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Flow-based Methodologies for Synthesis of Complex Chemical Structures

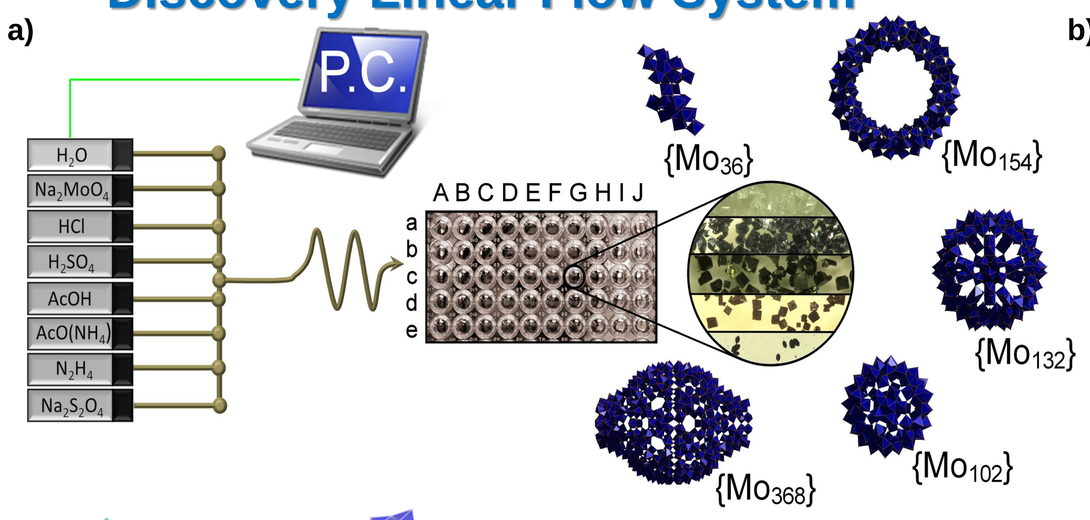
Introduction

In recent years, new methodologies for the synthesis of polyoxometalates (POMs) have gained importance. In early 2010, a paper was published in Science where it was demonstrated that a flow system can lead to interesting effects in the self-assembly processes of polyoxometalates.[1] Hence, new flow-based approaches are being devised as new methodologies for synthesizing a wide range of different inorganic structures and studying complex systems. To demonstrate these new synthetic approaches, two flow setups have been designed to screen reaction parameter space to explore the self-assembly processes occurring in complex chemical structures.

Discovery Linear Flow System

A conventional linear flow system (Figure 1a) has been setup to apply discovering the array and perform ratio-dependent reaction conditions for complex inorganic structures. As shown in Figure 1b, a general flow approach for giant molybdenum-based POMs such as $\{Mo_{154}\}$, $\{Mo_{132}\}$ and $\{Mo_{368}\}$ have been achieved.[2]

Discovery Linear Flow System



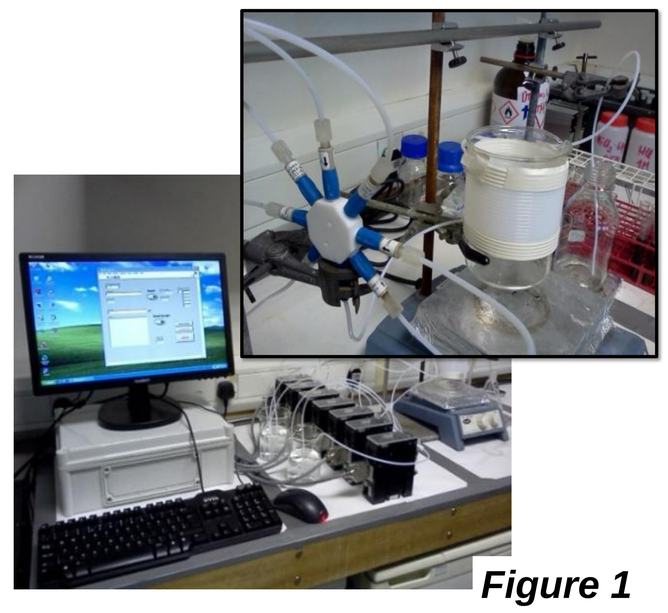
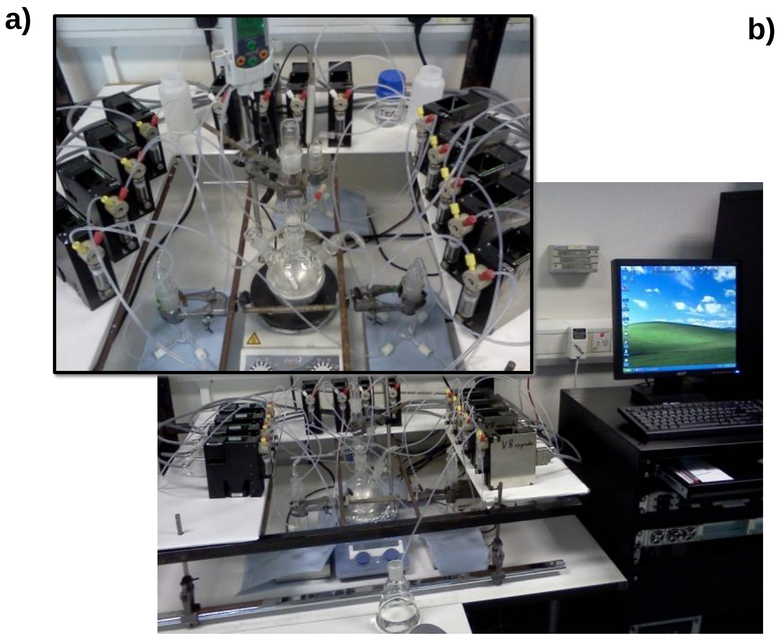


