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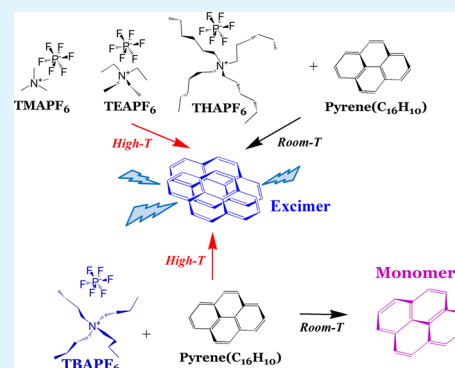
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S Supporting Information

ABSTRACT: Pyrene (Py) excimer, through its unique fluorescence quenching, exhibits high sensitivity and high selectivity in detecting specific electron-deficient molecules, providing a potential platform for sensing technology, optical switch, and probing hydrophobicity of molecular environment. In solution state, its quenching mechanism has been well-studied. However, there remain many unknown properties regarding the quenching mechanism of the solid-state Py excimer. In this paper, the effects of a series of tetra-alkylammonium salts (with a variety of chain lengths and anions) on Py excimer quenching are investigated to identify the controlling parameters of the fluorescence quenching in the binary system. Several experimental approaches including steady-state fluorescence spectroscopy, UV absorption, ¹³C-nuclear magnetic resonance (NMR) spectra, X-ray diffraction, scanning electron microscopy, and time-dependent fluorescence decay are employed to seek for the fundamental understanding of the quenching mechanism. The result indicates a unique quenching effect of tetrabutylammonium cation on the pyrene excimer, and which is not observed in the other cations with different chain lengths (the same associated hexafluorophosphate anions). Meanwhile, hexafluorophosphate anion (in the presence of tetrabutylammonium) is able to effectively retain Py excimer fluorescence when the system is prepared by evaporating solvent at high temperature. It is also confirmed that dynamic quenching is involved in the process. Hydrophobic environment around Py molecules shows strong correlation with the formation of Py excimer. The knowledge obtained in this study provides the insights to how the interaction between salt and Py molecule affects the excimer fluorescence.

KEYWORDS: fluorescence quenching, explosive sensing, high-T solvent annealing, thin film, size of organic salts, perturbing excimer



1. INTRODUCTION

Pyrene (Py) is a polycyclic aromatic hydrocarbon molecule made of four fused benzene rings without heteroatoms.¹ One remarkable feature of such polycyclic aromatic hydrocarbons is their significant fluorescence due to their electron-rich structures. This fluorescence can be effectively quenched by certain electron deficient molecules, providing a useful platform to detect these specific molecules.² In this regard, Py and its derivatives in solution and solid state have been successfully applied to many fields such as sensors for ions,^{2–6} explosives,^{7–12} optical switches,^{13,14} monitors for micellar formations,^{15–17} and biological probes for DNA and RNA.^{18–20} In spite of its many applications, the origin of solid-state Py excimer fluorescence has not been systematically studied (except the case of π – π stacking²¹) as most research efforts have been made on synthesis of various Py derivatives.^{4,15,17,18,21–23}

Two types of emission from the excited states of Py molecules are commonly observed: the ultraviolet (UV) emission (370 to 400 nm) from unassociated excited monomers (M_1^*) and a blue emission (440–490 nm) from Py excimers (E^*). The latter forms due to the interaction between a ground-state monomer (M_1) and an excited

monomer (M_1^*).^{1,24} The intermolecular distance (d) between Py, can dictate the types of fluorescence: ~ 1 nm for monomer and $0.4 \text{ nm} < d < 1 \text{ nm}$ for excimer.^{1,22,25–27} In the solution state, the formation of Py excimer is mostly attributed to molecular diffusion process.^{1,22,24} Therefore, a high Py concentration enhances the formation of Py excimers until self-quenching occurs.²⁸ Another factor that promotes the formation of Py excimer is the long lifetime of Py monomer, τ_M (~ 450 ns) and high monomer quantum efficiency ($\Phi_M = 0.6$ in cyclohexane).^{1,22,29} However, in the solid state, the formation and quenching mechanisms of excimer are likely different from the solution state due to its relatively low molecular diffusivity.^{30–32}

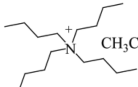

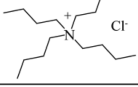


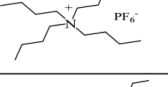
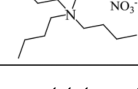
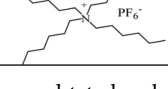
It has been reported that Py excimer in a simple ternary electrospun mixtures containing tetrabutylammonium hexafluorophosphate (TBAPF₆) and polystyrene (PS) can be effectively quenched in the presence of a trace amount (at a parts per billion level) of nitro-explosives (e.g., nitroaromatic, nitroglycerin, or nitroamine compounds) over a short period of

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Table 1. List of a Series of Tetraalkylammonium Salts in This Study^a

Name	Molecular weight (g/mol)	Name	Molecular weight (g/mol)
 TBA Acetate	301.52	 TMAPF ₆	219.11
 TBACl	277.92	 TEAPF ₆	275.22
 TBABF ₄	329.27	 TBAPF ₆	387.43
 TBANO ₃	304.47	 THAPF ₆	499.64

^aTMA, TEA, and THA represent tetramethylammonium, tetraethylammonium, and tetrahexylammonium cations, respectively.

time (in 6 min).⁷ A recent report showed that the Py excimer fluorescence in a Py/PS/TBAPF₆ film can also be greatly enhanced by high solvent vapor pressure induced by temperature, indicating that the solvent molecules (tetrahydrofuran (THF) in this case) promote certain configurations of Py to form excimers.³³ Since both PS and TBAPF₆ can, in principle, affect the Py excimer fluorescence, it is difficult to differentiate the contribution of individual components to the Py fluorescence in the ternary system.

This paper presents a systematic study on the effects of the chemical structure of anions and the chain lengths of a series of tetra-alkylammonium salts on the Py excimer quenching in a binary system (namely, Py and salt) in both solution and solid states. The important parameters that control the Py excimer are therefore determined. The fluorescence lifetime provides an insight into the excimer quenching mechanism (most likely dynamic quenching). The polarity around and mobility of Py molecules are also correlated with the excimer fluorescence. There is a unique chain length of the tetra-alkylammonium cation (namely tetrabutyl), which significantly perturbs the formation of Py excimer, while a specific anion, for example, PF₆⁻, shows capability of restoring the excimer under a high-*T* drying process. The insignificant nanostructural changes characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) of different Py/salt systems suggest that the quenching caused by TBAPF₆ may not be related to the formation of a new crystalline structure or topological variations.

2. EXPERIMENT

2.1. Materials and Procedures. *Materials.* All the chemical components of salts listed in Table 1, pyrene (Mw 202.25g/mol), and acetone (purity >99.9%) were purchased from Sigma-Aldrich and used as received.

Sample Preparation for Solutions. Py in acetone solution was prepared at different concentrations (10⁻⁴, 10⁻³, 10⁻², 5 × 10⁻², 10⁻¹, and 2 × 10⁻¹ M, respectively). To investigate the effect of salts on the Py fluorescence emission, the Py/salt binary mixtures were prepared in the acetone at a fixed salt-to-Py weight ratio (71.2:28.8 by weight). All concentrations of different salts in the solutions are under the critical

micellation concentrations (CMC) confirmed by dynamic light scattering (DLS).

