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REVIEW

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Triazatruxene-based materials for organic electronics and optoelectronics

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10,15-Dihydro-5*H*-diindolo[3,2-*a*:3′,2′-*c*]carbazole (triazatruxene or triindole), which is an aromatic and C_3 symmetric planar π-extended conjugated structure, has attracted a great deal of interest due to its exceptional solubility, high thermal stability, rich-electronic properties and easy modification. Over the past ten years, owing to the advances in the synthesis of triazatruxene derivatives, the scope of applications of this attractive building block has been extended to organic electronics, two-photon absorption, nonlinear optics, fluorescent sensors, *etc.* This review aims at summarizing investigations into triazatruxene-based organic electronic materials from synthesis and self-assembly to optoelectronic properties to achieve a better understanding on the structure–function relationships and to explore their extensive applications. The potential of these highly promising scaffolds in future research will also be put forth.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) have become an important class of materials owing to their unique optical and electronic properties and wide potential applications in organic electronic devices, such as organic field-effect transistors (OFETs),[1–5] organic photovoltaics (OPVs),[6–8] and organic light-emitting diodes (OLEDs).[9–12] The development of new PAHs, especially large π-systems, in organic electronics and functional nanomaterials has become a vital issue.[13–15] Among various polycyclic aromatic compounds, 10,15-dihydro-5*H*-diindolo-[3,2-*a*:3′,2′-*c*]carbazole (triazatruxene or triindole) is a C_3 symmetric planar π-extended conjugated structure that can be regarded as a symmetric indole cycle-trimer.[16–18] It can also be formally considered as an overlapping framework of three carbazole units and act as an electron donating unit.[18–21] Owing to its planar extended π system and its electron-rich structure, this C_3-symmetric molecule offers great potential application in non-linear optics (NLO),[22] two-photon absorption (TPA),[23] OLEDs,[24–27] OPVs,[28,29] liquid crystal displays (LCDs),[19,30,31] OFETs, organic lasers,[32] as well as fluorescent sensors.[16,33] This polyarene exists in the form of two possible isomers, *i.e.* triazatruxene and isotriazatruxene, only differing in the way the carbazole moieties arrange (Fig. 1).[34,35] The first reports on

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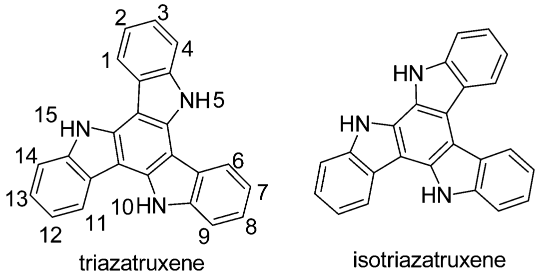

Fig. 1 Structure of triazatruxene and isotriazatruxene.

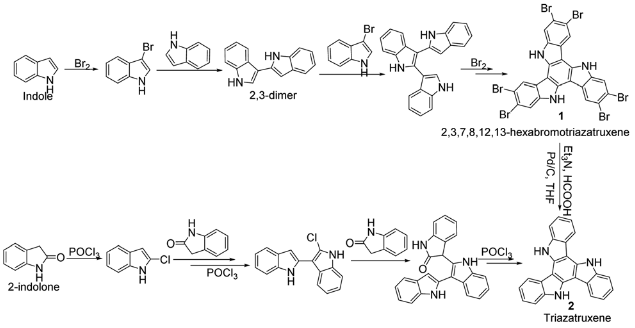

Fig. 2 Possible reaction mechanism for the formation of hexabromotriazatruxene **1** and triazatruxene **2** by two common methods.

the synthesis of triazatruxene and isotriazatruxene were demonstrated in 1980.[36,37] Based on the pioneering work in 1980, triazatruxene was synthesized through the Ullmann coupling of 1-iodo-*N*-methylindole with the activated copper.[36] In the meantime, asymmetric isotriazatruxene was afforded by cyclotrimerization of the *O*-acetate of indoxyl.[37] Although the selective preparation of each isomeric form is now well established, the symmetric form has still received much more attention than the asymmetric one and this review will only focus on the symmetric one. Concerning triazatruxene, Eissenstat *et al.* realized its simple synthetic method starting from 2-indolone with $POCl_3$[38] in 1995 and then Robertson *et al.* accomplished the synthesis beginning from indole with bromine in 2000.[39] Since then, triazatruxene derivatives have been widely utilized in various optoelectronic applications, such as NLO, TPA, OFETs, OPVs, OLEDs, and LCDs. In this review, we discuss the design strategy, self-assembly properties, and the device performance of triazatruxene-based materials. This review aims at pointing out the impact and added value brought by the presence of triazatruxene moieties in various organic electronic materials. The potential of these highly appealing building blocks in future design and development of organic electronic materials will also be included.

Synthesis of triazatruxene derivatives

Generally, triazatruxene can be synthesized by the trimerization of indole and 2-indolone in the presence of bromine and $POCl_3$, respectively, as depicted in Fig. 2. In addition, indole, when treated with excess bromine, can form hexabromotriazatruxene. As for the reaction of indole with bromine, one equivalent of bromine would be sufficient to complete the cyclotrimerization in principle. However, only the 2,3-dimer was isolated under these conditions, whereas three equivalents were necessary to obtain the brominated symmetric indole trimers (2,3,7,8,12,13-hexabromotriazatruxene (**1**)).[39] In particular, the synthesis of unsubstituted triazatruxene (**2**) has been reported by isolation of hexabromotriazatruxene and subsequent dehalogenation.[24,40] As a first synthetic approach, the mixtures of indole and three

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equivalents of Br_2 in acetonitrile were stirred overnight at room temperature. Then, the obtained hexabromotriazatruxene was washed and recrystallized, taking advantage of the low solubility of this intermediate compound. The dehalogenation was realized by reduction with formic acid in triethylamine in the presence of a Pd/C catalyst, affording unsubstituted triazatruxene. For the other synthetic approach, unsubstituted triazatruxene was directly synthesized by the symmetric cyclotrimerization of 2-indolone in $POCl_3$ at 100 °C in a quite high yield (Fig. 2).[16,17,38] This is a much simpler way to obtain unsubstituted triazatruxene in terms of time and yields.

Functionalized triazatruxenes are interesting organic electronic materials with unique organic optoelectronic properties. Most of the functionalization studies have mainly focused on the NH-sites and peripheral benzene rings.[18,19,41,42] Alkyl chains are usually introduced at the N5, N10, and N15 positions under basic conditions. For instance, the *N*-alkylated triazatruxene **3** was synthesized by simple alkylation of triazatruxene under basic conditions (Fig. 3). High photoconductivity was observed in the amorphous state, and the spontaneous crystallization of the films led to a photocurrent enhancement of up to four orders of magnitude.[43] Alkyl chains have also been introduced into the peripheral benzene rings of triazatruxene. As shown in Fig. 3, compound **5** was prepared in this way by *N*-alkylation and 6-fold Sonogashira coupling. Subsequent hydrogenation of the triple bonds afforded **6**, and further removal of the protected groups gave compound **7**. Their high HOMO (highest occupied molecular orbital) energy levels (−4.92 to −4.99 eV) indicated that they were likely to be hole transporters. It is worth noting that these compounds can also efficiently self-assemble into columnar structures.[20]

Due to the planar and C_3-symmetric structure of triazatruxene, a large quantity of triazatruxene-based materials have been explored, such as starburst molecules with C_3-symmetry,[24,26,44–46] dumbbell-shaped molecules,[29,47] D–π–A linear molecules,[48,49] dendrimers,[50,51] conjugated microporous polymers,[52] and triazafullerene, *etc.*[21,40] Basic reactions regarding the functionalization of triazatruxene include electrophilic substitution reactions at the NH-positions. Usually, the aryl and other conjugated groups are linked to triazatruxene through a coupling reaction on the periphery. According to the molecular topology shapes of conjugated triazatruxene derivatives, we classify them into star-shaped molecules, dumbbell-shaped molecules, and D–π–A linear molecules.

