Nafion-Induced Metal-Metal Interactions in a Platinum(II) Terpyridyl Acetylide Complex: a Luminescent Sensor for Detection of Volatile Organic Compounds

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The platinum(II) terpyridyl acetylide complex [Pt(terpy)(C≡CR)]ClO$_4$ (terpy＝2,2'：6'2''-terpyridine, R＝CH$_2$CH$_2$CH$_3$) (**1**) was incorporated into Nafion membranes. At high loading the dry membranes exhibit intense photoluminescence with λ_{max} at 707 nm from the ^{3}MMLCT state, which was not observed in fluid solution. Upon exposure to the vapor of polar volatile organic compounds (VOC), this photoluminescence was significantly red-shifed. This process was fully reversible when the VOC-incorporated membrane was dried in air. The dramatic and reversible changes in the emission spectra made the Nafion-supported complex as an interesting sensor candidate for polar VOC.

Introduction

The design of new solid-state sensor materials that can selectively adsorb volatile organic compounds (VOC) and produce measurable color and/or luminescence changes is of potential significance in the sense of environmental and public safety control.[1-5] The use of metal complexes as optical sensors for VOC detection has been reported, and most of them are based on the susceptibility of metal-to-ligand charge transfer (MLCT) and/or metal-metal-to-ligand charge transfer (MMLCT) absorption and emission energies to the subtle changes in the micro-environment around the metal complex molecules.[6-10] In 1995, Mann and co-workers[6,7] reported that the solid of the double salts [PtL$_4$][M(CN)$_4$] (L＝arylisonitrile; M＝Pt, Pd) has the structures composed of stacked square planar complexes, and is spectroscopically sensitive to the presence of VOC vapors (exhibiting shifts in absorption and emission maxima). In 1997, Balch and co-workers[8] observed that when a colorless trimeric Au(I) complex is irradiated with long-wavelength UV light, subsequent contact with solvent results in an intense yellow luminescence. Eisenberg and co-workers[1] reported that interaction of a dimeric Au(I) dithiocarbamate complex [Au(S$_2$CN-(C$_5$H$_{11}$)$_2$)]$_2$ in its cast film with VOC vapors results in both a dramatic color change and an enhanced luminescence. In 2000, Cariati and Ford and their coworkers[9] reported that exposure of the polymeric solid [CuI(4-

methylpyridine)]$_\infty$ to liquid or vapor toluene leads to disappearance of its room-temperature blue emission and the appearance of a yellow emission characteristic of the [CuI(4-methylpyridine)]$_4$ tetramer, and the process is reversed when the latter was exposed to liquid or vapor of *n*-pentane. Recently, Che and co-workers[10] reported that cyclometalated complexes [Pt(L)py]$^+$ and [Pt(L)]$^+$ (HL＝4,6-diphenyl-2,2'-bipyridine, py＝pyridine) immobilized in Nafion and anchored in silica respectively show changes in photoluminescence excited states from ^{3}MLCT to ^{3}MMLCT or vice versa upon exposure to VOC.

Platinum(II) polypyridine complexes show absorption and emission properties susceptible to the changes in micro-environment.[11-13] Perturbation of metal-metal and/or ligand-ligand interactions by VOC may cause changes in photoluminescence energy, and this can be used as the operating principle for the design of luminescent sensor devices. In the present work we use a platinum(II) terpyridyl acetylide complex (**1**, Figure 1) as a luminescent probe and incorporate it into Nafion film. Nafion represents a unique family of polymers, which consists of a perfluorinated backbone, and short pendant chains terminated by sulfonic groups.[14-16] When swollen in polar solvents, particularly in water or methanol, the sulfonic head groups are clustered together in solvent-containing pockets within the perfluorocarbon matrix. The solvent-swollen Nafion can incorporate high concentration of organic dyes and

Nafion membrane

Chin. J. Chem., 2004, Vol. 22, No. 10   **1205**

metal complexes, thus raising the possibility of obtaining high local concentration of organic molecules and inorganic cations. These optically transparent membrane systems are readily amenable to spectroscopic investigations, and are suitable for manufacture of luminescent sensor devices. At high loading, **1** in Nafion exhibits photoluminescence from [3]MMLCT excited state. Exposure of the dry **1**-incoporated Nafion film to a polar VOC vapor results in significant shift in the emission maximum.
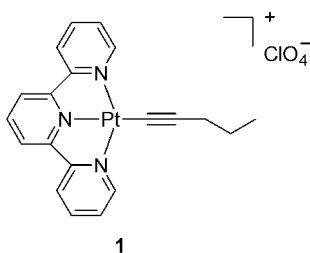
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Figure 1 Structure of platinum(II) terpyridyl acetylide complex.

