



Symmetrical fluorescent oligothiophene and benzene centered bispyrenoimidazole derivatives with double *n*-dodecyl chains showing high thermal stability



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ABSTRACT

A family of symmetrical oligothiophene (dithiophene, terthiophene, and quaterthiophene) or benzene centered bispyrenoimidazole derivatives, having the same coplanar pyrenoimidazole terminal groups at each side, has been synthesized via Radziszewski, N-alkylation, and the following Pd(PPh₃)₄ catalyzed Suzuki and Stille coupling reactions. Double *n*-dodecyl chains are introduced to the molecules at the same time in order to increase their solubility in organic solvents. UV–vis and fluorescence spectra as well as thermal properties have been studied. The results demonstrate that compound **4** with a benzene linker displays the strongest fluorescence intensity, and oligothiophene centered bispyrenoimidazole derivatives **5–7** show obvious bathochromic shifts compared with benzene centered compound **4**. It is worth mentioning that this family of compounds exhibits excellent thermal stability with the decomposition temperature higher than 400 °C even if the incorporation of double *n*-dodecyl chains. Furthermore, X-ray single-crystal structures of one representative compound **4** (CHCl₃)₂ and an intermediate **3** have been described.

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Pyrene and their derivatives have received considerable attention because of their potential applications in molecular electronic and optical devices such as dye-sensitized solar cells (DSSCs),¹ organic light-emitting diodes (OLEDs),² and organic field-effect transistors (OFETs).³ As an important organic intermediate consisting of four fused benzene rings,^{4–10} pyrene is a polycyclic hydrocarbon compound having the advantages of excellent thermal and optical stabilities as well as ease of synthetic modification. Based on this concept, a variety of pyrene derivatives bearing either electron-donating and/or electron-withdrawing groups have been studied in the literature, and most of reported compounds focused on the fine tuning of the conjugated aromatic core.^{11–17}

Pyrenoimidazole with additional exocyclic aromatic π -linkers could be conveniently synthesized via one step reaction between pyrene-4,5-dione and aldehyde. For example, a series of pyrenoimidazoles containing various functional chromophores has been reported on the application for deep blue light-emitting materials, and all of them display high thermal stability.¹⁸ In addition, several organic dyes containing pyrenoimidazole donors and cyanoacrylic acid acceptors have been synthesized for DSSC investigations, and

the optoelectrical properties of these dyes can be tuned by changing the conjugation lengths of π -linkers.¹

In our previous work, a series of oligothiophene based heterocyclic aromatic compounds with terminal thienyl, imidazolyl, and pyridyl groups has been described.^{19–21} Moreover, temperature-dependent semiconducting and photoresponsive properties of self-assembled nanocomposite films and nanodevices fabricated from these compounds have been explored.^{22,23} Our motivation herein is to investigate new pyrenoimidazole extended heterocyclic aromatic compounds with excellent optoelectrical and thermal properties, which could be promising candidates for the study of molecular electronics. To the best of our knowledge, there is no report on oligothiophene and benzene centered compounds with two terminal pyrenoimidazole groups to date. In this Letter, we focus on the symmetrical oligothiophene and benzene centered heterocyclic aromatic derivatives capped by the same coplanar pyrenoimidazole groups at each side. In our experiments, long *n*-dodecyl chains are selected to increase the solubility of resultant compounds in conventional organic solvents, and it is found that the resultant molecules with molecular weight more than 900 still exhibit both strong fluorescence emission and high thermal stability. Control experiments reveal that shorter alkyl chains like *n*-butyl and *n*-octane could not increase the solubility effectively

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and longer alkyl chain such as *n*-cetyl would lead to lower yields.²⁴ In addition, it is suggested that the introduction of branched alkyl chains may cause negative effects on the thermal stability for the final compounds.²⁵

