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Site-selective [2 + 2 + *n*] cycloadditions for rapid, scalable access to alkynylated polycyclic aromatic hydrocarbons†

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Polycyclic aromatic hydrocarbons (PAHs) are attractive synthetic building blocks for more complex conjugated nanocarbons, but their use for this purpose requires appreciable quantities of a PAH with reactive functional groups. Despite tremendous recent advances, most synthetic methods cannot satisfy these demands. Here we present a general and scalable [2 + 2 + *n*] (*n* = 1 or 2) cycloaddition strategy to access PAHs that are decorated with synthetically versatile alkynyl groups and its application to seven structurally diverse PAH ring systems (thirteen new alkynylated PAHs in total). The critical discovery is the site-selectivity of an Ir-catalyzed [2 + 2 + 2] cycloaddition, which preferentially cyclizes tethered diyne units *with preservation of other (peripheral) alkynyl groups*. The potential for generalization of the site-selectivity to other [2 + 2 + *n*] reactions is demonstrated by identification of a Cp_2Zr-mediated [2 + 2 + 1]/metallacycle transfer sequence for synthesis of an alkynylated, selenophene-annulated PAH. The new PAHs are excellent synthons for macrocyclic conjugated nanocarbons. As a proof of concept, four were subjected to alkyne metathesis catalysis to afford large, PAH-containing arylene ethylene macrocycles, which possess a range of cavity sizes reaching well into the nanometer regime. Notably, these high-yielding macrocyclizations establish that synthetically convenient pentynyl groups can be effective for metathesis since the 4-octyne byproduct is sequestered by 5 Å MS. Most importantly, this work is a demonstration of how site-selective reactions can be harnessed to rapidly build up structural complexity in a practical, scalable fashion.

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Introduction

The recent surge of interest in molecular carbon nanoscience is driven by the pursuit of atomic precision in larger nanostructures (*e.g.* graphene nanoribbons and carbon nanotubes)[1] and by the extraordinary properties displayed by molecular nanocarbons themselves.[2] Large polycyclic aromatic hydrocarbons (PAHs) represent a transition in the continuum between molecules and nanostructures. These structurally diverse compounds exhibit promise for a range of applications due to their exceptional photophysical and electronic properties, and their ability to organize into functional assemblies *via* π-stacking.[3] Since most carbon nanostructures are comprised of fused rings, PAHs are their natural synthetic building blocks. For example, the polymerization of PAH monomers may offer the best approach for growing atomically precise graphene nanoribbons[4] and the synthesis of carbon nanotubes and fullerenes from belt- and bowl-shaped PAH precursors should eventually be feasible.[5] PAHs are also attractive as components of many other types of functional materials, including polymers,[6] macrocycles,[7] and metal and covalent organic frameworks.[8]

The synthesis of PAHs is challenging since it requires regioselective fusions of many rings. Recently, much progress has been made to address this challenge,[1,2a,9] and metal-mediated cycloadditions have proven particularly valuable due to their efficacy in the formation of aromatic rings.[10] This research group is focused on development of a unified approach to PAH synthesis (Scheme 1a), based on divergent [2 + 2 + *n*] cycloadditions of biaryl-tethered diynes or dinitriles (**A**) to give highly functionalized PAHs (**B**).[11] Importantly, since only one conformational degree of freedom is frozen out with each cyclization, the minimal loss of entropy contributes to excellent yields[11a,b] and enables the use of more challenging dinitrile[11c] substrates.

