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Luminescent Optical Detection of Volatile Electron Deficient ² Compounds by Conjugated Polymer Nanofibers

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Supporting Information 8

ABSTRACT: Optical detection of volatile electron deficient 9 analytes via fluorescence quenching is demonstrated using ca. 10 200 nm diameter template-synthesized polyfluorene nanofibers 11 as nanoscale detection elements. Observed trends in analyte 12 quenching effectiveness suggest that, in addition to energetic 13 factors, analyte vapor pressure and polymer/analyte solubility 14 play an important role in the emission quenching process. 15 Individual nanofibers successfully act as luminescent reporters 16 of volatile nitroaromatics at subparts-per-million levels. 17 Geometric factors, relating to the nanocylindrical geometry 18



of the fibers and to low nanofiber substrate coverage, providing a less crowded environment around fibers, appear to play a role in 19

providing access by electron deficient quencher molecules to the excited states within the fibers, thereby facilitating the 20

pronounced fluorescence quenching response. 21

etection of trace amounts of electron deficient com-22 pounds is important for a number of applications 23 24 including screening for hidden explosives, humanitarian 25 demining, and environmental monitoring, as well as criminal 26 and forensic investigations.^{1,2} In recent years, due to the 27 increasing threat from terrorism and organized crime, and the 28 consequent demand for improved security for citizens and 29 infrastructure, much attention has focused on detection of 30 explosives such as nitroaromatics (TNT, TNB), nitramines 31 (RDX, HMX, Tetryl), nitrate esters (PETN, nitrocellulose), 32 and organic peroxides (TATP, HMTD). Molecules that are not 33 explosive themselves, but present as impurities (DNT) or tags 34 (DMNB) in common formulations, can also be target analytes. 35 To detect explosives with high sensitivity and high selectivity, 36 many detection methods have been explored, including gas 37 chromatography, mass spectroscopy, ion mobility spectroscopy 38 and trained canine teams.^{2–4} However, these approaches are 39 either bulky, expensive, or require time-consuming training and 40 operation, limiting their deployment to fixed site screening at 41 major transportation hubs or government buildings.⁵

Optical addressed sensors have advantages in terms of 42 43 sensitivity, speed, portability, and cost-effectiveness, as well as 44 offering a variety of transduction schemes for signal retrieval.^{1,5} 45 Sensors for detection of explosive compounds have focused on $_{\rm 46}$ colorimetric and fluorescence detection methods, $^{6-8}$ with a 47 number of sensors based on organic and inorganic conjugated 48 polymers, small molecule fluorophores, metallo-organic com-49 plexes, and molecularly imprinted polymers reported.^{6,9-14} 50 While each class of chemical explosives presents their own set

of challenges for detection, nitroaromatics present particular 51 difficulties for gas phase sensors due to their low vapor 52 pressures.¹⁵ However, these electron deficient analytes bind 53 strongly to the electron-rich polymer thin films typically used, 54 while the subsequent fluorescence quenching response is 55 amplified by the molecular wire configuration of the 56 chromophores.^{14,16,17} The Fido explosives sensing platform, 57 based on this amplifying fluorescent polymers (AFP) approach, 58 is capable of detecting a range of nitrated explosive vapors.^{18,19} 59 Although most optically addressed detectors have been based 60 on planar transducer formats such as spun cast thin films or 61 spotted arrays, one-dimensional (1D) nanostructures such as 62 nanowires, nanotubes, and nanofibers have been attracting 63 increasing attention as chemical and biological sensors.²⁰⁻²⁷ ₆₄ Organic 1D nanostructures, possessing the processability and 65 high photoluminescence (PL) efficiency of their constituent ₆₆ molecular components,^{28–30} also offer advantages for sensing ₆₇ applications including their high surface-to-volume ratios and 68 analyte diffusion into the organic matrix, which is more difficult 69 for inorganic semiconductor nanowires or glass nanofibers.^{31,32} 70 The long-range exciton migration intrinsic to the well-71 organized molecular arrangement within these nanostructures 72 magnifies the fluorescence quenching response to surface 73 adsorbed analytes.^{10,17,33} 74

