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Invited feature article

## Stimuli-responsive side chains for new function from conjugated materials



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## ABSTRACT

This article describes several projects in our laboratory relating to stimuli-responsive conjugated materials using functional side chain moieties. Although side chain engineering has become increasingly important in controlling the packing of conjugated materials, these groups have typically been reserved for imparting solubility to otherwise insoluble materials. By incorporating solubilizing side chains through photocleavable nitrobenzyl linkers, new conjugated polymers behave as negative photoresists upon exposure to ultraviolet light with minimal photobleaching. Our approach enables photopatterning and solution-based fabrication of multilayer conjugated polymer films without the use of orthogonally soluble materials. Work to understand the electronic effects of the aromatic side chain substituents in these materials led to the subsequent discovery of aromatic interactions between side chains and main chains that control the conformations of solid-state phenylene-ethynylene oligomers, including highly twisted conjugated backbones. Such materials, when appropriately substituted, display reversible piezochromic and mechanofluorochromic behavior.

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### 1. Introduction

Conjugated materials, including both conjugated polymers and small-molecule oligomers, generally feature extended  $\pi$ -conjugation in at least one direction through some combination of aromatic and/or heteroaromatic rings and exocyclic double or triple bonds. The resulting delocalization of molecular orbitals and electron density can give these materials important optical and electronic properties, such as luminescence, exciton transport, and conductivity. Conjugated polymers have the potential to combine the properties of traditional plastics with these optoelectronic features for use in a range of applications including transistors, light-emitting devices, sensors, and photovoltaics [1–6]. Although these materials still have the key disadvantage of generally poorer performance and robustness than inorganic semiconducting materials, they offer a wide range of potential advantages including mechanical flexibility, toughness, wide tunability of properties through changes in chemical structure, and high-volume, low-cost processing from solution.

Realization of many of the advantages of conjugated materials requires their solubility. Solubility is important for both (i) synthesizing polymers with high molecular weight, which has

been shown to improve performance in a number of examples, and (ii) enabling fabrication of coatings using solution-based techniques such as spray coating or inkjet printing. Most extended, unsubstituted conjugated polymers such as poly(thiophene) and poly(acetylene) are, however, intractable in organic solvents. A highly generalizable design paradigm for conjugated polymers has therefore emerged, with long, often branched, alkyl substituents attached as pendants onto the conjugated backbone of the polymer. When present in sufficient density, length, and branching, such ‘solubilizing chains’ render conjugated polymers fully soluble, enabling film fabrication using standard solution processing techniques. These chains are generally considered functionally orthogonal to the optical and electronic properties of isolated conjugated polymer chains, which the chemical structure of the conjugated backbone dictates, provided that the alkyl chains do not introduce steric buttressing between adjacent rings. In addition to changing the length and branching structure of alkyl chains, broader approaches to altering the structures of side chains on conjugated polymers have included hydrophilic oligoether chains, fluorinated chains, conjugated side-chains, and end-functionalized side-chains, including ionic and siloxane functionalization [7,8]. Not surprisingly, the influence of side chains on the properties and performance of conjugated polymers increases in the solid state, where the side chains can affect parameters such as  $\pi$ -stacking distances and lamellar spacing between conjugated chains. Although largely limited to empirical approaches with

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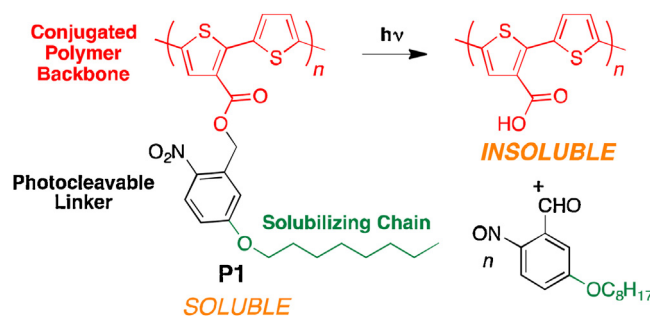


Fig. 1. Prototype example of a CP with photocleavable solubilizing chains.

individual trends being polymer-specific, side chain engineering – the optimization of side chain structure to maximize both solubility and device performance – is becoming an increasingly popular aspect of developing functional conjugated materials [7–12].

