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Abstract

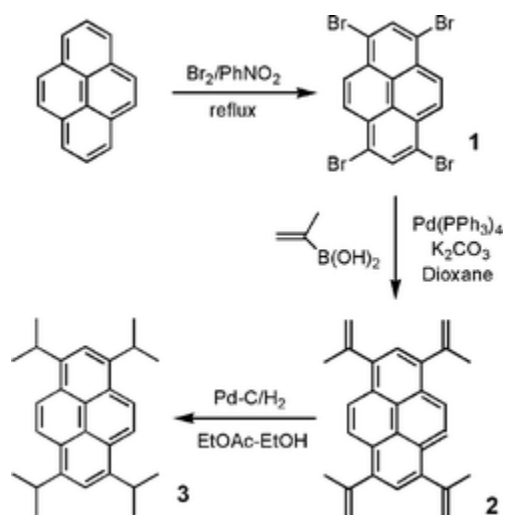
A practical synthesis of **1,3,6,8-tetraisopropylpyrene** and the isolation and X-ray structural characterization of its monomeric cation radical salt are described.

Pyrene has been extensively utilized as a fluorescent probe for studying the conformational changes in proteins in solution owing to its long excited-state lifetime and characteristic excimer formation due to its self association.¹ The ability of pyrene to self associate into ordered structures has also been exploited in its usage as liquid crystalline materials.² In stark contrast, it is this ability of π - π stacking and excimer formation in solution and solid state that has limited the usage of pyrene as an emissive material in organic light-emitting diodes (OLED's) and related applications.³

Although, pyrene undergoes selective and quantitative bromination at the 1,3,6,8-positions to produce the corresponding tetrabromopyrene,⁴ attempted electrophilic substitutions to functionalize the pyrene core at the 1,3,6,8-positions with isopropyl groups, and thereby sterically congesting the flat fluorophore,⁵ led to complex mixtures of polyalkylated pyrenes from which the separation of the desired isomer was rather tedious.⁶

Our continuing interest in the design and syntheses of stable organic cation radicals or hole carriers, which are of fundamental importance to organic materials science,⁷ led us to obtain an efficient and scalable route for the preparation of 1,3,6,8-tetraisopropylpyrene (**3**) and demonstrate the efficacy of sterically hindered tetraisopropylpyrene for the isolation and X-ray crystallographic characterization of its monomeric cation-radical salt. The details of these findings are described herein.

After several failed attempts, in our hands, to synthesize **3** by Friedel–Crafts alkylation,^{5,6} we resorted to a different approach as summarized in Scheme 1. Thus, a 4-fold Suzuki coupling between the readily-available 1,3,6,8-tetrabromopyrene,⁴ and isopropenylboronic acid,⁸ afforded cleanly the 1,3,6,8-tetraisopropenylpyrene (**2**) in >92% isolated yield. A catalytic hydrogenation of **2** over 10% Pd-C in a mixture of ethyl acetate–ethanol furnished **3** in quantitative yield. It was noted that under these hydrogenation conditions, the reduction of the pyrene core was not observed.



Scheme 1 Synthesis of 1,3,6,8-tetraisopropylpyrene (**3**).

The absorption spectrum of **3** in dichloromethane was characteristically similar to that of the parent pyrene with a modest bathochromic shift (~ 30 nm) owing to the alkyl substitutions. Furthermore, unlike the parent pyrene⁹ which showed a broad featureless excimer emission centered at ~ 472 nm in the concentration range studied (0.05–0.1 M), the tetraisopropylpyrene **3** showed only the monomeric emission (Fig. 1). As such, the observation of monomeric emission for **3** suggests that the bulky isopropyl groups exert sufficient steric

inhibition to prevent a face to face approach of ~ 3.5 Å necessary for an efficient π -stacking¹⁰ and consequent excimer formation (Fig. 1, right).

