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Synthesis and photophysical properties of some 6,6"- functionalized terpyridine derivatives

Research Article

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Abstract: The synthesis and photophysical properties of several 6,6" symmetrically substituted 4'-aryl-2,2':6',2"-terpyridine derivatives are reported herein. The UV-Vis spectra in acetonitrile as well as in dichloromethane show two intense bands in the UV areas 252-262 nm and 275-290 nm while the fluorescence emission spectra are only slightly influenced by chemical derivatization.

Keywords: *Terpyridines • SN and SE Reactions • UV-Vis Spectra • Fluorescence • Fluorescence Quantum Yield*

1. Introduction

Terpyridines have attracted strong research interest due to their potential applications in coordination chemistry [1], asymmetric catalysis [2], chemo-therapeutics [3] and supramolecular chemistry [4]. Their distinct photophysical characteristics create the possibility to design new functional materials such as light-emitting devices [5]. In particular 4'-aryl-substituted terpyridines are known to possess interesting fluorescent properties and can be used in oligonucleotide derivatization [6], construction of photo- and redox-active complexes [7] and in synthesis of fluorescent-labeled proteins and peptides [8]. Frequently, a fine-tuning of terpyridines fluorescence color induced by chemical modification is required for a better performance of photofunctional systems [9]. On the other hand, tuning fluorophores to desirable photophysical properties is still a difficult task and structural alteration can easily modify their emission properties. Anyhow, the introduction of different aromatic substituents at 4'-position of the terpyridine unit can lead to quite dramatic effects on the fluorescence intensities and, in some cases, the wavelength of emission [10]. Variation of the emissive properties can also be achieved by symmetrical substitution at positions 6,6" of the terpyridine ring but, to the best of our knowledge, no extensive investigation of photophysical properties for these type of compounds has been done so far. In addition, maintaining the same aromatic unit in the position 4' and inserting either electron withdrawing groups (F, Cl, Br) or electron donating groups (NH_2, CH_3, OCH_3, and $N(CH_3)_2$) at positions 6,6" of the terpyridine ring can modify absorption and emission properties. We therefore became interested in examining the photophysical properties of symmetrically disubstituted terpyridines and, in this contribution, we present the synthesis and UV-Vis and fluorescence properties of a series of known and new 6,6"-symmetrically disubstituted 4'-aryl-terpyridines **I** (Fig. 1). A study of their absorption and emission properties is detailed herein.

2. Experimental Procedure

Chemicals and solvents of commercial grade were used without further purification. ^1H, and ^{13}C NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 at room temperature on Bruker Avance300 and Avance400 spectrometer (δ in ppm, *J* in Hz) at ^1H operating frequencies of 300.13 MHz and 400.13 MHz (75 MHz and 100 MHz for ^{13}C); spectra were referenced using the solvent signal as internal standard. The mass spectra (MALDI+) were recorded from $CHCl_3$ solutions on a MALDI-TOF Microflex (Bruker) spectrometer (DCTB as matrix); APCI mass spectra were

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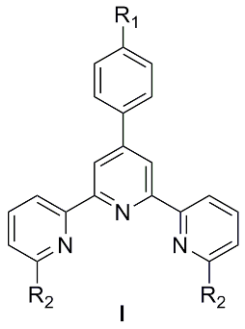

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Figure 1. 6,6"-symmetrically disubstituted 4'-aryl-terpyridines.

recorded on an Agilent 6320 ion trap mass spectrometer in positive mode. Elemental analyses were carried out on a Perkin-Elmer 2400-B microanalyser. The UV–Vis absorption spectra (230–500 nm) were measured with a Perkin Elmer Lambda 35 UV-Vis spectrophotometer and the luminescence spectra (285–750 nm) were obtained with a Perkin Elmer LS 55 Luminescence at 20°C. Relative quantum yields were calculated using 2-aminopyridine in ethanol as standard (excitation at 285 nm, Φ = 0.37). All solvents used for spectrophotometric measurements were degassed prior to use. Melting points were measured with a Kleinfeld melting point apparatus and are uncorrected. Thin layer chromatography (TLC) was conducted on silica gel 60 F254 TLC plates purchased from Merck. Preparative column chromatography was performed using PharmPrep 60 CC (40–63 μm) silica gel purchased from Merck. Chemicals and solvents were purchased from Merck or Acros and were used without further purification.

