Electronic Supplementary Information for

A tetrathiafulvalene vinylogue-based double-layer polymer thin film as a highly sensitive and selective TNT sensor

Farshid Shahrokhi and Yuming Zhao*

Department of Chemistry, Memorial University of Newfoundland
St. John’s, NL, Canada A1B 3X7
Email: yuming@mun.ca

Table of Content

1. Experimental .................................... S-2
2. NMR Spectra for New Compounds .......... S-8
3. Detailed Results of UV-Vis Titration Experiments ................................................. S-21
4. Detailed Results of Differential Pulse Voltammetric Titrations ......................... S-22
5. Optical Profiling and SEM Images of Polymer Films ......................................... S-26
1. Experimental

1.1 General

Chemicals were purchased from commercial suppliers and used directly without purification. All reactions were conducted in standard, dry glassware. Evaporation and concentration were carried out with a rotary evaporator. Flash column chromatography was performed with 240-400 mesh silica gel, and thin-layer chromatography (TLC) was carried out with silica gel F254 covered on plastic sheets and visualized by UV light. Melting points (m.p.) were measured using an SRS OptiMelt melting point apparatus and are uncorrected. $^1$H and $^{13}$C NMR spectra were measured on a Bruker Avance III 300 MHz multinuclear spectrometer. Chemical shifts ($\delta$) are reported in ppm downfield relative to the signals of the internal reference SiMe$_4$ or residual solvents (CHCl$_3$: $\delta_H = 7.24$ ppm, $\delta_C = 77.2$ ppm; CH$_2$Cl$_2$: $\delta_H = 5.32$ ppm, $\delta_C = 54.0$ ppm). Coupling constants ($J$) are given in Hz. Infrared spectra (IR) were recorded on a Bruker Alfa spectrometer. MALDI-TOF MS analysis was performed on Bruker 9.4T Apex-Qe FTICR system. High-resolution APPI-TOF MS analysis was done on a GCT premier Micromass Technologies instrument. UV-Vis absorption spectra were measured on a Cary 6000i spectrophotometer. Surface topography of polymer thin films was visualized by using a New View 8000 3D optical surface profiler (Zygo Corporation) and FEI MLA 650F scanning electron microscope (SEM). Samples for SEM imaging were subjected to Au sputter coating before analysis. Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) analyses were carried out in a standard three-electrode setup controlled by a BASi Epsilon potentiostat. Experimental conditions were set up as follows. CV analysis: glassy carbon or indium tin oxide (ITO) coated glass as the working electrode, Pt wire as the counter electrode, Ag/AgCl as the reference electrode, scan rate = 100 mV/s. DPV analysis: glassy carbon as the working electrode, Pt wire as the counter electrode, Ag/AgCl as the reference electrode, step E = 4 mV, pulse width = 50 ms, pulse period = 200 ms, scan rate = 20 mV/s. All samples were measured in CH$_2$Cl$_2$ using Bu$_4$NBF$_4$ as electrolyte.

1.2 Synthetic procedures

4,4’-((9H-Fluoren-9-ylidene)methylene)dibenzaldehyde (5)

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{Br} & \quad \text{Br}
\end{align*}
\]

9-((Dibromomethylene)-9H-fluorene (3) (0.500 g, 1.489 mmol), 4-formylphenylboronic acid (4) (0.665 g, 4.46 mmol), cesium carbonate (2.418 g, 7.440 mmol), THF (25 mL), and deionized water (10 mL) were added to 50 mL round-bottomed flask. The mixture was bubbled with N$_2$ flow for 5 min, and then Pd(PPh$_3$)$_4$ (0.172 g, 0.148 mmol) was added. The reaction mixture was stirred under N$_2$ and heated at reflux 24 h. The reaction mixture was next cooled down to room temperature, poured into a separatory funnel including water, and extracted twice with CH$_2$Cl$_2$. 

