

行政院國家科學委員會補助專題研究計畫成果  
結案報告

計畫名稱：有機電激發光元件用新摻雜材料之設計  
與合成(3/3)

計畫類別：整合型計畫

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計畫主持人：陳金鑫 教授

執行機構：國立交通大學應用化學系

國立交通大學電子資訊研究中心

中華民國九十一年九月十六日

## 研究成果報告

本實驗室自參與國科會專題研究計劃以來，致力於合成新穎的有機發光材料以及元件的開發，已有豐碩的成果。在第一年的計劃中，經由國科會、交大應用化學系及交大電子資訊中心的資助下，積極展開實驗室的建立，真空薄膜蒸鍍機及周邊設備的設計與組裝。經過一年的努力，設備趨於完善，率先成立『有機發光元件研究實驗室』，為國內學術界第一個專攻有機發光二極體(Organic Light Emitting Diode, OLED)平面顯示技術的研究團隊。

邁入第二年計劃後，本實驗室分為有機合成組以及元件製程組，各司其職，並且相互合作。有機合成組負責開發新穎的有機發光摻雜材料，並改良合成步驟，進而配合元件製程的進度，提供所需的材料。而元件製程組則負責元件製程方面，除了負責將材料應用於元件上外，亦需改善元件結構，以增加發光效率、光色之純度與元件的穩定度，盡可能將材料發揮至極至。這種專業經營的研究管理模式，不但在台灣為首創，在世界 OLED 的研發單位中，也屬一流，同時亦備受業界的肯定。

OLED 的發展，是以全彩化的平面顯示器為最高目標邁進，目前紅、藍、綠三原色的摻雜材料都已開發出來，但卻尚未達到令人滿意的地步，故仍需持續地研發新穎的、更好的三原色摻雜材料。基於本

實驗室致力推動 OLED 的精神，進入計劃第三年，無論在發展新穎紅、藍、綠有機發光材料上有相當傑出的成果外，在元件製程方面亦有所嶄獲。

在紅光摻雜物方面，由於 4-(dicyanomethylene)-2-*t*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB) 是目前最好的紅光摻雜物之一，並且陸續被 Kodak 與 Sanyo 應用在主動式 OLED。本實驗室為了改善紅光元件的光色、濃度驟熄現象、發光效率與熱穩定性等問題，博士班學生溫世文，成功地合成新穎紅光摻雜物 2-2-(*tert*-butyl)-6-[(*E*)-2-(1,1,7,7-tetramethyl-8-phenyl-2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinolin-9-yl)-1-ethenyl]-4*H*-4-pyranylidene malononitrile (DCJTB-P)，其由關鍵中間體 8-bromo-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinolin-9-carbaldehyde 經由 Suzuki coupling 與 Knoevenagel condensation 而得，此化合物以 DCJTB 為基礎，並在 julolidine 結構中(C)-8 的位置改以苯環取代，成功地防止雙鍵自由旋轉，增加分子的剛硬度，因而提昇熱穩定度，並且也稍微地改善了光色，此篇發表於今年二月 ICCT (International Chemical Conference, Taipei) 會議中(附件十三)。博士班學生李世男，於 DCJTB 之 julolidine 結構中的(C)-8 位置用一推電子基取代，合成出新的紅光摻雜物 2-2-(*tert*-butyl)-6-[(*E*)-2-(1,1,7,7-tetramethyl-8-methoxy-2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinolin-9-yl)-1-ethenyl]-4*H*-4-pyranyl

idenmalononitrile (DCJTB-OR)，此篇亦發表在今年 ICCT 會議中(附件十五)。另外，碩士班學生劉醇炘與游宗燁，經由實驗發現，調整電洞傳輸層 NPB 的膜厚，替換電洞注入層將 CuPc 改為  $CF_x$  以平衡電荷傳輸，並且利用雙摻雜的技術，得到一最佳的紅光元件 ITO(170 nm)/ $CF_x$ (50 nm)/NPB(110 nm)/Alq<sub>3</sub>+rubrene(5 %)+DCJTB(x %)(30 nm)/Alq<sub>3</sub>(55 nm)/LiF(1 nm)/Al(200 nm)。當電流密度為 20 mA/cm<sup>2</sup>，螢光效率可達 3.24 cd/A，CIE<sub>x,y</sub> 座標(0.643, 0.354)，成功地改善了紅光元件的發光效率與光色。此篇已於今年八月二十一日在韓國所舉辦的 2002 國際資訊顯示 IMID (International Meeting on information Display) 會議中發表(附件十七)。

在綠光摻雜物方面，本實驗室簡金雄合成 10-(2-benzothiazolyl)-9-methyl-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-benzo[*l*]pyrano[6,7,8-*ij*]quinolizin-11-one (C-545MT)，此綠光摻雜物以 Alq<sub>3</sub> 為主發光體，在摻雜濃度為 2 %到 12 %的範圍間，其發光效率均可維持在 7.8 cd/A 左右，顯示在 coumarin 中 C(4)-的位置以一甲基取代，立體效應增加，抗濃度驟熄的現象比 C-545T 提昇十倍，雖然發光效率不如現在市場上所熟知的 C-545T，但此高抗濃度驟熄的現象是前所未見的，而此篇專利已在申請中(附件七和十二)。另外博士班學生李孟庭則發明出另一 coumarin 系列的新穎綠光摻雜物 10-(2-benzothiazolyl)-1,3,3,7,7-pentamethyl-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-benzo[*l*]pyrano[6,7,

8-*ij*]quinolizin-11-one (簡稱為 C-545P), 其熱穩定性比 C-545T 好, 發光效率也比 C-545T 提昇 10%, 且較 C-545T 更具有抗濃度驟熄效應; 值得一提的是, C-545P 特殊的分子結構, 可突破 C-545T 的專利, 進而提昇國內 OLED 在國際市場上的競爭力, 此篇專利包材料與元件已在申請中(附件八、九、十五和十八)。

在藍光摻雜物方面, 本實驗室元件製程組經實驗發現, 當改變發光層的膜厚時, 發光效率也會隨之而改變, 進而找出最佳藍光主發光體 9,10-*di*(2-naphthyl)anthracene (ADN)的膜厚以及 tetra(*t*-butyl)-perylene (TBP)的最佳摻雜濃度之藍光元件 ITO(170 nm)/CuPc(15 nm)/NPB(40 nm)/ ADN+2% TBP(30 nm)/Alq<sub>3</sub>(20 nm)/LiF(1 nm)/ Al (200 nm)。當電流密度為 20 mA/cm<sup>2</sup>, 發光效率可達 5.1 cd/A, CIE<sub>x,y</sub> 座標(0.15, 0.22), 此篇已發表於今年六月在上海所舉辦的 2002 國際合成金屬科技研討 ICSM (International Conference on Science and Technology of Synthetic Metal)會議中(附件十六)。

另外, 本實驗室博士後研究員班如曼在有機材料合成方面亦有所貢獻, 其中包含研究 DCJTB 的關鍵中間體, 發現導致 DCJTB 量產不易的原因乃是在合成中間體 tetramethyljulolidine (TMJ)時, 會伴隨另一副產物的生成, 並且利用不同的酸催化以及反應溫度的改變, 也會影響 TMJ 的產率, 此篇將發表在 *Tetrahedron Lett.* **2002**(附件一)。另

外，在 *Molecules* 期刊中即將發表一篇合成 indole 化合物之新方法(附件二)。

近兩年間，本實驗室更發表四篇的科譜教育文章，希望將 OLED 的科技知識普及化，推廣 OLED 輕、薄、彩、美、廉、易(攜帶)、多(元化)應用的優點，不遺餘力，更提供許多最新的 OLED 國內外情報(附件三、四、五和六)。

總結此三年計劃，自我評估覺得成果極為豐碩，其分項研究成果細目與附件如下：

## 研究成果細目

碩士論文：

1. 楊文坪：新綠色螢光摻雜物材料應用在有機電激發光顯示的合成與性質的研究(八十九年十一月)。
2. 蔡宗韋：新型綠色摻雜物的合成及其在有機電激發光上的應用(八十九年九月)。
3. 楊景仲：新穎藍色發光體的設計與合成及其應用在有激發光二極體的性質研究(九十年七月)。
4. 簡金雄：抗濃度驟熄之新型有激發光二極體綠色螢光摻雜材料的設計與研究(九十年七月)
5. 李世男：應用在有機電激發光顯示器之新紅色螢光摻雜物的合成性質與研究(九十年七月)
6. 李孟庭：有機電激發光元件之新穎綠色客發光體材料的合成與應用(九十一年七月)
7. 顏嘉國：9, 10-[二(2-萘基)]蒽應用於藍光與紅光有機電激發光元件之性質研究(九十一年七月)

期刊：

1. **Synthetic Study of Tetramethyljulolidine – A key intermediate toward the synthesis of red dopant DCJTb for OLED applications**  
Banumathy Balaganesan, Shih-Wen Wen and Chin H. Chen \*  
*Tetrahedron Letters* (manuscript TL-020513-071 - accepted for publication)
2. **An Unusual Reaction of *N*-Methyl-*p*-toluidine with 1,3-Dichloroacetone – A New Indole Synthesis**  
Banumathy Balaganesan and Chin H. Chen\*  
*Molecules* (manuscript MCP020304 – accepted for publication).
3. **A Highly Robust Green Fluorescent Dopant for Organic Light-Emitting Devices**  
Chin H. Chen, Chin-Hsiung Chien, Tswen-Hsin Liu  
*Thin solid film* (in press)

科譜教育：

1. 新世紀的 "鑫" 科技--有機電激發光二極體平面顯示器技術--  
簡金雄, 陳金鑫\*, *物理雙月刊*, 23, 2, 307(2001).
2. 交大 OLED 平面顯示技術的推展與近況--鄭榮安, 陳金鑫\*,  
*交大有聲雜誌*, 390, 28(2002).
3. 前瞻性 OLED 的展望——可撓曲式有機發光二極體之開發現況  
--鄭榮安, 陳金鑫\*, *電子與材料*, 11, 37(2001).
4. 二十一世紀的明星產業-有機發光二極體平面顯示器技術--  
簡金雄, 陳金鑫\*, *光電科技*, 24, 78(2001).



專利：

1. 中華民國專利：陳金鑫，簡金雄 -- 具有高度抗濃度驟熄效應的新型綠色螢光摻雜物之有機電激發光裝置(專利申請號碼 090116194)
2. 中華民國專利：陳金鑫，李孟庭 -- 新型綠色有機電激發光材料 (專利申請號碼 091102076)
3. 中華民國專利：陳金鑫，李孟庭，顏嘉國 -- 具抗濃度驟熄效應的新型綠色螢光摻雜物之有機電激發光裝置 (專利申請號碼 091103308)
4. 中華民國專利：陳金鑫，溫世文 -- 新型有機電激發光材料中間體 (專利申請號碼 091103308)

國際會議邀請演講：

1. **Tetramethyl Julolidine – A key intermediate in the synthesis of the red dopant DCJTb for OLED applications**  
Chin H. Chen, Banumathy. B and Shih-Wen Wen  
*International Conference of Electroluminescence III, Los Angeles(ICELE), Sep 5-9, 2001.*
2. **A Highly Robust Green Fluorescent Dopant for Organic Light Emitting Devices**  
Chin H. Chen, Chin-Hsiung Chien and Tswen-Hsin Liu  
*Abs. Intern. Conf. Mater. Adv. Tech. (ICMAT 2001), Singapore, 2001.*

- 3. Design and Synthesis of New Red dopants for Organic Electroluminescent Devices**  
Shih-Wen Wen and Chin H. Chen  
*International Chemical Conference, Taipei(ICCT), Feb 23-26, 2002.*
- 4. Synthesis and Characterization of New Red dopants for Electroluminescence**  
Shih-Nan Lee, Tswen-Hsin Liu, Chia-Kuo Yen and Chin H. Chen  
*International Chemical Conference, Taipei(ICCT), Feb 23-26, 2002.*
- 5. Efficient Green Coumarin Dopants for Organic Light Emitting Device**  
Meng Ting Lee, Chia-Kuo Yen, Wen Ping Yang and Chin H. Chen  
*International Chemical Conference, Taipei(ICCT), Feb 23-26, 2002.*
- 6. Blue Emitters of 9,10-di-(2-naphthyl)anthracene in OLEDs**  
Tswen-Hsin Liu, Wen Jian Shen, B. Banumathy, Chia-Kuo Yen, Chung-Yeh Iou, Hsian-Hung Chen and Chin H. Chen  
*International Conference on Science and Technology of Synthetic Metals(ICSM), Shanghai, June 29-July 5, 2002.*
- 7. DCJTb Doped Red Emitters in OLED**  
Tswen-Hsin Liu, Chung-Yeh Iou, Shih-Wen Wen and Chin H. Chen  
*International Meeting on Information Display(IMID), Korea, Aug 21-23, 2002.*
- 8. Efficient Green Fluorescent Dopants for Organic Light Emitting Devices**  
Meng Ting Lee, Chia-Kuo Yen, Wen Ping Yang and Chin H. Chen  
*Eurodisplay Conference, France, Oct 1-4, 2002.*

# 附件一

## Synthetic study of tetramethyljulolidine – a key intermediate toward the synthesis of the red dopant DCJTB for OLED applications

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**Abstract** – The formation and characterization of a novel chiral sulfonic acid derivative obtained during the synthesis of 1,1,7,7-tetramethyljulolidine (TMJ), a key intermediate towards the red dopant 4-(dicyanomethylene)-2-*t*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran (DCJTB) used for organic electroluminescent devices, upon *bis*-annulation of *N,N*-bis(4-methyl-2-butenyl)aniline is described.

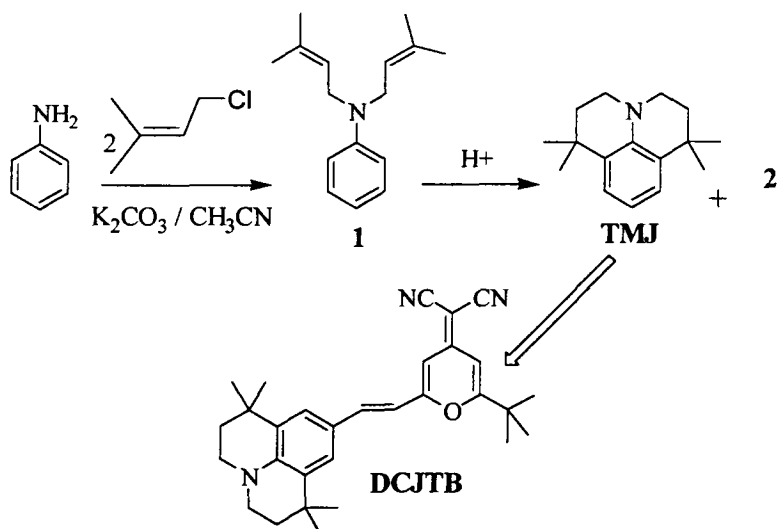
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Organic electroluminescent devices are of growing interest in various display applications due to their high luminous efficiency and capability of emitting many colors throughout the visible spectrum. Commercial interest in organic light emitting diode (OLED) technology has been the vital driving force in fueling the recent research and development activities.<sup>1,2</sup>

4-(Dicyanomethylene)-2-*t*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran, (DCJTB) is one of the best fluorescent dopants of choice for the red emitter of *tris*(8-hydroxyquinolino)aluminium hosted OLED's including Pioneer's recently demonstrated passive matrix full color prototype and Kodak / Sanyo's 2.4-in and 5.5-in low temperature poly silicon full color active matrix OLED displays. The cost of manufacturing DCJTB is prohibitively high owing to the synthetic complications of one of the key intermediates, 1,1,7,7-tetramethyljulolidine (TMJ), which can be prepared in two steps from aniline and 1-chloro-3-methyl-2-butene (Scheme 1). The low yield (~30%) obtained in the acid catalyzed *bis*-annulation prompted us to reinvestigate the reaction and analyze the products of the above reaction.

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**Scheme 1** Synthesis of DCJTB

*N,N*-bis(4-Methyl-2-butenyl)aniline **1** was prepared by the conventional *N*-alkylation of aniline with two equivalents of 1-chloro-3-methyl-2-butene in the presence of  $K_2CO_3$  at reflux. This compound was then subjected to a *bis*-annulation in the presence of an acid catalyst to form the key intermediate TMJ.

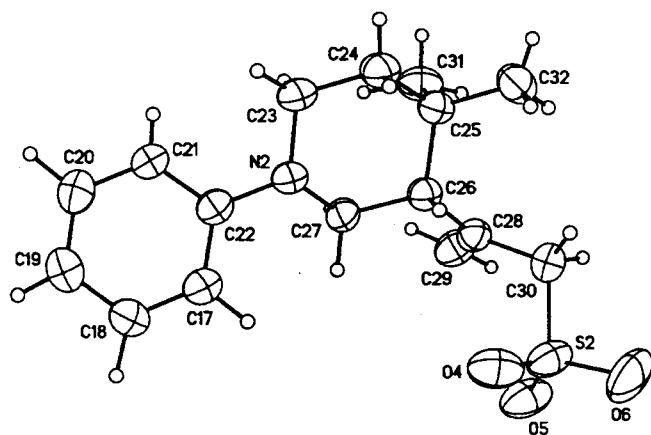
Different acid catalysts were employed to effect the *bis*-annulation. The starting material was found to remain unaffected in the presence of weak acids like *p*-toluene sulfonic acid, methane sulfonic acid and acetic acid. Strong acids such as aqueous perchloric acid, trifluoroacetic acid and trifluoromethane sulfonic acid led to the formation of TMJ in infinitesimal quantities along with an inseparable polar mixture. In the presence of concentrated sulfuric acid at 0°C, TMJ was obtained in 37% yield in addition to a major quantity of an insoluble material. To enhance the yield of TMJ, the temperature of the reaction was raised to about 30°C. This, in fact, led to a further decrease in the yield of TMJ (34%) accompanied with a proportionate increase in the formation of the insoluble by-product (Table 1). Moreover, in both cases, conc. sulfuric acid was taken in large excess (about three v/w equivalents), which led to a voluminous precipitation during the basic work-up of the reaction, which in turn made the process of filtration more tedious. Hence, we decided to use a combination of acids to avoid the above said complexities.

Various proportions of methane sulfonic acid and sulfuric acid were prepared (v/v equivalents - 1:1, 2:1, 4:1) to catalyze the formation of TMJ. A decrease in the concentration of sulfuric acid resulted in a drastic decrease in the yield of TMJ (Table 1). However, the insoluble by-product **2** was obtained predominantly (59%) when a 1:1 mixture of methane sulfonic acid: sulfuric acid was used, which provoked our interest in characterizing and studying its formation.

Table 1. Yields of TMJ and **2** obtained by catalysis using various proportions of sulfuric acid and methane sulfonic acid.

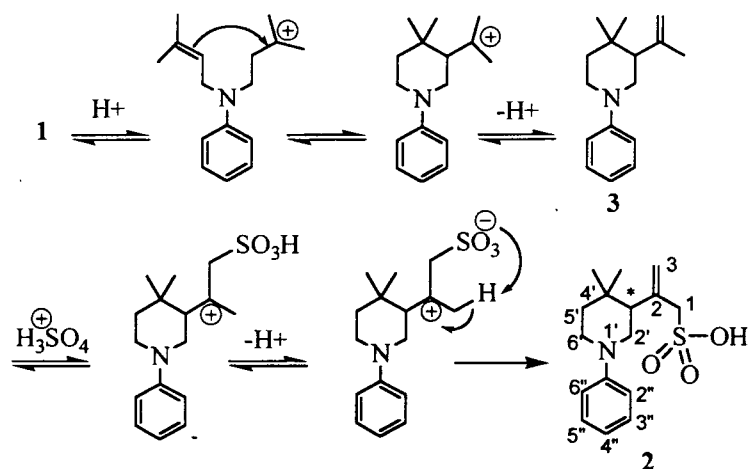
Entry	Acid / solvent	Temperature (°C)	Time (h)	Yield of TMJ (%)	Yield of <b>2</b> (%)
1	Conc.H <sub>2</sub> SO <sub>4</sub>	0	0.5	37	20
2	Conc.H <sub>2</sub> SO <sub>4</sub>	0-30	3	34	22
3	H <sub>2</sub> SO <sub>4</sub> : CH <sub>3</sub> SO <sub>3</sub> H (1:1)	0	1	16	59
4	H <sub>2</sub> SO <sub>4</sub> : CH <sub>3</sub> SO <sub>3</sub> H (1:2)	0-30	3	10	22
5	H <sub>2</sub> SO <sub>4</sub> : CH <sub>3</sub> SO <sub>3</sub> H (1:4)	0-30	3	<5	-

The mass spectra of compound **2** showed peaks at  $m/e$  309 ( $M^+$ ) and at 229 ( $M^+ - SO_3H + 1$ ), indicating that product **2** must bear a  $-SO_3H$  group in its skeleton. The unsymmetrical nature of the <sup>1</sup>H-NMR spectrum suggested that the compound might have undergone an unexpected rearrangement during the acid-catalyzed *bis*-annulation. The <sup>13</sup>C NMR showed three quaternary, four methines, five methylenes and two methyls. A methylene at 116.88 ppm indicated the presence of an exocyclic double bond whose protons resonated at 5.28 and 4.94 ppm as singlets. Based on a detailed analysis of both one and two dimensional NMR spectroscopic techniques (<sup>1</sup>H-<sup>1</sup>H COSY, <sup>1</sup>H-<sup>13</sup>C HETCOR), the structure was found to be consistent with that of **2**.<sup>3</sup> It was further unequivocally confirmed by a single crystal X-ray diffraction studies.<sup>4</sup>



Single X-ray diffraction of compound **2**

A plausible mechanism for the formation of 2-(4',4'-dimethyl-1'-phenyl-3'-piperidyl)-2-propene-1-sulfonic acid **2** is presented in Scheme 2.



### Scheme 2

The mechanism is likely to involve an intramolecular “ene” reaction in the presence of acid <sup>5</sup> to form the intermediate **3**. Subsequently the exocyclic double bond of **3** undergoes sulfonation in the presence of sulfuric acid to form the sulfonic acid **2**. To summarize, we have characterized and proposed a plausible mechanism for the formation of the by-product, a novel chiral sulfonic acid derivative **2** obtained during the synthesis of TMJ, a key intermediate towards the red dopant DCJTb for organic electroluminescent devices upon *bis*-annulation of *N,N*-bis(4-methyl-2-butenyl)aniline **1**. It was also found that **2** is a water-soluble compound and hence can be eliminated easily to furnish highly pure TMJ.

### Acknowledgements

We like to thank the National Science Council, Taiwan, Republic of China for providing a post-doctoral fellowship for B.B. The authors gratefully acknowledge the help of L. W. Kelts of Eastman Kodak Company, Rochester, New York for providing the 500 MHz NMR spectroscopic data and the Department of crystallography, NTHU for single crystal X ray diffractational analyses.

### References

1. Chen, C. H.; Tang, C. W.; Shi, J; Klubek, K. P. *Macromol. Symp.* **1997**, *125*, 49-58.
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3. Typical Experimental Procedure: To a mixture of methane sulfonic acid and sulfuric acid (1:1 v/v equivalents, 5 mL), *N,N*-bis(4-methyl-2-butenyl) aniline (**1**, 2.5 g, 11 mmol) was added at 0°C and the mixture stirred for an hour. After complete disappearance of the starting material (monitored by TLC), the reaction mixture was poured onto ice and extracted using dichloromethane ( 3 x 300 mL).

The organic layer was washed with saturated NaHCO<sub>3</sub> solution and water, dried over anh. MgSO<sub>4</sub> and the solvent was evaporated to dryness to yield TMJ (4 g, 16%). During basification of the aqueous layer of the reaction mixture using saturated NH<sub>4</sub>OH solution, compound **2** crystallized as needles (2.0 g, 59%).

Spectral characteristics of **2**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz) δ 0.86 (s, 3H), 0.95 (s, 3H), 1.43 (m, 1H), 1.66 (dt, *J*=13.5, 2.5 Hz, 1H), 2.55 (dd, *J*=12.0, 4.5 Hz, 1H), 2.85 (m, 2H), 3.35 (dd, *J*=12.5, 3.0 Hz, 1H), 3.45 (dd, *J*=12.5, 3.0 Hz, 1H), 3.55 (q, *J*=13.25 Hz, 2H), 4.94 (s, 1H), 5.28 (s, 1H), 6.82 (t, *J*=8.0 Hz, 1H), 6.95 (d, *J*=7.8 Hz, 2H), 7.22 (t, *J*=8.0 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 19.74, 30.66 (2Me's), 32.70 (C-4'), 40.08 (CH<sub>2</sub>, C-5'), 45.44 (CH<sub>2</sub>, C-6'), 49.26 (CH, C-2'), 50.32 (CH<sub>2</sub>, C-2'), 61.89 (CH<sub>2</sub>, C-1), 116.18 (2CH's, C-2'', C-6''), 116.88 (CH<sub>2</sub>, C-3), 118.96 (CH, C-4''), 129.32 (2CH's, C-3'', C-5''), 142.60 (C-2), 151.11(C-1'').

