

Cyclometalated Pt(II) complex with bidentate Schiff-base ligand displaying unexpected cis/trans isomery

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Platinum complexes, and in general luminescent d^6 and d^8 derivatives, containing π -conjugated ligands with N and/or C donor atoms, have attracted widespread research interest for the applications in optoelectronics, chemo/biosensors, bioimaging and medicinal chemistry.^[1] Schiff base, O^N , bidentate ligands are versatile and tunable structures, easy to prepare, and have been widely applied in the development of metal catalysts. On the contrary, transition-metal Schiff base complexes are less studied and developed in optoelectronics.

In this communication we report the design and synthesis of prototype Pt(II) complexes carrying a C^N ancillary ligand (i.e. 1-phenyl-pyrazole (Hppz) and 2-phenyl-pyridine (Hppy)) and the 2-hydroxy-1-naphthyl-(N-phenyl)-imine (**HNpOPh**) O^N one. These complexes have been synthesized as depicted in Figure 1 reacting intermediate **PtMD** or **PtMM** with the HO^N ligand.

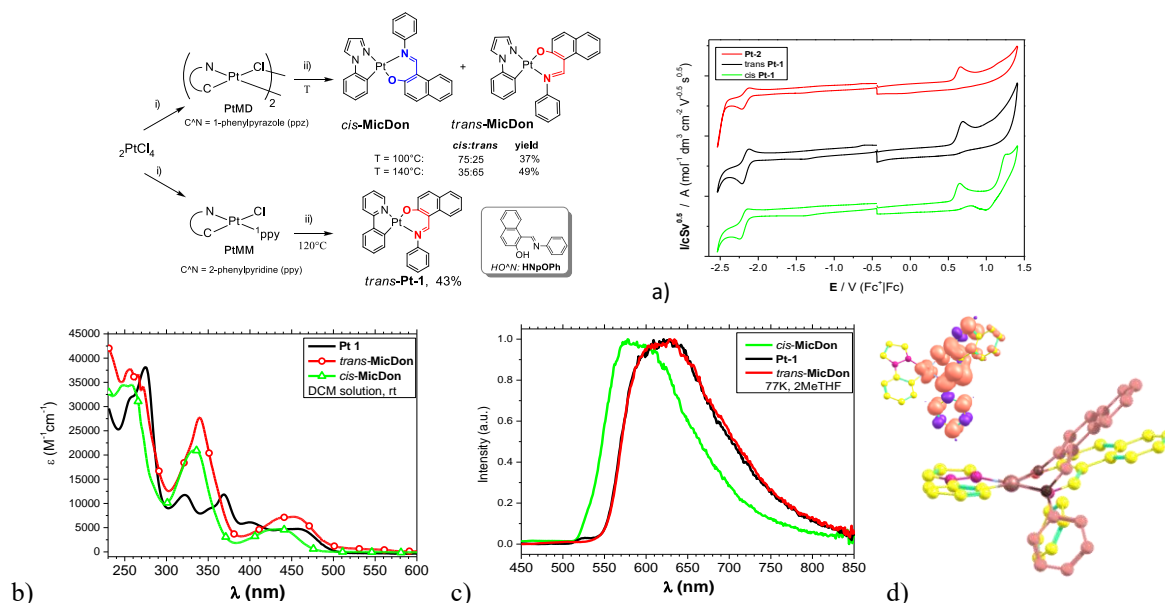


Figure 1. *Left panel*: Synthetic route to complexes **MicDon** and **Pt-1**, isolated yields are indicated. i) Hppz or Hppy, 2-ethoxyethanol/H₂O, 80°C, Ar; ii) 2-ethoxyethanol, Na₂CO₃, **HNpOPh**, Δ , Ar. *Panel a*: Cyclic voltammeteries in DCM. *Panel b*: Absorption spectra in DCM. *Panel c*: emission spectra at 77K. *Panel d*: calcd. triplet spin density (top), and ground (yellow) to triplet (pink) state geometry distortion in *trans*-**MicDon**

Unexpected and worth standing result, is that the new Pt(II) complex (**MicDon**) can be obtained in both its *cis* and *trans* forms as defined in Figure 1,^[2] while only the *trans* isomer of **Pt-1** forms.^[3] This results from the *trans* influence exerted by the phenyl-pirazole ligand which makes the *cis* isomer thermodynamically accessible.

Cis/trans isomers of **MicDon** were easily isolated by chromatography and structurally characterized by HPLC-MS, NMR and X-Ray diffraction. The results from the combined electrochemical, photophysical and DFT studies demonstrated that most of the electronic properties of the complexes are determined by the O[^]N ligand. In fact the first mono-electronic oxidation involves the Pt center plus O[^]N ligand, while the first reduction, partially reversible, involves the O[^]N ligand (Fig. 1a). Complexes adopting *trans* configuration show similar absorption (Fig. 1b), emission (Fig. 1c) and excited state features scarcely influenced by the C[^]N ligand (ppy or ppz). On the other hand, the *cis* isomer absorption and emission are overall blue shifted and the complex has a higher luminescence efficiency. Large excited state distortion (Fig. 1d) quenches the emission of the complexes but in diluted solution but they become highly luminescent in rigid matrix and the emissions are assigned to the perturbed ³LC states centered on the NpOPh ligand.

Funding: Regione Lombardia (decreto 3667/2013) project TIMES “Tecnologie e materiali per l’utilizzo efficiente dell’energia solare” and Progetto Integrato Regione Lombardia and Fondazione CARIPLO (decreti 12689/13, 7959/13), Azione 1 e 2, "SmartMatLab centre" and Cariplo Foundation grant 2013-1766

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