

# 國立台北科技大學工程學院一百零三學年度第二學期第四次 院學術審議委員會會議紀錄

時間：中華民國一百零四年七月十四日（星期二）中午 12 時

地點：工程學院研討室

主持人：張添晉院長

聯絡人：徐寶崇(4522)

學術審議委員：曾添文、翁文慧（請假）、鍾仁傑（請假）、唐自標、陳貞光、  
陳水龍（請假）、尹世洵（請假）、蘇昭瑾、張淑美、曾昭衡、  
章裕民、丁原智（請假）、張本秀

壹、會議開始

貳、提案討論：

案由一、工程科技博士班有機高分子組博士生林清隆（學號：94679018）  
提學位考試案。

說明：

一、依據工程科技研究所博士班修業辦法第五條研究成果「本所博士班學生在論文口試前，須有兩篇論文在國內外重要學術會議或期刊發表（含已被接受者），**兩篇中必須有一篇在 SCI 期刊發表**，除指導教授外，為第一作者。」規定辦理。

二、林同學已通過資格考試，現依規定提出之博士論文發表檢核表如附件，請審議。

決議：通過。

參、臨時動議：無。

肆、散會（下午 1 時）

國立台北科技大學工程科技研究所博士論文發表檢核表

100 年 6 月 27 日院務會議修訂通過

申請人姓名	學號	組別	申請日期
林清隆	94679018	高分子	104 年 6 月 26 日

一、SCI、EI 期刊論文

序號	論文名稱 (含作者)	論文出處 (含期刊名稱、期(卷)數及頁碼)	發表日期	作者排名 (請填阿拉伯數字)	論文類別 (請勾選)
1	Improved photovoltaic performances of dye-sensitized solar cells with ZnO films co-sensitized by metal-free organic sensitizer and N719 dye	Organic Electronics	2015/06 accept	1 含指導教授 不含指導教授	V SCI <input type="checkbox"/> EI
2	New Fluorous Bipyridine Ligands for Copper-Catalyzed Atom Transfer Radical Polymerization of Methyl Methacrylate in the Thermomorphic Mode	Journal of Applied Polymer Science, Vol. 110, 2531-2537 (2008)	2008	1 含指導教授 不含指導教授	V SCI <input type="checkbox"/> EI
3	Synthesis of Well-defined Block CoPolymer Electrolytes Using Atom Transfer Radical Polymerization	Synthetic Metals, Vol. 154, 21-24 (2005)	2005	2 含指導教授 不含指導教授	V SCI <input type="checkbox"/> EI
4					V SCI <input type="checkbox"/> EI

二、其他期刊 (不屬於 SCI、EI 期刊) 及國內、國際研討會論文

序 號	論 文 名 稱 ( 合 作 者 )	論文出處 (含期刊名 稱、期(卷)數及頁碼)	發表 日期	作者排名 (請填阿拉伯數字)	論文類別 (請勾選)
1	Graphene oxide-Ag nanocomposite: Synthesis ,Characterization and Optical Properties	101 年化學學會 NC008	2012	2	含指導教授 <input type="checkbox"/> 其他期刊 <input type="checkbox"/> 國際研討會 V 國內研討會
2	Characterizatin and Morphology Study MEHPPV-POSS/ PCBM bulk heterojunction on Polymer Solar Cells	100 年高分子學會	2011	1	含指導教授 <input type="checkbox"/> 其他期刊 V 國際研討會 <input type="checkbox"/> 國內研討會
3	Characterizatin and Morphology Study Polythiophene derivatives / PCBM bulk heterojunction on Polymer Solar Cells	2009 TACT	2009	1	含指導教授 <input type="checkbox"/> 其他期刊 <input type="checkbox"/> 國際研討會 V 國內研討會
4	Effect of annealing treatment on morphology of PPV derivatives/fullerene film	97 年化學會 AC161	2008	1	含指導教授 <input type="checkbox"/> 其他期刊 <input type="checkbox"/> 國際研討會 V 國內研討會
5	Synthesis, Characterization and Photoelectric Properties of poly(2-thiophen-3-yl-benzothiazole)	97 年化學會 AC166	2008	2	含指導教授 <input type="checkbox"/> 其他期刊 <input type="checkbox"/> 國際研討會 <input type="checkbox"/> 國內研討會
6	Synthesis of thiophene and benzothiadiazcle contained copolymer and its application on polymer solar cell	96 年化學會 MC0159	2007	2	含指導教授 <input type="checkbox"/> 其他期刊 <input type="checkbox"/> 國際研討會 V 國內研討會
7	Characterization and Morphology Study Polythiophene derivatives / PCBM bulk heterojunction on Polymer Solar Cells	96 年化學會 MC0211	2007	2	含指導教授 <input type="checkbox"/> 其他期刊 <input type="checkbox"/> 國際研討會 V 國內研討會
8	Preparation and Characterization of Conducting Polyaniline/PET Composite film	96 年化學會 OC0024	2007	1	不含指導教授 V 國內研討會

