Supporting Information

Table of Contents

General Experimental

All reagents and solvents were purchased from commercial suppliers and used without further purification. Container **2** was synthesized according to literature procedures[1]. ^{1}H NMR spectra were recorded on a Bruker AVANCE III HD (400 MHz). FT-IR spectra were recorded on a ThermoFisher Nicolet iS10 spectrometer. UV-Vis spectroscopy was recorded on a Cary 100 spectrometer (Agilent). The fluorescence spectroscopy was conducted on a RF-6000 fluorescence spectrometer (Shimadzu). Dynamic light scattering (DLS) and ζ-potential were recorded on a Zetasizer Nano ZS instrument (Malvern). Transmission electron microscopy (TEM) was carried out on a Tecnai G2 F20 S-Twin (FEI) instrument. Elemental Analysis was performed on a Vario EL Elemental Analyzer (Analysemsysteme GmbH).

Synthetic Procedures

Polymer **1**: container **2** (150 mg, 0.125 mmol) and dimethyl sulfoxide (10 mL) was heated at reflux for 5 h. After removing excess dimethyl sulfoxide by rotary evaporation, the residue was dried under high vacuum. A solution of dextran (M_w = 40K, 80 mg) and diisopropylethylamine (0.5 mL, 3 mmol) in DMSO (15 mL) was added and stirred at 50 °C for 8 h. The product was poured into water (80 mL) and dialyzed (MWCO 3500) against water. The residual solution was lyophilized to yield polymer **1** as a white solid (136 mg, 78%).

^{1}H NMR (400 MHz, 20 mM NaD_2PO_4): 6.83 (s, 4H), 5.65 (d, *J* = 14.6 Hz, 2H), 5.55 (d, *J* = 15.6 Hz, 4H), 5.48 (d, *J* = 8.4 Hz, 2H), 5.46 (d, *J* = 8.4 Hz, 2H), 5.35 (d, *J* = 16.0 Hz, 4H), 4.97 (d, *J* = 2.4 Hz, 9.8H), 4.50 (d, *J* = 15.6 Hz, 4H), 4.38 (d, *J* = 15.6 Hz, 4H), 4.26 (d, *J* = 15.6 Hz, 4H), 4.29 (d, *J* = 15.6 Hz, 4H), 4.16 (d, *J* = 14.6 Hz, 2H), 3.99-3.89 (m, 19.6H), 3.75-3.68 (m, 19.6H), 3.58-3.48 (m, 19.6H), 1.80 (s, 6H), 1.76 (s, 6H).

FT-IR (cm^{-1}): 3680m, 3400s, 1725s, 1617s, 1479s, 1450s, 1420s, 1016s, 806m.

Elemental Analysis $(C_6H_{10}O_5)_{9.8}(C_{50}H_{50}N_{16}O_{19})_1(H_2O)_{39}$: C 37.65%; H 6.56%; N 6.46%. Calculated: C 37.62%; H 6.52%; N 6.45%.

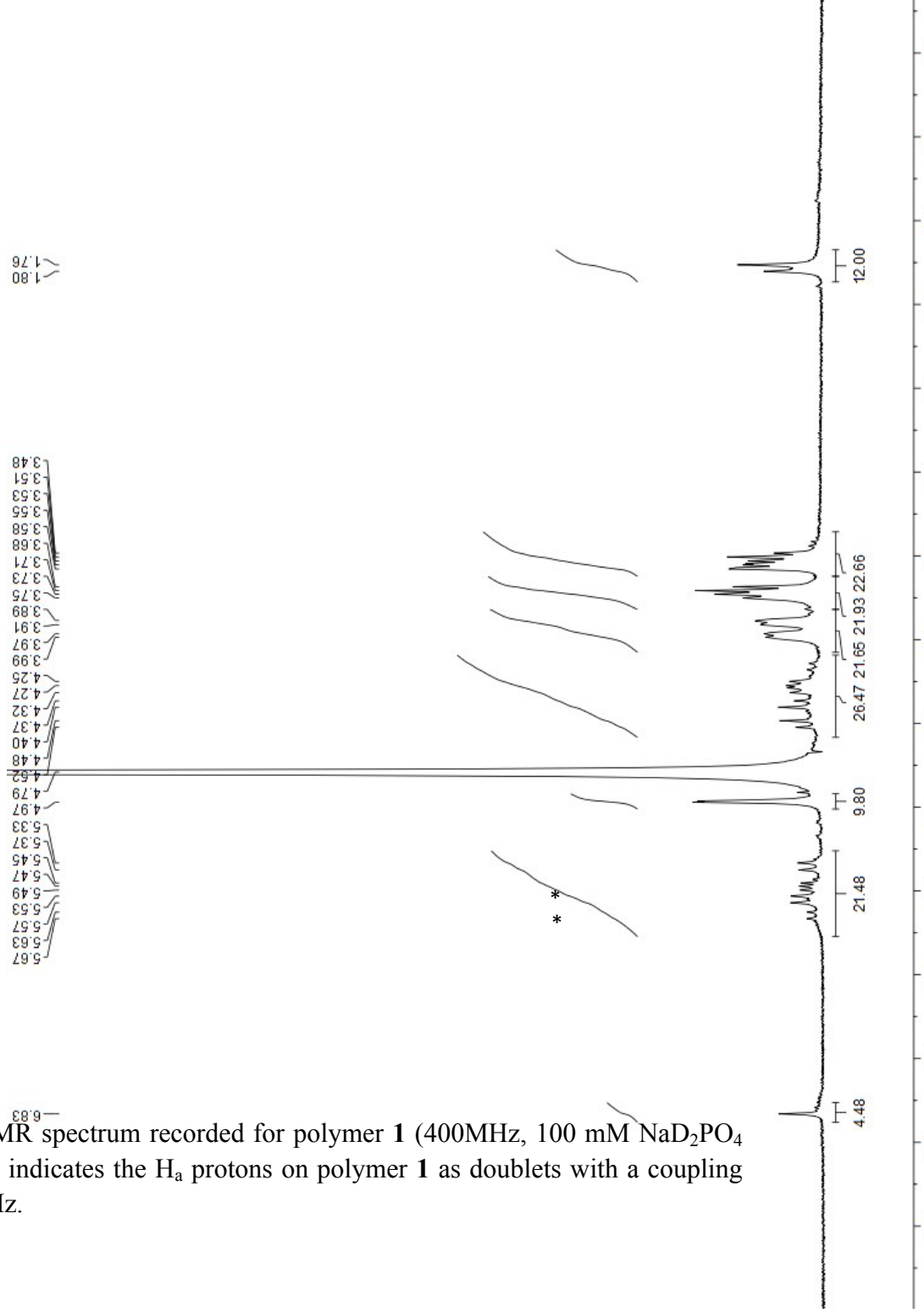


Figure S1. ^{1}H NMR spectrum recorded for polymer **1** (400MHz, 100 mM NaD_2PO_4 buffer, pD 7.4). * indicates the H_a protons on polymer **1** as doublets with a coupling constant of 15.6 Hz.

