

## Project C: Nanostructured Luminescent and Sensory Materials

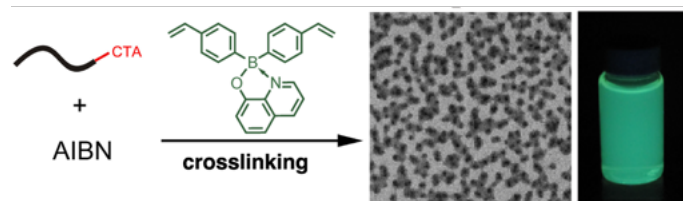
In this project, we use controlled polymerization methods to prepare luminescent boron-containing block and star (co)polymers, study their supramolecular assembly, and explore imaging and sensing applications. Fluorescent homopolymers, amphiphilic block copolymers, and star polymers were obtained by reversible addition-fragmentation chain transfer (RAFT) (co)polymerization of the corresponding styryl-type organoboron quinolate, triarylborane, and diarylborinic acid monomers.

### 1) Luminescent Organoboron Quinolate Block Copolymers and Star Polymers [C1-C4].

We chose organoboron quinolates as the chromophores because of their advantageous characteristics that include (i) strong and easily tunable emission, (ii) high stability in aqueous media, and (iii) facile derivatization. Amphiphilic block copolymers with PEO and PNIPAM were successfully prepared. In selective solvents, the block

copolymers self-assembled into vesicles, spherical, or extended branched aggregates as confirmed by dynamic light scattering (DLS) and transmission electron microscopy (TEM) studies. To promote supramolecular assembly and enable the generation of hybrid materials, a series of pyridine-functionalized boron quinolate monomer was also prepared. As polymeric Lewis bases, the pyridine-functionalized block copolymers are able to form supramolecular complexes with metal ions and Lewis acids. For example, coordination of  $ZnCl_2$  to styrene block copolymer in chloroform triggered the formation spherical micelles as well as larger aggregates.  $ZnCl_2$  was chosen for these studies because as a  $d^{10}$  ion it is not optically active itself, allowing us to study in detail the effect of self-assembly on the absorption and fluorescence properties. In contrast, the supramolecular co-assembly with zinc *meso*-tetraphenylporphyrin (ZnTPP, shown) in cyclohexane as a selective solvent for PS resulted in extended branched structures with controllable emission properties. Energy transfer from the boron chromophores to the ZnTPP moieties was observed for these supramolecular complexes.

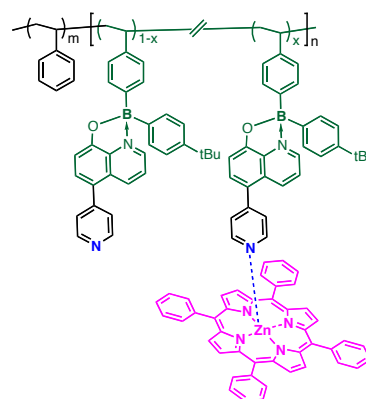
In an alternative approach, well-defined luminescent particles could be generated from a boron quinolate cross-linker and a polymeric chain transfer agent (CTA) as illustrated schematically. Well-defined star architectures with a luminescent core were successfully obtained as confirmed by GPC-MALLS, NMR, DLS, and TEM analysis. Star polymers that are derived from PNIPAM-*b*-PS were found to further aggregate in water to form strongly green-luminescent superstructures. Given their highly regular size and strong emission, these star polymers could prove useful for biological imaging applications. Similarly, organoboron



star polymers with pyridyl pendant groups were prepared by arm-first RAFT polymerization using a novel luminescent organoboron cross-linker in combination with linear P4VP polymer as a chain transfer agent. The P4VP stars lend themselves to further functionalization at the periphery in a similar way as described in the case of block copolymer micelles above.

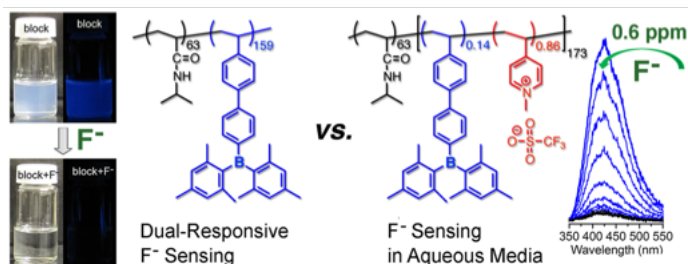
### 2) Luminescent Tricoordinate Organoboron Polymers for Anion Detection [C5-C6].

