

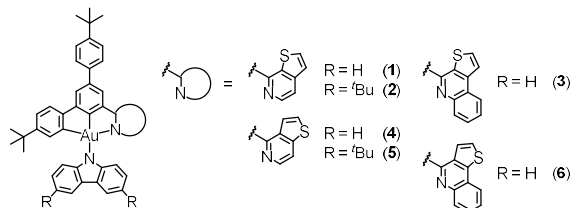
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Design and synthesis of yellow- to red-emitting gold(III) complexes containing isomeric thienopyridine and thienoquinoline moieties and their applications in operationally stable organic light-emitting devices

Lok-Kwan Li, Cathay Chai Au-Yeung, Man-Chung Tang, Shiu-Lun Lai, Wai-Lung Cheung, Maggie Ng, Mei-Yee Chan,* Vivian Wing-Wah Yam*
Institute of Molecular Functional Materials and Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, P. R. China

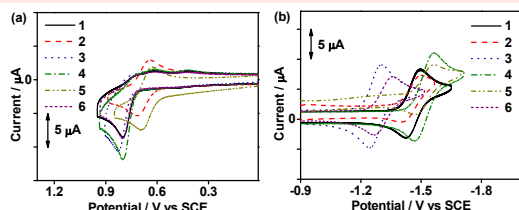
Introduction

A new class of isomeric thienopyridine and thienoquinoline-containing carbazolygold(III) complexes **1–6** has been designed and synthesized.



Through incorporating six different *N*-heterocycles into the cyclometalating ligand, these isomeric gold(III) complexes have been found to exhibit distinctly different photophysical, electrochemical and electroluminescence properties. The investigation of the isomeric effect and extended π -conjugation of the *N*-heterocycles has never been reported in gold(III) systems, and is also scarcely reported in the widely studied iridium(III) and platinum(II) systems. Considering the radical anion stability and the resonance structures of the *N*-heterocyclic moieties, we believe that a proper choice of the isomer in the emitting material could lead to prolonged device operational lifetimes.

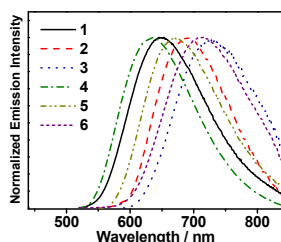
Electrochemical Studies



Cyclic voltammograms for (a) oxidative and (b) reductive scans of **1–6** in degassed dichloromethane (0.1 M $n\text{Bu}_4\text{NPF}_6$) at 298 K.

- Quasi-reversible reduction waves: ligand-centered reduction of C⁺A⁻N ligand;
- The first oxidation processes: carbazole ligand-centered oxidation

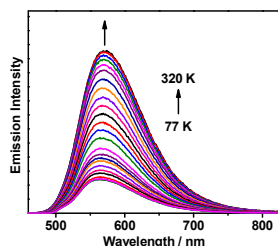
Photophysical Properties



Structureless emission bands in toluene for **1–6**, with peak maximum ranging from 635 to 730 nm, excited state lifetimes of 0.1–0.3 μs and high radiative decay rates (k_r) on the order of 10^5 s^{-1} , were assigned to the LLCT [$\pi(\text{carbazole}) \rightarrow \pi^*(\text{C}^+\text{A}^-\text{N})$] origin.

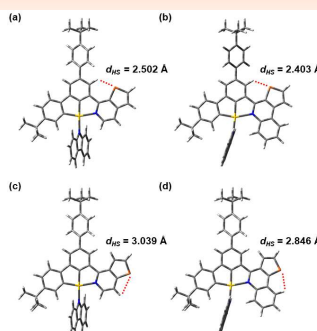
Normalized emission spectra of **1–6** in degassed toluene at 298 K.

