Supplementary Information for: On-Surface Structural and Electronic Properties of Spontaneously Formed Tb_2Pc_3 Single Molecule Magnets

Jack Hellerstedt[*,1,2], Aleš Cahlík[*,1,2], Martin Švec[1,2], Bruno de la Torre[1,2], María Moro-Lagares[1,2], Taras Chutora[1,2], Barbora Papoušková[2], Giorgio Zoppellaro[2], Pingo Mutombo[1], Mario Ruben[3,4], Radek Zbořil[2], and Pavel Jelinek[†,1,2]

[1]Institute of Physics of the Czech Academy of Sciences, v.v.i., Cukrovarnická 10, 162 00 Praha 6, Czech Republic
[2]Regional Centre of Advanced Technologies and Materials, Palacký University, Šlechtitelû 27, 78371 Olomouc, Czech Republic
[3]Karlsruhe Institute of Technology, Institute of Nanotechnology Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
[4]Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), CNRS-Université de Strasbourg, 67034 Strasbourg, France
[*]These authors contributed equally to this work
[†]email: jelinekp@fzu.cz

July 13, 2018

Substrate Registration and Unit Cell

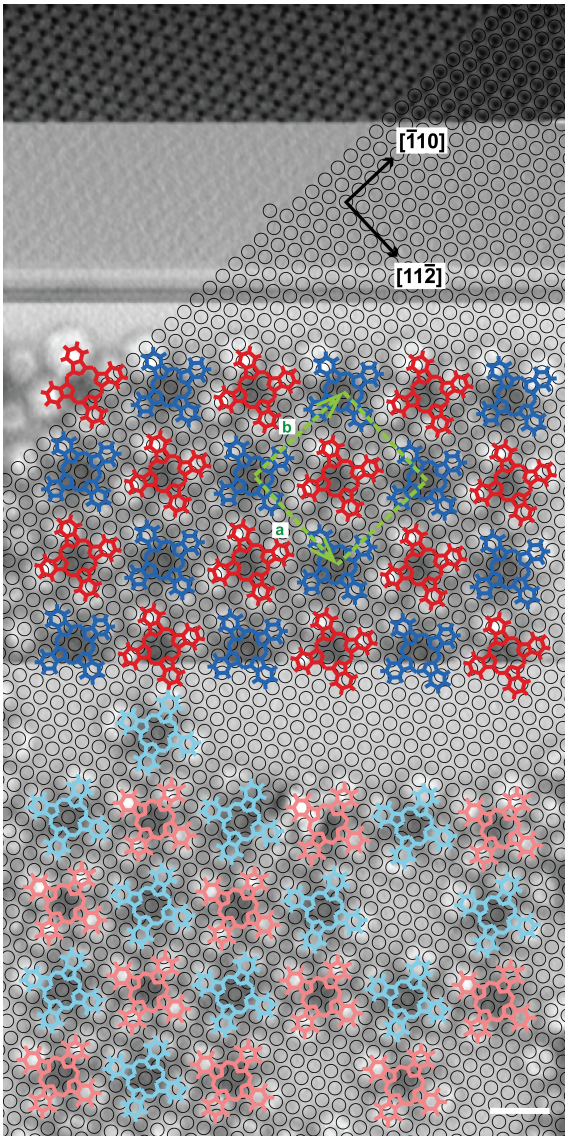


Figure S1: nc-AFM image showing atomic registration of Ag(111), $TbPc_2$ (dark red/blue), and Tb_2Pc_3 (light red/blue). Overlay of Ag(111) lattice, and top ligand orientations for each species.

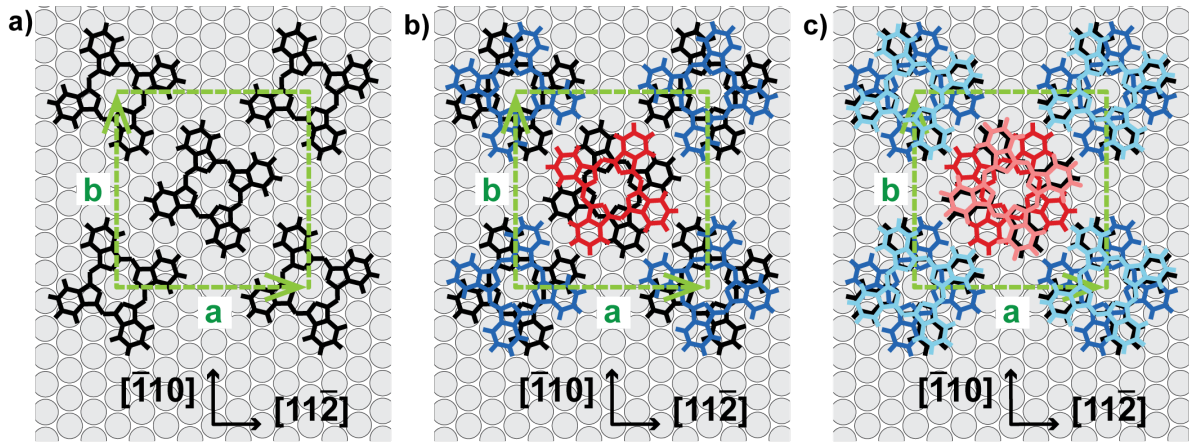


Figure S2: Molecular unit cell: a) configuration of bottom Pc on the Ag(111). b) second layer of Pc added in dark red/blue. c) third layer added in light red/blue. Ag(111) lattice directions are labeled in numbers at bottom, molecule unit cell is indicated with green arrows.

