

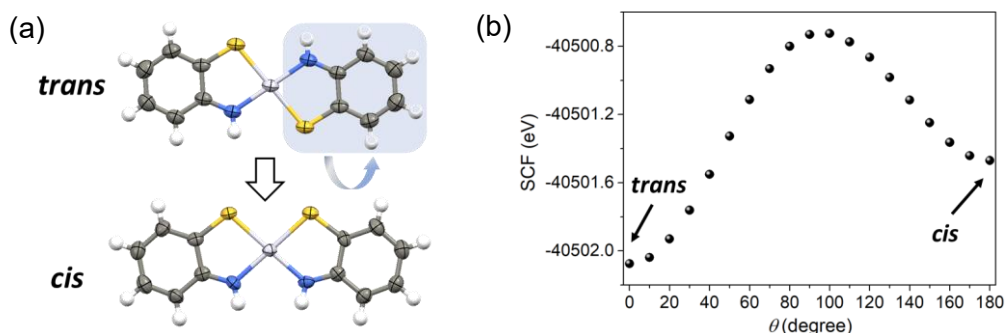
Trans-cis Isomerism of Pt Complexes with *o*-Aminobenzenethiol Ligand

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Trans and *cis* isomers of Pt complexes have received widespread acceptance as a clinical drug for the treatment of various diseases.¹ In this study, a N,S-donor ligand, *o*-aminobenzenethiol, was reacted with Pt(II) salt in aqueous methanol solution under ambient atmosphere.² The neutral π -planar complexes, *trans*- and *cis*-Pt(itsq)₂ (itsq^{•−} represents the *o*-iminothiosemiquinonate π -radical; Figure a), were simultaneously harvested as dark-blue solids. Equilibrium dynamics for the *trans-cis* isomerization of the Pt complexes was evaluated by ¹H NMR spectroscopy in five kinds of organic solvents. It is found that the *trans* isomer is dynamically more stable than the *cis* isomer in most solvents and that the isomerization process is entropically controlled possibly *via* a solvent association mechanism. In addition, DFT calculations predicted that the *trans* isomer is 0.60 eV more stable than the *cis* isomer with a rotational barrier of 1.35 eV (Figure b).

Proton-coupled electron transfer (PCET) plays a pivotal role in biological and chemical processes.³ Molecules with π -electron systems, where the π -conjugation can be reconstructed by attaching or detaching protons, have been investigated to realize the PCET behavior. Metal complexes with π -ligands bearing Lewis acidic/basic sites are of great interest in understanding the PCET. In this study, we address the PCET behavior of the Pt complexes based on the pH-dependent absorption and electrochemical spectra in solution state. Given that the *trans* and *cis* isomers have different two-dimensional layered structures, i.e., those based on monomer and dimer units, respectively, the present system may provide a feasible platform for investigating the effect of molecular packing on the proton-electron coupled electron conduction and magnetism. The results are also discussed in detail.



- 1) M. J. Abrams, B. A. Murrer, *Science* **1993**, 261, 725. 2) K. Matsumoto, I. Fukutomi, I. Kinoshita, S. Ooi, *Inorg. Chim. Acta* **1989**, 158, 201. 3) a) T. Mitani, G. Saito, H. Urayama, *Phys. Rev. Lett.* **1988**, 60, 2299. b) M. H. V. Huynh, T. J. Meyer, *Chem. Rev.* **2007**, 107, 5004.