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# Regioselective late-stage functionalization of tetraphenylenes: rapid construction of double helical architectures and potential hole transport materials†‡

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Herein we report a novel approach for diversification of tetraphenylene *via* regioselective late-stage iodination followed by atom(s) insertion into the resulting cyclic iodonium salts. Thus, the steric hindrance effect of *tert*-butyl facilitates the regioselective synthesis of two cyclic iodonium salts of 2,7,10,15-tetra-*tert*-butyltetraphenylene. In addition, two more cyclic iodonium salts of 2,7,10,15-tetranitrotetraphenylene were also readily synthesized due to the *meta*-position induced effect of the electron-withdrawing $NO_2$ group. Subsequent functionalization of these tetraphenylene-based cyclic iodonium salts *via* diverse atom(s) insertion processes led to several tetraphenylene-based [8 + *n*] and [*n* + 8 + *n*] fused rings including fascinating double helical architectures. This newly developed late-stage functionalization methodology was also successfully applied to rapid synthesis of potential hole transport materials, thereby demonstrating its robust synthetic value in both tetraphenylene chemistry and materials science.

## Introduction

Tetraphenylene (**1**) is a nonplanar molecule featuring two opposite pairs of benzene rings that are oriented alternatively above and below the plane of the central cyclooctatetraene, featuring a distinct saddle-shaped structure with two types of C–C bonds in different lengths (Fig. 1).[1,2] It is noteworthy that appropriate substitutions on the benzene rings of **1** impair the symmetry of **1**, providing versatile chiral tetraphenylene derivatives.[1d,3] With the unique three-dimensional geometry and chiral properties, studies of tetraphenylenes have led to extensive applications in a variety of research fields, such as supramolecular chemistry,[4] asymmetric catalysis,[5] materials science,[6] covalent-organic frameworks,[7] *etc.*

Since the first synthesis of **1** was reported in 1943,[2a] numerous approaches towards the bottom-up construction of the tetraphenylene core have been reported.[1g–i] Generally, there are mainly five methods, which are summarized in Scheme 1A: (1) Diels–Alder cycloaddition between 1,2,5,6-dibenzocyclooctа-3,7-diynes and furans followed by deoxygenation,[8] (2) metal-mediated pyrolysis of biphenylenes followed by annulative dimerization,[9] (3) rhodium-catalyzed double [2 + 2 + 2] cycloaddition of triynes,[10] (4) metal-catalyzed or metal-mediated (cross)coupling of 2,2′-disubstituted biphenyls or 2-halobiphenyls,[3,4d,5b,11] and (5) cyclization of *o*-quateraryls by the Scholl reaction.[12] Indeed, over several decades, these methods have their merits and were employed efficiently in the synthesis of various tetraphenylenes. However, the limitations and disadvantages of these methods are also obvious because the starting materials rely on pre-functionalized building blocks and are usually accompanied by synthetic difficulties. Therefore, an efficient synthesis of highly functionalized tetraphenylenes has always been a synthetic challenge.

Late-stage functionalization has emerged as an appealing and versatile strategy for expanding the diversity of complex

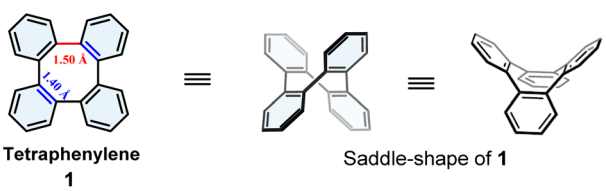


Fig. 1 Structure of tetraphenylene (**1**).

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† This article is dedicated to the memory of Professor Chin-Kang Sha.

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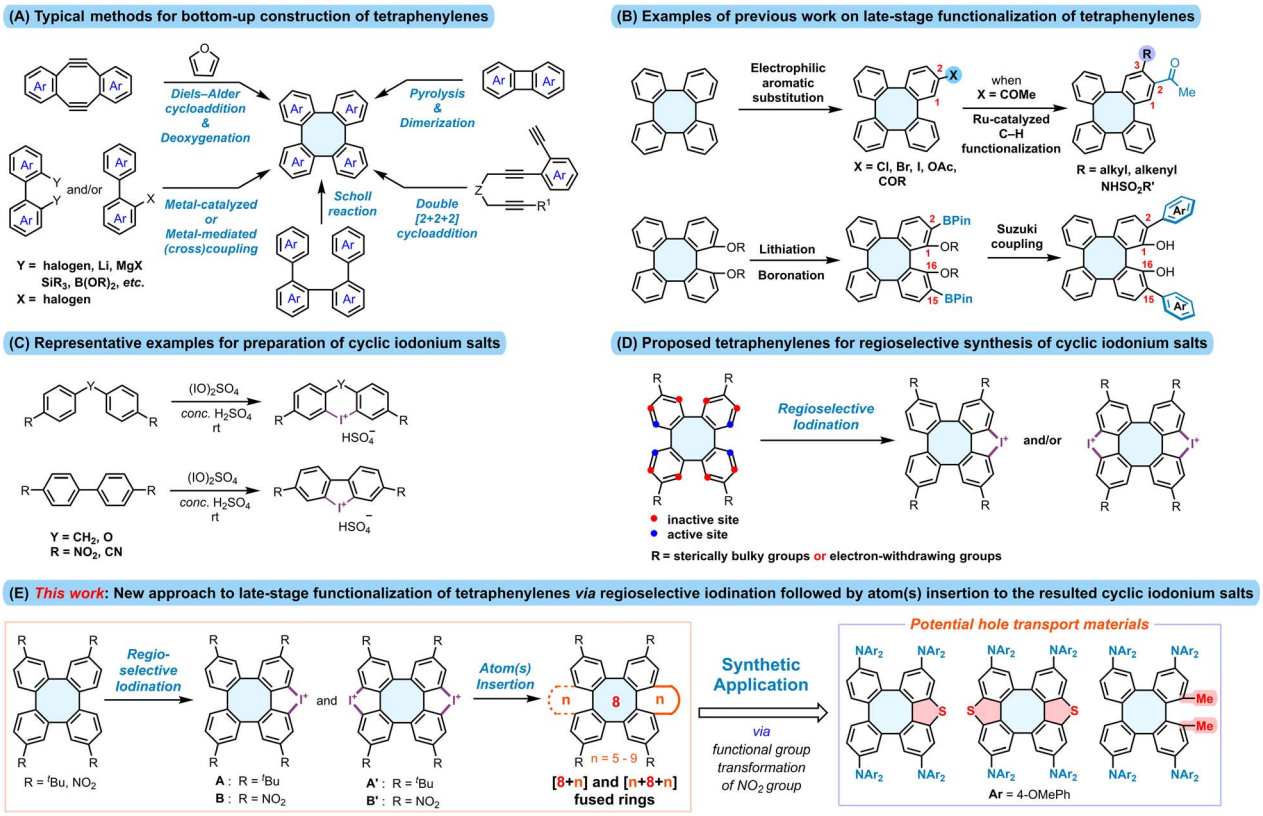


