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Acetate binding induces fluorescence enhancement in tryptophan ligands

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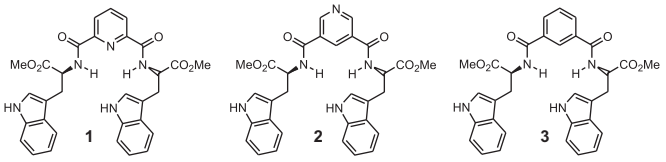
ABSTRACT

The anion coordination properties of bis-tryptophan dicarboxamide ligands **1**–**3** were investigated using fluorescence and ^{1}H NMR spectroscopy. It was observed that the coordination of acetate anions to these ligands produced emissions at 381 nm with gradual enhancement of fluorescence. In comparison, fluoride produced minor enhancement, the addition of chloride, bromide and nitrate anions caused quenching of ligand fluorescence. ^{1}H NMR studies revealed that the ligands coordinated to the acetate anions through the indole and amide NH groups.

1. Introduction

Supramolecular chemistry of anions has rapidly emerged as an important focus of research due to its potential implications in the development of receptors for anion recognition [1] and transport [2]. Among the various motifs that have been explored for the binding and recognition of anions, the most prominent ligands include pyrrole- and pyridine-derivatives [3,4] based on amide and/or urea frameworks [5]. The anion coordination ability of the indole motif has also been studied recently [6,7] in order to understand the nature of interactions for halides vis-à-vis other anions. Although several indole-based anion receptors have been reported, the anion coordination ability of bis-tryptophan ligands remains relatively unexplored. In fact, the role of tryptophan (*cf.* indole) in anion coordination and binding has attracted attention following the elucidation of the halide binding site in *haloalkane dehalogenase* [8]. In this connection, unraveling the potential of tryptophan-based ligands in anion coordination becomes immensely relevant [9], analogous to the cation–π interactions involving various cations with indole and tryptophan derivatives [10].

The significance of tryptophan (*cf.* indole) derivatives also emanates from its versatile fluorescence properties which can be modulated depending on the ligand environment [9,11]. An important question in this regard was the anion coordination ability of the tryptophan amide motif and its effect on the fluorescent responses of the ligand. With this motivation, we investigated three tryptophan-derived dicarboxamides ligands **1**–**3** as potential ligands for anion coordination using fluorescence spectroscopy and ^{1}H NMR spectroscopy.



2. Results and discussion

2.1. Synthesis and characterizations of ligands 1–3

Ligands **1** and **3** were obtained in moderate yields by reacting tryptophan methyl ester with pyridine-2,6-dicarbonyl chloride and benzene-1,3-dicarbonyl chloride, while ligand **2** was obtained by coupling pyridine-3,5-dicarboxylic acid with tryptophan methyl ester using EDC hydrochloride and HOBT methodology (Supplementary materials). Subsequently, ligands **1**–**3** were purified by chromatography and characterized using UV–visible, fluorescence and ^{1}H/^{13}C NMR spectroscopy.

We were able to crystallize ligand **1** from acetonitrile as yellow prisms in the orthorhombic P2(1)2(1)2 space group and the X-ray structure [12] indicated that the two indole groups adopted a folded conformation in the solid state. Apparently, another polymorph of this ligand was isolated from methanol–dichloromethane solution wherein the indole motifs adopted partially open conformations [9c]. Close inspection of the X-ray structure revealed intramolecular hydrogen bonds (Fig. 1) between the amide NH as donors with the pyridine(N) and ester group as acceptors. The hydrogen

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bonds parameters for the intramolecular amide NH/pyridine–N and the amide NH/ester–O interactions were found to be 2.285 Å (< N–H · · · N 108°) and 2.616 Å (< N–H · · · O 104°) respectively. In addition, the solid-state packing structure exhibited intermolecular hydrogen bonds involving indole NH and the ester C = O (2.842 Å, < N–H · · · N 164°) which resulted in the formation of hydrogen bonded chains.

On the basis of crystallographic evidence, we reasoned that **1** could adopt intramolecularly hydrogen bonded conformations such as **1a** and **1b** in the presence of suitable anionic guests (Scheme 1). We hypothesized that the ligands would interact with anions via the indole NH and/or the amide NH groups, which in turn, would reflect in the quenching or enhancement of fluorescence emission [13].

2.2. UV–visible and fluorescence studies

The absorption spectra of **1**, **2** and **3** recorded in acetonitrile (Fig. 2a) were strikingly similar with λ_{max} 285 nm, characteristic of tryptophan absorptions [9c]. We recorded the fluorescence spectra of **1** in acetonitrile [14], and observed two emissions at 373 and 455 nm (Fig. 2b) when irradiated at 300 nm; the long wavelength emission possibly arises from excimer emission for this system [15]. In comparison, irradiation of **2** and **3** at 300 nm produced a broad emissions centered at 439 nm ($\lambda_{em,\ max}$) and 335 nm ($\lambda_{em,\ max}$) respectively. The emission quantum yields were found to be 0.14(3) for **1**, 0.05(6) for **2** and 0.06(5) for **3** with reference to tryptophan [15].

