

## A Re-evaluation of the Photophysical Properties of 1,4-Bis(phenylethynyl)benzene: A Model for Poly(phenyleneethynylene)

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**Abstract:** Photophysical measurements, recorded in aerated cyclohexane at 283 K, indicate that 1,4-bis(phenylethynyl)benzene behaves in a conventional manner, undergoing emission from the lowest vibrational level of the first excited singlet state; there is no evidence for aggregation of this material in cyclohexane solution in the concentration range  $(1-250) \times 10^{-6} \text{ mol dm}^{-3}$ . However, in highly viscous, low-temperature glasses, the material does exhibit inhomogeneous fluorescence behavior, and wavelength-dependent excitation and emission spectra, indicative of a slow rate of relaxation of conformers of the excited states compared to the rate of fluorescence.

### 1. Introduction

Many ethynylated aromatic systems, such as 1,4-bis(phenylethynyl)benzenes, 9,10-bis(phenylethynyl)anthracenes, 2,5-bis(phenylethynyl)thiophenes, and 2,5-bis(phenylethynyl) metalacyclopentadienes, display interesting structural, electronic, nonlinear optical, and luminescent properties. The stiff, linear nature of these compounds often results in liquid-crystalline behavior,<sup>1</sup> and it is interesting to note that many of the models used to rationalize the phase behavior assume cylindrical symmetry along the ethynyl axis. The fluorescent and electroluminescent properties of both molecular and polymeric systems based upon these motifs have prompted speculation about the suitability of these compounds for alternatives to poly(phenylene)vinylene (PPV) as emitting layers in electroluminescent devices.<sup>2</sup> The conjugated  $\pi$ -system has led to the development of molecular wire-like architectures,<sup>3</sup> for which remarkably low resistivities have been measured.<sup>4</sup>

The origin of many of these fascinating properties may be directly attributed to the extended, linear  $\pi$ -conjugation that runs along the principal molecular axis which, at any point in time,

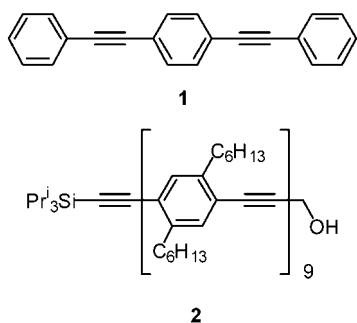
is dependent upon the relative orientation of the planar aromatic moieties. Indeed, it has recently been claimed that conformational changes may be used to modify the conductive properties of a 1,4-bis(phenylethynyl)benzene derivative, giving rise to a molecular switch.<sup>5</sup> The HOMO-LUMO gap in these materials, and hence their emissive properties, will vary with the effective conjugation length, which in turn will alter their photo- and electroluminescence characteristics. To engineer molecular devices based upon conjugated frameworks, a firm grasp of the factors that control the geometry of the compound, and hence the  $\pi$ -conjugation pathway, in both the ground and excited states is required.

We,<sup>1c,6</sup> and others,<sup>1-5,7</sup> have had an interest in the chemistry and properties of compounds featuring phenylethynyl motifs for some time. The barrier to rotation about the alkynyl-aryl single bond is very low, estimated at less than 1 kcal/mol,<sup>8</sup> and engineering control over the molecular conformation in materials derived from the elementary framework **1** (Chart 1) is a significant challenge. Nevertheless, a number of groups have recently reported success in achieving a degree of such control after constraining molecular and polymeric materials in Langmuir films,<sup>9</sup> or self-assembled monolayers,<sup>10</sup> as well as through use of intramolecular tethers.<sup>11</sup>

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Chart 1. Compounds **1** and **2**

In terms of measurements concerned with the dynamic processes of materials based upon the core framework of **1**, Sluch et al. have undertaken picosecond time-resolved emission studies of a substituted nonamer **2** (Chart 1).<sup>12</sup> Their results are consistent with a thermally populated distribution of ground-state conformations and a first excited state with a considerably larger barrier to rotational distortion from the lowest energy planar orientation. The viscosity of the solvent medium was also shown to play a significant role in the dynamic process, with high-viscosity solvents hindering the relative torsional motion of the aryl groups. Similar models have been proposed<sup>13</sup> to account for the photophysical properties of 1,4-bis(anthracenyl-9-ethynyl)benzene<sup>6c</sup> and 1,4-bis(phenylethynyl)anthracene.<sup>6c,7a-c</sup>

We were greatly intrigued by a recent report of a series of photophysical measurements of the parent species 1,4-bis(phenylethynyl)benzene (**1**).<sup>14</sup> This report described the observation of significant and systematic shifts in the fluorescence emission spectrum of **1** with excitation wavelength. The observation of two discrete spectral profiles, rather than a smooth transition from one spectral profile, clearly indicated the presence of two, spectroscopically distinct species in solution. These species were attributed to two discrete configurational

isomers of **1**, i.e., a planar structure and a twisted form. If true, this observation would have profound implications for the behavior of these materials in a range of applications, as well as being an example of very unusual photophysical behavior.

