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A sequential cyclization/π-extension strategy for modular construction of nanographenes enabled by stannole cycloadditions†

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The synthesis of polycyclic aromatic hydrocarbons (PAHs) and related nanographenes requires the selective and efficient fusion of multiple aromatic rings. For this purpose, the Diels–Alder cycloaddition has proven especially useful; however, this approach currently faces significant limitations, including the lack of versatile strategies to access annulated dienes, the instability of the most commonly used dienes, and difficulties with aromatization of the [4 + 2] adduct. In this report we address these limitations *via* the marriage of two powerful cycloaddition strategies. First, a formal Cp_2Zr-mediated [2 + 2 + 1] cycloaddition is used to generate a stannole-annulated PAH. Secondly, the stannoles are employed as diene components in a [4 + 2] cycloaddition/aromatization cascade with an aryne, enabling π-extension to afford a larger PAH. This discovery of stannoles as highly reactive – yet stable for handling – diene equivalents, and the development of a modular strategy for their synthesis, should significantly extend the structural scope of PAHs accessible by a [4 + 2] cycloaddition approach.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a versatile class of organic compounds with diverse applications as components of electronic devices such as OLEDs, OFETs, and OPVs,[1–3] as well as in biology and medicine.[4] In general, the utility of these compounds stems from the diverse array of properties that can be synthetically controlled by tuning (for example) molecular shape, edge structure, and functionality.[5,6] Despite established advances in PAH chemistry, there remain substantial synthetic limitations that restrict possible architectures and new applications.

The main challenge associated with PAH synthesis is the lack of general, reliable methods for the selective fusion of aromatic rings, which generally rely on harsh conditions or specific functional handles to facilitate fusion. Significant effort has gone into developing such strategies,[7] and several reaction classes have emerged to greatly expand the diversity of accessible PAHs. These include oxidative couplings such as the Scholl reaction, electrophilic cyclization of alkynes,[8] radical cascades, annulative π-extension,[9] transition metal mediated [2 + 2 + *n*] cycloadditions,[10–13] and the Diels Alder reaction.[14]

The Diels Alder reaction, or [4 + 2] cycloaddition, has attracted particular interest in the synthesis of PAHs due to its versatility and operational simplicity.[14,15] For this application, dienes capable of undergoing facile aromatization after cycloaddition are necessary, and several systems are commonly employed. Perhaps the most ubiquitous are furans which generate epoxy-bridged intermediates, with aromatization occurring in a second, deoxygenation step (Scheme 1a).

While this method has proven valuable, particularly in the synthesis of sterically crowded acenes known as twistacenes,[16] it suffers from low overall yields and poor functional group tolerance due to the harsh aromatization step. Thus, the development of diene sources that undergo spontaneous aromatization is of high interest. There are three commonly employed dienes of this type: cyclopentadienones,[17–19] thiophene dioxides,[20,21] and oxadiazinones.[22–24] In each case, the cycloaddition intermediate aromatizes with liberation of a gas. Although these examples generate aromatic products in a single step, the electron-withdrawing character of the eliminated substituent (CO, SO_2, and CO_2) causes the dienes to be sluggish partners for standard Diels Alder reactions. This generally corresponds to limited yields for cycloadditions with benzynes, despite their promise as crucial building blocks in syntheses of nanocarbons.

Another significant roadblock in the application of these dienes to nanographene synthesis is the challenge of incorporating them into complex fused ring systems. Annulated furans

