JOC Article

Synthesis and Studies of the Properties of a Liquid-Crystalline Quaterrylenebis(dicarboximide) by ^{1}H NMR and UV−vis Spectroscopies

Suk-Wah Tam-Chang,* Wonewoo Seo, and Isaac K. Iverson†

Department of Chemistry, University of Nevada, Reno, Nevada 89557

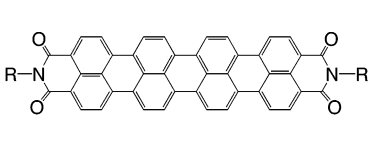
tchang@chem.unr.edu

Received November 7, 2003

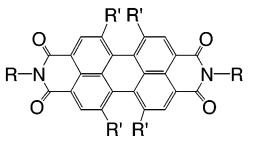
The synthesis of an ionic quaterrylenebis(dicarboximide) **1a**, a long-wavelength absorbing mesogen, is described. When compared with its analogue **2a**, an ionic perylenebis(dicarboximide), the aromatic protons of **1a** exchange with deuterium of concentrated D_2SO_4 at a dramatically faster rate. In addition, stronger aggregation in aqueous media was observed for **1a**.

Introduction

The design and synthesis of long-wavelength absorbing and emitting compounds is an important area of research.[1−6] Near-infrared (NIR) absorbing and emitting dyes have potential applications in optical recording, thermally written displays, laser printers, laser filters, infrared photography, and fiber-optic communications.[1,4] Long-wavelength dyes can also be used in optical applications in conjunction with commercially available GaAlAs lasers that emit at 780 nm. In a recent communication,[7] we reported the design of an ionic quaterrylenebis(dicarboximide) **1a** that possesses long-wavelength absorbing and lyotropic (solvent dependent) liquid-crystalline properties. The self-organization of **1a** (driven by π-stacking and hydrophobic interactions in aqueous media) into a liquid-crystalline phase allowed the control of the molecular orientation of **1a** in thin solid films, producing a linear polarizer of light at long wavelengths.[7]



1a, R= $(CH_2)_2NEt_2H^+$ $HCOO^-$
1b, R = $C_{12}H_{25}$
1c, R = C_6H_3-2,6-Pr^i_2



2, R'=H, R= $(CH_2)_2NEt_2$
2a, R'=H, R= $(CH_2)_2NEt_2H^+$ Cl^- (or $HCOO^-$)
2-d$_4$, R'=D, R= $(CH_2)_2NEt_2$
2b, R'=D, R= $(CH_2)_2NEt_2H^+$ Cl^-

In the family of arenebis(dicarboximide)s, quaterrylenebis(dicarboximide)s are the more conjugated analogues of perylenebis(dicarboximide)s. Liquid-crystalline perylenebis(dicarboximide)s have received much attention in the past few years because of their unique properties resulting from the combination of their liquid-crystalline (thermotropic or lyotropic), photophysical, semiconducting, and photoconducting properties.[8−13] The availability of an efficient procedure for the synthesis of liquid-crystalline quaterrylenebis(dicarboximide)s will stimulate research on the novel properties and applications of this more conjugated member of arenebis(dicarboximide)s. Despite the fact that elegant synthetic procedures were reported by Müllen et al. for nonionic quaterrylenebis(dicarboximide)s **1b**,**c**,[5,6] those procedures are not applicable to the synthesis of ionic **1a** because the alkyl amino groups of **1a** modify its reactivity and solubility compared to **1b**,**c**.[6] In this paper, we describe an effective and less expensive procedure that led to the synthesis of **1a** in high yield. In addition, we report detailed studies of the properties of **1a** and its analogue **2a** by ^{1}H NMR and UV−vis spectroscopy. A further understanding of the properties of **1a** is important for the future design of long wavelength absorbing mesogens, optimizing properties, and developing new applications.

Results and Discussion

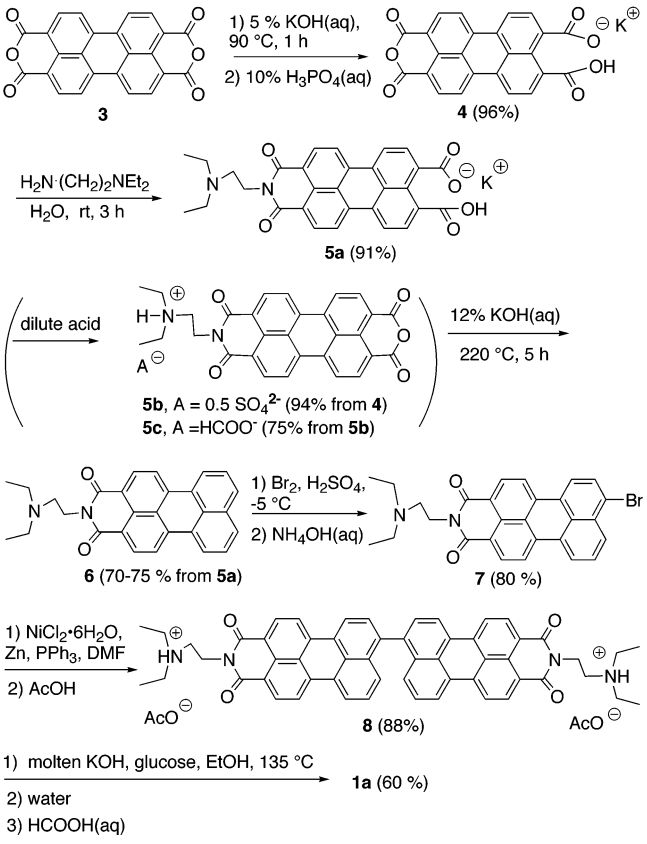
Synthesis of 1a. The synthetic route to **1a** is outlined in Scheme 1. Monoanhydride salt **4** was prepared ac-

† Present address: GE Osmonics, 5951 Clearwater Drive, Minnetonka, MN 55343.

(1) Law, K. Y. *Chem. Rev.* **1993**, *93*, 449−486.
(2) Thompson, R. B. In *Topics in Fluorescence Spectroscopy, Vol. 4, Probe Design and Chemical Sensing*; Lakowicz, J. R., Ed.; Plenum Press: New York, 1994; pp 151−222.
(3) Lakowicz, J. R. *Principles of Fluorescence Spectropscopy*, 2nd ed.; Kluwer Academic/Plenum Publishers: New York, 1999.
(4) Emmelius, M.; Pawlowski, G.; Vollmann, H. W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1445−1600.
(5) Quante, H.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1323−1325.
(6) Geerts, Y.; Quante, H.; Platz, H.; Mahrt, R.; Hopmeier, M.; Bohm, A.; Müllen, K. *J. Mater. Chem.* **1998**, *8*, 2357−2369.
(7) Tam-Chang, S. W.; Seo, W.; Iverson, I. K.; Casey, S. M. *Angew. Chem., Int. Ed.* **2003**, *42*, 897−900.
(8) Iverson, I. K.; Tam-Chang, S.-W. *J. Am. Chem. Soc.* **1999**, *121*, 5801−5802.
(9) Würthner, F.; Thalacker, C.; Sautter, A.; Schärtl, W.; Ibach, W.; Hollricher, O. *Chem. Eur. J.* **2000**, *6*, 3871−3886.
(10) Würthner, F.; Thalacker, C.; Diele, S.; Tschierske, C. *Chem. Eur. J.* **2001**, *7*, 2245−2253.
(11) Gregg, A. B.; Cormier, R. A. *J. Am. Chem. Soc.* **2001**, *123*, 7959−7960.
(12) Gronheid, R.; Hofkens, J.; Köhn, F.; Weil, T.; Reuther, E.; Müllen, K.; De Schryver, F. C. *J. Am. Chem. Soc.* **2002**, *124*, 2418−2419.
(13) Lukas, A. A.; Zhao, Y.; Miller, S. E.; Wasielewski, M. R. *J. Phys. Chem. B* **2002**, *106*, 1299−1306.

