Supporting Information

Investigation of Ester and Amide Linker based Porous Organic Polymers for Carbon Dioxide Capture and Separation at Wide Temperatures and Pressures

Ruh Ullah[1 ξ], Mert Atilhan[1*], Baraa Anaya[1], Shaheen Al-Muhtaseb[1], Santiago Aparicio[2], Hasmukh Patel[3 ξ], Damien Thirion[4] and Cafer T. Yavuz[4,5*]

[1]*Department of Chemical Engineering, Qatar University, PO Box 2713, Doha, Qatar*

[2]*Department of Chemistry, University of Burgos, 09001 Burgos, Spain*

[3]*Department of Chemistry, Northwestern University, Evanston, IL 60208, USA*

[4]*Graduate School of EEWS, KAIST, 373-1 Guseong Dong, Yuseong Gu, Daejeon 305-701, Republic of Korea*

[5]*Department of Chemistry, KAIST, 373-1 Guseong Dong, Yuseong Gu, Daejeon 305-701, Republic of Korea*

**Corresponding Authors and* [ξ]*Equal contribution*

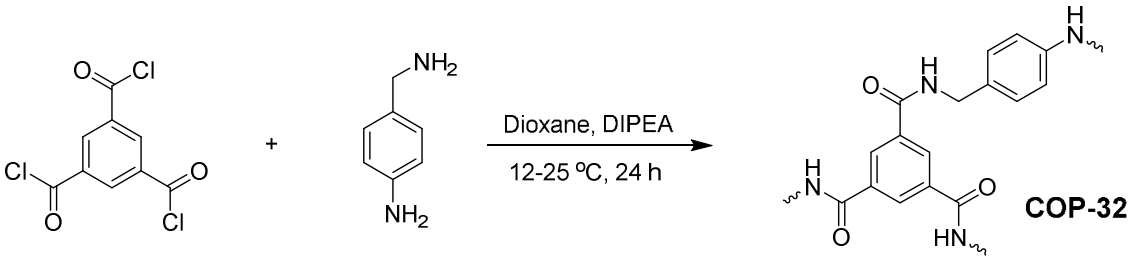
mert.atilhan@qu.edu.qa and yavuz@kaist.ac.kr

Materials

N,N-Diisopropylethylamine, 1,3,5-benzene tricarbonyltrichloride, 4-aminobenzylamine, 1,4-phenylenediamine, 1,3-phenylenediamine, hydroquinone, phloroglucinol, bisphenol A, dioxane, and ethanol were obtained from TCI, Japan.

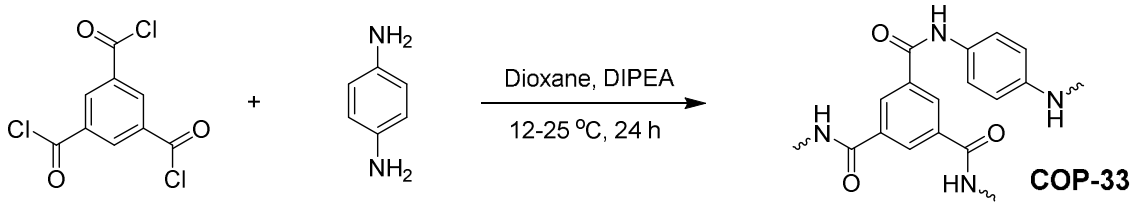
Synthesis of covalent organic polymers (COPs-32, 33, 34, 35, 36, 37)

