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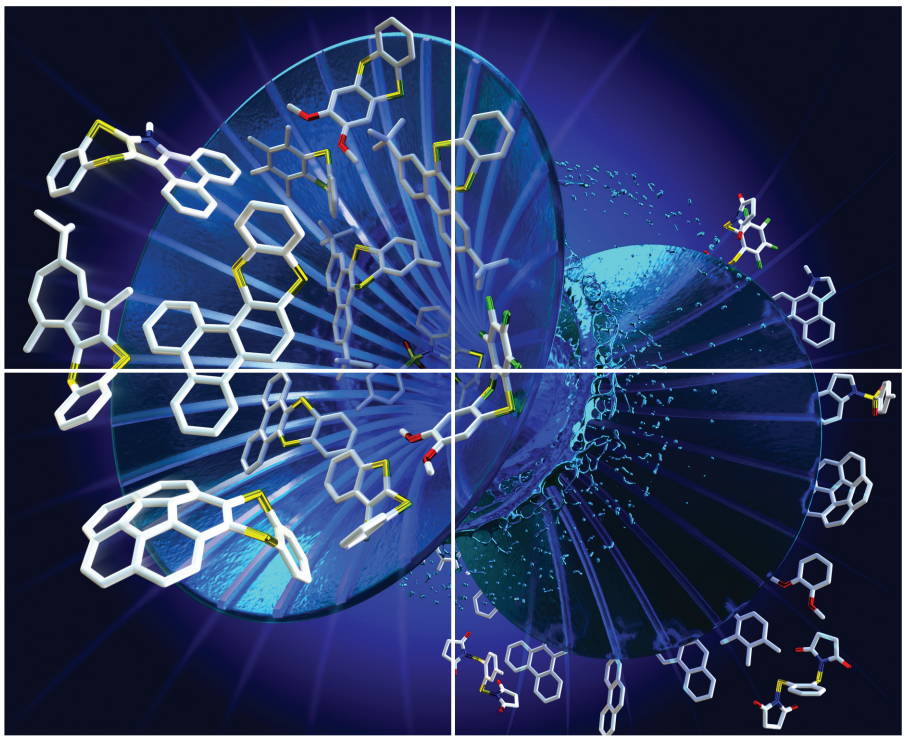

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One-step synthesis of polycyclic thianthrenes from unfunctionalized aromatics by thia-APEX reactions†

Kou P. Kawahara,[a] Hideto Ito *[a] and Kenichiro Itami *[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.

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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[2a,3] and development of organic chemical reactions[4] 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**),[6d] thermally activated delayed fluorescence (TADF) (compound **B**),[6d] C–H functionalization of aromatic compounds (compound **C**),[4] semiconductivity (compound **D**),[7l] and host–guest capability for fullerenes (compound **E**).[3]

To meet the high demands of π-extended thianthrenes as functional molecules, easy and rapid synthetic methods are highly desired. Representative synthetic methods of thianthrene derivatives are shown in Fig. 2A. For example, symmetric thianthrene structures can be constructed utilizing arenethiols as starting materials with fuming H_2SO_4 and reductants such as zinc and $SnCl_2$ (Fig. 2A-1).[8] Besides, using S_2Cl_2 and Lewis acids such as $AlCl_3$, symmetric thianthrenes can be directly synthesized from unfunctionalized aromatic substrates, while the applicable substrates are limited to simple

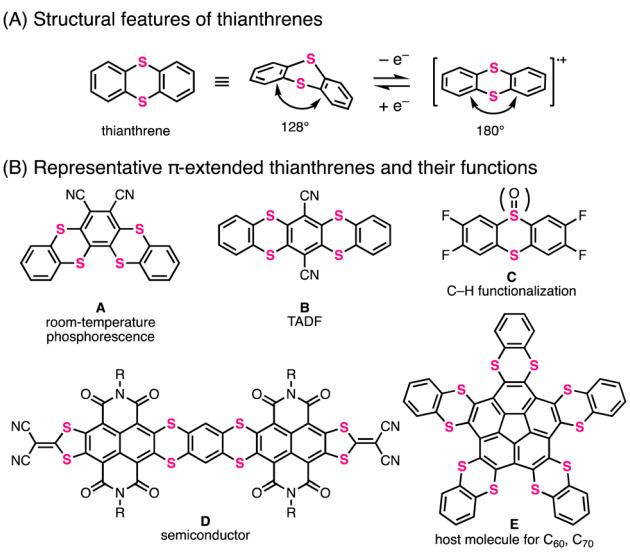


Fig. 1 π-Extended thianthrenes: structures, properties, and applications.

