ORIGINAL PAPER

Synthesis and Spectroscopic Studies of 3,6-Diphenyl-2,5-Dihydropyrrolo[3,4-C]Pyrrole-1,4-Dion's N,N'-Dialkyl Derivatives

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Abstract 3,6-diaryl-2,5-dihydro-1,4-diketopyrrolo[3,4-c] pyrrole-1,4-dione (DPPD) derivatives are used commercially as red pigments, because of their color strength, brightness, and very low solubility in most common solvents. These products, although highly colored, appear to be of limited value as dyes, since they show a tendency to form an aggregate when incorporated into a solvent. Monoalkyl and dialkyl derivatives of DPPD were synthesized and then characterized with IR, ^{1}HNMR, UV-Vis absorption and emission spectroscopy. Molar absorption coefficient, singlet energy level and Stokes' shift values of DPPD derivatives were declared. Monoalkyl and dialkyl derivatives of DPPD's solubilities were measured from saturated solutions of dimethylformamide (DMF), tetrahydrofuran (THF), dichloromethane (DCM), acetonitrile (ACN) and toluene and they are compared with each other.

Keywords Diketopyrrolopyrrole ·
Fluorescence spectroscopy · Photocharacterization ·
Solubility calculation · Dye · Synthesis

Introduction

3,6-diaryl-2,5-dihydro-1,4-diketopyrrolo[3,4-c]pyrrole-1,4-diones (DPPD) are currently of considerable commercial importance as high performance pigments. These organic chromophores have been intensely studied by chemists at Ciba to find out whether they can be used as products in various areas, e.g. for coloring of construction plastics,

fibres and surface coatings such as automotive paints, prints and inks.

The success of these compounds as pigments relies, in part, on their high light fastness and very low solubility in most common solvents. This state of low solubility is presumed to result from 2-dimensional network by intermolecular hydrogen bonds (N...H...O) combined with Π-Π and Van der Waals interactions of the aryl substituents between layers of molecules [1].

A number of electronic applications have been suggested for diketopyrrolopyrroles as charge generating materials for laser printers [2] and information storage systems [3]. In order to design novel photorefractive materials, the incorporation of the chromophoric DPPD derivatives into polymers was achieved first by Yu et al. [4]. Later, Tieke and co-workers realized two different series of DPPD-containing polymers, thus, aliphatic co polyesters and co polyurethanes [5], via their N-alkylated lactam groups, have been prepared by Suzuki coupling. They have been also used as p-conjugated material [6] towards electronic applications as OLED materials. The chromophoric biheterocycle DPPD with a variable basic core structure was introduced into liquid crystal research by Praefcke and co-workers [7]. The essential feature of this anisotropic material is its N-alkylation in combination with aryl moieties in 3- and 6-position bearing long alkyl-chains. Variation of the substitution pattern and the length of alkyl chains are versatile tools inducing different phase types [8]. Hence, even thermomesomorphic DPPD-containing polymers [9] and amphiphilic DPPD derivatives exhibiting lyotropic phase behaviour are known [10]. The interesting liquid crystalline and optical (fluorescence emission) properties of DPPD show that these materials are very promising towards advanced applications, e.g. organic voltaics [11]. These superior characteristics of DPPD encouraged us to do further research regarding their

