Decay of the Exciton in Quaterthiophene-Terminated Alkanethiolate Self-Assembled Monolayers on Au(111)

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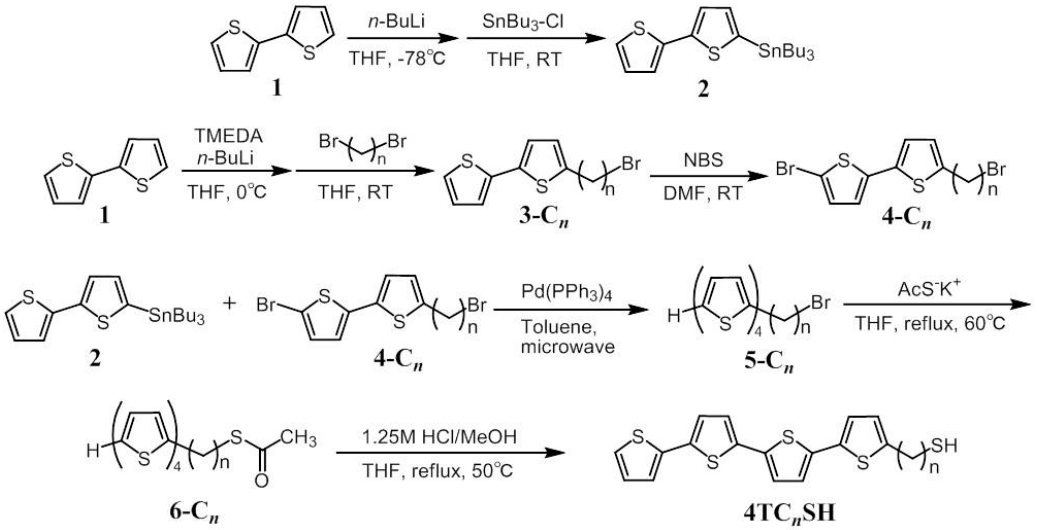
1. Synthesize of 4TC$_n$SH

1.1. General information

Compounds **4TC$_3$SH**, **4TC$_5$SH**, **4TC$_7$SH**, **4TC$_9$SH**, and **4TC$_{13}$SH** were synthesized according to the modified synthetic route of previous report [S1], as shown in **Scheme 1**. Compound **2** was synthesized according to the reported procedure [S2]. Through our synthesis procedure, all reactions were carried out under a nitrogen atmosphere. Solvents of the highest purity grade were used as received. Unless stated otherwise, all reagents were purchased from commercial sources and used without purification. Column chromatography was performed on silica gel, KANTO Chemical silica gel 60N (40–50 μm). Thin-layer chromatography plates were visualized with UV light. Microwave irradiation was performed by a Biotage Initiator Ver. 2.5. ^{1}H NMR spectra were recorded on a JEOL ECS-400 spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. Data are reported as follows: chemical shift δ (ppm), multiplicity (s = singlet, d = doublet, dd = double doublet t = triplet, q = quartet, m = multiplet), coupling constant J (Hz), and integration. High resolution mass spectrum (HRMS) was obtained atmospheric pressure chemical ionization method using LTQ Orbitrap XL at the Elemental Analysis Section of Comprehensive Analysis Center (CAC), ISIR, Osaka University.

Scheme 1.



