

# 行政院國家科學委員會補助專題研究計畫成果報告

低聚反式（亞芳香基亞乙烯）衍生物  
和尿素衍生物的合成與研究  
The Synthesis of Oligo(arylene-(*E*)-vinylene)s and their  
Derivatives; and The Synthesis of Organic Ureas

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## 中文摘要

新型低聚反式(亞芳香基亞乙烯) DPBP-PPV 的開發與電致發光的應用。

關鍵詞：電致發光、PPV、藍光放射材料

## 英文摘要

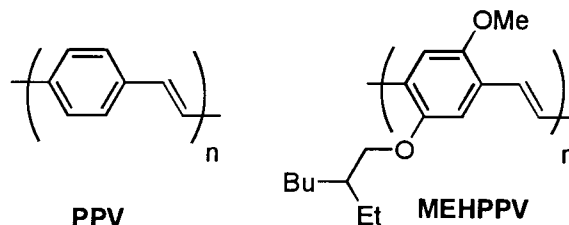
The synthesis and application of poly(2,2'-diphenylbiphenyl-4,4'-ylenevinylene-2'',5''-bistrimethylsilyl-*para*-phenylenevinylene) (DPBP-PPV), a novel blue-light emitting polymer was reported. The EL spectrum of DPBP-PPV is almost identical with its PL spectrum. By blending with PBD, the devices show a high external efficiency of 0.2% with the highest brightness of 300 cd/m<sup>2</sup>.

Keywords: electroluminescence, PPV, blue-light emission.

## 報告內容

Since the first demonstration of electroluminescence (EL) from poly(*para*-phenylenevinylene) (PPV) by Cambridge group [1], research concerning EL of  $\pi$ -conjugated polymers rapidly grows during the last decade. Due to the high intrinsic luminescent efficiency of PPV, many derivatives have therefore been synthesized and investigated in order to control the color of the emission, to facilitate solution processing, and to enhance the external efficiency of EL devices [2]. Among these, tuning the color of emission is of particular

important because an array of display requires integration of the red, green, and blue emitting components. To control the emissive properties of PPV solid films, a lot of recent efforts have been devoted to the study of substituent effects on the electronic and optical properties. Famous examples such as the family of MEHPPV that carries electron-donating alkoxy groups on the phenylene units red-shifting the emission wavelength from the parent green-light to into red region [3]. Other examples of introducing either electron-deficient aromatic



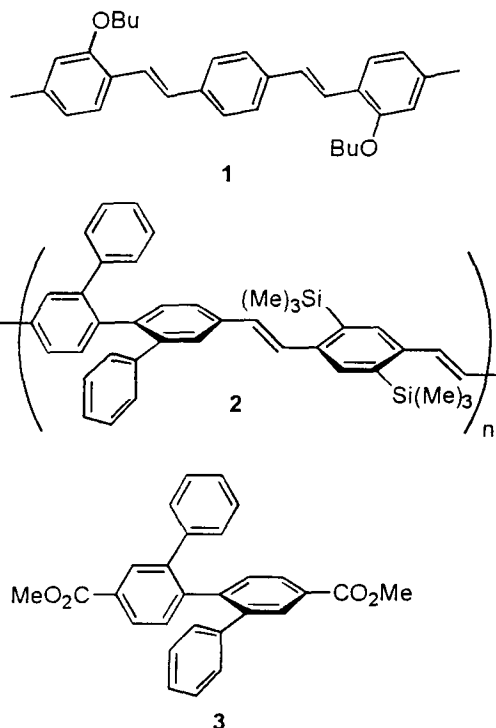
rings or electron-withdrawing groups on the vinylene units have also been reported [4,5]. In addition, blue-light EL polymers based on oligo-*para*-phenylenevinylene (OPPV) as side-chains or as segments on the backbone have also been developed [6].

In this work, we focus our attention on developing a new class of blue light emitting polymers based on the PPV skeleton. The desired polymers should have reasonably good solubility in common organic solvents and be able to form high quality thin-films through spin-coating process. In addition, the ideal emission bandwidth should be narrow and have an emission wavelength within 435-480 nm. In an ideal case, the polymers should have minimal percentage of sp<sup>3</sup> components that may significantly reduce the charge mobility in the matrix [7].

A survey of the previous literature

reveals that the EL behavior and the emission bandwidth of OPPV based polymers are not always consistent with their PL characteristics, and are difficult to predict.

