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Paper

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## UV-Induced Fluorescence Recovery and Solubility Modulation of Photocaged Conjugated Oligomers

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This article describes photoactivatable conjugated oligomers that show both increased fluorescence quantum yield and pH-dependant solubility upon irradiation with UV light. Sonogashira coupling between ester-substituted phenylacetylenes and alkoxy-substituted diiodo phenylene-vinylenes yielded conjugated phenylene-ethynylene/phenylene-vinylene oligomers. Oligomers with nitrobenzyl ester moieties had quenched fluorescence in polar solvents; UV irradiation restored their quantum yield of fluorescence to that of corresponding alkyl ester-substituted oligomers. These photocaged oligomers also exhibited UV-induced changes in solubility consistent with photogeneration of carboxylic acids. This approach is therefore effective at tuning the properties of conjugated organics with light after traditional synthetic operations, and has potential for use in photoactivatable fluorophores or solution-processable multilayer devices.

### Introduction

This article describes conjugated oligomers that have both increased fluorescence efficiency and pH-dependant solubility upon irradiation with UV light. We anticipate this strategy will be applicable to new caged fluorophores and solution-processed multilayer organic devices. Conjugated materials behave as organic semiconductors: they can conduct holes and electrons, and have mobile excitons upon excitation. Such materials have therefore become increasingly popular for a number of applications, such as photovoltaics,<sup>1</sup> sensors,<sup>2</sup> and light-emitting devices.<sup>3</sup> They offer several unique advantages over inorganic semiconductors; for example, when substituted with solubilizing groups, many conjugated materials are solution-processable, enabling coating techniques that do not require high temperature or vacuum, such as spin-casting and roll-to-roll processing.<sup>4</sup> In addition, properties such as intensity of fluorescence or solubility depend on chemical structure, which chemists can tune through rational design and the modularity of many of the chemical transformations (such as cross-coupling) used in their syntheses.

The most common approach for tuning the properties of conjugated polymers is to design and synthesize different monomers and corresponding polymers, with each polymer prepared having a given set of properties. Post-polymerization modification of conjugated polymers that have reactive functional groups, such as substitution of terminal bromides with trimethylamine or esterification of carboxylic acids,<sup>5-7</sup> is also a common strategy. A valuable alternative strategy is to develop materials that have tunable properties after traditional synthetic operations or processing is complete. Successful approaches to the post-processing tuning of conjugated polymers have included

thermally cleavable esters<sup>8-10</sup> or acid-labile tetrahydropyran-protected alcohols<sup>11, 12</sup> on poly(thiophene) backbones. Solution-processed thin films of these materials become hard and insoluble and display increased chromophore density and stability upon thermolysis.<sup>13-15</sup>

We are interested in developing photochemical strategies for tuning the properties of conjugated materials after the completion of traditional synthetic steps. Photochemical processes have the advantage that many of the properties of light are easy to control. These properties include spatiotemporal distribution, intensity, wavelength, and polarization. Much of the work in this area has focused on photochemical control of the solubility of specially designed conjugated polymers, akin to negative-tone photolithography. These examples, to our knowledge, have relied either on photoinduced heating<sup>16, 17</sup> or photoacid generators<sup>11</sup> to promote loss of a labile solubilizing group. Other studies have focused on photochemically controlling fluorescence efficiency of conjugated polymers through switching of a photochromic pendant group<sup>18-22</sup> or photochemical synthesis of a conjugated backbone from a precursor material.<sup>23, 24</sup> In this paper, we report conjugated oligomers, substituted with nitrobenzyl esters (NBEs), that show photoactivated changes in fluorescence quantum yield and solubility.

The molecules discussed in this paper contain two key structural elements. One is a conjugated backbone that contains both phenylethynyl (PE) and phenylvinyl (PV) linkages. There have been a number of reports of conjugated polymers that include a combination of these two structural moieties.<sup>25-27</sup> Such polymers offer a unique combination of properties, such as high quantum yield of fluorescence ( $\Phi_F$ ), red-shifted absorbance and