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Current strategies employed to enhance the sensitivity of 1D 75 76 nanostructures for sensing applications are focused on the structure-level design by controlling the structure morphol-77 78 ogy.^{34,35} The structures of various 1D nanomaterials, and their 79 hierarchical assemblies including meshes and nanoarrays, 80 effectively influence the absorption and diffusion behaviors of 81 the analyte.^{18,36,37} Therefore, considerable efforts have been 82 placed on optimizing the 1D structures and assemblies to 83 achieve high sensitivity, selectivity and fast time response.³⁸ 84 Besides tailoring the morphology and size of the nanostruc-85 tures, binary and multicomponent materials have investigated 86 to achieve superior sensing performance.³⁹ Doping is 87 commonly used to achieve controlled changes to photophysical 88 characteristics and consequent enhancements of sensing 89 performance.³⁴ The composite nanostructures can not only 90 combine the properties of different compounds but also ⁹¹ generate new functionality based on intermolecular interactions ⁹² and energy transfers.^{40,41} In this article, we report on the 93 luminescent optical detection of volatile electron deficient 94 compounds by conjugated polymer nanofibers based on 95 poly(9,9-dioctylfluorenyl-2,7-diyl), (PFO). The performance 96 of dense arrays of luminescent PFO nanofibers for gas phase 97 detection of trace amounts of 2,4-dinitrotoluene (DNT), 98 anthraquinone (AQ), and duroquinone (DQ) analytes was 99 compared with that of a thin film based sensor format prepared 100 using the same parent material. Following this, the effect of 101 packing density on the fluorescence quenching response is 102 investigated. Finally, detection of nitroaromatics at subparts-103 per-million levels is demonstrated on individual nanofibers by 104 scanning confocal microscopy and photoluminescence spec-105 troscopy.

106 EXPERIMENTAL METHODS

Materials. Porous alumina membranes with nominal pore 107 108 diameters of 200 nm were purchased from Whatman Ltd. 109 Poly(9,9-dioctylfluorenyl-2,7-diyl), PFO, with a polydispersity 110 index of 3.0 and a weight-average of 100 000 (PS standards) was purchased from H.W. Sands Corp. Sulfuric acid (H₂SO₄; 111 112 95-98%), sodium hydroxide, anhydrous tetrahydrofuran (THF), chloroform (CHCl₃), hydrochloric acid (HCl; 37% 113 114 in water), methanol, acetone, decane, 2,4-dinitrotoluene (2,4-115 DNT; 97%), duroquinone (DQ; 97%), and anthraquinone 116 (AQ; 98%) were purchased from Sigma-Aldrich, Ltd. All 117 reagents and solvents were used without further purification. 118 Deionized water (>16.1 MΩ cm, Milli-Q, Millipore) was used 119 for all aqueous solutions.

Preparation of Polyfluorene Nanofibers. A concen-120 121 trated solution of PFO (60 mg/mL) was prepared by dissolving 122 the polymer in anhydrous THF in a sealed amber glass vial, while heating to 60 °C and stirring vigorously for 30 min. The 123 solution was allowed cool to room temperature. Alumina 124 125 membranes were sonicated in methanol and air-dried prior to use. A 50 μ L drop of polymer solution was deposited on top of 126 127 a membrane. A glass coverslip was placed on top of the drop, facilitating penetration of the solution into the template pores. 128 129 A weight of ca. 2.5 kg was applied overnight. Following this, 130 excess material was removed from the template surface by scraping with a razor blade. The template, with embedded 131 132 nanofibers, was soaked in aqueous NaOH (3 M) for 12 h to 133 dissolve the alumina host. The NaOH solution was removed 134 and the nanofiber residue was gently washed three times with 135 deionized water and once with acetone before finally dispersing 136 the fibers in decane (with sonication for ca. 2 s). Random arrays

of nanofibers were prepared by depositing 5 μ L droplets of 137 fibers, suspended in decane, onto clean glass coverslips followed 138 by drying overnight in air.

Imaging and Optical Measurements. Scanning electron 140 microscopy (SEM) images were acquired using a field emission 141 instrument (FEI Quanta 3D DualBeam SEM, FEI) operating at 142 beam voltages of 1-10 kV. Atomic force microscopy (AFM) 143 images were acquired in tapping mode using a calibrated 144 instrument (Innova, Bruker AXS) with commercial tapping 145 mode probes (typical radius of curvature ca. 8 nm, front/side 146 cone angles of $15 \pm 2^{\circ}/17.5 \pm 2^{\circ}$ respectively and nominal 147 spring constant of 20-80 N/m; MPP-11123-10, Bruker AXS). 148 No processing was applied to data apart from background plane 149 subtraction. Luminescence microscopy images were acquired 150 using an upright epi-fluorescence microscope (BX51, Olympus) 151 equipped with a 100 W halogen lamp and a thermoelectrically 152 cooled color CCD camera (Fast1394 QICAM, QImaging). 153 UV-vis absorption spectra were acquired using a double-beam 154 spectrophotometer (V-650, Jasco) equipped with an optional 155 60 mm integrating sphere (ISV-722, Jasco). Photoluminescence 156 (PL) spectra were recorded using a luminescence spectrometer 157 equipped with a pulsed Xe short arc discharge lamp and 158 Czerny-Turner monochromators (QuantaMaster 40, Photon 159 Technology International). 160