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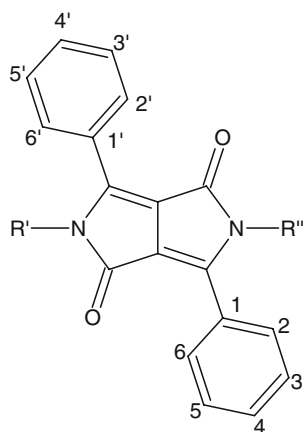Izmir, Turkey
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Fig. 1 Schematic structures of the N-alkyl and N,N'-dialkyl DPPD derivatives. R and R' refer substituted groups; methyl, butyl, hexyl and dodecyl. **a** 3,6-diphenyl-N,N'-dimethylpyrrolo[3,4-c]pyrrole-1,4-dione **b** 3,6-diphenyl-N-butylpyrrolo[3,4-c]pyrrole-1,4-dione **c** 3,6-diphenyl-N,N'-dibutylpyrrolo[3,4-c]pyrrole-1,4-dione **d** 3,6-diphenyl-N-hexylpyrrolo[3,4-c]pyrrole-1,4-dione **e** 3,6-diphenyl-N,N'-dihexylpyrrolo[3,4-c]pyrrole-1,4-dione **f** 3,6-diphenyl-N-dodecyl-pyrrolo[3,4-c]pyrrole-1,4-dione **g** 3,6-diphenyl-N,N'-didodecylpyrrolo[3,4-c]pyrrole-1,4-dione
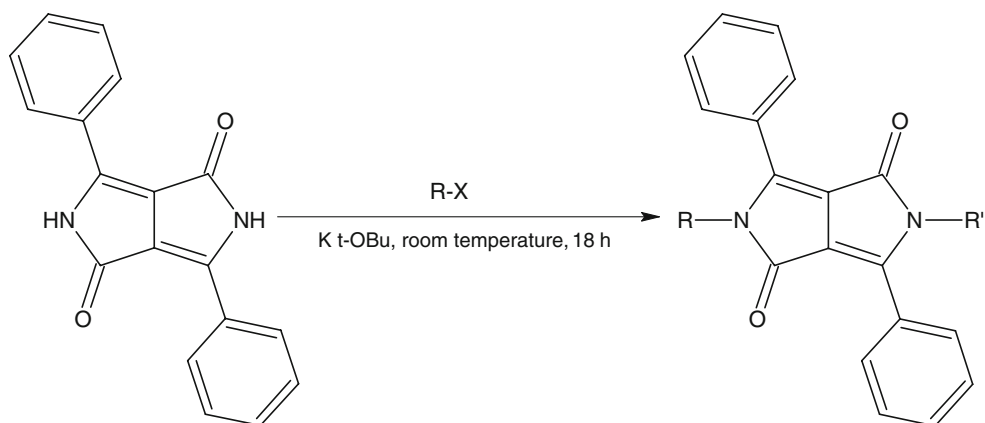
photostabilities and solubilities in different media. In this work, alkylation of 2,5-dihydro derivatives of DPPD was carried out via the nitrogen atoms in order to improve and test their solubility characteristics. This article describes synthesis, photocharacterization and solubility measurements of DPPD derivatives in different media. Figure 1 shows schematic structures of the seven different N-alkyl and N,N'-dialkyl DPPD derivatives.

Experimental

Instrumental

Melting points were determined on a Barnstead Electrothermal 9,100 apparatus. IR spectra were recorded on a Perkin-Elmer Spectrum BX FTIR spectrometer as a KBr

pellet. NMR spectra were recorded on a Unity Inova 500 (Varian) Instrument and chemical shifts are expressed in ppm downfield from $SiMe_4$. Absorption spectra were recorded using a Shimadzu 1601 UV-Visible spectrophotometer. Steady state fluorescence emission and excitation spectra were measured using Varian Cary Eclipse Spectrofluorometer with a Xenon flash lamp as the light source.

Reagents

All of the reagents were obtained from Merck and Fluka. Solvents used for chromatographic separation and recrystallization were of chromatographic grade. Solvents for the spectroscopic studies were of analytical grade and used without further purification.

Synthesis

3,6-diaryl-2,5-dihydro-1,4-diketopyrrolo[3,4-c]pyrrole-1,4-dione was prepared following the literature procedure [12]. Alkylation of the nitrogen atoms was carried out in presence of potassium t-butoxide as a base in 1-methyl-2-pyrrolidinone [13]. Employed alkylating agents were methyl-4-toluene-sulphonate, 1-iodobutane, 1-bromohexane, 1-chlorododecane (See Fig. 2).

3,6-diphenyl-2,5-dihydro-1,4-diketopyrrolo[3,4-c]pyrrole-1, 4-dione

The procedure used for synthesis of 3,6-diphenyl-2,5-dihydro-1,4-diketopyrrolo[3,4-c]pyrrole-1,4-dione: Benzonitrile (21.7 mmol) was added, under stirring and nitrogen atmosphere, to a solution of sodium t-amyl oxide [from sodium (21.7 mmol)] in dry t-amyl alcohol (45 cm^3). Diethyl succinate (10.8 mmol) was then added portion wise over 4 h and heating continued for a further 1 h. The mixture was stirred for 16 h at 25°C and then added to an ice-cooled mixture of concentrated hydrochloric acid (2.2 cm^3) and methanol (20 cm^3). The bright red precipitate