Films. Film samples were prepared for the following studies: (1) differentiate the quenching effects of PS and TBAPF₆ on the Py excimer, and (2) investigate the possible mechanisms of the organic salts affecting the emission of Py excimer. In part (1), ternary Py/PS/TBAPF₆ samples were made at various compositions of TBAPF₆ (from 13 to 63 wt %), where the concentration of Py remains constant (i.e., 18.3 wt %). One of the compositions (TBAPF₆/Py/PS = 18.3:36.3:45.4) showed high quenching efficiency in the presence of 2,4-DNT in our previous study.⁸ A binary film composed of Py/PS (1:2 by weight) was also made to compare with the ternary Py/PS/TBAPF₆ film of the same Py/PS ratio. To study the controlling parameters of the salts, binary systems containing both Py and a series of tetra-alkylammonium salts were prepared at a fixed salt-to-Py weight ratio of (71.2:28.8) and a constant Py concentration (0.02 g/mL) in acetone. All the films were made by solvent evaporation at either high-*T* (100 °C) or room-*T*. The glass substrates were first preheated to the desired temperature and allowed to equilibrate for ~1 h. Then, a 100 μL of the Py/salt solution was placed on the preheated substrate for 2 min and let it cool at room-*T* until fully dried.

2.2. Characterization. The fluorescence emission, ¹³C NMR, and lifetime of fluorophores in Py/salt films were characterized in this study.

- (1) Fluorescence and UV absorption: The fluorescence spectra were measured by a steady-state fluorescence spectrometer (Fluorolog, Jobin Yvon Horiba). The excitation wavelength of 334 nm for the Py/salt was chosen based on the maximum UV absorption, except that a wavelength of 350 nm was used for the films containing PS. The emission spectra were monitored through a 1 mm slit over the wavelength range of 350–600 nm and normalized by the maximum intensity in the corresponding spectrum. In this study, the fluorescence ratio of excimer-to-monomer, $I_{\text{exc}}/I_{\text{mon}}$, is used as an index to evaluate the content of Py excimer. The absorption spectra were recorded on a UV–visible spectrophotometer (Cary 50, Agilent Technologies).
- (2) ¹³C NMR: The solid-state ¹³C cross-polarization magic-angle spinning (CPMAS) NMR spectra were acquired using a Bruker DMX 300 NMR spectrometer operating at a field strength of 7.05 T and a resonance frequency of 300 MHz for ¹H and 75.4 MHz for ¹³C. Chemical shifts were obtained based on an external reference sample, solid glycine (carbonyl at 176.5 ppm). ¹³C NMR measurements were taken in the absence or presence of the salts.

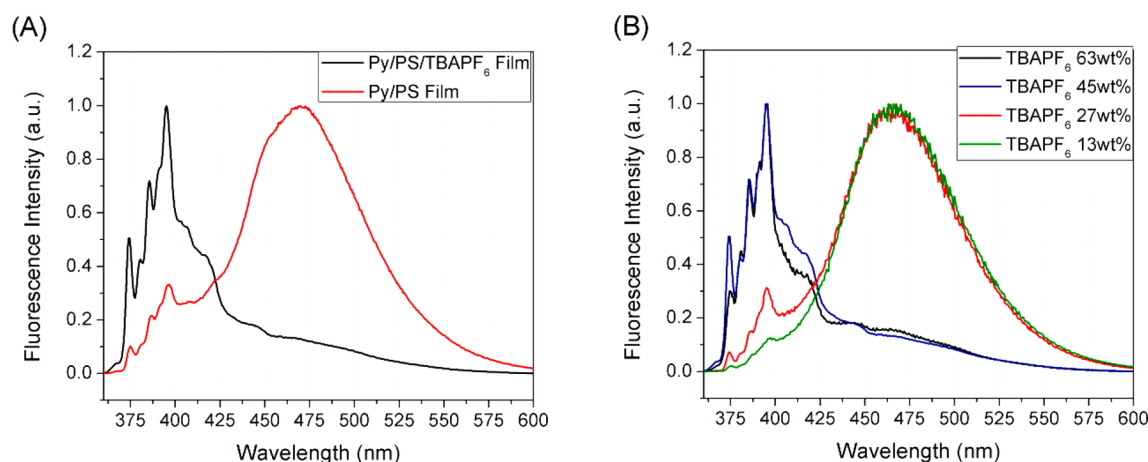


Figure 1. Fluorescence spectra (excited at 350 nm) of (A) Py/PS/TBAPF₆ film (black) and Py/PS film (red) prepared by room-*T* evaporation. (B) Py/PS/TBAPF₆ films prepared at room-*T* with different salt compositions, 63 wt % (black), 45 wt % (blue), 27 wt % (red), and 13 wt % (green), respectively.

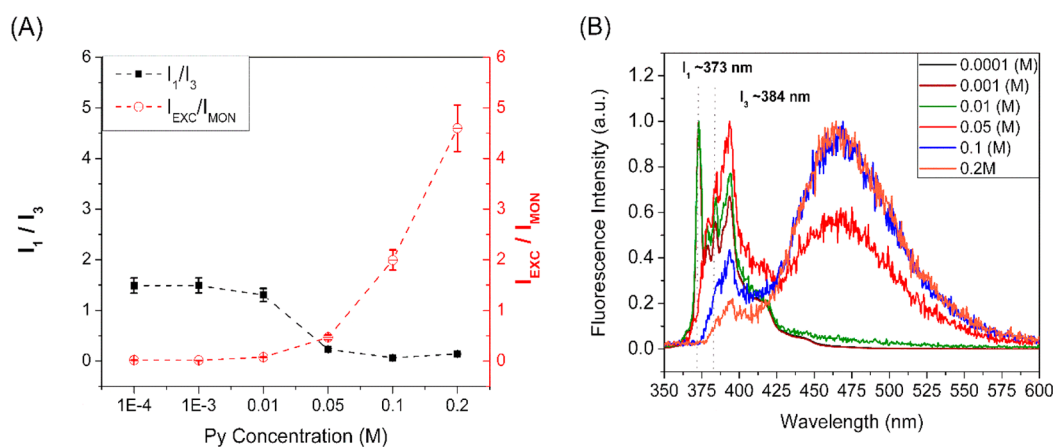


Figure 2. (A) The ratios of $I_{\text{exc}}/I_{\text{mon}}$ (open circles, red) and I_1/I_3 (solid squares, black) as a function of Py concentration. The $I_{\text{exc}}/I_{\text{mon}}$ increases and I_1/I_3 decreases with increased Py concentration. The error ranges of these values are within 10%. (B) The fluorescence emission spectra (excited at 343 nm) of Py in acetone solution at different concentrations (M). (10^{-4} , 10^{-3} , 10^{-2} , 5×10^{-2} , 10^{-1} , and 2×10^{-1} , respectively).

- (3) Fluorescence lifetime measurement: the samples were excited with a pulse diode laser (PicoQuant) at 405 nm with a repetition rate of 2.5 MHz. The emission of the samples was focused onto an avalanche photodiode (PicoQuant) using a 450 nm long-pass spectral filter to examine excimer alone. The fluorescence decay was recorded using a time-dependent single photon counting module (PicoHarp300, PicoQuant). The data were then normalized by the maximum intensity in the corresponding decay curves and the initial background intensity was subtracted.
- (4) SEM: the morphology of films was measured by the JEOL 6335F Field Emission SEM (SM-6335F), a cold cathode field emission scanning electron microscope, which provides a resolution of 1.5 nm at 15 kV and 5.0 nm at 1 kV.
- (5) XRD: the XRD pattern of the film was obtained through a regular θ - 2θ configuration by a Bruker D8 Advance X-ray Diffractometer with a 2.2 kW Cu anode sealed tube. The XRD data were analyzed after background subtraction and expressed in an arbitrary unit.

