

SUPPORTING INFORMATION

Synthesis of oligothiophene derivatives

3,3''',4',4''''-tetrahexyl-2,2':5',2'':5'',2''':5''',2''''-quiquethiophene (1): ¹H NMR (300 MHz, CDCl₃, δ): 7.19 (d, J=5.2 Hz, 2H), 7.12 (s, 2H), 6.99 (s, 2H), 6.96 (d, J=5.2 Hz, 2H), 2.82 (t, J=7.2 Hz, 8H), 1.72 (m, 8H), 1.37 (m, 24H), 0.93 (m, 12H). ¹³C NMR (100 MHz, CDCl₃, δ): 139.86, 139.65, 135.75, 134.30, 130.48, 130.25, 130.10, 128.76, 125.86, 123.62, 31.72, 30.75, 30.69, 30.61, 30.33, 29.49, 29.32, 29.30, 29.25, 29.00, 22.67, 14.13; MS (MALDI-TOF) m/z: [M + H]⁺ calcd. for C₅₇H₃₅N₃OS₂, 749.337; found, 749.324.

3,3''',3''''',4'-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-quiquethiophene]-5-carbaldehyde (2) ¹H NMR (300 MHz, CDCl₃, δ): 9.84 (s, 1H), 7.60 (s, 1H), 7.20-7.11 (m, 3H), 6.98-6.92 (m, 3H), 2.88-2.79 (m, 8H), 1.77-1.63 (m, 8H), 1.47-1.25 (m, 24H), 0.93 (m, 12H). ¹³C NMR (300 MHz, CDCl₃, δ): 182.52, 141.18, 140.28, 140.22, 140.09, 139.74, 139.10, 136.54, 134.89, 134.52, 132.78, 132.63, 130.44, 130.33, 130.12, 129.92, 128.76, 126.48, 125.95, 123.70, 31.67, 31.65, 31.60, 30.64, 30.56, 30.52, 30.23, 29.46, 29.42, 29.37, 29.28, 29.25, 29.22, 29.13, 22.62, 22.58, 14.10; MS (ESI-Mass) m/z: [M + H]⁺ calcd. for C₄₅H₆₀OS₅, 777.325; found, 777.510.

(E)-2-cyano-3-(3,3''',3''''',4'-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-quiquethiophen]-5-yl)acrylic acid (3): ¹H NMR (300 MHz, CDCl₃, δ): 8.04 (s, 1H), 7.60 (s, 1H), 7.46 (d, J=5.2 Hz, 1H), 7.25 (s, 1H), 7.24 (s, 1H), 7.22 (s, 1H), 7.06 (s, 1H), 7.04 (d, J=5.2 Hz, 1H), 2.88-2.79 (m, 8H), 1.77-1.63 (m, 8H), 1.47-1.25 (m, 32H), 0.93 (m, 12H); ¹³C NMR (100 MHz, CDCl₃, δ): 173.85, 148.69, 143.97, 143.70, 143.45, 143.34, 140.05, 138.87, 138.20, 136.50, 136.32, 134.24, 133.92, 133.90, 133.79, 132.45, 129.85, 129.55, 127.63, 127.44, 122.31, 106.70, 35.54, 35.50, 35.41, 34.45, 34.31, 33.83, 33.39, 33.33, 33.25, 33.11, 33.05, 26.53, 26.50, 26.45, 17.86; MS (MALDI-TOF) m/z: [M + H]⁺ calcd. for C₄₈H₆₁NO₂S₅, 844.338; found, 844.282.

(E)-2,5-dioxopyrrolidin-1-yl 2-cyano-3-(3,3''',3''''',4'-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-quiquethiophen]-5-yl)acrylate (4): A mixture of (3) (0.178 g, 0.21 mmol), N-hydroxysuccinimide (1.05 mmol) and EDC (2.1 mmol) in dichloromethane (20 mL) was stirred at room temperature for 24 h. The mixture was extracted by dichloromethane and then the solvent was removed under reduced pressure. The residue was filtered by dichloromethane/hexane. Yield 74% (0.147 g). Dark red solid, ¹H NMR (300 MHz, CDCl₃, δ): 8.29 (s, 1H), 7.65 (s, 1H), 7.24-7.11 (m, 4H), 6.94-6.91 (m, 2H), 2.88-2.79 (m, 8H), 1.77-1.63 (m, 8H), 1.47-1.25 (m, 36H), 0.93 (m, 12H); ¹³C NMR (100 MHz, CDCl₃, δ): 168.60, 159.42, 149.04, 145.76, 143.47, 140.87, 140.58, 140.22, 139.78, 137.00, 134.68, 134.59, 134.55, 132.28, 131.84, 131.68, 130.30, 130.13, 129.82, 128.77, 126.74, 125.99, 123.75, 114.59, 31.67, 31.65, 31.61, 31.55, 30.62, 29.92, 29.49, 29.43, 29.34, 29.29, 29.24, 29.19, 29.12, 25.59, 22.61, 22.56, 14.08, 14.05; MS (MALDI-TOF) m/z: [M + H]⁺ calcd. for C₅₂H₆₄N₂O₄S₅, 941.354; found, 941.365.

