S&R 8 (10/15)

RGC Ref.: M-HKU702-12
(please insert ref. above)

The Research Grants Council of Hong Kong
SRFDP & RGC ERG Joint Research Scheme
Completion Report

(Please attach a copy of the completion report submitted to the Ministry of Education by the Mainland researcher)

Part A: The Project and Investigator(s)

1. Project Title

Phosphorescent Metal Complexes for Solar Energy Conversion Reactions

2. Investigator(s) and Academic Department/Units Involved

	Hong Kong Team	Mainland Team
Name of Principal Investigator *(with title)*	Chi Ming CHE	Zhong-Min SU
Post	Chair Professor	Professor
Unit / Department / Institution	Department of Chemistry / The University of Hong Kong.	College of Chemistry / Northeast Normal University
Contact Information	Pokfulam Road, Hong Kong.	Changchun 13000, Jilin, PRC.
Co-investigator(s) *(with title and Institution)*	Lai-Fung CHAN (Assistant Professor, The Hong Kong Polytechnic University), David Lee PHILLIPS (Professor, The University of Hong Kong)	Yun GENG (Lecturer, Northeast Normal University), Guo-Gang SHAN (Postdoctoral Fellow, Northeast Normal University)
PhD student(s) (with period of involvement)	Name: Yin-Ming NG Institution: The University of Hong Kong Period from1 March 2013 to 29 Feb 2016 Name: Qingyun WAN Institution: The University of Hong Kong Period: 1 Sept 2014 to 29 Feb 2016	Name: Shui-Xing WU Institution: Northeast Normal University Period from1 March 2013 to 29 Feb 2016 Name: Hai-Bin LI Institution: Northeast Normal University Period: 1 Sept 2014 to 29 Feb 2016 Name: Yong WU Institute: Northeast Normal University Period: 1 March 2013 to

		29 Feb 2016

Note: The Hong Kong project team must involve at least one research postgraduate student pursuing a Doctor of Philosophy degree at the UGC-funded university (PhD student) at any time throughout the project period.

3. Project Duration

	Original	Revised	Date of RGC/ Institution Approval *(must be quoted)*
Project Start date	1 March 2013		
Project Completion date	29 Feb 2016		
Duration *(in month)*	36		
Deadline for Submission of Completion Report	28 Feb 2017		

Part B: The Completion Report

5. Project Objectives

5.1 Objectives as per original application

1. To use both TDDFT / ab initio multi-configuration self-consistent field calculations and ultrafast laser spectroscopic measurements to delineate the roles of metal ions played in the generation, formation, and decay of long-lived electronic excited states.

2. To develop metal photo-catalysts including those of inexpensive 1st row transition metals.

3. To develop new metal complexes which display electronic excited states with lifetimes over hundreds of microseconds.

4. To develop highly robust, heterogeneous metal catalysts for photochemical oxidation reactions.

5. To train young scientists with skills and knowledge in Synthetic Chemistry, Computational Chemistry and Ultrafast Laser Spectroscopy and to contribute to the development of Hong Kong and Mainland China as world leading centers of excellence in the areas of Transition Metal Photo-physics and Photochemistry and Phosphorescent Molecular Materials.

5.2 Revised Objectives

Not applicable

6. Research Outcome

Major findings and research outcome
(maximum 1 page; please make reference to Part C where necessary)

The research conducted with this funding has aided the development of new classes of transition metal complexes. In essence, we have accomplished the followings:

