Improved Synthesis of β-Ketoenamine-Linked Covalent Organic Frameworks via Monomer Exchange Reactions

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I. Materials and Instrumentation

Materials

All reagents were purchased from commercial sources and used without further purification or prepared from them. Reactions were monitored by thin layer chromatography (TLC) carried out on EMD 250µm silica gel 60-F254 plates. Visualization was performed by irradiation with UV light and a potassium permanganate stain.

Instrumentation

Nuclear Magnetic Resonance. ¹H NMR spectra were acquired on a Varian Inova 500 MHz and an Agilent 400 MHz spectrometer. Spectra were recorded at 25 °C and calibrated using residual solvent as an internal reference (CDCl₃: 7.26 ppm for ¹H NMR). Solid state ¹³C Cross Polarization Magic Angle Spinning (CP-MAS) NMR spectra of covalent organic frameworks were recorded on a Varian 400 MHz using a spin rate of 10,000 Hz and calibrating using adamantane as an external standard.

Infrared Spectroscopy. Infrared spectra were recorded on a Nicolet iS10 Fourier-Transform Infrared (FT-IR) Spectrometer equipped with a ZnSe ATR attachment and are uncorrected.

Elemental Analysis. Elemental analyses were performed by Robertson Microlit Libraries.

Scanning Electron Microscopy. Covalent organic frameworks were coated with osmium (9 nm) and imaged using a Hitachi SU8030 SEM (working distance and accelerating voltage included in each SEM figure).

Gas Adsorption. Gas adsorption isotherms were conducted on a Micromeritics ASAP 2420 Accelerated Surface Area and Porosity Analyzer. Typically, 20-50 mg samples were transferred to dried and tared analysis tubes equipped with filler rods and capped with a

Transeal. The samples were heated to 40 °C at a rate of 1 °C/min and evacuated at 40 °C for 20 min. They were then heated to 100 °C at a rate of 1 °C/min heat, evacuated at 100 °C until the outgas rate was $\leq 0.3 \mu$ mHg/min (holding the samples at 100 °C for 5 h was sufficient), and the tube was reweighed to determine the mass of the activated sample. The tube was then transferred to the analysis port of the instrument. UHP-grade (99.999% purity) N₂ was used for all adsorption measurements. N₂ isotherms were generated by incremental exposure to nitrogen up to 760 mmHg (1 atm) in a liquid nitrogen (77 K) bath. Oil-free vacuum pumps and oil-free pressure regulators were used for all measurements. Brunauer-Emmett-Teller (BET) surface areas were calculated from the linear region of the N₂ isotherm at 77 K within the pressure range P/P0 of 0.05 – 0.10. All linear fits had a minimum R² value of 0.999.

Powder X-Ray Diffraction. Powder X-ray diffraction (PXRD) patterns were obtained at room temperature on a STOE STADI MP or STOE STADI P powder diffractometer equipped with an asymmetric curved Germanium monochromator (CuK α 1 radiation, λ = 1.54056 Å) and one-dimensional silicon strip detector (MYTHEN2 1K from DECTRIS). The line focused Cu X-ray tube was operated at 40 kV and 40 mA. The as-obtained powder samples were sandwiched between two acetate foils (polymer sample with neither Bragg reflections nor broad peaks above 10° 20) mounted in flat plates with a disc opening diameter of 8 mm, and measured using transmission geometry in a rotating holder. The patterns were recorded in the 20 range of 0 – 32° for an overall exposure time of 6 min. The instrument was calibrated against a NIST Silicon standard (640d) prior to the measurement.

Sonication. Sonication was performed with a Branson 3510 ultrasonic cleaner with a power output of 100W and a frequency of 42 kHz.

II. Experimental Procedures for Covalent Organic Framework Monomers

N-aryl Benzophenone Imine of Benzidine

The benzophenone imine of benzidine was synthesized using a reported procedure.¹ NMR data is consistent with previously reported spectra.

Synthesis of 2,4,6-Tris(4-aminophenyl)-1,3,5-triazine

2,4,6-Tris(4-aminophenyl)-1,3,5-triazine (TAZ) was synthesized using a reported procedure.² NMR data is consistent with previously reported spectra.

