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# Ladder π-conjugated materials with main group elements*

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*Abstract*: Ladder-type π-conjugated skeletons are promising building units for new materials for organic electronics, wherein their annelated coplanar structures enhance the π-conjugation, leading to a set of desirable properties such as intense fluorescence and high carrier mobility. As a new entry into this class of skeletons, we now disclose two series of ladder molecules, i.e., silicon- and carbon-bridged oligo(*p*-phenylenevinylene)s and thiophene- and selenophene-based heteroacenes. The former ladder molecules contain the silole substructure in which the silicon bridges affect the electronic structure and thus photophysical properties through the σ*–π* conjugation. The latter heteroacenes can be recognized as the heteroatom analogs of acenes and may be promising materials for organic thin film transistors. These two series of molecules have been synthesized based on newly developed intramolecular cyclizations of acetylenic compounds.

*Keywords*: ladder oligo(*p*-phenylenevinylene)s; silicon; heteroacenes; intramolecular cyclization; fluorescence.

## INTRODUCTION

π-Conjugated molecules are key materials for a broad spectrum of applications in organic electronics, and their importance has been rapidly increasing in recent years. One crucial issue in their molecular designs is how to create molecules that have desirable electronic structures as well as desirable solid-state structures. In this regard, our research includes two key terms, "ladder molecule" and "main group elements."

For the ladder π-conjugated molecules, their most significant virtue may be their rigid coplanar structures that promise enhanced π-conjugation, leading to a set of desirable properties, such as an intense luminescence and high carrier mobility. In the last decade, the persistent interest in this field has led to the synthesis of various fascinating ladder molecules [1], such as ladder oligo- or poly(*p*-phenylene)s with carbon [2] or heteroatom bridges [3], polyacenes and heteroacenes [4], and related π-conjugated systems [5].

On the other hand, main group element-containing π-conjugated molecules have also received recent keen attention [6]. Among the elements, we particularly focused our attention on the elements from groups 13 to 16, such as B, Si, P, S, and Se. These main group compounds have notable features such as effective orbital interactions, diversity in coordination numbers, and unique structural features

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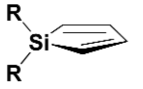
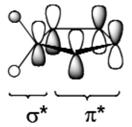
around the main group element atoms. Exploiting these characteristic features in the designs would lead to new materials with unique functions and properties [7]. Among these, the orbital interaction is particularly important in terms of electronic tuning [8]. For example, in the silole ring, a silicon analog of cyclopentadiene, its lowest unoccupied molecular orbital (LUMO) consists of the orbital interaction ($\sigma^*$–$\pi^*$ conjugation) between the $\sigma^*$ orbital of two $\sigma$-bonds and the $\pi^*$ orbital of the butadiene moiety [9]. This orbital interaction effectively decreases the LUMO level and makes this ring attractive as a building unit for new electron-accepting $\pi$-systems [10]. In fact, one of the silole derivatives we recently synthesized, 2,5-bis(bipyridyl)silole **1**, has a significantly high performance as an electron-transporting material for organic light-emitting diodes [11] and is currently one of the high-level standard materials in this field [12]. This fact well demonstrates how important the orbital interaction between the main group elements and $\pi$-conjugated frameworks is in the designs of new $\pi$-conjugated materials. Recent theoretical calculations also suggest that this type of orbital interaction effectively occurs not only in other five-membered ring systems, such as borole and phosphole [13], but also in the polymeric systems consisting of these heterole rings [14].