Scheme 1 (A) Typical methods for bottom-up construction of tetraphenylenes; (B) examples of previous work on late-stage functionalization of tetraphenylenes; (C) representative examples for preparation of cyclic iodonium salts; (D) proposed tetraphenylenes for regioselective synthesis of cyclic iodonium salts; (E) late-stage functionalization of tetraphenylenes *via* regioselective iodination followed by atom(s) insertion, and application in synthesis of hole transport materials.

scaffolds.[13] Apart from the aforementioned bottom-up methods for the construction of the cyclooctatetraene core, direct late-stage functionalization of tetraphenylenes is a concise and valuable strategy to address the diversity of tetraphenylenes, particularly for unsymmetrically substituted tetraphenylenes.[14] As shown in Scheme 1B, in 2016, Zhang and co-workers reported the late-stage transition-metal-catalyzed halogenation, acetoxylation and carbonylation of **1**, providing a variety of 2-substituted tetraphenylenes.[14h] Later, they further developed carbonyl directed ruthenium-catalyzed *ortho* C–H functionalization of 2-acetyltetraphenylene, leading to a variety of 2,3-disubstituted tetraphenylene derivatives.[14i] Recently, our group has devised a reliable method for the realization of a library of 2,15-disubstituted 1,16-dihydroxytetraphenylenes, whose pathway involves a late-stage lithiation/boronation process to afford a key 2,15-bis-borylated intermediate, allowing for subsequent Suzuki coupling reactions.[5f] Although these late-stage functionalization methodologies have provided excellent results for the synthesis of various tetraphenylenes, there are still significant limitations such as (1) electrophilic aromatic substitutions are only applicable to the synthesis of mono-substituted tetraphenylenes, (2) the access to multi-substituted tetraphenylenes relies on the use of *ortho*-directing groups, (3) it is usually hard to precisely predict the substituted positions of tetraphenylenes due to the random reaction sites of four benzene rings, and so on. Thus, to date, reliable and practical strategies on late-stage functionalization of tetraphenylenes to afford their respective highly functionalized derivatives remain sparse. It is still desirable to develop new late-stage functionalization strategies for the precise and divergent synthesis of polyfunctional tetraphenylenes.

Over the past decade, the applications of cyclic diaryliodonium salts in the construction of complex molecules as an effective late-stage functionalization methodology have witnessed significant progress; therefore the preparation of cyclic diaryliodonium salts has been well established.[15] One of the attractive and efficient methods for the synthesis of cyclic diaryliodonium salts is that 4,4′-disubstituted diaryls were directly used to react with iodosyl sulfate (Scheme 1C).[16] Inspired by the synthetic simplicity of cyclic diaryliodoniums and their abundant and various transformations,[15a] we opine that meticulous manipulation of tetraphenylenes bearing suitable substituents (such as sterically bulky $^t$Bu groups and electron-withdrawing $NO_2$ groups) could regioselectively afford similar cyclic iodonium salts for further functionalization, leading to structurally diverse tetraphenylene derivatives (Scheme 1D). Herein we report a novel approach for diversification of **1** *via* regioselective late-stage iodination followed by insertion of atoms into the resulting cyclic iodonium salts. These approaches afforded various structurally well-defined tetraphenylene-based [8 + *n*] and [*n* + 8 + *n*] fused-

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ring compounds with aesthetic architectures such as fascinating double helical frameworks. Furthermore, this methodology was also successfully applied to a rapid synthesis of several potential hole transport materials (Scheme 1E).