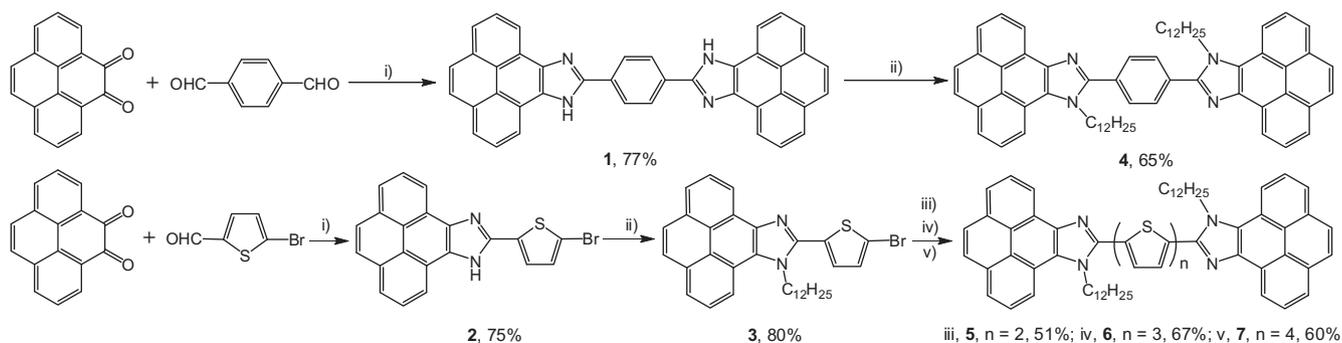
As shown in Scheme 1, bispyrenoimidazole precursor **1** was synthesized through the Radziszewski reaction in a high yield of 75% between pyrene-4,5-dione and terephthalaldehyde in the presence of ammonium acetate and glacial acetic acid. Subsequent *N*-alkylated reaction of compound **1** proceeded successfully in the presence of NaH as a base in a yield of 65%, and the target compound **4** with double *N*-substituted *n*-dodecyl chains was obtained. As expected, the solubility of compound **4** in common organic solvents has been greatly improved in comparison with that of compound **1**. Similarly, monopyrenoimidazole compound **3** with an *n*-dodecyl substituted imidazole ring could also be prepared by the same strategy. The desired dithiophene, terthiophene, and quaterthiophene centered bispyrenoimidazole derivatives **5–7** were prepared via Pd(PPh₃)₄ catalyzed Suzuki and Stille coupling reactions between intermediate **3** and bis(pinacolato)diboron, 5-bis(trimethylstannyl)thiophene, or 5,5'-bis(trimethylstannyl)-2,2'-bithiophene in satisfied yields, where all the reactions could be monitored directly by an UV-light detector excited at 365 nm with the color of fluorescence emission altering from wathet blue to red.

All symmetrical bispyrenoimidazole compounds **4–7** with extended heterocyclic aromatic structures show characteristic absorptions at 373–451 nm in their electronic spectra (Fig. 1), corresponding to the π – π^* transitions between adjacent aromatic heterocycles. In comparison with benzene centered bispyrenoimidazole

compound **4**, the absorption peaks of oligothiophene centered bispyrenoimidazole derivatives **5–7** are much broader at low energy band, and their maximum UV–vis absorption wavelengths (λ_{\max}) display obvious bathochromic shifts of 31–61 nm because of the existence of more electron-rich thiophene rings. In addition, 15 and 30 nm red shifts of λ_{\max} are observed for **6** and **7** compared with that of **5**, indicative of the alteration of their extended conjugation π system from 2 to 4 thiophene rings.

It is also noted that this family of pyrenoimidazole based compounds is florescence active exhibiting green to yellow and red luminescence (455–566 nm). On the one hand, compound **4** shows an extraordinarily strong fluorescence peak at 455 nm with the luminescence quantum yield (Φ) of 0.52 (Table 1). On the other hand, similar bathochromic shifts have been found to different extents in the fluorescence emission spectra of compounds **5–7**, but the measured Φ values for **5**, **6**, and **7** are much lower as 0.16, 0.14, and 0.15 (Table 1). In comparison with the benzene centered compound **4**, the oligothiophene centered compounds **5–7** have stronger intramolecular electron transfer due to the presence of electron-rich thiophene donors, which may lead to the fluorescent quench.^{26,27} These results strongly indicate that not only the number of central thiophene rings but also the type of bridging units of bispyrenoimidazole can significantly affect the spectroscopic properties.

