π-Extended Star-Shaped Polycyclic Aromatic Hydrocarbons based on Fused Truxenes: Synthesis, Self-Assembly, and Facilely Tunable Emission Properties

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Abstract: A new set of star-shaped polycyclic aromatic hydrocarbons (PAHs) based on naphthalene-fused truxenes, TrNaCr (n = 1–4), were synthesized and characterized. The synthesis involved a microwave-assisted six-fold Suzuki coupling reaction, followed by oxidative cyclodehydrogenation. Multiple dehydrocyclization products could be effectively isolated in a single reaction, thus suggesting that the oxidative cyclodehydrogenation reaction involved a stepwise ring-closing process. The thermal, optical, and electrochemical properties and the self-assembly behavior of the resulting oxidized samples were investigated to understand the impact of the ring-fusing process on the properties of the star-shaped PAHs. Distinct bathochromic shift of the absorption maxima (λmax) revealed that the molecular conjugation extended with the stepwise ring-closing reactions. The optical band-gap energy of these PAHs varied significantly on increasing the number of fused rings, thereby resulting in readily tunable emissive properties of the resultant star-shaped PAHs. Interestingly, the generation of rigid “arms” by using perylene analogues caused TrNaC2 and TrNaC3 to show significantly enhanced photoluminescence quantum yields (PLQYs) in solution (Φ = 0.65 and 0.66, respectively) in comparison with those of TrNa and TrNaC1 (Φ = 0.08 and 0.16, respectively). Owing to strong intermolecular interactions, the TrNa precursor was able to self-assemble into rod-like microcrystals, which could be facilely identified by the naked eye, whilst TrNaC1 self-assembled into nanosheets once the naphthalene rings had fused. This study offers a unique platform to gain further insight into—and a better understanding of—the photophysical and self-assembly properties of π-extended star-shaped PAHs.

Introduction

Polycyclic aromatic hydrocarbons (PAHs), which can be regarded as nanographene fragments, have regained much attention since graphene was first isolated by Novoselov, Geim, and co-workers in 2004.[9] Because of their characteristic electronic and self-assembly properties, PAHs represent a promising class of active organic materials for a variety of electronic devices, such as organic field-effect transistors (OFETs),[8] organic solar cells (OSCs),[9] and organic light-emitting diodes (OLEDs).[10] In particular, small and medium-sized PAHs have attracted much interest owing to their excellent photoluminescence properties, high carrier mobility, and outstanding resistance towards oxidation, as well as their well-designed structures.[10]

Growing attention has been paid to the synthesis of PAHs, in particular from the perspective of materials chemistry.[11] At the beginning of the 20th Century, Scholl, Clar and Mansfeld[1] first committed to the synthesis and study of PAHs. Then, Müllen and Pisula[12] made great contributions to this field, enabling PAHs to be synthesized in high yields under mild conditions. The synthesis of structurally well-defined PAHs has opened up the possible preparation of specific nanographenes by using bottom-up approaches.[8, 9] In contrast to top-down methods,[13] that involve “cutting” graphene, which don’t allow the structure and size distribution of the nanographenes to be controlled, bottom-up syntheses can achieve purified nanographenes with explicit structures and predictable properties.[11]

Unlike the small (even zero) energy gaps in graphenes, which hinder their application in electronic devices, nanographenes have bigger energy gaps and the ability to adjust their (opti-
cal) band gaps through appropriate design of their sizes and edge structures.\textsuperscript{12,13} However, most graphenes possess extremely low solubility and tend to stack and aggregate in common solvents, which makes them difficult to integrate into devices.

