Low-cost catalyst for light-activated radical polymerisation

Radical chemistry has greatly affected polymer science, allowing an increasingly large diversity of polymers to be made robustly and reliably. More recently, with the development of reversible deactivation radical polymerisation (RDRP), polymers can be synthesised with controlled and near uniform molecular weights, allowing precision at the atomic scale. The continual introduction of novel photocatalytic radical chemistry into existing RDRP processes has led to a rapidly propagating area of polymer research in recent years. The Polymer Nanostructures Group at the University of Sydney, led by Markus Müllner, has recently introduced bismuth oxide (a visible band gap semiconductor) as a heterogeneous photocatalyst for polymerisation by photo-induced electron transfer (PET) that operates at room temperature and with visible light (Hakobyan K., Gegenhuber T., McErlean C.S.P., Müllner M. Angew. Chem. Int. Ed. 2019, 58, 1828-32). Bismuth oxide introduces favourable properties to PET-RDRP, such as low toxicity, reusability, low cost, and ease of removal from the reaction mixture. Formidable control normally associated with degenerative chain-transfer polymerisations, such as macromolecular design by interchange of xanthate (MADIX) and reversible additionfragmentation chain-transfer (RAFT) polymerisation, was observed. Homopolymers and diblock copolymers with differently activated monomers were successfully synthesised, while the PET process allowed excellent temporal control of the polymerisations.





Altering photochemistry with static electric fields

It has recently been shown that static electric fields can be used to catalyse non-electrochemical reactions, opening up a new approach to chemical catalysis. Now, researchers at the Australian National University have expanded electrostatic catalysis into the realm of molecular excited states. Using state-ofthe-art computational methods, they have shown that static electric fields can be used as an approach to modifying the relative energies of different types of excited state in a predictable and significant manner (Hill N.S., Coote M.L. J. Am. Chem. Soc. 2018, 140, 17800-4). They showed that the energies of two

types of excited state with different wavefunction symmetries can be altered in opposite directions, providing the ability to invert their ordering, in order to enhance certain desirable photochemical properties. These field effects can be harnessed using carefully placed charged functional groups (CFGs) in the form of acids or bases, which can be turned on or off by simple changes in pH. These oriented electric fields could allow the design and synthesis of a new generation of highly efficient photoactive molecules that may find application in a wide range of industrial, synthetic, and biochemical applications.

Relating structure and charge transfer in electroactive MOFs

A key structural feature of photosynthetic organisms such as purple bacteria is a cofacially arranged photoreaction trap, often described as the 'special pair'. This cofacial system plays a vital role in facilitating the conversion of light to chemical energy, by stabilising the photo-excited mixedvalence radical state through a process called intervalence charge transfer (IVCT). This intriguing phenomenon has been the focus of a number of qualitative biomimicry studies using discrete organic molecules, mostly based on porphyrin derivatives. However, quantitative experimental and theoretical studies on model inorganic systems have been limited. Recent research led by Deanna D'Alessandro from the University of Sydney with colleagues Bowen Ding, Carol Hua and Cameron Kepert has now demonstrated subtle structure-function relationships that govern through-space IVCT in metalorganic frameworks (MOFs) with

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cofacially aligned ligands (Ding B., Hua C., Kepert C.J., D'Alessandro D.M. *Chem. Sci.* 2019, **10**, 1392–400). This work follows a previous report from the same group that revealed a new mechanism for charge transfer interactions in MOFs (*J. Am. Chem. Soc.* 2018, **140**, 6622–30). Uncovering structure–activity relationships in MOF materials that emulate processes in natural systems, and establishing methods for quantifying their charge transfer properties, represents an important advance in fine tuning solidstate materials for device applications.