Supplementary Information

Supramolecular Purification of Aromatic Polyester Monomers from Chemical Depolymerization

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Synthetic Characterization

Synthesis of bis(2-hydroxyethyl) isophthalate, BHEI

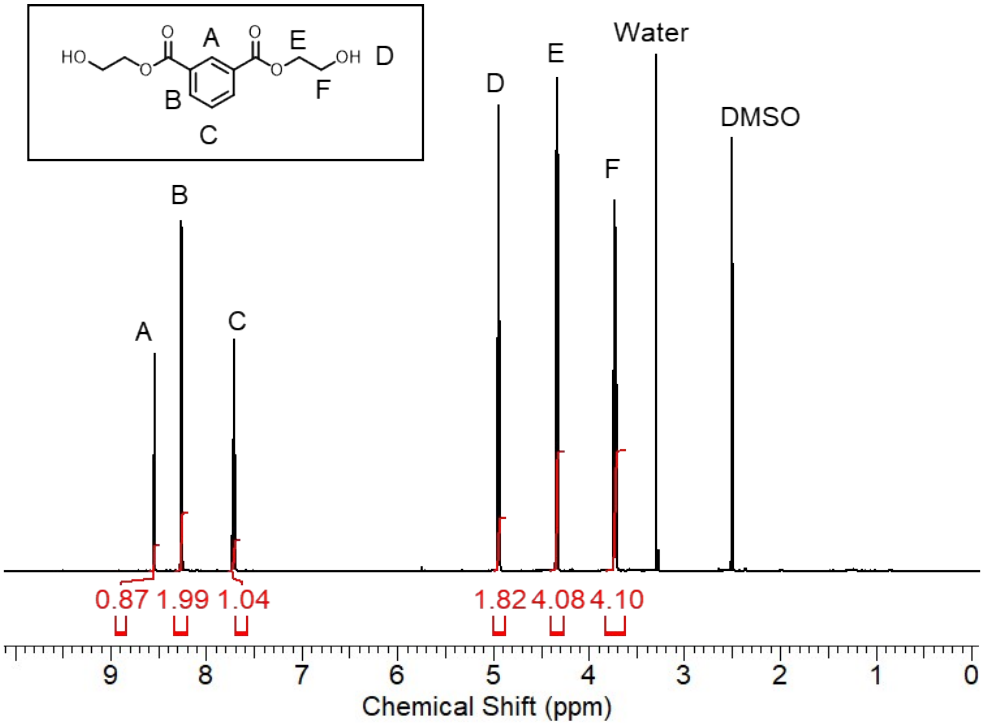

Figure S1. ^{1}H NMR spectra (500 MHz, DMSO-d6) of BHEI monomer.

Synthesis of Crosslinked Cyclodextrin Polyurethanes

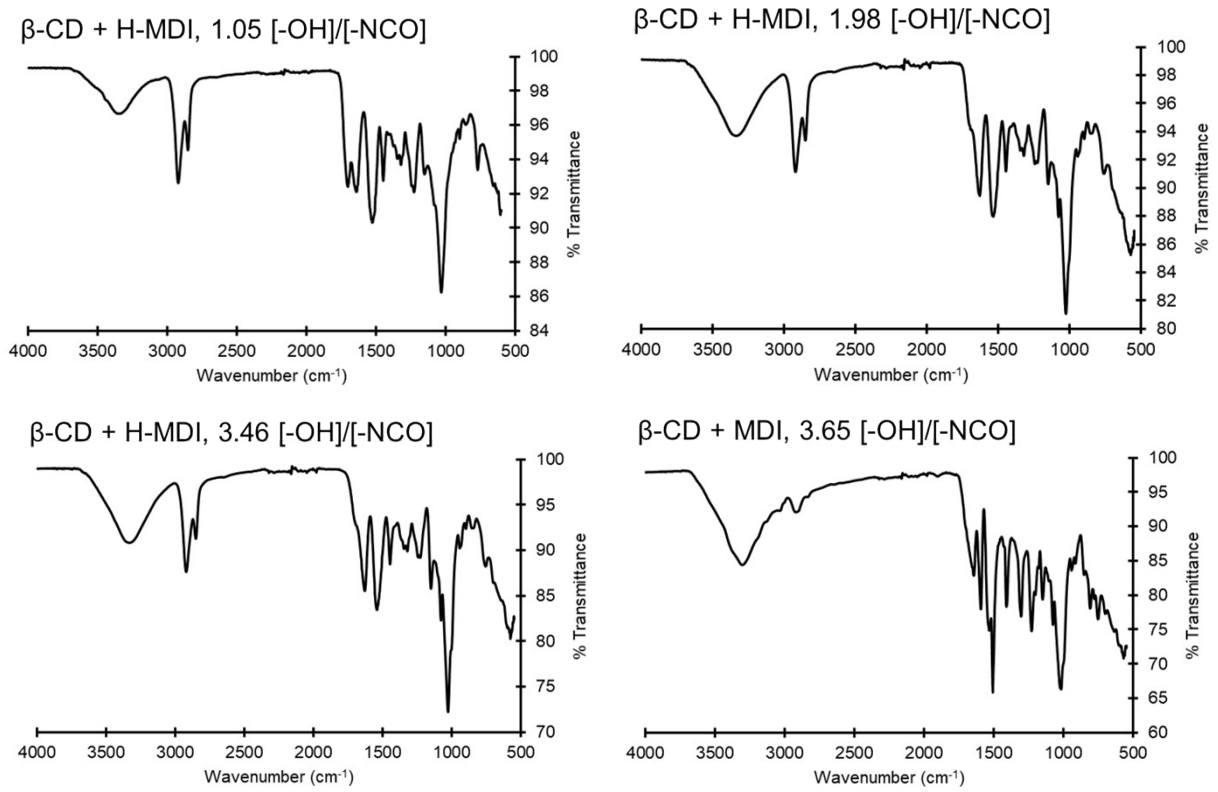

Figure S2. FTIR spectra of urethane crosslinked β-CD particles.

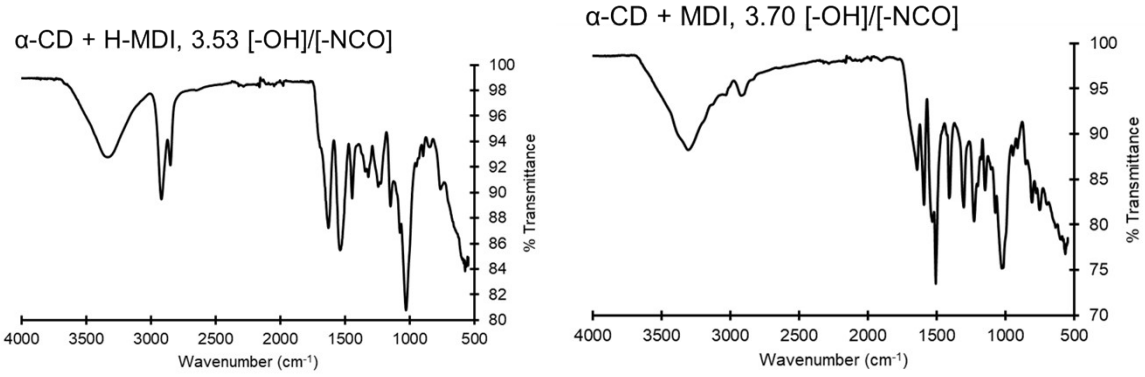

Figure S3. FTIR spectra of urethane crosslinked α-CD particles.

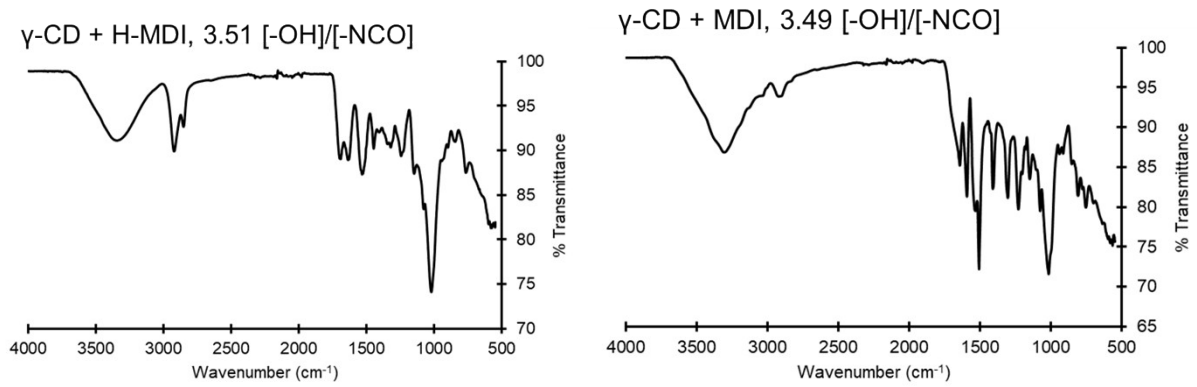

Figure S4. FTIR spectra of urethane crosslinked γ-CD particles.

