ICT-based Alkynylpyrene†

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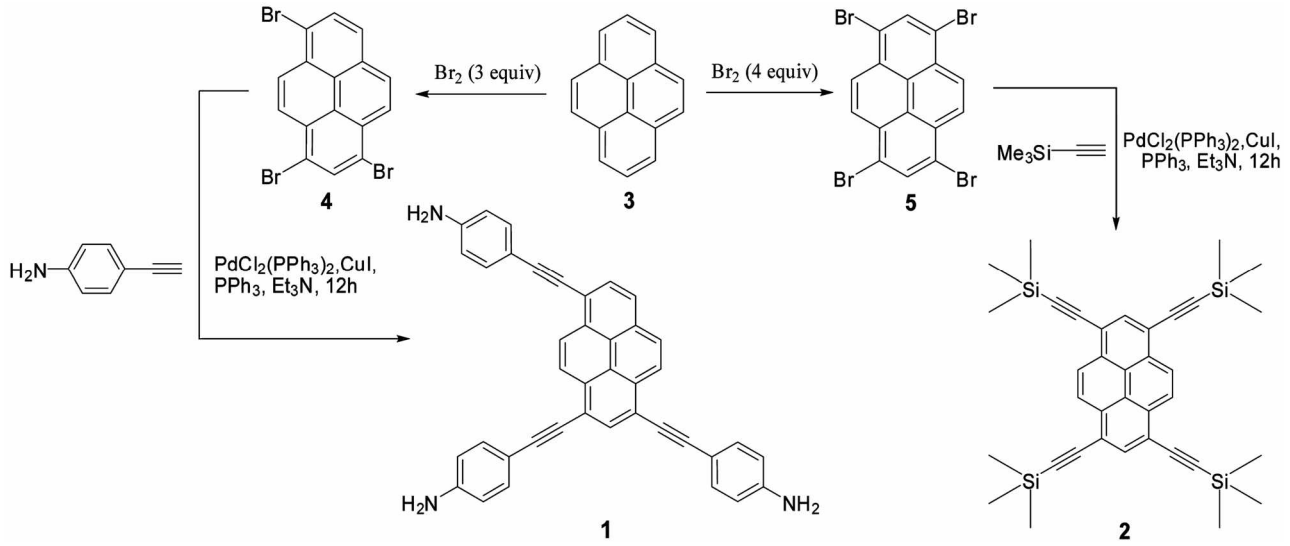
Pyrene derivatives are increasingly gaining attention as valuable and versatile tools in various areas of chemical biology and material research.[1] Due to their advantage in photophysical properties, pyrene derivatives have been widely used as microenvironment sensors, organic light emitting diodes, fluorescent polymers, dendrimers, and photoactive polypeptides.[1]

Intramolecular charge transfer (ICT) in organic molecules have been widely investigated to understand the factors controlling the charge separation and charge recombination related to electronic devices.[2] Besides, introduction of *Donor-Acceptor ICT* system to fluorophores through π-conjugation *via* C=C or C≡C bond has been well known to make their absorption and emission bands bathochromically moved.[3,4] This molecular system that absorbs and emits in longer wavelength region is useful in a biological research such as DNA, RNA, and peptide probe. Therefore, it is expected that if any suitable substituents are introduced to *Donor-Accept* system, it would be possible to obtain organic materials exhibiting red shifted fluorescence emission followed by having potential applications in biological fluorescence probe and electronics such as electro-optic devices, light-emitting diodes, and field effect transistors.

Previously, various synthetic alkynylpyrenes were synthesized and it was found that introduction of alkynyl groups to pyrene nuclei induces an effective extension of π-conjugation to give a largely enhanced fluorescence emission compared with the parent pyrene itself.[5] Furthermore, the alkynylpyrenes group is known to maintain their fluorescence intensities even under aerated conditions, giving rise to an additional useful feature for practical uses. However, so far, only a few alkynylpyrene having both donors and acceptor (ICT molecular) has been reported.[6]

In this regard, we have synthesized a new ICT material 1,3,6-tris(anilinoethynyl)pyrene in which alkynylpyrene as a acceptor is linked to -PhNH$_2$ as a donor and now report on studies of its synthetic methods and ICT mechanism by absorption and fluorescence emission properties.

