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Photochemical Synthesis of Aldehydes in the Solid Phase

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A substituted anthraquinone (AQ), previously shown to photochemically generate benzaldehyde in methanol solution, was attached to a commercially available resin via an 11 carbon tether and an amide bond. Photolysis of the polymer-bound AQ with visible or 350 nm UV light resulted in the formation of benzaldehyde in yields of 50−55% as determined by HPLC. The phenolic positions in the polymer were then alkylated using benzyl bromide and 1-iodo-3-(4-nitrophenyl)propane in a coupling reaction with K_2CO_3 as a base and a solution-phase proton shuttle. Photolysis of these alkylated polymers resulted in the formation of benzaldehyde (54−89%) and 3-(4-nitrophenyl)-propanal (58−67%). The yields of both aldehydes dropped considerably with subsequent realkylation and photolysis, and the polymer beads began to show signs of deterioration. This is the first time that aldehydes have been made photochemically on a solid-supported phase.

Introduction

Solid-phase, photochemical processes continue to receive considerable attention in the literature. For example, compounds irradiated in the solid phase have been reported to undergo the Norrish type II process,[1] cyclization,[2] and dimerization reactions.[3] In the past decade or so, a number of solid-phase photoprocesses have been found that lead to chiral products with enantiomeric excess (ee) values over a wide range.[4−7]

Solid-phase photochemistry techniques have played an important role in the area of polymer-supported synthesis. Recent developments in parallel and combinatorial syntheses have sparked considerable interest in new solid-phase methods involving amorphous polymers.[8] One obvious goal of anchoring a reaction site to an insoluble polymer is to facilitate workup and product isolation. A requirement for performing photochemical synthesis on polymers is that the polymer should not absorb strongly in the UV−visible region that is needed to excite the reactive functional group. Since polystyrene resins only absorb weakly above 300 nm, they can be used to anchor photosystems that require long-wavelength UV or visible light for activation. Currently, there are relatively few examples of light-mediated processes on solid supports in the literature. Perhaps the most important of these are photolabile linkers that are used in solid-phase peptide synthesis.[9a−c] Recently, the photochemical desulfurization of thiol groups anchored to a solid support was reported as the first example of a photoprocess in the solid phase that can be carried out using visible light.[9d]

At the outset of this work one of our goals was to attach a substituted anthraquinone (AQ) to a polymer for the purpose of preparing aldehydes under mild conditions using visible or long wavelength UV. We wanted to do this by taking advantage of a photochemical process that we have studied extensively in our laboratory, where we have shown that photoexcited 1-alkoxy- and 1-(benzyloxy)-9,10-anthraquinones (**1**, with R = phenyl or cyclopropyl and X = butyl or benzyl, for example) undergo facile conversion to their corresponding anthrahydro-

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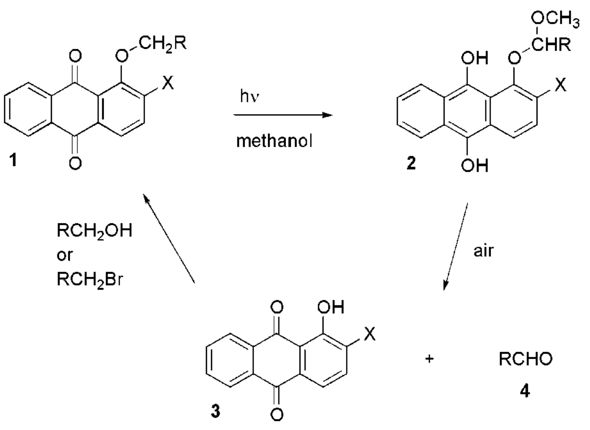
Scheme 1



quinones (**2**) in methanol (Scheme 1).[10] This transformation, which is believed to occur via short-lived biradicals,[11] can be viewed as an intramolecular redox reaction between the AQ and the alkoxy group at the 1-position. Upon exposure to air, the intermediate anthrahydroquinone is rapidly converted to a substituted 1-hydroxy-9,10-anthraquinone (**3**) and the corresponding aldehyde (**4**). This photoprocess can be used to make aldehydes, including acid-sensitive ones, in yields of 50−80%.[12] A second goal of this work was to be able to show that this substituted AQ (**1**), covalently attached to a polymer, could be alkylated and realkylated at the 1-position to make a variety of aldehydes. Herein, we demonstrate that both of these goals were achieved and provide the first example of a photochemical, solid-phase synthesis of aldehydes.

