69597)
				HOMO-1 \rightarrow LUMO (0.11986)
GAzPh-NPh2	2.1152	586.17	1.1207	HOMO \rightarrow LUMO (0.70729)

Table S6. Results of $S_0 \rightarrow S_1$ transitions of GAz derivatives at the ground state from TD-DFT calculations



Figure S8. (A) The NBOs and (B) Kohn–Sham orbitals involving 3c-4e bond of **GAziPr-Br** and the stabilization energy of donor–acceptor interactions (isovalue = 0.03). E⁽²⁾: The second-order perturbation stabilization energy.



Figure S9. (A) The NBOs and (B) Kohn–Sham orbitals involving 3c-4e bond of **GAzPh-Br** and the stabilization energy of donor–acceptor interactions (isovalue = 0.03). E⁽²⁾: The second-order perturbation stabilization energy.



Figure S10. (A) The NBOs and (B) Kohn–Sham orbitals involving 3c-4e bond of **GAzPh-tBu** and the stabilization energy of donor–acceptor interactions (isovalue = 0.03). E⁽²⁾: The second-order perturbation stabilization energy.



Figure S11. (A) The NBOs and (B) Kohn–Sham orbitals involving 3c-4e bond of **GAzPh-Th** and the stabilization energy of donor–acceptor interactions (isovalue = 0.03). E⁽²⁾: The second-order perturbation stabilization energy.



Figure S12. (A) The NBOs and (B) Kohn–Sham orbitals involving 3c-4e bond of **GAzPh-NPh2** and the stabilization energy of donor–acceptor interactions (isovalue = 0.03). E⁽²⁾: The second-order perturbation stabilization energy.



Figure S13. The results of NBO calculations of the GAz compounds focused on energy levels of one of the LP(O1)s and LP(O2)s which contribute to construct HOMOs and LUMOs (isovalue = 0.03).

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Coordinates for optimized structures with theoretical calculation

Center	Atomic	Atomic	Coordinates (Angstroms)			
Number	Number	Туре	Х	Y	Z	
1	6	0	-2.523572	-2.490416	-0.037592	
2	6	0	-3.896082	-2.486044	-0.056364	
3	6	0	-4.5534	-1.238628	-0.061662	
4	6	0	-3.87507	-0.040026	-0.047825	
5	6	0	-2.459171	-0.027701	-0.025859	
6	6	0	-1.774397	-1.285878	-0.022749	
7	7	0	-0.423789	-1.451555	-0.009095	
8	7	0	0.402279	-0.475101	0.00405	
9	6	0	1.767177	-0.804975	0.014205	
10	6	0	2.622413	0.323746	0.027413	
11	6	0	4.01476	0.116555	0.03897	
12	6	0	4.496229	-1.179253	0.036804	
13	6	0	3.652818	-2.30158	0.023466	
14	6	0	2.283745	-2.104813	0.012187	
15	8	0	-1.827115	1.103529	-0.012518	
16	32	0	0.110883	1.595214	0.016198	
17	8	0	2.085125	1.520221	0.029989	
18	35	0	6.392083	-1.463002	0.053051	
19	35	0	-6.465933	-1.222578	-0.09003	
20	6	0	-0.021196	2.507047	-1.739011	
21	6	0	0.271586	1.538976	-2.895887	
22	6	0	0.876057	3.751625	-1.801326	
23	6	0	-0.001386	2.472599	1.791341	
24	6	0	-0.057926	1.435438	2.923907	
25	6	0	-1.161195	3.474024	1.880004	
26	1	0	-1.967077	-3.41974	-0.033929	
27	1	0	-4.463225	-3.405864	-0.067502	
28	1	0	-4.391827	0.909828	-0.053468	
29	1	0	4.672532	0.974394	0.05004	

