

Syntheses, Characterization, and Photophysics Studies of Photoactive Chromophore 2-Naphthyl-Labeled $[n]$ -Ladderanes

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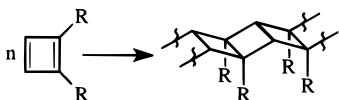
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Abstract: The syntheses and characterization of a series of saturated ladderanes **3**, oligomers of 1,3-cyclobutadiene-1,2-dicarboxylate diesters with pendant 2-naphthyl groups, are described. Absorption and fluorescence spectra provide evidence for a ground state through-space interchromophore interaction that becomes stronger with an increasing number of pendant aryl groups. A new fluorescence band ($\lambda_{\text{max}} = 303$ nm) observed in the tetramer (**3c**) and pentamer (**3d**) as blue-shifted from the monomer ($\lambda_{\text{max}} = 335$ nm) was assigned as emission from an imperfectly stacked chromophore array. Nonexponential fluorescence decays of all four oligomers, obtained by single photon counting, are accommodated well by conformations attained from a molecular mechanics geometry optimization. In the solid state, the monomeric precursor of the family, tricarbonyl[di-2-naphthylmethyl 1,2,3,4- η -1,3-cyclobutadiene-1,2-dicarboxylate]iron (**2**), exists as highly stable channel solvate under ambient conditions.

Introduction

Much effort has been directed recently toward the syntheses of organic soluble, unsaturated ladder polymers because of their promising electronic properties.^{1,2} In contrast, only a few representatives of chromophore-appended, fully saturated rigid ladder polymers (ladderanes) have been studied.^{3,4} However, these rigid, fully saturated backbones would be useful scaffolds onto which antenna chromophores might be affixed. The resulting oligomers and polymers would provide interesting modes for understanding long distance interchromophore interactions along a fixed σ framework.^{5–7}

Multifused cyclobutane rings possess several promising properties as key components for such rigid architectures, and it has been speculated that analogous



ladderanes might be used in future molecular optoelectronic devices.^{8–10} Based on recent progress in synthesizing the higher ladderanes,⁴ we here report the syntheses and characterization of a series of ladderane oligomers **3** in which pendant aryl groups are used as probes for conformational rigidity and for interchromophore electronic interactions (Scheme 1). We also describe the steady state absorption, excitation, and emission characteristics of this family, as measured by single photon counting. We note in passing that with higher molecular weight

members of this series (illustrated here with **3d**) that one face of the polymer chain will be decorated with the aryl groups, whereas the other will resemble a simple polyvinylene. We will be interested in the future whether these faces, with quite different physical characteristics, might provide interesting macromolecular properties, combining characteristics of two classes of commercially important polymers.

Experimental Section

General. Melting points were measured by a Melt-temp apparatus (uncorrected). Infrared spectra were recorded on a Nicolet 510P FT-IR spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded on a General Electric GN-500 (500 MHz) spectrometer or a Bruker AC-500 (500 MHz) or a Bruker AC-250 (250 MHz) spectrometer. Chemical shifts are reported as δ value relative to internal solvent or TMS. High-resolution mass spectra were recorded on a VGZAB2-E (VG Analytical LTD., Manchester, U.K.) mass spectrometer. Fast atom bombardment (FAB) mass spectra were performed on a Finnigan TSQ 70 instrument with the sample in a 3-nitrobenzyl alcohol (NBA) matrix. The X-ray data were collected at 183 K on a Siemens P4 diffractometer, equipped with a Nicolet LT-2 low-temperature device and using a graphite monochromator with Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Absorption spectra were recorded on a Hewlett-Packard 8451A diode array spectrophotometer. Fluorescence spectra were recorded on a SLM Aminco SPF-500C spectrofluorometer. Fluorescence quantum yields Φ_F ($\lambda_{\text{ex}} = 280$ nm) were measured by comparing the integrated emission intensity with that of 1-naphthol standard ($\Phi_F = 0.21$).¹¹ Extinction coefficients (ϵ) were determined from Beer's law. Single photon counting experiments were performed at the Center for Fast Kinetics Research at the University of Texas at Austin.

Samples used for all spectroscopic measurements were purified by thin layer chromatography and were analytically pure (>99%). NMR and high-resolution mass spectra were consistent with the assigned structures (see Supporting Information). The optical densities of all sample were kept between 0.1 and 0.2 (about 1×10^{-5} to 4×10^{-5} M naphthyl chromophore in degassed spectral grade THF) to avoid aggregation and other intermolecular interactions. For single photon counting experiments, degassed THF solutions of the probe molecule at room temperature were excited at 286 nm and monitored at 335 nm.

Materials. Anhydrous THF was freshly distilled from Na/benzophenone under N_2 . Dry acetone was obtained by distillation from

