J Fluoresc (2017) 27:271–280
DOI 10.1007/s10895-016-1954-5

ORIGINAL ARTICLE

Facile Synthesis and Photophysical Characterization of New Quinoline Dyes

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Received: 18 August 2016 / Accepted: 19 October 2016 / Published online: 27 October 2016

Abstract This paper describes the synthesis of new quinoline derivatives, molecules that has been long interest in the organic and medicinal chemistry. Through the Multicomponent Reaction (MCR), an important tool in modern synthetic methodology, that generate products with good structural complexity, in addition to economy of atoms and selectivity, we provide easy access to the preparation of quinoline derivatives. The reactions were promoted by niobium pentachloride, as a Lewis acid. Subsequently, the synthesis of new aminoquinoline derivatives with good yields was performed using Pd/C and hydrazine. The photophysical investigations of quinoline derivatives show the substituent effect on the optical properties characterization was done by absorption and photoluminescence measurements with quantum yields of up to 83 %, the presence of the amino group at position 6 at the quinoline backbone was crucial for obtaining these increased quantum yields. Results show that these molecules may have potential use for a variety of applications and mainly attracts attention because of its wide potential of applicability in optoelectronic devices.

Keywords Niobium pentachloride · Multicomponent reactions · Quinoline derivatives · Photoluminescence · Fluorescence quantum yields

Electronic supplementary material The online version of this article (doi:10.1007/s10895-016-1954-5) contains supplementary material, which is available to authorized users.

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Introduction

The development of new synthetic strategies for the efficient production of organic compounds is very important, especially when it comes to compounds such as quinoline derivatives which have a variety of applications in many areas and are present in various natural products and drugs [1, 2]. Thus, this compound has been the subject of numerous research groups. Besides the great biological applicability of the quinoline derivatives, such as anti-inflammatory [3, 4], anti-cancer [5–9], anti-hypertensive [10–13], antibacterial [14–17] and antifungal [18, 19] agents, there are also several studies aiming to take advantage of their excellent mechanical properties. For example, their application in polymer chemistry, organic electronics and optoelectronics [20–24]. Also, the aminoquinolines that act as fluorophores show potential performance as organic semiconductors [25]. In addition, some derivatives of substituted quinolines have been used as ligands for the preparation of phosphorescent complexes used in organic light-emitting diodes (OLEDs) [26–28]. The diphenylaminoquinolines have shown to be a promising luminescent organic material with emission in blue range [29, 30]. Other derivatives are presented as potential candidates for applications in fiber optics, photonics and light emitting diodes [31–34]. The literature shows that quinoline backbone is found in several natural products [35].

For dye applications in OLEDs, it is known that a higher value of short-circuit current density (Jsc) is assigned to molecules bearing a broad and intense absorption spectrum [36]. This is the case of molecules containing the quinoline backbone as π spacer, where the increase in the energy conversion efficiency reaches 6.07 % [36]. Zhang et al. showed a great improvement in OLEDs luminescence efficiency and brightness when quinoline derivatives were used [37].

Some classical methods of synthesis are described in the literature to give support for new synthesis [38–68]. Because of this potential applicability of quinoline derivatives, many research groups have geared their efforts towards the development of new efficient and low cost synthetic methods. For the synthesis of quinoline derivatives, several types of catalysts may be used. It has also been shown that acid catalysts are superior to some of the basic types of reactions [44].

Therefore, in this work we describe the facile synthesis and the optical characterization of new nitroquinoline and aminoquinoline derivatives, compounds with potential application as dyes in organic electronic devices.

