

Chemosensory Performance of Molecularly Imprinted Fluorescent Conjugated Polymer Materials

Jiahui Li, Claire E. Kendig, and Evgueni E. Nesterov,*

Supporting Information

General Procedures. All reactions were performed under an atmosphere of dry nitrogen. Melting points were determined in open capillaries and are uncorrected. Column chromatography was performed on silica gel (Sorbent Technologies, 60 Å, 40-63 µm) slurry packed into glass columns. All solvents were additionally purified and dried by standard techniques. High purity Pd(PPh₃)₄ was obtained from Strem Chemicals, Inc. All other reagents were obtained from Aldrich and Alfa Aesar and used without further purification. ¹H and ¹³C NMR spectra were recorded at 300 MHz and 75 MHz respectively, and are reported in ppm downfield from tetramethylsilane. FT-IR spectra of solid samples were recorded on Bruker Tensor 27 FT-IR spectrometer equipped with a total internal reflection module. UV-visible spectra were recorded on Varian Cary 50 UV-Vis spectrophotometer. Fluorescence studies were carried out with a PTI QuantaMaster4/2006SE spectrofluorimeter. Fluorescence quantum yields were determined using ethanol solution of Coumarin 6 as a standard (solution samples, Φ = 0.78¹) and ~ 1 mM 9,10-diphenylanthracene in PMMA spin-cast film (solid films, Φ = 0.83²). Cyclic voltammetry (CV) measurements were carried out in a standard 3-electrode electrochemical cell in 0.1 M Bu₄NPF₆ solution in CH₂Cl₂ as an electrolyte with 3 mm diameter glassy carbon or 2 mm diameter Pt button working electrode, Pt wire auxiliary electrode, and Ag/Ag⁺ reference electrode using Autolab PGSTAT 302 potentiostat from Eco Chemie. The data were corrected by the CV of ferrocene performed under the same conditions immediately before and after the measurements. GPC analyses were performed with Agilent 1100 chromatograph equipped with two PLgel 5 mm MIXED-C columns connected in series, using THF as a mobile phase, and calibrated against polystyrene standards. Polymer samples for fluorescence quenching studies were prepared using Laurell Technologies WS-400B-6NPP spin processor. Scanning Electron Microscopy images were acquired with Hitachi S-3600N microscope. High resolution mass spectra were obtained at the LSU Department of Chemistry Mass Spectrometry Facility using an ESI or MALDI-TOF method, and a peak matching protocol to determine the mass and error range of the molecular ion.

Synthetic details.

2,5-diiodo-1,4-hydroquinone (4) was prepared as described in the literature.³

1,4-Bis((diethylene glycol monomethyl ether)oxy)-2,5-diiodobenzene (5). A mixture of 14.5 g (0.04 mol) of **4**, 43.8 g (0.16 mol) of diethylene glycol monomethyl ether *p*-toluenesulfonate,⁴ 22.1 g (0.16 mol) of K₂CO₃, and 0.66 g (0.04 mol) of KI in 500 ml of methyl ethyl ketone was stirred at 100 °C for 48 h. After concentrating in vacuo, the dark brown residue was dissolved in CH₂Cl₂, and the solution was washed successively with 10% aqueous KOH solution, water and brine, and dried over Na₂SO₄. Concentration in vacuo afforded crude product as a brown solid, which was recrystallized from *n*-heptane – toluene mixture to give 18.4 g (81%) of **5** as a light-brown crystalline material, mp 90-92 °C. ¹H NMR (CDCl₃) δ 7.25 (s, 2H), 4.14-4.10 (m, 4H), 3.91-3.87 (m, 4H), 3.81-3.77 (m, 4H), 3.61-3.57 (m, 4H), 3.41 (s, 6H). HRMS *m/e* 588.9569 (M+Na)⁺ (calcd for C₁₆H₂₄O₆NaI₂ 588.9560).

1,4-Bis((diethylene glycol monomethyl ether)oxy)-2,5-diethynylbenzene (6). A mixture of 17.0 g (0.03 mol) of **5**, 8.8 g (12.6 ml, 0.09 mol) of (trimethylsilyl)acetylene, 1.44 g (7.5 mmol) of CuI, and 0.69 g (6.0 mmol) of Pd(PPh₃)₄ in 350 ml of toluene – *i*Pr₂NH (7:3) mixture was stirred at 70 °C in a sealed flask for 48 h. After cooling down to room temperature, the mixture was passed through a short column with silica gel eluted with CHCl₃. The solution was concentrated in vacuo, the resulting residue was dissolved in 200 ml of methanol, and added dropwise to a solution of 4.0 g (0.07 mol) of KOH in 500 ml of methanol. After stirring for 40 min, the mixture was poured into water, extracted with ether, the organic phase was washed successively with water, conc. NH₄Cl solution, water, brine, and dried over Na₂SO₄. Concentration in vacuo afforded solid material, which was dissolved in ethyl acetate – hexane (2:1) mixture and passed through a short column with silica gel. After concentration in vacuo, the resulting solid was recrystallized from hexane – CH₂Cl₂ mixture to give 4.4 g (41%) of **6** as a brown crystalline material, mp 88-90 °C. ¹H NMR (CDCl₃) δ 7.01 (s, 2H), 4.19-4.16 (m, 4H), 3.90-3.87 (m, 4H), 3.78-3.75 (m, 4H), 3.59-3.56 (m, 4H), 3.40 (s, 6H), 3.32 (s, 2H).

