

Title: 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.

Highlights:

- The expansion of side chains of conjugated materials to impart function is described.
- *o*-Nitrobenzyl linkers on conjugated backbones yield insolubility upon UV photolysis.
- Varied inductive effects of non-conjugated side chains can perturb HOMO-LUMO gaps.
- Aromatic side chain/main chain interactions can twist phenylene-ethynylenes
- Piezochromism and mechanofluorochromism occur in a twisted phenylene-ethynylene.

Keywords: side chain engineering, conjugated polymers, nitrobenzyl, photolithography, piezochromism, aromatic interactions

## 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 influence parameters such as  $\pi$ -stacking distances and lamellar spacing between conjugated chains. Although largely limited to empirical approaches with 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]

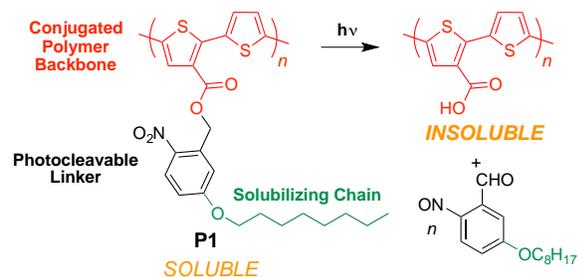
Given that flexible side chains can occupy up to 50% of the molecular weight of conjugated oligomers or polymers, it is reasonable to consider the integration of moieties into this chemical space for the design of stimuli-responsive conjugated materials. In fact, appending stimuli-responsive groups in 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.

### 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]

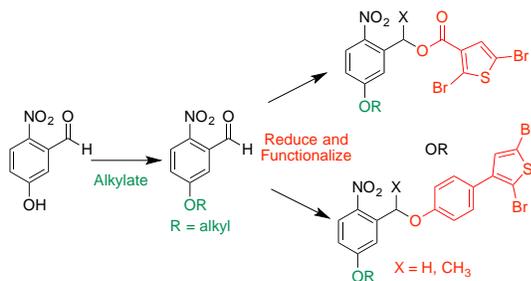
Our approach to photopatternable conjugated polymers rests on the concept that the vast majority of conjugated polymers require flexible side chains for solubility, and that their removal should render materials insoluble. In addition, solubilizing side chains causes several problems for organic electronic 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 Figure 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.



**Figure 1.** Prototype example of a CP with photocleavable solubilizing chains.

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 Figure 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 be cleaved. Subsequent reaction at the benzylic position both defines the structure of the photolysis leaving group and installs the second component to be separated upon

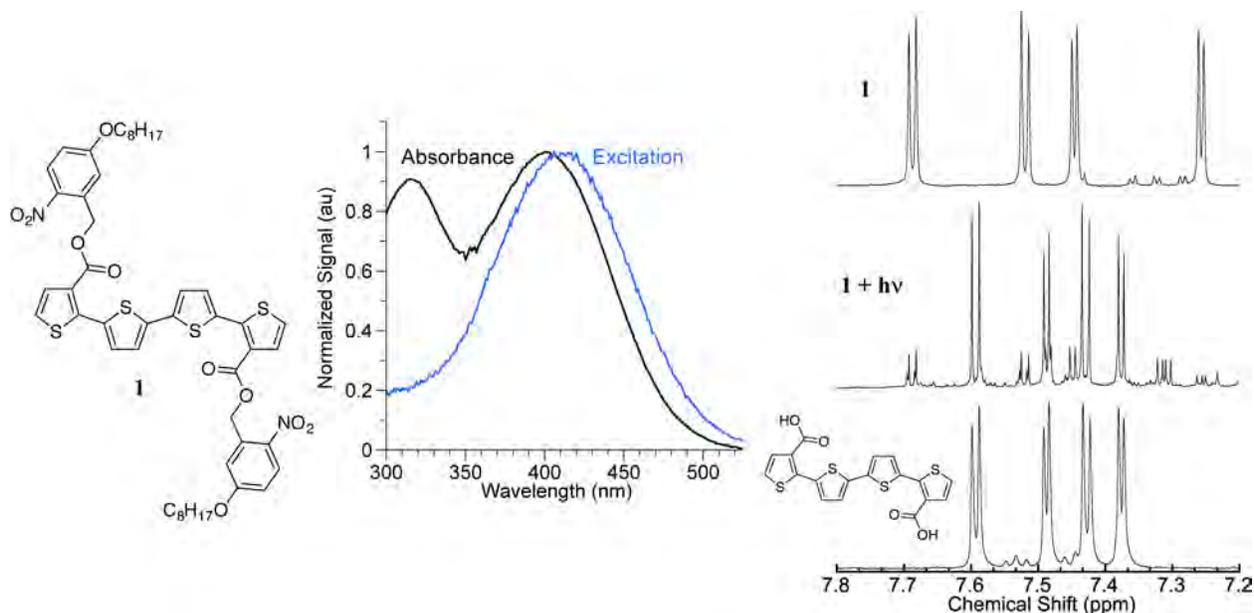
photolysis, which in our experiments are dihalogenated thiophene-based monomer units suitable for cross-coupling polymerizations.