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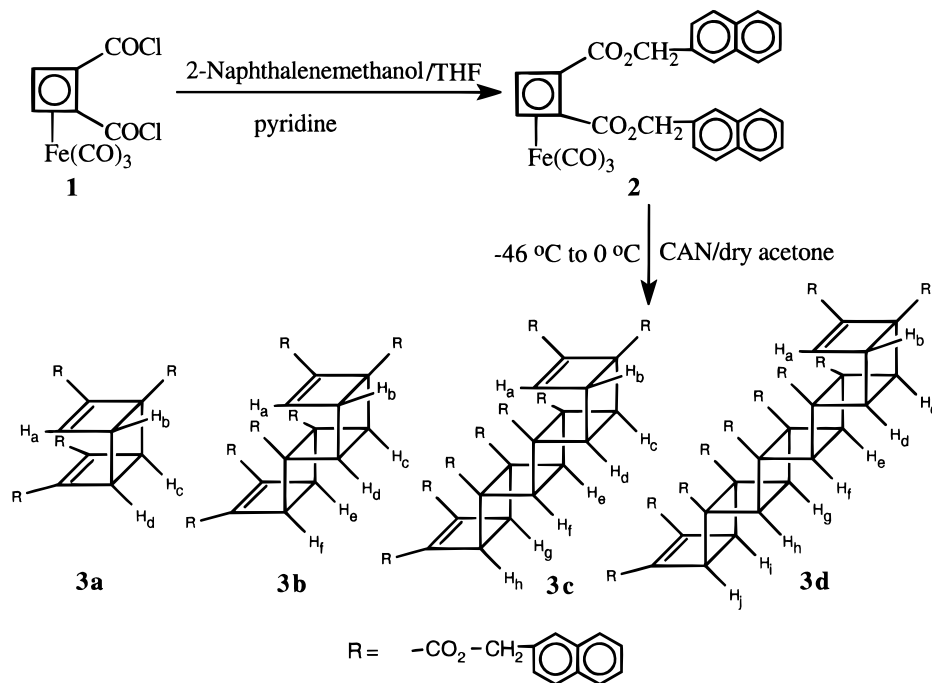
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Scheme 1. Syntheses of Rigid Saturated Ladderanes Bearing Attached Arenes

KMnO₄ and again from anhydrous CaSO₄. Deoxygenation of solvent was accomplished by at least 5 freeze–pump–thaw cycles. Air-sensitive compounds were handled in a He-filled drybox. All other chemicals and dry solvents were purchased from Aldrich and were used as received.

Synthesis. Tricarbonyl[1,2,3,4- η -1,3-cyclobutadiene-1,2-dicarbonyl]iron (**1**)¹² was esterified with 2-naphthylmethanol. Oxidative polymerization with ceric ammonium nitrate (CAN) gave oligomers **3a–d**.

Tricarbonyl[di-2-naphthylmethyl 1,2,3,4- η -1,3-cyclobutadiene-1,2-dicarboxylate]iron (2**).** 2-Naphthalenemethanol (1.6 g, 10 mmol) in minimal dry THF was added to a solution of bis(acid chloride) **1** (300 mg, 0.95 mmol) in 6.0 mL of dry pyridine. After standing for 15 min, the reaction mixture was heated 15 min at 50 °C. Water was then poured into the reaction mixture, and the mixture was extracted with ether. The extract was dried (anhydrous MgSO₄), filtered, and evaporated under vacuum, and the residue was chromatographed on neutral alumina with benzene and benzene–ether as eluents. A second chromatographic purification (on silica gel eluted with benzene), followed by recrystallization from benzene–hexane, gave 0.23 g (42%) of pure **2** as yellow needles: mp 146–148 °C; FT-IR (KBr) 2066, 2002, 1995, 1983, and 1730 cm⁻¹.

Syntheses of [*n*]-Ladderanes (3**).** A thick slurry of **2** (150 mg, 0.27 mmol) and ceric(IV) ammonium nitrate (0.73 g, 1.34 mmol) in a minimal amount of dry acetone was stirred at 0 °C for 3–4 h. Water was added and the mixture was extracted by CH₂Cl₂. Solvent was removed from the residue to give a yellow oil. Dimer [3]-ladderane (**3a**) and trimer [5]-ladderane (**3b**) co-eluted upon chromatography on silica gel with chloroform–hexane mixture as eluent. Separation of **3a** and **3b** was obtained by repeated chromatography on preparative TLC eluted by ethyl acetate:hexane (3:7), which afforded 54 mg of pure [3]-ladderane (**3a**) (33%) and 48 mg of pure [5]-ladderane (**3b**) (29%). When the same reaction (220 mg of **2**, 0.40 mmol) was run at –20 °C, followed by the same workup as above except elution in preparative TLC by 1–2% acetone in CH₂Cl₂, 14 mg (7%) of tetramer [7]-ladderane (**3c**) was isolated in addition to **3a** and **3b**. When the same reaction (670 mg of **2**, 1.2 mmol) was repeated at –46 °C for 6 days, followed by –20 °C for 1 month, 15 mg (2%) of pentamer [9]-ladderane (**3d**) was isolated after repeated column chromatography (silica gel) and preparative TLC using 3% acetone in CH₂Cl₂ as an elutant, in addition to larger quantities of **3a**, **3b**, and **3c**.

[3]-Ladderane (3a**):** Absorption (THF) λ_{max} ($\epsilon \times 10^{-3}$) 228 (285), and 272 (22.4) nm; $\Phi_{\text{F}} = 0.003$.

[5]-Ladderane (3b**):** Absorption (THF) λ_{max} ($\epsilon \times 10^{-3}$) 228 (426), and 272 (33.8) nm; $\Phi_{\text{F}} = 0.005$.

[7]-Ladderane (3c**):** Absorption (THF) λ_{max} ($\epsilon \times 10^{-3}$) 228 (511), and 272 (39.1) nm; $\Phi_{\text{F}} = 0.007$.

[9]-Ladderane (3d**):** Absorption (THF) λ_{max} ($\epsilon \times 10^{-3}$) 228 (579), and 274 (457) nm; $\Phi_{\text{F}} = 0.008$.

