

行政院國家科學委員會專題研究計畫 成果報告

利用第一原理之計算方法探討鎘化硒奈米粒子與不同配位
體分子間之電荷移轉機制
研究成果報告(精簡版)

計畫類別：個別型
計畫編號：NSC 95-2112-M-002-052-
執行期間：95年08月01日至96年10月31日
執行單位：國立臺灣大學材料科學與工程學系暨研究所

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報告附件：出席國際會議研究心得報告及發表論文

處理方式：本計畫可公開查詢

中華民國 97年01月28日

利用第一原理之計算方法探討鎘化硒奈米粒子與不同配位體分子間
之電荷移轉機制(結案報告)

NSC(95-2112-M-002-052)

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**The following result has been accepted for publication in Journal of Materials
Chemistry (2008) (SCI, 4.29)**

Introduction

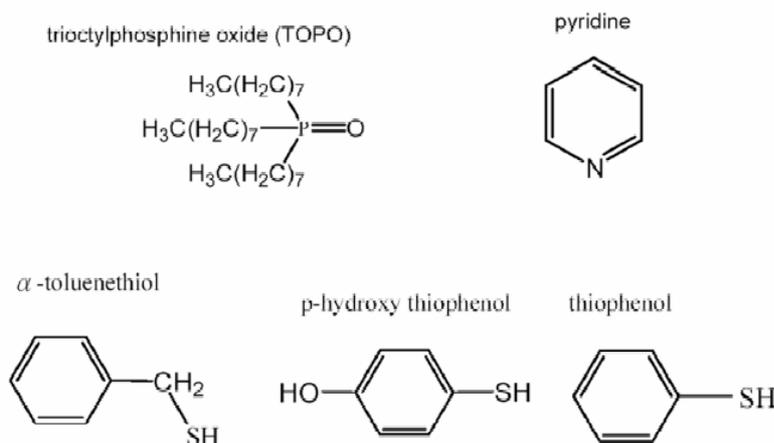
Research concerning the size-dependent optical properties of colloidal semiconductor quantum dots has had increasing interest during the past decade because of their applications: primarily involving CdSe nanocrystals as a platform for photostable luminescent biological labels^{1,2}, solar cells³⁻⁵, and light-emitting devices⁶⁻⁹. The quantum dots are usually surrounded by a ligand capping layer to prevent their coagulation. The nature of the ligand strongly affects the luminescent properties of quantum dots¹⁰. Synthesized CdSe nanocrystals are covered with organic ligands containing bulky (C8-C18) alkyl groups attached through the classic organometallic route¹¹ and the numerous “greener” modifications¹²⁻¹⁷. CdSe nanocrystals that are coated with inorganic materials, such as CdS, ZnS, or ZnSe layers for biological labeling applications, can improve the fluorescence quantum yield¹⁸ and in the case of ZnS or ZnSe, decrease the toxicity of the quantum dot. The use of a shell with higher

band gap materials such as CdS, ZnS, ZnSe, or long chain bulky alkyl group ligands (acting as a potential barrier) is not suitable for applications involving charge transfer. In order to facilitate electron transfer, ligand exchange with a conducting pentathiophene derivative has been reported¹⁹. Other surface ligand exchange reactions on CdSe nanocrystals using pyridines^{10,11,20}, thiols^{10,12,21,22}, amines¹⁵, and derivatized phosphine oxides²³ have also been reported.

Despite the importance of surface exchange reactions with organic ligands for the application of semiconductor nanocrystals, the surfaces of nanocrystals are poorly understood. This is especially true with regard to how the organic capping layer influences the optical and photoelectric properties of CdSe nanocrystals. In this paper, we examine hole transfer from photoexcited CdSe quantum dots to hole accepting ligands: thiophenol and p-hydroxy thiophenol and compare the results with none hole accepting ligands: TOPO and α -toluenethiol. We analyzed these systems with PL spectra and time-resolved PL decay spectra. Our results suggest that thiophenol and p-hydroxy thiophenol transfer the photogenerated hole in CdSe very effectively. The results of current-voltage (I-V) measurement showed the short-circuit current density of thiophenol capped CdSe quantum dots to be an order higher than that of TOPO.

