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Supporting Information

Chemical Tailoring of β-Cyclodextrin-Graphene Oxide for Enhanced Per- and Polyfluoroalkyl Substances (PFAS) Adsorption from Drinking Water

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1. ^{1}H NMR and ^{13}C-NMR

Mono-6-deoxy-6-tosyl-β-cyclodextrin (tosyl-βCD)

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.73 (d, J= 8.4Hz, 2H), 7.41 (d, J= 8.4Hz, 2H), 5.81 – 5.62 (m, 14H), 4.82 - 4.74 (m, 7H), 4.48 – 4.41 (m, 6H), 4.34-4.29 (m, 1H), 4.19-4.14 (m, 1H), 3.63 – 3.16 (m, 40H, overlapped signal with H_2O), 2.40 (s, 3H) ppm.

Mono-6-deoxy-6-azido-β-cyclodextrin (N_3-βCD)

^{1}H NMR (500 MHz, DMSOd_6): δ = 5.75-5.64 (m, 14H), 4.88-4.83 (m, 7 H), 4.54-4.47 (m, 6H), 3.77−3.56 (m, 28 H), 3.41-3.29 (m, 14 H, overlapped signal with H_2O) ppm.

^{13}C NMR (125 MHz, DMSOd_6): δ = 102.3-101.6 (m), 83.0, 81.8-81.4 (m), 73.0−72.0 (m), 60.1-59.7 (m), 51.1 (CH_2N_3) ppm.

Mono-6-deoxy-6-amino-β-cyclodextrin (C_0-βCD)

^{1}H NMR (500 MHz, D_2O): δ = 5.09 (bs, 7 H), 3.99−3.86 (m, 26H), 3.67-3.51 (m, 13H), 3.49 (t, J= 9.0Hz, 1H), 3.13(d, J= 12Hz, 1H), 2.90 (dd, J= 14.5Hz, J= 7.0Hz, 1H) ppm.

^{13}C NMR (125 MHz, D_2O): δ = 102.3, 102.1, 83.3, 81.6, 81.3, 73.5−72.3, 60.7, 41.7 (CH_2N) ppm.

Mono-6-deoxy-6-ethylenediamine-β-cyclodextrin (C_2-βCD)

^{1}H NMR (500 MHz, D_2O): δ = 5.09 (bs, 7H), 4.00-3.87 (m, 26H), 3.68-3.49 (m, 14H), 3.09-3.06 (m, 1H), 2.98-2.94 (m, 2H), 2.91-2.86 (m, 1H), 2.83-2.80 (m, 2H) ppm.

^{13}C NMR (125 MHz, D_2O): δ = 101.8, 101.5, 81.0, 80.9, 73.0, 72.9, 72.9, 72.0, 71.7, 71.7, 70.4, 60.2, 48.8, 38.7 ppm.

Mono-(6-(1,6-hexamethylenediamine)-6-deoxy)-β-Cyclodextrin (C_6-βCD)

^{1}H NMR (400 MHz, D_2O): δ = 5.14 (d, J= 3.8Hz, 1H), 5.11-5.08 (m, 6H), 3.99-3.82 (m, 26H), 3.68-3.56 (m, 13H), 3.44 (t, J= 9.2Hz, 1H), 3.10 (bd, J= 12Hz, 1H), 2.93 (t, J= 8.0Hz, 2H), 2.80 (dd, J= 8.8Hz, J= 13.2Hz, 1H), 2.63 (bt, J= 7.6Hz, 2H), 1.69-1.60 (m, 2H), 1.55-1.45 (m, 2H), 1.29-1.45 (m, 4H) ppm.

^{13}C NMR (125 MHz, DMSO-d_6): δ =102.6, 102.4, 82.1, 73.5, 72.9, 72.5, 60.4, 50.0, 49.8, 41.4, 32.3, 30.0, 27.0, 26.6. ppm.

Mono-(6-(1,12-dodecanediamine)-6-deoxy)-β-Cyclodextrin (C_{12}-βCD)

^{1}H NMR (500 MHz, D_2O): δ = 4.95 (bs, 7H), 3.79-3.55 (m, 26H), 3.51-3.42 (m, 12H), 3.23-3.21 (m, 1H), 2.98-2.94 (d, J= 14Hz, 1H), 2.85-2.77 (m, 2H), 2.63 (bt, J= 14Hz, 1H) ppm, 1.56-1.49 (m, 3H), 1.31-1.13 (m, 20H) ppm.

