One-step synthesis of polycyclic thianthrenes from unfunctionalized aromatics by thia-APEX reactions†

Kou P. Kawahara,a Hideto Ito a,⁎b and Kenichiro Itami a,⁎a,b

In this paper, thia-APEX reactions affording π-extended thianthrene derivatives from unfunctionalized aromatics are described. By utilizing S-diimidated 1,2-arenedithiols as benzene-1,2-dithiol dication synthons, new benzodithiine arms were fused to the unfunctionalized aromatic substrates in one step, affording π-extended thianthrenes in 21–87% yields. The present thia-APEX reaction occurs with equimolar amounts of aromatic substrates and S-diimidated 1,2-arenedithiols and a catalytic amount of TFOH, which is advantageous for the efficient creation of novel π-extended thianthrenes. In addition, the unique solid state packing structures and photophysical properties of the synthesized π-extended thianthrenes were elucidated in this study.

Introduction

Thianthrene is a six-membered sulfur-containing heterocyclic compound consisting of a dibenzo-fused 1,4-dithiine ring in which two sulfur atoms are embedded diagonally (Fig. 1A).1 Neutral thianthrene adopts a bent structure whose C–S–C angle is ca. 128°, whereas it reversibly transforms into a planar structure in the radical cation state.1c,2 The redox behavior and cationic-state capability of thianthrene can be utilized for supramolecular chemistry,3,4 and development of organic chemical reactions4 and cathode materials.5 Moreover, the thianthrene structure is favorable for electron-donation and intersystem crossing due to the electron-richness and heavy atom effect of sulfur atoms.6 By utilizing these functionalities, π-extended thianthrenes have been developed in recent years.3–7 Fig. 1B shows the representative thianthrene-based materials with unique reactivities and optoelectronic and supramolecular properties: room-temperature phosphorescence (compound A),3,6 thermally activated delayed fluorescence (TADF) (compound B),6 C–H functionalization of aromatic compounds (compound C),4 semiconductivity (compound D),7 and host–guest capability for fullerenes (compound E).3

Fig. 1 π-Extended thianthrenes: structures, properties, and applications.

†Electronic supplementary information (ESI) available: Syntheses, NMR, UV-vis absorption, emission, DFT calculations and crystallographic table. CCDC 2223785 (3ea), 2223786 (3ca) and 2241075 (3fa). For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d2qo02058k

aGraduate School of Science, Nagoya University, Chikusa, Nagoya 464-8602, Japan
bInstitute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, Chikusa, Nagoya 464-8602, Japan

View Article Online
View Journal | View Issue
benzene derivatives. Alternatively, SAr-type homoannulation reactions using ortho-halogenated areniethiols and a base are also useful for the preparation of symmetric thianthrenes. Furthermore, cross-annulation reactions using aryl-dithiols and 1,2-dihaloarenes are frequently employed to construct unsymmetric thianthrene structures and large organic frameworks consisting of multiple thianthrene bridges (Fig. 2A-2). In this method, the characteristics of multistep transformations and the low availability of arene dihaloarenes in larger aromatic systems would diminish the synthetic utility and efficiency of the whole synthetic process. One early example of one-step synthesis of thianthrenes was reported by Sato and coworkers in 1988 (Fig. 2B). They used benzophenanthriphen (BPT) and AlCl₃ for cross-annulation of unfunctionalized arenes with a dithiene framework, achieving the one-step synthesis of various thianthrenes. However, this reaction requires excess amounts of trifluoroacetic acid (TFA) instead of TfOH, which would diminish the synthetic utility and applicability of substrates would be needed to advance the synthetic chemistry of thianthrenes.

