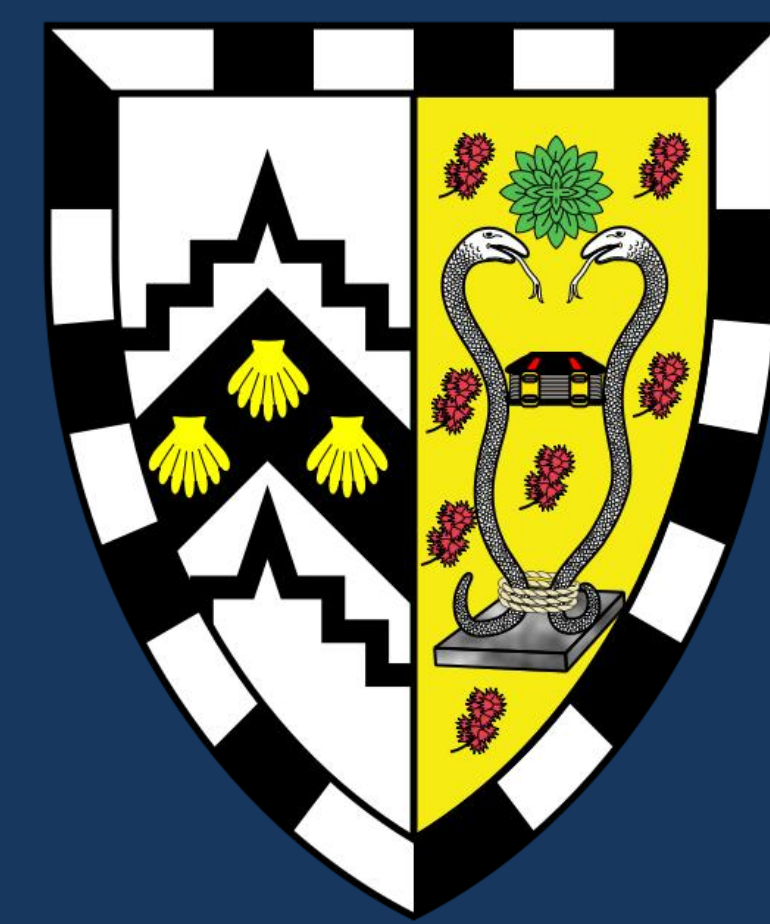


Towards Iminoboronate Polymers as Dynamically Adaptable, Photoactive Materials



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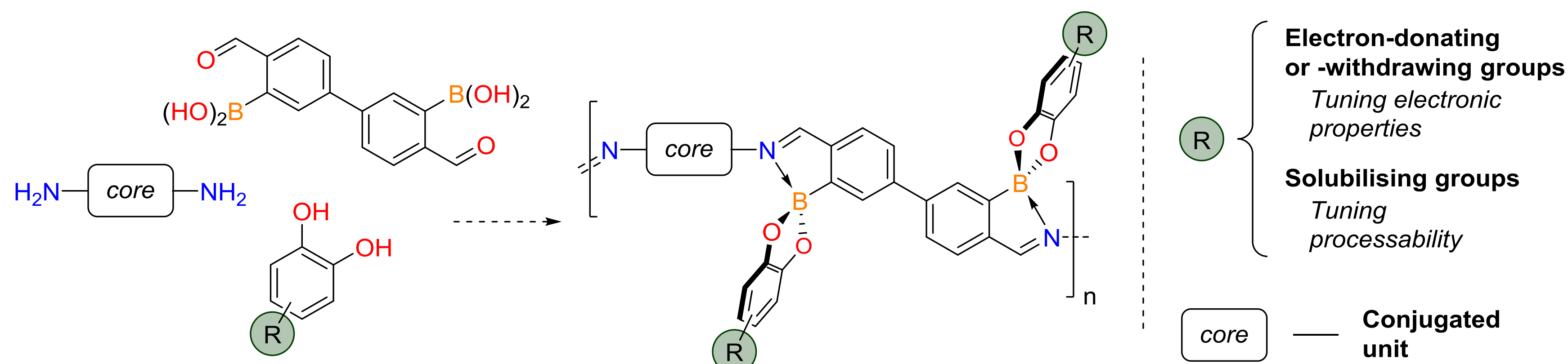
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Introduction

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 tuneable and adaptable to changes in environmental conditions.^{1,2} Such materials have been used for the development of applications in sensing³ as well as self-healing materials.⁴

Iminoboronate esters hold great potential for complex self-assembling systems based on the reversible condensation of 2-formylphenylboronic acids, primary amines, and diols.⁵ 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 catechols and iminoboronate stability as well as optical properties using model systems. The nature of the optical transitions of oligo(iminoboronate)s have also been investigated using computational modelling.