[a]*Graduate School of Science, Nagoya University, Chikusa, Nagoya 464-8602, Japan*
[b]*Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, Chikusa, Nagoya 464-8602, Japan*

†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

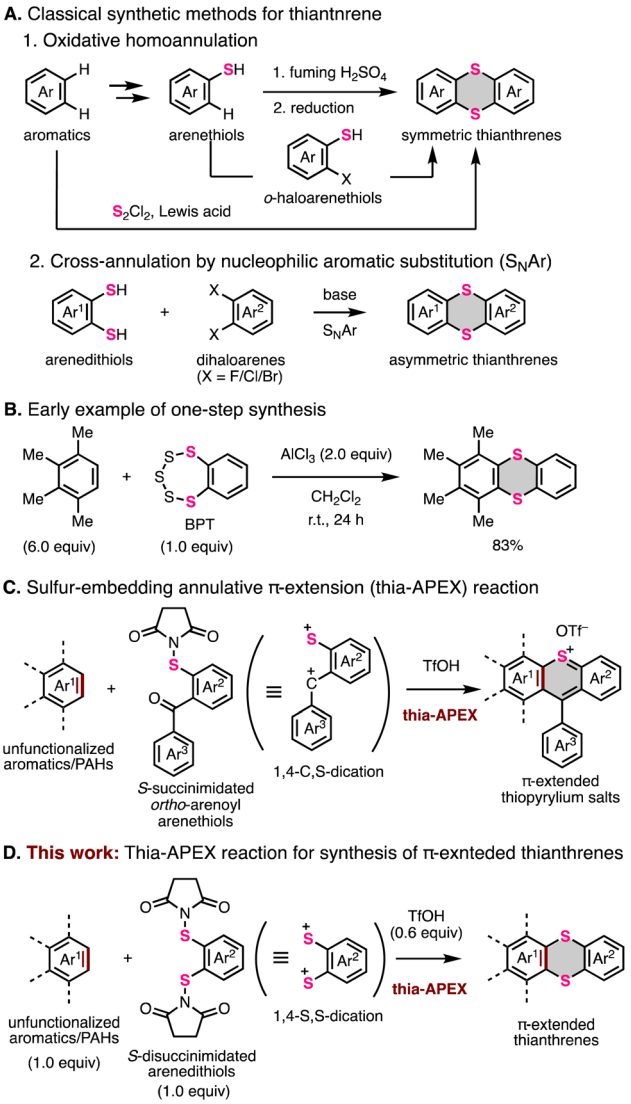


Fig. 2 Conventional synthetic methods for thianthrenes and one-step synthesis using sulfur-embedding annulative π-extension (thia-APEX).

