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ELECTRONIC SUPPLEMENTARY INFORMATION

Optimized photoelectrochemical water splitting with tandem polymer solar cells

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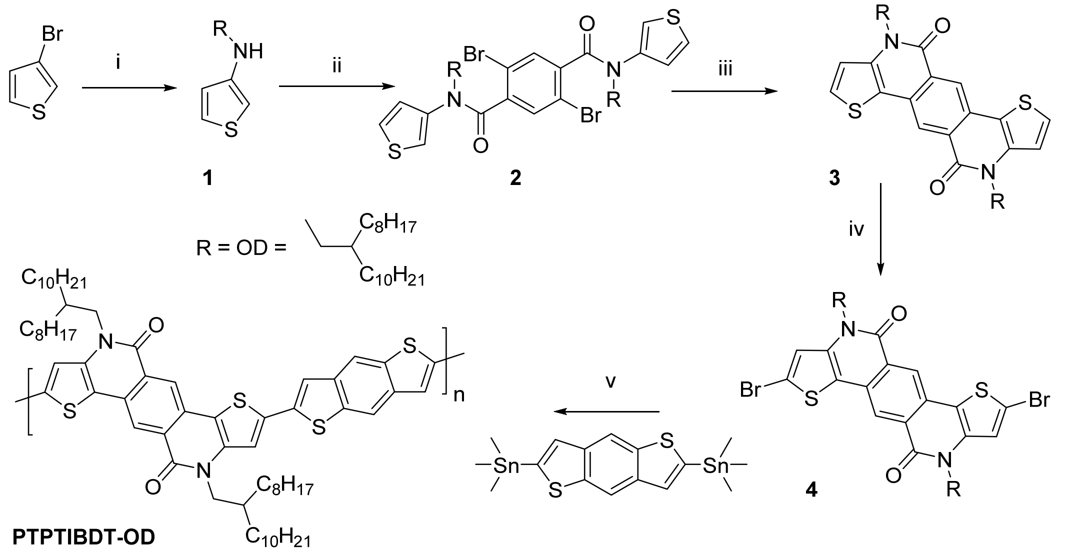
General procedures and methods

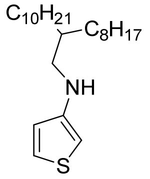
All starting materials and reagents were purchased from commercial suppliers unless stated otherwise. All ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Varian Mercury Spectrometer using $CDCl_3$ as solvent with tetramethylsilane (TMS) as internal standard. The given values are in ppm relative to TMS (0 ppm). UV-vis-NIR optical absorption spectra were recorded on a Perkin-Elmer Lambda 900 spectrometer in a chloroform solution in a quartz cell or a thin film spin coated on a glass substrate. Cyclic voltammetry (CV) was conducted under inert atmosphere using an Autolab PGSTAT30 with a three electrode setup equipped with an ITO working electrode covered with a spin coated polymer film, silver counter electrode and a silver electrode coated with silver chloride (Ag/AgCl) as quasi reference electrode in combination with ferrocene/ferrocenium (Fc/Fc^+) as internal standard. A 1 M solution of tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in acetonitrile was used as the electrolyte. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) was measured on a PerSeptive Biosystems Voyager – DE PRO spectrometer using either α-cyano-4-hydroxycinnamic acid (CHCA) and/or trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrices. Molecular weights for the polymers were determined with an Agilent high temperature GPC equipped with a PDA detector, RI detector and LS detector and with a Plgel 10μm Mixed B column using ODCB at 140 °C as eluent.

Synthesis



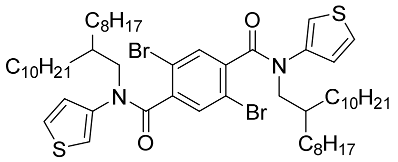
Scheme S1 – Synthesis of TPTI monomer and subsequent PTPTIX polymers. (*i*) 3-Bromothiophene, 2-octyldodecylamine, CuI, K_3PO_4, dimethylaminoethanol (DMAE), 90 °C, 2 d. 35%. (*ii*) 2,5-Dibromoterephthalic acid, $SOCl_2$, DCM, 24 h, then, Et_3N, DCM, room temperature, overnight. (*iii*) $Pd(OAc)_2$, PCy_3HBF_4, K_2CO_3, dimethylamine (DMA), 120 °C, overnight. (*iv*) NBS, DCM, 0 °C to room temperature, 2 h. (*v*) Pd_2dba_3, PPh_3, toluene/DMF (9/1), 115 °C, overnight.