N-aryl Benzaldehyde Imine of Benzidine

The benzaldehyde imine of benzidine was synthesized using a reported procedure. ³ NMR data is consistent with previously reported spectra.

Aldehyde Monomers

Triformylbenzene (Arcos[®]) is commercially available and was used without further purification. Triformylphloroglucinol was prepared according to a reported procedure, and NMR data is consistent with reported spectra.⁴

III. Experimental Procedures for Covalent Organic Frameworks

Synthesis of Imine-Linked Covalent Organic Frameworks

Imine-linked COFs were synthesized using literature procedures which reported the greatest crystallinity and surface area for that particular COF. While a general procedure is detailed below, the capacity of the Schlenk tube, solvent, and amine monomer quantities are included in **Table S1**. The identity of solvents used in the hot washing procedure are listed in Table S2.

General Procedure

To a flame-dried Schlenk tube, 1 mmol of 1,3,5-triformylbenzene (TFB, 0.162 g) and the aminefunctionalized monomer (1 mmol of trifunctional linkers or 1.5 mmol of difunctional linkers) were added followed by the solvent thoroughly washing the sides of the tube. The tube was sonicated for ten minutes at room temperature. Acetic acid was subsequently added directly to the reaction mixture which was then degassed via three freeze-pump-thaw cycles (vacuum <50 mTorr). The tube was ultimately sealed under a N₂ atmosphere and placed in a 120 °C pre-heated oil bath for three days. The reaction was removed from the oil bath, allowed to cool, and the insoluble product that formed was collected via vacuum filtration. Acetone was used to thoroughly rinse the reaction flask. The collected solid was transferred to a 125 mL Erlenmeyer flask, stirred in hot solvent, and filtered while hot. This procedure was repeated for a total of four washes. The collected material was then transferred to a tared vial and dried at 120 °C under vacuum (~20 mTorr).

Table S1. Imine-Linked COF Synthetic Conditions						
COE	Tube	Amine Monomer	Solvent	Solvent	AcOH	AcOH
001	Capacity (mL)	Solveni	Vol. (mL)	Molarity	Vol. (mL)	
BND-TFB ¹	50	BND ^a -Benzophenone Imine	1:1 Diox ^f :Mes ^g	10.0	6	1.68
TAZ-TFB ⁵	200	TAZ ^b	10:1 Diox:Mes	50.6	6	3.80
TAPB-TFB ⁶	50	TAPB°	3:1 THF ^h :Mes	10.0	6	0.10
DAFL-TFB ⁷	50	DAFL ^d	1:1 o-DCB ⁱ :DMA ^j	14.3	3	2.39
TAPA-TFB ⁶	50	TAPA ^e	3:1 THF:Mes	10.0	6	1.00

^a 1,1'-biphenyl-4,4'-diamine (benzidine)

^b4,4',4"-(1,3,5-triazine-2,4,6-triyl)tris-benzenamine

^c 5'-(4-aminophenyl)- [1,1':3',1"-Terphenyl]-4,4"-diamine

^d2,7-diaminofluorene

^e N¹,N¹-bis(4-aminophenyl)-1,4-benzenediamine

^g mesitylene

^h tetrahydrofuran

ⁱ ortho-dichlorobenzene

^jN,N-dimethylacetamide

^f1,4-dioxane

	Was	sh 1	Was	h 2	Wasl	h 3	Was	sh 4
COF	Solvent	Temp.	Solvent	Temp.	Solvent	Temp.	Solvent	Temp.
BND-TFB	DMF	90	DMF	90	Acetone	60	Ethanol	80
TAZ-TFB	DMF	90	DMF	90	Acetone	60	Ethanol	80
TAPB-TFB	DMF	90	Methanol	60	Methanol	60	Methanol	60
DAFL-TFB	THF	60	THF	60	Acetone	60	Acetone	60
TAPA-TFB	DMF	90	DMF	90	Acetone	60	Ethanol	80

Table S2. Imine-Linked COF Wash Conditions

Table S3	3. Imine-Linke	d COF Yields an	d Porosity
COF	S_{BET} (m ² g ⁻¹)	Yield	COF Color
BND-TFB	1948	211 mg (55%)	Orange
TAZ-TFB	1399	317 mg (69%)	Pale Yellow
TAPB-TFB	922	435 mg (95%)	Pale Yellow
DAFL-TFB	933	269 mg (88%)	Yellow-Brown
TAPA-TFB	814	380 mg (70%)	Orange

