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FEATURE ARTICLE

Triazole: a unique building block for the construction of functional materials**Michal Juriček, Paul H. J. Kouwer and Alan E. Rowan****Received 4th February 2011, Accepted 14th April 2011*

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Over the past 50 years, numerous roads towards carbon-based materials have been explored, all of them being paved using mainly one functional group as the brick: acetylene. The acetylene group, or the carbon–carbon triple bond, is one of the oldest and simplest functional groups in chemistry, and although not present in any of the naturally occurring carbon allotropes, it is an essential tool to access their synthetic carbon-rich family. In general, two strategies towards the synthesis of π -conjugated carbon-rich structures can be employed: (a) either the acetylene group serves as a *building block* to access acetylene-derived structures or (b) it serves as a *synthetic tool* to provide other, usually benzenoid, structures. The recently discovered copper-catalysed azide–alkyne cycloaddition (CuAAC) reaction, however, represents a new powerful alternative: it transforms the acetylene group into a five-membered heteroaromatic 1*H*-1,2,3-triazole (triazole) ring and this gives rise to new opportunities. Compared with all-carbon aromatic non-functional rings, the triazole ring possesses three nitrogen atoms and, thus, can serve as a ligand to coordinate metals, or as a hydrogen bond acceptor and donor. This Feature Article summarises examples of using the triazole ring to construct *conjugation*- and/or *function*-related heteroaromatic materials, such as tuneable multichromophoric covalent ensembles, macrocyclic receptors or responsive foldamers. These recent examples, which open a new sub-field within organic materials, started to appear only few years ago and represent “a few more bricks” on the road to carbon-rich functional materials.

Introduction

There is no doubt that, since the first experimental evidence for the formation of buckminsterfullerene (C₆₀) in 1985,¹ all-carbon and carbon-rich π -conjugated structures have

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relationship between the molecular structure and function of organic materials and their synthesis.

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attracted and inspired scientists more than any other class of compounds.² Owing to their ability to self-assemble by means of π - π interactions and unique electronic properties, carbon-rich materials, both natural and synthetic, have shown their great potential in applications varying from simple dyes to functional devices. To this end, three Nobel Prizes have been awarded for the discoveries of carbon-based functional materials: fullerenes (1996), conductive polymers (2000) and graphene (2010); and each of them has, at the time of the discovery, triggered a new carbon revolution. In parallel, scientists became fascinated with the design and synthesis of new carbon allotropes and their carbon-rich analogues, and over the past decades, numerous approaches towards carbon-based materials have been developed. Among these, substructures of two-dimensional graphene,³ graphyne and graphdiyne^{4,5} have received the most attention (Scheme 1). One functional group, more than any other, however, played a role of the carbon brick that paved the road towards carbon-based materials.

Acetylene as a unique synthetic tool

The acetylene group, or the carbon-carbon triple bond, is one of the oldest and simplest functional groups in chemistry and a ubiquitous structural feature of both natural and synthetic organic molecules.⁶ Its rigid and π -conjugated structure makes the acetylene group an outstanding candidate for the construction of unsaturated molecular scaffolds. Although not present in any of the naturally occurring carbon allotropes, it is an essential tool to access their synthetic carbon-rich family. Furthermore, its unsaturated, high-energy structure makes the carbon-carbon triple bond a very attractive functional group for further postmodification by numerous synthetic transformations.

In general, two strategies towards the synthesis of π -conjugated carbon-rich structures can be employed using the acetylene group: (a) as a building block or (b) as a synthetic tool. In the former case, the carbon-carbon triple bond is integrated in the π -conjugated system; in the latter case, it is employed and subsequently postmodified to provide other, usually benzenoid, π -conjugated structures. The most powerful transformations, widely used in both strategies, are schematically summarised in Scheme 1 using the cutouts of graphyne, graphdiyne and graphene.

The main tools for the construction of acetylene-derived π -conjugated structures are the Sonogashira cross-coupling reaction^{7,8} (violet), alkyne metathesis⁹ (blue), and the Glaser and Cadiot-Chodkiewicz reactions¹⁰ (green): methods that are widely used in the synthesis of oligomeric, polymeric and cyclic cutouts of graphyne and graphdiyne.^{4,5} The Diels-Alder and cyclotrimerisation reactions³ (orange), belonging to the pool of cycloaddition reactions, together with the Bergman cyclisation reaction¹¹⁻¹³ (red) represent the main tools for the construction of benzenoid cutouts of graphene, such as polycyclic aromatic hydrocarbons (PAHs).¹⁴

Huisgen cycloaddition reaction

In addition to the above mentioned synthetic tools employing acetylene to construct rigid, π -conjugated structures, the [3 + 2] cycloaddition of alkynes represents an alternative class of potentially useful reactions. In particular, the Huisgen 1,3-dipolar cycloaddition with azides, leading to di- or trisubstituted 1*H*-1,2,3-triazoles (simply referred to as triazoles), is of special interest (Scheme 2).¹⁵

Analogous to [4 + 2] and [2 + 2 + 2] cycloadditions of alkynes which result in the formation of the aromatic, six-membered benzene ring (Scheme 1, orange), the azide-alkyne cycloaddition (AAC) reaction results in the formation of the heteroaromatic, five-membered triazole ring. Compared with benzene and other all-carbon aromatic cycles, however, the triazole ring provides, besides the π -conjugated character, an additional function: as a result of its coordinating and hydrogen-bond-accepting/-donating abilities, it can serve as a unique *functional building block*.

