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A systematic study on the absorption and fluorescence properties of 2,4,6-triaryl and tripyridylpyridines

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Eight different 2,4,6-triaryl, and tripyridylpridines compounds were synthesized and their fluorescent properties were studied by using steady-state and time-resolved fluorescence and UV-Vis absorption spectroscopy techniques in 6 different solvents. Especially, 2,4,6-triarylpyridines showed strong fluorescence properties with high fluorescence quantum yields but small Stokes shifts.

Key Words: 2,4,6-triarylpridine, 2,4,6-tripyridylpridine, fluorescence, UV-Vis absorption, fluorescence quantum yield, fluorescence lifetime.

Introduction

Prompted by rapidly expanding applications of organic fluorescent materials for electroluminescence (EL), dye-lasers, sensors, probes, and phototherapeutic agents, development of new fluorescent organic compounds with high functionality has been

the subject of intense study for more than a decade.[1−4] Pyridines are of interest because of the occurrence of their saturated and partially saturated derivatives in biologically active compounds and natural products, such as NAD nucleotides, pyridoxol (vitamin B6), and pyridine alkaloids.[5,6] Kröhnke type pyridines[7,8] and other substituted pyridines including the related terpyridines[9,10] are prominent building blocks in supramolecular chemistry because of their π-stacking ability, and directed H-bond formation. 2,4,6-Triarylpyridines are

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structurally related to symmetrical triaryl-thiopyrylium, -selenopyrylium and –telluropyrylium photosensitizers, which have been recommended for photodynamic cell-specific cancer therapy.[11,12] For these reasons, these compounds have attracted considerable attention in recent years. However, to the best of our knowledge, no systematic study has been undertaken to elucidate the photophysical behavior of 2,4,6-triaryl, and –tripyridylpyridines compounds.

In this research, 2,4,6-triaryl, and –tripyridylpyridines were synthesized and reported the spectroscopic and photophysical properties of these compounds. All the dyes were studied in 6 different solvents by UV-Vis absorption spectroscopy then by steady-state and time resolved fluorescence spectroscopy.

Experimental

All solvents were reagent grade. All chemicals were purchased from Aldrich and Merck. Melting points were measured on Electrothermal 9100 apparatus. IR spectrums (KBr disc) were recorded on a Jasco FT/IR-430 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 400 instrument. Elemental analyses were obtained from a LECO CHNS 932 Elemental Analyzer.

General procedure for the synthesis of 2,4,6-triaryl and tripyridylpyridines (3a-3h): A mixture of aldehyde derivative (10 mmol), acetophenone derivative (20 mmol) and ammonium acetate (40 mmol) in DMF (5 mL) was heated in a sealed tube (oil bath temperature = 150 °C) for 3 h. Reaction mixture was extracted with EtOAc (3 × 20 mL), and dried over anhydrous Na_2SO_4. Removing of solvent gave the solid product. The crude product was crystallized with *n*-hexane/ EtOAc (1:9).

2,4,6-Triphenylpyridine (3a): Colorless solid, mp. 133-135 °C; (KBr) 3061, 3031, 1615, 1593, 1549, 1399, 1210, 1038, 1017, 874, 708, 648 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$)δ 8.28 (brd, J = 8 Hz, 4H, ArH), 7.95 (s, 2H, PyridineH), 7.79 (brd, J = 8 Hz, 4H, ArH), 7.61-7.57 (m, 6H, ArH), 7.54-7.47 (m, 3H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 150.2, 139.6, 130.1, 129.2, 129.1, 129.0, 128.8, 127.3, 127.2, 117.2; Anal. Cald for $C_{23}H_{17}N$: C, 89.87; H, 5.57; N, 4.56. Found: C, 89.54; H, 5.42; N, 4.67.