2-Naphthalenylmethyl Trimethylacetate (4**).** Over a period of 10 min, trimethylacetyl chloride (0.5 g, 4.6 mmol) was added to a solution of 2-naphthalenemethanol (0.5 g, 3.2 mmol) in dry THF (10 mL) with pyridine (1 mL), which was maintained at 0 °C by immersion in an ice–water bath. After the addition was complete, the mixture was warmed to 25 °C and stirred for 1 h. Water was added and the mixture was extracted with ether. The ether extract was washed with HCl (0.1 N), NaHCO₃ (saturated), and NaCl (saturated) and dried over MgSO₄ (anhydrous). After removal of solvent, the residue was chromatographed on a silica gel column using ethyl acetate–hexane mixture as eluent. After removal of solvent under vacuum, pure **4**, 0.53 g (68%), was obtained as a slightly yellow oil: absorption (THF) λ_{max} ($\epsilon \times 10^{-3}$) 228 (84), and 274 (5.6) nm; $\Phi_{\text{F}} = 0.12$.

Results and Discussions

Synthesis and Characterization. Treating the bis(acid chloride) **1** with 2-naphthalenemethanol in the presence of pyridine afforded **2** as yellow crystals, Scheme 1. Oxidative decomposition of **2** by ceric ammonium nitrate (CAN) released free 1,2-disubstituted cyclobutadiene which then participated in an FMO-controlled Diels–Alder reaction³ to give dimer **3a**, trimer **3b**, tetramer **3c**, and pentamer **3d**. High concentrations of the slurry of the monomer derived from **2** and low temperatures favored higher ladderane formation, as had been shown by previous studies with simpler monomers.⁴ The same reaction was run at 0, –20, and –46 °C followed by –20 °C in order to access to the higher ladderane oligomers. The low-temperature approach was marred by the very slow rate of reaction (about a month at the lowest temperature). Attempts to crystallize the ladderanes failed because of their polymer-like properties.

The structural assignments for **3a–d** are based on expected chemical shifts, coupling constants, and COSY (¹H–¹H and

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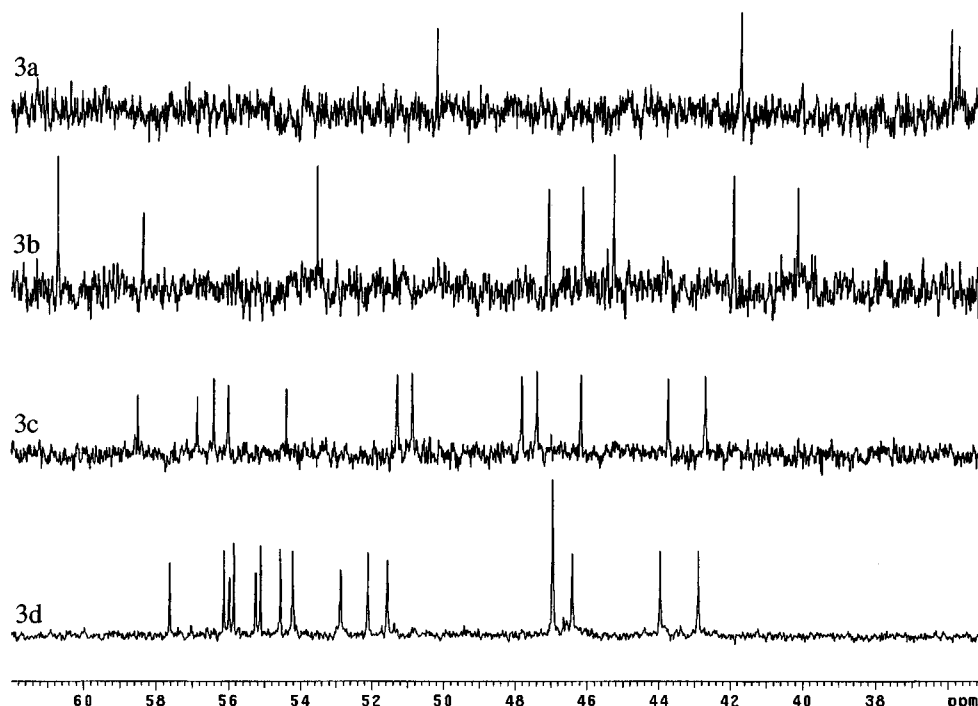


Figure 1. ^{13}C NMR (CDCl_3 , 500 MHz) spectra (aliphatic backbone regions) of **3a–d**.