1.2. Synthesis

*Synthesis of **3-C9***: **1** (2.03 g, 12.2 mmol), and *N*,*N*,*N*',*N*'-tetramethylethylenediamine (TMEDA; 2.0 mL, 13.4 mmol) was placed in a two-necked round-bottomed flask and dissolved with THF (6 mL). *n*-BuLi (1.6 M hexane solution, 8.43 mL, 13.5 mmol) was added to the mixture at 0°C. After stirring for 1 h at room temperature (RT), the mixture was placed in a dropping funnel and added dropwise to a solution of 1,9-dibromononane (5.22 g, 18.2 mmol) in THF (30 mL). After further stirring for 8 h, the reaction was quenched by the addition of water, and the organic layer was separated. The aqueous layer was extracted with hexane, and the combined organic layer was washed with water and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane) to give **3-C9** (1.15 g, 25%). Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.14 (dd, J = 4.9, 0.8 Hz, 1H), 7.08 (dd, J = 3.3, 0.8 Hz, 1H), 6.96 (m, 2H), 6.68 (d, J = 3.0 Hz, 1H), 3.39 (t, J = 7.5 Hz, 2H), 3.00 (t, J = 7.5 Hz, 2H), 1.83 (m, 2H), 1.66 (m, 2H), 1.33 (m, 10H).

*Synthesis of **3-C3**, **3-C5**, **3-C7**,* and ***3-C13***: These compounds were synthesized by following the procedure used for the preparation of **3-C9** with yields of 29, 33, 24, and 43%, respectively.

*^{1}H NMR of **3-C3***: ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.16 (dd, J = 6.0, 0.8 Hz, 1H), 7.09 (dd, J = 3.0, 0.8 Hz, 1H), 6.98 (m, 2H), 6.72 (d, J = 3.0 Hz, 1H), 3.45 (t, J = 7.5 Hz, 2H), 2.98 (t, J = 7.5 Hz, 2H), 2.20 (m, 2H).

*^{1}H NMR of **3-C5***: ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 6.92 (dd, J = 4.8, 0.8 Hz, 1H), 6.90 (dd, J = 2.7, 0.8 Hz, 1H), 6.81 (m, 2H), 6.68 (d, J = 3.0 Hz, 1H), 3.40 (t, J = 7.5 Hz, 2H), 2.80 (t, J = 7.5 Hz, 2H), 1.90 (m, 2H), 1.70 (m, 2H), 1.55 (m, 2H).

*^{1}H NMR of **3-C7***: ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.16 (dd, J = 5.2, 0.8 Hz, 1H), 7.08 (dd, J = 3.1, 0.8 Hz, 1H), 6.96 (m, 2H), 6.65 (d, J = 3.0 Hz, 1H), 3.39 (t, J = 7.5 Hz, 2H), 2.88 (t, J = 7.5 Hz, 2H), 1.85 (m, 2H), 1.68 (m, 2H), 1.38 (m, 6H).

*^{1}H NMR of **3-C13***: ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.15 (dd, J = 5.8, 0.8 Hz, 1H), 7.06 (dd, J = 3.0, 0.8 Hz, 1H), 6.96 (m, 2H), 6.62 (d, J = 3.0 Hz, 1H), 3.39 (t, J = 7.5 Hz, 2H), 2.95 (t, J = 7.5 Hz, 2H), 1.85 (m, 2H), 1.67 (m, 2H), 1.33 (m, 18H).

*Synthesis of **4-C9***: **3-C9** (374 mg, 1.01 mmol) was placed in a recovery flask and dissolved in DMF (10 mL). *N*-bromosuccinimide (NBS; 200 mg, 1.10 mmol) was added to the mixture. After stirring for 1 h at RT, the reaction was quenched by the addition of water. The aqueous layer was extracted with EtOAc, and the combined organic layer was washed with water and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane) to give **4-C9** (430 mg, 93%). Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 6.91 (dd, J = 4.8, 0.8 Hz, 1H), 6.89 (dd, J = 3.1, 0.8 Hz, 1H), 6.84 (d, J = 3.0 Hz, 1H), 6.65 (d, J = 3.0 Hz, 1H), 3.39 (t, J = 7.5 Hz, 2H), 2.90 (t, J = 7.5 Hz, 2H), 1.84 (m, 2H), 1.66 (m, 2H), 1.33 (m, 10H).

Synthesis of ***4-C3***, ***4-C5***, ***4-C7***, and ***4-C13***: These compounds were synthesized by following the procedure used for the preparation of **4-C9** with yields of 90, 95, 93, and 91%, respectively.

