Supporting Information

Rational Design of A Fluorescent Poly(*N*-aryleneindole ether sulfone) Switch by Cation–π Interactions

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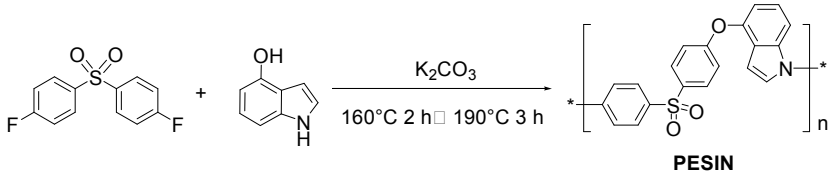
I. General remarks of optical spectroscopic studies

The studies on the binding properties of **PESIN** were carried out in *N*,*N*-dimethylformamide (DMF)/H_2O (99:1, v/v). A variety of aromatic heterocyclic hydrochlorides including pyridine hydrochloride (Py·HCl), pyridine hydrobromide (Py·HBr), pyridine sulfate ($Py·H_2SO_4$), quinoline hydrochloride (Qu·HCl), imidazole hydrochloride (IM·HCl) and benzimidazole hydrochloride (BIM·HCl) were also dissolved in aqueous solutions (v/v, DMF/H_2O = 99:1). Sodium hydroxide and triethylamine hydrochloride were both dissolved in water. DMF was either HPLC or spectroscopic grade and water was distilled for twice. All solutions were prepared using volumetric syringes, pipettes, and volumetric flasks. The stock solutions of fluorophores and analytes were freshly prepared and used for each measurement. Each time a 3 mL of receptor was filled in a quartz cell of 1 cm of optical path length, and the stock solution of hydrochloride was added into a quartz cell dropwise using a micro-syringe. The volume of analyte stock solution added was less than 100 μL to remain the concentration of receptor unchanged. Absorption spectra were detected on a SHIMADZU UV-3150 uv-vis-NIR sprectrophotometer. Fluorescent emission spectra were collected on a PerkinElmer LS-55 fluorescence spectrometer.

II. Synthesis of poly(*N*-aryleneindole ether sulfone) sensor (PESIN)

To a three-necked flask (25 mL) equipped with magnetic stirrer, an argon outlet, inlet, and water-cooled condenser, 4-hydroxyindole (4.0 mmol), 4,4'-difluorodiphenyl sulfone (4.0 mmol), K_2CO_3 (8 mmol), and NMP (10.0 mL) were added. The reaction mixture was evacuated and flushed with high-purity argon. This procedure was repeated three times. The reaction mixture was heated to 160 ^oC under stirring for 2h, and then the temperature was subsequently brought to 190 °C and maintained at this temperature for 3h. The resulting polymer solution was allowed to slowly cool to room temperature, and subsequently poured into cold water, filtered, washed with water and methanol, and then dried at 100 °C under vacuum (yield 96%). FT-IR spectrum (KBr pellet, cm^{-1}): 3094, 1685, 1592, 1519, 1321, 1247, 752; ^1H NMR (600 MHz, DMSO-d_6): δ = 6.46 (s, 1H), 6.89 (s, 1H), 7.09 (d, J = 20.4 Hz, 2H), 7.23 (s, 1H), 7.55 (s, 1H), 7.69 (s, 1H), 7.84 (m, 6H) ppm; Anal.Calcd for $(C_{20}H_{13}NO_3S)_n$ $(347.39)_n$: C, 69.15; H, 3.77; N, 4.03; Found: C, 68.96; H, 3.80; N, 4.00.

