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Synthesis, twofold oxidative cyclization and dual emission of diaryl-substituted benzodithieno [5.5.5.6]fenestranes

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The syntheses of three 3,8-diaryl-substituted benzodithieno[5.5.5.6]fenestranes (BDTFs) and two doubly *o*-phenylene-bridged BDTFs are presented. These syntheses require careful consideration of the steric and electronic factors of the thiophene-fused polycyclic system. The electron-rich bis(3,4-dimethoxyphenyl)-BDTF displays a dual fluorescence profile where the long-wavelength emission is attributed to exciplex emission, as supported by concentration- and solvent-dependent fluorescence experiments as well as fluorescence lifetime studies. In contrast, the less electron-rich diphenyl-BDTF shows a much weaker exciplex emission, whereas the two cyclized analogues show only monomer emission. Additional emission measurements of model compounds reveal that the through-space interaction between the electron-rich 3,4-dimethoxyphenyl groups and the benzo unit may be crucial to the exciplex formation. Single-crystal X-ray diffraction of one of the twofold oxidatively cyclized BDTFs shows the highly distorted thiophene–benzene moieties and also multiple short contacts that involve the sulfur atoms and the bridgehead methine groups of the fenestrane core. This work demonstrates that there still exist vastly unexploited properties of (hetero)arene-fused fenestranes due to their unique three-dimensionally arranged aromatic units.

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Introduction

Fenestranes are a class of polycyclic compounds bearing four mutually connected rings.^{1–3} Small-ring fenestranes containing one,^{4–9} two^{5,10,11} or three^{12,13} cyclobutane rings were synthesized, as driven historically by the hypothetical planarization of their central quaternary carbon atom.^{14–18} On the other hand, construction of the less strained, more symmetrical [5.5.5.5]fenestrane skeleton was pioneered by Cook *et al.*^{19,20} and by Keese *et al.*^{21,22} starting from late the 1970s. Arene fusion came into play when Kuck and Böge reported the syntheses of tetrabenzo[5.5.5.5]fenestrane (**1**, also known as fenestrindane)²³ and tribenzo[5.5.5.6]fenestrane (**2**)²⁴ (Fig. 1a). Indeed, the former compound has opened up an avenue for the outward molecular extension around the [5.5.5.5]fenestrane core to yield geometrically unique, nonplanar polyaromatic structures. For example, we merged two hexa-*peri*-hexabenzocoronene subunits with fenestrindane²⁵ and incorporated *o*-phenylene units across its bays, generating four fused

cycloheptatriene rings (**3a** and **3b**, Fig. 1b)^{26–29} Moreover, extension of **1** with four *m*-quaterphenylene units was achieved generating macrocyclic substructures.³⁰

Recently, we disclosed the synthesis of a series of isomeric benzodithieno[5.5.5.6]fenestranes (BDTFs), such as **4** and **5** (Fig. 1c).³¹ The realm of heterocyclic fenestrane chemistry has thus progressed from heteroatom substitution (aza-,^{32,33} oxa-substitution^{34–38} or both³⁹) within the fenestrane core to heteroarene annulation at the core. BDTFs **4** and **5** can be easily derivatized at the reactive thiophene rings, without any need to protect the bridgeheads by methyl groups (which is necessary for the all-benzene analogues **1** and **2**).^{40,41} We envisioned that a similar *o*-phenylene bridge present in **3a** can be introduced to BDTF **5** to generate the nonplanar polycyclic aromatic skeleton of **8H** and **8CHO** (Fig. 1d). The pursuit of structures like **8H** and **8CHO** is driven by the potential applications of thiophene-based polycyclic arenes reported as light-emitting diodes,⁴² field-effect transistors,^{43–45} near-infrared⁴⁶ photovoltaic units,^{47,48} and ferroelectric⁴⁹ and redox-active switching materials.⁵⁰ Series of atomically precise, thiophene-fused graphene nanoribbons with different shapes and lengths were also reported in the light of establishing structural control for optoelectronic applications.^{51,52} Besides the *o*-phenylene-bridged BDTFs **8H** and **8CHO**, we also aimed at investigating