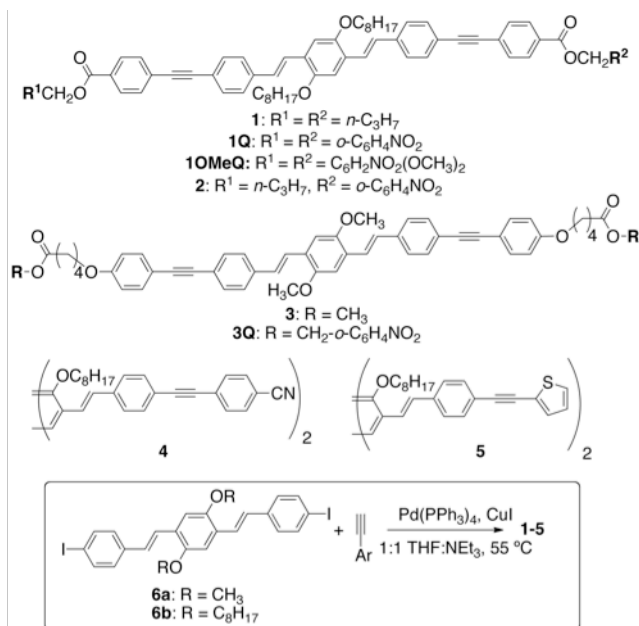
emission spectra as compared to similarly substituted poly(phenylene ethynylene)s (PPEs), and reduction potentials and oxidative stabilities that are more favorable than those of poly(phenylene vinylene)s (PPVs).<sup>25</sup> As such, they are a potentially useful but underutilized class of conjugated materials. Moreover, only several individual reports have been published concerning the synthesis and properties of corresponding oligomeric structures,<sup>28-30</sup> even though conjugated oligomers can be rigorously purified and identified, and can also serve as active components of devices. We chose PE/PV oligomers because they have substantial absorbance in the visible region of the spectrum, where photocleavable nitrobenzyl esters do not absorb light, but still allow installation of these esters using the functional group-tolerant Sonogashira reaction. Additionally, the five-arene conjugated oligomer backbone we used has been shown to be a suitable model for the photophysical properties of the corresponding P(PE/PV) conjugated polymers.<sup>31</sup>

The second structural element of our design is the *o*-nitrobenzyl ester group. This moiety is both photolabile upon irradiation with UV light<sup>32</sup> and a fluorescence quencher by photoinduced electron transfer (PET). Caged fluorophores have become important tools in applications such as cellular imaging.<sup>33</sup> Although other novel photochemical strategies for caged fluorophores have been reported,<sup>34-36</sup> nitrobenzyl groups remain a popular chemical strategy in the design of photoactivatable fluorescent dyes and quantum dots.<sup>37-43</sup> In addition to fluorescence modulation by PET, nitrobenzyl groups can “cage” other properties such as drug release, electrostatic interactions, or bioactivity.<sup>44-46</sup>

## Results and Discussion

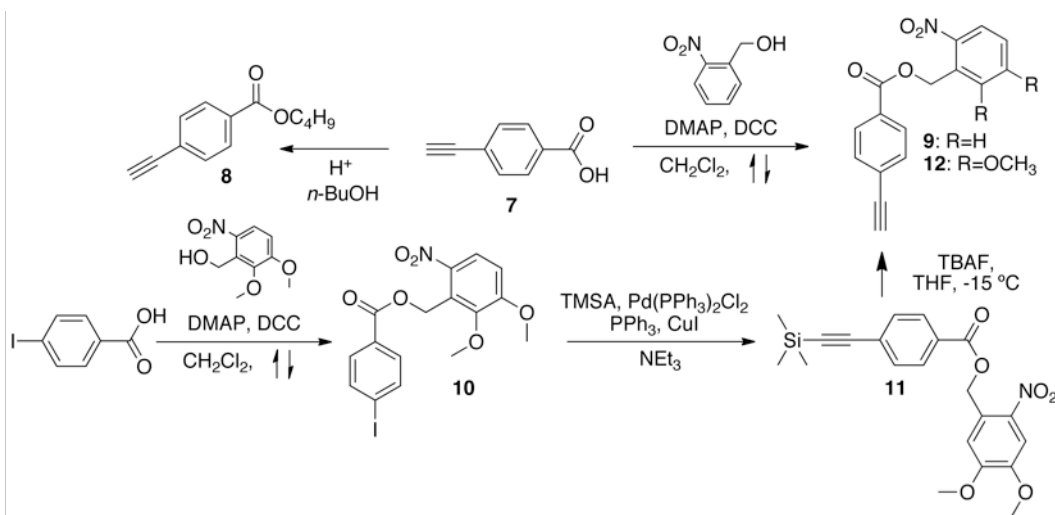
### Synthesis of Conjugated Oligomers

We initially targeted symmetrically-substituted 5-ring PE/PV derivatives (Figure 1) that bore either fluorescence quenching, photolabile nitrobenzyl esters (**1Q**, **1OMeQ**, **3Q**) or photoinert alkyl esters (**1**, **3**). The preparation of symmetrically substituted benzoic ester-terminated PE/PV derivatives (**1**, **1Q**, **1OMeQ**) followed a convergent pathway, as shown in Figures 1 and 2. We



