Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Polymer Multilayer Films Regulate Macroscopic Fluid Flow and Power Microfluidic Device via Supramolecular Interaction

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1. Synthesis of Mono-6-(p-Tolylsulfonyl)-β-Cyclodextrin (Ts-*O*-β-CD)

6-*O*-Ts-β-CD was prepared according to reported method[1] with little modification as shown in figure S1. 25g of β-CD was suspended in 209 mL of water and 2.73 g of NaOH in 8.75 mL of water was added dropwise to the previous solution. The suspension turned to be homogeneous. The solution was immersed into an ice-water bath, and then 6.3 g of TsCl in 12.5 mL of acetonitrile was dripped slowly. White precipitation was occurred immediately and the solution was further stirred for 2 h at 25 °C. Later the suspension was cooled overnight at 4 °C. Through suction filtration, the resulting precipitate was retrieved and recrystallized 3 times from hot water. The product was vacuum-dried at 50 °C. Yield: 20%. ^{1}H NMR (DMSO-d_6) δ: 2.44 (s, 3H, CH_3), 3.41-3.74 (m, H-3,5,6) overlap with HOD, 4.21-4.53 (m, 6H, C6-OH), 4.80 (s, 7H, H-1 of CD), 7.43-7.77 (dd, 4H, aromatic tosyl) (see Figure S2).

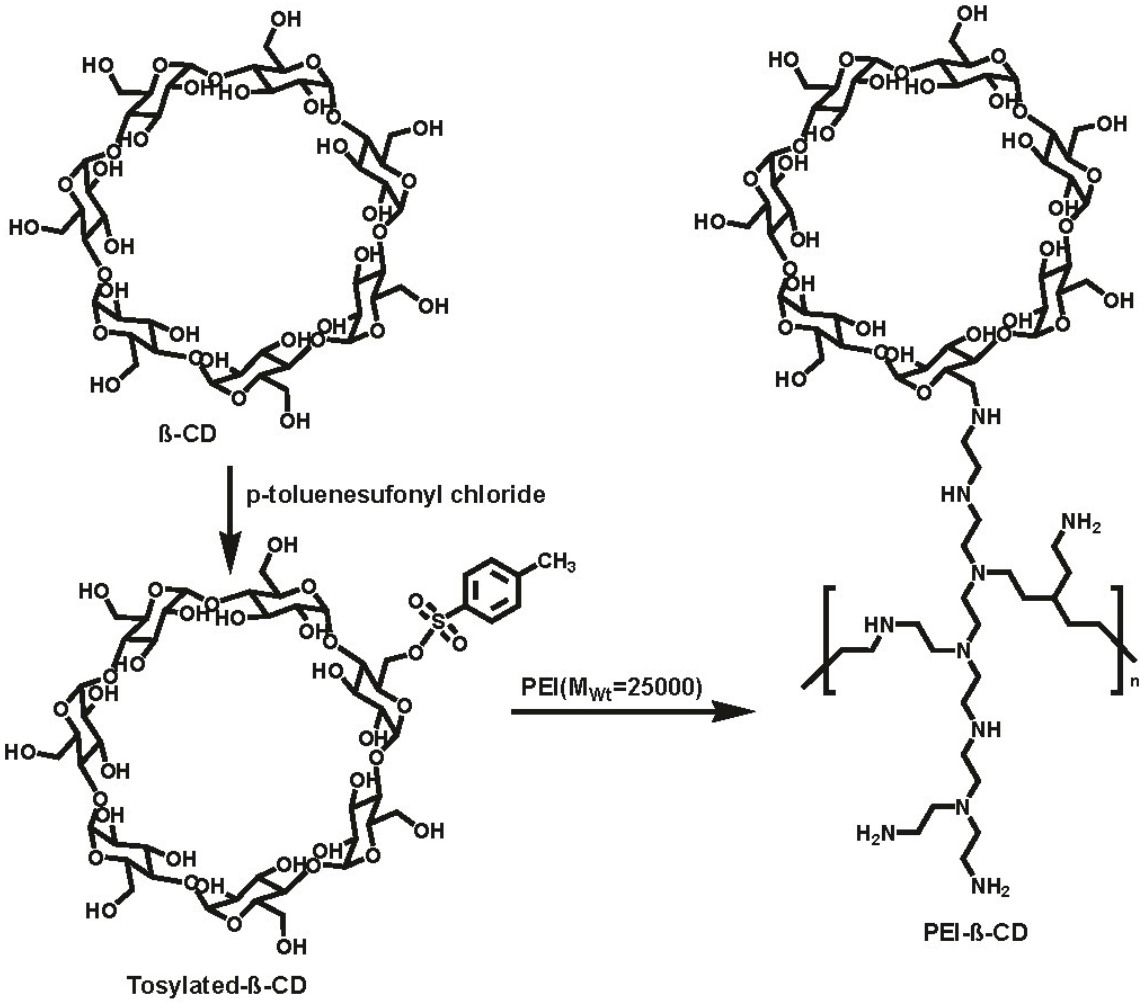


Figure S1. Synthesis of cyclodextrin functionalized polyethyleneimine (PEI-β-CD).

