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Search for Conglomerate in Set of [7]Helquat Salts: Multigram Resolution of Helicene–Viologen Hybrid by Preferential Crystallization

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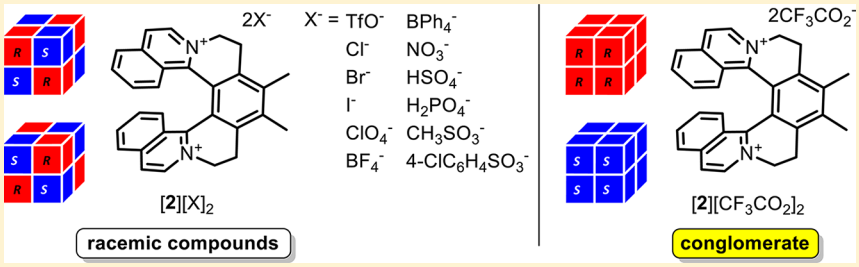
Supporting Information



ABSTRACT: Investigation of a set of 12 [7]helquat salts by X-ray crystal diffraction led to identification of conglomerate behavior in bis(trifluoroacetate) salt [**2**][CF_3CO_2]$_2$. This is to demonstrate that a systematic search for conglomerates can be performed for a given helicenoid enabling straightforward multigram resolution via preferential crystallization. Subsequently, preferential crystallization of this chiral helicene–viologen hybrid has been established to obtain pure *P* and *M* enantiomers on a multigram scale, 5 g each. Furthermore, preparation of nonracemic samples of [7]helquat **2** via diastereomeric (*R*,*R*)-dibenzoyltartrate salts is described, and determination of absolute configuration and racemization barrier is also reported.

INTRODUCTION

Conglomerates are substances that form two separate enantiomeric solid phases upon crystallization of their racemates (Figure 1a).[1,2]

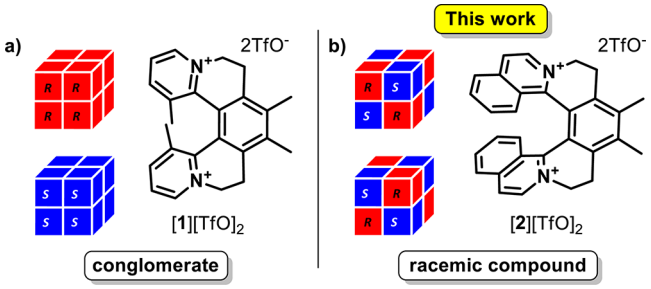


Figure 1. (a) [5]Helquat derivative [**1**][TfO]$_2$ happens to be a conglomerate enabling resolution via preferential crystallization (PC), whereas (b) [7]helquat [**2**][TfO]$_2$ is a racemic compound and is therefore unsuitable for PC.

However, only 5–10% of racemates exhibit conglomerate behavior. Despite this relatively low natural occurrence, conglomerates have been instrumental for preparative stereochemistry since its dawn in 1848, when Pasteur manually separated enantiomers of sodium ammonium tartrate.[3] Today, conglomerates are pivotal to a high mass-throughput resolution process called preferential crystallization (PC),[1,4] which is used in industry. Another, particularly powerful technique relying on conglomerates is a recently discovered attrition-induced deracemization based[5] on Viedma ripening.[6]

In our recent studies, we introduced helquats, which represent a structural link between helicenes[7] and viologens (Scheme 1).[8] Our efforts have been driven by a hypothesis that crossbreeding rich fields of viologens and helicenes will lead to interesting[9] and applicable chemistry. In the search for straightforward and robust methods to prepare our novel helicene–viologen hybrids in enantiopure form,[10] we turned to explore conglomerates. In the context of the growing importance of conglomerates and the impressive breakthroughs reported in this field in the last years,[11] conglomerates of helicenes and their congeners are attractive and remain underused. In spite of the fact that conglomerates in the helicenoid structural family have been detected relatively frequently[12−14] in the past (e.g., [7]helicene,[14e] Scheme 1), until recently,[12] they have not been employed to obtain enantiomers of helical aromatics on multigram scale.

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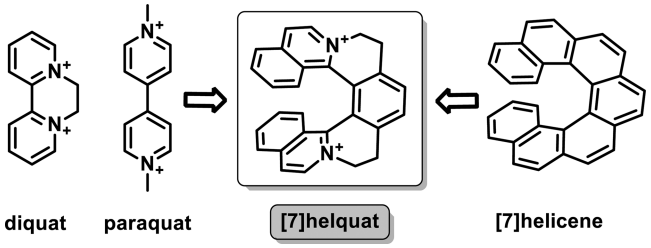
Scheme 1. Helquats Represent a Structural Link between Helicenes and Herbicides Diquat and Paraquat



Unfortunately, at the moment, there is no reliable method to predict if a particular compound will be a conglomerate.[15] This represents a major restriction to applicability of conglomerates. Although it is generally referred to 5−10% frequency of occurrence of conglomerates, the actual proportion may be as high as 20%, at least in some compound classes.[16,17] Interestingly, in 1981, Jacques group studied a set of more than 500 salts and estimated that probability of finding conglomerate in salts is 2 or 3 times greater than in the family of covalent racemates.[18] According to a recently published rule of thumb, it is expected that screen of dozens of salts for a given chiral amine (or acid) usually leads to identification of at least one conglomerate.[19]

Herein, we report our results on an active search for a conglomerate in a set of salts of [7]helquat **2** (Figure 2). Next, with

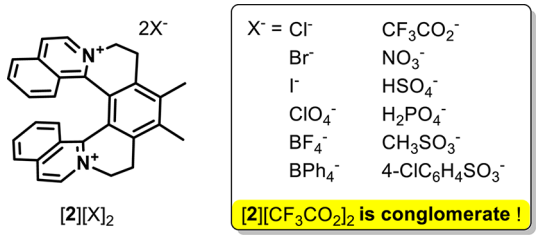


Figure 2. To find a conglomerate, a set of 12 [7]helquat salts $[\mathbf{2}][X]_2$ was prepared from $[\mathbf{2}][TfO]_2$ by anion exchange.

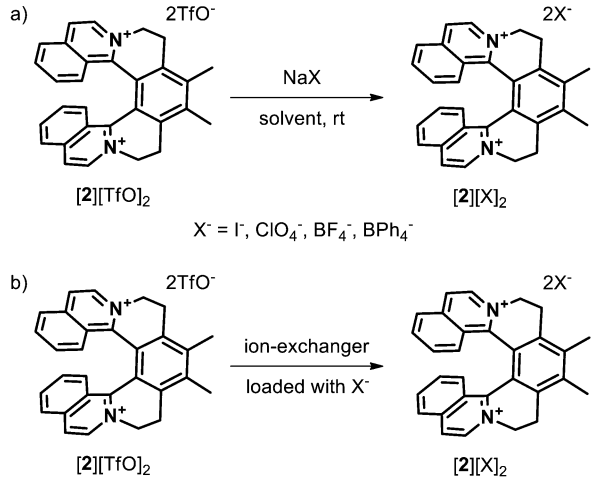
helquat $[\mathbf{2}][CF_3CO_2]_2$ identified as a conglomerate, we describe PC to obtain *P* and *M* enantiomers on multigram scale (5 g of each enantiomer). This is to demonstrate that systematic investigation of various salts for a given helical dication leads to identification of a conglomerate suitable for straightforward multigram resolution via PC.

RESULTS AND DISCUSSION

Our recent discovery that [5]helquat derivative $[\mathbf{1}][TfO]_2$ forms a conglomerate was serendipitous. By employing PC, we were able to take advantage of this finding to obtain 10 g of each enantiomer of helical salt $[\mathbf{1}][TfO]_2$.[12] As the preparative power of PC to obtain nonracemic helicenes and helicene-like compounds in multigram quantities is attractive and remains underused, we became interested in expanding this useful approach. To demonstrate that the preparative utility of this method can be more general, we set out to search actively for conglomerates in [7]helquat series.

Synthesis of [7]Helquat Salts $[\mathbf{2}][X]_2$. The [7]helquat bistriflate $[\mathbf{2}][TfO]_2$ did not show conglomerate behavior.[20] We reasoned that systematic investigation of various salts for a given helical dication will eventually lead to identification of a conglomerate. With the given helical dication [**2**], this task is reduced to the synthesis of a set of salts with various anions and probing their solid phase behavior. The $[rac\text{-}\mathbf{2}][TfO]_2$ was converted to a set of twelve salts by anion exchange adopting either simple precipitation experimental protocol in case of iodide, perchlorate, tetrafluoroborate, and tetraphenylborate (Scheme 2a), or alternatively, ion-exchange resin technique for the remaining eight salts was used (Scheme 2b).

Scheme 2. Preparation of a Series of Salts of [7]Helquat [2] by (a) Precipitation and (b) Anion-Exchange Resin Technique



Search for Conglomerate. With the 12 salts in hand, we began to search for conglomerate. Second Harmonic Generation (SHG) developed by Coquerel group[21] as the attractive approach for scanning solids for conglomerate behavior was not available to us. Therefore, we opted for X-ray crystal diffraction measurement as a way to detect conglomerates.[22] Whereas $[\mathbf{2}][Cl]_2$, two different polymorhps of $[\mathbf{2}][Br]_2$, $[\mathbf{2}][I]_2$, $[\mathbf{2}][ClO_4]_2$, $[\mathbf{2}][BF_4]_2$, $[\mathbf{2}][BPh_4]_2$, $[\mathbf{2}][NO_3]_2$, $[\mathbf{2}][HSO_4]_2$, $[\mathbf{2}][H_2PO_4]_2$, $[\mathbf{2}][CH_3SO_3]_2$, and $[\mathbf{2}][4\text{-}ClC_6H_4SO_3]_2$ all crystallized as racemic compounds, trifluoroacetate salt $[\mathbf{2}][CF_3CO_2]_2$ formed a conglomerate. Specifically, $[P\text{-}\mathbf{2}][CF_3CO_2]_2$ crystallized in the tetragonal space group $P4_32_12$, that belongs to one of the 11 pairs of enantiomorphic space groups, consequently the $[M\text{-}\mathbf{2}][CF_3CO_2]_2$ enantiomer would crystallize in the second space group, namely in $P4_12_12$. The quality of 8 crystal structures out of the 12 prepared salts allowed their full X-ray characterization.[23] In all 8 cases, the racemate crystallized as a racemic compound. The five remaining salts were not of sufficient crystallographic quality to allow full X-ray crystal characterization; however, it was possible to assign the space group in all salts measured (Table 1). Based on the information regarding the space group in these five salts, it can be concluded that [7]helquat [**2**] perchlorate, tetrafluoroborate, dihydrogenphosphate, and 4-chlorobenzenesulfonate crystallize as racemic compounds, whereas [7]helquat [**2**] trifluoroacetate forms a conglomerate. The confirmation of the conglomerate behavior in case of trifluoroacetate salt $[\mathbf{2}][CF_3CO_2]_2$ came with the initial successful PC trials on a 1 g scale (see the Experimental Section for details).

Preferential Crystallization with 5 g Samples of $[\mathbf{2}][CF_3CO_2]_2$. A graphical summary of the key steps in PC of [7]helquat [**2**] trifluoroacetate is provided in Scheme 3. The procedure takes place in two-step cycles, and the results from

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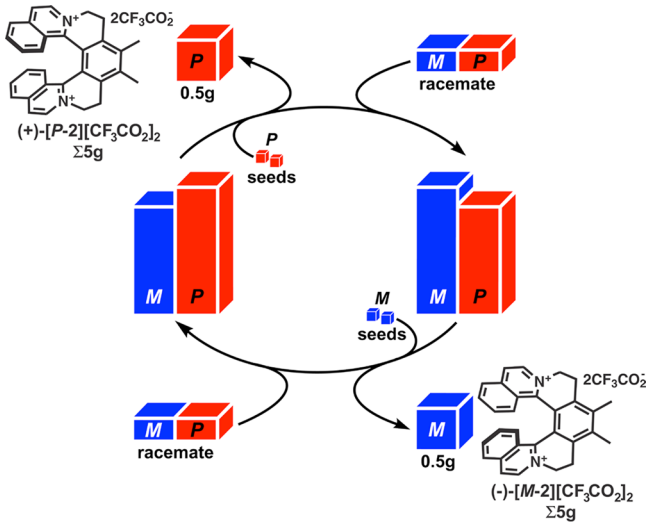
Table 1. Selected Crystal Structure Characteristics of the Prepared [7]Helquat Salts[a]

	X⁻ =						
[**2**][X]$_2$	Cl^-	Br^-	Br^-	I^-	ClO_4^-	BF_4^-	BPh_4^-
CCDC no.	861621	861619	861620	857138	857141[b]	857140[b]	861625
chemical formula	$C_{30}H_{26}N_2{\cdot}2Cl$	$C_{30}H_{26}N_2{\cdot}2Br$	$C_{30}H_{26}N_2{\cdot}2Br$	$C_{30}H_{26}N_2{\cdot}2I$	$C_{30}H_{26}N_2{\cdot}2(ClO_4)$	$C_{30}H_{26}N_2{\cdot}2(BF_4)$	$C_{30}H_{26}N_2{\cdot}2(BC_{24}H_{20})$
crystal system	orthorhombic	monoclinic	orthorhombic	orthorhombic	monoclinic	monoclinic	triclinic
space group	*Pnna*	$P2_1/c$	*Pccn*	*Pccn*	$P2_1/n$	$P2_1/n$	$P\bar{1}$
	X⁻ =						
[**2**][X]$_2$	$CF_3CO_2^-$	NO_3^-	HSO_4^-	$H_2PO_4^-$	$CH_3SO_3^-$	4-$ClC_6H_4SO_3^-$	
CCDC no.	857139[b]	861624	861622	861617[b]	861623	861618[b]	
chemical formula	$C_{30}H_{26}N_2{\cdot}2(C_2F_3O_2)$	$C_{30}H_{26}N_2{\cdot}2(NO_3)$	$C_{30}H_{26}N_2{\cdot}2(HSO_4){\cdot}H_2O$	$C_{30}H_{26}N_2$	$C_{30}H_{26}N_2{\cdot}2(CH_3SO_3)$	$C_{30}H_{26}N_2$	
crystal system	tetragonal	monoclinic	tetragonal	tetragonal	orthorhombic	orthorhombic	
space group	$P4_32_12$	$P2_1/c$	$I4_1/acd$	$P4_2/mbc$	*Pbcn*	*Pca* 2_1	

[a]For details, see the Supporting Information. [b]The quality of the X-ray data allowed us to determine the space group only.

