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Blue emitting *Butterfly*-Shaped 1,3,5,9-Tetraarylpyrenes: Synthesis, Structures, and Physical Properties

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ABSTRACT

Novel *butterfly*-shaped, *highly fluorescent stable* monomers of the type 7-*tert*-butyl-1,3,5,9-tetrakisarylpyrene were synthesized by the Suzuki-Miyaura coupling reaction of the new bromopyrene derivative 7-*tert*-butyl-1,3,5,9-tetrabromopyrene with the corresponding arylboronic acids.

The design and synthesis of efficient electroluminescent materials based on polyaromatic hydrocarbons (PAH) has been under investigation for well over a decade.¹ Pyrene and its derivatives² are important members of the polyaromatic hydrocarbon family (PAHs) that have exhibited several advantages: (1) solution processable, (2) good thermal stability, (3) enhanced charge carrier mobility, and (4) intense luminescence efficiency. Indeed, polyaromatics have been employed in organic light-emitting diodes (OLEDs)^{2,3} as well as in other optoelectronic devices,⁴ and as fluorescence probes.⁵ However, the use of pyrene as an efficient emitting material in OLED applications has been somewhat limited, primarily because the planar structure has a tendency to form π -aggregates/excimers thereby quenching the fluorescence in concentrated solution or in the solid state. To suppress the aggregation, many research groups have focused on exploring the availability of methods for the functionalization of the pyrene core. In general, the 1-, 3-, 6-, and 8-positions of pyrene preferentially undergo electrophilic aromatic substitution (S_EAr) reactions. Thus, various pyrene derivatives (see SI) can be easily accessed depending on the experimental conditions.^{2,6} On the other hand, the 4-,

5-, 9- and 10- positions of the parent pyrene are susceptible to bromination in the presence of iron powder, in the presence of sterically bulky *tert*-butyl groups located at the 2- and 7-positions as positional protective groups.⁷ Even on extending the reaction time, pentabromide pyrene derivative would be obtained.⁸ Besides electrophilic substitution of pyrene, Harris showed an efficient, one-step synthetic approach to catalyze the oxidation of the K-region of pyrene using ruthenium chloride.¹¹ Müllen *et. al.*¹⁰ have developed an asymmetric functionalization method to direct bromine atoms to the K-region without the need for *tert*-butyl groups. Additionally, in our laboratory, we also reported the selective formation of the 5-mono- and 5,9-di-substitution products from 7-*tert*-butyl-1,3-dimethylpyrene by formylation and acetylation depending on the type of Lewis acid catalyst deployed.¹² More recently, the 1- and 3- positions of pyrene were brominated using 2-*tert*-butylpyrene; the *tert*-butyl group on the pyrene ring protects the ring from electrophilic attack at the 6,8-positions.⁹

Based on the previously mentioned research, we decided to exploit a new intermediate in order to develop a series of pyrene related materials for further

applications. Our initial efforts attempted to synthesize 7-*tert*-butyl-1,3,4,5,9,10-hexabromo-pyrene (**3**) using iron powder to catalyze its formation from 2-*tert*-butylpyrene in different solvents, however efforts using CH₂Cl₂, nitrobenzene, and benzene, all failed. A bromo atom substituted at the 1- and 3- positions of pyrene would sterically hinder the 4- and 10- positions, thereby enabling regioselective substitution at the 5- and 9- positions. Since the 7-position of the pyrene core has been protected, four bromines atoms can be introduced at the 1-, 3-, 5-, 9- positions by electrophilic bromination of 2-*tert*-butylpyrene in the presence of iron powder. The 7-*tert*-butyl-1,3,5,9-tetrabromopyrene (**2**) was prepared and purified successfully in excellent yield. To the best of our knowledge, this is the first example of a method to halogenate pyrene not only in the activated sites but also in the K-region. The intermediate **2** has two advantages:^{2a} (1) the active sites at the 1- and 3- positions could give C-functionalized pyrene by Suzuki/Sonogashira coupling reactions to avoid aggregation; (2) the K-region (5-, 9- positions) affords a strategy to extended conjugated systems to larger PAHs by cyclization reaction.