GAzPh-iPr

30	1	0	4.069575	-3.29899	0.022163
31	1	0	1.599742	-2.942556	0.001788
32	1	0	-1.071016	2.809063	-1.794483
33	1	0	-0.395474	0.672504	-2.89139
34	1	0	0.137861	2.04862	-3.856246
35	1	0	1.302368	1.174946	-2.861089
36	1	0	0.628423	4.479675	-1.023215
37	1	0	0.755569	4.253019	-2.768069
38	1	0	1.928574	3.485588	-1.686318
39	1	0	0.949066	3.009286	1.861761
40	1	0	0.794518	0.75131	2.902405
41	1	0	-0.048259	1.939069	3.8966
42	1	0	-0.974352	0.839667	2.87635
43	1	0	-1.0896	4.258555	1.121085
44	1	0	-1.157402	3.965042	2.859544
45	1	0	-2.125348	2.977488	1.755307

GAzPh-Br

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Туре	Х	Y	Z
1	6	0	-3.83576	-0.512314	-0.000535
2	6	0	-2.422343	-0.510027	-0.000189
3	8	0	-1.786319	0.624993	-0.000487
4	32	0	0.120675	1.118256	0.000079
5	35	0	6.420821	-1.878728	-0.000035
6	35	0	-6.434944	-1.677455	-0.000574
7	1	0	-4.349487	0.43932	-0.001062
8	6	0	-3.873373	-2.956993	0.000544
9	6	0	-4.523282	-1.707731	-0.00015
10	1	0	-4.444832	-3.874208	0.000823
11	6	0	-2.499854	-2.968275	0.000795
12	6	0	-1.745563	-1.768575	0.000432
13	1	0	-1.947967	-3.900273	0.001271
14	6	0	2.631256	-0.142545	0.000333

15	6	0	4.024466	-0.329139	0.000192
16	8	0	2.078091	1.050493	0.000434
17	1	0	4.673469	0.535453	0.000117
18	6	0	4.522498	-1.619645	0.000153
19	6	0	3.692726	-2.751651	0.000232
20	1	0	4.121685	-3.74388	0.000218
21	6	0	1.79003	-1.278334	0.000367
22	6	0	2.321384	-2.571998	0.000323
23	1	0	1.647374	-3.417842	0.000365
24	7	0	-0.394106	-1.93891	0.000534
25	7	0	0.42498	-0.960332	0.000336
26	6	0	0.004201	2.020643	1.745148
27	6	0	0.005025	2.020558	-1.745129
28	6	0	-1.233009	2.242541	2.36556
29	6	0	-1.30736	2.916473	3.582323
30	6	0	-0.147363	3.380718	4.197881
31	6	0	1.087587	3.171192	3.58914
32	6	0	1.16444	2.498149	2.371865
33	6	0	1.165484	2.498899	-2.370806
34	6	0	1.089259	3.171872	-3.588158
35	6	0	-0.145282	3.380467	-4.198051
36	6	0	-1.305496	2.915356	-3.583561
37	6	0	-1.231767	2.241519	-2.366705
38	1	0	-2.139569	1.889358	1.893484
39	1	0	-2.273115	3.078011	4.048551
40	1	0	-0.205866	3.904191	5.145881
41	1	0	1.995092	3.531583	4.061002
42	1	0	2.126643	2.341155	1.903825
43	1	0	2.127385	2.342559	-1.901933
44	1	0	1.996931	3.532921	-4.059192
45	1	0	-0.203293	3.90388	-5.146115
46	1	0	-2.270938	3.076152	-4.05069
47	1	0	-2.138507	1.887693	-1.895466

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Туре	Х	Y	Z
1	6	0	-3.86318	-2.9934	-0.00036
2	6	0	-4.56328	-1.76264	-0.0004
3	6	0	-3.82582	-0.58285	-0.0004
4	6	0	-2.41882	-0.56727	-0.00034
5	6	0	-1.73194	-1.8176	-0.00032
6	6	0	-2.48808	-3.01245	-0.00034
7	1	0	-4.40078	-3.93033	-0.00035
8	1	0	-4.31377	0.384255	-0.00045
9	1	0	-1.93754	-3.94574	-0.00033
10	6	0	2.631117	-0.16191	0.000025
11	6	0	1.800622	-1.30013	-0.00026
12	6	0	4.026296	-0.33569	0.000056
13	6	0	4.5919	-1.6055	-0.00016
14	6	0	3.728463	-2.72995	-0.00041
15	6	0	2.356598	-2.58495	-0.00045
16	1	0	4.631434	0.559968	0.000277
17	1	0	4.14513	-3.72917	-0.00057
18	1	0	1.697279	-3.44263	-0.00065
19	7	0	-0.37875	-1.9838	-0.00033
20	7	0	0.433459	-0.99918	-0.0002
21	8	0	2.06548	1.02976	0.000274
22	8	0	-1.78562	0.577625	-0.00036
23	6	0	-6.10046	-1.69443	-0.00042
24	6	0	6.11357	-1.82665	-0.00014
25	32	0	0.108125	1.071043	0.000119
26	6	0	-6.75182	-3.0898	-0.00045
27	6	0	-6.57894	-0.93941	1.262178
28	6	0	-6.57895	-0.93936	-1.26297
29	6	0	6.900815	-0.50403	0.000035
30	6	0	6.513975	-2.62608	1.262334
31	6	0	6.514026	-2.62578	-1.2628

