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<td>Yang, Wenlong; University of Nevada Reno, Chemistry Monteiro, Jorge; University of Nevada Reno, Chemistry de Bettencourt-Dias, Ana; University of Nevada Reno, Chemistry Chalifoux, Wesley; University of Nevada Reno, Chemistry</td>
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A New Thiophene-Functionalized Pyrene, Peropyrene, and Teropyrene via a Two- or Four-fold Alkyne Annulation and Their Photophysical Properties

Wenlong Yang, Jorge H. S. K. Monteiro, Ana de Bettencourt-Dias and Wesley A. Chalifoux*

Department of Chemistry, University of Nevada, Reno

1664 N. Virginia St., Reno, NV 89557 (USA)

E-mail: wchalifoux@unr.edu
Abstract: A thiophene-functionalized pyrene, peropyrene, and teropyrene were synthesized through a two- or four-fold alkyne annulation reaction promoted by triflic acid. All of the target compounds were fully characterized spectroscopically and the structure of the peropyrene analogue was unambiguously confirmed by X-ray crystallography. A significant red-shift in the absorption and emission properties as a function of extended conjugation was observed by UV-vis and fluorescence spectroscopy. This alkyne annulation strategy is a useful method for the conversion of smaller polycyclic aromatics to larger ones, such as nanographenes.

Key words: thiophene, pyrene, peropyrene, teropyrene, annulation
Pyrene derivatives have attracted a lot of attention due to their easy modifiability and wide range of applications.\textsuperscript{1,2} Most reported pyrene derivatives involve four-fold substitution either at the 1,3,6,8-positions\textsuperscript{3} or 4,5,9,10-positions;\textsuperscript{4} there are only a few reported methods for the direct functionalization at the 2,7-positions\textsuperscript{5-7} or at the 4,10-positions.\textsuperscript{8-11} Therefore, new methods that provide access to a broader scope of substituted pyrenes are of value. Larger derivatized pyrenacenes (homologues of pyrene) would be of significant value, as their extended conjugation should lead to interesting optical and electronic properties. However, larger pyrenacenes, such as peropyrenes and teropyrenes, are rarely reported, presumably due to their difficult preparation and functionalization.\textsuperscript{12} Recently, peropyrene attracted attention due to its potential use as a singlet fission material; still, poor performance was observed and it was proposed that this could be rectified through the incorporation of substituents.\textsuperscript{13} The first teropyrene was reported by Misumi in 1975, but this compound was only characterized by UV-vis spectroscopy, presumably due to its poor solubility.\textsuperscript{14} Bodwell and coworkers reported the synthesis of a series of bent teropyrenes (teropyrenophanes), which were fully characterized spectroscopically and their structures confirmed by X-ray crystallography.\textsuperscript{15-17} All the reported methods to generate pyrenacenes rely either on cyclodehydrogenation or oxidation. Recently, we described a new method for the synthesis of para-alkoxyphenyl-functionalized pyrenes, peropyrenes, and teropyrenes through a non-oxidative alkyne annulation reaction promoted by triflic acid (TfOH).\textsuperscript{11} All resulting target compounds showed excellent solubility in common organic solvents, greatly simplifying their
characterization. We also successfully applied this method for the bottom-up synthesis of narrow and soluble graphene nanoribbons.\(^{18}\) Electron-rich ethynylaryl moieties are required for this cyclization method and thus we envisioned that ethynylthiophene may also undergo a facile annulation. Thiophene substituents are commonly employed as good electron-donating moieties with interesting intrinsic photophysical properties,\(^{19,20}\) and capable of undergoing numerous useful chemical transformations. Therefore, introducing thiophene groups into pyrenes, peropyrenes, and teropyrenes would be of much interest, allowing one to tune the optical and electronic properties of these materials. Herein, we report an efficient approach to generate thiophene-functionalized pyrenes, peropyrenes, and teropyrenes via a two- or four-fold annulation reaction of alkynes promoted by TfOH.