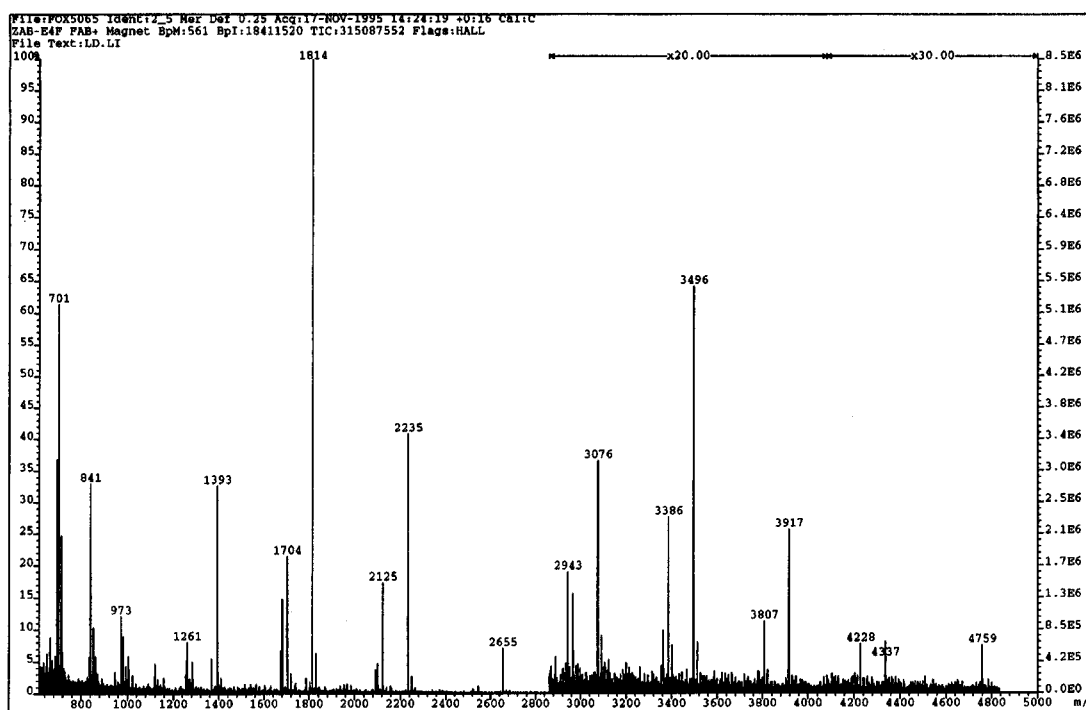


Figure 2. Mass spectrum (FAB, NBA) of the oligomer **3** reaction mixture obtained at the lowest temperature.

^1H – ^{13}C) spectra. In the region between 35 to 62 ppm in the ^{13}C NMR spectrum, dimer **3a** has four characteristic aliphatic ring carbon peaks, trimer **3b** has eight, tetramer **3c** has twelve, and the pentamer **3d** has sixteen (Figure 1). Two of the carbon peaks corresponding to the aliphatic ring carbons in **3d** overlap at 46.94 ppm as a result of the diminishing effect of the asymmetry of the initiator end. The three-dimensional structures of **3a–d** were confirmed by ^1H NMR spectroscopy employing Nuclear Overhauser (NOE) experiments to establish the indicated spatial relationships.

FAB mass spectroscopy (Figure 2) clearly showed that ladderane oligomers containing up to eleven repeating units had been synthesized at the lowest temperature. The peaks at 841, 1261, 1704, 2235, 2655, 3076, 3496, 3917, 4337, and 4759

correspond to 2, 3, 4, 5, 6, 7, 8, 9, 10, and 11 monomer repeat units, respectively.¹³ However, attempts to separate the higher ladderane oligomers ($n \geq 11$) by preparative TLC failed because of the very low yields of those higher oligomers.⁴

X-ray Crystal Structure Determination of 2. Crystals grew as yellow blocks by slow evaporation of solvent from a CDCl_3 solution in an NMR tube. The data crystal was a prism with approximate dimensions $0.26 \times 0.33 \times 0.38$ mm. X-ray crystal analysis¹⁴ revealed that **2** and CDCl_3 form a 1:1 solvate complex and lie on a crystallographic mirror plane at $x, 1/4, z$. The dihedral angle between the two 2-naphthyl rings is 53.8° . The CDCl_3 solvate appears to be encapsulated by the 2-naphthyl

(13) $(\text{M} + \text{H})^+$, $(\text{M} + \text{Na})^+$, and $(\text{M} + \text{Cs})^+$ are directly observed instead of M^+ .

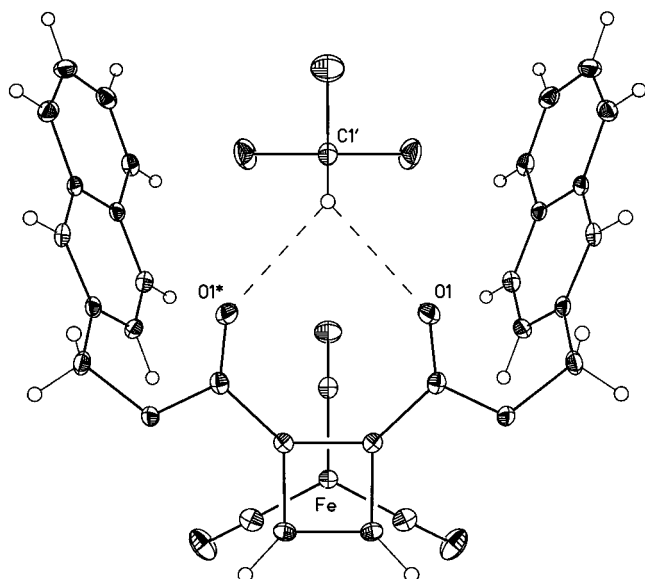


Figure 3. Crystal structure of **2** (complex 1:1 with CDCl_3).

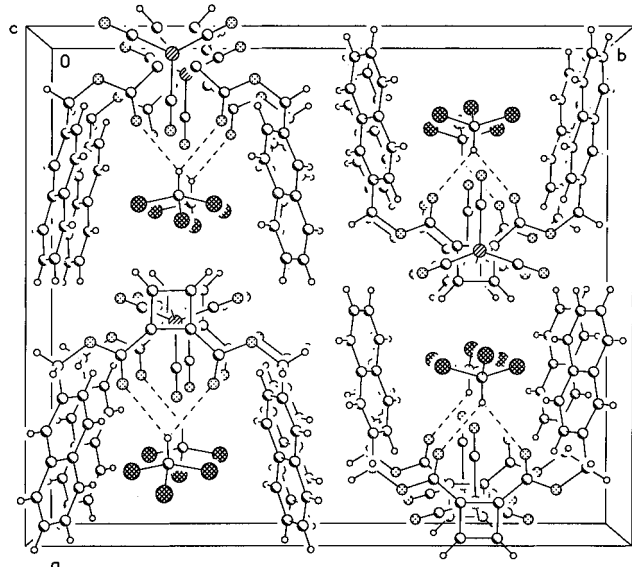


Figure 4. Stereoscopic representation of crystal **2** (complex 1:1 with CDCl_3).

rings within H-bonding distance of the two carbonyl oxygen atoms of the complex (Figure 3). The distance between the carbonyl oxygen and the deuterium atom ($\text{D}\cdots\text{O}$) is 2.56 Å. The packing morphology of this complex (Figure 4) indicates stacking of one complex on top of the other along the *c* axis to create long channels into which the CDCl_3 solvates are held. Given the fact that two chlorine atoms from CDCl_3 point directly toward the two 2-naphthyl rings, we suspect that there might exist a weak intermolecular interaction involving a charge-transfer interaction between the π -electron system of a pendant 2-naphthyl group and a chlorine atom in CDCl_3 . Previous studies showed that such charge-transfer interactions between aromatic molecules and CCl_4 appear to be general phenomena in the solution,¹⁵ and that similar interactions between chloroform and aromatic groups might be expected in the solid state.