Experimental

Materials and Instrumentation

All reactions were performed under air atmosphere, unless otherwise specified. Acetonitrile was distilled from calcium hydride. All commercially available reagents were used without further purification. The $NbCl_5$ used was supplied by Companhia Brasileira de Metalurgia e Mineração (CBMM). Thin-layer chromatography was performed on 0.2 mm Merck $60F_{254}$ silica gel aluminum sheets, which were visualized with a vanillin/methanol/water/sulfuric acid mixture, molybdate or UV-365 nm irradiation. Bruker DRX 400 spectrometer was employed for the NMR spectra ($CDCl_3$ solutions) using tetramethylsilane as internal reference for ^1H and $CDCl_3$ as an internal reference for ^{13}C. A Bruker FTIR model VERTEX 70 was used to record IR spectra (neat). HRMS analyses were recorded in a micrOTOF (Bruker), with ESI-TOF detector working on positive mode. Absorption spectra in the UV-Vis region were obtained in an apparatus from Molecular Devices (Model SpectraMax M2) using a quartz cuvette of 1 cm light path at room temperature. Fluorescence emission curves were obtained using a spectrophotometer BioTek microplate (Model Synergy H1).

Quantum yields were analyzed by adjusting the solution absorption using the UV-Vis to ca. 0.05 at 325–393 nm wavelength, the output was measured using the luminescence spectrophotometer at the same wavelength and comparing it to the known 9,10-diphenylanthracene standard using Eq. 1:

Equation 1: Quantum yield calculation using 9,10-diphenylanthracene

$$\Phi_f = \Phi_{std} x \frac{A_{std} F}{A F_{std}} x \frac{n^2}{n^2_{std}}$$

Φ is the fluorescence quantum yield, A is the absorption of the excitation wavelength, F is the area under the emission curve, and n is the refractive index of the solvents used. Subscript *std.* denotes the standard. The compounds were solubilized in ethanol and the concentration maintained at about 5×10^{-6} mol.L^{-1} to follow the protocol for analysis [69].

Synthesis

General Procedure for the Synthesis of Nitroquinoline Derivatives

To a solution of $NbCl_5$ (50 mol%) in 7.0 mL of anhydrous acetonitrile, maintained at room temperature, under air atmosphere, we added a solution of *p*-nitroaniline (1.0 mmol), phenylacetylene (1.0 mmol) and benzaldehyde derivatives **(2a–x)** (1.0 mmol) in 3.0 mL of anhydrous acetonitrile. The reaction mixture was quenched with water (3.0 mL) after 96 h. The mixture was extracted with ethyl acetate (10.0 mL). The organic layer was separated and washed with saturated sodium bicarbonate solution (3 × 10.0 mL), saturated brine (2 × 10.0 mL), and then dried over anhydrous magnesium sulfate. The solvent was removed under vacuum. The resulting mixture obtained was recrystallized in CH_3OH. In some cases more than one recrystallization process was needed [70].

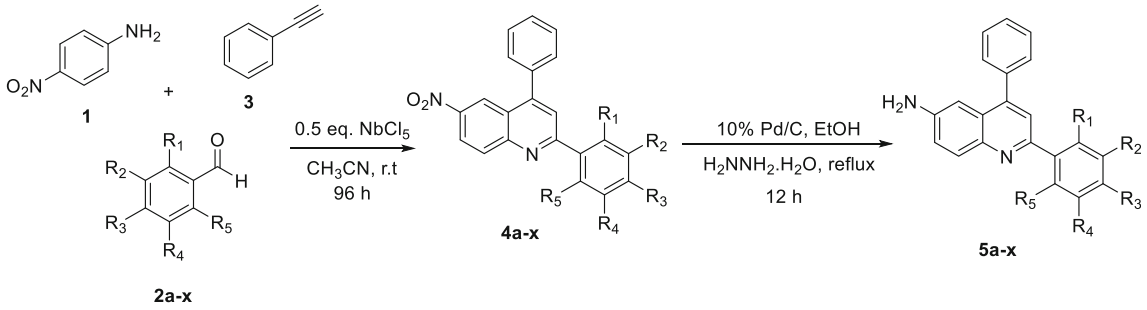
General Procedure for the Synthesis of Aminoquinoline Derivatives

An ethanol suspension (20.0 mL) of quinoline derivative (**4a–x**) (1.0 mmol) was heated to 50.0 °C in the presence of 10%Pd/C and 2.00 mL of hydrazine monohydrate was added over 30 min to this suspension. The reaction mixture became clear as the reaction proceeded. It was kept at reflux for another 12 h. Upon completion of reaction, the mixture was filtered over Celite twice to remove the Pd/C catalyst. Ethanol was removed under reduced pressure. The crude product was recrystallized from isopropanol. Note: the crystals grew slowly [25].

