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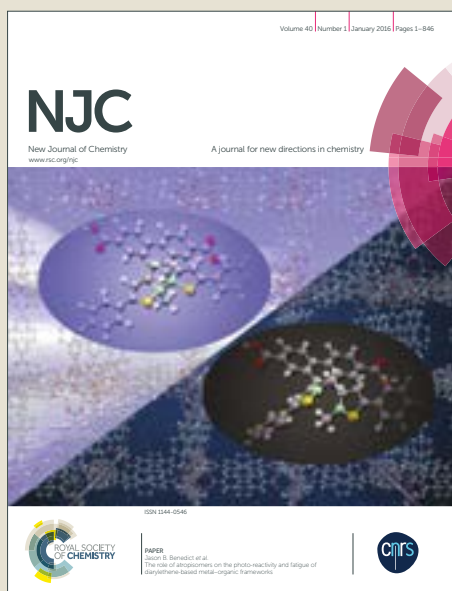
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Subphthalocyanine basicity: reversible protonation at the azomethine bridge.

 Yann Bernhard,^a Vivian Lioret^a and Richard A. Decréau^a

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Abstract: Subphthalocyanine (SubPc) could be reversibly protonated at the azomethine bridge. This phenomenon was examined by addressing the pKa of the acid (TFA, MSA, TMSA) and the SubPc electron-withdrawing properties of the peripheral isoindolic substituents (F₁₂ vs H₁₂ and NO₂), which tunes the basic character of the azomethine moiety. The protonation of up to three azomethines was suggested and monitored spectrophotometrically: appearance of new absorption bands at 610, 630 nm and 660 nm, together with marked colour change from purple to blue to green. Evidence of such a protonation was also shown by significant changes in the ¹H-NMR spectrum and new bands in the infrared spectrum.

Introduction. Subphthalocyanines (SubPc) are tris-isoindole analogues of phthalocyanines.¹ They are used as synthons in the synthesis of A3B phthalocyanines, and also in various photonic processes, such as photovoltaics,² and optical imaging.³ The chemistry of this domed structure has been explored obviously on the ring opening chemistry front,⁴ but also on the apical substitution at the Boron atom.⁵ Reaction with an acid is also of interest: it may drastically affect both the reactivity and the optical properties of the macrocycle. Reactivity with Lewis acids was examined for the apical substitution reaction:⁶ in the presence of aluminium trichloride, a reaction with SubPc takes place leading to a blue coloration that is interpreted as the interaction of AlCl₃ with bridging nitrogen atoms (acide-base interaction). Reactivity with Brønsted acid was also mentioned, through the possibility to achieve the protonation of azomethine bridges of subphthalocyanines with H₂SO₄.^{1b} Prior reports on the protonation of porphyrins and phthalocyanines has also been reported. For example, mixing phthalocyanines in sulfuric acid or TFA leads to the formation of brown species, that may be

interpreted as the protonation of one or several azo-bridges.^{7ad} As we were working on the protonation of subphthalocyanines (the actual study) a careful study came up addressing the basicity of azomethine in phthalocyanines depending upon the nature of the substituents at the 4,5 or 3,6 positions.^{7cd} Herein, we report a detailed study on the reaction of SubPc with Brønsted acids: the reversible protonation of H₁₂/F₁₂ subphthalocyanines was examined with a series of acids the pKa of which range from ca. -15 to 0 (table 1). Hence, such a study explored the possibility to achieve the protonation of up to three azomethine bridges (Fig 1).⁴ Protonations were examined by UV/Vis, ¹H-NMR and infrared spectroscopies.

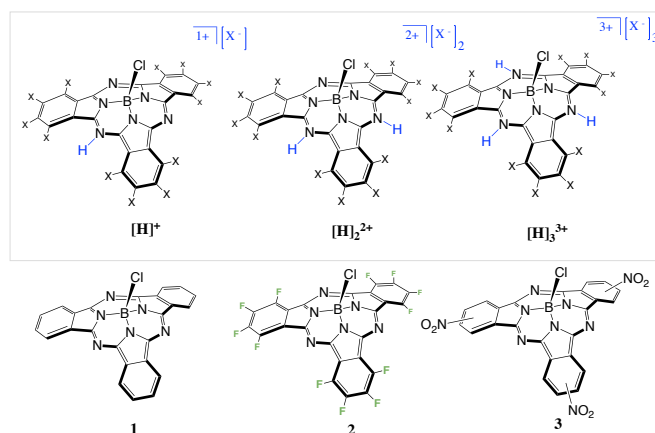
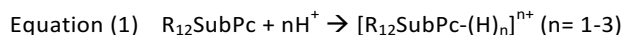