Syntheses of **3a** [12], **4** [12], **5** [12] and **6a** [6] are described elsewhere.

6,6"-dibromo-4'-[4"'-(hydroxymethyl)phenyl]-2,2':6',2"-terpyridine (3b)

2-acetyl-6-bromopyridine (0.58 g, 2.92 mmol) was added to 50 mL MeOH solution of 4-(hydroxymethyl) benzaldehyde (0.20 g, 1.46 mmol), NaOH (0.05 g, 1.46 mmol) and 10 mL aq. NH_4OH 25%. The reaction mixture was refluxed for 2 days and then let to reach room temperature. The precipitate formed was filtered, washed with water and cold methanol. The crude product was purified by column chromatography on silica gel (AcOEt:Petroleum Ether=1:1, R_f = 0.4) to afford **3b**. (Yield 0.37 g, 52%) Appearance: white solid, mp. 251-252°C. ^{1}H NMR (300 MHz, *CDCl$_3$*) δ ppm: 8.69 (s, 2H, $H_{3'}$, $H_{5'}$), 8.59 (d, 2H, H_3, $H_{3''}$, ^3J = 7.8 Hz), 7.88 (d, 2H, $H_{2'''}$, $H_{6'''}$, ^3J = 8.4 Hz), 7.72 (t, 2H, H_4, $H_{4''}$ ^3J = 7.8 Hz), 7.54 (overlapped signals, 4H, $H_{3'''}$, $H_{5'''}$, H_5, $H_{5''}$), 4.81 (s, 2H, -C$\underline{H_2}$OH). ^{13}C NMR (75 MHz, *CDCl$_3$*) δ ppm: 156.45, 153.68, 149.74, 142.56, 140.84, 138.55, 136.03, 127.50, 126.66, 126.52, 119.33, 118.83, 63.41. MS (*MALDI+/DCTB*): $[M+H]^+$ *m/z:* 496.20, 498.20, 500.20; $[M+Na]^+$ *m/z:* 518.20, 520.20, 522.20; $[M+K]^+$ *m/z*: 534.10, 536.10, 538.10. Anal. Calcd. for $C_{22}H_{15}Br_2N_3O$: C, 53.15; H, 3.04; Br, 32.14; N, 8.45; found: C, 53.19; H, 3.13; Br, 32.05; N, 8.43.

6,6"-dibromo-4'-[4"'-(methoxymethyl)phenyl]-2,2':6',2"-terpyridine (3c)

2-acetyl-6-bromopyridine (1.60 g, 8.02 mmol) was added to 120 mL MeOH solution of 4-(bromomethyl) benzaldehyde (0.80 g, 4.01 mmol), NaOH (0.16 g, 4.01 mmol) and 30 mL aq. NH_4OH 25%. The reaction mixture was refluxed for 2 days and then let to reach room temperature. The formed precipitate was filtered and washed with water and cold methanol and the crude product was purified by column chromatography on silica gel (CH_2Cl_2:Petroleum Ether=2:1, R_f = 0.7) to afford **3c**. (Yield 1.12 g, 54%) Appearance: white solid, mp. 155ºC. ^{1}H NMR (300 MHz, *CDCl$_3$*), δ ppm: 8.68 (s, 2H, $H_{3'}$, $H_{5'}$), 8.58 (dd, 2H, H_3, $H_{3''}$, ^3J = 7.8 Hz, ^4J = 0.6 Hz), 7.86 (d, 2H, $H_{2'''}$, $H_{6'''}$, ^3J = 8.1 Hz), 7.71 (t, 2H, H_4, $H_{4''}$, ^3J = 7.8 Hz), 7.51 (overlapped signals, 4H, H_5, $H_{5''}$, $H_{3'''}$, $H_{5'''}$), 4.56 (s, 2H, -CH_2-O-), 3.43 (s, 3H, -O-CH_3). ^{13}C NMR (75 MHz, *CDCl$_3$*) δ ppm: 157.16, 154.32, 150.38, 141.57, 139.40, 139.11, 137.34, 128.18, 128.15, 127.38, 119.95, 119.67, 74.17, 58.14. MS (*MALDI+/DCTB*): $[M+H]^+$ *m/z:* 509.9, 511.9, 513.9; $[M+Na]^+$ *m/z:* 531.8, 533.8, 535.8; $[M+K]^+$ *m/z*: 547.8, 549.8, 551.8. Anal. Calcd. for $C_{23}H_{17}Br_2N_3O$: C, 54.04; H, 3.35; Br, 31.26; N, 8.22; found: C, 53.99; H, 3.31; Br, 31.33; N, 8.25.