The molecular structures of precursor **3** and solvate complex of benzene centered bispyrenoimidazole **4**·(CHCl₃)₂ are further confirmed by single-crystal X-ray analysis, and their crystallographic data are summarized in Table S11. As shown in Figure 2a, the



Scheme 1. Synthetic routes for oligothiophene and benzene centered bispyrenoimidazole derivatives **4–7** with double *n*-dodecyl chains. Reagents and conditions: (i) NH₄OAc (10 equiv), AcOH, 110 °C, 4 h; (ii) 1-bromododecane (5 equiv), NaH (3 equiv), DMF, 105 °C, 8 h; (iii) bis(pinacolato)diboron (1 equiv), Pd(PPh₃)₄ (0.05 equiv), KOH (5 equiv), dioxane/H₂O, reflux, 8 h; (iv) 2,5-bis(trimethylstannyl)thiophene (0.5 equiv), Pd(PPh₃)₄ (0.1 equiv), toluene, reflux, 10 h; (v) 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (0.5 equiv), Pd(PPh₃)₄ (0.1 equiv), toluene, 12 h.

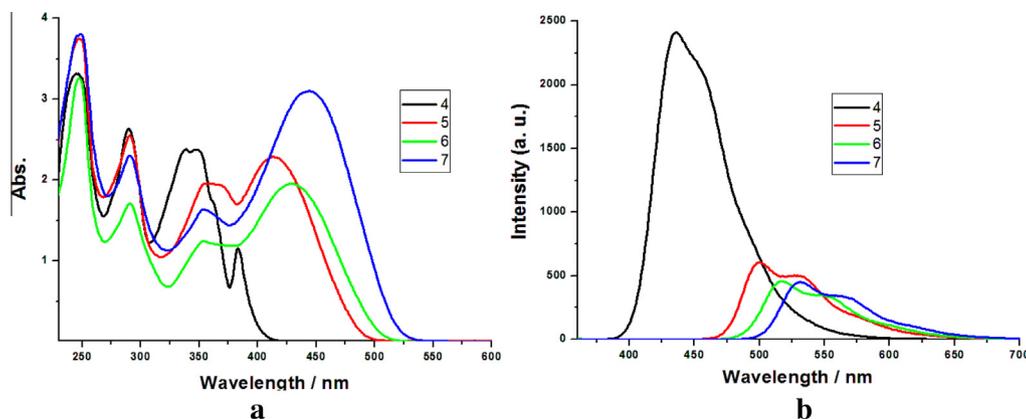


Figure 1. UV–vis absorption spectra (a) and fluorescence emission excited at 350 nm (b) for compounds **4–7** in their dichloromethane solutions at room temperature with the same concentration of $5.0 \times 10^{-5} \text{ mol L}^{-1}$.

Table 1

Wavelengths of electronic absorption and fluorescence emission spectra as well as quantum yields of fluorescence of **4–7**^a

Compound	UV-vis absorption	Fluorescence emission	ϕ_s^c
	λ_{\max} (nm) ($\log \epsilon$ M ⁻¹ cm)	λ_{\max} (nm) (λ_{ex}) ^b	
4	383 (4.37), 348 (4.68), 339 (4.68)	436 (350)	0.52
		0.11	
		416	
		0.05	
		448	
		0.70	
		459	
0.69			
5	414 (4.66), 356 (4.59)	529, 500 (350)	0.16
6	429 (4.59), 354 (4.40)	517 (350)	0.14
7	444 (4.79), 354 (4.52)	566, 532 (350)	0.15

^a All samples were measured at the same concentration of 5.0×10^{-5} mol L⁻¹ in dichloromethane solutions.

^b Excited at 350 nm.

^c Using anthracene ($\phi_{\text{std}} = 0.27$) as the fluorescence standard.