1,4-Bis((diethylene glycol monomethyl ether)oxy)-2,5-bis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethen-1-yl)benzene (7). A mixture of 2.26 g (6.24 mmol) of **6**, 1.75 g (2.00 ml, 13.7 mmol) of pinacolborane, and 0.16 g (0.62 mmol) of ZrCp₂HCl in 25 ml of 1,2-dichloroethane was stirred in a sealed flask at 65 °C for 72 h. After cooling down to RT, the reaction mixture was poured into water, and extracted with ether. The organic phase was washed with water, brine, and dried over Na₂SO₄. Concentration in vacuo afforded crude product as brown oil. The crude product

was passed through a column with silica gel eluted with ethyl acetate – hexane (3:1) to afford a yellow solid. Final recrystallization from hexane – CH₂Cl₂ afforded 2.1 g (54%) of **7** as a bright-yellow crystalline material, mp 124-126 °C. ¹H NMR (CDCl₃) δ 7.72 (d, *J* = 20.0 Hz, 2H), 7.10 (s, 2H), 6.15 (d, *J* = 20.0 Hz, 2H), 4.17-4.13 (m, 4H), 3.90-3.87 (m, 4H), 3.77-3.74 (m, 4H), 3.62-3.59 (m, 4H), 3.42 (s, 6H), 1.31 (s, 24H). HRMS *m/e* 641.3634 (M+Na)⁺ (calcd for C₃₂H₅₂B₂NaO₁₀ 641.3644).

(2,4,6-Triisopropylphenyl)methanol (9a). A solution of *t*-BuLi (6.24 ml of 1.7 M solution in pentane, 10.6 mmol) was added dropwise to a stirred at -75 °C solution of 1.0 g (3.5 mmol) of 2,4,6-triisopropylbromobenzene **8** in 30 ml of THF. The resulting mixture was stirred for 1 h at -75 °C, followed by dropwise addition of 0.111 g (3.7 mmol) of paraformaldehyde in 10 ml of THF. The reaction mixture was stirred at -75 °C for 1 h, and allowed to warm to room temperature overnight. It was poured into conc. NH₄Cl solution, and extracted with ether. The combined organic phase was washed with water, brine, and dried over Na₂SO₄. After concentration in vacuo, the resulting crude product was passed through a column with silica gel eluted with ethyl acetate – hexane (1:2) mixture. This afforded 0.6 g (72%) of **9a** as a colorless crystalline material, mp 95-96 °C. ¹H NMR (CDCl₃) δ 7.05 (s, 2H), 4.78 (d, *J* = 5.3 Hz, 2H), 3.38 (septet, *J* = 7.0 Hz, 2H), 2.89 (septet, *J* = 7.0 Hz, 1H), 1.29 (d, *J* = 7.0 Hz, 12H), 1.22 (d, *J* = 7.0 Hz, 6 H), 1.19 (t, *J* = 5.0 Hz, 1H). HRMS *m/e* 257.1887 (M+Na)⁺ (calcd for C₁₆H₂₆ONa 257.1875).

2,5-Diiodobenzoyl chloride (10). A mixture of 4.0 g (10.8 mmol) of 2,5-diiodobenzoic acid and 5.0 ml (68.7 mmol) of thionyl chloride was refluxed for 2 h. After allowing to cool down to RT, unreacted thionyl chloride was distilled out, and the crude product was recrystallized from hexane to afford 3.7 g (88%) of **10** as a colorless crystalline material, mp 93-94 °C. ¹H NMR (CDCl₃) δ 8.31 (d, *J* = 2.0 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.56 (dd, *J*₁ = 8.3, *J*₂ = 2.0 Hz, 1H).

