Photophysical Properties of Coplanar and Twisted 1,4-Bis(9-ethynylanthracenyl)benzene. Rotational Equilibration in the Excited States of Diarylalkynes

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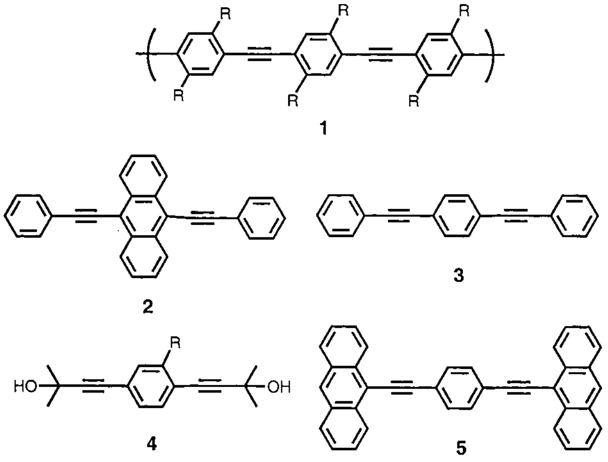
We report the synthesis and photophysical properties of 1,4-bis(9-ethynylanthracenyl)benzene. Results in dilute hexane solutions give a very high fluorescence quantum yield ($\Phi = 0.97$) and a lifetime of $\tau = 1.8$ ns. Studies at different temperatures, viscosities, and micromorphologies, as well as excited-state semiempirical calculations, indicate that conformations having aryl groups coplanar absorb and emit at wavelengths that are longer than those that have their aryl groups orthogonal or twisted. A simple MO picture is consistent with essentially frictionless aryl group rotation in the ground state and a relatively high rotational barrier in cummulene-like excited states.

1. Introduction

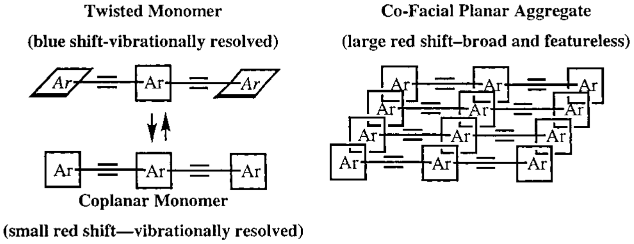
Compounds possessing aromatic chromophores linearly conjugated by alkyne linkages (Scheme 1) are characterized by good luminescence properties, and by efficient charge and energy transfer. Due to efficient electronic communication between adjacent chromophores, arylalkynes are commonly used in the preparation of conducting polymers,[1] energy-harvesting assemblies,[2] ultrasensitive sensors,[3] and molecular electronics devices.[4]

One of the current challenges in the design and development of functional materials based on poly(arylalkynes) is the optimization of their emission intensities, which tend to decrease upon concentration in thin films or in bulk solids. Along with changes in quantum efficiency due to self-quenching, red shifts in absorption and emission have been primarily explained in terms of chromophore aggregation.[5] However, we have recently shown that coplanarization and twisting of aryl groups may have small but significant contributions to the spectral shifts observed upon changes in temperature,[6] phase, and micromorphology.[7,8] Although the effects of conformational changes on the photophysics of linearly conjugated chromophores with planar aromatic groups and double bonds have been extensively documented,[9] analogous interpretations of experimental shifts have not been considered in the case of poly(arylalkynes). One could speculate that the cylindrical symmetry of the triple bond π-system should result in uninterrupted conjugation for all the orientations of conjugated aromatic groups. However, a simple molecular orbital analysis and the expected changes in excited-state bond orders analyzed in the case of **3** (Scheme 1) suggested otherwise.[7] On the basis of our observations with compounds **1**−**4**, we have proposed a working model (Scheme 2) that may account for the effects of aggregation and planarization.[7,8,10] We have proposed that conformational changes should result in small spectral shifts retaining high emission yields and vibrational structure. Aggregation effects, in contrast, should give rise to more shifted, excimer-like emission, with a loss of vibrational structure and shorter lifetimes that result from self-quenching. To test our model we would like to investigate a set of arylethynyl chromophores with a range of rotational dynamics, ground-state association properties, and excited-state lifetimes. In this paper we report the synthesis and photophysical properties of 1,4-bis(9-ethynylanthryl)benzene **5**. Compound **5** has a nearly quantitative fluorescence quantum yield ($\Phi = 0.97$) and a lifetime of $\tau = 1.8$ ns. The singlet-state lifetime of **5** falls between those of compounds **2** ($\tau = 3.8$ ns) and **3** ($\tau = 0.8$ ns), which we have shown to be close to the time scales for conformational equilibration in the excited state. Studies were carried out in dilute hexane, methylcyclohexane, and mineral oil solutions, as well as in polyethylene films. With measurements at different temperatures, viscosities, and micromorphologies, we document a series of photophysical observations consistent with the model shown in Scheme 2.

