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Title: New Applications of Photolabile Nitrobenzyl Groups in Polymers

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ABSTRACT: This article describes progress in the author's laboratory in two new areas of photoresponsive polymers: 1) photochemical control of electrostatics, and 2) conjugated materials with photocleavable pendants. In both cases, incorporation of *o*-nitrobenzyl esters (NBEs) imparts this photoreactivity. NBE-derivatized, ROMP-derived polycations form positive photoresist LbL films that dissolve in base upon irradiation. NBE-derivatized conjugated oligomers show photoactivated fluorescence, while NBE-substituted polythiophenes are negative photoresists due to photolysis of solubilizing alkyl chains.

Introduction

Stimuli-responsive materials encompass a wide variety of functional surfaces, polymers, composites, particles, etc., which show a macroscopic change in properties upon application of an external stimulus.^[1] A few examples of the many target applications of stimuli-responsive materials are chemical sensing, mechanical actuation, and targeted delivery. Researchers have designed materials that respond to a variety of stimuli, such as temperature, electrical potential, magnetic fields, chemical concentration, and light. Light has several unique characteristics that make it a particularly promising stimulus, such as control over when and where light irradiates a sample (spatiotemporal control), stoichiometry (through a combination of power and time of irradiation), and energy. Depending on its properties, light can also permeate through solid-state materials, which simplifies its delivery as a stimulus

relative to more traditional chemical reagents. These features of light and its reactions with light-responsive polymers have been the cornerstone of transformative technologies such as photolithography,^[2] a key step in the fabrication of microprocessors. Recently, interest in using light to induce novel function in polymers has accelerated. The focus of our laboratory's research is to use our grounding in physical organic chemistry to rationally design and understand the properties of new organic materials with targeted photoresponsive characteristics. This article describes our laboratory's progress in two new areas of photoresponsive polymers: 1) photochemical control of electrostatics, and 2) conjugated materials with photocleavable pendants.

There is a broad spectrum of structural moieties with highly predictable photochemical reactivities that are readily integrated into polymeric structures. General classes of these moieties include^[3]: 1) photochemically promoted addition reactions, which are in some cases reversible as a function of the wavelength of light used, such as [2+2] cycloadditions of coumarins, 2) reversible photoisomerizations, in which the isomerism is either stereochemical (such as *cis*- and *trans*-azobenzenes) or structural (such as the spiro[pyran-merocyanine] photoisomerization), and 3) photochemical dissociations,^[4] such as the photochemical cleavage of *para*-hydroxyphenacyl or *ortho*-nitrobenzyl (ONB) groups. Although its photochemical reactivity has been known for decades, the ONB structural unit is experiencing a renaissance in the context of polymers and materials science—Coughlin, Theato, and colleagues reviewed the applications of the ONB moiety in these fields in early 2012.^[5] This surge in activity is in part because of the numerous advantages of the ONB group: it is readily prepared and derivatized, it is applicable to a variety of 'caged' functional groups including amines, acids, and alcohols, and it retains its photochemical reactivity in many solvents and in the solid state.

Despite its disadvantages, which are that it generates byproducts that absorb light competitively, that only ultraviolet light is efficient at inducing its photolysis, and that a

potentially toxic byproduct, *o*-nitrosobenzaldehyde, is formed upon photolysis, the ONB group is among the most popular of photolabile moieties in polymer science. Material platforms that use ONB-containing polymers include, photosensitive block copolymer micelles for targeted delivery,^[6] which can release cargo upon photochemical conversion of the hydrophobic block in the micelle core to a soluble hydrophilic block,^[7] cleavage a photosensitive junction between two blocks, or photolysis of a main chain comprising many ONB groups.^[8] Microphase segregation of ONB-functionalized block copolymers also allows the photochemical production of nanoporous films.^[9,10] Stimuli-responsive hydrogels with photolabile crosslinks is another new class of photosensitive polymeric materials currently undergoing rapid development.^[11-16] Incorporation of ONB groups into organic materials has also enabled new approaches to thin film photopatterning in applications, for example, of protein patterning, microfluidics, and organic electronics.^[17-20]