**Figure 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.

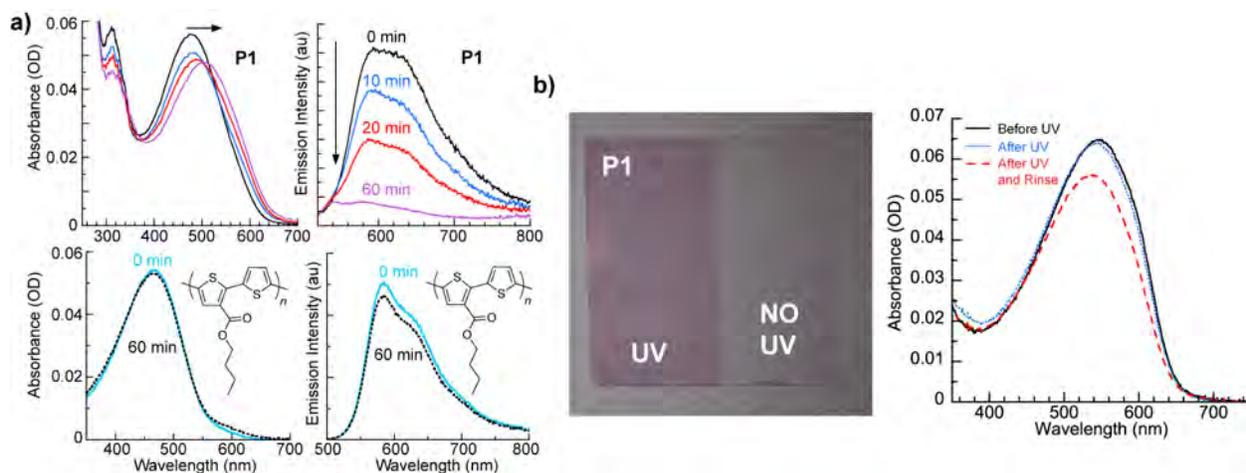
Our initial research focused on determining if photochemical cleavage was possible given that the excited state energy of the ONB chromophore is higher than that of conjugated backbones?[37] We chose thiophene-based conjugated backbones because they have greater photochemical robustness than materials that have exocyclic double bonds such as poly(phenylene vinylene)s or quaternary sites such as poly(fluorene)s.[29] We prepared polymer **P1** (Figure 1) which contains octyl chains linked to the backbone through ONB ester groups, using Stille polymerization of the appropriately functionalized 2,5-dibromothiophene and commercially available 2,5-bis(trimethylstannyl)thiophene.

The results of two experiments established that energy transfer from the ONB group to the thiophene-based conjugated chromophore would not inhibit photocleavage significantly (Figure 3). First, comparing the excitation and absorbance spectra of **1**, a small molecule quarterthiophene analog of **P1**, showed that excitation of the ONB ester chromophore around 315 nm does not yield emission from the quarterthiophene backbone in CH<sub>2</sub>Cl<sub>2</sub>. Second, <sup>1</sup>H NMR spectroscopy of a UV-irradiated sample of **1** in DMSO-*d*<sub>6</sub> shows the expected diacid as the major product. We expected these results, as photocleavable ONB groups have been used in a number of photoactivatable fluorophores that have HOMO-LUMO gaps lower than ONB,[40-42] including from our laboratory.[43]



**Figure 3.** *Left:* Structure of small-molecule polymer analog **1** with photocleavable alkyl chains. *Middle:* UV/vis absorbance and excitation spectra ( $\lambda_{em} = 540$  nm) of **1** in CH<sub>2</sub>Cl<sub>2</sub>, which demonstrates that absorbance by the ONB functional group at 315 nm does not lead to significant fluorescence from the quarterthiophene chromophore. *Right:* <sup>1</sup>H NMR spectra (in DMSO-*d*<sub>6</sub>) of **1**, a crude sample of photolyzed **1** after irradiation at 365 nm, and independently synthesized expected photolysis product. Adapted with permission from Reference 37. Copyright 2012 American Chemical Society.

The absorbance spectrum of **P1** shifted bathochromically upon irradiation at 365 nm at  $\sim 10$  mW/cm<sup>2</sup> in deoxygenated CH<sub>2</sub>Cl<sub>2</sub>. This observation, together with the measured quenching of fluorescence, are indicative of agglomeration, aggregation, and planarization of polymer chains expected upon insolubilization. These spectroscopic changes are in strong contrast to oligomer **1**, which showed no significant changes in the absorbance intensity of the quarterthiophene chromophore. Finally, an analogous polymer without the nitrobenzyl groups showed no significant changes in absorbance or emission intensity upon irradiation under identical conditions for the same amount of time (60 minutes).