Herein we describe the synthesis, the characterization, and photophysical behavior of **1** and **2**, and the application of **2** in light emitting diodes. To gain insight into the photophysical properties of OPPV based materials, 1,4-distyrylbenzene **1** was used as a probe to investigate the excitation and emission characters of OPPVs.



OPPV **1** was purified twice by sublimation at 180 °C under vacuum ( $5 \times 10^{-5}$  torr). The concentration dependent steady-state fluorescence spectra for **1** in toluene were collected from a typical right-angle detection fluorescence spectrometer equipped with a 1 x 1 cm quartz cuvette. The spectrum for a highly diluted solution ( $10^{-6}$ M) of **1** shows a maximum centered at 440 nm with the electronic-vibrational (vibronic) couplings ranged from 400-480 nm. Gradually increasing the concentration of **1** from  $10^{-6}$ M to  $10^{-2}$ M alters the pattern of the emission spectra as well as their emission intensity. The first vibronic emission band peaked at 415 nm gradually disappears while the second and the third vibronic emission bands peaked at 440 nm and 470 nm remain [8].

Examination of its absorption spectrum as well as the excitation spectrum reveals that **1** has a strong absorption peaked at 370 nm with a tailing extended to 430 nm. At high concentrations, self-absorption mechanism may occur that reduces the emission below 430 nm [9]. In extreme cases, emissions below 430 nm would probably be significantly suppressed under the typical experimental conditions. This possibility was supported by the frontal-surface fluorescence spectrometric experiment [9] which gives rise to a shoulder at 420 nm. To obtain further support for the self-absorption mechanism, a liquid thin-film of a  $10^{-2}$  M solution of **1** was employed in the fluorescent experiment in order to minimize the path-length for self-absorption process [10]. Under these conditions, normal emission spectrum was obtained.

Vacuum deposition of **1** on a quartz plate would lead to an amorphous solid film. The photoluminescence spectrum shows only one major emission at 450 nm with a shoulder appeared at 490 nm. Although the energy-transfer mechanism may be more complicated in aggregated or solid state [11], similar to that in highly concentrated solution, the first vibronic band at 415 nm disappears. The appearance of the emission shoulder at 490 nm may due to either an emission arising from the low-energy  $0 \rightarrow n$  vibronic transition or from the partial crystallization areas of the solid-film, in comparison to the identical emission wavelength of the single crystals of **1** [12].

All these results indicate that the complicated vibronic emission spectrum of OPPV could be simplified through the self-absorption or energy transfer mechanism in the solid film, leading to a single major emission with narrow bandwidth. The higher energy vibronic emission may be re-absorbed and channelled to the desired lower energy blue light emission. In addition, the emission spectrum may become narrower if the crystallinity or the formation of highly ordered aggregation [12] could be suppressed.

On the basis of the above conclusions, polymer **2** was rationally designed and

synthesized. Due to the non-planer conformation of the biphenyl units [13], each of the OPPV units will be confined as an independent unit and non-conjugated with each other. More importantly, the phenyl substituents on the biphenyl units would hinder the rotation of the biphenyl backbone, prohibiting the biphenyl unit from coplanarization in the excited state and maintaining the OPPV fluorophore as an independent blue light emitting unit. In addition, the presence of the phenyl side chain would increase the solubility of **2** as well as reduce its tendency towards crystallization [14].

Polymer **2** is reasonably soluble in  $\text{CHCl}_3$  and highly soluble in 1,2-dichlorobenzene. The soluble portion of polymer **2** in  $\text{CHCl}_3$  prepared accordingly has an weight-average molecular weight  $M_w = 2400$  relative to the polystyrene standard in gel permeation chromatography (GPC) measurements with  $M_w/M_n = 1.7$ . No obvious glassy transition temperature was observed on the basis of differential scanning calorimetry (DSC) analysis scanning from 50-300 °C. Polymer **5** has extremely good thermal stability. The thermogravimetric analysis (TGA) trace indicated decomposition at 400 °C (5% weight loss) under  $\text{N}_2$ . No elimination of small molecule was observed below this temperature, indicating the high degree of conjugation had been formed during the polymerization reaction.

