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Impacts of host-guest assembly on photophysical and photocatalytic properties of heterogenized molecular photosensitizer and catalysts

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Abstract

This review focuses on taking porous matrixes as 'molecular containers' to tune and regulate photophysical and photocatalytic properties of molecular photosensitizers and catalysts for application in solar energy conversion. The host-guest assemblies feature with a physical separation of catalytic sites as well as a precise preorganization of photosensitizer and catalytic species in close spatial proximity. The host-guest effects on the photophysical processes, such as energy dissipating nonradiatively or radiatively and photoinduced energy- or electron-transfer, and on the photocatalytic processes, such as regulating mass transfer, diverting reaction pathway with preferable intermediate species, and modulating reaction dynamics, are demonstrated. The geometrical confinement of molecular catalysts and photosensitizers to construct the enzyme-like microenvironments, provides a promising avenue to mimic the sophisticated natural photosynthesis.

Keywords: host-guest effect, molecular photosensitizer, molecular catalysts, photophysical properties, photocatalysis

1. Introduction

The high-efficiency utilization and transformation of renewable energy has been raised to an unprecedented height at present, in view of the sustainable development and the future of the mankind. Natural photosynthesis is a prototype to transform renewable solar energy to chemical energy based on PSI and PSII with fundamental reaction cascades, that are carried out by precisely organized molecular components in a smart protein matrix. Taking nature as an example, artificial photosynthesis manipulates light-harvesting antennae and redox-active centers to fulfill the conversion of small molecules of H_2O, CO_2, and NH_3 *et al.* to solar fuels. The atom-efficient molecular complex catalysts, paired with molecular chromophores, are promising candidates in artificial photosynthesis advantaged by outstanding intrinsic activities, definite active sites as well as fundamental insights into catalytic mechanism.[1] However, the vulnerability of homogenous molecular systems under reaction conditions has to be circumvented for the practical application in solar fuels production.

An emerging strategy of host-guest assembly, heterogenizing molecular systems into porous architectures as isolated sites sterically, could maintain the intrinsic activities of molecular systems meanwhile promote their sustainability and recyclability. Significantly, the integration of molecular guests with porous hosts could engender a microenvironment substantially different from that corresponding to the homogenous bulk solution, such as hydrophobicity/hydrophilicity, electrostatics, numerous apertures and constrained void spaces. The host-guest assembly provides an unexpected opportunity to modulate the photophysical properties of bound-guest species, dictate the diffusion of the substrate and ions, and stabilize higher-energy transition states or radical intermediates,[2] reminiscent of natural enzymes procedure.[3,4, 5,6,7,8-10,11] The numerous porous architectures could serve as host containers to accommodate molecular guests of photosensitizers and catalysts, such as period mesoporous silica (PMS),[12] metal-organic frameworks (MOFs), and covalent organic frameworks (COFs) *et al*. Among them, the modular nature of MOFs, constructed by organic-ligand backbones linking inorganic-node building blocks, affords a versatile platform to hierarchically organize light-harvesting antennae and catalytic centers with controllable position, mutual distance, and relative orientation.[3,4, 13] which could optimize energy migration and electron transfer required for efficient artificial photosynthesis.[14-16,17]

The host-guest assemblies of molecular photosensitizer and catalysts with a variety of MOF hosts had been well reviewed for photocatalysis.[3, 10, 11, 13-15, 18-20] However, the insights of host-guest effects in these heterogenous host-guest assemblies remain plenty of scopes for fundamental research, especially in comparison with the relatively mature field of homogenous supramolecular coordination self-assembly.[21,22] In this contribution, we will specifically focus on the host-guest effects on photophysical processes and photocatalytic process during artificial photosynthesis for solar fuels production. The design and classification of host-guest assembly is first described in view of spatial population of guest species within MOF hosts, together with a brief depiction of assembling strategy. Next, the host-guest effects on photophysical processes are separated discussed based on photo-active MOFs and photo-inert MOFs. Then, the host-guest effects on photocatalytic reaction are depicted from two aspects of spatial confinement and the resultant mass transfer. Finally, attempts to understand the intertwined host-guest effects in future are suggested.

2. The design, classification and synthesis of heterogenous host-guest assembly

Benefiting from the development of inorganic chemistry and synthetic chemistry, various molecular complexes have sprung up for artificial photoconversion, such as a simple molecule with single light-harvesting/redox-active function or double functions, and a photochemical molecular device (PMD) with covalent linkage of photosensitizing center and catalytic unit as a single molecular entity.[23, 24] These guest molecules can be incorporated into MOF host as inorganic-node building blocks, organic-linker backbones, porous inclusion or scaffold defects *via* crystal engineering.[25,26-28] Therefore, the versatility of host-guest assembly can be designed with the types and positions of guest molecules.

Given the initial light harvesting by molecular photosensitizers to drive a desired excited state redox reaction, the photo-response of functional-MOF host is taken to classify the host-guest assembly into photo-active host and photo-inert host, shown in **Figure 1**. As the photo-active host (top panel), MOF is constructed by photo-functional organic linkers, where engineered molecular photosensitizers are installed at organic linkers *via* modifying, grafting or exchanging,[23] or light-harvesting functions are carried by organic linkers intrinsically, such as porphyrin-derived ligands and 2-aminoterephthalic acid ligands.[29, 30] As to the photo-inert host (bottom panel), MOF is an “innocent” container, where molecular photosensitizers are positioned to MOF cavity or stuck in MOF scaffolds as structural imperfects.