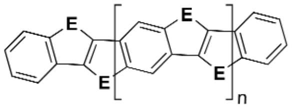


**Silole**

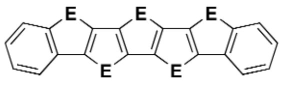


**LUMO of Silole**

**1**



**2** (E = SiR$_2$ or CR$_2$)

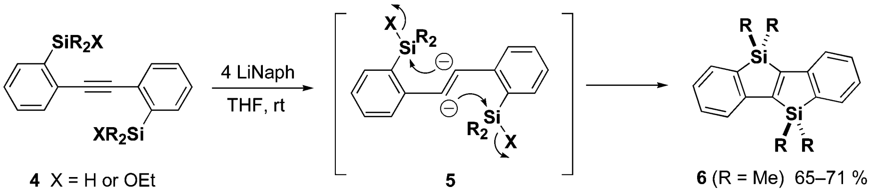


**3** (E = S or Se)

On the basis of these considerations, we have chosen two types of ladder molecules as the target molecules, that is, the element-bridged ladder oligo(*p*-phenylenevinylene)s **2** and the thiophene- and selenophene-based heteroacenes **3**. The former ladder systems are attractive not only as a model system for fully ladder poly(*p*-phenylenevinylene)s, but also as a fundamental framework for low-molecular-weight functional materials. Nevertheless, these types of ladder systems have not been synthesized except for the simplest stilbene derivatives with carbon [15], silicon [16], or heteroatom bridges [17]. On the other hand, the thiophene- and selenophene-based heteroacenes have also attracted much attention as the heteroatom analogs of linearly fused acenes, such as pentacene, which have been the most widely studied in the field of organic thin film transistors [18]. However, only limited examples have been reported in the literature, including dibenzo-annulated dithieno[3,2-*b*:2',3'-*d*]thiophene [19], fused oligothiophenes consisting of five or seven thiophene rings [20,21], and a fully fused polythiophene [22]. These are mostly due to the lack of useful synthetic routes in terms of efficiency as well as accessible structural diversity. Under these backgrounds, we commenced this research for the exploration of a conceptually new synthetic methodology for these two ladder $\pi$-conjugated systems. We now disclose two types of new intramolecular cyclizations of acetylenic compounds.

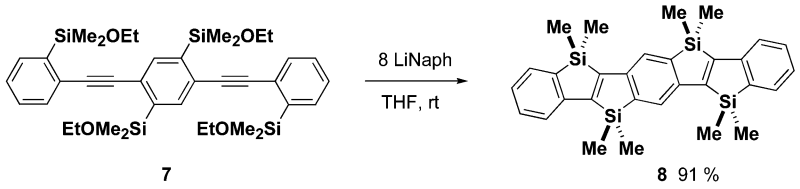
## INTRAMOLECULAR REDUCTIVE CYCLIZATION

As a general and facile synthetic route to the bis-silicon-bridged stilbene (5,10-disila-5,10-dihydroindeno[2,1-*a*]indene) skeleton, we developed a new intramolecular reductive cyclization (Scheme 1) [23]. Thus, bis(*o*-silylphenyl)acetylenes **4** are employed as the starting material and are treated with a reducing agent, such as lithium naphthalenide. A two-electron reduction takes place at the acetylene moiety to formally produce a dianionic intermediate **5**, which further undergoes a subsequent double cyclization to yield the desired bis-silicon-bridged stilbene skeleton **6**. The key point of this reaction is the choice of the leaving group on the silicon moiety: the leaving group must be inert toward the lithium naphthalenide, and, therefore, we chose hydrogen or alkoxy group.



**Scheme 1**

It is noteworthy that the cyclization proceeds efficiently in the case of a diacetylenic starting material, as shown in Scheme 2. When compound **7** was treated with excess lithium naphthalenide, the cyclization simultaneously proceeded on the two acetylene moieties to give the desired compound **8**. Its yield exceeded 90 %, demonstrating that this reaction almost quantitatively proceeds. The crystal structure analysis proved that this compound indeed has a flat coplanar π-conjugated framework. The dihedral angle between the central benzene and outer phenyl rings is only 3.9°.

