

Electronic Supporting Information for

Heterocirculenes as a new class of organic semiconductors

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Experimental details

The charge carrier mobilities of OFETs were calculated in the saturation regime from a plot of the square root of the drain current vs. gate voltage using the following equation:

$$I_D = C_i \mu (W / 2L)(V_G - V_T)^2$$

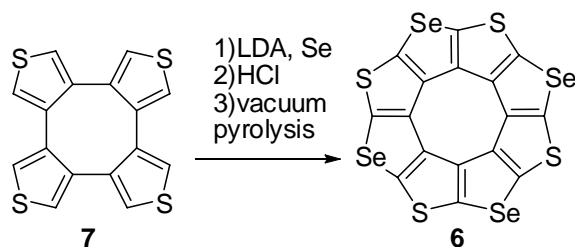
where I_D is the drain-source current, C_i is the capacitance per unit area of the gate dielectric (18 nF/cm²), L is the channel length, W is the channel width, and V_T and V_G are the threshold voltage and gate-source voltage, respectively.

Materials

Octathio[8]circulene **5** was synthesized as described earlier.¹

Tetrathiotetraselenocirculene **6** was synthesized following the same procedure and replacing the sulphur powder with selenium. Diisopropylamine (9.9 mL, 70 mmol) was added to a suspension of tetrathiothiophene **7** (0.985 g, 3.00 mmol) in anhydrous diethyl ether (150 mL) under argon, and the mixture was cooled to -20 °C. A solution of n-butyllithium in hexanes (23.2 mL of 2.5 M solution, 58 mmol) was added, and the mixture was allowed to warm to 0 °C and stirred for 30 min. Powdered selenium (3.79 g, 48 mmol) was then added, and the reaction was stirred for 24 h at room temperature. Acidic work-up and washing with water and diethyl ether gave a dark-red precipitate which was subject to vacuum pyrolysis at 0.04-0.05 torr at 450-600 °C. The unreacted selenium and target circulene precipitated in neighboring zones of the tube. The lighter-colored fraction containing target circulene was separated and the product was purified by repeated vacuum sublimation to give **6** (950 mg, 50% yield) as an insoluble white-creamy powder. HRMS (EI): 639.5543 (calcd. for C₁₆S₄Se₈ 639.5544). Found: C, 32.38; H, 0.00; N, 0.00; S, 22.83; Calcd. for C₁₆S₄Se₄: C, 30.20, H, 0.00; N, 0.00; S, 20.16.

