

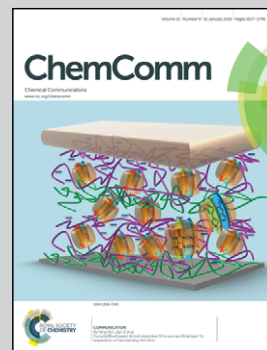


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Functional helquats: helical cationic dyes with marked, switchable chiroptical properties in the visible region

Remarkable chiroptical properties of the new helquat dyes are due to the unique combination of a cationic hemicyanine chromophore and a helicene-like motif. The magnitude of the ECD response and the pH switching along with their positioning in the visible region are unprecedented among heliceneoids.

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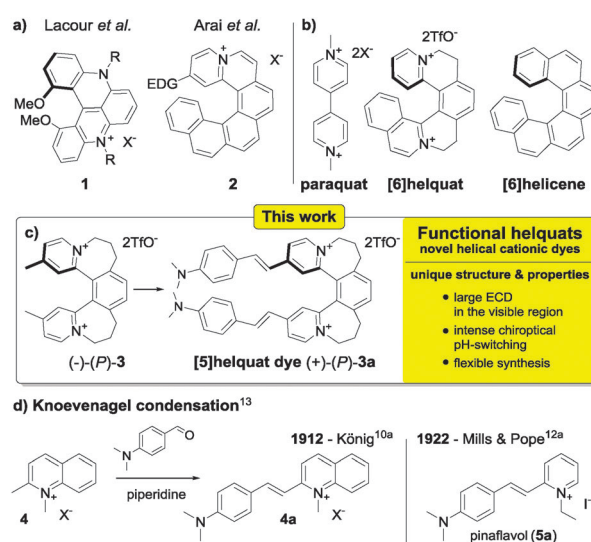
# Functional helquats: helical cationic dyes with marked, switchable chiroptical properties in the visible region†

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**Helquat dyes are the first helicene-like cationic styryl dyes obtained as separate enantiomers. Their remarkable chiroptical properties are due to the unique combination of a cationic hemicyanine chromophore and a helicene-like motif. The magnitude of the ECD response and the pH switching along with their positioning in the visible region are unprecedented among heliceneoids.**

Cationic dyes receive great attention due to their widely useful photophysical properties.<sup>1</sup> This field played a pivotal role in transforming organic chemistry from a purely academic effort into a highly profitable industrial endeavour.<sup>2</sup> However, chiral cationic dyes are attractive yet surprisingly underdeveloped,<sup>3,4</sup> compared to achiral dyes. Specifically, cationic dyes based on a helicene structure<sup>5</sup> remain largely overlooked. Rare exceptions are helicinium systems from the groups of Lacour<sup>6</sup> and Arai<sup>7</sup> (e.g. **1**, **2**, Scheme 1a). The seldom visited territory of helical cationic dyes promises compounds with significant chiral properties such as sizeable chiroptical response in the visible region.

We introduced recently helquats as a structural link between helicenes and viologens (Scheme 1b).<sup>8</sup> The present work is motivated by an expectation that methyl-substituted helquats will lead to an original class of helically chiral cationic dyes (e.g. (+)-(P)-**3a**, Scheme 1c) with unique properties, opening up



**Scheme 1** (a) Rare examples of helical cationic dyes;<sup>6,7</sup> (b) structural relationship of [6]helquat with paraquat and [6]helicene; (c) one-step diversification strategy providing access to a range of helical dyes from a common methyl-substituted helquat precursor as presented in this paper; (d) synthesis of hemicyanine dye **4a** as reported by Walter König in 1912<sup>10a</sup> and structure of pinaflavol (**5a**) prepared analogously by Knoevenagel condensation.<sup>13</sup> EDG = electron-donating group.

