J. Org. Chem. 1990, 55, 49–57 49

Dimerization Reactions of Cyanine Radical Dications

R. L. Parton* and J. R. Lenhard

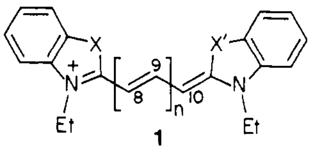
Research Laboratories—Photographic Products Group, Eastman Kodak Company, Rochester, New York 14650

Received February 15, 1989

Radical dications formed during the one-electron oxidation of representative cationic dicarbocyanine (pentamethine) dyes that lack alkyl substitution on the even-numbered carbon atoms of the methine chain were found to undergo irreversible dimerization in methanol or acetonitrile solution. Deprotonation of the resultant UV-absorbing dimer gives a dicationic bis-dye whose spectral properties are similar to those of the parent dye. These bis-dyes are susceptible to further oxidation via a reversible two-electron mechanism to yield a highly unsaturated, cross-conjugated, tetracationic species. The chemistry of radical dications derived from the one-electron oxidation of carbocyanine (trimethine) dyes was found to depend on the nature of the dye heterocycle as well as the degree of alkyl substitution in the methine chain. Some thiacarbocyanine radical dications irreversibly dimerized and gave products analogous to those observed for dicarbocyanines. A persistent radical dication was obtained by the one-electron oxidation of an indolocarbocyanine and a chain-substituted thiacarbocyanine dye.

Cyanine dyes are widely used as spectral sensitizers in homogeneous[1,2] and heterogeneous[3–7] photoredox systems, although they are most recognized for their use in silver halide photography.[8,9] In many applications, the dye essentially functions as an electron donor, whereby an electron is transferred from the optically excited dye to an acceptor molecule or crystal. The initial dye product of such a photosensitization event is the corresponding monooxidized, radical form of the dye. Prior studies of cyanine dye redox chemistry have largely focused on the determination of one-electron oxidation and reduction potentials of dyes and on the correlation of these data with photosensitization efficiency.[10–13] In only a few instances has the fate of the cyanine dye radical been investigated.[10,14,15]

As depicted in 1, the general cyanine dye structure involves two heterocyclic nuclei that are linked by a conjugated chain containing an odd number of methine carbons. The positive charge is extensively delocalized between the nitrogen atoms. The length of the conjugated chain and the nature of the terminal groups are both important in determining the spectral absorption wavelengths of these dyes. Historically, the terms simple cyanine ($n = 0$), carbocyanine ($n = 1$), and dicarbocyanine ($n = 2$) have been used to designate dye structures having one, three, and five methine carbons in the chain, respectively.



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X=S,O,Se,–CH=CH–,C(CH$_3$)$_2$

The one-electron oxidation of a cationic dye would initially generate the corresponding radical dication. The principal resonance forms associated with the oxidized dye indicate that the radical character would reside primarily on the nitrogen atoms and on the even-numbered carbon atoms of the polymethine chain. This alternation of electron density is consistent with the EPR results of Oehling and Baer obtained for electrolytically formed cyanine and carbocyanine dye radicals.[16]

The stability of cyanine, carbocyanine, and dicarbocyanine radical dications, as measured by their anodic cyclic voltammetric response, is markedly dependent on the type and extent of substitution in the polymethine chain of the dye. The various radical dications are susceptible to radical–radical dimerization at the even-methine carbons, and hence methine chain substituents would be expected to impart both steric and electronic effects which would influence the radical reactivity.[17] We have recently isolated the dimers derived from cationic dicarbocyanine dyes bearing one or more alkyl substituents at the even-numbered positions of the pentamethine chain. For a series of these compounds, we found the dimerization reaction to be reversible in acetonitrile at room temperature[15] (eq 1).

$$2\text{dye}^+ \underset{+2e^-}{\overset{-2e^-}{\rightleftarrows}} 2\text{radical}^{2+} \rightleftarrows \text{dimer}^{4+} \tag{1}$$

The C···C bond dissociation energy in the dimers of variously substituted dicarbocyanines was evaluated from the temperature dependence of UV–vis spectra and was found to range from 12.2 to 16.8 kcal/mol. The persistence of the radical dication was related to electronic stabilization by the alkyl substituent(s) and to the amount of steric strain in the respective dimers.

This paper describes the dimerization reaction mechanisms and products associated with one-electron oxidation of dicarbocyanine dyes that lack alkyl substitution on the even-numbered carbon atoms (8, 10, or 12) of the pentamethine chain. In contrast to the substituted analogues,

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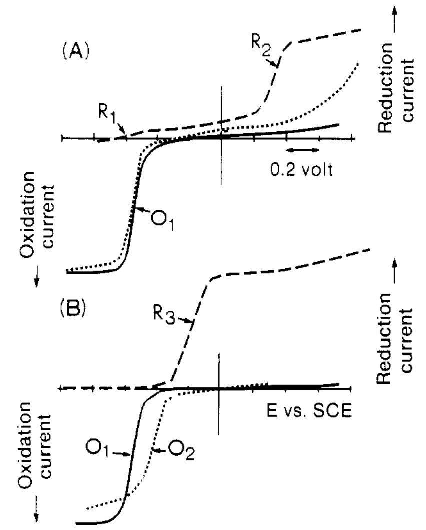
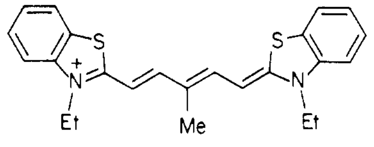


Figure 1. Stirred-solution voltammograms obtained during the controlled-potential electrolysis of ca. 0.5 mM solutions of **2** (A) and **3** (B) in $CH_3CN/TBABF_4$: before (—) and after (- - -) electroxidation at 0.7 V; after (···) subsequent reduction at 0.1 V; solutions of **2** also contain pyridine (10^{-5} M); recorded at a Pt disk electrode, sweep rate 20 mV/s.

the radical coupling process for these dyes was found to be totally irreversible. Moreover, the dimers exhibit a structurally dependent reactivity of their own as they are susceptible to deprotonation and further oxidation. In addition, we have extended our investigations to include dyes of the carbocyanine class and report on the mechanisms and products of their chemical oxidation.[18]

Results and Discussion

Dicarbocyanines. Figure 1 compares stirred-solution voltammograms (ssv) recorded at a Pt disk (0.1 cm^2) electrode during the controlled-potential electrolysis of dicarbocyanine dyes **2** and **3** in acetonitrile. The solid, dashed, and dotted curves of Figure 1 represent the voltammograms recorded before oxidation, after exhaustive electrooxidation at 0.7 V, and after subsequent reduction at 0.1 V, respectively. For each of the curves A and B, the magnitude of the limiting current is directly proportional to the concentration of electroactive species in solution (dye, radical dication, dimer, etc.). The ssv for the initial dye solution, Figure 1A, shows a wave, O_1, at 0.6 V, which corresponds to the one-electron oxidation of **2** to the radical dication. In the ssv recorded after electrooxidation has been accomplished (at a second Pt gauze electrode, 0.1 m^2, poised at 0.7 V), only a trace of radical is detected at R_1.



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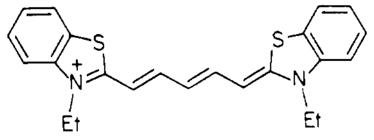

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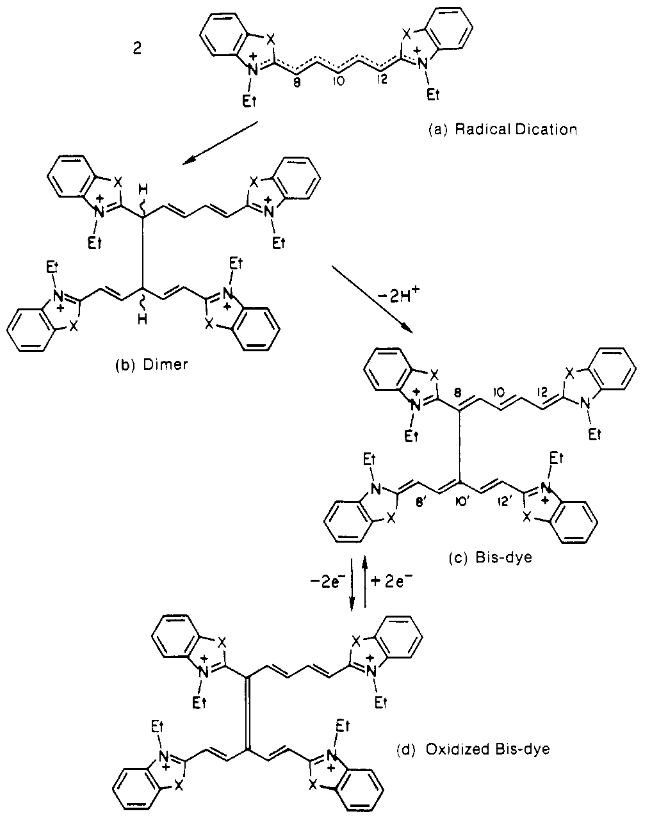
Scheme I



This behavior is consistent with rapid dimerization of the radical dication of **2**. A new wave, R_2, associated with the reduction of the stable dimer, appears at −0.4 V. Subsequent exhaustive reduction of this solution at 0.1 V, a potential capable of reducing the trace radical ion present but not sufficient to directly reduce the dimer,[19] results in nearly complete regeneration of **2** (O_1 is restored). The data of Figure 1A, are consistent with the reversible dimerization of **2** according to eq 1.