Previously, we have devoted our efforts toward the development of a one-step annulative π-extension (APEX) reaction and a heteroatom-embedding APEX (hetero-APEX) reaction for efficient and rapid access to large polycyclic aromatic hydrocarbons (PAHs), polycyclic heteroarenes and nanographenes from readily available unfunctionalized aromatics. Recently, we also developed a sulfur-embedding APEX reaction for the one-step synthesis of π-extended thiopyrylium salts (Fig. 2C). In this reaction, S-succinimidated ortho-arenyl areniethiols work as 1,4-C,S-dication π-extensions in the presence of TFOH, and thus a one-step sequence of annulative C=S/C=C bond formation and dehydrative aromatization of unfunctionalized aromatics occurs with high regioselectivity. To further explore the potential of the thia-APEX strategy, we tested whether 1,2-arendithiols having two succinimide groups will work as 1,4-S₅,S-dications, which would enable the one-step fusion of a benzodithiene ring onto unfunctionalized aromatics. Herein, we report a new thia-APEX reaction using S-diimidated 1,2-arendithiols for the efficient one-step synthesis of π-extended thianthrenes under mild reaction conditions. Furthermore, some characteristic photophysical properties and structural features of the newly synthesized π-extended thianthrenes were elucidated by X-ray crystallographic analysis, measurements of absorption and emission, and density functional theory (DFT) calculations.

Results and discussion

First, we newly prepared S-diimidated 1,2-benzenedithiol from 1,2-benzenedithiol (2a) (see the ESI† for details) and investigated the thia-APEX reaction of 1,2-dimethoxybenzene (1a) with 2a as a π-extending agent (Table 1). When a mixture containing 1a (0.20 mmol, 1.0 equiv.), 2a (1.1 equiv.), and trifluoromethanesulfonic acid (TFOH, 2.3 equiv.) in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP, 1.0 mL) was stirred at 80 °C under air for 13 h, the desired thia-APEX reaction proceeded to afford 2,3-dimethoxythianthrene (3aa) in 38% yield along with the demethylated by-product 4 in 25% yield (entry 1). The use of an excess amount of 2a or a mixed solvent of 1,2-dichloroethane (DCE) and HFIP (ν/ν = 1:1) increased the yields of 3aa with decreased formation of 4 (entries 2 and 3). The use of DCE alone as the solvent resulted in a higher yield than the use of HFIP as the solvent (entries 4–7). In this regard, the HFIP molecule or H₂O in HFIP might be involved in the deprotection of OMe to give 4. To our delight, the use of a smaller amount of TFOH (ca. 0.6 equiv.) and a stoichiometric amount of 2a was suitable for increasing the yield of product 3aa (99% NMR yield, entry 7). The use of trifluoroacetic acid (TFA) instead of TFOH dramatically decreased the yield of...
Thia-APEX reactions also proceeded on unfunctionalized product 3aa, implying the need for a strong acid for activating the S–N bonds (entry 8). Elevating the temperature to 100 °C resulted in an increased yield of 4 along with the decomposition of 3aa (entry 9). Finally, we found that the use of an equimolar amount of 1a and 2a in the presence of 0.6 equiv. of TfOH in DCE at room temperature (23 °C) are the best reaction conditions for the present thia-APEX reaction, and thus succeeded in exclusively obtaining 3aa in 83% isolated yield (entry 10). Compared to the early report on one-step thianthrene synthesis by Sato,12 the present thia-APEX reaction realized a 1 : 1 cross-annulation between the unfunctionalized arenne and the π-extending agent with catalytic amounts of an acid even at room temperature.

