

Review

Designing bipyridine-functionalized zirconium metal–organic frameworks as a platform for clean energy and other emerging applications



Thach N. Tu^{a,b}, My V. Nguyen^{a,c}, Ha L. Nguyen^{a,d}, Brian Yulianto^e, Kyle E. Cordova^{d,f}, Selçuk Demir^{g,*}

^a Vietnam National University–Ho Chi Minh City (VNU-HCM), Ho Chi Minh 721337, Viet Nam

^b Bach Khoa University, VNU-HCM, Ho Chi Minh 721337, Viet Nam

^c University of Science, VNU-HCM, Ho Chi Minh 721337, Viet Nam

^d Center for Research Excellence in Nanotechnology, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

^e Research Center of Nanosciences and Nanotechnology, Institut Teknologi Bandung, Bandung 40132, Indonesia

^f Berkeley Global Science Institute, University of California, Berkeley, Berkeley, CA 94720, USA

^g Department of Chemistry, Faculty of Arts and Sciences, Recep Tayyip Erdogan University, Rize 53100, Turkey

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ABSTRACT

Metal–organic frameworks (MOFs) are a class of crystalline and porous materials with modular structural features. This modularity has allowed MOFs to be designed and synthesized with adjustable pore sizes and shapes leading to ultrahigh porosity. Among the tens of thousands of known MOF structures, zirconium-based MOFs (Zr-MOFs) have attracted attention not only for their structural properties but also their superior chemical and thermal stabilities, which are critical for a myriad of practical applications. In particular, bipyridine (BPY) functionalized Zr-MOFs have been received recognition for their interesting intrinsic properties, which arise from various post-modification pathways. The fact that post-modification is readily available for such MOFs paves the way towards anchoring specific components (functional groups, metal complexes, and nanoparticles) via the bipyridine docking centers, thus endowing this MOF platform with the capability to chemically alter and enhance the bulk material's properties. Throughout this review, an emphasis is placed on the preparation of BPY-functionalized Zr-MOFs, their characterization, and subsequent applications, such as electrocatalytic or photocatalytic hydrogen evolution reactions, heterogeneous molecular catalysis, and gas storage for renewable energy. Furthermore, this review highlights the design and applications of materials from the viewpoint of materials design and the necessity and importance of installing complexity to achieve synergistic interactions. Finally, our perspective for future applications is introduced with the expectation of providing useful information to those interested in this specific MOF platform.

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* Corresponding author.

E-mail address: selcuk.demir@erdogan.edu.tr (S. Demir).

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1. Introduction

Metal–organic frameworks (MOFs), a new generation of highly advanced porous materials, provide a platform for solving global environmental problems. The beauty of MOF materials, which are governed by the principles of reticular chemistry, lies in the fact that the proper selection of constituent building blocks results in designable crystal structures owning adjustable pore sizes and shapes, and tunable internal chemical environments [1]. These features have endowed MOFs with the ability to be applied to a range of applications, including gas storage and separation [2,3], catalysis [4], drug delivery [5], proton conducting applications [6,7], and molecular sensing [8]. Recently, zirconium-based MOFs

(Zr-MOFs) have gained much interest not only due to their high thermal and chemical stability, which are vastly superior to other known MOFs, but also because of their performance in a variety of applications, including catalysis and clean energy (Fig. 1) [9–13]. Together with the advances in the synthesis of new MOF materials [14–17] adopting diverse topologies [18–23], significant efforts have focused on decorating and post-synthetically functionalizing the interior surface of Zr-MOFs for enhancing their performance in specific, novel applications. Among these, bipyridine-functionalized (BPY) Zr-MOFs have stood out primarily due to the ability to modify their structures through various post-synthetic modification pathways in order to anchor specific components (functional groups, metal complexes, nanoparticles) via

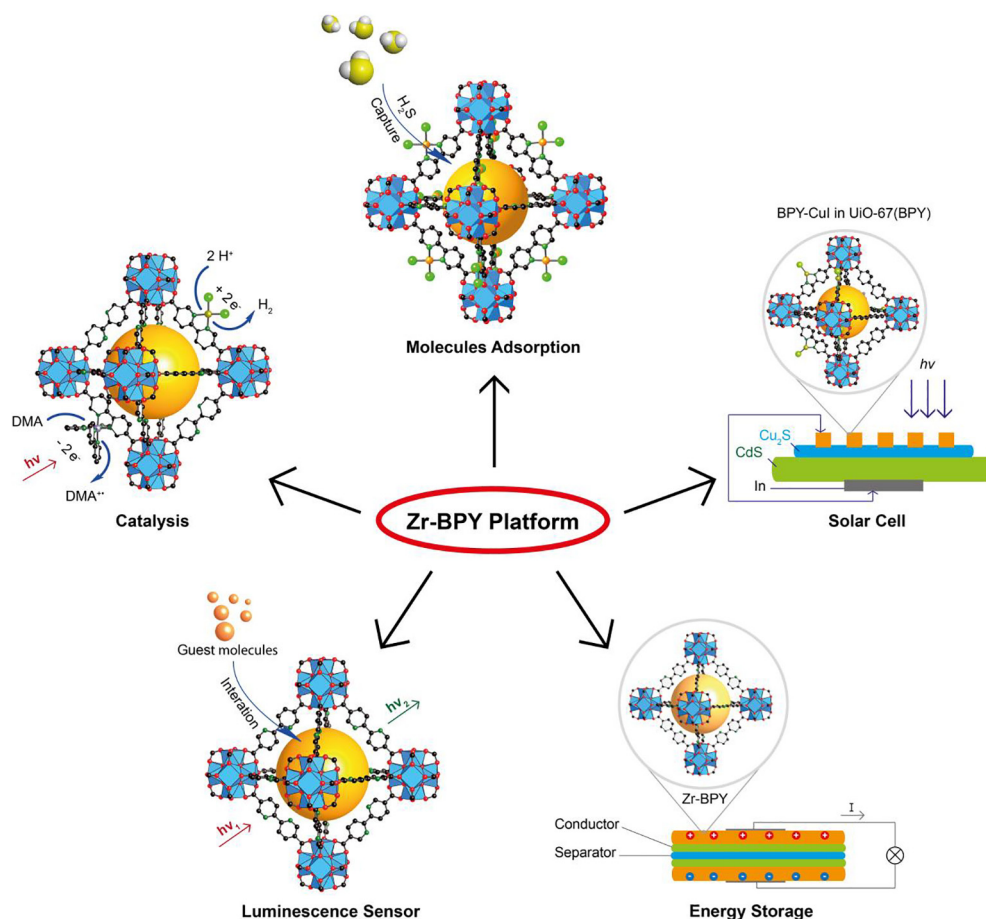


Fig. 1. Schematic illustration of different pathways toward applications of UiO-67(BPY).

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