Given that flexible side chains can occupy up to 50% of the molecular weight of conjugated oligomers or polymers, it is reasonable to consider the integration of moieties into this chemical space for the design of stimuli-responsive conjugated materials. In fact, appending stimuli-responsive groups in side chains has been central in the development of CPs intended for applications in chemical sensing, in which interaction or reaction of the pendant with the target analyte causes changes in color, luminescence efficiency, luminescence spectrum, or resistivity [4,13]. Our own laboratory's research in this area, which we summarize herein, has been to expand the utility of this chemical space – the non-conjugated side chains of conjugated materials – to control their optoelectronic properties and impart new stimuli-responsive function. We focus here on two such specific areas: (1) photocleavable side chains to control solubility, and (2) side chain/main chain interactions to control optical properties.

## 2. Photocleavable side chains

The use of light as a stimulus for responsive materials has a unique combination of advantageous characteristics: (i) the spatiotemporal control of incident light is usually straightforward, (ii) dynamic, precise, and instantaneous control over the energy (wavelength of light) and stoichiometry (intensity) of the stimulus, (iii) transparency of many forms of matter to light, and (iv) other readily controlled features due to the wave nature of light, such as phase, interference, and polarization. Keeping in mind the enormous importance of photolithography to electronics, it is not surprising that the concept of directly photopatternable

organic electronic materials have found significant interest [14–26].

Our approach to photopatternable conjugated polymers rests on the concept that the vast majority of conjugated polymers require flexible side chains for solubility, and that their removal should render materials insoluble. In addition, solubilizing side chains causes several problems for organic electronic materials: (i) they take up large fractions of active layer volume, (ii) labile bonds in these chains are primary sources of photochemical decomposition [27–29], (iii) as they render most conjugated polymers soluble in the same solvents, fabricating stratified, multilayer devices using only solvent-based techniques can restrict the materials used to those that are orthogonally soluble [30,31]. Several previously known approaches use thermally- or acid-labile tertiary carboxylic esters to cleave solubilizing chains from CP backbones [32–35]. Light can also serve as an indirect stimulus that renders these types of polymers insoluble, either through photothermal heating with infrared light or photoacid/photobase generators [17,19,24,36]. In contrast, our design focuses on the use of photolabile linkers to perform the same function using light as the direct stimulus that induces insolubility of the polymer. Our overall design for photocleavable solubilizing chains is shown in Fig. 1: photolabile *o*-nitrobenzyl (ONB) linkers connect solubilizing alkoxy chains to CP backbones [37]. Irradiation of solution-deposited films with ultraviolet light cleaves the photolabile linkers, causing the CP to be insoluble.

We chose ONB groups as the photolabile linkers for several reasons [38,39]: (i) The radical mechanism of their cleavage does not require the presence of a highly polar environment such as water to stabilize an ion pair, and (ii) as shown in Fig. 2, synthetic elaboration of the ONB core as a bifunctional linker is often straightforward using the commercially available 2-nitro-5-hydroxybenzaldehyde. Reaction of the phenol group with alkylating or acylating agents appends desired functionality to

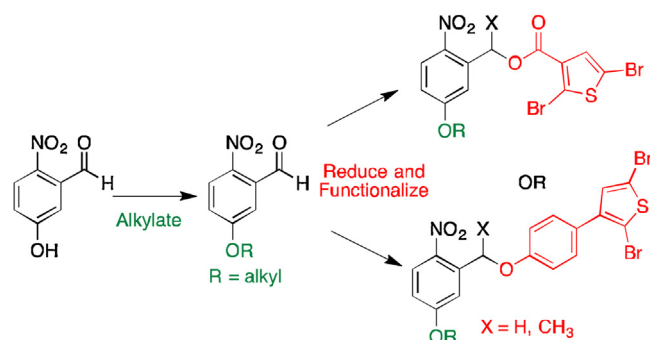


Fig. 2. General approach for synthesizing monomers with ONB-linked solubilizing chains suitable for conjugated polymer synthesis through cross-coupling polymerizations. Although examples shown here are only those that our group has published, this strategy is highly generalizable for functionalizing both the phenol and the benzylic position.

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