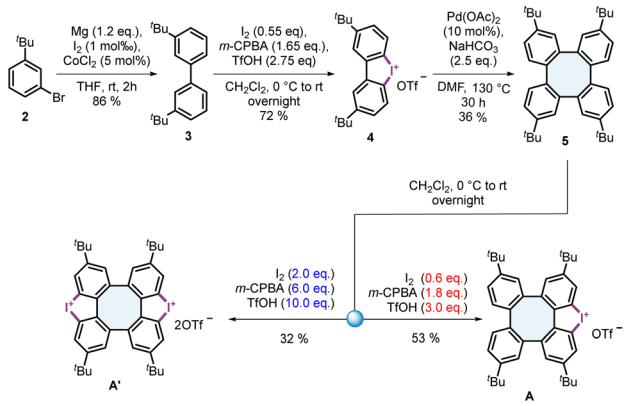
## Results and discussion

### Synthesis of cyclic iodonium salts of tetraphenylenes

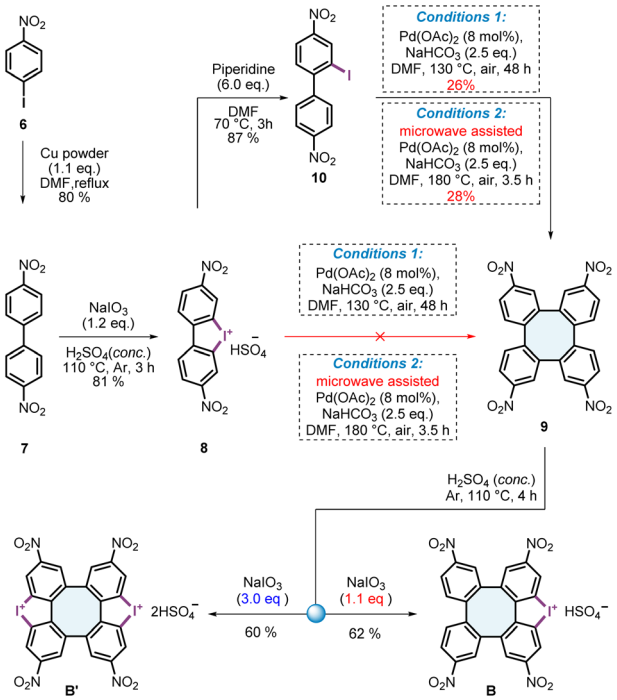
To date, a number of methods for preparing cyclic aryliodoniums have been established.[15a] For example, early in the 1950s, Hwang and co-workers built up a very simple and efficient method to prepare six-membered cyclic diaryliodonium salts *via* the reaction of 4,4′-disubstituted diaryls and iodosyl sulfate in concentrated sulfuric acid.[16a,b] Later, five-membered cyclic diaryliodonium salts of 4,4-dinitrobiphenyl were readily achieved under the same reaction conditions.[16c] On the other hand, a literature report revealed that the sterically bulky $^t$Bu group on the benzene ring could hinder iodination of the *ortho*-positions.[17] Thus, these elegant synthetic studies featuring operational simplicity have inspired us to attempt to realize similar tetraphenylene-based cyclic iodonium salts.

As shown in Scheme 2, initially we adopted a cobalt-catalyzed homo-coupling reaction of *in situ* generated magnesium bromide of 1-bromo-3-*tert*-butylbenzene (**2**) to provide biaryl **3** with good yield (86%).[18] Subsequently, biaryl **3** was treated with $I_2$, m-CPBA and TfOH in $CH_2Cl_2$ at 0 °C, generating the cyclic iodonium salt **4** in 72% yield under mild conditions.[19] Then, a palladium-catalyzed annulative dimerization of **4** in the presence of $NaHCO_3$ offered 2,7,10,15-tetra-*tert*-butyltetraphenylene (**5**) in 36% yield.[11e,20] Finally, treatment of **5** with $I_2$, m-CPBA and TfOH successfully furnished cyclic iodonium salt **A** in 53% yield.[19] Under similar conditions, bis-cyclic iodonium salt **A′** was also obtained in a yield of 32% by increasing the amounts of $I_2$, m-CPBA and TfOH.

Likewise, 2,7,10,15-tetranitrotetraphenylene-based cyclic iodonium salts **B** and **B′** were synthesized as described in Scheme 3. Initially, 1-iodo-4-nitrobenzene (**6**) went through a Cu-mediated Ullmann coupling to generate 4,4′-dinitrobiphenyl (**7**) with a yield of 80%. Subsequent treatment of **7**




Scheme 2 Synthetic route of tetraphenylene **5** and its cyclic iodonium salts A and A′.




Scheme 3 Synthetic route of tetraphenylene **9** and its cyclic iodonium salts B and B′.

with $NaIO_3$ in concentrated sulfuric acid at 110 °C directly provided cyclic iodonium salt **8** in 81% yield.[21] However, a straightforward palladium-catalyzed annulative dimerization of **8** did not give expected 2,7,10,15-tetranitrotetraphenylene (**9**).[11e,20] Alternatively, reduction of **8** with piperidine successfully delivered 2-iodo-4,4′-dinitrobiphenyl (**10**) with 87% yield.[22] Then, biphenyl **10** underwent a palladium-catalyzed annulative dimerization in the presence of $NaHCO_3$ at 130 °C for 48 h to furnish **9** with a yield of 26%.[11e] Of note, a microwave-assisted reaction under the same conditions could significantly shorten the reaction time from 48 h to 3.5 h, but did not improve the reaction yield (28%). Finally, tetranitrotetraphenylene **9** was subjected to 1.1 equivalents of $NaIO_3$ in concentrated sulfuric acid at 110 °C, successfully giving the cyclic iodonium salt **B** in 62% yield.[21] The bis-cyclic iodonium salt **B′** was successfully obtained in 60% yield by using 3.0 equivalents of $NaIO_3$ under the same conditions.

### Functionalization of tetraphenylenes enabled by atom(s) insertion into cyclic iodonium salts

With cyclic iodonium salt **A** in hand, we tried a series of reactions to form a variety of [8 + *n*] fused rings. Thus, cyclic iodonium salt **A** was first employed for the synthesis of a family of [8 + 5] fused rings by insertion of various atoms including nitrogen, oxygen, sulfur, and selenium (Scheme 4). 4-Methoxyaniline (**11**) readily reacted with **A** under the catalyzed system of $Cu(OAc)_2$ with $Na_2CO_3$ refluxing in ethylene glycol/$^i$PrOH, providing a nitrogen insertion compound **12** with a yield of 52%.[23] Then, a copper-catalyzed oxygen insertion of **A** was also realized, yielding an oxygen-bridged tetraphenylene **13** (50%).[24]

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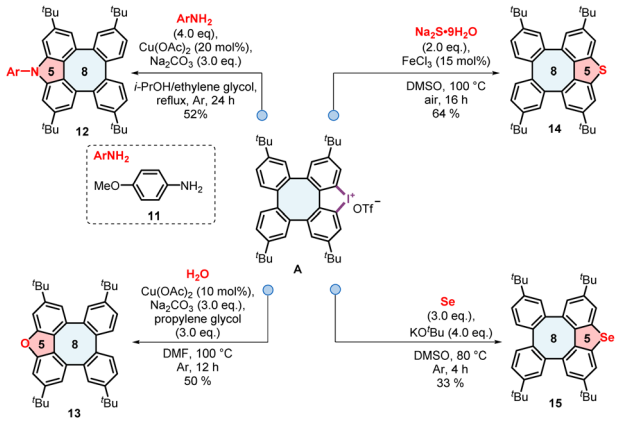
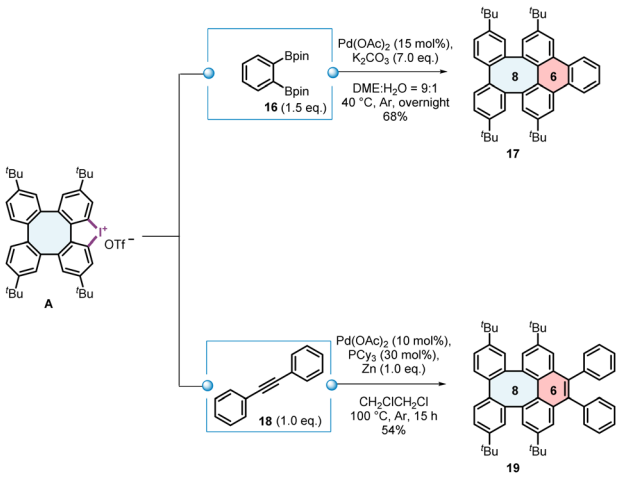



Scheme 4 Syntheses of [8 + 5] fused rings.

