〈Research Paper〉

Efficient Fluorescence Quenching of *tert*-butyl substituted Phthalocyanines with Picric Acid

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Abstract: Two *tert*-butyl substituted phthalocyanines(Pcs), in metal-free and metallated forms, were synthesized and the fluorescence responses toward various nitro derivatives, including picric acid(PA), 2,4-dinitrotoluene(DNT), 1,4-dinitrobenzene(DNB), 4-nitrotoluene(NT), nitrobenzene(NB), 1,4-benzoquinone(BQ), and nitromethane(NM) were investigated. Among the various nitro derivatives, current Pc derivatives exhibited efficient and exclusive fluorescence quenching in the presence of picric acid, which was readily observed by a naked eye. Quenching efficiency was estimated by the Stern-Volmer relationship, in which quenching constant, K_{SV}, was calculated to be in the range of $10^4 M^{-1}$. It was also found out that the aggregational behaviors of these Pcs are heavily dependent on the nature of solvent systems, subsequently affecting the quenching efficiency.

Keywords: *phthalocyanine, aggregates, chemosensor, nitroaromatic compound, picric acid*

1. Introduction

Nitroaromatic compounds(NACs) is of significant concern for homeland security, battlefield protection, and industrial and environmental safety control[1]. Furthermore, NACs are important constituents of many unexploded land mines worldwide[2]. Therefore, detection of NACs is very important when combating terrorism, maintaining national security, and providing environmental safety.

Various methods have been used for the detection of nitroaromatics including GC-MS, ion-mobility spectroscopy(IMS), surface-enhanced Raman spectroscopy, and various other spectroscopic techniques[3].

However, these methods cannot be used in the field due to their high cost, lack of selectivity, and sensitivity. As a result, fluorescence signaling is a key in-field choice due to its high detection sensitivity and selectivity[4]. Among various NACs, Picric acid(PA), whose explosive power is higher than that of TNT, is a well-known for its explosive, poisonous and carcinogenic properties[5,6]. Furthermore,

the use of PA in the manufacture of rocket fuel, fireworks, and matches releases a large quantity of it into the environment[7,8].

Phthalocyanines(Pcs) exhibit interesting properties that are useful for diverse applications, such as optical storage, electrophotography, photovoltaic cells, and sensing devices, mainly due to their high stability, architectural flexibility, and diverse coordination properties[9]. Pcs with their extended electron-rich aromatic structure give rise to high extinction coefficients in the long wavelength regions. These unique features have triggered intense interests in its use for several promising fields based on their excellent spectroscopic characteristics.

The interactions of Pc derivatives, in most cases, are based on energy or electron transfer processes, because of the presence of *p*-electron conjugated ring system. In spite of the fascinating reports to date, it has not yet been reported in the literature about the interaction of Pc with NACs. Hence, in the present investigation, we prepared two *tert*-butyl substituted phthalocyanines, in metal-free and metallated forms, with an intention to examine the spectral responses of Pcs with NACs, more specifically PA. Metal-free Pc1

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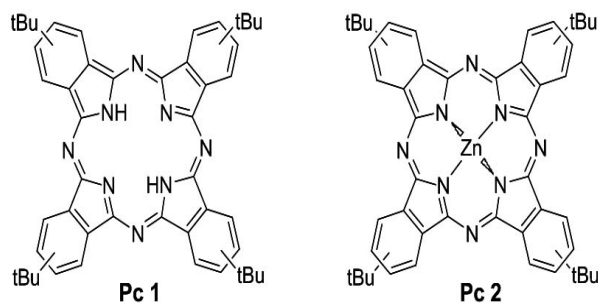
Scheme 1. Chemical structures of *tert*-butyl substituted phthalocyanines(Pcs), in metal-free Pc1 and metallated Pc2

and metallated Pc2 were synthesized according to the reported procedure(Scheme 1)[10].

It was envisaged that, through current investigation, the electron-rich nature of two Pcs may play an important factor in the detection of some electron deficient NACs.