1. Synthesis of COP-32



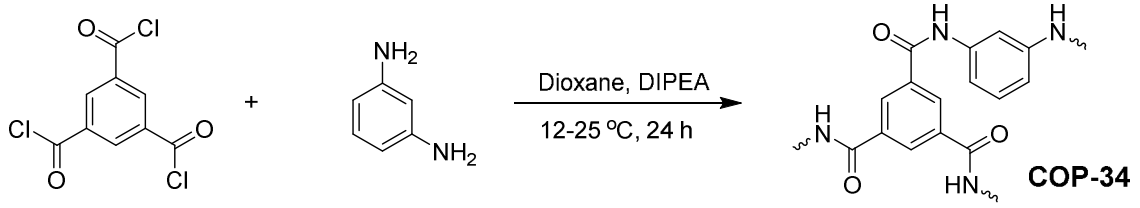
DIPEA (6.55 mL, 37.6 mmol) was added to 4-aminobenzylamine (1.86 g, 15.23 mmol) dissolved in 1,4-dioxane (250 mL) at room temperature. The 1,4-dioxane solution (50 mL) with 1,3,5-benzene tricarbonyltrichloride (2.5 g, 9.42 mmol) was added drop-wise to the above solution with continuous stirring at 12-14 °C in the atmospheric condition. Once the addition was finished, the reaction mixture slowly heated up to room temperature and it was stirred for 24 h. The precipitate was washed with 1,4-dioxane and soaked in ethyl alcohol three times over the period of 12 h. The obtained product, COP-32, was dried at room temperature under vacuum for 2 h and subsequently it was dried at 110 °C in vacuum for 5 h. Yield: 82 %.

2. Synthesis of COP-33



DIPEA (6.55 mL, 37.6 mmol) was added to 1,4-phenylene diamine (1.65 g, 15.23 mmol) dissolved in 1,4-dioxane (250 mL) at room temperature. The 1,4-dioxane solution (50 mL) with 1,3,5-benzene tricarbonyltrichloride (2.5 g, 9.42 mmol) was added drop-wise to the above solution with continuous stirring at 12-14 °C in the atmospheric condition. Once the addition was finished, the reaction mixture slowly heated up to room temperature and it was stirred for 24 h. The precipitate was washed with 1,4-dioxane and soaked in ethyl alcohol three times over the period of 12 h. The obtained product, COP-33, was dried at room temperature under vacuum for 2 h and subsequently it was dried at 110 °C in vacuum for 5 h. Yield: 86 %.

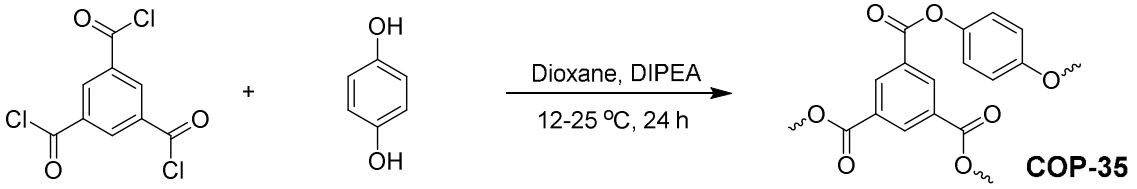
3. Synthesis of COP-34



DIPEA (6.55 mL, 37.6 mmol) was added to 1,3-phenylene diamine (1.65 g, 15.23 mmol) dissolved in 1,4-dioxane (250 mL) at room temperature. The 1,4-dioxane solution (50 mL) with 1,3,5-benzene tricarbonyltrichloride (2.5 g, 9.42 mmol) was added drop-wise to the above solution with continuous stirring at 12-14 °C in the atmospheric condition. Once the addition was finished, the reaction mixture slowly heated up to room temperature and it was stirred for 24 h. The precipitate was washed with 1,4-dioxane and soaked in ethyl alcohol

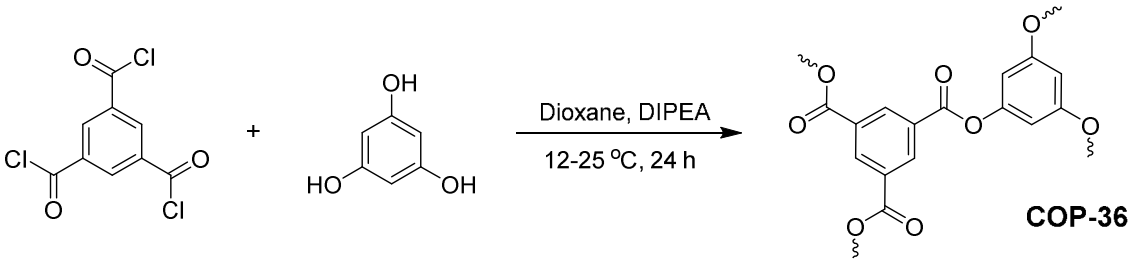
three times over the period of 12 h. The obtained product, COP-34, was dried at room temperature under vacuum for 2 h and subsequently it was dried at 110 °C in vacuum for 5 h. Yield: 80 %.

