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Helquats: A Facile, Modular, Scalable Route to Novel Helical Dications

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Dedicated to Professor Rudolf Zahradník on the occasion of his 80th birthday

Electroactive paraquat **1** and diquat **2** (Figure 1) are widely used herbicides produced in ton quantities every year.[1] Due to their powerful electron-accepting character they are exceptional electron-transfer quenching agents. Research into these dicationic species spearheaded the development of supramolecular science and led to the evolution of molecular devices.[2] Extensive studies into their properties in biological and photocatalytic systems,[3] and their molecular recognition capabilities further testify to the unique position of these privileged dications.

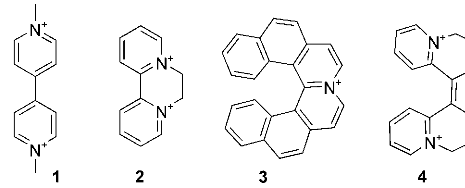
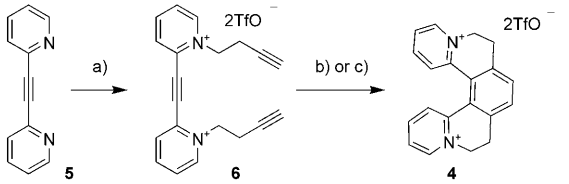


Figure 1.

The comparatively unexplored realm of helically chiral N-heterohelicenia[4,5] (e.g., **3**, ref. [4b,c]) represents a platform on which to simultaneously expand the fields of cationic N-heteroaromatics,[6] helicenes, and heterohelicenes.[7] The possibility of combining the remarkably diverse application potentials of these areas, is particularly attractive.

Herein, we report the synthesis, and properties of helical extended diquat **4** (helquat **4**) and derivatives thereof that bear resemblance to both diquat **2**, and azoniahelicene **3**. In the synthesis of the parent helquat **4**, we capitalize on the fact that a facile pyridine-type nitrogen quaternization protocol (**5**→**6**, Scheme 1) developed for monocation synthesis by Vaquero, Cuadro et al.[8] can be beneficially combined with a reliable entry to helical scaffolds based on [2+2+2]-triyne cycloisomerization pioneered by Starý and Stará.[9] Thus, triyne **6** is prepared in high yield from the known pyridine precursor **5** (ref. [10]) and the key [2+2+2] cycloisomerization **6**→**4** is effected in minutes with Wilkinson's catalyst [Rh(PPh$_3$)$_3$Cl] in acetonitrile under microwave conditions. The practicality of the protocol is underscored by the fact that a simple ethyl acetate wash of the crude product removes the catalyst affording helquat **4** as the triflate salt in good purity on milligram to gram scales. X-ray crystal structure analysis unambiguously confirms the identity of **6**



Scheme 1. a) TfOCH$_2$CH$_2$C≡CH, CCl$_4$, CH$_2$Cl$_2$, 40 °C, 23 h, 83 %; b) [Rh(PPh$_3$)$_3$Cl] (5 mol %), MeCN, MW, 30 min, 90 °C, 99 %; c) [Cp*Ru(cod)Cl] (10 mol %), H$_2$O/DMSO 99:1, air, 30 min, 100 °C, 94 %. Tf = trifluoromethanesulfonyl.

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and **4** (Figure 2).[11] The reaction **6**→**4** is, to our knowledge, the first example of metal-catalyzed [2+2+2] cycloaddition of cationic N-heteroaromatics reported to date.[12]