Synthesis of β-Ketoenamine-Linked Covalent Organic Frameworks via Monomer Exchange of the Corresponding Imine-Linked Frameworks

Upon synthesizing an imine-linked covalent organic framework with a quality that matches or surpasses that reported in the literature, that material was again subjected to solvothermal conditions now in the presence of 1,3,5-triformylphloroglucinol (TFP). After the reaction's completion, the reaction mixture and product were extracted with ethyl acetate to obtain the displaced 1,3,5-triformylbenzene (TFB).

General Procedure

To a flame-dried Schlenk tube, 0.4 mmol (see section XIV for other stoichiometric studies) each of 1,3,5triformylphloroglucinol (0.084g) and the corresponding imine-linked covalent organic framework (0.4 mmol) were added followed by dioxane:mesitylene (1:1, 4.0 mL) thoroughly washing the sides of the tube. The tube was sonicated for ten minutes at room temperature. 6M acetic acid (0.67 mL) was subsequently added directly to the reaction mixture which was then degassed via three freeze-pump-thaw cycles (vacuum <50 mTorr). The tube was ultimately sealed under a N₂ atmosphere and placed in a 120 °C pre-heated oil bath for three days. The reaction was removed from the oil bath, allowed to cool, and the insoluble product that formed was collected via vacuum filtration. Ethyl acetate (\sim 75 mL) was used to thoroughly rinse the reaction tube and wash the product obtained by filtration. This filtrate contains triformylbenzene which was saved for later extraction. The collected solid (from filtration) was transferred to a 125 mL Erlenmeyer flask, stirred in hot DMF (75 mL at 90 °C for 30 min.), and filtered while hot. This procedure was then repeated using DMF (75 mL at 90 °C for 30 min.) followed by acetone (75 mL at 60 °C for 30 min) and absolute ethanol (75 mL at 80 °C for 30min). The collected material was then transferred to a tared vial and dried at 120 °C under vacuum (~20 mTorr). The filtrate from above was transferred to a separatory funnel and the organic fraction was then washed with brine, collected, filtered through cotton, and evaporated in vacuo to yield an off-white solid. The mass of this compound was recorded and a ¹H NMR sample was obtained in CDCl₃.

Table S4. β -Ketoenamine-Linked COF Conditions, Yields, and Porosity					
COF	Quantity of Corresponding Imine-Linked COF (mg)	S _{BET} (m ² g ⁻¹)	Yield	COF Color	
BND-TFP	154	1536	169 mg (98%)	Orange	
TAZ-TFP	185	1148	178 mg (87%)	Dark Orange	
TAPB-TFP	184	815	138 mg (68%)	Dark Orange	
DAFL-TFP	161	460	167 mg (93%)	Red-Brown	
TAPA-TFP	159	823	146 mg (82%)	Red	

Synthesis of β-Ketoenamine-Linked Covalent Organic Frameworks by Direct Condensation

 β -ketoenamine-linked covalent organic frameworks were synthesized directly from an amine monomer, or a protected analog of an amine monomer, and TFP to compare their materials quality with those COFs obtained using monomer exchange. Synthetic conditions were identical to those detailed in the previous section for synthesizing β -ketoenamine-linked covalent organic frameworks via monomer exchange. No ethyl acetate extraction of the reaction mixture and product was performed. **IV. Covalent Organic Framework Structures**



Figure S1. Structures of β -ketoenamine-linked COFs. (A) BND-TFB COF, (B) TAZ-TFP COF, (C) TAPB-TFP COF, (D) DAFL-TFP COF, (E) TAPA-TFP COF.



Figure S2. Structures of β -ketoenamine-linked COFs. (A) BND-TFB COF, (B) TAZ-TFP COF, (C) TAPB-TFP COF, (D) DAFL-TFP COF, (E) TAPA-TFP COF.

V. Powder X-Ray Diffraction Patterns of Covalent Organic Frameworks





Figure S3. PXRD pattern for BND-TFB COF.



Figure S4. PXRD pattern for TAZ-TFB COF.



Figure S5. PXRD pattern for TAPB-TFB COF.