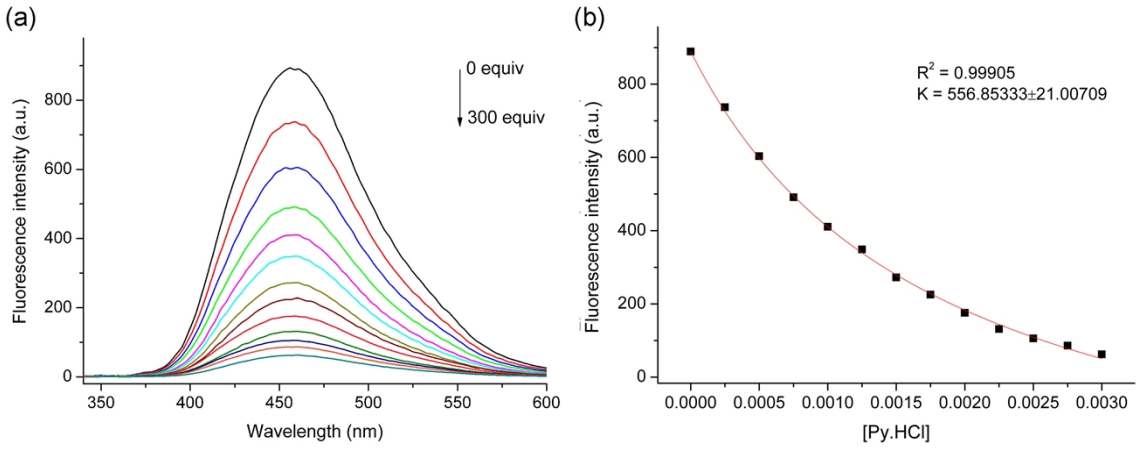


Scheme S1. Synthesis of **PESIN** *via* C–N/C–O coupling reaction.

III. Binding studies of PESIN with pyridine hydrochloride and quinoline hydrochloride

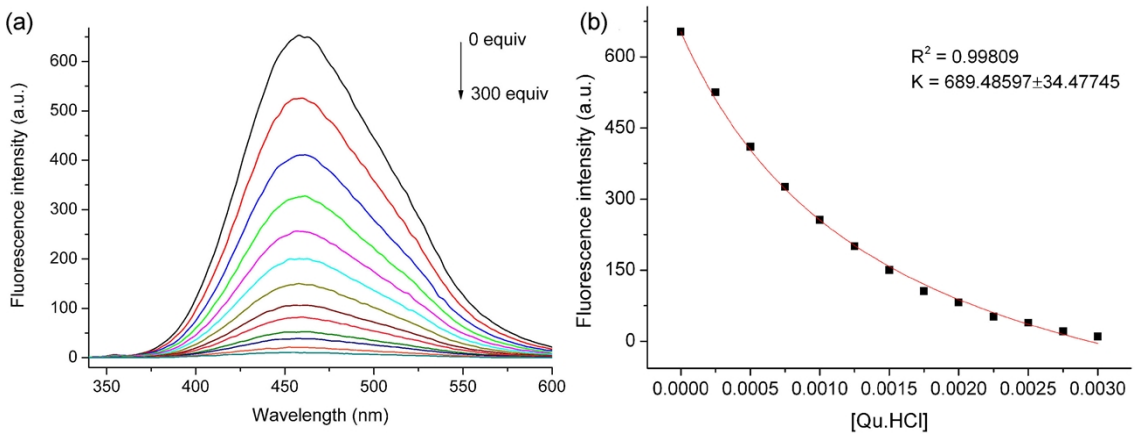
The apparent association constant K is determined by the nonlinear curve fitting method[1] (eqn. (1)). C_H and C_G are the concentrations of sensor **PESIN** and pyridine hydrochloride (Py·HCl) or quinoline hydrochloride (Qu·HCl), respectively. F_0 is the fluorescence intensity of **PESIN** before the addition of hydrochlorides. F_{lim} is the lowest value that the fluorescence intensity can reach after the addition of hydrochlorides and can be left as a floating parameter in the analysis if it cannot be determined accurately. K can thus be obtained by the nonlinear least squares analysis of F_{cal} versus C_G.

$$F = F_0 + \frac{F_{lim} - F_0}{2}\{1 + \frac{C_G}{C_H} + \frac{1}{KC_H} - [(1 + \frac{C_G}{C_H} + \frac{1}{KC_H})^2 - 4\frac{C_G}{C_H}]^{1/2}\} \qquad (1)$$



$$K = (5.57 \pm 0.21)\times 10^2\ M^{-1}$$

Figure S1. (a) Fluorescent titration spectra of **PESIN** (10 μM) upon addition of pyridine hydrochloride in 99:1 (v/v) of DMF/H_2O (λ_{exc} = 320 nm, slits = 5.0 nm, 3.5 nm). (b) The association constant K obtained by nonlinear curve fitting at the emission of 458 nm.



$$K = (6.89 \pm 0.34) \times 10^2\ M^{-1}$$

Figure S2. (a) Fluorescent titration spectra of **PESIN** (10 μM) upon addition of quinoline hydrochloride in 99:1 (v/v) of DMF/H_2O (λ_{exc} = 320 nm, slits = 5.0 nm, 3.5 nm). (b) The association constant *K* obtained by nonlinear curve fitting at the emission of 458 nm.

