


Month 2019 NbCl₅ Promoted the Efficient Synthesis of Phthalein Derivatives: Optical Characterization and Solvatochromic Effect

Vitor Fernandes Moreno, Giovanni Carvalho dos Santos, Gyordanna Mayara Gaspar da Costa, Marcelo Henrique Ayala Gomes, and Luiz Carlos da Silva-Filho* 

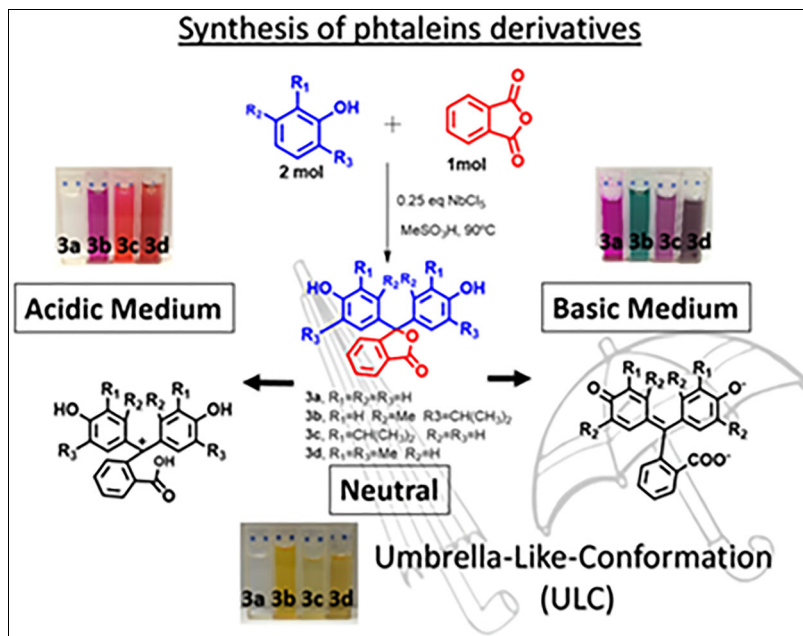
Laboratory of Organic Synthesis and Processes (LOSP), Department of Chemistry, School of Sciences, São Paulo State University (UNESP), Bauru, São Paulo 17033-360, Brazil

*E-mail: luiz.carlos@unesp.br

Received May 31, 2019

DOI 10.1002/jhet.3664

Published online 00 Month 2019 in Wiley Online Library (wileyonlinelibrary.com).



Organic dyes derived from phthaleins have a large number of industrial applications and can be synthesized using a Lewis acid by Friedel–Crafts acylation, followed by an addition reaction to the carbonyl compound. This work aims to investigate the use of NbCl₅ as a catalyst for the acylation reaction. The behavior of the phthalein derivatives in several solvents and when subjected to different pH conditions was studied. These compounds showed a color-changing effect depending on the pH and solvent, making them useful for applications as indicators. The phthaleins change their conformations depending on the condition of the medium. Photophysical studies of these compounds were carried out through their UV–Vis absorption spectra. Here, we show the umbrella-like conformation change of phthalein derivatives that depend on the solvent and the pH of the medium.

J. Heterocyclic Chem., **00**, 00 (2019).

INTRODUCTION

Each year, new niobium-containing compounds appear as catalysts in organic synthesis [1,2]. Some types of studied reactions involving the application of niobium compounds in organic synthesis include tetrahydropyridine synthesis, the Povarov multicomponent reaction, Friedel–Crafts acylation, β -mercaptan preparation, synthesis of 3,4-dihydropyrimidinones (Biginelli reaction), synthesis of β -keto-esters, Diels–Alder and aza-Diels–Alder reactions, aldehyde and imine allylation, nucleophilic additions to *N*-acyl-iminium ions, aldol and aza-aldol reactions, the Sakurai reaction, γ -keto-esters, cross-coupling reactions, coupling reactions

of carbonyl compounds, reduction reactions, and one-pot synthesis of quinoline derivatives, among others [1]. In these cited syntheses, the compound that has been studied the most is niobium pentachloride. The pentacationic niobium has unfilled valence orbitals (4d orbitals). Thus, this compound is highly electrophilic, so it can act as a Lewis acid, catalyzing various organic reactions [2].

Within the reactions, the Friedel–Crafts acylation reaction developed by Charles Friedel and James Crafts in 1877 is aimed at replacing a hydrogen of the aromatic ring with substituent groups that may be alkyl or acyl, so they are denominated respectively: Alkylation reactions and acylation reactions both occur by electrophilic aromatic substitution [3]. This alkylation reaction

involves replacing the hydrogen of the aromatic ring with an alkyl group, which was previously attached to a halogen. The reaction only occurs in the presence of a catalyst that acts as a Lewis acid. The reaction of this work is based on a Friedel–Crafts acylation reaction, which takes place at two moments in the process, and the reaction catalyst is niobium pentachloride, which, as discussed previously, has great potential to be the good Lewis acid that the reaction requires [4].

Organic dyes derived from phthaleins have a large number of applications, such as paints, adhesives, insecticides, food colorings, cosmetics, and pH (potential hydrogen) indicators [5–7]. Phthalates also have promising biomedical applications, including use in cell viability detection, blood and urine analyses, genomics, and treatment of diseases associated with amyloidosis, among others [8,9]. Phthalein derivatives can be synthesized from the reaction between two equivalents of the phenolic derivative with one equivalent of the anhydride derivative in the presence of different catalysts, among which we can mention: AlCl_3 , SnCl_4 , ZnCl_2 , and H_2SO_4 , among others [10]. One of the main applications of phthalein derivatives is as pH indicator dyes because their carbonic structures can change their configuration depending on the pH of the media in which they are found. In their acidic or neutral forms, the phthalein derivatives do not exhibit coloration. However, in a basic medium, the solution usually acquires strong colors ranging from pink to violet through blue. At basic pHs, the total conjugation of all the π electrons present in the phthalein derivative occurs, causing this derivative to

absorb visible light wavelengths [11]. Phenolphthalein, one of the simplest phthalein derivatives, is widely used as an indicator of acid–base titrations, as it changes from colorless to carmine at a pH close to 8, indicating the titration turning point [6]. The structural forms that the phenolphthalein assumes according to the pH or according to the solvent can be seen in Figure 1. Lopez Arbeloa and co-workers proposed a model to explain the different forms of rhodamine derivatives [12]. The same explanation can be used in phthalein derivatives. This model was called umbrella-like motion and is based on the open and closed structure of the lactonic ring present in these compounds [12].

