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Solid-state red emission of boron–fluorine complexes with extended π-conjugated structure

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ABSTRACT

Two unique boron–fluorine complexes bearing extended conjugated structure were designed and synthesized facilely. These compounds absorb in visible region and emit red light in solutions with large Stokes shift. However, emission red-shift was observed with concentration increasing, showing typical *J*-aggregated fluorescence. Due to the *J*-aggregate formation, red emissions were observed in solid state for both compounds.

1. Introduction

Fluorescence has been recognized as one the most sensitive and powerful tools for various applications, including biomedical monitoring, sensing, and also photoelectric devices [1]. During the recent decades, it has been of great interest for researchers to search chromophores with high fluorescent intensity (large absorption coefficient and high quantum yield). Till now, a large number of chromophores have been found to emit intensely in solution, and some have even been commercially available, such as Rhodamine derivatives, cyanine dyes, etc. However, photoelectric devices based on fluorescent organic solids demand that these compounds can preserve their photophysical properties in the solid state [2]. Most chromophores developed till now don't meet this requisite because fluorescent dyes usually have flat π-conjugated structures, which tend to form excimers and aggregate via parallel π-π stacking. Especially for red fluorescent materials, they are usually polar in nature and possess π-extended system, which makes them much easier to aggregate in solid state.

Aggregate-induced emission enhancement (AIEE) dyes have aroused great interest because these dyes emit intense fluorescence in solid states. Most AIEE dyes reported till now emit blue to green fluorescence. Recently, red-emissive dyes with aggregate-induced emission enhancement (AIEE) are reported by several groups. One popular strategy is to introduce red chromophores conjugatedly to small AIEE molecules, and then intramolecular charge transfer would induce the red chromophores to emit in solid state [3]. Another strategy is to construct conjugated D-π-A structure, and *N,N′*-dimethyl moieties are mostly adopted as donor [4]. *N,N′*-dimethyl groups can rotate freely in solutions to result in energy lost via non-irradiative decay. But the rotation can be inhibited in solid state, resulting in fluorescence enhancement in nanoparticles and solid powders. Due to the intramolecular charge transfer (ICT) characteristic, they unusual have large Stokes shift, especially in polar conditions. [5] Some other strategies are also proved to be successful, such as embedding red-emissive dyes into matrix or inhibiting parallel π–π stacking through polymerization [6]. Till now, it's still challenging to construct NIR solid-emissive dyes with high efficiency, although they are especially important for OLED [7].

Typical boron–fluorine derivatives (typically BODIPY) are a class of excellent dyes, which usually show intense emission (high fluorescent quantum yield and absorption coefficient) in organic solutions, excellent photo-stability and chemical stability. They comprise most requisites for applications in various research fields, such as sensor, bio-imaging [8], and photosensitizer [9]. Near-IR BODIPY dyes can be easily prepared by extending its π-conjugation system. But typical BODIPY dyes tend to aggregate to form non-emissive species in solid state due to its highly planar structure, especially for red emissive BODIPYs. Some strategies have been proved to be effective to prevent parallel packing, such as introducing bulky isolator [10], construction of non-covalent

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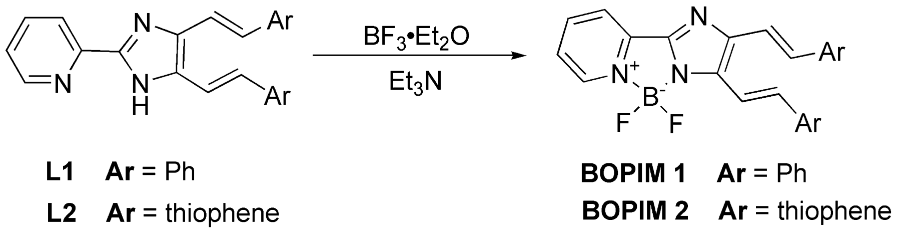

Scheme 1. Synthesis of red-emissive BOPIM dyes.

bond to facilitate non-parallel supramolecular interactions [11]. During the recent years, we developed a class of unique solid-emissive boron–fluorine dyes (BOPIM), using heterocyclic rings instead of pyrroles [12]. These dyes can form series of intermolecular non-covalent bonds, and these interactions help to inhibit formation of parallel-packing induced aggregates. The synthesized dyes are structurally simple and emit from blue to orange color. Then it came to our mind that boron–fluorine dyes with long-wavelength emission in solid state may be obtained by extending the π-conjugation of BOPIM dyes. Herein, we described the synthesis (Scheme 1) and characterization of π-extended structures based on BOPIM chromophore.

