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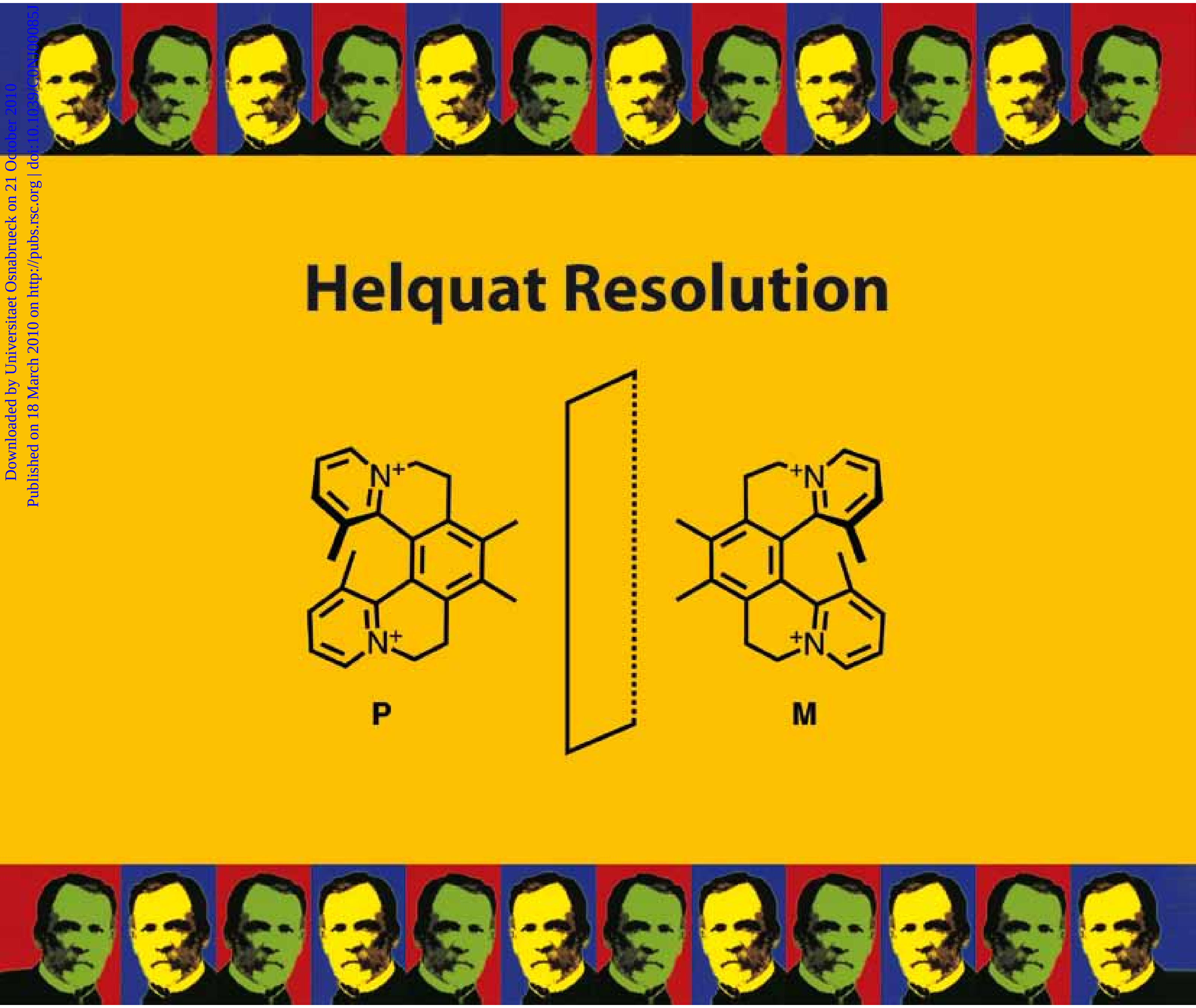