Scheme 3. Simplified Graphical Summary of Preferential Crystallization[a]



[a]Nine repetitions of this cycle led to 5 g samples of each enantiomer of [7]helquat [**2**][CF_3CO_2]$_2$.

the individual crystallization runs are listed in Table 2. In the representative example (run 15) enantioenriched [**2**]-[CF_3CO_2]$_2$ (5.00 g, 5.0% ee in favor of the *P* enantiomer) was dissolved in 150 mL of acetonitrile. The solution was allowed to stir for 30 min at room temperature for "sterilization".[24] To the stirred acetonitrile solution (stirring rate 280 rpm) was added 250 mL of ethyl acetate in one portion. Immediately after that, 3.7 mg of seeds of enantiopure (+)-[*P*-**2**][CF_3CO_2]$_2$ was added to the supersaturated solution to facilitate crystallization of the major *P* component. Because the *P* enantiomer was supersaturated with respect to the *M* enantiomer, it crystallized preferentially upon seeding from the stirred mixture. After 18 min, the mixture was filtered, and polarimetric analysis of the precipitate showed its enantiomeric enrichment in favor of the *P* enantiomer (0.83 g, $[\alpha]_D$ = +530.3, 83.1% ee). The filtrate exhibited enantiomeric excess in favor of the opposite enantiomer (i.e., *M*), thus enabling continuation of the process after the sample was supplemented with racemate to 5 g. By following the next crystallization step, this time starting with the sample enriched in the *M* enantiomer (run 16), 1.04 g of precipitate was obtained ($[\alpha]_D$ = −515.0, 80.7% ee), leaving the filtrate enriched in the *P* enantiomer. By repeating this cyclic procedure nine times, both enantiomers of the [7]helquat [**2**][CF_3CO_2]$_2$ were obtained in multigram quantities in enantioenriched form. Finally, all *P* fractions were combined (see Tables 2 and 6) and recrystallized twice to give 5 g of (+)-[*P*-**2**]-[TfO]$_2$ (>96% ee). Similarly, all *M* fractions were combined and recrystallized twice resulting in 5 g of (−)-[*M*-**2**][TfO]$_2$ (>96% ee). Enantiocomposition analysis of the two multigram samples after recrystallization was performed using chiral capillary electrophoresis (CE) with a heptakis(2,3-di-*O*-acetyl-6-*O*-sulfo)-*β*-cyclodextrin chiral selector.[25]

Table 2. Summary of Individual Runs during Preferential Crystallization Experiments

		[7]helquat collected (g)			
run no.	[*rac*-**2**][CF_3CO_2]$_2$ added (g)	(*P*)	ee_P (%)	(*M*)	ee_M (%)
1	4.79	0.79	84.0		
2	1.01			0.66	84.3
3	0.42	0.69	86.3		
4	0.82			0.82	86.8
5	0.75	0.92	86.0		
6	0.93			0.83	83.3
7	0.68	0.62	88.2		
8	0.45			0.95	50.1
9	0.86	0.66	87.6		
10	0.68			0.78	78.9
11	0.83	0.65	88.5		
12	0.58			0.43	87.0
13	0.38	0.63	87.2		
14	0.65			0.69	84.0
15	0.61	0.83	83.1		
16	0.84			1.04	80.7
17	1.07	0.69	86.9		
18	0.74			0.85	84.3
	0.78				
total	17.87[a]	6.48		7.05	

[a]5 g of scalemic sample recovered (6.8% ee_P).

Chromatography-Free Synthesis of Racemic [7]-Helquat Derivative [*rac*-2][TfO]$_2$. [7]Helquat **2** bistriflate was prepared via a three-step procedure in gram quantities as depicted in Scheme 4. The synthetic sequence consisted of Sonogashira coupling and bisquaternization followed by [2 + 2 + 2] cycloisomerization.[26] Of particular note are the chromatography-free purification protocols employed in this study. The reaction mixture after the Sonogashira coupling was filtered and the compound **3** was obtained in 61% yield after

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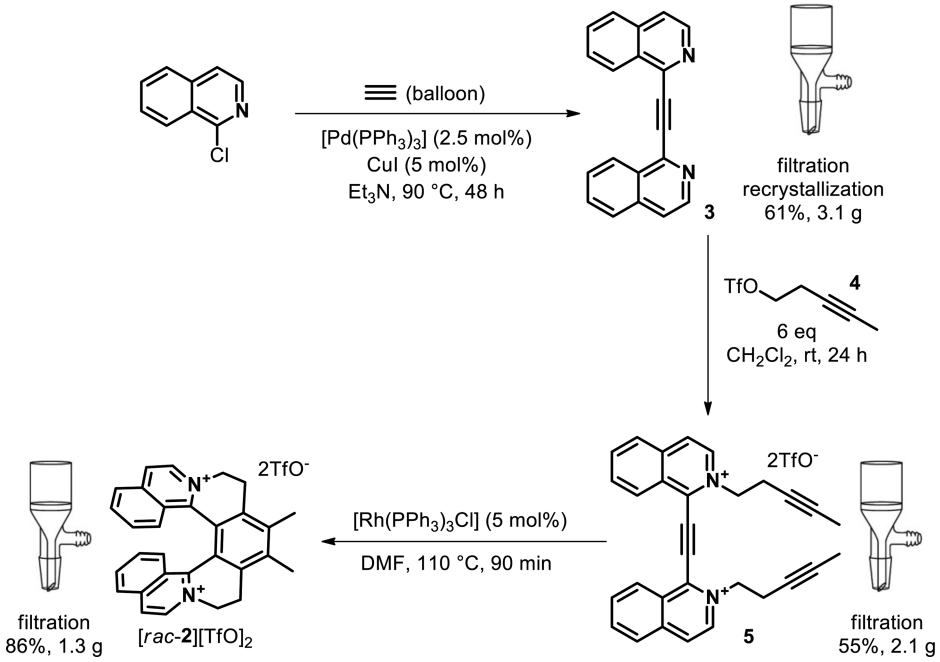
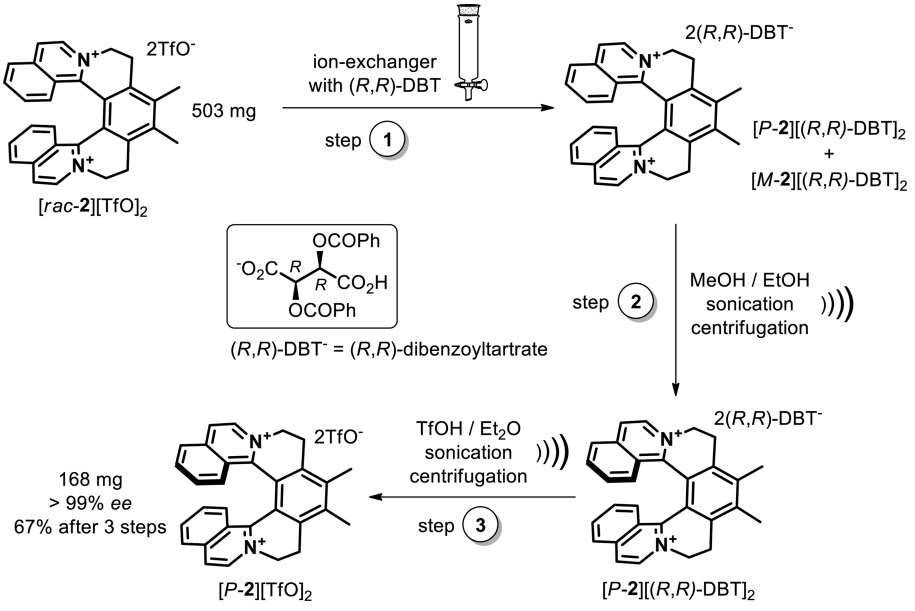
Scheme 4. Three-Step Synthetic Entry to Racemic [7]Helquat Derivative [*rac*-2][TfO]$_2$



Scheme 5. Resolution of [*rac*-2][TfO]$_2$ via Diastereomeric Salts



recrystallization of the crude product from cyclohexane. Compound **3** was then subjected to bisquaternization, giving the triyne **5** in 55% yield after straightforward sonication of the crude product in mixture of ethyl acetate and acetone (see Figure S1 (Supporting Information) for the X-ray crystal structure of **5**).[27] The final [2 + 2 + 2] cycloaddition gave the [7]helquat **2** bistriflate in 86% yield after simple removal of the volatiles from the reaction mixture followed by sonication of the residue in binary solvent composed of ethyl acetate and acetone. All three synthetic steps in the described procedure are exclusively skeleton-building, which makes the preparative entry to [*rac*-**2**][TfO]$_2$ very direct. By repeating this three-step synthetic sequence, more than 20 g of the racemic [*rac*-**2**][TfO]$_2$ was accumulated for the resolution studies.

Resolution of [*rac*-2][TfO]$_2$ via Diastereomeric Salts. Practical resolution procedure of [*rac*-**2**][TfO]$_2$ via diastereomeric salts was developed prior to our PC efforts (Scheme 5). This first-generation resolution approach opened an entry to the two enantiomers of [7]helquat **2** before the conglomerate was identified, and the multigram PC protocol was pursued. This initial resolution campaign secured not only samples of the two enantiomers of high ee (>96% ee, milligram quantities) needed as seeds for PC experiments but also allowed us to produce a multigram sample of low ee (5% ee, 5 g), which was essential for our multigram PC study. The resolution procedure for [7]helquat **2** via diastereomeric dibenzoyltartrate salts is based on a protocol previously established for [5]helquat.[28]

The triflate salt of racemic helquat [*rac*-**2**][TfO]$_2$ was converted to a mixture containing two diastereomeric (*R*,*R*)-

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dibenzoyltartrate salts, [*P*-**2**][(*R*,*R*)-DBT]$_2$ and [*M*-**2**][(*R*,*R*)-DBT]$_2$, using ion-exchange resin technique (step 1 in Scheme 5). We found that the less soluble diastereomer [*P*-**2**][(*R*,*R*)-DBT]$_2$ was readily separated by repeated trituration of the mixture containing the two diastereomeric salts with binary solvent composed of MeOH and EtOH, which selectively dissolves [*M*-**2**][(*R*,*R*)-DBT]$_2$. By employing this straightforward procedure, a 268 mg quantity of [*P*-**2**][(*R*,*R*)-DBT]$_2$ was prepared (step 2). Chiral CE using sulfated β-cyclodextrin chiral selector[25] showed that diastereomeric purity was greater than 96% de. The subsequent ion exchange of the dibenzoyltartrate anions for the triflate anions (step 3) was effected by sonicating the suspension of solid [*P*-**2**][(*R*,*R*)-DBT]$_2$ diastereomer in solution of trifluoromethanesulfonic acid in diethyl ether. This interesting process, [*P*-**2**][(*R*,*R*)-DBT]$_2$ → [*P*-**2**][TfO]$_2$, is a solid to solid transformation, and the resulting helquat ditriflate salt is separated by centrifugation of the suspension followed by supernatant removal. The [7]helquat [*P*-**2**][TfO]$_2$ was thus obtained without any loss of enantiomeric purity as confirmed by CE (>96% ee). The enantiomeric salt [*M*-**2**][TfO]$_2$ was obtained by analogous procedure using (*S*,*S*)-dibenzoyltartrate anion.

Determination of Absolute Configuration and Racemization Barrier of [7]Helquat 2. The absolute configuration of the (+)-[*P*-**2**][TfO]$_2$ was assigned by single-crystal X-ray analysis (Figure S1, Supporting Information). The [7]-helquat **2** is thus no exception to the general empirical helicity rule that *P*-configured helicenoids are dextrorotatory.[29]

To determine the racemization barrier of the resolved helquat (+)-[*P*-**2**][TfO]$_2$, its stirred solution in DMSO was heated at 100 °C under argon atmosphere, and samples were taken after each 30 min. The progress of the racemization was followed by chiral CE using a heptakis(2,3-di-*O*-acetyl-6-*O*-sulfo)-β-cyclodextrin chiral selector.[25] Analysis of the data allowed estimation of the rate constant k, activation free energy ΔG, and racemization half-life $T_{1/2}$ (Table 3, see the Experimental Section for details).