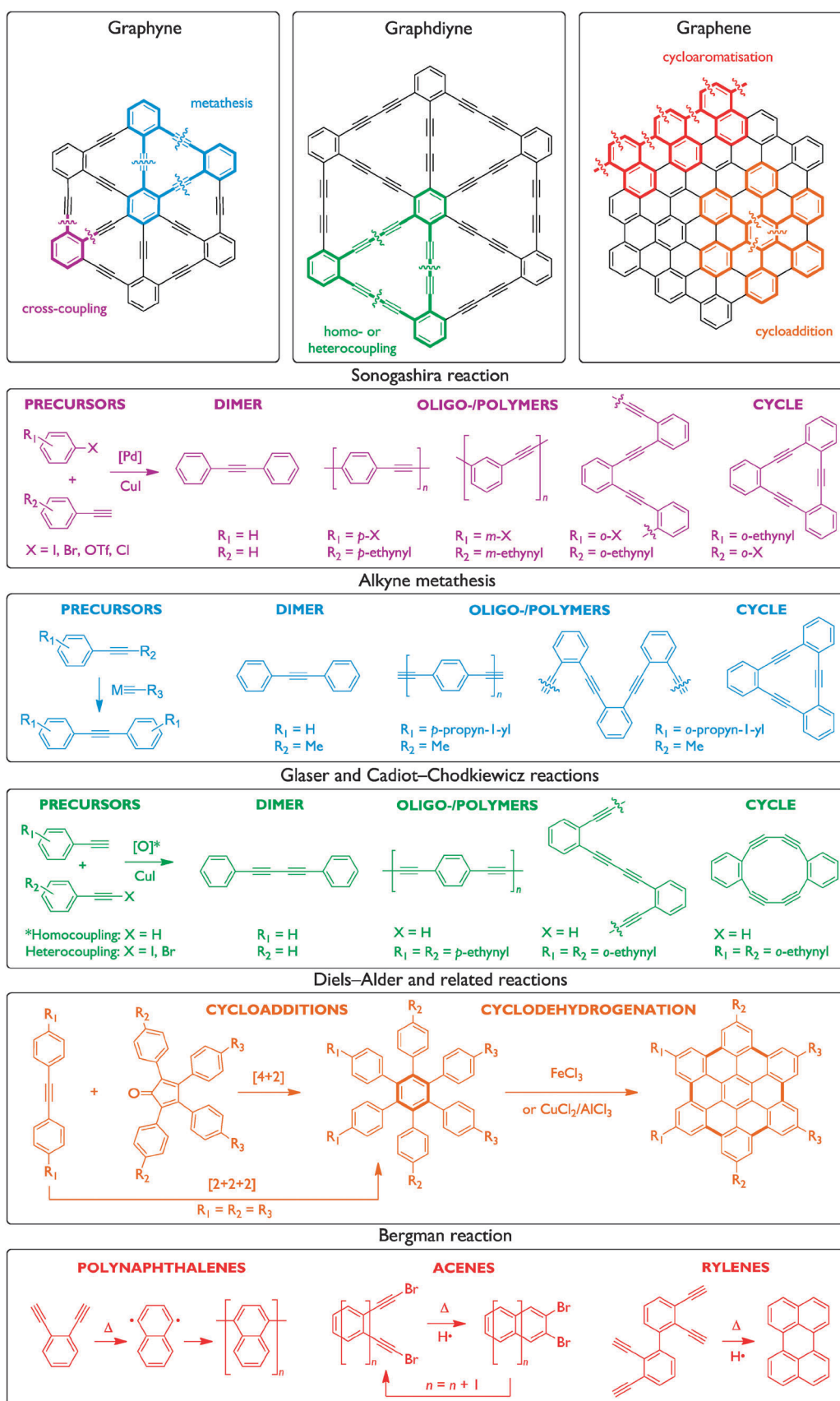
The thermal AAC reaction (Scheme 2, violet) has been known for more than a century, the first example, employing azidobenzene and diethyl but-2-ynedioate, being reported by Michael in 1893.¹⁶ The thorough investigation of this reaction by Huisgen and coworkers,¹⁷ however, was not carried out until six decades later, in the 1950s–1970s, while studying the larger family of 1,3-dipolar cycloaddition reactions.¹⁸ Although the AAC reaction is highly exothermic, its high activation barrier results in exceedingly low reaction rates for unactivated reactants even at elevated temperature.¹⁹ Furthermore, a mixture of two regioisomers **1** and **2** is usually formed when an unsymmetrically substituted alkyne is employed.

It was not until 2002, when the number of publications dealing with utilisation of the AAC reaction rapidly increased.²⁰⁻²² The introduction of the copper(i) catalyst, independently discovered by Tornøe/Christensen/Meldal²³ and Rostovtsev/Green/Fokin/Sharpless,²⁴ led to major improvements in both rate and regioselectivity of the copper-catalysed azide-alkyne cycloaddition (CuAAC) reaction (blue). The use of a copper(i) catalyst drastically changes the reaction mechanism (orange) and results in the exclusive formation of the 1,4-disubstituted product **2**. Although the precise nature of the reactive alkynyl copper species is not completely understood,²⁵ it is clear that copper acetylide species **5** are formed and these are the productive components of the reaction mechanism.²⁶ As a result, the CuAAC reaction is restricted to terminal acetylenes.

