Synthesis of 3,4,6-Triaryl-2-Pyridone Derivatives and Their Fluorescent Properties

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We previously reported that 3,4,6-triaryl-α-pyrone derivatives exhibited greenish-yellow fluorescence in the solid state, but did not exhibit fluorescence in solution at all.[1-4] This unusual fluorescent properties are caused by fixing the 6-aryl group of the pyrones, and are the result of molecular packing. These interactions induce a pathway for radiative decay, which is associated with intense fluorescence emission only in the solid state. If the oxgen atoms in the pyrones are replaced by nitrogen units, the resulting pyridones would show unique fluorescent properties.

Scheme 1. Synthesis of pyridones

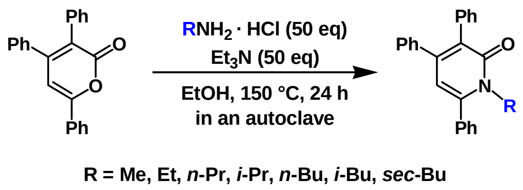
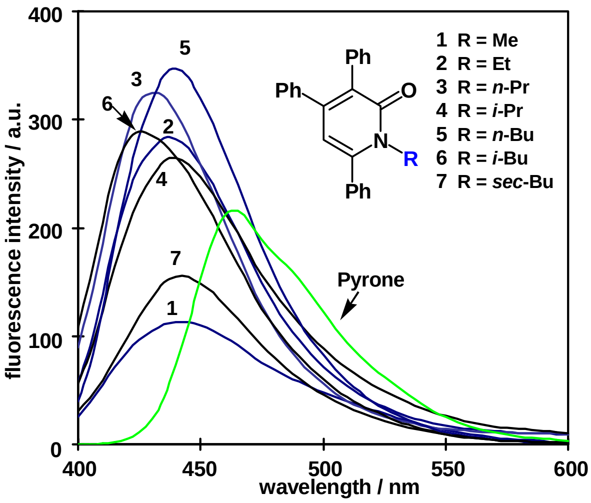
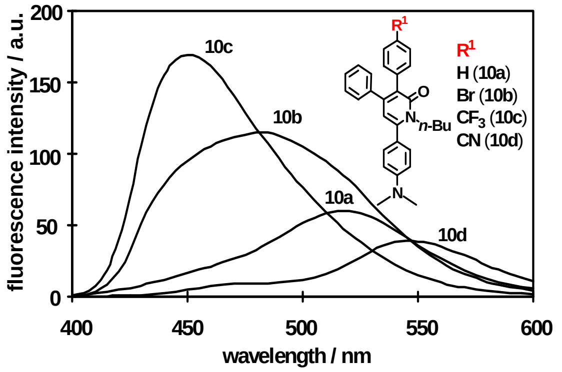


Figure 1. Fluorescence spectra of **1-7** in the powdered form



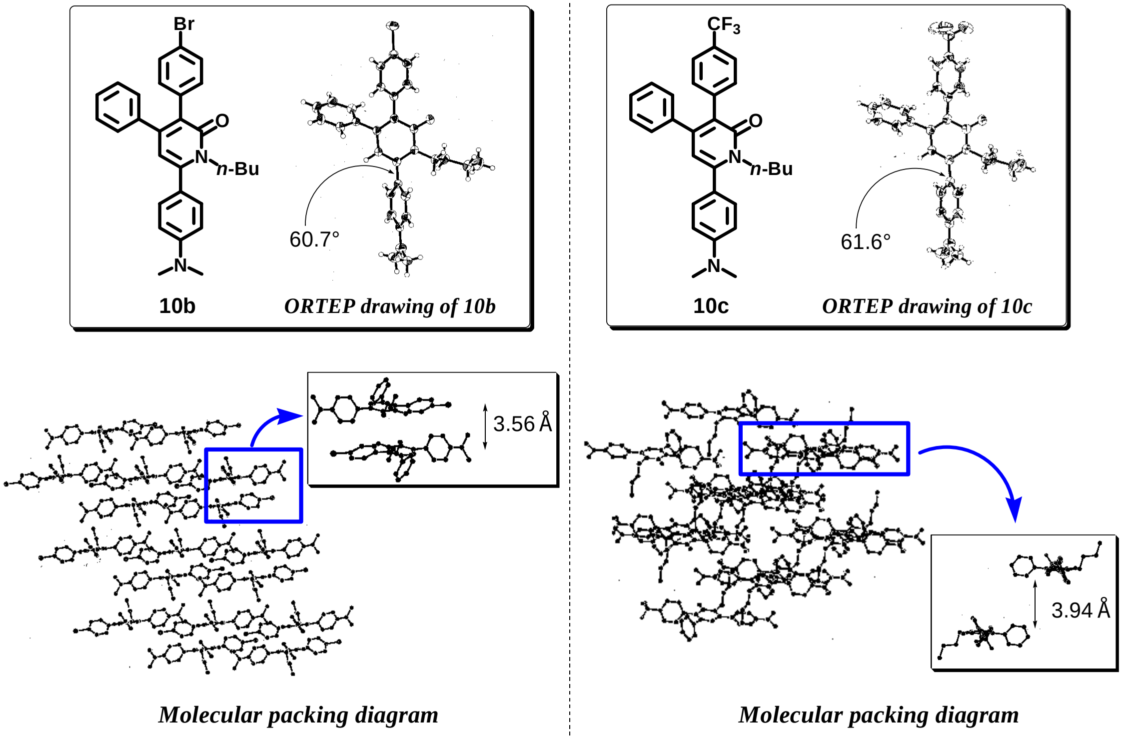
From these points of view, we synthesized 3,4,6-triaryl-2-pyridone derivatives and investigated the relationship between their fluorescent properties and crystal structures. The pyridone derivatives were readily synthesized in good yields by the reaction of the corresponding pyrones with primary amines (Scheme 1). Fluorescent spectra of the pyridones were blue-shifted compared with these of pyrones. Among the pyridones, *N*-*n*-butyl pyridone emitted an intense blue fluorescence in the solid state

Figure 2. Fluorescence spectra of **10a-10d** in the powdered form



(Figure 1). To change the properties extensively, the pyridones having electron-withdrawing and -donating aryl groups at 3- and 6-positions were prepared. The introduction of dimethylamino group to *para*-position of the 6-aryl group and cyano group to 3-aryl group caused red-shift due to intramolecular charge transfer (Figure 2). To investigate the difference in fluorescence spectra, X-ray crystallographic analyses were performed on **10b** and **10c** (Figure 3). Although both the aryl groups at the 6-position were twisted from the planes of the pyridones by about 60°, the molecular packings of them were quite different. Namely, the crystal packing arrangement of the molecules of **10b** was parallel to each other and the intermolecular distance was 3.56 Å. In contrast to the structure, **10c** was arranged in a zig-zag fashion and the interplaner distance of molecules was 3.94 Å. The difference of the interplaner distance of each compounds would influence the fluorescence intensities, which is explained by intermolecular energy transfer.

Figure 3. Crystal structures and molecular packing diagrams of **10b** and **10c**



Molecular packing diagram *Molecular packing diagram*

Reference:

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