Supporting Information for

Direct Detection of Ultralow Trace Amount of Isocyanates in Air Using Fluorescent Conjugated Polymer

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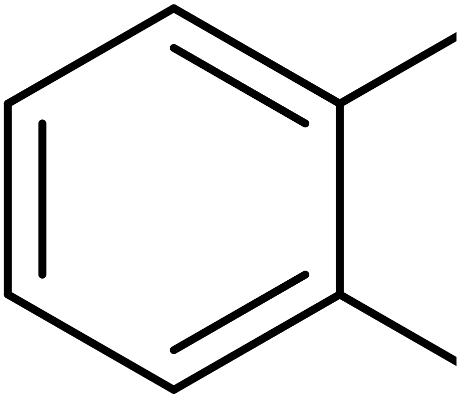
Materials and Methods

Toluene was dried and distilled over CaH_2 under an atmosphere of dry argon. Tetrahydrofuran was dried and distilled over benzophenone and sodium under an atmosphere of dry argon. Anthracene, benzoquinone, *p*-chloranil, n-butyllithium, ethynyltrimethylsilane, tin(II) chloride dehydrate, 4-bromobenzophenone, zinc dust, titanium tetrachloride, acetic acid, Tetrakis(triphenylphosphine)palladium(0), copper (I) iodode, diisopropylamine 1,1,2,2-tetrachloroethane, all isocyanates and all other reagents were purchased as a reagent grade from Aldrich and used without further purification. Potassium hydroxide and all the other solvents were purchased from Caledon laboratories limited and used without further purification.

Fisher-John's melting point apparatus was used for recording the melting points of all the synthesized compounds by thin disc method. Care was taken to ensure that the heating was done at a steady rate. The melting points were not corrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance Digital 300 and 400 MHz (300, 400 and 75, 100 MHz for ^1H and ^{13}C NMR, respectively). Resonances were quoted on the δ scale relative to tetramethylsilane (TMS, δ = 0) as an internal standard. For ^{1}H-NMR spectra, the following abbreviations have been used: s = singlet, d = doublet, t= triplet, q = quartet, m= multiplet. Infrared measurements were performed on a Varian 1000 FT-IR Scirinitar series spectrophotometer. The following abbreviations have been used in IR spectra: s = strong, m = medium, w = weak, br. = broad, sh = sharp. The measuring mode was %T (percentage transmittance). The bands were expressed in cm^{-1} (per centimeter). Mass spectra were measured with a Micromass Quattro LC ESI (EI). The UV-Vis spectra were recorded on a Perkin-Elmer Lambda 900 UV-Vis-NIR spectrometer at room temperature. The fluorescence spectra of all samples were measured in a quartz cuvette with a path length 1cm in Shimadzu RF-1501 spectroflurometer.



Scheme S1. The synthesis of monomer **1.**

Scheme S2. The synthesis of monomer **2**

9,10-Dihydro-9,10-o-benzenoanthracene-1,4-dione (III). Under an argon atmosphere in a two-neck flask, a mixture of anthracene (**I**) (10.0 g, 56.0 mmol) and *p*-benzoquinone (**II**) (20.27 g, 112.0 mmol) in 70 mL acetic acid was refluxed with vigorous stirring for 2.5 h. The reaction progress was monitored by TLC (Hexane: Acetone, 3:1). The resulting reaction mixture was poured into water and after filtering the crude was washed with hot water. The crude product was then purified by silica gel column chromatography using hexane as a first eluting solvent and then chloroform as a second one. Compound **III** (11.9432 g, 72.0%) was then obtained as yellow solid after removing the solvent. Product **III** (m.p 293.0 ^{0}C, lit ^{5} m.p 292-296 ^{0}C): ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.41 (4H, m), 7.06 (4H, m), 6.52 (2H, s), 5.81 (2H, s). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 183.54, 151.93, 150.96, 143.58, 135.40, 125.98, 125.48, 124.44, 124.26, 47.36. IR (NaCl Plate, cm^{-1}): 2980 (ν_{CH}).

