Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Cyclopentadithiophene-Benzoic Acid Copolymers as Conductive Binders for Silicon Nanoparticles in Anode Electrode of Lithium Ion Batteries

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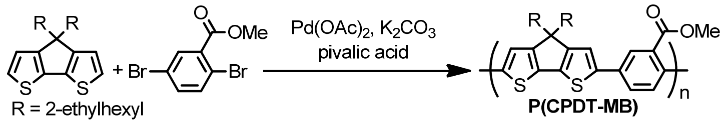
1. General methods and synthesis of compounds

1.1 General methods

Methyl-2,5-dibromobenzoate, $Pd(OAc)_2$ and pivalic acid were purchased from Sigma-Aldrich and used without further purification. 4,4-Bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene was synthesised by modification of established procedures.[S1] Synthesis was performed under a nitrogen atmosphere using standard Schlenk techniques. ^1H NMR spectra were obtained using a Bruker 500 MHz spectrometer. Polymer molecular weight was determined by GPC in tetrahydrofuran (THF) solution using a JASCO 880-PU pump and JASCO 870-UV/VIS detector (referenced to polystyrene standards). UV-Vis absorption spectra were recorded on a JASCO U-670 UV-Vis spectrophotometer. CV was performed at 0.10 V s^{-1} in a DY2300 electrochemical analyzer with a three-electrode cell, Ag/AgCl as reference electrode, platinum wire as counter electrode and platinum plate as the working electrode in nitrogen-purged anhydrous 0.10 M tetrabutylammonium hexafluorophosphate acetonitrile solution at room temperature. Onsets of oxidation and reduction peak potentials were used in the calculation of HOMO and LUMO energy levels.

S1. P. Coppo and M. L. Turner, *J. Mater. Chem.*, 2005, **15**, 1123.

1.2 Synthesis of P(CPDT-MB) by direct arylation polymerization



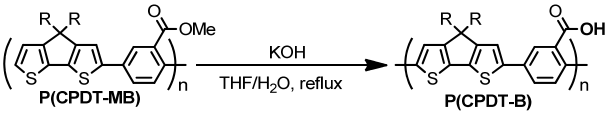
Reaction conditions are summarized in Table S1. Typical reaction conditions (entry 12) are described as follows. Anhydrous pivalic acid (3.8 mg, 0.037 mmol), potassium carbonate (42.8 mg, 0.31 mmol), and catalyst $Pd(OAc)_2$ (0.012 mmol, 2.8 mg, 0.1 eq.) was added to a solution of monomers CPDT (50.0 mg, 0.124 mmol) and methyl-2,5-dibromobenzoate (36.5 mg, 0.124 mmol) in anhydrous *N*-methylpyrrolidone (NMP) (1.24 mL) in a 10 mL Schlenk tube. The solution was purged with nitrogen gas for 5 min, then the mixture was stirred at 80 °C for 8 h. After polymerisation, the resulting mixture was precipitated into 100 ml methanol. The precipitate was collected by vacuum filtration and then washed by Soxhlet extraction with ethanol and methylethylketone and extracted into chloroform. The chloroform fraction was concentrated under reduced pressure and reprecipitated into methanol. The precipitate was collected using centrifugation at 5000 rpm for 4 min and dried in vacuum to obtain a dark orange powder (451 mg, 85% yield and 281 mg, 53% yield after Soxhlet extraction). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.966, 7.01, and 7.27 (s, 2H, 3-cyclopentadithiophene), 7.48 (s, ^{1}H, aromatic), 7.67 (s, ^{1}H, aromatic), 7.87 (s, ^{1}H, aromatic), 3.81 (s, 3H, OCH_3), 1.92 (br, 4H, CH_2). GPC (polystyrene standards in THF): M_n = 53,000, M_w/M_n = 2.59. UV-vis: λ_{max} = 465 nm in THF, λ_{max} = 467 nm in film.