Other Species

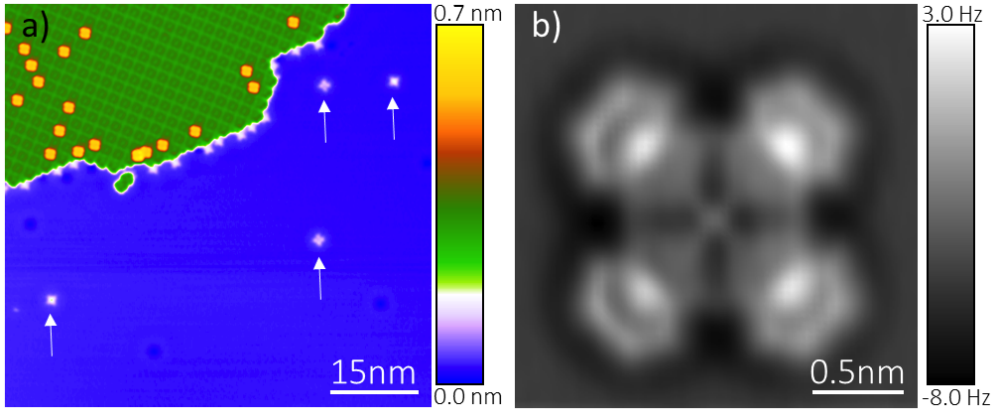


Figure S3: a) STM topography image of $TbPc_2$, Tb_2Pc_3 and occupied Pc molecules. Residual Pc molecules are observed at the edge of a $TbPc_2$-Tb_2Pc_3 island, and on the bare terrace (marked with white arrows). $V_{bias} = 0.2$ mV, I = 20 pA. b) AFM high resolution image with CO-functionalized tip of a single Pc molecule with occupied center that could be TbPc. Compare to Katoh et. al.[1]

KPFM Parabolas

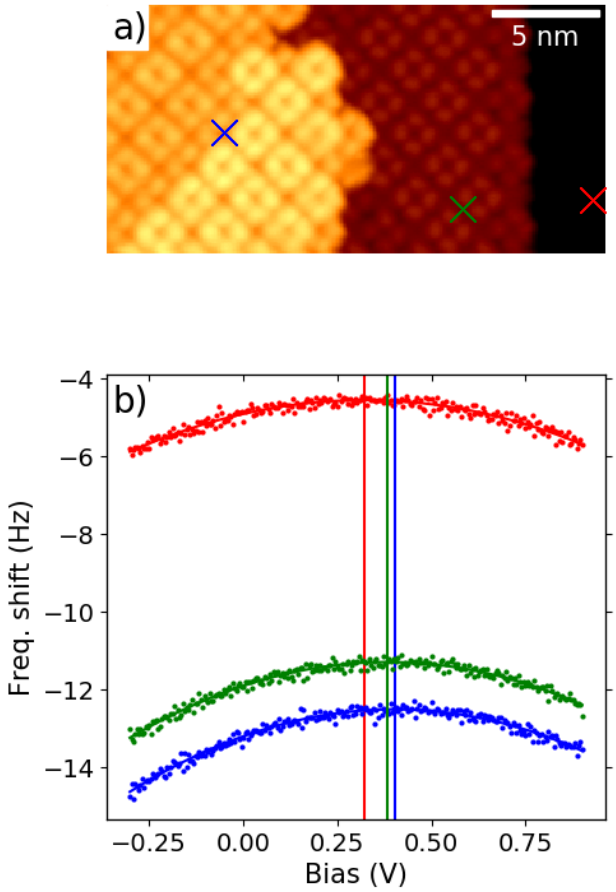


Figure S4: a) Overview STM topography (V_{bias} = 100 mV, I = 10 pA) with the Kelvin probe parabola locations indicated with colored crosses. b) At the marked locations, $\Delta f(V_{bias})$ is recorded at identical heights above the sample. Vertical lines indicate the V_{CPD} parabolic cusp for each curve.

nc-AFM comparison with simulation

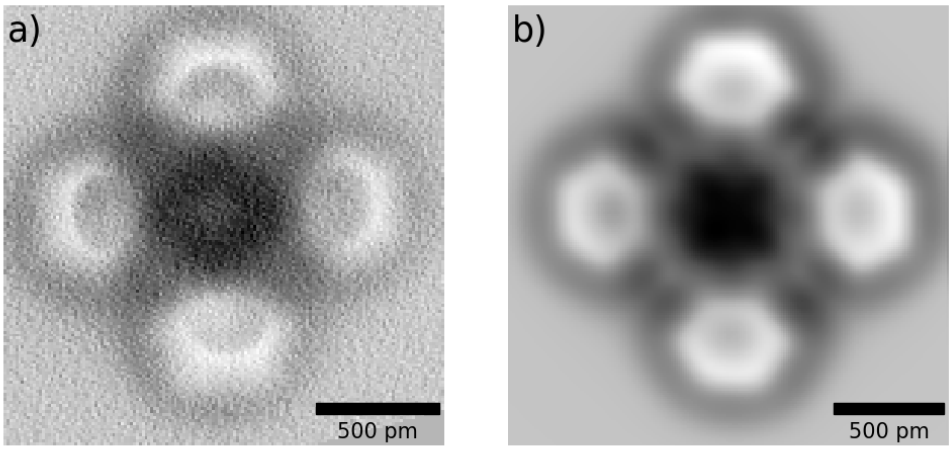


Figure S5: a) High resolution image of isolated Tb_2Pc_3 molecule. b) Simulated nc-AFM image of Tb_2Pc_3 molecule.

Data Analysis Methods

The analysis and preparation of these figures was aided by the use of the scipy[2] and matplotlib[3] python libraries as well as WSxM.[4]

Chemical Analysis

Experimental Methods (MALDI MS)

The Synapt G2-S mass spectrometer (Water, Manchester, UK) equipped with MALDI interface was used for recording the spectral data. The Nd:YAG laser (355 nm) had a pulse rate of 1 kHz at energy level 400 (corresponding to cca 80 μJ); the sample plate voltage was 0 V. The spectra were obtained in positive/negative mode in the range of 50-2000 Da, scan time 1 s, inter-scan delay 0.015 s. The instrument was calibrated before the experiments using red phosphorus in acetone as a reference.

Sample/ matrix preparation and deposition

10 mg of the matrix (2,5- dihydroxybenzoic acid) was dissolved in 1 mL of the solution methanol/ CH_2Cl_2 (1:1, v/v). Saturated solutions of the samples in $CHCl_3$ were subsequently prepared. 2 μL of the matrix was deposited on the MALDI spot and allowed to dry completely before a second 2 μL deposit. Once dry, the plate was inserted in the MALDI source and the prepared spots were analysed.

