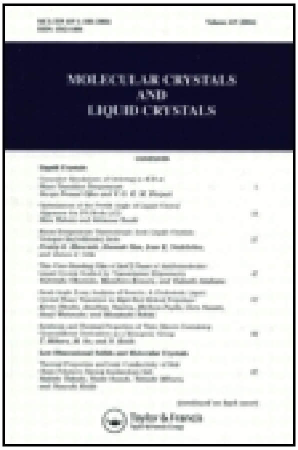

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Luminescent Properties of Pentacene Derivatives with Naphthalene Moiety

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Luminescent Properties of Pentacene Derivatives with Naphthalene Moiety

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Pentacene moiety in electro-optical device which includes solar cell and organic light-emitting diodes (OLEDs) has attracted lots of interest because of its high carrier mobility and dopant property. We synthesized new conjugated compounds, 6,13-diphenylpentacene(DPP), 6,13-dinaphthalen-1-yl-pentacene(DNP) and 6,13-di-naphthalen-2-yl-pentacene(2-DNP) based on pentacene by using of tin(II) chloride dihydrate catalyst. All compounds showed photoluminescent (PL) maximum wavelength at around 620 nm and 660 nm. As solute concentration of DPP increases, the PL peak intensity at 660 nm rapidly increases as well as the overall PL intensity normally increases. This experimental result was only observed in 1-DNP, on the other hand, this tendency was not found in 2-DNP. We suppose the result can be explained by steric interaction between naphthyl moieties.

Keywords: cyclic voltammetry; electroluminescence; pentacene derivatives

1. INTRODUCTION

For the past decades, great successes have been made in the field of organic light-emitting diodes (OLEDs). Green and blue OLEDs with high efficiency, good color coordinate value, and long lifetime have been reported [1,2]. However, the performance of red fluorescent OLEDs material compared to other OLEDs materials is still not satisfactory [3–5]. Presently, most high-performance red OLEDs are made by doping a red dye into a suitable host [6,7]. The reported dopants

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Address correspondence to Jong-Wook Park, Department of Chemistry/Center for Nanotechnology Research, The Catholic University of Korea, Pucheon, 420-734, Korea. E-mail: hahapark@catholic.ac.kr include pyran-containing compound [5,8,9], porphyrin compound [4,10–12], europium chelate complexes [13–15] and diphenylpentacene compound [16,17].

In particular, pentacene derivatives have been extensively investigated in organic thin film transistor (TFT) and photovoltaic research [18–20]. In here, we report the synthesis and photoluminescent (PL) properties of new 6,13-dinaphthalene-1-ly-pentacene (1-DNP) and 6,13-Di-naphthalen-2-yl-pentacene (2-DNP) as pentacene derivatives.

2. EXPERIMENT

2.1. Material and Characterization

6,13-Pentacenequinone (99%), phenyllithium (1.9 M solution in diethyl ether), 1-bromonaphthalene (97%), 2-boronaphthalene (97%), n-buthyllithium (1.6 M solution in hexanes) were purchased from Aldrich and used without further purification unless it noted otherwise. Solvents were purified by normal procedures and handled under moisture free atmosphere.

^{1}H-NMR spectra were recorded with Bruker, Avance DPX-300 NMR spectrometer in $CDCl_3$ and chemical shift were recorded in ppm units with the residual proton solvent resonance. FAB-Mass spectra were measured with JEOL, JMS-AX505WA.

