

Chapter 3: Solvato and acidochromic properties of compounds 4i-q

Solvent effect plays an important role in the photophysical properties of organic molecules. Acidochromic compounds have applications in sensor techniques and medical diagnostics. They can response to pH variations *via* protonation/deprotonation processes by showing different absorption spectra.³⁵ The present study investigates the spectral behaviors of the new Schiff bases **4i-q** derivatives (Fig. 53) and their pH sensing behavior.

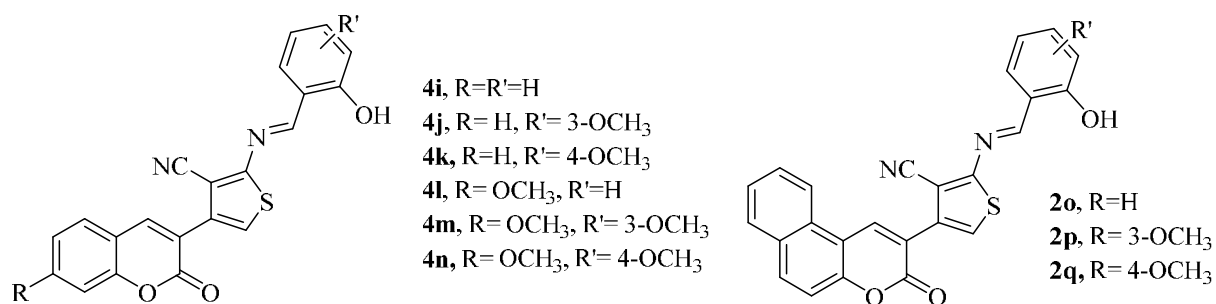
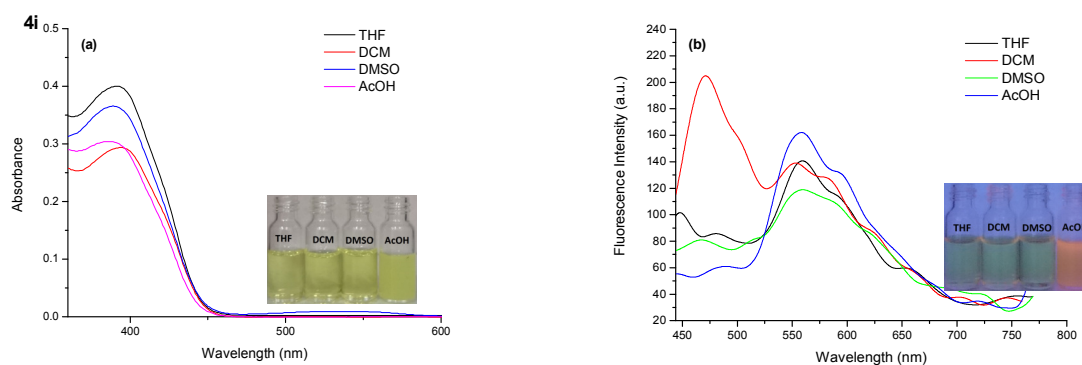
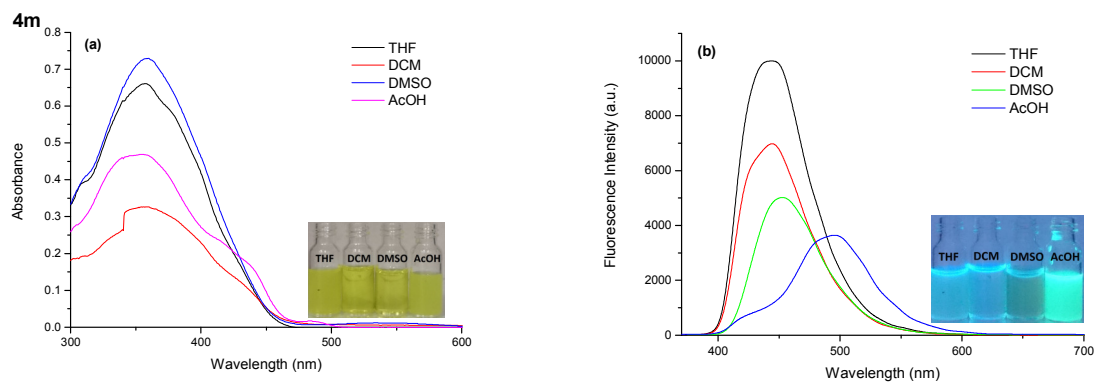
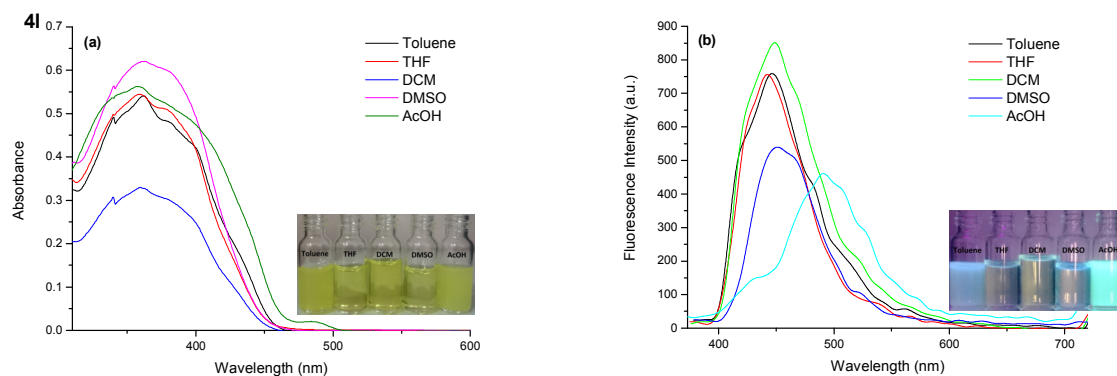
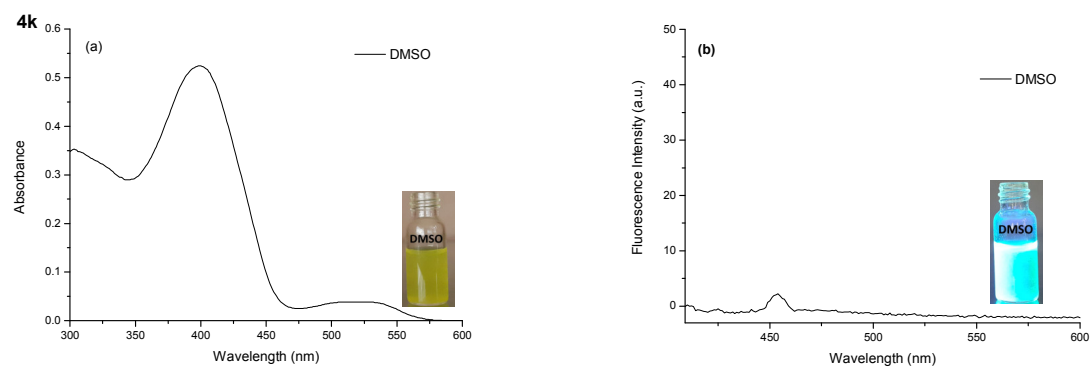
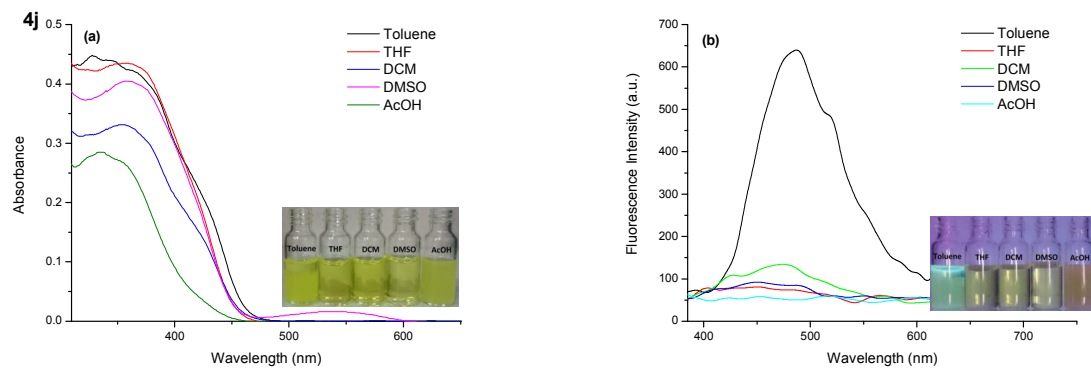