PL Emission Quenching Studies. The emission quench- 161 ing response of PFO thin films and nanofiber arrays to vapors 162 of electron deficient analytes was ascertained by inserting one 163 such sample at a time into a sealed quartz cuvette containing 164 solid 2,4-DNT, DQ, or AQ at room temperature. The analyte 165 material had been presealed in the cuvette for 1 h in advance in 166 order to allow it reach its equilibrium vapor pressure. After a 167 certain time period had elapsed, the PFO sample was removed 168 from the cuvette and a PL spectrum was immediately recorded. 169 Thin film and nanofiber samples (on coverslips) were mounted 170 at 45° to the incident beam using a home-built coverslip holder 171 in a quartz cuvette that was placed into the cuvette holder of 172 the QuantaMaster 40 system. The solid quencher was placed at 173 the bottom of the cuvette to avoid direct contact with the 174 polymer sample on the coverslip. As a result, only vapors from 175 the analyte interacted with the PFO polymer sample. Single 176 nanofiber emission measurements were carried out using a 177 scanning confocal PL microscope (MicroTime 200, PicoQuant 178 GmbH) equipped with a 402 nm pulsed picosecond laser 179 diode. 180

RESULTS AND DISCUSSION

Polyfluorene Nanofibers. PFO nanofibers were prepared 182 under ambient conditions via solution-assisted wetting of 183 porous anodized alumina membrane templates. Following 184 synthesis, the nanofiber-filled template was attached to an 185 adhesive carbon pad and the alumina host was selectively 186 dissolved in aqueous NaOH (3 M). The remaining nanofibers 187 were rinsed with deionized water and dried under nitrogen gas 188 flow. Scanning electron microscopy (SEM) images of a 189 freestanding PFO nanofiber array following selective removal 190 of the template are shown in Figure 1a and b. The data 191 fl demonstrate that close-packed forests of nanofibers were 192 formed ($\sim 10^9$ nanofibers/cm²). Statistical analysis of the 193 SEM image data indicated a mean nanofiber diameter of 208 194 \pm 30 nm, in good agreement with the nominal template pore 195 diameter; see Figure 1c. The fibers exhibited a smooth outer 196 surface morphology without obvious structural defects. 197

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Figure 1. (a and b) Scanning electron microscopy images of a "forest" of nanofibers following selective dissolution of the alumina template. (c) Histogram of nanofiber diameters obtained following SEM image analysis. The solid red line is a Gaussian fit to the diameter distribution. (d) Epi-fluorescence image of a random PFO nanofiber array on a glass substrate.

An epi-fluorescence microscopy image of a dense array of 198 199 nanofibers that was deposited onto a glass substrate from a 200 decane suspension is shown in Figure 1d. Nanofiber length, L, 201 was found to range between 2 and 40 μ m, and mean fiber 202 length was found to be 15 \pm 2 μ m. Some degree of radial 203 curvature was observed for the majority of the fibers, indicating 204 the flexibility of these nanostructures. Uniform blue photo-205 luminescence with a low emission background was observed 206 along the full lengths of the fibers, indicating that the nanofiber 207 formation and extraction protocols provided dispersions of 208 robust, discrete high-aspect ratio PFO nanofibers in a format 209 suitable for deposition of nanofiber arrays. Additionally, the density of the deposited arrays could be readily tuned from 210 dense, multilayer surface coverage to well-dispersed, submono-211 212 layer surface coverage by appropriate dilution of the nanofiber 213 suspension.

Typical intensity-normalized absorption and PL spectra 214 215 acquired for a random PFO nanofiber array on glass are shown in Figure 2. The absorption spectrum of the nanofiber 216 array exhibited a band at ca. 395 nm (fwhm of ca. 110 nm) with 217 a shoulder near 407 nm and a pronounced low energy peak at 218 441 nm, the latter features being characteristic of the $S_0 \rightarrow S_1$ 219 220 0–1 and 0–0 transitions of β -phase PFO, respectively, and 221 indicated that a fraction of β -phase chains had formed within the amorphous phase matrix of the PFO nanofibers.^{42,43} The 222 long wavelength tail in this spectrum (above 450 nm) was 223 attributed to a degree of optical scattering by the nanofiber 224 array.⁴⁴ The PL spectrum of the nanofiber array exhibited 225 comparatively narrow emission peaks (viz. the PL spectrum of 226 an as-spun PFO thin film shown in Figure SI.1, Supporting 227 Information) at 441, 467, and 500 nm, indicative of a narrowed 228 229 distribution of emitting PFO chain segments with increased 230 effective conjugation lengths. This spectrum was characteristic 231 of the S₁ \rightarrow S₀ 0–0 transition, with associated vibronic replicas, 232 of β -phase PFO.^{42,45}

 f_2

²³³ The fraction of β -phase material present within the fibers was ²³⁴ estimated by deconvoluting the absorption spectrum by fitting ²³⁵ it with three Gaussian functions using a nonlinear least-squares



