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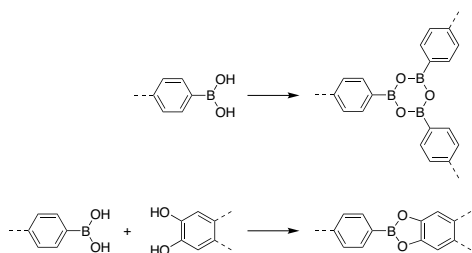
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Covalent Organic Framework (COF) Linkers

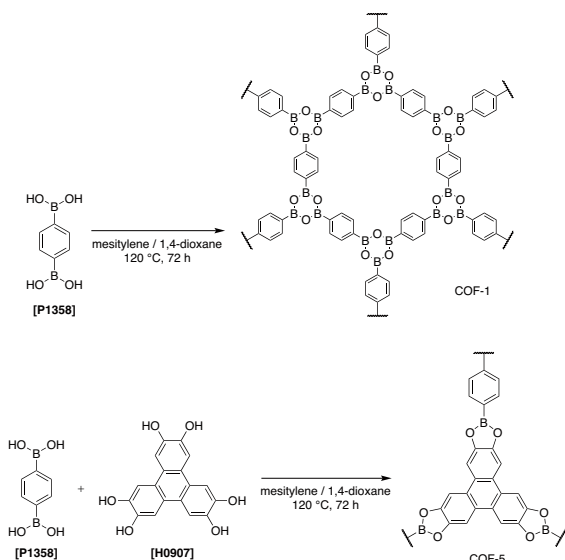
Covalent organic frameworks (COFs) are crystalline organic frameworks consisting of a network structure made of covalent bonds.^{1,2)} COFs are classified as porous crystalline materials similar to metal-organic frameworks (MOFs)/porous coordination polymers (PCPs) and zeolites. They include 2D COFs, 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

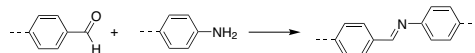


The self-condensation of boronic acids to produce boroxines and the condensation of boronic acids and catechols to produce boronic esters are the first synthetic strategies to synthesize COFs (Scheme 1).¹⁾ The advantages of boroxine-based COFs and boronic ester-based COFs include their tendency to have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

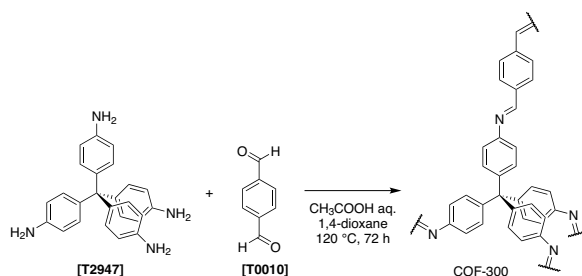


Scheme 1. Synthesis of COF-1 and COF-5¹⁾

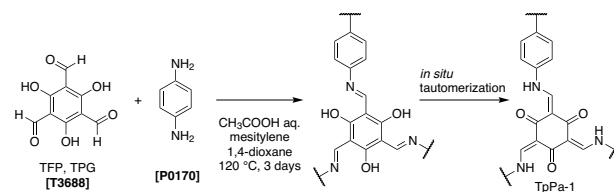
● Imines



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.

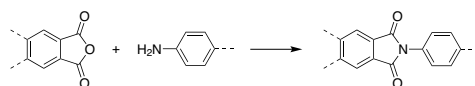


Scheme 2. Synthesis of COF-300⁴⁾



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.