Fig. 2 Alkylation process of the 3, 6-diaryl-2, 5-dihydro-1, 4-diketopyrrolo[3,4-c]pyrrole-1,4-dione

Table 1 UV-vis spectroscopic data (λ / nm and ε / L mol^{-1} cm^{-1}) and solubility (C_x / mol L^{-1}) of DPPD derivatives in dichloromethane

Solvent	R	λ	ε	C_x	λ^f_{max}	$\Delta\lambda$	E_s
Dichloromethane	N,N-dimethyl	473	24,200	$4,79 \times 10^{-2}$	525	52	60,32
	N-butyl	465	20,150	$1,32 \times 10^{-2}$	521	56	61,35
	N,N-dibutyl	467	13,500	$6,16 \times 10^{-1}$	527	60	61,10
	N-hexyl	469	38,000	$6,8 \times 10^{-3}$	521	52	60,83
	N,N-dihexyl	466	20,900	1,95	527	61	61,22
	N-dodecyl	465	27,800	$1,29 \times 10^{-2}$	521	56	61,35
	N,N-didodecyl	468	37,900	$5,59 \times 10^{-2}$	528	60	60,96

was filtered off, washed with methanol and dried under vacuum (Yield 31%).

Molecular structures were revealed by means of IR and H^1 NMR spectroscopy.

N-alkyl and N,N'-dialkyl derivatives of 3,6-diphenyl-2, 5-dihydro-1,4-diketopyrrolo[3,4-c]pyrrole-1,4-dione

The procedure used for synthesis of N-alkyl and N, N'-dialkyl derivatives of 3,6-diphenyl-2,5-dihydro-1,4-diketopyrrolo[3,4-c]pyrrole-1,4-dione: 3,6-diphenyl-2,5-dihydro-1,4-diketopyrrolo[3,4-c]pyrrole-1,4-dione was stirred in 1-methyl-2-pyrolidinone at room temperature. Potassium-tert-butoxide was added under nitrogen atmosphere. After that, n-alkyl halide was added and stirred for 18 hours. The mixture was poured into the water. The precipitate was filtered off and crude product was purified by column chromatography using (1:3) ethyl acetate/n-hexane as eluent. Re-crystallization was performed from methanol for all derivatives.

The following N-alkyl derivatives of DPPD (1a-g) have been synthesized.

N,N'-dimethyl DPP (1a)   as dark red crystals (28 %); mp 255°C; IR (KBr): $\upsilon_{=C-H}$ 3000, υ_{-C-H} 2700-2800, $\upsilon_{-C=O}$ 1665; ^{1}H NMR (CDCl$_3$) : δ (ppm) 2.98ppm (s, 3H)

N-butyl DPP (1b)   red-orange crystals (32 %); mp 132°C ; IR (KBr): υ_{-N-H} 3500, $\upsilon_{=C-H}$ 3059, υ_{-C-H} 2857-2925, $\upsilon_{-C=O}$ 1657; ^{1}H NMR (CDCl$_3$) : δ (ppm) 3.844 (t, 2H); 1.610 (p, 2H); 1.288 (h, 2H); 0.87 (t,3H)

N,N'-dibutyl DPP (1c)   red-orange crystals (35 %); mp 240°C ; IR (KBr): $\upsilon_{=C-H}$ 3059-3137, υ_{-C-H} 2871-2927, $\upsilon_{-C=O}$ 1673; ^{1}H NMR (CDCl$_3$) : δ (ppm) 3.6 (t, 2H); 1.47 (p, 2H); 1.43 (h, 2H); 0.94 (t, 3H)

N-hexyl DPP (1d)   orange crystals (62 %);mp 123°C; IR (KBr): υ_{-N-H} 3665, $\upsilon_{=C-H}$ 3054-3142, υ_{-C-H} 2852-2926, $\upsilon_{-C=O}$ 1653; ^{1}H NMR (CDCl$_3$) : δ (ppm) 3.83 (t, 2H); 1.65 (p, 2H); 1.44 (p, 2H); 1.36 (p, 2H); 1.3 (h, 2H); 0.83 (t, 3H)