Table S1. The parameter for calculation of the number of attached OT groups

The weight of each particle	2.2×10 ⁻¹³ mg/ea
The surface area of each particle	6362 nm ² /ea
The number of OT in 1 mg of particle	4.8×10 ⁻⁸ mol
The number of the attached OT group on each particle	9.4×10 ⁻²¹ mol/ea or 5700/ea
The number of the attached OT on nm ² (packing density)	0.89/nm ²

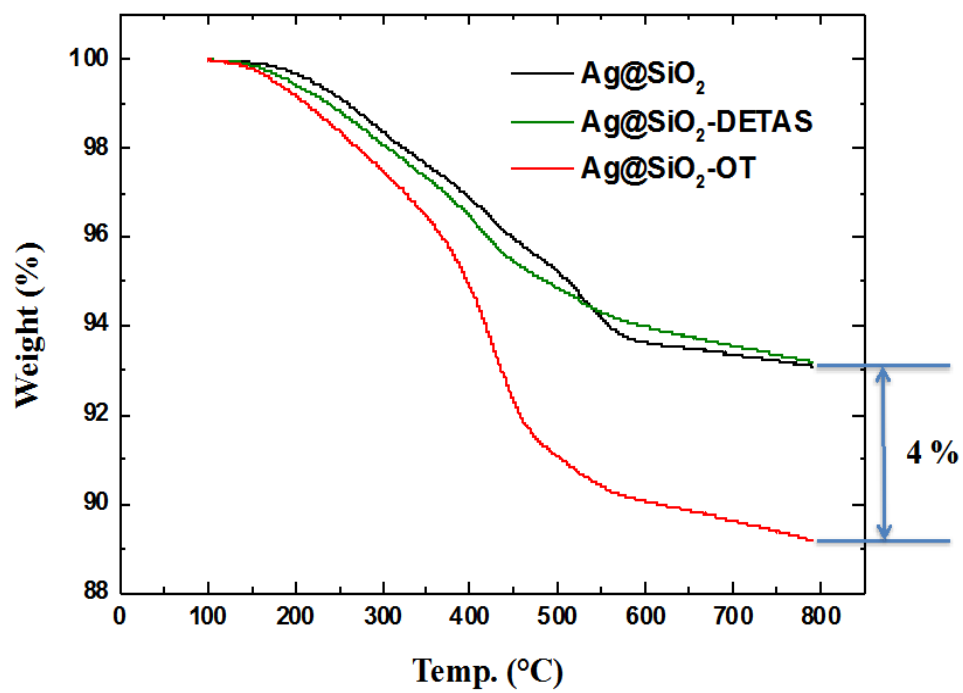


Figure S1. TGA results of surface modified silver nanoparticles

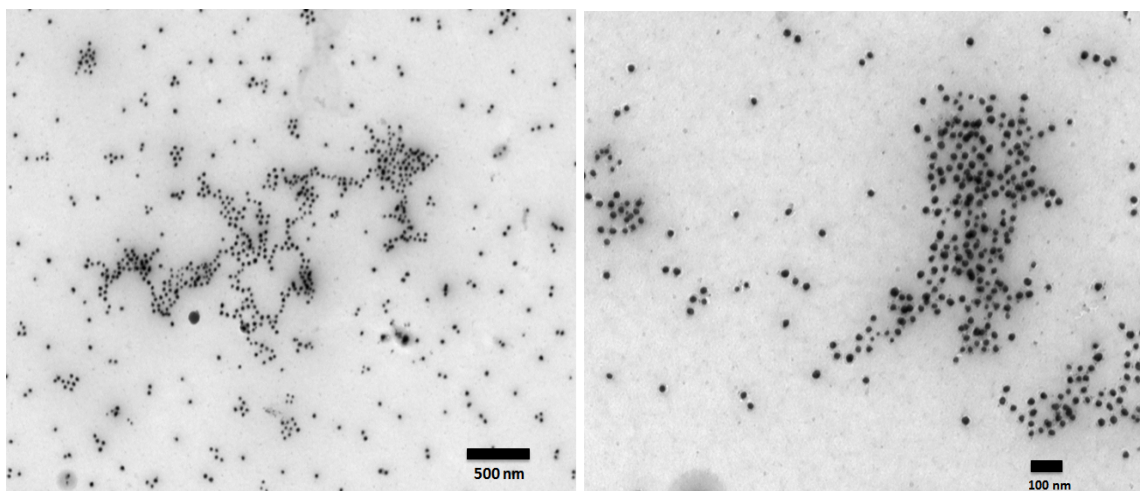


Figure S2. TEM images of P₃HT:PCBM film with 3 wt% of :Ag@SiO₂ composite films

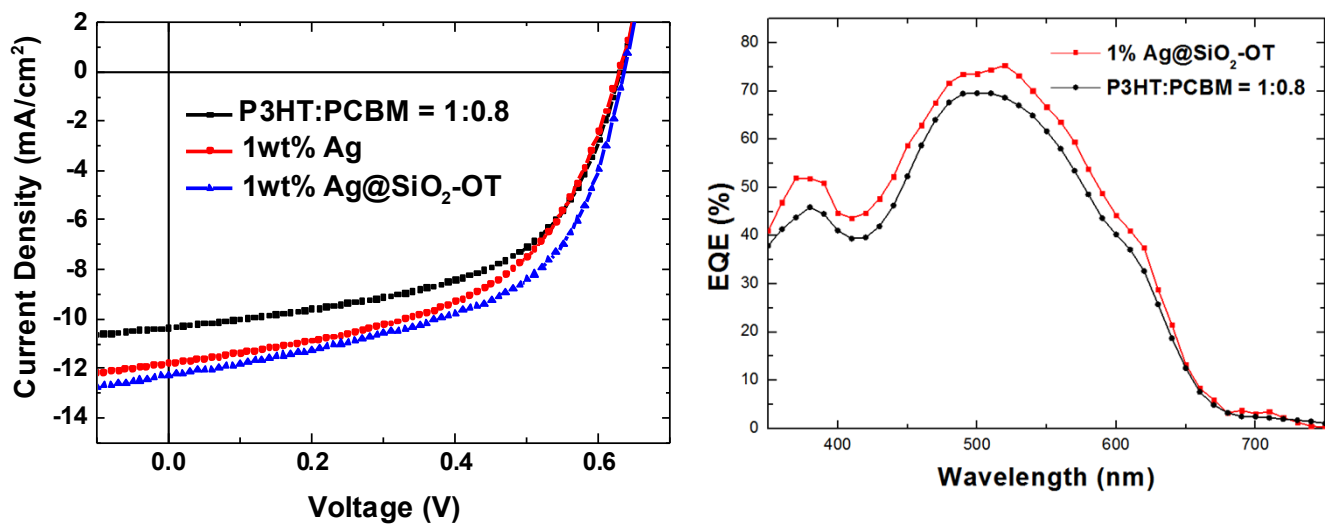


Figure S3. *I-V* curves (left) and IPCEs (right) of P₃HT:PCBM (1:0.8) based solar cells with nanoparticle components.