10.1021/jo030342y CCC: $27.50
Published on Web 03/23/2004

SCHEME 1. Synthetic Scheme of 1a



cording to a procedure reported by Tröster.[14] To a suspension of **4** in water was added an aqueous solution of *N*,*N*-diethylethylenediamine to yield compound **5a** in 91% yield. In contrast to the procedure reported for the synthesis of the analogous intermediate for **1b**,**c** that required the use of a metal catalyst, expensive solvent such as NMP or quinoline, heating, and laborious purification steps, the synthesis for **5a** occurred in water at room temperature without any catalysts. To further simplify the procedure and reduce the time cost, compound **5a** was used directly to prepare intermediate **6** eliminating the preparation and isolation of **5b** (although compound **5a** could be converted to the sulfate salt **5b** or the formic salt **5c** for characterization purposes). Decarboxylation of **5a** in KOH at 220 °C in a closed steel vessel produced monoimide **6** in about 70% yield.

Attempts to prepare compound **7** by the reaction of **6** with elementary bromine in an inactive solvent (e.g., Br_2 in methylene chloride)[6] or other brominating agents such as *N*-bromosuccinimide[15] and pyridinium tribromide[16] were unsuccessful. A byproduct was obtained in addition to recovery of unreacted compound **6**. The ^{1}H NMR spectrum of the byproduct suggested the loss of an ethyl group resulted from oxidative cleavage by bromine.[17,18] Bromination of **6** was successful using Br_2 in concentrated sulfuric acid[19] resulting in a high yield of **7** (80%). The concd H_2SO_4 used as an active solvent protonated the amino groups of **6**, thus protecting them from oxidative cleavage in addition to increasing the solubility of **6**.

The next step involved the homocoupling of **7** to form the biperylenebis(dicarboximide) **8**. Expensive organometallic catalysts such as Ni(cod)$_2$ (cod = 1,5-cyclooctadiene) and tetrakis(triphenylphosphine)nickel(0) (generated from zinc and bis(triphenylphosphinenickel(II) chloride) have been used for the synthesis of **1b**,**c**.[5,6] Instead, we employed simple, inexpensive organic and inorganic compounds (zinc dust, triphenylphosphine, and $NiCl_2{\cdot}6H_2O$) as reagents.[20−22] Because Ni^0 is generated in situ, special air-free handling conditions are not necessary. Ni^0-mediated coupling of **7** readily produced compound **8** in high yield (88%). Using a molten KOH/EtOH medium along with the presence of excess equivalents of glucose as an oxidant,[6,23] compound **8** was converted to the desired quaterrylenebis(dicarboximide) that precipitated out from the reaction mixture upon addition of water. The conversion of the amino groups of the quaterrylenebis(dicarboximide) into cationic groups was achieved by reaction with formic acid to produce the formate salt **1a**.

Studies of 1a and 2a by ^{1}H NMR Spectroscopy. Studies of 2a in Concentrated D_2SO_4 by ^{1}H NMR Spectroscopy. Variable-temperature ^{1}H NMR studies of **2a** ($\sim 10^3$ M) in concd D_2SO_4 (D-99%, 96−98% solution in D_2O) were performed. At room temperature, two well-resolved doublets were observed for the aromatic protons suggesting that no significant aggregation of the molecules occurred (Figure 1). There was no observable change in peak shapes or intensities after the temperature of the sample was increased from 25 to 55 °C in about 5 min or further increased to 85 °C (in another 5 min). However, the deuterium of the solvent exchanged with the aromatic protons after heating at 105 °C for more than 3 d. The slow rate of deuterium exchange allowed product **2b** to be isolated readily in 87% yield (Scheme 2). The ^{1}H NMR spectrum of **2b** in CF_3COOD showed a sharp singlet for the aromatic protons that integrated to four protons only (when the CH_3 protons peak was assigned a value of 12).

Studies of 1a in Concentrated D_2SO_4 by ^{1}H NMR Spectroscopy. ^{1}H NMR studies of **1a** were performed under conditions similar to those employed for **2a**. The integrated area of the peak for CH_3 protons was assigned a value of 12, and the integrated area of the aromatic resonances was determined with reference to the CH_3 peak. The ^{1}H NMR spectrum of a freshly prepared solution of **1a** in D_2SO_4 showed three distinct resonances at 8.9, 8.7, and 8.4 ppm for the aromatic protons (Figure 2a). The total integrated area of these peaks was about 16. The relatively sharp peaks observed for the aromatic protons indicated that there was no significant aggrega-

(14) Tröster, H. *Dyes Pigments* **1983**, *4*, 171−177.
(15) Konishi, H.; Aritomi, K.; Okano, T.; Kiji, J. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 591−593.
(16) Reeves, W. P.; King, R. M. *Synth. Commun.* **1993**, *23*, 855−859.
(17) Deno, N. C.; Fruit, R. E. *J. Am. Chem. Soc.* **1968**, *90*, 3502−3506.
(18) Micallef, A. S.; Bott, R. C.; Bottle, S. E.; Smith, G.; White, J. M.; Matsuda, K.; Iwamura, H. *J. Chem. Soc., Perkin Trans. 2* **1999**, 65−71.
(19) Derbyshire, D. H.; Waters, W. A. *J. Chem. Soc.* **1950**, 573−577.
(20) Nauman, C.; Langhals, H. *Synthesis* **1990**, 279−281.
(21) Langhals, H.; SüBmeier, F. *J. Prakt. Chem.* **1999**, *341*, 309−311.
(22) Tiecco, M.; Testaferri, L.; Tingoli, M.; Chianelli, D.; Montanucci, M. *Synthesis* **1984**, 736−738.
(23) Bradley, W.; Pexton, F. W. *J. Chem. Soc.* **1954**, 4432−4435.

