Supporting Information

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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 \(\zeta\)-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<sub>w</sub> = 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%).

<sup>1</sup>H NMR (400 MHz, 20 mM NaD<sub>2</sub>PO<sub>4</sub>): 6.83 (s, 4H), 5.65 (d, <i>J</i> = 14.6 Hz, 2H), 5.55 (d, <i>J</i> = 15.6 Hz, 4H), 5.48 (d, <i>J</i> = 8.4 Hz, 2H), 5.46 (d, <i>J</i> = 8.4 Hz, 2H), 5.35 (d, <i>J</i> = 16.0 Hz, 4H), 4.97 (d, <i>J</i> = 2.4 Hz, 9.8H), 4.50 (d, <i>J</i> = 15.6 Hz, 4H), 4.38 (d, <i>J</i> = 15.6 Hz, 4H), 4.26 (d, <i>J</i> = 15.6 Hz, 4H), 4.29 (d, <i>J</i> = 15.6 Hz, 4H), 4.16 (d, <i>J</i> = 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<sup>-1</sup>): 3680m, 3400s, 1725s, 1479s, 1450s, 1420s, 1016s, 806m.

Elemental Analysis (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>9.8</sub>(C<sub>50</sub>H<sub>50</sub>N<sub>16</sub>O<sub>19</sub>)·(H<sub>2</sub>O)<sub>39</sub>: 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$_2$PO$_4$ 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$_2$PO$_4$ 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$_2$PO$_4$ 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$_2$PO$_4$ buffer (100 mM, pH 7.4). [2] represents the mole concentration of container 2 conjugated to polymer 1.

(A)
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 NaH₂PO₄ buffer (pH = 7.4, λₑₓ = 350 nm); (B) plot of I₀-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 ($K_a = (3.7 \pm 0.1) \times 10^4\ M^{-1}$)
Figure S6. (A) Fluorescence spectra from the titration of dye 5 (10 μM) with container 2 (0 – 312 μM) in 10 mM NaH$_2$PO$_4$ 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$_2$O/Na$_2$PO$_4$, 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$_h$. 

![Diagram of molecule 6]
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$_2$PO$_4$ 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 NaD₂PO₄ buffer, pD =7.4) of mole fraction (χ) of 6 versus Δδ·χ. 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 NaD₂PO₄ buffer, pD =7.4) of mole fraction (χ) of 7 versus Δδ·χ. 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$_2$PO$_4$ 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**
**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 was used to determine quantum yield $\Phi_F$ by using a standard samples with known $\Phi_F$ value. Here we choose quinine sulfate as the standard samples in 0.1 M H$_2$SO$_4$. For the measurement, standard and test samples were prepared in a 10 mm cuvette with an absorbance of 0.024 at 350 nm. $\lambda_{ex} = 350$ nm, slit width: 5 nm/5 nm. Quantum yield was calculated according to the following equation:

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

where subscripts $X$ and $S$ refer to test sample and standard sample, respectively; $\Phi$ 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); $\Phi_S$ is 0.55 based on literature report.$^3$

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**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 °C. After washing three times with PBS, the cells were imaged by confocal microscopy with the excitation wavelength at 405 nm.
References