SCHEME 1



SCHEME 2



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2. Experimental Section

2.1. Materials and Methods. All starting materials were of reagent grade and used without further purification. Solvents for reaction and photophysical measurements were either distilled or of spectroscopic grade. ^{1}H and ^{13}C NMR spectra were obtained on an AMS 360 (360 MHz), Bruker ARX400 (400 MHz), or Avance Bruker ARX500 (500 MHz) spectrometer. ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ with TMS as an internal standard, unless otherwise noted. IR spectra were obtained on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. UV−vis spectra were acquired on an HP 8453 spectrometer. High-resolution electron impact (EI-HiRes) mass spectra were obtained on a VG Autospec (Micromass, Beverly, MA) spectrometer. Melting points were determined using a MEL-TEMP II apparatus equipped with a Fluke 50S K/J thermometer. Column chromatography was performed using silica gel (40 μm, 32−63 μm, Scientific Absorbents Incorporated).

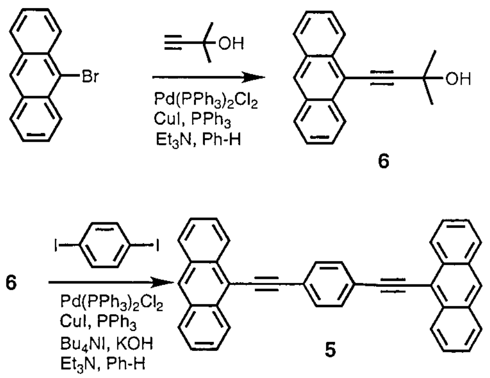
*1-(9′-Anthracenyl)-3-hydroxy-3-methyl-1-butyne (**6**).* Compound **6** was prepared by Pd(0)-catalyzed coupling of 9-bromoanthracene and 2-methyl-3-butyn-2-ol as previously reported.[11]

*1,4-Bis-(9-ethynylanthryl)benzene (**5**).*[12] A mixture of ethynylanthracene **6** (0.40 g, 100 mol %), 1,4-diiodobenzene (0.218 g, 50 mol %), CuI (0.293 g, 100 mol %), $PdCl_2(PPh_3)_2$ (0.218 g, 20 mol %), PPh_3 (0.60 g, 150 mol %), Bu_4NI (2.270 g, 400 mol %), crushed KOH (1.74 g, 2000 mol %), and Et_3N (2.2 mL of 1000 mol %) were suspended in 50 mL of deoxygenated benzene in a 100-mL three-necked round-bottom flask equipped with a magnetic stir bar and water condenser. The reaction was refluxed for ca. 16 h and quenched with saturated NH_4Cl after all of the ethynylanthracene **6** had reacted. The biphasic mixture was separated, and the aqueous layer was extracted three times with Et_2O. The combined organic layers were washed twice with deionized water, washed once with brine, and dried over anhydrous $MgSO_4$. After concentrating in vacuo, compound **5** was obtained as orange-red prisms (ca. 30% yield). Crystals of **5** turned dark upon heating to 190 °C, brown at 250 °C, and then finally melted at 280−283 °C (lit. 292 °C, dec).[12] The spectral data obtained was consistent with that previously reported in ref 12: e.g., ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.68 (d, $J = 8.7$ Hz, 4H), 8.48 (s, 2H), 8.05 (d, $J = 8.4$ Hz, 4H), 7.85 (s, 4H), 7.65 (m, 4H), 7.55 (m, 4H). (KBr, cm^{-1}): 3048, 2923, 2195, 1505, 881, 830, 726; MS (EI) m/z 478.2 (M^+, 100%), 239.0 (M^{2+}, 30%); HRMS (EI) $m/z/(M^+)$ calcd for $C_{38}H_{22}$ 478.1721, obsd 478.1717.

