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Fluorescence Study of Dehydroabietic Acid-Based Bipolar Arylamine-Quinoxalines

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The absorption and fluorescence spectra, lifetimes and quantum yields of a series of triarylamine-quinoxaline bipolar compounds, with and without the bulky dehydroabietic acid group, have been studied in toluene solution. This bulky group is introduced to improve solubility and thermal properties of these systems. It is shown that this does not affect their spectral or photophysical behavior. The compounds show relatively strong fluorescence, with the emission maximum strongly dependent upon the substituents present. Oxidation potentials have also been determined in acetonitrile solution, and again indicate that introduction of the resin acid moiety has no effect on these properties.

KEY WORDS: Fluorescence; triarylamines; quinoxalines; dehydroabietic acid.

INTRODUCTION

The area of molecular electronics has developed to the state of maturity where organic and polymeric semiconductor systems are now finding commercial applications, and are being intensively studied for use in areas such as light-emitting diodes (LEDs), thin film transistors and photovoltaic systems [1,2]. For many of these applications, efficiency is increased dramatically in the presence of charge-transporting molecules, such as aromatic amines for holes [3] and quinoxalines for electrons [4,5]. There is also considerable interest in the use of bipolar molecules in these devices, where both electron and hole-transporting groups are present [4–6]. For applications in LEDs, knowledge of the photophysical characteristics of the charge-transporting materials are fundamental for optimizing device properties, and are also valuable for the design of potential new blue-light emitters. In addition, the processability of molecules for these applications is an important property. Solvent-based methods, such as spin coating, have proved particularly attractive for preparing thin film devices. However, these require both high solubility in volatile solvents and compounds which do not crystallise readily. We have recently shown that triarylamines with a resin acid moiety have excellent solubility and film-forming properties which make them good candidates as hole transport layers [7,8]. We extend this study to dehydroabietic acid-based triarylamine-quinoxaline bipolar compounds with potential for device applications. Introduction of bulky groups into aromatic amines can affect both the spectra and photophysics of these compounds [9]. We have therefore compared their behavior with the corresponding compounds without this group, and report a study of their fluorescence behavior in toluene solution.

EXPERIMENTAL

Materials

The structures of a series of bipolar compounds featuring dehydroabietic acid-based quinoxalines acceptors fused to various triarylamine donors (**1–4**) and the analogues (**5–8**) used in this study are given in Fig. 1. They have been synthesized following a two-step procedure as

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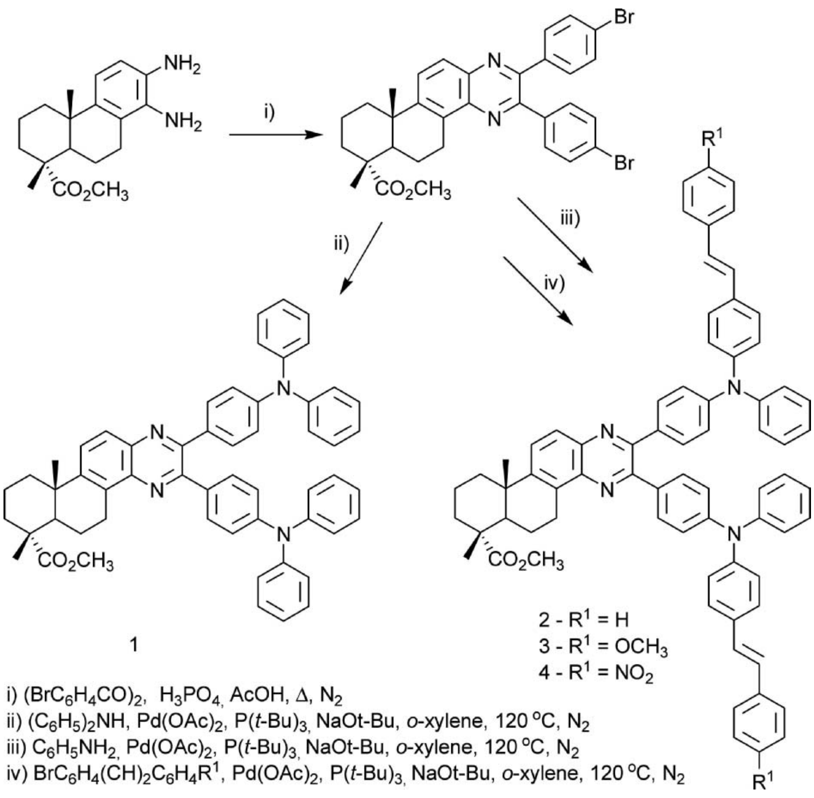