Synthesis of cyclodextrin crosslinked with perfluorinated bis-cyanobenzenes

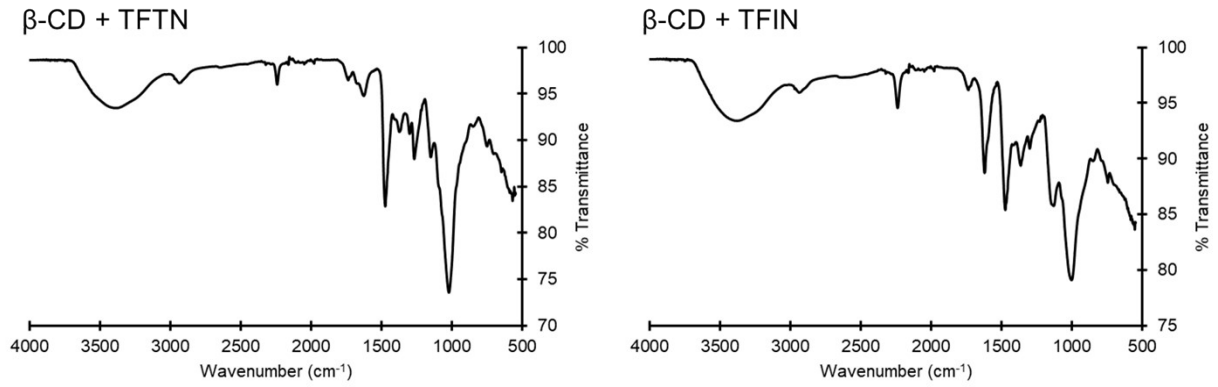

Figure S5. FTIR spectra of aromatic crosslinked β-CD particles.

Absorbance After Soxhlet Extraction

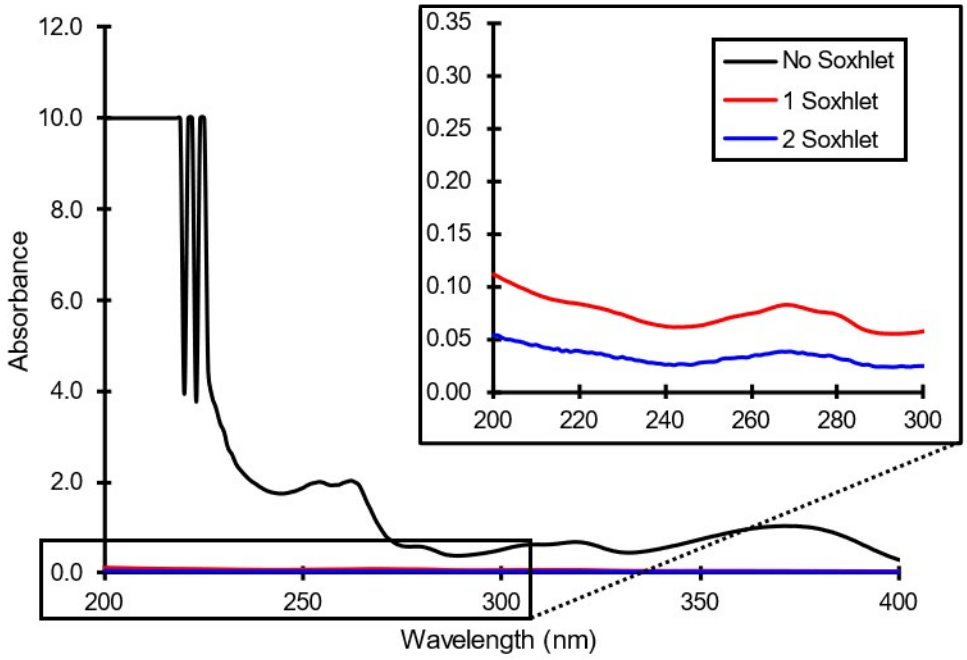

Figure S6. UV-Vis of water exposed to as synthesized particles, after the first Soxhlet purification with H_2O and MeOH, and after the second Soxhlet extraction with H_2O and MeOH. Removal of UV-active species requires two extractions for quantifying the extraction efficacy.

Elemental Analysis Results

From elemental analysis data the cyclodextrin content of each absorbent was calculated. For polyurethanes:

$$\frac{mmol\ cyclodextrin}{g\ adsorbent} = \frac{1000 \times \left(100 - \frac{\%N \times DI_{mw}}{14.007}\right)}{\left(\frac{CD_{mw}}{100}\right)} \#(equation\ S1)$$

For cyclodextrin crosslinked with perfluorinated bis-cyanobenzenes:

$$\frac{mmol\ cyclodextrin}{g\ adsorbent} = \frac{1000}{100 \times 42} \times \left(\frac{\%C}{12.011} - \frac{\%N \times 8}{2 \times 14.007}\right) \#(equation\ S2)$$

Where DI_{mw} is the molecular weight of the diisocyanate crosslinker, CD_{mw} is the molecular weight of the cyclodextrin used, and %C and %N come from the raw data. Whole numbers 42, 8, and 2 are the number of carbons in β-cyclodextrin, carbons in the fluorinated crosslinkers, and nitrogens in the fluorinated crosslinkers, respectively. The molar mass of carbon and nitrogen used were 12.011 and 14.007 respectively, and factors of 100 are present to convert from the mass percentages in the raw data.

The urethane expression was straightforward to derive because no mass is lost during the reaction of diisocyanates. The expression for cyclodextrin crosslinked with perfluorinated bis-cyanobenzenes was more complex because HF is lost as the reaction proceeds. The general method of the derivation began by using %N to find the mols of crosslinker incorporated in a given mass. Crosslinker was presumed the exclusive source of nitrogen. The mass of carbon from the crosslinker could then be calculated from this and subtracted from the total carbon in the same given mass. Remaining carbon was attributed exclusively to the cyclodextrin, enabling the calculation of mmol CD/g.

All samples were analyzed in triplicate. The average is reported below.

Entry #	Cyclodextrin	Crosslinker	Functional group ratio [-OH]/[-NCO] or [-OH]/[-F]	Incorporated cyclodextrin (mmol/g)
1	β	H-MDI	1.05	0.071
2	β	H-MDI	1.98	0.344
3	β	H-MDI	3.46	0.385
4	α	H-MDI	3.53	0.301
5	γ	H-MDI	3.51	0.434
6	α	MDI	3.70	0.407
7	β	MDI	3.65	0.415
8	γ	MDI	3.49	0.344
9	β	TFTN	1.93	0.601
10	β	TFIN	1.95	0.527

Binding Constant Derivation

Binding constants for polyester monomers with cyclodextrins were measured using a chemical titration procedure adapted from reference S3.[S3] For this, a series of ten aqueous solutions were prepared with an initial monomer concentration of ≈ 1.0 x 10-4 M and an increasing loading of the desired cyclodextrin between 0 and 300 equivalents, depending on the specific system. Fluorescence emission spectra were then taken at room temperature (21 ± 1 °C) for each solution within 3 hours of their preparation. Fluorescence intensity was taken from an emission wavelength of 307 nm for DMI and BHEI while the emission wavelength used for DMT and BHET was 327 nm. Each system was investigated in triplicate experiments.