4. Synthesis of COP-35



DIPEA (6.55 mL, 37.6 mmol) was added to hydroquinone (1.67 g, 15.23 mmol) dissolved in 1,4-dioxane (300 mL) at room temperature. The 1,4-dioxane solution (50 mL) with 1,3,5-benzene tricarbonyltrichloride (2.5 g, 9.42 mmol) was added dropwise to the above solution with continuous stirring at 12-14 °C in the atmospheric condition. Once the addition was finished, the reaction mixture slowly heated up to room temperature and it was stirred for 24 h. The precipitate was washed with 1,4-dioxane and soaked in ethyl alcohol three times over the period of 12 h. The obtained product, COP-35, was dried at room temperature under vacuum for 2 h and subsequently it was dried at 110 °C in vacuum for 5 h. Yield: 82 %.

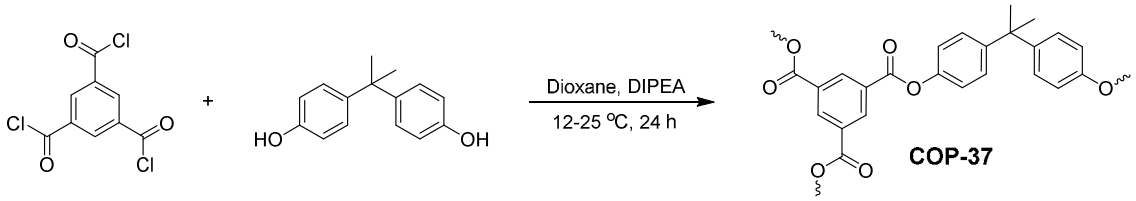
5. Synthesis of COP-36



DIPEA (6.55 mL, 37.6 mmol) was added to phloroglucinol (1.19 g, 9.42 mmol) dissolved in 1,4-dioxane (200 mL) at room temperature. The 1,4-dioxane solution (40 mL) with 1,3,5-benzene tricarbonyltrichloride (2.5 g, 9.42 mmol) was added dropwise to the above solution

with continuous stirring at 12-14 °C in the atmospheric condition. Once the addition was finished, the reaction mixture slowly heated up to room temperature and it was stirred for 24 h. The precipitate was washed with 1,4-dioxane and soaked in ethyl alcohol three times over the period of 12 h. The obtained product, COP-36, was dried at room temperature under vacuum for 2 h and subsequently it was dried at 110 °C in vacuum for 5 h. Yield: 77 %.

6. Synthesis of COP-37



DIPEA (6.55 mL, 37.6 mmol) was added to bisphenol-A (3.47 g, 15.23 mmol) dissolved in 1,4-dioxane (300 mL) at room temperature. The 1,4-dioxane solution (50 mL) with 1,3,5-benzene tricarbonyltrichloride (2.5 g, 9.42 mmol) was added dropwise to the above solution with continuous stirring at 12-14 °C in the atmospheric condition. Once the addition was finished, the reaction mixture slowly heated up to room temperature and it was stirred for 24 h. The precipitate was washed with 1,4-dioxane and soaked in ethyl alcohol three times over the period of 12 h. The obtained product, COP-37, was dried at room temperature under vacuum for 2 h and subsequently it was dried at 110 °C in vacuum for 5 h. Yield: 74 %.