4. Compound **2** was crystallized from acetonitrile:water.

2-(4',4'-dimethyl-1'-phenyl-3'-piperidyl)-2-propene-1-sulfonic acid **2** was found to be a *dl*-pair as seen from the X-ray diffractive pattern.

Crystal data for compound **2**: C<sub>32</sub>H<sub>58</sub>N<sub>2</sub>O<sub>13</sub>S<sub>2</sub>, *M* = 742.92 (*dl*-pair), monoclinic, space group - P2 (1)/c at a temperature 294(2) K and wavelength = 0.71073 Å, *a* = 20.7836(18) Å, *α* = 90°, *b* = 9.7131(9) Å, *β* = 117.156(2)°, *c* = 21.9556(19) Å, *γ* = 90°, *U* = 3943.7(6) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.251 mg/m<sup>3</sup>; absorption coefficient = 0.196 mm<sup>-1</sup>, *F*(000) = 1600, crystal size = 1.10 x 0.15 x 0.10 mm<sup>3</sup>; *θ* range for data collection = 1.10 to 28.28°, index ranges -23 ≤ *h* ≤ 26, -12 ≤ *k* ≤ 12, -28 ≤ *l* ≤ 24, reflections collected = 22977, independent reflections = 8752 [*R*(int) = 0.0728], completeness to *θ* = 28.28° is 89.6 %, absorption correction = empirical, max. and min. transmission = 0.8960 and 0.4552, refinement method = full-matrix least-squares on *F*<sup>2</sup>, data / restraints / parameters = 8752 / 0 / 442, goodness-of-fit on *F*<sup>2</sup> = 1.124, final *R* indices [*I*>2σ(*I*)] *R*1 = 0.0761, *wR*2 = 0.2203; *R* indices (all data) *R*1 = 0.1260, *wR*2 = 0.2533, largest diff. peak and hole = 0.582 and -0.597 e.Å<sup>-3</sup>. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-181958. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

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Supplementary Material

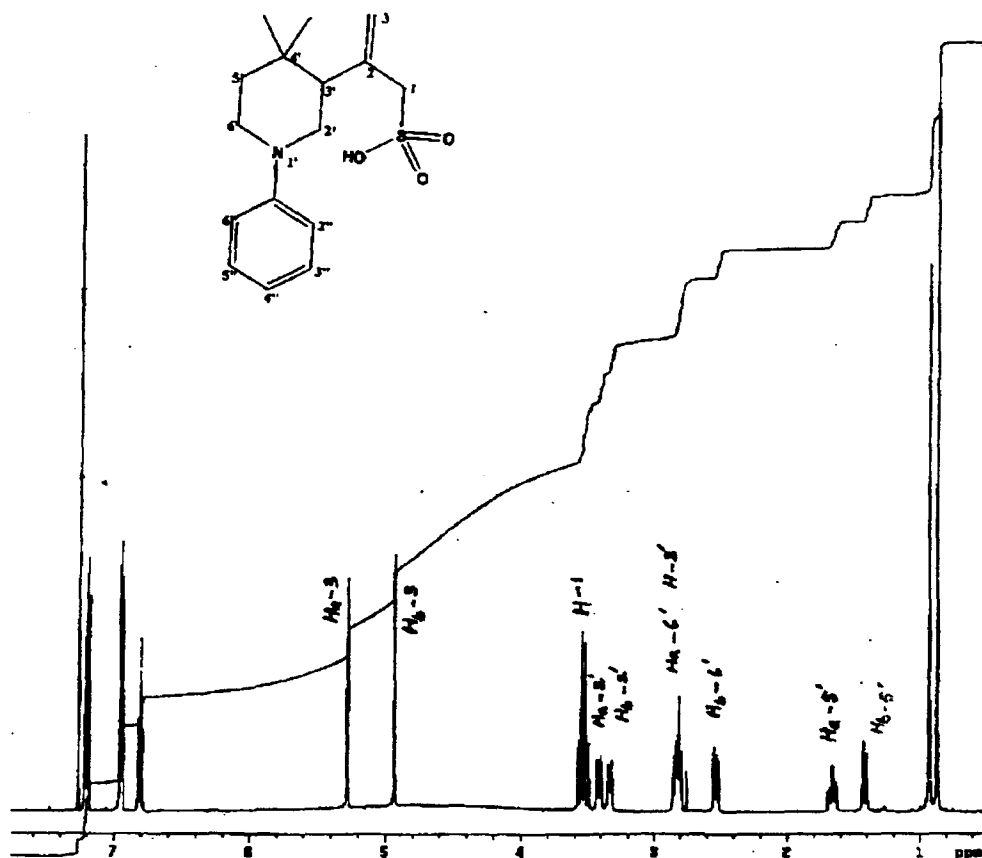


Figure 1 <sup>1</sup>H-NMR spectrum of compound 2



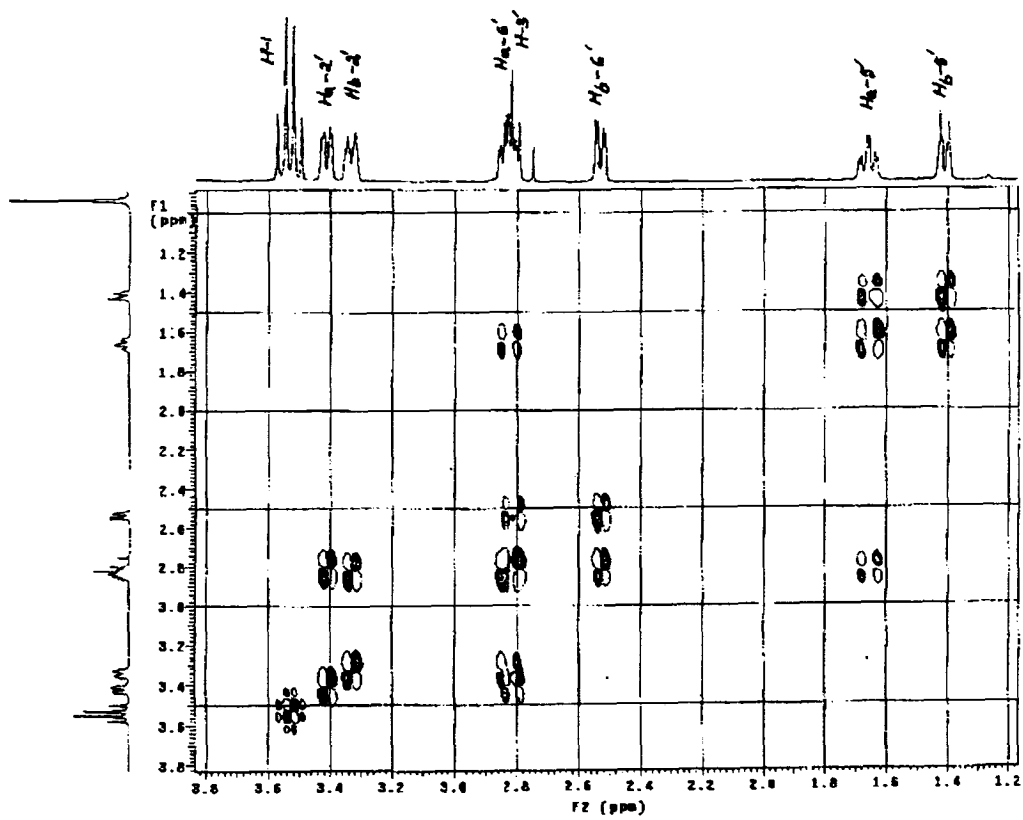


Figure 2 <sup>1</sup>H-<sup>1</sup>H COSY spectrum of compound 2

## An Unusual Reaction of *N*-Methyl-*p*-toluidine with 1,3-Dichloroacetone – A New Indole Synthesis

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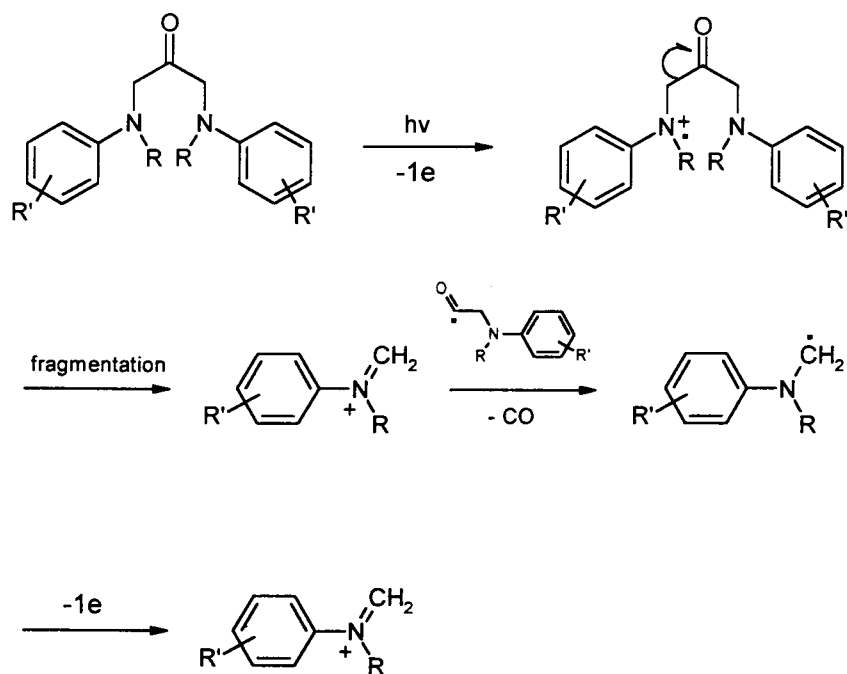
**Abstract:** An unusual synthesis of an indole derivative from *N*-methyl-*p*-toluidine and 1,3-dichloroacetone is described. The mechanism of the formation of the indole derivative is proposed to involve an annulation of the key iminium intermediate and the structure of which is elucidated by means of one and two dimensional high resolution NMR spectroscopy and is confirmed by single X-ray crystallography.

**Keywords:** Synthesis, 1,3-dichloroacetone, 2-methyl-3-(aniliny)indole, iminium intermediate, annulation.

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### Introduction

There is a continuing need for enhanced photosensitization in the field of silver halide photography. Considerable work amply demonstrates the ability of certain organic electron donating molecules, when incorporated into a silver halide emulsion, to provide a two electron sensitizing effect alone or in combination with cyanine dyes [1]. In the course of our study towards the search for new two electron sensitizing donors, we were interested in the synthesis of the novel 1,3-dianiliny substituted acetones. These type of donors are potentially capable of producing two electrons upon irradiation and subsequent fragmentation as shown in scheme 1.



Scheme 1

Based on the consideration of redox potentials of the fragmented anilinylium radical, we targeted at *bis*-1,3-(*N*-methyl-*p*-toluidinylium)acetone. As there was no precedence in the literature on the synthesis of the target compound, we decided to explore the direct synthesis by reacting two equivalents of *N*-methyl-*p*-toluidine (1) with 1,3-dichloroacetone (2) in the presence of two equivalents of a tertiary base as an acid scavenger, which in turn led to a novel indole derivative. The formation and mechanism of the indole derivative is described in this paper.

### Results and Discussion

Different bases such as triethylamine (TEA), pyridine, *N,N*-dimethyl-4-aminopyridine (DMAP), 1,5-diazabicyclo[4.3.0]non-5-ene and 2,6-lutidine were employed to synthesize 1,3-(*N*-methyl-*p*-toluidinylium)acetone from *N*-methyl-*p*-toluidine (1) and 1,3-dichloroacetone (2). The reactant 2 was found to form crystalline quaternary salts with both TEA and DMAP and could not be pushed further to react with 1 in methylene chloride to form the expected product. Reaction with 1 did occur in presence of other bases but led to inseparable complex mixtures.

When four equivalents of *N*-methyl-*p*-toluidine (1) was used *in lieu* of the additional acid scavenger, a cleaner reaction product was obtained [2]. The crystalline colourless product exhibited a mass of 278 (M<sup>+</sup>), 18 units lesser (corresponds to one equivalent of water) than the desired mass for *bis*-1,3-(*N*-methyl-*p*-toluidinylium)acetone (M<sup>+</sup>, 296). <sup>1</sup>H NMR revealed five distinct methyl groups with no detectable

alkyl protons in the upfield. The aromatic protons exhibited only one  $A_2B_2$  quartet (4H) with overlapping signals integrating for three additional protons. The  $^{13}\text{C}$  NMR showed seven quaternary, seven methine and five methyl carbon resonances. It did not exhibit any peak in the downfield region higher than 147.9 ppm, indicating the absence of a carbonyl group, which was further supported by the absence of any discernible carbonyl stretching band in the IR spectrum. The unsymmetrical nature of the NMR spectrum suggested that one of the aromatic protons might have undergone an unexpected rearrangement during the alkylation. To assign the chemical shifts in the structural elucidation of the newly formed reaction product, a combination of homonuclear and heteronuclear correlation spectroscopic techniques ( $^1\text{H}$ - $^1\text{H}$  COSY,  $^1\text{H}$ - $^{13}\text{C}$  HETCORR) were employed. Based on the above data, two structures namely **A** and **B** as represented in Fig.1 are found to be consistent.

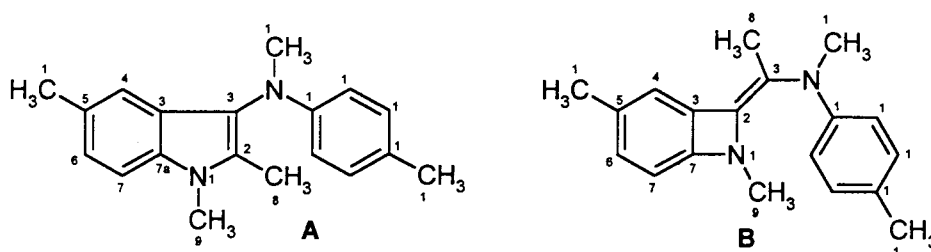


Fig. 1

As the above NMR analyses could not differentiate the two structures **A** and **B**, the  $^1\text{H}$ - $^{13}\text{C}$  long range correlation spectroscopy (LRHETCORR) was analyzed for delineating the correct structure. A long range correlation between H4 and C3 was observed which confirmed the structure **A** to be more appropriate. This is also a more likely structure since the ring system of benzoazetidone with an exocyclic double bond as in **B** is very strained and hence appears unlikely. The structure **A** was also unequivocally confirmed by a single crystal x-ray diffraction (Fig. 2).

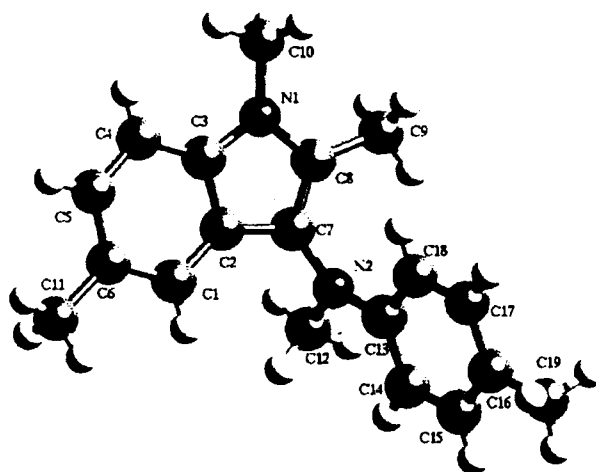
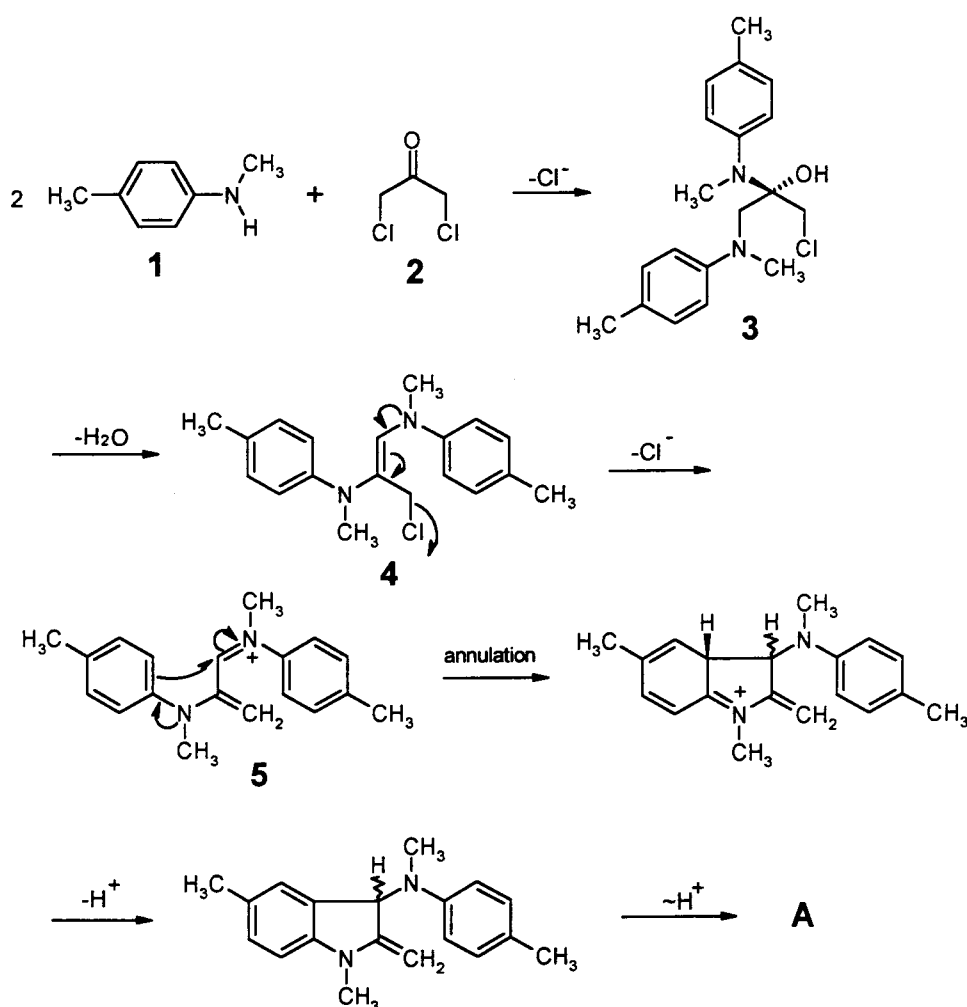


Fig. 2 Single X-ray Diffraction of compound A. (The atom labeling is different from the chemical nomenclature of A.)

A plausible mechanism which leads to the formation of the 2-methylindole derivative A is proposed in scheme 3:

The mechanism is likely to involve the initial formation of the mono-*N*-alkylated derivative resulted by displacing the first chloride, which undergoes a Mannich type reaction to form the intermediate 3. Subsequently, 3 eliminates a water molecule to form the key enamine intermediate 4 probably by a general acid catalysis. Displacement of the second chloride led to the formation of the key iminium intermediate 5, which undergoes an *ortho*-annulation to yield the 3-(*N*-methyl-*p*-toluidinyl)-1,2,5-trimethylindole (A).



**Scheme 3**

Due to pharmacological interest, substituted indoles are of importance to synthetic chemists [2,3]. Farfran *et al* reported the synthesis of 3-alkyl indole derivative from a secondary aniline and an ethanolic solution of glyoxal at elevated temperatures in low yields [4]. In our study, we could accomplish the

formation of a 2-alkyl indole derivative, hitherto unreported, by reacting *N*-methyl-*p*-toluidine (1) with 1,3-dichloroacetone (2) at room temperature in moderately good yield.

### Conclusion

We have showed an unusual reaction between *N*-methyl-*p*-toluidine (1) and 1,3-dichloroacetone (2) to form the 2-methyl indole derivative and a likely mechanism has been proposed to explain the formation of the product.

### Acknowledgements:

We like to thank the National Science Council, Taiwan, R.O.C. for providing a post-doctoral fellowship for B.B. Part of this work was done at the Kodak Research Laboratory, Rochester, New York in collaboration with Dr. Antony Williams, who provided the high resolution NMR spectral analysis. The authors are also grateful to the Analytical Science Division of Eastman Kodak Company for the X-ray diffraction crystallography.

### Experimental

#### General

<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained using a Varian Gemini 200 NMR and were recorded at 300 and 75 MHz respectively. All reagents and chemicals were obtained from Aldrich Chemical Company (USA) and were used as received unless otherwise noted. The X-ray crystallographic data were collected on an Enraf Noius CAD-4 diffractometer in the  $\omega$ -2 $\theta$  scan mode using graphite monochromated Mo K $\alpha$  radiation. These structures were solved by direct methods using SHELXTL package. All of the structures were refined on F<sup>2</sup> using SHELXL93.

To a solution of 1.27 g (10 mmol) of 1,3-dichloroacetone in 10 mL of methylene chloride was added 5.15 mL (40 mmol) of *N*-methyl-*p*-toluidine. The reaction mixture which turned dark brown quickly was allowed to stir at r. t. for several days. During this time, the colour of the reaction mixture slowly changed from reddish orange to essentially colourless. After the complete disappearance of the starting material (monitored by tlc), the mixture was washed with water, dried with magnesium sulfate and concentrated on a rotary evaporator. The residue was subjected to a flash column chromatography using CH<sub>2</sub>Cl<sub>2</sub> / heptane mixture (1: 4) as the eluent to yield a colourless solid A (1.9 g, 68%). M.p 97-98° C (hexane).

#### Spectral Data

- (1) <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 2.46 (s, 3H); 2.49 (s, 3H); 2.62 (s, 3H); 3.53 (s, 3H); 3.83 (s, 3H); 6.82 (d, J = 8.0, 2H); 7.22 (d, J = 8.0, 2H); 7.24 (dd, J = 7.8, 1.4, 1H); 7.34 (s, 1H); 7.44 (d, J = 8.0, 1H).  
(2) <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 9.6 (CH<sub>3</sub>, C-8); 20.2 (CH<sub>3</sub>, C-15); 21.3 (CH<sub>3</sub>, C-10); 29.6 (CH<sub>3</sub>, C-9); 39.7

(CH<sub>3</sub>, C-16); 108.5 (CH, C-7); 112.2 (2-CH's, C-12, C-12'); 117.6 (CH, C-4); 120.3 (C-3); 122.4 (CH, C-6); 124.6 (C-3a); 125.0 (C-14); 128.3 (C-5); 129.4 (2-CH's, C-13, C-13'); 133.1 (C-2); 134.0 (C-7a); 147.9 (C-11).

(3) Anal. calcd for C<sub>19</sub>H<sub>22</sub>N<sub>2</sub> (278.39): C, 81.97; H, 7.97; N, 10.06.

Found: C, 82.03; H, 8.01; N, 10.09

### Crystallographic Data

#### Crystal Data and structure refinement for A

Empirical formula	C <sub>19</sub> H <sub>22</sub> N <sub>2</sub>
Formula weight	278.39
Temperature	298(2)K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 2(1)/c
Unit cell dimensions	a = 6.481(1) Å α = 90 ° b = 11.936(2) Å β = 94.12(3)° c = 21.181(4) Å γ = 90 °
Volume	1634.3(5) Å <sup>3</sup>
Z	4
Density (calculated)	1.131 g / cc
Absorption coefficient	0.066 mm <sup>-1</sup>
F(000)	600
Crystal size	0.2 x 0.2 x 0.4 mm
θ range for data collection	1.93 to 23.18°
Index ranges	-7 ≤ h ≤ 7, 0 ≤ k ≤ 13, 0 ≤ l ≤ 23
Reflections collected	2324
Independent reflections	2324 [R (int) = 0.0000]
Refinement method	Full matrix least squares on F <sup>2</sup>
Data/ Restraints/ parameters	2324 / 0 / 194
Goodness of fit on F <sup>2</sup>	1.057
Final R indices [I > 2σ(I)]	R1 = 0.0535, wR2 = 0.1504
R indices (all data)	R1=0.0664, wR2 = 0.1643

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*Samples Availability:* Available from the authors.