Herein, we report the synthesis of a series of star-shaped PAHs based on naphthalene-fused truxenes (TrNaC\textsubscript{n}, \(n = 1\)–4; Figure 1) with facilely tunable photoelectrical properties by using a stepwise ring-closing reaction. In our previous work, we demonstrated that star-shaped molecules could effectively depress aggregation.\textsuperscript{14} Truxene has been recognized as a raw material for constructing large polyarenes and fragments of fullerenes. Alkyl substituents on the truxene core also contribute to improving the solubility of PAHs in common organic solvents. The thermal, optical, electrochemical, and self-assembly properties of the resulting stepwise-oxidized PAHs with subtle structural changes were investigated at length. Ring-fused product TrNaC\textsubscript{1} exhibited good thermal stability with a high decomposition temperature (\(T_{\text{d}}\)) of 413 °C, higher than that of the TrNa precursor (\(T_{\text{d}} = 397 °C\)). The optical band-gap energies of these PAHs, as recorded from the UV/Vis absorption spectra, varied significantly with the number of fused rings, thereby resulting in facilely tunable emissive properties for the resultant star-shaped PAHs. Interestingly, with the generation of rigid perylene analogue arms, TrNaC\textsubscript{2} and TrNaC\textsubscript{3} showed significant enhancement in their photoluminescence quantum yields (PLQYs) in solution (\(\eta = 0.65 \text{ and } 0.66\), respectively) in comparison with those of TrNa and TrNaC\textsubscript{1} (\(\eta = 0.08 \text{ and } 0.16\), respectively). More interestingly, clearly different self-assembly behaviors were observed for the ring-fused TrNaC\textsubscript{1} and the TrNa precursor, in which TrNaC\textsubscript{1} self-assembled into nanosheets whereas TrNa assembled into rod-like microcrystals.

**Figure 1.** Synthesis of TrNaC\textsubscript{n}. TBAB = tetra-n-butylammonium bromide, MW = microwave irradiation.

### Results and Discussion

#### Synthesis

Since the first investigation by Müllen and co-workers\textsuperscript{15} in 2000, the iron(III) chloride (FeCl\textsubscript{3})/nitromethane (CH\textsubscript{3}NO\textsubscript{2}) catalyst system has been widely used as a mild and effective Lewis oxidant/acid catalyst for the synthesis of nanographenes through a solution-mediated oxidative cyclodehydrogenation reaction. Figure 1 shows the chemical structures of a series of target star-shaped PAHs, which contain two types of edge structures with fjord and bay regions. Our synthesis of the target molecules began with a six-fold Suzuki cross-coupling reaction\textsuperscript{14a,b} between hexabromotritruxene (TrBr) and 2-naphthylboronic acid, as shown in Figure 1. To promote multiple coupling reactions, we employed microwave irradiation, which has been shown to promote higher yields of the products, cleaner reactions with easier workup, and shorter reaction times.