To modify the surface of CdSe quantum dots with different organic ligands, we employed a ligand exchange procedure. The TOPO ligand on the surface of the CdSe quantum dots was removed by repeat pyridine washing. The CdSe quantum dot powder containing TOPO was re-dispersed in pyridine (99%, Acros) to remove TOPO. Washed CdSe quantum dots were precipitated by adding excess hexane (99%, Fluka) and then isolated by centrifugation. This exchange procedure was repeated 6 times. Most of the TOPO on the surface of the CdSe quantum dots are exchanged by pyridine. To remove the surface pyridine, CdSe quantum dots were kept in vacuum over night. To passivate the surface of the quantum dot with thiophenol (99%, Acros) or α -toluenethiol (99%, Acros), bare CdSe quantum dots (0.2g) were re-dispersed in a mixture of 25g benzene (99%, Fluka) and 0.1mole of either thiophenol or α -toluenethiol. The solution was left to stir for 1 day in Ar flow at 70°C. At the end of the exchange reaction, the nanocrystals were recovered as a precipitate by adding an excess of hexane to the solution. This ligand exchange cycle was repeated three times. Finally, the CdSe quantum dots passivated with thiophenol or α -toluenethiol were stored in Ar environment at -10°C. For p-hydroxy thiophenol capped quantum dots, bare CdSe nanocrystals (0.2g) were re-dispersed in a mixture of 25g methanol and 0.3g p-hydroxy thiophenol (99%, Tokyo Kasei). The reaction was left to stir for 1 day in Ar environment at 70°C. After the exchange reaction, nanocrystals were

precipitated by excess hexane. We repeated the above ligand exchange cycle three times. The nanocrystals passivated with p-hydroxy thiophenol were also stored in Ar atmosphere at -10°C .



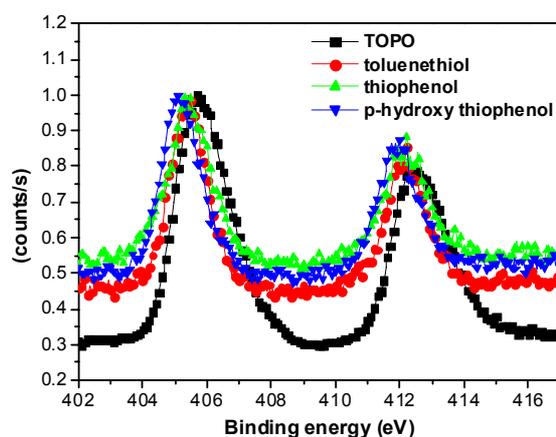
圖五：不同之 ligand 分子之結構

Results and discussion

High-resolution XPS spectra were used to study the surface chemistry of ligand encapsulated CdSe nanoparticles (Figure 1). The TOPO capped CdSe quantum dot has Cd3d_{5/2} peak ranged from 405 to 406eV, with a normal distribution centered at 405.6eV which agrees with previously reported data²⁴ of $405.6 \pm 0.2\text{eV}$ (Figure 1(a)); Se 3d peak ranged from 53 to 56eV, with a normal distribution centered at 54.4eV which also agrees with the literature data²⁴ of $54.6 \pm 0.2\text{eV}$ (Figure 1(b)). The Cd 3d_{5/2} and Cd 3d_{3/2} of XPS spectra of different ligand capped CdSe quantum dots (α -toluenethiol, thiophenol, and p-hydroxy thiophenol) deviates from those of the TOPO capped CdSe quantum dots. This implies their surface states are different from those