Photochemical Control of Electrostatics

Intermolecular forces that dictate how molecules and collections of molecules behave on microscopic and macroscopic scales are electrostatic in nature. Ion-ion, ion-dipole, hydrogen bonding, dipole-dipole, and induced dipole interactions all depend on like charges repelling and opposite charges attracting. Controlling electrostatic forces with external stimuli is therefore fertile ground for new and useful responsive materials. In one approach to controlling electrical charge on polymers with light not further discussed here, we demonstrated that the photoisomerization of some photochromic polymers enables photochemical control of the sign and rate of charge accumulation by contact electrification—the separation of charge when contacting materials separate.^[21] Here we discuss another of our projects in this area: photolabile polyelectrolyte multilayer films.

The layer-by-layer (LbL) technique for fabricating coatings, which uses alternating exposure of a surface to two solutions, each containing a polymer that interacts with the other, is a versatile and useful technique.^[22] Advantages of LbL include a simple processing design,

control over nanoscale thickness, and ease in coating non-planar and irregularly shaped substrates. Although different types of intermolecular interactions can hold LbL films together, the charge-charge interactions between oppositely charged polyelectrolytes are the most common. Our goal in this study was to use light to switch the attractive charge-charge interactions, which are required to assemble the film, to repulsive charge-charge interactions by switching the polycationic component of the film to a polyanionic structure.

ROMP for synthesis of NBE-containing polymers

Effective radical polymerizations of nitrobenzyl-containing monomers can be challenging because nitroaromatic groups can participate in radical termination reactions, and often require high concentration (2-3 M) and low conversion ($\leq 30\%$) of monomer.^[23] Although acceptable for highly soluble monomers that are not highly elaborated synthetically, these constraints on reaction conditions were unacceptable for our needs. To address this pervasive problem, we investigated the utility of the non-radical chain-growth ring-opening metathesis polymerization (ROMP)^[24,25] for preparation of NBE-functionalized polymers.^[26] Exposing NBE-substituted norbornene monomers **1** or **2** to any of the commercially available Grubbs ruthenium carbene metathesis catalysts resulted in complete consumption of monomer. As has been observed for other ROMP polymerizations,^[27] the first- or third-generation Grubbs catalysts generally polymerized **1** in a well-controlled fashion, with product polymers that had polydispersity indices less than 1.3 and that showed a linear relationship between number-average molecular weight and initial ratio of monomer to catalyst. Our use of ROMP for preparation of NBE-containing diblock copolymers was further evidence of the living nature of the polymerization of monomer **1**.

Given the success of ROMP with monomer **1**, we prepared monomer **3**, a structurally analogous molecule with a cationic quaternary ammonium group attached to the norbornene through a photosensitive NBE linker (Figure 2). As observed with **1**, and in strong contrast to our failed attempts at radical polymerization of an analogous methacrylate derivative, ROMP

of monomer **3** gave complete conversion to polymer **P3** in less than 1 hour at room temperature.

Photolabile Polyelectrolyte Multilayers

We then prepared and characterized photosensitive polyelectrolyte multilayers with **P3** as the polycationic component.^[28] Alternating and repeated dipping of a planar quartz substrate in a DMF solution of **P3** and an aqueous solution of the commercially available polyanion poly(styrene sulfonate) (PSS) yielded polyelectrolyte multilayer films that we characterized using several methods. UV/vis absorbance spectrophotometry of the films showed bands due to both the PSS and the nitroaromatic ring of **P3**. Also, the sign of the zeta potential of **P3**/PSS-coated polystyrene microspheres after each deposition step was the same as the sign of the previously deposited polyelectrolyte.

