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Review

Formation of oriented and patterned films of metal–organic frameworks by liquid phase epitaxy: A review

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ABSTRACT

In the last years, the interest in metal–organic frameworks (MOFs) and other crystalline coordination networks (CCNs) expanded from their extraordinarily high porosity to other fascinating properties, such as the electronic and magnetic coupling between the metal centers (and sometimes the ligands). To explore and utilize these properties, these frameworks have to become deposited onto solid surfaces, such as electrodes. In this review, we summarize and discuss the state of the art in growing surface-bound metal–organic frameworks (SURMOFs) from the view of a surface scientist. We will briefly describe selected applications, which require MOF thin films rigidly anchored to solid, conducting or transparent substrates and will also point out that in several cases the superb structural quality of SURMOFs allows to use them as model system for studying crucial intrinsic properties of MOF materials, including diffusion of guest species and the formation of surface barriers. An emphasis is put on the methods for localized depositions (patterning) and future developments are envisioned.

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Nomenclature

General

AFM	atomic force microscopy
ALD	atomic layer deposition
CCNs	crystalline coordination networks
CD	circular dichroism
DMSO	dimethylsulfoxide
DPN	dip-pen nanolithography
DXP	*N*,*N*′-bis(2,6-dimethylphenyl)-3,4,9,10-perylenetetracarboxylic diimide
EBL	electron beam lithography
FTO	fluorine-doped tin oxide
FWHM	full width at half maximum
IPER	irradiation-promoted exchange reaction
IRMOF	isoreticular metal organic framework
IRRAS	infrared reflection absorption spectroscopy
ITO	indium tin oxide
LbL	layer-by-layer
LPE	liquid phase epitaxy
MBE	molecular beam epitaxy
MOF	metal–organic framework
μCP	micro-contact printing
NR	nano-rod
NP	nano-particle
NW	nano-wire
PCP	porous coordination polymer
PDMS	poly(dimethylsiloxane)
PSM	post-synthesis modification
QCM	quartz crystal microbalance
SAM	self-assembled monolayer
SBU	secondary building unit
SEM	scanning electron microscopy
SPR	surface plasmon resonance
SURMOF	surface mounted metal–organic framework
TCNQ	tetracyanoquinodimethane
ZIF	zeolitic imidazolate framework

ligands

abIM	5-azabenzimidazole
adc	9,10-anthracenedicarboxylate
ada	4,4′-azobenzenedicarboxylate
bdc	1,4-benzenedicarboxylate
BME-bdc	2,5-bis(2-methoxyethoxy)-1,4-benzenedicarboxylate
bipy	4,4′-bipyridine
bpdc	biphenyl-4,4′-dicarboxylate
btc	1,3,5-benzenetricarboxylate
btdd	bis(1*H*-1,2,3-triazolato[4,5-b],[4′,5′-*i*])dibenzo[1,4]dioxin
chdc	cyclohexane-1,4-dicarboxylate
da-sbdc	diazido-stilbenedicarboxylic acid
dabco	1,4-diazabicyclo[2.2.2]octane
Dcam	(1R,3S)-(+)-camphoric acid
dmtpdc	2′,5′-dimethyl-[1,1′:4′,1″-terphenyl]-4,4″-dicarboxylic acid
dmcapz	3,5-dimethyl-4-carboxypyrazolate
dobdc	2,5-dioxido-1,4-benzenedicarboxylate
dot	dioxidoterephthalate
dpndi	*N*,*N*′-di(4-pyridyl)-1,4,5,8-naphthalenetetracarboxydiimide
F_4bdc	tetrafluorobenzene-1,4-dicarboxylate
Ica	imidazolate-2-carbaldehyde
mIm	2-methylimidazole
NH_2-bdc	2-amino-1,4-benzenedicarboxylate
N_3-bdc	2-azidobenzene-1,4-dicarboxylate
ndc	1,4-naphtalene dicarboxylate
NO_2-ip	5-nitroisophthalate
$p(ep)_2dc$	1,4-bis(4-carboxyphenylethinyl)-2,5-dimethoxybenzene
ppdc	pentaphenyl dicarboxylate
pz	pyrazine
tpdc	1,4-di(4-carboxyphenyl)benzene
qpdc	[1,1′,4′,1″,4″,1‴-quaterphenyl]-4,4‴-dicarboxylate
TCPP	5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin

MOFs

CAU-1	Christian-Albrechts-University, $[Al_4(OH)_2(OCH_3)_4(H_2N\text{-}bdc)_3]$
DA-MOF	Zn_2P_2L, P = [5,15-di(4-pyridylacetyl)-10,20-diphenyl] porphyrinatozinc-(II), L = 1,2,4,5-tetrakis(4-carboxyphenyl)benzene)
HKUST-1	$[Cu_3(btc)_2]$
IRMOF-9	$[Zn_4O(bpdc)_3]$ interpenetrated
IRMOF-10	$[Zn_4O(bpdc)_3]$
MIL	Material Institut Lavoiser
MIL-100(Fe)	$Fe_3OF(btc)_2$
MIL-101(Fe)	$Fe_3OCl(bdc)_3$
MIL-88B(Fe)	$Fe_3O(bdc)_3$
MOF-5	$[Zn_4O(bdc)_3]$
MOF-508	$[Zn_2(bdc)_2(bipy)]$
NAFS-1	CoTCPP-py-Cu
NAFS-2	TCPP-Cu
PPF-5	pillared paddlewheel porphyrin framework 5
UiO	University of Oslo
UiO-66	$Zr_6O_4(OH)_4(bdc)_6$
UiO-67	$Zr_6O_4(OH)_4(bpdc)_6$
UiO-68-NH_2	$Zr_6O_4(OH)_4(NH_2\text{-}tpdc)_6$
ZIF-8	$Zn(mIm)_2$
ZIF-22	$Zn(abIm)_2$
ZIF-90	$Zn(Ica)_2$
Zn-CID-5	$Zn(NO_2\text{-}ip)(bipy)$

SAMs

APTES	3-aminopropyltriethoxysilane
CMMT	9-carboxy-10-(mercaptomethyl)triptycene
HDT	1-hexadecanethiol
MHDA	16-mercaptohexadecanoic acid
MPA	3-mercaptopropionic acid
MUDA	11-mercaptoundecanoic acid
ODS	octadecylsiloxane
PhTES	phenyltriethoxysilane

1. Introduction

The application of coordinative bonds for the construction of large molecular assemblies has opened several new areas in polymer and solid state chemistry. Summarized under the term "coordination polymers", supramolecular architectures in one, two, and three dimensions have been prepared, characterized and explored with regard to applications [1–5]. Due to their general composition from metal atoms (or clusters) and various ligands, they offer an enormous structural and functional flexibility. The three-dimensional materials with translational symmetry have been termed crystalline coordination networks (CCNs), in case these networks enclose voids, the term metal–organic frameworks (MOFs) has been established [6]. Another class of coordination networks containing pores, but not necessarily with a periodic