Figure 2. Intensity-normalized absorption (mauve line) and emission (blue line) spectra (λ_{ex} : 407 nm) of a random array of PFO nanofibers deposited on a glass substrate. (inset) Plot of three Gaussian functions (solid gray lines) and a background Gaussian function (dashed gray line) that were fitted to the nanofiber array absorption spectrum (solid black line). The sum of all four Gaussians is shown (red line).

algorithm; see Figure 2, inset.⁴⁶ An additional Gaussian was fit ²³⁶ to the data to account for the background signal, mainly due to ²³⁷ optical scattering from the nanofiber array. The amount of β - ²³⁸ phase was estimated by dividing the combined area of the ²³⁹ Gaussians centered at 407 and 441 nm by the total area of all ²⁴⁰ the fitted Gaussians (neglecting the contribution from the long ²⁴¹ wavelength tail). An upper limit value for the β -phase fraction ²⁴² of 7% was determined.⁴⁷

Overall, the spectroscopic data indicated that a fraction of the 244 amorphous phase PFO molecules, with initially random 245 molecular chain conformations, had adopted the more planar 246 and extended 2₁ helical molecular conformation of the β -phase 247 during synthesis;⁴⁸ see Scheme SI.3, Supporting Information. 248 The nanofiber emission spectra were completely dominated by 249 this fraction, due either to Förster-type energy transfer or to 250 singlet exciton migration from the glassy phase to the lower 251 energy β -phase.^{43,45,49} Formation of the β -phase within 252 polymer fibers was attributed to the action of mechanical 253 stresses that arose during solution-assisted filling of the alumina 254 template pores and, afterward, during solvent evaporation.^{42,50}

PL Quenching of Films and Nanofiber Arrays. The 256 photoluminescence behaviors of β -phase containing PFO thin 257 films and nanofibers in the presence of vapors of an electron 258 deficient analyte were compared by exposing individual samples 259 to solid analyte material (that was presealed in cuvettes for 1 h 260 in advance in order to allow the analyte reach its equilibrium 261 vapor pressure) for specific periods of time prior to measuring 262 PL spectra. PL spectra acquired for a typical, ca. 6.5 nm thick, 263 β -phase containing PFO film on a glass substrate following 264 exposure to DQ vapors for 0, 10, 30, 60, 120, 180, 300, and 600 265 s, respectively, are shown in Figure 3a. For comparison, PL 266 f3 spectra acquired under identical conditions for a typical dense, 267 random array of PFO nanofibers on a glass substrate are shown 268 in Figure 3b. As expected, both film and nanofiber spectra were 269 dominated by β -phase emission. Additionally, exposure to DQ 270 vapors resulted in a marked and rapid quenching of both film 271 and nanofiber emission. The time dependence of the quenching 272 responses, determined by monitoring the intensity of the 0-1 273 emission peaks (centered at 467 nm) as a function of exposure 274 time indicated a decrease in film emission intensity of 73% after 275 10 s, which progressed to 86% after 60 s. In contrast, nanofiber 276 array emission responded more gradually during exposure to 277



Figure 3. (a) PL spectra recorded for a typical β -phase containing PFO thin film on exposure to DQ vapor for different times. (b) Analogous data measured for a typical dense, random array of PFO nanofibers. (c) PL spectra recorded for a thin film on exposure to 2,4-DNT vapor for different times. (d) Analogous data measured for a dense nanofiber array. (e–g) Extent of PL quenching (decay of 0–1 peak intensity) for film (blue lines) and nanofiber array (red lines) samples as a function of exposure to DQ, 2,4-DNT, and AQ, respectively. Note: for all, $\lambda_{ex} = 401$ nm.

278 DQ vapor, with a decrease in nanofiber emission intensity of 279 31% after 10 s, which progressed to 50% after 60 s; see Figure 280 3e.

PL spectra acquired for a typical β -phase containing PFO 281 282 film following exposure to 2,4-DNT vapors are shown in Figure 3c. For comparison, PL spectra acquired under identical 283 conditions for a typical dense, random array of PFO nanofibers 284 are shown in Figure 3d. Exposure to 2,4-DNT vapors resulted 285 in rapid emission quenching. The quenching responses 286 indicated a decrease in film emission intensity of 48% after 287 10 s, which progressed to 59% after 60 s. Again, nanofiber array 288 emission responded more gradually, with a decrease in fiber 289 emission intensity of 13% after 10 s, which progressed to 30% 290 after 60 s; see Figure 3f. Finally, the time dependent quenching 291 responses observed for a β -phase containing PFO film and a 292 dense, random array of PFO nanofibers following exposure to 293 AQ vapors are compared in Figure 3g. Exposure to AQ vapors 294 resulted in a notably slow quenching of emission. A decrease in 2.95 film emission intensity of 4% after 10 s, which progressed to 5% 296 after 60 s, was observed, while nanofiber emission intensity 297 decreased by 2% after 10 s and progressed to only 3% after 60 s. 298 PL Quenching Mechanism and Trends. Since the 299 300 wavelength range of the PFO emission was far above the 301 absorption range of the analytes (see Figure SI.5, Supporting 302 Information), emission quenching by excited state energy 303 transfer was considered unlikely. Therefore, the observed

