

Supporting information

For

Supramolecular Assemblies of Glycoclusters with Aggregation-Induced Emission for Sensitive Phenol Detection

Die Li,^{†‡} Jing Chen,^{†‡} Xiaoling Xu,^{†‡} Chunyang Bao,^{†‡} Qiang Zhang^{†‡*}

[†] Key Laboratory of New Membrane Materials, Ministry of Industry and Information Technology, School of Environmental and Biological Engineering, Nanjing University of Science and Technology, Nanjing 210094, P. R. China.

[‡] Institute of Polymer Ecomaterials, School of Environmental and Biological Engineering, Nanjing University of Science and Technology, Nanjing 210094, P. R. China.

*Email: zhangqiang@njust.edu.cn

Materials

β -cyclodextrin (β -CD, 97%, Sigma-Aldrich) was recrystallized twice from water and dried in a vacuum oven at 100 °C for two days prior to use. Copper (I) Bromide (98%, Sigma-Aldrich) was washed sequentially with acetic acid and ethanol and dried under vacuum. 1, 3, 2-Dioxaborolane, 2, 2'-[[[(1E)-1, 2-diphenyl-1, 2-ethenediyl]di-4, 1-phenylene]bis[4, 4, 5, 5-tetramethyl - (TPE-Bpin₂)] was obtained from AIEgen Biotech (HK) and directly used for the synthesis of 4, 4'-(1, 2-diphenylethene-1, 2-diyl)bis(1, 4-phenylene) (TPEDB).^{1, 2} 1-(2'-propargyl) D-ribose, 1-(2'-propargyl) D-mannose, 1-(2'-propargyl) D-glucose,^{3, 4} and *Heptakis*-(6-deoxy-6-azido)- β -cyclodextrin (CD@N₃)^{5, 6} were synthesized according to previous reports. All the other reagents and solvents were obtained from Aladdin (China) and used without further purification unless otherwise stated.

Analytical techniques

¹H NMR spectra were recorded at 25 °C with a Bruker AV 500M spectrometer using deuterated solvents obtained from Aladdin. Fourier transform infrared (FTIR) spectra was recorded on a Nicolet iS5 FTIR spectrometer using an iD7 diamond attenuated total reflectance optical base. Transition electron microscopy (TEM) images were acquired by FEI TECNAI G2 20 TEM microscope equipped with LaB6 filament. Surface area measurements were conducted on ASAP 3020 system (Micromeritics, USA). The sample was degassed at 90 °C for 72 h and then backfilled with N₂. The N₂ isotherms were generated by incremental exposure to ultrahigh-purity nitrogen up to 1 atm in a liquid nitrogen (77 K) bath. The specific surface area of the samples was calculated by BET model, and the pore size distribution was determined by

Brett-Joyner-Halenda (BJH) method. The size and size distribution of nanoparticles were measured by dynamic light scattering (DLS) using a ZetaPALS variable temperature analyzer (Brookhaven Instruments, UK). The fluorescence spectrums were recorded on a Shimadzu RF-6000 spectrofluorometer.

Synthesis of persubstituted cyclodextrin-based glycoclusters *via* CuAAC (CD@Ribose, CD@Glucose and CD@Mannose).

Synthesis of three different kinds of cyclodextrin-based glycoclusters was conducted. Alkyne-functionalized pyranoses (including mannose, glucose) and furanose (ribose) were synthesized *via* similar procedure as previous report.⁶ Took CD@Ribose for example, A solution of 1-(2'-propargyl) D-ribose (1.5 g, 8 mmol), CD@N₃ (1.3 g, 1 mmol), bpy (62 mg, 0.4 mmol) in DMF (10 ml) was deoxygenated by three freeze-pump-thaw cycles. The solution was then transferred *via* cannula under nitrogen into a Schlenk tube, previously evacuated and filled with nitrogen, containing CuBr (29 mg, 0.2 mmol). The resulting solution was stirred at 50 °C for 24 h. When the reaction was completed, the reaction mixture was purged with air for 1 h. Most of the DMF could be removed either under high vacuum or by compressed air blowing overnight. Anhydrous methanol was then added into this concentrated deep blue solution to get a precipitate. The upper layer blue solution was removed and the precipitate was carefully collected and washed with anhydrous methanol to get a white powder. To increase the isolated conversion, the solution was collected and concentrated *via* rotary evaporator and precipitated into methanol again. The above procedure was repeated at least five times in order to remove DMF, excess alkyne ribose and Cu / bpy residues. The collected precipitate was soluble in

water and passed through a short neutral alumina column to remove the residue copper and the final product could be recovered as white powder after freeze drying (1.6 g, yield: 61%).

CD@Mannose and CD@Glucose were prepared *via* similar procedure as previous report,⁶ with yields of 86% and 88% respectively.