For a PAH to be a useful synthon, it must be available in appreciable quantities *and* be suitably functionalized, but this set of requirements has proven difficult to achieve. Given their high carbon content and synthetic versatility, alkynyl substituents are attractive for the elaboration of PAHs into more complex functional materials.[12] Such substituents are especially useful for macrocyclization reactions to give arylene ethynylene macrocycles (AEMs),[13] cycloarylenes,[14] and other exotic

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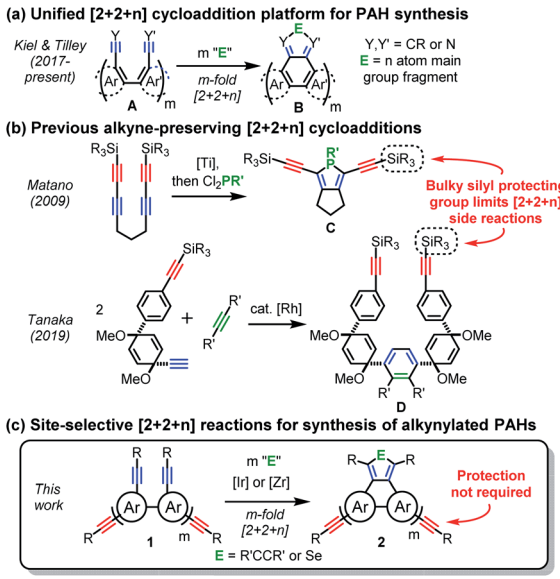


Scheme 1

macrocycles.[15] These and related macrocyclic nanocarbons[5c,7,16] represent a broad structural class of tremendous interest for their internal cavities and unique spatial arrangements of carbon-rich building blocks.

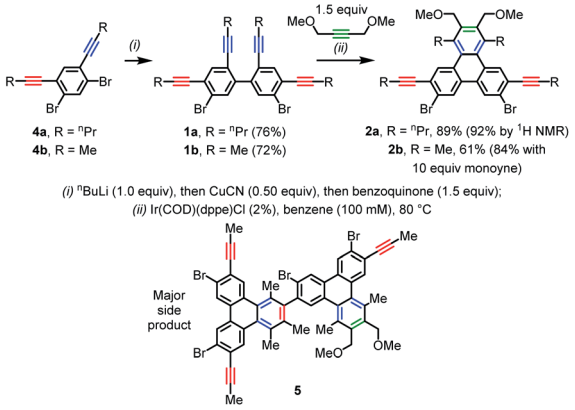
Alkynyl groups are usually installed onto PAHs from the corresponding halide (*via* Sonogashira coupling) or carbonyl (*via* nucleophilic attack), but these precursors are limited in number given the established regiochemical preferences for halogenation or oxidation. Other widely employed methods to access carbonyl-containing precursors involve Friedel–Crafts-type cyclizations or Diels–Alder/oxidation sequences, but these also offer limited structural diversity. Perhaps most importantly, these routes add synthetic steps and usually involve harsh conditions. *Thus, a more direct entry to alkynylated PAHs that bypasses traditional intermediates would be highly desirable*. Relevant previous work by the Matano[17] and Tanaka[15b] groups (Scheme 1b) demonstrated use of [2 + 2 + *n*] reactions to produce alkynylated synthetic intermediates **C** and **D** *en route* to oligomeric (non-PAH) products. Importantly, in both cases, one of the alkynes on the starting material was protected by a bulky silyl group, which minimizes the many possible deleterious cycloaddition side reactions.[18] The efficiency described above for cycloadditions of biaryl-tethered diynes (**A**) suggested that these transformations might be site-selective[19] and select for tethered diyne units (*i.e.* with preservation of peripheral, non-tethered alkynyl groups), as shown in Scheme 1c. This would alleviate the need to protect one of the alkynes, which would greatly simplify the syntheses of oligo(alkynyl)arylene precursors (**1**) and provide direct access to valuable alkynylated PAHs (**2**).

Here we describe development of the strategy of Scheme 1c, which was found to be possible with both Ir-catalyzed [2 + 2 + 2] and Cp_2Zr-mediated [2 + 2 + 1] cycloadditions. This previously unrecognized site-selectivity gives rapid access to alkynylated PAHs, which is demonstrated with thirteen examples, representing seven different ring systems (Schemes 2–4). The [2 + 2 + 1] variant also offers the possibility of a divergent annulation with heterocyclic rings. Due to the streamlined precursor syntheses and generally high yields, multigram quantities of alkynylated PAHs are easily accessed, which is critical for their intended use as synthetic intermediates. As a proof of concept, four of the new PAHs were exploited as synthons for macrocyclic nanocarbons *via* alkyne metathesis reactions of their alkynyl groups (Scheme 5). Three of these structurally complex macrocycles are derived from previously unknown PAH ring systems. More importantly, they possess a range of internal cavity sizes reaching well into the nanometer regime.