quenching response was assigned to photoinduced electron 304 transfer from the excited PFO to the electron deficient analytes. 305 The overall free energy change, ΔG° , may be approximated by 306

$$\Delta G^{\circ} = E(P/P^{+\circ}) - \Delta E_{0-0} - E(Q/Q^{+\circ})$$

where $E(P/P^{+\circ})$, ΔE_{0-0} , and $E(Q/Q^{+\circ})$ are the oxidation 307 potential of the PFO polymer, the lowest singlet 0–0 excitation 308 energy of the polymer and the reduction potential of the 309 analyte, respectively.⁵¹ $E(P/P^{+\circ})$ and ΔE_{0-0} values for glassy 310 phase PFO are 1.6 V (vs SCE)⁵² and 2.90 eV, respectively. 311 $E(Q/Q^{+\circ})$ values for 2,4-DNT, AQ, and DQ are -1.0, -0.9, 312 and -0.8 V (vs SCE), calculated from various different 313 electrochemical and optical measurement data; see Table 314 SI.1, Supporting Information.⁵³⁻⁵⁷ This results in ΔG° values 315 between -0.30 and -0.50 eV; see Scheme SI.4, Supporting 316 Information, for a schematic of the oxidative electron transfer 317 process. 318

The uptake, M(t), of an analyte by a thin film over a given 319 exposure time period can be calculated by 320

$$M(t) = 2M(\infty)\sqrt{\frac{Dt}{\pi L^2}}$$

where *D* is the diffusion coefficient of the analyte within the 321 film, $M(\infty)$ is the mass uptake at the equilibrium point, taken 322 as *SV* where *S* is the solubility of the analyte within the film and 323



Figure 4. (a and b) Representative epi-fluorescence microscopy images of dense and disperse random nanofiber arrays, respectively. (c and d) Emission spectra (λ_{ex} : 401 nm) recorded for typical disperse nanofiber arrays on exposure to DQ and 2,4-DNT vapors, respectively, for different times. (inset) Extent of emission quenching (decay of 0–1 peak intensity) during exposure to DQ (blue) and 2,4-DNT (red), respectively.

324 V its volume, L is the film thickness (cm), and t is the total 325 exposure time.⁵⁸ To estimate the uptake of, e.g., 2,4-DNT by a 326 PFO thin film, mean values of $D(1.1 \times 10^{-9} \text{ cm}^2/\text{s})$ and S(29) $_{327} \times 10^{-6}$ g/cm³) for 2,4-DNT were obtained for five different polymers with comparable diffusivity and solubility to PFO.⁵⁹ 32.8 Given that the PFO films were 2.42 cm² in area and 6.5 nm 32.9 330 in thickness, the total 2,4-DNT uptake after 18 s (ca. 50% 331 emission quenching) was estimated to be ca. 1.0×10^{-8} g or 5.9 $_{332} \times 10^{-11}$ mol. The total amount of PFO polymer within the film 333 was ca. 1.57×10^{-6} g (bulk PFO density of ca. 1 g cm⁻³ 334 without compression)⁴³ giving a total number of 9,9-335 dioctylfluorenyl monomers of ca. 5×10^{-9} M. Consequently, 336 the molar ratio of uptaken 2,4-DNT molecules to the total 337 number of available emissive fluorene monomers was about 338 1:85, indicating that emission quenching likely occurred via an 339 amplified luminescence quenching process mediated by PFO 340 polymer chains (which permitted exciton migration within the 341 film) rather than via direct quencher analyte-chromophore 342 interaction.⁶⁰ Since the film thickness was on the order of the exciton migration range (0-5 nm) measured for amorphous 343 PFO,⁶⁰ this amplified quenching process facilitated effective 344 quenching of film emission with a 2,4-DNT exposure time of 345 only a few minutes. 346

While a strong, negative exergonicity (ΔG°) facilitates 347 emission quenching, the quenching rate (EQ) is also related 348 to the polymer-analyte binding strength $(K_{\rm b})$ and the vapor 349 pressure of the quenching analyte molecules (VP) by the 350 expression EQ $\infty [\exp(-\Delta G^{\circ})^2] K_{\rm b} VP.^{10}$ This is pertinent to 351 the present study since the quenching effectiveness of the 352 analytes above (DQ > 2,4-DNT > AQ) differed from the 353 relative magnitudes of the reaction exergonicities (DQ > AQ > 354 355 2,4-DNT); see Figure 3e-g. While it was not possible to obtain 356 exact values for the polymer-analyte binding constants $(K_{\rm b})$, 357 polymer-analyte interactions may be considered in terms of the 358 free energy of mixing, i.e., $\Delta G_{\rm M} = \Delta H_{\rm M} - T\Delta S_{\rm M}$.⁶¹ $\Delta H_{\rm M}$ may 359 be estimated from $\Delta H_{\rm M} = \Phi_{\rm A} \Phi_{\rm P} (\delta_{\rm A} - \delta_{\rm P})^2$, where $\Phi_{\rm A}$ and $\Phi_{\rm P}$