Scheme 1. Proposed assembly of conjugated iminoboronate polymers from a diamine, a substituted catechol, and bis(2-formylphenylboronic acid), affording a highly modular set of materials.

Results and Discussion

Stability and Dynamic Behaviour

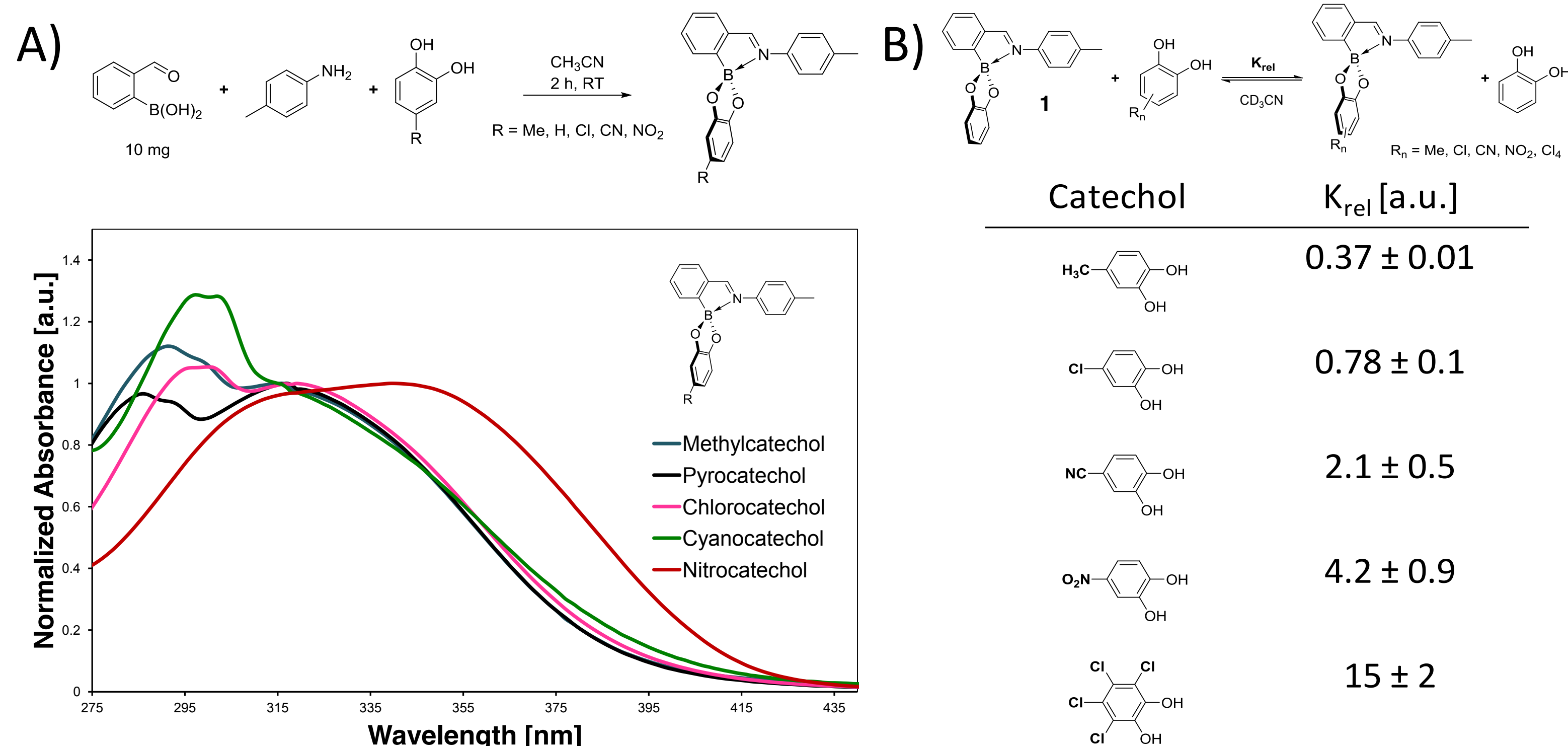


Figure 1. A) Model iminoboronate formation using a series of substituted catechols and their respective UV-Vis spectra in CH₃CN. B) Competitive-binding of substituted catechols and associated K_{rel} data.