## 附件三

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### 新世紀的 ”鑫” 科技--有機電激發光二極體平面顯示器技術

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如果說液晶顯示器 (Liquid Crystal Display, 簡稱 LCD) 是二十世紀平面顯示器的發展史中, 一個令人驚喜的里程碑, 那麼有機發光二極體 (Organic Light-Emitting Diodes, 簡稱 OLED) 則是人類在二十一世紀所夢想追求能超越 LCD 的平面顯示技術。為什麼這麼說呢? 因為二十一世紀的時代是一個 ”3C” 的時代, 也就是通訊 (Communication)、電腦 (Computer) 與消費性電子器材 (Consumer Electronics) 的時代, 在這樣的生活當中, 各種小型的電子用品將時時伴隨著我們, 如上網購物、收發電子郵件、安排行程、打電話等, 都可隨時隨地進行, 人機之間的接觸越來越頻繁, 人機之間也將以平面顯示器為主要的溝通介面, 相對的, 人們對顯示器的要求也會越來越高, 例如輕薄短小、精緻靈敏、色彩鮮艷、省電等, 而能將這些特性集於一身的, 就是 OLED。因此, 在不久的將來, 跟紙張一樣厚度的電視螢幕、捲軸式的電子書刊 (e-paper) 或行動電話、色彩亮麗的手機螢幕等產品將會出現在我們的生活中, 無庸置疑的, 這將會使我們未來的生活更加的亮麗鮮豔、多采多姿。

既然 OLED 想要與 LCD 競爭新世紀主流平面顯示器的地位, 那他必定有著許多 LCD 所沒有的優點, 我們將一些 OLED 的特性列舉如下:

- 自發光, 視角廣達 165°以上
- 反應時間快 ( $\sim 1 \mu s$ )
- 高亮度 (100-14000 cd/m<sup>2</sup>)
- 高流明效率 (16-38 lm/W)
- 低操作電壓 (3-9V DC)
- 面板厚度薄 (2 mm)
- 可製作大尺寸與可撓曲性面板
- 製程簡單, 具有低成本的潛力 (30-40% of TFT-LCD)

綜合以上各種 OLED 的特性所製成的顯示器, 將不會有 LCD 從側面看就看不清楚的問題; 也不會有 LCD 影像殘留及畫面跳動的情況; 不但便宜, 而且省電; 相較於 LCD, 顏色更鮮艷, 對比更鮮明; 而小於 2 mm 厚度的全彩面板更是只有 OLED 才能作到。

這樣吸引人的特性, 到底 OLED 是怎樣辦到的呢? 以下我們針對 OLED 的發光原理與發展歷史作一簡介:

OLED 又可稱為有機電激發光 (Organic Electroluminescence, 簡稱 OEL), 簡單的說, 就是將一外加偏壓, 使電子電洞分別經過電洞傳輸層 (Hole Transport Layer) 與電子傳輸層 (Electron Transport Layer) 後, 進入一具有發光特性的有



機物質，在其內再結合時，形成一"激發光子" (exciton) 後，再將能量釋放出來而回到基態 (ground state)，而這些被釋放出來的能量中，由於所選擇的發光材料的不同，可使部份能量以不同顏色的光的形式釋放出來，而形成 OLED 的發光現象 (圖一)。

最早在 1963 年時，Pope 發表了世界上第一篇有關 OLED 的文獻，當時使用數百伏特的電壓通過 Anthracene 晶體時，觀察到發光的現象。雖然有一些後續的研究，不過這項成果並未受到重視。一直到 1987 年美國柯達公司的 Tang 與 VanSlyke 等人發明真空蒸鍍及三層結構 (圖二) 的小分子 OLED 元件後，OLED 的效能大幅躍進至具有深厚商業應用的潛力。自此之後，OLED 便在業界、學界掀起了一股無法阻擋的旋風與魅力。而 1990 年英國劍橋大學的 Friend 等人成功的開發出以塗佈方式將多分子應用在 OLED 上，即 Polymer LED，亦稱為 PLED。不但再引發第二波研究熱潮，更確立了 OLED 在二十一世紀產業中所佔有的重要地位。

在發明此元件的過程中，陰陽兩極材料的發現也是重要的一環。陰極的金屬必需具備低功函數 (work function) 的特性，才能有效的將電子注入有機層內，鎂 (Mg) 的功函數夠低 (3.5eV)，也相當穩定，十分符合元件的要求。而當鎂銀 (Ag) 以十比一的比例形成合金後，少量的銀可以提供成長區 (nucleating site) 給鎂，使得鎂可以順利的在有機層上成膜。這樣的合金與比例便成為後續研究的範本。另外鋰 (Li) 金屬 (1.4eV) 的化合物如 LiF、Li<sub>2</sub>O 等，與鋁 (Al) 金屬 (3.4eV) 的化合物，也是另一種普遍使用在陰極上的材料。而在陽極的選擇上，則必需是一個高功函數又可透光的材質，這樣的選擇並不多，所以 ITO (indium tin oxide) 這樣的金屬氧化物，不但具有 4.5eV-5.3eV 的高功函數，且性質穩定又透光，便成了最佳的選擇。延用至今，這兩者仍是目前 OLED 元件中最常被使用的陰陽極材料。

在後續的研究當中發現，OLED 可藉由在發光層中摻雜一不等濃度的摻雜物 (dopant)，使得主發光體 (host) 的能量得以轉移至摻雜物上而改變原本主發光體的光色以及發光的效率，不但可得到紅、藍、綠三色的 OLED 元件，也因此使得 OLED 朝著全彩化顯示器的目標又前進一大步。然而在這當中，各種材料的選擇是非常關鍵的，必需考慮材料本身的物理性質，如能階差、熱性質、形態學等，所以要找出一個合適的 OLED 材料，不論是電洞傳輸材料、電子傳輸材料、主發光材料以及不同光色的摻雜物，都需要科學家們一再的研究與改良，才能達到要求。一些目前常用的有機材料如圖三。

另外一個攸關 OLED 顯示器效果的重要關鍵，就是顯示器的驅動方式。就目前來說，OLED 的驅動方式可分為被動式矩陣 (passive matrix，即 PM-OLED) 與主動式矩陣 (active matrix，即 AM-OLED) 兩類 (基本電路設計如圖四)，其中被動式矩陣架構較簡單 (其立體剖面圖如圖五)，成本也較低，但必需在高脈衝電流下操作，才能達到適合人眼觀賞的亮度，因 OLED 的亮度與所通過的電流密度成正比，太高的操作電流不但會使電路效率及壽命降低，因為掃描的關係

使其解析度也受限制，因此 PM-OLED 比較適合於小尺寸的產品。相反的，AM-OLED 雖然成本較昂貴、製程較複雜（仍比 TFT-LCD 容易），但其每一個畫素（pixel）皆可記憶驅動信號並可獨立與連續驅動，且效率較高，適用於大尺寸與高解析度之高資訊容量的顯示產品。

在目前最新的文獻中，科學家們兵分兩路的從發光原理及受質材質上著手。利用三重態（triplet）的發光，把先前光物理上不能發光的而損失掉的能量用來發光（見圖一），大大的將 OLED 的發光效率躍進了三倍以上，流明效率可躍升到 38 lm/W。另外在受質的材質上，科學家也研究以可撓曲的塑膠面板來替代現有的玻璃面板，或是以透明的導電材質取代現有的金屬電極，使得光可以從陰極面或兩面發出。另外也有許多關於白光 OLED 的研究，未來有希望用以取代目前以燈泡為主的各種光源。可想而知的，這些研究將會進一步擴展 OLED 在未來產品的應用。

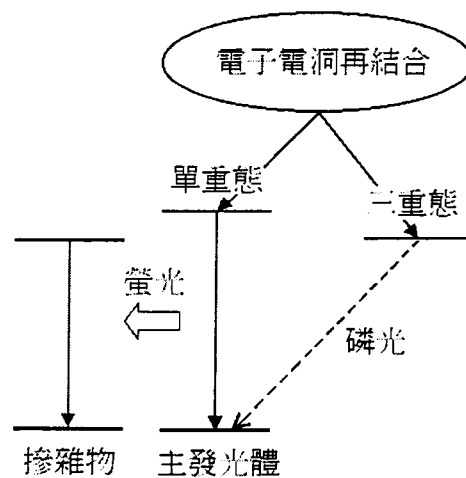
簡而言之，OLED 的遠景與商機，是任何有眼光的產商都不會錯過的，世界上各大光電、電子與化學廠商，都紛紛加入競爭的行列。其中以美國柯達（Kodak）在小分子 OLED 居於領導地位，並且在 1999 年與日本的三陽公司（Sanyo）共同發表的全球第一座 5.5 吋的主動式全彩化 OLED 顯示器（如圖六）；英國 CDT 公司則在多分子 PLED 領先群倫，也在 1998 年開發出主動式單色 PLED 顯示器；日本的 Pioneer 在 1997 年推出多彩的汽車音響面板，並在 2000 年將多彩 OLED 應用在美國摩托羅拉（Motorola）”Timeport” 的手機面板上，是全球第一間量產 OLED 產品的公司；而臺灣的銖寶公司則在 1999 年成立並與美國柯達公司合作，成為全球第二家、臺灣第一家量產 OLED 的公司；緊接著在 2001 年，新成立的東元激光也宣布與美國柯達公司合作，預計明年即可量產，成為全球第三家量產 OLED 的公司。目前世界各大廠商無不以全彩 OLED 為首要目標，如日本的 SONY 公司即發表了最新消息，要在 2003 年量產目前全球最大尺寸的 13 吋 OLED 平面顯示器。一波波的最新消息中，一再的顯現出 OLED 在全球大廠眼中無窮的魅力。

在這樣的一股趨勢之中，臺灣的產界、學界怎麼會任憑機會溜走？銖德公司旗下的銖寶公司，宏碁集團所屬的達基科技，東元集團轉投資的東元激光，國聯光電旗下的聯仲科技，勝華電子所屬的勝園科技等，另外傳統化工產業的奇美集團，臺塑集團旗下的南亞科技，以及永信化學公司等，在國內各著名大學相關科系、研究機關的支援下，無不投入大筆資金、招兵買馬，摩拳擦掌準備抓住這個機會與世界各大廠商一較高下，期望能擺脫過去以代工為主的產業形態，一躍登上產業金字塔的頂端。

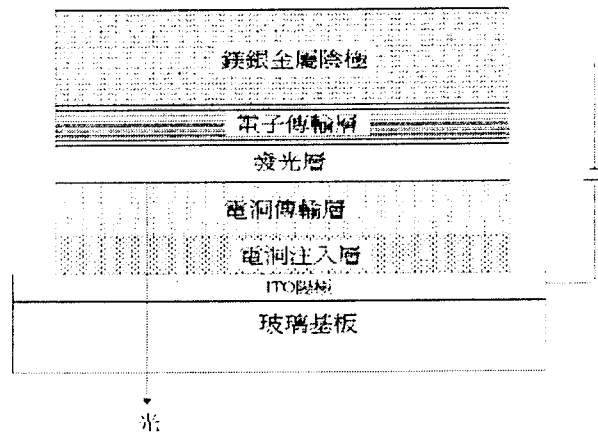
在這個新世紀之初，可以預見 OLED 會是未來發出耀眼光芒的一項光電整合產業，我們何其有幸能在這個關鍵時刻，貢獻自己一份心力，不論是物理、化學、電子、電機、材料、光電等各種人才，都是發展 OLED 所急需的生力軍。唯有我們共同努力，才能讓 OLED 展現耀眼的光芒，也讓臺灣在世界科技舞臺發光，更能讓這個明日之”鑫”的科技真正實現在你我的生活之中。

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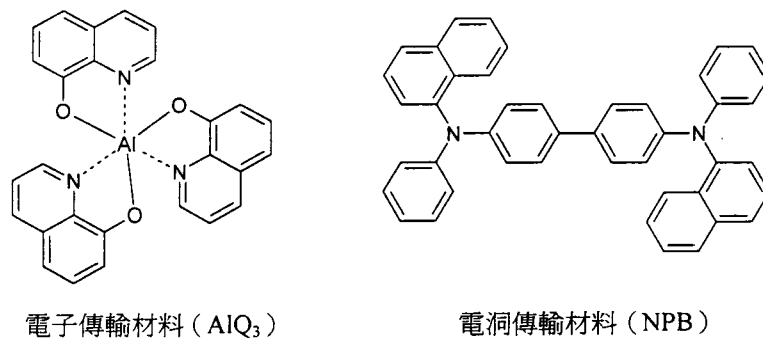
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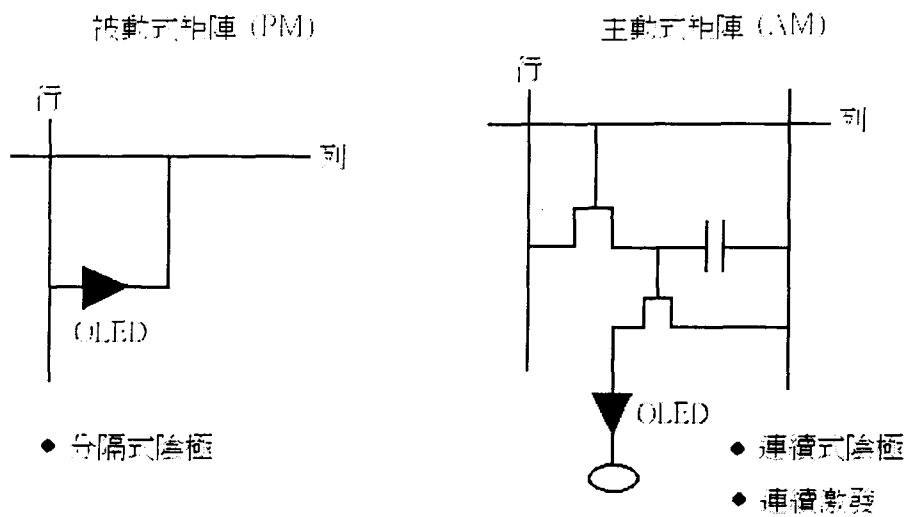
圖一，OLED 發光原理



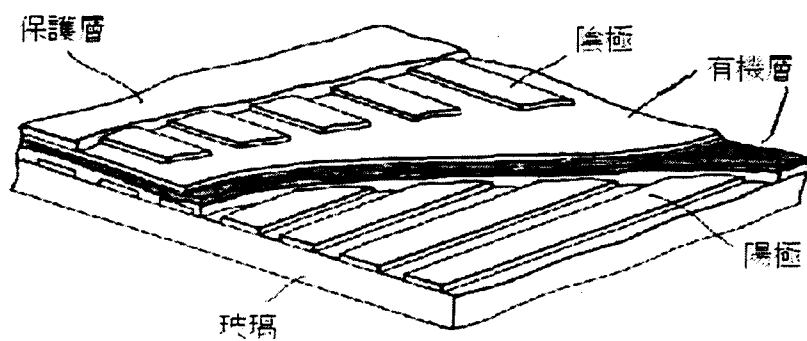
圖二，目前最為普遍使用的三層式 OLED 元件結構



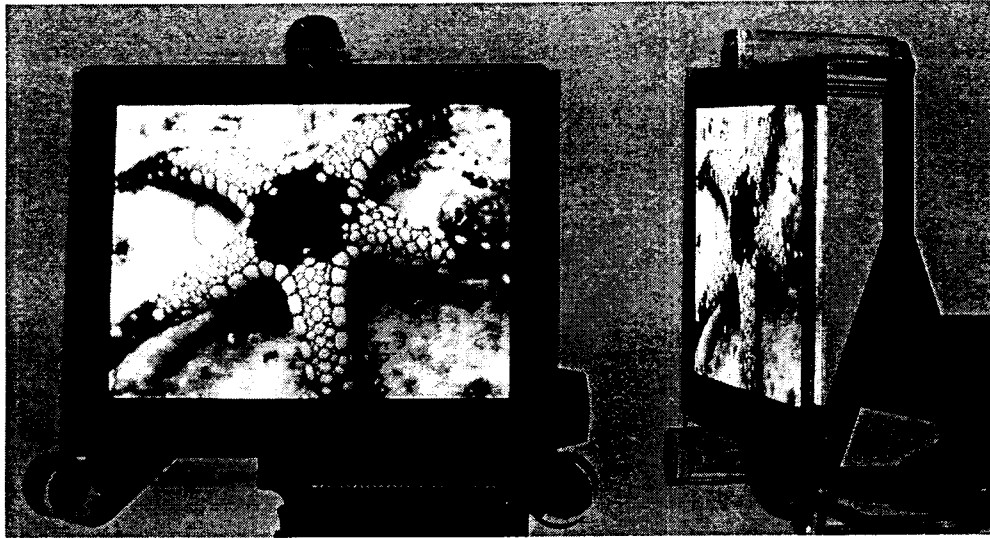
圖三，OLED 常用的傳輸層材料



圖四，被動式矩陣與主動式矩陣的電路原理



圖五，被動式矩陣 OLED 的剖面圖



圖六，柯達與三陽在 1999 年推出的主動式全彩 OLED 顯示器

## 附件四

交大有聲雜誌 2002, 390, 28.

### 交大 OLED 平面顯示技術的推展與近況

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#### 一、什麼是有機發光二極體(OLED)：

有機發光二極體(OLED)近來已成為國內外非常熱門的一項科技，此被視為下一世紀的平板顯示技術，其元件的基本結構其實相當簡單，只需【玻璃基板／ITO(陽)電極／電洞注入層／電洞傳輸層／發光層／電子傳輸層／(陰)電極】而已，全部的有機層薄膜厚度加起來不到  $0.15\ \mu\text{m}$ ，連封裝加乾燥劑 (desiccant) 整個顯示板 (Panel) 厚度不過 2 mm；其原理是利用有機發光體的半導體特性，於元件中的陽極及陰極通入直流電壓，藉由電子與電洞的結合以光的形式釋放出能量。它除了具有 LCD 之輕薄、省電與全彩化的優點外，它還有 LCD 所沒有的自發光 (self-emissive)、廣視角 (達 160 度)、高發光效率、高應答速度 (達  $1\ \mu\text{sec}$ ) 等特點。因具有全彩、高亮度、輕薄短小等特性，國內目前也有許多家大廠投入研發製造的行列，未來將可能成為國內繼 TFT-LCD 後另一光電主力產品。

#### 二、交通大學 OLED 研究中心的催生與 OLED 實驗室的成立：

面對國內光電產業一片有機電激發光顯示器(OLED)的投資熱，因國內學術單位尚未有具規模的研究單位及實驗室，學生對此新興技術與材料也較為陌生。交大校長張俊彥有感國內高科技引進的必要性，兩年前邀請陳金鑫教授回國開課，並積極為 OLED 研究中心催生。經多方爭取，在國科會、友達科技及富臨科技共同協助下，交通大學於 2001 年五月十五日率先成立『有機發光元件研究實驗室』，成為國內學術界第一個專攻 OLED 平面顯示技術的研究團隊。該實驗室負責人~應用化學系陳金鑫教授，正是國內業界亟欲取得授權的柯達公司 OLED 專利發明人之一，也是柯達公司三十五篇專利的原創人；OLED 研究群經由陳教授在短短兩年苦心的經營下已漸漸成長茁壯，而該研究群目前成員為 12 位，其中碩士生八位、博士生三位及一名印度籍博士後研究員。在該中心正式啟用的同時，於電子資訊大樓國際會議廳舉行開幕典禮，並由國際顯示協會(SID)中華民國總會、國立交通大學、國科會產學計劃主辦，日本真空技術集團、中日經貿發展基金會及中華民國真空科技學會協辦「OLED 技術與發展趨勢」研討會。是日到場祝賀，全台灣產官學研齊聚一堂，嘉賓雲集逾 450 人，這是台灣自

有 OLED 研發以來最大的一次盛會。臨場還有本實驗室發表的研究壁報、PLED 元件展示(如圖 1 所示)及現場參觀，工商時報及電子時報在 90 年 5 月 14 日都有大幅刊登及詳盡的報導(圖 2 為當日交大 OLED 研究群在會場的合照及會場展示)。

### 三、國科會產學計劃的申請與推動：

在 2000 年七月 OLED 研究群申請並通過為期三年(2000 年十月至 2003 年九月)國科會的產學研究計劃，且於當年度開始執行，參與的機構除了交通大學外，在產業界方面合作的廠商包括了友達光電及富臨科技。該產學計劃主要的研究方向是以「可撓曲式有機發光二極體(FOLED)」為主軸，結合交通大學及產業界協同研發具前瞻性且經濟效益宏大的「FOLED」平面顯示元件、材料、封裝及製程的關鍵技術。這為期三年的計劃重點方向包括如下：

- 開發透明導電體成膜在可撓曲型塑膠基板之製程與設備。
- 研發防滲透水、氧氣的透明導電塑膠基板之保護層材料與元件封裝技術。
- 設計、合成改善有機發光二極體的關鍵材料及元件的設備製程，以搭配可撓曲式塑膠材質的基板。
- 建立 Flexible OLED (FOLED) 製程相關技術，以移轉合作廠商，落實本計劃研發成果的經濟效益。

計劃的第一年已完成的重點在於硬體設備規劃與建造，週邊檢測設備的設立及中型 OLED 真空薄膜蒸鍍機的引進、組裝、配備、試機等。其中包括座落在國立交通大學電子資訊中心地下室一萬級無塵室的落成(圖 3 為無塵式建構過程)，及黃光室 ITO 基板的圖案化，及有機發光二極體檢測實驗室的建立。

### 四、教育部整合性卓越計劃的發展方針：

由於 OLED 在產業界及學術界持續的發燒，相關科技也日新月異，基於教學研究的熱忱與使命感的促擁下使得陳金鑫教授決定於同年度著手策劃教育部卓越計劃，並以「尖端顯示技術基礎研究—有機發光二極體尖端材料與元件的研發」作為研究主題，於次年(2001 年)十一月通過該項研究計劃與經費。研究總計劃將由開發尖端有機發光顯示用“小分子”及高效率低溫複晶矽薄膜電晶體



(LTPS)驅動基板為重心，配合光物理與化學的研究，及上放光(top-emitting)，高開口率 OLED 元件的製作與檢測，最後並加以防水、氧的構裝以期達到國際水準的高效率，高穩定性的全彩主動矩陣式發光二極體元件，及計畫完成製作一中小型 QVGA 全彩主動式有機發光平面顯示元件。基於各個專長領域的整合性以提昇研究成效，因此邀請參與計畫的學者分別由跨校與跨領域的精英組成團隊來執行，而各個專長研究領域及方向如下：

- (1) 尖端有機發光材料的設計與合成：由交大應用化學所陳登銘教授主持及中研院化學所陳錦地博士協助。
- (2) 高效率低溫複晶矽薄膜電晶體基板的開發與驅動系統的組合：由交大電機及電子研究所鄭晃忠教授主持。
- (3) 高效率上放光 OLED 元件製程的開發及光物理與化學的研究：由交大電子資訊研究中心陳金鑫教授主持，及清大化學所劉行讓教授協助。
- (4) 上放光 OLED 元件封裝材料與技術的開發：由交大材料所謝宗雍教授主持。

本計畫專注在“低分子” OLED 尖端材料與元件的研發，並發揮化學有機合成的專長，在整個計畫的構想、組織架構、運作與執行方面才可達到精簡、有效率，上、中、下游一以貫之，並收立竿見影之效。另一方面由於工研院材料所年初也宣佈要開發類似 Kodak/Sanyo 的低分子全彩低溫多晶矽主動式 OLED 平面顯示器面板。本計畫決定採取一種不同於工材所用的“全彩化”技術，以避免不必要的重複以節省國家的資源，開闢多元化的 OLED 技術，造就多方面未來平面顯示技術的人才。

在於有機化學專長領域方面，“低分子” OLED 研究重心在於開發一種參重態(triplet)的藍光材料，以參重態與單重態(或參重態)橘紅光之間的能量轉換及光物理機制的研究，進而組合成一種可用於 OLED 平面顯示技術的高效率，可開關式的光束 (switchable and pixelated) 白光源，由於單重態(singlet)的能量限制一般都無法突破 25% 的發光瓶頸，只有研究現今世界各國都在追求的參重態藍光材料，其衍生的白光才能達到 100% 的內部量子效率。全彩化的方法，我們將引用台灣現有的彩色濾光板(CFA)的技術來達成。為了使 OLED 發光的效率再提昇，我們將引用上放光(top-emitting)的元件構造來配合交大自己研發的高效率複晶矽 TFT 主動驅動基板。這種元件構造由於它的開口率(Aperture Ratio)大可達 80%，3 倍於 Kodak/Sanyo 用的下放光 TFT 元件，可使 TOLED 元件用白光加 RGB CFA 的全彩化亮度足以媲美目前 Kodak/Sanyo 所發表的全彩 LTPS TFT AMOLED 面板。