2. Experimental

2.1 Materials

The chemicals used in the synthesis, 4-*tert*-butyl phthalonitrile, $ZnCl_2$, dimethylaminoethanol(DMAE), 1,8-diazabicyclo[5.4.0]undec-7-ene(DBU), 1-pentanol, were obtained from Sigma-Aldrich(Korea), and used as received with no further purification.

2.2 Synthesis

Derivative Pc1: 4-*tert*-butylphthalonitrile(1.0g, 5.43 mmol) was dissolved in 10mL of *n*-pentanol and the mixture was stirred for 10min. After DBU (1,8-diazabicyclo[5.4.0]undec-7-ene, 0.2mL, catalyst) was added to the reaction mixture, the mixture was stirred and heated to 145°C and it was refluxed for 12h. After finishing the reaction, the mixture was cooled to room temperature. Excess *n*-pentanol was removed under reduced pressure. The crude product was dissolved in 250mL of $CHCl_3$ and washed by a large amount of water. After removal of $CHCl_3$, the crude product was purified by silica gel column chromatography using hexane as eluent and Pc1 was obtained as a deep blue powder.

^{1}H-NMR δ(400 MHz, $CDCl_3$): 1.88(s, 36H), 8.17(s,

4H), 9.02(br, 8H); MALDI-Mass: 738.817(M$^+$).

Derivative Pc2: 4-*tert*-butylphthalonitrile(1.0g, 5.43mmol) and $ZnCl_2$(0.185g, 1.36mmol) were dissolved in 3mL of dimethylaminoethanol(DMAE) and the mixture was stirred and heated to 145°C and it was refluxed under argon for 15h. After finishing the reaction, the mixture was cooled to room temperature. Excess DMAE was removed under reduced pressure. The crude product was dissolved in 250mL of $CHCl_3$ and washed by a large amount of water. After removal of $CHCl_3$, the crude product was purified by silica gel column chromatography using hexane as eluent and Pc2 was obtained as a deep blue powder.

^{1}H-NMR δ(400 MHz, $CDCl_3$): 1.64(s, 36H), 7.88(s, 4H), 9.55(br, 8H); MALDI-Mass: 800.340(M$^+$).

2.3 Property investigation

The synthesis of *tert*-butyl substituted phthalocyanines was confirmed by MALDI-Mass measurements(Korea Basic Science Institute, KBSI), in which α-Cyano-4-hydroxy cinnamic acid was employed as matrix. The UV-Vis spectra were obtained from Lambda 7 spectrometer(Perkin Elmer). The photoluminescence emission spectra were collected by using LS-45 spectrofluorophotometer(Perkin Elmer), with a cuvette of 1cm path-length. SEM images were obtained using a FE-SEM apparatus(JEOL Scanning Microscope JSM-6700F).

3. Results and Discussion

Both *metal*-free Pc1 and metallated Pc2 revealed well-defined UV-vis spectra, with sharp Q-bands centered at 660-695nm, indicating monomeric species in solution(Figure 1(a)). While there observed no significant features in the B-bands, the Q-band of Pc1 is split into two absorption bands with maxima at 660 and 695nm. The splitting of the Q-band was attributed to extended p conjugation of Pc aggregates as a consequence of intramolecular electronic coupling between the Pc subunits[11].
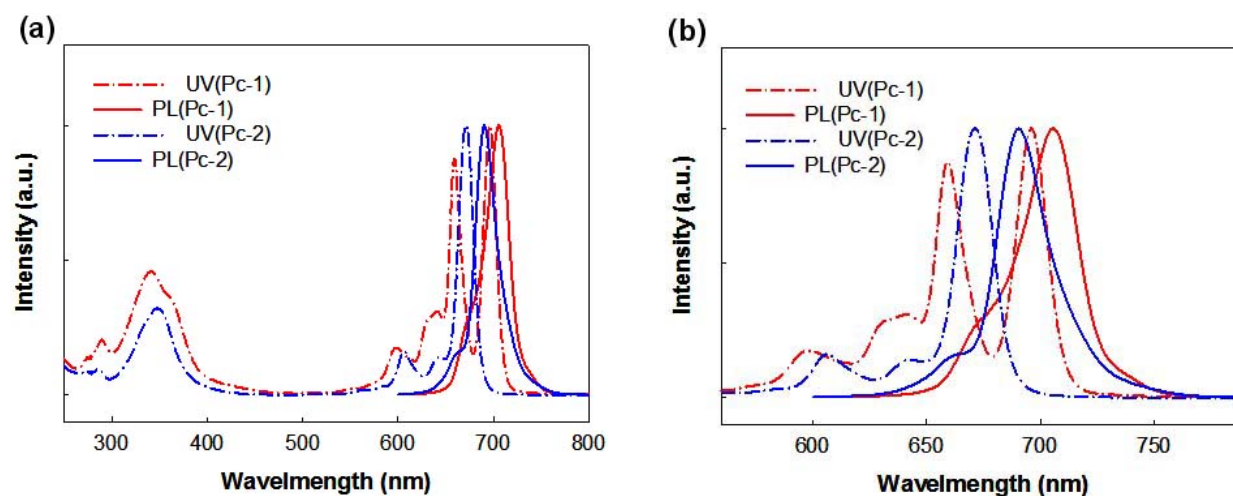
A previous report indicated that enhanced p-p