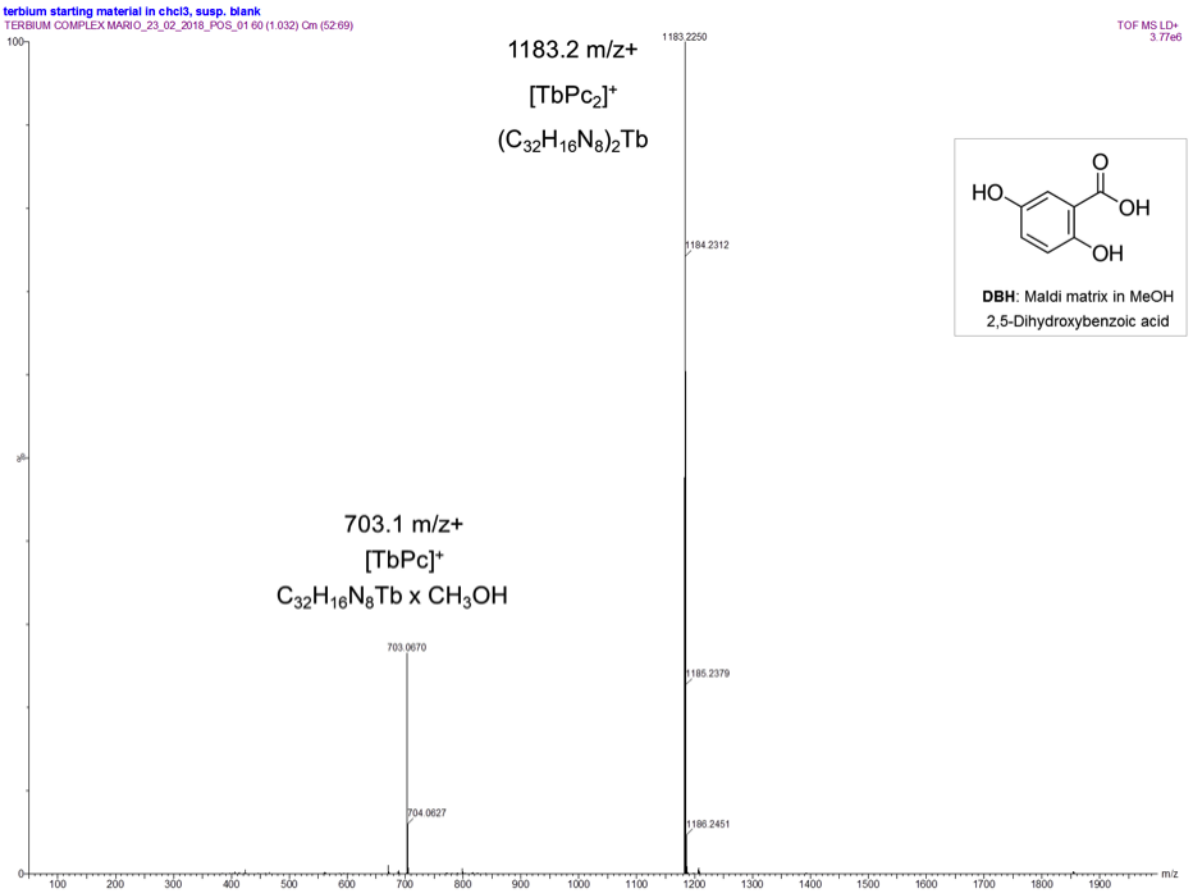


Figure S6: MALDI-MS mass spectroscopy analysis using 2,5-dihydroxybenzoic acid (DBH) matrix in MeOH of neat $TbPc_2$ (solvents $CHCl_3$/MeOH) before UHV deposition, acquired in positive mode. Note the presence of half-decker Tb ring (TbPc, $C_{32}H_{16}N_{18}Tb$) together with double-decker Tb complex ($TbPc_2$, $[(C_{32}H_{16}N_{18})_2Tb]$).

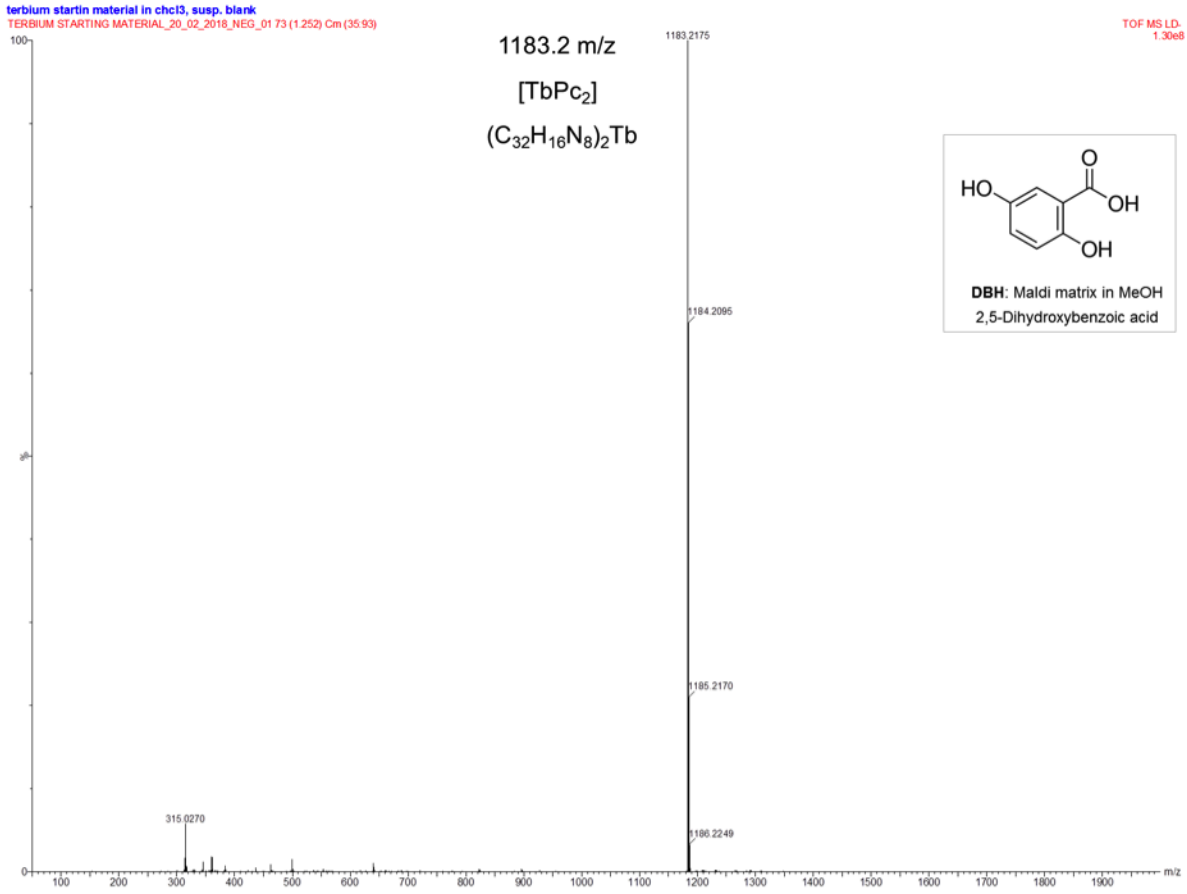


Figure S7: MALDI-MS mass spectroscopy analysis using 2,5-dihydroxybenzoic acid (DBH) matrix in MeOH of neat $TbPc_2$ (solvents $CHCl_3$/MeOH) acquired in negative mode, with the dominating double-decker $TbPc_2$ signal $[C_{32}H_{16}N_{18}Tb]$.

