Catalytic molecular motors: fuelling autonomous movement by a surface bound synthetic manganese catalase†

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A molecular approach to the powering of multi-component nano-devices capable of autonomous translational and rotational motion through the conversion of chemical to kinetic energy is reported.

The effective use of nano- and microscale machinery capable of driving linear and rotary motion is essential to the proper functioning of living cells. The construction of artificial molecular machines, ubiquitous in nature, remains, however, a major contemporary challenge. The recent development of molecular based systems including shuttles, rotors, muscles, switches, elevators, motors and processive catalysts has brought the prospect of synthetic molecular based ‘mechanical machines’ within sight. Nevertheless the required ‘fuelling’ of the motion of these molecular systems remains a major hurdle. Indeed, central to the function of nanoscopic (e.g. ATP-synthase, which employs H\(^+\) gradients) and macroscopic (e.g. ATP-driven actin filaments in muscle tissue, controlled by Ca\(^{2+}\) gradients) molecular devices employed by nature is the ability to convert chemical to mechanical energy. Although light-powered molecular devices, such as the first molecular motor capable of performing repetitive unidirectional rotary motion, developed in our group, hold considerable potential towards driving changes in wholly molecular systems, as demonstrated recently in liquid crystal films, the movement of larger assemblies (i.e. 10\(^{-4}\)–10\(^{-9}\) m) requires concerted action of several molecular motors or significantly greater power to effect rotational and translational motion. The high power density required might be achievable through the use of chemical energy. Indeed Kelly and coworkers have demonstrated that rotary motion can be induced by sequential chemical conversions. An attractive alternative to the application of complex chemical transformations to drive molecular devices is provided by the approach taken recently by the groups of Whitesides, Sen, Mallouk and Crespi, and Ozin and Manners, in which the decomposition of H\(_2\)O\(_2\) on the surface of microscopic composite (bi-)metallic objects is employed to achieve translational and/or rotational movement through the creation of localised [O\(_2\)] gradients. The nature of the motion induced by this approach was found to be critically dependent on both the particle dimensions and the ability to localise the production of O\(_2\). The use of a synthetic oxygen evolving complex might be of considerable advantage to future (non-metallic) micro- and nanoscale molecular machines, as it can be easily (chemically) modified, tether length can be adjusted, and local catalyst density is controllable. Furthermore, it offers the possibility to control oxygen evolution down at the molecular level. A synthetic molecular system capable of chemically driven motion still remains a major hurdle, however, due to the requirement to be able to immobilise molecular catalysts on particles with retention of catalyst function. Furthermore the integrity of the multicomponent system created must not be compromised during the conversion of chemical to kinetic energy.

Here, we report our preliminary results on autonomous movement of microparticles (μ-particles) via a [covalently] tethered synthetic catalase mimic. The design (Fig. 1) of a molecular based device capable of converting chemical energy to kinetic energy, comprises three key elements: an object (micro- or nanoparticle, complex or macro-molecule) to be transported, a spacer/tether and a catalyst for converting chemical energy to kinetic energy. The new highly efficient catalase mimic, [(Mn(II)(L\(_2\))\(_2\)(RCO\(_2\))\(_2\))]\(^+\) (I) (where HL is 2-[[di(2-pyridyl)methyl]amino][methyl]phenol) developed within our group, is well suited to such a role. Its high rate of disproportionation of H\(_2\)O\(_2\) to H\(_2\)O and O\(_2\) (i.e. catalase activity) and the ability to attach the catalyst covalently, through either the ligand L\(^-\) or more promisingly the bridging carboxylate group, allows for facile fixation to the surface of nano- and micro-scale objects through chemical modification.

Designed as a functional model for dinuclear Mn-catalase enzymes, ligand HL, bearing a phenol, tertiary amine and two pyridine binding sites, was synthesised. Complexation with Mn(CIO\(_2\))\(_2\) in the presence of carboxylic acids provided dinuclear Mn\(_{10}\)Mn\(_{10}\)-complexes 1a and 1b (Scheme 1). X-ray analysis of the benzoate complex 1a confirms the bridging nature of the phenolates and the carboxylate (Fig. 2, see also ESI†). The ability of 1 to catalyse H\(_2\)O\(_2\) disproportionation was demonstrated in several solvents with turn over frequencies (T.O.F.) of ~0.27 s\(^{-1}\) at 25 °C (i.e. CH\(_3\)CN, 30% aq. H\(_2\)O\(_2\)).