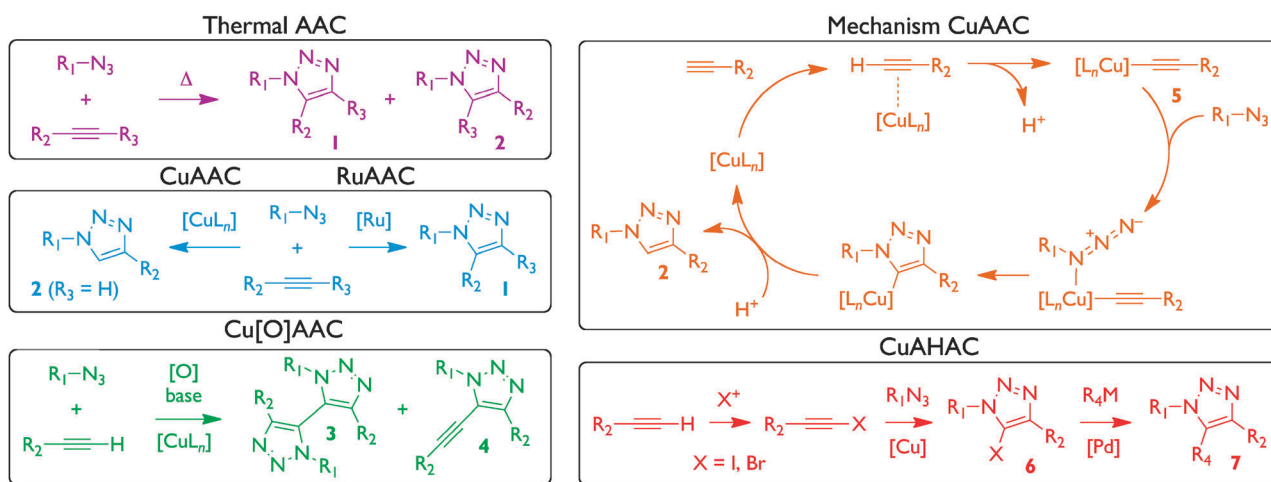


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Scheme 1 Acetylene transformations leading to π -conjugated structures employing acetylene: (a) as a building block (violet, blue and green) and (b) as a synthetic tool (orange and red).



Scheme 2 Variations of the Huisgen 1,3-dipolar azide-alkyne cycloaddition (AAC) reaction ([CuL_n] denotes either a single-metal centre CuL_n or an oligonuclear cluster Cu_xL_n).

Compared with the thermal AAC process, the rate of the CuAAC reaction is increased by a factor of 10^7 making it conveniently fast at and below room temperature. The reaction is not significantly affected by most organic and inorganic functional groups, nor steric or electronic factors, and proceeds in many protic and aprotic solvents, including water. Moreover, CuAAC reactions are easy to perform and give rise to their intended products in very high yields with little or no side products.²⁶ As such, the CuAAC reaction meets all criteria of “click chemistry”, a term defined by Sharpless in 2001 for the reactions that are “modular, wide in scope, give very high yields, generate only inoffensive byproducts...” and are “stereospecific (but not necessarily enantioselective).”²⁷

Other metals known to catalyse various acetylenic transformations (among others Ag(I), Pd(0/II), Pt(III), Au(I/III) and Hg(II)) have so far not yielded effective catalysts for the conversion of azides and terminal alkynes to 1,4-disubstituted triazoles.²⁶ In 2005, ruthenium cyclopentadienyl complexes, however, were found to catalyse the formation of the complementary 1,5-di- ($R_3 = H$) and 1,4,5-trisubstituted triazoles **1** from azides and, both terminal and internal alkynes, respectively.²⁸ While the scope and functional group tolerance of the RuAAC reaction (blue) are excellent, the reaction is more sensitive to the solvents and the steric demands of the azide substituents than the CuAAC reaction.²⁹

In parallel to these developments, several synthetic variations of the CuAAC reaction, leading to 1,4,5-trisubstituted triazole derivatives, have been developed (Scheme 2). These include the oxidative copper-catalysed azide-alkyne cycloaddition (Cu[O]AAC) reaction³⁰ leading to **3** and **4** (green) and the copper-catalysed azide-haloalkyne cycloaddition (CuAHAC) reaction³¹ leading to **6** (red). In all cases, the reaction conditions were optimised and the desired products were obtained in excellent to quantitative yields. Following this approach, multi-step one pot procedures are feasible. For instance, three-step reaction, including the iodoacetylene formation, CuAHAC and cross-coupling reactions, leading to **7** can be carried out in high yields.^{32,33} In addition, various

1,4,5-trisubstituted triazole derivatives (**7**) were prepared by substitution of the hydrogen atom in the 5-position of the triazole moiety that was formed *via* the standard CuAAC reaction; these methods have recently been reviewed.³⁴

Triazole-derived materials

“There is more function to the 1,2,3-triazole unit than first meets the eye.”³⁵

Since its discovery, the CuAAC reaction has found numerous applications, varying from traditional organic synthesis to advanced materials.^{20–22} Advantageous properties, such as high chemical stability, strong dipole moment, heteroaromatic character and hydrogen-bond-accepting/-donating ability,³⁶ enable the triazole ring to interact productively in several ways with (biological) molecules, organic and inorganic surfaces and materials. For example, triazole can serve as a unique hydrolytically-stable replacement for the amide bond.³⁷ Since this Feature Article highlights recent results on functional triazole-derived materials, it is not intended to cover all work on CuAAC reactions, which has shown a substantial growth over the past decade.

From the perspective of making oligo-/polymeric (1D) and dendrimeric (2D and 3D) networks using the CuAAC reaction, numerous studies have been published.^{38–41} In all these examples, however, the triazole moiety was used only as a covalent linkage and the formed macromolecular structures comprised mainly of aliphatic subunits. Additionally, the ability of the triazole moiety to coordinate metals and serve as a ligand or cationic receptor was also demonstrated.^{42–49} Yet, studies where the CuAAC reaction would be employed as a synthetic tool towards the preparation of extended π -conjugated carbon-rich hetero-structures have only started to appear few years ago.^{35,50–68} Among these, several unique examples, employing the triazole unit as a functional building block in responsive materials, are present. These are based either on cation-N(triazole)^{52,61,63} (coordination) or, hydrogen-N(triazole)⁶³ and anion-H(triazole)^{35,57–59,62} (hydrogen bonding) interactions. The properties resulting from the conjugation- and function-related characteristics of

the triazole group in π -conjugated materials available to this date are briefly discussed in the following sections.