\textsuperscript{14a,b} After optimizing the microwave conditions, including the solvent system, reaction temperature, and reaction time, we found that the optimal reaction conditions were heating at 150 °C for 40 min in THF with [Pd(PPh\textsubscript{3})\textsubscript{4}] as a catalyst. Thus, the desired compound, TrNa, was obtained in good purity and high yield (60–80%). Subsequently, we wondered whether we could obtain \(\pi\)-expanded planar structures by using the oxidative cyclization reaction. Thus, the solution-based cyclodehydrogenation reaction was performed in dry CH\textsubscript{3}Cl\textsubscript{2} at 0 °C for 30 min (see the Supporting Information). First, FeCl\textsubscript{3} was added (4 equivalents per C–C bond), and three spots were clearly observed by thin layer chromatography (TLC). After careful purification by using standard column chromatography on silica gel, the resultant compounds were characterized by using mass spectrometry (MALDI-TOF) and the three spots were attributed to the loss of six, eight, and 10 hydrogen atoms. As shown in Figure 2a, a compound that had lost 12 hydrogen atoms was also obtained, but only in a small amount (ca. 1%), which was rather challenging to separate. We speculated that the structures of these four aromatic hydrocarbon derivatives were TrNaC\textsubscript{1}, TrNaC\textsubscript{2}, TrNaC\textsubscript{3}, and TrNaC\textsubscript{4}, respectively, as shown in Figure 2b. Next, we screened various reaction conditions, including different reactant concentrations, reaction temperatures, and amounts of catalyst, but failed to improve the yield of TrNaC\textsubscript{4}. \(\textsuperscript{1}H\) NMR and MS (MALDI-TOF) analyses were used to monitor the oxidative cyclization reaction. Thus, TrNa and TrNaC\textsubscript{n} (\(n = 1–4\)) were unambiguously characterized by using mass spectrometry, as shown in Figure 2. All of the compounds were readily soluble in common organic solvents, such as CH\textsubscript{3}Cl\textsubscript{2}, CHCl\textsubscript{3}, and THF, which enabled their purification by using column chromatography. These results showed that multiple dehydrocyclization samples could be effectively isolated from one reaction, thus suggesting that the oxidative cyclodehydrogenation reaction involved a stepwise ring-closing process, which provided us with a deeper understanding of the cyclodehydrogenation reaction. Firstly, the oxidative cyclodehydrogenation reaction is an electrophilic process.\textsuperscript{16} Moreover, the reaction is a stepwise ring-closing process.\textsuperscript{17} According to frontier orbital theory,
electrons on the highest occupied molecular orbitals (HOMOs) have a certain charge-density distribution on each atom and electrophilic reactions take place on atoms with larger HOMO densities. Thus, we concluded that the HOMO distribution would determine the location of electrophilic attack (Figure 3). Compared with the HOMO densities at the active sites of TrNa, TrNaC1, TrNaC2, and TrNaC3, the TrNa precursor had a relatively high HOMO density (7.51%), which ensured that the reaction took place in high yield. However, the densities of the HOMOs at the active sites of the partly ring-fused molecules (TrNaC1, TrNaC2, TrNaC3) decreased with increasing number of closed rings (from 3.09% to 0.0007%). In particular, for TrNaC2 and TrNaC3, there was minimal electron density at the 8,8′-position of the naphthalene arms (Figure 3), which may be the reason why it was challenging to obtain higher yields of TrNaC4.