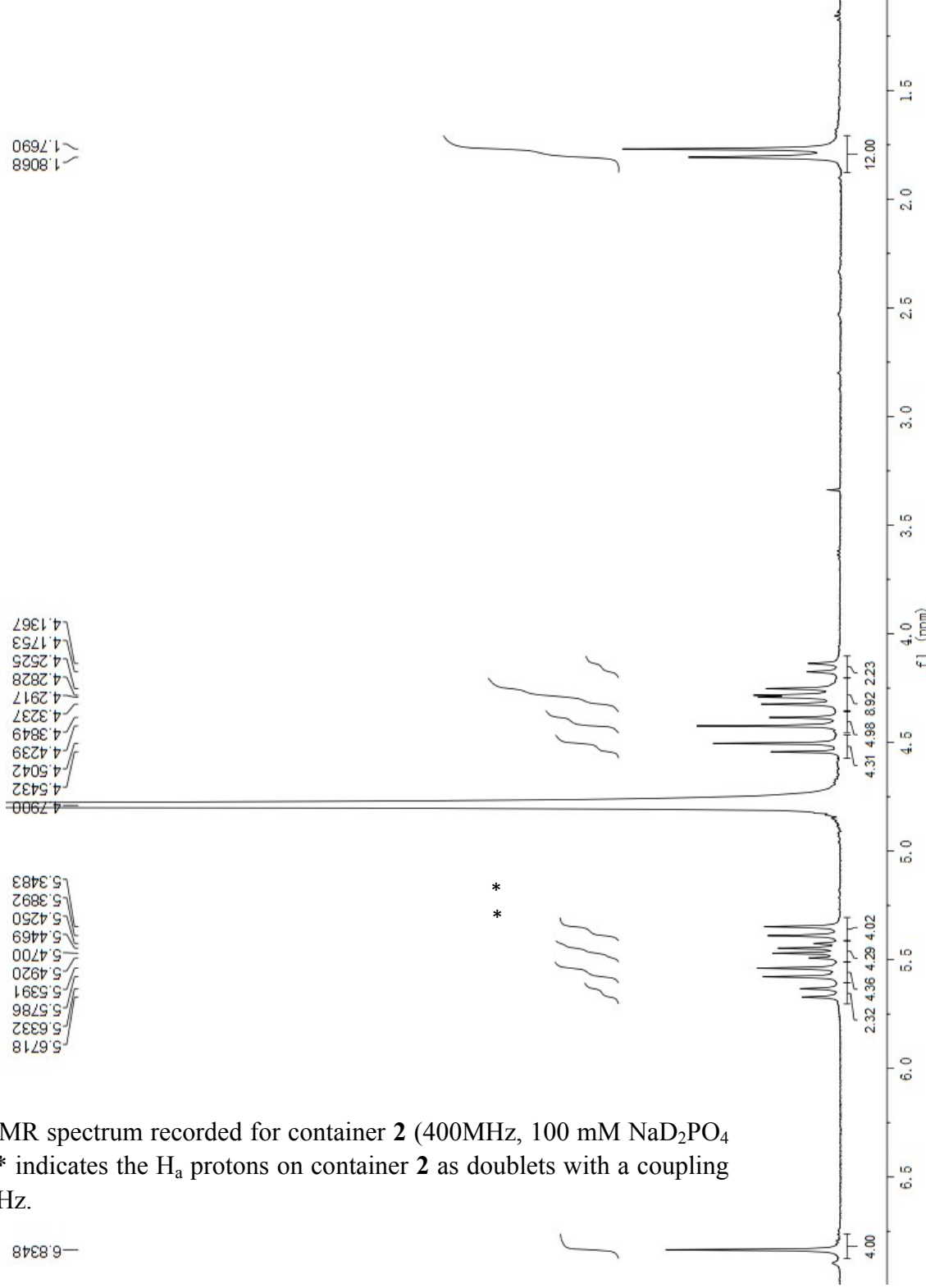
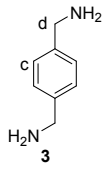


Figure S2. ^{1}H NMR spectrum recorded for container **2** (400MHz, 100 mM NaD_2PO_4 buffer, pD 7.4). * indicates the H_a protons on container **2** as doublets with a coupling constant of 15.6 Hz.

Spectra for host-guest study



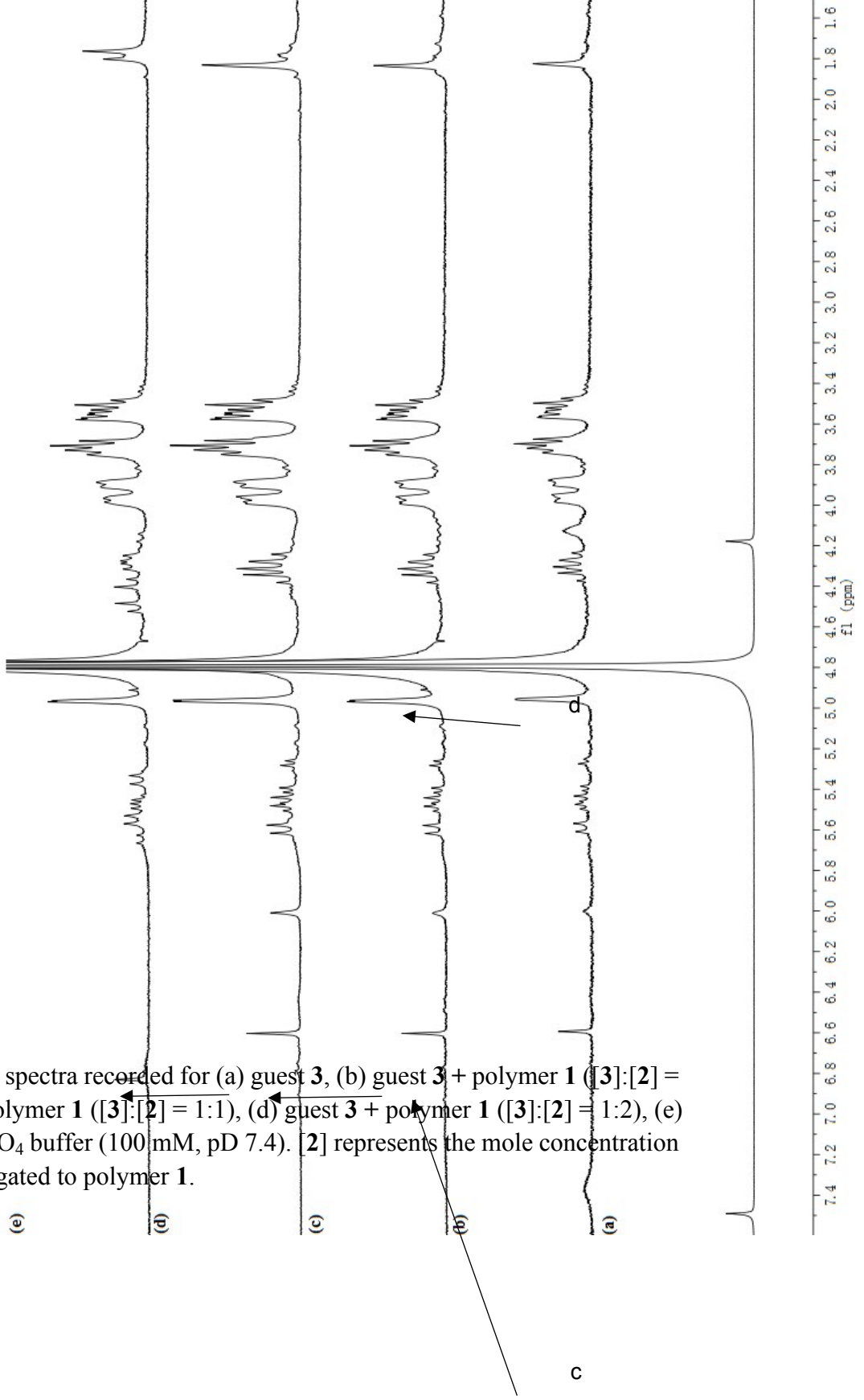


Figure S3. ^{1}H NMR spectra recorded for (a) guest **3**, (b) guest **3** + polymer **1** ([**3**]:[**2**] = 2:1), (c) guest **3** + polymer **1** ([**3**]:[**2**] = 1:1), (d) guest **3** + polymer **1** ([**3**]:[**2**] = 1:2), (e) polymer **1** in NaD_2PO_4 buffer (100 mM, pD 7.4). [**2**] represents the mole concentration of container **2** conjugated to polymer **1**.

