Effect of Solvent on the Spectroscopic, Electrochemical and Spectroelectrochemical Properties of Near–Infrared Oxovanadium(IV) $\alpha,\alpha'$–Octapentoxypythalocyanine

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A near-infrared oxovanadium(IV)-$\alpha,\alpha'$-octapentoxypythalocyanine (oxo-V(IV)-Pc) has been synthesized and characterized. Solvent-dependent optically spectroscopic and electrochemical investigations including UV-vis absorption and magnetic circular dichroism (MCD) spectroscopy, cyclic voltammetry (CV), DPV and multi-scan rate CV electrochemistry measurements were carried out to give in-depth understanding of the electronic structure of this oxo-V(IV)-Pc. Both $\alpha,\alpha'$-substituents and solvent polarities have large influence on the electronic structure of this NIR absorbed oxovanadium(IV)-phthalocyanine.

Keywords: Phthalocyanine, oxovanadium complexes, near infrared absorption, solvent polarity, magnetic circular dichroism, cyclic voltammetry, spectroelectrochemistry.

Влияние растворителя на спектральные, электрохимические и спектроэлектрохимические свойства $\alpha,\alpha'$–октапентоксифталоцианината оксованадия(IV), поглощающего в ближней ИК области

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В работе получен и охарактеризован оксованадий(IV)-$\alpha,\alpha'$-октапентоксифталоцианин, поглощающий в ближней ИК области. С помощью спектральных и электрохимических методов, включая спектроскопию электронного поглощения и магнитного кругового дихроизма, циклическую вольтамперометрию, дифференциальную пульссирующую вольтамперометрию, было показано, что природа $\alpha,\alpha'$-заместителей и полярность растворителя оказывают значительное влияние на электронную структуру полученного комплекса.

Ключевые слова: Фталоцианин, комплексы оксованадия, поглощение в ближней ИК области, полярность растворителя, магнитный круговой дихроизм, циклическая вольтамперометрия, спектроэлектрохимия.
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Introduction

Currently, there are increased research interests in phthalocyanines (Pcs) including fundamental theories to industrial applications.[1] The large π-system of phthalocyanines can lead to strong absorption and emission in the red/near-infrared (NIR) region, and exhibit relatively high molar extinction of the lowest energy π→π* band (usually referred to as the Q band), which is considerably more intense than the corresponding bands in the spectra of porphyrins and tetraazaporphyrins.[2] Although the red-shift of the Q bands of phthalocyanine can be achieved to longer wavelength region through fused-ring-expansion with benzene rings to form naphthalocyanine (Nc)[3] and then anthracocyanine (Ac),[4] the significant destabilization of HOMO level makes these compounds unstable. Additionally, the absence of peripheral substituents are also issues with stability. In contrast, Pcs with substituents at both peripheral (β)- and non-peripheral (α-) positions generally exhibit enhanced solubility, especially the α-substituted Pcs revealed more satisfied results due to its deformed molecular structures.[5] On the other hand, introduction of electron donating substituents at α-positions results in a greater destabilization of the highest occupied molecular orbital (HOMO) state relative to the lowest unoccupied molecular orbital (LUMO) state leading to the red-shift of the Q band absorption in metallophthalocyanines (MPcs) and hence lower first oxidation potentials, since there are large MO coefficients at these positions in the HOMO of the π-system.[6] NIR phthalocyanines have excellent light, weather and thermal resistances, and these complexes find applications such as optical active materials, the high-valence metallo-phthalocyanines have various potential applications such as optical active materials, on nonlinear optical materials and catalysis, [8] and thus have found applications in the selective evaluation of compounds arising from fused-ring expansion. Oxovanadium(IV)phthalocyanine.

Materials and Instruments

Virgin grade α-dichlorobenzene, CH₂Cl₂ and DMF for spectroscopic and electrochemical measurements was purchased from the Aladdin reagent company of Shanghai. Other chemicals and solvents were of analytical pure grade and were obtained from the Shanghai Guoyao Co. which were dried or distilled prior to use.

Experimental

Chemicals

Analytical pure N,N-dimethylmethanamide (DMF) for electrochemical measurements was purchased from the Aladdin Reagent Company of Shanghai, and freshly distilled before use. All other chemicals and solvents were analytical pure grade and were purchased from the Shanghai Guoyao Company. All solvents were dried and distilled prior to use.