are the volume fractions of analyte and polymer, respectively, 360 and δ_A and δ_p are the corresponding solubility parameters.⁶¹ 361 Since a negative ΔG_M is required for solubility, ΔH_M and $(\delta_A - 362 \delta_p)^2$ (i.e., $\Delta \delta$) should be as small as possible. The Hansen 363 solubility parameters for PFO and the analytes⁶¹ were used to 364 estimate $\Delta \delta$ for each of the three polymer/analyte pairs; see 365 Tables SI.2 and SI.3 of the Supporting Information. 366

Qualitatively, for $\Delta\delta$ < 1 analyte and polymer are expected to 367 be miscible, for $\Delta \delta = 1$ the components will be partially 368 miscible, and for $\Delta \delta > 1$ the components will become 369 progressively immiscible.⁶² Importantly, the order of the 370 magnitudes of the $\Delta\delta$ values estimated for each of the three 371 polymer/analyte pairs was consistent with their observed 372 quenching effectiveness. The role of the vapor pressure of the 373 analyte molecules (VP) in influencing EQ was also considered. 374 Again, the relative magnitudes of the equilibrium vapor 375 pressures were consistent with the observed order of quenching 376 effectiveness. The more effective PFO quenching response was 377 observed in the presence of DQ, with a vapor pressure of DQ 378 $(2.88 \times 10^{-3} \text{ mm Hg}, \text{ or } 2324 \text{ ppb, at } 25 \text{ °C})$, followed by 2,4- 379 DNT (1.47 \times 10⁻⁴ mm Hg, or 118 ppb, at 25 °C) and AQ 380 $(1.16 \times 10^{-7} \text{ mm Hg, or } 0.1 \text{ ppb, at } 25 \text{ °C})$, respectively.⁶³ 381

Role of Sample Morphology. From consideration of $_{382}$ Figures 3e–g, it is apparent that the EQ for each of the analytes $_{383}$ was greater for the ca. 6.5 nm thick β -phase containing PFO $_{384}$ thin films than for the PFO nanofiber arrays. Concerning the $_{385}$ morphology of the latter samples, dense nanofiber arrays were $_{386}$ typically observed to comprise multilayers of nanofibers $_{387}$ distributed in randomly stacked, disorganized arrangements; $_{388}$ see Figure 4a. To probe the effect of nanofiber density and $_{389}$ f4 substrate surface coverage on the emission quenching response $_{390}$ of the arrays, lower density nanofiber arrays were prepared $_{391}$ using a diluted (×4) nanofiber/decane suspension; see Figure $_{392}$ 4b. PL spectra acquired of disperse nanofiber arrays, comprised $_{393}$ of submonolayers of disperse, randomly distributed nanofibers $_{394}$ on glass substrates, following exposure to DQ or 2,4-DNT $_{395}$

396 vapors are shown in Figure 4c and d, respectively. Exposure to 397 the DQ and 2,4 DNT vapors resulted in a prompt and 398 significant quenching of nanofiber array emission. The time 399 dependence of the quenching responses, determined by 400 monitoring the intensity of the 0-1 emission peaks (at ca. 401 467 nm) as a function of duration of exposure to DQ vapor, 402 indicated a decrease in disperse nanofiber array emission 403 intensity of 73% after 10 s, which progressed to 87% after 60 s; 404 see Figure 4d, inset. While exposure to 2,4-DNT vapor resulted 405 in slightly less pronounced emission quenching, the time-406 dependent quenching responses indicated a decrease in 407 disperse nanofiber array emission intensity of 53% after 10 s, which progressed to 69% after 60 s. Therefore, the emission 408 409 quenching responses of disperse PFO nanofiber arrays were 410 markedly improved over the responses measured for dense 411 nanofiber arrays and were very similar to those measured for β -412 phase containing PFO thin films; see Figure 3e and f. 413 Specifically, the emission quenching responses to DQ vapor 414 were practically identical for thin films and disperse fiber arrays (extent of array quenching at 60 s/extent of film quenching at 415 $_{416}$ 60 s = 87%/86% = 1.01) while the responses measured during exposure to 2,4-DNT vapor were slightly more pronounced for 417 nanofiber arrays than for thin films (extent of array quenching 418 at 60 s/extent of film quenching at 60 s = 69%/59% = 1.17). 419 The observation that disperse arrays of ca. 200 nm diameter 420 421 PFO nanofibers could act as luminescent reporters of the 422 selected volatile electron deficient compounds and that, during 423 exposure to these analyte vapors, they exhibited an emission 424 quenching response which was comparable to that of the ca. 6.5 425 nm thick PFO films (see Figure SI.5, Supporting Information), 426 was very encouraging since the greater thickness of the fibers 427 might have been expected to reduce their relative response. In 428 this regard, assuming similar porosities and polymer-analyte 429 interactions for the solution processed PFO films and 430 nanofibers, a slower quenching response could be plausibly 431 expected for the fibers as a result of the longer times that might 432 be required for analyte molecules to diffuse into the interior of 433 the material during the quenching process.