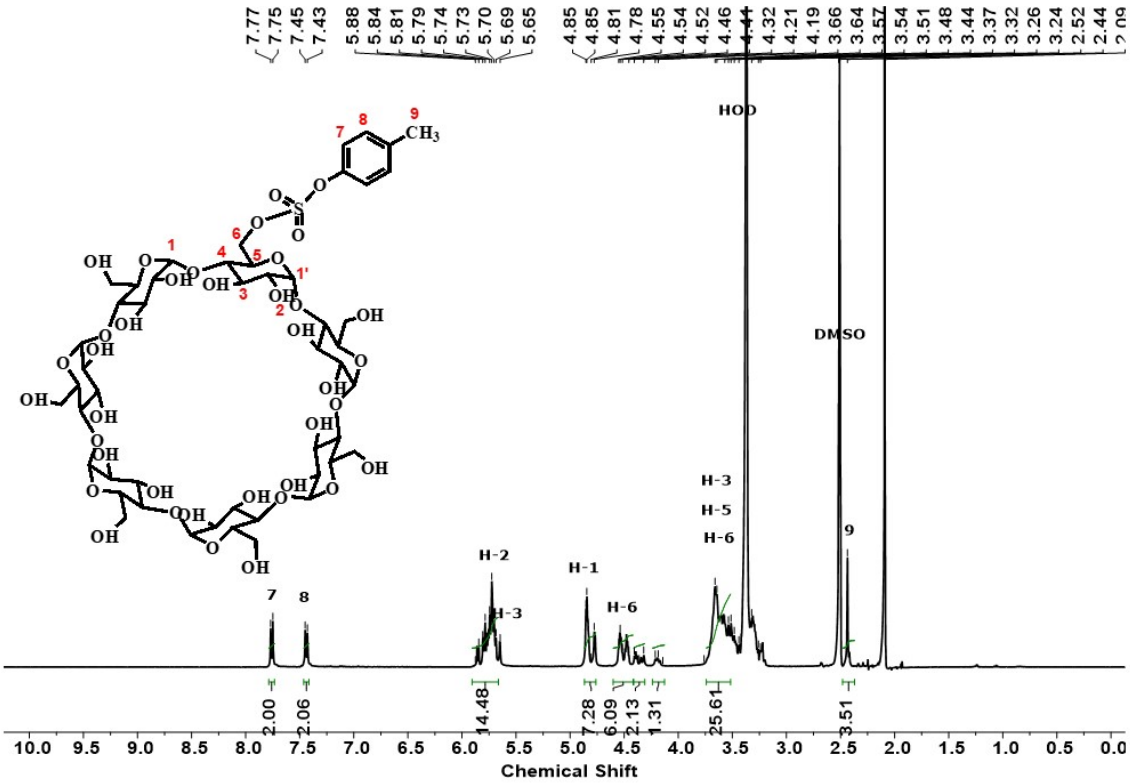


Figure S2. 400 MHz 1H NMR spectra of Tosyl-β-CD in DMSO-d_6.

