香 港 大 學
THE UNIVERSITY OF HONG KONG

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Poster No.: C6
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Intended Major: Chemistry
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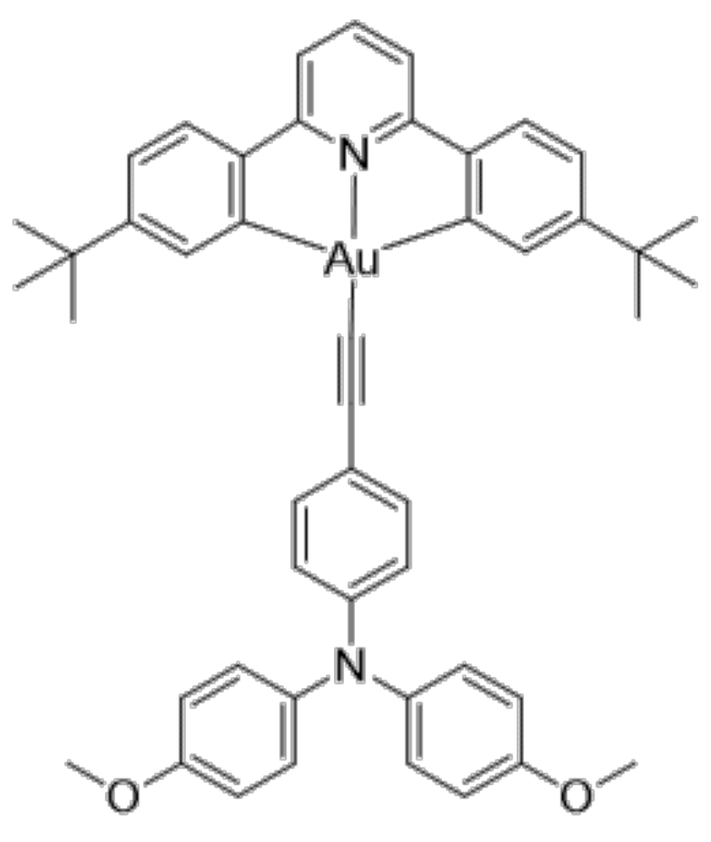
Design, Synthesis, Photophysical and Electrochemical Study of Luminescent Cyclometalated Gold(III) Complexes