Table S1. Reaction conditions for direct arylation polymerization [a]

Entry	Solvent	Temp. (°C)	Time (h)	$Pd(OAc)_2$ (eq)	M_n [b]	[b]	Yield [c] (%)
1	NMP	80	10	0.01	1500	1.35	8
2	NMP	100	10	0.01	1900	1.23	10
3	NMP	80	20	0.01	990	1.22	9
4	NMP	100	20	0.01	1300	1.26	10
5	NMP	80	10	0.1	2500	1.74	51
6	NMP	100	10	0.1	6900	2.36	85
7	NMP	80	20	0.1	7800	2.72	80
8	NMP	100	20	0.1	4800	1.97	45
9	NMP	90	20	0.1	7400 (11400)	2.32 (2.44)	80 (44)
10	DMAc	80	20	0.1	16600	2.68	9
11	DMAc (anhy.)	80	20	0.1	62300	2.58	79 (3)
12	NMP (anhy.)	80	8	0.1	40000 (53000)	3.27 (2.59)	85 (53)

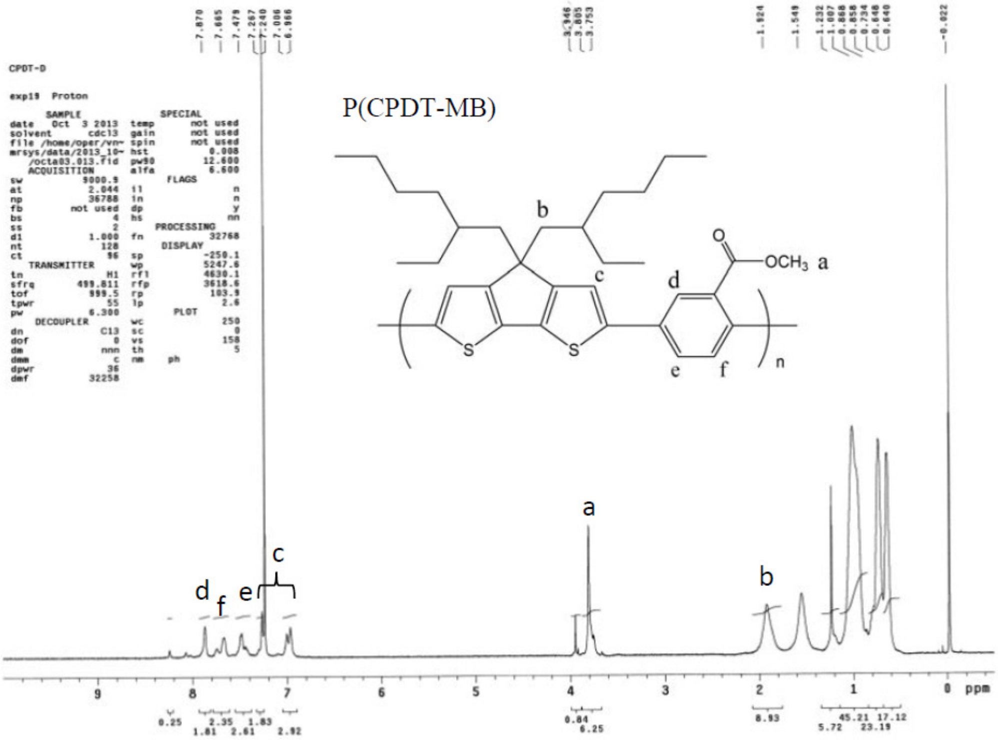
[a] Reactions were carried out in the presence of anhydrous pivalic acid (0.3 eq.) and K_2CO_3 (2.5 eq.) and 0.1M monomer concentration. [b] Calculated from gel permeation chromatography (GPC) measurements carried out using THF as the solvent and calibrated by polystyrene standards. M_n and M_w/M_n after Soxhlet extraction is noted in brackets. [c] Yield after Soxhlet extraction is noted in brackets.