The preparation of thiophene-functionalized pyrene 7, peropyrene 10 and teropyrene 13 begins with the synthesis of a common coupling partner, dialkynylboronic ester 4 (Scheme 1a). Compound 3 was prepared via a double Sonogashira cross-coupling reaction of 1 with 2 to give compound 3 in 90% yield. Compound 3 underwent lithium-halogen exchange upon treatment with \(n\)-butyllithium and was then allowed to react with isopropoxyboronic acid pinacol ester to provide dialkynylboronic ester 4 in good yield. With compound 4 in hand, we first endeavoured to prepare 2,6-dialkynylbiphenyl 6 by a Suzuki coupling reaction between 4 and 5 at 85 °C (Scheme 1b). To our disappointment, only a trace amount of 6 was formed under these conditions along with uncharacterized side-products. Fortunately, we found that these side reactions could be dramatically reduced by
simply decreasing the reaction temperature to 65~70 °C. This provided compound 6 in 58% yield. We extended these cross-coupling conditions to substrates 8 and 11 to produce the cyclization precursors 9 and 12 in modest (49% and 28%, respectively) yields. From precursors 6, 9, and 12, our plan was to invoke the alkyne annulation reaction using a Brønsted acid. In our previous study, higher yields and cleaner reactions were observed when TFA was added first to promote partial cyclization of the substrates followed by addition of TfOH to complete the reaction. In this work, we report that the slow addition via syringe pump of TfOH diluted in CH₂Cl₂ at 0 °C results in good yields and clean reactions. These reaction conditions produced thiophene-functionalized pyrene 7, peropyrene 10, and teropyrene 13 in respectable yields of 60%, 72% and 56%, respectively. It should be noted that this corresponds to roughly an impressive 87% yield per alkyne cyclization for compound 13.
Scheme 1. a) Synthesis of boronic ester 4: Reagents and conditions: i) Pd(PPh$_3$)$_2$Cl$_2$, Cul, THF/Et$_3$N, r.t., 14 h, 90%; ii) (a) n-butyllithium (n-BuLi), THF, –78 °C, 30 min; (b) isopropoxyboronic acid pinacol ester, –78 °C to r.t., 73%. b) Synthesis of thiophene substituted pyrene 7, peropyrene 10, and teropyrene 13. Reagents and conditions: iii) Pd(PPh$_3$)$_4$, K$_2$CO$_3$, THF/H$_2$O, 65~70 °C, 12~48 h, 58% (6), 49% (9), 28% (12); iv) TfOH, DCM, 0 °C to r.t., 60% (7), 72% (10), 56% (13).

Single crystals of peropyrene 10 suitable for X-ray crystallographic analysis were obtained (Figure 1a). The peropyrene 10 backbone is slightly more twisted as compared to the phenyl-substituted peropyrene we reported previously$^{11}$ with an
overall end-to-end twist angle of 24°. Interestingly, the sulphur atoms in both thiophenes point in the same direction causing slight differences in the splay angle of each bay region in 10, with values of 17° and 20° (Figure 1b). The twisting is attributed to the steric repulsion between the thiophene moiety and the hydrogen substituent within the bay region. A slip-stacked face-to-face molecular packing was found with a minimum interplanar spacing of 3.4 Å (Figures 1c-d).

**Figure 1.** a-b) Thermal ellipsoid plots (ellipsoids at 50% probability, hydrogen atoms omitted for clarity) of peropyrene 10, showing the splay angle values; c-d) molecular packing of peropyrene 10, showing the interplanar spacing (alkyl chains, tert-butyl groups, and hydrogen atoms were omitted for clarity).
The absorption spectra of the pyrene 7, peropyrene 10, and teropyrene 13 products are shown in Figure 2. The compounds absorb in the UV and visible region, and the absorption bands show a characteristic vibrational progression. The increase in conjugation from compound 7, over 10, to 13 is mirrored in the bathochromic shift of the absorption bands and the observed increase in molar absorptivity ($\varepsilon$) (Figures S1(a) and S1(b)). The determined $\varepsilon$ values for 7 ($2.0 \times 10^4$ M$^{-1}$ cm$^{-1}$ at 359 nm), 10 ($4.9 \times 10^4$ M$^{-1}$ cm$^{-1}$ at 469 nm) and 13 ($6.7 \times 10^5$ M$^{-1}$ cm$^{-1}$ at 572 nm) are in the same order of magnitude as for similar reported compounds.$^{4,11,21,22}$

![Absorption Spectra](https://mc06.manuscriptcentral.com/cjc-pubs)

**Figure 2.** Absorption spectra of the compounds 7 (black line), 10 (red line) and 13 (blue line) obtained in toluene with concentration $1 \times 10^{-6}$ M.

