

Supporting information for

Sustainable synthetic approach to π - conjugated arylacetylenic semiconductors for bulk heterojunction solar cells

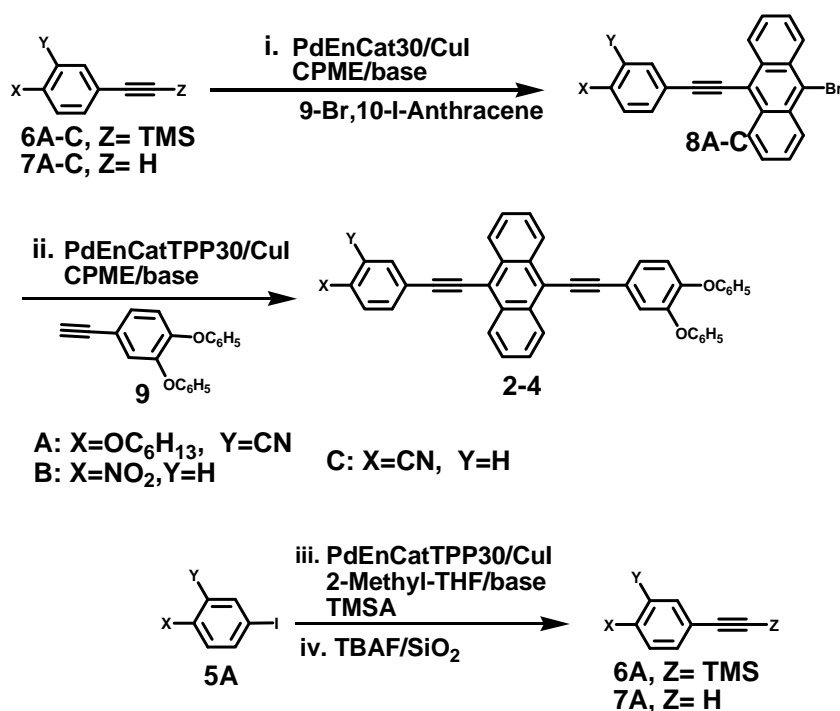
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Materials Synthesis.

Scheme S1. Synthetic routes to semiconductors **2-4**



2-(Hexyloxy)-5-[(trimethylsilyl)ethynyl]benzonitrile 6A. 2-(Hexyloxy)-5-iodobenzonitrile^{S1} **5A** (0.5 mmol), diisopropylamine (106 μ l, 0.75 mmol), trimethylsilylacetylene (106.3 μ L, 0.75 mmol), PdEnCatTPP30 (0.025 g, 0.01 mmol), CuI (0.0019 g, 0.01 mmol), and degassed 2-Methyl-THF (0.5 ml) were placed in a screw-capped vial equipped with a magnetic stirrer. Next, the mixture was stirred at 30°C for 18 h, then CH₂Cl₂ was added (1 ml), and the catalyst recovered by filtration. The mixture was subsequently diluted with CH₂Cl₂ (2 ml), washed with water (3ml x 2), dried over Na₂SO₄, filtered and evaporated to dryness to afford pure **6** (98% yield, yellow oil). ¹H-NMR (400 MHz, CDCl₃) δ : 0.23 (s, 9H), 0.91 (t, J=12.0 Hz, 3H), 1.33 (m, 4H), 1.48 (m, 2H), 1.84 (m, 2H), 4.06 (t, J= 6.5, 2H), 6.88 (dd, J=8.8 Hz, 2.1, 1H), 7.57 (dd, J=8.8, 2.13, 1H), 7.64 (d, J=2.0 Hz). ¹³C-NMR (CDCl₃, δ): 161.7, 137.9, 136.6, 118.7, 118.6, 113.1, 104.1, 100.9, 95.0, 71.2, 31.5, 29.5, 25.6, 22.6, 13.9, -0.3.

E-factor= [0.164 g (2-(hexyloxy)-5-iodobenzonitrile) + 0.076 g (diisopropylamine) + 0.408 g (2-methyl-THF) + 0.1474 g (trimethylsilylacetylene) + 0.0019 g (CuI) + 0.025 (PdEnCatTPP30) + 3.97 g (CH₂Cl₂) + 6.0 g (H₂O) – 0.146 g (product x yield)]/ 0.146 g= **72.91**

Not accounting for drying agent.

5-Ethynyl-2-(hexyloxy)benzonitrile 7A. In a screw capped vial equipped with a magnetic stirrer 2-(hexyloxy)-5-[(trimethylsilyl)ethynyl]benzonitrile **6A** (0.5 mmol) and SiO₂-supported TBAF (0.0625 g, 0.05 mmol; 1.25 mmol/g) were added, and the resulting mixture was left under vigorous stirring at 30°C. After 3 hours, ethyl acetate (1 ml) was added. The catalyst was then filtered off and washed with ethyl acetate (1.5 ml). The solvent was removed under vacuum to give compound **7A** as a yellow oil Yield: 95%. ¹H-NMR

(400 MHz, CDCl₃) δ: 7.05 (d, J=8.2 Hz, 1H), 6.99 (m, 1H), 6.08 (d, J=8.2 Hz, 1H), 3.97 (m, 2H), 2.98 (s, 1H), 1.81 (m, 4H), 4.52 (m, 2H), 1.34 (m, 2H), 0.92 (m, 3H). ¹³C-NMR (CDCl₃, δ): 161.7, 138.9, 137.6, 118.6, 113.4, 113.8, 101.3, 82.5, 78.9, 71.2, 31.5, 29.5, 25.6, 22.6, 13.9.

E-factor = [0.149 g (2-(hexyloxy)-5-[(trimethylsilyl)ethynyl]benzonitrile) + 0.0625 g (TBAF/SiO₂) + 2.25 g (ethyl acetate) – 0.108 g (product x yield)]/0.108 g = **21.7**

5-[(10-Bromo-9-anthryl)ethynyl]-2-(hexyloxy)benzonitrile 8A. In a screw capped vial equipped with a magnetic stirrer 5-ethynyl-2-(hexyloxy)benzonitrile **7A** (0.43 mmol), degassed cyclopentyl methyl ether (CPME, 0.66 ml), 9-iodo,10-bromo-anthracene (0.149 g, 0.39 mmol), diisopropylamine (1.063 g, 10.53 mmol), CuI (0.00074g, 0.0039 mmol), and PdEnCat30 (0.029g, 0.011 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 55°C. After 18 hours, the crude mixture was diluted with CHCl₃ (2 ml), the catalyst was filtered off, and the solvent removed under vacuum to give 9-bromo-10-[4-hexyloxy-(3-nitrophenyl)ethynyl]anthracene **8**. The crude product was purified by flash silica gel chromatography (eluent: petroleum ether/dichloromethane 9/1). Yield: 88% (yellow crystals); ¹H NMR (CDCl₃, δ): 8.60 (m, 1H), 7.95 (m, 4H), 7.92 (d, J=8.5 Hz, 1H), 7.64 (m, 4H), 7.02 (d, J=8.5 Hz, 1H), 4.15 (m, 2H), 1.90 (m, 4H), 1.27 (m, 4H), 0.94 (m, 3H); ¹³C-NMR (CDCl₃, δ): 161.5, 143.2, 141.9, 134.3, 134.2, 130.9, 130.1, 126.3, 126.2, 123.9, 118.4, 113.5, 101.4, 95.6, 93.0, 71.2, 31.5, 29.5, 25.6, 22.5, 13.9. An. Calcd. For: C₂₉H₂₄BrNO: C, 72.20; H, 5.01; N, 2.90%. Found: C, 72.29; H, 5.00; N, 2.88%.

E-factor = [0.097 g (5-ethynyl-2-(hexyloxy)benzonitrile) + 0.149 g (9-bromo,10-iodoanthracene) + 0.57 g (cyclopentyl methyl ether) + 0.00074g (CuI) + 1.063 g (diisopropylamine) + 0.029 g (PdEnCat30) + 2.98 g (CHCl₃) + 20 g (SiO₂) + 104.33 g (petroleum ether) + 11.40 g (CH₂Cl₂) – 0.165 g (product x yield)]/0.165 g = **851.2**

9-Bromo-10-(4-nitrophenylethynyl) anthracene 8B. Prepared by coupling 9-bromo-10-iodoanthracene with 4-nitro-ethynylbenzene **7B** (1:1.1), following the above procedure. The crude product was purified by recrystallization from toluene (2x25ml) to give the pure compound as yellow needles. Yield: 94%; ¹H NMR (CDCl₃, δ): 8.56 (m, 4H), 8.26 (d, J= 11.2 Hz, 2H), 7.84 (d, J= 11.2 Hz, 2H), 7.6 (m, 4H).^{S3}

E-factor: *vide infra*

4-[(10-Bromo-9-anthryl)ethynyl]benzonitrile 8C. Prepared by coupling 9-bromo-10-iodoanthracene with 4-ethynyl-benzonitrile **7C** (1:1.1), following the procedure described for bromoderivative **8A**. The crude product was purified by crystallization from toluene (30 ml) to give the pure compound as yellow crystals. Yield: 89%; ¹H NMR (CDCl₃, δ): 8.53 (m, 4H), 7.76 (m, 2H), 7.67 (m, 2H), 7.58 (m, 4H).^{S4}

E-factor: *vide infra*

5-[(10-[[3,4-Bis(hexyloxy)phenyl]ethynyl]-9-anthryl)ethynyl]-2-(hexyloxy)benzonitrile (2). In a screw capped vial equipped with a magnetic stirrer 3,4-bis(hexyloxy)ethynylbenzene **9** (0.130 g, 0.43 mmol),

degassed cyclopentyl methyl ether (CPME, 0.66 ml), bromoderivative **8A** (0.39 mmol), diisopropylamine (2.126 g, 21.06 mmol), CuI (0.0029 g, 0.015 mmol), and PdEnCatTPP30 (0.082 g, 0.033 mmol) were consecutively added and the resulting mixture was left under vigorous stirring at 50°C. After 20 hours, the crude mixture was diluted with CHCl₃ (2 ml), the catalyst was filtered off, and the solvent removed under vacuum to give 9-bromo-10-[4-hexyloxy-(3-nitrophenyl)ethynyl]anthracene **8**. This latter was purified by recrystallization from ethyl acetate (2x25ml) to give the pure compound as orange needles. Yield: 67%. ¹H-NMR (CDCl₃, δ): 8.69 (m, 3H), 8.61 (m, 3H), 7.96 (s, 1H), 7.57 (m, 1H), 7.52 (m, 3H), 7.26 (m, 1H), 7.02 (m, 1H), 6.94 (m, 1H), 4.10 (m, 4H), 1.88 (m, 6H), 1.51 (m, 6H), 0.92 (m, 6H); ¹³C-NMR (CDCl₃, δ): 14.0, 22.5, 22.6, 25.5, 25.7, 28.8, 29.2, 29.3, 31.4, 31.6, 69.2, 69.52, 76.7, 76.9, 77.3, 86.9, 99.6, 112.5, 113.4, 115.4, 116.7, 125.3, 126.6, 126.9, 127.4, 131.9, 132.1, 136.7, 160.6. An. Calcd. For: C₄₉H₅₃NO₃: C, 83.60; H, 7.59; N, 1.99. Found: C, 83.72; H, 7.60; N, 1.97%.

