Electronic Supplementary Information (ESI) for

Host molecules inside metal-organic frameworks: host@MOF and guest@host@MOF (Matrjoschka) materials

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Table S1 Examples of the synthetic approaches and applications of representative host@MOF and guest@host@MOF materials.

Material	Host molecule	Approach	Application	Ref
Porphyrin@MOF				
M@TMPyP@MOM−2 (M=Mn^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+})	$[H_2TMPyP]^{4+}[p\text{-tosyl}^-]_4$	Bottle−around−ship Post−synthetic metalation	Cyclohexane oxidation	44
Pt@TMPyP@MOM−2	$[H_2TMPyP]^{4+}[Cl^-]_4$	Bottle−around−ship	Sulfide ion sensing	45
M@4SP@HKUST−1(Cu, Zn) M = Fe^{3+}, Mn^{3+}	$[H^+]_4[H_24SP]^{4-}$	Bottle−around−ship	Monooxygenation	46
M@TMPyP@MOM−n (M = Fe^{2+}, Co^{2+}, Mn^{2+}) (n=4, 5, 6)	$[H_2TMPyP]^{4+}[p\text{-tosyl}^-]_4$	Bottle−around−ship	Olefin oxidation	47
Cd@TMPyP@MOM−10(Cd)	$[H_2TMPyP]^{4+}[p\text{-tosyl}^-]_4$	Bottle−around−ship	−	48
Mn@TMPyP@MOM−10(Mn)	$[H_2TMPyP]^{4+}[p\text{-tosyl}^-]_4$	Post−synthetic metal exchange	Epoxidation of trans−stilbene	48
Cu@TMPyP@MOM−10(CdCu)	$[H_2TMPyP]^{4+}[p\text{-tosyl}^-]_4$	Post−synthetic metal exchange	Epoxidation of trans−stilbene	48
Cd@TMPyP@MOM−11(Cd)	$[H_2TMPyP]^{4+}[p\text{-tosyl}^-]_4$	Bottle−around−ship	CO_2 adsorption	49
Mn@TMPyP@ZIF−8	$[H_2TMPyP]^{4+}[I^-]_4$	Bottle−around−ship	Cyclic addition of CO_2 with epoxide	50
Zn@TMPyP@PCN−224	$[H_2TMPyP]^{4+}[I^-]_4$	Impregnation	Cyclic addition of CO_2 with epoxide	51
Fe@TCPP in HKUST-1(Cu)	H_2TCPP	Bottle−around−ship	Electrochemical DNA sensing	52
Phthalocyanine@MOF				
M@PcF_{16}@MIL−101(Cr) M= Fe^{3+}, Ru^{2+}	H_2PcF_{16}	Impregnation	Oxidation of tetralin	54
M@Pc@bio−MOF−1 (M= Co^{2+}, Ni^{2+}, Cu^{2+})	H_2Pc	Ship−in−bottle	Styrene epoxidation	55
M@Pc@MIL−101 (M= Cu^{2+}, Co^{2+}, Ni^{2+})	H_2Pc	Ship−in−bottle	Oxidative amidation	56
Cu@Pc@MIL-101(Cr)	H_2Pc	Ship−in−bottle	Styrene epoxidation	57
Cu@Pc@MIL-100(Fe)	H_2Pc	Ship−in−bottle	Styrene epoxidation	57
Crown ether@MOF				
18C6@ZIF-67/18C6@ZIF-8 membrane	18C6	Bottle−around−ship	Selective Li^+/K^+ and Na^+/K^+ transport	58
BCE@ZIF-7	BCE	Bottle−around−ship	-	59
M@BCE@ZIF-7 (M=Li^+, Mg^{2+}, Al^{3+})	BCE	Bottle−around−ship	Selective Li^+/Mg^{2+} transport	59
DB15C5@UiO-66	DB15C5	Bottle−around−ship	Selective K^+/Mg^{2+} transport	60
DB18C6@UiO-66	DB18C6	Bottle−around−ship	Selective K^+/Mg^{2+} transport	60
B15C5@ZIF-8	B15C5	Bottle−around−ship	C_3H_6/C_3H_8 separation	61
Calixarene@MOF				
CA−1@MOF−5	CA−1	Bottle−around−ship	−	62
Pd@CA−2@MOF−5	CA−2	Bottle−around−ship	Hydrogenation of 2−butyne−1,4−diol	63

Note: the structures of representative host molecules can be seen in Fig. 2. The reference number and content are consistent with those in the main text.

