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ARTICLE

Synthesis of 2- and 6-thienylazulenes by palladium-catalyzed direct arylation of 2- and 6-haloazulenes with thiophene derivatives

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Taku Shoji,^{*a,b} Akifumi Maruyama,^b Takanori Araki,^a Shunji Ito,^c and Tetsuo Okujima^d

Preparation of 2- and 6-thienylazulene derivatives was established by the palladium-catalyzed direct cross-coupling reaction of 2- and 6-haloazulenes with the corresponding thiophene derivatives in good yield. Several thienylazulene derivatives were also conducted to the reaction with 2-chloroazulene derivative in the presence of the palladium-catalyst to afford the thiophene derivatives with two azulene functions in good yield.

Introduction

Azulene has attracted the interest of many research groups owing to its unusual properties as well as its beautiful blue color.¹ Recently, much attention has been focused on thienylazulene derivatives and their polymeric materials owing to their application to organic electronic materials such as field effect transistors (FETs), photovoltaics (PVs), light-emitting diodes (LEDs), and so on.² Therefore, we have advanced with development of an efficient synthetic method for 2- and 6-thienylazulene derivatives that should contribute to the construction of the organic materials.³

Since the 2- and 6-positions of azulene derivatives are usually inert to the electrophilic substitution reactions in contrast to the high reactivity at those of 1- and 3-positions,⁴ we have developed several synthetic procedures for 2- and 6-arylazulene derivatives by utilizing transition-metal-catalyzed cross-coupling reactions (e.g., Suzuki–Miyaura and Stille cross-coupling reactions) of 2- and 6-azulenyl metal reagents.⁵ Although the azulenyl metal reagents were useful for the preparation of polyaromatic systems with multiple 2- and 6-azulenyl groups, preparation of the metal reagents for the transition-metal-catalyzed reactions sometimes causes difficulty and the most promising azulenylborane reagents are relatively unstable and undergo easy hydrolysis to afford hydrocarbon derivatives.⁶ Murafuji and co-workers also

reported the synthesis of biaryl-type compounds containing 2-amino-6-azulenyl moiety by Suzuki–Miyaura cross-coupling reaction of the corresponding aryl halides with 6-borylazulene derivative, which is prepared by Miyaura–Ishiyama borylation reaction of **3** (structure of **3** is shown in Scheme 1).^{7,8} Although the borylation of **3** proceeds relatively efficient with good product yield (73%), the total yield of the desired biaryl-type compounds from **3** become relatively low due to the two-step protocols (i.e., borylation and the following cross-coupling reaction).⁷ We have also reported an efficient synthetic procedure by utilizing aryl- and heteroarylmagnesium ate complexes including with 2- and 3-thienyl derivatives, which are generated in situ from the corresponding aryl and heteroaryl halides, to afford 2- and 6-(aryl- and heteroaryl)azulenes in sufficient yield.^{3,9} However, the procedure also requires the prior preparation of aryl- and heteroarylmagnesium ate complexes under the dehydrated conditions. Because the functionalized azulene derivatives should become a promising candidate for the production of advanced materials,^{2,10} development of a more general and an efficient method for the preparation of azulene derivatives with 2- and 6-thienyl substituents from readily available reagents would have great importance.

Recently, transition-metal catalyzed direct arylation have attracted interest as a cross-coupling reaction for the next generation.¹¹ Especially, Fagnou and co-workers have developed a direct arylation reaction by palladium-catalyzed C–H bond activation as a new type of the cross-coupling reaction.¹² In 2011, Schipper and Fagnou have also reported the synthesis of thiophene based organic electronic materials by the palladium-catalyzed direct arylation of thiophene derivatives with the corresponding aryl halides.¹³ Since the reaction proceeds in high yield without using an organometallic counterpart, many thienylarenes and their polymers have been prepared by the procedure.¹⁴ Although the direct arylation reaction seems to be an effective synthetic procedure, there is no report for the application of such a

^a Department of Chemistry, Faculty School of Science, Shinshu University, Matsumoto 390-8621, Nagano, Japan.