Reference:

1. a) D. K. Ryan, J. H. Weber, *Anal. Chem.* **1982**, *54*, 986-990; b) B. Valeur, J. Pouget, J. Bouson, M. Kaschke, N. P. Ernsting, *J. Phys. Chem.* **1992**, *96*, 6545-6549; c) R.-H. Yang, K.-A. Li, K.-M. Wang, F.-L. Zhao, N. Li, F. Liu, *Anal. Chem.* **2003**, *75*, 612-621.

IV. Binding studies of PESIN with pyridine, triethylamine hydrochloride and hydrochloride

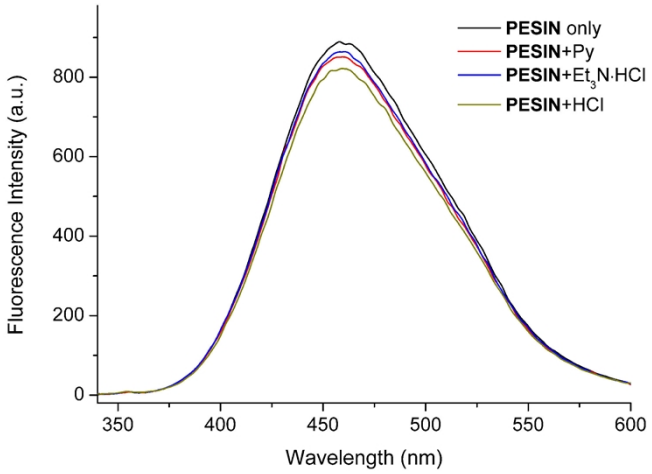


Figure S3. Fluorescence spectra of **PESIN** (10 μM) upon addition of 300 equiv of pyridine, triethylamine hydrochloride and hydrochloride, respectively, in 99:1 (v/v) of DMF/H_2O, excited at 320 nm.

V. Optimized geometries of PESIN solution with pyridine hydrochloride (Py·HCl)

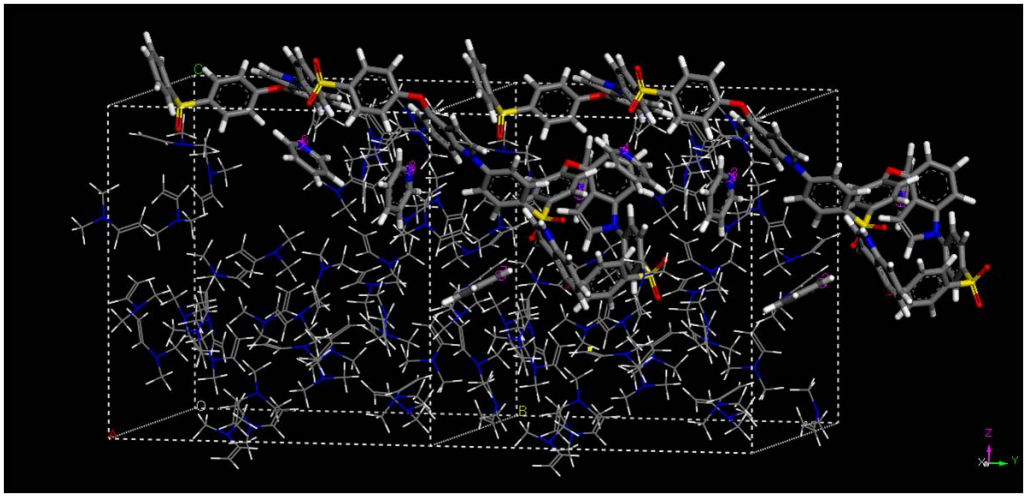


Figure S4. Polymer solution (**PESIN**, pyridine hydrochloride and DMF) after structure and energy optimization.