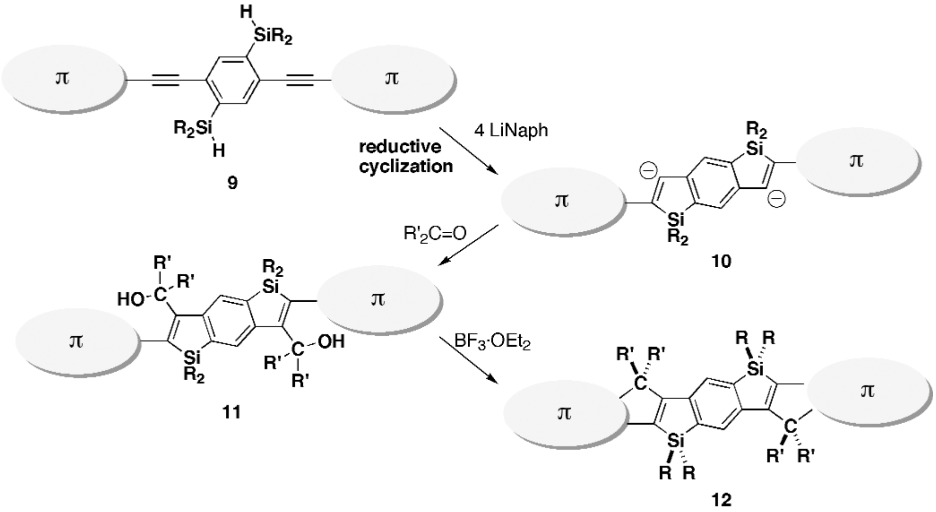


**Scheme 2**

On the basis of this new cyclization, we have so far synthesized a series of derivatives, including the all silicon-bridged stilbene **6** and distyrylbenzenes **8** [23], stilbene-based π-conjugated polymers [24], partially bridged silaindene derivatives [25], and the silicon- and carbon-bridged ladder oligo(*p*-phenylenevinylene)s [26]. Among these, the next section will focus on the synthesis of the last class of molecules.

## SILICON- AND CARBON-BRIDGED LADDER OLIGO(*p*-PHENYLENEVINYLENE)S

Our strategy to access the fully bridged ladder oligo(*p*-phenylenevinylene)s is schematically outlined in Scheme 3, in which we employ acetylenic starting materials **9** containing only one silyl group per one acetylene moiety [26]. This type of substrate similarly undergoes the reductive cyclization to produce a dianionic intermediate **10**, which can be trapped with a ketone to produce the corresponding dialcohol **11**. In the presence of a Lewis acid, finally, the dialcohol undergoes the Friedel–Crafts-type annulation to produce the desired silicon- and carbon-bridged ladder π-conjugated system **12**. Notably, in Scheme 3, the diethynylbenzene moiety **A** serves as the synthetic equivalent of a 5-ring fused spacer unit **A'**, that connects two π-conjugated moieties (Chart 1). On the basis of this idea, we carried out the synthesis of an 11-ring fused compound **14** (Chart 2). Thus, we first introduced two fluorene units into the terminal positions of the diethynylbenzene **A**. The cyclization of the resultant compound **13** proceeded at the two acetylene moieties to produce the corresponding diol, which subsequently underwent the Friedel–Crafts annulation in the presence of $BF_3 \cdot OEt_2$ to produce the fully fused compound **14**. Similarly, a 13-ring fused oligo(*p*-phenylenevinylene) **16** was also synthesized by employing a tetraacetylenic compound **15** as the starting material. In this case, the cyclization simultaneously proceeded at four acetylenic moieties. The subsequent Friedel–Crafts annulation gave the fully fused 13-ring π-conjugated compound **16** in good yield. This is the longest example of the ladder oligo(*p*-phenylenevinylene) reported so far. X-ray crystallography proved that these fused π-conjugated systems have highly coplanar π-conjugated frameworks and the lengths of the molecules are about 2.5 and 2.9 nm for **14** and **16**, respectively.