Binding constants were determined based on the correlation between deceasing fluorescence intensity and the initial concentrations of the monomer guest molecule G and the cyclodextrin host molecule H. The generalized binding equilibria between the guest, host, and complex HG with binding constant K_b for a 1:1 stoichiometry can be described as

$$K_b = \frac{[HG]}{[H][G]} \ \#(equation\ S3)$$

A solution containing all three components would have a fluorescence intensity F_{soln} equal to

$$F_{soln} = k_G[G] + k_H[H] + k_{HG}[HG] \#(equation\ S4)$$

Where k_G, k_H, and k_{HG} are the combined fluorescence constants for the guest, host and complex respectively assuming a 1.0 cm cuvette. Noting that the host cyclodextrin is non fluorescent (k_H=0) and that the equilibrium guest concentration can be expressed as

$$[G] = [G]_o - [HG] \#(equation\ S5)$$

We can rewrite the solution fluorescence intensity at equilibrium as:

$$F_{soln} = k_G[G]_o - k_G[HG] + k_{HG}[HG] \#(equation\ S6)$$

A solution of pure guest monomer may be prepared, and the fluorescence intensity F_G directly measured.

$$F_G = k_G[G]_o \#(equation\ S7)$$

Subtracting the solution fluorescence intensity from that of the initial guest molecule fluorescence intensity allows us to predict the changes in fluorescence as a function of the complex concentration

$$\Delta F = F_G - F_{soln} = k_{HG}[HG] - k_G[HG] = \Delta k[HG] \#(equation\ S8)$$

Where

$$\Delta k = k_G - k_{HG} \#(equation\ S9)$$

The equilibrium concentration of the complex HG for a given solution can be written exclusively in terms of the known values $[G]_o$ and $[H]_o$, and the unknown binding constant.

$$[HG] = \frac{1}{2}\left\{\left([G]_o + [H]_o + \frac{1}{K_b}\right) - \sqrt{\left([G]_o + [H]_o + \frac{1}{K_b}\right)^2 - 4[H]_o[G]_o}\ \right\} \#(equation\ S10)$$

Substituting this expression we arrive at an equation with two unknowns, Δk and K_b, and three known values, $[G]_o$,$[H]_o$, and ΔF.

$$\Delta F = \frac{1}{2}\Delta k\left\{\left([G]_o + [H]_o + \frac{1}{K_b}\right) - \sqrt{\left([G]_o + [H]_o + \frac{1}{K_b}\right)^2 - 4[H]_o[G]_o}\right\} \#(equation\ S11)$$

For each titration solution, the experimental value of ΔF was calculated. A least squares nonlinear regression was then performed using Microsoft Excel and the Solver add-in to calculate the values of Δk and K_b.

Binding stoichiometry was confirmed to be 1:1 by analysis of the residual error between experimental and regression values of ΔF as described in reference S4.[S4] Briefly, residual errors from an accurate binding model are expected to be completely random, while those from an inaccurate model would likely follow an observable pattern. Residual errors in our experiments do not follow any distinct or repeatable trends.

Fluorescence Excitation/emission Wavelength Determination

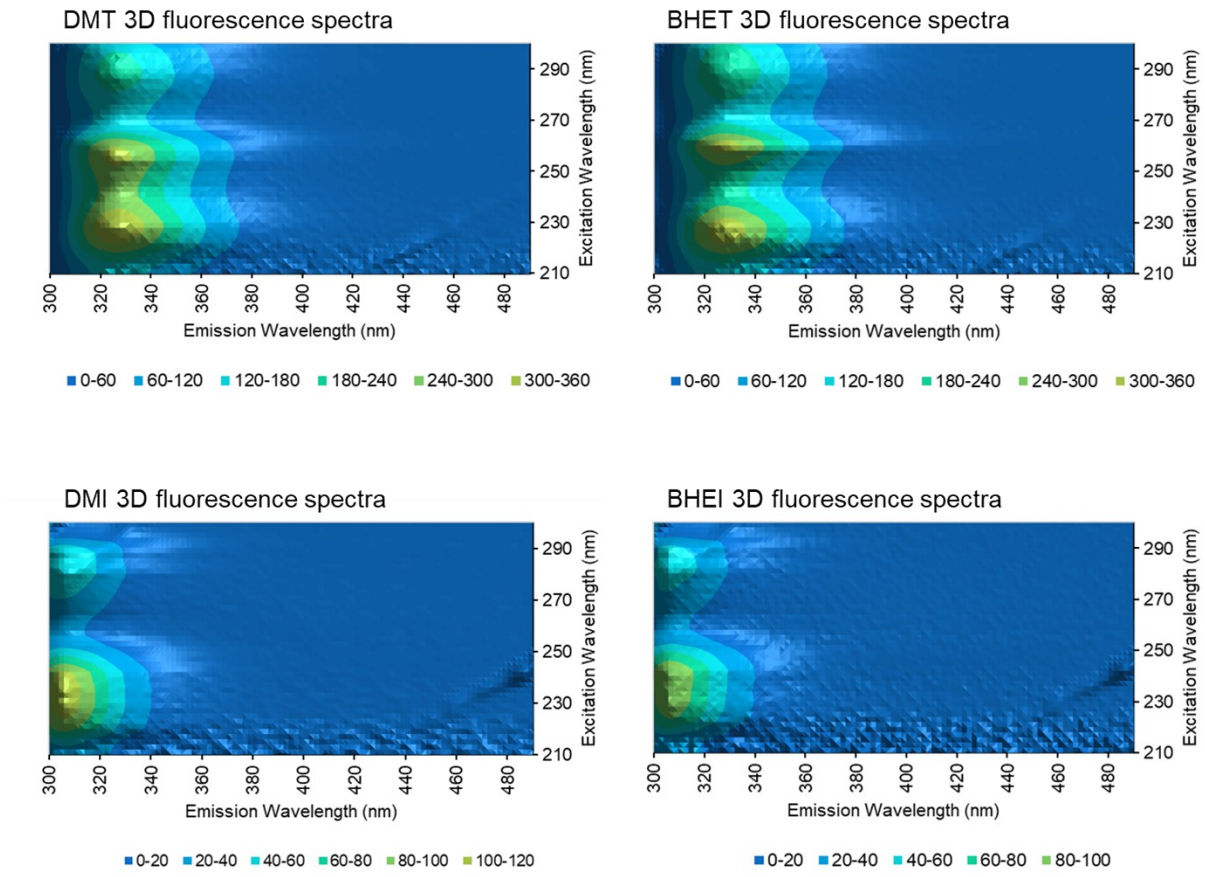

Figure S7. 3D fluorescence excitation/emission spectra to determine the excitation wavelength for each monomer.

Binding Constant Measurements

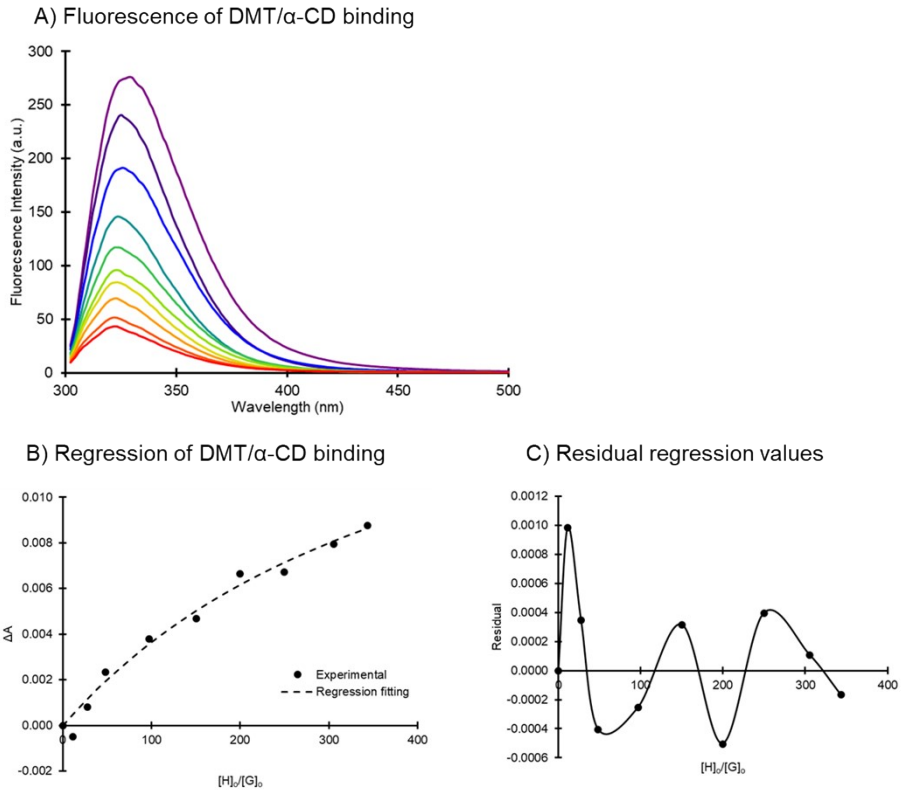

Figure S8. (A) Fluorescence titration of DMT/α-CD and (B) regression fit to determine binding constant along with the (C) residual regression values consistent with 1:1 stoichiometry.