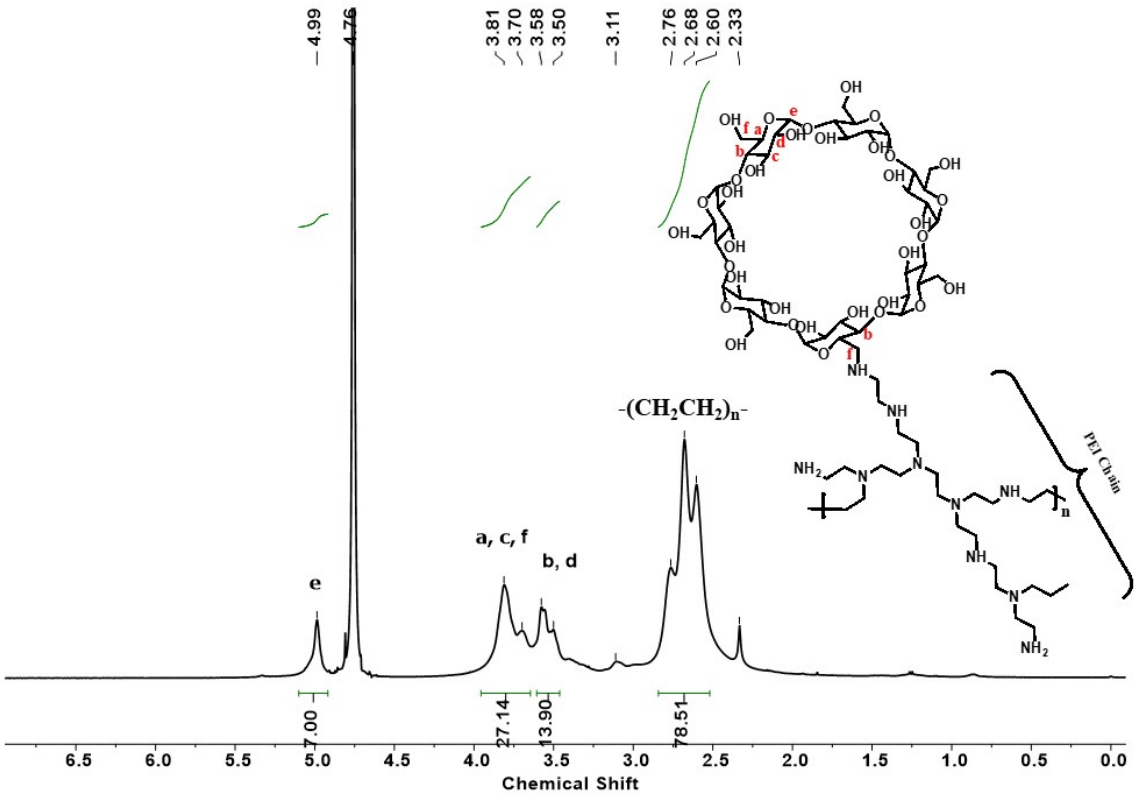
2. Synthesis of PEI-β-CD

PEI-β-CD was prepared according to the reported procedure.[2] The procedure is shown in Figure S1. Briefly, 0.5 g of PEI in 20 ml dimethyl sulfoxide (DMSO) was reacted with 3.8 g of 6-*O*-Ts-β-CD prepared as described above. The solution was stirred in a nitrogen environment at 70°C for 3 days. After that, the product was dialyzed in water for 3 days with a MWCO 12kDa membrane. After dialysis, PEI-β-CD was obtained by freeze-drying. Yield: 35% The β-CD grafting level per PEI chain was analyzed by ^{1}H NMR (D_2O) is approximately 7.91%. δ: 4.99 (s,7H, H(e) of CD), 3.81 (m, 28H, H(a), H(c), H(f) of CD), 3.58 (m, 14H, H(b) and H(d) of CD), 2.33-2.76 (m, 78, methylene of –CH_2CH_2-) (see Figure S3). From the integrated area of (S1) of H1 of β-CD and the integrated peak area (S2) of PEI from 2.76 to 2.33, the degree of β-CD substitution (DS) to PEI was calculated according to the following formula[3]:

DS = (S1/7)/ [(S2-4S1)/4].

The distinctive adsorption peaks of β-CD are at 1030 cm^{-1} (C–O stretching vibration involving ether linkage in glucose unit), 944 cm^{-1} (skeletal vibration involving α-1,4 linkage), 756 cm^{-1} (ring breathing vibration), and 577 cm1 (pyranose ring vibration) in the FTIR

spectrum. The four adsorption bands mentioned above appeared at the corresponding positions in the β-CD PEI spectra but were absent in the PEI spectrum, confirming that β-CD

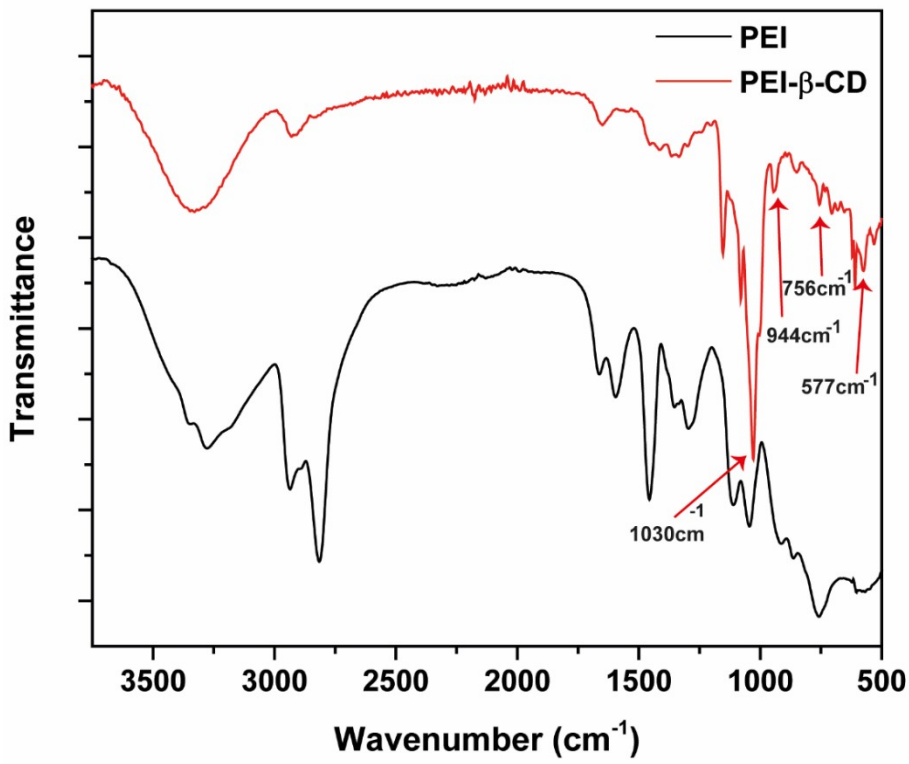


had been covalently grafted onto PEI as shown in figure S4.

Figure S3. 400 MHz 1H NMR spectra of PEI-β-CD in D_2O.

Figure S4. FTIR spectra of β-CD, PEI, and β -CD-PEI.

3. Synthesis of Ferrocenecarboxylic Acid



Ferrocenecarboxylic acid was synthesized according to the following two-step reaction (see Figure S5).[4]

