Synthesis and characterization of a luminescence podand bridged dipyridyl platinum(II) complex

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Abstract. We have designed and synthesized an aromatic podand containing two dipyridyl platinum complexes in both ends of the podand, of which the luminescence in solution is reversibly fabricated by adding equal equivalent of dibenzylammonium hexafluorophosphate and base. The results are obtained by absorption and emission spectroscopy and \(^1\)H NMR spectroscopy.

1. Introduction

It is well established that one of the most used means to modulate the luminescence is to control component molecule packing and consequent intermolecular interactions. Much attention is being devoted currently to the host-guest recognition, in which the photochemical and photophysical properties of each component can be modified profoundly upon complexation\(^1\)-\(^7\). Such recognition interactions have been used in the design of crown ethers and dialkylammonium ion systems for a variety of applications, on the basis of a cooperative combination of [N–H···O] and [C–H···O] hydrogen bonds and π–π stacking interactions. On the other hand, in the past few decades square-planar platinum(II) complexes have been extensively explored due to their capability to exhibit rich photophysical properties\(^8\)-\(^10\). Scientist have reported a square-planar platinum(II) complex based on dibenzo[24]crown-8\(^11\) (Pt-Crown), as shown in scheme 1, which exhibited that upon addition of trifluoroacetic acid (TFA) to a solution of Pt-Crown in CH\(_2\)Cl\(_2\), significant decrease in the luminescence intensities was observed.

However, it is well-known that podands are open chain crown ethers, which has the various potential applications. Owing to the ion-binding properties, ionophoric properties, podands have been widely studied.\(^12\)-\(^14\) For example, podands have been studied as delivery vehicles for biological molecules and alkali metal ions, ligands for organometallic catalysts, precursors for anticancer drugs, fluorescent sensors for heavy metals, precursors of nanomaterials with novel electronic, magnetic and optical properties, and reagents for the extraction of radionuclides and rare-earth elements and chiral amino acids. However, host-guest recognition is rarely explored in podand-based system.

In this context, we have combined podand with platinum(II) complexes to design a podand bridged dipyridyl platinum(II) complex (compound 1), as shown in scheme 1. The luminescence responses can be triggered by adding acid/base. Upon treatment of the solution of compound 1 with acid and base, the luminescence intensity was enhanced and decreased, respectively, together with a reversible change of NMR signals. The change of luminescence intensity is in sharp contrast to the situation of Pt-Crown system mentioned in the previous literature\(^11\).
2. Experiment

The synthetic pathways of compound 1 are shown in scheme 2. The synthesis of 5-(bromomethyl)-2, 2'-bipyridine (bipyBr) and dibenzylammonium hexafluorophosphate (2-H-PF₆) (scheme 1) are according to the previous literature. Compound 4 is reacted with bipyBr to produce compound 3. Compound 3 is stirred with Pt(DMSO)₂Cl₂ to produce compound 2, which is followed by CuI catalyzing to produce the compound 1. The structure of the compound 1 was investigated by NMR and ESI-MS spectra. The photophysical features have been studied by ¹H NMR spectroscopy and absorption and emission spectroscopy to explain the interactions of compound 1 and 2-H-PF₆.

2.1. Materials and Reagents:
Tetrakis(triphenylphosphine)platinum(0) (99%), phenylacetylene, methacrolein, 2-acetylpyridine, 4-toluene sulfonyl chloride (98.5%), iodine (99.8%) were commercially available and used as received. Triethylamine and all solvents were purified by standard procedures. NMR spectra were recorded with a 400 MHz spectrometer. Chemical shifts are reported on the δ scale relative to tetramethylsilane. Emission spectra were recorded in an air-equilibrated solution. ¹H NMR titrations of the samples was measured on a 400 MHz spectrometer, and deuterated solvents were used from freshly opened bottle. Titration experiment was performed in chloroform-d solutions. ESI-MS Experiments were recorded on a solariX Fourier transform ion cyclotron mass spectrometer resonance.