3. RESULTS AND DISCUSSION

Figure 1A shows the fluorescence spectra (excited at 350 nm) of two polymer thin films prepared by solvent evaporation at room temperature: Py/PS/TBAPF₆ and Py/PS, respectively. In spite of the same weight Py/PS ratio, the excimer emission

peak (465 nm) is prominent in the PS/Py film but nearly nonexistent in the presence of TBAPF₆, indicating that TBAPF₆ effectively quenches the Py excimer. A follow-up study was conducted on a ternary system (Py/PS/TBAPF₆) where the composition of TBAPF₆ varies from 13 wt % to 63 wt % (with a constant Py concentration of 18 wt %) as shown in Figure 1B. The result indicates nearly complete quenching of the Py excimer in the films as the TBAPF₆ concentrations \geq 45 wt %. To further explore the interaction of the salt and Py as well as its influence on the fluorescence of Py excimer, films composed of Py and other tetra-alkylammonium salts with a variety of anions and cations in place of TBAPF₆ were studied in both solution and solid states.

3.1. Salt Effects on the Formation of Py Excimer in Solution State. It has been known that $I_{\text{exc}}/I_{\text{mon}}$ in solution state is governed by the molecular mobility (i.e., diffusion) and the concentration of Py molecules.^{24,34,35} In this study, the polarity around Py determined by its monomer emission is also investigated to correlate with $I_{\text{exc}}/I_{\text{mon}}$. The five vibronic fine structures of the pyrene monomer give rise to five fluorescence peaks from 370 to 400 nm (namely, from I_1 to I_5), depending on the polarity of its environment. The higher the I_1/I_3 value, the more polar is the solvent environment.^{36–38} Although the

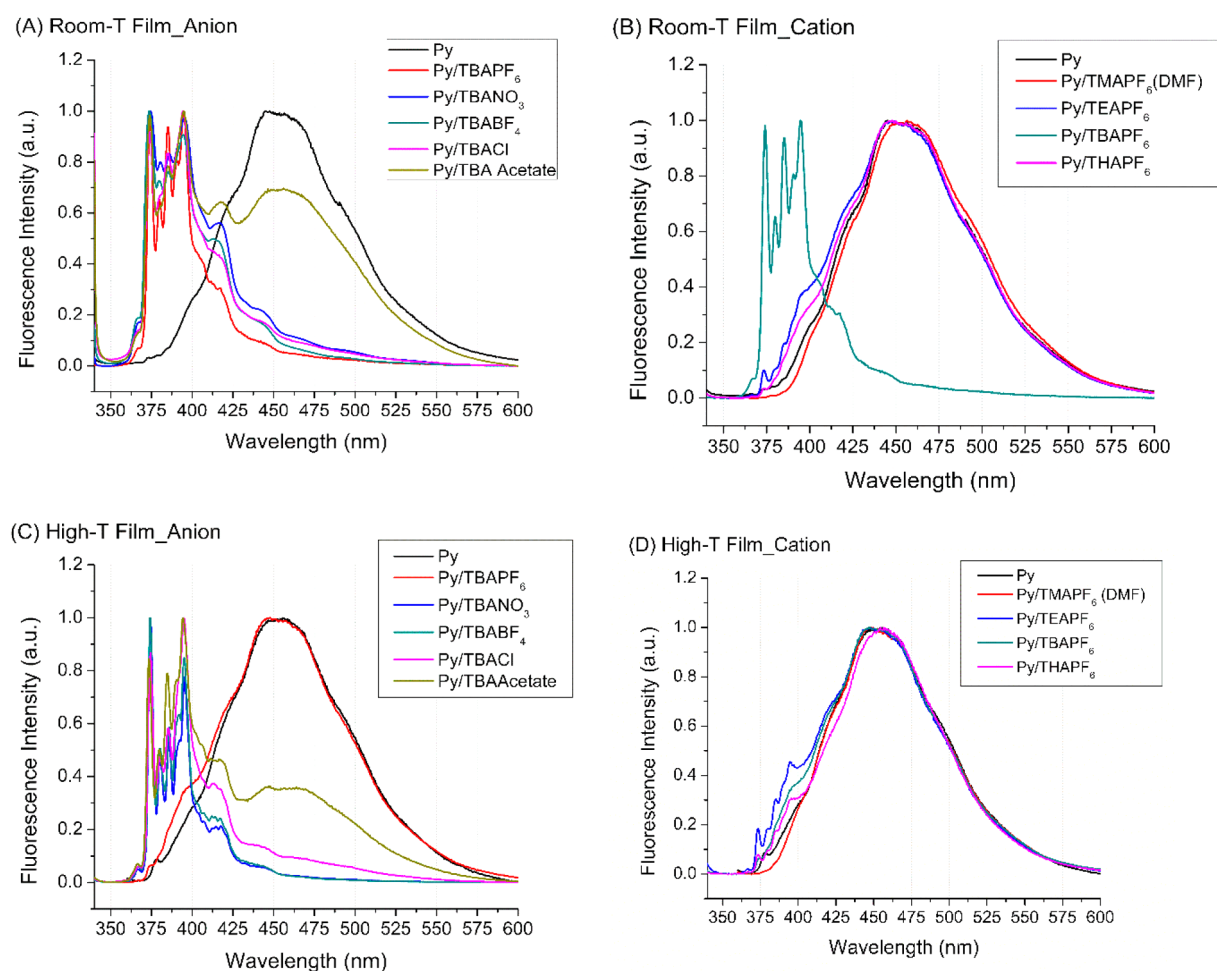


Figure 3. Fluorescence spectra (excited at 334 nm) of the films composed of Py and a variety of salts (A) and (B) contain the measurements of room-*T* prepared films, while (C) and (D) contain the measurements of high-*T* prepared films. (A) and (C) illustrate the fluorescence spectra of the films composed of Py/TBA⁺ (different anions): Py (black), Py/TBAPF₆ (red), Py/TBANO₃ (blue), Py/TBAPF₄ (green), Py/TBACl (pink), and Py/TBA acetate (light green), respectively; (B) and (D) illustrate the fluorescence spectra of the films composed of Py/PF₆[−] (different cations): Py (black), Py/TMAPF₆ (red), Py/TEAPF₆ (blue), Py/TBAPF₆ (green), and Py/THAPF₆ (pink), respectively.

formation of Py excimers ($I_{\text{exc}}/I_{\text{mon}}$) and the polarity of the Py environment (I_1/I_3) have been previously reported together,^{39,40} they have not been closely examined and correlated because the studied Py concentrations were low thus resulting in insignificant excimer emission. Figure 2A shows that the emission of Py excimer in acetone is enhanced drastically (high $I_{\text{exc}}/I_{\text{mon}}$) above 0.05 M of the Py concentration, where the polarity of Py also starts to decrease (low I_1/I_3), representing that the hydrophobic environment around Py is strongly related to the formation of excimer in the solution. In regards to Py concentration, Figure 2B indicates that the excimer intensity decreases significantly as the Py concentration is lower than 0.05 M.

A similar approach was taken to evaluate the effect of various tetra-alkylammonium salts on the fluorescence of Py excimer, including a series of salts associated with the same cation (i.e., TBA⁺ chain) but different anions as well as another series of salts which have the same anion (i.e., PF₆[−]) but different chain lengths of tetra-alkylammonium. The $I_{\text{exc}}/I_{\text{mon}}$ increases and the I_1/I_3 decreases with increased Py concentration regardless of the types of salts (listed in Table S1 Supporting Information), revealing no significant dependence of the chemical structures of the salts on the formation of Py excimer in solution state.