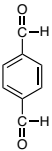
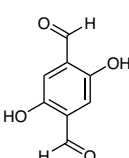
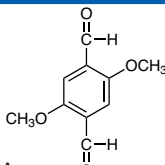
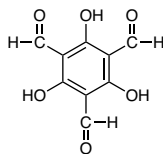
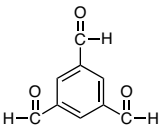
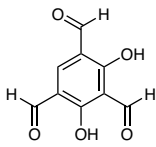
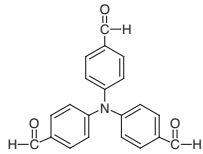
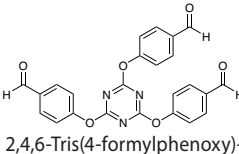
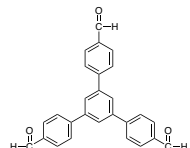
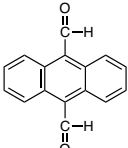
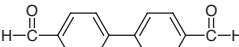
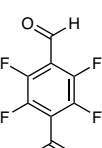
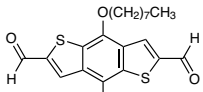
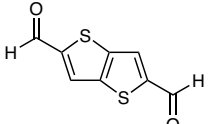
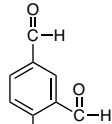
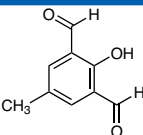
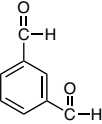
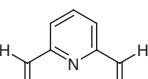
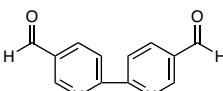
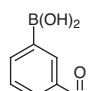
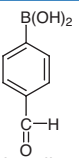
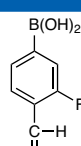
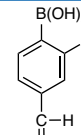
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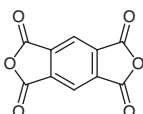
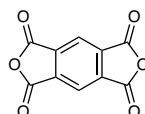
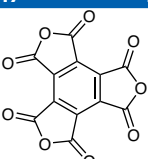
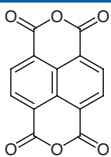
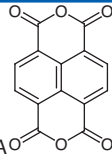
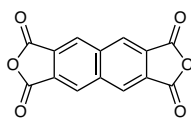
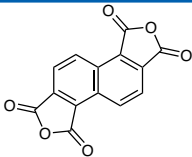
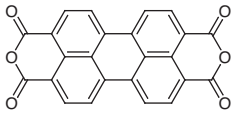
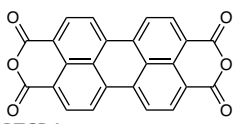
Amine Linkers

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T1457 5g 25g	P1691 5g 25g	D3390 1g 5g	D3180 25g	D2893 1g 5g
<chem>Cc1c(N)c(C)c(N)c(C)c1C</chem> TMPD CAS RN: 3102-87-2	<chem>Nc1ccc(S(=O)(=O)O)cc1N</chem> 1,4-Phenylenediamine- 2-sulfonic Acid CAS RN: 88-45-9	<chem>Nc1ccc(cc1)-c2ccc(N)cc2</chem> 4,4''-Diamino-<i>p</i>-terphenyl CAS RN: 3365-85-3	<chem>Nc1ccc2c(=O)c3cc(N)ccc3c(=O)c2c1</chem> 2,6-Diaminoanthraquinone CAS RN: 131-14-6	<chem>Nc1ccc2cc(N)ccc2n1</chem> [2,2'-Bipyridine]- 5,5'-diamine CAS RN: 52382-48-6
D3430 1g 5g	M0220 25g 500g	T2332 1g 5g	T2728 5g 25g	T3695 1g 5g
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T3909 200mg 1g	M3538 1g	T2947 200mg 1g	T1494 100mg	D0077 5g 25g
<chem>Nc1ccc(cc1)Oc2ccc(Oc3ccc(N)cc3)cc2</chem> 1,3,5-Tris(4-amino- phenoxy)benzene CAS RN: 102852-92-6	<chem>Nc1nc2n(C(=N1)N)nc(N)c2N</chem> Melem CAS RN: 1502-47-2	<chem>Nc1ccc(cc1)C2(Cc3ccc(N)cc3)C2(NC(=O)c4ccc(N)cc4)</chem> TAM CAS RN: 60532-63-0	<chem>Nc1nc2c3c(N)nc(NC(=O)c4ccc(N)cc4)c3nc2c1</chem> 5,10,15,20-Tetrakis(4- aminophenyl)porphyrin CAS RN: 22112-84-1	<chem>Nc1ccc(cc1)-c2ccc(N)cc2</chem> 3,3'-Diaminobenzidine CAS RN: 91-95-2
D0078 5g 25g	D2312 5g 25g	D1344 25g 100g	T0253 1g 5g	D0822 25g
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<chem>Nc1ccc2c(c1)ccc3cc(N)ccc32</chem> 2,7-Diaminofluorene CAS RN: 525-64-4	<chem>Nc1ccc2c(c1)ccc3cc(N)ccc32</chem> 2,7-Diaminofluorene Dihydrochloride CAS RN: 13548-69-1	<chem>Nc1ccc(cc1)[N+](=O)[O-]</chem> 2-Nitro- 1,4-phenylenediamine CAS RN: 5307-14-2	<chem>Nc1cc(N)c(Cl)c(Cl)c1</chem> 2,5-Dichloro- 1,4-phenylenediamine CAS RN: 20103-09-7	<chem>Nc1cc(S)cc(S)c1N</chem> 2,5-Diamino-1,4-benzenedithiol Dihydrochloride CAS RN: 75464-52-7
D2183 25g 100g	D4628 5g 25g	T0334 1g	T0337 5g 25g 500g	A1211 25g
<chem>Cc1cc(N)cc(N)c1C</chem> 2,5-Diamino-<i>p</i>-xylene CAS RN: 6393-01-7	<chem>Cc1cc(N)ccc1N</chem> 2,5-Diaminotoluene CAS RN: 95-70-5	<chem>Nc1ccc(N)cc1N</chem> 1,2,4-Triaminobenzene Dihydrochloride CAS RN: 615-47-4	<chem>Nc1nc2c(N)nc(N)nc2n1</chem> Melamine Monomer CAS RN: 108-78-1	<chem>NC(=O)c1ccc(N)cc1</chem> 4-Aminobenzohydrazide CAS RN: 5351-17-7
C1426 5g 25g 100g				
<chem>N[C@H]1CCCC[C@@H]1N</chem> <i>trans</i>-1,4- Cyclohexanediamine CAS RN: 2615-25-0				