Preparation of the solutions used in investigation

*Preparation of Stock Solution of TPEDB in Carbonate Buffer.*⁷ A stock solution of TPEDB with a concentration of 10 mM was first prepared by dissolving 0.105 g (250 μ mol) TPEDB in 25 mL DMSO. The solution was stored in a refrigerator under 4 °C before use. Subsequently, into a 100 mL volumetric flask, K₂CO₃ (1.120 g), KHCO₃ (0.190 g) and deionized water (80 mL) were added. After adding 3 mL of DMSO into the carbonate buffer, 1 mL of the stock solution of TPEDB in DMSO (10 mM) was added under stirring. The volume of the solution was increased to 100 mL by adding appropriate amount of deionized water. The resultant solution of TPEDB (100 μ M) in the carbonate buffer (pH 10.5, 4% DMSO) was stirring for 15 min before use. The stock solution of TPEDB (1000 μ M, 4% DMSO) in carbonate buffer was prepared follow the same process.

Preparation of Glycoclusters, Saccharides and Phenols Solution in Deionized Water. The aqueous solutions of glycoclusters (CD@Ribose, CD@Glucose, CD@Mannose) of 200 μ M and 2000 μ M, saccharides (ribose, glucose, mannose), and phenols (catechol, resorcinol) of 10 μ M and 100 μ M were prepared successively for use.

Preparation of mixed solutions and determination of fluorescence intensity

Preparation of Mixture of TPEDB and CD@Saccharides. To prepared a solution of TPEDE (10 μM) with 50 μM of CD@Saccharides (CD@Ribose, CD@Glucose, CD@Mannose) in the carbonate buffer containing 0.4% DMSO, 1.0 mL of the stock solution of CD@Saccharides (200 μM) and 2.6 mL of deionized water were added to 0.4 mL of a stock solution of TPEDB (100 μM) in the carbonate buffer containing 4% DMSO. After shaking for a few seconds, the solution was allowed to stand for 30 min before its FL spectrum was measured. Similarly, the solution of TPEDE (10 μM) in 0.4% DMSO with different concentration of CD@Saccharides was adjusted by adding an appropriate amount of CD@Saccharides (200 μM) and deionized water.

Preparation of Solution of TPEDB and CD@Saccharides Containing an Analyte. 0.4 mL of the solution of TPEDB (100 μM) in the carbonate buffer containing 4% DMSO and 0.2 mL of a solution of CD@Saccharides (200 μM) were added into a vial and shaken for 30 min, followed by the addition of 3.2 mL of a solution of analyte (10 μM) (ribose, glucose, mannose, catechol, resorcinol) and 0.2 mL of deionized water. After shaking for a 30 min, a solution of TPEDB (10 μM) with CD@Saccharides (10 μM) and 8 μM of interferent in the carbonate buffer containing 0.4% DMSO was obtained. The solution was allowed to stand for 30 min before its FL spectrum measured. The solutions of TPEDB (10 μM) and CD@Saccharides (10 μM) containing interferences of different concentrations were prepared by adding appropriate amount of interference solutions (10 μM or 100 μM) and deionized water.

In order to measure the FL spectrum under high concentration, the concentration of each solution was increased by a factor of ten, and the mixed solutions were prepared according to the same procedure.

Preparation of Simulated Sewage and Mixture of TPEDB and CD@Riboser Containing Simulated Sewage with different concentration. 11 mg catechol, 29 mg sodium dodecyl sulfate (SDS), 60 mg emulsifier OP-10, 10 mg glycerol and 17 mg cellulose were dissolved into 10 mL water in turn to prepare simulated sewage with each component concentration of 10 mM, then dilute to 100 μ M and 10 μ M for standby.

0.4 mL of the solution of TPEDB (100 μ M) in the carbonate buffer containing 4% DMSO and 0.2 mL of a solution of CD@Ribose (200 μ M) were added into a vial and shaken for 30 min, followed by the addition of simulated sewage and deionized water with corresponding volume to test the fluorescence intensity of simulated sewage with different concentrations.

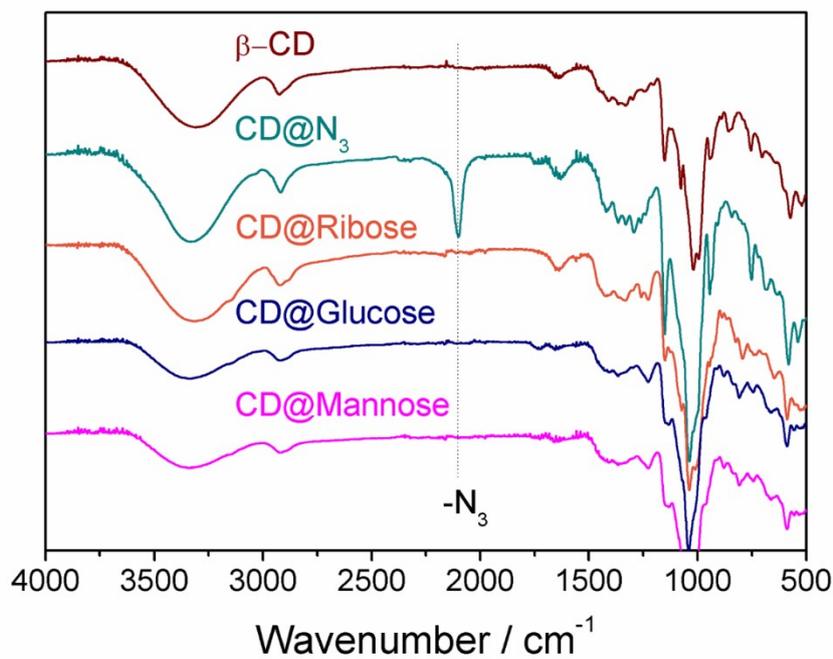


Figure S1. FTIR spectra of β -CD and its derivatives.