S-2
The organic layers were combined and dried over MgSO₄. After filtration and concentration under gentle heating and reduced pressure, the resulting residue was subjected to silica gel column chromatography (hexanes/EtOAc, 9:1) to give pure compound 5 (0.471 g, 1.219 mmol, 82%) as a yellow crystalline solid. m.p.: 199–202 °C; IR (neat): 3054, 2833, 2735, 1692, 1596, 1562, 1432, 1202, 1164 cm⁻¹; ¹H NMR (300 MHz, CD₂Cl₂): δ 10.07 (s, 2H), 7.95 (d, J = 8.4 Hz, 4H), 7.72–7.67 (m, 2H), 7.57 (d, J = 8.1 Hz, 4H), 7.27 (td, J = 7.5, 1.0 Hz, 2H), 6.95 – 6.88 (m, 2H), 6.58 (dt, J = 7.9, 0.8 Hz, 2H) ppm; ¹³C NMR (75 MHz, CD₂Cl₂): δ 192.02, 148.53, 142.04, 141.25, 138.23, 136.57, 136.41, 130.77, 130.67, 128.99, 127.15, 125.44, 119.94 ppm; HRMS (APPI-TOF, positive mode): m/z calcd for C₂₈H₁₈O₂ [M]+ 386.1307, found 386.1295. X-ray.

9-(Bis(4-(2,2-dibromovinyl)phenyl)methylene)-9H-fluorene (6)

![Chemical structure of 9-(Bis(4-(2,2-dibromovinyl)phenyl)methylene)-9H-fluorene (6)]

Compound 5 (1.043 g, 2.699 mmol), CBr₄ (4.470 g, 13.51 mmol), PPh₃ (5.663 g, 21.62 mmol), CH₂Cl (50 mL) were added to a 100 mL round-bottomed flask. The reaction mixture was stirred at room temperature for 1.5 hours and then subjected to vacuum filtration. The solids collected were extracted with CH₂Cl₂ and the organic layers were combined and concentrated under reduced pressure. The resulting residue was subjected to silica gel column chromatography (hexanes/CH₂Cl₂, 4:1) to give pure compound 6 (1.734 g, 2.484 mmol, 92%) as a pale yellow solid. m.p.: 213–216 °C; IR (neat): 3019, 1595, 1500, 1439, 1402, 1256, 1113, 1018, 785, 765 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.72 (d, J = 7.5 Hz, 2H), 7.65 (d, J = 8.2 Hz, 4H), 7.57 (s, 2H), 7.40 (d, J = 8.3 Hz, 4H), 7.32–7.24 (m, 2H), 7.00–6.93 (m, 2H), 6.70 (d, J = 7.9 Hz, 2H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 143.68, 142.86, 140.75, 138.51, 136.50, 135.36, 135.23, 130.22, 129.03, 128.14, 126.68, 125.01, 119.54, 90.31 ppm; HRMS (APPI-TOF, positive mode): m/z calcd for C₄₈H₂₉Br₈ [M + H]+ 693.8123, found 693.8142.

2,2'-(((9H-fluoren-9-ylidene)methylene)bis(4,1-phenylene))bis(methaneylelylidene))bis(4,5-bis(methylthio)-1,3-dithiole) (9a)
Compound 5 (0.151 g, 0.391 mmol), 4,5-bis(methylthio)-1,3-dithiole-2-thione (8a) (0.265 g, 1.173 mmol), and P(OMe)₃ (15 mL) were added to a 100 mL round-bottomed flask. The flask was placed in an oil bath heated at 145 °C and kept in it for 5 h. After that, the reaction mixture was subjected to under vacuum distillation at the same temperature to remove unreacted P(OMe)₃. The residue was subjected to silica gel column chromatography (hexanes/EtOAc, 7:3) to give pure compound 9a (0.189 g, 0.254 mmol, 65%) as a deep-orange oil. Caution: the product is quite sensitive to air and light, and it needs to be stored in a fridge immediately after purification to prevent significant decomposition. IR (neat): 3054, 3021, 2990, 2918, 2852, 1567, 1540, 1502, 1443, 1314, 1184 cm⁻¹; ¹H NMR (300 MHz, CD₂Cl₂): δ 7.71 (d, J = 7.3 Hz, 2H), 7.38–7.32 (m, 4H), 7.30–7.21 (m, 6H), 6.94 (td, J = 7.7, 1.2 Hz, 2H), 6.77 (d, J = 7.9 Hz, 2H), 6.57 (s, 2H), 2.45 (s, 6H), 2.43 (s, 6H) ppm; ¹³C NMR (75 MHz, CD₂Cl₂): δ 145.45, 140.84, 140.69, 139.32, 136.91, 134.77, 133.98, 131.08, 128.11, 128.01, 127.51, 126.94, 125.33, 125.00, 119.79, 114.48, 19.40, 19.31 ppm; HRMS (APPI-TOF, positive mode): m/z calcd for C₇₄H₁₀₂S₈ [M]⁺ 1246.5747, found 1246.5708.