2,4,6-Triisopropylbenzyl 2,5-diiodobenzoate (11a). A mixture of 0.84 g (2.1 mmol) of **10**, 0.50 g (2.1 mmol) of **9a**, and 0.29 g (2.4 mmol) of 4-(*N,N*-dimethylamino)pyridine in 40 ml of CH₂Cl₂ was stirred at room temperature for 24 h. The reaction mixture was poured into 10% aqueous HCl, extracted with ether, washed with conc. NH₄Cl solution, water and brine, and dried over Na₂SO₄. Concentration in vacuo afforded white solid which was recrystallized from hexane to yield 1.0 g (80%) of **11a** as a colorless crystalline material, mp 115-117 °C. ¹H NMR (CDCl₃) δ 8.02 (d, *J* = 2.2 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.43 (dd, *J*₁ = 8.4, *J*₂ = 2.2 Hz, 1H), 7.08 (s, 2H), 5.50 (s, 2H), 3.30 (septet, *J* = 6.9 Hz, 2H), 2.92 (septet, *J* = 7.0 Hz, 1H), 1.29 (d, *J* = 6.9 Hz, 12H), 1.28 (d, *J* = 7.0 Hz, 6H). HRMS *m/e* 613.0052 (M+Na)⁺ (calcd for C₂₃H₂₈O₂NaI₂ 613.0071).

Benzyl 2,5-diiodobenzoate (11b) was prepared following the procedure for compound **11a**. Reaction of 0.62 g (1.58 mmol) of **10**, 0.17 g (0.16 ml, 1.58 mmol) of benzyl alcohol **9b**, and 0.22 g (1.80 mmol) of 4-(*N,N*-dimethylamino)pyridine in 30 ml of CH₂Cl₂ afforded, after column chromatography purification, 0.51 g (70%) of **11b** as a colorless oil. ¹H NMR (CDCl₃) δ 8.09 (d, *J* = 1.3 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.50-7.30 (m, 6H), 5.37 (s, 2H). HRMS *m/e* 464.8849 (M+H)⁺ (calcd for C₁₄H₁₁O₂I₂ 464.8848)

1,3,5-Triiodobenzene (12) was prepared following the literature procedure,⁵ mp 182-185 °C (lit.⁶ mp 183 °C).

Polymer P1. A mixture of 100 mg (0.162 mmol) of **7**, 39.5 mg (0.070 mmol) of **5**, 10.3 mg (0.017 mmol) of **11a**, 21.7 mg (0.048 mmol) of **12**, 4.0 mg (0.0035 mmol) of Pd(PPh₃)₄, 134 mg (0.97 mmol) of K₂CO₃, and 200 mg (0.69 mmol) of sodium dodecyl sulfate in 30 ml of water – toluene – ethanol (10 : 1 : 4) mixture was stirred at 1000 rpm in a sealed Schlenk flask at 75 °C for 72 h. After cooling down to room temperature, the reaction mixture was poured into acetone, centrifuged, and supernatant solution was discarded. The solid residue was transferred into water, ultrasonicated for 40 min, separated, and washed successively with water, methanol, and acetone, each time upon ultrasonication. Finally, the product was dried in vacuo to afford 40 mg (50%) of the polymer **P1** as a red powder.

Polymer P2. A solution of lithium *n*-propyl mercaptide (1.0 ml of ~0.5 M solution in HMPA, prepared as described in literature⁷) was added to the polymer **P1** (25 mg) suspended in 5 ml of HMPA placed in a Schlenk flask. The flask was sealed, and the reaction mixture was ultrasonicated at room temperature for 1.5 h. The resulting mixture was poured into methanol, supernatant solution was removed by centrifugation, and the solid residue was washed with methanol. The solid product was refluxed with a mixture of 20 ml of methanol and 1 ml of conc. HCl for 24 h, separated, and washed with boiling methanol in a Soxhlett extractor. This was followed by washing successively with methanol and acetone, each time upon ultrasonication. The resulting product was dried in vacuo. This afforded 14 mg (60%) of **P2** as an orange powder.

Polymer P3. The polymer was prepared following the procedure for polymer **P1**. Reaction of 100.0 mg (0.162 mmol) of **7**, 71.9 mg (0.127 mmol) of **5**, 18.7 mg (0.032 mmol) of **11a**, 4.0 mg (0.0035 mmol) of Pd(PPh₃)₄, 134 mg (0.97 mmol) of K₂CO₃, and 200 mg of sodium dodecyl sulfate in 30 ml of water – toluene – ethanol (10 : 1 : 4) mixture afforded 20 mg (20%) of the polymer **P3** as a red powder. ¹H NMR (CDCl₃) δ 7.47 (br. s, 2H), 7.21 (s, 2H), 4.39-4.10 (m, 4H), 4.10-3.85 (m, 4H), 3.85-3.68 (m, 4H), 3.68-3.46 (m, 4H), 3.39 (br. s, 6H). The spectrum also shows signals belonging to

the template. Integration of the template signals at 5.53 (s, 2H of template) and 1.28 (m, 18H of template) allowed to estimate the fraction of the template to be ~10%. GPC analysis: M_n 9500 Da, PDI 1.65.