3.2. Py Excimer Fluorescence in Solid State in the Presence of Salts. Effect of Salt Structures and Film Preparation Methods. In solid state, the effect of salts on the formation of Py excimer differs significantly from that in solution. The fluorescence spectra of Py/salt thin films made from the solutions by solvent evaporation at two different temperatures (25 and 100 °C) are investigated. Figure 3A–D illustrates the fluorescence spectra of the Py/salt thin films. In contrast to the solution state, the excimer quenching in the films is strongly affected by the chemical structures of the salts. When comparing different anions in the case of TBA⁺ cation [Figure 3A], most of the films show low Py excimer fluorescence except for that of Py/TBA acetate. However, when we compare the effect of different cations [Figure 3B], an unexpected phenomenon is observed that the excimer fluorescence is only inhibited by TBAPF₆, a salt with a specific chain length of four carbons, while both Py/TEAPF₆ and Py/THAPF₆ films show a strong excimer peak. Since TMAPF₆ (tetramethylammonium PF₆) is not soluble in acetone, the Py/TMAPF₆ film was made by evaporation from a Py/TMAPF₆/dimethylformamide (DMF) solution, where both Py and TMAPF₆ are soluble. The emission spectrum also shows high excimer fluorescence. The result indicates that only TBAPF₆ has a quenching effect on Py excimer as prepared at room-*T*.

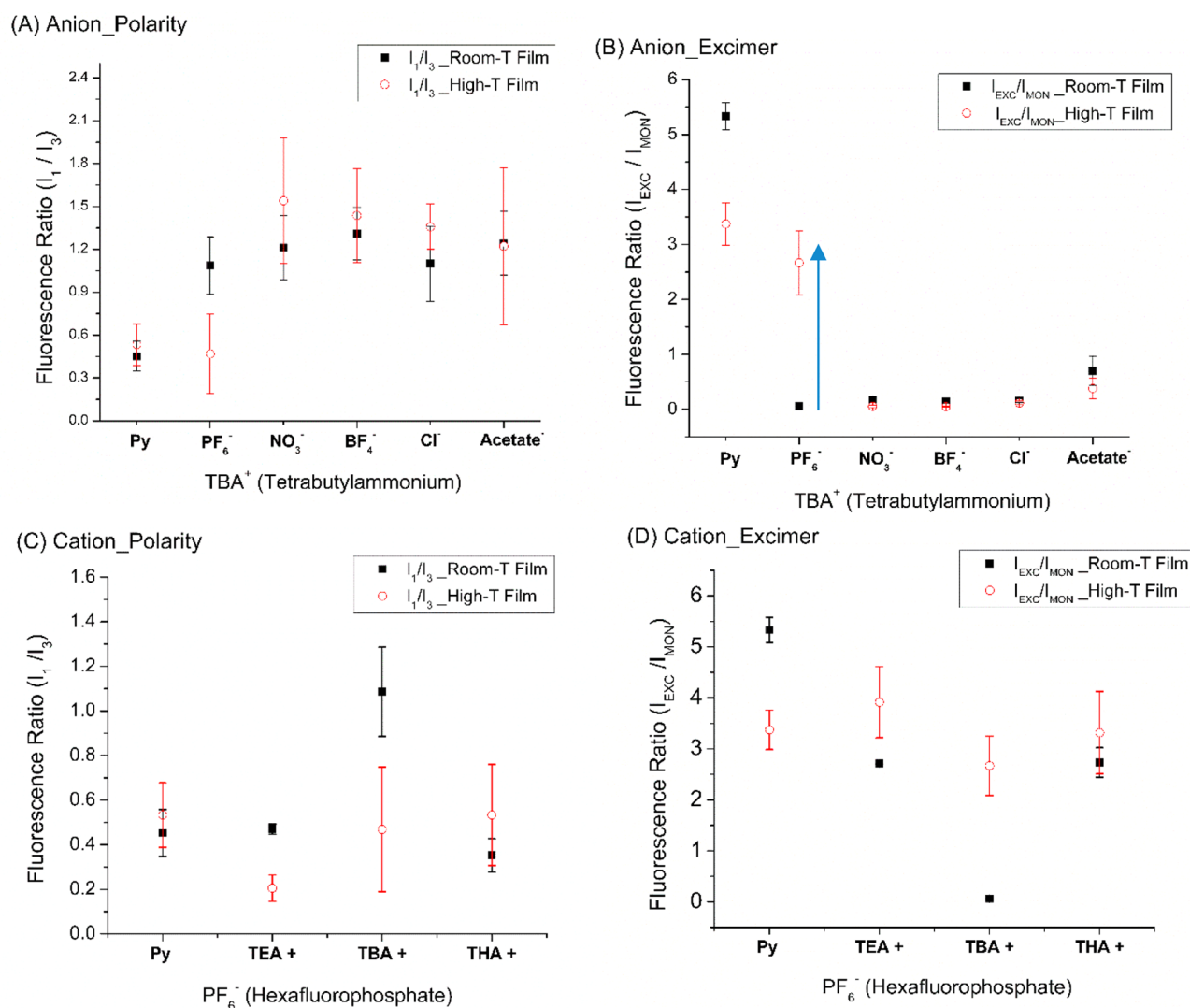


Figure 4. Fluorescence intensity ratio of (A) I_1/I_3 (B) I_{exc}/I_{mon} of Py/TBA⁺ salt films prepared via room-T (■, black) and high-T (○, red) evaporation; (C) I_1/I_3 (D) I_{exc}/I_{mon} of Py/PF₆⁻ salt films prepared via room-T (■, black) and high-T (○, red) evaporation.

Figure 3C,D shows the fluorescence spectra of thin films (Py in various salts) prepared at high-T (100 °C) evaporation. This preparation method is chosen because enhanced excimer was found in the ternary film composed of Py/PS/TBAPF₆ under the same process.³³ Here, a significant difference in I_{exc}/I_{mon} is also found between the high-T and room-T evaporation films in the binary Py/TBAPF₆ system. However, the other Py/salt systems do not show strong temperature dependence in excimer fluorescence. Apparently, TBAPF₆ behaves differently from the other salts in this study.

Previously, it has also been reported that the excimer fluorescence of the ternary film (PS/Py/TBAPF₆) increases significantly after annealing the film under a high solvent vapor pressure.³³ The enhancement of excimer fluorescence could be explained by high solvent vapor pressure inducing the formation of Py excimers.³¹ The same approach is applied to the binary system, i.e., Py/TBAPF₆. However, high vapor pressure annealing under either acetone or THF does not change the Py excimer fluorescence in this case (Figure S1 in Supporting Information). The result suggests that PS serves an essential role as a plasticizer in the presence of high solvent vapor pressure, providing the required mobility for the Py or

salt molecules to reorganize themselves in the molecular configuration of Py excimer. Note that the solvation power of vapor phase is not equivalent to that in the solution state. We further annealed the high excimer fluorescence Py/TBAPF₆ film (made by solvent evaporation at high-T) at 100 °C for 1 h to investigate the effect of high thermal energy on quenching (Figure S2 in Supporting Information). Unlike the ternary system where a nearly complete excimer quenching took place,³³ no significant change of Py excimer fluorescence intensity was observed in the binary system, indicating that the previous excimer fluorescence quenching in the Py/PS/TBAPF₆ film after 1 h of high-T annealing²⁴ was attributed to the enhanced mobility of Py and TBAPF₆ as associated with the highly mobile PS chains induced by high temperature (above the glass transition temperature of PS). However, in the Py/TBAPF₆ system, there is no such mechanism for mobility enhancement in absence of PS chains.

