Super-Sensitive Protonation Behavior of Trifluoroethoxy-Substituted Phthalocyanines and Their Application to Solvent Discrimination

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ABSTRACT: The super-sensitive protonation behavior of trifluoroethoxy-substituted phthalocyanines (TFEO-Pcs) was carefully studied using UV–vis and fluorescence spectroscopy, as well as computational calculations. The practical utility of TFEO-Pcs in sensor technology was demonstrated by identifying chloroform samples from different commercial sources.

INTRODUCTION

Phthalocyanines (Pcs), that is, planar 18 π-electron aromatic compounds that consist of four isoindoline units, are well-known functional dyes, whose unique electronic and optical properties have led to applications in advanced materials such as dye-sensitized solar cells, photodynamic therapy drugs, catalysts for organic reactions, chemical sensors, and electronic devices.1 In the interest of industrial applications, control over the aggregation of Pc macrocycles is of prime importance, as aggregated Pcs exhibit low solubility and less attractive optical properties.2 For the last decade, our group has been interested in trifluoroethoxy-substituted Pcs (TFEO-Pcs),3 as these show outstanding stability and solubility in various organic solvents as well as nonaggregation properties because of the presence of the highly lipophilic trifluoroethoxy (TFEO) group at their peri-positions. The purely nonaggregation properties of the TFEO-Pcs lead to sharp Q-bands, which are attractive for applications in chemical sensors in terms of clarity and responsivity.4 During our research on the design, synthesis, and spectral properties of TFEO-Pcs and their derivatives,5 we noticed that TFEO-Pcs are extremely sensitive toward their protonation in solvents (Figure 1a).5 The UV–vis spectra of TFEO-Pcs are highly solvent- and concentration-dependent, which can be observed even by the naked eye. The protonation of Pcs has been well investigated because protonated Pcs are expected to find applications in various areas because of their electronic properties, which include absorption, fluorescence, aggregation, and photochemical features upon protonation.6,7 Although the protonation of Pcs regularly requires acids, TFEO-Pcs are spontaneously protonated, even in neutral chlorinated solvents such as chloroform.5 Thus, TFEO-Pcs exhibit a very high susceptibility for the acceptance of protons via the nitrogen atom at the meso-position (Figure 1b), which is increased by the influence of the TFEO group at the α-position.6 Even though it is possible in some cases to visually examine solvent acidity because of drastic color changes, we describe herein the response of TFEO-Pcs to protons quantitatively, which allows applications in super-sensitive proton sensors. In addition to this experimental investigation, these phenomena were investigated theoretically using density functional theory (DFT) calculations.

RESULTS AND DISCUSSION

To create a reference frame for protonated TFEO-Pcs, we initially investigated the UV–vis spectra of four A4-type Pcs, that is, 16TFEO-Pc,* 8TFEO-Pc, 4TFEO-Pc, and 1Bu-Pc upon addition of trifluoroacetic acid (TFA) in trifluorotoluene (Figure 2, Table 1, and Figure S11). In the absence of TFA, 16TFEO-Pc, 8TFEO-Pc, 4TFEO-Pc, and 1Bu-Pc exhibit maximum absorption wavelengths (λmax) at 711.5, 712.5, 690.0, and 677.5 nm, respectively. Upon addition of TFA, the maximum absorption wavelengths of all Pcs were shifted bathochromically over two steps, depending on the concentration of TFA. The corresponding peaks (λ1 and λ2) were attributed to the monoprotonated and diprotonated Pcs, respectively. Interestingly, the values for the wavelength shift of 16TFEO-Pc (Δλ1 = 57.5 nm), 8TFEO-Pc (Δλ1 = 59.0 nm), and 4TFEO-Pc (Δλ1 = 46.0 nm) are larger than that of 1Bu-Pc (Δλ1 = 22.0 nm). These results suggest that the interaction between the TFEO substituents at the α-position with the proton at the meso-position affects the peak shift. Subsequently, we determined the equilibrium constants (K) between the nonprotonated Pcs and the monoprotonated Pc (PcH•) by titration, and the results are summarized in Table

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1. Among all compounds examined, 8TFEO-Pc exhibits the largest value of \( K (15.1 \times 10^5 \text{ M}^{-1}) \), whereas that of 4TFEO-Pc (\( K = 7.62 \times 10^5 \text{ M}^{-1} \)) decreases by reducing the number of TFEO substituents at the \( \alpha \)-position. Although the number of TFEO substituents at the \( \alpha \)-position does not change, the \( K \) value of 16TFEO-Pc (1.70 \( \times \) 10^5 M\(^{-1} \)) also decreases because of the strong electronegativity of the fluorine atom. The \( K \) value of tBu-Pc (1.61 \( \times \) 10^5 M\(^{-1} \)), which does not contain any TFEO substituents, is the smallest among all compounds examined. Accordingly, 8TFEO-Pc is the most sensitive toward protonation and exhibits the most drastic changes to its UV−vis spectrum upon protonation.