FTIR Analysis of COPs materials

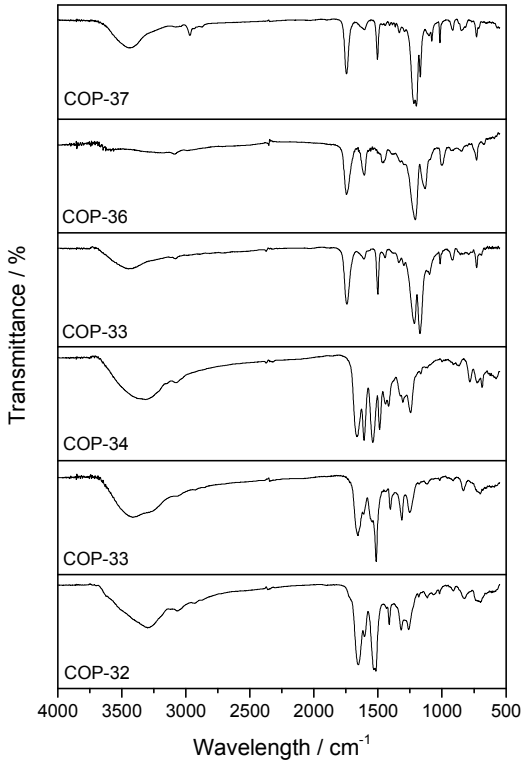


Figure S1. FT-IR spectra of COPs-32-37

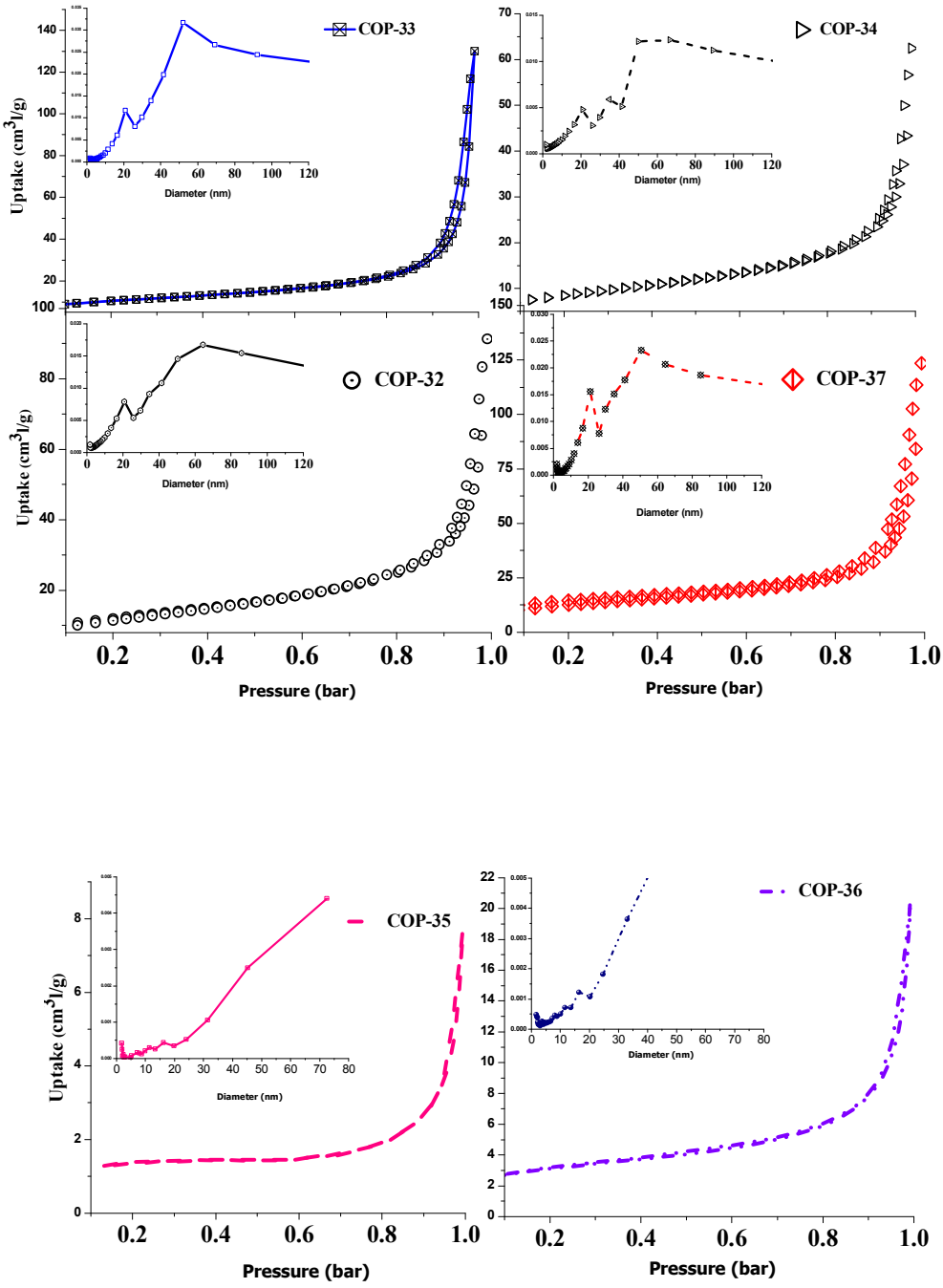


Figure S2a. Liquid nitrogen adsorption desorption isotherms indicating porosity of materials, whereas the inlet shows pore size distribution.

