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Photoinduced Aggregation of Polythiophenes

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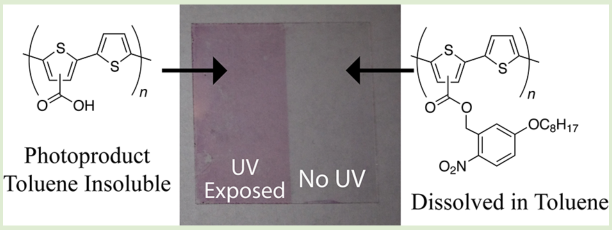
S *Supporting Information*

ABSTRACT: This letter describes thiophene-based materials that undergo photoinduced aggregation or precipitation upon irradiation with UV light. The only solubilizing side chains on these materials are photocleavable by connection through photolabile nitrobenzyl esters. While quaterthiophene oligomers yield diacids that remain soluble in dichloromethane at micromolar concentrations upon exposure to ultraviolet light, the polymeric analog shows both red-shifted absorbance and heavily quenched fluorescence, consistent with aggregation due to photochemical cleavage of solubilizing alkyl chains. Thin films of this polymer also resisted dissolution in organic solvent upon irradiation, suggesting applicability in the construction of multilayer solid-state devices.



Conjugated polymers (CPs) have useful optoelectronic properties that make them increasingly important in a variety of applications.[1,2] Although the performance of organic materials in these applications often does not match that of more traditional inorganic semiconductors, organics offer exquisite control over properties through tools of synthetic chemistry, as well as the potential for inexpensive solution-based processing over large areas and for mechanically flexible devices. Polythiophenes (PTs) are among the most popular of conjugated materials; their advantages include high carrier mobility, good photo-oxidative stability, red-shifted absorbance from many other classes of materials, and the availability of techniques for well-controlled synthesis.

Solubilizing side chains on conjugated polymers are ubiquitous because of their necessity for using the frequently cited advantage of solution-based processing: the parent structures of materials such as PT and poly(phenylene-vinylene) are insoluble without them. These groups, however, cause a number of problems with potential devices that use these polymers. For example, it is challenging to make layered structures that contain several soluble materials; solutions to this problem have included polymers that are orthogonally soluble and polymer cross-linking upon deposition.[3] Solubilizing side chains also occupy volume with optoelectronically inert groups and contribute to photochemical degradation of conjugated polymers.[4]

Previously published work has shown that PT derivatives bearing tertiary esters can be cleaved thermally, resulting in loss of the solubilizing ester side chain and improved stability of devices prepared with such procedures.[5−7] Further heating results in decarboxylation to the parent poly(thiophene) structure.[8] Visible or infrared light can also heat PT derivatives with tertiary esters[9] or tetrahydropyran[10,11] protecting groups locally for photopatternable materials. In addition, there are a variety of other strategies for photoinduced changes in CP solubility,[12,13] such as photo-cross-linking and photochemical schemes for conversion of soluble precursor polymers to insoluble CPs.[14−16]

The photochemical cleavage of nitrobenzyl groups is a versatile reaction that has found utility in applications from targeted delivery of therapeutics to surface patterning.[17,18] Cleavage of nitrobenzyl groups from fluorophores is also a known strategy for "uncaging" the fluorescence of dyes and other emitters.[19−22] For example, *ortho*-nitrobenzyl esters can yield photochemically modulated solubility of phenylene-ethynylene/phenylene-vinylene conjugated oligomers.[23] These compounds also showed photoinduced increased fluorescence efficiency upon cleavage of NB groups with UV light due to the cleavage of the fluorescence quenching nitroaromatic groups from the fluorophore. In this study, we demonstrate UV-mediated photocleavage of nitrobenzyl groups substituted with solubilizing alkyl chains from both oligothiophenes and polythiophenes. Our hypothesis was that photolysis of solubilizing chains would yield insoluble polythiophenes. To test this hypothesis, we prepared symmetrically substituted quarterthiophene derivatives containing solubilizing alkyl chains that were either photocleavable through photolabile nitrobenzyl esters or photoinert alkyl esters substituted in the 3- or 5-position of the terminal thiophene rings.

