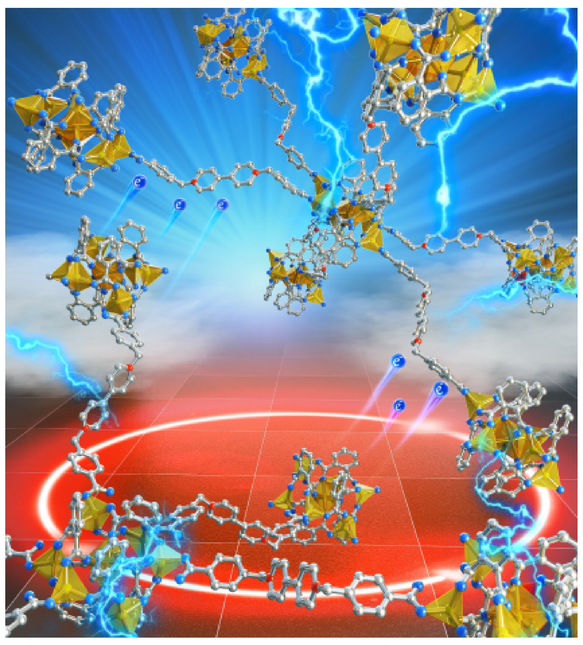
J. Am. Chem. Soc., 2019, DOI:10.1021/jacs.9b04930



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X-ray and UV Dual Photochromism, Thermochromism, Electrochromism, and Amine-Selective Chemochromism in an Anderson-like Zn_7 Cluster-Based 7-Fold Interpenetrated Framework

(J. Am. Chem. Soc.2019, DOI:10.1021/jacs.9b04930)

Abstract

Smart materials are highly desirable over the recent decade due to the growing demand of complicated nature. Stable stimuli-responsive smart materials exhibit widespread potential for applications in smart windows, sensors, separators, chemical valves, and release platforms but are rare. Despite being good candidates, viologen-based multifunctional smart materials are still a challenging task for chemists. To obtain such materials, the judicious strategy is to introduce polynuclear metal–carboxylate clusters as electron donors into a stable framework to increase chromic sensitivity. Toward this endeavor, we have synthesized a novel viologen-based polymer with a unique Anderson-like metal–carboxylate cluster, $[Zn_7(bpybc)_3(o\text{-}BDC)_6]\cdot 2NO_3\cdot 6H_2O$ (bpybc = 1,1′-bis(4-carboxyphenyl)-4,4′-bipyridinium, o-BDC = *o*-benzenedicarboylic acid) (**1**), which is a particular 7-fold interpenetrated framework with a 3D **pcu** network in which bpybc ligand as the linker and $Zn_7O_{30}C_{12}$ as the second building unit (Zn_7 SBU) were used as 6-connected nodes. More importantly, it shows excellent chromic behavior in response to multiple external stimuli especially soft X-ray and UV dual light, temperature, electricity, and organic amines, which stand out in the viologen-based polymers. Interestingly, the coloration process of **1** from “core” to “edge” is observed upon heating at the appropriate temperature, which has not yet been found in other reported thermochromic materials. Of particular interest for **1** is the couple of quaternary stimuli-sensitive abilities because it simultaneously meets the following conditions: (i) the capability of withstanding high light, higher temperature, extreme pH, and other harsh conditions; and (ii) the high sensitivity to external stimuli keeping away from photodegradation, thermal relaxation, side reactions, and so on. To be noted, **1** has high thermal stability and chemical stability, which are excellent advantages as smart materials. To further develop possible practical utilization, **1** has been doped into the polymer matrixes to construct a hybrid film, which not only keeps the response to external stimuli but also significantly improves the repeatability of the photochromic process, indicating that a new smart device with multi-stimuli-responsive functions will emerge successively in the future.

文章全文链接：https://pubs.acs.org/doi/10.1021/jacs.9b04930

上一篇： Appl. Catal. B: Environ., 2019, 243, 175-182
下一篇： Applied Catalysis B: Environmental, 2019, 243, 693-702