**Figure 1.** Structures of conjugated oligomers described in this study, and general reaction conditions for their preparation.

prepared the central diiodide components with either dimethoxyphenylene (**6a**) or dioctyloxyphenylene rings (**6b**) via a modified literature procedure of Horner-Wadsworth-Emmons olefination of the corresponding diposphonate with 4-iodobenzaldehyde.<sup>29</sup> We prepared the terminal alkynes by Sonogashira coupling of methyl 4-iodobenzoate and trimethylsilylacetylene (TMSA), followed by simultaneous deprotection of the silyl group and hydrolysis of the methyl ester in a refluxing solution of sodium hydroxide gave the common precursor 4-ethynyl benzoic acid (**7**).<sup>47</sup> Acid-catalyzed esterification of **7** with *n*-BuOH yielded butyl 4-ethynylbenzoate (**8**), which we used because PE/PV derivatives with methyl esters tended to be poorly soluble. *N,N'*-dicyclohexylcarbodiimide (DCC)-mediated esterification of **7** with 2-nitrobenzyl alcohol gave photolabile terminal alkyne **9**. Sonogashira coupling



**Figure 2.** Synthesis of terminal alkynes for benzoic ester PE/PV oligomers

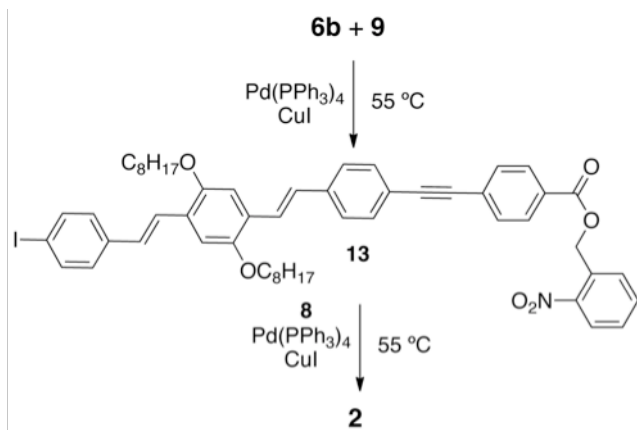


Figure 3. Synthesis of unsymmetric oligomer 2.

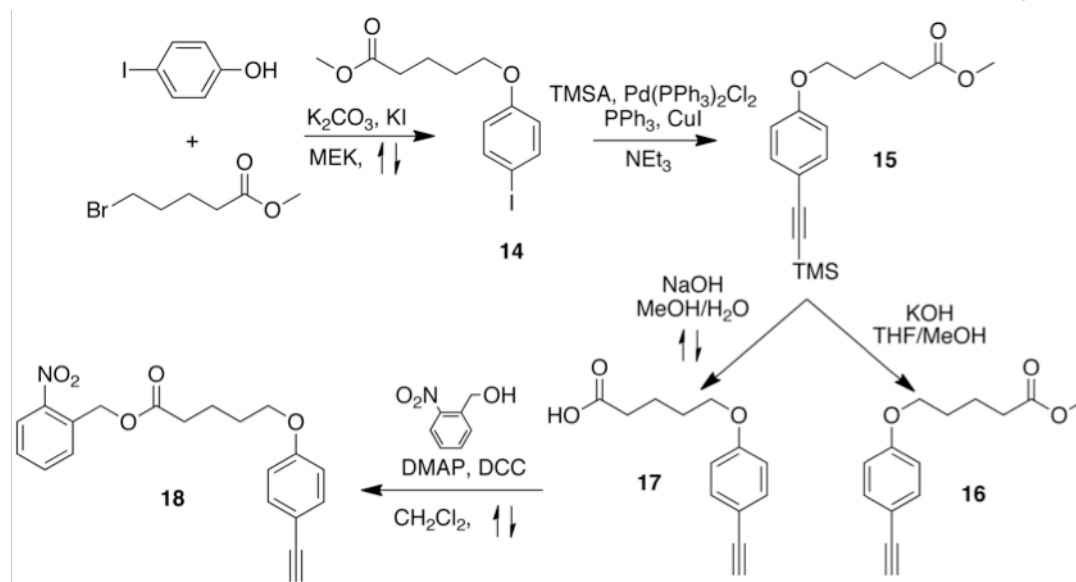


Figure 4. Synthesis of alkoxy-terminated PE/PV oligomers.

between **6b** and **8** or **9** gave the target PE/PV oligomers **1** and **1Q**.

