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.

General information
State: Published
Organisations: Department of Physics, Neutrons and X-rays for Materials Physics, Department of Chemistry, Northwestern University, Argonne National Laboratory, North Carolina State University
Number of pages: 9
Pages: 7475-7483
Publication date: 2016
Peer-reviewed: Yes

Publication information
Journal: Journal of Physical Chemistry A
Volume: 120
Issue number: 38
ISSN (Print): 1089-5639
Ratings:
BFI (2018): BFI-level 1
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 1
Scopus rating (2017): CiteScore 2.75 SJR 1.17 SNIP 0.964
Web of Science (2017): Impact factor 2.836
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 1
Scopus rating (2016): CiteScore 2.64 SJR 1.252 SNIP 0.958
Web of Science (2016): Impact factor 2.847
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 1
Scopus rating (2015): CiteScore 2.78 SJR 1.148 SNIP 1.074
Web of Science (2015): Impact factor 2.883
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 1
Scopus rating (2014): CiteScore 2.65 SJR 1.159 SNIP 1.069
Web of Science (2014): Impact factor 2.693
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 1
Scopus rating (2013): CiteScore 2.64 SJR 1.205 SNIP 1.109
Web of Science (2013): Impact factor 2.775
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 1
Scopus rating (2012): CiteScore 2.78 SJR 1.513 SNIP 1.127