E-factor = [0.130 g (3,4-bis(hexyloxy)ethynylbenzene) + 0.188 g (**8A**) + 0.57 g (cyclopentyl methyl ether) + 0.0029 g (CuI) + 2.126 g (diisopropylamine) + 0.082 g (PdEnCatTPP30) + 2.98 g (CHCl₃) + 45.10 g (ethyl acetate) – 0.186 g (product x yield)]/0.186 g = **274.1**

9-[[3,4-Bis(hexyloxy)phenyl]ethynyl]-10-[[4-nitrophenyl]ethynyl]anthracene (3). Prepared by coupling compound **8B** and 1,2-bis(hexyloxy)-4-ethynylbenzene (**9**) (1/1.1) following the procedure described for reaction between **8** and **9**. Yield: 69% (red crystals).^{S3} ¹H-NMR (CDCl₃, δ): 8.65 (m, 2H), 8.55 (m, 2H), 8.24 (d, J = 8.8 Hz, 2H), 7.80 (d, J = 8.7 Hz, 2H), 7.61 (m, 4H), 7.30 (d, 1H), 6.88 (d, 1H), 4.01 (m, 4H), 1.82 (m, 4H), 1.62–1.20 (m, 10H), 0.87 (s, 6H).

E-factor: *vide infra*

4-[(10-[[3,4-Bis(hexyloxy)phenyl]ethynyl]-9-anthryl)ethynyl]benzonitrile (4). Prepared by coupling compound **8C** and 1,2-bis(hexyloxy)-4-ethynylbenzene (**9**) (1/1.1) following the above procedure. Yield: 70% (red-orange crystals); m.p. 158°-159°C; ¹H-NMR (CDCl₃, δ): 8.65 (m, 2H), 8.56 (m, 2H), 7.81 (d, J=8.6 Hz, 2H), 7.69 (d, J=8.6 Hz, 2H), 7.61 (m, 4H), 7.29 (m, 1H), 7.20 (m, 1H), 6.88 (m, 1H), 4.32 (m, 4H), 1.82 (m, 6H), 1.47 (m, 6H), 1.21 (m, 4H), 0.83 (m, 6H). ¹³C-NMR (CDCl₃, δ): 150.4, 148.9, 132.3, 132.2, 132.0, 131.8, 128.3, 127.5, 127.2, 126.8, 126.7, 125.4, 120.3, 118.5, 116.7, 116.4, 115.2, 113.3, 111.6, 103.7, 100.2, 91.0, 84.8, 69.5, 69.2, 31.6, 29.2, 29.1, 25.7, 22.6, 14.0. An. Calcd. For: C₄₃ H₄₁ NO₂: C, 85.54; H, 6.84; N, 2.32. Found: C, 85.48; H, 6.85; N, 2.30%.

E-factor = [0.130 g (3,4-bis(hexyloxy)ethynylbenzene) + 0.191 g (**8C**) + 0.57 g (cyclopentyl methyl ether) + 0.0029 g (CuI) + 2.126 g (diisopropylamine) + 0.082 g (PdEnCatTPP30) + 2.98 g (CHCl₃) + 45.10 g (ethyl acetate) – 0.211 g (product x yield)]/0.211 g = **241.56**

E-factor calculation for the preparation of [3,4-bis(hexyloxy)phenyl]ethynyltrimethylsilane 11 by the Sonogashira reaction of 0.5 mmol of 1,2-bis(hexyloxy)4-iodobenzene 10 with trimethylsilylacetylene.

- L. Valentini, D. Bagnis, A. Marrocchi, M. Seri, A. Taticchi, and J. M. Kenny *Chem. Mater.* 2008, **20**, 32 (SI):

E-factor= [0.202 g (1,2-Bis(hexyloxy)-4-iodobenzene) + 0.729 g (diisopropylamine) + 2.041 g (toluene) + 0.197 g (trimethylsilylacetylene) + 0.0077 g (CuI) + 0.0473 (PdCl₂(PPh₃)₂) + 30 g (SiO₂) + 49.7 g (CH₂Cl₂) + 140.05 g (C₆H₁₄) – 0.185 g (product x yield)]/0.185 g = **1204.3**

- **Optimized conditions:**

E-factor= [0.202 g (1,2-Bis(hexyloxy)-4-iodobenzene) + 0.075 g (diisopropylamine) + 0.204 g (2-methyl-THF) + 0.073 g (trimethylsilylacetylene) + 0.0019 g (CuI) + 0.025 (PdEnCatTPP30) + 3.97 g (CH₂Cl₂) + 6.0 g (H₂O) – 0.185 g (product x yield)]/0.185 g = **56.03**

Not accounting for drying agent.

Waste reduction: **95.3%**

E-factor calculation for the preparation of 3,4-Bis(hexyloxy)ethynylbenzene 9 by the de-silylation reaction of 0.5 mmol of bis(hexyloxy)phenyl]ethynyltrimethylsilane 11.

- L. Valentini, D. Bagnis, A. Marrocchi, M. Seri, A. Taticchi, and J. M. Kenny *Chem. Mater.* 2008, **20**, 32 (SI).

E-factor= [0.188 g ([bis(hexyloxy)phenyl]ethynyltrimethylsilane) + 0.189 g (TBAF in THF) + 3.32 g (THF) + 20 g (SiO₂) + 166 g (petroleum ether) + 60 g (CH₂Cl₂) – 0.138 g (product x yield)]/0.138 g=
1808.4

- **Optimized conditions:**

E-factor = [0.188 g ([bis(hexyloxy)phenyl]ethynyltrimethylsilane) + 0.0625 g (TBAF/SiO₂) + 2.25 g (ethyl acetate) – 0.146 g (product x yield)]/0.146 g= **16.1**

Waste reduction: **99.1%**

E-factor calculation for the preparation of 9-bromo-10-(4-nitrophenylethynyl) anthracene 8B by the Sonogashira reaction of 0.39 mmol of 9-bromo-10-iodoanthracene with 4-nitro-ethynylbenzene 7B.

- A. Marrocchi, A. Spalletti, R. Flamini, I., S. Ciorba, M. Seri, F. Elisei, and A. Taticchi, *J. Photochem. Photobiol. A* 2010, **211**, 162 (S2).

E-factor = [0.063 g (4-nitro-ethynylbenzene) + 0.149 g (9-bromo,10-iodoanthracene) + 1.80 g (toluene) + 0.0053 g (CuI) + 2.126 g (diisopropylamine) + 0.032 g (Pd(PPh₃)₄) + 40 g (SiO₂) + 265 g (CH₂Cl₂) + 520 g (petroleum ether) – 0.141 g (product x yield)]/0.141 g = **5879.6**

- **Optimized conditions:**

E-factor = [0.063 g (4-nitro-ethynylbenzene) + 0.149 g (9-bromo,10-iodoanthracene) + 0.57 g (cyclopentyl methyl ether) + 0.00074g (CuI) + 1.063 g (diisopropylamine) + 0.029 g (PdEnCat30) + 2.98 g (CHCl₃) + 43.25 g (toluene) – 0.147 g (product x yield)]/0.147 g = **326.2**

Waste reduction: **94.4%**

E-factor calculation for the preparation of 4-[(10-bromo-9-anthryl)ethynyl]benzonitrile 8C by the Sonogashira reaction of 0.39 mmol of 9-bromo-10-iodoanthracene with 4-ethynyl-benzonitrile 7C.

- R. Flamini, I. Tomasi, A. Marrocchi, B. Carlotti, A. Spalletti, *J. Photochem. Photobiol. A* 2011, **223**, 140 (S3)

E-factor = [0.052 g (4-ethynyl-benzonitrile) + 0.149 g (9-bromo,10-iodoanthracene) + 2.02 g (toluene) + 0.011 g (CuI) + 2.126 g (diisopropylamine) + 0.064 g (Pd(PPh₃)₄) + 40 g (SiO₂) + 331.25 g (CH₂Cl₂) + 487.5 g (petroleum ether) – 0.131 g (product x yield)]/0.131 g = **6588.1**

- **Optimized conditions:**

E-factor = [0.052 g (4-ethynyl-benzonitrile) + 0.149 g (9-bromo,10-iodoanthracene) + 0.57 g (cyclopentyl methyl ether) + 0.00074g (CuI) + 1.063 g (diisopropylamine) + 0.029 g (PdEnCat30) + 2.98 g (CHCl₃) + 25.95 g (toluene) – 0.137 g (product x yield)]/0.137 g = **223.7**

Waste reduction: **96.6%**

E-factor calculation for the preparation of 9-[[3,4-bis(hexyloxy)phenyl]ethynyl]-10-[[4-nitrophenyl]ethynyl]anthracene (3) by the Sonogashira reaction of 0.39 mmol of 9-bromo-10-(4-nitrophenylethynyl) anthracene 8B with 3,4-bis(hexyloxy)ethynylbenzene 9.