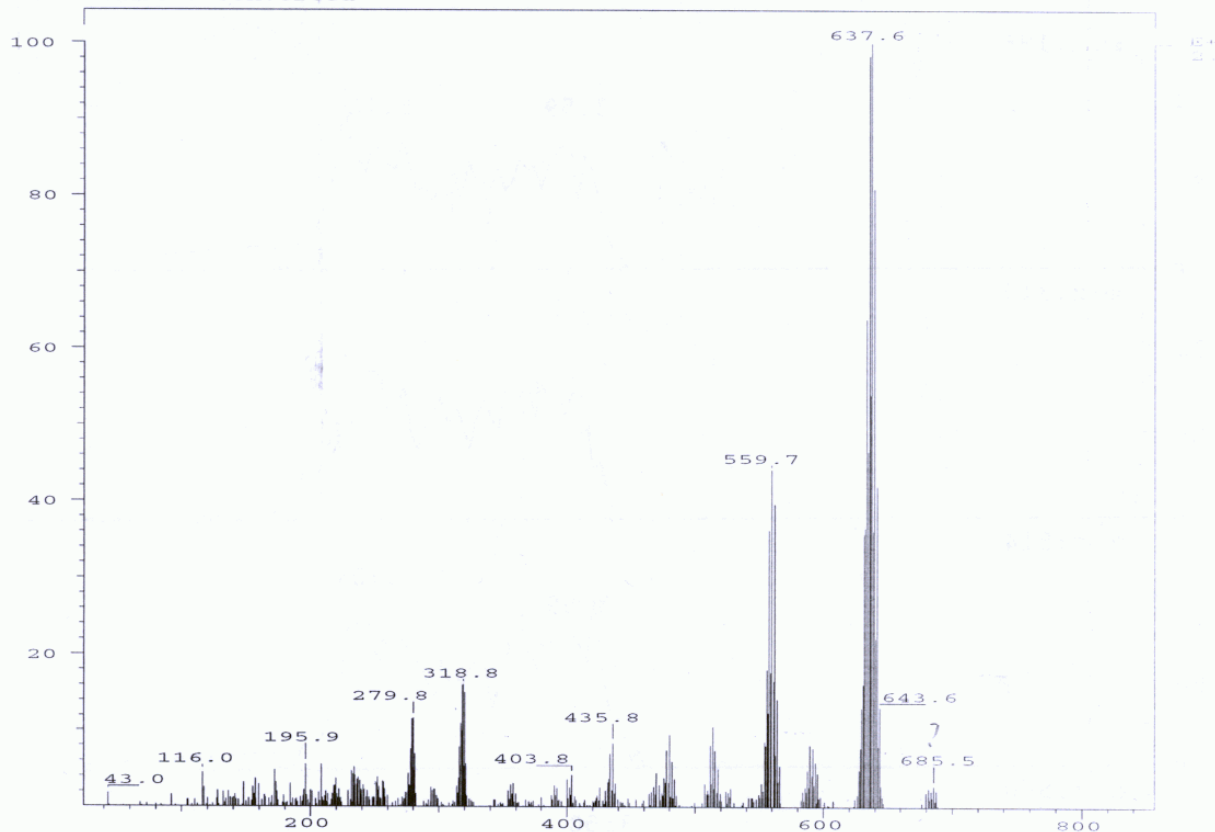
MS analysis has revealed that S/Se disproportionation has occurred at the high reaction temperature, with a trace amount of C₁₆S₃Se₄ (at m/z 685) and substantial amount of C₁₆S₅Se₃ (at m/z 589) present in the sample. According to single crystal X-ray crystallography² the disordered S/Se population corresponds to overall sulfur:selenium ratio of 3:2, which is also in line with the results of elemental analysis.



¹ K. Y. Chernichenko, V. V. Sumerin, R. V. Shpanchenko, E. S. Balenkova and V. G. Nenajdenko, *Angew. Chem. Int. Ed.*, 2006, **45**, 7367.

² O. Ivasenko, J. M. MacLeod, K. Chernichenko, E. Balenkova, R. V. Shpanchenko, V. G. Nenajdenko, F. Rosei and D. F. Perepichka, *to be published*.

SPEC: 2kch2-c1
 Samp: 639, C16S4Se4, fest, Aceton Elapse: 05:10.9 103
 Comm: Faden, 20'-1600' mit 120' /min Start: 120
 Mode: EI +VE +LMR BSCAN (EXP) UP HR NRM Study: DEP/EI, MAT90
 Oper: Tschuck Client: Krasovskiy, Knochel Inlet: DIP
 Data: CMASS : converted



LIST: 2kch2-c1 Elapse: 05:10.9 103
 Samp: 639, C16S4Se4, fest, Aceton Start: 120
 Comm: Faden, 20'-1600' mit 120' /min Study: DEP/EI, MAT90
 Mode: EI +VE +LMR BSCAN (EXP) UP HR NRM Inlet: DIP
 Oper: Tschuck Client: Krasovskiy, Knochel
 Limit: (0)
 Peak: (1648) C100.S4.Se4 R:D: -1.0 > 50.0
 Data: CMASS : converted