Table 3. Racemization Characteristics of [2][TfO]$_2$ Determined at 100 °C in DMSO on the Basis of Chiral Analysis by CE

T (°C)	k (h^{-1})	$\Delta G^{\ddagger}$ (kJ·mol^{-1})	$T_{1/2}$ (h)
100.0	0.021	129.5	16.5

CONCLUSION

In summary, a search for conglomerates in a set of 12 salts of [7]helquat **2** was carried out. Investigation of solid-state properties of the salts by X-ray crystal diffraction analysis led to identification of conglomerate behavior in bis(trifluoroacetate) salt [**2**][CF_3CO_2]$_2$. This approach takes advantage of helquat's ionic nature and represents a general method for seeking a conglomerate. As far as we know, active screening for conglomerates by exploring a series of salts of the same helicenoid skeleton has never been performed before. Next, with helquat [**2**][CF_3CO_2]$_2$ identified as a conglomerate we described preferential crystallization to obtain *P* and *M* enantiomer on multigram scale (5 g of each enantiomer). This represents an advantageous approach to preparation of multigram quantities of both enantiomers of helical dication **2**. Furthermore, a procedure for obtaining milligrams of nonracemic [7]helquat **2** via diastereomeric (*R*,*R*)-dibenzoyltartrate salts is reported, and determination of absolute configuration and racemization barrier is also described. We expect that the results presented in this report will resonate in the context of the development of chemistry of helicenes and their congeners[7a] as well as the recent breathtaking advances in chiral resolution technologies, namely those relying on conglomerates.[11,30]

EXPERIMENTAL SECTION

General Methods. Thin-layer chromatography (TLC) analysis was performed on silica gel plates (silica gel 60 F254-coated aluminum sheets) and visualized by UV (UV lamp 254/365 nm) and/or chemical staining with $KMnO_4$ [$KMnO_4$ (1% aq), Na_2CO_3 (2% aq)]. TLC analysis of organic cation salts was achieved using Stoddart's magic mixture[31] (MeOH/NH_4Cl_{aq}(2 M)/$MeNO_2$ 7:2:1) as eluent on silica gel plates. NMR spectra were measured using NMR spectrometers on the following frequencies: 600 MHz for ^{1}H, 151 MHz for ^{13}C, 61 MHz for ^{15}N; or 500 MHz for ^{1}H, 126 MHz for ^{13}C, 470 MHz for ^{19}F; or 400 MHz for ^{1}H, 101 MHz for ^{13}C, 377 MHz for ^{19}F. The solvents were $CDCl_3$ (δ_H = 7.26 ppm, δ_C = 77.00 ppm) with TMS as internal standard (δ_H = 0 ppm), acetone-d_6 referenced to the CHD_2COCD_3 peak (δ_H = 2.05 ppm) and to the CD_3COCD_3 (δ_C = 29.80 ppm), or DMSO-d_6 (δ_H = 2.50 ppm and δ_C = 39.50 ppm). ^{15}N NMR spectra were referenced to the nitromethane peak (δ_N = 0 ppm). Chemical shifts are given on a δ scale as parts per million (ppm); coupling constants (J) are given in hertz. Where indicated, the signal assignments in the NMR spectra are unambiguous; the numbering scheme is arbitrary and is shown in the inserts. Where assigned, all ^{1}H and ^{13}C resonance assignments are based on analysis of H,H-COSY, H,H-ROESY, H,C-HSQC, and H,C-HMBC spectra. HRMS ESI spectra were measured using an orbitrap mass analyzer. Specific rotations [α] at 589 nm (g/100 mL) were measured in methanol at 25 °C, and the concentrations range was c = 0.24−0.33 g per 100 mL unless stated otherwise. Dichloromethane and triethylamine were purified by way of distillation under argon over CaH_2 and were used directly after distillation. DMF was degassed immediately before use via the freeze−pump−thaw method. For preferential crystallization ethyl acetate for HPLC and acetonitrile for HPLC were used. All starting materials and reagents were obtained from commercial suppliers and used without further purification unless stated otherwise. Demineralized water was used unless otherwise stated. Demineralization was accomplished via filtration through ion exchange columns (Lewatit S100 for catex column, Lewatit MP500 for anex column) in a demineralization ion-exchange station type ID-PP and IDKP. Thermal racemization experiments were done in a commercially available block thermostat using a temperature regulator constructed at IOCB development workshops.

Capillary Electrophoresis (CE). Capillary electrophoresis (CE) measurements were carried out in an in-house built device.[32] Briefly, computer-controlled high voltage module CZE 2000 and pneumatic valves were used for delivery of separation voltage and performing capillary filling, flushing, and hydrodynamic injection of analytes, respectively. Zones of analytes were detected by UV absorbance at 206 nm. The Clarity data station (DataApex, Prague, Czech Republic) was employed for data acquisition and subsequent analysis. Evaluation of optical purity of the samples was based on the corrected (migration time normalized) peak areas.[33]

For chiral analysis, untreated fused silica capillaries with an outer polyimide coating of 50/375 μm id/od (Polymicro Technologies, Phoenix, AZ) were used in 29/40 cm effective/total length. A background electrolyte consisted of 22 mM sodium, 35 mM phosphate buffer, pH 2.4, and a chiral selector, 6 mM heptakis(2,3-di-*O*-acetyl-6-*O*-sulfo)-β-cyclodextrin heptasodium salt. Samples as ca. 10 mM aqueous solution were injected into the capillary hydrodynamically under a pressure of 300 Pa for 2 s. Separation voltage was −12 kV (i.e., cathode at the injection capillary end) at an ambient temperature of 22−25 °C (Figure 3).

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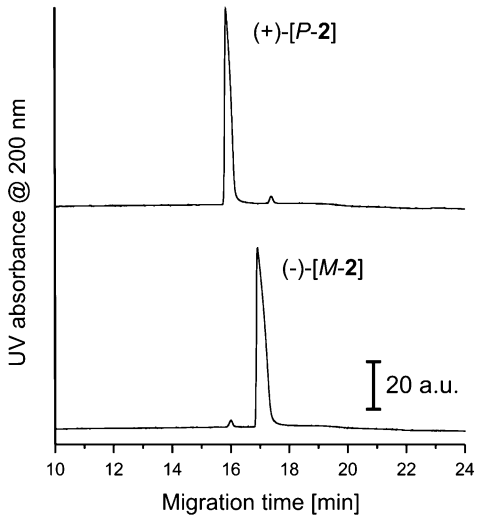
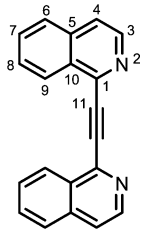


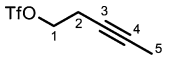
Figure 3. CE with heptakis(2,3-di-*O*-acetyl-6-*O*-sulfo)-*β*-cyclodextrin chiral selector showing the enantiomeric purity (≥96% ee) of the two multigram samples of (+)-[*P*-**2**][CF_3CO_2]$_2$ and (−)-[*M*-**2**][CF_3CO_2]$_2$ after recrystallization.

Synthesis of [*rac*-2][TfO]$_2$. *1,2-Di(isoquinolin-1-yl)ethyne (**3**).*



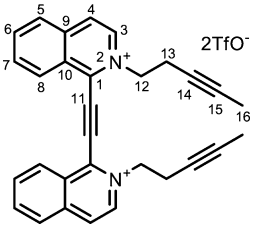
1-Chloroisoquinoline (5.93 g, 36.2 mmol), [Pd(PPh_3)$_4$] (1.05 g, 0.905 mmol, 2.5 mol %), and CuI (345 mg, 1.81 mmol, 5 mol %) in this order were placed in a Schlenk flask and placed under argon. Freshly distilled and degassed triethylamine (95 mL) was added. The flask was disconnected from the argon line and connected to the balloon filled with acetylene. The atmosphere was exchanged by way of piercing the septum with a long needle. The reaction was stirred at 90 °C for 48 h. Progress of the reaction was checked by TLC (hexane/ethyl acetate 50:50, product R_f = 0.35). Workup: The reaction mixture was cooled to rt, filtered through a Celite pad on a glass sinter and washed with ethyl acetate (2 L), and the volatiles from the solution were removed on a rotary evaporator. Cyclohexane (750 mL) was added to the crude product, and the mixture was stirred under reflux condenser (oil bath temperature 115 °C) for 1 h. Then the hot liquid was filtered through a preheated Celite pad on a glass sinter and concentrated until the first crystals appeared in the solution, and the mixture was then left in the refrigerator overnight. The crystals that formed were filtered on a glass sinter and dried, giving 3.10 g (61%) of brown-yellow solid. This protocol represents an improved procedure avoiding chromatography during purification of compound **3**. For previous procedures, see ref 8a,b. ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ = 7.90−7.95 (m, 4H, H-7 and H-8), 8.00 (dd, J = 5.6, 1.1 Hz, 2H, H-4); 8.12−8.15 (m, 2H, H-6); 8.71 (d, J = 5.6 Hz, 2H, H-3); 8.72−8.74 (m, 2H, H-9). ^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ = 90.9 (C-11), 122.4 (C-4), 127.1 (C-9), 128.2 (C-6), 129.7 (C-8), 130.4 (C-10), 131.9 (C-7), 136.8 (C-5), 143.9 (C-1), 144.2 (C-3). The analytical data are in agreement with literature.[8a,b]

*Alkynyl Triflate **4**, Pent-3-ynyl Trifluoromethanesulfonate.*[12]



3-Pentyn-1-ol (8.0 mL, 7.30 g, 86.7 mmol) was placed in a round-bottomed flask and placed under argon. Pyridine (6.8 mL, 6.78 g, 85.9 mmol, 0.99 equiv) was added followed by freshly distilled CH_2Cl_2 (80 mL), and this mixture was stirred at rt for 1 min. A Schlenk flask was placed under argon, and Tf_2O (15.0 mL, 25.22 g, 88.5 mmol, 1.02 equiv) was added by way of needle and syringe followed by CH_2Cl_2 (80 mL). The pyridine−alcohol mixture precooled to 0 °C was slowly added to the stirring solution of triflic anhydride cooled to 0 °C to keep the mixture cold. After completion of the addition, the mixture was stirred at 0 °C for 30 min. Workup: 30 mL of water was added to the mixture, the resulting mixture was stirred for 5 min, and then all of the material was transferred to a separatory funnel using additional 10 mL of CH_2Cl_2. The organic layer was separated, another portion of CH_2Cl_2 (60 mL) was added, and the water layer was extracted again. Combined CH_2Cl_2 layers were dried with $MgSO_4$ and filtered, and the solvent was carefully removed on rotary evaporator. The crude product was distilled in Kugelrohr to obtain 17.26 g (92%, 79.8 mmol) of alkynyl triflate **4** as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.78 (t, J = 2.5, 3H, H-5), 2.67 (tq, J = 6.9, 2.5 Hz, 2H, H-2), 4.53 (t, J = 6.9 Hz, 2H, H-1). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 3.3, 20.2, 71.7, 74.4, 79.4, 118.6 (q, J = 319.6 Hz). The analytical data are in agreement with literature.[34]

*Triyne **5**, 1,1′-(Ethyne-1,2-diyl)bis(2-(pent-3-yn-1-yl)isoquinolin-2-ium) Trifluoromethanesulfonate.*



The substrate **3** (1.50 g, 5.35 mmol) was placed in a Schlenk flask and put under argon. Freshly distilled CH_2Cl_2 (150 mL) was added, and the substrate was dissolved by stirring. Then the triflate **4** (6.95 g, 5.3 mL, 32.11 mmol, 6 equiv) was slowly added by syringe and needle. The flask was covered with aluminum foil and stirred at rt for 24 h. Workup: The mixture was transferred to a round-bottomed flask and the volatiles were removed on rotary evaporator. Ethyl acetate/acetone mixture (5:1) (70 mL) was then added to the residue, and the mixture was sonicated for 5 min giving a suspension of a brown powder. The suspension was centrifuged, and the supernatant was removed. Next, 60 mL of ethyl acetate/acetone 5:1 mixture was added, the suspension was sonicated and centrifuged, and the supernatant was removed. This sonication-centrifugation procedure was repeated once more to obtain 2.10 g of triyne **5** (55%) as a beige powder. Mp: 239−241 °C (acetone/ethyl acetate). R_f = 0.25 (SiO_2, eluent: Stoddart's Magic mixture 7:2:1 MeOH/2 M aq solution of NH_4Cl.$MeNO_2$).[31] ^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ = 1.75 (t, J = 2.5, 6H, H-16), 3.30−3.34 (m, 4H, H-13), 5.59 (t, J = 6.5, 4H, H-12), 8.33 (ddd, J = 1.1, 6.9, 8.7, 2H, H-7), 8.49 (ddd, J = 1.1, 6.9, 8.4, 2H, H-6), 8.64 (dt, J = 8.4, 1.0, 2H, H-5), 9.01 (dd, J = 1.0, 6.8, 2H, H-4), 9.18 (dq, J = 8.7, 0.9, 2H, H-8), 9.28 (d, J = 6.8, 2H, H-3). ^{13}C NMR (151 MHz, $(CD_3)_2CO$): δ = 3.2 (C-16), 21.8 (C-13), 61.2 (C-12), 74.3 (C-15), 82.1 (C-14), 96.2 (C-11), 128.8 (C-4), 129.3 (C-5), 129.9 (C-8), 131.1 (C-10), 134.4 (C-7), 138.5 (C-3), 138.6 (C-6 and C-9), 138.9 (C-1). ^{15}N NMR (60.8 MHz, $(CD_3)_2CO$): δ = −172.9. IR (KBr): $\tilde{\nu}$ (cm^{-1}) 3127w, 3078 m, 2233vw, 1623 m, 1607 m, 1389 m, 1340 m, 1273vs,sh, 1268vs, 1169s, 1029vs, 637s. MS (ESI) m/z: 595 [(M − TfO + MeOH)$^+$] (100), 563 [(M − TfO)$^+$] (8). HRMS (ESI) m/z: [(M − TfO)$^+$] ($C_{31}H_{26}F_3N_2O_3S$) calcd 563.1611, found 563.1611. Anal. Calcd for $C_{32}H_{26}F_6N_2O_6S_2$: C (53.93), H (3.68), N (3.93). Found: C (53.75), H (3.71), N (3.79).