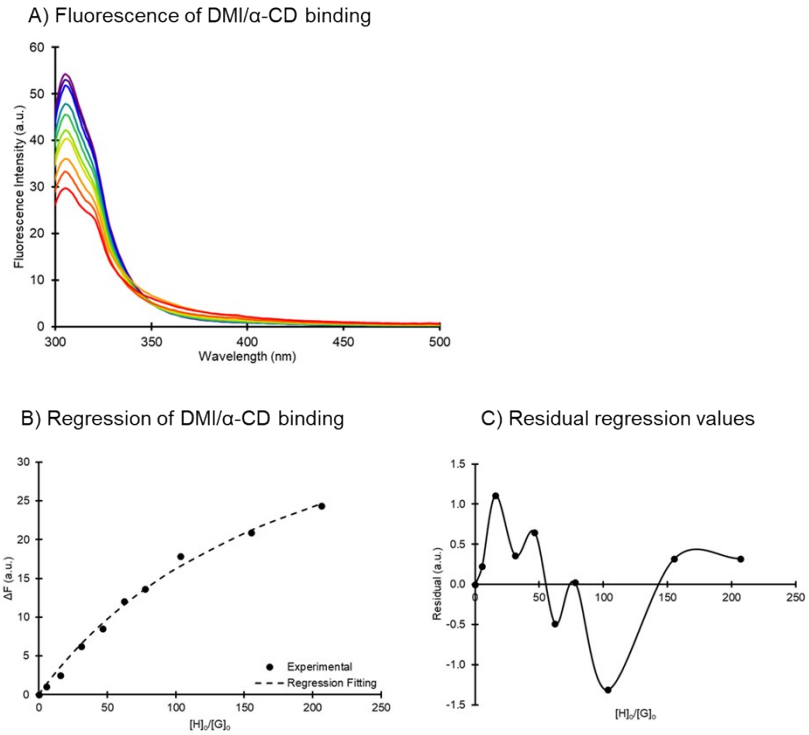

Figure S9. (A) Fluorescence titration of DMI/α-CD and (B) regression fit to determine binding constant along with the (C) residual regression values consistent with 1:1 stoichiometry.

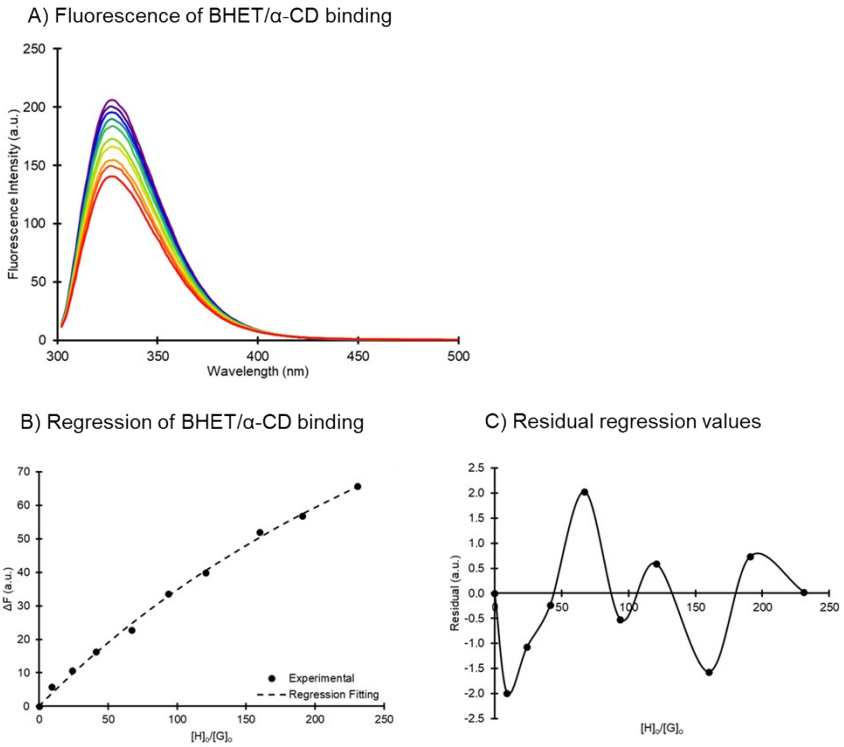

Figure S10. (A) Fluorescence titration of BHET/α-CD and (B) regression fit to determine binding constant along with the (C) residual regression values consistent with 1:1 stoichiometry.

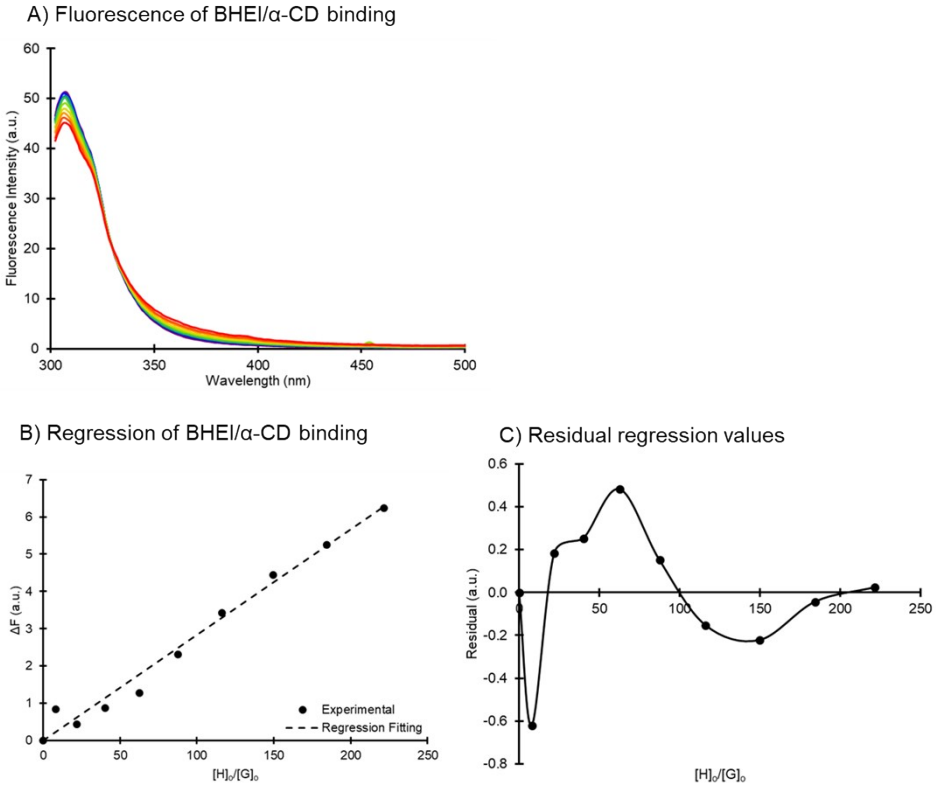

Figure S11. (A) Fluorescence titration of BHEI/α-CD and (B) regression fit to determine binding constant along with the (C) residual regression values consistent with 1:1 stoichiometry.