Results and Discussion

Synthesis and Characterization

Recently, our research group described the synthesis of quinoline derivatives through multicomponent reaction (MCR) between arylaldehydes, anilines and alkynes catalyzed by Niobium Pentachloride [71]. In this work, we describe the synthesis of nitroquinoline derivatives by MCRs, using the promoter $NbCl_5$, followed by the reduction of nitro groups for obtaining the aminoquinoline derivatives.



Scheme 1 Synthesis of aminoquinolines **5a–x** in two steps

The MCRs were conducted between *p*-nitroaniline (**1**) (1.0 eq.), benzaldehyde derivatives (**2a–x**) (1.0 eq.) and phenylacetylene (**3**) (1.0 eq.) under air atmosphere, room temperature, constant stirring and using anhydrous acetonitrile (CH_3CN) as solvent. $NbCl_5$ was used in the proportion of 50 % for each mol of benzaldehyde derivative used.

Reduction of nitro group in the nitroquinoline derivatives was conducted with hydrazine monohydrate in the presence of 10 % Pd/C (Scheme 1). The results are summarized in Table 1.

The MRCs in the presence of $NbCl_5$ showed good yields for the production of nitroquinoline derivatives, regardless of the benzaldehyde derivatives used. The results were better using derivatives containing electron withdrawing substituents, which improve the coordination of the benzaldehyde with the Lewis acid ($NbCl_5$) and facilitate the subsequent addition of the amine group of *p*-nitroaniline to the carbonyl group of the benzaldehyde [72]. The reactions with *m*-nitrobenzaldehyde and *p*-nitrobenzaldehyde (**4v** and **4x**) showed lower yields due to the poor solubility of these compounds. To support the good results of the first step, in Table 2

Table 1 Benzaldehyde derivatives utilized and reaction yields

Aldehyde	R_1	R_2	R_3	R_4	R_5	Nitroquinoline yield(%)[a]	Aminoquinoline yield(%)[a]
2a	H	H	H	H	H	93 (**4a**)	92 (**5a**)
2b	F	H	H	H	H	87(**4b**)	91 (**5a**)
2c	Cl	H	H	H	H	92(**4c**)	94 (**5a**)
2d	Br	H	H	H	H	81(**4d**)	93 (**5a**)
2e	H	F	H	H	H	75(**4e**)	84 (**5a**)
2f	H	Cl	H	H	H	98(**4f**)	92 (**5a**)
2g	H	Br	H	H	H	79(**4 g**)	90 (**5a**)
2h	H	H	F	H	H	98(**4 h**)	84 (**5a**)
2i	H	H	Cl	H	H	86(**4i**)	80 (**5a**)
2j	H	H	Br	H	H	98(**4j**)	87 (**5a**)
2k	OCH_3	H	H	H	H	93 (**4 k**)	74 (**5 k**)
2l	H	OCH_3	H	H	H	79 (**4 l**)	90 (**5l**)
2m	H	H	OCH_3	H	H	71 (**4m**)	85 (**5 m**)
2n	CH_3	H	H	H	H	83(**4n**)	65 (**5n**)
2o	H	CH_3	H	H	H	78(**4o**)	70 (**5o**)
2p	H	H	CH_3	H	H	82) (**4p**)	72 (**5p**)
2q	H	H	C_6H_5	H	H	98 (**4q**)	92 (**5q**)
2r	H	H	$N(CH_3)_2$	H	H	70) (**4r**)	91 (**5r**)
2s	H	H	$C(CH_3)_3$	H	H	78(**4s**)	93 (**5s**)
2t	CH_3	H	CH_3	H	CH_3	79 (**4t**)	89 (**5t**)
2u	H	H	SCH_3	H	H	75 (**4u**)	91 (**5u**)
2v	H	H	NO_2	H	H	56(**4v**)	84 (**5v**)
2x	H	NO_2	H	H	H	54(**4x**)	82 (**5x**)