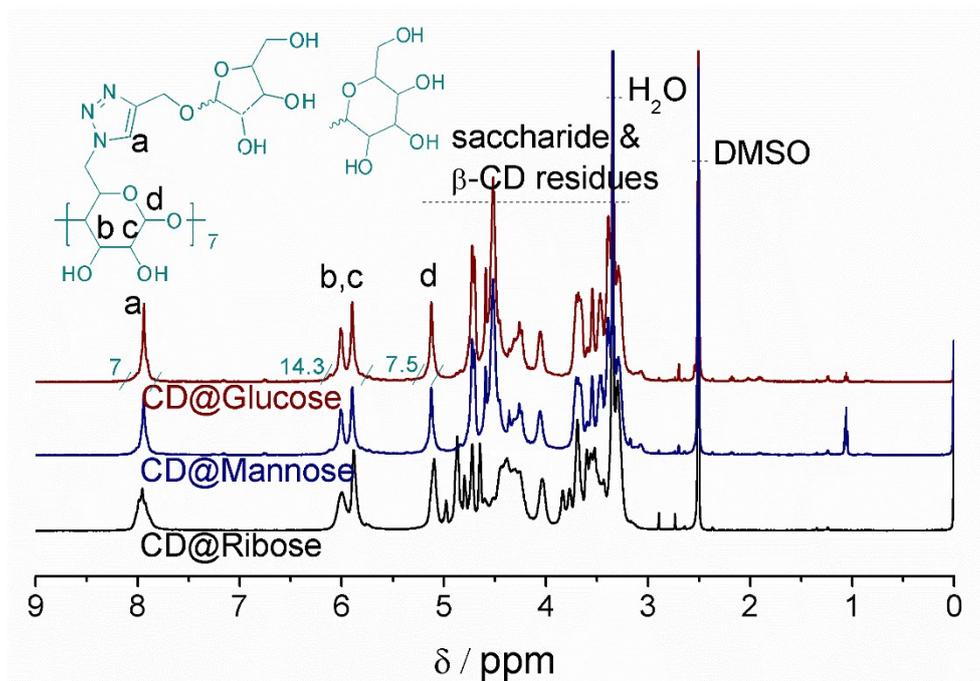


Figure S2. ^1H NMR spectra of CD@Ribose, CD@Glucose and CD@Mannose in $\text{DMSO-}d_6$.

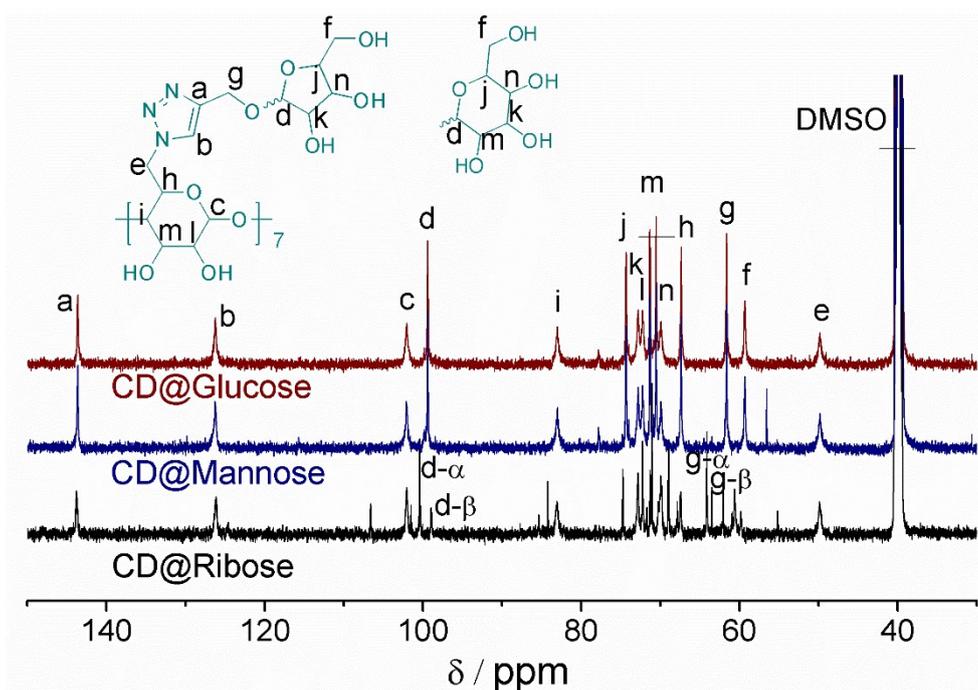


Figure S3. ^{13}C NMR spectra of CD@Ribose, CD@Glucose and CD@Mannose in $\text{DMSO-}d_6$.