We had not previously observed such anomalous behavior in several closely related systems,<sup>6</sup> and Grummt and colleagues have claimed the fluorescence spectrum of **1** is wavelength independent.<sup>7j</sup> Furthermore, neither we nor Grummt's group had seen the unusual low-energy shoulder ( $\lambda_{\text{max}} = 360$  nm) on the UV-vis profile of **1** reported by Levitus et al.<sup>14</sup> This prompted us to reexamine carefully the spectroscopic properties of **1** in solution.

## 2. Experimental Section

A sample of **1** was prepared by Sonogashira coupling of 1,4-diiodobenzene with phenylacetylene in diisopropylamine with a mixed Pd(PPh<sub>3</sub>)<sub>4</sub> (3%)/CuI (3%) catalyst.<sup>15</sup> The product was purified by recrystallization from toluene, yielding analytically pure material as determined by elemental analysis (C<sub>22</sub>H<sub>14</sub> requires C 94.97%, H 5.03%; found C 94.59% H 4.99%), <sup>1</sup>H and <sup>13</sup>C NMR, and GC-MS. UV-vis spectra were recorded with an ATI Unicam UV-2 spectrophotometer. Samples were held in silica cells with path lengths of 1, 2, 10, and 25 mm and the spectra recorded over the range 200–400 nm with a 1 nm data interval and a 2 nm band-pass. Fluorescence spectra were recorded with a Jobin-Yvon Horiba Fluorolog 3-22 Tau-3 spectrofluorimeter. The spectra of dilute solutions, with an absorbance of <0.1 in the range 250–400 nm, were recorded by using conventional 90° geometry, and a front-face geometry was used to study highly absorbing solutions. Both the excitation and emission spectra were fully corrected by using the manufacturers correction curves for the spectral response of the excitation and emission optical components. A spectral band-pass of 2.5 nm was used for both the excitation and emission monochromators. Excitation and emission matrices were acquired by recording the emission spectra over the range 300–500 nm and stepping the excitation wavelength from 230 to 400 nm in 2.5 nm increments. Fluorescence lifetimes were recorded with the same spectrometer operating in the phase-modulation mode. The phase shift and modulation were recorded over the frequency range 50–300 MHz, and the data fitted using the Jobin-Yvon software package. Low-temperature spectra were recorded in an Oxford Instruments DN1704 cryostat and temperature controller (ITC 6). A mixture of diethyl ether, 2-methylbutane, and ethanol in the ratio 5:5:2 (v/v), EPA, was used for the low-temperature studies since this forms an optically transparent glass at low temperatures.

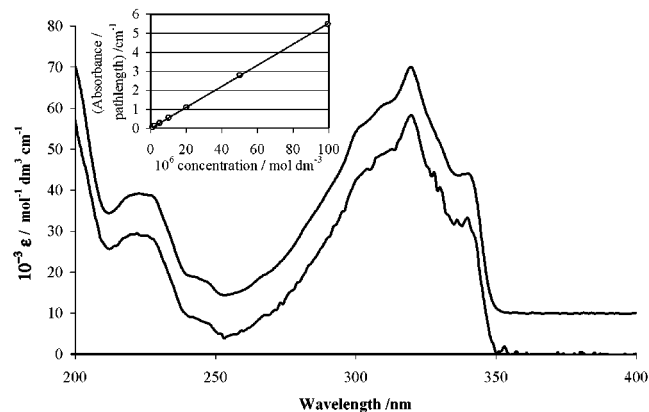
## 3. Results and Discussion

In cyclohexane solution, the UV-vis spectrum of **1** prepared in this manner is consistent with that published earlier by one of us,<sup>6e</sup> featuring a series of partially resolved absorption bands between 250 and 350 nm, with a sharp band-edge at the red end of the absorption profile (Figure 1). Similar spectra were observed in toluene, acetonitrile, and dioxane solutions.<sup>6e,7j,16</sup> A maximum extinction coefficient of  $58\,000 \pm 1\,000$  mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup> was determined at the 320 nm peak. The same spectral profile was obtained at concentrations from 10<sup>-6</sup> to 2.5 × 10<sup>-4</sup> mol dm<sup>-3</sup> in cyclohexane, with a linear dependence of the absorption upon concentration (Figure 1). The linear nature of the Beer-Lambert plot suggests that concentration-dependent aggregation phenomena are not significant in this solvent.