Results and discussion

The new strategy was initially envisioned as a solution to difficulties encountered in the synthesis of alkynylated triphenylenes such as **2a** and **2b** (Scheme 2) using classical ring fusion techniques (*e.g.* the Scholl reaction[20]). Notably, there was no literature precedent for, or suitable synthetic precursors to, the deceptively simple 2,7-dialkynyl-3,6-dihalo triphenylene substitution pattern. Since the starting dialkynyl dihalides **4a** and **4b** are available in only two steps and can be easily homocoupled to yield tetra(alkynyl)biphenylene precursors **1a** and **1b**,[11a] this strategy would provide streamlined access to triphenylenes **2a** and **2b** if the subsequent site-selective [2 + 2 + 2] reaction was successful. The most important step in the synthesis of precursors **1a** and **1b** is the highly selective *in situ* desymmetrization *via* Li/Br exchange that precedes the Cu-mediated oxidative homocoupling. This desymmetrization also streamlines the synthesis of all other oligo(alkynyl)arylene substrates in this manuscript (*e.g.* **1c–1l** in Scheme 3; see ESI for more details†).

The [2 + 2 + 2] pre-catalyst Ir(COD)(dppe)Cl, which can be isolated[21] or generated *in situ*[22a,b] from commercially available materials, proved to be highly effective for synthesis of model pentynylated triphenylene **2a**. This compound was isolated in a remarkable 89% yield under optimized conditions. The preservation of the pentynyl groups in **2a** was verified by ^{1}H and ^{13}C NMR spectroscopies (one propargylic methylene triplet and



Scheme 2 Model system for site-selective [2 + 2 + 2] reaction.

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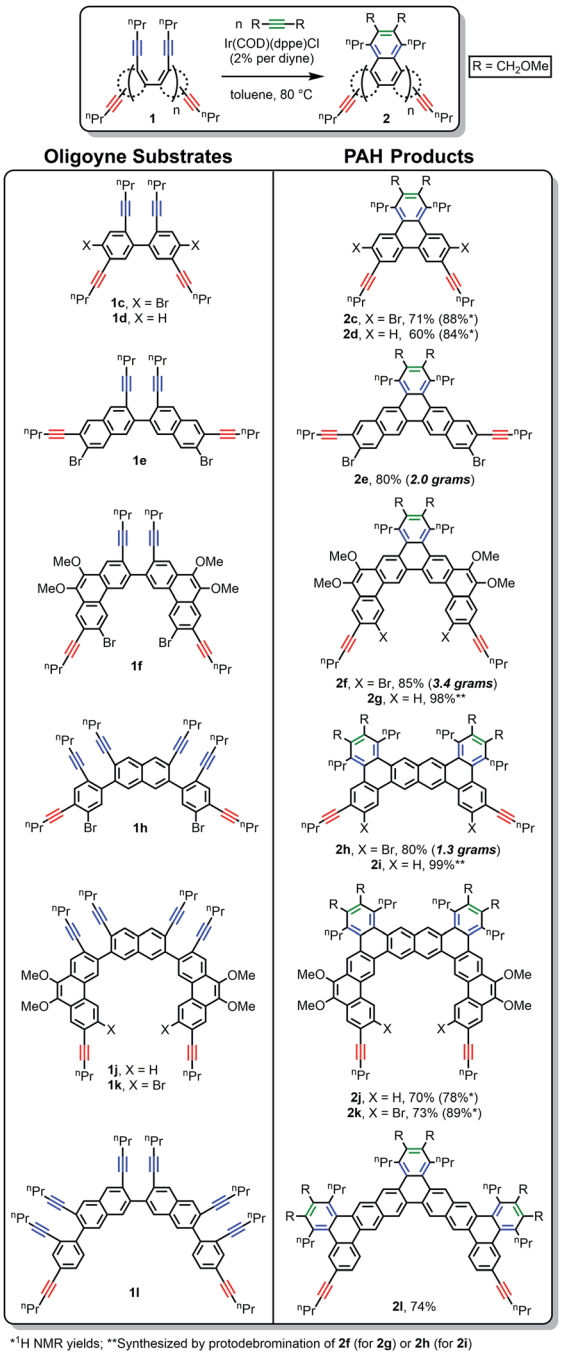