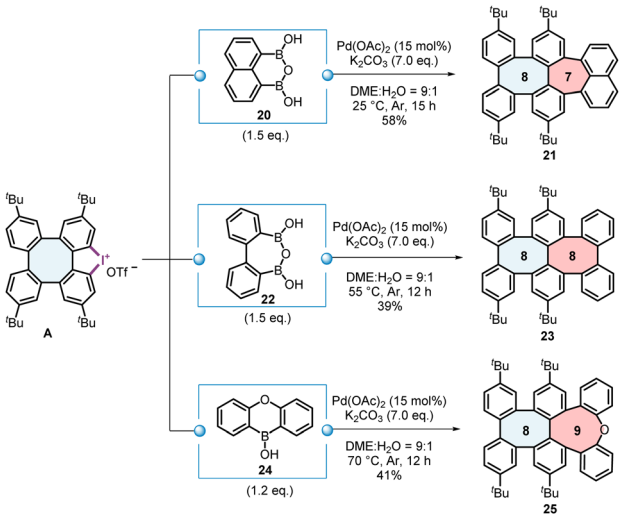
Notably, $H_2O$ was vital, acting as the oxygen source in this reaction. Treatment of **A** with $Na_2S{\cdot}9H_2O$ using $FeCl_3$ as a catalyst in DMSO at 100 °C generated a sulfur-containing compound **14** in 64% yield.[25] Additionally, the transition-metal-free selenium insertion into **A** in DMSO with KO$^t$Bu at 100 °C delivered **15** with an acceptable yield of 33%.[26]

After a family of [8 + 5] fused rings had been synthesized, the synthesis of [8 + 6] fused rings was also carried out (Scheme 5). The double Suzuki reaction between cyclic iodonium salt **A** and 1,2-diborylated **16** (ref. 27) at a lower temperature (40 °C) efficiently offered a [8 + 6] fused ring **17** in 68% yield.[11c] In addition, the [4 + 2] benzannulation between **A** and 1,2-diphenylethyne (**18**), utilizing a palladium-catalyzed protocol, delivered a [8 + 6] fused ring **19** in an acceptable yield of 54%.[28]

To expand the reaction scope, it was worth noting that the synthesis of [8 + 7], [8 + 8], and [8 + 9] fused rings by employing palladium-catalyzed coupling annulative reactions of cyclic iodonium salt **A** and various coupling blocks was also investigated (Scheme 6). The palladium-catalyzed double Suzuki coupling reaction between cyclic iodonium salt **A** and naphthalene-1,8-diboronic acid anhydride (**20**) led to the formation of **21** in 58% yield.[11c] Treatment of **A** with 1,1′-biphenyl-2,2′-



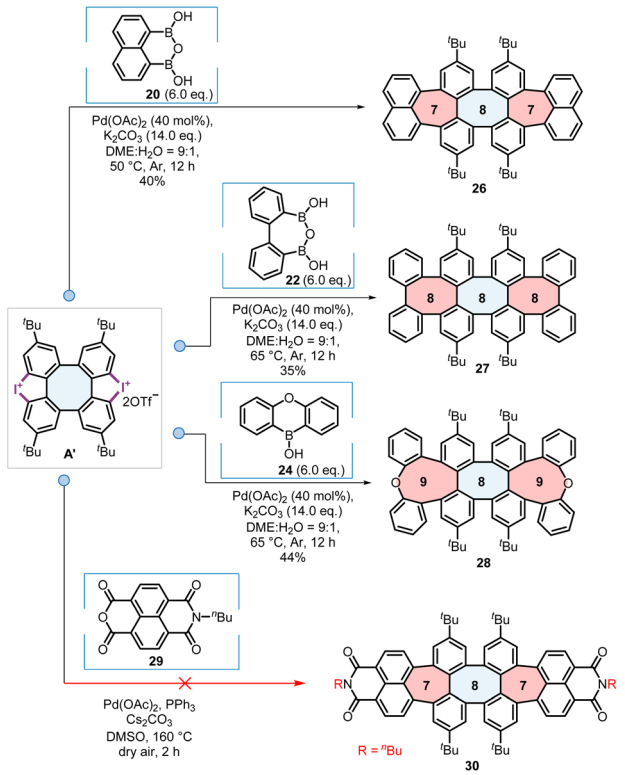

Scheme 5 Syntheses of [8 + 6] fused rings.




Scheme 6 Syntheses of [8 + 7], [8 + 8], and [8 + 9] fused rings.

diboronic acid anhydride (**22**) under the same Suzuki coupling conditions delivered the desired [8 + 8] fused ring **23** in a yield of 39%. Notably, dibenzoxaborininol **24**, which was obtained from diaryl ether following Fu's procedure,[29] was allowed to react with **A** to give a [8 + 9] fused ring **25** in 41% yield.

Moreover, palladium-catalyzed Suzuki coupling reactions of bis-cyclic iodonium salt **A′** and various coupling partners for the construction of [$n$ + 8 + $n$] fused rings were also investigated




Scheme 7 Syntheses of [7 + 8 + 7], [8 + 8 + 8], and [9 + 8 + 9] fused rings.

