Summer Research Fellowship (SRF)
2020 for Science Students

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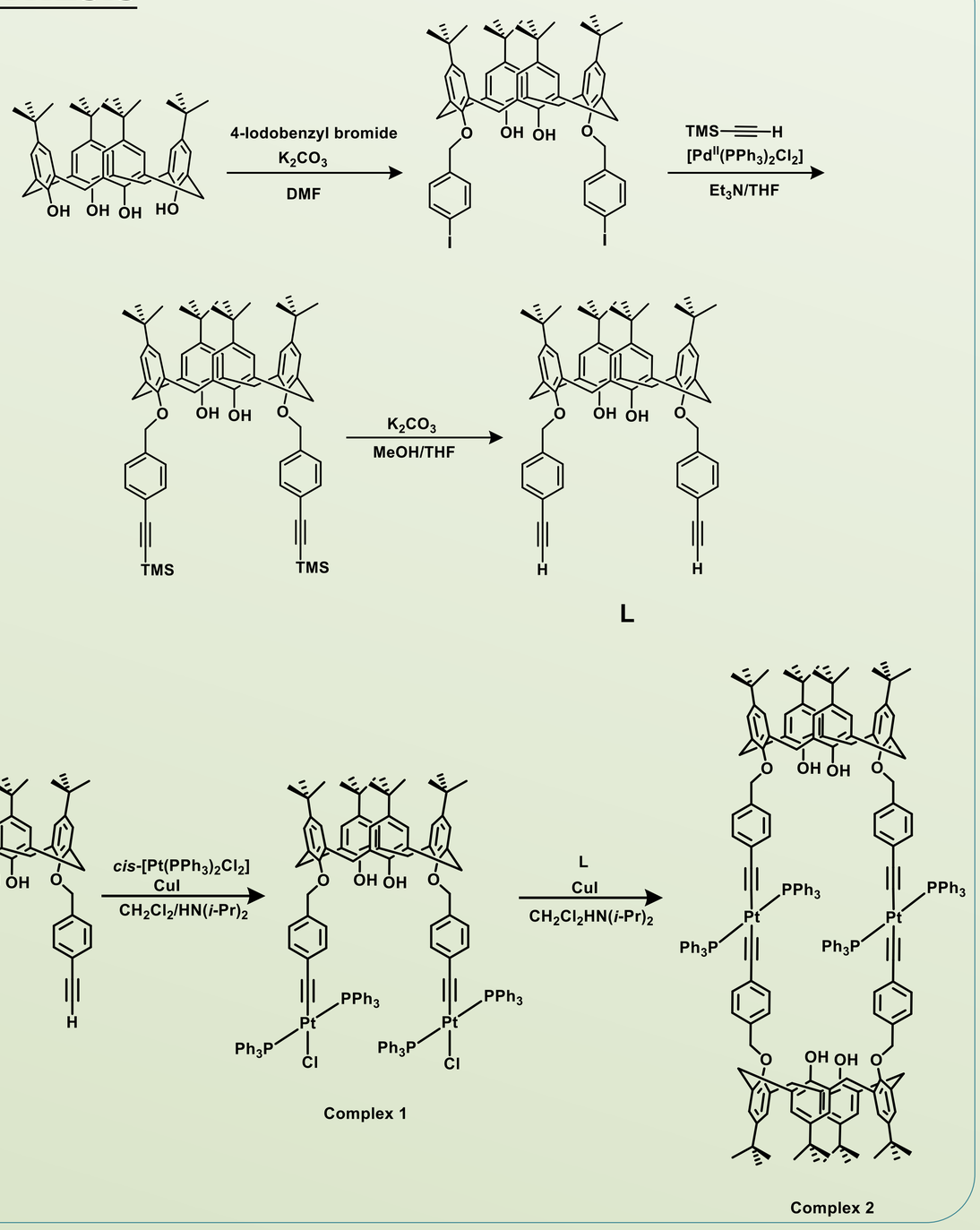
Design, Synthesis and Photophysical Studies of Luminescent Calix[4]arene-based Alkynylplatinum(II) Phosphine Complexes