As shown in Scheme 1, target compounds **1** and **2** are synthesized by Sonogashira coupling reaction.[7] Bromination of pyrene with **3** and **4** equivalents of bromine gave 1,3,6-tribromopyrene and 1,3,6,8-tetrabromopyrenes,[8] respectively. Cross-coupling of the 1,3,6-tribromopyrene with 4-ethynylaniline afforded 1,3,6-tris(anilinoethynyl)pyrene (**1**). 1,3,6,8-Tetrakis(trimethysilyl)pyrene was also synthesized in a similar manner to the corresponding trimethylsilyl-



Scheme 1. Synthesis of **1** and **2**.

†This paper is dedicated to Professor Sang Chul Shim on the occasion of his honorable retirement.

acethylene.

First of all, we took UV-Vis absorption spectroscopy of **2** which might not have the ICT motif such as electron donor. The absorption spectra pattern of **2** depicted in Figure 1(a) are similar to that of pyrene (or 1-methylpyrene),[9] but appear in longer wavelength (red shift) due to a π-conjugated extension to the pyrene. Interestingly, the UV-Vis spectra of **1** in which silicon unit is replaced by amino group show further red shifted by ~40 nm and broader band compared to that of **2**. This absorption pattern and extent of the red shift in **1** are similar to those of tetraethynylpyrene in same solvent,[10] suggesting that the large shift of the UV-Vis bands of **1** result mainly from the extended conjugation of the phenyl group to give an optimized ICT system.[6]

On the other hand, in the fluorescence spectra, we observed different types of the emission bands in **1** and **2**, respectively. As expected, **2** shows two distinct emission bands: normal emission at 435 nm and secondary vibronic band at 470 nm. This pattern is consistent with that of tetraethynylpyrene substituted benzene[10] in which there is no amino (electron donor) unit. Compound **1** having a electron donor, however, displays red-shifted broad band at 520 nm without any shoulder band at 470 nm like **2**. From the fluorescence spectral changes between **1** and **2**, one then can suggest that the amine group in **1** seem to influence on the effective ICT mechanism as an electron donor to pyrene.

To gain insight into the ICT in **1**, we performed fluorescence studies in variation of solvents with different polarity (Figure 2). The intensity in the fluorescence spectra was normalized to easily compare the wavelength changes in various solvents (Figure 2a). In hexane, **1** shows a typical pyrene emission bands. In more polar solvent such as THF, MeCN, and MeOH, it moves in turn to longer wavelengths along with disappearance of the secondary vibronic band (Figure 2a). The emission bands move significantly to the red by increasing solvent polarity, which is typically responsible for ICT feature.[6,11]

In consideration of the fluorescence intensity, we observed declining emission intensity as increasing solvent polarity as seen in Figure 2b.[12,13] The weakened intensity is attributable to the fact that in polar solvent, efficient non-radiative decay or electron transfer to the stabilized ICT excited state is preferentially executed. This is a well-established phenomenon, wherein decreased band gap between HOMO and LUMO increases the accessibility of non-radiative de-excitation pathways *via* vibronic coupling.[13,14] Although the normalized fluorescence spectra of **1** in MeOH is very similar to that in CH_3CN, the intensity in MeOH is lower than that in CH_3CN. This is probably due to an intermolecular H-bonding between MeOH and -NH_2 of **1**.[15]

The optical properties of fluorophores containing free electron pairs such as amino or hydroxy unit may change upon protonation which derives a band gap difference between HOMO and LUMO states. To investigate this sensory response of **1**, protonation by $HClO_4$ in THF, MeCN and MeOH was examined (Figure 3). Absorption bands of **1**

