

発光性クロミック金属錯体

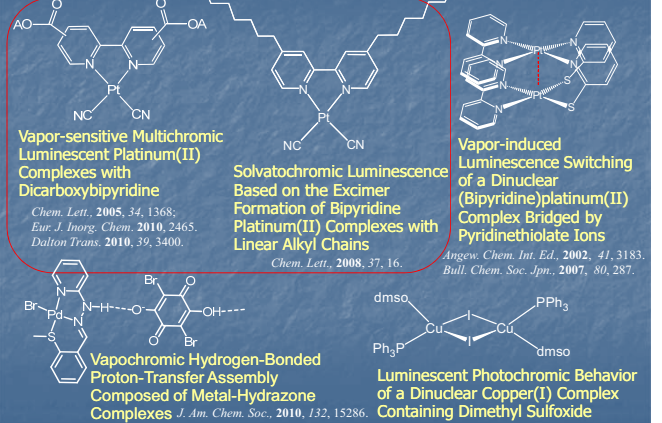
北海道大学大学院理学研究院 加藤昌子
Masako KATO, Hokkaido University



the construction of photofunctional metal complexes

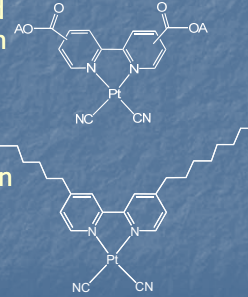
1

Luminescent metal complexes which respond to environmental stimuli



Today's Topics

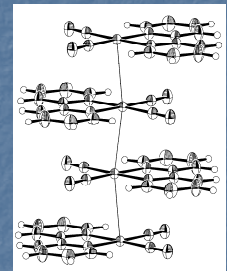
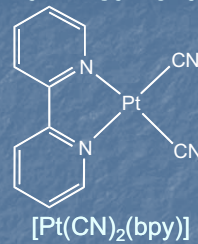
1. Outstanding Vapochromism and Vapor-induced Self-organization of Platinum(II) Complexes with Dicarboxybipyridine
2. Solvatochromic Luminescence Based on the Excimer Formation of Bipyridine Platinum(II) Complexes with Linear Alkyl Chains



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(2,2'-bipyridine)(Dicyanido)Platinum(II) with a Linear-chain Structure