^{13}C NMR (125 MHz, D_2O): δ = 102.1, 101.9, 80.9, 73.3, 73.2, 72.0, 71.9, 71.7, 65.9, 59.7, 39.7, 39.6, 28.5, 28.4, 28.2, 28.1, 27.9, 27.7, 25.6, 14.0 ppm.

2. Attenuated total reflection Infrared Spectroscopy (ATR-FTIR)

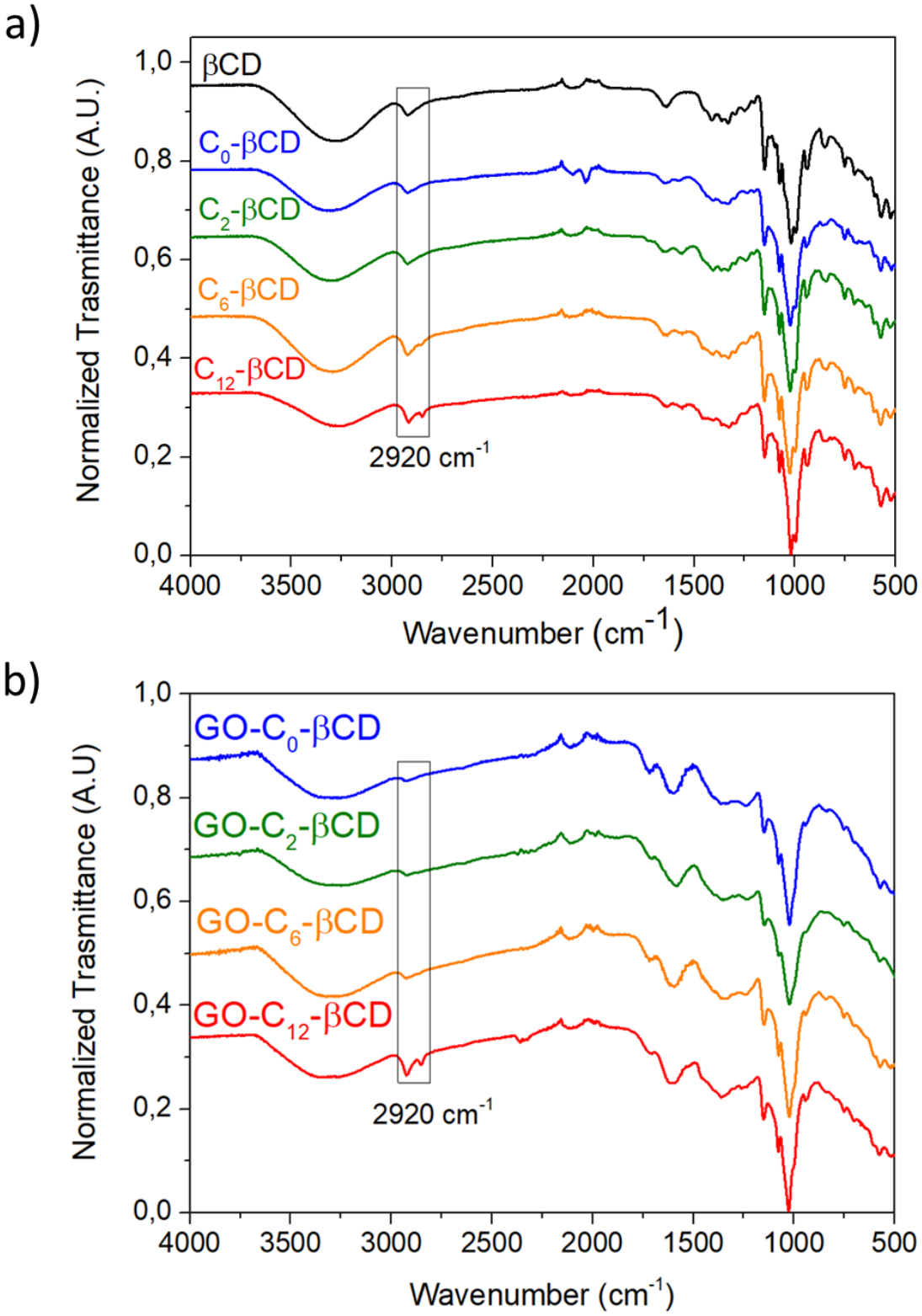


Figure S1. ATR-FTIR spectra of a) βCD (black), C_0-βCD (blue), C_2-βCD (green), C_6-βCD (orange), C_{12}-βCD (red), and b) GO-C_0-βCD (blue), GO-C_2-βCD (green), GO-C_6-βCD (orange), GO-C_{12}-βCD (red).