1.3 Synthesis of P(CPDT-B) by saponification



A mixture of P(CPDT-MB) (Entry 12 in Table S1) (100 mg) and KOH (581 mg) in a mixed solution (THF:H_2O = 10:1, 6.6 mL) was refluxed for 48 hours under a nitrogen atmosphere. After the reaction, the solution was concentrated in vacuum and the polymer was precipitated into water. Then, the polymer was suspended in 37% HCl aqueous solution and stirred at reflux temperature for 12 hours. The resulting polymer was filtered, washed with water and dried in vacuum to obtain dark orange powder (99.5 mg, 99% yield). GPC (polystyrene standards in THF): M_n = 17,000, M_w/M_n = 3.32. UV-vis: λ_{max} = 471 nm in THF, λ_{max} = 477 nm in film.

2. ^{1}H NMR spectrum



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CPDT-D

exp19  Proton

      SAMPLE                 SPECIAL
date    Oct  3 2013  temp        not used
solvent       cdcl3  gain        not used
file /home/oper/vn~  spin        not used
mrsys/data/2013_10~  hst            0.008
   /octa03.013.fid   pw90          12.600
   ACQUISITION       alfa           6.600
sw           9000.9            FLAGS
at            2.044  il                 n
np            36788  in                 n
fb         not used  dp                 y
bs                4  hs                nn
ss                2         PROCESSING
d1            1.000  fn             32768
nt              128           DISPLAY
ct               96  sp            -250.1
   TRANSMITTER       wp            5247.6
tn               H1  rfl           4630.1
sfrq        499.811  rfp           3618.6
tof           999.5  rp             103.9
tpwr             55  lp               2.6
pw            6.300             PLOT
    DECOUPLER        wc               250
dn              C13  sc                 0
dof               0  vs               158
dm              nnn  th                 5
dmm               c  nm       ph
dpwr             36
dmf           32258
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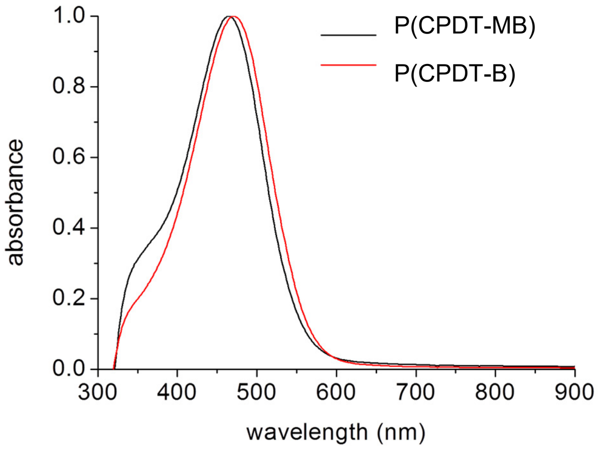
Figure S1. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of P(CPDT-MB).

3. Optical and electrochemical properties



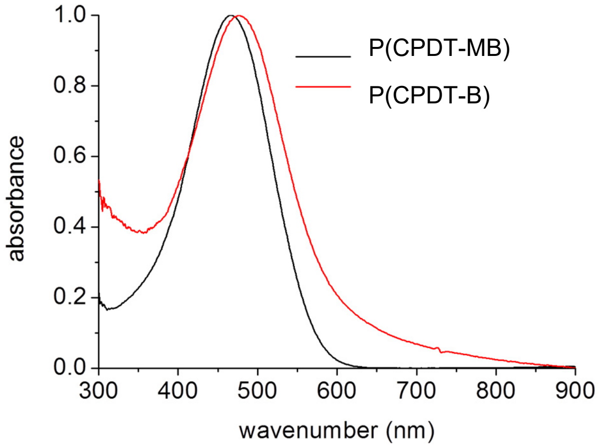


Figure S2. UV-vis absorption spectra of P(CPDT-MB) and P(CPDT-B) in THF solutions (top) and films (bottom).