Figure 1

Networked Reactor System



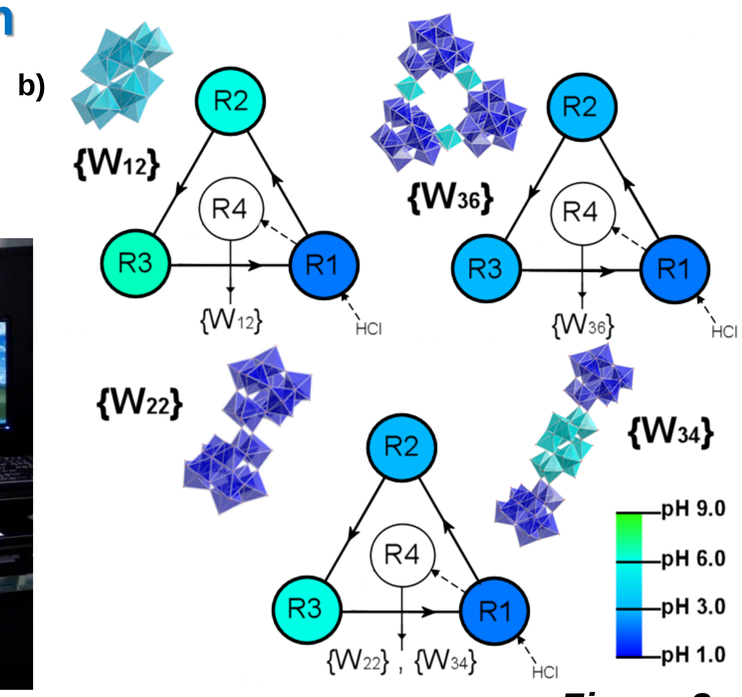


Figure 2

Networked Reactor System

A novel concept of networked 'one-pot' reaction array (Figure 2a) has been employed not only for synthesizing inorganic materials (i.e. POMs) but also for studying reaction networks in such complex chemical systems. As shown in Figure 2b, a wide range of structurally related isopolyoxotungstates (iso-POTs) have been successfully synthesized taking advantage of combining flow and batch conditions.