Hydrophobicity (I_1/I_3) and Excimer (I_{exc}/I_{mon}). Like the result in the solution state (Figure 2), the correlation of the hydrophobicity of Py surrounding with the Py excimer fluorescence is also studied in comparison of different salts in the solid state as shown in Figure 4. Figure 4A illustrates the I_1/I_3

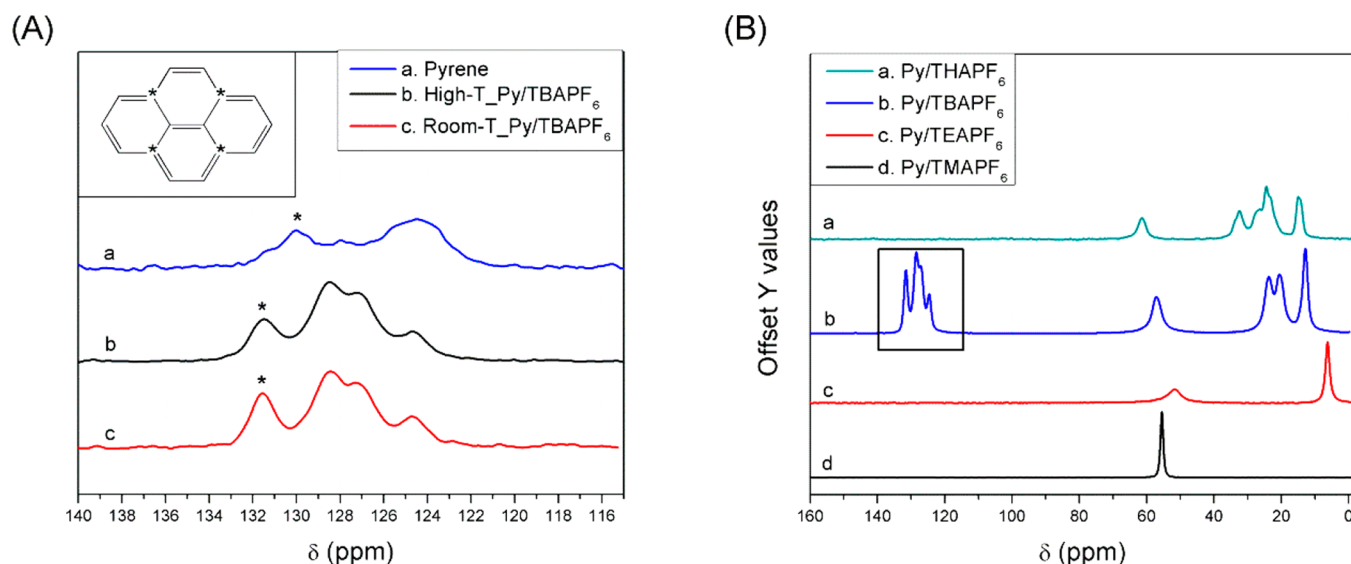


Figure 5. ^{13}C NMR spectra of (A) pure Py film (blue), Py/TBAPF₆ film prepared by high- T evaporation (black) and room- T evaporation (red), which is the blowup of the box in (B). The inset shows a pyrene molecule where the asterisks represent the carbons for the corresponding NMR shifts around 130–132 ppm. (B) Complete NMR spectra of Py/TMAPF₆ (black), Py/TEAPF₆ (red), Py/TBAPF₆ (blue), and Py/THAPF₆ (green) films prepared by room- T evaporation.

I_3 of several Py thin films containing TBA⁺ salts with different anions prepared at different temperatures. Except for the Py/TBAPF₆ film prepared at high T , all the other samples result in a more polar environment than Py itself judged by higher values of I_1/I_3 (>1). Figure 4B shows that the $I_{\text{exc}}/I_{\text{mon}}$ for the same series of TBA⁺ salts indicate low $I_{\text{exc}}/I_{\text{mon}}$ (<1) in most of the cases with the exceptions being the Py films and Py/TBAPF₆ film made at high T . The correlation of the Py excimer emission with its hydrophobic environment is consistent with that observed in the solution state (Figure 2). Figure 4C illustrates the I_1/I_3 of films made of Py and PF₆[−] anion with various chain lengths of tetra-alkylammonium cations. The result also shows a general feature of hydrophobic environment for Py (i.e., $I_1/I_3 < 1$) in the PF₆[−] films except for the Py/TBAPF₆ film prepared at room temperature. The same correlation of hydrophobicity with the formation of Py excimer is found in this series as shown in Figure 4D, where the Py/TBAPF₆ film made at room temperature shows almost no excimer fluorescence.

Several findings deduced from the results are worth noting. First, both solution and solid state results seem to suggest that the polar environment of Py molecules may strongly correlate with the excimer fluorescence – *the more hydrophobic, the higher the excimer fluorescence*. Note that in the previous ternary system (i.e., Py/PS/TBAPF₆ films) the hydrophobicity of Py environment is a required but not sufficient condition for high excimer fluorescence.³³ Examples of low I_1/I_3 but low $I_{\text{exc}}/I_{\text{mon}}$ were occasionally found in the solution casting film made of PS/Py/TBAPF₆. Second, the result of Figure 4A–D suggests that the *Py excimer quenching is mainly attributed to the TBA⁺ cation* instead of the anions (PF₆[−], BF₄[−], Cl[−], acetate[−], and NO₃[−]) based on the high $I_{\text{exc}}/I_{\text{mon}}$ observed in Py films containing tetra-alkylammonium cations with other chain lengths (such as TMA⁺, TEA⁺ and THA⁺). The unique quenching behavior induced by TBA⁺ salts is possibly due to the perturbation of the molecular configuration of Py excimer^{40–42} or the alternative nonradiative pathways. The detail of these scenarios will be discussed later. In regards to

anions, PF₆[−] does play a unique role in retaining high excimer fluorescence at high solvent vapor pressure (induced by high T) when the molecules are mobile enough, that is, from solution to solid state. Other anions do not show such effect. Note that no clear correlation between I_{exc} and topology was observed in previous study in a three-component (Py/PS/TBAPF₆) system.³³ Here to examine the effect of the topology on hydrophobicity (I_1/I_3) of the Py surroundings, SEM was also conducted (Figure S3, Supporting Information). The result shows no significant difference in the Py/TBAPF₆ films prepared at high and room T although they show very different $I_{\text{exc}}/I_{\text{mon}}$ and I_1/I_3 values (Figure 3). Moreover, no significant difference in SEM data was observed in the presence of different salts. This suggests that there is weak correlation, if any, between topology and the formation of Py excimer in the film.

Interactions between Pyrene and Salts. The fact that a strong correlation is revealed between the polarity around Py and the formation of Py excimer prompts us to study the effect of TBAPF₆ on the Py local molecular environment. Figure 5(A) shows the ^{13}C NMR spectra of three thin films: a pure Py film and two Py/TBAPF₆ films prepared at a high and a room temperature, which yield high and low $I_{\text{exc}}/I_{\text{mon}}$, respectively. It has been reported that Py has five peaks *in solution* in the spectra between 125–131 ppm (124.58 ppm, 124.81 ppm, 125.70 ppm, 127.25 ppm, 131.04 ppm, respectively⁴³), while only three of them are resolvable in our case [Figure 5A], possibly due to the lack of mobility in the solid state. Individual Py peaks are affected somewhat by TBAPF₆ to increase relative intensities of Py peaks. Another important finding in this study is that the peak at 130 ppm [marked as * in Figure 5A] shifts to 131.6 ppm. This result is consistent with a previous study⁴¹ where the interaction between polyaromatic hydrocarbon and quaternary alkylammonium group causes a NMR peak shift of several proton and C atoms. This shift is presumably due to the decrease in the symmetry of aromatic moiety attributed to the positively charged ammonium group polarizing the π -electrons of Py moiety.^{40,41,44} Figure 5B shows the ^{13}C NMR spectra of

Py/PF₆[−] salts films. Interestingly, the Py peaks around 125–132 ppm are only shown in Py/TBAPF₆ unlike other Py/salt films (i.e., Py/TMAPF₆, Py/TEAPF₆, Py/THAPF₆), indicating that Py interacts with TBAPF₆ very differently from other salts. The ¹³C NMR peaks below 60 ppm in Figure 5(B) are contributed by tetra-alkylammonium cations.