- Marrocchi, A. Spalletti, R. Flamini, I., S. Ciorba, M. Seri, F. Elisei, and A. Taticchi, *J. Photochem. Photobiol. A* 2010, **211**, 162.(S2)

E-factor = [0.130 g (3,4-bis(hexyloxy)ethynylbenzene) + 0.156 g (**8B**) + 2.02 g (toluene) + 0.011 g (CuI) + 2.126 g (diisopropylamine) + 0.064 g (Pd(PPh₃)₄) + 40 g (SiO₂) + 331.25 g (CH₂Cl₂) + 487.5 g (petroleum ether) – 0.148 g (product x yield)]/0.148 g = **5831.8**

- **Optimized conditions:**

E-factor= 305.3

[0.130 g (3,4-bis(hexyloxy)ethynylbenzene) + 0.156 g (**8B**) + 0.57 g (cyclopentyl methyl ether) + 0.0029 g (CuI) + 2.126 g (diisopropylamine) + 0.082 g (PdEnCatTPP30) + 2.98 g (CHCl₃) + 45.10 g (ethyl acetate) – 0.167 g (product x yield)]/0.167 g

Waste reduction: **94.8%**

Table S1. Optimization of the Sonogashira reaction of [4-(Hexyloxy)-3-nitro]iodobenzene **5** with trimethylsilylacetylene (TMSA)

Entry	Medium ^a	iPr ₂ NH (eq)	Catalyst (mol%)	CuI (mol%)	TMSA (eq)	Conversion (%) ^b
1	Toluene	14	PdEncatTPP30 (8)	8	4	32
2	THF	14	PdEncatTPP30 (8)	8	4	88
3	Cyclopentylmethyl ether	14	PdEncatTPP30 (8)	8	4	55
4	Ethanol 96%	14	PdEncatTPP30 (8)	8	4	13
5	2-methyl-THF	14	PdEncatTPP30 (8)	8	4	100
6	2-methyl-THF	14	PdEncatTPP30 (8)	8	2	100
7	2-methyl-THF	4	PdEncatTPP30 (8)	8	2	100
8	2-methyl-THF	1.5	PdEncatTPP30 (8)	8	1.5	100
9	2-methyl-THF ^c	1.5	PdEncatTPP30 (2)	2	1.5	92
10	2-methyl-THF ^d	1.5	PdEncatTPP30 (2)	2	1.5	92
11	2-methyl-THF ^e	1.5	PdEncatTPP30 (2)	2	1.5	100
12	2-methyl-THF	1.5	PdEncatTPP30 (2)	2	1.5	78 ^f
13	2-methyl-THF	1.5	PdEncatTPP30 (1)	1	1.5	39
14	2-methyl-THF	1.2	PdEncatTPP30 (2)	2	1.2	47
15	2-methyl-THF	1.05	PdEncatTPP30 (5)	5	1.05	72
16	2-methyl-THF	1.05	PdEncatTPP30 (2)	2	1.05	46
17	2-methyl-THF	1.05	Pd/C (2)	2	1.05	5
18	2-methyl-THF	1.05	Pd/Al ₂ O ₃ (2)	2	1.05	--
19	2-methyl-THF	1.05	PdEnCat30 (2)	2	1.05	--
20	2-methyl-THF	1.05	PdCl ₂ (PPh ₃) ₂ -polymer bound (2)	2	1.05	--

^a0.125 M; ^bReaction time: 18h, Reaction temperature: 30°C; ^cComplete conversion after 24 h, 99% yield; ^d 0.4 M; ^e 1M; ^f 2.5M

Table S2. Optimization of the de-silylation reaction of {[4-hexyloxy-, 3-nitrophenyl]ethynyl}(trimethyl)silane **6**.

Entry ^a	Catalyst (mol%)	Reaction time	Conversion (%)
1	TBAF ^b (100)	20 h	90
2	TBAF · H ₂ O (20)	10'	100
3	TBAF · H ₂ O (10)	15'	100
4	TBAF · H ₂ O (5)	15'	5
5	TBAF · H ₂ O (5)	2 h	5
7	Amb-F (20)	15'	3
8	Amb-F (20)	3 h	12
9	Amb-F (20)	20 h	36
10	Amb-F (20)	48 h	60
11	TBAF/SiO ₂ (20)	15'	100
12	TBAF/SiO ₂ (10) ^c	15'	55
13	TBAF/SiO ₂ (10) ^c	2 h	83
14	TBAF/SiO ₂ (10) ^c	3 h	100
15	TBAF/SiO ₂ (10) ^d	20 h	--
16	KF/Al ₂ O ₃ (10)	20 h	--
17	DABCO-F2 (10) ^e	20 h	21

^aSolFC; ^b1M in THF; ^cloading: 1.25 mmol/g; ^dloading: 0.29 mmol/g; ^eloading: 4.8 mmol/g

Table S3. Optimization of the Sonogashira reaction of 4-ethynyl-1-(hexyloxy)-2-nitrobenzene **7** with 9-bromo,10-iodoanthracene.^a

Entry	Medium ^b	iPr ₂ NH (eq)	Catalyst (mol%)	CuI (mol%)	Conversion (%) ^c
1	Toluene	45	PdEnCatTPP30 (4)	4	23
2	THF	45	PdEnCatTPP30 (4)	4	70
3	2-methyl-THF	45	PdEnCatTPP30 (4)	4	75
4	Ethanol 96%	45	PdEnCatTPP30 (4)	4	23
5	Cyclopentyl methyl ether	45	PdEnCatTPP30 (4)	4	100
6	Cyclopentyl methyl ether	36	PdEnCatTPP30 (4)	4	88
7	Cyclopentyl methyl ether	27	PdEnCatTPP30 (4)	4	87
8	Cyclopentyl methyl ether	18	PdEnCatTPP30 (4)	4	82
9	Cyclopentyl methyl ether ^d	27	PdEnCatTPP30 (4)	4	60
10	Cyclopentyl methyl ether ^e	27	PdEnCatTPP30 (4)	4	53
11	Cyclopentyl methyl ether ^f	27	PdEnCatTPP30 (4)	4	45
12	Cyclopentyl methyl ether	27	PdEnCat40 (4)	4	--
13	Cyclopentyl methyl ether	27	PdEnCatPolyTPP (4)	4	90
14	Cyclopentyl methyl ether	27	Pd/SiO ₂ (4)	4	5
15	Cyclopentyl methyl ether	27	Pd/Al ₂ O ₃ (4)	4	47
16	Cyclopentyl methyl ether	27	PdEnCat30 (4)	4	100
17	Cyclopentyl methyl ether	27	PdEnCat30 (4)	0.5	93
18	Cyclopentyl methyl ether	27	PdEnCat30 (4)	1	100
19	Cyclopentyl methyl ether	27	PdEnCat30 (3)	1	100
20	Cyclopentyl methyl ether	27	PdEnCat30 (2)	1	81

^a 1.1:1 Molar ratio; ^b 0.06 M; ^c Reaction time: 18h. Reaction temperature: 55°C; ^d 0.13 M; ^e 0.2 M; ^f 0.5M.

Table S4. Optimization of the Sonogashira reaction of 3,4- bis(hexyloxy)- ethynylbenzene **9** with 9-bromo-10-[4-hexyloxy-(3-nitrophenyl)ethynyl]anthracene **8**.

Entry	Medium ^b	iPr ₂ NH (eq)	Catalyst (mol%)	CuI (mol%)	Conversion (%) ^c
1	Toluene	45	PdEnCatTPP30 (4)	4	28
3	2-methyl-THF	45	PdEnCatTPP30 (4)	4	21
5	Cyclopentyl methyl ether	45	PdEnCatTPP30 (4)	4	25
6	Cyclopentyl methyl ether	45	PdEnCatTPP30 (6)	4	78
7	Cyclopentyl methyl ether	27	PdEnCatTPP30 (6)	4	75
8	Cyclopentyl methyl ether	27	PdEnCatTPP30 (6)	1	70
13	Cyclopentyl methyl ether	27	PdEnCatPolyTPP (4)	4	90
14	Cyclopentyl methyl ether	27	Pd/SiO ₂ (4)	4	--
15	Cyclopentyl methyl ether	27	Pd/Al ₂ O ₃ (4)	4	23
16	Cyclopentyl methyl ether	27	PdEnCat30 (4)	4	--

^a 1.1:1 Molar ratio; ^b 0.06 M; ^c Reaction time: 20h. Reaction temperature: 50°C.

Table S5. Optimization of the Sonogashira reaction of 1,2-Bis(hexyloxy)-4-iodobenzene **10** with trimethylsilylacetylene (TMSA)

Entry	Medium ^a	iPr ₂ NH (eq)	Catalyst (mol%)	CuI (mol%)	TMSA (eq)	Conversion (%) ^b
1	Toluene	14	PdEnCatTPP30 (8)	8	4	25
2	THF	14	PdEnCatTPP30 (8)	8	4	85
3	Cyclopentylmethyl ether	14	PdEnCatTPP30 (8)	8	4	50
4	Ethanol 96%	14	PdEnCatTPP30 (8)	8	4	9
5	2-methyl-THF	14	PdEnCatTPP30 (8)	8	4	100
6	2-methyl-THF	14	PdEnCatTPP30 (8)	8	2	100
7	2-methyl-THF	4	PdEnCatTPP30 (8)	8	2	100
8	2-methyl-THF	1.5	PdEnCatTPP30 (8)	8	1.5	100
9	2-methyl-THF ^c	1.5	PdEnCatTPP30 (2)	2	1.5	89
10	2-methyl-THF ^d	1.5	PdEnCatTPP30 (2)	2	1.5	89
11	2-methyl-THF ^e	1.5	PdEnCatTPP30 (2)	2	1.5	100
12	2-methyl-THF	1.5	PdEnCatTPP30 (2)	2	1.5	76 ^f
13	2-methyl-THF	1.5	PdEnCatTPP30 (1)	1	1.5	41
14	2-methyl-THF	1.2	PdEnCatTPP30 (2)	2	1.2	47
15	2-methyl-THF	1.05	PdEnCatTPP30 (5)	5	1.05	69
16	2-methyl-THF	1.05	PdEnCatTPP30 (2)	2	1.05	42
17	2-methyl-THF	1.05	Pd/C (2)	2	1.05	--
18	2-methyl-THF	1.05	Pd/Al ₂ O ₃ (2)	2	1.05	--
19	2-methyl-THF	1.05	PdEnCat30 (2)	2	1.05	--
20	2-methyl-THF	1.05	PdCl ₂ (PPh ₃) ₂ -polymer bound (2)	2	1.05	--

^a0.125 M; ^bReaction time: 18h, Reaction temperature: 30°C; ^cComplete conversion after 24 h, 99% yield; ^d 0.4 M; ^e 1M; ^f 2.5M

Table S6. Optimization of the de-silylation reaction of {[3,4-bis(hexyloxy)phenyl]ethynyl}(trimethyl)silane **11**.