Alkylation of commercially available 5-hydroxy-2-nitrobenzaldehyde with bromooctane yielded solubilized nitrobenzyl aldehyde **1**, which NaBH$_4$ reduced to yield nitrobenzyl alcohol **2** (Scheme 1). Condensation of **2** and 2-bromothiophene-3-carboxylic acid gave ester **3**, which upon palladium-catalyzed cross-coupling with 5,5′-bis(tributylstannyl)-2,2′-bithiophene gave quarterthiophene **O3** with photolabile solubilizing groups. For synthesis of derivative **O4** with photoinert carboxylic esters, acid-catalyzed esterification of 5-bromothiophene-2-carboxylic

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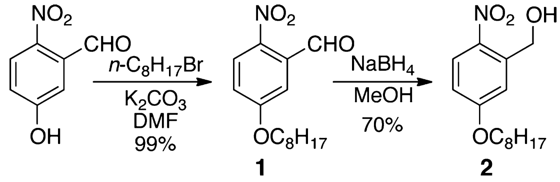
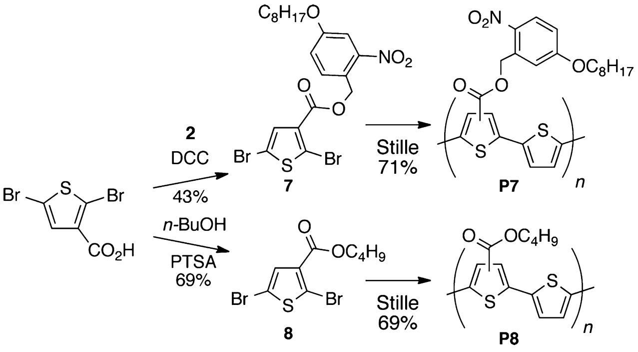
Scheme 1. Synthesis of Nitrobenzyl Alcohol 2



Scheme 3. Synthesis of Polythiophenes P7 and P8[a]



[a] “Stille”: Pd catalyst, 2,5-bis(trialkylstannyl)thiophene.

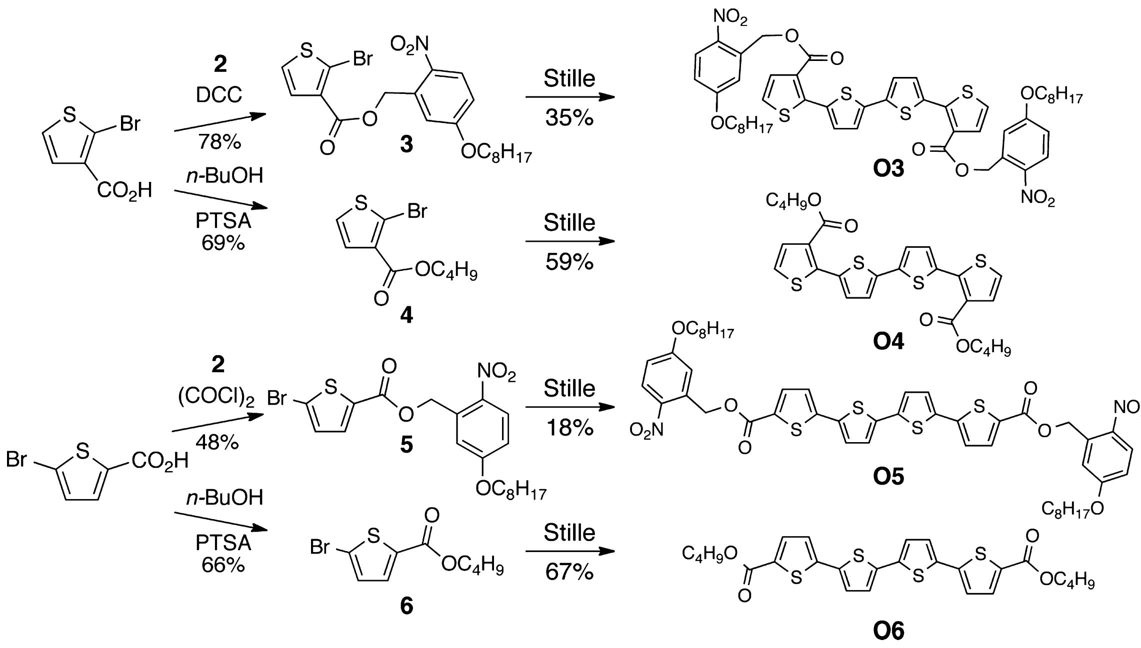
acid with *n*-BuOH gave ester **4**, which upon Stille coupling yielded quarterthiophene **O4**. A similar synthetic strategy yielded **O5** and **O6**, quarterthiophenes with photocleavable or photoinert esters in the 5-positions of the terminal rings (Scheme 2).