With the optimized conditions in hand, the scope of thia-APEX reactions using other aromatic substrates was examined (Fig. 3). When using S-dimethoxymethylated 3,4,5,6-tetrafluorobenzene-1,2-dithiol 2b with 1a, the thia-APEX reaction was less efficient, but afforded dimethoxystyrafluorothianthrene 3ab in 32% yield. In the reaction with 2a, 1,2,3,4-tetramethylbenzene (1b) was transformed to the corresponding thianthrene 3ba in 70% yield. Unfortunately, the thia-APEX reactions of electron-deficient aromatic substrates such as 1,2-difluorobenzene and ortho-phthalalodinitrile did not proceed, probably due to their lower nucleophilicities. Thianthrene 3ca was also obtained in 21% yield from phenanthrene (1c) and 2a. Although this reaction preferentially occurred at the K-region (C9, C10-position of phenanthrene: concave armchair edges in PAH), as same as the previous report,5aa,5b minor thia-APEX reactions at other regions and/or multi-thia-APEX reactions could result in lower yields of 3ca. In contrast, the thia-APEX reaction using 2,7-di-
tert-butylphenanthrene (1d) with 2a efficiently proceeded to afford dibenzothianthrene 3da in 87% yield. Besides, by employing the methylated π-extending agent 2c instead of compound 2a, di-tert-butylphenanthrene 1d was transformed to the corresponding dibenzothianthrene 3dc in 71% yield. Thanks to the bulky tert-butyl groups, the π-extensions on other regions such as the C1–C2, C2–C3 and C3–C4 positions are considered to be prevented. Moreover, the thia-APEX reaction of C2v-symmetric corannulene (1e) with 2a mainly afforded benzodithiine-fused corannulene 3ea in 35% yield, although multi-thia-APEX products were also observed in the reaction mixture to some extent. Besides, benzodithiine-fused triphenylene 3fa was obtained from pristine triphenylene (1f) in 39% yield. The structure of 3fa was elucidated by X-ray crystallographic analysis (see the ESI†). In this reaction, there is a possibility of the formation of other regioisomers and multi-thia-APEX products, which can decrease the yield of 3fa. Furthermore, benzothiophenone (1g) and 1-tosyl-1H-indole (1h) were used as heteroaromatic templates for thia-APEX reactions, and dibenzothiinothiophene 3ga and dibenzothiinopyrrole 3ha were obtained in 53% and 86% yields, respectively. Thia-APEX reactions also proceeded on unfunctionalized...
heteroaromatic rings. For example, the thia-APEX reaction of N-methyldibenzoindole 1, which was previously synthesized by us using the APEX reaction of N-methylpyrrole,15 with 2a took place to afford 3a in 42% yield. Finally, guaiazulene (1j) was subjected to the thia-APEX conditions, and compound 3ja was obtained in 25% yield (an average yield of four runs, see the ESIF for details) as a relatively unstable dark-green oil. In this reaction, the thia-APEX reaction selectively proceeded on the five-membered ring moiety.

Because new π-extended thianthrenes such as 3ca, 3ea and 3ja were easily accessed by the thia-APEX reaction for the first time, the photophysical properties as well as the electronic structures of 3ca, 3ea and 3ja were also investigated. First, dibenzothianthrene 3ca showed an absorption band in the UV region, and the longest wavelength absorption maximum appeared at 331 nm in CH2Cl2 (Fig. 4, green line). Thiianthrene 3ca emits strong blue-green fluorescence (fluorescence quantum yield (Φfl) = 24%) upon excitation with 330 nm light, and the emission maximum was observed at 497 nm in CH2Cl2 (Fig. 4, green dashed line). In the case of corannulene-fused thianthrene 3ea, an intense absorption maximum and a weak shoulder peak were observed at 304 nm and at 350–450 nm, respectively (Fig. 4, orange line). Moreover, thiianthrene 3ea showed a broad fluorescence spectrum having a peak top at 560 nm (Fig. 4, orange dashed line) and an orange emission in CH2Cl2. Both thiianthrene 3ca and 3ea showed Stokes shifts of ca. 160 nm, whose relatively large values were considered to be derived from large dynamic structural relaxations at their excited states.1,7,18 Furthermore, the fluorescence quantum yields of thianthrenes 3ca and 3ea were measured as 24% and 4%, respectively. Notably, the 24% quantum yield of 3ca was even larger than those of pristine phenanthrene and triphenylene (ca. 10%),16 which can be rationalized by the heavy atom effect of sulfur atoms and the prevention of quenching of fluorescence by its bent structure.17 Finally, we found that guaiazulene-fused benzodithiine 3ja shows a green color in CH2Cl2 and a weak and broad absorption band between 450–800 nm (Fig. S5†). This compound did not show fluorescence, which is strongly reflective of the nature of the guaiazulene core.