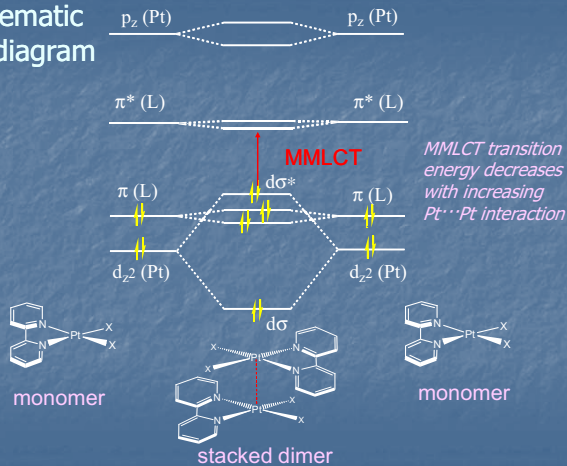


Red Form

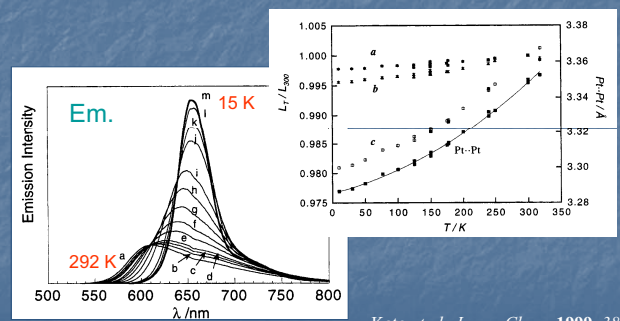
Pt...Pt = 3.34(1) Å at RT

→ Pt...Pt interactions

Schematic MO diagram



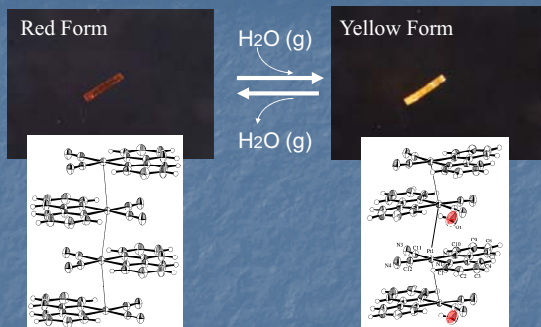
Temperature-dependent Luminescence Spectra and Structural Parameters for the Red Form of [Pt(CN)₂(bpy)]



a) 292, b) 260, c) 240, d) 220, e) 180, f) 160, g) 140, h) 120, i) 100, j) 60, k) 45, l) 30, m) 15 K.

Kato et al., *Inorg. Chem.*, 1999, 38, 1638-1641.

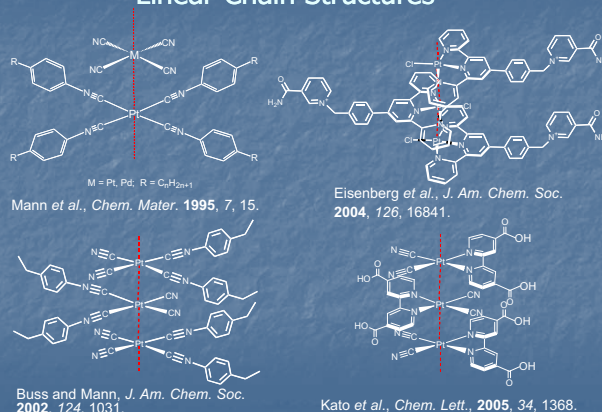
Vapochromism of [Pt(CN)₂(bpy)]



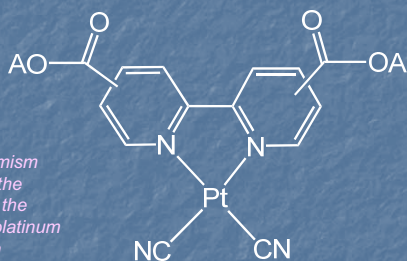
Pt...Pt = 3.3388(1) Å Pt...Pt = 3.3279(3), 4.6814(3) Å
 Pt...Pt...Pt = 168.59(4)° Pt...Pt...Pt = 132.89(1)°

Kishi & Kato, *Mol. Cryst. Liq. Cryst.*, **2002**, 379, 303-308.

Vapochromic Platinum(II) Complexes with Linear-Chain Structures



1. Outstanding Vapochromism and Vapor-induced Self-organization of Platinum(II) Complexes with Dicarboxybipyridine



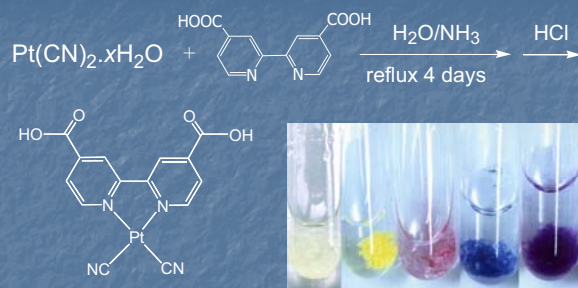
Vapochromism based on the change of the platinum-platinum interaction

[Pt(CN)₂(H₂dc bpy)] Na₂[Pt(CN)₂(dc bpy)]

Kato et al., *Chem. Lett.*, **2005**, 34, 1368.

Eur. J. Inorg. Chem. **2010**, 2465.