4'-(4"'-bromophenyl)-2,2':6',2"-terpyridine-6,6"-dicarboxylic acid (6b)

A solution of dinitrile **5** (0.70 g, 1.59 mmol) in acetic acid (50 mL) and conc. HCl (20 mL) was refluxed for 16 h. The precipitate formed upon cooling was collected by filtration, washed with water and dried to afford diacid **6b** (Yield 0.69 g, 92%). Appearance: white solid, mp. 210ºC. ^{1}H NMR (300 MHz, *DMSO-d$_6$*) δ ppm: 8.89 (overlapped signals, 4H, $H_{3'}$, $H_{5'}$, H_5, $H_{5''}$), 8.22 (overlapped signals, 4H, H_4 , $H_{4''}$, H_3, $H_{3''}$), 7.94 (d, 2H, $H_{3'''}$, $H_{5'''}$, ^3J = 8.7 Hz), 7.83 (d, 2H, $H_{2'''}$, $H_{6'''}$, ^3J = 8.7 Hz). ^{13}C NMR (75 MHz, *DMSO-d$_6$*) δ ppm: 165.14, 154.20, 154.04, 148.10, 147.16, 138.32, 135.91, 131.59, 128.62, 124.48, 123.61, 122.52, 118.25. MS (*MALDI+/DCTB*) $[M+H]^+$ *m/z*: 476.00, 478.00; $[M+Na]^+$ *m/z*: 498.00, 500.00; $[M+K]^+$ *m/z*: 514.00, 516.00. Anal. Calcd. for $C_{23}H_{14}BrN_3O_4$: C, 58.00; H, 2.96; Br, 16.78; N, 8.82; found: C, 58.08; H, 2.95; Br, 16.72; N, 8.80.

4'-(4"'-bromophenyl)-2,2':6',2"-terpyridine-6,6"-dicarboxylic acid dimethyl ester (6c)

Thionyl chloride (1.00 mL, 13.76 mmol) was added dropwise to cold methanol (50 mL). After the mixture was stirred for 15 min at room temperature, terpyridine derivative **6b** (1.00 g, 2.09 mmol) was added and the mixture refluxed for 5 h. After cooling, the white

