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Reversible and Highly Selective Fluorescent Sensor for Mercury(II) Based on a Water-soluble Poly(para-phenylene)s Containing Thymine and Sulfonate Moieties

Experimental Parts

Materials and Instruments

Reagents were purchased and utilized as received unless indicated otherwise. All solvents were purified using standard procedures. Evaporation and concentration in vacuum were carried out at water aspirator pressure. Column chromatography: SiO_2 (200-300 meshes). ^{1}H and ^{13}C NMR spectra were obtained at Bruker ARX400, ARX600 spectrometer using tetramethylsilane (TMS) as internal standard. MALDI-TOF mass spectrometric measurements were performed on a Bruker Biflex MALDI-TOF Spectrometer. EI mass spectrometric measurements were performed on a SHZMADZU GCMS-QP2010 puls Spectrometer. FTIR spectra were obtained at a Bruker Tensor 27 Spectrometer. UV/vis spectra were measured on a Hitachi U-3010 spectrophotometer. The Fluorescence Spectra were measured on Hitachi F-4500 fluorimeter. The thermal analysis was recorded on the TA-60WS Thermal Analyzer.

1,4-bis(3-bromopropoxy)-2,5-diiodobenzene (1) was synthesized from 1,4-diiodo-2,5-dimethoxybenzene according to the literature procedure. [1] 2-(5-Methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)acetic acid (5) and Sodium 3,3'-(2,5-diiodo-1,4-phenylene)bis(oxy)dipropane-1-sulfonate (8) were synthesized according to the stander

procedure reported in the literature. [2-3] And 1,4-phenylenediboronic acid (9) was purchased in from Aldrich.

Synthesis of 1,4-bis(3-azidopropoxy)-2,5-diiodobenzene (2) To a solution of 1 (604 mg, 1 mmol) in 10 mL N,N-dimethylformamide (DMF) was added sodium azide (390 mg, 6 mmol). After stirring for 12 h at 60 °C, the solvents were removed under vacuum. Purification of the crude product by silica gel column chromatography (eluent: petroleum/chloroform, 1:4) yielded pure product (485 mg, 92 %) as white solid. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.2 (s, 2H), 4.2 (t, 4H), 2.1 (m, 4H), 1.28 (t, 4H). ^{13}C NMR ($CDCl_3$, δ, ppm): 153, 123, 86, 67, 48, 29. MS (EI): m/z= 528 (M^+), 527 (M^+).

Synthesis of *di-tert*-butyl 3,3'-(2,5-diiodo-1,4-phenylene) bis (oxy) bis (propane-3,1-diyl) dicarbamate (3) To a solution of compound 2 (527 mg, 1 mmol) in mixture solvent tetrahydrofunan (THF)/water (3 mL/4 mL) was added PPh_3 (655 mg, 2.5 mmol). After stirring for 12 h at room temperature, $(Boc)_2O$ (554 mg, 2.5 mmol) was added and the reaction mixture was stirred for another 4 h. THF was removed at reduced pressure and the water layer was extracted with Et_2O for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under vacuum. Purification of the crude product by silica gel column chromatography (eluent: petroleum/chloroform, 2:1) yielded pure product (553 mg, 82 %) as white solid. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.18 (s, 2H), 5.07 (s, 2H), 4.02 (t, 4H), 3.4 (t, 4H), 2.03 (q, 4H), 1.44 (s, 18H). ^{13}C NMR (($CDCl_3$, δ, ppm): 156, 152, 122, 86, 79, 53, 38, 29, 28. MS (MALDI-TOF): M=676.3, 699.1($M+Na^+$), 715.1 ($M+K^+$).