Results and discussion

Incorporation and absorption properties of 1 in nafion membrane

The Nafion membranes used in the present work were their sodium form (Nafion-Na$^+$). Due to hydrophobic and electrostatic interactions, **1** was easily adsorbed into Nafion by immersing the polymer in a well-stirred solution of **1** in methanol. The amount of uptake of **1** by the membranes was determined by the difference in the absorbance of the solution before and after the addition of the Nafion membranes. The solubility of **1** in Nafion-Na$^+$ can be rather high (>13.8 mg per gram of Nafion). Figure 2 shows the absorption spectra of **1** in methanol-swollen Nafion as a function of the loading. Control experiments show that the absorption of Nafion membrane above 280 nm is negligibly weak. At low loading **1** exhibits vibronic-structured absorption bands at $\lambda < 350$ nm and a tail in the region of 350—500 nm in Curve 1.
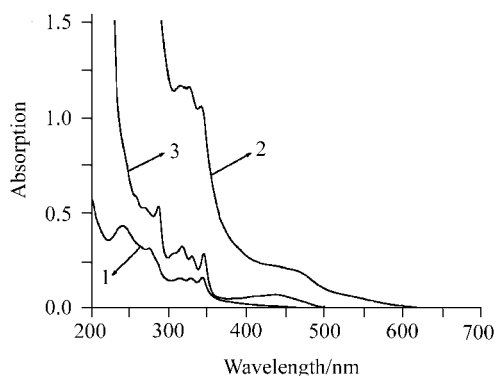
Figure 2 Absorption spectra of complex **1** in CH$_2$Cl$_2$ and in methanol-swollen Nafion (1) 0.69 mg/g of Nafion; (2) 13.8 mg/g of Nafion; (3) 5.7×10^{-3} mol/L in CH$_2$Cl$_2$.

With reference to previous spectroscopic work on platinum(II) terpyridyl complexes,[17-19] the absorption bands at $\lambda < 350$ nm are assigned to the intraligand(IL) transition of terpyridyl and acetylide ligands, while the low energy absorption in the region of 350—500 nm is assigned to the dπ(Pt)$\rightarrow\pi^*$(terpy) MLCT transition. At high loading, in addition to IL and MLCT transitions **1** also exhibits a less intense band in the region of 520—600 nm (Curve 2 in Figure 2). Since this band occurs only for high loading sample, we tentatively assign it to the [1]MMLCT transition. In this case **1** forms aggregates in Nafion, and the metal-metal interactions give rise to the MMLCT transition. Similar MMLCT transitions have previously been reported in [Pt$_2$L$_2$(μ-dppm)]-[ClO$_4$]$_2$ (HL = 6-phenyl-2,2'-bipyridine, dppm = Ph$_2$P-CH$_2$PPh$_2$),[20] [Pt$_2$(terpy)$_2$L]$^{3+}$ (HL = guanidine),[21] and [Pt$_2$(terpy)$_2$(μ-pz)]$^{3+}$ (pz = pyrazolate).[22] Figure 3 shows the simplified schematic molecular-orbital diagram of platinum(II) terpyridyl complexes.
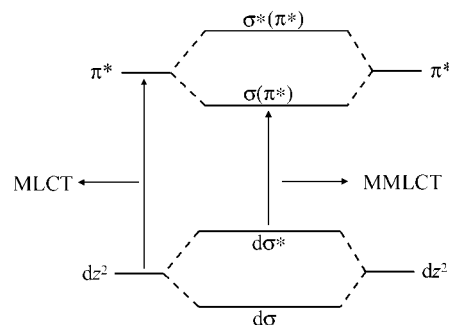
Figure 3 Simplified schematic molecular-orbital diagram of platinum(II) terpyridyl complexes.