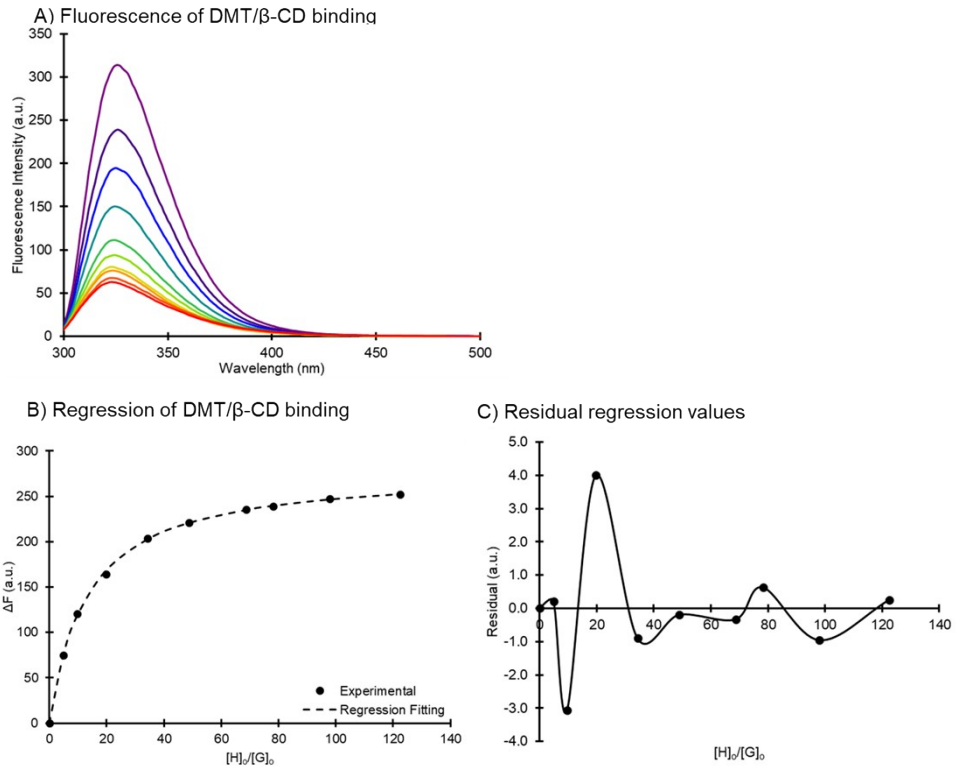

Figure S12. (A) Fluorescence titration of DMT/β-CD and (B) regression fit to determine binding constant along with the (C) residual regression values consistent with 1:1 stoichiometry.

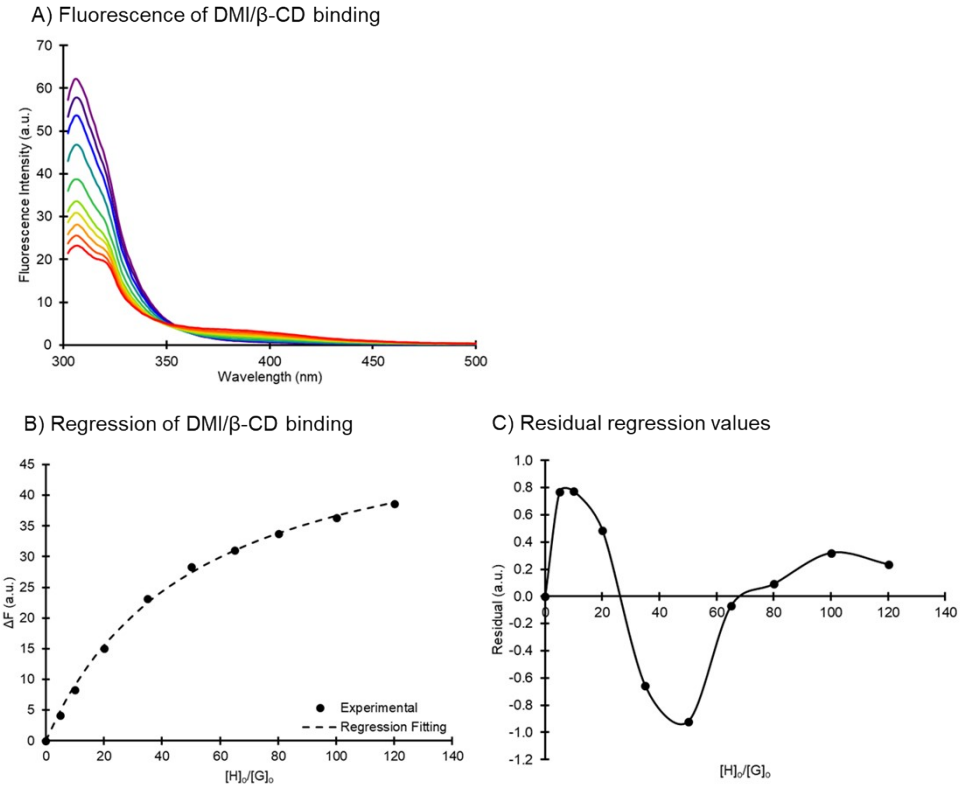

Figure S13. (A) Fluorescence titration of DMI/β-CD and (B) regression fit to determine binding constant along with the (C) residual regression values consistent with 1:1 stoichiometry.

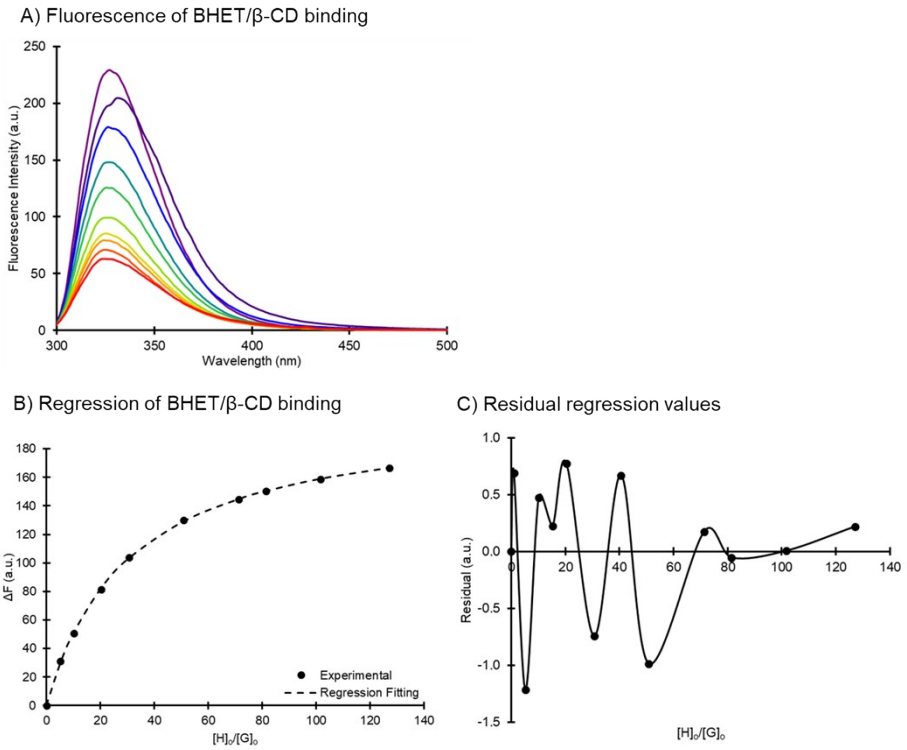

Figure S14. (A) Fluorescence titration of BHET/β-CD and (B) regression fit to determine binding constant along with the (C) residual regression values consistent with 1:1 stoichiometry.

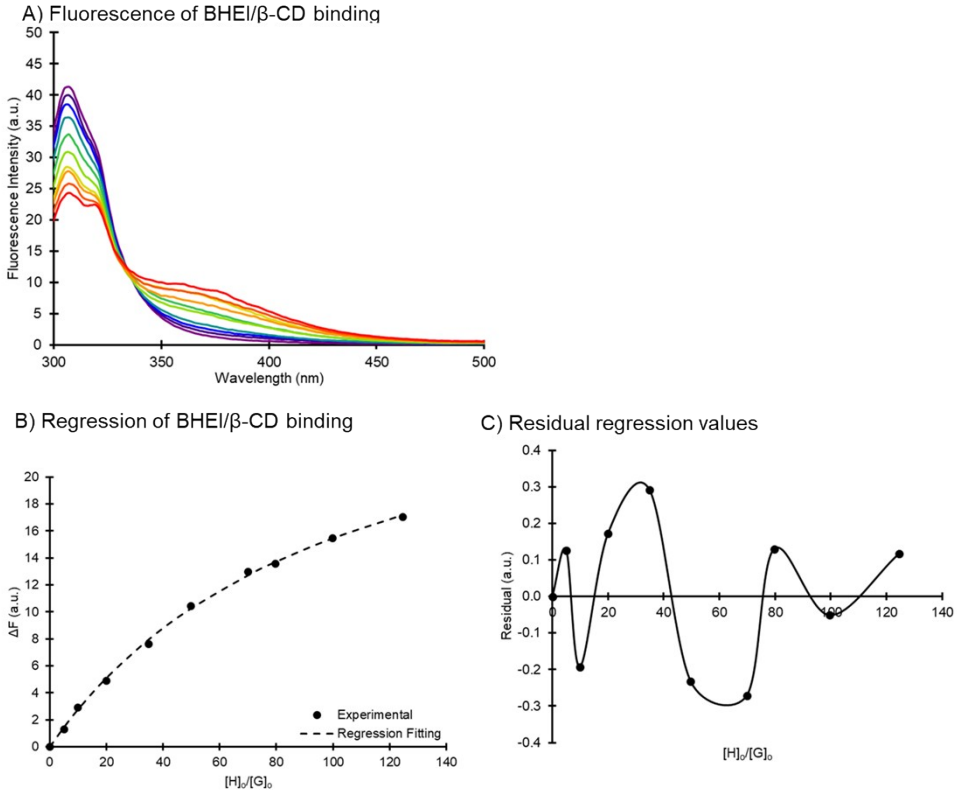

Figure S15. (A) Fluorescence titration of BHEI/β-CD and (B) regression fit to determine binding constant along with the (C) residual regression values consistent with 1:1 stoichiometry.