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LETTER
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Resolution of a configurationally stable [5]helquat: enantiocomposition analysis of a helicene congener by capillary electrophoresis

Resolution of a configurationally stable [5]helquat: enantiocomposition analysis of a helicene congener by capillary electrophoresis†‡

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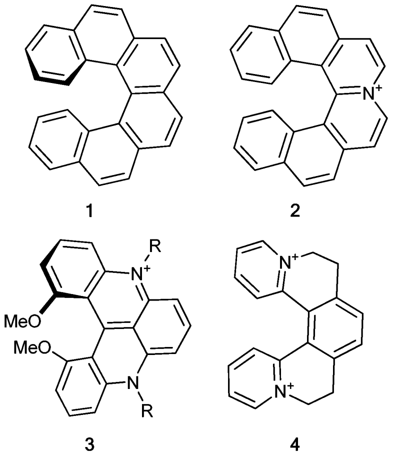
Racemic [5]helquat as a triflate salt has been synthesized using a robust, three-step procedure. Subsequent exchange of triflate anions for inexpensive (*R*,*R*)-dibenzoyltartrate anions *via* an ion exchange resin afforded two diastereoisomeric salts. Crystallization led to the resolution of the helquat (ee > 98%). This is the first time that a non-racemic helquat has been obtained; its helicity having been assigned and its racemization barrier determined. Capillary electrophoresis with a sulfated β-cyclodextrin chiral selector is introduced for the first time as a straightforward method to analyze the enantiocomposition of charged, helicene-like species.

Helicenes and similar aromatic helical systems continue to fascinate chemists due to their unique structure and properties (*e.g.* [6]helicene (**1**), Scheme 1).[1,2] In particular, their electronic properties and pronounced chirality are attractive for many branches of chemical research, such as molecular electronics, materials chemistry and catalysis.[3] As opposed to neutral helicene species, their cationic derivatives with quaternary nitrogen atoms in the helical backbone have been rather overlooked.[4] Rare exceptions have been investigations of azoniahelicenes (*e.g.* **2**)[4b,c] and recently described [4]heterohelicenia (**3**).[5]

To expand the portfolio of existing quaternary nitrogen-containing helicene-like molecules, we recently introduced helquats (helical extended diquats, *e.g.* **4**), which represent the missing structural link between helicenes and viologens.[6] This novel combination opens up an attractive field of research as both compound classes, *i.e.* helicenes and viologens, can be regarded as privileged from the point of view of their applications.[7] Helicenes and their congeners have been studied due to their unique three-dimensional arrangement, which suggests their use as inherently chiral scaffolds for catalyst design,[8] NMR chiral shift agents,[9] enantioselective sensing[10] and self-assembly.[11] On the other hand, viologens[12] have been extensively investigated as fast electron transfer catalysts,[12d] as constituents of electrochromic and data storage materials,[13] building blocks in supramolecular chemistry,[14] and bioactive compounds.[15]

Our recent publication introduced helquats as novel helicene-viologen hybrids and presented their synthesis in a racemic form.[6a] To explore the emerging potential of helquats and to address the issues that depend on their helical chirality, the preparative entry to non-racemic series is essential and needs to be developed. Herein, we report the resolution of configurationally stable [5]helquat (ref. 16) using inexpensive, enantiopure dibenzoyltartrate anions. Capillary electrophoresis (CE) with a sulfated β-cyclodextrin chiral selector is also introduced for the first time as a straightforward method to analyze the enantiocomposition of charged, helicene-like species.