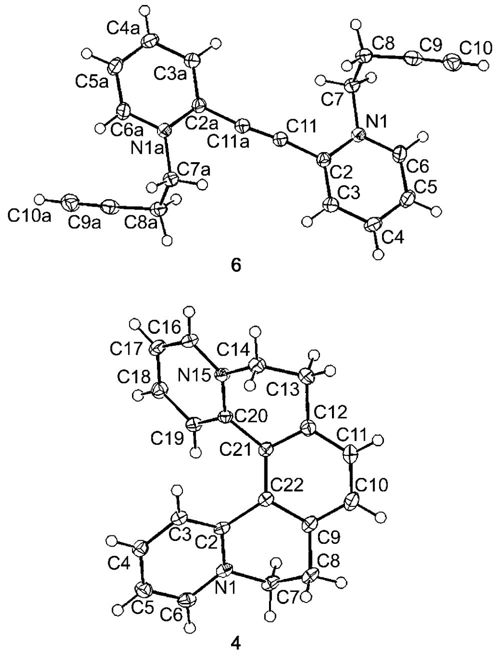


Figure 2. Molecular structures of **6** and **4** from single-crystal X-ray structure determination. Triflate counterions were omitted for clarity.

The key transformation **6**→**4** is also catalyzed by a known ruthenium catalyst [Cp*Ru(cod)Cl] (Cp* = pentamethylcyclopentadienyl, cod = 1,5-cyclooctadiene)[13] and can be conducted under unique aqueous aerobic conditions (Scheme 1), representing a rare metal-catalyzed example of air-tolerant [2+2+2] cycloadditions.[14] Although this reaction also proceeds at room temperature, it is slower with conversion reaching 25 % after 17 h. We note that this mild air- and water-tolerant process leads to the water-soluble blue fluorophore **4**.[15] The fluorescence spectrum obtained after excitation at 330 nm, shows a maximum at 400 nm and extends into the visible region, accounting for the blue fluorescence (Figure 3). The quantum yield was determined to be 0.14 with fluorescence lifetime of 3 ns (see Supporting Information for details).

Analysis by cyclic voltammetry showed the dication **4** to be reduced in two separate reversible one-electron steps at reduction potentials of −742 and −982 mV (vs. standard hydrogen electrode, scan rate 0.5 V s,$^{-1}$ see the corresponding cyclic voltammogram, Scheme 2, panel A).[16] In a UV/Vis spectroelectrochemical experiment, absorption bands of the three electrochemical states in the manifold **4**, **7**, and **8** were determined. The results obtained experimentally (Scheme 2, panel B upper) are in excellent agreement with the theoretical UV/Vis absorption bands of the three species **4**, **7**, and **8** obtained by ab initio calculations (TD-DFT with BMK functional and 6-31+G* basis set, Scheme 2, panel B lower). Interestingly, calculations show that if the reduced species **8** resided predominantly in its triplet state,[17] the UV/Vis absorption spectrum would exhibit no maximum in the region around 690 nm. The presence of this band in the experimentally determined UV/Vis spectrum strongly suggests that species **8** exists mostly in the singlet form (see Supporting Information for details). The corresponding triplet state of **8** is calculated to be 0.5 eV (48 kJ mol^{-1}) higher in energy as compared to the singlet ground state of **8**. Thus, the two electrochemical experiments supported by ab initio calculations suggest that helquat **4** parallels electrochemical proper-