Scheme 1.

depicted for (**1–4**) in Scheme 1. Thus, by a mild acid catalyzed condensation of two *ortho*-anilines, respectively, methyl 13,14-diaminodeisopropyldehydroabietate [10] or commercially available 1,2-diaminobenzene with dibromobenzil, the dibromoquinoxaline intermediates were prepared, which by reaction with different diarylamines gave the compounds (**1–4**) and (**5–8**). The amination reaction takes place rapidly by using the catalyst combination of $Pd(OAc)_2$ and a bulky and electron-rich phosphine, P(t-Bu)$_3$ [11]. The intermediates and the bipolar compounds (**1–4**) and (**5–8**) were purified by repeated recrystallization or column chromatography. Details of the synthesis and characterization will be given later [12].

Methods

Absorption and fluorescence spectra were recorded on a Shimadzu UV-2100 and a Jobin-Yvon SPEX Fluorolog 3-22 spectrometer, respectively. All the fluorescence spectra were corrected for the wavelength response of the system. Fluorescence quantum yields were measured using tetrathiophene ($\phi_F = 0.18$ in benzene) and pentathiophene ($\phi_F = 0.34$ in benzene) as standards [13]. Fluorescence decays were measured using a home-built time-correlated single photon counting (TCSPC) apparatus with a Horiba-JY-IBH nanoLED (373 nm) as excitation source, Jobin-Yvon monochromators, Philips XP2020Q photomultiplier, and Canberra instruments TAC and MCA. The fluorescence decays were analyzed employing the method of modulating functions [14]. Oxidation potentials were determined by cyclic voltammetry using an EG&G Princeton Applied Research Potentiostat Model 273A. A three-electrode system was used, with a platinum counter electrode, a platinum working electrode, and a KCl saturated calomel reference electrode (SCE). Tetrabutylammonium hexafluorophosphate was used as the supporting electrolyte. The electrochemical properties were determined in acetonitrile and all the other photophysical parameters were determined in toluene.

RESULTS AND DISCUSSION

The absorption spectra of dehydroabietic acid-based quinoxalines acceptors fused to various triarylamine donors (**1–4**) and their analogues (**5–8**) show strong

