

A Comparison of Linear Optical Properties and Redox Properties in Chalcogenopyrylium Dyes Bearing Ortho-Substituted Aryl Substituents and *tert*-Butyl Substituents

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A series of thiapyrylium pentamethine dyes (**4** and **12–15**) bearing 2,2'-di-*tert*-butyl-6,6'-diphenyl, 2,2'-di-*tert*-butyl-6,6'-bis(2,6-dimethylphenyl), 2,2'-di-*tert*-butyl-6,6'-bis(2-methylphenyl), 2,2',6,6'-tetrakis(2,6-dimethylphenyl), and 2,2',6,6'-tetrakis(2-methylphenyl) substituents, respectively, were prepared and their linear optical properties and electrochemical redox properties were measured and compared to thiapyrylium pentamethine dyes **3** and **5**. The *tert*-butyl and 2,6-dimethylphenyl substituents give nearly identical chromophores with respect to values of λ_{max} , molar extinction coefficients (ϵ), bandwidths at half-height ($\nu_{1/2}$), and lack of absorption in the visible spectrum. The 2-methylphenyl substituent imparts linear optical properties that are intermediate between those of the *tert*-butyl and phenyl substituents. The 2,6-dimethylphenyl and 2-methylphenyl substituents impart greater oxidative stability based on anodic shifts in oxidation potential.

Introduction

Commercial applications with inexpensive, near-infrared-emitting diode lasers have created a demand for near-infrared-absorbing dyes. Some of the more important applications include thermal imaging,¹ electrophotography,² optical recording,³ photography, and lithography.⁴ Near-infrared-absorbing dyes have also been used as filter elements in conjunction with near-infrared-emitting diode lasers.^{4,5} The 810–850-nm window is where many of the commercially available gallium-arsenide diode lasers emit. Chalcogenopyrylium dyes derived from the condensation of 2-methyl and 4-methyl chalcogenopyrylium salts with various carbonyl and dicarbonyl equivalents give methine and polymethine

dyes that have absorption maxima with large extinction coefficients in this window.^{4,6} For many applications, the near-infrared-absorbing dye should also be essentially colorless in the visible spectrum, which severely limits the types of substituents that can be incorporated along the chromophore.

The *tert*-butyl substituent has been used in the 2- and 6-positions of various chalcogenopyrylium dyes to give minimal absorption in the visible portion of the spectrum and intense, narrow absorption in the near-infrared (with typical bandwidths at half-height of $\leq 600 \text{ cm}^{-1}$).^{6a,b,7} The *tert*-butyl substituents also impart greater solubility to the chalcogenopyrylium dyes in organic solvents and minimize aggregation—properties that tend to minimize the formation of crystallites in coated films.

The *tert*-butyl substituent has one significant drawback in near-infrared-absorbing chalcogenopyrylium dyes. Because alkyl substituents are inductively electron donating,⁸ near-infrared-absorbing chalcogenopyrylium dyes with 2,6-di-*tert*-butyl or other alkyl substituents are more easily oxidized relative to dyes with aryl substituents.⁹ The ease of oxidation can lead to undesired redox processes both in the ground (typically, reactions of the dye with oxygen, ozone) and excited states (electron transfer from electron-rich ground-state molecules to the

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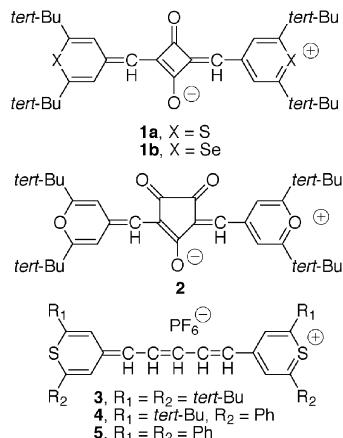
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CHART 1



low-energy SOMO of the excited-state dye) in various imaging applications, which can impact color reproduction and sensitometry.⁴ The 2,6-di-*tert*-butylthiapyrylium and selenopyrylium analogues of squarylium dyes **1** (Chart 1) have absorption maxima of 804 and 847 nm, respectively ($\epsilon > 300\,000\text{ M}^{-1}\text{ cm}^{-1}$), but oxidation potentials of +0.48 and +0.54 V vs the ferrocene/ferricinium couple (Fc/Fc⁺, $E^\circ = +0.40\text{ V}$), respectively.^{6a,7} The pyrylium croconate **2** (Chart 1) has an absorption maximum of 845 nm ($\epsilon > 100\,000\text{ M}^{-1}\text{ cm}^{-1}$) but an oxidation potential of +0.42 V vs Fc/Fc⁺.^{6a} Thiapyrylium pentamethine dye **3** (prepared according to Scheme 1) has an absorption maximum of 821 nm ($\epsilon = 384\,000\text{ M}^{-1}\text{ cm}^{-1}$, Figure S1 in Supporting Information) and an oxidation potential of +0.58 V vs Fc/Fc⁺.

In contrast to the *tert*-butyl group, the phenyl and other aryl groups are inductively electron withdrawing⁵ due in part to the greater electronegativity of the sp²-hybridized carbons. As shown in Table 1 for thiapyrylium pentamethine dyes **4** (prepared according to Scheme 1) and **5**^{3c} in which two and four *tert*-butyl substituents, respectively, have been replaced by phenyl substituents, oxidation potentials are more positive (+0.65 and +0.73 V vs Fc/Fc⁺ for **4** and **5**, respectively). However, absorption maxima are significantly longer for **4** and **5** relative to **3** (Table 1) and weak secondary bands are observed in the absorption spectra of **4** and **5** in the 400–450-nm window (Figures S2 and S3, respectively, in Supporting Information).