N-(2-octyldodecyl)thiophen-3-amine (1)



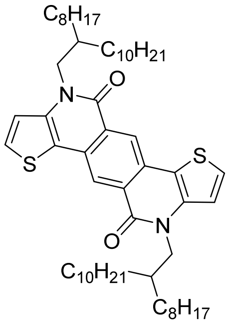
A mixture of 3-bromothiophene (11.023 g, 67.6 mmol), 2-octyldodecan-1-amine (13.7 g, 46 mmol), CuI (876 mg, 4.6 mmol) and grinded K_3PO_4 (17 g, 80 mmol) in dimethylaminoethanol (30 mL) was heated to 90 °C for 2 days under an argon atmosphere. The reaction was cooled to room temperature and filtered. The residue was washed with ethyl acetate and the filtrate concentrated and subjected to silica column chromatography (gradient heptane/dichloromethane 0 - 100%) to give 8.5 g (49%) of the air sensitive compound **1**. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.14 (dd, *J* = 5.1, 3.0 Hz, 1H), 6.61 (dd, *J* = 5.2, 1.5 Hz, 1H), 5.91 (dd, *J* = 3.1, 1.5 Hz, 1H), 3.57 (s, 1H), 2.97 (d, *J* = 6.1 Hz, 2H), 1.59 (p, *J* = 9.5, 4.6, 4.1 Hz, 1H), 1.37 – 1.15 (m, 32H), 0.88 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 149.10, 124.96, 119.91, 94.79, 77.31, 76.99, 76.67, 49.87, 37.80, 32.20, 31.91, 30.05, 29.66, 29.63, 29.60, 29.33, 26.78, 22.68, 14.11.

2,5-Dibromo-N^1,N^4-di(2-octyldodecyl)-N^1,N^4-di(thiophen-3-yl)terephthalamide (2)



2,5-Dibromoterephthalic acid (2.49 g, 7.7 mmol) was dissolved in dichloromethane (50 mL) with a few drops of DMF and $SOCl_2$ (3 mL) was added dropwise. The reaction was stirred at room temperature overnight and dried in vacuum to give the acid chloride that was re-dissolved in dichloromethane (15 mL). A solution of **1** (8.5 g, 22 mmol) and triethylamine (2 mL) in dichloromethane (30 mL) was added dropwise and the reaction was stirred overnight at room temperature. After addition of water, the organic fraction was extracted with chloroform and washed with brine, dried over $MgSO_4$ and purified via silica column chromatography to give 8.2 g (7.8 mmol) of **2** (71% yield). The product was directly continued in the next reaction.

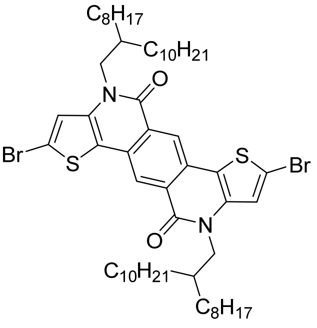
4,10-Di(2-octyldodecyl)-4,10-dihydrothieno[2',3':5,6]pyrido[3,4-*g*]thieno[3,2-*c*]isoquinoline-5,11-dione (3)



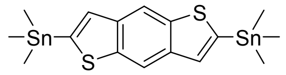
Compound **2** (8.2 g, 7.8 mmol) was dissolved in dimethylamine (100 mL) with $Pd(OAc)_2$ (87.5 mg, 390 µmol), PCy_3HBF_4 (287 mg, 780 µmol) and K_2CO_3 (1.2 g, 8.6 mmol) and heated under argon to 120 °C overnight. The reaction was cooled and water was added. The organics where extracted with chloroform and washed with brine, dried over $MgSO_4$ and concentrated before column chromatography with chloroform/heptane gradient (0% to 100%). The product containing fractions were combined, concentrated and recrystallized form ethanol with a little addition of chloroform. Filtration and drying gave **3** as yellow powder (1.47 g) in 21% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.86 (s, 2H), 7.48 (d, J = 5.4 Hz, 2H), 7.09 (d, J = 5.4 Hz, 2H), 4.23 (d, J = 7.8 Hz, 4H), 2.02 (q, J = 7.4, 6.6 Hz, 2H), 1.22 (d, J = 3.5 Hz, 64H), 0.85 (dt, J = 6.6 Hz, 10H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 161.58, 139.43, 129.99, 126.80, 126.09, 123.62, 117.94, 117.73, 77.31, 76.99, 76.67, 49.71, 37.11, 31.87, 31.84, 31.64, 29.95, 29.58, 29.55, 29.50, 29.30, 29.24, 26.66, 22.65, 22.62, 14.09, 14.06.