N,N'-dihexyl DPP (1e)   orange crystals (44 %);mp 243°C; IR (KBr): $\upsilon_{=C-H}$ 3055, υ_{-C-H} 2847-2911, $\upsilon_{-C=O}$ 1674; ^{1}H NMR (CDCl$_3$) : δ (ppm) 3.74 (t, 2H); 1.59 (p, 2H); 1.24 (6H, m); 0.82 (t, 3H)

N-dodecyl DPP (1f)   yellow-orange crystals (48 %); mp 110.8°C ; IR (KBr): υ_{-N-H} 3694, $\upsilon_{=C-H}$ 3059-3157, υ_{-C-H} 2847-2919, $\upsilon_{-C=O}$ 1666; ^{1}H NMR (CDCl$_3$) : δ (ppm) 3.83 (t, 2H); 1.59 (p, 2H); 1.25 (m, 18 H); 0.87 (t, 3H)

Table 2 UV-vis spectroscopic data (λ / nm and ε / L mol^{-1}cm^{-1}) and solubility (C_x / mol L^{-1}) of DPPD derivatives in acetonitrile

Solvent	R	λ	ε	C_x	λ^f_{max}	$\Delta\lambda$	E_s
Acetonitrile	N,N-dimethyl	468	12,100	$1,27 \times 10^{-3}$	522	54	60,96
	N-butyl	463	19,700	$1,15 \times 10^{-3}$	518	55	61,62
	N,N-dibutyl	461	11,650	$3,87 \times 10^{-2}$	524	63	61,89
	N-hexyl	462	18,350	$5,99 \times 10^{-4}$	518	56	61,75
	N,N-dihexyl	466	12,250	$4,3 \times 10^{-3}$	523	57	62,02
	N-dodecyl	463	23,000	2×10^{-4}	518	55	61,62
	N,N-didodecyl	464	11,350	$1,68 \times 10^{-4}$	524	60	62,02

Table 3 UV-vis spectroscopic data (λ / nm and ε / L mol^{-1}cm^{-1}) and solubility (C_x / mol L^{-1}) of DPPD derivatives in tetrahydrofuran

Solvent	R	λ	ε	C_x	λ^f_{max}	$\Delta\lambda$	E_s
Tetrahydrofuran	N,N-dimethyl	475	12,100	$8{,}87\times10^{-3}$	525	50	60,96
	N-butyl	467	19,700	$6{,}85\times10^{-2}$	521	54	61,62
	N,N-dibutyl	470	11,650	$3{,}35\times10^{-1}$	526	56	61,89
	N-hexyl	468	18,350	$1{,}8\times10^{-2}$	522	54	61,75
	N,N-dihexyl	470	12,250	$1{,}34\times10^{-1}$	527	57	62,02
	N-dodecyl	467	23,000	$3{,}39\times10^{-2}$	523	56	61,62
	N,N-didodecyl	470	11,350	$3{,}98\times10^{-2}$	528	58	62,02

N,N'-dildodecyl DPPD (1g) yellow-orange crystals (55 %); mp 180 °C; IR (KBr): $\upsilon_{=C-H}$ 3025, υ_{-C-H} 2847-2915, $\upsilon_{-C=O}$ 1679; ^{1}H NMR (CDCl$_3$) : δ (ppm) 3.74 (t, 3H); 1.58 (p, 2H);1.22 (m, 18 H); 0.88 (t, 3H)

Phenyl peaks at N-alkyl DPPDs': **2,4 and 6:** between 7.53-7.58; **6' and 2':** 7.84; **3' and 5':** 7.83; **3 and 5:** 8.33; **3 and 5:** 8.35; **4':** 7.22

Phenyl peaks at N,N'-alkyl DPPDs': **4 and 4':** between 7.51-7.56; **3 and 3':** 7.80; **5 and 5':** 7.80; **2,2' and 6,6':** 7.82. (See Fig. 1).

Results and discussion

Spectroscopic measurements

Absorption based studies

All of the DPPD derivatives were characterized in the solvents of dichloromethane (DCM), acetonitrile (ACN), tetrahydrofuran (THF), toluene and dimethylformamide (DMF) by means of absorption and emission spectroscopy. UV-Vis spectroscopy related data (absorption maximum (λmax; in nm), molar extinction coefficient (ε; in L mol^{-1} cm^{-1})) and solubilities (C_x; mol L^{-1}) of DPPD derivatives in all of the employed solvents were shown in Tables 1, 2, 3, 4 and 5 respectively.