5,6,7,12,13,14-Hexahydro-5,14:7,12-bis(o-benzeno)pentacene-6,13-dione (IV). Under an atmosphere of argon in a two-neck flask a mixture of compound **III** (11.0 g, 37.16 mmol), anthracene **I** (6.62 g, 37.16 mmol) and *p*-chloranil (9.27 g, 37.16 mmol) in 500 mL acetic acid was refluxed for 24 h. The progress of the reaction was monitored by TLC (Hexane:Acetone, 3:1 v/v). The resulting mixture was then cooled to room temperature and the filtered precipitate was washed with ether and dried in vacuum oven to give 16.61 g (92.0%) of compound **IV** as a yellow solid; m.p > 350 °C, lit.[5] m.p > 370 °C. ^{1}H-NMR (300 MHz, $CDCl_3$, ppm): δ 7.37 (8H, m), 6.99 (8H, m), 5.77 (4H, s). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 180.00, 150.96, 143.64, 125.48, 124.26, 47.36.

Compound V. In a flame dried two-necks round bottom flask, under an argon atmosphere **I** equivalent of n-butyllithium (33.34 mL, 82.55 mmol) in hexane was added dropwise to a solution of (trimethysilyl)acetylene (11.64 mL, 82.55 mmol) in 80 mL THF at 0 ^{0}C Before it was transferred to a solution of compound **IV** (16.0 g, 33.02 mmol) in 400 mL THF at 0 ^{0}C the mixture was kept at 0 ^{0}C for another 50 min. The reaction mixture was then warmed to room temperature. The reaction was monitored by TLC (Hexane: Acetone, 3:1). After overnight stirring 20 mL 10% HCl solution was added to the reaction mixture and the mixture was then extracted with chloroform .After removing the solvent hexane was added to the residue. Compound **V** (20.15 g, 89.62%) was collected by filtration as a mixture of *cis* and *trans* isomers. ^{1}H-NMR (300 MHz, $CDCl_3$, ppm): 7.35 (8H, m), 6.92 (8H, m), 5.50 (4H, s), 0.19 (18H, s). IR (KBr Pellet, cm^{-1}): 3498, 3257, 3068, 3019, 2959, 2897, 2173.

Compound VI. In a solution of compound **V** (5.0 g, 28.0 mmol) in 100 mL of acetone, a solution of tin (II) chloride dehydrate (4.13 g, 18.25 mmol) in 50% of acetic acid (50.0 mL) was added dropwise. This mixture was stirred at room temperature for another 24 h and the reaction progress was monitored by TLC (Hexane: Acetone, 3:1). After filtering the resulting solid it was dissolved in chloroform and washed with water and then sodium bicarbonate solution twice. The solvent was removed by the rotor-evaporation and the residue was precipitated in hexane. The resulting solid was dried in vacuum oven and collected as a white solid (3.50 g, 73%). m.p 417 °C, lit.[1] m.p 419 °C. ^{1}H-NMR (300 MHz, $CDCl_3$, ppm): 7.35 (8H, m), 6.96 (8H, m), 5.79 (4H, s), 0.50 (18H, s). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 144.86, 144.05, 129.19, 125.20, 123.77, 114.82, 102.48, 100.60, 52.07, 29.69, 1.01. IR (NaCl Plate, cm^{-1}): 2957(ν_{CH}).

Compound 1. In a solution of compound **VI** (2.80 g, 15.71 mmol) in THF (30 mL) and MeOH (30 mL) , a solution of KOH (2.0 g in 5 mL of H_2O) was added and the mixture was stirred at room temperature for 4 h.The progress of the reaction was monitored by TLC (Hexane: Dichloromethane, 3:1). The resulting solid product was filtered and washed with water and hexane. After dried in vacuum oven compound **1** was obtained as white solid powder (2.05 g, 95%). m.p 437 ^{o}C, lit.[1] m.p 439.5 ^{o}C. ^{1}H-NMR (300 MHz, $CDCl_3$, ppm): 7.37 (8H, m), 6.96 (8H, m), 5.84 (4H, s), 3.71 (2H, s). ^{13}C NMR (100 MHz, $C_2D_2Cl_4$ ppm): δ 144.06, 143.95, 124.90, 123.54, 113.57, 84.84, 78.03, 51.27. IR (KBr Pellet, cm^{-1}): 3303 ($\nu_{C\equiv C}$).

