Supporting Information

For the manuscript:

Supramolecular assembly of heterocirculenes in 2D and 3D

Experimental

Materials. Graphite (grade SPI-2) was obtained from SPI Supplies, and was cleaved prior to each experiment using adhesive tape. Propionic (99%), 1-hexanoic (99%), 1-heptanoic (99%) and 1-octanoic acid (98%) were purchased from Sigma Aldrich and were used without further purification. Sulflower and selenosulflower were prepared according to previously reported procedures.[1,2] Suspensions were prepared by either heating (up to the boiling point of the solvent used), sonication or simply stirring of small sample (~0.1-0.5 mg) of the corresponding heterocirculene in few drops of the appropriate TMA solution. A small drop of the freshly prepared suspension was applied on cleaved graphite substrate prior to scanning. In the experiments without TMA, suspensions of the heterocirculenes from different solvents (1,2,4 trichlorobenzene, CS2, DMSO, DMF, propionic, 1-hexanoic, 1-heptanoic and 1-octanoic acids) were tried yielding however no ordered structures.

STM imaging. STM images were acquired using either a NanoSurf EasyScan2 or a Digital Instruments Inc. (Veeco) NanoScope IIIa. Both microscopes were operated at ambient conditions, and images were obtained from the topography channel. Tips were cut from 80/20 PtIr wire (Goodfellow Corporation). Calibration of the piezoelectric positioners was verified by atomic resolution imaging of graphite (x and y-directions) and by the height of single steps on the graphite surface (z-direction). Atomic resolution was verified prior to the addition of solutions to the surface. Periodicity measurements were performed against dimeric TMA rows of TMA/1-docosanol SAMNs obtained simultaneously with TMA/sulflower domains by scanning 1-docosanol/TMA/sulflower/1-octanoic acid solution. Image processing was done using WSxM software.[3]

Calculations. All calculations were performed with density functional theory at B3LYP/6-31G(d) level implemented in GAUSSIAN 03.[4] *Cs* symmetry constrains were applied in calculations of a $(TMA)_6$·suflower and $(TMA)_6$ selenosuflower complexes. In modeling of the dimer $(TMA)_6$·$(suflower)_2$, all the coordinates of the $(TMA)_6$·suflower layer were preoptimized and freezed, while the second sulflower molecule was allowed to relax.

X-ray analysis. The powder pattern for **2** was taken with Stoe STADI P diffractometer ($CuK_{\alpha1}$-radiation, Ge monochromator, transmission mode, linear-PSD). Single crystal data collection was performed on CAD-4 (Enraf Nonius) diffractometer at room temperature. Structure calculations for

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[1] K. Yu. Chernichenko, V. V. Sumerin, R. V. Shpanchenko, E. S. Balenkova and V. G. Nenajdenko, *Angew. Chem. Int. Ed.*, 2006, **118**, 7527.

[2] A. Dadvand, F. Cicoira, K. Yu. Chernichenko, E. S. Balenkova, R. M. Osuna, F. Rosei, V. G. Nenajdenko and D. F. Perepichka, *Chem. Commun.*, **2008** in press.

[3] I. Horcas, R. Fernandez, J. M. Gomez-Rodriguez, J. Colchero, J. Gomez-Herrero, A. M. Baro, *Rev. Sci. Instrum.,* 2007, ***78***, 013705.

[4] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, 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, Gaussian, Inc., Wallingford CT, 2004.

single crystal data were carried out in the JANA2000 program.[5] Rietveld refinement was performed with the GSAS program package.[6] The initial model was taken from the single crystal data and restrained with soft bond restrains (±0.05 Å). Occupancies for (Se,S) positions were refined simultaneously with atomic coordinates while atomic displacement parameters were fixed as 0.025 for all atoms.

