# Supporting Information

# Electropolymerization of Poly (2H,2′H,4H,4′H-3,3′-SpiroBi [Thieno[3,4-b][1,4]Dioxepine on Counter Electrode for Platinum-free Dye Sensitized Solar Cells

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**Synthesis of spiroBiProDOT monomer**

An oven dried two neck 500 mL round bottom flask adjusted with Soxhlet extractor containing 4 Å molecular sieves under nitrogen atmosphere was charged with 300 mL of dry toluene, 3,4-DMT (3,4-dimethoxy thiophene, 4 g, 0.028 mol), pentaerythritol (23g, 0.17 mol), p-TSA (p-toluenesulphonic acid, 0.52 g, 2.76 mmol), consecutively, followed by refluxing for 3 days. Reaction mixture was monitored by TLC using 50 % toluene in hexane as an eluting solvent mixture. The black color mixture was cooled down and concentrated using rotary evaporator. Column chromatography was carried out to purify the spiroBiProDOT monomer using 200 mesh silica gel and dichloromethane as a solvent. Solid white powder with 69 % efficiency yield was calculated. $^{1}$H NMR (400 MHz, $CHCl_3$-$d_1$) δ: 4.08 (s, 8 H), 6.47 (s, 4 H).

**Table S1.** Photovoltaic results of the solar cells with modified $FTO_{poly\text{-}(spiroBiProDOT)}$ counter electrodes fabricated by two-step electropolymerization based on two applied potentials of 1.1 V and 10 V for various times.

| Applied potential (V) | Time (min) | Thickness (μm) | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | *FF* | $\eta$ (%) |
|---|---|---|---|---|---|---|
| 1.1<br>10 | 10<br>20 | 4.2-4.5 | 0.726 ± 0.03 | 14.76 ± 0.45 | 0.73 ± 0.015 | 7.9 ± 0.08 |
| 1.1<br>10 | 10<br>10 | 2.9-3.2 | 0.71 ± 0.05 | 11.58 ± 0.29 | 0.71 ± 0.22 | 6.3 ± 0.16 |
| 1.1<br>10 | 10<br>30 | 5.1-5.4 | 0.70 ± 0.11 | 10.12 ± 0.20 | 0.70 ± 0.17 | 5.5 ± 0.18 |

**Table S2**. Comparison of photovoltaic parameters of DSSCs based on Pt and polymer based counter electrodes.

| | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | *FF* | $\eta$ (%) | Ref. |
|---|---|---|---|---|---|
| Pt | 0.756 | 14.821 | 0.5795 | 6.493 | [1] |
| Pt + rGO | 0.753 | 17.553 | 0.5583 | 7.115 | |
| Pt | 0.720 | 16.47 | 0.62 | 7.35 | [2] |
| PEDOT (Solid state polymerization) | 0.710 | 16.26 | 0.61 | 7.04 | |
| Pt | 0.69 | 13.0 | 67.1 | 6.1 | [3] |
| CoS/PEDOT:PSS | 0.65 | 13.2 | 62.7 | 5.4 | |
| Pt | 0.749 | 15.66 | 0.73 | 8.31 | This study |
| Poly(spiroBiProDOT) | 0.726 | 14.76 | 0.73 | 7.9 | |
| PEDOT | 0.691 | 12.68 | 0.72 | 6.8 | |

* rGO: reduced graphene oxide, CoS: Cobalt sulfide nanoparticles, PSS: poly-(styrene sulfonic acid

References:


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