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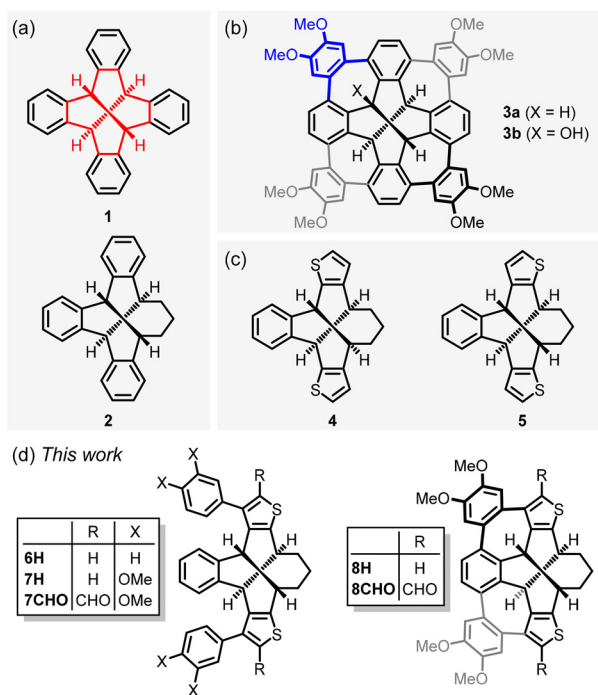


Fig. 1 (a) Benzoannulated fenestranes.^{23,24} The [5.5.5]fenestrane core of **1** is highlighted in red. (b) π -Extended fenestrindanes bearing fused cycloheptatriene rings.²⁶ An *o*-phenylene bridge is highlighted in blue. (c) Isomeric benzodithieno[5.5.5]fenestranes (BDTFs).³¹ (d) Novel diaryl-substituted and *o*-phenylene-bridged BDTFs reported herein.

the spectroscopic properties of their synthesis precursors, *i.e.* diaryl-BDTFs **7H** and **7CHO**. For a comparison of properties, diphenyl-BDTF **6H** was also synthesized as a less electron-rich counterpart of **7H**. In fact, these new BDTFs display spectral features markedly different from that of their all-benzene congeners, as shown below. In particular, we discuss the unexpected dual emissive nature of diaryl-BDTFs **6H** and **7H** and propose the mechanism underlying this phenomenon.

Results and discussion

Synthesis of diaryl-BDTFs

The parent unsubstituted BDTF **5** was prepared according to our reported procedure.³¹ Initially, we envisioned that the thiophene units of **5** could undergo palladium-catalyzed β -selective C–H arylation to directly yield the target diaryl-BDTF **6H**. Under the β -arylation conditions reported by Studer, Itami *et al.* (using 3,4-dimethoxyphenylboronic acid)⁵³ and by Larrosa *et al.* (using 4-iodoveratrole),⁵⁴ our starting material **5** remained mostly unreacted, supposedly due to the steric hindrance caused by the benzo unit. Consequently, we resorted to introducing reactive handles to the β -position of the thiophene rings of **5**. Scheme 1 shows the synthetic path toward the target diaryl-BDTFs. First, BDTF **5** was treated with *N*-iodosuccinimide (NIS) in the presence of acetic acid to afford the α,α' -diiodide **9** in 81% yield. In principle, **9** can iso-