1,2-bis (4-bromophenyl)-1,2-diphenylethene (2). In a flame-dried three-neck flask under argon atmosphere, an ice-cooled (-5 ^{o}C) suspension of zinc powder (12.50 g, 191.19 mmol) in THF (240 mL) was prepared and titanium tetrachloride (20.00 mL, 181.81 mmol) was slowly added to the suspension. The resulting mixture was refluxed for 4 h. After cooling to room temperature, a solution of 4-bromobenzophenone (10.00 g, 38.30 mmol) in THF (50 mL) was slowly added to the mixture, and the mixture was then refluxed overnight. After cooling to room temperature, the mixture was diluted with saturated aqueous sodium hydrogen carbonate solution (until no bubble come out) and dichloromethane and stirred for 5 h. The mixture was filtered through a Celite pad, and the filtrate was separated into an organic and an aqueous layers. The aqueous layer was extracted thrice with dichloromethane, and the combined organic layer was dried over MgSO4 and the solvent was evaporated under the reduced pressure. The resulting white crude product was purified by silica gel column chromatography using hexane as eluting solvent. Compound **2** was obtained as white powder (8.50 g, 90.55% yield) after removing the solvent. Compund **2**

was further purified by multiple recrystalization in ehanol:toluene (3:2) and hexane:ethyl acetate (8:2) and obtained as white crystal. ^{1}H-NMR (300 MHz, $CDCl_3$, ppm): δ 7.26 (4H, m), 7.15 (6H, m), 7.01 (4H, m), 6.90 (4H, m). ^{13}C-NMR (100 MHz, $CDCl_3$): 142.93, 142.83, 142.39, 142.29, 140.31, 132.87, 131.21, 131.11, 130.91, 128.02, 127.82, 126.95, 126.83, 120.80, 120.66. EI-MS calculated for [M^+] 490.23, found 490. IR (KBr Pellet, cm^{-1}): 1640 ($\nu_{C=C}$).

Polymer P1. In a flame dried two-necks 25 mL round-bottom flask, under an argon atmosphere monomer **1** (0.2513 g, 0.50 mmol) and dibromo-TPE (0.2451 g, 0.50 mmol) was added to diisopropylamine\anhydrous toluene (2.8:4.2, 7 mL). After degassed and purged with argon for 30 min, $Pd(PPh_3)_4$ (0.030 g, 5 mol %) and CuI (0.0047g, 5 mol%) was added. The mixture was heated at 90 ^oC for 48 h under argon. The reaction mixture was then dissolved in $CHCl_3$ and washed with aqueous NH_4Cl solution and dried over anhydrous MgSO4. The solvent was removed by rotor-evaporator and the residue was dissolved into $CHCl_3$ and precipitated with MeOH three times. After drying under vacuum at 80 ^oC for 5h, the polymers were obtained (0.3019 g, 71% of yield) as greenish-yellow powder.