Fig. 53. Structures of compounds 4i-q.

I. Absorption and Fluorescence Properties of compounds 4i-q

The solvatochromic behavior of the Schiff bases **4i-q** was studied in five solvents with different polarities; toluene, THF, DCM, DMSO and acetic acid. The results are represented in Fig. 54 and Table 8.





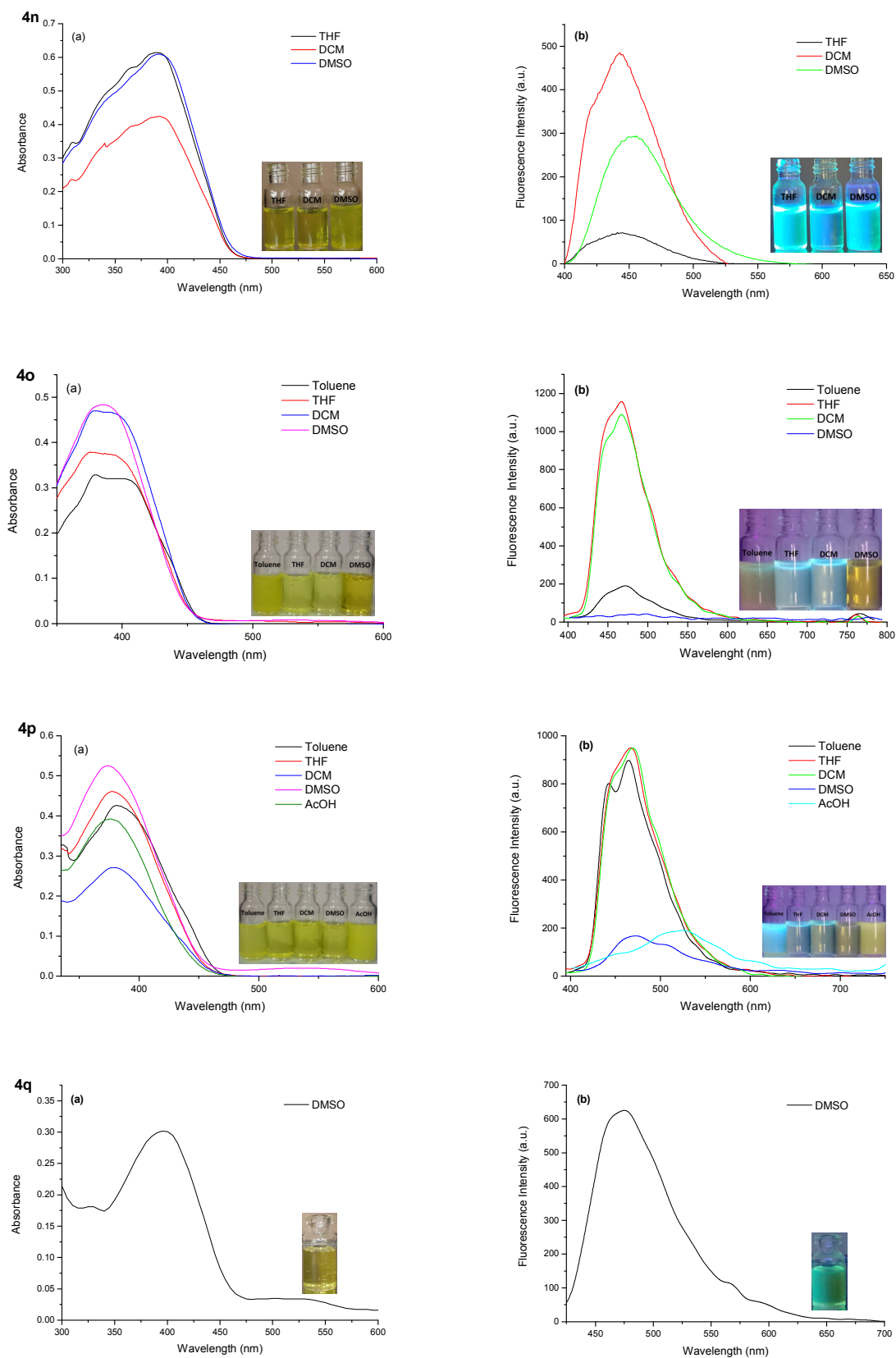


Fig. 54. (a) Absorption spectra and (b) Emission spectra of compounds **4i**, **4j**, **4k**, **4l**, **4m**, **4n**, **4o**, **4p** and **4q** in different solvents. Insets: Photographs of the solutions (1×10^{-3} M).

Table 8. Spectrophotometric properties of compounds **4i-q**.

Solvent ^[a]	4i				4j			
	λ_{abs} ^[b]	λ_{fl} ^[c]	Stokes shift ^[d]	ϵ ^[e]	λ_{abs} ^[b]	λ_{fl} ^[c]	Stokes shift ^[d]	ϵ ^[e]
Toluene	-	-	-	-	328	487	159	22200
THF	392	559	167	25800	357	449	92	29800
DCM	393	470-553	160	16000	355	447	92	20300
DMSO	389	560	171	23500	357	444	86	22300
Acetic acid	385	558	173	16600	335	478	143	10900
Solvent ^[a]	4k				4l			
	λ_{abs} ^[b]	λ_{fl} ^[c]	Stokes shift ^[d]	ϵ ^[e]	λ_{abs} ^[b]	λ_{fl} ^[c]	Stokes shift ^[d]	ϵ ^[e]
Toluene	-	-	-	-	361	446	85	39500
THF	-	-	-	-	359	442	83	27900