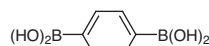
Aldehyde Linkers

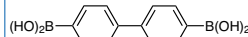
Aldehyde Linkers		T0010	D5510	D6056
		25g 100g 500g	1g 5g	1g 5g
				
		Terephthalaldehyde CAS RN: 623-27-8	DHTA CAS RN: 1951-36-6	DMA CAS RN: 7310-97-6
T3688	B6003	D6046	T2310	T4077
200mg 1g	200mg 1g	1g 5g	500mg	1g 5g
				
TPG CAS RN: 34374-88-4	BTA CAS RN: 3163-76-6	2,4,6-Triformylresorcinol CAS RN: 58343-11-6	Tris(4-formylphenyl)amine CAS RN: 119001-43-3	2,4,6-Tris(4-formylphenoxy)-1,3,5-triazine CAS RN: 3140-75-8
F1252	A2664	B2854	T4088	B5484
200mg 1g	1g 5g	1g 5g	1g 5g	200mg
				
TFPB CAS RN: 118688-53-2	9,10-Diformylanthracene CAS RN: 7044-91-9	BPDA CAS RN: 66-98-8	TFTA CAS RN: 3217-47-8	4,8-Bis(n-octyloxy)benzo[1,2-b:4,5-b']dithiophene-2,6-dicarbaldehyde CAS RN: 1668554-22-0
T3212	F0310	H0683	I0153	P0949
200mg 1g	1g 5g 25g	1g 5g	25g 100g 250g	1g 5g
				
Thieno[3,2-b]thiophene-2,5-dicarboxaldehyde CAS RN: 37882-75-0	4-Hydroxyisophthalaldehyde CAS RN: 3328-70-9	2-Hydroxy-5-methylisophthalaldehyde CAS RN: 7310-95-4	Isophthalaldehyde CAS RN: 626-19-7	2,6-Pyridinedicarboxaldehyde CAS RN: 5431-44-7
B6576	F0445	F0446	F1051	F1079
1g	1g 5g 25g	1g 5g	1g 5g	1g
				
[2,2'-Bipyridine]-5,5'-dicarbaldehyde CAS RN: 135822-72-9	3-Formylphenylboronic Acid CAS RN: 87199-16-4	4-Formylphenylboronic Acid CAS RN: 87199-17-5	3-Fluoro-4-formylphenylboronic Acid CAS RN: 248270-25-9	2-Fluoro-4-formylphenylboronic Acid CAS RN: 871126-22-2