RESULTS AND DISCUSSION

The synthesis was carried out as described in the literature by Sabnis, starting from the reaction between phenol (**1a**) and phthalic anhydride (**2**) on heating at 90°C in an inert atmosphere of N_2 [5]. In this first moment, the reaction proceeded for 300 min described in the literature, the reaction time was monitored through thin layer chromatography, and the objective of this reaction was to determine the way of reaction follow up. The synthesis also was performed under a N_2 atmosphere. The results of the assays with inert atmosphere (N_2) and air atmosphere show similar yield, 68% and 65%, respectively. Therefore, a normal air atmosphere was used for the continuation of the work. The next step was to optimize the synthesis by adding and subsequently

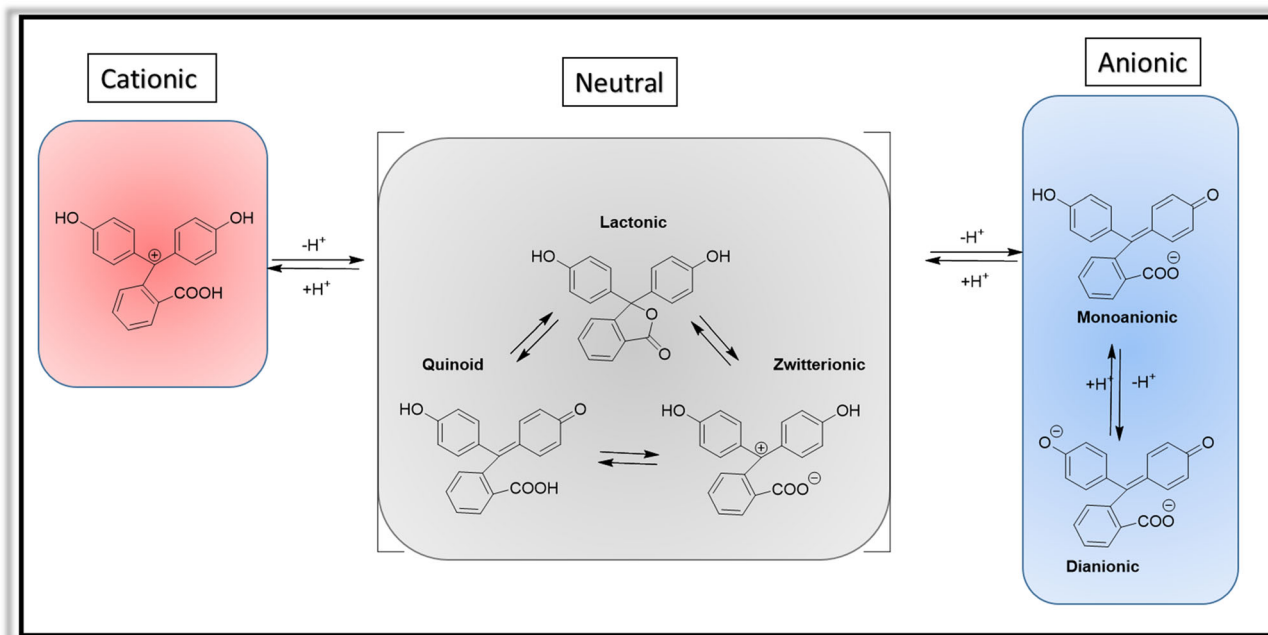


Figure 1. Structures of phenolphthalein in acid medium and in basic medium. [Color figure can be viewed at wileyonlinelibrary.com]

varying the ratio of NbCl_5 and the solvent used to obtain phenolphthalein (**3a**). The results of these first tests are shown in Scheme 1 and Table 1.

Analyzing the above table revealed that there was a significant product formation only when methanesulphonic acid (MeSO_3H) was used as the reaction solvent. An explanation for this result is that MeSO_3H is a polar, strong ($\text{pK}_a -2.6$), and protic solvent; this makes it act as a better Lewis acid than the other solvents tested, and this is due to a better stabilization of the reaction intermediate (ion acyl). Ethanol is also polar but does not have a proton available and thus does not act as a Lewis acid. The other solvents also have some characteristics (apolarity or the fact that they are aprotic) that do not aid in the formation of the phthalein derivatives. Another point observed in these initial tests was that the use of the proportions of 25 and 50 mol % of NbCl_5 provided the best yield for obtaining the compound **3a**. The decrease of the reaction time using NbCl_5 is also evidenced in the tests performed.

These same reactions were tested at room temperature; however, the formation of the products of interest was not observed even after 24 h of reaction. In addition, the literature reported that temperatures above 90°C degrade the product [5], so tests were not performed at higher temperatures or at reflux. Based on the results obtained and with the intention of using the lowest amount of NbCl_5 , the following reaction conditions were adopted: a concentration of 25 mol % of NbCl_5 , MeSO_3H as the reaction solvent, and heating at 90°C . Once under these conditions, the reaction is processed with a high yield, in a short reaction time, and using a low concentration of the catalyst. Other acids are known for the efficiency in the synthesis of these compounds; among them are perchloric acid ($\text{pK}_a -10$) and sulfuric acid ($\text{pK}_a -3$) [6]. Acids such as trifluoroacetic acid ($\text{pK}_a -0.25$) and acetic acid ($\text{pK}_a 4.76$) could not be tested for reacting with NbCl_5 .

The reactions were carried out starting from 2.0 mmol of the phenolic derivatives (**1a–d**) and with 1.0 mmol of the phthalic anhydride derivatives (**2**), using MeSO_3H and 25 mol % of NbCl_5 niobium pentachloride, as the Lewis acid, in a common atmosphere under heating at 90°C (Scheme 2 and Table 2).

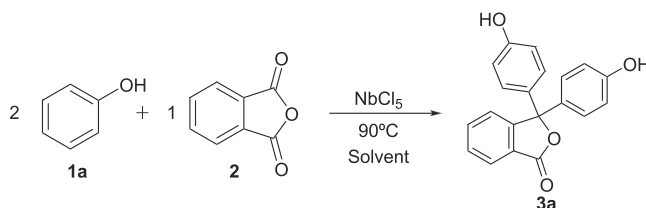
Table 1
Synthesis optimization.

