Luminescent properties of tetracyanoethylene combined with triphenylphosphine oxide

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Abstract. The spectral properties of tetracyanoethylene triphenylphosphine oxide complex were investigated. The reaction mechanism was studied deeply, and the luminescent properties were explored through fluorescence spectroscopy, UV spectroscopy and Raman spectroscopy. The experimental results showed that under certain conditions, the triphenylphosphine oxide with tetracyanoethylene can form stable charge transfer complex.

Keywords: triphenylphosphine oxide; tetracyanoethylene; charge transfer complex

1. Introduction
The alias of tetracyanoethylene (TCNE) is four cyano supersede ethylene. Middleton found that TCNE can almost react with all the electron-rich substance in 1958 [1]. With the study of functional organic materials, it is found that as a kind of strong stable electron acceptor TCNE expands the range of applications [2]. In the field of nonlinear optics, magnetism, electricity, etc, TCNE has broad application prospects. The stable radical anion formed by the tetracyanoethylene is a strong π acid [3], TCNE can interact with multiple types of electron donors, then formed a stable charge transfer complex. Triphenylphosphine oxide is mainly used for the synthesis of organic compounds, phosphate salts and other phosphorus compounds. The rigidity of the triphenylphosphine oxide skeleton and the basicity of the oxygen atoms can induce crystallisation of other compounds which are difficult to crystallize [4].

The charge transfer [5], also known as charge exchange. It is a charge transfer process occurring when a positive ion collides with a neutral atom, and in recent years, through the discovery of molecular structure, it made the appropriate adjustments and realized the luminous efficiency of the intramolecular charge transfer compounds is enhance, it has been widely applied in the field of organic electroluminescence [6].

The charge transfer complex, also known as electron donors-receptor complex [7]. In recent decades, due to the fact that many scientific researchers pay more attention to the concepts and theories of the charge transfer complex, the study of the relevant charge transfer complex is more in-depth. In general, according to the differences of receptor molecules the charge transfer complex can be divided into three types, σ-acceptor reagents [8] charge transfer complex, n-acceptor reagents [9,11] charge transfer complex and π-acceptor reagents [12-15] transfer complex. Compared with the original material, the molecular solubility, viscosity, absorption, stability and molar volume [16] of charge transfer complex will change in a certain extent. The application of charge transfer complex in
medicinal chemistry, analytical chemistry, semiconductor, biochemistry and other fields are more widely [17]. In this paper, the structural characterization of the triphenylphosphine oxide-tetracyanoethylene charge transfer complex was tested by using fluorescence spectrum [18,19], Raman spectrum and ultraviolet spectrum means [20].

2. Experimental

2.1. Instruments and reagents

2.2.1 The UV spectra. The mixture of triphenylphosphine oxide solution, tetracyanoethylene solution (0.3mL) and anhydrous ethanol were added to a stopper colorimetric tube. The sample was detected using UV-visible spectrophotometer, and then detected the buffer solution as a bland control.

2.2.2 The fluorescence spectra. The mixture of triphenylphosphine oxide solution, tetracyanoethylene solution (0.3mL) and anhydrous ethanol were added to a stopper colorimetric tube. The sample was placed in constant temperature water bath for 40 minutes at 30°C, and cooled to room temperature. The sample was measured using fluorescence spectrophotometer.

2.2.3 The Raman scattering. The liquid was injected into the OTA-LK-1 liquid sample cell using a 2 mL glass vial. The spectral range was from 300 cm⁻¹ to 3200 cm⁻¹, using carbon tetrachloride as the solvent. Based on the silver glass plate, the excitation source is an air-cooled argon ion laser (Spectra-Physics Model 163-C4260). The sample was detected using Roman spectrophotometer at 532nm, and Integration time is 30 s for 3 times, then take a parallel testing for 3 times.

3. Results and Discussion

3.1. UV spectra

The sample solution was prepared and tested at room temperature. The UV-visible absorption spectra were shown in figure 1.

![Figure 1](image1.png)

**Figure 1.** UV absorbance spectra of TCNE(a), triphenylphosphine oxide(b) and TCNE-triphenylphosphine oxide(c).

The results (figure 1) showed that (c) had the double absorption peaks at 224nm and 246nm, they were the characteristic absorption peaks of (a) and (b). And the maximum absorption peak of (c) at
246nm (the absorption value was 2.1). The absorption value of (c) compared with (a) and (b) had a significant increase, caused by $\pi-\pi^*$ transition, and it belongs to B absorption band.

### 3.2. fluorescence emission spectra

The fluorescence intensity of (a) and (b) with the excitation wavelength of 315nm was monitored at room temperature. The fluorescence curves were shown in figure 2. The maximum fluorescence emission peak of curve (a) is at 327nm. Compared with the maximum emission peak position of curve (b), the fluorescence emission peak of curve (a) is redshift. The phosphorus atom of triphenylphosphine oxide has a lone pair electrons, it can form a transition of the electron energy level with TCNE. And the fluorescence intensity of (a) enhanced significantly. It indicated that triphenylphosphine oxide and TCNE can form a charge-transfer complex which has good fluorescence properties.

### 3.3. Raman scattering

The resonance Raman scattering spectrum of TCNE-Ph$_3$P=O complex in CCl$_4$ solvent was measured experimentally at the incident light of 532nm, and for comparison, the static Raman scattering spectrum of TCNE in CCl$_4$ solvent was also detected (figure 3 and figure 4).

![Figure 3. Raman scattering spectrum of TCNE.](image1)

![Figure 4. Raman scattering spectrum TCNE triphenylphosphine oxide.](image2)

It is found that the Raman peak at 2512 cm$^{-1}$ was the strongest in the static Raman scattering spectrum, while the Raman peaks around 1200 cm$^{-1}$ and 1600 cm$^{-1}$ were much stronger than these at 2512 cm$^{-1}$ in the resonance Raman scattering spectrum. The vibrational modes were strongly coupled at 1200 cm$^{-1}$ and 1600 cm$^{-1}$ because of the intermolecular charge transfer, and that the intensity of the Raman peak enhanced remarkably.

### 3.4. Preliminary Reaction Mechanism

Tetracyanoethylene is an important strong electron acceptor, and can form charge transfer complexes with a variety of types of electron donor. The phosphorus atom of triphenylphosphine oxide has a lone pair of electrons, it reacted with tetracyanoethylene as an electron donor, and produced a charge transfer complex of type n-$\pi$ for the ratio of 1 to 1. The optimized structure was shown in figure 5.
4. Conclusions

In this paper, the influence of the intermolecular charge transfer (electronic transition) has been studied through the Fluorescence spectra, UV spectra and resonance Raman scattering. The results show that in carbon tetrachloride and ethanol, tetracyanoethylene with triphenylphosphine oxide forms stable charge-transfer complex.

Using intermolecular charge transfer, a series of tetrahydro-ethylene complexes has been prepared, a multi-functional complex fluorescent probes built, and a new applications of nucleic acid probes explored and developed. The drug probe is the main tool to improve the accuracy of diagnosis and analysis with composite probe.

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