merize to the β,β' -diiodide **10** in a halogen dance reaction (HDR).^{55,56} Thus, compound **9** was treated with lithium diisopropylamide (LDA) in a typical procedure.⁵⁷ After workup, we retrieved cleanly unsubstituted BDTF **5** (45% yield) without any traces of β,β' -diiodide **10** or unreacted **9**. We hypothesized that the large iodine atoms, when attached to the β -C atoms, would suffer steric clash with the protons at the inner positions of the benzo unit. As a result, HDR failed to take place, and the C–I bonds were reduced by LDA.^{58,59} Therefore, we pursued the HDR strategy with the α,α' -dibromide **11** instead of **9**. Compound **11** was synthesized from **5** using *N*-bromosuccinimide (NBS) and was isolated in 85% yield. The HDR of **11** was performed by use of 2,2,6,6-tetramethylpiperidide (LTMP) in this case,[†] and the desired β,β' -dibromide **12** was isolated in 74% yield, along with the β -monobromide **13** (24% yield). This successful HDR corroborates our hypothesis. The sites of halogenation in both **12** and **13** were unambiguously confirmed by X-ray crystallography (Fig. S1).[‡] Subsequently, the β,β' -dibromide **12** was subjected to Suzuki–Miyaura cross-coupling with 3,4-dimethoxyphenylboronic acid to yield bis(3,4-dimethoxyphenyl)-BDTF **7H** in 78% yield. Here, the electron-rich 3,4-dimethoxyphenyl group was chosen to facilitate the subsequent oxidative cyclization step.²⁶ In a similar manner, the less electron-rich diphenyl-BDTF **6H** was prepared from β,β' -dibromide **12** and phenylboronic acid and isolated in 86% yield. Both diaryl-BDTFs **6H** and **7H** were fully characterized by ¹H and ¹³C NMR spectroscopy and APCI mass spectrometry.

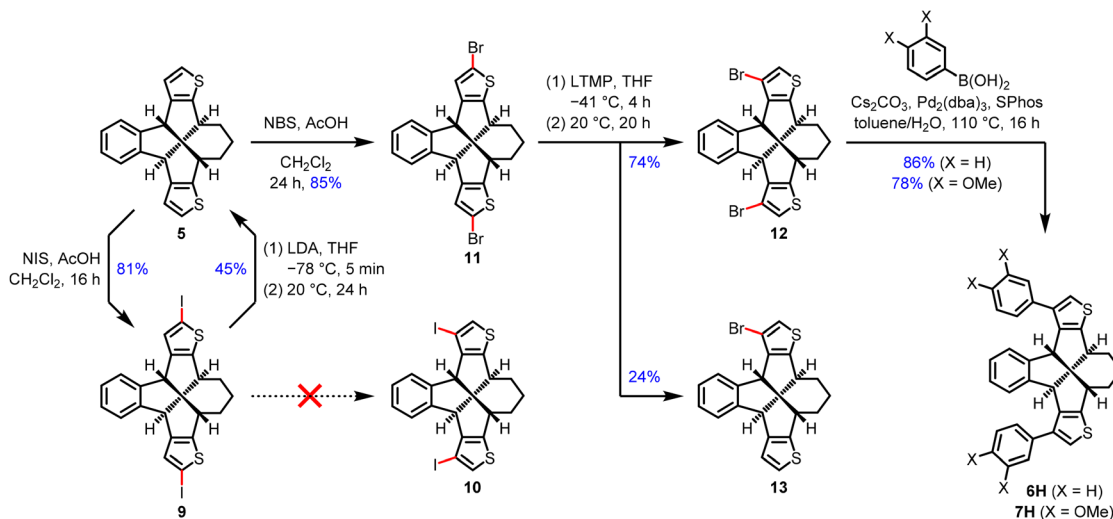
Oxidative cyclization of diaryl-BDTF

Under oxidative conditions, bis(3,4-dimethoxyphenyl)-BDTF **7H** can be expected to oligomerize or polymerize through the reactive unsubstituted α -positions of the thiophene rings.⁶⁰ Therefore, we decided to first block the thiophene rings of **7H** with the formyl group.⁶¹ As shown in Scheme 2, compound **7H** was treated with *n*-butyllithium followed by quenching with DMF to afford the dialdehyde **7CHO** in 68% yield. Subsequently, the key twofold oxidative cyclization of **7CHO** using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and triflic acid (TfOH) gave the desired doubly *o*-phenylene-bridged product **8CHO** in 74% yield. Notably, we did not observe any bridgehead-hydroxylated derivatives of **8CHO**, implying that the hydride abstraction of **8CHO** by DDQ was effectively impeded by the electron-withdrawing formyl groups. In contrast, the *o*-phenylene-bridged fenestrindane **3a** was found to undergo bridgehead-hydroxylation by DDQ and TfOH to give **3b** (Fig. 1).²⁸ Eventually, **8CHO** was converted to the target compound **8H** in 84% yield in a Haller–Bauer-type decarbony-

