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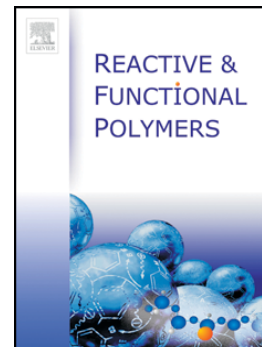
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Wei-Wei Liang, Yu-Shun Lin, Yu-Ying Lai, Yen-Ju Cheng

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Synthesis, characterization, and photovoltaic applications of donor-acceptor alternating and random copolymers based on a ladder-type nonacyclic structure

Wei-Wei Liang, Yu-Shun Lin, Yu-Ying Lai\* and Yen-Ju Cheng\*

Department of Applied Chemistry, National Chiao Tung University, 1001 University Road, Hsin-Chu, 30010 Taiwan

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E-mail: [yjcheng@mail.nctu.edu.tw](mailto:yjcheng@mail.nctu.edu.tw); [yuyinglai@nctu.edu.tw](mailto:yuyinglai@nctu.edu.tw)

Abstract

A nonacyclic building block **TPTPT** with the alternate thiophene and benzene subunits fastened by four bridging methylene groups was connected with various acceptors including diphenylquinoxaline (**QX**), thieno[3,4-c]pyrrole-4,6(5H)-dione (**TPD**), thieno[3,4-b]thiophene (**TT**) to afford donor-acceptor (D-A) alternating copolymers- **PTPTPTQX**, **PTPTPTPD**, and **PTPTPTTT** and random copolymers- **PTPTPTQX11**, **PTPTPTQX12**, **PTPTPTPD11**, **PTPTPTPD12**, **PTPTPTTT11**, and **PTPTPTTT12**. The thermal, optical, and electrochemical properties of these copolymers were measured and compared. The random copolymers all have higher glass transition temperature ( $T_g$ ) than the corresponding alternating copolymers. ONIOM (our own n-layered integrated molecular orbital and molecular mechanics) calculations suggest that the increase of planarity in the random copolymers arises from the introduction of thiophene units intercalating between donor and acceptor moieties. Bulk heterojunction (BHJ) polymer solar cells (PSCs) were fabricated on the basis of ITO/PEDOT:PSS/polymer:PC<sub>71</sub>BM/Ca/Al device configuration. When the acceptor is **QX** or **TPD**, the resultant alternating copolymers performed superior than the random counterparts. When the acceptor is **TT**, the high content of **TT** seems to be harmful to the device efficiency, which may relate with the strong quinoidal character of the **TT** unit. Overall, for the **TPTPT** core structure, in the used acceptors, the alternating-copolymer arrangement

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