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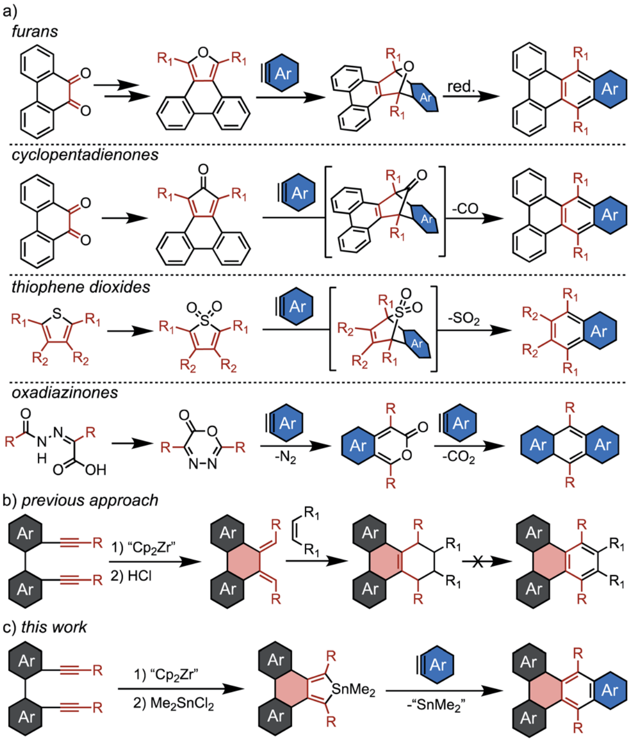


Scheme 1 (a) Commonly employed dienes for the synthesis of nanographenes *via* [4 + 2] cycloadditions; (b) prior development of a zirconocene coupling approach to the synthesis of PAHs from tethered diynes; (c) this work, combining the zirconocene coupling approach to PAH synthesis with π-extension *via* the [4 + 2] cycloaddition of stannoles.

and cyclopentadienones are most commonly generated from *o*-diones, and thus can only be appended to PAHs for which the diones are readily accessible. There are currently no straightforward ways to generate PAH-thiophene dioxides, and oxadiazinones are fundamentally incapable of being annulated to larger fused systems. Thus, the development of new strategies for appending reactive dienes to nanographene cores is critical for expanding the utility of Diels Alder cycloadditions in PAH synthesis.

Previously, this group attempted to resolve this issue *via* the use of a [2 + 2 + 1] zirconocene-mediated coupling of tethered diynes (Scheme 1b).[25] This strategy enabled the synthesis of a wide range of nanographenes from unfused precursors, and facile protodemetallation of the resulting zirconacycles generated PAH-appended dienes. Although the dienes were reactive towards dienophiles, aromatization of the resulting cycloaddition products was not possible.

To address this limitation, we sought to develop a new Diels Alder diene source that is broadly reactive with arynes and readily installed into a wide range of complex PAHs *via* the zirconocene coupling approach. To this end, several papers from Hitomi[26] and Neumann[27] that describe stannoles as sources of stannylene (:SnR_2) upon reaction with dienophiles served as inspiration. Although these studies focused primarily on the liberation of stannylene, they described high yields of the aromatic byproducts, indicating that stannoles not only undergo efficient [4 + 2] cycloadditions but also spontaneously aromatize upon liberation of divalent tin. Despite a few early observations, stannole cycloaddition chemistry has not been developed into a generally applicable methodology.[28,29] Although stannoles have been shown to be effective cross-coupling partners for direct annulation *via* Pd catalysis,[30,31] this is the first report of their general use as efficient dienes for [4 + 2] cycloadditions to generate π-extended polycyclic aromatic hydrocarbons.

In this contribution, stannoles are shown to be readily incorporated into a wide range of PAH structures using the zirconocene coupling of tethered diynes. These stannoles then serve as highly efficient dienes in Diels Alder cycloadditions with arynes (Scheme 1c), most strikingly from *ortho*-dihalo substrates which are generally incompatible with other spontaneously aromatizing dienes. Furthermore, in a demonstration of the potential for stannoles to engage in a more diverse array of cycloaddition reactions, one example is shown to undergo an unusual dimerization at high temperatures to generate a helically chiral, 1,2,4,5-cyclooctatetraene in exceptional yield (≥95%).

