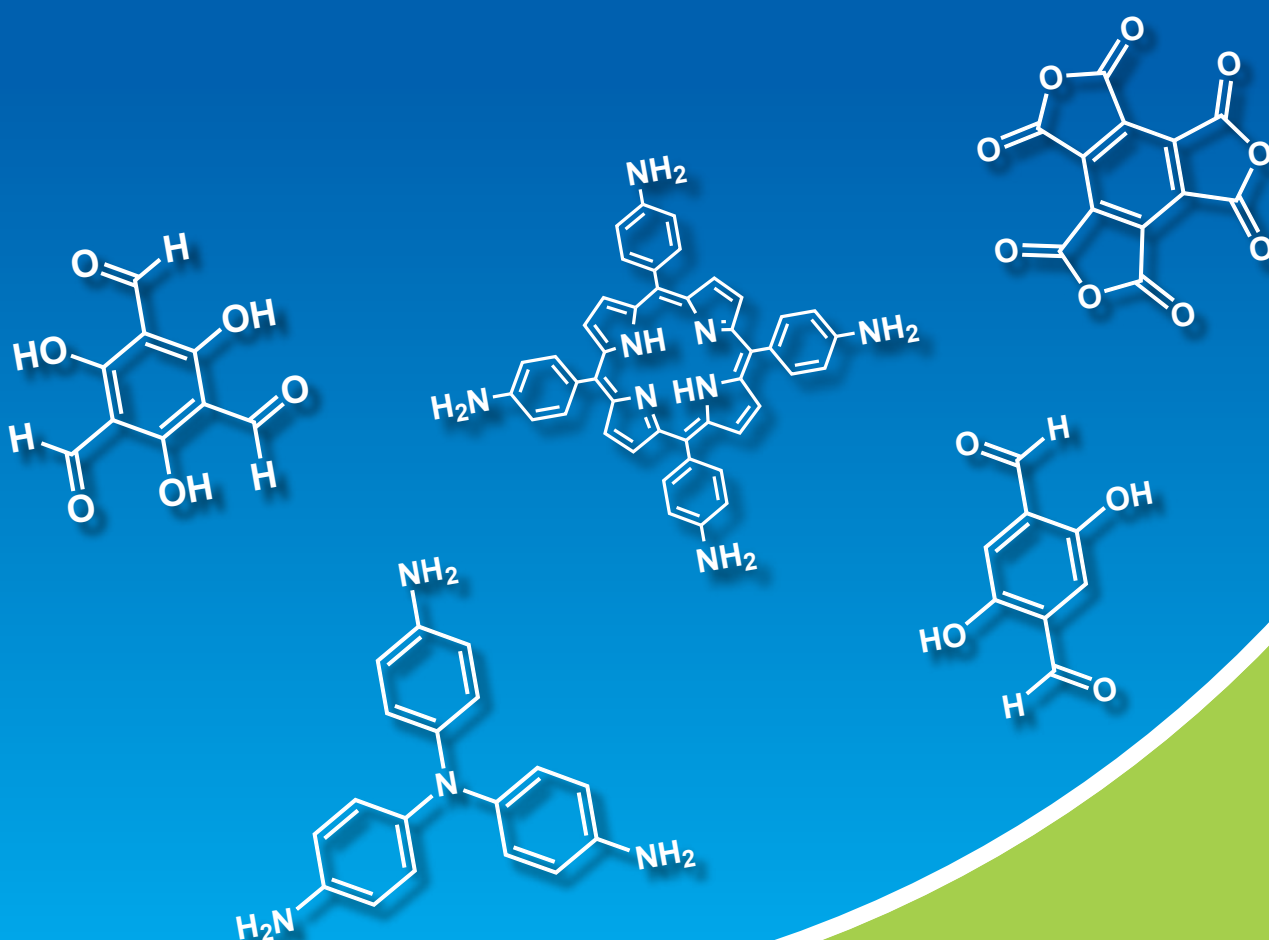


Covalent Organic Framework (COF) Linkers



Amine Linkers

Aldehyde Linkers

Carboxylic Anhydride Linkers

Boronic Acid Linkers

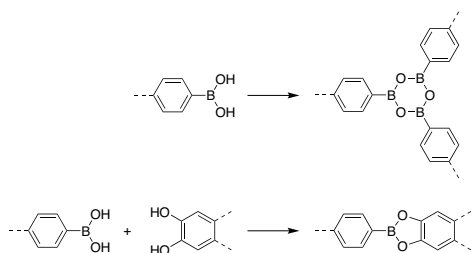
Other Linkers

Covalent Organic Framework (COF) Linkers

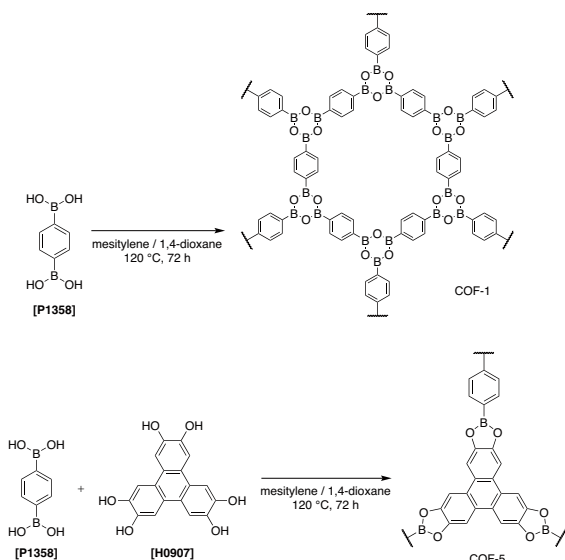
Covalent organic frameworks (COFs) are crystalline organic frameworks consisting of a network structure made of covalent bonds.^{1,2)} COFs are classified as porous crystalline materials similar to metal-organic frameworks (MOFs)/porous coordination polymers (PCPs) and zeolites. They include 2D COFs, which are constructed by stacking layers of 2D covalently bonded sheets, and 3D COFs, which are constructed by 3D connected frameworks. COFs are expected to be used as molecular storage or separation materials, catalysts, electronic materials, energy storage materials, battery materials, and drug delivery materials, due to their porosity, crystallinity, and structural diversity.

COFs are designed and synthesized by combining monomers, also known as linkers, according to intended topology. Some synthetic examples are shown below with synthetic strategies.

● Boroxines and boronic esters

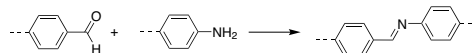