^b Department of Material Science, Graduate School of Science and Technology, Shinshu University, Matsumoto 390-8621, Nagano, Japan.

^c Graduate School of Science and Technology, Hiroshima University, Hiroshima 036-8561, Aomori, Japan.

^d Department of Chemistry and Biology, Graduate School of Science and Engineering, Ehime University, Matsuyama 790-8577, Ehime, Japan

† Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: Experimental, copies of ¹H and ¹³C NMR, UV/Vis spectra, cyclic and differential pulse voltammograms of reported compounds. See DOI: 10.1039/x0xx00000x

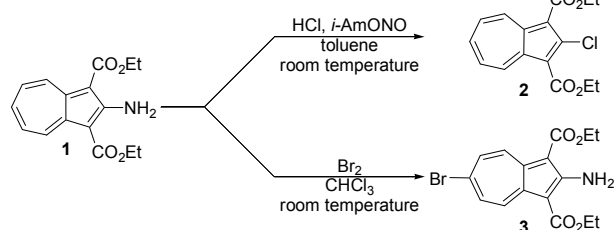
direct cross-coupling reaction to the azulene derivatives, so far. We have applied the method reported by Fagnou *et al.* to establish practical and efficient synthetic procedure for the preparation of 2- and 6-thienylazulene derivatives, which have growth potential to organic materials.

Herein, we describe an efficient synthesis of 2- and 6-thienylazulene derivatives **9–17** by the direct palladium-catalyzed cross-coupling reaction of 2-chloroazulene **2** and 6-bromoazulene **3** with several thiophene derivatives. 2,5-Di(azulenyl)thiophene derivatives **19–22** were also prepared by the reaction of **2** with thienylazulenes under the similar reaction conditions. Electronic properties of the new thienylazulenes obtained by this research were characterized by absorption spectroscopy and theoretical calculations. Electrochemical analysis of the compounds was also investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV).

Results and discussion

Synthesis

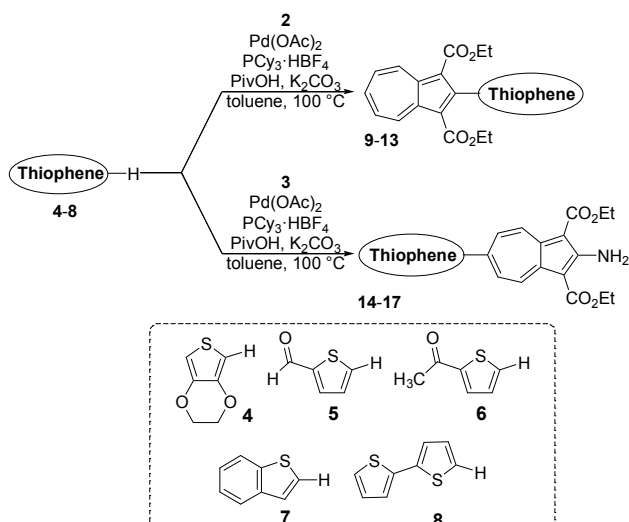
1,3-Bis(ethoxycarbonyl)-2-chloroazulene (**2**) and 2-amino-6-bromo-1,3-bis(ethoxycarbonyl)azulene (**3**) were prepared by Nozoe's procedure using 2-amino-1,3-bis(ethoxycarbonyl)azulene (**1**) as a starting material (Scheme 1).¹⁵



Scheme 1 Synthesis of 2-chloro- and 6-bromoazulene derivatives **2** and **3**.

We have attempted the cross-coupling of **2** and **3** with thiophene derivatives **4–8** by the catalytic system of 5 mol% Pd(OAc)₂, 10 mol% PCy₃·HBF₄ and 30 mol% pivalic acid (PivOH) in the presence of K₂CO₃, which has been previously reported by Schipper and Fagnou.¹³ The structure and yield of the products **9–17** are summarized in Table 1. Overview of the cross-coupling reaction is shown in Scheme 2.

