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ORIGINAL PAPER

Fluorescence Characteristics of Some Dehydroabietic Acid-Based Arylamines

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Abstract Absorption spectra and fluorescence data in nonpolar solvents are reported for seven novel dehydroabietic acid-based diarylamines, which have potential as components of hole transport layers for molecular electronic devices. This bulky group has been found to improve the possibilities for film formation of these compounds, and in this study we show that this does not significantly affect their fluorescence characteristics, which are similar to diphenylamine.

Keywords Fluorescence · Dehydroabietic acid · Diarylamines · Hole transport layers

Introduction

Since the first suggestions that organic molecules could function as active components in molecular electronic devices [1], 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 [2, 3]. Typically these systems involve thin films of organic material sandwiched between two electrodes. For many of these applications efficiency is dramatically increased if there is a charge transport layer. Aromatic amines are amongst the most important derivatives for hole transport in devices [4–16], and have been used in a wide range of structures, either as separate layers [2, 15], or covalently attached to light emitting layers [11, 17–19]. In addition, these compounds have been tested as blue emitters in organic LEDs [20], and as components of electroluminescent bipolar compounds [21]. Arylamines also find use in areas such as antioxidants [22, 23] and have potential for use as two-photon probes for imaging and other applications [24]. For all these applications, knowledge of the behaviour of the lowest excited singlet state is important.

In the search for added value compounds from the renewable feed stock rosin, it has been shown that arylamines can be synthesised with a resin acid moiety by palladium catalysed cross-coupling reaction of aryl halides with either primary amines or diarylamines [23]. For thin film device fabrication, compounds should form good amorphous layers which do not have a tendency to crystallise. We have recently shown that dehydroabietic acid-based arylamines are excellent candidates for hole transport [25–27; Burrows et al., submitted for publication], and that in the best cases light emitting diodes (LEDs) made using these compounds give similar performance to devices prepared with solution processed *N,N*-diphenyl-*N,N*-bis(3-methylphenyl)-1,1-diphenyl-4,4-diamine (TPD) [27], a commonly used hole transport material, while showing the advantage that they are much more stable against crystallisation. In addition, solvent-based deposition techniques, such as spin coating [28] and inkjet printing [29] are attractive for film preparation, and the decrease in

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the degree of crystallinity in these compounds is also likely to increase their solubility, and hence their use in such applications. However, arylamine photophysics is suggested to be strongly dependent on the molecular configuration [30, 31], and introduction of this bulky group may have a marked effect both on the energy of the lowest singlet state and on the fluorescence quantum yield. We have, therefore, carried out a study of the absorption and fluorescence properties of a series of dehydroabietic acid-based diarylamines to see to what extent these bulky groups affect their spectroscopy and photophysics. These diarylamines are the building blocks of both the triarylamines [25, 27; Burrows et al., submitted for publication] and arylamine–quinoxalines [26], which we are testing for applications as hole transport layers.

Experimental

Materials

The structures of the arylamines (**1**–**7**) used in this study are given in Fig. 1. Details of the synthesis and characterisation are given elsewhere [23, 32, 33]. On keeping at room temperature in solution for prolonged periods, compounds became coloured, possibly due to formation of oxidation and/or coupling products. They are, however, stable if kept at lower temperatures. All reagents were of the purest grade available, and solvents were further purified by standard techniques.