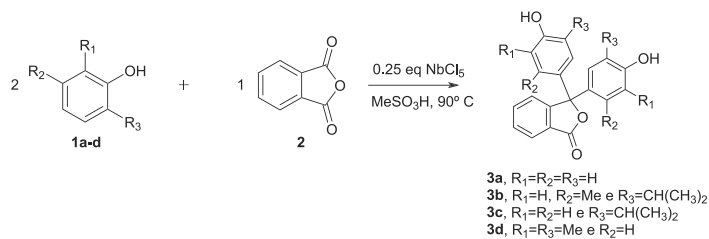
NbCl_5 (mol %)	Solvent	Reaction time (min)	Yield (%)
0	MeSO_3H	300	66
	EtOH	300	—
	AcOEt	300	—
	Hexane	300	—
	CH_2Cl_2	300	—
5	MeSO_3H	110	47
	EtOH	300	—
	AcOEt	300	—
	Hexane	300	—
	CH_2Cl_2	300	—
10	MeSO_3H	110	49
	EtOH	300	—
	AcOEt	300	—
	Hexane	300	—
	CH_2Cl_2	300	—
25	MeSO_3H	70	76
	EtOH	300	—
	AcOEt	300	—
	Hexane	300	—
	CH_2Cl_2	300	Traces
50	MeSO_3H	80	78
	EtOH	300	—
	AcOEt	300	—
	Hexane	300	—
	CH_2Cl_2	300	Traces
100	MeSO_3H	80	61
	EtOH	300	—
	AcOEt	300	—
	Hexane	300	—
	CH_2Cl_2	300	Traces

Obtaining different types of substitutions in phthalein derivatives is also justified by the fact that with the change of substituent types, the photochemical and photophysical properties can be altered by enhancing or decreasing the emission behavior and the absorption/emission maximum can be bathochromically shifted (shift to longer wavelengths in the spectrum, red-shift) or hypsochromically (shift to shorter wavelengths in the spectrum, blue-shift) [13].

Mechanistically, the reaction first proceeds through the formation of the acyl ion catalyzed by NbCl_5 . In sequence, the acyl ion reacts with a molecule of the phenolic derivative through a Friedel–Crafts acylation reaction,

Scheme 1. Optimization of synthesis of phthalein derivatives.



Scheme 2. Synthesis of phthalein derivatives in the presence of NbCl₅.**Table 2**

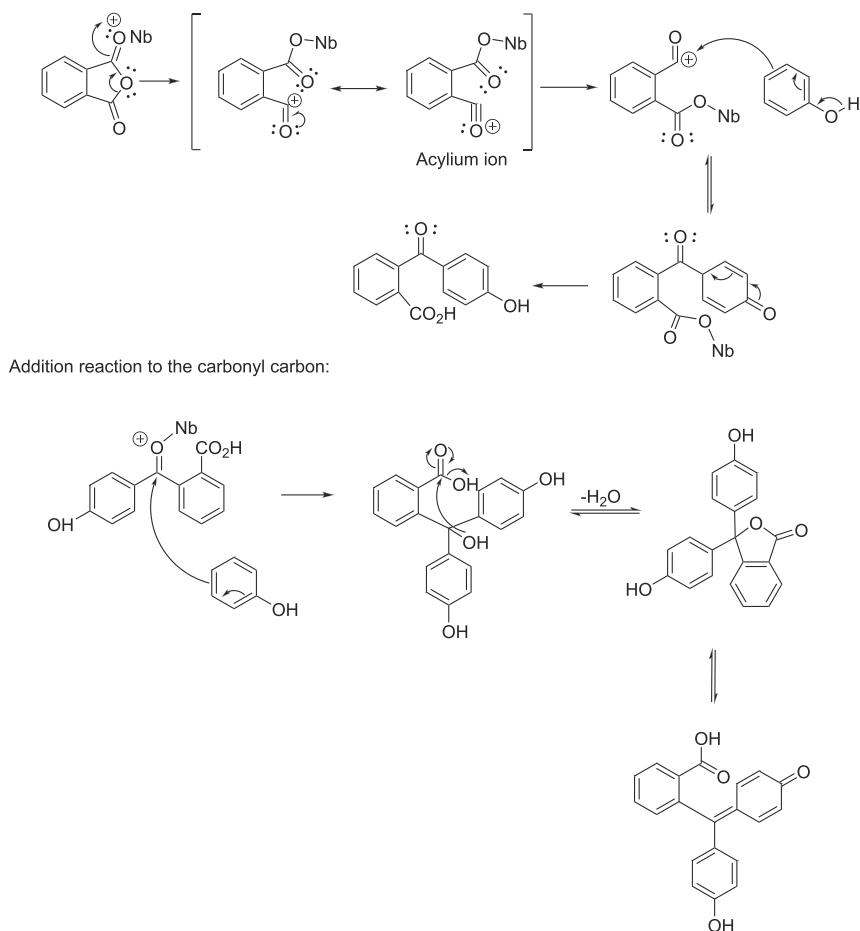
Results obtained for the synthesis of the phthalein derivatives.

Phenolic derivative	NbCl ₅		Product
	Reaction time (min)	Yield (%)	
	70	76	
	80	70	
	80	92	
	80	89	

forming the monoacylated adduct, an intermediate of the reaction. This adduct undergoes a nucleophilic attack on the second molecule of phenol, which binds to the carbocation that is formed when another molecule of the catalyst binds to the oxygen that is between the two aromatic rings; this characterizes an addition reaction followed by a proton transfer with loss of water to form the respective phthalein derivative (Scheme 3).

Analyzing Table 2, it can be noted that niobium pentachloride is a good Lewis acid for the synthesis of the phthalein derivatives, generating the products of interest in good reaction times and with good yields, showing the efficiency of NbCl₅ as a catalyst for this synthesis.

Optical properties of phthalein derivatives. Because of the extremely useful and known applications of phenolphthalein, the optical behavior of phthalein

Scheme 3. Mechanistic proposal for the synthesis of phthalein derivatives.

derivatives synthesized in acidic and basic media was investigated, by observing its color variation. H_2SO_4 at $\text{pH} = 1$ was used as the acidic medium and NH_4OH at $\text{pH} = 12$ as the basic medium.