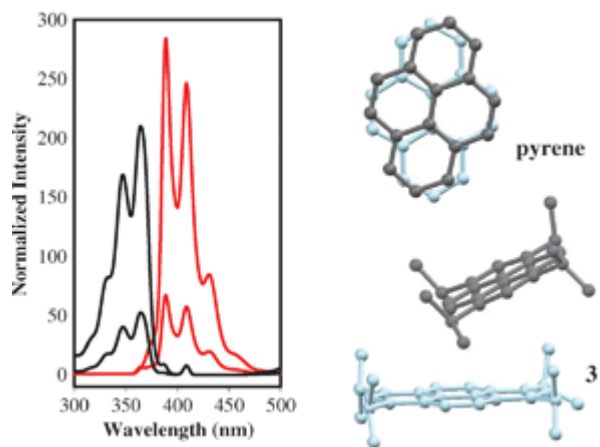


Fig. 1 Left: selected excitation (black lines) and emission (red lines) of **3** as dichloromethane solution ranging from a concentration of 1.66×10^{-6} M to 1.0×10^{-5} M. Right: calculated structures of dimeric pyrene and **3** using DFT at B3LYP-631G* level.

Next with sufficient quantities of the tetraisopropylpyrene at our disposal, it was subjected to electrochemical oxidation at a platinum electrode as a 2×10^{-3} M solution in dichloromethane containing 0.2 M *n*-Bu₄NPF₆ as the supporting electrolyte. The cyclic voltammograms (Fig. 2, left) consistently met the reversibility criteria at various scan rates of 100–500 mV s⁻¹, as they all showed cathodic/anodic peak current ratios of $i_a/i_c = 1.0$ (theoretical) as well as the differences between anodic and cathodic peak potentials of $E_{pa} - E_{pc} = 70$ mV at 22 °C. The reversible oxidation potential of **3** ($E_{ox} = 0.98$ V vs. SCE) was calibrated with added ferrocene as an internal standard ($E_{ox} = 0.45$ V vs. SCE). It is important to note that under similar conditions as above, the parent pyrene undergoes an irreversible electrochemical oxidation at $E_{ox} = 1.36$ V vs. SCE.

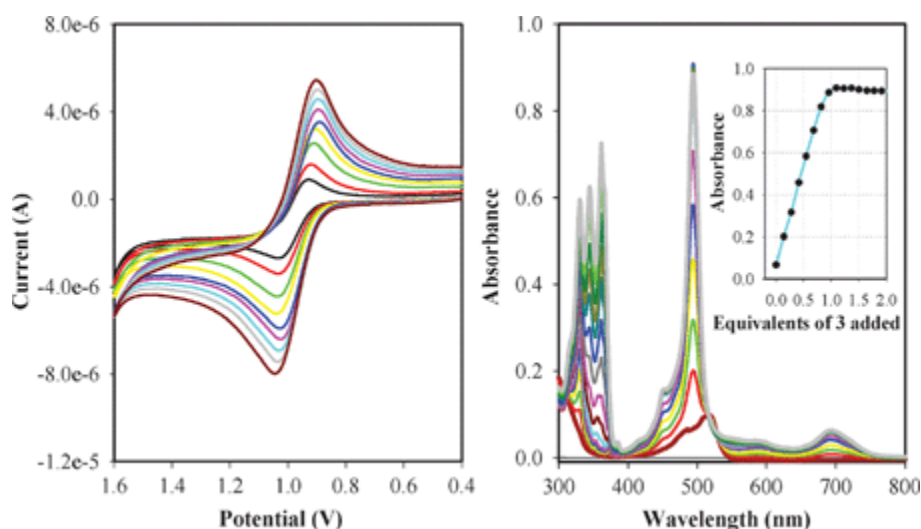
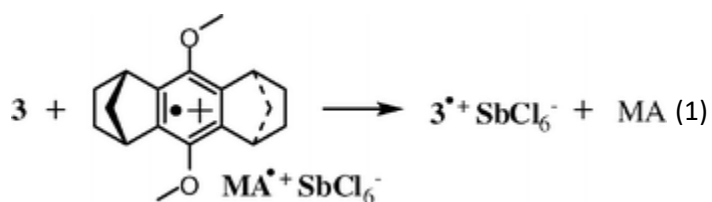