Results and Discussion

To achieve our first goal of attaching an anthraquinone to a polymer, a target anthraquinone had to be synthesized. Specifically, we considered the following three structural elements of the AQ photochemical polymer system. First, the linker connecting the AQ to the polymer needed to be long enough to make the AQ readily accessible to the reactant/solvent (methanol) during the photolysis. Second, it was desirable to attach the tether to the AQ at the 2-position because it is synthetically feasible to introduce an alkyl group at this position starting with commercially available 1-hydroxy-9,10-anthraquinone (**5**) and because the quantum yield increases with increasing size (i.e., steric bulk) of the substituent at this position.[10b] Finally, the functional group that was selected to covalently link the polymer to the AQ tether had to be stable to light and to the reaction conditions used in the alkylation of the polymer after the photolysis. AQ **10** satisfies all of these structural requirements, and its synthesis is outlined in Scheme 2.

Reaction of AQ **5** with commercially available 10-undecenal under Marshalk conditions[13] occurs regioselectively giving AQ **6** in a 46% yield with a tether of 11 carbons including an alkene group at the chain terminus. Coupling of the benzyl group to the oxygen at the 1-position occurs almost quantitatively to give AQ **7**. It should be noted that the choice of the alkyl group at this point in the synthesis establishes the identity of the aldehyde (benzaldehyde) that will be formed in the first cycle of the photolysis step.

Three more steps are needed to make the target compound. Hydroboration−oxidation of **7** gives alcohol **8** in 94% yield, and **8** is oxidized by chromic acid to give carboxylic acid **9** in 71% yield. AQ **10** is then formed in 79% yield from **9** via standard amide bond formation reaction conditions. On the basis of earlier work,[14] the *N*-hydroxysuccinimide (NHS) ester in **10** should react with an amine group in a resin to form an amide bond that covalently attaches the AQ to a polymer.

The covalent attachment of AQ **10** to a commercially available resin (polystyrene) containing NH_2 groups (0.4 mmol per g of resin) was carried out by stirring the resin beads in a THF solution of **10** at room temperature. Since AQs are yellow compounds, the progress of the reaction could be observed visually as the yellow color of the THF solution faded and the color of the beads changed from off-white to yellow. The resin beads were “loaded” with **10** at two different levels. In one loading experiment, equimolar amounts of **10** and the resin “NH_2 groups” were combined in an attempt to attach (via an amide linkage) AQs to all of the amine sites in the polymer. Not surprisingly, only 85% of the amine sites were loaded on the basis of the amount of unreacted **10** that was recovered. In a second loading experiment, we wanted to load 50% of the available amines in the polymer, so a 1:2 mole ratio of **10** to NH_2 groups was used. In this case, the loading was essentially quantitative and only a trace of **10** was recovered. The polymers with the 50 and 85% loadings are represented by structure **11** (R = Ph) and will be referred to hereafter as the partially loaded polymer (**PLP**) and fully loaded polymer (**FLP**), respectively.

One reason for loading the polymer at two different levels is that we wanted to know if all of the amines in the polymer would be able to react with **10**. Since we were unable to load the polymer completely, it is apparent that some of the amine groups in the polymer are inaccessible to solvent and/or AQ **10.** Another reason for loading the polymer at the lower level is that we were concerned that the presence of the AQs in the polymer might significantly change its properties. Since each AQ increases the mass of the polymer by 594 amu, an 85% loading results in a 20% increase in the mass of **FLP**. This could diminish its ability to swell in solvents like methanol and possibly reduce the yields of the aldehyde produced in the photolysis reaction.