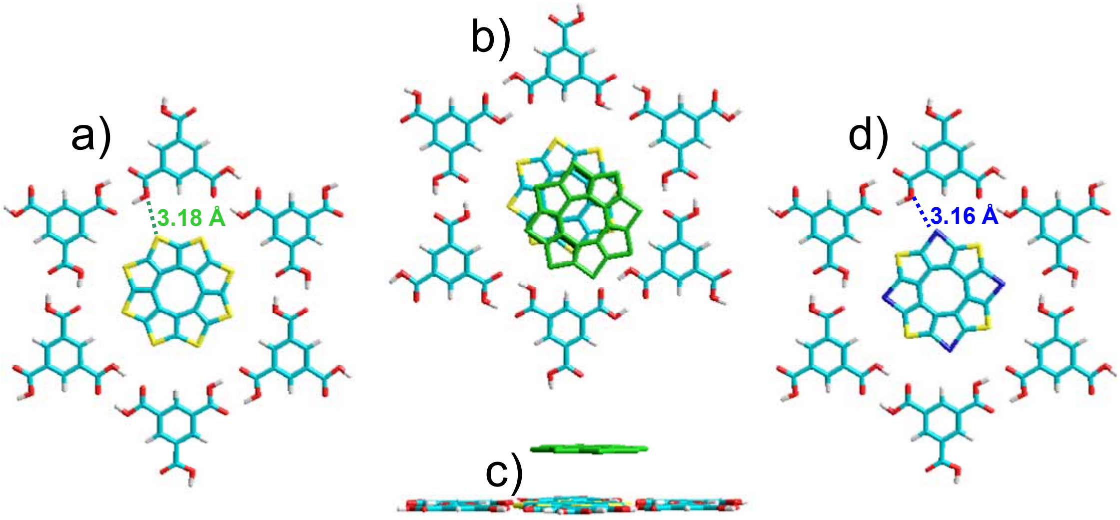
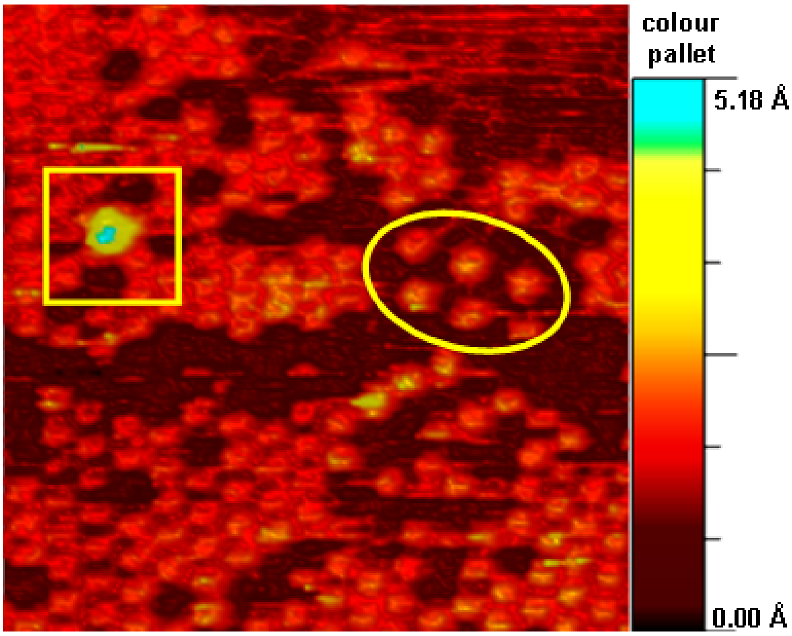


Figure S1. B3LYP/6-31G(d) optimized geometries of TMA-sulflower (a), its dimeric agglomerate (b, c) and TMA-selenosulflower (d). Colors assignment: carbon- cyan, hydrogen- white, oxygen- red, selenium- blue, sulfur- yellow, second layer molecule of the sulflower dimer is coloured in green.



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[5] V. Petriček, M. Dusek and L. Palatinus, Jana2000. Structure Determination Software Programs. Institute of Physics, Praha, Czech Republic, 2000.

[6] A.C. Larson and R.B. Von Dreele, Los Alamos National Laboratory Report LAUR, 1994, 86; B. H. Toby, *J. Appl. Cryst.* 2001, **34**, 210.

Figure S2. Selenosulflower island (marked with yellow square) together with small metastable domain of TMA-flower pattern filled with selenosulflower guests (yellow ellipse), deposited from propionic acid. Image parameters: 24.3×24.3 nm^2, I_t= 0.3 nA, U_t= 0.8 V.