The coupling reaction of **2** with 3,4-ethylenedioxythiophene (EDOT) (**4**) under the catalytic system gave **9** in 81% yield, along with bis-adduct **19** in 7% yield, although the reaction was carried out by utilizing aryl chloride as a substrate. It is well-known that the aryl chlorides are usually less reactive substrate toward the palladium-catalyzed cross-coupling reaction compared with aryl iodides and bromides.¹⁶ Relatively high yield of the coupling product is attributable to the electron-withdrawing nature of the two ethoxycarbonyl groups at the 1,3-positions of the azulene ring, which should increase the reactivity toward the oxidative addition process of the palladium catalyst.

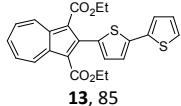
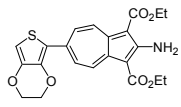
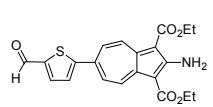
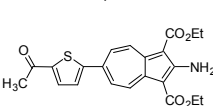
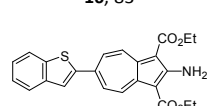


Scheme 2 Palladium-catalyzed cross-coupling reaction of **2** and **3** with thiophene derivatives **4–8**.

To examine the generality of the reaction with thiophene derivatives, we investigated the cross-coupling reaction of **2** with several commercially available thiophene derivatives **5–8** under the similar cross-coupling conditions (Table 1). 2-Formylthiophene (**5**) and 2-acetylthiophene (**6**) were reacted with **2** in the presence of the palladium catalyst to give the corresponding 2-thienylazulenes **10** and **11** in 90% and 89% yields, respectively (entries 2 and 3). The reaction of **2** with benzothiophene (**7**) gave the presumed substitution product **12** in 87% yield (entry 4). The desired mono-substitution product **13** was obtained in 85% yield along with di-substituted product **20** in 11% yield, when the reaction of **2** was carried out with two molar equivalent of 2,2'-bithiophene (**8**), which possesses a reactive site in each thiophene ring (entry 5).

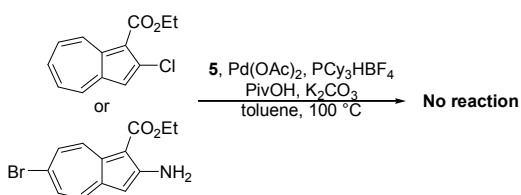
Table 1 Synthesis of 2- and 6-thienylazulene derivatives **9–17**.

Entry	Haloazulene	Thiophene	Product, Yield [%] ^a
1	2	4	9, 81
2	2	5	10, 90
3	2	6	11, 89
4	2	7	12, 87

5	2	8	 13 , 85
6	3	4	 14 , 80
7	3	5	 15 , 87
8	3	6	 16 , 83
9	3	7	 17 , 82
10	3	8	No reaction

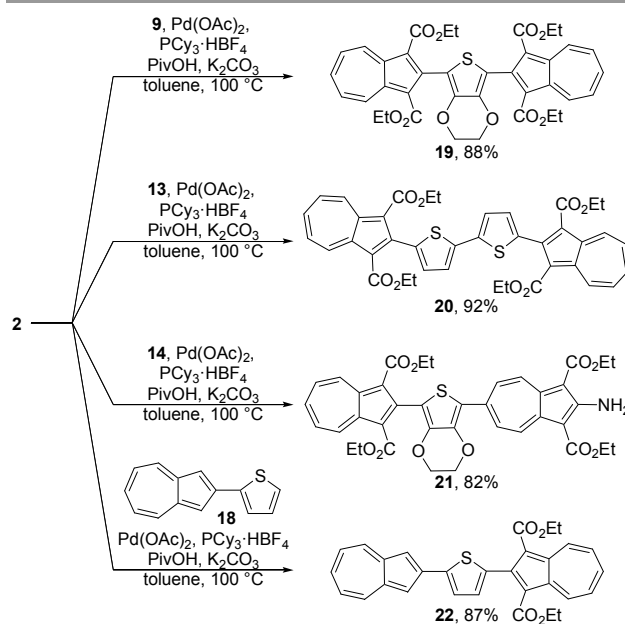
^a Isolated yield.