In our design **P3** becomes anionic upon irradiation and exposure to basic media, as the photoproduct is a polymer with a carboxylic acid on each repeat unit (Figure 2). Therefore, the energetically favorable cation-anion interactions become unfavorable anion-anion interactions, resulting in disruption of the film. Other groups have used analogous photochemical charge-switching strategies to control cellular uptake of nanoparticles or colloidal stability.^[29,30] PEM films that comprised **P3** and PSS were photolabile in a manner consistent with our design. Upon irradiation with UV light and rinsing with a weakly basic aqueous solution, only 10% of the absorbance of these films remained. Also consistent with our design was that the zeta potential of samples of UV-irradiated **P3**/PSS coated microspheres were negative, regardless of whether the last layer deposited was cationic or anionic polymer. The thickness of control PEM films that comprised PSS and the photoinert polycation poly(diallyldimethylammonium chloride) (PDAC) decreased by less than 10% upon exposure to identical irradiation and washing conditions. Finally, using the sequential nature of LbL film assembly, we restricted the photoresponsive polymer to the top halves of these PEM films by assembling layers of **P3**/PSS on top of layers of PDAC/PSS. UV

irradiation and rinsing of these films decreased their thicknesses by approximately a factor of 2, as measured both by UV/vis and profilometry.

Organic Semiconductors with Photocleavable Groups

Conjugated organic materials are key in a number of current and emerging technologies.^[31,32] They combine the optoelectronic characteristics of inorganic semiconductors, such as mobile charge carriers (holes or electrons) and excited states (excitons), with the structural variety and solution processing enabled by organic chemistry. Studies of the photoresponsive characteristics of new conjugated polymers often focus on correlating their structures and morphologies to photophysical processes and incorporating them into optoelectronic devices for various applications. In addition, there have been studies of conjugated polymers that contain photochromic moieties to enable reversible photoswitching of polymer properties.^[33] As an alternative, we are interested in combining photocleavable moieties with conjugated materials; this approach enables irreversible removal of a structural component of the polymer, which yields rationally designed light-activated changes in properties.

Photoreactive Conjugated Oligomers

Our first study in this area focused on the photoresponsive properties of five-ring conjugated oligomers that contained both exocyclic triple and double bonds between rings; an example of the new molecules used is **PEPV-1** in Figure 3.^[34] In this molecule, the central double bonds gave a larger bathochromic shift than triple bonds would, while the triple bonds enabled the final synthetic reactions for each molecule to be functional group tolerant Sonogashira couplings. The hypothesis of this study was that the nitroaromatic group would act as fluorescence quencher of the conjugated backbone of **PEPV-1**, and that therefore UV-induced photolysis would result in an “unquenching” of fluorescence. Indeed, as Figure 3 shows, the nitrobenzyl groups did quench the fluorescence of the conjugated oligomer, with the quantum yield of **PEPV-1** depending on the polarity of the solvent, consistent with

photoinduced electron transfer (PET) quenching. The quantum yield of control molecule **PEPV-2**, which had butyl esters in both terminal positions, remained high in all solvents.

Figure 3 also shows that our design for unquenching the fluorescence of conjugated materials was successful: the fluorescence quantum yield of **PEPV-1** increased by a factor of 5 (from 0.13 – 0.7) after UV irradiation. In contrast, **PEPV-2** showed no photochemically induced change in quantum yield from ~ 0.7 upon irradiation under identical conditions. Neither of the molecules showed any change in the shapes of their emission spectra after irradiation. Structurally analogous conjugated oligomers with two nitrobenzyl ester groups instead of one showed similar behavior. Finally, as the product of photolysis is a carboxylic acid, the solubility of the products of the NBE-substituted PEPV conjugated oligomers changed upon irradiation: upon exposure of these molecules to aqueous base and UV light, the resulting deprotonated carboxylates precipitated from CH₂Cl₂ while acidification yielded CH₂Cl₂-soluble carboxylic acids.

Photoreactive Oligothiophenes and Polythiophenes

This initial study in using nitrobenzyl groups to develop conjugated oligomers with phototunable properties was, to our knowledge, the first such demonstration of this strategy. In an effort to extend this approach to conjugated polymers and improve the photostability of the conjugated backbone, we examined oligo- and polythiophenes with photolabile solubilizing chains.^[35] Polythiophenes are more photochemically stable than materials with exocyclic main chain double bonds such as poly(phenylene-vinylene)s or the PEPV oligomers discussed previously.^[36] In addition, to increase the difference in solubility characteristics before and after photolysis, we altered our design such that the only solubilizing alkyl chains on our thiophene-based materials were bound to photocleavable groups. Using Stille coupling, we prepared quarterthiophene derivatives with these NBE moieties on the terminal rings, as well as polythiophenes with solubilizing NBE groups on every other thiophene ring. The effect of the nitrobenzyl esters on the quarterthiophene oligomers was analogous to the

PEPV oligomers: in comparison to the quarterthiophene oligomers that had only *n*-butyl esters, the nitrobenzyl groups quenched the oligothiophene fluorescence with higher efficiency in polar solvents than in non-polar solvents, and photolysis of NBE-substituted quarterthiophenes increased the fluorescence quantum yield.