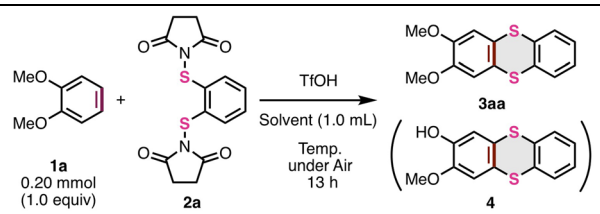
benzene derivatives.[4b,9] Alternatively, S_NAr-type homoannulation reactions using *ortho*-halogenated arenethiols and a base are also useful for the preparation of symmetric thianthrenes.[10] Furthermore, cross-annulation reactions using aryldithiols and 1,2-dihaloarenes are frequently employed to construct unsymmetric thianthrene structures and large organic frameworks consisting of multiple thianthrene bridges (Fig. 2A-2).[2c,5a,7c,e,h–k,11] In this method, the characteristics of multistep transformations and the low availability of arene dithiols and 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).[12] They used benzopentathiepin (BPT) and $AlCl_3$ for cross-annulation of unfunctionalized arenes with a dithiine framework, achieving the one-step synthesis of various thianthrenes. However, this reaction requires excess amounts of unfunctionalized aromatics to ensure a high yield. Due to this limitation, it seems difficult to apply it to the synthesis of larger aromatics. Therefore, the development of a more efficient and rapid synthetic method with a broad scope 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)[13,14] reaction and a heteroatom-embedding APEX (hetero-APEX)[15] reaction for efficient and rapid access to large polycyclic aromatic hydrocarbons (PAHs), polycyclic heteroaromatics and nanographenes from readily available unfunctionalized aromatics. Recently, we also developed a sulfur-embedding APEX (thia-APEX) reaction for the one-step synthesis of π-extended thiopyrylium salts (Fig. 2C).[15o] In this reaction, *S*-succinimidated *ortho*-arenoyl arenethiols work as 1,4-*C*,*S*-dication π-extending agents 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-arenedithiols having two succinimide groups will work as 1,4-*S*,*S*-dications, which would enable the one-step fusion of a benzodithiine ring onto unfunctionalized aromatics. Herein, we report a new thia-APEX reaction using *S*-diimidated 1,2-arenedithiols 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,-hexafluoroisopropyl alcohol (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 (v/v = 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 H_2O 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

Table 1 Optimization of the reaction conditions for the thia-APEX reaction of **1a** with **2a**



Entry	2a (equiv)	TfOH (equiv)	Solv.	Temp.	Yield of 3aa[a]	Yield of 4[a]
1	1.1	2.3	HFIP	80 °C	38% (38%)	16% (25%[c])
2	2.0	2.5	HFIP	80 °C	57%	0%
3	1.0	2.4	DCE/HFIP[b]	80 °C	65%	17%
4	1.0	2.3	DCE	80 °C	71%	19%
5	1.0	1.1	DCE	80 °C	50%	26%
6	2.0	2.3	DCE	80 °C	65%	0%
7	1.0	0.64	DCE	80 °C	99% (78%)	0%
8[c]	1.1	0.62 (TFA)	DCE	80 °C	3%	0%
9	1.0	2.2	DCE	100 °C	34%	25%
10	1.0	0.62	DCE	23 °C	>99% (83%)	0%

TfOH: trifluoromethanesulfonic acid; HFIP: 1,1,1,3,3,3-hexafluoroisopropyl alcohol; DCE: 1,2-dichloroethane; TFA: trifluoroacetic acid. [a] ^{1}H NMR yields determined using CH_2Br_2 as the internal standard, and isolated yields in parentheses. [b] A mixed solvent of HFIP/DCE (v/v = 1 : 1) was used. [c] TFA was used instead of TfOH.

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 **3a** (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 arene 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*-diimidated 3,4,5,6-tetrafluorobenzene-1,2-dithiol **2b** with **1a**, the thia-APEX reaction was less efficient, but afforded dimethoxytetrafluorothianthrene **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*-phthalodinitrile 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,[15a,o] 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-