2,2'-((((9H-fluoren-9-ylidene)methylene)bis(4,1-phenylene))bis(methaneclylidene))bis(4,5-bis(decylthio)-1,3-dithiole) (9b)

Compound 5 (0.151 g, 0.391 mmol), 4,5-bis(decylthio)-1,3-dithiole-2-thione (8b) (0.561 g, 1.173 mmol), and P(OMe)₃ (15 mL) were added to a 100 mL round-bottomed flask. The flask was placed in an oil bath heated at 145 °C and kept in it for 5 h. After that, the reaction mixture was subjected to under vacuum distillation at the same temperature to remove unreacted P(OMe)₃. The residue was subjected to silica gel column chromatography (hexanes/EtOAc, 7:3) to give pure compound 9b (0.221 g, 0.286 mmol, 65%) as a deep-orange oil. Caution: the product is quite sensitive to air and light, and it needs to be stored in a fridge immediately after purification to prevent significant decomposition. IR (neat): 3054, 3021, 2990, 2918, 2852, 1567, 1540, 1502, 1443, 1314, 1184 cm⁻¹; ¹H NMR (300 MHz, CD₂Cl₂): δ 7.71 (d, J = 7.3 Hz, 2H), 7.38–7.32 (m, 4H), 7.30–7.21 (m, 6H), 6.94 (td, J = 7.7, 1.2 Hz, 2H), 6.77 (d, J = 7.9 Hz, 2H), 6.57 (s, 2H), 2.45 (s, 6H), 2.43 (s, 6H) ppm; ¹³C NMR (75 MHz, CD₂Cl₂): δ 145.45, 140.84, 140.69, 139.32, 136.91, 134.77, 133.98, 131.08, 128.11, 128.01, 127.51, 126.94, 125.33, 125.00, 119.79, 114.48, 19.40, 19.31 ppm; HRMS (APPI-TOF, positive mode): m/z calcd for C₇₄H₁₀₂S₈ [M]⁺ 1246.5747, found 1246.5708.
to give pure compound 9b (0.366 g, 0.293 mmol, 75%) as a deep-orange oil. Caution: the product is quite sensitive to air and light, and it needs to be stored in a fridge immediately after purification to prevent significant decomposition. IR (neat): 3054, 3021, 2920, 2850, 1566, 1540, 1501, 1442, 1184 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 7.72 (d, \(J = 7.5\) Hz, 2H), 7.35 (d, \(J = 8.4\) Hz, 4H), 7.32–7.20 (m, 6H), 6.97–6.90 (m, 2H), 6.79 (d, \(J = 7.9\) Hz, 2H), 6.56 (s, 2H), 2.85 (td, \(J = 7.3, 2.5\) Hz, 8H), 1.72–1.59 (m, 8H), 1.36–1.19 (m, 56H), 0.96–0.81 (m, 12H) ppm; \(^{13}\)C NMR (75 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 145.17, 140.52, 140.24, 139.02, 136.66, 134.42, 134.02, 130.81, 127.94, 127.75, 127.13, 126.59, 125.22, 125.02, 119.45, 113.70, 36.35, 36.27, 32.19, 32.17, 29.84, 29.82, 29.61, 29.60, 29.42, 22.97, 22.96, 14.19 ppm; HRMS (APPI-TOF, positive mode): \(m/z\) calcd for C\(_{74}\)H\(_{102}\)S\(_8\) [M]\(^+\) 1246.5747, found 1246.5708.

\(4,4',4'',4'''-(((9H-fluoren-9-ylidene)methylene)bis(4,1-phenylene))bis(ethene-2,1,1-riyl))tetrabenzaldehyde (7)\)