Then, the diminished Py peak in the ¹³C NMR (from 120 to 134 ppm) may be related to the reduced amount of Py monomers in the cases of Py/TMAPF₆, Py/TEAPF₆ and Py/THAPF₆. In this regard, it is speculated that the marginal differences between the ¹³C NMR spectra of the two Py/TBAPF₆ films prepared via room-*T* and high-*T* evaporation [Figure 5A] is possibly due to the same local environment of Py monomer left with a specific molecular interaction regardless of existence of excimer. Besides NMR, XRD was also performed on the sample to investigate the correlations between crystalline structures of Py/salts films and the formation of Py excimer under different procedures as shown in Figure 6. Note that

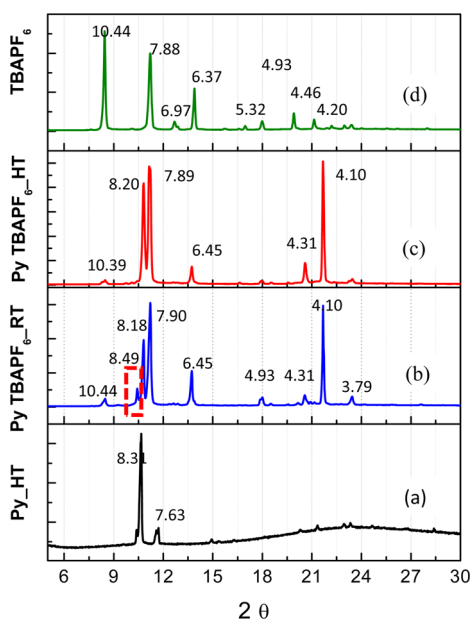


Figure 6. XRD spectra of different films (a) Py (black) (b) room-*T* prepared Py/TBAPF₆ (blue) (c) high-*T* prepared Py/TBAPF₆ (red) (d) TBAPF₆ (green). The *d*-spacings corresponding to the individual peak positions are shown in Å. A new peak is found in the spectrum of room-*T* prepared Py/TBAPF₆ film (framed by the red rectangle).

both Py and the associated salt contain crystalline structures yielding diffraction peaks. Although a significant difference in the $I_{\text{exc}}/I_{\text{mon}}$ was observed in high-*T* and room-*T* prepared Py/TBAPF₆ films (Figure 3), their XRD data (Figure 6) are similar except for a new peak indicative of a *d*-spacing of 8.49 Å (marked in red box) observed in case of room-*T* prepared Py/TBAPF₆. This peak is not originated from Py or TBAPF₆ according to any possible combination of Miller indices (Table S2). However, this peak was only observed in this sample but not revealed in other Py/salt films, which contain, either TBA⁺ or PF₆[−] (Figure S4, Supporting Information), leading to inclusive interpretation for this special *d*-spacing.

Lifetime and Excitation of Py Excimer in the Presence of TBAPF₆. Although the hydrophobicity of the Py environment and the unique effect of TBAPF₆ on the Py excimer fluorescence are observed, the mechanism of Py excimer quenching demands further investigation. As mentioned

previously, two possible mechanisms may take place: static quenching, where the quenchers (i.e., salt) and the fluorophores (i.e., Py) form nonfluorescent complexes and dynamic quenching, where the same excited fluorophores undergo nonradiation pathways to relax from the excited to the ground state. The two scenarios can be distinguished by the lifetime of the fluorophore (e.g., Py excimer in this case), which is inversely proportional to the sum of rate constants from all relaxation processes, *k*, as expressed in eq 1.²⁴

$$\tau = \frac{1}{k} = \frac{1}{(k_f + k_{nr})} \quad (1)$$

where *k_f* and *k_{nr}* are the rate of fluorescence and the sum of rates of nonradiative processes (e.g., internal conversion and vibration relaxation, intermolecular energy transfer, and intersystem crossing, etc.), respectively. Therefore, the invariant lifetime indicates static quenching where *k_{nr}* = 0, while in the case of dynamic quenching (associating with a finite positive value of *k_{nr}*) shorter lifetime should be expected.

In this study, the fluorescence lifetime was measured to investigate the origin of Py excimer quenching mechanism by the TBA⁺ salts. The fluorescence intensity decay can be described by the following equation:

$$\frac{I(t)}{I_{\text{max}}} = \sum_i A_i e^{-k_i t} = \sum_i A_i e^{-t/\tau_i} \quad (2)$$

where *A_i*, *τ_i* represent the fractions and lifetime of each relaxation process, respectively.

Note that the lifetime of fluorescence in this study was measured with wavelengths above 450 nm from Py excimer. Figure 7A shows the excimer fluorescence decays of the Py and Py/TBAPF₆ in the solution state and the two decay curves practically collapse on top of each other, indicating that TBAPF₆ has no effect on Py excimer fluorescence in solution state, consistent with the steady-state fluorescence result shown in Table S1. In addition, all the other solutions containing Py/TBA⁺ salts (various anions) also yield the same decay pattern as that of Py solution further confirming the above statement (Figure S5 in the Supporting Information). In comparison with solution, the fluorescence intensity of Py excimer in the Py thin film decays much slower as shown in Figure 7B, suggesting that the fluorescence lifetime of the Py excimer is shorter in the solution state than that in the solid state. This may be due to the increased frequency of collisions of Py excimers with surrounding solvent molecules and/or solvent dipole perturbation. It has been reported that the excited-state molecule can interact with the surrounding solvent molecules whose polarity may significantly affect the de-excitation of Py returning to the ground state.⁴⁵ These excited-state solute/solvent interactions (i.e., dipole-induced dipole interaction between Py and solvent) often result in characteristic emission spectra as well as in the lifetime of the excited molecules.⁴⁵

In Figure 7C, the high-*T* prepared Py/TBAPF₆ film appears a very similar decay pattern as that of the Py film, indicative of a similar decay mechanism. Though both decay curves of Py and high-*T* prepared Py/TBAPF₆ films can be described with a single exponential decay reasonably well, better fits are obtained by a double exponential decay with a major population (>95.4%) of short-lifetime *τ*₁ of ~12 ns and a minor population (<4.6%) of slightly different long-lifetimes *τ*₂, 31.8 and 41.6 ns for Py and Py/TBAPF₆, respectively (Table S2 in Supporting Information). This observation lends itself to a possible