2.2. The synthesis of compound 1:
The suspension compound 2 (60 mg, 0.048 mmol), CuI (2.1 mg, 0.011 mmol) in dichloromethane was under N₂ atmosphere, followed by addition of triethylamine (0.7 mL), and the mixture was stirred at rt for 12 h. Solvent was removed under reduced pressure, and the crude product was purified by flash chromatography with CH₂Cl₂/MeOH (15:1, v/v) mixture solution as the eluent to get orange solid. The orange solid was recrystallized by dichloromethane/ether to yield orange powder (47 mg), in 65% yield. ¹H NMR (400 MHz, CDCl₃): δ 8.81 (s, 4H), 8.15 (d, J = 8 Hz, 2H), 8.05 (d, J = 8 Hz, 2H), 7.93 (t, J = 8 Hz, 2H), 7.80 (d, J = 8 Hz, 2H), 7.57 (q, J = 8 Hz, 8H), 7.31-7.22 (m, 14H), 6.67 (m, 4H), 4.53 (s, 4H), 4.01 (t, J = 4 Hz, 4H), 3.81 (t, J = 4 Hz, 4H), 3.76 (m, J = 4 Hz, 8H), 3.61 (m, 8H). High resolution mass spectrum m/z: caculate [C₇₂H₆₆N₄NaO₈Pt₂]⁺: 1527.4069; found: 1527.4032 (Figure S6). See the Supporting Information for the details on their synthesis and characterization of compound 2-5, and the experiments.

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Scheme 1. Structure of compound Pt-crown⁵, compound 1 and 2-H-PF₆.

Scheme 2. Synthetic routes for compound 1 and compound 2.
3. Results and Discussions

3.1. \(^1\)H NMR Spectroscopy:

The spectrum of the compound 1 in CHCl\(_3\) solution is shown in Figure 1a. Upon addition of equivalent 2-H-PF\(_6\) in CD\(_3\)CN solution to the NMR tube, the spectrum shown in Figure 1b was obtained, in which, the methylene proton H\(_2\) on compound 1 were shifted upfield from \(\delta = 4.50\) to 4.40 ppm. The aromatic protons H\(_6\), H\(_7\), H\(_8\) in phenylacetylene ligand are shifted upfield, which was pointed out in Figure 1. And, the signals of dipyridyl ligand protons of compound 1 were broadened and aggregated to such an extent. Furthermore, a broad peak at 7.18 ppm was clearly assigned to the protons H\(_{Arc}\) of 2-H-PF\(_6\) hosted by the compound 1, whereas the signal at 7.44 and 7.39 ppm was assigned to the protons H\(_{Aruc}\) adjacent to the uncomplexed 2-H-PF\(_6\). This phenomenon was assigned to the presence of strong \(\pi-\pi\) stacking interactions in the system of compound 1 and 2-H-PF\(_6\). Subsequently, upon the addition of one equivalent of N-tert-butyl-N',N',N'',N'',N''',N'''-hexamethylphosphorimidic triamide (P\(_1\)-t-Bu) to the same NMR tube, followed by spectroscopic analysis, resulted in the spectrum shown in Figure 1c, which is essentially the same as that illustrated in Figure 1a, except that there are additional peaks arising from the presence of protons in the dibenzylammonium, indicating that the recognition was reversible. These observations suggest that addition of 2-H-PF\(_6\) to the compound 1 results in aggregation through host–guest interactions, in which, \(\pi-\pi\) stacking interactions play a key role, and that can be reversed by adding base.

![Figure 1. \(^1\)H NMR (400 MHz, 25 °C) spectra of (a) compound 1 (in CDCl\(_3\), 2.5x10\(^3\)mol·L\(^{-1}\)), (b) of a 1:1 mixture of 2-H-PF\(_6\) and compound 1 (CDCl\(_3\)/CH\(_3\)CN, 100:4) and (c) of a 1:1:1 mixture of, compound 1 and P\(_1\)-t-Bu (CDCl\(_3\)/CH\(_3\)CN, 100:4).](image)

3.2. The photophysical properties of the system:

The UV-vis absorption spectra (Figure 2) of compound 1 in CDCl\(_3\) solutions exhibit intense ligand-centered absorption bands at ca. 270 nm along with a broad low-energy absorption at 403 nm, arising likely from MLCT and LLCT states\(^{17}\). Upon addition of equivalent 2-H-PF\(_6\), the absorption bands between 390 and 500 nm of compound 1 showed a slight blue shift in comparison with that in compound 1, which could be basically recovered by further adding equivalent of P\(_1\)-t-Bu.

