JOC The Journal of Organic Chemistry

Note

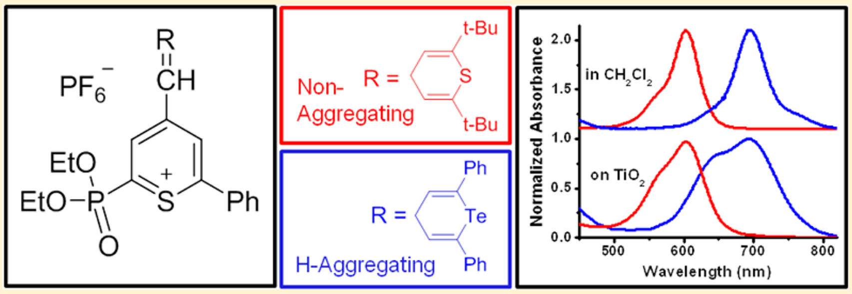
pubs.acs.org/joc

Synthesis and Photoelectrochemical Performance of Chalcogenopyrylium Monomethine Dyes Bearing Phosphonate/Phosphonic Acid Substituents

Matthew A. Bedics, Kacie R. Mulhern, David F. Watson,* and Michael R. Detty*

Department of Chemistry, University at Buffalo, The State University of New York, Buffalo, New York 14260-3000, United States

Ⓢ *Supporting Information*



ABSTRACT: Chalcogenopyrylium monomethine dyes were prepared via condensation of a 4-methylchalcogenopyrylium compound with a chalcogenopyran-4-one bearing a 4-(diethoxyphosphoryl)phenyl substituent (or the phosphonic acid derivative). The dyes have absorbance maxima of 603−697 nm in the window where the solar spectrum is most intense. The dyes formed H-aggregates on TiO_2, increasing the light-harvesting efficiency of the dyes. Shortcircuit photocurrent action spectra were acquired to evaluate the influence of dye structure on the photoelectrochemical performance.

Nanocrystalline TiO_2 is a wide-bandgap semiconductor[1−5] used in dye-sensitized solar cells (DSSCs).[6−8] Effective DSSCs require dyes to adhere to and persist on the semiconductor surface and to absorb light efficiently, inject electrons into the semiconductor, and oxidize an electron donor in the electrolyte.[7−10] More efficient DSSCs absorb light available in the near-infrared (NIR) region of the solar spectrum, which contains approximately half of the sun's usable energy,[11] and use a sensitizer absorbing in the NIR with a cosensitizer with high efficiency in the visible spectrum.[12] Sensitizer aggregation, which broadens the electronic spectrum, can be beneficial to the overall efficiency of the DSSC.[13−17]

Chalcogenopyrylium dyes absorb into the NIR,[18−20] and X-ray structural analysis has shown that chalcogenopyrylium monomethine dyes have an essentially planar structure.[18] The contributions of the chalcogen atoms to the electronic structure of these compounds (particularly with respect to HOMO and LUMO levels) has been examined in detail.[18] Chalcogenopyrylium compounds form H- and J-aggregates in polymer films and are effective photosensitizers in electrophotographic applications.[21−23] In order to evaluate chalcogenopyrylium compounds in DSSCs, anchoring groups must be introduced that persist on TiO_2. Phosphonate anchoring groups have surface-adduct formation constants to TiO_2 that are much greater than those for carboxylic acids.[15,24−28] Herein, we describe the synthesis of several chalcogenopyrylium monomethine dyes containing a phosphonate linker for attachment to nanocrystalline TiO_2 and preliminary results of their photoelectrochemistry on nanocrystalline TiO_2, which include absorbance at >700 nm.

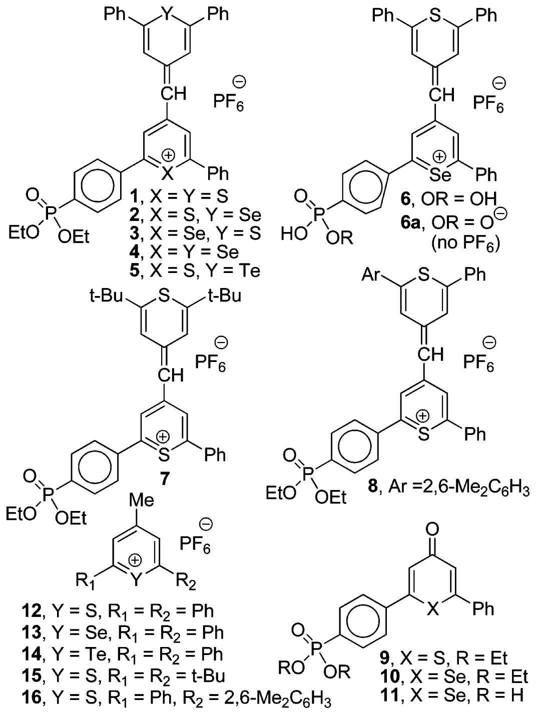
Dyes **1−8** (Chart 1) were prepared as representative chalcogenpyrylium dyes to examine the effect of the chalcogen atoms on the wavelengths of absorbance of light, the effectiveness of the phosphonate as a linking group, and the photoelectrochemical performance of DSSCs containing the dyes. Dyes **7** and **8** have bulky substituents to mimimize aggregation, allowing the impact of aggregation on TiO_2 on photoelectrochemical performance to be assessed directly.

Condensation of a phosphonate-containing chalcogenopyranone **9−11** with a 4-methylchalcogenopyrylium salt **12−16** (prepared following literature procedures)[18,20,29] should give **1−8** (Chart 1) on the basis of literature precedent.[19,21] While phosphonate-containing chalcogenopyranones **9−11** have not been described, 4-bromophenyl-substituted chalcogenopyranones **17** or **18** (Scheme 1) seem to be appropriate precursors for introduction of the phosphonate group via Pd-catalyzed coupling of diethyl phosphite.[30] Addition of the elements of H_2S or H_2Se to 1,5-diaryl-1,4-pentadiyn-3-one **19** formally allows the preparation of **17** and **18**.[31] Pentadiynone **19** can be prepared from addition of a metal phenylacetylide to the known 4-bromophenylpropargyl aldehyde (**20**)[32] followed by oxidation of the intermediate 1,5-diaryl-1,4-pentadiyn-3-ol **21** that is formed.[31,33,34]

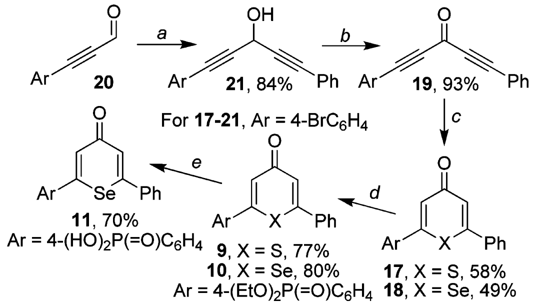
Received: June 20, 2013
Published: July 30, 2013

dx.doi.org/10.1021/jo401280s | *J. Org. Chem.* 2013, 78, 8885−8891

Chart 1



Scheme 1. Synthesis of Chalcogenopyranones 9−11[a]

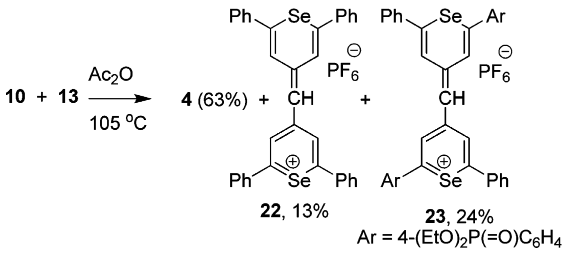


[a] Reagents: (a) PhCCMgBr, THF; (b) MnO_2, CH_2Cl_2; (c) (1) NaOEt, EtOH, (2) Na_2S or Na_2Se; (d) HP(=O)$(OEt)_2$, Pd$(OAc)_2$, dppf, KOAc, Et_3N, THF; (e) Me_3SiCl, NaI, CH_3CN/CH_2Cl_2.