Table S1 (continued) Examples of the synthetic approaches and applications of representative host@MOF and guest@host@MOF materials.

Material	Host molecule	Approach	Application	Ref
Cavitand@MOF				
$MeMeCH_2$@*mer*−ZIF−10	$MeMeCH_2$	Bottle−around−ship	-	65
$MeMeCH_2$@*rho*−$Zn_{16}Im_{32}$	$MeMeCH_2$	Bottle−around−ship mechanosynthesis	-	64
Cucurbituril@MOF				
CB6@MIL−101−36 (36 wt% of CB6)	CB6	Wet−impregnation	CO_2 sorption and CO_2/CH_4 separation	25
CB6@MIL−101−Cl−31 (31 wt% of CB6)	CB6	Impregnation	SO_2 adsorption	70
MC5@MIL−100(Fe)-23 (23 wt% of MC5)	MC5	Bottle−around−ship	Pb^{2+} removal	39
Metal organic polyhedron@MOF				
M_6L_4@MIL−101(Cr)	M_6L_4	Ship−in−bottle	Oxidation of benzyl alcohol	34
NH_2-MOP@DUT−68(Zr)	NH_2-MOP or $H_2N-M_4L_6$	Ship−in−bottle	Proton conductivity	72
MOP-3@PCN−777	MOP-3	Impregnation	Proton conductivity	73
NH_2-MOP@MOA	NH_2-MOP or $H_2N-M_4L_6$	Bottle−around−ship	Oxoanion removal	74

Note: the structures of representative host molecules can be seen in Fig. 2. The reference number and content are consistent with those in the main text.

Table S2 Examples of the synthetic approaches and applications of representative enzyme@MOF as host@MOF materials.

Material	Enzymes	Approach	Application	Ref
MP-11@Cu-MOF	MP-11 (1.1 nm×1.7 nm×3.3 nm)	Impregnation	Oxidation of methylene blue	75
MP-11@Tb-mesoMOF	MP-11 (1.1 nm×1.7 nm×3.3 nm)	Impregnation	Oxidation of 3,5-Di-t-butylcatechol	76
Cyt c@Tb-mesoMOF	Cyt c (2.6 nm×3.2nm×3.3 nm)	Impregnation	-	77
Protease@MIL-101-NH_2	Protease (2.85 nm)	Impregnation	Proteolytic activity for glycyl-L-tyrosine-	78
HRP@PCN-333(Al)	HRP (4.0 nm×4.4 nm×6.8 nm)	Impregnation	Oxidation of o-Phenylenediamine	79
Cyt c@PCN-333(Al) MP-11@PCN-333(Al)	Cyt c (2.6 nm×3.2nm×3.3 nm) MP-11 (1.1 nm×1.7 nm×3.3 nm)	Impregnation	Oxidation of ABTS	79
cutinase@NU-1000(Zr) cutinase@PCN-600(Zr)	Cutinase	Impregnation	Hydrolysis of PNPB	80
HRP/GOx@PCN-888	GOx (6.0 nm×5.2 nm×7.7 nm) HRP (4.0 nm×4.4 nm×6.8 nm)	Impregnation	Oxidation of glucose; Oxidation of ABTS	81
Cyt c@ZIF-8	Cyt c (2.6 nm×3.2nm×3.3 nm)	Bottle−around−ship	Detection of H_2O_2	83
FCAT@ZIF-90 FCAT@MAF-7 FCAT@ZIF-8	FCAT (4.4 nm×4.9 nm×5.6 nm)	Bottle−around−ship	H_2O_2 degradation	84
nano BCL@MTV-ZIFs	BCL	Bottle−around−ship	Kinetic resolution of (R,S)-2-octanol	85
Cyt c@NKMOF-101-Zn	Cyt c (2.6 nm×3.2nm×3.3 nm)	Bottle−around−ship	Oxidation of ABTS	86
α-G/GOx@Cu-MOF	*α*-glucosidase and GOx	Bottle−around−ship	Hydrolysis and oxidation of maltose	87
CRL@ZIF-8	CRL	Bottle−around−ship	Hydrolysis of PNPB	88
urease@ZIF-8 HRP@ZIF-8	Urease HRP (4.0 nm×4.4 nm×6.8 nm)	Bottle−around−ship	Hydrolysis Oxidation	89
catalase@ZIF-90	catalase	Bottle−around−ship	H_2O_2 degradation	90
OPAA@PCN-128y	OPAA (4.4 nm×4.4nm×7.8 nm)	Impregnation	Detoxifying DFP and Soman	104
β-G@Cu(PABA)	β-Glucosidase	Bottle−around−ship	Hydrolysis of cellulose	105
GOx/HRP@ZIF-8	GOx (6.0 nm×5.2 nm×7.7 nm) HRP (4.0 nm×4.4 nm×6.8 nm)	Bottle−around−ship	Oxidation of glucose and ABTS	107
FaldDH/FateDH@ZIF-8	FaldDH and FateDH	Bottle−around−ship	Photocatalytic CO_2 reduction	108

