Supporting Information

Conjugated Polyelectrolyte Containing a High Density of Pendant Phenylboronic Acid Groups for Dopamine Detection

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1. Experimental

1.1 Synthesis of monomer 1 (M1).

2,7-Dibromo-9,9-bis(3'(N,N-dimethylamino)propyl)fluorene (M1). To a stirred mixture of 2,7-dibromofluorene (3.05 g, 9.4 mmol) and 60 ml dimethyl sulfoxide (DMSO), under argon were added tetrabutylammonium bromide (60 mg) and 8 mL of a 50 wt.% aqueous solution of sodium hydroxide. 20 mL DMSO solution of 3-dimethylamino propyl chloride hydrochloride (3.5 g, 22 mmol) was added dropwise to the mixture. The reaction mixture was stirred at room temperature for 6 hours, and then diluted with 50 mL of water to dissolve all the salts. Extract the product with ether (3×100 mL) and wash with water (3×100 mL) and saturated sodium chloride (100 mL). The organic layer is combined, dried by MgSO₄, filtered, and the solvent is removed under reduced pressure to give a solid. Recrystallization of the crude solids from MeOH/H₂O to give white crystals as the final product (2.15 g, yield 47.8%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.52 (d, 2H), 7.47 (s, 3H), 7.44 (s, 1H), 1.99 (m, 14H), 1.69 (s, 4H), 0.75 (m, 4H). FTIR (cm⁻¹): 2965, 2937, 2856, 2822, 2776, 1454, 1403, 1371, 1272, 1130, 1052, 1016, 673. Elemental Anal. Calcd for C₂₃H₃₀Br₂N₂ (%): C, 55.89; H, 6.12; N, 5.67. found: C, 55.31; H, 6.04; N, 5.91.

1.2 Synthesis of monomer 2 (M2).

2,5-Dibromohydroquinone. Hydroquinone (4.26 g, 0.039 mol, dissolved in 20 mL of acetic acid) was placed into a 500 mL Schlenk flask, followed by the dropwise addition of 4 mL of bromine (dissolved in 18 mL of acetic acid) over a period of 3 h. The reaction mixture was stirred overnight at 0 °C. The resulting solid after filtration was recrystallized over methanol/deionized water to give pure white crystals, which were collected and dried in vacuum overnight (3.52 g, yield 32.9%).

1,4-Bis(3'-(N,N-dimethylamino)propyl)-2,5-Dibromobenzene. 2,5-Dibromohydroquinone (2.67 g, 10 mmol) and 3-(Dimethylamino) propyl chloride hydrochloride (3.16 g, 20 mmol) were placed into a 100 mL flask, and then dissolved in dimethyl sulfoxide (DMSO) (30 mL) with the aid of magnetically stirring. Then KOH (8.4 g, 0.15 mol), which was ground into a fine powder in advance, was added.
The reaction mixture was stirred overnight at 20°C. Then the reaction mixture was poured into ice water and allowed to stand for 12 hours. The mixture is filtered through a Buchner funnel under reduced pressure. The solid was washed three times with ice water to give a white solid (3.75 g, yield 42.8%).

**2,5-Bis(3’-(N,N-dimethylamino)propyl)-1,4-di(trimethylsilylethynyl)benzene.** 1,4-Bis(3’-(N,N-dimethylamino)propyl)-2,5-Dibromobenzene (2.18 g, 5 mmol), CuI (0.026 g, 0.14 mmol), (PPh₃)₂PdCl₂ (0.145 g, 0.20 mmol), and diisopropylamine (20 mL) were added to a 100 mL round bottom flask under argon atmosphere. The substrate was stirred until dissolved and trimethylethynyl silicon (1.5 mL) was added dropwise to the mixture. The mixture was stirred at room temperature for 1 hour and then refluxed for 12 hours. The reaction was terminated and cooled to room temperature. After filtration, the filtrate was collected and the solvent was removed under reduced pressure to give a black solid. The crude product was purified by silica gel column chromatography (dichloromethane/ethyl acetate/triethylamine, 100:50:1, v/v). After removing the solvent, a brown product (2.05 g, yield 86.9%) was obtained.