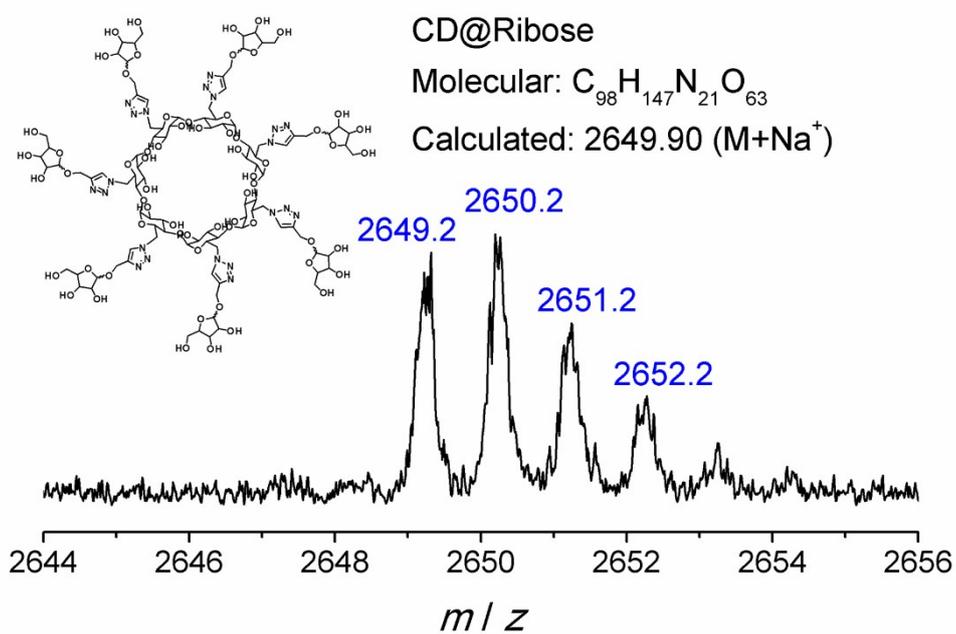


Figure S4. MALDI-ToF MS spectrum of CD@Ribose.

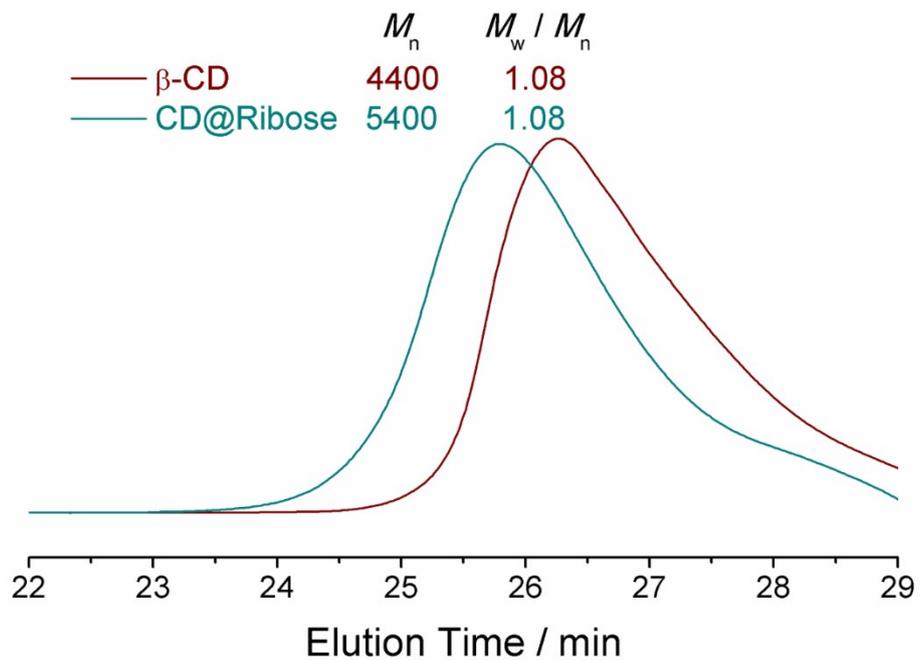


Figure S5. SEC elution traces of β -CD and CD@Ribose.