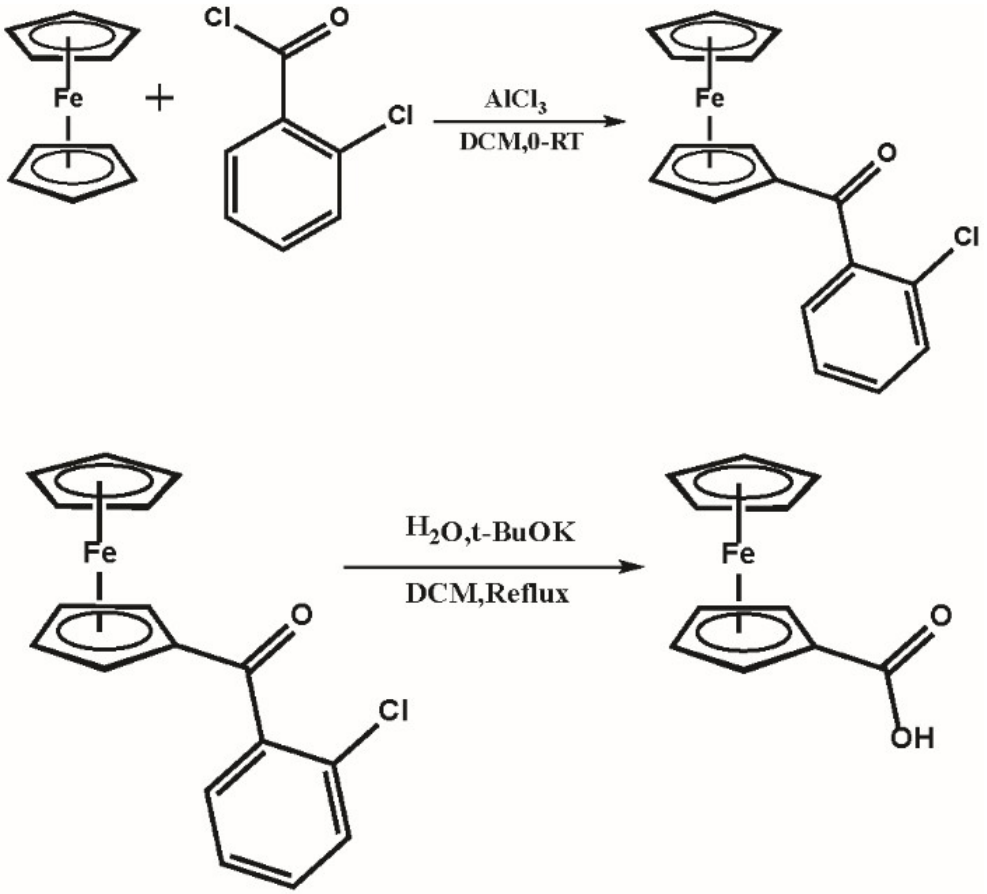


Figure S5. Synthesis of ferrocenecarboxylic acid.

3.1 Synthesis of 2-chlorobenzoyl ferrocene

A 250 mL dried three-necked round-bottomed flask equipped with a funnel for the addition of air-sensitive solids and a two-necked adapter holding a thermometer and a gas inlet tube was used for the following reaction. The flask was maintained at an inert atmosphere. Into the flask 3g(16.1mmol) of ferrocene,2.82g (16.1mmol) of 2-chlorobenzoyl chloride, 35ml of dichloromethane and 2.23 g (16.8 mmol) of anhydrous aluminum chloride was added through the funnel. Then the flask was immersed in an ice bath and aluminium chloride was added slowly in order to maintain the flask temperature below 5° C. The appearance of instant deep blue color indicated that the reaction was occurring and the mixture was kept for another 30 minutes in ice cold water. Later it was kept for 2 hours at room temperature. After the reaction, 50 mL of water was added carefully to the solution mixture for work up with dichloromethane yielding 4.9 g (94%) of (2-chlorobenzoyl)ferrocene as a viscous, red liquid, which gradually solidifies. Yield: 94% ^{1}H NMR ($CDCl_3$) δ: 4.27(s,5H, Cp),4.59(t,2H Cp),4.74(t,2H, Cp),7.34(dt,1H, phenyl),7.40(dt,1H, phenyl),7.44(dd,1H, phenyl),7.50(dd,1H, phenyl) (see Figure S6).

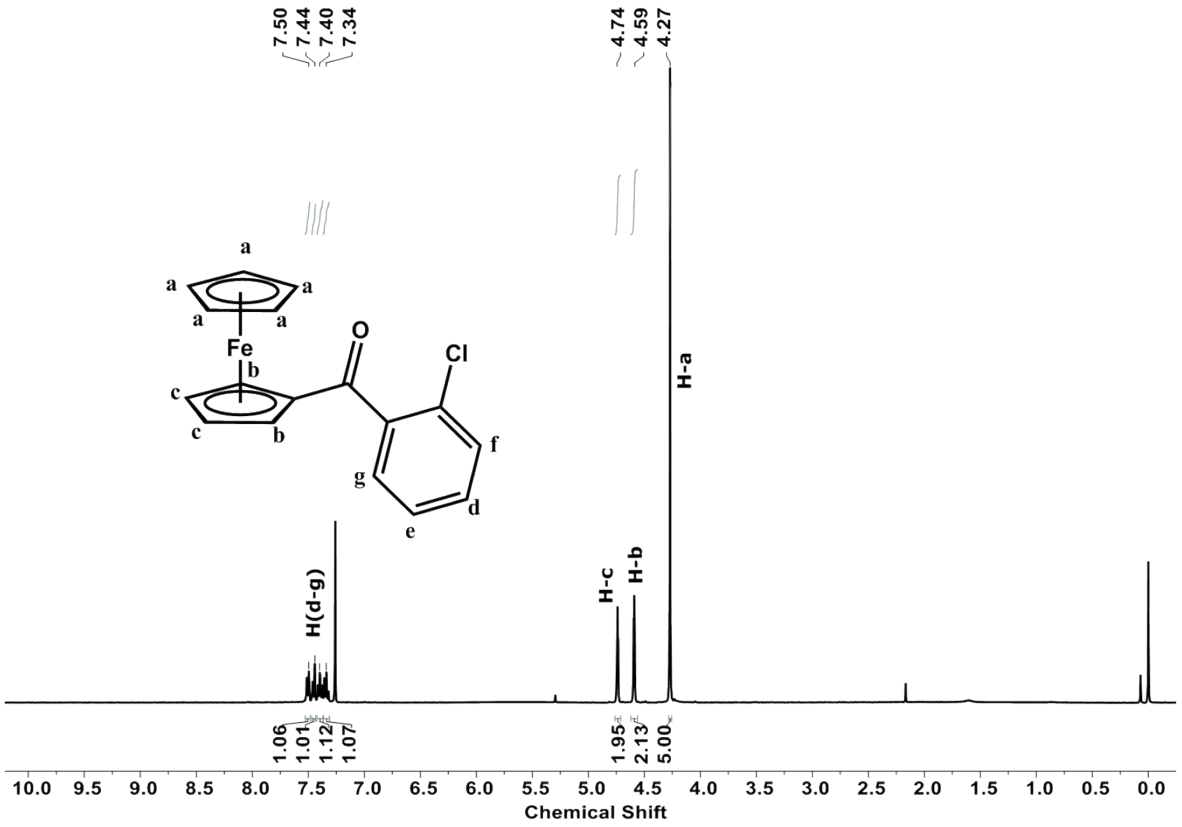


Figure S6. ^{1}H NMR spectra of 2-chlorobenzoyl in $CDCl_3$.