The photolysis of **PLP** and **FLP** was carried out by stirring the polymer beads in 90% aqueous methanol in the presence of air and irradiating them with visible or 350 nm light (Scheme 3). Similar results were obtained by performing the photolysis in the absence of oxygen followed by exposure to air. Periodically, the photolysis was interrupted and the methanol solution was analyzed for its aldehyde content using HPLC. If a significant amount of aldehyde was present, the photolysis solution was replaced with fresh aqueous methanol and the

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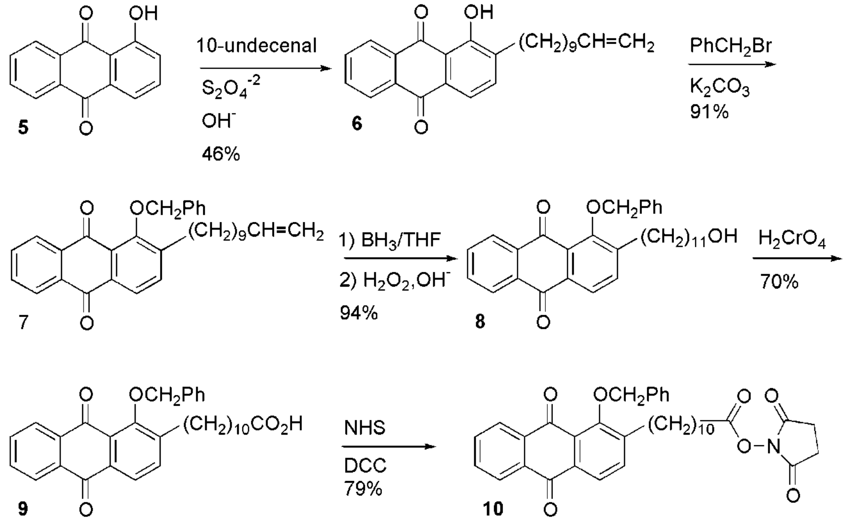
Scheme 2



Scheme 3

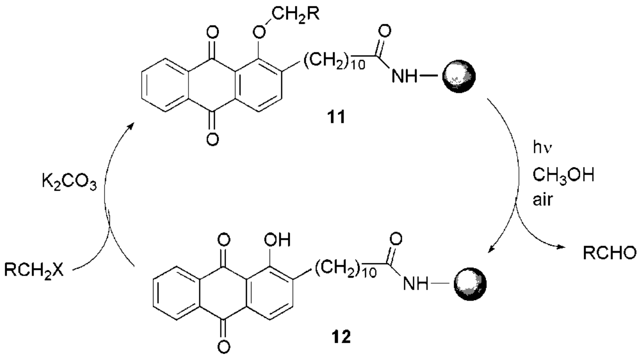


Table 1. Aldehyde Yields (%) from the Photolysis of Solid-Phase Polymers[a]

polymer	PhCHO	**13**[b]
PLP[c]	50[e]	
FLP[d]	55[e]	
alkylated **PLP**	89[f]	54[f]
alkylated **FLP**	58[f]	67[f]
realkylated **PLP**	30[g]	
realkylated **FLP**	25[g]	

[a] Visible light (tungsten lamp). [b] p-NO_2-Ph-CH_2CH_2CHO. [c] Polymer **11** loaded with AQ **10** at 50% of its NH_2 sites. [d] Polymer **11** loaded with AQ **10** at 85% of its NH_2 sites. [e] Yield is based upon the number of AQs in the polymer. [f] Yield is based upon the number of phenols in the polymer prior to alkylation. [g] Yield is based upon the number of phenols in the polymer prior to realkylation.

photolysis was continued. Total irradiation times of about 30 h were needed to complete the photolysis, and benzaldehyde yields of 50–55% (Table 1) were obtained from **PLP** and **FLP**.

The yield of benzaldehyde from these solid-phase polymers is about 20% lower than the yield of benzaldehyde from the photolysis of 1-benzyloxy-2-butyl-9,10-anthraquinone in methanol.[12] One possible reason for the lower yield of benzaldehyde from the solid-phase AQ is that some of the AQs in these polymers are inaccessible to solvent. Support for this hypothesis comes from our observation of a small solvent effect during the photolysis. The yield of benzaldehyde is 5–10% higher in 90% aqueous methanol than in pure methanol or in methanol with higher percentages of water (i.e., 70 and 80% aqueous methanol). If the polymer swells the most in 10% aqueous methanol and the accessibility of methanol to the AQs increases with the swelling of the polymer, this would account for the highest yield of benzaldehyde in 10% aqueous methanol.

