

Properties and structure of two fluorinated 1,10-phenanthrolines



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ABSTRACT

We report the synthesis, X-ray structure, absorbance and emission of 4,7-bis(4-fluorophenyl)-1,10-phenanthroline and 4,7-bis-(4'-trifluoromethyl-biphenyl-4-yl)-1,10-phenanthroline. 4,7-Bis(4-fluorophenyl)-1,10-phenanthroline was synthesized by successive Skraup reactions and features absorbance at 274 nm and emission at 384 nm while 4,7-bis-(4'-trifluoromethyl-biphenyl-4-yl)-1,10-phenanthroline featured absorbance at 283 nm and emission at 400 nm. The structures show molecular stacking of the phenyl groups and phenanthroline structure and longitudinal fluorine atom associations within the crystal lattice. Furthermore, the three fused rings of the 4,7-bis(4-fluorophenyl)-1,10-phenanthroline unit exhibited torsion up to 13.97(9)° throughout the crystal lattice whereas no torsion is observed for 4,7-bis-(4'-trifluoromethyl-biphenyl-4-yl)-1,10-phenanthroline.

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1. Introduction

1,10-Phenanthrolines are a widely used class of hetero aromatic compounds that consist of a central structure of three fused rings with adjacent nitrogen atoms. Historically, 1,10-phenanthrolines were produced using *ortho*-nitroaniline as the initial compound, and as such, the 1,10-phenanthroline structure is sometimes referred to as *ortho*-phenanthroline. This class of compounds is commonly used by themselves or for chelation of Lewis acid centers such as the ions of metals. 1,10-Phenanthrolines have found applications in enzyme inhibition [1], in the creation of luminescent compounds with a wide variety of metal centers [2], in the photometric determination of the ferrous ion and in the determination of organometallic reagents [3], and in various types of organic electronics [4].

Phenanthroline compounds (either as single molecules or as coordination ligands) are extensively used materials, and fluorination has become popular in recent years due to the electronic or physical properties imparted by one or more fluorine atoms [5]. The fluorinated phenanthrolines being reported were synthesized in an attempt to increase compatibility with fluorinated polymeric materials and as chelators for metal ions or atoms. In our previous

reports we used phosphorescent metal-phenanthroline complexes in a fluorinated polymer as oxygen sensors [6], and we reported osmium fluorinated 1,10-phenanthroline complexes in organic light emitting devices [7]. Here, we report the physical characterization of two fluorinated 1,10-phenanthrolines: 4,7-bis(4-fluorophenyl)-1,10-phenanthroline (**1**), and 4,7-bis-(4'-trifluoromethyl-biphenyl-4-yl)-1,10-phenanthroline (**2**).

2. Results and discussion

1 was synthesized by contacting 3-chloro-1-(4-fluoro-phenyl)-propan-1-one with *o*-nitroaniline in a mixture of arsenic acid and *o*-phosphoric acids by using successive Skraup reactions [8]. After the first Skraup reaction, the nitro moiety was reduced to an amine and the Skraup process repeated to yield the desired fluorinated phenanthroline. Using a similar procedure to the synthesis of **1**, a brominated phenanthroline (4,7-bis(4-bromophenyl)-1,10-phenanthroline) was synthesized and subsequently reacted with trifluoromethanebenzene boronic acid in a palladium mediated coupling to yield **2** (Fig. 1). The identity of species **1** and **2** was confirmed by mass spectrometry, ¹H NMR, and single crystal X-ray crystallography.

The absorbance, emission, and excitation of **1** and **2** are shown in the supplementary materials. **1** features an absorbance peak at 274 nm with an extinction coefficient of 40,000 ± 10% L mol⁻¹ cm⁻¹ at 20 °C and **2** has an absorbance peak at 283 nm with an extinction