The *tert*-butyl substituent does not extend the π -chromophore in contrast to aryl substituents. As a logical extension, the electron-withdrawing character of aryl substituents could be used to tailor oxidation potentials without extending the π -chromophore if the aryl group were held orthogonal to the dye π -framework. Furthermore, the orthogonal aryl substituents should eliminate secondary absorption bands in the visible spectrum. We describe a series of thiapyrylium pentamethine dyes incorporating 2,6-dimethylphenyl or 2-methylphenyl substituents in the 2- and 6-positions of the thiapyrylium ring whose linear optical properties are nearly identical with those of thiapyrylium pentamethine dye **3**, but whose electrochemical oxidation potentials are more positive (anodic) than that of dye **3** with *tert*-butyl substituents.

Results and Discussion

Thiapyrylium pentamethine dye **3** was prepared according to Scheme 1 in which 4-methylthiapyrylium³ hexafluorophosphate **6a** was condensed with cyanine **7** in a one-to-one mixture of acetic acid/acetic anhydride with catalytic sodium acetate as a base to give dye **3** in 78% isolated yield. The remaining dyes of this study were prepared in a similar manner from the appropriate salt **6**.

The 4-methylthiapyrylium salts **6b–f** were prepared according to Scheme 2. The addition of a lithium acetylide to an arylpropargyl aldehyde **8** gave the corresponding 1,4-pentadiyn-3-ol **9**, which was then oxidized to the corresponding pentadiyn-3-one **10** with MnO₂ in CH₂Cl₂. The addition of Na₂S to diynones **10** in NaOEt/EtOH under controlled conditions⁷ gave thiapyranones **11**. Addition of MeMgBr to the carbonyl groups of **11** followed by elimination with HPF₆ gave the 4-methylthiapyrylium hexafluorophosphate salts **6**.

The preparation of arylpropargyl aldehydes **8b** and **8c** from the addition of the lithium acetylides of 2,6-dimethylphenylethyne¹¹ and 2-methylphenylethyne¹² to methyl formate was not complicated by competitive addition of the acetylide to the resulting arylpropargyl aldehyde **8**. Further addition to give the 1,5-diaryl-1,4-pentadiyn-3-ol occurred only under more forcing conditions with an excess of acetylide as described below. The propargyl aldehydes **8b** and **8c** were isolated in 63% and 69% yields, respectively, as air-sensitive oils.

The addition of lithium *tert*-butylacetylide to commercially available phenylpropargyl aldehyde (**8a**) gave diynol **9b** in 92% isolated yield. The addition of stoichiometric lithium *tert*-butylacetylide to arylpropargyl aldehydes **8b** and **9c** gave diynols **9c** and **9d** in 78% and 57% isolated yields, respectively. The addition of acetylides derived from 2,6-dimethylphenylethyne or 2-methylphenylethyne to arylpropargyl aldehydes **8b** or **8c** was more sluggish and useful yields were realized when a 3-fold excess of the acetylide was employed. Diynols **9e** and **9f** were isolated in 78% and 70% yields, respectively. All of the diynols **9** were prone to air oxidation to give the corresponding diynones **10** so the diynols **9** were converted directly to diynones **10** in 91–95% isolated yield with MnO₂ in CH₂Cl₂.

The addition of Na₂S to the diynones **10** to give thiapyranones **11** was somewhat problematic. While the 2-*tert*-butyl-6-phenylthiapyranone **11b** was isolated in 68% yield, thiapyranones **11c–f** were isolated in only 18–22% yield. The increased steric demands of 2-methyl and 2,6-dimethyl substituents on the phenyl ring may contribute to the lower yields. The major byproducts in these reactions, while not fully characterized, were consistent with the addition of Na₂S across two diynone units as well as oligomeric products from further additions.

The addition of MeMgBr to the thiapyranones **11b–f** followed by dehydration with aqueous HPF₆ gave the 4-methylthiapyrylium hexafluorophosphate salts **6b–f** in

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SCHEME 1

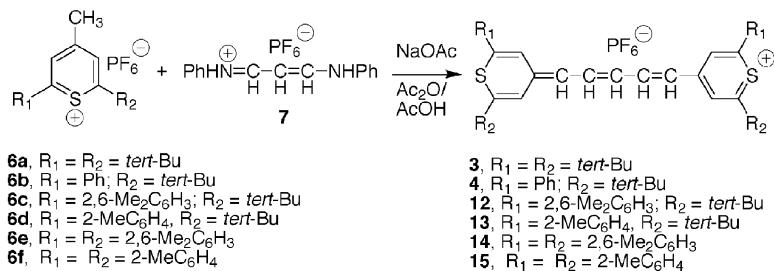
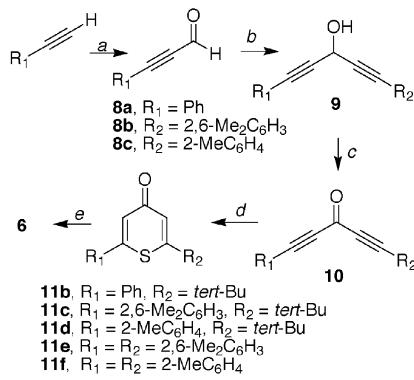