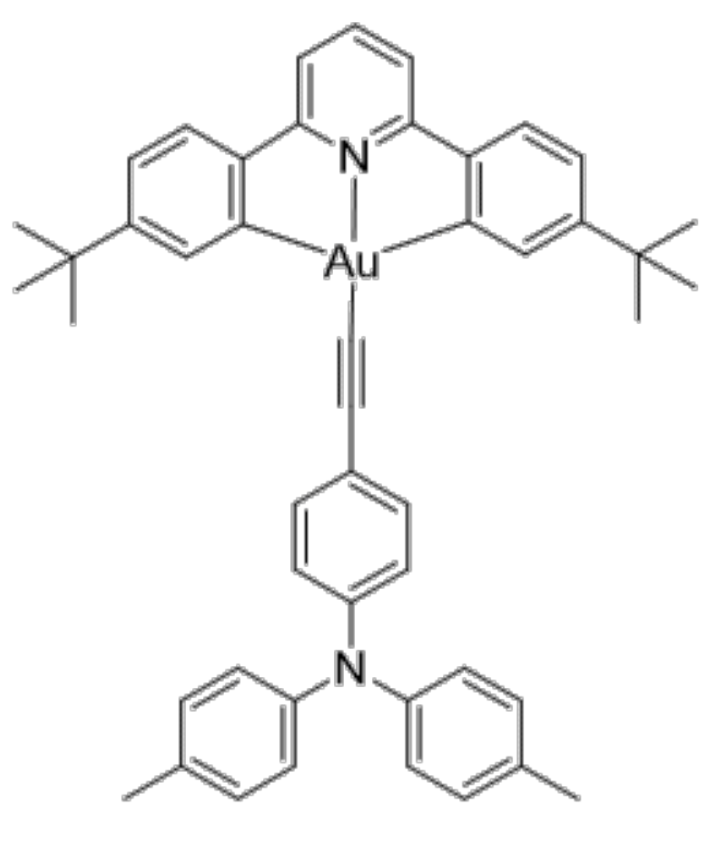
Introduction

Gold(III) complexes with strong *σ*-donating ligands, such as alkynyl and aryl ligands, have been found to possess enhanced photophysical properties such as room-temperature photoluminescence and electroluminescence. These enhanced properties have made such alkynylgold(III) complexes attractive for optoelectronic applications such as organic light-emitting diodes (OLEDs). It has also been demonstrated that the charge transfer properties of the gold(III) complexes can be readily tuned through the modification of their alkynyl ligands. In addition, the rich electrochemical properties, high stability and environmental benignity of gold(III) complexes have made them promising candidates for use in organic memory devices. Recent works have utilized different classes of alkynylgold(III) C^N^C complexes for the fabrication of organic memory devices with binary and ternary memory performances.

In this study, three alkynylgold(III) complexes with varying substituents on the triphenylamine-based alkynyl ligand have been designed, synthesized and characterized. The effects of varying electron-donating strengths on the photophysical and electrochemical properties of the complexes have been investigated.



(1)



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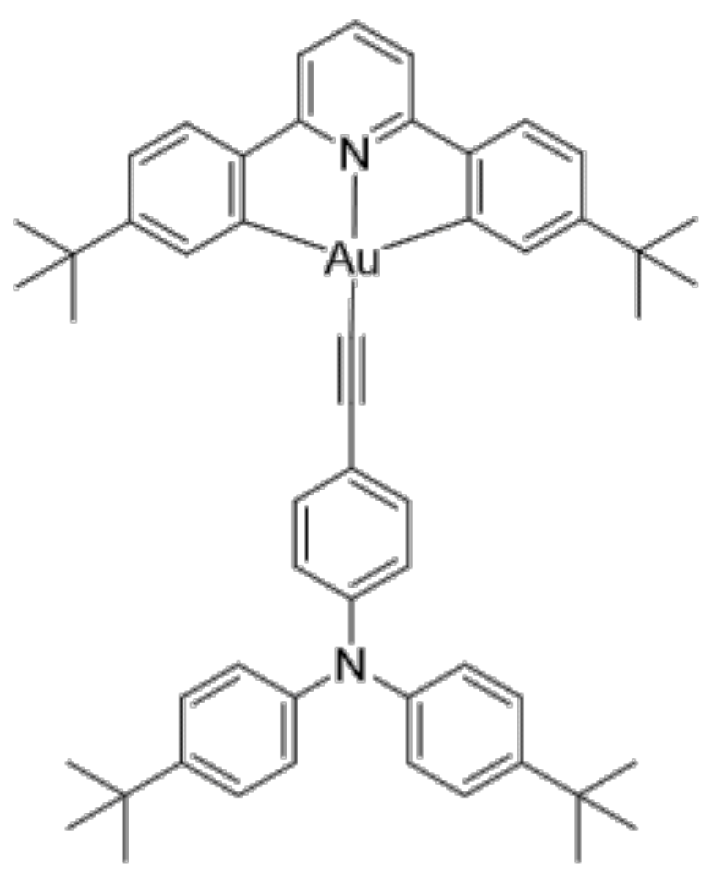

