Electronic Supplementary Information (ESI)

Conducting Polymer as Anion-Responsive Chemical Fuse

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Experimental Section

General Considerations. All reagents were purchased from commercial suppliers and used as received unless otherwise noted. CH_2Cl_2 and CH_3CN used for electrochemical studies were saturated with nitrogen and purified by passage through activated Al_2O_3 columns under nitrogen (Innovative Technology SPS PureSolv MD4). Spectroscopic grade CH_2Cl_2 and DMSO were used for UV–vis measurements. The compounds [2,2':5',2''-terthiophene]-3',4'-diamine¹ and methyl 2,2-diethoxyacetimidate² were prepared according to literature procedures. All air-sensitive manipulations were carried out under nitrogen atmosphere by standard Schlenk-line techniques.

Physical Measurements. ¹H NMR and ¹³C NMR spectra were recorded on a 400 MHz Agilent 400-MR DD2 Magnetic Resonance System or a 500 MHz Varian/Oxford As-500 spectrometer. Chemical shifts were referenced to internal standard of tetramethylsilane (as $\delta = 0.00$ ppm), or referenced to residual solvent peaks if the internal standard was not contained in the solvents.³ High-resolution electrospray ionization (ESI) mass spectra were obtained on an ESI-Q-TOF mass spectrometer (Compact, Bruker Daltonics Inc). FT-IR spectra were recorded on a Shimadzu IRTracer-100 FT-IR Spectrophotometer. Elemental analysis was performed by a Perkin Elmer 2400 Series II CHNS/O Analyzer. UV–vis spectra were recorded on an Agilent 8453 UV–vis spectrophotometer with ChemStation software.

Electrochemistry. Electrochemical studies were carried out with an Autolab model PGSTAT204 (Metrohm). A three-electrode configuration consisting of a working electrode (platinum button electrode, ITO-coated glass electrode, or 5- μ m interdigitated microelectrode), a Ag/AgNO₃ (0.05 M in CH₃CN with 0.1 M *n*-Bu₄NPF₆) reference electrode, and a platinum coil counter electrode was used. Drain current measurements were carried out at a 10 mV/s scan rate with a 40 mV offset potential between the two working electrodes. All electrochemical potentials were reported with respect to the Cp₂Fe/Cp₂Fe⁺ redox couple unless otherwise noted.

Electropolymerization and Characterization. Thin films of P1a and P1b were grown by repeated potential sweeps (between -0.2 and +1.0 V vs Ag/Ag⁺; scan rate = 50 mV/s) of CH₂Cl₂ solution samples (0.5 mM). The polymer-modified electrode was washed repeatedly with CH₂Cl₂ prior to further characterizations. In situ spectroelectrochemical measurements were carried out using a polymer-modified ITO-coated glass electrode, a platinum coil counter electrode, and a

¹ P. Li, O. Fenwick, S. Yilmaz, D. Breusov, D. J. Caruana, S. Allard, U. Scherf and F. Cacialli, *Chem. Commun.*, 2011, **47**, 8820–8822.

² Y. Hattori, M. Nishikawa, T. Kusamoto, S. Kume and H. Nishihara, *Chem. Lett.*, 2014, 43, 1037–1039.

³ G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176–2179.

Ag/AgNO₃ (0.05 M in CH₃CN with 0.1 M n-Bu₄NPF₆) reference electrode immersed in a quartz UV–vis cell. Films were grown on the surface of the working electrode and washed with CH₂Cl₂. The polymer-modified electrode was transferred to a cuvette containing fresh electrolyte. The UV–vis spectra were taken at 100 mV intervals using Ocean Optics FLAME-S-XR1 spectrometer. The thickness of the film was determined using an atomic force microscope (XE-70, Park systems), and used to calculate the conductivity (σ) of the film by using poly(3-methylthiophene) as a reference. 4–6

Structural Disassembly by Hydrogen Bonding Acceptor Anions. Thin film samples of electropolymerized P1a on ITO-coated glass electrodes were immersed in CH_2Cl_2 solution samples of various anions (5 μ M) for 15 sec. Cyclic voltammograms of the electrode and UV–vis spectra of the supernatant solutions were measured before and after exposure to anions. For the conductivity measurements, 5- μ m interdigitated microelectrodes were used instead of ITO-coated glass electrodes.