The reversibility and products of the oxidation of **3** are quite different from that of **2** as evidenced by the corresponding ssv curves (B) obtained during electrolysis of **3**. Specifically, in the voltammetric data obtained after the electrooxidation step (dashed curve) no wave R_1 and relatively little R_2 is present. A new wave R_3 appears at 0.25 V. Furthermore, upon re-reduction of the electrooxidized solution at 0.1 V, **3** is *not* regenerated. Instead, a new product is formed that exhibits an oxidation wave at ca. 0.4 V (O_2).

Results parallel to those of Figure 1 were obtained in experiments exploring the chemical oxidation of dicarbocyanines **2** and **3** with mild oxidants such as Ag^+ or Fe^{3+}. Oxidation of a methanol/water solution of **2** with excess ferric chloride affords an isolable, UV absorbing, tetracationic dimer (λ_{max} = 342 nm, ϵ_{max} = 8.5 × 10^4 M^{-1} cm^{-1}). Reducing a solution of the dimer with iodide or aqueous ascorbic acid regenerates dye **2** (λ_{max} = 647 nm, ϵ_{max} = 24.2 × 10^4 M^{-1} cm^{-1}). In contrast, treatment of a deep blue solution of **3** (λ_{max} = 650 nm, ϵ_{max} = 24.6 × 10^4 M^{-1} cm^{-1}) in aqueous acetonitrile/methanol with excess ferric ion affords an orange solution having a broad, relatively weak absorption centered at 470 nm. On subsequent treatment of this solution with iodide ion or ascorbic acid the reaction mixture again became bright blue. The product was

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[18] Irreversible dimerization of unsubstituted quinocyanine (monomethine) radical dications was proposed by J. Chang of Kodak's Research Laboratories. A similar mechanism is proposed here for carbocyanine (trimethine) dyes.

[19] Direct electrochemical reduction of the dimers derived from simple cyanines (n = 0) results in regeneration of the parent dye.[18]

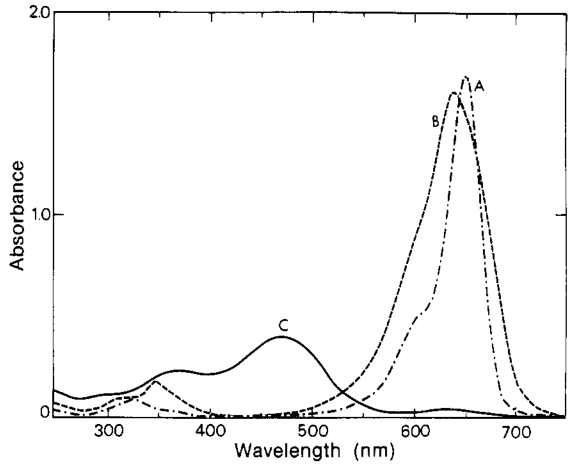

Figure 2. UV–vis spectra in acetonitrile for 6.8 μM solutions of (A) dye 3, (B) bis-dye 3c, and (C) oxidized bis-dye 3d.

precipitated by the addition of aqueous KPF$_6$ and isolated as a dicationic salt. Field desorption mass spectrometry and ^{1}H NMR analysis indicated the product to be a bis-dye, that is, two dye 3 molecules covalently bonded together at the pentamethine linkage. UV–vis spectra measured for the products from the oxidation of 3 are shown in Figure 2.

Scheme I is proposed to describe the reaction pathways and products associated with the chemical or electrochemical oxidation of 3 (where X = S). Radical dication, dimer, bis-dye, and oxidized bis-dye species will subsequently be designated a, b, c, and d, respectively. The radical dication **3a** formed as the result of one-electron oxidation of dye 3 undergoes a rapid and irreversible dimerization reaction. Radical–radical coupling can occur at pentamethine-chain positions of high radical density, i.e., 8, 10, and 12, where positions 8 and 12 are equivalent. Although coupling at the 8,12 positions is statistically favored, the 10 position is the least sterically hindered. The coupling product formed initially is an unstable tetracationic dimer (**3b**). ^{1}H NMR analysis of subsequent products indicates that the 8,10′ isomer is preferentially formed during the dimerization process. The methine protons at the coupling position in the dimer are quite acidic due to the influence of the iminium groups, and as a consequence, the dimer readily deprotonates in methanol or acetonitrile solution.[20] The deprotonation process reestablishes the π-system in the constituent chromophores of the molecule and yields the dicationic bis-dye **3c** (λ_{max} = 638 nm, ϵ_{max} = 24.0 × 10^4 M^{-1} cm^{-1}, Figure 2). The bis-dye is itself electroactive and can be reversibly oxidized in a two-electron process at a potential considerably lower (ca. 250 mV) than that of the original dye. In most experiments, the oxidation of **3** will be driven beyond the bis-dye stage because of the low E_{ox} of **3c** and result in an overall loss of two electrons per chromophore.

The product obtained from a two-electron oxidation of **3c** is the tetracationic species **3d**. Compound **3d** has a cross-conjugated π-system and, in contrast to **3c**, does not have a resonating charge between the nitrogen atoms. As shown in Figure 2, curve C, **3d** exhibits a visible absorption band at shorter wavelengths (λ_{max} = 470 nm, CH$_3$CN) and with a much lower extinction than the bis-dye precursor. Compound **3d** could be isolated and characterized; however, dilute solutions of **3d** in acetonitrile were fairly unstable. Decomposition occurred with partial regeneration of the bis-dye **3c**, and the rate of decomposition was accelerated by the addition of water. The mechanism for this reaction is under investigation.

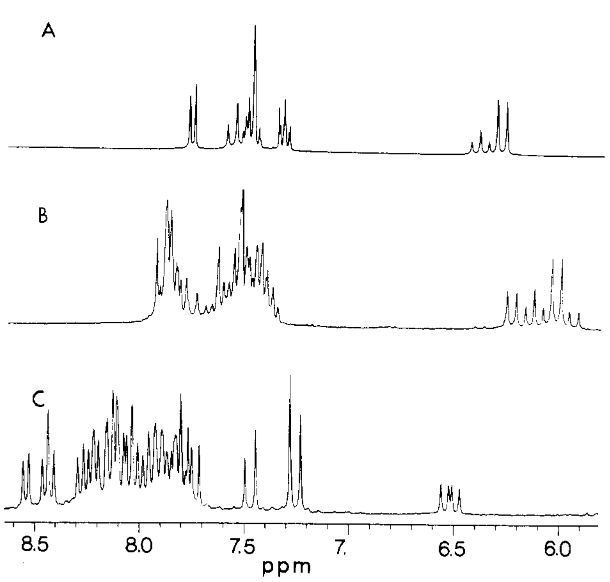

Figure 3. Proton NMR spectra (300 MHz, in CD$_3$CN): (A) dye **3**; (B) bis-dye **3c** (primarily 8,10′ isomer; the doublet at 5.93 ppm is due to the presence of some 10,10′ isomer); (C) **3d**.

Compound **3d** (E_{red} = +0.37 V) can be easily reduced with ascorbic acid or iodide ion back to the bis-dye. ^{1}H NMR analysis indicates that samples of the bis-dye contain primarily the 8,10′ isomer. Figure 3 shows a portion of the ^{1}H NMR spectra (CD$_3$CN) of dye **3**, bis-dye **3c**, and compound **3d**. The protons on the even-numbered carbons of the methine chain of a cyanine dye are shifted upfield relative to the protons on the odd-numbered carbons.[21] Thus dye **3** has absorptions for the C-10 and C-8, C-12 protons at δ 6.42 (t, J = 12.5 Hz, 1 H) and δ 6.32 (d, J = 13.1 Hz, 2 H), respectively. The spectrum of the bis-dye **3c** (8,10′ isomer) has absorptions for the C-10 methine proton, δ 6.12 (t, J = 12.5 Hz, 1 H), the C-12 proton, δ 6.23 (d, J = 13.0 Hz, 1 H), and the two equivalent protons at the 8′ and 12′ positions, δ 6.02 (d, J = 13.5 Hz, 2 H). Crude samples also contain approximately 10% of the 10,10′ isomer which has four equivalent upfield methine protons (8, 8′, 12, 12′), δ 5.93 (d, J = 13.4 Hz). The 8,8′ isomer was not detected. Compound **3d**, which is not a cyanine per se, has a more complex spectrum. The chemical shifts of the methine protons on carbons 8′ and 12′ (as well as 9′ and 11′) are no longer magnetically equivalent since rotation about the 8–10′ bond is not possible. The chemical shifts of these protons cannot be assigned unambiguously. However, COSY and NOE experiments allowed tentative assignment for some of the methine protons. The C-10 proton absorbs at δ 6.51 (dd, J = 10.8 Hz, J = 15.3 Hz, 1 H), the C-12 and C-9′ (or C-11′) protons overlap at δ 7.25 (d, J = 15.3 Hz, 2 H), and the C-8′ (or C-12′) proton absorbs at δ 7.46 (d, J = 15.5 Hz, 1 H).

Space-filling (CPK) molecular models of **3c** indicate that steric crowding involving the heterocyclic nuclei prohibits the two individual chromophores in **3c** from lying in the same plane (with collinear pentamethine chains). The chromophoric units are necessarily twisted from one another but need not be orthogonal. The molecular models indicate a range of acceptable angles in which steric in-

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[20] Water in these solvents is probably acting as a base in these experiments. The appearance of the ssv curves is sensitive to the moisture content of the electrolyte.