TABLE 1. A Comparison of the Linear Optical and Electrochemical Properties of Thiopyrylium Dyes 3–5 and 12–15

dye	R ₁	R ₂	λ_{\max}^a nm	$\log \epsilon^a$	$\nu_{1/2}^b$ cm ⁻¹	ox ^{c,d}		red ^c		ΔE , V
						Ep _a , V (vs Fc/Fc ⁺)	Ep _c , V (vs Fc/Fc ⁺)	Ep _a , V (vs Fc/Fc ⁺)	Ep _c , V (vs Fc/Fc ⁺)	
3	t-Bu	t-Bu	821	5.58	593	+0.58	-0.56	-0.48	-0.48	1.10
4	t-Bu	Ph	855	5.44	738	+0.68	-0.44	-0.36	-0.36	1.08
5	Ph	Ph	893	5.40	748	+0.65	-0.40	-0.34	-0.34	1.02
12	t-Bu	2,6-Me ₂ C ₆ H ₃	831	5.38	623	+0.73	-0.47	-0.39	-0.39	1.16
13	t-Bu	2-MeC ₆ H ₄	836	5.30	687	+0.69	-0.52	-0.44	-0.44	1.17
14	2,6-Me ₂ C ₆ H ₃	2,6-Me ₂ C ₆ H ₃	841	5.54	608	+0.84	-0.36	-0.30	-0.30	1.17
15	2-MeC ₆ H ₄	2-MeC ₆ H ₄	855	5.38	752	+0.78	-0.39	-0.31	-0.31	1.13

^a In CH₂Cl₂. ^b Bandwidth at half-height. ^c In CH₂Cl₂ at a Pt-disk electrode with a scan rate of 0.1 V s⁻¹ with 0.2 MBu₄NBF₄ as supporting electrolyte with the ferrocene/ferricinium couple as the reference electrode. ^d Irreversible peak potential. ^e Ep_a - E°.

SCHEME 2



^a Key: (a) *i*. BuLi, THF, -78 °C; *ii*. HCO₂Me, -78 °C;
 (b) *i*. R₂CCH₂, BuLi, -78 °C; *ii*. add to **8**; (c) MnO₂, CH₂Cl₂; (d) Na₂S, NaOEt/EtOH; (e) *i*. MeMgBr; *ii*. HPF₆

72–84% isolated yields following recrystallization. The condensation of the 4-methylthiapyrylium salts **6b–f** with cyanine **7** gave dyes **4** and **12–15** in 56–62% isolated yield following recrystallization.

(a) Linear Optical Properties of Thiapyrylium Pentamethine Dyes 3–5 and 12–15. The absorption spectra of dyes **3–5** and **12–15** are shown in Figures S1–S7, respectively, in the Supporting Information. The wavelengths of the absorption maxima (λ_{\max}) and the molar extinction coefficients (ϵ) for dyes **3–5** and **12–15** are compiled in Table 1. The bandwidths at half-height ($\nu_{1/2}$) for these dyes are also compiled in Table 1.

The substitution of a 2,6-dimethylphenyl substituent for a *tert*-butyl substituent gives a 10-nm bathochromic shift in λ_{\max} with minimal increase in $\nu_{1/2}$ in comparing dyes **3**, **12**, and **14**. In comparison, substitution of the 2-methylphenyl substituent for a *tert*-butyl substituent gives 15–19-nm bathochromic shifts in λ_{\max} , but gives significant increases in values of $\nu_{1/2}$ (a 94-cm⁻¹ increase

from **3** to **13** and a 65-cm⁻¹ increase from **13** to **15**). The linear optical properties of dye **15** with four 2-methylphenyl substituents are nearly identical with those of dye **4** with two *tert*-butyl and two phenyl substituents. Importantly, all of the dyes **12–15** have intense absorbance at λ_{\max} with molar extinction coefficients, ϵ , > 180 000 M⁻¹ cm⁻¹.

(b) Electrochemical Oxidation and Reduction Potentials.

Oxidation and reduction potentials for dyes **3–5** and **12–15** were determined by cyclic voltammetry and values of Ep_a for the irreversible oxidation of the thiapyrylium dye and values of E° for the reversible cation/neutral radical couple are compiled in Table 1. Substitution of either a 2,6-dimethylphenyl or a 2-methylphenyl group for a *tert*-butyl group gives an anodic (positive) shift in the oxidation potential. In comparing dyes **3**, **13**, and **15**, each substitution of a 2-methylphenyl substituent for a *tert*-butyl group gives a 10-mV anodic shift. In comparing dyes **3**, **12**, and **14**, sequential substitution of a 2,6-dimethylphenyl substituent for a *tert*-butyl group gives 15- and 11-mV anodic shifts.

In earlier work, we demonstrated that the energy of the absorbed photon at λ_{\max} was directly proportional to the energy difference, ΔE , between the oxidation and reduction potentials for chalcogenopyrylium dyes.⁶ Not surprisingly, values of ΔE for **12–15** (1.13–1.17 V, Table 1) are comparable to ΔE for dye **3** (1.10 V) and the anodic shift observed in oxidation potentials upon substitution of 2,6-dimethylphenyl and 2-methylphenyl substituents for *tert*-butyl groups is accompanied by a corresponding shift in the reduction potential.