3. Thermogravimetric analysis (TGA)

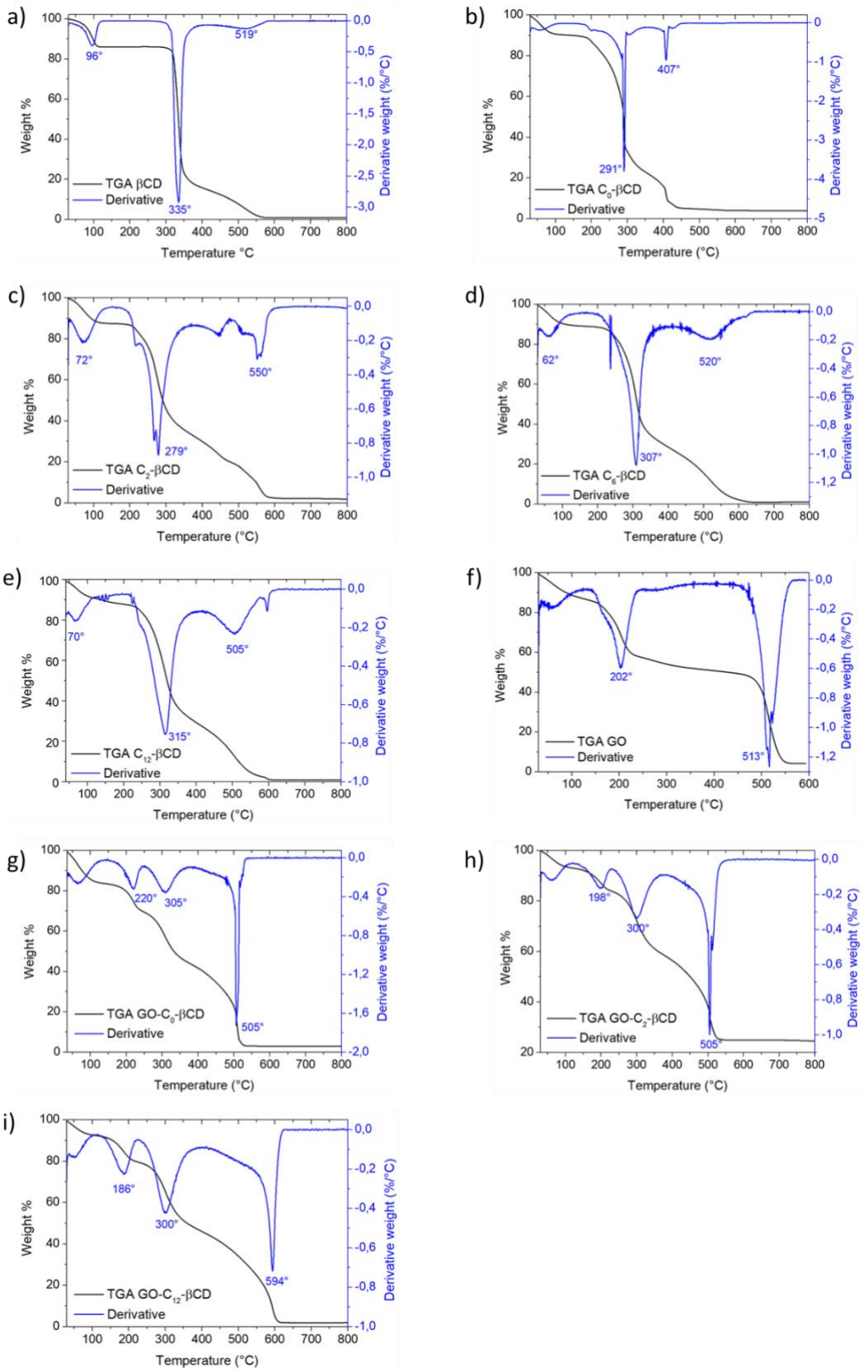


Figure S2. TGA of a) βCD, b) C_0-βCD, c) C_2-βCD, d) C_6-βCD, e) C_{12}-βCD, f) GO, g) GO-C_0-βCD, h) GO-C_2-βCD, i) GO-C_{12}-βCD (10 °C/min in air).