[21] Scheibe, G.; Seiffert, W.; Wengenmayr, H.; Jutz, C. *Ber. Bunsenges. Phys. Chem.* **1963**, *67*, 560.

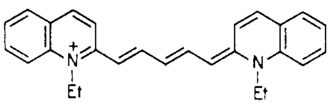
Table I. Spectral and Electrochemical Data for Cyanines and Their Oxidation Products in Acetonitrile[a]

compd[b]	wavelength, nm	$10^{-4}\epsilon$, M^{-1} cm^{-1}	E_{ox}, V	E_{red}, V
3	650	24.6	0.630	−0.885
3c	638	24.0	0.37	
3d	472, 367[c]	5.8, 3.4		
4	706	25.5	0.513	−0.884
4b	344, 243[d]	5.5, 8.3		−0.50
4c	692, 658	27.2, 20.7	0.27	
4d	441, 377, 243	4.8, 4.5, 6.3		
5	639	23.2	0.775	−0.820
5c	639, 589	23.1, 16.4	0.67	
5d	486, 406	4.3, 5.1		
6	580	23.8	0.697	−1.045
6c	574	20.5	0.41	
6d	450	5.2		
7	660	25.7	0.65	−0.87
7c	650	7.2		
7d	496	26.7		
8	645	13.8	0.625	−0.980
8b	345	4.8		−0.50
9	554	15.0	0.902	−1.060
9h	545, 520	12.1, 11.8	0.55	
9i	434	4.2		
10	593	15.5	0.77	−1.068
10h	582, 552	10.5, 10.3	0.43	
10i	504	3.5		
11	571	11.4		
11f	363	5.5		
12	578	15.4	0.745	−1.138
12e	472	8.2		
13	544	14	1.088	−1.000
13e	480	6.5		

[a] Redox potentials for dyes were measured by phase-selective second-harmonic ac voltammetry and are reproducible within a few millivolts. Data for oxidation products were obtained by cyclic voltammetry and are accurate to ±0.01 V. All potentials were measured in $CH_3CN/0.1$ M $TBABF_4$ and are reported vs Ag/AgCl. [b] See text for compound designations. [c] In methylene chloride/acetonitrile 85:15. [d] In methylene chloride/acetonitrile 90:10.

teractions are minimized. Steric crowding in cyanine dyes is known to be accompanied by a lowering of ϵ_{max} and a broadening of the spectral absorption band.[22,23] The fact that the visible absorption band of the bis-dye is substantially broader than that of the parent dye is consistent with some degree of residual crowding in the bichromophoric molecule **3c**.

In examining the chemical and electrochemical oxidation of other unsubstituted dicarbocyanine dyes we found Scheme I to be a general reaction mechanism that describes the chemistry of this dye class.[24] The relative distributions of products, however, was found to be strongly dependent on the nature of the cyanine heterocycle. For example, in acetonitrile or methanol solution, the chemical oxidation of the dicarbocyanine derived from 2-quinoline, **4** (λ_{max} = 706 nm, CH_3CN), does not proceed to the extent found for the benzothiazole analogue **3**. While dimerization of the radical dication derived from **4** is rapid and irreversible, the methine protons of the dimer of **4** (i.e., **4b**) are less acidic than those in **3b**. In acetonitrile, **4b** was isolable as the PF_6 salt (λ = 344 nm, CH_3CN). Deprotonation of the dimer **4b** to yield the corresponding bis-dye **4c** (λ_{max} = 692 nm, CH_3CN) could be accomplished in acetonitrile solution by the addition of base (pyridine or triethylamine).[25] On the other hand, for the dicarbocyanines derived from 3,3′-dimethylindole (dye **5**), benzoxazole (dye **6**), and benzoselenazole (dye **7**), oxidation to the analogous tetracationic species **5d**, **6d**, and **7d** was facile. Spectral and electrochemical data obtained for the dyes and their corresponding oxidation products are listed in Table I.[26]



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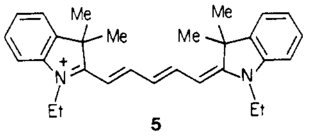

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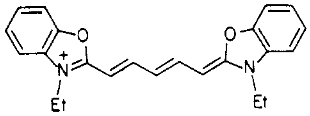

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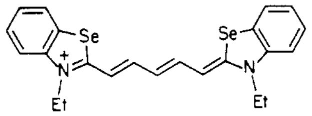

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Steric features specific to a nucleus of a dicarbocyanine also influence the coupling position found in the corresponding dimeric oxidation products. The particular isomer(s) afforded by oxidation via the described methods depends on the degree of residual crowding[27] involving the heterocycle and the pentamethine carbons. For instance, in the relatively unhindered dye **3**, a mixture of bis-dye isomers was obtained with the statistically favored 8,10′ isomer being dominant. For dye **4**, on the other hand, where the 3,3′ hydrogens of the quinoline nucleus crowd the adjacent methine carbons, radical coupling is seen to predominantly occur at the central position of the methine chain.[28] Steric crowding of carbons 8 and 12 is enhanced in compound **5** where the *gem*-dimethyl groups of the indole nucleus selectively inhibits radical–radical coupling at these methine carbons. The bis-dye **5c** could be isolated in good yield and, according to ^1H NMR analysis, consisted almost exclusively of the 10,10′ isomer.

The electrochemical data shown in Figure 1 together with data presented previously[15] demonstrate that alkyl substituents positioned on the even-numbered carbons of the methine chain have a significant effect on the oxidation chemistry of dicarbocyanine dyes. Surprisingly, dye **2**, which contains only a 10-methyl group, undergoes a reversible dimerization, whereas unsubstituted analogs **3**, **6**, and **7** irreversibly dimerize. The 10-methyl substituent in **2** has the capacity to electronically stabilize the radical,[29]

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(22) Brooker, L. G. S.; White, F. L.; Heseltine, D. W.; Keyes, G. H.; Dent, S. G.; Van Lare, E. J. *J. Photogr. Sci.* **1953**, *1*, 173.

(23) Brooker, L. G. S.; White, F. L.; Sprague, R. H.; Dent, S. G.; Van Zandt, G. *Chem. Rev.* **1947**, *41*, 325.

(24) Scheme I outlines the general oxidation route for dicarbocyanine dyes but shows the isomer (8,10′) preferred for dye **3**. Other dicarbocyanines may yield different isomers or isomer distributions.

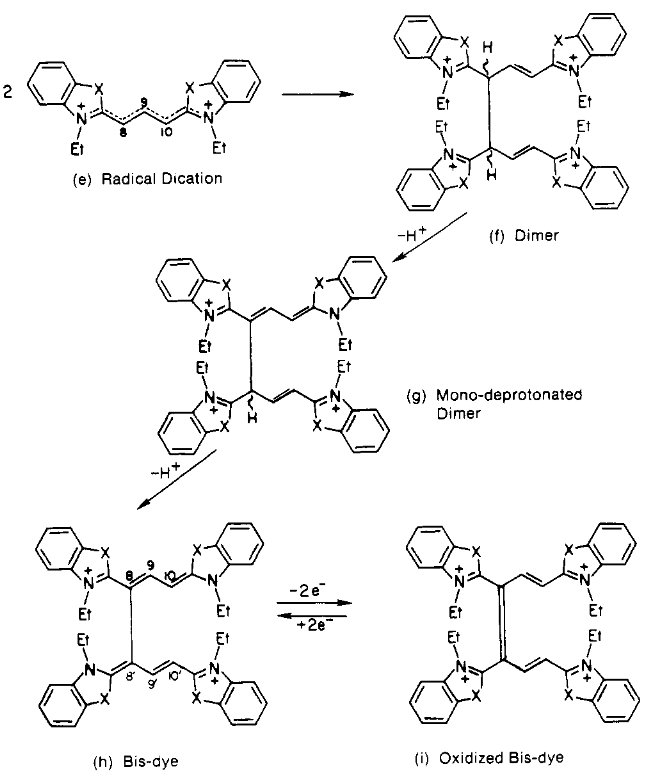
(25) Treatment of dimer **4b** with base also yields decomposition products in which the chromophore is destroyed.

(26) For some dyes (**6** and **7**) electrolysis solutions were pumped to a Hewlett-Packard 8450A diode array spectrophotometer equipped with a 1-mm quartz spectral flow cell for measurement of absorption spectra.

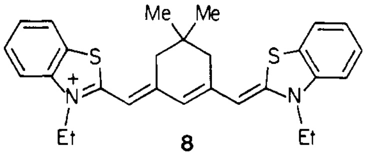
(27) Residual crowding as defined in ref 22 refers to steric interactions involving the heterocycle and the hydrogens of the methine chain. For a given heterocyclic nucleus, residual crowding effects are independent of the length of the methine chain.

(28) In dicarbocyanines **3**, **5**, **6**, and **7**, the first, third, and fifth carbon atoms of the polymethine chain are numbered 8, 10, and 12, respectively. Due to the additional carbon in the quinoline nucleus, the corresponding methine carbons in dye **4** are properly numbered 9, 11, and 13.