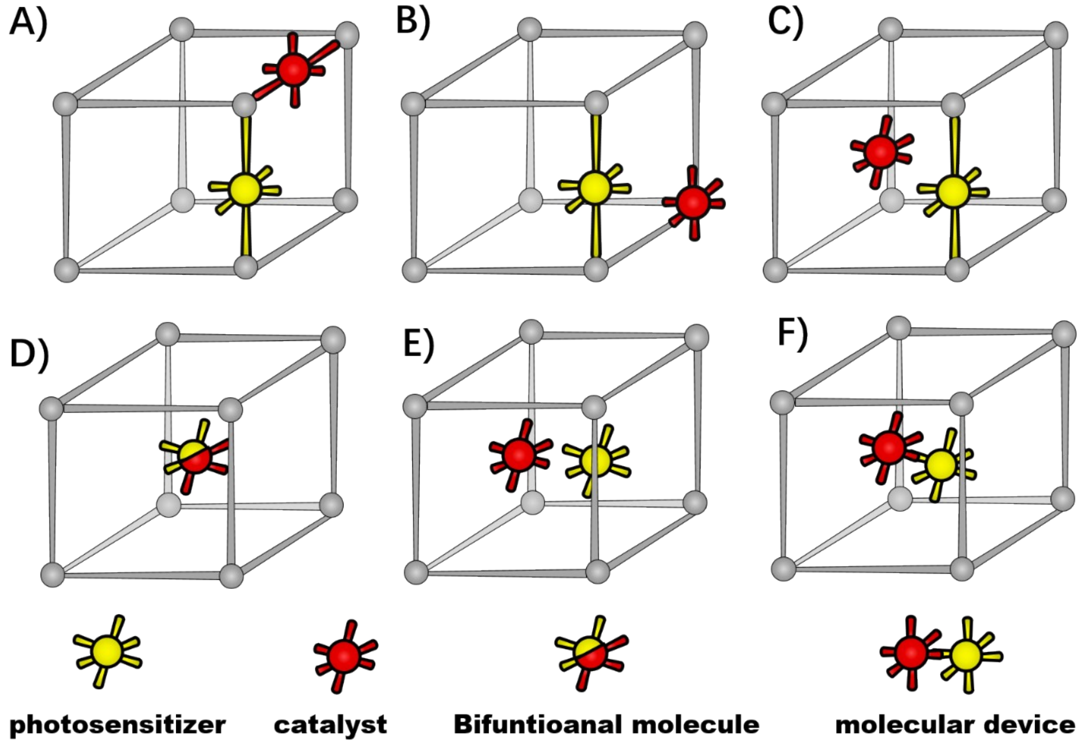

Figure 1. The design and classification of host-guest assemblies discussed in this Review. (A-C) photo-active MOFs with chromophores anchoring on organic linkers and catalytic sites respectively populating on organic linker, vertices/nodes and porous cavity, and (D-F) photo-inert MOFs encapsulating with a single molecule bearing photo-responsive and redox-active dual role, double molecules acting as a chromophore and a catalyst separately, and a photochemical molecular device with covalent linkage of photosensitizing center and catalytic unit. The chromophore and catalyst are highlighted in yellow and red, respectively.

For the photo-active hosts, molecular redox-active catalysts could be incorporated into MOFs' functional-organic linkers, metal vertices or porous cavity to form host-guest assembly.[26-28, 30, 31] So far, various molecular photosensitizers and catalysts had been integrated into MOFs as functional-organic linkers through the routine synthetic strategies of mixed-ligand multivariate approach, post-synthetic exchange and sequent post-synthetic metalation (**Figure 2A**),[5, 29, 31-33,34] such as Ru and Ir-based molecular photosensitizers,[33, 35-38] Ru-based water oxidation catalysts,[39-41] Pt-based H_2 evolution catalysts,[33, 42] and Mn, Re and Ir-based CO_2 reductive catalysts,[36, 43] *et al*. In these cases, molecular catalysts are installed into functionalized linkers, where the structural tailoring of guest molecules is necessary to fit the inherent organic-linker length. As a complement, a molecular catalyst could be built around MOF node itself. A rare example is Lin`s work of direct incorporating the redox-active Ru_2 centers as metal vertices of photoactive porphyrin MOFs.[30] Alternatively, molecular catalysts could be accommodated into MOFs' cavity with a "ship-in-a-bottle" strategy,[44] where the molecular dimensions are matched with inner spaces of MOFs' cavities. For example, Co-dioxime-diimine was trapped into the cavities of a photo-active NH_2-MIL-125(Ti) for light-driven H_2 production,[29] and a Ru-based catalyst was covalently incorporated into the cages of MIL-101(Cr) through "amide bond" as bridges.[45] An active catalyst of ruthenium complex with dimension larger than aperture size of a MOF host was encapsulated into the pores of zirconium-based UiO-66 for hydrogenation of CO_2, taking advantage of aperture-opening events resulting from dissociative linker exchange **(Figure 2B)**.[46]

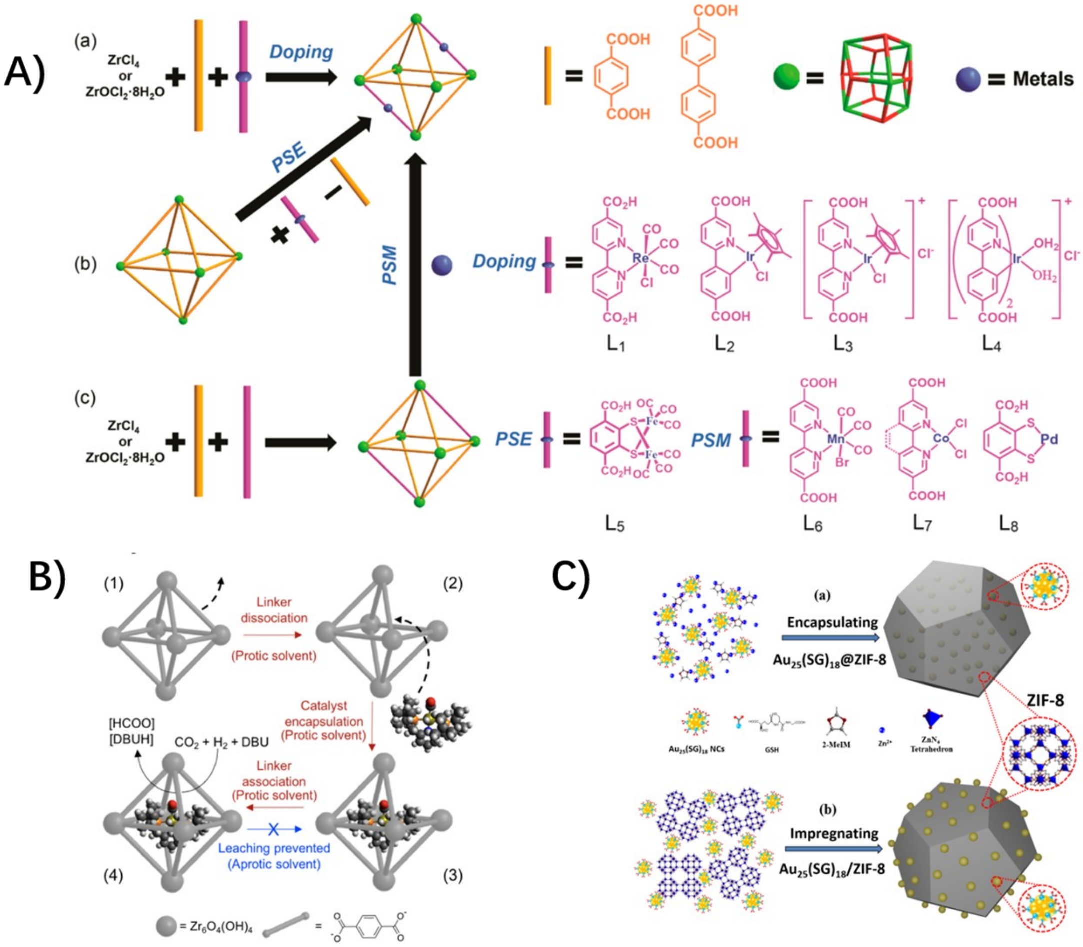

Figure 2. (A) Synthetic strategy of (a) mixed-ligand multivariate approach (doping), (b) post-synthetic exchange (PSE) and (c) post-synthetic metalation (PSM). Reprinted with permission from ref. 34. Copyright 2017 American Chemical Society. (B) A "ship-in-a-bottle" strategy of aperture-opening encapsulation. Reprinted with permission