Entry ^a	Catalyst (mol%)	Reaction time	Conversion (%)
1	TBAF ^b (100)	20 h	90
2	TBAF · H ₂ O (20)	15'	100
3	TBAF · H ₂ O (10)	15'	100
4	TBAF · H ₂ O (5)	15'	3
5	TBAF · H ₂ O (5)	2 h	6
6	TBAF · H ₂ O (5)	20 h	55
7	Amb-F (20)	15'	5
8	Amb-F (20)	3 h	36
9	Amb-F (20)	20 h	84
10	Amb-F (20)	48 h	100
11	TBAF/SiO ₂ (20)	15'	100
12	TBAF/SiO ₂ (10) ^c	15'	45
13	TBAF/SiO ₂ (10) ^c	2 h	73
14	TBAF/SiO ₂ (10) ^c	3 h	100
15	TBAF/SiO ₂ (10) ^d	20 h	5
16	KF/Al ₂ O ₃ (10)	20 h	--
17	DABCO-F2 (10) ^e	20 h	21

^a SolFC; ^b 1M in THF; ^c loading: 1.25 mmol/g; ^d loading: 0.29 mmol/g; ^e loading: 4.8 mmol/g

Table S7. Optical band gaps for compounds **1-4** in solution (CHCl₃) and as thin-films.

Donor	$(E_g^{opt})_{soln}$ (eV)	$(E_g^{opt})_{film}$ (eV)
1	2.49	2.98
2	2.45	2.22
3	2.36	2.36
4	2.38	2.49

Table S8. FET performance parameters measured under vacuum for anthracene-based arylacetylenes **1**, **3**, and **4** films spin-cast from chloroform.

Semiconductor	T _a ^a (°C)	μ ^b (cm ² V ⁻¹ s ⁻¹)	I _{on} /I _{off}	V _t (V)
1	-	4.3x10 ⁻⁵	1.2x10 ⁴	-59
	40	4.0x10 ⁻⁵	2.3x10 ⁴	-32
	60	3.2x10 ⁻⁵	2.7x10 ⁴	-35
	80	no activity	-	-
	120	no activity	-	-
3	-	5.5x10 ⁻⁵	7.7x10 ¹	-70
	40	2.0x10 ⁻⁶	3.2x10 ¹	-40
	60	4.7x10 ⁻⁶	2.7x10 ¹	-74
	80	no activity	-	-
	120	no activity	-	-
4	-	4.0x10 ⁻⁴	4.9x10 ²	5
	40	3.2x10 ⁻⁴	1.2x10 ³	-1
	60	4.9x10 ⁻³	1.5x10 ³	-8
	80 ^b	3.4x10 ⁻²	1.0x10 ⁵	-4
	120	no activity	-	-

^aT_a= annealing temperature. ^bAnnealing time: 2h

Table S9. Summary of diffraction-derived d-spacing (d), computed molecular lengths (l), and calculated molecular long axis tilt angles (φ) in semiconducting film of compounds **1-4** spin-coated from chloroform solution.

Semiconductor	d-spacing (d, Å) ^a	Molecular length (l, Å) ^b	Tilt angle (φ , deg) ^c
1	26.8	33.3	36.4
2	27.6	33.3	34.0
3	18.9	27.6	46.8
4	39.9	27.6	-

^aMinority phases are not reported; ^bSemiempirical AM1 calculations; ^cWith respect to substrate normal.
 $\varphi = \cos^{-1}(d/l)$

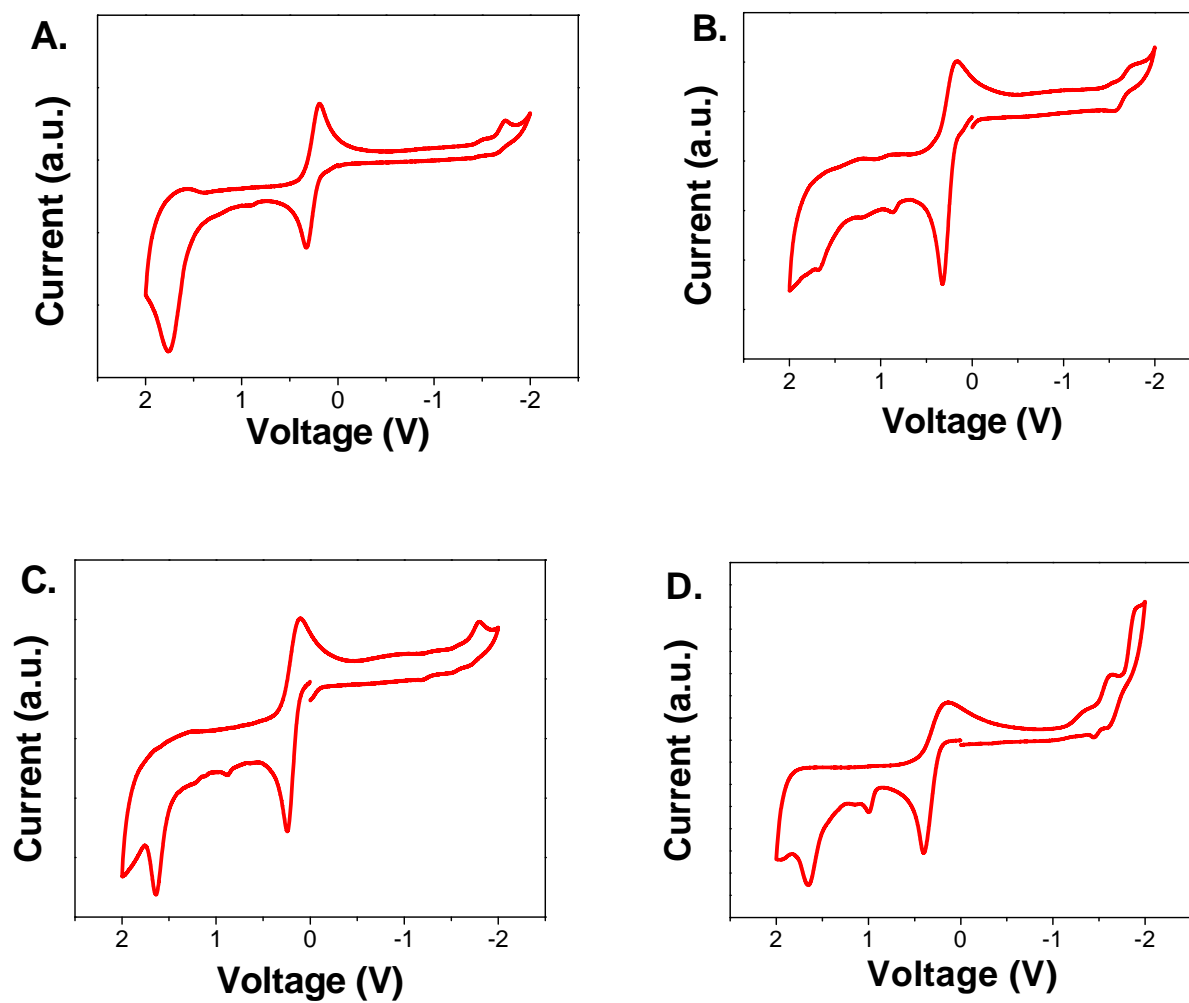


Figure S1. CV curves of anthracene derivatives **1-4** in 0.1 M $\text{Bu}_4\text{N}^+\text{PF}_6^-$ solution in CH_2Cl_2 at a scan rate of 100 mV/s. Ferrocene was used as internal standard.