DCM	-	-	-	-	360	449	89	32600
DMSO	399	460	61	30800	364	451	87	28400
Acetic acid	-	-	-	-	358	491	133	23500
Solvent ^[a]	4m				4n			
	λ_{abs} ^[b]	λ_{fl} ^[c]	Stokes shift ^[d]	ϵ ^[e]	λ_{abs} ^[b]	λ_{fl} ^[c]	Stokes shift ^[d]	ϵ ^[e]
Toluene	-	-	-	-	-	-	-	-
THF	357	444	87	46100	389	441	52	31300
DCM	359	444	85	36800	391	443	52	25400
DMSO	357	453	94	38200	391	456	65	37700
Acetic acid	354	496	142	23400	-	-	-	-
Solvent ^[a]	4o				4p			
	λ_{abs} ^[b]	λ_{fl} ^[c]	Stokes shift ^[d]	ϵ ^[e]	λ_{abs} ^[b]	λ_{fl} ^[c]	Stokes shift ^[d]	ϵ ^[e]
Toluene	379	473	94	26300	381	443-465	84	22500
THF	377	467	90	28300	378	467	89	30700
DCM	379	467	88	34200	377	469	92	38100
DMSO	386	480	94	20900	374	472	93	39200
Acetic acid	-	-	-	-	376	527	151	24500
Solvent ^[a]	4q							

	$\lambda_{\text{abs}}^{[b]}$	$\lambda_{\text{fl}}^{[c]}$	Stokes shift ^[d]	$\epsilon^{[e]}$
Toluene	-	-	-	-
THF	-	-	-	-
DCM	-	-	-	-
DMSO	395	475	80	-
Acetic acid	-	-	-	-

^[a] In order of their increasing E_{T}^{N} values;¹⁴ ^[b] long-wavelength absorption maximum, in nm; ^[c] fluorescence emission maximum, in nm; ^[d] Stokes shift in nm; ^[e] extinction coefficient, $\text{cm}^{-1}\text{M}^{-1}$.