from ref. 46. Copyright 2018 American Chemical Society. (C) A “bottle-around-a-ship” strategy of coordination assisted self-assembly. Reprinted from ref. 47 with permission from Wiley-VCH.

The preceding host-guest assemblies rely upon the photo-active hosts with functionalized organic linkers for molecular catalysts installation. Another class of photo-inert hosts, serve as the physical scaffolds to isolate the light-harvesting and redox-active molecules with a confined environment exerted around bound guest species. In this condition, we develop a universal “bottle-around-a-ship” way of coordination assisted self-assembly to integrate molecular guests into MOFs (**Figure 2C**),[47-49] where the incarcerating molecular complexes coordinate with MOFs nodes or organic linkers improperly prior to building of MOFs, concomitantly generating the structural imperfects and defects around these mismatch-sites. The unique superiority of this strategy is to break through the limitation on the structure and dimension of molecular guests. In our previous works, a Ru(bda)L_2-based water oxidative catalyst, an atomically precise $Au_{25}(SG)_{18}$ nanoclusters, and a PMD of octahedral metal-organic cage (MOC) of $[Pd_6(RuL_3)_8]^{28+}$ (MOC-16) comprising multiple photosensitive ruthenium-units and catalytic palladium-units,[50, 51] had been successfully encapsulated into MOFs’ scaffolds of ZIF-8 and/or UiO-66 as their high tolerances to structural defects. [48, 49, 51] In our ensuing works unpublished, a Re-based molecular catalyst and a couple of Re and Ru molecular complexes have been incorporated into MOF hosts, and the relevant work is underway. Anyway, the extending of guest molecular types provides an unprecedented opportunity to mimic natural photosynthesis.

3. The photophysical properties of host-guest assembly

Artificial photoconversion begins with the light-harvesting of chromophores to achieve high-energy excitation state, followed by a serial of excited state dynamic processes in ultrafast timescale, involving radiative and nonradiative relaxation concomitantly electron and energy transfer. In these steps, the electron and energy transfer steps, either with or without the participation of electron donors or acceptors, induce the redox-activity of catalytic centers to trigger the consequent catalytic conversion along with breaking and making of chemical bonds, obeying macro-kinetic law. In homogenous molecular system, the photophysical processes of metal-organic complexes, such as polypyridyl Ru(II) and Ir(II) chromophores, *et al.*, could be adjusted easily based on the universal regulations of coordination engineering and synthesis chemistry. In a counterpart of host-guest assembly, the photophysical properties of heterogenized chromophores within MOFs are inevitably influenced by the host-guest effects, which could be further reflected to the following catalytic performance. Understanding the mechanistic aspects of light-initiated dynamics between bound chromophores and the surrounding array of host, catalytic sites or electron and hole mediates, is pivotal for artificial photosynthesis.

In this section, the host-guest effects are separated discussed based on photo-active MOFs and photo-inert MOFs. For the photo-active MOFs with inherent or acquired photo-active ligands, the chromophores are covalently assembled into MOF hosts adopting precise spatial organization as part of MOF crystals, thereby, the photoinduced electron- and electron-transfer involves the quasi-intramolecular host-guest transitions, such as ligands to ligands, ligands to nodes, or ligands to inclusive guests. In contrast, the photo-inert MOFs serve as molecular containers to provide a microenvironment different from homogenous bulk solution, therefore, the photophysics of guest chromophores are more sensitive to the polarity and the steric, geometric and torsional constraints, which are induced by the noncovalent interactions of hydrogen bonding, π-π stacking, electrostatic interaction, van der Waals force *et al.*

3.1 The photo-induced energy- or electron-transfer with photo-active MOFs

Photo-induced energy transfer (EnT): The photo-induced energy transfer (EnT) within organic solids typically takes place *via* the movement of localized excitation or excitons, i.e., tightly bound electron-hole pairs,[52] which could be mainly described using Förster and Dexter models as long- and short-range processes, respectively. Organizing chromophores into the extended architectures with different MOF functionalities, could manipulate EnT pathways, such as, ligand-to-ligand, metal-to-metal, metal-to-ligand (or ligand-to-metal), and guest-to-MOF,[13] in terms of spatial separation and relative orientation of chromophores.

For photo-active MOFs with light-harvesting organic linkers, the directional and efficient long-range energy transport has been studied in two model systems incorporating ruthenium-based and porphyrin-based units.[19,53,54] The rapid intra-MOF energy migration over long distances dominated the photophysical process of Ru(II) (2,2'-bipyridine)$_3$-derived Zr-MOF of UIO-67, and the facile intracrystal site-to-site energy migration appeared in isomorphous UIO-67 with mixed Ru(II)/Os(II) (2,2'-

bipyridine)$_3$-derived building blocks.[54,55,56] In photo-active MOFs composed of Zn(II) porphyrin struts, the photogenerated exciton migrated directionally over a distance of p to ~45 porphyrin struts within its lifetime.[57]

The intended destination of exciton migration is productive dissociation into electrons and holes in a specific site to take part in solar fuel production, although it has yet to be experimentally explored so far. In photo-active MOFs composed of 1,1,2,2-tetrakis(4-(pyridin-4-yl)phenyl)-ethene (tppe) ligand (**Figure 3A**), the efficient host-to-guest energy transfer from tppe ligands to inclusion guests of Rho6G, ended up the mobile exciton on a dye molecule within its emission lifetime.[58] In two MOFs constructed from truxene-derived ligands and zinc nodes, following the exciton migration *via* ligand-to-ligand energy exchange, a coumarin guest within MOF cavity acted as an energy trap to quench the excitation *via* host-to-guest energy transfer.[59] In this example, exciton migration "through-space" jumping over longer distance, rather than routine step-by-step random hopping, was proposed to estimate the EnT efficiency (**Figure 3B**). [59]

