Synthesis, Structure, and Photophysical Studies of a Pair of Novel Rigid Bichromophoric Systems Bearing a Methyl Viologen Acceptor Unit

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The rigid bichromophoric systems **7a**·$2BF_4$ and **7b**·$2BF_4$, comprising either a dimethoxybenzene (**a**) or dimethoxynaphthalene (**b**) unit, each covalently linked through a six-bond norbornylogous bridge to a methyl viologen unit, were synthesized with a view to studying long-range intramolecular energy (EnT) and/or electron (ET) transfer. X-ray crystallography has been used to illustrate that **7b**·$2BF_4$ has the ability to undergo self-organization on crystallization to form extended linear arrays within the crystal lattice. Preliminary photophysical studies on **7b**·$2BF_4$ indicate the presence of an additional rapid nonradiative process (rate constant > 2.5×10^{10} s^{-1}) in the bichromophore compared to a model dimethoxynaphthalene unit, and possible explanations for this process are presented.

Introduction

An important goal in chemistry is the rational design of multichromophoric supramolecular systems that are capable of efficient transport and utilization of either electronic excitation or electrons.[1] In this respect, there remains a pressing need to gain a deeper understanding of those factors that govern the dynamics of energy-transfer (EnT) and electron-transfer (ET) processes.[2,3] This need is being addressed by a number of research groups who have synthesized a variety of rigid, covalently-linked multichromophoric systems in which interchromophoric separations and orientations are well-defined.[4−8]

Our approach to the design of model multichromophoric assemblies is based on the attachment of chromophores to rigid norbornylogous bridges[4a,6] of variable, but controllable, length and configuration—the first representatives of which are the recently reported triads, such as **1(m)** (Chart 1).[7]

Photophysical studies on these systems revealed that photoinduced ET occurred with high quantum efficiency and showed that the resulting giant charge-separated states ($^+$DMA−DMN−DCV$^-$) were reasonably long-lived (*ca.* 60 ns), at least for the *anti* isomers.[8,9] These encouraging results have led us to attempt the synthesis of tetrads of the type **2** that incorporate, in addition to two naphthoquinone groups, terminal porphyrin donor and methyl viologen (MV^{2+}) acceptor chromophores. Retrosynthetic considerations led immediately to **3a** and **3b** (Chart 2) as key components for the construction of

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(9) The *syn* and *anti* isomers are those in which the *ethano* and *methano* bridges of the respective bicyclo[2.2.2]octane and norbornane units directly fused to the DMN ring are, respectively, *syn* and *anti* with respect to one another.

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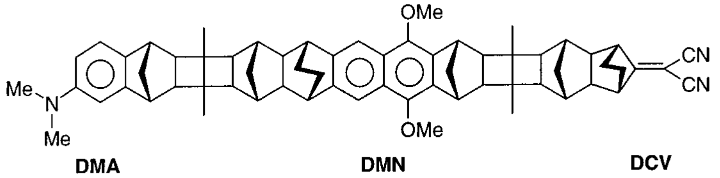
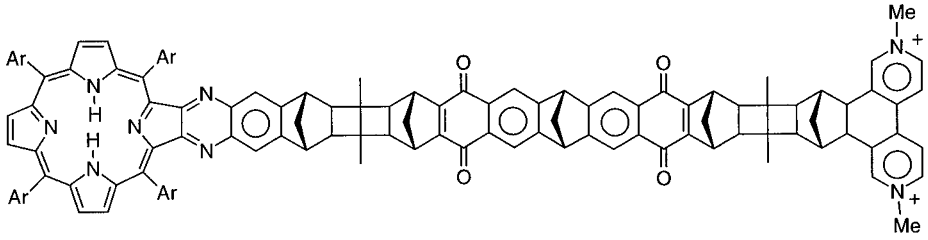
Chart 1

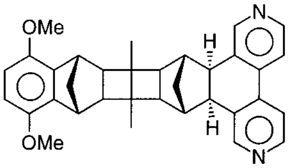


1(m)

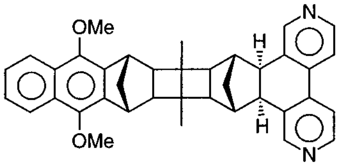


2 $2X^-$

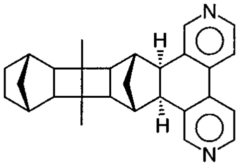
Chart 2



3a

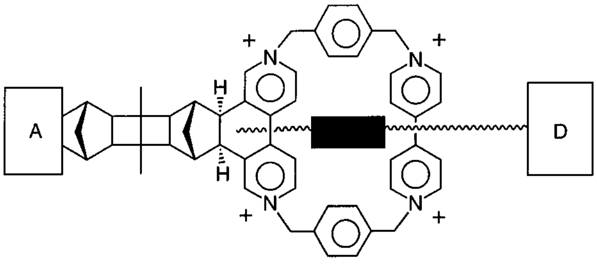


3b



3c

Chart 3



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the right-hand bridge of **2** and related systems. The attractiveness of **3a** and **3b** is further enhanced by the possibility of employing them in the form of Stoddartian boxes,[10] of the type **4** (Chart 3), or as components of large supramolecular assemblies.