Next, the absorption properties and electronic structures of π-extended thianthrenes 3ca and 3ea were evaluated by DFT and time-dependent DFT (TD-DFT) calculations using the Gaussian 16 program18 at the B3LYP/6-31+G(d,p) level of theory19 and by consideration of the solvent effect using the integral equation formalism-polarizable continuum model (IEF-PCM)20 in CH2Cl2. As shown in Fig. 5, the energy levels of the HOMO and LUMO of 3ca were calculated to be −5.90 eV and −1.74 eV, respectively. While the HOMO of 3ea is mainly localized on the 1,4-dithiine moiety, the LUMO of 3ca is localized to some extent on the phenanthrene moiety. A similar HOMO and LUMO localization tendency was also found in 3ea, and the energy levels of the HOMO and LUMO of 3ea were calculated to be −5.96 eV and −2.20 eV, respectively. Compared with the HOMO and LUMO energy levels of pristine phenanthrene (HOMO: −6.12 eV; LUMO: −1.43 eV) and corannulene (HOMO: −6.35 eV; LUMO: −2.01 eV), the effect of

---

**Fig. 4** Absorption and emission spectra of π-extended thianthrenes 3ca and 3ea in CH2Cl2. Excitation wavelengths for fluorescence (FL) measurements: 330 nm (3ca) and 405 nm (3ea). The pictures of emission color were taken using the concentrated solutions of each compound under 365 nm of UV light irradiation.

**Fig. 5** Representative frontier orbitals of 3ca (A) and 3ea (B) (isovalue = 0.02). Geometry optimization and energy calculations were conducted at the B3LYP/6-31+G(d,p) level of theory.
benzodithiine-fusion is slightly more predominant in increasing the energy levels of the HOMO (Δ = +0.22 and +0.39 eV) rather than in decreasing those of the LUMO (Δ = −0.31 and −0.19 eV). As a result, the HOMO–LUMO energy gaps of 3ca and 3ea are reduced by 0.53–0.58 eV compared with phenanthrene and corannulene. As shown in Table 2, the calculated excitation wavelength (λ_{TD-DFT}) of the HOMO → LUMO transition of thianthrene 3ca was 347.21 nm (f = 0.0993), which is consistent with the experimental longest wavelength absorption of 3ca as a weak peak (λ_{abs} = 331 nm). Besides, the second and third excitation attributed to HOMO → LUMO+1 and HOMO−1 → LUMO transitions was calculated to be 334.84 nm (f = 0.0023) and 299.47 nm (f = 0.2015), respectively. The latter allowed excitation is considered to be the shoulder absorption peak around 290 nm. With regard to 3ea, the electron transitions in three lowest energies were also estimated to be 395.93 nm (f = 0.0162, HOMO → LUMO), 388.71 nm (f = 0.0229, HOMO → LUMO+1) and 356.73 nm (f = 0.0000, HOMO−1 → LUMO+1), whose small or zero values of f show a good agreement with the weak shoulder absorptions between 350 to 450 nm. Moreover, the HOMO−1 → LUMO+1 transition (λ_{TD-DFT} = 356.73 nm, f = 0.0000) of 3ea was determined as a forbidden transition.

Next, we performed the structural analyses of 3ca and 3ea by X-ray crystallographic analysis. Single crystals of 3ca and 3ea were obtained by recrystallization from chloroform/pentane by a vapor diffusion method. In the X-ray crystallographic analysis of 3ca, two pairs of two molecules were observed in a unit cell, and both pairs consist of two molecules arranged in a pseudo-C_{2} symmetry, whose dithiine cores are directed in the same axis with ca. 127° bent angles (Fig. 6A). Each pair is directed in the opposite direction and positioned in a C_{i} symmetry, forming the two pseudo-enantiomeric pairs of two racemic molecules (Fig. 6A–C). Furthermore, each molecule is aligned in the direction of the b axis, forming columnar stacks, maintaining ca. 3.6 Å of intermolecular distance, which indicates weak π–π interactions of 3ca molecules.21 This characteristic columnar packing is identical to that of unsubstituted thianthrene.22 In the X-ray crystallographic analysis of 3ea, the bent angle of the thianthrene moiety in 3ea was found to be 126°, which is also closely identical to those of 3ca and unsubstituted thianthrene (Fig. 6D).21 Besides, the dangling benzodithiine arm is bent toward the concave face of the corannulene core, which forms a ladle-like shape. The one-dimen-

Table 2 | Results of TD-DFT calculations at the B3LYP/6-31+G(d,p) level of theory in CH2Cl2 (IEF-PCM). λ_{TD-DFT}: estimated excitation wavelength; f: oscillator strength; λ_{abs}: the experimental observed longest wavelength absorption in CH2Cl2.