**2,5-Bis(3’-(N,N-dimethylamino)propyl)-1,4-diethynylbenzene(M2).** 2,5-Bis(3’-(N,N-dimethylamino)propyl)-1,4-di(trimethylsilylethynyl)benzene (1.42 g, 3 mmol) was dissolved in 20 mL of tetrahydrofuran in a 100 mL flask, and then 6 mL of n-Bu₄NF (1 M) dissolved in tetrahydrofuran was added. The mixture was stirred for 0.5 h at room temperature. After finishing the reaction, 30 mL of deionized water was added to the reaction mixture and extracted with 3×100 mL of dichloromethane. The organic phases were combined and anhydrous sodium sulfate was added to remove the water. The excess solvent was removed by rotary evaporation under reduced pressure to give the crude product, which was purified by dichloromethane/petroleum ether (2:1, v/v) on a neutral alumina column. The solvent was removed to obtain a light brown solid (0.82 g, yield 83.1%).¹H NMR (400 MHz, CDCl₃, ppm): δ 6.98 (s, 2H), 4.03 (t, J = 8.5 Hz, 4H), 3.33 (s, 2H), 2.48 (t, J = 9.6 Hz, 4H), 2.25 (s, 12H), 1.95 (t, 4H). FTIR (cm⁻¹): 3160, 2966, 2938, 2854, 2817, 2775, 1492, 1459, 1386, 1226, 1033, 964, 873, 730. Elemental Anal. Calcd for C₂₀H₂₈N₂O₂ (%): C, 73.14; H, 8.95; N, 8.53. found: C, 67.71; H, 8.32; N, 8.18.
1.3 Synthesis of 4-bromomethylphenylboronic acid pinacol ester

**4-bromomethylphenylboronic acid.** 4-methylphenylboronic acid (4.02 g, 30 mmol), 2 mL of bromine and 40 mL of carbon tetrachloride were added to a 250 mL flask. The mixture was slightly heated for several minutes, followed by stirring at room temperature and under ambient light for 48 h. Afterwards, the solid was filtered and washed three times with hexane to give a white solid (4.72 g, 73.5%).

**4-bromomethylphenylboronic acid pinacol ester.** To a stirred 250 mL flask was added 4-bromomethylphenylboronic acid (2.4 g, 11 mmol), pinacol (1.45 g, 12 mmol) and ether (30 mL), and finally acetic acid (1.8 mL) was added dropwise. The reaction was carried out at room temperature for 3 h. After finishing the reaction, 100 mL of dichloromethane was added to the flask. The mixture was washed with 100 mL of deionized water which was repeated for three times, and the organic layer was collected and combined, and then dried with anhydrous sodium sulfate. Removing solvent produced a colorless solid (2.65 g, 81.3%). \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm): \(\delta 7.78\) (d, \(J=7.8\) Hz, 2H), 7.39 (d, \(J=7.8\) Hz, 2H), 4.49 (s, 2H), 1.34 (s, 13H).

2. Schemes, Figures, and Tables

![Scheme S1](image-url)

**Scheme S1.** The synthetic routes of the monomers.
Scheme S2. The synthetic route of 4-bromomethylphenylboronic acid pinacol ester.

Figure S1. $^1$H NMR spectra of M1 in CDCl$_3$.

Figure S2. $^{13}$C NMR spectra of M1 in CDCl$_3$. 
Figure S3. $^1$H NMR spectra of M2 in CDCl$_3$.

Figure S4. $^{13}$C NMR spectra of M2 in CDCl$_3$. 
Figure S5. $^1$H NMR spectra of PFPE-NMe$_2$ in CDCl$_3$.

Figure S6. $^1$H NMR spectra of PFPE-PBA in CD$_3$OD.
**Figure S7.** FTIR spectra of the monomers and the polymers.