Scheme 3 Generalization of the site-selective [2 + 2 + 2] reaction to more complex PAHs.

two quaternary alkynyl resonances, respectively) and high-resolution mass spectrometry. The choice of Ir(COD)(dppe)Cl as pre-catalyst was informed both by its exceptional efficiency in [2 + 2 + 2] reactions involving biphenyl-tethered diynes[11b] and by Takeuchi's demonstration of its ability to furnish alkynylated benzene products[22a,b] (in [2 + 2 + 2] reactions involving a 1,3-diyne reactant).

Since the peripheral pentynyl groups (shown in red) in the starting material (**1a**) and product (**2a**) are virtually identical, it was anticipated that competing *inter*molecular cycloadditions involving these groups would necessitate extensive screening and optimization efforts. In contrast, the yield of this transformation was fairly insensitive (82–93%) to wide ranges of values for several critical parameters, including concentration (10–300 mM), monoyne equivalents (1.0–5.7), catalyst loading (1–10%), and reaction time (1–10 h), as discussed further in the ESI (Tables S1–S3†). Under the optimized conditions, there was a notable decrease in yield (61%) for triphenylene **2b**, which has less sterically demanding propynyl groups. The major side product was dimeric **5** (8–18% by ^{1}H NMR, depending on concentration), resulting from a cycloaddition between the product (**2b**) and starting material (**1b**). Dilution from to 10 mM (from 100 mM) did not improve the yield. Notably, the yield of **2b** increased to 84% with a larger excess of monoyne (10 equiv.), and side product **5** was not observed. Since bulkier pentynyl groups provided higher yields in the model system, they were used for the remaining examples below.

The site-selective [2 + 2 + 2] reaction proved to be a general means to access alkynylated PAHs, as demonstrated by the isolation of **2c–2l** (Scheme 3). Precursors **1c–1l** were synthesized in a modular fashion *via* standard C–C bond-forming reactions (see Schemes S1–S3 for details†), all of which were streamlined by Li-mediated desymmetrization reactions as mentioned above. From the same benzene, naphthalene, and phenanthrene building blocks, a range of different shapes, sizes, and alkynyl group substitution patterns were obtained *via* onefold, twofold, or threefold cycloadditions. Notably, the decrease in yields in the absence of the sterically demanding Br groups *ortho* to the alkynes (for **2d** and **2j** relative to **2c** and **2k**) was relatively small. This suggests that *ortho* substituents play a smaller role than the substituent on the alkynyl group in shutting down undesirable intermolecular side reactions. Also, the size of the PAH building blocks does not appear to play a large role. This can be seen by the comparable yields for **2a** (89%), **2e** (80%), and **2f** (85%), which were derived from cycloadditions of biphenylene (**1a**), binaphthalene (**1e**), and biphenanthrene (**1f**) precursors, respectively. Interestingly, the generally good-to-excellent yields do not correlate with the number of required cycloadditions. For example, a twofold cycloaddition produced **2j** in 70% yield, whereas a threefold cycloaddition produced **2l** in 74% yield. The substitution patterns of the new PAHs would be difficult or impossible to access using previous synthetic methodology, even for the deceptively simple triphenylene systems **2a–d**. Represented among these examples are the first known tribenzo[*a*,*h*,*o*]pentaphene (**2f–g**), tribenzo[*a*,*h*,*o*]phenanthro[2,3-*q*]hexaphene (**2j–k**), and pentabenzo[*a*,*c*,*j*,*q*,*s*]heptaphene (**2l**) ring systems. Perhaps most importantly, since high dilution is not necessary (diyne concentration = 100 mM), the new strategy is highly scalable. For example, **2e**, **2f**, and **2h** were isolated on 2.0, 3.4, and 1.3 gram scales, respectively.