of the TOPO capped CdSe quantum dots. However, their Se 3d peak positions rarely deviate from the TOPO capped CdSe quantum dots. It has been reported that the thiol functional groups of ligands will complex with the Cd atoms of the CdSe surfaces to form Cd-S- structures^{10,12,21-22}. A. Puzder et al. calculated the binding energy of phosphine oxide to the CdSe quantum dot facets^{25,26}. They find that the dominant binding interaction is between oxygen atoms in the ligands and cadmium atoms on the quantum dot surfaces. Our results imply the ligands: TOPO, thiophenol, α -toluenethiol, and p-hydroxy thiophenol bind much stronger to the Cd atoms than to Se atoms of the CdSe quantum dots. Oxide peaks as a doublet near 55eV for Se 3d²⁷ and 405eV for Cd 3d²⁴ were not observed for exchanged ligands on CdSe quantum dots. This indicates that the ligand exchange on the quantum dots is complete and the exchanged quantum dots are in good quality. In order to check that the exchanged ligands really bond on the surfaces of CdSe quantum dots, XPS spectra of the C region was taken. The C atoms of saturated aliphatic TOPO were monitored for the C 1s peak position and found to range from 284 to 287eV, with a normal distribution centered about 285.3eV²⁸. The C atoms of aromatic ligands were monitored for the C 1s peak positions of thiophenol, α -toluenethiol, and p-hydroxy thiophenol, and found to center about 284.7eV²⁹. These results imply that the thiophenol, α -toluenethiol, and p-hydroxy thiophenol were successfully capped on the surfaces of CdSe quantum dots.

The 282.8eV peak positions of thiophenol and α -toluenethiol represent the C-Si bond³⁰ from using a silicon substrate in the XPS experiment. To determine the amount of ligands per weight of CdSe quantum dots, elemental analysis was performed. Because there is only one S atom per each molecule of thiophenol, α -toluenethiol, and p-hydroxy thiophenol molecule respectively, we can determine the concentration of ligand by moles of S atoms per 100g CdSe quantum dots (Table 1). If we assume that the TOPO ligands on the surface of CdSe quantum dots were completely replaced by thiophenol, α -toluenethiol, and p-hydroxy thiophenol ligands respectively, then the amount of CdSe per mole of each ligand can be determined. Finally, the moles of S atoms for each ligand on the surface of CdSe quantum dots should be the same. Table 1 shows that the concentration of S atoms for each ligand is similar. This result also indicates the ligand exchange between TOPO and other ligand is complete.



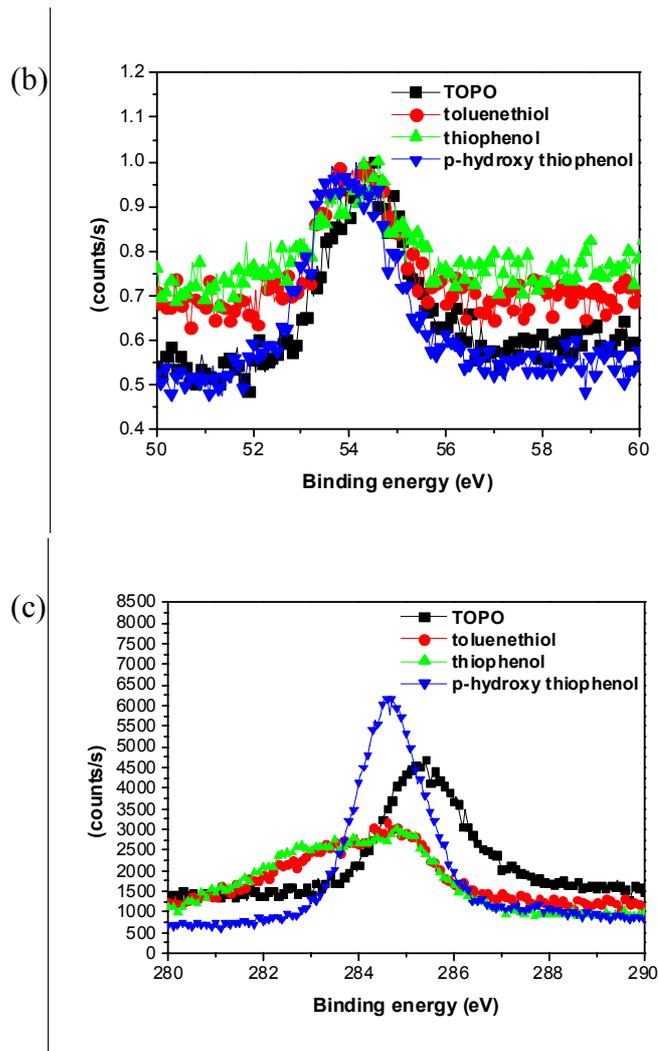
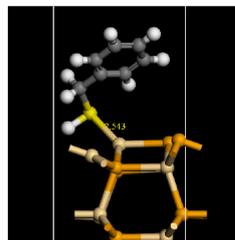


