DESIGN OF LUMINESCENT rE(I) AND Ir(III) COMPLEXES FOR PHOTOCATALYSIS AND STIMULI-RESPONSIVE MATERIALS

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Rational ligand design enables the development of new classes of luminescent Re(I) and cyclometalated Ir(III) complexes as efficient visible-light photocatalysts, in which systematic tuning of excited-state energetics directly translates into catalytic reactivity. Incorporation of strongly π-accepting ligands, such as isocyanoborate and isocyanoantimonate, into Re(I) diimine platforms affords charge-neutral, intensely emissive complexes with enhanced excited-state redox potentials, thereby enabling activation of a broad range of substrates under visible irradiation [1]. To further improve robustness and efficiency, photostable Re(I) platforms featuring carbene ligands have also been developed; these complexes promote photocatalytic CO_2 reduction under visible light [2], addressing a key limitation of conventional *fac*-$[Re(CO)_3(diimine)X]$ systems, which typically require UV excitation.

Complementary Ir(III) photocatalysts provide long-lived triplet excited states capable of driving challenging electron-transfer processes, including the selective activation of fluorinated alkyl halides. To improve practicality and recyclability, heterogeneous photocatalysts have been prepared by immobilizing these transition-metal complexes on solid supports [3]. By immobilizing the photocatalyst on receptor-containing solid-supported materials, selective activation of substrates can also be achieved. Emission-quenching and time-resolved studies elucidate bimolecular electron-transfer events between immobilized excited states and solution-phase substrates, establishing correlations between electron-transfer efficiency, catalytic performance, and selectivity. Finally, introduction of a related class of acyclic carbene ligands into luminescent Ir(III) complexes yields mechanochromic systems, highlighting opportunities to integrate photocatalysis with stimuli-responsive materials [4,5].

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[1] (a) W.-K. Chu, C.-C. Ko, K.-C. Chan, S.-M. Yiu, F.-L. Wong, C.-S. Lee, V. A. L. Roy, *Chem. Mater.* **2014**, *26*, 2544; (b) Y. Fan, S.-C. Cheng, S.-L. Chan, C.-C. Ko, *Inorg. Chem.* **2026**, 65, in press.

[2] (a) A. Maurin, C.-O. Ng, L.-J. Chen, T.-C. Lau, M. Robert, C.-C. Ko, *Dalton Trans.* **2016**, 14524; (b) Y. Feng, C.-O. Ng, K.-M. Tong, S.-C. Cheng, C.-C. Ko, *Energy Fuels* **2021**, 19170; (c) P.-Y. Ho, S.-C. Cheng, F. Yu, Y.-Y. Yeung, W.-X. Ni, C.-C. Ko, C.-F. Leung, T.-C. Lau, M. Robert, *ACS Catal.* **2023**, *13*, 5979.

[3] (a) Y.-L. Xiao, Y.-K. Chun, S.-C. Cheng, C.-O. Ng, M.-K. Tse, E. N.-Y. Lei, R.-Y. Liu, C.-C. Ko, *Catal. Sci. Technol.* **2021**, *11*, 556; (b) R. Liu, S.-C. Cheng, Y. Xiao, K.-C. Chan, K.-M. Tong, C.-C. Ko, *J. Catal.* **2022**, *407*, 206. (c) Y. Xiao, X. Lu, S.-C. Cheng, M.-K. Tse, J. Liang, H. Huang, W. Tu, C.-C. Ko, X. Zhu, L. Wang, Y. Zhou, Y. Yao, Z. Zou, *J. Catal.* **2023**, *426*, 52.

[4] (a) J. Han, K.-M. Tang, S.-C. Cheng, C.-O. Ng, Y.-K. Chun, S.-L. Chan, S.-M. Yiu, M.-K. Tse, V. A. L. Roy, C.-C. Ko, *Inorg. Chem. Front.* **2020**, *7*, 786; J. Han, Y.-K. Chun, S.-L. Chan, S.-C. Cheng, S.-M. Yiu, C.-C. Ko, *CCS Chem* **2022**, *4*, 2354.

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