The synthesis of helical dication **5** proceeded in the three-step sequence of Sonogashira coupling, bis-quaternization and [2 + 2 + 2] cycloisomerization (Scheme 2).[17,18] We note that the presented synthesis is particularly straightforward to perform and represents a modified version of the general protocol we introduced recently.[6] Smooth Sonogashira coupling of commercially available bromopyridine **6** with gaseous acetylene lead to bis-pyridine **7**, which was isolated *via* flash chromatography according to the previously published



Scheme 1

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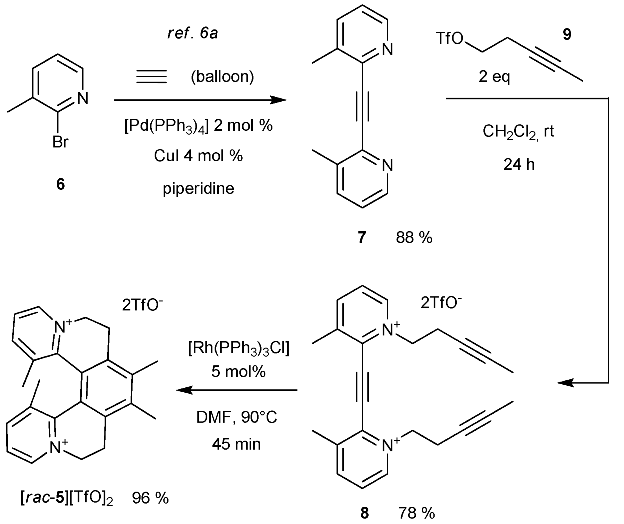
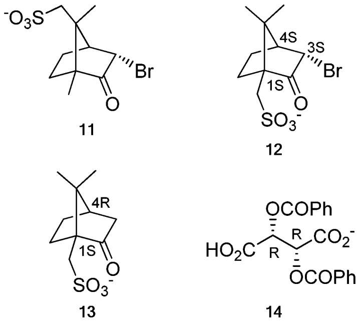
† Dedicated to Professor Jiří Klinot.

‡ Electronic supplementary information (ESI) available: For experimental procedures, spectroscopic characterization data, CE and details on measurement and simulation of ECD. See DOI: 10.1039/c0nj00085j



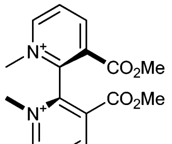
Scheme 2 The three-step synthesis of racemic [5]helquat (**5**).



Scheme 3 Enantiopure anions.

procedure.[6] We found that the next step, bis-quaternization **7** → **8**, worked efficiently in dichloromethane, obviating the use of environmentally problematic tetrachloromethane, the solvent we used in our first generation synthesis of helquats.[6] Finally, the key helicity-forming [2 + 2 + 2] cycloisomerization reaction (**8** → [*rac*-**5**][TfO]$_2$) was effected by the Wilkinson catalyst, with dimethylformamide (DMF) as the solvent of choice.[19] In DMF, the reaction proceeded in high yield, and the characteristic colour change from green to red accompanied the reaction's progress.

