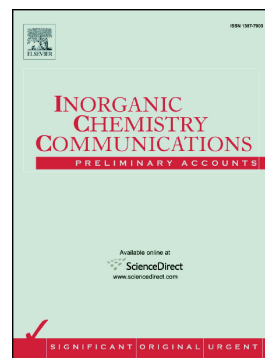


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3-D Organic-Inorganic Hybrid Architecture Based on Tröger's Base: Synthesis, Supramolecular Structure, and Aggregation-Induced Emission Properties

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Abstract

An organic-inorganic hybrid solid (DMDP)[Hg(SCN)₄] (1) (DMDP = 2,8-(6*H*,12*H*-5,11-methanodibenzo[*b,f*]diazocineylene)-di(*p*-ethenyl-*N*-methyl-pyridinium) was designed and synthesized. X-Ray structural analysis reveals that it comprises a 3-D interpenetrating superstructure that 1-D inorganic anionic chains {[Hg(SCN)₄]²⁻]_∞ penetrates into 2-D organic (DMDP)²⁺ cationic network. Photoluminescence investigation show that compound **1** exhibits a typical aggregation-induced emission (AIE) properties.

Key words: Crystal engineering, interpenetrating superstructure, Tröger's Base, aggregation-induced emission

Organic-inorganic hybrid solid materials have been received considerable attention because of their fascinating architectures as well as their potential applications in catalysis, gas storage, optoelectronics, sensors, and so on^[1-7]. Crystal engineering^[8-10] towards this end is to understand and utilize coordinate/covalent forces^[11] and/or weaker noncovalent forces such as hydrogen bonding,^[12,13] C–H... π interaction,^[14-17] π ... π interaction,^[18,19] halogen bonds^[20-22] and other scarcely interactions such as metal–metal,^[23,24] S...S,^[25-29] Se...Se^[30-32] interactions *etc.* to construct supramolecular frameworks. Supramolecular self-assembly of pre-selected reactants is an important method to synthesize new hybrid materials possessing fascinating architectures and properties. The dipyrindinium cations and their derivatives are of considerable interest due to their physical properties and applications in biology and photochemistry.^[33-37] Our previous work about dipyrindinium salts based on Tröger's Base (TB)^[38] shown interesting optical properties.^[39,40] On the other hand, mercury-tetra-thiocyanate [Hg(SCN)₄]²⁻, as a stable molecular ion, has been employed as important inorganic building blocks for constructing inorganic-organic assemblies with various organic molecules.^[41-44] The combining of dipyrindinium organic cation and [Hg(SCN)₄]²⁻ inorganic anion in a hybrid solid may create unusual structure and properties. In this work, we report the synthesis and X-ray crystallographic study of a novel hybrid architecture in which the inorganic mercury-tetra-thiocyanate anionic chains {[Hg(SCN)₄]²⁻]_∞ penetrates the organic dipyrindinium cationic network. We also discuss the photophysical properties of **1**.

The X-ray structure of compound **1** reveals that it crystallizes in the monoclinic space group *Pccn* and its asymmetric unit contains one [Hg(SCN)₄]²⁻ divalent anion and one (DMDP)²⁺ divalent cation (Fig. 1). The mercury (II) centre,

which has distorted tetrahedral coordination environment, coordinated to four thiocyanate S atoms (S1, S2, S1*, and S2*). The Hg(II) –S, S–C, and C≡N distances are 2.504(2)–2.571(2) Å, 1.643(9)–1.644(8) Å, and 1.130(9)–1.136(10), respectively. The S–Hg–S angles vary between 102.07(13) and 120.55 (10)°. The Hg–S–C bond is bent with the Hg–S–C angles varying in the range of 96.8(3) and 100.5(3)°. For the (DMDP)²⁺ cation, the dihedral angle between the two benzene rings constituting the TB framework is 89.9°. The torsion angles between the benzene rings C9–C14 and the adjacent pyridine rings N1–C7 is 6.6°, indicating that the benzene rings and the adjacent pyridine rings are almost coplanar. Excellent coplanarity of the conjugated moiety

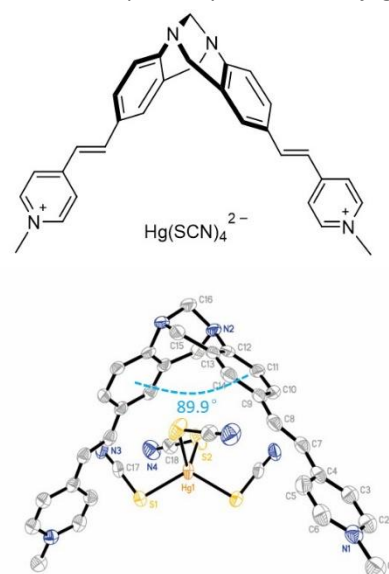


Fig. 1 Molecular structure and ORTEP drawing of **1** showing the 30% probability ellipsoids. The hydrogen atoms have been omitted for clarity.

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