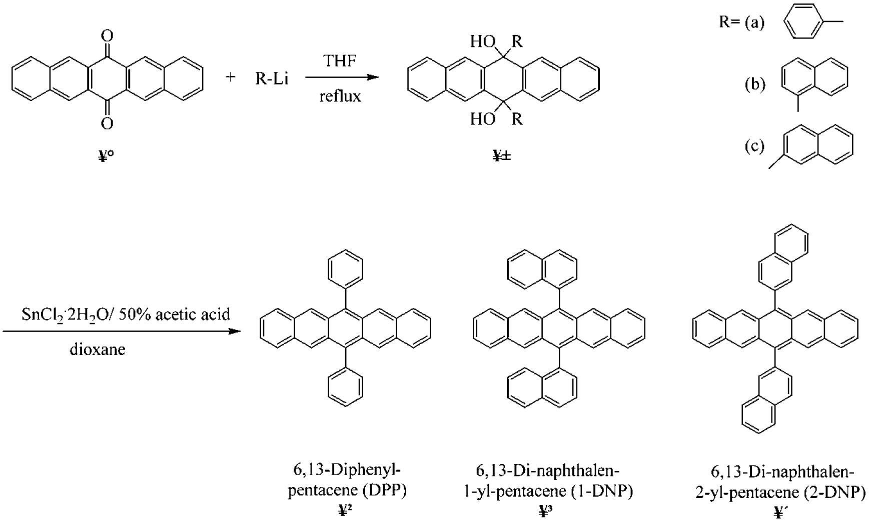
The optical absorption spectra were measured by a HP 8453 UV-VIS-NIR Spectrometer. Perkin Elmer luminescence spectrometer LS55 was used for photoluminescence spectroscopy.

2.2. Synthesis of 6,13-Dinaphthalene-1-ly-P entacene (1-DNP, IV)

6,13-Diphenylpentacene (DPP, III), 6,13-dinaphthalen-1-yl-pentacene (DNP, IV) and 6,13-di-naphthalen-2-yl-pentacene (2-DNP, V) were synthesized as Scheme 1.

A solution of 1-bromonaphthalene (2 ml, 16.2 mmol) in THF (50 ml) was stirred under N_2 and cooled to -78°C in a dryice/aceton bath. Upon cooling, 8.1 ml (16.2 mmol) of n-butyllithium was added to make metal-halogen exchange and 6,13-pentacenequinone (I) (500 mg, 1.6 mmol) was added to the yellow solution, and the mixture was refluxed for 7 hrs. Orange color product of diol (II) was recrystallized under hexane-EA solvent after common work-up process. (631 mg, 70% yield).

To a stirred solution of 6,13-di-naphthalen-1-yl-5a,6,13,13a-tetrahydro-pentacene-6,13-diol (II) (500 mg, 1.0 mmol) in 1,4-dioxane (50 ml)



SCHEME 1 Synthesis of 6,13-Diphenylpentacene (DPP, III) 6,13-dinaphthalen-1-yl-pentacene (DNP, IV) and 6,13-Di-naphthalen-2-yl-pentacene (2-DNP, V).

was added a suspension of tin(II) chloride dihydrate (10 g) in 50% aqueous acetic acid (10 ml). The reaction mixture was wrapped in foil and heated to 50 ~ 60°C for 3 hrs. As a result, a deep purple powder (IV) was isolated (400 mg, 80% yield).

Synthesis of 6,13-Di-naphthalen-2-yl-pentacene (2-DNP, V) was proceeded in the same method as 1-DNP's.

3. RESULTS AND DISCUSSION

We synthesized pentacene derivatives, DPP (III), 1-DNP (IV) and 2-DNP (V) by using reduction elimination reaction under Tin catalyst as shown in Scheme 1. These products were purified with recrystallization and typical silica column method to get highly pure purple color powder. The structure was identified by NMR, IR, UV-Visible spectroscopies and FAB-Mass analysis. As the second step reaction proceeded, OH peak in NMR and IR data completely disappeared in all compounds (DPP (III), 1-DNP (IV) and 2-DNP (V)). The resulting products are soluble in common organic solvents, such as chloroform and THF. 1-DNP (IV) showed higher melting temperature value at about 272°C than DPP (III) (254°C) and 2-DNP (V) (160°C). It means that 1-DNP (IV) shows the strongest interaction between molecules compared to DPP (III) and 2-DNP (V). Since thermal stability is a