Table S2. Optical and electrochemical properties of polymers.

Polymer	λ_{max}/nm		E_{pa}/V vs AgCl/Ag
	in THF	in film	
P(CPDT-MB)	465	467	1.61
P(CPDT-B)	471	477	1.73

4. Battery fabrication and measurements

4.1 Preparation of electrodes

Nano-silicon powder (Alfa aesar, particle diameter ≦50 nm, specific surface area 70-80 m^2/g) was used as active material for anodes, and the conjugated polymers, P(CPDT-MB) and P(CPDT-B), were used as conductive binders. In the process of fabrication, the conductive binders were dissolved in THF. The conductive binder and nano-silicon powder (weight ratio = 1:2) were mixed in 4 mL sample bottle with adequate solvent stirred in Planetary Centrifugal Mixer (Thinky Mixer ARM-310) to obtain well-mixed slurry. The resulting slurry was used to coat copper foil using 100 μm blade with 8 V constant speed by home-made doctor blade. Then, the electrode film was dried in vacuum oven at 110 °C for 8 h.

4.2 Trimming of electrode sheets

The resulting electrode film was cut into several rounded films with 13 mm diameter using a cutting machine (P1300-A, UBIQ). Then, the rounded electrode films were weighed to calculate the weight and density. Loading of the electrode films is in a range of 0.6-0.7 mg/cm^2.

4.3 Assembly of batteries

All half coin cells (CR2032, width: 20 mm, height: 32 mm) were assembled in the glove box (UNILAB-B, MBraun) under argon atmosphere (H_2O value < 1 ppm, O_2 value < 5 ppm), and sealed by a capping machine (C2000-A, UBIQ). The half coin cells are composed of front cover, reed, spacer, lithium metal, separator, electrode sheet and back cover (ordering from top to bottom). The electrolyte contains 1:1 volume ratio of EC (ethylene carbonate, Alfa aesar) and DEC (diethyl carbonate, Alfa aesar).

4.4 Cycle life test of lithium ion batteries

The half coin cells were measured at constant current mode by charging/discharging machine (BAT-750B). The charging/discharging rates at 0.1, 0.2, 0.5, 1.0 and 2.0 C correspond to 360, 720, 1800, 3600 and 7200 mA/g, respectively. The first cycle was measured at 0.1 C for activating all internal silicon. The cut-off voltages of discharge and charge were set at 0.01 V and 1.5 V, respectively. The results of cycle life test are summarized in Fig. 4 (all specific capacities were calculated based on total weight of anode of electrode). The columbic efficiencies were also tested and shown in Fig. S3. The battery fabricated from P(CPDT-B) shows stable efficiency around 100% even after 60 cycles, whereas P(CPDT-MB) is quickly degraded.

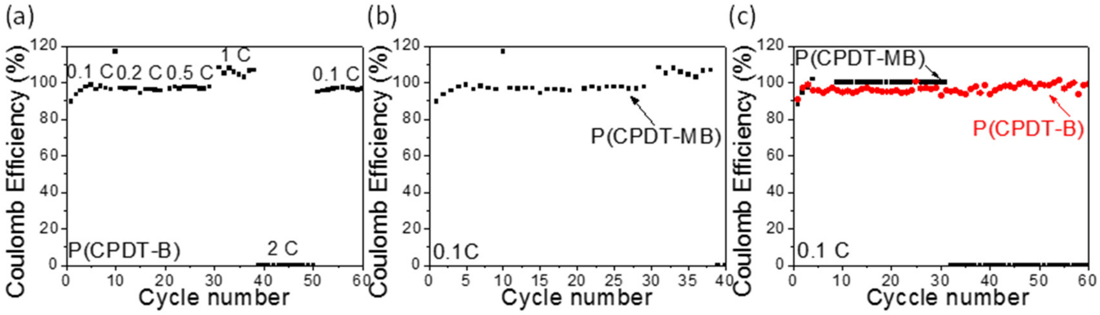


Figure S3. Columbic efficiencies of lithium ion batteries at various Coulomb rates for (a) P(CPDT-B) and (b) P(CPDT-MB). (c) Columbic efficiencies of lithium ion batteries at a constant rate at 0.1 C.