This strategy was subsequently generalized to include a formal [2 + 2 + 1] reaction, as shown in Scheme 4. Heating an equimolar mixture of **1m** and $Cp_2Zr(pyr)(Me_3SiC{\equiv}CSiMe_3)$[23] (an isolable source of "Cp_2Zr") in hexanes, isolation of the crude zirconacyclopentadiene intermediate (**2m**) *via* filtration, and

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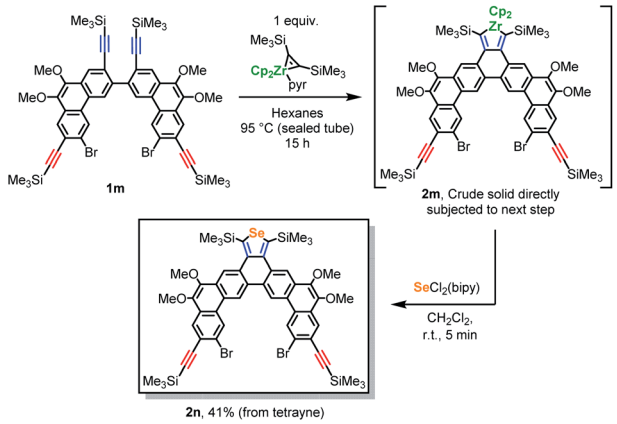
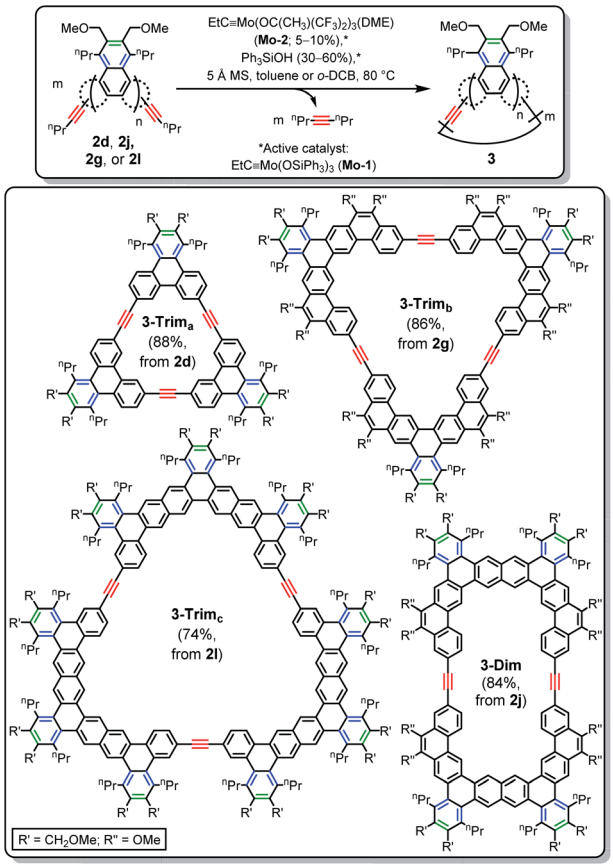


Scheme 4 Extension of the strategy to include a Cp_2Zr-mediated formal [2 + 2 + 1] reaction.