[1] 4 publications in international chemistry journals including Chemical Communications, Organometallics, Chemistry – An Asian Journal and New Journal of Chemistry.
[2] 7 presentations on this research topic were delivered in international conferences.
[3] Both the electronic structures and binding properties of chalcogenolate-bridged molecular wheels of ruthenium and osmium $[M(ER)_2(CO)_2]_n$ (M = Ru or Os, E = S or Se, R = alkyl or aryl group, and n = 6 or 8) have been studied with DFT calculations. [New J Chem., 2013, 37, 1811] (Appendix A)
[4] A gold(III) complex having an avidin functional group has been synthesized. It shows long-lived phosphorescence with quantum yield and lifetime of up to 5 % and 115 μs respectively in solution at room temperature. Upon conjugation with biotin, the as-formed conjugate could act as staining agent for proteins and DNA, and drug carrier to organelles under cellular conditions. [Chem. Commun. 2015, 51, 8547] (Appendix B)
[5] Ir(III) complexes supported by a novel tetradentate trianionic O^N^C^O ligands and two axial neutral ligands have been synthesized and characterized. They display phosphorescence with quantum yields and lifetimes of up to 51 % and 2.5 μs respectively at room temperature. [Organometallics, accepted] (Appendix C)
[6] Cu(I) complexes displaying emission with color ranging from green to red demonstrated excellent performance in OLEDs. [Chem. Asian J., accepted] (Appendix D)
[7] Cyclometalated Pt(II) complexes $[Pt(thpy)X]^+$ has been prepared (Hthpy = 2-(2'-thienyl)pyridine; X = bis-phosphine or bis-carbene) and characterized. They exhibit dual fluorescence-phosphorescence with relative intensities being sensitive to the the auxiliary ligand X. DFT/TDDFT calculations suggest that the excitation-dependent emission behaviour arise from the difference in k_{ISC} from S_1 and S_2 to the triplet manifold. The explanation is in quantitative agreement with the results obtained from femtosecond time-resolved spectroscopic measurements. [Chem. Sci., under review] (Appendix E)
[8] Cyclometalated gold(III) alkyl complexes exhibit phosphorescence with emission quantum yields and lifetimes of up to 0.40 and 180 μs respectively at room temperature. Their capacity of acting as catalyst for light-induced oxidative C-H bond functionalization has been explored. [Inorg. Chem., under review] (Appendix F)
[9] A series of luminescent cyclometalated Pt(II) complexes were encapsulated into MOFs via cation exchange. The resultant Pt^{II}@MOFs composites displayed strong phosphorescence of ^{3}MMLCT nature. They could act as hetereogenous catalysts for dehydrogenation of alcohol to ketone and hydrogen via hydrogen atom abstraction. [Manuscript under preparation] (Appendix G)
[10] A series of *trans*-Dioxo and nitrido rhenium(V) complexes supported by bis-carbene ligands were synthesized. They exhibit room temperature phosphorescence with emission

quantum yields of up to 77 % in solutions. DFT calculations and femtosecond time-resolved spectroscopic measurements have been conducted to examine the structure of the emissive $^3[(d_{xy})^1(d_{\pi*})^1]$ excited states. Their excited state reactivities have also been examined by emission quenching and photochemical reactions with alkyl bromides. [Manuscript under preparation] (Appendix H)

Potential for further development of the research and the proposed course of action *(maximum half a page)*

The development of materials exhibiting long-lived excited state is an important area of contemporary research. By combining synthesis, computation analysis and ultrafast spectroscopic measurements, we have been able to comprehensively analyse the properties exhibited by these materials. The achievements accomplished in this project gave significant insights into the design and structure-property relationship in transition metal complexes. Given the enormous impact of this field of research, we will continue to work on the development of luminescent transition metal complexes.

7. The Layman's Summary

(describe in layman's language the nature, significance and value of the research project, in no more than 200 words)

The rational design and synthesis of new materials that can effectively absorb light and utilize the energy in organic transformations is one of the most pursued areas in current scientific research. Upon absorption of light, a material can attain a highly reactive, long-lived excited state that can perform bimolecular multi-electron and atom transfer reactions. As the lifetime of the excited species is critical to the efficiency of such light-induced event, transition metal compounds are excellent candidates for investigation because the spin-orbit coupling effect induced by the heavy metal ions can assist the effective generation of highly reactive triplet state species from singlet ground state. The aims of this project are to make new metal complexes that display long-lived triplet excited state upon light irradiation, and investigate their properties by means of spectroscopic measurement and computational studies. By combining the expertise of different research groups, we have been able to understand the structure-property relationship of these materials, which in turn aids the design of better materials for the aforementioned purposes. Their applications in light-energy conversion have also been explored.

Part C: Research Output

8. Peer-reviewed journal publication(s) arising directly from this research project

(Please attach a copy of each publication and/or the letter of acceptance if not yet submitted in the previous progress report(s). All listed publications must acknowledge RGC's funding support by quoting the specific grant reference.))