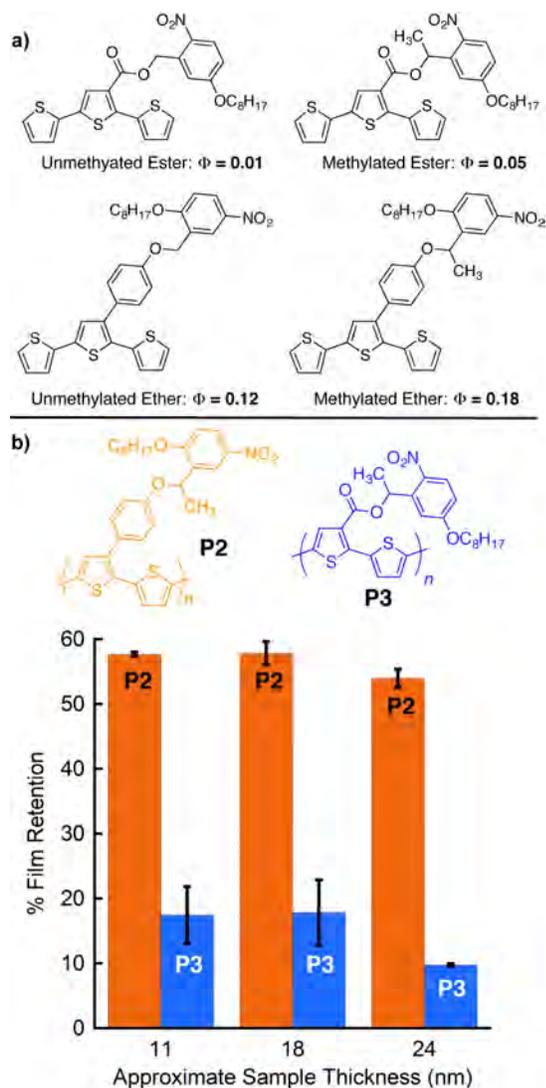
**Figure 4** a. Photoinduced changes in the absorbance and emission spectra of **P1** (top) and an analogous polythiophene without ONB linkers (bottom) illustrating the spectroscopic changes in deoxygenated  $\text{CH}_2\text{Cl}_2$  during irradiation at 365 nm at  $\sim 10 \text{ mW/cm}^2$ . b. Photoinduced insolubility of a thin film of **P1** spun-cast on a glass slide. Adapted with permission from Reference 37. Copyright 2012 American Chemical Society.

More importantly, this photoinduced insolubility persists when **P1** is a thin film. Figure 4b shows both a photograph of a thin film of **P1** on a glass cover slip after irradiating half of the film at 365 nm for 30 minutes under ambient conditions, and rinsing with toluene. The unirradiated polymer dissolved fully in toluene, while the irradiated side was largely insoluble and remained on the substrate. UV/vis spectra taken before irradiation, after irradiation, and after rinsing show less than 5% bleaching of the polythiophene after irradiation. Between 8-14% of the absorbance decreased upon rinsing with toluene. Based on GPC and UV/vis analysis, the soluble fraction of irradiated films are primarily oligomeric chains.

We next focused optimizing photolysis reactions because although these polythiophene derivatives appear to resist extensive photobleaching,[29] other polymers may not be as persistent. Previous work has demonstrated that, because of benzylic radical character that develops in the H-atom abstraction step of ONB photolysis, increasing radical stabilization through either i) additional alkyl substitution at the benzylic position,[44] or ii) electronic effects of the leaving group can increase the photoreaction quantum yield.[45] We therefore prepared terthiophene oligomers (Figure 5a) and analogous polymers that vary in the structure of ONB leaving group—as either carboxylic acids or phenols, and the substitution in the benzylic positions—either as methylenes or methines.[46]

The trend of quantum yield of photolyses of the terthiophene derivatives in chloroform, determined using  $^1\text{H}$  NMR spectroscopy and chemical actinometry, followed the expected trend (Figure 5). Note that these quantum yields are corrected for the competitive absorbance of the conjugated backbone and reflect the efficiency of photolysis only taking into consideration those photons absorbed by the ONB group. The type of unsubstituted ONB ester derived from a primary alcohol that we used in the initial study showed the lowest quantum yield of approximately 1%, in agreement the literature.[45] In contrast, the ONB ether with a phenol leaving group had a quantum yield of  $\sim 12\%$ , consistent with increased radical-stabilizing effect of the ether. Methylation at the benzylic position increased quantum yields significantly—to 5% for the ester and 18% for the ether. Therefore, relative to our initial ONB ester design, we

