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Cationic [6]Helicenes: Tuning (Chir)Optical Properties up to the Near Infra-Red

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ABSTRACT

The intramolecular condensation of ortho substituents of triaryl carbenium ions can lead to the formation of cationic helicenes. These chiral and configurationally stable molecules exhibit extended optical properties reminiscent of their parent methylum ions. Among them, cationic [6]helicenes are particularly interesting as orthogonal late-stage functionalization strategies allow the introduction of a variety of auxochromes with different regiochemistry. Intense chiroptical properties can thus be tailored in the far red and up to the near infra-red (NIR) spectral windows. A wealth of applications can be foreseen, in particular in material sciences.

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1. Introduction

Helicenes, which are ortho condensed polyaromatics, are inherently chiral due to the steric repulsion of their termini. Configurationally stable, they can be isolated as (*M*) or (*P*)-enantiomers. Cationic helicenes based on triaryl carbenium scaffold exhibit strong absorption and emission properties in the visible spectral range [1]. Moreover with this family of derivatives, variations of the heteroatoms inside the helicene skeleton are possible, affording compounds with rich electronic properties. Among them, cationic diaza **1** and dioxo [6]helicenes **2** are particularly attractive (Fig. 1), as late-stage functionalization strategies allow a fine tuning of their (chir)optical properties up to the NIR [2].

2. Synthesis and Late-Stage functionalization

Somewhat counter intuitive, cationic diaza [6]helicene **1** is an electron-rich species. It can thus readily react with electrophiles (Fig. 1). Under kinetic control, nitration or bromination reactions occur selectively at positions 8 and 10 [2–3]. Further derivatizations are then possible with such building blocks. Dinitro and dia-

mino derivatives **3** and **4** are obtained *via* this synthetic route (Fig. 2a). Under protic conditions allowing thermodynamic equilibration, regioselectivities of the electrophilic additions are reversed and addition reactions are observed at positions 3 and/or 15 (Fig. 1), leading for instance to mono- and bis-tetracenes **7** and **8** after further elaboration (Fig. 2b) [4].

Diaza **1** can also react as electrophile in oxidative nucleophilic addition reactions, but its electron-rich nature limits the reaction scope (Fig. 1, see also for instance reaction products **5** and **6** in Fig. 2a) [2–3]. Conversely, the electron-poor dioxo analogue **2** readily reacts in such transformations (Fig. 1), allowing in particular the oxidative addition of nucleophilic indolenine moieties in positions 5 and/or 13 (compounds **9** and **10**, Fig. 2c) [5]. Synthetic routes to compounds **1** – **10** are given in the Supporting Information.

3. Optical and chiroptical properties

Focusing on diaza **1**, functionalization of positions 8 and 10 from one side, and 5 and 13 from the other, allows a fine tuning of the optical properties (Fig. 2a) [3]. At positions 8 and 10, introduction of electron-withdrawing groups (EWG) such as nitro moieties (compound **3**) induces a strong hypsochromic shift of the absorption maximum (λ_{abs} 560 nm vs. 614 nm for **3** and **1**, respectively). Conversely, electron-donating groups (EDG) like amino substituents lead to bathochromic shifts of the absorption (for

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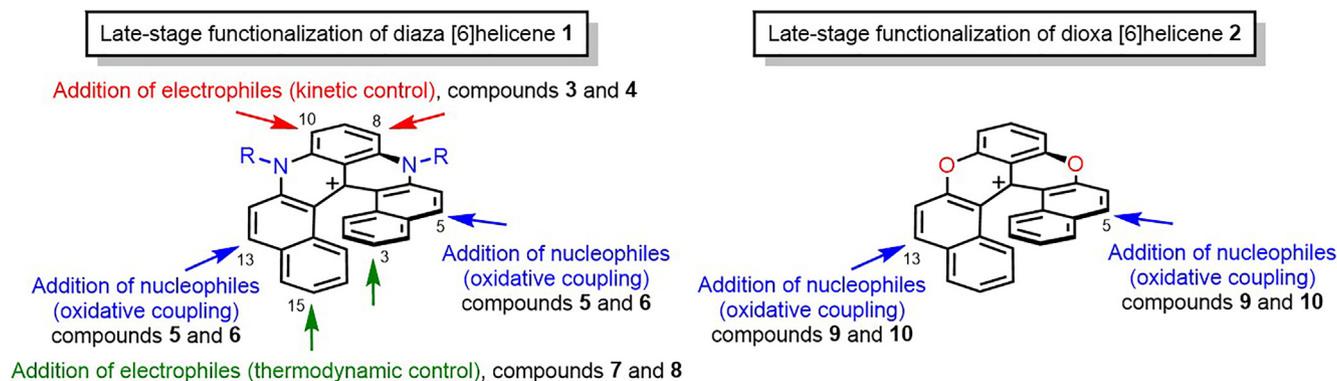


Fig. 1. Late-stage functionalization patterns of diaza **1** and dioxo [6]helicenes **2**. *M* enantiomer shown.

