第一部分 自由基對前驅物 1-對甲苯磺醯基-苯咪唑及其衍生物之合成與光化學研究

第二部分 4,4′-二羧基聯吡啶釕錯合物之合成及其太陽能電池之應用

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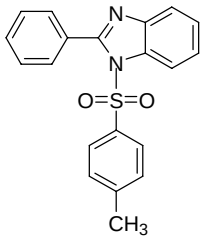
中文摘要

本篇論文主要的部分為一系列自由基對前驅物 1-對甲苯磺醯基-苯咪唑及其衍生物 **55**、**56**、**57** 的合成與低溫 EPR 光譜之研究。化合物 **55** 於 77 K，MTHF 低溫介質，230-325 nm 波長光源照射後，可觀測到一組明顯之三重態 EPR 訊號，其 zfs 參數為$|D/hc|$ = 0.0144 cm^{-1} 與$|E/hc|$ = 0.0020 cm^{-1}。另外化合物 **55** 與自由基捕捉試劑 **MNP** 於常溫，$CDCl_3$ 溶劑，254 nm 波長光源之照光反應，可分別單離出 Photo-Fries 重排產物 **72**、**73**，以及自由基捕捉產物 **Ts-MNP**，此一結果說明了化合物 **55** 在上述的照光條件下，屬於自由基對前驅物物種 **84**，其化學量子產率為 0.24 ± 0.07；另一方面，以 m-xylene 單位連結，屬於兩組三重態自由基對之前驅物 **56**，於照光後可觀測到一組

三重態 EPR 訊號物種 **85** 及 **86**，而非五重態物種，且於 77 K 溫度所測得的 *D´*值較化合物 **55** 來的小; 最後在化合物 **57** 的 77 K (MTHF 低溫介質) EPR 實驗裡，並未如預期觀測到三組三重態自由基對加上一組四重態的 EPR 光譜訊號，這顯示化合物 **57** 於低溫條件下較為不活性，此一部分已經經由低溫介質下照光的 UV/vis 實驗證實 (由日本 Itoh 博士代為完成)。

第二部分為染料敏化 TiO_2 太陽能電池之染料合成研究。藉由相關文獻報導，*Cis*-di(thiocynato)bis(2,2´-bipyridyl-4,4´-dicarboxylate) ruthenium (Ⅱ)，通稱 N3 dye，具有光能轉換效率 (10-12 %) 之高量子效率，為首要合成的目標化合物，另外，也嘗試合成相似衍生物 **92**。進一步的工作須待尋找出取代 N3 dye 且同樣能應用於染料敏化 TiO_2 太陽能電池的化合物。



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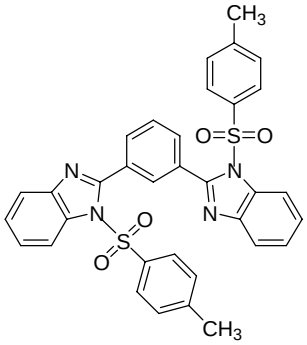

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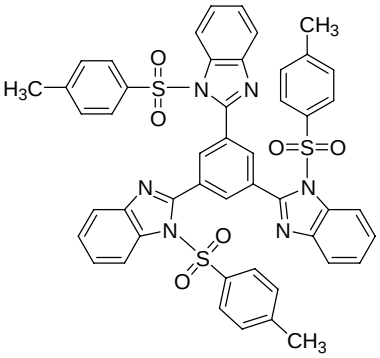

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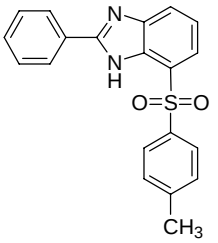

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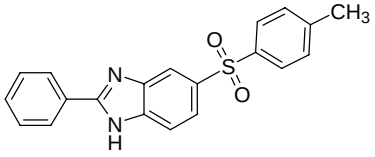

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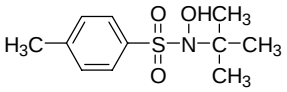
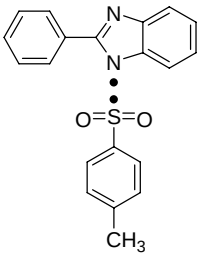


Ts-MNP



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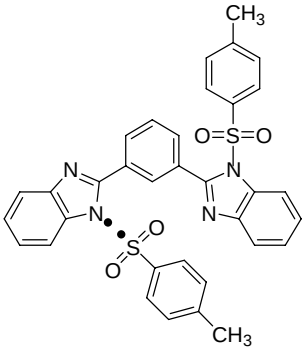

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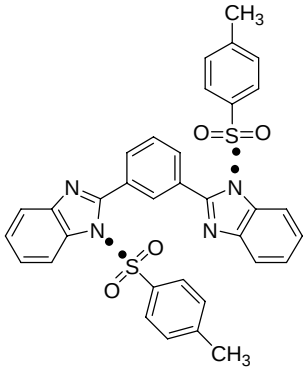

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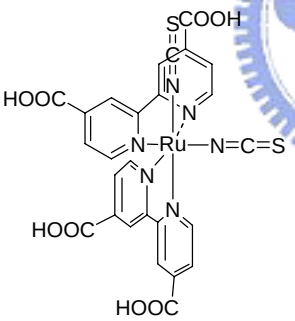
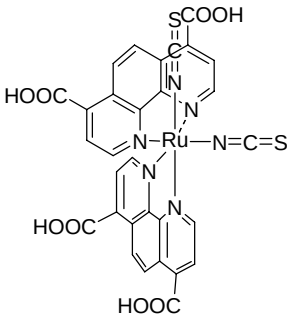