2.2. UV−vis and Steady-State Fluorescence Spectra. Absorption spectra were obtained with a Hewlett-Packard 8453 spectrophotometer. Fluorescence spectra were recorded with a Spex-Fluorolog II spectrofluorimeter and corrected for nonlinear instrumental response. The fluorescence quantum yield of **5** was measured using 9,10-diphenylanthracene in cyclohexane as a reference.[13]

2.3. Time-Resolved Fluorescence Decays. The fluorescence decays were measured with a time-correlated single photon counting fluorimeter (Edinburgh Instruments, Model FL900CDT) equipped with a pulsed H_2 discharge lamp operating at 0.4 bar. When necessary, the fluorescence intensity was attenuated to obtain an average number of detected fluorescence photons lower than 1% of the excitation source repetition rate (40 kHz). The experimentally measured luminescent emission was deconvoluted from the instrumental response to obtain the decay. The instrumental response was measured using a LUDOX suspension as a scattering sample, setting both monochromators at the emission wavelength of the sample.

SCHEME 3



2.4. Dichroic Spectroscopy. The orientation of the transition dipole moment of compound **5** was determined by the stretched polymer method.[14] Samples of linear low-density polyethylene (Scairfilm SL-1, 4 mils) from DuPont Canada were extensively washed with chloroform prior to exposure to concentrated solutions of **3**. Films were stretched to about 4 times their original length prior to incorporation of the substrate. Crystalline residues and externally adsorbed samples were removed by exposing the film to nonswelling solvents such as ethanol. Dichroic spectra were measured in a Shimadzu 3101-PC UV−vis−NIR instrument equipped with a Glan-Taylor calcite polarizer in the sample beam. A detailed description of the method used in this work was published previously.[7]

2.5. Semiempirical Calculations. The geometries of the molecules were optimized using the AM1 method, and the electronic spectrum and transition moment directions were computed using the ZINDO/S method as implemented in the Hyperchem package.[15] The CI matrix was computed using 201 lowest, single excited configurations.

3. Results and Discussion

3.1. Sample Preparation and Fluorescence Measurements in Solution. Compound **5** was prepared in two steps from 9-bromoanthracene as illustrated in Scheme 3. Pure samples of compound **5** were obtained by recrystallization after column chromatography. Compound **5** is a pale yellow solid that dissolves well in several solvents. The lowest energy electronic transition in nonpolar solvents is relatively broad and occurs between 350 and 470 nm with a λ_{max} at 429 nm. Figure 1 shows the room-temperature excitation and emission spectra obtained with compound **5** in cyclohexane solution at ambient temperature. There is an excellent agreement between the UV−vis absorption and fluorescence excitation spectrum in solution

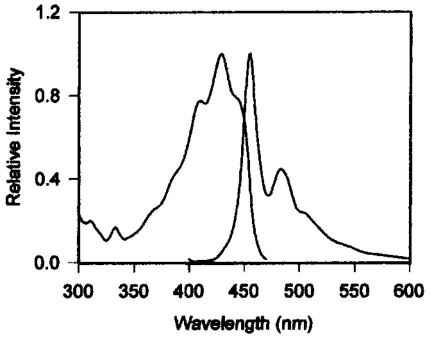


Figure 1. Excitation and emission of **5**. Spectra were collected in 10^{-5} M cyclohexane solution at room temperature. The emission and excitation wavelengths were 500 and 355 nm, respectively.