<table>
<thead>
<tr>
<th></th>
<th>λ_{TD-DFT}</th>
<th>f</th>
<th>Electronic transition (coefficient)</th>
<th>λ_{abs}</th>
</tr>
</thead>
<tbody>
<tr>
<td>3ca</td>
<td>347.21 nm</td>
<td>0.0993</td>
<td>HOMO → LUMO (0.67256)</td>
<td>331 nm</td>
</tr>
<tr>
<td></td>
<td>334.84 nm</td>
<td>0.0023</td>
<td>HOMO → LUMO+1 (0.61319)</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>299.47 nm</td>
<td>0.2015</td>
<td>HOMO−1 → LUMO (0.56362)</td>
<td>—</td>
</tr>
<tr>
<td>3ea</td>
<td>395.93 nm</td>
<td>0.0162</td>
<td>HOMO → LUMO (0.68456)</td>
<td>350–450 nm</td>
</tr>
<tr>
<td></td>
<td>356.73 nm</td>
<td>0.0000</td>
<td>HOMO−1 → LUMO+1 (0.61773)</td>
<td>—</td>
</tr>
</tbody>
</table>

Fig. 6 | Structures of π-extended thianthrene 3ca: (A) structure and ORTEP drawing of 3ac with 50% probability, (B) side view of a unit cell, (C) top view of a unit cell, (D) structure and ORTEP drawing of 3ea with 50% probability, (E) ORTEP drawing of the columnar packing structure of 3ea, and (F) an extracted dimer structure with distances of π–π and CH/π interaction in units of Å.

sional columnar packings of 3ea are aligned in an antiparallel manner to the neighboring molecular columns, counteracting the dipole moments of each column (Fig. 6E). Focusing on the distances between two neighboring molecules, each corannulene core is longitudinally aligned at 3.3 Å intervals, which are smaller than the sum of the van der Waals radii of two carbon atoms, indicative of the existence of the π–π interaction.21 Furthermore, the distances between the peripheral C–H bond in the corannulene core and the carbon atoms in the dangling benzene ring are less, and ranged from 2.7 to 2.9 Å. These values are within the sum of the van der Waals radii of one hydrogen and one carbon atom, showing the existence of CH/π interactions (Fig. 6F).21 Depicting isosurfaces of non-covalent interaction (NCI) plot analysis using the NCIPLOT 4.0 program,24 green isosurfaces, which indicate weak non-covalent interactions, are visually and clearly confirmed between the corannulene cores (π–π) and between the corannulene core and the benzene ring (CH/π) (Fig. 7). Because unsubstituted corannulene in the solid state shows a disordered arrangement derived from CH/π interactions, the thianthrene arms are considered to contribute to the formation of the
of benzodithiine arms were calculated to be 7.31 kcal mol$^{-1}$ (Fig. 6). The inversion barriers corresponding to the inversion ture was also observed by X-ray crystallographic analysis 3ea-ladle was the most stable conformer in 3ea, and a spoon-shaped one (3ea-spoon) in the ground and transition states were optimized at the B3LYP/6-31+G(d,p) level of theory. The structure of 3ea was extracted from the data of X-ray crystallographic analysis.

