

## Triplet Bandgap Engineering Using an Ion-Trapped Single Dye for Color-Tunable Phosphorescence at Cryogenic Temperatures

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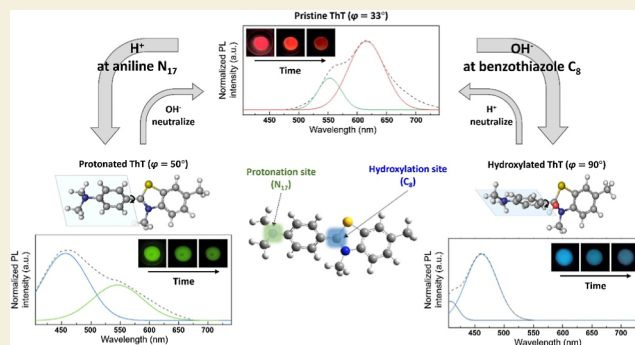
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**ABSTRACT:** This study interprets the changes in the molecular structure resulting from the ion trap of a single dye, thioflavin T (ThT), where the proton and hydroxide directly combine. The triplet emission characteristics with altered bandgap at cryogenic temperatures were analyzed using chemical analysis and quantum calculation. In ThT solutions with added hydrochloric acid, H<sup>+</sup> binds to N<sub>17</sub> in the aniline group resulting in protonation, while upon the addition of sodium hydroxide, OH<sup>-</sup> binds to C<sub>8</sub> in the benzothiazole leading to hydroxylation. Ion binding not only affects intramolecular charge distribution but also alters the dihedral angle of the rotor for energy minimization, calculated as 50° for protonated ThT and 90° for hydroxylated ThT compared to the pristine state (33°). At a cryogenic temperature of 77 K, where the nonradiative energy relaxation process is suppressed, triplet emission lasting for ~1 s was observed, exhibiting different luminescent colors depending on the kind of trapped ions. In 1 mM ThT solution, the ion trapping resulted in the bandgap changes, resulting in red, green, and blue emissions for pristine, protonated, and hydroxylated states, respectively, which can also be reversed. However, at a relatively high concentration of 10 mM, strong interactions between ThT molecules prevented ion trapping.

**KEYWORDS:** thioflavin T, cryogenic temperature, photoluminescence, protonation, hydroxylation



## INTRODUCTION

Thioflavin T (ThT) is a water-soluble organic cationic dye molecule widely used as a fluorescent probe to detect amyloid fibrils.<sup>1–4</sup> It consists of a benzothiazole group, an aniline group, and a freely rotating C–C bond shared between the two groups. It has recently been reported that its fluorescence intensity increases when combined with nucleic acid<sup>5,6</sup> and G-quadruplex,<sup>7,8</sup> and it is a suitable fluorescent probe in the field of biosensing. In general, ThT emits fluorescence from the singlet state at room temperature via the following mechanism. ThT is converted from a locally excited state, where the dihedral angle ( $\varphi$ ) of the benzothiazole and dimethylaniline rings is 33° in a low-viscosity solvent such as water, to a twisted intramolecular charge transfer (TICT) state of 90° with internal rotation (Figure 1a). It then returns to the ground state at 33° and emits weak fluorescence because it undergoes a nonradiative process.<sup>9–11</sup>

Most of the pure organic fluorescence organic luminophores, such as ThT, do not contain heavy metal ions or halogen ions to promote spin–orbit coupling at room temperature.<sup>12–15</sup> Therefore, intersystem crossing (ISC) and triplet exciton populations cannot occur, thereby resulting in only fluorescence, which is a radiative energy transfer from the lowest singlet state (S<sub>1</sub>) to the singlet ground state (S<sub>0</sub>). However, at a cryogenic temperature of 77 K, the molecular motion and

phonon vibrations are extremely suppressed. This reduces the nonradiative relaxation of the triplet state so that phosphorescence can be expressed even in pure organic materials. In ThT molecules, intramolecular rotation causes TICT and reduces the emission efficiency at room temperature. At cryogenic temperatures, molecular motion is confined to a rigid matrix, and TICT is suppressed, thus emitting intense light. Photoluminescence (PL) color control of the molecule is achieved by changing the substituent, adjusting the type and ratio of the dopant, and using a vertical stacking device.<sup>16–20</sup> Molecules can form new covalent bonds by directly bonding with cations or anions. The molecular structure of ThT can be easily altered by ion trapping with protons or hydroxides, which are mainly used for pH control. When a proton (H<sup>+</sup>) or hydroxide (OH<sup>-</sup>) was added to the ThT solution, each ion was bound to the ThT molecule in the solution.<sup>21,22</sup> We can expect the bandgap of the ThT molecules to be simply modulated by altering the electron arrangement and internal charge transfer.

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