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Supplementary information

Advances and Challenges in the Creation of Porous Metal Phosphonates

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Table S1. Synthesis Protocol for Porous Metal Phosphonates.

Metal Precursor	Phosphonic Linker	Synthesis Method	Final Morphology	References
$ZrOCl_2$	Mono-alkyl phosphonic acids and their dialkyl ester	Direct precipitation in HF (aqueous media)	Lamellar hexagonal particles (10–100 μm)	[1]
$Th(NO_3)_4$ $ZrOCl_2$	Mono-terphenyl and bis-terphenylene PA	Direct precipitation in HF (dioxane/water)	Lamellar particles	[2]
$ZrOCl_2$	α,ω-bis(phosphonic acid) alkyl or aryl linker	Direct precipitation in HF	Lamellar thin films	[3]
$ZrOCl_2$	Butane DPA, benzene DPA,bis(phosphono methyl) DPA, diphenyl DPA with H_3PO_4	Direct precipitation in HF (DMSO/water)	Lamellar structure with mesoporosity	[4]
Zr (IV) fluoro complexes	3,3′, 5,5′-TMBPDA	Direct precipitation in HF	Lamellar structure with inter-layer microporosity	[5]
$ZnCl_2$	Phenyl-DPA Biphenylyl-DPA	Co-condensation in water	Lamellar structure	[6]
$CuSO_4$ 5H_2O & $CuNO_3$ 2.5H_2O	Phenyl-DPA and Biphenylyl-DPA	Co-condensation in water under reflux or hydrothermal conditions	Lamellar structure	[7]
$CuSO_4$ 5H_2O & $ZnCl_2$	Ethylene-DPA and Propylene-DPA	Co-condensation in water	Lamellar structure	[8]
$ZrOCl_2$	Benzene DPA + H_3PO_4	Direct precipitation in HF	Lamellar particles with micro/mesoporosity	[9]
$Zn(NO_3)_2$ & $Cd(NO_3)$	Bis(methylene) phenyl-PA	Co-condensation in water	Lamellar structure	[10]
$ZnCl_2$	Phenyl DPA with H_3PO_4	Hydrothermal in water	Lamellar with slit-shape pores 6.6 nm	[11]
$Mn(ac)_2$ & $Zn(ac)_2$	NMIB-DPA	Hydrothermal in EtOH/water	Lamellar structure with 3D porous framework	[12]
$Co(ac)_2$	Octyl DPA	Co-condensation & Hydrothermal in water (HF)	1D polymeric network and Layered structure	[13]
$SnCl_4$	Phenyl PA	Hydrothermal in HF	Micro and mesoporous	[14]
$Sn(CO_2)_2$	Phenyl DPA	Hydrothermal in water	3D non-porous layered structure	[15]

$SnCl_4$	Phenyl PA Methyl PA	Hydrothermal in HF	Layered spherical globules with micro/mesoporosity	[16]
$SnCl_4$	PPPA	Direct precipitation followed by hydrothermal in HF	Supermicroporous layered particles	[17]
$SnCl_4$ $ZrOCl_2$	PPPA PPA	Direct precipitation in HF	Layered micro and mesoporous structure	[18]
$SnCl_4$	Phenyl-PA Biphenyl-PA	Hydrothermal in HF	Layered nano-sized particles with micro/mesoporosity	[19]
$SnCl_4$ $ZrOCl_2$	bpyBPAE + Methyl PA	Hydrothermal in DMSO (HF)	Small nanoparticles (<15 nm) with micro/mesoporosity	[20]

Abbreviations: PA = Phosphonic acid; DPA = Diphosphonic acid; 3,3′,5,5′-TMBDPA = Tetramethylbiphenyldiphosphonic acid; NMIB = N-methyliminobis(methylenephosphonic acid); PPPA = 4-(4′-phosphonophenoxy)phenyl phosphonic acid; PPA = Phenylphosphonic acid; and bpyBPAE = Tetraethyl 2,2′-bipyridinediyl-5,5′-bis(phosphonate).

Table S2. Phosphonate—MOFs.