Addition of PhC≡CMgBr (deprotonation of phenylacetylene with EtMgBr) to **20** gave diynol **21** (Scheme 1), which was oxidized with MnO_2 in CH_2Cl_2 to give **19** in 78% overall yield. Sodium ethoxide catalyzed addition of EtOH to **19** to give an unisolated mixture of enol ethers,[31] to which was then added Na_2S or Na_2Se to give **17** or **18**. Pd$(OAc)_2$-catalyzed coupling of diethyl phosphite to **17** and **18** gave **9** and **10**.[30] Phosphonate **10** was converted to phosphonic acid derivative **11** using iodotrimethylsilane generated in situ from chlorotrimethylsilane and NaI in CH_2Cl_2/CH_3CN.[35−37]

While condensation of **12**−**16** with **9**−**11** should lead directly to dyes **1**−**8**, "scrambling" of the chalcogenopyrylium rings can occur if concentrations of reactants are too high, reaction times are too long, or the chalcogenopyranone is limiting reagent.[38] As shown in Scheme 2, 0.2 M **10** and 0.2 M **13** were heated 10 min at 105 °C in Ac_2O to give a mixture of **4** (63%), known tetraphenyl derivative **22**[21] (24%), and **23** with two phosphonate groups (13%) upon workup. The products in the mixture were identified by mass spectrometry and ^{1}H NMR spectroscopy (Supporting Information). The major product was the expected **4** with m/z 741.0552 for $C_{39}H_{34}O_3P^{80}Se_2$ (calcd m/z 741.0576) and a "methine" CH signal at δ 7.015. Dye **22**[21] displayed m/z 605 for $C_{35}H_{25}{}^{80}Se_2$ and a "methine" CH signal at δ 6.97. The third product **23** gave m/z 877.0837 for $C_{43}H_{43}O_6P_2{}^{80}Se_2$ (calcd m/z 877.0865) and a "methine" CH signal at δ 7.05. In order to confirm the ^{1}H NMR assignments given for the "scrambled" products, pure **4** (described below) was spiked with ~10 mol % of authentic **22** with the methine signal of **22** appearing at higher field than that of **4** (Supporting Information).

Scheme 2. Scrambling of Chalcogenopyrylium Rings in the Synthesis of 4



The reaction was repeated with 0.11 M **10** and 0.10 M **13** in Ac_2O at 105 °C for 2 min. Dye **4** was isolated in 83% yield, and neither **22** nor **23** was detected in the reaction mixture. These concentrations were employed at 105 °C in the preparation of the remaining dyes with the 4-methylchalcogenopyrylium compound as limiting reactant. No "scrambled" products were observed, and yields are compiled in Table 1. Reaction times were a function of chalcogen atom and steric bulk at the 2- and 6-positions. Condensations were slowest with thiopyrylium compounds **15** (with two *tert*-butyl substituents, 30 min reaction time), **12** (15 min), and **16** (15 min). Condensations with selenopyrylium compound **13** were complete after 2 min and with telluropyrylium compound **14**, after 1 min.

Table 1. Synthetic Yields, Absorption Maxima (λ_{max}), and Molar Extinction Coefficients (ε) in CH_2Cl_2, and Saturation Surface Coverages (Γ_0) on Nanocrystalline TiO_2 for Dyes 1−5, 7, and 8[a]

compd	% yield	λ_{max}, nm	ε, M^{-1} cm^{-1}	Γ_0, mol cm^{-2}
1	89	630	$(1.31 \pm 0.03) \times 10^5$	$(6.8 \pm 1.7) \times 10^{-8}$
2	79	655	$(1.18 \pm 0.03) \times 10^5$	$(4.2 \pm 0.2) \times 10^{-8}$
3	93	651	$(1.27 \pm 0.02) \times 10^5$	$(5.5 \pm 0.6) \times 10^{-8}$
4	83	677	$(1.27 \pm 0.02) \times 10^5$	$(7.3 \pm 1.0) \times 10^{-8}$
5	56	697	$(1.29 \pm 0.01) \times 10^5$	$(4.1 \pm 0.4) \times 10^{-8}$
6/**6a**	65	653	$\sim 1.0 \times 10^5$	$(1.0–1.5) \times 10^{-7}$ [b]
7	88	603	$(1.08 \pm 0.02) \times 10^5$	$(3.7 \pm 1.1) \times 10^{-8}$
8	88	625	$(1.18 \pm 0.01) \times 10^5$	$(4.3 \pm 0.8) \times 10^{-8}$

[a] Error limits are standard deviations based on a minimum of 4 films/measurement. [b] Assumes ε of ~1.0×10^5 for both **6** and **6a** in a 60:40 mixture of **6** to **6a**.

Dye **6** (Chart 1) was prepared from **11** and **12** by heating at 105 °C in AcOH for 5 min as an equal volume of Ac_2O was added slowly and then for an additional 25 min. Dye **6** was isolated as a 60:40 mixture of **6** and its zwitterionic form **6a**, with an absorbance maximum (λ_{max}) for the mixture of 653 nm, in 65% combined yield. Attempts to isolate the zwitterionic form **6a** were unsuccessful, as were attempts to protonate and isolate only **6**. Consequently, other phosphonic acid derivatives were not prepared for study.

Values of λ_{max} (603−697 nm) for the electronic absorbance spectra of **1**−**8** in CH_2Cl_2 solution are compiled in Table 1 and fall in the window where the solar spectrum is most intense. In the higher dielectric solvent CH_3CN, blue shifts of 3−7 nm are observed relative to CH_2Cl_2. Normalized absorbance spectra for **1**−**8** in both solvents are shown in Figure S1 of the Supporting Information. Values of the molar extinction coefficient (ε) vary between 1.08 × 10^5 and 1.31 × 10^5 M^{-1} cm^{-1} (Table 1). Increasing the size of the chalcogen atom gives a red-shift in λ_{max}, which has been previously reported for chalcogenopyrylium[18,20] and chalcogenoxanthylium dyes[39] as well as in π-excessive heterocyclic systems such as the polychalcogenophenes.[40] Values of ε for dyes **1** and **3**−**5**, which vary in structure only in the heteroatoms, have no significant differences among them. Dye **2**, where Se has been substituted for S, has a lower value of ε that is significantly different from the other dyes **1** and **3**−**5**. Lower values of ε with Se substitution have been observed in other chalcogen-containing systems.[41] Oscillator strengths for dyes **1**−**8** fall in the range 0.57−0.62 and are not different from one another in a statistically significant way.