With this protonation reference frame in hand, the concentration-dependent (1.0 \( \times \) 10\(^{-6} \) to 1.0 \( \times \) 10\(^{-4} \) M) UV−vis spectra of 16TFEO-Pc, 8TFEO-Pc, 4TFEO-Pc, and tBu-Pc were recorded (Figures 3 and S12). The absorption spectra of 16TFEO-Pc and 8TFEO-Pc in chloroform show two peaks for the protonated state and nonprotonated state in the Q band region. Thus, the protonation should be due to proton-containing impurities (e.g., HCl) in chloroform. Furthermore, we noticed that the peaks for the protonated states increase with decreasing concentration of the compounds (16TFEO-Pc: \( \log \varepsilon_{\text{max}} = 4.42−5.23 \); 8TFEO-Pc: \( \log \varepsilon_{\text{max}} = 4.85−5.16 \)) as the abundance ratio of protons in chloroform increases relative to the concentration of the compounds. 

**Table 1. Maximum Absorption Wavelengths (\( \lambda_{\text{max}}; \lambda_0: \) No Additive, \( \lambda_1: \) Addition of TFA (1st time) and \( \lambda_2: \) Addition of TFA (2nd time)) and Equilibrium Constants (\( K \)) for 16TFEO-Pc, 8TFEO-Pc, 4TFEO-Pc, and tBu-Pc in PhCF\(_3\) (1.0 \( \times \) 10\(^{-5} \) M)**

|                | \( \lambda_0 \) (nm) | \( \lambda_1 \) (nm) | \( \lambda_2 \) (nm) | \( \Delta \lambda_1 \) (nm) | \( \Delta \lambda_2 \) (nm) | \( K \) (M\(^{-1} \)) |
|----------------|----------------------|----------------------|----------------------|-----------------------------|-----------------------------|--------------------------|
| 16TFEO-Pc      | 711.5                | 769.0                | 802.5                | 57.5                        | 91.0                        | 1.70 \( \times \) 10^5   |
| 8TFEO-Pc       | 712.5                | 771.5                | 817.5                | 59.0                        | 91.0                        | 15.1 \( \times \) 10^5    |
| 4TFEO-Pc       | 690.0                | 736.0                | 768.0                | 46.0                        | 78.0                        | 7.62 \( \times \) 10^5    |
| tBu-Pc         | 677.5                | 699.5                | 738.0                | 22.0                        | 60.5                        | 1.61 \( \times \) 10^5    |

\^\( \Delta \lambda_1 = \lambda_1 − \lambda_0 \). \^\( \Delta \lambda_2 = \lambda_2 − \lambda_0 \).

**Figure 1. Protonation at the meso-position of Pcs.**

**Figure 2.** (a) UV−vis spectra of 8TFEO-Pc (1.0 \( \times \) 10\(^{-5} \) M in PhCF\(_3\)). (b) TFA titration plot for 8TFEO-Pc in PhCF\(_3\).**

**Figure 3.** Concentration-dependent UV−vis spectra of (a) 16TFEO-Pc and (b) 8TFEO-Pc in chloroform.
to the quantity of the compound. Simultaneously, the peaks of the nonprotonated states decrease (16TFEO-Pc: log $\varepsilon_{\text{max}} = 5.17 \pm 4.73$; 8TFEO-Pc: log $\varepsilon_{\text{max}} = 5.03 \pm 4.71$). A similar protonation behavior was observed in dichloromethane, whereas such phenomena did not occur in 1,4-dioxane, toluene, or trifluorotoluene. The protonation of 8TFEO-Pc was saturated (1.0 × 10$^{-5}$ M) at a higher concentration than that of 16TFEO-Pc (6.0 × 10$^{-6}$ M). This result suggests that the basicity of 8TFEO-Pc is more suitable for the detection of protons than that of 16TFEO-Pc. On the other hand, $^8$Bu-Pc was only partially protonated at low concentrations, which suggests desirable basicity for Pcs that contain TFEO substituents at the $\alpha$-position.

Subsequently, we measured the steady-state fluorescence spectra of 8TFEO-Pc in different organic solvents (Figure 4).