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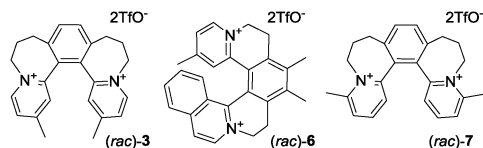
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intriguing application opportunities for chiral sensing<sup>9</sup> or chiroptical pH-switching<sup>25–27</sup> (**3k** and **7k**, Scheme 5). Here, we describe such dyes and demonstrate their remarkable chiroptical properties such as large electronic circular dichroism (ECD) in the visible region and prominent switching of the chiroptical response by pH. The magnitude of the ECD response and the pH-switching effect along with their positioning in the visible region are unprecedented among heliceneoids.

Reacting arylaldehydes with methyl-substituted cationic heteroaromatics to produce hemicyanine dyes<sup>10,11</sup> (e.g. **4** → **4a**, Scheme 1d) has been since the early 20th century the enabling technology that led to sensitizers widely used in photography (e.g. pinaflavol).<sup>12</sup> This transformation (Knoevenagel condensation,<sup>13</sup>





**Scheme 2** Structures of novel racemic methyl-substituted helquats used in this work. For synthetic details, see the ESI,<sup>†</sup> Section S3.

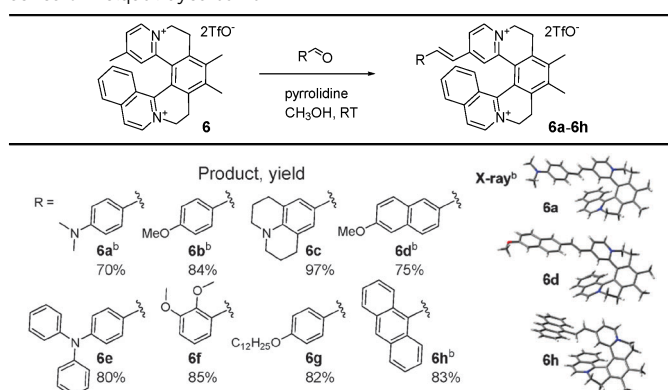
Scheme 1d) is generally reliable, selective, experimentally simple, and versatile.<sup>14</sup> At the outset of the present study, we proposed novel methyl-substituted helquat dye precursors **3**, **6**, and **7** (Scheme 2) as dye precursors suitable for Knoevenagel condensation.

Our approach relies on a convenient three-step synthesis of the methyl-substituted helquats,<sup>8a,c</sup> involving [2+2+2] cycloaddition.<sup>15</sup> This strategy affords racemic helquat dye precursors **3**, **6**, and **7** in gram quantities (Scheme 2, for synthetic details, see the ESI,<sup>†</sup> Sections S3A–S3C).

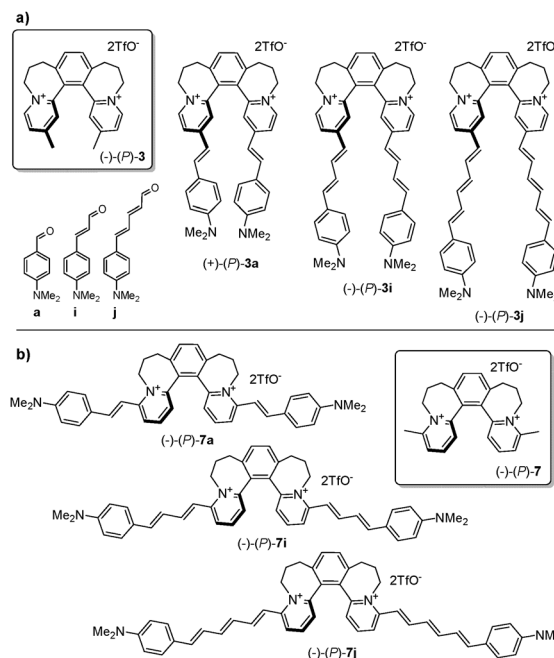
Using [6]helquat **6** demonstrates the potential of our approach, reacting with various arylaldehydes to give a series of dyes **6a–h** (Table 1). Their triflate salts are typically easy to purify by precipitation. From the three methyl groups in helquat **6**, only the one attached to a pyridinium moiety proved to be reactive in the Knoevenagel condensations. Precursors **3** and **7** show that helquats with two active methyl groups can be used for double Knoevenagel condensations (e.g. **3** → **3a**, **7** → **7a**, Scheme 3 and Sections S3G and S3H, ESI<sup>†</sup>).