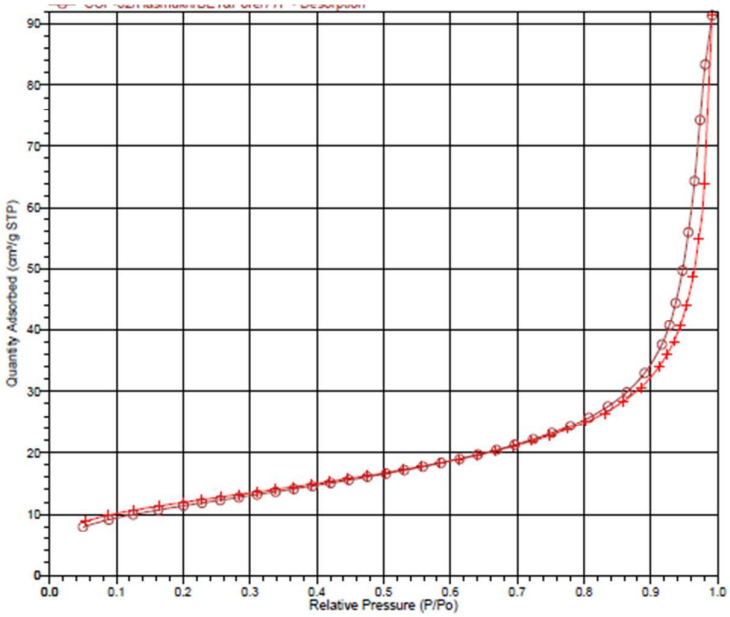


Figure S2b. Nitrogen adsorption desorption isotherms of COP-32 obtained from BET machine.

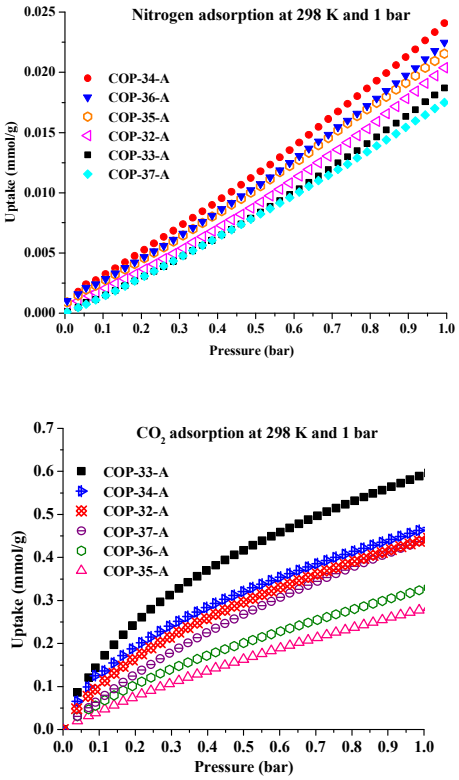


Figure S3. CO_2 and N_2 adsorption of COPs-32-37 at 298 K and up to 1 bar

Liquid Nitrogen adsorption desorption analysis

Table S1. Maximum adsorption of N_2, CO_2 and CH_4 by COP materials at 10 bars

Material	**CO_2 (mmol/g)**		**CH_4 (mmol/g)**		**N_2 (mmol/g)**		**Selectivity (CO_2:N_2:CH_4)**	
Temperature	**298 K**	**323 K**	**298 K**	**323 K**	**298K**	**323K**	**298 K**	**323 K**
COP-32	1.11	0.80	0.22	0.08	0.08	0.04	13.9:1:2.8	20:1:2
COP-33	1.44	0.98	0.41	0.29	0.61	0.26	3.5:1:1.5	3.8:1:1.1
COP-34	1.12	0.78	0.41	0.19	0.18	0.057	6.2:1:2.3	13.7:1:3
COP-35	0.82	0.55	0.18	0.13	0.08	0.06	10.3:1:3	9.2:1:2.2
COP-36	0.56	0.37	0.07	0.019	0	0	-	-
COP-37	1.14	0.72	0.19	0.11	0.21	0	-	-