



Photochromism, Electrical Properties, and Structural Investigations of a Series of Hydrated Methylviologen Halobismuthate Hybrids: Influence of the Anionic Oligomer Size and Iodide Doping on the Photoinduced Properties and on the Dehydration Process

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Syntheses, X-ray structural analyses, thermal behaviors, photochromism, and electrical properties of a series of methylviologen (MV²⁺) halobismuthate hybrids, namely, (MV)₃[Bi₄Cl₁₈](H₂O)_y (1a, y~1.7), (MV)₄[Bi₆Cl₂₆](H₂O)_y (2a, y~1.7), (MV)₄[Bi₆Cl_{25.6}I_{0.4}](H₂O)_y (3a, y~1.5), and (MV)₄[Bi₆Cl_{24.6}I_{1.4}](H₂O)_y (4a, y~1.3), are reported. Because of the thermal effect of a UV lamp or as a result of being heated up to 100 °C, all of the above compounds undergo a complete (1a, 2a, and 3a) or a partial (4a) dehydration together, in 2a and 3a, with an impressive structural reorganization involving a 90° rotation of methylviologen dimers and, in 3a, a new Cl/I distribution, finally leading to (MV)₃[Bi₄Cl₁₈] (1b), (MV)₄[Bi₆Cl₂₆] (2b), (MV)₄[Bi₆Cl_{25.6}I_{0.4}] (3b), and (MV)₄[Bi₆Cl_{24.6}I_{1.4}](H₂O)_x (4a, x ~ 0.65), respectively. In its turn, 4a (x ~ 0.65) undergoes an abrupt structural change at 160 °C when water molecules are completely removed, leading to (MV)₄[Bi₆Cl_{24.6}I_{1.4}] (4b). Obviously, the two first dehydrated phases can be considered as the n = 2 (1b) and n = 3 (2b) members of the (MV)_(2n+2)/2[Bi_{2n}Cl_{8n+2}] family, and the ultimate member (n = ∞) with an infinite 1D double-chain inorganic framework, namely, (MV)[Bi₂Cl₈], has already been reported. According to the results of structural refinements, some positions of the Cl atoms in the [Bi₆Cl₂₆]⁸⁻ anionic cluster of 3a and 4a have been occupied by I atoms, finally leading to iodide-doped materials of the 2a type (percentage of doping: 3a, 1.5%; 4a, 5.4%). Upon UV irradiation, yellow crystals of 2a and 3a (which become 2b and 3b because of the thermal effect of the UV lamp) or yellow crystals of 2b, 3b, and 4a undergo a color change to black crystals (in the case of 2b), as observed in (MV)[Bi₂Cl₈], or light-brown crystals (in the cases of 3b and 4a). These photochromic properties are probably due to the photoinduced electron transfer from the anionic part to the methylviologen dications. In contrast, no color change is observed when yellow crystals of 1a or 1b and the iodide-doped (MV)[Bi₂Cl_{8-ε}I_ε] material are irradiated. Because the relative positions of methylviologen to the host anionic frameworks are comparable in all structures (the N...Cl distances are about 3.4 Å), these results indicate that such kinds of photochemical reactions depend on the dimension of the anionic networks, as well as the iodide doping. The single-crystal electrical conductivity measurements of 2b before and after irradiation were carried out between 150 and 393 K. The results prove that both of them are semiconductors with weak room temperature conductivity and that the band gap of the irradiated crystal (2b, 0.35 eV) is much smaller than that of the original hybrid 2a (1.0 eV).

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