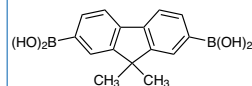
Carboxylic Anhydride Linkers

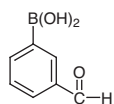
Carboxylic Anhydride Linkers				
B0040 25g 100g 500g		P2103 5g 25g		M3617 1g 5g
				
PMDA CAS RN: 89-32-7		PMDA (purified by sublimation) CAS RN: 89-32-7		Mellitic Trianhydride CAS RN: 4253-24-1
N0369 25g 250g	N0755 1g 5g	N1128 1g 5g	N1247 1g	P0972 25g 100g 500g
				
NTCDA CAS RN: 81-30-1	NTCDA (purified by sublimation) CAS RN: 81-30-1	2,3,6,7-NTCDA CAS RN: 3711-01-1	1,2,5,6-NTCDA CAS RN: 3711-03-3	PTCDA CAS RN: 128-69-8
P2102 1g				
				
PTCDA (purified by sublimation) CAS RN: 128-69-8				

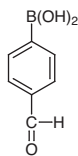
Boronic Acid Linkers

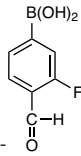
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BDPA
CAS RN: 4612-26-4

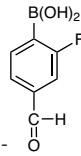
B2490 1g 5g

BPDA
CAS RN: 4151-80-8

D4701 1g

(9,9-Dimethyl-9H-fluorene-2,7-diyl)diboronic Acid
CAS RN: 866100-14-3

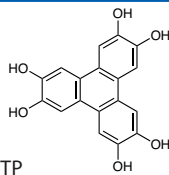
F0445 1g 5g 25g

3-Formylphenylboronic Acid
CAS RN: 87199-16-4

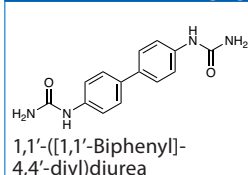
F0446 1g 5g

4-Formylphenylboronic Acid
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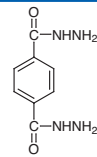
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3-Fluoro-4-formylphenylboronic Acid
CAS RN: 248270-25-9

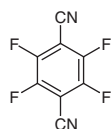
F1079 1g

2-Fluoro-4-formylphenylboronic Acid
CAS RN: 871126-22-6

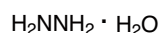
Other Linkers

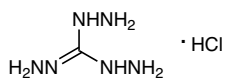
H0907 1g 5g

HHTP
CAS RN: 4877-80-9

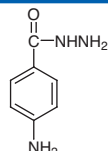
B6577 1g 5g

1,1'-([1,1'-Biphenyl]-4,4'-diyl)diurea
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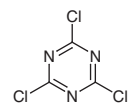
T0758 25g 500g

Terephthalic Dihydrazide
CAS RN: 136-64-1

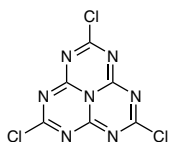
T1050 1g 5g 25g

Tetrafluoroterephthalonitrile
CAS RN: 1835-49-0

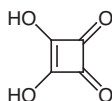
H0172 25mL 500mL

Hydrazine Monohydrate
CAS RN: 7803-57-8

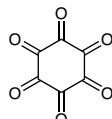
T4080 1g 5g

N,N',N''-Triaminoguanidine Hydrochloride
CAS RN: 5329-29-3

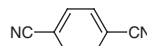
A1211 25g

4-Aminobenzohydrazide
CAS RN: 5351-17-7

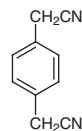
C0460 25g 500g

Cyanuric Chloride
CAS RN: 108-77-0

T4145 1g

Heptazine Chloride
CAS RN: 6710-92-5

D1399 5g 25g

Squaric Acid
CAS RN: 2892-51-5

T0876 1g 5g

Triquinoyl
CAS RN: 527-31-1

T0016 25g 100g 500g

Terephthalonitrile
CAS RN: 623-26-7

X0061 5g 25g

1,4-Phenylenediacetonitrile
CAS RN: 622-75-3

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Россия +7(495)268-04-70

Казахстан +7(7172)727-132

Киргизия +996(312)96-26-47

Адрес: <https://tci.nt-rt.ru/> || эл.почта: tic@nt-rt.ru