(c) Singlet-Oxygen Generation by Dyes 4 and 12–15. Self-sensitized generation of singlet oxygen in solution is not a concern for the dyes of this study. The quantum yields for singlet oxygen generation [$\phi(^1\text{O}_2)$] for **4** and **12–15** were all < 0.0005 [100% efficiency has $\phi(^1\text{O}_2) = 1.0$] in MeOH solution.

Summary and Conclusions

In conclusion, strong, narrow absorbance bands characterize chalcogenopyrylium dyes bearing 2,6-di-*tert*-butyl substituents. In polymethine systems, the wavelengths of absorption extend into the near-infrared. Thiapyrylium pentamethine dye **3** has $\lambda_{\text{max}} = 821$ nm with a molar extinction coefficient of 384 000 M⁻¹ cm⁻¹. While dye **3** has excellent optical properties for compatibility with near-infrared-emitting diode lasers, it is very easily oxidized with $E_{\text{pa}} = +0.58$ V (vs Fc/Fc⁺), which limits its utility. The 2,6-dimethylphenyl substituent is very similar to the *tert*-butyl substituent with respect to impact on λ_{max} and band shape as measured by $\nu_{1/2}$, but dyes bearing this substituent have more anodic (positive) oxidation potentials relative to dyes with *tert*-butyl substituents. The 2-methylphenyl substituent is intermediate between the *tert*-butyl group and the phenyl group with respect to optical properties, but also imparts more anodic (positive) oxidation potentials relative to dyes with *tert*-butyl substituents. Synthetically, the 2,6-dimethylphenyl and 2-methylphenyl substituents are easily introduced into the thiapyrylium framework at the 2- and 6-positions.

Experimental Section

General Methods. 2,6-Di-*tert*-butyl-4-methylthiapyrylium hexafluorophosphate **6a** was prepared as described in ref 3a. Quantum yields for singlet oxygen were measured in MeOH at 25 °C, using methods we have previously described.¹⁴

Preparation of 2-(1,1-Dimethylethyl)-6-phenylthiapyran-4-one (11b). Diynone **10b** (5.13 g, 24.4 mmol) was dissolved in a 0.25 M solution of NaOEt in EtOH (488 mL) that was stirred at room temperature for 10 min and then added to a solution of Na₂S prepared from sulfur (0.94 g, 29.3 mmol) and NaBH₄ (1.48 g, 39.0 mmol) in a 0.25 M solution of sodium ethoxide in ethanol (488 mL). (These reagents were heated at reflux until all sulfur was dissolved and the color of the solution changed from green to white.) The reaction mixture was stirred for 1 h at ambient temperature and was first filtered through Celite and then concentrated. The products were extracted from an aqueous workup with EtOAc and the organic extracts were washed with brine, dried over MgSO₄, and concentrated. The product was purified via chromatography on SiO₂ eluted with EtOAc to give 4.05 g (68%) of **11b** as a yellow oil: ¹H NMR (400 MHz, CDCl₃): δ 7.57 (m, 2 H), 7.45 (m, 3 H), 7.10 (s, 1 H), 7.00 (s, 1 H), 1.40 (s, 9 H); ¹³C NMR (125 MHz CDCl₃): δ 182.7, 165.9, 153.0, 136.3, 130.4, 129.1, 126.8, 126.2, 125.0, 38.3, 30.5; IR (film, NaCl) 1613 cm⁻¹; HRMS (EI) *m/z* 244.0922 (calcd for C₁₅H₁₆OS: 244.0931). Anal. Calcd for C₁₅H₁₆OS: C, 73.73; H, 6.60. Found: C, 73.38; H, 6.41.

Preparation of 2-(1,1-Dimethylethyl)-6-(2,6-dimethylphenyl)thiapyran-4-one (11c). Diynone **10c** (0.44 g, 1.8 mmol), sulfur (0.070 g, 2.2 mmol), and NaBH₄ (0.11 g, 2.9 mmol) were treated as described for the preparation of **11ab**. Following chromatography on SiO₂ eluted with 20% EtOAc/hexanes and recrystallization from CH₃CN, thiapyranone **11c** was isolated in 0.105 g (20%) yield as a white crystalline solid, mp 105–106 °C: ¹H NMR (300 MHz, CDCl₃): δ 7.24 (t, 1 H, *J* = 7.5 Hz), 7.12 (d, 2 H, *J* = 7.5 Hz), 7.02 (s, 1 H), 6.75 (s, 1 H), 2.23 (s, 6 H), 1.38 (s, 9 H); ¹³C NMR (125 MHz, CDCl₃): δ 183.1, 167.5, 153.3, 136.4, 135.3, 129.5, 129.3, 128.0, 125.3, 38.6, 30.7,

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20.1; IR (KBr) 1621 cm⁻¹; HRMS (ES) *m/z* 273.1313 (calcd for C₁₇H₂₀OS + H: 273.1313). Anal. Calcd for C₁₇H₂₀OS: C, 74.95; H, 7.40. Found: C, 74.62; H, 7.48.