3.2 Synthesis of Ferrocenecarboxylic acid

A 250mL dried three-necked round-bottomed flask equipped with and a reflux condenser and an inert atmosphere were maintained through one end of the flask. Into this 25 mL of dry 1,2-dimethoxyethane,3.45 g (30.8mmol) of potassium tert-butoxide, 167 μL (9.2 mmol) of water was added with stirring producing a slurry to which the crude2.5g(7.7mmole) (2-chlorobenzoyl)ferrocene was added. The red solution was stirred and refluxed under nitrogen for 2 hours. As the reaction proceeds the color fades to tan and after 1 hour at reflux, the reaction mixture was cooled and poured into 100mL of water. The resulting solution was washed with three 15mL portions of diethyl ether which are combined and back-extracted with two 5mL portions of 10% aqueous sodium hydroxide. The aqueous phases were then combined and acidified with concentrated hydrochloric acid. The precipitate was collected by filtration and air-dried yielding 1.5 g (80% from ferrocene) of ferrocenecarboxylic acid as an air-stable yellow powder. Yield: 85% ^{1}H NMR (DMSO-d_6) δ:4.19 (s,5H, Cp),4.38(t,2H, Cp),4.72(t,2H, Cp),7.97(s,1H, COOH) (see Figure S7).

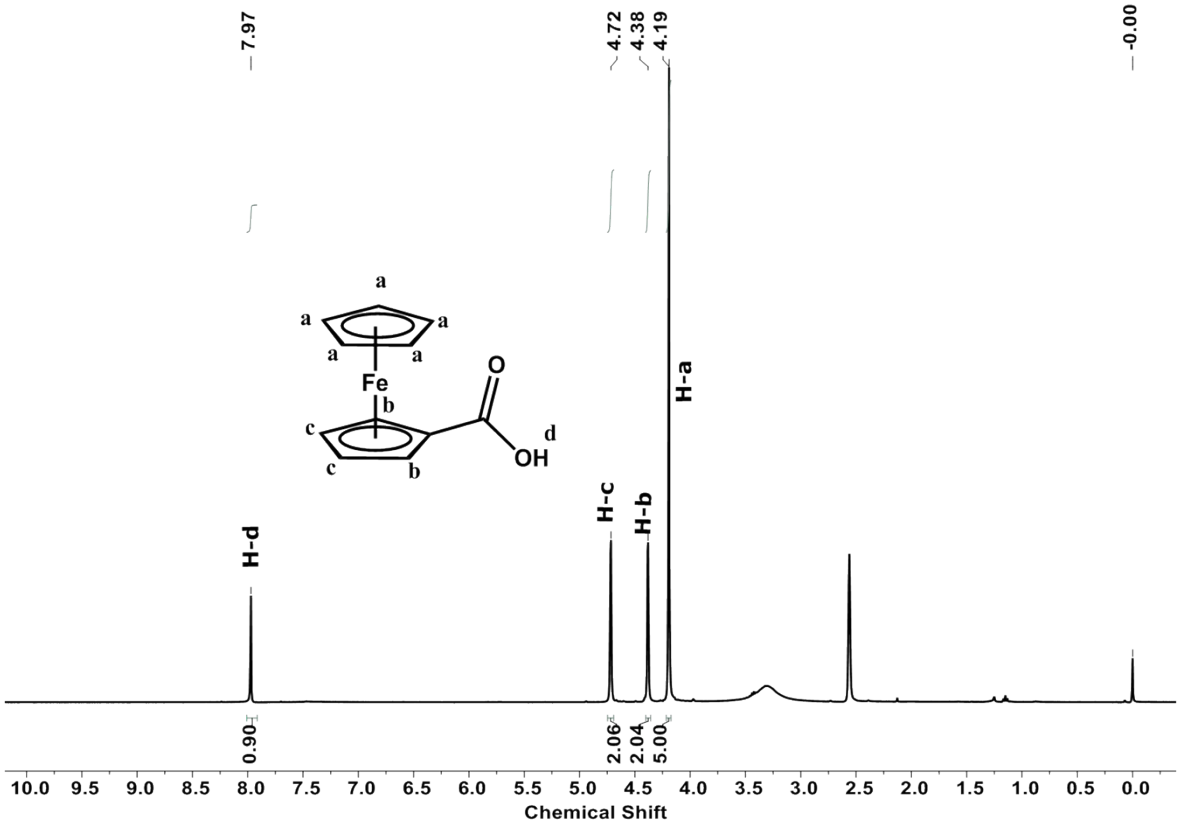


Figure S7: 400MHz ^{1}H NMR spectra of ferrocenecarboxylic acid in DMSO-d_6.