Films of TiO_2 were functionalized by immersion in ∼2 mM CH_2Cl_2 solutions of **1**−**8**. Amounts of the adsorbed dyes per projected surface area (surface coverages, Γ_0, in mol cm^{-2}) were determined by quantifying the concentration of dye in adsorption solutions before and after exposure to TiO_2 films.[42] Values of Γ_0 are compiled in Table 1 for **1**−**8** and vary from 3.7 × 10^{-8} to 7.3 × 10^{-8} mol cm^{-2} for the diethyl phosphonates. The phosphonic acid derivatives **6**/**6a** gave somewhat greater coverage [(1.0−1.5) × 10^{-7} mol cm^{-2}] than the phosphonate derivatives. Exact values cannot be ascertained because of the **6**/**6a** mixture.

Figure 1 shows absorbance spectra of dyes **1**, **7**, and **8** on TiO_2 films compared to absorbance spectra in CH_2Cl_2. On TiO_2, **1** has developed a higher energy band relative to the solution spectrum, consistent with the formation of an H-aggregate on the surface. Dyes **2**−**6** show similar formation of H-aggregates (Figure S2, Supporting Information). Dye **7** with bulky *tert*-butyl substituents has more limited H-aggregation, presumably because of the steric hindrance of face-to-face interactions, and the absorbance spectra on TiO_2 and in CH_2Cl_2 are similar. Dye **8**, with a bulky 2,6-dimethylphenyl substituent, also limits face-to-face interactions. Some H-aggregation is observed with **8** on TiO_2, but much less than observed with **1**. By varying the concentration of the adsorbing solution, the extent of H-aggregation by **1**, **7** and **8** upon adsorption to TiO_2 can be varied (Figure S3, Supporting Information).

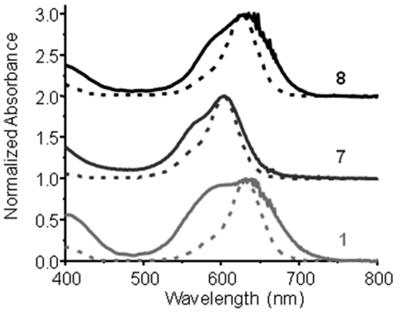


Figure 1. Normalized UV−visible absorption spectra for dyes **1**, **7** (offset 1 au), and **8** (offset 2 au) in CH_2Cl_2 (dashed lines) and on TiO_2 (solid lines).

Nanocrystalline TiO_2 films on FTO-on-glass electrodes (TiO_2/FTO) were functionalized with **1**−**8**. Short-circuit photocurrent action spectra [incident photon to current efficiencies (IPCE) vs wavelength] were acquired to evaluate the influence of dye structure on the photoelectrochemical performance of DSSCs. Overlaid absorptance and photocurrent action spectra are shown in Figure 2 for dyes **1**, **7**, and **8** and in Figure S4 (Supporting Information) for dyes **2**−**6**. (Absorptance equals the fraction of photons absorbed, or one minus the transmittance.) For dyes **1**−**4**, absorptance was ≥0.90 from 570−575 nm through 675−725 nm (95−150 nm-wide regions). For dyes **7** and **8** with reduced aggregation, absorptance was ≥0.90 over a smaller region: 590−625 nm (35-nm wide) for **7** and 588−670 nm (82-nm wide) for **8**. Dye

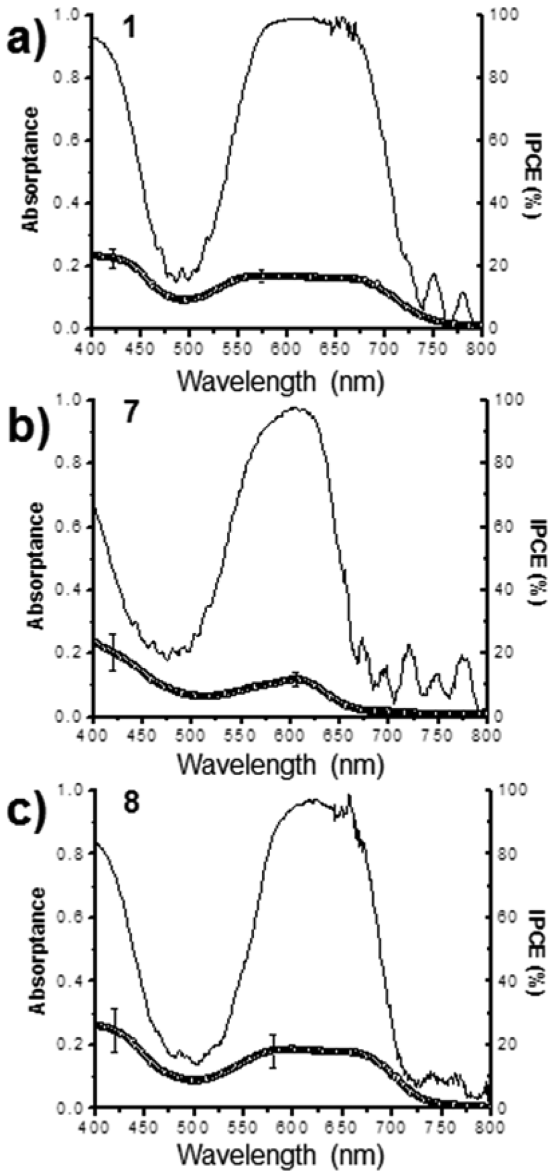


Figure 2. Absorptance (*y*-axis left) and IPCE (*y*-axis right) spectra for dyes (a) **1**, (b) **7**, and (c) **8**. Error bars are ±1 standard deviation based on a minimum of 3 runs.

5 displayed absorptance ≥0.90 between 600 and 750 nm, and dye **6**, between 540 and 755 nm (215 nm).

White-light photocurrent−photovoltage (J−V) data were also acquired. Values of open circuit voltage (V_{oc}), short-circuit photocurrent density (J_{sc}), fill factor (FF), and global energy-conversion efficiencies (η) were low (η < 0.1% for all films) (Table S1, Supporting Information).

The correspondence between absorptance and IPCE spectra for dyes **1**−**8** indicates that **1**−**8** sensitized TiO_2 through excited-state electron injection. The impact of aggregation on IPCE values was determined by examining the window for each dye where values of IPCE are ≥10%. For **1**−**6**, this region is a plateau where IPCE values are comparable over both the aggregate region and the unaggregated dye. For **1**, IPCE was ≥10% between 475 and 710 nm; for **2**, between 500 and 725 nm; for **3**, between 500 and 735 nm; and for **4**, between 550 and 725 nm (Figure S4, Supporting Information). Dye **5** displayed IPCE values ≥10% only over the 400−450-nm range, but had IPCE ≥ 5% from 400 to 775 nm (Figure S4, Supporting Information). Dye **6**, in contrast, displayed values of IPCE ≥10% over the 400−750-nm window (Figure S4, Supporting Information). All six of these dyes formed an H-aggregate. Dye **7**, in contrast, displayed IPCE values ≥10% only over the 570−625-nm range (Figure 2), consistent with little H-aggregation on the film. Dye **8** displayed IPCE values ≥10% over the 525−700-nm range (Figure 2), which includes some aggregate formation.