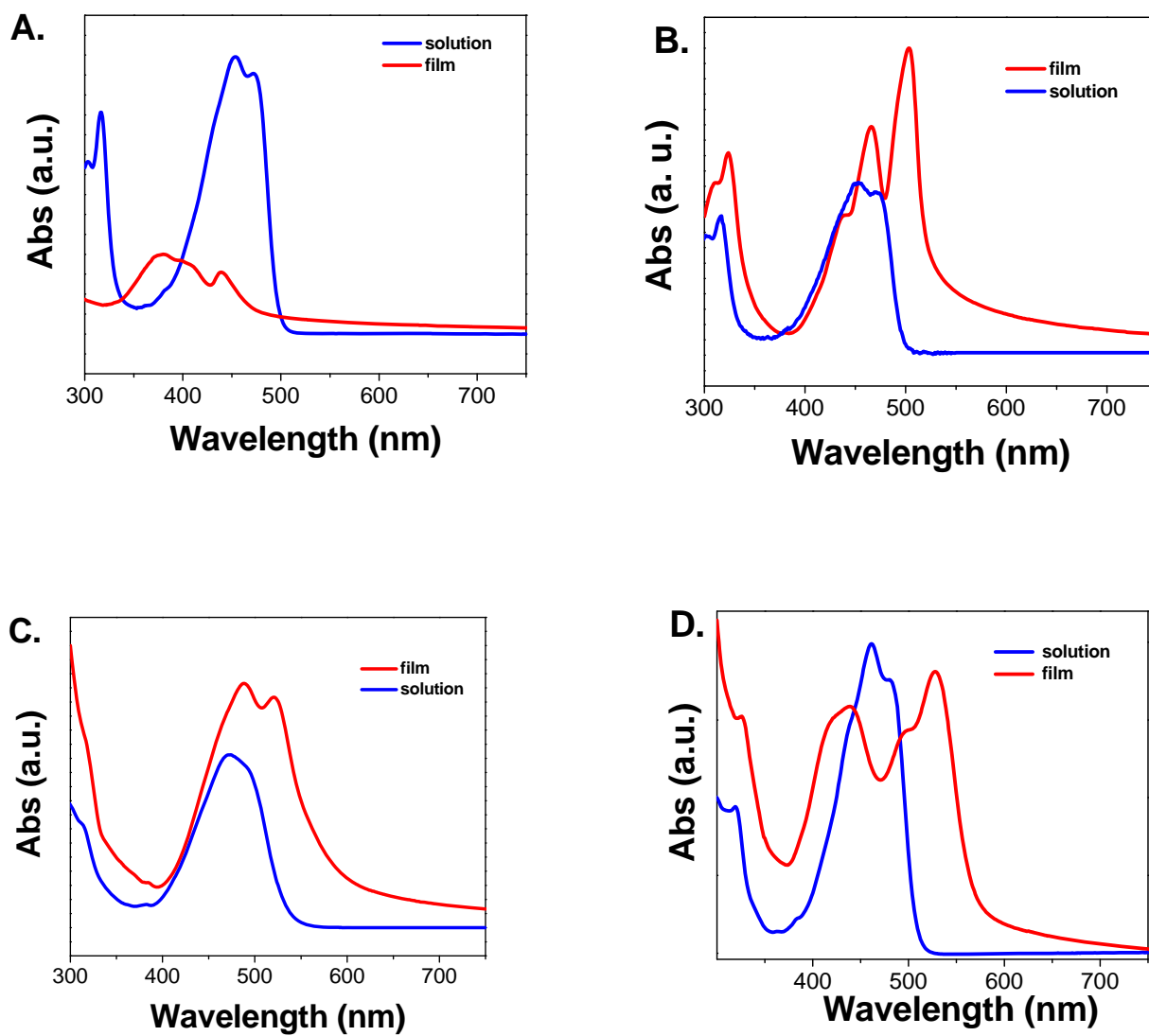


Figure S2. Optical absorption spectra for pristine semiconductors **1-4** in solution and as thin films on glass substrates.

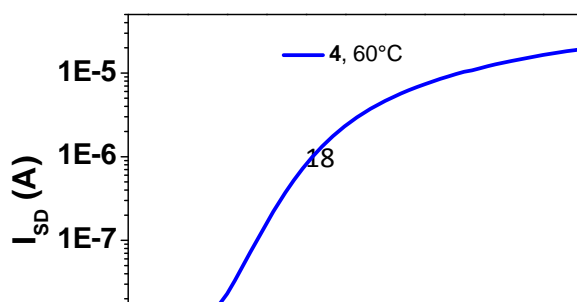
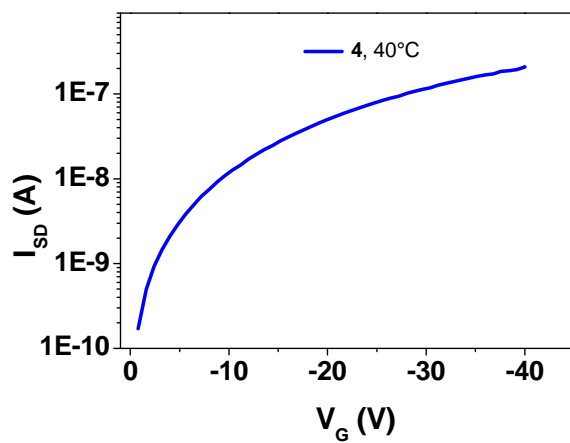
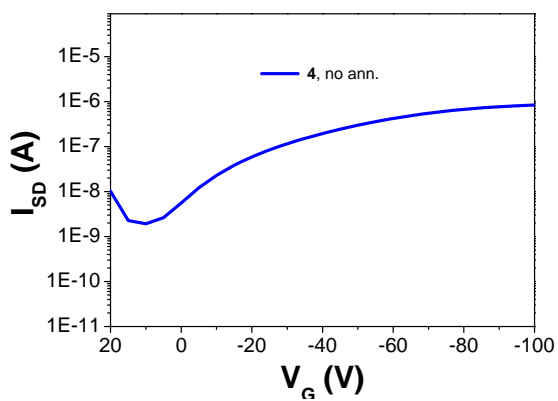
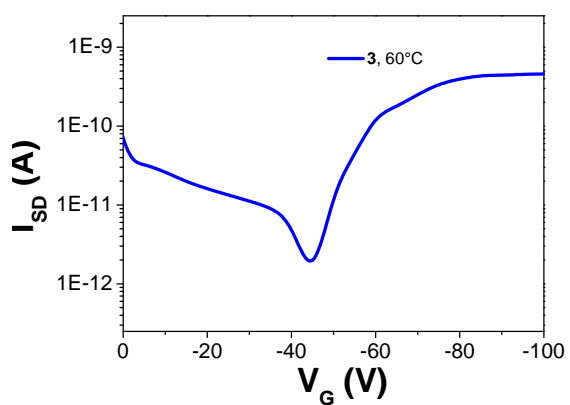
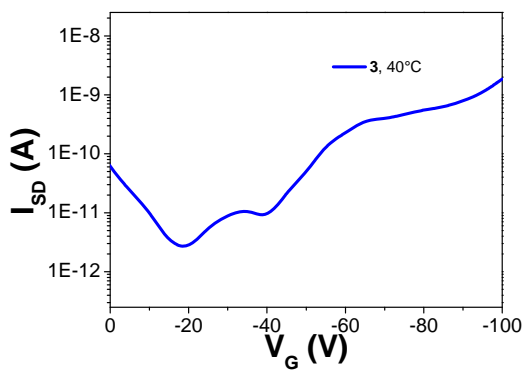
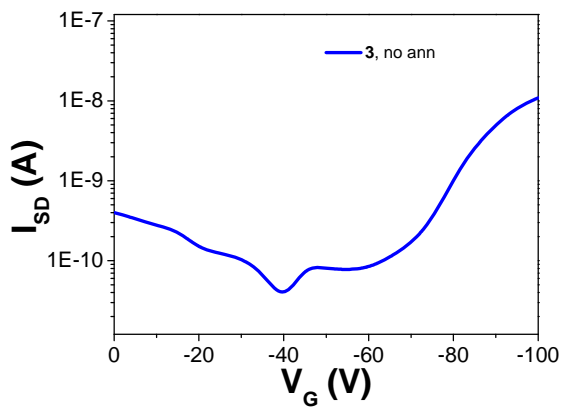
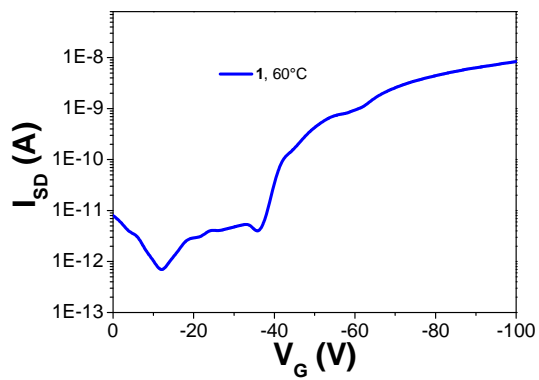
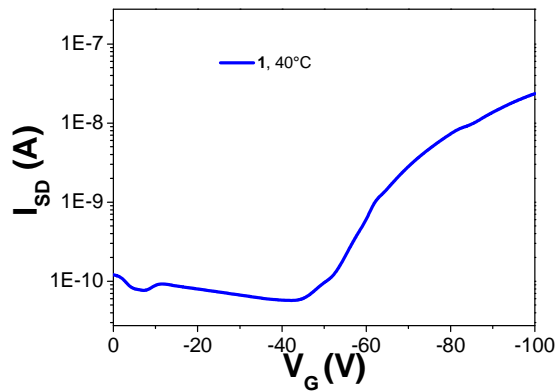
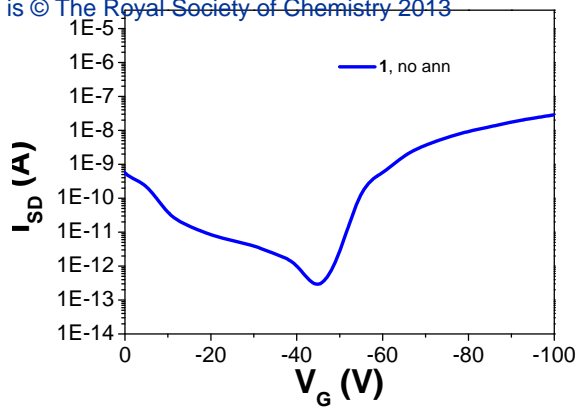


Figure S3. FET transfer plots of arylacetylenes **1**, **3**, and **4** spin cast from chloroform onto Si/SiO₂ substrates and annealed at the indicated temperatures. Devices measured in vacuum.