Figure S6. PXRD pattern for DAFL-TFB COF.



Figure S7. PXRD pattern for TAPA-TFB COF.

β-Ketoenamine-Linked COFs Synthesized by Monomer Exchange



Figure S8. PXRD pattern for BND-TFP COF.



Figure S9. PXRD pattern for TAZ-TFP COF.



Figure S10. PXRD pattern for TAPB-TFP COF.



Figure S11. PXRD pattern for DAFL-TFP COF.



Figure S12. PXRD pattern for TAPA-TFP COF.

β-Ketoenamine-Linked COFs Synthesized by Direct Condensation



Figure S13. PXRD pattern for BND-TFP COF synthesized directly from benzidine-benzophenone and triformylphloroglucinol.



Figure S14. PXRD pattern for BND-TFP COF synthesized directly from benzidine-benzaldehyde and triformylphloroglucinol.



Figure S15. PXRD pattern for DAFL-TFP COF synthesized directly from amine monomer and triformylphloroglucinol.



Figure S16. PXRD pattern for TAPA-TFP COF synthesized directly from amine monomer and triformylphloroglucinol.

VI. Nitrogen Adsorption Isotherms of Covalent Organic Frameworks with BET Plot Insets





Figure S17. Nitrogen adsorption isotherm for BND-TFB COF.



Figure S18. Nitrogen adsorption isotherm for TAZ-TFB COF.



Figure S19. Nitrogen adsorption isotherm for TAPB-TFB COF.



Figure S20. Nitrogen adsorption isotherm for DAFL-TFB COF.



Figure S21. Nitrogen adsorption isotherm for TAPA-TFB COF.

β-Ketoenamine-Linked COFs Synthesized by Direct Condensation



Figure S22. Nitrogen adsorption isotherm for BND-TFP COF.



Figure S23. Nitrogen adsorption isotherm for TAZ-TFP COF.



Figure S24. Nitrogen adsorption isotherm for TAPB-TFP COF.



Figure S25. Nitrogen adsorption isotherm for DAFL-TFP COF.



Figure S26. Nitrogen adsorption isotherm for TAPA-TFP COF.

β-Ketoenamine-Linked COFs Synthesized by Direct Condensation



Figure S27. Nitrogen adsorption isotherm for BND-TFB COF synthesized directly from benzidinebenzophenone and triformylphloroglucinol.



Figure S28. Nitrogen adsorption isotherm for BND-TFP COF synthesized directly from benzidinebenzaldehyde and triformylphloroglucinol.



Figure S29. Nitrogen adsorption isotherm for DAFL-TFP COF synthesized directly from amine monomer and triformylphloroglucinol.



Figure S30. Nitrogen adsorption isotherm for TAPA-TFP COF synthesized directly from amine monomer and triformylphloroglucinol.

VII. Pore Size Distributions of Covalent Organic Frameworks

Imine-Linked COFs Synthesized Using Reported Conditions



Figure S31. Pore size distribution of BND-TFB COF.



Figure S32. Pore size distribution of TAZ-TFB COF.



Figure S33. Pore size distribution of TAPB-TFB COF.



Figure S34. Pore size distribution of DAFL-TFB COF.



Figure S35. Pore size distribution of TAPA-TFB COF.

β-Ketoenamine-Linked COFs Synthesized by Monomer Exchange



Figure S36. Pore size distribution of BND-TFP COF.



Figure S37. Pore size distribution of TAZ-TFP COF.



Figure S38. Pore size distribution of TAPB-TFP COF.



Figure S39. Pore size distribution of DAFL-TFP COF.



Figure S40. Pore size distribution of TAPA-TFP COF.

β-Ketoenamine-Linked COFs Synthesized by Direct Condensation



Figure S41. Pore size distribution of BND-TFP COF synthesized directly from benzidine-benzophenone and triformylphloroglucinol.



Figure S42. Pore size distribution of BND-TFP COF synthesized directly from benzidine-benzaldehyde and triformylphloroglucinol.



Figure S43. Pore size distribution of DAFL-TFP COF synthesized directly from amine monomer and triformylphloroglucinol.



Figure S44. Pore size distribution of TAPA-TFP COF synthesized directly from amine monomer and triformylphloroglucinol.