4.5 Electrochemical impedance analysis

The impedance measurements were carried out using VSP Bio-logic with a frequency range of 0.01-100000 Hz. The equivalent circuit model (Figure S4) was applied to simulate the resistance and ionic conductivity of the polymers, where R1 and R2 are the resistance of electrolyte and charge transfer, respectively. The ionic conductivity was calculated by the following formula: $\sigma = (1/R) \times (d/S)$. The charge transfer resistance R was calibrated by EC-Lab software.

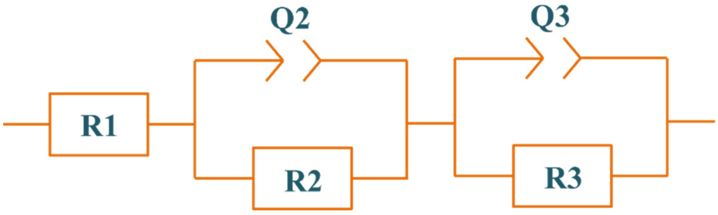


Figure S4. Equivalent circuit model for the electrochemical impedance analysis

5. DC conductivity test

Polymer films were prepared by a drop casting method, in which THF solution of the polymer was casted between two copper plates on a glass substrate and dried in vacuum. The electric resistance was measured using DY2300 electrochemical analyzer with a scan rate of 1 V s^{-1}, as shown in Fig. S5. The electrical conductivity σ' was calculated from the equation:

$\sigma' = (1/R') \times (L/A)$

where R', A and L are resistance, area of the polymer film and length between two electrodes, respectively.

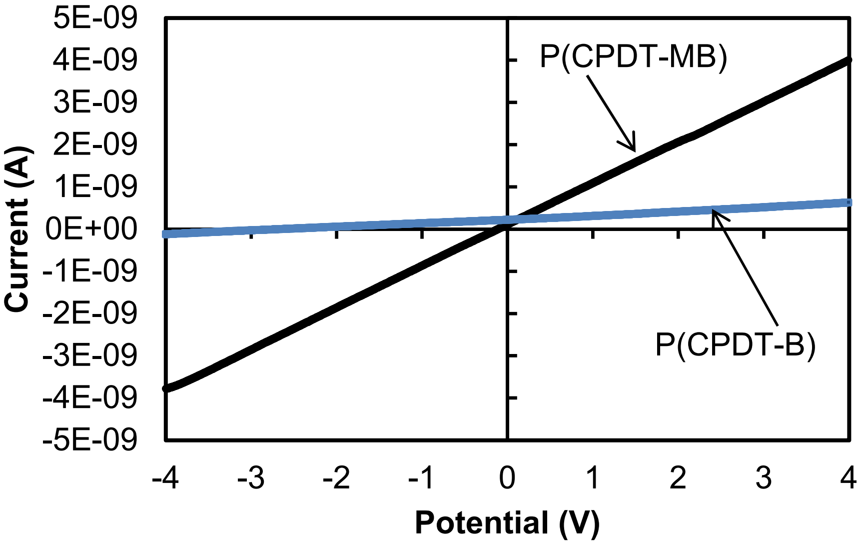


Figure S5. DC resistance tests of films of P(CPDT-MB) and P(CPDT-B)

Table S3. Results of DC measurement

Polymer	Electric resistance (S^{-1})	Electric conductivity(S cm^{-1})
P(CPDT-MB)	1.0×10^{9}	2.1×10^{-8}
P(CPDT-B)	1.1×10^{10}	3.1×10^{-9}