In this paper, we present the synthesis of **3a** and **3b**, the model system **3c**, and their bismethylated derivatives **7a**−**c**·2BF$_4$, respectively (Scheme 1). We report the single-crystal X-ray diffraction determination, as well as electrochemical and photophysical studies on compound **7b**·2BF$_4$.

Results and Discussion

Synthesis. The syntheses of **3a**−**c**, which are outlined in Scheme 1, entail appending the 4,4′-dipyridyl unit to the known[6a,7] six-bond bridge systems **6a**−**c** using a variation of the aryl−aryl coupling method developed by de Meijere *et al.*[11] The palladium(II)-catalyzed coupling (Pd(OAc)$_2$, PPh$_3$, ^{n}Bu$_4$NBr, K$_2$CO$_3$, DMF) of 3-bromopyridine with the norbornene analogues[6a] **6a**−**c** afforded the bipyridine derivatives **3a**−**c**, respectively. Substitution of the readily available 3-bromopyridine for the 3-iodopyridine employed by de Meijere *et al.*[11] was found to have no detrimental effect upon the yields of the reaction, in our hands. The yields of **3a**−**c** were highest when the coupling was performed under dilute conditions (approximately 0.01 M in alkene). The moderate yields obtained (20−40%) for this reaction are lowered when compared to the optimized values reported for norbornene (45%) and dicyclopentadiene (56%).[11] Quaternization (Me$_3$OBF$_4$, CH$_2$Cl$_2$) of the bipyridine nitrogens occurred readily and in reasonable yields (typically 60−70%) to produce **7a**$^{2+}$−**7c**$^{2+}$ as their tetrafluoroborate salts.

X-ray Crystal Structure. Red crystals suitable for X-ray crystallography were obtained by the vapor diffusion of diethyl ether into an acetonitrile solution of **7b**·2BF$_4$. The results of the determination are consistent with the expected stereochemistry and connectivities. The structure[12] of **7b**·2BF$_4$ reveals the presence of an approximately C_s symmetric molecule with a mirror plane perpendicular to the major molecular axis. The *exo*-orientation of the 5,6-dihydro-3,8-phenanthroline unit (Figure 1a) is consistent with the known[13] strong tendency for *exo* attack on the norbornene ring. The average planes of the dimethoxynaphthalene and viologen units are parallel. The centroid−centroid distance from the

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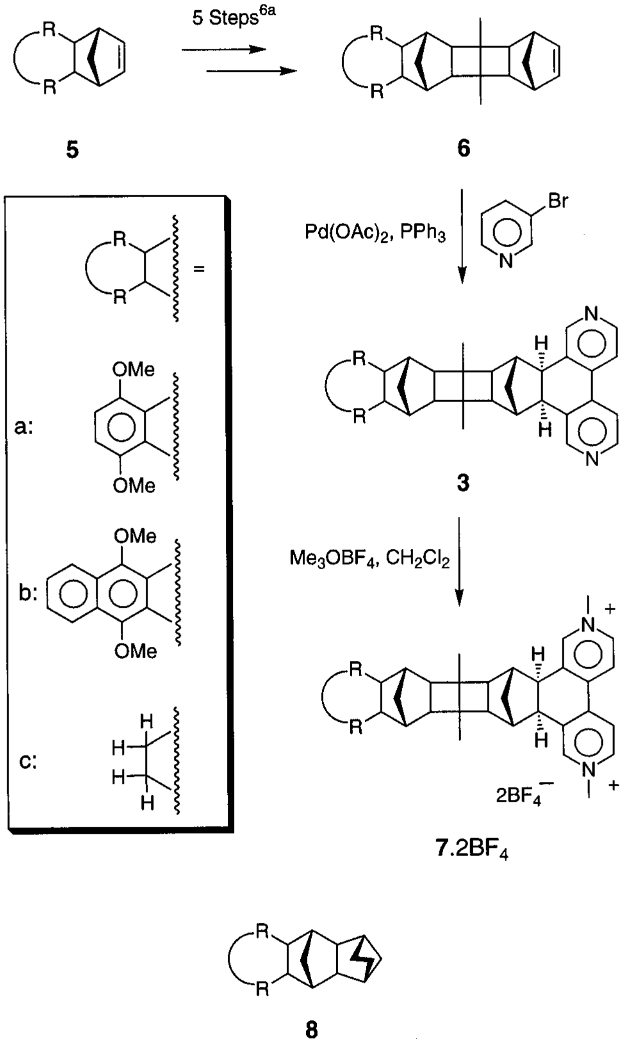
[10] Anelli, P. L.; Ashton, P. R.; Ballardini, R.; Balzani, V.; Delgado, M.; Gandolfi, M. T.; Goodnow, T. T.; Kaifer, A. E.; Philp, D.; Pietraszkiewicz, M.; Prodi, L.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Vicent, C., Williams D. J. *J. Am. Chem. Soc.* **1992**, *114*, 193.

[11] Albrecht, K.; Reiser, O.; Weber, M.; Knieriem, B.; de Meijere A. *Tetrahedron* **1994**, *50*, 383.