Thermal Properties

The thermal properties of cyclodehydrogenation precursor TrNa and main product TrNaC1 were investigated by using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) under an inert nitrogen atmosphere (Figure 4). Good thermal stability of TrNaC1 was demonstrated by its high decomposition temperature ($T_d$, which corresponded to 5% weight loss) of 413 °C, whilst TrNa showed a lower decomposition temperature of $T_d = 397$ °C. According to these results, the ring closure from TrNa to TrNaC1 led to improved thermal properties. Moreover, the glass transition temperature of TrNaC1 was 132 °C, whilst TrNa exhibited an exothermic peak ($T_c$) at 146 °C, after an endothermic melting state. The exothermic peak corresponded to a phase transition into a stable crystalline form. As revealed by the DSC curve, TrNa exhibited...
higher crystallinity than TrNaC1, which matched well with the X-ray diffraction (XRD) patterns (see below), in which TrNa exhibited stronger and sharper diffraction peaks than TrNaC1.

Photophysical Properties

Owing to the good solubility of fused TrNaC1, TrNaC2, and TrNaC3 in common solvents, such as CH₂Cl₂, THF, and trichlorobenzene, it was possible to record the UV/Vis absorption and fluorescence emission spectra of TrNaC1, TrNaC2, and TrNaC3, as well as of the TrNa precursor, as solutions in THF to investigate the changes in their optical properties after locking the naphthalenyl rings of TrNa. The absorption and emission spectra were measured as dilute solutions in THF (1 x 10⁻⁶ M) and as neat films, as shown in Figure 5. The TrNa precursor exhibited only one absorption band in solution (at 331 nm), whilst the ring-fused products exhibited two main absorption bands. One major band at 325 nm and another peak at 369 nm were observed for TrNaC1. TrNaC2 and TrNaC3 exhibited one major peak at about 345 nm and another absorption band with two shoulder peaks at 400 and 424 nm, which was characteristic of rigid fused rings. These two types of absorption band were mainly attributed to the π→π* transition of the core and the π→π* transition of the fused arms. The absorption bands of the fused products showed a significant bathochromic shift compared to those of the TrNa precursor, thus implying extension of the π-conjugation. However, no clear bathochromic shift was observed on moving from TrNaC1 to TrNaC3, thus indicating that there was no significant π-delocalization between the fused arms and the central truxene core. Interestingly, TrNaC2 and TrNaC3, which contained rigid large planer perylene analogue arms, showed a distinctly different absorption band at about 420 nm, which may be characteristic of ring-fused perylene analogue arms. On the formation of the perylene analogue arms, the intensity of the characteristic peaks gradually increased on moving from TrNaC2 to TrNaC3. This phenomenon was consistent with the result that the energy gap decreased with increasing conjugation length in the molecules. Furthermore, the optical band gap could be determined from the onset of the UV/Vis absorption spectra.

The emission spectra of precursor TrNa and ring-fused TrNaCn in THF are shown in Figure 5b. Like most rigid π-conjugated systems, the fluorescence spectra of TrNaC2 and TrNaC3 were distinct mirror images of their absorption spectra, with the presence of two main peaks in dilute solution at 432 and 458 nm. Notably, the intensity of the second peak at about
458 nm increased with the extension of conjugation. Unlike the dual peaks for TrNaC2 and TrNaC3, TrNa and TrNaC1 only exhibited one main peak with less well-defined shoulders in their emission spectra.

The UV/Vis spectra of the corresponding thin films were broadly in accordance with the solution-phase spectra, whilst the corresponding fluorescence spectra showed a gradual bathochromic shift on moving from TrNa to TrNaC3. This phenomenon could be ascribed to the idea that molecules aggregated more effectively in the solid state, with gradual increased rigidity. In other words, the emission properties of the resulting nanographenes could be facilely adjusted by controlling the number of restricted phenyl rings in a single system.

To further investigate their optical properties, the PLQYs (as $\times 10^{-1} \text{m}$ solutions in THF and neat films) and fluorescence transients of TrNa and TrNaCn were determined and the key data are summarized in Table 1. The solution-phase PLQY of TrNa ($\eta = 0.08$) was small because the intramolecular rotation of the multiple naphthyl arms non-radiatively deactivated its excited states. The solution-phase PLQYs for TrNaC1, TrNaC2, and TrNaC3 were 0.16, 0.65, and 0.66, respectively, which suggested that the PLQY gradually increased with extension of the π-conjugation. In particular, TrNaC2 and TrNaC3 showed higher PLQYs in solution ($\eta = 0.61–0.66$) than TrNa and TrNaC1 ($\eta = 0.08–0.16$), thus indicating that the large rigid perylene chromophores played a key role in improving the PLQY. The formation of rigid perylene units may have helped to enhance the radiative pathways that led to a higher PLQY, with red-shifted emission peaks. Moreover, the PLQYs of TrNaC2 and TrNaC3 in the solution state were larger than the corresponding solid-state PLQYs ($\eta = 0.25–0.28$). A decrease of more than 2.5-fold for $\eta$ in the neat films indicated the presence of significant quenching, which correlated well with the large π-conjugated coplanar system. The fluorescence transients of TrNa and the fused products were investigated to study their excited-state relaxation dynamics. As shown in Figure 6, the transients were measured at the maximum fluorescence band for $\times 10^{-1} \text{m}$ solutions in THF and in films that had been excited at the first peak of the fluorescence spectra; the data for the fluorescence lifetimes ($\tau$) are listed in Table 1. The excited-state relaxation of samples in solution followed a similar single-exponential-decay profile, except for the TrNa precursor. The estimated fluorescence lifetimes were $\tau = 6.58–12.30$ ns for the ring-fused samples and progressively decreased with an increasing number of π-conjugated rings. The fluorescence transients for the thin films exhibited non-exponential behavior, including fast relaxation of the excited state within the first 2 ns and relatively slow relaxation thereafter. The short component of the transient lifetime in the thin films was mainly ascribed to non-radiative relaxation, which resulted from exciton migration during the initial decay stage. Thus, the decrease of $\eta$ by