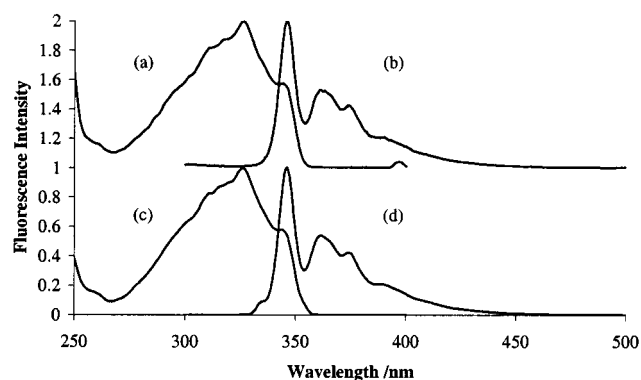
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**Figure 1.** UV absorption spectra of  $1 \times 10^{-6}$  (lower trace) and  $250 \times 10^{-6}$  mol dm $^{-3}$  (upper trace) solutions of **1** in cyclohexane at 293 K. The upper trace has been offset by  $10\,000$  mol $^{-1}$  dm $^3$  cm $^{-1}$  for clarity. The inset shows the absorbance at the peak, 320 nm, as a function of concentration. The value obtained for  $250 \times 10^{-6}$  mol dm $^{-3}$  falls on this line but has been omitted for clarity.

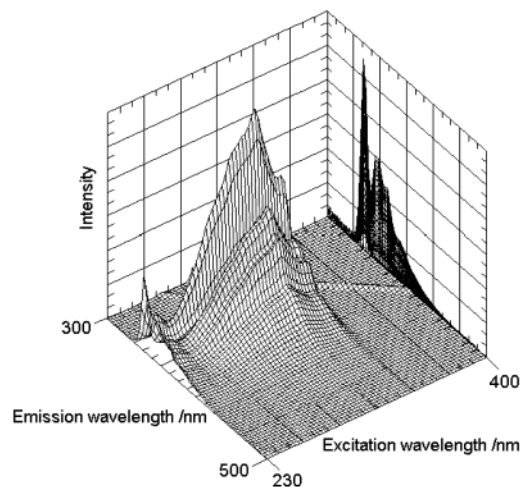


**Figure 2.** Normalized fluorescence excitation and emission spectra obtained from a  $1 \times 10^{-6}$  mol dm $^{-3}$  solution of **1** in cyclohexane. The excitation spectra a and c were obtained by using emission wavelengths of 450 and 350 nm, respectively, and the emission spectra b and d were obtained by using excitation wavelengths of 270 and 340 nm, respectively. The small peak at 397 nm in spectrum b is due to Raman scatter from the solvent. Both the excitation and emission monochromators were set to 2.5 nm fwhm.

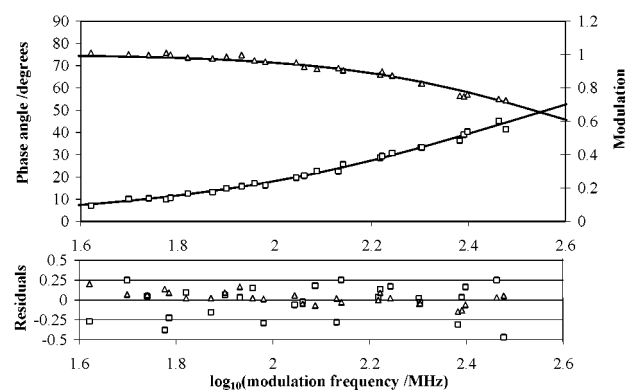
Crucially, the spectra do not exhibit the shoulder at 360 nm described by Levitus et al.<sup>14</sup>

Fluorescence emission spectra were collected by using excitation wavelengths from 230 to 400 nm (Figure 2). We observed constant emission band profiles across this range of excitation wavelengths. The emission spectrum is similar to that observed by Levitus et al. using short excitation wavelengths, and shows some vibrational fine structure with peaks at 346, 362, and 375 nm, tailing to the red.<sup>14</sup> Excitation spectra of the emission were independent of the selected emission wavelength and closely resemble the UV–vis absorption spectrum.