However, the improved emission quenching performance 434 435 observed for the disperse nanofiber arrays suggested that 436 geometric factors relating to the lower substrate coverage, 437 providing a less crowded environment around each of the 438 fibers, may play a role in the quenching response. Specifically, 439 the cylindrical geometry of the disperse, randomly distributed 440 fibers may offer a significant advantage over planar thin films for vapor detection, as sensor size and shape are known to deeply 441 affect the time required to capture a given number of analyte 442 molecules. For example, for a hemicylindrical sensor, it has 443 been shown that the time required to accumulate analyte 444 molecules on the sensor surface via static diffusion is 445 significantly shorter than that required for a disk-shaped 446 sensor.⁶⁴ Likewise, it has been predicted, and experimentally 447 confirmed, that the response time for moisture diffusion into a 448 cylindrical polymer sensor structure may be up to 10-fold 449 shorter than that for a thin film sensor of identical thickness 450 and composition.65 451

452 Although a trade-off does exist between the average response 453 time and minimum concentration of analyte molecules that is 454 detectable by a sensor operating in a diffusion-limited regime, it 455 has been shown that, for the same response times, the detection 456 limit of a nanofiber sensor may still be 3–4 orders of magnitude 457 higher than that of a planar sensor.⁶⁶ These observations justify 458 the use of nanofibers in certain sensing applications and, for the PFO nanofibers employed in this work, the geometric factors 459 associated with the disperse nanofiber arrays likely facilitated 460 access by the electron deficient quencher molecules to the 461 excited states within the fibers enabling prompt quenching 462 responses. 463

Single Nanofiber PL Quenching. Further studies were 464 carried out on individual PFO nanofibers in order to explore 465 the ultimate level of miniaturization attainable for this nanofiber 466 based sensor format. To this end, single nanofiber optical 467 measurements were undertaken using a time-resolved laser 468 scanning confocal photoluminescence microscopy and spec- 469 troscopy system; see Figure 5. In a typical experiment, a 470 f5



Figure 5. (a) PL spectra recorded for a single nanofiber before and after exposure to a nearby solid 2,4-DNT pellet. (inset) Scanning confocal emission intensity images of the fiber before and after exposure; arrows indicate the location at which data were acquired. (b) Emission intensity versus time trace measured for the nanofiber prior to and during exposure to the 2,4-DNT material. Note: for all, $\lambda_{ex} = 402$ nm.

scanning confocal emission intensity image and a location 471 specific PL spectrum (λ_{ex} : 402 nm) were first recorded for a 472 selected nanofiber on a glass substrate under ambient 473 conditions. To prevent photobleaching, data were recorded 474 quickly (images: 2 ms pixel integration time; spectra: 30 s 475 integration time) at an incident excitation power $<0.1 \text{ nW/cm}^2$. 476 Then, to ensure that the nanowire emission output was stable, 477 the integrated emission intensity ($\lambda > 430 \text{ nm}$) was recorded in 478 real time for 30 s at which point a solid pellet of 2,4-DNT 479 material (51 mg) was gently placed into position at a height of 480 5 mm above the nanofiber sample; see Scheme SI.2, Supporting 481 Information. The nanofiber emission intensity was subse- 482 quently recorded over a period of ca. 6 min. Following this, a 483 second scanning confocal emission intensity image and 484 spectrum were recorded for the fiber. Emission intensity 485 images of a typical selected nanofiber that were recorded prior 486 to and following exposure to 2,4-DNT in this manner are 487

488 shown in the inset to Figure 5. The nanofiber exhibited a 10-489 fold decrease in emission intensity that was uniform along the 490 full length of the fiber, i.e., no residual emission "hot spots" 491 were observed. Corresponding PL spectra measured at a 492 location on the nanofiber before (black line) and after (red 493 line) exposure are shown in the main panel of Figure 5a. 494 Clearly, exposure resulted in an almost complete quenching of 495 the nanofiber emission. (Note that the apparent slight red shift 496 in the wavelength position of the 0-0 emission peak was an 497 artifact caused by the low transmission of the 430 nm long pass 498 filter.)