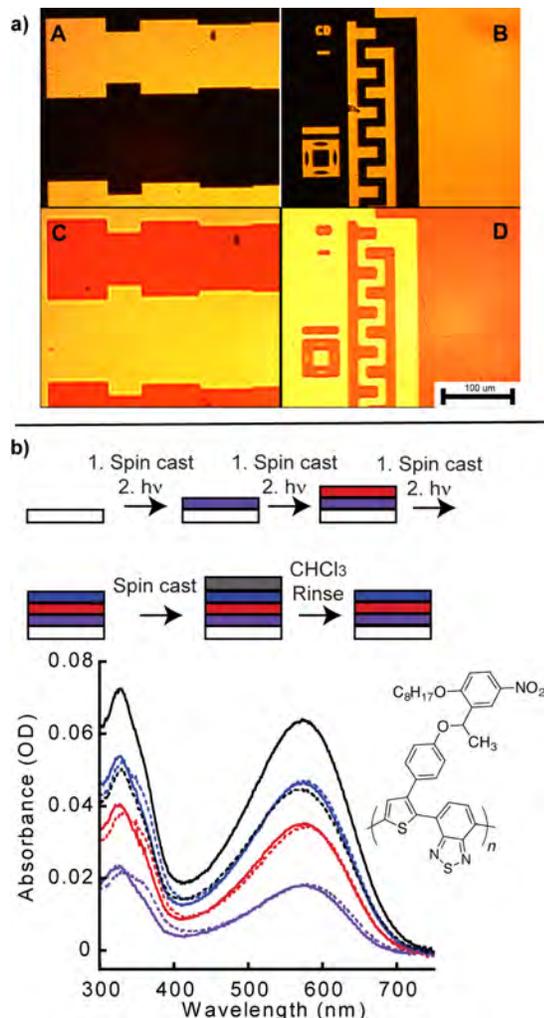
realized a nearly 20-fold increase of solution phase photocleavage efficiency through ONB optimization. The photoinduced retention of spun-cast thin films of the poly(thiophenes) also depended strongly on the structure of the ONB group with a similar trend. For example, after 4 minutes of irradiation and rinsing with  $\text{CHCl}_3$ , only ~15% of visible absorbance remained for a 24 nm-thick film of methylated ONB ester polythiophene **P3**; identical treatment yielded 60% retention of methylated ONB ether polythiophene **P2**.



**Figure 5.** a. Increase in photolysis quantum yield (365 nm) as with increase in stabilization of benzylic radical intermediate. b. Increased retention of thin films of polythiophene with ONB ether cleavable group relative to ONB ester cleavable group after 4 minutes of exposure to 365 nm and immersion in chloroform for 30 seconds. Adapted with permission from Reference 46. Copyright 2015 American Chemical Society.

This approach of photochemical cleavage of solubilizing chains also addresses the problem of all-solution processed multilayer films of conjugated materials. Alternating steps of solution deposition through spin casting and irradiation with UV light results in stratified films of, in the example shown in Figure 6b, a donor-acceptor poly(thiophene-*alt*-benzothiadiazole) with photocleavable solubilizing chains. In addition, the photoinduced nature of rendering these

polymers insoluble enabled patterning by irradiation through a photomask. Finally, although these particular polymers showed only low hole mobility values ( $\sim 10^{-5} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ) when incorporated into thin film transistors, it is noteworthy that their performance before photolysis and rinsing was similar to that observed after photolysis and rinsing, suggesting potential in materials optimized for their semiconducting characteristics.