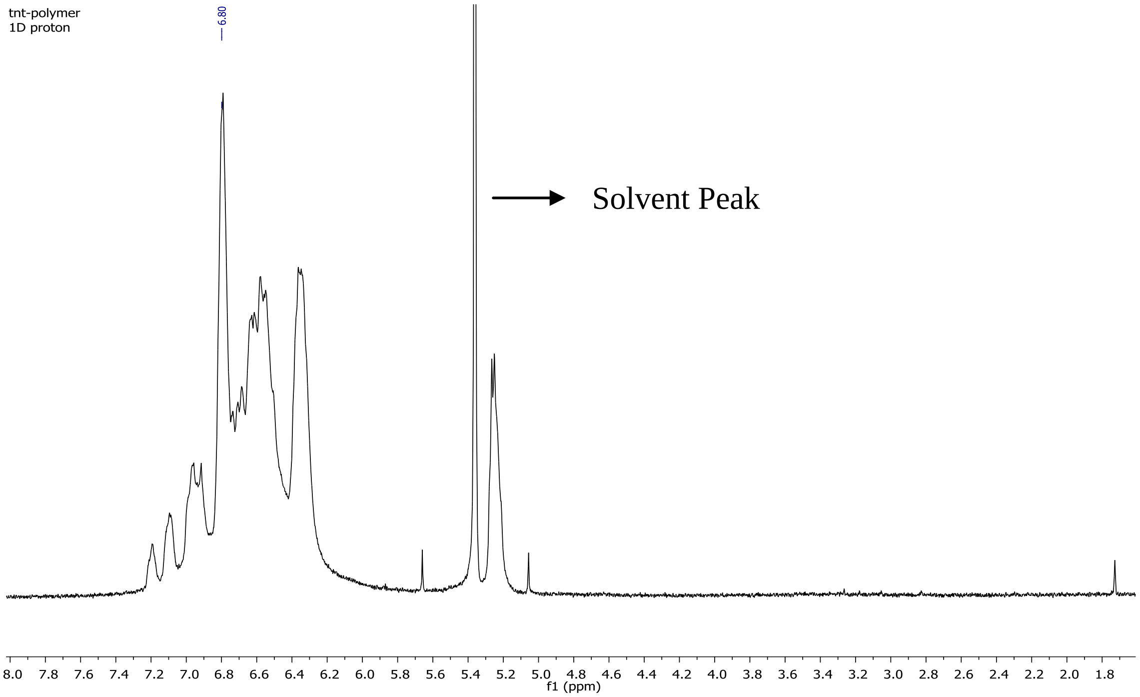


Figure S1. ^{1}H-NMR spectrum of polymer **P1** (300 MHz, $C_2D_2Cl_4$)

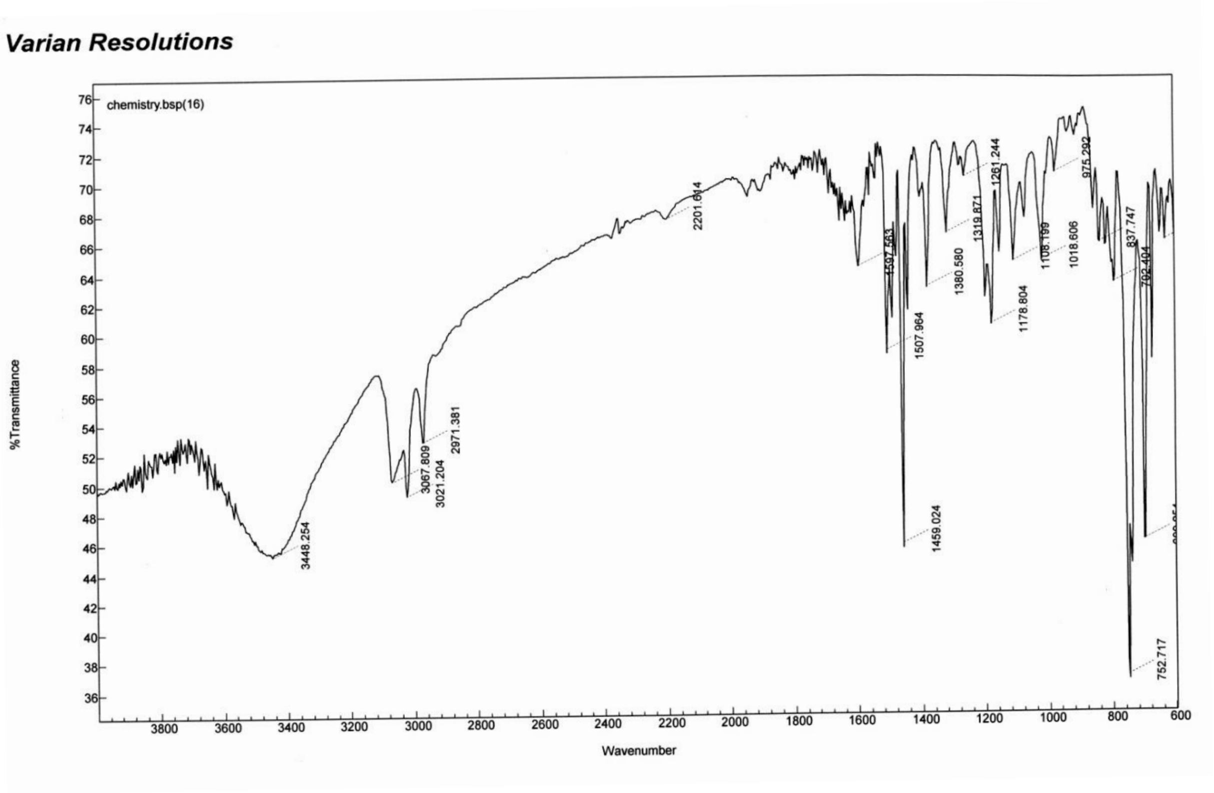


Figure S2. IR spectrum of polymer **P1** (KBr pellet).