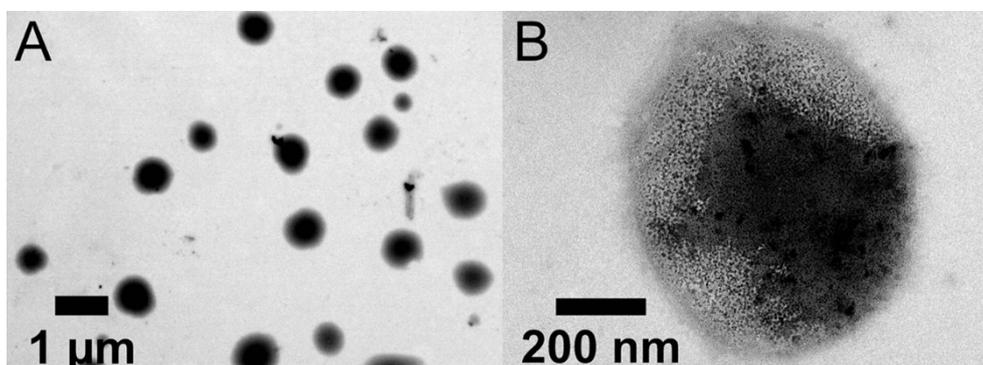


Figure S6. TEM images of dispersed TPEDB / CD@Ribose nanospheres.

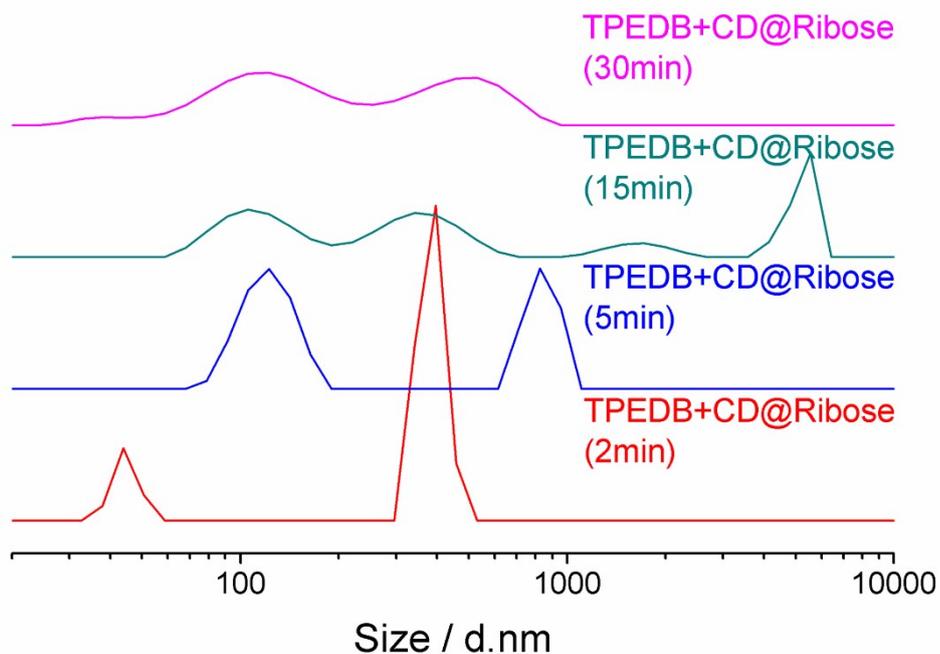


Figure S7. Particle size of the mixture of TPEDB in the carbonate buffer containing 4% DMSO (1 mM) and CD@Ribose aqueous solution (1 mM).

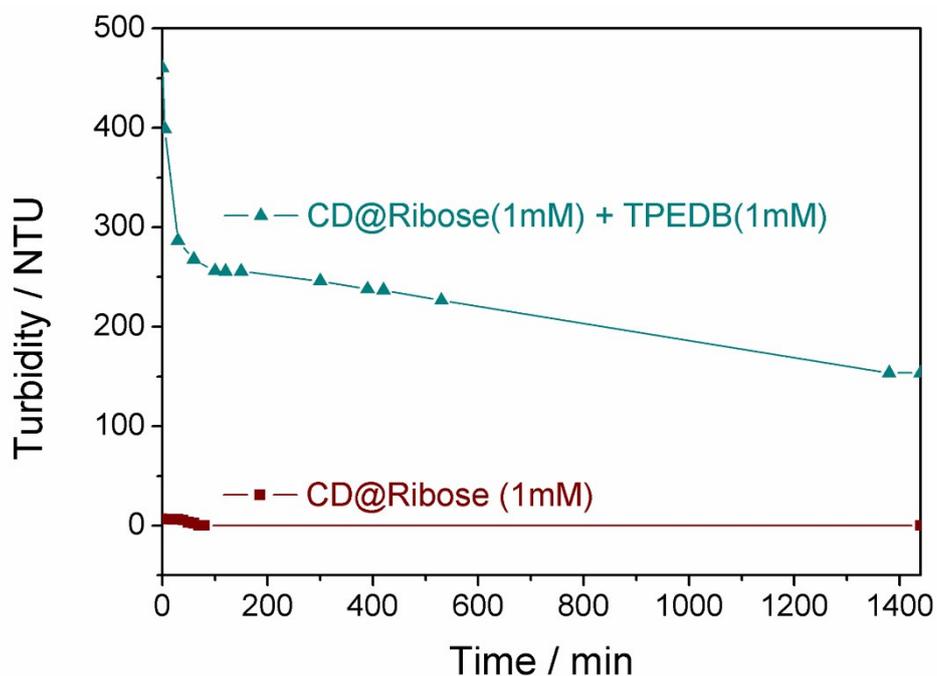


Figure S8. Turbidity curves of CD@Ribose aqueous solution (1 mM) and its mixture with TPEDB in the carbonate buffer containing 4% DMSO (1 mM).