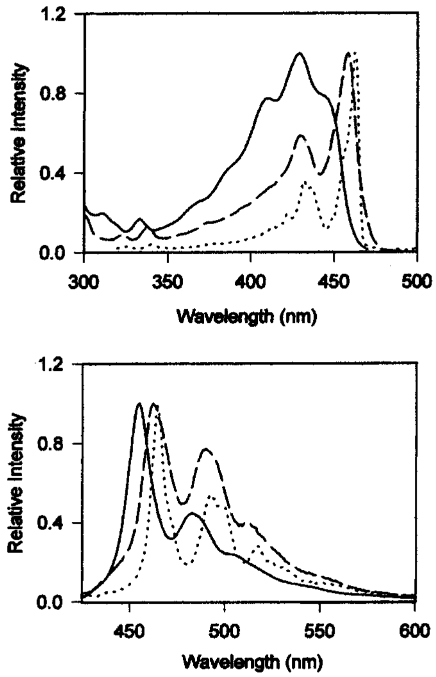


Figure 2. Effects of planarization on the excitation (top) and emission (bottom) of compound **5**. The spectra were collected with either an emission wavelength of 500 nm or an excitation of 355 nm. Solid lines correspond to measurements in cyclohexane at 300 K; dashed lines correspond to measurements in polyethylene film at 300 K; dotted lines correspond to measurements in a methylcyclohexane matrix at 77 K.

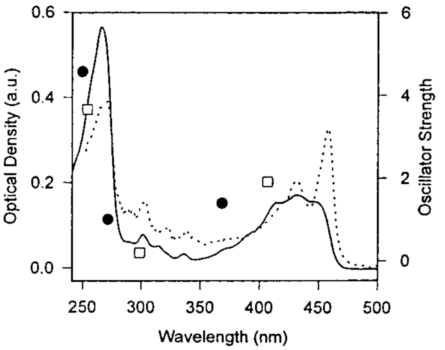


Figure 3. Room-temperature UV−vis absorbance of **5** in cyclohexane (solid line) and in polyethylene (dotted line). The ZINDO/S method was used to calculate the electronic transitions for a 90° twisted conformation (filled circles) and for the planar conformation (open squares). The two lowest energy transitions of each conformer are polarized along the long molecular axis.

(compare Figures 1 and 3). The lack of excitation wavelength dependence in the emission spectra confirmed the high purity of our samples and suggests that full conformational equilibration occurs in the excited state (vide infra). The intense green emission of **5** extends between 425 and 600 nm and is characterized by two vibrational maxima at 455 and 483 nm and by two shoulders near 507 and 545 nm. The most striking features of the excitation and emission spectra are the poor vibrational resolution of the excitation and their poor mirror image symmetry. A fluorescence quantum yield of $\Phi_F = 0.97$ was determined in methylcyclohexane at 300 K using 9,10-diphenylanthracene as a standard. Lifetime measurements carried out by time-correlated single photon counting at 300 K and at 77 K revealed a very small difference with values of 1.8 and 1.9 ns, respectively, indicating that neither vibrational relaxation nor intersystem crossing are important modes of relaxation for the singlet excited state of the 1,4-bis(9-ethynylanthryl)benzene chromophore.

3.2. Fluorescence Studies in Low-Temperature Glasses and in Polyethylene Films. Given that twisted and coplanar rotamers are predicted to have different electronic transitions, an equilibrium change that favors a given conformation should be spectroscopically detectable for compound **5**. It is expected that changes in temperature, viscosity, and micromorphology will affect the equilibrium population and the conformational dynamics of poly(arylalkynes). As illustrated by the spectra shown in the top panel of Figure 2, measurements carried out with dilute solutions in methylcyclohexane (MCH) at 77 K revealed a remarkable change in the excitation spectrum. A relatively small shift to the red was accompanied by a large increase in vibrational resolution. A concomitant intensity redistribution gave rise to the appearance of the specular relation between excitation and emission that characterizes the rigid anthracene chromophores. The emission spectrum obtained in MCH at 77 K, shown with a dashed line in the bottom panel in Figure 2, underwent a small (ca. 10 nm) red shift and a small increase in the resolution of the vibronic transitions. To confirm the conformational origin of these changes, we also exploited the micromorphological changes resulting from adsorption of chromophores into high-density polyethylene. The adsorption of organic compounds into polyethylene occurs at the boundary between amorphous and crystalline regions;[16] we proposed that these offer a strong interaction between coplanar conformations and flat crystalline surfaces. High-density polyethylene films also have the added advantage of aligning molecules along the stretching direction, thus allowing determination of the direction of transition dipole moments.[17] The results obtained with compound **5** in polyethylene are shown in Figure 2 with excitation and emission spectra plotted with a dashed line. The polyethylene spectra are very different from those obtained in fluid solution and are quite similar to those obtained in MCH at 77 K. Similar to results in the low-temperature glasses, the most dramatic changes occur in the excitation spectrum where the longest wavelength vibrational transition is now the most pronounced. Accompanying this change is a relative decrease in intensity of the higher energy bands at 430 and 415 nm which restores the mirror-image symmetry of the excitation and emission spectra. A comparison of polyethylene emission at 300 K and MCH emission at 77 K reveals more subtle changes. The intensities of the lower energy transitions are slightly higher in the polymer matrix at ambient temperature, suggesting a slightly greater proportion of noncoplanar conformers.