Good quality thin-films of **2** with the thickness of 650-800 Å could easily be obtained through spin-coating from a chloroform solution (13 mg/mL). The thickness of the thin-film was evaluated by using ellipsometry. An absorption maximum at 375 nm and an emission at 450 nm are characteristics for distyrylbenzenes [2c], indicating that the distyrylbenzene units are more or less non-conjugated with each other. The emission spectrum shows a blue color peaked at 450 nm with a narrow full width at half-maximum (FWHM) of 55 nm, ranged from 440-495 nm. Relative small Stokes-shift of 75 nm for **2**, in comparison to a large value of about 170 nm for **3** in solution, suggests that the rotation and coplanarization

of the biphenyl unit in the excited state is retarded.

The indium-tin oxide (ITO) coated glass electrodes used for the preparation of EL devices were pretreated with poly(styrenesulfonic acid) /poly(3,4-ethylenedioxythiophene) (PEDOT) as a hole-injection layer. The polymer films were spin-coated at 5000 rpm from  $\text{CHCl}_3$  solutions with a concentration of 13 mg/mL, giving films of 800 Å thickness. A layer of Mg/Ag (10:1) contacts were then deposited on top of the polymer under vacuum at pressures below  $1 \times 10^{-6}$  torr.

LEDs fabricated with polymer **2** show bright emission easily observable under normal room illumination. The turn-on voltage of 13 V is close to the 15 V for the PPV polymer, using Al as the electrode. Significant reduction of the turn-on voltage and enhancement of the external quantum efficiency by doping with PBD indicates an imbalanced injection of opposite charges in the original polymer matrix (Table 1). We believe that the electron injection is less efficient than the hole injection, and therefore requiring PBD, a good electron-transport material, to balance the electron injection and optimize the performance of the device. Other factors such as the change of interface properties or morphology of the polymer matrix may also significantly affect the performance of LED devices. Similar to the PPV series, polymer **2** should have a good hole-transport behavior. Doping with hole-transport compounds such as N,N,N'-tetraphenyl-1,1'-biphenyl-4,4'-diamine (TPB) only enhances the background current without increasing the brightness of the device, and therefore retarding the quantum efficiency of the EL.

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Table 1  
Performance of the ITO/PEDOT/DPBP-PPV, PBD, TPB/Mg devices.

	DPBP-PPV/PBD/TPB (weight ratios)		
	(100:0:0)	(100:40:0)	(100:40:40)
External quantum efficiency (%)	< 0.1	0.2	0.015
Brightness (cd/m <sup>2</sup> )	80	300	200

## 國科會補助國外會議報告

### 第六屆國際材料會議 - 亞洲會議，香港

(7月24日到7月27日)

### 第六屆國際華人有機會議，上海

(7月28日到7月31日)

台灣大學化學系梁文傑教授

第六屆國際材料會議在香港城市大學召開，相互觀摩，獲益良多。台灣方面出席講員有工研院劉佳明博士與本人。該會議不乏國際知名科學家參與，包括 D. Bradley, Z. H. Kafafi, J. Kido, Y. Shirato, W. Huang, J. J. Kim, K. Seki, M. Fujihira 等教授參加。除了在會議上作學術交流外，本人還參觀城市大學物理與材料系及其實驗室，對該大學與現代化物理與材料實驗室設計有進一步瞭解。

城市大學物理與材料實驗室，編制與台灣一般國立大學相當，但個別教授的實驗室空間充裕。以李述湯教授為首領導下，形成有國際競爭力的研究小組。專攻光電材料、奈

米材料與表面材料。對於人口和資源較少的香港而言，此等集中資源編制有利於強化該校的競爭力，這一點足可讓我們借鏡。本人是次講題為「Synthesis and Characterization of Poly(2,2'-diphenylbiphenyl-4,4'-ylenevinylene-2'',5''-bis(trimethylsilyl)-*para*-phenylenevinylene), a New Efficient Blue-light Emitting Polymer」。之後本人隨之赴上海參加第六屆國際華人有機會議。此次國際華人有機會議，台灣代表三十餘人，濟濟一堂，共襄盛舉。世界華人化學家相互觀摩。中研院院士楊念祖教授暢談光化學的過去與未來，得益良多。此外又參觀上海有機所。上海有機所正與香港的幾所大學合作，推動有

機合成計劃，亦與外資化  
工合作，進行藥物發展研  
究。此等擴大合作，有利

於強化世界競爭力，這一  
方面我們應借鏡。