It is possible to observe interesting results in the study carried out, because all the solutions showed significant changes in their coloration when they go from an acid medium to an alkaline medium [14]. This effect is known as halochromism [15–18]. Details of these studies are as follows.

In Figure 2, we see the spectra acquired at the moment of turning, where there are still species that were not fully protonated (acid medium) or deprotonated (basic medium) (Fig. S14 shows all the compounds together). The spectra with total conversion of the structures are in Figs S10, S11, S12, and S13. The quantity of each acid/base added in the solution is in the caption of the spectra (Figs S10–S13), ranging from 0.5–10 000 μL of acid/base in 3 mL of ethanol solution with $\sim 10^{-4}$ M of each compound. In these figures, which show the spectral titration, we can see the halochromic effect on all

phthalin derivatives. In general, we see the appearance and consequent increase of the band assigned to the protonated species in acid medium while the decrease of the band assigned to the neutral form. The same happens in a basic environment, where we see the emergence of the deprotonated species.

As seen in the titration spectra of the compounds (Figs S10–S13), each derivative has different limiting regions for the detection of changes in the medium (acid or basic). Derivative **3a** shows no change in acid medium (H_2SO_4), but in basic media, it is able to identify a change in pH from the addition of 250 μL of NH_4OH , reaching an addition limit of 8000 μL ($\text{pH} 9.5$ – 12). Derivative **3b** is the most sensitive, showing a detection of 1 μL for the acid, going up to 250 μL ($\text{pH} 7$ – 5), and to the base 5 μL at 8000 μL ($\text{pH} 7.5$ – 12). Compounds **3c** and **3d** showed an acidic detection starting at 750 μL to 3000 μL ($\text{pH} 5.5$ – 1). In basic media, both started at 250 μL ($\text{pH} 9.5$), but **3c** goes up to 5000 μL ($\text{pH} 12$) while **3d** is limited to 3000 μL ($\text{pH} 12$). We can observe in the spectra the increase in the intensity of the absorption band attributed

to the acidic and basic forms. Also, the decrease of the band assigned to the neutral form is observed. Thus, we generally observe a moderate detection limit for compounds **3a**, **3c**, and **3d** ranging from the range of 10^{-6} to 10^{-5} mol/L for both acid and base. For compound **b**, we found detection limit of 10^{-9} to 10^{-6} mol/L for the acid medium and 10^{-8} to 10^{-5} mol/L for the basic medium, which is a good limit

compared with the literature [19]. The first observation is that at alkaline pH, the phthalate derivatives acquire a dianionic structure, and the presence of the alkyl groups stabilizes this negative charge by induction. All compounds in basic media have three absorption bands. The first around 275 nm. As seen in Figure 2 and Table 3, the second band ranges from 361 to 404 nm, and the last

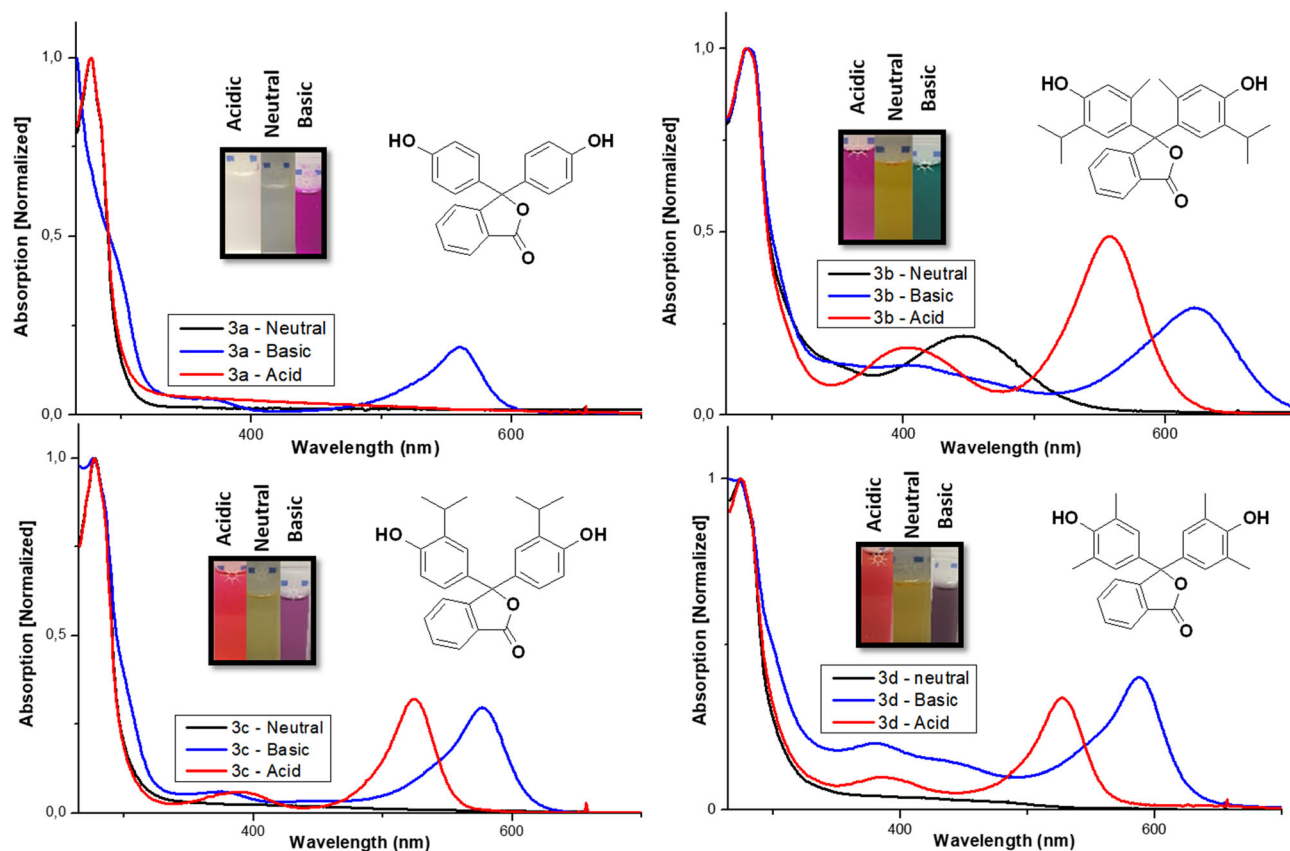


Figure 2. Absorption properties of phthalain derivatives in acidic, neutral, and basic media in ethanol 1×10^{-4} M (halochromism effect). [Color figure can be viewed at wileyonlinelibrary.com]

Table 3

Absorption properties of phthalain derivatives in acidic, neutral, and basic media.