Except that of solubility, all other photophysical constants were also checked in solid matrix of PVC (See Table 6).

The gathered absorption and emission spectra of N,N-dihexyl and N,N-didodecyl DPPD were presented in Figs. 3 and 4, respectively.

The DPPD derivatives (from 1a to 1g) exhibited similar absorption maxima (around 467 nm) in the solvents of DCM, ACN, THF and DMF. All of the DPPD derivatives exhibited red shifts in the range of 6-13 nm in their absorption maxima in toluene with respect to acetonitrile or tetrahydrofuran. These red shifts can be attributed to the $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions arising from solvent polarity differences. Blue shifts of 30 nm or more arise from hydrogen bond formation between the solvent protons and the non-bonded electron pair of the solute. In our case, the absence of such large blue shifts reveals the deficiency of hydrogen bond formation in all of the used solvents. The DPPD derivatives exhibited very efficient absorbance bands (around 467 nm) and high molar extinction coefficients in all of the employed solvents. The molar extinction coefficients measured in DCM were approximately 2-fold of the other solvents.

The data shown from Table 1–Table 5 reveal that DPPD derivatives absorb best in DCM.

Emission based studies

The emission spectroscopy related data of fluorescent DPPD derivatives were shown from Table 1–6. Maximum emission wavelength (λ_{max}^f in nm), Stokes' shift ($\Delta\lambda$ in nm) and singlet energy values (E_s) were measured or

Table 4 UV-vis spectroscopic data (λ / nm and ε / L mol^{-1}cm^{-1}) and solubility (C_x / mol L^{-1}) of DPPD derivatives in toluene

Solvent	R	λ	ε	C_x	λ^f_{max}	$\Delta\lambda$	E_s
Toluene	N,N-dimethyl	481	14,200	$1{,}8\times10^{-2}$	532	51	59,31
	N-butyl	474	16,650	$1{,}3\times10^{-1}$	525	51	60,19
	N,N-dibutyl	473	16,250	$3{,}2\times10^{-1}$	532	59	60,32
	N-hexyl	467	28,000	$1{,}42\times10^{-3}$	525	58	61,10
	N,N-dihexyl	471	14,650	$1{,}6\times10^{-1}$	533	62	60,57
	N-dodecyl	468	25,900	$6{,}61\times10^{-3}$	525	57	60,96
	N,N-didodecyl	471	29,250	2×10^{-2}	533	62	60,32

Table 5 UV-vis spectroscopic data (λ / nm and ε / L mol^{-1}cm^{-1}) and solubility (C_x / mol L^{-1}) of DPPD derivatives in dimethylformamide

Solvent	R	λ	ε	C_x	λ^f_{max}	$\Delta\lambda$	E_s
Dimethylformamide	N,N-dimethyl	474	14,500	$2,67 \times 10^{-2}$	528	54	60,39
	N-butyl	469	13,500	$6,5 \times 10^{-2}$	523	54	60,83
	N,N-dibutyl	465	12,000	$2,67 \times 10^{-1}$	529	64	61,35
	N-hexyl	470	15,000	$5,87 \times 10^{-2}$	524	54	60,70
	N,N-dihexyl	461	14,000	$2,1 \times 10^{-2}$	528	67	61,10
	N-dodecyl	466	17,200	$1,8 \times 10^{-2}$	523	57	61,22
	N,N-didodecyl	470	18,000	2×10^{-4}	529	59	61,10

calculated for the conventional solvents and solid matrix of PVC. The DPPD derivatives from 1a to 1g exhibited emission wavelengths between 518-533 nm in all of the employed solvents. Except that of 1-d and 1-f all of the DPPD derivatives exhibited further emission wavelengths in toluene with respect to other solvents.

In agreement with literature, the maximum emission wavelengths of all derivatives (except that of 1-a) were increased when immobilized in the polymer matrix of PVC [14]. The red shifts from ACN to PVC were 43 nm, 11 nm, 41 nm, 14 nm, 40 nm and 10 nm for 1-b, 1-c, 1-d, 1-e, 1-f and 1-g respectively. Red shift of absorption and emission of DPPD derivatives can be attributed to enhanced conjugation in immobilized polymer phase by hindrance of vibrational and rotational motions.