This synthetic strategy was generally applicable; we prepared **1OMeQ**, which is identical to **1Q** except that each photolabile ester contains two methoxy groups. Esterification of 4-iodobenzoic acid yielded aryl iodide **10**, and subsequent Sonogashira coupling with TMSA and deprotection of the silyl group with tetrabutylammonium fluoride gave terminal acetylene **12**. Sonogashira coupling between **12** and diiodide **6b** gave the target bis(dimethoxynitrobenzyl ester)-substituted PE/PV oligomer **1OMeQ**. In addition, as illustrated in Figure 3, lowering the stoichiometry of the terminal alkyne in the Sonogashira reaction between **6b** and **9** gave a separable mixture of the singly coupled (**13**) and doubly coupled (**1Q**) products; subsequent coupling of **13** with **8** yielded unsymmetrically substituted **2**, which had the same conjugated backbone as the other derivatives, but only one labile NBE quencher, as opposed to the symmetric derivatives, which each had zero or two NBE groups.

We used our modular synthetic approach to prepare other

derivatives with different substituents at the terminal positions, including alkoxy-terminated PE/PV analogs **3** and **3Q** (Figure 4). Alkylation of 4-iodophenol with methyl 5-bromopentanoate, followed by Sonogashira coupling with TMSA, gave common precursor **15**. Deprotection of the silyl group with KOH in THF/methanol for 30 minutes yielded terminal unit **16**, while deprotection with NaOH in refluxing water/methanol resulted in both deprotection of the silyl group and hydrolysis of the methyl ester, yielding acid **17**. DCC-mediated esterification of **17** with 2-nitrobenzyl alcohol gave NBE-functionalized terminal acetylene **18**. We used identical Sonogashira coupling conditions with methoxy-substituted diiodide **6a** and either **16** or **18**, yielding alkoxy-substituted PE/PV analogs **3** and **3Q**, without and with photolabile NBE groups, respectively. Additional examples of the modularity of our synthetic approach are oligomers with different terminal electron withdrawing groups (a benzonitrile derivative, **4**) or terminal heteroaromatic rings (a thiophene

derivative, **5**).

#### Absorbance and Fluorescence of Conjugated Oligomers

Table 1 summarizes photophysical parameters of oligomers **1-5**; all of the PE/PV oligomers have absorption maxima around 420 nm with extinction coefficients of approximately  $8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ , and fluorescence maxima between 470 and 490 nm in solvents such as THF and  $\text{CH}_2\text{Cl}_2$  (DCM). As we expected from our experimental design, the absorbance and fluorescence spectra of **3**, which lacks clear donor-acceptor character, is between those of similarly substituted phenylene-ethynylenes<sup>48</sup> ( $\lambda_{\text{max}} = 383 \text{ nm}$ ,  $\lambda_{\text{em}} \sim 430 \text{ nm}$ ) and phenylene-vinylenes<sup>49</sup> ( $\lambda_{\text{max}} = 426 \text{ nm}$ ,  $\lambda_{\text{em}} = 500 \text{ nm}$ ) that have the same number of arenes and exocyclic multiple bonds reported in the literature. The quantum yields of fluorescence of all the oligomers that do not have NBE moieties are high ( $0.7 < \Phi_f < 0.8$ ) in all solvents investigated (benzene,  $\text{CH}_2\text{Cl}_2$ , THF, and acetonitrile). Figure 5 shows normalized absorbance and emission spectra of compounds **1** and **3** in  $\text{CH}_2\text{Cl}_2$ .

Donor-acceptor interactions between the central

dialkoxyphenylene (a common structural component among all oligomers studied here) and the terminal rings of these five-ring systems result in a bathochromic shift of the optical spectra: molecules terminated with electron donating alkoxy (**3**, **3Q**) units show absorbance maxima under 420 nm, while the molecules terminated with electron withdrawing esters (**1**, **1Q**, **1OMeQ**) or nitriles (**4**) show absorbance maxima slightly above 420 nm. These interactions have a more significant impact on emission spectra, with a shift of 24 nm between **3** (472 nm) and **4** (496 nm) in CH<sub>2</sub>Cl<sub>2</sub>. Molecules with stronger donor-acceptor character are also solvatochromic: compound **1** has maximal fluorescence intensity at 470 nm in hexanes and 497 nm in acetonitrile ( $\Delta E = 0.14$  eV).