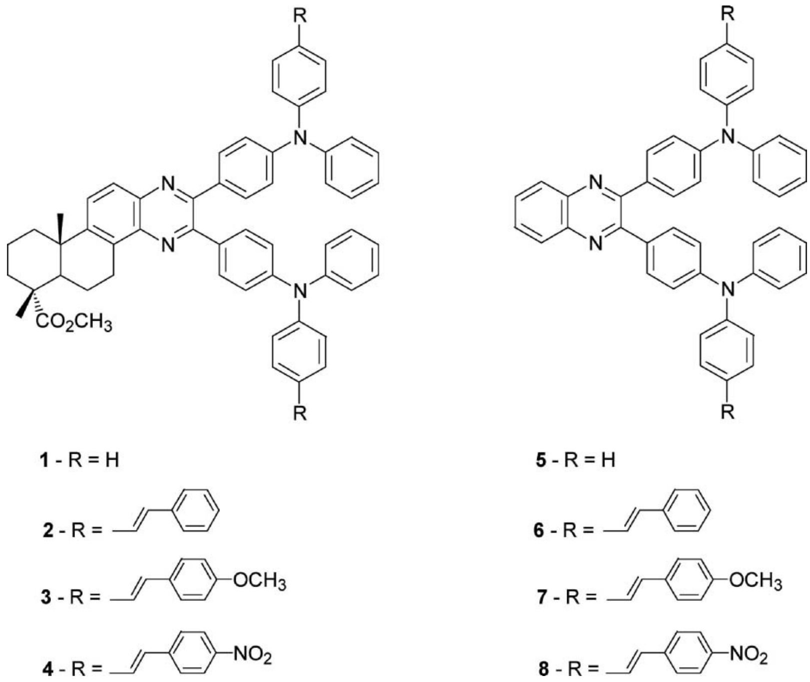

Fig. 1. Structures of a series of bipolar compounds featuring dehydroabietic acid-based quinoxalines acceptors fused to various triarylamine donors (**1**–**4**) and their analogues (**5**–**8**).

absorption bands and their maximum absorption wavelengths are shown in Table I. As examples, the absorption spectra for compounds **1** and **4** are given in Figs. 2 and 3, respectively. It can be seen that the absorption maxima can be tuned significantly by changing the substituents on the arylamine rings, but it is not affected by the presence of the dehydroabietic acid moiety. The molar extinction coefficients (ε) were obtained with five solutions of different concentrations. Good Beer–Lambert plots were obtained in all cases, and the slope of the plot of the absorption values (at the maximum wavelength of absorption) vs. the concentration values gives us the ε values shown in Table I.

The fluorescence spectra for compounds **1** and **4** are shown in Figs. 2 and 3, respectively. As can be seen in Table I, the emission maxima can also be tuned over a wide range by changing the substituents on the arylamine rings, while the presence of the dehydroabietic acid moiety slightly shifts the emission maxima towards longer wavelengths (10–17 nm) with the exception of compound **8**. There is no significant correlation between spectral data and oxidation potentials, suggesting that the triarylamine group only plays a relatively minor role in the lowest energy excited state. For compound **5**, the absorption and emission properties are similar to literature data for this compound [6], except for a somewhat lower value for

Table I. Electrochemical and Photophysical Properties of a Series of Bipolar Compounds Featuring Dehydroabietic Acid-Based Quinoxalines Acceptors Fused to Various Triarylamine Donors (**1**–**4**) and Their Analogues (**5**–**8**)

Cpd	E_{ox} (V)[a]	λ_{abs} (nm)	ε_{max} (M^{-1} cm^{-1})	λ_{em} (nm)	ϕ_F	τ_F (ns)	k_F (10^9 s^{-1})
1	1.03	400	26786	465	0.315	1.80	0.175
5	1.05	403	25746	475	0.334	2.20	0.152
2	0.83	368	39102	472	0.350	2.07	0.169
6	0.84	368	75085	487	0.348	2.69	0.129
3	0.84	367	97057	480	0.344	2.41	0.143
7	0.85	365	46062	497	0.378	3.22	0.117
4	0.88	428	55614	558	0.513	2.69	0.191
8	0.89	428	78397	552	0.502	2.69	0.187

[a] In acetonitrile.