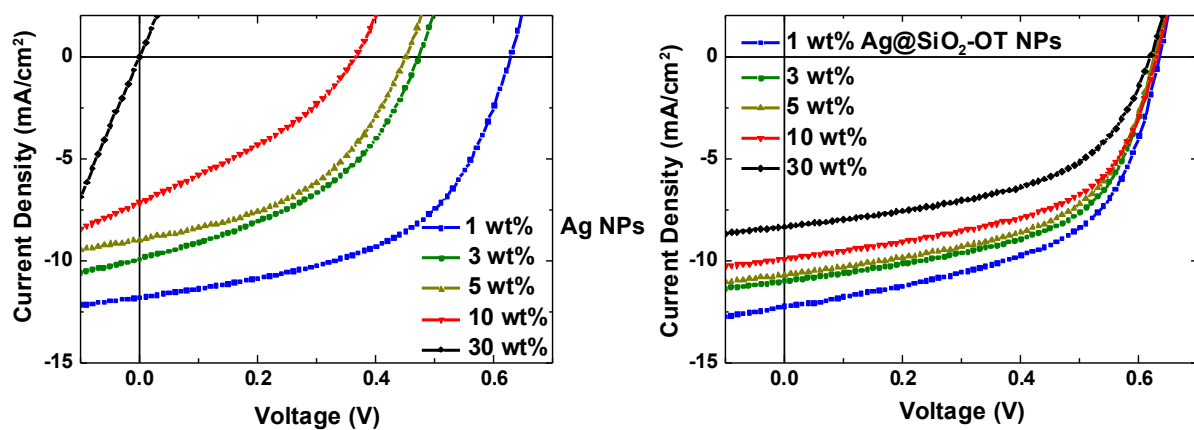


Figure S4. *I-V* curves of P₃HT:PCBM (1:0.8) based solar cells with various amounts of Ag@SiO₂-OT NPs (right) and Ag NPs (left).

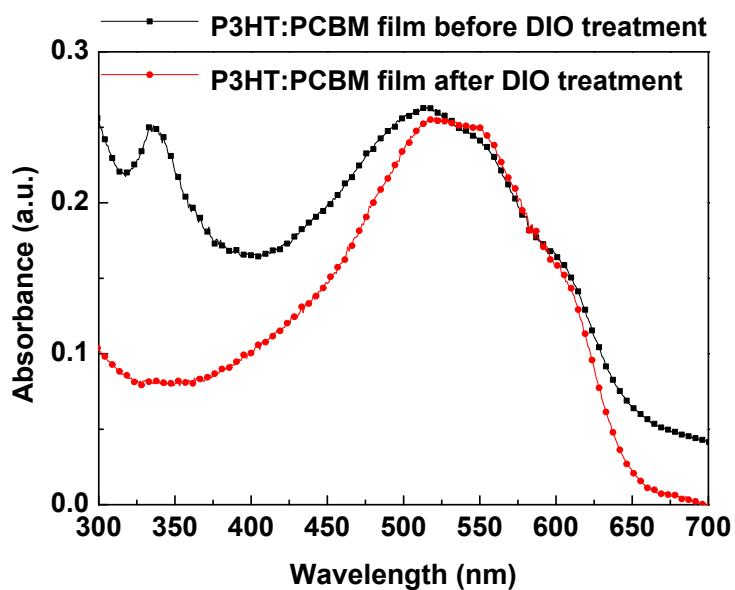


Figure S5. Absorption spectra of P3HT:PCBM blend film before and after DIO treatment.

Table S2. The photovoltaic performance of polymer solar cells with various concentrations of nanoparticles.

Types of NPs	NP ratio		V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (ave)	PCE (max)
	whole NPs (wt%)	Ag content (wt%)					
Ref	0	0	0.62 ± 0.01	10.28 ± 0.40	0.54 ± 0.02	3.44 ± 0.12	3.59
Ag@SiO ₂ -OT	1	0.66	0.63 ± 0.01	11.42 ± 0.45	0.55 ± 0.01	4.02 ± 0.17	4.25
	3	2	0.62 ± 0.01	10.71 ± 0.49	0.54 ± 0.01	3.57 ± 0.16	3.82
	5	3.33	0.62 ± 0.01	10.55 ± 0.35	0.54 ± 0.02	3.54 ± 0.16	3.65
	10	6.6	0.62 ± 0.01	9.73 ± 0.35	0.54 ± 0.01	3.23 ± 0.10	3.38
	30	20	0.61 ± 0.01	7.98 ± 0.26	0.52 ± 0.01	2.56 ± 0.08	2.65
Ag	1	1	0.63 ± 0.01	11.37 ± 0.35	0.53 ± 0.01	3.78 ± 0.09	3.88
	3	3	0.47 ± 0.00	9.38 ± 0.54	0.42 ± 0.01	1.85 ± 0.14	2.01
	5	5	0.45 ± 0.01	8.72 ± 0.27	0.43 ± 0.02	1.70 ± 0.13	1.86
	10	10	0.35 ± 0.01	6.75 ± 0.56	0.34 ± 0.02	0.79 ± 0.08	0.88
	30	30	n.a.	n.a.	n.a.	n.a.	n.a.