Mass	Intensity	%RA	%RIC	Delta	R+D	Composition
278.8210	*	306928	11.59			
279.8255	*	309250	11.68			
315.7764	*	207654	7.84			
316.7764	*	290323	10.97			
317.2819	*	263005	9.93			
317.7771	*	423165	15.98			
318.2771	*	287823	10.87			
318.7732	*	426022	16.09			
319.7766	*	397811	15.03			
435.7547	*	220153	8.32	0.6	9.0	C8.S2.Se2
479.7209	*	248185	9.37			
511.6858	*	212832	8.04	0.4	17.0	C16.S4.Se2
513.6799	*	276218	10.43			
553.6511	*	224616	8.48			
554.6529	*	212296	8.02			
555.6494	*	477266	18.03			
556.6493	*	327819	12.38			
557.6499	*	957032	36.15			
558.6531	*	467446	17.66			
559.6502	*	1166293	44.05			
560.6553	*	438520	16.56			
561.6507	*	1046307	39.52			
563.6444	*	375313	14.18			
589.5907	*	213368	8.06			
591.6034	*	203547	7.69			
629.55602	*	345138	13.04			
630.5567	*	426736	16.12			
631.5575	*	943998	35.66			
632.5597	*	965602	36.47			
633.5614	*	1691590	63.90			
634.5606	*	1229679	46.45			
635.5562	*	2601306	98.26			
636.5540	*	1427692	53.93			
637.5572	*	2647372	100.00			
638.5575	*	954889	36.07			
639.5543	*	2140110	80.84	0.0	17.0	C16.S4.Se4
640.5531	*	583861	22.05			
641.5509	*	1108979	41.89			
642.5685	*	209797	7.92			
643.5508	*	346388	13.08			

Quantum chemical calculations

Density Functional Theory Calculations have been performed at B3LYP/6-31G(d,p) level as implemented in Gaussian 03W.³ The frequency check was done on the optimized structures to confirm that they are true minima. The reorganization energies were calculated as a sum of relaxation energies of a radical cation (from the geometry of a neutral molecule) and of a neutral molecule (from the geometry of a radical cation), as described earlier.⁴

Thin film deposition and device fabrication

Films were deposited at room temperature by vacuum sublimation in a home-built evaporator at pressure $\sim 1 \times 10^{-6}$ Torr and deposition rates ranging between 0.2–1 Å sec⁻¹. The films were deposited on circular Au source/drain (bottom-contact) electrodes patterned on 190 nm-thick SiO₂ thermally grown on heavily n-doped (Sb) Si ($\rho \approx 0.01$ – 0.02 Ohm cm). SiO₂ substrates have a Root Mean Roughness (rms) of 0.2 nm. The heavily doped n-Si substrate was used as common gate electrode. The thickness of the electrodes was 25 nm. A Cr thin film (3 nm) was used as adhesion layer. Patterning was achieved by lift off.⁵ Prior to deposition, substrates were cleaned by sonication in acetone and isopropyl alcohol followed by exposure to O₂ plasma. The channel lengths and widths of the devices were 6 μm and 1880 μm, respectively.

Electrical measurements

Electrical measurements were carried out in the dark, at room temperature and under nitrogen atmosphere (99.998 %) using a semiconductor parameter analyzer (Hewlett Packard 4145 B).

AFM measurements

AFM measurements were performed using a DI-Enviroscope system (Veeco Instruments) operated in intermittent contact (tapping) mode. The cantilevers used were the NSC 35 series from Micromesh, with resonance frequencies between 150–300 kHz. According to the supplier, the tip's radius of curvature at the apex is 10 nm.

³ G.W.T.M.J. Frisch, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H.P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A. D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, and J.A. Pople, 03, Revision D.01 ed., Gaussian, Inc., Wallingford, CT, **2004**.

⁴ N. E. Gruhn, D A. da Silva Filho, T. G. Bill, M. Malagoli, V. Coropceanu, A. Kahn and J.-L. Brédas, *J. Am. Chem. Soc.*, 2002, **124**, 7918

⁵ C. Santato, F. Cicoira, P. Cosseddu, A. Bonfiglio, *Appl. Phys. Lett.*, 2006, **88**, 163511.