Scheme II



as well as to introduce a certain amount of steric strain in the dimer. The relative importance of electronic versus steric factors in determining the reversibility of the dimerization process was not obvious from the available data. This issue was addressed by examining the oxidation of 9,11-neopentylene-substituted dicarbocyanine 8 (λ_{max} = 645 nm, ϵ_{max} = 13.8 × 10^4 M^{-1} cm^{-1}, CH_3CN). CPK molecular models indicate that the neopentylene bridge should introduce considerable steric strain in the corresponding dimer formed by coupling at either the 8, 10, or 12 methine carbon atoms. The particular alkyl substitution in this dye, however, solely occupies the *odd-numbered* methine carbons and therefore is not expected to electronically stabilize the radical to an appreciable extent because of the low radical electron density at these methine positions. Cyclic voltammetry data show 8 undergoes an



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irreversible one-electron oxidation in acetonitrile. Controlled-potential coulometry experiments (oxidation at 0.7 V followed by reduction at 0.1 V) confirmed that the coupling reaction was indeed irreversible. Chemical oxidation of 8 (ferric ion in acetonitrile) affords a tetracationic dimer product, **8b** (λ_{max} = 345 nm, ϵ_{max} = 4.8 × 10^4 M^{-1} cm^{-1}, CH_3CN), which could be isolated. Overall, these results indicate that electronic stabilization is critical both to the persistence of the radical and to the reversibility of the radical coupling process.

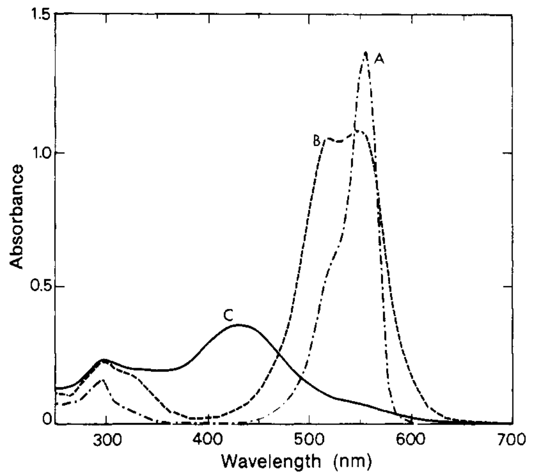
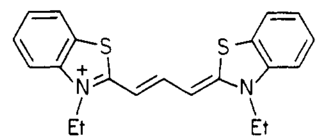
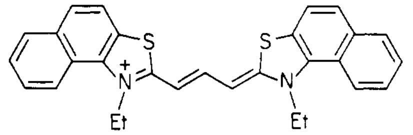


Figure 4. UV-vis spectra for 9.1 μM solutions of (A) dye **9**, (B) bis-dye **9h**, and (C) oxidized bis-dye **9i**, in acetonitrile.

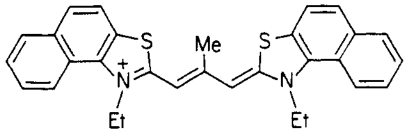
Carbocyanines. Radical dications generated via one-electron oxidation of unsubstituted carbocyanine dyes are also subject to dimerization at the even-numbered carbons of the methine chain. The products and reaction mechanisms associated with the oxidation of carbocyanines are analogous to those outlined for dicarbocyanines, with the notable exception that removal of the methine protons from the coupling carbons of carbocyanine dimers sometimes occurs in a stepwise manner. Scheme II is offered as a general mechanism for the oxidation of carbocyanine dyes but specifically depicts the products associated with the oxidation of **9**. Radical dication, dimer, monodeprotonated dimer, bis-dye, and oxidized bis-dye species derived from *carbocyanine* dyes will subsequently be designated e, f, g, h, and i, respectively. Spectral and electrochemical data obtained for the products isolated from the chemical (ferric chloride or tris(4-bromophenyl)aminium hexachloroantimonate[30,31]) or electrochemical (preparative-scale coulometry) oxidation of dyes **9–11** are listed in Table I.



9



10



11

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(29) Alkyl groups can stabilize the radical by hyperconjugation. In addition, examination of resonance forms in which the radical is localized on the chain indicates that two iminium functional groups are present. Electron-releasing by alkyl groups via hyperconjugation combined with the electron-accepting ability of the iminium functional groups may provide enhanced radical stabilization. This effect has been referred to as "captodative" (Stella L.; Janousek Z.; Merenyi R.; Viehe H. G. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 691), as "merostabilization" (Baldock R. W.; Hudson P.; Katritzky A. R.; Soti F. *Perkin Trans.* **1974**, *1*, 1422), and as a "push-pull effect" (Balaban A. T.; Caproiu M. T.; Negoita N.; Baican R. *Tetrahedron* **1977**, *33*, 2249.

(30) Bell, F. A.; Ledwith, A.; Sherrington, D. C. *J. Chem. Soc. C* **1969**, 2719.

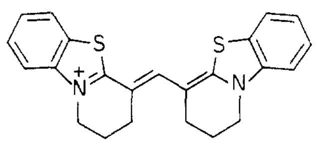
(31) Due to the high E_{ox} of dyes **9** and **10**, chemical oxidation required the use of the more powerful oxidant tris(4-bromophenyl)aminium hexachloroantimonate.

Oxidation of **9** (λ_{max} = 554 nm, ϵ_{max} = 15.0 × 10^4 M^{-1} cm^{-1}) in acetonitrile initially yields a solution with UV–vis absorption bands at λ = 305 and 575 nm. The 305-nm band corresponds to the dimer formed via coupling of radical dications at the 8,8′ positions. The dimer **9f** has two acidic methine protons with distinctly different pK_a's. On standing, monodeprotonation of **9f** occurs in acetonitrile affording **9g** (λ_{max} = 575 nm) which was too unstable to isolate. Addition of base (pyridine or triethylamine) to the solution of **9g** gave a species having a broad absorption at λ = 545 nm that was isolated, purified, and identified by ^{1}H NMR spectroscopy and field desorption mass spectrometry as the bis-dye **9h** (λ_{max} = 545, 520 nm, ϵ_{max} = 12.1 × 10^4, 11.8 × 10^4 M^{-1} cm^{-1}, CH_3CN, see Figure 4B).[32]

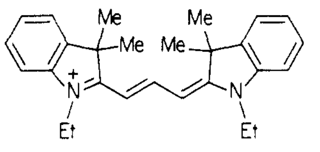
It is notable that deprotonation of **9f** occurs in a manner allowing observation of **9g**, whereas, under similar experimental conditions, the corresponding protons in the homologous dicarbocyanine dimer **3b**, although undoubtedly having different pK_a's, are both removed under the reaction conditions. This reactivity difference is probably related to steric factors associated with coupling at the 8,8′ methine carbons. Removal of the first proton from **9f** essentially yields a carbocyanine dye that has a bulky substituent at the 8-methine position. Molecular models indicate the quaternary nuclei in **9g** to be twisted from planarity. The twisted structure may be responsible for the lower acidity of the methine proton. Similar steric congestion in dicarbocyanine dimers is not encountered since radical coupling produces 8,10′ and 10,10′ isomers.[33]

Dyes **10** and **11** dimerized in a manner identical with that found for **9**. The bis-dye **10g** was readily isolated; however, treatment of the dimer of **11**, **11f**, with base resulted in decomposition of the dimer and loss of the chromophore. Apparently, the steric congestion added by the 9-methyl substituent further reduces the acidity of the methine protons in **11f**.[34]

Like radical dications derived from dicarbocyanine dyes, the one-electron oxidized forms of carbocyanine dyes are stabilized by alkyl substitution at the even-numbered carbons of the methine chain. The carbocyanine dye **12**, which contains trimethylene bridging groups at the 8- and 10-methine carbons, exhibits reversible, one-electron cyclic voltammetry (measured at 0.1 V/s) in acetonitrile solution. The electrochemical data indicate that the half-life of the radical dication form of **12** (**12e**) is at least 5 min. Radical persistence in **12e** is attributed to electronic stabilization by the alkyl substituents and to steric hindrance to dimerization. As indicated by their anodic cyclic voltammetric response, radical dications of dyes having no methine chain substituents or containing a methyl group at the odd-numbered (9) methine carbon undergo irreversible dimerization on the millisecond time scale. Irreversible cyclic voltammetry was observed for dyes **9–11** in experiments using potential scan rates ranging from 20 mV/s to 1000 V/s.



12



13

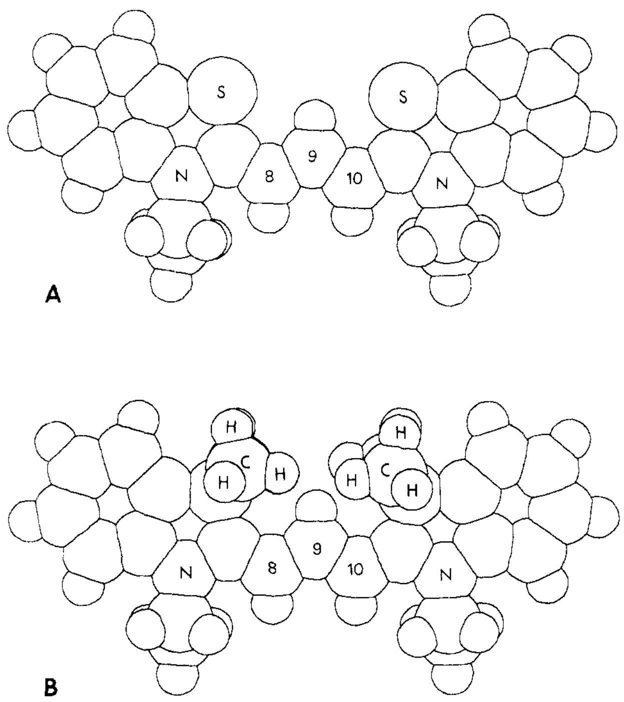


Figure 5. Computer-generated representations of (A) 3,3′-diethylthiacarbocyanine **9** and (B) 3,3′-diethyl-1,1′-dimethylindolocarbocyanine **13**.