treatment of a CH_2Cl_2 solution of **2m** with $SeCl_2$(bipy)[11b] afforded selenophene-annulated dibenzo[*a*,*o*]pentaphene **2n** in 41% isolated yield. The silyl groups on **1m** were chosen since they often lead to *reversible* [2 + 2 + 1] cycloadditions involving zirconocene,[14,24] and **2m** was expected to be the thermodynamic product (entropy should favor monomeric **2m** over the oligomeric products that would result from intermolecular cycloadditions[14]). Indeed, the site-selectivity of this reaction appears to occur under thermodynamic control. Thus, when **1m** was treated with 1.0 equiv. of $Cp_2Zr(pyr)(Me_3SiC{\equiv}CSiMe_3)$ (in benzene-d_6 due to solubility concerns), **2m** was observed in only 20% yield after 10 min at 22 °C, along with starting **1m** (30%), a complex mixture of unidentified products (likely oligomers), and no remaining $Cp_2Zr(pyr)(Me_3SiC{\equiv}CSiMe_3)$. Temperatures up to 90 °C did not lead to notable increases in **2m**, but after 18 h at 105 °C the yield of **2m** increased to 45%.[25] Importantly, **2m** is expected to be a versatile synthon for the installation of a range of other heterocycles using well-developed zirconacycle transfer chemistry.[26]

The angular disposition of the alkynyl groups in PAHs **2c–d** and **2f–l** makes them attractive for macrocyclization *via* alkyne metathesis, which often provides AEMs in a high yielding, scalable fashion.[27] PAHs are intriguing building blocks for more complex AEMs, as has been demonstrated on a number of occasions.[28] However, for all but the smallest PAHs (phenanthrene and carbazole), such AEMs have been produced by routes that are difficult to scale or generalize, probably due to difficulties associated with accessing appropriately functionalized PAH precursors. The site-selective [2 + 2 + 2] cycloaddition presented above directly addresses those difficulties.

For the macrocyclization reactions of Scheme 5, the Fürstner-type metathesis catalyst[29] "$EtC{\equiv}Mo(OSiPh_3)_3$" (**Mo-1**) was employed. In analogy to the approach taken by Moore,[30] we found that **Mo-1** can be conveniently generated *in situ* by treatment of easily-prepared $EtC{\equiv}Mo(OC(CH_3)(CF_3)_2)_3(DME)$ (**Mo-2**)[31] with 6 equiv. of Ph_3SiOH (see ESI for details on this ligand exchange†). Triphenylene ethynylene macrocycle **3-Trim$_a$** was isolated in excellent yield (88%) after treatment of **2d** with a 5% loading of **Mo-1** in the presence of 5 Å molecular sieves[29] (16 h at 80 °C in



Scheme 5 New PAHs as synthons for large arylene ethynylene macrocycles.

toluene). The identity of **3-Trim$_a$** was unambiguously determined by ^{1}H and ^{13}C NMR spectroscopy (the former showed the absence of propargylic methylene resonances and the latter showed only one quaternary alkynyl resonance) and MALDI-TOF. As is often the case for alkyne metathesis macrocyclizations,[27c,d] minimal purification was required (elution of the reaction mixture through a plug of silica gel followed by precipitation with MeOH), and high dilution was not necessary. Attempts at the macrocyclization of the analogous, Br-substituted **2c** yielded a complex mixture that contained only small amounts of macrocycle, even at higher (20%) catalyst loading.

Remarkably, the synthesis of **3-Trim$_a$** demonstrates that 5 Å MS are effective for sequestration of the byproduct 4-octyne, which is imperative for the high yield. Fürstner's 2010 discovery[29] that alkyne metathesis reactions can be driven by sequestration of (smaller) 2-butyne has played a critical role in the continued rise of this synthetic methodology.[32] As a result, the use of propynyl groups has become ubiquitous since the easily-sequestered 2-butyne byproduct is produced, but the installation of propynyl groups requires either gaseous propyne (for Sonogashira coupling) or expensive propynyl magnesium bromide solution (for Kumada coupling). The high-yielding synthesis of **3-Trim$_a$** (and the other macrocycles presented below) demonstrates that pentynyl groups may provide a cheaper, more convenient alternative to propynyl groups.