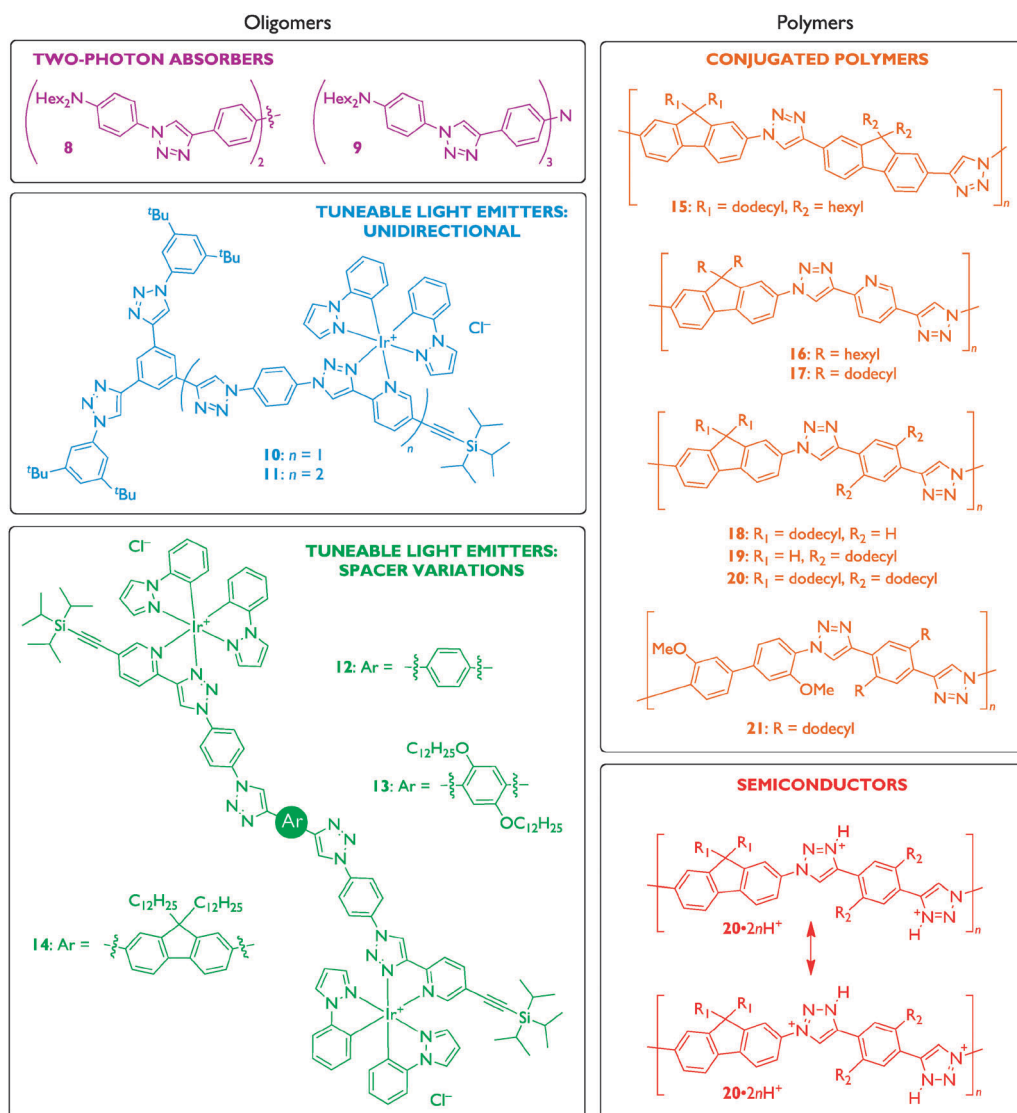
Conjugation-related triazole-derived materials

The triazole moiety is a nitrogen-rich, strongly electron-deficient heterocycle. Although according to molecular modelling⁶⁵ and X-ray crystallography⁶⁹ the triazole moiety is known to be flat, several independent studies^{50,53,55,65–67} indicate that the conjugation in triazole-derived hetero-aromatic structures is not extended through the triazole moiety (or sometimes postulated as through the formally sp^3 hybridised nitrogen atom (N-1) of triazole).⁵⁶ As a consequence, the CuAAC approach represents an efficient tool to link various (hetero-)aromatic/chromophoric units into a covalent ensemble, leading to materials with interesting properties (Scheme 3).