The cross-coupling reaction of 6-bromoazulene derivative **3** with thiophenes **4–8** was also examined under the similar catalytic conditions with those of the reaction of **2**. As summarized in Table 1, the coupling products **14–17** were obtained in good yield, except for the reaction with **8** that resulted into the recovery of the substrate. The reaction of **3** with EDOT gave the presumed 6-thienylazulene derivative **14** in 80% yield as a sole product (entry 6). 6-Thienylazulene derivatives **15** and **16** with formyl and acetyl group, respectively, at the 5-position of the thiophene ring were obtained in good yield (**15**: 87%, **16**: 83%) by the reaction of **3** with the corresponding thiophene derivatives (entries 7 and 8). The compound **3** also reacted with **7** effectively to give the presumed coupling product **17** in 82% yield (entry 9). To investigate the effect of carbonyl function on the azulene ring, the cross-coupling reaction of 2-chloro-1-ethoxycarbonylazulene and 2-amino-6-bromo-1-ethoxycarbonylazulene with **5** was also examined, but resulted into the complete recovery of the starting materials. Thus, the two electron-withdrawing groups at the both 1- and 3-positions of the azulene ring are essential for the success of the coupling reaction (Scheme 3).



Scheme 3 An attempt to the cross-coupling reaction of 2-chloro-1-ethoxycarbonylazulene and 2-amino-6-bromo-1-ethoxycarbonylazulene with **5**.

Recently, Katagiri *et al.* reported the preparation of 5,5'-di(2-azulenyl)-2,2'-bithiophene and 2,5-di(2-azulenyl)thieno[3,2-b]thiophene, which could be applied to organic field-effect transistors (OFETs), by Suzuki–Miyaura cross-coupling reaction.^{2e} However, their procedure requires 2-iodoazulene¹⁷ that is limited availability. If the thienylazulenes prepared by this research undergo the cross-coupling reactions, a new and facile synthetic route to di(azulenyl)thiophene derivatives could be established. Thus, the cross-coupling reaction of **2** with the thienylazulenes **9**, **13**, **14** and **18**³ was investigated to access the thiophene derivatives with two azulene functions. The structure and yield of the products **19–22** are summarized in Scheme 4. As expected, the cross-coupling reaction of **2** with **9** in the presence of 5 mol% Pd(OAc)₂, 10 mol% PCy₃·HBF₄ and 30 mol% PivOH provided 2,5-di(2-azulenyl)EDOT (**19**) in 88% yield as a sole product. As similar to the results on the preparation of **19** described above, the reaction of **2** with 2,2'-bithiophene derivative **13** in the presence of the palladium-catalyst gave 5,5'-di(2-azulenyl)-2,2'-bithiophene derivative **20** in 92% yield. Asymmetrically substituted di(azulenyl)thiophene derivatives **21** and **22** were also obtained in 82% and 87% yields, respectively, when the reaction of **2** were carried out with **14** and **18** in the presence of the palladium catalyst. These results imply the potential of the cross-coupling reaction to access the novel π-electron systems containing thienylazulene moieties, since the products **19–22** were obtained in high yield.



Scheme 4 Preparation of di(azulenyl)thiophene derivatives **19–22**.

Spectral properties

These new compounds **9–17** and **19–22** were fully characterized on the basis of their spectral data, as summarized in the Electronic Supplementary Information (ESI). The NMR spectroscopic assignment of the reported

compounds was confirmed by COSY, HMQC and HMBC experiments. HRMS of the compounds **9–17** and **19–22** ionized by EI or FAB showed the expected molecular ion peaks. These results are consistent with the given structure of these products.