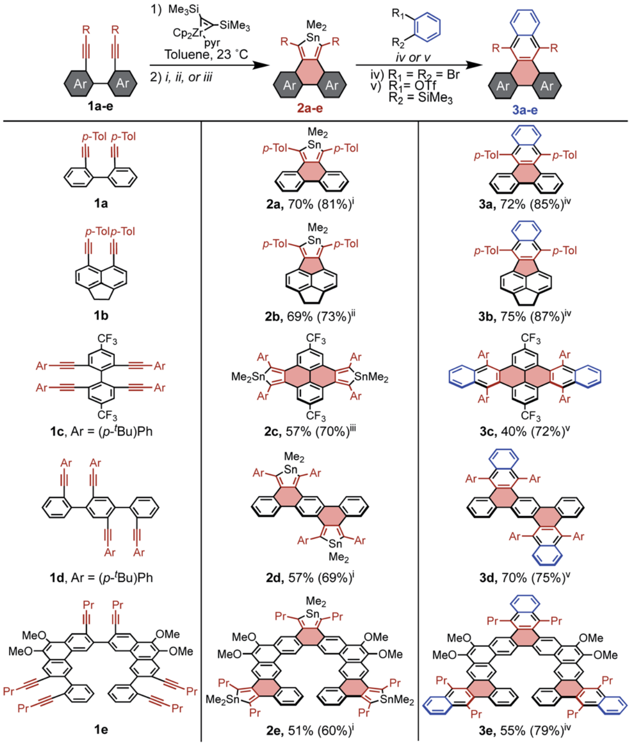
Results and discussion

It seemed that stannoles could be appended to PAHs *via* zirconocene coupling of tethered alkynes, followed by transmetalation to the stannole *via* the CuCl-mediated conditions developed by Takahashi.[32] This strategy was initially tested on **1a** to confirm that the reaction conditions were effective for previously unexplored tethered diynes (Scheme 2). It was determined that the sequence can either be performed in a stepwise manner through isolation of the intermediate zirconacycle, or in a convenient one-pot procedure using the Negishi protocol in essentially the same yield (see page S7† for all reported preparations).

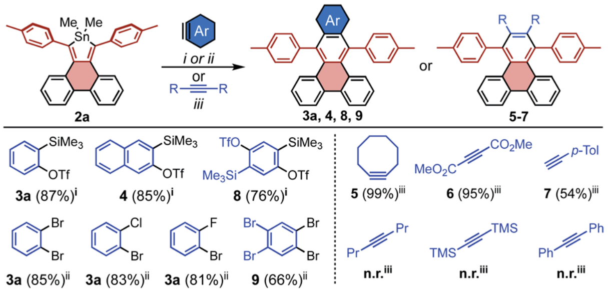
Beyond the model stannole **2a**, it is possible to construct more complex stannole-containing PAHs using this methodology (Scheme 2). Zirconocene coupling of alkynes may also be used to generate PAHs containing 5-member rings, which can similarly undergo transmetalation to stannoles as evidenced by the synthesis of stannole **2b** in 73% yield. The efficiency of stannole formation makes it possible to synthesize bis- and tris-stannoles in good yield, which enables the construction of more complex diene-containing PAH architectures such as **2c–2e**, which would be difficult to access by established methods.

Compound **2a** was utilized as a model system to explore the reactivity of stannoles for [4 + 2] cycloadditions with benzyne, beginning with the widely used and mild benzyne precursor 2-$(Me_3Si)C_6H_4(OTf)$. Initially, simple mixing of **2a**, the benzyne precursor, and the soluble fluoride source $[nBu_4N][Ph_3SiF_2]$ in toluene furnished **3a** in 78% yield by ^1H NMR spectroscopy after some optimization (page S18†). A significant improvement to 88% was seen upon addition of dimethylacetylenedicarboxylate (DMAD) as a stannylene trap,[25] but no other commonly employed traps were effective (diphenyl disulfide, diacetyl, butylbromide).