A further key favorable feature of our strategy is that a single non-racemic methyl-helquat such as (–)-(*P*)-**3** (Scheme 3a) provides access to a whole range of non-racemic (*P*)-configured dyes. To this end, racemic helquat **3** is resolved *via* a dibenzoyltartrate method<sup>16</sup> into (–)-(*P*)-**3** and (+)-(*M*)-**3** (Section S3D, ESI<sup>†</sup>). The former is transformed into (*P*)-configured dyes **3a**, **3i**, and **3j** (Scheme 3a). The absolute configuration of both enantiomeric series of dyes derived from **3** is established unambiguously by helicity assignment of (*M*)-**3** and (*M*)-**3a** by X-ray crystallography (Section S7, ESI<sup>†</sup>). Similarly, a series of dyes **7a**, **7i**, and **7j** (Scheme 3b and Section S3H, ESI<sup>†</sup>) are synthesized as both enantiomers from the respective precursors (–)-(*P*)-**7** and (+)-(*M*)-**7**.

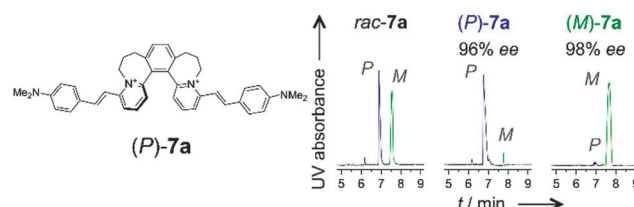
**Table 1** Use of [6]helquat **6** in Knoevenagel condensation to obtain a series of helquat dyes **6a–6h**<sup>a</sup>



<sup>a</sup> Typical conditions: **6** (0.07 mmol), arylaldehyde (5 eq.), pyrrolidine (5 eq.), 60–120 min. <sup>b</sup> For X-ray data, see the ESI, Section S7. Full experimental data, see Section S3F.



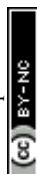
**Scheme 3** (a) Three representative (*P*)-configured helquat dyes **3a**, **3i**, and **3j** obtained from the precursor (–)-(*P*)-**3** via Knoevenagel condensation with respective aldehydes; (b) the isomeric (*P*)-configured dyes **7a**, **7i**, and **7j** derived from (–)-(*P*)-**7**. For (*M*)-configured dyes and further details, see the ESI,<sup>†</sup> Sections S3G and S3H.



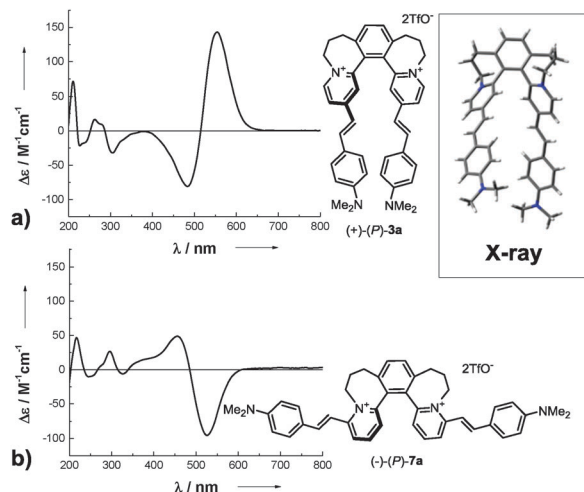
**Fig. 1** Results from chiral analysis of the racemic and non-racemic samples of helquat dye **7a** by CE with a sulfated  $\gamma$ -cyclodextrin selector. Analysis established the enantiomeric purity of the non-racemic dyes to be greater than 95% ee in (*P*)- as well as (*M*)-series. See Section S4 (ESI<sup>†</sup>) for details.