2,4,6-Tri(4-hidroxyphenyl)pyridine (3b): Colorless solid; mp. 143-145 °C; IR (KBr) 3365, 3065, 1599, 1514, 1274, 1235, 1023, 1003, 952, 826, 761 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6)δ 9.76 (brs, -OH), 8.15 (brd, J = 8.8 Hz, 4H, ArH), 7.88 (s, 2H, PyridineH), 7.81 (brd, J = 8.8 Hz, 4H, ArH), 6.77 (brd, J = 8.4 Hz, 2H, ArH), 6.68 (brd, J = 8.4 Hz, 2H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6)δ 162.4, 158.9, 156.7, 155.7, 130.9, 130.7, 129.7, 129.0, 128.7, 116.4, 115.9; Anal. Cald for $C_{23}H_{17}NO_3$: C, 77.73; H, 4.82; N, 3.94. Found: C, 77.71; H, 4.85; N, 3.96.

2,4,6-Tri-tolylpyridine (3c): Colorless solid; mp. 173-175 °C; IR (KBr) 3028, 2980, 2917, 2858, 1599, 1542, 1509, 1421, 1388, 1392, 1293, 1240, 1111, 728 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$)δ 8.20 (brd, J = 8 Hz, 4H, ArH), 7.91 (s, 2H, PyridineH), 7.71 (brd, J = 8 Hz, 2H, ArH), 7.42-7.38 (m, 6H, ArH), 2.53 (s, 6H, -CH_3), 2.50 (s, 3H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$)δ 157.4, 149.9, 139.9, 138.9, 137.1, 136.3, 129.8, 129.5, 127.1, 116.3, 21.4, 21.3; Anal. Cald for $C_{26}H_{23}N$: C, 89.36; H, 6.63; N, 4.01. Found: C, 89.12; H, 6.37; N, 4.08.

2,4,6-Tris(4-methoxyphenyl)pyridine (3d): Colorless solid, mp. 134-135 °C; (KBr) 3072, 3003, 2959, 2835, 1614, 1542, 1509, 1360, 1127, 1073, 1000, 968, 833, 632 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (brd, J = 8.8 Hz, 4H, ArH), 7.75 (s, 2H, PyridineH), 7.69 (brd, J = 8.8 Hz, 2H, ArH), (brd, J = 8.8 Hz, 6H,

ArH), 3.89 (s, 6H, -OCH_3), 4.88 (s, 3H, -OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 160.3, 156.8, 149.4, 132.4, 131.5, 128.4, 128.3, 115.2, 114.5, 114.0, 55.4, 55.3; Anal. Cald for $C_{26}H_{23}NO_3$: C, 78.57; H, 5.83; N, 3.52. Found: C, 78.34; H, 5.62; N, 3.67.

2-(6-(pyridin-2-yl)-4-(pyridin-3-yl)pyridin-2-yl)pyridine (3e): Yellowish crystals, mp. 230 ^{o}C; IR (KBr) 3065, 3029, 1617, 1589, 1535, 1515, 1179, 830, 813, 558, cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.08 (brs, 2H), 7.73-8.65 (m, 4H), 8.36-8.33 (m, 5H), 8.03 (brs, 2H), 7.61-7.52 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$)δ 155.7, 151.3, 150.4, 149.4, 147.2, 140.8, 138.6, 137.4, 126.5, 125.8, 121.6, 121.3, 119.7; Anal. Cald for $C_{20}H_{14}N_4$: C, 77.40; H, 4.55; N, 18.05. Found: C, 77.44; H, 4.72; N, 18.28.

2,4,6-Tri(pyridine-2-yl)pyridine (3f): A yellow solid; mp. 228-230 °C; IR (KBr) 3075, 3048, 3032, 1582, 1540, 1452, 891, 798, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$)δ 9.12 (s, 2H), 8.81 (d, J = 4.4 Hz, 1H), 8.87 (d, J = 4.5 Hz, 2H), 8.68 (d, J = 7.9 Hz, 2H), 8.00 (d, J = 7.9 Hz, 1H), 7.92-7.83 (m, 3H), 7.37-7.35 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)δ 156.1, 156.0, 155.0, 150.0, 149.1, 148.7, 136.9, 136.8, 123.9, 123.8, 121.4, 121.3, 118.7; Anal. Cald for $C_{20}H_{14}N_4$: C, 77.40; H, 4.55; N, 18.05. Found: C, 77.12; H, 4.67; N, 18.39.

