Butterfly Deformation Modes in a Photoexcited Pyrazolate-Bridged Pt Complex Measured by Time-Resolved X-Ray Scattering in Solution

Pyrazolate-bridged dinuclear Pt(II) complexes represent a series of molecules with tunable absorption and emission properties that can be directly modulated by structural factors, such as the Pt-Pt distance. However, direct experimental information regarding the structure of the emissive triplet excited state has remained scarce. Using time-resolved wide-angle X-ray scattering (WAXS), the excited triplet state molecular structure of [Pt(ppy)(μ-t-Bu₂pz)]₂ (ppy = 2-phenylpyridine; t-Bu₂pz = 3,5-di-tert-butylpyrazolate), complex 1, was obtained in a dilute (0.5 mM) toluene solution utilizing the monochromatic X-ray pulses at Beamline 11IDD of the Advanced Photon Source. The excited-state structural analysis of 1 was performed based on the results from both transient WAXS measurements and density functional theory calculations to shed light on the primary structural changes in its triplet metal-metal-to-ligand charge-transfer (MMLCT) state, in particular, the Pt-Pt distance and ligand rotation. We found a pronounced Pt-Pt distance contraction accompanied by rotational motions of ppy ligands toward one another in the MMLCT state of 1. Our results suggest that the contraction is larger than what has previously been reported, but they are in good agreement with recent theoretical efforts and suggest the ppy moieties as targets for rational synthesis aimed at tuning the excited-state structure and properties.

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