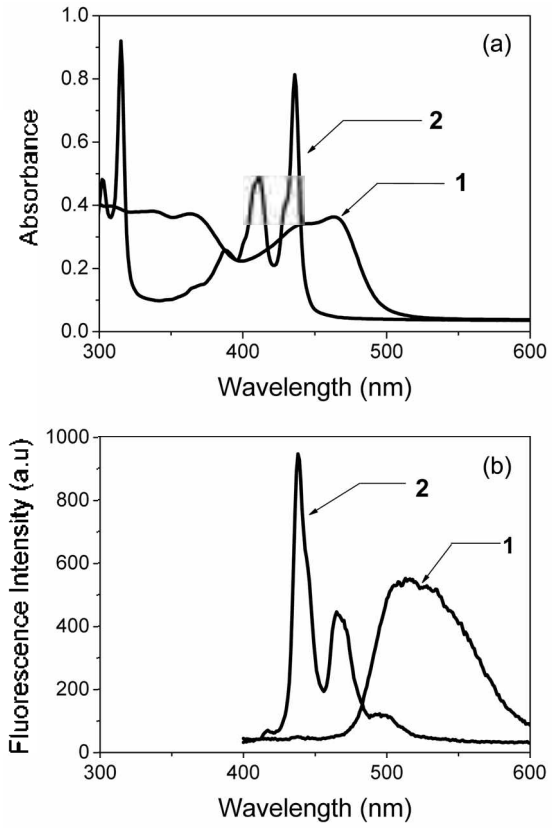


Figure 1. UV-Vis absorption spectra (a) and fluorescence emission spectra (b) of **1** and **2**, respectively, in THF.

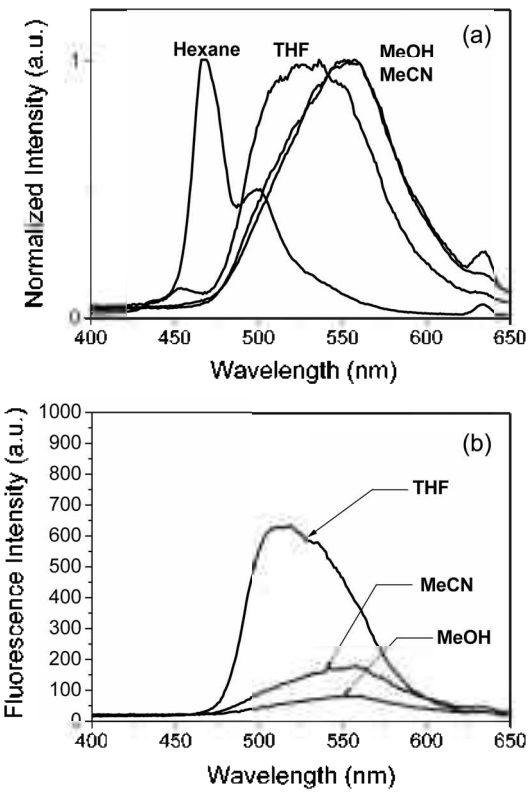


Figure 2. (a) Normalized emission spectra of **1** and (b) emission spectra of **1** (3 μM) in various solvents in differing polarity, respectively. Excitation at 316 nm.

