

Supporting information

Synthesis, structure-fluorescence relationships and density functional theory studies
of novel naphthalimide-piperazine-pyridine-based polystyrene sensors for Hg(II)
detection

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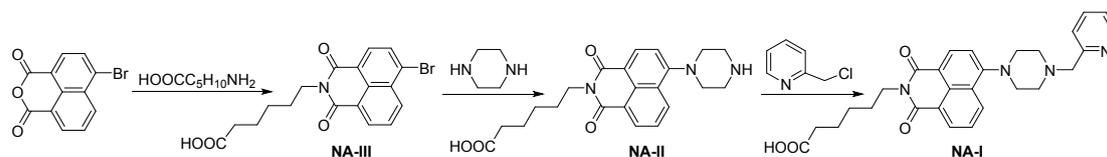
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Synthesis of 6-(1,3-dioxo-6-(4-(pyridin-2-ylmethyl)piperazin-1-yl)-1H-benzo[de]isoquinolin-2(3H)-yl)hexanoic acid (NA-I)



Scheme S1 Synthetic route of compound **NA-I**

6-(6-Bromo-1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl)hexanoic acid (NA-III)¹

4-Bromo-1,8-naphthalic anhydride (4 mmol, 1.11 g) and 6-aminocaproic acid (4.8 mmol, 0.63 g) were dissolved in ethanol (60 mL). The reaction mixture was stirred and refluxed for 6 h. The solvent was removed under reduced pressure, and then refrigerated. Pure **NA-III** (1.17 g, yield 75%) was obtained as a grey solid following filtration, washing with cold ethanol and then drying. ¹H NMR (400 MHz, DMSO-*d*₆): δ = 8.52 (q, *J* = 7.2 Hz, 2H, ArH), 8.28 (d, *J* = 7.6 Hz, 1H, ArH), 8.17 (d, *J* = 8.0 Hz, 1H, ArH), 7.96 (t, *J* = 7.6 Hz, 1H, ArH), 4.00 (t, *J* = 7.6 Hz, 2H, CH₂), 2.21 (t, *J* = 7.2 Hz, 2H, CH₂), 1.67-1.51 (m, 4H, CH₂), 1.38-1.31 (m, 2H, CH₂); ESI-MS: *m/z* calcd for C₁₈H₁₆BrNO₄ [M-H]⁻: 388.02; found: 387.97.

6-(1,3-Dioxo-6-(piperazin-1-yl)-1H-benzo[de]isoquinolin-2(3H)-yl)hexanoic acid (NA-II)²

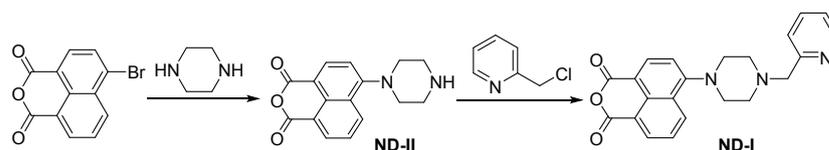
Compound **NA-III** (3 mmol, 1.17 g) and piperazine (9 mmol, 0.78 g) were dissolved in 2-methoxyethanol (40 mL). The reaction mixture was refluxed for 4 h under N₂ protection. The solvent was removed under reduced pressure, and then the residue was purified via flash column chromatography on silica gel (CH₂Cl₂: CH₃OH = 3:1, v/v) to afford **NA-II** as a yellow solid (0.51 g, yield 43%). ¹H NMR (400 MHz, DMSO-*d*₆): δ = 8.51 (q, *J* = 7.6 Hz, 2H, ArH), 8.42 (d, *J* = 8.0 Hz, 1H, ArH), 7.83 (q, *J* = 7.6 Hz, 1H, ArH), 7.42 (d, *J* = 8.0 Hz, 1H, ArH), 4.02 (t, *J* = 7.2 Hz, 2H, CH₂), 3.46-3.42 (m, 8H, CH₂), 2.21 (t, *J* = 7.6 Hz, 2H, CH₂), 1.66-1.51 (m, 4H, CH₂), 1.37-1.30 (m, 2H, CH₂); ESI-MS: *m/z* calcd for C₂₂H₂₄N₃O₄ [M+H]⁺: 396.19; found: 396.24.

6-(1,3-Dioxo-6-(4-(pyridin-2-ylmethyl)piperazin-1-yl)-1H-benzo[de]isoquinolin-2(3H)-yl)hexanoic acid (NA-I)³

To a solution of 2-(chloromethyl)pyridine hydrochloride (4.6 mmol, 0.75 g) in acetonitrile (40 mL) was added K₂CO₃ (7.6 mmol, 1.05 g) aqueous solution (20 mL). Then compound **NA-II** (3.0