Polymer P4. The polymer was prepared starting from 10 mg of polymer **P3** following the procedure for polymer **P2**. This yielded 5 mg (50%) of the polymer **P4** as an orange powder. 1H NMR ($CDCl_3$) δ 7.43 (d, $J \sim 14$ Hz, 2H), 7.18 (br. s), 4.39-4.10 (m, 4H), 4.10-3.85 (m, 4H), 3.85-3.68 (m, 4H), 3.68-3.46 (m, 4H), 3.37 (br. s, 6H). The template was not detectable by 1H NMR analysis. GPC analysis: M_n 12500 Da, PDI 2.06.

Polymers P5 and P6. The polymer **P5** was prepared following the procedure described for the polymer **P1**. Reaction of 60.0 mg (0.097 mmol) of **7**, 23.8 mg (0.042 mmol) of **5**, 4.6 mg (0.010 mmol) of **11b**, 13.2 mg (0.029 mmol) of **12**, 3.35 mg (0.0029 mmol) of $Pd(PPh_3)_4$, 80.3 mg (0.582 mmol) of K_2CO_3 , and 150 mg of sodium dodecyl sulfate in 20 ml of water – toluene – ethanol (10 : 1 : 4) mixture afforded 15 mg (50%) of the polymer **P5** as an orange-red powder. This polymer (10 mg) was converted to **P6** following the procedure for the polymer **P2**. This yielded 6 mg (60%) of **P6** as an orange powder.

2,4,6-Trinitrotoluene (TNT) and **1-tert-butyl-2,4-dinitrobenzene (BDNB)** were prepared according to literature procedures.^{8,9} *Caution: TNT is high explosive and should be handled only in small quantities.*

Vapor phase fluorescence quenching studies.

Polymers were spin-cast from ~1 mg/ml solutions in $CHCl_3$ (for **P3** and **P4**) or from ~1 mg/ml suspensions in $CHCl_3$ (for **P2** and **P6**) on 22×22 mm microscope glass cover slides at 2500 rpm in nitrogen atmosphere. A polymer-covered slide was attached inside a 40×40×10 mm quartz fluorescent cell containing cotton wool mixed with a solid quencher at the bottom. The cell was immediately capped and placed into a sample compartment of a spectrofluorimeter, and fluorescence spectra were automatically recorded at specified time intervals, using a customized program written in Macro Command Editor of PTI FeliX32 software.

Additional figures.

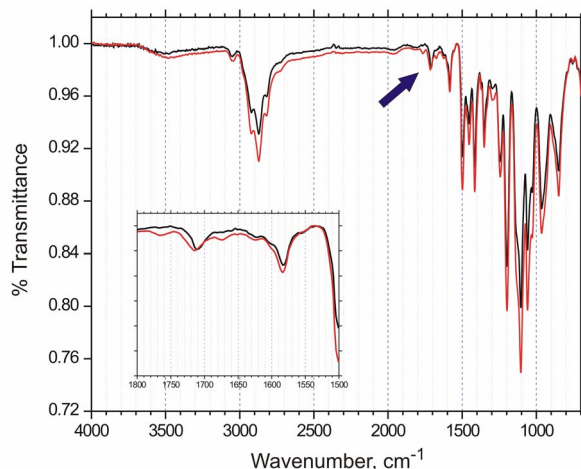


Figure S1. FT-IR spectra of the polymers **P5** and **P6**. Black trace corresponds to the polymer **before** template removal (**P5**), red trace corresponds to the MICP **P6**. The carbonyl stretching frequency bands used to determine the extent of template removal are shown with blue arrows, and the area around this signal is expanded in the inset. The frequency shift is $\sim 6\text{ cm}^{-1}$.

References.

- (1) Reynolds, G. A.; Drexhage, K. H. *Opt. Commun.* **1975**, *13*, 222-225.
- (2) Osaheni, J. A.; Jenekhe, S. A. *J. Am. Chem. Soc.* **1995**, *117*, 7389-7398.
- (3) Zhou, Q.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 7017-7018.
- (4) Snow, A. W.; Foos, E. E. *Synthesis* **2003**, 509-512.
- (5) Gan, Z.; Roy, R. *Can. J. Chem.* **2002**, *80*, 908-916.
- (6) Beinhoff, M.; Karakaya, B.; Schluter, A. D. *Synthesis* **2003**, 79-90.
- (7) Bartlett, P. A.; Johnson, W. S. *Tetrahedron Lett.* **1970**, 4459-4462.
- (8) Dorey, R. C.; Carper, W. R. *J. Chem. Eng. Data* **1984**, *29*, 93-97.
- (9) Dangel, B. D.; Godula, K.; Youn, S. W.; Sezen, B.; Sames, D. *J. Am. Chem. Soc.* **2002**, *124*, 11856-11857.