\[
\begin{align*}
\text{Compound 6} & \quad (0.642 \text{ g}, 0.919 \text{ mmol}), \quad \text{4-formylphenylboronic acid (4) (0.685 g, 4.599 mmol)}, \\
& \quad \text{cesium carbonate (2.989 g, 9.197 mmol)}, \quad \text{THF (50 mL)}, \quad \text{and deionized water (15 mL) were added to 250 mL round-bottomed flask. The mixture was bubbled with N}_2 \quad \text{flow for 5 min and then Pd(PPh}_3\text{)}_4 \quad (0.212 \text{ g}, 0.184 \text{ mmol}) \quad \text{was added. The reaction mixture was stirred under N}_2 \quad \text{and heated at reflux 24 h. The mixture was next cooled down to room temperature, poured into a separatory funnel including water, and extracted twice with CH}_2\text{Cl}_2. \quad \text{The organic layers were combined and dried over MgSO}_4. \quad \text{After filtration and concentration under gentle heating and reduced pressure, the resulting residue was subjected to silica gel column chromatography (hexanes/EtOAc, 4:1) to give pure compound 7 (0.514 g, 0.643 mmol, 70%) as a yellow crystalline solid. m.p.: 255 °C (dec.); IR (neat): 3043, 3023, 2922, 2823, 2733, 1694, 1598, 1562, 1385, 1303, 1205, 1164 cm}\(^{-1}\); \(^1\)H NMR (300 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 10.02 (s, 2H), 10.01 (s, 2H), 7.90–7.83 (m, 8H), 7.67 (d, \(J = 7.3\) Hz, 2H), 7.50–7.43 (m, 8H), 7.27–7.22 (m, 4H), 7.15–7.07 (m, 8H), 6.97–6.92 (m, 2H), 6.60 (d, \(J = 7.9\) Hz, 2H) ppm; \(^{13}\)C NMR (75 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 192.17, 192.07, 148.68, 146.67, 144.62, 142.52, 141.74, 140.97, 138.94, 137.11, 136.47, 136.28, 135.24, 131.80, 131.73, 130.75, 130.68, 130.27, 130.23, 128.65, 128.42, 126.87, 125.35, 119.86 ppm; HRMS (APPI-TOF, positive mode): \(m/z\) calcd for C\(_{58}\)H\(_{38}\)O\(_4\) [M]\(^+\) 798.2770, found 798.2743.\)
2,2',2'',2''''-((((((9H-fluorene-9-ylidene)methylene)bis(4,1-phenylene))bis(ethene-2,1,1-triyl))tetrakis(benzene-4,1-diyl))tetrakis(methanelylidene))tetrakis(4,5-bis(decylthio)-1,3-dithiole) (2)

Compound 7 (0.103 g, 0.129 mmol), 8b (0.370 g, 0.774 mmol), and P(OMe)3 (6 mL) were added to a 50 mL round-bottomed flask. The flask was placed in an oil bath heated at 145 °C and kept in it for 5 h. After that, the reaction mixture was subjected to under vacuum distillation at the same temperature to remove unreacted P(OMe)3. The residue was subjected to silica gel column chromatography (hexanes/EtOAc, 98:2) to give pure compound 2 (0.228 g, 0.090 mmol, 70%) as a deep-orange oil. Caution: the product is quite sensitive to air and light, and it needs to be stored in a fridge immediately after purification to prevent significant decomposition. IR (neat): 3022, 2920, 2850, 1567, 1542, 1504, 1462, 1412, 1018 cm⁻¹; ¹H NMR (300 MHz, CD₂Cl₂): δ 7.67 (d, J = 7.5 Hz, 2H), 7.34 (d, J = 8.5 Hz, 4H), 7.27–7.15 (m, 14H), 7.12–7.04 (m, 10H), 7.00–6.93 (m, 2H), 6.67 (d, J = 7.9 Hz, 2H), 6.48 (s, 4H), 2.89–2.73 (m, 16H), 1.62 (dq, J = 16.8, 9.1, 8.2 Hz, 16H), 1.25 (d, J = 14.1 Hz, 112H), 0.91–0.84 (m, 24H) ppm; ¹³C NMR (75 MHz, CD₂Cl₂): δ 145.42, 143.01, 141.49, 140.71, 139.01, 138.17, 137.87, 136.17, 136.07, 134.57, 133.30, 133.25, 131.10, 130.31, 129.94, 128.20, 128.14, 127.99, 127.82, 127.37, 126.98, 126.74, 125.30, 125.19, 119.57, 114.12, 36.51, 36.44, 32.35, 30.31, 30.29, 30.18, 30.13, 30.01, 29.98, 29.77, 29.58, 28.98, 28.95, 28.92, 23.13, 14.35 ppm; MS (MALDI-TOF, positive mode, DCTB as matrix): m/z calcd for C₁₅₀H₂₀₆S₁₆O [M + O]⁺ 2535.16, found 2535.15.