In order to resolve the racemic [5]helquat dication [*rac*-**5**], we aimed to take advantage of the different solubilities and/or crystallization abilities of the two diastereoisomeric salts formed from the racemic helquat dication with an enantiopure anion. Related cation **3** has previously been resolved *via* diastereoisomeric salt formation with the enantiopure, hexacoordinated phosphorus BINPHAT anion.[5a,20] We were also inspired by the resolution procedure reported in 1950 by Aziz and Breckenridge,[21] who resolved the racemate of atropisomeric bipyridinium species **10** *via* crystallization of a α-bromocamphor-π-sulfonate[22] salt (Scheme 3). In this context, the exchange of the achiral triflate anion in [*rac*-**5**][TfO]$_2$ for enantiopure anions derived from a chiral pool seemed to be a reasonable starting point for our resolution attempts.[23] Breckenridge's group used the precipitation of diiodide salt [**10**]I$_2$ with silver bromocamphorsulfonate Ag[**11**] to prepare the mixture of the two diastereoisomeric salts. By way of contrast, we relied on an ion exchange resin to conveniently convert helquat bistriflate [*rac*-**5**][TfO]$_2$ into diastereoisomeric salts [*P*-**5**][**12**]$_2$ and [*M*-**5**][**12**]$_2$. Although the ion exchange procedure worked well, various subsequent crystallization experiments with the mixture of diastereoisomeric salts [*P*-**5**][**12**]$_2$ and [*M*-**5**][**12**]$_2$ unfortunately led to no measurable enrichment in either the precipitates or the mother liquor, as judged by CE with a sulfated β-cyclodextrin chiral selector (see discussion of CE in the next section). A similar situation was faced in the case of a mixture of [*P*-**5**][**13**]$_2$ and [*M*-**5**][**13**]$_2$, where, similarly, no successful resolution by crystallization occurred. After this initial study, racemic [5]helquat as its triflate salt was converted into a mixture containing two diastereoisomeric (*R*,*R*)-dibenzoyltartrate salts,[24] [*P*-**5**][**14**]$_2$ and [*M*-**5**][**14**]$_2$, using a reliable ion exchange resin technique (Scheme 4). We were pleased to find that in this case, diffusion of ethanol vapours into a methanolic solution of a mixture containing [*P*-**5**][**14**]$_2$ and [*M*-**5**][**14**]$_2$ led to the exclusive formation of [*P*-**5**][**14**]$_2$ crystals, thus enabling resolution. The diastereoisomeric purity of the crystals obtained from several crystallization experiments was consistently greater than 98% de, as shown by CE with a sulfated β-cyclodextrin chiral selector (Fig. 1). Subsequently, by using ion-exchange resin the resolved crystals of (+)-[*P*-**5**][**14**]$_2$ are transformed to ditriflate (+)-[*P*-**5**][TfO]$_2$, and its enantiomeric purity was checked by CE. This enantiocomposition analysis showed that no loss of stereointegrity of the sample occurred during the ion exchange procedure, as evidenced by the single peak in the electropherogram of (+)-[*P*-**5**][TfO]$_2$. At this point, we concluded that **5** has a sufficiently high configurational stability associated with its helix to allow convenient handling of its solutions at rt.



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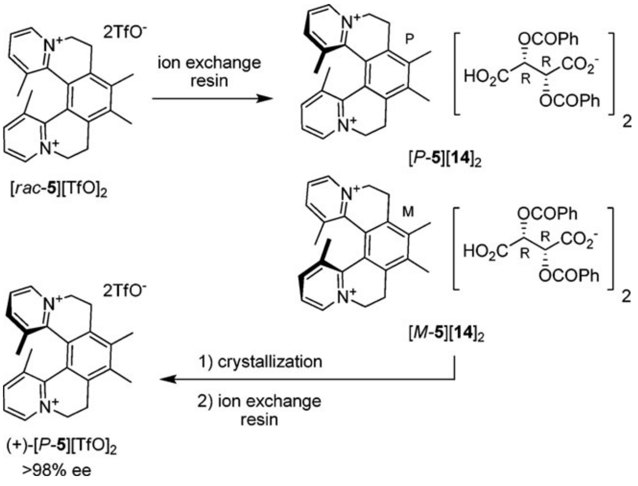
Reliable and fast enantiocomposition analysis was key to the direct evaluation of our resolution attempts. HPLC with a



Scheme 4 Resolution of racemic helquat [**5**][TfO]$_2$ *via* diastereoisomeric salts.

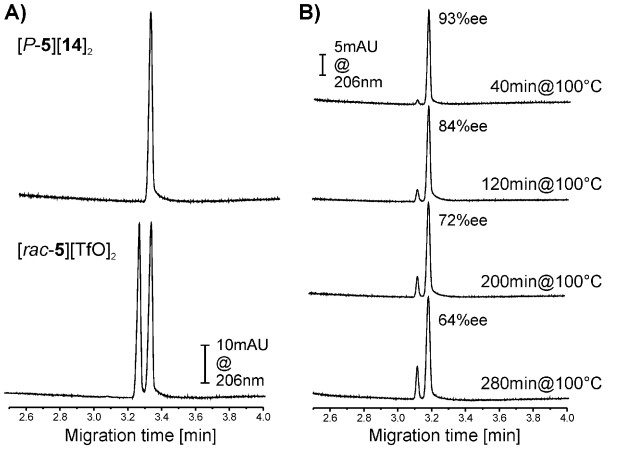


Fig. 1 CE with a sulfated β-cyclodextrin chiral selector: (A) enantiocomposition analysis of [*rac*-**5**][TfO]$_2$ and [*P*-**5**][**14**]$_2$, (B) monitoring of the racemization progress of [*P*-**5**][TfO]$_2$.[30]