INTRODUCTION

Supramolecular chemistry has aroused extensive research interest in recent years. Calix[n]arenes, a class of macrocyclic oligomers with substituted phenol as monomeric unit, can serve as a molecular scaffold for the construction supramolecular assembles.[1-3] In particular, calix[4]arene is widely employed as an important building block owing to their unique molecular structures, tunable molecular conformation, and versatile functionalization at both the lower and upper rims.[4] Moreover, the incorporation of metal complexes into calix[4]arene scaffold can give rise to intriguing spectroscopic and luminescent properties, rendering the construction of interesting luminescent supramolecular architectures.[5-8] Yam and co-workers reported the self-assembly of gold(I) alkynylcalix[4]crown-6 complex into luminescent tetranuclear gold(I) complexes, with the four gold(I) in special rhomboidal array.[9] As an extension on the study of the application of calix[4]arene-based metal complexes, the same group also reported luminescent calix[4]arene-based platinum(II) and gold(I) complexes as chemosensors for sensing potassium[10] and aluminum ion[11] respectively, based on their drastic spectroscopic changes upon ion-binding. In view of the rich spectroscopic and luminescent properties of square-planar alkynylplatinum(II) phosphine complexes,[12,13] it would be an attractive candidate for the construction of interesting supramolecular structures. It is envisaged that the incorporation of alkynylplatinum(II) phosphine complexes into calix[4]arene scaffold can give rise to various interesting luminescent supramolecular architectures.

In the present study, two novel calix[4]arene-based alkynylplatinum(II) phosphine complexes **1** and **2** have been successfully synthesized and characterized. Their photophysical properties have been examined.

SYNTHESIS



CONCLUSION

Two luminescent calix[4]arene-based alkynylplatinum(II) phosphine complexes have been successfully synthesized and characterized. Their photophysical properties are studied. With further modification on the calix[4]arene-based alkynyl ligand as well as the phosphine ligand, more interesting luminescent supramolecular architectures are expected, providing further insight into the development of luminescent functional materials for various applications.

Acknowledgement

I would like to present my sincere appreciation to my supervisor Professor Vivian Wing-Wah Yam for her inspiration and support. Also, I would like to gratefully thank Miss Jenny Yuk-Wa Yeung for her patient guidance and motivating teaching throughout the whole project.

UV-VIS ABSORPTION SPECTROSCOPY

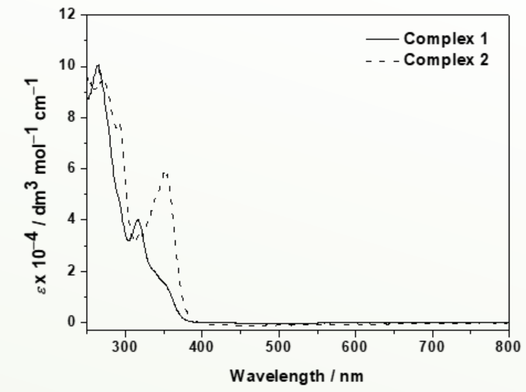


Figure 1. UV-Vis absorption spectra of complexes **1** and **2** in dichloromethane solutions at 298 K.

Table 1. UV-vis absorption data of complexes **1** and **2** in dichloromethane solutions measured at 298 K.

Complex	λ_{abs} / nm (ε / mol^{-1} dm^3 cm^{-1})
1	265 (100445), 315 (40115), 352 (14620, sh)
2	270 (95050), 291 (76990, sh), 353 (58600)

The UV–vis absorption spectra of both complexes in dichloromethane solutions at 298 K display intense absorption bands at around 260–320 nm and 350 nm, with extinction coefficients in the order of 10^4 mol^{-1} dm^3 cm^{-1}.