In all of the employed solvents the Stokes' shift values were in the range of 51-67 nm. When doped into the PVC the Stokes' shift values of DPPD derivatives of 1b, 1d and 1e increased 31 nm, 24 nm and 28 nm respectively (See Table 1–6). Small differences in the Stokes' shifts of the molecules in solvent phase can be attributed to differences in solvent polarities but the decrease of Stokes' shift in polymer film arises from lowered difference of equilibrium geometries between ground and excited states in immobilized phase with respect to solutions. Large Stokes' shift is desirable for fluorescence measurements and solid state components because the high Stokes' shift values allow the emitted fluorescence photons to be easily distinguished from the excitation photons, leading to the possibility of very low background signals. Stokes' shift exceeding 30 nm is

recommended for easy visualization and sensitive detection. The Stokes' shift values of 60-85 nm in PVC matrix permit the usage of DPPDs in the construction solid-state optics.

An efficient intersystem crossing from singlet (S2) to T2 and singlet (S1 or S2) to T1 have to occur in solutions of DPPD derivatives. Singlet energy of DPPDs in polymer film matrix, E_s around 59 kcal mol^{-1}, is observed to be lowered about 0.74-1.39 kcal mol^{-1}, with respect to E_s of DPPDs in solutions (See Table 1–5). This result may be taken as an evidence of lessened singlet-triplet intersystem crossings of DPPDs in polymer film matrix, with respect to solutions, in support of enhanced fluorescence emission.

Table 6 UV-vis spectroscopic data (λ / nm and ε / L mol^{-1}cm^{-1}) of DPPD derivatives in PVC matrix

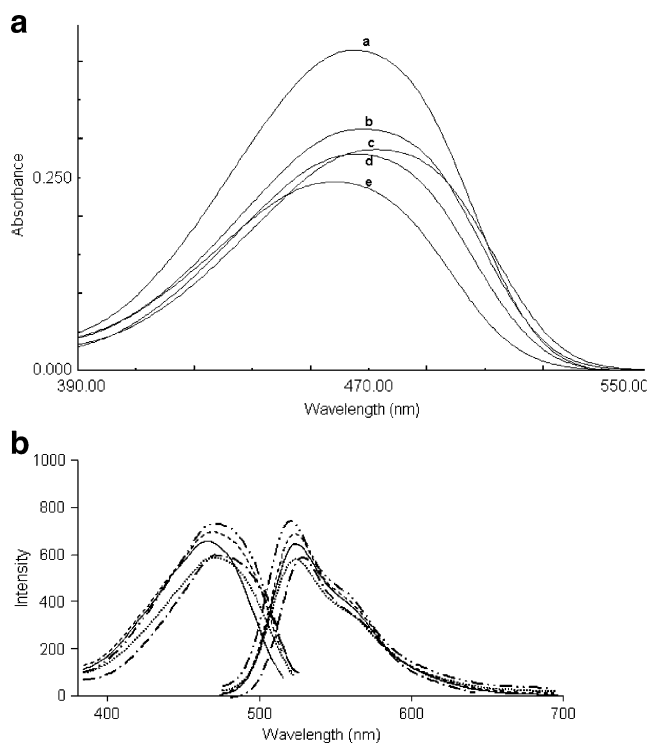| Matrix	R	λ	ε	λ^f_{max}	$\Delta\lambda$	E_s
PVC	N-butyl	479	62,000	561	82	59,6
	N,N-dibutyl	474	93,000	535	61	60,39
	N-hexyl	477	105,400	559	82	59,8
	N,N-dihexyl	474	106,800	537	63	60,39
	N-dodecyl	473	52,600	558	85	60,32
	N,N-didodecyl	474	94,000	534	60	60,39

Fig. 3 A Absorption spectrum of N,N-dihexyl DPPD: **a** DCM, λ^{ab}_{max} = 466 nm, **b** THF, λ^{ab}_{max} = 470 nm, **c** Toluene, λ^{ab}_{max} = 471 nm, **d** ACN, λ^{ab}_{max} = 466 nm, **e** DMF, λ^{ab}_{max} = 461 nm. (B) Emission spectrum of N,N-dihexyl DPPD : (1) THF, λ^{em}_{max} = 527 nm, (2) DCM, λ^{em}_{max} = 527 nm, (3) ACN, λ^{em}_{max} = 523 nm, (4) Toluene, λ^{em}_{max} = 533 nm, (5) DMF, λ^{em}_{max} = 528 nm. — · · —THF, — — — -DCM, ————ACN, — · — -Toluene, - - - - - - - - - - - -DMF

Solubility studies

Solubilities of the DPPD derivatives were extracted from absorption based spectral data. Absorption spectra of dilute (2×10^{-5} M) and saturated solutions of DPPD derivatives were recorded in all of the employed solvents. In order to obey the Lambert-Beer's law the saturated solutions were studied in µM level, after real concentration was calculated.