VI. Binding studies of PESIN with pyridine hydrochloride (Py·HCl), pyridine hydrobromide (Py·HBr), pyridine sulfate (Py·H_2SO_4)

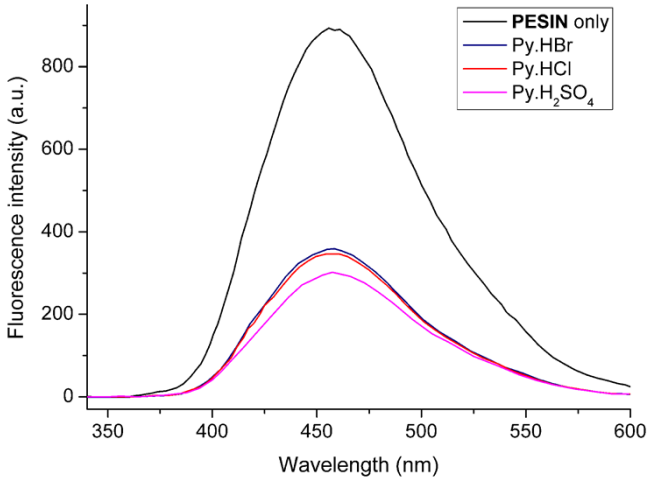


Figure S5. Fluorescence spectra of **PESIN** (10 μM) upon addition of 125 equiv of pyridine hydrochloride (Py·HCl), pyridine hydrobromide (Py·HBr) and pyridine sulfate (Py·H_2SO_4), respectively, in 99:1 (v/v) of DMF/H_2O, excited at 320 nm.

VII. Calculation of the detection limit

The typical limit of detection (LOD) is obtained by using the equation followed:

$$LOD = \frac{3 \times SD}{S}$$

Where SD is the standard deviation of the background (blank **PESIN**) and S is the sensitivity. S can be obtained from the slope of the linear fit.

VIII. IR spectra of PESIN

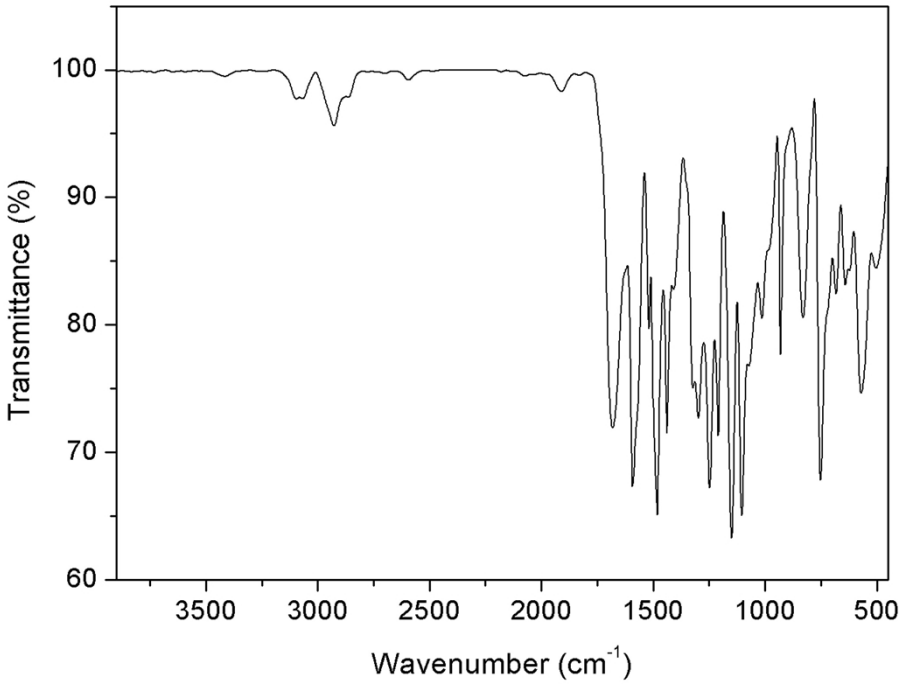


Figure S6. The IR spectrum of polymer **PESIN**.

IX. Copy of ^{1}H NMR spectra of PESIN