另外，在上放光 TOLED 元件的結構上，尚急需創新的，就是它的封裝技術與材料，本計畫將從尖端的奈微米複合材料來從事各種相關的研究，以期在 OLED 封裝技術上有所突破，貢獻於台灣的光電業界。

## 五、結論：

OLED 在台灣短短數年當中，已被炒的如火如荼，雖然業界已在拼命迎頭追趕，反觀學術界在這方面的研究還有待整合、加強及努力，今後三、五年內國內在 OLED 領域所需的人才培養，正是本計劃所要做的主要工作，而交大 OLED 團隊在新穎材料的開發及發光元件製作專長培訓更是不可或缺的重要一環。其實在 OLED 這未來的主要平面顯示技術裡，可能發明的空間已經不多，時間更是有限、刻不容緩，如果相關產官學研部門不能在這二、三年內大刀闊斧的投入研發，鼓勵創新、挑戰未來，一旦錯過這個重要的時機，以後再追恐怕只會更加吃力、事倍功半，可期待的績效有限。因此交大 OLED 研究實驗室的成立不僅可培養、訓練學生相關 OLED 知識及實驗技術；未來更會成為產學界共同實驗室。而實驗室內設有一日本真空集團提供的全新中型可製作全彩化的真空薄膜蒸度機台更使得研究環境如虎添翼，這些得來不易的成果將使得交大在產學界相關領域的地位再度提昇與肯定。

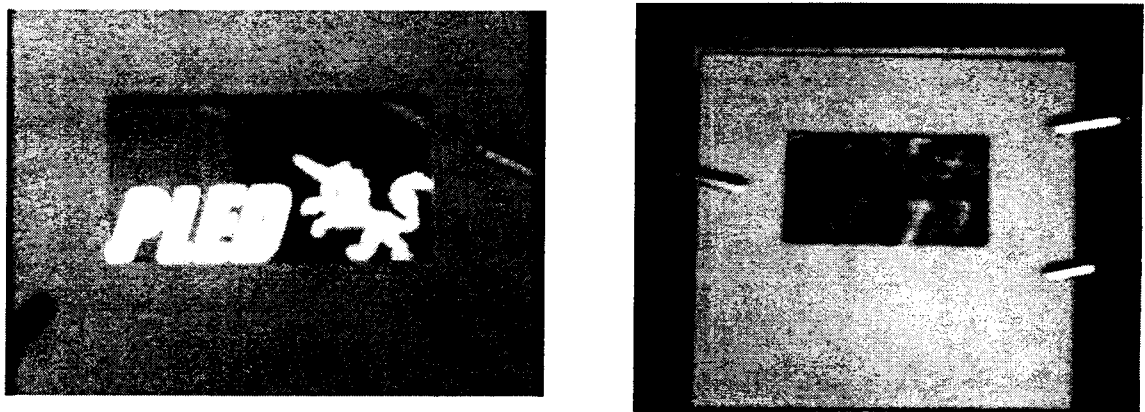


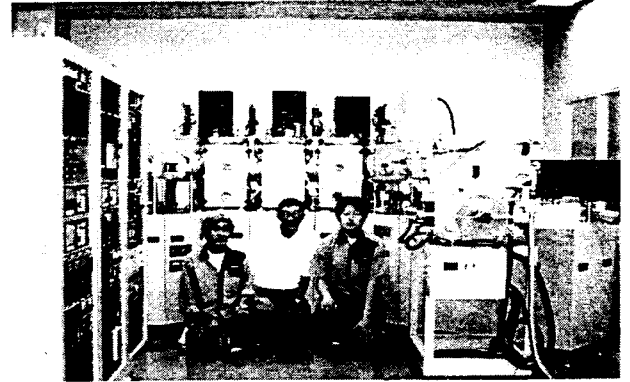
圖 1 交大 OLED 實驗室開幕當天所展示之 PLED 元件。



圖 2 交大『有機發光元件研究實驗室』研究群在會場的合照。



圖 3-1 5 月 10 號機台初步組裝



3-2 5 月 15 號無塵室落成

## 附件五

*電子材料* 2001, 11, 37.

### 前瞻性 OLED 的展望——可撓曲式有機發光二極體之開發現況

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#### 摘要：

有機發光二極體(Organic Light Emitting Diode; 簡稱 OLED)可說是本世紀當紅的新興產業，主要是因為 OLED 顯示器具有：1、自發光，視角廣達 165°以上，2、反應時間快(~1  $\mu$ s)，3、高發光效率，4、低操作電壓(3~9 V DC)，5、面板厚度薄(2 mm)，6、可製作大尺寸與可撓曲性面板及 7、製程簡單，具有低成本的潛力(比 TFT-LCD 便宜 30~40%)。本篇文章將就 OLED 產業、學界及可撓式有機發光二極體(Flexible Organic Light Emitting Diode; 簡稱 FOLED)基材與傳統導電透明玻璃 OLED 元件間的差異做一簡單介紹。

關鍵字(Keywords)：有機發光二極體(OLED)，可撓曲式有機發光二極體(FOLED)，電激發光(electroluminescence)，顯示器(display)，可撓曲式(Flexible)。

#### 緒論：

平面顯示器(Flat Panel Display, 簡稱 FPD)是目前最重要的光電產品之一，與日常生活有緊密相關性。當進入了二十一世紀後，人們需要性能更好、更能符合未來生活需求的新一代平面顯示器，來迎接這個“3C”，[即電腦，(Computer)、通訊(Communication)、消費性電子器材(Consumer Electronics)]及“3G”(即第三代行動電話)時代的來臨。近幾年來世界知名的廠商及學術研發機構以大筆的資金投入 OLED 研發的行列，放眼望去，有機發光二極體其具有的輕、薄、靈、巧、彩、美、小等特性，是最能符合未來人們對平面顯示器的要求一項技術，

### OLED 的發展現況

OLED 的發展，是以全彩化的平面顯示器為最高目標在前進，目前紅、藍、綠三原色的摻雜材料都已成功的開發出來了，但是卻尚未達到完全令人滿意的地步，仍需要持續地研究開發新的、更好的三原色摻雜材料，尤其是藍光及紅光。另外白光材料也是最近的一項研究重點，希望能用來作為照明光源或是液晶顯示器螢幕的背光源，期能大幅減少目前白光光源所佔的空間與重量。

在 1998 年，美國的 Baldo 等人研究出以銥金屬錯合物(iridium complex)製成的元件，可以把原先三重態中流失的能量補救回來，得以將 OLED 元件的發光效率大幅提昇三倍以上，是近來 OLED 技術開發上的一大突破。

由於 OLED 的製程較 LCD 簡單，成本亦只有 LCD 的 30%~40%，因此成為

商業應用的一大優點，然而目前在製成全彩化顯示器的製程中，最為關鍵的技術有三點：1、全彩化像素（color pixelation scheme）的技術，2、高解析度（high resolution）畫素的形成，3、驅動電路的設計。

值得一提的是這幾年來，科學家正在研究以塑膠基板取代玻璃基板，製成可撓曲式的 OLED，即 Flexible OLED，也稱為 FOLED，如果能順利研發成功，則類似筆捲式行動電話的商品（如圖一），將不再是如好萊塢電影“Red Planet”中的科幻情節了。

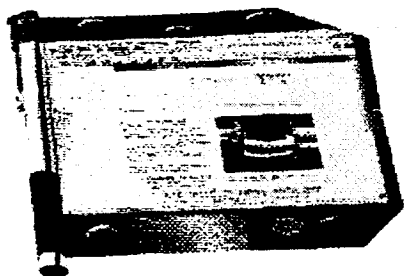
## OLED 目前業界的投資現況

1996 年，日本 Pioneer 的 256x64 畫素綠光顯示器問世，是全球首次宣布將 OLED 應用在商品上，從此 OLED 商品化的腳步向前大步邁進，全球大廠在此領域上的競爭也更加白熱化。1997 年，Pioneer 繼續推出多彩的 OLED 汽車音響面板，並在 2000 年與美國摩托羅拉（Motorola）合作，將多彩 OLED 應用在

“Timeport” 手機面板上。另外，美國的柯達公司也是 OLED 技術的領先者之一，不但握有多項 OLED 相關基本專利，它也在 1999 年與日本三洋（Sanyo）合作共同開發全球第一座採用低溫多晶矽（LTPS）薄膜電晶體驅動的 2.4 吋及 5.2 吋主動式全彩化 OLED 顯示器。在高分子發光二極體(Polymer Light Emitting Diode；簡稱 PLED)方面，英國的 CDT 公司於 1998 年推出主動式的單色 PLED 顯示器。日本的 Toshiba 公司則宣布將在 2002 年 4 月量產全彩的 PLED 顯示器。日本的 SONY 公司日前剛發表最新消息，宣布要在 2003 年量產目前全球最大尺寸的 13 吋 OLED 平面顯示器。此外歐美日等地還有數十間著名廠商紛紛投入 OLED 相關產業中（表一）而形成一個彼此激勵的激烈競爭局面。

在國內的業界方面，幾家大廠如鍊德公司旗下的鍊寶公司、東元集團轉投資如：東元激光；宏碁集團所屬的友達科技、勝華電子所屬的勝園科技、國聯光電旗下的聯宗科技、奇美集團下的奇美光電、南亞科技、永信化學公司、光磊科技、國碩光電、翰立科技、精碟科技、昱鐳光電、悠景科技等十數家公司，皆先後投入台灣 OLED 及 PLED 市場進行研究與開發（表二），可說是近年來少見的一股風潮。

根據 Display Search 的調查，OLED 顯示器在 2000 年的收益為 240 萬美金，相較於 1999 年提升了 100%。該調查也預測 2005 年收益將提升到 33 億美金，其成長可謂爆炸性的發展，猶如“麻雀變鳳凰”的情節。



圖一、筆捲式的電子商品

表一、國外 OLED 廠商

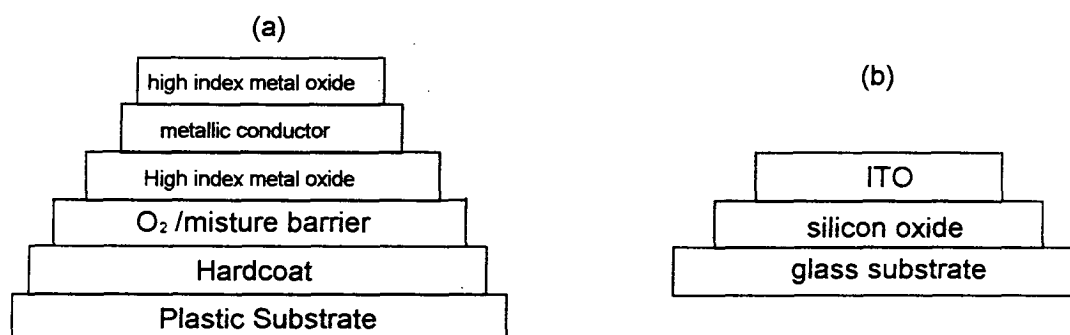
企業名		材料	量產時間
柯達	(美)	小分子	持有專利
Dow Chemical	(美)	高分子	材料供應商
UNIAx	(美)	高分子	
Dupont	(美)	—	
Universal Display	(美)	小分子	
eMagin	(美)	小分子	2001年
CDT	(英)	高分子	持有專利
西門子	(德)	高分子	2002年左右
德國IBM	(德)	高分子	2002年左右
飛利浦	(荷)	高分子	2002年左右
LG電子	(韓)	小分子	2001年
三星 / NEC	(日韓)	小分子	2001年
SEIKO-EPSON	(日)	高分子	2002年左右
三洋電機	(日)	小分子	2002年初, 動畫面板
Pioneer	(日)	小分子	1998年, 動畫面板2002年秋季
TDK	(日)	小分子	2000年, 動畫面板2002年左右
日本精機	(日)	小分子	2002年
Stanley電氣	(日)	高分子	2001年被動式面板
TOYOTA汽車	(日)	高分子	
SONY	(日)	—	2003年
東芝	(日)	小分子 / 高分子	2002年4月
住友電工	(日)	—	
住友化學	(日)	高分子	材料供應商
出光興產	(日)	小分子	材料供應商
東洋Ink製造	(日)		材料供應商
大日本印刷	(日)		

表二、國內 OLED 廠商

企業名		材料	量產時間
鍊德	(台)	小分子 / 高分子	2000年, 動畫面板2002年
勝華	(台)	小分子	
達碁	(台)	—	
永信	(台)	小分子	
光磊	(台)	小分子	
東元	(台)	小分子	
國碩	(台)	小分子	
聯宗	(台)	小分子	
精碟	(台)	高分子	
翰立	(台)	高分子	
奇美	(台)	小分子	
悠景	(台)	小分子	
南亞	(台)	小分子	

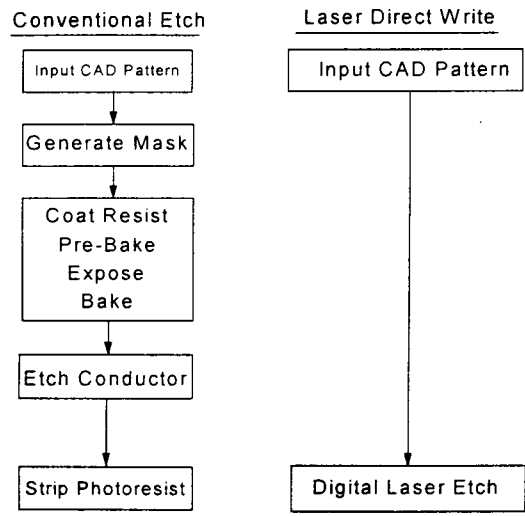
## FOLED 基板特性簡介與傳統導電玻璃基板比較：

過去 OLED 顯示器主要以剛硬的玻璃或矽晶元為基材，相較於一般傳統玻璃導電透明基板的特性，塑膠基板的優點有：便宜、易加工、質地輕且可任意撓曲。然而，典型的塑膠基板對水的穿透度為  $100-10^{-1} \text{ g/m}^2/\text{day}(25^\circ\text{C})$ ，其無法完全阻隔水汽及氧氣的穿透而加速元件老化，導致所製成的元件無法連續操作達 10000 小時，因此也就無法直接符合商業上的需求。圖二為 FOLED 透明塑膠基板與傳統導電玻璃基板結構圖，為了達到阻隔水氧的目的，其必需在塑膠基板和無機導電層之間塗覆緻密的特殊材料以防止水氧值的滲透及擴散。因為有機及無機材質間界面的問題，因此阻隔層材料的選取必需在塗覆過程中能無缺陷地均勻成膜(defect-free)、不會產生針孔(pinholes)、高透光性及避免對可見光的吸收，並以多層膜的製程方式來達成 FOLED 基板機能需求。



圖二、可撓曲式透明導電塑膠基板結構 (a)與傳統玻璃導電透明基板結構 (b)。

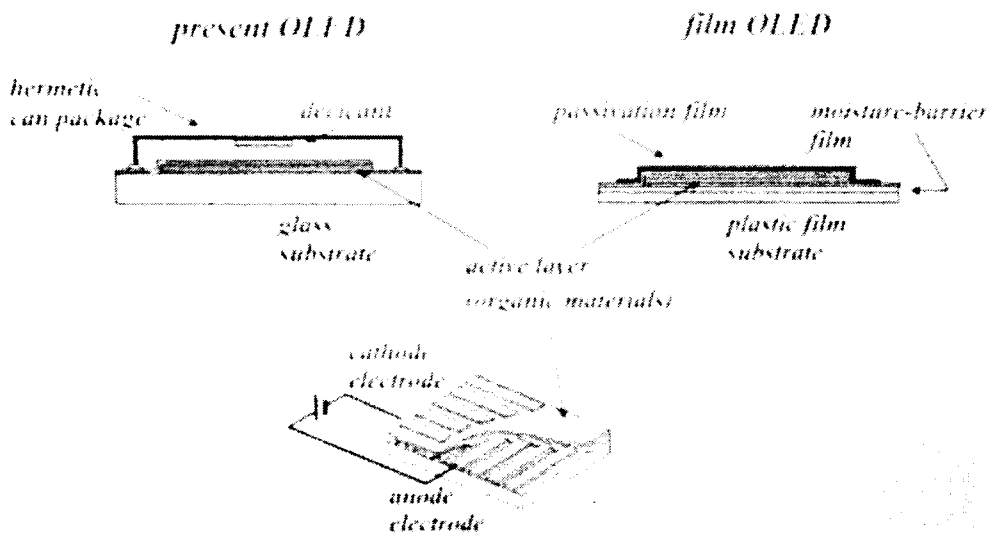
在基板表面圖樣化(patterning)技術中的圖案蝕刻方面(如圖三所示)，相較於傳統蝕刻法利用光阻膜予以曝光、顯影及濕式蝕刻完成圖形，透明導電塑膠基板則是可直接利用雷射光束在基板上蝕刻出圖案，其優點在於該方法不需光阻膜及光罩，且能因應顧客或消費者的需求任意改便圖案，省去一些煩瑣或不必要的製程。



圖三、傳統玻璃基板蝕刻與雷射光束方法蝕刻之比較。

傳統玻璃導電透明基板與透明塑膠導電透明基板元件結構之比較：

圖四是一般普遍常見以透明導電玻璃為基板的 OLED 與可撓式 FOLED 元件結構之比較圖，在傳統玻璃基板製成的 OLED 構造中包含了金屬電極(鎂/銀合金)、電子傳輸層、發光層、電動傳輸層、電洞注入層、陽極(ITO)及玻璃基板；相較於一般剛性基材所構成的元件結構，FOLED 構造除了多出防水、氧保護層及塑膠基板取代剛硬性基板外，其餘結構皆大同小異

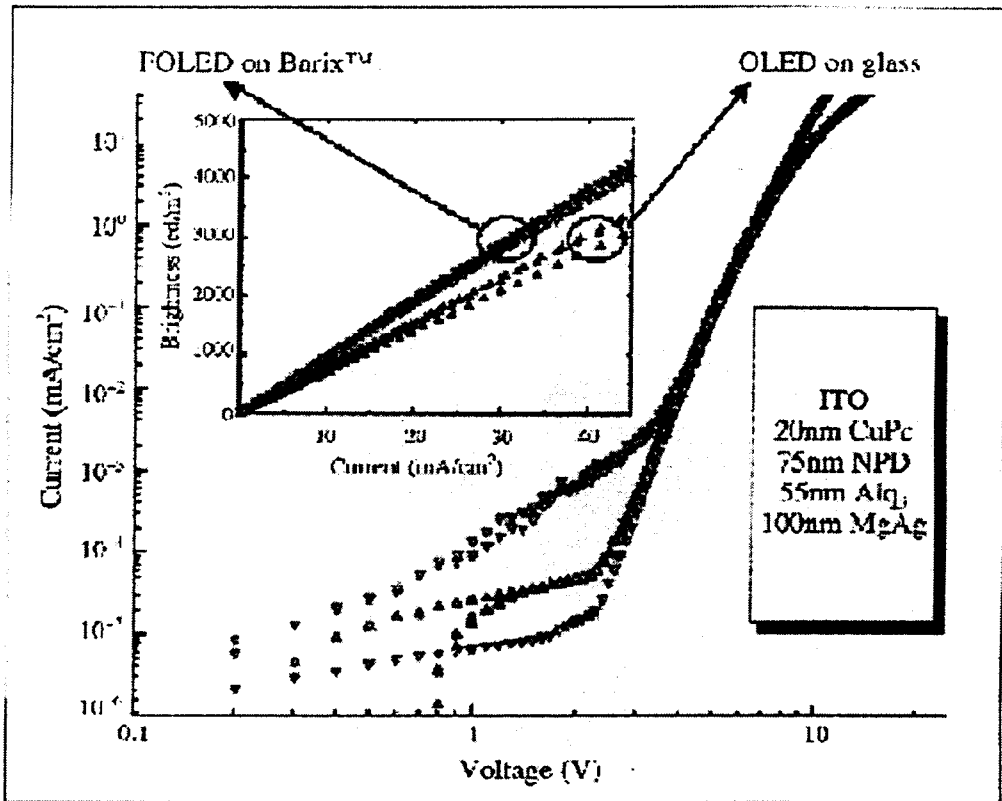


圖四、目前最為普遍使用的三層式 OLED 元件與 FOLED 元件構造之比較。

圖五為 Michael S. Weaver 等人以傳統熱蒸鍍方法將 OLED 小分子分別蒸鍍到傳統玻璃透明導電基板(▲)及可撓式透明導電塑膠基板(▼)所測得之電流-驅動電壓-量度(I-V-L)圖。由圖中電流-電壓及電流-量度的關係圖中我們不難發現塑膠基板所製成的元件效能並不亞於傳統 ITO 玻璃所製成的元件。而圖六則是由



Universal Display Corp.(簡稱 UDC)以塑膠導電透明基板所製成的 FOLED 元件。



圖五、 OLEDs 在傳統 ITO 透明導電玻璃基板(▲)及可撓式透明導電塑膠基板 (▼)所製成元件之電流(I)-電壓(V)-亮度(L)的關係曲線圖。



圖六、 可撓曲式 128x64 畫素單色被動式矩陣顯示器，基板厚度為 0.175 mm。

## FOLED 塑膠基板的研發：

FOLED 研發已慢慢形成一股熱潮，因此許多研究機構也意會到塑膠基板開發的重要性，而紛紛投入研發的行列。如新光碟片基材-環烯烴共聚物 mCOC (Metallocene based Cyclic Olefin Copolymer, 以下簡稱 mCOC) 材料於 1954 年由美國 DuPont 設廠生產，因為它具極優異的光學性、高透明度與耐熱性 (高玻璃轉移溫度)、質輕、低吸溼、耐熱及優異的加工流動性、高耐熱、高光學特性、絕佳阻水、阻氣性及耐酸鹼溶劑等特性。因此歐、美、日等國多家大廠，包括 Hoechst、BF Goodrich、Nippon Zeon、Mitsui、Japan Synthetic Rubber、Idemitsu 等以及國內工研院化工所，皆大力投入 COC 材料之研究開發。極有潛力用於取代 TFT LCD、OLED、PLED 等顯示器用的玻璃基板，達到全塑膠化平面顯示器輕、薄及不易破裂之特性要求。表三列出目前商業上高分子材料對水、氧的穿透率，而目前 LCD 常用的塑膠基板主要材質為 polyester 及環氧樹脂，其它基材如：polyether-polysulfones(PES)、PET、polyimide、polyether-polyimide 及 polycarbonates(PC)等也在 FOLED 導電透明基板研究的行列中。

Sample	Oxygen Permeation Rate (cc/m <sup>2</sup> /day)		Water vapor Permeation (g/m <sup>2</sup> /day <sup>†</sup> )	
	23°C	383°C	232°C	383°C
	Native 7 mil PET (DuPont)	7.62	-	-
Teijin – LCD film	<2	-	<5	-
Polaroid – LCD film	<1.0	-	-	-
Barix <sup>™</sup> 100	<0.005	<0.005*	-	0.46 <sup>†</sup>
Barix <sup>™</sup> 100 / ITO	<0.005	<0.005*	-	0.011 <sup>†</sup>
Barix <sup>™</sup> 200 / ITO	<0.005	<0.005*	-	<0.005 <sup>†</sup>
Barix <sup>™</sup> 500 / ITO	<0.005	<0.005*	-	<0.005 <sup>†</sup>

