

# Flexible dual-action colorimetric-electronic amine sensors based on *N*-annulated perylene diimide dyes

*(Supporting Information)*

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## 1. Materials and Methods

**Materials:** All reactants, reagents and solid supports used were purchased from Sigma-Aldrich, Fisher Scientific, the Printability and Graphic Communications Institute (ICI) or DuPont Teijin Films. All solvents and materials purchased were used as received without further purification.

**Nuclear Magnetic Resonance (NMR):** All  $^1\text{H}$ , and  $^{13}\text{C}$  spectroscopy experiments were recorded with a Bruker AVIII HD 500 MHz spectrometer. All experiments were performed in tetrahydrofuran- $d_8$  (THF- $d_8$ ). Chemical shifts were referenced to residual solvent and reported in parts per million (ppm).

**UV-Visible Spectroscopy (UV-Vis):** Optical absorption measurements were performed using an Agilent Technologies Cary 60 UV-Vis Spectrophotometer in ambient conditions. All solution UV-Vis spectra were measured using 10 mm quartz cuvettes using tetrahydrofuran (THF), dimethylsulfoxide (DMSO), or 2-methyl-tetrahydrofuran (MeTHF) as solvents. Stock solutions (*ca.* 1 mM) were prepared and diluted to concentrations between  $10^{-6}$  –  $10^{-5}$  M, then used to construct calibration curves for determining molar absorptivity. To measure the spectrum of deprotonated species, solutions of analyte were prepared in  $10^{-4}$  M 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU). To demonstrate the reversibility of this transformation, DBU and trifluoroacetic acid were added alternatively (Figure S12).

**Photoluminescence Spectroscopy (PL):** All PL emission measurements were performed using an Agilent Technologies Cary Eclipse fluorescence spectrometer at room temperature. All PL spectra were measured using 10 mm quartz cuvettes using THF or MeTHF as solvents. Solutions were diluted to concentrations *ca.*  $10^{-6}$  M.

**Solubility Measurements:** Calibration curves were generated as previously described for UV-Visible Spectroscopy. Saturated solutions of an analyte were prepared in *ca.* 0.3 mL of solvent, MeTHF. Solutions were filtered through a 0.4  $\mu\text{m}$  PVDF syringe filter and diluted until UV-Vis absorption fell within the calibration curve; dilution factors ranged from  $2 \times 10^3$  to  $5 \times 10^4$ . Concentration of saturated solutions was calculated according to the Beer-Lambert Law and dilution factor.

**Film Casting:** Films of styrene butadiene styrene (SBS) were slot-die coated on a flexible polyethylene terephthalate (PET) substrate from a 50 mg/mL solution of SBS in *o*-xylene. Analyte molecules were then cast on top from a 20 mg/mL solution of analyte in MeTHF (S-PDIN-H,  $\text{SO}_2$ -PDIN-H) or butylamine (PDIN-H). Additional deprotonated films were cast from a 20 mg/mL solution from the appropriate solvent with 5 v% DBU. Additional films were spin-coated on a flexible PET substrate or on ozone-cleaned glass substrates. For glass films, film thickness was measured using a KLA Alpha Step D-500 stylus profiler.

### Spectroscopic Studies on Amine Exposure:

**Solution:** A solution of analyte in DMSO (5  $\mu\text{M}$ ) and a solution of butylamine (3 mM) with analyte (5  $\mu\text{M}$ ) were prepared. The initial spectrum of 3 mL of the analyte solution was measured. To the cuvette was added 10  $\mu\text{L}$  aliquots of the butylamine solution. The cuvette was inverted 3 times to mix and allowed to equilibrate for 1 minute prior to measurement. Limits of detection (LoD) were determined by plotting the absorbance of the deprotonated species to the protonated species against the concentration of *n*-butylamine in solution. LoD was defined as the minimum concentration of *n*-butylamine at which an increase in the absorbance ratio was observed.

**Film:** Films of analyte molecule on SBS coated PET were slot-die coated as previously described. Films were fixed to the inside of a 3.5 mL sealable quartz cuvette. The initial spectrum of the film is measured.

To the cuvette is added an aliquot (20  $\mu\text{L}$ ) of butylamine. The change in absorbance is tracked over time, collecting spectra every 15 s.

**Device Fabrication:** The PDI-based amine sensors were fabricated on silver (Ag) interdigitated electrodes (IDE) printed on clear polyethylene terephthalate (PET) substrate, sizing 25 mm x 20 mm, with 250 mm finger width and 100 mm gap. The IDE platform is provided by ICI. The substrates were washed with isopropyl alcohol prior to coating the films. The tin oxide nanoparticles ( $\text{SnO}_2$  NPs) and PDI solutions were slot-die coated on top of the IDE at same coating speed of 40 cm/min and optimized pump rate conditions to form 15 mm wide films. The substrates were kept at 40  $^\circ\text{C}$  during the coating process. Firstly, the  $\text{SnO}_2$  NPs solution (Avantama N31, 2.5 wt.% in butanol) was sonicated for 5 minutes, after slot-die coated at a 55 mL/min pump rate and then, devices were annealed on a hot-plate for 10 minutes at 100  $^\circ\text{C}$  to evaporate the residual solvent. For the PDI films, 20 mg/mL solutions of S-PDIN-H and  $\text{SO}_2$ -PDIN-H in 2Me-THF were slot-die coated on top of the  $\text{SnO}_2$  NPs film at 45 mL/min pumping rate. For the PDIN-H, films were printed from 10 mg/mL solution in *n*-butylamine at 55 mL/min pumping rate. The devices were annealed for 10 minutes on a hot-plate at 100  $^\circ\text{C}$  for a complete evaporation of the remaining solvent in the film.