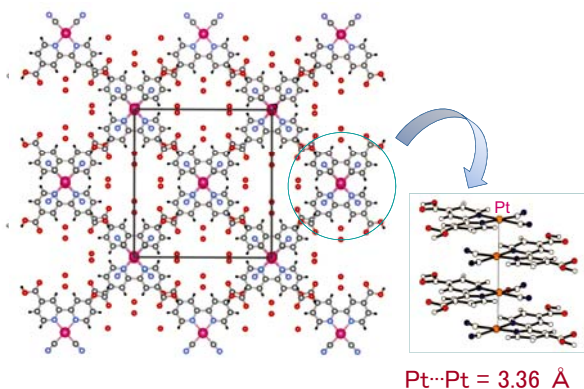
Synthesis of [Pt(CN)₂(H₂dc bpy)]



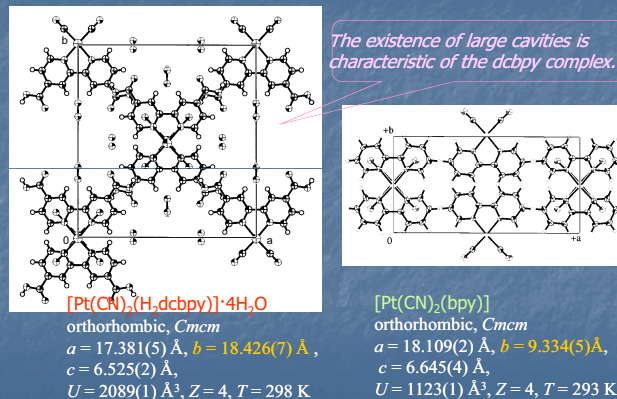
Recrystallization: DMF / 2M HCl
 NH₃ aq / HCl or AcOH

pH = 5 4 3 <2
 [Pt(CN)₂(H₂dc bpy)] · NH(CH₃)₂ [Pt(CN)₂(H₂dc bpy)] · 4H₂O
 [Pt(CN)₂(H₂dc bpy)] · 2H₂O

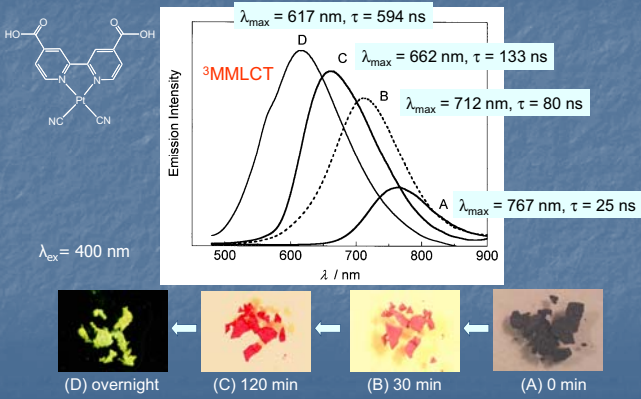
Packing Structure of [Pt(CN)₂(4,4'-H₂dc bpy)] · 4H₂O (Red Form)



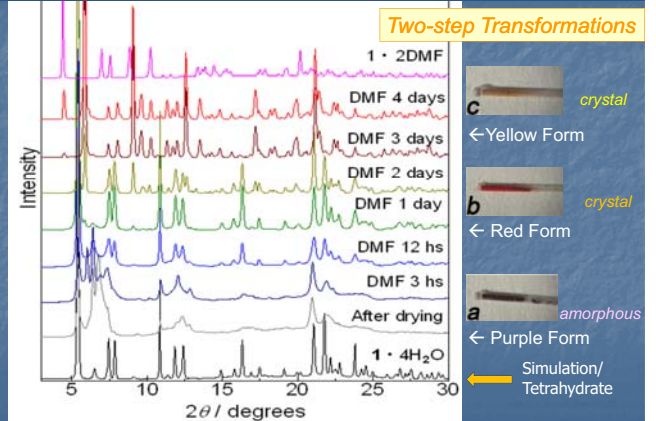
Comparison of the Packing Structures for the Red Forms of [Pt(CN)₂(H₂dc bpy)] · 4H₂O and [Pt(CN)₂(bpy)]