precipitate formed was filtered and washed several times with cold ethanol and dried to afford compound **6c** (Yield 0.81 g, 78%). Appearance: white solid, mp. 268-269°C. ^{1}H NMR (300 MHz, *CDCl$_3$*) δ ppm: 8.84 (d, 2H, H_5, $H_{5''}$, ^3J = 7.8 Hz), 8.78 (s, 2H, $H_{3'}$, $H_{5'}$), 8.19 (d, 2H, H_3, $H_{3''}$, ^3J = 7.8 Hz), 8.03 (t, 2H, H_4, $H_{4''}$, ^3J = 7.8 Hz), 7.77 (d, 2H, $H_{3'''}$, $H_{5'''}$, ^3J = 8.7 Hz), 7.67 (d, 2H, $H_{2'''}$, $H_{6'''}$, ^3J = 8.7 Hz), 4.06 (s, 6H, -O-CH_3). ^{13}C NMR (75 MHz, *CDCl$_3$*) δ ppm: 165.79, 156.19, 155.23, 149.69, 147.57, 137.92, 137.24, 132.96, 132.13, 129.05, 125.28, 124.62, 119.71, 52.92. MS (*MALDI+/DCTB*) $[M+H]^+$ *m/z*: 504.10, 506.10; $[M+Na]^+$ *m/z*: 526.10, 528.10; $[M+K]^+$ *m/z*: 542.10, 544.10. Anal. Calcd. for $C_{25}H_{18}BrN_3O_4$: C, 63.57; H, 3.84; Br, 16.92; N, 8.90; found: C, 63.59; H, 3.84; Br, 16.81; N, 8.99.

4'-(4"'-bromophenyl)-6,6"-bis(hydroxymethyl)-2,2':6',2"-terpyridine (6d)

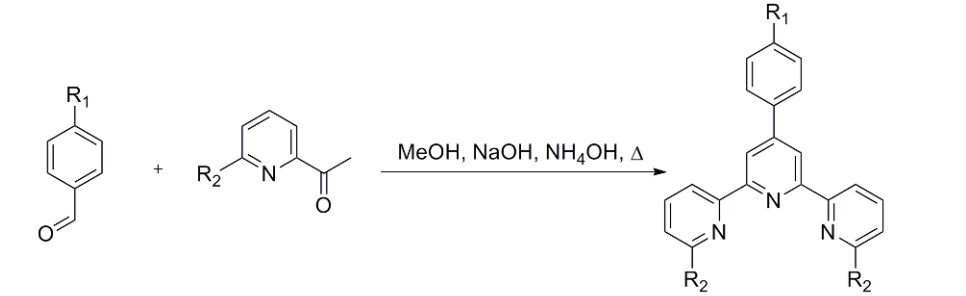
$NaBH_4$ (0.20 g, 5.28 mmol) was added to a suspension of diester **6c** (0.30 g, 0.59 mmol) in absolute ethanol (25 mL) and the mixture was stirred at room temperature for 3 h and then it was refluxed for 1h. After cooling, the solvent was evaporated, saturated aqueous $NaHCO_3$ (30 mL) was added and the solution was heated to boiling. The cold mixture was filtered off and washed with water to afford **6d** (Yield 0.22 g, 88%). Appearance: white solid, mp. 295°C. ^{1}H NMR (300 MHz, *DMSO-d$_6$*) δ ppm: 8.67 (s, 2H, $H_{3'}$, $H_{5'}$), 8.52 (d, 2H, H_3, $H_{3''}$, ^3J = 5.7 Hz), 8.03 (t, 2H, H_4, $H_{4''}$, ^3J = 5.7 Hz), 7.87 (d, 2H, $H_{3'''}$, $H_{5'''}$, ^3J = 6.6 Hz), 7.80 (d, 2H, $H_{2'''}$, $H_{6'''}$, ^3J = 6.6 Hz), 7.59 (d, 2H, H_5, $H_{5''}$, ^3J = 5.7 Hz), 5.57 (s, 2H, -OH), 4.71 (s, 4H, -CH_2-OH). ^{13}C NMR (75 MHz, *DMSO-d$_6$*) δ ppm: 161.64, 155.66, 153.73, 148.11, 137.72, 136.71, 132.15, 128.96, 122.78, 120.87, 118.97, 117.65, 64.31. MS (*MALDI+/DCTB*) $[M+H]^+$ *m/z* = 448.30, 450.30; $[M+Na]^+$ *m/z*: 470.30, 472.30; $[M+K]^+$ *m/z*: 486.20, 488.20. Anal. Calcd. for $C_{23}H_{18}BrN_3O_2$: C, 61.62; H, 4.05; Br, 17.82; N, 9.37; found: C, 61.57; H, 4.13; Br, 17.72; N, 9.33.