**Measurement Procedures:** To measure the sensitivity of devices upon exposure to different amine concentrations, the fabricated sensors were put inside a 1.5 L glass container at room temperature ( $\sim 22$   $^\circ\text{C}$ ) and under ambient conditions, and a specific concentration of the analyte was dropped inside it with a micro pipette. The concentration of the volatile organic solvent was calculated using the following equation:

$$C(\text{ppm}) = \frac{v(\text{mL}) \times d(\text{g/mL}) \times R(\text{L atm/mol K}) \times T(\text{K})}{p(\text{atm}) \times V_s(\text{L}) \times M_w(\text{g/mol})} 10^6$$

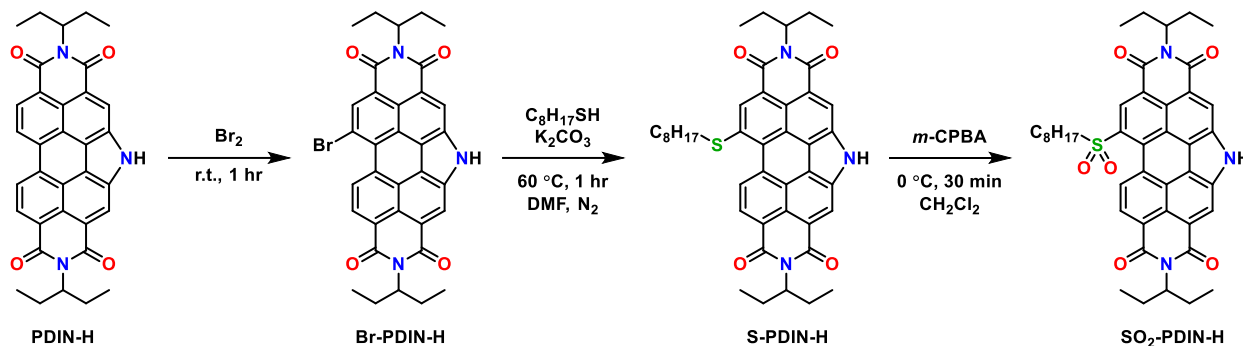
where  $C$  is the analyte vapour concentration,  $v$  the volume of the liquid analyte,  $d$  the density of analyte,  $R$  the ideal gas constant,  $T$  the ambient temperature,  $p$  the ambient pressure,  $V_s$  the volume of the container, and  $M_w$  the molecular weight of the analyte. For example, if we want to obtain the concentration of *n*-butylamine as 100 ppm, substitute it into the formula to calculate the required volume (considering a 1.5 L container):

$$100(\text{ppm}) = \frac{v(\text{mL}) \times 0.7414(\text{g/mL}) \times 0.08206(\text{L atm/mol K}) \times 295(\text{K})}{1(\text{atm}) \times 73.14(\text{g/mol}) \times 1.5(\text{L})} 10^6$$

The *n*-butylamine volume we should take after calculation is  $v = 0.62$   $\mu\text{L}$ .

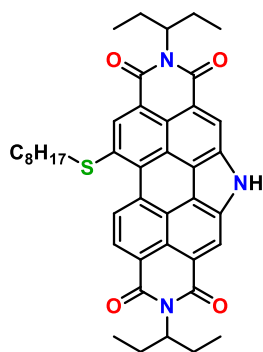
**Electrical Characterization:** The electrical characterization was performed using a Keithley 2460 Source Meter, with I-V curves of devices measured between a range [-10 V:10 V] and a 0.2 V fixed step. The measurements were conducted on devices before exposed to the gas analyte and at every 30 s during exposure. As can be seen in Figure S17, the I-V curves demonstrate a linear conductivity behavior over the entire voltage range for the different concentrations tested. The corresponding conductance ( $G = \text{current/voltage}$ ) was calculated by the slope of the I-V curves, and to correct for differences in resistance between devices, the response ratio of the device before and under exposure ( $DG/G_0$ ) is obtained as  $\Delta G/G_0 = (G - G_0)/G_0$ , where  $G_0$  is the conductance of device before exposed to the analyte and  $G$  is the conductance achieved during exposure.

## 2. Synthetic Procedures



**Figure S1.** Synthetic Scheme for S-PDIN-H and SO<sub>2</sub>-PDIN-H.

### S-PDIN-H



Starting material (Br-PDIN-H) was prepared following literature procedure.<sup>[1]</sup>

Br-PDIN-H (1.2 g, 1.9 mmol, 1 eq.) was combined with K<sub>2</sub>CO<sub>3</sub> (1.87 g, 13 mmol, 7 eq.) in an oven-dried 250 mL round-bottom flask (rbf). The rbf was sealed with a rubber septum and purged with N<sub>2</sub> for 15 minutes. To the flask was added dry, degassed dimethylformamide (100 mL) and octanethiol (1 mL, 5.7 mmol, 3 eq.). The dark blue solution was sparged an additional 15 minutes before being placed in a 60 °C bead bath and left to stir 1 hour, until thin-layer chromatography indicated consumption of starting material. Upon reaction completion, the solution was poured into 2M HCl (200 mL) and organics extracted with ethyl acetate (4 x 50 mL). The solvent was dried with NaSO<sub>4</sub> and removed by rotary evaporation.

Solids were re-dissolved in minimal CH<sub>2</sub>Cl<sub>2</sub> and loaded onto a silica gel plug. The plug was eluted first with a (10:1) hexanes:ethyl acetate mixture, followed by neat ethyl acetate to collect the desired product. The solvent was removed by rotary evaporation and the resulting red solid was slurried in pentane and collected by vacuum filtration. Yield: 1.15 g, 88%.

<sup>1</sup>H NMR (500 MHz, THF) δ (500 MHz, THF) 11.52 (s, 1H), 8.63 (d, *J* = 7.4 Hz, 1H), 8.37 (s, 1H), 8.23 (d, 7.4 Hz, 1H), 8.05 (s, 1H), 7.98 (s, 1H), 5.17 (tt, *J* = 6.4 Hz, 8.9 Hz, 1H), 5.05 (p, *J* = 7.5 Hz, 1H), 3.17 (t, *J* = 7.5 Hz, 2H), 2.40 (m, 4H), 2.09 (m, 4H), 1.88 (p, *J* = 7.5 Hz, 2H), 1.66 (p, *J* = 7.5 Hz, 2H), 1.38 (m, 8H), 1.10 (t, *J* = 7.3 Hz, 6H), 1.08 (t, *J* = 7.5 Hz, 6H), 0.95 (t, *J* = 6.8 Hz, 3H).

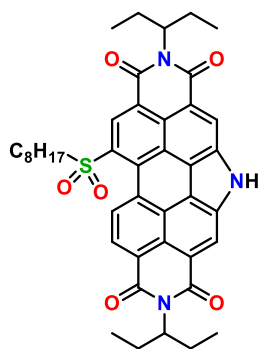
<sup>13</sup>C NMR (126 MHz, THF) δ 164.1, 139.4, 132.4, 131.7, 131.5, 127.4, 126.6, 124.4, 123.0, 120.8, 120.3, 120.0, 117.6, 116.9, 116.1, 66.9, 57.2, 57.1, 33.4, 31.9, 29.3, 29.2, 29.2, 28.2, 25.1, 24.8, 22.6, 13.5, 11.4, 11.2.