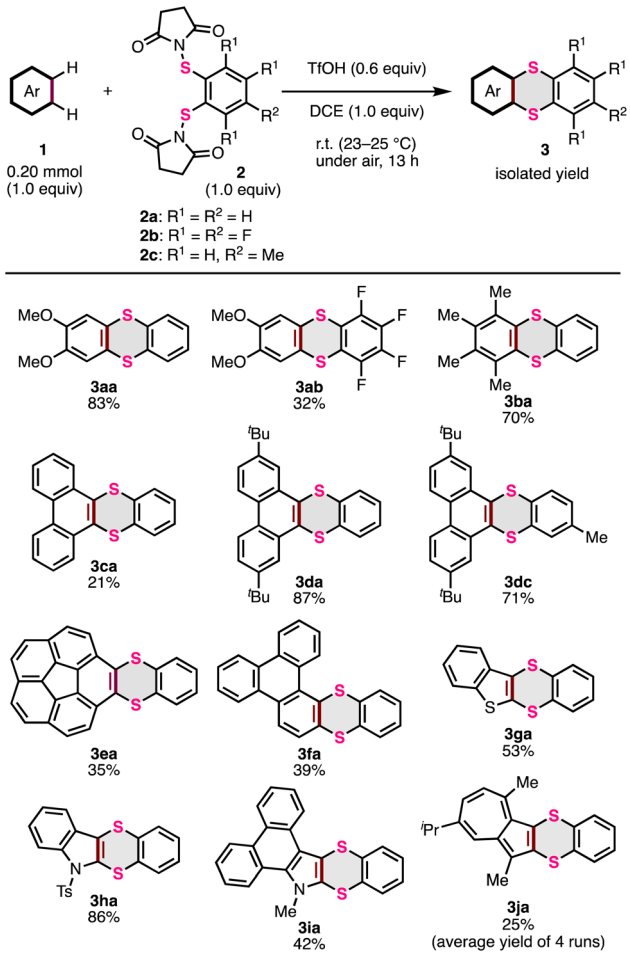


Fig. 3 Scope of substrates in the thia-APEX reaction.

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 C_{5v}-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, benzo[*b*]thiophene (**1g**) and 1-tosyl-1*H*-indole (**1h**) were used as heteroaromatic templates for thia-APEX reactions, and dibenzodithiinothiophene **3ga** and dibenzodithiinopyrrole **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 **1i**, which was previously synthesized by us using the APEX reaction of *N*-methylpyrrole,[14g] with **2a** took place to afford **3ia** 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 ESI† 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 CH_2Cl_2 (Fig. 4, green line). Thianthrene **3ca** emits strong blue-green fluorescence (fluorescence quantum yield (Φ_F) = 24%) upon excitation with 330 nm light, and the emission maximum was observed at 497 nm in CH_2Cl_2 (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, thianthrene **3ea** showed a broad fluorescence spectrum having a peak top at 560 nm (Fig. 4, orange dashed line) and an orange emission in CH_2Cl_2. Both thianthrene **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.[1,7j] 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 CH_2Cl_2 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 program[18] at the B3LYP/6-31+G(d,p) level of theory[19] and by consideration of the solvent effect using the integral equation formalism-polarizable continuum model (IEF-PCM)[20] in CH_2Cl_2. 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 **3ca** 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

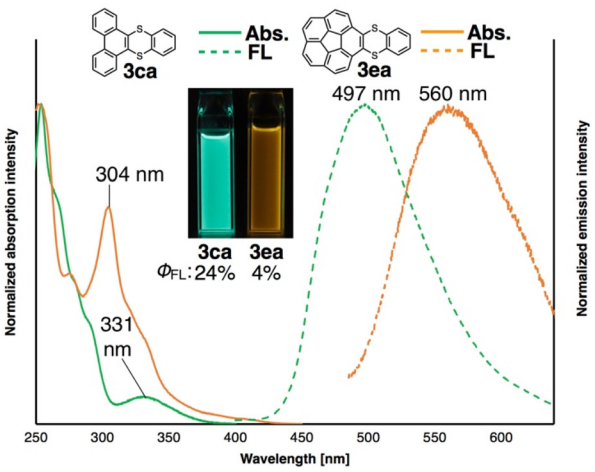


Fig. 4 Absorption and emission spectra of π-extended thianthrenes **3ca** and **3ea** in CH_2Cl_2. Excitation wavelengths for fluorescence (FL) measurements: 330 nm (**3ca**) and 405 nm (**3ea**). The pictures of emission color were taken using the concentrated solutions of each compound under 365 nm of UV light irradiation.