Capillary electrophoresis (CE) with sulfated cyclodextrin chiral selectors<sup>17</sup> allows direct enantiocomposition analysis of the new dyes (e.g. **7a**, Fig. 1 and Section S4, ESI<sup>†</sup>). This analysis confirms that the stereointegrity of the helix persists during the Knoevenagel condensations forming dyes shown in Scheme 3 and Section S3G and S3H (ESI<sup>†</sup>).<sup>18</sup>

The non-racemic dyes show notable chiroptical properties. Compound (+)-(*P*)-**3a** exhibits a large molar rotation ( $[\phi]_D^{20} = +223\,830 \text{ deg cm}^2 \text{ dmol}^{-1}$ ), and exciton coupling<sup>19</sup> leads to significantly intense Cotton effects in ECD spectra in the visible region (Scheme 4a and Section S5, ESI<sup>†</sup>). Specifically, the dye with right-handed helicity (+)-(*P*)-**3a** shows a strong positive ECD band at 555 nm ( $\Delta\epsilon = +143 \text{ M}^{-1} \text{ cm}^{-1}$ ). While the prominent chiroptical response of many helicenoids in the UV region is documented amply in the literature,<sup>5,20</sup> systems with substantial ECD in the visible are very rare.<sup>21,22</sup> Thus, in







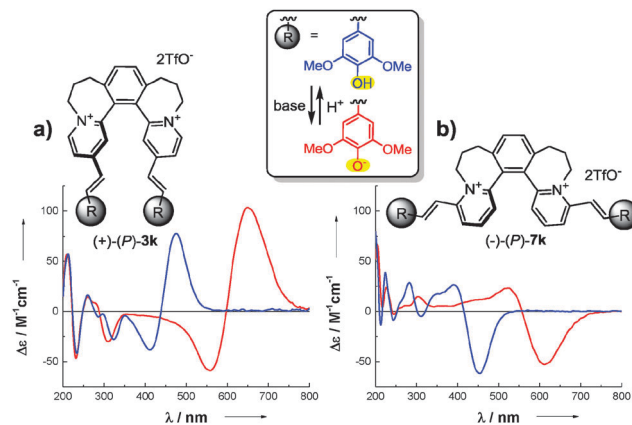
**Scheme 4** Opposite Cotton effects in the visible region of isomeric dyes of the same absolute configuration: ECD spectra of (a) (+)-(P)-3a and (b) (-)-(P)-7a. Inset: X-ray geometry of (P)-configured scaffold of 3a.

this spectral region, the title dyes exhibit the most intense ECD bands among the helicenoids known.

The dye (-)-(P)-7a is a positional isomer of (+)-(P)-3a. The former also shows significant molar rotation ( $[\phi]_D^{20} = -100880 \text{ deg cm}^2 \text{ dmol}^{-1}$ ) and a markedly strong visible Cotton effect ( $\Delta\epsilon = -96 \text{ M}^{-1} \text{ cm}^{-1}$  at 527 nm, Scheme 4b). However, it is noteworthy that, despite their same absolute configuration, (+)-(P)-3a and (-)-(P)-7a display opposite visible Cotton effects (compare Scheme 4a and b). Also, this phenomenon is observed consistently for the other two isomeric pairs, (-)-(P)-3i/(-)-(P)-7i and (-)-(P)-3j/(-)-(P)-7j (Section S5, ESI†).<sup>23</sup> This effect is verified by first-principles calculations at several levels of theory (Section S6, ESI†). The ECD spectra simulated for (P)-3a and (P)-7a reproduce the experimental results in all major features (Fig. S35 and S37, ESI†).<sup>24</sup> Transitions between orbitals of the opposite symmetry with respect to the  $C_2$  axis of the molecule give rise to positive ECD in (P)-3a and negative ECD in (P)-7a. On the other hand, transitions between orbitals of the same symmetry give rise to negative ECD in (P)-3a and positive ECD in (P)-7a (see Fig. S39 and S41 and Tables S13 and S15, ESI†).

