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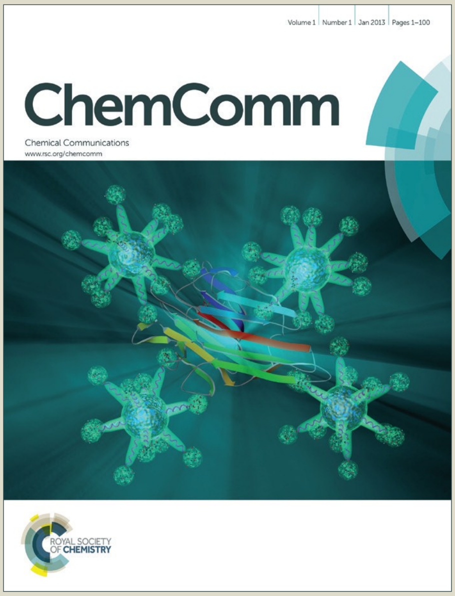

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Parent and Trisubstituted Triazacoronenes: Synthesis, Crystal Structure and Physicochemical Properties †

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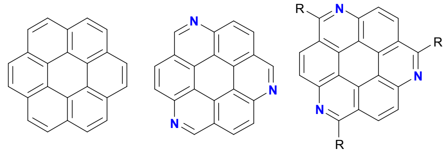
A four-step synthesis of C_3-symmetric parent 1,5,9-triazacoronene (TAC) and its derivatives was achieved using a three-fold Bischler-Napieralski cyclization as a key step. Single crystal X-ray diffraction of 1b (R = *n*-Bu) demonstrates that the azacoronene core is perfectly co-planar and the molecules adopt favorable 2-D "brick-wall" arrangement with strong π-π interactions. The unique stacking, tunable photophysical and electronic properties, and high thermal stability should make them promising candidates for emissive and electron-transport materials.

Polycyclic aromatic hydrocarbons (PAHs) have been the subject of intense research over the past decade owing to their potential applications in futuristic organic electronics, such as organic light-emitting diodes, field-effect transistors, and solar cells.[1] Coronene occupies a special place among PAHs, which is an intriguing D_{6h} symmetric disc-shaped nanographene[2-3] with zigzag periphery, perfectly delocalized π-system and the ideal size for processing techniques.[4]

Chemical doping of heteroatoms to the lattice of aromatics is an effective strategy to modulate their intrinsic physicochemical properties.[5] Among the potential dopants, electronegative nitrogen, with a smaller atomic radius and one more electron than carbon, is considered to be one of the fascinating elements for this purpose.[6] However, in a sharp contrast with the prosperity of other *N*-doping aromatics, the sparse literature precedent of azacoronenes is surprising and likely arises from the lack of efficient synthetic approaches.[7] Recently, Liu *et al.* reported the synthesis of diazacoronenes which have shown significant potentials as a promising electron donor for the development of high performance organic materials.[8] In 2010, Wei *et al.* reported an elegant synthesis of triazacoronene derivatives bearing six-methoxyl groups in the periphery which were indispensable for the nitration and Pictet–Spengler cyclization during the construction of triazacoronene core.[9] In general, introduction of electron-donating alkoxyl groups represents a general strategy for the successful synthesis of many aromatics.[3c,4d,10-11] These groups not only facilitate the synthesis but also improve the solubility or tune the properties. However, introduction of alkoxyl groups is occasionally double-edged as they will inevitably perturb on the intrinsic physicochemical properties, impede effective π-stacking and preclude further extension of the π-system. Not surprisingly, it was revealed by X-ray analysis that the azacoronenes with six methoxys lacked of apparent π-π interactions in the solid state which are generally considered to be of great importance for applications.[9]

Parent triazacoronene **1a** remains elusive although it has been addressed in previous studies.[9,11] The difficulties for the synthesis of **1a** and its derivatives, such as **1b-1i**, lie in the challenge of the final cyclization step, by Bischler-Napieralski reaction for instance, which is conceptually more favorable for electron-rich substrates.[10-12] Herein, we demonstrate that parent **1a** and **1b-1i** were effectively synthesized through a rational design and appropriate reaction conditions. Our goal was three-fold: (a) to get insight into the intrinsic properties of TACs by excluding the influence of any activation group (alkyl or alkoxyl); (b) to enhance intermolecular orbital overlap by



Coronene

1a
Parent Triazacoronene

1b-i
R = alkyl, aryl, CF_3

Fig. 1 Coronene and triazacoronenes (TACs).