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(Scheme 7). First, a [7 + 8 + 7] fused ring **26** was obtained in 40% yield by a palladium-catalyzed coupling reaction between bis-cyclic iodonium salt **A′** and naphthalene-1,8-diboronic acid anhydride (**20**).[11c] Then, the palladium-catalyzed coupling reaction between **A′** and diboronic acid anhydride **22** afforded an octaphenylene **27** in 35% yield. It is interesting to note that a [9 + 8 + 9] fused ring **28** was easily obtained in an acceptable yield (44%) by a twofold atom insertion process. The fascinating double helical structure **28** (CCDC 2381518) was revealed by an X-ray diffraction analysis (Fig. 2).[30] Unluckily, the palladium-catalyzed coupling reaction between **A′** and naphthalene carboxamide **29** could not deliver the expected diimide-containing **30**.[31]

Oligotetraphenylenes are a class of interesting molecules, featuring an artificial double helical architecture with fascinating molecular configurations and extensive application prospects.[6j–l,32] As shown in Scheme 8, Rajca and coworkers first reported a convergent synthetic route to octaphenylene **33** based upon stepwise connection and annelation of two molecules of 1,16-dibromotetraphenylene **31** bearing *tert*-butyl substituents. In their work, double lithium–bromine exchange of **31** followed by the oxidative coupling of the resulting dilithiotetraphenylene **32** with $CuBr_2$ gave the target **33** in a mere 4% yield, suffering from tedious and time-consuming purification steps.[32a] Notably, our new method shows robust synthetic advantage on the construction of double helical structures. In comparison, the microwave-assisted palladium-catalyzed annulative dimerization of **A** streamlines the synthetic steps of **33** and eventually delivered the double helical octaphenylene **33** in a yield of 21% with operational simplicity.

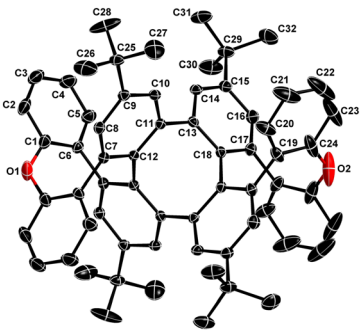
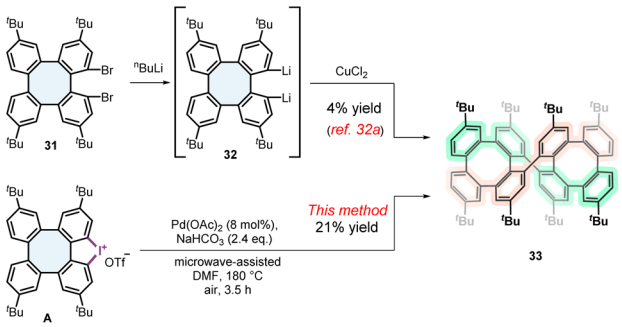



Fig. 2 X-ray diffraction analysis of **28**. Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity.




Scheme 8 Application in synthesis of double helical structure **33**.

## Application in rapid synthesis of potential hole transport materials

Over the last two decades, there has been considerable progress in the development of perovskite solar cells (PSCs).[33] Hole transport materials (HTMs) are a key component of PSCs due to their vital role in adjusting the charge dynamics.[34] Generally, an ideal HTM candidate for PSCs should possess the following features: (1) appropriately aligned energy levels with perovskites: the highest occupied molecular orbital (HOMO) level must be less negative than the valence band of perovskites for efficient hole capture, while the high-lying lowest unoccupied molecular orbital (LUMO) level ensures low electron affinity to block electron recombination at interfaces, (2) high hole mobility and conductivity: HTMs should have excellent transporting ability of free charge carriers for reducing charge losses, (3) good solubility: HTMs should be well dissolved in nonpolar and aprotic solvents for facilitating hole transport layer formation, and (4) high thermal and photochemical stability and high hydrophobicity: the stability of HTMs and their protection of perovskites from water are an efficient strategy for retarding the degradation of PSCs in a long-term durable photovoltaic operation; a high glass transition temperature of the HTM enables structural changes induced by continuous sunlight exposure to be avoided. In addition, development of HTMs requires a simple synthetic process in order to reduce the cost.

It is well known that **spiro-OMeTAD** is the most widely used HTM in PSCs due to its rigid spiro structure, which suppresses molecular aggregation, thus resulting in amorphous film-forming performance.[35] Similarly, the tetraphenylene core offers a nonpolar and rigid molecular backbone to avoid π–π stacking and forms a thermally stable amorphous phase. Therefore, the tetraphenylene framework in replacement of the spiro core would lead to a new family of HTMs. In this regard, Wang and co-workers developed two tetraphenylene-based HTMs (**OTP-OMeDPA** and **OTPE-OMeDPA**) with good power conversion efficiency (PCE) for PSCs.[6g] As shown in Fig. 3, by employing **OTP-OMeDPA** and **OTPE-OMeDPA** respectively with the same dopant in the hole transporting layer, PSC devices were fabricated with an excellent PCE of 20.6% and 21.5%, respectively, in comparison with that of 19.4% for **spiro-OMeTAD**. Notably, **OTPE-OMeTPA** presents an improved PCE in comparison with its counterpart **OTP-OMeDPA** probably due to its extended π-conjugation. These results opened a promising avenue for the modification of tetraphenylenes for the development of higher performance HTMs. Inspired by our methodology enabling rapid diversification of tetraphenylenes, we further investigated the modification of **OTP-OMeDPA** with the aim of improving the performance of potential HTMs.