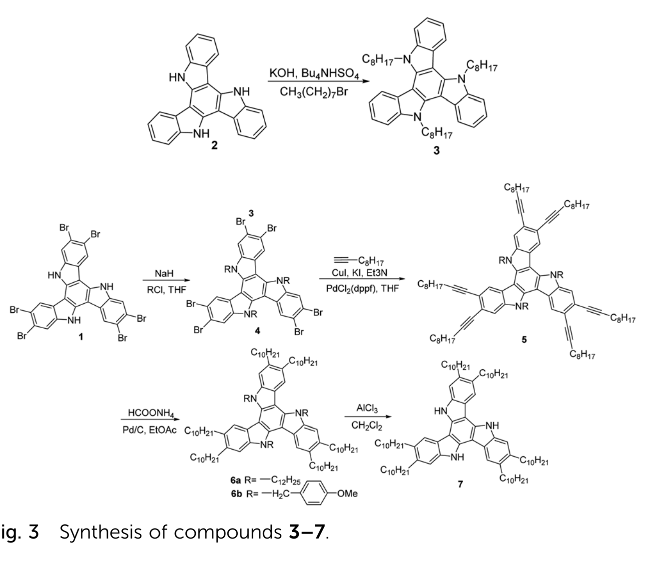


Fig. 3 Synthesis of compounds **3–7**.

Star-shaped molecules

Star-shaped molecules feature a core unit which may or may not provide conjugated links between arms that radiate like spokes from a central axle. The arms of the macromolecules usually consist of linear oligomers or irregular conjugated chains lacking a formal repeat unit.[53,54] Similar to dendrimers, star-shaped molecules possess well-defined molecular structures as well as superior chemical purity. In addition, they retain the excellent film-forming properties, solution processability and precisely designable properties of polymers in device fabrication. Star-shaped molecules also have distinct advantages over linear structures because of their conformational effects, intramolecular charge transfer and energy transfer, self-assembly and thermal behaviors. More importantly, a star-shaped architecture with conjugated arms would generate new electrical, optical, and morphological properties in the system.

Generally, synthesis of well-defined, highly substituted branched star-shaped structures is difficult because of intractable multiple couplings and arduous and time-consuming repetitive synthetic steps, and the overall yields are low. Thus, a facile and powerful methodology that can facilitate this procedure is highly desirable. This is particularly important for complex material syntheses that generally require multistep synthetic procedures. The lengthy reaction sequence and the associated difficulty have often discouraged scientists from widely exploiting these materials. In recent studies, Lai *et al.* have first developed a facile and powerful microwave-enhanced multiple coupling methodology.[42] A family of well-defined star-shaped compounds **8–13** with triazatruxene as the core and oligofluorenes as the branches has thus been conveniently constructed within minutes by microwave-enhanced multiple Suzuki coupling reactions (Fig. 4).[20,26,42] The results demonstrate that microwave heating allows rapidly and efficiently obtaining structurally complex monodisperse star-shaped macromolecules with high yield and purity.

Maintaining the same triazatruxene core, star-shaped molecules with different side arms were investigated. In the case of oligothiophenes as the side arms, the increasing effective conjugation length can not only render the absorption and emission peaks redshifted, but also increase the isotropic transition temperature.[55] Star-shaped molecules bearing *N*-alkylcarbazole,[41] and *N*-phenylcarbazole[56] branches were also developed and displayed similar redshifts of the absorption spectral peaks with the introduction of phenyl groups.

In addition, alkyl chains have also been introduced into the peripheral benzene rings of triazatruxene (**5–7**).[31] These materials combined the good hole transport properties of the triazatruxene unit with the supramolecular organization typical of discotic

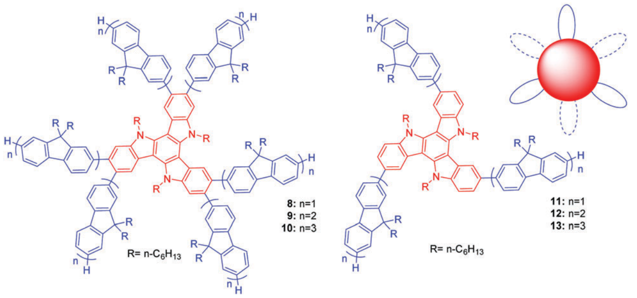


Fig. 4 Chemical structures of star-shaped compounds **8–13**.

liquid crystals. Moreover, the particularly high values of the HOMO energy levels make such substances well suitable for all the applications where charge injection from an electrode is required.

The construction of star-shaped molecules is not restrained by linking a core and branches through a single bond. With the aim of expanding the library of triazatruxene derivatives, a family of triazatruxene-based polycyclic aromatics was constructed. By employing an elegant oxidation by $FeCl_3$, triphenylene and triazatruxene were connected by sharing the same benzene rings (Fig. 5).[57] This strategy greatly expands the π-conjugated planes, and, at the same time, maintains the maximum rigidity of the molecule. As a result, the star-shaped triphenylene-fused triazatruxenes exhibit good thermal stability and thermotropic liquid crystalline behaviors. The charge carrier mobilities of these extended triazatruxene samples were determined using the space-charge limited-current (SCLC) technique and high hole mobilities. Interestingly, the longer alkyl-chain-substituted compound (**15**) could gelate in multi-solvents owing to their strong intermolecular interactions.

Dumbbell-shaped molecules

Dumbbell-shaped molecules couple two chromophores through either a flexible alkyl spacer or a rigid aromatic linkage. As another way to extend the π-conjugated length, the synthetic approach to dumbbell-shaped molecules is more facile compared with that of star-shaped molecules.[52–54] Due to its C_3-symmetric structure, triazatruxene plays the role of conjugated spacers or end groups rather than cores in the dumbbell-shaped molecules.

A series of extended π-conjugated twin molecules based on triazatruxenes were synthesized, of which the triazatruxenes were connected by rigid diketopyrrolopyrrole (DPP), benzo[2,1,3]-thiadiazole (Btz), pyridal[2,1,3]thiadiazole (Pytz), or thieno[1,2,5]-thiadiazole (Ttz) linkages by Pd^0-catalyzed Suzuki coupling (Fig. 6). The large steric end groups of triazatruxenes effectively suppress the aggregation of these π-conjugated molecules. The optical properties of the twin molecules are strongly affected by the π-linkages owing to their different π-conjugated lengths and torsion angles with triazatruxenes. By means of introducing triazatruxenes as end groups into the diketopyrrolopyrrole unit,[29] a good balance is achieved between planarity and solubility. It promotes end-to-end π–π interactions in adjacent molecules and leads to favorable morphologies of active layers in blend with low ratios of PCBM derivatives.