Figure 2. XPS peaks of CdSe quantum dots in three regions: (a) Cd 3d, (b) Se 3d, and (c) C 1s.

Result – CdSe (100) with Alpha



- The adsorption distance : 2.54 Å
- The binding energy : 0.81 eV
- $\Delta Q = 0.54$ (e)
(From S to Cd)

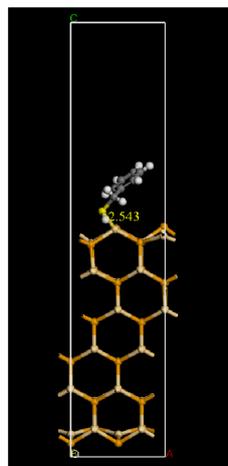


Figure.3 Relaxed structure of CdSe+Thiophenel

	Φ (eV)	E_b (eV)	ΔQ (e)
CdSe	5.38		
CdSe + alpha	5.24	0.81	0.54
CdSe + hydroxy	4.86	0.47	0.28
CdSe + thio	5.18	0.59	0.30
CdSe + topo	4.69	0.97	0.51

Table I. Calculated workfunction, binding energy, charge transfer for CdSe nanoparticles with different ligands.

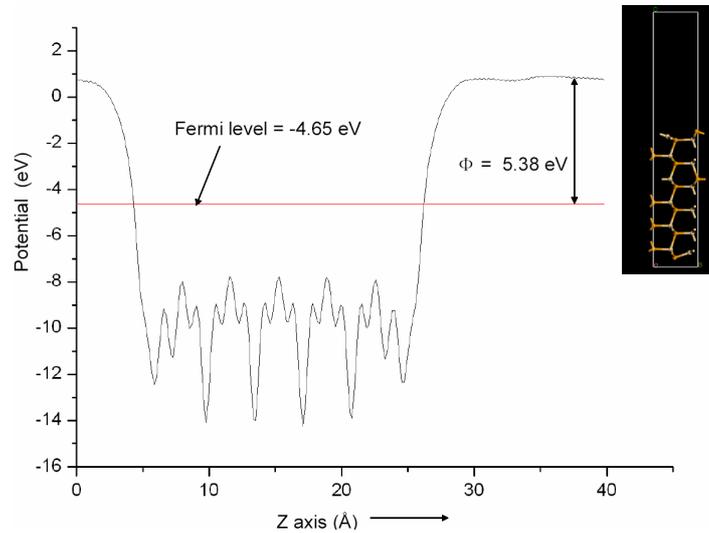


Figure.4 Calculated workfunction profile of CdSe surface.