Fig. 2 Left: cyclic voltammograms of 2×10^{-3} M **3** in CH₂Cl₂ containing 0.2 M *n*-Bu₄NPF₆ at scan rates between 100 and 500 mV s⁻¹. Right: spectral changes upon the reduction of 1.33×10^{-5} M MA⁺ by incremental addition

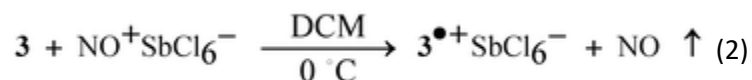
of **3** in dichloromethane at 22 °C. Inset: a plot of increase in absorbance of **3**^{•+} (monitored at 494 nm) against the equivalent of added **3**.

The electrochemical reversibility and relatively low oxidation potential of **3**, prompted us to generate its cation radical by chemical oxidation using a stable aromatic cation radical salt (MA^{•+} SbCl₆⁻; $E_{red} = 1.11$ V vs. SCE) as a one-electron oxidant.¹¹ Thus Fig. 2 (right) shows the spectral changes attendant upon an incremental addition of sub-stoichiometric amounts of tetraisopropylpyrene to a 1.3×10^{-5} M MA^{•+} [λ_{max} (log ϵ) = 518 nm (3.86)] in dichloromethane at 22 °C. Furthermore a plot of formation of the tetraisopropyl pyrene cation radical (*i.e.* increase in the absorbance at 494 nm) against the increments of added neutral **3** (see inset of Fig. 2, right), established that MA^{•+} was completely consumed after the addition of 1 equiv. of **3**; and the resulting highly structured absorption spectrum of **3**^{•+} [λ_{max} = 330, 345, 362, 494 (log ϵ = 4.83), 451 (sh), 590, and 695 nm] remained unchanged upon further addition of neutral **3** (*i.e.* eqn (1)).



The green-colored solution of the **3**^{•+} SbCl₆⁻ is highly persistent and did not show any decomposition at room temperature during the course of 12 hours. Moreover, a reduction of a dichloromethane solution of **3**^{•+} with zinc dust regenerated neutral **3** quantitatively, which further lends support to the high stability of the **3**^{•+}. As in the neutral tetraisopropylpyrene which showed no signs of aggregation (*i.e.* Fig. 1), the formation of the dimeric cation radical resulting from the cofacial stacking of **3**^{•+} with neutral **3**, was not observed as judged by the singular absence of the charge-resonance transition in the NIR region in the presence of a large excess of **3**. Note that the parent pyrene cation radical readily forms a dimeric cation radical with characteristic absorption bands at 395 and 520 nm together with a broad charge-resonance transition centered at ~1600 nm.¹²

The high stability of the tetraisopropylpyrene cation radical in solution prompted us to isolate its crystalline salt by chemical oxidation using nitrosonium hexachloroantimonate as a 1-e⁻ oxidant according to the stoichiometry in eqn (2).



Thus, a solution of **3** in anhydrous dichloromethane was added to crystalline NO⁺ SbCl₆⁻ under an argon atmosphere at ~0 °C. The gaseous nitric oxide produced was entrained by bubbling argon through the solution to yield a green-colored solution, which upon spectrophotometric analysis indicated the formation of **3**^{•+} SbCl₆⁻ (see Fig. 2). An excellent crop of dark-colored crystals, suitable for X-ray crystallographic studies, were obtained by a slow diffusion of toluene into the above solution of **3**^{•+} during a period of 2 days at -20 °C.