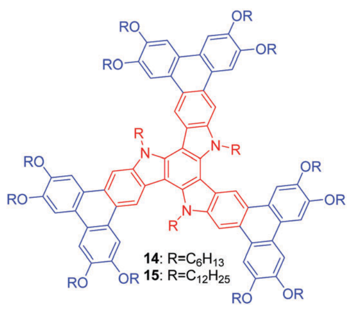


Fig. 5 Chemical structures of star-shaped compounds **14–15**.

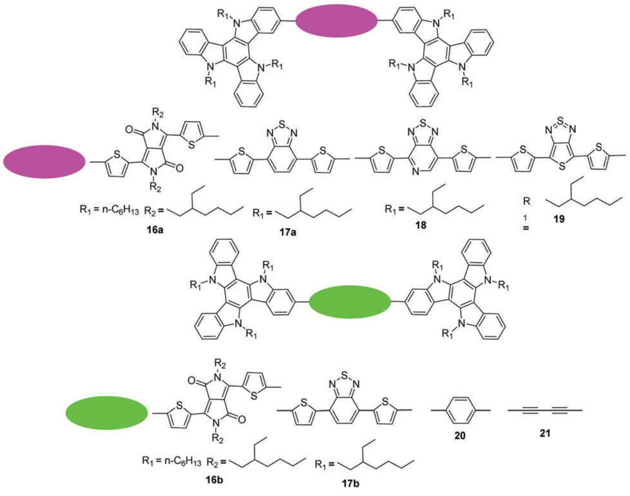


Fig. 6 Chemical structures of dumbbell-shaped compounds **16–21**.

Since the lowest unoccupied molecular orbital (LUMO) levels could be modulated through intramolecular energy transfer in D–A–D molecules, Nicolas *et al.* prepared a family of gradient π-conjugated D–A–D molecules (**17–19**). In these dumbbell-shaped molecules, a triazatruxene unit was employed as an electron donor (D), whereas Btz, Pytz, or Ttz was used as an electron acceptor (A). As for compounds **17–19**, the HOMO energy levels are mainly governed by the first oxidation potential of the triazatruxene fragment which leads to a similar HOMO level for all these compounds. Unlike HOMO levels, the LUMO levels are strongly dependent on the nature of the central withdrawing unit. As the electron withdrawing strength increases, the LUMO values decrease from −3.60 to −3.84 and to −3.92 eV for compounds **17a**, **18** and **19**, respectively. Thus, similar electrochemical data are obtained for **17a** and **17b**, showing that the functionalization position (*meta* or *para*) to the triazatruxene fragment has little influence on HOMO–LUMO properties. In 2015, Gómez-Lor *et al.* synthesized two new dimers with two triindole subunits (**20** and **21**) bound together through different linkers (*p*-phenylene or diacetylene groups). The results demonstrated that the optoelectronic properties of the triindole dimers were strongly influenced by the nature of the π-linkers; the diacetylenic bridge allowed better electronic delocalization.[58] These data draw a conclusion that the optical properties and energy levels are mainly governed by the nature of the central core. In this way, the optical properties and energy levels can be controlled by changing the central units.

D–π–A linear molecules

Most of the organic optoelectronic materials are characterized by an electron donor, a π-conjugated bridge, and an electron acceptor (D–π–A).[59–61] Triazatruxene, owing to its unique discotic π-extended and electron-rich aromatic structure, has been used to produce various functional materials.[16,43,62–64] Benefiting from its strong intramolecular charge transfer characteristics, synthetic flexibility, and high stability, novel triazatruxene-based D–π–A linear molecules were recently designed and synthesized for organic electronics. First synthesis of triazatruxene-based D–π–A linear molecules (**22–24**) was reported in 2011 (Fig. 7),[48] demonstrating large absorption coefficients and fluorescence quantum yields as well as interesting electrochemical properties. The molecule **23** exhibited interesting photovoltaic effects in bulk heterojunction solar cells, due to the good hole mobility imparted by the triazatruxene entity. From this initial report, numerous D–π–A linear structures were developed with different π-bridges and acceptors. Inspired by the strong intramolecular charge transfer characteristics of triazatruxene, Zhu *et al.* first reported the application of triazatruxene in dye-sensitized solar cells (DSSCs). All sensitizers (**25–27**) have shown significant performance in DSSCs with a PCE of over 5%, and the highest PCE value is up to 6.1% with a thiophene (**25**) as a π-linker.[65] The results demonstrate that the triazatruxene-based D–π–A linear molecule can produce high photocurrent density and is a promising candidate for DSSCs. Then, they synthesized two novel D–π–A linear organic dyes with a rhodanine-3-acetic acceptor applied as photosensitizers for DSSCs.[49] They exhibited high light-harvesting ability, efficient electron injection ability, and enhanced PCE.

Self-assembly properties of triazatruxenes

To achieve organic electronics based on π-conjugated systems, a detailed understanding of the supramolecular interactions between individual π-conjugated molecules has become one of the most challenging scientific research areas. Supramolecules can be formed by the self-assembly of organic molecules through different kinds of intermolecular interactions such as π–π stacking, van der Waals and hydrogen bonding interactions. To develop high-performance optoelectronic devices, a better understanding and control of interactions among molecules is necessary.

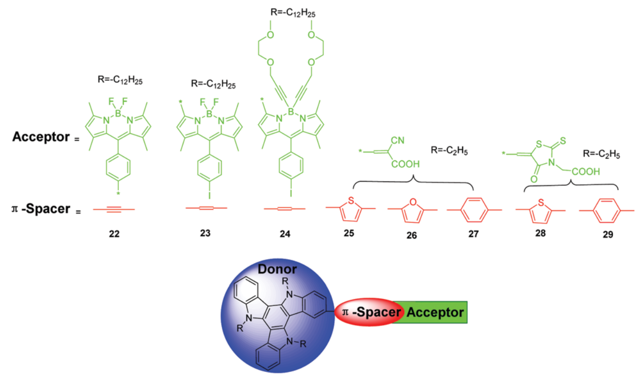


Fig. 7 Chemical structures of D–π–A linear compounds **22–29**.

Among all noncovalent interactions, π–π stacking is considered as one of the main driving forces for the formation of a 1D assembly of organic conjugated molecules. By modulating the size of conjugated planes, the types and the length of side chains, or the external conditions, such as temperature, solvent, and concentration, different morphologies including wires and tubes were achieved.[43,45,66] Gómez-Lor *et al.* developed a family of stable hexagonal columnar mesophases **30–37** based on triazatruxene, and investigated their different self-assembly behaviors with various peripheral substituents (Fig. 8).[67] Through investigating the influence of the electronic characteristics of the peripheral substituents on their self-association behaviors, they found that improving the electron-donating properties of the terminal *p*-phenyl substituents facilitated self-assembly while electron-withdrawing groups inhibited aggregation. Consequently, the self-assembly properties of triazatruxene derivatives can be tuned by means of modulating the electronic characteristics of the peripheral substituents. In addition, the self-assembly process at different solvent compositions shows that the stacking tendency strongly depends on the polarity of the solvent. Subsequently, a series of *N*-(hetero)arylmethyl triazatruxenes (**38–45**) were also synthesized.[64,68] According to the theoretical investigations and X-ray crystallographic analysis, they confirmed that this is the preferred all-*syn* conformation in the solid state. In addition, compound **42** crystallizes and forms C_3-symmetric dimeric cagelike complexes. Guest molecules of chloroform and water are confined within the resulting cavities with stabilization by different intermolecular interactions; this highlights the potential of these compounds in the construction of supramolecular systems. In 2010, Wu *et al.* reported a new family of enlarged π-conjugated discotic mesogens *via* the fusion of three triphenylene units into a triazatruxene core.[57] Highly ordered columnar superstructures and an unusual gelation behavior in different solvents were observed, further proving the strong intermolecular interactions in the new π-systems (Fig. 9). Based on polarizing optical microscopy (POM) images, X-ray diffraction (XRD) and differential scanning calorimetry (DSC) data, it is found that annealing of the bulk

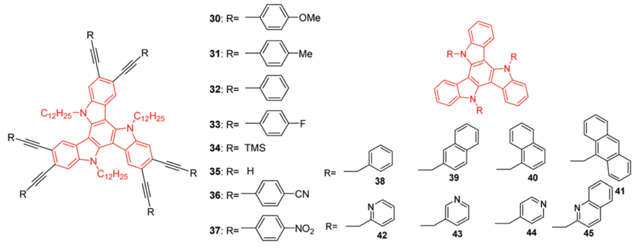


Fig. 8 Chemical structures of compounds **30–45**.

