the construction of photofunctional metal complexes

Today’s Topics

1. Outstanding Vaporochromism 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

Temperature-dependent Luminescence Spectra and Structural Parameters for the Red Form of [Pt(CN)_2(bpy)]

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

\[
\text{[Pt(CN)\(_2\)(bpy)]}
\]

Red Form

Pt···Pt = 3.34(1) Å at RT

\( \rightarrow \) Pt···Pt interactions

\[
\begin{align*}
\text{Em.} &\quad 15 \text{ K} \\
\text{Emission Intensity} &\quad \text{Emission Wavelength (nm)}
\end{align*}
\]


Pt···Pt interactions
Vapochromism of \([\text{Pt(CN)}_2(\text{bpy})]\)

Red Form

Yellow Form

Pt–Pt = 3.338(1) Å

Pt–Pt = 168.59(4)°


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

\[\text{Pt(CN)}_2(\text{H}_2\text{dcbpy})\]

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


Synthesis of \([\text{Pt(CN)}_2(\text{H}_2\text{dcbpy})]\)

\[
\begin{align*}
\text{Pt(CN)}_2.x\text{H}_2\text{O} + \text{HOOC-} & \quad \text{H}_2\text{O/\text{NH}_3 \text{HCl}} \\
\text{DMF} & \quad \text{reflux 4 days} \\
\text{Recrystalization:} & \quad \text{DMF} \\
\text{pH = 5} & \quad 4 \\
\text{H}_2\text{O/\text{NH}_3 \text{HCl} or AcOH} & \quad 3 < 2
\end{align*}
\]


Comparison of the Packing Structures for the Red Forms of \([\text{Pt(CN)}_2(\text{H}_2\text{dcbpy})]\)·4\text{H}_2\text{O} and \([\text{Pt(CN)}_2(\text{bpy})]\)

The existence of large cavities is characteristic of the dcbpy complex.

Packing Structure of \([\text{Pt(CN)}_2(4,4'-\text{H}_2\text{dcbpy})]\)·4\text{H}_2\text{O} (Red Form)

Pt–Pt = 3.36 Å
Luminescence Spectral Changes for the Purple Form of [Pt(CN)2(4,4'-dcbpy)] upon Exposure to DMF Vapor

$\lambda_{\text{max}} = 617 \text{ nm}, \tau = 594 \text{ ns}$

$\lambda_{\text{max}} = 662 \text{ nm}, \tau = 133 \text{ ns}$

$\lambda_{\text{max}} = 712 \text{ nm}, \tau = 80 \text{ ns}$

$\lambda_{\text{max}} = 787 \text{ nm}, \tau = 25 \text{ ns}$

Vapochromic Transformation for [Pt(CN)2(H2dcbpy)]

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

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

Changes in Powder X-ray Diffraction (PXRD) Pattern of [Pt(CN)2(4,4'-dcbpy)] upon Exposure to DMF Vapor

Two-step Transformations

$\lambda_{\text{max}} = 767 \text{ nm}, \tau = 25 \text{ ns}$

$\lambda_{\text{ex}} = 400 \text{ nm}$

Powder X-ray diffraction patterns of [Pt(CN)2(H2dcbpy)] 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.

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

The Plot of the Emission Energy for [Pt(CN)2(H2dcbpy)] in the Solid State Against the Dipole Moment of Vapor Molecules

Vapor molecules ⇒ higher polarity
Luminescence ⇒ higher energy
Pt···Pt interactions ⇒ weaker

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

- Expansion of 2D network to 3D structure by using metal cations

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

- \( \text{MeOH Suspension of } [\text{Pt(CN)}_2(\text{H-dcbpy})] \)
- Recrystallization (\( \text{H}_2\text{O}/\text{MeOH}/\text{Et}_2\text{O} \))
- \( \text{Na}_2[\text{Pt(CN)}_2(\text{dcbpy})] \) pale yellow crystals
- \( \text{Na}_2[\text{Pt(CN)}_2(\text{dcbpy})] \) \( \cdot \) \( 5\text{H}_2\text{O} \)