We have devised a strategy to prepare chalcogenopyrylium monomethine dyes bearing a phosphonate or phosphonic acid group, which can function as a linker to semiconductor surfaces. The chalcogenopyrylium monomethine dyes prepared by this strategy efficiently harvest visible and NIR light. Moreover, like chalcogenorhodamine dyes that we have previously evaluated,[13−16] dyes **1**−**6** show improved light-harvesting efficiency and higher values of IPCE upon formation of H-aggregates. In contrast, **7** and **8**, which are less prone to form aggregates, have reduced light-harvesting efficiency. Aggregates of other dyes have been shown to have poorer IPCEs than their monomeric counterparts,[43] but orientation of the aggregates relative to the semiconductor surface was not well-defined.

The chalcogenopyrylium compounds can accommodate great structural diversity and the results presented here suggest that additional chalcogenopyrylium dyes should be designed and evaluated in DSSCs for enhanced photoelectrochemical performance. Similar chemistry can be used to facilitate incorporation of the phosphonate/phosphonic acid linker on compounds with absorbance even further into the infrared.

■ EXPERIMENTAL SECTION

1-(4-Bromophenyl)-5-phenylpenta-1,4-diyn-3-ol (21). EtMgBr (3.0 M, 11.2 mL, 34 mmol) was added dropwise to a tetrahydrofuran (THF, 60 mL) solution of phenylacetylene (3.94 mL, 35.9 mmol) at 0 °C. The resulting solution was stirred for 0.5 h at 0 °C and then for an additional 0.5 h at ambient temperature. The solution was cooled to −78 °C, and **20** (4.95 g, 23.7 mmol), dissolved in THF (30 mL), was added via cannula. After 1 h at −78 °C, the reaction mixture was stirred for an additional 2 h at ambient temperature. The reaction was quenched with 10 mL of MeOH and then was poured into saturated NH_4Cl (50 mL). Products were extracted with CH_2Cl_2 (3 × 75 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated. The resulting oil was purified via chromatography on SiO_2 with CH_2Cl_2 as eluent (R_f 0.62) to yield 6.15 g (84%) of **21** as a white solid: mp 99.5−100.5 °C; IR (KBr) 3320 (OH), 2232 ($C\equiv C$) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50−7.46 (m, 4 H), 7.36−7.32 (m, 5 H), 5.57 (d, 1H, J = 12 Hz), 2.54 (d, 1 H, J = 11.5 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 133.3, 131.9, 131.6, 128.9, 128.3, 132.2, 121.8, 120.9, 87.1, 85.68, 84.8, 83.5, 53.2; HRMS [ESI, high-resolution, double focusing magnetic sector (HRDFMagSec)] m/z 309.9958 (calcd for $C_{17}H_{11}O^{79}Br^+$ 309.9993).

1-(4-Bromophenyl)-5-phenylpenta-1,4-diyn-3-one (19). 1-(4-Bromophenyl)-5-phenylpenta-1,4-diyn-3-ol (**20**, 2.88 g, 9.26 mmol) and MnO_2 (8.05 g, 92.6 mmol) in CH_2Cl_2 (30 mL) were stirred for 1 h at ambient temperature. The mixture was filtered through Celite, and the filtrate was concentrated to give 2.66 g (93%) of **19** as a pale yellow solid that was used without further purification: mp 105.5−106.5 °C; IR (KBr) 2207 ($C\equiv C$), 1615 ($C=O$) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (AA′BB′, 2 H, J = 8 Hz), 7.57 (AA′BB′, 2H, J = 8 Hz), 7.52−7.49 (m, 3 H), 7.42 (t, 2 H, J = 8.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5, 134.5, 133.3, 132.0, 131.3, 128.7, 126.1, 119.3, 118.3, 92.0, 90.0, 89.3; HRMS (ESI, HRDFMagSec) m/z 307.9836 (calcd for $C_{17}H_9O^{79}Br^+$ 307.9837).

2-(4-Bromophenyl)-6-phenyl-4*H*-thiopyran-4-one (17). Sulfur (0.171 g, 5.34 mmol), $NaBH_4$ (0.202 g, 5.34 mmol) and 0.25 M NaOEt in EtOH (40.0 mL) were heated at reflux for 4 h. In another flask, **21** (1.50 g, 4.85 mmol) was dissolved in THF (10.0 mL) and then added to 0.25 M NaOEt in EtOH (40 mL). After stirring for 10 min, this mixture was then added to the S/$NaBH_4$ mixture. This resulting mixture was heated at reflux for 20 min and poured into 100 mL of water, and products were extracted with EtOAc (3 × 50 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated. The resulting solid was purified via chromatography on SiO_2 eluted with 20% EtOAc/CH_2Cl_2 (R_f 0.50) to yield 0.97 g (58%) of **17** as an off-white solid: mp 179.0−180.0 °C; IR (KBr) 1625 cm^{-1} ($C=O$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65−7.63 (m, 4 H), 7.53−7.51 (m, 5 H), 7.23 (s, 1 H) 7.20 (s, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 182.1, 153.0, 151.8, 135.9, 134.9, 132.6, 130.8, 129.4, 128.3, 127.2, 127.1, 126.9, 125.3; HRMS (ESI, HRDFMagSec) m/z 342.9777 (calcd for $C_{17}H_{11}O_1{}^{79}BrS + H^+$ 342.9787).

2-(4-Bromophenyl)-6-phenyl-4*H*-selenopyran-4-one (18). Selenium (0.215 g, 2.72 mmol), $NaBH_4$ (85.6 mg, 2.72 mmol) and 0.25 M NaOEt in EtOH (30 mL) were heated at reflux for 1.5 h. In another flask, **21** (0.700 g, 2.26 mmol) was dissolved in THF (5.0 mL), added to 0.25 M NaOEt in EtOH (20 mL), and stirred for 10 min before addition to the Se/$NaBH_4$ mixture. The resulting mixture was heated at reflux for 20 min and poured into 100 mL of water, and products were extracted with EtOAc (4 × 50 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated. The resulting solid was purified via chromatography on SiO_2 eluted with 20% EtOAc/CH_2Cl_2 (R_f 0.50) to yield 0.43 (49%) of **18** as a white solid: mp 165.5−167.0 °C; IR (KBr) 1605 cm^{-1} ($C=O$); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.66−7.62 (m, 4 H), 7.52−7.50 (m, 5 H), 7.24 (s, 1 H), 7.22 (s, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 184.2, 155.3, 153.9, 137.5, 136.6, 132.6, 131.0, 129.4, 128.3, 128.3, 128.1; HRMS (ESI, HRDFMagSec) m/z 391.9148 (calcd for $C_{17}H_{11}O_1{}^{79}Br^{80}Se + H^+$ 391.9138).