[12] (a) Compound **7b**·2BF$_4$ (C$_{40}$H$_{42}$N$_2$O$_2$·2BF$_4$; M_r = 756.4) crystallized in the monoclinic space group $P2_1/m$ with cell dimensions of a = 14.147(2) Å, b = 18.571(1) Å, c = 14.287(8) Å, β = 93.925(5)°, and V = 3744.8(7) Å^3 and an occupation of Z = 4 in the unit cell. Data were collected at 20 °C with an Enraf-Nonius CAD-4 diffractometer using nickel-filtered copper radiation (λ = 1.5418 Å), to a maximum 2θ = 120°, giving 5739 unique reflections; the structure was determined by direct phasing and Fourier methods and solved by MULTAN80 and refinement used RAELS, yielding R = 0.099, R_w = 0.130 for 2281 independent reflections with $I > 3\sigma(I)$.

[13] Freeman, F. *Chem. Rev.* **1975**, *75*, 439.

Scheme 1



closest ring of the naphthalene unit to the 4,4′-carbon−carbon bond of the viologen unit is 10.9 Å. A *syn* relationship is observed between the methoxy groups of the naphthalene unit, which is common to such structures.[14]

Within the crystal lattice of **7b**·2BF$_4$, the molecules are coaligned along the crystallographic *b* direction with the tetrafluoroborate counterions forming a parallel channel between adjacent organic arrays (Figure 1b). There is a proximal relationship between the DMN and MV^{2+} units with an intermolecular ring centroid−4,4′-C−C bond separation of 3.4 Å, possibly indicating a degree of π−π stabilization in this portion of the π-electron donor−acceptor complex,[15] which gives rise to the red color of the crystals. The repeat separation between adjacent bipyridinium units is 14.3 Å.

Electrochemistry. The first oxidation and first reduction potentials for **7a**·2BF$_4$ and **7b**·2BF$_4$, and the model compounds **7c**·2BF$_4$ and **8a** and **8b**, are recorded in Table 1. The bichromophores **7a**·2BF$_4$ and **7b**·2BF$_4$ and the model compound **7c**·2BF$_4$ possess identical reduction potentials, thereby attesting to the lack of any significant electronic communication between the two chromophores in the former pair of molecules. In a similar fashion, both the dimethoxybenzene unit of **7a**·2BF$_4$ and the dimethoxynaphthalene unit of **7b**·2BF$_4$ were oxidized at the same potentials as the model compounds **8a** and **8b**, respectively.

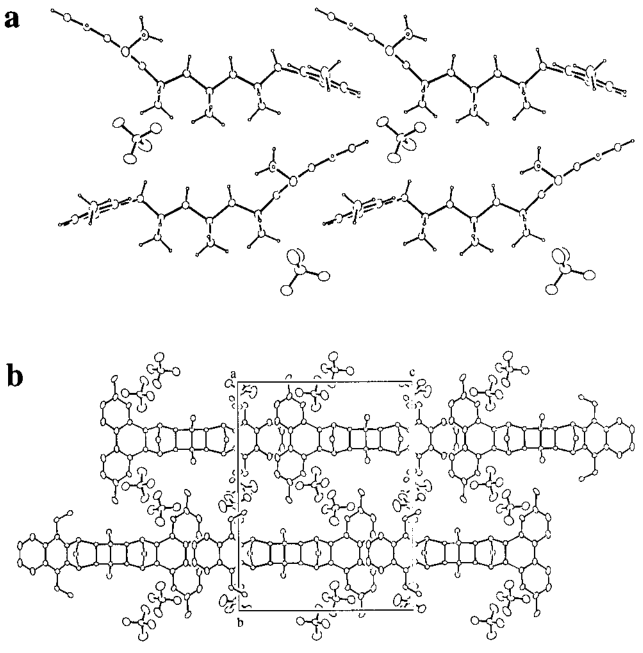


Figure 1. (a) Part of the polar stack of π-donors and π-acceptors that extends along the crystallographic *b*-direction and (b) a view down the crystallographic *a* direction showing the colinear nature of the stack, respectively, of the solid-state structure of **7b**·2BF$_4$.

Table 1. Reduction (E^1) and Oxidation (E^2) Potentials (*vs* Ag/AgCl) of 3a,b and Viologens 7a−c·2BF$_4$ (25 °C, MeCN, Fc/Fc$^+$ Internal Reference, Scan Rate 100 mV s^{-1})

compd	$E^{1,a}$	$E^{2,a}$
8a		+1.26
8b		+1.12
7a	−0.42	+1.26
7b	−0.42	+1.12
7c	−0.42	

[a] Values are ±0.01 V.