The absorption maxima and their coefficients ($\log \epsilon$) in the UV/Vis spectra for 2- and 6-thienylazulenes **9–17** and di(azuleny)thiophenes **19–22** are summarized in the ESI. 2-Thienylazulenes **9–13** showed characteristic weak absorptions in the visible region at around 520 nm arising from the azulene system (see the ESI). These absorption bands of the 2-thienylazulenes **9–13** displayed the slight bathochromic shift compared with that of the parent compound **23** without the thienyl function (Fig. 1). Thus, the thienyl group at the 2-position on the azulene ring should contribute to the extension of the π -conjugation, respect to the result on the UV/Vis spectra. Moreover, compounds **9** and **13** in CH_2Cl_2 exhibited relatively strong absorptions at around $\lambda_{\text{max}} = 420$ nm, which may be assigned to the intramolecular charge transfer (ICT) absorption band from the electron-rich thiophene ring to the 2-azuleny moiety, because this band could not be displayed in that of **10** and **11**, which possess an electron-withdrawing carbonyl group at 5-position on the thiophene ring, and also that of compound **12**.

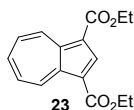


Fig. 1 Structure of 1,3-bis(ethoxycarbonyl)azulene (**23**).

On the other hand, compounds **14–17** exhibited a strong absorption band at around $\lambda_{\text{max}} = 450$ nm, which could not be observed in that of **1** (Fig. 2). The absorption maxima of **14–17** were nearly equal to each other, although the substituent on the thiophene ring is varied. Therefore, contribution of the ICT characters between azulene and thiophene moieties to this band should be relatively low as respect to the results on the UV/Vis spectra.

Recently, Hawker and co-workers reported the 4,7-bis(2-thienyl)azulene shows the emission in acidic solvent, due to the protonation of azulene ring.^{2c} We also investigated the fluorescent study of thienylazulenes **9–17** and bis(azuleny)thiophenes **19–22** in both neutral and acidic solvent, but no fluorescence was observed under the measurement conditions likewise usual azulene derivatives.

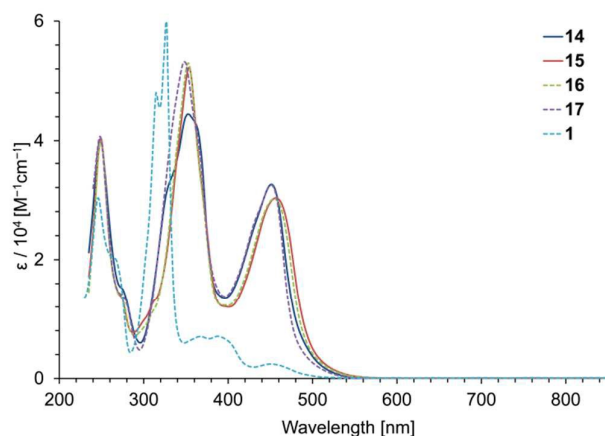


Fig. 2 UV/Vis spectra of **14** (blue line), **15** (red line), **16** (light-green dotted line), **17** (purple dotted line) and **1** (light-blue dotted line) in CH_2Cl_2 .

To examine the theoretical aspects of the spectroscopic properties depending on the substitution position of these series, molecular orbital calculations were performed on **9** and **14**, as well as **1** and **23** for comparative studies, as model compounds, using time-dependence density functional theory (TD-DFT) at the B3LYP/6-31G** level (Table 2).¹⁸ The frontier Kohn–Sham orbitals of **1**, **9**, **14** and **23** are shown in the ESI.

Judging from a comparison of the experimental and the theoretical UV/Vis spectra, the absorption maxima of **9** at $\lambda_{\text{max}} = 419$ nm could be assigned to transitions, which originated from the HOMO located on the azulene and EDOT moieties to the LUMO located on the azulene ring (Fig. S–41 in the ESI). Thus, the absorption band of **9** at $\lambda_{\text{max}} = 419$ nm could be attributed to some ICT characters of the transitions from EDOT to azulene moieties as predicted by the comparison with the substituents effect on the thiophene ring in this band. The longest absorption maxima of **9** at $\lambda_{\text{max}} = 528$ nm is considered as the π - π^* transition (HOMO and HOMO–1 to LUMO) of the substituted azulene-ring itself. The slight bathochromic shift for the longest wavelength absorption of **9** compared with that of **23** should be attributed to the lower HOMO–LUMO gap due to the extension of π -electron system, as respect to the TD-DFT calculation.