Although *ortho*-dihalo precursors to arynes generally require harsher reaction conditions, they are highly valuable building



Scheme 2 Substrate scope of stannole synthesis and subsequent π-extension *via* [4 + 2] cycloaddition with benzyne. For **2a–2e**, yields represent total isolated yield across two steps from the diyne, while yields from isolated zirconacycles are given in parenthesis. For **3a–3e**, *in situ* yields as determined by ^{1}H NMR spectroscopy are given in parenthesis. Reagents and conditions: (i) Me_2SnCl_2, CuCl, LiCl, toluene, 23 °C; (ii) Me_2SnCl_2, CuCl, LiCl, toluene, 60 °C; (iii) Me_2SnCl_2, CuCl, $ZnCl_2$, toluene, 23 °C; (iv) 1,2-dibromobenzene (1.2 equiv.), ^{n}BuLi (1.1 equiv.), toluene, 23 °C; (v) 2-(Me_3Si)C_6H_4(OTf) (1.1 equiv.), [NBu_4] Ph_3SiF_2 (3.3 equiv.), dimethylacetylenedicarboxylate (1.5 equiv.), toluene, 60 °C.



Scheme 3 Benzyne and alkyne substrate scope for [4 + 2] cycloadditions with model stannole system **2a**. Given yields were determined *in situ via* ^{1}H NMR spectroscopy. Reagents and conditions: (i) aryne (1.1 equiv.), [*n*Bu_4N][Ph_3SiF_2] (3 equiv.), dimethylacetylenedicarboxylate (1.5 equiv.), toluene, 60 °C (ii) aryne (1.2 equiv.), ^{n}BuLi (1.1 equiv.), toluene, 23 °C; (iii) alkyne (2.5 equiv.), toluene, 100–160 °C.

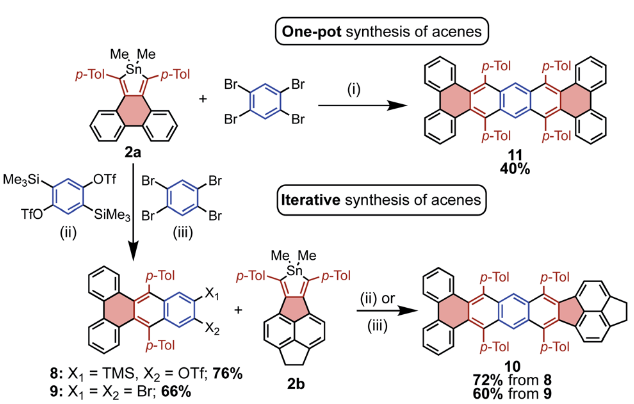
blocks due to their availability. Significantly, stannoles are robust in the presence of ^{n}BuLi, and treatment of *o*-dibromobenzene with ^{n}BuLi at 23 °C in the presence of stannole **2a** resulted in the formation of **3a** in 85% yield. This efficient transformation contrasts with the absence of analogous reactions involving cyclopentadienones, thiophene dioxides, and pyrones, which are ostensibly reactive toward organolithium species.

Generalization of these cycloaddition conditions to stannoles **2b–2e** enabled facile access to π-extended PAHs **3b–3e**. In each case except **2d**, stannoles were compatible with both types of benzyne precursors, and the method that resulted in the higher isolated yield is reported in Scheme 2. It is believed that the reaction of **2d** with *o*-dibromobenzene failed due to its very limited solubility in aromatic solvents, making its reaction with the generated benzyne too sluggish to compete with benzyne decomposition.

The range of additional benzyne sources that are compatible with [4 + 2] cycloadditions to stannoles was further explored using **2a** as a model system. For the *ortho*-Me_3Si-OTf derivative of naphthalene, the cycloaddition product **4** was accessed in 85% yield, suggesting the generality of these conditions to other *ortho*-Me_3Si-OTf PAHs. Other dihalo reactant partners may be employed, as observed for 2-chloro and 2-fluorobromobenzene which both gave **3a** in greater than 80% yield (Scheme 3).

