

## 摘要

本研究主要是在聚 3-己烷基噻吩高分子 (poly(3-hexylthiophene), P3HT) 末端進行缺電子基團 (electron-deficient moieties, EDM) 的改質，並從薄膜電晶體與太陽能電池元件效率上的差異瞭解 EDM 末端修飾所帶來的效應。另一方面，則是設計出一系列在薄膜電晶體應用上具有高電洞遷移率與傑出熱穩定性的 thienoisindigo (TIG) 予體-受體共聚高分子。而其可分為三部分。

第一部分，在 P3HT 末端修飾方面，為了維持能促使 rr-P3HT 獲得高效率元件表現的光吸收能力、分子鏈堆疊與電性，各 P3HT 控制在具有高規則度與大於 50 kD 的重量平均分子量之情況。未封端 P3HT-end-H/Br 是以簡易的 GRIM method 聚合，之後，再利用 *in-situ* method 轉換為末端具有 EDM 功能性缺電子基團改質的 end-functionalized P3HT。在 EDM 直接與相連的 3-hexylthiophene 片段參與共軛之下，透過其拉電子能力的驅使，end-functionalized P3HT 可些微降低能階與提升末端附近的共面性。然而，在分子鏈排列時，相較於具有立體位阻而會破壞分子鏈間堆疊的 3,4,5-triphenyl-4H-1,2,4-triazole (TAZ)，具有平面結構的 2,5-diphenyl-1,3,4-oxadiazole (OXD) 末端基，則能促使 P3HT-end-OXD 沿著側鏈方向形成較 P3HT-end-H/Br 緊密的堆疊，而可增加薄膜的結晶度。因此，相較 P3HT-end-TAZ ( $\mu_h = 1.8 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ )，P3HT-end-OXD 薄膜電晶體的電洞遷移率，可由 P3HT-end-H/Br 的  $2.9 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  改善至  $3.8 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ 。

第二部分，我們也將先前所使用的 P3HT 應用至以 PCBM 為受體的太陽能電池系統。同樣地，透過 EDM 拉電子能力的驅使，end-functionalized P3HT 不但可些微降低 HOMO 能階以使元件獲得較高

的開環電壓，並且能因末端處結構共面性的改善而誘導能量轉移的發生，以致延長激子生命週期供予激子擴散至兩相界面進行解離。再者，與 PCBM 混摻時，P3HT-end-OXD 可在不改變兩相相分離的情況下，透過其末端微量平面的 OXD 提供如添加劑之功效，改善分子鏈規則度，使混摻薄膜能具有較高的吸收係數與載子傳輸特性，進而有效地貢獻於元件的短路電流密度與填充係數。因此，P3HT-end-OXD:PCBM 太陽能電池的功率轉換效率，可由原先 P3HT-end-H/Br:PCBM 的 3.28 % 提升至 4.24 %。反之，P3HT-end-TAZ:PCBM 太陽能電池則會因由末端龐大 TAZ 破壞混摻薄膜結晶度與導致 PCBM 聚集而具有極差的效率 (PCE = 0.5 %)。

第三部分，在 TIG 予體-受體共聚高分子分子設計方面，我們以延伸主鏈共軛長度與增強分子鏈間吸引力之概念開創一系列具有高遷移率的 TIG 予體-受體共聚高分子。選擇 thieno[3,2-*b*]thiophene (TT) 或 (*E*)-2-(2-(thiophen-2-yl)vinyl)thiophene (TVT) 兩者雜環分子為予體與 TIG 共聚，合成出四個新式的 TIG 予體-受體共聚高分子。再者，並也使用噻吩分子封端，以消除末端基缺陷對電晶體效率的影響。這一系列 TIG 共聚高分子，不但有延長至 1300 nm 的寬廣吸收光譜，並且具備匹配金電極的 HOMO 能階 (-5.15 至 -5.29 eV) 可供電洞注入。當適宜的條件下，相較於 C8C12TIG-TVT 與 C10C14TIG-TVT 的 0.29 與 0.42 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>，C8C12TIG-TT 可展現出一般未經特殊製備的 TIG 高分子電晶體中最高 0.69 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> 的電洞遷移率。這個效率的表現，是歸因於 TT 有相較 TVT 高的平面度與強的供電子能力所導致。因此，在所有 TIG 系列高分子文獻，C8C12TIG-TT 分子鏈在基材表面可形成具有 3.528 Å 最短  $\pi$ - $\pi$  堆疊距離之規則層狀的 edge-on 排列構型，而能獲得有效的分子鏈間載子傳遞。然而，值得注意的是，C8C12TIG-TT 分子鏈的排列方向有一臨界排列轉變，當薄膜退火溫度高到 300 °C 時，則會使得更多含量的分

子鏈以 face-on 型態方式堆疊，造成遷移率的下降。此外，這一系列 TIG 共聚高分子亦能伴隨有不會受到熱效應牽絆的良好電流開關比與閾值電壓 ( $I_{\text{on}}/I_{\text{off}} > 10^4$  與  $1.5 < V_{\text{th}} < 2.8$ )，而具有相當傑出的熱穩定性。

在 P3HT 末端改質的研究結果，顯示出分子鏈末端基亦是對元件效率不可忽略的影響因素之一，而其缺陷可透過適當的 EDM 加以修飾，但改善的功效卻會取決於 EDM 的大小和平面性。而這個微結構修飾於 P3HT 的成功，亦反映出此方法可延伸應用至其它高分子材料的潛力，以再提升元件效率。至於，在 TIG 共聚高分子部分，則可為其於薄膜電晶體應用上帶來進一步的進展，以及對這類型高分子的分子設計提供一些有價值的參考資訊。



## Abstract

The study mainly explore the effect of modified poly(3-hexylthiophene) (P3HT) by end-capping with electron-deficient moieties (EDM) on thin film transistor (TFT) and polymer solar cell (PSC) performance. On the other hand, it demonstrates to design a series of high hole mobility and excellent thermal stability thienoisindigo (TIG)-based D-A copolymers for TFT application. This research can be divided into three parts.