2,4,6-Tri(pyridine-3-yl)pyridine (3g): A yellow solid; mp. 269-271 °C; IR (KBr) 3086, 3050, 3034, 1588, 1544, 1457, 893, 796, 700 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6)δ 9.40 (s, 2H), 9.1 (s, 1H), 8.64-8.58 (m, 4H), 8.30-8.28 (brd, J = 7.6 Hz, 1H), 8.20 (s, 2H), 7.54-7.47 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6)δ 152.6, 149.8, 148.9, 148.6, 148.2, 147.7, 135.8, 135.2, 134.3, 130.5, 125.3, 123.9, 118.2; Anal. Cald for $C_{20}H_{14}N_4$: C, 77.40; H, 4.55; N, 18.05. Found: C, 77.02; H, 4.85; N, 18.66.

2,4,6-Tri(pyridine-4-yl)pyridine (3h). A yellow solid; mp. 348-351 °C; IR (KBr) 3070, 3053, 3032, 1580, 1557, 1367, 966, 848, 625, 509 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6)δ 8.91-8.87 (m, 4H), 8.56-8.52 (m, 4H), 8.25 (s, 2H), 7.75-7.73 (d, J = 8.4 Hz, 2H), 7.46-7.44 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6)δ 163.6, 150.5, 149.0, 145.7, 145.8, 130.6, 128.6, 127.9, 125.9; Anal. Cald for $C_{20}H_{14}N_4$: C, 77.40; H, 4.55; N, 18.05. Found: C, 77.00; H, 4.79; N, 18.36.

Photophysical assays

Absorption spectra of the samples were taken with a Shimadzu UV-3101PC UV–VIS–NIR spectrophotometer and fluorescence spectra were taken with a Shimadzu RF-5301PC spectrofluorophotometer. The temperature of the samples was controlled using a Grant W14 circulating water bath during the absorption and fluorescence spectra measurements and, therefore, ambient temperature was used.

Fluorescence decay lifetime measurements were carried out with a LaserStrobe Model TM-3 lifetime fluorophotometer from Photon Technology International.[13] The excitation source consisted of a pulsed nitrogen laser/tunable dye laser combination. All samples were excited at 337 nm in which absorbance of each sample was approximately 0.10 to eliminate inner filter effects. The decay curves were collected over 200 channels using a nonlinear time scale with the time increment increasing according to arithmetic progression. This approach enhances temporal resolvability of heterogeneous decays by providing higher data density (shorter time increments) at shorter times, whereas the time increments gradually increase at longer times. The fluorescence decays were analyzed with the lifetime distribution analysis software from the instrument supplying company. The quality of fits was assessed by χ^2 values and weighed residuals.

Fluorescence quantum yields (Φ_f) were determined by comparison with a reference solution. For this

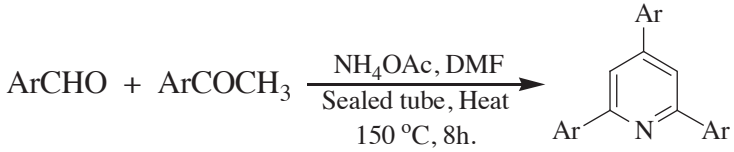
purpose, the following relation has been applied to calculate relative fluorescence quantum yields.[14]

$$\Phi_s = \Phi_r \left(\frac{D_s}{D_r}\right) \left(\frac{n_s}{n_r}\right)^2 \left(\frac{1-10^{-A_r}}{1-10^{-A_s}}\right)$$