1,2-Bis(4,5-bis(methylthio)-1,3-dithiol-2-ylidene)-1,2-bis(4-((4,5-bis(methylthio)-1,3-dithiol-2-ylidene)methyl)phenyl)(9H-fluoren-9-ylidene)methyl)pheny lethane (10)
Compound 9a (0.050 g, 0.067 mmol), iodine (0.051 g, 0.20 mmol), and CH2Cl2 (10 mL) were added to a 100 mL round-bottom flask. The reaction mixture was stirred under N2 at room temperature for 5 min. Then 60 mL of the aqueous solution of saturated Na2S2O3 was added to the reaction and the mixture was kept stirring for another 15 min. The mixture was poured into a separatory funnel, and the aqueous layer was separated and extracted with CH2Cl2 twice. The organic layers were combined and dried over MgSO4. After filtration and concentration under gentle heating and reduced pressure, the resulting residue was subjected to silica gel column chromatography (hexanes/CH2Cl2, 7:3) to give compound 10 (0.019 g, 0.013 mmol, 20%) as a red semi-solid. IR (neat): 3054, 3022, 2918, 2851, 1565, 1537, 1501, 1443, 1427, 1185, 967 cm⁻¹; ¹H NMR (300 MHz, CD2Cl2): δ 7.72–7.68 (m, 4H), 7.56–7.51 (m, 3H), 7.39–7.34 (m, 8H), 7.31–7.16 (m, 10H), 6.98–6.91 (m, 3H), 6.89–6.81 (m, 2H), 6.78 (d, J = 7.9 Hz, 2H), 6.66 (d, J = 7.9 Hz, 2H), 6.57 (s, 2H), 2.45 (s, 6H), 2.44 (s, 6H), 2.42 (s, 6H), 2.41 (s, 6H) ppm; HRMS (APPI-TOF, positive mode): m/z calcd for C76H58S16 [M]⁺ 1482.0070, found 1482.0091.
2. NMR Spectra for New Compounds

Fig. S-1 $^1$H NMR (300 MHz, CD$_2$Cl$_2$) spectrum of compound 5.
Fig. S-2 $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$) spectrum of compound 5.
Fig. S-3 $^1$H NMR (300 MHz, CDCl$_3$) spectrum of compound 6.
Fig. S-4 $^{13}$C NMR (75 MHz, CDCl$_3$) spectrum of compound 6.
Fig. S-5 $^1$H NMR (300 MHz, CD$_2$Cl$_2$) spectrum of compound 9a.
Fig. S-6 $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$) spectrum of compound 9a.
Fig. S-7 $^1$H NMR (300 MHz, CD$_2$Cl$_2$) spectrum of compound 9b.
Fig. S-8 $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$) spectrum of compound 9b.
Fig. S-9 $^1$H NMR (300 MHz, CD$_2$Cl$_2$) spectrum of compound 7.
Fig. S-10 $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$) spectrum of compound 7.
Fig. S-11 $^1$H NMR (300 MHz, CD$_2$Cl$_2$) spectrum of compound 2.
Fig. S-12 $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$) spectrum of compound 2.
Fig. S-13 $^1$H NMR (300 MHz, CD$_2$Cl$_2$) spectrum of compound 10.
3. Detailed Results of UV-Vis Titration Experiments

Solutions of compounds 9a and 2 in CHCl₃ were subjected to titrations with nitrobenzene, 2,4-dinitrobenzene (DNT), and 2,4,6-trinitrobenzene (TNT), respectively. Detailed results are summarized in the following figure. Attempts to extract binding constants from the titration data, however, were not successful due to poor spectral fitting.

**Fig. S-14** (A) UV-Vis titration results of compound 9b (4.00 × 10⁻⁵ M in CHCl₃, 298 K) with nitrobenzene (from 0 to 27.4 molar equiv). (B) UV-Vis titration results of compound 9b (4.00 × 10⁻⁵ M in CHCl₃, 298 K) with 2,4-dinitrotoluene (from 0 to 11.6 molar equiv). (C) UV-Vis titration results of compound 9b (2.00 × 10⁻⁵ M in CHCl₃, 298 K) with 2,4,6-trinitrotoluene (from 0 to 7.43 molar equiv). (D) UV-Vis titration results of compound 2 (3.97 × 10⁻⁵ M in CHCl₃, 298 K) with nitrobenzene (from 0 to 27.1 molar equiv). (E) UV-Vis titration results of compound 2 UV-Vis titration results of compound 2 (3.97 × 10⁻⁵ M in CHCl₃, 298 K) 2,4-dinitrotoluene (from 0 to 11.7 molar equiv). (F) UV-Vis titration results of compound 2 UV-Vis titration results of compound 2 (1.98 × 10⁻⁵ M in CHCl₃, 298 K) 2,4,6-trinitrotoluene (from 0 to 7.5 molar equiv).
4. Detailed Results of Differential Pulse Voltammetric Titrations