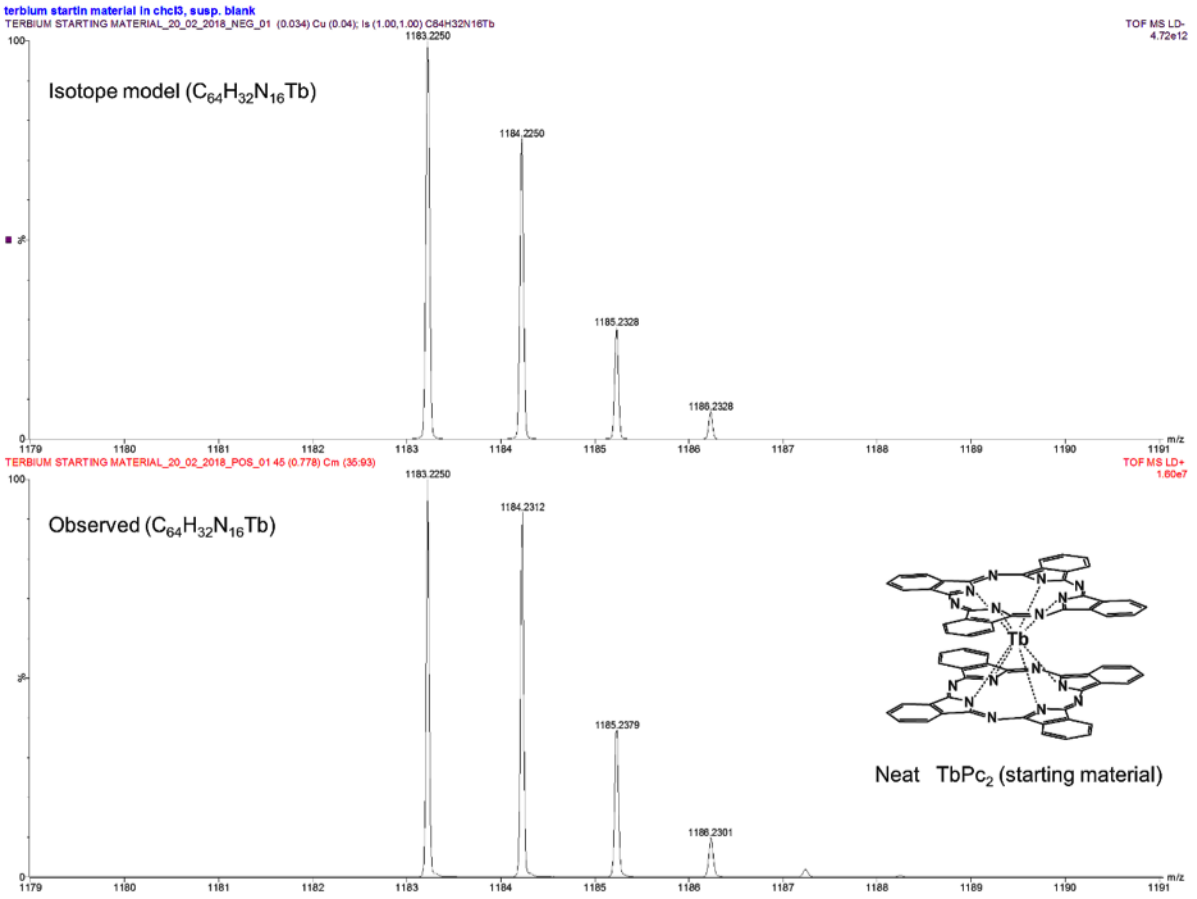
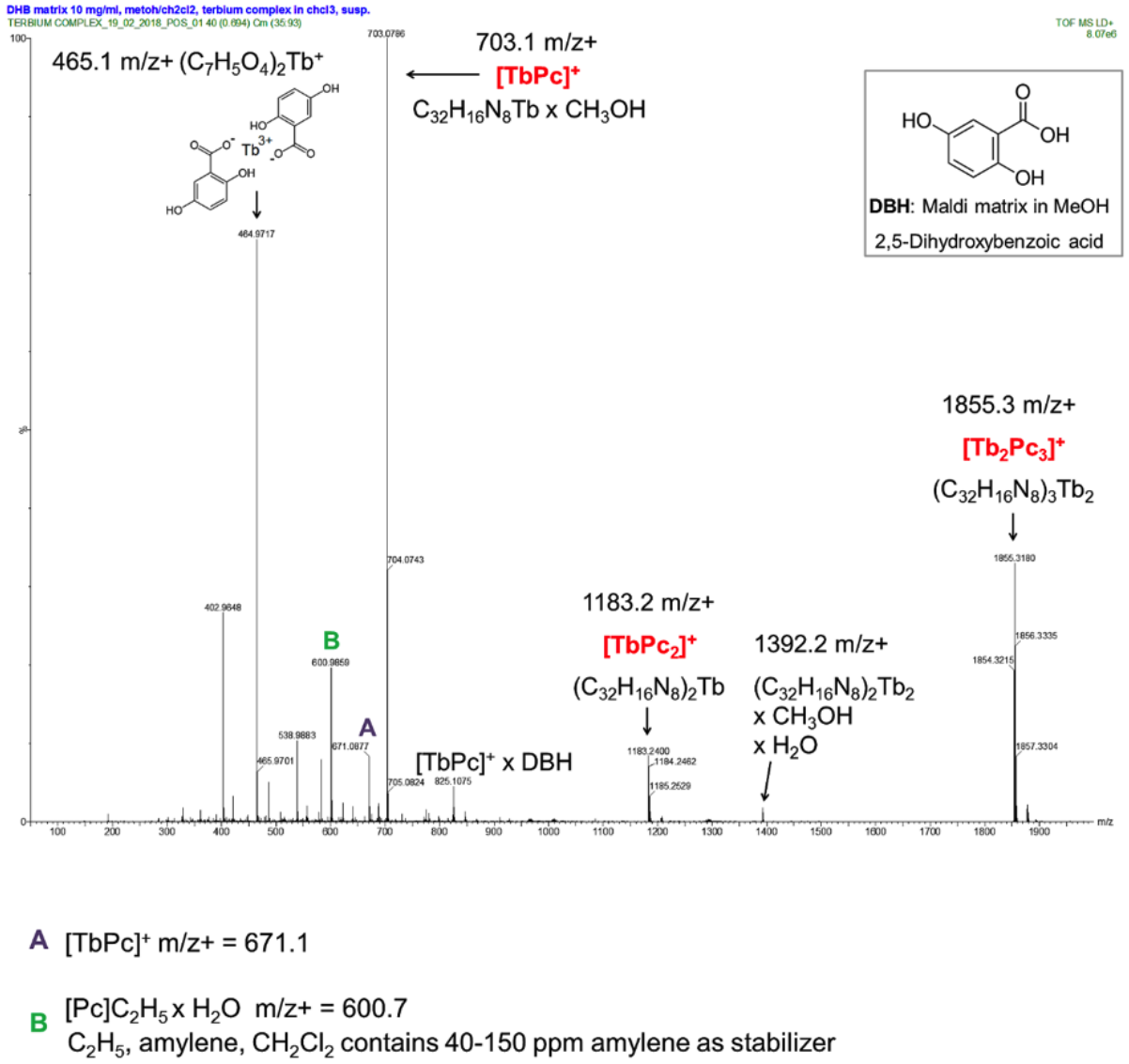