Diethyl [4-(4-oxo-6-phenyl-4*H*-thiopyran-2-yl)phenyl]-phosphonate (9). Triethylamine (0.102 mL, 0.732 mmol) was added to palladium acetate (4.1 mg, 0.018 mmol), 1,1′-bis-(diphenylphosphino)ferrocene (20.2 mg, 0.0364 mmol), KOAc (7.1 mg, 0.072 mmol) in THF (5.0 mL). The resulting solution was heated at reflux for 15 min prior to the addition of diethyl phosphite (93 μL, 0.73 mmol) and **17** (0.250 g, 0.728 mmol). The resulting mixture was heated at reflux for 24 h and then diluted with CH_2Cl_2 (10 mL) and water (10 mL). The organic layer was dried over $MgSO_4$ and concentrated. The resulting oil was purified via chromatography on SiO2 first using 40% EtOAc/CH_2Cl_2 and then 10% MeOH/EtOAc as eluent (R_f 0.58) to yield 0.225g (77%) of **9** as an off-white solid: mp 128.5−129.5 °C; IR (KBr) 1613 cm^{-1} ($C=O$); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.92 (dd, 2H, J = 12.5, 7.5 Hz), 7.78 (dd, 2H, J = 8.0, 3.5 Hz), 7.70−7.68 (m, 2H), 7.55−7.53 (m, 3H), 7.21(s, 1H), 7.20 (s, 1H), 4.13 (m, 4H), 1.33 (t, 6H, J = 7 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 182.0, 153.2, 151.8, 139.7, 135.8, 132.7, 132.5, 132.6, 132.5, 130.9, 130.0, 129.4, 128.0, 127.2, 127.0, 126.9, 126.8, 62.4 (d, $^2J_{CP}$ = 4.7 Hz), 16.3 (d, $^3J_{CP}$ = 5.7 Hz); HRMS (ESI, HRDFMagSec) *m/z* 401.0971 (calcd for $C_{21}H_{21}O_4PS + H^+$ 401.0976).

Diethyl [4-(4-oxo-6-phenyl-4*H*-selenopyran-2yl)phenyl]-phosphonate (10). Palladium acetate (3.6 mg, 0.016 mmol), 1,1′-bis(diphenylphosphino)ferrocene (17.8 mg, 0.0321 mmol), KOAc (6.3 mg, 0.064 mmol), THF (5 mL), Et_3N (98 μL, 0.70 mmol), diethyl phosphite (82 μL, 0.64 mmol) and **18** (0.250 g, 0.641 mmol) were treated as described for the preparation of **9**. The isolated oil was purified by chromatography on SiO_2 eluted first with 40% EtOAc/CH_2Cl_2 and then with 10% MeOH/EtOAc (R_f 0.64) to yield 0.229 g (80%) of **10** as an off-white solid: mp 99.5−100.5 °C; IR (KBr) 1608 cm^{-1} (C=O); ^{1}H NMR (500 MHz CD_2Cl_2) δ 7.94 (dd, 2 H, *J* = 13.0, 8.0 Hz) 7.69 (dd, 2 H, *J* = 8.5, 4.0 Hz) 7.61−7.59 (m, 2 H) 7.52−7.51 (m, 3 H), 4.18 (m, 4 H), 1.36 (t, 6 H, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.0, 155.4, 153.8, 141.2, 137.3, 132.7, 132.6, 131.6, 130.7, 130.1, 129.3, 129.0, 128.1, 126.9, 126.7, 126.7, 62.3 (d, $^2J_{CP}$ = 5.8 Hz), 16.2 (d, $^3J_{CP}$ = 6.6 Hz); HRMS (ESI, HRDFMagSec) *m/z* 449.0415 (calcd for $C_{21}H_{21}O_4P^{80}Se + H^+$ 449.0421).

4-(4-Oxo-6-phenyl-4*H*-selenopyran-2-yl)phenylphosphonic acid (11). Trimethylsilyl chloride (0.142 mL, 1.12 mmol) was added dropwise to NaI (0.168 g, 1.12 mmol) in anhydrous CH_3CN (2.0 mL) and anhydrous CH_2Cl_2 (2.0 mL). After 0.5 h of stirring, selenopyranone **10** (0.100 g, 0.224 mmol) was added, and the resulting mixture was stirred overnight. The dark red mixture was quenched with MeOH (2.0 mL) and poured into 1 M HCl (50 mL). Potassium hydroxide pellets were added until the solution became a light brown color. The mixture was washed with EtOAc (2 × 25 mL). The pH of the aqueous solution was lowered to approximately 1 with concentrated HCl, and products were extracted with EtOAc (3 × 25 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The product was precipitated from EtOAc with hexanes to yield 61.2 mg (70%) of **11** as a light brown powder: mp 220−222 °C; ^{1}H NMR (500 MHz, $(CD_3)_2S{=}O$) δ 11.38 (s, 2 H), 7.81−7.80 (m, 4 H), 7.74 (dd, 2 H, *J* = 1.5, 7.5 Hz), 7.56 (m, 3 H), 7.39 (s, 1 H), 7.29 (s, 1 H); ^{13}C NMR (75 MHz, $(CD_3)_2S{=}O$) δ 183.0, 154.1, 153.2, 139.0, 137.9, 136.8, 135.5, 131.6, 131.5, 131.0, 129.6, 128.0, 127.4, 126.7, 126.7, 126.5. HRMS (EI, HRDFMagSec) *m/z* 392.9805 (calcd for $C_{17}H_{13}O_4P^{80}Se + H^+$ 392.9795).

General Procedure for the Preparation of Monomethine Dyes 1−8. 4-((2-(4-(Diethoxyphosphoryl)phenyl)-6-phenyl-4*H*-thiopyran-4ylidene)methyl)-2,6-diphenylthiopyrylium hexafluorophosphate (1). Thiopyranone **9** (50.0 mg, 0.125 mmol), 4-methyl-2,6-diphenylthiopyrylium hexafluorophosphate (**12**, 46.4 mg, 0.114 mmol), and Ac_2O (0.500 mL) were heated at 105 °C for 15 min. The solution was diluted with Et_2O (2.5 mL), and the resulting solid was isolated by filtration. The solid was recrystallized from CH_3CN/ether to yield 71.8 mg (89%) of **1** as a metallic dark blue solid: mp 124.0−125.5 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.14−7.98 (m, 6 H), 7.86 (dd, 2 H, *J* = 8.0, 3.5 Hz), 7.79 (t, 6 H, *J* = 7.0 Hz), 7.68−7.61 (m, 9 H), 6.85 (br s, 1 H) 4.15 (m, 4 H), 1.35 (t, 6 H, *J* = 7.0 Hz); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 157.4, 155.9 (br), 154.5, 153.9 (br), 153.2, 139.1, 135.7, 135.5, 134.2, 133.3, 133.2, 132.6, 132.5, 131.8, 130.3,130.2, 127.6, 127.5, 127.4, 126.8, 123.6, 62.9 (d, $^2J_{CP}$ = 5.7 Hz), 16.5 (d, $^3J_{CP}$ = 6.9 Hz); HRMS (EI, HRDFMagSec) *m/z* 645.1694 (calcd for $C_{39}H_{34}O_3PS_2^+$ 645.1692). Anal. Calcd for $C_{39}H_{34}O_3PS_2{\cdot}PF_6$: C, 59.24; H, 4.33. Found: C, 59.11; H, 4.47.