We extended our approach to analogous polythiophenes with either photolabile or photoinert solubilizing esters on alternating rings. *N,N′*-Dicyclohexylcarbodiimide (DCC)-mediated esterification of 2,5-dibromothiophene-3-carboxylic acid with nitrobenzyl alcohol **2** yielded photolabile monomer **7**, whereas acid-catalyzed esterification of 2,5-dibromothiophene-3-carboxylic acid with *n*-BuOH yielded the photoinert monomer **8**. Each of these monomers was amenable to step-growth polymerization with 2,5-bis(trialkylstannyl)thiophene under Stille coupling conditions with either $Pd(PPh_3)_4$ or $Pd_2(dba)_3/P(o\text{-tolyl})_3$ to yield polythiophenes **P7** and **P8** (Scheme 3).

The Supporting Information shows height-normalized absorbance and emission spectra of nitrobenzyl oligomer **O3** and polymer **P7** in CH_2Cl_2, while Table S1 summarizes relevant optical data of all conjugated thiophene materials. The absorbance spectra of these materials are consistent with expectations based on their chemical structures. Each compound has a band in the visible region of the spectrum corresponding to the (π,π^*) excitation of conjugated thiophene chains; the bands of the quarterthiophene oligomers (λ_{max} 400−425 nm) are at higher energy than the polymers (λ_{max} 480 nm), consistent with the number of conjugated rings in the structures. In addition, **O3**, **O5**, and **P7** show an additional band at 315 nm due to the presence of the *para*-alkoxynitroaromatic group.

To understand the effect of the nitroaromatic groups on the excited state of the conjugated thiophene backbones, we characterized the fluorescence spectra of these materials. Like the UV/vis spectra, the emission spectra of polymers **P7** and **P8** is red-shifted (610 nm) from the quarterthiophene oligomers. The excitation spectra of **O3**, **O5**, and **P7** show no peaks attributable to the nitrobenzyl group, which indicates that energy transfer from the photocleavable moieties is not competitive with other excited-state processes and that, besides competitive absorbance of the UV light, the coupling of the two chromophores should not interfere with photocleavage. The quantum yields of fluorescence (Φ_F) of nitrobenzyl-substitued **O3**, **O5**, and **P7** depend strongly on solvent, with quenching more efficient in more polar solvents (CH_2Cl_2 and CH_3CN) than in the less polar solvent benzene. Those fluorophores without nitrobenzyl groups (**O4**, **O6**, and **P8**) had fluorescence quantum yields that did not vary as a function of solvent

Scheme 2. Synthesis of Quaterthiophene Oligomers O3−O6[a]



[a] “Stille”: 5,5′-bis(tributylstannyl)-2,2′-bithiophene, $Pd(PPh_3)_4$, DMF.

polarity. These trends are consistent with photoinduced electron transfer quenching of the nitrobenzyl-substituted fluorophores.

To photocleave solubilizing nitrobenzyl groups from conjugated thiophene-based materials, we irradiated samples with 365 nm light from a Hg/Xe lamp with a power density of 10 mW/cm^2. To minimize the photo-oxidative degradation that is known to occur with conjugated materials, we deoxygenated all samples by bubbling with argon gas. We monitored both absorbance and fluorescence spectra as a function of irradiation time. Figure 1 shows the response of both the absorbance and fluorescence spectra of oligomer **O3** in CH_2Cl_2 as a function of UV irradiation time. Regioisomer **O5** showed qualitatively similar behavior to that described below for **O3**; these data are summarized in the Supporting Information. The absorbance band at 315 nm decreased, consistent with photolysis of the nitroaromatic group.