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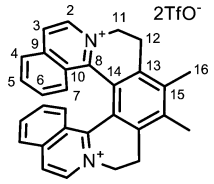
*10,11-Dimethyl-8,9,12,13-tetrahydrodiisoquinolino[1,2-a:2′,1′-k][2,9]phenanthroline-7,14-diium Trifluoromethanesulfonate, [**2**][TfO]$_2$.*



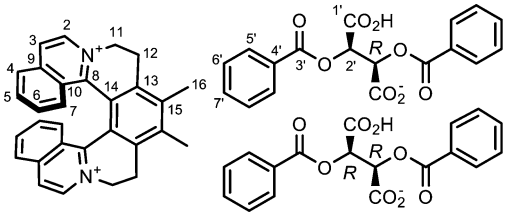
The substrate **5** (1.50 g, 2.1 mmol) and [Rh(PPh$_3$)$_3$Cl] (97 mg, 0.105 mmol, 5 mol %) were placed in a Schlenk flask and put under argon. Degassed DMF (150 mL) was added, and the mixture was stirred at 110 °C for 90 min. Workup: The mixture was transferred to a round-bottomed flask, and the volatiles were removed on rotary evaporator. Next, 100 mL of ethyl acetate/acetone mixture (5:1) was added to the residue, and the mixture was sonicated for 5 min giving a suspension of a brownish powder. The suspension was centrifuged and the supernatant was removed. Then, 60 mL of ethyl acetate/acetone 5:1 mixture was added, the suspension was sonicated and centrifuged, and the supernatant was removed. This sonication−centrifugation procedure was repeated once more to obtain 1.30 g of helquat [**2**][TfO]$_2$ (86%) as a beige powder. Mp: 319−321 °C (acetone/ethyl acetate). R_f = 0.36 (SiO$_2$, eluent: Stoddart's Magic mixture 7:2:1 MeOH/2 M aq solution of NH$_4$Cl·MeNO$_2$).[31] ^{1}H NMR (600 MHz, (CD$_3$)$_2$CO): δ = 2.55 (s, 6H, H-16), 3.34 (bdt, J = 0, 4.0, 15.4 Hz, 2H, H-12), 3.75 (ddd, J = 2.0, 3.3, 16.8, 2H, H-12), 5.26 (bdt, J = ≠ 0, 3.3, 14.1, 2H, H-11), 5.29 (ddd, J = 2.0, 4.0 13.8, 2H, H-11), 7.48 (ddd, J = 1.2, 7.0, 8.1, 2H, H-6), 7.61 (ddd, J = 0.9, 1.2, 8.5, 2H, H-4), 7.61 (ddd, J = 1.1, 7.0, 8.5, 2H, H-5), 7.71 (ddt, J = 1.1, 8.1, 0.6, 2H, H-7), 8.04 (bd, J = 0, 6.6, 2H, H-3), 8.81 (dt, J = 6.6, 0.7, 2H, H-2). ^{13}C NMR (151 MHz, (CD$_3$)$_2$CO): δ = 17.2 (C-16), 26.2 (C-12), 55.6 (C-11), 125.3 (C-3), 126.2 (C-14), 126.7 (C-4), 127.1 (C-10), 128.5 (C-7), 132.2 (C-6), 137.0 (C-5), 137.3 (C-2), 138.7 (C-9), 140.8 (C-13), 142.4 (C-15), 151.3 (C-8). ^{15}N NMR (60.8 MHz, (CD$_3$)$_2$CO): δ = −182.1. IR (KBr): $\tilde{\nu}$ (cm^{-1}) 1629 m, 1609w, 1571w, 1553w, 1509w, 1477vw, 1403w, 1380w, 1359w, 1275vs, 1263vs, 1224 m, 1161 m, 1140 m, 1030s, 768w, 639 m, 573w, 517 m. MS (ESI) m/z: 563 [(M-TfO)$^+$] (100), 414 [(M-2TfO)$^+$] (70), 207 [(M-2TfO)$^{2+}$] (10). HRMS (ESI) m/z: [(M − TfO)$^+$] (C$_{31}$H$_{26}$O$_3$N$_2$F$_3$S) calcd 563.1611, found 563.1610. Anal. Calcd for C$_{32}$H$_{26}$F$_6$N$_2$O$_6$S$_2$: C (53.93), H (3.68), N (3.93). Found: C (53.91), H (3.73), N (3.81).

Preparation of Anion-Exchange Resin. *Step A.* Strongly basic anion-exchange resin in Cl$^-$ cycle (Dowex 1 × 2, chloride form, 16−100 mesh) was mixed with water in a column equipped with a Teflon tap. For uninterrupted smooth flow of liquid through the ion-exchanger column a sinter S0 or a piece of cotton-wool plug at the bottom part of the column is recommended. The amount of resin used for the experiment was measured in terms of resin volume (in Cl$^-$ cycle) in water. Generally, for 100 mg of the [7]helquat [**2**][TfO]$_2$ to be exchanged, 10 mL of the resin in the initial Cl$^-$ cycle was necessary. The resin was allowed to swell in demineralized water for ca. 12 h. Switching from a Cl$^-$ cycle to an OH$^-$ cycle was done by passing 2 M aq NaOH through the resin (for 10 mL of the resin 150 mL was used). Completion of the exchange determined by the absence of Cl$^-$ anions was checked by taking a few drops of the basic solution aside to a small vial, acidifying it with a few drops of aq HNO$_3$ (1:1) solution, until the universal pH-paper test detected acidic reaction, and finally adding two drops of 0.1 M aq AgNO$_3$ solution. Completely clear solution in this test indicated the absence of Cl$^-$ anions (absence of AgCl precipitate). At that point, demineralized water (100 mL for the mentioned volume) was run through the resin until neutral reaction of the liquid was detected (universal pH paper test). Subsequently, water was exchanged to MeOH by washing the column with sufficient amount of MeOH (50 mL for the mentioned volume). All bubbles were removed by mixing the resin with a long needle or by stoppering the column and turning it gently upside down and back so that all beads of the resin nicely mixed with MeOH and no bubbles remained. Consequently, the resin in OH$^-$ phase was loaded with the appropriate anions as described below (in step B).

Step B. A 0.2 M solution of the selected acid in MeOH or water was passed through the ion-exchanger after step A with the flow rate of approximately 2 drops per second until the liquid at the outlet was acidic (as checked by universal pH paper). The amount of the 0.2 M acidic solution for the initial 10 mL of the ion-exchanger in the Cl$^-$ phase was approximately 50 mL. For the individual acids, see the respective sections below. The column was then stoppered and mixed by turning it gently upside down and back so that all the resin beads mixed entirely with the methanolic or aqueous solution and no bubbles remained. This was very important, as it eliminated residual OH$^-$ anions which can react with the base-sensitive dicationic species. After this, MeOH (100 mL for the initial 10 mL of the resin) was run through the column until neutral reaction was detected in the eluent at the bottom of the column. At this point, the resin was ready for exchange of anion in helquat salts as described in the Experimental Section.

Resolution of Racemic [7]Helquat [*rac*-2][TfO]$_2$ via Diastereomeric Salts. *Step 1: Transformation of [rac-**2**][TfO]$_2$ to [rac-**2**][(R,R)-DBT]$_2$. rac-10,11-Dimethyl-8,9,12,13-tetrahydrodiisoquinolino[1,2-a:2′,1′-k][2,9]phenanthroline-7,14-diium (2R,3R)-2,3-Bis-(benzoyloxy)-3-carboxypropanoate, [rac-**2**][(R,R)-DBT]$_2$.* A solution of [*rac*-**2**][TfO]$_2$ (503.2 mg, 0.706 mmol) in 50 mL of MeOH was allowed to sink in an ion-exchange resin (50 mL) loaded with (*R*,*R*)-DBT$^-$ anions. Then 500 mL of MeOH was used to remove the substrate from the ion-exchange resin completely as determined by TLC. Workup: The volatiles from the solution of the product were removed on a rotary evaporator giving 727.2 mg of crude [*rac*-**2**][(*R*,*R*)-DBT]$_2$ as a yellow solid ([α]$_D$ = −20.1, c = 0263, DMSO). Complete exchange of triflate anions was verified by the absence of a signal in ^{19}F NMR.

*Step 2: Separation of Diastereomeric Salts To Produce [P-**2**][(R,R)-DBT]$_2$. (P)-10,11-Dimethyl-8,9,12,13-tetrahydrodiisoquinolino[1,2-a:2′,1′-k][2,9]phenanthroline-7,14-diium (2R,3R)-2,3-Bis(benzoyloxy)-3-carboxypropanoate, [P-**2**][(R,R)-DBT]$_2$*



A mixture of MeOH/EtOH 1:1 (50 mL) was added to the crude [*rac*-**2**]-[(*R*,*R*)-DBT]$_2$ (727.2 mg). The mixture was shortly sonicated and filtered rinsing the flask walls with EtOH (10 mL). The solid was then washed with ethyl acetate (20 mL). This procedure involving sonication in a MeOH/EtOH mixture was repeated once more with 50 mL and once with 10 mL of this solvent mixture. After this triple sonication−filtration procedure, diastereomer [*P*-**2**][(*R*,*R*)-DBT]$_2$ (268.5 mg, 0.238 mmol, 67%) was obtained as a yellow solid ([α]$_D$ = +385.6, c = 0.258, DMSO, 99.8% ee). The ratio of the diastereomers was checked by CE. Mp: 143−145 °C (MeOH/EtOH). R_f = 0.33 (SiO$_2$, eluent: Stoddart's Magic mixture 7:2:1 MeOH/2 M aq solution of NH$_4$Cl/MeNO$_2$).[31] ^{1}H NMR (600 MHz, DMSO-d_6): δ = 2.60 (s, 6H, H-16), 3.27 (ddd, J = 7.0, 12.0, 16.4 Hz, 2H, H-12), 3.69 (dt, J = 16.4, 2.8, 2H, H-12), 5.66 (s, 2H, H-2′), 5.21 (ddd, J = 2.7, 7.0, 14.2, 2H, H-11), 5.23 (ddd, J = 3.2, 12.0, 14.2, 2H, H-11), 7.44 (ddd, J = 1.3, 6.9, 8.6, 2H, H-6), 7.45−7.48 (m, 4H, H-6′), 7.52 (dq, J = 8.6, 0.9, 2H, H-7), 7.59−7.62 (m, 4H, H-7′), 7.69 (ddd, J = 1.1, 6.9, 8.1, 2H, H-5), 7.78 (ddt, J = 1.3, 8.1, 0.8, 2H, H-4), 7.89−7.91 (m, 4H, H-5′), 8.14 (dd, J = 0.8, 6.7, 2H, H-3), 8.8 (d, J = 6.7, 2H, H-2). ^{13}C NMR (151 MHz, DMSO-d_6): δ = 16.6 (C-16), 24.8 (C-12), 53.8 (C-11), 70.8 (C-2′), 123.9 (C-3), 124.7 (C-14), 125.5 (C-10), 125.6 (C-7), 127.1 (C-4), 128.5 (C-6′), 129.0 (C-5′), 129.3 (C-4′), 130.6 (C-6), 133.3 (C-7′), 134.6 (C-5), 136.1 (C-2), 137.0 (C-13), 139.4 (C-15), 140.6 (C-9), 149.4 (C-8), 164.6 (C-3′), 167.3 (C-1′). IR (KBr): $\tilde{\nu}$ (cm^{-1}) 3090w, 3066w, 3034vw, 3011vw, 1721vs, 1625 m, 1603 m, 1584vw, 1571w, 1552w, 1507w, 1474vw, 1432vw, 1402vw, 1380vw, 1356w, 1266s, 1177w, 1113 m, 718s, 689w. MS (ESI) m/z: 771 [(M − DBT)$^+$] (10), 413 [(M − 2DBT − H)$^+$] (100), 207 [(M − 2DBT)$^{2+}$] (67). HRMS

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(ESI) m/z: [(M − DBT)$^+$] ($C_{48}H_{39}N_2O_8$) calcd 771.27009, found 771.26991.

Step 3: Anion Exchange from [P-2][(R,R)-DBT]$_2$ to [P-2][TfO]$_2$ via Sonication. [*P*-**2**][(*R*,*R*)-DBT]$_2$ (268.5 mg, 0.238 mmol, $[\alpha]_D$ = +385.6, *c* = 0.258, DMSO, 99.8% ee) was sonicated with TfOH/Et_2O 1:99 mixture (8 mL) for 5 min. The solid softened during the first sonication, and after that the clear supernatant was removed. Next, another portion of the TfOH solution (8 mL) was added, the mixture was again sonicated and the soft solid turned less soft and finally a yellowish powder formed. The mixture was centrifuged and the supernatant was removed. This sonication−centrifugation procedure with TfOH solution was repeated once more and the resulting solid was three times sonicated in pure diethyl ether, centrifuged, and the supernatant was removed to get rid of the excess triflic acid. Product [*P*-**2**][TfO]$_2$ was obtained as a yellowish solid (168.2 mg, 0.236 mmol, 99%, $[\alpha]_D$ = +572.7, *c* = 0.271, MeOH, 99.8% ee). The enantiomeric purity was checked by CE. This enantiocomposition analysis by CE showed that no loss of stereointegrity of the sample occurred during the ion-exchange procedure. Mp: 308−310 °C (Et_2O).

Procedure To Obtain [M-2][TfO]$_2$. The procedure to obtain compound [*M*-**2**][TfO]$_2$ was analogous to that described for [*P*-**2**][TfO]$_2$ in steps 1−3 above. (*S*,*S*)-Dibenzoyl tartrate anion was used instead of (*R*,*R*)-dibenzoyltartrate anion. Initial anion exchange starting with [*rac*-**2**][TfO]$_2$ (313.9 mg, 0.440 mmol) gave crude [*rac*-**2**][(*S*,*S*)-DBT]$_2$ (855.4 mg, $[\alpha]_D$ = +59.0, *c* = 0.251, DMSO). Next, [*M*-**2**][(*S*,*S*)-DBT]$_2$ was isolated (76.8 mg, 0.068 mmol, $[\alpha]_D$ = −375.0, c = 0.237, DMSO, 98.2% ee. Mp: 145−147 °C MeOH/EtOH). Finally, [*M*-**2**][TfO]$_2$ was obtained as a yellow solid (46.5 mg, 0.065 mmol, 30% of *M* enantiomer, $[\alpha]_D$ = −572.4, *c* = 0.261, MeOH, 98.2% ee; mp 306−308 °C, Et_2O).

Racemization Barrier of [7]Helquat [*P*-2][TfO]$_2$. The racemization was performed in a block heater with the temperature set so that the actual temperature in the reaction vessel was as required. [*P*-**2**][TfO]$_2$ (2.2 mg, 3.09 μmol) was dissolved in distilled DMSO (0.3 mL), transferred to an NMR tube, and purged with argon. This tube was put into the hole of the block-heater filled with a Rotitherm heating medium. The real temperature was gauged with a probe put to a neighboring hole not touching the walls. The measurement was performed at 100 °C. Before the beginning of the process, a sample for CE analysis (ca. 10 μL) was taken with a capillary. The NMR tube was then heated and samples for CE were taken with a capillary every 30 min (each sample ca. 10 μL). The experiment was finished after 210 min. The decreasing amount of [*P*-**2**][TfO]$_2$ in the mixture as followed by CE is listed in Table 4 and plotted in a graph in Figure 4.