Reactions of stannoles with common alkynes were also explored. Generally, **2a** reacted rapidly and efficiently at moderate temperatures with activated internal alkynes such as strained cyclooctyne and electron-deficient dimethyacetylene dicarboxylate, to furnish **5** and **6** in 99% and 95% yields, respectively. The unactivated terminal alkyne 4-ethynyl toluene required elevated temperature but gave reasonable conversion to the unsymmetrical PAH **7** in 54% yield (Scheme 3, R,R = H, *p*-Tol). The unactivated internal alkynes 4-octyne, bis(-trimethylsilyl)acetylene, and diphenyl acetylene were generally unreactive, even at highly elevated temperatures (160 °C in mesitylene).

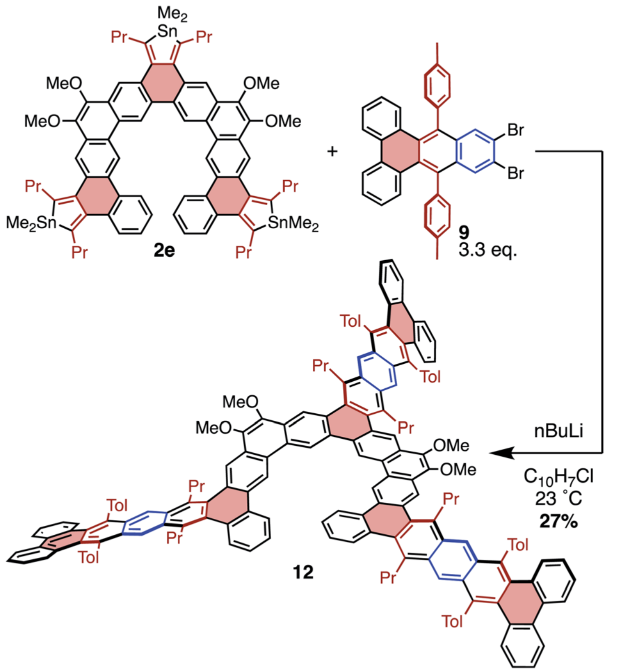
The efficiency with which stannoles undergo cycloadditions with arynes makes them desirable substrates for the synthesis of extended π-systems through multiple, successive cycloadditions. To this end, conditions were developed for the iterative addition of stannoles to bifunctional aryne precursors. Stannole



Scheme 4 Synthesis of acenes *via* the multiple addition of stannoles to benzynes. Reagents and conditions: (i) aryne (0.5 equiv.), ^{n}BuLi (1.1 equiv.), toluene, 23 °C; (ii) aryne (1.1 equiv.), [nBu_4N][Ph_3SiF_2] (3 equiv.), DMAD (1.5 equiv.), toluene, 60 °C; (iii) aryne (2 equiv.), ^{n}BuLi (1.1 equiv.), toluene, 23 °C.

2a was treated with 1.1 equivs of a bis-benzyne precursor under standard conditions for Me_3Si-OTf precursors, and this afforded the desired mono-addition product **8** in 76% isolated yield (Scheme 3). A larger excess of the aryne precursor (2 equiv.) increased the yield of **8** to 85% (see page S13†). Similarly, treatment of stannole **2a** with an excess of 1,2,4,5-tetrabromobenzene (2 equiv.) and ^{n}BuLi (1.1 equiv.) afforded the mono-addition product **9** in 66% isolated yield. Both **8** and **9** participated in a second cycloaddition with stannole **2b** to give unsymmetrical acene **10** in 72 and 60% yields, respectively (Scheme 4). One-pot double-addition of stannole **2a** to 0.5 equivalents of 1,2,4,5-tetrabromobenzene was also successful, to generate tetrabenzopentacene **11** in 40% yield.