Fig. 1 Top: examples of protonation states in subphthalocyanines. Bottom: protonation of aza-bridges in X₁₂-Subphthalocyanine (X = H, F), i.e. subphthalocyanine **1**, hexadecafluorophthalocyanine **2**, or tris-nitro-subphthalocyanine **3**.³ The synthesis of species **1-3** was reported previously.^{3a-c}

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† Footnotes relating to the title and/or authors should appear here. Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

UV-Vis. Organic acids as opposed to inorganic acids were used to achieve the synthesis of protonated subphthalocyanine in order to prevent the presence of water presumably responsible for the

instability of such protonated species. Herein protonation studies were carried out using trifluoroacetic acid (TFA, $pK_a = 0.3$), methanesulfonic acid (MSA, $pK_a = -1.9$) and trifluoromethanesulfonic acid (TMSA, $pK_a = -14.9$). A spectrophotometric titration was achieved by monitoring the absorbance upon addition of acid, hence allowing to demonstrate the first protonation step. Upon addition of TFA to a solution of H_{12} SubPc **1** an absorption band lying at 610 nm shows up, while the main band decays at the same time, while an isobestic point was observed. Judging from the evolution of the band, it seems that TFA is not strong enough to complete the protonation of the SubPc (Figure 2 (top), Table 1). The absorbance of protonated **1** decreases very slowly over time (Figure 2 (bottom)). The decay is small after 2h (ca < 10%), and is about 40-50% after 8h.

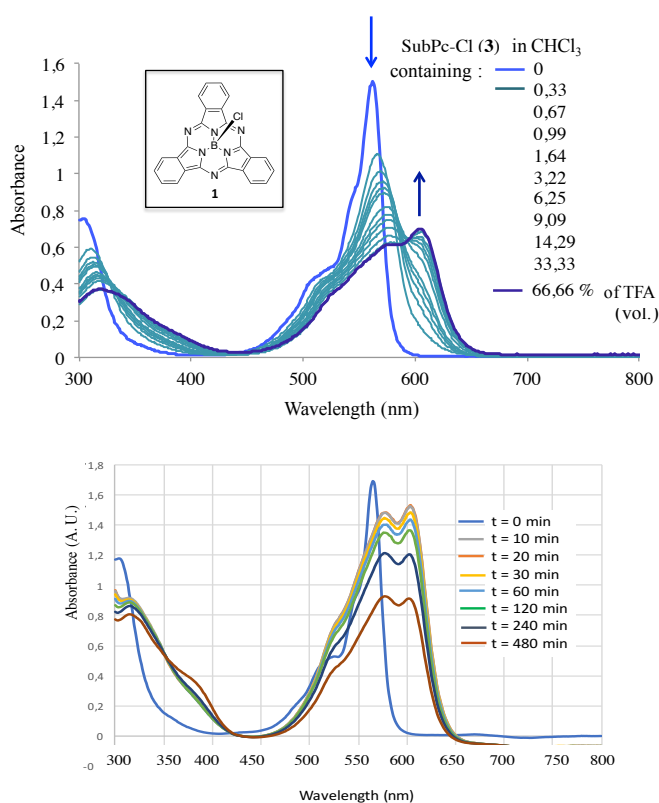


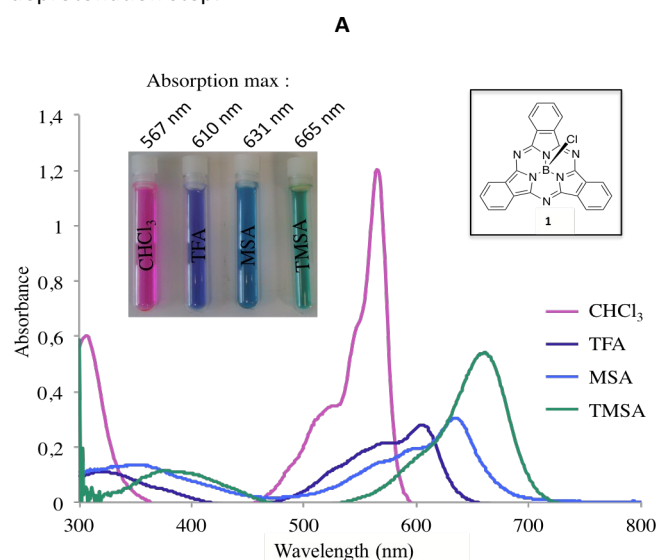
Fig. 2 Titration with TFA. *Top.* Overlapping of absorption spectra of **1** in chloroform with increasing amounts of TFA. *Bottom.* Monitoring the absorbance of protonated **1** over time (decay becomes substantial after 2h).