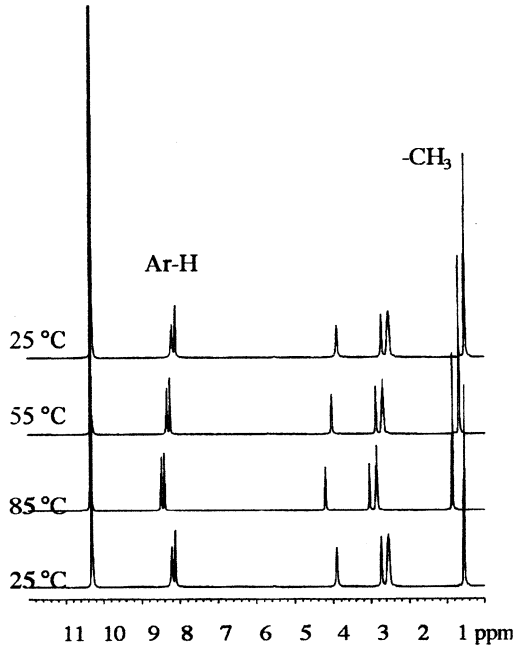
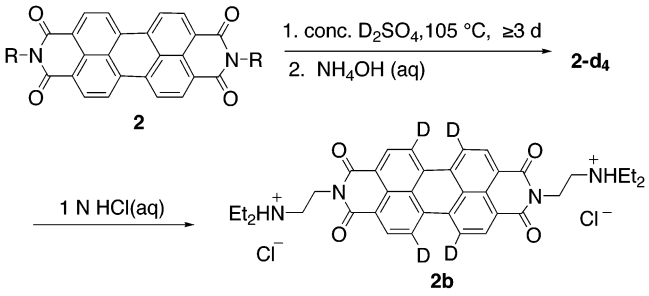


FIGURE 1. Offset spectra (500 MHz) showing the effect of heating for short durations on the ^{1}H NMR spectrum of **2a** (3 × 10^{-2} M) in concd D_2SO_4 (D-99%, 96−98% solution in D_2O).

SCHEME 2. Synthetic Scheme of 2b



tion of the molecules in concd D_2SO_4. At elevated temperatures, the resonance peaks for the aromatic protons broadened and rapidly decreased in intensity (Figure 2b,c). After the temperature of the solution was raised to 55 °C in about 5 min, significant broadening of the aromatic resonances occurred and the integrated area of these peaks decreased (Figure 2b). Upon further increasing the temperature to 85 °C in another 5 min, the aromatic resonances disappeared completely (Figure 2c). When the solution was allowed to cool back to 25 °C under vacuum, the aromatic peaks did not reappear. However, when the solution was cooled in the capped NMR tube or allowed to expose to air for a few hours, a very weak broad peak appeared in the aromatic region (Figure 2d).

Because the extent of aggregation of molecules in a solution should decrease with increased temperature, the broadening of the resonance peaks observed did not result from the aggregation of molecules in concd D_2SO_4. Furthermore, the aromatic peaks were not restored to the original shape or intensity after the solution was cooled back to 25 °C, suggesting that the disappearance of the aromatic peaks was caused by a permanent chemical change. The observed changes may be attributed to the rapid exchange of the aromatic protons

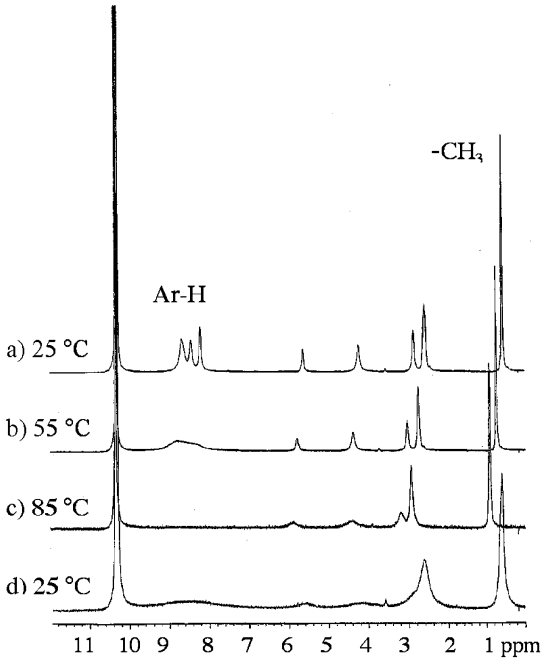


FIGURE 2. Offset spectra (500 MHz) showing the effect of temperature on the ^{1}H NMR spectrum of **1a** (1 × 10^{-2} M) in concentrated D_2SO_4.

with the deuterium of D_2SO_4 to yield a mixture of isomers, therefore broadening the peaks and decreasing the intensity of the aromatic resonances. Because of the high rate of exchange, attempts to isolate isotopically pure isomers of the deuterium labeled **1a** by quenching of the reaction with KOD and D_2O were not successful. The broadening of aliphatic peaks of **1a** in D_2SO_4 is not clearly understood.

Deuterium exchange of **1a** in concd D_2SO_4 also occurred at room temperature but at a slower rate. After storage at room temperature for about 3 d, significant broadening of the peaks occurred and the total integrated area decreased to a relative value of about 13. A further decrease in the intensity to a relative value of 12 was observed after 7 d. Interestingly, deuterium exchange was not mentioned for the aromatic protons of the quaterrylene rings of **1c**, although deuterium exchange with D_2SO_4 was reported for the protons on the phenyl substituents at the imide positions of **1c**.[6]

Studies of 1a in Deuterated Trifluoroacetic Acid (CF_3COOD) by ^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of a freshly prepared sample of **1a** in CF_3COOD (D-99.5%) showed very broad overlapping resonance signals (from about 6−8 ppm) for the aromatic protons. The relative integrated area of the aromatic peaks was about 16, indicating that the extent of deuterium exchange in the freshly prepared sample was insignificant and the broadening of peaks was resulted from aggregation of the compound in CF_3COOD. Upon storage of the solution at room temperature, the shape and the integrated area of the aromatic peaks changed slowly. After a total of 3 d, the integrated area of the peaks for the aromatic protons decreased to about 15, with a further reduction in intensity to about 13 in 7 d. These results showed that deuterium exchange of the aromatic protons of **1a** in CF_3COOD occurred at room temperature (al-

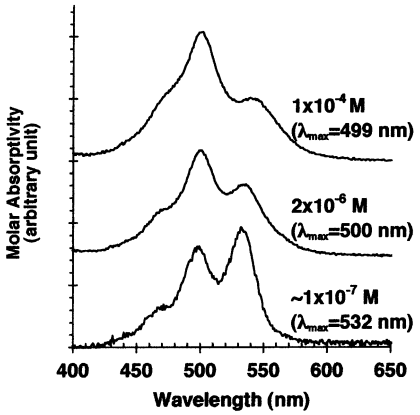


FIGURE 3. Offset spectra showing the effect of concentration of **2a** on the electronic absorption spectrum of **2a** in water at 25 °C.

though at a slower rate than in concd D_2SO_4) presumably because of the lower acidity of CF_3COOD compared to D_2SO_4.