[a] Yields of isolated products after recrystallization

are shown the yields when compared to others catalysts [24, 73–80], we note that the $NbCl_5$ promotes MCRs with good yields in milder conditions. The efficiency of this catalyst is highlighted by the conduction of reactions at room temperature and pressure, and air atmosphere. These factors could reduce the cost of large-scale production.

The second reaction step, the reduction of the nitro group in all nitroquinoline derivatives, was successfully obtained and presented good yields. An exception was the halogenated nitroquinoline derivatives, in which the reductive reactional condition also resulted in the dehalogenation of the products, obtaining only the compound **5a** as product. An explanation for this fact is the small amount of reagents used in our experiments, a condition different from those described in the literature. Indeed, Pd-catalyzed hydrogenolysis of carbon-halogen bonds with hydrazine as a hydrogen donor is a long known method, but it is usually performed with large amounts of catalyst and/or reducing agent [81–85]. In short, this study has shown that the conversion of polysubstituted quinolines with fluorides, bromides and chlorides into corresponding quinoline dehalogenated can be efficiently performed with ethanol in the presence of hydrazine as hydrogen donor and catalytic amounts of Pd/C. The chemical structures of the resulting nitroquinoline and aminoquinoline derivatives were confirmed by ^1H NMR, ^{13}C NMR, IR and HRMS spectra.

Photophysical Properties

As it is well known, substituents have a key effect on the properties of fluorophores. In this study, we add different types of substituents at various positions to examine the effects on absorption, emission and fluorescence quantum yield. The photophysical characteristics were investigated in CH_3CH_2OH solutions.

Table 3 Maximum absorption wavelength (λ_{max}) for quinoline derivatives

Compound	λ_{max}(nm) ethanol	Compound	λ_{max}(nm) ethanol
4a	335	**5a**	375
4b	326	**5a**	375
4c	375	**5a**	375
4d	332	**5a**	375
4e	331	**5a**	375
4f	332	**5a**	375
4g	332	**5a**	375
4h	337	**5a**	375
4i	341	**5a**	375
4j	341	**5a**	375
4k	343	**5k**	370
4l	341	**5l**	373
4m	357	**5m**	373
4n	379	**5n**	370
4o	341	**5o**	373
4p	356	**5p**	373
4q	360	**5q**	373
4r	393	**5r**	388
4s	344	**5s**	373
4t	358	**5t**	370
4u	369	**5u**	376
4v	332	**5v**	385
4x	325	**5x**	373

UV-Vis Absorption Properties

The data of UV-Vis absorption are summarized in Table 3 in 10^{-3} mol. L^{-1}EtOH solution.

The absorption spectra of the nitroquinoline derivatives in ethanol are characterized by strong absorption peaks centered

Table 2 Comparison of the data reported in literature and the products obtained in the synthesis of 6-nitro-2,4-diphenylquinoline (**4a**)

	Catalyst	Solvent	Temperature (C°)	Time (min)	Yield (%)
1	$NbCl_5$	CH_3CN	r.t.	5760	93
2	YCl_3	----	180 (MW) [c]	8	63
3	$K_5CoW_{12}O_{40}.3H_2O$	----	90 (MW)	10	90
4	$Fe(OTf)_3$	----	100	180	69
5	In/HCl	H_2O	Reflux	1080	77
6	H_2SO_4	CH_3COOH	Reflux	240	93
7	K-10 [a]	----	100 (MW)	10	72
8	$Zn(OTf)_2$	[hmim]PF_6 [b]	90	120	90
9	$In(OTf)_3$	----	110 (MW)	300	87
10	$FeCl_3$	CH_3CN	Reflux	45	61