Table 4. Data from the Racemization Study of [*P*-2][TfO]$_2$ in DMSO at 100 °C As Followed by CE

time (min)	*P* (%)	*M* (%)	ee$_P$ (%)	ln(ee$_P$)
0	100.0	0.0	100.0	4.605170
36	98.9	1.0	97.9	4.583947
60	98.0	2.0	96.0	4.564348
90	96.4	3.6	92.8	4.530447
120	96.5	3.5	93.0	4.532599
150	95.5	4.5	91.0	4.510860
180	93.8	6.2	87.6	4.472781
210	92.7	7.3	85.4	4.447346

Racemization process is a combination of two elemental processes: (*P*)-enantiomer converts to (*M*)-enantiomer with rate constant *k* and (*M*)-enantiomer converts to (*P*)-enantiomer with the same rate constant *k*. When these two processes are combined, the enantiomeric excess (ee) of one enantiomer (or optical rotation of the sample) decays also by first order kinetics with rate constant 2*k* (eq 1, decay of enantiomeric excess ee$_P$ according to first-order kinetics)

$$ee_P = ee_{P0} \cdot e^{-2kt} \quad (1)$$

where ee$_{P0}$ is the initial enantiomeric excess of [*P*-**2**][TfO]$_2$.

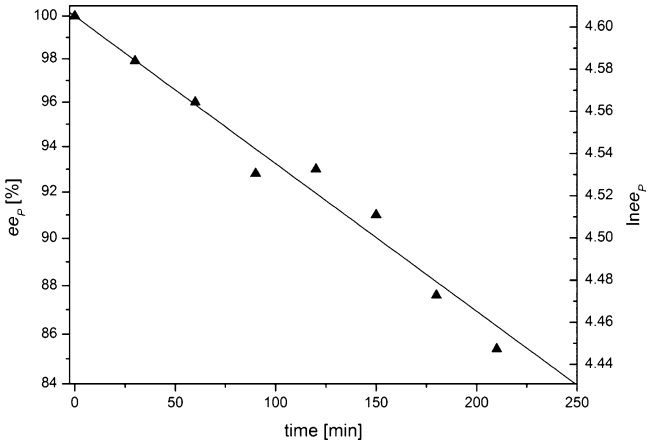

Figure 4. Racemization of [*P*-**2**][TfO]$_2$ in DMSO at 100 °C. Dependence of natural logarithm of the enantiomeric excess ln(ee$_P$) on time as determined by CE.

Ee$_P$ from CE experiment thus decays according to the first order kinetics. The natural logarithm of ee$_P$ was plotted against time and a trendline was calculated as a straight line. This trendline in the form $y = -2kx + a$ gave the kinetic constant 2*k*. From this value, half-life of racemization can be calculated (eq 2, half-life expressed using rate constant *k*):

$$T_{1/2} = \frac{\ln 2}{2k} \quad (2)$$

According to the theory of transition state, rate constant *k* can be transformed into activation Gibbs energy. This is the barrier of interconversion of one enantiomer into the other. The Gibbs free energy was calculated using eq 3 (Gibbs free energy calculation), where R = 8.314472 J·K^{-1}·mol^{-1} is the gas constant, T is the thermodynamic temperature (in K), k is a kinetic constant obtained from the measurement, h = 6.62606896 × 10^{-34}, J·s is Planck's constant, k_B = 1.3806504 × 10^{-23} J, and K^{-1} is Boltzmann constant.

$$\Delta G^{\ddagger} = -RT \ln \frac{kh}{k_B T} \quad (3)$$

The experimental value was thus $\Delta G^{\ddagger}$ = 129.5 kJ·mol^{-1} (measured at 100 °C) determining the half-life to be 16 h 33 min at 100 °C (Table 3).

Preferential Crystallization Attempts with [2][TfO]$_2$. *Attempt 1.* [7]Helquat [**2**][TfO]$_2$ (100.0 mg) enantioenriched in (−)-[*M*-**2**][TfO]$_2$ ($[\alpha]_D$ = −40.9, *c* = 0.286, MeOH, 6.8% ee) was dissolved in acetone (40.0 mL), and the solution was then stirred at rt for 30 min. Ethyl acetate (40.0 mL) was then added followed immediately by seeds of (−)-[*M*-**2**][TfO]$_2$ (0.8 mg, 98% ee). The mixture was stirred at rt for 20 min (400 rpm), the mixture was centrifuged, and the supernatant was removed. (−)-[*M*-**2**][TfO]$_2$ (40.3 mg) ($[\alpha]_D$ = −9.7, *c* = 0.279, MeOH, 1.6% ee) was obtained as a yellow solid. The supernatant was concentrated to dryness giving 60.6 mg of a yellow solid enantioenriched in (−)-[*M*-**2**][TfO]$_2$ ($[\alpha]_D$ = −15.7, *c* = 0.273, MeOH, 2.5% ee).

Attempt 2. [7]Helquat [**2**][TfO]$_2$ (100.0 mg) enantioenriched in (−)-[*M*-**2**][TfO]$_2$ ($[\alpha]_D$ = −42.2, *c* = 0.263, MeOH, 7.0% ee) was dissolved in acetone (40.0 mL), and the solution was then stirred at rt for 30 min. Ethyl acetate (40.0 mL) was then added followed immediately by seeds of (−)-[*M*-**2**][TfO]$_2$ (0.8 mg, 98% ee). The mixture was stirred at rt for 15 min (250 rpm) and centrifuged, and the supernatant was removed. (−)-[*M*-**2**][TfO]$_2$ (8.4 mg) ($[\alpha]_D$ = −14.4, *c* = 0.243, MeOH, 2.4% ee) was obtained as a yellow solid. The supernatant was concentrated to dryness giving 93.7 mg of a yellow solid enantioenriched in (−)-[*M*-**2**][TfO]$_2$ ($[\alpha]_D$ = −54.2, *c* = 0.258, MeOH, 9.0% ee).

Anion Exchange To Seek Conglomerate. *General Procedure for Anion Exchange via Anion-Exchange Resin.* The ion-exchange

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Table 5. ^{1}H NMR Data of the Individual Salts of [7]Helquat 2 (600 MHz, DMSO-d_6, 300 K)[a]

	hydrogen no.										
anion	H-2	H-3	H-4	H-5	H-6	H-7	H-11a	H-11b	H-12a	H-12b	H-16
Cl^-	8.98	8.18	7.80	7.70	7.47	7.54	5.26	5.29	3.27	3.70	2.61
Br^-	8.70	8.01	7.71	7.64	7.42	7.44	5.08	5.12	3.19	3.63	2.56
I^-	8.90	8.16	7.79	7.70	7.45	7.53	5.21	5.27	3.28	3.70	5.61
ClO_4^-	8.88	8.15	7.78	7.70	7.44	7.52	5.20	5.24	3.27	3.70	2.61
BF_4^-	8.80	8.15	7.78	7.70	7.44	7.52	5.20	5.23	3.27	3.70	2.61
BPh_4^-	8.85	8.12	7.76	7.67	7.42	7.51	5.17	5.20	3.23	3.66	2.59
$CF_3CO_2^-$	8.91	8.16	7.77	7.70	7.44	7.53	5.21	5.25	3.27	3.70	2.61
NO_3^-	8.89	8.16	7.78	7.70	7.44	7.52	5.24	5.24	3.27	3.70	2.61
HSO_4^-	8.89	8.16	7.78	7.70	7.44	7.52	5.21	5.23	3.27	3.70	2.61
$H_2PO_4^-$	8.85	8.12	7.76	7.67	7.42	7.51	5.17	5.20	3.23	3.66	2.59
$CH_3SO_3^-$	8.90	8.16	7.78	7.70	7.45	7.52	5.24	5.24	3.27	3.70	2.61
4-$ClC_6H_4SO_3^-$	8.89	8.15	7.78	7.69	7.44	7.52	5.20	5.24	3.26	3.68	2.59

[a]The chemical shifts correspond to the center values of each multiplet.

resin in OH^- cycle was loaded with the corresponding acid using 0.2 M solution of the acid in MeOH (in case of CF_3CO_2H, H_2SO_4, H_3PO_4, CH_3SO_3H, and 4-$ClC_6H_4SO_3H$) or in water (HNO_3 and HBr). [*rac*-**2**][TfO]$_2$ was dissolved in MeOH (for amounts see the individual procedures below) and transferred to the ion-exchange resin column. The solution was allowed to slowly (1−2 drops per second) sink in the ion-exchange resin and MeOH was then used to elute the helquat out of the resin. The volatiles from the resulting solution were removed on rotary evaporator and the product was recrystallized from a suitable mixture of solvents (see the individual procedures below for details). In case of X^- = Cl^-, the anion-exchange resin in Cl^- cycle was used as obtained from the supplier without any additional modification. The yields of salts after the individual anion exchanges ranged from 59 to 95% depending on the respective anions. The following series of salts was prepared this way: [*rac*-**2**][X]$_2$ (X^- = Cl^-, Br^-, $CF_3CO_2^-$, NO_3^-, HSO_4^-, $H_2PO_4^-$, $CH_3SO_3^-$, and 4-$ClC_6H_4SO_3^-$).

General Procedure for Anion Exchange via Precipitation. The starting [*rac*-**2**][TfO]$_2$ was dissolved in acetone and the corresponding inorganic salt (NaI, $NaClO_4{\cdot}H_2O$, $NaBF_4$, $NaBPh_4$) dissolved in acetone was added. A precipitate formed either immediately or in a few minutes. The mixture was then stirred overnight, filtered, sonicated in acetone twice, and centrifuged, and the supernatant was removed. The yields ranged from 66 to 98%. The following series of salts was prepared this way: [*rac*-**2**][X]$_2$ (X^- = I^-, ClO_4^-, BF_4^-, and BPh_4^-). The ^{1}H NMR data for the individual salts discussed in this section are summarized in Table 5.

10,11-Dimethyl-8,9,12,13-tetrahydrodiisoquinolino[1,2-a:2′,1′-k][2,9]phenanthroline-7,14-diium Chloride, [rac-2][Cl]$_2$. The starting [*rac*-**2**][TfO]$_2$ (200.0 mg, 0.280 mmol) was dissolved in 20 mL MeOH and transferred to a column containing 20 mL of the ion-exchange resin loaded with Cl^- anions. The solution was allowed to slowly sink in the ion-exchange resin, and then an additional 60 mL of MeOH was passed through the resin to elute the helquat. The volatiles from the solution were removed on rotary evaporator. 0.5 mL of MeOH was added to dissolve the product followed by 5 mL of acetone causing precipitation. The mixture was sonicated, centrifuged, and the supernatant was removed. The product [*rac*-**2**][Cl]$_2$ was obtained as a yellow solid in 60% yield (80.9 mg, 0.167 mmol). Mp: >350 °C (MeOH/acetone). R_f = 0.33 (SiO_2, eluent: Stoddart's Magic mixture 7:2:1 MeOH/2 M aq solution of $NH_4Cl/MeNO_2$).[31] ^{13}C NMR (101 MHz, DMSO-d_6): δ = 16.8, 24.9, 53.8, 124.0, 124.8, 125.5, 125.8, 127.2, 130.8, 134.7, 136.3, 137.1, 139.5, 140.7, 149.5. IR (KBr): $\tilde{\nu}$ (cm^{-1}) 3053w, 2924vw, 1625vs, 1607 m, 1569 m, 1547 m, 1505 m, 1476w, 1455w, 1401 m, 1381 m, 1359s, 878vw, 811vs, 670w. MS (ESI) *m*/*z*: 513 [(M − Cl)$^+$] (50), 413 [(M − 2Cl − H)$^+$] (32), 207 [(M − 2Cl)$^{2+}$] (100). HRMS (ESI) *m*/*z*: [(M − Cl)$^+$] ($C_{30}H_{26}ClN_2$) calcd 449.17790, found 449.17839. Anal. Calcd for $C_{30}H_{28}Cl_2N_2O$: C (71.57), H (5.61), N (5.56). Found: C (71.26), H (5.57), N (5.23).

10,11-Dimethyl-8,9,12,13-tetrahydrodiisoquinolino[1,2-a:2′,1′-k][2,9]phenanthroline-7,14-diium Bromide, [rac-2][Br]$_2$. The starting [*rac*-**2**][TfO]$_2$ (84.0 mg, 0.118 mmol) was dissolved in 10 mL of MeOH and transferred to a column containing 20 mL of the ion-exchange resin loaded with Br^- anions. The solution was allowed to slowly sink in the ion-exchange resin, and then an additional 100 mL of MeOH was passed through the resin to elute the helquat. The volatiles from the solution were removed on rotary evaporator. MeOH (0.5 mL) was added dissolving the solid followed by 5 mL of acetone causing precipitation. The mixture was sonicated and centrifuged, and the supernatant was removed. The product [*rac*-**2**][Br]$_2$ was obtained as a yellow solid in 86% yield (58.7 mg, 0.102 mmol). Mp: >350 °C (MeOH/acetone). R_f = 0.33 (SiO_2, eluent: Stoddart's Magic mixture 7:2:1 MeOH/2 M aq solution of $NH_4Cl/MeNO_2$).[31] ^{13}C NMR (101 MHz, DMSO-d_6): δ = 16.8, 24.9, 53.9, 124.0, 124.8, 125.6, 125.8, 127.2, 130.8, 134.7, 136.2, 137.1, 139.5, 140.7, 149.5. IR (KBr): $\tilde{\nu}$ (cm^{-1}) 3045w, 1623vs, 1605 m, 1569 m, 1549 m, 1506 m, 1475w, 1458w, sh, 1401 m, 1381 m, 1359s, 877vw, 814s, 670w. MS (ESI) *m*/*z*: 413 [(M − 2Br − H)$^+$] (56), 207 [(M − 2Br)$^{2+}$] (100). HRMS (ESI) *m*/*z*: [(M − Br^-)$^+$] ($C_{30}H_{26}N_2Br$) calcd 493.12739, found 493.12707. Anal. Calcd for $C_{30}H_{27}Br_2N_2O_{1/2}$: C (61.77), H (4.67), N (4.80), Br (27.39). Found: C (61.92), H (4.52), N (4.58), Br (27.36).