Interestingly, the yields of benzaldehyde from the photolysis of **PLP** and **FLP** are similar. This result shows that the higher level of loading did not significantly reduce the fraction of AQs in the polymer accessible to solvent and therefore able to undergo photolysis. Furthermore, it appears that the higher loading did not significantly change the properties of the polymer.

In the alkylation of the solid-phase **AQ**, the phenolic OH group at the 1-position in **12** (i.e., the polymers resulting from the photolysis of **PLP** and **FLP**) must be converted to OCH_2R so that the photolysis can be repeated to produce either more of the same aldehyde or a different one. The Mitsunobu reaction (RCH_2OH, PPh_3, DEAD, THF) and direct coupling (RCH_2X, K_2CO_3) accomplish this solution-phase transformation in high yield. When **12** was reacted with benzyl alcohol under Mitsunobu conditions and the polymer was irradiated at 350 nm in 90% aqueous methanol, only 10–15% yields of benzaldehyde were obtained.[15] This was an unexpected result since Mitsunobu reactions with one substrate in the solid phase are well-known, including examples in which a modified triarylphosphine is attached to a polymer,[16] a modified DEAD is attached to a polymer,[17] and, most applicable to our case, in which a phenolic group is attached to a polymer.[18a,b] Perhaps the low yield from the Mitsunobu reaction of **12** is the consequence of having free NH_2 groups in the polymer that react with one of the intermediates.[18c] This seems unlikely, however, given that these same NH_2 groups appeared to be inaccessible to AQ **10** in THF.

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(15) Yield is based upon the number of OH groups at the 1-position in **12**, which is known from the photolysis.

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Our initial attempts to convert **12** to **11** by direct coupling were also unsuccessful. Treatment of **12** with triethylamine or LDA to deprotonate the phenolic proton in the polymer followed by its reaction with excess RCH_2X failed to give a polymer that produced significant amounts of aldehyde when irradiated. Since substituted 1-hydroxy-9,10-anthraquinones are alkylated in high yield in acetone or 2-butanone solution using K_2CO_3 as an insoluble base, we decided to try these reagents, recognizing that a proton shuttle would be needed to transfer a proton from the solid-phase AQ to the insoluble K_2CO_3. Use of 1-hydroxy-9,10-anthraquinone as a proton shuttle with benzyl bromide as the alkylating agent in the conversion of **12** to **11** and subsequent photolysis led to a benzaldehyde yield of 89% using the **PLP** and a 54% yield of benzaldehyde from **FLP** (see Table 1). Using the proton shuttle method with 1-iodo-3-(4-nitrophenyl)-propane as the alkylating agent gave (after photolysis) 58 and 67% yields of 3-(4-nitrophenyl)propanal (**13**) from **PLP** and **FLP**, respectively. Thus, these experiments show that the polymer can be reloaded with different alkyl groups and can be used to make both aliphatic and aromatic aldehydes. The potential for repeated use seems to be limited, however. When the polymer was reloaded a second time using benzyl bromide, only a 20−30% yield of benzaldehyde was obtained. Furthermore, after three reloading/photolysis procedures, the beads had become discolored and their texture was gummy, indicating that the polystyrene support was deteriorating. Since visible light was used to irradiate these polymers, it seems unlikely that the degradation of the support was caused by the light source.

Conclusions

We have shown that an appropriately substituted anthraquinone, previously used for the photochemical generation of benzaldehyde under very mild conditions, can be covalently linked to a polymer and irradiated with light to generate benzaldehyde in good yields. Since this polymer can be alkylated and realkylated with different alkyl halides, this method can be used in a general way to make aryl and alkyl aldehydes in good yields. Although a solid-phase synthesis of aldehydes has been reported recently,[19] this is, to our knowledge, the first example of a photochemical, solid-phase synthesis of aldehydes.