\*38°C, 90% RH, 100% O<sub>2</sub>

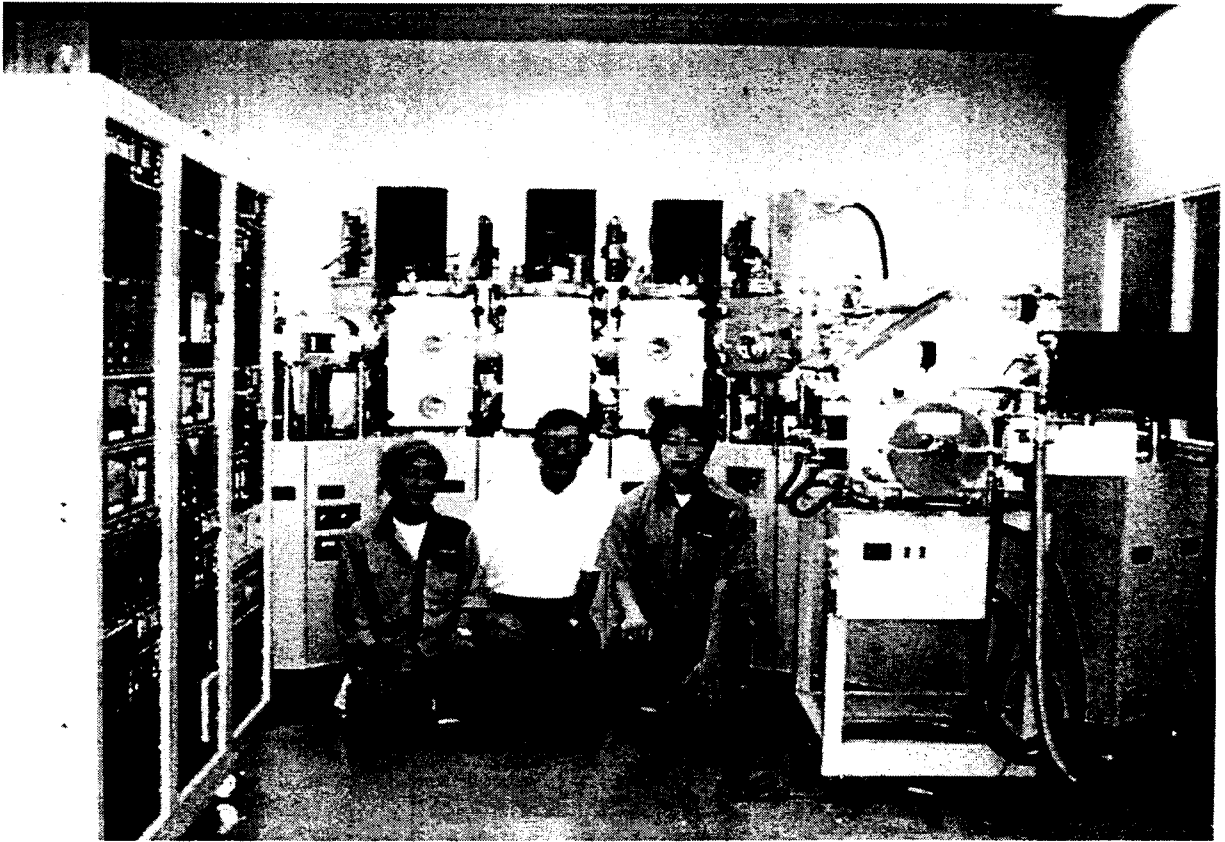
<sup>†</sup>383°C, 100% RH

表三、目前商業上使用高分子基板材料的水氣及氧氣穿透率。

在國內學術界方面，國立交通大學在國科會的經費援助及張俊彥校長的全力支持下，於 2001 年 5 月與達基科技、富臨科技合作成立國立交通大學「有機發光元件製作實驗室」，不僅建立一間一萬級的無塵室，更引進日本真空(ULVAC)的 SOLCIET 中型蒸鍍機，是目前台灣學術界最先進的一所實驗室，並將全力投入 OLED 及 FOLED 的研究及發展。「可撓曲式發光二極體」(FOLED)是歐、

美、日等國先進的實驗室目前最熱門的研究課題之一，加上有機材料具有良好的可撓曲性，較易製作在塑膠基板上以達到未來攜帶型所需「輕、便、小、彩、省、美、多」的要求。因此在國科會產學合作計畫通過下，將「可撓曲式有機發光二極體」列入重要發展方向，配合 ULVAC 的 SOLCIET 蒸鍍機組(圖七)研發前瞻性且經濟效益宏大的 Flexible OLED (FOLED) 平面顯示元件、材料、封裝及製程技術。其主要研發方向歸納如下：

- 開發透明導體成膜在可撓曲型塑膠基板之製程與設備。
- 研發防滲透水、氧氣的透明導電塑膠基板之保護層材料與元件封裝技術。
- 設計、合成改善有機發光二極體的關鍵材料及元件的設備製程，以搭配可撓曲式塑膠材質的基板。
- 建立 FOLED 製程相關技術，以移轉合作廠商，落實本計劃研發成果的經濟效益。



圖七、於 2001 年五月組裝完成並座落於國立交通大學「有機發光元件製作實驗室」之 ULVAC 的 SOLCIET 蒸鍍機組。圖中人物由左而右依序為日籍工程師中火田敏春先生、產學計劃主持人陳金鑫教授及日籍工程師佐藤麻世先生。(照片由台灣日真工程師陳建文先生提供)

#### 結論：

FOLED 展現了其傲人的 FPD 發展優勢與前景，如質輕、耐衝擊性及符合潮流需求，但為了能提早將這門技術市場化，FOLED 元件的封裝(packaging)與圖樣化

(patterning)將是決定該產品問世的關鍵，因此尋求及開發更高效能的塑膠基板及封裝技術將是刻不容緩的重要課題。

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- 1、Michael S., Weaver et al., *Information Display*, Vol. 17, No. 5&6, pp. 26-29, 2001.
- 2、Hagen K., Thomas N. J., *Solid State Tech.*, vol. 43, No. 3, pp.63-77.
- 3、Staff, *Solid State Tech.*, vol. 44, No. 3, pp.32-42.

## 附件六

光電科技 2001, 24, 78.

### 二十一世紀的明星產業-有機發光二極體平面顯示器技術

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平面顯示器 (Flat Panel Display, 簡稱 FPD) 是目前最重要的光電產品之一, 其與日常生活的緊密相關性, 使得光電業界多年來莫不持續不斷地努力研發新型的平面顯示器, 以追求更完美的功能。主流的平面顯示技術也一路從陰極射線管 (Cathode Ray Tube, 簡稱 CRT) 顯示器發展到了液晶顯示器 (Liquid Crystal Display, 簡稱 LCD)。尤其當進入了二十一世紀後, 人們需要性能更好、更能符合未來生活需求的新一代平面顯示器, 來迎接這個“3C”(即電腦, Computer、通訊, Communication、消費性電子器材, Consumer Electronics) 及“3G”(即第三代行動電話) 時代的來臨。放眼望去, 有機發光二極體 (Organic Light-Emitting Diodes, 簡稱 OLED) 其具有的輕、薄、靈、巧、彩、美、小等的特性, 是最能符合未來人們對平面顯示器的要求的一項技術, 也因此在全球光電相關的產學界掀起了一股研究熱潮, 國內外許多大廠也紛紛投入大量人力與資金加以研究, 其所具有的商業應用潛力, 可說是二十一世紀高科技產業界中, 一顆閃亮耀眼的巨星。

在此文章中, 我們針對 OLED 的發展歷史與原理、OLED 的發展現況、OLED 目前業界的投資現況, 做一完整的介紹。

#### \* OLED 的發展歷史與原理

OLED 也可稱為有機電激發光 (Organic Electroluminescence, 在日本常被稱為 OEL), 最早是在 1963 年由 Pope 教授所發現, 當時他以數百伏特的偏壓施加於 Anthracene 的晶體上, 觀察到發光的現象, 是最早的文獻報導。由於其過高的電壓與不佳的發光效率, 在當時並未受到重視。一直到 1987 年美國柯達公司的 C. W. Tang 及 Steve Van Slyke 發表以真空蒸鍍法製成多層式結構的 OLED 元件, 可使電洞電子侷限在電子傳輸層與電洞傳輸層之界面附近再結合, 大幅提高了元件的性能, 其低操作電壓與高亮度的商業應用潛力吸引了全球的目光, 從此開啓 OLED 風起雲湧的時代。而 1990 年英國劍橋大學的 Friend 等人成功的開發出以塗佈 (spin coating) 方式將多分子應用在 OLED 上, 即 Polymer LED, 亦稱為 PLED, 對 OLED 的發展有推波助瀾之效, 也使得 OLED 的未來更形寬廣。

OLED 發光的原理是利用一正向外加偏壓, 使電洞電子分別經過電洞傳輸層 (Hole Transport Layer) 與電子傳輸層 (Electron Transport Layer) 後, 進入一具有發光特性的有機物質, 在其內再結合時, 形成一“激發光子” (exciton) 後, 利用發光材料的特性, 將能量以光的形式釋放出來而回到基態 (ground state), 如

圖一所示。而這些釋放出來的能量當中，通常由於發光材料的選擇及電子自旋的特性 (spin state characteristics)，只有 25% (單重態到基態, singlet to ground state) 的能量可以用來當作 OLED 的發光，其餘的 75% (三重態到基態, triplet to ground state) 是以磷光或熱的形式回歸到基態。由於所選擇的發光材料能階 (band gap) 的不同，可使這 25% 的能量以不同顏色的光的形式釋放出來。

小分子 OLED 的元件是以真空蒸鍍法 (vacuum deposition) 將有機材料成膜在受質 (substrate) 上，目前較為一般研究常用的元件構造如圖二所示，以低功函數 (work function) 的鎂銀合金 (10:1) 為陰極，AlQ<sub>3</sub> 為電子傳輸層，NPB 為電洞傳輸層，CuPc 為電洞注入層，以高功函數、導電且透明的 ITO (indium tin oxide) 玻璃為陽極，在 AlQ<sub>3</sub> 與 NPB 之間則夾有一發光層，是將少許的高螢光摻雜物 (fluorescent dopant) 分散 (disperse) 在主發光體 (host emitter) 內所構成的，適當的摻雜物不僅可以改變主發光體的光色，也可以提高發光效率及增進 OLED 元件的操作穩定性。隨著全球科學家不斷的研究，元件構造也常做修正，不過大致不脫此類型元件的原理。

#### \* OLED 的發展現況

OLED 的發展，是以全彩化的平面顯示器為最高目標在前進，目前紅、藍、綠三原色的摻雜材料都已成功的開發出來了，但是卻尚未達到完全令人滿意的地步 (如圖三)，仍需要繼續的研究開發新的、更好的三原色摻雜材料，尤其是藍光及紅光。另外白光材料也是最近的一項研究重點，希望能用來作為照明光源或是液晶螢幕的背光源，可大幅減少目前白光光源所佔的空間與重量。

在 1998 年，美國的 Baldo 等人研究出以銥金屬錯合物 (iridium complex) 製成的元件，可以把原先三重態中流失的能量補救回來，將 OLED 元件的發光效率大幅提昇三倍以上，是近來 OLED 技術開發上的一大突破。

這幾年來，科學家正在研究以塑膠基板取代玻璃基板，製成可撓曲式的 OLED，即 Flexible OLED，也稱為 FOLED，其元件構造如圖四所示，如果能順利研發成功，則類似筆捲式行動電話的商品 (如圖五)，將不再是如好萊塢電影，“Red Planet” 中的科幻情節了。

由於 OLED 的製程較 LCD 簡單，成本亦只有 LCD 的 30%~40%，也是商業應用的一大優點。而目前在製成全彩化顯示器的製程中，最為關鍵的技術有三點：1. 全彩化像素 (color pixelation scheme) 的技術，2. 精細 (high resolution) 像素的形成，3. 驅動電路的使用。分別介紹如下：

1. 全彩化像素的技術：顯示器的螢幕是由許多的像素所構成，全彩化的顯示器就是因為組成每一個像素的副像素 (sub-pixel) 能發出紅、藍、綠三原色的光 (如圖六)，將此三原色加以組合變化即可發出任意顏色的光，因此如何構成三原色的像素，就是 OLED 目前的重要課題之一。經過十多年的研究，全球大廠發展出幾種不同的全彩化像素技術，大致可分為三類，簡介於表一，目前為止並沒有哪一類型佔有絕對的優勢，不過並排式的三原色全彩化技術比較普遍，因

爲此法的發光效率沒有被耗損，但是製程與量產比較困難。

2. 精細像素的形成：越精密的像素，形成的影像就越精緻，因此各加廠商莫不積極的研究。目前以美國 Kodak/日本 Sanyo 與日本 Pioneer 的技術發展較爲成功，如圖七所示。另外英國的 CDT 公司與 EPSON 合作，嘗試將噴墨印刷技術（ink-jet printing）應用到像素形成上，也在努力研究中。

3. 驅動電路的使用：一般來說，OLED 顯示器都驅動方式分爲被動式（passive matrix，即 PM-OLED）與主動式（active matrix，即 AM-OLED）兩類，其電路設計原理如圖八所示。被動式適合用在小尺寸的面版，因爲其瞬間亮度與陰極掃描列數成正比，所以需要在高脈衝電流下操作，會使像素的壽命縮短。且因爲掃描的關係也使其解析度受限制，但成本低廉、製程簡單是其一大優點。主動式恰與被動式特性相反，雖然成本較昂貴、製程較複雜（仍比 TFT-LCD 容易），但每一個像素皆可連續與獨立驅動，並可記憶驅動信號，不需在高脈衝電流下操作，效率較高，壽命也可延長，適用於大尺寸、高解析度之高資訊容量的全彩化 OLED 顯示產品。

由此可知，當這些問題能一一克服改善之時，OLED 全彩顯示器將再向前邁進一大步，這項技術造福人們生活的時刻也即將到來。

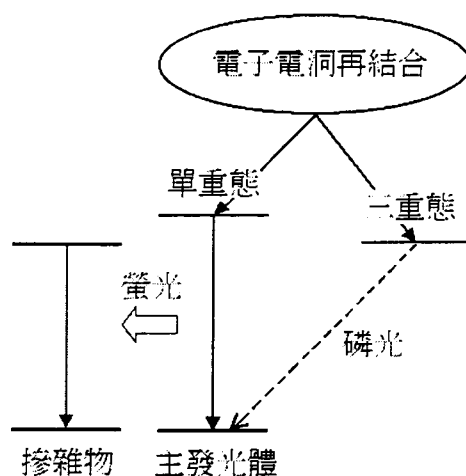
#### \* OLED 目前業界的投資現況

1996 年，日本 Pioneer 的 256x64 像素綠光顯示器問世，是全球首次宣布將 OLED 應用在商品上，從此 OLED 商品化的腳步向前大步邁進，全球大廠在此領域上的競爭也更加白熱化。1997 年，Pioneer 繼續推出多彩的 OLED 汽車音響面板（圖九），是相當有名的一項商品。並在 2000 年與美國摩托羅拉（Motorola）合作，將多彩 OLED 應用在“Timeport”手機面板上（圖十）。另外美國的柯達公司也是 OLED 技術的領先者之一，不但握有多項 OLED 相關基本專利，也在 1999 年與日本三洋（Sanyo）合作共同開發全球第一座採用低溫多晶矽（LTPS）薄膜電晶體驅動的 2.4 吋主動式全彩化 OLED 顯示器（圖十一），是領先群倫的產品。另外在 PLED 方面，英國的 CDT 公司於 1998 年推出主動式的單色 PLED 顯示器，是高分子方面的先驅。日本的 Toshiba 公司則宣布將在 2002 年 4 月量產全彩的 PLED 顯示器。日本的 SONY 公司日前剛發表最新消息，宣布要在 2003 年量產目前全球最大尺寸的 13 吋 OLED 平面顯示器（圖十二）。另外歐美日等地還有數十間著名廠商紛紛投入 OLED 相關產業中（表二），形成一個彼此激勵的激烈競爭局面。由以上可以發現，OLED 全面商品化的時程正在一步步的逼近中。

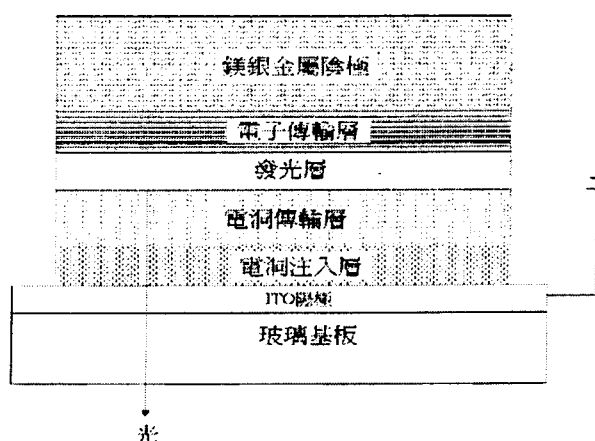
在國內的業界方面，幾家大廠如銻德公司旗下的銻寶公司，東元集團轉投資的東元激光，宏碁集團所屬的達碁科技，勝華電子所屬的勝園科技，國聯光電旗下的聯宗科技，奇美集團下的奇美光電，南亞科技，永信化學公司等，以及光磊科技、國碩光電、翰立科技、精碟科技、悠景科技等十數家公司，皆先後投入台灣 OLED 市場，進行研究與開發（表三），可說是近年來少見的一股風潮。

另外在國內學術界方面，國立交通大學在國科會的經費援助、張俊彥校長的全力支持以及美國柯達公司 C.W. Tang 的造訪諮詢（圖十三）之下，於今年 5 月與達基科技、富臨科技合作成立國立交通大學「有機發光元件製作實驗室」，不僅建立一間一萬級的無塵室，更引進日本真空的 SOLCIET 中型蒸鍍機，是目前台灣學術界最先進的一所實驗室，將全力用以投入 OLED 及 FOLED 的研究與發展。而其他如台大、清大、中研院、工研院工材所等學術研究單位，亦對國內 OLED 產業提供了源源不絕的人才與豐富的相關研究成果。

OLED 目前仍然有材料上、製程量產上的問題有待突破，但是其深具商業應用潛力的動人魅力，卻是不可抵擋的，也因此才能吸引全球如此多的廠商投入研究。然而 OLED 是一項整合性的產業，單打獨鬥並不能大步邁進，只有各項領域的人才分工合作、各展所長，才能攜手同行。期待這項二十一世紀的閃亮新星，能在不久的將來，綻放他耀眼的光芒，並使得人們的生活更加便利與精彩。