The ^1H NMR studies indicate that deuterium exchange is dramatically faster for the aromatic protons of **1a** than **2a**. In concd D_2SO_4, deuterium exchange of the aromatic protons of **1a** is complete after heating the sample from 25 to 85 °C in about 10 min while the deuterium exchange of the aromatic proton of **2a** required heating at 105 °C for about 3 d. Deuterium exchange of these compounds presumably occurs by an electrophilic aromatic substitution mechanism involving the formation of a cationic intermediate. Better resonance stabilization of the rate-determining transition state (that leads to the cationic intermediate) by the more conjugated compound **1a** would lower the activation barrier and increase the reaction rate. The high reactivity of quaterrylenebis(dicarboximide)s toward electrophilic substitutions has two implications. (1) Care should be taken in the sample preparation, storage, and interpretation of results of analytical studies of quaterrylenebis(dicarboximide)s in deuterated acids. (2) The aromatic rings of quaterrylenebis(dicarboximide)s may be functionalized readily for modulating their solubilities and lyotropic liquid-crystalline properties and for further extending the λ_{max} value to longer wavelengths, thus allowing the optimization of these properties for technological exploitations.

Electronic Transition Properties of 1a and 2a. To gain better understanding of the effect of solvents on the aggregation and the electronic transition properties of **1a**, the absorption properties of **1a** were studied by UV−vis spectroscopy and compared to the properties of the less conjugated analogue **2a**. The studies were limited to water, HCOOH(aq), TFA, and concd H_2SO_4 as solvents because of the low solubility of **1a** and **2a** in other common solvents.

Electronic Transition Properties of 2a in Water. The visible absorption spectrum of **2a** in water showed a blue shift in the λ_{max} value as the concentration of **2a** increased from $\sim 10^{-7}$ to $\sim 10^{-4}$ M (Figure 3), suggesting the formation of H-aggregates (in which the molecules were stacked in a ladder-like fashion).[24] The extent of

(24) Czikklely, V.; Forsterling, H. D.; Kuhn, H. *Chem. Phys. Lett.* **1970**, *6*, 207−210.

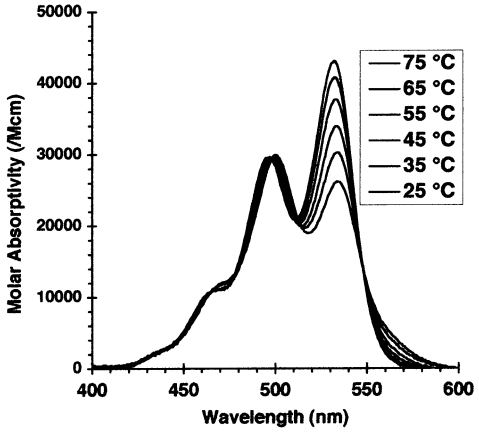


FIGURE 4. Effect of temperature on the electronic absorption of **2a** (6×10^{-7} M) in water.

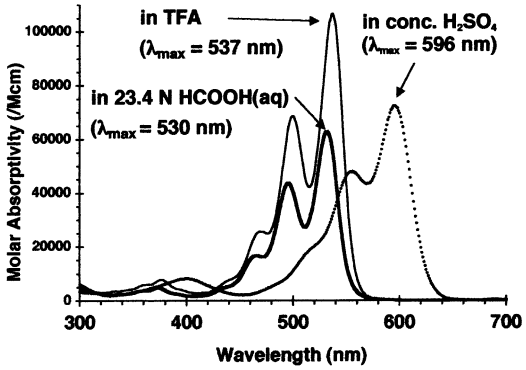


FIGURE 5. Electronic absorption spectra of a 3.4×10^{-4} M solution of **2a** in 23.4 N HCOOH(aq) (bold line), 2×10^{-4} M solution of **2a** in TFA (solid line), and a 3×10^{-4} M solution in concd H_2SO_4 (dots) at 25 °C.

aggregation decreased as the temperature increased. The spectrum of a 6×10^{-7} M solution of **2a** at 75 °C showed a λ_{max} value of 534 nm and a less intense peak at ~500 nm that were attributed to the monomer of **2a** (Figure 4). Since the monomer peak at ~500 nm overlapped with the absorption peak of the higher aggregates, a smaller change in the intensity with temperature was observed for the absorption peak at ~500 nm compared to the peak at 534 nm.

Electronic Transition Properties of 2a in HCOOH(aq), TFA, and Concentrated H_2SO_4. Despite the large change in solvent acidity from water to 23.4 N HCOOH(aq) or TFA, the spectral shapes and λ_{max} values of a 3.3×10^{-4} M solution of **2a** in 23.4 N HCOOH(aq) and a 2×10^{-4} M solution of **2a** in TFA (Figure 5) were similar to that observed for the monomer of **2a** in a 10^{-7} M solution in water at elevated temperature. In addition, there was no change in the absorption spectrum when the concentration of **2a** decreased from 2×10^{-4} to 2×10^{-6} M indicating that there was no significant aggregation of **2a** in 23.4 N HCOOH(aq) or TFA. The large difference in the extent of aggregation of **2a** in these acidic solvents compared to water may be due to two reasons: (1) the complete protonation of the terminal amino groups of **2a** in these acidic solvents increases the electrostatic repulsion among the molecules and (2) different entropically driven hydrophobic or

TABLE 1. Dependence of the Value of λ_{Max} of the Electronic Transition of 1a on the Concentration of HCOOH(aq) and 1a

[HCOOH] (N)	[**1a**] (μM); λ_{max} (nm)		
23.4	0.5; 738	5; 719	50; 705
21.0	0.2; 697	2; 689	20; 683
16.7	0.4; 694	n.a.	n.a.
1.2	0.4; 677	n.a.	n.a.

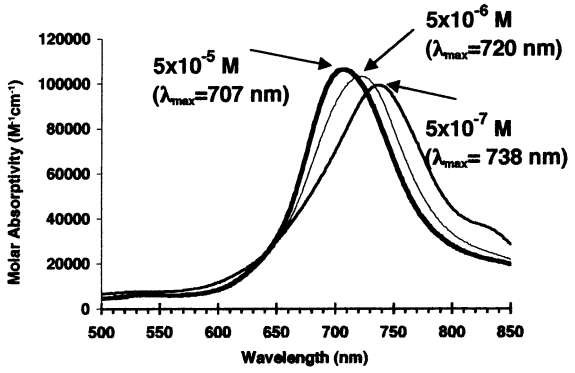


FIGURE 6. Effect of the concentration of **1a** in 23.4 N HCOOH(aq) on the electronic absorption of **1a** at 25 °C.

solvophobic interactions in these solvents compared to water.

In concd H_2SO_4, the spectral shape of the absorption spectrum of **2a** was similar to that in 23.4 N HCOOH(aq) or TFA; however, the λ_{max} value is shifted to about 60 nm longer in wavelength (Figure 5). Since the studies by ^{1}H NMR spectroscopy showed that the rate of electrophilic substitution of the aromatic protons of **2a** in concd H_2SO_4 was very slow at room temperature, protonation of the perylene ring of **2a** could be excluded. The cause of the large red shift of the λ_{max} value in concd H_2SO_4 is not clear. It may be attributed to a general solvent effect, although protonation of the carbonyl function of **2a** cannot be excluded.