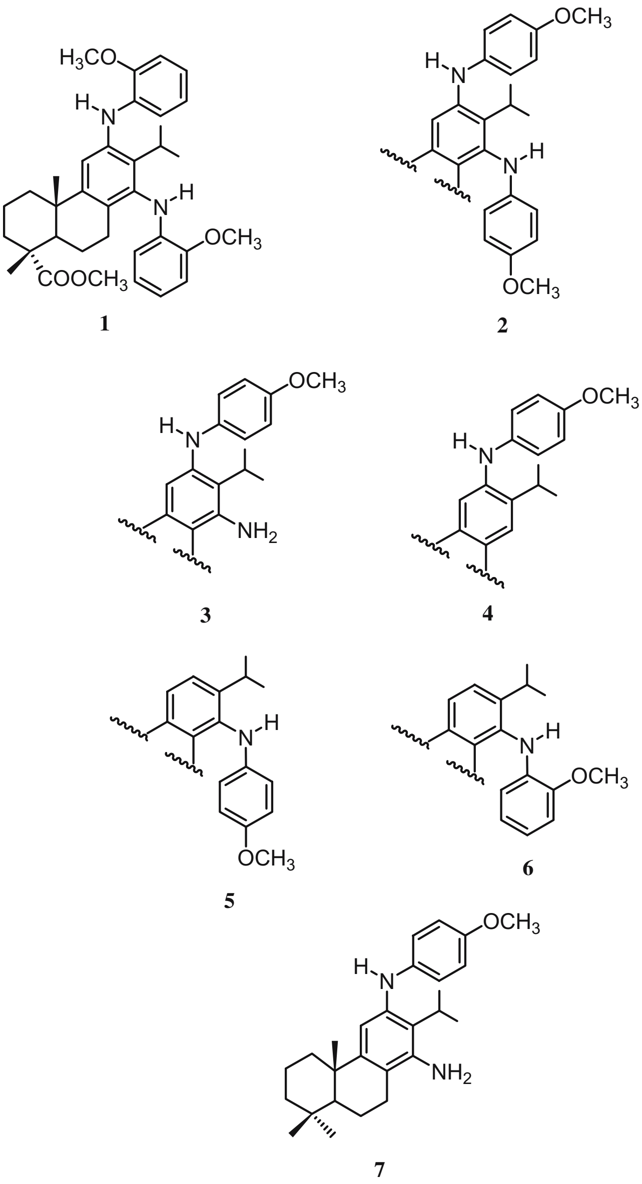

Fig. 1 Structures of arylamines studied

Equipment and methods

Absorption spectral measurements were made on solutions in 1 cm quartz cuvettes on a Shimadzu UV-2100 Spectrophotometer. Molar absorption coefficients were determined from slopes of absorbance as a function of concentration for a series of solutions for each compound at various concentrations. Fluorescence spectra and quantum yields were measured in 1 cm quartz cuvettes using 90 degree geometry on a Jobin Yvon-Spex Fluorolog 3-22 instrument. Emission and excitation spectra were corrected for variation in spectral response of the light source (a 450 W Xenon lamp) and detector. Quantum yields were determined for optically matched solutions from the ratio of integrated corrected emission spectra [34]. Dithiophene (Φ_f=0.014 in methylcyclohexane [35]) and *p*-(dimethylamino)benzethyne (Φ_f=0.26 in heptane [36]) were tested as references. Somewhat higher values were obtained in the latter case, and values reported here used this reference. The electrochemical instrumentation for cyclic voltametry (CV) consisted of an EG&G Princeton Applied Research Potentiostat Model 273A, connected to the data acquisition software (EG&G PAR Electrochemical Analysis Model 273 version 3.0). A three-electrode system was used, with a platinum counter electrode, a platinum working electrode, and a potassium chloride saturated calomel reference electrode (SCE). A 10^{-1} M solution of tetrabutylammonium hexafluorophosphate in acetonitrile was used as the supporting electrolyte. The solutions used in the cyclic voltammetry studies were 5 mM diarylamine in 0.1 M of supporting electrolyte. Solutions were degassed and kept under nitrogen throughout each experiment. Measurements were conducted at 25±0.1°C using a sweep rate of 50 mV s^{-1}. Further details are given elsewhere [23; Burrows et al., submitted for publication].

Fluorescence decays were measured using a home-built Time-Correlated Single Photon Counting apparatus with an N_2 filled IBH 5000 coaxial flashlamp as excitation source, Jobin–Ivon monochromator, Philips XP2020Q photomultiplier, and Canberra instruments Time-to-amplitude converter and Multichannel Analyser. Alternate measurements (1,000 counts per cycle), controlled by Decay® software (Biodinâmica-Portugal), of the pulse profile at 337 or 356 nm and the sample emission were performed until $1–2\times10^4$ counts at the maximum were reached [37]. The fluorescence decays were analysed using the modulating functions method of Striker with automatic correction for the photomultiplier "wavelength shift" [38].

Results

Absorption spectra were run of the seven dihydroabietic acid-based diarylamines in cyclohexane, heptane, methanol and acetonitrile solutions. These showed relatively strong absorptions, with maxima in *n*-heptane or cyclohexane in the 243–249 and 276–284 (296 for compound **1**) nm regions, and weaker maxima or shoulders around 320–330 nm. Typical spectra for compounds **1** and **5** are shown in Fig. 2 and data for absorption maxima and molar absorption coefficients are summarised in Table 1. From the above data, we assign the weak peak or shoulder around 325 nm to the $S_0\rightarrow S_1$ transition. The lowest energy band in diarylamines is predominantly π,π^*, although there may be mixing involving some charge transfer from the nitrogen [30]. Only very small red shifts (1–5 nm) were observed in the absorption maxima in the 280 nm region on going to the polar solvents methanol and acetonitrile. With the long wavelength band, again only minor effects of solvent polarity were observed, although it was difficult to obtain quantitative information since this tended to merge with the tail of the 280-nm band in the polar solvent acetonitrile.