Metal Precursor	**Phosphonic Linker**	**Synthesis Method**	**Final Morphology**	**References**
Hydrous TiO_2	Methylene DPA	Hydrothermal in HF/water	3D framework with layered structure—Non-porous	[21]
$CoCl_2$ & $Co(ac)_2$ $NiCl_2$ & $Ni(ac)_2$	N,N′-PBMDPA	Hydrothermal in water	Hexagonal array of channels with 10 Å pores	[22]
Hydrous TiO_2 $AlCl_3$	N,N′-PBMDPA	Hydrothermal in HF/water	3D framework with microporosity	[23]
$Zn(ClO_4)_2$	DHBP	Co-condensation in water & reflux with DMF	3D porous structure with microporosity (10 Å pores)	[24]
$Pb(ac)_2$ $ZnCl_2$	EDTP	Hydrothermal in water/EtOH	Open-framework with tunnels & microporous	[25]
$Pb(NO_3)_2$	N,N′-PBMDPA	Hydrothermal in water	3D supramolecular framework	[26]
$ZrOCl_2$	PBMPA	Co-condenastion/Precipitation in water (NH4F or HF)	Layered framework	[27]
$Zn(NO_3)_2$	BDPEt	Co-condensation (THF/water)	3D network with channels of ~4.5A°	[28]
$CuCl_2$	BDPEt BDPMe	Co-condensation (EtOH/water)	Layered pillar structure with VdW interaction	[29]
$CuCO_3{\cdot}Cu(OH)_2$	BDPA Amino triazole	Co-condensation (MeOH/water)	Pillared interlayer architecture with apparent pores	[30]
$Ni(ac)_2$	N,N′-PBMDPA	Hydrothermal in water	3D frameworks with 0.9 nm pores	[31]
$Co(ac)_2$	N,N′-BPBMDPA	Hydrothermal in water	3D honeycomb architecture with pores of 1.8 nm	[32]
$BaBr_2{\cdot}2H_2O$	Octaethyl pyrene-1,3,6,8-tetraphosphonate	Hydrothermal in EtOH/water	3D framework made up by crosslink of 1D chains	[33]
$SnCl_4$	BTBP	Hydrothermal in MeOH	Amorphous microporous (~8.5 Å)	[34]
$CuSO_4$, NiO, $NiSO_4$, & $MnSO_4$	BTTMT TMB-BTTMT	Hydrothermal in water	2D double-layered structure with 1D	[35]

			tunnel with aperture of 3.5 Å × 7.0 Å	
$ZrOCl_2$	BTBP	Direct precipitation in HF	Non-porous honeycomb-like motif	[36]
$ZrOCl_2$	TTBMP	Direct precipitation in HF	Permanent microporosity & channels of (~5–10 Å)	[37]
$Al_2(SO_4)_3$	TMB-TTMT	Hydro(solvo)thermal in EtOH/water	3D framework with hexagonal channels (1.2 nm width)	[38]
$ZrCl_4$	BTBP	Direct precipitation & Hydrothermal (HF)	3D amorphous and semi-crystalline framework with microporosity (10 Å pores)	[39]
$ZrOCl_2$	TTBMP	Direct precipitation in HF	2D layered structure with no porosity	[40]

Abbreviations: DPA = Diphosphonic acid; N,N′-PBMDPA = N,N′-piperazine bis(methylenephosphonic acid); DHBP = 1,4-dihydroxy-2,5-benzenediphosphonate; EDTP = N,N,N′,N′-ethylenediaminetetrakis(methylenephosphonic acid); PBMPA = Piperazine-N,N′-bis(methylenephosphonic acid); BDPEt = 1,4-benzenediphosphonate bis(monoethyl ester); BDPMe = 1,4-benzenediphosphonate bis(monomethyl ester); BDPA = Benzene-1,4-diphosphonic acid; BTTMT = Benzene-1,3,5-triyltris(methylene)triphosphonic acid; TMB-BTTMT = (2,4,6-trimethylbenzene-1,3,5-triyl)tris(methylene)triphosphonic acid; BTBP = 1,3,5-tris(4-phosphonophenyl) benzene; TTBMP = 2,4,6-tris(4-(phosphonomethyl)phenyl)-1,3,5-triazine; and TMB-TTMT = 2,4,6-trimethylbenzene-1,3,5-triyl-tris(methylene)triphosphonic acid.

Table S3. Mesoporous Metal Phosphonates—Templated.