Since radical coupling in carbocyanine radical dications is limited to the methine carbons adjacent to the heterocyclic nuclei, the effect of steric interactions introduced by residual crowding[27] inherent to a heterocycle can be pronounced. Correlation of molecular structures with the radical dication reactivities for carbocyanine dyes derived from benzothiazole (**9**) and 3,3-dimethylindole (**13**) demonstrate this point. Figure 5 shows computer-generated representations of **9** and **13** in which the geometries were optimized by using molecular mechanics.[35] Figure 5A shows that the sulfur atoms in **9** do not appreciably crowd the methine chain and thus are not expected to impede radical coupling at carbons 8 or 10. This molecular structure is consistent with the rapid and irreversible dimerization of the radical dication of **9**. In contrast, the molecular structure of dye **13**, as shown in Figure 5B, is seen to be significantly crowded. The gem dimethyl groups of the indole nucleus, in conjunction with the *N*-ethyl groups, clearly occupy the space surrounding the sites of high radical density. Radical persistence in a close analogue of **13** has been demonstrated.[16] We have found **13** to exhibit reversible cyclic voltammetry in acetonitrile at potential sweep rates ranging from 20 mV/s to 200 V/s. The half-life of the radical dication of **13** has been mea-

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(32) Consistent with this mechanism, careful treatment of bis-dye **9h** with trifluoroacetic acid regenerates the spectrum associated with dye **9g**.

(33) Increasing the chain length in a thiacyanine dye increases the pK_a of the dye: Beretta P.; Jaboli A. *J. Photogr. Sci. Eng.* **1974**, *18*, 197. Herz, A. H. *J. Photogr. Sci. Eng.* **1974**, *18*, 207. If only electronic factors were important, it seems likely that deprotonation of **9f** should be favored over that of **3b**; however, the opposite is observed. This suggests that steric factors have a major effect.

(34) In addition, the specific molecular configuration of **11f** may make the removal of the remaining proton kinetically slow for steric reasons.

(35) Molecular mechanics forces were calculated by using MacroModel (the Columbia Chemistry Molecular Modelling System, 1988). Graphic display of the structures was accomplished by using the software package Chem-X, developed and distributed by Chemical Designs Ltd., Oxford, England.

sured to be ca. 30 min in acetonitrile solution.[36] Radical persistence in **13** is attributed here to steric hindrance to dimerization.

Summary and Conclusions

The chemistry of radical dications formed by the one-electron oxidation of carbocyanine and dicarbocyanine dyes was found to depend on the nature of the dye heterocycle and on the degree of alkyl substitution in the polymethine chain. Unless prevented by steric factors, the radical dications are susceptible to dimerization at the even-numbered carbon atoms of the polymethine chain. For dicarbocyanine radicals bearing one or more alkyl substituents at the even-methine positions, the dimerization reaction is found to be reversible. Similar reversibility in the dimerization of analogous carbocyanine radicals has not yet been demonstrated. Other carbocyanine and dicarbocyanine radical dications, which are unsubstituted or are substituted exclusively on odd-numbered methine carbons, undergo a dimerization reaction that is totally irreversible. Deprotonation of the resultant UV-absorbing dimers reestablishes π-electron delocalization in these molecules, giving dicationic bis-dyes whose spectral properties are similar to that of the parent dye. These bis-dyes are susceptible to further oxidation via a reversible two-electron mechanism to yield highly unsaturated, cross-conjugated, tetracationic species.

Extensive synthetic procedures for generating cyanine dyes of diverse molecular structure have been reported.[37] The degree of steric congestion in these molecules can be controlled by substituent modifications involving either the heterocyclic nuclei or the polymethine chain. As demonstrated in this report, the radical dications derived from cyanine dyes offer excellent models in which to study the interplay of the electronic and steric effects on radical stability and persistence.

Experimental Section

Materials. 3,3′-Diethylthiadicarbocyanine iodide, 1,1′-diethyl-2,2′-dicarbocyanine iodide, and 3,3′-diethyloxadicarbocyanine iodide were commercially available (Kodak Laboratory Chemicals). Other dyes were synthesized by previously established procedures.[37] Dyes obtained with iodide counterions were converted to hexafluorophosphate or tetrafluoroborate salts by dissolving the dye in methanol/water, adding aqueous potassium hexafluorophosphate (Alfa) or sodium tetrafluoroborate (MCB), and diluting with water as necessary to precipitate the dye. Dye purity was established by ionographic analysis, thin-layer chromatography, and comparison of the dye extinction coefficient with established standards when possible. Ferric chloride hexahydrate (Kodak Laboratory Chemicals) was ground to a fine powder before use. Tris(4-bromophenyl)aminium hexachloroantimonate (Aldrich) was used as received. Tetrabutylammonium tetrafluoroborate (TBABF$_4$, Kodak Laboratory Chemicals) for electrochemistry was recrystallized three times from ethanol/water mixtures and dried in vacuo. Acetonitrile (MCB spectrograde) for electrochemistry was dried over 4-Å molecular sieves (Kodak Laboratory Chemicals, baked at 400 °C).

Apparatus. Electrochemical measurements were performed using a Princeton Applied Research Corp. (PAR) 173 potentiostat in conjunction with a PAR 175 universal programmer, PAR 179 digital coulometer, and PAR 124A lock-in amplifier. A Hewlett-Packard 239A low-distortion oscillator was used in ac measurements. Formal oxidation and reduction potentials were obtained via phase-selective second-harmonic ac voltammetry (quadrature component) at an applied frequency of 400 Hz (16-mV peak-to-peak signal) as described previously.[10] Voltammetric data were obtained at 22 °C at a platinum disk electrode (0.02 cm^2). Controlled-potential coulometry was performed with a PAR 337A cell system equipped with a Pt gauze working electrode (67 cm^2). Compounds **6c**, **6d**, **7c**, and **7d** were not isolated in solid form. The data listed in Table I for these oxidation products were obtained by direct analysis of electrolysis solutions. Solutions of **6d** and **7d** were prepared by exhaustive two-electron electrolysis at 0.8 V. Subsequent conversion of the respective products to **6c** and **7c** was accomplished by reduction at 0.1 V. Assignment of spectral data to a particular oxidation product was made on the basis of the similarities in the redox behavior noted for the unsubstituted dicarbocyanines **3**–**7**. All potentials were measured vs the NaCl saturated calomel electrode and converted to the Ag/AgCl reference by adding 40 mV. UV–vis spectra were recorded on a Perkin-Elmer Lambda 5 spectrophotometer. Nuclear magnetic resonance (^{1}H and ^{13}C NMR) spectra chemical shifts are reported in δ units, parts per million (ppm) downfield from tetramethylsilane, and were measured by using a General Electric QE-300 or IBM WP270SY spectrometer. Mass spectra (MS) were obtained on a field desorption instrument. Microanalyses were performed at Kodak's facilities. Melting points were obtained on a Thomas-Hoover apparatus using open capillary tubes and are uncorrected.

3,3′-Diethylthiadicarbocyanine Hexafluorophosphate (3). The iodide salt was converted to the hexafluorophosphate salt: mp 246–249 °C; λ_{max} = 650 nm (CH$_3$CN), ϵ_{max} = 24.6 × 10^4 M^{-1} cm^{-1}; ^{1}H NMR (CD$_3$CN) δ 1.39 (t, J = 7.2 Hz, 6 H), 4.25 (q, J = 7.2 Hz, 4 H), 6.32 (d, J = 13.1 Hz, 2 H), 6.42 (t, J = 12.5 Hz, 1 H), 7.35 (td, J = 7.3 Hz, J = 1.5 Hz, 2 H), 7.48–7.62 (m, 6 H), 7.79 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ((CD$_3$)$_2$SO) δ 12.49, 41.31, 99.99, 113.02, 120.69, 122.89, 124.89, 125.40, 127.97, 140.92, 150.35, 163.22. Anal. Calcd for $C_{23}H_{23}N_2S_2{\cdot}PF_6$: C, 51.5; H, 4.3; N, 5.2. Found: C, 51.5; H, 4.2; N, 5.2.

8,10′-Bis(3,3′-diethylthiadicarbocyanine) Bis(hexafluorophosphate) (3c). Ferric chloride hexahydrate (450 mg, 1.67 mmol) in 15 mL of water was added to a solution of **3** (400 mg, 0.75 mmol) in 50 mL of acetonitrile and 25 mL of methanol. The color of the reaction mixture rapidly turned from deep blue to orange. After stirring 10 min, the solution was filtered and then combined with a solution of ascorbic acid (500 mg, 2.84 mmol) in 75 mL of methanol/water (50:50). The reaction mixture became bright blue. The solution was filtered into 50 mL of water containing potassium hexafluorophosphate (750 mg, 4.08 mmol), and the mixture was diluted with 200 mL of water. The resulting precipitate was allowed to settle, collected, washed with water, and dried, affording 350 mg (87% yield) of **3c**: mp 183–186 °C (dec); λ_{max} = 638 nm (CH$_3$CN), ϵ_{max} = 24.0 × 10^4 M^{-1} cm^{-1}. ^{1}H NMR analysis indicated a mixture of 90% of the 8,10′ isomer and 10% of the 10,10′ isomer as determined by integration of the methine protons. ^{1}H NMR (CD$_3$CN) for the major isomer: δ 1.15 (t, J = 7.2 Hz, 6 H), 1.26 (t, J = 7.2 Hz, 3 H), 1.58 (t, J = 7.2 Hz, 3 H), 4.18 (m, 6 H), 4.56 (q, J = 7.2 Hz, 2 H), 6.02 (d, J = 13.5 Hz, 2 H), 6.12 (t, J = 12.5 Hz, 1 H), 6.23 (d, J = 13.0 Hz, 1 H), 7.3–8.0 (m, 20 H). The minor isomer had a doublet at δ 5.93 (J = 13.4 Hz). Field desorption mass spectrum: m/e, 925 $(M{\cdot}PF_6)^+$, 535 $(M{\cdot}(PF_6)_2)^{2+}$. Anal. Calcd for $C_{46}H_{44}N_4S_4{\cdot}2PF_6$: C, 51.5; H, 4.1; N, 5.2. Found C, 51.4; H, 4.1; N, 5.1. The product was recrystallized twice from methylene chloride/ethanol, and a sample of a pure 8,10′ isomer was obtained (50 mg, 12% yield), mp 210.5–211.5 °C (dec).