6,6"-bis(bromomethyl)-4'-(4"'-bromophenyl)-2,2':6',2"-terpyridine (6e)

A mixture of dry DMF (40 mL) and PBr_3 (0.42 mL, 4.44 mmol) was stirred for 15 min at room temperature. The diol **6d** (0.49 g, 1.11 mmol) was added and the mixture was heated at 60ºC for 1 h and then stirred at room temperature overnight. After neutralization with aqueous $NaHCO_3$ (saturated, 20 mL), the precipitate was filtered and washed with cold water and acetonitrile. The solid was purified by column chromatography on silica gel (AcOEt:Petroleum Ether=1:3, R_f = 0.66) to afford **6e** (Yield 0.42 g, 68%). Appearance: white solid, mp. 211-213°C. ^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm: 8.71 (s, 2H, $H_{3'}$, $H_{5'}$), 8.58 (dd, 2H, H_3, $H_{3''}$, ^3J = 7.8 Hz, ^4J = 0.9 Hz), 7.88 (t, 2H, H_4, $H_{4''}$, ^3J = 7.8 Hz); 7.77 (d, 2H, $H_{3'''}$, $H_{5'''}$, ^3J = 8.7 Hz), 7.67 (d, 2H, $H_{2'''}$, $H_{6'''}$, ^3J = 8.7 Hz), 7.52 (dd, 2H, H_5, $H_{5''}$, ^3J = 7.8 Hz, ^4J = 0.9 Hz), 4.68 (s, 4H, -CH_2-Br). ^{13}C NMR (100 MHz, *CDCl$_3$*) δ ppm: 156.32, 155.71, 155.61, 149.18, 137.90, 137.58, 132.20, 128.93, 123.67, 123.48, 120.52, 119.03, 34.11. MS (*MALDI+/DCTB*): $[M+H]^+$ *m/z*: 571.90, 573.80, 575.90, 577.9; $[M+Na]^+$ *m/z*: 593.80, 595.80, 597.80, 599.80. Anal. Calcd. for $C_{23}H_{16}Br_3N_3$: C, 48.12; H, 2.81; Br, 41.75; N, 7.32; found: C, 48.31; H, 2.87; Br, 41.67; N, 7.31.

3. Results and Discussions

Our initial approach focused on the synthesis of different 6,6" symmetrically substituted 4'-aryl-2,2':6',2"-terpyridine substrates. Terpyridines **3a-c** were easily obtained, in fair to good yields, using typical procedures [11] (Scheme 1). Condensation of aromatic aldehyde **1a** with 2-acetylpyridine **2a** and aldehyde **1b** with 2-acetyl-6-bromopyridine **2b** afforded **3a** and **3b**, respectively. When **1c** was treated with **2b** in the presence of methanol and NaOH, methoxymethyl substituted terpyridine **3c** was obtained. Attaching different functional groups, like Br (**3a**), CH_2OH (**3b**) and CH_2OCH_3 (**3c**), to the phenyl group at position 4' can not only open many pathways toward the construction of advanced supramolecular

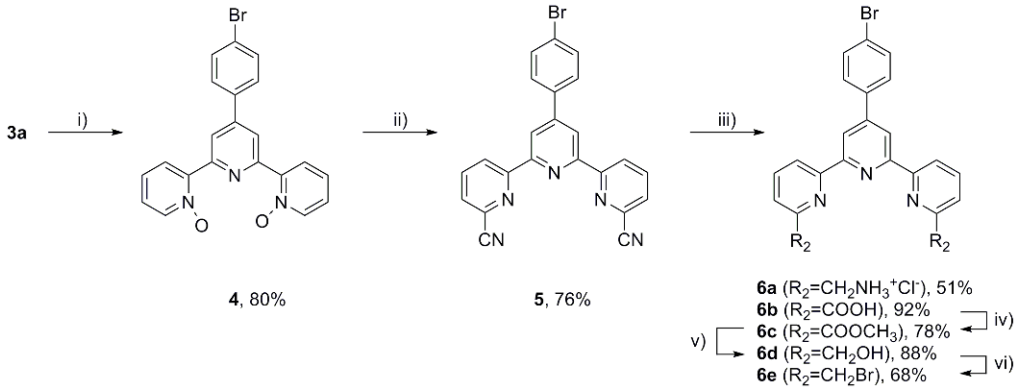


1a (R_1=Br)
1b (R_1=CH_2OH)
1c (R_1=CH_2Br)