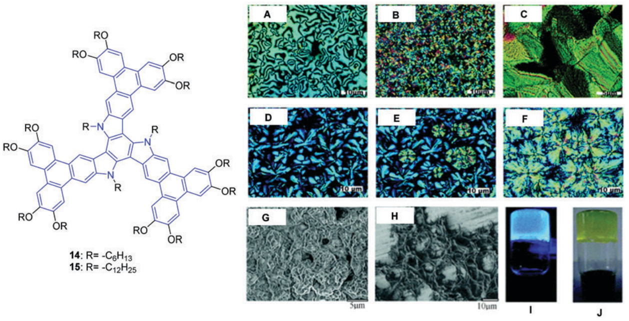


Fig. 9 Chemical structures of star-shaped compounds **14–15**; polarized optical microscopy (POM) images of the drop-cast thin film of: (A) **14** at 115 °C, (B) **14** at 75 °C, (C) **14** at 60 °C, (D) **15** at 95 °C, (E) **15** at 68 °C, and (F) **15** at 63 °C; SEM images of (G) **15** in the xerogel and (H) **15** in thin films prepared by drop-casting a toluene solution onto a copper substrate and the organic gel formed in toluene under (I) a UV lamp (excited with 365 nm light) and (J) natural light.

materials in the liquid crystalline phase can improve their molecular order and facilitate highly ordered columnar superstructures at room temperature. They also found that the long aliphatic alkyl chains in **15** can enhance the intercolumn association, especially in nonpolar hydrocarbon solvents. However, no gelation behaviors were noticed in the shorter aliphatic-chain-substituted **14**. It indicates that the length of peripheral alkyl groups of triazatruxene dominates the self-assembly behaviors of the aggregates. Considering the above possibility of tuning the intermolecular interactions between triazatruxene units by means of adjusting the electronic characteristics of the peripheral substituents or *N*-substituents, the solvent and the length of peripheral alkyl, these studies have provided interesting hints for the design of new triazatruxene-based materials with improved self-assembly properties. By controlling the self-assembled arrays, highly oriented films could also be constructed for the development of molecule-based electronic devices.

Optoelectronic applications of triazatruxenes

OLEDs

Since the pioneering studies of Tang and Van Slyke on OLEDs, significant advances have been achieved. For the devices, multilayer sandwiched structures are generally adopted to govern the different functions of charge injection and transport as well as emission.[11,69,70] Despite remarkable progress, there are several important challenges. One of the greatest challenges is the inferior performance of blue OLEDs to that of green and red ones.[71–73] Typically, as key blue light-emitting chromophores, fluorene and its derivatives have drawn much attention. However, one drawback of fluorene based blue-emitting materials is an occurrence of long wavelength emission after annealing the films in air or long-time operation of OLEDs.[74–77] Unfortunately, the long-wavelength emission owing to the formation of ketone defects or excimers/aggregates prevents fluorene derivatives from being excellent blue emitters. As analogues of fluorene, carbazole units have been regarded as the promising potential candidates for eliminating the contribution of fluorenone to the long wavelength emission with good hole transporting characteristics. Triazatruxene is composed of three overlapping carbazole units annulated by sharing a central benzene unit. Therefore, triazatruxene derivatives are potential interesting blue-emitting materials with good hole transporting properties.

In 2006, Lai *et al.* reported a facile and powerful strategy to achieve a novel series of six-arm monodisperse compounds **8–10** based on triazatruxene and fluorene units, which initiated the application of triazatruxene in OLEDs.[26] With the configuration of ITO/PEDOT:PSS/**10** (spin-cast, 130 nm)/Ba/Al, a single-layer EL device based on **10** achieved highly efficient (2.07 cd A^{-1}, EQE of 2.0%) and pure-deep-blue EL with standard CIE coordinates of (0.15, 0.09) and good color stability, which suggested that this kind of material was considerably promising in achieving high-performance solution processable blue OLEDs. With this work, the more pronounced contribution of fluorenone defects to the long wavelength emission in fluorene-based EL blue materials seems to be approbated to some degree, and these triazatruxene core/oligofluorene branch macromolecules also show the enhanced solid-state luminescence and low-threshold lasing.[25]

Three-arm star-shaped oligofluorene/triazatruxene hybrids **11–13** have also been developed by Lai *et al.*[24] The introduction of kinked arms and triazatruxene not only depressed the aggregation and crystallization of these rigid molecules with decreased symmetry but also tuned the HOMO energy levels for better hole-injection/transport ability. Thus, this strategy provided an effective approach in the design of stable amorphous molecular materials for OLEDs or other organic electronic applications. A **13**-based solution-processed single-layer EL device achieved the best device performance with a rather low turn-on voltage (3.3 V @ 1 cd m^{-2}) and a high device efficiency (EQE 2.16%, 1.56 cd A^{-1} @ 2382 cd m^{-2}) as well as a high brightness (L_{max} 7714 cd m^{-2} with EQE 1.6%) with CIE coordinates of (0.16, 0.15). These results suggest that the triazatruxene with a kinked star-shaped architecture is beneficial for realizing high-performance solution-processed stable blue EL devices.

Apart from the oligofluorene, constructing triazatruxene-based star-shaped molecules with phenylcarbazole branches is an effective method to not only improve the thermal and morphological stabilities but also achieve bifunctional properties of light emission and hole transporting owing to the relatively weak π-donors of phenylcarbazole units. For this purpose, the starburst 9-phenylcarbazole/triazatruxene hybrids **46–47** were synthesized and characterized (Fig. 10).[56] Deep blue emission (λ_{max}, 423–434 nm) was obtained both in solution and as films. Good thermal stability and amorphous properties as well as appropriate HOMO energy levels and large band gaps (3.18–3.26 eV) show that these starburst 9-phenylcarbazole/triazatruxene materials are the promising light-emitting and/or hole-transporting materials as well as host materials for triplet emission. In order to study the impacts of peripheral substituents on optoelectronic properties, Gómez-Lor *et al.* synthesized a series of differently substituted star-shaped

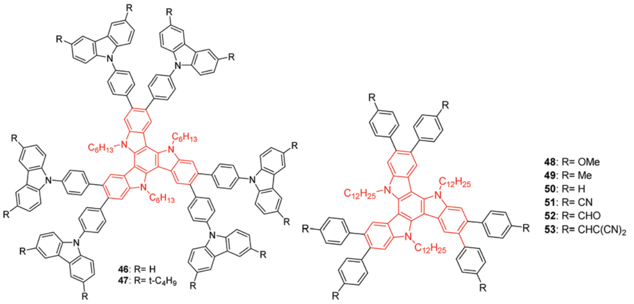


Fig. 10 Chemical structures of star-shaped compounds **46–53**.

hexaaryl-triazatruxenes **48–53** (Fig. 10).[78] In that process, the deep blue emission was unchanged by donor peripheral substituents while an increasing acceptor characteristic produced a reduced optical gap and an increased Stokes shift, eventually leading to the appearance of a new electronic level. In addition, a single-layer OLED was fabricated by solution processing with the structure of ITO/PEDOT:PSS/active layer/Ca/Al. Among all these materials, the most electron-rich derivative **48** with six donor methoxy groups performed the best. As presented in this study, the material not only showed higher emission efficiency in the solid state due to aggregation-induced fluorescence enhancement, but also achieved higher mobility with efficient carrier transport in the whole operating voltage range.