Scheme 2. Synthetic route to compound **4**, **5**

The synthesis of target compound **4** is depicted in Scheme 2. Pyrene was first mono-*tert*-butylated to afford the 2-*tert*-butylpyrene (**1**), which was then treated with Br₂ (4 equivalents) in CH₂Cl₂ at room temperature in the presence of iron powder, yielding the desired 7-*tert*-butyl-1,3,5,9-tetrakisbromo-pyrene **2** in high yield (83.5 %). Compound **2** is a white solid powder, which is slightly soluble in common organic solvents, such as CH₂Cl₂ and CHCl₃. The ¹H NMR spectrum showed three singlets between δ 8.47–8.80 ppm region (Ha, Hb, Hc), and a singlet for the pyrene protons in the ratio 2:2:1, consistent with the symmetrically substituted structure of **2**.

In the present study, we report the synthesis, structure, optical and electrochemical characterization of a series of *butterfly*-shaped pyrene-core derivatives of the type 7-*tert*-butyl-1,3,5,9-tetraarylpyrene (**4**), which utilized the key starting material **2** by reacting in a Suzuki cross-coupling reaction with the corresponding arylboronic acids under Pd-catalyzed conditions in the presence of an excess amount of toluene (65–71 % isolated yields, see SI). The molecular structure of the

compounds of type **4** were characterized by their ¹H/¹³C NMR spectra, single crystal X-ray diffraction, FT-IR spectroscopy, mass spectroscopy, and by elemental analysis. As a comparison, the aromatic aldehyde **4c** was condensed with 4-*tert*-butylaniline to afford the Schiff base **5**, and 1,3,6,8-tetrakis(4-methoxyphenyl)pyrene (**6**) was synthesized according to the modified literature procedure.¹³ The 7-*tert*-butyl-1,3,5,9-tetraarylpyrenes **4** were soluble in common organic solvents such as toluene, CH₂Cl₂, CHCl₃, THF, acetonitrile, and *N,N*-dimethyl-formamide, and exhibited excellent thermal stability under air/N₂. The key thermal data for the pyrene derivatives **4** are summarized in Table 1.

Figure 1. X-ray structure of compounds **4a** and **4b**

Single crystals of **4a** (CCDC 917256), **4b** (CCDC 917257) and **6** (CCDC 915429) were grown from a mixture of CH₂Cl₂ and MeOH and were investigated by X-ray crystallography to establish the structure. All crystal structures were found to belong to the monoclinic crystal system with space group *P*2₁/*c* for **4a** and **6**, and *P*2₁/*n* for **4b**. As shown in Figure 1, these terminal moieties adopt a reasonably twisted conformation with a substantial dihedral angle relative to the pyrene ring (46.2–68.0°), and torsion angles of 49.4–70.5° between the pyrene and phenyl rings, whilst for the pyrene and methoxyphenyl rings, the torsion angles were 48.1–56.2°. In the presence of a *tert*-butyl group at the 7-position of pyrene, the four terminal moieties twist with reasonable dihedral angles relative to the pyrene cores. This conformation effectively prevents π–π stacking and releases the steric interactions in the solid state. Only C–H⋯π interactions were observed and impact on molecular geometries as well as prevent the excimer formation in the solid state.¹⁶ The packing of molecules of **4a** and **4b** reveal the 2D self-assembled planar solid-state structure (see SI). The comparison compound **6** exhibited a sandwich-like 3D structure self-assembled in solid state via C–H⋯π bond interactions overlapping the porous two-dimensional networks. A chloroform molecule was encapsulated in the molecular channel by a hydrogen bonding C45–H45⋯O4 (2.506 Å) interaction (see SI).

The UV/vis absorption and fluorescence spectra of **4**, **5** and **6** were investigated in dilute dichloromethane and in a thin film (see Figure 2). The four compounds exhibit two prominent absorption bands between 298–308 nm and 373–391 nm, and the optical absorption spectrum of

Table 1. The photophysical and electrochemical properties of compounds **4**, **5** and **6**.