The emission decay trace of the CHCl\(_3\) solution recorded at 662 nm was deconvoluted as a bi-exponential functions (FigureS8), giving a luminescence lifetime of 8.99 ns\((\alpha = 20.82\%)\) and 57.14 ns \((\alpha = 79.18\%)\). The bi-exponential decay recorded at 662 nm is due to the superimposition of the fluorescence band (which is responsible for the measured short time of 8.99 nm) with the phosphorescence one (responsible for the measured long time of 57.14 ns). The internal quantum yields of compound 1 in CHCl\(_3\) solution is 4.55%.
Figure 2. UV-vis absorption and emission spectra of compound 1 (2.5×10⁻⁵ mol·L⁻¹) in CHCl₃ solution (black), 1:1 mixture of 2-H·PF₆ and compound 1 (CDCl₃/CH₃CN, 100:1) (red), a 1:1:1 mixture of 2-H·PF₆, compound 1 and P₁-t-Bu (CDCl₃/CH₃CN, 100:1) (blue).

Upon excitation at λₑₓ = 420 nm, the CHCl₃ solution of compound 1 exhibited a strong luminescence band centered at 662 nm in Figure 2, which was assigned to the mixtures of MLCT and ³MLCT luminescence. Upon addition of equivalent 2-H·PF₆, the band was blue shifted to 655 nm together with an increase in its intensity. The enhancement of emission intensity is in contrast to the situation of Pt-Crown system, of which the emission intensity decreased, mentioned in the previous literature. Besides, and the blue shift of ³MLCT emission has been confirmed to be the aggregation of luminescence compound. Further treatment of this solution with equivalent P₁-t-Bu completely restored the luminescence to the original level. We deduce that the novel increase of emission intensity was attributed to the podand-like structure, and the slight blue shift was attributed to aggregation of compound 1.

Figure 3. UV-vis absorption and emission spectra of compound 2 (2.5×10⁻⁵ mol·L⁻¹) in CHCl₃ solution (black), 1:1 mixture of 2-H·PF₆ and compound 2 (CDCl₃/CH₃CN, 100:1) (red) at rt.

To clarify the mechanism of this unusual luminescence behavior, we further studied interactions of the model compound 2 with 2-H·PF₆. The UV-vis absorption spectra of compound 2 are shown in Figure 3. The spectra consist of high intensity absorption bands below 350 nm, which can be attributed to ligand ³π-π* transitions, and a broad, moderately intense absorption band at 390 nm assign to metal-to-ligand charge transfer (MLCT) transition. Upon addition of equivalent 2-H·PF₆, the absorption bands has a very slight change in comparison with that in compound 1. Upon excitation at λₑₓ = 390 nm, the solution of compound 2 exhibited a very weak MLCT luminescence band centered at 450 nm and a ³MLCT luminescence band centered at 550 nm. Upon addition of equivalent 2-H·PF₆, the luminescence intensity is increased slightly, which was in contrast to the situation of compound 1 and 2-H·PF₆ mentioned above. Considering the structure difference between compound 1 and compound 2, the change of emission bands in compound 1 and 2-H·PF₆ were attributed to the presence of π-π stacking interactions mainly at the part of phenylacetylene ligand, as revealed by its ¹H NMR spectrum.
4. Conclusion

In summary, we have fabricated a luminescence system based on podand bridged dipyridyl platinum(II) complexes, by adding equivalent 2-H-PF₆ to a solution of compound 1 in CHCl₃ on the basis of the π-π interactions between phenylacetylene ligand and 2-H-PF₆. The host–guest recognition leads to a novel enhancement of emission intensity and a slight aggregation of the compound 1 and 2-H-PF₆, as shown in NMR spectrum and emission spectrum. And the changes can be fully reversed upon the addition of equal equivalent of base. We conclude that podand-like structure plays an important role in the unusual luminescence change. Therefore, podands can be promising candidates for constructing smart materials through functionalizing. We believe that the novel synthetic host can attract more attention, and its synthesis and applications will become a new and attractive research topic in the near future.

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