The self-condensation of boronic acids to produce boroxines and the condensation of boronic acids and catechols to produce boronic esters are the first synthetic strategies to synthesize COFs (Scheme 1).¹⁾ The advantages of boroxine-based COFs and boronic ester-based COFs include their tendency to have good crystallinity, large surface area, and high thermal stability.

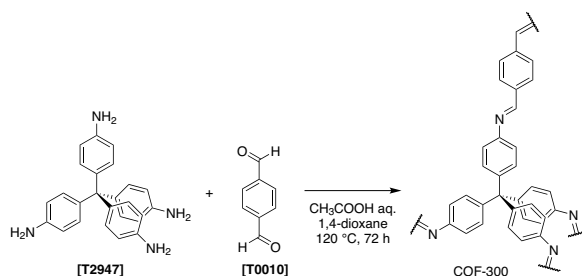


Scheme 1. Synthesis of COF-1 and COF-5¹⁾

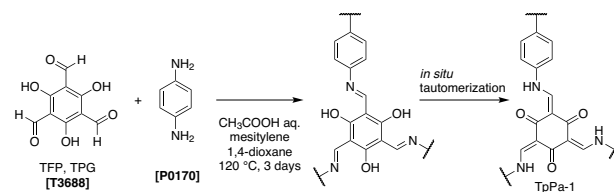
● Imines



Imine-linked covalent organic framework, synthesized by condensation of aldehydes and amines, was first reported in 2009 (Scheme 2),⁴⁾ and imine-based COFs are now the most widely reported COFs. Imine-based COFs have higher chemical stability compared to boroxines and boronic esters. In addition, several researchers have reported post-synthetic modification or functionalization of imine-based COFs, such as the synthesis of COFs for CO₂ capture through the post-synthetic modification and functionalization of imine-based structures.⁵⁾ In 2012, it was reported that β -ketoenamine-type COFs can be synthesized by using 2,4,6-triformylphloroglucinol (TPG, TFP) as an aldehyde linker (Scheme 3).⁶⁾ These compounds have recently received a lot of attention due to their stability towards acids and bases.