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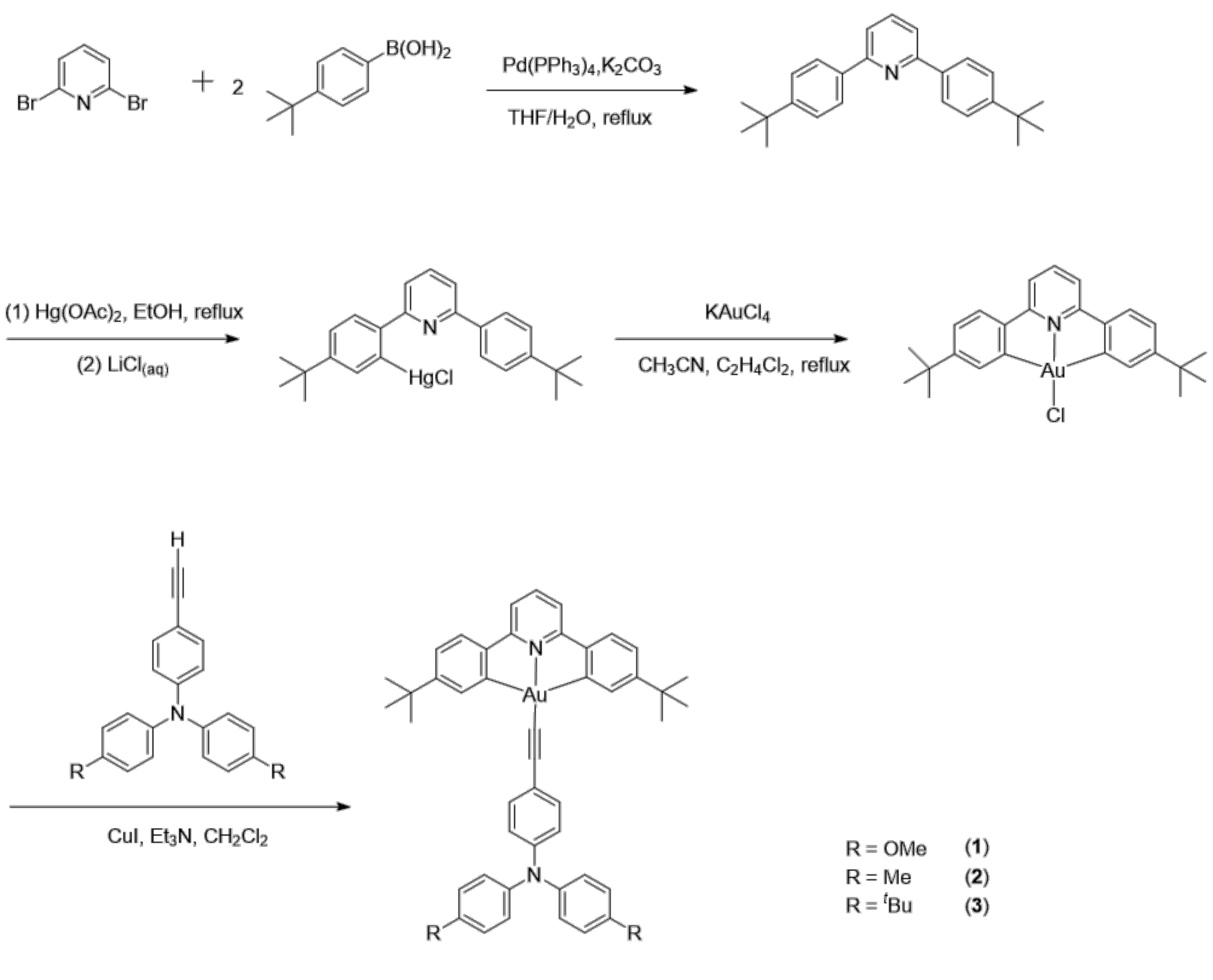
Synthesis



Acknowledgement

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References

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Photophysical Properties

- All three complexes exhibit intense absorption bands at 280–350 nm, and less intense vibronic-structured absorption bands at around 370–430 nm.
- These absorption bands are assigned as the intraligand (IL) [$\pi \rightarrow \pi^*$(C^N^C)] transitions with some charge transfer character from the *tert*-butylphenyl moiety to the central pyridine unit.
- Absorption tails that extended to 470 nm are attributed to ligand-to-ligand charge transfer (LLCT) [π(C≡C–C_6H_4–N(C_6H_4–R)$_2$) $\rightarrow \pi^*$(^{t}BuC^N^C^{t}Bu)] transitions; with mixing of IL [$\pi \rightarrow \pi^*$(C^N^C and C≡C–C_6H_4–N(C_6H_4–R)$_2$)] transitions.