	Absorption (nm) (ϵ [10^4 L/mol/cm])			Absorption spectral shift (nm)	
	Acidic medium	Neutral medium	Basic medium	Neutral to acidic medium	Neutral to basic medium
3a	275 [0.75]	276 [0.75] ~400 ^a [0.02]	265 [0.97] 361 [0.10] 560 [0.51]	—	160
3b	281 [0.47] 403 [0.12] 557 [0.24]	281 [0.47] 446 [0.09]	281 [0.25] 404 [0.15] 622 [0.58]	111	176
3c	275 [0.61] 384 [0.61] 524 [2.35]	275 [0.53] ~400 ^a [0.01]	275 [0.47] 375 [0.25] 577 [1.65]	124	177
3d	275 [0.57] 387 [0.54] 528 [2.15]	275 [0.33] ~400 ^a [0.01]	275 [0.52] 381 [0.29] 588 [1.87]	128	188

^aShoulder.

band is around 600 nm. In acidic, basic, or neutral media, the compounds show an intense band at approximately 280 nm, which can be attributed to the three phenyl rings that shows the open form of the molecule.

An exception in neutral behavior was compound **3b**, which showed other bands under this condition, unlike the other three molecules. In this compound, we can see a band at 446 nm in a neutral medium. In an acid medium, besides the bands already mentioned, we observed the appearance of a new band in three compounds (**3b** = 557 nm, **3c** = 524 nm, and **3d** = 528 nm). The methyl and isopropyl groups are responsible for the different behaviors of **3b**, **3c**, and **3d** in acidic conditions. These groups are electron donors and stabilize the central charge formed in the molecule in its cationic form. Another factor responsible for the absorption in the visible light spectrum is the fact that the isopropyl group is bulky and causes steric hindrance that forces the molecule to seek a more stable conformation, in the case here, a quinoidal structure (in neutral pH conditions) and a cationic structure (for acidic conditions). Different to compound **3a**, the other compounds in neutral media have a shoulder of low molar absorptivity in the spectrum around 400 nm, which

explains the yellowish coloration of the solutions (this band is more intense in **3b**).

As can be seen in Figure 3 and Table 4, except for compound **3a** (phenolphthalein), all other compounds present colors in the various solvents used. The colors vary from shades of yellow to red under neutral conditions in the five solvents studied (Fig. S15 shows all the compounds together). Derivatives **3a**, **3c**, and **3d** show an intense absorption band ranging from 272 to 279 nm in the solvents used. Nevertheless, in compounds **3c** and **3d**, we can see an additional shoulder of low molar absorptivity around 400 nm. This last band justifies

Table 4

The solvent effect in absorption properties of phthalein derivatives.

	Absorption measurement in different solvents (nm)				
	EA	DMSO	EtOH	MeOH	THF
3a *	276	278	276	276	273
3b	280; 409	282; 430	281; 446	281; 447	275; 413
3c *	277	279	275	277	272
3d *	275	276	275	275	273

*The compounds showed a shoulder from the band around 280nm until 420nm.

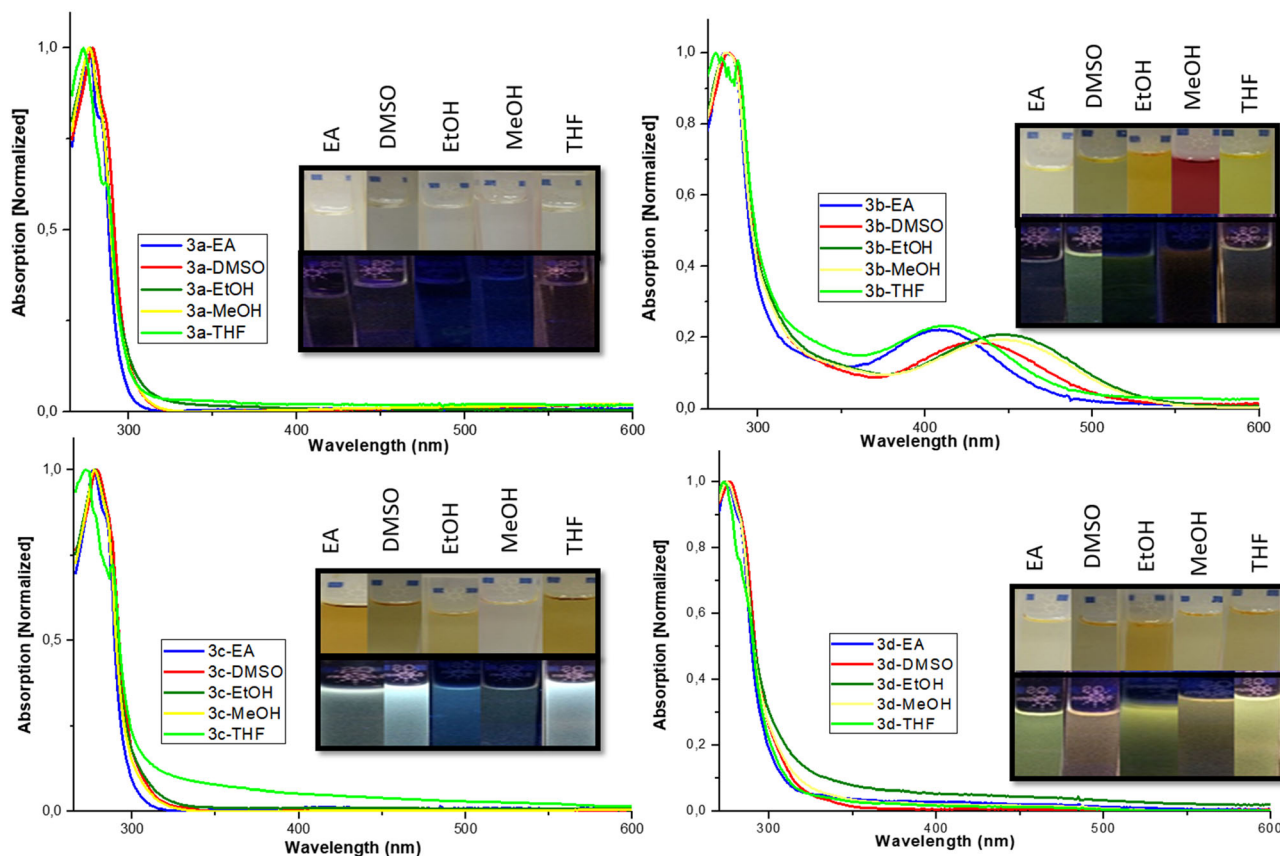


Figure 3. The solvent effect in absorption properties of phthalein derivative [10^{-5} M]. [Color figure can be viewed at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com)]

the yellowish color of these compounds in solution. The derivative **3b** had two absorption bands: the first around 275–282 nm and the second around 409–447 nm.