3.3. Absorption Measurements in Polyethylene Films. In agreement with fluorescence excitation measurements, a comparison of the UV−vis absorption of **5** in solution and in polyethylene films indicates a change in the conformer population upon incorporation of the compound in the polymer. The results in Figure 3 show a dramatic enhancement of the longer wavelength intensities and an overall increase in the vibronic resolution of the sample. Linear dichroism measurements with compound **5** suggested that the lowest energy transition in the polymer, between ca. 400 and 470 nm, is essentially homogeneous. Absorbance differences when measurements were carried out with linearly polarized light, either parallel (E_Z) or perpendicular (E_Y) to the polyethylene stretching direction, gave a dichroic ratio $E_Z/E_Y = 1.77$. Assuming that this a pure transition along the principal molecular axis, and knowing that most molecules adopt preferred orientations along the stretching direction,[18] one may calculate orientation factors $K_Z = 0.47$ and $K_Y = 0.26$. Orientation factors are a measure of the degree of

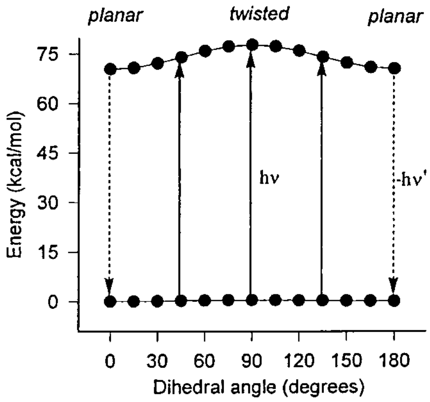


Figure 4. Conformational energies for the ground state and first excited state of compound **5**. The solid line near 0 kcal/mol illustrates the ground-state rotational surface with a maximum of ca. 0.3 kcal/mol. An equilibrium mixture of rotamers is responsible for the heterogeneity of the absorption spectrum (upward arrows). Excited-state equilibration in fluid solvents within its 1.8 ns lifetime is responsible for the homogeneous emission from the coplanar conformer (downward arrows).

alignment and are a function of molecular shape.[14] The orientation factors determined for compound **5** are consistent with those expected for an ellipsoidal shape. They can be compared with those obtained with compound **3**, which behaves as a nearly ideal rigid rod which aligns almost perfectly ($K_Z \approx 1$, $K_Y \approx 0$),[8] and with compound **2**, which has a greater degree of orientation than **5** as suggested by the larger orientation factors along the stretching *Z*-direction ($K_Z = 0.72$ and $K_Y = 0.22$).[7]

3.4. Semiempirical Calculations: Ground- and Excited-State Conformational Potentials. The semiempirical methods AM1 and ZINDO/S were used to calculate the conformational dependence of the lower electronic energy transitions of compound **5**. A portion of the ground-state rotational potential was calculated with the AM1 method for structures where the external anthryl groups were rotated in a paralleled fashion by 15° increments with respect to the plane of the central phenyl ring. The resulting ground state potential is essentially flat, with energy differences between the coplanar mimimum and the twisted maximum of only 0.3 kcal/mol (Figure 4). Single point Franck−Condon transition energies calculated with the ZINDO/S method for each ground-state geometry were used to construct an excited-state potential shown in Figure 4. The CI matrix was computed with the lowest 201 single excited-state configurations, and the wavelength, orientation of the dipole moment, and oscillator strength were determined for each transition. The results in Figure 4 indicate an excited-state rotational potential with a coplanar minimum and an orthogonal maximum with an estimated energy difference of 7 kcal/mol.