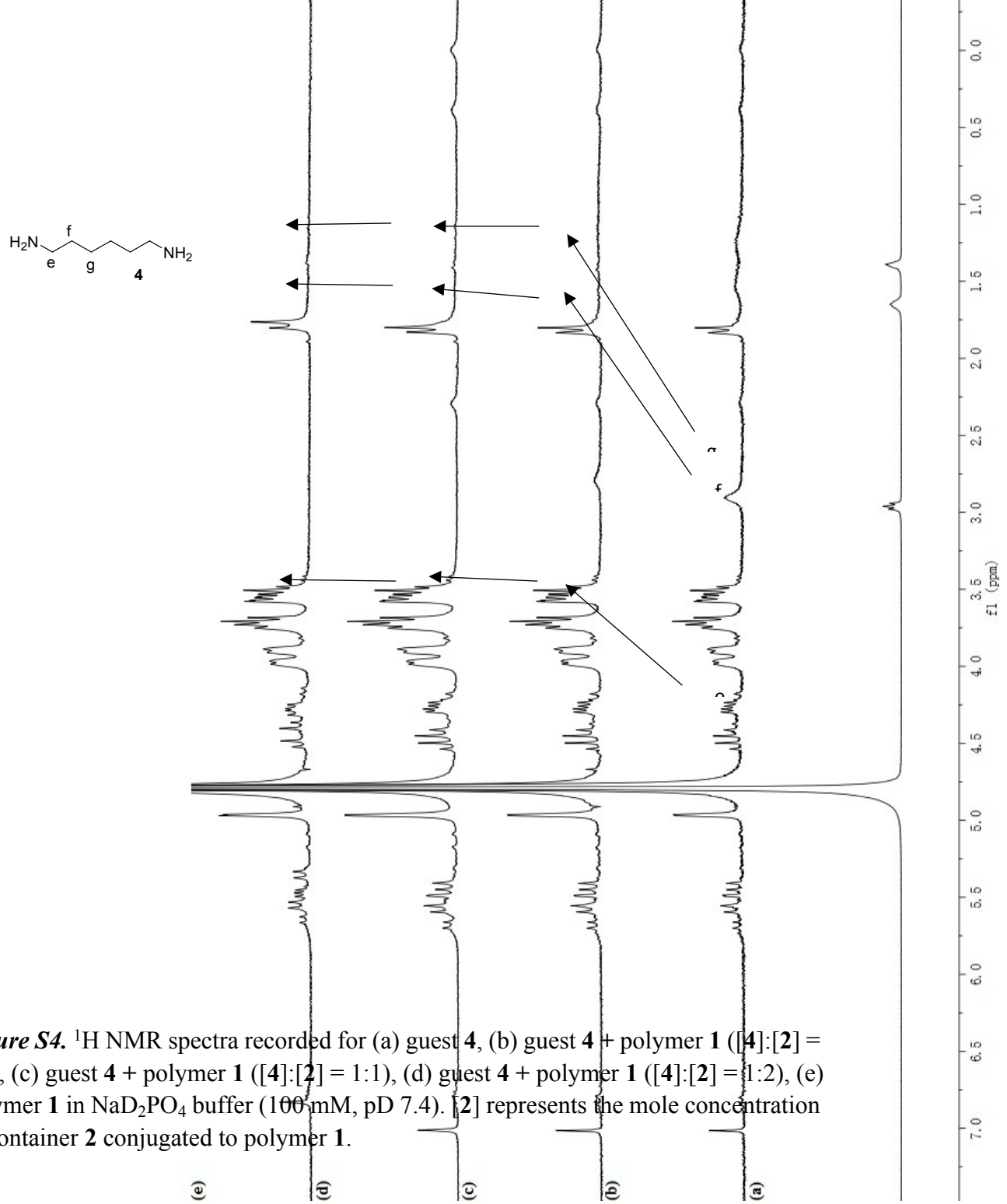
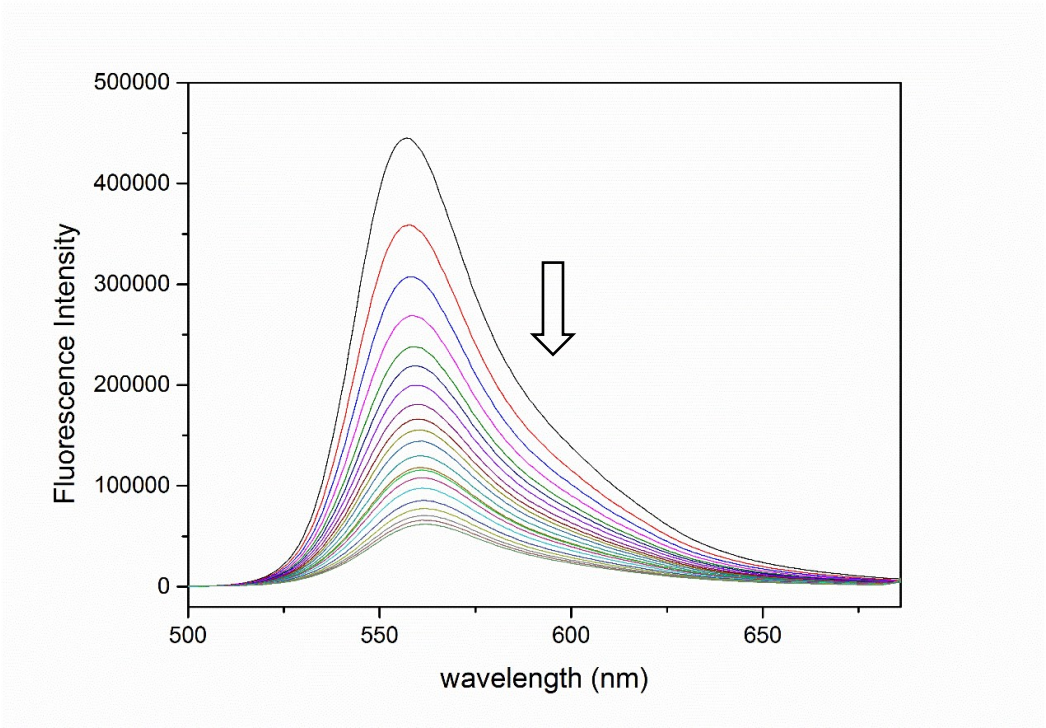


Figure S4. ^{1}H NMR spectra recorded for (a) guest **4**, (b) guest **4** + polymer **1** ([**4**]:[**2**] = 2:1), (c) guest **4** + polymer **1** ([**4**]:[**2**] = 1:1), (d) guest **4** + polymer **1** ([**4**]:[**2**] = 1:2), (e) polymer **1** in NaD_2PO_4 buffer (100 mM, pD 7.4). [**2**] represents the mole concentration of container **2** conjugated to polymer **1**.