Experimental Section

General. The amine-containing resin (0.4 mmol of NH_2 groups per g of resin) was purchased from Argonaut Technologies, Inc. (P/N 800007). Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra (250 MHz) were recorded from solutions in $CDCl_3$, and chemical shifts are reported in parts per million (ppm, δ) downfield from internal Me_4Si (TMS). Mass spectra were obtained using electron ionization on a quadrupole instrument. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. Infrared spectra were recorded on a FT-IR instrument either as thin films on sodium chloride plates or as powdered mixtures with KBr. HPLC analyses were made using a C-18 reverse-phase column, a UV−vis detector, and methanol−water mixtures as the eluting solvent. Photolyses were carried out using a slide projector for visible light (300 W) and a Rayonet Chamber Reactor with 350 nm bulbs for UV light.

1-Hydroxy-2-(10-undecenyl)-9,10-anthraquinone (6). To 250 mL of 1:1 (v/v) methanol−water was added 2.77 g (12.3 mmol) of 1-hydroxy-9,10-anthraquinone followed by 11.20 g of NaOH and 12.36 g of $Na_2S_2O_4$. Under argon, the mixture was heated in an oil bath at 70−75 °C for 30 min. After the dropwise addition of 14.3 g (85.0 mmol) of 10-undecenal, the mixture was heated at reflux for 3 days. After cooling to room temperature, the reaction mixture was poured over ice and acidified with concentrated HCl. The precipitate that formed with stirring was collected by vacuum filtration. Chromatography of this material on silica gel followed by elution with hexane−methylene chloride (4:1) gave a yellow solid that was recrystallized from heptane giving 2.13 g (46.0%) of **6** as yellow crystals: mp 101−102 °C; IR (KBr) 3073, 2923, 2855, 1672, 1635, 1590, 1437, 1360, 1299, 911, 767, 700 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 13.05 (s, 1H), 8.26−8.34 (m, 2H), 7.75−7.84 (m, 3H), 7.52 (d, $J = 7.68$ Hz, 1H), 5.73−5.91 (m, 1H), 4.90−5.04 (m, 2H), 2.79 (t, $J = 7.69$ Hz, 2H), 2.06 (q, $J = 6.91$ Hz, 2H), 1.60−1.72 (m, 2H), 1.23−1.45 (m, 12H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 188.89, 182.23, 160.83, 139.43, 139.21, 136.33, 134.44, 133.89, 133.71, 133.71, 131.18, 127.21, 126.80, 119.24, 115.31, 114.12, 33.82, 29.95 (2), 29.53, 29.49, 29.14 (2), 29.04, 28.93. Anal. Calcd for $C_{25}H_{28}O_3$: C, 79.75; H, 7.50; Found: C, 79.39; H, 7.65.

1-Benzyloxy-2-(10-undecenyl)-9,10-anthraquinone (7). To a solution of 1.12 g (2.97 mmol) of **6** in 75 mL of 2-butanone (freshly distilled from CaH_2) were added 4.00 g of anhydrous K_2CO_3 and 2.00 g (11.7 mmol) of benzyl bromide. The mixture was heated at reflux under argon for 4 h during which time the color changed from deep red to yellow. The mixture was cooled and vacuum filtered to remove the potassium salts. The solvent was removed under reduced pressure in a rotary evaporator. The yellow oil residue was dissolved in hexane and cooled producing a yellow solid that was collected by vacuum filtration. The solvent was removed from the mother liquor, and the resulting oil was chromatographed on silica gel and eluted with hexane−methylene chloride (ca. 1:1) providing a yellow solid. The yellow solids were combined and recrystallized from hexane giving 1.27 g (91%) of **7** as yellow crystals: mp 65.5−66.0 °C; IR (KBr) 2922, 2849, 1671, 1583, 1464, 1324, 1278, 1026, 979, 714 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.23−8.33 (m, 2H), 8.12 (d, $J = 7.92$ Hz, 1H), 7.72−7.81 (m, 2H), 7.64 (d, $J = 7.92$ Hz, 3H), 7.32−7.49 (m, 3H), 5.74−5.93 (m, 1H), 5.08 (s, 2H), 4.90−5.05 (m, 2H), 2.73 (t, $J = 7.62$ Hz, 2H), 2.05 (q, $J = 7.13$ Hz, 2H), 1.52−1.68 (m, 2H), 1.20−1.44 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 183.00, 182.64, 157.47, 145.78, 139.14, 137.30, 135.61, 134.86, 134.04, 133.77, 133.41, 132.66, 128.53, 128.37, 128.15, 127.28, 126.57, 125.90, 123.64, 114.19, 76.21, 33.84, 30.56, 30.25, 29.63, 29.51 (2), 29.14 (2), 28.96. Anal. Calcd for $C_{32}H_{34}O_3$: C, 82.37; H, 7.34; Found: C, 82.10; H, 7.39.

