Supplementary Material (ESI) for Chemical Communications

Highly selective recognition of lead ion in water by podand fluoroionophore/γ-cyclodextrin complex sensor

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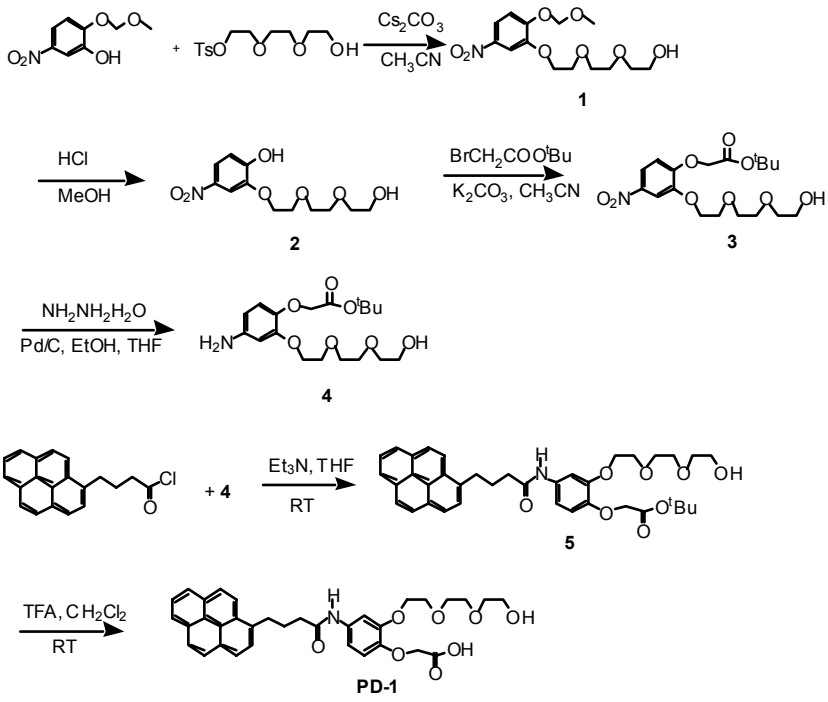
1. Synthesis of **PD-1**

Scheme A. Synthesis of **PD-1**



Preparation of 2-(2-{2-[2-methoxymethoxy]-5-nitrophenoxy}ethoxy)ethoxy)-1-ethanol (1). To a solution of 2-(methoxymethoxy)-5-nitrophenol (1.19 g, 6.0 mmol) in acetonitrile (100 mL) was added cesium carbonate (2.93 g, 9.0 mmol) and the reaction mixture was stirred for 1 h at reflux.[1] To the reaction mixture

2-[2-(2-hydroxyethoxy)ethoxy]ethyl-4-methylbenzenesulfonate (1.82 g, 6.0 mmol) was added and refluxed for 3 h. After completion of reaction, the precipitate was filtered through pad of Celite. After evaporation of solvent, the residue was extracted with methylene chloride (2x 30 mL), washed with water (2x30 mL), and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by flash column chromatography (SiO_2, ethyl acetate) to give desired product in 78% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.83-7.87 (m, 2H), 7.20-7.22 (d, 1H, *J*= 8.7 Hz), 5.32 (s, 2H), 3.59-4.30 (m, 12 H), 3.52 (s, 3H). Mass: 331 (M^+).

Preparation of 2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}-4-nitrophenol (2). To a solution of compound **1** (1.54 g, 4.6 mmol) in methanol (30 mL) was added conc-HCl (2 mL) and the reaction mixture was stirred for 1 h at 60^{o}C.[2] The solvent was evaporated and residue was extracted with methylene chloride (2x 30 mL), washed with saturated aqueous sodium bicarbonate solution (2x20 mL), washed with water (2x20 mL), and dried over $MgSO_4$. Evaporation of solvent gave the desired product in 90% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68-7.80 (m, 2H), 6.96-6.98 (d, 1H, *J*= 8.7 Hz), 3.56-4.13 (m, 12H). Mass: 287 (M^+).