[a] Montmorillonite $[(Na,Ca)_{0,3}(Al,Mg)_2Si_4O_{10}(OH)_2.nH_2O]$

[b] 1-hexyl-3-methylimidazolium hexafluorophosphate

[c] MW- Microwave irradiation

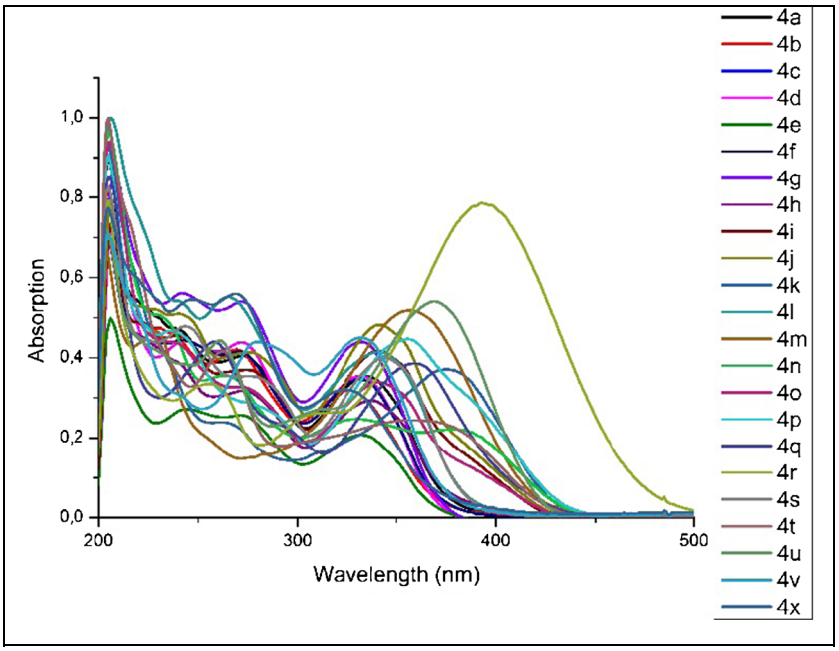


Fig. 1 UV-Vis absorption of nitroquinoline derivatives (**4a–x**) in ethanol

at 250–280 nm and 325–393 nm probably due to π-π* and n-π* transitions, which are characteristics of conjugated quinoline backbone and phenyl side chains with or without substituents. The absorption spectra of ethanolic solutions (10^{-3} mol.L^{-1}) of nitroquinoline derivatives are depicted in Fig. 1.

Analyzing the effect of the substituent groups using **4a** (6-nitro-2,4-diphenylquinoline) as the reference compound, it can be observed a general tendency by which the compounds containing electron withdrawing substituents showed lower values of λ_{max} when compared to electron donors. We also observed that electron withdrawing substituents have greater absorption when in *para* position. Electron withdrawing groups such as nitro (NO_2), in *meta* or *para* position showed hypsochromic shift. The same was observed in the halogen substituents (F, Cl and Br) in *ortho* and *meta* positions, except chlorine in *ortho* position. A bathochromic shift was observed for these halogens in *para*. On the other hand, electron donor