Electronic Transition Properties of 1a in Aqueous Formic Acid Solution. Compound **1a** is insoluble in water but very soluble in formic acid. Studies in HCOOH(aq) indicated that extensive aggregation of **1a** occurred and the λ_{max} of electronic transition of **1a** varied with the concentrations of HCOOH(aq) and **1a** (Table 1). In HCOOH (aq, 23.4 N), the absorption spectrum of a 5 $\times$ 10^{-7} M solution of **1a** showed a very broad peak at 738 nm and a shoulder at 830 nm (Figure 6). Furthermore, a blue shift in λ_{max} value was observed as the concentration of **1a** increased. As the concentration of HCOOH decreased, the λ_{max} of **1a** shifted to shorter wavelengths (Table 1).

These results are consistent with the formation of H-aggregates[24] of **1a** in formic acid resulting in a blue-shift of the absorption maximum (λ_{max}) of the dimer and higher aggregates compared to the monomer peaks. Strong π-stacking and hydrophobic interactions among the molecules of **1a** in aqueous solutions were expected because of the presence of the large conjugated ring structure. The extent of aggregation increased as the concentration of **1a** increased and the concentration of HCOOH(aq) decreased. This resulted in incomplete protonation of the terminal amino groups of **1a** and reduced the electrostatic repulsion among the molecules.

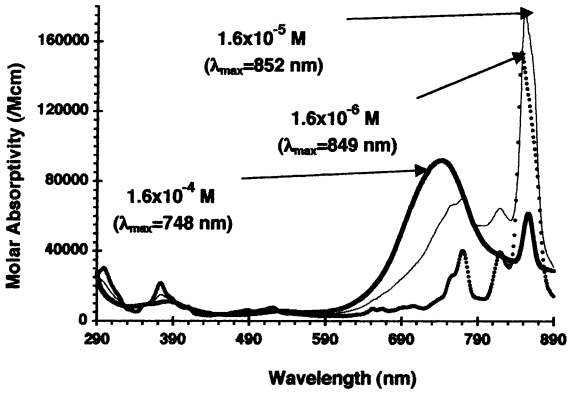


FIGURE 7. Dependence of the electronic absorption spectrum of **1a** on the concentration of **1a** in TFA at 25 °C. (Bold line) 1.6 $\times$ 10^{-4} M; (thin solid line) 1.6 $\times$ 10^{-5} M; (dotted line) 1.6 $\times$ 10^{-6} M of **1a**.

The study of the effect of temperature on the electronic transition properties of **1a** in 23.4 N HCOOH(aq) further confirms the formation of H-aggregates.[7] The absorption spectrum of **1a** (5 $\times$ 10^{-7} M) showed a broad absorption band with a λ_{max} at ~740 nm and a shoulder at ~825 nm at 25 °C. At high temperatures (e.g., 85 °C), the extent of aggregation decreases causing a shift in the λ_{max} of the solution to ~770 nm and an increase in the intensity of the shoulder at ~825 nm.[7]

Visible Absorption Spectroscopic Studies of 1a in TFA. In TFA, the visible absorption spectra of **1a** varied with the concentration of **1a** (Figure 7). At ~10^{-4} M, a broad band with a λ_{max} value of ~750 nm and a small sharp peak at ~850 nm were observed. The broad band observed for the 10^{-4} M solution of **1a** was presumably caused by the aggregation of **1a** in TFA. This result is consistent with the significant broadening of the aromatic peaks observed in the ^{1}H NMR spectrum of a freshly prepared solution of **1a** in D-TFA. The extent of aggregation decreased as the concentration of **1a** decreased. At ~10^{-6} M, the peak at 750 nm decreased in intensity and red-shifted to ~770 nm. A small peak at 825 nm emerged, and the sharp peak at ~850 nm increased significantly in intensity.

Electronic Transition Properties of 1a in Concentrated H_2SO_4 (aq, ~98%). The electronic absorption spectrum of **1a** in concd H_2SO_4(aq) was similar to that of **1a** in TFA at low concentration (e.g., 10^{-6} M) of **1a**. The spectrum of **1a** (1 $\times$ 10^{-5} M) in concd H_2SO_4(aq) at 25 °C showed an intense sharp band at 856 nm and a weak peak at 772 nm (Figure 8). No significant change in the spectral shape and the λ_{max} of **1a** was observed when the concentration of **1a** was reduced to about 10^{-6} or 10^{-7} M suggesting that the sharp peak observed is not due to the formation of J-aggregates (in which the molecules are stacked in a staircase fashion).[25] This conclusion is consistent with the observation of relatively sharp peaks in the ^{1}H NMR spectrum for the aromatic protons of a freshly prepared solution of **1a** in D_2SO_4. A sharp and intense absorption peak is reported for **1c** in concd H_2SO_4 (although at longer wavelength, 907 nm, than that of **1a**) and is attributed to the protonation of

(25) Harrison, W. J.; Mateer, D. L.; Tiddy, G. J. T. *Faraday Discuss.* **1996**, *104*, 139−154.

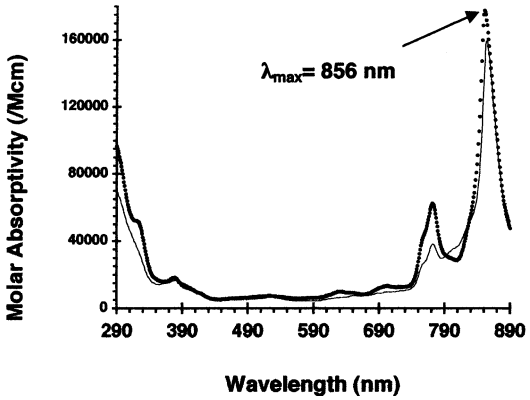


FIGURE 8. Effect of the concentration of **1a** on the UV−vis spectrum of **1a** in concd H_2SO_4. Only the spectra of the solutions of 1.4×10^{-5} M (solid line) and 1.4×10^{-6} M (dotted line) are shown for clarity.

the carboxamide functions of **1c**.[6] Because deuterium exchange of the aromatic protons of **1a** occurred in concd D_2SO_4 and D-TFA at room temperature, protonation of the aromatic ring of the monomer in concd H_2SO_4 and TFA may also contribute to the sharp absorption band at 856 nm.

In summary, the electronic transition properties and extent of aggregation of **1a** and **2a** varied with the solvent, the concentration of **1a** and **2a**, and temperature. H-aggregate formation of **2a** occurred at room temperature in water but not in 23.4 N HCOOH(aq), TFA, or concd H_2SO_4(aq). Because of the large aromatic surface of **1a** compared to **2a**, there is stronger π-stacking and hydrophobic interactions. Consequently, **1a** was insoluble in water and substantial H-aggregates formation occurred in HCOOH(aq) and TFA. Since the aggregation of molecules in solutions is a prerequisite to the formation of a lyotropic liquid-crystalline phase, the observation of the formation of chromonic liquid-crystalline phases of **2a** in water[8] and **1a** in HCOOH(aq)[7] is consistent with the results reported in this paper. In concd H_2SO_4(aq), studies by ^{1}H NMR and visible spectroscopy showed that no significant aggregation of **1a** was observed. The cause of the sharp intense peak at 856 nm in the visible absorption spectrum of **1a** in concd H_2SO_4 is not clear. It may be attributed to protonation of the aromatic ring or the carbonyl functions. Large variations in the spectral shape and λ_{max} value of **1a** (from about 675 nm to 850 nm) can be attained depending on the solvent, concentration of **1a**, and temperature, allowing the modulation of the optical properties **1a** without any irreversible chemical modification of **1a**.