Thus, a series of **OTP-OMeDPA**-based molecules including **2Me-OTP-OMeDPA**, **S-OTP-OMeDPA**, and **2S-OTP-OMeDPA** were synthesized *via* π-conjugation modification of the central eight-

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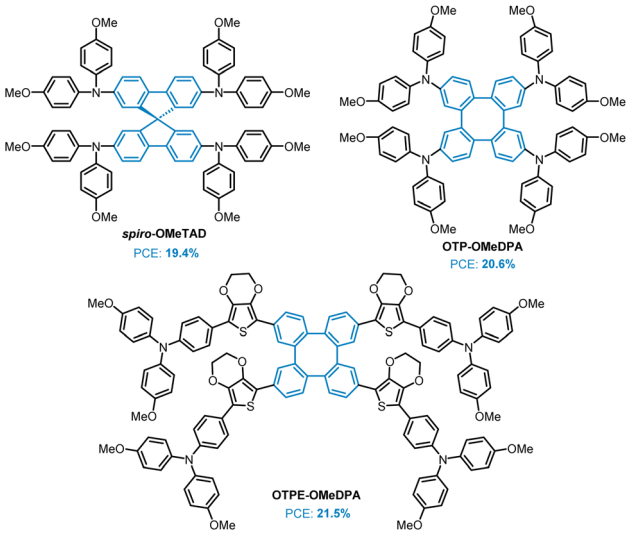
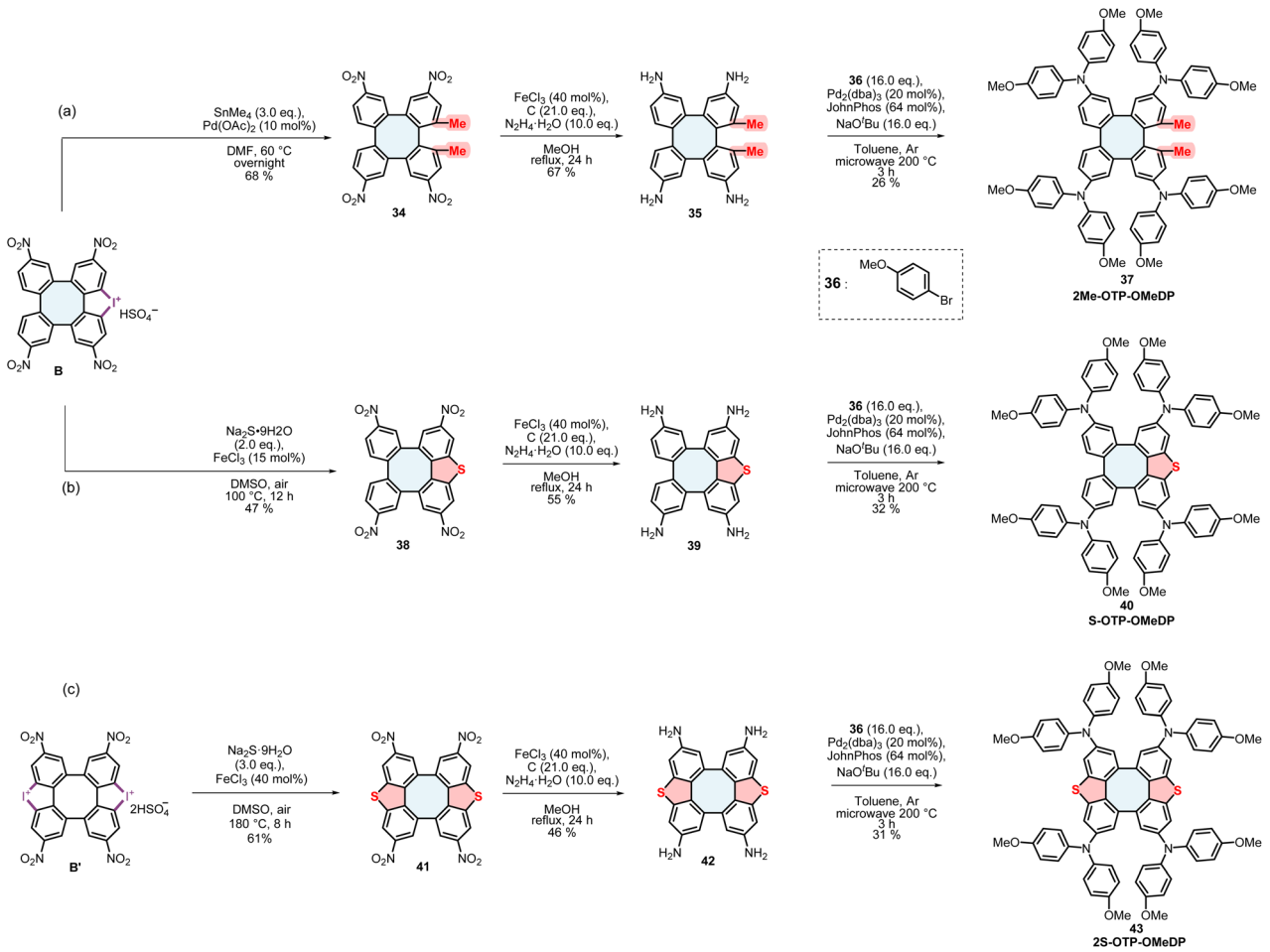



Fig. 3 Structure of representative hole transport materials.

membered ring (Scheme 9).[14e] A palladium-catalyzed double Stille coupling of cyclic iodonium salt **B** and $SnMe_4$ led to the formation of dimethyltetranitrotetraphenylene (**34**),[36] which was allowed to undergo a $FeCl_3$-catalyzed reduction by hydrazine hydrate[11h] to give tetraaminotetraphenylene **35** followed by Buchwald–Hartwig amination[37] with bromide **36** to furnish **2Me-OTP-OMeDPA** (Scheme 9a). Then, the sulfur atom was chosen as the bridging unit of the tetraphenylene core. Consequently, the reaction involving an Fe(III)-catalyzed sulfur insertion into **B** afforded a sulfur-bridged product **38** in a yield of 47%.[25] Subsequently, **38** was allowed to undergo similar reduction and amination procedures to furnish the desired **S-OTP-OMeDPA** (Scheme 9b). In addition, by treatment of bis-cyclic iodonium salt **B′** with $Na_2S\cdot 9H_2O$ catalyzed by $FeCl_3$ in DMSO at 180 °C for 8 h, the disulfur-bridged compound **41** was also obtained in 61% yield. Likewise, subsequent $FeCl_3$-catalyzed reduction of **41** and Buchwald–Hartwig amination of **42** worked smoothly to deliver **2S-OTP-OMeDPA** in an acceptable yield (Scheme 9c).