The intensity of the structureless emission band of **1** doped in MCP at 20 wt% is found to **drastically increase by almost 5-fold** from 77 to 320 K. The excited-state lifetimes were found to be almost unchanged in the range of 200 K (1.5 μs) to 320 K (1.4 μs), suggesting that the thermal up-conversion process is almost complete under those temperature conditions. These, together with the $\Delta E_{S_1-T_1}$ value of 0.004 eV computed by time-dependent density functional theory (TDDFT) calculations, as well as the **high k_r , on the order of 10^5 s^{-1}** in both solution and solid-state thin films, are indicative of **TADF behavior** in the carbazolygold(III) complex.



Emission spectra of the thin film of 20 wt% **1** doped in MCP upon increasing the temperature from 77 to 320 K.

Computational Studies



The distances between the S and H atoms in the *N*-heterocyclic moieties of (a) **1**, (b) **3**, (c) **4** and (d) **6** at the optimized ground-state geometries.

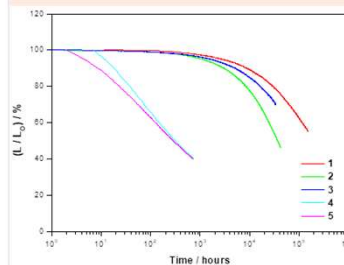
Density functional theory (DFT) and time-dependent DFT (TDDFT) calculations were performed to gain a deeper insight into

- electronic structures
- origins of the electronic transitions
- nature of the emissive states
- geometries of the S_1 and T_1 states of **1**, **3**, **4** and **6**

The position of the sulfur atom plays an important role in **controlling the dipole–dipole interaction and the steric repulsion** within the complex, which would influence the HOMO–LUMO energy gap and the molecular packing of the complexes in the solid state.

The presence of the dipole–dipole interaction in **1** and **3** would allow them to have a **more stable radical anion** in their excited states than **4** and **6**.

Electroluminescence Studies



Relative luminance, L/L_0 , of vacuum-deposited devices based on **1–5** as a function of operation time projected at an initial luminance of 100 cd m^{-2} .

- Vacuum-deposited based on 2-thpy-containing complexes, **4** and **5**, exhibited LT_{70} values of **86** and **55 h** at 100 cd m^{-2} , respectively.
- The devices based on 1-thpy-containing complexes, **1** and **2**, demonstrated **long LT_{70} values of 63,258 and 15,760 h** at 100 cd m^{-2} . The higher operational stability could be rationalized by the **relatively higher radical anion stability** of **1–3** (See computational studies).
- Solution-processed and vacuum-deposited OLEDs based on these complexes showed maximum EQEs of **7.9 %** and **14.5 %**, respectively.

Conclusion

- A new class of carbazolygold(III) complexes containing isomeric *N*-heterocyclic moieties has been designed and synthesized, in which their emission energies have been effectively tuned to span from **yellow to red**, with **high PLQYs of over 80 %** in solid-state thin films.
- The isomeric *N*-heterocyclic moieties have been found to significantly perturb the photophysical, electrochemical and EL properties. Notably, **the use of 1-thpy and 1-thq rather than 2-thpy and 2-thq moieties could render an extra stabilization to the gold(III) complexes**, leading to a long device operational stability with LT_{70} of ca. 63,200 h and LT_{50} of ca. 206,800 h at 100 cd m^{-2} in the gold(III)-based OLEDs.
- It is presented that the present work would provide important insights into the development of robust and highly luminescent gold(III) complexes, as well as the identification of stable molecular motifs for designing efficient emitters.

Reference

Li, L.-K.; Au-Yeung, C. C.; Tang, M.-C.; Lai, S.-L.; Cheung, W.-L.; Ng, M.; Chan, M.-Y. and Yam, V. W.-W. *Mater. Horiz.*, **2022**, 9, 281–293.

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Contact information

Presenter: Chai Cathay Au-Yeung (aychai@hku.hk); Corresponding authors: Mei-Yee Chan (chanmym@hku.hk), Vivian Wing-Wah Yam (wwwyam@hku.hk)