32	1	0	-7.83968	-2.98345	-0.00054
33	1	0	-6.4776	-3.66788	-0.88685
34	1	0	-6.47775	-3.66786	0.886004
35	1	0	-7.67173	-0.88735	1.276938
36	1	0	-6.19463	0.082036	1.294936
37	1	0	-6.2507	-1.45067	2.171101
38	1	0	-6.25069	-1.45057	-2.17192
39	1	0	-7.67174	-0.88733	-1.27773
40	1	0	-6.19468	0.082103	-1.29569
41	1	0	7.973141	-0.71672	0.000032
42	1	0	6.683637	0.098396	-0.88592
43	1	0	6.683598	0.098178	0.886127
44	1	0	7.595418	-2.79289	1.275532
45	1	0	6.025323	-3.60203	1.299167
46	1	0	6.242536	-2.08133	2.17053
47	1	0	6.025376	-3.60172	-1.29988
48	1	0	6.24262	-2.08081	-2.17087
49	1	0	7.59547	-2.79258	-1.27599
50	6	0	-0.01006	1.988709	1.740886
51	6	0	-0.00961	1.989644	-1.7402
52	6	0	1.144893	2.500691	-2.35072
53	6	0	1.065421	3.182617	-3.56305
54	6	0	-0.16731	3.367071	-4.18451
55	6	0	-1.32196	2.868258	-3.58614
56	6	0	-1.24425	2.186254	-2.37381
57	6	0	1.144293	2.499394	2.351998
58	6	0	1.064494	3.180733	3.564637
59	6	0	-0.16841	3.36496	4.185808
60	6	0	-1.32291	2.866509	3.586853
61	6	0	-1.24488	2.185089	2.374215
62	1	0	2.104967	2.360057	-1.87296
63	1	0	1.969045	3.569489	-4.02164
64	1	0	-0.22809	3.897263	-5.12879
65	1	0	-2.28612	3.009231	-4.06267

66	1	0	-2.14577	1.805369	-1.9135
67	1	0	2.104497	2.358952	1.874445
68	1	0	1.968003	3.567318	4.023693
69	1	0	-0.22945	3.894707	5.130325
70	1	0	-2.28721	3.007318	4.063147
71	1	0	-2.14629	1.804495	1.913438

Center Atomic Atomic Coordinates (Angstroms) Y Ζ Х Number Number Type 1 6 0 -6.03495 -1.72036 -0.03738 2 0 1 -6.28124 0.733705 -3.72496 3 6 0 -8.51387 -1.44464 -0.24902 4 0 6 -8.15796 -2.67386 0.228378 5 8 0 1.795499 -0.01941 0.623366 32 6 0 0.099666 -0.09893 1.127504 7 6 0 2.468843 -2.97533 -0.10511 8 6 0 2.419864 -0.52228 -0.04874 9 1 0 -0.01602 4.332591 0.411381 0 10 16 -7.12877 -0.45731 -0.56649 0 0.346967 11 6 -6.75116 -2.83073 12 1 0 1.90763 -3.90156 -0.13363 13 1 0 4.382016 -3.90479 -0.17557 14 6 0 1.722041 -1.76942-0.06941 15 6 0 3.826439 -0.54556 -0.05865 16 6 0 4.546275 -1.73798 -0.0914 0 17 6 -0.11709 3.838107 -2.97165 0 18 6 6.007423 -1.74439 -0.09826 19 0 6.859111 -2.758950.2796576 20 0 6 8.233285 -2.427020.15799721 6 0 8.429579 -1.16073 -0.31712 22 6 0 -1.20283 2.758796-2.07811 23 1 0 6.508134 -3.70757 0.662464