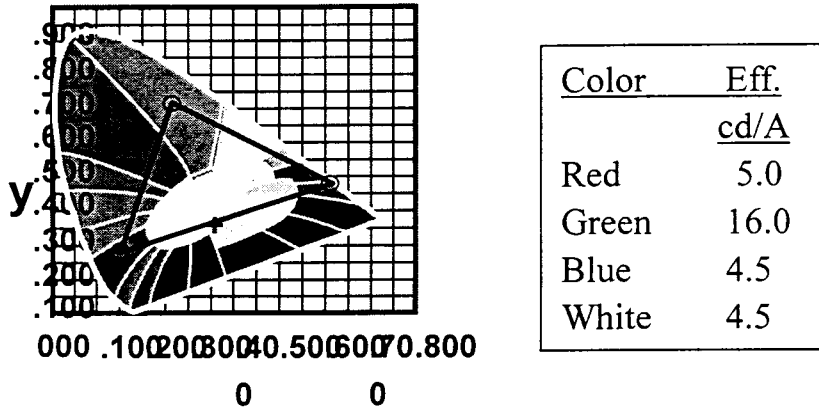


圖一、OLED 發光原理

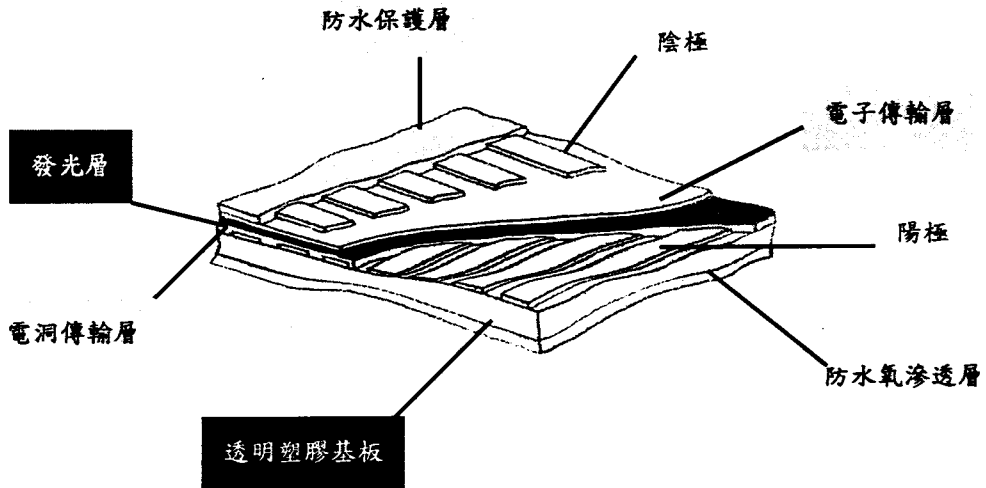


圖二，目前最為普遍使用的三層式 OLED 元件結構

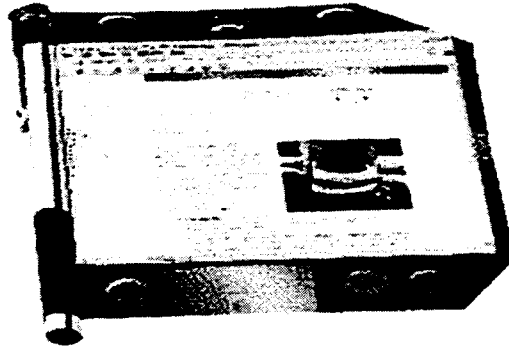




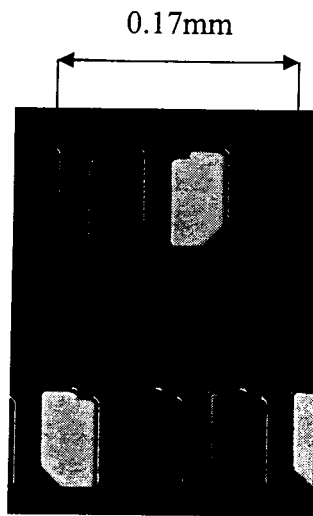
圖三、目前紅、藍、綠、白四色 OLED 元件的發光效率



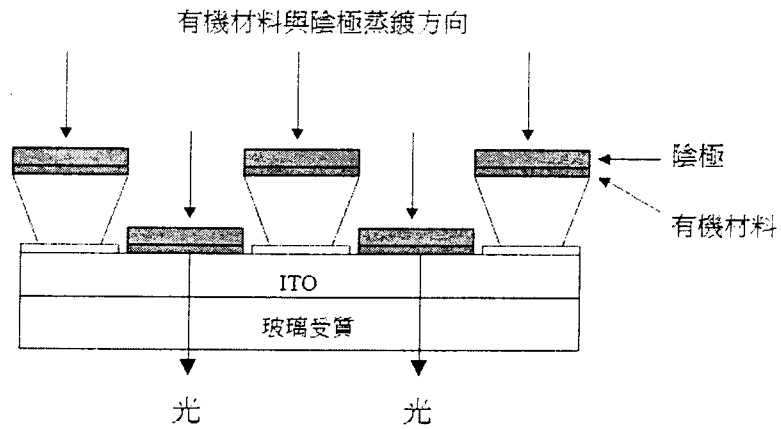
圖四、FOLED 元件構造



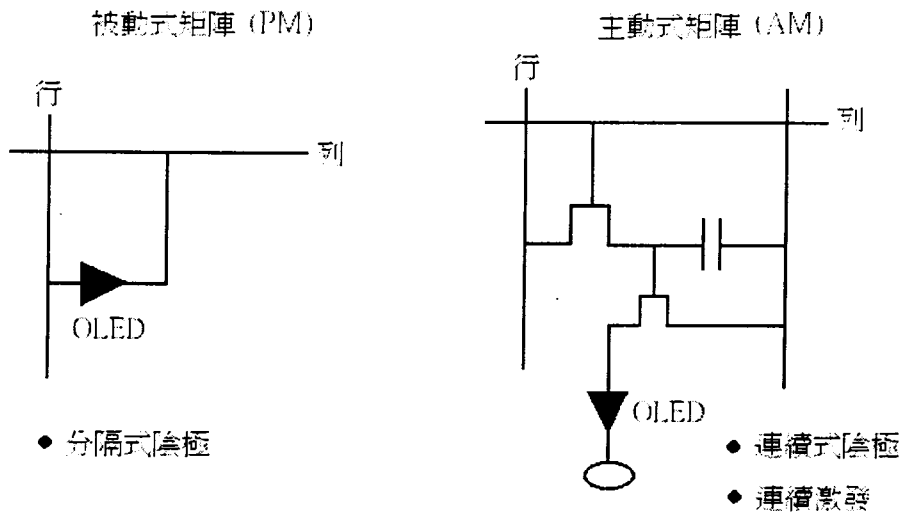
圖五、筆捲式的電子商品



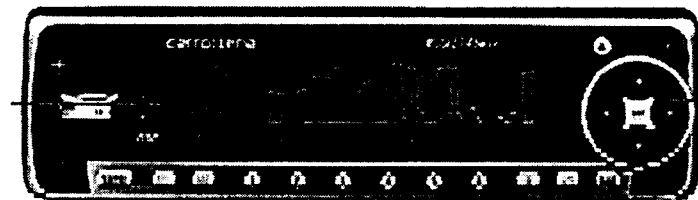
圖六、單一像素中副像素的排列法



圖七、Pioneer 與 Kodak 的像素製法



圖八、被動式矩陣與主動式矩陣的電路原理



圖九、Pioneer 於 1997 年所推出的汽車音響面版

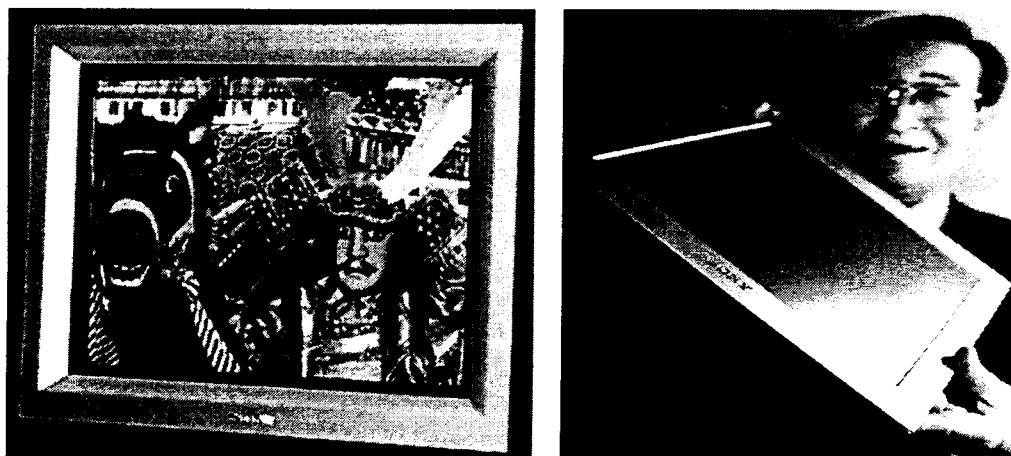


圖十、採用多彩 OLED 面板的 Motorola “Timeport” 手機



圖十一、柯達與三洋在 1999 年推出的 2.4 吋主動式全彩 OLED

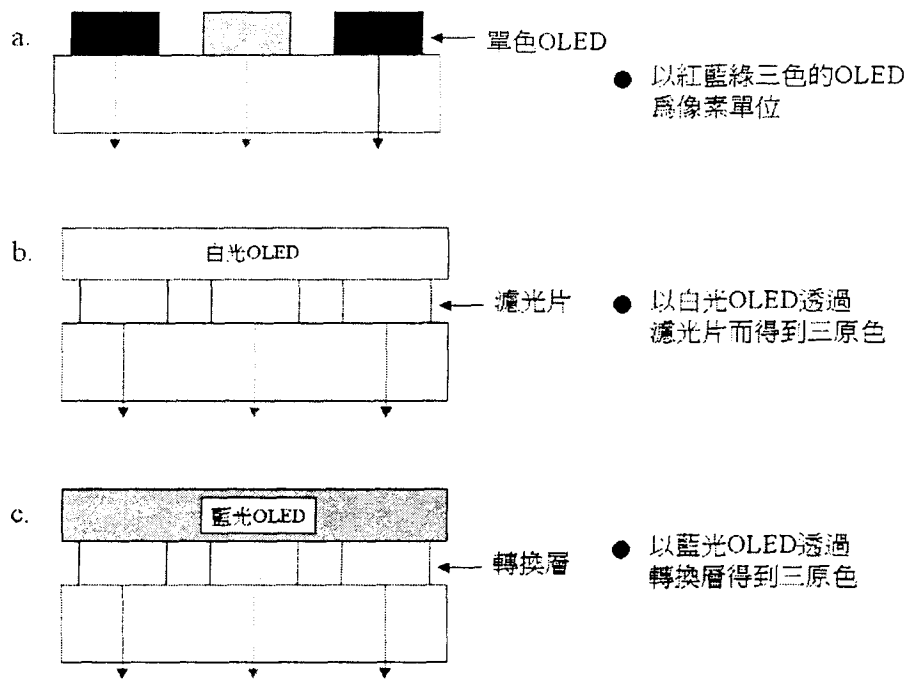
顯示器



圖十二、SONY 將在 2003 年量產目前全球最大尺寸的 13 吋 OLED  
平面顯示器



圖十三、美國柯達公司的 C. W. Tang 於 2000 年 12 月造訪  
新竹交通大學 OLED 實驗室



表一、五種像素結構的簡介：a.並排式三原色法，b.白光濾光法  
c.藍光轉換法。

企業名		材料	量產時間
柯達	(美)	小分子	持有專利
Dow Chemical	(美)	高分子	材料供應商
UNLAX	(美)	高分子	
Dupont	(美)	—	
Universal Display	(美)	小分子	
eMagin	(美)	小分子	2001年
CDT	(英)	高分子	持有專利
西門子	(德)	高分子	2002年左右
德國IBM	(德)	高分子	2002年左右
飛利浦	(荷)	高分子	2002年左右
LG電子	(韓)	小分子	2001年
三星 / NEC	(日韓)	小分子	2001年
SEIKO-EPSON	(日)	高分子	2002年左右
三洋電機	(日)	小分子	2002年初, 動畫面板
Pioneer	(日)	小分子	1998年, 動畫面板2002年秋季
TDK	(日)	小分子	2000年, 動畫面板2002年左右
日本精機	(日)	小分子	2002年
Stanley電氣	(日)	高分子	2001年被動式面版
TOYOTA汽車	(日)	高分子	
SONY	(日)	—	2003年
東芝	(日)	小分子 / 高分子	2002年4月
住友電工	(日)	—	
住友化學	(日)	高分子	材料供應商
出光興產	(日)	小分子	材料供應商
東洋Ink製造	(日)		材料供應商
大日本印刷	(日)		

表二、國外 OLED 廠商

企業名		材料	量產時間
錐德	(台)	小分子/高分子	2000年, 動畫面板2002年
勝華	(台)	小分子	
達基	(台)	—	
永信	(台)	小分子	
光磊	(台)	小分子	
東元	(台)	小分子	
國碩	(台)	小分子	
聯宗	(台)	小分子	
精碟	(台)	高分子	
翰立	(台)	高分子	
奇美	(台)	小分子	
悠景	(台)	小分子	
南亞	(台)	小分子	

表三、國內 OLED 廠商



# 附件七

## 發明專利說明書

一、發明名稱： 中文：具有高度抗濃度驟熄效應的新型綠色螢光摻雜物之有機

電激發光裝置

英文：Organic Electroluminescent Device with New Green

Fluorescent Dopants

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## 附件八

### 發明專利說明書

一、發明名稱： 中文：新型綠色有機電激發光材料  
英文：Novel Green Organic Electroluminescent Materials

二、發明人： 姓名：1.陳金鑫 Chin Hsin Chen  
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## 附件九

### 發明專利說明書

一、發明名稱： 中文：具抗濃度驟熄效應的新型綠色螢光摻雜物之有機電激發發光裝置

英文：Organic Electroluminescent Device with New Green Fluorescent Dopants

二、發明人： 姓名：1.陳金鑫 Chin Hsin Chen  
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# 附件十

## 發明專利說明書

一、發明名稱： 中文：新型有機電激發光材料中間體  
英文：New Intermediates for Organic  
Electroluminescent Materials

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之3

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## 附件十一

### **Tetramethyljulolidine – A key intermediate in the synthesis of the red dopant DCJTB for OLED applications**

Chin H. Chen, Banumathy, B and Shih-Wen Wen

(International Conference of Electroluminescence III, Los Angeles, (ICEL-3), Sep 5-9, 2001.)

Organic electroluminescent devices are of growing interest in various display applications due to their high luminous efficiency and capability of emitting many colors throughout the visible spectrum. Commercial interest in organic light emitting diode (OLED) technology has been the vital driving force in fueling the recent research and development activities.<sup>1,2</sup>

4-(Dicyanomethylene)-2-*t*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran, (DCJTB) is one of the best fluorescent dopants of choice for the red emitter of *tris*(8-hydroxyquinolato)aluminium hosted OLED's including Pioneer's recently demonstrated passive matrix full color prototype and Kodak / Sanyo's 2.4-in and 5.5-in low temperature poly silicon full color active matrix OLED displays. The cost of manufacturing DCJTB is prohibitively high owing to the synthetic complications of one of the key intermediates, 1,1,7,7-tetramethyljulolidine (TMJ), which can be prepared in two steps from aniline and 1-chloro-3-methyl-2-butene (Scheme 1). The low yield (~30%) obtained in the acid catalyzed *bis*-annulation prompted us to reinvestigate the reaction and analyze the products of the above reaction.

**A Highly Robust Green Fluorescent Dopant  
for Organic Light-Emitting Devices**

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Department of Applied Chemistry & Microelectronics and Information Systems Research Center  
National Chiao Tung University, Hsinchu, Taiwan 300, Republic of China

**Abstract:** A novel coumarin derivative, 10-(2-benzothiazolyl)-9-methyl-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-benzo[*l*]pyrano[6,7,8-*ij*]quinolizin-11-one, abbreviated as C-545MT, when doped in AlQ<sub>3</sub> as green emitter in OLED has the unusual property of resistance to concentration quenching and the sustaining of its EL luminance efficiency (~7.8 cd/A) over a wide range of doping concentration (2– 12%) which is more than ten times that of C-545T.

Single crystal XRD evidence is presented that the difference in doping behaviors can be linked to the difference in molecular packing as well as volume of unit cell of the perspective dopant crystals. Twisted molecular geometry of C-545MT that is distorted by the steric effect of C (4)-methyl substituent could prevent the undesirable molecular aggregation from occurring at high concentration thus delaying the onset of quenching.

*Keywords:* OLED, Electroluminescent, Green dopant, Coumarin, Concentration quenching, Synthesis, x-ray crystallography, photoluminescence.

## 1. Introduction

Strategically substituted 7-amino-3-(2-benzothiazolyl)coumarins based on the laser dyes, C-6 and C-545 have been widely used as green dopants in AlQ<sub>3</sub>-hosted organic electroluminescent devices [1]. Their popularity derives from the fact that these highly fluorescent coumarin derivatives when doped at their optimal concentrations usually produce

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very high EL efficiencies and a fairly sharp emission (FWHM ~60 nm) whose color and EL properties can be further refined by structural modifications. One notable example is the green dopant, 10-(2-benzothiazolyl)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-benzo[*l*]pyrano[6,7,8-*ij*]quinolizin-11-one, better known as C-545T (Fig. 1) which has an optimal doping concentration in AlQ<sub>3</sub> about 1% and a flat cd/A curve over a wide range of drive current is found to be particularly suitable for passive dot-matrix OLED display applications [2].

However, upon further examination of the relationship between EL efficiency (cd/A) and doping concentration, it is revealed that the luminance efficiency of C-545T tends to drop rather quickly after peaking at around 1%. Further, as the doping concentration gets too high, a shoulder at the long-wavelength edge of its emission begins to grow which ultimately will result in an undesirable shift of hue. This narrow window of optimal doping concentration and the lack of robustness in process control for fabrication of the doped emitter can be disadvantageous in production where high display quality assurance is required. It is believed that the early onset of concentration quenching phenomenon is usually caused by the tendency of most coumarin dyes to aggregate or dimerize at high concentration. Several studies have shown that the positions in coumarin molecules that most likely to take part in a photo-induced [2+2] cyclization are the C(3)=C(4) *sp*<sup>2</sup> double bond [3]. As a result, all of these photochemical reactions will lead invariably to products that are no longer fluorescent due to the destruction of the emissive chromophore originally present in the coumarin nucleus.

To study the effect of substitution at the C(4)-position of C-545T on the possible “delaying” of onset of concentration quenching, we report herewith the discovery of a very unusual coumarin derivative, 10-(2-benzothiazolyl)-9-methyl-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-benzo[*l*]pyrano[6,7,8-*ij*]quinolizin-11-one, designated as C-545MT (Fig. 1), which possess the unprecedented property of resistance to concentration quenching and the

sustaining of its EL luminance efficiency over a wide range of doping concentration from 2% to 12% (v/v) which is more than x10 that of C-545T.

## 2. Photoluminescence Studies of C-545MT and C-545T

The thermal and solution photoluminescent properties of C-545T [4] vs. C-545MT [5] are compared in Table 1. In general, the melting point ( $T_m$ ), glass transition temperature ( $T_g$ ) and thermal decomposition temperature ( $T_d$ ) of C-545MT are lower than those of C-545T. While the fluorescence spectra in  $\text{CH}_3\text{CN}$  are similar at around 516 nm, their relative fluorescence quantum yields are quite different with C-545TM being only 73% that of C-545T. From the absorption spectra and cyclic voltammograms, the HOMO/LUMO levels of C-545T and C-545MT are estimated to be 5.24/2.80 eV and 5.28/2.80 eV, respectively. The donating nature of the methyl group at C-4 of the coumarin nucleus lowers the HOMO of C-545MT for about 0.04 eV while the LUMO level remains unaffected. As expected, the emission of C-545MT is slightly hypsochromic with respect to that of C-545T due to a wider bandgap. However, the unusually large difference of 31 nm in Stoke shift suggests that either the ground state or the excited state geometry of these dopants may be quite different.

Thin film samples of solid-state photoluminescence of C-545T and C-545MT doped in  $\text{AlQ}_3$  at various concentrations are prepared by vacuum co-deposition on cleaned quartz surface and measured on the Acton Research Spectro Pro-150 Fluorimeter with the excitation set at 400 nm. For clarity, only PL spectra of optimally doped C-545T at 0.5% and C-545MT at 2% are compared in Fig. 2. From this illustration, the advantage of C-545TM in delaying the onset of concentration quenching (x4) over C-545T is already evident. The solid PL emission  $\lambda_{\text{max}}$  of C-545MT at 517 nm is also slightly blue-shifted from that of C-545T at 522 nm. It is also interesting to note that the emission (FWHM 63 nm) of C-545MT is actually 5 nm narrower than



its corresponding solution spectrum, contrary to C-545T (FWHM 61 nm) which is broader as what is normally observed for most other dopants.

#### 4. Single Crystal X-ray Crystallographic Analyses of C-545MT and C-545T

In order to explore further on this unusual property of resistance to concentration quenching by CH<sub>3</sub>-substituent at C(4) exerted on C-545T molecule, single crystal X-ray diffraction analyses were performed on both dopants using the Bruker Smart CCD instrument. Both single crystals can be grown from ethanol and their perspective 3-dimensional drawings are depicted in Fig. 3 in which all hydrogens are omitted for clarification. Some of the significant differences in structure, unit cell and packing distance are also compared in Table 2.

Twisted angle along the C7-C8 bond as defined by the planes occupied by the coumarin ring and the benzothiazole moiety of C-545MT is 21.7° which is more than x2 of that of C-545T (10°). With essentially identical C7-C8 bond length of 1.49 Å, the larger twisted angle of C-545MT can be attributed to the crowding effect of the neighboring CH<sub>3</sub>-group in order to relieve the steric compression. The large deviation from planar configuration of the C-545MT chromophore that is important for efficient fluorescence could also explain its lower quantum yield with respect to C-545T.

The major difference appears to be in their perspective molecular packing with C-545T in space group P2(1)/c and C-545MT in P2(1)/n. C-545T has 4 molecules per unit cell with a volume of 2242 Å<sup>3</sup> while C-545MT has 8 with a unit cell volume of 4835 Å<sup>3</sup>. The calculated molecular density of C-545T (1.275 Mg/m<sup>3</sup>) is therefore denser than that of C-545MT which has a density of 1.221 Mg/m<sup>3</sup>. The tighter packing between molecules of C-545T is presumably arisen from its near planar molecular geometry which allows for better stacking than C-545MT as compared in Fig. 4. This difference in packing as observed by the x-ray diffraction analyses

could be one of the key evidences for rationalizing the difference in doping behavior of C-545MT vs C-545T in AlQ<sub>3</sub> hosted OLEDs.

## 5. Electroluminescence Studies of C-545MT vs. C-545T

The organic EL devices were fabricated by vapor deposition according to published procedures [8]. The sequence of deposition and respective layer thickness were: [ITO (1000 Å)/ CuPc (150Å) / NPB (600 Å) / v% dopant + AlQ<sub>3</sub> (375 Å) / AlQ<sub>3</sub> (375 Å) / Mg : Ag (10:1, 2000 Å)]. The EL device were completed with encapsulation in a dry argon glove box. The structures of NPB and AlQ<sub>3</sub> have been disclosed previously. The EL luminance and C.I.E. chromaticity values were measured using a Photo Research PR-650 spectrophotometer.

The most striking difference between devices doped with C-545MT and C-545T is that the former is extremely resistant to concentration quenching. Fig. 5 shows the I-V-L curves of C-545MT doped at 7.5% level with insert showing the overlay of its similar EL and solid PL spectra at their respective optimal doping concentration. The turn-on voltage is around 5.5 V and the luminance at 100 mA/cm<sup>2</sup> is 8,170 cd/m<sup>2</sup> with a luminance efficiency reaching 8.1 cd/A. For comparison, the corresponding EL efficiency of C-545T at concentration > 6% dopant level would have fallen below 4 cd/A. The advantage in delaying of concentration quenching is further illustrated in Fig. 6 in which the luminance efficiency of C-545MT vs C-545T is plotted over a wide range of doping concentration from 0 to 12.5% (v/v). It is noted that although C-545T has a higher efficiency of 9.3 cd/A at its optimal doping level of 1%, it tends drop to rather quickly at higher concentration. On the contrary, the EL efficiency of C-545MT reaches a plateau of around 7.8 cd/A which is sustained throughout the doping concentration spanning from 2% to as high as 12.5%. This robustness in processing can be of great advantage in production where large window of doping control may be necessary to maintain the highest display luminance quality.

Further advantage of C-545MT in its capability of maintaining its emissive color over a wide range of doping concentration is illustrated in Fig. 7 in which the luminance of the device driven at 20 mA/cm<sup>2</sup> is plotted against the doping concentration along with the corresponding 1931 C.I.E. coordinates. The desirable flat cd/A response over drive current for passive dot-matrix OLED applications has also been observed for C-545MT doped AlQ<sub>3</sub> emitter at concentration range throughout 2-12%.

### **Summary**

We have discovered an unusual green coumarin dopant C-545MT which is highly robust and resistant to concentration quenching in AlQ<sub>3</sub> host matrix as doped emitter in OLEDs. The luminance efficiency of C-545MT is sustained around 7.8 cd/A over a wide doping concentration range of 2-12% (v/v) which is more than ten times that of C-545T. Single crystal XRD evidence is presented that the difference in doping behaviors can be linked to the difference in molecular packing as well as volume of unit cell of the perspective dopant crystals of C-545MT and C-545T. Twisted molecular geometry of C-545MT which is distorted by the steric effect of C(4)-methyl substituent could prevent the aggregation from occurring at high concentration thus delaying the onset of quenching.

### **Acknowledgement**

This work is supported in part by Grants from the National Sciences Council of the Republic of China (NSC-90-2216-E-009-003) and the R&D Foundation of NCTU.

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**List of figure and table captions:**

Fig. 1. Molecular structures of C-545T and C-545MT.

Fig. 2. Thin film solid PL of C-545T and C-545MT doped in AlQ<sub>3</sub>.

Fig. 3. Single crystal x-ray crystallographic structures of C-545T and C-545MT.

Fig. 4. Comparison of molecular packing in unit cells of C-545T vs C-545MT

Fig. 5. I-V-L curve of green C-545MT Device (7.5% doped in AlQ<sub>3</sub>).

Fig. 6. Comparison of luminance efficiency vs doping concentration of C-545T and C-545MT.

Fig. 7. Doping concentration vs luminance and 1931 CIE coordination of C-545MT.

Table 1. Thermal and spectroscopic properties of C-545T vs C-545MT in acetonitrile.

Table 2. Comparison of x-ray crystallographic data of C-545T and C-545MT.

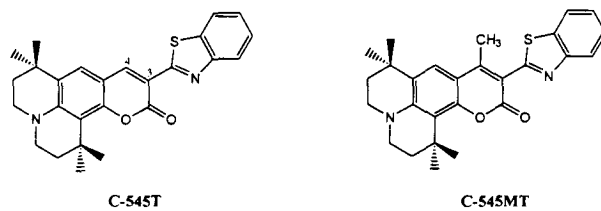


Fig. 1. Molecular structures of C-545T and C-545MT.

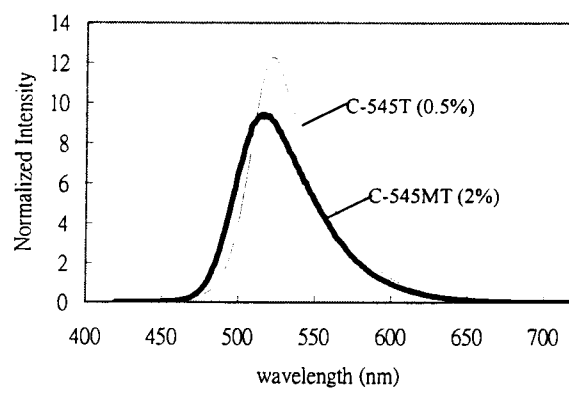


Fig. 2. Thin film solid PL of C-545T and C-545MT doped in AlQ<sub>3</sub>.

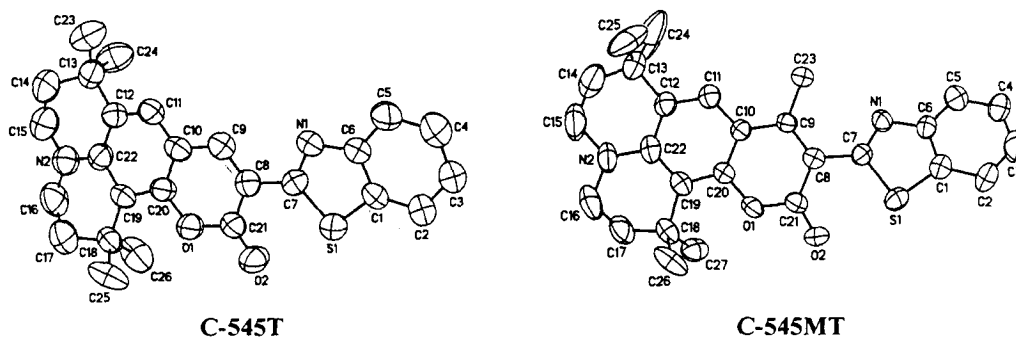


Fig. 3. Single crystal x-ray crystallographic structures of C-545T and C-545MT.



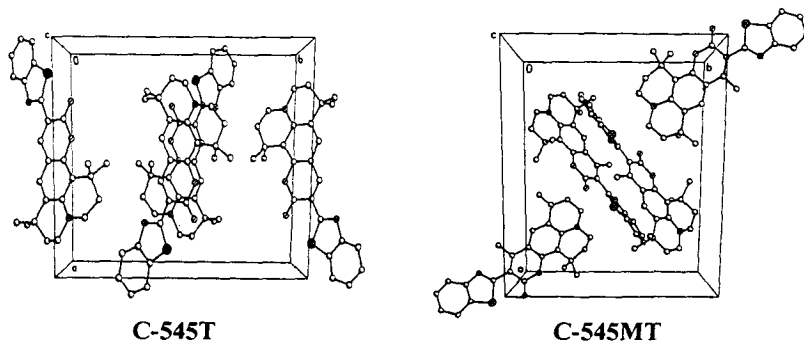


Fig. 4. Comparison of molecular packing in unit cells

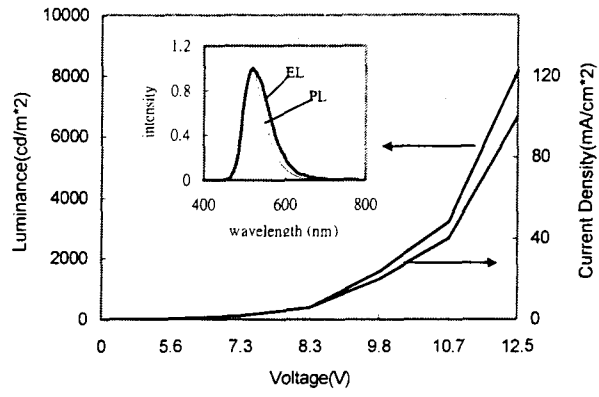


Fig. 5. I-V-L curve of green C-545MT Device (7.5% doped in AlQ<sub>3</sub>).