Beyond the star-shaped compounds, Lai and Huang's group also synthesized a family of hyperbranched polymers **54–56** (Fig. 11) based on triazatruxene, which exhibited strong blue emission in both solution and solid states.[50] The photophysical properties of conjugated hyperbranched polymers were found to be strongly dependent on the branching degree. Hyperbranched polymers with a higher branching degree and lower content of linear fluorene units exhibited better photophysical properties, manifesting narrower emission spectra and relatively high quantum efficiency as well as improved thermal spectral stability. This phenomenon can be explained by the fact that the compact and global three-dimensional hyperbranched polymer structure with a higher branching degree is more effective to limit the interchain aggregation and π–π stacking. Hence, the resulting triazatruxene-containing polyfluorenes are attractive active materials for optoelectronic applications, *i.e.* efficient blue EL.

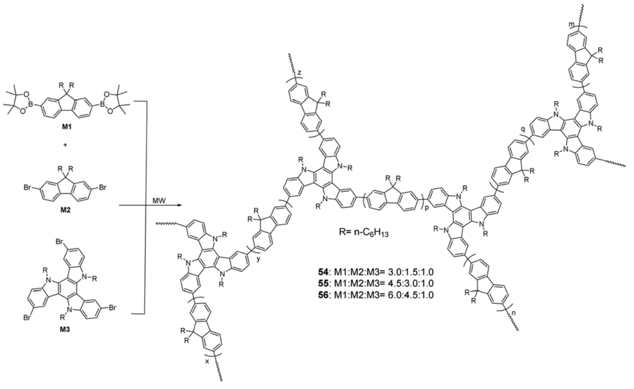


Fig. 11 Synthesis routes towards **54–56**. Conditions: microwave heating, pressurized-vessel, Pd(PPh$_3$)$_4$, THF; (i) 100 °C, 5 min; (ii) 150 °C, 15 min; (iii) phenylboronic acid, 150 °C, 5 min; (iv) bromobenzene, 150 °C, 5 min.

Liquid crystals

Liquid crystals are commonplace in technological devices, such as watches, computer displays, and temperature and pressure monitors. In the meantime, they are central to our technological lifestyles. Classically, liquid crystalline materials are based on a structural motif which could be classified as rod-like and as disc-like. In the last decade, discotic liquid crystals have attracted increasing interest because of their unique self-organization behaviors into columnar structures. Owing to one-dimensional high charge carrier mobilities along the columnar stacks, these materials can be widely employed as conducting layers in organic electronic devices.[79–81]

Triazatruxene, a disk-like molecule with C_3-symmetry, has been recently investigated as a novel building block for the construction of discotic liquid crystals. Manickam *et al.* first proposed the possibility of inducing a discotic mesophase based on a triazatruxene core.[82] Gómez-Lor *et al.* synthesized several hexasubstituted triazatruxene compounds (Fig. 12) from the known symmetrical hexabromotriindole, utilizing Sonogashira coupling reactions as the key step.[19] It was revealed that these compounds had different thermal properties. Compounds **58** and **59** melt into the isotropic liquid without showing any mesomorphism, while compounds **60** and **61** exhibited stable hexagonal columnar mesophases over a wide temperature range. Highly ordered triazatruxene-related liquid crystals **62–68** (Fig. 12) with an extended π-aromatic system were synthesized and achieved using six-fold Suzuki coupling of known *N*-dodecylhexabromotriazatruxene with different boronic acids substituted in *para* with groups of different electronic characteristics.[30,31] Compounds **62–63** and **67–68** melt in the isotropic liquid without forming any mesophase, whereas compounds **64** and **66** substituted with six electron-donating alkoxy chains showed mesomorphism upon heating. Comparison of **64** and **66** showed that the chain length can increase the temperature range of the mesophases. It is indicated that the influence of the peripherally attached groups on the mesomorphic and electronic properties not only provides interesting insights into the intrinsic nature of the interactions involved in mesophase formation in these compounds but also offers a great opportunity to further tune their physical properties. To achieve high charge mobility in

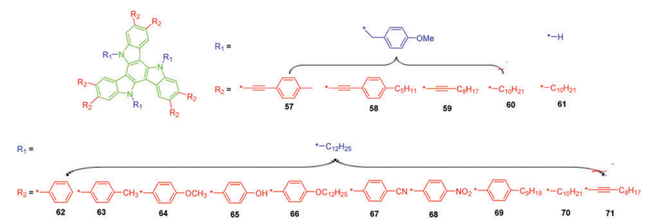


Fig. 12 Chemical structures of hexasubstituted triazatruxene compounds **57–71**.

discotic liquid-crystals, hexasubstituted triazatruxene compounds **69–71** have been synthesized by Gómez-Lor.[31] Their research showed that the carrier mobility mostly depends on the stacking distance between molecules, which usually decreases upon increasing the order. Moreover, the incorporation of alkyne spacers has been identified to efficiently increase the supramolecular order in the discotic mesophases, thus simultaneously reducing the distance between molecules in the stack, and resulting in the discotic liquid crystalline material with the highest hole mobility.

It is well-known that increasing the core size can result in a higher tendency to form mesophases. A series of π-extended discotic liquid crystalline triazatruxenes **72–75** (Fig. 13) were also reported by Gómez-Lor's group.[30] Among these materials, **72** is not a liquid crystal while compounds **73–75** form ordered hexagonal columnar mesophases. Extending the conjugation in these materials and attaching peripheral electron-donor substituents have been found to be highly beneficial for their mesomorphism. Chi *et al.* synthesized a discotic liquid crystal based on oligothiophene fused triazatruxenes **76** using a microwave-assisted Stille cross-coupling reaction. This material with a large core size could possess the strongest π–π interaction in a concentrated solution and show an isotropic temperature at 185 °C.[55] According to the investigation, the expansion of the conjugation upon cyclization of thiophene moieties was beneficial for increasing the transition temperatures and the phase widths of the columnar structures. Based on this idea, two larger π-conjugation discotic liquid crystals **77** and **78** based on the triazatruxene core were constructed using diamine-diketone condensation as the key expansion step with different solubilizing chains attached at the periphery.[83] The resulting discotic molecules showed good thermal stability and columnar liquid crystalline properties. Due to their large π-conjugation structure, they showed a tendency to aggregate and possessed a weak intramolecular charge transfer nature which diminished their fluorescence. Mobilities up to 0.14 $cm^2\ V^{-1}\ s^{-1}$ and 0.69 $cm^2\ V^{-1}\ s^{-1}$ were obtained for **77** and **78**, respectively, hence qualifying them as prominent charge transporting materials.