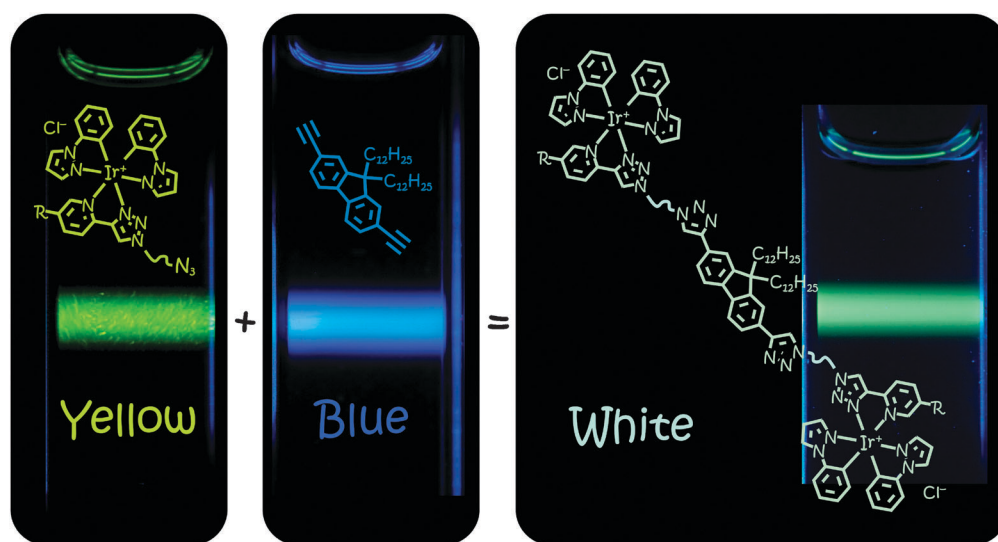
In oligomeric push–pull systems **8** and **9** (violet), the triazole linkers play an important role as both non-conjugating connectors and electron-withdrawing units favouring charge

separation (CS).⁶⁷ As a result, full transparency and significant two-photon absorption in the visible region are combined in these chromophores. The fast formation of the CS excited state, which strongly absorbs in the visible region and has a lifetime of several nanoseconds, is of interest for optical limiting applications.

The studies of the photophysical properties of triazole-derived multi-chromophoric oligomers **10–14**⁵⁰ (blue and green) and polymers **15–21**^{65,66} (orange) revealed that the optical properties are independent of molecular weight, *i.e.*, there is only poor electron or energy transport (through triazole) between the chromophoric units which retained their individual properties. In the first case, a series of hetero-aromatic triazole–pyridine-derived ligands and their luminescent iridium(III) complexes **10–14**, bearing two additional cyclometalating ligands, were synthesised and studied. These studies revealed that the photophysical properties of **10–14** were not significantly altered by changes within the structure: the number of iridium centres (blue) and the spacer properties



Scheme 3 Conjugation-related representative examples of triazole-derived oligomeric (**8–14**) and polymeric (**15–21**) structures as potential materials for organic optoelectronics.



Scheme 4 White-like emission of **14** containing both iridium (yellow emission) and fluorene (blue emission) chromophores, as observed by a naked eye.

(green). Accordingly, very little interaction (through space or through the backbone) between the iridium centres within one molecule was observed, indicating that each iridium centre retained its individual properties. The results show that this approach can be generally applied towards covalently linked multichromophoric systems with potential application, for instance, in the design and preparation of tuneable light emitters. As a demonstration of this concept (Scheme 4), a single molecule white-light emitter **14** was constructed from two iridium centres (yellow emission) and a fluorene unit (blue emission).⁵⁰

Quantum mechanical calculations on two model compounds, based on 1,4-diphenyl-1*H*-1,2,3-triazole, indicated that the conjugation in these systems is interrupted due to a distinct location of the frontier molecular orbitals (FMOs) on different parts of the molecule; the HOMO is predominantly located on the former alkyne part and the LUMO is located on the former azide part of the cycloadduct. Protonation in the 3-position of the triazole group in **20** (Scheme 3, red) resulted in the decrease of the HOMO–LUMO gap and more delocalised FMOs as indicated by a red shift of the emission maximum and a broader and less structured emission profile.⁶⁵ The use of electron-donating bisalkyne and electron-withdrawing bisazide precursors is expected to further lower the band gap of the oligo-/polymers, which then become of interest as potential organic semiconductors.

Other studies concerning the conjugation-related characteristics of the triazole unit include the modulation of the fluorescence emission upon clicking⁶⁸ or metal coordination⁶⁰ and the construction of push–pull systems employing triazole as a π -conjugated linker.⁵⁶ The interruption of conjugation in the latter case has a positive effect: the longest wavelength charge-transfer absorptions are found for systems with inefficient ground-state donor–acceptor conjugation.

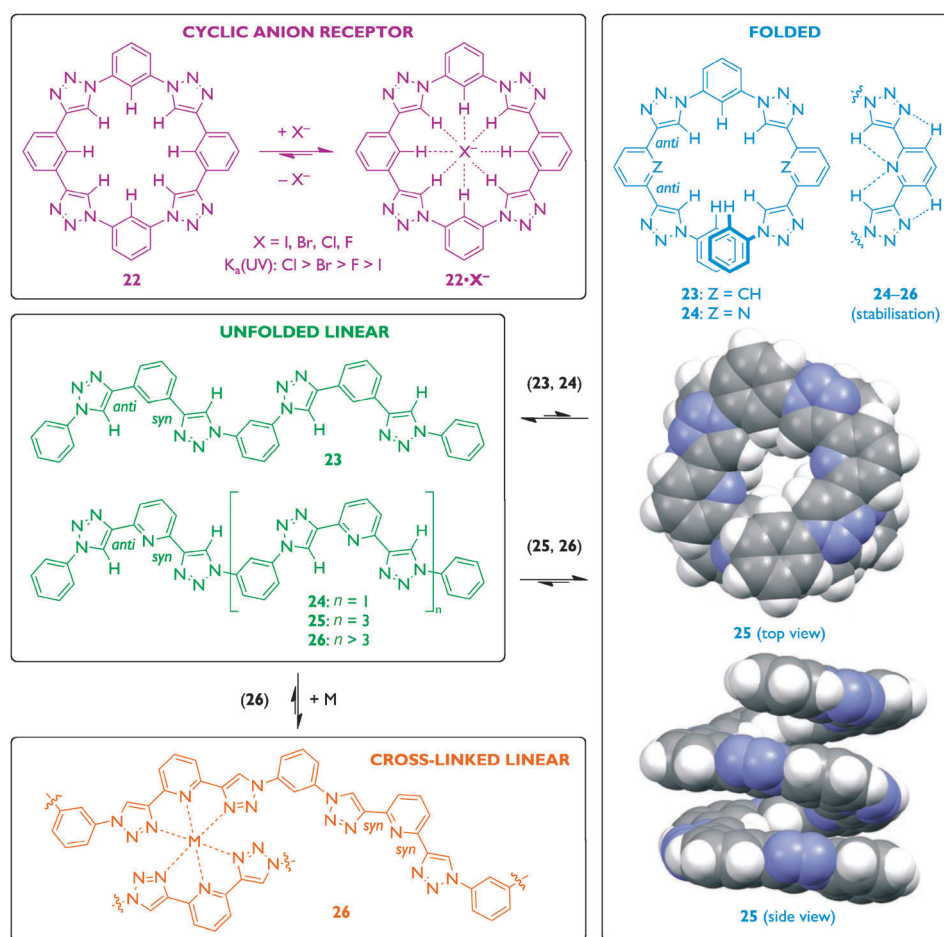
Function-related triazole-derived materials