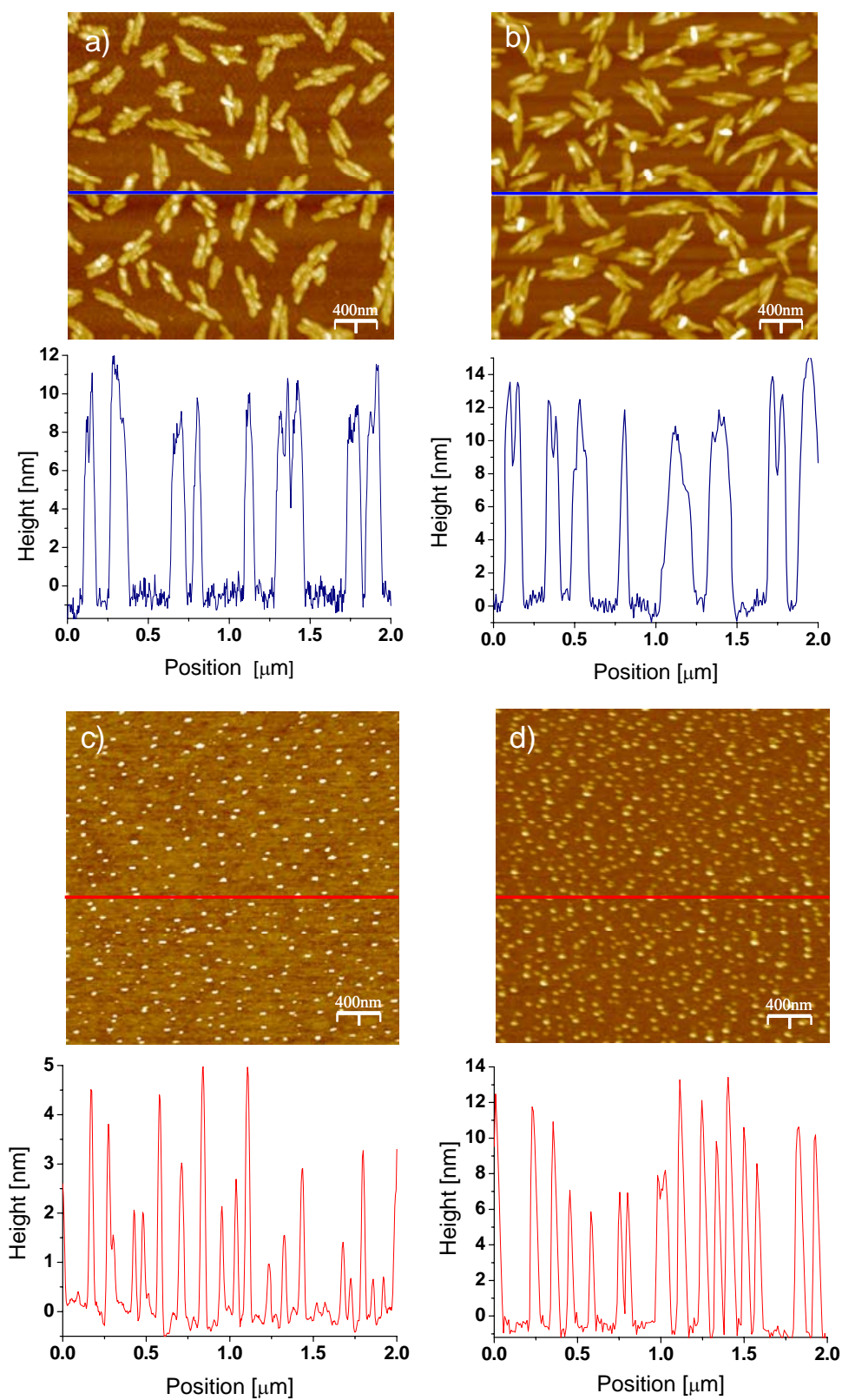


Figure S1: AFM Micrograph ($2\ \mu\text{m}\times 2\ \mu\text{m}$) images and corresponding height histogram of thin films of sulflower **5** (a,b) with the deposition time of 1 min, 2 min, respectively; tetraselenotetrathio[8]circulene **6** (c,d) with the deposition time of 1 min, 2 min, respectively. Films grown on SiO_2/Si substrate at room temperature (deposition rate= $0.2\ \text{\AA}/\text{s}$).