Where D_S and D_r are the integrated area under the corrected fluorescence spectra for the sample and reference, n_S and n_r are the refractive indexes of the sample and reference, respectively. A_S and A_r are the absorbance value for the sample and reference at the excitation wavelength, respectively. The reference used for this study is tryptophan at 1.0×10^{-6} M in water. This reference has a known fluorescence quantum yield of 0.13 in this condition.[15]

Results and discussion

In this study, aldehyde and acetophenone derivatives containing electron donating group, such as -OH, -CH_3, -OCH_3, -NH_2, were particularly chosen. A treatment of appropriate amount of aldehyde (1 equiv.) with acetophenone derivatives (2 equiv.) and ammonium acetate (4 equiv.) in DMF in sealed tube (at 150 °C oil bath temperature) for 3 h afforded the target products in excellent yields (Scheme 1) and (Table 1). The structures of the known compounds **3a**,[5] **3c**,[16] **3d**,[7] **3e**[17], and **3f**[18] were corroborated by comparison of their mp values, elemental analyses and their spectral data (IR ^{1}H and ^{13}C NMR spectra) with those authentic samples. The structures of other compounds **3b**, **3g**, and **3h** were characterized on the basis of spectral data.



1 **2** **3**

Scheme 1

Table 1. Synthesized compounds.

Entry	Ar	Ar[1]	Yield (%)[a]	mp (°C) (Lit.)
3a	Ph	Ph	81	133-135 (134-135)[5]
3b	*p*-OH-Ph	*p*-OH-Ph	70	143-145
3c	*p*-CH_3-Ph	*p*-CH_3-Ph	87	173-175 (176-177)[16]
3d	*p*-OCH_3-Ph	*p*-OCH_3-Ph	85	134-135 (136-137)[7]
3e	2-Pridyl	3-Pridyl	78	230 (232)[17]
3f	2-Pridyl	2-Pridyl	70	228-230 (232)[18]
3g	3-Pridyl	3-Pridyl	50	269-271
3h	4-Pridyl	4-Pridyl	73	348-351

[a]Isolated yields

UV-Vis and fluorescence properties of compounds **3a-3h** have been studied in different solvents. It is well known that UV-Vis absorption and fluorescence spectra of chemical compounds may be influenced by the

surrounding medium and the change in the absorption and emission bands are often accompanied by a change in the polarity of the medium. For this purpose, we measured the absorption and fluorescence spectra (for instance, the absorption and the fluorescence spectra of **3c** in studied solvents were given in Figures 1a and 1b.) of 1×10^{-5} solutions of compounds **3a-3h** in 6 different solvents (CH_2Cl_2, $CHCl_3$, CH_3CN, CH_3OH, $CH_3CO_2C_2H_5$, and DMSO), which have a different solvation character.

The spectral data, quantum yields, and lifetime (τ_f) values are listed in Table 2 for **3a-3e** and Table 3 for **3f-3h.**

Table 2. Photophysical and spectral properties of **3a-3d** in different solvents.