4. X-Ray photoelectron spectroscopy (XPS)

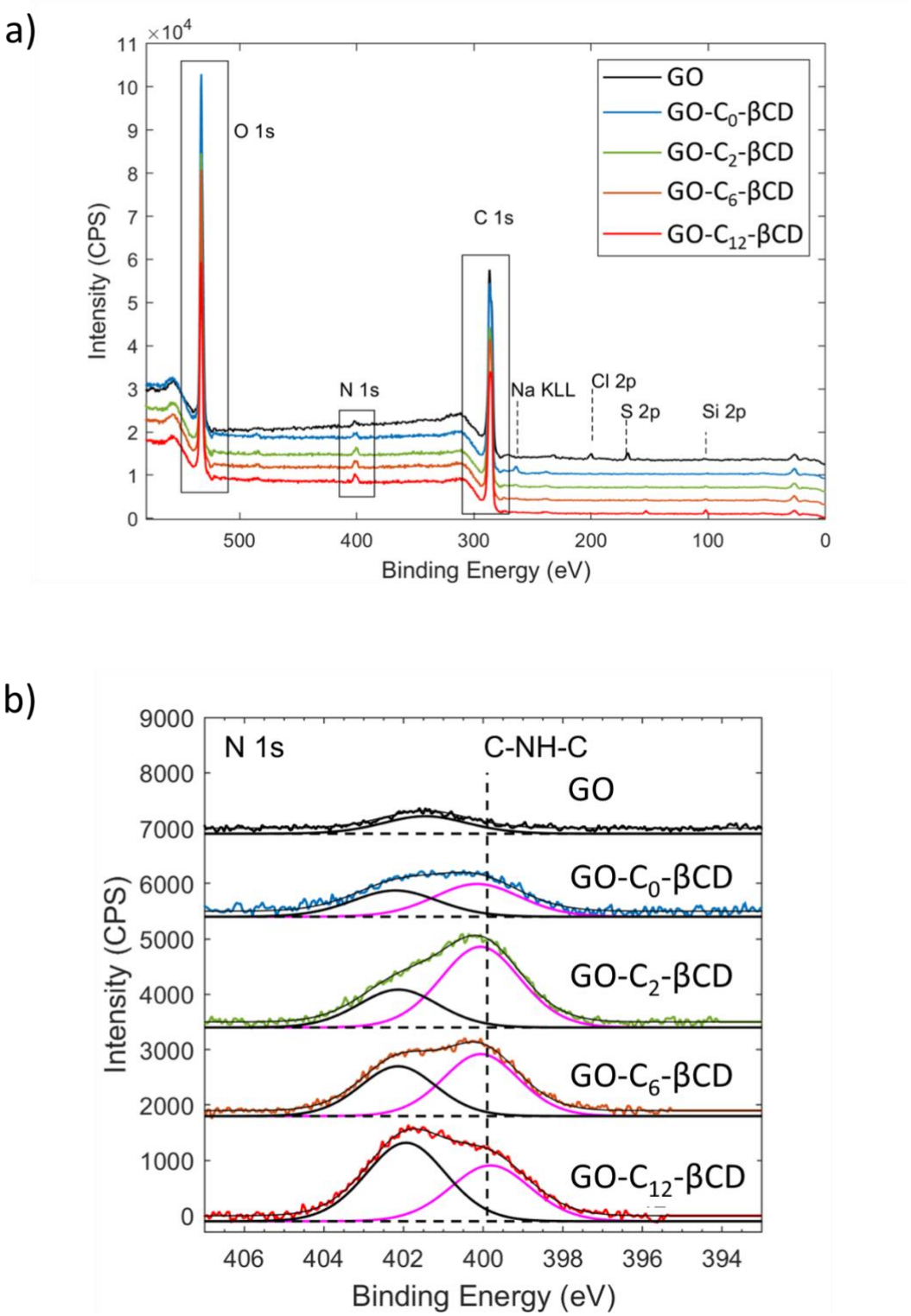


Figure S3. a) XPS survey spectra and b) N 1s signals of GO (black), GO-C_0-βCD (blue), GO-C_2-βCD (green), GO-C_6-βCD (orange), and GO-C_{12}-βCD (red). N 1s was fitted by two voigt curves with binding energies at: i) 400.0 eV (C-NH-C, magenta line) and ii) 402.0 eV (other N atoms, black line). All spectra was shifted for better visualization.