	pK_a	H_{12} -SubPc 1	F_{12} -SubPc 2	Estimated number of protonated azomethynes H_{12} / F_{12}
$CHCl_3$		567	575	0 / 0
TFA	0.3	610	575	1 / 0
MSA	-1.9	631	629	2 / 2
TMSA	-14.9	665	674	3 / 3

Table 1 . H_{12} vs F_{12} Subphthalocyanine absorption bands upon protonation with acids of decreasing pK_a values.

When subphthalocyanine **1** was in the presence of a stronger acid, such as TMSA or MSA, new absorption bands appeared, together with color changes from pink to purple, blue, and green, respectively. When SubPc **1** was in solution in MSA ($pK_a = -1.9$) its absorption spectrum shows the appearance of an absorption band at 631 nm (Fig 3A, pale blue line). When **1** was in solution in TMSA ($pK_a -14.9$) the maximum absorption band that could be detected lies at 665 nm (Fig 3A, green line). When SubPc was in solution in a dichloromethane/TMSA mixture (1:1 vol.) as opposed to pure TMSA, the compound precipitates, which may be an indication that the formed compound is a multi-charged species (i.e. protonated at several azomethine bridges). The same set of studies was carried out with electro-deficient subphthalocyanine **2** that bears 12 electron-withdrawing fluorine atoms. When **2** was in solution in strong acids, such as MSA and TMSA (Figure 3B), absorption bands at 665 nm (blue line) and 674 nm (green line) appeared, which is reminiscent of the results with H_{12} -SubPc **1**. However, when **2** was in less acidic TFA ($pK_a = 0.3$) protonation does not seem to occur as no shift in the absorption band was noticed (Fig. 3B, pink line, table 1), i.e. the UV/Vis shift corresponding to a mono-protonated species is almost not observed). This set of UV/Vis titrations seems to indicate that the titration of the azomethine bridges is a function of the electron density of the macrocycle.

Reversibility. Upon addition of water or a non nucleophilic base to a solution of the protonated subphthalocyanine, subsequent disappearance of the absorption bands of the protonated species occurs, whereas that of the starting subphthalocyanine is usually restored. Hence, such a protonation process occurring at the azomethine bridges appears to be *reversible*. However, species protonated with MSA and TMSA appear to be less stable during the deprotonation step.



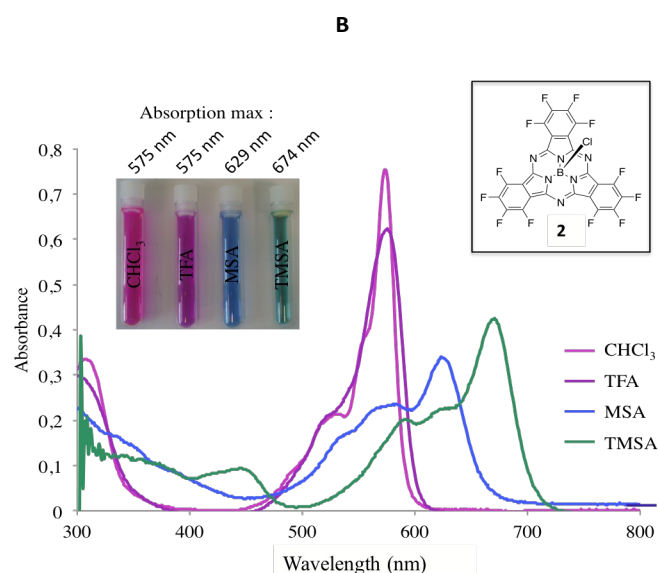


Fig. 3. UV/Vis of H₁₂ (A, top)/F₁₂ (B, bottom) Subphthalocyanines 1,2 in solution in chloroform (pink), TFA (dark blue (top) or purple (bottom)), MSA (pale blue), and TMSA (green). Insert: color of a solution of the respective end-products of compounds 1 and 2 in solution in chloroform, TFA, MSA, and TMSA).