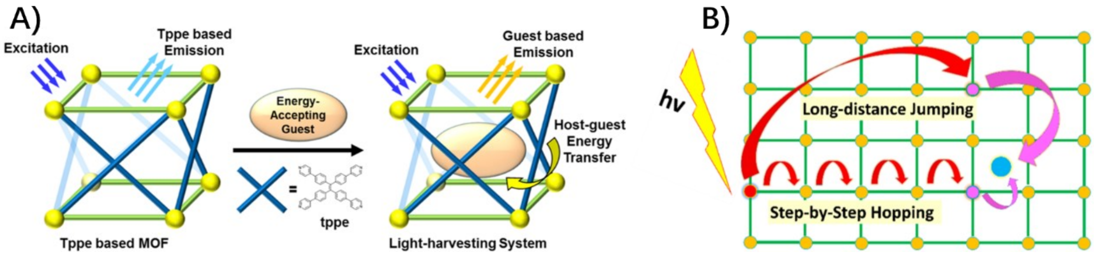

Figure 3. (A) Energy transformation from tppe-based MOF to spatially confined energy-accepting guest. Reprinted with permission from ref. 58. Copyright 2018 American Chemical Society. (B) Two distinct pathways in exciton migration on a network of chromophores with step-by-step nearest neighbour hopping and long-distance jumping. Reprinted from ref. 59 with permission from American Chemical Society.

Photo-induced electron transfer (ET): The photo-induced electron transfer (ET) between chromophores and catalytic centers could be utilized for generation of reactive species in photo-active MOFs. The electron transport in frameworks could be electron hopping or band transport, related to the position of photo-active chromophores and redox-active sites. Both types of transport can either occur through-space (such as through π-π interactions) or through-bonds (by pairing electron donors and acceptors).[11] So far, a wide range of host-guest assemblies have been explored to utilize the photo-induced electron transfer between host and guest molecules for H_2 evolution and CO_2 reduction.[29, 35,33] Herein some typical examples are given, classifying by ET pathways of ligand-to-ligand, ligand-to-node, and ligand-to-inclusion.

Ligand to ligand: In a photo-functional UiO-67 with $[Ru(dcbpy)(bpy)_2]^{2+}$ (bpy: bipyridine, dcbpy: dicarboxylate bipyridine) chromophores as light-absorbing linkers, the catalytic moieties of $Pt(dcbpy)Cl_2$ and $Co(dcbpy)Cl_2$ were respectively incorporated as a second type of functionalized linker.[60, 61] The possibility that charge transfer from photoexcited Ru moiety to catalytic Pt and Co moiety occurred, which accounted for the photocatalytic proton reduction. In another case, a light harvesting moiety of $[Ru(bpy)_2(dcbpy)]^{2+}$ and a catalytic complex of $[Re(CO)_3(dcbpy)Cl]^+$ were co-installed into MOF-253, constructed from Al-O clusters and dicarboxylate bipyridine.[62] The facilitated photocatalytic CO_2 reduction in Ru-MOF-253-Re, relative to MOF-253-Re, supported the presence of a charge transfer between the light harvesting moiety and the catalytic moiety (**Figure 4A**). This efficient charge transfer was also highlighted when grafting a $Ru(bpy)_3$-based photosensitizer and a $Re(CO)_3Cl$-based catalyst into MOF-808.[63] Notably, a highly efficient self-healing system was developed in a bipyridine-embedded UiO-type MOF with arrangement of diimine sites closely and densely surrounded the H_2-evolving catalyst of $Pt^{II}(L)Cl_2$ and photosensitizer of $Ir^{III}(ppy)_2(L)$ (L: 2,2’-bipyridine-5,5’-dicarboxylate, ppy: phenylpyridine) (**Figure 4B**),[33] which presented a persistent H_2 evolution for 6.5 days at least, contrast to the homogeneous counterpart for 7.5 h.

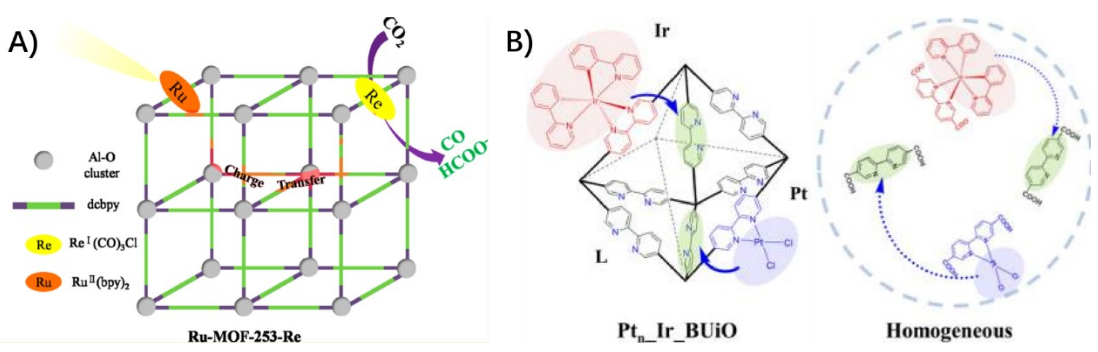

Figure 4. (A) The proposed ligand-to-ligand electron transfer from a light harvesting moiety of $[Ru(bpy)_2(dcbpy)]^{2+}$ to a catalytic complex of $[Re(CO)_3(dcbpy)Cl]^+$.

Reprinted with permission from ref. 62. Copyright 2018 American Chemical Society. (B) Schematic operation principle of self-Healing MOF (Pt_n_Ir_BUiO) and the corresponding homogeneous system. Reprinted with permission from ref. 33. Copyright 2016 American Chemical Society.