The calculated transitions for the fully coplanar conformation and the conformation where the two anthryl groups are at 90° with respect to the central phenyl ring are superimposed with the experimental data in Figure 3. Transitions corresponding to the planar conformation are depicted by open squares, and transitions corresponding to the twisted conformer are depicted by filled circles. Calculations indicate that the three lowest energy transitions in the coplanar conformation are red-shifted with respect to the analogous transition of the twisted conformation. These results support the assignment of the spectra obtained in polyethylene films and in MCH at 77 K to the lowest energy, all-planar conformation of compound **5**. An increase in the intensities in the lower energy portion of the absorption band as the samples change from solution to glasses or to polymer is well accounted for by the calculations. The ZINDO/S method also suggests that the two lowest energy transitions by 400 and 300 nm are oriented along the acetylene axes, while the higher energy transition near 250 nm is oriented perpendicular to the acetylene bond and along the plane of the anthracene units. With respect to the changes in conformational populations and equilibration brought by sample freezing, it is noteworthy that the oscillator strength for the two conformations is of similar magnitude. This is consistent with the nearly identical radiative rates determined under conditions where different conformers predominate at 300 K and at 77 K.

The results obtained in MCH at 77 K and in polyethylene at room temperature raise an important question: *Why does planarization cause major changes in the excitation spectrum of* **5** *but only minor changes in the emission?* Given that the emission spectrum reflects the dynamics of the excited state, we conclude that the lower energy species, the excited-state planar rotamer, must be the emitter in all cases. This is in contrast to the variability in the excitation and absorption spectra of **5**, where the dynamics and equilibrium populations of the ground state are reflected. The spectral observations with compound **5** can all be explained in terms of the energy diagram in Figure 4. Population of all rotamers in the ground state at ambient temperature gives rise to broad absorption bands, as is characteristic of heterogeneous samples with multiple absorbers. However, with an excited-state lifetime of 1.8 ns, nearly complete equilibration along the excited-state potential must occur, such that emission can only be observed from structures close to that of the low-energy coplanar conformer. Excited-state equilibration is also responsible for the invariability of the emission spectrum upon changes in excitation wavelength in solution at ambient temperature. When experiments are conducted at 77 K, or at ambient temperatures in polyethylene films, the main absorbing and emitting species should be the coplanar rotamer.

3.5. Slowing Down Excited Conformational Dynamics with High-Viscosity Mineral Oil. According to the above model, one should be able to introduce wavelength dependence in excitation and emission measurements by slowing down the conformational dynamics in the excited state so that equilibration cannot be attained within the 1.8 ns lifetime. The simplest way to test this model, in a qualitative fashion, would be to inhibit the internal dynamics of the ground and excited states by increasing the viscosity of the solvent. To accomplish this, we carried out measurements in mineral oil.

We initially found that fluorescence measurements of compound **5** in mineral oil at 300 K were identical to those in cyclohexane at the same temperature. However, both the excitation and emission spectra exhibited a strong wavelength dependence when the mineral oil was cooled to −78 °C. As indicated by the spectra (a)−(d) in the top frame of Figure 5, the excitation spectrum became increasingly blue-shifted as the emission wavelength was changed between 540 and 480 nm. Since excited-state rotational equilibration should be incomplete under those conditions, we interpret changes in the absorption envelope as indicative of changes in the emitting species. By sampling emission at shorter wavelengths, one observes increasing contributions from the twisted rotamers. Consistently, the emission spectrum, which had been previously assigned to the equilibrated coplanar rotamer, was significantly blue-shifted and broadened as the excitation wavelength was shifted from 450 to 300 nm. An emission spectrum obtained upon excitation at 312 nm in Figure 5 shows a significant decrease in vibrational resolution and a broad shoulder between 430 and 480 nm, which

