

Phosphorescence spectra of dinuclear platinum(II) complexes: Relation between electronic structure of excited state and intersystem crossing

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Recently, phosphorescence spectra of dinuclear platinum(II) complexes have drawn a lot of interests. For instance, a pyrazolate-bridged platinum(II) complex (**1**; Scheme 1)¹ with two bipyrimidines (bpym)s and a pyridinethiolate-bridged complex (**2**)² with two phenylpyridines (ppy)s exhibit interesting phosphorescence spectra. The phosphorescence of **1** is completely quenched in CH₃CN solution but observed in solid phase, while that of **2** is observed in both CH₃CN solution and solid phase. We wish to report geometries and electronic structures of the lowest energy singlet (S₁) and triplet (T₁) excited states of **1** and **2** and to clarify the reason of the difference in their phosphorescence spectra.

Geometries of **1** and **2** in the S₁ and T₁ states were optimized by the broken-symmetry DFT(B3PW91) and the usual DFT(B3PW91) methods, respectively. Spin-orbit interaction was evaluated with the one-electron part of the Breit-Pauli Hamiltonian with the CAS-CI wave function.

In CH₃CN solution, the electronic structure of **1** in the S₁ and T₁ states is assigned as the charge transfer excited state, where one-electron excitation occurs from the dσ*(Pt-Pt) antibonding orbital to the π* orbital of bpym (Fig. 1). These dσ*(Pt-Pt) and π*(bpym) orbitals are delocalized on two Pt-bpym moieties. These S₁ and T₁ states take the C_{2v} symmetry. In solid phase, on the other hand, the electronic structures of **1** in the S₁ and T₁ states are characterized as the π-π* excited state of bpym (Fig. 1). It is noted that these π(bpym) and π*(bpym) orbitals are localized on one bpym. These S₁ and T₁ states take the C₁ symmetry. The spin-orbit interaction between the S₁ and T₁ states is zero in the C_{2v} symmetry but not equal to zero in the C₁ symmetry because of the symmetry of the one-electron part of the Breit-Pauli Hamiltonian. Thus, the S₁ → T₁ intersystem crossing hardly occurs in CH₃CN solution, but it effectively occurs in solid phase. This is one of the reasons why the T₁ → S₀ phosphorescence of **1** is completely quenched in CH₃CN solution but observed in solid phase.

The electronic structures of **2** in the S₁ and T₁ states are assigned as the charge transfer excited state in both CH₃CN solution and solid phase (Fig. 1). These S₁ and T₁ states take the C₂ symmetry, in which the spin-orbit interaction is present between the S₁ and T₁ states. Because the S₁ → T₁ intersystem crossing easily occurs in both experimental conditions, the T₁ → S₀ phosphorescence is observed in **2**.

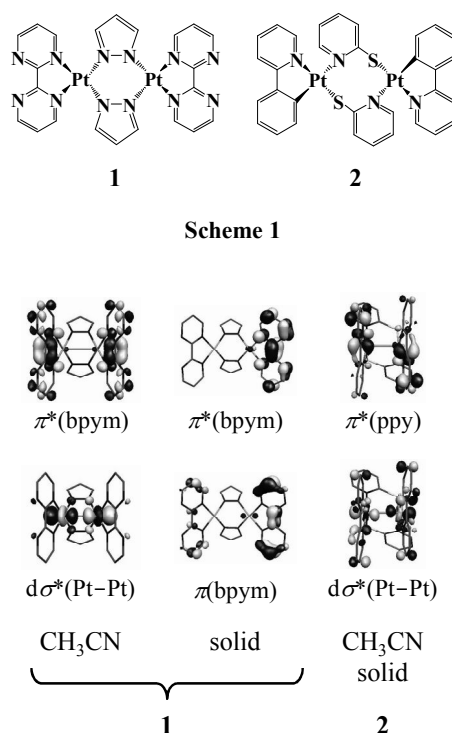


Fig. 1 Singly occupied molecular orbitals (SOMOs) in the S₁ and T₁ states of **1** and **2**

(1) K. Umakoshi, Y. Kim, M. Onishi, S. Ishizaka, and N. Kitamura, private communication. (2) T. Koshiyama, A. Omura, and M. Kato, Chem. Lett. **33**, 1386 (2004).