^{1}H NMR of ***4-C3***: ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 6.93 (dd, J = 4.3, 0.8 Hz, 1H), 6.90 (dd, J = 3.0, 0.8 Hz, 1H), 6.83 (d, J = 3.0 Hz, 1H), 6.71 (d, J = 3.0 Hz, 1H), 3.44 (t, J = 7.5 Hz, 2H), 2.97 (t, J = 7.5 Hz, 2H), 2.22 (m, 2H).

^{1}H NMR of ***4-C5***: ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 6.95 (dd, J = 4.3, 0.8 Hz, 1H), 6.90 (dd, J = 2.9, 0.8 Hz, 1H), 6.83 (d, J = 3.0 Hz, 1H), 6.63 (d, J = 3.0 Hz, 1H), 3.41 (t, J = 7.5 Hz, 2H), 2.83 (t, J = 7.5 Hz, 2H), 1.89 (m, 2H), 1.74 (m, 2H), 1.53 (m, 2H).

^{1}H NMR of ***4-C7***: ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.16 (dd, J = 5.3, 0.8 Hz, 1H), 7.08 (dd, J = 3.0, 0.8 Hz, 1H), 6.96 (d, J = 3.0 Hz, 1H), 6.68 (d, J = 3.0 Hz, 1H), 3.40 (t, J = 7.5 Hz, 2H), 2.80 (t, J = 7.5 Hz, 2H), 1.86 (m, 2H), 1.69 (m, 2H), 1.43 (m, 6H).

^{1}H NMR of ***4-C13***: ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 6.93 (dd, J = 5.0, 0.8 Hz, 1H), 6.90 (dd, J = 3.2, 0.8 Hz, 1H), 6.81 (d, J = 3.0 Hz, 1H), 6.67 (d, J = 3.0 Hz, 1H), 3.38 (t, J = 7.5 Hz, 2H), 2.81 (t, J = 7.5 Hz, 2H), 1.85 (m, 2H), 1.68 (m, 2H), 1.35 (m, 18H).

Synthesis of ***5-C9***: **2** (470 mg, 1.0 mmol), **4-C9** (420 mg, 0.94 mmol), $Pd(PPh_3)_4$ (54 mg, 0.007 mmol), and toluene (5 mL) were placed in a microwave-proof-walled glass vial equipped with a snap cap. The glass vial was purged with argen, securely sealed, and heated in a microwave reactor, keeping the temperature at 180°C for 5 min. After removal of the solvent under reduced pressure, the residue was isolated by column chromatography on silica gel (hexane/$CHCl_3$ = 7/3) to give **5-C9** (173 mg, 35%). Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.20 (dd, J = 3.0, 0.8 Hz, 1H), 7.15 (dd, J = 3.0, 0.8 Hz, 1H), 6.95-7.08 (m, 6H), 6.67 (d, J = 3.0 Hz, 1H), 3.39 (t, J = 7.5 Hz, 2H), 2.78 (t, J = 7.5 Hz, 2H), 1.84 (m, 2H), 1.67 (m, 2H), 1.33 (m, 10H).

Synthesis of ***5-C3***, ***5-C5***, ***5-C7***, and ***5-C13***: These compounds were synthesized by following the procedure used for the preparation of **5-C9** with yields of 42, 40, 45, and 43%, respectively.

^{1}H NMR of ***5-C3***: ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.21 (dd, J = 4.9, 0.8 Hz, 1H), 7.16 (dd, J = 3.4, 0.8 Hz, 1H), 6.99-7.08 (m, 6H), 6.84 (d, J = 3.0 Hz, 1H), 3.45 (t, J = 7.5 Hz, 2H), 2.98 (t, J = 7.5 Hz, 2H), 2.21 (m, 2H).