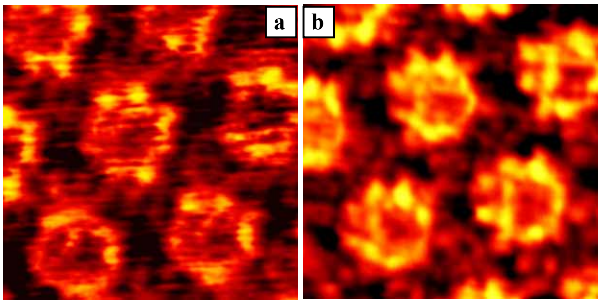

Figure S3. Individual petals are often observed smeared together, making difficult to distinguish their exact positions. Image parameters: (a) TMA-sulflower, 3.6×3.6 nm^2, I_t=0.3 nA, U_t=+0.5 V; (c) TMA-selenosulflower, 3.6×3.6 nm^2, I_t=0.3 nA, U_t=+0.3 V.

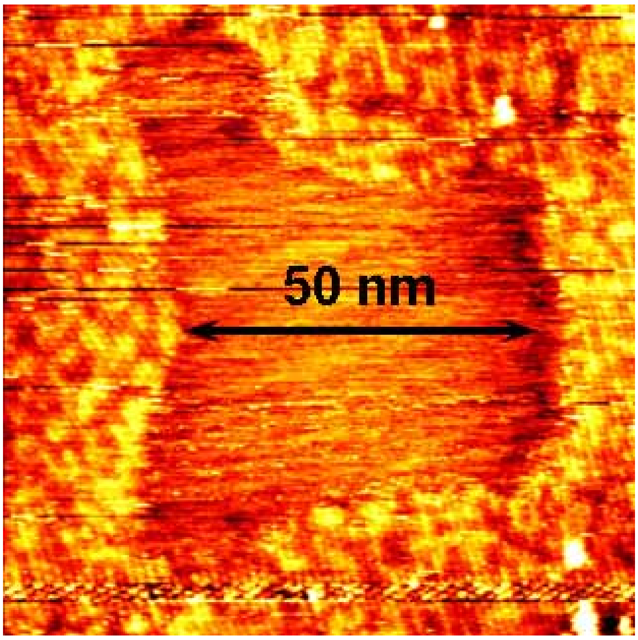

Figure S4. Tip assisted desorption of TMA-selenosulflower SAMN. This image was taken immediately after slow scanning at I_t=1.00 nA, U_t=+0.05 V in a 50×50 nm^2 area by zooming out to 90×90 nm^2 and scanning at I_t=0.3 nA, U_t=+0.8 V.

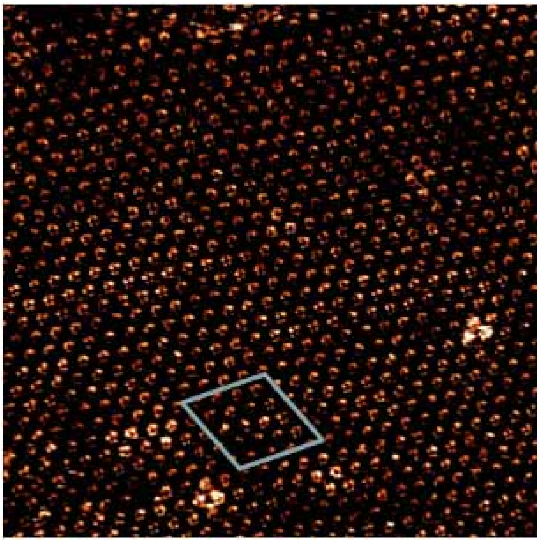

Figure S5. Moiré pattern (MP) of sulflower/chicken-wire SAMN with blue rhombus representing its unit cell (a~7 nm). No FFT analysis was possible due to very low contrast of this MP. The image parameters: 44.5×44.5 nm^2, I_t=0.3 nA, U_t=+0.3 V.