Results and Discussion

Solvent Dependent Spectroscopy

The spectroscopic properties of oxo-V(IV)Pc in both low-polar solvent CH₂Cl₂ and polar solvent DMF are shown.
in Figure 2. The UV-vis spectra of 1 is characteristic sharp of metallo-phthalocyanines, but the Q bands lie at a significantly longer wavelength than those of normal oxo-V(IV)Pcs without substituent groups (λ = 695 nm in chlorobenzene).

In the low-polar solvent CH₂Cl₂, (Figure 2, left, bottom), the Q-band absorption of oxo-V(IV)Pc exhibits main absorption bands at 788 and 703 nm. The Soret band of 1 appears at 338 nm, and an extra band at 479 nm can be assigned as intramolecular charge-transfer band. In the case of oxo-V(IV)Pc in DMF (Figure 2, right, bottom), the Q-band absorption exhibits a mirror red-shift to 792 nm. Similarly, the Soret band appears at 349 nm and the charge transfer band appears at 473 nm. On the other hand, the magnetic cicular dichroism (MCD) spectra of oxo-V(IV)Pc is also typical of metallo-phthalocyanines,[13] showing a clear Faraday A-term type of curve associated with the Q₂ absorption peak at λ = 788 nm in CH₂Cl₂ (Figure 2). In the Soret band region, three bands were observed at λ = 336, 358 and 498 nm, and the additional band at around 490 nm can be plausibly assigned to a transition involving the ether oxygen lone pairs n-π* transition.[14] Similar shape of the MCD signals of oxo-V(IV)Pc in DMF were observed, but slightly shifted to the longer wavelength region. The assigned Faraday A-term type of curve associated with the Q₂ absorption peak at λ = 792 nm in DMF was detected (Figure 2), and Soret bands were appeared at λ = 323, 369 and 410 nm, respectively. Solvent dependent UV-vis measurements (Figure 3) were also carried in various organic solvents containing different solvent polarities, including CH₂Cl₂, toluene, ethylacetate, DMF and benzonitrile in order to further insight understand the solvent dependent spectroscopic properties of this oxo-V(IV)Pc 1. It is known that the red-shift of the Q-band absorptions is a function of the solvent's refractive index,[15] and Table 1 also shows the red-shift of the Q-band absorptions based on the increase of the solvent polarities.

**Solvent Dependent Electrochemistry**

Electrochemical measurements were performed to give further in-depth understand of the electronic properties of this α,α'-substituted phthalocyanines, since it is well established that the HOMO and LUMO energies of phthalocyanine derivatives correlate well with their first oxidation and reduction potentials. Electrochemical measurements were carried out in low-polar solvent o-dichlorobenzene and polar solvent DMF containing 0.1 M TBAP to gain further insight into the electronic properties, and the redox potentials E½ values derived cyclic and differential pulse voltammetry (CV and DPV) measurements. The voltammograms for oxo-V(IV)Pc in low-polar o-dichlorobenzene and polar solvent DMF was detected at various scan-rates from 10-500 mV in both low-polar CH₂Cl₂ and polar DMF (Figure 5), provide an insight into the reversibility of the system on an experimental time-scale. The good linear correlations observed for plots of peak current versus v½ for oxo-V(IV)Pc (Figure 6) confirm that all of the oxidation and reduction processes are diffusion controlled.

**Solvent Dependent Spectroelectrochemistry**

In order to confirm further the effect of the solvent polarities on the spectroelectrochemistry properties, thin-layer UV-visible spectra during the first and second reduction and/or oxidation of oxo-V(IV)Pc 1 were carried out in both low polar solvent o-dichlorobenzene and polar solvent DMF. The comparison of spectral changes at different potential values for reversible processes were shown in Figure 7. During the first reduction process, the electroreduced oxo-V(IV)Pc 1 reveals the significant decrease of the main absorption band (Q-band), but the further increase of the additional bands in the visible region in the DMF solution. In addition to measure the spectral changes of further electroreduced oxo-V(IV)Pc 1, the changes were only observed in the DMF measurements, and this clearly show that the solvent effects have large influence on the electroreduced spectral changes. The electrooxidized spectral changes were also measured in both o-dichlorobenzene and DMF, no significant difference was observed based on the different solvent measurements. Since the 2nd oxidation process of 1 in DMF is irreversible, thus the spectroelectrochemistry was not further proceded under this experiment conditions.

