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Synthesis and fluorescence properties of DMCX$^+$—a stable oxygen-bridged [4]helicenium dye

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ABSTRACT

A one-step synthesis of the stable [4]helicenium dye, 1,13-dimethoxy-chromeno[2,3,4-*kl*]xanthenium hexafluorophosphate (DMCX$^+$) from the readily available tris(2,6-dimethoxyphenyl)carbenium ion is reported. The crystal structure, the chemical stability, and dye properties of the DMCX$^+$ helicenium system are described.

Cationic triphenylmethane dyes have been known and used for more than a century.[1,2] The dyes are potent colorants, but it is the hetero-bridged triphenylmethylium dyes that have received the most attention. Bridging two of the triphenylmethylium arms, with either oxygen or nitrogen, forms the intensely studied xanthenium and acridinium dyes.[3–6] Bridging of all the arms results in the formation of a triangulenium dye:[7–12] these are promising fluorophores that have been studied in supramolecular assemblies,[13–22] as materials,[23,24] for their photophysical properties,[25–30] and as phase-transfer catalysts.[31]

If only two heteroatom-bridges are introduced in the triphenylmethylium system, [4]helicenium structures are obtained. The helical framework is inherently chiral, which makes the [4]helicenium compounds interesting chiral equivalents of the bridged triphenylmethylium dyes.[32,33] The [4]helicenium ions can also be considered as a new charged subclass of the heterohelicenes. A phosphorus [4]heterohelicene has been reported,[34] and research involving heterohelicenes appears frequently.[35–45]

The [4]helicenium dyes have the general structure shown in Figure 1. The parent [4]helicene and [4]helicenium ions are not locked structures and the enantiomers cannot be resolved.[46–48] Addition of methoxy groups at the 1 and 13 positions gives rise to a substantial isomerization barrier and stable left and right handed isomers.[32] While the nitrogen-bridged [4]helicenium dyes (X = Y = NR, DMQA$^+$) have been studied extensively,[49–55] only a single paper from 2010 by Lacour and co-workers reports a five-step synthesis and resolution of the oxygen-bridged [4]helicenium derivative; 1,13-dimethoxy-chromeno[2,3,4-*kl*]xanthenium (X = Y = O, DMCX$^+$).[56] In a theoretical study, we showed that the observed racemization barrier of the DMCX$^+$ ion may be strongly influenced by the formation of leuco-adducts.[32] The formation of leuco-adducts will in turn depend on the cation stability (the pK_{R+} value). Similarly leuco-adducts will influence the optical properties. For these reasons, studies of the cation stability and optical properties of DMCX$^+$ salts with non-nucleophilic counterions are of importance if we are to understand the properties of the new helicenium dyes. In this Letter, we report a simplified one-step synthesis, the single crystal structure, studies of the cation stability, and the fluorescent properties of DMCX·PF$_6$.

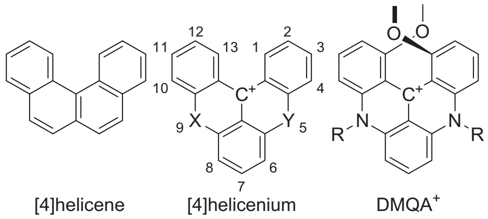

Figure 1. Structures of [4]helicene and [4]helicenium ions.

DMCX$^+$ can be envisaged as an intermediate in the synthesis of trioxatriangulenium (TOTA$^+$) from tris(2,6-dimethoxyphenyl)carbenium derivative **1** as shown in Scheme 1, which takes place in

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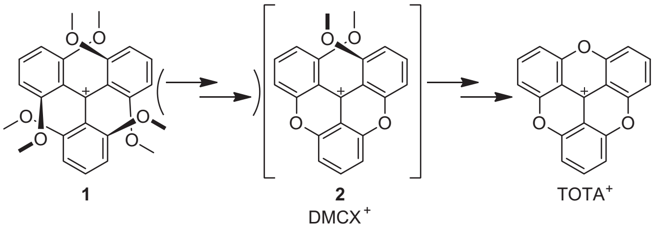
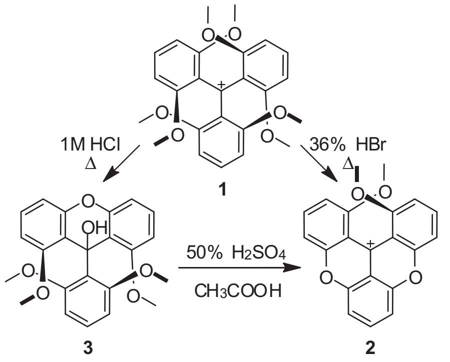


Scheme 1. Reaction of **1** in pyridine hydrochloride at 180 °C.

molten pyridine hydrochloride at elevated temperatures.[7] However, this was not the case as it was found that cleavage of the methyl ethers was substantially faster than bridge formation. The cationic triphenylmethylium dyes (e.g. **1**) can be readily observed by MALDI-TOF mass spectrometry.[10,57] However, when monitoring the reaction in Scheme 1, DMCX$^+$ was not observed at any point. When the reaction was run to 50% conversion and the reaction mixture purified, no trace of DMCX$^+$ was observed. The temperature effect was investigated by running the reaction in a mixture of pyridine and pyridinium hydrochloride between 100 and 180 °C, and in pure pyridine hydrochloride between 180 and 220 °C, in 20 °C intervals. These studies showed that dealkylation and bridge formation in pyridine hydrochloride were not a viable route to DMCX$^+$.