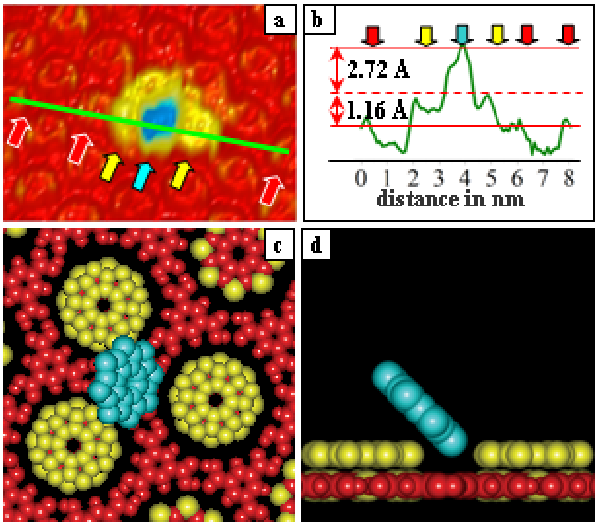

Figure S6. Alternative appearance of an island of sulflower (a), corresponding line-profile (b) and its tentative model (c, d). The image parameters: 6.4×8.7 nm^2, I_t=0.13 nA, U_t=+1.2 V.

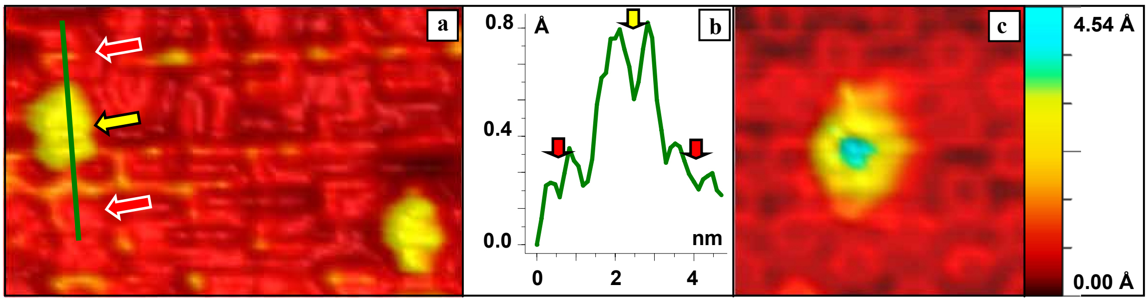

Figure S7. STM images of sulflower dimers (a), corresponding line-profile (b) and a sulflower island (c) formed upon slow drying of a TMA-sulflower 1-octanoic acid suspension and observed at low tunneling voltage. After approaching at ‘graphite settings’ (I_t=1.0 nA, U_t=+0.05 V) the area was continuously scanned at I_t=0.3 nA, U_t=+0.3 V for over 1h. During that time gradual appearance and growth of aggregates ((a) and (b)) was observed.

X-ray structure discussion.

The distribution of selenium and sulfur atoms in the "sunflower" molecule found from diffraction data is not ordered. However, it is not simply random occupation as one could expect. Three different position types are present in the structure (Fig.S8). The first position (S1) is mainly occupied by Se atom (0.653(15)). The second one (S2) has nearly close ratio between Se and S atoms (0.525(14) and 0.475(14), respectively). In contrast, two remaining (S3 and S4) positions are mainly occupied by sulfur atoms with ratio of about 4:1. These positions are alternated around the molecule. The (Se,S)–C separations are decreased with a reduction of the selenium content from 1.86Å to 1.79Å that corresponds to decreasing of the atomic radius. Simultaneously the C–(Se,S)–C angles are increased from 84.8(4)° to 86.7(4)°. The molecule is practically flat. Molecular stacking in the unit cell is quite similar to that observed earlier in sulflower.

The lattice parameters for both single crystal and powder samples taken at room temperature are the same taking into account the estimated standard deviations (esd's). The experimental and calculated patterns are also very close (Fig. S9) although the samples belong to different batches. This may indicate that the real composition of the compound $C_{16}S_{4.683}Se_{3.317}$ is nearly constant. Indeed, the powder diffraction refinement yielded close composition, namely $C_{16}S_{4.72}Se_{3.28}$ that can be considered as the same taking into account precision of the refinement using the powder diffraction data. The obtained values are rather close to those found in the single crystal refinement and confirm the suggestion that a distribution of the Se and S atoms in the structure is not exactly 1:1.