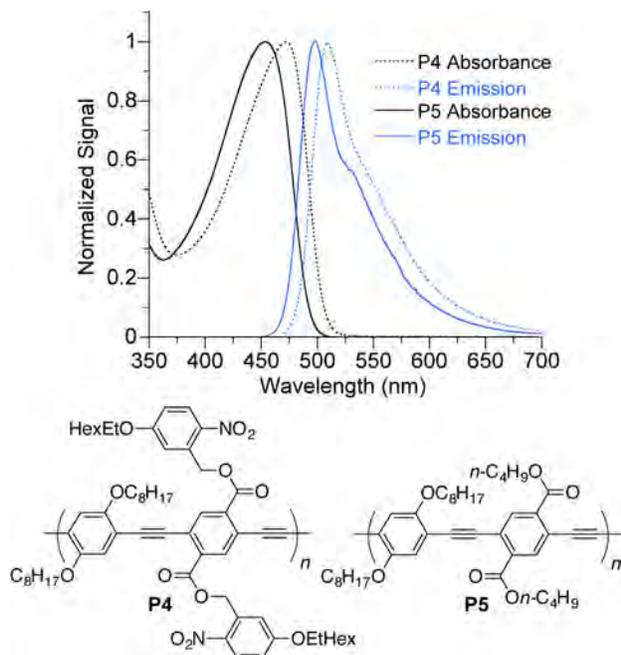


**Figure 6.** a. Photochemical patterning of polythiophene with methylated ONB linkers; panels A and B are photomask images, panels C and D are images of the patterned polymer film. . b. Absorbance spectra of a multilayer thin film made from sequential deposition and irradiation. Solid lines are immediately following deposition, dotted lines are after irradiation and rinsing with  $\text{CHCl}_3$ . The fourth and final layer (black) was not irradiated so the dotted line is simply after rinsing away the fourth layer as it still remained soluble with no irradiation. Adapted with permission from Reference 46. Copyright 2015 American Chemical Society.

### Direct Electronic Effects of Side Chains

In related investigations of the potential utility of photocleavable ONB side chains for conjugated materials, our planned research took several unexpected turns, initiated by a relatively minor observation shown in Figure 7. In an effort to expand the classes of polymers for which these cleavable side chains would be applicable, we prepared poly(phenylene

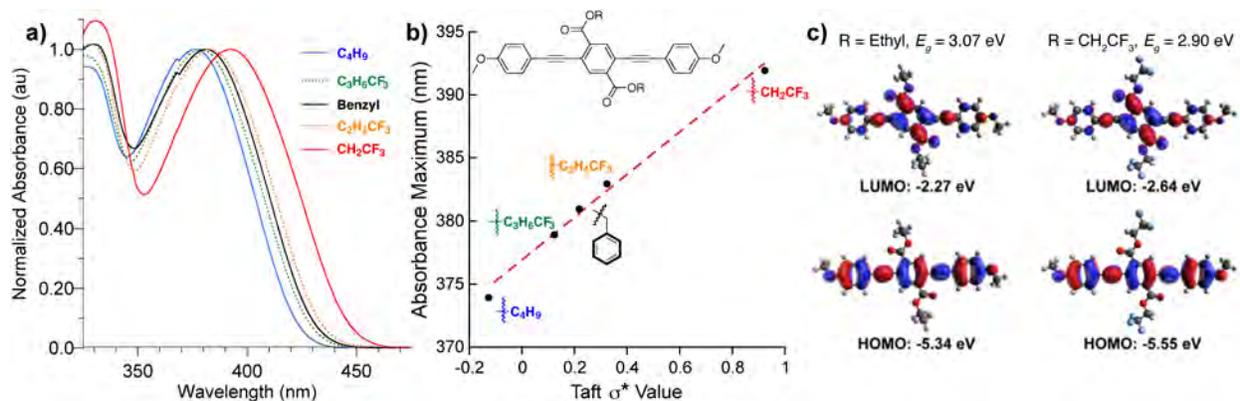
ethynylene) (PPE) **P4**, which comprises alternating dialkoxyphenylene rings and terephthalate rings with ONB-linked alkyl chains; control polymer **P5** has the same formally conjugated backbone but lacks ONB linkers between the alkyl chains and each terephthalate. We noted that, in contrast to other molecules that we had prepared with ONB ester substituents, the presence of the ONB esters made the HOMO-LUMO gap of **P4** smaller than that of alkyl ester-functionalized **P5**, even though these groups were not conjugated formally to the PPE backbone—the absorbance and emission maxima are shifted by 18 nm and 11 nm, respectively, in CH<sub>2</sub>Cl<sub>2</sub>. A similar effect persisted in the thin films of these materials. Moreover, close examination of our thiophene-based materials revealed an analogous trend. Although modest in magnitude, we pursued the question of the origin of this effect, as the tuning of the non-conjugated units of side-chains is not a common strategy for tuning the optical properties of conjugated materials.



**Figure 7.** Initial observation of different optical spectra of **P4** and **P5**, which have the same formally conjugated backbone, in CH<sub>2</sub>Cl<sub>2</sub>. Adapted with permission from Reference 50. Copyright 2014 American Chemical Society.

Polymeric materials bring a number of potential advantages to functional materials, such as toughness and mechanical flexibility. Nevertheless, polymers in general, and conjugated polymers in particular, have poor structural homogeneity due to both distributions in molecular weights in each sample generated, as well as the degree to which defects are incorporated into the backbones of conjugated polymers, such as diyne linkages in PPEs prepared by Sonogashira couplings.[47] Homogeneous, rigorously purified and characterized conjugated oligomers, on the other hand, abrogate these challenges of interpretation due to sample heterogeneity.[48, 49] To check that the observed differences between optical spectra of these polymers was not due to this heterogeneity, we prepared three-ring phenylene-ethynylene (PE) small-molecule analogs of these polymers that vary only in the alkoxy groups of the central terephthalate ring (Figure 8).[50] The difference in the optical absorbance and emission spectra of these molecules in CH<sub>2</sub>Cl<sub>2</sub> demonstrate that as the alkoxy groups of the terephthalate increase in electron