Synthesis of N,N'- (3,3'- (2,5-diiodo-1,4-phenylene) bis(oxy) bis (propane-3,1-diyl)) di (2-thyminacetic acid) (6) To a solution of compound 3 (338 mg, 0.5 mmol) in 2 mL CH_2Cl_2 trifluoroacetic acid (114 mg, 0.32 mL, 5 mmol) was added dropwise in 2 min. After stirring for 2 h at room temperature, the solvents were removed under vacuum. The residue was dissolved in 6 mL CH_2Cl_2, and triethylamine (101 mg, 0.7 mL, 5 mmol) was added. After stirring for 1 h, the solvent was removed under vacuum. The yielded white powder was dissolved in 6 mL of CH_2Cl_2, then a solution of 5 (184 mg, 1 mmol) and DhbtOH (328 mg, 1 mmol) in 5 mL of DMF was added. EDCI (230 mg, 1.15 mmol) and 4-dimethyl-aminopyridine (146 mg, 1.15 mmol) was added to the reaction mixture at 0 °C. After stirring for 1 h the solution was allowed to be warmed up to room temperature and further stirred for another 28 h. The reaction mixture was washed successively with saturated citric acid aqueous solution (3 × 20 mL) and water (2 × 30 mL). Then the aqueous layer was extracted with CH_2Cl_2 for three times. The combined organic phase was dried over anhydrous Na_2SO_4 and was removed under vacuum. The residue was washed with $CHCl_3$ and dried under vacuum to afford a white powder (212 mg, Yield 27 %). ^{1}H NMR (DMSO, δ, ppm): 11.51 (s, 2H), 8.44 (t, 2), 7.42 (s,2H), 7.33 (s,2H), 4.37 (s, 4H), 4.01 (t, 4H), 3.28, (t,4H), 1.84 (q, 4H), 1.37 (s, 6H). ^{13}C NMR (DMSO, δ, ppm): 167, 165, 153, 151, 143, 123, 108, 87, 68, 50, 36, 29, 12. MS (MALDI-TOF): M= 808.3, 808.3(M), 831.3 ($M + Na^+$), 847.2 ($M + K^+$). FTIR (KBr, cm^{-1}): 3293, 3056, 1673, 1565, 1464, 1383, 1212, 765, 641.

Synthetic procedure PBTS 1,4-phenylenediboronic acid (7) (22.2 mg, 0.13 mmol), monomer 6 (77 mg, 0.104 mmol) and monomer 8 (32 mg, 0.026mmol), a solution of K_2CO_3 (2 mL, 2 M), DMF (3 mL) and THF (4 mL) were mixed together in a flask. The mixture was

stirred at room temperature for 0.5 h under nitrogen atmosphere. After the addition of the catalyst [$PdCl_2(dppf)CH_2Cl_2$, 3 mol % with respect to the monomers], the mixture was heated to 70 °C for 48 h. After that, the reaction mixture was concentrated under vacuum, dissolved in H_2O, and dialyzed for 48 h with 3000 g/mol cutoff membrane, concentrated and dried, giving CPs as tan solid. (Yield: 36 mg, 46 %. ^{1}H NMR (DMSO, δ, ppm): 11.2 (b, N-H thymine) 8.18 (b, H-N-C=O), 7.68 (b, H-Ar, H-C=C), 5.75 (s, -NHCO), 4.32 (b, $PhOCH_2$-), 4.03 (b, CO-CH_2-thymine), 3.43 (b, -CH_2SO_3Na, -CH_2NHCO), 1.98 (b, -CH_2CH_2-SO_3Na, -CH_2CH_2NHCO), 1.73 (b, -CH_3). FTIR (KBr, cm^{-1}): 3295, 2954, 1658, 1626, 1573, 1403, 1378, 1280, 1208, 1044, 832, 703, 618.

Synthetic procedure for PBS 1,4-phenylenediboronic acid (22.2 mg, 0.13 mmol), monomer 7 (81.2 mg, 0.13mmol), a solution of K_2CO_3 (2 mL, 2 M), DMF (3 mL) and THF (4 mL) were mixed together in a flask. The mixture was stirred at room temperature for 0.5 h under nitrogen atmosphere. After the addition of the catalyst [$PdCl_2(dppf)CH_2Cl_2$, 3 mol % with respect to the monomers], the mixture was heated to 70 °C for 48 h. After that, the reaction mixture was concentrated under vacuum, dissolved in H_2O, and dialyzed for 48 h with 3000 g/mol cutoff membrane, concentrated and dried, giving PBS as tan solid. Yield: 20 mg, 36 %. ^{1}H NMR (D_2O, δ, ppm): 7.41 (b, H-Ar), 4.12 (b, $PhOCH_2$-), 3.14 (b, -CH_2SO_3Na), 2.14 (b, -CH_2CH_2 SO_3Na). FTIR (KBr, cm^{-1}): 2922, 1627, 1495, 1406, 1280, 1188, 1045, 833, 702, 613.

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