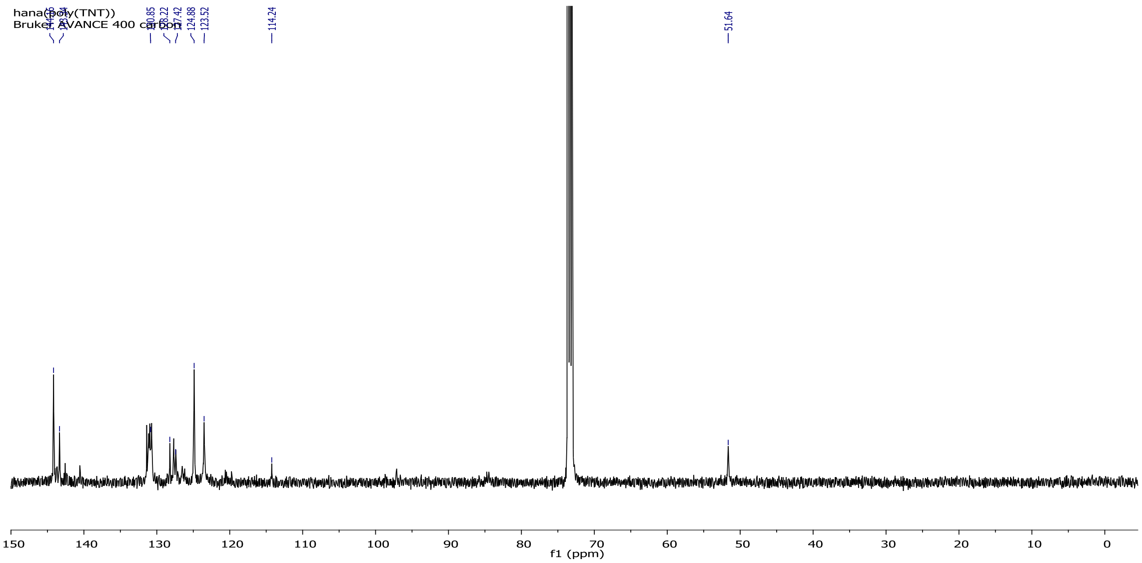


Figure S3. ^{13}C -NMR spectrum of polymer **P1** (100 MHz, $C_2D_2Cl_4$)

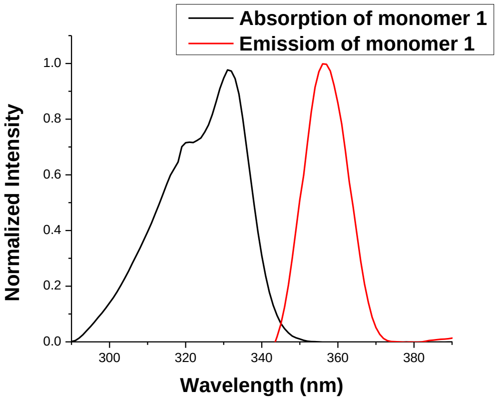


Figure S4. Normalized absorption and emission spectra of monomer **1** in 1,1,2,2-tetrachloroethane.

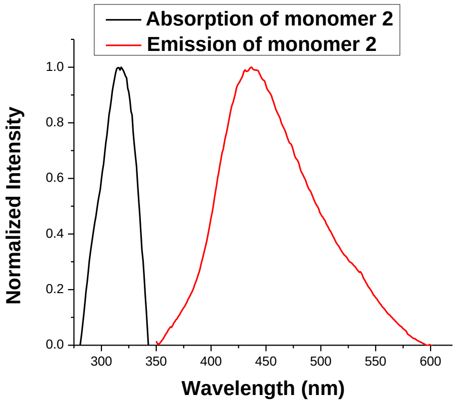


Figure S5. Normalized absorption and emission spectra of monomer **2** in $CHCl_3$