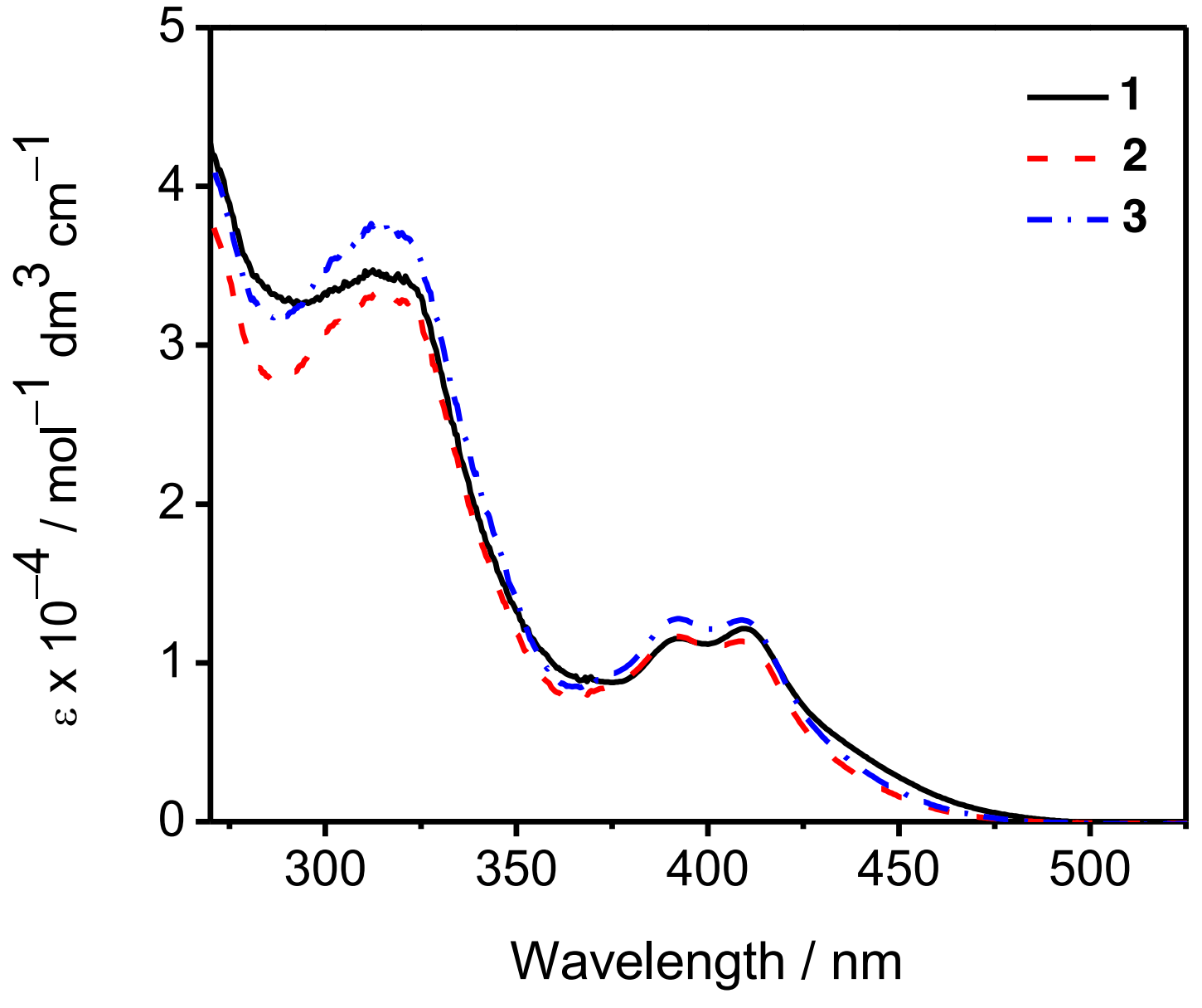

Figure 1. UV–vis absorption spectra of complexes **1–3** in dichloromethane solutions at 298 K.