(14) Crystallographic summary for $(\text{C}_{28}\text{H}_{20}\text{O}_4)\text{Fe}(\text{CO})_3\text{-CDCl}_3$. Yellow needles from CDCl_3 , orthorhombic, $Pnma$, $Z = 4$ in a cell of dimensions $a = 19.832(1)$, $b = 23.276(2)$, $c = 6.1419(4)$ Å, $V = 2835.2(3)$ Å³, $\rho_{\text{calc}} = 1.59$ g·cm⁻³, $F(000) = 1384$. A total of 6943 reflections were measured, 3317 unique ($R_{\text{int}} = 0.038$). The structure was refined on F^2 to an $R_w = 0.0874$, with a conventional $R = 0.0359$, with a goodness of fit = 1.010 for 207 refined parameters.

In this solvate complex, the 2-naphthyl rings bend toward CDCl_3 along $\text{C}_9\text{-C}_{10}$ with a small but significant dihedral angle of $3.6 \pm 0.3^\circ$, which is a strong and direct indication of a weak intermolecular interaction between a chlorine atom and the aromatic naphthalene ring, most probably of charge-transfer character. Therefore, we conclude that the 2-naphthyl groups contribute significantly to the stability of the solvate co-crystal: this crystal showed no deterioration or solvent loss under ambient laboratory conditions for 6 months and could withstand several cycles of evacuation. One set of stacked **2** is aligned antiparallel to those of the other set, thus canceling any net dipole. This packing morphology might be useful for designing controlled, well-ordered, and predictable solid state organic crystals.¹⁶

Molecular Modeling of the Conformations of **3a-d**.

Figure 5 shows the calculated optimal structures of **3a-d** (stick-rod model, top; space-filling model, bottom) obtained by minimization using force field mechanics within the Cache program (Cache Scientific, Version 3.8) at the MM2 level with 3000 iterations per structure. The end-to-end lengths of these ladderanes are estimated to be 11 Å for **3a**, 21 Å for **3b**, 24 Å for **3c**, and 26 Å for **3d**. The end-to-end length of the cyclobutane ring skeleton is about 3.0 Å for **3a**, 5.8 Å for **3b**, 8.5 Å for **3c**, and 11.3 Å for **3d**. Therefore, this family of 2-naphthyl-labeled ladderanes can be thought of as nanometer-sized chromophore-labeled supramolecular clusters. Upon increasing the chromophore loading from **3a** to **3d**, the chromophores at the center of the ladderanes are forced to adopt an imperfect quasi-face-to-face stacking conformation, Figure 5. The backbone rigidity makes it difficult to attain in these intramolecular interactions the optimal geometry observed for freely diffusive intermolecular excimers or excited state dimers.

Photophysics Studies of Oligomers **3a-d** and Model Compound **4**.

The absorption maxima (Figure 6) of **3a-d** are essentially identical, with maxima at 228 nm and around 272 nm. Because of the different number of chromophores in these ladderanes, only the normalized extinction coefficients (ϵ) of the 2-naphthyl ${}^1\text{B}_b$ (228 nm) and ${}^1\text{L}_a$ (~270 nm) bands are compared (Figure 7A). The individual 2-naphthyl chromophores of **3a** and **3b** in the ground state are nearly identical, whereas the extinction coefficients decrease gradually from **3b** to **3c** and to **3d**, which is consistent with an increase in the number of interacting chromophores. Interestingly, a plot of the ϵ of **3b**, **3c**, and **3d** against the reciprocal of the number of 2-naphthyl units (Figure 7B) is linear with an intercept value ϵ of about $40\,000\text{ M}^{-1}\text{ cm}^{-1}$, corresponding to a ladderane with infinite chain length. Such a structure would closely resemble a one-dimensional crystal.

The observed change of ϵ in **3a-d** agrees well with molecular modeling studies. In **3a** and **3b**, there are no closely packed 2-naphthyl chromophores. However, two pairs and four pairs of closely stacked 2-naphthyl chromophores are found in **3c** and **3d**, respectively (Figure 5). The decrease in ϵ originating from a pair of stacked 2-naphthyl chromophores is calculated as about $3300\text{ M}^{-1}\text{ cm}^{-1}$. Because of broadening of the ${}^1\text{L}_a$ band caused by Davydov splitting, deconvolution and quantitative description of the half-width of this band proved difficult.