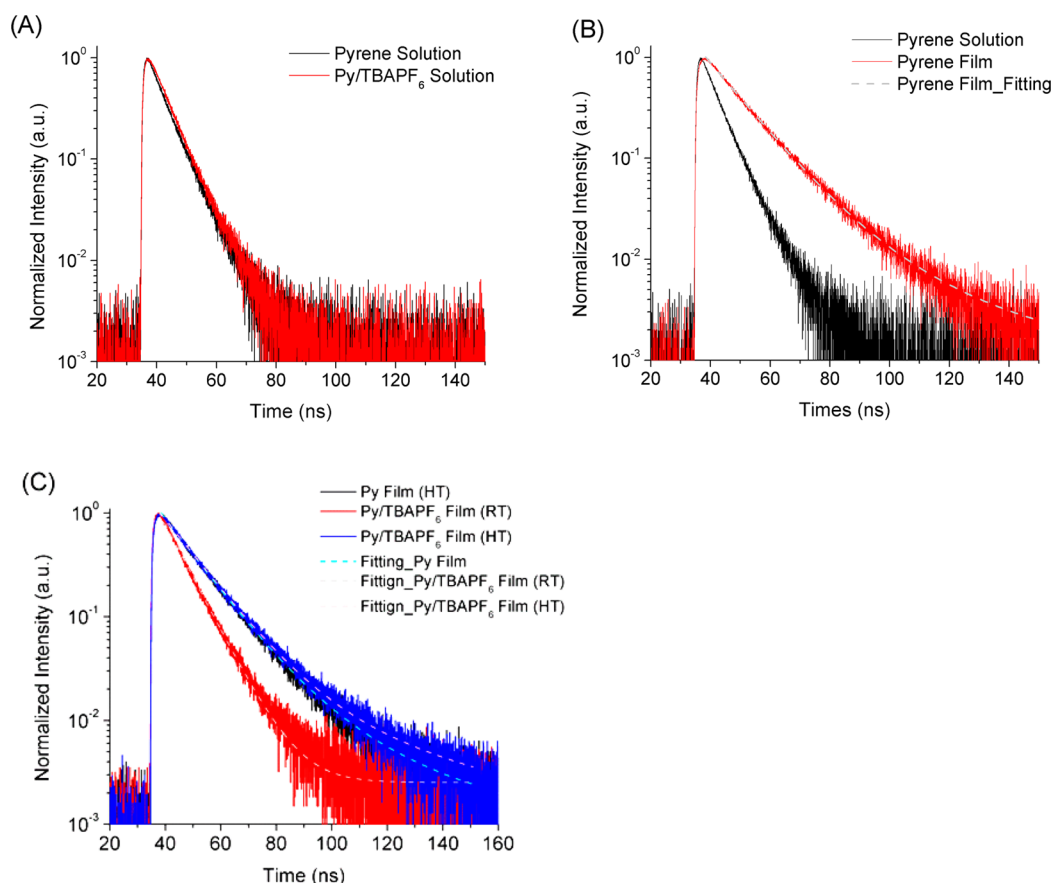


Figure 7. Fluorescence lifetime measurements of (A) pure Py (black) and Py/TBAPF₆ (red) solutions, (B) pure Py solution (black) and film (red) and (C) Py film (black), room-*T* prepared Py/TBAPF₆ film (red), and high-*T* prepared Py/TBAPF₆ film (blue). The dotted lines are the best fits (see Supporting Information).

(A) Monitored at $\lambda_{em} = 375$ nm (monomer)

(B) Monitored at $\lambda_{em} = 455$ nm (excimer)

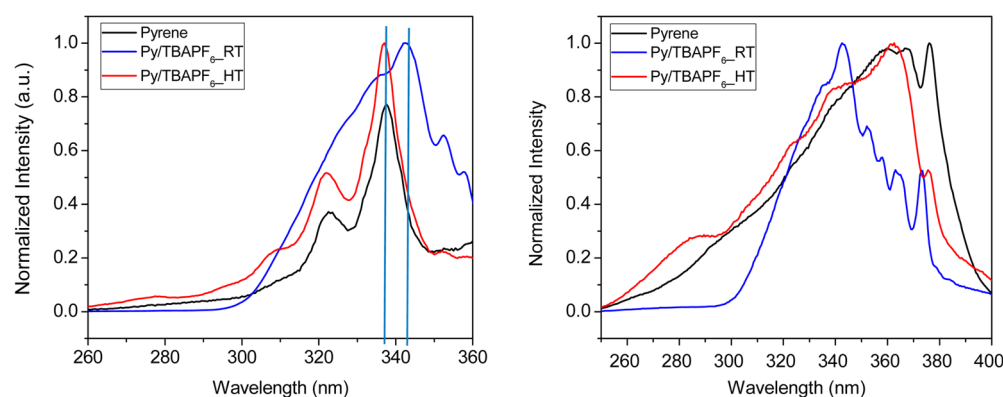


Figure 8. Fluorescence excitation spectra of Py (black), room-*T* prepared Py/TBAPF₆ film (blue), and high-*T* prepared Py/TBAPF₆ film (red), monitored at two emission wavelengths (A) 375 nm (I_{mon}) and (B) 455 nm (I_{exc}).

explanation that the majority of Py molecules in the high-*T* prepared Py/TBAPF₆ thin films follow a similar relaxation pathway compared with those in the Py film. Note that the lifetime of Py thin film prepared at room-*T* shows the same decay rate as that of the high-*T* prepared film (data not shown) and that both films have the same excimer fluorescence (Figure 3). In the case of a binary system (i.e., Py/TBAPF₆), a drastic difference in the fluorescence is found between room-*T* and high-*T* prepared films. To further confirm the relationship

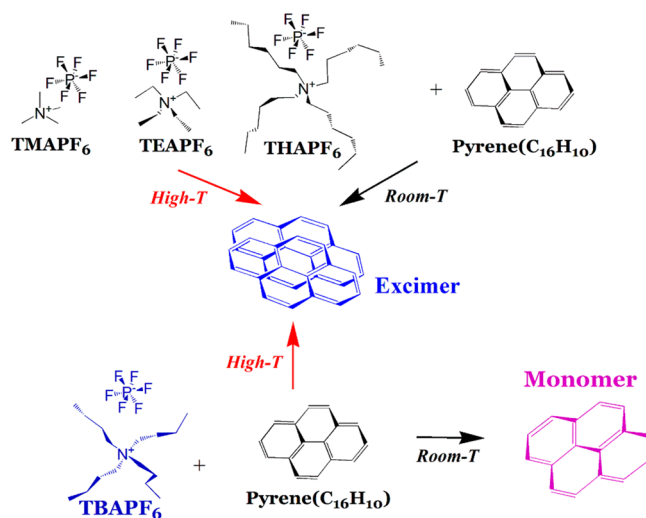
between the excimer fluorescence intensity and its lifetime decay, the decay pattern of room-*T* prepared Py/TBAPF₆ film [Figure 7C red curve] was also examined. The result can be fitted well by a single exponential decay with a much smaller τ_1 of 8.4 ns (Table S2 in Supporting Information). The shorter lifetime in room-*T* prepared Py/TBAPF₆ film compared with those of the Py and high-*T* Py/TBAPF₆ films ($\tau_1 \approx 12$ ns) indicates a dynamic quenching process involving fast non-radiative pathways. An effort is also made to fit the decay

through a linear combination of an independent single exponential decay and the double-exponential decay parameters obtained from the high-*T* prepared Py/TBAPF₆ data (Equations S1 and S2 in Supporting Information). However, the best fitting coefficient of the double-exponential decay is practically 0, indicating that there is no contribution from the same decay mechanism found in the room-*T* prepared Py/TBAPF₆ film as that of the Py or high-*T* prepared Py/TBAPF₆ films (Table S3 in Supporting Information). On the basis of eqs 1 and 2, the fast decay (i.e., smaller τ_1) in the room-*T* prepared Py/TBAPF₆ film is attributed to a larger k_{nr} than that of the high-*T* prepared Py/TBAPF₆ film if the intrinsic k_f remains constant.

