HIGH STABILITY MOLECULAR NON-LINEAR OPTICAL SWITCHES BASED ON POLYOXOMETALATES

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Nothing travels faster than light. For this reason, optoelectronic and all-optical computing and telecommunications promise revolutionary increases in performance: through greater speed, higher parallelism and lower energy consumption.[1] The potential is well illustrated by the far higher speed and bandwidth achieved by fibre optic telecommunications *vs* copper wire. To realise light-based devices, however, new materials are required for construction of miniaturized optical and optoelectronic components. In particular, optical computers will need optical transistors (switches), able to modify the properties of an incoming laser light beam in response to an external electrical or optical stimulus (Figure 1).

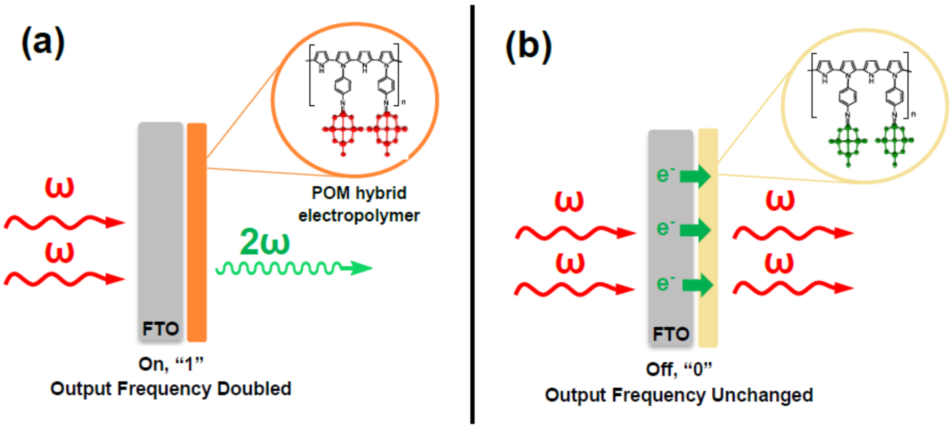

Figure 1 Prototype optoelectronic switch, consisting of an NLO active POM electropolymer on a conductive glass support: **(a)** Oxidized, "On" state, the incoming laser beam is frequency doubled by the polymer; **(b)** Reduced, "Off" state, where one-electron reduction switches off the NLO activity.

Non-linear optical (NLO) materials enable doubling or tripling of the frequency of laser light, and so can form the basis of optical switches.[2] However, materials with the required combination of a rapid and strong NLO response, rapid high contrast photo- or redox switching, near infinite stability to on-off cycling, and low cost are elusive. We are developing organoimido polyoxometalates (POMs), based on earth abundant elements, as redox-active NLO chromophores that can be electropolymerized to form prototype optoelectronic switches. Because POMs accept electrons with no structural change,[3] electron transfer occurs rapidly and their reduced states are stable. We recently performed the first experimental measurements of 2nd order NLO (frequency doubling) coefficients, and the first spectroelectrochemical measurements, on such species.[4] These indicate that significant non-linearities result from strong ligand-to-polyoxometalate charge transfer transitions, which can be completely extinguished, and completely regenerated by electroreduction and oxidation of the $\{NMo_6O_{18}{}^{2-/3-}\}$ acceptor unit. Thus, the materials are a promising starting point for molecule-based NLO switches.

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