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蔡淑美、郭華

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林清隆	張淑美教授	張淑美	
簽章	張淑美	張淑美	

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Accepted letter

Ms. Ref. No.: ORGELE-D-15-00276R1

Title: Improved photovoltaic performances of dye-sensitized solar cells with ZnO films co-sensitized by metal-free organic sensitizer and N719 dye  
Organic Electronics

Dear Prof. LuYin Lin,

I am pleased to confirm that your paper "Improved photovoltaic performances of dye-sensitized solar cells with ZnO films co-sensitized by metal-free organic sensitizer and N719 dye" has been accepted for publication in Organic Electronics.

Your accepted manuscript will now be transferred to our production department and work will begin on creation of the proof. If we need any additional information to create the proof, we will let you know. If not, you will be contacted again in the next few days with a request to approve the proof and to complete a number of online forms that are required for publication.

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Thank you for submitting your work to this journal.

With kind regards,

Chihaya Adachi, PhD

Editor  
Organic Electronics

Comments from the Editors and Reviewers:

Reviewer #1: The authors have replied and revised the manuscript as reviewer's comments and suggestions. In particular, they explained the argument on the electrochemical impedance analysis in detail. Now, the manuscript could be accepted directly.

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Manuscript Number: ORGELE-D-15-00276

Title: Improved photovoltaic performances of dye-sensitized solar cells with ZnO films co-sensitized by metal-free organic sensitizer and N719 dye

Article Type: Research Paper

Keywords: co-sensitization; dye-sensitized solar cells; incident photon-to-current conversion efficiency; metal-free; organic sensitizer; zinc oxide

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Order of Authors: Shu-Mei Chang, Professor; Ching-Lung Lin; Ying-Jiun Chen; Hung-Chia Wang; Wei-Chen Chang; LuYin Lin

**Abstract:** The co-sensitization is an effective way to enhance the spectral responses of the dye-sensitized solar cells (DSSCs) by using multiple dyes to absorb different parts of the solar spectrum. The organic sensitizers of the triphenylamine derivatives, W3 and W4 dyes, are synthesized with complementary light absorption spectra to that of the commercially available N719 dye. The main absorption peaks are at 400 to 500 nm and 500 to 600 nm for the triphenylamine derivatives and the N719 dye, respectively. Owing to the outstanding cell performance and the higher absorption coefficient, the W4 dye was applied to co-sensitize with the N719 dye. A wide absorption wavelength (400 to 700 nm) for light harvesting is obtained for the co-sensitized ZnO film soaking in the N719 dye for 2 h and subsequently in the W4 dye for 1.5 h, and thereby an light-to-electricity conversion efficiency ( $\eta$ ) value of 4.34% is achieved for the pertinent DSSC, which is higher than those of the cells sensitized with individual W4 dye (3.38%) and N719 dye (3.76%). The co-sensitized ZnO film cannot only possess wider light absorption range but also better sensitizer coverage since the small size of the organic dye (W4) can adsorb on the gaps between the three dimensional N719 dye on the ZnO surface. The electrochemical impedance spectroscopy (EIS) and the incident photo-to-current conversion efficiency (IPCE) are utilized to analyse the interfacial resistance and the wavelength-dependent light-to-electricity efficiency for the DSSCs, respectively.