The crystal structure of **3**^{•+} SbCl₆⁻ revealed that cationic tetraisopropylpyrene moieties pack in a herringbone arrangement (see Fig. 3, left) with a pair of embedded toluene molecules.[‡] One of the two crystallographically independent toluene molecules forms an individual 1:1 complex with **3**^{•+} while the other toluene molecule and the counteranion (SbCl₆⁻) fill the space between the herringbone stacks of **3**^{•+} (see Fig. 3, left).[§]

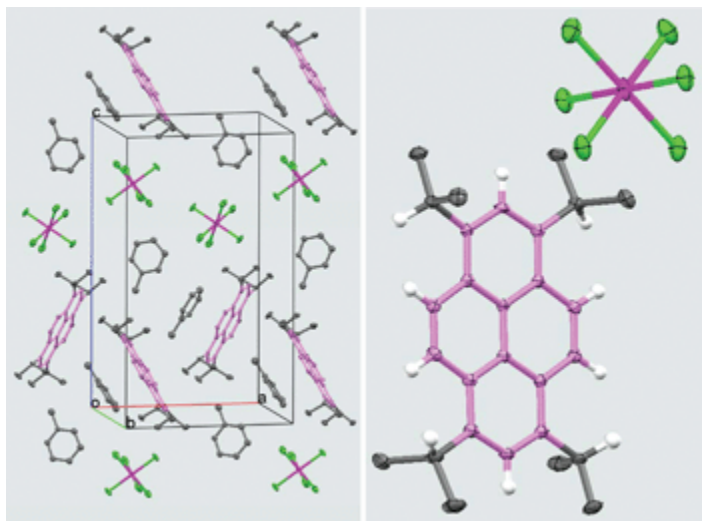


Fig. 3 The ORTEP diagram of 3^+ SbCl_6^- cation radical salt (right), with the packing diagram (left) showing that the **toluene** molecules are embedded between the herringbone stacks of 3^+ . (The thermal ellipsoids are drawn with 55% probability.)

A closer look at the bond length changes in the cation radical 3^+ , together with a comparison with its neutral form, the structure of which was established by X-ray crystallography, points to the following important observations: (i) one electron oxidation causes no perceptible change in the bonds marked **A** (d_A 139 pm) and **E** (d_B 142 pm). (ii) The increased aromatization of the two internal rings of the **pyrene** molecule on oxidation occurs by a simultaneous lengthening of the short external bonds **B** and **D** by 2.2 and 2.9 pm, respectively, and shortening of the adjacent long bonds **C** by 2.1 pm. Interestingly, the bonds which undergo most dramatic lengthening in 3^+ (*i.e.* bonds **B** and **D**) are the bonds on which the HOMO resides, *i.e.* Fig. 4 (right). (iii) The central bond **F** undergoes a shortening of 1.8 pm in order to accommodate the changes in the bond lengths of various annulenic bonds (*i.e.* **B**, **C**, and **D**).

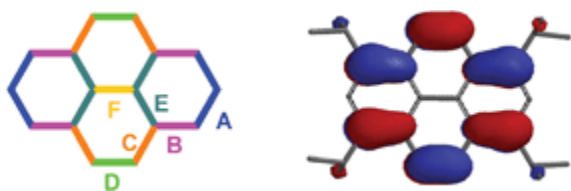


Fig. 4 Left: lettering scheme for the **pyrene** skeleton. Right: showing the localization of the HOMO of **3**, obtained by DFT calculations at the B3LYP-631G** level, on bonds labelled **B** and **D**.