Conclusions

This paper describes a detailed procedure for the synthesis of quaterrylenebis(dicarboximide) **1a**. To the best of our knowledge, **1a** is the first example of a quaterrylenebis(dicarboximide) that possesses an ionic pendant group and displays lyotropic liquid-crystalline properties. Future studies will include the functionalization of the aromatic rings of **1a** to extend the absorption wavelength beyond 850 nm and the detailed studies of the liquid-crystalline properties of **1a** and its derivatives.

Experimental Section

***N,N′*-Bis(2-(*N″,N″*-diethylamino)ethyl)perylene-3,4:9,10-bis(dicarboximide) (2) and *N,N′*-Bis(2-(*N″,N″*-diethylammonium)ethyl)perylene-3,4:9,10-bis(dicarboximide)-1,6,7,12-*d*$_4$-dihydrochloride (2b).** A total of 8.0 g (20 mmol) of perylene-3,4,9,10-tetracarboxylic acid was suspended in 80 mL of water, and the mixture was heated to 100 °C. A total of 8.0 mL (57 mmol) of *N,N*-diethylethylenediamine was added, and the reaction mixture was refluxed overnight. After the solution was cooled to room temperature, the product was filtered, washed with 1% KOH(aq) and water, and dried under vacuum to give 11 g (88%) of **2**. Compound **2** was converted to **2a** by reaction with HCl(aq) or converted to **2b** by the procedure described below. In a glass vial, 1.00 g (1.71 mmol) of bis-(2-(*N,N*-diethylamino)ethyl)perylene-3,4:9,10-bis(dicarboximide) **2** was dissolved in 9.15 g of concd D_2SO_4. The solution was transferred to a 10-mm NMR tube, and it was put into a sand bath at 105 °C for at least 3 d. ^{1}H NMR spectra of the solution were obtained periodically during the time period to monitor the integration of the signals for the aromatic protons relative to those for the aliphatic protons. The solution was then poured into 60 mL of double distilled water, and the tube was rinsed with water. An NH_4OH(aq) solution (prepared by adding 45 mL of concentrated NH_4OH (assay 28−30%) to 55 mL of water) was carefully added to the sulfuric acid solution to give a resulting solution of pH 10. It was sonicated for 5 min and allowed to sit overnight. The precipitate was filtered, washed with about 200 mL of 3.2 M NH_4OH(aq), and allowed to dry in air overnight. The solid was dissolved in 100 mL of 1 M HCl(aq), and 75 mL of water was added. The solvent was evaporated to dryness with a rotary evaporator under reduced pressure from an aspirator. The solid recovered was dried under vacuum to yield 0.992 g (1.49 mmol, 87%) of **2b**. The regioselectivity indicated for the deuterium labeling in **2b** was inferred from reactivity patterns reported in the literature for the perylenetetracarboxylic acids and anhydrides.[26,27] **2**: ^{1}H NMR (300 MHz, CF_3COOD) δ 8.78 (4H, Ar−H), 8.75 (4H, Ar−H), 4.72 (t, 4H, ^3J (H,H) = 5 Hz, α-CH_2), 3.64 (t, 4H, ^3J (H,H) = 5.5 Hz, β-CH_2), 3.45 (unresolved q, 8H, −NC$H_2$$CH_3$), 1.40 (t, 12H, ^3J (H,H) = 7 Hz, CH_3) ppm; ^{13}C NMR (75 MHz, CF_3COOD) δ 166.1, 136.5, 133.2, 129.4, 126.5, 124.5, 121.5, 52.4, 49.2, 36.4, 7.4 ppm; IR (KBr) ν 2969, 1695, 1654, 1593, 1579 cm^{-1}; UV−vis (3.3×10^{-4} M in HCOOH, 23.40 N) λ_{max} (ϵ, M^{-1} cm^{-1}) 496 (43 655), 531 (62 773), 468 nm (16 530). **2b**: ^{1}H NMR (300 MHz, CF_3COOD) δ 8.80 (s, 4H, Ar-H), 4.77 (t, 4H, ^3J (H,H) = Hz, α-CH_2), 3.69 (t, 4H, ^3J (H,H) = Hz, β-CH_2), 3.50 (unresolved q, 8H, −NC$H_2$$CH_3$), 1.45 (t, 12H, ^3J (H,H) = 7 Hz, CH_3) ppm; ^{13}C NMR (125 MHz, CF_3COOD) δ 166.1, 136.5, 133.2, 129.4, 126.5, 124.5, 121.5, 52.4, 49.2, 36.4, 7.4 ppm; IR (KBr) ν 2941, 1695, 1655, 1588, 1433, 1392, 1309 cm^{-1}; HRMS (FAB, *m/z*) calcd for $C_{36}H_{33}D_4N_4O_4$ ($M^{2+} - H^+$), 593.3066; found 593.3092; mp 290 °C dec.

Monopotassium Salt of 2-(*N,N*-Diethylamino)ethylperylene-9,10-dicarboximide-3,4-dicarboxylic Acid (5a). Monopotassium salt **4** (9.82 g, 21.9 mmol), prepared according to the procedure reported by Tröster,[14] was suspended in water (300 mL) at room temperature. *N,N*-Diethylethylenediamine (10.63 g, 89.60 mmol) dissolved in 50 mL of water was added slowly to the suspension of **4**. The mixture was stirred for 3 h at room temperature. Acetone (1 L) was added into the resulting red solution to induce precipitation. The mixture was allowed to stand overnight, and the resulting brick red precipitate was collected using suction filtration. The residue was resuspended in acetone, and the mixture was refluxed for 1 h. The brick red solid was then isolated by vacuum filtration, washed with acetone, and dried under vacuum at 120 °C overnight to yield 10.9 g (19.9 mmol, 91%) of **5a** as a brick red solid.

(26) Rogovik, V. I.; Shirokii, K. I.; El'tsov, A. V. *Zh. Org. Khim.* **1980**, *16*, 867−872.
(27) Rohr, U.; Schlichting, P.; Böhm, A.; Gross, M.; Meerholz, K.; Bräuchle, C.; Müllen, K. *Angew. Chem., Int. Ed.* **1998**, *37*, 1434−1437.