- Formation of model iminoboronates from 2-formylphenylboronic acid, *p*-toluidine, and substituted catechols proceeds very efficiently in CH₃CN at room temperature (Figure 1A).
- ¹H 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_{rel} , Figure 1B).

Iminoboronate Fluorescence

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

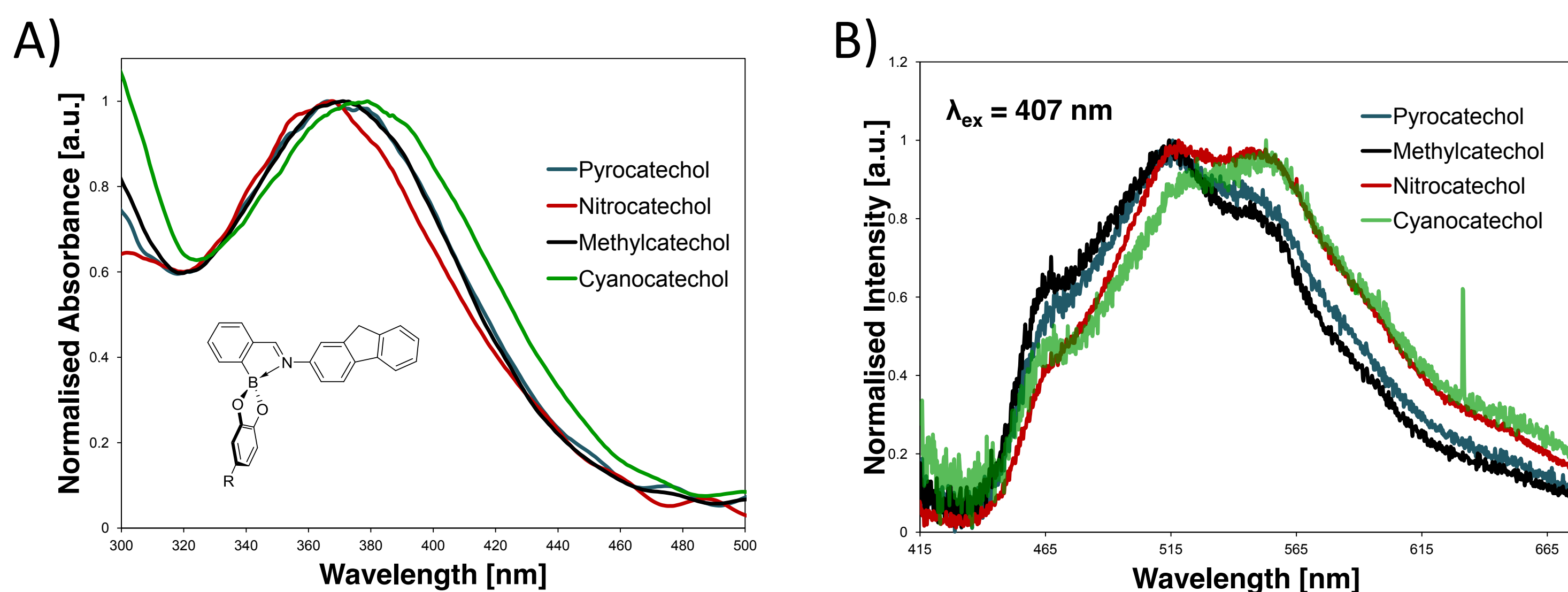


Figure 2. A) UV-Vis spectra of 2-aminofluorene based iminoboronates suspended in polystyrene film. B) Fluorescence spectra of iminoboronates in polystyrene film.

- Emission of fluorene-based iminoboronates is more intense in polystyrene matrix than in CH₃CN solution (Figure 2B).

- Increased quantum yield is likely due to matrix-induced hindered rotation of the fluorene unit, freezing out rotational relaxation pathways and increasing planarisation.

- Other non-radiative pathways still remain and limit the emission intensity of the model iminoboronates.