Ligand to node: In photo-active MOFs composed of porphyrin-derived tetracarboxylate ligands and catalytic centers of Ru_2 secondary building units (SBUs), the proximity of Ru_2 SBUs to porphyrin ligands facilitated multielectron transfer from excited porphyrins to Ru_2 SBUs, which enabled efficient visible-light-driven hydrogen evolution reaction (**Figure 5A**).[30] Similarly, visible-light-excitation of Eu-Ru(phen)$_3$-MOF, the electron injection from Ru(phen)$_3$-derived ligands into the nodes of dinuclear Eu(III)$_2$ clusters was confirmed by the fluorescence quenching to generate the dinuclear Eu(II)$_2$ active sites, which drove the selective reduction CO_2 to formate in a two-electron process (**Figure 5B**).[64]

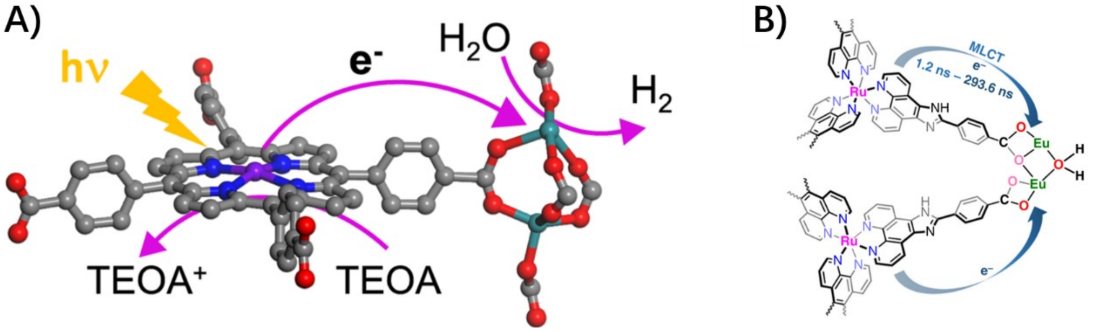

Figure 5. (A) The ligand-to-node multielectron transfer from excited porphyrin-linkers to Ru_2 SBUs. Reprinted with permission from ref. 30. Copyright 2018 American Chemical Society. (B) Schematic light-induced electron transfer from Ru-metalloligand photocenter to catalytic Eu_2 oxo-cluster center in Eu-Ru(phen)$_3$-MOF. Reprinted from ref. 64.

Ligand to inclusion: The proton reductive center of [Fe_2S_2] was incorporated into a Zn (II) porphyrin-derived zirconium-MOF through post-binding to porphyrin zinc center. The electron transfer, between the photo-active porphyrin linkers and the reactive [Fe_2S_2] center, was facilitated due to their close vicinity and chemical bonding nature.[31] An example related to multi-electron transfer was mentioned here, in which, the negatively charged polyoxometalate (POMs) were accommodated into the cavity of cationic MOFs yielding with di-positively charged $[Ru(bpy)_3]^{2+}$-derived linker through electrostatic interaction. The multi-electron injection from excited Ru photosensitizer to the encapsulated POMs enabled efficient visible-light-driven hydrogen production (**Figure 6A**).[65] In addition, the bidirectional electron transfer from $[Ru(bpy)_3]^{2+}$-based ligands to the encapsulated copper (II) clusters within cavities was proposed in Cu-Ru-MOF hybrid catalyst for catalytic CO_2 selective hydrogenation to ethanol (**Figure 6B**).[66] In this case, the Cu^I species could be generated *via* single-electron transfer from photoexcited $[Ru(bpy)_3]^{2+}$-based ligands to initial Cu^{II} centers, meanwhile, Cu^I species could be photo-oxidatively regenerated from Cu^0 *via* photoexcited Ru^{2+}.

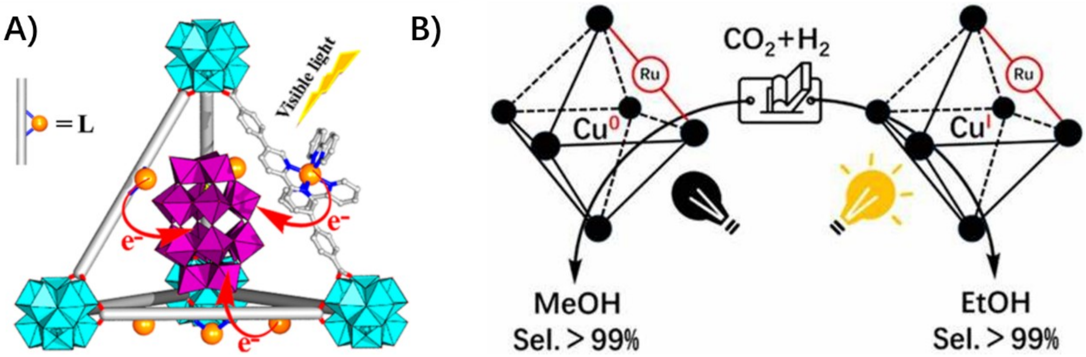

Figure 6. (A) The ligand-to-inclusion multi-electron injection from excited Ru photosensitizer to the encapsulated POMs. Reprinted with permission from ref. 65. Copyright 2015 American Chemical Society. (B) The bidirectional electron transfer from $[Ru(bpy)_3]^{2+}$-based ligands to the encapsulated copper (II) clusters within cavities in Cu-Ru-MOF hybrid catalyst. Reprinted with permission from ref. 66. Copyright 2020 American Chemical Society.

In summary, the proximity of chromophores to catalysts oriented within the host-guest assembly, facilitates the electron transfer intra-assembly *via* a pseudo-intramolecular pathway. As a result, the host-guest assembly gives better photocatalytic performances compared with their homogenous counterparts. As to the presence of external species to take part in electron transfer, the oxidative and reductive quenching could take place at the assembly-solution interface or the assembly cavity, where the mass transfer has to be considered (*vide supra*).

3.2 The photophysical process of host-guest assembly with photo-inert MOFs

For photo-inert MOFs, the hosts are photophysically unremarkable and serve as containers for molecule guests based on their porous structures and accommodation ability. In this condition, the complete isolation and restriction of guest molecules within MOF rigid skeletons, will inevitably modulate the photophysical properties of incarcerated guests without altering their chemical structures. The detailed energy dissipation following the photoexcitation of chromophores includes the non-radiative channels of vibration and rotation relaxation and intersystem crossing (ISC) from ^{1}MLCT to ^{3}MLCT, the ensuing radiative and nonradiative deactivation of ^{3}MLCT excited state, and the desired electron transfer from excited states of photocenter to catalytic center, *et al*. In this section, the photophysical process of host-guest assembly are depicted in light of the type of incarcerated guests, a single molecule, double molecules and a PMD molecule.

Single molecule assembling: The photophysical properties of three RuL_3@InBTB MOFs were studied by photoluminescence (PL) technique (**Figure 7**),[67] where three cationic $[Ru(bpy)_3]^{2+}$ (bpy: 2,2'-bipyridine), $[Ru(phen)_3]^{2+}$ (phen: 1,10-phenanthroline), and $[Ru(bpz)_3]^{2+}$ (bpz: 2,2'-bipyrazine) were encapsulated into the mesopores of a three-dimensional InBTB MOF (H_3BTB=1,3,5-benzenetribenzoic acid) through cation-exchange. In comparison with control bulk sample, the host-guest encapsulation induced a blueshifted PL emission band of $[Ru(bpy)_3]^{2+}$ in $Ru(bpy)_3$@InBTB, in addition to a prolonged average lifetime of triplet excited state (^{3}MLCT) through retarding nonradiative decay. In contrast, the PL emission band position remained unaltered for $Ru(phen)_3$@InBTB, while shifted to long-wavelength region for $Ru(bpz)_3$@InBTB. These dramatic disparities should be related to the spatial orientations of three RuL_3^{2+} ions and distinct nanoscale environments in InBTB channels.