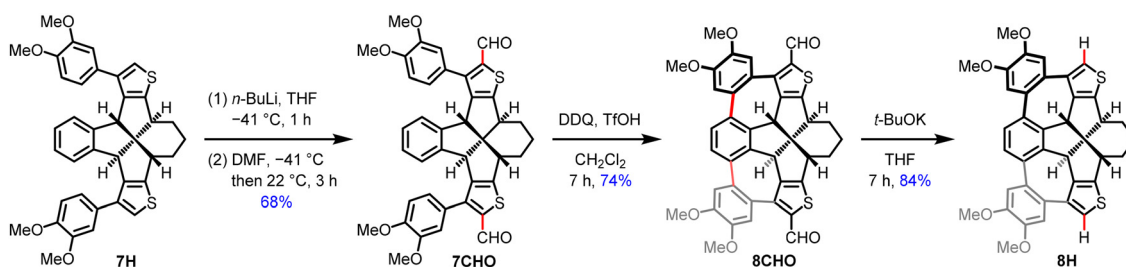
[†] Unlike LDA, the base LTMP lacks α -hydrogen atoms. LTMP was chosen originally to prevent the reductive debromination of β,β' -dibromide **12** via the hydride transfer mechanism. It turned out that the β -monobromide **13** still emerged as a minor product using LTMP as the base, meaning the single-electron transfer mechanism for reductive debromination was operative.^{58,59}

[‡] Deposition numbers 2039282 (for **12**), 2039283 (for **13**), and 2212499 (for **8CHO**) contain the supplementary crystallographic data for this paper.





Scheme 1 Synthesis of diaryl-BDTFs **6H** and **7H** from unsubstituted BDTF **5** utilizing the halogen dance reaction.



Scheme 2 Overall double oxidative cyclization of diaryl-BDTF **7H** involving diformylated intermediates.

lation mediated by potassium *tert*-butoxide.^{62,63} The identity of all new compounds was confirmed by ¹H and ¹³C NMR spectroscopy and mass spectrometry. In addition, the structure of the *o*-phenylene bridged BDTF **8CHO** was unequivocally established by X-ray crystallography.

Crystal structure of the *o*-phenylene-bridged BDTF **8CHO**

Slow evaporation of an ethyl acetate solution of the BDTF **8CHO** yielded single crystals suitable for X-ray diffraction analysis, which fully corroborated the proposed molecular structure.[‡] The crystal structure of **8CHO** belongs to the triclinic *P* $\bar{1}$ space group. The average dihedral angle of the peripheral benzene–benzene bay regions is 37.8° (Fig. 2a), whereas that of the outer thiophene–benzene bay regions is 45.8° (Fig. 2b). In comparison, the respective benzene–benzene dihedral angles of the fourfold *o*-phenylene-bridged fenestrindane **3a** have a range of 28.9–35.4°.²⁶ Clearly, the large dihedral angle of the thiophene–benzene moiety in **8CHO** is due to the markedly different geometry of the thiophene ring as compared to that of a benzene ring. The nonplanarity of a ring can be quantified by averaging the distances of the constituting atoms from their own mean plane.⁶⁴ The seven-membered rings of **8CHO** have a nonplanarity of *ca.* 29 pm, which is 16% larger than that of the cycloheptatriene rings of **3a** (*ca.* 25 pm). The two C–C–C