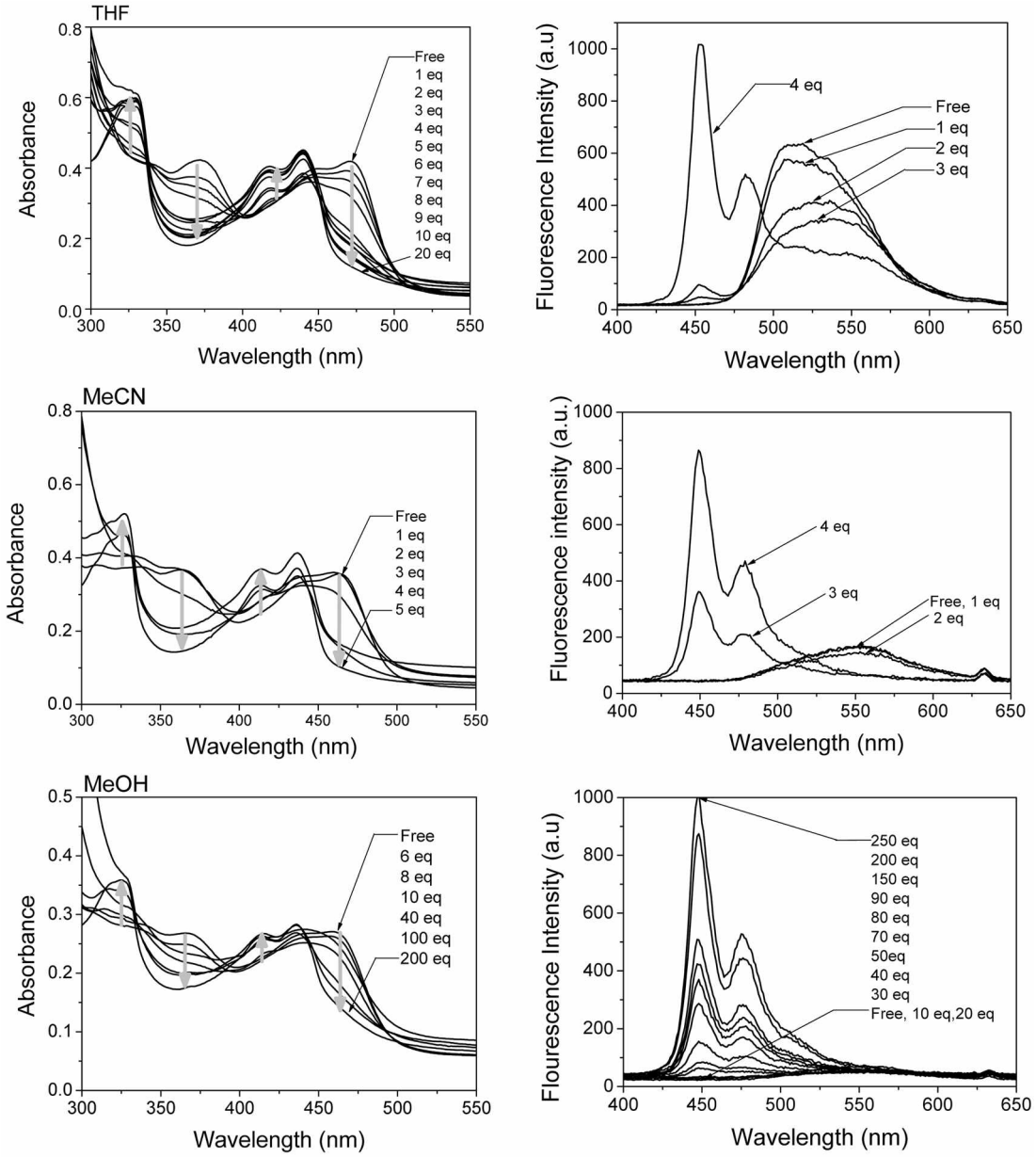


Figure 3. UV/visible absorption and emission spectra (λ_{ex} = 316 nm) of **1** (3 μM) upon addition of various amounts of $HClO_4$ in THF, MeCN, and MeOH, respectively.