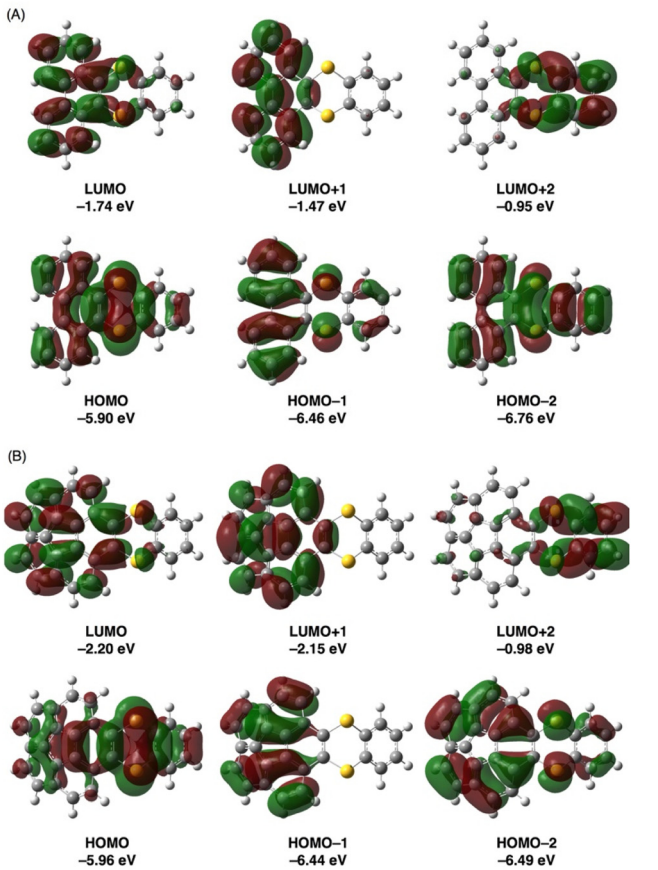


Fig. 5 Representative frontier orbitals of **3ca** (A) and **3ea** (B) (isovalue = 0.02). Geometry optimization and energy calculations were conducted at the B3LYP/6-31+G(d,p) level of theory.

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 ($\lambda_{TD\text{-}DFT}$) 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 ($\lambda_{TD\text{-}DFT}$ = 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).[1,22] Besides, the dangling benzodithiine arm is bent toward the concave face of the corannulene core, which forms a ladle-like shape. The one-dimensional 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).[23] 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

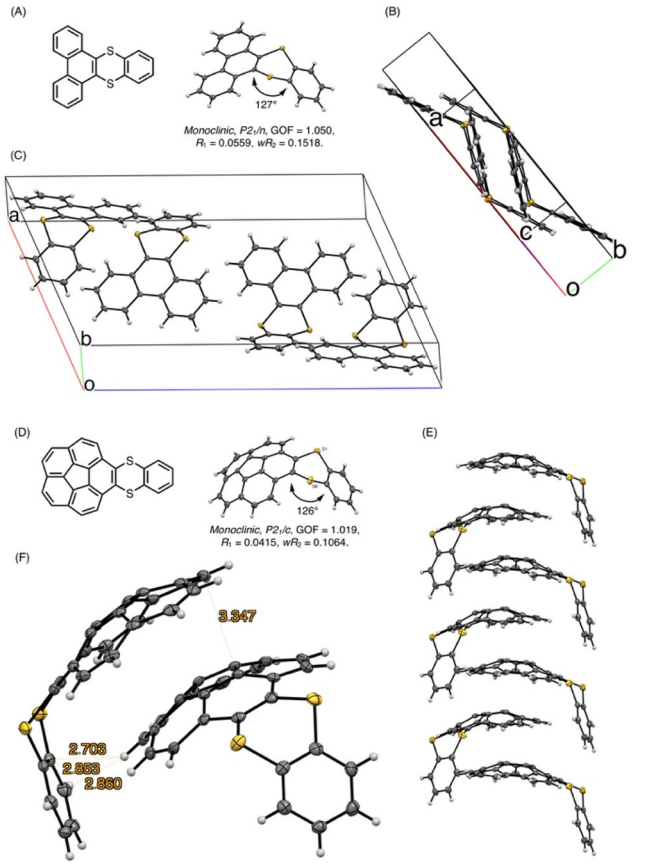


Fig. 6 Structures of π-extended thianthrene **3ca**: (A) structure and ORTEP drawing of **3ac** with 50% probability, (B) side view of a unit cell, (C) top view of a unit cell, (D) structure and ORTEP drawing of **3ea** with 50% probability, (E) ORTEP drawing of the columnar packing structure of **3ea**,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