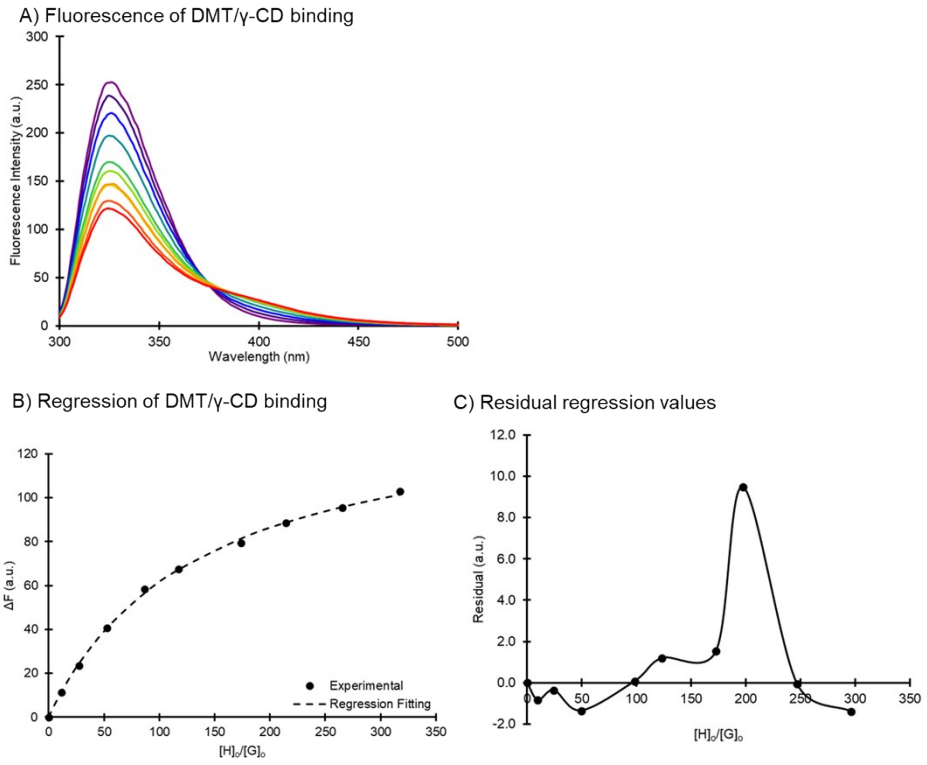

Figure S16. (A) Fluorescence titration of DMT/γ-CD and (B) regression fit to determine binding constant along with the (C) residual regression values consistent with 1:1 stoichiometry.

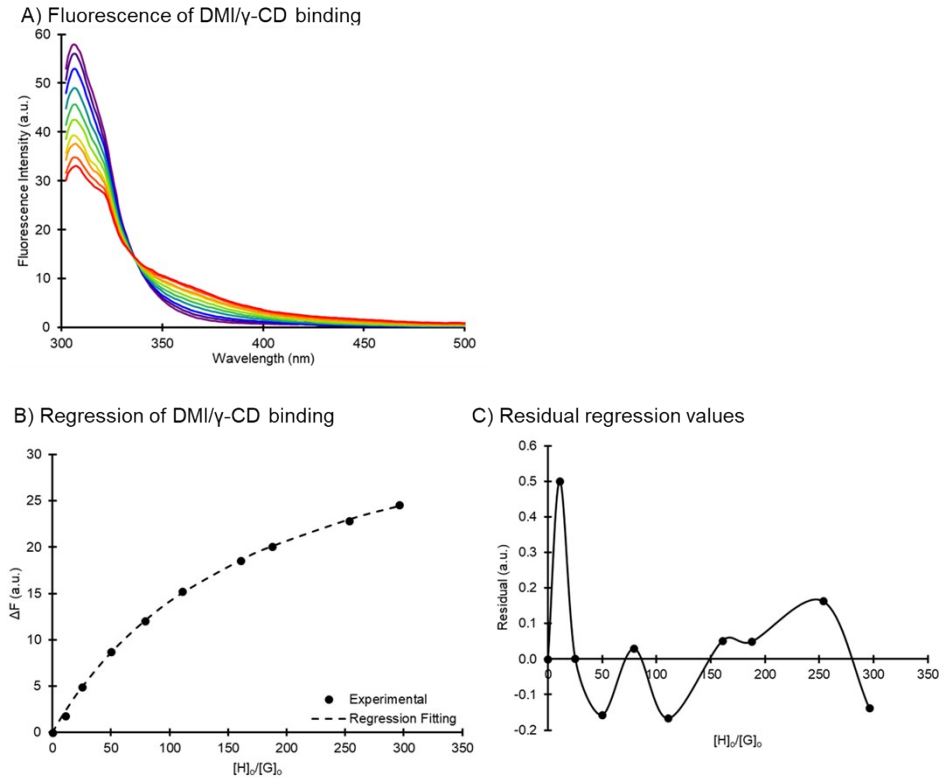

Figure S17. (A) Fluorescence titration of DMI/γ-CD and (B) regression fit to determine binding constant along with the (C) residual regression values consistent with 1:1 stoichiometry.

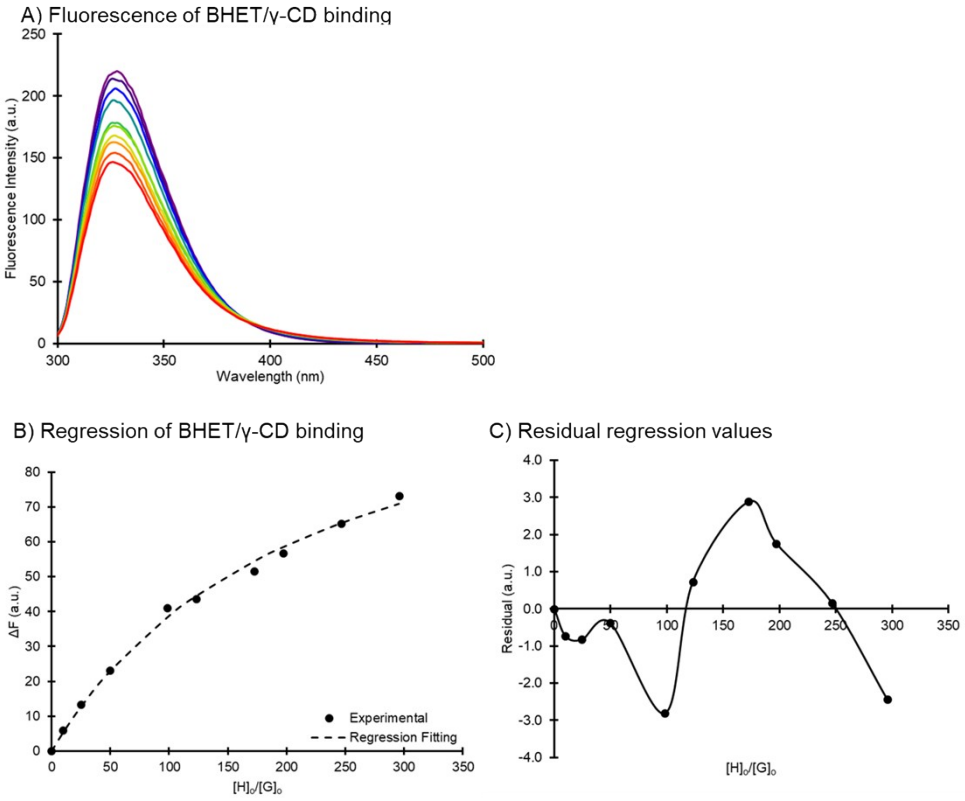

Figure S18. (A) Fluorescence titration of BHET/γ-CD and (B) regression fit to determine binding constant along with the (C) residual regression values consistent with 1:1 stoichiometry.

