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SYNTHESIS AND PHOTOPHYSICAL STUDIES OF FLUORESCENT IRON COMPLEX FOR SENSITIZER APPLICATIONS

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ABSTRACT

Inorganic coordination complexes for dye-sensitized solar cells (DSSC) are cheaper substitutes for silicon-based solar cells and have been actively investigated in the past 3 decades. In this report, Here, a homoleptic iron complex with phenanthroline descendant - 3,4,7,8-tetramethyl-1,10-phenanthroline has been synthesized. Optimal synthesis conditions have been proposed based on the experimental yield. Photophysics of synthesized complexes in various solvents has been explored using UV-vis spectroscopy, FTIR spectroscopy, Raman spectroscopy, steady-state, and time-domain luminescence methods. The synthesized complex shows a possible candidate as a dye for DSSC. The synthesized complex shows a metal-to-ligand charge transfer character, which is critical for sensitizer application.

Keywords: Homoleptic, Iron Complex, Spectroscopy, Phenanthroline, DSSC.

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INTRODUCTION

Year after year, the global energy demand is on the rise. In accordance with forecast estimates, to meet the growing demand from the population and economy, by 2030 it will be necessary to increase the energy capacity by at least 1.7 times relative to the contemporary level. If we take Uzbekistan as an example of a developing country, 85% of electricity in the republic is produced using (burning) natural gas. Therefore, the decreasing volume of gas can affect the production of electricity. Moreover, the increase in atmospheric carbon dioxide levels is another issue. Thus, the development of renewable energy sources remains an important issue. Since Uzbekistan is a sunny country, the use of solar energy has great prospects. Currently, almost all solar power is generated by pure silicon-based solar cells. As dominant in the solar cell market, silicon-based solar cells suffer from several shortcomings, counting cost, weather dependence, space requirements, environmental concerns, rigidity, and production costs.[1] Therefore, exploring new alternatives to solar cells has been a crucial topic for researchers worldwide. Research on dye-sensitized solar cells (DSSC) began after the pioneering work of researchers in the early 1990s.[2] DSSC is cost-effective, easily fabricated, and environmentally friendly. Among many transition metal complexes, Ruthenium(II) complexes have been the most intensively studied and become the backbone of the DSSC realm. Those complexes have been used as dye sensitizers widely because of their remarkable advantages. Despite being so "good", there are obstacles related to ruthenium which is notoriously very expensive, low abundant, and toxic. Therefore, one could be concerned with other alternatives to ruthenium complexes. Thus, numerous articles are dedicated to homiletic and heteroleptic copper(I) complexes,[3-6] where most copper dyes suffer several issues such as low molar absorptivity, short excited state lifetime, and lability. Replacing ruthenium with even heavier metals was reported elsewhere.[7,8] Different complexes of metals of iron triads were dominantly found to be good mediators in DSSC. Some other reports also addressed using for dyes DSSC. One of the earliest appeared in the early 2010s and utilized the Ni(II) complex as a sensitizer.[9] Although photovoltaic function was detected, the

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low performance was caused by a short-lived excited state fluorescence lifetime. Likewise, other counterparts in 3d row, iron complexes were found very effective red-ox mediators in DSSC applications because of their high redox potential.[10,11] Bipyridine, ferrocene, and other ligands were chosen to reach higher efficiency. Iron (II) complexes have not yet been reported widely as a sensitizer dye in DSSC. Its unique electronic structure may pave the way for new sensitizer applications. Here we report the synthesis of the Iron(II) complex with the more bulky ligand. Different spectral techniques were applied to assess its features, and potential phenomena were elucidated.

EXPERIMENTAL

Materials and Methods

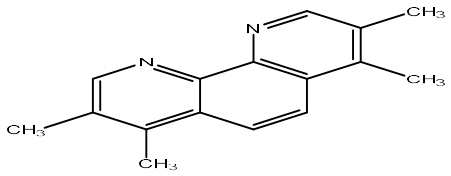
3,4,7,8-tetramethyl-1,10-phenanthroline (tmphen) (Scheme-1), ammonium hexafluorophosphate - NH_4PF_6 purchased from Haihang Industry Co., Ltd (PRC); ethanol (EtOH), iron(II) sulfate heptahydrate – $FeSO_4 \cdot 7H_2O$, analytical grade and used as purchased.