2,8-Dibromo-4,10-di(-octyldodecyl)-4,10-dihydrothieno[2',3':5,6]pyrido[3,4-*g*]thieno[3,2-*c*]isoquinoline-5,11-dione (4)

A mixture of **3** (1.0 g, 1.13 mmol) dissolved in dichloromethane (50 mL) was cooled to 0 °C before adding NBS (402 mg, 22.26 mmol). As a precipitate formed, chloroform was added after 2 h. Small portions of NBS were added until thin layer chromatography (TLC) showed full conversion. Column chromatography with chloroform/heptane gradient (0% to 100%) gave the desired product that was subsequently recrystallized from ethanol with a small amount of chloroform. After filtration and drying **4** (980 mg) was obtained as a shiny yellow compound in 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.59 (s, 2H), 7.03 (s, 2H), 4.12 (d, $J = 4.1$ Hz, 4H), 2.05 – 1.87 (m, 2H), 1.44 – 1.12 (m, 64H), 0.85 (dt, $J = 6.8$ Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 160.95, 138.78, 129.21, 126.70, 123.26, 120.82, 118.72, 115.07, 77.32, 77.00, 76.68, 49.71, 36.97, 31.89, 31.85, 31.50, 29.95, 29.61, 29.56, 29.51, 29.32, 29.27, 26.54, 22.66, 22.64, 14.10, 14.08. MALDI-TOF *m/z*: 1042.47 ($M^{+\cdot}$, 100%).



2,6-Bis(trimethylstannyl)benzo[1,2-b:4,5-*b*']dithiophene



Benzo[1,2-*b*:4,5-*b*']dithiophene (250 mg, 1.32 mmol) was dissolved in THF (20 mL) and cooled to −78 °C. Four equivalents of *tert*-butyllithium (1.6 M in hexanes, 3.30 mL, 5.28 mmol) were added dropwise. After 1 h the reaction was warmed to room temperature for a short period and then cooled to −78 °C again before quenching the reaction with chlorotrimethylstannane (1.0 M in THF, 5.30 mL, 5.28 mmol). After addition the reaction was allowed to warm to room temperature and stirred for another 2 h. The reaction mixture was then concentrated in vacuum and re-dissolved in heptane. The salts were filtered off and the procedure was repeated three times. The resulting product was then recrystallized twice from ethanol to give 186 mg of white crystals. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.28 (s, 2H), 7.42 (s, 2H), 0.44 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.71, 141.30, 138.56, 130.92, 115.05, 77.32, 77.00, 76.68, -8.37.

PTPTIT-OD

Equimolar amounts of **4** (80.9 mg, 77.5 µmol) and 2,6-bis(trimethylstannyl)benzo[1,2-b:4,5-b']dithiophene (40.0 mg, 77.5 µmol) were put in a Schlenk tube with Pd_2dba_3 (1.42 mg, 1.55 µmol) and PPh_3 (1.63 mg, 6.20 µmol) and put under argon. The mixture is dissolved in toluene/DMF (9/1) (2 mL) and argon was bubbled through for 15 min. before heating the reaction to 115 °C overnight. After cooling the polymer was precipitated in methanol and filtered through a Soxhlet thimble. Soxhlet extraction with acetone, heptane and dichloromethane was used to wash residual catalyst and lower molecular weight fractions and the final polymer was extracted with chloroform and again precipitated in methanol and filtered over a PTFE filter to give 50 mg of PTPTIT-OD. GPC (ODCB, 140 °C) M_n 35.4 kg mol^{-1}, PDI = 5.0, λ_{max} = 526 nm.