Organic field-effect transistors (OFETs)

OFETs have drawn intensive attention due to their potential applications in ink-jet printed flexible sensors, logic circuits, radiofrequency identification tags, and displays.[84–86] Therefore, significant efforts have been made toward the development of high performance conjugated semiconductors used as the active layer in OFETs because of their solution-processability and mechanical stability.[87] Organic semiconducting materials are commonly classified as p-type, n-type and bipolar semiconducting materials. Among these, p-type semiconducting materials with high hole mobility have been developed over a decade since most of the semiconducting materials are known to have an excess of π-electrons in nature.

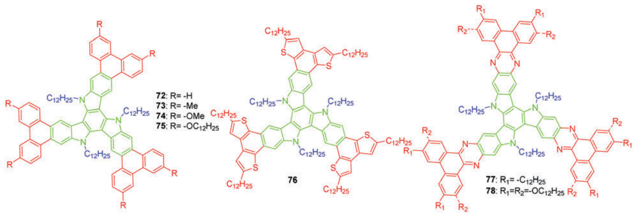


Fig. 13 Chemical structures of π-extended discotic liquid crystalline compounds **69–78**.

Carbazole derivatives have been widely studied as p-type semiconductors due to their electron-donating capabilities. Triazatruxene, as an extended π-system in which three carbazole units share an aromatic ring, shows good hole transporting properties.[64,88] The charge transport properties of triazatruxene derivatives have been reported by SCLC, yielding hole mobility values of about 2.8 $cm^2\ V^{-1}\ s^{-1}$.[66] However, OFETs based on triazatruxene are scarce.[44] Gómez-Lor *et al.* reported OFETs based on *N*-methyltriazatruxene single crystals, achieving the mobility up to 0.4 $cm^2\ V^{-1}\ s^{-1}$.[62] Additionally, they also tried to fabricate uniform transparent films based on *N*-dodecyltriazatruxene oxidized with trifluoroacetic acid (TFA). According to the *I–V* characteristics of the films, they showed much lower mobility compared with single crystals. Charge transport in OFETs based on triazatruxene strongly depended on the molecular order and morphology of the organic semiconductor thin films. Recently, Velasco's group employed *N*-trimethyltriazatruxene as a vacuum-deposited active layer in standard bottom-gate top-contact (BGTC) OFETs.[89] According to the electrical measurements, the mobility increased by enhancing the π-conjugation, which was highly dependent on the extended π-conjugated cores. Mobility up to 10^{-2} $cm^2\ V^{-1}\ s^{-1}$ was achieved with *N*-trimethyltriazatruxene, which presented good air-stability and durability under air conditions, for longer periods of up to 5 months.

Two-photon absorption (TPA) and nonlinear optics (NLO)

TPA is the simultaneous absorption of two photons by a molecule in order to excite a molecule from the ground state to the excited state. A lot of octupolar multibranched derivatives were studied for their TPA properties. The coherent coupling between the branches would significantly increase the TPA cross-section. As a result, triazatruxene could be a good candidate because of its large π-conjugated plane, rich electronic characteristics, and C_3-symmetry.

In the first work based on triarylboryl attached to triazatruxene by an ethenylene or ethynylene linker (Fig. 14), the compounds **79a** and **80a** showed TPA cross-sections of δ = 2100 and 2500 GM (at 810 nm by femtosecond pulses in THF), respectively.[23] Moreover, the TPA cross-sections of 2,7,12-substituted compounds (**79a** and **79b**) are significantly larger than those of their 3,8,13-isomers (**80a** and **80b**). According to the results, the ethenylene π-linker is better than the ethynylene linker, and the 2,7,12-substituted structure is superior to the 3,8,13-isomers.

In 2011, Chi *et al.* reported the synthesis of a series of triazatruxene-based star-shaped octupolar compounds **81–83** (Fig. 15) with intramolecular ''push–pull'' characteristics.[90] These chromophores showed an obvious solvatochromic effect and large Stokes shifts due to the photoinduced intramolecular charge transfer (ICT). They exhibited large TPA cross-sections

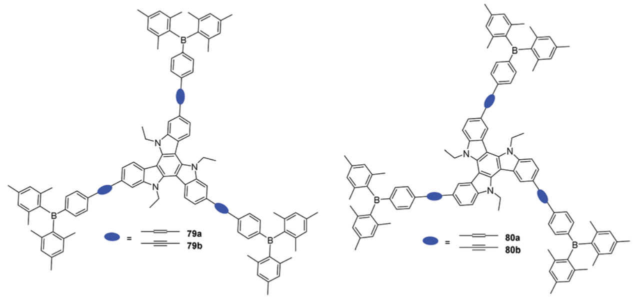


Fig. 14 Chemical structures of star-shaped octupolar compounds **79–80**.

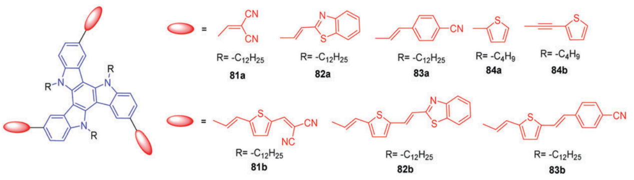


Fig. 15 Chemical structures of star-shaped octupolar compounds **81–84**.

ranging from 280 to 1620 GM in the near-infrared (NIR) region. Compound **83b** showed the largest TPA action cross-section of 564 GM and could be a potential two-photon fluorescent probe. In addition, all the compounds displayed good thermal stability and photostability. Then, Yuan *et al.* reported two similar octupolar triazatruxene molecules (**84a** and **84b**) functionalized with thiophene units.[91] These studies demonstrate that triazatruxene is an excellent central electron-rich donor for constructing octupolar optoelectronic molecules.

Besides TPA, Pérez-Moreno *et al.* reported NLO application based on triazatruxenes with different conjugation lengths and peripheral substituents.[22] They found that the linear optical properties of hexasubstituted triazatruxenes depended slightly on the length of the conjugated system and strongly on the electron-accepting/withdrawing strength of the peripheral groups. The strong wavelength dependence of the first hyperpolarizability values around resonance is clearly shown to be overwhelmed by dispersion effects, which is not determined by the charge-transfer pattern in these octupolar materials. This finding provides insight into independent tuning of the linear absorptive properties, determined by the charge-transfer pattern. Recently, Fang's group also reported NLO application based on C_3-symmetric *N*-phenyltriazatruxene with a remarkable second-NLO intensity, which was 5 times that of KH_2PO_4.[92]

Organic photovoltaics (OPVs)

OPVs are promising cost-effective alternatives to silicon-based solar cells, and possess light-weight, low-cost, and flexibility advantages.[93] As mentioned above, triazatruxene derivatives have high hole mobility, two-photon absorption properties, and a large π-conjugated structure. In addition, electron-donating triazatruxene units provide both a good π–π stacking ability due to the perfectly flat conjugated core, and high solubility because of easy alkylation of the indole moieties. Triazatruxene has been proven to be a well-adapted structure with excellent electron-donating and hole transporting materials for high-efficiency solution-processed bulk heterojunction (BHJ) organic solar cells and DSSCs.