Martin and Smith reported that refluxing **1** in 1 M HCl(aq) afforded the tetramethoxy-xanthenol **3** in quantitative yield (Scheme 2).[7] Thus, other ether-cleaving reagents can be used to make bridged triphenylmethylium dyes starting from **1**. It is evident that a combination of ether-cleaving reagent and heat is required for the process to occur. Taking these facts into account, a series of experimental conditions were tested. Various concentrations of sulfuric, hydrobromic, and hydrochloric acid in water and acetic acid were used at temperatures from 80 to 130 °C. Using sulfuric acid, the starting material was converted into unidentified compounds without a trace of DMCX$^+$ being formed. By using hydrochloric acid the xanthenium ion was formed quantitatively, as reported by Martin and Smith, but only a trace of the DMCX product was observed, which could not be isolated. It was evident from MALDI-TOF that the ethers of **1** were cleaved, but DMCX$^+$ was not formed to any appreciable extent. Starting from isolated **3** allowed for the formation of DMCX$^+$ in a limited yield <5% by using 50% sulfuric acid in glacial acetic acid (Scheme 2).

It was found that the balance between dealkylation and bridge formation was best in aqueous hydrobromic acid, with the highest yield being obtained after 120 min at 120 °C. Using these reaction conditions, the title compound was isolated as its PF_6^- salt in a yield of 135 mg (15%), with an additional 10% recovered material as the fully ring-closed TOTA$^+$. Thus, DMCX$^+$ can be obtained in one step from **1** using ether-cleaving reagents. The low yield is similar to the overall yield of the previous reported five-step synthesis.



Scheme 2. Synthesis of DMCX$^+$ (**2**).

Deep-orange feather-like crystals of DMCX·PF_6 were grown from dichloromethane/ethanol allowing the structure of the helical DMCX$^+$ ion to be studied in detail by a single crystal X-ray analysis (CCDC 842400). The structure is shown in Figure 2. The space group is C 2/c and both the M- and P-enantiomers were present in symmetry equivalent sites. The bottom aromatic ring is in-plane with the central carbon and the two oxygen bridges. The two phenyl arms are symmetrically twisted out of the molecular plane in opposite directions creating a helical pitch of 2.7 Å. A detailed comparison of bond lengths showed that DMCX$^+$ was essentially isostructural to DMQA$^+$, except when considering the helical pitch. We recently calculated the helical pitch of DMQA$^+$ and DMCA$^+$ as 49° and 43.0°, respectively; the values determined in the crystals are lower at 42–44° for DMQA$^+$ and at 39° for DMCX$^+$.[32,49] Although the absolute value predicted by the calculations is too high by 4–7° the difference between DMQA$^+$ and DMCA$^+$ is well-predicted. The values found indicate that the electron-donating ability of the 1,13-methoxy groups is more strongly required in the DMCX$^+$ system, resulting in a lower helical pitch. This is to be expected when comparing the donor strength of oxygen and nitrogen.[4]

In our synthesis and that reported by Lacour et al., the triiodide salt of DMCX$^+$ is formed. To investigate the photophysics of DMCX$^+$ it is vital that no triiodide remains. This can be controlled by examining the absorption spectrum of DMCX$^+$ as shown in Figure 3. A dip in the absorption is present around 300 nm, where triiodide absorbs. If any triiodide remains it can be seen in this window in the DMCX$^+$ absorption. Inspection of the absorption spectrum of DMCX$^+$ shows that it is a yellow–red dye with a weak absorption in the yellow and a stronger absorption in the blue–green part of the spectrum. The absorption bands at 375 and 450 nm correspond to absorptions in xanthenium systems.[27] A contribution to the high energy band derives from the absorption of the chromenylium unit.[58] The two red absorptions must be due to transitions localized over the entire conjugated system. It should be stated that these findings are in direct conflict with the circular dichroism and absorption spectrum reported in the 2010 paper by Lacour and co-workers, where only UV transitions were observed.[56] This discrepancy is assigned to some undesired side reaction leading to the formation of a leuco-adduct in the I_3^- salt first reported.[32,33,59]

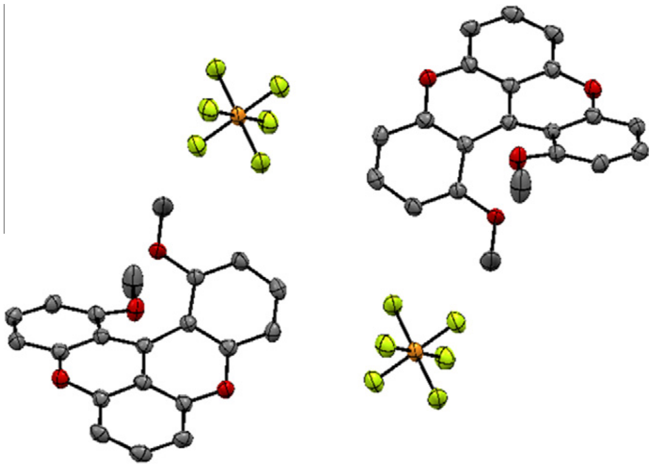


Figure 2. Crystal structure of DMCX·PF_6 (CCDC 842400), both enantiomers are shown. The packing is a slipped stack with the next DMCX$^+$ unit lying over the PF_6^- of this layer. Hydrogen atoms are not shown for clarity. Thermal ellipsoids are shown at the 50% probability level.

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