appear at 375 and 475 nm regardless of solvent species (THF, MeCN or MeOH). Upon addition of $HClO_4$, however, both absorption maxima of **1** are found to decline with concomitant appearance of new bands at 325 and 430 nm. The blue shifts is due to the fact that protonation on aniline group suppress the conjugation from a phenyl unit to an ethynyl bridge.[6,14] In THF, gradual addition of $HClO_4$ to **1** leads to markedly diminished fluorescence emission at 520 nm along with a rather weak appearance at 455 nm. Upon addition of 4 eq $HClO_4$ to **1**, fluorescence emission is completely shifted to 455 nm with a maximum intensity. In MeCN, the emission of **1** upon addition of 3 eq $HClO_4$ shows a complete blue-shift from 555 to 455 nm (Δ=100 nm). We also observed a same fluorescence shifting pattern of **1** in MeOH. Addition of 1-4 eq $HClO_4$ did not give any pronounced changes compared to free **1**. Further addition of $HClO_4$ upto 250 eq produced a similar blue-shift like in the case of other solvents used. The blue shift in all different solvent is obviously because the energy gap between HOMO and LUMO becomes larger than that of free ligand, inducing that no longer ICT is executed in the protonated ammonium unit upon the protonation.[14]

In conclusion, we synthesized tris(anilinoethynyl)pyrene (**1**) and tetrakis(trimethylsilyl)pyrene (**2**). Solvatochromic studies reveal that aniline of **1** play a role as an electron donor to pyrene, giving rise to a solid evidence of its ICT characteristic. Protonation to **1** using $HClO_4$ gives blue shifts in both absorption and emission spectra regardless of solvent species, attributable to the HOMO-LUMO energy gap increased by blocking the ICT. The molecule **1** is potentially

useful as H^+ sensor and as organic light emitting materials in the fabrication of light emitting device.

Experimental Section

Materials: Reagents were purchased from commercial sources and were used without further purification. 1,3,6-Tribromopyrene (**4**), 1,3,6,8-tetrabromopyrene[8] (**5**), tetrakis(trimethylsilyl)pyrene[10] (**2**) have been previously reported and were synthesized according to the published procedures.

Spectroscopic measurements: Fluorescence spectra were recorded with a RF-5301PC spectrofluorophotometer. The perchloric acid solutions were prepared in THF, MeCN and MeOH. Stock solutions of **1** and **2** were prepared in hexane, THF, MeCN, and MeOH. For all measurements, excitation was made at 316 nm with excitation slit widths at 1.5 nm and emission slit widths at 3 nm. Fluorescence titration experiments were performed using 3.0 μM solution of **1**.

1,3,6-Tris(anilinoethynyl)pyrene (1). Tribromopyrene (100 mg, 0.22 mmol), [$PdCl_2(PPh_3)_2$] (15 mg, 0.02 mmol), CuI (2 mg, 0.1 mmol), PPh_3 (5 mg, 0.02 mmol), and the 4-ethynylaniline (160 mg, 1.32 mmol) were added to a degassed solution of triethylamine (10 mL) and THF (10 mL) under N_2. The resulting mixture was refluxed for 12 hours under the nitrogen atmosphere. After removal of the solvent *in vacuo*, water (50 mL) and CH_2Cl_2 (50 mL) were added and organic layer was separated. The organic layer was dried over anhydrous $MgSO_4$, and the solvent was evaporated *in vacuo* to give a red orange solid which purified by column chromatrography on silica gel with ethyl acetate: hexane (8:1) to provide 41 mg (33%) of **1** as a red orange solid. mp: 213-217 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.74 (s, 2H, pyrene), 8.63 (d, 1H, pyrene, J = 7.9 Hz), 8.37 (s, 1H, pyrene), 8.15-8.07 (m, 3H, pyrene), 7.6 (d, 6H, aniline, J = 7.9 Hz), 6.74 (d, 6 H, aniline, J = 7.9 Hz). ^{13}C NMR ($CDCl_3$): δ 148.1, 133.5, 132.5, 127.2, 124.3, 119.7, 118.7, 113.4, 112.7, 93.3, 87.1 ppm. FAB MS m/z (m^+): Calcd, 547.65. Found, 547.50.

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