**Scheme 3**

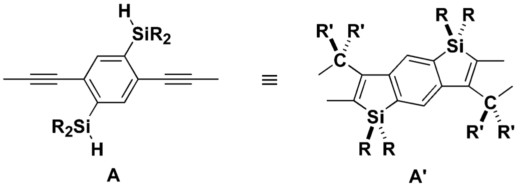


**Chart 1**

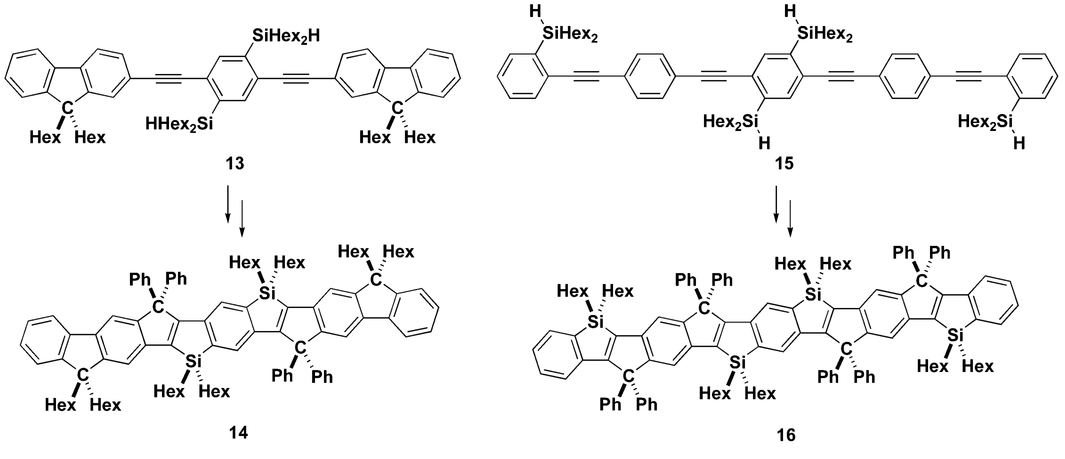


**Chart 2**

## SILICON EFFECT ON THE FLUORESCENCE PROPERTIES

One interesting issue in this chemistry is how the silicon atoms affect the photophysical properties. Figure 1 shows a comparison of the fluorescence spectra in THF between the bis-silicon-bridged stilbene **6** and its carbon analog **17** [23]. While the carbon-bridged compound does not show a fluorescence in the visible region due to its rather short π-conjugation length, the silicon-bridged one exhibits an intense blue emission. In terms of the fluorescence maximum wavelength, about a 60-nm red shift is observed from **17** ($\lambda_{\mathrm{max,em}}$ 367 nm) to **6** ($\lambda_{\mathrm{max,em}}$ 426 nm). This substantial effect is related to the contribution of the σ*–π* conjugation in the silole substructure in **6**. According to the theoretical calculation at the HF/6-31G(d) level of theory, the LUMO of **6** is 0.55 eV lower than that of the carbon analog **17** due to the orbital interaction.

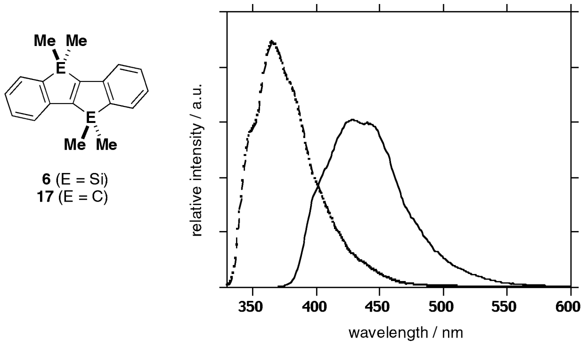


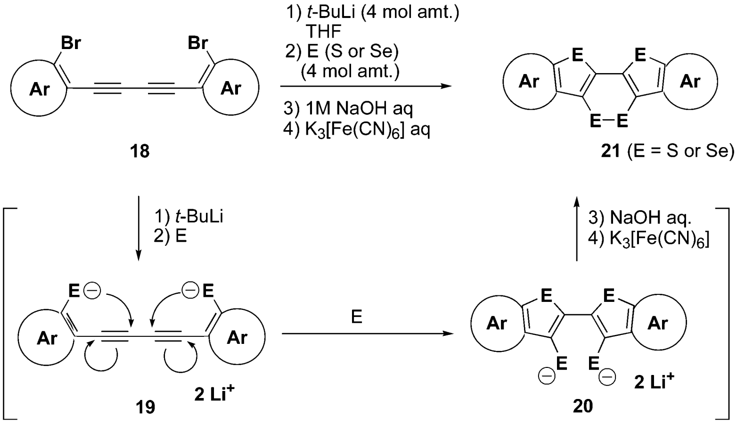
**Fig. 1** Fluorescence spectra of compounds **6** (solid line) and **17** (dashed line) in THF.

While the detailed study of the fluorescence properties of a series of bridged distyrylbenzenes revealed that the incorporation of the silicon bridges into the ladder oligo(*p*-pheneylenevinylene)s tends to slightly decrease the fluorescence quantum yield [27], the extended ladder molecules still exhibit an intense fluorescence. Thus, the 11- and 13-ring fused systems **14** and **16** show intense green and yellow fluorescences at 499 and 523 nm, with the quantum yield of 0.40 and 0.59, respectively.