2-(Diethoxymethyl)-4,6-di(thiophen-2-yl)-1*H***-thieno[3,4-***d***]imidazole (2).** An oven-dried 100-mL Schlenk flask was charged with [2,2':5',2"-terthiophene]-3',4'-diamine (345 mg, 1.25 mmol), methyl 2,2-diethoxyacetimidate (799 mg, 4.96 mmol), and anhydrous EtOH (5 mL). The mixture was sparged with Ar for 20 min, and treated with trifluoroacetic acid (0.1 mL). The resulting red solution was stirred at r.t. for 4 h, and concentrated under reduced pressure. Flash column chromatography on SiO₂ (hexanes:EtOAc = 2:1, v/v) furnished **2** as a yellow solid (423 mg, 1.08 mmol, yield = 87%). ¹H NMR (400 MHz, CDCl₃, 298 K): δ 9.04 (s, 1H), 7.48 (br, 1H), 7.22 (d, J = 5.0 Hz, 2H), 7.10 (br, 1H), 7.05–7.03 (m, 2H), 5.63 (s, 1H), 3.79 (dt, J = 14.2, 7.1 Hz, 2H), 3.69 (dt, J = 14.2, 7.1 Hz, 2H), 1.27 (t, J = 7.1 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, 298 K): δ 160.9, 146.7, 135.4, 135.2, 133.6, 128.1, 124.4, 124.2, 123.6, 122.6, 116.1, 104.4, 97.3, 77.2, 63.0, 15.2. FT-IR (ATR, cm⁻¹): 2974, 1521, 1479, 1431, 1371, 1327, 1268, 1178, 1114, 1056, 1013, 976, 906, 847, 811, 742, 687. Anal. Calcd for C₁₈H₁₈N₂O₂S₃: C, 55.36; H, 4.65; N, 7.17. Found: C, 55.23; H, 4.60; N, 7.26.

4,6-Di(thiophen-2-yl)-1*H*-thieno[3,4-*d*]imidazole-2-carbaldehyde (3). To a THF (15 mL) solution of 2 (423 mg, 1.08 mmol) was added aq HCl (2 M, 6 mL). The mixture was stirred at 65 °C for 2.5 h, cooled to r.t., and poured into a sat'd aq solution of Na₂CO₃ (50 mL). The organic fraction was extracted with ethyl acetate (4 × 50 mL). The combined extracts were dried over anhyd Na₂SO₄, filtered, and concentrated under reduced pressure to afford crude **3** as a dark purple solid (317 mg), which was carried on to the next step without further purification.

2-(1*H*-Benzo[*d*]imidazol-2-yl)-4,6-di(thiophen-2-yl)-1*H*-thieno[3,4-*d*]imidazole (1a). To a mixture of crude 3 (317 mg), *o*-phenylenediamine (331 mg, 3.06 mmol), and DMF (10 mL) was added *p*-TsOH·H₂O (95.2 mg, 0.50 mmol). The mixture was stirred at r.t. for 4 h, and poured into a sat'd aq solution of Na₂CO₃ (50 mL). The organic fraction was extracted with ethyl acetate (3 × 50 mL). The combined extracts were dried over anhyd Na₂SO₄, filtered, and concentrated under reduced pressure. Flash column chromatography on SiO₂ (hexanes:EtOAc = 3:1, v/v) furnished **1a**

⁴ G. Zotti and G. Schiavon, *Synth. Met.*, 1990, **39**, 183–190.

⁵R. P. Kingborough and T. M. Swager, J. Am. Chem. Soc., 1999, **121**, 8825–8834.