N-substituted *n*-dodecyl tail and the sulfur atom of its neighboring thiophene ring in **3** are found to point toward the same direction, exhibiting the *cis* configuration. The dihedral angle between pyrenoimidazole and thiophene ring is 12.3(2)°. However, two N-substituted *n*-dodecyl tails in **4**·(CHCl₃)₂ display the *trans* conformation related to the whole molecular plane, and the two side pyrenoimidazole rings are not coplanar to the central benzene ring with the same dihedral angle of 44.1(1)°. Unlike the serrated *n*-dodecyl chain in **3**, two *n*-dodecyl chains in **4**·(CHCl₃)₂ are partially twisted (the second and the third carbon atoms counted from substituted nitrogen atom) against the pyrenoimidazole ring.

The crystal packing view of **4**·(CHCl₃)₂ and **3** is shown in Figure 3 and Figure S11, respectively. In **4**·(CHCl₃)₂, strong π - π stacking interactions are found between neighboring pyrene and imidazole rings with the centroid-to-centroid separation of 3.623(5) Å. Similarly, effective π - π stacking interactions are observed in **3** between adjacent aromatic rings with the centroid-to-centroid separations of 3.654(6) and 3.789(6) Å. By checking the latest version of CCDC database on pyrenoimidazole based compounds, it is found that

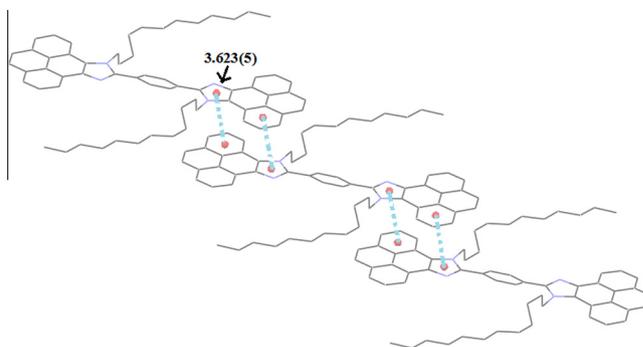


Figure 3. Perspective view of packing structure of **4**·(CHCl₃)₂ with π - π stacking interactions (Å). Hydrogen atoms and solvent molecules are omitted for clarity.

there is only one structural example of square-grid copper(II)-organic framework based upon a ligand prepared from the reaction between pyrene-4,5,9,10-tetraone and 4-carboxybenzaldehyde.²⁸ So this is the first structural report on pyrenoimidazole based compounds.

The thermal stability of heterocyclic aromatic compounds has an important impact on the optoelectronic performance, which is one of the most important parameters for their preparation and application. However, π -conjugated organic compounds with the decomposition temperature higher than 400 °C are not very common, especially for those incorporating long alkyl chains in their molecular structures to increase the solubility and make easier the spectral characterizations. In this work, all four oligothiophene and benzene centered bispyrenoimidazole derivatives bearing double *n*-dodecyl chains have been checked by the thermogravimetric analysis (TGA), and the TGA curves of **4–7** indicate that they can remain unchangeable when the temperature is below 400 °C. So it is concluded that the introduction of *n*-dodecyl chains to bispyrenoimidazole system could not only promote effectively the solubility in common organic solvents, but also keep high thermal stability (Fig. 4).

In summary, synthetic, structural, thermal, and spectral comparisons have been carried out for a series of symmetrical oligothiophene and benzene based bispyrenoimidazole derivatives. The

