Journal of Molecular Structure 1047 (2013) 194–203

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Synthesis and fluorescence emission properties of 1,3,6,8-tetraarylpyrenes

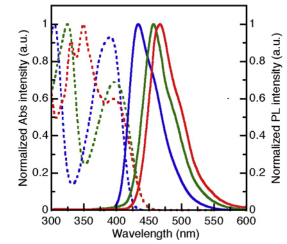
Jian-Yong Hu[a], Xing Feng[a], Hirotsugu Tomiyasu[a], Nobuyuki Seto[a], Ummey Rayhan[a], Mark R.J. Elsegood[b], Carl Redshaw[c], Takehiko Yamato[a,*]

[a] *Department of Applied Chemistry, Faculty of Science and Engineering, Saga University, Honjo-machi 1, Saga-shi, Saga 840-8502, Japan*
[b] *Chemistry Department, Loughborough University, Loughborough LE11 3TU, UK*
[c] *Department of Chemistry, The University of Hull, Hull HU6 7RX, UK*

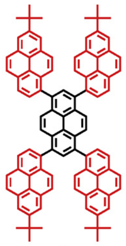
HIGHLIGHTS

- A series of 1,3,6,8-tetraarylpyrenes have been synthesized in high yields.
- All compounds emit very bright fluorescent emissions, from *deep-blue* to *pure-blue* in solution.
- Tetrapyrenyl and tetrafluorenyl groups suppress π···π stacking in the solid state.

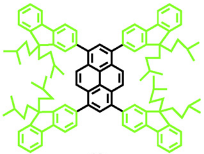
GRAPHICAL ABSTRACT



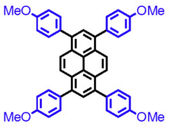
Normalized absorption (dotted line) and fluorescence (solid line) spectra of 1,3,6,8-tetrakis(7-*tert*-butylpyren-2-yl)pyrene (**8**) (red line), 1,3,6,8-tetrakis[9,9-bis-(3-methylbutyl)-*9H*-fluoren-2-yl]pyrene (**10**) (green line) and 1,3,6,8-tetrakis(4-methoxyphneyl)pyrene (**12**) (blue line) in CH_2Cl_2 at ~10^{-6} M concentration at 25 °C.



8



10



12

ARTICLE INFO

Article history:
Received 15 January 2013
Received in revised form 23 April 2013
Accepted 23 April 2013
Available online 11 May 2013

Keywords:
Pyrene
Suzuki cross-coupling reaction
Tetraarylpyrenes
Tetrafluorenylpyrenes
Fluorescence emission properties

ABSTRACT

Three types of stable pyrene-based highly fluorescence (blue) compounds, 1-, 1,6-bis, 1,8-bis and 1,3,6,8-tetrakis(7-*tert*-butylpyrenyl)pyrenes and 1,3,6,8-tetrakis[9,9-bis(3-methylbutyl)-9*H*-fluoren-2-yl]pyrene, were successfully synthesized via a Pd/Cu-catalysed Suzuki cross-coupling reaction of the corresponding bromopyrenes with 7-*tert*-butyl-1-pyrenylboronic ester or 2-[9,9-bis(3-methylbutyl)-9*H*-fluoren-2-yl]-4,4,5,5-tetramethyl[1,3,2]dioxaborolane, respectively. All compounds have good solubility in common organic solvents and high thermal stability with melting points up to 270 °C; the exceptions are the isomeric 1,6-bis-, and 1,8-bispyrenyl-substituted pyrenes. All products show high extinction coefficients of absorption ($\lambda_{max} \approx 349$–396 nm) and high quantum yields ($\lambda_{max} \approx 432$–465 nm; $\Phi_f \approx 0.75$–0.99) in dichloromethane solution, and emit strong fluorescence in the visible region ranging from *deep-blue* to *pure-blue* on increasing the number of substituents. This data suggests that such systems have promise as blue emitters in organic light-emitting device (OLED) applications (OLED = organic light emitting diode). Crystal structures were determined for 1,3,6,8-tetrakis [9,9-bis(3-methylbutyl)-9*H*-fluoren-2-yl] pyrene and 1,3,6,8-tetrakis(4-methoxyphenyl)pyrene.

