Strategy for Improved Photoconversion Efficiency in Thin Photoelectrode Films by Controlling π-Spacer Dihedral Angle

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Benzo[*c*][1,2,5]thiadiazole (BT) has been used in dye-sensitized solar cells (DSCs) for its light-harvesting abilities.^[1,2] However, as a strongly electron deficient unit, BT causes rapid back electron transfer (BET), which in turn lowers the photo conversion efficiency (PCE) of devices.^[3] Herein, we report a powerful strategy for retarding BET by controlling both the photoelectrode thickness and π -spacer dihedral angle. To achieve this, we introduced planar (**BT-T**) or twisted π -spacers (**BT-P**, **BT-MP**, and **BT-HT**) between BT units and anchoring groups, and used different photoelectrode thicknesses between 1.8 and 10 µm (Fig. 1).

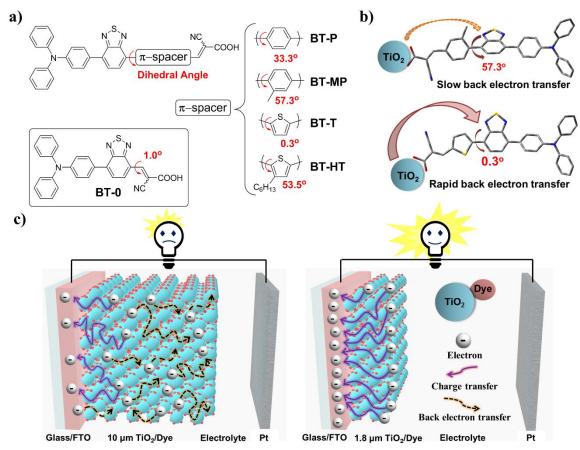


Figure 1. a) Chemical structures of BT-series showing dihedral angles between BT and π -spacers. Schematic figures: b) back electron transfer with different π -spacers, and c) enhancement of charge collection efficiency in a thin 1.8 µm photoelectrode compared with a thicker 10 µm photoelectrode.

Computational and experimental results show that twisted π -spacers were more efficient at retarding BET than the planar π -spacer. However, BET was found to be less important than expected, and light harvesting efficiency (LHE) played a critical role as the thickness of the photoelectrode decreased because charge collection efficiency was enhanced. The planar dye **BT-T** obtained the highest LHE, this value remained unusually high even in 1.8 µm photoelectrodes. As a result, **BT-T** gave a PCE of 6.5% ($J_{sc} = 13.56 \text{ mA/cm}^2$, $V_{oc} = 0.67 \text{ V}$ and FF = 0.72) in thin 1.8 µm photoelectrodes with 3.5 µm scattering layers, which represented a roughly 40% enhancement compared to the PCE in 10 µm photoelectrodes (4.76%). Overall, these results provide a novel approach to achieving ultrathin and highly efficient flexible DSCs.

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