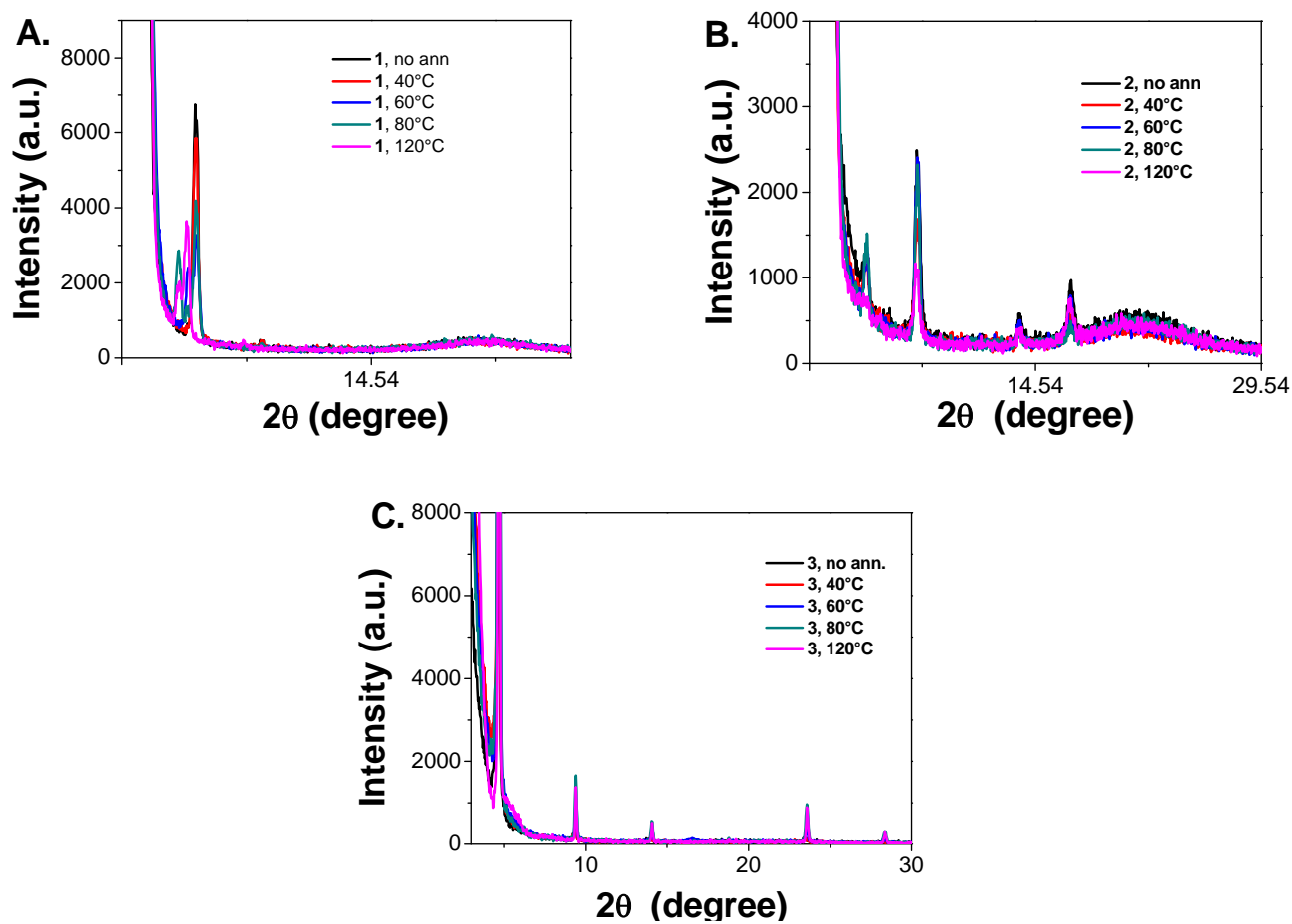
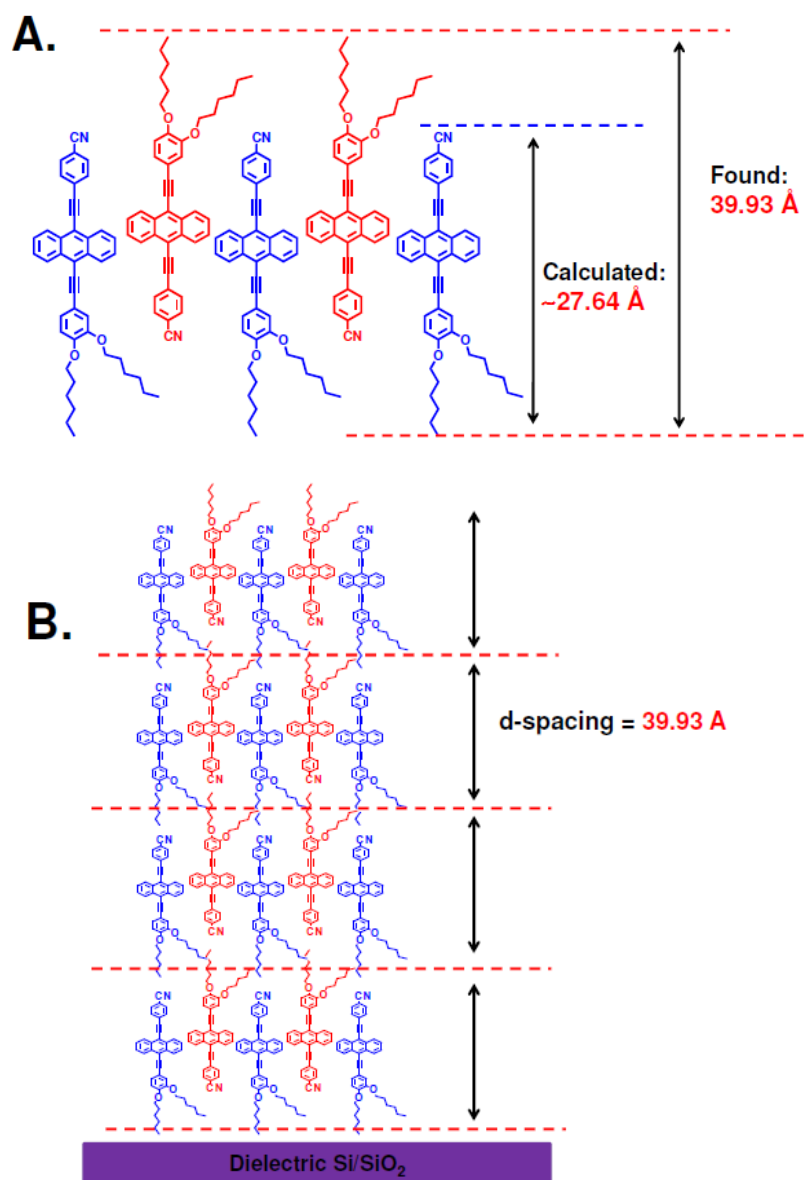
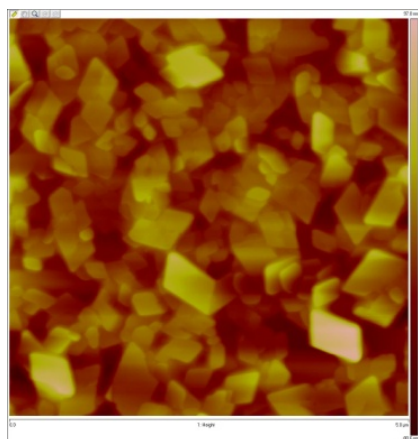


Figure S4. θ - 2θ X-ray diffraction data for spin-cast films of the semiconductors **1-3** annealed at the indicated temperatures and spin-cast from chloroform on Si/SiO₂ substrates.

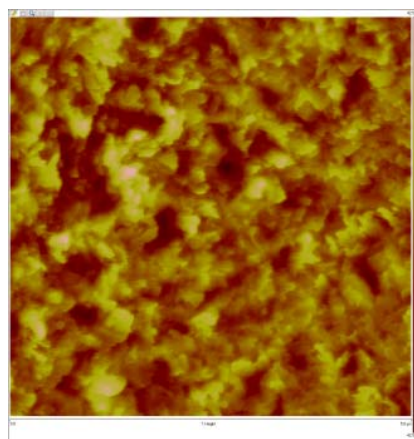


Figure

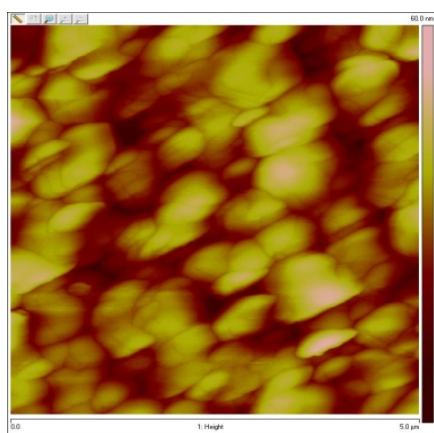
S5.



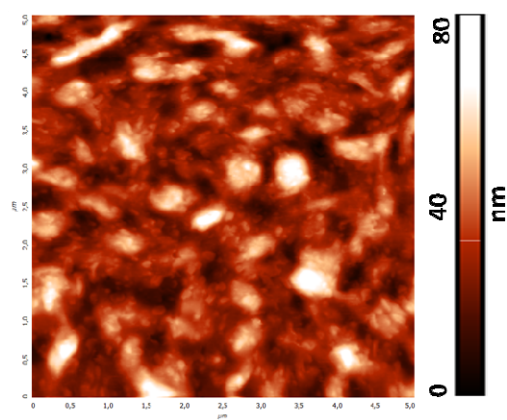
(A.)



(B.)

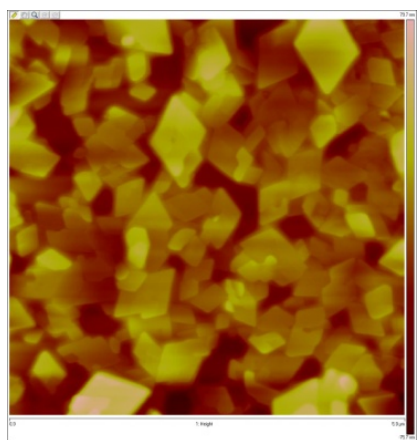


(C.)