Photophysical Studies.[16] There is considerable overlap of the absorption spectra of the individual dimethoxynaphthalene (DMN) and MV^{2+} chromophores. The DMN absorption spectrum has an onset near 340 nm and a maximum at 290 nm, while for MV^{2+} the onset of the spectrum is near 370 nm with a maximum at 280 nm (cf. Figure 2). The DMN model compound **8b** has a fluorescence maximum at 377 nm (Figure 2) and a fluorescence lifetime of 7.6 ± 0.1 ns. In contrast, no fluorescence could be detected from the MV^{2+} model compound **7c**·2BF$_4$ in acetonitrile. This observation is consistent with previous studies on methyl viologen, which have concluded its fluorescence quantum yield $<10^{-4}$ with an estimated singlet excited-state lifetime <1 ps.[17]

For the bichromophoric system **7b**·2BF$_4$, fluorescence from the DMN chromophore is dramatically quenched

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[14] Golka, A.; Craig, D. C.; Paddon-Row M. N. *Aust. J. Chem.* **1994**, *47*, 101−110. Craig, D. C.; Oliver, A. M.; Paddon-Row, M. N. *J. Chem. Soc., Perkin Trans. 1*, **1993**, 197.

[15] Hunter, C. A; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525. Ferguson, S. B.; Sanford, E. M.; Seward, E. M.; Diederich, F. *J. Am. Chem. Soc.* **1991**, *113*, 5410. Hunter, C. A. *Chem. Soc. Rev.* **1994**, *23*, 101. Amabilino, D. B.; Anelli, P. L.; Ashton, P. R.; Brown, G. R.; Córdova, E.; Godínez, L. A.; Hayes, W.; Kaifer, A. E.; Philp, D.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Tolley, M. S., Williams D. J. *J. Am. Chem. Soc.* **1995**, *117*, 11142.

[16] All photophysical studies were carried out in MeCN solution at 293 K.

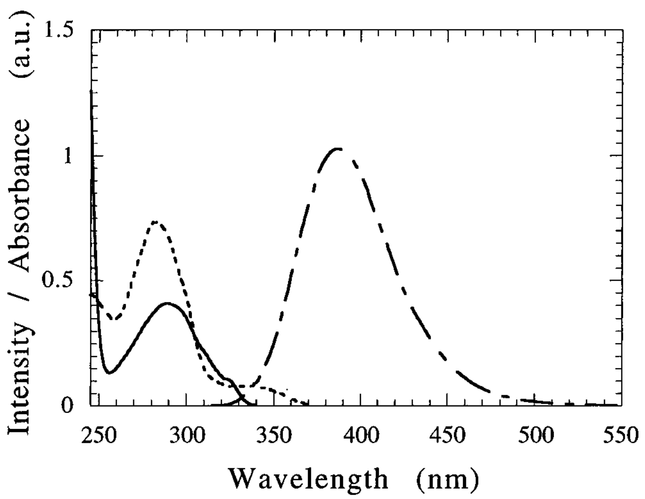

Figure 2. Absorption spectra in acetonitrile solution of the model dimethoxynaphthalene unit **8b** (solid line), the model methyl viologen **7c**·$2BF_4$ (dotted line), and the fluorescence spectrum of **8b** (dashed line) in acetonitrile solution at 293 K.

compared to the model compound. For excitation at 292 nm (and after correcting for competitive absorption by the methyl viologen) we estimate the fluorescence is quenched more than 200-fold corresponding to a DMN excited-state lifetime of < 40 ps (which is the resolution limit of our instrumentation). This indicates that in the bichromophoric compound there is a competing nonradiative process with a rate constant $>2.5 \times 10^{10}$ s^{-1}. The additional nonradiative process in **7b**·$2BF_4$ can be either electron transfer (ET) or energy transfer (EnT). The free energy change (ΔG) for photoinduced intramolecular ET in a bichromophoric system can be estimated using the approach of Weller:[18]

$$\Delta G = e(E^{\mathrm{ox}}(\mathrm{D}) - E^{\mathrm{red}}(\mathrm{A})) - E_{\mathrm{oo}} - \left(\frac{e^2}{4\pi\epsilon_{\mathrm{o}}\epsilon_{\mathrm{s}}R_{\mathrm{c}}}\right) - \frac{e^2}{8\pi\epsilon_{\mathrm{o}}}\left(\frac{1}{r^+} + \frac{1}{r^-}\right)\left(\frac{1}{37.5} - \frac{1}{\epsilon_{\mathrm{s}}}\right)$$

Calculation of ΔG for photoinduced ET in $\mathbf{7b}^{2+}$ requires the donor and acceptor redox potentials ($E^{\mathrm{ox}}(\mathrm{D}) = 1.12$, $E^{\mathrm{red}}(\mathrm{A}) = -0.42$ from Table 1), the lowest singlet excitation energy for DMN ($E_{\mathrm{oo}} = 3.87$ eV), the center-to-center interchromophore distance ($R_{\mathrm{c}} = 10.86$ Å), and the effective donor and acceptor radical cation and anion radii ($r^+ \approx r^- \approx 4.5$ Å).[6b] In acetonitrile (dielectric constant, $\epsilon_{\mathrm{s}} = 37.5$), ΔG is calculated to be -2.33 eV, indicating that photoinduced electron transfer is thermodynamically highly feasible. If electron transfer occurs after photoexcitation, formation of the reduced viologen species, MV^+, with a characteristic absorption near 500 nm might be observed.[17] However, transient absorption studies following flash photolysis of **7b**·$2BF_4$, which resulted in excitation of either the MV^{2+} group (355 nm) or both DMN and MV^{2+} species (266 nm), led to no detectable transient formation of MV^+ within the 7 ns time resolution of our laser flash photolysis system.