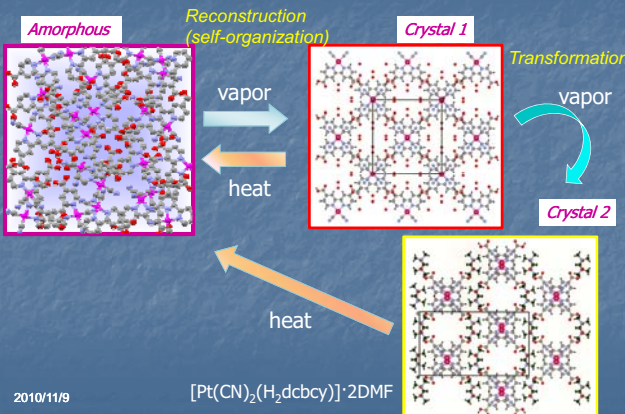
Luminescence Spectral Changes for the Purple Form of $[\text{Pt}(\text{CN})_2(4,4'\text{-dcbpy})]$ upon Exposure to DMF Vapor



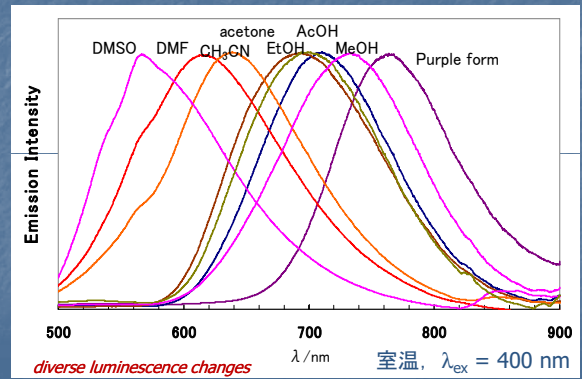
Changes in Powder X-ray Diffraction (PXRD) Pattern of $[\text{Pt}(\text{CN})_2(\text{H}_2\text{dcbpy})]$ upon Exposure to DMF Vapor



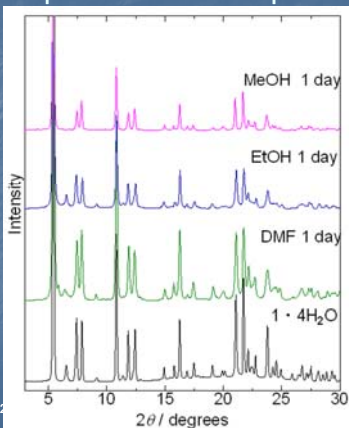
Vapochromic Transformation for $[\text{Pt}(\text{CN})_2(\text{H}_2\text{dcbpy})]$



Luminescence Spectral Changes of the Purple Form upon Exposure to Various Vapors

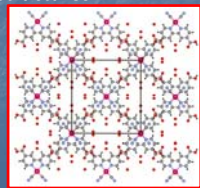


Powder X-ray diffraction patterns of $[\text{Pt}(\text{CN})_2(\text{H}_2\text{dcbpy})]$ on exposure to various vapors

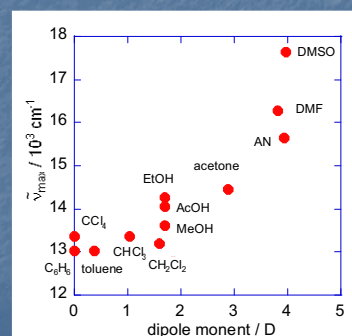


The 1st step for the reconstruction is essentially the same.

The complex uptakes vapor molecules to form the 3D network structures.