As the homogeneity of the fluorescence spectrum is of vital importance to the question of whether this material has any dual emission characteristics, we have also recorded the excitation–emission matrix, EEM, of a dilute solution of **1** in cyclohexane, illustrated in Figure 3. These data further confirm the homogeneity of the excitation and emission spectra. The emission spectrum of a more concentrated solution of **1**,  $250 \times 10^{-6}$  mol dm $^{-3}$ , was recorded by using a front-face geometry that reduces, but does not entirely eliminate, inner-filter effects. The observed spectrum shows a similar spectral profile to that of very dilute solutions, but the blue-shifted band at 350 nm has a reduced intensity. This is not an unusual phenomenon, and it can be



**Figure 3.** Fluorescence excitation and emission matrix obtained from a  $1 \times 10^{-6}$  mol dm $^{-3}$  solution of **1** in cyclohexane. The emission spectra have been projected onto the right-hand-side panel. The ridge of small peaks that appear at excitation wavelengths longer than 350 nm are the result of Rayleigh scatter by the sample.



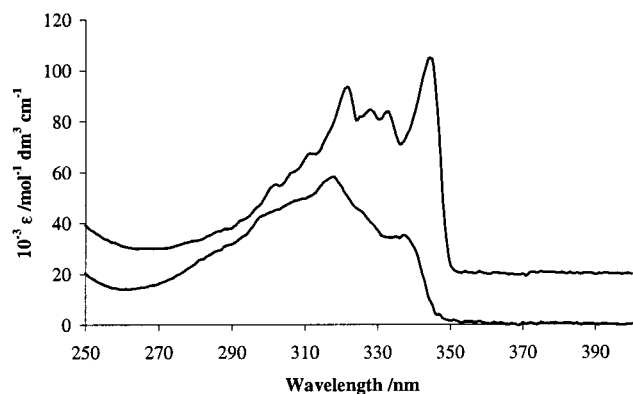
**Figure 4.** Data obtained by the phase-modulation technique for the determination of the fluorescence lifetime of **1** in aerated cyclohexane, using excitation at 320 nm and emission at 360 nm. The curves show the fit of the phase (squares) and modulation (triangles) for a single-exponential decay with a lifetime of 0.53 ns. The normalized residuals are shown below.  $\chi^2 = 0.80$ .

explained by the effects of reabsorption in these optically dense solutions<sup>17,18</sup> rather than the effects of co-facial aggregation proposed elsewhere.<sup>7e</sup>

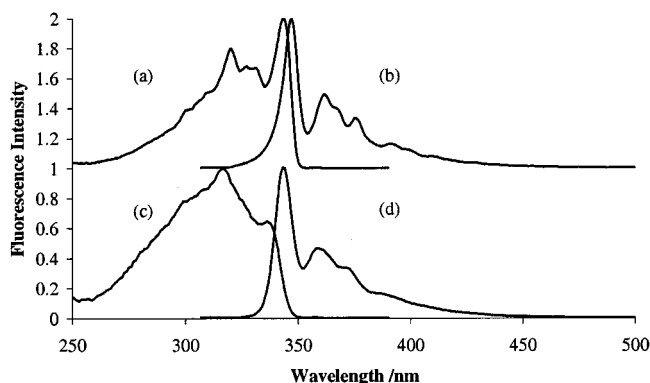
Fluorescence lifetimes, determined by the phase-modulation technique from cyclohexane solutions, gave a value for **1** of  $0.63 \pm 0.05$  ns, which was found to be independent of the excitation and emission wavelengths used, consistent with our data reported earlier.<sup>6e</sup> A typical fit is illustrated in Figure 4. Similarly, Bircner et al. found the fluorescence lifetime of **1** to vary between 0.59 (toluene) and 0.69 ns (methylcyclohexane).<sup>7j</sup> This is much shorter than reported by Levitus et al., where values ranged between 0.74 and 0.97 ns depending upon the excitation and emission wavelengths used.<sup>14</sup> Their data were obtained by using the method of time-correlated single-photon counting, and close examination of the fluorescence decay plot presented in ref 14 shows that the instrument response profile of the equipment was rather long,  $> 1$  ns, and that a relatively small number of counts were acquired.<sup>19</sup> A system containing

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**Figure 5.** Absorption spectra of **1** in EPA at 298 (lower trace) and 77 K (upper trace). The spectra have been corrected for changes in solvent density and the low-temperature spectrum is shown offset by  $20\,000\text{ mol}^{-1}\text{ dm}^3\text{ cm}^{-1}$  for clarity.