Note: The reference number and content are consistent with those in the manuscript.

Table S2 (continued) Examples of the synthetic approaches and applications of representative enzyme@MOF as host@MOF materials.

Material	Enzymes	Approach	Application	Ref
GOx@ZIF-8	GOx (6.0 nm×5.2 nm×7.7 nm)	Bottle−around−ship	Detection of glucose	110 111
GOx/HRP@DNA/ZIF-8	GOx (6.0 nm×5.2 nm×7.7 nm) HRP (4.0 nm×4.4 nm×6.8 nm)	Bottle−around−ship	Detection of glucose	112
GOx@MAF-2	GOx (6.0 nm×5.2 nm×7.7 nm)	Bottle−around−ship	Detection of glucose	113
GOD@GA-Ni/Cu-MOF	GOD	Impregnation	Detection of glucose	114
Urease@ZIF-8	Urease	Bottle−around−ship	Detection of urea	115
UOx/HRP@ZIF-8	Urate oxidase HRP (4.0 nm×4.4 nm×6.8 nm)	Bottle−around−ship	Detection of uric acid	115
β-Gal/Ox/HRP@ZIF-8	β-galactosidase and oxidase and HRP	Bottle−around−ship	Detection of lactose	115
Peptide-HRP@ZIF-90	HRP (4.0 nm×4.4 nm×6.8 nm)	Bottle−around−ship	Detection of SPARC	116
Lac@MCS/UiO-66-NH_2	Laccase	Impregnation	Tetracycline detection	117
Cas12a@MAF-7	Cas12a nuclease	Impregnation	Detection of SARS-CoV-2 RNA	118

Note: The reference number and content are consistent with those in the manuscript.

Abbreviations and acronyms used in Table S1 and Table S2:

For MOFs:

MOM = metal-organic material as a series of specific MOFs;

HKUST = Hong Kong University of Science and Technology;

HKUST-1 = a MOF composed of Cu_2 nodes and trimesic acid ligands;

ZIF = Zeolitic Imidazolate Framework;

ZIF-8 = a ZIF composed of zinc ions and 2-methylimidazole ligands;

ZIF-67 = a ZIF composed of cobalt ions and 2-methylimidazole ligands;

ZIF-7 = a ZIF composed of zinc ions and benzimidazole ligands;

ZIF-90 = a ZIF composed of zinc ions and imidazole-2-carboxaldehyde ligands;

PCN = Porous Coordination Network;

PCN-224 = a MOF composed of Zr_6 nodes and meso-5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin;

PCN-777 = a MOF composed of Zr_6 nodes and 4,4′,4″-*s*-triazine-2,4,6-triyl-tribenzoate;

PCN-333 = a MOF composed of aluminum ions and 4,4′,4″-*s*-triazine-2,4,6-triyl-tribenzoate ligands;

PCN-600 = a MOF composed of Fe_3 nodes and tetrakis (4-carboxyphenyl) porphyrin ligands;

PCN-888 = a MOF composed of aluminum trimeric cluster and heptazine based tritopic ligand;

PCN-128y = a MOF composed of Zr_6 nodes and (4′,4‴,4⁗,4⁗′-(ethene-1,1,2,2-tetrayl)tetrakis(([1,1′-biphenyl]-4-carboxylic acid))) (H_4ETTC);

MIL = Material Institute Lavoisier;

MIL-101(M) = a MOF composed of M_3O (M= Cr, Fe,) nodes and terephthalic acid ligands;

MIL-101-NH_2 = a MOF composed of Cr_3O nodes and 2-aminoterephthalic acid ligands;