In addition to its heteroaromatic character, the function-related properties of the triazole unit have also been studied

and, to this date, several examples of unique triazole-derived functional materials have been described.^{54,57–59,61–63} In this concept, the term “function” designates the coordination and hydrogen-bond-accepting ability of the nitrogen atoms in the 2- or 3-positions, and the hydrogen-bond-donating ability of the hydrogen atom in the 5-position. While the ability of triazole to serve as a ligand or hydrogen-bond acceptor is not unusual, the C–H hydrogen-bond-donating ability has emerged as a new non-covalent binding motif. The polarised character of the C–H bond originates from the presence of three electronegative nitrogen atoms, localised in the ring. As a result, a large dipole moment of approximately 5 D is generated and its axis is almost co-linear with the C–H bond. Accordingly, the triazole’s anion- and cation-affinities are reinforced by the ion–dipole interactions.³⁵

Illustrative examples of the triazole-derived functional materials that are available to this end, **22–29**, and which can bind anions, cations or both, are depicted in Schemes 5 and 6, and Fig. 1. Conjugation-related materials **10–14**, described in the previous section (Scheme 3), also fit into this category: the triazole group serves as a functional building block that coordinates to iridium(III). In the case of **22–26**, the heteroaromatic character of these molecules is responsible for their size- and shape-persistent structures, which is important for achieving strong host–guest binding. Moreover, the other introduced (hetero-)aromatic moieties can serve as additional hydrogen-bond acceptors (pyridine) and donors (benzene) to further increase the binding affinities of the host.

The first type of triazole-derived materials described in the literature can be represented by one of the two structural motifs: macrocyclic triazolophane **22** or linear foldamers **23–26** (Scheme 5; the side chains are omitted for clarity). In both of these structures, the triazole-1,4-diyl units are connected through the 1,3-phenylene or pyridine-2,6-diyl spacers which can adopt three different conformations: *anti–anti*, *anti–syn* and *syn–syn*. While in **22**, all spacers are restricted to adopt the *anti–anti* conformation (violet), in **23–26**, all three conformations (and their combinations) are



Scheme 5 Function-related representative examples of triazole-derived structures: cyclic anion receptor **22** and linear anion-/cation-responsive foldamers **23–26**; side chains are omitted for clarity.

possible. In the case when all spacers adopt the *anti-anti* conformation, **23–26** have helically folded structures (blue); in all other cases, their structures are unfolded (green and orange). When pyridine-2,6-diyl spacers are employed (**24–26**), the *anti-anti* conformation is preferred to the other two, due to hydrogen-bond stabilisation as depicted in Scheme 5 (blue).⁶³ Additionally, the folded structures of **25** and **26**, which display two or more complete turns, are further stabilised by a significant number of π - π stacking contacts.⁵⁸

The majority of the binding affinity in the case of cyclic receptor **22** arises from the pre-organised structure, in which the polarised triazole C–H bonds and the positive ends of the triazole dipoles point towards the centre of the cavity. As a consequence, **22** shows a strong binding affinity towards all halide anions (violet).⁵⁷ What is remarkable, however, is that this association occurs solely with the use of C–H...X hydrogen bonds and arises from within a neutral receptor. Both triazole and phenylene C–H bonds take part in the binding process and the following order of the C–H hydrogen-bond donor strengths was observed: triazole > N-linked phenylene > C-linked phenylene. Moreover, each electron-donating group weakens the anion-binding-affinity and this effect is bigger when the substituent is localised on the phenylene unit linked to the triazole through the nitrogen

atom. The binding of the halides is size-selective; the Cl^- and Br^- anions bind inside the cavity stronger than the too-small F^- and the too-large I^- anions, by 1.5 and almost 3 orders of magnitude, respectively. A remarkably large binding constant was observed for the Cl^- ion ($\sim 10^7 \text{ M}^{-1}$) in non-polar solvents, when each of the four benzene rings in **22** was equipped with a *tert*-butyl substituent.

In contrast to **22**, the analogous open-chain oligomer **23** preferably adopts unfolded conformations, which are in equilibria. The folded conformation, however, is strongly preferred in the presence of anion templates. As a result of this conformational change, the triazole protons and the protons in the 2-position of the 1,3-phenylene moiety are projected inwards, with the two terminal phenyl rings overlapping to generate a folded structure similar to that of triazolophane **22** (blue).^{57,59} Compared with cyclic **22**, the size selectivity is shifted in favour of the larger Br^- and I^- halides over Cl^- and the anion-binding-affinities of **23** are much-reduced, emphasising the extreme importance of pre-organisation.