The absence of an observable transient absorption associated with radical ions on the nanosecond timescale of our instrumentation might be attributable to rapid (<7 ns) recombination of the charge-separated state. This is reasonable since the energy difference between the ground state, DMN$-MV^{2+}$, and the charge-separated state, DMN^+-MV^+, is *ca.* 1.54 eV[19] and may be of similar magnitude to the combined solvent and internal reorganisation energies. Under these conditions, Marcus theory predicts that the activation energy barrier to charge-recombination will be small and lower than that for charge separation. The low barrier to the back-electron transfer process could contribute to very fast charge recombination. However, a further possibility is that singlet−singlet EnT from excited DMN to the MV^{2+} moiety followed by rapid nonradiative relaxation competes effectively with any ET process. There is a significant overlap of the DMN (donor) fluorescence spectrum with the MV^{2+} absorption profile (cf. Figure 2), which is a requirement for Förster dipole−dipole EnT.[20] In addition, we have demonstrated previously that a norbornylogue bridge linking two chromophores can mediate orbital overlap-dependent EnT mechanisms (Dexter-type or short-range interactions) via a "superexchange" process, thereby substantially increasing the rate.[21] An unambiguous assignment of the quenching mechanism requires further investigation beyond the scope of the present work. However, we could reasonably expect that in compounds of type **2**, which contain a terminal porphyrin moiety and in which intramolecular EnT from the locally excited porphyrin to MV^{2+} is energetically not possible, that ET will be the preferred pathway upon excitation of the porphyrin.

Conclusions

In this paper, we described the preparation and characterization of **7a**−**c**·$2BF_4$ model compounds bearing a viologen unit and donor-substituted aryl chromophores linked together *via* rigid norbornylogous hydrocarbon bridges. Preliminary photophysical studies demonstrate that **7b**·$2BF_4$ undergoes a rapid nonradiative decay processes compared to the model **8b**, which could be associated with energy- or electron-transfer processes.

With $\mathbf{7}^{2+}$, we have attached a new electron acceptor—namely the viologen unit—onto the norbornylogous bridge, thereby broadening our ongoing research into the effects of distance, solvent, bridge configuration, and driving force on the dynamics of intramolecular energy- and electron-transfer processes in multichromophoric systems. Our present directions include replacing the donor chromophores in order to study electron transfer. The distinctive properties of $\mathbf{7}^{2+}$ represent the basis of an approach to studying electron transfer that employs use of the noncovalent bonding interactions to bring electron donors and acceptors together. Systems such as $\mathbf{7}^{2+}$ also become important compounds with which to probe the effect of counterions on electron transfer.

Experimental Section

General Methods. Chemicals were purchased from Aldrich and used as received. Solvents were dried, and reagents were purified where necessary using literature methods.[22] Compounds **5a** and **5b** were prepared according to published

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[17] Mau, A. W.-H.; Overbeek, J. M.; Loder, J. W.; Sasse, W. H. F. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 869.

[18] Weller, A. *Z. Phys. Chem.* **1982**, *133*, 93.

[19] $E^{\mathrm{ox}}(\mathrm{D}) - E^{\mathrm{red}}(\mathrm{A}) = 1.12 - (-0.42) = 1.54$ eV.

[20] Turro, N. J. *Modern Photochemistry*; Benjamin: Menlo Park, 1978; Chapter 9.

[21] Scholes, G. D.; Ghiggino, K. P.; Oliver, A. M.; Paddon-Row, M. N. *J. Phys. Chem.* **1993**, *97*, 11871.

[22] Perrin D. D., Armarego, W. L., Ed. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: New York, 1988.

literature.[6,7] Thin-layer chromatography (TLC) was carried out on aluminum sheets precoated with Merck 5735 Kieselgel 60F. Column chromatography was carried out using Kieselgel 60 (0.040−0.063 mm mesh, Merck 9385). Melting points are uncorrected. Microanalyses were carried out by Dr. H. Pham, University of New South Wales. Low-resolution mass spectra (MS) were obtained using either electron impact (EIMS) or matrix-assisted laser desorption (MALDI) mass spectrometry in conjunction with a 3,5-dihydrobenzoic acid matrix. Nuclear magnetic resonance (NMR) spectra were recorded at 300 MHz for proton frequency and 75 MHz for carbon frequency using the DEPT pulse sequence.

Photophysical Experiments. Solutions of the compounds in spectroscopic grade MeCN were made up to a maximum optical density of 0.2 (concentration $< 10\ \mu$M) and were thoroughly degassed by repeated freeze−pump−thaw cycles. Measurements were carried out at 293 K. Fluorescence decay profiles were obtained by the time-correlated single-photon counting technique using an excitation wavelength of 292 nm. Full details of the instrumentation and data analysis procedures may be found elsewhere.[23] Transient absorption experiments were performed using a laser flash photolysis apparatus that comprised a Nd:YAG laser (continuum) with frequency-tripled (355 nm) and frequency-quadrupled (266 nm) output. Transient species generated by the absorption of 5 mJ excitation pulses (pulse width 7 ns) were monitored at right angles to the excitation using a pulsed 150 W high-pressure xenon lamp, photomultiplier tube, and digital oscilloscope.

