

shows exceptional thermal stability up to 200°C whereas **2** which is fully dehydrated at 100°C, begins to collapse after 110°C.

[1] Yaghi O., Li Q., *MRS Bulletin* 2009, 34, 682. [2] Naik A. D., Dürst M. M., Léonard A., Tinant B., Marchand-Brynaert, Su B. L., Garcia Y., *Cryst. Growth Des.* 2010, 10.1021/cg901473. [3] Naik A. D., Marchand-Brynaert J., Garcia Y., *Synthesis* 2008, 149.

**Keywords:** MOF, crystal engineering, supramolecular chemistry

#### FA4-MS31-P17

**Zn<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>4</sub> and Zn<sub>7</sub>O<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>10</sub> – Syntheses and Crystal Structures.** Nina van Gellecom<sup>a</sup>, Georgi Genchev<sup>a</sup>, Walter Frank<sup>a</sup>, <sup>a</sup>*Institut für Anorganische und Strukturchemie II, Heinrich-Heine Universität Düsseldorf, Germany*  
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The first examples of zinc trifluoroacetates were reported in 1939 by F. Swarts [1]. These salts were found to be suitable precursors for the preparation of ZnO:F, which is of interest for the semiconductor research [2]. So far, only micro-crystalline samples or solvates of zinc trifluoroacetates have been described. Here we report on the syntheses and the crystal structures of the parent Zn<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>4</sub> (**1**) and of Zn<sub>7</sub>O<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>10</sub> (**2**). Single-crystals of **1** have been obtained by the thermolysis of In(O<sub>2</sub>CCF<sub>3</sub>)<sub>3</sub> in the presence of elemental zinc at 240 °C under static vacuum. **1** crystallizes in the monoclinic space group *P*2<sub>1</sub>/*c* with lattice parameters of *a* = 11.558(2) Å, *b* = 12.561(3) Å, *c* = 16.602(5) Å, and β = 134.121(17) ° with *Z* = 4. The structure is composed of two crystallographically independent Zn atoms that are linked by three trifluoroacetate groups. These fragments are connected by a further trifluoroacetate anion to form chains along [010]. Single-crystals of **2** have been prepared by the thermolysis of Ce(O<sub>2</sub>CCF<sub>3</sub>)<sub>3</sub> in the presence of zinc powder under reduced pressure at 320 °C. **2** crystallizes in the triclinic space group *P*1̄ with lattice parameters of *a* = 10.754(3) Å, *b* = 13.543(5) Å, *c* = 17.634(5) Å, α = 68.323(5) °, β = 89.772(5) ° and γ = 66.634(4) ° and with *Z* = 2. In the crystal of **2** the Zn<sub>7</sub>O<sub>2</sub> fragments, which are composed of two edge-sharing Zn<sub>4</sub>O tetrahedrons, are coordinated by ten trifluoroacetate groups. These fragments are linked by a bridging trifluoroacetate group to form chains along [001].

[1] Swarts F., *Bull. Soc. Chim. Belg.*, 1939, 48, 176. [2] Klingshirn C., *ChemPhysChem*, 2007, 8, 782.

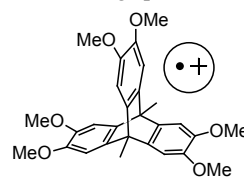
**Keywords:** zinc compounds, single-crystal X-ray diffraction, thermal behaviour

#### FA4-MS31-P18

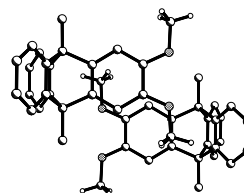
**Novel 2D Assembly of Triptycene Cation Radicals vs. Traditional 1D Motifs** Sergey V. Lindeman, Khushabu Thakur, Rajendra Rathore *Department of Chemistry, Marquette University, Wisconsin, USA*  
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A series of triptycene derivatives with varying number of *o*-dimethoxy substituents along with their corresponding cation