UV-vis absorption and fluorescence spectra of the potential hole transport materials **2Me-OTP-OMeDPA**, **S-OTP-OMeDPA**, and **2S-OTP-OMeDPA** as well as **OTP-OMeDPA** in $CH_2Cl_2$ were investigated (Fig. 4). The absorption maximum ($\lambda_{max}$) of **OTP-OMeDPA** at 307 nm showed a conspicuous blue shift but a narrow absorption band in comparison with that of **spiro-OMeTAD** ($\lambda_{max}$ = 383 nm, see Fig. S1 in the ESI‡).[38] The absorption curves of **2Me-OTP-OMeDPA** ($\lambda_{max}$ = 307 nm) similar




Scheme 9 Rapid synthesis of potential hole transport materials (a) **2Me-OTP-OMeDPA**, (b) **S-OTP-OMeDPA**, and (c) **2S-OTP-OMeDPA**.

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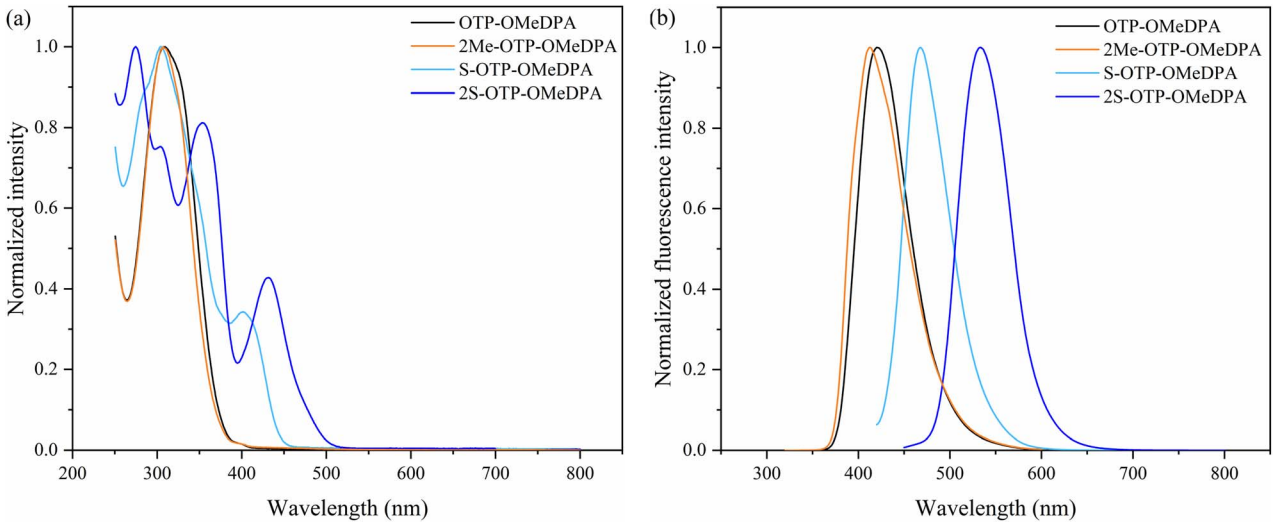


Fig. 4 (a) UV-vis absorption spectra normalized at the peak value in solution ($5 \times 10^{-5}$ M in $CH_2Cl_2$); (b) fluorescence spectra normalized at the peak value in solution ($5 \times 10^{-5}$ M in $CH_2Cl_2$); the fluorescence spectra of **OTP-OMeDPA**, **2Me-OTP-OMeDPA**, **S-OTP-OMeDPA** and **2S-OTP-OMeDPA** were recorded with excitation at 307, 307, 420, and 432 nm, respectively.

to that of **OTP-OMeDPA** indicated that the insertion of the two methyl groups did not affect the π-conjugation of the tetraphenylene skeleton much. Sulfur inserted derivatives **S-OTP-OMeDPA** ($\lambda_{max} = 420$ nm) and **2S-OTP-OMeDPA** ($\lambda_{max} = 432$ nm) exhibited a significant red shift in comparison with **OTP-OMeDPA**, which is attributed to the formation of larger conjugated fragments after sulfur was inserted into the bay area of the tetraphenylene core.[14e] Fluorescence spectra showed that **OTP-OMeDPA**, **2Me-OTP-OMeDPA** and **2S-OTP-OMeDPA** had relatively large Stokes shifts of around 80–113 nm, while **S-OTP-OMeDPA** showed a small Stokes shift of 48 nm. All of them possessed higher Stokes shifts than **spiro-OMeTAD**, whose Stokes shift was 43 nm (see Fig. S2 in the ESI‡). These results suggested a more significant change in the geometric configuration of the tetraphenylene-based HTMs than that of **spiro-OMeTAD** and thus benefited in the infiltration and pore-filling for forming compact hole-transporting layers to protect perovskites.[39]

To preliminarily evaluate their potential application in HTMs, parameters including half-wave potentials for the oxidation waves ($E_{ox}$), HOMO energy levels ($E_{HOMO}$), and LUMO energy levels ($E_{LUMO}$) of tetraphenylene-based **OTP-OMeDPA**, **2Me-OTP-OMeDPA**, **S-OTP-OMeDPA**, and **2S-OTP-OMeDPA** as well as **spiro-OMeTAD** were determined and are summarized in Table 1.[6g,34f] Cyclic voltammograms (CVs) of the tetraphenylenes (Fig. 5) and **spiro-OMeTAD** (see details in Fig. S3 in the ESI‡) were measured in THF solutions with 0.1 M $^nBu_4NPF_6$ employing $FeCp_2^+/FeCp_2$

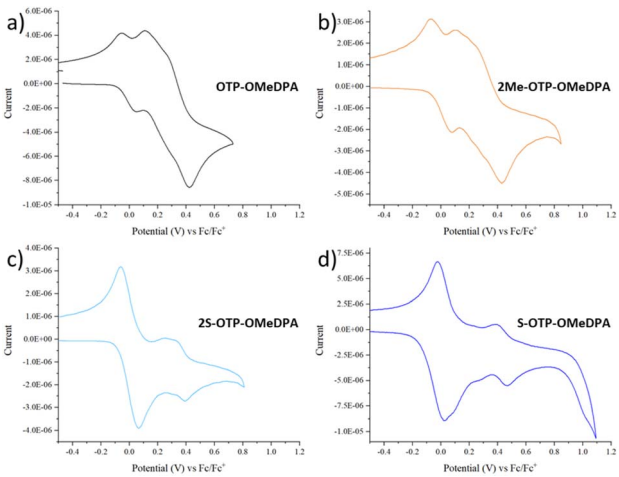


Fig. 5 Cyclic voltammograms of (a) **OTP-OMeDPA**; (b) **2Me-OTP-OMeDPA**; (c) **S-OTP-OMeDPA**; and (d) **2S-OTP-OMeDPA** recorded in THF with $FeCp_2^+/FeCp_2$ as the internal standard.