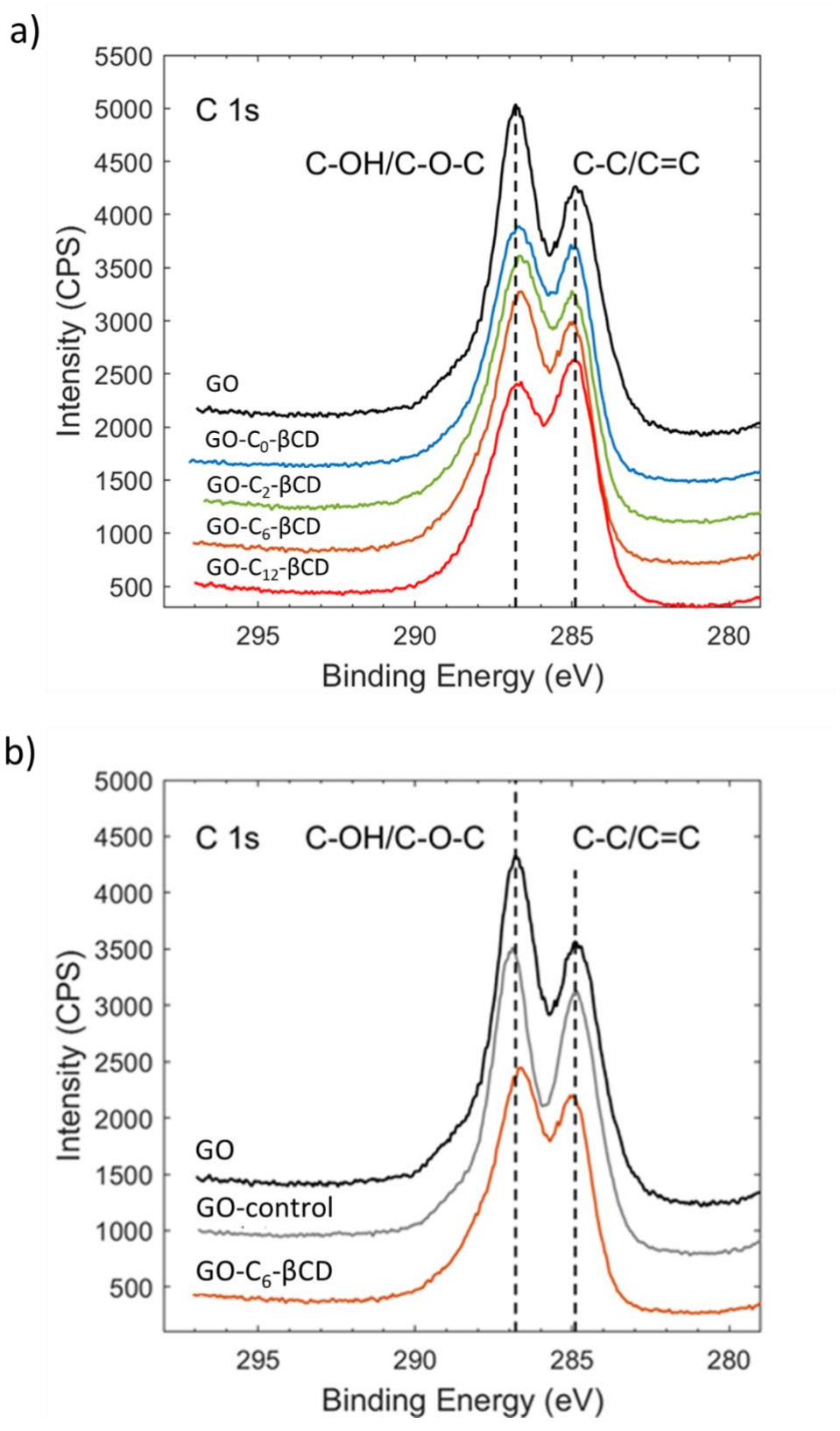


Figure S4. C 1s XPS signal of a) GO (black), GO-C_0-βCD (blue), GO-C_2-βCD (green), GO-C_6-βCD (orange), GO-C_{12}-βCD (red), and b) GO (black), GO-control (grey) and GO-C_6-βCD (orange).