bond angles across the fenestrane core (α and β) reflect the degree of planarization of the central quaternary carbon atom (around a perfectly planar tetracoordinate carbon atom, $\alpha = \beta = 180^\circ$). The X-ray structural analysis of **8CHO** gave $\alpha = 115.9^\circ$ and $\beta = 113.6^\circ$, which does not exceed significantly the corresponding bond angles of the parent BDTF **5** (115.3, 111.3°)³¹ and of the β,β' -dibromide **12** (116.4, 110.7°). As shown in Fig. 2c, the cyclohexane ring (highlighted in purple) of the [5.5.5.6]fenestrane core exhibits disorder as the twist conformation (left) and the half-chair conformation (right). In principle, the two conformations are interconvertible through a single transition state by moving just two carbon atoms in opposite directions.⁶⁵ In the twist conformation, the molecular symmetry of **8CHO** is roughly *C*₂. In the crystal lattice, a plethora of short contacts involving the bridgehead C–H bonds, the sulfur atoms and the aldehyde groups are observable (Fig. S3).

UV–Vis absorption spectroscopy

The UV–Vis absorption spectra of diaryl-BDTFs **6H**, **7H** and **7CHO**, as well as their corresponding doubly cyclodehydrogenated derivatives **8H** and **8CHO** are shown in Fig. 3. Bis(3,4-dimethoxyphenyl)-BDTF **7H** exhibited a broad, featureless absorption profile above 250 nm without any distinct



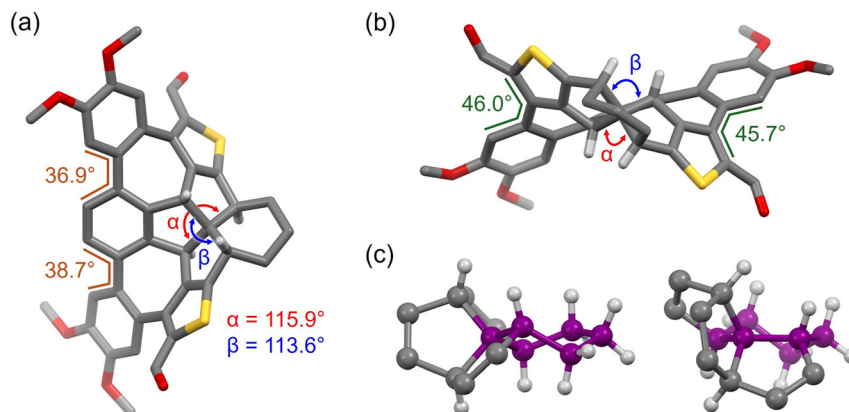


Fig. 2 Molecular structure of **8CHO** determined by single-crystal X-ray diffraction. (a) and (b) Structure of the approximately C_2 -symmetrical conformer in two different perspectives. Hydrogen atoms (except the bridgehead methines) are omitted for clarity. (c) Ball-and-stick diagrams of the [5.5.5.6]fenestrane core of **8CHO** where the six-membered ring (highlighted in purple) displays disorder: twist conformation (left) and half-chair conformation (right).

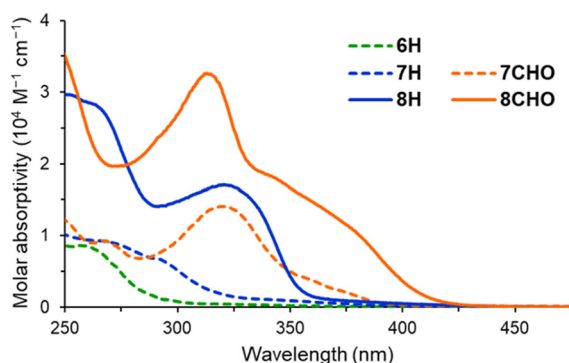


Fig. 3 UV-Vis absorption spectra of BDTFs **6H**, **7H**, **7CHO**, **8H** and **8CHO** (chloroform, 50 μ M).

maximum. In contrast, the diformylated derivative **7CHO** showed two absorption maxima at 267 and 320 nm. The latter, more intense peak is attributed to the $\pi \rightarrow \pi^*$ transition of the thiophene–benzene moiety. The absorption band beyond 340 nm may originate from the $n \rightarrow \pi^*$ transition due to a sulfur-to-aldehyde charge transfer (CT).