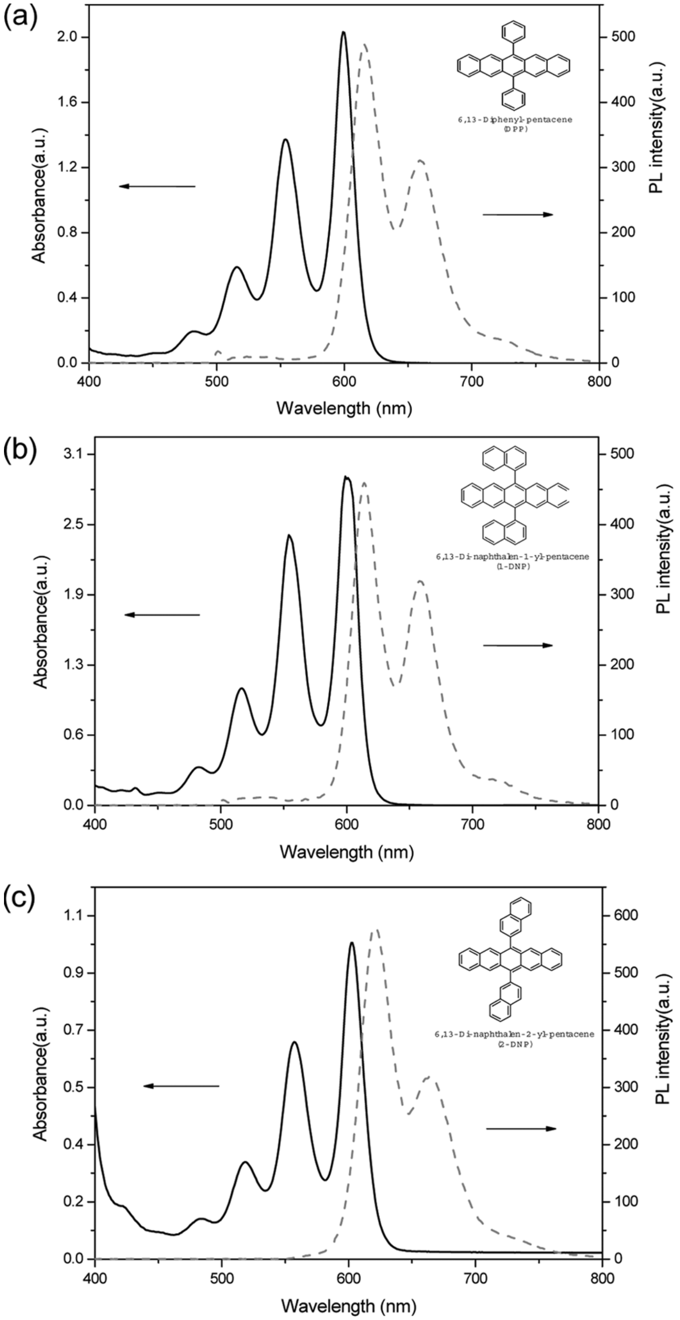
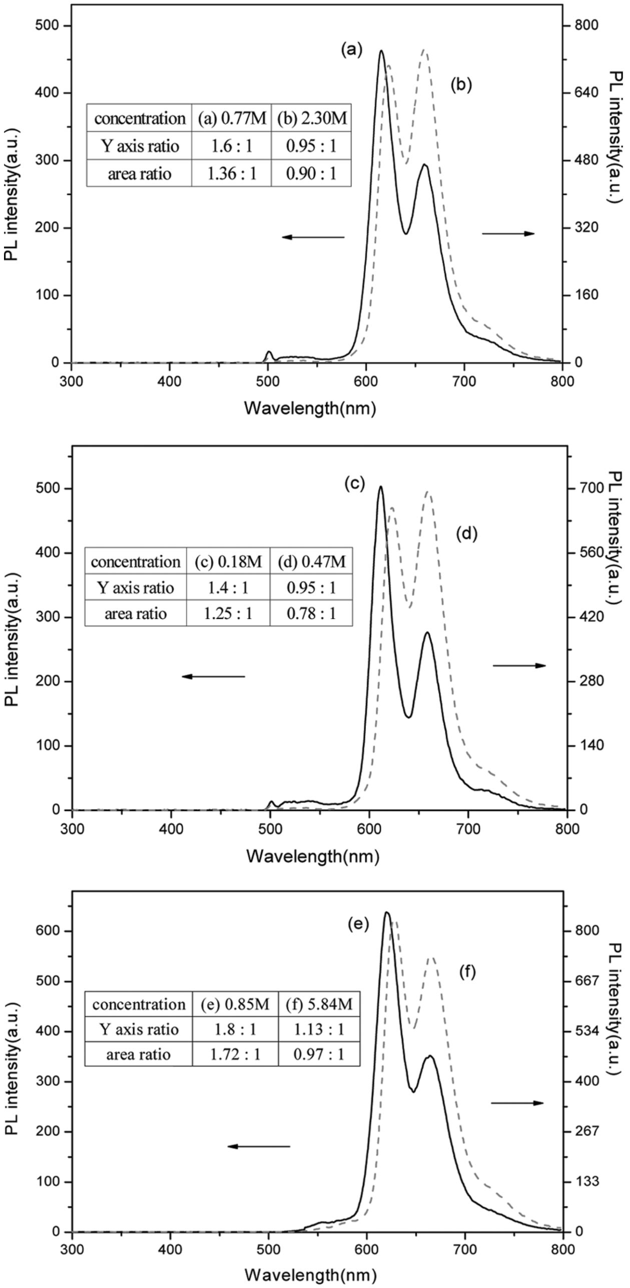