GAzPh-Th

24

9.041668

-3.09758

0.416986

0

1

25	1	0	9.361975	-0.65421	-0.5135
26	6	0	-1.16527	3.52432	-3.24145
27	6	0	0.036423	3.70904	-3.92089
28	6	0	-0.03642	2.164072	-1.57516
29	16	0	6.933277	-0.35208	-0.62497
30	6	0	-2.63	-0.08645	0.062801
31	6	0	-1.80242	-1.22776	-0.03873
32	6	0	-4.01994	-0.2554	0.064974
33	6	0	-4.58328	-1.52929	-0.04038
34	6	0	-3.7305	-2.6566	-0.15009
35	6	0	-2.35944	-2.50783	-0.14489
36	1	0	-4.63942	0.62602	0.175102
37	1	0	-4.16098	-3.64235	-0.26883
38	1	0	-1.70002	-3.36056	-0.23418
39	7	0	-0.43632	-0.93217	-0.02283
40	7	0	0.372412	-1.92374	-0.07069
41	8	0	-2.05468	1.094876	0.167956
42	1	0	-8.87488	-3.43948	0.49379
43	1	0	-9.5029	-1.05833	-0.44114
44	6	0	1.202428	3.127015	-3.42937
45	6	0	1.167142	2.362355	-2.26533
46	6	0	0.097122	1.91143	1.896387
47	6	0	-1.03289	2.315193	2.621869
48	6	0	-0.89815	2.900784	3.878911
49	6	0	0.366072	3.096661	4.429427
50	6	0	1.496768	2.705844	3.715941
51	6	0	1.363816	2.118194	2.459943
52	1	0	-2.13975	2.616638	-1.55688
53	1	0	-2.07749	3.975323	-3.61671
54	1	0	0.064357	4.303709	-4.82754
55	1	0	2.142702	3.267219	-3.95156
56	1	0	2.078057	1.918696	-1.88744
57	1	0	-2.01699	2.169699	2.197444
58	1	0	-1.78339	3.204213	4.427247

59	1	0	0.469897	3.552583	5.408083
60	1	0	2.485045	2.857296	4.13641
61	1	0	2.247251	1.819136	1.912215

GAzPh-NPh2

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Туре	X	Y	Z
1	6	0	-2.46608	2.513077	-0.04294
2	6	0	-3.8346	2.514493	-0.05067
3	6	0	-4.53933	1.27714	-0.06733
4	6	0	-3.81963	0.079759	-0.07615
5	6	0	-2.41756	0.062928	-0.06175
6	6	0	-1.71352	1.309767	-0.04571
7	7	0	-0.368	1.463777	-0.04061
8	7	0	0.4449	0.470008	-0.02006
9	6	0	1.811094	0.764472	-0.02748
10	6	0	2.640248	-0.37656	0.070283
11	6	0	4.028729	-0.21548	0.078867
12	6	0	4.589592	1.061033	-0.02237
13	6	0	3.745412	2.192741	-0.12699
14	6	0	2.373402	2.041622	-0.12425
15	8	0	-1.7881	-1.08253	-0.09327
16	32	0	0.105155	-1.57402	0.058781
17	8	0	2.058662	-1.55785	0.174008
18	6	0	-0.13411	-2.41044	1.829313
19	6	0	0.0781	-2.58936	-1.63252
20	7	0	5.991237	1.228579	-0.03378
21	6	0	6.58812	2.356759	0.596184
22	6	0	7.627475	3.051247	-0.03667
23	6	0	8.220955	4.144553	0.585528
24	6	0	7.780917	4.571958	1.83724
25	6	0	6.743417	3.886345	2.466673
26	6	0	6.154777	2.781989	1.858958
27	6	0	6.832849	0.248201	-0.63495