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

- Pt-Pt = 4.927(1), 5.927(1) Å

Changes in the powder X-ray diffraction pattern of 1A

- \( \text{Vapor-induced self-organization} \)
- \( \text{Hydrophilic vapor} \)
- \( \phi = 0.27 \)
- \( \text{Amorphous solid of } \text{Na}_2[\text{Pt(CN)}_2(\text{dcbpy})] \cdot \text{2H}_2\text{O} \) (1A)

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

- Luminescence spectral changes
- \( \lambda_{\text{ex}} = 400 \text{ nm} \)

Summary 1

- Vapochromic platinum complexes
- Multichromic luminescence controlled by hydrogen networks
2. Solvatochromic Luminescence Based on the Excimer Formation of Bipyridine Platinum(II) Complexes with Linear Alkyl Chains

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


\[ \text{X} = \text{Cl}^-, \text{CN}^-, n = 5, 7, 9, 11 \]

\[ \text{[PtX}_2(\text{dC}_n\text{bpy})] \]

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

**Synthesis of the Platinum Complexes**

\[ \text{K}_2[\text{PtCl}_4] \]
\[ \xrightarrow{\text{H}_2\text{O (acidic)}} \]
\[ \text{[PtCl}_2(\text{dC}_n\text{bpy})] \text{ yellow crystals} \]

\[ \text{[Pt(CN)}_2\text{]}_2\text{H}_2\text{O} \]
\[ \xrightarrow{\text{dC}_n\text{bpy}, \text{DMF} / \text{NH}_3 \text{aq reflux}} \]
\[ \text{[Pt(CN)}_2(\text{dC}_n\text{bpy})] \text{ white crystals} \]

\[ \text{dC}_n\text{bpy} = 4,4’-\text{dialkyl-2,2’-bipyridine} \]

\[ n = 5, 7, 9, 11 \]

Crystal Structure of \[ \text{[Pt(CN)}_2(\text{dC}_9\text{bpy})] \cdot \text{CH}_3\text{CN} \]

**Emission Spectra of the White Crystals of [Pt(CN)]_2(dC_9bpy)**

\[ \lambda_{\text{ex}} = 350 \text{ nm} \]

\[ \lambda_{\text{em}} = 360 \text{ nm} \]

\[ \text{[Pt(bpy)(en)}_2\text{ClO}_4] \text{ crystals at RT} \]


**Absorption and Emission Spectra of [Pt(CN)]_2(dC_9bpy) in CHCl_3 at Different Concentrations**

\[ \lambda_{\text{ex}} = 340 \text{ nm} \]

\[ \lambda_{\text{em}} = 404 \text{ nm} \]

\[ \lambda_{\text{em}} = 394 \text{ nm} \]

**Concentration-dependent Luminescence of [Pt(CN)]_2(dC_9bpy) in CHCl_3**

Absorption and Emission Spectra of [Pt(CN)]_2(dC_9bpy) at Room Temperature

\[ \text{Abs.} \]

\[ \text{Em.} \]

\[ \lambda_{\text{ex}} = 340 \text{ nm} \]

\[ \lambda_{\text{em}} = 404 \text{ nm} \]

\[ \lambda_{\text{em}} = 394 \text{ nm} \]
Excimer Fluorescence Spectra of Pyrene

A: 10^{-2} M
B: 7.75 \times 10^{-3} M
C: 5.5 \times 10^{-3} M
D: 3.25 \times 10^{-3} M
E: 10^{-3} M
G: 10^{-4} M

Schematic energy diagram for excimer formation


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Emission Spectra of [Pt(CN)_{2}(dC_{9}bpy)] in Methanol at RT

A: 1.1 \times 10^{-5}
B: 2.2 \times 10^{-5}
C: 4.4 \times 10^{-6}
D: 8.8 \times 10^{-6}

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Emission and Absorption Spectra of [Pt(CN)_{2}(dC_{9}bpy)] in Toluene at RT

\( \lambda_{ex} = 340 \text{nm} \)

\( \lambda = 2.2 \times 10^{-1} \text{M} \)
\( \tau = 0.1 \mu \text{s} \)

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Emission Spectral Changes of [Pt(CN)_{2}(dC_{9}bpy)] in the Different Ratios of CHCl_{3}/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, [PtX_{2}(dC_{n}bpy)] (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.