HRMS (MALDI, [M-2H]<sup>+</sup>) calculated: 686.3047; detected: 686.3062; Δ = 2.2 ppm

Elemental Analysis theoretical (%): C 73.33, H 6.59, N 6.11, S 4.66; found (%): C 72.98, H 6.56, N 6.01, S 4.38

UV-vis λ (x 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>, THF solution): 440 nm (1.0); 471 nm (2.4); 503 nm (3.2); 540 nm (5.1)

### SO<sub>2</sub>-PDIN-H:



S-PDIN-H (1.15 g, 1.7 mmol, 1 eq.) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (75 mL) in a 250 mL rbf. The solution was stirred over an ice-water bath 10 minutes to cool to 0 °C. *meta*-chloroperoxybenzoic acid (0.95 g, 4.3 mmol, 2.5 eq., 77%) was added, the reaction was removed from the ice-water bath and the reaction was left to stir 30 minutes, until TLC indicated the reaction had completed. Following completion, saturated NaHCO<sub>3</sub> solution (150 mL) was poured into the reaction and the resulting mixture stirred 5 minutes. The organic extracts were then washed with saturated NaHCO<sub>3</sub> (3 x 30 mL). The organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub>, and solvent removed by rotary evaporation. The resulting solids were recrystallized from CH<sub>3</sub>OH and collected by vacuum filtration, yielding a red solid. Yield: 0.8 g, 67%.

<sup>1</sup>H NMR (500 MHz, THF) δ 12.44 (s, 1H), 9.75 (d, *J* = 8.5 Hz, 1H), 9.43 (s, 1H), 8.83 (s, 1H), 8.80 (s, 1H), 8.59 (d, *J* = 8.5 Hz, 1H), 5.18 (m, 2H), 3.41 (dd, 6.8 Hz, 9.9 Hz, 2 H), 2.44 (m, 4H), 2.05 (m, 4H), 1.70 (m, 2H), 1.23 (p, *J* = 7.4 Hz, 2H), 1.03 (m, 20H), 0.75 (t, *J* = 6.9 Hz, 3H).

<sup>13</sup>C NMR (126 MHz, THF) δ 164.1, 136.7, 133.4, 132.9, 131.5, 129.8, 129.2, 126.6, 123.7, 122.6, 121.4, 119.6, 118.5, 117.9, 66.9, 57.6, 57.3, 51.5, 31.5, 28.8, 28.7, 27.9, 25.0, 24.9, 24.8, 22.3, 22.0, 13.3, 11.0, 11.0.

HRMS (MALDI, [M+Na]<sup>+</sup>) calculated: 742.2921; detected: 742.2929; Δ = 1.1 ppm

Elemental Analysis theoretical (%): C 70.07, H 6.30, N 5.84, S 4.45; found (%): C 69.79, H 6.25, N 5.64, S 4.13

UV-vis λ (x 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>, THF solution): 464 nm (1.6); 500 nm (3.2); 535 nm (5.3)

### 3. $^1\text{H}$ , $^{13}\text{C}$ NMR Spectra

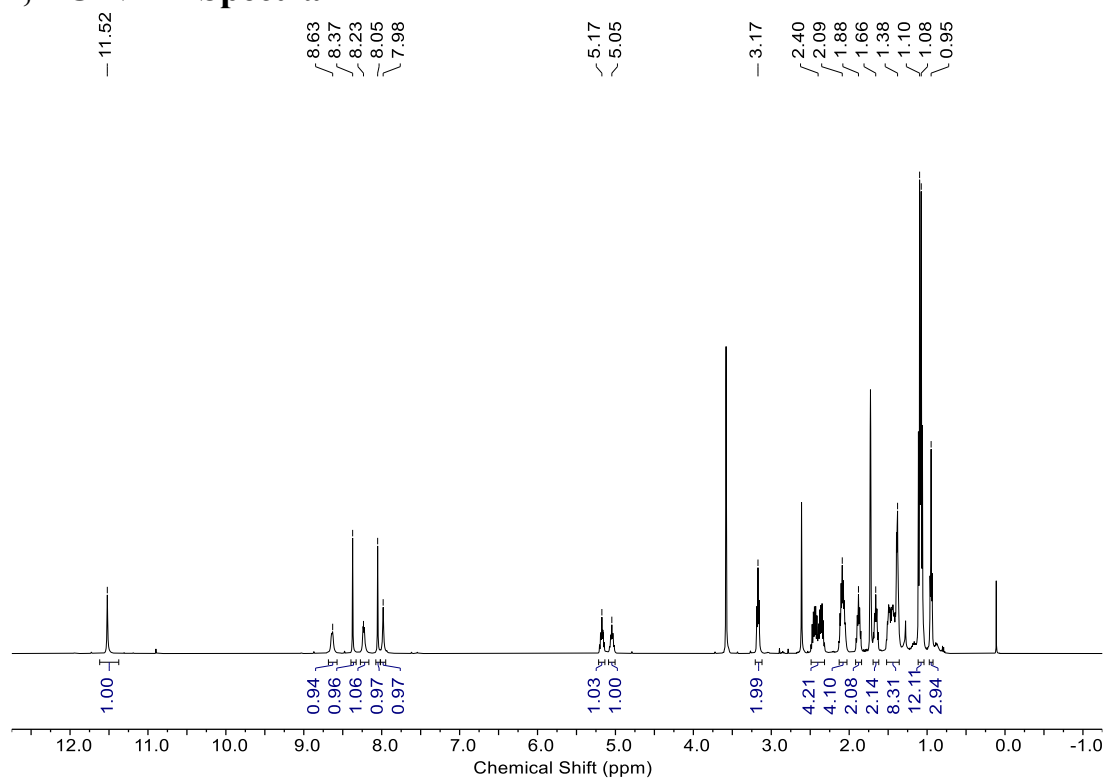


Figure S2.  $^1\text{H}$  NMR Spectrum of S-PDIN-H in  $\text{THF-}d_8$ .