In the absorption spectrum of the doubly cyclized derivative **8CHO**, we observed an enhanced intensity, a blue-shifted absorption maximum (313 nm) and a longer absorption edge (428 nm) relative to **7CHO**. The small blue shift may indicate that the molecule actually becomes less extensively conjugated upon cyclization. This phenomenon is opposite to the red shift observed when tetrakis(3,4-dimethoxyphenyl)fenestrindane, the precursor of **3a**, was doubly cyclized in a similar fashion.²⁶ The peculiarity can be resolved by realizing the thiophene–benzene moiety in **7CHO** is “more coplanar” than the corresponding biphenyl moiety in tetraarylfenestrindanes. This is because, in the former case, the geometry of thiophene renders a diminished steric clash of protons across the bay regions.^{66,67} Consequently, cyclization of **7CHO** distorts the di-

hedral angle of the thiophene–benzene moiety to a larger value (45.8° based on X-ray data). The extension of the absorption edge of **8CHO** pinpointed an intensified $n \rightarrow \pi^*$ transition after cyclization. Similarly, this can be rationalized by the weakened thiophene–benzene conjugation, which in turn strengthens the sulfur–aldehyde interaction within the thiophene ring. In line with this, in the absorption spectrum of the decarbonylated derivative **8H**, the sulfur-to-aldehyde CT band is absent. The absence of the formyl group in **8H** leads to a greater thiophene–benzene conjugation, and thus a slightly red-shifted absorption maximum at 321 nm.

Fluorescence spectroscopy

The fluorescence spectra of BDTFs **7H**, **7CHO**, **8H** and **8CHO** were measured in chloroform (Fig. 4). Notably, the spectrum of bis(3,4-dimethoxyphenyl)-BDTF **7H** showed two emission maxima at 335 and 450 nm. The latter peak is much more intense and broader than the former. On the contrary, the spectra of BDTFs **7CHO**, **8H** and **8CHO** showed a single emission maximum at 443, 378 and 482 nm, respectively. These three emission wavelengths reveal the same trend as the absorption onsets (Table S2). In other words, these emissions involve the transition from the first electronically excited state (S_1) to the ground state (S_0). For the anomalous dual emitter **7H**, the short-wavelength emission at 335 nm can be assigned likewise to the $S_1 \rightarrow S_0$ transition.

To decipher for **7H** the physical origin of the second emission band at 450 nm, we hypothesized that an excited molecule of **7H** at S_1 is associated with another molecule of **7H** at S_0 , forming a complex that fluoresces at a longer wavelength. Such a complex is known as an excimer if the two constituent molecules are identical, and as an exciplex if they are different.⁶⁸ Note that **7H** was synthesized as a racemate, so the excited complex can be homochiral and/or heterochiral. Hence, we hereafter use the less stringent term “exciplex” rather than “excimer” to describe this complex. The hypothesis



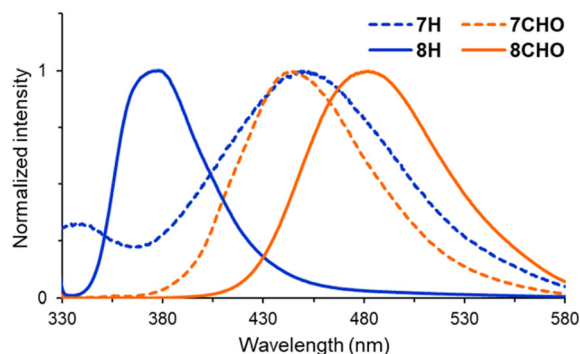


Fig. 4 Emission spectra (chloroform, $\lambda_{\text{ex}} = 300$ nm) of BDTFs **7H**, **7CHO**, **8H** and **8CHO** ($c = 50 \mu\text{M}$ except for **8H** $c = 2.5 \mu\text{M}$).