(A)



(B)

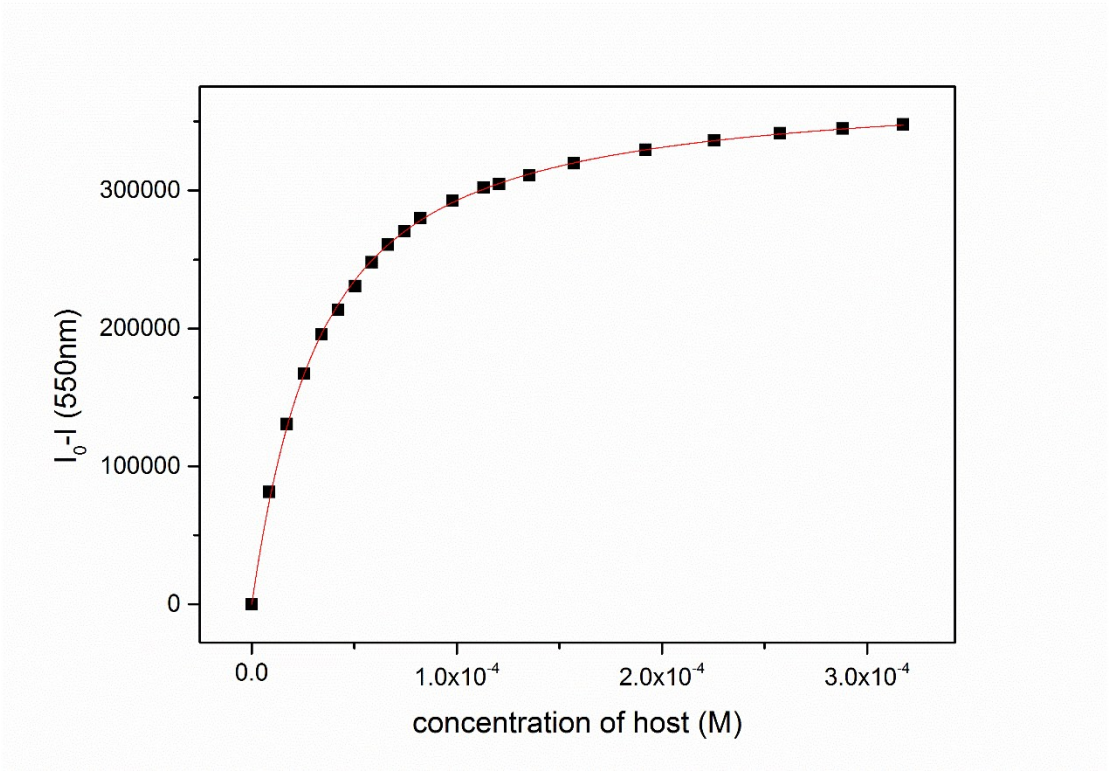
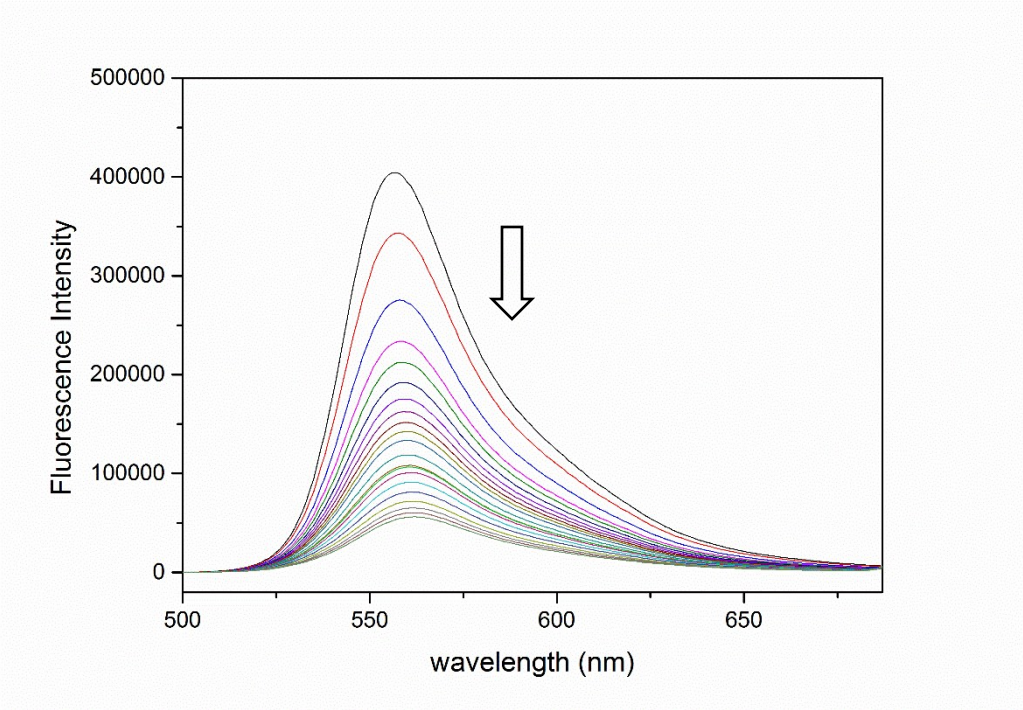


Figure S5. (A) fluorescence spectra from the titration of dye **5** (10 μM) with polymer **1** (calculated for container **2** concentration, 0 – 317 μM) in 10 mM NaH_2PO_4 buffer (pH =7.4, λ_{ex} = 350 nm); (B) plot of I_0-I (550 nm) as a function of container **2** concentration. The solid line represents the best non-linear fitting of the data to a 1:1 binding model ($K_a = (3.7 \pm 0.1) \times 10^4$ M^{-1})

(A)



(B)

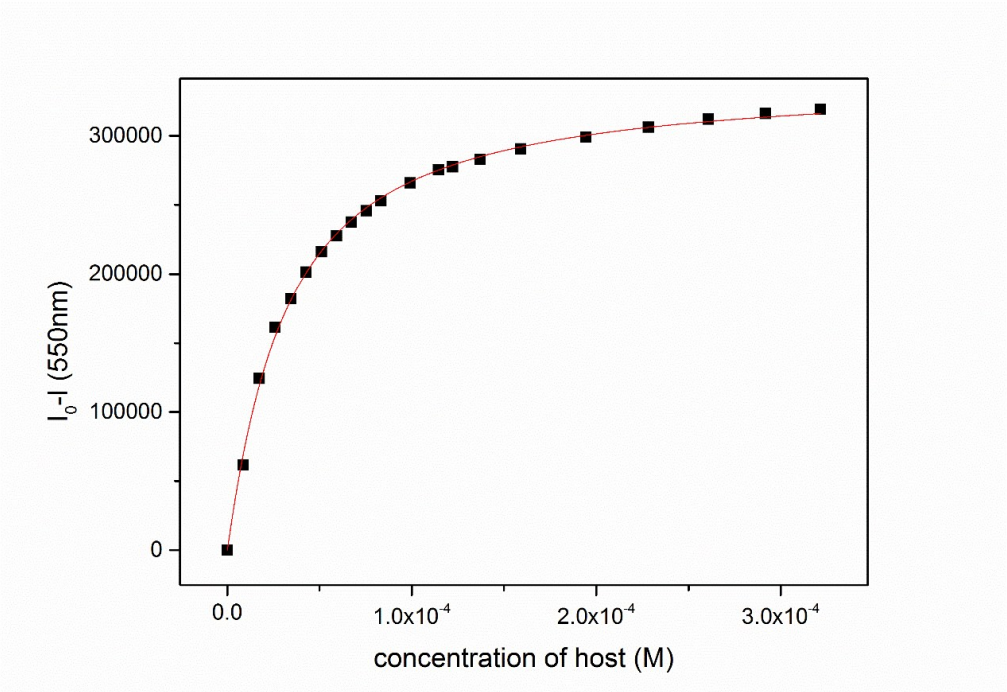


Figure S6. (A) fluorescence spectra from the titration of dye **5** (10 μM) with container **2** (0 – 312 μM) in 10 mM NaH_2PO_4 buffer (pH = 7.38, λ_{ex} = 350 nm); (B) plot of I_0-I (550 nm) as a function of **2** concentration. The solid line represents the best non-linear fitting of the data to a 1:1 binding model ($K_a = (3.8 \pm 0.1) \times 10^4$ M^{-1})