![Fig. 1](image-url) Design of a system propelled by a catalase mimic.
Covalent immobilisation of the catalyst via the bridging carboxylate ligand was achieved using the p-formyl-functionalised complex 1b, which was attached to aminopropyl-modified silica microparticles (40–80 µm) in ethanol–acetonitrile through imine formation (Scheme 2). Multiple rigorous washing steps (EtOH, CH3CN, CH2Cl2 and Et2O) of the µ-particles were performed to remove residual, non-covalently bound, complex 1b. The modification of the µ-particles via an imine bridge was confirmed by IR spectroscopy and electrochemistry (see ESI†), through comparison of the aminopropyl-functionalised particles, its iminobenzoic acid analogue, and the particles functionalised with 1b as well as free complex. The immobilised catalytic system obtained was found to be robust to detachment (i.e. retains activity, IR and redox properties are unaffected, see ESI†) from the µ-particles and exhibited high activity towards H2O2 disproportionation as observed with the free catalyst (e.g. 1a). The modified particles were recoverable by filtration and could be recycled several times without significant loss in activity. The characteristic imine absorption at 1645 cm⁻¹ is not affected by H2O2 decomposition and IR spectra of functionalised µ-particles are unaffected by catalase activity. Kinetic and thermodynamic parameters of H2O2 decomposition by functionalised µ-particles as well as free complex 1b (5 wt%) were obtained by Eyring plot analysis,¹⁹ showing first order kinetics (w.r.t. [H2O2]) with large negative entropy of activation (kₐ = 3.09 × 10⁻³ s⁻¹, ΔS° = -288.62 J K⁻¹mol⁻¹ for the free complex 1b and kₐ = 1.51 × 10⁻³ s⁻¹, ΔS° = -291.07 J K⁻¹mol⁻¹ for the 1b-functionalised microparticles).

In order to study the movement induced by O₂ formation, a thin liquid film, containing a dilute suspension (in CH3CN or glycerol) of the 1b-functionalised µ-particles, mixed with non-functionalised µ-particles (40–80 µm) as reference, on a microscope glass slide, were monitored after addition of a 5% H2O2 solution in CH3CN. O₂ evolution was observed as small O₂ bubbles appearing on only the catalyst-functionalised µ-particles. Both linear and rotary

Scheme 1

Fig. 2 X-ray structure of 1a.

Scheme 2
The measured rotational speed for the depicted particle is 1.55 rad s\(^{-1}\). This motion can also be observed in the more viscous solvent glycerol (Fig. 4).

Interestingly, the autonomous movement of micro-sized particles is induced. The exact mechanism by which propulsion of the particles takes place (recoil from \( \text{O}_2 \) bubbles\(^{13}\), interfacial tension gradient\(^{13}\)) and the parameters governing the dynamics of the system need further investigation. The principle introduced here, to use a designed molecular catalyst to induce motion, is currently explored in the controlled motion of nanoparticles and functional molecules.

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Notes and references

17. Chemical formula: \([\text{C}_{62}\text{H}_{41}\text{Mn}_{2}\text{N}_{5}\text{O}_{40}\text{Cl}_{2}O_{2}]^{+}\); \( M = 939.18 \text{ g mol}^{-1}\); Unit cell dimensions \( a = 15.226(2) \text{ Å} (\alpha = 90^\circ), \ b = 12.924(2) \text{ Å} (\beta = 115.157(9)^\circ), \ c = 10.946(4) \text{ Å} (\gamma = 90^\circ), \ V = 2153.6(6) \text{ Å}^3; T = 130 \text{ K}; \) monoclinic C2; \( Z = 2; \gamma (\text{Mo } K_\alpha) \text{ cm}^{-1} = 7.1; \) \( wR(F) = 0.0778 \text{ for } 4691 \) reflections with \( F^2 \geq 0 \text{ and } R(F) = 0.0303 \text{ for } 4481 \) reflections with \( F^2 \geq 4 \sigma(F) \text{ and } 375 \) parameters, Flack parameter \( (X) = 0.428(15) \); CCDC number 268595. See http://wwrsc.org/suppdata/cc/b/b5b50502/h for crystallographic data in CIF or other electronic format.
18. \( \text{CH}_2\text{Cl}_2, \text{MeOH}, \text{CH}_3\text{CN} \text{ and glycerol were tested and gave satisfactory results.} \)