2a (R_2=H)
2b (R_2=Br)

3a (R_1=Br, R_2=H), 70%
3b (R_1=CH_2OH, R_2=Br), 52%
3c (R_1=CH_2OCH_3, R_2=Br), 54%

Scheme 1. Synthesis of terpyridines **3a-c**



Scheme 2. *Reagents and conditions:* i) m-CPBA, CH_2Cl_2, r.t.; ii) $(CH_3)_3SiCN$, CH_3COCl, CH_2Cl_2, r.t.; iii) BH_3•THF, THF, HCl, (**6a**); AcOH, HCl, Δ, 16h, (**6b**); iv) $SOCl_2$, MeOH, Δ, 5h, (**6c**); v) $NaBH_4$, EtOH, (**6d**); vi) DMF, PBr_3, (**6e**)

Table 1. Absorption and emission details of terpyridines **3a-6e** in acetonitrile and dichloromethane.

Compound	λ_{abs} (nm) (log10 ε) ACN	λ_{em} (nm)[a]	Φ ACNa	λ_{abs} (nm) (log10 ε) DCM	λ_{em} (nm)	Φ DCM[a]
3a	254 (4.50), 276 (4.54)	356	0.17	255 (4.52), 278 (4.59)	358	0.24
3b	255 (4.41), 289 (4.51)	355	0.15	256 (3.46), 290 (3.57)	357	0.20
3c	254 (4.40), 288 (4.47)	356	0.11	256 (4.35), 290 (4.44)	357	0.15
4	252 (4.21), 275 (4.14)	353	0.02	255 (4.53), 278 (4.60)	357	0.06
5	259 (4.54), 283 (4.45)	353	0.16	262 (4.51), 285 (4.44)	354	0.22
6a	256 (3.29), 282 (3.29)	354	0.08	258 (3.59), 284 (3.63)	359	0.08
6b	260 (4.20), 282 (4.09)	353	0.10	262 (4.47), 284 (4.40)	361	0.16
6c	259 (4.63), 280 (4.51)	355	0.19	262 (4.62), 284 (4.49)	362	0.43
6d	254 (4.30), 282 (4.33)	358	0.26	255 (4.34), 284 (4.44)	361	0.23
6e	262 (4.67), 281 (4.61)	357	0.04	260 (3.62), 285 (3.58)	358	0.09

[a]*Relative quantum yields were determined by using 2-aminopyridine (Φ = 0.37, excitation at 285 nm, in ethanol) as standard compound.*

structures, but may also affect the emission properties of these compounds.

Terpyridine **3a** was further functionalized (Scheme 2) to symmetrically substituted derivatives by oxidation with *m*-CPBA to give *N,N*"-dioxide intermediate **4** [6] which was then subjected to a Reissert-Henze-type reaction to obtain the 6,6"-dicarbonitrile **5** [12]. Reduction of dinitrile **5** with diborane, afforded the bis(aminomethyl) derivative **6a**, isolated as its hydrochloride salt [6]. Hydrolysis of **5** to carboxylic derivative **6b** was performed in acetic acid in a very good 92% yield. Esterification of acid **6b** with methanol allowed the preparation of the methyl ester **6c** in 78% yield, which was further reduced with $NaBH_4$ in dry ethanol to afford **6d** in 88% yield. Bromomethyl substituted phenyl terpyridine **6e** was obtained in 68% yield by treatment of **6d** with PBr_3 in anhydrous DMF.