	Solvent	λ_{abs}(nm)	λ_{ems}(nm)	Φ_f	τ (ns)	χ^2
3a	DMSO	261	360	0.44 ± 0.02	2.72 ± 0.05	0.97
	CH_3OH	253	357	0.55 ± 0.01	2.63 ± 0.04	0.88
	CH_3CN	254	354	0.52 ± 0.02	2.29 ± 0.02	0.78
	CH_3CO_2Et	253	347	0.42 ± 0.03	2.50 ± 0.02	0.82
	$CHCl_3$	254	353	0.28 ± 0.03	2.04 ± 0.02	0.90
	CH_2Cl_2	255	351	0.45 ± 0.04	2.23 ± 0.04	1.00
3b	DMSO	269	359	0.56 ± 0.01	2.79 ± 0.04	0.95
	CH_3OH	262	362	0.70 ± 0.01	2.66 ± 0.04	0.82
	CH_3CN	263	360	0.71 ± 0.02	2.80 ± 0.02	0.74
	CH_3CO_2Et	262	352	0.60 ± 0.02	2.89 ± 0.02	0.75
	$CHCl_3$	264	359	0.37 ± 0.02	2.45 ± 0.01	0.93
	CH_2Cl_2	265	357	0.59 ± 0.03	2.53 ± 0.01	0.77
3c	DMSO	285	376	0.58 ± 0.01	3.04 ± 0.06	1.03
	CH_3OH	280	379	0.70 ± 0.02	2.55 ± 0.04	0.98
	CH_3CN	280	374	0.74 ± 0.02	3.03 ± 0.04	0.99
	CH_3CO_2Et	280	365	0.68 ± 0.02	3.02 ± 0.02	0.78
	$CHCl_3$	281	372	0.39 ± 0.02	2.49 ± 0.02	0.82
	CH_2Cl_2	281	372	0.67 ± 0.01	2.89 ± 0.03	0.92
3d	DMSO	285	378	0.29 ± 0.01	2.78 ± 0.03	0.71
	CH_3OH	280	385	0.30 ± 0.01	1.42 ± 0.02	0.65
	CH_3CN	276	373	0.54 ± 0.01	3.09 ± 0.03	0.68
	CH_3CO_2Et	278	366	0.47 ± 0.02	2.85 ± 0.02	0.95
	$CHCl_3$	278	379	0.28 ± 0.02	2.19 ± 0.04	0.84
	CH_2Cl_2	274	369	0.50 ± 0.01	2.74 ± 0.04	0.70

λ_{abs}: maximum absorption wavelength, λ_{ems}: fluorescence emission maximum wavelength, Φ_f: fluorescence quantum yield, τ: fluorescence lifetime.

Table 3. Photophysical and spectral properties of **3e-3h** in different solvents.

	Solvent	λ_{abs}(nm)	λ_{ems}(nm)	Φ_f	τ (ns)	χ^2
3e	DMSO	282	359	0.01 ± 0.01	0.36 ± 0.01	0.84
	CH_3OH	280	354	0.10 ± 0.02	0.71 ± 0.01	0.65
	CH_3CN	280	354	0.18 ± 0.02	1.37 ± 0.02	0.63
	CH_3CO_2Et	279	353	0.16 ± 0.02	1.45 ± 0.02	0.66
	$CHCl_3$	281	357	0.11 ± 0.01	1.32 ± 0.03	0.74
	CH_2Cl_2	280	356	0.19 ± 0.01	1.45 ± 0.03	0.75
3f	DMSO	257-272	357	0.04 ± 0.00	0.38 ± 0.01	1.02
	CH_3OH	242-270	354	0.21 ± 0.03	2.00 ± 0.01	0.85
	CH_3CN	243-272	350	0.21 ± 0.03	1.73 ± 0.01	0.98
	CH_3CO_2Et	251-271	346	0.19 ± 0.02	2.44 ± 0.03	1.00
	$CHCl_3$	243-271	348	0.17 ± 0.01	1.47 ± 0.02	0.87
	CH_2Cl_2	246-273	350	0.20 ± 0.02	1.83 ± 0.02	0.88
3g	DMSO	279	357	0.01 ± 0.00	0.01 ± 0.00	0.89
	CH_3OH	279	352	0.06 ± 0.00	0.55 ± 0.01	0.77
	CH_3CN	277	351	0.11 ± 0.00	0.59 ± 0.01	0.92
	CH_3CO_2Et	278	349	0.09 ± 0.00	1.13 ± 0.01	0.69
	$CHCl_3$	279	353	0.09 ± 0.00	0.89 ± 0.01	1.00
	CH_2Cl_2	278	353	0.13 ± 0.01	0.92 ± 0.01	0.97
3h	DMSO	277	356	0.01 ± 0.00	0.12 ± 0.01	0.87
	CH_3OH	278	352	0.10 ± 0.00	0.48 ± 0.01	0.95
	CH_3CN	279	351	0.12 ± 0.00	0.61 ± 0.01	0.80
	CH_3CO_2Et	278	352	0.11 ± 0.01	1.11 ± 0.02	0.85
	$CHCl_3$	278	353	0.10 ± 0.01	0.98 ± 0.01	1.03
	CH_2Cl_2	279	352	0.18 ± 0.01	1.24 ± 0.01	1.05