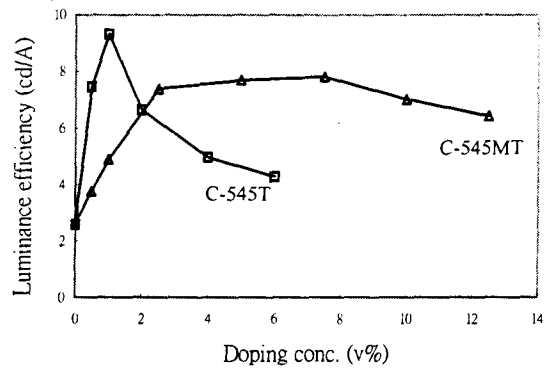


Fig. 6. Comparison of luminance efficiency vs doping concentration of C-545T and C-545MT.

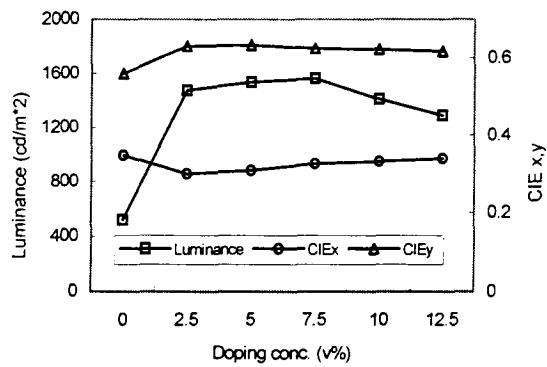


Fig. 7. Doping concentration vs luminance and 1931 CIE coordination of C-545MT.

dopant	T <sub>m</sub>	T <sub>g</sub>	T <sub>d</sub>	abs. $\lambda$ max	fl. $\lambda$ max	FWHM	Stoke's shift	$\Phi^{PL}$
C-545T	230°C	100°C	318°C	476 nm	516 nm	56 nm	40 nm	1.0
C-545MT	158°C	64°C	304°C	444 nm	515 nm	68 nm	71 nm	0.73

Table 1. Thermal and spectroscopic properties of C-545T vs C-545MT in acetonitrile.

dopant	twisted angle	space group	unit cell vol.	Z value	C7-C8 bond	Calc. density
C-545T	10°	P2(1)/c	2242 Å <sup>3</sup>	4	1.490 Å	1.275 Mg/m <sup>3</sup>
C-545MT	21.7°	P2(1)/n	4835 Å <sup>3</sup>	8	1.486 Å	1.221 Mg/m <sup>3</sup>

Table 2. Comparison of x-ray crystallographic data of C-545T and C-545MT.

## Design and Synthesis of New Red Dopants For Organic Electroluminescent Devices

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Fluorescent dopants play a key role in enhancing the EL efficiency, tuning the color and influencing the operational stability of OLED devices that are fabricated by using Alq as the host emitter. To drive down the material cost and to achieve the highest possible EL grade of purity, design of highly fluorescent dopants that can be readily synthesized in high yield, purified and scaled up to production scale become important. For co-deposition with Alq by carefully controlled resistive heating, T<sub>g</sub> and thermal gravimetric properties need also to be considered. In this talk, highlights of our recent work at the OLED laboratory of NCTU in the design and synthesis of several new red fluorescent dopants related to 4-(dicyanomethylene)-2-*t*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran (DCJTB) will be presented along with their PL and EL properties used as red emitters in OLEDs.

**Design and Synthesis of DCJTB-Based Fluorescent Dopants  
for  
Organic Light-Emitting Devices**

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Abstract:

4-(Dicyanomethylene)-2-*t*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran (DCJTB) has been widely used as red dopant in Alq-hosted organic electroluminescent devices. In order to improve the colorimetry as well as the efficiency of OLED device, synthesis of materials with high purity, good fluorescence quantum yield and low propensity for concentration quenching is important. Through molecular design, several modified red dopants based on DCJTB by introducing a steric donating group at the C-8 position of the julolidyl ring have been prepared and fabricated as doped emitters in OLEDs. This poster will present their PL and EL performance data in comparison with those of DCJTB.



## A New Green Dopant For Organic Electroluminescent Devices

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Fluorescent dopants play a key role in enhancing the EL efficiency, tuning the color and influencing the operational stability of OLED devices. In green emitting materials, 10-(2-benzothiazolyl)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-benzo[*l*]pyrano-[6,7,8-*ij*]quinolizin-11-one, better known as C-545T, has been widely used as green dopant in Alq-hosted organic electroluminescent device with high EL efficiency and a sharp emission (FWHM ~ 60nm). In this paper, the design and synthesis of a new coumarin-based electrofluorescent dopant C-545P will be presented and its PL and EL properties will be benchmarked with those of C-545T.

# Doped Blue Emitters of 9,10-di(2-naphthyl)anthracene in Organic Electroluminescent Devices

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Received 1 July 2002; accepted 2002

## Abstract

Blue EL emission of 9,10-di(2-naphthyl)anthracene (ADN) based emitter in OLED is highly dependent upon its thickness and attenuated by the microcavity effect of the emitter. By carefully tuning the thickness of ADN and optimizing the doping concentration of TBP, one of the highest efficiencies reported for the anthracene based blue emitter at 6.6 cd/A with a CIE of  $x = 0.13$ ;  $y = 0.21$  is achieved.

*Keywords:* opto-electronic devices, electroluminescence, thin-film structures

## 1. Introduction

Tetra(*t*-butyl)perylene (TBP) doped in 9,10-di(2-naphthyl)anthracene (ADN) has been reported to produce efficient blue emission in OLED with a luminance efficiency of  $\sim 3.4$  cd/A and a CIE coordinates of  $x = 0.15$ ;  $y = 0.23$ . This doped device is also one of the few blue OLEDs that have been demonstrated to be stable [1] with a half life of 4,000 h starting from an initial luminance of 636 cd/m<sup>2</sup>. Further studies of this blue ADN emitter revealed however, that its EL performance was not always reproducible nor was the nature of this device robust. Both luminance and color were found to be dependent upon the thickness of each of the organic layers of the device with the emitting layer appeared to be the most sensitive. Slight variation of the thickness of emitter could result in the grow-in of two extraneous shoulders in the green region around 500 nm and 540 nm in addition to the main EL emission at  $\lambda_{\max} \sim 460$  nm which corresponds to the solid PL of ADN. Evidence will be presented in this paper which supports that the variation in EL performances and emission spectrum are mainly due to an optical effect rather than what was commonly believed to be the formation of exciplex [2] or the shift of recombination zone within the emitter [3].

## 2. Experimental

The device architecture was [ITO (1700Å)/CuPc (150Å)/NPB (400Å)/ADN + TBP ( $x$  Å)/Alq<sub>3</sub> (200Å)/LiF (10Å)/Al (2000Å)] and the structure of this blue host and dopant studied in this report is shown in Fig. 1 where CuPc was the hole injection layer, NPB the hole transport material, ADN was the blue host, TBP was the blue dopant and Alq<sub>3</sub> was the electron transport backing layer. Prior to organic deposition, the ITO coated glass plate was thoroughly cleaned by scrubbing, sonication, vapor degreasing, and oxygen plasma treatment. Devices were fabricated under the vacuum of  $10^{-6}$  Torr in a thin-film evaporation coater following a published protocol [4].

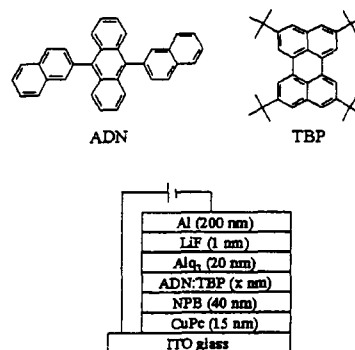


Fig. 1 Device structure and blue host and dopant materials.

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Table 1. EL performance comparison of doped and undoped TBP/ADN blue emitters.

Thickness CuPc/NPB/ADN/Alq <sub>3</sub> (nm)	Concentration TBP (%)	EL peak (nm)	Luminance at 20 mA/cm <sup>2</sup> (cd/m <sup>2</sup> )	Lum. Yield (cd/A)	CIE coordinates (x,y)	Voltage (V)	Efficiency (lm/W)
25/50/30/40	2	465	636	3.4	0.15,0.23	9.7	1.10
15/40/30/20	0	456	763	3.8	0.16,0.17	8.6	1.39
15/40/130/20	0	456	550	2.8	0.15,0.09	18.2	0.48
15/40/30/20	1	464	1311	6.6	0.13,0.21	8.9	2.33

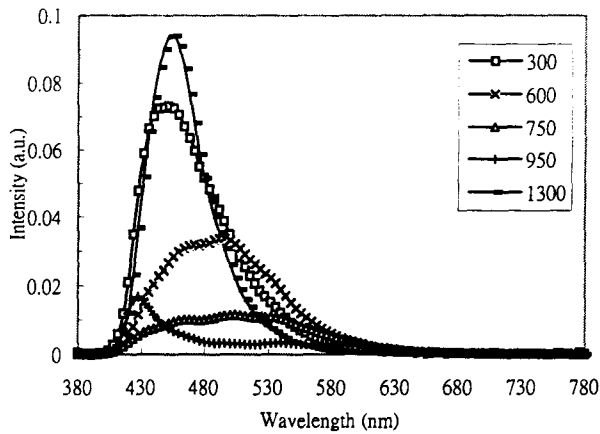


Fig. 2. EL spectra of ADN vs. film thickness

### 3. Results and Discussion

Fig. 2 shows the unnormalized EL spectra of the undoped devices where the thickness of the blue ADN emitter layer was systematically increased from 300 Å to 1300 Å. The blue emission at around 460 nm is noted to broaden and its intensity dropped sharply as the thickness of the emitter layer increased to 600 Å and 750 Å, respectively. Further increase in thickness was observed to recover the blue emission beginning at ~950 Å and maximized at 1300 Å when the full EL spectrum of ADN was restored with a narrower FWHM. This periodicity of changing emissive pattern which can no longer be explained by the shift of the exciton recombination zone is best rationalized by the weak microcavity effects of the ADN emitter in OLED [5].

To eliminate the possibility of exciplex formation in interpreting the EL spectral behavior with respect to thickness variations, we replaced the NPB (I<sub>p</sub> -5.2eV) with TPD (I<sub>p</sub> -5.5eV) in our device structure and fabricated a series of devices by varying the ADN emitter thickness accordingly. It was reasoned that if the broad emission at around 540 nm were indeed produced by the exciplex formation at the ADN/NPB interface, the replacement of TPD with a higher I<sub>p</sub> should alleviate it. The fact that similar periodicity of emissive pattern remained for TPD device suggests the exciplex emission does not appear to play a role in the ADN based blue device.

These findings allow us to optimize the blue device structure by doping with TBP at various concentrations in ADN emitter with different thickness. Their EL device performances in terms of luminance efficiency and CIE

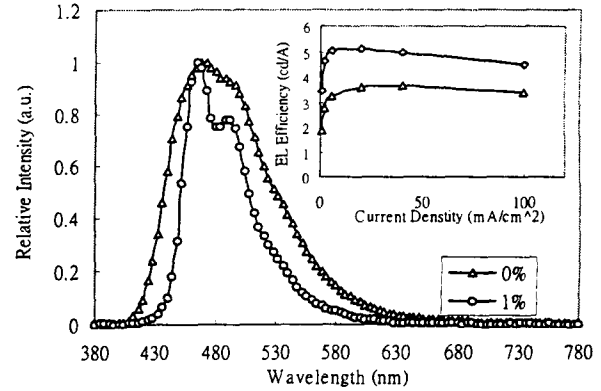


Fig. 3. EL spectra of doped and undoped TBP/ADN blue devices

coordinates are tabulated and benchmarked against Kodak's recent result [1] in Table 1. Increasing the thickness of ADN to 1300 Å resulted in producing a much saturated blue emission at CIE  $x = 0.15$ ;  $y = 0.09$  albeit at a lower luminance efficiency (2.8 cd/A) and a higher drive voltage (18.2V) which could be due to the unbalanced carriers for recombination in the thicker ADN layer. The optimized doping concentration of TBP in the device with 300 Å of ADN was determined to be around 1% which produced a blue emission peaking at 464 nm with a CIE  $x = 0.13$ ;  $y = 0.21$ . At the drive current density of 20 mA/cm<sup>2</sup> and 8.9V, this blue device achieved a luminance of 1311 cd/m<sup>2</sup> which corresponds to a luminance efficiency of 6.6 cd/A and a power efficiency of 2.33 lm/W that are among the best ever reported for electrofluorescent OLEDs. Fig. 3 shows the comparison of this doped EL spectrum with that of the undoped device with the insert depicts the relationship between the luminance efficiencies (cd/A) and drive currents of both devices. The near "flat" efficiency response with respect to drive current is particularly desirable for passive matrix OLED flat panel display applications.

We thank the National Sciences Council of Taiwan, R.O.C. for financial support of this research.

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## DCJTB Doped Red Emitters in OLED

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R.O.C.Phone : +886-3-5712121x59200 , E-mail : [fredchen@eic.nctu.edu.tw](mailto:fredchen@eic.nctu.edu.tw)**Abstract**

We have studied the device optimization of red DCJTB dye doped Alq<sub>3</sub> emitters in OLED. By varying the hole injection materials, thickness of hole-transport (NPB) layer and by evaporation with rubrene as co-dopant, efficiencies of 3.24 cd/A and near saturated CIE color coordinates of  $x = 0.643$ ,  $y = 0.354$  was achieved without needing additional doping of hole-trap with NPB. From experiments with film thickness variation, it is concluded that the improved EL performance and color saturation are due to the synergistic effects of microcavity, device structural optimization as well as optimal doping of DCJTB with rubrene. We believe this luminance efficiency for red is by far one of the best ever reported for dye-doped electrofluorescent OLEDs.

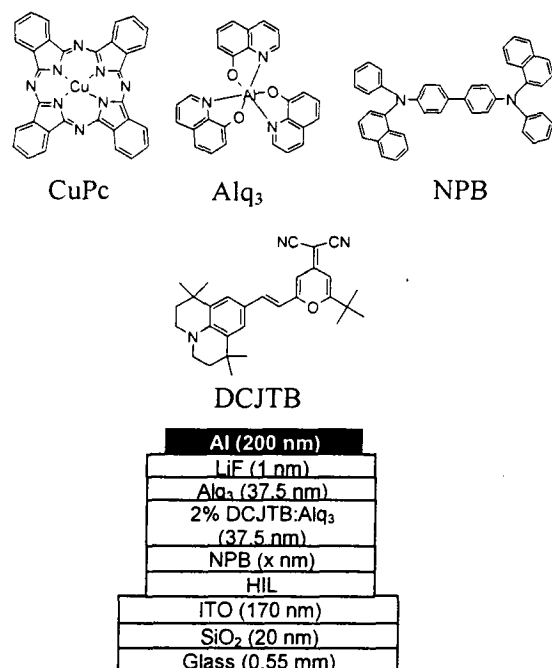
**1. Introduction**

Organic light-emitting devices (OLED) have received considerable attention due to their potential application in flat-panel displays. For full color display applications, it is necessary to demonstrate a set of primary RGB emitters with sufficiently high luminous efficiencies of proper proportion and a matching set of chromaticity in order to achieve a desired white emission with the right CIE coordinates. Such emitters can, in principle, be obtained using a guest-host doped system utilizing a single host matrix dispersed with various RGB guest dopants leading to EL of desirable hues [1]. Typically, the green OLED emitter has the highest efficiency [2] followed by the blue [3] which leaves red as the weakest link in the triad whose balanced overall luminance can be critical in the making of a good full color passive matrix [4] as well as active matrix display [5].

An archetypical red dopant material used for many of today's OLED displays on the market is 4-(dicyanomethylene)-2-*t*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran, better known as DCJTB [6]. Despite of the fact that DCJTB is an excellent red fluorescent dye with solution PL  $\lambda_{\max} \sim 620$  nm and a

quantum efficiency  $\eta > 90\%$ , the optimally doped EL in Alq<sub>3</sub> tends to appear orange which is due to the contamination of green emission from the host emitter. Although the color saturation can be improved by higher level of doping, its luminance is greatly compromised due to the onset of concentration quenching. As a result, red color approaching chromaticity coordinates of CIE  $x,y = [0.65, 0.35]$  could only be obtained at dopant concentration of higher than 3% when the luminance has dropped well below its plateau. By adding 5% of rubrene as a red emitting assist dopant with 2% DCJTB in Alq<sub>3</sub>, Hamada and coworkers at Sanyo [7] was able to achieve a luminance efficiency of 2.1 cd/A with CIE  $x,y = [0.64, 0.35]$ . Subsequently, the Kodak/Sanyo team discovered [8] that by adding ~6% of NPB as hole-trapping dopant to the above emitting system simultaneously, the efficiency could be further improved to 2.8 cd/A with a starting luminance of 550 cd/m<sup>2</sup> at 20 mA/cm<sup>2</sup> and near saturated red chromaticity coordinates of CIE  $x,y = [0.65, 0.34]$ . The encapsulated device structure disclosed in that report was [Glass/ITO (anode)/150 nm NPB (hole transport)/37.5 nm Alq<sub>3</sub> with dopants (emitter)/37.5 nm Alq<sub>3</sub> (electron transport)/LiF (e-injecting)/200 nm Al (cathode)] which showed a remarkable projected operational half-life of 8,000 h at ambient conditions. It is believed that this EL performance was one of the best for a red fluorescent dye-base OLED emitter including the 1,1'-dicyano-substituted *bis*(styryl-naphthalene) derivatives (BSN) recently reported by Sony [9].

For full color display, the red emitter of OLED still needs to be improved further to save power consumption and the Kodak/Sanyo's 3-dopant process involving DCJTB, rubrene and NPB is also in need of simplification. We have restudied the red emitter based on DCJTB and rubrene in this paper by varying the hole-injecting materials, film thickness of the hole-transport layer and doping concentration. It was found the luminance efficiency and color of DCJTB doped emitters can indeed be greatly improved by



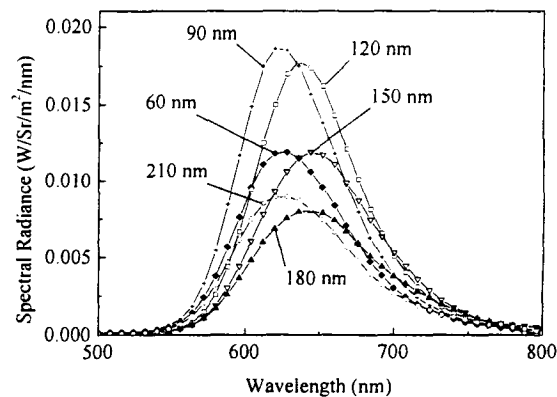
**Figure 1** Structure of doped device and materials

device optimization without the additional doping of hole-trapping material in the emitter.

## 2. Experimental

The device architecture was [ITO (170 nm)/HIM (15 nm)/NPB (x nm) /x% DCJTB: Alq<sub>3</sub> (37.5 nm) /Alq<sub>3</sub> (37.5 nm)/LiF (1 nm)/Al (200 nm)] and the structures of materials are shown in Fig. 1 where CuPc and CHF<sub>3</sub> were used as the hole injection materials (HIM), NPB the hole transport material, DCJTB was the red dopant, Alq<sub>3</sub> was the host emitter as well as the electron transport backing layer. The ITO/glass used was 0.7 mm thick which contained a passivation layer of 20 nm of SiO<sub>2</sub> and its sheet resistance was about 10 Ω/□. In this work, we used two different hole injection materials of 15 nm of copper phthalocyanine (CuPc) and CHF<sub>3</sub> plasma polymerized anode modification layer [10] to study the effect on luminance efficiency.

Prior to organic deposition, the ITO coated glass plate was thoroughly cleaned by scrubbing, sonication, vapor degreasing, and oxygen plasma treatment. Devices were fabricated under the vacuum of about 10<sup>-6</sup> Torr in a thin-film evaporation coater following a published protocol [11]. All organic layers were prepared by vapor deposition using resistively heated tantalum boats. Typically, the deposition rate was 4

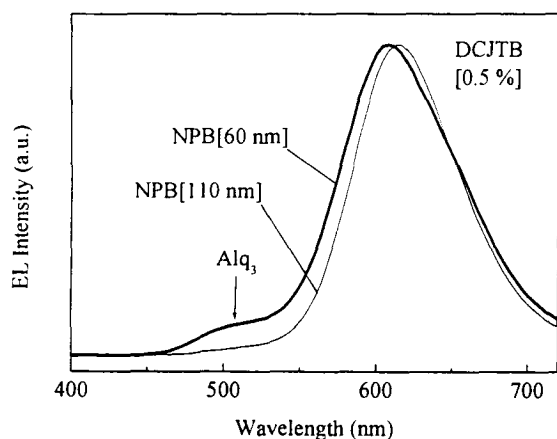


**Figure 2** Effects of NPB film thickness on the EL spectra

Å/s and the substrate to evaporant source distance was about 30 cm. The dopant was coevaporated from resistively heated graphite boat which was controlled by a temperature controller and monitored through a thermocouple attached to the side of the boat. By careful control of the dopant boat temperature, it was possible to precisely coevaporate a determined amount of dopant dispersed into the Alq<sub>3</sub> emitter layer as measured in v/v %. After the deposition of the organic layers and without a vacuum break, the LiF and Al cathode electrode were deposited in sequence on top of the organic layers using separately controlled sources. The active area of the EL device, defined by the overlap of the ITO and the cathode electrodes, was 0.1 cm<sup>2</sup>. The EL emission spectra (taken normal to device) and current-voltage-luminance characteristics of the devices were measured in a dry box with a diode array rapid scan system using a Photo Research PR650 spectrophotometer and a computer-controlled programmable DC source.

## 3. Results and discussion

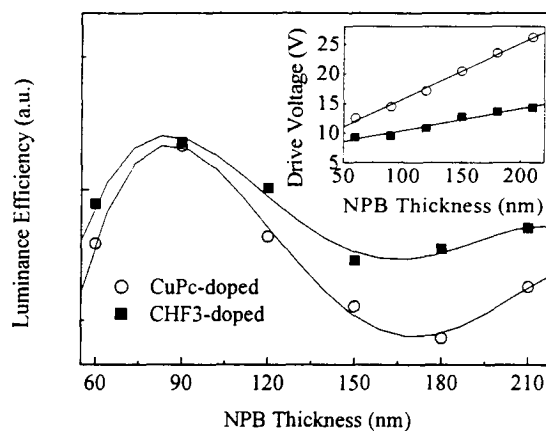
To determine if there was any microcavity effect on the coupling out efficiency of the red emission of DCJTB doped device, we began by first studying the basic device architecture using CuPc (15 nm) as the HIM by varying the thickness of hole transport layer (NPB). Fig. 2 shows the plots of EL spectra of 2% DCJTB doped device at various NPB layer thickness that was varied from 60 nm to 210 nm at 30 nm intervals. The red emission due to DCJTB was found to shift gradually from 624 nm to around 648 nm and back to 630 nm again as the NPB thickness increases from 60 nm to 210 nm with corresponding change of



**Figure 3 Comparison of EL spectra of NPB [60 nm] and [110 nm] doped cells**

FWHM from 80 nm to 100 nm to 88 nm. The EL intensities in terms of radiance ( $\text{W}/\text{Sr}/\text{m}^2$ ) were observed to also have changed in a cyclical fashion along with the thickness. This periodicity of emissive pattern can be rationalized by the optical (multiple-beam) interference effect [12] caused by the Lambertian nature of the emission generated in the center of a half-cavity created by the reflective cathode mirror and the transparent ITO/glass substrate in OLED. At lower doping concentration of 0.5% DCJTb, this effect is more prominent as shown in Fig. 3 in which the EL spectrum of the device with thicker NPB of 110 nm shows no residual  $\text{Alq}_3$  emission (near 510 nm) while that of the device with 60 nm of NPB is still contaminated with the host green emission due to incomplete Förster energy transfer. From these experiments, the best thickness of NPB layer was therefore determined to be between 90 – 120 nm in consideration of both coupling out efficiency and emissive color.

Although the thicker NPB device of 110 nm can improve the red emission at a lower doping concentration of DCJTb, it was not without cost with CuPc (15 nm) as HIM. As shown in the inset of Fig. 4, the increase of NPB thickness will cause the drive voltage of these devices to rise sharply. By replacing CuPc with plasma polymerized  $\text{CHF}_3$  polymer as hole injection and anode modification layer, the situation can be dramatically improved. By plotting the luminance efficiency against NPB thickness of these two devices, it was noted the amplitude of periodical variance as revealed in their respective EL efficiency



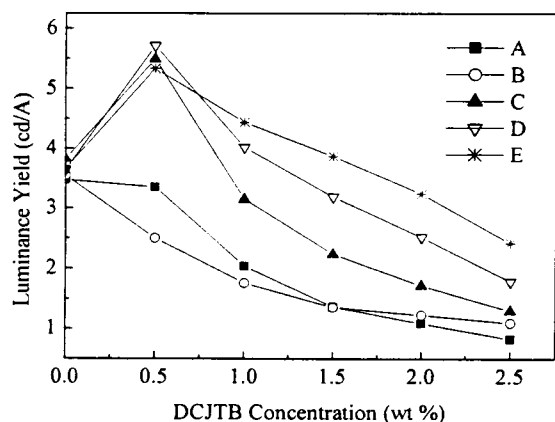
**Figure 4 Current efficiency vs. thickness of NPB layer for CuPc(○) and  $\text{CHF}_3$ (■) devices. Inset: drive voltage as a function of the NPB film thickness.**

appears also less for the device made of  $\text{CHF}_3$  than that of CuPc.

