

## Design and Synthesis of a New Non-Fullerene Acceptor for High-Performance Photomultiplication-Type Organic Photodiodes

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Herein, a new non-fullerene acceptor is designed and synthesized by introducing thienylenevinylene (TV) groups into the conventional 2,2' - [[6,6,12,12-tetrakis(4-hexylphenyl)-6,12-dihydrodithieno[2,3-d':2',3' - d']-s-indaceno[1,2-b:5,6-b']dithiophene-2,8-diyl]bis[methyldiyne(3-oxo-1H-indene-2,1(3H)-diylidene)]]bis[propanedinitrile] (ITIC) structure. As a result, TV-ITIC acceptor has an extended  $\pi$ -conjugation length, which not only lowers energy bandgap and lowest unoccupied molecular orbital (LUMO) level, but also increases the volumetric portion of the aliphatic chain, improving its hydrophobic properties, which improves miscibility with the donor polymer semiconductor, poly(3-hexylthiophene-2,5-diyl) (P3HT). All of these photophysical properties are beneficial for efficient exciton separation, electron trapping, and charge injection abilities of PM-OPDs compared to those obtained with conventional ITIC. Because of such synergetic contributions of TV-ITIC to the photomultiplication mechanism, the resulting optimized PM-OPD exhibits a high external quantum efficiency (>74,000%) and a large specific detectivity (>10<sup>12</sup> Jones).