⁶ Absolute conductivity (σ) is related to drain current by $\sigma = \left(\frac{i_d}{V_d}\right) \left(\frac{W}{n \cdot T \cdot L}\right) \cdot A$, where i_d = drain current, V_d = offset voltage, W = sample width, n = number of interface, T = film thickness, L = electrode length and A = correction factor. A is determined by measuring the conductivity of poly(3-methylthiophene) using the same setup, which has maximum conductivity of 60 S cm⁻¹. For further information, see refs 4 and 5.

as a red solid (238 mg, 0.588 mmol, 54%, combined yield of two-step synthesis from **2**). ¹H NMR (400 MHz, DMSO- d_6 , 298 K): δ 13.40 (s, 1H), 13.36 (s, 1H), 7.87–7.79 (m, 2H), 7.63–7.48 (m, 4H), 7.34 (dd, J = 14.0, 8.2 Hz, 2H), 7.18 (br, 2H). ¹³C NMR (100 MHz, DMSO- d_6 , 298 K): δ 174.5, 154.3, 148.0, 143.5, 142.9, 135.0, 134.4, 128.8, 128.2, 125.1, 124.2, 124.0, 122.6, 119.5, 112.4, 112.4, 104.5, 62.4, 39.5.⁷ FT-IR (ATR, cm⁻¹): 3147, 1613, 1516, 1464, 1406, 1370, 1349, 1321, 1290, 1216, 1117, 1074, 986, 930, 901, 850, 837, 801, 765, 737, 673, 639. HRMS (ESI) calcd for C₂₀H₁₂N₄S₃ [M + H]⁺ 405.0297, found 405.0299.

1-Methyl-2-(1-methyl-1*H*-benzo[*d*]imidazol-2-yl)-4,6-di(thiophen-2-yl)-1*H*-thieno[3,4*d*]imidazole (1b). To a mixture of 1a (61.9 mg, 0.151 mmol) and K₂CO₃ (83.5 mg, 0.604 mmol) in DMF (5 mL) was added methyl iodide (0.030 mL, 0.50 mmol). The reaction mixture was stirred at r.t. for 24 h, and poured into H₂O (50 mL). The organic fraction was extracted with ethyl acetate (3 × 50 mL). The combined extracts were dried over anhyd Na₂SO₄, filtered, and concentrated under reduced pressure. Flash column chromatography on SiO₂ (hexanes:EtOAc = 5:1, v/v) furnished 1b as a yellow solid (60.6 mg, 0.140 mmol, yield = 93%). ¹H NMR (500 MHz, CDCl₃, 298 K): δ 7.87 (d, J = 8.0 Hz, 1H), 7.53–7.49 (m, 3H), 7.42 (td, J = 8.1, 0.9 Hz, 1H), 7.39–7.34 (m, 2H), 7.29 (dd, J = 5.1, 1.0 Hz, 1H), 7.21 (dd, J = 3.5, 1.1 Hz, 1H), 7.12 (dd, J = 5.2,3.6 Hz, 1H), 7.09 (dd, J = 5.0, 3.7 Hz, 1H), 4.37 (s, 3H), 4.18 (s, 3H). ¹³C NMR (125 MHz, CDCl₃, 298 K): δ 152.6, 146.1, 142.8, 142.7, 137.4, 136.5, 135.4, 133.1, 128.1, 127.8, 127.8, 126.7, 124.7, 124.5, 123.7, 123.2, 120.7, 118.0, 110.3, 102.8, 34.8, 32.8. FT-IR (ATR, cm⁻¹): 3067, 2946, 1623, 1513, 1451, 1438, 1408, 1354, 1326, 1287, 1236, 1200, 1154, 1059, 1006, 968, 952, 908, 851, 811, 796, 764, 729, 693. HRMS (ESI) calcd for C₂₂H₁₆N₄S₃ [M + H]⁺ 433.0610, found 433.0612.