28	6	0	6.535205	-0.25963	-1.90612
29	6	0	7.361728	-1.21357	-2.48999
30	6	0	8.502696	-1.66335	-1.82677
31	6	0	8.805586	-1.15304	-0.56608
32	6	0	7.975553	-0.20985	0.032119
33	7	0	-5.93817	1.271521	-0.0595
34	6	0	-6.6664	0.160949	0.47219
35	6	0	-7.67548	-0.4442	-0.28332
36	6	0	-8.40056	-1.50823	0.245443
37	6	0	-8.12083	-1.98563	1.524068
38	6	0	-7.11285	-1.38437	2.276723
39	6	0	-6.39264	-0.31216	1.76043
40	6	0	-6.68326	2.346349	-0.63368
41	6	0	-6.36431	2.835372	-1.9059
42	6	0	-7.10271	3.877336	-2.45863
43	6	0	-8.17528	4.430221	-1.76131
44	6	0	-8.50173	3.935021	-0.49992
45	6	0	-7.75937	2.90366	0.066173
46	1	0	-1.90849	3.441628	-0.01624
47	1	0	-4.38239	3.445745	-0.02373
48	1	0	-4.32969	-0.87341	-0.10642
49	1	0	4.652508	-1.09436	0.170069
50	1	0	4.182538	3.177194	-0.2247
51	1	0	1.717457	2.897154	-0.21382
52	1	0	7.964798	2.728303	-1.01401
53	1	0	9.023586	4.672204	0.082332
54	1	0	8.241557	5.427849	2.31657
55	1	0	6.397114	4.202807	3.444296
56	1	0	5.358186	2.243314	2.357239
57	1	0	5.654729	0.09497	-2.42772
58	1	0	7.118478	-1.59738	-3.4745
59	1	0	9.147632	-2.4025	-2.28747
60	1	0	9.686564	-1.49882	-0.03683
61	1	0	8.20834	0.177483	1.016538

62	1	0	-7.8881	-0.07678	-1.27996
63	1	0	-9.17984	-1.97093	-0.34948
64	1	0	-8.68348	-2.81744	1.931459
65	1	0	-6.89313	-1.74274	3.276037
66	1	0	-5.61566	0.161453	2.348079
67	1	0	-5.54031	2.396205	-2.45497
68	1	0	-6.8459	4.247893	-3.4446
69	1	0	-8.75248	5.237072	-2.19748
70	1	0	-9.33233	4.359613	0.052533
71	1	0	-8.00841	2.524121	1.049713
72	6	0	-1.41468	-2.68275	2.330549
73	6	0	0.977802	-2.78565	2.596443
74	6	0	0.81238	-3.40591	3.83331
75	6	0	-1.57863	-3.30681	3.565263
76	6	0	-0.46555	-3.66766	4.321201
77	1	0	1.972317	-2.59234	2.217535
78	1	0	1.684434	-3.68613	4.414386
79	1	0	-2.28408	-2.40499	1.749712
80	1	0	-2.57743	-3.51127	3.93598
81	1	0	-0.59346	-4.1519	5.283387
82	6	0	-1.10233	-2.74983	-2.37049
83	6	0	1.24791	-3.20626	-2.09955
84	6	0	1.236394	-3.95688	-3.27328
85	6	0	-1.11172	-3.49846	-3.54566
86	6	0	0.057501	-4.10348	-4.00046
87	1	0	2.167316	-3.09179	-1.54126
88	1	0	2.15092	-4.42679	-3.61899
89	1	0	-2.01575	-2.28955	-2.01917
90	1	0	-2.03468	-3.60926	-4.1048
91	1	0	0.049605	-4.6867	-4.91505

Graphical Abstract

<Title>

Enhancement of Near-infrared Emission Based on Hypervalent Germanium(IV)-Fused Azobenzene Compounds with Electron-donating Groups

<Authors' names>

Masayuki Gon, Misao Yaegashi, Kazuo Tanaka*

<Summary>

We synthesized hypervalent germanium-fused azobenzene (GAz) compounds with distorted trigonal bipyramidal geometry. They exhibited near-infrared (NIR) emission and their optical properties were highly enhanced by introducing electron-donating groups. The strategy is useful for creating novel NIR luminescent materials based on heteroatoms.

<Diagram>