The NBE-derivatized polythiophene **PT-NBE**, however, showed different behavior, consistent with aggregation of polymers upon cleavage of the solubilizing chains. Upon UV photolysis under identical conditions, the λ_{max} of the visible absorbance band shifted to the red in CH₂Cl₂ and toluene, while in THF there was no corresponding red shift. In addition, instead of the increase in fluorescence quantum yield observed with the oligomers, irradiation of the NBE-substituted polythiophene caused polymer fluorescence quenching in toluene and CH₂Cl₂, but not in THF. Our observations—bathochromic shifting of absorbance and fluorescence quenching—are typical for conjugated polymer aggregation, and are consistent with our design of light-induced cleavage solubilizing chains. In all cases, the photolytic stability of the conjugated backbones were excellent, as demonstrated by the lack of significant degradation of absorbance and emission intensity upon irradiation of control materials that had butyl esters in place of the NBEs.

As demonstration of further evidence for our model of photoinduced aggregation of polythiophenes, as well as the potential applicability of this approach, we irradiated thin films of **PT-NBE** to determine the effect of photolysis of solubilizing chains on film solubility. As shown in Figure 4, the solubility of **PT-NBE** in toluene reduced dramatically upon irradiation at 365 nm for 30 minutes: the absorbance of the film decreased only 8–14% decrease upon rinsing with toluene. Areas not irradiated with UV light remained freely soluble in toluene.

Outlook

Our work summarized here demonstrates new approaches for imparting important classes of polymer materials—conjugated polymers and layer-by-layer films—with photoresponsive properties using *o*-nitrobenzyl ester groups. Potential applications of our

new photoreactive conjugated systems are in the construction of multilayer optoelectronic films that require only solution-based processing, and combine the benefits of several previously published approaches, such as the room-temperature reactivity of photochemical crosslinking,^[37] and the post-deposition removal of solubilizing chains that occurs with thermally cleavable polymers,^[38] which is known to increase polymer stability and improve optoelectronic performance.^[39,40] Photoactivatable fluorophores based on conjugated systems may show higher sensitivity than known photoactivatable small-molecule dyes^[41,42] because of amplification of quenching by exciton migration. Critical for all potential applications of photolabile conjugated polymers is that, as we have shown for polythiophenes, some conjugated polymers can withstand the UV irradiation required to cleave nitrobenzyl groups.

Degradable films and capsules of polyelectrolyte films have been identified as potential delivery vehicles;^[43-46] our new approach could make this a photolytic process with the advantages of spatiotemporal precision. In addition, because layer-by-layer assembly allows for control of chemical functionality as a function of film thickness, we are investigating if our approach can control film thickness as a function of irradiation wavelength using differentially absorbing photolabile groups,^[47] a generally viable concept as shown using structurally elaborated alkanethiolate self-assembled monolayers.^[48]

Realization of these goals in useful applications, however, will require additional fundamental understanding, development, and optimization of these concepts and materials. For example, a consistent feature of all the approaches discussed here is the ONB group, which has advantages of straightforward synthetic modification and installation and a photolysis reaction that occurs in a variety of environments. Weaknesses of the ONB group include reactive byproducts and the requirement for ultraviolet light. Potential solutions to these challenges include photolysis induced by two-photon absorption^[49,50] or the use of NIR upconversion strategies,^[51] and the use of other photolabile groups that do not generate highly reactive byproducts, such as the NPPOC group.^[52] In addition, our group has been

investigating polymers that respond to singlet oxygen ($^1\text{O}_2$),^[53] which can be generated using long wavelength light and appropriate sensitizers;^[54] the potential use of NIR-absorbing sensitizers with $^1\text{O}_2$ -reactive polymers represents another potential alternative to circumventing these technical challenges.