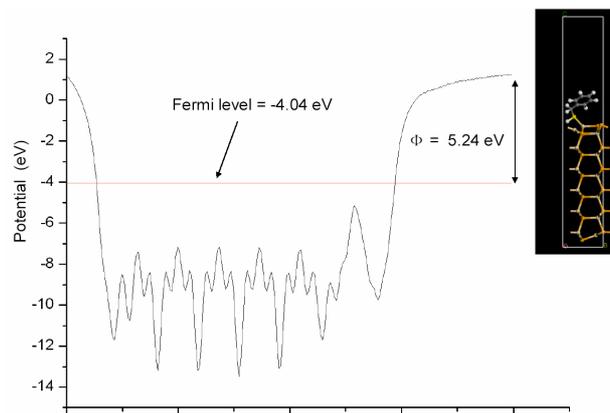


Figure.5 Calculated workfunction profile of CdSe surface after bonding with ligand molecules.

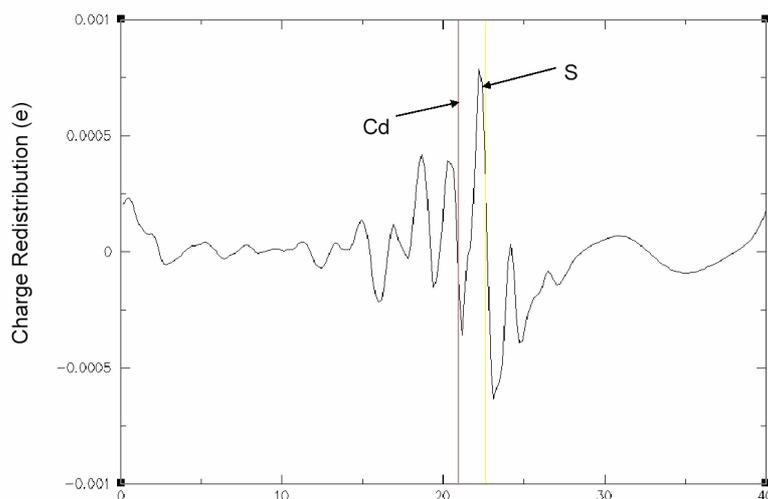
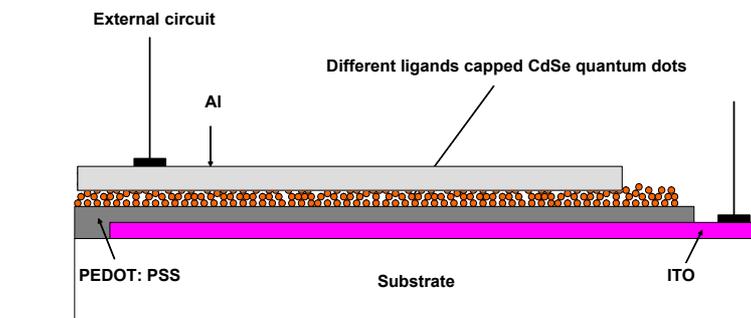


Figure.6 Calculated charge transfer profile of CdSe surface+TOPO.

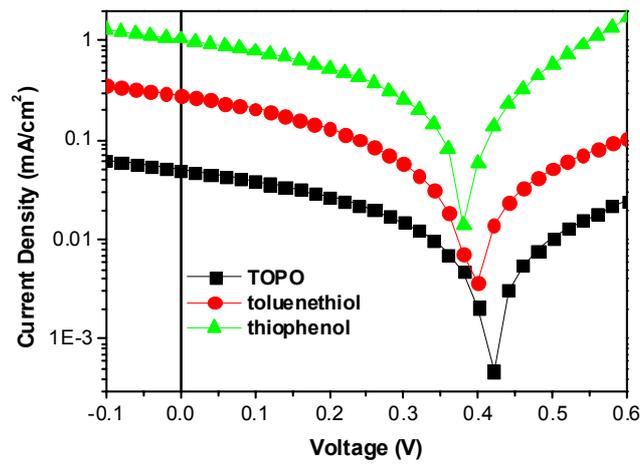
To demonstrate that efficient hole transfer and charge transport are present in aromatic ligand capped CdSe quantum dots, we fabricated a photovoltaic device by spin-coating a solution of 2% by weight CdSe quantum dots onto an indium tin oxide glass substrate coated with PEDOT: PSS, then vacuum deposited an aluminum electrode (Figure 7(a)). Three photovoltaic devices were fabricated using an active layer consisting of TOPO capped CdSe quantum dots, α -toluenethiol capped CdSe quantum dots, and thiophenol capped CdSe quantum dots. Since p-hydroxy thiophenol ligand capped CdSe quantum dots dissolved in ethanol that can attack the PEDOT: PSS layer, a photovoltaic device for p-hydroxy thiophenol ligand was not prepared. I-V characteristics of fabricated devices were generated under illumination of simulated an A.M. 1.5 global solar light at $100\text{mW}/\text{cm}^2$, and shown in Figure 7(b). The I_{sc} of different ligands in increasing order are: thiophenol > α -toluenethiol > TOPO. These results are consistent with the lifetime data described above. π -electrons in the thiophenol can facilitate efficient charge transport and charge separation, thus an order increase in I_{sc} was observed as compared with the I_{sc} of insulating TOPO. The efficient charge separation at the interface between thiophenol ligand and CdSe