Sulfate (5b) or Formate Salt (5c) of 2-(*N,N*-Diethylamino)ethylperylene-9,10-dicarboximide-3,4-dicarboxylic Anhydride. Compound **4** (2.09 g, 4.66 mmol) was suspended in 35 mL of double-distilled water and cooled to 0 °C in an ice bath. A total of 2 mL of *N,N*-diethylethylenediamine (14.2 mmol, 3 equiv) was dissolved in 5 mL of water and added dropwise to the suspension of **4**. The mixture was stirred for 3 h and gradually warmed to room temperature. It was then acidified with 0.5 M sulfuric acid. The orange precipitate that formed was filtered, washed with 0.1 M sulfuric acid, and dried under vacuum to give 2.57 g (4.37 mmol, 94% yield) of **5b**. For characterization purposes, the formate salt **5c** was also prepared by dissolving 1.10 g of the isolated material (**5b)** in 125 mL of 23.4 N formic acid, and then 75 mL of EtOH was added followed by 125 mL of dibutyl ether that was layered on slowly. The mixture was allowed to sit overnight to allow for complete precipitation. The bright red solid was filtered and washed with excess acetone and dried to give 0.75 g (75% recovery). All characterization was performed with the formate salt unless otherwise noted: ^{1}H NMR (300 MHz, CF_3COOD) δ 8.71 (d, 2H, ^3J (H,H) = 8 Hz; Ar-H), 8.51 (unresolved multiplet, 4H, Ar-H), 8.33 (d, 2H, ^3J (H,H) = 8 Hz, Ar-H), 8.08 (s, 1H, formate proton), 4.81 (unresolved t, 2H, α-CH_2), 3.87 (unresolved t, 2H, β-CH_2), 3.64 (multiplet, 4H, $-NCH_2CH_3$), 1.53 (t, 6H, ^3J (H,H) = 7 Hz, CH_3) ppm; ^{13}C NMR (125 MHz, CF_3COOD) δ 167.5, 163.4, 138.4, 137.1, 136.5, 135.4, 133.0, 131.1, 127.9, 127.8, 126.9, 126.7, 124.2, 119.5, 55.2, 50.5, 38.3, 9.3 ppm; IR (KBr) ν 1767, 1724, 1697, 1654, 1595 cm^{-1}; MS (FAB, *m/z*) calcd for $C_{30}H_{23}N_2O_5$ (M^+) 491, found 491; mp 258 °C.

2-(*N,N*-Diethylamino)ethylperylene-3,4-dicarboximide (6). Compound **5a** (5.43 g, 9.93 mmol) and KOH (5.67 g, 86.8 mmol) were placed in a Teflon cup. Double-distilled water (80 g) was added. After sonication for 30 min, the Teflon cup was then placed inside a 325-mL stainless steel reactor vessel with a steel lid. The closed reactor vessel was completely submerged in a sand bath in a detonation safe room. The temperature was ramped to 220 °C and maintained for 12 h. *Caution: Careful control of the temperature is required to prevent pressure buildup beyond the safety limit of the steel reactor used. The use of a steel reactor with a safety pressure release valve is strongly recommended. The reaction vessel should be cooled back to room temperature before opening the lid.*

The reactor was cooled to room temperature and opened. The resulting metallic brick red suspension was washed out with excess amount of water into a filter funnel and collected by suction filtration. The resulting residue was washed with water until the filtrate was colorless. After drying under vacuum, the residue was dissolved in $CHCl_3$ (200 mL), and the insoluble solid was removed by suction filtration. The solution in $CHCl_3$ was added to a basic alumina pad. The basic alumina was eluted with acetone/$CHCl_3$ (v/v = 2:8). The eluent was collected until the eluent became colorless. The solvent was then evaporated to give compound **6** as red needlelike crystals in 70% yield. Other attempts gave **6** in as high as 75% yield: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, 2H, ^3J (H,H) = 7.5 Hz, Ar-H), 7.93 (d, 2H, ^3J (H,H) = 7 Hz, Ar-H), 7.81 (d, 2H, ^3J (H,H) = 7.5 Hz, Ar-H), 7.67 (d, 2H, ^3J (H,H) = 8.5 Hz, Ar-H), 7.38 (t, 2H, ^3J (H,H) = 8.5 Hz, Ar-H), 4.23 (t, 2H, ^3J (H,H) = 8 Hz, α-CH_2), 2.80 (t, 2H, ^3J (H,H) = 8 Hz, β-CH_2), 2.71 (q, 4H, ^3J (H,H) = 7 Hz, $-NCH_2CH_3$), 1.15 (t, 6H, ^3J (H,H) = 7 Hz, CH_3) ppm; ^{13}C NMR (125 MHz, CF_3COOD) δ 168.6, 142.9, 136.2, 135.6, 135.2, 132.0, 129.7, 129.3, 129.0, 128.3, 128.1, 122.5, 119.1, 54.6, 51.5, 38.7, 9.8 ppm; UV−vis (2.1 × 10^{-4} M of the acetate salt in H_2O) λ_{max} (ϵ, M^{-1} cm^{-1}) 491 nm (18 000); UV−vis (2.5 × 10^{-4} M in $CHCl_3$) λ_{max} (ϵ, M^{-1} cm^{-1}) 489 (36 000), 508 nm (34 000); IR (KBr) ν 2965, 2806, 1688, 1649, 1592, 1571 cm^{-1}; HRMS (DEI, *m/z*) calcd for $C_{28}H_{24}N_2O_2$ (M^+) 420.1838, found 420.1822.

2-(*N,N*-Diethylamino)ethyl-9-bromoperylene-3,4-dicarboximide (7). In a 250-mL round-bottom flask were mixed together 1.20 g (2.85 mmol) of **6** and 65 mL of concentrated sulfuric acid. The mixture was cooled to −5 °C, and then 0.19 mL of Br_2 was added dropwise with a syringe. The reaction mixture was stirred vigorously at −5 °C for 1 h. While still cold, the reaction mixture was poured into 250 mL of prechilled water in a 1000-mL recovery flask in an ice bath, and the pH of the resultant solution was adjusted to pH 8−9 by slowly adding about 170 mL of 30% NH_4OH(aq). A bright red precipitate formed, and the suspension was sonicated for 3 h to ensure complete deprotonation of the amine. The solid was filtered and washed with 300 mL of 5% NH_4OH(aq). The product was dried under vacuum to yield 1.41 g (2.81 mmol, 98%) of bright red solid **7**. Compound **7** can be further purified by recrystallization in a 1% triethylamine/DMF solution. The filtered solid was washed with ether and dried under vacuum to recover 80% of **7**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, 1H, ^3J (H,H) = 8 Hz, Ar-H), 8.31 (d, 1H, ^3J (H,H) = 8 Hz, Ar-H), 8.14 (d, 1H, ^3J (H,H) = 7.8 Hz, Ar-H), 8.12 (d, 1H, ^3J (H,H) = 8.5 Hz, Ar-H), 8.06 (d, 1H, ^3J (H,H) = 7.5 Hz, Ar-H), 7.99 (d, 1H, ^3J (H,H) = 8 Hz, Ar-H), 7.85 (d, 1H, ^3J (H,H) = 8 Hz, Ar-H), 7.69 (d, 1H, ^3J (H,H) = 8 Hz, Ar-H), 7.54 (t, 1H, ^3J (H,H) = 7.5 Hz, Ar-H), 4.29 (t, 2H, ^3J (H,H) = 8 Hz, α-CH_2), 2.82 (t, 2H, ^3J (H,H) = 8 Hz, β-CH_2), 2.71 (q, 4H, ^3J (H,H) = 8 Hz, $-NCH_2CH_3$), 1.14 (t, 6H, ^3J (H,H) = 7.5 Hz, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.8, 163.7, 136.2, 136.1, 132.8, 131.3, 1313, 131.2, 130.0, 129.4, 129.4, 128.8, 128.8, 128.1, 126.2, 126.1, 124.2, 123.5, 121.2, 121.2, 120.6, 120.3, 50.1, 47.9, 38.3, 12.6 ppm; UV−vis (5.6 × 10^{-5} M, $CHCl_3$) λ_{max} (ϵ, M^{-1} cm^{-1}) 513 (35 600), 488 nm (36 000); IR (KBr) ν 2966, 1693, 1647, 1592, 1562 cm^{-1}; HRMS (FAB, *m/z*) calcd for $C_{28}H_{24}BrN_2O_2$ (MH^+) 499.1021, found 499.1004; mp 246 °C dec.