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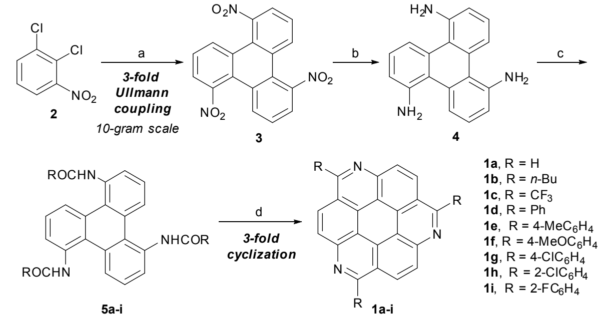
self-assembly of the aromatics moieties; (c) to reserve the peripheral C-H bonds for further π-extension or functionalization.

As shown in Scheme 1, the key intermediate 1,5,9-trinitrotriphenylene **3** was readily prepared through a three-fold Ullmann coupling reaction from inexpensive dichloride **2** by modifying the method reported by Mugnier and Laviron in 1979.[13] Catalytic hydrogenation of compound **3** afforded triamine **4** in a quantitative yield, which reacted with anhydrides or acyl chlorides to afford triamides **5a-5i** in moderate to excellent yields. However, the final 3-fold cyclization was difficult in the absence of alkoxyl or alkyl activating groups. We speculate the transformation of **5** to **1** presumably involves three successive ring closures: carbonium-ion formation being followed by intramolecular electrophilic attack. The final ring closure is more challenging due to the strong deactivation effect by the formed two electron-deficient pyridine rings. Amide **5d** was initially investigated due to its easier carbonium-ion formation and less sensitivity towards hydrolysis.[14] Typical conditions for Bischler-Napieralski cyclization, such as polyphosphoric acid at 150 °C or refluxed $POCl_3$, failed to give the desired product, instead leading to *mono*- and/or *di*-cyclized products or hydrolysis. Gratefully, ionic liquid of molten aluminum chloride – sodium chloride ($AlCl_3$-NaCl)[15] at 220 °C (Method A) was found to be effective affording **1d** in 64% yield. It was worth noting that the composition of this ionic liquid played an important role (Table S1). To our delight, the condition was applicable to various TACs, even for pristine **1a** and **1h**-**1i** bearing *ortho* substituents (Table S2). The only exceptions were **1c** (R = CF_3) with strong electron-withdrawing groups, and **1f**, of which the methoxy groups were not compatible with the strong Lewis acidic condition. Gratefully, a combination of $POCl_3$ and P_2O_5 at 120 °C (Method B) could afford **1f** in 67% yield. Amazingly, **1c** could also be obtained albeit in only 15% yield. To the best of our knowledge, it was the first example to prepare a 2-perfluoroalkylated phenanthridine-type compound directly from the corresponding amide, which was commonly prepared through palladium-catalyzed cyclization of perfluoroacetimidoyl chloride[16] or isocyanide insertion.[17] We ascribe it to the delocalization of the charge through a large π-system despite the strong –*I* effect of trifluoromethyl substituent. Evaluation of Method B revealed that it was also applicable to other TACs except **1a** and **1h-1i** with *ortho* substituents. Therefore, Method B is complementary to Method A for the synthesis of a variety of TACs.



Scheme 1 Synthesis of triazacoronenes. Conditions: (a) Cu, DMF, reflux, 12 h, 53%; (b) H_2 (1 atm), Pd/C, EtOAc–EtOH (10 : 1, *v*/*v*), rt, quant.; (c) Anhydride or RCOCl, base, solvent, 43-89%; (d) Method A: NaCl-$AlCl_3$, 220 °C, or Method B: $POCl_3$–P_2O_5, 120 °C, 50–79%, 15% for **1c**.

Most of TACs are soluble in dichloromethane or a mixed solvent of dichloromethane and methanol. The proton NMR spectra were recorded either in $CDCl_3$-CD_3OD or $CDCl_3$-CF_3COOD. The sparingly solubility of **1c** precludes solution ^{13}C NMR characterization; however, ^1H NMR, ^{19}F NMR and HRMS (MALDI TOF-MS/DHB matrix) confirmed the structure. The structure of **1h** was confirmed by variable-temperature ^1H NMR due to the existence of atropisomers at room temperature (Figure S1). The ^1H NMR signals of the peripheral protons located in the range of 9.0–10.0 ppm similar to coronene (8.85 ppm).[18]