Electrochemistry. Experiments were conducted at 25 °C in a one-compartment cell containing a glassy carbon working electrode, a Pt-wire auxilary electrode, and a Ag/AgCl quasireference electrode (−40 mV relative to the saturated calomel electrode (SCE)). As internal reference redox system, the Fc/Fc^+ couple (Fc = ferrocene) was used with a redox potential measured to 0.507 V (vs Ag/AgCl).[24] Measurements were made on (saturated or 0.7 mM) solutions of each sample in dry freshly distilled acetonitrile containing Bu_4NBF_4 (0.1 M, Aldrich) as supporting electrolyte with a scan rate of 100 mV s^{-1}.

Crystallography. Reflection data were measured with an Enraf-Nonius CAD-4 diffractometer in $\theta/2\theta$ scan mode using nickel-filtered copper radiation ($\lambda = 1.5418$ Å). Reflections with $I > 3\sigma(I)$ were considered observed. The structure was determined by direct phasing and Fourier methods. The structure has independent cations positioned across the symmetry planes, and these are related by approximate 2-fold screws lying within the planes and parallel to a. The asymmetric unit therefore consists of two half-cation molecules and two BF_4 anions. The methoxy carbons and both anions exhibit positional disorder. The relatively small number of observed reflections, together with the disorder and pseudosymmetry, gave rise to severe refinement problems, and constrained refinement was necessary to achieve satisfactory convergence. Positional parameters of the cation atoms were refined independently, but corresponding distances in the two molecules were constrained to approach equality. A set of subsidiary coordinates with tetrahedral geometry was used to define a BF_4 group, and the disordered anions were defined by transformation of the set of subsidiary coordinates to one of four local axial systems, each refineable for rotation and translation. The coordinates of the subsidiary atoms were refined, but the ideal tetrahedral geometry was maintained. The relative occupancies of the components of each disordered group were refined. Hydrogen atoms were included in positions calculated each cycle. Two 15-parameter TLX rigid-body models were used to describe the thermal motions of the cations, and another two were used for the disordered anions. Hydrogen atom thermal motions were included with the appropriate group.

Refinement converged at R of 0.099, which is rather higher than normal, but is reasonable considering the poor data quality and refinement difficulties. Reflection weights used were $1/\sigma^2(F_o)$, with $\sigma(F_o)$ being derived from $\sigma(I_o) = [\sigma^2(I_o) + (0.04I_o)^2]^{1/2}$. The weighted residual is defined as $R_w = (\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}$. Atomic scattering factors and anomalous dispersion parameters were from *International Tables for X-ray Crystallography*.[25] Structure solution was by MULTAN80[26] and refinement used RAELS.[27] ORTEP-II[28] was used for the structural diagram.[29]

(8aα,9*β*,9aα,9b*β*,9cα,10*β*,15*β*,15aα,15b*β*,15cα,16*β*,16aα)-11,14-Dimethoxy-9b,15b-dimethyl-8b,9,9a,9c,10,15,15a,-15c,16,16a-decahydro-9,16:10,15-dimethanonaphtho[2′,3″:3′,4′]cyclobuta[1′,2′:3,4]cyclobuta[1,2-*b*]benzo[*f*][3,8]-phenanthroline (3a). To a solution of palladium(II) acetate (29 mg, 0.13 mmol) and triphenylphosphine (0.14 g, 0.52 mmol) in anhydrous DMF (10 mL) under an argon atmosphere were added K_2CO_3 (0.78 g, 6.4 mmol), $^nBu_4NBr$ (1.16 g, 3.6 mmol), and 3-bromopyridine (0.82 g 5.2 mmol), and the mixture was warmed to 70 °C for 30 min. A solution of **6a** (0.9 g, 2.6 mmol) and palladium(II) acetate (29 mg, 0.13 mmol) in anhydrous DMF (170 mL) was added to the solution at 70 °C over 16 h via a syringe pump. On completion of the addition, the mixture was warmed to 120 °C for 24 h and then cooled to room temperature, and dichloromethane (150 mL) was added. The resulting suspension was filtered, and the filtrate was extracted with HCl (2 M, 2 × 100 mL). The combined aqueous solutions were washed with dichloromethane (100 mL), and then solid NaOH was added until the mixture reached pH 13. The resulting suspension was extracted with dichloromethane (5 × 50 mL), the combined organic solutions were washed with H_2O (5 × 100 mL) and brine (100 mL) and then dried ($MgSO_4$), and the solvent was removed under reduced pressure to give a brown solid that was recrystallized from dichloromethane/methanol to yield **3a** as a white solid (0.49 g, 38%): mp > 300 °C; MS (EI) m/z 502 $[M]^+$; ^1H NMR (300 MHz, $CDCl_3$) δ 0.88, (s, 6H), 1.38 (d, $J = 11.3$ Hz, 1H), 1.54 (m, 2H), 1.73 (d, $J = 9.5$ Hz, 1H), 2.09 (s, 2H), 2.30 (s, 2H), 2.45 (s, 2H), 3.15 (s, 2H), 3.52 (s, 2H), 3.81 (s, 6H), 6.62 (s, 2H), 7.62 (d, $J = 5.4$ Hz, 2H), 8.47 (d, $J = 5.4$ Hz, 2H), 8.49 (s, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 9.3, 30.0, 40.1, 41.8, 43.3, 43.8, 49.5, 49.8, 52.9, 56.0, 109.0, 116.1, 132.8, 136.6, 136.5, 147.8, 152.3, 155.0. Anal. Calcd for $C_{34}H_{34}O_2N_2$: C, 81.2; H, 6.8; N, 5.6. Found C, 81.4; H, 6.9; N, 5.5.