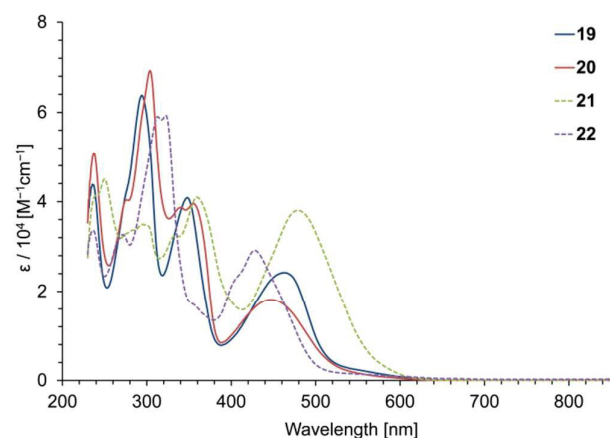
The calculations revealed that the longest absorption band of **1** in the visible region is caused by π - π^* transition (HOMO–1 to LUMO) of azulene-ring itself, which could be assigned as normal orbital types of HOMO–LUMO transition of azulene nucleus¹⁹ (Table 2 and Fig. S–43 in the ESI). The strong absorption band at $\lambda_{\text{max}} = 433$ (sh) and 451 nm of **14** is revealed as the transition from the HOMO and HOMO–1 to LUMO and LUMO+1, spread in both azulene and EDOT moieties (Fig. S–42 in the ESI). Thus, the EDOT moiety contributes to the lower HOMO–LUMO gap and also strength of the transition efficiency. Thus, thienyl function contributes to the extension of π -electron system in this 2-aminoazulene derivative, effectively, because these bands could not be observed as strong absorption bands in that of **1** (Table 2). The conclusion is consistent to the little substituent effect of this absorption band.

Table 2 Electronic transitions for **9**, **14**, and **1** and **23** as references, derived from the computed values based on B3LYP/6-31G** method and experimental values

Sample	Experimental	Computed value	Composition of band ^[a] (amplitude)
	λ_{\max} (log ϵ)	λ_{\max} (strength)	
9	419 (3.81)	428 (0.2199)	H \rightarrow L (0.9074)
	528 (2.79)	492 (0.0084)	H-1 \rightarrow L (0.9316) H \rightarrow L (0.2227)
14	433 sh (4.42)	397 (0.4374)	H \rightarrow L (0.8650)
	451 (4.51)	431 (0.0133)	H-1 \rightarrow L (0.8654) H \rightarrow L+1 (0.4710)
1	388 (3.85)	366 (0.0121)	H-1 \rightarrow L+1 (0.6578) H \rightarrow L (0.7285)
	404 sh (3.76)	403 (0.0122)	H-1 \rightarrow L (0.8803)
	452 (3.37)		
23	505 (2.81)	464 (0.0075)	H \rightarrow L (0.9680)

[a] H = HOMO, L = LUMO

The UV/Vis spectra of di(azulenyl)thiophene derivatives **19–22** showed characteristic strong absorption bands in the visible region (Fig. 3), similar with those of 2- and 6-thienylazulene derivatives. The extinction coefficients were found to increase with the number of substituted azulene rings. Moreover, absorption maxima of di(azulenyl)thiophene derivatives **19–22** exhibited the slight bathochromic shift relative to that of the corresponding thienylazulenes **9**, **13** and **14**. These results suggest that the π -conjugation is effectively expanded by the thiophene ring substituted by two azulene rings.

**Fig. 3** UV/Vis spectra of **19** (blue line), **20** (red line), **21** (light-green dotted line) and **22** (purple dotted line) in CH_2Cl_2 .