Compound **3b** shows the second absorption band in the various solvents, because as already mentioned, the isopropyl group favors the open quinoidal form that is conjugated and absorbs in the visible light spectrum. Although methanol has no difference in relation to ethanol in the shift, we see that methanol has a higher epsilon value (higher intensity), due to the higher solubility of the compound in methanol. The compounds, when irradiated with 365-nm UV light, showed weak emissions, except **3a** (phenolphthalein) that does not show luminescence behavior.

The absence of phenolphthalein emission (**3a**) has already been reported in the literature [20]. This happens because in phenolphthalein, we have a great thermal deactivation due to the freedom of oscillation, but the participation of the triplet state in non-radiative deactivation also has an effect on this process. Despite the cuvette images showing the fluorescence of these other derivatives, the fluorescence emission measurements did not show well-defined spectra with a single emission band.

In addition, the intensity of this emission measure by the fluorescence quantum yield (Φ_f) is very low. For this reason, we cannot assign maximum emission wavelength values to these compounds in the media. The emission spectra images of the compounds in the various solvents and with acid–base effects can be seen in Figures S16, S17, and S18 in the Supporting information.

EXPERIMENTAL

Structures in acid (cationic) and basic (mono and dianionic) structures are already known and do not present many structural modifications. However, in the neutral form, we have three forms that can be determined in the understanding of the spectral structure in the different solvents studied. The molecular rearrangement can be analyzed by molecular modeling using the B3LYP functional. The groundstate geometries were optimized by density functional theory using the Becke three-parameter Lee–Yang–Parr exchange–correlation functional (B3LYP) and electronic structure method (6–31 + G(d,p) basis set) [21–24]. This information can show us the most stable

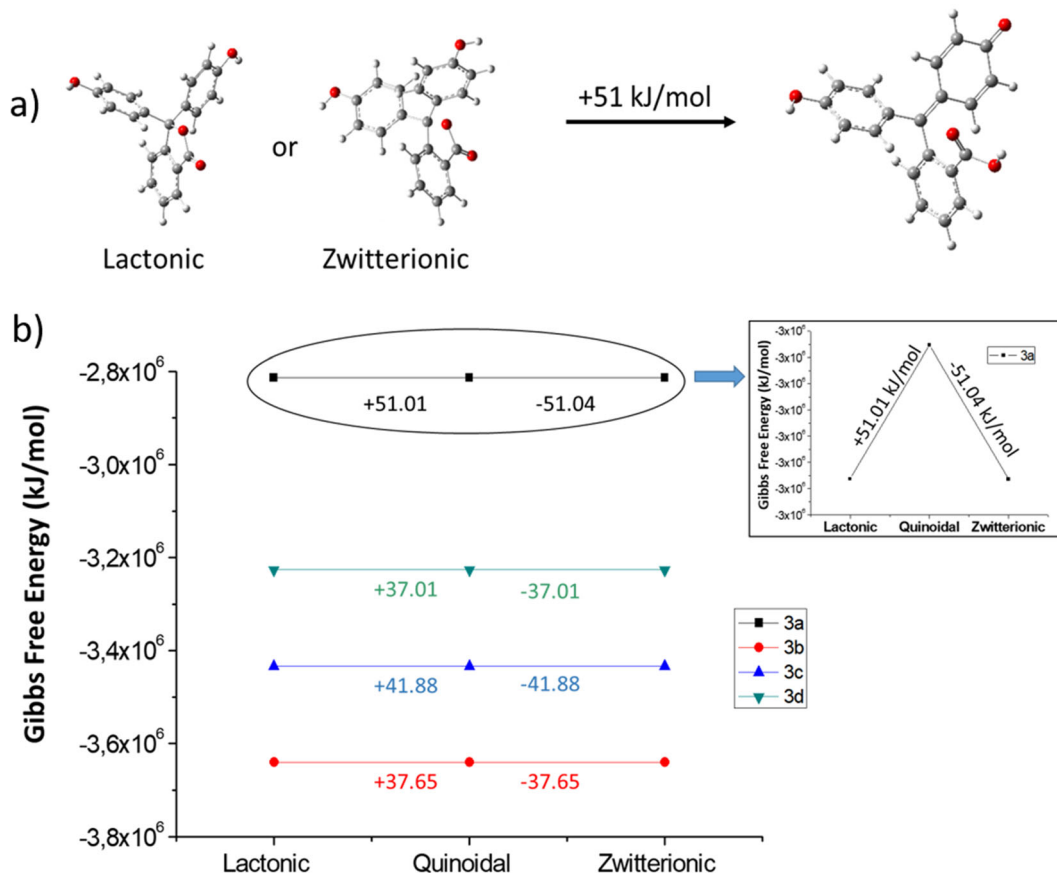


Figure 4. (a) B3LYP calculation of molecular rearrangement. (b) Gibbs free energy diagram. [Color figure can be viewed at wileyonlinelibrary.com]