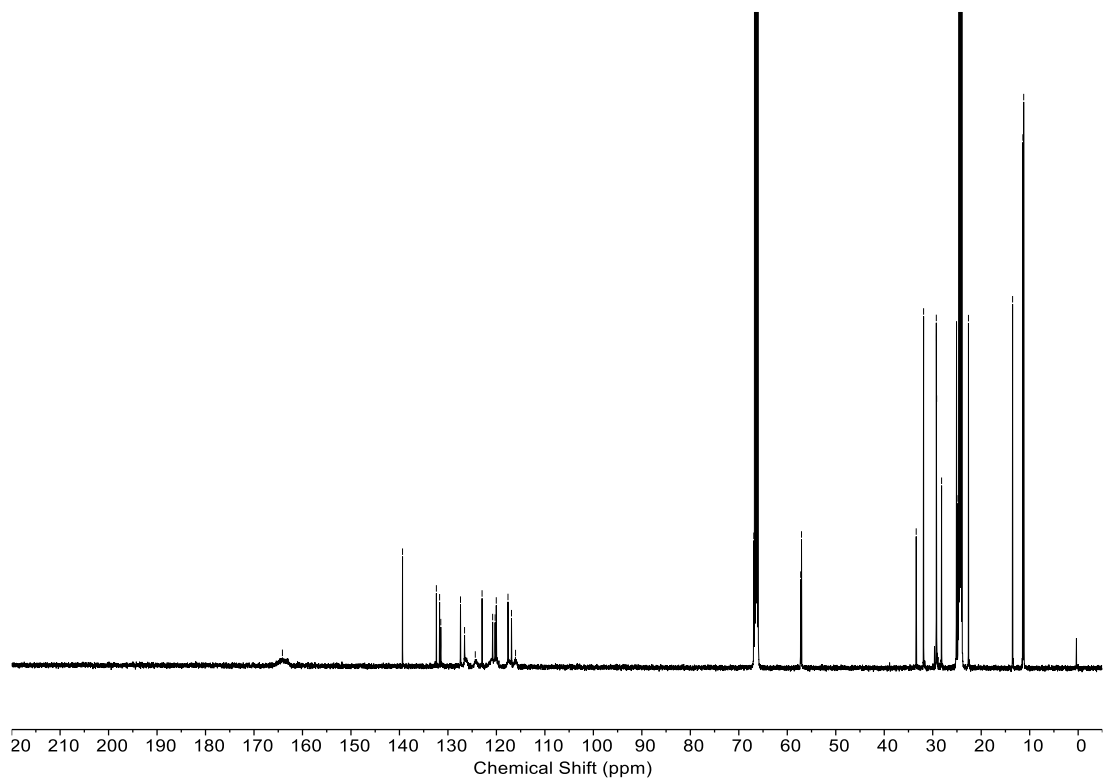
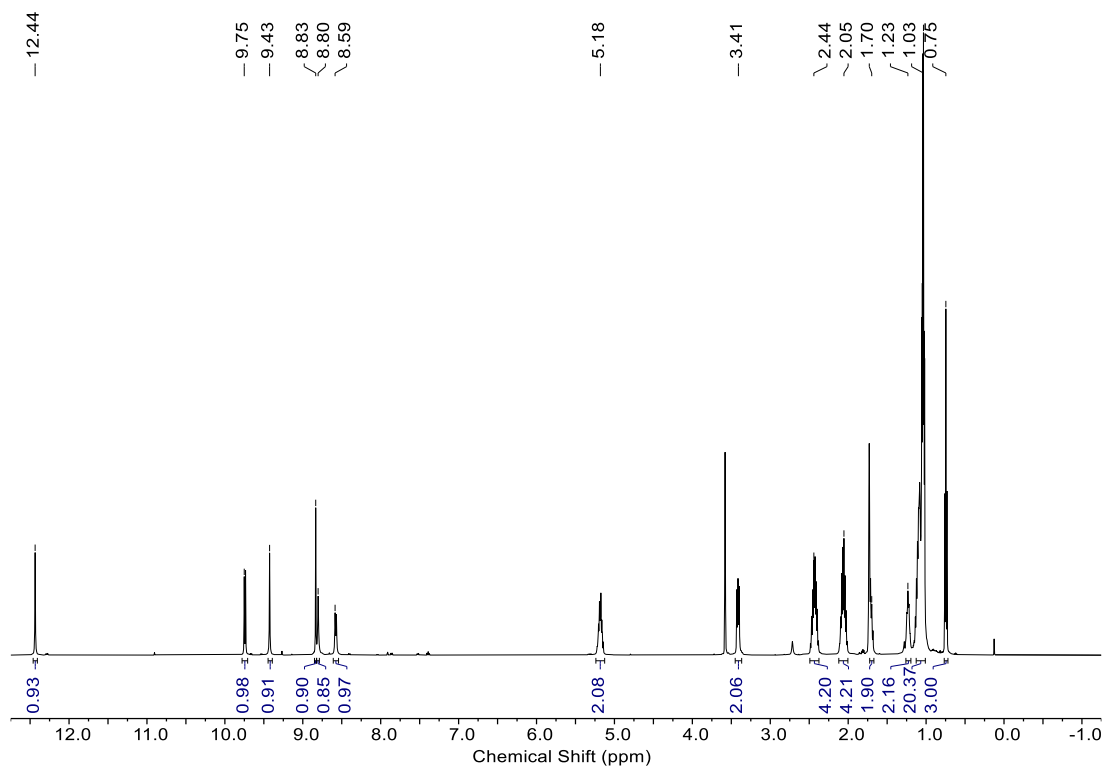
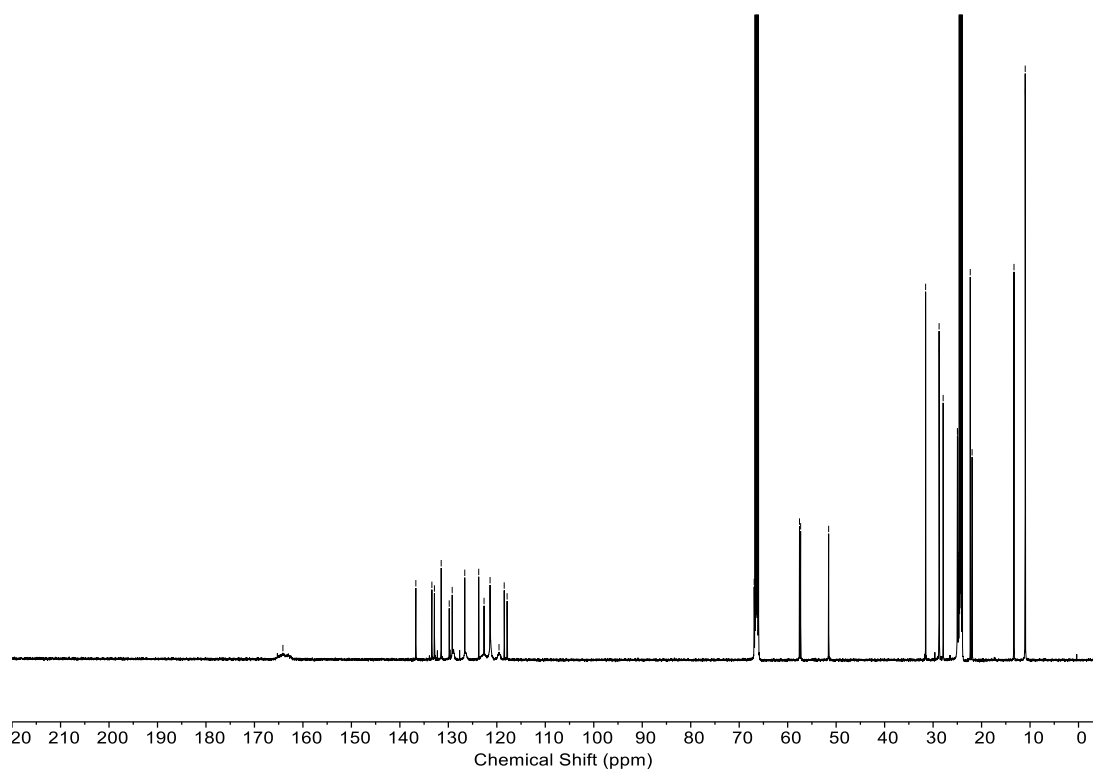