The absorption spectra of **1** in organic solvents were also examined and Curve 3 in Figure 2 gives an example. It was found that as the polarity of the solvent increases, the MLCT absorption band shifts to the short wavelength. For example, the λ_{max} of the MLCT band shifts from *ca*. 438 nm in dichloromethane to 412 nm in methanol. As shown in Curve 2, the λ_{max} of the MLCT transition of **1** incorporated in methanol-swollen Nafion is at 466 nm, much longer than that in dichloromethane. This suggests that the environment around the molecules of **1** in methanol-swollen Nafion is less polar than that in dichloromethane. Considering the hydrophobicity and the charge of **1**, it is likely that the molecules of **1** are located in the fluorocarbon/methanol interface of the membrane. This allows electrostatic interaction of the platinum(II) cations of **1** with the sulfonate headgroup in Nafion as well as interaction of the terpyridyl ligands of **1** with the hydrophobic domain of Nafion. In contrast to the Nafion sample, even for the saturated solution in organic solvents the absorption properties of **1** were found to follow Beer's law and no MMLCT absorption band was observed. Evidently, only in Nafion the concentration of **1** can be high enough to allow molecules of **1** to form aggregates.

Emission of 1 and its response to VOC

In degassed dichloromethane solution at room temperature **1** displays intense photoluminescence in the region of 500—700 nm with λ_{max} at 570 nm (Figure 4, Curve 2). The photoluminescence quantum yield, determined by the optical dilute method[23] using a degassed acetonitrile solution of [Ru(bpy)$_3$](PF$_6$)$_2$ as the reference (Φ_{em}=0.062),[24] was *ca.* 0.30. With reference to previous spectroscopic study on platinum(II) terpyridyl acetylide complexes,[17,18] this photoluminescence is assigned as arising from the $d\pi(Pt)\rightarrow\pi^*$(terpy) ^{3}MLCT state. Increasing in the concentration of **1** in dichloromethane resulted in no change in the photoluminescence energies. In contrast, the photoluminescence of Nafion-incorporated **1** depends on the loading. The Nafion membranes incorporating **1** were dried in air, and then their photoluminescence was detected. The emission spectra are shown in Figure 4. At low loading, the Nafion membrane exhibits an intense emission at λ_{max} of 553 nm (Curve 1), which is comparable to the ^{3}MLCT emission of **1** in dichloromethane at room temperature. However, as the loading is increased, a new emission with λ_{max} at 707 nm is detected, and its intensity increases at the expense of the ^{3}MLCT band. At the loading greater than 13.8 mg/g Nafion, only the 707 nm emission band is observed (Curve 3). With reference to the previous work on platinum (II) terpyridyl acetylide complexes,[17,18] this emission is assigned to originating from the ^{3}MMLCT state.
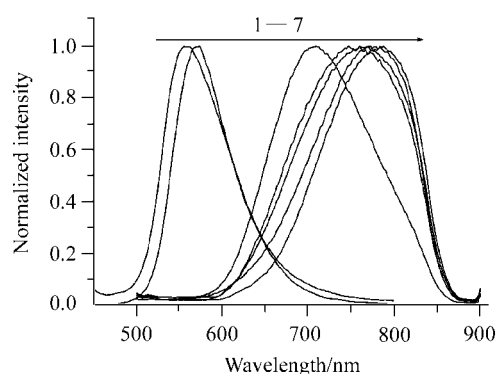

Figure 4 Normalized emission spectra of **1** in CH$_2$Cl$_2$ and in Nafion upon exposure to the vapor of polar VOC (1) in dry Nafion at loading of 0.69 mg of **1**/g Nafion, λ_{ex}=424 nm; (2) in CH$_2$Cl$_2$ solution, λ_{ex}=438 nm; (3) in dry Nafion at loading of 13.38 mg of **1**/g Nafion, λ_{ex}=466 nm; (4)—(7) Sample 3 exposure to CH$_3$CN, C$_2$H$_5$OH, CH$_3$COCH$_3$, CH$_3$OH respectively, λ_{ex} =466 nm).

We examined the response of the emission of the Nafion-incorporated **1** to the vapors of VOC with the high loading sample, for which only the ^{3}MMLCT emission band appears. When the dry membrane is exposed to the vapors of polar VOC at their equilibrium vapor pressure in a closed cell for 20 min, the ^{3}MMLCT emission band is significantly red-shifted as shown in Figure 4 (Curves 4—7). For example, upon exposure of the dry membrane to methanol vapor, the emission band

is red-shifted in *ca.* 81 nm. This shift in emission is fully reversible: after the VOC vapor-incorporated Nafion membrane was dried in air at room temperature, the λ_{max} of the emission shifted to 707 nm again. Such emission shift implies that incorporation of polar VOC into the Nafion matrix significantly increases the intermolecular metal-metal and/or ligand-ligand interactions of **1**. This would raise the HOMO of the metal center (dσ^*) and/or would low the LUMO of the ligand [$\sigma(\pi^*)$] as illustrated in Figure 3, hence resulting in the reduction of the energy of the ^{3}MMLCT state. We found that upon exposure of the dry membrane to non-polar VOC such as dichloromethane and cyclohexane the emission showed no notable shift in energy. Probably, Nafion can not incorporate such non-polar VOC, thus the interactions of the intermolecular metal-metal and/or ligand-ligand of the metal complex are not significantly disturbed.