Preparation of 2-(1,1-Dimethylethyl)-6-(2-methylphenyl)thiapyran-4-one (11d). Diynone **10d** (0.25 g, 1.1 mmol), sulfur (0.043 g, 1.3 mmol), and NaBH₄ (0.067 g, 1.8 mmol) were treated as described for the preparation of **11b**. Following chromatography on SiO₂ eluted with 20% EtOAc/hexanes, thiapyranone **11d** was isolated in 0.051 g (18%) yield as a colorless oil: ¹H NMR (300 MHz, CDCl₃): δ 7.2 (m, 4 H), 7.03 (d, 1 H, *J* = 1.2 Hz), 6.83 (d, 1 H, *J* = 1.2 Hz), 2.34 (s, 3 H), 1.39 (s, 9 H); ¹³C NMR (75 MHz, CDCl₃): δ 182.7, 166.9, 153.5, 136.0, 135.9, 131.1, 130.0, 129.4, 129.3, 126.3, 125.4, 38.6, 30.7, 20.1; IR (film, NaCl) 1613 cm⁻¹; HRMS (ES) *m/z* 281.0959 (calcd for C₁₆H₁₈OS + Na: 281.0976). Anal. Calcd for C₁₆H₁₈OS: C, 74.38; H, 7.02; Found: C, 74.19; H, 7.11.

Preparation of 2,6-Bis(2,6-dimethylphenyl)thiapyran-4-one (11e). Diynone **10e** (0.20 g, 0.69 mmol), sulfur (0.028 g, 0.84 mmol), and NaBH₄ (0.44 g, 1.1 mmol) were treated as described for the preparation of **11b**. Following chromatography on SiO₂ eluted with 20% EtOAc/hexanes and recrystallization from CH₃CN, thiapyranone **11e** was isolated in 0.050 g (22%) yield as a white crystalline solid, mp 168–170 °C: ¹H NMR (300 MHz, CDCl₃): δ 7.25 (t, 2 H, *J* = 7.5 Hz), 7.13 (d, 4 H, *J* = 7.5 Hz), 6.87 (s, 2 H), 2.29 (s, 12 H); ¹³C NMR (125 MHz, CDCl₃): δ 183.0, 155.0, 136.5, 135.2, 130.5, 129.9, 128.4, 20.4; IR (CCl₄) 1619 cm⁻¹; HRMS (ES) *m/z* 343.1120 (calcd for C₂₁H₂₀OS + Na: 343.1133). Anal. Calcd for C₂₁H₂₀OS: C, 78.71; H, 6.29. Found: C, 78.73; H, 6.32.

Preparation of 2,6-Bis(2-methylphenyl)thiapyran-4-one (11f). Diynone **10f** (0.70 g, 2.5 mmol), sulfur (0.096 g, 3.0 mmol), and NaBH₄ (0.15 g, 4.0 mmol) were treated as described for the preparation of **11b**. Following chromatography on SiO₂ eluted with 20% EtOAc/hexanes and recrystallization from CH₃CN, thiapyranone **11f** was isolated in 0.15 g (22%) yield as a white crystalline solid, mp 144–146 °C: ¹H NMR (300 MHz, CDCl₃): δ 7.2–7.35 (m, 8 H), 6.99 (s, 2 H), 2.39 (s, 6 H); ¹³C NMR (125 MHz, CDCl₃): δ 182.2, 154.9, 136.2, 135.9, 131.5, 130.3, 130.4, 129.6, 126.7, 20.4; IR (KBr) 1614 cm⁻¹; HRMS (EI) *m/z* 292.0904 (calcd for C₁₉H₁₆OS: 292.0922). Anal. Calcd for C₁₉H₁₆OS: C, 78.05; H, 5.52. Found: C, 77.87; H, 5.13.

General Procedure for the Preparation of 4-Methylthiapyrylium Hexafluorophosphate Salts. Preparation of 2-(1,1-Dimethylethyl)-6-phenyl-4-methylthiapyrylium Hexafluorophosphate (6b). Thiapyranone **11b** (4.05 g, 16.6 mmol) was dissolved in THF (70 mL) and cooled to 0 °C. A solution of 1.4 M methylmagnesium bromide (60 mL, 84 mmol) in ether was added and the reaction mixture was stirred at room temperature for 15 min. The solution was then poured into acetic acid and 5 mL of a 60% solution of HPF₆ was slowly added until the solution darkened. The reaction mixture was then poured into water and the green crystals were collected by filtration. The crude product was recrystallized from CH₃CN to give **6b** in 4.64 g (72%) yield as a light green powder, mp 178 °C: ¹H NMR (500 MHz, CD₃CN): δ 8.64 (s, 1 H), 8.56 (s, 1 H), 7.95 (d, 2 H, *J* = 7.6 Hz), 7.76 (m, 1 H), 7.70 (m, 2 H), 2.88 (s, 3 H), 1.62 (s, 9 H); ¹³C NMR (125.5 MHz, CD₃CN): δ 186.1, 169.0, 167.4, 134.8, 134.7, 134.4, 131.2, 129.3, 42.5, 30.9, 26.0; λ_{max} (CH₂Cl₂) 367 nm (ϵ 41 400 ± 800 M⁻¹ cm⁻¹); MS (ES) *m/z* 243 (M⁺ for C₁₆H₁₉S, 243). Anal. Calcd for C₁₆H₁₉F₆PS: C, 49.48; H, 4.93. Found: C, 49.27; H, 4.95.