The excitation spectra were also collected at specific wavelengths to provide the insight into the electronic states of Py in the presence TBAPF₆. The excitation of Py from the ground-state (S_0) to the higher electronic energy levels of S_1 , S_2 , S_3 , and S_4 can be observed around 372, 334, 272, and 243 nm, respectively, in different solvents (i.e., cyclohexane, CH₂Cl₂).⁴⁶ In this study, we focus on the excitation level from $S_0 \rightarrow S_2$ transition between 334 and 345 nm which was commonly observed in the fluorescence of Py. Figure 8 shows the excitation spectra of Py, room-*T* and high-*T* prepared Py/TBAPF₆ films at emission wavelengths, λ_{em} of 375 and 455 nm at the vicinities of monomer and excimer fluorescence, respectively. The peak in the excitation spectrum of the room-*T* prepared Py/TBAPF₆ film observed at $\lambda_{em} = 375$ nm is found at 343 nm, indicating a red shift from 337 nm which are observed in both high-*T* prepared Py/TBAPF₆ and Py films [Figure 8A]. This suggests a lower energy electronic level of S_2 in the case of room-*T* prepared Py/TBAPF₆. A practically invariant excitation spectrum of the room-*T* prepared Py/TBAPF₆ film is observed at $\lambda_{em} = 450$ nm (excimer) compared with that at $\lambda_{em} = 375$ nm (monomer) as shown in Figure 8B. However, the range of the excitable wavelengths becomes broader for the high-*T* prepared Py/TBAPF₆ and Py films (compared with the corresponding room-*T* spectra), representing the formation of Py excimers.^{22,47} This result suggests that the room-*T* prepared Py/TBAPF₆ film has drastically different the electronic and vibronic levels from those of the high-*T* prepared Py/TBAPF₆ and Py films, leading to the nonradiative pathways, which quench the Py excimer.

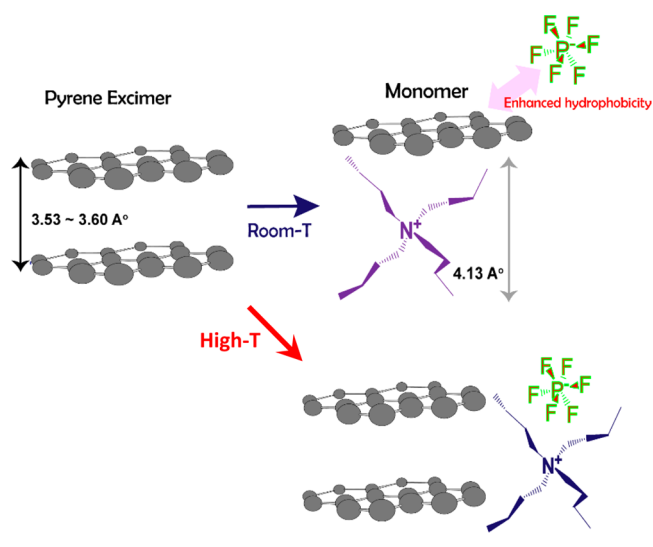
Further Insights to the Effect of TBAPF₆. Scheme 1 summarizes the observation of the formation of Py excimer in the presence of different chain lengths of quaternary ammonium salts and procedures. The fact that the Py/TBAPF₆ thin film prepared at room *T* appears to be the only condition inhibiting the formation of Py excimer indicates the carbon chain length of the tetra-alkylammonium is the key parameter of quenching. This phenomenon can be explained by two effects: the size of tetra-alkylammonium cation and the ion association as described below. It has been reported that the proximity of Py molecules is an important factor in forming Py excimer (0.353–0.360 nm) with different configurations (i.e., slipped parallel, graphite type, and crossed).⁴⁸ Note that the van der Waals size of tetra-alkylammonium cation increases with increased carbon chain length: TMA⁺ (0.270 nm) < TEA⁺ (0.336 nm) < TBA⁺ (0.413 nm) < THA⁺ (0.442 nm).⁴⁹ As the cation size increases slightly larger than the intermolecular distance between Py molecules to form an excimer (in the case of TBA⁺), the fluorescence quenching reaches its maximum. However, further increased size of the cation (e.g., THA⁺) does not affect the excimer fluorescence intensity. The fact suggests

Scheme 1. Formation of Py Excimer in the Presence of Different PF₆[−] Associated Salts under a High-*T* or Low-*T* Thin-Film Preparation Procedure



that an optimal cation size is presumably the key perturb the molecular configuration of Py excimer, resulting in the quenching of Py excimer. Since Py has a higher electron negativity (due to the high density of π -electron), it is speculated that tetraalkylammonia cation might be able to insert between the Py excited dimer if the size is smaller than or comparable to the intermolecular distance between Py (as shown in Scheme 2).

Scheme 2. Proposed Scheme of the Formation of Py Excimer with TBAPF₆ under a High-*T* or Low-*T* Thin-Film Preparation Procedure, Respectively



The excimer fluorescence may be quenched when the Py intermolecular distance is significantly perturbed by the comparable size of cation as observed in the presence of TBA⁺. Cations with smaller sizes (e.g., TMA⁺ and TEA⁺) do not affect the excimer spacing, while those with larger size (e.g., THA⁺) cannot insert between the Py molecules.

The hydrophobic and temperature dependence of the quenching mechanism can be also explained by the association between the anions and cation (namely TBA⁺ in this case). It has been reported that the ion association constant depends on

not only the properties of the ions (ion radius and ion charge) but also the nature of the solvent medium.⁵⁰ On the basis of the Denison and Ramsey equation, the ion association increases upon the elevation of temperature.⁵¹ It is presumed that the increased ion association between TBA⁺ and PF₆⁻ during the high-*T* evaporation (in the presence of the solvent) may weaken the interaction between TBA⁺ and Py excimer, thus restoring the Py excimer fluorescence as shown in Scheme 2. Moreover, weaker interaction between PF₆⁻ and solvent upon the elevation of temperature has been reported,⁵⁰ suggesting a more hydrophobic environment induced by PF₆⁻. Therefore, the increased *T* can effectively enhance not only the hydrophobicity of the Py environment but also the PF₆⁻ association with TBA⁺, leading to less perturbation of the formation of Py excimer.

To the best of our knowledge, this report presents the first observation of inhibited formation of Py excimer due to the different cation chain lengths of quaternary ammonium and the peculiar phenomenon of retaining excimer intensity (only in the case of TBAPF₆) of a high-*T* prepared film.

4. CONCLUSION

The effect of different chemical structures of salts on the formation of Py excimer has been investigated. In solution state, the Py concentration is mostly responsible for the formation and quenching of Py excimer nearly independence of the salts since the process is mainly controlled by the diffusion of Py. On the contrary, the chemical structures of salts show a significant effect on the Py excimer quenching in solid state. The cation with butyl chain length (TBA⁺) results in significant quenching of the Py excimer, while methyl (TMA⁺), ethyl (TEA⁺), and hexyl (THA⁺) chains have little or no effect on the Py excimer emission. This result indicates that subtle variation of the cationic size may lead to drastic quenching of Py excimer. The excimer fluorescence is found closely related to the polarity around the Py molecules, that is, the higher I_1/I_3 , the lower $I_{\text{exc}}/I_{\text{mon}}$. The result of the fluorescence lifetime measurement indicates that the low $I_{\text{exc}}/I_{\text{mon}}$ in Py/TBAPF₆ films prepared at room *T* is mainly caused by nonradiative “dynamic quenching” processes. Moreover, the $I_{\text{exc}}/I_{\text{mon}}$ of Py/TBAPF₆ film is restored by high-*T* evaporation method, which however does not promote Py excimers with other anions in study. Such temperature dependence implies that the ion interaction or hydrophobicity between the PF₆⁻ anion and TBA⁺ cation may change drastically upon variation of temperature during the drying process. Nevertheless, once the relative molecular orientation (or position) between Py and TBAPF₆ is “locked” in, thermal energy (up to 100 °C) shows no effect on the fluorescence in solid state due to low molecular mobility (in contrast to the system containing PS). To the best of our knowledge, such peculiar effects of TBA⁺ and PF₆⁻ on the Py excimer quenching are reported for the first time.

■ ASSOCIATED CONTENT

Supporting Information

Table of data relating I_1/I_3 as a function of [Py], fluorescence emission spectra, SEM images, tables of data indicating lattice parameters and Miller indexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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