Finally, the emission intensity versus time trace was acquired 499 500 at the same location on the nanofiber; see Figure 5b. Prior to placement of the 2,4-DNT material near the nanofiber, a stable 501 502 emission trace, with an average intensity of ca. 55 counts/ms, was recorded. Immediately following placement, as 2,4-DNT 503 molecules volatilized from the surface of the solid sample, 504 entered the ambient atmosphere and diffused toward the 505 506 nanofiber, a dramatic decrease in nanofiber emission intensity 507 was observed. Under these conditions, the local concentration 508 of 2,4-DNT molecules in the vicinity of the nanofiber was 509 expected to be considerably less than that obtained using the 510 cuvette approach (i.e., equilibrium vapor pressure) employed 511 during the thin film and nanofiber array measurements 512 described above. Remarkably, for the single nanofiber, emission 513 was observed to rapidly drop by ca. 10% after only 1 s, by 50% 514 after 6 s, and by ca. 82% after 60 s. The good agreement 515 observed between data obtained during multiple measurements 516 at different locations along different fibers confirmed that the 517 reduction in nanofiber emission intensity were due to analyte-518 induced emission quenching and not to localized photo-519 bleaching. To estimate the vapor pressure of 2,4-DNT s20 molecules at the nanofiber surface, an approximation in terms 521 of diffusion from a planar surface using Fick's law, made by 522 considering that the pellet dimensions were substantially 523 greater than those of the nanofiber, was used:

$$\frac{\partial \phi}{\partial t} = D \frac{\partial^2 \phi}{\partial x^2}$$

s24 where *D* is the 2,4-DNT diffusivity in air $(0.203 \text{ cm}^2/\text{s})^{67}$ and ϕ 525 is the flux of 2,4 DNT molecules. The resulting 1D solution is

$$\phi(x, t) = \phi(0, 0) \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right)$$

526 Using this, and assuming that $\phi(0,0)$ is proportional to the 527 saturation vapor pressure of 2-4,DNT (140 ppb at 25 °C),⁶³ 528 the vapor pressure at the surface of the nanofiber array sample 529 1 s after placement of the pellet was estimated to be 25 ppb. 530 Assuming this represents the detection limit of the nanofiber ⁵³¹ sensor, this compares very well with current commercially ⁵³² available explosive sensors.^{18,19}

533 CONCLUSION

534 The photoluminescence behavior of PFO nanofiber arrays 535 changes markedly in the presence of vapors of electron 536 deficient analytes, which cause significant quenching of 537 nanofiber emission via an amplified luminescence quenching 538 process. The observed order of analyte quenching effectiveness 539 is DQ > 2,4-DNT > AQ indicating that, in addition to energetic 540 factors, analyte vapor pressure and polymer/analyte solubility 541 plays an important role in the emission quenching process. 542 Examination of the emission quenching responses of submonolayers of disperse, randomly distributed nanofibers, 543 permits detection of nitroaromatics at subppm levels by 544 individual nanofibers. The observation that individual ca. 200 545 nm diameter PFO nanofibers exhibit an emission quenching 546 response competitive with that of ca. 6.5 nm thick PFO films, 547 suggests that geometric factors relating to the lower nanofiber 548 substrate coverage, providing a less crowded environment 549 around the fibers, combined with the nanocylindrical fiber 550 geometry, play a role in providing access by the electron 551 deficient quencher molecules to the excited states within the 552 fibers thereby facilitating the quenching response. 553

The results confirm that such nanostructures may success- 554 fully act as luminescent nanoscale vapor sensors and 555 demonstrate the performance that may be achieved by 556 controlling the structure and morphology of sensor transducer 557 elements at the nanoscale. Practical application of the PFO 558 nanofibers for volatile compound sensing requires a portable, 559 cost-effective device with full data connectivity for field 560 operations.⁶⁸ Ozcan and co-workers demonstrated fluorescent 561 imaging of single nanoparticles, viruses, and DNA fragments on 562 a smartphone-based optical reader,^{69,70} which was later used for 563 detection of parts-per-billion level detection of mercury 564 contamination in real world water samples.⁷¹ More recently, 565 Ming et al. reported the development of low-cost chip-based 566 wireless multiplex diagnostic device using a smartphone-based 567 optical reader.⁷² The excellent responsivity and signal-to-noise 568 ratios exhibited by the PFO nanofibers lend themselves to this 569 smartphone based approach for realization of an optical sensor 570 platform, with rapid response times and subparts-per-million 571 detection levels. 572

ASSOCIATED CONTENT

Supporting Information

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Further experimental details. Characteristics of PFO thin films 575 and their luminescence responses to analytes. Key physical 576 parameters of the conjugated polymer/analyte system. 577 Comparative quenching responses of PFO thin films, nanofiber 578 arrays, and single nanofibers. This material is available free of 579 charge via the Internet at http://pubs.acs.org. 580

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Notes	585

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