FIGURE 1 Normalized absorption (solid line) and fluorescence (dashed line) spectra of (a) DPP (III), (b) 1-DNP (IV), and (c) 2-DNP (V) in toluene.



concentration	(a) 0.77M	(b) 2.30M
Y axis ratio	1.6 : 1	0.95 : 1
area ratio	1.36 : 1	0.90 : 1

concentration	(c) 0.18M	(d) 0.47M
Y axis ratio	1.4 : 1	0.95 : 1
area ratio	1.25 : 1	0.78 : 1

concentration	(e) 0.85M	(f) 5.84M
Y axis ratio	1.8 : 1	1.13 : 1
area ratio	1.72 : 1	0.97 : 1

FIGURE 2 Photoluminescence spectra of (a) DPP 0.77 M toluene solution, (b) DPP 2.30 M toluene solution, (c) 1-DNP 0.18 M toluene solution, (d) 1-DNP 0.47 M toluene solution, (e) 2-DNP 0.85 M toluene solution, and (f), 2-DNP 5.84 M toluene solution.

critically important issue in determining lifetime of OLEDs, 1-DNP (IV) is expected to be very useful for improving device materials.

Figure 1 shows UV-Visible and photoluminescence (PL) spectra of DPP (III), 1-DNP (IV) and 2-DNP (V) toluene solutions. The maximum absorbance of all products appeared at around 482 nm, 517 nm, 554 nm and 600 nm, which are originated from the π-π^* transition of conjugated double bond [16,17]. The energy band gaps of DPP (III), 1-DNP (IV) and 2-DNP (V) were estimated to be 2.04 eV (III), 2.04 eV (IV) and 2.04 eV (V) from the analysis of absorption edge with a plot of (hv) vs. $(\alpha hv)^2$, where α, h, and v are absorbance, Plank's constant, and the frequency of light, respectively.

In Figure 1, all compound showed similar red PL spectrum tendency under the different solute concentration such as 0.77 M DPP, 0.18 M 1-DNP and 0.85 M 2-DNP solution. PL maximum wavelength appeared at around 620 nm and 660 nm.

We also observed PL intensity variation as a function of solute concentration. Figure 2 and caption text show a certain solute concentration value for making same PL intensity of two peaks at 620 nm and 660 nm. Figure 2 (a), (c) and (e) are typical PL spectra of 6,13-disubstituted pentacene derivatives, Figure 2 (b), (d) and (f) show similar PL intensity of 620 nm and 660 nm peak. As solute concentration of DPP increased, PL peak intensity at 660 nm rapidly increased as well as overall PL intensity increased. This result tendency was also observed in 1-DNP, and the changed PL intensity of two peaks (620 nm, 660 nm) was shown at more than 0.47 M 1-DNP concentration. In 2-DNP solution case, peak intensity of 660 nm increased as the concentration of solute solution increased but there was no the reversed phenomena of two PL peaks even though solute concentration was more than 5.84 M. These results might be due to the capability of molecular interaction, 2-DNP has relatively lower packing ratio and molecular interaction than 1-DNP's because of steric hinderance of 2-naphthyl bulky group. Therefore, There is no special increase of the longest PL maximum value 660 nm peak which might be caused by the interaction between molecules. These molecular interaction differences between 1-DNP and 2-DNP confirm with melting point result. CV, PL and EL properties of these derivatives in solid film states will be reported in the other paper.

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