Columnar packing structure. In addition, the columnar packing structure of thianthrene 3ea is the first example of mono-benzodithiine-fused corannulene$^{3,7,e}$ whereas there are a lot of other rim-region-fused or rim-region-substituted corannulene derivatives showing a similar columnar stacking ability.$^{28}$ We expect that the columnar stacking achieved by the simple structural motif of benzodithiinocorannulene can provide a fruitful insight into the application of corannulene-based functional materials in organic electronics$^{26}$ and supramolecular chemistry$^{27}$ as well as host-guest chemistry.$^{3}$

To obtain insights into the bent structures of thianthrenes 3ca and 3ea in crystalline and solution states, their inversion barriers were examined using DFT calculations. The structures of thianthrenes 3ca and 3ea in the ground and transition states were optimized at the B3LYP/6-31+G(d,p) level of theory. 3ca has only one stable bent structure (see the ESI†), whereas 3ea has two stable structures, a ladle-shaped one (3ea-ladle) and a spoon-shaped one (3ea-spoon), because of the inversion of the corannulene core and the benzodithiine arm (Fig. 8). 3ea-ladle was the most stable conformer in 3ea, whose structure was also observed by X-ray crystallographic analysis (Fig. 6). The inversion barriers corresponding to the inversion of benzodithiine arms were calculated to be 7.31 kcal mol$^{-1}$ for TS1$_{3ca}$ and 7.47 kcal mol$^{-1}$ for TS1$_{3ea}$. The values of TS1$_{3ca}$ and TS1$_{3ea}$ are larger than that of pristine thianthrene (5.1 kcal mol$^{-1}$, at the B3LYP/6-31+G(d,p) level),$^{28}$ indicating that the PAH structures of phenanthrene and corannulene make the inversion barriers of benzodithiine arms higher. Furthermore, the transition state of corannulene core flipping in 3ea (TS2$_{3ea}$) was optimized and its barrier was calculated to be 9.72 kcal mol$^{-1}$. This value is also closely identical to that of pristine corannulene.$^{29}$ In conclusion, newly synthesized 3ca and 3ea were found to be hybrid molecules of thianthrene and PAHs. Their bent structures and conformational changes reflect the nature of both thianthrene and PAH cores well.

Conclusions

By using S-diimidated 1,2-benzenedithiol derivatives as new π-extending agents, thianthrenes and π-extended thianthrenes were efficiently obtained by the thia-APEX reaction of unfunctionalized aromatic substrates in one step. In addition, the characteristic photophysical and electronic properties and structural features of thia-APEX products were elucidated by UV-vis absorption and emission spectroscopy, DFT calculations and X-ray crystallographic analysis. In particular, the π-extended thianthrenes having phenanthrene and corannulene cores (3ca and 3ea) showed emission properties with larger Stokes shifts. 3ea showed higher fluorescence quantum yields than pristine phenanthrene and triphenylene. Regarding corannulene-fused thianthrene 3ea, 1D-columnar packing in the solid state was observed, which is in stark contrast to pristine corannulene. The newly developed thia-APEX reaction is expected to contribute to the rapid and efficient creation of unique π-extended thianthrenes having various aromatic cores.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the JST-CREST program (JPMJCR19R1 to H. I.), the JSPS KAKENHI (JP19H05463 to K. I., JP20K21192 and JP21H01931 to H. I.), and the Noguchi Research Foundation and the Foundation of Public Interest of
Tatematsu (to H. I.). K. P. K. gratefully acknowledges the JSPS Research Fellowship for Young Scientists (DC1). We thank Mr. Hiroki Shudo for helping with the X-ray crystallographic analysis and taking pictures of sample solutions. NMR spectroscopy and MS measurements were conducted using resources from the Chemical Instrumentation Facility (CIF), Research Center for Materials Science (RCMS), and Institute of Transformative Bio-Molecules (ITbM), Nagoya University. Calculations were performed using the resources of the Research Center for Computational Science, Okazaki, Japan (Projects: 21-IMS-C070 and 22-IMS-C069) and the SuperComputer System, Institute for Chemical Research, Kyoto University.

References


15 Representative examples of the hetero-APEX reaction:


The fluorescent quantum yields of the commercially available pristine phenantrene and corannulene in CH₂Cl₂ were measured using a spectrofluorometer in our laboratory (see the ESI†), and determined to be 3% and 1%, respectively. These values were lower than those reported in the literature (14% and 7%): ref. 16a and b and J. Mack, P. Vogel, D. Jones, N. Kaval and A. Suttona, The development of corannulene-based blue emitters, Org. Biomol. Chem., 2007, 5, 2448.