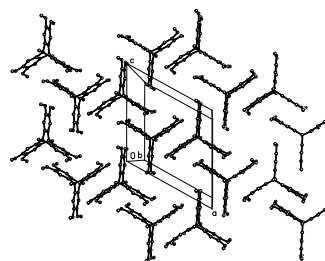
radical salts has been synthesized. The methoxy-substituted benzene rings possess a lower oxidation potential whereas the lengths of their C<sub>Ar</sub>-O bonds provide a very sensitive indicator of the positive charge associated with the corresponding arene ring (i.e. 5.3 pm bond contraction per unit charge). The triptycene molecules were designed as a 3-



dimensional π-delocalized alternative to traditional planar 2-dimensional ion-radical substrates. Using highly precise low-temperature (100 K) X-ray structural data, the intra-molecular electronic interaction/delocalization was identified both in the neutral molecules and in the corresponding cation radicals. Specifically, C<sub>Ar</sub>-O bonds in the neutral triptycenes are progressively elongated by up to 1.0 pm with increasing electron donicity of the molecules whereas C<sub>Ar</sub>-O bonds in the corresponding cation radicals are additionally shortened by 2.0 pm (per unit charge) for interacting dimethoxy-substituted benzene rings. Importantly, both the neutral molecules and their cation-radical salts have a very uniform/conserved association mode of the dimethoxy-substituted arene rings in



crystals. They form close anti-parallel couples that are strengthened by multiple C-H...π hydrogen bonds and dipole-dipole interactions. These forces are further strengthened in the crystals of the cation radicals being assisted by favorable π-π interactions. The regular association of triptycene rings produces 2-dimensional layers with continuous electronic π-π delocalization throughout the plane of the layers via combination of intra- and inter-molecular charge resonance. This packing mode is principally different from the traditional



1-dimensional stacking of the planar aromatic ion radicals and hence opens new avenues in supramolecular design of the next-generation electronic materials for photovoltaic applications.

**Keywords:** supramolecular self-assembly, cation radical salts, charge resonance

#### FA4-MS31-P19

**Synthetic Polymers in Biological Environment.** Jindřich Hašek, Jan Dohnálek, Tereza Skálová, Jarmila Dušková, Andrea Štěpánková, Petr Kolenko *Institute of Macromolecular Chemistry, Academy of Science, 16206 Praha 6, Czech Republic*  
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Many practical applications where synthetic polymers are in a direct contact with bio-macromolecules are known. Positive and also some negative consequences of polymer activity in

biological environment have been reported in pharmacology, food industry, cosmetics. Examples include e.g. the preferred uptake of large macromolecules into the cell (EPR effect), decreased degradation of macromolecular drugs, enhancement of life-time of bio-macromolecules in blood circulation, etc. However, no systematic explanations of these effects on molecular level have been reported.

Structure determination of classical polymers has always been difficult because of a lack of regularity and a lack of structural elements implicitly forming the exact 3D fold of bio-macromolecules and ensuring the identical conformation of all macromolecules in the measured sample. Other difficulties lie in polydispersity resulting from a statistical nature of polymerization process, generally high intrinsic flexibility of polymers, and also from high molecular weight. This all leads to an impossibility to grow well equilibrated crystals and thus the crystalline grains in polymers are in all cases of a very low diffraction quality.

The experimentally determined structures of polymers are reviewed in the first part of the “Structure database of polymers – PolyBase” [1]. Generally, the polymer stacking in the crystalline state is well based on experiment, but the detailed molecular structure is prevalingly a subject of imposed restrains on bond lengths and angles.

The second part of PolyBase is formed by polymer fragments firmly adsorbed on protein surface [2] as it is observed by X-ray diffraction techniques. Water soluble polymers dissolved in large water basins observed in many protein crystals [3] often form characteristic patterns on protein surface. As the polymer conformation here is formed or at least strongly influenced by weak attractive and repulsive interactions between polymers and proteins, it is more descriptive to call this part of PolyBase a “Database of Protein-Polymer Interactions”. The 3D structure of a polymer here is usually determined by protein and thus whole PDB file [4] involving polymer molecules and also proteins should be analysed together and is therefore retained in the PolyBase.

The intermolecular interactions are strongly dependent on distribution of function groups on the protein surface under discussion. Therefore the structures are grouped according to the dominating interaction. The most important include: hydrogen bridges to the positively charged side chain of K, R, H (the positive charges of Lys, Arg, His are usually encapsulated by H-bond acceptors of the polymer); H-bonds to the side chains of E,D,Q,N; H-bonds to S,T,Y,W; H-bonds to main chain amino groups; H-bonds to the main chain carbonyls; hydrophobic interaction between protein and polymer.

The research is supported by GA CR 305/07/1073.

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 [2] Hašek J., *Zeitschrift für Kristallogr.* (2006) 23, 613. [3] Skálová T. et al, *J. Appl. Crystallogr.* (2010), in press. [4] Berman H.M. et al, *Nucleic Acid Research* (2000) 235-242.

**Keywords: protein crystal, hydrophilic polymers, PEGylation**