Figure 1. (a) UV-Vis and emission spectra of Pc1 and Pc2. Magnified spectra around Q-bands are represented in (b).

interaction among the molecules of metal-free phthalocyanine derivative[12]. Fluorescence emission spectra were collected with an excitation wavelength of 340nm in the THF:water(6:4) mixture(Figure 1(b)).

Both Pcs exhibited a mirroring of the Q-band in the 680-710nm region; Pc1 showed a red shift by 15nm compared to that of Pc2 due to longer conjugation length, as observed in UV spectra.

Now we turned our attention to the influence of nitroaromatic compounds(NACs) on Pc derivatives. The objective here was to investigate the spectral response of Pc to NACs. Photographic images of Pc1 was taken in the presence of nitroaromatic compounds (NACs), including picric acid(PA), 1,4-dinitrobenzene (DNB), 2,4-dinitrotoluene(DNT), nitrobenzene(NB), 4-nitrotoluene(NT), 1,4-benzoquinone(BQ), and nitromethane (NM)(Figure 2(a)).

The influence of NACs is easily recognized from inspection of the solutions under UV light ($l_{exciation}$=365nm). Obviously, PA was distinguished from other NACs, exhibiting a fluorescence quenching. Almost 95% fluorescence quenching was observed with the addition of 40 equivalents of PA; this could be easily observed by the naked eye. Such significant response in the emission of Pc1 were observed only with PA. The fluorescence intensities of both Pcs with various NACs were measured and summarized in Figure 2(b). In competitive experiments in the presence of PA and DNB, no significant variation in the quenching efficiency was observed with or without DNB(Figure 2(c)).

It is evident that the most electron-deficient aromatic compound, PA, caused the largest fluorescence quenching, i.e. the greater the number of electron-