Excitation spectra of **3a-d** and model compound **4** are shown in Figure 8A (normalized at 273 nm). The excitation spectrum of **4** is identical to that of naphthalene itself (not shown for clarity) with maxima at 273 nm, which is therefore assigned to the unperturbed 2-naphthyl group. Two features are clear in the spectra: first, the optical density at around 248 nm increases consistently from **4** to **3a**, **3b**, **3c**, and **3d**, until for **3c** and **3d**, a new band actually appears at 248 nm. Second, another new

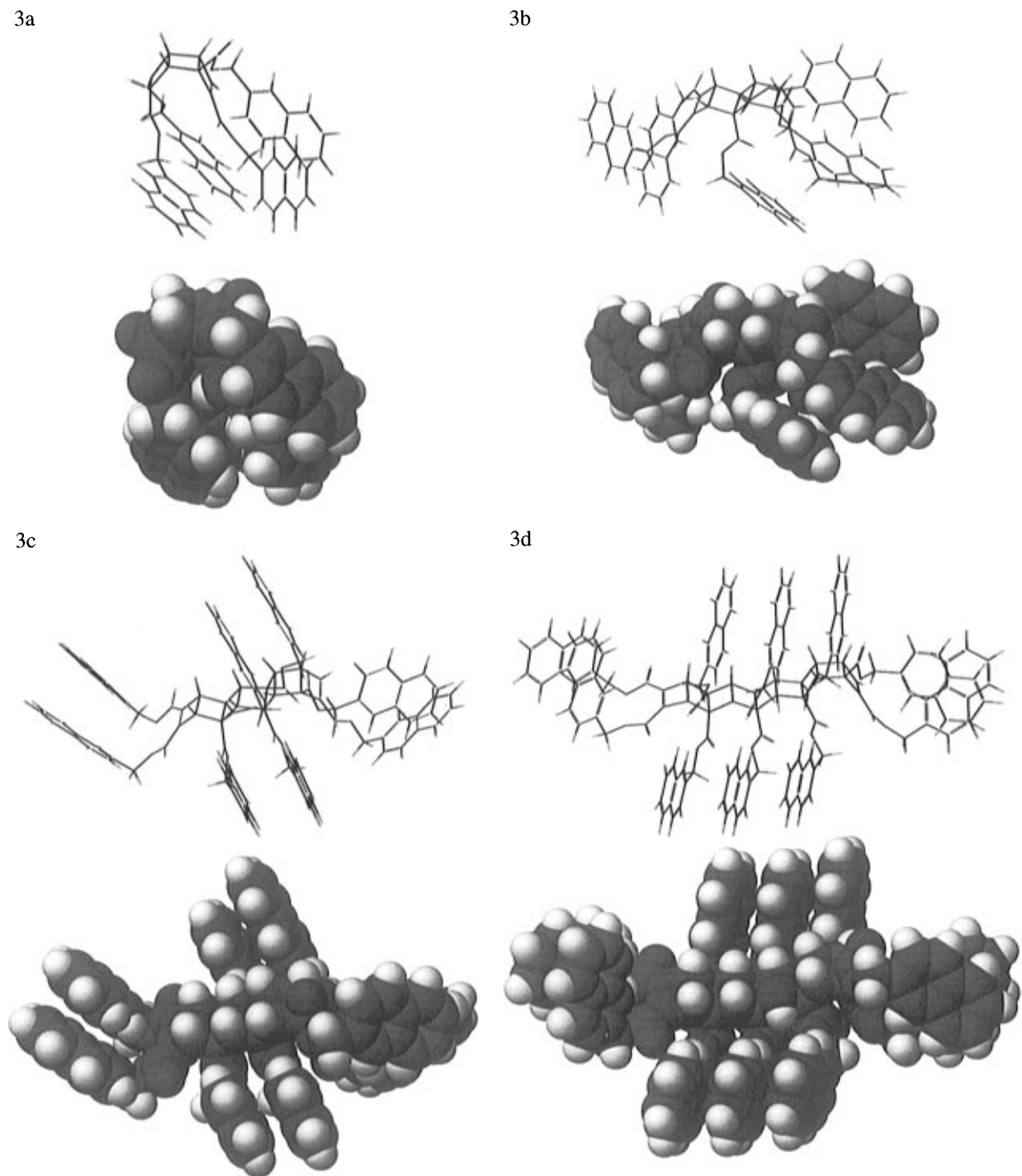
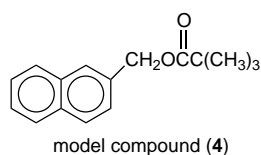


Figure 5. Computer-generated models of minimum energy conformation for **3a–d**.

band around 303 nm present in **3a–d** is absent in **4**. The



difference excitation spectra between **3a–d** and **4** (Figure 8B) illustrate the ground state properties of this family. The resulting spectra derive essentially from secondary intramolecular chromophore interactions, in this case, by through-space interactions attained by chromophore stacking. The increase in intensity to the blue (248 nm) and to the red (303 nm) of the ground state unperturbed 2-naphthyl excitation band is attributed to the

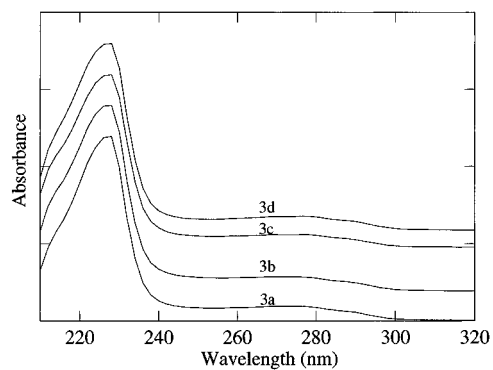


Figure 6. Absorption spectra of **3a–d** in degassed THF at room temperature.