VIII. Covalent Organic Framework Stability Studies

Procedure

Seven 20 mL vials were obtained, and 50 mg of BND-TFB COF was added to each vial. Similarly, 50 mg of BND-TFP COF was added to each of seven 20 mL vials. Hydrochloric acid and sodium hydroxide solutions with concentrations of 3, 6, and 9 M were prepared and individually added to a vial for each COF. H₂O was added to the seventh vial for each COF. All H₂O used was purified by reverse osmosis, and approximately 10 mL of solution was added to each vial. All vials were sealed with a cap, and those containing acidic or basic solutions were stored at room temperature for seven days. The vials containing H₂O were sealed with Teflon tape and a cap and heated to 100 °C on a hot plate for 7 days. After 7 days, each COF sample was collected by vacuum filtration thoroughly rinsing the sides of the sample vial with acetone. The material was then transferred to a new 20 mL vial along with a stir bar. The product was washed with hot DMF x 2 (T = 90 °C), acetone (T = 60 °C), and ethanol (T = 80 °C) stirring and heating on a hot plate. All washes were 30 minutes in length, and the product was collected between washes by vacuum filtration. After completing all four washes, the collected material was transferred to a tared vial and dried at 120 °C under vacuum (~20 mTorr). The samples were massed after drying, and the percentage recoveries are recorded in **Table S5**. PXRD patterns were obtained for samples recovered with sufficient yield.

Table S5. Stability Test Percent Recoveries					
Condition	BND-TFB	BND-TFP			
Condition	(Imine)	(β-ketoenamine)			
Boiling H ₂ O	68.2	84.4			
3M HCI	6.4	78.0			
6M HCI	0.2	76.8			
9M HCI	0.0	78.2			
3M NaOH	104.4	69.2			
6M NaOH	97.6	68.4			
9M NaOH	84.2	69.6			





Figure S45. Summary of stability study results.



Figure S46. PXRD pattern of BND-TFB as synthesized.



Figure S47. PXRD pattern of BND-TFB after exposure to boiling H₂O for 7 days.



Figure S48. PXRD pattern of BND-TFB COF after exposure to 3M HCl for 7 days.



Figure S49. PXRD pattern of BND-TFB COF after exposure to 3M NaOH for 7 days.



Figure S50. PXRD pattern of BND-TFB COF after exposure to 6M NaOH for 7 days.



Figure S51. PXRD pattern of BND-TFB COF after exposure to 9M NaOH for 7 days.



Figure S52. PXRD pattern of BND-TFP COF as synthesized.



Figure S53. PXRD pattern of BND-TFP COF after exposure to boiling H₂O for 7 days



Figure S54. PXRD pattern of BND-TFP COF after exposure to 3M HCl for 7 days.



Figure S55. PXRD pattern of BND-TFP COF after exposure to 6M HCl for 7 days.



Figure S56. PXRD pattern of BND-TFP COF after exposure to 9M HCl for 7 days.



Figure S57. PXRD pattern of BND-TFP COF after exposure to 3M NaOH for 7 days.



Figure S58. PXRD pattern of BND-TFP COF after exposure to 6M NaOH for 7 days.



Figure S59. PXRD pattern of BND-TFP COF after exposure to 9M NaOH for 7 days.

IX. Solid State ¹³C Cross Polarization Magic Angle Spinning (CP-MAS) NMR of Covalent Organic Frameworks



Figure S60. CP-MAS spectra of imine-linked BND-TFB (top) and β -ketoenamine-linked BND-TFP (bottom) formed by monomer exchange.



Figure S61. CP-MAS spectra of imine-linked TAZ-TFB (top) and β -ketoenamine-linked TAZ-TFP (bottom) formed by monomer exchange.



Figure S62. CP-MAS spectra of imine-linked TAPB-TFB (top) and β -ketoenamine-linked TAPB-TFP (bottom) formed by monomer exchange.



Figure S63. CP-MAS spectra of imine-linked DAFL-TFB (top) and β -ketoenamine-linked DAFL-TFP (bottom) formed by monomer exchange.



Figure S64. CP-MAS spectra of imine-linked TAPA-TFB (top) and β -ketoenamine-linked TAPA-TFP (bottom) formed by monomer exchange.