Titled molecular	$\lambda_{\text{max}}^{\text{abs}}$ (nm) solns ^a / films ^b		$\lambda_{\text{max}}^{\text{PL}}$ (nm) solns ^a / films ^b		Φ^{c} solns / thin films	LUMO (eV)	HUMO (eV)	HOMO-LUMO ΔE (eV)	T_g^{d}	T_m^{d} (°C)	T_d^{e} (°C)
4a	373	380	412	410	0.92 / 0.75	-1.58	-5.01	3.43	93	292	350.1
4b	379	369	421	443	0.90 / 0.72	-1.36	-4.76	3.40	94	276	410.0
4c	386	400	469	471	0.56 / 0.48	-2.45	-5.66	3.21	94	301.5	328.8
5	355		467	--	--	-2.12	-5.25	3.13	--	265.6	430.2
6	391	405	434	488	0.94/-	-1.47	-4.71	3.24	--	270.5	--

^a Maximum absorption wavelength measured in dichloromethane at room temperature. ^b Measured in thin neat films. ^c Measured in dichloromethane and in neat thin films, respectively. ^d Melting temperature (T_m) obtained from differential scanning calorimetry (DSC) measurement. ^e Decomposition temperature (T_d) obtained from thermogravimetric analysis (TGA).

4c was very broad and less well resolved in the range from 330 to 420 nm. For substituents bearing electronic donating or accepting groups at the *para*-position of the phenyl ring, the compounds have a slight red shift and followed the order **6**(OMe)>**4c**(CHO)>**4b**(OMe)>**4a**(H); similar influences on the photophysical properties of compounds have been noted previously.^{9b,14} Compounds **4** and **6** exhibited absorption λ_{max} values that were significantly red-shifted in comparison to the parent 2-*tert*-butylpyrene (338 nm). For the Schiff base **5**, the bulky blocking group (the 4-*tert*-butylphenylamine moiety) was introduced at the *para*-position of the benzene rings in order to expand the π -conjugation of the butterfly-shaped system. The broad absorption spectrum had λ_{max} at 355 nm, which indicated that the delocalization of the π electrons was extended over a large area of the molecule.

Figure 2. (a) Normalized UV-vis absorption and (b) emission spectra of compounds **4** recorded in dichloromethane at ca. 10^{-5} – 10^{-6} M at 25°C. (c) emission spectra in thin film (d) photographs of blue emission from the films of **4** (left→right).

For thin film absorption, compounds of type **4** have slightly broader spectra with a red shift (5–14 nm) in comparison to that observed in solution (Table 1). This was ascribed to aggregate formation in the solid-state. In the case of compound **6** however, an unusual zigzag type absorption spectrum curve was observed in the solid-state, and the maximum absorption band at λ 391 nm suggested that the 1,3,6,8-tetrakis(4-methoxy-phenyl)pyrene (**6**) possessed extensive intermolecular interactions as a film

(see SI). Figures 2b and 2c reveal that the butterfly-shaped compounds **4** emit very bright, sharp and deep blue fluorescence, both in solution and in the solid-state. The emission maxima at 412 nm for **4a** and 421 nm for **4b** reveal a smaller red shift than compound **6** (λ_{max} = 434 nm). For **4c**, the presence of the CHO moiety, caused a significant red-shift and a broadened emission maximum (λ_{max}) at 469 nm in dilute dichloromethane. Interestingly, when the extended terminal 4-*tert*-butylphenyliminophenyl groups were replaced by the carbaldehyde group in **4c**, a similar emission maximum at 469 nm with weak fluorescence intensity occurred. Nevertheless, no excimer emission was observed in this butterfly-shaped tetraarylpyrene system.