The Plot of the Emission Energy for $[\text{Pt}(\text{CN})_2(\text{H}_2\text{dcbpy})]$ in the Solid State Against the Dipole Moment of Vapor Molecules

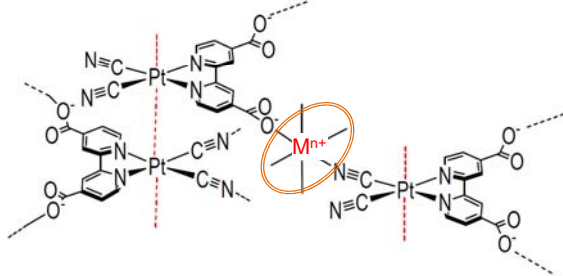


Vapor molecules \Rightarrow higher polarity \Rightarrow luminescence \Rightarrow higher energy \Rightarrow Pt...Pt interactions \Rightarrow weaker

Good sensor for organic vapors

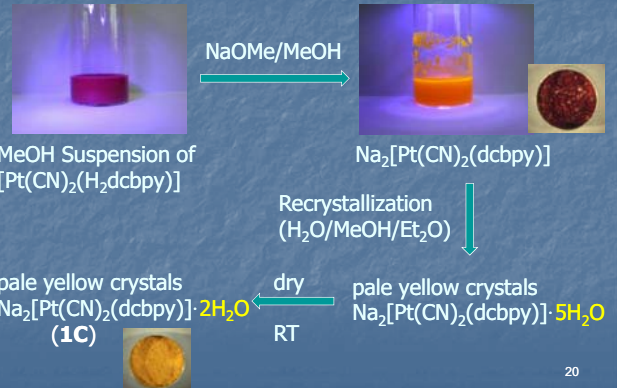
Vapour-Induced Amorphous–Crystalline Transformation for $\text{Na}_2[\text{Pt}(\text{CN})_2(\text{dcbpy})]$

vapo expansion of 2D network to 3D structure
 syste by using metal cations
 bonding interactions