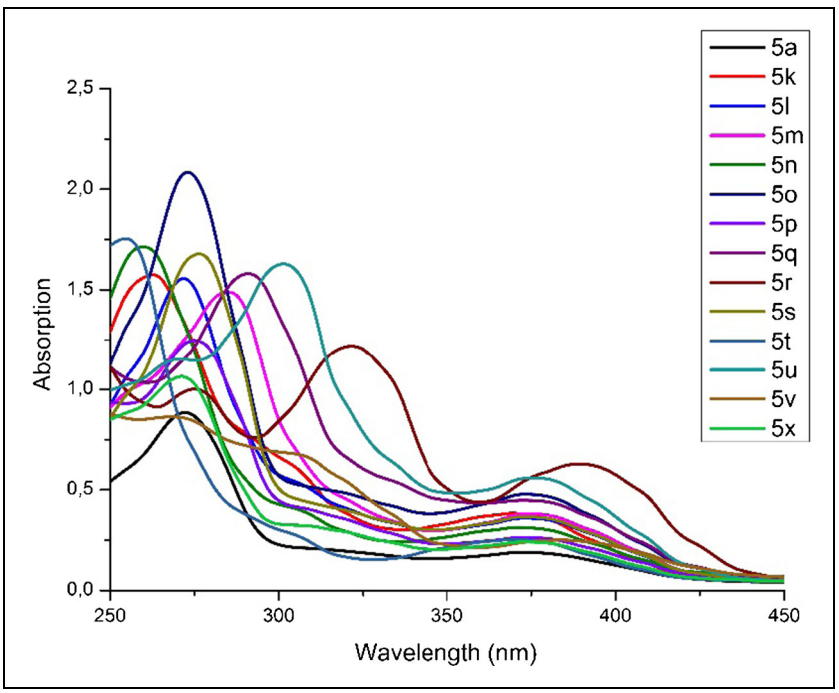


Fig. 2 UV-Vis absorption of aminoquinoline derivatives (**5a–x**) in ethanol

substituents, such as methoxy (341–375 nm) and methyl (341–379 nm) in any position, *tert*-butyl group (344 nm) and thioether group (369 nm), also exhibited a bathochromic shift. The compound that showed higher λ_{max} was **4r** (393 nm) having dimethylamine as substituent, an electron donating group. This phenomenon may be explained taking into account the presence of a pair of non-bonding electrons that are capable of interacting with π electrons of the aromatic ring. Phenyl substituent had a bathochromic shift (360 nm) because it has effectively extended the conjugation of the molecule.

The change of electron withdrawing groups (NO_2) by the electron donating group (NH_2) had profound influence in the spectral properties. As it can be observed, a difference of 40 nm was seen between molecule **4a** and **5a**, a bathochromic shift due to the change of the electron withdrawing groups (NO_2) by the electron donating group (NH_2) at position 6 at the quinoline backbone. In general, due to the strong influence of amino group at position 6, no significant alteration was observed by changing the substituents on the phenyl ring in position 2 (370 nm to 376 nm) (Fig. 2). Molecules **5n** and **5r** were exceptions when compared to **4n** and **4r**, exhibiting a slight hypsochromic shift. There was a large bathochromic shift in molecules with the amino groups **5v** (385 nm) and **5x** (373 nm). Again, *para* position showed higher values compared to other positions.

Emission Fluorescence Properties

Figure 3 shows the fluorescence emission of quinoline derivatives.

Similar to the absorption effects, the fluorescence behavior was also affected by the substituents and their positions. Molecules **4a–x** mostly show a similar behavior in the shift.

Table 4 Photophysical data obtained from UV-Vis absorption and fluorescence emission of quinoline derivatives