The compounds are non fluorescent solids showing one absorbance maxima in all the solvents, ranging between 328-399 nm. The yellowish color of the solutions explains the appearance of the absorbance bands in the same region (Insets, Fig. 54).

The emission spectra were recorded with the excitation wavelengths corresponding to the maximum absorption bands. According to the substituent the properties vary, for **4i**, **4j** and **4k**, prepared from the simple coumarin, the emission spectra had to be recorded at a high concentration and with a slit width of 5 nm for both excitation and emission, in order to get good signals. An increase in the extent of the π -electron system (i.e. degree of conjugation) leads to an increase in the fluorescence intensity, thus compounds **4l**, **4m** and **4n** with a methoxy group at the 7-position of the coumarin ring and compounds **4o**, **4p** and **4q** with a conjugated phenyl group, had the best emission spectra.

The compounds exhibited high fluorescence intensity in toluene except for **4i**, **4k**, **4m**, **4n** and **4q** which were not soluble in it. A red shift in the emission spectra for **4l**, **4m** and **4p** was observed in acetic acid. The Stokes shifts of all the compounds soluble in acetic acid were greater than in the other solvents. Compounds **4k** and **4q** were only soluble in DMSO with an absorption and emission maxima of 399 nm and 460 nm, respectively, for **4k**, and 395 nm and 475 nm for **4q**.

II. Acidochromic properties of compounds 4i-q

The acidochromic properties of compounds **4i-q** were evaluated by adding increasing concentrations of TBAOH to a solution of **4i-q** in DMSO (2×10^{-5} M). The neutral compounds had one absorption maxima near the visible region (357-399 nm), addition of TBAOH led to a bathochromic shift of 115-180 nm, of the main peak, and new bands in the visible region appeared (512-538 nm), accompanied by a dramatic color change of the solutions from light yellow to pink. This long wavelength absorption band is a characteristic of the deprotonation of the OH group.

As depicted in Fig. 55a, the addition of 5 equivalents of TBAOH to a DMSO solution of **4i** led to a large bathochromic shift of 144 nm. A new band at 533 nm appeared while the band at 389 nm underwent a hypochromic shift along with the formation of an isosbestic point, and accompanied by a color change of the solution from pale yellow to pink. For compounds **4i**, **4j** and **4k**, the hypochromic shift of the original bands at 389, 340 and 399 nm, respectively, was more pronounced than for the other compounds (Fig. 55). For example, as can be seen in Fig. 56, for **4p** the hypochromic shift of the peak at 374 nm, was not intense like for the three compounds mentioned above. For compounds **4n** and **4q** the original bands at 397 nm went through a hypochromic shift plus a hypsochromic shift of 53 and 31 nm, respectively, after the addition of TBAOH (Fig. 57).

The largest bathochromic shift was 180 nm, and was observed with compound **4j**.