1. Introduction

Organic light-emitting devices (OLEDs) have seen remarkable development in the past two decades due to their potential application in full-color flat-panel displays and solid-state lighting [1–4]. The three primary colors of red, green and blue (RGB) are essential for full-color displays. However, compared to red and green-based OLEDs, blue OLEDs show relatively poor performance due to the intrinsic wide-energy band-gap nature of blue emitters. Thus, blue emitting compounds with good color purity and high efficiency are particularly worthy of study.

---

* Corresponding author. Tel.: +81 952 28 8679; fax: +81 952 28 8548.
E-mail address: yamatot@cc.saga-u.ac.jp (T. Yamato).

0022-2860/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.molstruc.2013.04.074

Organic compounds such as polycyclic aromatic hydrocarbons (PAHs) (e.g. naphthalene, anthracene, pyrene, perylene, etc.) and their derivatives are suitable for developing RGB emitters for OLED applications owing to their excellent fluorescent properties [5–10]. In particular, these compounds have strong π-electron delocalization characteristics and can be substituted with a range of functional groups, which may be used for OLED materials with a tunable wavelength. Numerous RGB emitting compounds derived from naphthalene, anthracene, perylene and fluorene have been widely reported for OLED applications. However, the use of pyrene and its derivatives as blue emitters in OLEDs is limited because of the formation of π-aggregates/excimers in solution at high concentration and in the solid-state, which can lead to additional long-wavelength emission and a decrease of fluorescence quantum yield. This problem has been mainly solved by the introduction of bulky or heavily branched side chains into the pyrene molecule or co-polymerization with a suitable bulky co-monomer. Recently, it was reported that pyrene derivatives could be used as blue-emitting compounds in OLEDs via the introduction of long or branched side chains [11–15]. Furthermore, the synthesis of a pyrene-based fluorescent dendrimer has also been reported, wherein the core unit is a 1,3,6,8-tetrasubstituted pyrene and the peripheral units contain monosubstituted pyrene units [11,16–21].

On the other hand, fluorene is a PAH molecule with a rigid biphenyl plane. The C9 site of the fluorene molecule can be easily functionalized, which provides for the possibility of improved solubility and processability, and of controlling the excimer formation in the excited state [22–24]. Recently, fluorene-based compounds have been extensively used as thermally stable and efficient emissive OLED materials [25–29] and as high carrier transport organic field-effect transistors (OFETs) material [30–32].

In this study, pyrene was chosen as a π-conjugation center core because of its excellent fluorescence properties [33], its electron-acceptor nature [34,35], and its good performance in solution [36]. Substituted fluorenyl groups were introduced into pyrene molecules to invoke high solution and solid-state photoluminescence (PL) quantum yields [35], and in order to block the interchain interactions. To improve solubility and thermal stability, two long alkyl groups were introduced at the C9 position of the fluorene moiety [37,38]. The substituted pyrenyl groups were introduced because they are highly emissive, bulky, and rigid, and were expected to improve the fluorescence quantum yield and thermal stability. We were interested in investigating the structure–property relationships between the π-center pyrene core and the increasing number of substituents or the use of different substituents. Thus, we report herein the synthesis and fluorescence emission properties of 1-, 1,6-bis-, 1,8-bis- and 1,3,6,8-tetrakis-(7-*tert*-butylpyrenyl)pyrenes and 1,3,6,8-tetrakis[9,9-bis(3-methylbutyl)-9*H*-fluoren-2-yl]pyrene.

2. Experimental

The $^1H/^{13}C$ NMR spectra were recorded at 300 MHz and 75 MHz on a Nippon Denshi JEOL FT-300 NMR spectrometer in $CDCl_3$ with Me_4Si as an internal reference. The IR spectra were obtained as KBr pellets on a Nippon Denshi JIR-AQ2OM spectrometer. Mass spectra were obtained on a Nippon Denshi JMS-HX110A Ultra-high Performance Mass Spectrometer at 75 eV using a direct-inlet system. Elemental analyses were performed by Yanaco MT-5. Gas–liquid chromatograph (GLC) analyses were performed by Shimadzu gas chromatograph, GC-14A; silicone OV-1, 2 m; programmed temperature rise, 12 °C min^{-1}; carrier gas nitrogen, 25 mL min^{-1}. UV–Vis spectra were recorded on a Perkin Elmer Lambda 19 UV/VIS/NIR spectrometer. Emission spectra were performed in a semi-micro-fluorescence cell (Hellma®, 104F-QS, 10 × 4 mm, 1400 μL) with a Varian Cary Eclipse spectrophotometer.