10,11-Dimethyl-8,9,12,13-tetrahydrodiisoquinolino[1,2-a:2′,1′-k][2,9]phenanthroline-7,14-diium Iodide, [rac-2][I]$_2$. The starting [*rac*-**2**][TfO]$_2$ (66.0 mg, 0.093 mmol) was dissolved in 20 mL of acetone, and NaI (140.2 mg, 0.926 mmol, 10 equiv) in 1 mL acetone was added at once. Immediately after the addition the solution turned dark and an orange precipitate formed. The mixture was stirred at rt for 4 h. Workup: The mixture was transferred to two vials, centrifuged, and the supernatant was removed. The remaining solids were twice sonicated in 1 mL of acetone and centrifuged, and the supernatants were removed. The product [*rac*-**2**][I]$_2$ was obtained as a dark orange solid in 98% yield (60.5 mg, 0.091 mmol). Mp: >350 °C (acetone). R_f = 0.33 (SiO_2, eluent: Stoddart's Magic mixture 7:2:1 MeOH/2 M aq solution of $NH_4Cl/MeNO_2$).[31] ^{13}C NMR (101 MHz, DMSO-d_6): δ = 16.9, 24.9, 53.9, 124.0, 124.8, 125.6, 125.8, 127.2, 130.8, 134.7, 136.2, 137.1, 139.5, 140.7, 149.5; IR (KBr): $\tilde{\nu}$ (cm^{-1}) 3044w, 1623vs, 1605 m, 1568 m, 1548 m, 1505 m, 1474w, 1437 m, 1400 m, 1379 m, 1357 m, 877vw, 819 m, 810s, 670w; MS (ESI) *m*/*z*: 541 [(M-I)$^+$] (2), 414 [(M-2I)$^+$] (75), 207 [(M-2I)$^{2+}$] (100). HRMS (ESI) *m*/*z*: [(M-I)$^+$] ($C_{30}H_{26}N_2I$) calcd 541.11352, found 541.11328. Anal. Calcd for $C_{30}H_{27}I_2N_2O_{1/2}$: C (53.20), H (4.02), N (4.14). Found: C (53.18), H (4.04), N (3.90).

19,20-Dimethyl-1,2,17,18-tetrahydrodiisoquinolino[1,2-a:2′,1′-k][2,9]phenanthroline-3,16-diium Perchlorate, [rac-2][ClO$_4$]$_2$. The starting [*rac*-**2**][TfO]$_2$ (65.1 mg, 0.091 mmol) was dissolved in 20 mL of acetone, and $NaClO_4{\cdot}H_2O$ (130.9 mg, 0.913 mmol, 10 equiv) in 5 mL of acetone was added at once. In less than 1 min a precipitate formed from the homogeneous mixture. The mixture was then stirred overnight. Workup: The suspension was transferred to three vials and centrifuged, and the supernatants were removed. To each vial was

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added 4 mL of acetone, the contents were sonicated and centrifuged, and the supernatants were removed. The product [*rac*-**2**][ClO_4]$_2$ was obtained as a yellow solid in 78% yield (43.6 mg, 0.071 mmol). Mp: >350 °C (acetone). R_f = 0.33 (SiO_2, eluent: Stoddart's Magic mixture 7:2:1 MeOH/2 M aq solution of NH_4Cl/$MeNO_2$).[31] ^{13}C NMR (101 MHz, DMSO-d_6): δ = 16.8, 24.9, 53.8, 124.0, 124.8, 125.6, 125.7, 127.2, 130.8, 134.7, 136.2, 137.1, 139.5, 140.7, 149.5. IR (KBr): $\tilde{\nu}$ (cm^{-1}) 1626 m, 1608w, 1570w, 1551w, 1508w, 1476w, 1443w, 1402w, 1381w, 1358w, 1102s, 1096vs, br, 878vw, 826 m, 670vw, 624 m. MS (ESI) *m*/*z*: 513 [(M − ClO_4)$^+$] (4), 413 [(M − 2ClO_4 − H)$^+$] (100), 207 [(M − 2ClO_4)$^{2+}$] (36). HRMS (ESI) *m*/*z*: [(M − ClO_4)$^+$] ($C_{30}H_{26}O_4N_2Cl$) calcd 513.15756, found 513.15772. Anal. Calcd for $C_{30}H_{26}Cl_2N_2O_8$: C (58.74), H (4.27), N (4.57). Found: C (58.49), H (4.25), N (4.43).

*19,20-Dimethyl-1,2,17,18-tetrahydrodiisoquinolino[1,2-a:2′,1′-k][2,9]phenanthroline-3,16-diium Tetrafluoroborate, [rac-**2**][BF_4]$_2$.* The starting [*rac*-**2**][TfO]$_2$ (60.0 mg, 0.084 mmol) was dissolved in 20 mL of water, and $NaBF_4$ (94.3 mg, 0.842 mmol, 10 equiv) in 0.5 mL water was added at once. In 2 min a precipitate formed from the homogeneous mixture. The mixture was then stirred overnight. Workup: The suspension was transferred to three vials and centrifuged, and the supernatants were removed. To each vial 0.5 mL water was added, the contents were sonicated and centrifuged, and the supernatants were removed. This procedure with water (0.5 mL for each vial) was repeated once more. The product [*rac*-**2**][BF_4]$_2$ was obtained as a yellow solid in 79% yield (38.6 mg, 0.066 mmol). Mp: >350 °C (water). R_f = 0.33 (SiO_2, eluent: Stoddart's Magic mixture 7:2:1 MeOH/2 M aq solution of NH_4Cl/$MeNO_2$).[31] ^{13}C NMR (101 MHz, DMSO-d_6): δ = 16.8, 24.9, 53.8, 124.0, 124.8, 125.6, 125.7, 127.2, 130.8, 134.7, 136.2, 137.1, 139.5, 140.7, 149.5. IR (KBr): $\tilde{\nu}$ (cm^{-1}) 1626 m, 1608w, 1570w, 1551w, 1508w, 1403w, 1381w, 1359w, 1123 m, 1084vs, 1062vs, 878vw, 826 m, sh, 672vw, 533vw. MS (ESI) *m*/*z*: 501 [(M − BF_4)$^+$] (100), 413 [(M − 2BF_4 − H)$^+$] (25), 207 [(M − 2BF_4)$^{2+}$] (76). HRMS (ESI) *m*/*z*: [(M − BF_4)$^+$] ($C_{30}H_{26}N_2BF_4$) calcd 501.21197, found 501.21200. Anal. Calcd for $C_{30}H_{26}B_2F_8N_2$: C (61.26), H (4.46), N (4.76). Found: C (61.06), H (4.27), N (4.67).

*19,20-Dimethyl-1,2,17,18-tetrahydrodiisoquinolino[1,2-a:2′,1′-k][2,9]phenanthroline-3,16-diium Tetraphenylborate, [rac-**2**][BPh_4]$_2$.* The starting [*rac*-**2**][TfO]$_2$ (57.0 mg, 0.080 mmol) was dissolved in 5 mL of acetone, and $NaBPh_4$ (276.5 mg, 0.800 mmol, 10 equiv) in 5 mL of acetone was added at once. In 10 min a precipitate formed from the homogeneous mixture. The mixture was stirred overnight. Workup: The suspension was transferred to three vials and centrifuged, and the supernatants were removed. To each vial was added 2 mL of acetone, the contents were sonicated and centrifuged, and the supernatants were removed. The solids were combined, sonicated in 2 mL acetone, and centrifuged, and the supernatant was removed. The product [*rac*-**2**][BPh_4]$_2$ was obtained as a yellow, light-sensitive solid in 66% yield (55.6 mg, 0.053 mmol). Mp: 249−251 °C (acetone). R_f = 0.33 (SiO_2, eluent: Stoddart's Magic mixture 7:2:1 MeOH/2 M aq solution of NH_4Cl/$MeNO_2$).[31] ^{1}H NMR (600 MHz, DMSO-d_6): see Table 5 and 5.76−6.81 (m, 8H in anion), 6.89−6.95 (m, 16H in anion), 7.15−7.21 (m, 16H in anion). ^{13}C NMR (101 MHz, DMSO-d_6): δ = 16.8, 24.9, 52.8, 124.0, 124.8, 125.6, 125.8, 127.2, 130.8, 134.7, 136.2, 137.1, 139.5, 140.7, 149.5/ IR (KBr): $\tilde{\nu}$ (cm^{-1}) 3054 m, 3038 m, 1622 m, 1606 m, 1578 m, 1569 m, 1551w, 1507w, 1478 m, 1441w, 1426 m, 1401w, 1380w, 1356 m, 1266w, 1188vw, 1176vw, 1153w, 883vw, 826 m, 814w, 750 m, 735vs, 670vw/ MS (ESI) *m*/*z*: 414 [(M − 2BPh_4)$^+$] (100). HRMS (ESI) *m*/*z*: [(M − BPh_4)$^+$] ($C_{54}H_{46}BN_2$) calcd 733.37486, found 733.37610.

*10,11-Dimethyl-8,9,12,13-tetrahydrodiisoquinolino[1,2-a:2′,1′-k][2,9]phenanthroline-7,14-diium 2,2,2-Trifluoroacetate, [rac-**2**][CF_3CO_2]$_2$.* The starting [*rac*-**2**][TfO]$_2$ (76.6 mg, 0.108 mmol) was dissolved in 10 mL of MeOH and transferred to a column containing 20 mL of the ion-exchange resin loaded with $CF_3CO_2^-$ anions. The solution was allowed to slowly sink in the ion-exchange resin, and then an additional 100 mL MeOH was passed through the resin to elute the helquat completely (as checked by TLC and UV detection at the outflow). The volatiles from the solution were removed on a rotary evaporator. The residue was dissolved in 1 mL of 2-butanone and the solid precipitated upon addition of 5 mL of ethyl acetate. The mixture was sonicated and centrifuged, and the supernatant was removed. The product [*rac*-**2**][CF_3CO_2]$_2$ was obtained as a yellow solid in 77% yield (53.2 mg, 0.083 mmol). Mp: >350 °C (2-butanone/ethyl acetate). R_f = 0.33 (SiO_2, eluent: Stoddart's Magic mixture 7:2:1 MeOH/2 M aq solution of NH_4Cl/$MeNO_2$).[31] ^{13}C NMR (101 MHz, DMSO-d_6): δ = 16.8, 24.9, 53.8, 124.0, 124.8, 125.6, 125.7, 127.2, 130.8, 134.7, 136.2, 137.1, 139.5, 140.7, 149.5. IR (KBr): $\tilde{\nu}$ (cm^{-1}) 3062vw, 1687vs, 1624 m, 1607w, 1568w, 1550w, 1506w, 1475vw, 1440w, 1403w, 1382w, 1359w, 1201s, 1129 m, br, 879vw, 833w, 818 m, 803w, 718w, 673vw. MS (ESI) *m*/*z*: 527 [(M − CF_3CO_2)$^+$] (1), 413 [(M − 2CF_3CO_2 − H)$^+$] (82), 207 [(M − 2CF_3CO_2)$^{2+}$] (100). HRMS (ESI) *m*/*z*: [(M − CF_3CO_2)$^+$] ($C_{32}H_{26}N_2O_2F_3$) calcd 527.19409, found 527.19445. Anal. Calcd for $C_{34}H_{28}F_6N_2O_5$: C (62.01), H (4.29), N (4.25). Found: C (62.05), H (4.20), N (4.02).

*10,11-Dimethyl-8,9,12,13-tetrahydrodiisoquinolino[1,2-a:2′,1′-k][2,9]phenanthroline-7,14-diium Nitrate, [rac-**2**][NO_3]$_2$.* The starting [*rac*-**2**][TfO]$_2$ (73.5 mg, 0.103 mmol) was dissolved in 10 mL of MeOH and transferred to a column containing 20 mL of the ion-exchange resin loaded with NO_3^- anions. The solution was allowed to slowly sink in the ion-exchange resin, and then an additional 100 mL of MeOH was passed through the resin to elute the helquat completely (as checked by TLC and UV detection at the outlet). The volatiles from the solution were removed on rotary evaporator. 2-Butanone (5 mL) was added, the suspension was sonicated and centrifuged, and the supernatant was removed. The product [*rac*-**2**][NO_3]$_2$ was obtained as a yellow solid in 89% yield (49.2 mg, 0.091 mmol). Mp: >350 °C (2-butanone). R_f = 0.33 (SiO_2, eluent: Stoddart's Magic mixture 7:2:1 MeOH/2 M aq solution of NH_4Cl/$MeNO_2$).[31] ^{13}C NMR (101 MHz, DMSO-d_6): δ = 16.8, 24.9, 53.9, 124.0, 124.8, 125.6, 125.7, 127.2, 130.8, 134.7, 136.2, 137.1, 139.5, 140.7, 149.5. IR (KBr): $\tilde{\nu}$ (cm^{-1}) 3063w, br, 1624 m, 1607w, 1570w, 1550w, 1507w, 1475w, 1437w, 1402 m sh, 1384vs, 1354vs, br, 878vw, 671vw. MS (ESI) *m*/*z*: 413 [(M − 2NO_3 − H)$^+$] (100), 207 [(M − 2NO_3)$^{2+}$] (83). HRMS (ESI) *m*/*z*: [(M − NO_3)$^+$] ($C_{30}H_{26}N_3O_3$) calcd 476.19687, found 476.19669. Anal. Calcd for $C_{30}H_{26}N_4O_6$: C (66.91), H (4.87), N (10.40). Found: C (66.58), H (4.81), N (9.86).