Preapartion of *tert*-butyl 2-(2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}-4-nitro phenoxy)acetate (3). To a solution of compound **2** (1.19 g, 4.1 mmol) in acetonitrile (50 mL) was added potassium carbonate (0.84 g, 6.1 mmol) and the reaction mixture was stirred for 1 h at reflux. To the reaction mixture, *tert*-butyl bromoacetate (0.97 g, 5.0 mmol) in acetonitrile (10 mL) was added slowly for 2 h using syringe pump and reaction was continued for additional 3 h at reflux. After completion of reaction, the precipitate was filtered through pad of Celite. After evaporation of solvent, the residue was extracted with methylene chloride (2x30 mL), washed with water (2x30 mL), dried over $MgSO_4$. The solvent was evaporated and the residue was purified by flash column chromatography (SiO_2, ethyl acetate) to give desired product in 75% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84-7.89 (m, 2H), 6.81-6.84 (d, 1H, *J*= 8.7 Hz), 4.69 (s, 2H), 3.60-4.30 (m, 12 H), 1.48 (s, 9H). Mass: 401 (M^+)

Preparation of *tert*-butyl 2-(4-amino-2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy} phenoxy)acetate (4). To a solution of compound **3** (1.2 g, 3.0 mmol) in 50 mL of

ethanol-THF (3:7) was added hydrazine monohydrate (0.9 g, 18.0 mmol) and 10% palladium on carbon (0.1 g) and the reaction mixture was stirred for 12 h at reflux.[3] After completion of reaction, the precipitate was filtered through pad of Celite. After evaporation of solvent, the residue was extracted with methylene chloride (2x 50 mL), washed with water (2x40 mL), dried over $MgSO_4$. After evaporation of solvent the desired product was obtained in 95% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.71-6.74 (d, 1H, J= 8.4 Hz), 6.27-6.28 (d, 1H, *J*= 2.4 Hz), 6.17-6.20 (m, 1H), 4.45 (s, 2H), 3.57-4.09 (m, 12H), 1.47 (s, 9H). Mass: 371 (M^+)

Preparation of *tert*-butyl 2-(4-{1-pyrenyl}butyramide-2-{2-[2-(2-hydroxy -ethoxy)ethoxy]ethoxy}phenoxy)acetate (5). To a solution of 1-pyrenebutyric acid (0.29 g, 1.0 mmol) in benzene (20 mL), oxalyl chloride (0.29 g, 2.0 mmol) and *N,N*-dimethylformamide (2 mL) were added and the reaction mixture was stirred for 12 h at room temperature. The solvent was evaporated and the residue was dissolved in tetrahydrofuran (20 mL). To the solution, triethylamine (0.20 g, 2.0 mmol) and **4** (0.37 g, 1.0 mmol) was added and stirred for 2 h at room temperature. After completion of the reaction, solvent was evaporated and the resulting residue was dissolved in methylene chloride (30 mL), washed with water (2x30 mL), and dried over $MgSO_4$. After evaporation of solvent the residue was purified by flash column chromatography (SiO_2, ethyl acetate) to give desired products in 55% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82-8.28 (m, 9H), 7.21 (d, 1H, *J*= 2.1 Hz), 6.98-7.01 (m, 1H), 6.72-6.75 (d, 1H, *J*=8.7Hz), 4.50 (s, 2H), 3.46-4.13 (m, 12 H), 3.36-3.41 (t, 2H, *J*=14.4 Hz), 2.24-2.35(m, 4H), 1.45 (s, 9H). Mass: 641 (M^+).

Preparation of 2-(4-{1-pyrenyl}butyramide-2-{2-[2-(2-hydroxyethoxy)ethoxy] -ethoxy}phenoxy)acetate (PD-1). The compound **5** (0.40 g, 0.62 mmol) and trifluoroacetic acid (1.0 mL) were dissolved in methylene chloride (30 mL) and the mixture was stirred for 2 h at room temperature. After completion of reaction, the reaction solution was washed with water (2x30 mL) and dried over $MgSO_4$. After evaporation of solvent the residue was purified by flash column chromatography (SiO_2, methylene chloride : methyl alcohol = 1:1) to provide the desired product in 73% yield. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 9.79 (s, 1H, NH), 7.95-8.42 (m, 10H, pyrenyl+OH), 7.31 (d, *J* = 1.6 Hz, 1H, ArH), 7.06 (dd, *J* = 8.1 Hz, 1.6 Hz, 1H, ArH), 6.78 (d, *J* = 8.1 Hz,