Metal Precursor	Phosphonic Acid	Template	Synthesis Method	Final Morphology	References
$Al(OiPr)_3$	MDPA	ODTMACl	Co-condensation at RT in water	Amorphous, Mesoporous (1.8 nm pores)	[41]
$Al(OsBu)_3$	EDPA	CTAB	Atrane route, Co-precipitation in water	Amorphous, Mesoporous (hexagonal)	[42]
$AlCl_3$	MDPA	Brij-56/58 F68, F127 P123	Co-condensation in EtOH/water followed by EISA	Amorphous Mesoporous (p6m)	[43]
$Al(OiPr)_3$ $AlCl_3$	MDPA EDPA PDPA	CTAB	Co-condensation in water and EtOH/water	Amorphous with Mesoporosity	[44]
$SnCl_4$	PPA	SDS	Hydrothermal	Semi-crystalline, Micro and mesoporous	[45]
$ZrOCl_2$	PPA	-	Hydrothermal in water	Amorphous, Inter-particle mesoporosity	[46]
$Al(OsBu)_3$	H3PMP	CTAB	Atrane route, Co-precipitation in water	Amorphous with mesoporosity	[47]
$Ti(OiPr)_4$	TPPhA	-	Non-hydrolytic condensation in THF	Amorphous with inter-particle porosity	[48]
$V(O)(OiPr)_3$	TPPhA	-	Non-hydrolytic condensation in DMSO	Amorphous with inter-particle porosity	[49]

$Ti(OBu)_4$	HEDP (β-CD)	PS beads	Hydrothermal in EtOH/water	Amorphous, Inter-particle mesoporosity & macroporous	[50]
$Ti(OBu)_4$	HEDP EDTMP	-	Hydrothermal in EtOH/water	Amorphous, plate-like particles & slit shaped inter-particle mesoporosity	[51]
$Ti(OBu)_4$	HEDP	F127 P123	Co-condensation in EtOH followed by EISA	Amorphous, Inter-particle mesoporosity	[52]
$TiCl_4$	EDTMP	Brij-56	Cryogenic condensation in EtOH followed by hydrothermal and EISA	Amorphous, p6mm Mesophase	[53]
$TiCl_4$	HEDP	CTAB	Cryogenic condensation in EtOH followed by hydrothermal treatment	Amorphous, la3d cubic mesophase	[54]
$Ti(OBu)_4$	HEDP EDTMP	-	Hydrothermal in EtOH/water	Amorphous with hierarchical meso/macroporosit y	[55]
$Ti(OBu)_4$	EDTMP DTPMP	-	Hydrothermal in EtOH/water	Crystalline (anatase domains) with phosphonate cap and hierarchical meso/macroporosit y	[56]
$AlCl_3$	BDPA	F127	Co-condensation in EtOH/water	Amorphous, Cubic mesoporous (Im3m)	[57]
$AlCl_3$	DEPT DPAEP DPEP	F127	Co-condensation in EtOH/water	Amorphous, mesoporous thin film	[58]
$Ti(OiPr)_4$	bBzP bPyP	-	Non-hydrolytic sol gel hydrothermal in toluene	Anatase crosslinked bisphosphonates with inter-crystal mesopores	[59]

Abbreviations: MDPA = Methylenediphosphonic acid; EDPA = Ethylenediphosphonic acid; PDPA = Propylenediphosphonic acid; PPA = Phenylposphonic acid; H3PMP = 1-phosphonomethylproline; TPPhA = Tetrakis-1,3,5,7-(4-diethylphosphonatophenyl) adamantane; HEDP = 1-hydroxyethane 1,1-diphosphonic acid; EDTMP = Ethylenediamine tetra(methylene phosphonic acid); DTPMP = Diethylenetriamine penta(methylene phosphonic acid); BDPA = 1,4-phenylene diphosphonic acid; DEPT = 2,5-bis(diethoxyphosphoryl) thiophene; DPAEP = Diethyl (N-diethylphosphonomethylcarbonyl)aminoethyl phosphonate; DPEP = Diethyl 2-(2′-diethylphosphonoethoxy)ethylphosphonate; bBzP = 4,4′-bis(diethylphosphonomethyl)biphenyl; and bByP = tetraethyl 2,2′-bipyridine-5,5′-bisphosphonate.

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