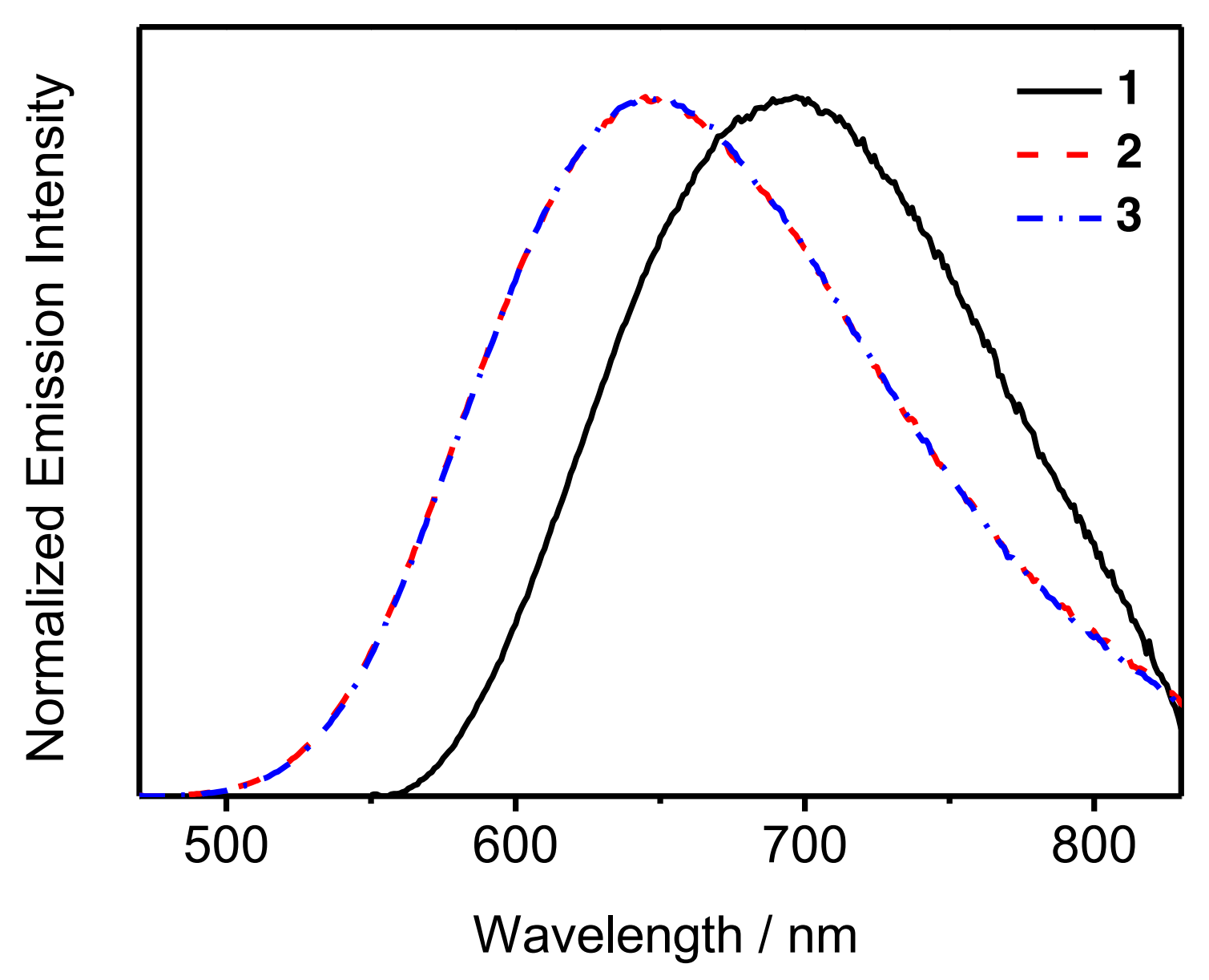

Figure 2. Normalized emission spectra of complexes **1–3** in degassed dichloromethane solutions at 298 K.