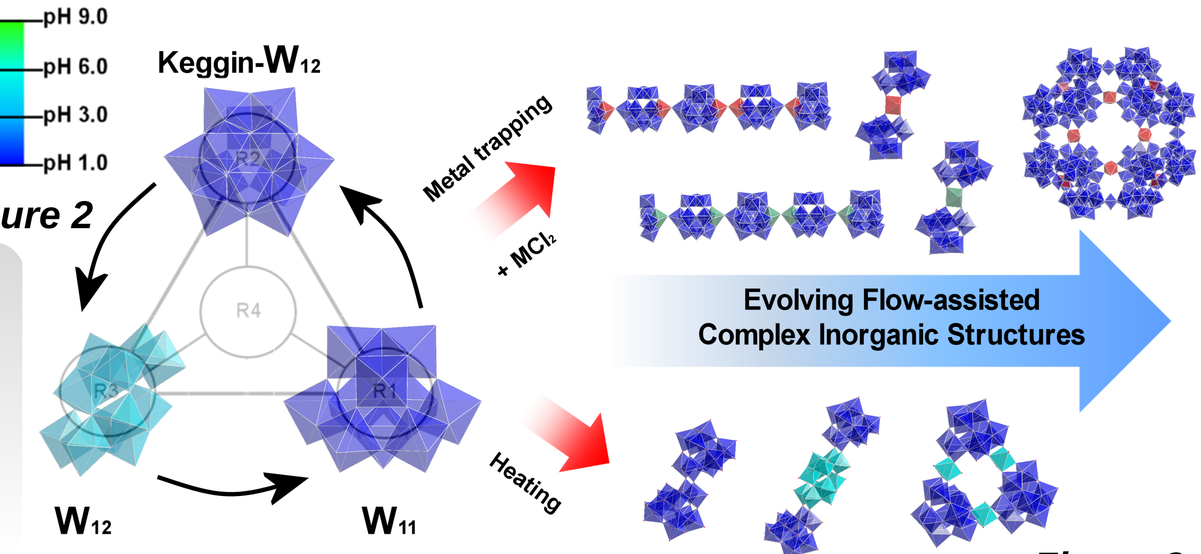


Figure 3

Complex Chemical Structures

As depicted in Figure 3, the NRS enables us to observe and explore transient nano-sized structures, by adding metal chloride salt (MCl_2) to the tungsten-based building block clusters, which gives the products by flow-assisted metal trapping-type process for large polyoxometalates. The UV monitoring (Figure 4a in R3, 4b in R1) and pH tuning in NRS has allowed the isolation of the biggest tungsten-based nano-sized $[H_{16}W_{200}Co_8O_{660}(H_2O)_{40}]^{88-} \equiv \{W_{200}Co_8\}$, as product of a multiple metal-trapping process (Figure 5).[3]

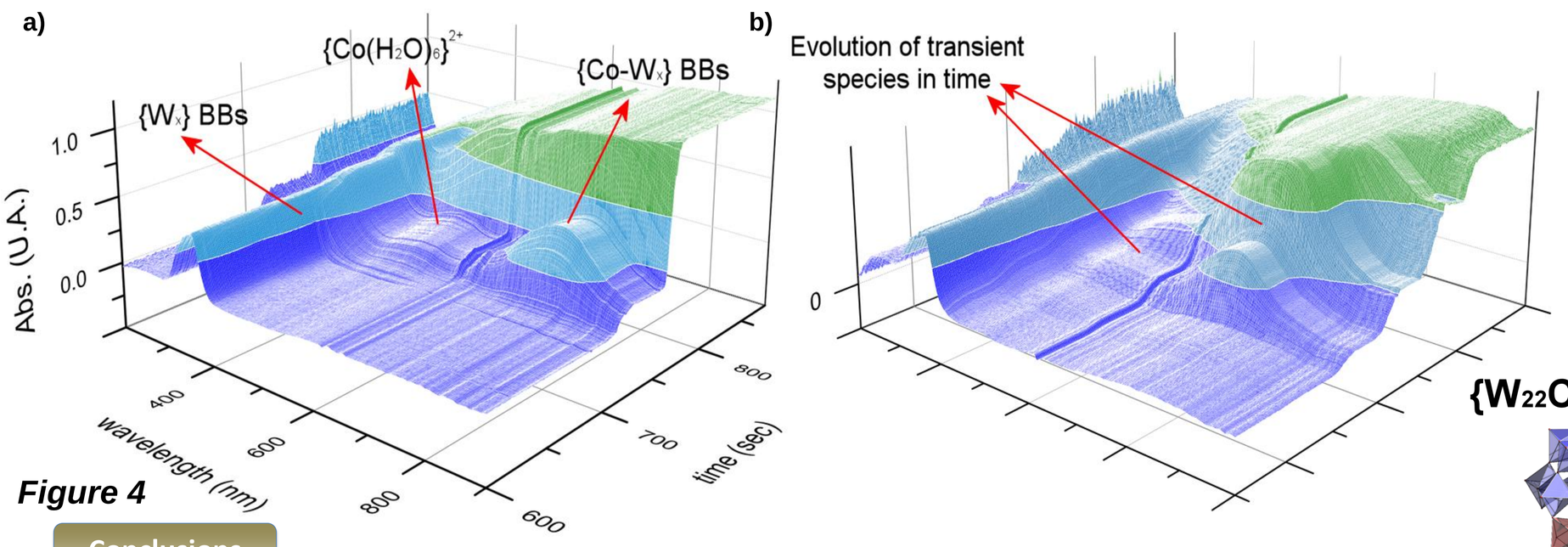


Figure 4

Conclusions

Two flow-based approaches are presented for synthesis of inorganic materials (i.e. polyoxometalates) allowing the discovery of nano-sized structures by screening the reaction parameters in a fundamentally new way. Additionally, the NRS allows us to perform 'one-pot' networking reactions efficiently and, simultaneously, online measurements for monitoring a real control over the self-assembly in polyoxometalates.

References

[1] Haralampos N. Miras, Geoff J. T. Cooper, De-Liang Long, Hartmut Bögge, Achim Müller, Carsten Streb, Leroy Cronin *Science* **2010**, 327, 72-74.

[2] Craig J. Richmond, Haralampos N. Miras, Andreu R. de la Oliva, Hongying Zang, Victor Sans, Leonid Paramonov, Charalampos Makatsoris, Ross Inglis, Euan K. Brechin, De-Liang Long, Leroy Cronin *Nature Chemistry* **2012** (in press).

[3] Andreu R. de la Oliva, Victor Sans, Haralampos N. Miras, Jun Yan, Hongying Zang, Craig J. Richmond, De-Liang Long, Leroy Cronin *Angewandte Chemie International Edition* **2012** (submitted).

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