Because the studied DPPD derivatives consist of the lipophilic pyrrolopyrrole group, lipophilic flank substituents and polar carbonyl groups, they could be dissolved in low-polar lipophilic (toluene) slightly polar (tetrahydrofuran, dichloromethane) and in polar (acetonitrile, dimethylformamide) solvents.

The experimental results obtained on the solubility of different DPPD derivatives should be interpreted in terms of the change of the molecular bulkiness and the change of the molecular lipophilicity on the substitution [15].

Tables 1–5 present data on solubilities of various DPPDs in the solvents of toluene (dielectric constant; D=2.4 Debye), tetrahydrofuran (D=7.5), dichloromethane (D= 9.1), dimethylformamide (D=37) and acetonitrile (D=38). In these solvents the solubility of the studied compounds is
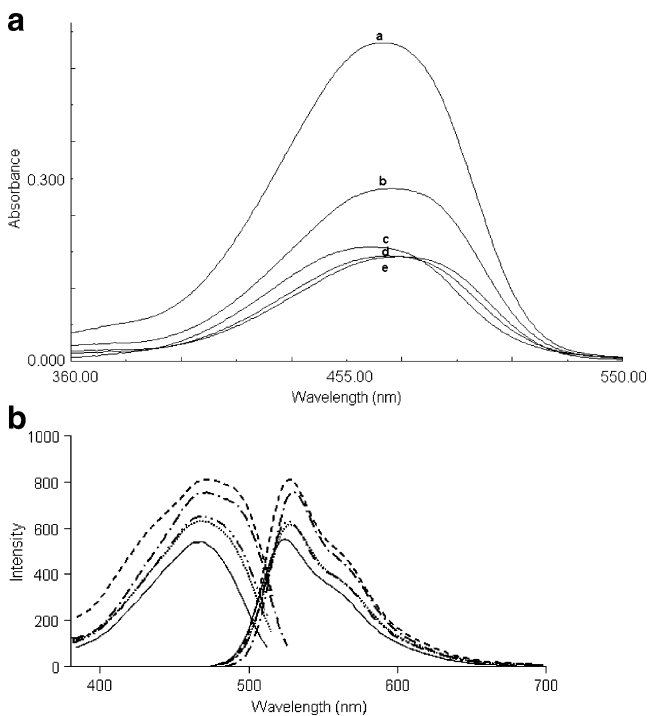
a

b

Fig. 4 **a** Absorption spectrum of N,N-didodecyl DPPD: **a** DCM, λ_{max}^{ab} = 468 nm, **b** THF, λ_{max}^{ab} = 470 nm, **c** ACN, λ_{max}^{ab} = 464 nm, **d** DMF, λ_{max}^{ab} = 470 nm, **e** Toluene, λ_{max}^{ab} = 471 nm(**b**) Emission spectrum of N, N-didodecyl DPPD : (1) DCM, λ_{max}^{em} = 528 nm, (2) Toluene, λ_{max}^{em} = 533 nm, (3) THF, λ_{max}^{em} = 528 nm, (4) DMF, λ_{max}^{em} = 529 nm, (5) ACN, λ_{max}^{em} = 524 nm. – – – – ·DCM, — · — ·Toluene, — · · —THF, -------------DMF, ————ACN
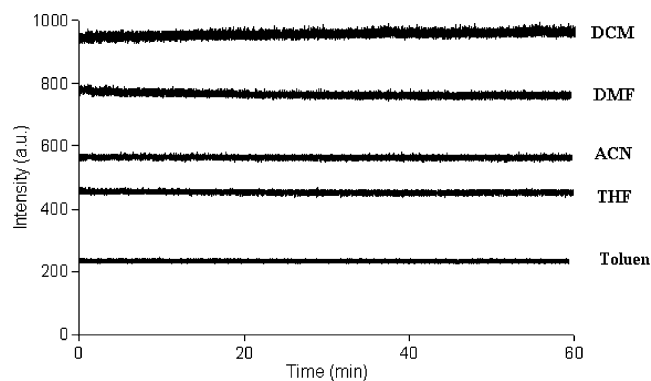
Fig. 5 Phostability results of N,N-dihexyl DPPD in all studied solvents