X. Fourier-Transform Infrared Spectroscopy of Covalent Organic Frameworks



Figure S65. FT-IR spectra of imine-linked BND-TFB (top) and β -ketoenamine-linked BND-TFP (bottom) formed by monomer exchange.



Figure S66. FT-IR spectra of imine-linked TAZ-TFB (top) and β -ketoenamine-linked TAZ-TFP (bottom) formed by monomer exchange.



Figure S67. FT-IR spectra of imine-linked TAPB-TFB (top) and β -ketoenamine-linked TAPB-TFP (bottom) formed by monomer exchange.



Figure S68. FT-IR spectra of imine-linked DAFL-TFB (top) and β -ketoenamine-linked DAFL-TFP (bottom) formed by monomer exchange.



Figure S69. FT-IR spectra of imine-linked TAPA-TFB (top) and β -ketoenamine-linked TAPA-TFP (bottom) formed by monomer exchange.

Table S6. Elemental Analysis of COFs: Predicted and Measured						
		C		Ν		Η
COE	Predicted	Measured	Predicted	Measured	Predicted	Measured
COP	(%)	(%)	(%)	(%)	(%)	(%)
BND-TFB	84.35	82.34	10.93	10.55	4.72	4.79
TAZ-TFB	77.91	74.45	18.17	16.79	3.92	4.15
TAPB-TFB	86.25	83.24	9.14	8.74	4.61	4.70
DAFL-TFB	85.05	81.75	10.44	8.87	4.51	4.45
TAPA-TFB	81.39	79.51	14.06	13.43	4.55	4.52
BND-TFP	74.99	73.54	9.72	8.74	4.19	4.17
TAZ-TFP	70.58	68.95	16.46	13.93	3.55	3.63
TAPB-TFP	78.09	75.83	8.28	7.24	4.17	4.17
DAFL-TFP	75.99	73.26	9.33	7.23	4.03	3.96
TAPA-TFP	72.64	71.58	12.55	11.09	4.06	4.12

XI. Elemental Analysis of Covalent Organic Frameworks

XII. Scanning Electron Microscopy of Covalent Organic Frameworks



Figure S70. Scanning electron microscopy images of BND-TFB COF.



Figure S71. Scanning electron microscopy images of BND-TFP COF



Figure S72. Scanning electron microscopy images of TAZ-TFB COF



Figure S73. Scanning electron microscopy images of TAZ-TFP COF



Figure S74. Scanning electron microscopy images of TAPB-TFB COF



Figure S75. Scanning electron microscopy images of TAPB-TFP COF



Figure S76. Scanning electron microscopy images of DAFL-TFB COF



Figure S77. Scanning electron microscopy images of DAFL-TFP COF.



Figure S78. Scanning electron microscopy images of TAPA-TFB COF



Figure S79. Scanning electron microscopy images of TAPA-TFP COF

XIII. ¹H NMR Spectra of Monomer Exchange Extracts



Figure S80. ¹H NMR spectra of extracts for β -ketoenamine-linked COFs obtained by monomer exchange. The reaction mixture and product were extracted with ethyl acetate yielding the displaced 1,3,5-triformylbenzene. All spectra were taken in CDCl₃.

XIV. Stoichiometric Studies of Linker Exchange

Imine-linked BND-TFB COF was subjected to monomer exchange reaction conditions in the presence of varying equivalents (0.5 eq, 1.0 eq, 1.5 eq) of 1,3,5-triformylphloroglucinol (TFP). After three days, the obtained COFs were analyzed by FTIR, PXRD, and surface area, and the soluble organics were extracted and analyzed by 1H NMR.