*19,20-Dimethyl-1,2,17,18-tetrahydrodiisoquinolino[1,2-a:2′,1′-k][2,9]phenanthroline-3,16-diium Hydrogen Sulfate, [rac-**2**][HSO_4]$_2$.* The starting [*rac*-**2**][TfO]$_2$ (41.9 mg, 0.059 mmol) was dissolved in 10 mL of MeOH and transferred to a column containing 20 mL of the ion-exchange resin loaded with HSO_4^- anions. The solution was allowed to slowly sink in the ion-exchange resin, and then an additional 100 mL of MeOH was passed through the resin to elute the helquat. The volatiles from the solution were removed on rotary evaporator. Acetone (5 mL) was added, the suspension was sonicated and centrifuged, and the supernatant was removed. The product [*rac*-**2**][HSO_4]$_2$ was obtained as a yellow solid in 95% yield (33.9 mg, 0.056 mmol). Mp: >350 °C (acetone). R_f = 0.33 (SiO_2, eluent: Stoddart's Magic mixture 7:2:1 MeOH/2 M aq solution of NH_4Cl/$MeNO_2$).[31] ^{13}C NMR (101 MHz, DMSO-d_6): δ = 16.8, 24.9, 53.9, 124.0, 124.8, 125.6, 125.7, 127.2, 130.8, 134.7, 136.3, 137.1, 139.5, 140.7, 149.5. IR (KBr): $\tilde{\nu}$ (cm^{-1}) 3060w, 2471w,vbr, 2108w, vbr, 1624s, 1606 m, 1569 m, 1549 m, 1506w, 1475w, 1439 m, 1402 m, 1381 m, 1357 m, 1226vs, 1185s, 1163s, 1058 m, 1045s, 888vw, 821s, 670vw, 579s. MS (ESI) *m*/*z*: 511 [(M − HSO_4)$^+$] (2), 413 [(M − 2HSO_4 − H)$^+$] (100), 207 [(M − 2HSO_4)$^{2+}$] (98). Anal. Calcd for $C_{30}H_{30}N_2O_9S_2$: C (57.50), H (4.83), N (4.47). Found: C (57.08), H (4.76), N (4.26).

*19,20-Dimethyl-1,2,17,18-tetrahydrodiisoquinolino[1,2-a:2′,1′-k][2,9]phenanthroline-3,16-diium Dihydrogen Phosphate, [rac-**2**][H_2PO_4]$_2$.* The starting [*rac*-**2**][TfO]$_2$ (59.8 mg, 0.084 mmol) was dissolved in 10 mL of MeOH and transferred to a column containing 20 mL of the ion-exchange resin loaded with $H_2PO_4^-$ anions. The solution was allowed to slowly sink in the ion-exchange resin, and then an additional 100 mL of MeOH was passed through the resin to elute the helquat. The volatiles from the solution were removed on rotary evaporator. The residue was partially dissolved in 1 mL of MeOH and sonicated, and 1 mL of acetone was added to precipitate the solid. The mixture was again sonicated and centrifuged, and the supernatant was

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removed. The product [*rac*-**2**][H_2PO_4]$_2$ was obtained as a yellow solid in 94% yield (47.9 mg, 0.079 mmol). Mp: 260−262 °C (MeOH/acetone). R_f = 0.33 (SiO_2, eluent: Stoddart's Magic mixture 7:2:1 MeOH/2 M aq solution of NH_4Cl/$MeNO_2$).[31] ^{13}C NMR (101 MHz, DMSO-d_6): δ = 17.0, 25.1, 54.0, 124.2, 124.9, 125.7, 125.9, 127.4, 131.0, 134.9, 136.4, 137.3, 139.7, 140.9, 149.7. IR (KBr): $\tilde{\nu}$ (cm^{-1}) 1625 m, 1605w, 1571 m, 1551 m, 1507 m, 1476w, 1448w, 1431w, 1404w, 1380 m, 1356 m, 1068 m, br, 975vs, br, 891 m, 879 m, 502 m, br. MS (ESI) *m*/*z*: 207 [(M − 2H_2PO_4)$^{2+}$] (100). HRMS (ESI) *m*/*z*: [(M − 2H_2PO_4)$^+$] ($C_{30}H_{26}N_2$) calcd 207.10425, found 207.10438.

*19,20-Dimethyl-1,2,17,18-tetrahydrodiisoquinolino[1,2-a:2′,1′-k][2,9]phenanthroline-3,16-diium Methanesulfonate, [rac-**2**][CH_3SO_3]$_2$.* The starting [*rac*-**2**][TfO]$_2$ (57.1 mg, 0.080 mmol) was dissolved in 10 mL of MeOH and transferred to a column containing 20 mL of the ion-exchange resin loaded with $CH_3SO_3^-$ anions. The solution was allowed to slowly sink in the ion-exchange resin, and then an additional 100 mL of MeOH was passed through the resin to elute the helquat. The volatiles from the solution were removed on rotary evaporator. MeOH (0.5 mL) was added, dissolving it, followed by 5 mL of ethyl acetate causing precipitation. The mixture was sonicated and centrifuged, and the supernatant was removed. The product [*rac*-**2**][CH_3SO_3]$_2$ was obtained as a yellow solid in 94% yield (45.5 mg, 0.075 mmol). Mp: >350 °C (MeOH/ethyl acetate). R_f = 0.33 (SiO_2, eluent: Stoddart's Magic mixture 7:2:1 MeOH/2 M aq solution of NH_4Cl/$MeNO_2$).[31] ^{1}H NMR (600 MHz, DMSO-d_6): see Table 5 and 2.29 (s, 6H in anion). ^{13}C NMR (101 MHz, DMSO-d_6): δ = 16.8, 24.9, 53.9, 124.0, 124.8, 125.6, 125.7, 127.2, 130.8, 134.7, 136.3, 137.1, 139.5, 140.7, 149.5. IR (KBr): $\tilde{\nu}$ (cm^{-1}) 3063w, 2929vw, 1626 m, 1606w, 1570w, 1550w, 1506w, 1476w, 1420w, sh, 1403w, 1380w, 1358 m, 1281s, sh, 1208vs, 1195s, 1183vs, 1051 m 1038s, 878vw, 773 m, 551 m. MS (ESI) *m*/*z*: 509 [(M − CH_3SO_3)$^+$] (1), 413 [(M − 2CH_3SO_3 − H)$^+$] (52), 207 [(M − 2CH_3SO_3)$^{2+}$] (100). HRMS (ESI) *m*/*z*: [(M − 2CH_3SO_3)$^{2+}$] ($C_{30}H_{26}N_2$) calcd 207.10425, found 207.10422. Anal. Calcd for $C_{32}H_{33}N_2O_{6.5}S_2$: C (62.62), H (5.42), N (4.56). Found: C (62.40), H (5.36), N (4.38).

*19,20-Dimethyl-1,2,17,18-tetrahydrodiisoquinolino[1,2-a:2′,1′-k][2,9]phenanthroline-3,16-diium 4-Chlorobenzenesulfonate, [rac-**2**][4-Cl$C_6H_4SO_3$]$_2$.* The starting [*rac*-**2**][TfO]$_2$ (91.3 mg, 0.128 mmol) was dissolved in 10 mL of MeOH and transferred to a column containing 20 mL of the ion-exchange resin loaded with 4-Cl$C_6H_4SO_3^-$ anions. The solution was allowed to slowly sink in the ion-exchange resin, and then additional 100 mL MeOH was passed through the resin to elute the helquat. The volatiles from the solution were removed on rotary evaporator. The residue was dissolved in 0.5 mL of MeOH and sonicated, and 10 mL of ethyl acetate was added to precipitate the solid. The mixture was again sonicated and centrifuged, and the supernatant was removed. The product [*rac*-**2**][4-Cl$C_6H_4SO_3$]$_2$ was obtained as a yellow solid in 99% yield (101.2 mg, 0.127 mmol). Mp: 149−151 °C (MeOH/acetone). R_f = 0.33 (SiO_2, eluent: Stoddart's Magic mixture 7:2:1 MeOH/2 M aq solution of NH_4Cl/$MeNO_2$).[31] ^{1}H NMR (600 MHz, DMSO-d_6): see Table 5 and 7.34−7.38 (m, 4H in anion), 7.56−7.60 (m, 4H in anion). ^{13}C NMR (101 MHz, DMSO-d_6): δ = 16.8, 25.0, 53.9, 124.0, 124.8, 125.6, 125.8, 127.3, 127.5, 127.7, 130.8, 133.0, 134.7, 136.3, 137.1, 139.5, 140.8, 147.2, 149.6/ IR (KBr): $\tilde{\nu}$ (cm^{-1}) 3060w, 1625 m, 1606w, 1572w, 1553w, 1507w, 1474 m, 1357 m, 1230vs,sh, 1217vs, 1202vs, 1118 m, 1095w, 1031s, 1006s, 751s, 711w, 483 m. MS (ESI) *m*/*z*: 605 [(M − Cl$C_6H_4SO_3$)$^+$] (9), 413 [(M − 2Cl$C_6H_4SO_3$ − H)$^+$] (50), 207 [(M − 2Cl$C_6H_4SO_3$)$^{2+}$] (100). HRMS (ESI) *m*/*z*: [(M − Cl$C_6H_4SO_3$)$^+$] ($C_{36}H_{30}O_3N_2ClS$) calcd 605.16602, found 605.16619. Anal. Calcd for $C_{42}H_{34}Cl_2N_2O_6S_2$: C (63.23), H (4.30), N (3.51), Cl (8.89), S (8.04). Found: C (62.83), H (4.19), N (3.24), Cl (8.90), S (8.15).

Preferential Crystallization Experiments with [2][CF_3CO_2]$_2$. *Exchange from [P-**2**][TfO]$_2$ to [P-**2**][CF_3CO_2]$_2$ and from [M-**2**][TfO]$_2$ to [M-**2**][CF_3CO_2]$_2$. (P)-10,11-Dimethyl-8,9,12,13-tetrahydrodiisoquinolino[1,2-a:2′,1′-k][2,9]phenanthroline-7,14-diium Trifluoroacetate, [P-**2**][CF_3CO_2]$_2$.* A solution of [*P*-**2**][TfO]$_2$ (168.2 mg, 0.236 mmol, $[\alpha]_D$ = +572.7, *c* = 0.271, MeOH, 98.3% ee) in 20 mL of MeOH was allowed to sink in the ion-exchange resin (20 mL) loaded with $CF_3CO_2^-$ anions. Then, an additional 200 mL of MeOH was used to elute the product from the ion-exchange resin completely (checked by TLC). Workup: The volatiles from the solution were removed on rotary evaporator giving crude [*P*-**2**][CF_3CO_2]$_2$. The solid was shortly sonicated in 3 mL of 2-butanone, then 5 mL ethyl acetate was added, the mixture was sonicated once more and centrifuged, and the supernatant was removed. The product [*P*-**2**]-[CF_3CO_2]$_2$ was obtained as a yellow solid in 99% yield (151.0 mg, 0.236 mmol, $[\alpha]_D$ = +636.7, c = 0.250, MeOH, 99.8% ee; mp: >350 °C MeCN/ethyl acetate). Chiral CE confirmed that no loss of stereointegrity of the sample occurred during the ion-exchange procedure.

*(M)-10,11-Dimethyl-8,9,12,13-tetrahydrodiisoquinolino[1,2-a:2′,1′-k][2,9]phenanthroline-7,14-diium Trifluoroacetate, [M-**2**][CF_3CO_2]$_2$.* [*M*-**2**][CF_3CO_2]$_2$ was prepared similarly to the *P* enantiomer. Starting from [*M*-**2**][TfO]$_2$ (46.5 mg, 0.065 mmol, $[\alpha]_D$ = −572.4, *c* = 0.261, MeOH, 98.2% ee) a yellow solid of [*M*-**2**][CF_3CO_2]$_2$ was obtained (40.9 mg, 0.064 mmol, 98% yield, $[\alpha]_D$ = −626.7, *c* = 0.272, MeOH, 98.3% ee, mp >350 °C MeCN/ethyl acetate). Chiral CE confirmed that no loss of stereointegrity of the sample occurred during the ion-exchange procedure.

*Obtaining Seeds Used in Preferential Crystallization of [7]-Helquat [**2**][CF_3CO_2]$_2$.* The individual runs of preferential crystallization experiments were seeded with enantioenriched crystalline material prepared as follows:

*Seeds of (+)-[P-**2**][CF_3CO_2]$_2$.* The sample of [7]helquat [**2**]-[CF_3CO_2]$_2$ enriched in (+)-[*P*-**2**][CF_3CO_2]$_2$ (567.4 mg, $[\alpha]_D$ = +547.2, *c* = 0.262, MeOH, 85.8% ee) was dissolved in 25.0 mL of acetonitrile. 50.0 mL of ethyl acetate was added and a precipitate formed in a few seconds. The mixture was shortly sonicated and filtered. (+)-[*P*-**2**][CF_3CO_2]$_2$ was isolated as a yellow solid (384.4 mg, $[\alpha]_D$ = +630.0, *c* = 0.286, MeOH, 98.8% ee; acc to CE 95.1% ee). The solid was finely powdered with a pestle in an agate mortar and used for seeding in PC.

*Seeds of (−)-[M-**2**][CF_3CO_2]$_2$.* The sample of [7]helquat [**2**]-[CF_3CO_2]$_2$ enriched in (−)-[*M*-**2**][CF_3CO_2]$_2$ (414.1 mg, $[\alpha]_D$ = −559.2, c = 0.252, MeOH, 87.7% ee) was dissolved in 18.0 mL of acetonitrile. Ethyl acetate (36.0 mL) was added, and a precipitate formed in a few seconds. The mixture was shortly sonicated and filtered. (−)-[*M*-**2**][CF_3CO_2]$_2$ as a yellow solid (279.5 mg, $[\alpha]_D$ = −612.7, *c* = 0.320, MeOH, 96.1% ee, acc to CE 97.4% ee) was isolated. The solid was finely powdered with a pestle in an agate mortar and used for seeding in PC.