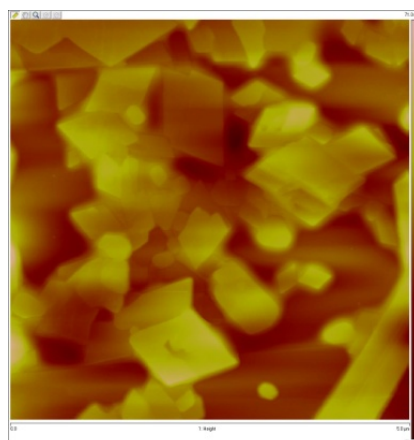


(D.)

Figure S6. Tapping mode AFM images ($5 \times 5 \mu\text{m}$) of films of (A.) **1**, (B.) **2**, (C.) **3**, and (D.) **4** spin-cast from chloroform on Si/SiO₂ substrates.



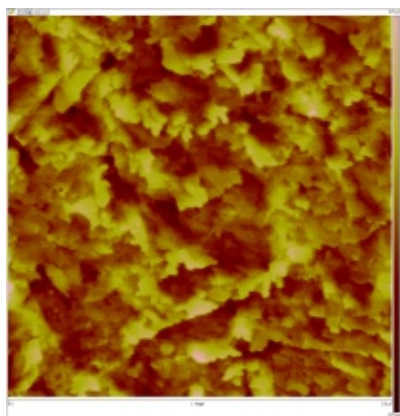
(A.)



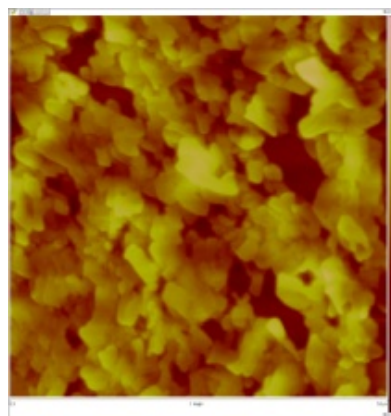
(B.)

Figure S7. Tapping mode AFM images ($5 \times 5 \mu\text{m}$) of films of **1** spin-cast from chloroform on Si/SiO₂

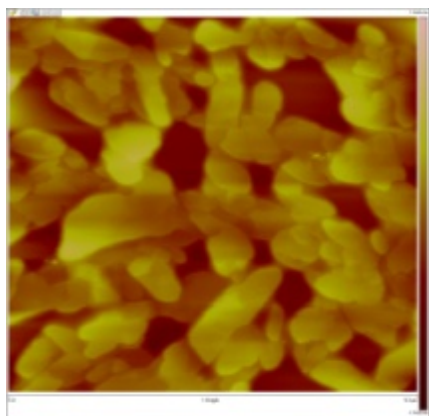
substrates annealed at (A.) 40°C, (B.) 60°C



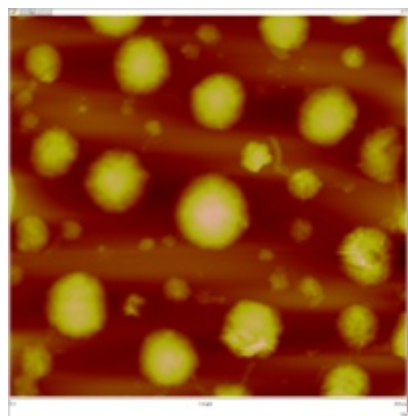
(A.)



(B.)

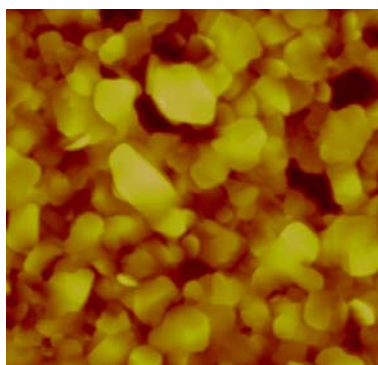


(C.)

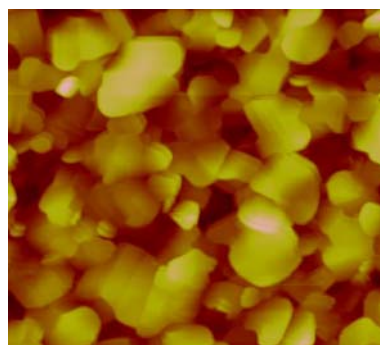


(D.)

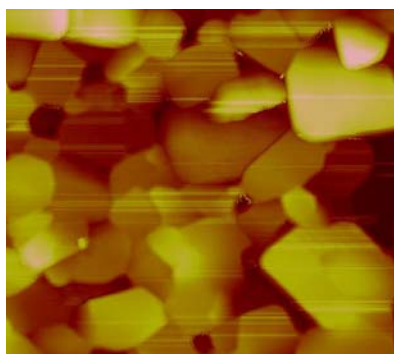
Figure S8. Tapping mode AFM images ($5 \times 5 \mu\text{m}$) of films of **2** spin-cast from chloroform on Si/SiO₂ substrates annealed at (A.) 40°C, (B.) 60°C, (C.) 80°C, and (D.) 120°C



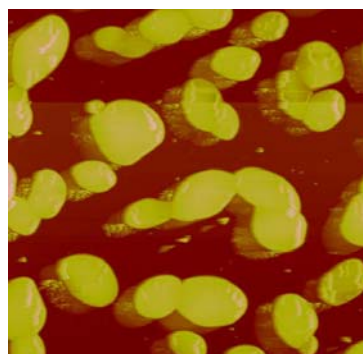
(A.)



(B.)



(C.)



(D.)

Figure S9. Tapping mode AFM images ($5 \times 5 \mu\text{m}$) of films of **3** spin-cast from chloroform on Si/SiO₂ substrates annealed at (A.) 40°C, (B.) 60°C, (C.) 80°C, and (D.) 120°C

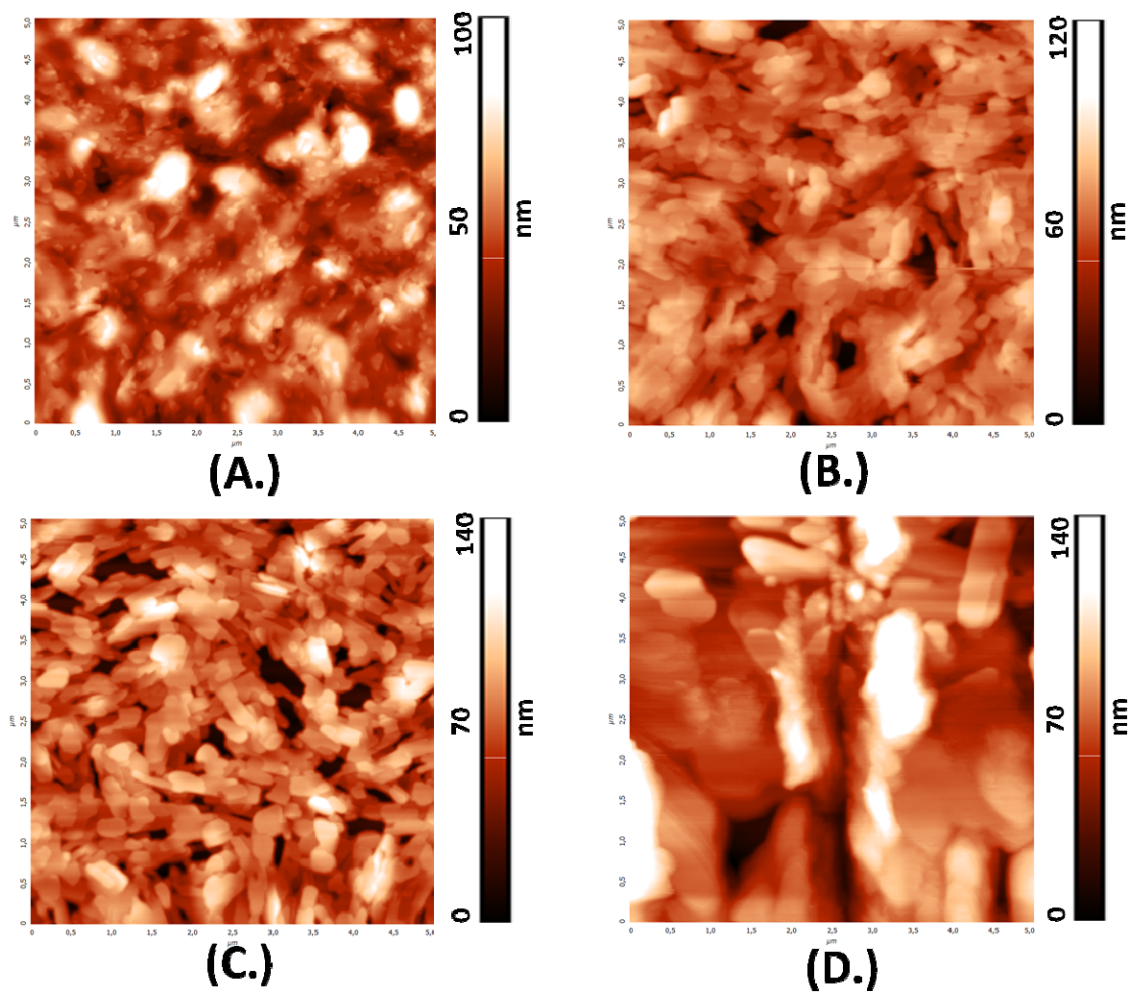


Figure S10. Tapping mode AFM images (5×5 μm) of films of 4 spin-cast from chloroform on Si/SiO₂ substrates annealed at (A.) 40°C, (B.) 60°C, (C.) 80°C, and (D.) 120°C