mmol, 1.19 g) was added slowly and the reaction mixture was refluxed for 10 h. The solvent was removed under reduced pressure, and then the residue was purified via flash column chromatography on silica gel (CH₂Cl₂: CH₃OH = 3:1, v/v) to afford **NA-I** as a yellow solid (1.21 g, yield 83%). ¹H NMR (400 MHz, CDCl₃): δ = 8.63 (d, *J* = 4.4 Hz, 1H, ArH), 8.45 (q, *J* = 7.2 Hz, 2H, ArH), 8.36 (d, *J* = 8.4 Hz, 1H, ArH), 7.72 (m, *J* = 1.2 Hz, 1H, ArH), 7.63 (t, *J* = 8.0 Hz, 1H, ArH), 7.50 (d, *J* = 8.0 Hz, 1H, ArH), 7.24 (d, *J* = 8.0 Hz, 1H, ArH), 7.18 (d, *J* = 8.0 Hz, 1H, ArH), 4.13 (t, *J* = 7.6 Hz, 2H, CH₂), 3.85 (s, 2H, CH₂), 3.31 (t, *J* = 7.2 Hz, 4H, CH₂), 2.87 (t, *J* = 7.2 Hz, 4H, CH₂), 2.38 (t, *J* = 6.8 Hz, 2H, CH₂), 1.73 (t, *J* = 6.8 Hz, 4H, CH₂), 1.50 (t, *J* = 7.0 Hz, 2H, CH₂); ESI-MS: *m/z* calcd for C₂₈H₃₀N₄O₄ [M+H]⁺: 487.23; found: 487.26.

Synthesis of 6-[4-(2-pyridinylmethyl)-1-piperazinyl]-1*H*,3*H*-Naphtho[1,8-*cd*]pyran-1,3-dione (**ND-I**)



Scheme S2 Synthetic route of compound **ND-I**

6-(1-Piperazinyl)-1*H*,3*H*-naphtho[1,8-*cd*]pyran-1,3-dione (**ND-II**)

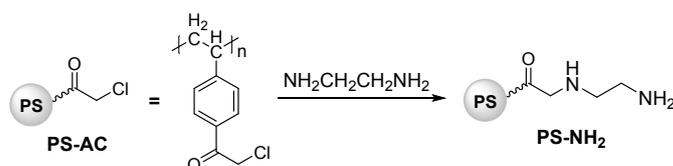
4-Bromo-1,8-naphthalic anhydride (4 mmol, 1.11 g) and piperazine (5 mmol, 0.43 g) were dissolved in 2-methoxyethanol (30 mL). The reaction mixture was stirred and refluxed for 4 h. The solvent was removed under reduced pressure, and the residue was recrystallized from ethanol to afford **ND-II** as a yellow solid (0.99 g, yield 88%). ¹H NMR (400 MHz, DMSO-*d*₆) δ = 9.00 (s, 1H, NH), 8.61-8.45 (m, 2H, ArH), 7.88 (t, *J* = 7.6 Hz, 1H, ArH), 7.47 (d, *J* = 8.0 Hz, 1H, ArH), 3.46 (t, *J* = 4.0 Hz, 4H, CH₂), 3.33 (t, *J* = 4.0 Hz, 4H, CH₂). ESI-MS: *m/z* calcd for C₁₆H₁₄N₂O₃ [M+H]⁺: 283.11; found: 283.06.

6-[4-(2-Pyridinylmethyl)-1-piperazinyl]-1*H*,3*H*-Naphtho[1,8-*cd*]pyran-1,3-dione (**ND-I**)³

To a solution of 2-(chloromethyl)pyridine hydrochloride (4.6 mmol, 0.75 g) in acetonitrile (40 mL) was added K₂CO₃ (7.6 mmol, 1.05 g) aqueous solution (20 mL). Then compound **ND-II** (3.0 mmol, 0.85 g) was added slowly and the reaction mixture was refluxed for 10 h. The solvent was removed under reduced pressure, and then the residue was purified via flash column

chromatography on silica gel (CH₂Cl₂: CH₃OH = 50:1, v/v) to afford **ND-I** as a yellow solid (0.57 g, yield 51%). ¹H NMR (400 MHz, CDCl₃) δ 8.62 (d, *J* = 4.0 Hz, 1H, ArH), 8.56 (d, *J* = 7.2 Hz, 1H, ArH), 8.55 (d, *J* = 7.2 Hz, 1H, ArH), 8.47 (q, *J* = 7.6 Hz, 1H, ArH), 7.72 (t, *J* = 7.6 Hz, 2H, ArH), 7.47 (d, *J* = 8.0 Hz, 1H, ArH), 7.22 (d, *J* = 8.0 Hz, 2H, ArH), 3.84 (s, 2H, CH₂), 3.39 (t, *J* = 4.4 Hz, 4H, CH₂), 2.88 (t, *J* = 4.4 Hz, 4H, CH₂). ESI-MS: *m/z* calcd for C₂₈H₃₀N₄O₄ [M+H]⁺: 374.15; found: 374.09.

Synthesis of aminated polystyrene microspheres (PS-NH₂)



Scheme S3 Synthetic route of aminated polystyrene microspheres (PS-NH₂)

Chloroacetylated polystyrene microspheres **PS** (1.0 g, 4.7 mmol) were swollen with THF (30 mL) overnight, then ethane-1,2-diamine (10 mmol, 0.6 g), NaHCO₃ (0.5 mmol, 0.042 g) and methanol (20 mL) were added. The reaction mixture was stirred and refluxed for 12 h. The microspheres were purified by filtration, washed with methanol and water for several times, then dried under vacuum at 30°C for 24 h to afford **PS-NH₂**. The average NH₂ content of **PS-NH₂** was 2.7 mmol/g, which was analyzed by conductometric titration.^{4,5}

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