The fluorescence spectra show only one emission band, which was attributed to nonprotonated 8TFEO-Pc, in 1,4-dioxane (725 nm), toluene (725 nm), and trifluorotoluene (717 nm). In chloroform, on the other hand, two emission bands corresponding to nonprotonated 8TFEO-Pc (718 nm) and protonated 8TFEO-Pc (775 nm) were observed, and these disappeared upon addition of pyridine. Furthermore, the peak for protonated 8TFEO-Pc was also observed in trifluorotoluene containing 1 vol % of hexafluoroisopropanol (HFIP). In the case of pure HFIP as the solvent, a new peak was observed at a longer wavelength (815 nm). These results demonstrate that a protonation at the meso-position affects not only the UV–vis but also the fluorescence properties.

To investigate potential applications in proton sensors, the UV–vis spectra of 8TFEO-Pc were measured using chloroform from different commercial sources (Figure 6). 8TFEO-Pc was partially protonated at low concentration in extremely pure chloroform from Sigma-Aldrich, which uses amylene stabilizers (Figure 6a). In contrast, chloroform obtained from KANTO (Figure 6c) and TCI for high-performance liquid chromatography (HPLC) (Figure 6e) is of lower purity and afforded yellow-green solutions indicative of high levels of monoprotonated 8TFEO-Pc. On the other hand, EtOH-stabilized chloroform from Sigma-Aldrich (Figure 6b) and Kishida (Figure 6d) did not suggest any protonation of 8TFEO-Pc. In addition, the color of the 8TFEO-Pc solutions did not change in chloroform (Figure 6f) that was distilled from KANTO (Figure 6c). Consequently, 8TFEO-Pc is able to visualize slight differences of the solvent conditions.

To further examine the color change upon protonation, we carried out DFT calculations using the SPARTAN 14 program, whereby a nonsubstituted Pc was used as a model compound. The energies of the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), and the LUMO + 1 of Pc and the protonated Pcs were calculated at the B3LYP/6-31G(d,p) level of theory. Although the LUMO is twofold degenerate in the nonprotonated state, these orbitals split into two unoccupied molecular orbitals with stabilization energy upon protonation because of its unsymmetrical structure. Although there should be two isomers in the deprotonated state, that is, an “adjacent” protonated state and an “opposite” protonated state, only the latter was used for the calculations, given its stabilization (adjacent state: $-9,050$ J/mol vs opposite state: $-9,050$ J/mol). It should also be noted that the orbital energy level was stabilized upon protonation. Furthermore, the energy gap between the LUMO and the HOMO decreases with increasing number of protons added except for the triprotonated state.

Subsequently, time dependent (TD)-DFT calculations at the $\omega$B97X-D/6-31G(d,p) level of theory were carried out to examine the bathochromic shift of the Q-band upon protonation.
protonation (Table 3). The results of these theoretical calculations agree nicely with the experimental observations, that is, the calculated absorption wavelength for the HOMO → LUMO transition increased with the number of protons added.

**CONCLUSIONS**

We have demonstrated that A4-type Pcs that contain TFEO substituents at the α-position are sensitive to the presence of protons. These Pc derivatives can reversibly accept protons that exist in solution, resulting in a color change of the solution according to the acidity of the solution. Especially, 8TFEO-Pc is super sensitive to protons, which allows distinguishing chloroform samples from different commercial suppliers. Such Pc derivatives should thus be expected to find applications in proton sensors.

**EXPERIMENTAL SECTION**

**General Information.** All reactions were performed in oven-dried glassware under a positive pressure of nitrogen. The solvents were transferred via a syringe and were introduced into the reaction vessels through a rubber septum. All solvents were purified by a standard method. All of the reactions were monitored by thin-layer chromatography (TLC) carried out on a 0.25 mm Merck silica gel (60-F254). The TLC plates were visualized with UV light and 7% phosphomolybdic acid or KMnO4 in water/heat. Column chromatography was carried out on a column packed with silica gel (60N spherical neutral size 50−63 μm). The 1H NMR (300, 700 MHz), 19F NMR (282 MHz), and 13C NMR (176 MHz) spectra for the solution in acetone-d6 (δ 2.05 ppm for 1H NMR, δ 206.26 ppm for 13C NMR) were recorded on Varian Mercury 300 and JEOL 700 NMR spectrometers. Chemical shifts (δ) are expressed in ppm downfield from internal C6F6 (−162.2 ppm) for 19F NMR. UV−vis spectra were recorded on a JASCO V-530 spectrometer. IR spectra were recorded on a JASCO FT/IR-200 spectrometer. Fluorescence spectra were recorded on a JASCO FP-6200 fluorospectrometer. Matrix-assisted laser desorption ionization time-of-flight (MALDI−TOF) mass spectra were taken on Shimadzu AXIMA CFR Plus. Chloroforms for UV−vis spectra were purchased from Sigma-Aldrich.