X-ray Crystallographic Studies on 1a. Single crystals of 1a were prepared by slow evaporation of hexanes/ethyl acetate solution (1:4, v/v) of this material. A red crystal (approximate dimensions $0.79 \times 0.566 \times 0.516 \text{ mm}^3$) was placed onto a nylon loop with Paratone-N oil, and mounted on an XtaLAB AFC12 (RINC): Kappa dual home/near diffractometer. The data collection was carried out using Cu K α radiation and the crystal was kept at T = 93 K. A total of 23101 reflections were measured (7.458° $\leq 2\theta \leq 159.658^{\circ}$). The structure was solved with SHELXT⁸ using direct methods, and refined with SHELXL⁹ refinement package of OLEX2.¹⁰ A total of 7825 unique reflections were used in all calculations. The final R1 was 0.0849 ($I \geq 2\sigma(I)$) and wR2 was 0.2444 (all data).

 $^{^{7}\,}$ The resonances of two aromatic carbons were not found due to tautomerization.

⁸ G. M. Sheldrick, Acta Cryst., 2015, A71, 3–8.

⁹ G. M. Sheldrick, Acta Cryst., 2015, C71, 3–8.

¹⁰ O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. Appl. Cryst., 2009, 42, 339–341.

	$1a \cdot H_2O$
Chemical formula	$C_{20}H_{12}N_4S_3\cdot H_2O$
Formula weight	422.53
Crystal system	triclinic
Space group	$P\overline{1}$
Color of crystal	red
a (Å)	12.1280(2)
b (Å)	12.4060(3)
c (Å)	13.9115(3)
α (°)	67.688(2)
β (°)	84.053(2)
γ (°)	77.848(2)
Volume (Å ³)	1892.37(7)
Z	2
R_{int}	0.0881
Final R indices $[I \ge 2\sigma(I)]$	R1 = 0.0849, wR2 = 0.2359
Final R indices [all data]	R1 = 0.0905, wR2 = 0.2444
Goodness-of-fit on F^2	1.059

Table S1. X-ray Crystallographic Data of 1a.

Density Functional Theory (DFT) Calculations. All density functional theory (DFT) calculations were conducted using Gaussian '09 suite package.¹¹ Ground-state geometry optimizations of 1a and 1b were performed using B3LYP hybrid functional with Grimme's D3 dispersion correction (B3LYP-D3)¹² with cc-pVTZ basis set, and the conductor-like polarizable continuum model (CPCM) using dichloromethane as a solvent.¹³ The dihedral angles between the two imidazole rings were calculated as 0.2° for **1a**, and 25.5° for **1b** (Fig. S4).

Atom	х	У	Z	Atom	x	у	Z
С	3.275546	-4.985599	-0.012858	Н	3.979238	-5.800273	-0.036805
\mathbf{C}	1.912413	-5.037095	0.014728	Η	1.356382	-5.962763	0.015626
\mathbf{C}	1.306391	-3.757021	0.041788	Η	0.241840	-3.585817	0.065581
\mathbf{C}	2.216449	-2.720895	0.034504	Η	0.680528	3.618486	0.992707
\mathbf{S}	3.847903	-3.354677	-0.007170	Η	1.895848	5.912175	0.704579
\mathbf{C}	1.920760	-1.315807	0.057473	Η	4.286617	5.622431	-0.347627
\mathbf{C}	0.679607	-0.700021	0.065046	Η	-0.938981	2.069393	0.019653
\mathbf{C}	0.742473	0.721666	0.076280	Η	-3.208137	-2.004752	-0.020054
\mathbf{C}	2.002644	1.267972	0.076619	Н	-6.115877	-2.405645	-0.082500
\mathbf{S}	3.147122	-0.067456	0.080431	Н	-8.189832	-1.044077	-0.115510
\mathbf{C}	2.395874	2.651377	0.096159	Η	-8.099161	1.411556	-0.095459
\mathbf{C}	1.655895	3.723545	0.542221	Η	-5.924406	2.611231	-0.041401
\mathbf{C}	2.321618	4.967661	0.400579				
\mathbf{C}	3.565866	4.848730	-0.144257				
\mathbf{S}	3.939692	3.202369	-0.516549				
Ν	-0.635388	-1.121800	0.040570				
\mathbf{C}	-1.334793	-0.007512	0.033397				
Ν	-0.569949	1.134562	0.057631				
\mathbf{C}	-2.776389	0.062757	0.005250				
Ν	-3.555429	-1.059840	-0.019638				
\mathbf{C}	-4.863818	-0.639720	-0.043671				
\mathbf{C}	-4.792341	0.773803	-0.031655				
Ν	-3.473330	1.179537	-0.000955				
\mathbf{C}	-6.074887	-1.325649	-0.073778				
\mathbf{C}	-7.226095	-0.554078	-0.091943				
\mathbf{C}	-7.173461	0.852707	-0.080433				
С	-5.967227	1.531023	-0.050358				