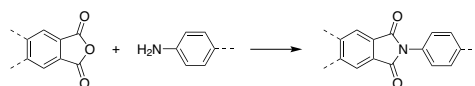


Scheme 2. Synthesis of COF-300⁴⁾



Scheme 3. Synthesis of TpPa-1⁶⁾

● Imides



Imide-linked COFs obtained by condensation of carboxylic anhydrides and amines have also been reported⁷⁾ and are expected to be applied to battery materials⁸⁾ and CO₂ capture materials.⁹⁾

● Other synthetic strategies

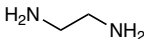
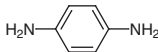
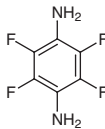
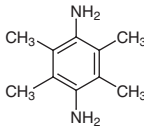
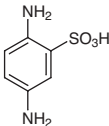
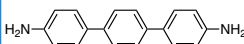
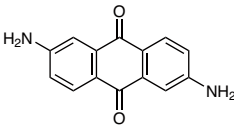
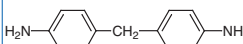
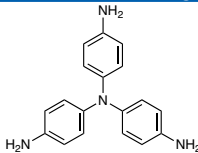
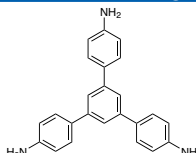
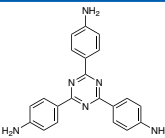
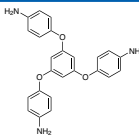
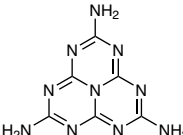
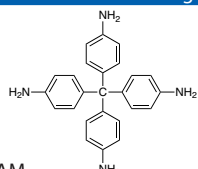
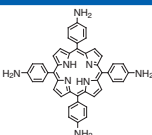
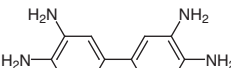
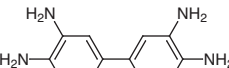
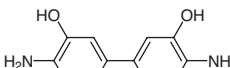
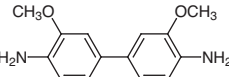
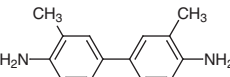
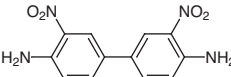
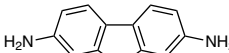
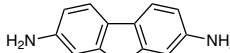
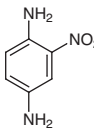
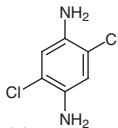
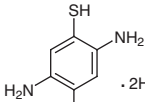
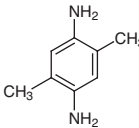
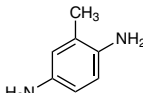
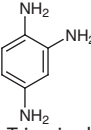
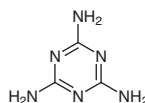
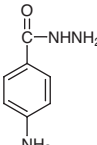
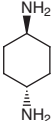
COFs constructed by other linkers besides imines, imides, and boroxines have been realized. Linkers other than amines, aldehydes, carboxylic anhydrides, and boronic acids are used as linkers to prepare these COFs. For example, hydrazone-type

COFs synthesized using hydrazines and aldehydes^{10,11)} and ionic COFs synthesized using 1,2,3-triaminoguanidinium chloride¹²⁾ were reported.