Procedure

To a flame-dried Schlenk tube, 1,3,5-triformylphloroglucinol [(a) 42 mg, 0.2 mmol, 0.5 equiv; (b) 84 mg 0.4 mmol, 1.0 equiv; (c) 126 mg, 0.6 mmol, 1.5 equiv) and imine-linked BND-TFB COF (154 mg, 0.4 mmol, 1.0 equiv) were added followed by dioxane:mesitylene (1:1, 4.0 mL) thoroughly washing the sides of the tube. The tube was sonicated for ten minutes at room temperature. 6M acetic acid (0.67 mL) was subsequently added directly to the reaction mixture which was then degassed via three freeze-pump-thaw cycles (vacuum <50 mTorr). The tube was ultimately sealed under a N₂ atmosphere and placed in a 120 °C pre-heated oil bath for three days. The reaction was removed from the oil bath, allowed to cool, and the insoluble product that formed was collected via vacuum filtration. Ethyl acetate (~75 mL) was used to thoroughly rinse the reaction tube and wash the product obtained by filtration. This filtrate contains soluble organics which was saved for later extraction. The collected solid (from filtration) was transferred to a 125 mL Erlenmeyer flask, stirred in hot DMF (75 mL at 90 °C for 30 min.), and filtered while hot. This procedure was then repeated using DMF (75 mL at 90 °C for 30 min.) followed by acetone (75 mL at 60 °C for 30min) and absolute ethanol (75 mL at 80 °C for 30min). The collected material was then transferred to a tared vial and dried at 120 °C under vacuum (~20 mTorr). The filtrate from above was transferred to a separatory funnel and the organic fraction was washed with water and brine, then collected and dried with magnesium sulfate, filtered through cotton, and evaporated in vacuo to yield an off-white solid. The mass of this compound was recorded and a ¹H NMR sample was obtained in CDCl₃.

Table S7. BND-TFP COF from stoichiometric studies: Yields, and Porosity					
equivalents TFP used	activated COF Yield	S_{BET} (m ² g ⁻¹)	COF Color	Mass recovery of soluble organics	
0.5 equiv	152 mg	675	Orange (lighter)	35 mg	
1.0 equiv	169 mg	1536	Orange	52 mg	
1.5 equiv	161 mg	1311	Orange (darker)	59 mg	



Figure S81. Comparison of FT-IR spectra of β -ketoenamine-linked BND-TFP synthesized using various equivalents of triformylphloroglucinol (TFP) versus imine-linked BND-TFB COF.

Figure S82. ¹H NMR spectra of extracts for β -ketoenamine-linked BND-TFP COFs obtained by monomer exchange using varying equivalents of triformylphloroglucinol (TFP) versus standard TFB and TFP.

Figure S83. PXRDs of β -ketoenamine-linked BND-TFP COFs obtained by monomer exchange using varying equivalents of triformylphloroglucinol (TFP) versus imine-linked BND-TFB COF.

Figure S84. Surface Area Analysis of β -ketoenamine-linked BND-TFP COFs obtained by monomer exchange using varying equivalents of triformylphloroglucinol (TFP).

XV. Simulation and Refinement of COF Structures

Crystal modeling of the COF structures was carried out using the Materials Studio (ver.5.0) suite of programs by Accelrys.⁸ The initial structures were constructed piecewise starting with a primitive hexagonal unit cell with space group P6. The a cell parameter was estimated according to the distance between the center of the vertices for each COF, and c parameter was arbitrarily chosen as 3.35 Å. The structures were optimized using the Geometry Optimization routine including energy minimization with cell parameters optimization, using the parameters from the Universal Force Field. Calculation of the simulated powder diffraction patterns and Pawley refinements were performed in the Materials Studio Reflex Plus Module using a Bragg-Brentano geometry. The observed diffraction patterns were subjected to a polynomial background subtraction and then to Pawley refinement wherein peak profile were refined using the Pseudo-Voigt peak shape function and asymmetry was corrected using the Berar-Baldinozzi function. Crystallite size was then estimated by the LeBail method which was Pawley refined to the experimental data. Surface area calculations were carried out using a Connolly surface calculation using the appropriate parameters for nitrogen as the adsorbed gas.

Table S8. Calculated & Predicted COF Characteristics					
COF	Average Domain Size (nm)	Calculated Pore Size (Å)	Connolly Surface Area (m²/g)		
BND-TFB	143	25.1	3027		
BND-TFP	117	25.0	2714		
TAZ-TFB	52	13.9	2698		
TAZ-TFP	71	13.8	2515		
TAPB-TFB	48	15.5	2893		
TAPB-TFP	40	14.9	2750		
DAFL-TFB	29	24.4	2247		
DAFL-TFP	29	24.2	1960		
TAPA-TFB	203	13.9	3192		
TAPA-TFP	163	13.8	2694		

XVI. Calculated and Modeled COF Characteristics

XVII. References

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