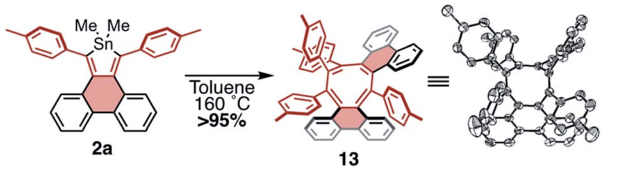
To further explore possibilities for this cycloaddition chemistry in producing unusual PAH structures, the molecular "lobster-shaped" compound **12** was chosen as a target that would be difficult to obtain using other methodologies (Scheme 5). Compound **12** was generated from stannole **2e** and benzyne precursor **9** in a manner similar to that previously described; however, due to the insolubility of **9**, 1-chloronaphthalene was used as a solvent to fully solubilize both components prior to benzyne formation. From these conditions, **12** was isolated in 27% yield, indicating an efficiency of approximately 65% per cycloaddition. Compound **12** displayed a propensity to aggregate in solution, producing sharp resonances in ^{1}H NMR spectra only at concentrations below 0.4 mM. This is likely a function of the significant π-extension in this molecule, as similar compound **3e** does not display this behavior in solution. This aggregation behavior complicates assessment of purity for **12**, as the isolated material still displays some broad resonances in addition to sharp peaks associated with unaggregated **11** (by ^{1}H NMR spectroscopy). The broad resonances may be due to impurities or partial aggregation. Despite this, MALDI unambiguously confirms the presence of **12**, and does not display peaks corresponding to over- or under-substitution in the range of 500–3000 amu (Fig. S54†). This suggests that the broadness observed by ^{1}H NMR spectroscopy is likely due to aggregation rather than the presence of major impurities.



Scheme 5 Synthesis of a π-extended helicene.

Given the facile elimination of divalent tin during the cycloadditions described above, it seemed possible that stannoles might undergo other cycloaddition–elimination processes. To explore the possibility of dimerization *via* cycloaddition, stannole **2a** was heated to 160 °C in toluene-d_8 in a sealed reaction vessel and the reaction mixture was monitored by ^{1}H NMR spectroscopy. Over a period of 12 h a new species formed in exceptionally high yield (>95%) displaying 4 tolyl CH_3 resonances of equal intensity and lacking any discernible resonances from dimethyltin. This is consistent with a product that is a highly unsymmetrical dimer, formed by elimination of Me_2Sn. Single crystals of the product were grown by slow diffusion of hexanes into a concentrated sample in $CDCl_3$, and X-ray crystallography confirmed the product as compound **13**, a helically chiral 1,2,4,5-cyclooctatetraene (COT) (Scheme 6). While there is a literature report of a COT with this substitution pattern,[33] it was formed as a minor product; to our knowledge, this is the first observation of a high-yield, selective synthesis of this type of substituted COT. This result highlights the potential for stannoles as versatile diene sources for a range of cycloadditions, making them valuable divergent building blocks for the synthesis of conjugated molecules.

The photophysics of **3b–3e**, **4**, **11**, and **12** were investigated by UV-vis and fluorescence spectroscopy (Fig. 1). The fine structure in the absorbance spectra displays significant sensitivity to the pattern of ring fusion, with **3c–3e** displaying different relative intensities of the three main absorption bands. However, the absorption onset ($\lambda_{\text{abs}}^{\text{onset}}$), and consequently the optical HOMO–LUMO gap (E_{opt}), are fairly consistent for the series at 3.03, 2.90, and 2.90 eV respectively (Table 1). The incorporation of a five-member ring into **3b** significantly alters the shape of the absorption spectrum, and imbues the structure with a notably smaller E_{opt} of 2.86 eV than **3a** despite their similarly sized π-system. Increasing the length of the acene fragment in these systems bathochromically shifts the absorption onset and decreases the HOMO–LUMO gap, with dibenzotetracene **4** reaching 2.70 eV, and tetrabenzopentacenes **11** and **12** reaching 2.35 and 2.38 eV respectively. The fluorescence spectra of the six fully benzenoid structures display similar shapes with two broad peaks, while **3b** displays three. The trends in fluorescence maximum ($\lambda_{\text{em}}^{\text{max}}$) mirror those in absorption onset, with **3c–3e** displaying highly similar maxima at 434, 435, and 451 nm



Scheme 6 Formal [4 + 4] dimerization of stannoles to generate a helically chiral cyclooctatetraene.