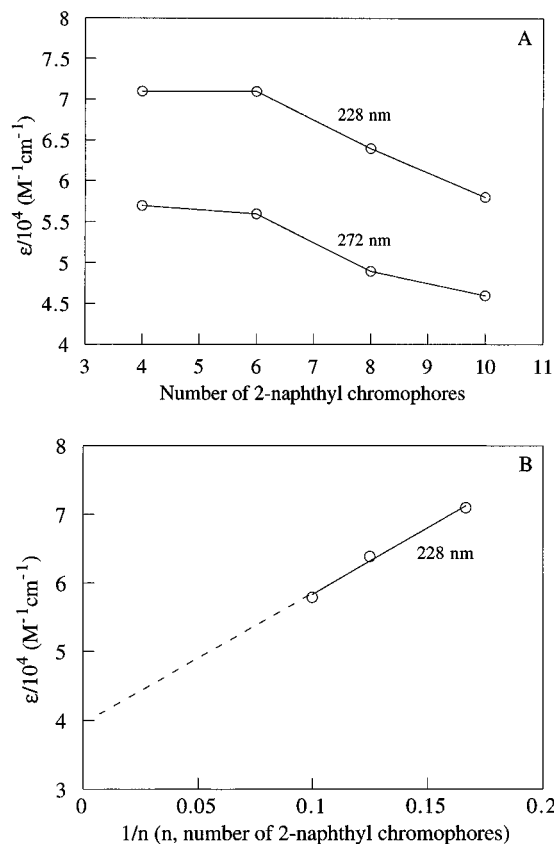


Figure 7. Dependence of the extinction coefficient on (A) the number of 2-naphthyl chromophores present in **3a–d** and (B) the reciprocal of the number of 2-naphthyl chromophores.

imperfectly stacked 2-naphthyl chromophores.¹⁷ Such a hypochromic effect has been observed previously¹⁸ in the nematic phase of a liquid crystalline poly(aryl cinnamate) where strong chromophore aggregation occurs. Direct excitation to the 303-nm band leads to no useful information since the emission is too weak to be meaningful.

When excited at 280 nm, dimer **3a** and trimer **3b** show characteristic 2-naphthyl monomer emissions at 335 nm and higher energy shoulders at around 303 nm. Tetramer **3c** and pentamer **3d** clearly exhibit resolved blue-shifted peaks at 303 nm (Figure 9A). To elucidate the identity of species responsible for these high-energy emissions, the wavelength dependences of the fluorescence spectra were examined. Upon excitation at 260 nm or 280 nm, **3a** and **3b** show essentially identical spectra. However, better definition and additional fine structure are observed at 303 nm in the fluorescence spectra of **3c** and **3d** (Figure 9B). The normal 2-naphthyl monomer emission component can also be seen, as shown by the emission peaks at 335 nm (Figure 9B). Figure 9C shows the emission spectra of **3a–d** obtained upon excitation at 230 nm: two peaks are observed at 303 and 335 nm in **3c** and **3d**, whereas only one peak at around 335 nm and a shoulder around 303 nm are seen in **3a** and **3b**. As expected for a single unperturbed chromophore, **4** exhibits wavelength-independent fluorescence emission upon excitation at 230, 260, or 280 nm. The fluorescence quantum yields in ladderanes **3** are much lower than in **4**. Self-quenching may be responsible for the low quantum yields, although the quantum yield increases gradually from **3a** to **3d** (Table 1).

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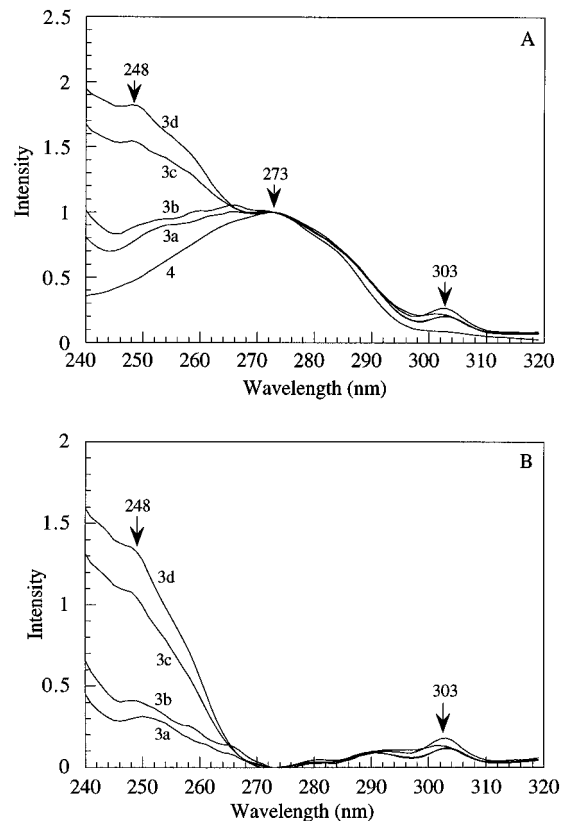


Figure 8. Steady state fluorescence excitation spectra of **3a–d** and **4** in degassed THF at room temperature monitored at 335 nm: (A) normalized at 273 nm; and (B) difference excitation spectra between **3a–d** and **4**.

These steady state emission studies suggest that two distinct environments exist for the 2-naphthyl chromophores in the ground states of **3c** and **3d**. Upon excitation at 280 nm, isolated naphthyl units emit strongly; an aggregated (imperfectly stacked) structure emits ($\lambda_{\text{max}} = 303$ nm) predominantly upon excitation at 260 nm. Upon excitation at 230 nm, both the isolated and aggregated chromophores emit, and the resulting fluorescence is a superposition of the fluorescence of these two species.

Although the fluorescence emission spectra of **3a–d** (Figure 9A) show predominant monomer and aggregate emission upon excitation at 280 or 260 nm, respectively, excimer emission at around 400 nm in both cases is barely detectable. When compared with the closest polymer analog, poly(2-naphthylmethyl methacrylate),¹⁹ **3a–d** show an excimer-to-monomer emission ratio (I_e/I_m) only about 0.15 to 0.2, whereas that of the polymer analog is close to one. The rigid backbone in these ladder oligomers thus apparently inhibits approach to a geometry optimal for excimer emission.