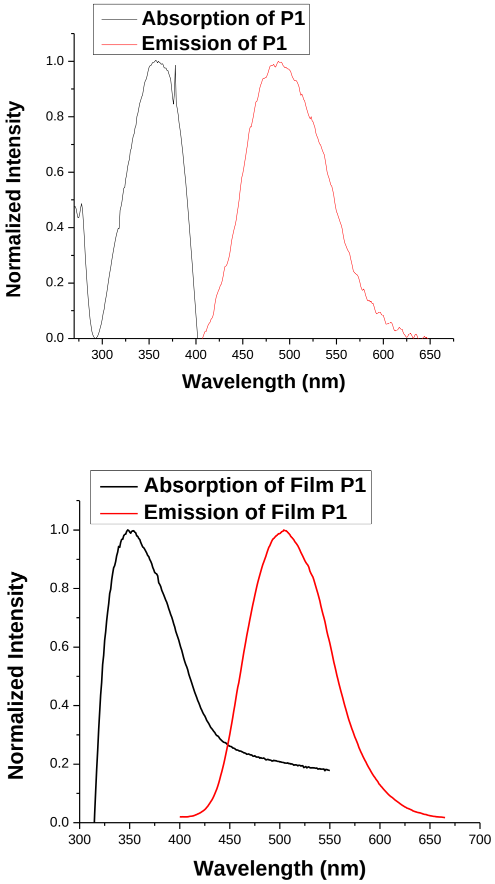


Figure S6. Normalized absorption and emission of polymer **P1** in (a) THF solution (b) film.

Figure S7. Structures of target isocyanates

Table S1. Vapor concentration of isocyanates[1]

Isocyanate	Vapor pressure (mmHg)	Vapor concentration (pg/mL)	Molarity of NCO group10^{-9} (mol/L)	Mw (g/mol)
PPDI	$<6.0 \times 10^{-3}$	52.46	0.655	160.13
TDI	<0.01	95.09	1.092	174.15
MDI	4.5×10^{-6}	0.062	4.9×10^{-4}	250.56
PI	1.4	9105.14	76.44	119.12
MeOPI	0.107	871.33	5.842	149.15
NO_2PI	6.84×10^{-3}	61.29	37.35	164.12
HDI	5.26×10^{-3}	48.34	0.287	168.22
IPDI	3.0×10^{-4}	3.64	0.033	222.28

Film Preparation

Films were coated on glass substrates by spin coating process. Polymer solution was spin-coated from 1,1,2,2 tetrachloroethane (TCE) solutions onto a glass plate (microscope slide, 20 × 20 × 1 mm) and spun at 1000 rpm by using a Chemat KW-4B spin-Coater. Then the films were dried for overnight at 80 ^{o}C under argon atmosphere. To prepare 4-80 nm thick films, 5-10 mg of polymer in 1.5 mL of solvent were used. The thickness of the films ranged from 4-80 nm, as measured using a Tencor Instrument Alpha-Step 200 surface profiler (uncertainty ± 0.01 Å) and by Atomic Force Microscopy (AFM) (uncertainty ± 0.2 nm).

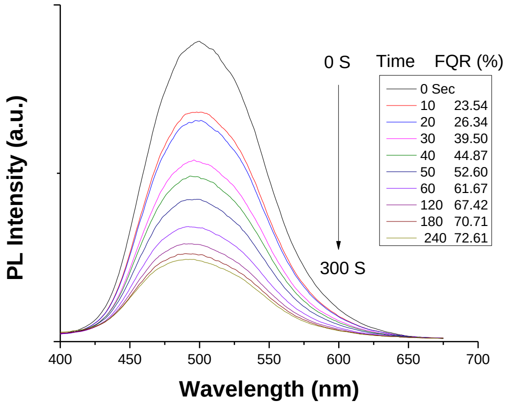


Figure S8. The time-dependent fluorescence intensity of **P1** film (7nm) upon exposure to HDI vapor (room temperature) from 0 s to 240 s.

