Synthesis, Crystal Structure, and Spectral Characterization of Novel Three-dimensional Supramolecular Networks with One-dimensional Channels Based on Keggin-type Polyoxoanions and Mixed-Valence Dibenzotetrathiafulvalenes

Dongmei Shi^a, Yaguang Chen^a, Haijun Pang^a, Fanxia Meng^a, Yu Sun^a, Kun Liu^a, and Hongbo Liu^{a, b}

^a Key Laboratory of Polyoxometalates, Science of Ministry of Education, College of Chemistry, Northeast Normal University, Changchun 130024, P. R. China

^b Department of Pharmaceutics, Changchun Medical College, Changchun 130031, P. R. China

Reprint requests to Dr. Yaguang Cheng. E-mail: chenyg146@nenu.edu.cn

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A new organic/inorganic salt formed by mixed-valence dibenzotetrathiafulvalene (DBTTF) radical cations and the spherical Keggin-type polyoxometalate anions $[H_3BW_{12}O_{40}]^{2-}$ was obtained by electrochemical oxidation of the donor in an acetonitrile and a 1,2-dichloroethane solution containing the polyanion. The compound has been characterized by X-ray diffraction, elemental analysis, EPR, IR and Raman spectroscopy. X-Ray diffraction experiments have revealed that the compound consists of heteropolyanions, water molecules and DBTTF radical cations. The organic radicals form trimers and dimers *via* π - π stacking; moreover, the polyoxoanions and the organic donors are also held together by hydrogen bonding interactions. In their packing arrangement, a three-dimensional supramolecular network with one-dimensional channels along the *b* axis is established with uncoordinated water molecules residing in the channels.

Key words: Radical Cation Salts, Electrochemical Oxidation, Polyoxometalate, DBTTF, Supramolecular