withdrawing character, from alkyl to 2,2,2-trifluoroethyl, the HOMO-LUMO gap decreases, as depicted by a plot of maximum wavelength of absorbance versus the Taft parameter for each alkoxy group.[51, 52] Supported by DFT calculations, we concluded that increased inductive electron-withdrawing effects of the alkoxy groups decreased the energies of the LUMOs of this class of donor-acceptor molecules, which are largely localized on the terephthalate ring, more than the energies of the HOMOs. In conclusion, this study demonstrated that simply exchanging non-conjugated side-chains could be useful for tuning the HOMO-LUMO gaps of conjugated materials in solution without changing the formally conjugated backbone.

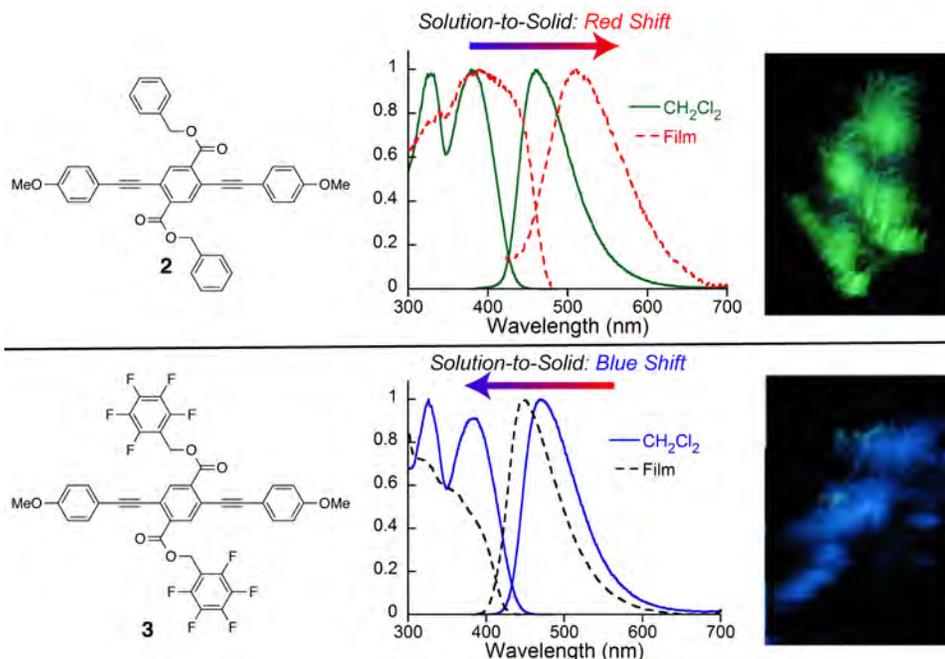


**Figure 8.** Understanding the effect of formally non-conjugated side-chains on the electronic spectroscopy of three-ring oligo-PE compounds in CH<sub>2</sub>Cl<sub>2</sub>. a) Normalized absorbance spectra CH<sub>2</sub>Cl<sub>2</sub>; b) Dependence of absorbance maximum on Taft  $\sigma^*$  parameter of alkoxy substituent of central terephthalate ring; c) Results of DFT calculations of two geometry-optimized examples, as calculated using the B3LYP functional and the 6-31G (d,p) basis set. Adapted with permission from Reference 50. Copyright 2014 American Chemical Society.

### Side Chain/Main Chain Aromatic Interactions That Dictate Conformation

Although understanding how chemical structure affects molecules in solution is important, understanding their behavior in the solid-state is arguably even more important, as most applications of conjugated materials require that they be neat solids or even more complicated microphase separated mixtures, as in the case of bulk heterojunction solar cells. Our ability to predict, design, and optimize the behavior of conjugated materials as ensembles of molecules in the solid-state, however, lags behind significantly our ability to do so for isolated, solvated molecules.[53] The absence of solvent often increases the importance that even comparatively small changes of side-chain chemical structure, such as extending the branching point of flexible side chains further from the conjugated backbone,[10, 11, 54-59] have in the properties of conjugated materials. The importance of this point for our molecules was clear when simply looking at solid samples of the molecules such as those in Figure 8. All of these molecules, including the benzyl ester-substituted **2** (Figure 9) has a yellow color with blue/green or green luminescence upon irradiation with UV light. In stark contrast, the solid of molecule **3** with pentafluorobenzyl ester substituents appears colorless and has deep blue luminescence (Figure 9) These unexpected observations, in which non-conjugated side-chains play a decisive role in the key properties of conjugated materials as solids, spurred us to investigate these molecules further.[60]