Table 1 Absorption maxima and molar absorption coefficients for arylamines **1**–**7** in heptane solution

Compound	Absorption maximum (nm)	Molar absorption coefficient ($M^{-1}cm^{-1}$)
1	249	23,600
	276	20,300
	296	15,100
2	243	12,500
	284	20,200
	329	3,500
3	248	29,500
	283	13,900
	329sh	2,700
4	243	10,300
	284	16,400
	329	2,700
5	245	14,500
	276	6,700
	316	3,200
6	247	15,800
	276	7,000
	296	5,500
7	246	13,200
	283	6,050
	329	1,800

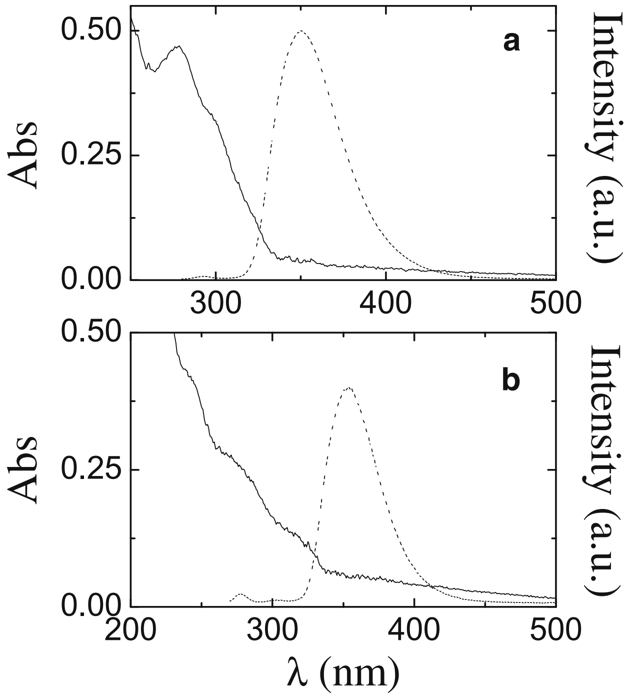

Fig. 2 Absorption (*solid line*) and fluorescence (*dotted line*) spectra in *n*-heptane solution of **a** compound **1** and **b** compound **5**

Fluorescence spectra were run in heptane and cyclohexane solutions, and very similar spectra were observed in the two solvents, showing in all cases a single broad emission, with maximum around 350–360 nm. Typical spectra are shown in Fig. 2, and data are summarised in Table 2. Fluorescence excitation spectra were also run, and showed onset of emission occurred with excitation in the 320–330 nm region, confirming that the $S_0\rightarrow S_1$ transition in these compounds corresponds to the weak shoulder in the absorption spectrum in this region. Energies of the lowest singlet state of the arylamines were determined from the intersection of the fluorescence emission and excitation spectra, and are given in Table 2, in addition to the values of the first oxidation potentials (E_p). These were taken from previous studies [23], except for compound **7**, which was measured here. The oxidation potentials are similar to those of the commonly used hole transport material TPD [12, 27].

The energies of the lowest singlet states are close to those previously reported for diphenylamine (3.86 eV [39]), and show that the bulky decahydronaphthalene moiety of the diarylamines does not markedly perturb this. There is rough correlation (not shown) between the energies of the lowest

Table 2 Fluorescence emission maxima and lowest excited singlet state energies of arylamines **1**–**7** in heptane solution and first oxidation potential (E_p) in acetonitrile

Compound	Emission maximum (nm)	S_1 energy (eV)	E_p (V)[a]
1	352	3.81	0.79
2	373	3.70	0.68
3	373	3.71	0.61
4	373	3.83	0.69
5	357	3.77	0.70
6	356	4.00	0.83
7	375	3.73	0.57

[a] Values determined in acetonitrile solution with a saturated calomel reference electrode and taken from ref. 23, except compound **7**, which was determined in this study.

singlet excited states and the oxidation potentials of these compounds (correlation coefficient r=0.80), which is similar to what has been reported for related systems [40, 41]. Whilst the importance of this relationship should not be exaggerated, it is a consequence of the fact that both parameters depend on the HOMO-LUMO energy gap, and supports the values of the singlet energies reported here. Qualitatively, the presence of two amine groups lowers both the singlet energy and oxidation potentials, in agreement with what is observed with other aromatic amines [42].