2,2′-(4-(3-Ethyl-2-benzothiazolio)-3-(2-(3-ethyl-2-benzothiazolio)vinyl)-1,3,5,7-octatetraene-1,8-diyl)bis(3-ethylbenzoliazolium) tetrakis(hexafluorophosphate) (3d) was prepared by addition of ferric chloride hexahydrate (400 mg, 1.5 mmol in 15 mL of water) to a solution of **3** (300 mg, 0.56 mmol) in 50 mL of acetonitrile and 25 mL of methanol. After stirring for 10 min, the solution was poured into 150 mL of methanol/water (50:50), potassium hexafluorophosphate (1.0 g, 5.4 mmol) in 75 mL of water was added, and the solution was then diluted to 400 mL with water. After chilling overnight at 5 °C, the orange precipitate was collected, washed with water, and dried, affording 360 mg of product (95% yield), mp 153–156 °C (dec). The product was dissolved in 20 mL of acetonitrile and filtered into 400 mL of ethyl acetate, and **3d** was collected (230 mg, 61% yield): mp 157–160 °C (dec); λ_{max} = 472 nm (CH$_2$Cl$_2$/CH$_3$CN (85:15)), ϵ_{max} = 5.8 × 10^4 M^{-1} cm^{-1}; ^{1}H NMR (CD$_3$CN) δ 1.47 (m, 6 H), 1.62

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[36] Lenhard, J., unpublished results.

[37] Hamer, F. M. In *The Chemistry of Heterocyclic Compounds*; Weissberger, A., Ed.; Interscience: New York, 1964; Vol. 18.

(m, 6 H), 4.60 (q, J = 7.3 Hz, 2 H), 4.80 (m, 6 H), 6.51 (dd, J = 10.8 Hz, J = 15.3 Hz, 1 H), 7.25 (d, J = 15.3 Hz, 2 H), 7.46 (d, J = 15.5 Hz, 1 H), 7.7–8.3 (m, 17 H), 8.43 (t, J = 8.3 Hz, 2 H), 8.54 (d, J = 8.2 Hz, 1 H); ^{13}C NMR (CD_3CN) δ 12.76, 13.13, 13.27, 13.41, 44.90, 45.40, 45.61, 47.37, 116.10, 117.72, 120.47, 122.66, 123.62, 123.66, 123.93, 124.33, 124.91, 128.79, 128.85, 129.13, 129.32, 129.41, 129.62, 129.82, 130.15, 130.22, 130.56, 130.76, 132.16, 136.81, 137.43, 139.85, 139.93, 140.80, 141.04, 142.22, 145.35, 166.70, 168.30, 169.09, 169.20. Anal. Calcd for $C_{46}H_{44}N_4S_4 \cdot 4PF_6$: C, 40.6; H, 3.3; N, 4.1. Found: C, 40.6; H, 3.3; N, 4.1.

1,1′-Diethyl-2,2′-dicarbocyanine (4) was used either as the iodide salt (Eastman) or it was converted to the hexafluorophosphate salt: mp >250 °C; λ_{max} = 706 nm (CH_3CN), ϵ_{max} = 25.5 × 10^4 M^{-1} cm^{-1}; ^{1}H NMR ($(CD_3)_2SO$) δ 1.40 (m, 6 H), 4.46 (m, 4 H), 6.34 (d, J = 12.3 Hz, 2 H), 6.65 (t, J = 12.3 Hz, 1 H), 7.44 (td, J = 7.3 Hz, J = 2.6 Hz, 2 H), 7.71–8.08 (m, 12 H); ^{13}C NMR ($(CD_3)_2SO$) δ 12.19, 42.71, 105.29, 115.79, 119.30, 123.07, 124.62, 124.71, 128.99, 132.42, 135.58, 138.64, 149.61, 150.70. Anal. Calcd for $C_{27}H_{27}N_2 \cdot PF_6 \cdot {}^1/_2H_2O$: C, 60.8; H, 5.3; N, 5.3. Found C, 61.0; H, 5.2; N, 5.2.

Dimer 4b was prepared by addition of ferric chloride hexahydrate (300 mg, 1.1 mmol in 15 mL of water) to 4 (hexafluorophosphate counterion, 520 mg, 1.0 mmol) dissolved in 50 mL of acetonitrile containing 25 mL of methanol. The blue solution immediately turned brown. After stirring for 5 min, the solution was filtered into 150 mL of methanol/water (50:50), and potassium hexafluorophosphate (1.0 g) was added in 100 mL of water. The mixture was diluted to a volume of 450 mL with water, and the solid formed was collected, washed with water, and dried under vacuum affording 570 mg (85% yield) of **4b**: mp 165–169 °C (dec); λ = 344 nm (CH_2Cl_2/CH_3CN (90:10)), ϵ = 5.45 × 10^4 M^{-1} cm^{-1}; ^{1}H NMR (CF_3CO_2D) δ 1.4–2.2 (m, 12 H), 5.0–5.8 (m, 10 H), 7.1–7.9 (m, 6 H), 8.0–8.8 (m, 22 H), 8.9–9.4 (m, 4 H). Anal. Calcd for $C_{54}H_{54}N_4 \cdot 4PF_6 \cdot H_2O$: C, 47.7; H, 4.1; N, 4.1. Found: C, 47.4; H, 4.0; N, 4.1.

11,11′-Bis(1,1′-diethyl-2,2′-dicarbocyanine) Bis(hexafluorophosphate) (4c). **4** (Iodide counterion, 2.0 g, 4.0 mmol) in 900 mL of warm methanol was combined with ferric chloride hexahydrate (2.0 g, 7.4 mmol) in 600 mL of water. The mixture was filtered, and triethylamine (2.0 g, 20.0 mmol) was added, generating a deep blue solution. This was filtered into 300 mL of water containing potassium hexafluorophosphate (5.0 g, 27.2 mmol), and the resulting precipitate was collected and dried (1.0 g, 48% yield). A portion of the product (260 mg) was purified by dissolving it in the minimum amount of methylene chloride and filtering this solution into 150 mL of methanol with stirring. The solution was gently warmed until crystals began forming. After standing at room temperature for two days **4c** was collected (120 mg): mp 218–223 °C (dec); λ_{max} (CH_3CN) = 692 nm, ϵ_{max} = 27.2 × 10^4 M^{-1} cm^{-1}; ^{1}H NMR (CD_3CN) δ 1.23 (t, J = 7.0 Hz, 12 H), 4.24 (q, J = 7.0 Hz, 8 H), 5.95 (d, J = 13.5 Hz, 4 H), 7.45 (td, J = 6.9 Hz, J = 1.2 Hz, 4 H), 7.65–7.80 (m, 12 H), 7.94 (s, 8 H), 8.18 (d, J = 13.5 Hz, 4 H); ^{13}C NMR ($(CD_3)_2SO$) δ 11.79, 42.97, 103.58, 115.95, 119.26, 124.74, 125.10, 126.05, 129.12, 132.69, 136.37, 138.57, 149.25, 151.19. Field desorption mass spectrum, m/e 378 (M^{2+}), 756 (M^+). Anal. Calcd for $C_{54}H_{52}N_4 \cdot 2PF_6 \cdot H_2O$: C, 60.8; H, 5.1; N, 5.3. Found: C, 61.0; H, 5.0; N, 5.3.

2,2′-(3,4-Bis(2-(1-ethyl-2-quinolinio)vinyl))-1,3,5-hexatriene-1,6-diyl)bis(1-ethylquinolinium) tetrakis(hexafluorophosphate) (4d) was prepared by combining 250 mg (0.24 mmol) of **4c** in 50 mL of methanol with ferric chloride hexahydrate (500 mg, 1.8 mmol) in 25 mL of water with stirring. The blue solution became yellow and was added to a solution of potassium hexafluorophosphate (1.0 g) in 150 mL of water. The product precipitated, was collected, washed with water, and dried (260 mg). This material was purified by dissolving it in 20 mL of dry acetonitrile and filtering it into 150 mL of ethyl acetate with stirring. The solid formed was collected and dried, affording 130 mg (41% yield) of **4d**: mp 149–169 °C (dec); λ_{max} (CH_3CN) = 441 nm, ϵ_{max} = 4.8 × 10^4 M^{-1} cm^{-1}; ^{1}H NMR (CD_3CN) δ 1.60 (t, J = 7.3 Hz, 12 H), 4.95 (q, J = 7.3 Hz, 8 H), 7.49 (d, J = 15.7 Hz, 4 H), 7.98 (d, J = 15.7 Hz, 4 H), 7.96 (d, J = 8.5 Hz, 4 H), 8.20 (t, J = 8.0 Hz, J = 1.0 Hz, 4 H), 8.3–8.45 (m, 12 H), 8.95 (d, J = 8.8 Hz, 4 H). Anal. Calcd for $C_{54}H_{52}N_4 \cdot 4PF_6 \cdot H_2O$: C, 47.9; H, 4.0; N, 4.1. Found: C, 47.7; H, 3.9; N, 4.0.