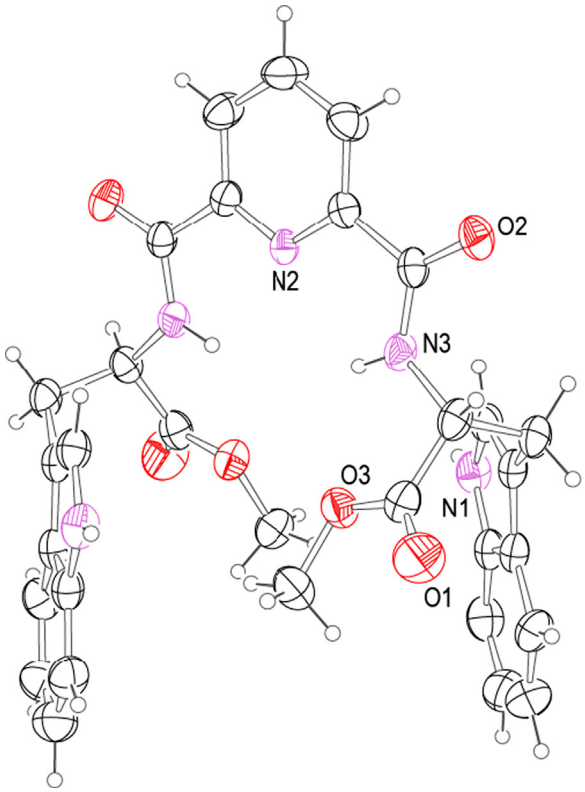


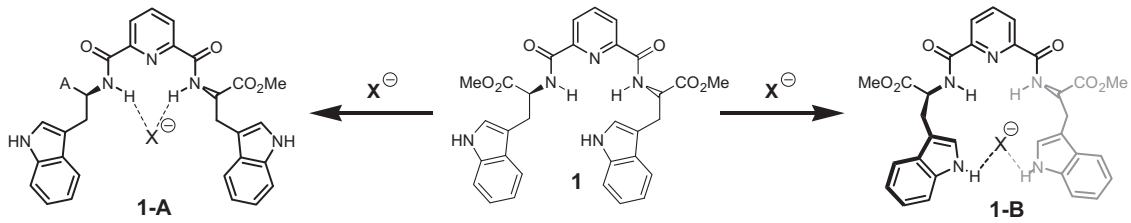
Fig. 1. X-Ray crystal structure of 1 (thermal ellipsoids drawn to 50% probability).

In the next experiment, we investigated the effects of acetate, fluoride, chloride, bromide and nitrate anions on ligand **1** using steady-state fluorescence spectroscopy. As shown in Fig. 3, the addition of acetate anions (as tetramethyl ammonium salt) to **1** in acetonitrile produced a new emission at 381 nm (as shown in Fig. 3a,b) with a shoulder at 368 nm; further addition of acetate ions (> 10 equiv., Fig. 3c) produced 5-fold enhancement of fluorescence emission at 381 nm ($Ka \sim 2890\ M^{-1}$, fitted on the 1:1 binding model) [16]. Similar fluorescence enhancement was observed upon addition of NaOAc to **1**, which substantiated the coordination of acetate to the ligand. In comparison, we observed that the addition of fluoride ions (upto 10 equiv.) to **1** in acetonitrile caused only minor enhancement of the fluorescence emissions at 373 and 455 nm (Fig. 3d), whereas the addition of chloride, bromide and nitrate anions induced quenching [17] of the ligand fluorescence.

In the same way, titration of **2** with acetate anions produced a new emission with maxima at 381 nm (Fig. 4a–c), and the addition of 5 equivalents of acetate anions caused 10-fold increase in fluorescence ($Ka \sim 3290\ M^{-1}$). Again, the addition of fluoride caused minor enhancement (Fig. 4d) of fluorescence for the emissions at 439 nm. However, the addition of chloride, bromide and nitrate anions caused quenching (Fig. 4d) of the ligand fluorescence.

Similar enhancement of fluorescence was observed upon addition of acetate anions (> 10 equiv.) to solution of ligand **3**, whereas the addition of other anions produced minor quenching effects (Fig. 5). In comparison to ligands **1** and **2**, we found that in this case, the acetate anions caused the emission to occur at 368 nm with shoulder at 381 nm. On the basis of the fluorescence titration plots, we calculated $Ka = 1670\ M^{-1}$, which indicated facile coordination of acetate to the bis-tryptophan ligand.

The association constants for **1**, **2** and **3** with selected anions were determined by fluorescence titration methods and presented in Table 1. The emissions observed at 381 nm for ligands **1** and **2** upon addition of acetate anions were significant (with upto 10-fold enhancement for the latter), given the prominent differences in the fluorescence emissions of **1** and **2** in their pristine states. Similar fluorescence changes were noted for ligand **3** upon coordination of acetate anions which apparently originated from intermolecular charge transfer (ICT) between the indole rings of the ligand; such intramolecular charge transfer (ICT) interactions have been observed with coumarin ligands upon addition of bisulfite [18], as well as for indole-based ligand upon coordination of Zn(II) cations [19,20]. Further indications in this regard were obtained from the fact that the presence of water or methanol substantially suppressed the effects of acetate anion on ligand fluorescence. We found that the characteristics of the emission profiles for the ligands **1**–**3** upon acetate binding (Scheme 1) are reminiscent of di-tryptophan structures [21]. On the other hand, the addition of halide ions causes quenching of fluorescence apparently via photo-induced electron transfer pathway [3,22].



Scheme 1. Possible anion coordination modes for ligand **1**.