The experimental observations of the bond length changes upon 1-electron oxidation of **3** were found to be in reasonable agreement with the calculated values using DFT calculations at the B3LYP-631G** level (see Table 1).⁴³

Table 1 Experimental and theoretical bond lengths of the neutral and cation radical of **3** presented in picometres (pm)

Bond type	B3LYP/6-31G**			X-Ray data		
	3	3⁺	Δ	3	3⁺	Δ
A	139.6	139.5	-0.1	138.9 (3)	138.6 (2)	-0.3
B	141.7	144.0	+2.3	141.1 (3)	143.5 (3)	+2.4
C	143.5	142.4	-1.1	143.4 (3)	141.2 (3)	-2.2
D	135.9	138.0	+2.1	134.7 (3)	137.5 (3)	+2.8
E	143.4	143.0	-0.4	142.7 (3)	142.4 (3)	-0.3
F	144.0	143.1	-0.9	144.5 (3)	142.7 (4)	-1.8

In summary, a simple and practical synthesis of **1,3,6,8-tetraisopropylpyrene (3)** has been accomplished from readily available precursors. The emission and absorption spectroscopy of the neutral and cationic **3** clearly show that the π -stacking is inhibited owing to the presence of bulky isopropyl groups. The isolation and X-ray crystal structure determination of **3⁺** SbCl₆⁻ as well as DFT calculations provide unequivocal evidence that introduction of a cationic charge (or polaron) in **3** largely affects the bonds on which the HOMO resides. Studies are underway for a more comprehensive investigation of the steric modulation of the π -stacking in various polyaromatic hydrocarbons.

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Footnotes

† Electronic supplementary information (ESI) available: Synthetic details of **3** and procedure for the isolation of its cation radical. Crystallographic data for CCDC 674750 and 674751. See DOI: [10.1039/b800168e](https://doi.org/10.1039/b800168e)

‡ *Crystal structure data for 3*. A suitable crystal ($0.20 \times 0.18 \times 0.06 \text{ mm}^3$) of **3** was obtained from a mixture of dichloromethane–acetonitrile solution at 22 °C. MW = 370.55, triclinic, space group $P\bar{1}$, $a = 11.3272(7)$, $b = 12.6764(7)$, $c = 16.9660(12) \text{ \AA}$, $\alpha = 94.595(4)^\circ$, $\beta = 92.311(4)^\circ$, $\gamma = 115.064(3)^\circ$, $D_c = 1.123 \text{ Mg m}^{-3}$, $V = 2192.2(2) \text{ \AA}^3$, $Z = 4$. The total number of reflections measured were 25 845, of which 7547 reflections were symmetrically non-equivalent. Also note that unit cell contained one molecule in a general position and two half molecules lying about their inversion centres. Final residuals were $R1 = 0.0644$ and $wR2 = 0.1740$ for 7547 reflections with $I > 2\sigma(I)$. *Crystal structure data for [3⁺ SbCl₆⁻, 2C₇H₈]*. A suitable crystal ($0.51 \times 0.23 \times 0.14 \text{ mm}^3$) of **3⁺** SbCl₆⁻ was obtained from a mixture of dichloromethane–toluene solution at -30 °C. MW = 889.27, orthorhombic, space group $Pnma$, $a = 13.8054(3)$, $b = 12.5572(3)$, $c = 23.6942(6) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $D_c = 1.438 \text{ Mg m}^{-3}$, $V = 4107.56(17) \text{ \AA}^3$, $Z = 4$. The total number of reflections measured were 34 504, of which 3746 reflections were symmetrically non-equivalent. Final residuals were $R1 = 0.0268$ and $wR2 = 0.659$ for 3746 reflections with $I > 2\sigma(I)$. Note that all four components have crystallographically imposed mirror symmetry. CCDC numbers of complexes **3** and **[3⁺ SbCl₆⁻, 2C₇H₈]** are 674750 and 674751.

§ Note that a cofacial arrangement between the toluene and **3⁺** at an inter-planar separation of 3.5 Å may stabilize the cationic tetraisopropylpyrene *via* an electron-donor acceptor interaction. Also note that both the toluene molecules are rotationally disordered (within their respective molecular planes) with the occupations of the minor components being 23 and 37%.