Figure S3.  $^{13}\text{C}$  NMR Spectrum of S-PDIN-H in  $\text{THF-}d_8$ .



**Figure S4.**  $^1\text{H}$  NMR Spectrum of  $\text{SO}_2$ -PDIN-H in  $\text{THF-}d_8$ .



**Figure S5.**  $^{13}\text{C}$  NMR Spectra of  $\text{SO}_2$ PDIN-H in  $\text{THF-}d_8$ .

## 4. Mass Spectra

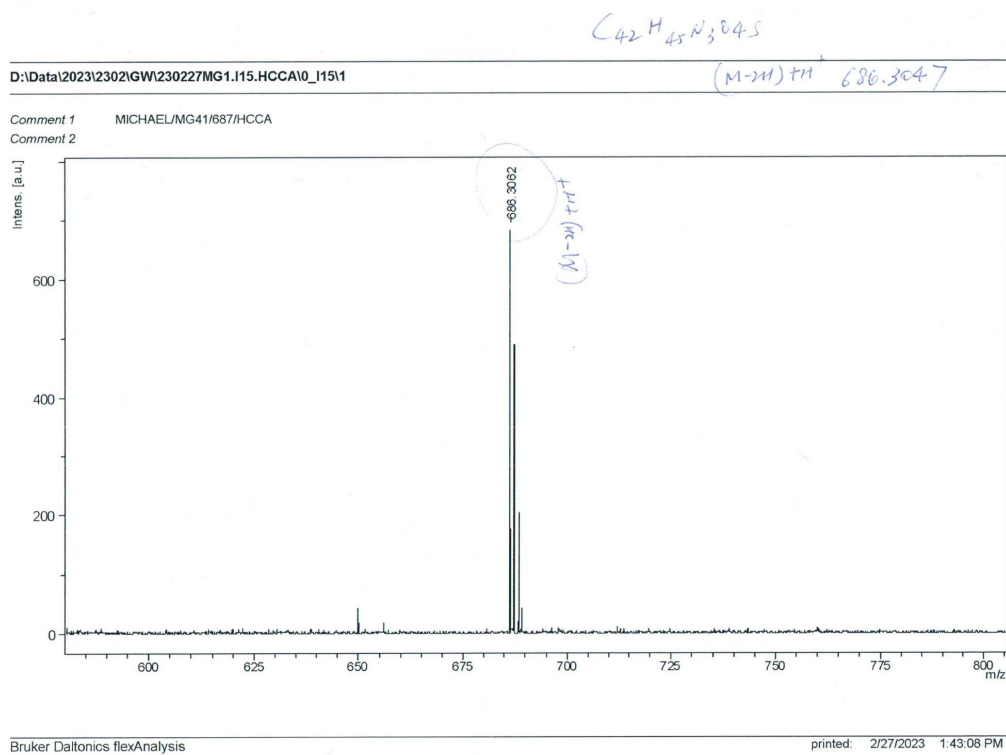


Figure S6. MALDI-TOF mass spectrum of S-PDIN-H

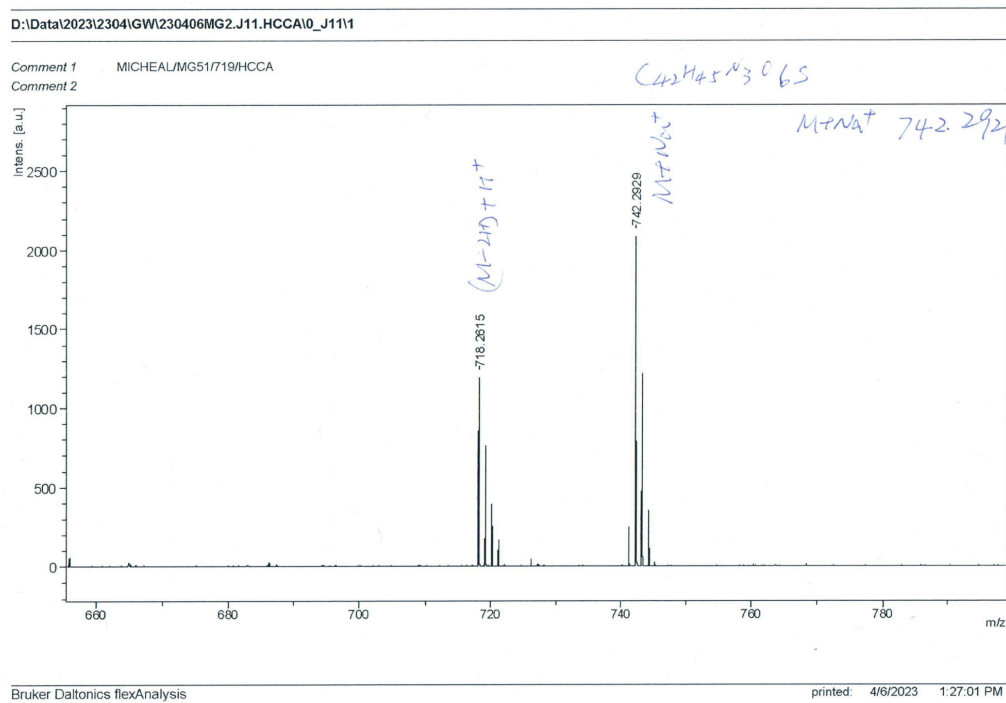


Figure S7. MALDI-TOF mass spectrum SO<sub>2</sub>-PDIN-H



## 5. CHNS Elemental Analysis

University of Calgary Department of Chemistry EA				Date:	10-25-2023
Name:	MICHAEL	Group:	GW		
Sample:	MGSP-1	Weight (mg):	2.185		
%C (Actual):	72.98	%C (Theoretical):	73.33		
%H (Actual):	6.56	%H (Theoretical):	6.59		
%N (Actual):	6.01	%N (Theoretical):	6.11		
%S (Actual):	4.38	%S (Theoretical):	4.66		