In 2011, Ziessel *et al.* reported three triazatruxene-based D–π–A linear derivatives (**22–24**) which were prepared by a sequence of reactions involving either cross-coupling reactions promoted by Pd complexes or a Knoevenagel reaction, leading to a vinyl linker.[48] Due to the introduction of triazatruxene units, the dyes exhibited large absorption coefficients and achieved ideal PCE in bulk heterojunction solar cells. To further improve the photoelectric conversion efficiency, they further introduced two triazatruxene units into one molecule and designed two triazatruxene-diketopyrrolopyrrole dumbbell-shaped D–π–A–π–D molecules (**16a** and **16b**) for OPVs.[29] In this work, a high PCE of 5.3% was obtained, which was the top value for solution-processed small-molecule BHJ solar cells based on triazatruxenes. Then, they constructed a series of similar dumbbell-shaped molecules (**17–19**).[47] According to the results, the intermolecular π–π packing in the amorphous solid state is mainly influenced by the triazatruxene units bearing bulky side-chains, while the optical properties and energy levels are tuned by the central acceptor. In other words, triazatruxene acts as a structural platform in thin films for pure or blended active layers and the optoelectronic properties are independently driven by the choice of the central core. These materials exhibited 3.5% of PCE, which was among the highest values reported so far for soluble amorphous small molecule based organic photovoltaic devices. To solve the problems of low PCE and poor film-forming properties of small molecules, Bo *et al.* reported two triazatruxene-cored star-shaped molecules **85–86** (Fig. 16).[28] For **85**, the triphenylamine donor unit is on the periphery of the star-shaped molecule and the benzothiadiazole acceptor unit is located at the center of the arm. However, as for **86**, only the acceptor unit is located at the periphery of the star molecule. The BHJ organic solar cells were fabricated with the device structure of ITO/PEDOT:PSS/**85** or **86**:$PC_{71}BM$/LiF/Al. The PCEs of 2.05% and 2.29% were achieved for **85** and **86**, respectively. Due to the relatively wide optical band gaps and high HOMO energy levels, the PCE of triazatruxene based solar cells is still low. To broaden the photo-absorption region and reduce the band gap, Ziessel *et al.* introduced stronger acceptor

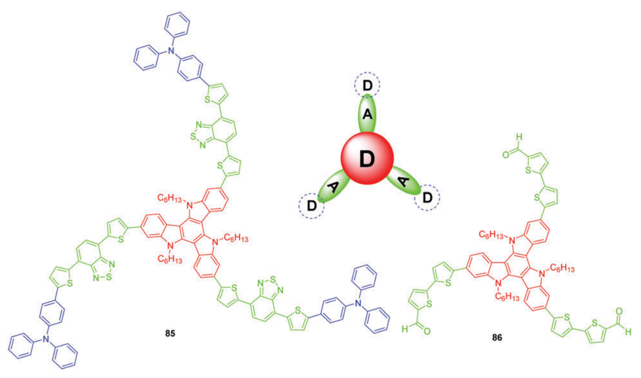


Fig. 16 Chemical structures of star-shaped compounds **85–86**.

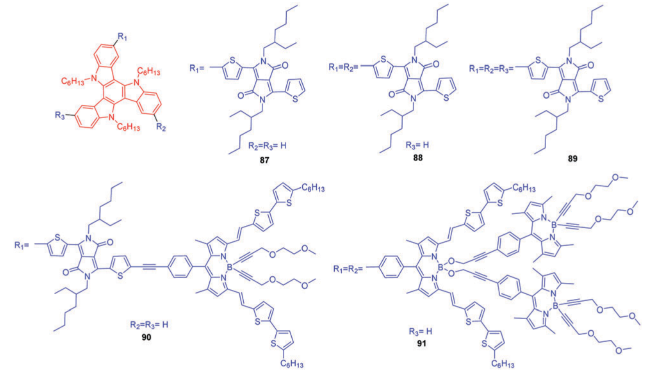


Fig. 17 Chemical structures of the functionalized triazatruxene compounds **87–91**.

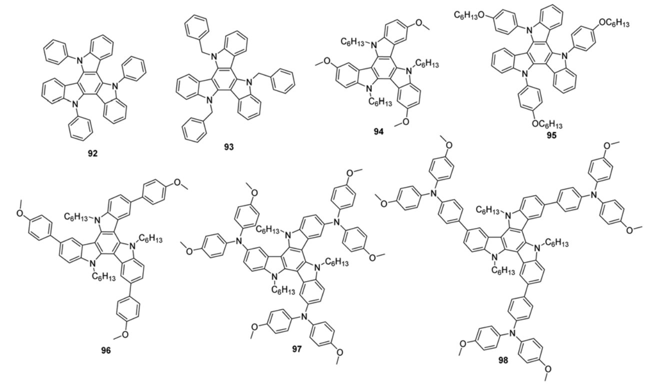


Fig. 18 Chemical structures of the triazatruxene-based hole-transporting materials **92–98**.

units such as diketopyrrolopyrrole and boron dipyrromethene into the triazatruxene core and reported a series of panchromatic absorbing chromophores **87–91** (Fig. 17).[94] All the dyes displayed strong and wide absorption in the near-UV and visible region of the solar spectra (400–750 nm), with intramolecular cascade energy transfer enabling photon concentration and fluorescence at approximately 740 nm.

Besides BHJ organic solar cells, DSSCs are also an important application in organic photovoltaics. For DSSCs, the main parameters that control the sensitizer efficacy are its strong absorption over the visible spectrum, a profitable mutual arrangement of both the donating and accepting groups to optimize the electronic transfer from the donor to the acceptor. Finally, the capacity of the sensitizer was adsorbed at the surface of the TiO_2 electrode. Interestingly, bulkiness and rigidity of the triazatruxene core could efficiently prevent molecular aggregation of most of the materials studied in DSSCs, since the ultimate power output of the solar cells is intimately correlated with the control of the molecular organization at the nanoscale. Zhu *et al.* synthesized a class of D–π–A type dyes (**25–27**) consisting of a triazatruxene moiety as the electron donor, thiophene, furan, and benzene acting as π-conjugated linkers and 2-cyanoacylic acid acting as the electron acceptor.[65] The solar cell based on **25** showed the highest PCE of 6.10%, with a short-circuit photocurrent density (J_{sc}) of 14.7 mA cm^{-2}, an open-circuit photovoltage (V_{oc}) of 670 mV, and a fill factor (FF) of 0.62 under standard conditions. It is indicated that the triazatruxene-based sensitizer can produce high photocurrent density and is a promising candidate for DSSCs. Recently, they reported two similar triazatruxene-based D–π–A type dyes **28** and **29** with a rhodamine acceptor linked by thiophene and benzene conjugations, respectively.[49] Among them, the dye bridged by benzene exhibited better light-harvesting ability, more efficient electron injection ability, and higher PCE.

Of particular interest in the field of OPVs is the development of triazatruxene-based photoactive materials. More recently, hole-transporting materials have attracted great attention due to the need for highly efficient and stable OPVs. In 2012, Ma *et al.* reported two p-type triazatruxene derivatives, triazatruxene and *N*-trimethyltriazatruxene, as solution processable hole transporting materials for use in OPVs with bilayer and inverted structures.[95] They both showed excellent hole extracting and transporting as well as electron blocking capabilities. The PCE of the devices with the hole transporting layer (HTL) increased from 0.16 to 0.71% for triazatruxene and 0.87% for *N*-trimethyltriazatruxene, respectively. Kwon *et al.* reported two hole-extraction materials **92** and **93** (Fig. 18), for their application in OPVs.[96] These materials acted as the hole-extraction layer (HEL) in the organic solar cells, increasing both V_{oc} and J_{sc}. More importantly, the SubPc (subphthalocyanine chloride)/C60 and SubNc (subnaphthalocyanine chloride)/C60 OPVs with a **93** HEL showed impressive 35.9% and 29.1% improvements in PCE compared to reference devices. Recently, Zheng *et al.* also applied the molecule **93** as an exciton blocking layer (EBL) for improving the performance of PHJ cells.[97] The PCE of the organic solar device based on **93** as an EBL increased from 1.25% to 1.70%, indicating its great promise as an EBL.