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Since the presence of bulky Br substituents appears to inhibit macrocyclization with **Mo-1** as catalyst, attention was focused on "Br-free" **2g**, **2i**, **2j**, and **2l**. Due to the larger sizes of these PAHs, the solvent was switched to *o*-dichlorobenzene (*o*-DCB) to limit the possibility of kinetic traps *via* precipitation of oligomeric or polymeric intermediates. Subjection of **2j**, **2g**, and **2l** to the slightly modified metathesis conditions afforded the elliptical macrocycle **3-Dim** and large, triangular macrocycles **3-Trim$_b$** and **3-Trim$_c$** in good to excellent isolated yields. While the yield of the largest of these macrocycles (**3-Trim$_c$**) improved on dilution (from 43% at 25 mM to 74% at 9 mM), this is still quite concentrated for a macrocyclization reaction. Since no well-defined side products were observed in any case, purification was again streamlined. Unfortunately, subjection of **2i** to the conditions of Scheme 5 produced an intractable mixture composed primarily (~95% by mass) of insoluble material that could not be characterized. It is important to note that, except for the modest dilution in the case of **3-Trim$_c$**, we have not attempted to optimize any parameter in these reactions.

In general, the new PAHs (**2a–n**) and macrocycles (**3**) are highly soluble in chlorinated solvents (>100 mg mL^{-1}) and insoluble in saturated hydrocarbons (*e.g.* hexanes) and more polar solvents (*e.g.* acetone and EtOH). The exception is **3-Dim**, which is only moderately soluble in chloroform (15–20 mg mL^{-1}). The solution behavior of the new AEMs (**3**) and their PAH precursors (**2d**, **2j**, **2g**, and **2l**) were investigated by variable concentration ^{1}H NMR spectroscopy. The chemical shifts in chloroform-*d* of all except **3-Dim** and **3-Trim$_b$** are independent of concentration (see Fig. S74–S81†), which suggests that the high solubility results from limited aggregation *via* π-stacking. This is likely a result of the alkyl groups in the bay positions, which induce non-planarity. In contrast, despite this alkyl group substitution, the ^{1}H NMR spectra of **3-Dim** and **3-Trim$_b$** in chloroform-*d* solution exhibit significantly broadened aromatic resonances with chemical shifts that depend upon concentration, which suggests aggregation *via* π-stacking.

The UV/vis absorption and emission spectra of AEMs (**3**) and their monomeric precursors (**2**) display the typical features of large, highly benzenoid PAH systems,[3a] including high molar absorptivities (up to 5.0×10^5 M^{-1} cm^{-1}, for **3-Trim$_c$**), relatively large optical HOMO–LUMO gaps (between 2.8 to 3.3 eV), and fluorescence (see Table S4 and Fig. S82–S86†). Despite the large increases in the sizes of the π-systems as a result of macrocyclization of **2** to form **3**, the expected red shifts in absorption maxima range from small (21 nm for **3-Dim**) to modest (54 nm for **3-Trim$_a$**). More strikingly, very small decreases in optical HOMO–LUMO gap (≤0.15 eV) and emission maxima (≤12 nm) are observed. Thus, to a large extent, the new PAH-containing AEMs retain the properties of their PAH precursors.

Conclusions

The results presented above demonstrate how the newly discovered site-selectivity of an Ir-catalyzed [2 + 2 + 2] cycloaddition enables streamlined construction of complex nanocarbons. Here, the [2 + 2 + 2] reaction was used in concert with an orthogonal alkyne metathesis macrocyclization to provide scalable, two-step access to large, PAH-containing AEMs. Several opportunities are available for the introduction of structural and functional diversity, which might be systematically exploited to perturb self-assembly, photophysical, or electronic properties of a specific AEM, or to access entirely new AEMs. It is important to note, however, that the targeted AEMs represent only a proof of concept; the intermediate alkynylated PAHs **2a–n** are valuable synthons for a range of other conjugated nanocarbons, including expanded helicenes, cycloarenes, and other macrocyclic nanocarbons. Such applications are the focus of continuing efforts in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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