(8bα,9*β*,9aα,9b*β*,9cα,10*β*,17*β*,17aα,17b*β*,17cα,18*β*,18aα)-11,16-Dimethoxy-9b,17b-dimethyl-8b,9,9a,9c,10,17,17a,-17c,18,18a-decahydro-9,18:10,17-dimethanoanthraceno-[2″,3″:3′,4′]cyclobuta-[1′,2′:3,4]cyclobuta[1,2-*b*]benzo[*f*]-[3,8]phenanthroline (3b). The title compound was prepared from of **6b** (2.0 g, 5.0 mmol) following the procedure described for compound **3a**: yield 0.55 g (20%); white solid; mp 226−230 °C dec; MS (EI) m/z 554 $[M]^+$; ^1H NMR (300 MHz, $CDCl_3$) δ 0.94 (s, 6H), 1.42 (d, $J = 11.0$ Hz, 1H), 1.57 (d, $J = 11.0$ Hz, 1H), 1.70 (d, $J = 9.5$ Hz, 1H), 1.93 (d, $J = 9.5$ Hz, 1H), 2.31 (s, 2H), 2.36 (s, 2H), 2.49 (s, 2H), 3.18 (s, 2H), 3.70 (s, 2H), 4.02 (s, 6H), 7.45 (m, 2H), 7.62 (d, $J = 5.4$ Hz, 2H), 8.10 (m, 2H), 8.47 (d, $J = 5.4$ Hz, 2H), 8.52 (s, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 9.5, 30.0, 40.5, 41.8, 42.7, 44.4, 49.4, 50.7, 53.0, 61.9, 116.1, 122.0, 125.0, 127.8, 132.7, 135.0, 136.3, 144.3, 147.9, 152.4. Anal. Calcd for $C_{38}H_{36}0_2N_2{\cdot}0.5H_2O$: C, 81.3; H, 6.6; N, 5.0. Found: C, 81.3 H, 6.6; N, 4.8.

(8bα,9*β*,9aα,9b*β*,9cα,10*β*,13*β*,13aα,13b*β*,13cα,14*β*,14aα)-9b,15b-Dimethyl-8b,9,9a,9c,10,11,12,13,13a,13c,14,14a-dodecahydro-9,14:10,13-dimethanobenzo[2″,3″:3′,4′]cyclobuta[1′,2′:3,4]cyclobuta[1,2-*b*]benzo[*f*][3,8]-phenanthroline (3c). The title compound was prepared from of **6c** (0.6 g, 2.6 mmol) following the procedure described for

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compound **3a**: yield 0.36 g (35%); white solid; mp 256−258 °C; MS (EI) *m/z* 394 $[M]^+$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.71, (s, 6H), 1.10 (m, 2H), 1.19 (d, *J* = 10.3 Hz, 1H), 1.30 (d, *J* = 10.3 Hz, 1H), 1.48 (m, 4H), 2.06 (s, 4H), 2.20 (s, 2H), 2.47 (s, 2H), 3.16 (s, 2H), 7.58 (d, *J* = 5.1 Hz, 2H), 8.42 (d, *J* = 5.1 Hz, 2H), 8.48 (s, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 9.4, 28.5, 29.9, 34.9, 35.9, 41.8, 45.2, 49.3, 52.6, 53.1, 116.0, 132.9, 136.2, 147.6, 152.3. Anal. Calcd for $C_{28}H_{30}N_2$: C, 85.2; H, 7.7; N, 7.1. Found: C, 85.5; H, 7.4; N, 6.9.