4-((2-(4-(Diethoxyphosphoryl)phenyl)-6-phenyl-4*H*-thiopyran-4-ylidene)methyl)-2,6-diphenylselenopyrylium hexafluorophosphate (2). Thiopyranone **9** (50.0 mg, 0.125 mmol), 4-methyl-2,6-diphenylselenopyrylium hexafluorophosphate (**13**, 51.7 mg, 0.114 mmol), and Ac_2O (1.0 mL) were heated at 105 °C for 2.0 min. Workup as described for **1** gave 75.6 mg (79%) of **2** as a metallic dark blue solid: mp 142−144 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.16−8.10 (m, 4 H), 8.00 (dd, 2 H, *J* = 8.0, 12.5 Hz), 7.86 (dd, 2 H, *J* = 3.5, 8 Hz), 7.79 (d, 2 H, *J* = 7.5 Hz), 7.74 (d, 4 H, *J* = 7.5 Hz), 7.68−7.61 (m, 9 H), 6.95 (br s, 1 H), 4.15 (m, 4 H), 1.35 (t, 6 H, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 161.7, 156.8, 154.7, 154.4, 153.8, 153.6, 138.9, 137.6, 135.5, 133.9, 133.3, 133.2, 132.7, 132.3, 130.3, 129.2, 128.4, 127.5, 127.5, 127.4, 126.7, 124.1, 62.9 (d, $^2J_{CP}$ = 5.7 Hz), 16.5 (d, $^3J_{CP}$ = 6.8 Hz); HRMS (EI, HRDFMagSec) *m/z* 693.1119 (calcd for $C_{39}H_{34}O_3PS^{80}Se^+$ 693.1126). Anal. Calcd for $C_{39}H_{34}O_3PSSe{\cdot}PF_6$: C, 55.92; H, 4.09. Found: C, 55.85; H, 4.42.

4-((2-(4-(Diethoxyphosphoryl)phenyl)-6-phenyl-4*H*-selenopyran-4-ylidene)methyl)-2,6-diphenylthiopyrylium hexafluorophosphate (3). Selenopyran-4-one **10** (50.0 mg, 0.112 mmol), 4-methyl-2,6-diphenylthiopyrylium hexafluorophosphate (**12**, 41.5 mg, 0.102 mmol), and Ac_2O (0.500 mL) were heated at 105 °C for 15 min. Workup as described for **1** gave 79.5 mg (93%) of **3** as a metallic dark blue solid: mp 124.5−126 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.20−7.96 (m, 6 H), 7.80 (d, 6 H, *J* = 7.5 Hz), 7.73- 7.59 (m, 11 H), 6.96 (br s, 1 H), 4.15 (m, 4 H), 1.35 (t, 6 H, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 158.2, 154.7, 153.3, 141.0, 137.6, 135.3, 133.25, 133.17, 132.7, 132.2, 131.7, 130.3, 130.2, 127.54, 127.42, 127.36, 127.3, 126.7, 62.8 (d, $^2J_{CP}$ = 5.8 Hz), 16.5 (d, $^3J_{CP}$ = 6.6 Hz); HRMS (EI, HRDFMagSec) *m/z* 693.1134 (calcd for $C_{39}H_{34}O_3PS^{80}Se^+$ 693.1126). Anal. Calcd for $C_{39}H_{34}O_3PSSe{\cdot}PF_6$: C, 55.92; H, 4.09. Found: C, 55.85; H, 4.15.

4-((2-(4-(Diethoxyphosphoryl)phenyl)-6-phenyl-4*H*-selenopyran-4-ylidene)methyl)-2,6-diphenylselenopyrylium hexafluorophosphate (4). Selenopyran-4-one **10** (50.0 mg, 0.112 mmol), **13** (46.3 mg, 0.102 mmol), and Ac_2O (1.0 mL) were at 105 °C for 2.0 min. Workup as described for **1** gave 74.9 mg (83%) of **4** as a metallic dark blue solid: mp 133−135 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.20- 8.07 (m, 4 H) 7.98 (dd, 2 H, *J* = 12.5, 8.0 Hz), 7.81 (dd, 2 H, *J* = 7.5, 3.0 Hz), 7.75−7.73 (m, 6 H), 7.69−7.60 (m, 9 H), 6.97 (s, 1 H), 4.15 (m, 4 H), 1.35 (t, 6 H, *J* = 6.5 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 163.2, 160.9, 158.3, 155.1, 153.7 141.2, 137.6, 137.4, 133.4, 133.3, 133.0, 132.6, 132.4, 131.1, 130.4, 130.3, 129.7, 128.1, 127.6, 127.5, 127.4, 62.8 (d, $^2J_{CP}$ = 5.6 Hz), 16.5 (d, $^3J_{CP}$ = 6.6 Hz); HRMS (EI, HRDFMagSec) *m/z* 741.0552 (calcd for $C_{39}H_{34}O_3P^{80}Se_2^+$ 741.0571). Anal. Calcd for $C_{39}H_{34}O_3PSe_2{\cdot}PF_6{\cdot}H_2O$:[44] C, 51.90; H, 4.02. Found: C, 51.85; H, 3.80.

4-((2-(4-(Diethoxyphosphoryl)phenyl)-6-phenyl-4*H*-thiopyran-4-ylidene)methyl)-2,6-diphenyltelluropyrylium hexafluorophosphate (5). Thiopyran-4-one **9** (50.0 mg, 0.112 mmol), 4-methyl-2,6-diphenyltelluropyrylium hexafluorophosphate (**14**, 46.3 mg, 0.102 mmol), and Ac_2O (1.0 mL) were heated at 105 °C for 1.0 min. The solution was then diluted with diethyl ether, and the resulting solid was isolated by filtration. Workup as described for **1** was followed by purification by column chromatography eluted first with 10% EtOAc/CH_2Cl_2 and then with 30% EtOAc/CH_2Cl_2 to yield 56.4 mg (56%) of **5** as a green solid: mp 144.5−147.5 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.17 (s, 2 H), 8.13 (s, 1 H), 8.07 (s, 1 H), 7.99 (dd, 2 H, *J* = 8.5, 12.5 Hz), 7.85 (dd, 2 H, *J* = 3.5, 8.5 Hz), 7.76 (d, 2 H, *J* = 8.5 Hz), 7.68−7.57 (m, 13 H), 6.97 (s, 1H), 4.15 (m, 4 H), 1.35 (t, 6 H, *J* = 7.0 Hz); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 160.9, 156.4, 156.1, 154.3, 152.6, 141.0, 138.7, 138.7, 135.3, 133.9, 133.1, 132.9, 132.3, 131.7, 131.4, 130.1, 130.0, 128.7, 127.2, 127.1, 127.0, 62.7 (d, $^2J_{CP}$ = 5.8 Hz), 16.2 (d, $^3J_{CP}$ = 5.7 Hz); HRMS (EI, HRDFMagSec) *m/z* 743.1025 (calcd for $C_{39}H_{34}O_3PS^{130}Te^+$ 743.1023). Anal. Calcd for $C_{39}H_{34}O_3PSTe{\cdot}PF_6{\cdot}H_2O$:[44] C, 51.80; H, 4.01. Found: C, 51.51; H, 3.81.

2,6-Diphenyl-4-((2-phenyl-6-(4-phosphonophenyl)-4*H*-selenopyran-4-ylidene)methyl)thiopyrylium hexafluorophosphate (6). Acetic anhydride (3.0 mL) was slowly added over 5 min to **11** (70.0 mg, 0.203 mmol) and **12** (83.0 mg, 0.203 mmol) in AcOH (3.0 mL) at 105 °C. The resulting mixture was heated for an additional 25 min at 105 °C. Workup as described for **1** gave 89.8 mg (65%) of a 60:40 mixture of **6** and its zwitterionic form as a dark blue solid: mp >260 °C; ^{1}H NMR (500 MHz, 2:1 CD_3OD:CD_2Cl_2) δ 8.24 (s, 2 H), 8.10 (s, 2 H), 7.95 (dd, 2 H, *J* = 8.0, 13.0 Hz), 7.79 (d, 6 H, *J* = 7.5 Hz), 7.71 (d, 2 H, *J* = 7 Hz), 7.64−7.52 (m, 9 H) 6.91 (s, 1 H); HRMS (EI, HRDFMagSec) *m/z* 637.0521 (calcd for $C_{35}H_{26}O_3PS^{80}Se^+$ 637.0500). Anal. Calcd for $[C_{35}H_{26}O_3PSSe{\cdot}PF_6]_{0.60}{\cdot}[C_{35}H_{25}O_3PSSe]_{0.40}$: C, 58.13; H, 3.57. Found: C, 58.22; H. 3.55.