quantum dot produces a 3 fold increase in the I_{sc} of α -toluenethiol. This short-circuit current density is considerable when compared to literature results on organic bilayer structure photovoltaic cells³⁹⁻⁴². Device made from thiophenol capped CdSe quantum dots exhibited the highest I_{sc} indicating an efficient hole transfer and charge transport. Figure 7(c) shows the external quantum efficiency (EQE) plots of the CdSe quantum dots photovoltaic devices with different ligands. For each sample, the EQE spectral response matches the lowest energy feature in the absorption spectrum. The shape of the photocurrent spectral response follows the absorption spectrum. No photocurrent is observed for excitation below the band edge suggesting that optical excitation of charges directly out of sub-bandgap trap states makes a negligible contribution to the photocurrent. The spectral response is clear evidence that free carriers originate from electron-hole pairs created within individual quantum dots. The EQEs of thiophenol capped CdSe quantum dots, α -toluenethiol capped CdSe quantum dots, and TOPO capped CdSe quantum dots at 555nm are 12.2%, 3.6%, and 1.7% respectively. This result coincides with the I_{sc} values of I-V measurement under AM 1.5 irradiation which the order of charge transfer efficiency are thiophenol > α -toluenethiol > TOPO. We can conclude that as the bulky ligand (TOPO) capped CdSe quantum dots was replaced by aromatic ligand (thiophenol) capped CdSe quantum dots, the charge transport improves substantially to yield an enhancement by a factor of approximately



10.

(b)



(c)

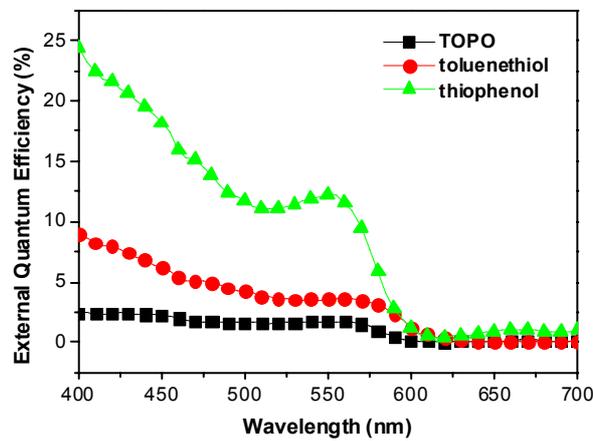


Figure 3. (a) The device structure consists of a CdSe quantum dots with different ligands active layer sandwiched between an aluminum electrode and a hole transport

In addition, the variation of open circuit of the photovoltaic devices also shows a good consistence with the calculated workfunction results.