5. Elemental analysis

Table S1. Element content (wt. %) of C_0-βCD ($C_{42}H_{71}NO_{34}$), C_2-βCD ($C_{44}H_{76}N_2O_{34}$), C_6-βCD ($C_{48}H_{84}N_2O_{34}$), and C_{12}-βCD ($C_{54}H_{96}N_2O_{34}$).

		Element content (wt. %)				
		C	**H**	**N**	**S**	**O**
C_0-βCD	**calculated**	44.5	6.3	1.2	-	48.0
	found	37.5	6.5	1.8	0.09	49.6
C_2-βCD	**calculated**	44.9	6.5	2.4	-	46.2
	found	38.0	6.9	2.4	0.1	47.9
C_6-βCD	**calculated**	46.8	6.9	2.3	-	44.1
	found	41.1	7.1	1.8	0.03	48.2
C_{12}-βCD	**calculated**	49.2	7.4	2.1	-	41.3
	found	44.8	7.7	2.2	0.09	43.8

Table S2. Atomic composition and atomic ratios of βCD, C_0-βCD, C_2-βCD, C_6-βCD, C_{12}-βCD, GO, GO-control, GO@βCD, GO-C_0-βCD, GO-C_2-βCD, GO-C_6-βCD, and GO-C_{12}-βCD.

	Atomic composition (%)					Molar ratio			
	C	**H**	**N**	**S**	**O**	**C/O**	**C/H**	**C/N**	**O/C**
βCD	23.39	51.12	0.00	0.04	25.45	**0,92**	**0,46**	-	**1,09**
C_0-βCD	24.35	50.45	1.00	0.02	24.17	**1.01**	**0.48**	**24.31**	**0.99**
C_2-βCD	24.00	51.97	1.29	0.03	22.71	**1.06**	**0.46**	**18.57**	**0.95**
C_6-βCD	25.15	51.73	0.96	0.03	22.12	**1.14**	**0.49**	**26.07**	**0.88**
C_{12}-βCD	26.08	53.69	1.08	0.02	19.14	**1.36**	**0.49**	**24.17**	**0.73**
GO	40.05	28.60	0.08	0.46	30.81	**1.30**	**1.40**	-	**0.77**
GO-control	39.14	31.02	0.10	0.08	29.65	**1.32**	**1.26**	-	**0.76**
GO@βCD	44.08	26.12	0.03	0.30	29.47	**1.50**	**1.69**	-	**0.67**

GO-C_0-βCD	32.03	38.51	0.35	0.03	29.08	**1.10**	**0.83**	**91.33**	**0.91**
GO-C_2-βCD	34.54	40.69	0.90	0.02	23.86	**1.45**	**0.85**	**38.31**	**0.69**
GO-C_6-βCD	34.69	41.53	0.75	0.02	23.01	**1.51**	**0.84**	**46.28**	**0.66**
GO-C_{12}-βCD	33.73	42.94	1.02	0.02	22.29	**1.51**	**0.79**	**32.99**	**0.66**

