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Ab Initio Study of Substituted Pyrenes for Blue Organic Light-Emitting Diodes

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Ab Initio Study of Substituted Pyrenes for Blue Organic Light-Emitting Diodes

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Luminescence efficiency of pyrene molecule is very low because of the aggregation effect of planar pyrene molecules. However, 1,3,6,8-tetra-substituted pyrenes with large electron donating group were reported to give a bright blue fluorescence [1]. In this paper, 1,6-bi-substituted and 1,4,6,9-tetra-substituted pyrenes as well as 1,3,6,8-tetra-substituted pyrenes were studied to find out the possibilities as the blue fluorescent materials of organic light-emitting diodes (OLEDs) [2–4]. Geometrical and electrical calculations were performed by **ab initio** *methods. HF/3-21G(d) basis set was used for the geometry optimization of the ground electronic states of those compounds. The geometry of the low-lying excited electronic state was optimized using configuration interaction with single excitation (CIS) method. The vertical and adiabatic transition energies were calculated by time-dependent density functional theory (TD-DFT) using the B1LYP functional with 6-31G(d) basis set. From calculational results, it was explained that the change in fluorescence wavelength was affected by the position and the number of substituents, through analyzing the change of energy levels of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of pyrene. Some of substituted pyrenes showed possibilities as stronger fluorescent materials. New efficient emitting materials for OLEDs were proposed from the calculation results obtained by tuning the position, the number of substitution and the species of substituting moiety.*

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1. INTRODUCTION

Organic light emitting diodes (OLEDs) have been the subject of great interest due to their potential application to the flat panel display. Since the first report on the multilayered OLED structure by Tang and coworkers [5], structures of OLEDs and emitting materials have been developed very fast. Especially, the development of pure red (R), green (G) and blue (B) emitting materials is the most important point for the advance of full-color display. However, the study on the blue emitting material is especially difficult because blue luminescence need high energy gap between HOMO and LUMO.

Organic materials such as the semiconducting π-conjugated compounds, called as Polycyclic Aromatic Hydrocarbons (PAHs) materials (e.g., naphthalene, anthracene, pyrene, perylene etc.) [6–10], are known to be suitable for applications in OLEDs. Although the semiconducting π-conjugated compounds and their derivatives widely have been used as emitting materials in OLED, their uses were expressly limited as emitting materials, because they consist of π-aggregates/excimers of planar molecules. The formation of π-aggregates/excimers leads to the excimer emission and low quantum efficiency, where the excimer emission appears in the long wave region in comparison with the main emission.

Pyrene as shown in Figure 1 is also known to be one of the semiconducting π-conjugated emitting materials. Some theoretical results from semi-empirical [1,11] and ***ab initio*** methods [12,13] have been reported, where absorption and emission peaks of pyrene were located

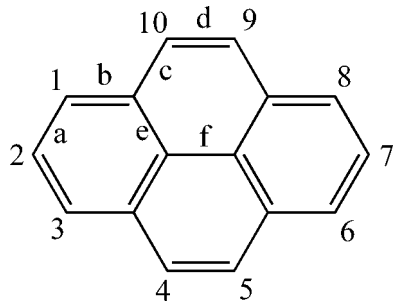


FIGURE 1 The structure of pyrene.

310 ~ 340 nm and 360 ~ 380 nm, respectively [14–16]. However pyrene is not suitable for use as an emitting material because of the formation of π-aggregates/excimers and low luminescence efficiency. In a previous article [1], it was proposed that the introduction of long or branched side chains is possible to solve those problems, where authors have substituted moieties at 1,3,6,8-positions of pyrene to increase the luminescence efficiency and change emission wavelength.

In this article, we have substituted moieties at 1,4,6,9-positions and 1,6-positions as well as 1,3,6,8-positions to increase luminescence efficiency and change luminescence wavelength. And geometrical structures and optical properties of those substituted pyrenes were characterized. And then, newly designed pyrene derivatives are proposed as new blue material possible to emit pure blue color.

