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Anion-binding properties of ureidoquinoline and its turn-on fluorescence in the presence of fluoride anions

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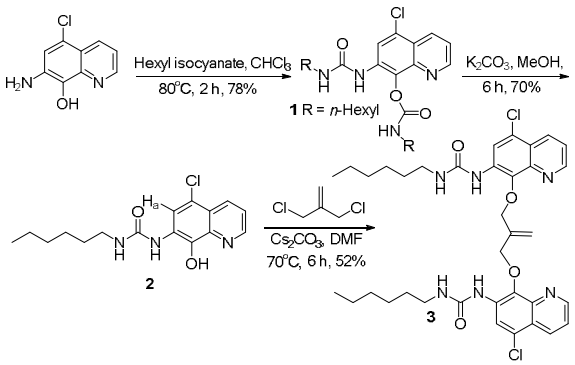
ABSTRACT

The anion-binding properties of ureidoquinoline, a derivative of 8-hydroxyquinoline, were investigated. In the presence of anions, ureidoquinoline exhibits turn-on fluorescence rather than its fluorescence being quenched or shifted. These properties are rare for phenol-based sensors. In particular, ureidoquinoline binds to $H_2PO_4^-$ and BzO^-, while F^- binds to ureidoquinoline *via* its hydrogen bonds when less than 2 equiv. of F^- are present. With more than 2 equiv. of F^-, the phenolic OH group of ureidoquinoline is deprotonated. Under such conditions, ureidoquinoline emits intense fluorescence. Under the condition, ureidoquinoline can be used for the detection of fluoride anions under illumination from a laboratory hand-held UV lamp or using a spectrofluorometer.

In supramolecular chemistry, new receptors that recognize both neutral and charged species have drawn the attention of researchers. Of particular interest are colorimetric or fluorescent sensors that detect target species and can provide qualitative (or quantitative) analytic information simply by analyzing the changes in their optical signals.[1] These sensors often afford rapid and convenient analysis techniques for the target species compared to methods based on instrumental analysis. Generally, fluorescent sensors are preferred over colorimetric sensors because of their superior sensitivity. Thus, there have been many efforts to develop new fluorophores that possess selective characteristics for analytes.[1, 2] To date, many chromophores have been developed, and each chromophore has its own merits. However, 8-hydroxyquinoline-based chromophores have been relatively less explored, but they have been modified to be sensors for anions[3] and cations[4], and materials[5] for organic light-emitting diodes (OLEDs). Recently, our group reported that bis-ureidoquinoline (**3**) exhibits turn-on fluorescence in the presence of F^-, which occurs *via* the NH groups of bis-ureidoquinoline hydrogen bonding to F^- (Scheme 1).[3a, 6] In the previous study, bis-ureidoquinoline (**3**) was synthesized from two molecules of ureidoquinoline (**2**), which was in turn obtained from **1** as shown in Scheme 1. We also recognized and partly understood the anion-binding properties of **2**. However, they were not reported because the binding properties of **2** were quite different from that of **3**. Thus, we report the detailed anion-binding properties of ureidoquinoline here. The unique anion-binding behavior of **2** is attributed to the phenolic OH of **2**. Specifically, while bis-ureidoquinoline **3** selectively binds to F^-, **2** binds to $H_2PO_4^-$ and BzO^-. However, F^- deprotonates the phenolic OH group of **2** in the presence of more than 2 equiv. of F^-. Moreover, by itself, **2** exhibits very weak fluorescence, but it emits intense fluorescence in the presence of more than 2 equiv. of F^-.



Scheme 1. Syntheses of ureidoquinoline (**2**) and bis-ureidoquinoline (**3**).

To evaluate the anion-binding properties of **2**, it was titrated with various anions in the form of tetrabutylammonium (TBA) salts. In the absence of F^-, **2** shows a sharp UV absorption band

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