Preparation of 2-(1,1-Dimethylethyl)-6-(2,6-dimethylphenyl)-4-methylthiapyrylium Hexafluorophosphate (6c). Thiapyranone **11c** (0.22 g, 0.80 mmol) was treated with 1.4 M MeMgBr in ether (1.7 mL, 2.4 mmol) and HPF₆ as described for **6b** to give **6c** in 0.27 g (82%) yield, mp 152 °C: ¹H NMR (300 MHz, CDCl₃): δ 8.63 (s, 1 H), 8.15 (s, 1 H), 7.39 (t, 1 H, *J* = 7.5 Hz), 7.23 (d, 2 H, *J* = 7.5 Hz), 3.04 (s, 3 H), 2.14 (s, 6 H), 1.69 (s, 9 H); ¹³C NMR (125.5 MHz, CD₃CN): δ 189.6, 168.6, 168.1, 138.2, 137.4, 135.4, 133.3, 131.9, 128.9, 42.5, 30.5, 25.9, 20.3; HRMS (ES) *m/z* 271.1532 (calcd for C₁₈H₂₃S: 271.1520).

Anal. Calcd for $C_{18}H_{23}F_6PS$: C, 51.92; H, 5.97. Found: C, 51.77; H, 6.03.

Preparation of 2-(1,1-Dimethylethyl)-6-(2-methylphenyl)-4-methylthiapyrylium Hexafluorophosphate (6d). Thiapyranone **11d** (0.100 g, 0.39 mmol) was treated with 1.4 M $MeMgBr$ in ether (1.2 mL, 1.7 mmol) and HPF_6 as described for **6b** to give **6d** in 0.13 g (84%) yield, mp 147 °C: 1H NMR (300 MHz, CD_3CN) δ 8.62 (s, 1 H), 8.41 (s, 1 H), 7.3–7.7 (m, 4 H), 2.88 (s, 3 H), 2.35 (s, 3 H), 1.61 (s, 9 H); ^{13}C NMR (125.5 MHz, CD_3CN) δ 187.3, 168.9, 166.4, 137.3, 134.5, 132.6, 132.1, 131.2, 127.4, 127.1, 126.6, 30.4, 30.1, 25.6, 19.6; HRMS (ES) m/z 257.1361 (calcd for $C_{17}H_{21}S$: 257.1364). Anal. Calcd for $C_{17}H_{21}F_6PS$: C, 50.74; H, 5.26. Found: C, 50.92; H, 5.51.

Preparation of 2,6-Bis(2,6-dimethylphenyl)-4-methylthiapyrylium Hexafluorophosphate (6e). Thiapyranone **11e** (0.080 g, 0.25 mmol) was treated with 1.4 M $MeMgBr$ in ether (1.0 mL, 1.4 mmol) and HPF_6 as described for **6b** to give **6e** in 0.09 g (78%) yield, mp 176 °C: 1H NMR (300 MHz, $CDCl_3$) δ 8.40 (s, 2 H), 7.39 (t, 2 H, J = 7.5 Hz), 7.25 (d, 4 H, J = 7.5 Hz), 3.15 (s, 3 H), 2.22 (s, 12 H); ^{13}C NMR (125.5 MHz, CD_3CN) δ 173.1, 170.6, 139.4, 137.2, 133.0, 132.3, 129.1, 26.4, 20.4; HRMS (ES) m/z 319.1530 (calcd for $C_{22}H_{23}S$: 319.1520). Anal. Calcd for $C_{22}H_{23}F_6PS$: C, 56.89; H, 4.99. Found: C, 56.83; H, 5.03.

Preparation of 2,6-Bis(2-methylphenyl)-4-methylthiapyrylium Hexafluorophosphate (6f). Thiapyranone **11f** (0.080 g, 0.27 mmol) was treated with 1.4 M $MeMgBr$ in ether (1.0 mL, 1.4 mmol) and HPF_6 as described for **6b** to give **6f** in 0.10 g (84%) yield, mp 156 °C: 1H NMR (300 MHz, $CDCl_3$) δ 8.40 (s, 2 H), 7.0–7.6 (m, 8 H), 3.03 (s, 3 H), 2.49 (s, 6 H); ^{13}C NMR (125.5 MHz, CD_3CN) δ 176.5, 171.7, 142.7, 142.2, 138.8, 137.9, 137.4, 136.5, 132.6, 30.8, 24.8; HRMS (ES) m/z 291.1203 (calcd for $C_{20}H_{19}S$: 291.1207). Anal. Calcd for $C_{20}H_{19}F_6PS$: C, 55.05; H, 4.39. Found: C, 54.83; H, 4.22.