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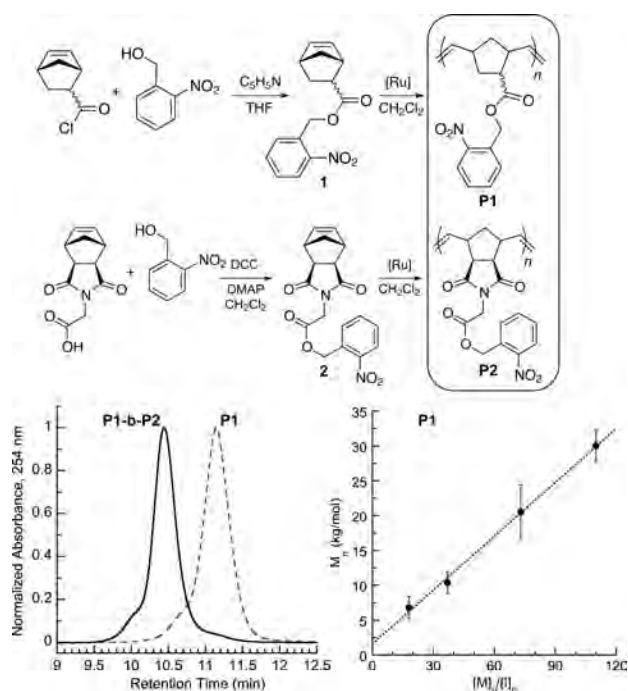


Figure 1. Top: Synthesis of NBE-substituted norbornene-based monomers (**1**, **2**) and polymers (**P1**, **P2**). Bottom Left: GPC chromatograms demonstrating block-copolymer synthesis of NBE-substituted norbornene monomers. Bottom Right: Linear dependence ($R = 0.998$) of number-average molecular weight of **P1** on the molar ratio of monomer to initiator. Reprinted with permission from ref. 26. Copyright 2011 American Chemical Society.