Complex	Absorption λ_{max} / nm (ε_{max} / $dm^3mol^{-1}cm^{-1}$)	Emission λ_{max} / nm (τ_o / ns)	Φ_{sol}[a]
1	312 (34600), 392 (11525), 411 (12095)	697 (82)	0.01
2	312 (32945), 391 (11620), 409 (11365)	647 (62)	0.07
3	313 (37795), 391 (12720), 409 (12700)	647 (61)	0.07

Table 1. Photophysical data of complexes **1–3** in dichloromethane solutions measured at 298 K.

[a] The relative luminescence quantum yield was measured at room temperature with a degassed solution of [Ru(bpy)$_3$]Cl_2 in acetonitrile (Φ = 0.06, excitation wavelength at 436 nm) as the reference.

- In degassed dichloromethane solution at 298 K, complexes **1–3** display structureless emission bands centered at 650–700 nm, which are assigned as originating from excited states of LLCT [π(C≡C–C_6H_4–N(C_6H_4–R)$_2$) $\rightarrow \pi^*$(^{t}BuC^N^C^{t}Bu)] nature.
- The incorporation of electron-donating dialkyl-amino and dialkoxy-amino substituents on the phenylalkynyl ligands results in higher-lying π[C≡C–C_6H_4–N(C_6H_4–R)$_2$] orbitals and thus narrower highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) energy gaps for the LLCT emissions.
- The red-shift is especially significant for **2**, due to the stronger electron-donating power of its methoxy substituent over the alkyl substituents on **1** and **3**.