![Scheme 1. Molecular structure of oxo-V(IV)Pc.](image)
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Figure 1. $^1$H NMR spectra of 1 in CD$_2$Cl$_2$.

Figure 2. UV-vis absorption and MCD spectra of 1 in CH$_2$Cl$_2$ (up) and DMF (bottom).

Scheme 1. Energy difference of electrochemistry measurements in low-polar $o$-DCB and polar DMF of oxo-V(IV)Pc.

Figure 3. Q-band absorptions of UV-vis spectra of oxo-V(IV)Pc in various organic solvents.
Figure 4. Cyclic voltammetry (CV) and DPV measurements of oxo-V(IV)Pc in o-dichlorobenzene (left) and DMF (right).

Figure 5. Multi-scan rate of cyclic voltammetry (CV) measurements of oxo-V(IV)Pc in o-dichlorobenzene (left) and DMF (right).

Table 1. Values of Q-band UV-vis absorptions of oxo-V(IV)Pc in various solvents.

<table>
<thead>
<tr>
<th></th>
<th>CH\textsubscript{2}Cl\textsubscript{2}</th>
<th>Toluene</th>
<th>Ethylacetate</th>
<th>DMF</th>
<th>PhCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxo-V(IV)Pc</td>
<td>788 nm</td>
<td>787 nm</td>
<td>789 nm</td>
<td>792 nm</td>
<td>810 nm</td>
</tr>
</tbody>
</table>

Table 2. Electrochemistry measurements of various oxo-V(IV)Pc derivatives.

<table>
<thead>
<tr>
<th>Molecular Structure</th>
<th>Reduction</th>
<th>Oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Solvent</td>
<td>V\textsuperscript{III}Pc\textsuperscript{-2}/V\textsuperscript{III}Pc\textsuperscript{-3}</td>
</tr>
<tr>
<td>Oxo-V(IV)Pc</td>
<td>o-DCB</td>
<td>-1.85</td>
</tr>
<tr>
<td>OV[Pc(Bu)_4]</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>-</td>
</tr>
<tr>
<td>OV[PcF\textsubscript{16}]</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>-1.41</td>
</tr>
<tr>
<td>OV[Pc(SC\textsubscript{5}H\textsubscript{11})\textsubscript{8}]</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>-1.14</td>
</tr>
<tr>
<td>Oxo-V(IV)Pc</td>
<td>DMF</td>
<td>-1.88\textsuperscript{a}</td>
</tr>
<tr>
<td>OV[Pc(OCH\textsubscript{3}(t-Bu))\textsubscript{4}]</td>
<td>DMF</td>
<td>-2.07</td>
</tr>
<tr>
<td>OV[Pc(C\textsubscript{8}H\textsubscript{17})\textsubscript{4}]</td>
<td>DMF</td>
<td>-1.94</td>
</tr>
</tbody>
</table>

\textsuperscript{a}: irreversible processes
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Figure 6. The dependence of square root of the scan-rate ($v^{1/2}$) on the peak current ($i_p$) for the all oxidations and reductions of oxo-V(IV)Pc in o-dichlorobenzene (up) and DMF (bottom) containing 0.1 M TBAP.
**Conclusions**

A oxo-V(IV)Pc having main absorption band in NIR region has been synthesized and characterized. Solvent dependent spectroscopy, electrochemistry and spectro-electrochemistry studies were carried out including UV-vis, magnetic circular dichroism (MCD) spectra, CV, DPV, multi-scan rate CV and thin-layer spectroelectrochemistry to give detailed understanding the effect of the substituents and solvent polarities on the electronic structures of this near-infrared oxo-V(IV)Pc. Considered NIR phthalocyanines have a wide range of potential applications in various high-tech fields, such as NIR optical recording materials and in IR radiation filters. The studies about solvent dependent electronic structure provide useful information for future rational molecular design, characterization, and potential applications.

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**References**


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