Conclusion

We have successfully compared the aromatic ligand capped CdSe quantum dots through ligand exchange with TOPO capped CdSe quantum dots using experimental and theoretical method. The photovoltaic devices made of CdSe quantum dots with

different ligands under A.M. 1.5 global solar conditions show that the short-circuit current density of thiophenol capped CdSe quantum dot is 10 times larger than that of TOPO capped CdSe quantum dots and 3 times larger than that of α -toluenethiol capped CdSe quantum dots which indicate very effective hole transport with aromatic ligands and quick charge separation at the interface of CdSe quantum dots. We have demonstrated that directly linking ligands to CdSe quantum dots will enhance their PL quenching and photoelectric properties.

Publication List 2006~2007

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出席國際會議研究心得報告及發表論文

(NSC 95-2112-M-002-052)

台大材料系 陳俊維(Chun-Wei Chen)

本次會議是在於 7/11~7/19 於捷克之布拉格所舉行之 47th microsymposium ADVANCED POLYMER MATERIALS FOR PHOTONICS AND ELECTRONICS, 由 Institute of Macromolecule 及捷克應用化學學會舉辦。此會議是在高分子電子材料領域有多年傳統之會議，每年會針對高分子電子材料不同應用，作特別之討論。值得一提的是領域，主辦單位 Institute of Macromolecule 為世界上第一個隱形眼鏡發明之單位。此會議此次主要是針對有機太陽能電池之理論與實驗研究，作特別之探討。

比較特別之 talk 為

1. Material requirements for organic solar cells. The structure - property correlation of low-bandgap transporters **by C.J. Brabec** (*Konarka Technologies, Linz, Austria*)
2. High open-circuit voltage photovoltaic devices based on modified carbon nanotube blend - polybithiophene heterojunctions
3. Optoelectronic devices with defined polymer-polymer heterojunctions by **D. Neher** (*University of Potsdam, Germany*)
4. Managing photoexcited states in conjugated polymers by **G. Wegner** (*Max Planck Institute of Polymer Research, Mainz, Germany*)
5. Bistable optical recording and fluorescence patterning in a highly luminescent polymer film **S.Y. Park** (*Seoul National University, Korea*)
6. Multiple functionalities of pendent charge transport moiety in electroluminescent conjugated polymers by **S.A. Chen** (*National Tsing-Hua University, Hsinchu, Taiwan*)
7. Charge carrier transport in ambipolar organic field-effect devices by **W. Brütting**

(University of Augsburg, Germany)

8. Novel digital nonvolatile memory devices based on semiconducting polymer thin films
9. Managing photoexcited states in conjugated polymers
10. Non-coherently excited photon up-conversion: sun-spectrum engineering and solar cells
11. Optoelectronic devices with defined polymer-polymer heterojunctions
12. Energy transfer and charge trapping processes in poly(*N*-vinylcarbazole) doped with iridium complexes
13. Electronic transport properties vs structural organization of thin layers of different regioregular polythiophene derivatives: effect of chain length and processing conditions

本次會議，我所發表之論文題目為” Nanostructured polymer/metal oxide solar cell by all-solution processes”，主要是利用 ZnO 奈米柱與導電高分子及 TiO₂ 奈米柱混成材料所製成之太陽能電池，此種材料為非常環保之太陽能電池材料，免於過去以 CdSe 為主之有機及無機混成材料為主。我們的結果已於日前發表於 *Journal of Materials Chemistry*, 17, 4571, 2007 (SCI, 4.29)

感想與心得

這是令人感覺非常愉快的一次雙邊交流活動，主辦單位熱心親切，安排議程與參訪活動內容豐富，會議地點環境幽美，加上優質的食宿交通，除了讓大家有機會從事科學問題之討論，也深深體會到捷克其人文涵養的厚實。在日新月異的科學領域裡，積極推展國際合作與資源分享，在提高我們的競爭力與能見度上的確有其重要性。

攜回資料名稱及內容

攜回資料為 Proceedings : ADVANCED POLYMER MATERIALS FOR PHOTONICS AND ELECTRONICS，內容含所有會議議程及論文摘要。