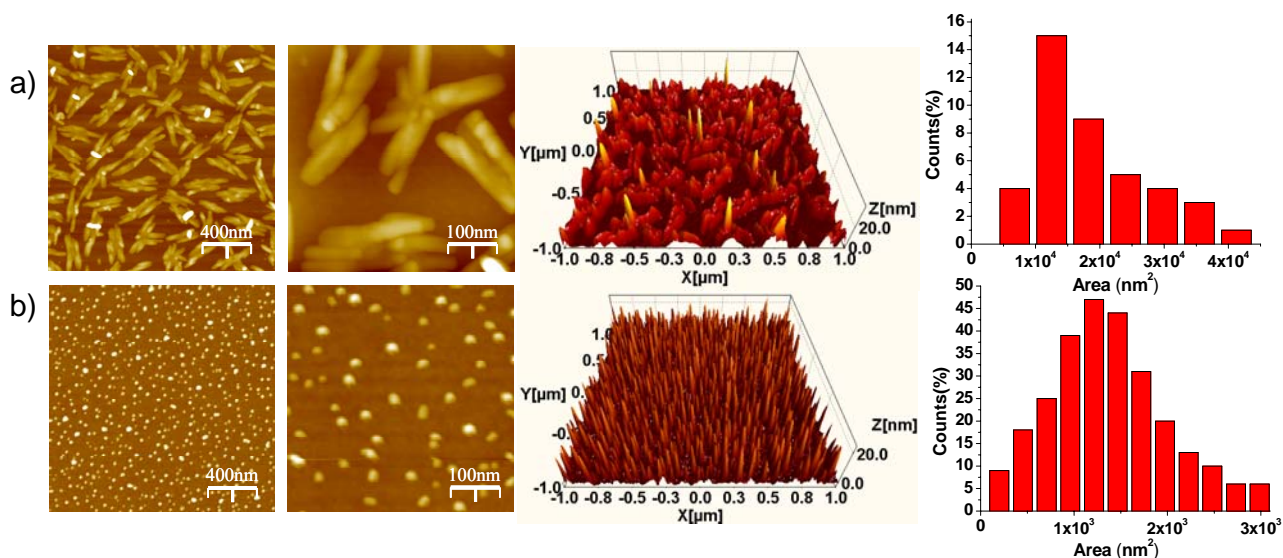


Figure S2: AFM Micrograph (2 μm × 2 μm and 500 nm × 500 nm), corresponding 3D images of early stage thin film growth, and corresponding area histogram of a) sulflower **5** and b) tetraselenotetrathio[8]circulene **6** on SiO₂/Si substrate at room temperature (deposition rate = 0.2 Å/s)