University of Calgary Department of Chemistry EA				Date:	10-25-2023
Name:	MICHAEL	Group:	GW		
Sample:	MGSP-2	Weight (mg):	2.159		
%C (Actual):	72.78	%C (Theoretical):	73.33		
%H (Actual):	6.71	%H (Theoretical):	6.59		
%N (Actual):	5.94	%N (Theoretical):	6.11		
%S (Actual):	4.44	%S (Theoretical):	4.66		

Figure S8. CHNS elemental analysis of S-PDIN-H

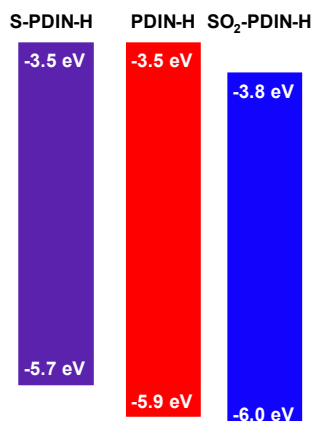
University of Calgary Department of Chemistry EA				Date:	12-20-2023
Name:	MICHAEL	Group:	GW		
Sample:	MG60-1	Weight (mg):	1.786		
%C (Actual):	69.59	%C (Theoretical):	70.07		
%H (Actual):	6.21	%H (Theoretical):	6.30		
%N (Actual):	5.70	%N (Theoretical):	5.84		
%S (Actual):	4.30	%S (Theoretical):	4.45		

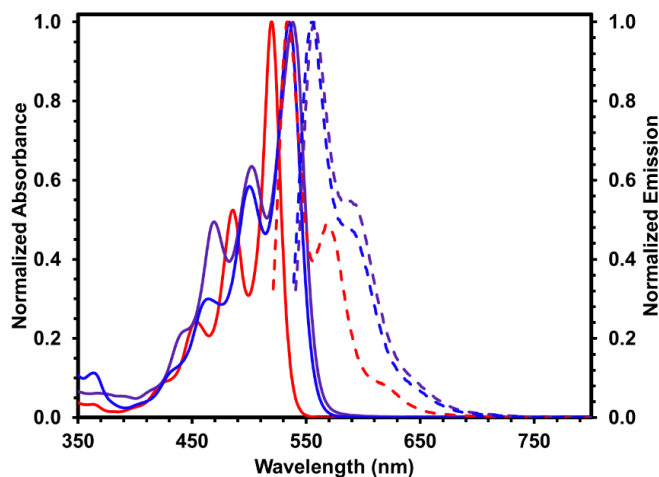
University of Calgary Department of Chemistry EA				Date:	12-20-2023
Name:	MICHAEL	Group:	GW		
Sample:	MG60-2	Weight (mg):	1.393		
%C (Actual):	69.79	%C (Theoretical):	70.07		
%H (Actual):	6.25	%H (Theoretical):	6.30		
%N (Actual):	5.64	%N (Theoretical):	5.84		
%S (Actual):	4.13	%S (Theoretical):	4.45		

Figure S9. CHNS elemental analysis of SO<sub>2</sub>-PDIN-H

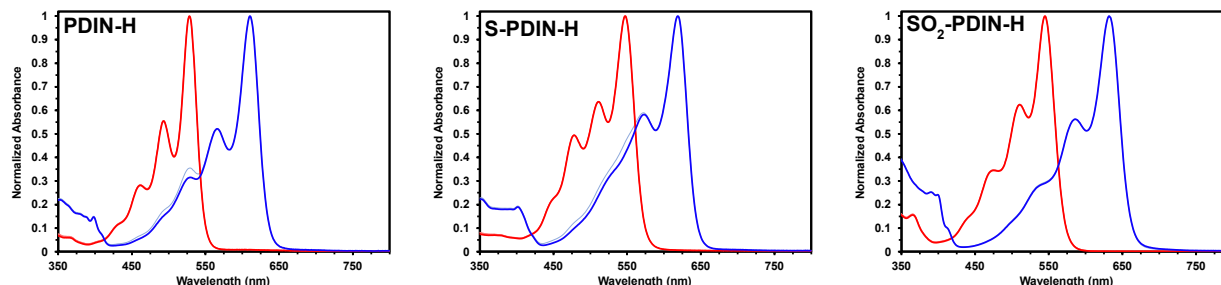
## 6. Additional Optical, Electronic and Film Characterization



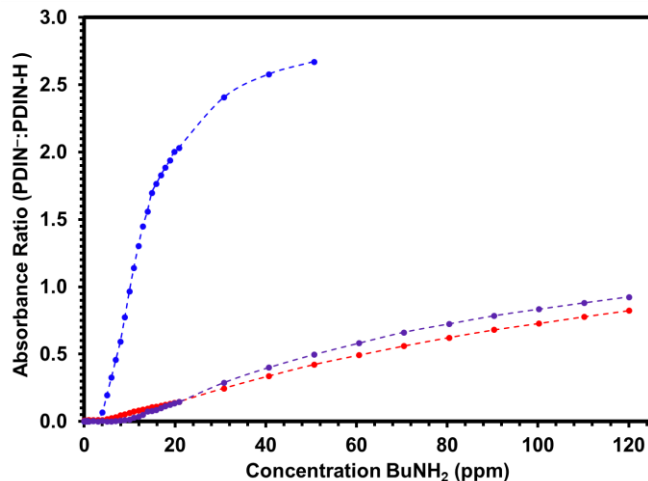
**Figure S10.** Energy level diagram for PDIN-H (red), S-PDIN-H (purple) and SO<sub>2</sub>-PDIN-H (blue). Orbital energies obtained from cyclic voltammetry data in dichloromethane according to  $E_{\text{LUMO}} = -4.8 \text{ eV} - E_{1/2, \text{Red1}}$ ; or  $E_{\text{HOMO}} = -4.8 \text{ eV} - E_{1/2, \text{Ox1}}$ .