Table S1. Summary of crystallographic information for $C_{16}S_{4.683}Se_{3.317}$

Parameter \ Composition	$C_{16}S_{4.683}Se_{3.317}$
Formula weight	604.2
Crystal system	monoclinic
Space group	$P2_1/m$ [14]
a (Å)	4.0290(8)
b (Å)	16.680(3)
c (Å)	11.270(2)
β (deg.)	94.30(3)
Volume (Å^3)	755.3(2)
Z	2
Temperature (K)	293
Color	Colorless
No. of measured/independent reflection ($I \geq 2\sigma$), R_{eq}	2731/1032, 0.033
R/R_{all} ($I > 2\sigma(I)$)/GOF	0.064/0.078/1.35

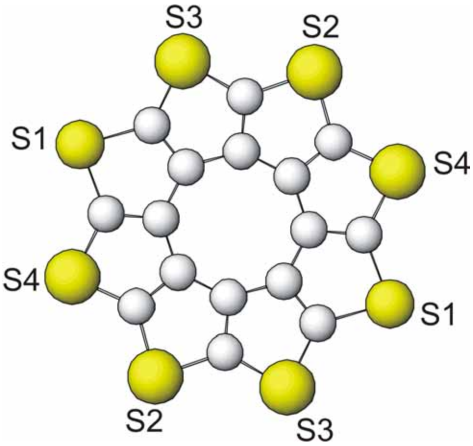

Figure S8. Mixed (Se,S) positions in the $C_{16}S_{4.683}Se_{3.317}$ structure.

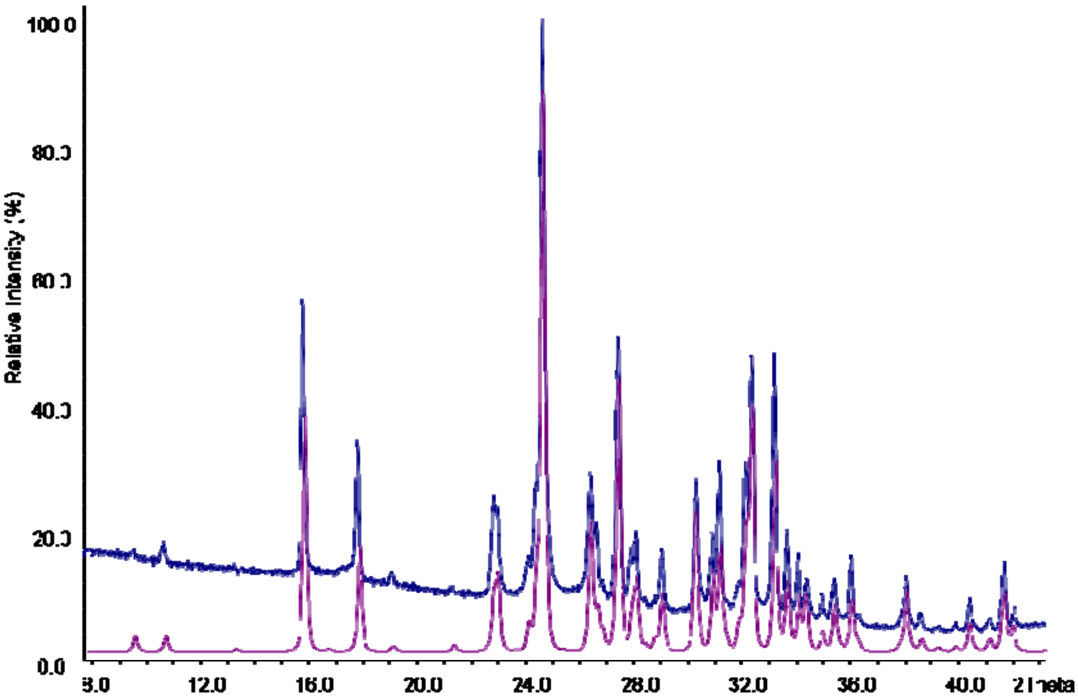

Figure S9. Experimental (blue) and calculated (cyan) XRD pattern for selenosulflower **2**.