N3 dye



92

Part Ⅰ Synthesis and Photochemistry of a series of radical pair precursors contain 1-toluene sulphonyl benzimidazoles and their derivatives

Part Ⅱ Synthesis of (4,4´-dicarboxylate-2,2´-bipyridyl) ruthenium complexes applied in the solar cells

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Department of Applied Chemistry

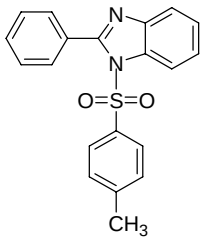
National Chiao Tung University

Abstract

The major part of this thesis is about the syntheses and EPR studies of a series of radical pair precursors (**55**, **56** and **57**) which contain *1*-toluene sulphonyl benzimidazoles as the key components. The photolysis (230-325 nm) of **55** at 77 K in a MTHF matrix gave EPR signals characteristic of a randomly oriented triplet radical pair and its zero-field splitting parameters are determined to be $|D/hc|$ = 0.0144 cm^{-1} and $|E/hc|$ = 0.0020 cm^{-1}, respectively. Furthermore, the photolysis of **55** in the presence of MNP in $CDCl_3$ at room temperature gave not only the Photo-Fries rearrangement products **72** and **73**, but also the radical trapping product, **Ts-MNP**. The results support that **55** is a good precursor for radical pair under photochemical conditions, and the overall photochemical quantum yield for radical pair formation is determined to

be 0.24 ± 0.07. The photolysis of **56,** a precursor for two triplet radical pairs linked by a meta-xylene unit, gave EPR signals which are consistent with a triplet species rather than a quintet species and the *D´* value of **85** and **86** is smaller than **84** taken at 77 K. Finally, the photolysis of **57** at 77 K in MTHF glassy matrix did not show EPR signals of the predicted three triplet states plus a quartet state. Compound **57** was found to be inert under low temperature glassy matrixes which was confirmed by a low temperature UV/vis study at the same matrixes (carried out by Dr. Itoh in Japan).

In part Ⅱ, the preparation of dye sensitized TiO_2 solar cells was carried out. *Cis*-di(thiocynato)bis(2,2´-bipyridyl-4,4´-dicarboxylate) ruthenium (Ⅱ), the N3 dye, which has the record high quantum efficiency (10-12%) for light to energy transfer was out first target compound. A similar analogue, **92**, was also synthesized. Further work is needed before we can find a substitute for the N3 dye in Dye Sensitized Solar Cells.



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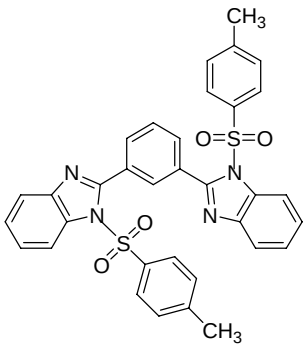

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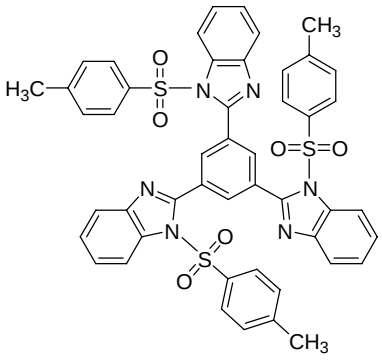

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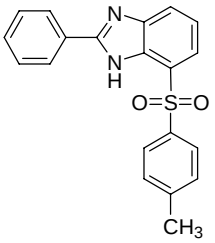

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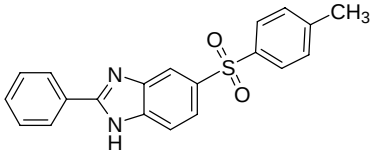

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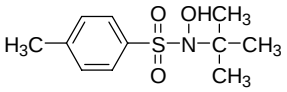

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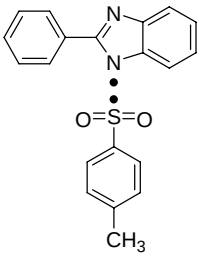

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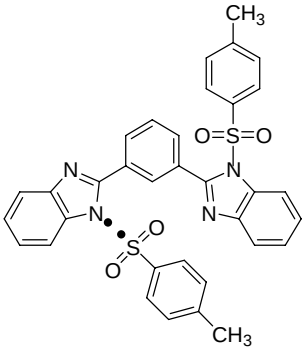

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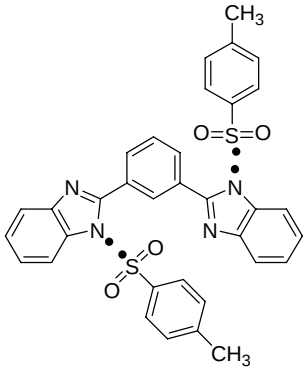

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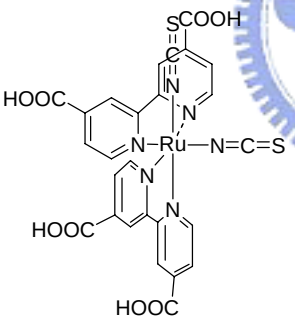
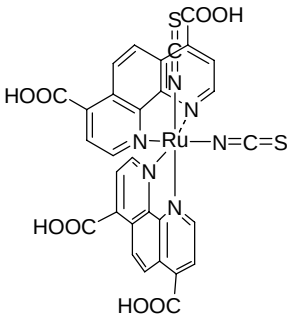


N3 dye



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