Table 1 Oxidation potentials and frontier molecular orbital energy levels of HTM candidates

| Compound | $\lambda_{edge}$ [a] (nm) | $E_{gap}$ [b] (eV) | $E_{ox}$ [c] (V) | $E_{HOMO}$ [d] (eV) | $E_{LUMO}$ [e] (eV) |
|---|---|---|---|---|---|
| **spiro-OMeTAD** | 414.6 | 2.99 | 0.35 | −5.45 | −2.46 |
| **OTP-OMeDPA** | 371.6 | 3.34 | 0.27 | −5.37 | −2.03 |
| **2Me-OTP-OMeDPA** | 380.6 | 3.31 | 0.27 | −5.37 | −2.06 |
| **S-OTP-OMeDPA** | 442.0 | 2.81 | 0.33 | −5.43 | −2.62 |
| **2S-OTP-OMeDPA** | 499.7 | 2.48 | 0.43 | −5.53 | −3.05 |

[a] The wavelength of the absorption edge ($\lambda_{edge}$) recorded in a solution ($5 \times 10^{-5}$ M in $CH_2Cl_2$). [b] HOMO–LUMO energy bandgap estimated from $\lambda_{edge}$, $E_{gap} = 1240/\lambda_{edge}$. [c] The half-wave potential *versus* $FeCp_2^+/FeCp_2$ for the oxidation wave. [d] $E_{HOMO} = -(5.10\ eV + eE_{ox})$. [e] Calculated from the HOMO–LUMO gap ($E_{gap}$) and the HOMO energy level ($E_{HOMO}$).

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as the internal standard to obtain the $E_{ox}$ values. From the CV curves shown in Fig. 5, the $E_{ox}$ values for the modified tetraphenylenes (**2Me-OTP-OMeDPA**, **S-OTP-OMeDPA**, and **2S-OTP-OMeDPA**) were found to be 0.27, 0.33 and 0.43 eV *vs.* $FeCp_2^+/FeCp_2$, which are equal to or slightly more positive than that of **OTP-OMeDPA** (0.27 eV *vs.* $FeCp_2^+/FeCp_2$) and therefore appropriate for energy alignment with the perovskite layer.[34f] The HOMO energy levels ($E_{HOMO}$) could be calculated from the $E_{ox}$ *vs.* $FeCp_2^+/FeCp_2$ using the equation $E_{HOMO} = -(5.10\ \text{eV} + eE_{ox})$.[40] In comparison, the HOMO energy levels of **2Me-OTP-OMeDPA** (−5.37 eV), **S-OTP-OMeDPA** (−5.43 eV) and **2S-OTP-OMeDPA** (−5.53 eV), which are equal to or slightly lower than that of **OTP-OMeDPA** (−5.37 eV) and **spiro-OMeTAD** (−5.45 eV), would enable efficient hole capture. Noteworthy is that the lower HOMO levels of **S-OTP-OMeDPA** and **2S-OTP-OMeDPA** are apparently associated with their extended S-bridged connection, leading to the n–π conjugation. In addition, the optical energy bandgap ($E_{gap}$) could be estimated from the longest absorption wavelength $\lambda_{edge}$, according to the equation $E_{gap} = 1240/\lambda_{edge}$ eV.[39] As a result, the LUMO energy levels ($E_{LUMO}$) could be estimated from the $E_{gap}$ and $E_{HOMO}$ according to the equation $E_{LUMO} = E_{HOMO} + E_{gap}$. The LUMO energy levels of **2Me-OTP-OMeDPA** (−2.06 eV), **S-OTP-OMeDPA** (−2.62 eV) and **2S-OTP-OMeDPA** (−3.05 eV) were found to be close to or lower than that of **OTP-OMeDPA** (−2.03 eV), exhibiting suitable reduction potentials for hole extraction from the perovskite layer.

## Conclusions

In summary, we reported a rapid and modular approach for late-stage atom(s) insertion into the tetraphenylene-based cyclic iodonium salts. The synthesis of tetraphenylene-based cyclic iodonium salts was successfully achieved through regioselective oxidative iodination oriented by both *tert*-butyl and nitro substituents. Atom(s) insertion reactions yielded a series of complex polycyclic hydrocarbons, featuring tetraphenylene-based [8 + *n*] and [*n* + 8 + *n*] fused-ring skeletons. It is worthy of note that functionalization of tetraphenylene cyclic iodonium salts could rapidly generate double helical architectures. Such appealing double helical frameworks with intrinsic chirality and potentially expandable π-conjugated systems should be of interest in the development of a new generation of advanced materials with interesting chiroptical properties. We believe that this work not only expands the diversity of tetraphenylene molecules, but also serves to inspire future widespread applications of tetraphenylene-based chiral systems in multiple fields of chiral optoelectronic materials. In addition, this late-stage atom(s) insertion strategy also enables a modular modification of the tetraphenylene-based hole transport materials. The three modified molecules show suitable properties for potential application as HTMs, indicating the robust synthetic potential of this strategy for the development of next generation HTMs.

## Data availability

The data supporting this article have been included as part of the ESI.‡ Crystallographic data for **28** have been deposited at the CCDC under 2381518 and can be obtained from **www.ccdc.cam.ac.uk/data_request/cif**, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

## Author contributions

X. Xu and H.-R. Ma performed the experimental work and data analysis. J.-F. Cui, X.-S. Peng and H. N. C. Wong conceived the project, supervised the investigation and wrote the manuscript. All authors discussed the results and contributed to the preparation of the final manuscript.

## Conflicts of interest

There are no conflicts to declare.

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