Incorporating two pH-active phenol units into our helically chiral bischromophoric dyes can engender an outstanding chiroptical pH-switchability. To this end, we have synthesized two dyes with phenol moieties, (+)-(P)-3k and (-)-(P)-7k (Scheme 5, Sections S31 and S3J, ESI†). For both of these compounds, pH changes trigger sizeable and reversible modulation of ECD response.<sup>25,26</sup> Notably, (+)-(P)-3k shows particularly intense chiroptical pH-switching ( $\Delta(\Delta\epsilon) = 100 \text{ M}^{-1} \text{ cm}^{-1}$  at 650 nm). The magnitude of this pH-switching effect and its positioning in the visible region are significant in general, and exceptional among helicenoids in particular.

In summary, this study introduces an original class of dicationic helical dyes with prominent chiroptical properties. The results are significant on multiple counts: (1) many non-racemic dyes are prepared easily from common precursors *via* a single-step Knoevenagel condensation; (2) the syntheses are



**Scheme 5** ECD switching between protonated (blue line) and deprotonated form (red line) of (a) (+)-(P)-3k and (b) (-)-(P)-7k.

convenient to perform and the products are typically easy to purify; (3) the new dyes show very intense ECD responses beyond the UV region due to a unique combination of a cationic hemicyanine chromophore with a helicene-like structural motif; (4) opposite Cotton effects in isomeric bis-chromophoric dyes of the same scaffold helicity are observed; (5) efficient pH-switching of the chiroptical responses is achieved ( $\Delta(\Delta\epsilon) = 100 \text{ M}^{-1} \text{ cm}^{-1}$  at 650 nm) and the magnitude of this pH-effect as well as its positioning in the visible region are unprecedented among helicenoids.<sup>27</sup> As the field of helical cationic dyes is extremely underdeveloped, helquat derivatives are attractive for many potential applications such as chiral environment-sensitive probes.

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- 23 For comparison of (M)-configured dye pairs (–)-(M)-**3a**/(+)-(M)-**7a**, (+)-(M)-**3i**/(+)-(M)-**7i**, and (+)-(M)-**3j**/(+)-(M)-**7j**, see Section S5 (ESI†).
- 24 ECD spectra simulations at various levels of theory: Section S6 (ESI†).
- 25 For a related non-cationic pH-responsive system, see: (a) S. E. Boiadjev and D. A. Lightner, *Tetrahedron: Asymmetry*, 1996, **7**, 2825; further examples with pH-switchable ECD response: (b) W. Lu, *et al.*, *J. Phys. Chem. A*, 2014, **118**, 283; (c) R. Lin, *et al.*, *Chem. – Eur. J.*, 2011, **17**, 2420; for recent example of acid–base chiroptical switching in an osmium complex with a [6]helicene ligand, see: (d) E. Anger, M. Srebro, N. Vanthuyne, C. Roussel, L. Toupet, J. Autschbach, R. Réau and J. Crassous, *Chem. Commun.*, 2014, **50**, 2854; see also references added in proof: (e) N. Saleh, B. Moore II, M. Srebro, N. Vanthuyne, L. Toupet, J. A. G. Williams, C. Roussel, K. K. Deol, G. Muller, J. Autschbach and J. Crassous, *Chem. – Eur. J.*, DOI: 10.1002/chem.201405176; (f) A. Wallabregue, P. Sherin, J. Guin, C. Besnard, E. Vauthey and J. Lacour, *Eur. J. Org. Chem.*, 2014, 6431.
- 26 Reviews on chiroptical switches: (a) J. W. Canary, *Chem. Soc. Rev.*, 2009, **38**, 747; (b) Z. Dai, J. Lee and W. Zhang, *Molecules*, 2012, **17**, 1247; (c) ref. 19a and references therein.
- 27 To the best of our knowledge, the only pH-triggered ECD switching in a helicenoid has been reported in a recent work on an organo-metallic osmium-helicene complex,<sup>25d</sup> having the main pH-switchable band located in the UV region. See also ref. 25e added in proof.