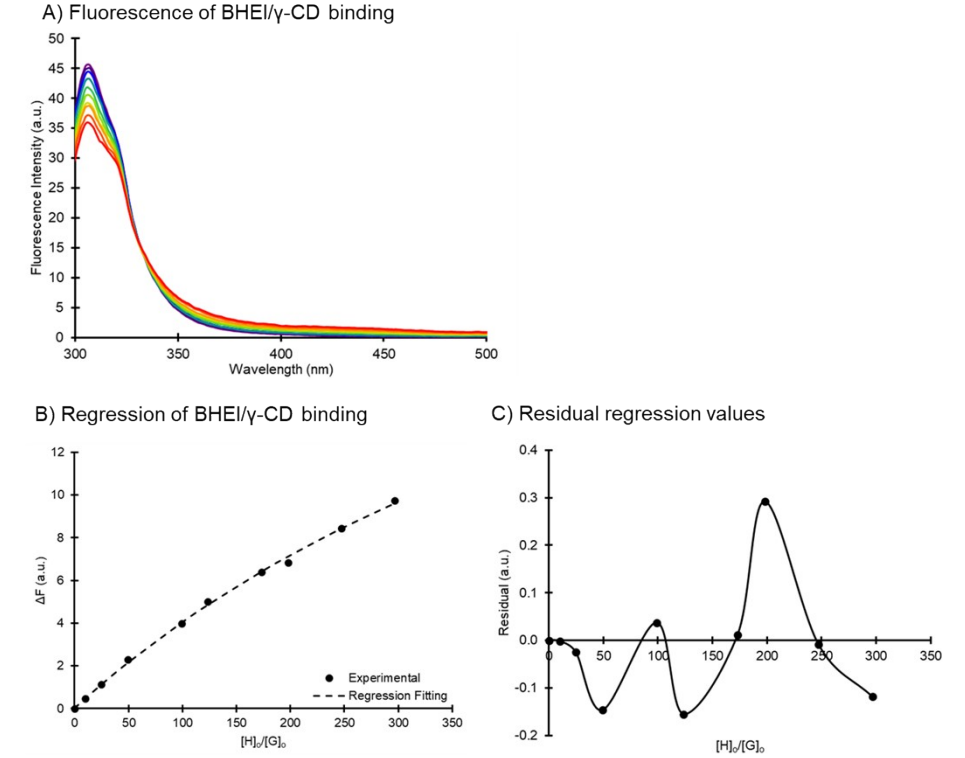

Figure S19. (A) Fluorescence titration of BHEI/γ-CD and (B) regression fit to determine binding constant along with the (C) residual regression values consistent with 1:1 stoichiometry.

Selective Extraction Experiments

A stock solution was prepared with equimolar amounts of isophthalate and terephthalate monomers, each at ≈ 5 x 10^{-5} M. The materials were dissolved in ultra-pure water using gentle heat and stirring, then cooled to room temperature. A graduated cylinder was used to measure out 25 mL of the solution into Erlenmeyer flasks containing a known mass of crosslinked cyclodextrin ≈ 100 mg. The solutions were gently swirled to expose all the adsorbent to the solution then were allowed to sit for 5-8 minutes. Crosslinked cyclodextrin was then removed by gravity filtration using Cytiva Whatman #2 filter paper that was prerinsed with copious amounts of ultra-pure water. Each experiment also included sample of the pure stock solution, and another where ≈ 100 mg of the crosslinked cyclodextrin was washed with 25 mL of ultra-pure water, each similarly filtered. These solutions enable us to determine changes in concentration before and after the extraction as well as confirm that the adsorbent is not contributing significantly to the solution background.

All solutions from the experiment were subsequently diluted by a factor of 5 and analyzed by UV-Vis to determine the changes is concentration. Isophthalate monomers were determined using their peak at 211 nm. Terephthalate monomers were analyzed at a wavelength of 256 nm. These wavelengths were selected to minimize the effect of one monomer on the others measures concentration. For every monomer system and wavelength, the desired component showed a molar absorptivity ≈ 16x greater than the other component, see the figure S20. Because all solutions measured had approximately the same concentration of isophthalates and terephthalates, even after extractions, correcting for the concentration of the other was unnecessary in standard experiments.

Concentration changes of each monomer Δ[G] were calculated as a percentage difference from the stock solution used for each experiment. Rather than calculate individual concentrations with a calibration curve, the % change is simply the difference in absorbance between stock and experimental solutions at the desired wavelength

$$\Delta[G]\% = \frac{A_{stock} - A_{extracted}}{A_{stock}} \times 100\% \#(equation\ S12)$$

Where A_{stock} and $A_{extracted}$ are the absorbance of the stock and extracted solutions respectively. Selectivity of the crosslinked cyclodextrin extraction was defined as the ratio of terephthalate and isophthalate concentration changes. This expression is a valid provided the stock solution is sufficiently close to an equimolar mixture of the two components.

$$Selectivity = \frac{\Delta[terephthalate]}{\Delta[isophthalate]} \#(equation\ S13)$$

Selective Extraction at Different Initial Monomer Concentrations:

Similar extraction experiments were performed on stock solutions with different starting ratios of DMT and DMI. The total concentration of each was kept at 1.0 x 10^{-4} M and monomer ratios of 1:3, 1:1 and 3:1 were used. Because the selectivity term defined above is only valid for the extraction of equimolar mixtures, it was decided to express differences in affinity for crosslinked cyclodextrin by comparing the initial mol fraction of DMT, χ_{DMT}(feed), to that removed by the absorbent, χ_{DMT}(extracted).

$$\chi_{DMT}(feed) = \frac{[DMT]_o}{[DMT]_o + [DMI]_o} \#(equation\ S14)$$

$$\chi_{DMT}(extracted) = \frac{\Delta[DMT]}{\Delta[DMT] + \Delta[DMI]} \#(equation\ S15)$$

Where $[DMT]_o$ and $[DMI]_o$ are the concentrations of the stock solution, and Δ[DMT] and Δ[DMI] are the positive changes in molar concentration between the stock and the extracted solutions.

In addition to modifying the expression of selectivity, the concentrations measured by UV-Vis were corrected for the residual absorbance of the comonomer in the mixture. An equation was derived for accurate concentrations. Absorbance values at 256 and 211 nm can be expressed as a linear combination of the absorbances from both DMT and DMI at these respective wavelengths as in equations S16 and S17. Solving these as a system of linear equations yields expressions for DMT and DMI concentrations (equations S18 and S19).

$$A_{256} = \varepsilon_{DMT,256}[DMT] + \varepsilon_{DMI,256}[DMI] \#(equation\ S16)$$

$$A_{211} = \varepsilon_{DMT,211}[DMT] + \varepsilon_{DMI,211}[DMI] \#(equation\ S17)$$

$$[DMT] = \frac{\varepsilon_{DMI,211}A_{256} - \varepsilon_{DMI,256}A_{211}}{\varepsilon_{DMI,211}\varepsilon_{DMT,256} - \varepsilon_{DMT,211}\varepsilon_{DMI,256}} \#(equation\ S18)$$

$$[DMI] = \frac{\varepsilon_{DMT,211}A_{256} - \varepsilon_{DMT,256}A_{211}}{\varepsilon_{DMT,211}\varepsilon_{DMI,256} - \varepsilon_{DMI,211}\varepsilon_{DMT,256}} \#(equation\ S19)$$

Where A_{256} and A_{211} are the measured absorbance values at 256 nm and 211 nm respectively, and molar absorptivities, ε, are identified with monomer and wavelength in subscript. Accurate molar absorptivities were determined by measuring a series of pure solutions at known concentrations and constructing calibration curves for both wavelengths. The table below gives these constants.