This is an important result if these compounds are to be considered as structural elements in efficient light harvesting polymers, because excimers act as excitation energy traps which, in turn, disrupt long distance excitation energy and electron transfer. Usually, bulky groups are introduced along a polymer to suppress excimer formation,^{19,20} but at the considerable expense of decreasing chromophore interaction and, consequently, efficiency of energy and electron transfer. Our results, combined with the previous studies in this group,^{6,21} clearly suggest that a rigid polymer backbone can efficiently suppress excimer formation without sacrificing long distance electronic coupling.

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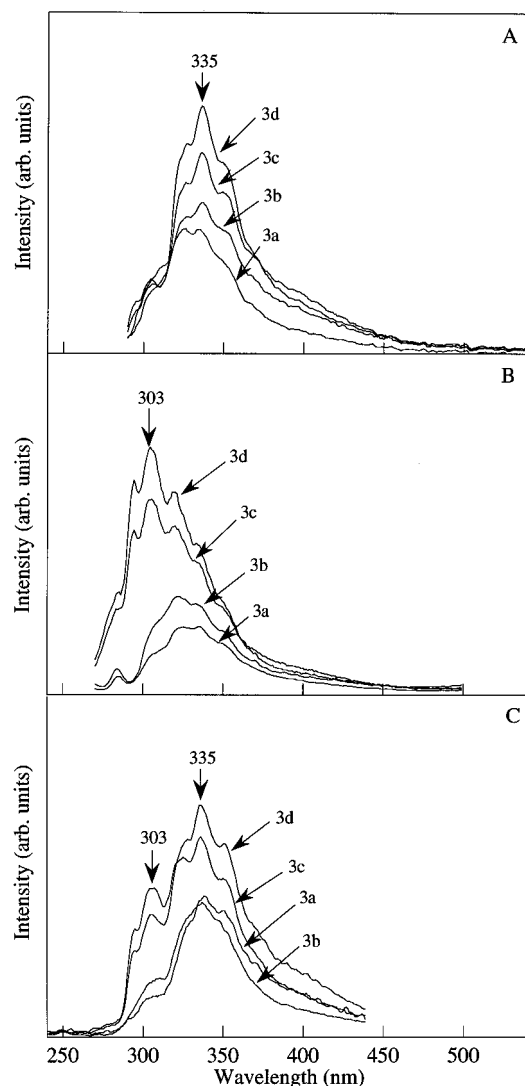


Figure 9. Steady state fluorescence emission spectra of **3a–d** in degassed THF at room temperature excited at (A) 280, (B) 260, and (C) 230 nm.

Table 1. Fluorescence Quantum Yields^a (Φ_F) of **3a–d** and **4**

	3a	3b	3c	3d	4
Φ_F ($\pm 5\%$)	0.003	0.005	0.007	0.008	0.12

^a $\lambda_{\text{ex}} = 280$ nm in degassed THF at room temperature.

Single Photon Counting Studies. The fluorescence decay of **4** could be analyzed by a single exponential function with a lifetime (τ) of 61 ns. This agrees closely with the reported lifetime (τ) of 2-methylnaphthalene (59 ns),²² showing that the excited state properties of the 2-naphthyl groups are retained in **4**. It is, therefore, reasonable to assume that analogous species could be observed in **3a–d** and that any deviation in the observed transient fluorescence decay of **3a–d** could be attributed to through-space chromophore interactions.

The single photon counting measurements of the decay of **3a–d** are nonexponential and can be satisfactorily analyzed only by a triexponential fitting of three decay components at around 0.5–1.1, 4.6–5.4, and 25–35 ns. Each of these decay times is significantly shorter than in **4**, and no contribution from a free isolated 2-naphthyl chromophore was evident. It is well-known that in an array of molecules it is impossible to construct a stationary state such that the excitation energy would be localized at a definite molecule.²³ Given the proximity of the

2-naphthyl chromophores in these ladderanes, extensive excitation energy migration or hopping is to be expected. Excited singlet lifetimes are often found to be shortened when excimer formation can take place.²⁴ However, single exponential fluorescence decay profiles have been previously reported for a bichromophore system (di-2-naphthyl-*n*-alkanes) with a lifetime nearly identical to its model compound (2-ethylnaphthalene) when exciton hopping rather than excimer formation was observed.²⁵ We therefore propose that through-space intramolecular electronic interactions among imperfectly stacked 2-naphthyl chromophores in **3a–d** are responsible for the observed nonexponential fluorescence decay. Because of the complicated kinetics associated with these nonexponential decay profiles, however, detailed assignments of the kinetic parameters have not been attempted.

Conclusions

The syntheses of the photoactive 2-naphthyl-labeled ladderanes described here provide good quantities of oligomers under conditions in which the identity of the incorporated group can be systematically altered. The controlled size of the ladderanes bearing different numbers of pendant chromophores permits quantitative study of the ground state conformation and how excited state photophysics are perturbed by the number of chromophores sampled by exciton hopping within the excited state lifetime. Absorption spectra, steady state fluorescence, and single photon counting studies clearly reveal extensive intramolecular electronic interaction in both the ground state and excited singlet state of this family.

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Supporting Information Available: ¹H and ¹³C NMR spectral data for **2**, **3a–d**, and **4**, X-ray experimental details for the crystal structure of the **2**–CDCl₃ (1:1) complex, and tables of positional and thermal parameters, bond lengths and angles, and torsion angles for (C₂₈H₂₀O₄)Fe(CO)₃–CDCl₃ (1:1) (12 pages). See any current masthead page for ordering and Internet access instructions.

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