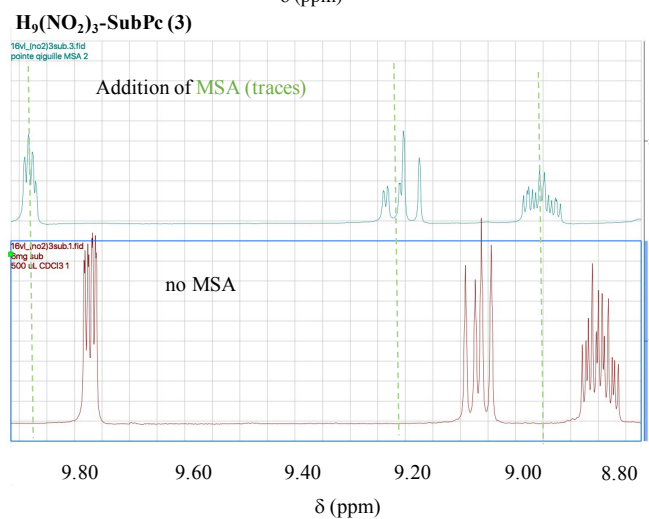
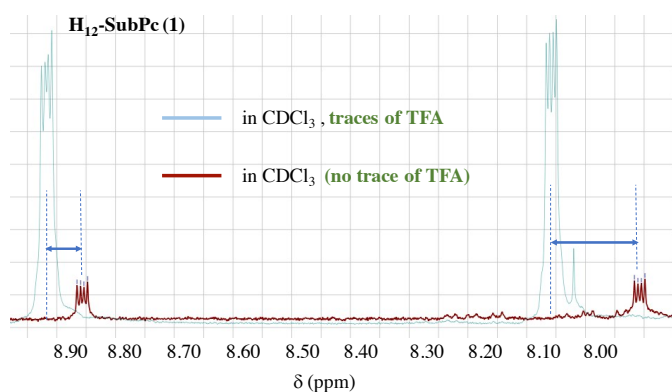


Fig. 4 ¹H-NMR spectra of protonated SubPc **3** (top) and **1** (bottom).

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¹H-NMR. Upon careful addition of trace amount of MSA, groups of peaks in the ¹H-NMR spectrum of H₉-(NO₂)₃-subphthalocyanine **3** are downfield shifted. When more acid was added the perturbation was more pronounced leading to a widespread series of peaks within the window of interest (no precipitation occurred). Hence, it suggests protonation at the subphthalocyanine azomethine bridge. The same trend was confirmed with H₁₂-subphthalocyanine **1**. However, a ¹H-NMR peak corresponding to an iminium-like protonated azomethine bridge (C⁺=N-H) could not be identified. Also, the spectrum measured in deuterated TFA showed changes in SubPc protons chemical shifts suggesting deuteration of the azomethine bridges.

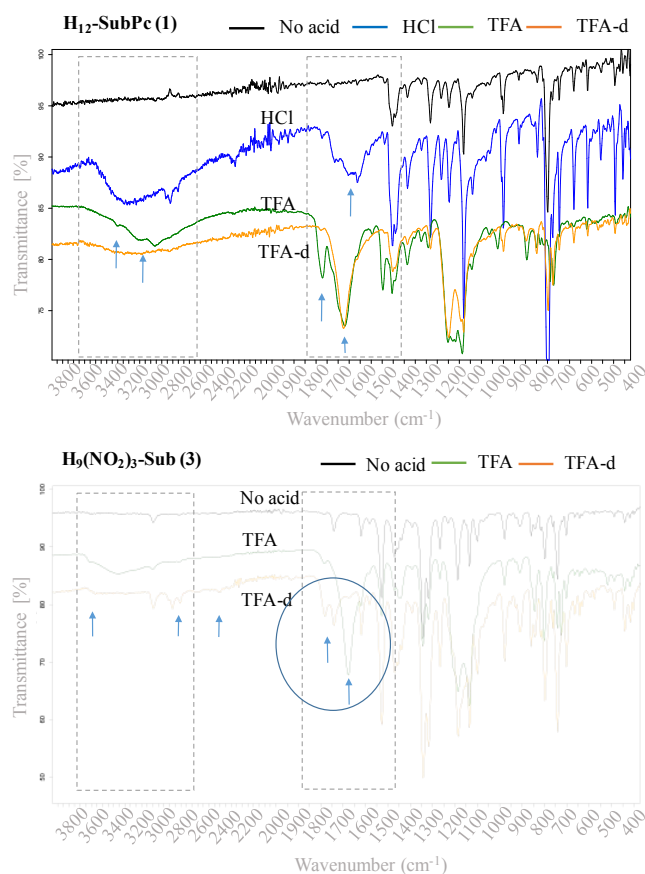


Fig. 5 Infrared spectra of protonated / non protonated SubPc.