UiO = University of Oslo;

UiO-66 = a MOF composed of Zr_6 nodes and 1,4-benzenedicarboxylic acid ligands;

UiO-66-NH_2 = a MOF composed of Zr_6 nodes and 2-aminoterephthalic acid ligands;

MOF-5 = a MOF composed of zinc ions and terephthalic acid ligands;

DUT = Dresden University of Technology;

DUT-68 = a MOF composed of Zr_6 nodes and 2,5-thiophenedicarboxylic acid ligands (H_2TDC);

NU = Northwestern University;

NU-1000 = a MOF composed of Zr_6 nodes and 1,3,6,8-tetrakis(p-benzoic acid)pyrene ligands;

MAF = Metal Azolate Framework;

MAF-7 = a MOF composed of zinc ions and 3-methyl-1,2,4-triazole ligands;

NKMOF-101-Zn = a MOF composed of zinc ions and squaric acid ligands;

MOA = Metal-organic aerogel;

For molecules:

$[H_2TMPyP]^{4+}[X]_4$ = 5,10,15,20-tetrakis(1-methyl-4-pyridinium)porphyrin,

X= *p*-tosyl$^-$, Cl^-, or I^- as shown in Fig. 2a, top;

$[H^+]_4[H_24SP]^{4-}$ = tetrakis(4-sulphonatophenyl)porphyrin as shown in Fig. 2a, middle;

H_2TCPP = meso-5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin as shown in Fig. 2a, bottom;

H_2Pc = phthalocyanine as shown in Fig. 2b, top;

H_2PcF_{16} = perfluorinated phthalocyanine as shown in Fig. 2b, bottom;

18C6 = 18-crown-6 as shown in Fig. 2c;

BCE = benzo-12-crown-4-ether as shown in Fig. 2d;

DB15C5 = dibenzo-15-crown-5 as shown in Fig. 2e;

DB18C6 = dibenzo-18-crown-6 as shown in Fig. 2f;

B15C5 = benzo-15-crown-5 as shown in Fig. 2g;

CA−1 = calix[4]arene derivate with carboxylic acid groups at ortho-position as shown in Fig. 2h ;

CA−2 = thiacalix[4]arene with carboxylic acid groups at ortho-position as shown in Fig. 2i;

$MeMeCH_2$ = a bowl-shaped cavitand with four methyl groups on both rims as shown in Fig. 2j;

MC5 = decamethylcucurbit[5]uril as shown in Fig. 2k;

CB6 = cucurbit[6]uril as shown in Fig. 2l;

M_6L_4 = an octahedral assembly with six Pd(II) nodes and four 1,3,5-tris(4-pyridyl)-2,4,6-triazine ligands, Fig. 2m;

$H_2N-M_4L_6$ = an amino-functionalized Zr-based tetrahedron with the formula of

$(\{[Cp_3Zr_3O(OH)_3]_4(NH_2\text{-}BDC)_6\}\cdot Cl_4)$ as shown in Fig. 2n;

MOP-3 = a nanosized cuboctahedron with the formula of $Na_6H_{18}[Cu_{24}(SO_3^-\text{-}m\text{BDC})_{24}(G)_{24}]$,

G represents coordinated solvent on Cu_2 node.

MP-11 = microperoxidase-11 with a molecular size of 1.1 nm×1.7 nm×3.3 nm;

Cyt c = cytochrome c with a molecular size of 2.6 nm×3.2nm×3.3 nm;

Protease with a molecular size of 2.85 nm;

HRP = horseradish peroxidase with a molecular size of 4.0 nm×4.4 nm×6.8 nm;

GOx = glucose oxidase with a molecular size of 6.0 nm×5.2 nm×7.7 nm;

FCAT = fluorescein-tagged catalase with a molecular size of 4.4 nm×4.9 nm×5.6 nm;

BCL = *Burkholderia cepacian* lipase;

α-G = *α*-glucosidase;

β-G = *β*-glucosidase;

OPAA = organophosphorus acid anhydrolase with a molecular size of 4.4 nm×4.4nm×7.8 nm;

PABA = *p*-aminobenzoic acid;

CRL = lipase from Candida rugosa;

GOD = glucose oxidase;

UOx = Urate oxidase;

ABTS = 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate;

PNPB = p-nitrophenyl butyrate;

DFP = diisopropyl fluorophosphate;

Soman = O-pinacolyl methyl fluorophosphonate;

SPARC = secreted protein acidic and rich in cysteine.