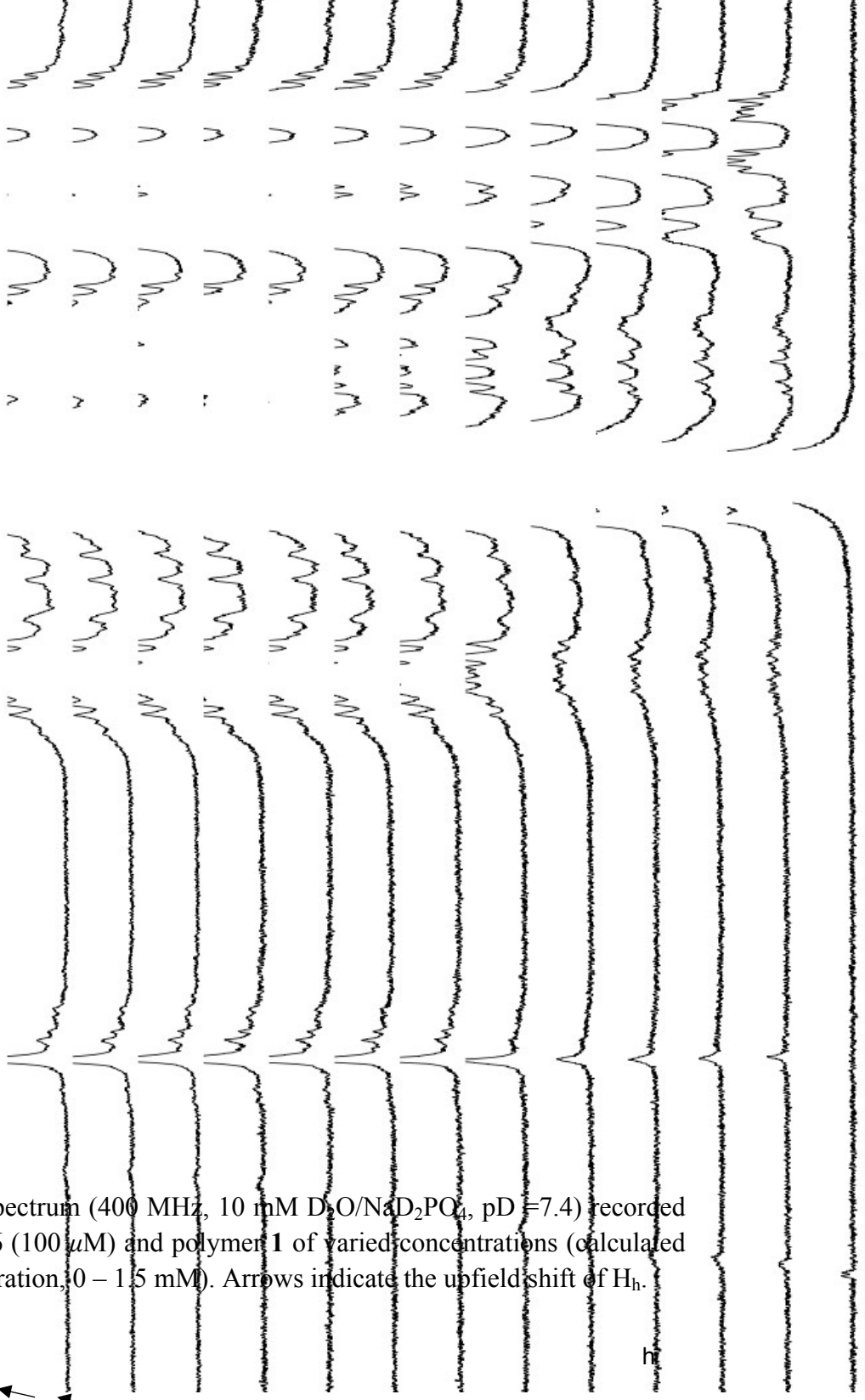
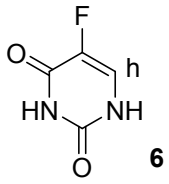


Figure S7. ^{1}H NMR spectrum (400 MHz, 10 mM D_2O/NaD_2PO_4, pD =7.4) recorded for a solution of drug **6** (100 μM) and polymer **1** of varied concentrations (calculated for container **2** concentration, 0 – 1.5 mM). Arrows indicate the upfield shift of H_h.



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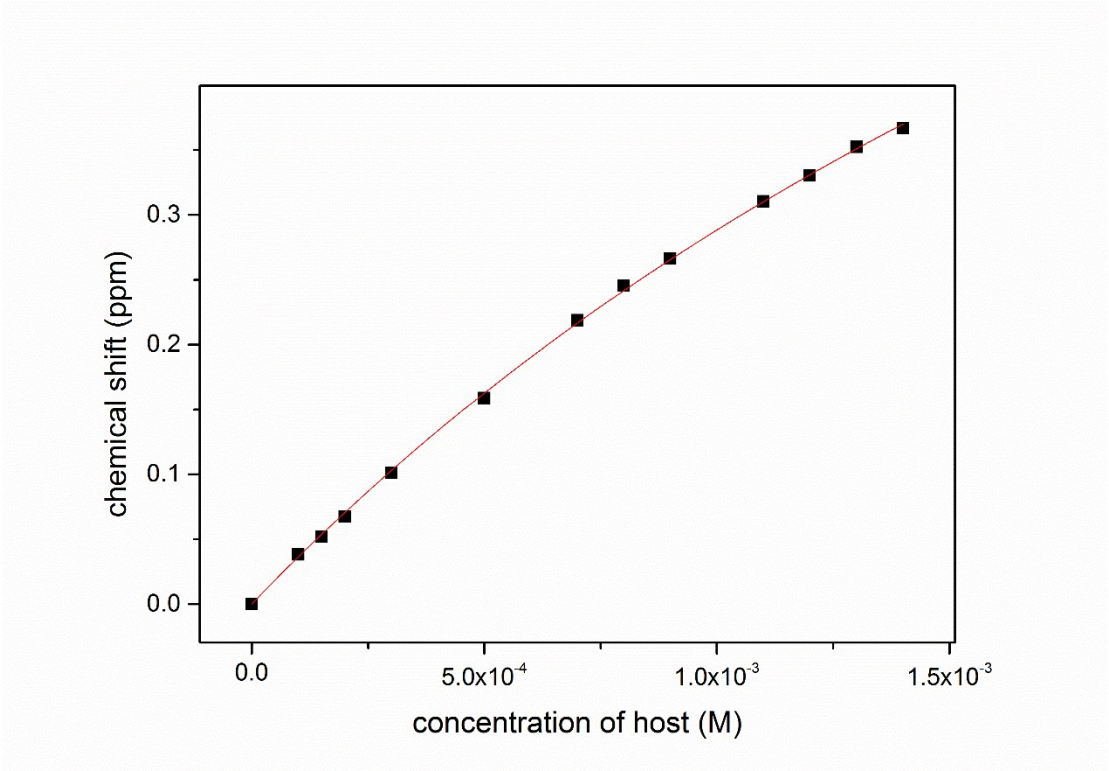


Figure S8. Plot of the chemical shift of H_g resonance on drug **6** as a function of container **2** (conjugated to polymer **1**) concentration. The solid line represents the best non-linear fitting of data to a 1:1 binding model ($K_a = (3.0 \pm 0.2) \times 10^2$ M^{-1}).