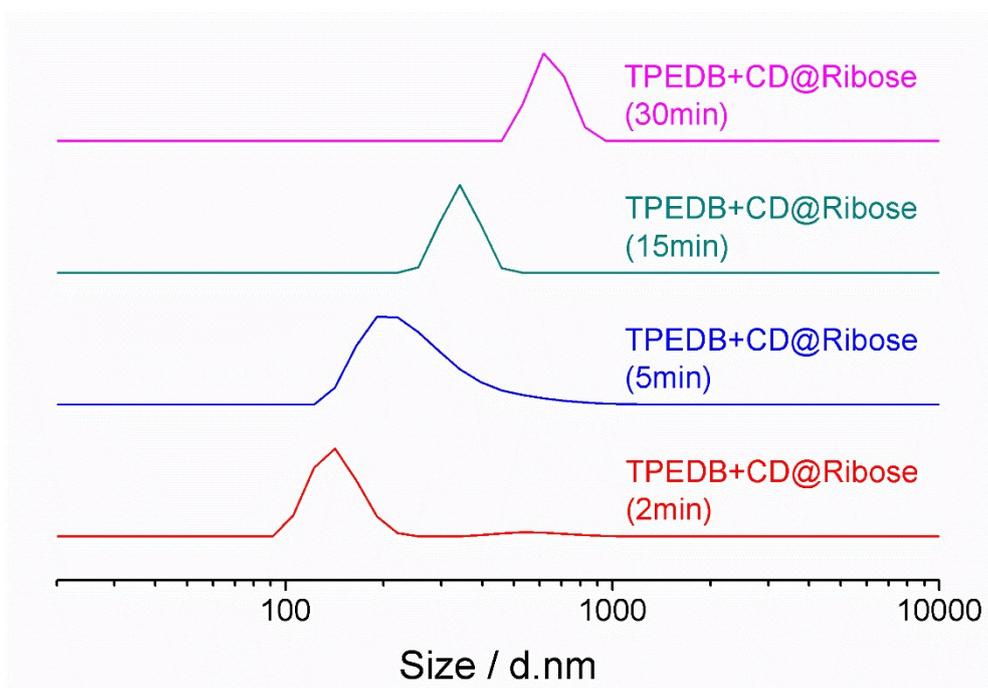


Figure S9. Particle size of the mixture of TPEDB in the carbonate buffer containing 4% DMSO (10 μ M) and CD@Ribose aqueous solution (10 μ M).

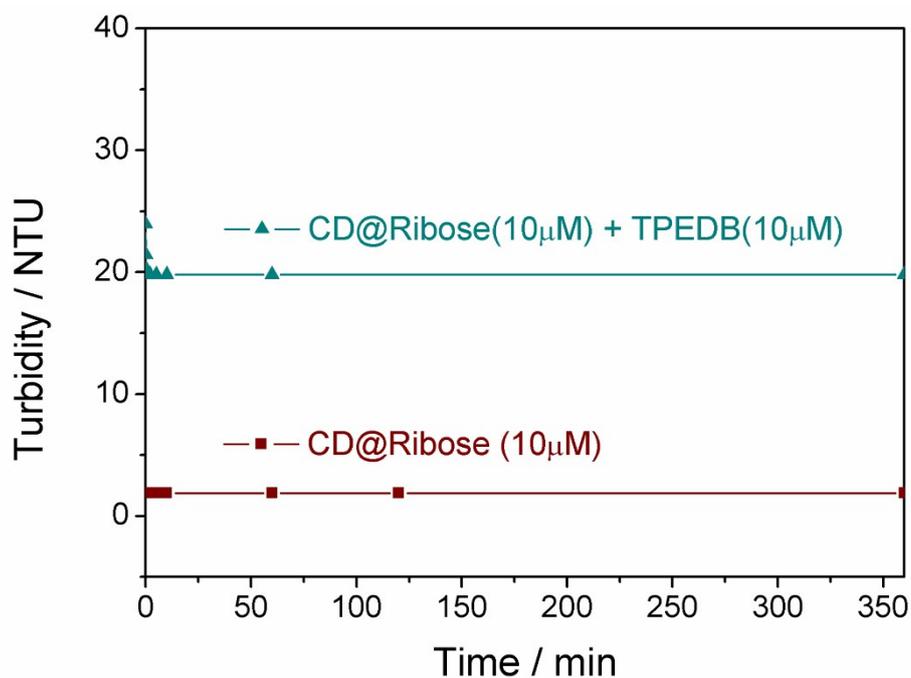


Figure S10. Turbidity curves of CD@Ribose aqueous solution (10 μ M) and its mixture with TPEDB in the carbonate buffer containing 4% DMSO (10 μ M).