6. Scanning electron microscopy (SEM)

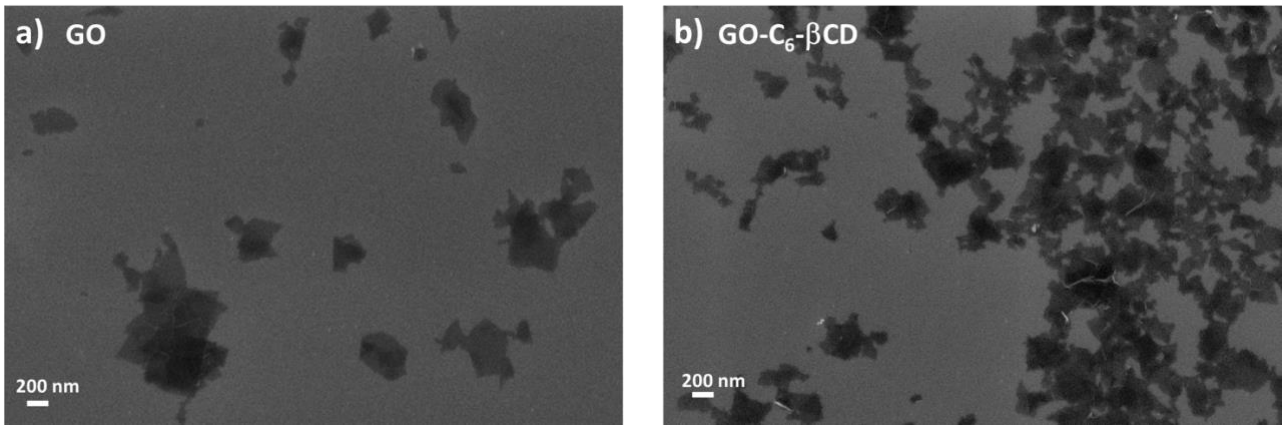
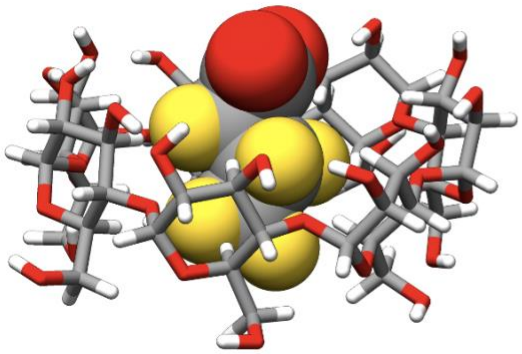


Figure S5. SEM images of a) pristine GO, and b) GO-C_6-βCD.

7. MD simulation of PFBA@βCD



	PFBA@βCD
van der Waals	-14.3
Electrostatic	4.7
E_{SURF}	-2.6
Total Affinity	-12.3

Figure S6. A representative snapshot, taken form MD simulation, of the interaction between PFBA and βCD. Computed total affinity and its contributions i.e., Van der Waals, electrostatic and non-polar solvation (Esurf) for PFBA inside βCD. All energies are reported in kcal mol^{-1}.

8. UPLC-MS/MS method

Table S3. Elution gradient used for PFBA analyses. Mobile phases: (A) MeOH:aqueous NH_4OAc 2 mM 95:5; (B) NH_4OAc 2 mM in MeOH.

Time (min)	Analytical pump		
	Flow (mL min^{-1})	A%	B%
0	0.3	100	0
1	0.3	80	20
5	0.3	60	40
6	0.3	100	0
8	0.3	100	0

Table S4. Elution gradient used for the analyses of the mixture of nine PFAS. Mobile phases: (A) MeOH:aqueous NH_4OAc 2 mM 95:5; (B) NH_4OAc 2 mM in MeOH.

Time (min)	Analytical pump		
	Flow (mL min^{-1})	A%	B%
0	0.3	100	0
1	0.3	80	20
6	0.3	55	45
13	0.3	20	80
15	0.35	5	95
17	0.35	5	95
18	0.3	100	0
21	0.3	100	0

Table S5. LC-MS/MS parameters for PFBA using UPLC-MS/MS ACQUITY UPLC H-Class PLUS – XEVO TQS Micro MS.

Analyte	Monitored transition (ES-)	Collision energy (eV)	Limit of quantification (µg/L)
Perfluorobutanoic acid (PFBA)	212.97→168.99	8	0.01

Table S6. LC-MS/MS parameters for the mixture of nine PFAS using UPLC-MS/MS ACQUITY UPLC H-Class PLUS – XEVO TQS Micro MS.

Analyte	Monitored transition (ES-)	Collision energy (eV)	Limit of quantification (µg/L)
Perfluorobutanoic acid (PFBA)	212.97→168.99	8	0.01
Perfluorodecanoic acid (PFOA)	412.98→168.98	18	0.01
Perfluoroundecanoic acid (PFNA)	462.96→218.97	16	0.01

Perfluorododecanoic acid (PFOS)	498.90→79.90	54	0.01
Perfluorotridecanoic acid (PFDA)	513.12→469.00	10	0.01
Perfluorotetradecanoic acid (PFUnDA)	562.96→519.06	10	0.05
Perfluorobutanesulfonic acid (PFDODA)	613.06→569.04	14	0.05
Perfluorohexanesulfonic acid (PFTrDA)	622.90→168.97	28	0.05
Perfluorooctanesulfonic acid (PFTA)	712.96→168.96	32	0.1