Fig. S-15 DPV profiles showing the responses of poly-1 thin film (deposited on glassy carbon) to nitrobenzene (NB) at varied concentrations. Experimental conditions: solvent: CH$_2$Cl$_2$; electrolyte: Bu$_4$NBF$_4$ (0.1 M); reference electrode: Ag/AgCl; counter electrode: Pt wire. Step E: 4 ms; pulse with: 50 ms; pulse amplitude: 50 mV; pulse period: 200 ms; scan rate: 20 mV s$^{-1}$.

Fig. S-16 DPV profiles showing the responses of poly-1 thin film (deposited on glassy carbon) to 2,4-dinitrobenzene (DNT) at varied concentrations. Experimental conditions: solvent: CH$_2$Cl$_2$; electrolyte: Bu$_4$NBF$_4$ (0.1 M); reference electrode: Ag/AgCl; counter electrode: Pt wire. Step E: 4 ms; pulse with: 50 ms; pulse amplitude: 50 mV; pulse period: 200 ms; scan rate: 20 mV s$^{-1}$.
Fig. S-17 DPV profiles showing the responses of poly-1 thin film (deposited on glassy carbon) to 2,4,6-trinitrobenzene (TNT) at varied concentrations. Experimental conditions: solvent: CH$_2$Cl$_2$; electrolyte: Bu$_4$NBF$_4$ (0.1 M); reference electrode: Ag/AgCl; counter electrode: Pt wire. Step E: 4 ms; pulse width: 50 ms; pulse amplitude: 50 mV; pulse period: 200 ms; scan rate: 20 mV s$^{-1}$.

Fig. S-18 (A) DPV profiles showing the responses of poly-2 thin film (deposited on glassy carbon) to nitrobenzene (NB) at varied concentrations. Experimental conditions: solvent: CH$_2$Cl$_2$; electrolyte: Bu$_4$NBF$_4$ (0.1 M); reference electrode: Ag/AgCl; counter electrode: Pt wire. Step E: 4 ms; pulse width: 50 ms; pulse amplitude: 50 mV; pulse period: 200 ms; scan rate: 20 mV s$^{-1}$. (B) Plot of DPV peak current against the concentration of nitrobenzene (NB).
Fig. S-19 (A) DPV profiles showing the responses of poly-2 thin film (deposited on glassy carbon) to 2,4-dinitrobenzene (DNT) at varied concentrations. Experimental conditions: solvent: CH$_2$Cl$_2$; electrolyte: Bu$_4$NBF$_4$ (0.1 M); reference electrode: Ag/AgCl; counter electrode: Pt wire. Step E: 4 ms; pulse with: 50 ms; pulse amplitude: 50 mV; pulse period: 200 ms; scan rate: 20 mV s$^{-1}$. (B) Plot of DPV peak current against the concentration of 2,4-dinitrobenzene (DNT).
Fig. S-20 (A) DPV profiles showing the responses of poly-2 thin film (deposited on glassy carbon) to 2,4,6-trinitrobenzene (TNT) at varied concentrations. Experimental conditions: solvent: CH$_2$Cl$_2$; electrolyte: Bu$_4$NBF$_4$ (0.1 M); reference electrode: Ag/AgCl; counter electrode: Pt wire. Step E: 4 ms; pulse with: 50 ms; pulse amplitude: 50 mV; pulse period: 200 ms; scan rate: 20 mV s$^{-1}$. (B) Plot of DPV peak current against the concentration of 2,4,6-trinitrobenzene (TNT).
5. Optical Profiling and SEM Images of Polymer Films

**Fig. S-21** Surface morphology of the thin film of **poly-1** electrochemically deposited on an ITO substrate.

**Fig. S-22** Surface morphology of the thin film of **poly-2** electrochemically deposited on an ITO substrate.
Fig. S-23 Optical profiling images for the surface morphology of the double-layer thin film of poly-2/poly-1 on an ITO substrate. (A) Scanned in the central area of the film, and (B) scanned on the edge of the film.
**Fig. S-24** SEM image of the surface of the double-layer thin film of poly-2|poly-1 on an ITO substrate.