General Procedure for the Preparation of Pentamethine Dyes. Preparation of 4-[4-[2-(1,1-Dimethylethyl)-6-phenyl]-4H-thiapyranylidene)methyl]-1,3-butadienyl-2-(1,1-dimethylethyl)-6-phenylthiapyrylium Hexafluorophosphate (4). Aniline (2.86 g, 30.0 mmol) and 1,1,3,3-tetramethoxypropane (1.99 g, 12.1 mmol) were dissolved in acetic acid (10 mL) and the solution heated to 80 °C for 15 min. The solution was removed from the heat and a 60% solution of hexafluorophosphoric acid (2 mL) was slowly added. The reaction mixture was then poured into water (200 mL) and the hexafluorophosphate cyanine salt **7** was collected as a yellow solid.¹³ Sodium acetate (0.023 g, 0.28 mmol), cyanine **7** (0.051 g, 0.14 mmol), and 4-methylthiapyrylium hexafluorophosphate **6b** (0.11 g, 0.28 mmol) were heated at 95 °C for 10 min in 0.75 mL of Ac_2O and 0.75 mL of HOAc. The reaction mixture was poured into water and the brown precipitate was collected by filtration. The dye was recrystallized by dissolving the crude dye in hot CH_3CN , cooling to ambient temperature, and then adding an equal volume of ether to induce crystallization upon standing. The resulting copper crystals were collected to give **4** in 0.058 g (62%) yield: mp 206.5–207.5 °C; 1H NMR (500 MHz, CD_3CN) δ 7.92 (t, 2 H, J = 13 Hz), 7.70 (m, 6 H), 7.53 (m, 8 H), 6.60 (t, 1 H, J = 13 Hz), 6.46 (d, 2 H, J = 13 Hz), 1.42 (s, 18 H); ^{13}C NMR (125 MHz, CD_3CN) δ 167.1, 152.9, 151.7, 149.3, 136.8, 134.7, 132.2, 131.2, 130.5, 129.4, 127.8, 126.1, 40.1, 30.7; λ_{max} (CH_2Cl_2) 855 nm (ϵ 275 000 \pm 8 000) $M^{-1} cm^{-1}$). Anal. Calcd for $C_{35}H_{37}F_6PS_2$: C, 63.05; H, 5.59. Found: C, 63.11; H, 5.52.

Preparation of 4-[4-[2,6-Bis(1,1-dimethylethyl)]-4H-thiapyranylidene)methyl]-1,3-butadienyl-2,6-bis(1,1-dimethylethyl)thiapyrylium Hexafluorophosphate (3). 2,6-Di-*tert*-butyl-4-methylthiapyrylium hexafluorophosphate (**6a**, 4.04 g, 0.0110 mol), $NaOAc$ (1.0 g, 0.012 mol), and cyanine **7** (1.84 g, 0.00500 mol) were heated to 90–95 °C in 25 mL of acetic anhydride and 25 mL of acetic acid for 0.5 h. (Temperature is critical, if the reaction reaches >100 °C, yields are dramatically reduced.) The reaction mixture was poured into 300 mL of water and stirred for 1 h. The solid was collected

by filtration and washed with 10% ethanol in ether to give copper–bronze crystals. A final wash with hot ethyl acetate removes the products of half reaction to give 2.67 g (90%) of dye **3**, mp 175–178 °C: 1H NMR (500 MHz, $CDCl_3$) δ 8.13 (t, 2 H, J = 13 Hz), 7.43 (br s, 4 H), 6.48 (t, 1 H, J = 13 Hz), 6.25 (d, 2 H, J = 13 Hz), 1.42 (s, 18 H); λ_{max} (CH_2Cl_2) 822 nm (ϵ 384 000 \pm 7 000 $M^{-1} cm^{-1}$). Anal. Calcd for $C_{31}H_{45}F_6PS_2$: C, 59.41; H, 7.24; S, 10.23. Found: C, 59.33; H, 7.28; S, 9.93.

Preparation of 4-[4-[2-(1,1-Dimethylethyl)-6-(2,6-dimethylphenyl)]-4H-thiapyranylidene)methyl]-1,3-butadienyl-2-(1,1-dimethylethyl)-6-(2,6-dimethylphenyl)thiapyrylium Hexafluorophosphate (12). Sodium acetate (0.016 g, 0.18 mmol), cyanine **7** (0.034 g, 0.093 mmol), and 4-methylthiapyrylium hexafluorophosphate **6c** (0.080 g, 0.17 mmol) were heated at 95 °C for 10 min in 0.5 mL of Ac_2O and 0.5 mL of HOAc as described for the preparation of dye **4**. Product yield was 0.085 g (60%) of **12** as a dark blue solid, mp 130 °C: 1H NMR (300 MHz, $CDCl_3$) δ 8.10 (br s, 2 H), 7.52 (s, 1 H), 7.49 (s, 1 H), 7.33 (t, 2 H, J = 7.5 Hz), 7.14 (d, 4 H, J = 7.5 Hz), 7.12 (br s, 2 H), 6.62 (br t, 1 H, J = 13 Hz), 6.38 (br d, 2 H, J = 13 Hz), 2.24 (s, 6 H), 2.18 (s, 6 H), 1.48 (s, 18 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.7, 154.4, 151.7, 144.3, 137.1, 130.4, 129.5, 128.6, 124.8, 120.3, 117.1, 31.2, 30.1, 20.7 (one signal overlapping); λ_{max} (CH_2Cl_2) 831 nm (ϵ 240 000 \pm 3 000 $M^{-1} cm^{-1}$). HRMS (ES) m/z 577.2968 (calcd for $C_{39}H_{45}S_2$: 577.2963). Anal. Calcd for $C_{39}H_{45}F_6PS_2$: C, 64.80; H, 6.27. Found: C, 64.53; H, 6.27.