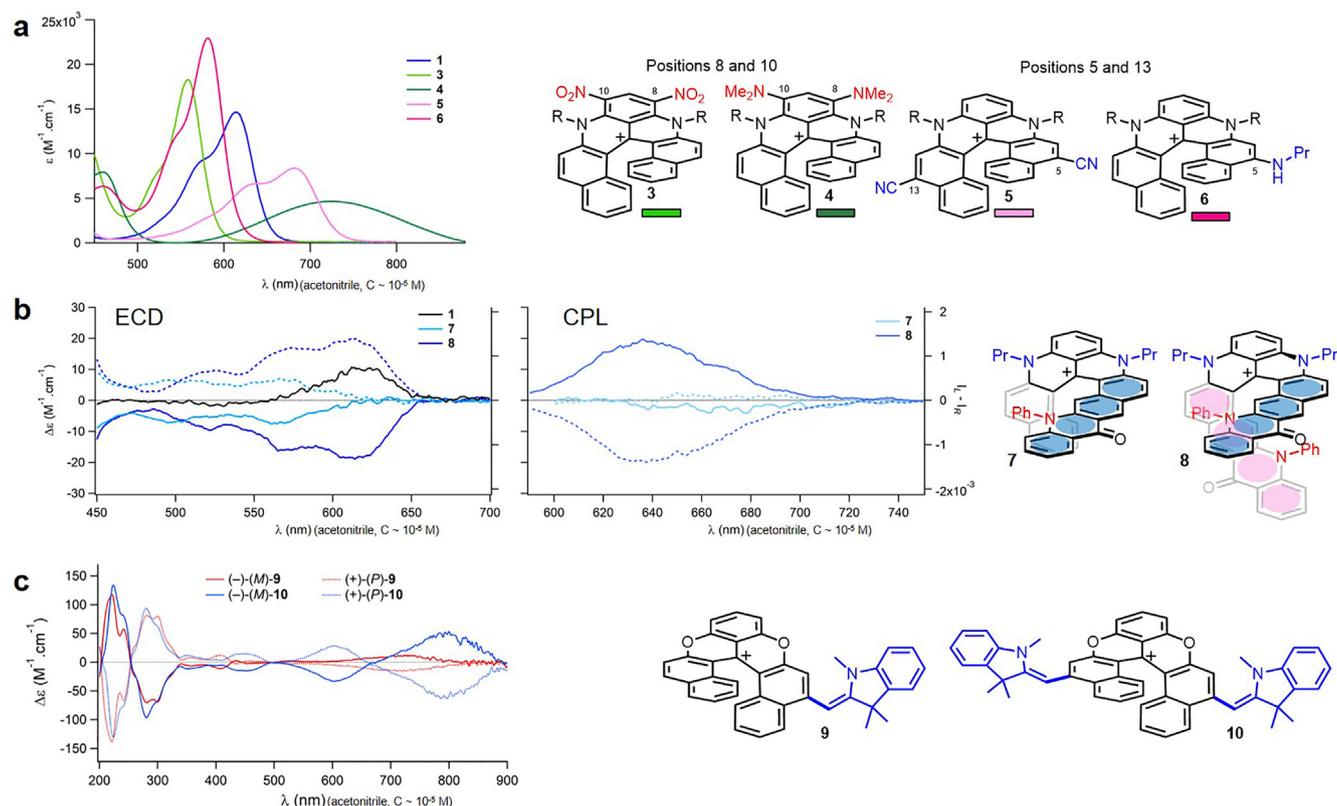


Fig. 2. (a) Absorption spectra of **1** and **3** – **6**; (b) ECD and CPL spectra of **7** and **8**; (c) ECD spectra of **9** and **10**.

instance, λ_{abs} 724 nm for **4**). The same trend is observed in fluorescence. The influence of the donating/withdrawing ability of the substituents is opposite at positions 5 and 13 (Fig. 2a). In this case, EWGs induce a redshift of the absorption (λ_{abs} 682 nm for **5**) contrary to EDGs which promote blueshifted absorption (λ_{abs} 582 nm for **6**). Again, similar tendencies are noticed in fluorescence.