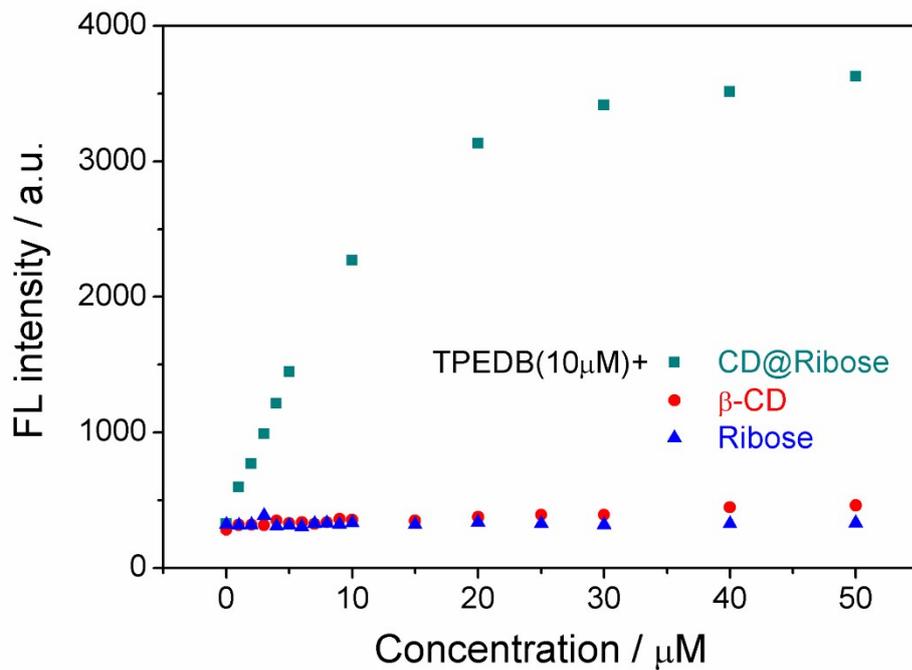


Figure S11. FL intensity of TPEDB (10 μM) at 470 nm with different concentrations of CD@Ribose, β-CD and ribose.

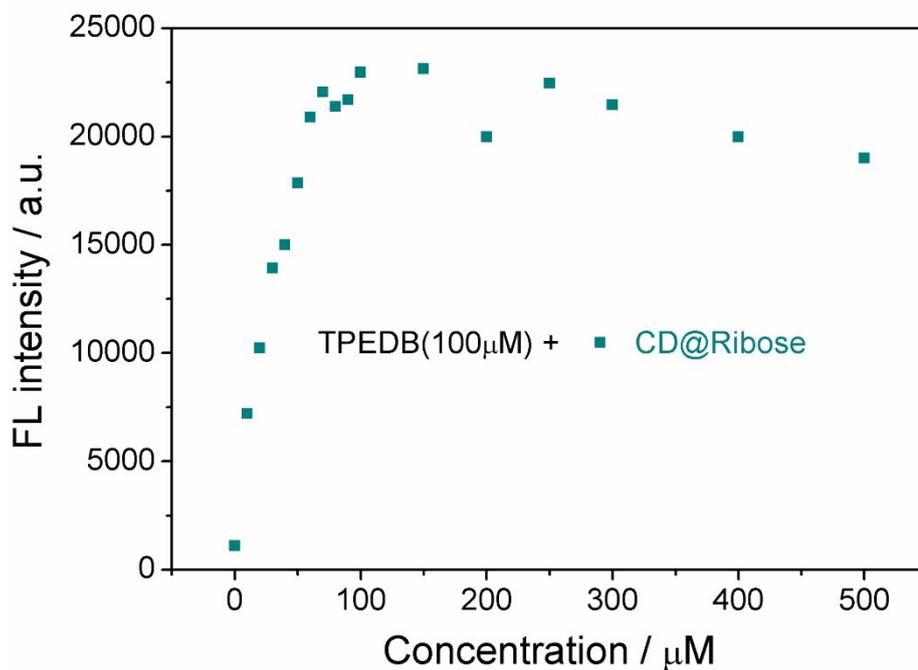


Figure S12. FL intensity of TPEDB (100 μM) at 470 nm with different concentration of CD@Ribose (0-500 μM).