Compound	λem	Δλst	Φfx (%)	Compound	λem	Δλst	Φfx (%)
4a	410	75	0.25	**5a**	470	95	65.33
4b	410	84	1.50	**5a**	470	95	65.33
4c	430	55	0.58	**5a**	470	95	65.33
4d	415	83	2.05	**5a**	470	95	65.33
4e	415	84	0.76	**5a**	470	95	65.33
4f	415	83	1.10	**5a**	470	95	65.33
4g	430	98	0.91	**5a**	470	95	65.33
4h	415	78	0.37	**5a**	470	95	65.33
4i	405	64	0.37	**5a**	470	95	65.33
4j	395	54	0.23	**5a**	470	95	65.33
4k	415	72	0.43	**5k**	466	93	69.92
4l	425	84	0.18	**5l**	469	96	69.57
4m	430	73	0.24	**5m**	469	96	70.18
4n	430	51	3.15	**5n**	466	93	53.64
4o	435	94	0.80	**5o**	469	96	80.32
4p	435	79	0.50	**5p**	469	96	59.53
4q	445	85	0.35	**5q**	466	96	72.92
4r	450	57	0.45	**5r**	475	87	51.70
4s	430	86	0.26	**5s**	469	96	73.03
4t	430	72	0.32	**5t**	466	96	49.16
4u	425	56	0.57	**5u**	472	99	83.48
4v	415	83	0.23	**5v**	472	87	24.15
4x	410	85	0.25	**5x**	469	90	14.66

When the difference in fluorescence intensity was analyzed, molecules **4n** and **4g** presented greater intensity. Fluorescence emission spectra of derivatives **5a–x** exhibited high intensity and showed similar values even by altering the substituents.

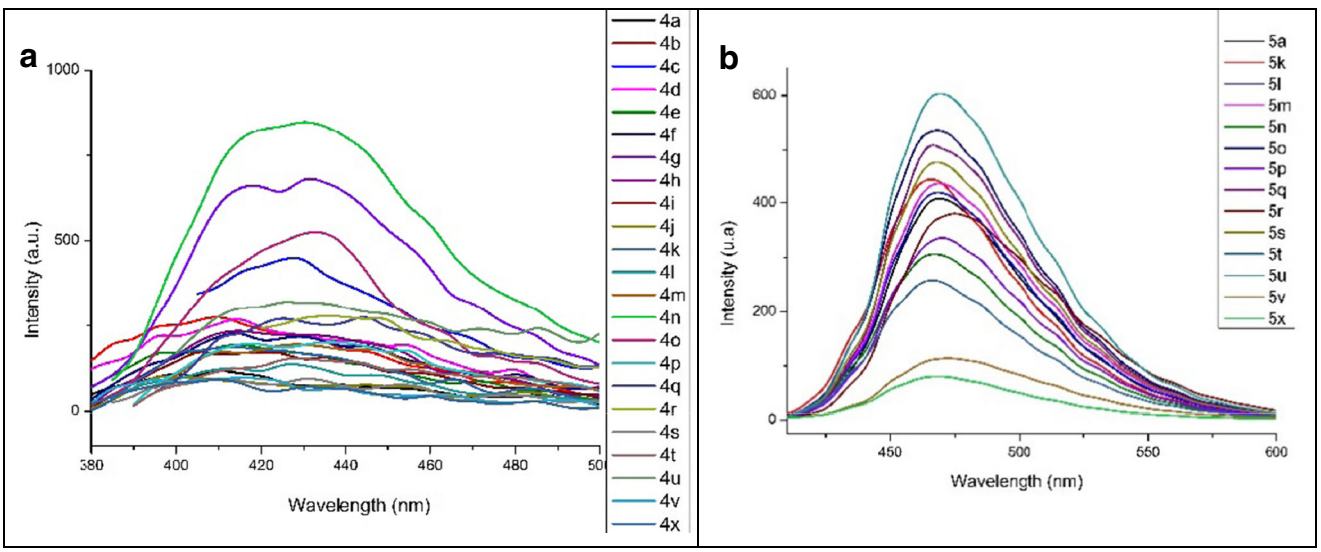


Fig. 3 **a** Fluorescence emission of nitroquinoline derivatives (**4a–x**) in ethanol. **b** Fluorescence emission of aminoquinoline derivatives (**5a–x**) in ethanol

