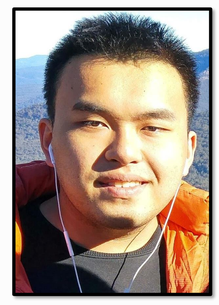
Exploring the frontiers of atom transfer radical polymerisation catalysts

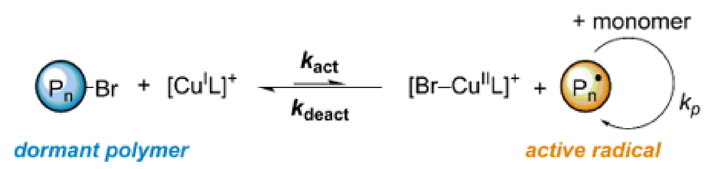
Alfred Fung, *Vincent Doan, Benjamin Noble, Michelle L Coote*

Research School of Chemistry, Australian National University, Canberra, ACT 0201, Australia
ARC Centre of Excellence for Electromaterials Science



Introduction

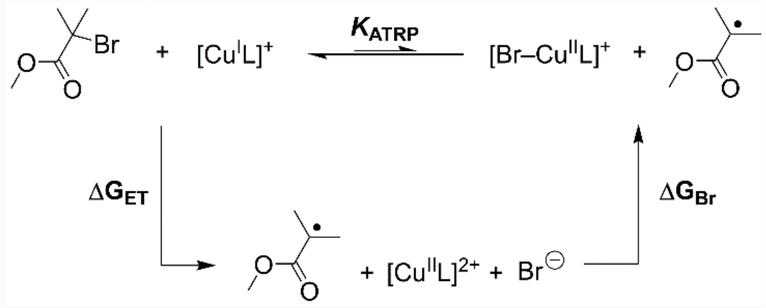
- Atom Transfer Radical Polymerisation (ATRP) is the most widely used form of Controlled Radical Polymerisation (CRP) techniques
- Reversible-deactivation of active radical chains as alkyl halides allows for control over dispersity



- In order to expand the utility of atom transfer techniques, new catalyst systems are required to expand it's substrate scope

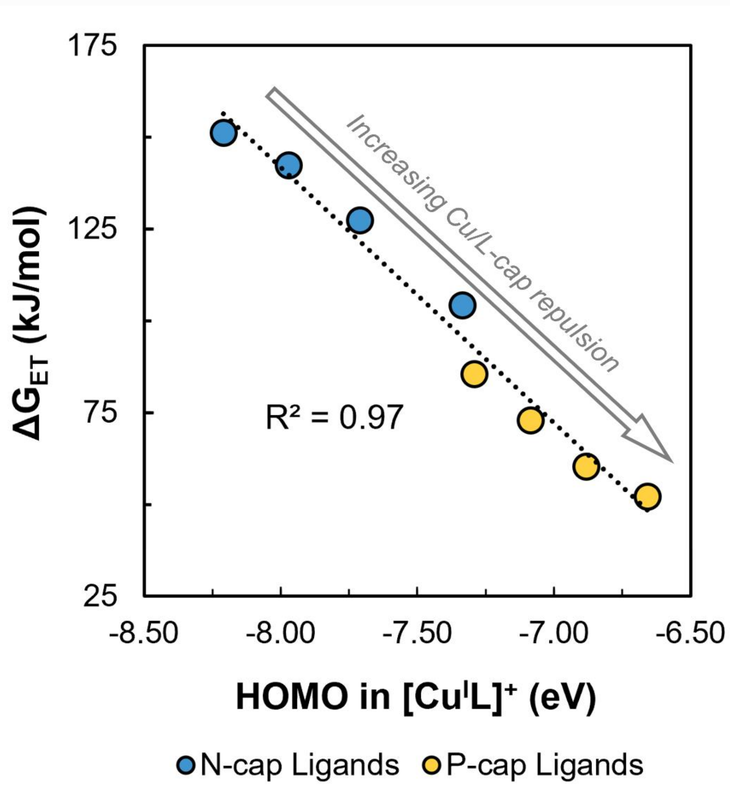
Computational Approach

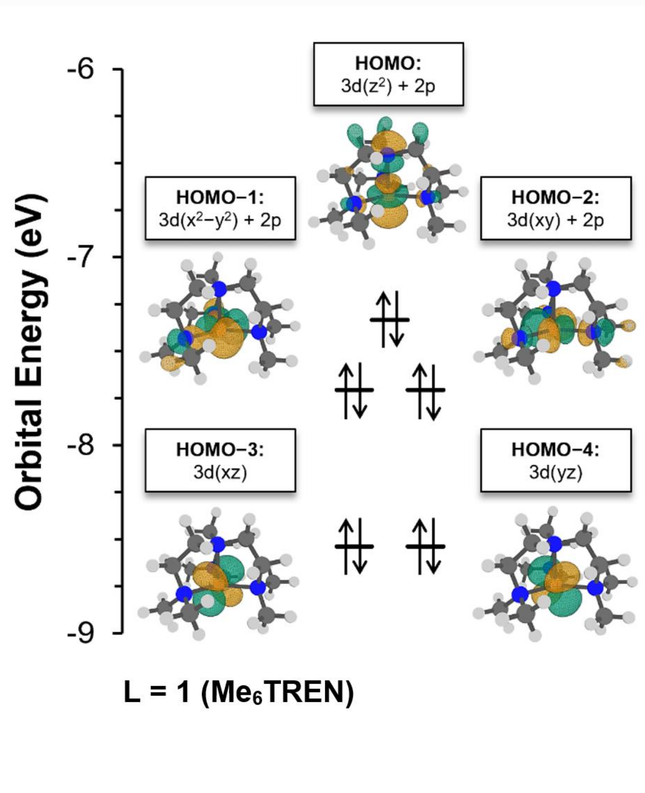
- Structure reactivity analysis used to establish the effectiveness of catalyst candidates in terms of electron transfer and halophilicity[1], Using benchedmarked methodology wB97XD/Def2TZVP and wB97XD/6-31G(d) with SSD for Cu.