Table S2. Cartesian Coordinates of the Optimized Ground-State Geometry of 1a.

¹¹ M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Boarone, B. Mennucci, G. A. Petersson et al. Gaussian '09, Gaussian, Inc.: Wallingford CT, 2009. ¹² S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.

¹³ M. Cossi, N. Rega, G. Scalmani and V. Barone, J. Comput. Chem., 2003, 24, 669-681.

Atom	х	у	Z	Atom	x	У	Z
С	-1.155577	5.588470	0.044786	Н	-0.583211	6.505726	0.067164
\mathbf{C}	-2.516256	5.435552	0.052999	Η	-3.210480	6.267176	0.083205
\mathbf{C}	-2.919853	4.072603	0.018890	Η	-3.955937	3.752777	0.019261
\mathbf{C}	-1.861205	3.183709	-0.016215	Η	-4.920203	-1.587702	-1.569851
\mathbf{S}	-0.331209	4.059959	-0.007464	Η	-6.061403	-3.858902	-0.873674
\mathbf{C}	-1.892910	1.745784	-0.052278	Η	-4.726535	-5.065629	1.051346
\mathbf{C}	-0.839966	0.841273	-0.103448	Η	5.927221	-2.817263	-0.353260
\mathbf{C}	-1.229992	-0.524498	-0.157233	Η	7.928601	-1.453711	0.125673
\mathbf{C}	-2.592181	-0.750256	-0.133501	Η	7.754077	0.953931	0.651808
\mathbf{S}	-3.391415	0.830502	-0.050172	Η	5.525787	2.086391	0.713173
\mathbf{C}	-3.408025	-1.948383	-0.069976	Η	-1.067596	-2.932456	-0.874746
\mathbf{C}	-4.551066	-2.236469	-0.783941	Η	0.260196	-3.291684	0.231590
\mathbf{C}	-5.167342	-3.464363	-0.405241	Η	0.575664	-2.843357	-1.473424
\mathbf{C}	-4.497770	-4.110668	0.598206	Η	3.958321	-3.482953	-0.689253
\mathbf{S}	-3.107106	-3.212998	1.122629	Η	2.568770	-3.007607	-1.656481
Ν	0.524342	0.952122	-0.127481	Η	2.376233	-3.430564	0.072920
С	0.986493	-0.289016	-0.204658				
Ν	-0.045530	-1.244911	-0.251000				
\mathbf{C}	2.460071	-0.449630	-0.122047				
Ν	3.288606	-1.560055	-0.295882				
\mathbf{C}	4.585307	-1.113340	-0.085603				
\mathbf{C}	4.472091	0.262108	0.211604				
Ν	3.156077	0.640163	0.183628				
\mathbf{C}	5.826408	-1.762058	-0.124628				
\mathbf{C}	6.948858	-0.986573	0.146277				
\mathbf{C}	6.848660	0.391048	0.447239				
\mathbf{C}	5.617517	1.029697	0.484189				
\mathbf{C}	-0.049934	-2.661478	-0.603983				
С	3.013624	-2.944314	-0.663139				

 Table S3. Cartesian Coordinates of the Optimized Ground-State Geometry of 1b.