In addition, the principal absorbance band at 400 nm did not decrease; we attribute the slight increase to byproducts from the nitrosoaromatic photolysis product. We therefore conclude that photochemical decomposition was not significant under these reaction conditions. Figure 1d, which shows that both the absorbance and emission spectra of control oligomer **O4** decreased less than 10% upon irradiation for 60 min, also supports this conclusion. Thiophene-based materials are more photochemically stable than phenylene-vinylene-based materials because they lack labile main chain exocyclic double bonds.[4] In addition, there was no significant shift in the absorbance peak, which indicated that the products of **O3** photolysis remained well-solvated. ^{1}H NMR spectroscopy of the photolysis reaction of **O3** in DMSO-d_6 was consistent with conversion to the dicarboxylic acid of the quaterthiophene, which we prepared independently by basic hydrolysis of **O4**.

During the irradiation, the fluorescence spectrum of **O3** retained the same spectral shape, but increased in intensity by a factor of 2 after 60 min of photolysis (Figure 1c). This corresponds to an increase in fluorescence quantum yield from 0.06 to 0.12. Given that the emission spectrum of **O4** shows <10% change upon identical irradiation conditions, these observations are consistent with cleavage of the nitrobenzyl ester quencher from the conjugated oligothiophene backbone preventing photoinduced electron transfer. This result is analogous to that which we observed with different nitrobenzyl-functionalized conjugated oligomers.[23]

Polymer **P7**, which is structurally analogous to oligomer **O3**, showed significantly different behavior upon photolysis (Figure 2). The maximal absorbance decreased by approximately 20% and red-shifted to λ_{max} = 507 nm after 60 min of irradiation at 365 nm in deoxygenated CH_2Cl_2; **P7** also showed similar behavior in toluene, while in THF **P7** showed a slight blue shift. In addition, the UV/vis spectrum of **P8**, which does not have photoreactive nitrobenzyl ester pendants, showed no change in CH_2Cl_2. We attribute these observations to photoinduced aggregation of **P7** in solvents of low polarity: red-shifted absorbance spectra is typical of aggregates of conjugated polymers,[24,25] and this interpretation is consistent with cleaving solubilizing chains from the backbone of the polythiophene to yield more polar carboxylic acid pendants.

Fluorescence data also supports photoinduced aggregation of polythiophene **P7** in toluene or CH_2Cl_2. In CH_2Cl_2, and in strong contrast to the results with conjugated oligomers **O3** and **O5**, the fluorescence intensity and quantum yield of **P7** decreased by a factor of 8 after 60 min of irradiation (Figure 2c). Self-quenching of polymer fluorescence is a common result of the interchain interactions that accompany conjugated polymer aggregation.[25] Irradiation in toluene yielded similar results at a slower rate of change, while irradiation in THF did not yield fluorescence quenching.