Figure S8: MALDI-MS mass spectroscopy analysis using 2,5-dihydroxybenzoic acid (DBH) matrix in MeOH of neat $TbPc_2$ (solvents $CHCl_3$/MeOH) (lower spectrum) before UHV deposition and its calculated isotopic distribution pattern (upper spectrum, isotope model).



A $[TbPc]^+$ m/z+ = 671.1

B $[Pc]C_2H_5 \times H_2O$ m/z+ = 600.7
C_2H_5, amylene, CH_2Cl_2 contains 40-150 ppm amylene as stabilizer

Figure S9: MALDI-MS mass spectroscopy analysis using 2,5-dihydroxybenzoic acid (DBH) matrix in MeOH of the recovered material from the evaporator crucible, following UHV annealing and surface deposition of the $TbPc_2$ material recorded in positive mode. The presence of the triple decker (Tb_2Pc_3), double-decker ($TbPc_2$) and half-decker (TbPc) signals are highlighted. Annealing time $t = 60$ min, annealing temperature, $T = 850$ K.

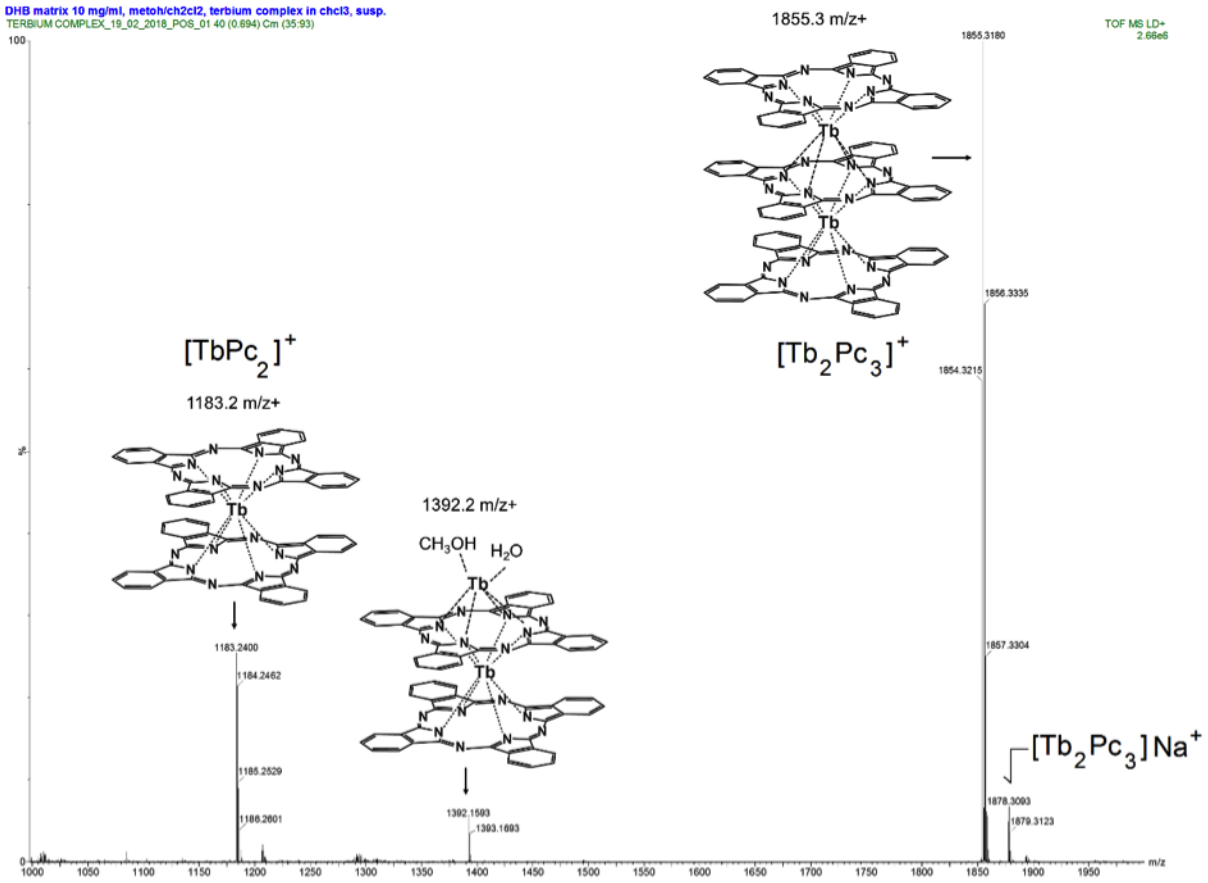


Figure S10: MALDI-MS mass spectroscopy analysis using 2,5-dihydroxybenzoic acid (DBH) matrix in MeOH of the recovered material from the evaporator crucible, following UHV annealing and surface deposition of the $TbPc_2$ material recorded in positive mode in the mass/z^+ region >1000. Annealing time t = 60 min, annealing temperature, T = 850 K.