	DBU	H ₁₂ -Sub (1)	(NO ₂) ₃ -Sub (3)
HCl	x	1655, 1688	x
	x	3278	x
TFA-H	1643, 1686	1671, 1772	1674
	x	3406, 3209, 3060	x
TFA-d	x	1671, 1772	x

Table 2 Infrared bands (cm^{-1}) addressing a protonation state in subphthalocyanines.

Infrared. Protonation and deuteration of the azomethine bridge was examined on $\text{H}_{12}\text{SubPc}$ (**1**), $\text{H}_9\text{SubPc}((\text{NO}_2)_3)$ (**3**) and diazabicycloundecene (DBU, as a possible control, although protonation at the tertiary amine is expected first) (Figure 5, Table 2) upon thorough comparison with the non-protonated parent species. Based on UV/Vis studies it is expected to lead to several protonation states. Upon addition of acid three sets of new bands appeared: A) A broad signal centered at 3278 cm^{-1} was found when HCl gas or TFA were added. Three distinct features could be seen when TFA was added, such as 3406 cm^{-1} , 3209 cm^{-1} , and 3060 cm^{-1} , some of which may correspond to an N-H stretching frequency in an iminium species. When deuterated TFA was used, a band that may correspond to an iminium $=^+\text{N-D}$ stretching frequency was found at 2400 cm^{-1} . Deuteration to afford N-D with lower stretching frequencies is in accordance with N-H/D stretching shifts found in the literature.⁸ B) Protonation of an imine results in an increase in the C=N frequency.⁸ First, the C=N stretching frequency (in a non-protonated / non-quaternized species) is typically found in the $1620\text{-}1680 \text{ cm}^{-1}$ window, and appeared to be 1620 cm^{-1} in the case of subphthalocyanines **1** and **2**. When HCl gas was added to $\text{H}_{12}\text{-SubPc}$ (**1**) a band at 1657 cm^{-1} appeared. When trifluoroacetic acid (TFA) was added, patterns possibly reminiscent of the trifluoroacetate ion were found,⁹ with bands at 1671 cm^{-1} and 1772 cm^{-1} ($\text{H}_{12}\text{SubPc}$ (**1**)), 1674 cm^{-1} ($\text{H}_9(\text{NO}_2)_3\text{SubPc}$ (**3**)) and 1686 cm^{-1} and 1643 cm^{-1} (DBU), respectively. When deuterated species was added, the band at 1671 cm^{-1} no longer appeared, bands around 1800 cm^{-1} and 2400 cm^{-1} appeared instead. Moreover, protonation also resulted in both shifting bands and leading to the apparition of new bands.

In summary, this set of experiments all combined provide a strong indication about the protonation of the subphthalocyanines azomethine bridges. Subphthalocyanines are usually quite stable in acidic conditions, provided the acid source is organic with no significant amount of water. Preliminary spectrophotometric titrations show the apparition of three new absorption bands, which may concur with the protonation of up to three azomethine bridges available in the SubPc moieties. Protonation of SubPc (at the azomethine bridge) was also evidenced by significant changes in the $^1\text{H-NMR}$ spectrum and new bands that appeared in the infrared spectrum addressing (N-H stretch) and other that were affected (C=N stretch). However, mass spectrometry analyses of a solution of SubPc **1** in solution in TFA did not show a M+1 / M+2 peak indicative of a mono-protonation / mono-deuteration processes, or more protonation/deuteration states ($z > 1$, when MSA was used). Overall such results on subphthalocyanine are relevant to other azomethine-containing species, such as phthalocyanines, salen, rhodopsin. Thorough titration studies are ongoing to determine the

equilibrium constant in various peripherally substituted subphthalocyanines addressing various electronic density (such as **1** and **2**).

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Protonation of subphthalocyanines azomethine bridges is reversible and was evidenced by UV/Vis, $^1\text{H-NMR}$ and IR.