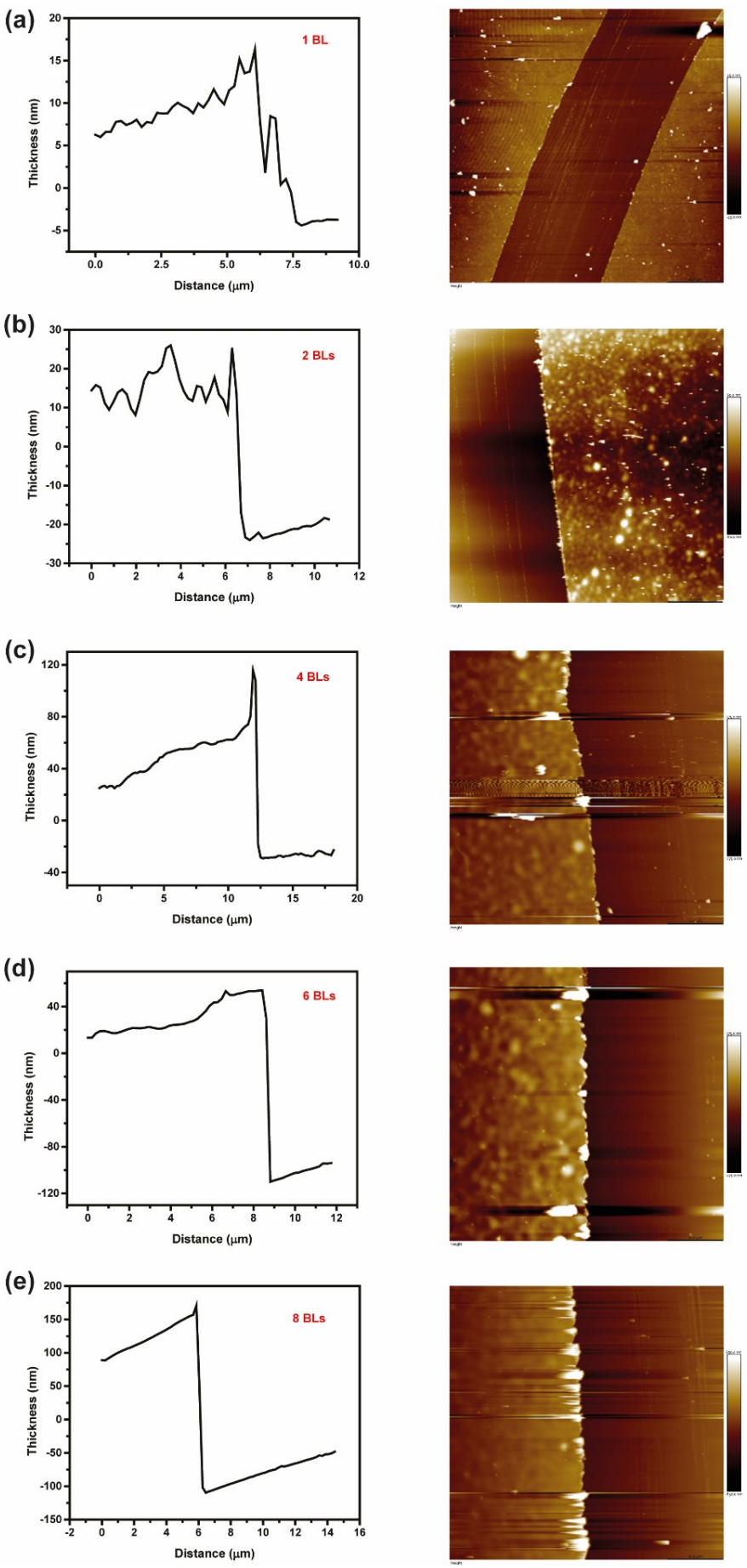


Figure S8. Thickness measurement using AFM (a) 1 BL (b) 2 BLs (c) 4 BLs (d) 6 BLs, and (e) 8 BLs.