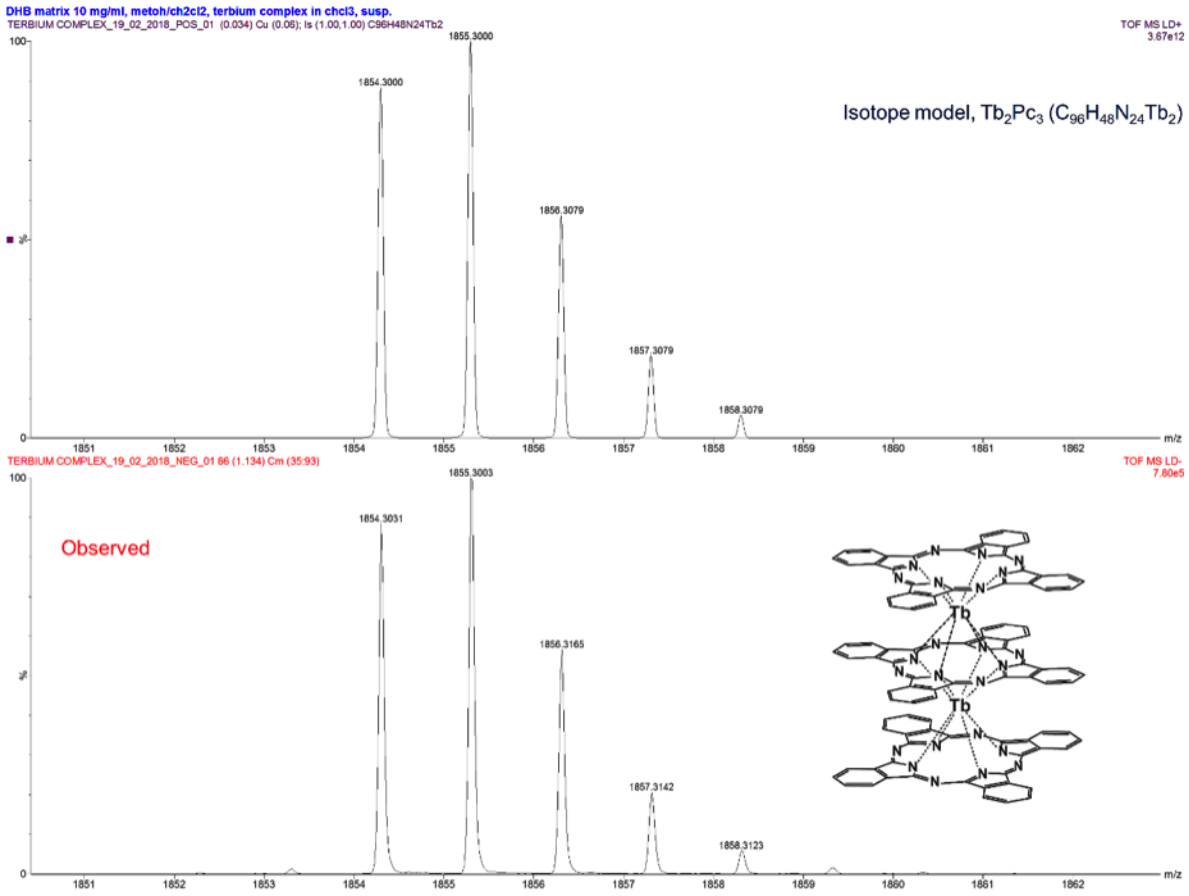


Figure S11: MALDI-MS mass spectroscopy analysis using 2,5-dihydroxybenzoic acid (DBH) matrix in MeOH of the recovered material from the evaporator crucible, following UHV annealing and surface deposition showing the presence of the triple-decker Tb_2Pc_3 (lower panel) with its calculated isotopic distribution pattern (upper panel). Annealing time $t = 60$ min, annealing temperature, $T = 850$ K.

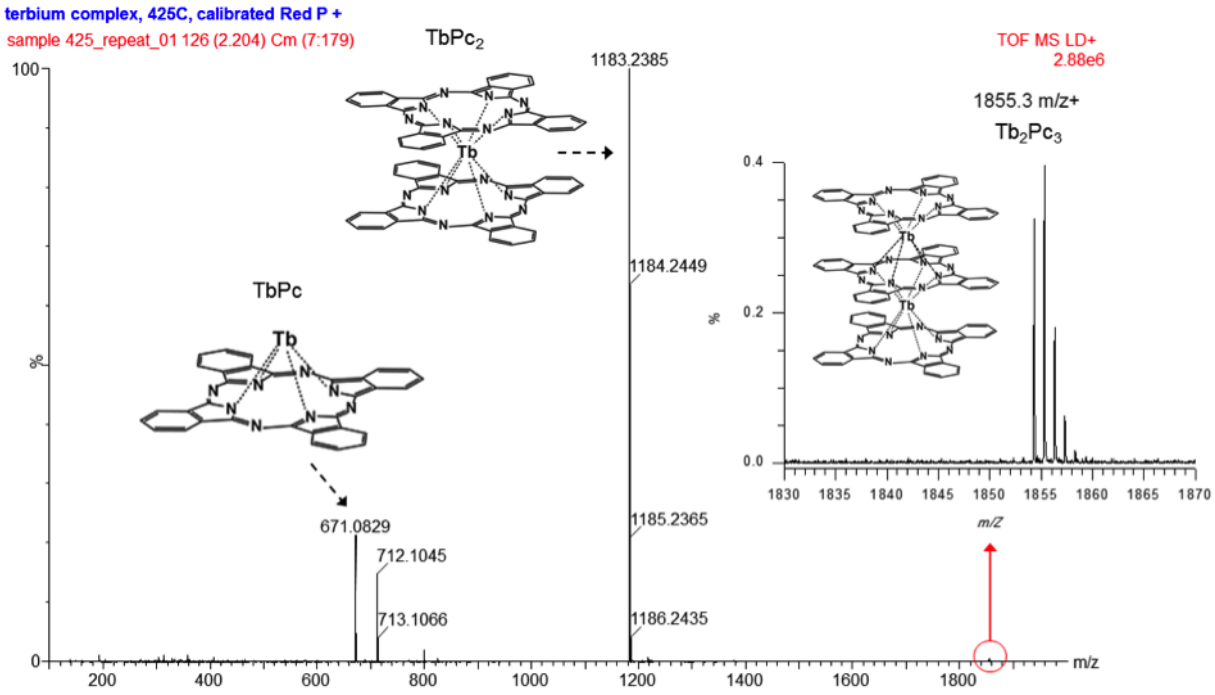


Figure S12: MALDI-MS mass spectroscopy analysis using 2,5-dihydroxybenzoic acid (DBH) matrix in MeOH of the $TbPc_2$ material (solvents $CHCl_3$/MeOH) recovered after annealing $T = 700$ K in the UHV chamber, acquired in positive mode. Annealing time $t = 10$ min.