In earlier work we had demonstrated that homopolymers that bear luminescent tricoordinate organoborane moieties as side chains can be prepared by post-polymerization modification procedures and are effective as sensory



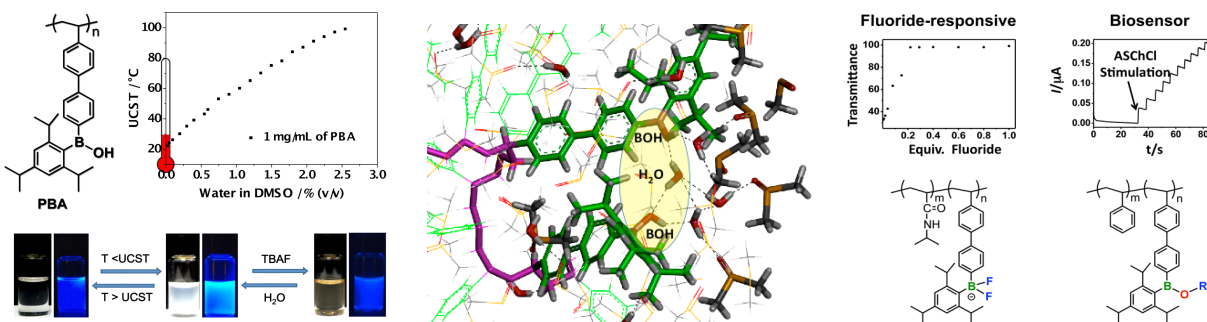
materials for anion detection. However, the poor solubility in aqueous media posed some obstacles and a straightforward approach to functional random and block copolymers was needed. Toward this end, we have recently developed RAFT polymerization techniques to give the first examples of luminescent, water-soluble block copolymers that contain luminescent tricoordinate arylborane monomers. We investigated the application of these polymers in the detection of fluoride anions. Highly

selective and sensitive fluoride detection ( $< 1$  ppm) was achieved by combining the fluorescent response upon anion binding with a physical response due to reversible aggregation of the polymer chains into micellar structures in DMF as a polar solvent (left side of Figure). Highly sensitive anion detection in aqueous solution was accomplished by introducing 4-vinylpyridine groups. Upon quaternization, the pyridinium moieties further promote anion binding through electrostatic interactions and therefore help overcome the high hydration enthalpy of fluoride anions (right side of Figure).



### 3) Luminescent Boronic and Borinic Acid Polymers as Stimulus-Responsive and Sensory Materials [C7-C10].

We have also a keen interest in the development of luminescent block copolymers that feature boronic and borinic acid groups as sensory and stimulus-responsive materials. In this respect we have recently developed a new class of borinic acid homo and block copolymers. Interestingly, we discovered that the homopolymer PBA shows a tunable upper critical solution temperature (UCST) in DMSO in the presence of small amounts of water. As the amount of water increases from 0 to 2.5 % (v/v), the UCST rises linearly from 20 °C to 100 °C (boiling point of water). Thus, the thermal responsive behavior can be tuned over a wide temperature range. We investigated the mechanistic aspects of this process by molecular dynamics simulations in a collaborative effort with researchers at the China University of Petroleum. The results indicate rapid and strong hydrogen-bond formation between BOH moieties and H<sub>2</sub>O molecules, which serve as crosslinkers to form an insoluble network.



Solutions of PBA in DMSO also show a reversible response to fluoride ions, which can be correlated to the presence of the Lewis acidic borinic acid groups. Upon addition of fluoride, the polymer becomes soluble because the functional R<sub>2</sub>BOH groups are converted to ionic [R<sub>2</sub>BF<sub>2</sub>]<sup>-</sup> groups, but it turns insoluble again upon addition of H<sub>2</sub>O which reverses this process. The highest detection efficiency was achieved with a PNIPAM block copolymer, PNIPMA-*b*-PBA. A styrene block copolymer, PS-*b*-PBA, was processed into a porous film with tunable pore size by drop-casting a THF solution in the presence of trace amounts of H<sub>2</sub>O. Upon immobilization of acetylcholine esterase, the resulting thin film was applied as an electrochemical biosensor for ASChCl substrate detection with some potential ramifications for organophosphorus and carbamate pesticides detection. The fact that the chemical structure and properties of these materials can be easily adjusted by modification of the organic substituents on boron indicates broad utility of this emerging class of smart materials.

**Other Related Collaborative Efforts [C11].** In a collaboration with Prof. G. Liu at USTC Hefei, we investigated in detail the effects of anions on the thermo-responsive properties. An inverted V-shaped series

$\text{CH}_3\text{COO}^- < \text{Cl}^- < \text{salt-free} > \text{NO}_3^- > \text{ClO}_4^- > \text{SCN}^-$  was observed for the anion-specific UCST of PBA in DMSO–H<sub>2</sub>O mixtures. This result indicates that both direct anion–polymer interactions and indirect solvent-mediated anion–polymer interactions are involved (and compete) in the specific anion effect on the UCST behavior of PBA. The dominant interactions change from direct anion binding to indirect anionic polarization of H-bonding as the anions change from chaotropes to kosmotropes. This work has been published in *J. Phys. Chem. B*.

Current efforts are aimed at further exploring the supramolecular chemistry and potential utility of borinic acid polymers, in catalysis applications. We have been targeting specifically polymers with more electron withdrawing 2,4-dichlorophenyl and 3,5-dichlorophenyl groups on boron.

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