Optical constants of PTPTIT-OD:[70]PCBM layers

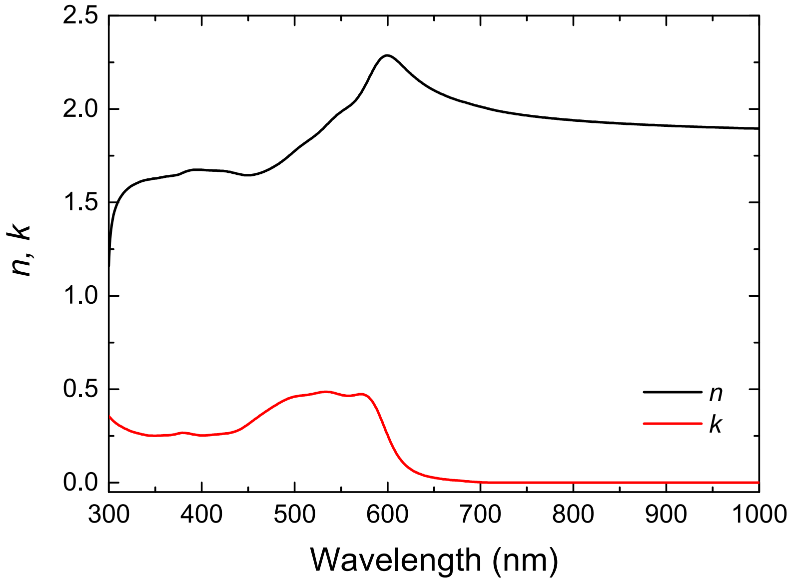


Fig. S1 Optical constants of PTPTIT-OD:[70]PCBM layers.

Catalyst stability

Stabilities of the catalysts used in the light-driven water splitting devices were separately tested with two-electrode measurements. Fig. S2a shows the stability of two RuO_2 catalysts deposited on a Ti plate for oxygen and hydrogen evolution reactions in 1.0 M KOH. The two-electrode measurements were performed at applied potentials of 1.65 V. The RuO_2 catalyst is known to be not completely stable for oxygen evolution reaction as it may oxidize further to one of its other states which are soluble.[S1] We have also observed that if a RuO_2 catalyst is continuously kept in 1.0 M KOH for two days without operating, noticeable decrease in its catalytic activity takes place. However if the catalyst is stored in air it quickly restores to its original performance level when contacted again with the electrolyte and enables stable operation up to at least 2 h (Fig. S2b). A detailed study on the stability of RuO_2 for hydrogen and oxygen evolution reactions in acid and alkaline media has been reported recently.[S2]

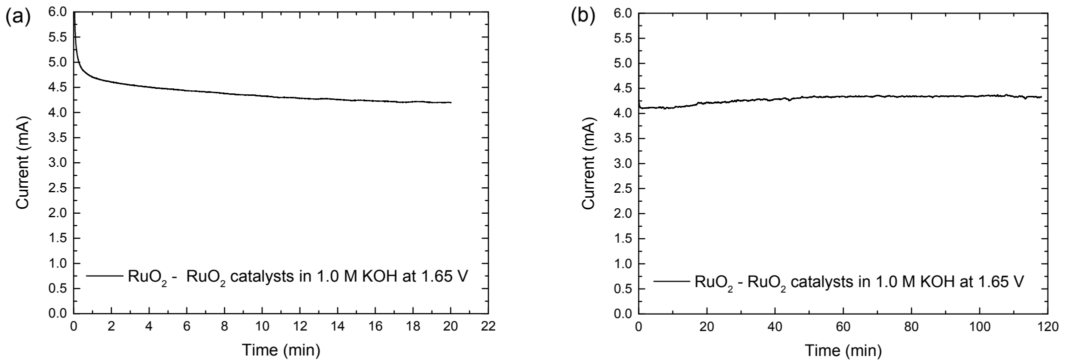


Fig. S2 Stability of RuO_2/RuO_2 catalysts in 1.0 M KOH. Two-electrode water splitting test potential of 1.65 V (a) 20 min. (b) 2 h. The catalyst used in panel (b) were stored in air and reached the same activity as freshly prepared catalyst (a) after a short time.

S1 K. Juodkazis, J. Juodkazytė, R. Vilkauskaitė, B. Šebeka and V. Jasulaitienė, *Chemija.*, 2008, **19**, 1.

S2 S. Cherevko, S. Geiger, O. Kasian, N. Kulyk, J.-P. Grote, A. Savan, B. R. Shrestha, S. Merzlikin, B. Breitbach, A. Ludwig and K. J. J. Mayrhofer, *Catal. Today*, 2016, **262**, 170.