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<th>Table 1. Photophysical properties of the TrNa precursor and the ring-fused products (TrNaCn).</th>
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<td><strong>Compound</strong></td>
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[a] Measured as a solution in THF ($\times 10^{-1} \text{m}$). [b] Measured as a thin film. [c] $\lambda_{\text{onset}}$ denotes the onset wavelength in the absorption spectra of the films. [d] $E_g^{\text{opt}}$ (optical energy gap) values were calculated from the absorption onset in the spectra of the films. [e] Estimated from the onset oxidation and reduction potentials by using $E_{\text{red}}^{\text{red}} = (E_{\text{onset}} + 4.477) \text{ eV}$, $E_{\text{ox}}^{\text{red}} = 0.03 \text{ eV}$. [f] Calculated from the HOMO and $E_{\text{lin}}$ value, which was estimated from the red edge of the longest absorption wavelength for the solid-state sample. [g] Fluorescence quantum yields in solution and the solid-state films, as measured on a quartz plate by using an integrating sphere.
about 25% in the thin films implied the presence of a non-radiative decay process. In addition, the longer decay component may primarily originate from stronger localized excitons, which would evade the fast non-radiative decay.

DFT Calculations

To further unravel the electronic structures of these PAHs, geometry optimization was performed at the B3LYP level of theory by using the Gaussian 09 simulation package. The HOMOs and LUMOs of these PAHs, as well as their corresponding energies, are shown in Figure 7. The band gaps for TrNa, TrNaC1, TrNaC2, and TrNaC3 were 3.97, 3.7, 3.17, and 3.14 eV, respectively. The calculated band gaps narrowed with extension of the conjugation, in accordance with the red-shifted optical absorption (see above).

Electrochemical Properties

The influence of the extent of conjugation or the planarity on the electrochemical properties of TrNa and TrNaCn was studied by using cyclic voltammetry (CV), as shown in Figure 8 and Table 1. A 0.1 M solution of tetrabutylammonium hexafluorophosphate (Bu4NPF6) in MeCN was used as the electrolyte in a standard three-electrode electrochemical cell. An internal reference ferrocene/ferrocenium (Fc/Fc+) redox couple was used to calibrate the measured potentials.

The HOMO energy levels of TrNaC1, TrNaC2, and TrNaC3 were −5.61, −5.29, and −5.25 eV, respectively. The energy gaps (Eg) of these molecules were estimated from the red edge of the longest absorption wavelength for the solid-state sample (Table 1). On the basis of the electrochemical data, we concluded that increasing the π-conjugation through cyclization could lead to a distinct negative shift of the first oxidation potential, linked to the higher-energy HOMO level. Fusion of the naphthalene unit into the truxene core made the generation of a radical cation easier, which was associated with higher oxidizability and a lower energy gap. This trend agreed with the results of the DFT calculations and the optical data.

Self-Assembly Characteristics

The solution processing of organic materials is a simple, inexpensive, and effective way of incorporating organic semiconductors into optoelectronic devices. In addition, molecules that exhibit macroscopic self-assembly properties always also show unique enhanced properties. Thus, it was necessary to study the relationship between molecular architecture and the self-assembly characteristics of these compounds in the solution state. As such, TrNa and TrNaC1 were separately dissolved in CH2Cl2 (as a “good solvent”) and MeOH was slowly added as a “poor solvent”; the volume ratio of CH2Cl2/MeOH could be varied from approximately 1:4 to 1:10. After aging for two or three days, the opaque solutions were drop-cast onto silicon wafers to investigate the self-assembly morphologies of TrNa and TrNaC1 by using a high-power optical microscope and the results are shown in Figure 9 and Figure 10, respectively. To our surprise, TrNa assembled into rod-like microcrystals with micrometer length that could be facilely identified by the naked eye. By comparison, TrNaC1 aggregated into nanosheets with rather small sizes.