Electrochemistry

To clarify the effect for substituent of thiophene and substitution position on the azulene ring toward the electrochemical properties in thienylazulenes **9–17** and di(azulenyl)thiophenes **19–22**, the redox behavior of those

compounds was examined by CV and DPV. The redox potentials (in volts vs. Ag/AgNO_3) of these compounds measured under a scan rate of 100 mVs^{-1} are summarized in Table 3. The reduction waves measured by CV and DPV are summarized in the ESI.

Table 3 Redox potentials^{a,b} of thienylazulene derivatives **9–17** and di(azulenyl)thiophenes **19–22**.

Sample	Method	E_1^{red} [V]	E_2^{red} [V]	E_3^{red} [V]
9	(DPV)	(-1.46)	(-1.82)	
10	(DPV)	(-1.35)	(-1.94)	
11	(DPV)	(-1.36)	(-1.83)	
12	(DPV)	(-1.48)		
13	(DPV)	(-1.23)	(-1.80)	
14	(DPV)	(-1.78)		
	CV	-1.44	-1.58	
15	(DPV)	(-1.42)	(-1.56)	(-1.78)
	CV	-1.50	-1.68	
16	(DPV)	(-1.48)	(-1.66)	(-2.02)
	CV	-1.64		
17	(DPV)	(-1.62)		
	(DPV)	(-1.41)	(-1.54)	
19	(DPV)	(-1.44)	(-1.82)	
20	(DPV)	(-1.39)	(-1.78)	
21	CV		-1.80	
	(DPV)	(-1.39)	(-1.78)	
22	(DPV)	(-1.23)	(-1.41)	(-1.91)

^a V versus Ag/AgNO_3 , 1 mM in benzonitrile containing Et_4NClO_4 (0.1 M), Pt electrode (internal diameter: 1.6 mm), scan rate = 100 mVs^{-1} and internal reference ($\text{Fc}/\text{Fc}^+ = +0.15 \text{ V}$). ^b Half-wave potentials E_{ox} and $E_{\text{red}} = (E_{\text{pc}} + E_{\text{pa}})/2$ on CV, E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively.

The electrochemical reduction of thiophene derivatives **9–13** with 2-azulenyl substituent at the 2-position exhibited irreversible two waves on DPV (see the ESI), which suggest the generation of unstable anionic species of **9–13** under the electrochemical reduction conditions. On the other hand, 6-thienylazulene derivatives **15–17** showed a one or two quasi-reversible waves on CV under the electrochemical reduction conditions.

The electrochemical reduction of **15** showed a reversible reduction waves at a half-wave potential of -1.44 V and -1.58 V on CV, which can be ascribed to the stepwise formation of a radical anionic and dianionic species produced by the reduction of both azulene and thiophene moieties. Further electrochemical reduction exhibited an irreversible wave at -1.78 V on DPV. Compound **16** also displayed quasi-reversible reduction waves, whose potentials were identified as -1.50 V and -1.68 V on CV, attributable to the formation of a radical

anionic and a dianionic species (Fig. 4). The electrochemical reduction of **17** exhibited quasi-reversible reduction wave, whose potential was identified as -1.64 V on CV. Different from the results on **15–17**, electrochemical reduction of **14** showed an irreversible reduction wave at -1.78 V on DPV, which might be ascribed to the electropolymerization of EDOT moiety²⁰ or decomposition of reduced species under the measurement conditions.

Previously, we have reported the redox behavior of several thienylazulene derivatives. In the study, electrochemical reduction of 6-thienylazulene derivatives showed reversibility on CV, although the 2-thienylazulenes displayed irreversible waves.^{3b} Since the 6-thienylazulene derivatives **15–17** also revealed the reversible reduction wave on CV, 6-azulenyl group on the thiophene ring should enhanced the stability toward the electrochemical reaction, rather than 2-azulenyl substituent.