Electrochemistry

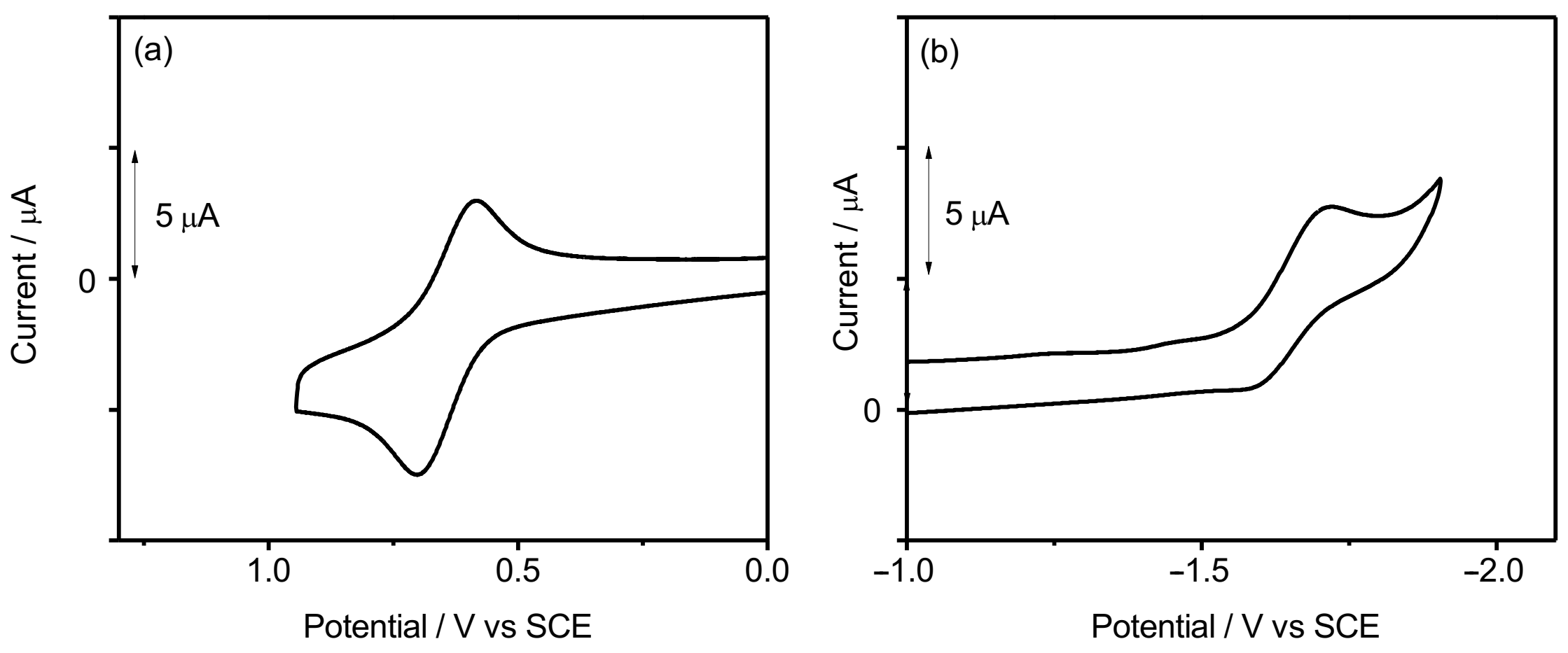

Figure 3. Cyclic voltammograms for the (a) oxidative and (b) reductive scans of complex **1.**

Table 2. Electrochemical data of complexes **1–3**.[a]

Complex	Oxidation $E_{1/2}$ / V vs. SCE[b] (ΔE_p / mV)[c]	Reduction [E_{pc} / V vs. SCE][d]	E_{HOMO} / eV[e]	E_{LUMO} / eV[f]	HOMO–LUMO / eV
1	+0.64 (99)	[–1.70]	–4.98	–2.64	2.34
2	+0.80 (68)	[–1.62]	–5.14	–2.72	2.42
3	+0.80 (93)	[–1.65]	–5.14	–2.69	2.45

[a] In CH_2Cl_2 solution with 0.1 M ^{n}Bu$_4$NPF$_6$ as supporting electrolyte at 298 K; working electrode, glassy carbon; scan rate = 100 mV s^{-1}.
[b] $E_{1/2} = (E_{pa} + E_{pc})/2$; E_{pa} and E_{pc} are the peak anodic and peak cathodic potentials, respectively.
[c] $\Delta E_p = (E_{pa} - E_{pc})$.
[d] E_{pc} refers to the cathodic peak potential for the irreversible reduction waves.
[e] E_{HOMO} levels were calculated from electrode potentials, i.e. $E_{HOMO} = -e(E_{pa}+(4.8-Fc^+/Fc))$ or $E_{HOMO} = -e(E_{1/2}+(4.8-Fc^+/Fc))$ in eV. (Fc^+/Fc = 0.46 V vs. SCE in CH_2Cl_2).
[f] E_{LUMO} levels were calculated from electrode potentials, i.e. $E_{LUMO} = -e(E_{pc}+(4.8-Fc^+/Fc))$ or $E_{LUMO} = -e(E_{1/2}+(4.8-Fc^+/Fc))$ in eV. (Fc^+/Fc = 0.46 V vs. SCE in CH_2Cl_2).

- Complex **1** has the least positive potential for oxidation when compared to complexes **2** and **3.**
- This could be ascribed to the stronger electron-donating ability of its methoxy substituent, which results in a higher-lying HOMO, and thus complex **1** is found to be more easily oxidized.
- The narrower HOMO–LUMO energy gap of **1** than **2** and **3** obtained from electrochemical studies is in line with the lower emission energy of **1** than **2** and **3** obtained in the photophysical studies.

Conclusion

In this study, three new alkynylgold(III) C^N^C complexes have been designed and synthesized, and their photophysical and electrochemical properties have been studied. Through the exploration and rationalization of the differences in properties of the three new complexes, a more in-depth understanding of the structure–property relationship of alkynylgold(III) C^N^C complexes is achieved.

It is hoped that the enhanced understanding of these metal complexes would assist scientists in designing metal complexes with fine-tuned properties, ultimately achieving the goal of synthesizing metal complexes which possess ideal properties for real life applications.