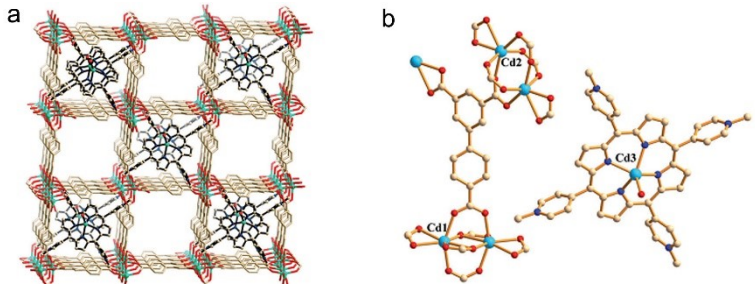

Fig. S1. a) View of the crystal packing in Cd@TMPyP@MOM−11(Cd); b) coordination environments of the Cd^{2+} ions in Cd@TMPyP@MOM−11(Cd). Turquoise Cd, beige C, red O, blue N. Reprocuced from ref. 49 with permission of Wiley-VCH Verlag GmbH & Co., Copyright 2012.

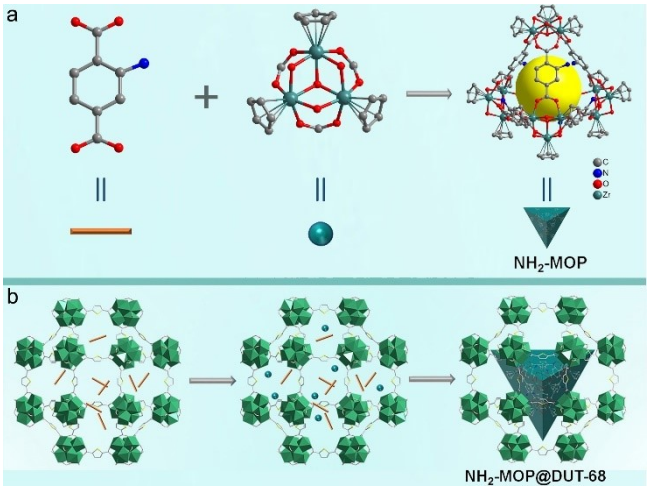

Fig. S2. a) Schematic preparation of the cuboctahedron NH_2-MOP, and b) the "ship−in−bottle" synthesis of NH_2-MOP@DUT−68. Adapted from ref. 72 with permission of Wiley-VCH Verlag GmbH & Co., Copyright 2021.

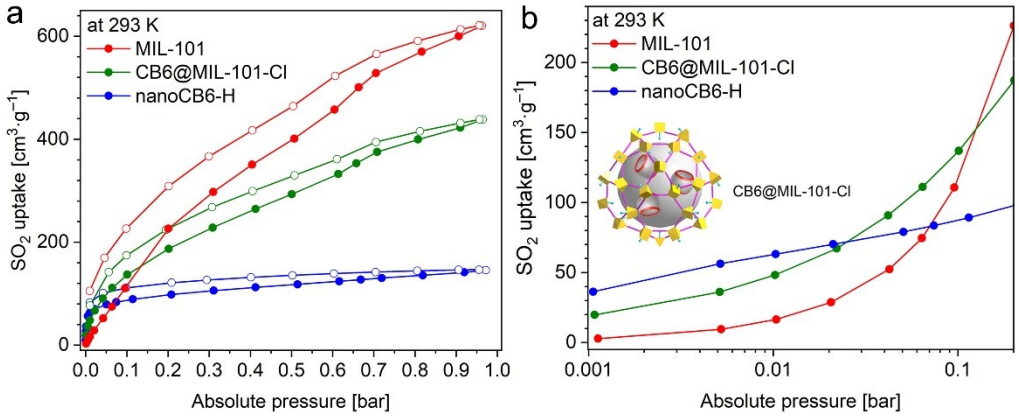

Fig. S3. SO_2 sorption isotherms of CB6@MIL−101−Cl−31 up to 1 bar at 293K and 298K, respectively. a) full pressure range, and b) low pressure range. Reproduced from ref. 70 with permission of the Royal Society of Chemistry, Copyright 2021.