2,6-Di-*tert*-butyl-4-((2-(4-(diethoxyphosphorylphenyl)-6-phenyl-4*H*-thiopyran-4-ylidene)methyl)thiopyrylium hexafluorophosphate (7). Thiopyran-4-one **9** (0.100 g, 0.250 mmol), 2,6-di-*tert*-butyl-4-methylthiopyrylium hexafluorophosphate (**15**, 83.6 mg, 0.227 mmol), and Ac_2O (1.0 mL) were heated at 105 °C for 3 h.

Workup as described for **1** gave 0.151 g (88%) of **7** as a purple solid: mp 211.5−213.5 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.98 (dd, 2 H, J = 8.5, 12.5 Hz), 7.92 (s, 2 H), 7.83 (m, 2 H), 7.74 (d, 2 H, J = 7.5 Hz), 7.63−7.58 (m, 3 H), 6.66 (s, 1 H), 4.14 (m, 4 H), 1.52 (s, 18 H), 1.34 (t, 6 H, J = 7.0 Hz); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 173.8, 155.8, 151.7, 133.27, 133.19, 132.1, 130.1, 127.3, 125.7, 122.5, 122.4, 62.9 (d, $^2J_{CP}$ = 5.8 Hz), 40.7, 31.1, 16.5 (d, $^3J_{CP}$ = 5.6 Hz); HRMS (EI, HRDFMagSec) m/z 605.2315 (calcd for $C_{35}H_{42}O_3PS_2^+$ 605.2307). Anal. Calcd for $C_{35}H_{42}O_3PS_2\cdot PF_6$: C, 55.99; H, 5.64. Found: 55.91; H, 5.48.

4-((2-(4-(Diethoxyphosphoryl)phenyl)-6-phenyl-4*H*-thiopyran-4-ylidene)methyl)-2-(2,6-dimethylphenyl)-6-phenylthiopyrylium hexafluorophosphate (8). Thiopyran-4-one **9** (0.100 g, 0.250 mmol), 2-(2,6-dimethylphenyl)-4-methyl-6-phenylthiopyrylium hexafluorophosphate (**16**, 99.1 mg, 0.227 mmol), and Ac_2O (0.50 mL) were heated at 105 °C for 15 min. Workup as described for **1** gave 81.7 mg (88%) of **8** as a metallic dark blue solid: mp 133.5−135.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.231 (s, 1 H), 8.09−8.08 (m, 2 H), 7.98 (dd, 2 H, J = 13.0, 8.0 Hz), 7.89 (dd, 2 H, J = 8, 3.5 Hz), 7.78 (d, 2 H, J = 7.0 Hz), 7.71−7.69 (m, 3 H), 7.61−7.53 (m, 6 H), 7.33 (t, 1 H, J = 7.5 Hz), 7.21 (d, 2 H, J = 7.5 Hz), 7.10 (s, 1 H), 4.23−4.09 (m, 4 H), 2.31 (s, 6 H), 1.36 (t, 6 H, J = 7.0 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 159.0, 157.5, 156.7, 154.7, 154.5, 153.9,139.0, 136.9, 135.7, 135.5, 134.3, 134.1, 133.4, 133.3, 132.7, 132.6, 132.2, 131.2, 130.9, 130.3, 130.3, 128.7, 127.6, 127.53, 127.47, 123.3, 62.9 (d, $^2J_{CP}$ = 5.4 Hz), 20.5, 16.5 (d, $^3J_{CP}$ = 6.1 Hz) ; HRMS (EI, HRDFMagSec) m/z 673.2012 (calcd for $C_{41}H_{38}O_3PS_2^+$ 673.1994). Anal. Calcd for $C_{41}H_{38}O_3PS_2\cdot PF_6\cdot(H_2O)_{0.5}$:[44] C, 59.49; H, 4.75. Found: C, 59.47; H, 4.78.

Preparation of Sensitized TiO_2 Electrodes. Nanocrystalline TiO_2 films were deposited onto glass microscope slides or fluorine-doped tin oxide (FTO)-coated glass (12−14 Ω/square), as described previously.[42] TiO_2 films were (4.1 ± 0.9) μm thick and consisted of anatase TiO_2 particles with average diameters of (36 ± 6) nm. For the FTO-coated glass electrodes, a dense TiO_2 blocking layer was added by spray pyrolysis before spreading the TiO_2. TiO_2 films were functionalized by immersion in concentrated (1−2 mM) solutions of the dyes in CH_2Cl_2 for at least 12 h. The functionalized films were dipped in CH_2Cl_2 or CH_3CN to remove nonadsorbed dye.

Surface Coverages of Dyes on TiO_2. Amounts of the adsorbed dyes per projected surface area, herein referred to as surface coverages, were determined by quantifying the concentration of dye in adsorption solutions before and after exposure to TiO_2 films. Values of λ_{max} of the dyes in CH_2Cl_2 (Table 1) were used to quantify concentrations of dyes and therefore the surface coverages.

Photoelectrochemistry. Short-circuit photocurrent action spectra and $J-V$ data were obtained as described previously.[13,45] A custom 500-μL Teflon cell housed the sensitized-FTO/TiO_2 working electrode and a Pt mesh counter electrode. The electrolyte was 0.05 M I_2, 0.5 M LiI, and 0.20 M HCl in CH_3CN. Higher photocurrents were measured when protons were added to the electrolyte, consistent with previous reports. TiO_2 films functionalized with N3 dye were characterized as controls. The electrolyte for FTO/TiO_2/N3 working electrodes consisted of 0.1 M LiI, 0.05 M I_2, 0.1 M guanidinium thiocyanate, 0.5 M 4tBP, and 0.6 M PMII in CH_3CN. UV−vis absorption spectra of sensitized-FTO/TiO_2 working electrodes were acquired before and after the acquisition of photoelectrochemical data. In a typical photoelectrochemical experiment, we acquired six short-circuit photocurrent action spectra and three $J-V$ data sets over the course of approximately 15 min for a given dye-functionalized TiO_2 electrode. Initial and final values of IPCE differed by 5−10% over the course of these experiments.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectral data for **1**−**11** and **17**−**23**, white-light photocurrent−photovoltage ($J-V$) data, normalized UV−visible absorption spectra for **2**−**6** in CH_2Cl_2 solution and on TiO_2 films, data for the extent of aggregation as a function of the concentration of adsorbing solution in dichloromethane, and absorptance and IPCE data for dyes **2**−**6**. These materials are available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: dwatson3@buffalo.edu; mdetty@buffalo.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the National Science Foundation (CHE-1151379) for support of this work. K.R.M. acknowledges the financial support provided by the Silbert Fellowship in Chemistry, Department of Chemistry, University at Buffalo.

■ REFERENCES

(1) Grätzel, M. *Acc. Chem. Res.* **2009**, *42*, 1788−1798.