(8aα,9*β*,9aα,9b*β*,9cα,10*β*,15*β*,15aα,15b*β*,15cα,16*β*,16aα)-*N*,*N*-Dimethyl-11,14-dimethoxy-9b,15b-dimethyl-8b,9,9a,9c,10,15,15a,15c,16,16a-decahydro-9,16:10,15-dimethanonaphtho[2″,3″:3′,4′]cyclobuta[1′,2′:3,4]cyclobuta[1,2-*b*]benzo[*f*][3,8]phenanthrolinium Bis(tetrafluoroborate) Trihydrate ($7a\cdot 2BF_4$). To a stirred solution of **3a** (0.12 g, 0.24 mmol) in anhydrous dichloromethane (2 mL) under an argon atmosphere was added trimethyloxonium tetrafluoroborate (0.1 g, 0.68 mmol), and the resulting white suspension was refluxed for 2 h. The mixture was cooled to room temperature, methanol (1 mL) was added, and the mixture was stirred for 30 min. The solvent was then removed under reduced pressure to give a bright orange solid that was recystallized from acetonitrile/methanol to yield **7a**·$2BF_4$ as a bright orange solid (0.11 g, 70%): mp 268−270 °C; MS (MALDI) *m/z* 532 $[M - 2BF_4]^+$; ^{1}H NMR (300 MHz, CD_3CN) δ 0.96, (s, 6H), 1.39 (m, 1H), 1.55 (m, 1H), 1.77 (m, 2H), 2.00 (s, 2H), 2.55 (s, 2H), 2.59 (s, 2H), 3.46 (s, 2H), 3.54 (s, 2H), 3.85 (s, 6H), 4.35 (s, 6), 6.73 (s, 2H), 8.48 (d, *J* = 6.6 Hz, 2H), 8.60 (d, *J* = 6.6 Hz, 2H), 8.77 (s, 2H); ^{13}C NMR (75.5 MHz, CD_3CN) δ 8.5, 30.0, 39.8, 41.2, 42.8, 43.6, 48.2, 49.7, 49.9, 52.6, 55.4, 109.3, 122.9, 135.9, 139.3, 140.5, 142.9, 147.7, 147.9. Anal. Calcd for $C_{36}H_{40}O_2N_2B_2F_8\cdot 3H_2O$: C, 56.9; H, 6.2; N, 3.7. Found: C, 57.1; H, 6.0; N, 3.6.

(8bα,9*β*,9aα,9b*β*,9cα,10*β*,17*β*,17aα,17b*β*,17cα,18*β*,18aα)-*N*,*N*-Dimethyl-11,16-dimethoxy-9b,17b-dimethyl-8b,9,9a,9c,10,17,17a,17c,18,18a-decahydro-9,18:10,17-dimethanoanthraceno[2″,3″:3',4']cyclobuta[1′,2′:3,4]cyclobuta[1,2-*b*]benzo[*f*][3,8]phenanthrolinium Bis(tetrafluoroborate) ($7b\cdot 2BF_4$). The title compound was prepared from **3b** (0.19 g, 0.34 mmol) following the procedure described for compound **7a**·$2BF_4$: yield 0.18 g (74%); mp > 300 °C; MS (MALDI) *m/z* 582 $[M - 2BF_4]^+$; ^{1}H NMR (300 MHz, CD_3CN) δ 1.03, (s, 6H), 1.43 (m, 1H), 1.77 (m, 1H), 1.78 (m, 1H), 2.00 (m, 1H), 2.34 (s, 2H), 2.58 (s, 2H), 2.66 (s, 2H), 3.48 (s, 2H), 3.79 (s, 2H), 4.04 (s, 6H), 4.35 (s, 6H), 7.53 (m, 2H), 8.12 (m, 2H), 8.49 (d, *J* = 6.6 Hz, 2H), 8.62 (d, *J* = 6.6 Hz, 2H), 8.78 (s, 2H); ^{13}C NMR (75.5 MHz, CD_3CN): δ 9.4, 30.6, 40.6, 41.6, 42.8, 44.8, 48.7, 50.1, 50.8, 53.0, 59.1, 122.1, 123.5, 125.3, 128.0, 135.1, 139.7, 140.8, 143.4, 144.3, 148.0. Anal. Calcd for $C_{40}H_{42}O_2N_2B_2F_8$: C, 63.5, H, 6.0; N, 3.7. Found: C, 63.8; H, 6.3; N, 3.5.

(8bα,9*β*,9aα,9b*β*,9cα,10*β*,13*β*,13aα,13b*β*,13cα,14*β*,14aα)-*N*,*N*-Dimethyl-9b,15b-dimethyl-8b,9,9a,9c,10,11,12,13,13a,13c,14,14a-dodecahydro-9,14:10,13-dimethanobenzo[2″,3″:3′,4′]cyclobuta[1′,2′:3,4]cyclobuta[1,2-*b*]benzo[*f*][3,8]phenanthrolinium Bis(tetrafluoroborate) Hydrate ($7c\cdot 2BF_4$). The title compound was prepared from **3c** (0.11 g, 0.28 mmol) following the procedure described for compound **7a**·$2BF_4$: yield 0.1 g (60%); white solid; mp > 300 °C; ^{1}H NMR (300 MHz, CD_3CN) δ 0.84, (s, 6H), 1.21 (m, 2H), 1.33 (m, 2H), 1.57−1.74 (m, 4H), 2.17 (s, 4H), 2.48 (s, 2H), 2.67 (s, 2H), 3.54 (s, 2H), 4.34 (s, 6H), 8.49 (d, *J* = 6.6 Hz, 2H), 8.58 (d, *J* = 6.6 Hz, 2H), 8.79 (s, 2H); ^{13}C NMR (75.5 MHz, CD_3CN) δ 8.6, 28.0, 30.0, 34.5, 35.8, 41.2, 45.0, 48.1, 49.5, 52.4, 52.9, 122.8, 139.3, 140.4, 142.9, 147.9. Anal. Calcd for $C_{30}H_{36}N_2B_2F_8.H_2O$: C, 58.5; H, 6.2; N, 4.5. Found: C, 58.8; H, 6.4; N, 4.5.

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