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**Table 2. Calculated Energy Levels of the Molecular Orbitals (eV)**

|          | HOMO     | LUMO     | LUMO + 1   | LUMO − HOMO |
|----------|----------|----------|------------|-------------|
| Pc−      | −4.94787 | −2.75968 | −2.75968   | 2.18819     |
| Pc−H     | −7.91433 | −6.05217 | −5.71472   | 1.86216     |
| Pc−H2    | −10.78380| −9.15418 | −8.70658   | 1.62962     |
| Pc−H3    | −13.68964| −12.04619| −11.95752  | 1.64345     |
| Pc−H4    | −16.46191| −14.99134| −14.99127  | 1.47057     |

**Table 3. Calculated Transition Energies (λ), Oscillator Strengths (f), and Configurations for Protonated Pc Models**

|          | λ (nm)  | f       | configuration                  |
|----------|---------|---------|--------------------------------|
| Pc−      | 610.55  | 0.4840  | HOMO → LUMO (93%)              |
|          | 610.47  | 0.4852  | HOMO → LUMO + 1 (93%)          |
| H2-Pc−   | 671.31  | 0.5449  | HOMO → LUMO (96%)              |
|          | 590.34  | 0.4131  | HOMO → LUMO + 1 (93%)          |
| H3-Pc−   | 726.66  | 0.6475  | HOMO → LUMO (98%)              |
|          | 642.74  | 0.4132  | HOMO → LUMO + 1 (92%)          |
|          | 367.91  | 0.1432  | HOMO − 1 → LUMO (54%)          |
|          |         |         | HOMO − 2 → LUMO + 1 (22%)      |
|          |         |         | HOMO − 6 → LUMO (11%)          |
| H4-Pc−   | 700.84  | 0.5277  | HOMO → LUMO (98%)              |
|          | 698.93  | 0.4812  | HOMO → LUMO + 1 (96%)          |
|          | 814.02  | 0.5556  | HOMO → LUMO (98%)              |
|          | 813.68  | 0.5560  | HOMO → LUMO + 1 (99%)          |

Only excited states with λ > 300 nm and f > 0.1 are shown.

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Figure 6. UV−vis spectra of 8TFEO-Pc in chloroform from (a) Sigma-Aldrich for ACS spectroscopy using amylene stabilizers (purity ≥ 99.8%); (b) Sigma-Aldrich for ACS spectroscopy using EtOH as a stabilizer (purity ≥ 99.8%); (c) KANTO for spectroscopy using amylene stabilizers (purity ≥ 99.0%); (d) Kishida for spectroscopy using EtOH as a stabilizer (purity ≥ 99.0%); (e) TCI for HPLC using amylene stabilizers (purity ≥ 99.5%); and (f) after distillation of (c).
for ACS spectroscopy using amylene stabilizers (purity ≥ 99.8%), Sigma-Aldrich for ACS spectroscopy using EtOH as a stabilizer (purity ≥ 99.8%), KANTO for spectroscopy using amylene stabilizers (purity ≥ 99.0%), Kishida for spectroscopy using EtOH as a stabilizer (purity ≥ 99.0%), and TCI for HPLC using amylene stabilizers (purity ≥ 99.5%).

**Synthesis of 8TFEO-Pc.** A suspension of 3-2,2,2-trifluoroethoxy)phthalonitrile (101.8 mg, 0.450 mmol) and ZnCl₂ (41.4 mg, 0.304 mmol) in 1.0 mL of N,N-dimethylmethanoethanol was heated at 130 °C and stirred at the same temperature for 4 h. After cooling to room temperature, the resulting mixture was diluted with water. Then, the green precipitate was collected by filtration and washed with water. The crude solid was purified by silica gel column chromatography (hexane/acetone = 8:2) to give 8TFEO-Pc (47.5 mg, 45%) as a green solid.

**Synthesis of 4TFEO-Pc.** A suspension of 3-2,2,2-trifluoroethoxy)phthalonitrile (101.8 mg, 0.450 mmol) and ZnCl₂ (41.4 mg, 0.304 mmol) in 1.0 mL of N,N-dimethylmethanoethanol was heated at 130 °C and stirred at the same temperature for 4 h. After cooling to room temperature, the resulting mixture was diluted with water. Then, the green precipitate was collected by filtration and washed with water. The crude solid was purified by silica gel column chromatography (hexane/acetone = 8:2) to give 4TFEO-Pc (70.1 mg, 64%), mixtures of isomers) as a green solid.

**Computational Method.** The geometries of model Pcs were optimized at the B3LYP/6-31G(d,p) level by using SPARTAN 14 program. Then, the HOMO and LUMO energy levels of model Pcs were calculated by using the optimized geometries at B3LYP/6-31G(d,p). These calculation results are summarized in Figure S14. The TD-DFT calculation was performed at the ωB97X-D/6-31G(d,p) level by using the optimized geometries which were calculated at the ωB97X-D/6-31G(d,p) level.

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