Table 2 Results of TD-DFT calculations at the B3LYP/6-31+G(d,p) level of theory in CH_2Cl_2 (IEF-PCM). $\lambda_{TD\text{-}DFT}$: estimated excitation wavelength; f: oscillator strength; λ_{abs}: the experimental observed longest wavelength absorption in CH_2Cl_2

	$\lambda_{TD\text{-}DFT}$	f	Electronic transition (coefficient)	λ_{abs}
3ca	347.21 nm	0.0993	HOMO → LUMO (0.67256)	331 nm
	334.84 nm	0.0023	HOMO → LUMO+1 (0.61319)	—
	299.47 nm	0.2015	HOMO−1 → LUMO (0.56362)	—
3ea	395.93 nm	0.0162	HOMO → LUMO (0.68456)	350–450 nm
	388.71 nm	0.0229	HOMO → LUMO+1 (0.65994)	—
	356.73 nm	0.0000	HOMO−1 → LUMO+1 (0.61773)	—

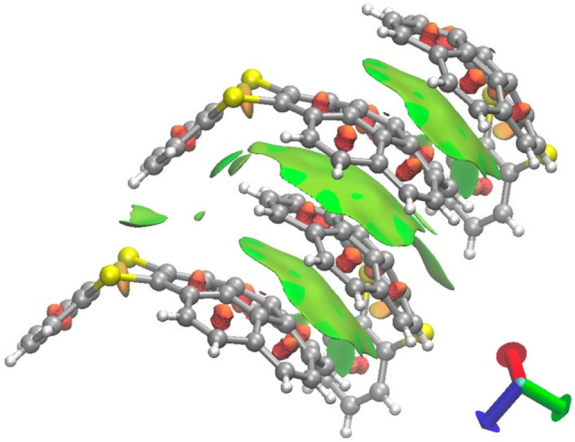


Fig. 7 NCI analysis and reduced density gradient isosurface (isosurface value = 0.3) using the NCIPLOT4 program for π-extended thianthrene **3ea**. Color code based on sign (λ_2) ρ was: −0.07 a.u. (blue) < 0.0 a.u. (green) < 0.07 a.u. (red). Blue and red isosurfaces show regions having attractive and repulsive interactions, respectively, and green isosurfaces show weak van der Waals interactions such as π−π interaction. The structure of **3ea** was extracted from the data of X-ray crystallographic analysis.

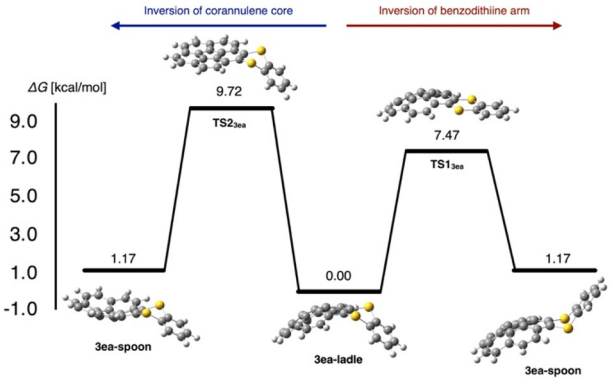


Fig. 8 Two possible pathways of the structural inversion of thianthrene **3ea** and their calculated barrier at the B3LYP/6-31+G(d,p) level of theory.

columnar packing structure. In addition, the columnar packing structure of thianthrene **3ea** is the first example of mono-benzodithiine-fused corannulene,[3,7e] whereas there are a lot of other *rim*-region-fused or *rim*-region-substituted corannulene derivatives showing a similar columnar stacking ability.[25] 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. **3ca** 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.

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