In the most recent years, a breakthrough in PCE has been achieved by replacing traditional dyes with organic–inorganic hybrid perovskite. Triazatruxene-based compounds as HTLs can also be applied in highly efficient perovskite solar cells. Ahmad *et al.* reported two solution-processable triazatruxene-based hole transporting materials **94** and **95** exploited in perovskite based solar cells.[98] Their HOMO–LUMO energy levels were well aligned with respect to perovskite energy levels. They found that the PCEs were 8.6% and 9.8% for **94** and **95** as HTLs, respectively, which were higher than that of the traditional hole transporting material Spiro-OMeTAD ever reported. Subsequently, they further optimized the structure and synthesized a class of new hole transporting materials **96–98**, comprising a triazatruxene core and electron-rich methoxy-engineered side arms.[99] A remarkable PCE of over 18% was observed for **96** with a compositive perovskite absorber, demonstrating the potential of triazatruxene-based materials as HTLs for highly efficient perovskite solar cells.

Fluorescent sensors

Recently, triazatruxene has been revisited in the context of developing new fluorescent sensors. Fluorescent sensors are a powerful tool for the detection of molecular entities in live cells or the recognition of chemicals such as gas or ions. As a first

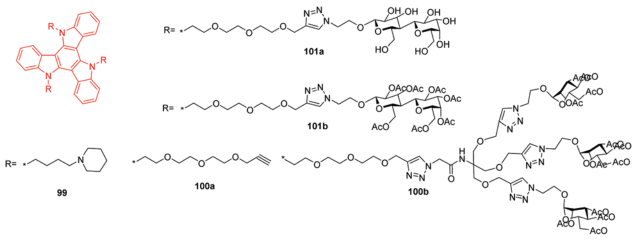


Fig. 19 Chemical structures of the triazatruxene-based fluorescent sensor materials **99–101**.

example of molecular probe **99** (Fig. 19) developed with triazatruxene, water-soluble sensors were specifically designed and prepared for the detection of G-quadruplex ligands.[16] The experimental and computational results showed that fluorescent sensor **99** can preferably recognize parallel G-quadruplex structures by end-stacking.[33] Subsequently, Li's group synthesized a series of triazatruxene-based compounds **100** as fluorescent sensors for concanavalin A.[100] They reported that the multivalent mannose-modified triazatruxenes exhibited specific binding with concanavalin A, but no binding to peanut agglutinin lectin or bovine serum albumin was observed. Fluorescent sensor **100b** readily dissolved in aqueous solution without aggregation and displayed strong fluorescence that was responsive to concanavalin A. Furthermore, the inhibitory ability of **100b** against ORN178-induced haemagglutination was also investigated, manifesting its selective binding with ORN178. Later, their group reported the lactose-functionalized triazatruxene derivatives **101**, which exhibited fluorescence quenching properties upon binding to peanut agglutinin (PNA) lectin.[101] Furthermore, **101a** exhibited a good selectivity for PNA and the concentration-dependent quenching upon binding to PNA was found with a Stern–Volmer quenching constant of 5.8×10^5 mol^{-1} L.

In 2012, Jiang *et al.* reported triazatruxene-based conjugated microporous polymers **102** (Fig. 20) as fluorescent sensors.[52] The fluorescent sensor **102** showed enhanced detection sensitivity and allowed for the rapid detection of arenes upon exposure to their vapors. It displayed prominent fluorescence enhancement in the presence of electron-rich arene vapors and drastic fluorescence quenching in the presence of electron-deficient arene vapors. In addition, the conjugated network facilitated exciton migration over the skeleton, the large surface area of the skeleton broadened the interface between the conjugated microporous polymers and the arene, and the micropores confined the arene molecules. These characteristics are inherent and endow **102** with a rapid response time and high sensitivity. Recently, Zheng *et al.* reported two triazatruxene based covalent organic frameworks (COFs) with a regular honeycomb lattice, **103** and **104**.[102] **103** also showed a rapid fluorescence-on and fluorescence-off nature towards electron rich and deficient arene vapors, respectively. After being exposed to electron-rich arene vapors, the enhanced fluorescence intensity can be recovered to normal levels after 5 min in an ambient atmosphere.

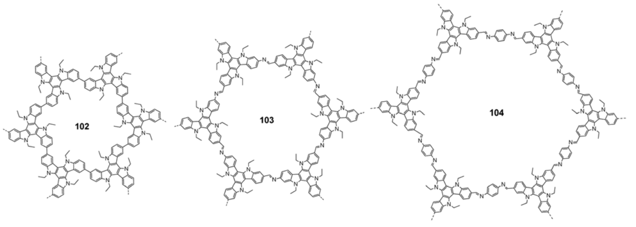
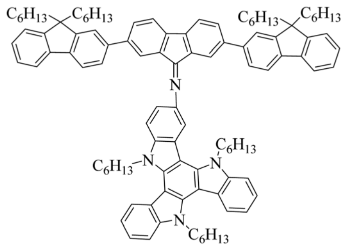


Fig. 20 Chemical structures of the triazatruxene-based fluorescent sensor materials **102–104**.



105

Fig. 21 Chemical structures of the triazatruxene-based fluorescent sensor materials **105**.

Recently, Lai's group designed a T-shaped Schiff-base triazatruxene derivative **105** which was the first report on triazatruxene-based fluorescent probes to detect HCl gas (Fig. 21).[103] The remarkable color change of **105** with turn-on behaviors in the presence of a trace amount of HCl gas was obviously observed by the naked eye. This study has opened up a new strategy to develop simple and sensitive fluorescent sensors for practical sensing applications.

Conclusions and perspectives

In this review, recent work on the synthesis, self-assembly properties and application of triazatruxene-based materials has been summarized. Due to the planar and C_3-symmetric structure of triazatruxene, a large quantity of star-shaped, dumbbell-shaped and D–π–A linear molecules have been synthesized, exhibiting good properties as organic semiconductors in optoelectronic devices or fluorescent sensors, and so on. The development of organic functional materials is advancing rapidly. Molecular design has led to remarkable advances in the creation of various organic semiconductors with diverse structures and properties. Triazatruxene, one of the giant polycyclic aromatic units, undoubtedly opens the door to develop high-performance semiconductors using new synthetic methods and new π-conjugated building blocks.

On the other hand, as we mentioned above, most triazatruxene derivatives are amorphous rather than crystalline in the solid state, which indicates that intermolecular packing is not ordered owing to the steric hindrance of alkyl or aryl chains and other groups at the N5, N10, and N15 positions. In this way, a relatively low performance is obtained in organic electronic devices such as OFETs and OPVs. As a consequence, the rational design of the molecular structure and the fine-tuned modulation of intermolecular interactions are indispensable, especially the latter, exerting a significant effect on the self-assembly behaviors, charge transporting properties, and further device performance. With continuing efforts to unravel the structure–property relationships that shed light on better understanding the rational chemical structure design towards high-performance functions, we look forward to achieving remarkable developments based on triazatruxenes in the coming near future.

Acknowledgements

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