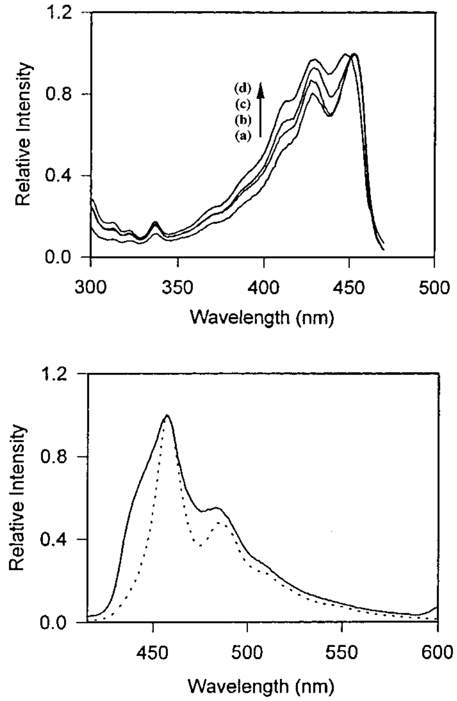
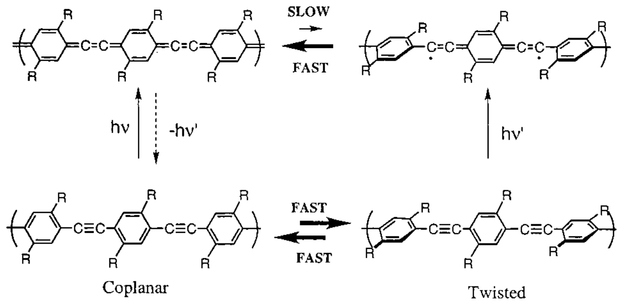


Figure 5. (top) Excitation spectra of compound **5** in mineral oil at −78 °C acquired by detection at (a) 540, (b) 520, (c) 500, and (d) 480 nm. (bottom) Emission spectra of compound **5** in mineral oil recorded by excitation at 312 nm at ambient temperature (solid line) and at −78 °C (dotted line).

SCHEME 4



we propose are indicative of the emission from nonequilibrated twisted conformers.

It is clear from the results in Figures 4 and 5 that the rotational dynamics of poly(arylalkynes) in ground and excited states are particularly interesting. It is well-known from ground-state calculations[19] and experiments with model compounds[20] that the energy barrier for aryl group rotation is very low, and possibly frictionless. Our results indicate that coplanar and twisted structures of compound **5** may coexist in solution in a relatively fast conformational equilibration, primarily determined by the temperature and viscosity of the medium. The excited-state rotational surface, in contrast, possesses important energetic features. As analyzed in our previous paper,[8] molecular orbital models show that the HOMO and the LUMO of diarylalkynes extend to varying degrees over the molecular frame as a function of the interaromatic rotational angle. The sign and magnitude of the atomic coefficients in the HOMO indicate that the bond order between alkynes and arenes remains single for all interaromatic dihedrals. In contrast, the sign and magnitude of the atomic coefficients in the LUMO give rise to cummulene-like structures, which becomes strongly dependent on orbital overlap (Scheme 4).[5,21] While Franck−Condon excitation energies from ZINDO/S semiempirical calculations suggest a barrier of 7 kcal/mol, relaxation in the excited-state potential may uncover further detail. The possible existence of a shallow minimum for twisted conformations in the excited state is currently being investigated.

4. Conclusions

The results reported with compound **5** illustrate the photophysical manifestations of planarization and twisting under conditions where intermolecular aggregation should be unimportant. From those results, we can draw several conclusions regarding the dynamic behavior of **5** in solution. At room temperature, **5** exists as an equilibrium mixture of all possible twisted and planar conformations. These rotamers absorb light with similar extinction coefficients, giving rise to the broad and poorly resolved excitation and absorption spectra. Upon excitation, the excited state undergoes equilibration along the excited-state surface within its 1.8 ns lifetime until it reaches the lowest energy coplanar structure, which undergoes radiative decay with high quantum yield. Experiments carried out in low-temperature glasses, polyethylene films, and viscous mineral oil reflect perturbations in the ground-state equilibrium population, as well as in the ground- and excited-state conformational dynamics. These results indicate that compounds with linearly conjugated aromatic groups and triple bonds should have conformationally dependent photophysical properties analogous to those of compounds that have linear conjugation through planar aromatic groups and double bonds.

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