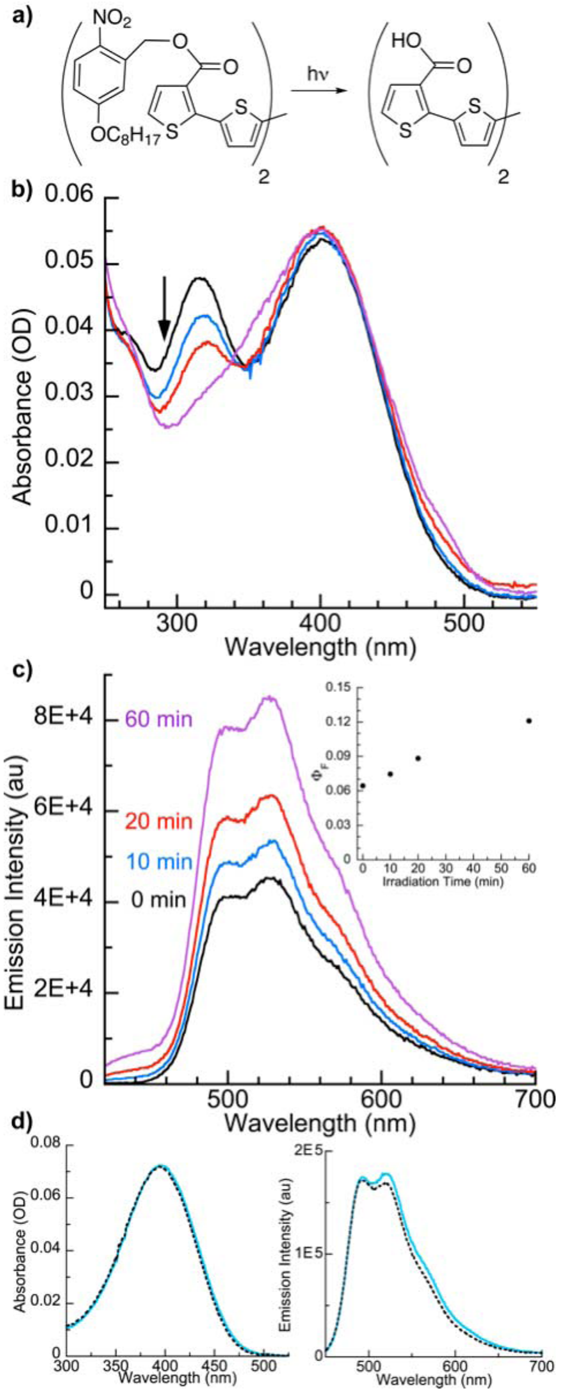


Figure 1. (a) Photolysis of oligomer **O3**, (b) response of absorbance spectrum, and (c) response of emission spectrum of a deoxygenated sample of **O3** in CH_2Cl_2 to 365 nm light at 0, 10, 20, and 60 min of irradiation. (d) Absorbance and emission spectra of **O4** before (solid blue line) and after (black dashed line) 60 min of irradiation at 365 nm.

The behavior of these polymers in the solid-state also supports the conclusion that **P7** forms aggregates insoluble in toluene or CH_2Cl_2 upon irradiation: Thin films of **P7** resisted