Conclusion

Upon incorporation in Nafion membranes the platinum(II) terpyridyl acetylide complex **1**, shows interesting absorption and luminescence properties. At high loading, **1** exhibits ^{1}MMLCT absorption in addition to ^{1}IL and ^{1}MLCT transitions, and photoluminescence from ^{3}MMLCT state. All these properties are not observed in organic solution. When the dry **1**-incorporated Nafion membrane is exposed to the vapor of polar VOC, the emission is dramatically red-shifted. Thus, this Nafion-supported complex may be used as sensor for polar VOC. An advantage in the application of such membranes in this field is that the membrane is optically transparent, thus readily amenable to spectroscopic measurements.

Experimental

Materials

Nafion membrane 117 with an equivalent weight of 1100 and thickness of 0.0175 cm was a product of Du Pont. Prior to use, the membranes were cleaned by boiling in concentrated nitric acid for 4 h and then thoroughly washed with distilled water and finally immersed in water for 24 h. The membranes in sodium form (Nafion-Na$^+$) were obtained by immersing the pretreated Nafion-H$^+$ membranes in 1 mol/L NaOH aqueous solution. Excess base was then removed by stirring the samples in water. Pentyne was a product of Aldrich Chemical Co. All the solvents were of analytical grade.

Pt[(terpy)(C≡C-C$_3$H$_7$)]ClO$_4$ (1)

[Pt(terpy)Cl]Cl was prepared by the literature method.[25] The mixture of 100 mg (0.20 mmol) of [Pt(terpy)Cl]Cl , 10 mg of CuI, 0.2 mL of (2.0 mmol) pentyne, 3 mL of DMF, and 4 mL of trimethylamine in a flask was sonicated under nitrogen for 8 h. To the mixture was added excess aqueous solution of NaClO$_4$. The

brown product was isolated, washed with water and ether. Subsequent recrystallization by diffusion of diethyl ether vapor into an acetonitrile solution of the product gave **1**. Yield 78%; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 1.02 (t, J=7.2 Hz, 3H), 1.52—1.61 (m, 4H), 7.86—7.89 (m, 2H), 8.43—8.65 (m, 7H), 9.00 (d, J= 5.7 Hz, 2H). The proton signal of $-CH_2-$ attached to the $C\equiv C$ was shielded by the proton in DMSO; FAB-MS (m/z): 495 (M[+]); Anal. calcd for $C_{20}H_{18}ClN_3O_4Pt$: C 40.38, H 3.05, N 7.06; found C 39.90, H 2.94, N 6.83.

Incorporation of 1 into Nafion membrane

The weighed Nafion membrane samples were immersed in a solution of **1** in methanol, and the solution was kept continuously stirred. At certain intervals the samples were taken out from the solution, thus samples adsorbing various amount of **1** were prepared. The amount of uptake of **1** by the membrane was determined by the difference in the absorbance of the solution before and after the addition of the Nafion membrane. The **1**-incorporated Nafion samples were dried in air.

Physical measurements and instrumentation

UV-vis spectra were obtained on a Shimadzu UV-1601PC spectrophotometer. Steady-state emission spectra were recorded on a Perkin Elmer LS50B spectrofluorometer. Elemental analysis was performed on a Carlo Erba 1106 elemental analyzer. ^{1}H NMR spectra were recorded on a Bruker-400 FT-NMR spectrometer with chemical shift relative to tetramethylsilane. FAB-MS spectra were run on a KYKY-ZHP mass spectrometer. The solutions of **1** in dichloromethane were purged with argon for 15 min for emission spectrum measurements. The quantum yields of the emission were obtained by the optical dilute method using a degassed acetonitrile solution of $[Ru(bpy)_3](PF_6)_2$ as a reference (Φ_{em}=0.062).[24] To study the response of the emission spectrum of **1**-incorporated Nafion membrane to VOC, the dry sample was first exposed to the vapor of VOC in a closed cell for 20 min, and then the emission spectrum was recorded.

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