Single crystals of **1b** suitable for X-ray crystallographic analysis were obtained as brilliant yellow needles by slow diffusion of CH_3CN into a solution of **1b** in THF. The structure of **1b** was unambiguously confirmed by X-ray crystallographic analysis (Figure 2). In contrast to azacoronene with hexa-alkoxyl groups,[9] the TAC core is disclosed to be perfectly flat with the dihedral angles less than 2°. Two of the side-chains are fully extended with *all-trans* confirmation and one is bent out of the plan of the TAC core to minimize the repulsions (Figure 2b and Figure S3). Bond-length alternation in extended π-conjugated molecules is important for discussing the nature of the π-system. The peripheral benzene and pyridine rings show significant bond alternation, while bonds lengths of the hub benzene are almost identical (1.42-1.43 Å) indicating single-bond character to certain extent. The C=C bond lengths of the rim (average 1.37 Å) are rather shorter than benzene. The rim C=N bonds (average 1.33 Å) are remarkably shorter than the flank (average 1.40 Å), thus having more double-bond characters. The crystal structure of **1b** is in good consistent with that predicted by density functional theory calculation

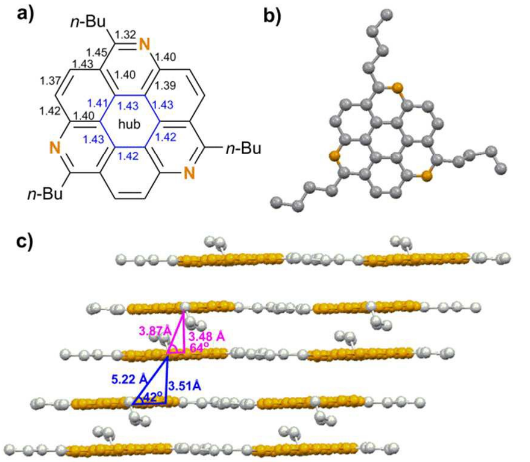


Fig. 2 X-ray crystal structures of TAC **1b**. (a) Molecular structure with bond lengths. (b) Top view. The nitrogen atoms are indicated in yellow. All H atoms have been omitted for clarity. (c) Crystal packing with face-to-face distances and offset angles (yellow color represents the TAC core).

(DFT) at B3LYP/6-31G(d) level (Figure S18). Nucleus-independent chemical shifts (NICS)[19] predict that the outer rings exhibit moderate aromaticity with NICS(0) values of -10.2 and -6.3 ppm respectively, whereas the central benzene ring is almost nonaromatic with a NICS(0) value of -0.4 ppm, sharing the same trend with NICS(1) results (Table S7).

The solid-state stacking has a great impact on the performance of materials because the transfer integral and reorganization energy are both highly dependent on the packing (arrangement) of the organic molecules. Compound **1b** adopted a two-dimensional (2-D) “brick-wall” arrangement with strong intermolecular interactions (Figure 2c),[20] having a striking difference from the none π-π interactions of azacoronenes bearing six alkoxyl groups in the periphery,[9] and the edge-to-face herringbone packing of coronene.[21] The adjacent molecules formed slipped stacks with a face-to-face distance of 3.48 Å slipped by 1.70 Å within the unit cell, and 3.51 Å slipped by 3.87 Å between unit cells. The offset angles between the TAC molecules are 64^{o} and 42^{o}, respectively, placing the alignment in the *J*-aggregate regime with significant overlap of the TACs aromatic cores.[22] Double C-H···N interactions were observed between the horizontally adjacent molecules, which might be responsible for the lamellar stacking (Figure S5). This unique arrangement has proven to be important for the performance as electronic materials for organic field-effect transistors (OFETs).[1h,23]

The UV-vis spectrum of **1a** in dichloromethane exhibits intense absorption bands at 275 nm, 317 nm (λ_{max}, logε = 4.82) and 351 nm, and a week absorption at 397 nm. The absorption spectra of **1b** is essentially the same as **1a**, while **1c** (R = CF_3) and **1d**-**1i** (R = aryl) are bathochromically shifted with respect to **1a** (Figure S6, Table S4). The dihedral angle between the core and the phenyl group of **1d** predicted by DFT calculation was 46° (Figure S16), which causes some extension of the π-conjugation to the azacoronene moiety, resulting in a narrower HOMO-LUMO gap and the observed red shift in absorption. All TACs have high values of molar extinction coefficient (5.9–9.6 × 10^4 $M^{-1}cm^{-1}$).