**Figure 6.** Normalized, corrected fluorescence excitation and emission spectra of **1** in EPA at (a, b) 77 and (c, d) 298 K determined with excitation at 320 nm and emission at 360 nm.

two distinct emitting species would be expected to show a biexponential decay, although the low signal-to-noise ratio and the unacceptably low reduced  $\chi^2$  values obtained for the single exponential decays may have prevented the authors from considering such fits.

At 77 K, the absorption spectrum of **1** in EPA shows changes in the absorption profile, with a significant increase in absorption at the red edge (Figure 5). Qualitatively, the excitation spectrum collected under these conditions is similar to the absorption spectrum and more like the mirror image of the emission spectrum, showing a strong (0,0) band and a small Stokes shift (Figure 6). Closer examination reveals a more complex behavior in the low-temperature glass, with some evidence of changes in the emission spectrum with excitation wavelength. For example, upon excitation at 350 nm, the red edge of the absorption band gives an emission spectrum with a sharp blue edge. However, for progressively shorter excitation wavelengths, this rising edge becomes less well-defined and the vibrational fine structure in the emission spectra show subtle but distinct shifts. This can only be attributed to the fact that in the low-temperature glasses we have a continuum of conformers, each with its own absorption and emission spectrum, and that on the fluorescence time scale these conformers are now long-lived, i.e., the rate of rotation of the phenyl rings with respect to one another is comparable to the fluorescence lifetime, 0.53 ns. We

propose that in the low-temperature glass there is a more limited range of conformations, with a greater bias toward the planar form. However, since the rotational barrier in the ground state is low, cooling to 77 K does not adequately reduce  $kT$  to limit the material to only the planar form.

Several models have been proposed to account for the dynamic behavior of **1** and structurally related systems on the basis of photophysical studies. Cherkasov et al. proposed a two-state model in which the aromatic rings adopt coplanar or orthogonal conformations to account for the low-temperature fluorescence behavior of 9,10-bis(phenylethynyl)anthracene.<sup>13a</sup> A similar description was proposed by Levitus et al. to account for their observations of **1**.<sup>14</sup>

However, in contrast to these hypotheses, we suggest that there is a continuum of rotational conformers of **1** in solution and that the distribution of these conformers in the ground electronic state changes with temperature.

Our observations and interpretations are therefore entirely in agreement with the conclusions of Sluch et al., who investigated the dynamics of the fluorescence of a substituted oligophenyleneethynylene, **2**.<sup>12</sup> Their work indicated that rotational relaxation occurred very rapidly in the excited state, with a recorded time constant of 60 ps, and they interpreted their data in terms of a quadratic coupling model. Using fast time-resolved emission spectroscopy, they demonstrated that the blue edge of the emission shifted in a subtle fashion at early times after excitation, evidence for the rapid planarization of the excited state. In their model, Sluch et al. suggest that the system behaves as though the potential well is very small in the ground electronic state but that in the first excited state the planar form is considerably more stable than the nonplanar conformers. Indeed, these interpretations are further supported by subsequent work on anthrylethynylenes reported by Garcia-Garibay's group.<sup>13b,c</sup>

#### 4. Conclusion

Photophysical measurements, recorded in aerated cyclohexane at 283 K, indicate that **1** behaves in a conventional manner, undergoing emission from the lowest vibrational level of the first excited singlet state. We see no evidence whatsoever for any anomalous excited state behavior that supports the presence of two distinct rotamers or aggregates in cyclohexane solution in the concentration range  $(1\text{--}250) \times 10^{-6}\text{ mol dm}^{-3}$ , and suggest that the data reported in the previous study involving excitation at wavelengths greater than 350 nm arise not from **1**, but rather from a second *chemically distinct species*, despite the careful efforts made by the authors to ensure sample purity.<sup>14,20</sup> However, there is evidence that in highly viscous, low-temperature glasses, the material does exhibit inhomogeneous fluorescence behavior, and that the excitation and emission spectra are wavelength dependent, indicative of a slow rate of relaxation of rotamers of the excited states compared to the rate of fluorescence.

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**Supporting Information Available:** Details of the synthesis and characterization of **1**, including  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra

and GC-MS (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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