2. COMPUTATIONAL METHODS

Calculations were processed by Gaussian 98 package. To optimize the geometry of the ground state (S_0), Hatree-Fork (HF) method with the 3-21G(d) basis set was used. Although HF method is low-level calculational method, it agrees well with the geometry of a molecule in the ground state. Table 1 shows agreement between computational and empirical results of pyrene molecule.

The vertical electronic excitation energy that includes some account of electron correlation was obtained using time dependent density functional theory (TD-DFT) with B3LYP/6-31G(d) basis set. In order to predict the fluorescence wavelengths of pyrene and its derivatives, geometries of pyrene and its derivatives were optimized using configuration interaction with all singly excited determinants (CIS) with the 3-21G(d). After the geometry optimization by CIS method, fluorescence wavelengths are estimated by TD-DFT using B1LYP functional with 6-31G(d).

TABLE 1 Comparison of Geometrical Data of Pyrene, Obtained by Experimental and Computational Methods where the Calculation was Performed Using HF/3-21G(d) Methods

	Length (Å)						Angle (°)			
	a	b	c	d	e	f	ab	bc	cd	ef
Exp.[14]	1.395	1.406	1.438	1.367	1.425	1.430	120.6	122.1	121.2	120.0
Cal.(HF/3-21G*)	1.382	1.390	1.445	1.338	1.410	1.430	120.6	122.2	121.2	120.0

3. RESULTS AND DISCUSSION

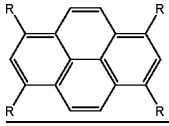
As shown in Figure 1, pyrene is a tetra cyclic hydrocarbon containing four fused aromatic rings, of which symmetry is $D2_h$. Sotoyama *et al*. [1] reported some of new substituted pyrenes, where the wavelength of 1,3,6,8-tetra(biphenylyl)pyrene [1,3,6,8-(bph)py] was reported as 446 nm. In this research, the wavelength of 1,3,6,8-(bph)py was computationally calculated as 452.3 nm which is similar to their experimental result. Table 2 shows their experimental results and our computational results of several materials. Calculated results did more redish shift, but agreed with experimental results in general.

To find out more efficient new blue material, we designed and substitute new moieties in some positions of pyrene. Used moieties are phenyl [ph], dimethylphenyl [dmp], biphenyl [bph], 3-phenylpyridine [ppy], 1H-imidazole [im], 1H-benzoimidazole [bim], benzo oxazole [box] and 1-methyl-1H-benzoimidazole [mbi]. And substituting positions are 1,3,6,8-, 1,6- and 1,4,6,9-positions. Newly designed compounds and moieties are shown in Figure 2.

Firstly, computational results of pyrene derivatives substituted at 1,3,6,8-positions were shown in Table 3. Among those derivatives, efficiencies of 1,3,6,8-tetra(phenylpyridine) pyrene [1,3,6,8-(ppy)py] and 1,3,6,8-tetra(benzo oxazole) pyrene [1,3,6,8-(box)py] were higher than that of 1,3,6,8-(bph)py. However their wavelengths were not suitable for the blue emission. The increase of the calculated wavelength of substituted pyrene's is because the nitrogen atom takes a role as electron withdrawer to lower HOMO value. And the increase of conjugation length also increases wavelength.