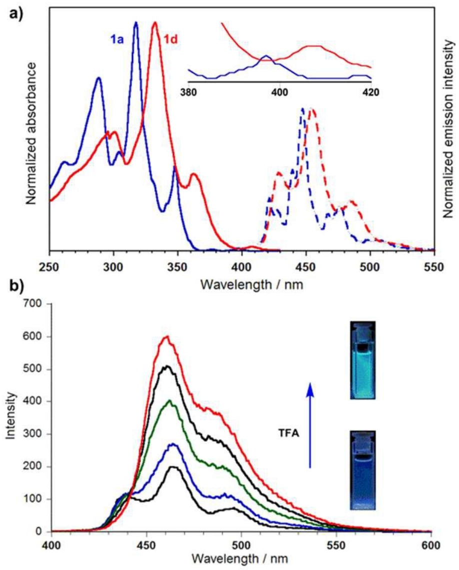


Fig. 3 (a) UV-vis absorption spectra (solid line) (*c* = 1 × 10^{-5} M) and emission spectra (dashed line) of **1a** (blue) and **1d** (red) in CH_2Cl_2. Inset: expansion of absorption spectra in the long-wavelength region. (b) Acid-induced photoluminescence changes of **1d**. Inset: photographs showing the visual fluorescence color changes under a 365 nm UV lamp.

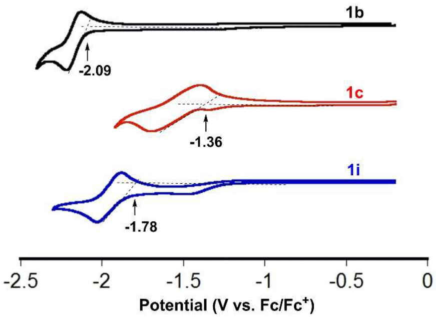


Fig. 4 Cyclic voltammograms of **1b**, **1c** and **1i** in CH_2Cl_2 (0.10 M *n*-Bu_4NPF_6). Scan rate: 100 mVs^{-1}. The arrows indicate the onset reductive potentials.

TACs **1a**-**1i** show strong blue emissions in solution under UV light with large stoke shifts around 130 nm (Figure S6-S7). As shown in Figure 3, the profiles of emission spectra of **1a** and **1d** are essentially the same displaying three characteristic and resolvable emission bands, and **1a** shows three apparent shoulders. Protonation of the nitrogen atoms by gradual addition of trifluoroacetic acid greatly enhances the fluorescence intensity and dramatically changes the UV-vis spectra (Figure 3b and Figure S8), indicating their possible applications as “turn-on” fluorescence proton sensors.

The electrochemical properties of representative TACs were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) (Figure 4 and Figure S9-S10). Compound **1b** shows a reversible reduction with a half-wave potential ($E_{1/2}$) at -2.17 V and an irreversible oxidation with peak potential (E_p) at 1.34 V. Similarly, **1c** shows one reversible reduction potential ($E_{1/2,}$ -1.53 V), shifted by 0.64 V with respect to **1b** resulting from the introduction of three electron-withdrawing CF_3 groups.[24] The LUMO levels of **1b**, **1c** and **1i** are estimated at -2.71, -3.44 and -3.02 eV, respectively based on the onset potentials of the reduction waves (Figure 4).[25] The HOMO level of **1b** is determined to be -5.94 eV, and the electrochemical band gap is 3.23 eV, near the optical gap (E_g^{opt}, 3.08 eV) deduced from the absorption edges. The LUMO levels of other aryl-substituted TACs (**1d**-**1h**) are estimated to be -3.0 eV approximately. These results suggest their high potentials as intrinsic n-type semiconducting materials.[26]

Furthermore, thermogravimetric analysis (TGA) of TACs indicates compound stability up to 400 ^{o}C (Figure S20), indicating their high potentials as robust organic materials.

In conclusion, C_3-symmetric pristine 1,5,9-triazacoronene as well as its derivatives with various substituents were concisely synthesized. TACs can be assembled utilizing inexpensive starting materials and are amenable to large-scale reactions. TACs **1a**-**1i** differ remarkably in solid stacking, photophysical and electrochemical properties from azacoronenes bearing alkoxyl groups. TACs **1a**-**1i** are promising candidates as n-type organic semiconductors. In addition, TACs especially those with *ortho*- substituted phenyl groups such as **1h** and **1i** can be elaborated for further extension of the π-system, which is currently underway. We hope more attentions to be paid to the pristine compounds of the numerous existed aromatics bearing alkoxyl and/or alkyl groups for investigating their intrinsic properties.

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