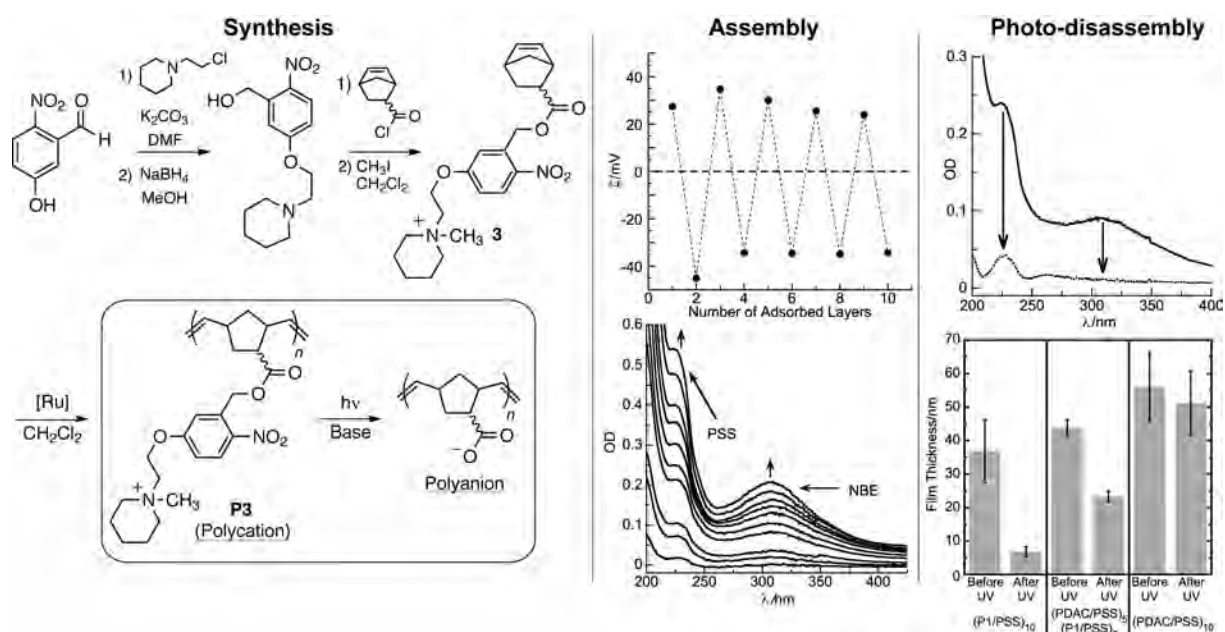


Figure 2. Left: Synthesis of photochemically charge-shifting polymer **P3**. Middle: LbL self-assembly of **P3/PSS** PEMs, as reflected by zeta potential measurements of LbL-coated microspheres (top) and absorbance spectra of an LbL-coated quartz slide. Right: Photochemical disruption of **P3/PSS** PEMs upon irradiation with $\lambda > 295$ nm monitored by absorbance spectra (top) and profilometry (bottom). Reproduced with permission^[28] from John Wiley and Sons.

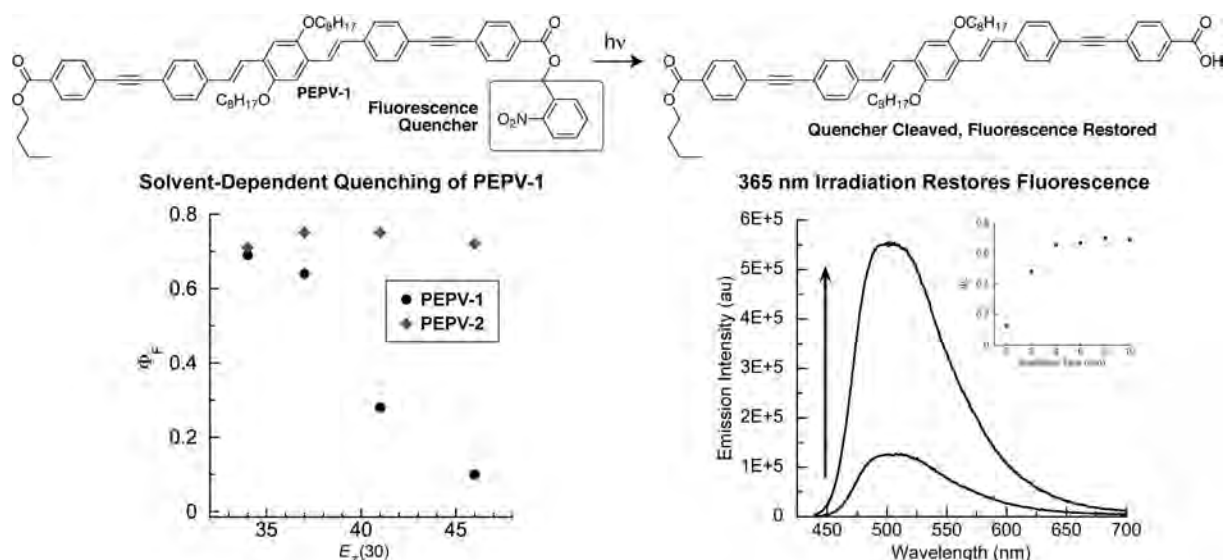


Figure 3. Top: Chemical structure and photochemical reaction of **PEPV-1**, a five ring conjugated phenylene-ethynylene/phenylene-vinylene oligomer with one terminal nitrobenzyl ester substituent. Bottom Left: Increasing solvent polarity causes increasing fluorescence quenching of **PEPV-1**, while the fluorescence quantum yield of **PEPV-2**, which has only *n*-butyl esters on both ends of the oligomer, remains at 0.70–0.75 regardless of solvent. Solvents were benzene, THF, CH_2Cl_2 , and acetonitrile. Bottom Right: Photolysis of **PEPV-1** at $\lambda > 295$ nm gives a 5-fold increase in fluorescence quantum yield.^[34] Reproduced by permission of The Royal Society of Chemistry.