In an additional study, an unprecedented behaviour of triazole-pyridine-derived responsive foldamer **25** was observed.⁵⁸ In polar solvent systems, the unfolded structure of oligomeric **25** (green) adopted an enantiomerically enriched helical conformation (blue) when equipped with chiral

oligo(ethyleneglycol) side chains. It was shown that the stabilisation of the helix by π - π stacking played an important role in this process; for example, the same experiments, performed on shorter oligomer **24**, indicated only a slight population of the helical conformation. The chirality transfer from the side chains to the backbone in **25** was unexpectedly followed by the helicity inversion upon the addition of achiral halide ion guests (Br^- and Cl^-). Although the process of folding and adopting the helical structure (driving force and stabilisation) is understood, the mechanism of the helicity inversion remains unclear. "It seems likely that the halide ions interact with the oligo(ethyleneglycol) side chains, thereby altering intramolecular chirality transfer to the (hetero)-aromatic backbone."⁵⁸ Taking into consideration the ability of **23** to bind halide ions, it is likely that the structural changes, resulting from binding of the halides inside the helix through hydrogen bonding, can also play an important role in the helicity inversion process.

The same type of structure as **24** and **25** can effectively bind also metals and protons, when the triazole-pyridine-triazole moiety adopts the *syn-syn* conformation and serves as a tridentate ligand (orange).⁶³ Similarly to **25**, longer oligomers, such as **26**, also adopt the helical conformation; due to the extended structure and larger number of π - π stacking units, however, the folded structure is stabilised in various solvents. Moreover, conformational change (*anti-anti* to *syn-syn*), resulting in unfolding of the helix, cross-linking and gel formation, takes place upon the addition of various metals (orange). Efficient gelation is based on the formation of the bridging metal complexes, which not only serve as cross-linking points but also impart various functions, potentially useful for the design of new magnetic (Fe) or emissive (Eu) materials.⁶¹

The second type of function-related triazole-derived materials is represented by a phthalocyanine (Pc) derivative **27** (Fig. 1), equipped with eight triazole groups on the periphery of the Pc core. The triazole groups do not only serve as a powerful synthetic tool to access a variety of these structures using the CuAAC reaction,⁷⁰ but also as functional building blocks that can coordinate to metals. The coordination of Pc **27** was followed by titration with $\text{Zn}(\text{OTf})_2$: the UV-vis spectrum of the final supramolecular aggregate exhibited an intense Q-band at 656 nm, which was hypsochromically shifted with respect to the parent Pc **27** that exhibited the Q-band at 697 nm (Fig. 1a). In addition, our recent studies have shown that the UV-vis titration reveals two break points (#1 and #2), corresponding to the coordination of **27** to $\text{Zn}(\text{II})$ in a ratio 1/1 and 1/2 (Fig. 1b). After this point, the spectrum does not change anymore, indicating a ratio 1/2 for the final structure $(\text{27})_2(\text{Zn})_4$ (Scheme 6), which remains stable for months. These results are further supported by our recent time-resolved fluorescence measurements, which are also indicative of the formation of a Pc dimer.⁷¹

The third type of function-related triazole-derived materials is represented by chiral binaphthyl-based polymers **28** and **29** (Fig. 2). It was shown that the (chir)optical and electronic properties of both polymeric species significantly changed upon the addition of transition metals and acids due to the

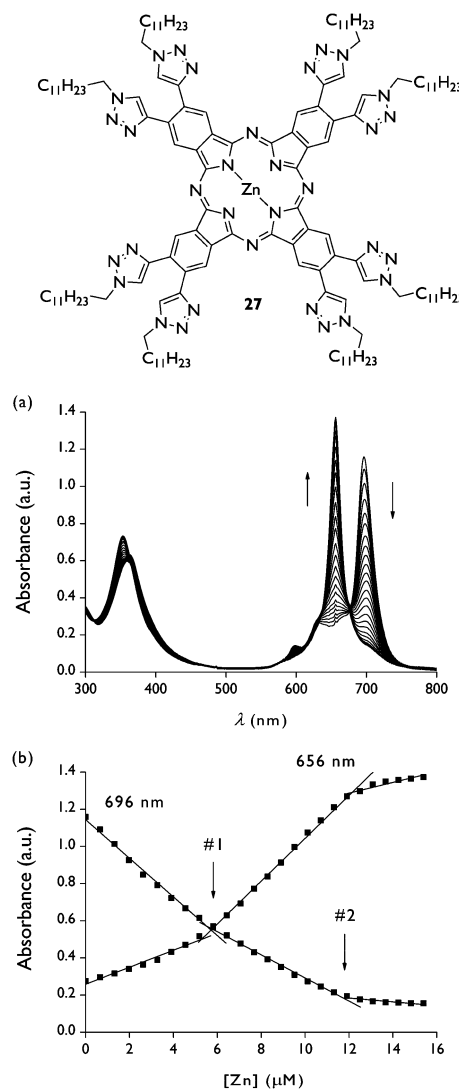
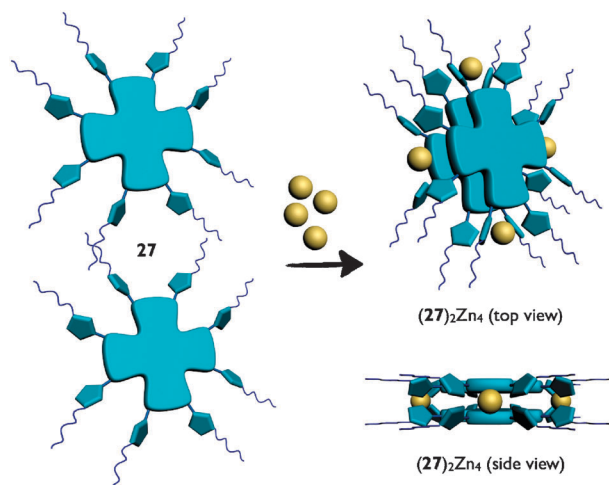


Fig. 1 Function-related example of triazole-derived structures, Pc **27**, and its titration with $\text{Zn}(\text{OTf})_2$ in THF: (a) UV-vis absorption titration curves and (b) absorbance decrease (696 nm)/increase (656 nm) versus zinc(II) concentration; $[\text{27}] = 6.6 \mu\text{M}$; $T = 298 \text{ K}$.