Pc(*phthalocyanine*), PA(*picric acid*), DNB(*1,4-dinitrobenzene*), DNT(*2,4-dinitrotoluene*), NB(*nitrobenzene*), NT(*4-nitrotoluene*), BQ(*1,4-benzoquinone*), NM(*nitromethane*)
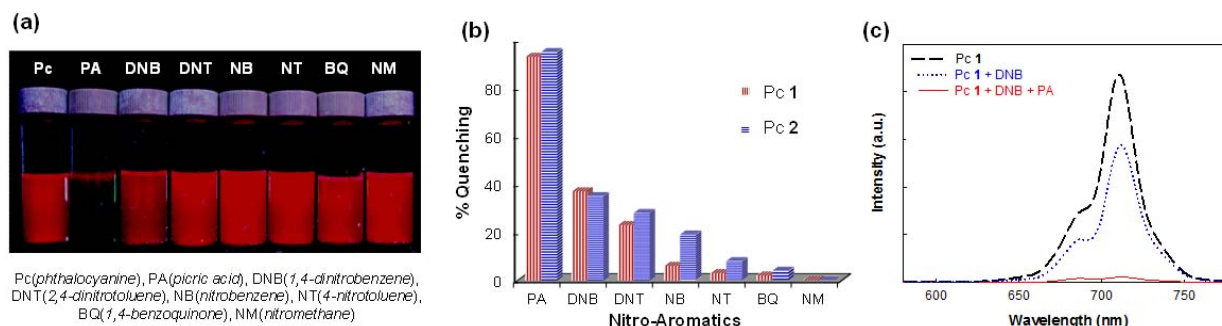
Figure 2. (a) Photographic images of Pc1(under 365nm UV light) upon addition of 40equivalents of various nitroaromatic compounds. (b) Bar diagrams of Pc1 and Pc2 after the addition of 40equiv. of various nitroaromatic compounds. (c) Fluorescence spectra of Pc1(10μM) upon sequential addition of 1,4-dinitrobenzene(DNB, 40equiv.) and picric acid(PA, 40equiv.). THF:water(6:4) mixture was used as solvent in all cases.
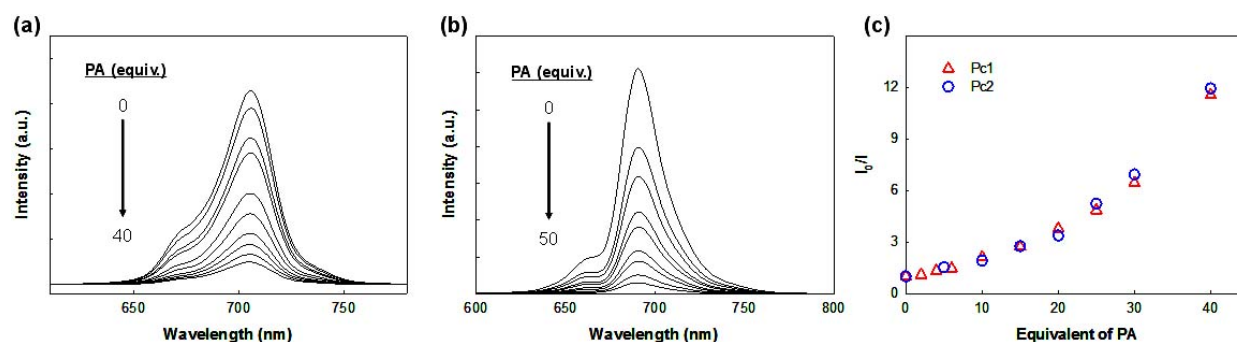
Figure 3. (a) Fluorescence spectra of Pc1(10μM) with the addition of picric acid(PA). (b) Fluorescence spectra of Pc2(10μM) with the addition of PA. (c) Stern-Volmer plots of Pc1 and Pc2 in response to PA in THF:water(6:4) mixture.

withdrawing nitro(-NO$_2$) groups present, the greater the degree of fluorescence quenching.

In order to obtain more insight concerning the mechanism, a Stern-Volmer plot was obtained from the fluorescence quenching titration(Figure 3), in which a linearity was maintained when the concentration of PA was below 200μM. However, when the concentration of PA was above 200μM, the plot moved upward. This non-linear nature of the plot indicates self-absorption or a combination of static and dynamic quenching or an energy transfer process between PA and Pc1[13].

We believe that, PA molecule interacts with the nitrogen atoms of the Pc derivatives and form non-fluorescent complex. From the linear part of the slope at low concentrations, the quenching constant of Pc1 for PA was calculated using the Stern-Volmer equation, $I_0/I = K_{SV}[A]+1$, where I_0 and I are the fluorescence intensities before and after the PA addition, respectively, $[A]$ is the molar concentration of PA, and K_{SV} is the quenching constant. The Stern-Volmer constant, K_{SV}, was $1.39 \times 10^4 M^{-1}$, which is higher than previous reports[14]. Similar, Pc2 exhibited selectivity toward PA, with a K_{SV} of $1.19 \times 10^4 M^{-1}$. The concentration required for the quenching of the fluorescence emission for Pc2 was 50 equivalents, which is slightly more than that for Pc1. It is believed that the smaller concentration of PA required for Pc1 results from its more electron-rich nature when compared with Pc2.