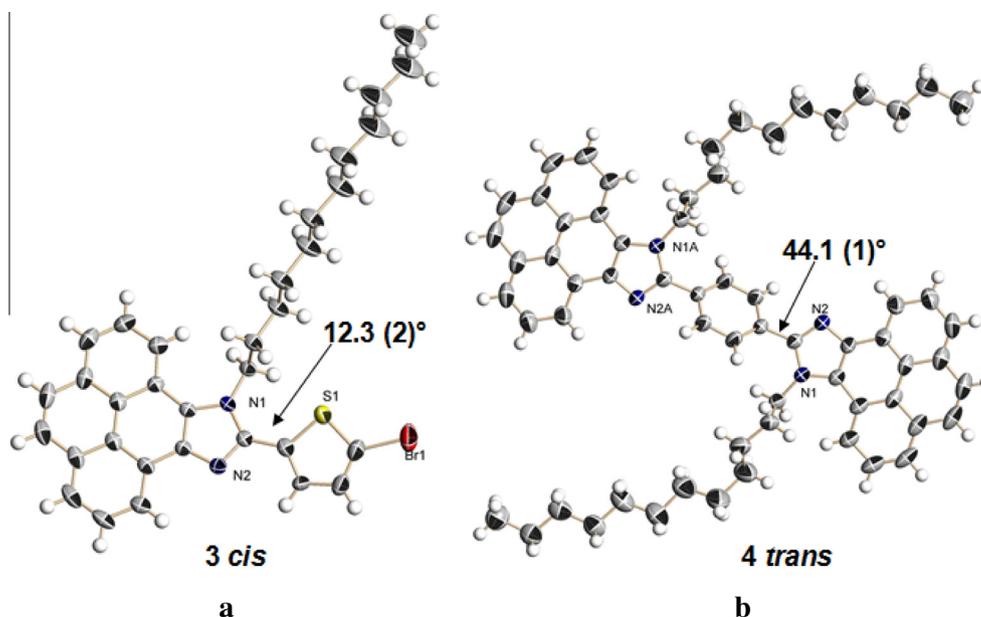


Figure 2. ORTEP diagrams (30% thermal probability ellipsoids) of the molecular structures of **3** (a) and **4**·(CHCl₃)₂ (b) showing the dihedral angles and relative configurations between adjacent aromatic heterocycles. The solvent molecules are omitted for clarity.

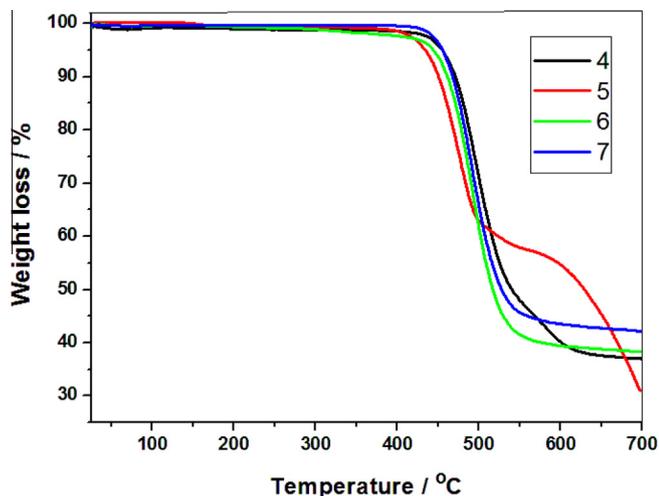


Figure 4. TGA curves of compounds 4–7.

extension of conjugation and the following N-alkylation of the pyrenoidimidazole chromophore by oligothiophene and benzene linkers have made them potentially useful candidates for thermally stable luminescent materials. These compounds display good fluorescence emission and thermal stability even if two *n*-dodecyl chains are present in their molecular structures. Additionally, single-crystal structures of a benzene centered bispyrenoidimidazole compound and an intermediate for preparing oligothiophene centered ones have been described for revealing their molecular conformation and crystal packing.

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Supplementary data

Experimental details, table of crystal data and structural refinements, view of the packing structure with π - π stacking interactions in **3**, ^1H , ^{13}C NMR and EI-TOF-MS spectra for related compounds. CCDC reference numbers 1012533–1012534 contain the supplementary crystallographic data for compounds **3** and **4**-(CHCl_3)₂ in this work. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the

Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK. Fax: +44 1223/336 033 (internat); e-mail: deposit@ccdc.cam.ac.uk].

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.tetlet.2014.09.003>.

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