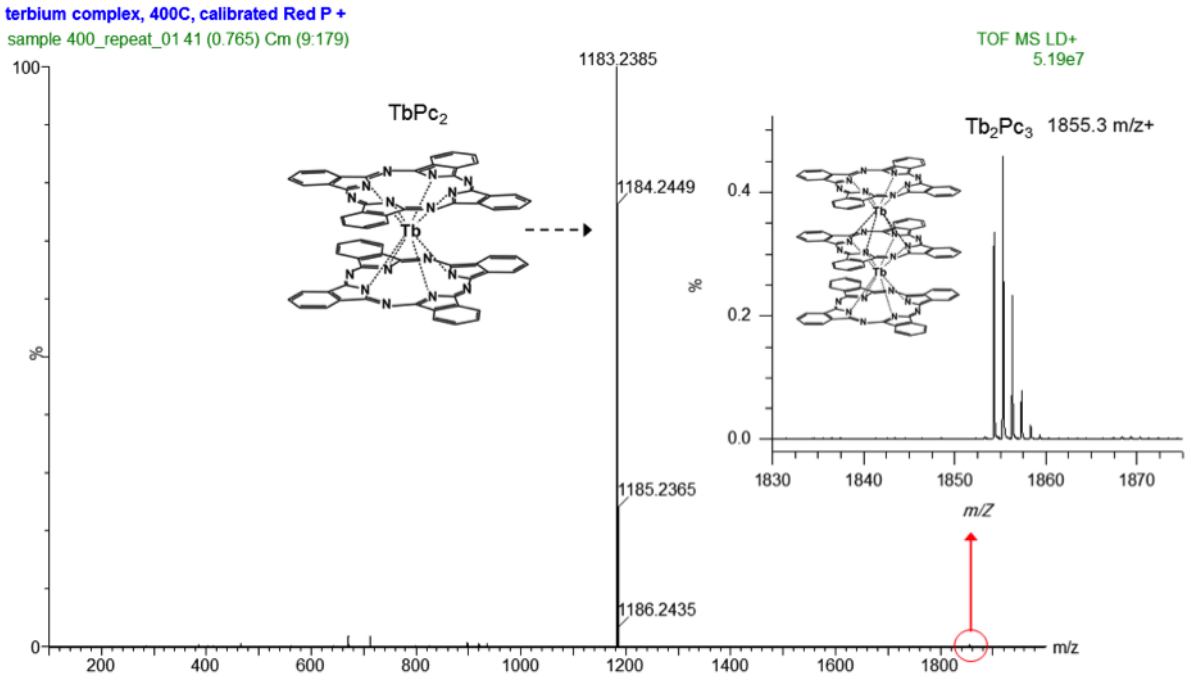


Figure S13: MALDI-MS mass spectroscopy analysis using 2,5-dihydroxybenzoic acid (DBH) matrix in MeOH of the $TbPc_2$ material (solvents $CHCl_3$/MeOH) recovered after annealing $T = 675$ K in the UHV chamber, acquired in positive mode. Annealing time $t = 10$ min.

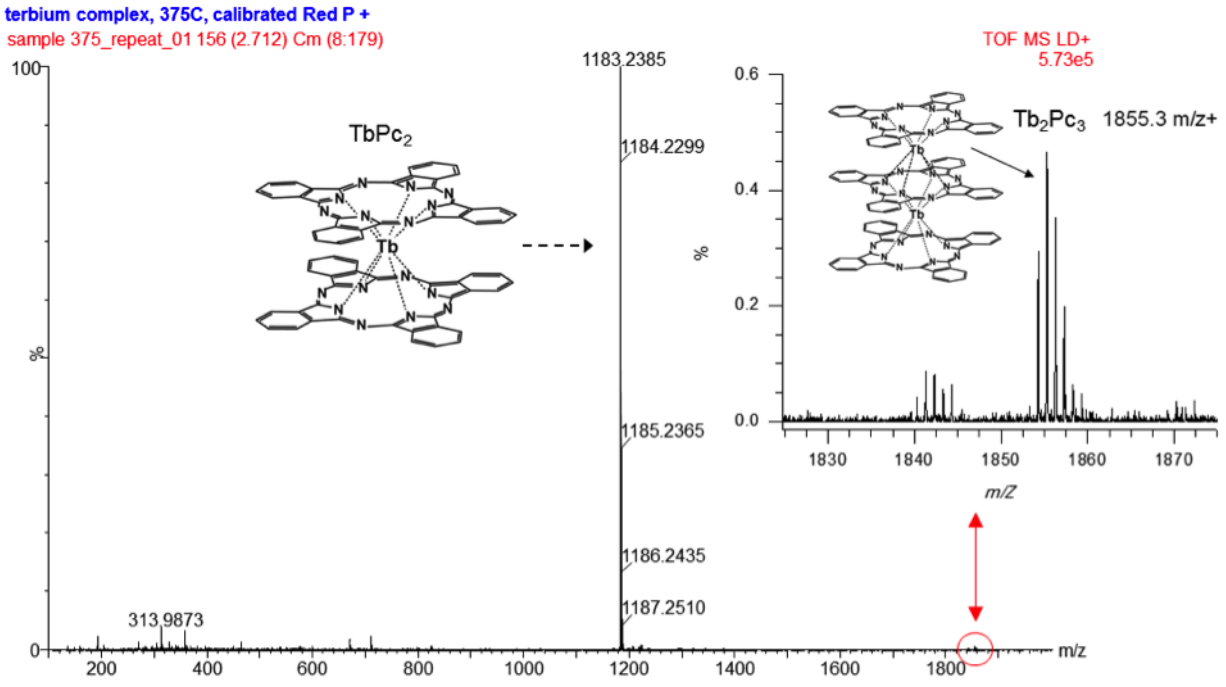


Figure S14: MALDI-MS mass spectroscopy analysis using 2,5-dihydroxybenzoic acid (DBH) matrix in MeOH of the $TbPc_2$ material (solvents $CHCl_3$/MeOH) recovered after annealing $T = 650$ K in the UHV chamber, acquired in positive mode. Annealing time $t = 10$ min.