**Figure S8.** GPC curve of PFPE-NMe₂ with polystyrene as a standard and THF as the eluent.

**Table S1.** The GPC data of PFPE-NMe₂.

<table>
<thead>
<tr>
<th></th>
<th>$\overline{M}_n$ (kDa)</th>
<th>$\overline{M}_w$ (kDa)</th>
<th>$D$</th>
<th>$\bar{X}_n$</th>
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</thead>
<tbody>
<tr>
<td>PFPE-NMe₂</td>
<td>6.2</td>
<td>14.0</td>
<td>2.26</td>
<td>18</td>
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Figure S9. Chemical Structures of PB, Tris and Gly.

Figure S10. Fluorescence spectra of PFPE-PBA in different buffers at different time: (a) Tris-NaOH (b) PB (c) Gly-NaOH. Buffer concentrations were fixed at 20 mM and the pH was set at 7.4. (d) Plots of fluorescence intensity of PFPE-PBA at 452 nm against the time in different buffers.
Figure S11. Fluorescence emission spectra of PFPE-PBA at different pHs, and (b) emission spectra after the addition of 15 μM DA, respectively, and (c) fluorescence intensities at 452 nm (black bars for the before and red bars for the after adding 15 μM DA and) and (d) fluorescence quenching efficiencies of PFPE-PBA at 452 nm. The quenching efficiency was calculated as $(1 - I/I_0) \times 100\%$, where $I_0$ is the fluorescence intensity of the initial PFPE-PBA solutions at 452 nm and $I$ is the fluorescence intensity at 452 nm after adding DA.
**Figure S12.** (a) Fluorescence spectra and (b) quenching efficiencies at 452 nm of PFPE-PBA solutions before and after the addition of DA (15 μM) in mixed solvents with different MeOH/H₂O volume ratios.

**Figure S13.** Stern-Volmer plots of PFPE-PBA with DA. The polymer concentrations were fixed at 5 × 10⁻⁵ with respect to the repeat unit. Kᵥ was calculated at low concentration of DA where the plots are approximately linear. I was the fluorescence intensity at 452 nm for PFPE-PBA.
Figure S14. Plot of fluorescence quenching efficiencies at 452 nm against the time after the adding 15 μM DA into PFPE-PBA solution.

Table S2. Comparison of the sensitivity and rapidity of the PFPE-PBA sensory system in this study with other sensory systems reported in the literature with regard to DA.

<table>
<thead>
<tr>
<th>Name</th>
<th>Method</th>
<th>LOD</th>
<th>Response Time</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>/</td>
<td>HPLC with fluorimetric</td>
<td>0.031 μg/mL</td>
<td>15 min</td>
<td>1</td>
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<tr>
<td>CuSrGO</td>
<td>Colorimetric</td>
<td>0.48 μM</td>
<td>&gt;15 min</td>
<td>2</td>
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<tr>
<td>Cu-MOXs-TMB-H2O2</td>
<td>Colorimetric</td>
<td>85 nM</td>
<td>20 min</td>
<td>3</td>
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<tr>
<td>rGO-SS</td>
<td>Electrochemical</td>
<td>&lt;1 μM</td>
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<td>4</td>
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<tr>
<td>N-CQDs (quantum dots)</td>
<td>Fluorescent chemosensing</td>
<td>35 nM</td>
<td>35 min</td>
<td>5</td>
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<tr>
<td>Ru-CIP-SDBS (Ru (II) complex)</td>
<td>Fluorescent chemosensing</td>
<td>6 nM</td>
<td>1 h</td>
<td>6</td>
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<tr>
<td>C-Au NCs (gold nanocluster)</td>
<td>Fluorescent chemosensing</td>
<td>1 nM</td>
<td>1 h</td>
<td>7</td>
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<tr>
<td>Material/Conjugate</td>
<td>Methodology</td>
<td>Fluorescence Sensing</td>
<td>KD (μM) / Sensitivity (ng/mL)</td>
<td>Time to Signal</td>
</tr>
<tr>
<td>-------------------</td>
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<tr>
<td>PBAQA (molecules)</td>
<td>Fluorescent chemosensing</td>
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<td>PFPBA NPs (nanoparticles)</td>
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<td>HRP–H₂O₂–PPESO₃ (Conjugated polymers)</td>
<td>Fluorescent chemosensing</td>
<td>0.14 μM</td>
<td>20 min</td>
<td>10</td>
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<tr>
<td>PFPE-PBA (Conjugated polyelectrolytes)</td>
<td>Fluorescent chemosensing</td>
<td>23 nM / 4.3 ng/mL</td>
<td>&lt;5 min</td>
<td>This work</td>
</tr>
</tbody>
</table>