***N,N′*-Bis(2-(*N″,N″*-diethylammonium)ethyl)-9,9′-biperylene-3,4:3′4′-bis(dicarboximide) Diacetate (8).** A total of 0.48 g (2.0 mmol) of $NiCl_2 \cdot 6H_2O$ was dissolved in 47 mL of DMF in a 100-mL round-bottom flask. Then the solution was warmed to 50 °C, and 2.10 g (8.0 mmol) of PPh_3 was added. After 10 min, 0.25 g (4.0 mmol) of zinc dust (325 mesh) was added. The solution changed color over the course of 30 min from blue to red. After heating at 50 °C for 1 h, 1.00 g (2.00 mmol) of **7** was added, and a condenser was fit to the round-bottom flask. After another 4.5 h, the reaction mixture was allowed to cool, and the product that precipitated was filtered, washed with acetone, and dried. The solid was then dissolved in 30 mL of boiling glacial acetic acid. After cooling, 70 mL of chloroform was added, and the solution was filtered through a pad of cellulose in a 60-mL fritted glass funnel. The cellulose was washed with excess chloroform. Most of the solvent was removed from the filtrate by evaporation. A total of 10 mL of chloroform and 100 mL of EtOAc was added. The solution was kept at ∼0 °C for 2 h. Then the precipitate was filtered off and washed with excess EtOAc. The resulting solid was dark purple/red and was sonicated with Et_2O and then filtered and washed with excess Et_2O in order to remove residual acetic acid. The solid was dried under vacuum to weigh 840 mg (0.88 mmol, 88%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (d, 2H, ^3J (H,H) = 8.5 Hz, Ar-H), 8.59 (d, 2H, ^3J (H,H) = 9 Hz, Ar-H), 8.58 (d, 2H, ^3J (H,H) = 8 Hz, Ar-H), 8.50 (d, 2H, ^3J (H,H) = 8 Hz, Ar-H), 8.46 (d, 2H, ^3J (H,H) = 7 Hz, Ar-H), 8.44 (d, 2H, ^3J (H,H) = 7.5 Hz, Ar-H), 7.72 (d, 2H, ^3J (H,H) = 8 Hz, Ar-H), 7.56 (d, 2H, ^3J (H,H) = 8 Hz, Ar-H), 7.50 (t, 2H, ^3J (H,H) = 6.8 Hz, Ar-H), 4.41 (unresolved t, 4H, α-CH_2−), 3.04 (broad, 4H, $-CH_2NR_2$), 2.93 (multiplet, 8H, $-NCH_2CH_3$), 2.04 (s, 6H, acetate $-CH_3$), 1.24 (t, 12H, ^3J (H,H) = 6.8 Hz, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.1, 140.8, 137.5, 137.3, 133.8, 131.9, 130.1, 129.7, 129.7, 129.6, 129.5, 128.4, 127.6, 126.9, 124.3, 123.6, 121.2, 121.1, 120.8, 120.6, 49.0, 47.6, 36.7, 11.2 ppm; UV (2.7 × 10^{-7} M in $CHCl_3$) λ_{max}(ϵ, M^{-1} cm^{-1}) 534 nm (47 000); IR (KBr) ν 3435, 1691, 1655, 1592, 1572, cm^{-1}; HRMS (FAB, *m/z*) calcd for $C_{56}H_{47}N_4O_4^+$ ($M^{2+} - H^+$) 839.3597, found 839.3607; mp >320 °C.

***N,N′*-Bis(2-(*N″,N″*-diethylammonium)ethyl)quaterrylene-3,4:13,14-bis(dicarboximide) Diformate (1a).** A total

of 1.01 g (1.20 mmol) of the acetate salt **8**, 10.0 g of D-glucose (55.5 mmol), approximately 150 g of KOH pellets (2.3 mol), and 200 mL of absolute ethanol were added to a 500-mL round-bottomed flask. The mixture was heated at 135 °C under nitrogen for 3 h. After cooling to room temperature, 200 mL of water was added to dissolve all of the KOH and glucose. The undissolved solid was filtered and washed with hot water (200 mL) and acetone. After drying under vacuum, the solid was dissolved in 23.4 N HCOOH (100 mL). Addition of diethyl ether to the formic acid solution resulted in the formation of a blue precipitate of **1a** and a red solid of the unreacted compound **8**. The solid mixture was filtered and dried under vacuum. The solid mixture was then refluxed in chloroform (200 mL) for 30 min. to dissolve the unreacted compound **8**, and the undissolved formate salt **1a** was filtered and washed with chloroform, and dried under vacuum to yield 0.51 g (0.51 mmol, 43%) of **1a**·$4H_2O$. Other attempts with longer times for the oxidative aromatization gave yields as high as 60%: ^{1}H NMR (300 MHz, D_2SO_4) δ 8.89 (br, Ar-H), 8.67 (br, Ar-H), 8.42 (br, A-H) (all three peaks integrate to 16 H); 5.78 (br, 2H, N−H), 4.46 (br, 4H, α-CH_2), 3.07 (br, 4H, β-CH_2), 2.80 (br, 8H, $-NCH_2CH_3$), 0.79 (unresolved t, 12H, CH_3) ppm; IR (KBr) ν 1685, 1647, 1573, 1361, cm^{-1}; HRMS (FAB, *m*/*z*) calcd for $C_{56}H_{45}N_4O_4$ ($M^{2+} - H^+$) 837.3441, found 837.3461. Anal. Calcd for $C_{58}H_{56}N_4O_{12}$ (**1a**·$4H_2O$): C, 69.59; H, 5.64; N, 5.60. Found: C, 69.92; H, 5.31; N 5.64; mp >320 °C.

Acknowledgment. S.-W.T.C. is grateful to the National Science Foundation for a Career Award and the support of this research (DMR-9876027). We appreciate the helpful suggestions of the reviewers.

Supporting Information Available: NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

JO030342Y