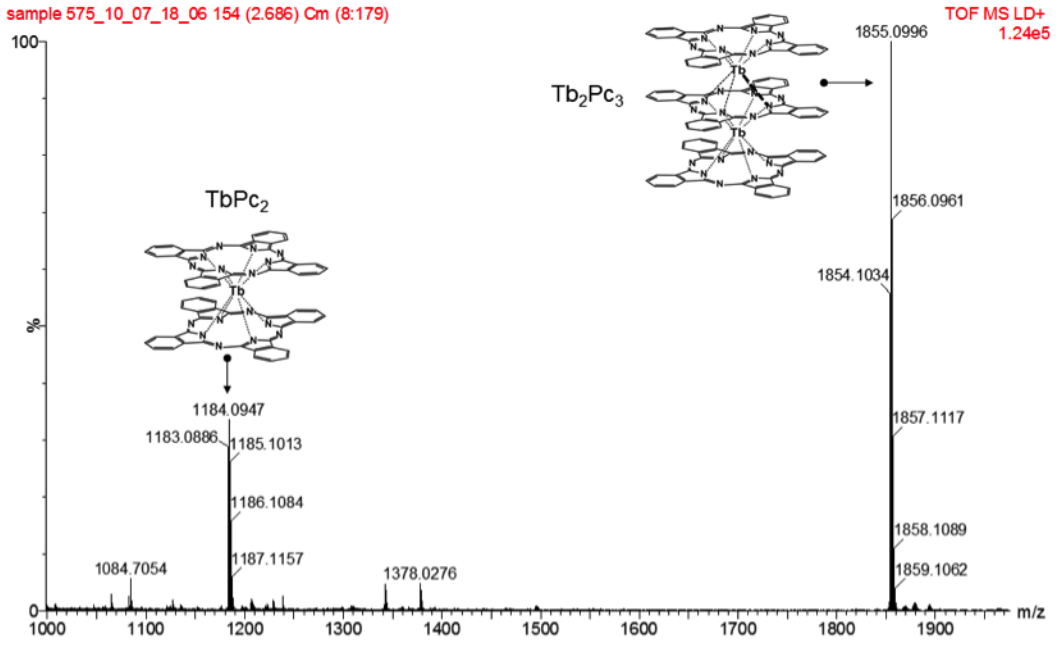


Figure S15: MALDI-MS mass spectroscopy analysis using 2,5-dihydroxybenzoic acid (DBH) matrix in MeOH of the recovered material from the STM crucible, following UHV annealing and surface deposition of the $TbPc_2$ material recorded in positive mode. Annealing time $t = 30$ min, annealing temperature $T = 850$ K.

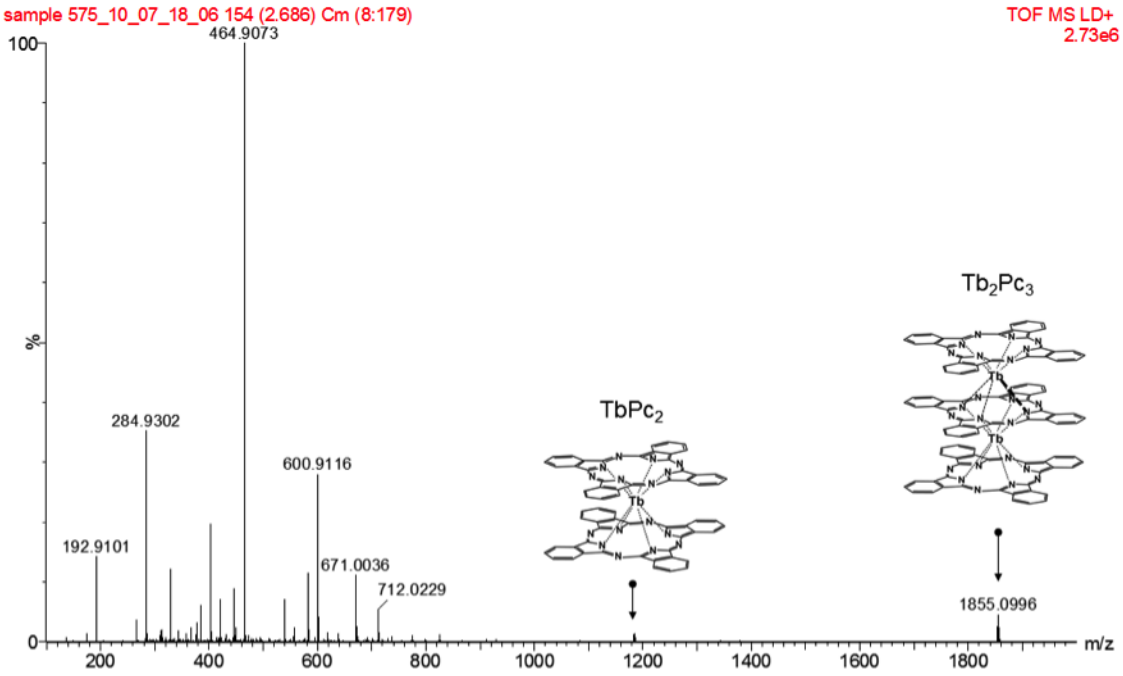


Figure S16: MALDI-MS mass spectroscopy analysis using 2,5-dihydroxybenzoic acid (DBH) matrix in MeOH of the recovered material from the STM crucible, following UHV annealing and surface deposition of the $TbPc_2$ material recorded in positive mode. Annealing time $t = 30$ min, annealing temperature $T = 850$ K.

References

1. Hill, S.; Datta, S.; Liu, J.; Inglis, R.; Milios, C. J.; Feng, P. L.; Henderson, J. J.; del Barco, E.; Brechin, E. K.; Hendrickson, D. N. *Dalton Transactions* **2010**, *39*, 4693.

2. van der Walt, S.; Colbert, S. C.; Varoquaux, G. *Computing in Science & Engineering* **2011**, *13*, 22–30.

3. Hunter, J. D. *Computing in Science & Engineering* **2007**, *9*, 90–95.

4. Horcas, I.; Fernndez, R.; Gmez-Rodrguez, J. M.; Colchero, J.; Gmez-Herrero, J.; Baro, A. M. *Review of Scientific Instruments* **2007**, *78*, 013705.