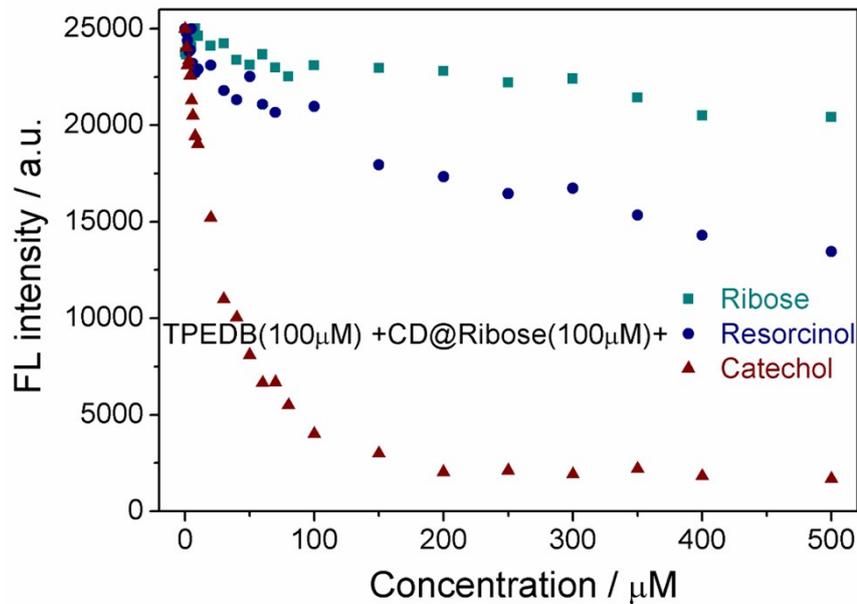


Figure S13. FL intensity of hypercrosslinked TPEDB (100 μM) / CD@Ribose (100 μM) aggregates at 470 nm in the presence of different concentration of analytes (monosaccharide, resorcinol and catechol).

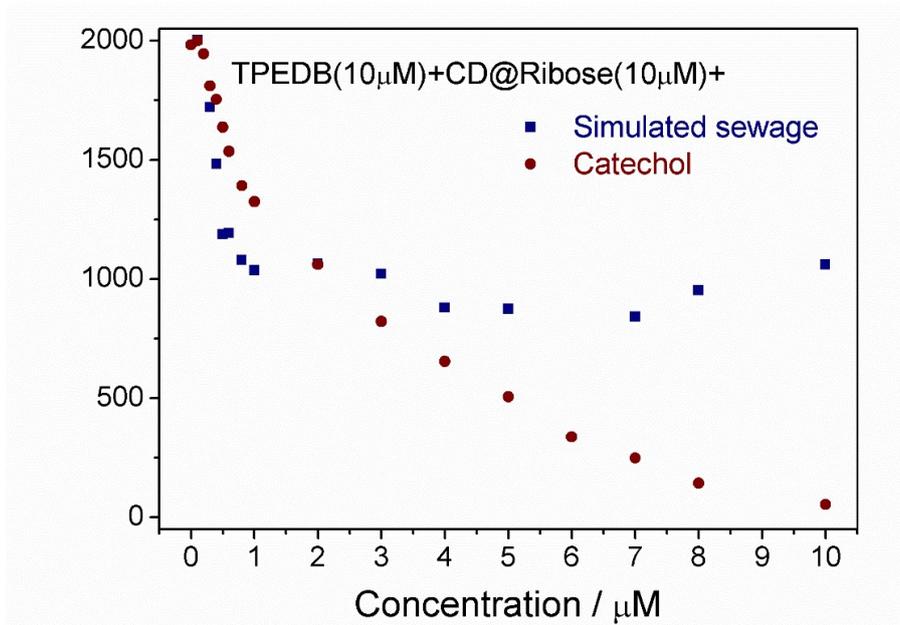


Figure S14. FL intensity of hypercrosslinked TPEDB (10 μM) / CD@Ribose (10 μM) aggregates at 470 nm in the presence of simulated sewage containing different concentrations of catechol.

REFERENCES

1. T. T. Kong, Z. Zhao, Y. Li, F. Wu, T. Jin and B. Z. Tang, *J. Mat. Chem. B*, 2018, **6**, 5986-5991.
2. S. Dalapati, E. Q. Jin, M. Addicoat, T. Heine and D. L. Jiang, *J. Am. Chem. Soc.*, 2016, **138**, 5797-5800.
3. Q. Zhang, S. Slavin, M. W. Jones, A. J. Haddleton and D. M. Haddleton, *Polymer Chemistry*, 2012, **3**, 1016-1023.
4. X. P. Liao, B. Y. Wang and Q. Zhang, *J. Mater. Chem. A*, 2018, **6**, 21193-21206.
5. K. Chmurski and J. Defaye, *Supramol. Chem.*, 2000, **12**, 221-224.
6. Q. Zhang, L. Su, J. Collins, G. S. Chen, R. Wallis, D. A. Mitchell, D. M. Haddleton and C. R. Becer, *J. Am. Chem. Soc.*, 2014, **136**, 4325-4332.
7. Y. Liu, C. M. Deng, L. Tang, A. J. Qin, R. R. Hu, J. Z. Sun and B. Z. Tang, *J. Am. Chem. Soc.*, 2011, **133**, 660-663.