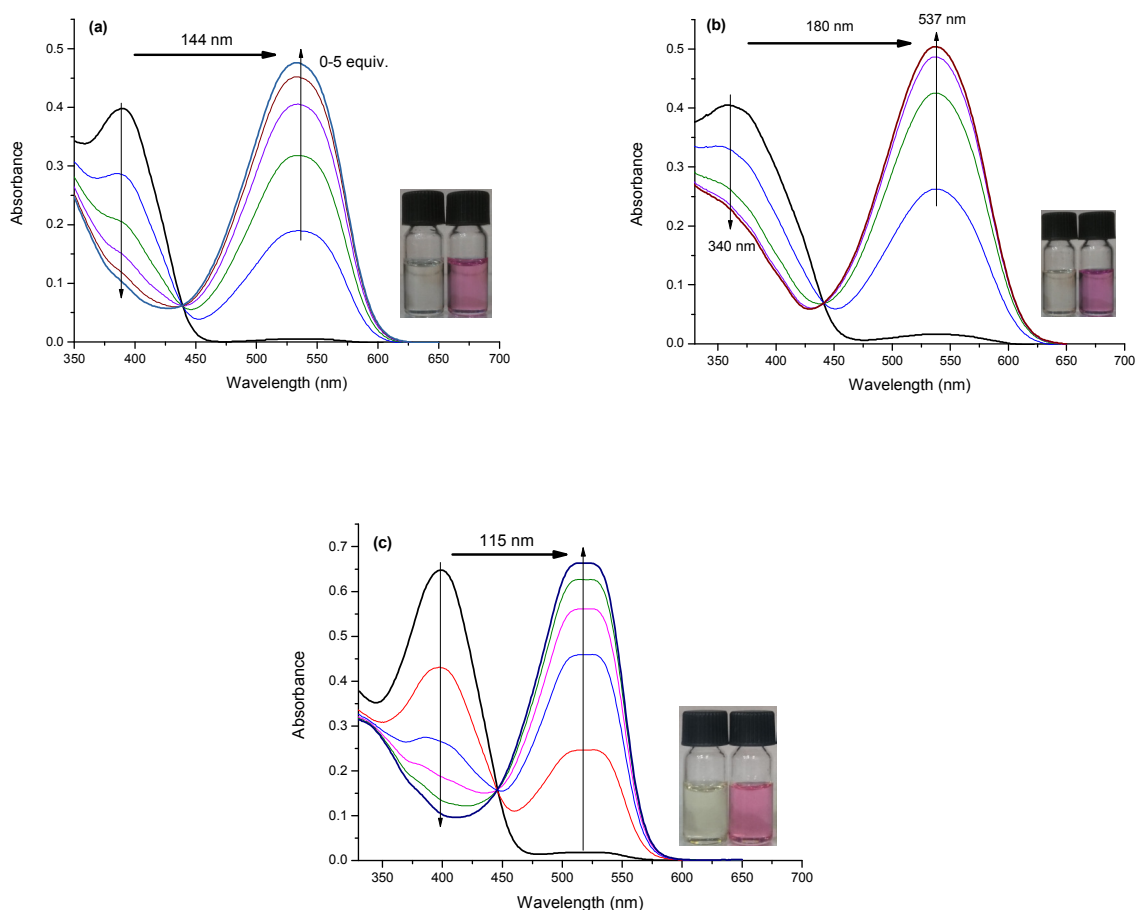


Fig. 55. UV-vis spectral changes of **4i** (a), **4j** (b) and **4k** (c) (2×10^{-5} M in DMSO) upon addition of TBAOH.

Insets: photographs of **4i**, **4j** and **4k** in DMSO before and after addition of TBAOH.

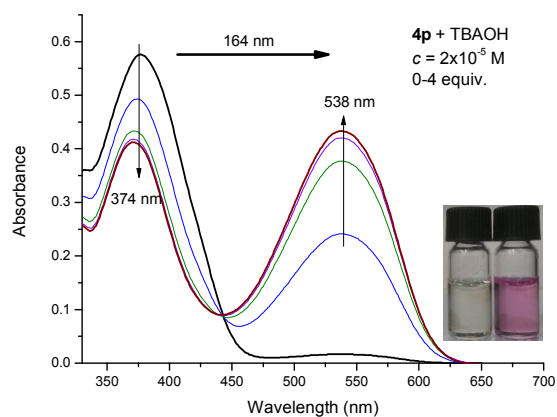


Fig. 56. UV-vis spectral changes of **4p** (2×10^{-5} M in DMSO) upon addition of TBAOH. Inset: photograph of **4p** in DMSO before and after addition of TBAOH.