λ_{abs}: maximum absorption wavelength, λ_{ems}: maximum emission wavelength, Φ_f: fluorescence quantum yield, τ: fluorescence lifetime

The fluorescence quantum yields for compounds **3a-3h** were determined and were found to be strongly emissive for **3a-3d** (while compounds **3e-h** displayed much lower quantum yields (Tables 1 and 2). For all compounds, no solvatochromic effect in the absorption and fluorescence spectra was observed in CH_2Cl_2, $CHCl_3$, CH_3CN, CH_3OH, $CH_3CO_2CH_2CH_3$, and DMSO. From DMSO to CH_2Cl_2 the emission spectra shift only 9 nm. It is the biggest shift for **3a** and **3d**.

The fluorescence lifetimes, which were monoexponential, were in the range of 2.04-3.09 ns for compounds **3a-3d** and decreased to 0.01-2.00 ns for **3e-3h**. The high magnitude in the fluorescence lifetimes and the fluorescence quantum yields are mainly originated from the increase in rigidity of the compound and lowering

of the non-radiative transition rate constant because of solute-solvent interactions.

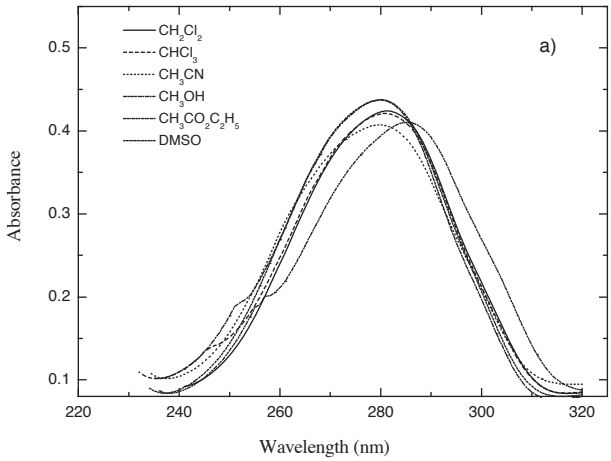


Figure 1a. The absorption spectra of **3c** in different solvents.

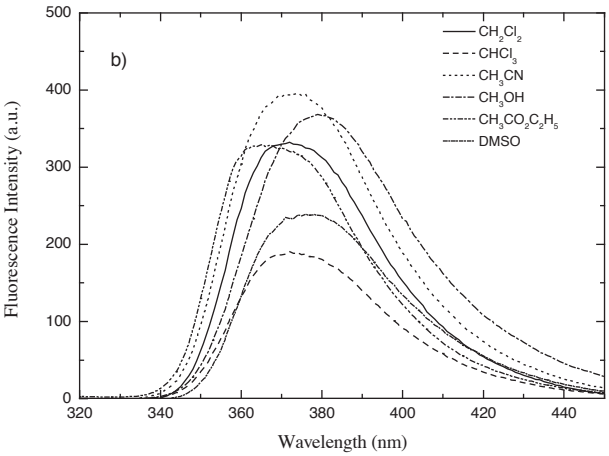


Figure 1b. The flourescence emission spectrum of **3c** in different solvents ($\lambda_{exc.} = 275$ nm).

Conclusion

As a result, the synthetic and photophysical properties displayed by these compounds indicate that they are promising candidates for fluorescent probes and fluorescent markers due to their strong fluorescence properties, especially compounds **3a-3d**.

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