found to be the lowest in acetonitrile. This is an expected result when the lipophilicity of DPPDs and the dipoles of the highly polar acetonitrile were considered together. The polarity of DPPDs remains constant for N-alkyl substitutions. But, the molecular bulkiness and the molecule's lipophilicity vary. Tables 1–5 reveal that, in the highly polar solvents of acetonitrile and dimethylformamide the solubility of N-alkyl derivatives decreases in the order of N-butyl> N-hexyl>N-dodecyl on going from n-butyl to n-dodecyl. This result could be explained by the aggregate formation tendency of n-dodecyl because of its greater lipophilicity in comparison with n-butyl. In case of slightly polar solvents of dichloromethane, tetrahydrofuran and toluene, the order is in the form of N-butyl> N-dodecyl>N-hexyl. The difference between low-polar and strongly polar solvents is that in low polar solvents, the N-dodecyl derivative becomes more soluble due to the similarities of polarities of solvent and solute.

The solubilities of N,N'-dialkyl derivatives decreases in the order of N,N'-dibutyl>N,N'-dihexyl>N,N'-didodecyl> N,N'-dimethyl respectively in the low polarity solvents of tetrahydrofuran and toluene. The solubility of the N,N'- dimethyl derivative should be evaluated in a different category since the lipophilicity became effective for alkyl
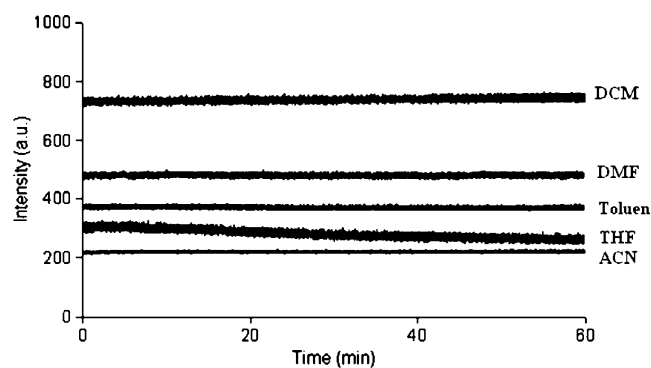
Fig. 6 Phostability results of N,N-didodecyl DPPD in all studied solvents

groups at least having four carbon chains. In the solvents of dimethylformamide and acetonitrile the solubility order is N,N'-dibutyl>N,N'-dihexyl>N,N'-dimethyl>N,N'-dido-decyl respectively.

Photostability studies

The photostabilities of DPPD derivatives were tested and evaluated in DCM, DMF, ACN, THF and Toluene. Using the xenon arc lamp, photostability tests of DPPD derivatives were carried out with a steadystate spectrofluorimeter in the mode of "Time Based Measurements". All of the fluorophores were excited at 467 nm and the data were acquired at their maximum emission wavelengths during one hour of monitoring.

The acquired data of N,N-dihexyl and N,N-didodecyl DPPD are shown in Figs. 5 and 6 respectively. The results of N,N-dihexyl and N,N-didodecyl DPPD were similar to the results of other DPPD derivatives.

Conclusion

In this work, monoalkyl and dialkyl derivatives of DPPD were characterized with absorption and emission spectroscopy. Molar absorption coefficient, singlet energy level, Stokes' shift values were declared. A study of the solubility of various DPPDs in different solvents has been performed by means of UV-Vis spectroscopy.

Except that of 1-a (N,N'-dimethyl derivative), all other derivatives can be concluded as monoalkyl/dialkyl complementary structures. Dialkyl derivatives (1-c (N,N'-dibutyl), 1-e (N,N'-dihexyl) and 1-g (N,N'-didodecyl)) are found to be more soluble with respect to their homolog monoalkyl derivatives (1-b (N-butyl), 1-d (N-hexyl) and 1-f (N-dodecyl)) in all of the employed solvents.

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