



The Templating Effect and Photochemistry of Viologens in Halometalate Hybrid Crystals

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Résumé en anglais Although the chemistry of viologens in solution has been thoroughly investigated, their intriguing functions in the crystalline state have been the subject of less attention. Recently, many hybrid structures incorporating viologen cations have been published, and a considerable number of them possess interesting properties in the solid state. Elaborate examination of these structures has indicated that peculiar interactions between the viologen dication and anions, including side contacts and face contacts, are very often encountered. This suggests that the viologen dications have a great influence on their surroundings at the atomic level. This remarkable templating effect is well demonstrated by a series of hybrids, in which the rare MX₅ (M = Bi^{III}, Sb^{III}; X = Cl, Br, I) inorganic chain of trans-connected octahedra is stabilised by a methylviologen dication; this leads to a new fascinating family of ferroelectrics. In contrast, owing to their unique structural features, viologen dications exhibit prominent photochemistry. Upon irradiation, viologen dications (V²⁺), with good electron-accepting abilities, are able to accept one electron from an electron donor, either an anion or a molecule, to afford stable separated charge state systems with photochromic properties resulting from the coloured V^{•+} radicals. This process takes place in the crystalline solid state and offers great opportunities to understand their structure-property relationships. The relationships discovered in the current system will guide subsequent rational syntheses to optimise the properties of the materials.

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