Catechol	CH ₃ CN Solution QY	PS Film QY
H ₃ C-C ₆ H ₃ (OH) ₂	0.33 %	1 %
H-C ₆ H ₃ (OH) ₂	0.22 %	1 %
NC-C ₆ H ₃ (OH) ₂	0.14 %	3 %
O ₂ N-C ₆ H ₃ (OH) ₂	0.10 %	0.5 %

Computational Modeling

- Molecular orbital calculations [DFT, wB97x-d 6-31G(d,p)] were performed on a series of simple iminoboronate 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.

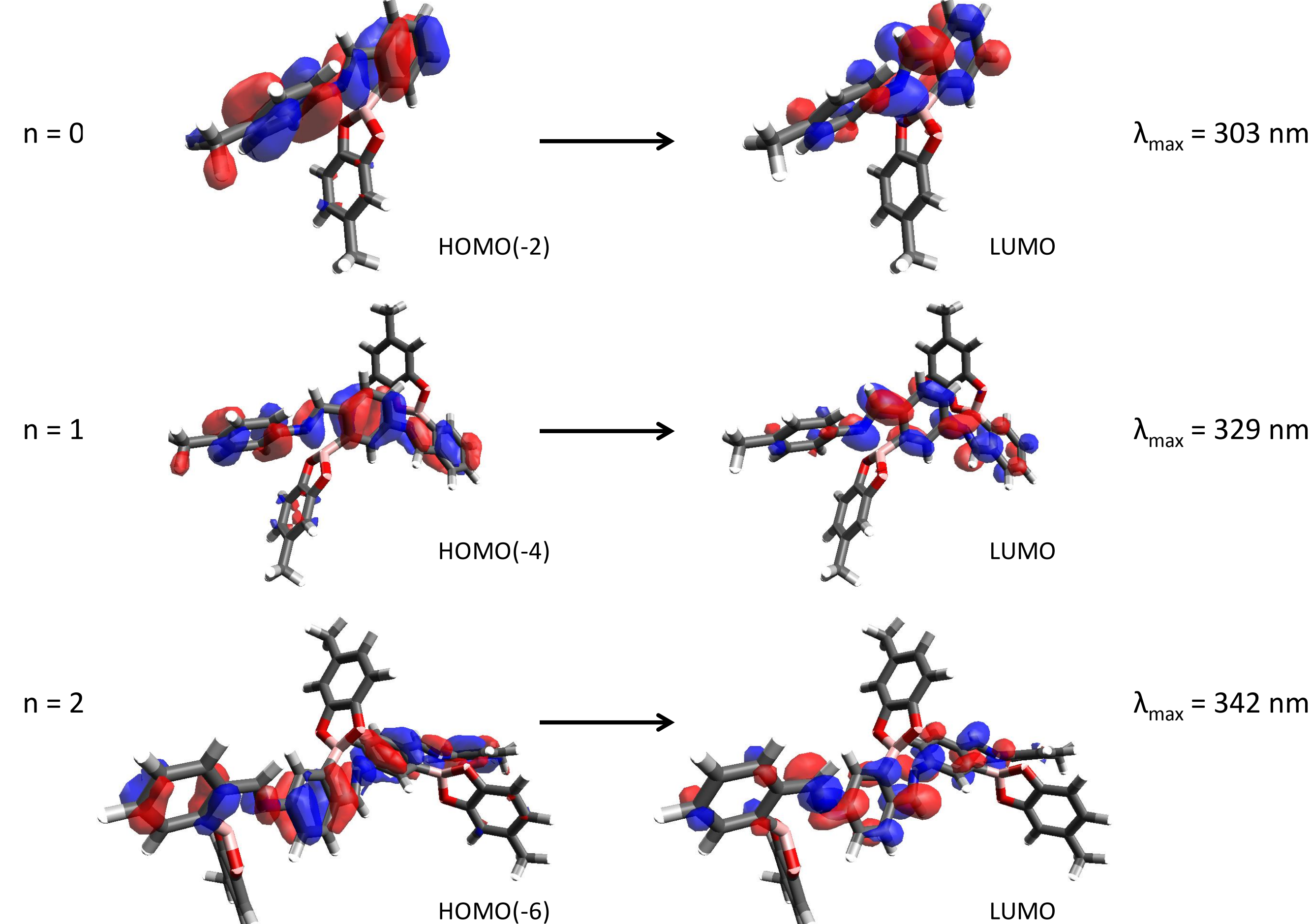


Figure 3. Calculated [DFT, wB97x-d 6-31G(d,p)] molecular orbitals of a series of oligo(iminoboronate)s. Transitions with the largest oscillator strengths chosen for visualisation.