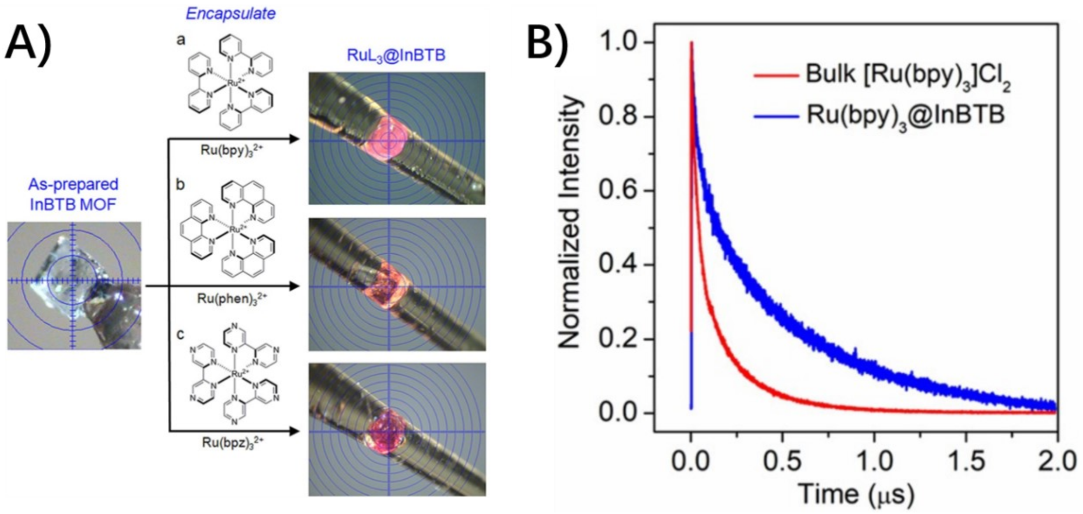

Figure 7. (A) Photo images of colorless as-prepared InBTB and color-changed RuL3@InBTB MOFs and (B) normalized time-resolved photoluminescence decay curves measured for bulk $[Ru(bpy)_3]Cl_2$ and $Ru(bpy)_3$@InBTB upon excitation at 470 nm. Adapted from ref. 67 with permission from Wiley-VCH.

Double molecules assembling: When encapsulating a photosensitizer and a catalyst simultaneously into photo-inert MOF framework, the separation of photosensitizer and catalyst in space and the energy migration or electron hopping through space is challenging, especially involving in the third component of sacrificial reagents. The imperfect or mismatched scaffolds of MOF hosts, could divert energy and charges away from catalysts. In this type of functional host-guest architectures, the tunability of pair wise encapsulation, including the species concentration, ratio and resultant distance, provides an opportunity to manipulate the photoinduced charge separation between neighbouring guests, the framework or media reactants. In an example of immersing a CO_2 reduction catalyst $[ReBr(CO)_3(4,4'\text{-dcbpy})]$ and a photosensitizer $[Ru\text{-}(bpy)_2(5,5'\text{-dcbpy})]Cl_2$ inside the cavities of UiO-68 and on the surface of UiO-66 (**Figure 8**), the elongating activity but decreasing reaction rate in ReRu-68 compared with ReRu-66, suggested the limited electron communication between a photosensitizer and a catalyst resided within MOF hosts randomly.[68]

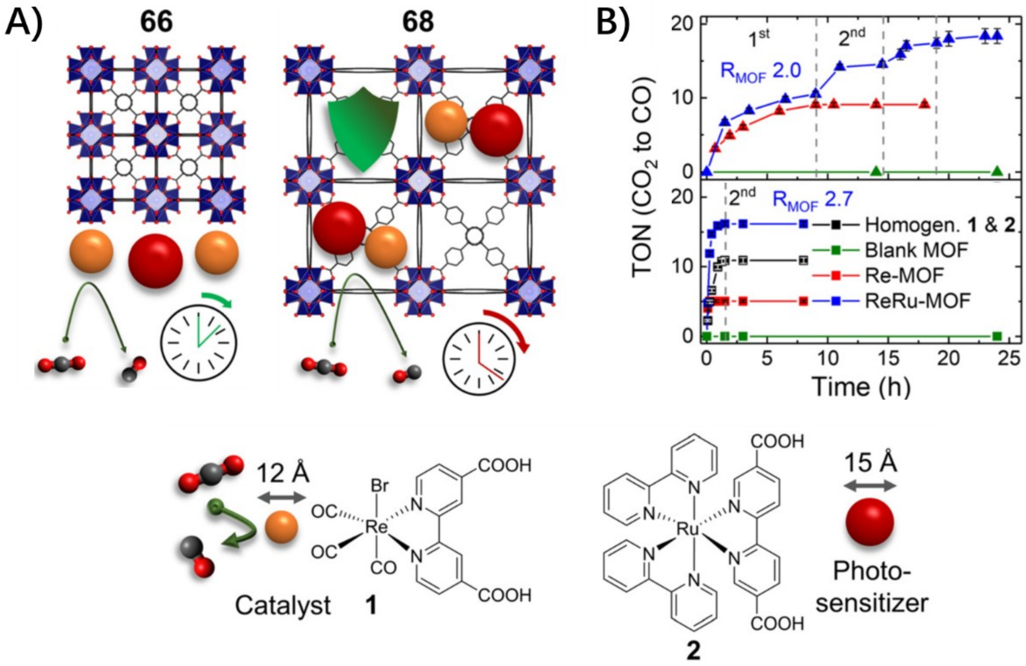

Figure 8. (A) Schematic concept behind catalytic performance differences and (B) accumulated TON vs. time plot for 66 (bottom) and 68 (top) with pristine MOFs

(green), Re-MOF (red), ReRuMOF (blue) with best-performing RMOF shown, homogeneous 1 and 2 (black). Adapted from ref. 68.