To verify the results of the optical images, SEM and TEM analyses were used to characterize their morphologies. After drop-casting aged opaque solutions onto silicon wafers and drying under vacuum, an ultrathin layer of gold was sputter-coated onto the silicon wafers and SEM characterization was performed at an accelerating voltage of 1.0 kV. Samples for the TEM analysis were obtained by drop-casting aged opaque solutions onto copper mesh and drying under vacuum. SEM and TEM images of TrNa and TrNaC1 are shown in Figure 11 and Figure 12, respectively. TrNa molecules exhibited lengths of tens-to-hundreds of microns and diameters of about 2 μm. In contrast, TrNaC1 assembled into nanosheets with lengths of about 4 μm. The increased planarity or π–π stacking interactions between the ring-fused naphthalenes might be the driving force for the self-assembly of TrNaC1 into nanosheets.

As shown in Figure 13, powder X-ray diffraction (XRD) measurements were used to further analyze the aggregates of TrNa and TrNaC1 and to elucidate their macroscopic morphologies. Both TrNa and TrNaC1 showed clear diffraction peaks within the range 2θ = 5–25°, thus indicating that they could self-assemble into ordered structures. Moreover, the sharp peaks for
TrNa and the relatively flat peaks for TrNaC1 suggested that TrNa assembled into a more-ordered superstructure in comparison to TrNaC1, in agreement with the observed microscale order in the crystalline structures of TrNa and the DSC analysis (see above). This phenomenon was attributed to “locked” π-π-stacking between the naphthalene arms, because the covalent bonds could direct the molecular orientation. According to recent studies, strong π-π stacking between small planar aromatic rings could induce aromatic molecules to assemble into macrostructures. Therefore, the planar naphthalene rings

Figure 9. Optical images of rod-like microcrystals of TrNa; scale bars: 100 µm (a), 20 µm (b).

Figure 10. Optical images of nanosheets of TrNaC1; scale bar: 100 µm (a), 20 µm (b).

Figure 11. a, b) SEM of rod-like microcrystals of TrNa; scale bars: 100 µm (a), 40 µm (b). c, d) TEM of rod-like microcrystals of TrNa; scale bars: 5 µm (c), 2 µm (d).

Figure 12. SEM and TEM analysis of TrNaC1 nanosheets; scale bar: 2 µm.

Figure 13. Powder XRD patterns of TrNa and TrNaC1.
of TrNa are beneficial for the formation of microscale crystals. In contrast, ring-fused structure TrNaC1, which contained “locked” π-stacking between naphthalene arms tended to adopt nanosheet structures.[1]

**Conclusion**

In summary, we have demonstrated a bottom-up synthetic approach towards a new set of π-extended star-shaped PAHs based on naphthalene-fused truxenes that exhibit facilely tunable emission properties. Multiple dehydrocyclization samples were effectively isolated from a single reaction, which confirmed that the oxidative cyclodehydrogenation reaction proceeded through a stepwise ring-closing process. Decreasing reactivity of the fused rings was observed with an increasing number of fusing steps. Clear enhancement in the fluorescence PLQY was observed for TrNaC2 and TrNaC3 compared to those of TrNa and TrNaC1, presumably because of the introduction of large rigid fused-pyrenyl rings. Furthermore, their (optical) band-gap energies could be regulated by increasing the number of closed rings with different edge structures (fold and bay regions). Interestingly, the self-assembly behavior of the resultant PAHs could also be facilely modulated by subtle tuning of the molecular structures. TrNaC1 self-assembled into nanosheets, whilst TrNaC2 assembled into rod-like microcrystals. This study offers a unique platform to gain further insight into—and better understanding of—the photophysical and self-assembly properties of π-extended star-shaped PAHs.

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