Changes of emission wavelengths and efficiencies were investigated through varying the number of substituents. Newly designed compound were 1,6-bi-substituted pyrenes. The substitution of two

TABLE 2 Experimental and Computational Data of Optical Properties of 1,3,6,8-substituted Pyrene Derivatives

	Exp.[1]	Cal. (TD-b1lyp/6-31G*)	
	λ_{exp} (nm)	λ_{cal} (nm)	Osc.
1,3,6,8-(ph)py	422	423.82	0.8321
1,3,6,8-(dmp)py	424	428.15	0.8871
1,3,6,8-(bph)py	446	454.30	1.1740

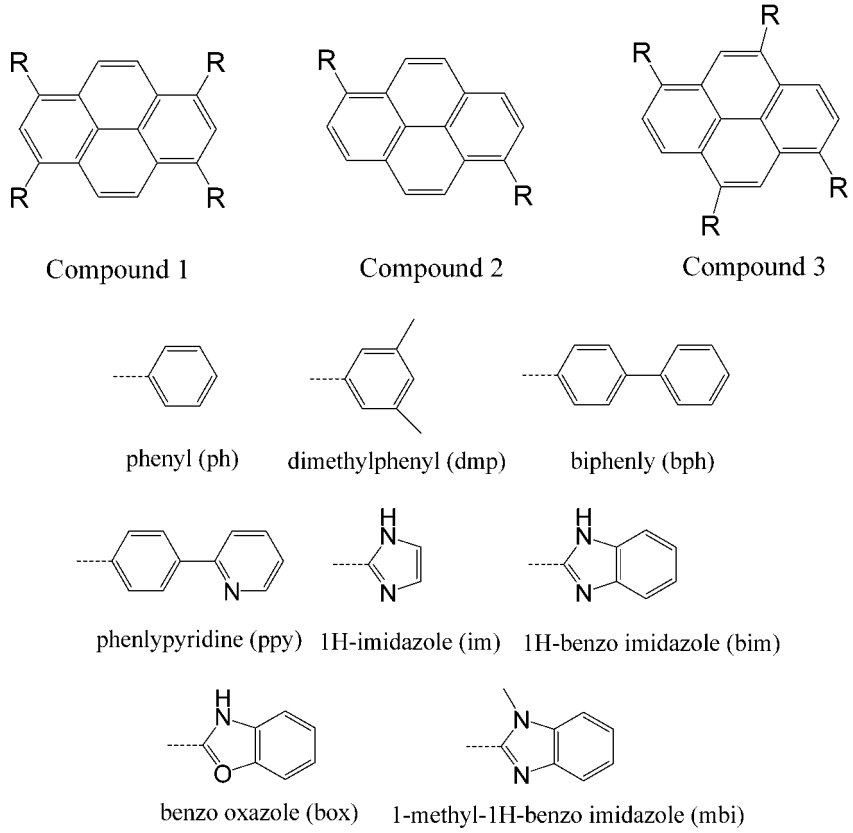
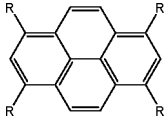


FIGURE 2 Compounds and moieties.

moieties less affects the energy gap between HOMO and LUMO than the tetra substituted pyrenes. Therefore emitting wavelength of pyrenes substituted at 1,6-positions shifted to blue region. The wavelengths of 1,6-bi-substituted pyrenes decreased than those of 1,3,6,8-tetra- substituted pyrenes about 30∼65nm. Especially, 1,6-bi(phenylpyridine) pyrene [1,6-(ppy)py], 1,6-bi(1H-benzoimidazole) pyrene [1,6-(bim)py], 1,6-bi(benzo oxazole) pyrene [1,6-(box)py] and 1,6-bi(1-methl-1H-benzo imidazole) pyrene [1,6-(mbi)py] were able to emit almost pure blue lights, of which wavelengths were 446.5 nm, 454.7 nm, 466.3 nm and 445.1 nm respectively, as shown in Table 4. Oscillation strengths were calculated as 1.4479, 1.3294, 1.4160 and 1.2167, respectively, which are better than that of 1,3,6,8-(bph)py. We expected that those materials are used as good blue emitting

TABLE 3 Calculated Fluorescent Wavelengths and Oscillation Strengths of Newly 1,3,6,8-tetra-substituted Pyrenes