Monomer, wavelength	Molar absorptivity ($M^{-1}\cdot cm^{-1}$)
$\varepsilon_{DMT,256}$	9660
$\varepsilon_{DMT,211}$	2295
$\varepsilon_{DMI,256}$	563
$\varepsilon_{DMI,211}$	36141

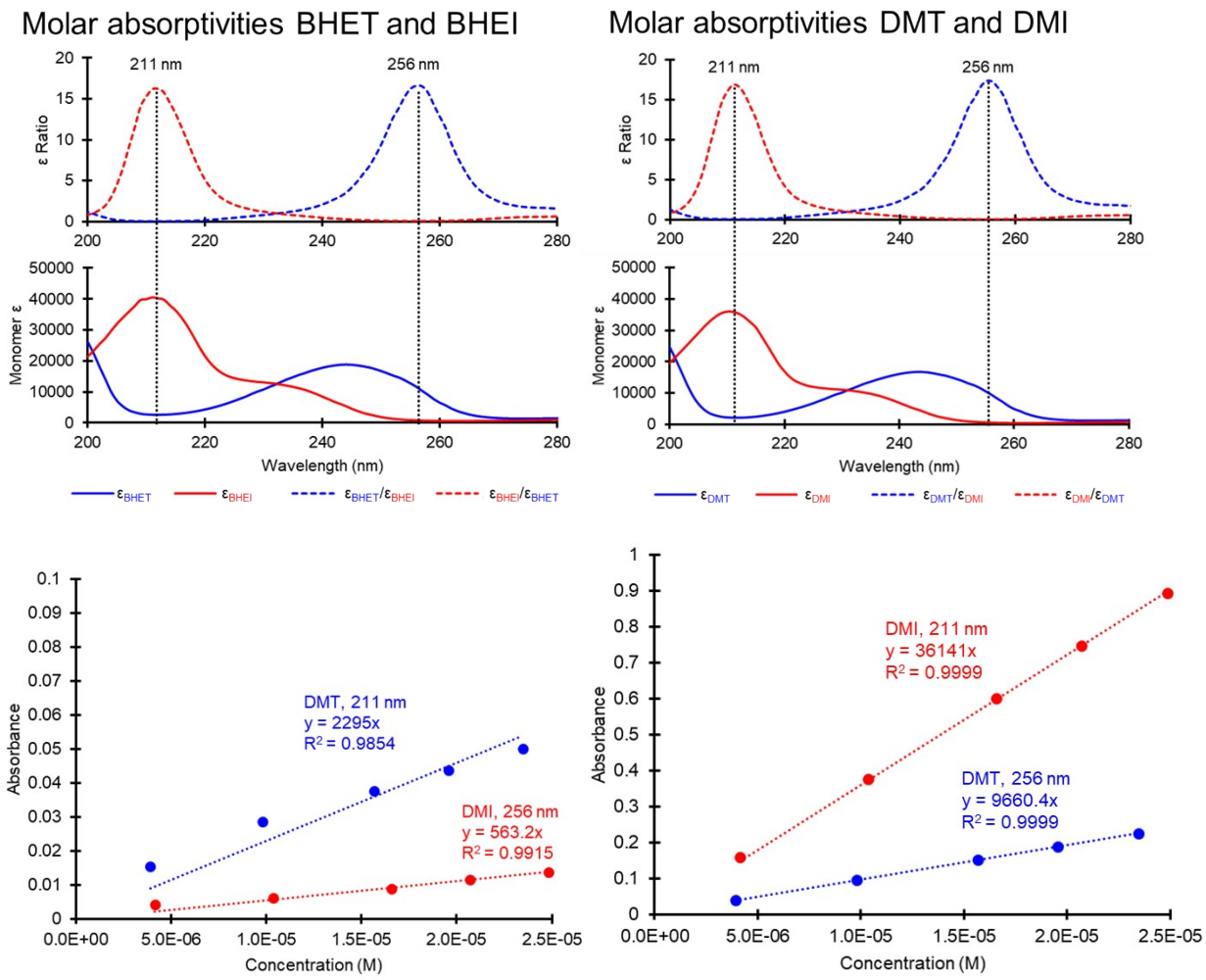

Figure S20. UV-Vis spectra of BHET, BHEI, DMT, and DMI peak intensities for determining molar absorptivity and calibration curves for concentration determination.

Bulk Extraction Efficiency Experiment

A 7.47 x 10^{-3} M solution of BHET was prepared in ultra-pure water using heat and gentle stirring. This concentration is near the saturation point, and BHET was observed to slowly crystalize if allowed to sit for more than ≈24 hours. To avoid this problem, the solution was cooled quickly by submerging it in a room temperature water bath and performing experiments shortly after.

As with earlier experiments, a known mass (≈165 mg) of crosslinked cyclodextrin was transferred to an Erlenmeyer flask and subsequently treated with 25.0 mL of the concentrated solution. A control flask without any adsorbent was also prepared. Gentle swirling was used to expose all adsorbent to the solution. The flasks were then sealed using parafilm and aluminum foil to prevent evaporation and were left for 15 hours without stirring or shaking. Each sample was then gravity filtered using filter paper that had been prerinsed with substantial amount of ultra-pure water. 120 µL of each filtrate was diluted to 50 mL total volume and UV-Vis was run. Absorbance measurements were taken at the 244 nm peak instead of 256 nm because there was no concern about signal overlap with comonomers in a pure guest solution.

The mass of BHET extracted per gram of absorbent was calculated as below. Changes in absorbance between stock and extracted solutions were again used in place of constructing a calibration curve.

$$\frac{mg\ extracted}{adsorbent\ mass\ (g)} = \frac{0.025\ L \times 0.00747\ M \times \left(\frac{A_{stock} - A_{extracted}}{A_{stock}}\right) \times 254.2\frac{g}{mol} \times 1000}{adsorbent\ mass\ (g)} \#(equation\ S20)$$

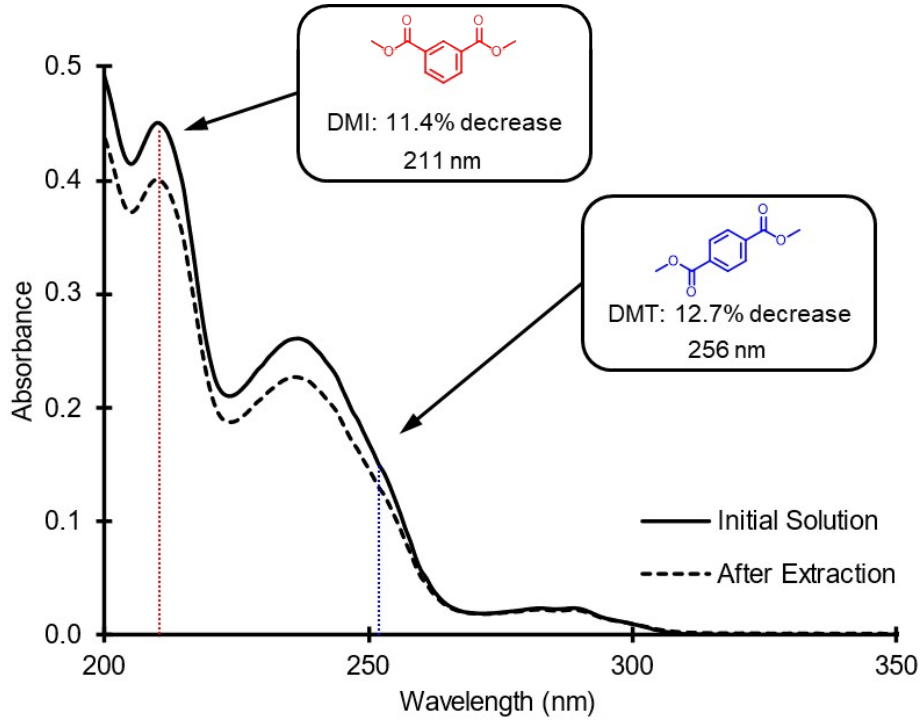

Figure S21. UV-Vis extraction with heterogeneous H-MDI/β-CD particles at a 1.05 [OH]/[NCO] ratio showing competitive extraction efficacy for each monomer component of DMI and DMT.

References

S1) S. Kawano, T. Kida, K. Miyawaki, Y. Fukuda, E. Kato, T. Nakano, M. Akashi. *Polymer Journal* **2015**, *47*, 443–448.

S2) A. Alsbaiee, B. J. Smith, L. Xiao, Y. Ling, D. Helbling, W. R. Dichtel. *Nature* **2016**, *529*, 190–194.

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S4) F. Ulatowski, K. Dąbrowa, T. Bałakier, J. Jurczak. *Journal of Organic Chemistry* **2016**, *81*, 1746–1756.

S5) D. B. Hibbert, P. Thordarson. *Chemical Communications* **2016**, *52*, 12792–12805.