Electron transfer

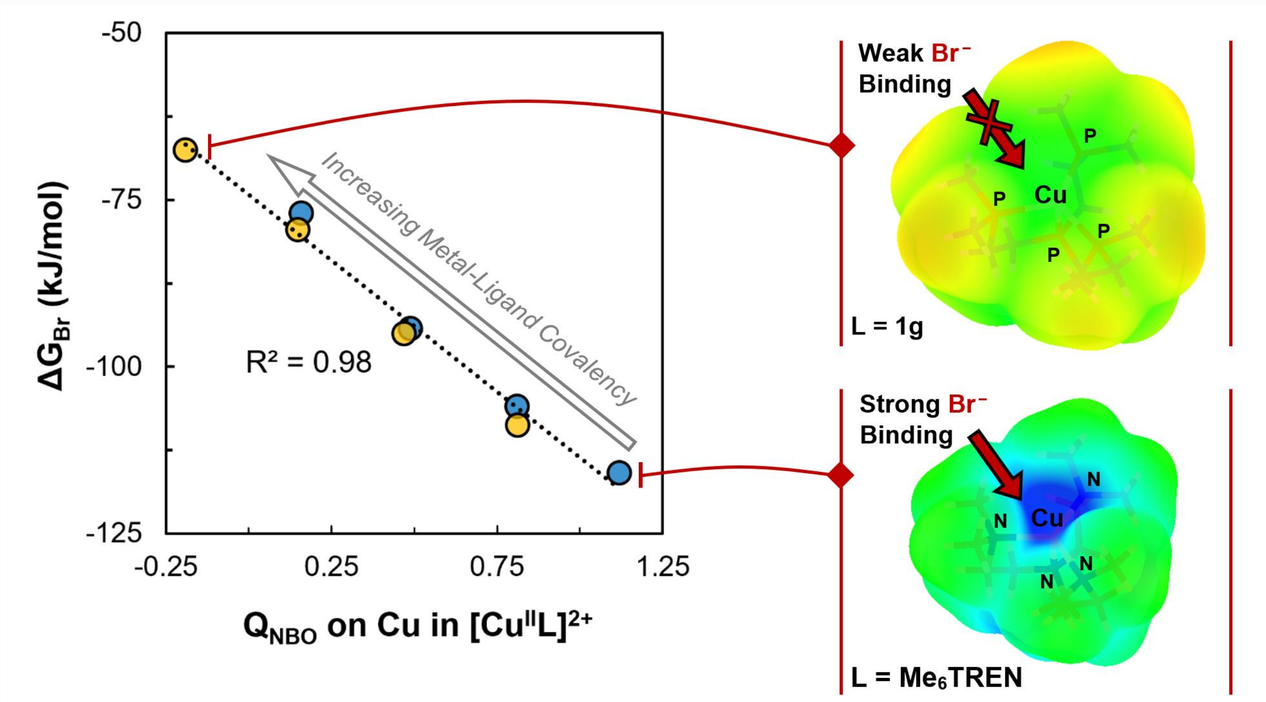
- Phosphorus substitutions upon existing ATRP ligands were designed in an attempt to improve the existing ATRP catalysts.
- Good ΔG_{ATRP} of P-capped TREN ligands originates from ΔG_{ET}.
- ΔG_{ET} strongly correlated to HOMO energy.
- Ligand cap atom forms part of the HOMO.





Halophilicity

- Phosphorus substituted ligands are out preformed by the nitrogen based ligand in terms of halophilicity.
- Br^- association is primary electrostatic.
- Retro-donation of electron density impairs halophilicity
- P-substitution reduces charge on Cu atom, regardless of position.
- No significant '*trans-influence*' from ligand cap.



Summary

- Both electron transfer and halophilicity plays an instrumental role to the overall K_{ATRP}
- The incorporation of phosphorus requires delicate balancing between ΔG_{ET} and ΔG_{Br}

Future Work

- Use the current design prompts to improve ΔG_{ET} and ΔG_{Br}
- Design and synthesise a new class of ATRP catalysts

1. Vincent Doan, Benjamin B. Noble, Alfred K.K. Fung, and Michelle L. Coote *The Journal of Organic Chemistry* **2019** *84* (23), 15624-15632 DOI: 10.1021/acs.joc.9b02915