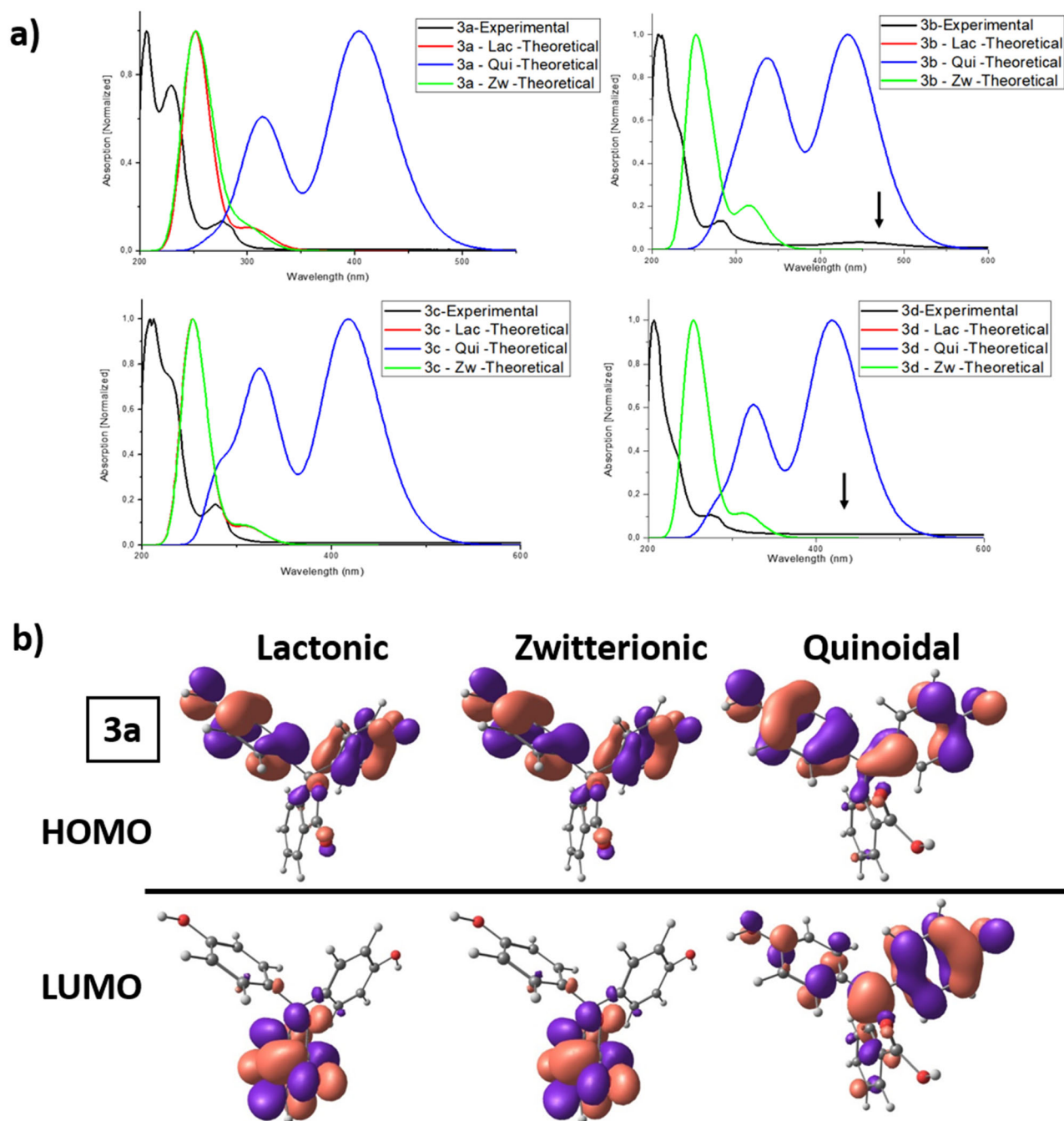


Figure 5. (a) Experimental and theoretical absorption graphic of phthalein derivatives, compounds **3a**, **3b**, **3c**, and **3d**. (b) Molecular orbitals of lactonic, zwitterionic, and quinoidal form, of phthalein **3a**. [Color figure can be viewed at wileyonlinelibrary.com]

structure and help explain the absorption of the compounds depending on the number of conjugated bonds. As we see in Figure 4, the structures of phthalein derivatives can assume different conformations depending on the medium. The lower Gibbs free energy shows that the more stable structure comes from the lactonic and zwitterionic structures that show almost the same energy for all the compounds. The quinoidal form gains about 37–51 kJ/mol as we can see in Figure 4a. In Figure 4b, the energy

differences among the compounds are shown. In Figure S19 and Table S1, we can see all the optimized structures and the Gibbs free energy of the four compounds in the lactonic, zwitterionic, and quinoidal forms [21–24].

In Figure 4b, it is observed that the Gibbs free energy for the compounds decreases in the following order $3a > 3d > 3c > 3b$. The lactonic and zwitterionic forms have similar energies. The major difference between the lactonic and zwitterionic forms of the quinoidal form

comes from compound **3a** that presents a difference of 51 kJ/mol. Compounds **3b** and **3d** show a difference of approximately 37 kJ/mol. Compound **3c** has an energy difference of approximately 42 kJ/mol.

In Figure 5a, we can see the experimental and theoretical spectrum of the phthalein derivatives. As shown here, the lactonic and zwitterionic forms exhibit a similar absorption spectrum with two bands, the first, intense, at approximately 250 nm and the second with lower intensity close to 320 nm. In the quinoidal form, we also have two absorption bands, the first near 340 nm and the second around 430 nm. The shape of the experimental curve, as well as the shift in the spectra, shows that in the conditions measured in ethanol solution, we have the lactonic and zwitterionic forms. However, in the experimental spectrum of compounds **3b** and **3d**, we see a band of low intensity above 400 nm. This band suggests that these compounds have a small amount in quinoidal form. This is proven by the more intense color of these compounds in ethanol. Another factor that justifies the presence of the quinoidal form is the small energy barrier of **3b** and **3d** that exists between the forms (37 kJ/mol). As already mentioned earlier, this is due to the fact that these compounds have relatively bulky substituents, which may, by steric hindrance, favor the quinoidal form.

In the molecular orbitals (MOs), we observed the same behavior for all derivatives (Fig. S20). Here, we showed only the MOs for compound **3a** (Figure 5b). A push-pull effect can be seen with well-localized MOs, showing a charge transfer character in the molecule (CT) [25]. In general, HOMO is located in the part of the phenol ring. LUMO in the lactonic and zwitterionic forms is located in the lactonic ring and in the carboxylate ion, respectively. Here, again, we observe the similarity in the lactonic and zwitterionic forms, where MOs are located in the same parts of the molecular structure. For the quinoidal form, we did not observe the push-pull effect on the molecule. HOMO and LUMO are located in the part of the molecule originating from the phenol.