With a diverse class of terpyridines in hand, we next investigated their photophysical properties. The absorption spectra of the phenyl substituted terpyridines, recorded in acetonitrile and dichloromethane, are shown in Fig. 2. Absorption spectra suggest some differences in the electronic band structures of **3a**-**6e** in acetonitrile as well as in dichloromethane. In the spectra recorded in acetonitrile, intense broad absorption bands are present in the areas 252-262 nm and 275-289 nm, respectively, and they are associated with π-π* transitions of the terpyridines. Generally, when compared to the reference compound **3a**, the maximum absorption bands of **3b**-**6e** are slightly shifted by appending either electron donating or electron withdrawing groups at the peripheral pyridines. The longest wavelengths of absorption in the UV-Vis spectrum of **3b** (λ_{max}= 255 and 289 nm) are broad and comparable in intensity (logε= 4.41 and 4.51, respectively) to that of the parent compound **3a** (Table 1); a bathochromic shift of 13 nm is observed. The introduction of CH_2OCH_3 group in **3c** decreases the molar absorptivity (logε=4.40 and 4.47) with absorption maxima similar to those observed for **3b** and not much different than those of **3a**. Interesting changes are noted when the absorption spectrum of **3a** is compared with that of its *N*-oxide **4**. Absorption maxima in these spectra show a slight hypsochromic shift (1-2 nm) and a decrease of the molecular extinction coefficient (*e.g.* for the longest wavelength absorption band at 275 nm from 4.54 in **3a** to 4.14 in **4**) is observed. Further insertion of CN groups in **5** caused only minor changes of the molecular extinction coefficients, as well as a slight bathochromic shift for the longest wavelength of absorption.

The absorption maximum of the right shoulder of **6a** was slightly red-shifted along with a significant decrease of the logε down to 3.29, probably due to

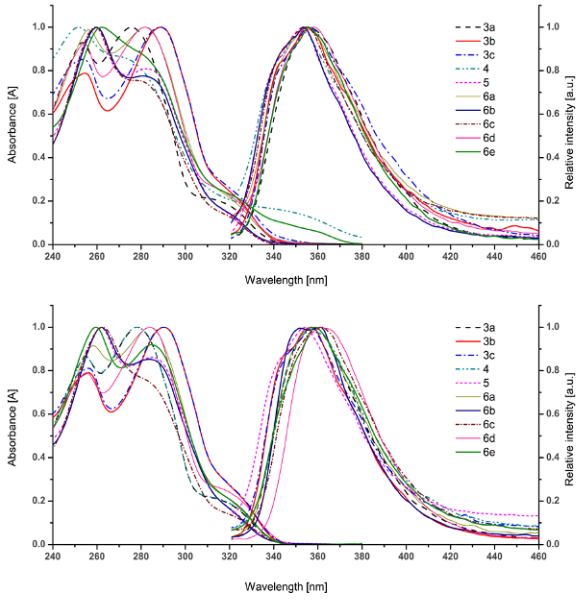


Figure 2. Normalized UV-Vis and emission spectra of **3a**-**6e** in acetonitrile (top) and dichloromethane (bottom) solution (298 K). UV-Vis spectra were recorded at concentrations varying from 1.8×10^{-5} M to 3.0×10^{-4} M and fluorescence spectra at concentrations varying from 2.2×10^{-8} M to 4.0×10^{-6} M. The excitation wavelength was 285 nm.

the poor solubility of **6a** in acetonitrile indicated by the somewhat opaque solution. Insertion of COOH group in **6b** resulted in a decrease of the absorptivity and a slight bathochromic shift, while $COOCH_3$ group in **6c** increases the molar absorptivity of the left shoulder. It can be clearly observed that the introduction of electron donating (CH_2OH) groups in **6d** resulted in a decrease of the molar absorptivity down to 4.30 and 4.33 as compared to **3a**, while introduction of CH_2Br in **6e** resulted in an increase of the absorptivity corroborated with a slight bathochromic effect.