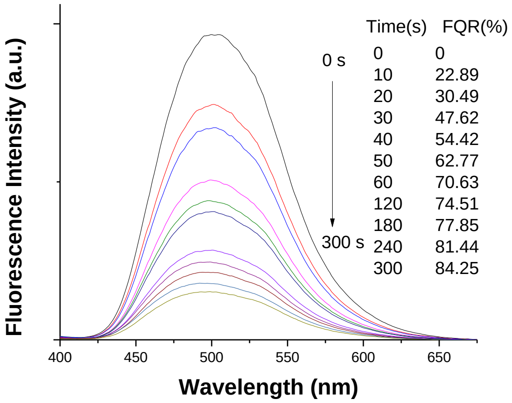


Figure S9. The time-dependent fluorescence intensity of **P1** film (4 nm) upon exposure to PPDI vapor (room temperature) from 0 s to 300 s.

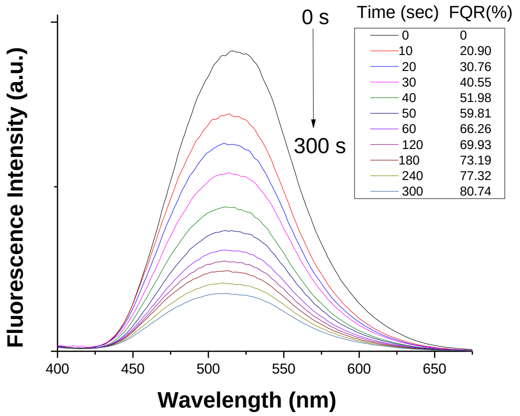


Figure S10. The time-dependent fluorescence intensity of **P1** film (4nm) upon exposure to PI vapor (room temperature) from 0 s to 300 s.

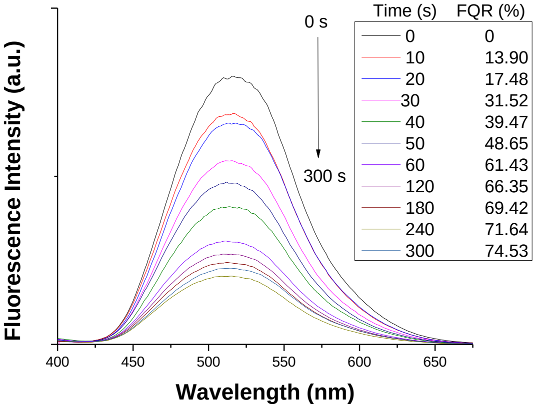


Figure S11. The time-dependent fluorescence intensity of **P1** film (4nm) upon exposure to NO_2PI vapor (room temperature) from 0 s to 300 s.

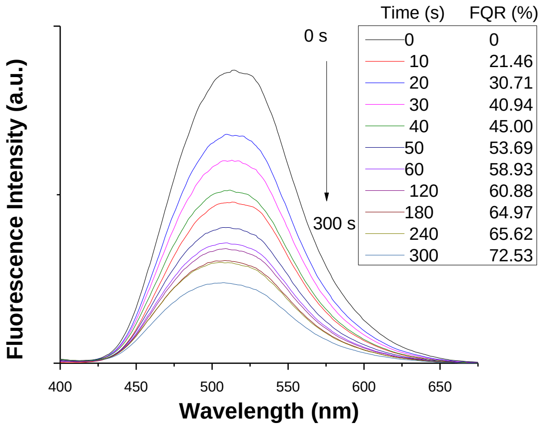


Figure S12. The time-dependent fluorescence intensity of **P1** film (4 nm) upon exposure to MeOPI vapor (room temperature) from 0 s to 300 s.

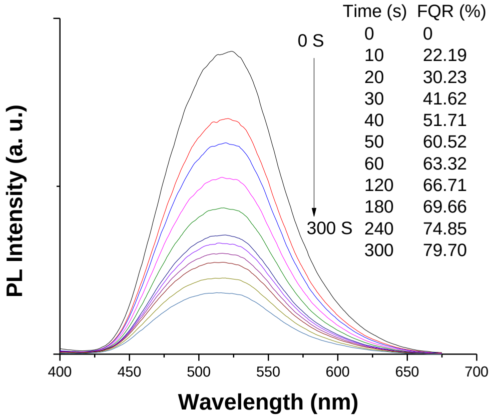


Figure S13. The time-dependent fluorescence intensity of **P1** film (7nm) upon exposure to TDI vapor (room temperature) at 0, 10, 20, 30, 40, 50, 60, 120, 180, 240 and 300 s.