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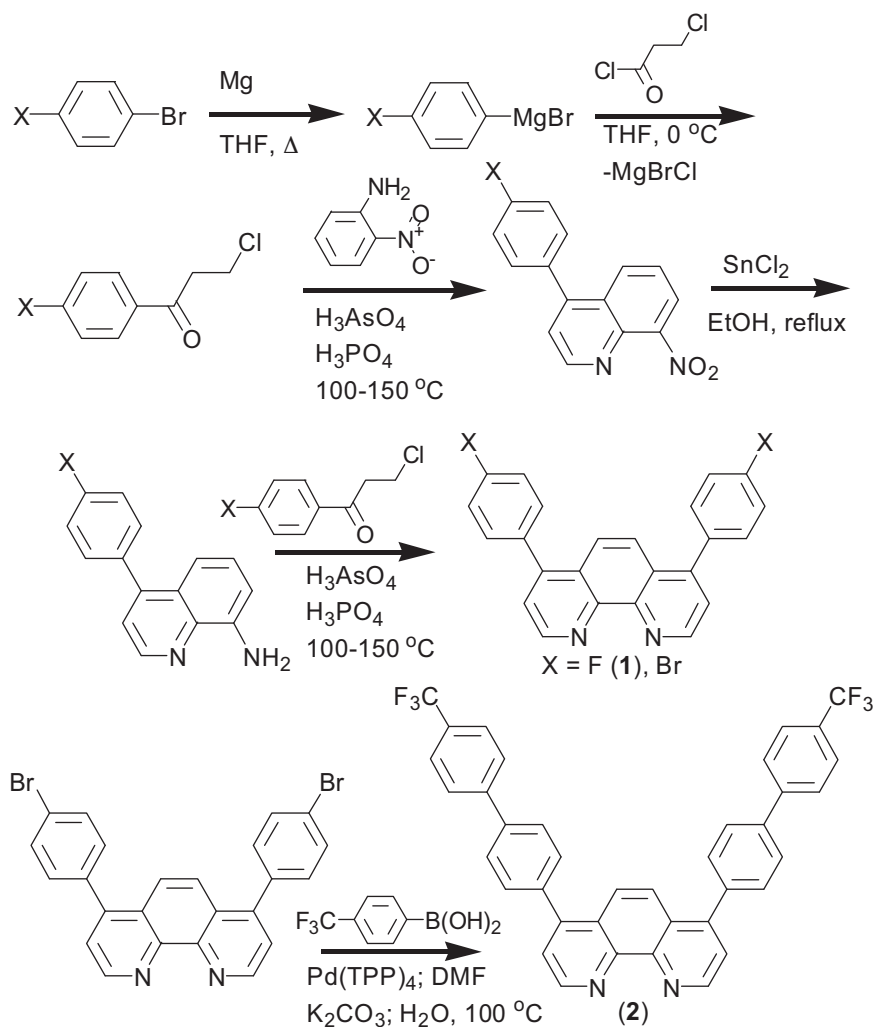


Fig. 1. Method to produce compounds **1** and **2**.

coefficient of $60,000 \pm 10\% \text{ L mol}^{-1} \text{ cm}^{-1}$ at 20 °C. **1** has an extinction coefficient of $13,500 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 300 nm which is similar to other phenyl derivatives [9]. **2** has a bathochromic shift and increased absorbance strength from that of **1**, both of which are consistent with its larger π structure. Both **1** and **2** are luminescent at 20 °C at a

concentration of 1.28×10^{-6} and $4.37 \times 10^{-6} \text{ mol L}^{-1}$ respectively. The luminescence of **1** is mostly in the UV. The structured Gaussian emission for **1** peaks at 384 nm and has a fwhm of 53 nm. **2** has emission that peaks at 400 nm with a fwhm of 61 nm. The bathochromic shift in the emission of **2** is consistent with the larger π

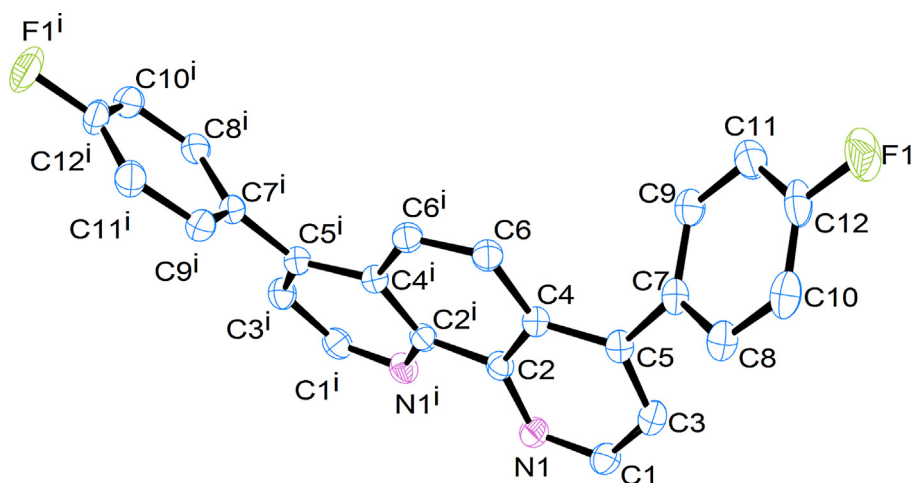


Fig. 2. Single crystal X-ray structure for **1** with 75% probability spheres. Hydrogen atoms removed for clarity.

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