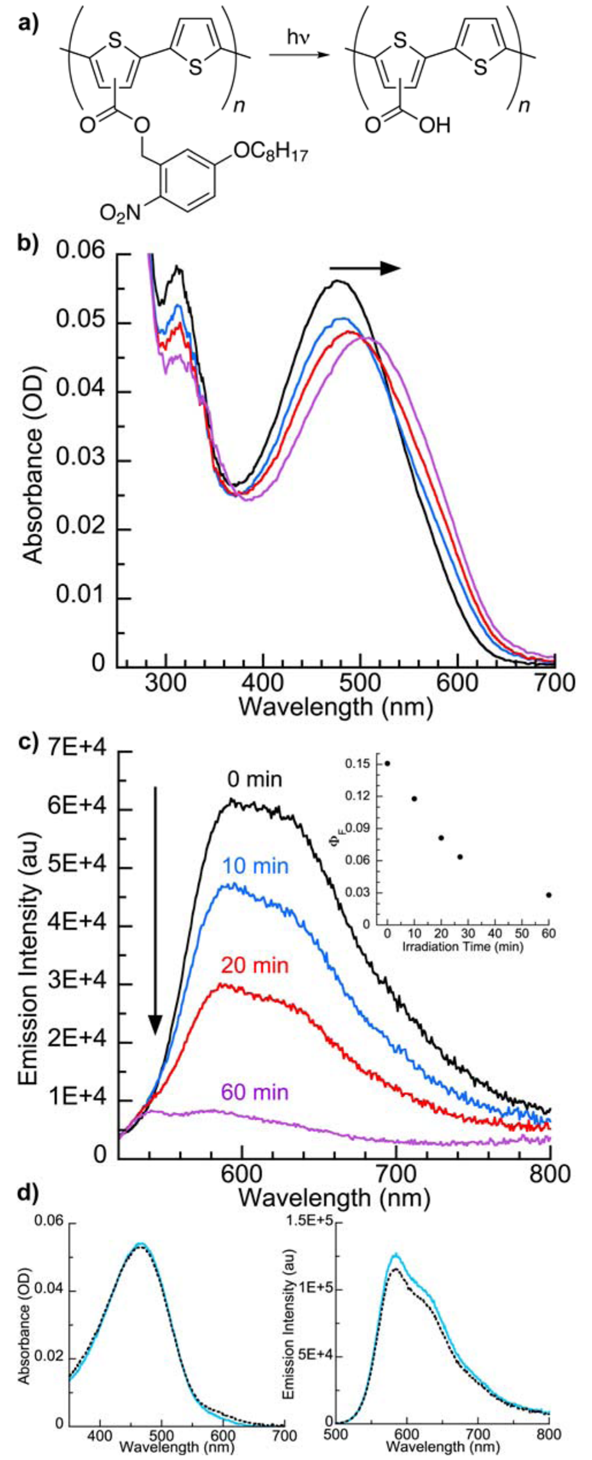


Figure 2. (a) Photolysis of polymer **P7**, (b) response of absorbance spectrum, and (c) response of emission spectrum of a deoxygenated sample of **P7** in CH_2Cl_2 to 365 nm light at 0, 10, 20, and 60 min of irradiation. (d) Optical spectra of **P8** before (solid blue line) and after (black dashed line) 60 min of irradiation at 365 nm.

dissolution in these solvents after UV irradiation, as determined by absorbance spectrophotometry, because of the photolytic cleavage of solubilizing groups from the polymer backbone. As shown in the Supporting Information, spun-cast films of **P7** on microscope coverslips dissolved readily in organic solvents at room temperature if not irradiated with UV light. When these films were irradiated with UV light, however, they underwent only an 11 ± 3% change in optical density after a combination of 30 min of irradiation at 365 nm under ambient conditions and rinsing with toluene (Figure 3). We attribute this decrease to dissolution of shorter polymer chains, chains with some unreacted pendants, or both. As shown in the Supporting Information and consistent with the lack of evidence for aggregation in THF as described above, polar aprotic solvents such as THF or DMSO significantly disrupt the irradiated polymer films, resulting in diminution of the absorbance of the films by 60−80%.

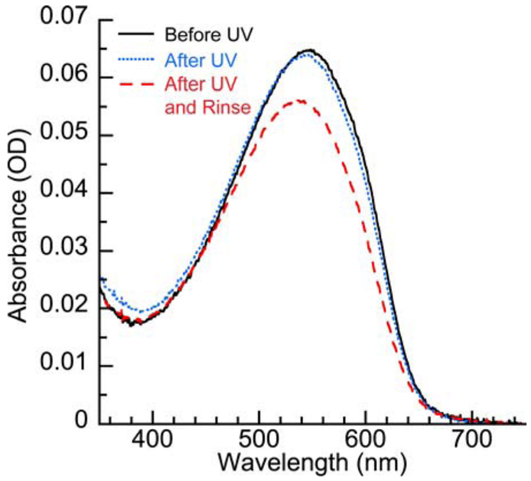


Figure 3. UV/vis spectra of a spun-cast film of **P7** before and after exposure to 365 nm light for 30 min. Rinsing the irradiated film with toluene resulted in only a 14% decrease in optical density.

In conclusion, we have demonstrated that incorporating solubilizing side chains through photocleavable linkers on thiophene-based conjugated materials enables photochemical control over intermolecular interactions and solubility of conjugated polymers both in organic solvent and as thin films. While quarterthiophenes remain soluble upon photolysis, an analogous polythiophene aggregates in organic solvents of low polarity upon photochemical cleavage of solubilizing groups. Films of photoresponsive polythiophenes undergo these photoinduced changes with a minimal amount of photobleaching, and resist dissolution upon photolysis. This approach complements previously reported approaches to the stimuli-responsive solubility of conjugated polymers while incorporating the advantages of using light as an external stimulus, such as spatiotemporal resolution.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of synthetic and photochemical experiments, additional supporting figures, and a table of photophysical data of thiophene-based materials. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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