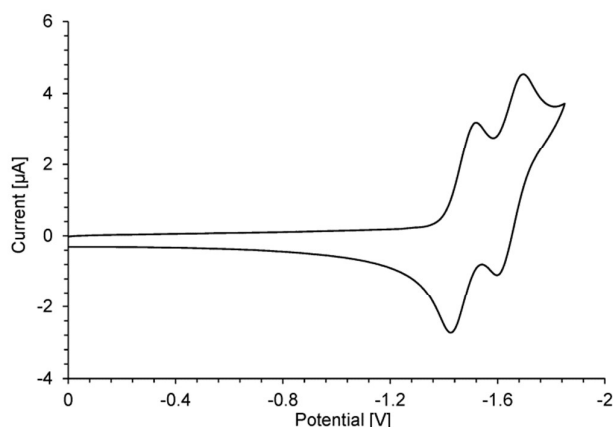


Fig. 4 Cyclic voltammogram of the reduction of **16** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte; scan rate = 100 mVs^{-1} .

The redox behavior of di(azulenyl)thiophene derivatives **19–22** was also examined by CV and DPV. Electrochemical reduction of **19** exhibited irreversible waves, whose potentials were identified as -1.41 V and -1.54 V by DPV. Electrochemical reduction of di(azulenyl)thiophenes **20** and **22** also showed irreversible waves, as similar with those of **19**. Cyclic voltammogram of **21** showed an irreversible wave following a quasi-reversible reduction wave (Fig. 5). The first irreversible and the second quasi-reversible waves should correspond to the stepwise reduction of 2-azulenyl and 6-azulenyl moieties. These results were also attributable to the destabilization of anionic species substituted by the 2-azulenyl moiety.

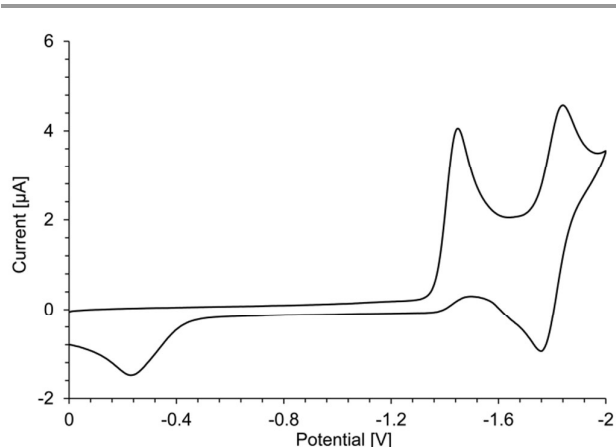


Fig. 5 Cyclic voltammogram of the reduction of **21** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte; scan rate = 100 mVs^{-1} .

Conclusions

In conclusion, we have described an efficient and direct synthetic method for 2- and 6-thienylazulenes, as well as that of di(azulenyl)thiophene derivatives. 2-Chloro- and 6-bromoazulenes **2** and **3** reacted with thiophene derivatives in the presence of $\text{Pd}(\text{OAc})_2$, $\text{PCy}_3\text{-HBF}_4$, PivOH and K_2CO_3 as catalyst to afford the corresponding 2- and 6-thienylazulenes **9–13** and **14–17** in high yield. Several di(azulenyl)thiophenes **18–21** were also prepared by the similar cross-coupling reaction of **1** with thienylazulenes **9**, **13**, **14** and **18**. Transition-metal-catalyzed aryl–aryl cross-coupling to access biaryl compounds usually requires both aryl halides and aryl organometallic reagents.²¹ The advantageous feature of the presented synthetic methodology is that these-type of reactions do not require the organometallic reagent such as arylboronic acid,^{8a} boronate ester,^{5c,6,7,8} stannane,^{5a,5b,6} silane,^{6,22} and so on. Thus, the presented procedure would be widely applicable for the synthesis of novel thienylazulene derivatives.

Analyses by CV and DPV showed that 6-thienylazulene derivatives **15–17** exhibited a quasi-reversible one or two-stage reduction wave owing to the generation of anionic species, although the 2-thienylazulene derivatives **9–13** displayed an irreversible wave. Thus, 6-thienylazulenes **15–17** may be expected to provide good performance organic electronics as respect to the stable redox properties.

To evaluate the scope of this class of molecules investigated by this research, the preparation of novel arylazulene derivatives by the palladium-catalyzed direct arylation and properties of those is now in progress in our laboratory.

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