1-Benzyloxy-2-(11-hydroxyundecyl)-9,10-anthraquinone (8). To 1.03 g (2.21 mmol) of **7** in 20 mL dry THF was added 2.0 mL (2.0 mmol) of 1.0 M BH_3−THF. The solution was heated in a 50 °C water bath for 30 min and then cooled to room temperature. After several drops of water had been added to quench excess BH_3, 5.20 mL of 2.0 M NaOH and 3.85 mL of 30% H_2O_2 were added. The reaction mixture was heated at a gentle reflux for 30 min. After cooling, the reaction mixture was diluted with 25 mL of CH_2Cl_2 and the aqueous layer was separated. The organic layer was washed with dilute HCl and water. After the organic layer was dried over sodium sulfate, the solvent was removed under reduced pressure in a rotary evaporator. The residue was chromatographed on silica gel and eluted with methylene chloride−hexane (1:1) giving starting material. This was followed by elution with methylene chloride−methanol (10:1) to give **8** as a yellow solid. Recrystallization from heptane−toluene (6:1) gave 1.092 g (94%) of **8** as yellow needles: mp 110.5°−111 °C; IR (KBr) 3420, 3066, 3032, 2925, 2854, 1667, 1601, 1455, 1428, 1374, 1311, 1263, 1212, 1188, 1157, 1046, 914, 843, 734, 699 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.14−8.36 (m, 2H), 8.12 (d, $J = 7.92$ Hz, 1H), 7.75−7.82 (m, 2H), 7.58−7.66 (m, 3H), 7.37−7.48 (m, 3H), 5.06 (s, 2H), 3.67 (t, $J = 6.6$ Hz, 2H), 2.72 (t, $J = 7.62$ Hz, 2H), 1.50−1.70 (m, 4H), 1.30 (br s, 14H); ^{13}C NMR (250 MHz,

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[19] Slavino, J. M.; Mervic, M.; Mason, H. J.; Kiesow, T.; Teager, D.; Airey, J.; Labaudiniere, R. *J. Org. Chem.* **1999**, *64*, 1823−1830.

$CDCl_3$) δ 183.22, 182.81, 157.48, 145.87, 137.23, 135.68, 134.89, 134.13, 133.79, 133.49, 132.68, 128.55 (2), 128.38, 128.18, 128.04, 127.33, 126.62, 125.93, 123.38, 75.28, 63.05, 63.04, 32.79, 30.56, 30.22, 29.53, 29.49 (2), 29.43 (2), 25.75. Anal. Calcd for $C_{32}H_{36}O_4$: C, 79.31; H, 7.49; Found: C, 79.82; H, 7.42.