was tested in two types of experiments. First, the emission spectra of **7H** dissolved in five additional solvents were obtained (Fig. 5a). In all cases, the first emission band at around 335 nm was present. Notably, the second emission band (450 nm in chloroform) was blue-shifted to 424, 434, 430 and 420 nm in toluene, THF, dichloromethane and acetonitrile, respectively. In ethanol, this second band is absent. Second, concentration-dependent fluorescence measurements of **7H** in chloroform revealed that the emission intensity at 450 nm decreased as the concentration of **7H** decreased (Fig. 5b). Similar concentration-dependent measurements of **7H** in acetonitrile and of diphenyl-BDTF **6H** in chloroform

(Fig. S4) showed dual emission, albeit with a less intense exciplex band. To sum up, both the solvatofluorochromism and the concentration dependence observed are in line with the hypothesis of exciplex formation.⁶⁹ Alternative reasons for a dual emission such as anti-Kasha emission⁷⁰ or formation of an intramolecular charge-transfer (ICT) state⁷¹ are refuted because these would be concentration-independent.

The lifetimes of both the monomer emission (335 nm) and exciplex emissions (450 nm) of **7H** were measured using time-correlated single photon counting (TCSPC) in two different solvents. The lifetime decay curves in chloroform and in acetonitrile were obtained and fitted by mono-exponential fitting. In chloroform, the lifetimes (τ) of the monomer and exciplex emissions are 1.68 and 10.61 ns, respectively (Fig. 5c). In acetonitrile, the lifetimes are 1.08 and 3.16 ns, respectively (Fig. 5d). Hence, the exciplex of **7H** is more stable in chloroform than in acetonitrile.

To understand the structural requisites of **7H** that enable exciplex formation, two control compounds were synthesized (Fig. 5e). The known compound **14**^{72,73} represents the isolated fluorophore present in BDTF **7H**. In addition, an isomer of **7H**, α,α' -bis(3,4-dimethoxyphenyl)-BDTF **15**, was prepared in 86% yield by coupling α,α' -dibromide **11** with 3,4-dimethoxyphenylboronic acid. Both compounds were subjected to fluorescence measurements in chloroform in the concentration range of 5–500 μM (Fig. S5). Compound **14** exhibited a single (monomer) emission at 340 nm even at a high concentration of 500 μM . This suggests that the fluorophore **14** alone is

