

Platinum complexes exhibiting intense luminescence and chromic phenomena

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Luminescent platinum complexes have attracted considerable attention as phosphorescent materials for organic light-emitting devices, photosensitizers for photocatalytic systems, and chromic materials for volatile organic compound (VOC) sensors. The most interesting point would be characteristic luminescence induced by self-assembly and the environment. We reported various mononuclear and dinuclear Pt(II) complexes which respond to organic vapor and mechanical stimulation by the changes in the stacking structures.^[1,2] This presentation focuses on the recent progress in our group regarding Pt(II) complexes exhibiting luminescence and chromic phenomena.

Pt(II)-diimine complexes bearing carboxy groups, $[\text{Pt}(\text{CN})_2(\text{L})]$ ($\text{L} = 4,4'$ -dicarboxy-2,2'-bipyridine, 4,7-dicarboxy-1,10-phenanthroline) (Fig.1(a)) exhibit multicolor vapochromic luminescence to various organic vapors in the solid state.^[3] These complexes form red-luminescent porous supramolecular frameworks from the purple amorphous form by absorbing alcoholic vapor. The color change occurs by the change of the Pt··Pt electronic interactions. Interestingly, the frameworks are kept after the included alcohol molecules has been removed, and the open form becomes acceptable to water vapor which was inactive to the original amorphous form. The framework can be destroyed by the mechanical grinding and reconstructed by the vapor exposure. Thus the complexes have shape-memory properties accompanied by the luminescence color changes.

By the introduction of cyclometalating ligands instead of diimine ligands, the improvement in the luminescence intensity is expected because of their strong ligand-fields. Taking this advantage, we have further developed luminescent chromic platinum complexes which have additional functionalities. A cyclometalated platinum complex with an amidato-bridged dinuclear framework, $[\text{Pt}_2(\mu\text{-aam})_2(\text{ppy})_2]$ (Haam = acetoamide, Hppy = 2-phenylpyridine) (Fig.1(b)) exhibits multi-step electrochromic behavior in addition to the luminescence.^[4] The features occur by the change of the assembled structures depending on the oxidation states of platinum ions including mixed-valence states. On the other hand, the tetra(*n*-butyl)ammonium salt of a cyclometalated Pt(II) complex, $[\text{Pt}(\text{CN})_2(\text{ppty})]^-$ (Hppty = *p*-tolyl-2-pyridine) (Fig.1(c)) realized very intense luminescence with the quantum yield more than 0.5.^[5] By the combination with the 1-ethyl-3-methylimidazolium ion with the anionic Pt(II) complex, the luminescent ionic liquid which exhibited thermochromic dual emission was fabricated. Another cyclometalated Pt(II) complex containing a carboxyl group, $[\text{Pt}(\text{pcppy})(\text{pic})]$ (Hpcppy = 2-(*p*-carboxyphenyl)pyridine, Hpic = picolinic acid) (Fig.1(d))

exhibits completely different luminescence properties from those of the unsubstituted complex, [Pt(ppy)(pic)].^[6] The carboxy group in [Pt(pcppy)(pic)] improves in the assembling properties of the platinum complex in both solid and solution states, which induces not only red ³MMLCT luminescence in the solid state but also aggregation-induced luminescence changes in a basic aqueous solution.

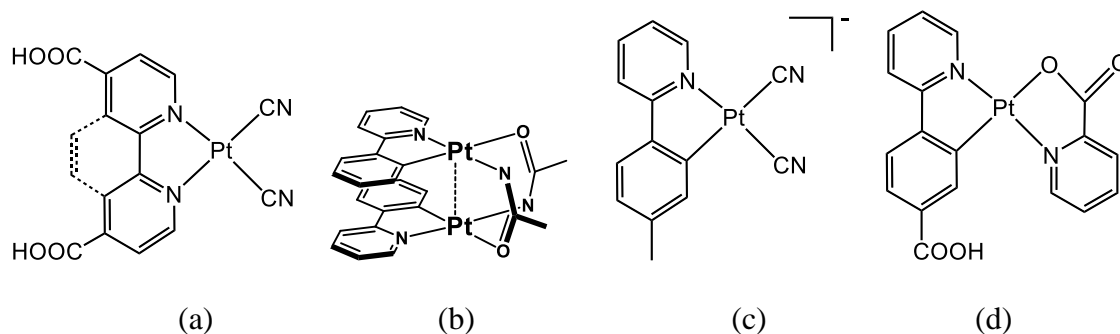


Fig. 1. Structural formulas of Pt(II) complexes.

References:

- [1] A. Kobayashi and M. Kato, *Eur. J. Inorg. Chem.*, **2014**, 4469. (Minireview)
- [2] M. Kato, *Bull. Chem. Soc. Jpn.*, **2007**, *8*, 287. (Accounts)
- [3] M. Kato, S. Kishi, Y. Wakamatsu, Y. Sugi, Y. Osamura, T. Koshiyama and M. Hasegawa, *Chem. Lett.*, **2005**, *34*, 1368; Y. Shigeta, A. Kobayashi, T. Ohba, M. Yoshida, T. Matsumoto, H.-C. Chang and M. Kato, *Chem., Eur. J.* **2016**, *22*, 2682.
- [4] M. Yoshida, N. Yashiro, H. Shitama, A. Kobayashi, and M. Kato, *Chem. Eur. J.*, **2016**, *22*, 491.
- [5] Ogawa, T.; Yoshida, M.; Ohara, H.; Kobayashi, A.; Kato, M. *Chem. Commun.* **2015**, *51*, 13377.
- [6] M. Ebina, A. Kobayashi, T. Ogawa, M. Yoshida, and M. Kato, *Inorg. Chem.* **2015**, *54*, 8876.