(2) Ardo, S.; Meyer, G. J. *Chem. Soc. Rev.* **2009**, *38*, 115−164.

(3) Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. *Chem. Rev.* **2010**, *110*, 6595−6663.

(4) Ooyama, Y.; Harima, Y. *Eur. J. Org. Chem.* **2009**, 2903−2934.

(5) Hodes, G. *J. Phys. Chem. C* **2008**, *112*, 17778−17787.

(6) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737−740.

(7) Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Müller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382−6390.

(8) Nazeeruddin, M. K.; Péchy, P.; Renouard, T.; Zakeeruddin, S. M.; Humphry-Baker, R.; Comte, P.; Liska, P.; Cevey, L.; Costa, E.; Shklover, V.; Spiccia, L.; Deacon, G. B.; Bignozzi, C.; Grätzel, M. *J. Am. Chem. Soc.* **2001**, *123*, 1613−1624.

(9) Nazeeruddin, M. K.; Humphry-Baker, R.; Liska, P.; Grätzel, M. *J. Phys. Chem. B* **2003**, *107*, 8981−8987.

(10) Yella, A.; Lee, H.-W.; Tsao, H. N.; Yi, C.; Chandiran, A. K.; Nazeeruddin, M. K.; Diau, E.W.-G.; Yeh, C.-Y.; Zakeeruddin, S. M.; Grätzel, M. *Science* **2011**, *334*, 629−634.

(11) Hamann, T. W.; Jensen, R. A.; Martinson, A. B. F.; Van Ryswyk, H.; Hupp, J. T. *Energy Environ. Sci.* **2008**, *1*, 66−78.

(12) Hardin, B. E.; Snaith, H. J.; McGehee, M. D. *Nat. Photonics* **2012**, *6*, 162−169.

(13) Mann, J. R.; Gannon, M. K.; Fitzgibbons, T. C.; Detty, M. R.; Watson, D. F. *J. Phys. Chem. C* **2008**, *112*, 13057−13061.

(14) Mulhern, K. R.; Detty, M. R.; Watson, D. F. *J. Phys. Chem. C* **2011**, *115*, 6010−6018.

(15) Mulhern, K. R.; Orchard, A.; Watson, D. F.; Detty, M. R. *Langmuir* **2012**, *28*, 7071−7082.

(16) Ehret, A.; Stuhl, L.; Spitler, M. T. *J. Phys. Chem. B* **2001**, *105*, 9960−9965.

(17) Kawasaki, M.; Aoyama, S. *Chem. Commun.* **2004**, 988−989.

(18) Detty, M. R.; McKelvey, J. M.; Luss, H. R. *Organometallics* **1988**, *7*, 1131−1147.

(19) Reynolds, G. A.; Drexhage, K. H. *J. Org. Chem.* **1977**, *42*, 885−888.

(20) Detty, M. R.; Murray, B. J. *J. Org. Chem.* **1982**, *47*, 5235−5259.

(21) *Topics in Applied Chemistry: Infrared Absorbing Dyes*; Matsuoka, M., Ed.; Plenum Press: New York, 1990.

(22) Detty, M. R.; Murray, B. J.; Perlstein, J. H. Telluropyrylium electron-accepting dye sensitizers for electron-donating photoconductive compositions. US Patent 4,365,017 (Dec, 1982).

(23) Detty, M. R.; Murray, B. J.; Perlstein, J. H. Benzotelluropyrylium diketonate electron-accepting dye sensitizers for electron-donating photoconductive compositions. US Patent 4,365,016 (Dec, 1982).

(24) Péchy, P.; Rotzinger, F. P.; Nazeeruddin, M. K.; Kohle, O.; Zakeeruddin, S. M.; Humphry-Baker, R.; Grätzel, M. *Chem. Commun.* **1995**, 65−66.

(25) Zakeeruddin, S. M.; Nazeeruddin, M. K.; Pechy, P.; Rotzinger, F. P.; Humphry-Baker, R.; Kalyanasundaram, K.; Grätzel, M. *Inorg. Chem.* **1997**, *36*, 5937−5946.

(26) Gillaizeau-Gauthier, I.; Odobel, F.; Alebbi, M.; Argazzi, R.; Costa, E.; Bignozzi, C. A.; Qu, P.; Meyer, G. J. *Inorg. Chem.* **2001**, *40*, 6073−6079.
(27) Park, H.; Bae, E.; Lee, J. J.; Park, J.; Choi, W. *J. Phys. Chem. B* **2006**, *110*, 8740−8749.
(28) Mann, J. R.; Nevins, J. S.; Soja, G. R.; Wells, D. D.; Levy, S. C.; Marsh, D. A.; Watson, D. F. *Langmuir* **2009**, *25*, 12217−12228.
(29) Panda, J.; Virkler, P. R.; Detty, M. R. *J. Org. Chem.* **2003**, *68*, 1804−1809.
(30) Kalek, M.; Jezowska, M.; Stawinski, J. *Adv. Synth. Catal.* **2009**, *351*, 3207−3216.
(31) Leonard, K.; Nelen, M.; Raghu, M.; Detty, M. R. *J. Heterocycl. Chem.* **1999**, *36*, 707−717.
(32) Tretyakov, E. V.; Tkachev, A. V.; Rybalova, T. V.; Gatilov, Y. V.; Knight, D. W.; Vasilevsky, S. F. *Tetrahedron* **2000**, *56*, 10075−10080.
(33) Detty, M. R.; Murray, B. J.; Seidler, M. D. *J. Org. Chem.* **1982**, *47*, 1968−1969.
(34) Detty, M. R.; Hassett, J. W.; Murray, B. J.; Reynolds, G. A. *Tetrahedron* **1985**, *45*, 4853−4859.
(35) Dhawan, B.; Redmore, D. *J. Org. Chem.* **1984**, *49*, 4018−4021.
(36) Blackburn, G. M.; Ingleson, D. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1150−1153.
(37) Peng, A.-Y.; Li, B.; Xun, Y.; Junying, L. *Synthesis* **2008**, 2412−2416.
(38) Detty, M. R.; Young, D. N.; Williams, A. J. *J. Org. Chem.* **1995**, *60*, 6631−6634.
(39) Calitree, B. D.; Donnelly, D. J.; Holt, J. J.; Gannon, M. K., II; Nygren, C.; Sukumaran, D. K.; Autschbach, J.; Detty, M. R. *Organometallics* **2007**, *26*, 6248−6257.
(40) Jahnke, A. A.; Seferos, D. S. *Macromol. Rapid Commun.* **2011**, *32*, 943−951.
(41) Stefan Haid, S.; Mishra, A.; Uhrich, C.; Pfeiffer, M.; Bäuerle, P. *Chem. Mater.* **2011**, *23*, 4435−4444.
(42) Mann, J. R.; Watson, D. F. *Langmuir* **2007**, *23*, 10924−10928.
(43) Khazraji, A. C.; Hotchandani, S.; Das, S.; Kamat, P. V. *J. Phys. Chem. B* **1999**, *103*, 4693−4700.
(44) Waters of crystallization were calculated by comparing the integral of water to undeuterated NMR solvent in the presence and absence of sample.
(45) Nevins, J. S.; Coughlin, K. M.; Watson, D. F. *ACS Appl. Mater. Interfaces* **2011**, *3*, 4242−4253.