In the visible region of the spectrum, conjugated oligomers that have bound NBE quenchers (**1Q**, **1OMeQ**, **2**, **3Q**) have solution absorption spectra that are nearly identical to analogous derivatives that do not have covalently bound quenchers (**1** and **3**), which indicates that the presence of the quenchers has minimal impact on the ground state conjugated chromophore. In the UV portion of the spectrum, the quenched molecules **1Q** and **1OMeQ** absorb significantly more light than **1**—up to 320 nm for nitrobenzyl esters and 390 nm for dimethoxynitrobenzyl esters (Supplementary Information)—consistent with known absorbances of the NBE moieties.<sup>50</sup> Excitation spectra of NBE-linked fluorophores show spectra that have the same shape as absorption spectra of the analogous unquenched fluorophores.

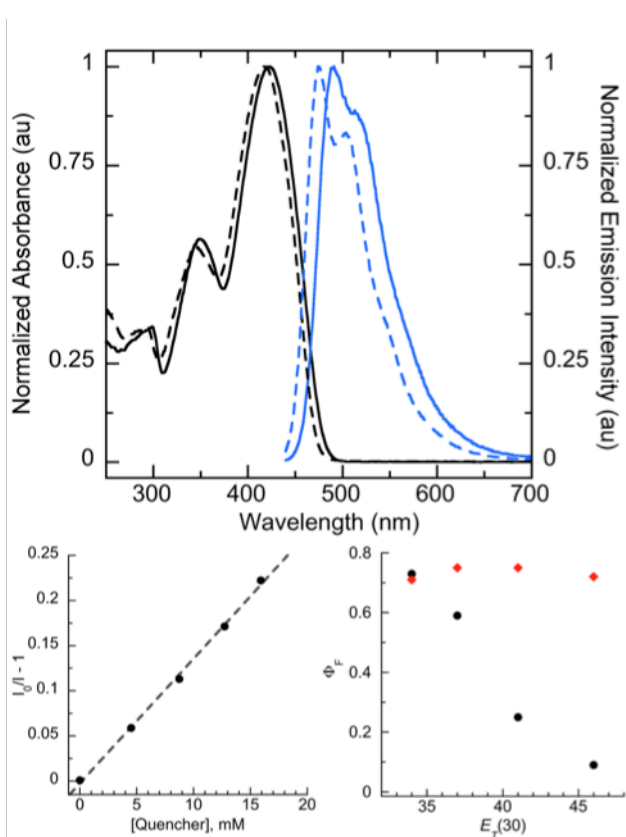
Steady-state Stern-Volmer analysis of 2-nitrobenzylacetate as a quencher of **3** resulted in a Stern-Volmer constant of 11–14 M<sup>-1</sup>, corresponding to bimolecular rate constant on the order of 10<sup>10</sup> M<sup>-1</sup>s<sup>-1</sup> (the experimentally determined lifetime of **3** was 1.1 ns). Consistent with this observation, the molecules with covalently bound NBEs had lower quantum yields of fluorescence than the molecules without covalently bound NBEs. For instance, the quantum yields of fluorescence of **1** and **1Q** in acetonitrile are 0.72 and 0.09, respectively. Monosubstituted **2** also showed quenched fluorescence, although it was 20–40% more fluorescent than **1Q**.

The difference in fluorescence efficiency between a conjugated oligomer and its analog that bears NBEs depends heavily on the polarity of the solvent: while  $\Phi_F$  of non-quenched molecules did not depend strongly on solvent,  $\Phi_F$  of quenched molecules decreased in solvents of higher polarity. In all examples studied

**Table 1.** Absorbance and Fluorescence of Conjugated Oligomers.

|              | $\lambda_{\max}$<br>(abs) <sup>a</sup> | $\lambda_{\max}$<br>(em) <sup>a</sup> | $\Phi_F^c$                    |      |      |          |
|--------------|--|---------------------------------------|-------------------------------|------|------|----------|
|              |  |                                       | C <sub>6</sub> H <sub>6</sub> | THF  | DCM  | ACN      |
| <b>1</b>     | 423 nm                                 | 491 nm                                | 0.71                          | 0.75 | 0.75 | 0.72     |
| <b>1Q</b>    | 424 nm                                 | 494 nm                                | 0.73                          | 0.59 | 0.25 | 0.09     |
| <b>1OMeQ</b> | 423 nm                                 | 493 nm                                | 0.69                          | 0.64 | 0.28 | 0.10     |
| <b>2</b>     | 424 nm                                 | 494 nm                                | 0.72                          | 0.65 | 0.31 | 0.13     |
| <b>3</b>     | 419 nm                                 | 472 nm                                | 0.74                          | 0.74 | 0.68 | <i>b</i> |
| <b>3Q</b>    | 418 nm                                 | 472 nm                                | 0.71                          | 0.66 | 0.52 | <i>b</i> |
| <b>4</b>     | 426 nm                                 | 496 nm                                | 0.77                          | 0.71 | 0.73 | 0.77     |
| <b>5</b>     | 422 nm                                 | 482 nm                                | 0.77                          | 0.72 | 0.77 | 0.75     |