^{1}H NMR of ***5-C5***: ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.21 (dd, J = 5.6, 0.8 Hz, 1H), 7.16 (dd, J = 3.0, 0.8 Hz, 1H), 6.96-7.05 (m, 6H), 6.68 (d, J = 3.0 Hz, 1H), 3.41 (t, J = 7.5 Hz, 2H), 2.82 (t, J = 7.5 Hz, 2H), 1.91 (m, 2H), 1.71 (m, 2H), 1.25 (m, 2H).

^{1}H NMR of ***5-C7***: ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.10 (dd, J = 5.3, 0.8 Hz, 1H), 7.05 (dd, J = 3.0, 0.8 Hz, 1H), 6.86-6.98 (m, 6H), 6.57 (d, J = 3.0 Hz, 1H), 3.30 (t, J = 7.5 Hz, 2H), 2.69 (t, J = 7.5 Hz, 2H), 1.75 (m, 2H), 1.59 (m, 2H), 1.30 (m, 6H).

^{1}H NMR of ***5-C13***: ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.23 (dd, J = 5.5, 0.8 Hz, 1H), 7.16 (dd, J = 3.3, 0.8 Hz, 1H), 6.95-7.08 (m, 6H), 6.68 (d, J = 3.0 Hz, 1H), 3.38 (t, J = 7.5 Hz, 2H), 2.81 (t, J = 7.5 Hz, 2H), 1.85

(m, 2H), 1.68 (m, 2H), 1.35 (m, 18H).

Synthesis of ***6-C₉*** : **5-C₉** (98 mg, 0.18 mmol) and potassium thioacetate (AcS^-K^+; 42 mg, 0.37 mmol) was placed in a recovery flask and dissolved in THF (5 mL). After stirring for 8 h at 60°C, the reaction was quenched by the addition of water. The aqueous layer was extracted with dichloromethane, and the combined organic layer was washed with water and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/$CHCl_3$ = 7/3) to give **6-C₉** (75 mg, 77%). Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.20 (dd, J = 5.4, 0.8 Hz, 1H), 7.16 (dd, J = 3.2, 0.8 Hz, 1H), 6.96-7.02 (m, 6H), 6.69 (d, J = 3.0 Hz, 1H), 2.85 (t, J = 7.5 Hz, 2H), 2.79 (t, J = 7.5 Hz, 2H), 2.31 (s, 3H), 1.57-1.66 (m, 4H), 1.30 (m, 10H).

Synthesis of ***6-C₃***, ***6-C₅***, ***6-C₇***, and ***6-C₁₃***: These compounds were synthesized by following the procedure used for the preparation of **6-C₉** with yields of 59, 73, 69, and 75%, respectively.

^{1}H NMR of ***6-C₃***: ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.20 (dd, J = 5.6, 0.8 Hz, 1H), 7.15 (dd, J = 3.0, 0.8 Hz, 1H), 6.96-7.06 (m, 6H), 6.72 (d, J = 3.0 Hz, 1H), 2.93 (t, J = 7.5 Hz, 2H), 2.86 (t, J = 7.5 Hz, 2H), 2.34 (s, 3H), 1.88 (m, 2H).

^{1}H NMR of ***6-C₅***: ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.20 (dd, J = 6.0, 0.8 Hz, 1H), 7.15 (dd, J = 3.0, 0.8 Hz, 1H), 7.02-7.10 (m, 6H), 6.68 (d, J = 3.0 Hz, 1H), 2.89 (t, J = 7.5 Hz, 2H), 2.79 (t, J = 7.5 Hz, 2H), 2.32 (s, 3H), 1.57-1.69 (m, 4H), 1.30 (m, 2H).

^{1}H NMR of ***6-C₇***: ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.20 (dd, J = 5.4, 0.8 Hz, 1H), 7.10 (dd, J = 3.4, 0.8 Hz, 1H), 6.95-7.08 (m, 6H), 6.66 (d, J = 3.0 Hz, 1H), 2.86 (t, J = 7.5 Hz, 2H), 2.81 (t, J = 7.5 Hz, 2H), 2.31 (s, 3H), 1.60-1.70 (m, 2H), 1.39 (m, 6H).