Fluorescence spectra were also run in acetonitrile and methanol solutions and were very similar to those in alkanes. Attempts were made to measure emission spectra in chloroform solutions. However, although fluorescence was observed, the solutions were not stable, probably due to photooxidation as has previously been reported for solutions of arylamines in chlorinated alkanes [43].

Fluorescence quantum yields (Φ_f) and lifetimes were determined in heptane or cyclohexane solutions and are given in Table 3. For all but one of the compounds, the fluorescence quantum yields are close to those reported for diphenylamine in EPA solution (Φ_f=0.11 [30]). With compound **6**, a markedly smaller value is observed, and although the explanation is not clear from its structure it is possible that there may be nonradiative deactivation via intramolecular proton transfer between the amine and *o*-methoxy group, as is seen in related systems [44, 45]. Fluorescence lifetimes are typically 1–2 ns. For three of the compounds (**1**, **4** and **7**), a smaller, longer lived component is observed, and may be associated with some degradation product. Radiative lifetimes were calculated from experimental lifetimes and quantum yields. They were also determined from the molar absorption coefficients ($\varepsilon_{\max}$) of the lowest energy absorption band using a modified form of the Strickler–Berg relationship, $\tau_{\mathrm{rad}} = 2.21 \times 10^{-8} / \left(\upsilon_{\max}^2 n^2 \varepsilon_{\max} \Gamma\right)$ where $\nu_{\max}$ and Γ are the absorption maximum and full-width in cm^{-1} and n is the solvent refractive index [46, 47]. Whilst the agreement between values calculated by the two methods is, in general, only moderate, all the values are consistent with assignment of π,π^* character to the lowest excited state. A major difficulty with the values calculated from the Strickler–Berg relationship is the accurate determination of the maximum and molar absorption coefficient of the lowest energy band.

In conclusion, absorption and fluorescence spectra have been measured for a series of dehydroabietic acid-based arylamines, and show that the presence of this bulky group does not markedly change their emission characteristics. Arylamines have already shown potential as light emitting layers in organic light emitting diodes [20], and the fact that the compounds studied here all emit in the near ultraviolet, and that they can be connected structurally to other groups by substitution of the amino nitrogen makes them good candidates in the search for the “Holy Grail” [48] of blue

Table 3 Fluorescence quantum yields, lifetimes and radiative lifetimes for arylamines **1**–**7**

Compound	Fluorescence quantum yield[a]	Fluorescence lifetime[b] (ns)	Radiative lifetime[c] (ns)	Calculated radiative lifetime[d] (ns)
1	0.186	1.89 (0.747)[e] 7.26 (0.196)[e]	10.2	3.9
2	0.105	0.70	6.7	20.9
3	0.111	0.86	7.7	27.1
4	0.100	1.09 (0.749)[e] 6.05 (0.161)[e]	10.9	27.1
5	0.183	2.11	11.5	21.1
6	0.027	2.27	84.1	10.8
7	0.101	1.12 (0.835)[e] 7.84 (0.163)[e]	11.1	40.6

[a] In *n*-heptane solution with *p*-(dimethylamino)benzethyne as reference.

[b] Values determined in methanol solution.

[c] Calculated from quantum yield (Φ_f) and lifetime (τ_{exp}) using $\tau_{\mathrm{rad}} = \tau_{\mathrm{exp}} / \Phi_f$.

[d] Calculated from molar absorption coefficient using modified Strickler–Berg relationship as described in the text.

[e] Relative amplitudes given in parenthesis.

LEDs. Synthesis and photophysical studies of other related amines are in progress to improve emission characteristics for these applications. Further, from overlap of absorption and emission and excitation spectra, the lowest excited singlet states in all cases are at higher energies than those of conjugated polymers used in polymer-based devices (<3.0 eV [49]). If derivatives based on these amines are used as hole transport layers in such systems, back energy transfer from polymer excited states is not likely to be an important energy loss mechanism.

Conclusions

A series of dehydroabietic acid-based diarylamines have been synthesised as potential components of hole transport layers for electrooptic devices. Incorporation of this bulky group has been found to enhance the solubility and film forming properties of this class of compounds without significantly affecting their spectroscopic or photophysical properties.

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