1,1′-Diethyl-3,3,3′,3′-tetramethylindolodicarbocyanine Hexafluorophosphate (5). The iodide salt was prepared by standard methods and converted to the hexafluorophosphate salt: mp 191–194 °C (dec); λ_{max} = 639 nm (CH_3CN), ϵ_{max} = 23.2 × 10^4 M^{-1} cm^{-1}; ^{1}H NMR (CD_3CN) δ 1.38 (t, J = 7.2 Hz, 6 H), 1.73 (s, 12 H), 4.09 (q, J = 7.2 Hz, 4 H), 6.23 (d, J = 13.8 Hz, 2 H), 6.55 (t, J = 13.8 Hz, 1 H), 7.28 (t, J = 8.6 Hz, 4 H), 7.44 (t, J = 7.4 Hz, 2 H), 7.51 (d, J = 7.4 Hz, 2 H), 8.11 (t, J = 13.2 Hz, 2 H); ^{13}C NMR ($(CD_3)_2SO$) δ 12.05, 27.02, 38.46, 48.87, 102.70, 110.78, 122.38, 124.64, 125.32, 128.38, 141.18, 141.51, 154.07, 172.20. Anal. Calcd for $C_{29}H_{35}N_2 \cdot PF_6$: C, 62.5; H, 6.3; N, 5.0. Found: C, 62.3; H, 5.9; N, 4.9.

10,10′-Bis(1,1′-diethyl-3,3,3′,3′-tetramethylindolodicarbocyanine) Bis(hexafluorophosphate) (5c). Ferric chloride hexahydrate (3.7 g, 13.7 mmol) was added portionwise to a solution of **5** (hexafluorophosphate counterion, 1.0 g, 1.8 mmol) in 75 mL of acetonitrile. The solution rapidly turned from dark blue to orange/red. The solution was filtered into a mixture of ascorbic acid (4.0 g, 22.8 mmol), 200 mL of methanol/water (50:50), and 2 mL of pyridine. The solution was filtered, and potassium hexafluorophosphate (8.0 g, 43.0 mmol) in 200 mL of water was added. An additional portion of 100 mL of water was added, and the product was collected and dried, affording 1.1 g of a green solid. The dye was purified by dissolving it in 80 mL of methylene chloride and adding 150 mL of toluene. After heating to reflux, the product crystallized out of solution, and it was collected and dried affording 440 mg (44% yield) of **5c**: mp 194–197 °C (dec); λ_{max} = 639 nm (CD_3CN), ϵ_{max} = 23.1 × 10^4 M^{-1} cm^{-1}; ^{1}H NMR (CD_3CN) δ 1.12 (t, J = 7.2 Hz, 12 H), 1.81 (s, 24 H), 3.93 (q, J = 7.2 Hz, 8 H), 5.82 (d, J = 14.2 Hz, 4 H), 7.21 (d, J = 7.8 Hz, 4 H), 7.30 (t, J = 7.3 Hz, 4 H), 7.41 (t, J = 7.8 Hz, 4 H), 7.55 (d, J = 7.3 Hz, 4 H), 8.34 (d, J = 14.2 Hz, 4 H); ^{13}C NMR ($(CD_3)_2SO$) δ 11.89, 27.02, 38.70, 49.14, 100.41, 111.05, 122.50, 125.12, 126.72, 128.46, 141.26, 152.86, 172.76. Anal. Calcd for $C_{58}H_{68}N_4 \cdot 2PF_6 \cdot 2H_2O$: C, 60.7; H, 6.3; N, 4.9. Found: C, 60.5; H, 6.0; N, 4.7.

2,2′-(3,4-Bis(1-ethyl-3,3-dimethyl-2-indolio)vinyl)-1,3,5-hexatriene-1,6-diyl)bis(1-ethyl-3,3-dimethylindolium) tetrakis(hexafluorophosphate) (5d) was prepared by combining ferric chloride hexahydrate (500 mg, 1.8 mmol) with **5c** (200 mg, 0.2 mmol) in 10 mL of acetonitrile. The orange solution was filtered into 150 mL of water containing potassium hexafluorophosphate (1.5 g, 8.2 mmol), and the mixture was diluted to 200 mL with water and chilled. **5d** was collected and dried, 150 mg (60% yield), mp 181–185 °C (dec). The product was unstable at dilute concentrations in acetonitrile and converted to the bis-dye on standing. Dilute solutions could be stabilized by using acetonitrile containing 10^{-4} M ferric chloride. In this solution the compound had peaks in the visible spectrum at λ = 486 nm (ϵ = 4.32 × 10^4 M^{-1} cm^{-1}) and λ = 406 nm (ϵ = 5.09 × 10^4 M^{-1} cm^{-1}); ^{1}H NMR (CD_3CN) δ 1.57 (t, J = 7.0 Hz, 12 H), 1.88 (s, 24 H), 4.60 (m, 8 H), 7.18 (d, J = 16.2 Hz, 4 H), 7.7–7.9 (m, 16 H), 8.15 (d, J = 16.2 Hz, 4 H); ^{13}C NMR (CD_3CN) δ 13.00, 23.95, 43.75, 53.19, 115.77, 122.65, 129.39, 131.01, 140.01, 143.90, 145.75. Anal. Calcd for $C_{58}H_{68}N_4 \cdot 4PF_6$: C, 49.7; H, 4.9; N, 4.0. Found: C, 50.1; H, 5.1; N, 4.1.

3,3′-Diethyl-9,11-neopentylenethiadicarbocyanine tetrafluoroborate (8) was prepared by standard procedures: mp 220–224 °C (dec); λ_{max} (CH_3CN) = 645 nm, ϵ_{max} = 13.8 × 10^4 M^{-1} cm^{-1}; ^{1}H NMR (CD_3CN) δ 1.10 (s, 6 H), 1.42 (t, J = 7.2 Hz, 6 H), 2.61 (s, 4 H), 4.36 (q, J = 7.2 Hz, 4 H), 6.22 (s, 2 H), 6.45 (s, 1 H), 7.40 (td, J = 7.0 Hz, J = 2.1 Hz, 2 H), 7.57 (m, 4 H), 7.98 (d, J = 7.7 Hz, 2 H). Anal. Calcd for $C_{28}H_{31}N_2S_2 \cdot BF_4$: C, 61.5; H, 5.7; N, 5.1. Found: C, 61.6; H, 5.6; N, 5.2.

Mixture of isomeric dimers (8b) was prepared by addition of ferric chloride hexahydrate (1.0 g, 3.7 mmol) in 10 mL of acetonitrile to a solution of 8 (500 mg, 0.9 mmol) in 25 mL of acetonitrile. The mixture was filtered into an aqueous solution of potassium hexafluorophosphate (1.5 g, 8.2 mmol), and the precipitate was collected and dried (580 mg, 84% yield): mp 154–158 °C (dec), λ_{max} = 345 nm (CH_3CN), ϵ_{max} = 4.8 × 10^4 M^{-1} cm^{-1}. The NMR spectrum indicated that a mixture of isomers was present; ^{1}H NMR (CD_3CN) δ 0.82–1.35 (series of s, 12 H), 1.45–1.77 (series of t, J = 6 Hz, 12 H), 2.32–3.07 (m, 8 H), 4.5–5.7 (m, 10 H), 7.1–7.4 (series of s, 4 H), 7.8–8.0 (series of m, 8 H), 8.0–8.4 (m, 8 H). Anal. Calcd for $C_{56}H_{62}N_4S_4 \cdot 4PF_6$: C, 44.9; H, 4.2; N, 3.7. Found: C, 44.5; H, 4.2; N, 3.7.

3,3′-Diethylthiacarbocyanine (9) was prepared as the iodide salt and converted to the tetrafluoroborate salt: mp >250 °C; λ_{max} (CH_3CN) = 554 nm, ϵ_{max} = 15.0 × 10^4 M^{-1} cm^{-1}; ^1H NMR (CD_3CN) δ 1.42 (t, J = 7.2 Hz, 6 H), 4.28 (t, J = 7.2 Hz, 4 H), 6.40 (d, J = 12.8 Hz, 2 H), 7.40 (m, 2 H), 7.55 (m, 4 H), 7.82 (overlapping d, J = 12.8 Hz, J = 8.0 Hz, 3 H); ^{13}C NMR ($(CD_3)_2SO$) δ 12.52, 41.42, 98.58, 113.24, 122.99, 125.07, 128.02, 140.68, 146.44, 164.06. Anal. Calcd for $C_{21}H_{21}N_2S_2{\cdot}BF_4{\cdot}H_2O$: C, 53.6; H, 4.9; N, 6.0. Found: C, 53.8; H, 4.6; N, 6.1.