Model Iminoboronate Dimers

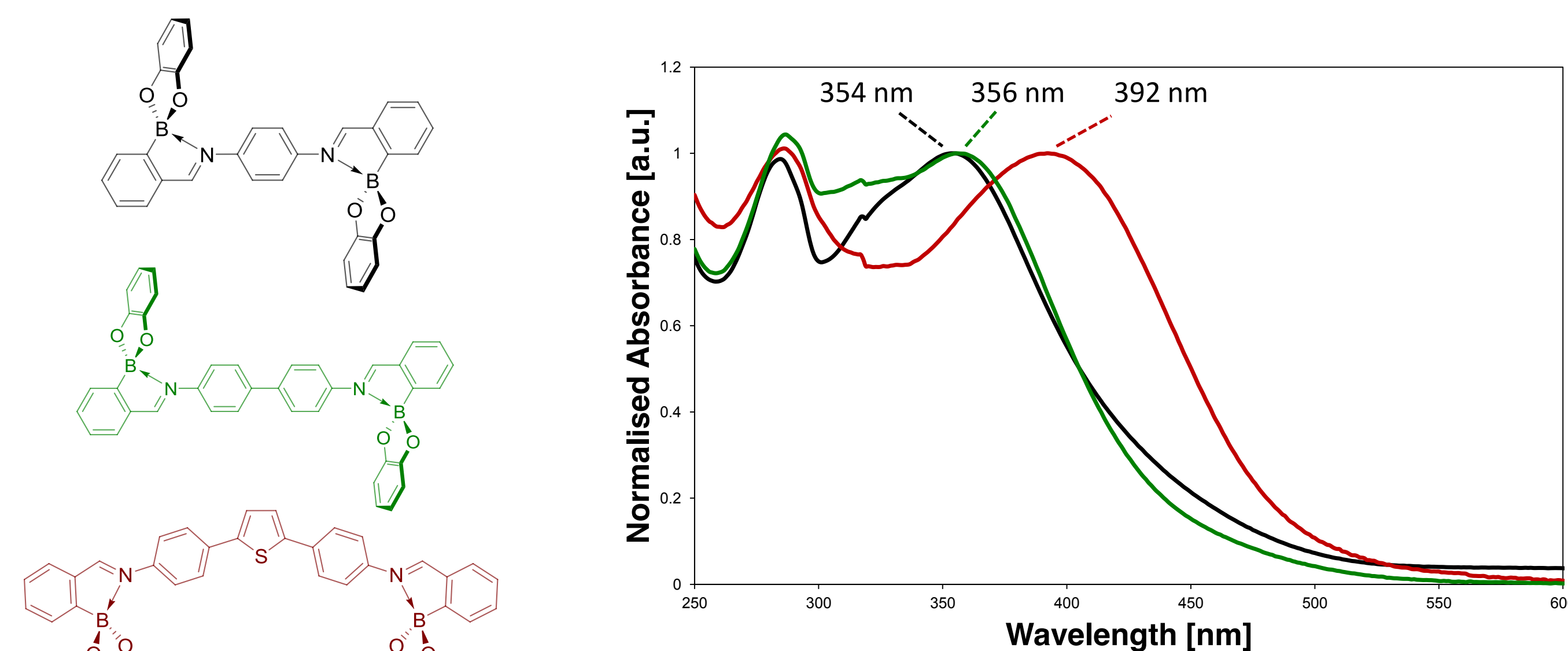


Figure 4. Structures of iminoboronate dimers and their UV-Vis spectra in CH₃CN.

- Absorbance spectra of iminoboronate dimers show a redshift in the 'backbone' transition compared to the homologous *p*-toluidine-pyrocatechol iminoboronate as well as the diamine precursors. This may support the proposed significance of main-chain orbital contributions to transitions of extended polymers.

Conclusions

- 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 iminoboronate transition becomes greatly localised on the oligomer backbone with increasing chain length (dominating potentially non-radiative CT transitions). Thus, it is likely that iminoboronate polymers (Scheme 1) will exhibit photoluminescent properties that may be tuneable based on the employment of different catechols and diamines.
- Iminoboronate dimers exhibit redshifted absorbance, perhaps indicating that backbone-localised orbitals contribute significantly to the main optical transition of extended iminoboronate systems.

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