*a* In CH<sub>2</sub>Cl<sub>2</sub>. *b* Not determined due to solubility. *c* Reported relative to Coumarin 6 in ethanol ( $\Phi_F = 0.78$ ).

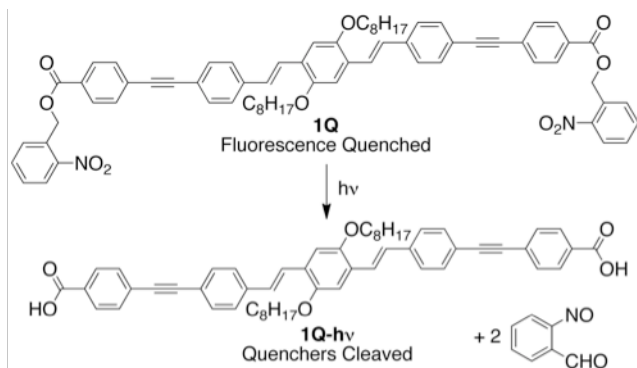


**Figure 5.** Top: Absorbance (black lines on left) and emission spectra (blue lines on right) of compounds **1** (solid lines) and **3** (dashed lines) in CH<sub>2</sub>Cl<sub>2</sub>. Bottom Left: Stern-Volmer plot showing fluorescence quenching of oligomer **3** by *o*-nitrobenzylacetate. Bottom Right: Dependence of quantum yield of fluorescence of **1** (red diamonds) and **1Q** (black circles) on the solvent parameter  $E_T(30)$ .

the ranking of quantum yield in solvents (numbers in parentheses are  $E_T(30)$  values) was benzene (34) > THF (37) > CH<sub>2</sub>Cl<sub>2</sub> (41) > acetonitrile (MeCN) (46). The effect is more pronounced in the ester-terminated analog, probably due to the proximity of the quencher to the fluorophore. In addition, the fluorescence spectra of pairs of non-quenched and quenched chromophores (**1** and **1Q**, for example) differ only in their fluorescence efficiency; the shapes of the emission spectra are indistinguishable. These observations support the conclusion that quenching occurs *via* photoinduced electron transfer,<sup>41</sup> as higher polarity solvents stabilize the charge-separated state resulting from electron transfer.

## Fluorescence Photorecovery

Figure 6 shows the photocleavage reaction of nitrobenzyl esters that we anticipated upon irradiation of the quencher-linked oligomers with UV light. Absorption of a photon gives a carboxylic acid and 2-nitrosobenzaldehyde as the products. Our design of these molecules was such that UV-induced photocleavage would break a bond connecting the nitroaromatic quencher and the conjugated fluorophore. This reaction would shut down the PET quenching pathway, because although

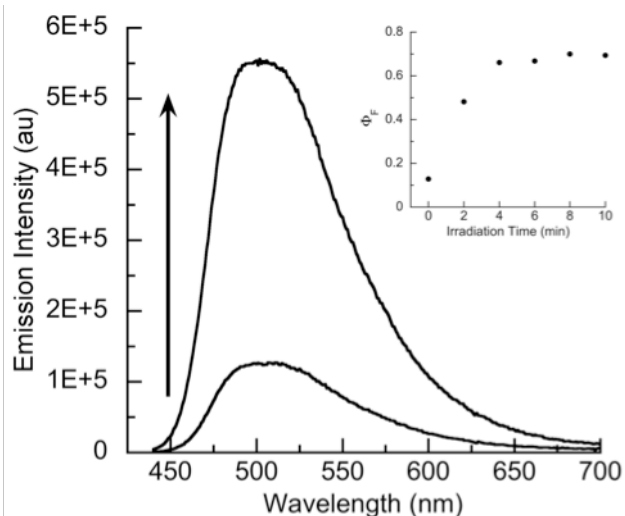


**Figure 6.** Photocleavage of nitrobenzyl ester quenchers from **1Q** to yield “unquenched” dicarboxylic acid **1Q-hv**.

quenching might still be energetically favorable, it would be diffusion-limited (*vide supra*:  $k_{sv} = 11\text{--}14 \text{ M}^{-1}$ ). We therefore expected that irradiation of the NBE-linked oligomers would enhance fluorescence, with the product a highly fluorescent conjugated carboxylic acid.