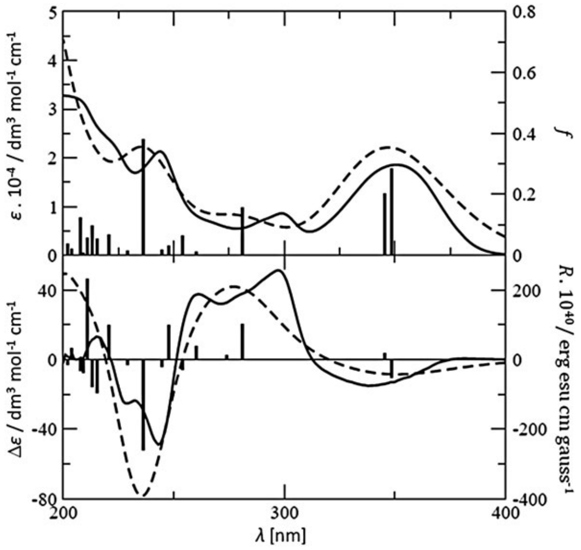


Fig. 2 Experimental and theoretical UV (top) and ECD (bottom) spectra of [*P*-**5**][TfO]$_2$. Experimental spectra (MeOH, c = 0.1 mM) are shown with solid lines and theoretical spectra with dashed lines. The positions and relative intensities of the oscillator strengths *f* and the rotatory strengths *R* for the respective electron excitations are shown by vertical bars. The calculated spectra were shifted to lower energy by 0.25 eV (see the ESI for details‡).

chiral stationary phase[25] and NMR chiral shift agents[26] are established tools for investigating the enantiocomposition of mixtures of helicene-like enantiomers. Although CE with a chiral selector is known to be a straightforward method to analyze the enantiocomposition of charged atropisomeric compounds,[27,28] to the best of our knowledge, it has never been reported in the context of the enantioseparation of helicene-like species.[29] To analyze the enantiocomposition of cation **5** in the salts [**5**][**14**]$_2$ and [**5**][TfO]$_2$, a chiral CE method was developed using sodium phosphate buffer as a background electrolyte and a commercially available sulfated β-cyclodextrin as a chiral selector.[30] The additional usefulness of this technique was apparent when it was put in use in an enantiocomposition analysis during our racemization study with (+)-[*P*-**5**][TfO]$_2$ (Fig. 1 and the next paragraph).

To determine the racemization barrier of the resolved helquat (+)-[*P*-**5**][TfO]$_2$, its stirred solution in water was heated in a CEM microwave apparatus[31] at 100 °C, and samples were taken after each 40 min. The samples exhibited gradually decreasing optical rotation values when inspected by polarimetry at two different wavelengths (589 and 546 nm). Analysis of this data set led to an activation free energy value $\Delta G^{\neq}$ = 127.2 kJ mol^{-1} and racemization half-life at 100 °C $T_{1/2}$ = 7.9 h (see the ESI for details‡). The racemization progress was simultaneously followed by enantiocomposition analysis, made possible by CE separation of the two enantiomers [*P*-**5**][TfO]$_2$ and [*M*-**5**][TfO]$_2$ using a sulfated β-cyclodextrin chiral selector (Fig. 1). The racemization data obtained from this CE study gave a $\Delta G^{\neq}$ value of 126.9 kJ mol^{-1}, which is in good agreement with the value based on optical rotation measurements.