## INTRAMOLECULAR TRIPLE CYCLIZATION

To access the other target molecules, the thiophene- or selenophene-based heteroacenes, we developed a general and versatile synthetic methodology based on a new intramolecular triple cyclization and the subsequent dechalcogenation reaction [28].

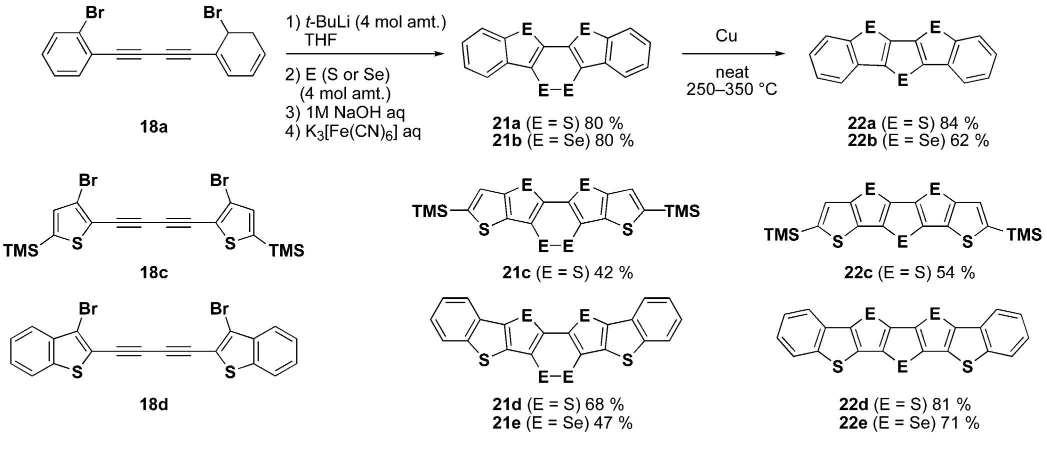
The intramolecular triple cyclization employs bis(*o*-haloaryl)diacetylenes **18** as the starting material, and constructs a heterole-1,2-dichalcogenin-heterole tricyclic structure in one pot, as shown in Scheme 4. This reaction includes three steps. The first step is the dilithiation of **18** with *t*-BuLi in THF, followed by trapping with a chalcogen element to produce a dianionic intermediate **19**. In the second step, the dianion centers attack the inner carbon atoms of the diacetylene moiety, followed by trapping with the remaining chalcogen element to afford a doubly cyclized intermediate **20**. Through the counter ion exchange by the addition of a 1 M NaOH aqueous solution, in the final step, potassium ferricyanide(III) is then employed as an oxidant to convert **20** to a fused 1,2-dichalcogenin compound **21**. Advantageously, this reaction proceeds not only with sulfur, but also with selenium. This is the first synthesis of 1,2-diselenin-containing fused π-conjugated compounds.



Scheme 4

## THIOPHENE- AND SELENOPHENE-BASED HETEROACENES

The transformation from the six-membered 1,2-dichalcogenin ring to the five-membered heterole ring can be easily achieved by the dechalcogenation reaction mediated by copper metal, according to Schroth's report [19]. Therefore, the combination of this triple cyclization with the dechalcogenation reaction is a general synthetic method for the synthesis of heteroacenes. In fact, on the basis of this procedure, we have synthesized a variety of heteroacene derivatives, including dibenzo-annulated dithieno[3,2-*b*:2',3'-*d*]thiophene **22a** and its selenophene analog **22b**, silyl-substituted pentathioacene **22c**, benzo-annulated pentathioacene **22d** and its selenophene derivative **22e**, in moderate to good yields, as shown in Scheme 5.



