Towards Iminoboronate Polymers as Dynamically Adaptable, Photoactive Materials

Evan N. Keyzer,† Dr Andrew J. Musser,§ Prof Richard H. Friend,§ Prof Jonathan R. Nitschke†

†Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK
‡Department of Physics, Cavendish Laboratory, University of Cambridge, J.J. Thomson Ave, Cambridge CB3 0HE, UK

*e-mail: ek405@cam.ac.uk

Plausible Iminoboronate Polymers

Introduction

Polymers built upon reversible bonds have the ability to interact with external stimuli and respond through reorganisation of their constituent building blocks, affording materials with properties that are tunable and adaptable to changes in environmental conditions. Such materials have been used for the development of applications in sensing as well as self-healing materials. Iminoboronate esters hold great potential for complex self-assembling systems based on the reversible condensation of 2-formylphenylboronic acids, primary amines, and diols. Polymers based on the iminoboronate ester motif represent a new class of dynamic, covalent, conjugated materials. The presence of two independently interchangeable dynamic covalent bonds (imine and boronate ester) opens up new opportunities to create a diverse set of functional materials (Scheme 1). Herein, we report fundamental investigations into the relationship between electron-donating/withdrawing groups and iminoboronate stability as well as optical properties using model systems. The nature of the optical transitions of oligo(aminoborinates) has also been investigated using computational modelling.

Results and Discussion

Stability and Dynamic Behaviour

- Formation of model iminoborinates from 2-formylphenylboronic acid, p-toluidine, and substituted catechols proceeds very efficiently in CH$_2$CN at room temperature (Figure 1A).
- +H NMR-monitored competitive-binding titrations of substituted catechols into a solution of 1 show that the iminoboronate motif is dynamic and stabilized by more electron-withdrawing catechols (larger $K_d$, Figure 18).

Iminoboronate Fluorescence

Since iminoborinates formed from p-toluidine were found to be non-emissive, 2-aminofluorene was adopted as a primary amine fluorophore to allow for investigation of iminoborinate photoluminescence.

- Emission of fluorene-based iminoborinates is more intense in poly styrene matrix than in CH$_2$CN solution (Figure 28).
- Increased quantum yield is likely due to matrix-induced hindered rotation of the fluorene unit, freeing out rotational relaxation pathways and increasing planarisation.
- Other non-radiative pathways still remain and limit the emission intensity of the model iminoborinates.

Computational Modeling

- Molecular orbital calculations (DFT, wB97x-d 6-31G(d,p)) were performed on a series of simple iminoborinate oligomers (left).
- The oscillator strength of the dominant transitions (backbone localised) increases relative to the low-energy CT transitions (catechol to backbone) with increasing chain length.
- The main transition redshifts as the molecule lengthens indicating that it has a significant contribution from the main-chain orbitals in the longer molecules.

Model Iminoboronate Dimers

- Absorption spectra of iminoborinate dimers show a redshift in the ‘backbone’ transition compared to the homologous p-toluidine-pyrocatechol iminoborate as well as the diamine precursors. This may support the proposed significance of main-chain orbital contributions to transitions of extended polymers.

- The iminoboronate motif is dynamic-covalent in nature and is stabilised by electron-withdrawing catechols, which may allow the polymeric materials to exhibit stimuli-responsive behaviour.

- As modelling suggests, the main iminoborinate transition becomes greatly localised on the oligomer backbone with increasing chain length (dominating potentially non-radiative CT transitions). Thus, it is likely that iminoborinate polymers (Scheme 1) will exhibit photoluminescent properties that may be tunable based on the employment of different catechols and diamines.

- Iminoborinate dimers exhibit redshifted absorbance, perhaps indicating that backbone-localised orbitals contribute significantly to the main optical transition of extended iminoborinate systems.

Conclusions

- There are several interesting possibilities for further work. Firstly, it is clear that the combination of the boronate ester with an amine is a potentially fruitful direction for future research.
- Secondly, there is scope for further investigation into the properties of these materials, particularly with regard to their potential applications in sensing and self-healing.

Bibliography