Figure 7 shows that UV photolysis of a sample of **2** in acetonitrile [with 0.03% butylated hydroxytoluene (BHT), *vide infra*] resulted in emission spectra consistent with these expectations. To perform these experiments, we used a 200 W Hg/Xe ozone-free lamp with a 295 nm high-pass filter. The quantum yield of fluorescence of the photolyzed sample reached a value similar that of **1** ( $\sim 0.7$ ) after 4 minutes of these irradiation conditions, while the shapes of both of emission and excitation spectra remained unchanged during the experiment. The recovery of emission efficiency also occurred in other solvents, such as THF or  $\text{CH}_2\text{Cl}_2$ , although the contrast in  $\Phi_F$  before and after photolysis was smaller because the fluorescence quenching of the unirradiated oligomers was not as efficient in solvents less polar than acetonitrile.

Figure 8 shows a comparison between the rates of recovery of quantum yield of benzoic ester-based oligomers **1Q**, **1OMeQ**, and **2** upon irradiation using a 365 nm interference filter. We observed recovery of fluorescence quantum yield within 20 min of irradiation of a 60/40 (v/v) THF/MeCN solution of disubstituted **1Q** or **1OMeQ** or monosubstituted **2**. The disubstituted molecules reach quantum yields (0.62–0.68) similar to that of the independently synthesized **1Q-hv** ( $0.7 \pm 0.07$ ). The UV-induced fluorescence recovery of **1OMeQ** was approximately two times faster than **1Q**: dialkoxy nitrobenzyl groups have  $\sim 5\times$  larger absorption cross-sections at 365 nm than unsubstituted nitrobenzyl groups, although they have lower quantum yields of reaction.<sup>50</sup> Control compound **1** did not show a statistically significant change in quantum yield during the irradiation, consistent with its lack of photocleavable moieties. The change in absorbance of all compounds under these irradiation conditions at 365 nm was 10% or less. Irradiation using shorter wavelength light (such as with a 295 nm long-pass filter) also resulted in a similar recovery of fluorescence quantum yield, but also resulted in more significant decomposition as reflected in decreases in absorbance for all compounds irradiated. Homolytic cleavage of the C-O bond in alkyl ethers is known to occur during irradiation of related materials in the absence of oxygen.<sup>51</sup> Addition of 0.03% BHT to the solutions significantly

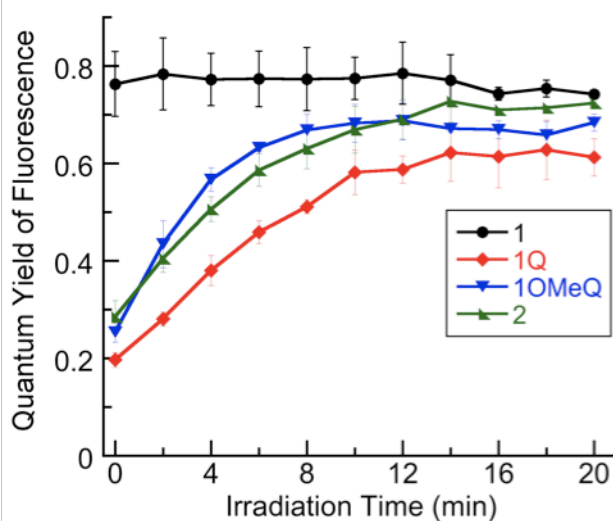


**Figure 7.** Emission intensity of monosubstituted conjugated oligomer **2** before and after 6 minutes of irradiation at  $\lambda > 295 \text{ nm}$  with a 200 W Hg/Xe lamp. *Inset:* Quantum yield of fluorescence vs. irradiation time.