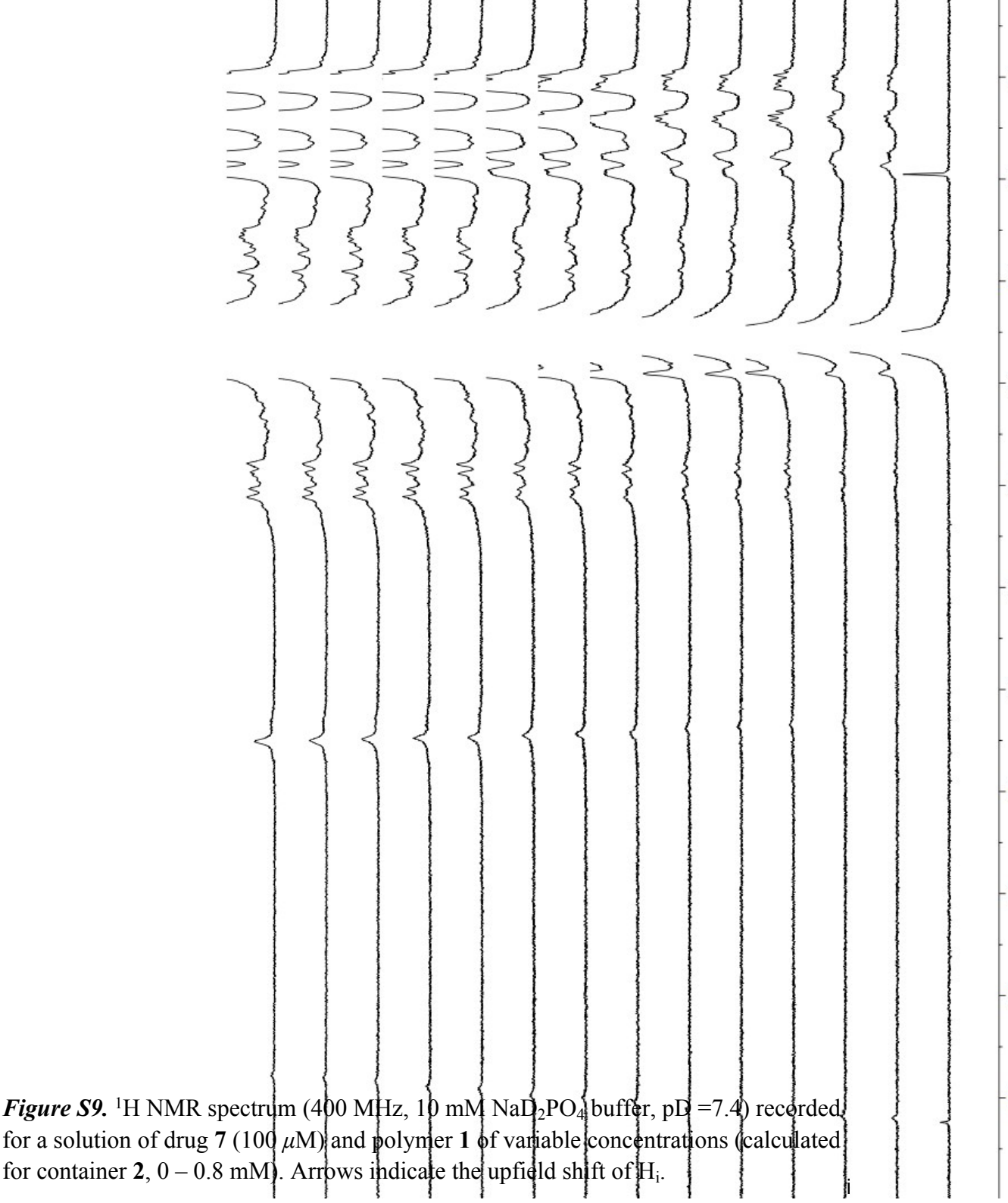


Figure S9. ^{1}H NMR spectrum (400 MHz, 10 mM NaD_2PO_4 buffer, pD =7.4) recorded for a solution of drug **7** (100 μM) and polymer **1** of variable concentrations (calculated for container **2**, 0 – 0.8 mM). Arrows indicate the upfield shift of H_i.

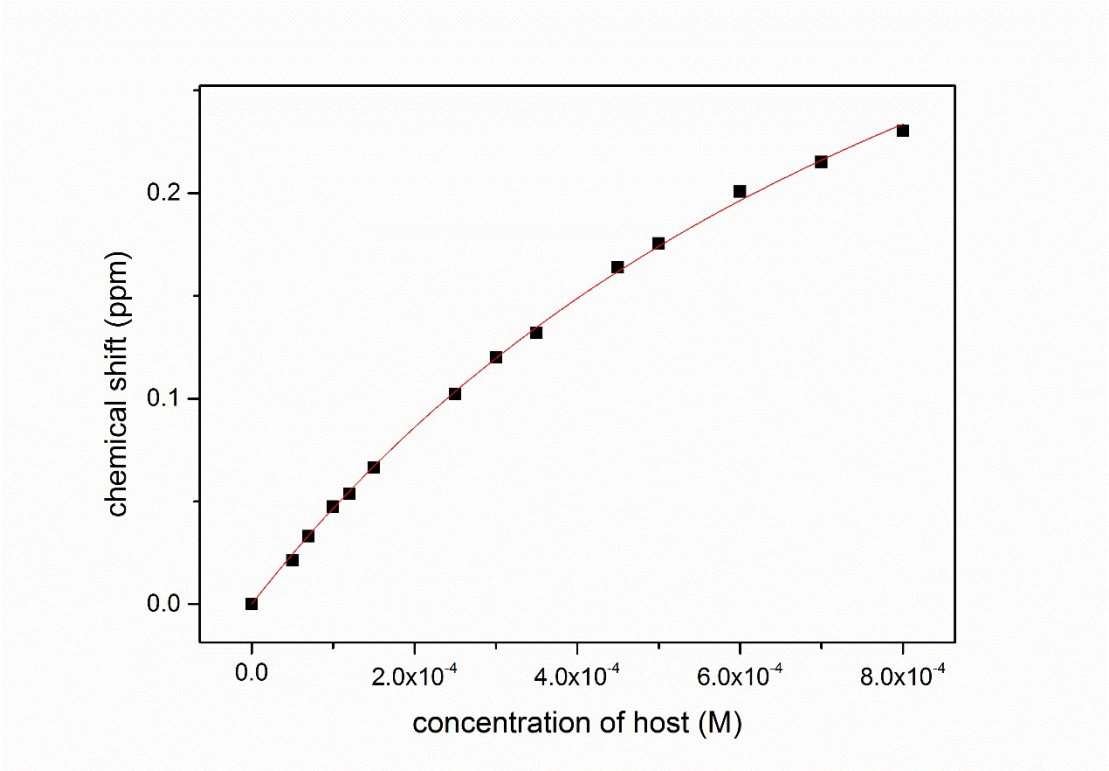


Figure S10. Plot of the chemical shift of H_i resonance on drug **7** as a function of container **2** (conjugated to polymer **1**) concentration. The solid line represents the best non-linear fitting of data to a 1:1 binding model ($K_a = (1.0 \pm 0.1) \times 10^3$ M^{-1})