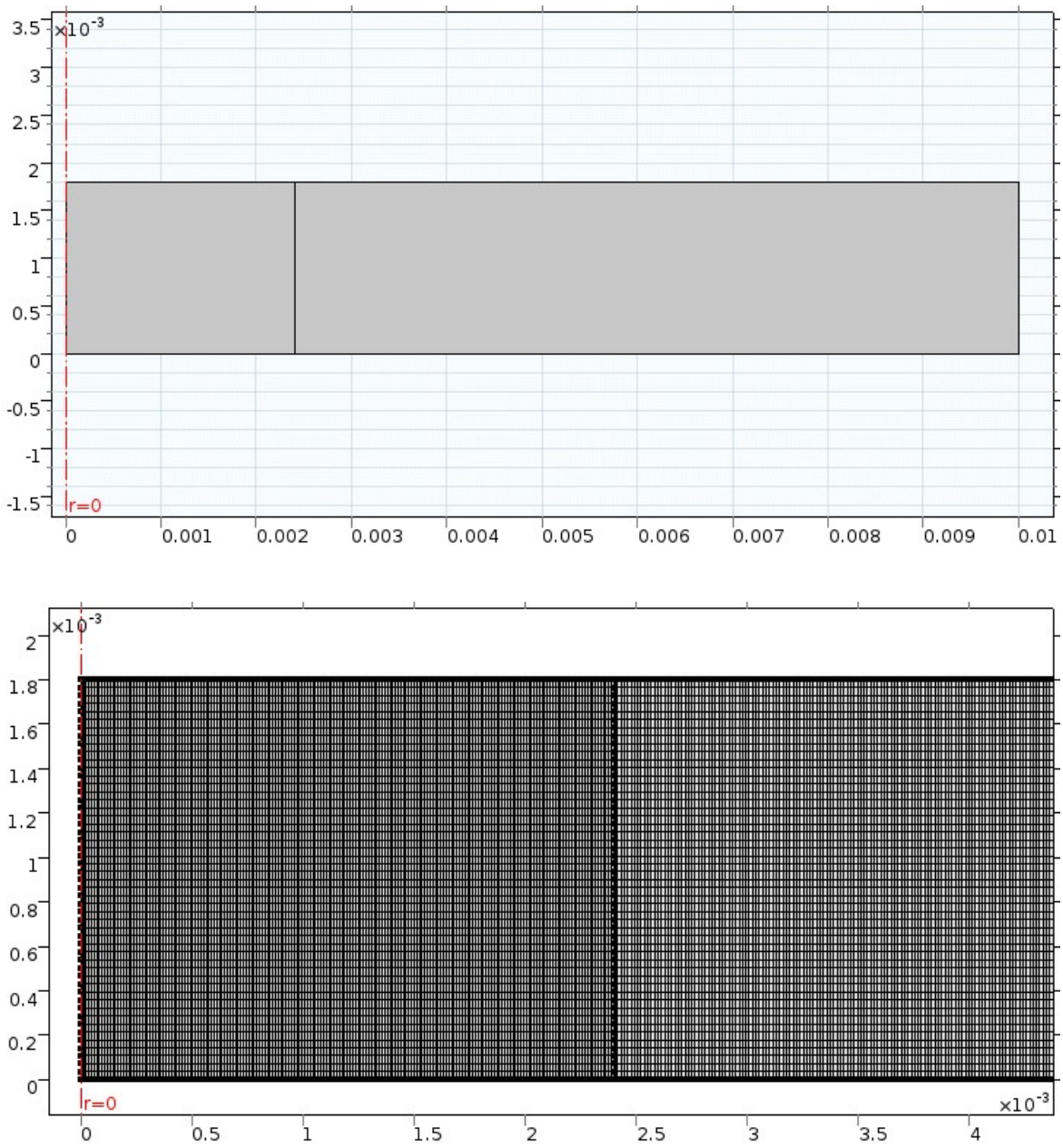


Figure S9: (a) Domain, and (b) Mesh used in the numerical study.

The geometry is shown in figure S9 (a). The model is axisymmetric with height of 1.8mm, width of 10 mm. The patch exists between center and *r* = 2.4mm. A mesh sensitivity test was done and a uniform mesh consisting of 50x1000 grids was found sufficient for the computations. Linear elements were used in the finite element method employed to solve the system of equations numerically.