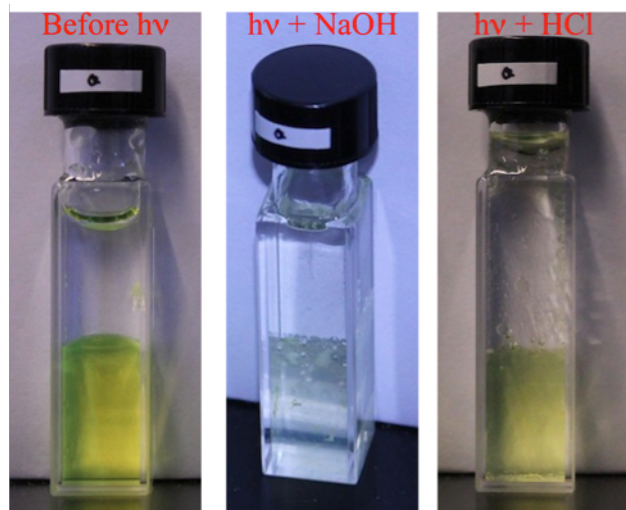
inhibited this decomposition, and did not affect the photorecovery of fluorescence efficiency significantly.

#### Photomodulation Of Solubility

During some of our attempts to synthesize PE/PV oligomers without long solubilizing alkoxy chains, we noted such derivatives tended to be only sparingly soluble—for example, a derivative with two methoxy groups on the central ring and a methyl ester on each terminal ring was not sufficiently soluble to obtain a  $^1\text{H}$  NMR spectrum of high quality. We therefore reasoned that photocleavage of nitrobenzyl ester groups could change the solubility of these conjugated oligomers, particularly because the photoproduct is an ionizable carboxylic acid. The photocleavage of nitrobenzyl esters is known to affect the



**Figure 8.** Dependence of quantum yield of caged (**1Q**, **1OMeQ**, **2**) or non-caged (**1**) conjugated oligomers as a function of UV irradiation time in 60/40 THF/MeCN (v/v) using a 365 nm interference filter.



solubility of metal complexes and polymer films for photopatterning applications<sup>52, 53</sup>

Figure 9 shows the result of a photolysis experiment using dinitrobenzyl ester **1OMeQ**. We irradiated a biphasic mixture of **1OMeQ** dissolved in  $\text{CH}_2\text{Cl}_2$  and an aqueous solution of 0.1 M NaOH with 365 nm light from a 200 W Hg/Xe for 45 min. After shaking the irradiated sample, the conjugated oligomer switched from being fully dissolved in the organic layer to being insoluble in both the organic and basic aqueous layer; it precipitated as a yellow solid. Acidification of the aqueous layer with HCl and agitation caused the chromophore to dissolve in the organic layer. Compound **1Q** showed similar behavior (ESI).

These observations are consistent with Figure 6: photolysis of **1Q** or **1OMeQ** yields the dicarboxylic acid, which is soluble in  $\text{CH}_2\text{Cl}_2$ . Deprotonation by the aqueous base, however, gives the disodium salt of the dicarboxylate, which is insoluble in both the aqueous and organic layers. The relative concentrations of diacid and dicarboxylate subsequently depend on pH. Three control experiments support this conclusion: i) the solubility of an identical biphasic sample of **1OMeQ** or **1Q** that is not irradiated does not change; therefore, hydrolysis of the nitrobenzyl ester was not occurring; ii) identical irradiation of a biphasic sample of **1**, which has no NBE groups, showed no change in solubility; therefore, any background photoreactions of the conjugated oligomer do not contribute to the observed change in solubility; iii) an independently synthesized sample of the diacid **1Q-hv** (by hydrolysis of **1** under basic conditions) shows the same dependence of solubility on pH as the irradiated sample of **1Q** or **1OMeQ**.

### Conclusion

Our work presents a novel strategy for altering the properties of conjugated materials with light. Here we demonstrated recovery of fluorescence and modulation of solubility with photolabile

nitrobenzyl esters. This approach is a new example of altering key macroscopic properties of these technologically important materials after synthetic and purification steps have been completed. We anticipate that our strategy will be useful in methods for constructing photopatterned multilayer films of conjugated polymers that do not require materials with orthogonal solubility, and for increasingly efficient photoactivatable fluorophores due to the amplification of fluorescence quenching in conjugated materials. Future work in our laboratory will focus on further tuning of the solubility of materials before and after photolysis, incorporation of NBEs into conjugated polymers, as well as addressing the current drawbacks of this approach, such as incorporating NBE groups into more photostable conjugated backbones,<sup>54</sup> and removing photolysis byproducts from solid-state samples.

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### Notes and references

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<sup>†</sup> Electronic Supplementary Information (ESI) available: Full experimental section, including synthetic procedures, absorbance and fluorescence spectra, and additional experimental details. See DOI: 10.1039/b000000x/

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