Molecular device assembling: In comparison with incorporating a photosensitizer and a catalyst separately, it is anticipated to encapsulate a PMD into MOF hosts, where the photosensitizer and catalyst are covalently linked as a single-component photocatalyst. An intramolecular electron transfer from the excited state of photosensitizer unit to the catalytic centre through the bridging ligand is expected to enhance the communication between them. The developed PMD could be a bimetallic assembly paired with covalent linking photosensitizer and catalysts, and a multi-metallic assembly comprised of multiple chromophores connected through bridging ligands to a catalytic site or multiple catalytic unites[24,69, 70]

In previous works, a metal-organic cage (MOC) was explored for H_2 evolution through assembling multiple photosensitive ruthenium-units and catalytic palladium-units within octahedral structure, which engendered the spatially separated but mutually equivalent multi-channel electron transfers from Ru sites to Pd sites (**Figure 9A**).[50,51,71,72] After encapsulating this MOC-16 into ZIF-8 and UiO-66 matrixes,[48, 49] the heterogenous host-guest assemblies inherit the distinctive feature of efficient and directional electron transfer in picosecond domain of MOC-16, while, the lifetimes of ^{3}MLCT excited-state are significantly elongating to microsecond scale, due to the inhibition of non-radiative vibrational relaxation by the rigid MOF-matrixes (**Figure 9B**). As a result, the extra high activities for H_2 generation were achieved.

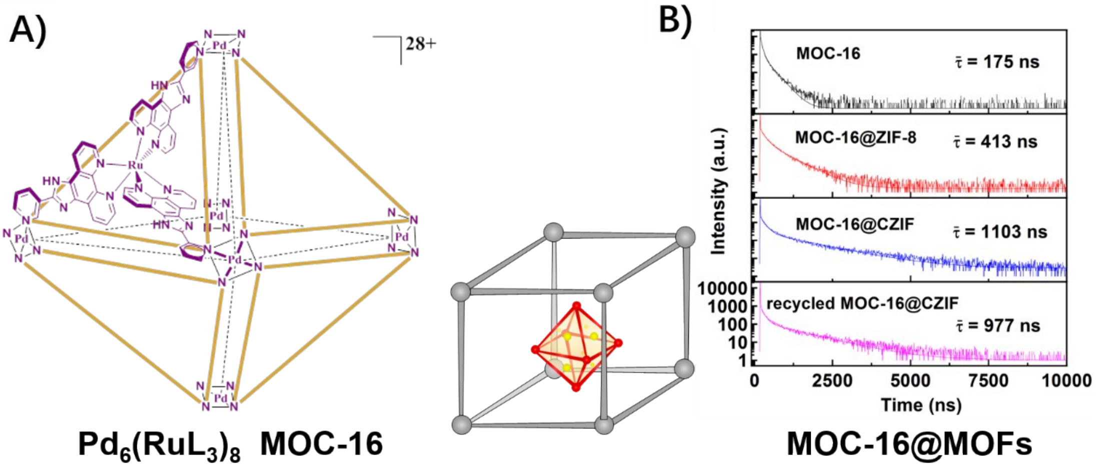

Figure 9. (A) The structure of a PMD of $Pd_6(RuL_3)_8$ metal-organic cage (MOC-16); and (B) time-resolved emission decay of ^{3}MLCT excited-state of MOC-16 and MOC-

16@MOFs. Reprinted with permission from ref. 49. Copyright 2019 American Chemical Society.

4. The spatial confinement and mass transport in host-guest assembly

Following the photoexcitation and a serial of photophysical events hereinbefore, the dark process of catalytic reaction should be considered for host-guest assemblies. Accompanied with the accommodation of functional units or the inclusion of guest species, MOF hosts will serve as a “nanoreactor” providing spatial confinement, while simultaneously allowing for small-molecule permeability by virtue of the permanent porosity, reminiscent of natural enzymes. Therefore, the spacial confinement and the resultant mass transfer in host-guest assembly are specifically discussed in this section.

Spatial confinement: The host-guest effects exert physical confinement to isolate and protect the chromophores and redox catalysts, concomitantly, chemical confinement to stabilize the high-energy intermediate species *via* host-guest noncovalent interactions that are difficult to access in the bulk solution.[73] Thereby, the reaction pathway could be diverted to achieve unprecedented reaction activities or rate enhancements, even though few literature precedents of such host-guest assembly for MOFs yet.

An example is post-metalating organic linkers of MOF-253 to immobilize Pt(bpy)$(Cl)_2$ moieties with both light-absorbing and catalytic functions (**Figure 10**).[42] The photocatalytic hydrogen evolution was ascribed to the cooperation of paired Pt(bpy)$(Cl)_2$ catalyst presumably *via* a Pt(II)-Pt(III)-hydride intermediate, a mechanism akin to that described in photocatalytically active diplatinum(II) complexes.[3,23, 42] In this case, the square channels of MOF-253 with closely spaced dcbpy units provide a space for pairs of dichloroplatinum (II) complexes to engender heterogeneous catalytic activity.

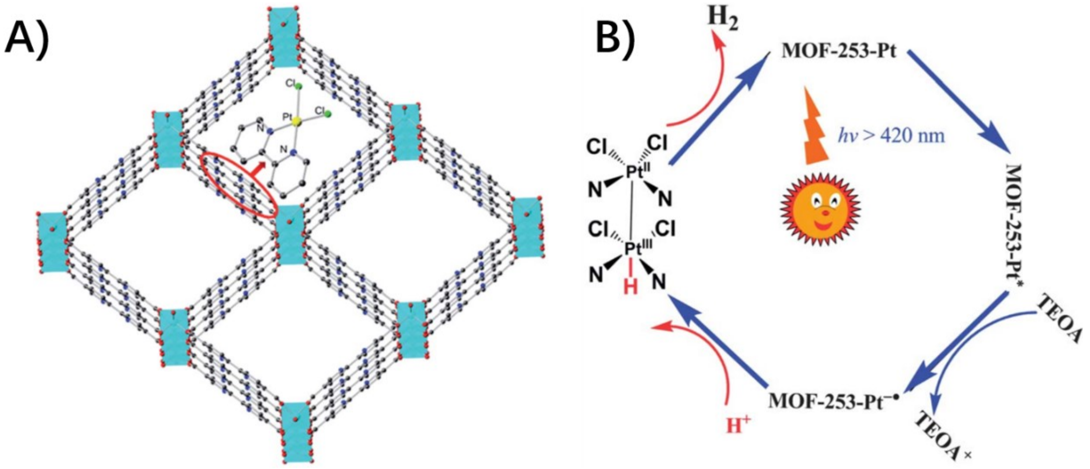

Figure 10. (A) Model structure of MOF-253-Pt, through post-synthetic modification of MOF-253 with $PtCl_2$ and (B) proposed reaction mechanism *via* pairs of dichloroplatinum (II) complexes for the photocatalytic H_2 evolution. Reproduced from ref. 42 with permission from the Royal Society of Chemistry.