Functionalizations at position 3 and/or 15 of diaza **1** do not alter the absorption / emission properties (Fig. 2b) [4]. The lowest energy transitions of mono- and bis-tetracenes **7** and **8** are centered on 615 and 616 nm, vs. 614 nm for **1**, and fluorescence maxima are observed between 653 and 658 nm for the three compounds with emission of similar intensities (ϕ_{flu} 21% – 31%). However, the accommodation of sterically demanding phenyl group(s) in the fjord region of **7** and **8** results in larger helical pitches. This phenomenon is reflected in their larger chiroptical response in electronic circular dichroism (ECD) and circularly polarized luminescence (CPL, Fig. 2b). In ECD, Cotton effects

increase at lower energy from $\Delta\epsilon$ 5 to 20 $\text{M}^{-1} \text{cm}^{-1}$ from **1** to **8**, and in CPL g_{lum} values as high as $1.4 \cdot 10^{-3}$ are observed for **8** [4].

Concerning dioxo **2**, additions of indolenine groups in positions 5 and/or 13 drastically perturb the (chir)optical properties of the dioxo helicene core (Fig. 2c) [5]. Introduction of such strong EDGs induces intense bathochromic and hyperchromic shifts of the absorption (ϵ 41000 $\text{M}^{-1} \text{cm}^{-1}$ at 727 nm for **9** and ϵ 84600 $\text{M}^{-1} \text{cm}^{-1}$ at 791 nm for **10**). Moreover, **9** and **10** fluoresce in the NIR (λ_{flu} up to 887 nm). In ECD (Fig. 2c), strong Cotton effect are observed in the far red and NIR, with $\Delta\epsilon$ values up to 60 $\text{M}^{-1} \text{cm}^{-1}$ around 790 nm for **10**.

4. Discussion

Electron-rich diaza [6]helicene **1** is best post-functionalized with electrophilic reagents, reactions happening at positions 8 and 10 under kinetic control, or 3 and 15 under thermodynamic

control. Conversely, electron-poor dioxa **2** is readily functionalized at positions 5 and 13 in oxidative coupling reactions with nucleophilic partners.

With diaza **1**, the absorption and emission properties can be tailored from the green to the far-red spectral window. Introduction of auxochromes at positions 5, 8, 10 and 15 impact the optical properties by tuning the energies of the frontier orbitals: at positions 8 and 10 by altering the HOMO level and at positions 5 and 13 the LUMO level. Similar trends and rational are observed within the closely related diaza [4]helicene family [6]. Substitutions at positions 3 and 15 do not influence the electronic properties. Moreover, the chiroptical properties can be tuned as well: introduction of steric bulk in the fjord region of the helicene increases the helical pitch, which results in an enhancement of the ECD and CPL properties.

The situation of dioxa **2** is different. The introduction of the indolenine moieties completely changes the nature of chromophores **9** and **10** compared to **2**. In mono-functionalized derivative **9**, a large charge delocalization from the electron-rich indolenine moieties to the electron-poor helicene core is observed, providing to this compound a cyanine character resulting in a hyperchromic and bathochromic shift of its absorption spectrum toward the very far-red. In compound **10**, the two indolenine moieties are electronically conjugated, as observed by cyclic voltammetry experiments [5]. The positive charge of **10** is thus completely delocalized over the whole molecule, from one indolenine to the other *via* the helicene core, enhancing further the cyanine character up to values usually observed for Cy7 and above [7]. Moreover, the chiral helicene core of **9** and **10** confers to those derivatives intense chiroptical properties up to the NIR.

5. Conclusion

Cationic diaza and dioxa [6]helicenes can be readily engaged into late-stage functionalization reactions. Orthogonal regioselectivities are achieved with electrophilic or nucleophilic partners, under kinetic or thermodynamic control. Compounds with intense

(chir)optical up to the NIR can be designed at will, opening the door for a wealth of applications, in particular in material sciences.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matpr.2022.05.098>.

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