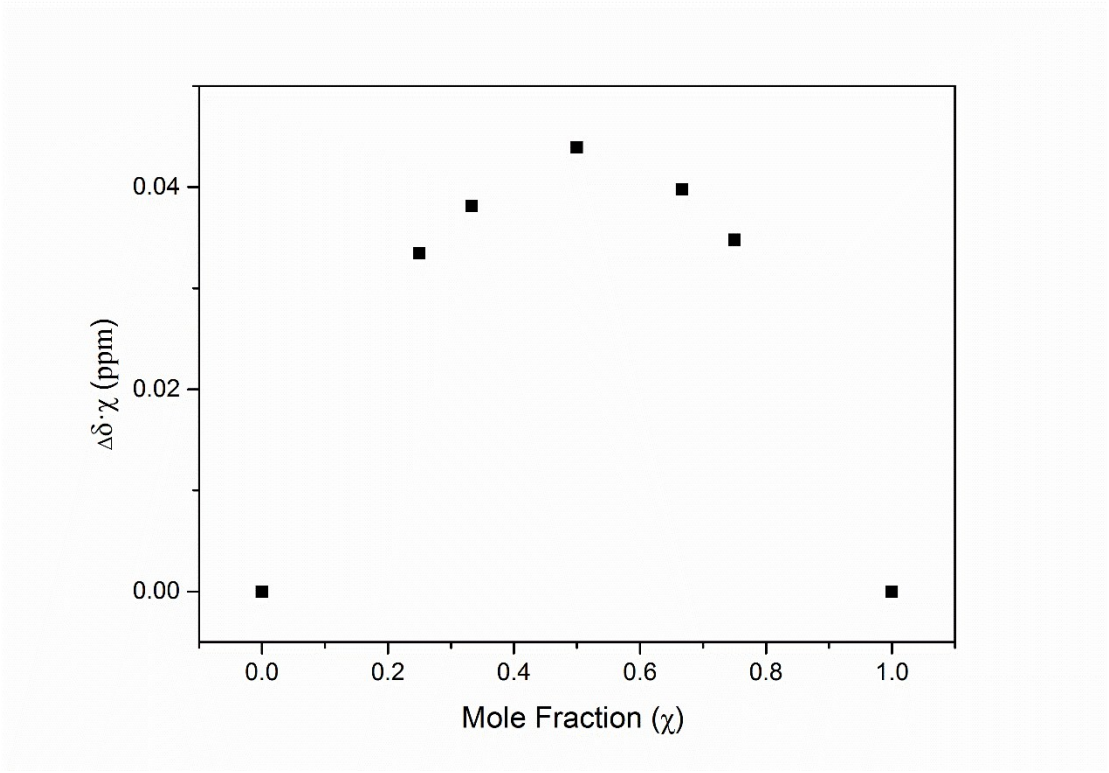


Figure S11. Job plot for drug **6** and polymer **1** ([**6**] + [container **2**] = 500 μM, 10 mM NaD_2PO_4 buffer, pD =7.4) of mole fraction ($\boldsymbol{\chi}$) of **6** versus $\Delta\boldsymbol{\delta}\cdot\boldsymbol{\chi}$. The plot indicates a 1:1 binding stoichiometry.

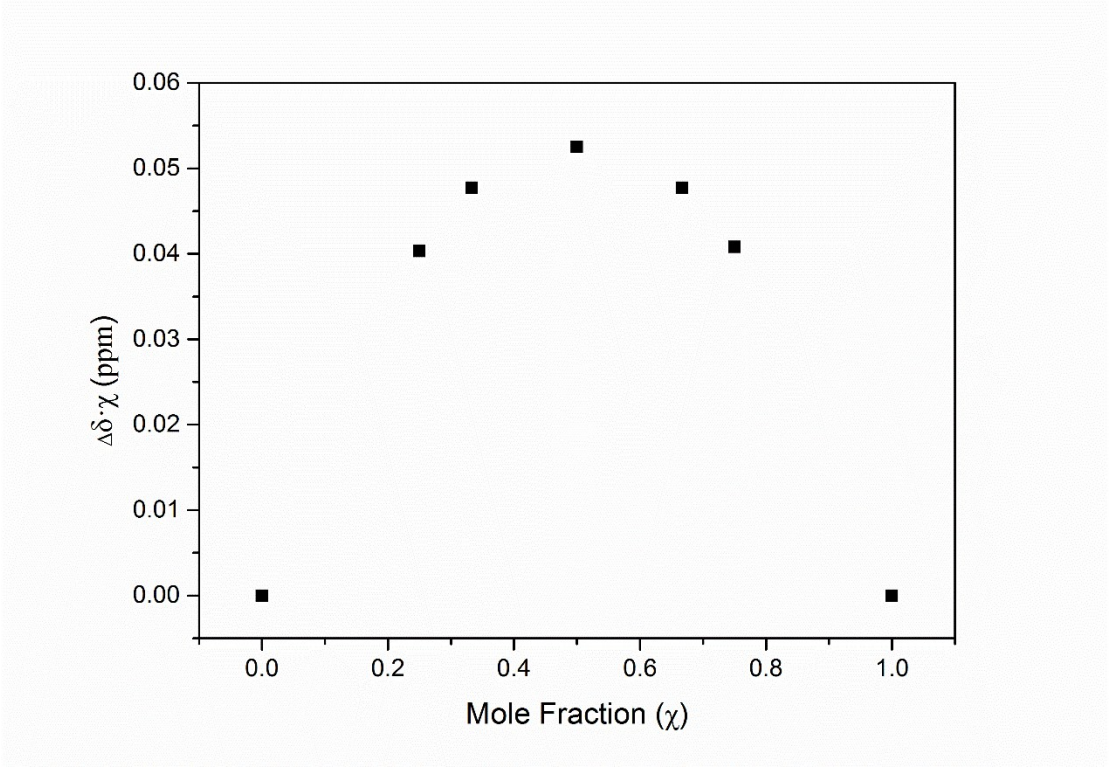


Figure S12. Job plot for drug **7** and polymer **1** ([**7**] + [container 2] = 500 μM, 10 mM NaD_2PO_4 buffer, pD =7.4) of mole fraction ($\boldsymbol{\chi}$) of **7** versus $\Delta\boldsymbol{\delta}\cdot\boldsymbol{\chi}$. The plot indicates a 1:1 binding stoichiometry.

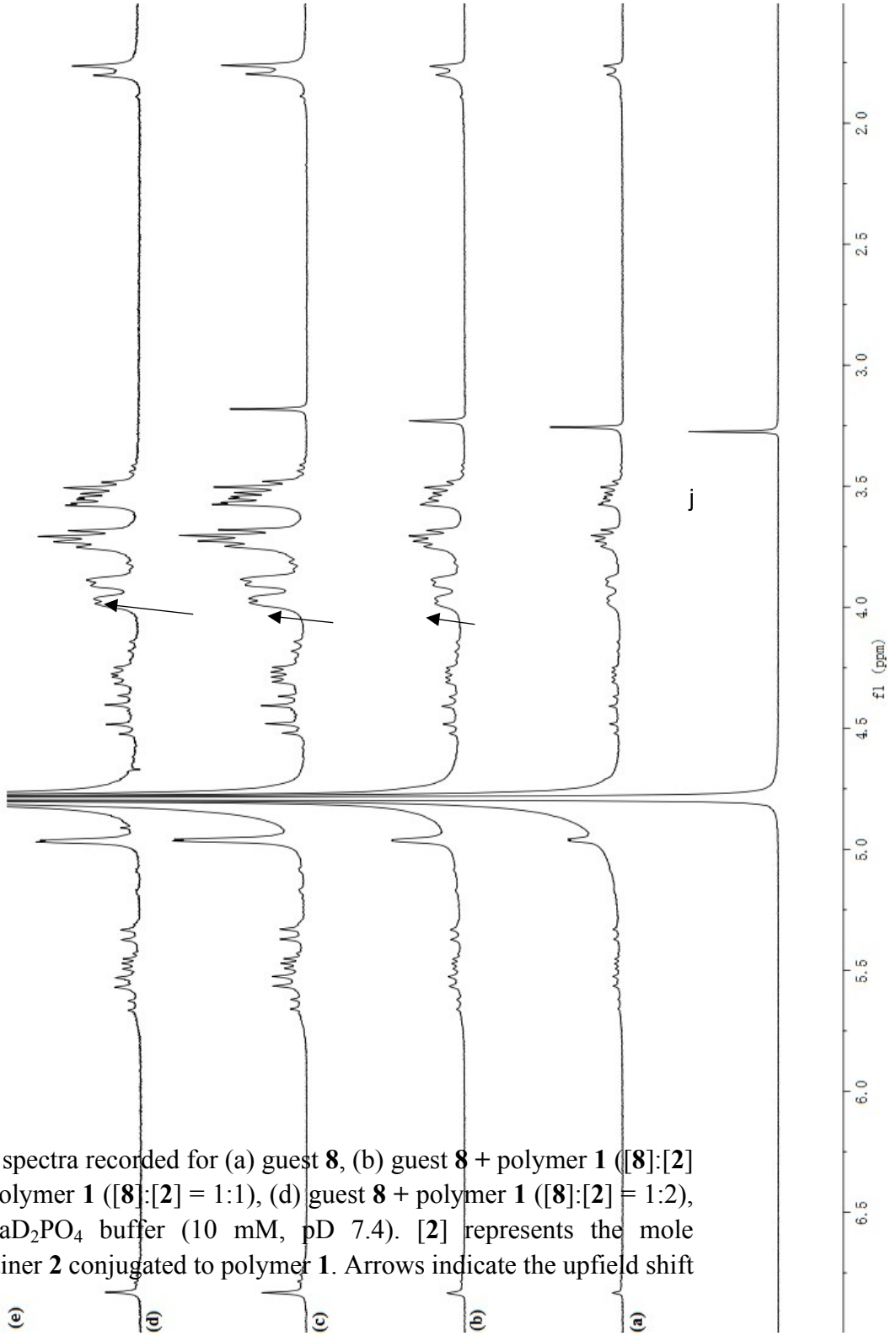
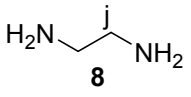