^{1}H NMR of ***6-C₁₃***: ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ7.21 (dd, J = 5.6, 0.8 Hz, 1H), 7.16 (dd, J = 3.0, 0.8 Hz, 1H), 6.95-7.08 (m, 6H), 6.68 (d, J = 3.0 Hz, 1H), 2.85 (t, J = 7.5 Hz, 2H), 2.78 (t, J = 7.5 Hz, 2H), 2.34 (s, 3H), 1.52-1.66 (m, 4H), 1.35 (m, 18H).

Synthesis of ***4TC₉SH***: **6-C₉** (75 mg, 0.14 mmol) was placed in a recovery flask and dissolved in THF (5 mL). Hydrogen chloride in methanol (1.25 M, 5 mL, 6.25 mmol) was added to the mixture. After stirring for 6 h at 50°C, the reaction was quenched by the addition of water. The aqueous layer was extracted with dichloromethane, and the combined organic layer was washed with aq. $NaHCO_3$ and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/$CHCl_3$ = 7/3) to give **4TC₉SH** (36 mg, 52%). Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS):δ 7.20 (dd, J = 5.4, 0.8 Hz, 1H), 7.16 (dd, J = 3.0, 0.8 Hz, 1H), 6.96-7.07 (m, 6H), 6.67 (d, J = 3.0 Hz, 1H), 2.78 (t, J = 7.5 Hz, 2H), 2.51 (q, J = 7.2 Hz, 2H), 1.53-1.72 (m, 4H), 1.24-1.42 (m, 11H). Exact mass Calcd for $C_{25}H_{28}S_5$: 488.0795. Found: 488.0790.

Synthesis of ***4TC₃SH***, ***4TC₅SH***, ***4TC₇SH***, and ***4TC₁₃SH***: These compounds were synthesized by following the procedure used for the preparation of **4TC₉SH** with yields of 25, 73, 70, and 78%, respectively.

*^{1}H NMR of **4TC$_3$SH***: ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.21 (dd, J = 5.3, 0.8 Hz, 1H), 7.16 (dd, J = 2.8, 0.8 Hz, 1H), 6.97-7.08 (m, 6H), 6.70 (d, J = 3.0 Hz, 1H), 2.93 (t, J = 7.5 Hz, 2H), 2.60 (q, J = 7.3 Hz, 2H), 1.98 (m, 2H), 1.37 (t, J = 7.5 Hz, 1H). Exact mass Calcd for $C_{19}H_{16}S_5$: 403.9856. Found: 403.9856.

*^{1}H NMR of **4TC$_5$SH***: ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.21 (dd, J = 5.0, 0.8 Hz, 1H), 7.16 (dd, J = 3.2, 0.8 Hz, 1H), 6.97-7.08 (m, 6H), 6.67 (d, J = 3.0 Hz, 1H), 2.81 (t, J = 7.5 Hz, 2H), 2.54 (q, J = 7.3 Hz, 2H), 1.62-1.71 (m, 4H), 1.41-1.57 (m, 3H). Exact mass Calcd for $C_{21}H_{20}S_5$: 432.0169. Found: 432.0167.

*^{1}H NMR of **4TC$_7$SH***: ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.21 (dd, J = 5.2, 0.8 Hz, 1H), 7.16 (dd, J = 3.0, 0.8 Hz, 1H), 6.96-7.087(m, 6H), 6.67 (d, J = 3.0 Hz, 1H), 2.79 (t, J = 7.5 Hz, 2H), 2.57 (q, J = 7.3 Hz, 2H), 1.55-1.72 (m, 4H), 1.30-1.44 (m, 7H). Exact mass Calcd for $C_{23}H_{24}S_5$: 460.0482. Found: 460.0480.