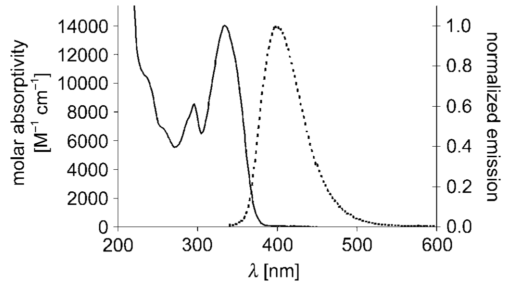
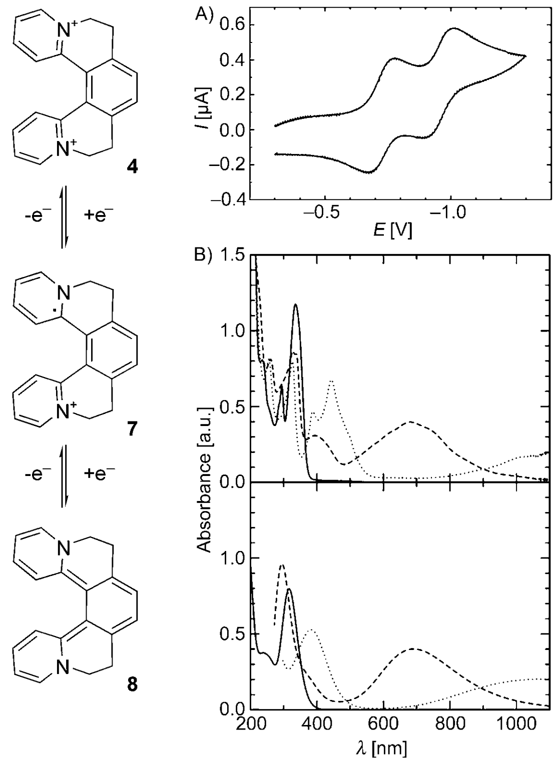


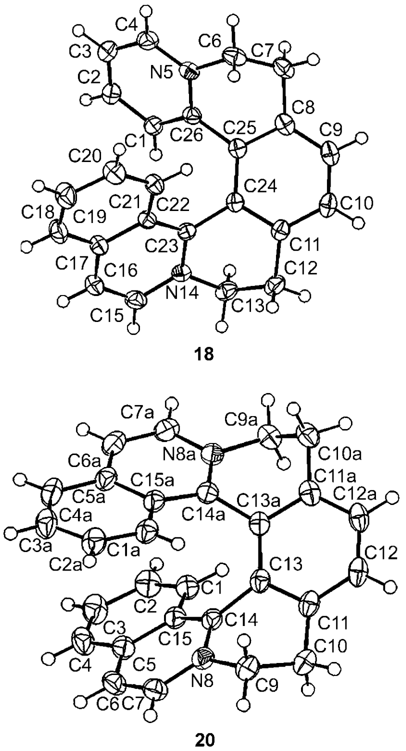
Figure 3. Absorption (solid line) and fluorescence (dotted line) spectra of helquat **4** in water.



Scheme 2. Reversible Weiz-type electrochemical manifold of **4**; panel A: cyclic voltammetry of **4** (0.4 mM) and $(n\mathrm{Bu}_4\mathrm{N})\mathrm{PF}_6$ (0.1 M) in acetonitrile; panel B upper: UV/Vis spectrum of **4** (3 mM) and $(n\mathrm{Bu}_4\mathrm{N})\mathrm{PF}_6$ (0.1 M) in acetonitrile (——), after the one-electron reduction (**7**, •••••) and in a fully reduced form (**8**, -----); Panel B lower: Ab initio calculated spectra of **4**, **7**, and **8** in acetonitrile. Counterions are omitted.

ties of diquat **2** (refs. [3b,16]) and thus belongs to an electrochemically privileged family of Weiz-type structures.[18]

To demonstrate the flexibility of the described synthetic protocol, a variety of helquats (Table 1) was synthesized. End-capped triyne **9** was transformed readily to hexasubstituted benzene derivative **10** showing that internal alkyne arms are well tolerated. Triyne **11**, with elongated tethers connecting the heterocyclic moiety with the pendant alkyne functionalities, also smoothly underwent cycloisomerization giving helquat **12** featuring two seven-membered rings. Significantly, introduction of diversity in the region anticipated to be crucial to the tuning of the helix inversion barrier[19] is also facile as exemplified by racemic syntheses of methyl-substituted helquats **14**, and **16**, and benzo-homologues, **18** and **20**. Structures of two representative examples of helical dications, **18** and **20**, are depicted in Figure 4.[20] Similarly to the synthesis of parent compound **4**, all helquats in Table 1 are isolated by a simple ethyl acetate wash of the crude product affording the helquats in good purity and high yields. Importantly, the seven helquats reported in this Communication can be accessed uniformly in only three steps from commercially available starting materials. Each three-step sequence entails a Sonogashira coupling, bisquaternization, and finally [2+2+2] cycloisomerization (see Supporting Information for details).