The photoluminescence spectrum of **4** as a thin-solid film presents a prominent maximum emission in the blue region (410 nm for **4a**, 443 nm for **4b** and 471 nm for **4c**). For **4a**, the wavelength of the emission maximum (λ_{max}) shows a slight hypsochromic shift in the solid state with respect to the dichloromethane solution spectrum (413 nm). This difference may be due to the different dielectric constant in the solid state versus dilute solutions.¹⁵ Compound **4b** displayed a slight red-shift (approx. 22 nm) compared to spectra recorded as dilute solutions (Table 1), thought to be due to aggregation. For **4c**, there was a slight red-shift (increased by 2 nm) in solution versus thin film. Compounds **4** also exhibited very high quantum yields (Φ^{c}) of ca. 0.92, 0.90 and 0.56 in solution and ca. 0.75, 0.72 and 0.48 in the solid state, respectively. There is thus potential for such systems as efficient pure-blue emitters. However, the fluorescence emission spectrum of **6** obtained in the solid state showed two emission bands at 488 nm and 564 nm. The longer wavelength band in the solid state is assigned to the emission of the excimer, which suggested compound **6** has strong aggregation in the solid state due to the absence of a *tert*-butyl group to suppress the intermolecular interactions in the molecular structure.

To further understand the electronic structures and optical properties of these novel butterfly-shaped pyrene derivatives **4**, **5** and **6**, DFT (B3LYP/6-31G*) calculations were performed. The frontier orbitals for **4** are shown in Figure 3, Table 1 and SI, the HOMO is delocalized over the entire pyrene framework for **4**, **5** and **6**, whereas the aryl substituent group or extended chain have limited

contributions to this system. Similarly, the LUMOs of **4a** and **4b** were also delocalized over the whole pyrene unit. However, it is remarkable that the LUMO of **4c** spreads over the entire pyrene framework, including the 4-formylphenyl unit. It is interesting to note that although enlarging the π conjugation by introducing the C=N bond in **5**, the terminal phenylimino groups do not contribute to the construction of the LUMO in **5**.

Figure 3. Computed molecular orbital plots (B3LYP/6-31G*) of selected compounds **4** and **5**. The lower plots represent the HOMOs, and the upper plots represent the LUMOs.

The electrochemical properties of **4** were investigated by cyclic voltammetry (CV). All compounds showed oxidation waves located at 1.48 V for **4a**; 1.35V and 1.73 V for **4b**, and 1.75V for **4c**, (versus ferrocenium/ferrocene (Fc^+/Fc)). All compounds display oxidation wave originating from the conjugation system of pyrene. The HOMO energy levels were calculated to be -5.49 eV for **4a**, -5.36 eV for **4b** and -5.73 eV for **4c**, respectively, from the onset of the first oxidation wave. The Energy gap (E_g) was estimated from UV-vis absorption (3.11eV for **4a**, 3.01 eV for **4b** and 2.88 eV for **4c**). The experimental data was found to closely correspond to the theoretically calculated data (See SI). The slight difference owing to the theoretical calculation being performed for the gas phase. The high reversibility of their redox processes demonstrated that the butterfly-shaped pyrene derivatives were stable, and suggested that the current molecular design may be suitable for applications in OLED-like optoelectronic devices. In particular, the low LUMO of **4c** can be used for hole-transportation in organic materials.

Figure 7. Cyclic voltammograms recorded for the compounds **4**

In conclusion, we have developed a new synthetic method for the construction of 7-*tert*-butyl-1,3,5,9-tetrabromopyrene (**2**), which is a key bromopyrene intermediate for designing and synthesizing efficient blue emitters. The *tert*-butyl group and the 4-fold functionalization efficiently suppressed molecular aggregation both in solution (UV-vis and fluorescence) and in the solid state (photoluminescence and crystal packing). This work provides a promising strategy to halogenate both at the active sites and in the K-region. Our current butterfly-shaped molecular design may provide an efficient strategy to achieve solid-state blue emitting materials for realizing full-color display of OLEDs. Further investigation of their applications in organic electroluminescent devices is in progress in our laboratory.

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Supporting Information Available Synthetic procedures and characterization data; this material is available free of charge via the Internet at <http://pubs.acs.org>.

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