8,8′-Bis(3,3′-diethylthiacarbocyanine) Bis(hexafluorophosphate) (9h). **9** (tetrafluoroborate counterion, 0.5 g, 1.1 mmol) was dissolved in 50 mL of dry acetonitrile. Tris(4-bromophenyl)aminium hexachloroantimonate (1.7 g, 2.1 mmol) was added; the deep red solution was stirred for 15 min and was then combined with 30 mL of methanol and poured into 300 mL of methanol/water (50:50) containing ascorbic acid (2.0 g, 11.4 mmol). The solution was chilled and then filtered to remove tris(4-bromophenyl)aniline. The filtrate was treated with 5 mL of pyridine and then combined with potassium hexafluorophosphate (2.0 g, 10.9 mmol) in 75 mL of water. A precipitate formed immediately. The solid was collected, washed with water, and dried, affording 0.50 g of **9h** (90% yield). The dye was purified by dissolving it in methylene chloride and filtering into hot ethanol. The reprecipitated material was collected and dried (150 mg, 26% yield), mp 213–218 °C (dec); **9h** had a broad absorption band, λ_{max} = 545, 520 nm (CH_3CN), ϵ_{max} = 12.1, 11.8 × 10^4 M^{-1} cm^{-1}; ^1H NMR (CD_3CN) δ 1.14 (t, J = 7.1 Hz, 6 H), 1.82 (t, J = 7.1 Hz, 6 H), 4.19 (q, J = 7.1 Hz, 4 H), 4.64 (q, J = 7.1 Hz, 4 H), 6.00 (d, J = 13.1 Hz, 2 H), 7.42–7.62 (m, 8 H), 7.66 (t, J = 7.7 Hz, 2 H, 7.75 (d, J = 7.7 Hz, 2 H), 7.82 (d, J = 8.1 Hz, 2 H), 7.86 (d, J = 7.9 Hz, 2 H), 7.98 (d, J = 13.1 Hz, 2 H); ^{13}C NMR ($(CD_3)_2SO$) δ 12.00, 13.88, 41.22, 45.14, 97.17, 105.10, 113.50, 114.22, 123.09, 125.17, 125.43, 125.72, 126.16, 128.15, 128.39, 140.76, 143.14, 144.09, 165.88, 168.79. Anal. Calcd for $C_{42}H_{40}N_4S_4{\cdot}2PF_6$: C, 49.5; H, 3.9; N, 5.5. Found: C, 49.1; H, 3.9; N, 5.5.

2,2′-(3,4-Bis(3-ethyl-2-benzothiazolio)-1,3,5-hexatriene-1,6-diyl)bis(3-ethylbenzothiazolium)) tetrakis(hexafluorophosphate) (9i) was prepared by dropwise addition of ferric chloride hexahydrate (400 mg, 1.5 mmol) in 25 mL of acetonitrile to a solution of **9h** (100 mg, 0.1 mmol) in 50 mL of acetonitrile. After addition, the solution was diluted to 500 mL with distilled water. The product precipitated, was collected, washed with water, and dried affording 50 mg (38% yield) of **9i**: mp 157–171 °C (dec); λ_{max} 434 nm (CH_3CN), ϵ_{max} 4.23 × 10^4 M^{-1} cm^{-1}. This compound can form with two 3-ethyl-2-benzothiazolio groups either cis or trans. The ^1H NMR (CD_3CN) of the major isomer was δ 1.40 (t, J = 7.0 Hz, 6 H), 1.67 (t, J = 5.8 Hz, 6 H), 4.55 (q, J = 7.0 Hz, 4 H), 4.90 (br m, 4 H), 7.05 (d, J = 15.6 Hz, 2 H), 7.38 (br m, 2 H), 7.80–7.95 (m, 4 H), 8.05–8.25 (m, 8 H), 8.48 (d, J = 8.0 Hz, 2 H), 8.60 (d, J = 8.0 Hz, 2 H). The absorptions for two of the methine protons (δ 7.38) and the methylene protons of two of the ethyl groups (δ 4.90) were broad. These peaks became sharp when the spectrum was recorded at 70 °C (δ 7.38 (d, J = 16 Hz, 2 H), 4.90 (q, J = 6 Hz, 4 H)). The original spectrum was obtained upon cooling to 30 °C. This behavior is consistent with the potential steric interactions present in the cis isomer. The presence of additional minor peaks in the spectrum, notably δ 7.26 (d, J = 15.6 Hz), suggests that 10–15% of the trans isomer is formed. Anal. Calcd for $C_{42}H_{40}N_4S_4{\cdot}4PF_6$: C, 38.5; H, 3.1; N, 4.3. Found: C, 38.4; H, 3.2; N, 4.3.

1,1′-Diethylnaphtho[1,2-*d*]thiazolocarbocyanine (10) was prepared as the *p*-toluenesulfonate salt: mp >250 °C; λ_{max} = 593 nm (CH_3CN), ϵ_{max} = 15.5 × 10^4 M^{-1} cm^{-1}; ^1H NMR ($(CD_3)_2SO$) δ 1.66 (t, J = 6.7 Hz, 6 H), 2.26 (s, 3 H), 4.70 (m, 4 H), 6.70 (d, J = 12.6 Hz, 2 H), 7.08 (d, J = 8.0, 2 H), 7.45 (d, J = 8.0 Hz, 2 H), 7.60 (t, J = 7.4 Hz, 2 H), 7.73 (t, J = 7.5, 2 H), 7.79 (d, J = 12.8, 1 H), 7.92 (d, J = 8.7 Hz, 2 H), 8.03 (t, J = 8.8 Hz, 4 H), 8.42 (d, J = 8.8 Hz, 2 H). Anal. Calcd for $C_{29}H_{25}N_2S_2{\cdot}C_7H_7SO_3$: C, 67.9; H, 5.1; N, 4.4. Found: C, 68.0; H, 5.1; N, 4.4.

8,8′-Bis(1,1-diethylnaphtho[1,2-*d*]thiazolocarbocyanine) Bis(hexafluorophosphate) (10h). Ferric chloride hexahydrate (4.0 g, 14.8 mmol) in 75 mL of water was added to a stirred solution of **10** (*p*-toluenesulfonate counterion, 1.0 g, 1.6 mmol) in 200 mL of methanol. After 15 min, ascorbic acid (5.0 g, 28.4 mmol) in 200 mL of water/methanol (50:50) and 7 mL of pyridine was added. After stirring an additional 10 min, potassium hexafluorophosphate (5.0 g, 27.4 mmol) in 150 mL of water was added. The precipitate formed was collected, washed with water, and dried, yielding 1.0 g of product. This material was dissolved in 50 mL of methylene chloride and filtered into 150 mL of ethanol. **10h** crystallized out (0.6 g, 62% yield), mp 215–217 °C (dec); this dye had a broad absorption spectrum, λ_{max} = 582, 552 nm (CH_3CN), ϵ_{max} = 10.5 × 10^4, 10.3 × 10^4 M^{-1} cm^{-1}; ^1H NMR (CD_3CN) d 1.48 (t, J = 7.1 Hz, 6 H), 1.78 (t, J = 6.9 Hz, 6 H), 4.62 (br m, 4 H), 5.26 (q, J = 6.9 Hz, 4 H), 6.14 (d, J = 13.2 Hz, 2 H), 7.55–8.00 (m, 16 H), 8.12 (m, 6 H), 8.38 (d, J = 8.4 Hz, 2 H), 8.70 (d, J = 8.7 Hz, 2 H). Anal. Calcd for $C_{58}H_{48}N_4S_4{\cdot}2PF_6{\cdot}2H_2O$: C, 55.5; H, 4.1; N, 4.5. Found: C, 55.8; H, 4.1; N, 4.4.

2,2′-(3,4-Bis(1-ethyl-2-naphtho[1,2-*d*]thiazolio)-1,3,5-hexatriene-1,6-diyl)bis(1-ethylnaphtho[1,2-*d*]thiazolium)) tetrakis(hexafluorophosphate) (10i) was prepared by dropwise addition of ferric chloride hexahydrate (1.0 g, 3.7 mmol in 20 mL of acetonitrile) to **10h** (250 mg, 0.21 mmol in 50 mL of dry acetonitrile). After 10 min, the solution was filtered into a solution of potassium hexafluorophosphate (2.0 g, 10.9 mmol) in 100 mL of water. The mixture was then diluted to 400-mL volume with water. After chilling, **10i** was collected, washed with water, and dried (240 mg, 76% yield): mp 170–180 °C (dec); λ_{max} (CH_3CN) = 504 nm, ϵ_{max} = 3.52 × 10^4 M^{-1} cm^{-1}. Adding excess tetrabutylammonium iodide to a 8 × 10^5 M acetonitrile solution of this compound regenerates the bis-dye **10h**, λ_{max} = 555 nm, ϵ_{max} = 10.4 × 10^4 M^{-1} cm^{-1}.

Acknowledgment. We thank Larry Kelts and Frank Michaels for some of the NMR measurements and Linda Knapp for some synthetic assistance.

Registry No. **2**, 80566-26-3; **3**, 123811-90-5; **3c**, 123811-92-7; **3d**, 123811-94-9; **4**, 123811-95-0; **4b**, 123811-97-2; **4c**, 123811-99-4; **4d**, 123834-24-2; **5**, 123812-00-0; **5c**, 123812-02-2; **5d**, 123834-26-4; **6**, 37069-76-4; **6c**, 123812-03-3; **6d**, 123812-04-4; **7**, 37069-84-4; **7c**, 123812-05-5; **7d**, 123812-06-6; **8**, 123812-07-7; **8b**, 123812-20-4; **9**, 61575-75-5; **9h**, 123812-09-9; **9i**, 123812-11-3; **10**, 123812-12-4; **10h**, 123812-14-6; **10i**, 123812-16-8; **11**, 15233-45-1; **11f**, 123812-17-9; **12**, 62203-10-5; **12e**, 123812-18-0; **13**, 38912-20-8; **13e**, 123812-19-1.