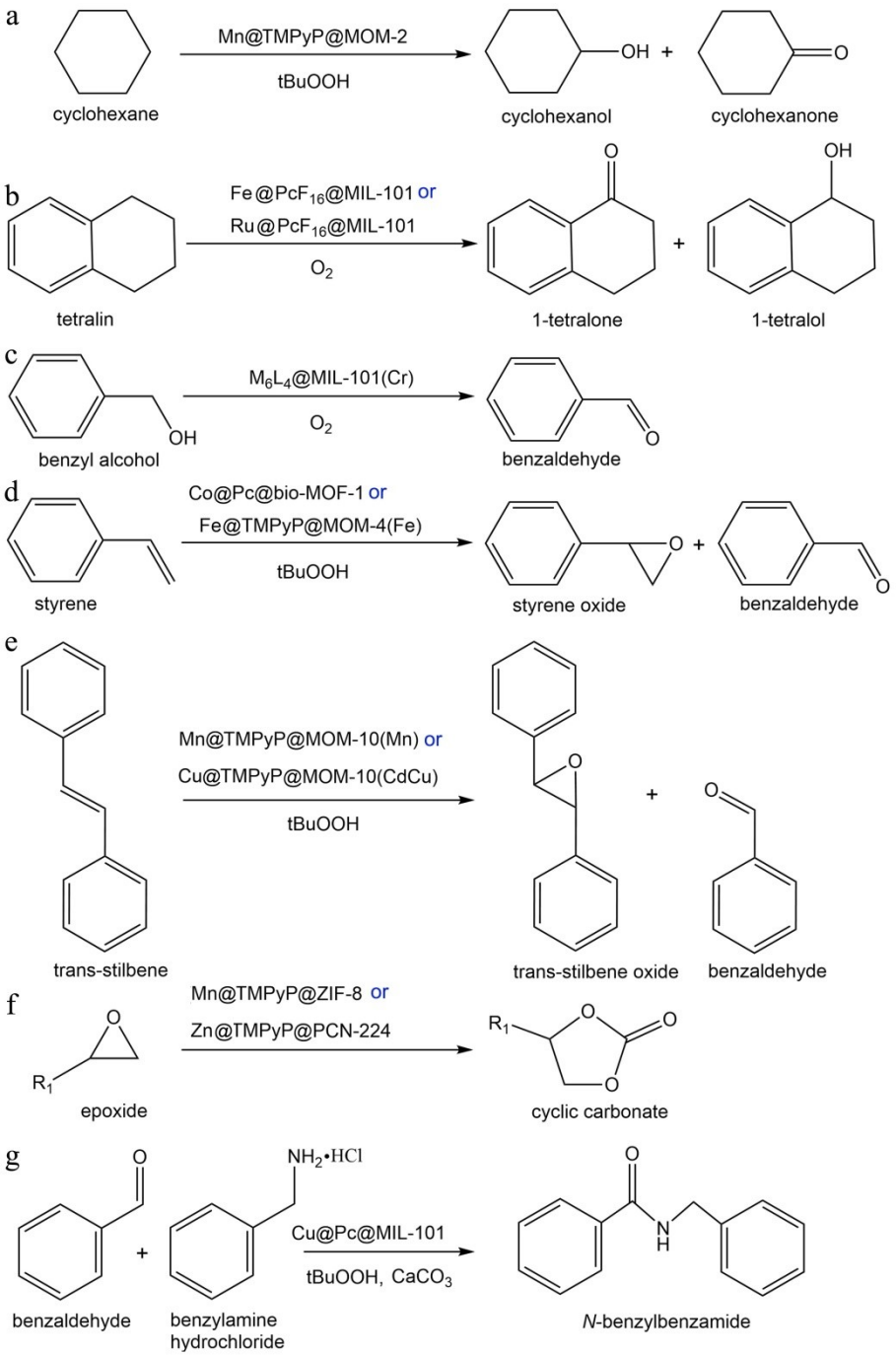

Fig. S4 Representative organic reactions catalyzed by host@MOF and metal@host@MOF materials. a) Oxidation of cyclohexane, b) oxidation of tetralin, c) oxidation of benzyl alcohol, d) oxidation of styrene, e) oxidation of trans−stilbene, f) cyclic carbonation, g) benzamide reaction. The used catalysts and oxidant/reagent are presented above and below the arrow, respectively.