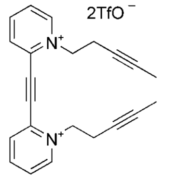
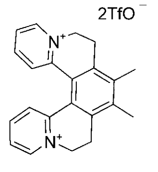
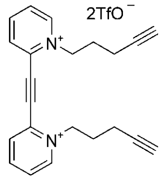
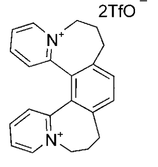
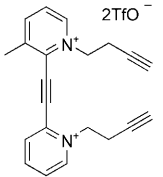
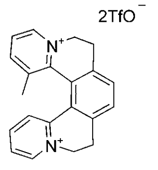
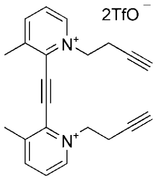
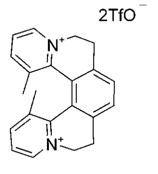
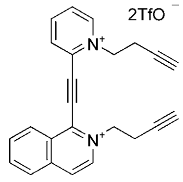
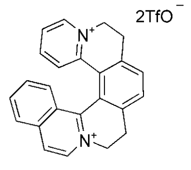
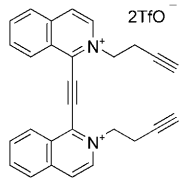
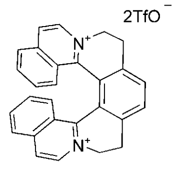


18

20

Figure 4. Molecular structures of **18** and **20** from single-crystal X-ray structure determination. Triflate counterions were omitted for clarity.

Table 1. Rhodium-catalyzed synthesis of helquats.

Entry[a]	Substrate	Product	Yield [%][b]
1	 **9**	 **10**	93[c]
2	 **11**	 **12**	91
3	 **13**	 **14**	94 93[d]
4	 **15**	 **16**	94[e]
5	 **17**	 **18**	76[f]
6	 **19**	 **20**	69[g]

[a] Reaction conditions: triyne (0.01–0.07 mmol), $[Rh(PPh_3)_3Cl]$ (5 mol%), MeCN, MW, 30 min, 90°C. [b] Yield of isolated product. [c] Reaction temperature 110°C. [d] EtOH, 0.5 g scale (0.9 mmol). [e] Reaction performed in EtOH, 90°C, 30 min, then 110°C, 30 min. [f] $[Rh(PPh_3)_3Cl]$ (10 mol%), EtOH, MW, 30 min, 110°C. [g] $[Rh(PPh_3)_3Cl]$ (10 mol%), EtOH, MW, 60 min, 120°C.

In conclusion, capitalizing on a [2+2+2]-cycloisomerization strategy, we have developed a robust three-step synthetic entry into a novel family of dications which we suggest to call helquats (helical extended diquats). They feature an electroactive-extended diquat-type motif in a helical arrangement. The evidence for the reversible electrochemical Weiz-type manifold in **4** and also regular columnar stacks in crystal structures of **4**, **18**, and **20** suggest the potential of helquats as electroactive functional elements of future nanoscience, for example, molecular electronics.[21] The conceptual simplicity, practicality, atom- and step-economy of the reported synthetic strategy will open this class of compounds for multidisciplinary research efforts ranging from organocatalysis to material applications to bio-applications. Potential uses of helical dications, structural tailoring to tune the singlet-triplet energy gap in fully reduced species such as **8**, and synthetic entry into non-racemic series are currently being pursued.

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Keywords: air-tolerant cycloisomerization · diquat · electrochemistry · helical structures · heteroaromatic cations

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