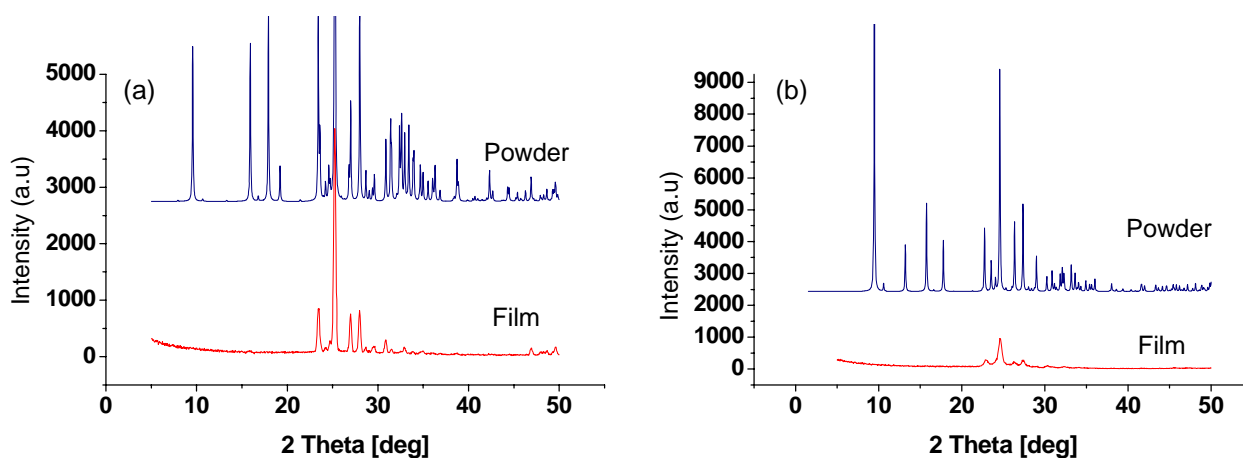


Figure S3: XRD pattern of (a) sulflower **5** (200 nm film, FWHM = 0.2755), and (b) tetraselenotetrathio[8]circulene **6** (200 nm film; FWHM = 0.51)

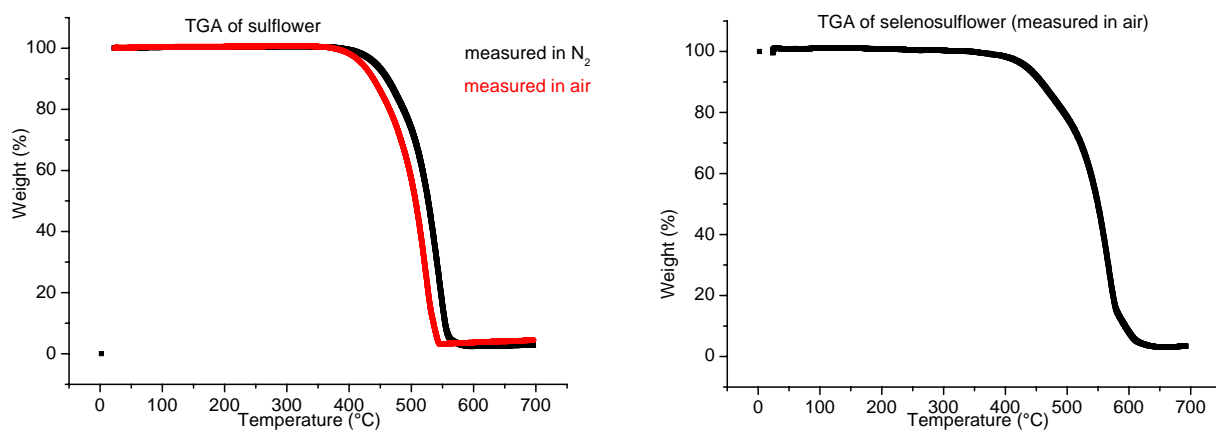


Figure S4: Thermogravimetric analysis (TGA) of sulflower **5** and selenosulflower **6** in ambient air and in nitrogen atmosphere.

Table S1: OFET characteristics of tetraselenotetrathio[8]circulene **6** fabricated at different substrate temperatures.

Temperature (C)	μ_h (cm ² /Vs)	V _T (V)	on/off
25	1×10^{-3}	-10	10^6
55	2×10^{-4}	-26	10^6
75	1×10^{-4}	-18	10^6
90	3×10^{-4}	-26	10^6
125	9×10^{-5}	-32	10^6