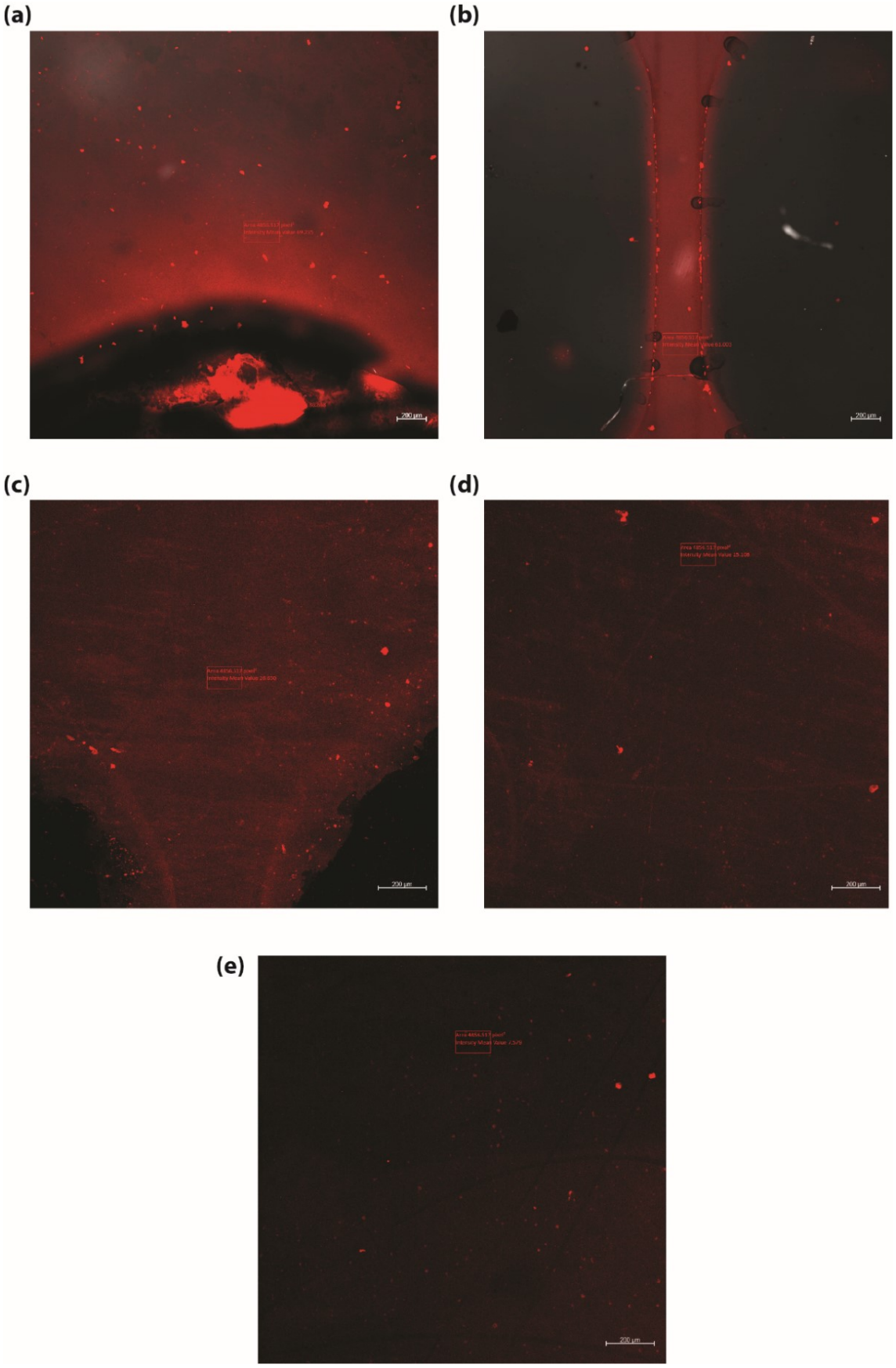


Figure S10: Confocal microscope images of dye release after addition of AdA (1mM) showing dye intensity at different points away from the coating (a) 0.3mm, (b) 4.5mm, (c) 11mm, (d) 14mm, and (e) 17mm.

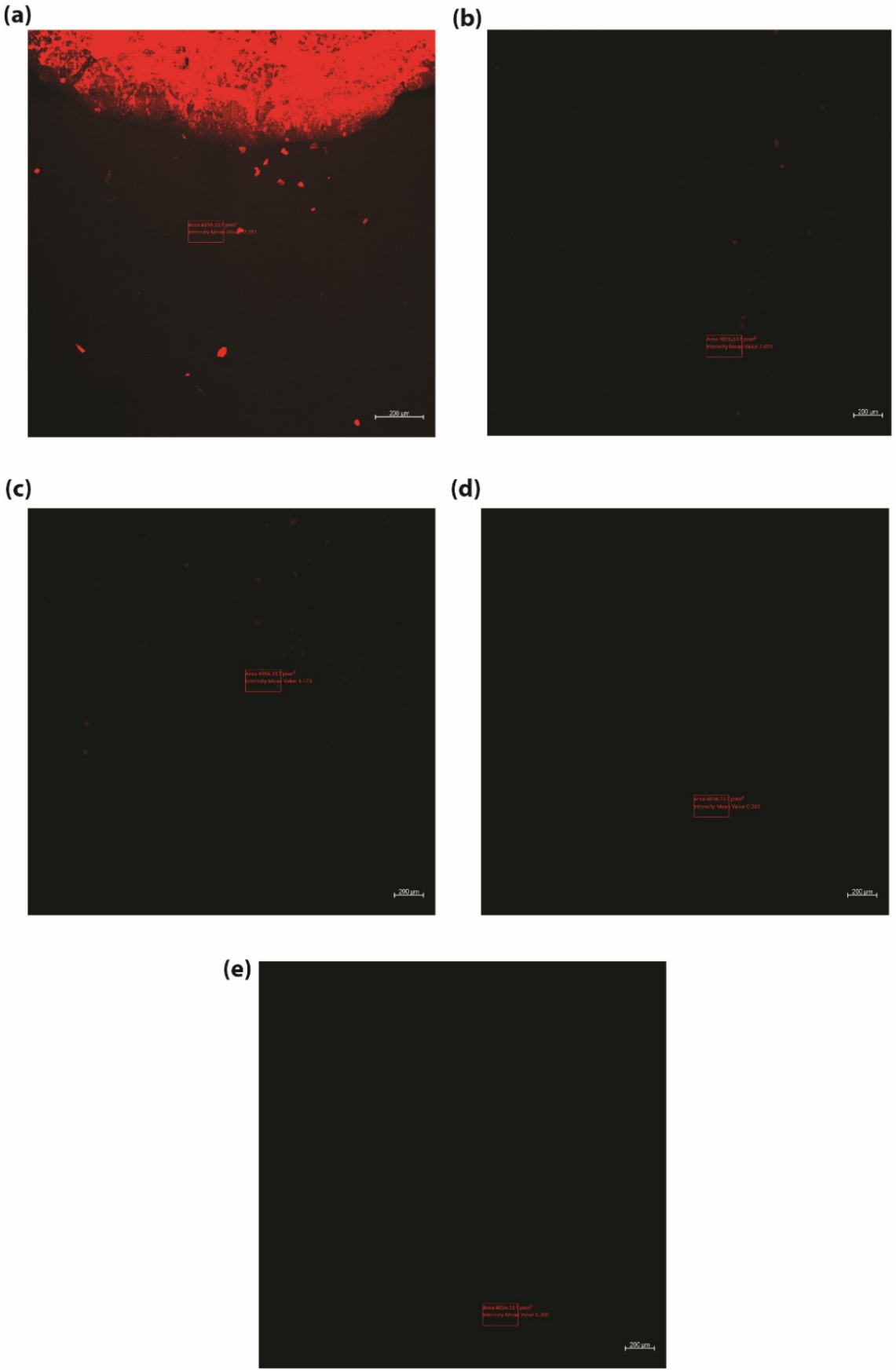


Figure S11: Confocal microscope images of dye release after adding aqueous solution without any competitive guest showing dye intensity at different points (a) 0.3mm, (b) 4.5mm, (c) 11mm, (d) 14mm, and (e) 17mm.

References

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3. X.-J. Han, Z.-Q. Dong, M.-M. Fan, Y. Liu, J.-H. Li, Y.-F. Wang, Q.-J. Yuan, B.-J. Li, S. Zhang, *Macromol. Rapid. Commun.*, 2012, **33**, 1055-1060.

4. Carboxylation of Aromatic Compounds: Ferrocenecarboxylic Acid *Org. Synth.*, 1977, **56**, 28.