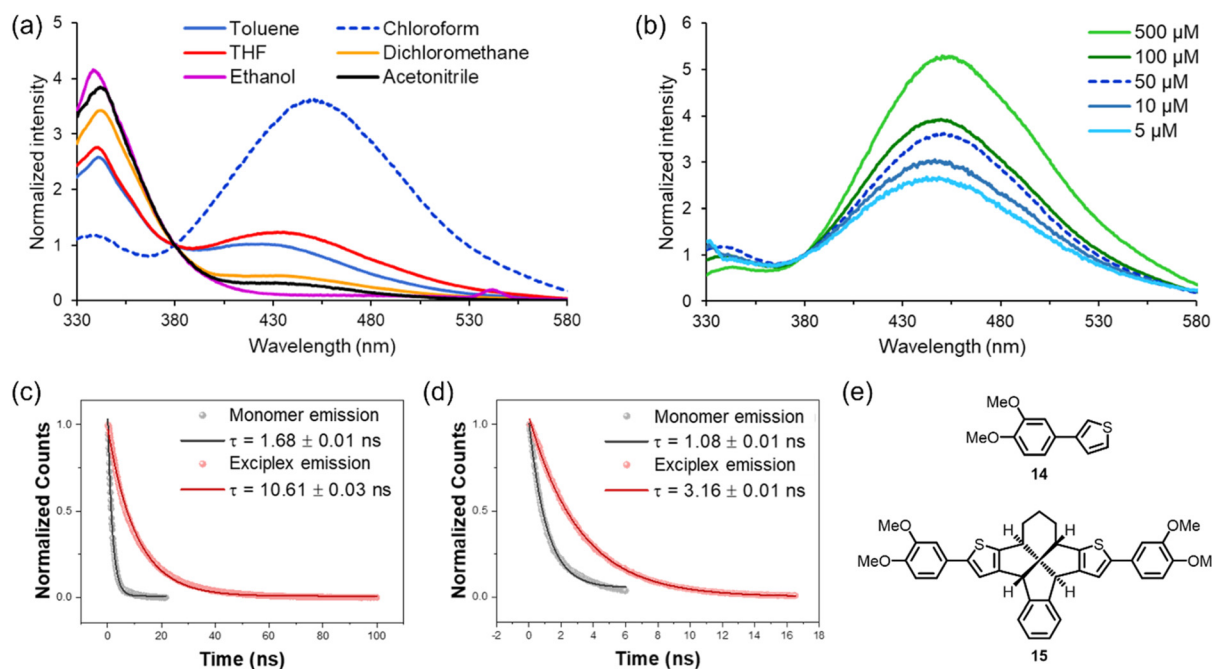


Fig. 5 (a) Solvent-dependent emission spectra of **7H** (50 μM , $\lambda_{\text{ex}} = 270$ nm in ethanol, 313 nm in acetonitrile, and 300 nm in the remaining four solvents). (b) Concentration-dependent emission spectra of **7H** (chloroform). Fluorescence decay curves of **7H** (c) in chloroform and (d) in acetonitrile ($\lambda_{\text{ex}} = 270$ nm). The monomer emission and exciplex emission are shown in black and red, respectively. (e) Structures of model compounds **14** and **15** synthesized.

incapable of exciplex formation. Likewise, the α,α' -diaryl-BDTF **15** showed only one monomer emission at 376 nm even at 500 μM . Both results pinpoint the necessity for the 3,4-dimethoxyphenyl groups in **7H** to interact through-space with the benzo unit. Although the exciplex geometry of **7H** is unclear and difficult to model, the β,β' -diaryl-BDTF constitution must be crucial to allow the formation of exciplex.

Conclusions

In this paper, we demonstrated the successful three-step transformation of benzodithieno[5.5.5.6]fenestrane **5** into β,β' -diaryl-BDTFs **6H** and **7H**, which are otherwise difficult to obtain *via* direct C–H activation methods. The overall double cyclization of bis(3,4-dimethoxyphenyl)-BDTF **7H** to yield the novel *o*-phenylene-bridged BDTF **8H** was achieved in three steps, involving the diformylated intermediates **7CHO** and **8CHO**. In the solid state, the *o*-phenylene-bridged BDTF **8CHO** shows a greater distortion at the seven-membered rings and a larger variety of short contacts compared to the all-benzene analogue **3**. Most surprisingly, both diphenyl-BDTF **6H** and bis(3,4-dimethoxyphenyl)-BDTF **7H** show dual emission. The origin of the long-wavelength emission was ascribed to the formation of the corresponding exciplexes, as corroborated by its solvatofluorochromic and concentration dependences as well as lifetime measurements. In summary, this work showcases that heteroarene-fused fenestranes, when suitably derivatized by π -extension, can exhibit unexpected photophysical properties that are not observed for the benzene-fused analogues.

Author contributions

M.-K. Lee performed the synthesis, data collection and data analysis. C.-F. Ng measured and refined the X-ray crystal structures. D. Kuck reviewed the data and edited the manuscript. W.-S. Wong formulated the project, reviewed the data and wrote the first draft. H.-F. Chow supervised the project and reviewed the data. All co-authors approved the final draft.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this study are available in the article and its supplementary information (SI). Supplementary information: experimental procedures and spectroscopic data. See DOI: <https://doi.org/10.1039/d5qo01298h>.

CCDC 2039282, 2039283 and 2212499 contain the supplementary crystallographic data for this paper.^{74a–c}

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