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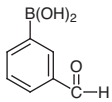
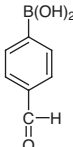
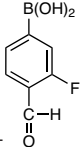
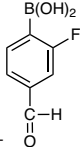
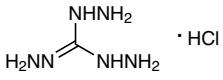
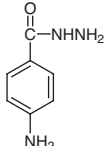
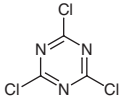
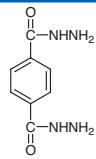
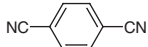
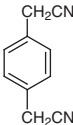
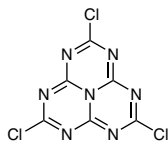
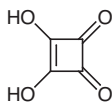
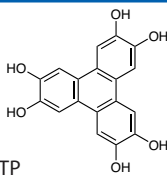
Amine Linkers

Amine Linkers			E0077	25mL 500mL	P0170	5g 25g 250g	T1110	1g	
									
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T1457	5g 25g	P1691	5g 25g	D3390	1g 5g	D3180	25g	M0220	25g 500g
									
TMPD CAS RN: 3102-87-2		1,4-Phenylenediamine- 2-sulfonic Acid CAS RN: 88-45-9		4,4''-Diamino- <i>p</i> -terphenyl CAS RN: 3365-85-3		2,6-Diaminoanthraquinone CAS RN: 131-14-6		4,4'-MDA CAS RN: 101-77-9	
T2332	1g 5g	T2728	5g 25g	T3695	1g 5g	T3909	200mg 1g	M3538	1g
									
TAPA CAS RN: 5981-09-9		TAPB CAS RN: 118727-34-7		4,4',4''-(1,3,5-Triazine- 2,4,6-triyl)trianiline CAS RN: 14544-47-9		1,3,5-Tris(4-amino- phenoxy)benzene CAS RN: 102852-92-6		Melem CAS RN: 1502-47-2	
T2947	200mg 1g	T1494	100mg	D0077	5g 25g	D0078	5g 25g	D2312	5g 25g
									
TAM CAS RN: 60532-63-0		5,10,15,20-Tetrakis(4- aminophenyl)porphyrin CAS RN: 22112-84-1		3,3'-Diaminobenzidine CAS RN: 91-95-2		DAB-4HCl Hydrate CAS RN: 868272-85-9 · 4HCl · xH2O		3,3'-Dihydroxybenzidine CAS RN: 2373-98-0	
D1344	25g 100g	T0253	1g 5g	D0822	25g	D0092	250mg 1g 5g 25g	D0093	5g 25g
									
<i>o</i> -Dianisidine CAS RN: 119-90-4		<i>o</i> -Tolidine CAS RN: 119-93-7		3,3'-Dinitrobenzidine CAS RN: 6271-79-0		2,7-Diaminofluorene CAS RN: 525-64-4		2,7-Diaminofluorene Dihydrochloride CAS RN: 13548-69-1 · 2HCl	
D0105	25g 500g	D1873	25g 250g	D2022	5g 25g	D2183	25g 100g	D4628	5g 25g
									
2-Nitro- 1,4-phenylenediamine CAS RN: 5307-14-2		2,5-Dichloro- 1,4-phenylenediamine CAS RN: 20103-09-7		2,5-Diamino-1,4-benzenedithiol Dihydrochloride CAS RN: 75464-52-7 · 2HCl		2,5-Diamino- <i>p</i> -xylene CAS RN: 6393-01-7		2,5-Diaminotoluene CAS RN: 95-70-5	
T0334	1g	T0337	5g 25g 500g	A1211	25g	C1426	5g 25g 100g		
									
1,2,4-Triaminobenzene Dihydrochloride CAS RN: 615-47-4 · 2HCl		Melamine Monomer CAS RN: 108-78-1		4-Aminobenzohydrazide CAS RN: 5351-17-7		<i>trans</i> -1,4- Cyclohexanediamine CAS RN: 2615-25-0			