The excitation and emission spectra are shown in Figure 3. The emission maxima (Table 1) are in the deep blue at 402 nm for 7, in the green at 486 nm for 10 and in the
orange-red at 590 nm for 13 and the emission bands for the latter show vibrational fine structure, analogous to the absorption and excitation spectra. The increased conjugation is reflected in the observed bathochromic shift of emission (Figures 2 and S1(c)) as well the decrease in the Stokes shift (Table 1). The observed emission spectra are mirror images of the excitation and absorption spectra, which indicates that the same states are involved in absorption and emission.

Figure 3. Excitation (left) and emission (right) spectra of (a) compound 7 (blue line) ($\lambda_{\text{exc}} = 359$ nm and $\lambda_{\text{em}} = 402$ nm), (b) compound 10 (green line) ($\lambda_{\text{exc}} = 467$ nm and $\lambda_{\text{em}} = 489$ nm) and (c) compound 13 (red line) ($\lambda_{\text{exc}} = 572$ nm and $\lambda_{\text{em}} = 590$ nm) in toluene at 298 K.

The emission lifetimes and efficiencies for all three compounds, summarized in Table 1, were measured in toluene. The emission lifetimes are $2.3 \pm 0.2$ ns (7), $1.9 \pm 0.1$ ns (10), and $4.4 \pm 0.3$ ns (13), which correspond to emissive rates of 0.0228,
0.2795 and 0.0927 ns\(^{-1}\), respectively. All decay curves were fit to a mono exponential (Figures S3, S4 and S5), indicating that emission occurs from one excited state. The emission efficiencies are 5.3 ± 0.6 (7), 53.1 ± 6.0 (10), and 40.8 ± 6.7 % (13). The lowest efficiency found for 7 is a result of the inefficient absorption and, most likely, losses due to radiationless decay due to the rotation of the thiophene rings on the side chain. In the case of 10 and 13, the increase in the absorption coefficient (Figure 2) contributes to an increase in the emission efficiencies. When compared to other pyrene, peropyrene and teropyrene derivatives reported by us,\(^{11}\) the presence of the thiophene group results in slightly decreased emission efficiencies. The emission lifetime of 7 is shorter than the previously reported pyrene derivative with phenyl substituents while, the emission lifetime of the compound 13 is longer.\(^{11}\) This is possibly due to small variances in the core structures (twist angle, splay angle, etc.).

**Table 1.** Absorption and emission maxima, Stokes shift, emission lifetimes (\(\tau\)), emission efficiencies (\(\Phi\)) and radiative rates (\(k_{rad}\)) obtained for the compounds in toluene.

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<tr>
<th>Compounds</th>
<th>Abs(_{\text{max}}) [nm]</th>
<th>Em(_{\text{max}}) [nm]</th>
<th>Stokes shift [cm(^{-1})]</th>
<th>(\tau) [ns(^{-1})]</th>
<th>(\Phi) [%]</th>
<th>(k_{rad}) [ns(^{-1})]</th>
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<td>359</td>
<td>402</td>
<td>2700</td>
<td>2.3 ± 0.2</td>
<td>5.3 ± 0.6</td>
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<tr>
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In summary, we have demonstrated a new method to prepare...
thiophene-functionalized pyrene, peropyrene, and teropyrene compounds through an alkyn e annulation reaction promoted by TFOH. All the target compounds were fully characterized and the structure of peropyrene was confirmed by X-ray crystallography. Increasing conjugation of the systems results in a red shift of absorption and emission maxima; the latter span the whole range of the visible spectrum and are accompanied by an increase in the emission efficiency. These properties make these easily accessible molecules interesting luminescent materials for a variety of optoelectronic applications.

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References:


(15) Merner, B. L.; Unikela, K. S.; Dawe, L. N.; Thompson, D. W.; Bodwell, G. J.


Table 2. Absorption and emission maxima, Stokes shift, emission lifetimes ($\tau$), emission efficiencies ($\Phi$) and radiative rates ($k_{rad}$) obtained for the compounds in toluene.

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Graphical Abstract