

Solid-State Emissive Chemosensors based on Boronate Supramolecules

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Molecular systems with enhanced emission properties in the solid-state involving aggregation have been attracted much attentions because of numerous applications in material science. Given that the sophisticated control of intra- and intermolecular effect on the emission enhancement is crucial, supramolecular organization is facile and profitable way. It is known that boronic acids reversibly form covalent bond with diols or catechols to produce ensemble systems through boronate esterification, which have been utilized as powerful building blocks in applications of not only sensing

and separation but also self-assembly. Therefore, boronate supramolecules with emission switching in the solid state is promising candidate for chemosensor design because chemical stimulus-induced transformation of the solid state could lead to a selective change in the emission. As a proof-of-principle, *gem*-di(boronic acid)-appended tetraphenylethylene (**DB-TPE**) was synthesized (Figure 1). Boronate esterification of **DB-TPE** with commercially available L- or D-tartaric acids led to preparation of chiral ensembles that showed enantioselective emission toward chiral diamines through enantiospecific aggregation.¹ On another front, it was found that reaction of **DB-TPE** with di(trimethylolpropane) in MeOH produced a [2+2] macrocycle (comprising two tetraphenylethylene units and two linkers) exclusively. Notably, it self-assembled as a stable nanoparticle in water to form blue-emissive nanoparticle ($\lambda_{em} = 483$ nm, $\lambda_{ex} = 365$ nm, $\Phi_F = 31\%$) with average diameter of 312 ± 44.6 nm.²

Other intriguing feature of boronate systems is to show room-temperature phosphorescence (RTP) behavior. Their unique properties involving afterglow with long lifetime have received much attention for their potential applications in the fields of lighting, sensing, imaging etc. In this study, we found that boronate microparticles (**BP**) obtained by sequential boronate esterification of benzene-1,4-diboronic acid and pentaerythritol showed RTP behavior with emission maximum of 494 nm when excited at 254 nm (Figure 2). Multi-color emission in water-dispersion state by grafting rhodamine B on the surface is discussed.

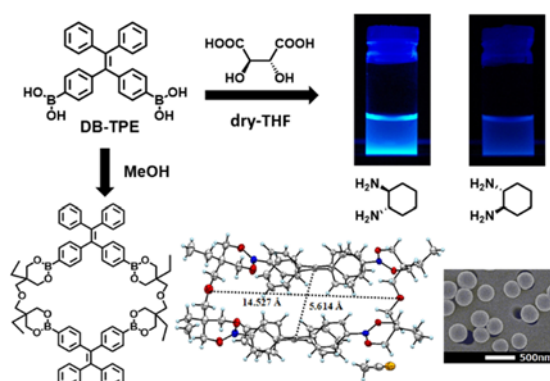


Figure 1. Functionalization of diboronic acid-appended TPE.

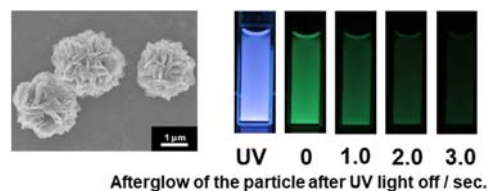


Figure 2. RTP behavior of boronate particles.

(1) Kawai, M.; Hoshi, A.; Nishiyabu, R.; Kubo, Y. *Chem. Commun.*, **2017**, 53, 10144–10147.

(2) Hoshi, M.; Kaneko, N.; Nishiyabu, R.; Kubo, Y. *J. Mater. Chem. C*, **2018**, 6, 11052–11062.

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He was Assistant Professor of Kochi University (1986 – 1992) and obtained PhD in 1990 from Osaka Prefecture University. After a Post-doctoral Fellow stay (1990 – 1991) in Prof. J. L. Sessler group at the University of Texas at Austin, since 1992, he has joined Saitama University as an Associate Professor, moving to Department of Chemistry at Tokyo Metropolitan University (TMU) as a Professor in 2008. He also was a researcher of Precursory Research for Embryonic Science and Technology (PRESTO) under Japan Science Technology Agency (1997 – 2000) and has concurrently been a researcher at Research Center for Gold Chemistry of TMU (2014 –) and at Research Center for Hydrogen Energy-based Society of TMU (2016 –). He has also been Research Fellow of Institute of Industrial Science, The University of Tokyo since 2017.

His research interest has focused on self-organization-based molecular systems and functional materials for applications in organic electronics.