Firstly, for end-group modification of P3HT, all P3HTs were controlled with high regioregularity and appropriate weight-average molecular weight (~50 kD) to maintain the original absorption capability, chain packing and electric property of rr-P3HT for efficient device performance. The uncapped P3HT-end-H/Br was polymerized *via* GRIM method and then converted to the end-functionalized P3HTs with EDMs in chain ends by *in-situ* method. Since EDMs participate the conjugation with nearly linked 3-hexylthiophene units, end-functionalized P3HTs can slightly lower energy levels and improve coplanarity of successive 3-hexylthiophene units near chain ends due to its electron-withdrawing capability. However, as polymer chains arrange, compared to the interruption of interchain packing by the steric hindrance of 3,4,5-triphenyl-4H-1,2,4-triazole (TAZ) in P3HT-end-TAZ, 2,5-diphenyl-1,3,4-oxadiazole (OXD) end-groups with the planar structure can promote P3HT-end-OXD form closer packing along the side chain direction than that of P3HT-end-H/Br, leading to the enhanced crystallinity in the thin film. For this reason the hole mobility of P3HT-end-OXD-based TFT can improve from P3HT-end-H/Br with a value of  $2.9 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  to  $3.8 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  relative to P3HT-end-TAZ ( $\mu_{\text{h}} = 1.8 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ).

Secondly, we also apply these previously used P3HTs to the PSC system with PCBM as acceptor. Similarly, end-functionalized P3HTs by electron-withdrawing capability of EDM end-groups not only can slightly lower HOMOs for the enhanced open-circuit voltage ( $V_{oc}$ ) of PSCs, but also can extend lifetime for exciton migration to the two-phase interface in the photoactive layer for efficient exciton dissociation due to the induced energy transfer by the improved coplanarity near chain ends. Furthermore, when blending with PCBM, planar OXD end-groups provide similar function as nonvolatile additives to assist P3HT-end-OXD in improving chain ordering without change of extent of phase separation in the blend film with PCBM, resulting in a promotion of absorption coefficient and charge carrier transport property for an effective contribution to short-circuit current density ( $J_{sc}$ ) and fill factor (FF) of the resulting device. Therefore, power conversion efficiency (PCE) of P3HT-end-OXD:PCBM-based PSC can be enhanced from P3HT-end-H/Br:PCBM of 3.28 % to 4.28 %. Whereas, P3HT-end-TAZ:PCBM-based PSC has the worst PCE of 0.50 % as a result of the disrupted crystallinity and unfavorable PCBM aggregations by bulky TAZ end-groups.

Thirdly, for the molecular design of TIG-based D-A copolymers, we develop a series of high mobility TIG-based D-A copolymers by the concept of extension of  $\pi$ -conjugation in the backbone and enhancement of interchain interaction of D-A moieties. The fused molecule, thieno[3,2-*b*]thiophene (TT) or (*E*)-2-(2-(thiophen-2-yl)vinyl)thiophene (TVT) was employed as the donor moiety in the synthesis of four new TIG-based D-A copolymers. Furthermore, thiophene molecules are introduced as end-cappers for these copolymers to

eliminate the influence of end-group defects on TFT performance. The series of TIG-based copolymers not only has a broad absorption band extended up to 1300 nm, but also gives a matched HOMO level (-5.15 to -5.29 eV) with gold electrodes, which is beneficial for charge injection. Compared to C8C12TIG-TVT ( $\mu_h = 0.29 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) and C10C14TIG-TVT ( $\mu_h = 0.42 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ), a highest hole mobility up to  $0.69 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  among reported TIG-based PTFTs with the general device fabrication can be achieved by C8C12TIG-TT under optimum conditions. This record performance is ascribed to TT with more planar structure and more electron-donating property than TVT. Therefore, C8C12TIG-TT chains take the ordered lamellar edge-on packing structure relative to the substrate with a shortest  $\pi$ - $\pi$  stacking distance of 3.43 Å among reported TIG-based copolymers for efficient interchain charge transport. However, it is worth noting C8C12TIG-TT at annealing temperature of 300 °C has a critical alignment transition of chain packing to form more chains with a face-on configuration, leading to a decrease in the mobility. In addition, the series of TIG-based copolymers also exhibits an outstanding thermal stability on device performance without annealing temperature-dependent on/off ratio and threshold voltage effects ( $I_{\text{on}}/I_{\text{off}} > 10^4$  and  $1.5 < V_{\text{th}} < 2.8$ ).

The effect of end-group modification of P3HT demonstrates that the structural defect of the polymer chain ends is a non-negligible influence on device performance, but can be tailored by appropriately functional EDMs. However, the efficacy depends strongly on the structure of EDM, such as size and planarity. Hence, the success of the fine modification in P3HT might also provide a promising route for other polymers for enhancement of device

performance. In the case of TIG-based D-A copolymers, the result provides further progress towards the use of TIG-based D-A copolymers for PTFT application and gives some valuable information for molecular design on this type of polymer.