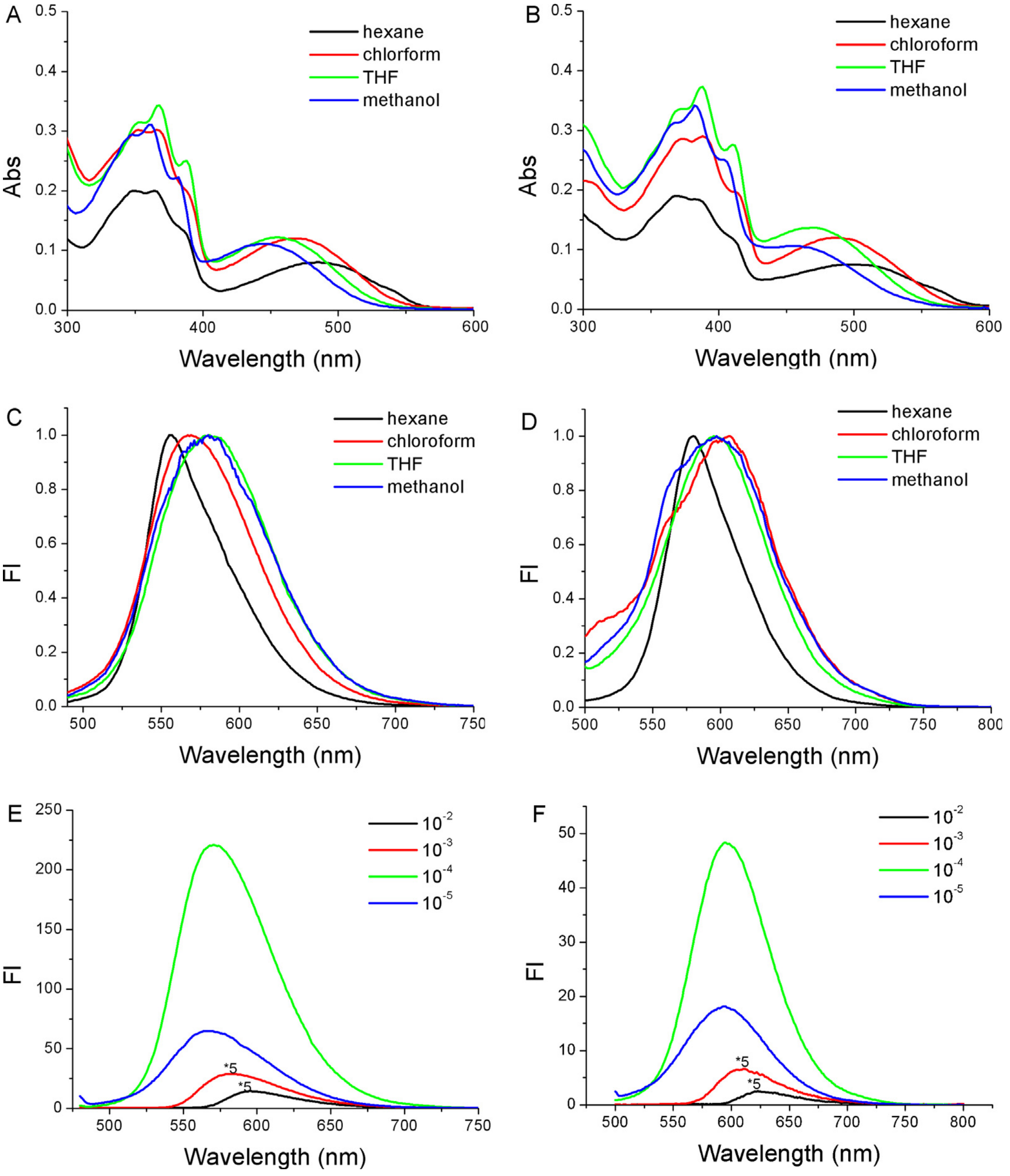

Fig. 1. (A) Absorption of BOPIM 1 in different solvents; (B) absorption of BOPIM 2 in different solvents; (C) fluorescence spectra of BOPIM 1 in different solvents; (D) fluorescence spectra of BOPIM 2 in different solvents; (E) concentration-dependent fluorescence spectra of BOPIM 1 in chloroform; (F) concentration-dependent fluorescence spectra of BOPIM 2 in chloroform.