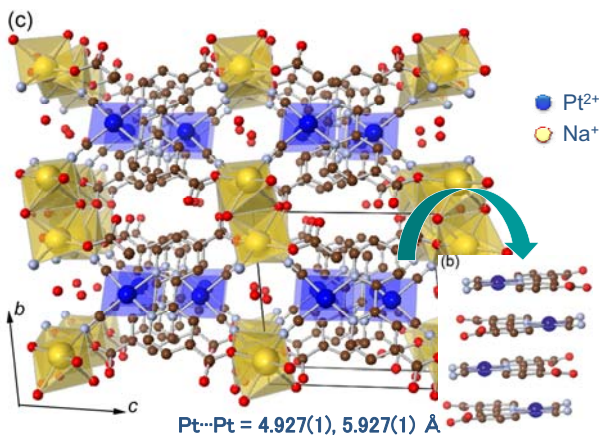
9 19

Preparation of $\text{Na}_2[\text{Pt}(\text{CN})_2(\text{dcbpy})]$

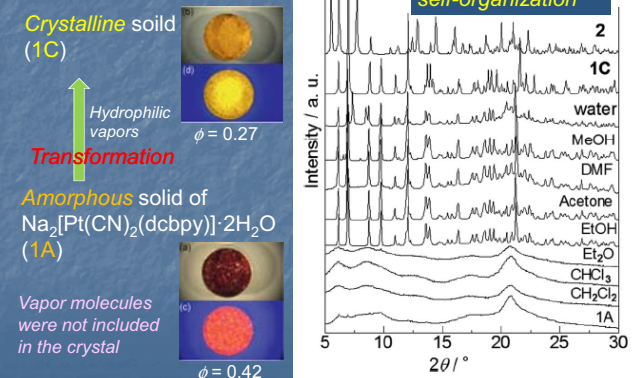


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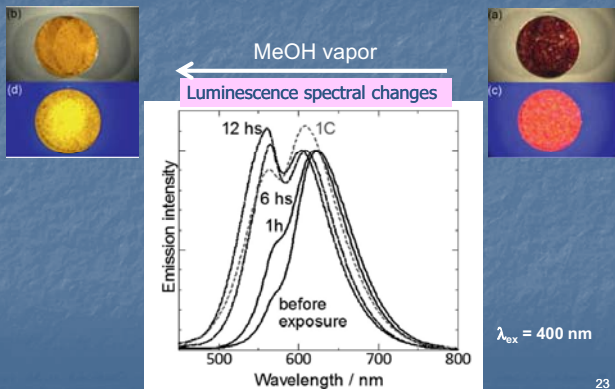
Crystal Structure of $\text{Na}_2[\text{Pt}(\text{CN})_2(\text{dcbpy})] \cdot 2\text{H}_2\text{O}$ (**1C**)



Changes in the powder X-ray diffraction pattern of **1A** $\text{Na}_2[\text{Pt}(\text{CN})_2(\text{dcbpy})] \cdot 2\text{H}_2\text{O}$



Vapochromic Behavior of $\text{Na}_2[\text{Pt}(\text{CN})_2(\text{dcbpy})] \cdot 2\text{H}_2\text{O}$ on Exposure to Methanol Vapors

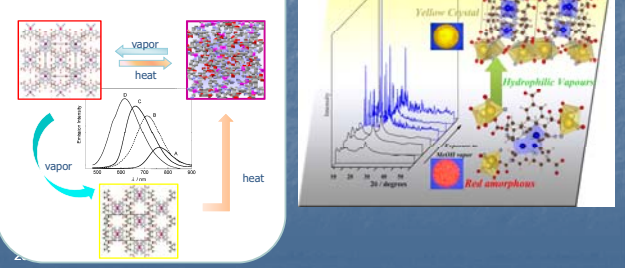


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Summary 1

vapochromic platinum complexes

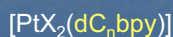
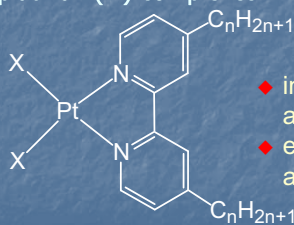
$[\text{Pt}(\text{CN})_2(4,4'\text{-H}_2\text{-dcbpy})]$ $\text{Na}_2[\text{Pt}(\text{CN})_2(4,4'\text{-dcbpy})] \cdot 2\text{H}_2\text{O}$
 Multichromic luminescence controlled by hydrogen networks
 Vapor-induced Self-organization



2. Solvatochromic Luminescence Based on the Excimer Formation of Bipyridine Platinum(II) Complexes with Linear Alkyl Chains

Kato et al., Chem. Lett., 2008, 37, 16.

Introduction of linear alkyl chains to bipyridine platinum(II) complexes

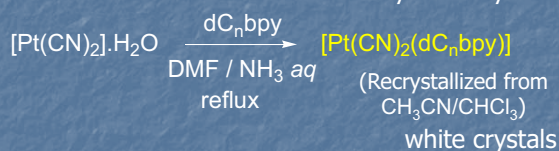
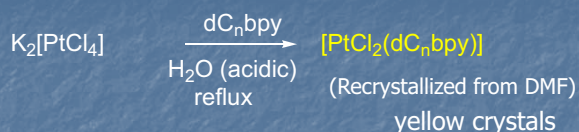


X = Cl⁻, CN⁻, n = 5, 7, 9, 11

- ◆ improve in solubility and amphiphilic properties
- ◆ enhance self-assembling ability and flexibility

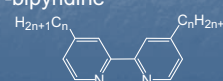
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Synthesis of the Platinum Complexes