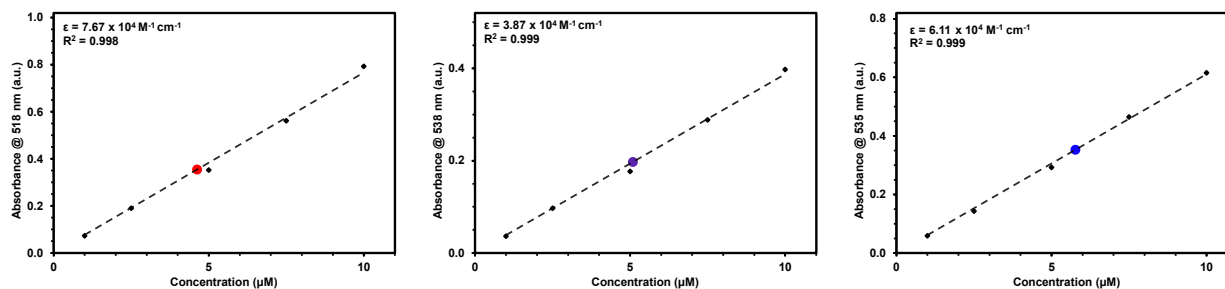
**Figure S11.** UV-Vis absorbance and emission spectra for PDIN-H (red), S-PDIN-H (purple) and SO<sub>2</sub>-PDIN-H (blue) in THF solution. Solid lines show absorbance spectra and dashed lines show emission spectra.



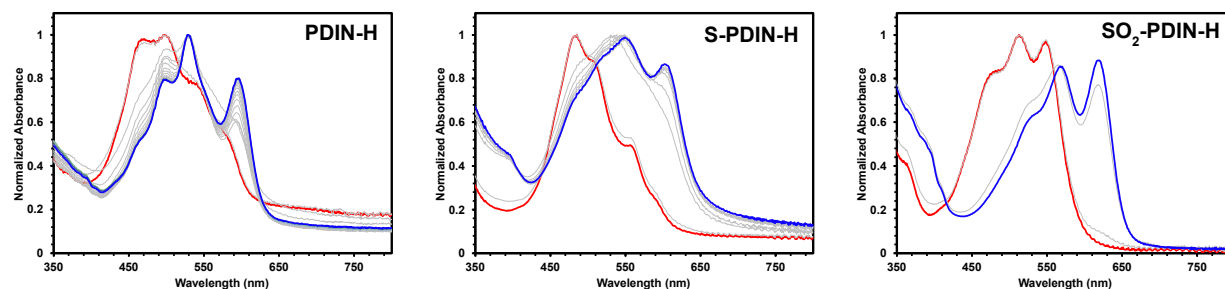
**Figure S12.** Normalized UV-Vis absorbance spectra for PDIN-H (left), S-PDIN-H (centre), and SO<sub>2</sub>-PDIN-H (right) with alternating equimolar additions of DBU (blue) and TFA (red). Subsequent additions are shown with colour desaturation. *Centre:* Normalized UV-Vis absorbance spectra for S-PDIN-H with alternating equimolar additions of DBU and TFA.



**Figure S13** Colorimetric response of solution phase sensing of BuNH<sub>2</sub> for PDIN-H (red), S-PDIN-H (purple) and SO<sub>2</sub>-PDIN-H (blue) on a linear x axis.



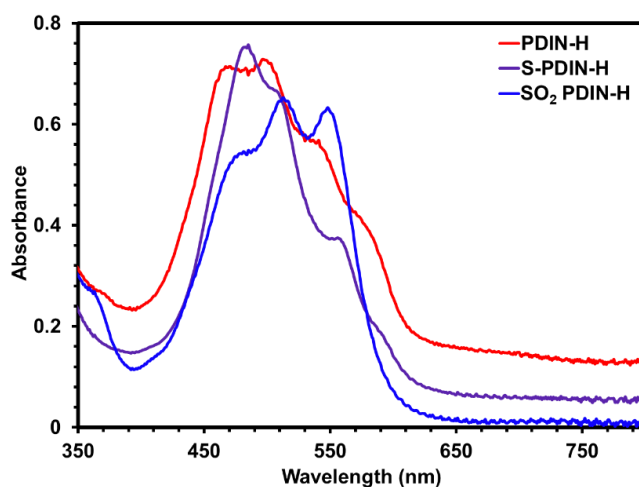
**Figure S14.** *Left:* Calibration curves for PDIN-H in MeTHF. Red spot shows the absorbance of a saturated solution of PDIN-H after dilution by a factor of 2000. *Centre:* Calibration curve for S-PDIN-H in MeTHF. Purple spot shows the absorbance of a saturated solution of S-PDIN-H after dilution by a factor of  $10^4$ . *Right:* Calibration curve for S-PDIN-H in MeTHF. Blue spot shows the absorbance of a saturated solution of PDIN-H after dilution by a factor of  $5 \times 10^4$ .



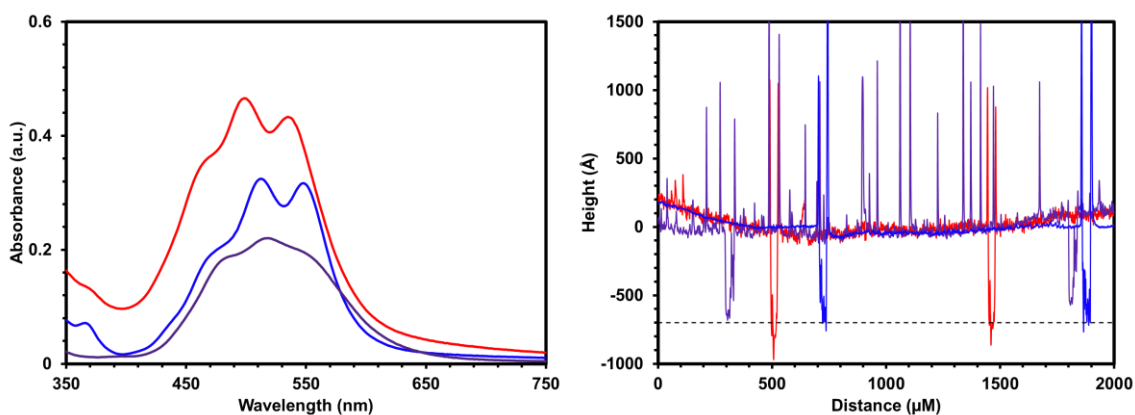
**Figure S15.** Film UV-Vis absorbance for PDIN-H (left), S-PDIN-H (centre) and SO<sub>2</sub>-PDIN-H (right) films upon exposure to 2  $\mu$ L n-butylamine in a  $\sim$ 5mL quartz cuvette. Each trace represents 15 seconds passing. Films are slot-die coated from MeTHF (S-PDIN-H, SO<sub>2</sub>-PDIN-H) or butylamine (PDIN-H) on top on a flexible PET substrate coated with SBS.