Synthesis of Complex

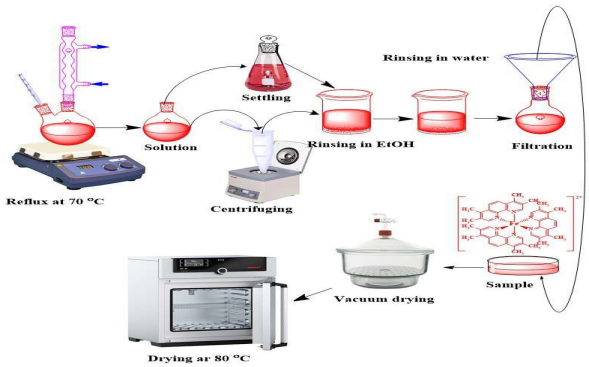
$FeSO_4 \cdot 7H_2O$ (0.06 mmol, 16.7 mg) was dissolved in 10 mL of doubly distilled water at 60 °C and 3,4,7,8-tetramethyl-1,10-phenanthroline (0.18 mmol, 42.5 mg) was dissolved and a hot solution was prepared and added dropwise to the hot salt solution, and the reflux reaction was carried out at 7 °C with constant stirring for 20 hours. Consequently, NH_4PF_6 (0.12 mmol, 19.6 mg) in 5 ml of deionized water was added dropwise and the hexafluorophosphate precipitate was obtained. As the reaction proceeded, the mixture turned dark red to pale red. After adding NH_4PF_6, the mixture was stirred for another hour. A precipitate then formed when the mixture cooled to room temperature. The obtained pale red complex precipitate was filtered through, rinsed several times with ethanol, dried at ambient temperature, and then in a drying oven for 18 h at 60 °C and 4 h at 80 °C respectively. The yield of the reaction is 80%. The entire process is summarized in Scheme 2.

Photophysical Studies

UV-vis spectrophotometer UV-2600 (Shimadzu, Japan) was used to record the absorption spectra of the complex. Chemical and structural characterization was carried out using the FITR spectrometer IRAffinity 1S (Shimadzu, Japan) equipped with an integrating sphere (MIRacle 10). Steady-state luminescence studies in various solvents were recorded on an RF-6000 spectrofluorometer (Shimadzu, Japan). Raman spectrum was recorded using the Renishaw Invia Raman spectrophotometer (Renishaw plc, UK). The lifetime of the complex was obtained at FluoTime 300 “Easy Tau” spectrometer (PicoQuant GmbH, Germany).



Scheme-1: Structure of 3,4,7,8-tetramethyl-1,10-phenanthroline (tmphen)



Scheme-2: Synthesis of $[Fe(tmphen)_3](PF_6)_2$

RESULTS AND DISCUSSION

As common knowledge, the solar irradiance spectrum peaks around 500 nm, and the intensity decays exponentially till the mid-IR region and beyond. To become a "good dye", the ideal complex has to exploit as much solar power as possible. In this regard, ruthenium complexes (N3, N719, black dye, etc.) have been playing as the "golden standard" since they were first discovered. Indeed, a long luminescence lifetime of a triplet state and a high quantum yield (almost equal to unity) play a pivotal role in these complexes. On the other hand, Iron(II) has an electronic configuration d^6 and an oxidation pathway similar to ruthenium(II).

Figure-1 shows the room temperature UV-vis and steady-state fluorescence spectra of $[Fe(tmphen)_3]^{2+}$ in acetonitrile. As can be seen from the UV-vis spectrum, it contains three distinct well-resolved peaks at 480, 510, and 540 nm. There are also two shoulders around 570 and 590 nm respectively. The distinct peak near 540 nm is notable, and we suggest it represents MLCT absorption. The room temperature emission spectrum is given as a red curve in the steady state fluorescence spectrum and the peak maximum is observed at 510 nm when the sample is excited at 440 nm.

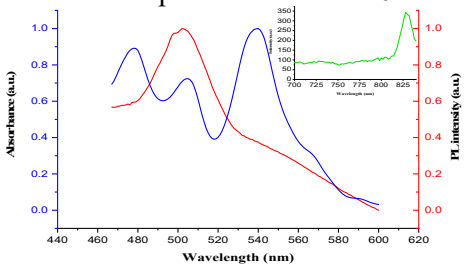


Fig.-1: Normalized UV-vis (Blue Curve) and Steady-State Fluorescence Spectra (red curve λ_{exc} = 440 nm and Green Curve in the Inset λ_{exc} = 540 nm) of $[Fe(tmphen)_3]^{2+}$ in Acetonitrile

Time-resolved fluorescence measurements revealed that the peak is considerably short-lived with a fluorescence lifetime of 9 ns (Fig.-2). The absence of any side chains in the ligand structure contributes to such fluorescence properties. Adding side chains to the ligand makes the molecule more rigid and opens new radiative pathways of deactivation. A considerably weak emission peak originating from the MLCT band also supports this idea. To the best of our knowledge, the emission peak around 825 nm could probably originated from a metal-to-ligand charge transfer (MLCT) excited state deactivation (see the inset of Fig.-1). To support our presumption, the absorption peak at 540 and the emission peak at 825 nm show a mirror image. To fully resolve the true nature of the peak at 825 nm, further research is needed.