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# New Fluorous Bipyridine Ligands for Copper-Catalyzed Atom Transfer Radical Polymerization of Methyl Methacrylate in the Thermomorphic Mode

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**ABSTRACT:** The atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) is often carried out under homogeneous conditions, so the residual metal catalyst in the polymer often influences the quality of the polymer and causes environmental pollution in the long run. Novel CuBr/4,4'-bis(R<sub>f</sub>CH<sub>2</sub>OCH<sub>2</sub>)-2,2'-bpy complexes (R<sub>f</sub> = *n*-C<sub>9</sub>F<sub>19</sub>, *n*-C<sub>10</sub>F<sub>21</sub>, or *n*-C<sub>11</sub>F<sub>23</sub>; 2,2'-bpy = 2,2'-bipyridine) are insoluble in toluene at room temperature yet readily dissolve in toluene at elevated temperatures to form homogeneous phases for use as catalysts in the ATRP reaction, and the Cu complexes

precipitate again upon cooling. The CuBr/4,4'-bis(*n*-C<sub>9</sub>F<sub>19</sub>CH<sub>2</sub>OCH<sub>2</sub>)-2,2'-bpy system produced the best results (e.g., polydispersity index by gel permeation chromatography = 1.26–1.41), in that the residual Cu content in the polymer was as low as 19.3 ppm when the ATRP of MMA was carried out in the thermomorphic mode. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2531–2537, 2008

**Key words:** atom transfer radical polymerization (ATRP); catalysts; gel permeation chromatography (GPC)

## INTRODUCTION

The search for recoverable catalysts is a major task in the field of catalysis.<sup>1</sup> Atom transfer radical polymerization (ATRP)<sup>2</sup> is an area of intense research because of the possibility of controlling the molecular weight, polydispersity index (PDI), and end-functionalized synthesis of the final polymer. ATRP typically uses one metal/ligand complex to mediate one growing polymer chain to achieve reasonable reaction rates. Consequently, the resulting polymer is often colored because of the residual metal.

Indeed, one of the limitations of ATRP for industrial development is the presence of a residual transition-metal catalyst in the final polymer, which is likely to cause environmental problems. Different purification methods have been proposed in the recent literature, but the most developed method is the immobilization of the ATRP catalyst onto organic or inorganic polymeric supports.<sup>3</sup> However, immobilized catalysts usually do not effectively

mediate the polymerization process. This may be attributed to a number of factors, including poor contact of the growing radical chain end to the deactivating species<sup>4</sup> and catalyst heterogeneity.<sup>5</sup>

Recently, more efficient heterogeneous,<sup>6</sup> two-component heterogeneous/homogeneous,<sup>7</sup> and thermoresponsive catalysts<sup>8</sup> have been reported. However, the relatively tedious preparation and recovery procedures might pose limitations for industrial applications. In 1999, Vincent et al.<sup>9</sup> reported the first example of a recyclable molecular catalyst for ATRP based on a fluorous biphasic system, which proved to be effective for catalyst recovery with the ATRP method. However, its expensive cost and low efficiency in controlling the molar masses of the polymers prevent it from being used in industrial applications.<sup>10</sup>

Gladysz and coworkers<sup>11,12</sup> recently introduced the solubility-based thermomorphic properties of heavy fluorous catalysts in organic solvents as a new strategy for performing homogeneous catalysis without a fluorous solvent. Catalyst recovery has been achieved by liquid/solid separation.<sup>13</sup> Vincent et al.<sup>14</sup> in 2004 also reported the solubility-based thermomorphic properties of a nonfluorous catalyst that is based on a long hydrocarbon chain (C<sub>8</sub>H<sub>17</sub>). Inspired by these works, we have been wondering if this approach could be extended, for particular cases, to catalysts carrying O-perfluoroalkylated 2,2'-bipyridine (2,2'-bpy) ligands. Reported here is

Additional Supporting Information may be found in the online version of this article.