- The high-energy absorption bands at 260–300 nm are assigned as intraligand (IL) [$\pi \rightarrow \pi^*$(phosphine)] transitions.
- The lower-energy absorption bands at 350 nm are assigned as an admixture of intraligand (IL) [$\pi \rightarrow \pi^*$(alkynyl)] and metal-to-ligand charge transfer (MLCT) [dπ(Pt) $\rightarrow \pi^*$(alkynyl)] transitions with predominantly IL character.

EMISSION SPECTROSCOPY

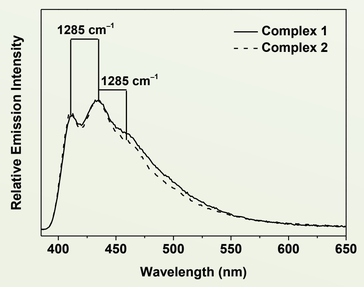


Figure 2. Normalized emission spectra of **1** and **2** in degassed dichloromethane solutions at 298 K.

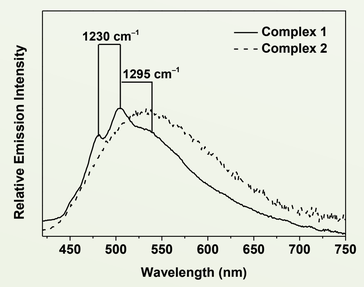


Figure 3. Normalized emission spectra of **1** and **2** in the solid state at 298 K.

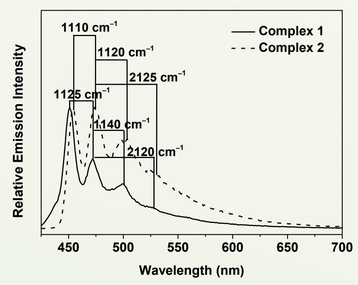


Figure 4. Normalized emission spectra of **1** and **2** in glass state at 77 K.

Table 2. Emission data of complexes **1** and **2**

Complex	Medium (T / K)	λ_{em} / nm (τ_0/μs)	Φ_{lum}[a]
1	CH_2Cl_2 (298)	412, 435, 460 (<0.1)	<0.01
	solid (298)	533 (<0.1)	
	solid (77)	456, 474, 505 (0.73)	
	glass (77)[b]	450, 474, 501, 527 (3.3)	
2	CH_2Cl_2 (298)	411, 434, 459 (<0.1)	<0.01
	solid (298)	479, 509, 545 (<0.1)	
	solid (77)	459, 478, 503, 531 (0.65)	
	glass (77)[b]	453, 476, 503, 530 (3.1)	

[a] **Relative luminescence quantum yield, measured by the optical diluted method using a degassed aqueous solution of quinine sulfate in 1.0 N sulfuric acid (Φ = 0.546, excitation wavelength at 365 nm) as reference.**

[b] **In EtOH / MeOH (4:1 v/v) glass.**

Upon photoexcitation at 365 nm, the complexes in degassed dichloromethane solutions at 298 K are weakly emissive, showing emission bands at around 410–460 nm (Figure 2).

- The emission bands are mainly derived from mixed ^{3}IL [$\pi \rightarrow \pi^*$(alkynyl)]/^{3}MLCT [dπ(Pt) $\rightarrow \pi^*$(alkynyl)] excited states, with predominantly IL character.
- The vibrational progressional spacings of the emission bands are around 1300 cm^{-1}, corresponding to the ν(C≡C) stretching modes of the triphenylphosphine ligand.
- Similar emission bands are observed in the solid state (Figure 3). In the glass state at 77 K (Figure 4), the emission spectra are dominated by vibronic structures with vibrational progressional spacings of around 1300 cm^{-1} and 2100 cm^{-1}, typical of the ν(C⎓C) and ν(C≡C) stretching modes, suggesting the involvement of the Ar-C≡C moiety in the emissive state.

References

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