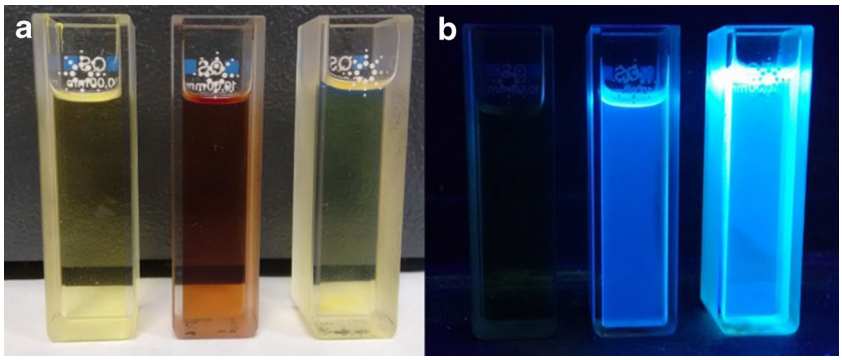


Fig. 4 **a** Ethanolic Solutions of **4a**, **5a** and **5u. b** Ethanolic Solutions of **4a**, **5a** and **5u** irradiated by 365 nm UV radiation

These high values are evidenced when compared to several standards of fluorescence as 9,10-diphenylanthracene which was the standard used for measures (**Φfx** = 90 % in ethanol) [70]. These results confirmed the strong influence of the amino group in the derivatives. The photophysical data of all synthetized compounds are showed in Table 4.

The fluorescence quantum yield (**Φ**f) is one of the most fundamental and important properties for materials with potential application in fluorescence imaging, optical devices, analysis and biosensing [86]. Here, we observed that the molecules **4a–x** with nitro group in position 6 do not present significant values of **Φ**f. In contrast, the presence of the amino group in this position was crucial for obtaining increased **Φ**f, as can be seen for aminoquinolines (**5a–x**) [25]. These high values of fluorescence quantum yield of fluorescence confirmed the importance of the amino group and demonstrated that fluorescence is not detected in aromatic compounds containing the nitro group, as seen in molecules **4a–x**. This is likely due to the existence of transitions $n \rightarrow \pi^*$, causing an efficient intersystem crossing process, and the great speed of the internal conversion processes $S_0 \rightarrow S_1$ [87].

Values of Stokes shifts are between 51 and 98 nm for compounds containing the nitro group (**4a–x**) and 87 to 100 nm for the aminoquinolines (**5a–x**). This shows energy loss in the excited state due to rearrangements or structural changes of molecules. In Fig. 4, compounds irradiated with ultraviolet light showed blue fluorescence for the aminoquinolines.

Conclusion

In conclusion, $NbCl_5$ proved to be an excellent catalyst for MCRs. The reactions were conducted in mild conditions, with low production cost and with good yields. The optical properties were dependent on the substituents, showing lower values of maximum absorption for the electron withdrawing substituents when compared to electron donors. The substituents positions were also important. Compounds **4a–x** exhibited low values of **Φ**f and aminoquinolines (**5a–x**) showed high values. In this context, compounds like **5r** are potential candidates for organic electronic devices. The results also show that the diamine quinoline derivatives **5v** and **5x** could be used as asymmetric monomers for the preparation of high performance polymers [25]. Due to the unquestionable importance of quinoline derivatives in several areas as the development of pharmaceuticals, dyes, chemical polymers and in electronic and organic optoelectronics devices, the MCRs methodology developed here is of great interest for those who study these molecules.

Acknowledgments The authors would like to thank Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) (Procs. 2013/08,697–0, 2012/24,199–8, 2015/00,615–0 and 2016/01,599–1), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) (Proc. 302,753/2015–0) and Pró-Reitoria de Pesquisa (PROPe-UNESP) for their financial support. We would also like to thank CBMM – Companhia Brasileira de Mineralogia e Mineração for the $NbCl_5$ samples. We express our special thanks to N. P. Lopes, J. N. Mendonça and J. C. Tomaz at the University of São Paulo in Ribeirão Preto for the HRMS analyses.

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