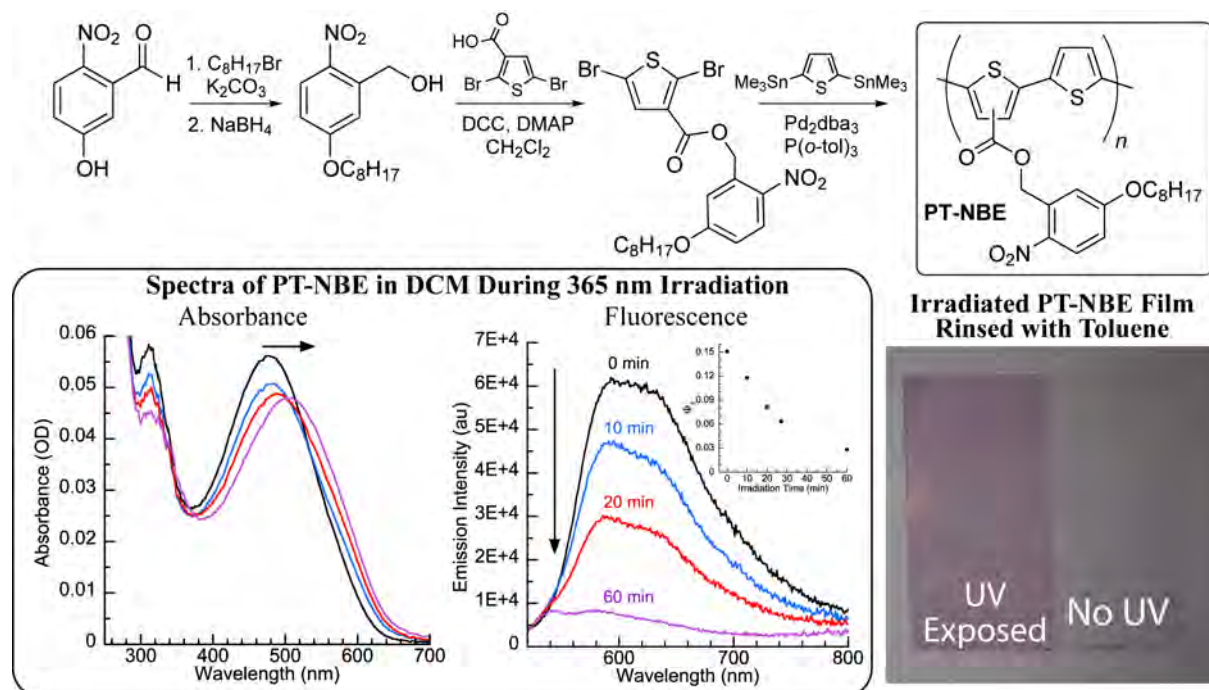


Figure 4. Top: Synthesis of **PT-NBE**, a polythiophene that only has solubilizing groups attached through photolabile nitrobenzyl ester linkers. Bottom Left: Irradiation of a dilute CH_2Cl_2 solution of **PT-NBE** at 365 nm shows a bathochromically shifted absorbance spectrum and strongly quenched fluorescence, consistent with light-induced aggregation of the polymers upon photolysis of the solubilizing chains. Bottom Right: Irradiation of a spun-cast thin film of **PT-NBE** leads to a toluene-insoluble polythiophene film. Reprinted with permission from ref. 35. Copyright 2012 American Chemical Society.

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Samuel Thomas has been an Assistant Professor of Chemistry at Tufts University, where his research focuses on new photoresponsive polymers, since 2009. He received a B.S. in Chemistry from the University of Rochester in 2000. After one year at Eastman Kodak, he earned his Ph.D. in 2006 under the supervision of Professor Timothy Swager at MIT. He then spent three years as a postdoctoral fellow with Professor George Whitesides at Harvard. Since starting at Tufts, Sam has received a 2009 DARPA Young Faculty Award, a 2010 Thieme Publishers Journal Award, and a 2012 NSF CAREER award.



New approaches to photoresponsive materials with nitrobenzyl esters are described using conjugated polymers and polyelectrolyte multilayer films that respond to UV light. Photocleavage of cations from polyelectrolytes in LbL films disrupts their integrity, and photolabile conjugated materials yield control over fluorescence efficiency and solubility with light.

S. W. Thomas III*

New Applications of Photolabile Nitrobenzyl Groups in Polymers