Spectroscopic evidence further confirmed the observations described above. As an example, benzyl terephthalate **2** shows a bathochromic shift in both absorbance and fluorescence upon transitioning from solution to a spun-cast thin film. This is typical behavior for phenylene-ethynylene small molecules and polymers, usually rationalized through a combination of planarization and aggregation in the solid-state.[47] Indeed, the single crystal X-ray structure of **2** shows a largely coplanar PE main chain (Figure 10), with inter-ring torsional angles of approximately  $10^\circ$ . Unlike alkyl-substituted conjugated molecules, for which the side chains are often in their fully extended form and do not interact with the main chain, the benzyl groups of **2** participate in clear intramolecular aromatic edge-face interactions with the main chain.[61, 62]

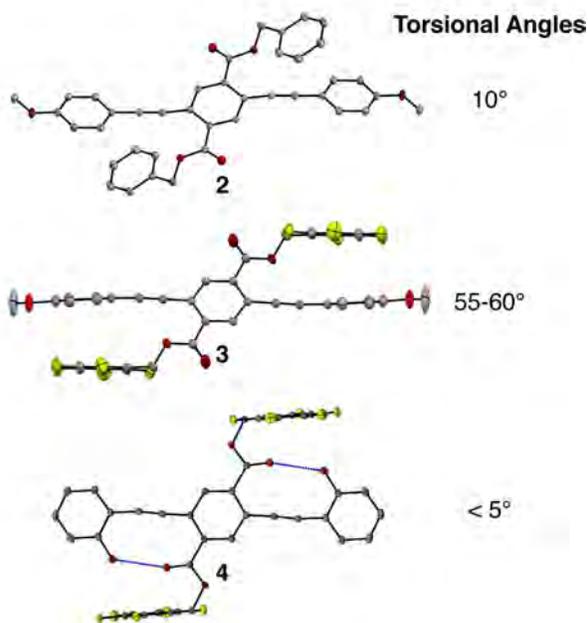


**Figure 9.** *Left and Middle:* Difference in shift of optical spectra between oligo(phenylene ethynylene)s **2** (a bathochromic shift) and **3** (a hypsochromic shift) upon transition from solution phase in  $\text{CH}_2\text{Cl}_2$  to solid-state. *Right:* Photographs of the fluorescence observed from solids of **2** and **3** upon irradiation with a hand-held UV-lamp. Adapted with permission from Reference 60. Copyright 2014, The Royal Society of Chemistry.

The spectroscopy of solid of molecule **3**, as expected based on our visual observations, instead shows *hypsochromic* shifts of its absorbance and fluorescence spectra upon transition from  $\text{CH}_2\text{Cl}_2$  solution to the solid-state. Much like **2**, the single crystal X-ray structure of **3** also reveals clear non-covalent interactions between the main chain and the perfluorinated benzyl side chains. In this case, however, the arenes interact cofacially because of the well-known opposite quadrupoles of non-fluorinated arenes and highly fluorinated arenes.[63, 64] To achieve a conformation that enables cofacial interactions, the PE backbone twists out of coplanarity, with inter-ring torsional angles between  $55\text{--}60^\circ$ . As has been observed in other OPE designs that yield twisted conformations, the resulting decreased conjugation causes the observed hypsochromic shift.[65–67] These cofacial interactions also occur between molecules in the crystal lattice, reinforcing the twisted conformation.

The contrast of **2** and **3** highlight how specific, discrete non-covalent interactions between the side-chains and main-chains of conjugated materials can control their conformations—and the

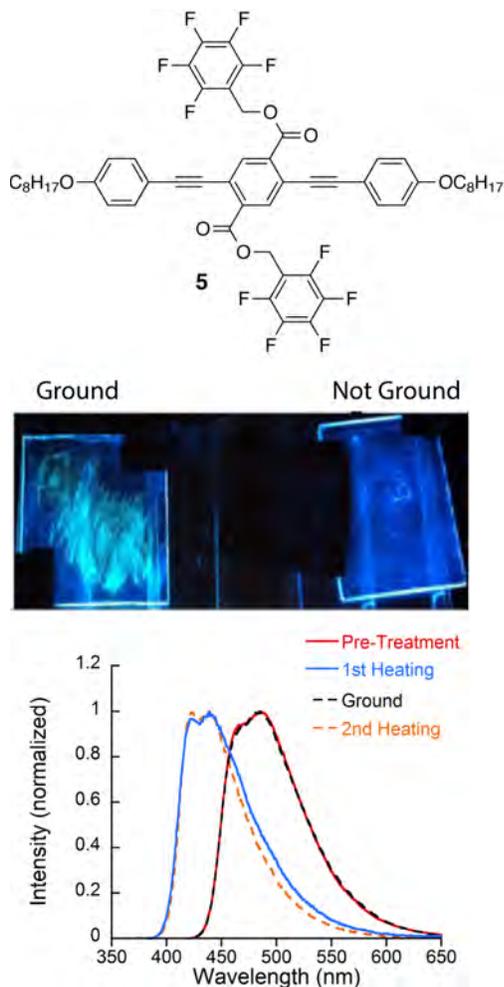
resultant optical properties—in the solid state. We reported several similar compounds with varying terminal rings on the 3-ring PE backbone that all showed hypsochromic shifting in the solid state caused by cofacial interactions between perfluorobenzyl ester side chains and the terminal conjugated rings. A key example of a molecule that did not follow this pattern was molecule **4**, in which intramolecular hydrogen bonding between the hydroxyl groups in the *ortho* position on the terminal phenylene rings and the carbonyl groups of the terephthalate, similar to those shown by Zhao and coworkers to promote OPE coplanarity,[68, 69] out-competed the arene-perfluoroarene cofacial interactions and yielded a highly planar backbone (Figure 10).[70]