Next we turn to the task of device optimization in attempts to maximize the luminance efficiency ( $\text{cd}/\text{A}$ ), power efficiency ( $\text{lm}/\text{W}$ ) as well as color saturation of DCJTb doped device in terms of  $\text{CIE}_{x,y}$  coordinates. This was accomplished by introducing 5% rubrene as the co-dopant along with the systematic change of dopant concentration of DCJTb. The structural variations in device are depicted in Table 1 with common features of anode of [ITO (170 nm)/ $\text{SiO}_2$  (20 nm)/glass (0.7 mm)] and cathode of [LiF (1 nm)/Al (200 nm)] omitted for clarification. Fig. 5 shows the plots of luminance yield against doping concentration of DCJTb of all five devices. With NPB at 60 nm and

**Table 1 Structural variations in device: glass (0.7 mm)/ $\text{SiO}_2$  (20 nm)/ ITO (170 nm)/HIL/HTL/EML/ETL/LiF (0.1 nm)/Al (200 nm)**

Device	HIL/HTL/EML/ETL
A	CuPc(15nm)/NPB(60nm)/ $\text{Alq}_3$ +DCJTb(x%)(37.5nm)/ $\text{Alq}_3$ (37.5 nm)
B	CuPc(15nm)/NPB(60nm)/ $\text{Alq}_3$ +rubrene(5%)+DCJTb(x%)(37.5nm)/ $\text{Alq}_3$ (37.5nm)
C	$\text{CHF}_3$ /NPB(110nm)/ $\text{Alq}_3$ +DCJTb(x%)(37.5nm)/ $\text{Alq}_3$ (37.5nm)
D	$\text{CHF}_3$ /NPB(110nm)/ $\text{Alq}_3$ +DCJTb(x%)(30nm)/ $\text{Alq}_3$ (55nm)
E	$\text{CHF}_3$ /NPB(110nm)/ $\text{Alq}_3$ +rubrene(5%)+DCJTb(x%)(30nm)/ $\text{Alq}_3$ (55 nm)

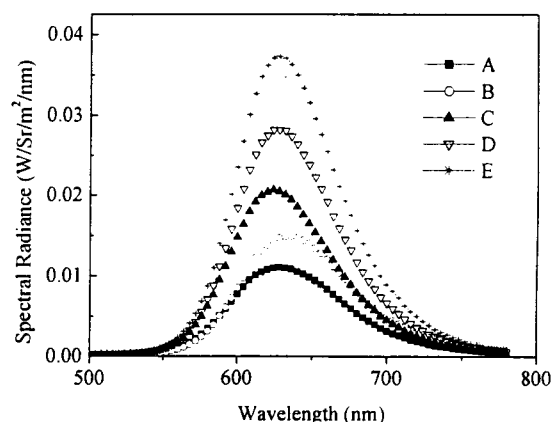


**Figure 5** EL efficiencies as a function of DCJTB doping concentration in Alq<sub>3</sub>

CuPc (15 nm) as HIM, both devices **A** and **B** as a group either without or with 5% rubrene co-doping showed dismally low EL efficiency as compared with devices **C** where NPB was 110 nm and CHF<sub>3</sub> was used as HIM. Dramatic improvement in luminance efficiency of device **C** at nearly all doping levels of DCJTB was noted by simply changing the thickness of NPB from 60 nm to 110 nm without rubrene. Further refinement of the thickness of the doped emitter (to 30 nm) as well as the Alq<sub>3</sub> electron transport layer (to 55 nm) to balance the charge-carriers resulted in further enhancement in efficiency in device **D** and **E**. The presence of 5% of rubrene co-dopant in the emitter layer of Device **E** appeared to prevent the drop of efficiency at higher doping region of DCJTB (from 1% - 2.5%). This is clearly advantageous as a near saturated red emission can be obtained only at DCJTB doping concentration of ~2%. The comparison of overall EL performance of 2% DCJTB doped devices of **A** – **E** is thus tabulated in Table 2. The corresponding EL spectra of these

**Table 2** Overall EL performance of 2% DCJTB doped devices @ 20 mA/cm<sup>2</sup>

Device	LumYield (cd/A)	CIE x	CIE y	Voltage (V)	Efficiency (lm/W)
A	1.09	0.632	0.363	11.34	0.3
B	1.23	0.648	0.350	11.00	0.35
C	1.99	0.635	0.362	10.28	0.61
D	2.52	0.641	0.356	9.23	0.86
E	3.24	0.643	0.354	8.53	1.19



**Figure 6** EL spectra of 2% doped DCJTB devices

devices expressed in spectral radiance of W/Sr/m<sup>2</sup> are overlaid in Fig. 6. The best DCJTB doped red OLED device based on the optimized device structure **E** can achieve a luminance efficiency of 3.24 cd/A at a drive current density of 20 mA/cm<sup>2</sup> with a near saturated color of CIE<sub>x,y</sub> coordinates of 0.643, 0.354.

#### 4. Conclusion

We have successfully fabricated one of the best red DCJTB doped OLED devices where a luminance efficiency of 3.24 cd/A with CIE<sub>x,y</sub> coordinates of 0.643, 0.354 and a power efficiency of 1.19 lm/W at drive current density of 20 mA/cm<sup>2</sup> and voltage of 8.53V was achieved. This jump in performance was accomplished by co-doping with 5% rubrene without needing the extra hole-trapping NPB present in the Alq<sub>3</sub> emitter. The dramatic improvement in efficiency is believed to arise from the synergistic effects of increasing the NPB film thickness, replacing CuPc with CHF<sub>3</sub> plasma polymerized hole injection layer as well as balancing of charge-carriers by device optimization. The enhancement of luminous efficiency in red emitter of OLED should prove to be valuable in realization of the full potential of full color OLED as one of the major flat panel displays of tomorrow.

#### 5. Acknowledgements

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# Efficient Green Fluorescent Dopants For Organic Light-Emitting Devices

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## Abstract

We have discovered a new family of green fluorescent dopants based on coumarin structure -- C-545P and C-545PB. When fabricated as doped emitter in Alq<sub>3</sub> hosted OLED devices, they show significant improvement in thermal properties, luminance efficiency and resistance to concentration quenching over the commercial dopant C-545T.

## 1. Introduction

One of the prototypical green dopants that is found in many of today's organic electroluminescent displays (OLED) on the market is 10-(2-benzothiazolyl)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-benzo[*l*]pyrano[6,7,8-*ij*]quinolizin-11-one, better known as C-545T [1]. It has a solution PL of  $\lambda_{\max}$  514 nm (in 1,2-dichloroethane) with FWHM = 40 nm and a quantum yield ~90%. At optimal doping in *tris*(8-hydroxyquinolino)aluminum (Alq<sub>3</sub>), C-545T was able to achieve a luminance efficiency of 8.7-10.5 cd/A and a power efficiency of 3.3-4.1 lm/W at 20 mA/cm<sup>2</sup> with CIE coordinates of  $x = 0.30-0.33$ ,  $y = 0.63-0.65$ , depending on device architecture and hole injection materials [2]. A sterically hindered di-*t*-butyl derivative, C-545TB with improved thermal and EL properties has also been patented later [3].

According to a recent market survey and cost analysis which was based on the projected worldwide demand of future OLED production, it was estimated that the total material cost of C-545T to the manufacturers alone could run as high as \$2.3 million by year 2003 [4]. One of the reasons for this exorbitant price can be attributed to the fact that most of these dopants are custom designed and meticulously synthesized. Besides, they are also protected by material patents and linked with various license restrictions which could limit their general availability and wide acceptability.

Nevertheless, on the road to commercialization of OLED flat panel displays, it is by no means enough to just consider the EL performance as the cost of various OLED materials that go into the device can be crucial in driving down the panel manufacturing cost and staying competitive in the marketplace amid the ubiquitous and dominant LC displays. At the OLED materials discovery laboratory of NCTU, we have been working on the design and synthesis of alternative and improved dopants that have the potential of replacing the proprietary materials on the market that are either expensive or difficult to obtain. For the purpose of designing a "plug-in" replacement dopant, it is particularly important to pay attention to the quality of emissive color as accepted by the customers at large. We define the "replacement" dopant as one that can improve the thermal properties, PL and EL efficiencies and aging characteristics of an existing dopant in an OLED product but leave the color of the

electroluminescent display unaffected by the replacement. In this paper, we wish to report the discovery of two such replacement dopants based on the generic structure of *coumarin* which are hereby abbreviated as C-545P and C-545PB. It will be shown that these new dopants fabricated as green emitters in Alq<sub>3</sub> based OLEDs could significantly improve the EL efficiency and thermal properties over the corresponding C-545T without compromising its emissive color.

## 2. Molecular Design and Characterization

The molecular design of this new family of dopants -- C-545P and C-545PB, is based on five (*penta*) strategically placed "methyl" steric spacers as contrasted to C-545T which only has four (*tetra*). The "P" family of dopants has the unique feature of having two *gem*-dimethyl groups situated alpha ( $\alpha$ ) to the nitrogen of the *julolidine* bearing the lone pair *p*-orbital. From the perspective of stereochemistry, the lack of molecular symmetry in the pattern of methyl substitution on *julolidyl* ring is expected to prevent molecular aggregation and delay the onset of quenching at high doping concentration as well.

The molecular structures of both C-545P and C-545PB were confirmed by single crystal x-ray diffraction crystallographic analysis using a Bruker Smart CCD instrument and their synthesis and additional spectral characterization are documented elsewhere [5]. The purity was checked by TLC as well as HPLC (> 99%), and their mass spectra revealed no extraneous peak other than the desired parent  $m/e = 444$  ( $M^+$  for C<sub>27</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>S) of C-545P and  $m/e = 556$  ( $M^+$  for C<sub>35</sub>H<sub>44</sub>N<sub>2</sub>O<sub>2</sub>S) of C-545PB, respectively.

Both single crystals of C-545P and C-545PB can be grown from dichloromethane/methanol and whose unit cells were found to belong to the space groups of P2(1)/c and P2(1)/n, respectively. Their perspective 3-D drawings of *dimeric* packing pattern in each of their perspective unit cell (viewed from the z-axis) are compared with that of C-545T [6] in Fig. 1 along with their corresponding chemical structures where all hydrogens are omitted for clarification. From the outset, there appears to reveal little difference or particular trend in going from C-545T to the "P" series in terms of unit cell volume, number of molecules/cell, calculated density or the nearest intermolecular packing distance in Table 1. All of these coumarin dopants show a pattern of D-A/A-D stacking where D represents the donor end of the electron-rich *julolidine* while A represents the acceptor end of the molecule. The most striking feature can only be observed by looking through the stack of each *dimeric* pair in each of the unit cell along the z-direction as graphically depicted in Fig. 1. The two C-545T molecules are seen to stack with the *p*-orbital of nitrogen of *julolidine* of one molecule pointing directly toward the carbonyl end of the coumarin ring of the other and *vice versa*. But, similar stack is made impossible by

Table 1. Comparison of x-ray crystallographic data

	Space group	Volume(Å <sup>3</sup> )	No. of molecules/ unit cell	Density(Mg/m <sup>3</sup> )	Nearest intermolecular packing distane(Å)
C-545T	P2(1)/c	2242	4	1.275	4.2
C-545P	P2(1)/c	2291.5	4	1.289	3.4
C-545PB	P2(1)/n	3077.4	4	1.202	5.2

the steric hindrance exerted by the *gem*-dimethyl groups substituted at  $\alpha$  to the nitrogen as in C-545P and C-545PB. As a result, their D-A/A-D stacks are shifted laterally from each other with the julolidyl ring over the benzothiazole in C-545P and *di*(*t*-butyl)benzothiazolyl rings over each other in C-545PB which appears to be separated apart the farthest in distance.

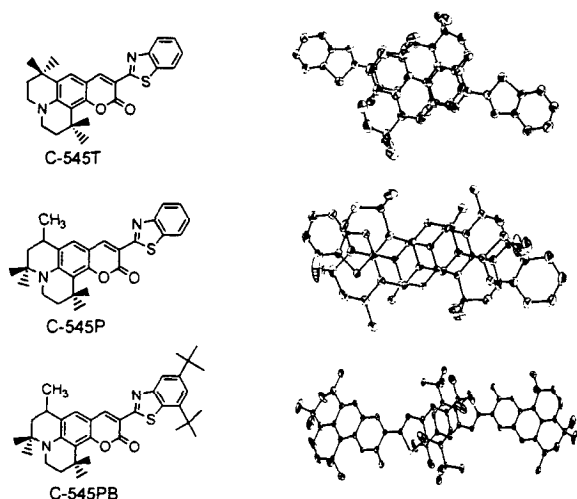


Figure 1. x-Ray single crystallographic images of C-545P, C-545PB and C-545T

### 3. Thermal and Photoluminescent Properties

By thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), the weight loss ( $T_d$ ) of C-545P and C-545PB is less than 5% upon heating to 343°C and 385°C, which are 25°C and 67°C thermally more stable than that of C-545T, respectively. The  $T_g$ 's of C-545P and C-545PB are 102°C and 156°C compared to 100°C of C-545T.

Solution (1,2-dichloroethane) absorption and PL spectra of these dopants are compared in Fig. 2. They are essentially identical with absorption  $\lambda_{max}$  at 480 nm and PL  $\lambda_{max}$  near 514 nm and FWHM about 48 nm. The relative quantum efficiencies are also similar with C-545PB slightly higher than those of C-545P and C-545T. These data confirm that the "P" series dopants enhance the thermal stability of C-545T but do not change fundamentally the photospectroscopic nature of the dye chromophore.

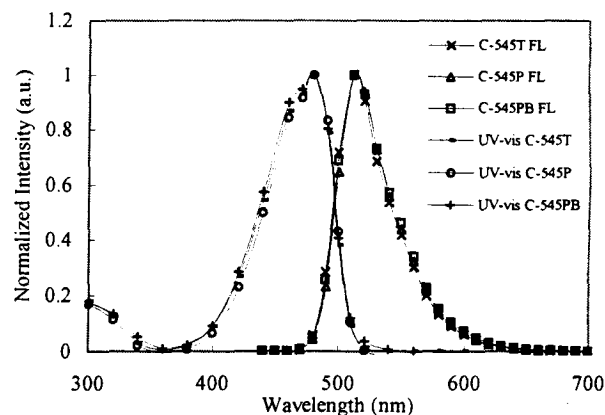


Figure 2. Solution absorption and photoluminescent spectra

### 4. Device Fabrication

The electroluminescent (EL) properties of C-545P and C-545PB are evaluated in the device structure of [ITO (170 nm)|copper phthalocyanine (CuPc, 15 nm)|1,4-bis[*N*-(1-naphthyl)-*N'*-phenylamino]biphenyl (NPB, 60 nm)|v% dopant + Alq<sub>3</sub> (37.5 nm)|Alq<sub>3</sub> (37.5 nm)|LiF (1 nm)|Al (200 nm)], where ITO on glass (0.7 mm) with 20 nm SiO<sub>2</sub> barrier layer was used as the substrate with a sheet resistance of ~10 Ω/□, CuPc as the hole-injection layer, NPB as the hole transport layer (HTL), v% dopant + Alq<sub>3</sub> as the emitter, Alq<sub>3</sub> as the electron transport layer and LiF as the electron-injection layer.

By CV measurements and the onset of absorption calculation, the bandgap energies of C-545P and C-545PB are estimated to be 2.4 eV with HOMO sits at -5.3 eV and LUMO at -2.9 eV that are identical to that of C-545T as well. As shown in Fig. 3, these dopants energy levels which lie right in between the LUMO (-2.7 eV) and HOMO (-5.5 eV) of host Alq<sub>3</sub> are ideal for Förster energy-transfer by exciton trap from Alq<sub>3</sub>.

Prior to the organic deposition, the ITO coated glass plate was patterned by conventional lithography and then thoroughly cleaned by scrubbing, sonication, vapor degreasing, and oxygen plasma treatment. All organic layers were prepared in a vacuum chamber (about 10<sup>-5</sup> Torr) by vapor deposition using resistively heated tantalum boats. Typically, the deposition rate was 4 Å/s and the substrate to evaporant source distance was about 30 cm. The dopant was coevaporated from resistively heated graphite boat which was controlled by a temperature controller and monitored through a thermocouple inserted into the bottom of the boat. By careful control of the dopant boat temperature, it was

possible to precisely coevaporate a determined amount of dopant dispersed into the  $\text{Alq}_3$  emitter layer as measured in v/v %. After the deposition of the organic layers and without a vacuum break, the ultra thin layer 10 Å of LiF followed by 2000 Å of Al was deposited through a patterned shadow mask on top of the organic layers using separately controlled sources to complete the cathode. The active area of the EL device, defined by the overlap of the ITO and the cathode electrodes, was 0.1  $\text{cm}^2$ . The EL emission spectra and current-voltage-luminance (B-I-V) characteristics of the devices without encapsulation were measured in ambient immediately after vacuum break with a diode array rapid scan system using a Photo Research PR650 spectrophotometer and a computer-controlled DC source.

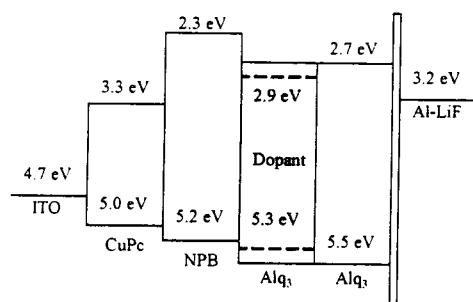


Figure 3. Energy diagram of doped green OLEDs

## 5. EL Results and Discussion

The plots of doping concentration (v/v%) in  $\text{Alq}_3$  vs luminance efficiency (cd/A) of C-545P, C-545PB and C-545T are compared in Fig. 4. Both C-545P and C-545T have their peak efficiencies found at around 1% with C-545P showing better luminance efficiency of 11.3 cd/A. At the optimal concentration, the emissive color of both devices expressed in terms of 1931 CIE coordinates are essentially identical at around  $x = 0.31$  and  $y = 0.65$ . From the profile of the curves, C-545P appears also to be slightly more resistant to concentration quenching than C-545T, particularly in the doping concentration range between 1 – 2% v/v. The turn-on voltage of C545P doped device was 4.5 V and at the drive voltage of 10 V, the device reached a brightness of 12000  $\text{cd/m}^2$ .

The best dopant to resist concentration quenching among the three is found in C-545PB whose luminance efficiency reaches 11.1 cd/A at 1% and remains essentially independent of doping concentration all the way through 4%. The robustness of C-545PB with di-*t*-butyl substituents against concentration quenching is consistent with the expectation of molecular design and the order of molecular packing as illustrated by its single crystal x-ray crystallographic analysis. At current density of 20  $\text{mA/cm}^2$  and a drive voltage of 8.8 V, its luminance was 2319  $\text{cd/m}^2$  with  $\text{CIE}_{x,y}$  coordinates of 0.33, 0.64 and the luminous power was 4.14  $\text{m/W}$ . The B-I-V plots of C-545PB at 3% doping level are shown in Fig. 5 in which the solid PL and EL spectra are overlaid in the insert. The nearly superimposable spectra are indicative of their identical nature of excited states and the extra di-*t*-butyl bulky spacers appear to alleviate the problem of excimer emission.

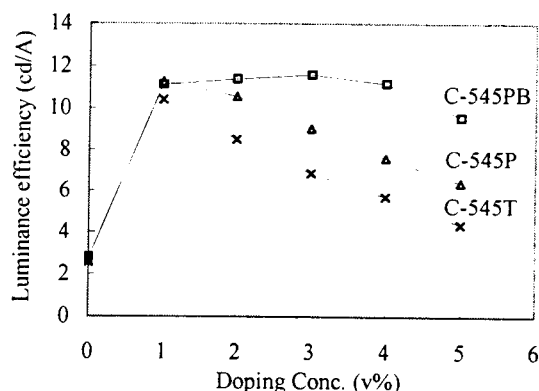


Figure 4. Comparison of doping concentration vs luminance efficiency

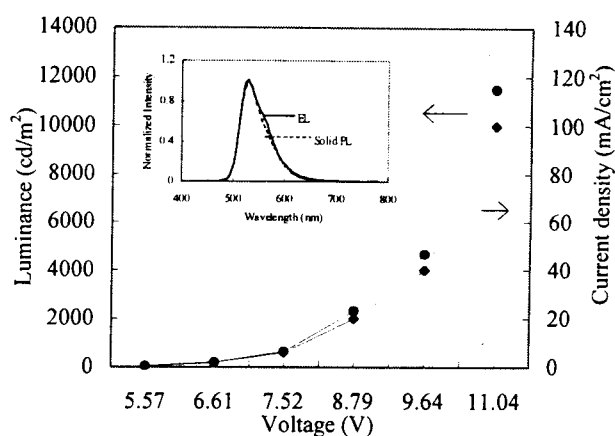


Figure 5. B-I-V of C-545PB at 3% doping in  $\text{Alq}_3$

Fig. 6 shows the comparison of devices doped with these three coumarin dopants at the optimal concentration of 1%, respectively. Like C-545T, both C-545P and C-545PB display a nearly flat response of luminance efficiency (cd/A) with respect to drive current densities from 10  $\text{mA/cm}^2$  to 100  $\text{mA/cm}^2$ . The replacement dopants also show a much steeper rise and early plateau in efficiency than C-545T at low drive current region. This is particularly desirable for the passive-matrix displays where the system would need to be capable of very high luminance at low voltage and to have a "flat" cd/A response with respect to drive voltage for IC chip design.

Finally, in Fig. 7, the emissive colors of C-545P, C-545PB and C-545T expressed in  $\text{CIE}_{x,y}$  coordinates are plotted against their respective doping concentration. The robust nature of the green C-545P as well as C-545PB doped emitter in terms of color variation is also comparable with that of C-545T which is well accepted in the OLED display community.

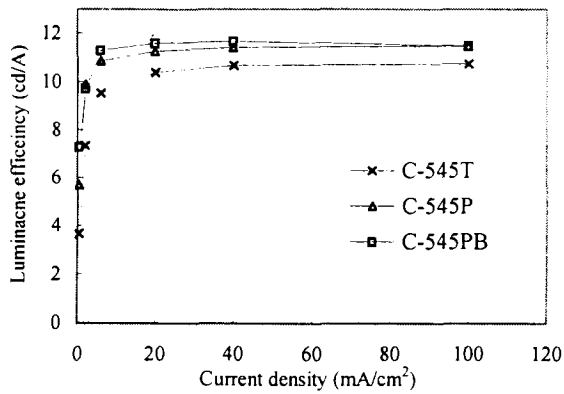


Figure 6. Luminance efficiency vs drive current comparison

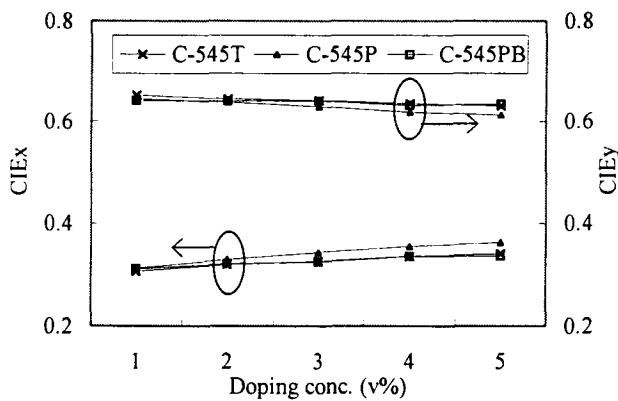


Figure 7. CIE coordinates vs doping conc. comparison

## 6. Conclusion

We have discovered a new family of green fluorescent dopant based on the generic structure of *coumrain* -- C-545P and C-545PB which can be used as "replacement" dopant for the commercial C-545T. When fabricated as doped emitter in Alq<sub>3</sub> hosted OLED devices, these new dopants show significant improvement in thermal properties and luminance efficiency as well as in their resistance to concentration quenching over C-545T.

## 7. Acknowledgement

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## 8. References

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