Preparation of 4-[4-[2-(1,1-Dimethylethyl)-6-(2-methylphenyl)]-4H-thiapyranylidene)methyl]-1,3-butadienyl-2-(1,1-dimethylethyl)-6-(2-methylphenyl)thiapyrylium Hexafluorophosphate (13). Sodium acetate (0.023 g, 0.28 mmol), cyanine **7** (0.044 g, 0.12 mmol), and 4-methylthiapyrylium hexafluorophosphate **6d** (0.10 g, 0.25 mmol) were heated at 95 °C for 10 min in 0.5 mL of Ac_2O and 0.5 mL of HOAc as described for the preparation of dye **4**. Product yield was 0.10 g (58%) of **13** as a dark blue solid, mp 144–146 °C: 1H NMR (500 MHz, CD_3CN) δ 7.93 (t, 2 H, J = 13 Hz), 7.5–7.2 (m, 12 H), 6.65 (t, 1 H, J = 13 Hz), 6.50 (d, 2 H, J = 13 Hz), 2.36 (s, 6 H), 1.44 (s, 18 H); ^{13}C NMR (125 MHz, CD_3CN) δ 168.3, 153.5, 151.5, 149.5, 137.0, 136.7, 132.0, 131.3, 130.4, 129.5, 127.3, 125.4, 124.2, 120.1, 40.0, 30.6, 20.0; λ_{max} (CH_2Cl_2) 836 nm (ϵ 198 000 \pm 5 000 $M^{-1} cm^{-1}$). HRMS (ES) m/z 549.2650 (calcd for $C_{37}H_{41}S_2$: 549.2656). Anal. Calcd for $C_{37}H_{41}F_6PS_2$: C, 64.80; H, 6.27. Found: C, 64.53; H, 6.27.

Preparation of 4-[4-[2,6-Bis(2,6-dimethylphenyl)]-4H-thiapyranylidene)methyl]-1,3-butadienyl-2,6-bis(2,6-dimethylphenyl)thiapyrylium Hexafluorophosphate (14). Sodium acetate (0.016 g, 0.18 mmol), cyanine **7** (0.034 g, 0.093 mmol), and 4-methylthiapyrylium hexafluorophosphate **6e** (0.080 g, 0.17 mmol) were heated at 95 °C for 10 min in 0.5 mL of Ac_2O and 0.5 mL of HOAc as described for the preparation of dye **4**. Product yield was 0.080 g (56%) of **14** as a dark blue solid, mp 162–164 °C: 1H NMR (500 MHz, $CDCl_3$) δ 7.76 (t, 2 H, J = 13 Hz), 7.48 (s, 2 H), 7.44 (s, 2 H), 7.16 (t, 4 H, J = 7.5 Hz), 7.04 (d, 8 H, J = 7.5 Hz), 6.66 (t, 1 H, J = 13 Hz), 6.40 (d, 2 H, J = 13 Hz), 2.18 (s, 24 H); λ_{max} (CH_2Cl_2) 841 nm (ϵ 348 000 \pm 7 000 $M^{-1} cm^{-1}$). HRMS (ES) m/z 673.2963 (calcd for $C_{47}H_{45}S_2$: 673.2963). Anal. Calcd for $C_{47}H_{45}F_6PS_2$: C, 68.93; H, 5.54. Found: C, 69.08; H, 5.39.

Preparation of 4-[4-[2,6-Bis(2-methylphenyl)]-4H-thiapyranylidene)methyl]-1,3-butadienyl-2,6-bis(2-methylphenyl)thiapyrylium Hexafluorophosphate (15). Sodium acetate (0.023 g, 0.28 mmol), cyanine **7** (0.051 g, 0.14 mmol), and 4-methylthiapyrylium hexafluorophosphate **6f** (0.11 g, 0.28 mmol) were heated at 95 °C for 10 min in 0.5 mL of Ac_2O and 0.5 mL of HOAc as described for the preparation of dye **4**. Product yield was 0.11 g (58%) of **15** as a dark blue solid, mp 134–136 °C: 1H NMR (500 MHz, CD_3CN) δ 7.70 (br t, 2 H, J = 13 Hz), 7.34 (br s, 4 H), 7.7–7.0 (m, 12 H), 6.48 (t, 1 H, J = 13 Hz), 6.30 (d, 2 H, J = 13 Hz), 2.21 (s, 12 H); ^{13}C NMR (125 MHz, CD_3CN) 153.7, 150.5, 149.4,

136.5, 135.6, 131.9, 131.2, 130.2, 130.1, 129.3, 127.2, 119.8, 19.8; λ_{max} (CH_2Cl_2) 854 nm (ϵ 240 000 \pm 3 000 $\text{M}^{-1} \text{cm}^{-1}$) HRMS (ES) m/z 617.8852 (calcd for $\text{C}_{43}\text{H}_{37}\text{S}_2$: 617.8859). Anal. Calcd for $\text{C}_{43}\text{H}_{37}\text{F}_6\text{PS}_2$: C, 67.70; H, 4.89. Found: C, 67.33; H, 4.86.

Electrochemical Procedures. The working electrode for cyclic voltammetry was a platinum disk electrode (diameter, 1 mm). The auxiliary and reference electrodes were silver wires. The reference for cyclic voltammetry was the Fc/Fc^+ couple at +0.40 V at a scan rate of 0.1 V s^{-1} . All samples were run in HPLC-grade dichloromethane that had been stored over 3A molecular sieves and freshly distilled prior to use. Tetraethylammonium fluoroborate was recrystallized from ethyl acetate–ether and then dried overnight at 80 °C before it was used as supporting electrolyte at 0.2 M. Nitrogen was used for sample deaeration.

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Supporting Information Available: Figures S1–S7 for the absorption spectra of dyes **3–5** and **12–15** and experimental procedures for the preparation of 2,6-dimethylphenylethyne, 2-methylphenylethyne, and compounds **8–10**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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