*Initial Preferential Crystallization Experiments. (+)-[P-**2**]-[CF_3CO_2]$_2$.* [7]Helquat [**2**][CF_3CO_2]$_2$ (1.00 g) enantioenriched in (+)-[*P*-**2**][CF_3CO_2]$_2$ ($[\alpha]_D$ = +34.9, 5.5% ee) was dissolved in 30.0 mL of acetonitrile stirred at rt for 30 min. Ethyl acetate (38.0 mL) was added followed immediately by seeds of (+)-[*P*-**2**][CF_3CO_2]$_2$ (4.8 mg). The mixture was stirred at rt for 30 min (280 rpm), and then the resulting precipitate was filtered, dried, and weighed. (+)-[*P*-**2**][CF_3CO_2]$_2$ (120.6 mg) ($[\alpha]_D$ = +563.1, 88.3% ee) was obtained as a yellow solid. The filtrate was concentrated to dryness giving 879.5 mg of a yellow solid enantioenriched in (−)-[*M*-**2**][CF_3CO_2]$_2$ ($[\alpha]_D$ = −45.3, 7.1% ee).

*(−)-[M-**2**][CF_3CO_2]$_2$.* [7]Helquat [**2**][CF_3CO_2]$_2$ (1.00 g) enantioenriched in (−)-[*M*-**2**][CF_3CO_2]$_2$ ($[\alpha]_D$ = −29.4, 4.6% ee) was dissolved in 30.0 mL of acetonitrile and stirred at rt for 30 min. Ethyl acetate (39.0 mL) was added followed immediately by seeds of (−)-[*M*-**2**][CF_3CO_2]$_2$ (4.8 mg). The mixture was stirred at rt for 40 min (280 rpm), and then the resulting precipitate was filtered, dried, and weighed. (−)-[*M*-**2**][CF_3CO_2]$_2$ (130.9 mg) ($[\alpha]_D$ = −536.6, 84.1% ee) was obtained as a yellow solid. The filtrate was concentrated to dryness giving 858.4 mg of a yellow solid enantioenriched in (+)-[*P*-**2**][CF_3CO_2]$_2$ ($[\alpha]_D$ = +54.7, 8.6% ee).

*Four Representative Procedures for Preferential Crystallization of [2][CF_3CO_2]$_2$ on 5 g Scale. (+)-[P-**2**][CF_3CO_2]$_2$.* [7]Helquat [**2**]-[CF_3CO_2]$_2$ (5.00 g) enantioenriched in (+)-[*P*-**2**][CF_3CO_2]$_2$ ($[\alpha]_D$ = +31.7, 5.0% ee) was dissolved in 150.0 mL of acetonitrile and stirred at rt for 30 min (280 rpm). Then 250.0 mL of ethyl acetate was added followed immediately by seeds of (+)-[*P*-**2**][CF_3CO_2]$_2$ (3.7 mg). This supersaturated solution was then stirred (280 rpm) for 18 min, and

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then the resulting precipitate was filtered, dried, and weighed. 833.8 mg of a yellow solid enriched in (+)-[*P*-**2**][CF_3CO_2]$_2$ ([α]$_D$ = +530.3, 83.1% ee) was obtained leaving the filtrate with excess of (−)-[*M*-**2**][CF_3CO_2]$_2$ (4.16 g, [α]$_D$ = −60.0, 9.4% ee).

Preparation of the Sample for the Next Round of PC. Racemic [7]helquat [**2**][CF_3CO_2]$_2$ (841.0 mg) was added to the filtrate concentrated to dryness. The mixture was dissolved in acetonitrile to enable homogenization, and the resulting solution was concentrated to dryness to obtain 5.00 g of solid material enantioenriched in (−)-[*M*-**2**][CF_3CO_2]$_2$ ([α]$_D$ = −42.0, 6.6% ee) ready for the next preferential crystallization step, this time toward (−)-[*M*-**2**][CF_3CO_2]$_2$ enantiomer.

*(−)-[M-**2**][CF_3CO_2]$_2$.* Material enriched in (−)-[*M*-**2**][CF_3CO_2]$_2$ enantiomer from the previous experiment (5.00 g, [α]$_D$ = −42.0, 6.6% ee) was dissolved in 150.0 mL of acetonitrile and stirred at rt for 30 min (280 rpm). Then 240.0 mL of ethyl acetate was added followed immediately by seeds of (−)-[*M*-**2**][CF_3CO_2]$_2$ (4.0 mg). This supersaturated solution was stirred (280 rpm) for 30 min, and then the resulting precipitate was filtered, dried, and weighed. A yellow solid (1.04 g) enriched in (−)-[*M*-**2**][CF_3CO_2]$_2$ enantiomer ([α]$_D$ = −515.0, 80.7% ee) was obtained leaving the filtrate with excess of (+)-[*P*-**2**][CF_3CO_2]$_2$ (3.93 g, [α]$_D$ = +82.0, 12.9% ee).

Preparation of the Sample for the Next Round of PC. Racemic [7]helquat [**2**][CF_3CO_2]$_2$ (1.07 g) was added to the filtrate concentrated to dryness. The mixture was dissolved in acetonitrile to enable homogenization, and the resulting solution was concentrated to dryness to obtain 5.00 g of solid material enantioenriched in (+)-[*P*-**2**][CF_3CO_2]$_2$ ([α]$_D$ = +55.5, 8.7% ee) ready for the next preferential crystallization step, this time toward (+)-[*P*-**2**][CF_3CO_2]$_2$ enantiomer.

*(+)-[P-**2**][CF_3CO_2]$_2$.* Material enriched in (+)-[*P*-**2**][CF_3CO_2]$_2$ enantiomer from the previous experiment (5.00 g, [α]$_D$ = +55.5, 8.7% ee) was dissolved in 150.0 mL of acetonitrile and stirred at rt for 30 min (280 rpm). Then 240.0 mL of ethyl acetate was added followed immediately by seeds of (+)-[*P*-**2**][CF_3CO_2]$_2$ (3.7 mg). This supersaturated solution was stirred (280 rpm) for 18 min, and then the resulting precipitate was filtered, dried, and weighed. A yellow solid (687.5 mg) enriched in (+)-[*P*-**2**][CF_3CO_2]$_2$ ([α]$_D$ = +554.3, 86.9% ee) was obtained leaving the filtrate with excess of (−)-[*M*-**2**][CF_3CO_2]$_2$ (4.26 g, [α]$_D$ = −46.8, 7.3% ee).

Preparation of the Sample for the Next Round of PC. Racemic [7]helquat [**2**][CF_3CO_2]$_2$ (741.8 mg) was added to the filtrate concentrated to dryness. The mixture was dissolved in acetonitrile to enable homogenization, and the resulting solution was concentrated to dryness to obtain 5.00 g of solid material enantioenriched in (−)-[*M*-**2**][CF_3CO_2]$_2$ ([α]$_D$ = −40.1, 6.3% ee) ready for the next preferential crystallization step, this time toward (−)-[*M*-**2**][CF_3CO_2]$_2$ enantiomer.

*(−)-[M-**2**][CF_3CO_2]$_2$.* Material enriched in (−)-[*M*-**2**][CF_3CO_2]$_2$ enantiomer from the previous experiment (5.00 g, [α]$_D$ = −40.1, 6.3% ee) was dissolved in 150.0 mL of acetonitrile and stirred at rt for 30 min (280 rpm). Then 240.0 mL of ethyl acetate was added followed immediately by seeds of (−)-[*M*-**2**][CF_3CO_2]$_2$ (3.6 mg). This supersaturated solution was then stirred (280 rpm) for 16 min, and then the resulting precipitate was filtered, dried, and weighed. A yellow solid (853.8 mg) enriched in (−)-[*M*-**2**][CF_3CO_2]$_2$ ([α]$_D$ = −536.8, 84.2% ee) was obtained leaving the filtrate with excess of (+)-[*P*-**2**][CF_3CO_2]$_2$ (4.22 g, [α]$_D$ = +55.1, 8.6% ee).

Preparation of the Sample for the Next Round of PC. Racemic [7]helquat [**2**][CF_3CO_2]$_2$ (784.5 mg) was added to the filtrate concentrated to dryness. The mixture was dissolved in acetonitrile to enable homogenization and the resulting solution was concentrated to dryness to obtain 5.00 g of solid material enantioenriched in (+)-[*P*-**2**][CF_3CO_2]$_2$ ([α]$_D$ = +43.3.4, 6.8% ee).

Results of the four selected consecutive procedures described above are summarized as entries 15−18 in Table 6. The results of the other 14 runs of preferential crystallization (7 runs in *P* cycle and 7 runs in *M* cycle) are also summarized in Table 6. The amounts of solid material collected after the individual crystallization runs were in range 0.43−1.04 g, and ee values in these fractions were in range 50−89%. When combined, all the (+)-[*P*-**2**][CF_3CO_2]$_2$ fractions gave 6.49 g of sample with 83.2% ee as determined by polarimetric measurement of the specific rotation. All the (−)-[*M*-**2**][CF_3CO_2]$_2$ fractions gave 7.06 g of sample with 80.7% ee. In the case of a less successful experiment (when either too much precipitate formed and its enantiomeric purity was low, or too little precipitate formed and the remaining supernatant was not sufficiently enantioenriched), all fractions were combined and the experiment was repeated. In the case of repeated failure, recrystallization of the starting material from acetonitrile/ethyl acetate is recommended. The success of the individual PC runs was probably governed by purity of the starting material and the solvents used (HPLC grade solvents are recommended as their use minimizes number of unsuccessful PC runs). The enantiomeric excess of the starting scalemic mixtures varied from 3 to 9% ee, and the PC experiments proceeded successfully within these starting ee values.

Table 6. Characteristics of Precipitates Obtained from the Individual Runs of Preferential Crystallization[a]

(*P*)-enantiomer				
run no.	mass of precipitate (g)	specific rotation [α]$^{25}_D$	ee$_P$ (%)	mass of pure enantiomer (g)
1	0.79	+535.6	84.0	0.67
3	0.69	+550.4	86.3	0.60
5	0.92	+548.3	86.0	0.79
7	0.62	+562.8	88.2	0.55
9	0.66	+558.8	87.6	0.58
11	0.65	+564.8	88.6	0.57
13	0.63	+556.5	87.3	0.55
15	**0.83**	**+530.3**	**83.1**	**0.69**
17	**0.69**	**+554.3**	**86.9**	**0.60**
$\Delta/\sum$	6.49		86.3[b]	5.60
(*M*)-enantiomer				
run no.	mass of precipitate (g)	specific rotation [α]$^{25}_D$	ee$_M$ (%)	mass of pure enantiomer (g)
2	0.66	−537.5	84.3	0.56
4	0.82	−553.7	86.8	0.72
6	0.83	−531.4	83.3	0.69
8	0.95	−320.0	50.2	0.48
10	0.78	−503.0	78.9	0.61
12	0.43	−554.9	87.0	0.38
14	0.69	−535.7	84.0	0.58
16	**1.04**	**−515.0**	**80.7**	**0.84**
18	**0.85**	**−536.8**	**84.2**	**0.72**
$\Delta/\sum$	7.06		78.9[b]	5.57

[a]Four representative procedures described in detail in the Experimental Section are shown in bold type. [b]ee calculated as weighted average. The ee values obtained on the basis of specific rotations of the two combined fractions were 83.2% ee for (*P*)- and 80.7% ee for (*M*)-enantiomer.

*Increasing ee of Samples of (+)-[P-**2**][CF_3CO_2]$_2$ and (-)-[M-**2**][CF_3CO_2]$_2$ after 18 Preferential Crystallization Runs in total.* Fractions after the individual cycles of preferential crystallization containing the same enantiomer (nine fractions of (*P*)- and nine of (*M*)-enantiomer) were combined to give two multigram samples of opposite helicity. These two fractions were recrystallized from acetonitrile/ethyl acetate mixture according to the following procedures.

*Recrystallization of (+)-[P-**2**][CF_3CO_2]$_2$.* A combined fraction (6.49 g) containing predominantly [7]helquat (+)-[*P*-**2**][CF_3CO_2]$_2$ ([α]$_D$ = +530.6, 83.2% ee) was dissolved in 200.0 mL of acetonitrile and stirred at rt for 30 min (280 rpm). Then 400.0 mL of ethyl acetate was added at once, and a precipitate formed within a few seconds after the addition was complete. This mixture was stirred for 5 min, sonicated for approximately 15 s, and filtered. The solid was washed with 100 mL of ethyl acetate and 100 mL of Et_2O. In the end it was dried under

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vacuum to obtain 5.44 g of solid material enriched in (+)-[*P*-**2**][CF_3CO_2]$_2$ ([α]$_D$ = +621.3). This solid was again dissolved in 160.0 mL of acetonitrile and stirred at rt for 30 min (280 rpm). 400.0 mL of ethyl acetate was added at once, and within a few seconds a precipitate formed. After stirring for 5 min and short sonication (15 s), the mixture was filtered, and the solids were washed with ethyl acetate followed by Et_2O. After drying, 5.027 g of nonracemic [7]helquat (+)-[*P*-**2**][CF_3CO_2]$_2$ was obtained (>96% ee determined by CE, Figure 3).

Recrystallization of (−)-[M-2][CF_3CO_2]$_2$. A combined fraction (7.06 g) containing predominantly [7]helquat (−)-[*M*-**2**][CF_3CO_2]$_2$ ([α]$_D$ = −515.3, 80.7% ee) was recrystallized twice following the procedure analogous to that for the (*P*)-enantiomer detailed in the preceding experiment. Nonracemic [7]helquat (−)-[*M*-**2**][CF_3CO_2]$_2$ (5.026 g) was obtained (>96% ee determined by CE, Figure 3).

■ ASSOCIATED CONTENT

Supporting Information

List of utilized chemicals, general procedure for preparation of anion-exchange resin, details on X-ray crystal structures, crystallographic information files (CIFs), and copies of NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

In memory of Professor Antonín Holý.

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