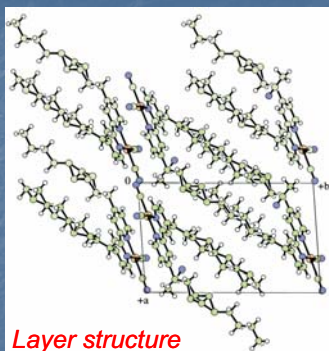
dC_nbpy = 4,4'-dialkyl-2,2'-bipyridine

n = 5, 7, 9, 11

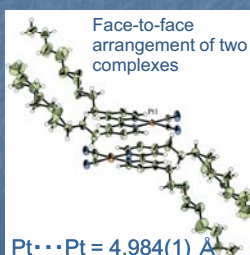


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Crystal Structure of [Pt(CN)₂(dC₉bpy)] · CH₃CN



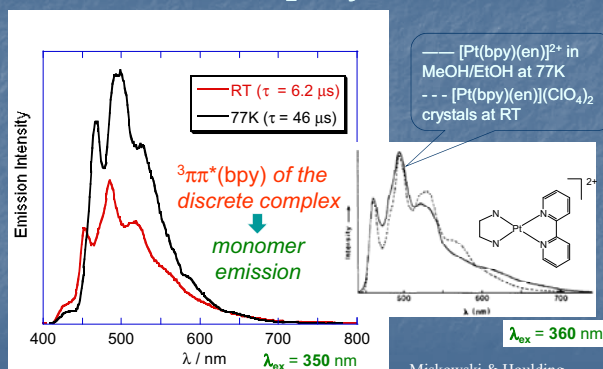
Layer structure



Pt...Pt = 4.984(1) Å

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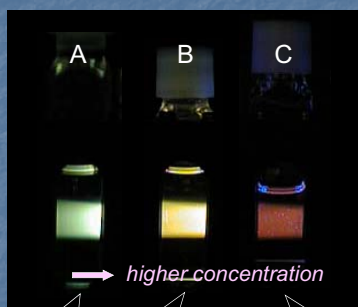
Emission Spectra of the White Crystals of [Pt(CN)₂(dC₉bpy)]



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Miskowski & Houlding, Inorg. Chem. 1989, 28, 1529.

Concentration-dependent Luminescence of [Pt(CN)₂(dC₉bpy)] in CHCl₃



higher concentration

2.2×10^{-4} M
($\lambda_{\text{ex}} = 340$ nm)

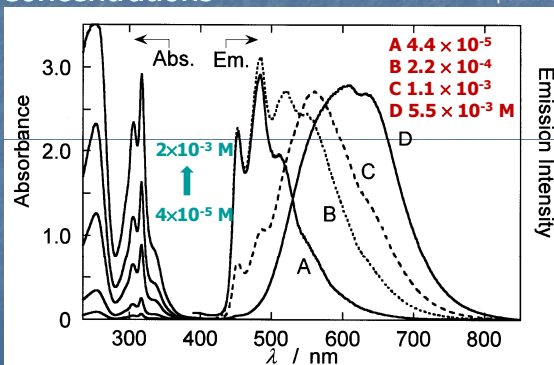
1.1×10^{-3} M
($\lambda_{\text{ex}} = 394$ nm)

5.5×10^{-3} M
($\lambda_{\text{ex}} = 404$ nm)

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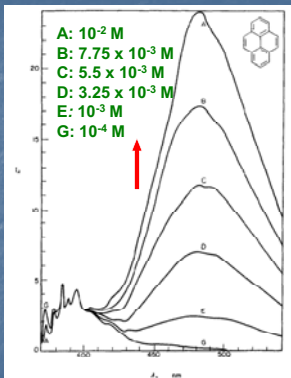
Absorption and Emission Spectra of [Pt(CN)₂(dC₉bpy)] in CHCl₃ at Different Concentrations

at Room Temperature

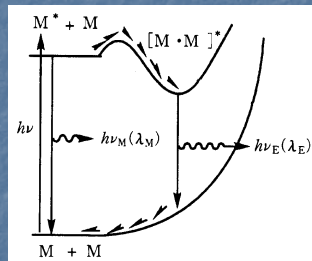


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Excimer Fluorescence Spectra of Pyrene