No significant shifts (±4 nm) of the absorption maxima of **3a**-**6e** were observed when dichloromethane was used as a solvent as compared to the spectra recorded in acetonitrile, but some variation occured in the molar extinction coefficient values. For instance, while the spectrum of **3a** recorded in dichloromethane has the same shape as the spectrum recorded in acetonitrile, for **3b** a dramatic decrease of molar absorptivity is observed (3.46, 3.57). While no solvent effect is noted for **3c,** in the case of **4** an increase of absorptivity is observed. Changes are also noted for terpyridines **6a** and **6b** which show an increased absorptivity, when compared to the same compounds in acetonitrile: the most dramatic decrease has been observed for **6e**.

The fluorescence properties of the synthesized terpyridines were also investigated in different solvents; details of emission spectra, recorded at various concentrations, are given in Fig. 2 and details of the emission maxima and fluorescence quantum yields (Φ**)** are shown in Table 1.

The maximum emission band of compounds **3a**-**6e** was located at about 353-358 nm when spectra were taken in acetonitrile, their fluorescence quantum yield being affected by the nature of the functional groups at the peripheral pyridine, while the emission profile was similar upon excitation at 285 nm. As it can be seen from the data collected in Table 1, the absorption maximum for each compound varies little in both CH_3CN and CH_2Cl_2.Thus, the emission spectrum of **3a** consists of one band with a maximum at 356 nm, red-shifted in comparison to 2,2':6',2"-terpyridine, which is known to have a fluorescence maximum at 338 nm [13]. Introduction of CH_2OH (**3b**) or CH_2OCH_3 (**3c**) group on the phenyl ring decreases the emission intensity when compared to **3a**, with values of the Φ = 0.15 and 0.11 in acetonitrile. As expected, *N*-oxide **4** has reduced emission intensity down to 0.02. Dinitrile **5** and compound **6c** show a similar Φ to that of **3a** indicating that the photophysical properties are less affected when CN or $COOCH_3$ groups are inserted, the intensity of emission of aminomethyl, carboxy and bromomethyl substituted terpyridines **6a**, **6b** and **6e** is significantly reduced, while the alcohol **6d** has an increased quantum yield when compared to **3a**. As can be seen from the data collected in Table 1, when the emission spectra were recorded in dichloromethane the quantum yield of the terpyridine **3a** increased to 0.24. Moreover, compounds which are modified by appending either electron-donating or withdrawing groups (**3b**, **3c**, **4**, **5**, **6b** and **6e**) also show higher efficiencies in comparison to the fluorescence quantum yields registered in acetonitrile. The values observed for **6a** and **6d** remain practically unchanged. In addition, the fluorescence intensity of compound **6c** increased twice in comparison to the value measured in acetonitrile (Φ=0.43).

Given the moderate value for the fluorescence quantum yield of **6c** in dichloromethane, we have tried to find other solvents to obtain higher fluorescence quantum yields for this compound, but fluorescence spectra registered in the low-solubilizing non-polar cyclohexane and the protic polar ethanol used as solvents showed a poorer fluorescence quantum yield for compound **6c** (Φ=0.28 and Φ=0.16, respectively).

The excitation spectra of compounds **3a**-**6e** were similar to the corresponding absorption spectra, showing that the emitting state is the lowest excited state.

4. Conclusions

New 6,6" symmetrically substituted 4'-aryl-2,2':6',2"-terpyridine substrates have been prepared and their UV-Vis and fluorescence spectra have been analyzed. We have noticed that the introduction of either electron donating or electron withdrawing groups modified the molar absorptivity as compared to terpyridine **3a**, and that most compounds showed red-shifted and differently shaped absorption spectra in comparison with the parent compound **3a**. Our results show also that the emission maximum wavelength of this class of compounds is only slightly modified by chemical change. Measurement of fluorescence quantum yield in acetonitrile and dichloromethane lead to low values (Φ=0.02-0.26) with the exception of the moderate value obtained for compound **6c** (Φ=0.43) in dichloromethane.

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