The Latest Status of Publications				Author(s) *(**bold** the authors belonging to the project teams and denote the corresponding author with an asterisk*)*	Title and Journal/ Book *(with the volume, pages and other necessary publishing details specified)*	Submitted to RGC *(indicate the year ending of the relevant progress report)*	Attached to this report *(Yes or No)*	Acknowledged the support of this Joint Research Scheme *(Yes or No)*	Accessible from the institutional repository *(Yes or No)*
Year of publication	Year of Acceptance *(For paper accepted but not yet published)*	Under Review	Under Preparation *(optional)*						
2013				YuHe Kan, Ken Chi-Hang Tso, Sharon Lai-Fung Chan,* Xiangguo Guan, Chi-Ming Che*	New Journal of Chemistry, 37, 1811-1816		Yes	Yes	Yes
2015				Johnson Lui-Lui Tsai, Anna On-Yee Chan, Chi-Ming Che*	Chemical Communications, 51, 8547-8550		Yes	Yes	Yes
	2017			Daqing Chen, Kai Li, Xiangguo Guan, Gang Cheng, Chen Yang, Chi-Ming Che*	Organometallics		Yes	Yes	No
	2017			Gary Kwok-Ming So, Gang Cheng,* Jian Wang, Xiaoyong Chang, Chi-Chung Kwok, Hongxing Zhang, Chi-Ming Che*	Chemistry – An Asian Journal		Yes	Yes	No

		V		Wai-Pong To, Glenna So Ming Tong, Chi-Wah Cheung, Chen Yang, Dongling Zhou, Chi-Ming Che*	Inorganic Chemistry		Yes	Yes	No
		V		Siu-Wai Lai, Kai Li, Glenna So Ming Tong, Chensheng Ma, Wai-Ming Kwok, Lili Du, David Lee Phillips, Chen Yang, Chi-Ming Che*	Chemical Science		Yes	Yes	No
			V	Chun-Yi Sun, Wai-Pong To, Faan-Fung Hung, Xin-Long Wang, Zhong-Min Su, Chi-Ming Che*			Yes	Yes	No

9. Recognized international conference(s) in which paper(s) related to this research project was/were delivered *(Please attach a copy of each delivered paper. All listed papers must acknowledge RGC's funding support by quoting the specific grant reference.)*

Month/Year/ Place	Title	Conference Name	Submitted to RGC *(indicate the year ending of the relevant progress report)*	Attached to this report *(Yes or No)*	Acknowledged the support of this Joint Research Scheme *(Yes or No)*	Accessible from the institutional repository *(Yes or No)*
July/2013/Michigan, USA	"Strongly Emissive Gold(III) and Platinum(II) Complexes with very Long-Lived Excited Emissive States. Molecular Design Studies, Photophysical Properties, and Applications"	The 20th International Symposium on the Photochemistry and Photophysics of Coordination Compounds (ISPPCC 20)	Yes	No	Yes	Yes
November/2013/Jeju, South Korea	"Phosphorescent Metal Complexes of Gold(III), Palladium(II) and Platinum(II) with Strongly Emissive, Long-Lived Triplet Excited States"	4th Asian Conference on Coordination Chemistry	Yes	No	Yes	Yes
July/2014/Dublin, Ireland	"Phosphorescent Metal Complexes with Long-Lived Electronic Excited States. Photophysics, Photocatalysis, and Material Applications"	ISACS13: Challenges in Inorganic and Materials Chemistry	Yes	No	Yes	Yes
July/2014/Singapore	"Luminescent Metal Complexes with a Planar Coordination Geometry"	The 41st International Conference on Coordination Chemistry (ICCC-41)	No	Yes	Yes	Yes

November/2014/Hong Kong	"Design on Strongly Phosphorescent Platinum(II) Complexes with Pincer-Type Ligands. Photophysics, Photochemistry and Applications"	UGC AoE on Institute of Molecular Functional Materials Research Symposium	No	Yes	Yes	Yes
April/2015/Shanghai	"Phosphorescent Metal Complexes"	The 5th Hong Kong-Shanghai-Muenster Joint Trilateral Symposium on Organometallic Chemistry	No	Yes	Yes	Yes
September/2015/Hong Kong	"Square Planar Metal Complexes"	Dedicated to Excellence: Hong Kong Symposium for Prof. Harry B. Gray's 80th Birthday	No	Yes	Yes	Yes

10. Student(s) trained *(Please attach a copy of the title page of the thesis.)*

Name	Degree registered for	Date of registration	Date of thesis submission/ graduation
Dr. Chunyi Sun	MPhil & Ph. D.	1 Sept 2009	31 July 2015
Mr. Xiting Zhang	Ph. D.	1 Sept 2012	31 May 2017
Mr. Chun Him Nathanael Lai	BSc (PolyU)	1 Sept 2011	
Mr. Claron Jiwen Niu	BSc (University of Chicago)	1 Sept 2014	

11. Other impact *(e.g. award of patents or prizes, collaboration with other research institutions, technology transfer, etc.)*

N.A.