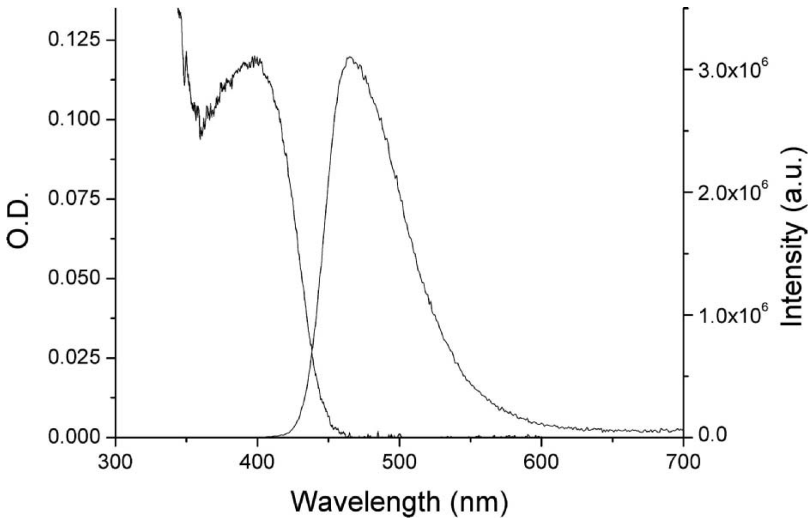

Fig. 2. Absorption (left, λ$_{\text{maximum}}$ 400 nm) and fluorescence (right, λ$_{\text{maximum}}$ 465 nm) spectra of compound **1** in toluene.

the fluorescence quantum yield in our study. For triarylamines, the compounds **1**–**8** show relatively high fluorescence quantum yields (ϕ_F, Table I), which are markedly affected by the substituents on the arylamine rings, with compounds **4** and **8** presenting the highest values. Since these compounds, having nitro groups, are likely to have the most polar-excited states of the compounds studied, it will be of considerable interest to study solvent effects on both absorption and fluorescence spectra. Studies are in progress on this. Further, the fact that the dehydroabietic acid moiety does not significantly affect the ϕ_F values, while it does enhance solubility, means that it will be possible to study compound **4** in a wide range of solvents to test its potential as a polarity probe. The fluorescence lifetimes (τ_F) and the fluorescence rate constants (k_F) are not significantly affected by the substituents on the arylamine rings and by the presence of the dehydroabietic acid moiety, suggesting that in this nonpolar solvent the substituents do not play any major part in the deactivation processes.

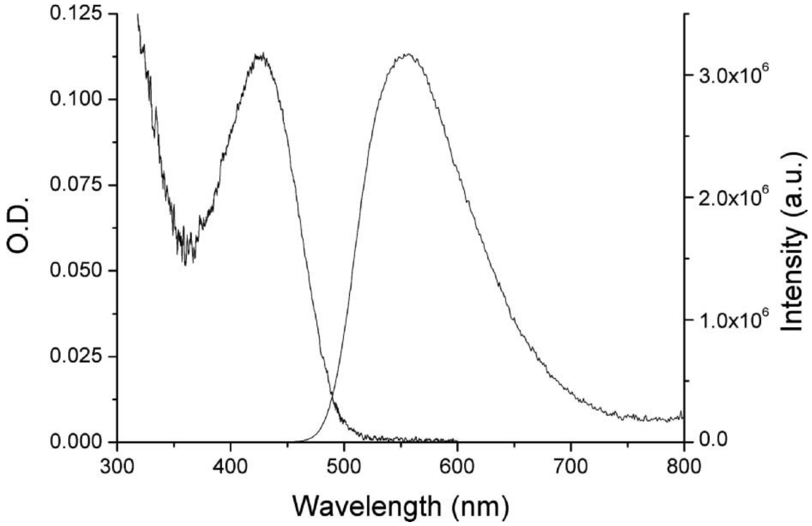

Fig. 3. Absorption (left, λ$_{\text{maximum}}$ 428 nm) and fluorescence (right, λ$_{\text{maximum}}$ 558 nm) spectra of compound **4** in toluene.

CONCLUSIONS

The photophysical properties of a series of bipolar compounds containing quinoxaline and triarylamine groups have been studied. They show strong absorption bands and relatively high quantum yields of fluorescence. The emission maxima can be tuned over a wide range of wavelengths (465–558 nm) by changing substituents on the arylamine rings. Thus, the presence of dehydroabietic acid moieties to enhance solubility does not significantly affect their photophysical properties.

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