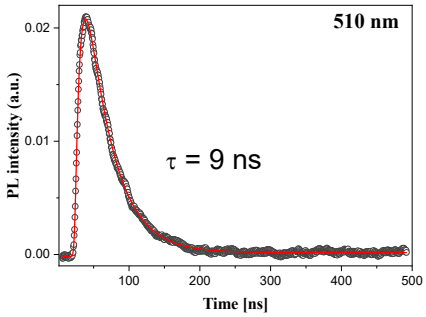


Fig.-2: Time-Resolved Emission Decay Curve of $[Fe(tmphen)_3]^{2+}$ in Acetonitrile

FTIR spectra of precursors and the obtained complex are given in Fig.-3. In the spectrum of $[Fe(tmphen)_3](PF_6)_2$ the functional group region is almost arid. The first group of absorption peaks is located in the range 1400 to 1700 cm^{-1} region, and assigned stretching vibrations of aromatic rings of tmphen ligand. Specifically, the C=N stretching band appears at 1596 cm^{-1}, and the C=C stretching band at 1574 cm^{-1}. A medium but narrow peak around 720 cm^{-1} originates from C–H bending vibrations. The second group of peaks is mostly dominated by the stretching vibrations of hexafluorophosphate anion centered around 870 cm^{-1}.

The following shifts in the vibrational frequencies support covalent coordination bond formation between a donor atom (nitrogen) and an acceptor (Iron(II) ion).C=N frequency shifted from 1612 cm^{-1} to 1596cm^{-}

[1], meanwhile, the frequency of the C=C conjugated bond of the aromatic carbons of phenanthroline shifted from 1565 cm^{-1} to 1574 cm^{-1} confirming the coordination takes place through a nitrogen atom.

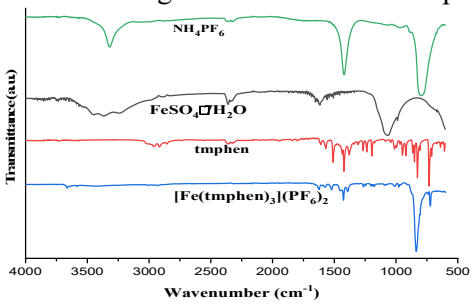


Fig.-3: Fourier Transform Infrared Spectra of Complex and Precursors

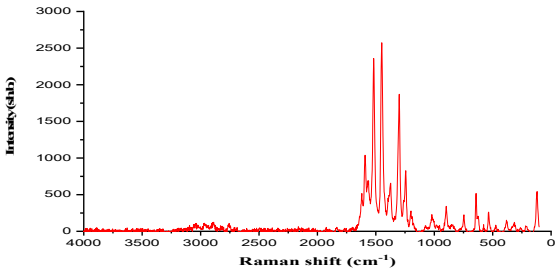


Fig.-4: Raman Spectrum of $[Fe(tmphen)_3]$ $(PF_6)_2$

The Raman spectrum which is shown in Fig.-4 is also consistent with the IR spectrum where most peaks have resided before 2000 cm^{-1}. In the Raman spectrum, three intense and narrow peaks are located at 1511, 1446, and 1300 cm^{-1} assigned to symmetric stretching vibrations of aromatic rings. Less intense Raman peak at 630 cm^{-1} attributed to P–F vibrations of hexafluorophosphate anion. The rate of non-radiative relaxation processes might be diminished after carefully selecting a bulkier ligand. During the study, the complex was dissolved in several solvents including both non-polar and polar, such as dimethyl sulfoxide, dimethylformamide, tetrahydrofuran, acetone, and acetonitrile. As discussed above, acetonitrile was more suitable as a solvent, and the complex exhibited unique photophysical properties. In the remaining solvents, the complex is either unstable or non-radiative processes have high rates.

CONCLUSION

Homoleptic Iron(II) complex synthesized choosing bulky phenanthroline derivative as a ligand. Its spectral properties showed a possible deactivation pathway from the triplet electronic state in acetonitrile. Time-resolved fluorescence studies another dominating deactivation pathway that has a short lifetime of 9 ns. Even though the prepared complex cannot compete with the Ruthenium(II) complex, it may glimpse new insight using 3*d* metals as a possible dye. Further studies may reveal the true nature of the second deactivation pathway.

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CONFLICT OF INTERESTS

The authors declare no competing financial interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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