**Figure S15.** Chemical structures of polyols.

**Figure S16.** Fluorescence spectra of PFPE-PBA before and after the addition of the two stock solutions of (a) serum and (b) artificial urine, respectively. The final concentrations of DA in PFPE-PBA solutions are labeled in the figures.
Figure S17. Digital photographs of PFPE-PBA solutions containing different concentrations of DA irradiated by a red laser pointer under natural light and under UV light (365 nm).

Figure S18. (a) Absorption spectrum of aqueous DA solution (0.5 mM). (b) Absorption spectra of PFPE-PBA upon addition of different concentrations of DA.

3. Additional Calculation and Discussions

3.1 Determining the Limit of Detection

The limit of detection (LOD) of PFPE-PBA to DA was calculated using linear regression theory, according to the following equations.

\[ S_a = \sqrt{\frac{\sum_{i=0}^{n}(x_i - \bar{x})^2}{n-1}} \]  

(S1)

\[ S = \frac{\Delta I}{\Delta c} \]  

(S2)
$\text{LOD} = \frac{3s_a}{|S|}$  \hspace{1cm} (S3)

$s_a$ represents the standard deviation of the fluorescence intensity of the initial polymer solution. The fluorescence intensity of the solution ($x_i$) was first measured and repeated 10 times to calculate the corresponding average intensity ($\bar{x}$), and then the standard deviation value ($s_a$) was calculated according to equation S1. Next, different concentrations of DA were added to the solution, whose fluorescence intensity varied linearly at low concentrations, and $s$ in equation S2 was the slope value. Finally, with the values of $s_a$ and $s$ as determined, the LOD for the system was calculated according to equation S3.

### 3.2 Determination of the Stern–Volmer Constant ($K_{SV}$)

The Stern-Volmer constant ($K_{SV}$) is calculated according to the following equation.

$$\frac{I_0}{I} = 1 + K_{SV}[Q]$$ \hspace{1cm} (S4)

$I_0$ is the initial fluorescence intensity at 452 nm of PFPE-PBA, $I$ is the fluorescence intensity at 452 nm of PFPE-PBA after adding DA, and $[Q]$ is the concentration of DA. $K_{SV}$ was calculated at low concentration of DA where the plots are approximately linear.

### 3.3 Determination of Recovery and RSD

Recoveries are calculated according to the following equation.

$$\text{Recovery} = \left(\frac{A}{B}\right) \times 100\%$$ \hspace{1cm} (S5)

$A$ is the known concentration of dopamine added, and $B$ is the value of the dopamine concentration determined using the fluorescence method. Fluorescence spectra were recorded before and after the addition of stock samples to polymer solutions, the value of $I_0/I$ at 452 nm was calculated, and the $B$ value was calculated from the linear portion of the Stern-Volmer curve at low concentrations in Figure S13.

The formula for calculating RSD is as follows.

$$RSD = \frac{SD}{\bar{x}}$$ \hspace{1cm} (S6)

$\bar{x}$ represents the average of the calculated results and $SD$ is the standard deviation.

$$SD = \sqrt{\frac{\sum_{i=0}^{n} (x_i-\bar{x})^2}{n-1}}$$ \hspace{1cm} (S7)
4. References


(9) Qian, C. G.; Zhu, S.; Feng, P. J.; Chen, Y. L.; Yu, J. C.; Tang, X.; Liu, Y.; Shen, Q.