1H, ArH), 4.41 (s, 2H, CH_2), 4.03 (m, 2H, CH_2), 3.75-3.76 (m, 2H, CH_2), 3.33-3.61 (m, 10H, CH_2), 2.39-2.42 (m, 2H, CH_2), 2.09 (m, 2H, CH_2). Mass: 585 (M^+). Anal. Calcd for $C_{34}H_{35}NO_8$: C, 69.73; H, 6.02; N, 2.39%. Found: C, 70.10; H, 6.31; N, 2.40%.

References

1) E. Weber, *Chem. Ber.* 1985, **118**, 4439.

2) J. Auerbach, S. M. Weinlab, *J. Chem. Soc., Chem. Comm.*, **1974**, 298.

3) S. Ram, R. E. Ehrenkaufer, *Synthesis*, **1988**, 91.

2. Effect of γ-CyD concentration on response function of the **PD-1**/γ-CyD complex.

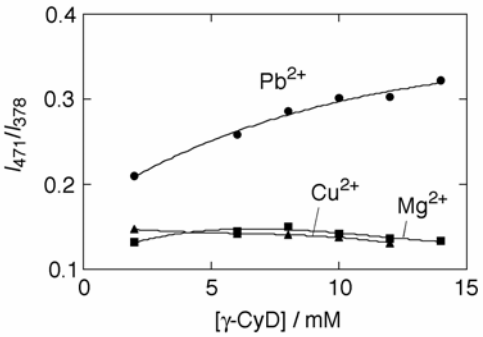


Fig. A Dependence of I_{471}/I_{378} on the γ-CyD concentration. **[PD-1]** = 2.0 x 10^{-6} M in 98% water/2% MeOH (v/v); $[M^{2+}]$ = 1.0 mM. Excitation wavelength, 328 nm. pH = 3.5 adjusted with 0.010 M acetate buffer.

3. Effect of p□ on response function of the **PD-1**/γ-CyD complex.

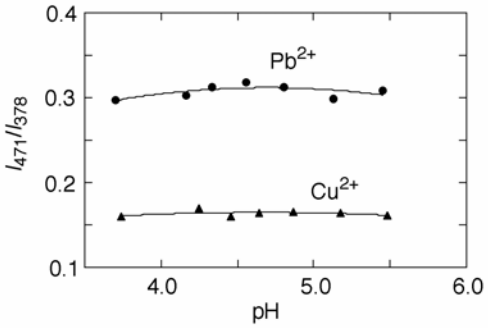


Fig. B Dependence of I_{471}/I_{378} on pH. **[PD-1]** = 2.0 x 10^{-6} M in 98% water/2% MeOH (v/v); $[M^{2+}]$ = 1.0 mM. Excitation wavelength, 328 nm. pH was adjusted with 0.010 M acetate buffer.

4. Metal ion selectivity of the **PD-1**/γ-CyD complex.

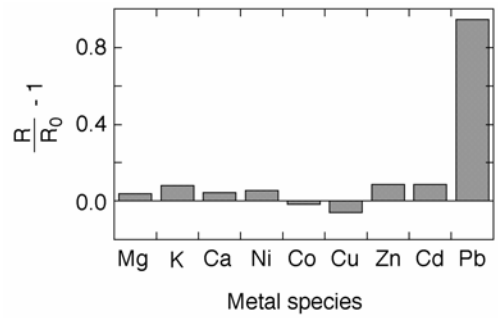


Fig. C Metal ion selectivity of **PD-1**/γ-CyD complex. **[PD-1]** = 2.0 x 10^{-6} M in 98% water/2% MeOH (v/v); [γ-CyD] = 12.0 mM. $[M^{2+}]$ = 1.0 mM. Excitation wavelength, 328 nm. pH = 4.3 adjusted with 0.010 M acetate buffer (I = 0.10 by $NaNO_3$). R_o and R denote I_{471}/I_{378} values in the absence and presence of metal cations.