**Figure S16.** Images of PDIN-H (left), S-PDIN-H (centre) and SO<sub>2</sub>-PDIN-H (right) films before and after exposure to n-butylamine. Top images are prior to amine exposure, bottom images are after exposure. Films are spin-coated from MeTHF (S-PDIN-H, SO<sub>2</sub>-PDIN-H) or butylamine (PDIN-H) on a flexible PET substrate with an anti-static coating to enable thick films.

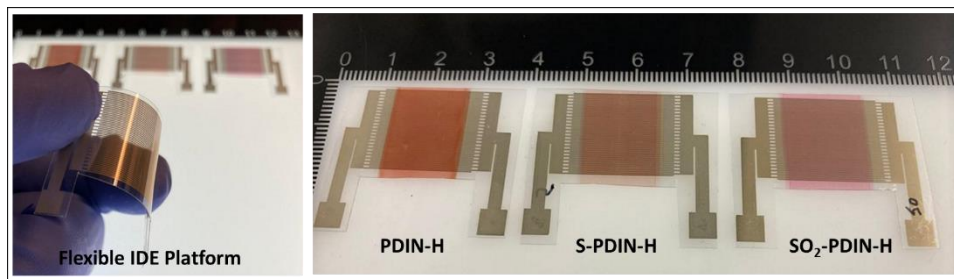


**Figure S17.** UV-Vis Film Absorbance Spectra for PDIN-H (red) S-PDIN-H (purple) and SO<sub>2</sub>-PDIN-H (blue). Films are slot-die coated from MeTHF (S-PDIN-H, SO<sub>2</sub>-PDIN-H) or butylamine (PDIN-H) on top on a flexible PET substrate coated with SBS.

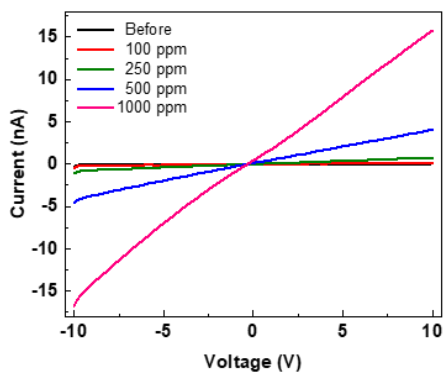


**Figure S18.** *Left:* UV-Vis Absorbance spectra for PDIN-H (red), S-PDIN-H (purple) and SO<sub>2</sub>-PDIN-H (blue) of films coated on ozone treated glass substrates. *Right:* Profilometry data showing film thickness for PDIN-H, S-PDIN-H and SO<sub>2</sub>-PDIN-H. Black dashed line shows 70 nm thickness. Films were spin-cast on ozone-cleaned glass substrates from MeTHF (S-PDIN-H, SO<sub>2</sub>-PDIN-H) or butylamine (PDIN-H).

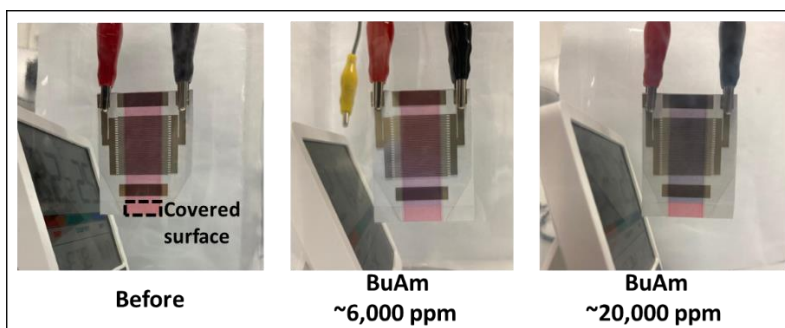
## 7. Additional Sensor Figures



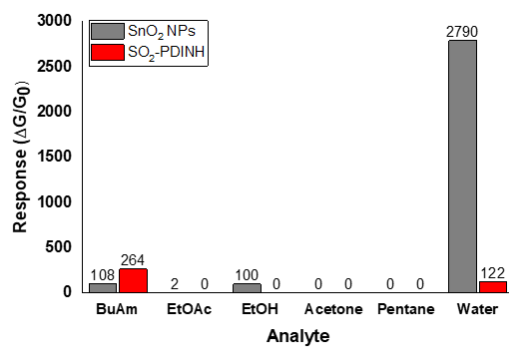
**Figure S19.** Pictures of the flexible IDE platform composed of silver electrodes printed on PET (left); and the respective sensors using PDIN-H, S-PDIN-H or SO<sub>2</sub>-PDIN-H. Sensors are fabricated by slot-die coating SnO<sub>2</sub> NPs from BuOH onto the flexible IDE platform. Active films are then slot-die coated from butylamine (PDIN-H), or MeTHF (S-PDIN-H, SO<sub>2</sub>-PDIN-H) on top of the SnO<sub>2</sub> NPs.



**Figure S20.** I-V curves for response of a sensor based on SnO<sub>2</sub>/SO<sub>2</sub>-PDIN-H when exposed to different concentrations of *n*-butylamine and measured over an applied voltage range of [-10 V: 10 V].



**Figure S21.** Image of SO<sub>2</sub>-PDINH sensor before (left) and under exposed to *n*-butylamine (right), highlighting the color change from pink to purple after deprotonation of the SO<sub>2</sub>-PDIN-H film. The bottom surface indicated was covered with tape, facilitating color comparison between the films.



**Figure S22.** Response of sensors to different analytes. For BuAm: 1000 ppm. For the other analytes, 100 uL solution was dropped inside the container. In ppm, the respective concentration was: EtOAc ~17000 ppm; EtOH ~28000 ppm; Acetone ~22000 ppm; Pentane: ~14000 ppm. For water, dropped 40 uL, ~36000 ppm (50% RH).

## 8. References

- [1] J. D. B. Koenig, W. E. Piers, G. C. Welch, *Chem. Sci.* **2021**, *13*, 1049–1059.