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# Synthesis of Well-defined Block Copolymer Electrolytes Using Atom Transfer Radical Polymerization

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## Abstract

A series of well-defined hydrophobic-hydrophilic di-blocks has been synthesized under environmentally friendly conditions through atom transfer radical polymerization (ATRP). The hydrophilic block is based on methoxy-capped oligo(ethylene glycol) methacrylate (nEGMA,  $n=4\sim5,8\sim9$ ) and the hydrophobic component is PMMA block. ATRP prepared PMMA-Br ( $M_n$  12000  $M_w/M_n$  1.37) was applied as a macroinitiator. Two solvent systems, acetone and mixed solvents of toluene/H<sub>2</sub>O (1/10), were employed. The acetone mediated polymerization gave the copolymer good control of molecular weight distribution (1.2) and rapid conversion. The toluene/H<sub>2</sub>O mediated polymerization provided the copolymer with a higher molecular weight but a less narrow polydispersity. The maximum conductivity was measured as  $4.8 \times 10^{-5}$  S/cm at 90 °C with di-block copolymer, (PMMA)<sub>x</sub>-b-(PnEGMA)<sub>y</sub> ( $n=8\sim9$ ,  $x/y$  ratio 3/1, contained ~67 wt% PEGMA), doped with Li salt ([EO:Li<sup>+</sup>] = 20:1). The conductivity at room temperature was  $ca\ 2 \times 10^{-6}$  S/cm.

**Keywords:** Atom transfer radical polymerization (ATRP), co-polymer, electrolyte.

## 1. Introduction

Amphiphilic block copolymers in selective solvents undergo macromolecular assembly to generate polymeric micelles and micelle-like aggregates which have been the subject of recent studies.[1–5] Under certain conditions, a net repulsion between the polymer blocks induces micro-phase separation into periodically spaced nanoscopic domains.[6] Selecting the hydrophilic block with a lithium-salt-solvating property enables the formation of a continuous ion-conducting pathway. The hydrophobic block with a solid-like property establishes the mechanical strength of the ion-conducting channels. Thus, this amphiphilic block copolymer is a potential candidate as a solid-state electrolyte for forming a thin film polymer lithium battery.

Most micelle-forming block copolymers prepared to date are based on hydrophilic poly(ethylene oxide) (PEO), and structural variations have been made mainly involving the hydrophobic block for example polyesters, polystyrene, poly(amino acids), poly(propylene oxide), and polyalkanes.[2,7–9] Although synthesized by numerous other research groups [10–12], various controlled structure hydrophilic copolymers have generally been prepared using ionic living polymerization chemistry under strictly anhydrous conditions. Water-soluble copolymers that could be

synthesized directly in aqueous media with precise control over their molecular weight distribution and copolymer architecture are a particularly interesting prospect. A few years ago, Matyjaszewski et al. [14] and Sawamoto et al.[15] independently developed transition metal catalyzed living free radical polymerization, which has subsequently come to be known as atom transfer radical polymerization (ATRP).[14] ATRP is generally initiated with an alkyl halide (R-X) and catalyzed using a transition metal complex, such as CuX/bpy.

The first example of aqueous ATRP was from Matyjaszewski et al., who found that ATRP of 2-hydroxyethyl acrylate can be conducted directly in water to obtain a final polymer with a narrow polydispersity, such as 1.34.[16] Following its discovery this study reported the facile ATRP of in acetone and in mix solvent (toluene/H<sub>2</sub>O) at room temperature, with various methoxycapped oligo(ethylene glycol) methacrylate (nEGMA,  $n=2,4\sim5,8\sim9$ ) (Fig. 1). A remarkably rapid rate of polymerization was observed, along with predetermined molecular weights with narrow molecular weight distributions in the range 1.2–1.4, indicating good living character.

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