Scheme 5

## STRUCTURAL FEATURES OF THE LADDER π-ELECTRON SYSTEMS

On the basis of the new intramolecular cyclization of acetylenic starting materials, we have synthesized two types of ladder molecules, the silicon- and carbon-bridged ladder molecules and the heteroacenes. Notably, these two series of compounds are very contrasting to each other in terms of molecular structures, as shown in Fig. 2. Thus, while the heteroacenes are very flat molecules without any substituents on the surface of the π-conjugated framework, the silicon- and carbon-bridged systems have a flat π-conjugated framework which is covered and insulated by the substituents on the silicon and carbon bridges. The flat π-conjugated structure in the heteroacenes is apparently beneficial for forming a close-packing structure and, therefore, these types of compounds are good candidates for applications to the organic thin film transistors. In fact, our preliminary study showed that the benzo-annulated pentathioacene **22d** has a high hole-career mobility comparable to that of pentacene [29]. In contrast, the latter structure in the silicon-bridged ladder systems is of a significant disadvantage in terms of the close π-stacking formation. However, exploiting this structural feature in the molecular design would give us a chance to construct a totally new self-assembly. For example, we recently found that one derivative of the bis-silicon-bridged stilbene, the dicarboxylic acid **23**, forms an interesting crystal packing structure [30]. As shown in Fig. 3, the dimeric motif of the carboxylic acid moiety forms one-dimensional network chains and the resultant chains are arranged in parallel to one another to form π-sheet-like structures, each of which is separated by the hexyl groups on the silicon atoms. Utilization of this self-assembly structure would lead to a new material with an interesting solid-state structure.

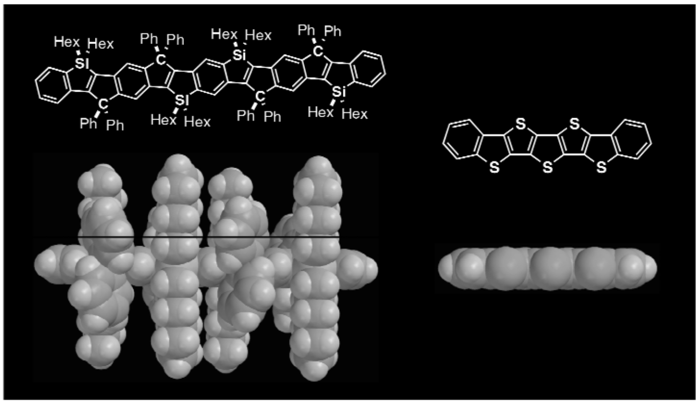
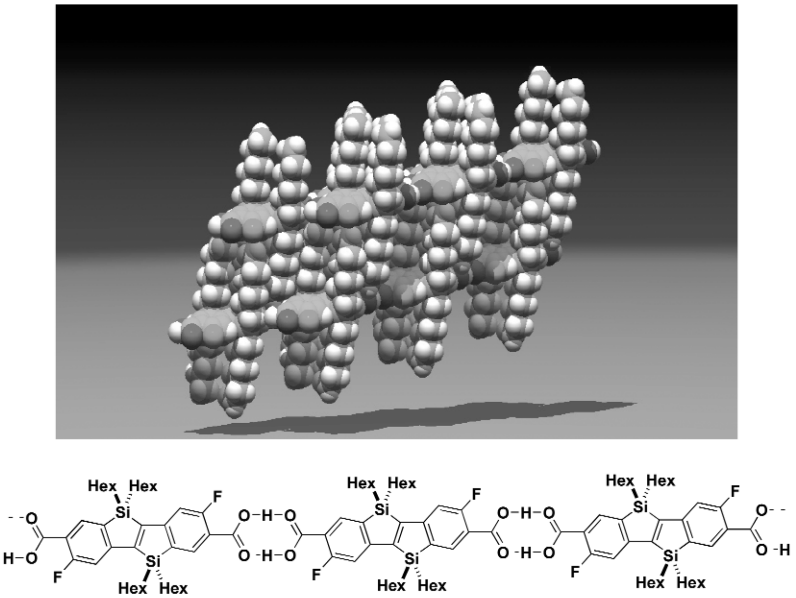


**Fig. 2** Side view of molecular structures: left, a structure of **16** determined by X-ray crystallography; right, a computer-generated structure of **22d**.



23

**Fig. 3** Crystal packing structure of Si-bridged-stilbenedicarboxylic acid **23**.

## CONCLUSION

In summary, our major subject in this research is to create a new series of ladder π-conjugated materials containing main group elements. On the basis of two types of new intramolecular cyclizations of acetylenic starting materials, we have established the synthetic routes to the silicon- and carbon-bridged oligo(*p*-phenylenevinylene)s and the thiophene- and selenophene-based heteroacenes. We are now going to do further structural modification of these ladder systems and use them in a broad spectrum of applications for organic electronics, such as light-emitting diodes and thin film transistors.

## ACKNOWLEDGMENTS

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