As we were not successful in obtaining sufficiently high quality single crystals of [*P*-**5**][**14**]$_2$ and [*P*-**5**][TfO]$_2$ to directly assign their configuration from the X-ray data, we relied on absolute configuration assignment using ECD spectroscopy.[32] The simulated ECD spectrum of [*P*-**5**] at the TDDFT/BMK/TZVP level calculated at the RI-DFTD/B3LYP/TZVP geometry[33] reproduced well the experimentally recorded spectrum. Specifically, the calculated signs, positions and intensities of the bands matched well with experiment (Fig. 2; detailed information can be found in the ESI‡). These data show that [5]helquat crystallizing as its (*R*,*R*)-dibenzoyltartrate salt has *P* helicity.

In summary, we have described the first resolution of a configurationally stable [5]helquat. Racemic [5]helquat as its triflate salt is converted into a mixture of two diastereoisomeric (*R*,*R*)-dibenzoyltartrate salts using an ion exchange resin. Association of the racemic helquat dication with enantiopure dibenzoyltartrate anions leads to two diastereoisomeric ion pairs. Subsequent, preferred crystallization of a single diastereoisomeric salt enables resolution. CE with a sulfated β-cyclodextrin chiral selector is introduced as a new method to analyze the enantiocomposition of charged, helicene-like species. We are currently working on extending the scope of the presented resolution procedure to other helquats.

Financial support by the Czech Science Foundation (203/09/1614, 203/09/0705, P207/10/2391, 203/08/1428) and IOCB (Z4 055 0506) is gratefully acknowledged. M. U. and P. Sla. acknowledge support from the Czech Ministry of Education (Research Project no. 6046137307). M. O. is a student of the International Max Planck Research School "Dynamical processes in Atoms, Molecules and Solids". We thank Dr I. Císařová, Mr P. Švec and Mrs N. Sarvašová for their experimental help, and Dr L. Adriaenssens for fruitful discussions.

Experimental

The sulfated β-cyclodextrin sodium salt was purchased from Aldrich (cat. no.: 389153). CE was carried out in home-made apparatus[34] equipped with a bare fused silica capillary with an outer polyimide coating, total/effective length 400/290 mm, id/od 50/375 μm (Polymicro Technologies, Phoenix, AR, USA) and a UV-absorption detector operating at a fixed wavelength of 206 nm. Enantiocomposition analyses were performed in a background electrolyte composed of 22 mM sodium, 35 mM phosphate buffer (pH 2.5) and a chiral selector of a 6 mM sulfated β-cyclodextrin. The analytes were dissolved in de-ionized water or methanol at *ca.* 1–2 mM concentration. They were injected into the capillary hydrodynamically by a pressure of 300–500 Pa for 3–5 s. Analyses were performed at a −12 kV separation voltage (cathode at the injection capillary end) at an ambient temperature of 22–25 °C. Chromatography and Electrophoresis Station Clarity (DataApex, Prague, CR) was employed for data acquisition and evaluation. The optical purity (ee) of analytes was determined from the ratio of the corrected (migration times normalized) peak areas of the separated enantiomers. CE analyses provided good reproducibility, the relative standard deviation (RSD) of the migration times was lower than 0.25% and the RSD of the determined enantiocomposition was lower than 2.1%.

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7 The concept of 'privileged' structures is useful in the field of chiral catalysis for classes of synthetic catalysts that are enantioselective over a wide range of different, mechanistically unrelated reactions, see: (*a*) T. P. Yoon and E. N. Jacobsen, *Science*, 2003, **299**, 1691; (*b*) In pharmaceutical research, for compound classes that are active against a number of different biological targets, see: B. E. Evans, K. E. Rittle, M. G. Bock, R. M. DiPardo, R. M. Freidinger, W. L. Whitter, G. F. Lundell, D. F. Veber and P. S. Anderson, *J. Med. Chem.*, 1988, **31**, 2235. In this sense, 'privileged' compound classes generally offer much more than one might imagine, *i.e.* a multitude of various applications that are unrelated and non-trivial to foresee. While this is certainly true for viologens, we believe it can also be claimed about helicenes.

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