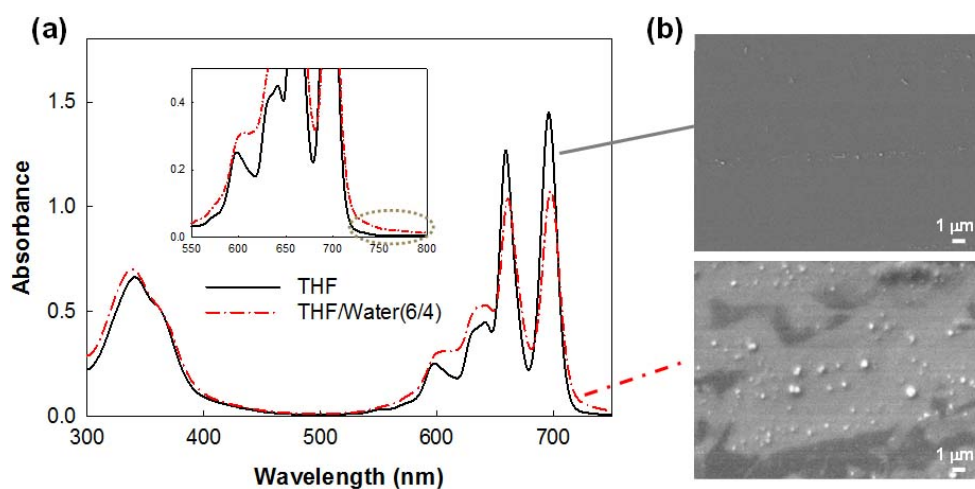It has been known that the morphologies of Pc derivatives were heavily affected by solvent compositions[15].

Figure 4. (a) UV-vis spectra of Pc1(10μM) in THF:water(6:4) mixture(black solid) and THF(red dotted). The inset enlarged UV spectra of Pc1 showing level-off tail. (b) SEM images of Pc1 showing more aggregates resulted from THF:water(6:4) mixture(lower), compared to the image obtained from THF(upper).

In order to examine the effect of solvent on the interaction with PA, we conducted the fluorescence titration of Pc1 toward various nitro derivatives in different solvent, THF-only condition. The exclusive quenching with PA remained unchanged, and Stern-Volmer constants in THF were found to be larger compared to those in THF:water(6:4) mixture, with K_{SV} of $2.76 \times 10^4 M^{-1}$ and $5.12 \times 10^4 M^{-1}$, respectively. In order to obtain insight into the role of solvents in this difference, UV-Vis spectra of Pc1 in the THF-only solution and THF:water(6:4) mixture were compared(Figure 4(a)), in which Pc derivatives in the THF:water(6:4) mixture led to the appearance of a leveling-off long wavelength tail that was absent in the THF-only solution; this tail was attributed to the Mie scattering due to the formation of aggregates. The formation of aggregates was observed in SEM measurements(Figure 4(b)), in which Pc1 in the THF:water(6:4) mixture showed the formation of aggregates[16]. In comparison, these aggregates were seldom found in THF-only solution. Thus, we can propose that these aggregates of Pc1 offer more diffusion channel for the excitons to migrate and allowing them to be more quickly annihilated by the PA molecules[17].

It is obvious that, from above result, the aggregational behaviors of Pcs are heavily dependent on the nature of solvent, subsequently affecting the quenching efficiency.

4. Conclusion

In summary, we synthesized two *tert*-butyl substituted phthalocyanines(Pcs), in metal-free and metallated forms. These Pc derivatives exhibited selective and efficient fluorescence quenching in the presence of picric acid, which was readily observed by a naked eye. In addition, it was found that the aggregates of Pc derivatives formed in aqueous mixture affected the sensitivity toward picric acid, producing slightly lower Stern-Volmer constant.

Acknowledgement

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