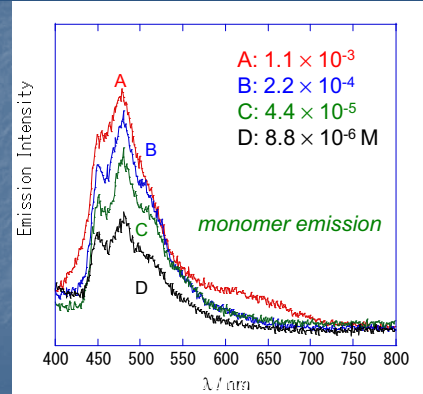


Schematic energy diagram for excimer formation



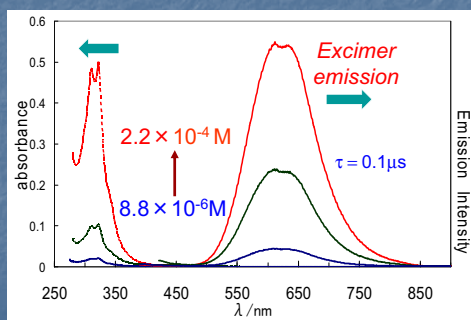
J. B. Birks & L. G. Christophorou, *Spectrochim. Acta*, 1963, 19, 401-410.
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Emission Spectra of [Pt(CN)₂(dC₉bpy)] in Methanol at RT



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Emission and Absorption Spectra of [Pt(CN)₂(dC₉bpy)] in Toluene at RT

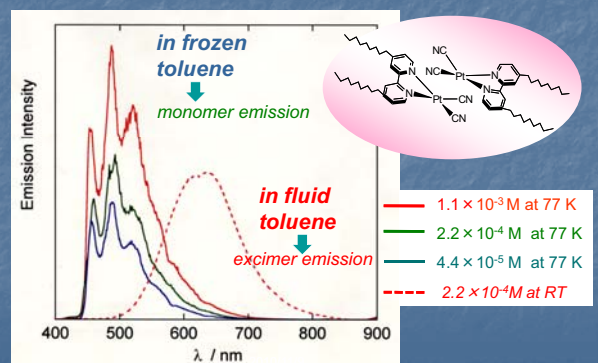


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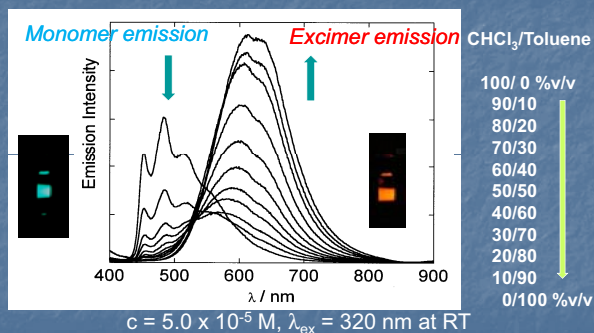
2010/11/9 λ_{ex} = 340nm

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Emission Spectra of [Pt(CN)₂(dC₉bpy)] in Toluene at 77 K



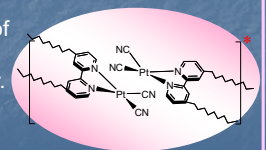
Emission Spectral Changes of [Pt(CN)₂(dC₉bpy)] in the Different Ratios of CHCl₃/Toluene



The complex exhibits solvent-sensitive luminescence depending on the formation of the excimer.

Summary 2

1. A series of bipyridine platinum(II) complexes bearing linear alkyl chains, [PtX₂(dC_nbpy)] (X = Cl⁻, CN⁻, n = 5-11) have been synthesized and characterized.
2. The layer structures were found for the complexes with C7-C11 chains in the crystal states.
3. These complexes are soluble in various organic solvents and the dicyanido complexes exhibit characteristic luminescence depending on solvents and the concentrations.
4. The solvatochromic behavior of the luminescence is attributed to the formation of the excimer.



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