Near-infrared Emissive Properties and Their Stimuli-responsiveness of π-Conjugated Polymers Based on Flexible Boron Complexes

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The stimuli-responsive luminescent properties are useful as chemical sensors. Especially, near-infrared (NIR) light-emitting materials can be high-sensitive sensors because of the possibility to convert small energy changes into large wavelength ones. To endow some stimuli-responsiveness, one of the promising properties is aggregation-induced emission (AIE), proposed by Tang.[1)] AIE luminogens (AIEgens) exhibit no or weak emission in solution but become highly emissive in aggregation or solid state. Recently, turn-on type NIR AIEgens have reported.[2)] However, the wavelength changes were limited due to the twisted structures which isolated the fluorophores. On the other hand, we have developed novel AIEgen boron-fused azobenzene complexes. Unlike common AIEgens, the π-conjugated system can be expanded, and drastic fluorescence wavelength changes are expected. In contrast, the copolymer constructed by the boron complex and a strong donor unit showed NIR emission in solution while the fluorescence drastically weakened in film, which phenomenon is called aggregation-caused quenching (ACQ).[3)]

In this work, we successfully developed AIE-active NIR emissive π-conjugated polymer **P-Me-BT** by introducing methyl group at boron. Comparing with conventional ACQ polymer **P-F-BT**, their photophysical properties were evaluated (Figure 1). Furthermore, their temperature-responsive luminescent properties were clarified (Figure 2). As the temperature decreased, both polymers aggregated and exhibited different changes of emission wavelength and intensity reflecting the difference of AIE and ACQ properties.

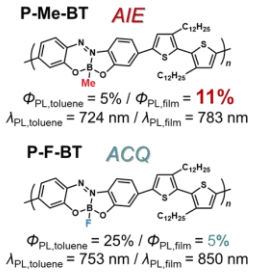

Figure 1. Chemical structures and photophysical properties of **P-Me-BT** and **P-F-BT**.

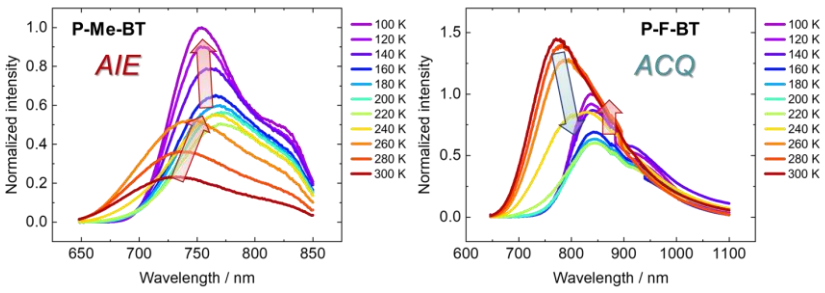

Figure 2. Variable temperature photoluminescence of **P-Me-BT** and **P-F-BT** in 2-methyltetrahydrofuran (1.0×10^{-5} M per repeating unit) at the condition from 300 to 100 K in 20 K increments, excited at wavelengths of absorption maxima.

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