Aldehyde Linkers

T0010 25g 100g 500g Terephthalaldehyde CAS RN: 623-27-8	D5510 1g 5g DHTA CAS RN: 1951-36-6	D6056 1g 5g DMA CAS RN: 7310-97-6
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T3688 200mg 1g TPG CAS RN: 34374-88-4	B6003 200mg 1g BTA CAS RN: 3163-76-6	D6046 1g 5g 2,4,6-Triformylresorcinol CAS RN: 58343-11-6	T2310 500mg Tris(4-formylphenyl)amine CAS RN: 119001-43-3	T4077 1g 5g 2,4,6-Tris(4-formylphenoxy)-1,3,5-triazine CAS RN: 3140-75-8
A2664 1g 5g 9,10-Diformylanthracene CAS RN: 7044-91-9	B2854 1g 5g BPDA CAS RN: 66-98-8	T4088 1g 5g TFTA CAS RN: 3217-47-8	B5484 200mg 4,8-Bis(<i>n</i> -octyloxy)benzo[1,2- <i>b</i> :4,5- <i>b'</i>]dithiophene-2,6-dicarbaldehyde CAS RN: 1668554-22-0	T3212 200mg 1g Thieno[3,2- <i>b</i>]thiophene-2,5-dicarboxaldehyde CAS RN: 37882-75-0
F0310 1g 5g 25g 4-Hydroxyisophthalaldehyde CAS RN: 3328-70-9	H0683 1g 5g 2-Hydroxy-5-methylisophthalaldehyde CAS RN: 7310-95-4	I0153 25g 100g 250g Isophthalaldehyde CAS RN: 626-19-7	P0949 1g 5g 2,6-Pyridinedicarboxaldehyde CAS RN: 5431-44-7	F0445 1g 5g 25g 3-Formylphenylboronic Acid CAS RN: 87199-16-4
F0446 1g 5g 4-Formylphenylboronic Acid CAS RN: 87199-17-5	F1051 1g 5g 3-Fluoro-4-formylphenylboronic Acid CAS RN: 248270-25-9	F1079 1g 2-Fluoro-4-formylphenylboronic Acid CAS RN: 871126-22-6	<div> <div>Carboxylic Anhydride Linkers</div> </div>	
		B0040 25g 100g 500g PMDA CAS RN: 89-32-7	P2103 5g 25g PMDA (purified by sublimation) CAS RN: 89-32-7	M3617 1g 5g Mellitic Trianhydride CAS RN: 4253-24-1
N0369 25g 250g NTCDA CAS RN: 81-30-1	N0755 1g 5g NTCDA (purified by sublimation) CAS RN: 81-30-1	N1128 1g 5g 2,3,6,7-NTCDA CAS RN: 3711-01-1	N1247 1g 1,2,5,6-NTCDA CAS RN: 3711-03-3	P0972 25g 100g 500g PTCDA CAS RN: 128-69-8
P2102 1g PTCDA (purified by sublimation) CAS RN: 128-69-8				
		P1358 1g 5g 25g BDPA CAS RN: 4612-26-4	B2490 1g 5g BPDA CAS RN: 4151-80-8	D4701 1g (9,9-Dimethyl-9H-fluorene-2,7-diyl)diboric Acid CAS RN: 866100-14-3
<div> <div>Boronic Acid Linkers</div> </div>				

F0445 1g 5g 25g  3-Formylphenylboronic Acid CAS RN: 87199-16-4	F0446 1g 5g  4-Formylphenylboronic Acid CAS RN: 87199-17-5	F1051 1g 5g  3-Fluoro-4-formylphenylboronic Acid CAS RN: 248270-25-9	F1079 1g  2-Fluoro-4-formylphenylboronic Acid CAS RN: 871126-22-6
Other Linkers			
T4080 1g 5g  N,N',N''-Triaminoguanidine Hydrochloride CAS RN: 5329-29-3	A1211 25g  4-Aminobenzohydrazide CAS RN: 5351-17-7	C0460 25g 500g  Cyanuric Chloride CAS RN: 108-77-0	T0758 25g 500g  Terephthalic Dihydrazide CAS RN: 136-64-1
T0016 25g 100g 500g  Terephthalonitrile CAS RN: 623-26-7	X0061 5g 25g  1,4-Phenylenediacetonitrile CAS RN: 622-75-3	T4145 1g  Heptazine Chloride CAS RN: 6710-92-5	D1399 5g 25g  Squaric Acid CAS RN: 2892-51-5
H0172 25mL 500mL $\text{H}_2\text{NNH}_2 \cdot \text{H}_2\text{O}$ Hydrazine Monohydrate CAS RN: 7803-57-8			
H0907 1g 5g  HHTP CAS RN: 4877-80-9			

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