Binding Studies of 1a by UV-vis Spectroscopic Titration. UV-vis titration was carried out in DMSO at T = 25 °C. Initial concentration of 1a was 32 μ M (= [H]₀), and aliquots of guest (AcO⁻) solution were delivered from the stock solution of $(n-Bu_4N)(OAc)$ (6 mM). In Fig. S1, changes in the absorbance at $\lambda = 520$ nm (black dots) are overlaid with the fitting curve (red line) as a function of [G]₀/[H]₀. The binding constant was determined by non-linear least-squares regression analysis^{14,15} with a 1:1 binding isotherm.



Fig. S1. Changes in the absorbance at $\lambda = 520$ nm vs [G]₀/[H]₀.



Fig. S2. ¹H NMR spectra of 1a (4 mM) in DMSO- d_6 obtained in the presence of 1 equiv of anions.

¹⁴ P. Thordarson, Chem. Soc. Rev., 2011, 40, 1305–1323.

¹⁵ Origin2017; OriginLab Corp.: Northampton, MA.



Fig. S3. FMO distribution diagrams (isovalue = 0.02) of DFT models of 1a ((a) and (b)) and 1b ((c) and (d)).



Fig. S4. Capped-stick representations of the energy-minimized DFT models of (a) 1a and (b) 1b (top, face-on view; bottom, side-on view).



Fig. S5. (a) Scan rate-dependent CV of P1a on Pt button electrode in monomer-free CH₂Cl₂ with n-Bu₄NPF₆ (0.1 M) as supporting electrolyte: (i) v = 100 mV/s; (ii) v = 75 mV/s; (iii) v = 50 mV/s; (iv) v = 25 mV/s. T = 298 K. (b) Anodic peak current of P1a as a function of scan rate.



Fig. S6. (a) Scan rate-dependent CV of P1b on Pt button electrode in monomer-free CH₂Cl₂ with *n*-Bu₄NPF₆ (0.1 M) as supporting electrolyte: (i) v = 100 mV/s; (ii) v = 75 mV/s; (iii) v = 50 mV/s; (iv) v = 25 mV/s. T = 298 K. (b) Anodic peak current of P1b as a function of scan rate.



Fig. S7. Cyclic voltammogram (black lines) and conductivity (red lines) of P1b on a 5- μ m interdigitated Pt microelectrode in CH₂Cl₂ with *n*-Bu₄NPF₆ (0.1 M) as supporting electrolyte. T = 298 K.



Fig. S8. Cyclic voltammograms of 1a obtained with repetitive voltage sweep (a) without and (b) with AcO^- anion (20 equiv) in CH_2Cl_2 with n-Bu₄NPF₆ (0.1 M) as supporting electrolyte.



Fig. S9. ¹H NMR (400 MHz) spectrum of 2 in CDCl_3 (T = 298 K).



Fig. S10. ¹³C NMR (100 MHz) spectrum of 2 in CDCl₃ (T = 298 K).



Fig. S11. ¹H NMR (400 MHz) spectrum of 1a in DMSO- d_6 (T = 298 K).



230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 Chemical Shift (ppm)

Fig. S12. ¹³C NMR (100 MHz) spectrum of 1a in DMSO- d_6 (T = 298 K).



Fig. S13. ¹H NMR (500 MHz) spectrum of 1b in CDCl₃ (T = 298 K).



Fig. S14. ¹³C NMR (125 MHz) spectrum of 1b in CDCl₃ (T = 298 K).

Author Contributions

Chungryeol Kim: Conceptualization, Data curation, Formal analysis, Investigation, Validation, Visualization, Writing – original draft, Writing – review & editing.

Dongwhan Lee: Conceptualization, Funding acquisition, Project administration, Resources, Visualization, Writing – original draft, Writing – review & editing.