

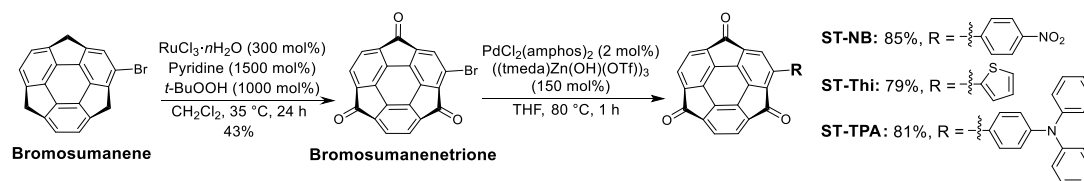
Solvent Dependency of the Charge Separation and the Near-Infrared Emission of Sumanenetrone-based Dyes

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Sumanenetrone (ST) is a triketone derivative of curved- π conjugated sumanene. It is known to show a strong electron-accepting ability close to C_{60} .¹ However, due to the low reactivity of the peripheral aromatic carbons and limited sequential approach to its functionalization, the derivatization of ST was not well investigated. We recently found an effective functionalization method to prepare various Donor-Acceptor (D-A) type ST derivatives that show unique emission properties. In this work, we report the synthesis of ST-based new D-A type molecules and their optoelectronic properties with a particular focus on the luminescence property of ST-TPA.

Synthesis of functionalized STs was achieved by recently reported Lewis acid-mediated Suzuki-Miyaura coupling reaction² using bromosumanenetrone, which can be prepared from previously reported bromosumanene³ through Ru-mediated oxygenation (Scheme 1).



Scheme 1. Synthesis of ST-based D-A type molecules.

All the derivatives showed two main absorption bands at both the UV range (250 nm to 500 nm) and the visible region reaching 800 nm, indicating their charge-transferring nature from the substituent to ST moiety. In the case of ST-NB and ST-Thi emission spectra, clear emission was observed in CH_2Cl_2 at 600 nm and 680 nm, respectively (Figure 1a).

Meanwhile, ST-TPA did not show emission in CH_2Cl_2 but showed strong NIR emission at 703 nm in Hexane (Figure 1b).

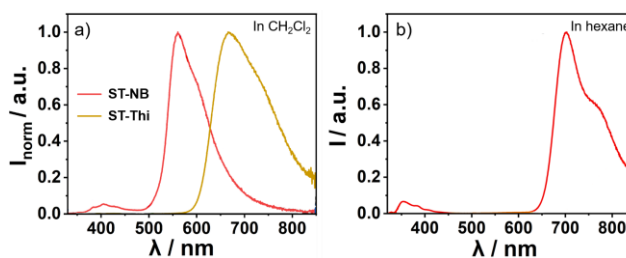


Figure 1. Emission spectra of a) ST-NB and ST-Thi (λ_{ex} = 320 nm), b) ST-TPA (λ_{ex} = 300 nm).

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