Scheme 6 Schematic representation of Pc **27** and the formation of its supramolecular aggregate $(\text{27})_2(\text{Zn})_4$ upon the addition of $\text{Zn}(\text{OTf})_2$.

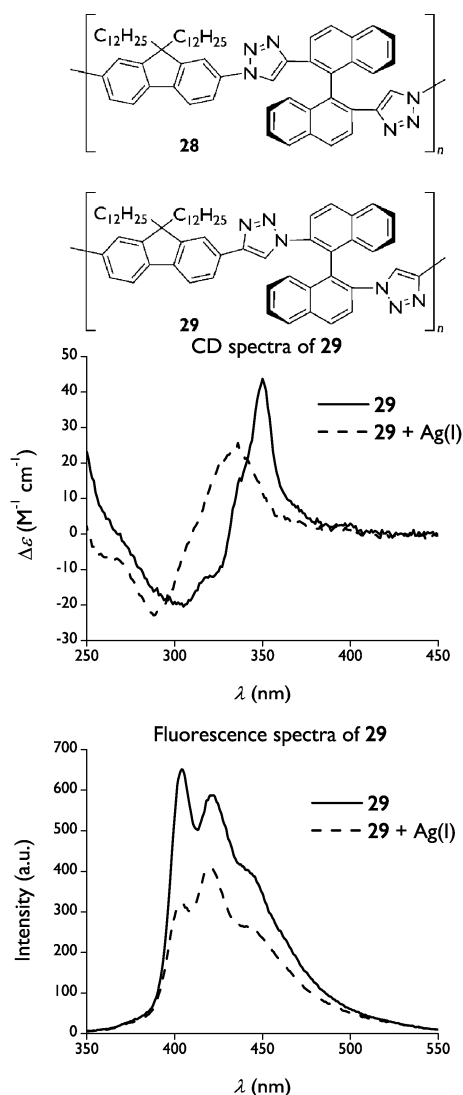


Fig. 2 Function-related examples of triazole-derived binaphthyl-based polymers, **28** and **29**, and the fluorescence and CD spectra of **29** before and after the addition of AgOTf.

coordination/protonation of the triazole moiety. The emission can be tuned upon the addition of Ag(I) resulting in a blue shift in the absorption and a decrease in the signal intensity in the CD spectra (Fig. 2). These changes are reversible upon the addition of organic base, highlighting the sensitive nature of the dihedral angle of the binaphthyl unit in these polymers.⁷¹

The last example that has only been synthesised recently, naphthalocyanine (Nc) **30**, combines both conjugation- and function-related properties of the triazole group (Fig. 3).⁷¹ Nc **30** possesses eight triazole groups fused to the Nc core *via* two carbon atoms, which results in the blue shift of the Q-band absorption maximum, compared with 2,3-Nc, due to the strong electron withdrawing character of the triazole unit. As a result, strong π - π aggregation behaviour, that can be fine-tuned upon doping with metals or guest molecules into the four half-cavities, is predicted for this class of molecules and is currently studied in our research group.

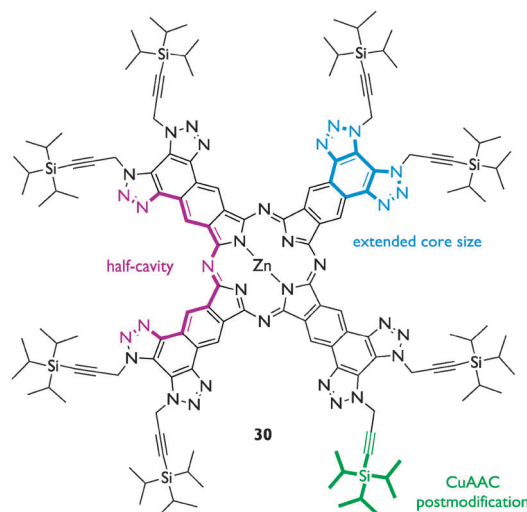


Fig. 3 Conjugation- and function-related example of triazole-derived materials, Nc **30**.

Conclusions

In addition to the acetylenic transformations, leading to acetylene-based or benzenoid π -conjugated structures, the CuAAC reaction represents another powerful synthetic tool. Compared with other acetylenic reactions, a five-membered heteroaromatic ring is formed instead of an aromatic all-carbon ring. Employing its coordination and hydrogen-bond-accepting/-donating abilities, the triazole group brings new design opportunities; in addition to its heteroaromatic character, it can also serve as a functional building block. The conjugation- and function-related triazole-based materials, available to date, only started to appear few years ago; these examples, however, have highlighted the huge potential for new applications in different directions and opened a new sub-field within organic materials. We anticipate that this new class of materials may be applied in, for instance, sensors and responsive devices with well-defined tuneable (opto)electronic properties, and believe that this review will motivate future research in this field and add another brick on the road to carbon-rich functional materials.

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