*^{1}H NMR of **4TC$_{13}$SH***: ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.20 (dd, J = 5.6, 0.8 Hz, 1H), 7.16 (dd, J = 3.0, 0.8 Hz, 1H), 6.96-7.07 (m, 6H), 6.67 (d, J = 3.0 Hz, 1H), 2.78 (t, J = 7.5 Hz, 2H), 2.51 (q, J = 7.3 Hz, 2H), 1.54-1.72 (m, 4H), 1.43-1.60 (m, 19H). Exact mass Calcd for $C_{29}H_{36}S_5$: 544.1421. Found: 544.1422.

[S1] Michalitsch, R.; ElKassmi, A.; Yassar, A.; Garnier, F. *J. Heterocyclic Chem.* **2001**, 38, 649-653.

[S2] Logtenberg, H.; van der Velde, H. M.; de Mendoza, P.; Areephong, J.; Hjelm, J.; Feringa, B. L.; Browne, W. R. *J. Phys. Chem. C* **2012**, 116, 24136-24142.

2. Alkylene Layer Thickness in 4TC$_n$S-SAM on Au(111)

The thickness of the -$(CH_2)_n$- chain layer, *d*, was estimated from *n* of 4TC$_n$S-SAMs on Au. As the IRAS results shown in Figure 1c of the main manuscript, only the vibrational modes directing perpendicular to the long -$(CH_2)_n$- axis were detectable, thereby the estimation of the tilting angle of the -$(CH_2)_n$- chain was impossible, as previously reported [S3]. Since the absolute absorption of CH_2 stretching mode for 4TC$_9$S-SAM is close to that for decanthiolate SAM, a similar structure of the -$(CH_2)_n$- chain in 4TC$_n$S-SAM is expected, i.e., the standing structure with a tilt angle θ of 30° from the surface normal, as shown in Figure S1. In addition, though the structure of Au-S-C anchor is not clear even for the alkanethiolate SAM on Au, it probably does not differ so much to that of the -$(CH_2)_n$- chain as shown in Figure S1. Assuming all *trans* configuration of the -$(CH_2)_n$- chain with typical values of d_{CC} = 1.53 Å and θ_{CC} =109.5°, the thickness *d* in 4TC$_n$S-SAMs on Au was estimated by

$$d = (n + 1)\, d_{cc} \cos\{(\pi - \theta_{CC})/2\} \cos\theta\,.$$

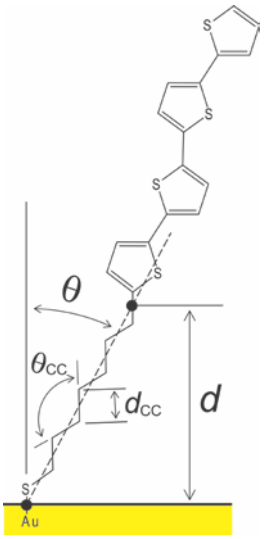


Figure S1. Schematic thiolate structure in 4TC$_9$S-SAM on Au(111).

[S3] Liedberg, B.; Yang, Z.; Engquist, I.; Wirde, M.; Gilius, U.; Götz, G.; Bäuerle, P.; Rummel, R.-M.; Ziegler, Ch.; Göpel, W. *J. Phys. Chem. B* **1997**, 101, 5951-5962.

3. Complete Reference in the Main Manuscript

The complete author list of Ref. 46 in the main manuscript is following

(46) Smits, E. C. P.; Mathijssen, S. G. J.; van Hal, P. A.; Setayesh, S.; Geuns, C. T.; Mutsaers, K. A. H. A.; Cantatore, E.; Wondergem, H. J.; Werzer, O.; Resel, R.; Kemerink, M.; Kirchmeyer, S.; Muzafarov, A. M.; Ponomarenko, S. A.; de Boer, B.; Blom, P. W. M.; de Leeuw, D. M.
Bottom-Up Organic Integrated Circuits. *Nature* **2008**, *455*, 956-959.