1-Benzyloxy-2-(11-carboxyundecyl)-9,10-anthraquinone (9). To a solution of 1.01 g (2.09 mmol) of **8** in 55 mL of acetone in a 40 °C water bath was added dropwise 1.47 mL of 2.06 M H_2CrO_4 (3.03 mmol). After 5 min, the reaction mixture was cooled in an ice bath, diluted with 40 mL of water, and extracted with ether (3 × 40 mL). The ether layers were combined and washed with 0.5 M NaOH (2 × 40 mL). The aqueous layer was acidified with HCl and extracted with methylene chloride (2 × 45 mL). Removal of the solvent under reduced pressure in a rotary evaporator gave a yellow solid that was chromatographed on silica gel and eluted with methylene chloride–acetone (2:1) to give 0.730 g (70%) of **9**. An analytically pure sample was obtained after several recrystallizations from toluene–heptane: mp 144–145 °C; IR (KBr) 3201, 2917, 2851, 1721, 1674, 1580, 1471, 1326, 1277, 1245, 1048, 979, 730, 710 cm $^{-1}$; H NMR (250 MHz, $CDCl_3$) δ 8.24–8.35 (m, 2H), 8.10 (d, $J = 7.92$ Hz, 1H), 7.75–7.83 (m, 2H), 7.58–7.65 (m, 3H), 7.37–7.49 (m, 3H), 5.06 (s, 2H), 2.72 (t, $J = 7.82$ Hz, 2H) 2.34 (t, $J = 7.50$ Hz, 2H), 1.53–1.68 (m, 4H), 1.20–1.38 (m, 12H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 183.20, 182.79, 180.06, 157.49, 145.86, 137.23, 135.68, 134.79, 134.12, 133.79, 133.48, 132.68, 128.54, 128.38, 128.18, 127.32, 126.62, 125.93, 123.68, 76.27, 34.09, 30.55, 30.21, 29.58, 29.38 (2), 29.2, 29.05, 24.68. Anal. Calcd. for $C_{32}H_{34}O_5$: C, 77.08; H, 6.87; Found: C, 77.18; H, 7.07.

1-Benzyloxy-2-(11-carboxyundecyl)-9,10-anthraquinone, NHS Ester (10). To a 50 mL round-bottom flask were added 0.720 g (1.44 mmol) of **9**, 0.342 g (1.66 mmol) of DCC, and 0.190 g (1.66 mmol) of NHS in 35 mL of dry THF. The reaction was monitored by TLC (silica gel, 9:1 CH_2Cl_2–MeOH). After ca. 25 h, the reaction mixture was cooled in an ice bath and vacuum filtered to remove the insoluble urea. Removal of the solvent from the mother liquor under reduced pressure in a rotary evaporator gave a solid residue that was chromatographed on silica gel and eluted with methylene chloride–acetone (20:1) to yield 0.675 g (79%) of **10** as a yellow solid. Recrystallization from toluene–hexane gave an analytically pure sample: mp 99–100 °C; IR (KBr) 2924, 2853, 1813, 1785, 1744, 1673, 1325, 1309, 1296, 1253, 1248, 1210, 1075, 726, 714 cm $^{-1}$; ^1H NMR (250 MHz, $CDCl_3$) δ 8.22–8.33 (m, 2H), 8.08 (d, $J = 7.92$ Hz, 1H), 7.70–7.82 (m, 2H), 7.62 (d, $J = 7.92$ Hz, 3H), 7.34–7.48 (m, 3H), 5.06 (s, 2H), 2.82 (s, 4H), 2.71 (t, $J = 7.82$ Hz, 2H) 2.60 (t, $J = 7.50$ Hz, 2H), 1.50–1.68 (m, 4H), 1.20–1.44 (m, 12H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 183.00, 182.63, 169.32, 168.68, 157.41, 145.75, 137.28, 135.63, 134.82, 134.07, 133.73, 133.44, 132.62, 128.52, 128.34, 128.15, 127.24, 126.52, 125.87, 123.60, 76.13, 30.90, 30.47, 30.18, 29.56, 29.38, 29.30, 29.28, 29.03, 28.72, 25.59, 24.56. Anal. Calcd for $C_{36}H_{37}NO_7$: C, 72.59; H, 6.26; N, 2.35; Found: C, 72.51; H, 6.12; N, 2.23.