CONCLUSION

It is concluded that NbCl₅ is a good catalyst for the synthesis of phthalein derivatives, because the reactions occur in low reaction times and with high yields, using low concentrations of NbCl₅ (25 mol %). These derivatives have good applications for use as acid-base indicators, obtaining good color variation at different pH values. The derivatives obtained absorptions within the range of the visible light spectrum and with high intensities of absorption when dissolved in alkaline

solution. The presence of alkyl groups stabilizes the negative charge of the anionic form of the dye, increasing the intensity of absorption in basic media. The presence of these alkyl groups in some cases can shift the absorption lengths of these derivatives bathochromically. Theoretical calculations using B3LYP functional helped us to show the differences in energy of the three different forms of each compound. In this study, we observed the greater stability of the lactonic and zwitterionic forms in relation to the quinoidal. This behavior was also seen in the MOs.

Acknowledgments. The authors would like to thank Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) (procs. 2012/24199-8, 2015/00615-0, 2016/01599-1, and 2018/14506-7), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) (proc. 302769/2018-8) and Pró-Reitoria de Pesquisa (PROPE-UNESP) for their financial support. We would also like to thank Companhia Brasileira de Mineralogia e Mineração (CBMM) for the NbCl₅ samples.

REFERENCES AND NOTES

- [1] (a) Henrique Arpini, B.; de Andrade Bartolomeu, A.; Andrade, K. Z.; Carlos da Silva-Filho, L.; Lacerda, V. *Curr Org Synth* 2015, 12(5), 570. (b) Dos Santos, G. C.; de Andrade Bartolomeu, A.; Ximenes, V. F.; da Silva-Filho, L. C. *J Fluoresc* 2017, 27, 271. (c) Martins, L. M.; de Faria Vieira, S.; Baldacim, G. B.; Bregadiolli, B. A.; Caraschi, J. C.; Batagin-Neto, A.; da Silva-Filho, L. C. *Dyes Pigm* 2018, 148, 81.
- [2] Andrade, Z.; Carlos, K. *Curr Org Synth* 2004, 1(4), 333.
- [3] (a) Gore, P. H. *Chem Rev* 1955, 55, 229. (b) Calloway, N. O. *Chem Rev* 1935, 17, 327. (c) Bandini, M.; Melloni, A.; Umami-Ronchi, A. *Angew Chem Int Ed* 2004, 43(5), 550.
- [4] (a) da Silva Barbosa, J.; da Silva, G. V. J.; Constantino, M. G. *Tetrahedron Lett* 2015, 56, 4649. (b) da Silva, B. H. S. T.; Bregadiolli, B. A.; Graeff, C. F. D. O.; da Silva-Filho, L. C. *ChemPlusChem* 2017, 82(2), 261.
- [5] Sabnis, R. W. *Tetrahedron Lett* 2009, 50, 6261.
- [6] Sabnis, R. W. *Handbook of Acid-Base Indicators*; CRC Press: Boca Raton, Fla, 2008.
- [7] Sabnis, R. W. *Color Technol* 2018, 134, 187.
- [8] Jha, A.; Garade, A. C.; Mirajkar, S. P.; Rode, C. V. *Ind Eng Chem Res* 2012, 51, 3916.
- [9] Sabnis, R. W. *Color Technol* 2018, 134, 347.
- [10] Kukreti, V.; Chamoli, R. P. *Dyes Pigm* 1996, 32, 15.
- [11] (a) Bhuchar, V. M.; Kukreja, V. P.; Das, S. R. *Anal Chem* 1971, 43(13), 1847. (b) Takezawa, H.; Akiba, S.; Murase, T.; Fujita, M. *J Am Chem Soc* 2015, 137, 7043.
- [12] Arbeloa, F. L.; Costela, A.; Arbeloa, I. L. *J Photochem Photobiol A Chem* 1990, 55, 97.
- [13] Lakowicz, J. R. *Principles of frequency-domain fluorescence spectroscopy and applications to cell membranes*; In *Fluorescence studies on biological membranes*; Springer: Boston, MA, 1988, pp 89–126.
- [14] Sabnis, R. W. *Phthalein Dyes*; In *Kirk-Othmer Encyclopedia of Chemical Technology*; Wiley-Interscience: Hoboken, N.J., 2000, pp 1–21.
- [15] Mukhopadhyay, A.; Mishra, A. K.; Jana, K.; Moorthy, J. N. *J Photochem Photobiol A Chem* 2017, 347, 199.
- [16] Benassi, E.; Carlotti, B.; Fortuna, C. G.; Barone, V.; Elisei, F.; Spalletti, A. *Chem A Eur J* 2015, 119, 323.
- [17] Yang, Z.; Qin, W.; Lam, J. W.; Chen, S.; Sung, H. H.; Williams, I. D.; Tang, B. Z. *Chem Sci* 2013, 4, 3725.

- [18] Schmitt, V.; Moschel, S.; Detert, H. *Eur J Org Chem* 2013, 2013, 5655.
- [19] Khan, M. I.; Mukherjee, K.; Shoukat, R.; Dong, H. *Microsyst Technol* 2017, 23, 4391.
- [20] Boguta, A.; Wróbel, D. *J Fluoresc* 2001, 11, 129.
- [21] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E., Robb, M. A.; Cheeseman, J. R.; Nakatsuji, H. *Gaussian 09*, revision A. 1. Gaussian Inc., Wallingford, 2009.
- [22] (a) Becke, A. D. *J Chem Phys* 1993, 98, 5648; (b) Ditchfield, R. H. W. J.; Hehre, W. J.; Pople, J. A. *J Chem Phys* 1971, 54, 724.
- [23] (a) Miertuš, S.; Scrocco, E.; Tomasi, J. *Chem Phys* 1981, 55, 117; (b) Mennucci, B. *Wiley Interdiscip Rev: Comput Mol Sc* 2012, 2, 386.
- [24] De Meyer, T.; Hemelsoet, K.; Van Speybroeck, V.; De Clerck, K. *Dyes Pigm* 2014, 102, 241.
- [25] Pavia, D. L.; Lampman, G. M.; Kriz, G. S.; Vyvyan, J. A. *Introduction to spectroscopy*. 4th ed.; United States: Cengage Learning, 2008, 579.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.