Photochromic Molecular Assemblies of Polyoxometalates and Diarylethenes

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Polyoxometalates (POMs) are molecular metal oxides composed of predominantly early transition metals in high oxidation states, however, there are now numerous exceptions. The remarkable structural, compositional, and resulting electronic diversity of POMs is undeniable and is responsible for these compounds attracting general interest across the sciences. ^[1-2] Intrigued by the opportunity that the combination of DAEs and POMs in a molecular assembly would present to investigate this balance of photochemical processes, we designed and prepared hybrids bringing together these components. In this presentation, I will discuss our experimental findings in terms of the solid-state properties, structure and stability in addition to the photochemical behaviour of the resulting compounds following excitation.

By using the molecular metal oxide $\{PMo_9O_{31}\}\$ as a building block, we have successfully taken advantage of well-defined surface reactivity that supports the ordering of ligands in the assembly *via* directional intramolecular contacts between the ortho hydrogen atoms of the pyridyl groups of the DAE and the adjacent terminal oxido ligands. In terms of molecular design, the principle objective was to mitigate coordination of the photochemically inactive (O_P) isomer, which was achieved due to steric implications imposed by $\{PMo_9O_{31}\}$, akin to our previous report using an alternative POM scaffold with only one point of coordination. ^[3-4]

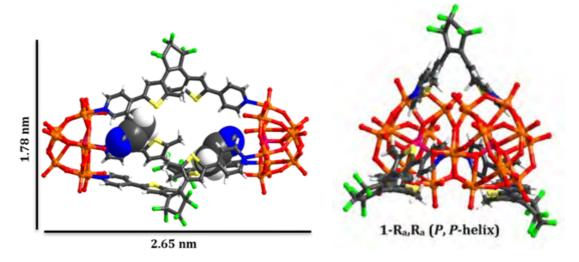


Figure 1. Graphical representation of the molecular capsule [(PM09O31)2(DAE)3]⁶⁻

[1] Gumerova, N., Rompel, A. (2018) Synthesis, structures and applications of electron-rich polyoxometalates, *Nat Rev Chem* **2**, 0112.

[2] Gao, Y., Choudhari, M., Such. G. K., Ritchie, C. (2022) Polyoxometalates as chemically and structurally versatile components in self-assembled materials, Chem.Sci., 13, 2510-2527.

[3] Xu, J., Volfova, H., Mulder, R. J., Goerigk, L., Bryant, G., Riedle, E., Ritchie, C. (2018) Visible-Light-Driven "On"/"Off"

Photochromism of a Polyoxometalate Diarylethene Coordination Complex, J. Am. Chem. Soc. 140, 33, 10482–10487.

[4] Choudhari, M., Xu, J., McKay, A., Guerrin, C., Forsyth, C., Ma, H. Z., Goerigk, L, O'Hair, R. A. J., Bonnefont., A.,

Ruhlmann, L., Aloise, S., Ritchie, C. (2022) A photo-switchable molecular capsule: sequential photoinduced processes, Chem. Sci., 13, 13732-13740.