**Figure 10.** Comparisons of X-ray crystal structures of analogous three-ring OPEs **2-4**. Adapted with permission from Reference 60. Copyright 2014, The Royal Society of Chemistry.

The sensitivity of conformation of this class of molecules highlighted for us that the shallow potential energy well of rotation about the PE linkage—on the order of 1 kcal/mol—allows control of conformation through balancing non-covalent interactions.[71] Along these lines, our group demonstrated reproducible and sensitive piezochromism (a change in color upon exertion of mechanical force) and mechanofluorochromism (a change in color of fluorescence upon exertion of mechanical force) of solids of **5**, an analog of **3** with octyloxy terminal groups (Figure 11).[72-74] Heating this solid above 80 °C yields blue emission, consistent with a twisted backbone; gently touching the solid manually with a spatula, however, results in bathochromic shifting of absorbance and fluorescence spectra. This change reverses above 80 °C, which corresponds to an endotherm observed only upon heating the ground sample. The extent to which i) planarization or ii) interchromophore aggregation contribute to the observed change in optical properties is currently unclear. Efforts toward understanding the force-induced polymorphism of **5** and related molecules are currently underway in our laboratory. Our observations are in line, however, with those of Xu and coworkers,[72] who have concluded that molecules that show aggregation-induced emission (AIE) also often show mechanofluorochromism. Although the molecules we discuss here are generally not examples of AIE (most are highly fluorescent in solution as well as in the solid), they do have in common with many AIE dyes a resistance to coplanarity, in our case due to favorable electrostatic

interactions between non-conjugated side chains and the conjugated main chain. As we suspect is occurring in our system, mechanical force-induced planarization and aggregation of such solids have been put forth as a source of kinetically trapped, metastable state of higher packing density and bathochromically-shifted optical spectra.



**Figure 11:** *Top:* Chemical structure of mechanofluorochrome **5**. *Middle:* Photograph of photoluminescence thin films of **5** before (*right*) and after (*left*) grinding. *Bottom:* Normalized photoluminescence emission spectra of thin films of **5** after four processing steps: solvent evaporation, heating at 90 °C, grinding, and heating to 90 °C again. Adapted with permission from Reference 60. Copyright 2014, The Royal Society of Chemistry.

## Conclusions

The broad research area of side-chain engineering is finding increasing interest as it becomes more evident that the non-conjugated side chains of conjugated oligomers and polymers can play a decisive role in determining the behavior of these optoelectronically active materials. Our particular approach, which complements the typical design paradigm of functionally orthogonal conjugated main chains and non-conjugated side chains, involves installing chemical moieties that are active participants in how conjugated materials interact with their environment. This research has yielded two new classes of stimuli-responsive solids i) thiophene-based conjugated polymers with ONB-based photocleavable side chains that behave as negative photoresists, and

ii) phenylene-ethynylenes with discrete aromatic interactions between side chains and main chains that show piezochromic and mechanofluorochromic properties. Current work in our laboratory is focusing on both i) ameliorating the disadvantages of our materials, such as the generation of byproducts upon ONB photolysis and the brittle nature of organic crystals as pressure-responsive materials, and ii) expanding their structural scope, such as the synthesis of near infrared-absorbing conjugated polymers with photocleavable side-chains for potential use in photovoltaics and PE-based mechanofluorochromic materials with broadened palettes of accessible colors. More broadly, we note that much of the research progress summarized in this article was the eventual product of following up on what seemed initially to be peculiar results regarding the optical properties of some molecules that we could have easily ignored. We believe firmly that such exciting outcomes are the natural and, frankly, inescapable products of careful and thorough fundamental research performed with interesting systems.

### Acknowledgement

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