3. Materials

The preparations of 1-bromopyrene (**2**), 1,6-di- and 1,8-di-bromopyrene (**3a** and **3b**), 1,3,6,8-tetrabromopyrene **(4)** from pyrene (**1**) have been previously reported [39]. 7-*tert*-butyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene (**5**) [40] and 2-[9,9-bis(3-methylbutyl)-9*H*-fluoren-2-yl]-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (**9**) [41] were prepared by the reported procedures.

3.1. Synthesis

*3.1.1. Synthesis of 7-tert-butyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene (**5**)*

The compound **5** was prepared in 55% yield from 1-bromo-7-*tert*-butylpyrene following by the reported procedure [40] as a white solid. mp 155–157 °C. ^1H NMR ($CDCl_3$, 300 MHz): $\delta_H = 1.49$ (s, 12H, Me), 1.59 (s, 9H, *t*Bu), 8.02 (d, $J = 9.0$ Hz, 1H, Py-H), 8.06 (d, $J = 9.6$ Hz, 1H, Py-H), 8.10 (d, $J = 4.2$ Hz, 1H, Py-H), 8.12 (d, $J = 2.7$ Hz, 1H, Py-H), 8.21 (d, $J = 1.5$ Hz, 1H, Py-H), 8.24 (d, $J = 1.8$ Hz, 1H, Py-H), 8.49 (d, $J = 7.8$ Hz, 1H, Py-H), 9.02 (d, $J = 9.3$ Hz, 1H, Py-H) ppm; MS *m*/*z*: 384 [M^+]; Anal. calcd. for $C_{26}H_{29}BO_2$ (384.32) C, 81.26, H, 7.61. Found C, 81.24, H, 7.62.

*3.1.2. Synthesis of 2-[9,9-bis(3-methylbutyl)-9H-fluoren-2-yl]-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (**9**)*

Similarly, compound **9** was obtained from 2-bromo-9,9-bis(3-methylbutyl)-9*H*-fluorene [42] in 70% yield as a colorless powder. mp 86–88 °C (Lit. [41] mp 86–88 °C).

*3.1.3. Synthesis of 1-(7-tert-butylpyren-1-yl)pyrene (**6**)*

1-Bromopyrene **2** (200 mg, 0.70 mmol), 7-*tert*-butyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene **5** (411 mg, 1.07 mmol), and $Pd(PPh_3)_4$ (109 mg, 0.07 mmol) and aqueous 2.0 M

Table 1
Summary of the crystal data of compound **10** and **12**.

Parameter	**10**	**12**
Empirical formula	$C_{108}H_{122}$	$C_{44}H_{34}O_4{\cdot}CHCl_3$
Formula weight [g mol^{-1}]	1420.06	746.13
Temperature [K]	150(2)	113(2)
Wavelength [Å]	0.71073	1.54187
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Crystal color	Pale yellow	Yellow
Crystal size [mm^3]	0.61 × 0.30 × 0.06	0.20 × 0.15 × 0.12
a [Å]	14.105(4)	14.076(3)
b [Å]	17.258(5)	9.7666(19)
c [Å]	19.659(6)	26.439(5)
α [°]	114.613(4)	90
β [°]	99.895(4)	95.169(15)
γ [°]	92.315(4)	90
Volume [$Å^3$]	4252(2)	3619.8(13)
Z	2	4
Density, calcd. [g m^{-3}]	1.109	1.369
Absorption coefficient [mm^{-1}]	0.062	2.653
F(0 0 0)	1540	1552.00
θ Range for data collection [°]	1.68–23.00	1.58–68.25
Reflections collected	23,833	35,591
Independent reflections	11,770	6558
Observed data [$F^2 > 2(F^2)$]	5167	4612
R_{int}	0.0764	0.0362
Restraints/parameters	279/1033	0/473
Goodness-of-fit on F^2	0.989	1.096
*R*1 [$F^2 > 2\sigma(F^2)$]	0.0815	0.0578
*wR*2 (all data)	0.2746	0.1852