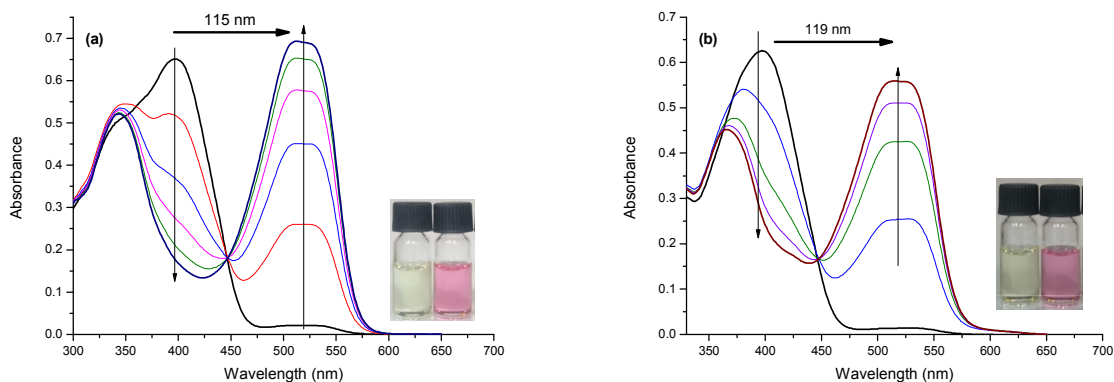


Fig. 57. UV-vis spectral changes of **4n** (a) and **4q** (b) (2×10^{-5} M in DMSO) upon addition of TBAOH. Insets: photographs of **4n** and **4q** in DMSO before and after addition of TBAOH.

Moreover, the original UV-vis spectra and the yellow color are recovered after addition of 3 equivalents of a TFA solution (Fig. 58 for **4i**), which is an evidence for the reversibility of the deprotonation that takes place.

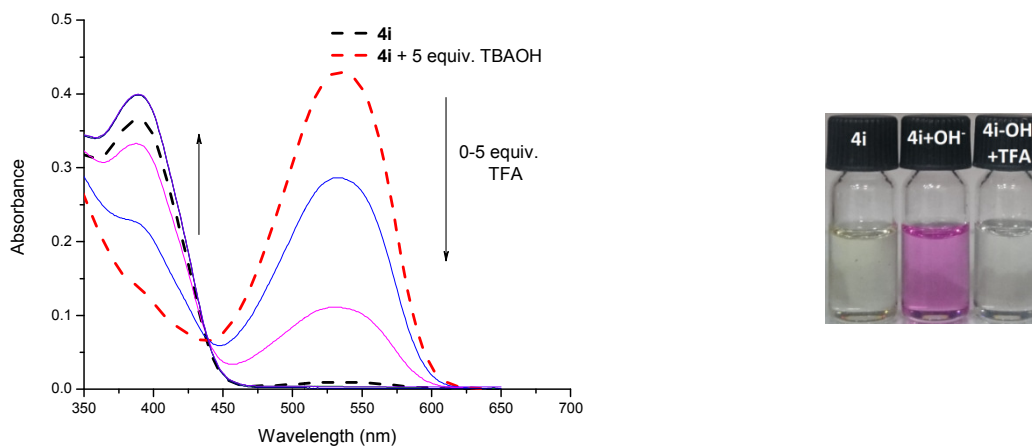


Fig. 58. Absorption spectra showing the reversibility of the acidochromic properties of **4i** (2×10^{-5} M in DMSO) after addition of TFA.

The deprotonation of these derivatives revealed the formation of new red shifted absorption bands with very large bathochromic shifts of the main bands, and a color change of the solutions from light yellow to pink, making them very good acidochromic pH sensors. Those changes are attributed to an increase in the ICT efficiency of the molecules. Similar acidochromic characteristics of the other compounds, as well as their reversibility, can be found in Figs. A30-A40 in Annex 1.

Conclusion

In summary, the solvato- and acidochromic properties of compounds **4i-q** have been reported. The absorption spectra are less sensitive to the solvent characteristics than the corresponding fluorescence spectra. Dramatic shifts in the absorption spectra as well as an obvious color change were observed upon treatment with TBAOH due to deprotonation of the $-\text{OH}$ group. Reversibility of absorbance intensity of the sensors shows that the system is stable in both basic and acidic media. The significant spectral and color changes could be attributed to an increase in the ICT character of the compounds.

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