Figure S13. ^{1}H NMR spectra recorded for (a) guest **8**, (b) guest **8** + polymer **1** ([**8**]:[**2**] = 2:1), (c) guest **8** + polymer **1** ([**8**]:[**2**] = 1:1), (d) guest **8** + polymer **1** ([**8**]:[**2**] = 1:2), (e) polymer **1** in NaD_2PO_4 buffer (10 mM, pD 7.4). [**2**] represents the mole concentration of container **2** conjugated to polymer **1**. Arrows indicate the upfield shift of H_j.

Supplementary TEM image



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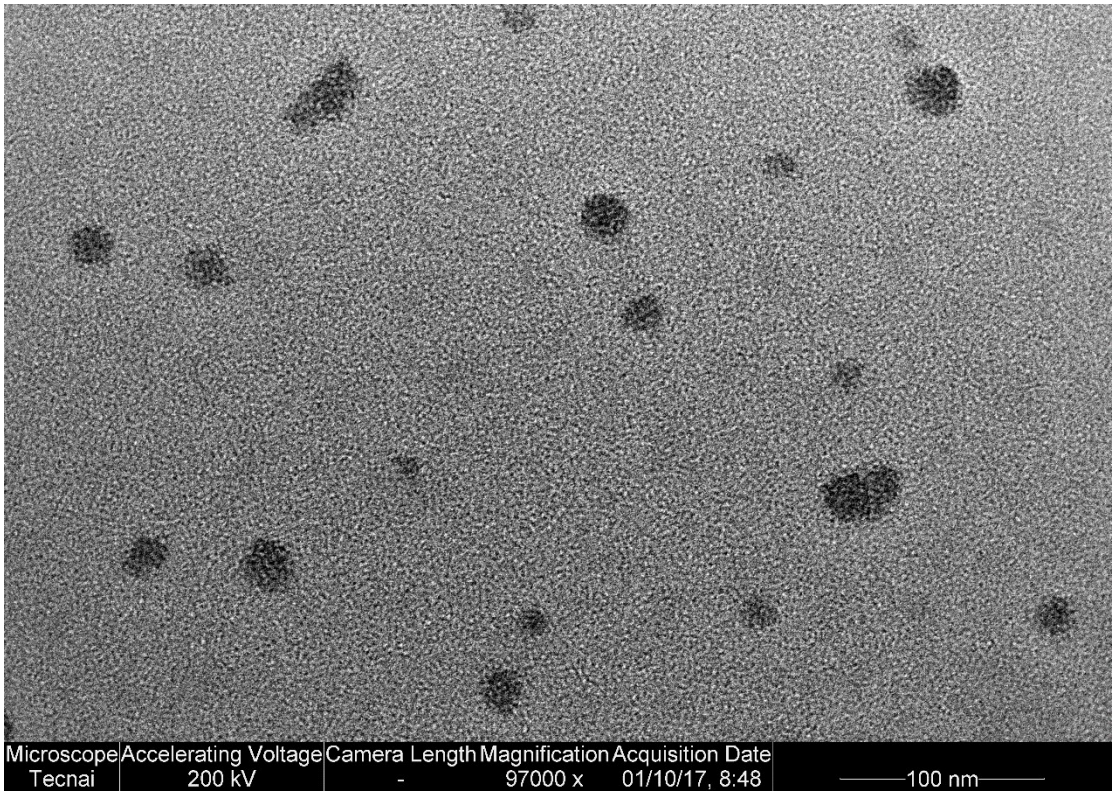

Figure S14. TEM image of 0.3 mg/mL polymer **1** and 0.6 mg/mL PEI in water after lyophilization.

Method for quantum yield determination

A comparative method[2] was used to determine quantum yield Φ_F by using a standard samples with known Φ_F value. Here we choose quinine sulfate as the standard samples in 0.1 M H_2SO_4. For the measurement, standard and test samples were prepared in a 10 mm cuvette with an absorbance of 0.024 at 350 nm. λ_{ex} = 350 nm, slit width: 5 nm/5 nm. Quantum yield was calculated according to the following equation:

$$\Phi_X = \Phi_S\left(\frac{A_S}{A_X}\cdot\frac{I_X}{I_S}\right)\left(\frac{n_x}{n_s}\right)^2$$

where subscripts *X* and *S* refer to test sample and standard sample, respectively; Φ represents the quantum yield; *A* represents the absorbance; *I* represents the integrated fluorescence intensity from corrected fluorescence spectra (400-600 nm); n represents the refractive index of the solution (n = 1.33 for dilute aqueous solution); Φ_S is 0.55 based on literature report.[3]

Solid phase luminescence

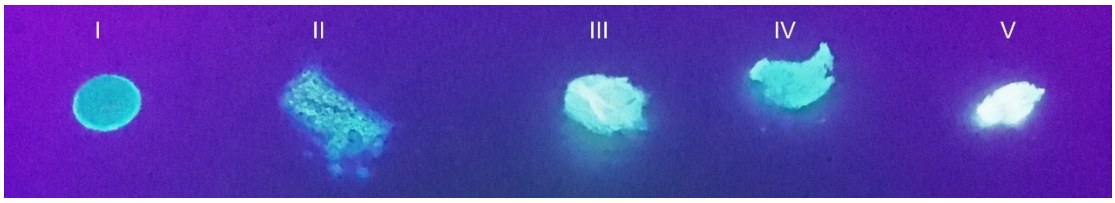

Figure S15. Luminescence images of PEI (Ⅰ), dextran (Ⅱ), polymer **1** (Ⅲ), lyophilized mixture of dextran and PEI (Ⅳ), lyophilized mixture of polymer **1** and PEI (Ⅴ) under UV irradiation (365 nm).

In vitro cytotoxicity assay

The cytotoxicity of polymer **1** and PEI was examined by CCK-8 assay with HeLa cells. HeLa cells were seeded in 96-plate wells (4000 cells/well) and cultured for 12 h. Then, the cells were treated with fresh medium (100 μL/well) containing polymer **1** alone, polymer **1** and PEI, or PEI alone at varied concentrations. After 24 h, CCK-8 solution (10 μL) was added to each well. After 3 h incubation, the absorbance was measured at 450 nm by a Microplate Reader (Biotek Synergy H1). The relative cell viability was calculated against blank (medium treated HeLa cells).

Bioimaging by confocal microscopy

Confocal laser scanning microscopic images were performed on an Olympus FV1000 confocal microscope with a 60 × oil-immersion objective lens. Cells were plated on 20 mm glass culture dish and were incubated overnight. The cells were washed with PBS and then incubated with polymer **1** (0.1 mg/mL) and PEI (0.033 mg/mL) for 10 h at 37 ºC. After washing three times with PBS, the cells were imaged by confocal microscopy with the excitation wavelength at 405 nm.

References

(1) Ma, D.; Zavalij, P. Y.; Isaacs, L. *J. Org. Chem.* **2010**, *75*, 4786–4795.

(2) Williams, A. T. R.; Winfield, S. A.; Miller, J. N. *Analyst* **1983**, *108*, 1067–1071.

(3) Melhush, W. H. *J. Phy. Chem.*, **1961**, *65*, 229-235.