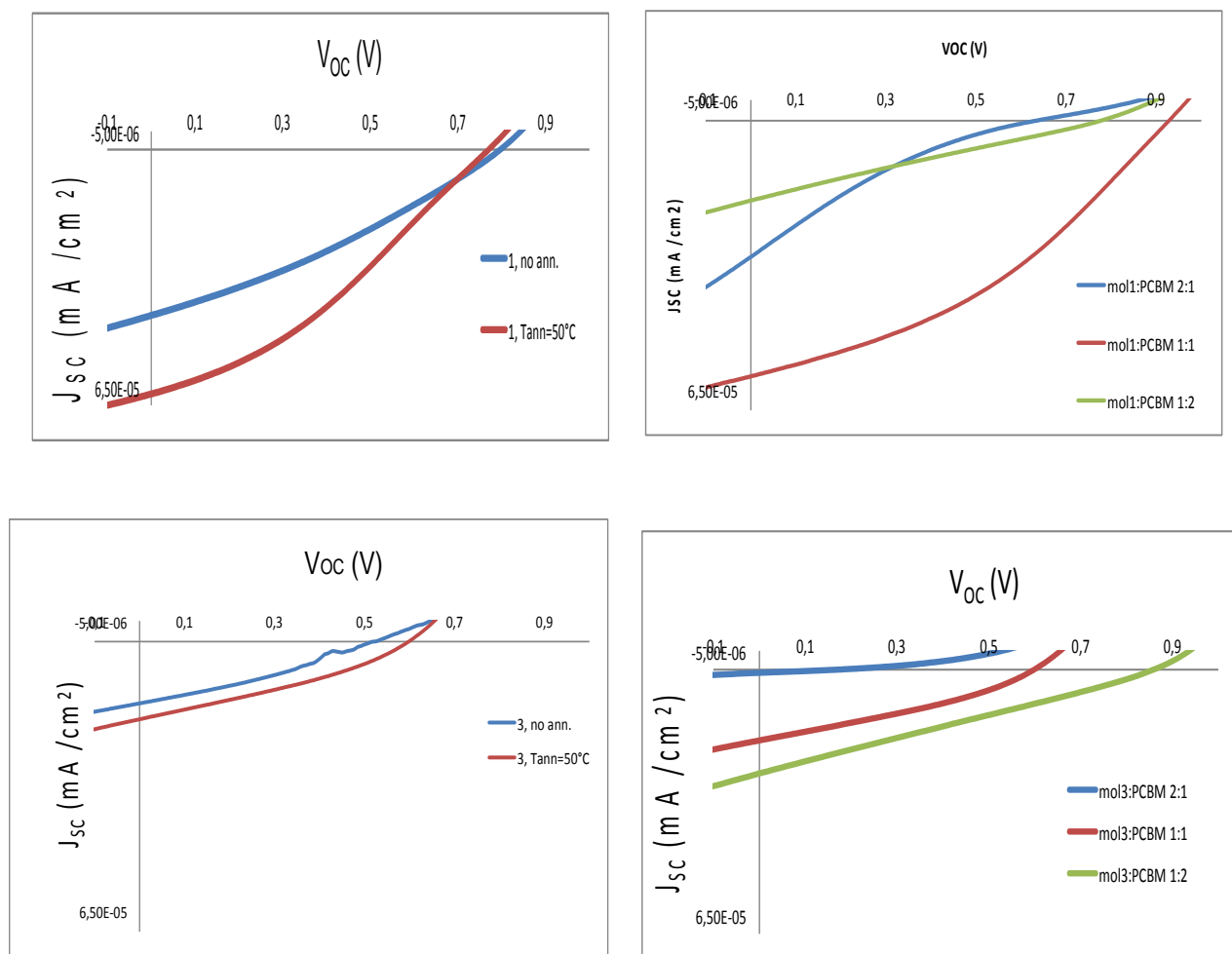
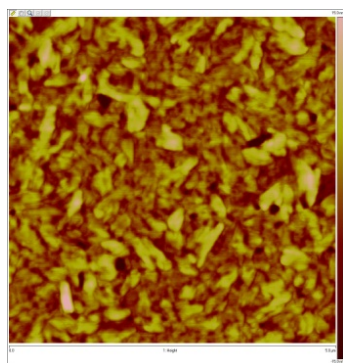
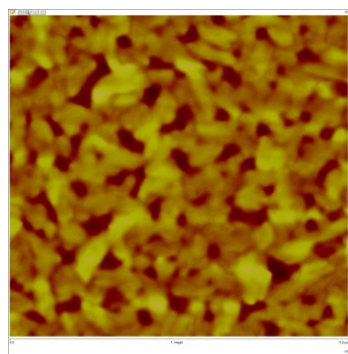


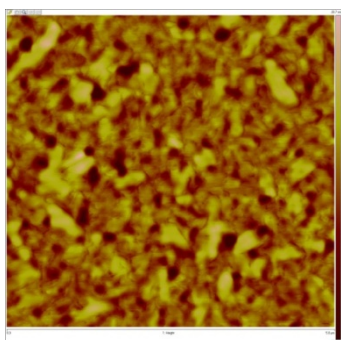
Figure S11. Current density (J)-Voltage (V) characteristics under illumination of optimized 1-, 3- /PCBM based BHJ devices.



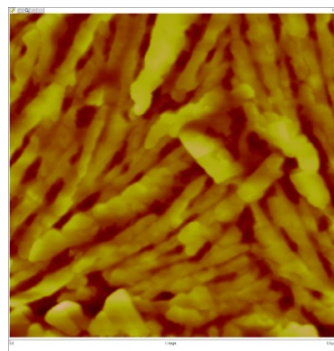
(A)



(B)

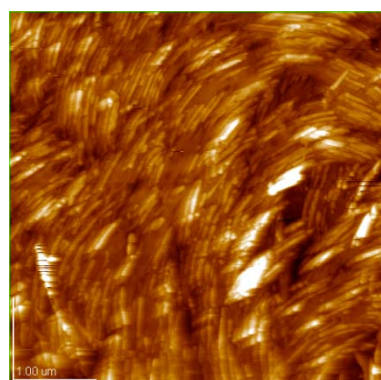


(C)

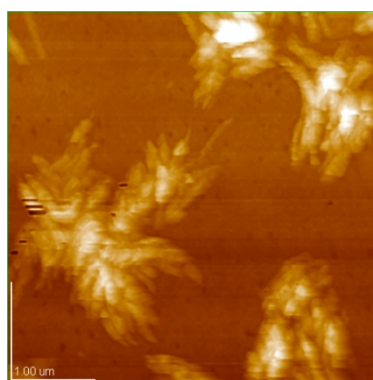


(D)

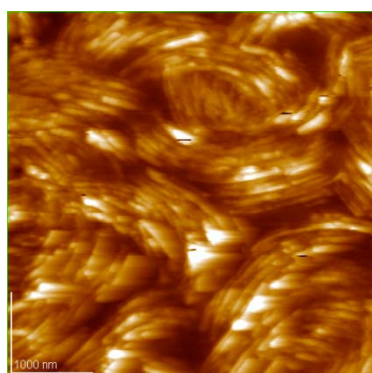
Figure S12. Tapping mode AFM images ($5 \times 5 \mu\text{m}$) of spin-coated films. A.) **1/PCBM 2:1**; B.) **1/PCBM 1:1**; C.) **1/PCBM 1:1** annealed at 50°C ; D.) **3/PCBM 2:1**



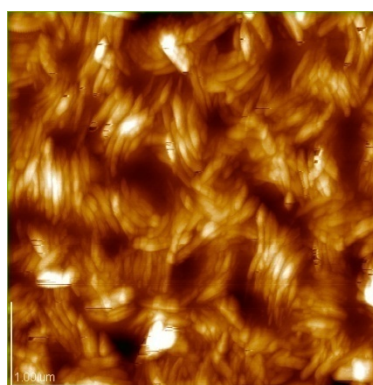
4/PCBM 1:2 $T_a = 50^\circ\text{C}$



4/PCBM 1:1 no annealing



4/PCBM 1:1 $T_a = 50^\circ\text{C}$



4/PCBM 2:1 no annealing

Figure S13. Tapping mode AFM images ($1\mu\text{m}\times 1\mu\text{m}$) of spin-coated 4/PCBM films as a function of D/A ratio, at the indicated annealing temperatures.

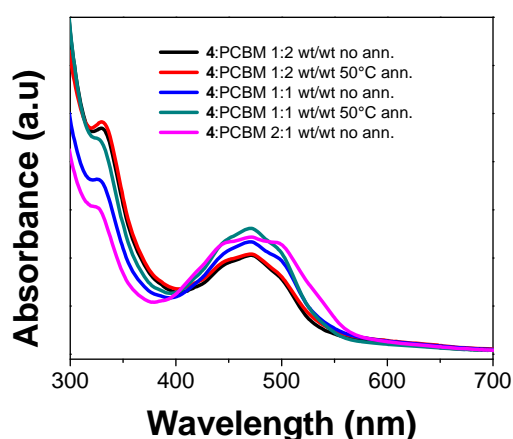
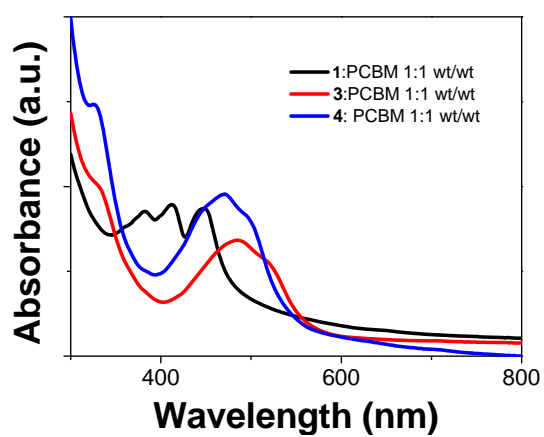


Figure S14. Absorption spectra for 1/PCBM, 3/PCBM and 4/PCBM blend films.

References

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- S2. A. Marrocchi, A. Spalletti, R. Flamini, I., S. Ciorba, M. Seri, F. Elisei, and A. Taticchi, *J. Photochem. Photobiol. A* 2010, **211**, 162
- S3. R. Flamini, I. Tomasi, A. Marrocchi, B. Carlotti, A. Spalletti, *J. Photochem. Photobiol. A* 2011, **223**, 140