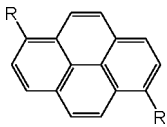


	Cal. (TD-b1lyp/6-31G*)			
	HOMO	LUMO	λ_{cal} (nm)	Osc.
1,3,6,8-(bph)py	–1.676	–4.773	453.30	1.1740
1,3,6,8-(ppy)py	–1.840	–4.764	484.22	1.2619
1,3,6,8-(im)py	–1.810	–4.625	484.21	0.8905
1,3,6,8-(bim)py	–2.292	–4.987	519.63	1.1579
1,3,6,8-(box)py	–2.632	–5.258	522.88	1.2764
1,3,6,8-(mbi)py	–2.033	–5.040	468.38	1.0936

materials; however the synthesis of bi-substituted pyrene was practically hard to process.

Another types of pyrene derivatives are 1,4,6,9-substituted pyrene derivatives. It is known that the electron population of HOMO in pyrene molecule is localized to 1, 3, 6 and 8 positions. The population of electrons in 4, 5, 9 and 10 positions is relatively less than that in 1, 3, 6 and 8 positions. And the population of electrons at 2, 7 positions hardly are negligible. Therefore 1, 3, 6 and 8 positions are very important to change energy gap between HOMO and LUMO. The variations of HOMO and LUMO of 1,4,6,9-substituted pyrenes are expected to be similar to those of 1,6-substituted pyrenes. Also 1,4,6,9-substituted pyrenes are known to be easy to synthesis. We calculated fluorescent

TABLE 4 Calculated Fluorescence Wavelengths and Oscillation Strengths of Newly 1,6-bi-substituted Pyrenes



	Cal. (TD-b1lyp/6-31G*)			
	HOMO	LUMO	λ_{cal} (nm)	Osc.
1,6-(bph)py	–1.599	–4.868	425.79	1.3430
1,6-(ppy)py	–1.806	–4.926	446.54	1.4479
1,6-(im)py	–1.595	–4.751	428.44	0.8998
1,6-(bim)py	–1.951	–4.990	454.66	1.3294
1,6-(box)py	–2.284	–5.214	466.26	1.4160
1,6-(mbi)py	–1.934	–5.058	445.11	1.2167

TABLE 5 Calculated Data of 1,4,6,9-(bph)py and 1,6-(bph)py

	1,4,6,9-(bph)py	1,6-(bph)py
HOMO	–1.554	–1.599
LUMO	–4.832	–4.868
λ_{cal} (nm)	424.08	425.79
Osc.	1.0358	1.3430

wavelength of 1,4,6,9-(bph)py, which is about 424.1 nm. This value was similar to 1,6-(bph)py of 425.8 nm. Calculational results are shown in Table 5. Even though our research was limited to 1,4,6,9-(bph)py, more research for 1,4,6,9-substituted pyrenes using other moieties will give possibilities to develop good blue emitting material.

4. CONCLUSION

In this study, structures and optical properties of pyrene and its derivatives emitting blue fluorescence were characterized using computational methods, and it was found that calculation results were in good agreement with the reported experimental data. We tried to reach in blue wavelength through changes of substitution positions as well as changes of various moieties. From the calculated results, the fluorescence wavelengths of newly designed substituted pyrenes gave about $425 \sim 520$ nm. Although synthesis of 1,6-substitued pyrenes are difficult, the wavelengths and efficiencies of 1,6-(ppy)py, 1,6-(bim)py, 1,6-(box)py and 1,6-(mbi)py are (446.5 nm and 1.4479), (454.7 nm and 1.3294), (466.3 nm and 1.4160) and (445.1 nm and 1.2167), respectively. These are enough to be new efficient blue emitting materials. We also proposed 1,4,6,9-substituted pyrenes. These substituted pyrenes are similar with 1,6-bi-substituted pyrenes because of a little effect of 4,9-positions. We confirmed those facts by comparison with 1,4,6,9-(bph)py and 1,6-(bph)py. Calculated wavelengths of 1,4,6,9-(bph)py and 1,6-(bph)py were 424.1 nm and 425.8 nm, respectively.

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