3-(4-Nitrophenyl)propanal (13). To a solution of 0.170 g (0.940 mmol) of 3-(4-nitrophenyl)-1-propanol in 15 mL of CH_2Cl_2 was added 0.304 g (1.41 mmol) of pyridinium chlorochromate. The reaction mixture was heated to reflux for 1.5 h, cooled, and combined with 35 mL of ether. After the solids were removed by gravity filtration, the solvents in the filtrate were evaporated under reduced pressure in a rotary evaporator. The crude product was chromatographed on silica gel and eluted with CH_2Cl_2 giving 0.111 g (66.1%) of analytically pure **13**: IR (film) 3068, 2944, 2900, 2830, 2728, 1723, 1610, 1577, 1525, 1452, 1394 cm $^{-1}$; ^1H NMR (250 MHz, $CDCl_3$) δ 9.75 (s, 1H), 8.04 (d, $J = 8.54$ Hz, 2H), 7.29 (d, $J = 8.55$ Hz, 2H), 2.97 (t, $J = 7.33$ Hz, 2H), 2.79 (t, $J = 7.33$ Hz, 2H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 200.36, 148.44, 146.50, 129.27, 123.72, 44.42, 27.75; MS (EI) *m/e* (rel intensity) 179 (40), 137 (32), 91 (35), 86 (65), 84 (100). Anal. Calcd for $C_9H_9NO_3$: C, 60.33; H, 5.06; N, 7.82. Found: C, 59.99; H, 5.27; N, 7.69.

Preparation of 85% Loaded Polymer 11 (FLP). To a 50 mL round-bottom flask were added 1.64 g of ArgoGel resin (0.66 mmol of NH_2 groups) and 30 mL of dry THF. The resin beads were stirred for 15 min to allow them to swell. A solution of 0.390 g (0.655 mmol) of **10** in 5 mL of THF was added to the beads. The flask was wrapped with aluminum foil and stirred for 48 h, after which time the yellow beads were collected by vacuum filtration. The beads were stirred with 20 mL of THF for 45 min, vacuum filtered, vacuum dried, and weighed. This process was repeated until the washings were colorless and the mass of the dried beads was constant (two more times). The faintly yellow filtrate and washings were combined, and the solvent was removed in a rotary evaporator under reduced pressure leaving a residue that contained 57 mg (0.096 mmol) of unreacted **10** and 64 mg (0.56 mmol) of NHS. Both of these quantities show indirectly that 85% of AQ **10** reacted with the resin. Reacting the resin with a 10% excess of **10** did not increase the loading.

Preparation of 50% Loaded Polymer 11 (PLP). The above procedure was followed starting with 1.68 g of resin (0.67 mmol of NH_2 groups) and 200 mg of **10** (0.336 mmol). The residue from the filtrate and washings contained only a trace of **10** and 39 mg (0.34 mmol) of NHS showing that the reaction occurred quantitatively and that the resin was 50% loaded.

General Procedure for the Photolysis of the Resin. Into a 50 mL round-bottom flask was introduced **FLP** or **PLP** (200–300 mg) and 50 mL of 90% aqueous methanol. The mixture was deoxygenated with N_2 and irradiated for 4–6 h with visible light (300 W tungsten bulb, slide projector). Air was then bubbled through the mixture for 20 min, and the aqueous methanol solution was carefully decanted from the beads. The aldehyde concentration was determined using HPLC. This procedure was repeated using new solvent until negligible amounts of aldehyde were formed. Yield calculations (Table 1) were based upon the number of AQs in the reactant polymer. Irradiation of the resin with 350 nm UV light using a Rayonet Chamber Reactor gave similar results.

General Procedure for Reloading of Resin. Polymer beads resulting from the photolysis of **FLP** or **PLP** were placed in a 50 mL round-bottom flask along with a large excess of K_2CO_3, 10 equiv of 1-hydroxy-9,10-anthraquinone for use as a proton shuttle, and 40 equiv of the desired halide in dry THF. The reaction was heated to 40–50 °C for ca. 3 days, during which time the beads became bright red while the solution turned from red to a faint yellow. The beads were vacuum filtered and washed with acetone, 50/50 water/methanol, and methanol, until the washings from the three solvents were colorless. The beads were then vacuum dried and irradiated following the general procedure above. The yield was calculated on the basis of the millimoles of aldehyde produced in the photolysis of the reloaded resin and the millimoles of available AQ-OH groups in the resin before reloading. The latter is equivalent to the millimoles of aldehyde formed in the previous photolysis.

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Supporting Information Available: Experimental procedures and spectral data for 1-bromo-3-(4-nitrophenyl)propane, 1-iodo-3-(4-nitrophenyl)propane, and 3-(4-nitrophenyl)-1-propanol. This material is available free of charge via the Internet at http://pubs.acs.org.

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