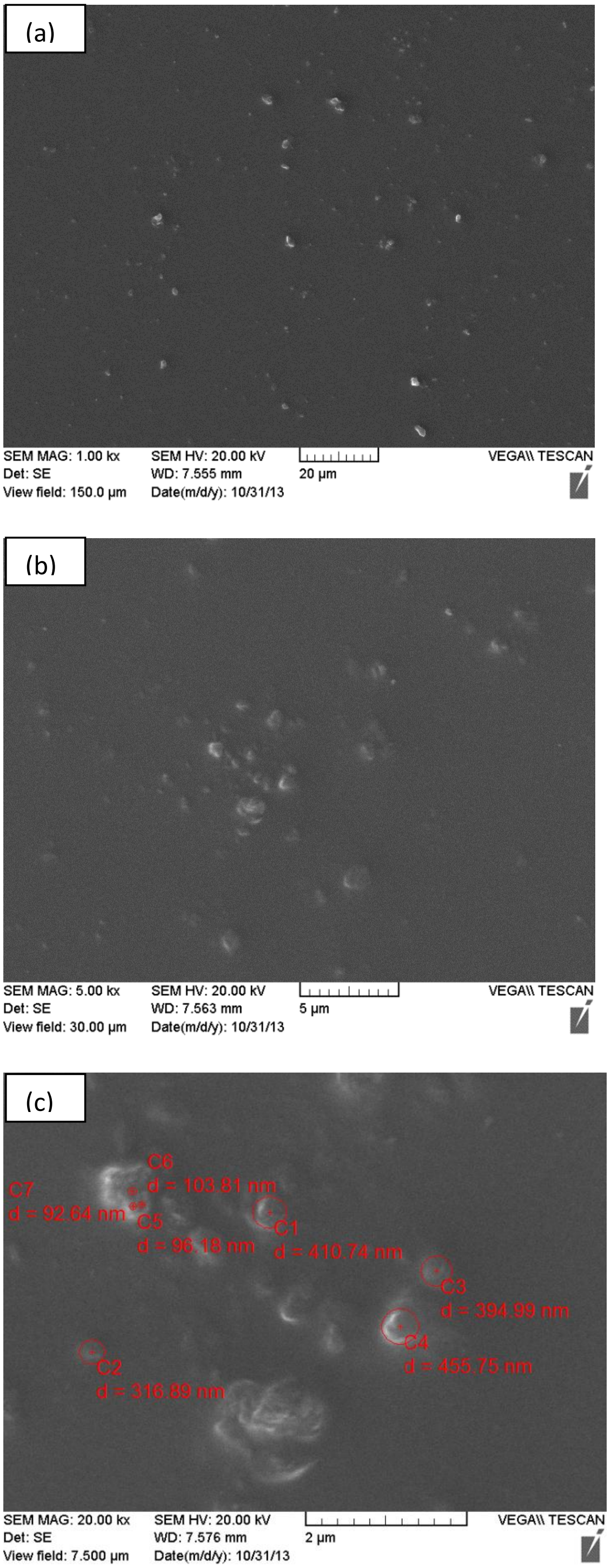


Figure S14. SEM images of polymer **P1** film on glass surface

REFERENCE

(1) (a) Sigma-Aldrich Inc. (TDI, HDI, NO_2PI); (b) NIOSH (National Institute for Occupational Safety and Health) (MDI); (c) NTP (Normal Temperature and Pressure) (PPDI); (d) IPCS (International Programme on Chemical Safety) (PI, MeOPI and IPDI).

(2) Reference 12 in the main text: (a) Québec, éditeur officiel, Réglementation sur la santé et sécurité autravail, décret 885-2001, Québec, 2001, Canada. (b) American Conference of Governmental Industrial Hygienists, Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices, Cincinnati, OH, 2004. (c) National Institute for Occupational Safety and Health Alert, Publication no. 1996-111, Cincinnati, OH, 1996. (d) Swedish National Board of Occupational Safety and Health, Occupational exposure limit values. Arbetarskyddsstyrelsens fösfattningssamling, AFS 2000: 3, Liber, Stockholm, Sweden, 2000. (e) Code of Federal Regulation (CFR), Government Printing Office, office of the federal register, 29 CFR *1910.1000, Washington DC, 1992.