Mass transport: MOF host could supply the spatial confinement with its rigid frameworks hereinbefore, in the meantime, the restricted diffusion (reactants, sacrificial reagents and products) by its numerous apertures (window, channel and cavity sizes) potentially results in kinetic bottlenecks, in comparison with bulk solution phase. As to the host-guest assembly, the aperture blockage, accompanying with guest incorporations, could further increase the limitation on mass transport as a result of steric hindrance.[74, 75] On the other hand, the porosity and hydrophilic/hydrophobic property of MOF scaffolds, could regulate the ionic and molecular transport, provide an environment that facilitates proton transfer, and deliver substrates to catalytic active species in close proximity.[11]

In our previous works,[48, 49] MOC-16 was incorporated into three matrixes of ZIF-8, UiO-66 and ZIF-8-derived-carbonate CZIF to intercompare the mass transfer based on wettability and porous structure (Figure 11). During H_2O splitting reaction for H_2 evolution, no activity appeared in hydrophobic MOC-16@ZIF-8, but high activities were observed at both hydrophilic MOC-16@UiO-66 and MOC-16@CZIF. The quantitative analysis indicated sacrificial reagent could permeate into porous UiO-66 to serve as two-electron donor, in sharp contrast to act as one-electron donor in nonporous CZIF matrix.

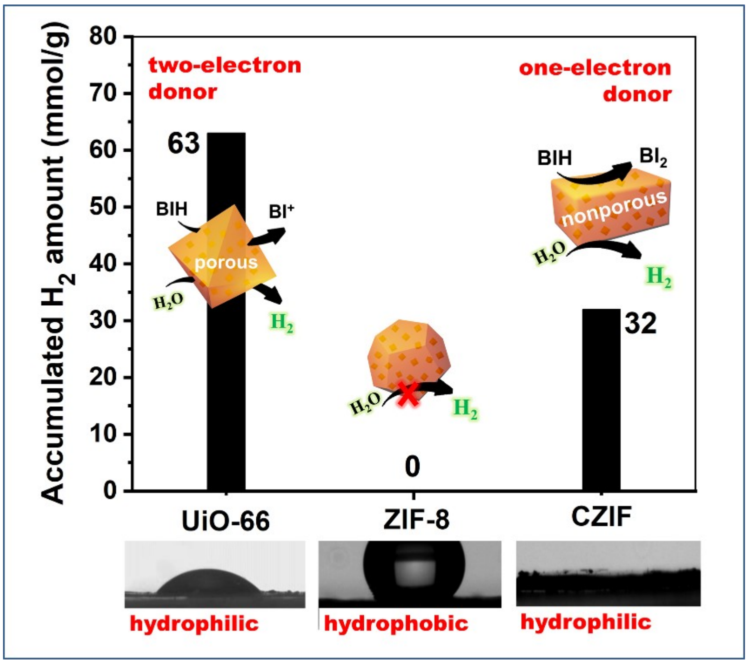

Figure 11. The host-guest effects on mass transfer based on wettability and porous structure of MOC-16 incorporating into three matrixes of ZIF-8, UiO-66 and ZIF-8-derived-carbonate CZIF. Reproduced from ref. 48 with permission from Wiley-VCH.

Notably, the stability of MOF hosts highly relies on the strength of coordination between metal-based nodes and organic struts, especially in the presence of sizable concentrations of aqueous hydroxide.[11] In our cases of MOC-16@ZIF-8 and Ru(bda)$_2$L@UiO-66 (bda: 2,2'-bipyridine-6,6'-dicarboxylic acid), the structural derivations of ZIF-8 and UiO-66 hosts with ligand replacements were concomitant with uptakes of carbonate and phosphate respectively in the presence of H_2O and CO_2 and phosphate buffer saline (PBS).[49, 76] Instructively, the isolation and integrity of guest molecules remained, meanwhile, presented the outstanding activity of H_2 evolution and the impressive turn-over number of O_2 evolution, respectively, in the presence of indispensable CO_2 atmosphere and PBS. An enzyme-like microenvironment in close vicinity to catalytic sites favorable for the proton delivery was proposed, where carbonate and phosphate as a proton mediator/relay to assist the proton and/or proton-couple electron transfer through hydrogen-bond network of water molecules (**Figure 12**).

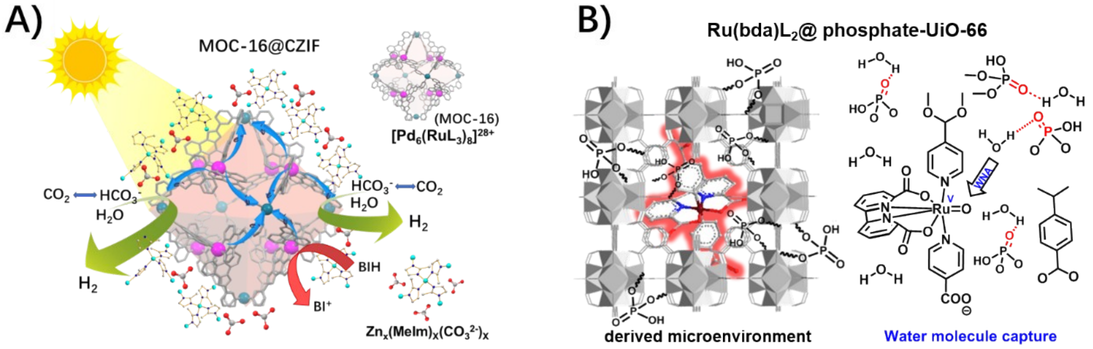

Figure 12. The uptakes of (A) carbonate in MOC-16@ZIF-8 and (B) phosphate in Ru(bda)$_2$L@UiO-66 (Reproduced from ref. 76 with permission from Elsevier), as a proton mediator/relay to assist the proton delivery through hydrogen-bond network of water molecules.

5. Conclusion and Perspectives

The review highlights the integration of molecular guests with MOF architectures enabling enzymes-like efficacy to isolate or preorganize photo-active and redox-active sites and manipulate the photophysical and photocatalytic properties. As an emergent field of heterogenous host-guest assembly, understanding and modeling of intertwined host-guest effects physically and chemically are still a great challenge. The precise synthesis to regulate the periodic population of guests throughout frameworks and govern the attainable guest capacity within porous host, and the specific characterization to determine the distances and angles between guest molecules as well as their molecular conformations, are indispensable to unravel the structure-property relationships. The high sensitive techniques and theoretical predictions are valuable in these investigations. The attempts to take advantages of host-guest assemblies for implementing artificial photosynthesis efficiently, are on the way.

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