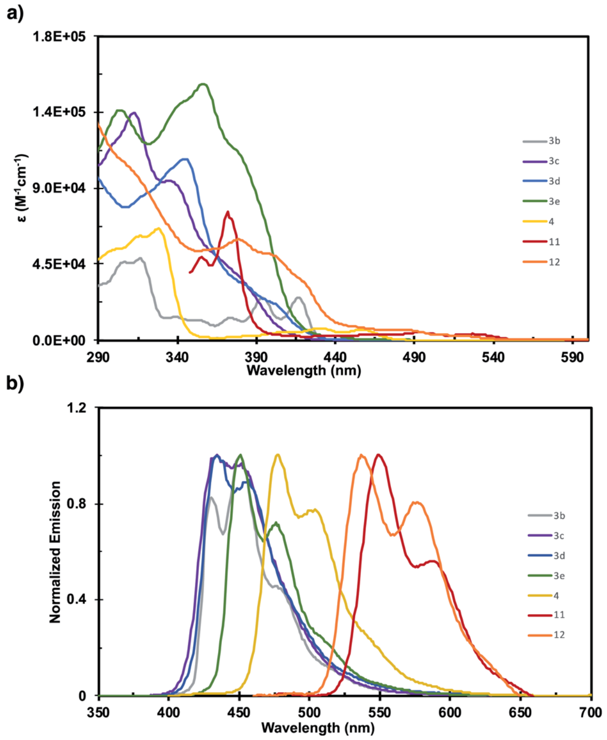


Fig. 1 Steady-state photophysics of **3b** (gray), **3c** (purple), **3d** (blue), **3e** (green), **4** (yellow), **11** (red), and **12** (orange). (a) UV-vis and (b) fluorescence spectroscopy acquired at 5×10^{-6} M in THF (**3b**, **3c**, **3d**, **3e**, **4**, **12**) and 1-chloronaphthalene (**11**). All fluorescence spectra were normalized to their respective λ_{max}.

Table 1 Summary of photophysical properties of key PAHs

Compound	$\lambda_{\mathrm{abs}}^{\mathrm{max}}$ (nm)	$\lambda_{\mathrm{abs}}^{\mathrm{onset}}$ (nm)	$\lambda_{\mathrm{em}}^{\mathrm{max}}$ (nm)	E_{opt} (eV)
3b	316	434	451	2.86
3c	312	409	434	3.03
3d	344	428	435	2.90
3e	357	428	451	2.90
4	327	459	477	2.70
11	372	527	551	2.35
12	308	521	538	2.38

respectively. **4**, **11**, and **12** are notably bathochromically shifted to 477, 551, and 538 nm respectively. These results highlight how orthogonal synthetic control over the core pattern of ring-fusion and the degree of π-extension enables tuning key aspects of the photophysical properties such as fine structure, HOMO–LUMO gap, and fluorescence.

Conclusions

In conclusion, stannoles represent a versatile diene source in [4 + 2] cycloadditions for the synthesis of π-extended aromatic systems. The high yielding cycloaddition–aromatization cascade and the broad compatibility with arynes suggest that stannoles can be superior to commonly employed cyclopentadienones for many applications in PAH synthesis, and their generation *via* [2 + 2 + 1] cycloadditions provides a complimentary approach to established methods for use of reactive dienes in the expansion of diverse PAH cores. Additionally, the high-yield formation of COT derivative **13** suggests that stannoles may be useful synthons for cycloadditions beyond [4 + 2], where their spontaneous aromatization is highly desirable for the synthesis of unusual conjugated ring structures.

Data availability

Crystallographic data for **13** has been deposited at the CCDC under 2121655.

Author contributions

H. M. B. and T. D. T. conceived of the idea. H. M. B. developed the methodology. D. D. B. expanded the methodology and substrate scope. H. M. B., D. D. B., and G. R. K. acquired the data for synthesis and characterization. R. C. H. acquired and analysed the crystallographic data for compound **13**. H. M. B., D. D. B., Y. L., and T. D. T. wrote and edited the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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