## **Iptycene-Based Fluorescent Sensors for Nitroaromatics and TNT**

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Abstract: Small-molecule fluorescent sensors (1-5) for the recognition of nitroaromatic compounds, such as 2,4-dinitrotoluene and the explosive TNT, were obtained by using a three-step dehydrohalogenation cycloaddition protocol. The interaction of the receptors and nitroaromatics was studied both in solution and in the solid state by using fluorescence spectroscopy and X-ray crystallography, respectively. It is shown that the iptycene receptors 1-5 provide a cavity suitable for binding nitroaromatic compounds in an edge-toface mode, rather than simple ringstacking interactions. The results obtained inspired us to develop an inexpensive, reliable and robust sensor for vapour detection of explosives. Poly-

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mer nanofibres are particularly suitable for the production of such TNT sensors as they accelerate the mass exchange between the polymer and the vapours of TNT. Quenching of the sensors took place within 1 min compared to 10 min for a glass-slide assay. Hence, the sensor performance can be improved by optimising the matrix material and morphology without resynthesising the sensor moieties.

### Introduction

The development of efficient, robust, reliable and portable methods for the detection of explosives is an issue in global security. The widespread use of nitro-compounds and nitroaromatics as explosive materials, both in civilian and military applications, makes them susceptible to illicit use. Moreover, TNT and its analogues are massively used in the fabrication of landmines and improvised explosive devices (IEDs).<sup>[1]</sup> This poses various threats to the civilian population as the landmines are expensive to remove and demining requires a significant expertise. It is estimated that 2.5 million new landmines and IEDs are fabricated every year and around 70 people are killed or injured daily by these weapons. The cost of disarming a single landmine is in the vicinity of 1000 US dollars.

State-of-the-art detection in public and military structures is performed by using trained canines, IR/Raman spectroscopy detectors, by X-raying the suspect containers, and with ion mobility spectrometry, an analytical technique capable of detecting vapours of explosive materials as well as narcotics or hazardous chemicals.<sup>[2a]</sup> Although these methods are considered highly efficient, their cost and portability is usually limited, particularly for stand-off detection. More-

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over, handheld instruments often suffer from diminished selectivity to interfering analytes, a condition frequently encountered in the field or in high-volume screening, such as landmine fields or in the case of shipping containers or crates.<sup>[2b]</sup>

Until recently, most of the research efforts in explosives sensing were oriented towards colorimetric/fluorescent single-molecule sensors, such as phosphole oxides,<sup>[3a]</sup> oligopyrroles,<sup>[3b,c]</sup> and calix[4]arenes,<sup>[3d]</sup> and fluorescent polymers in which fluorescence changes in the presence of nitroaromatic analyte. Interesting examples are anthracene-based Hbonded supramolecular polymers,<sup>[4a]</sup> iptycenes-based polyphenylene ethynylenes (PPE)<sup>[4b]</sup> or polyphenylenebutadiynylenes,<sup>[4c]</sup> polyacetylenes,<sup>[4d]</sup> polymetaloles,<sup>[4e]</sup> such as polysiloles,<sup>[4f]</sup> silica-supported metalloporphyrins,<sup>[4g]</sup> pyrene-copolyimides,<sup>[4h]</sup> poly(2-methoxy-(2'-ethylhexloxy)-p-phenylene-vinylene (MEH-PPV),<sup>[4j]</sup> dendrimers<sup>[5a,b]</sup> and metal-organic frameworks (MOFs).<sup>[6]</sup> However, many of these materials are relatively costly to prepare on a large scale and, to date, the only example of successful commercial application are Swager's iptycene amplifying polymers,<sup>[4b]</sup> which led to the development of the Fido<sup>®</sup> portable devices<sup>[7]</sup> by Nomadics, Inc.

We previously reported<sup>[8]</sup> on our synthetic efforts of small-molecule receptors 1-5 inspired by Swager's iptycene polymers (Figure 1).<sup>[4b]</sup> Receptors **1–6** exhibit fluorescence quenching upon coordination of nitroaromatics, presumably due to a photoinduced electron transfer mechanism (PET). To achieve the maximum efficiency of the PET process the fluorogenic fragment must be appended close to the electron-rich receptor. In this case, upon receptor (sensor) excitation, the electron in the LUMO of the receptor (donor) can be transferred to the LUMO of the nitroaromatic ana-

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Figure 1. Molecular structures of receptors 1-6.

lyte (acceptor). As a result, the excited state of the sensor does not relax with emission of light, that is, its fluorescence is quenched (Figure 2).



Figure 2. Mechanism of electron transfer between the  $S_1$  state of receptor, R, and the LUMO of a nitroaromatic compound, NA. a) The PET process prevents radiative decay from the  $S_1$  state; b) back electron transfer from NA<sup>-+</sup> to R<sup>++</sup> anion/cation radicals.

As shown in Figure 1, different fluorogenic fragments attached were in the 1,4-positions of the [1.1.1<sup>b</sup>.1.1]pentiptycene<sup>[9]</sup> central benzene ring. The steric congestion caused by the ortho-substituents of the fluorogenic fragments and the iptycene bridgehead hydrogen atoms is expected to constrain the 1,4-aryl fragments to assume an almost perpendicular alignment with respect to the central benzene ring. Unlike in the iptycene-phenyl ethynylene polymers,<sup>[4b, c]</sup> this perpendicular arrangement of the fluorogenic residues makes an effective conjugation with the iptycene unlikely, thereby increasing the HOMO-LUMO gap in 1–5. Conversely, the ethynylene moieties in 6 allow for efficient conjugation through the central benzene ring. This conjugation is likely to decrease the corresponding sensor LUMO energy, and potentially to reduce the driving force of the PET process. To investigate this point, sensor 6 was prepared to show the improved sensing efficacy of 1-5 with a direct attachment of aryl moieties.

Previously published iptycene sensors were of polymeric nature, which precluded insight into possible binding motifs of the nitroaromatics and iptycene receptors. Because sensors 1–5 are small molecules, an extensive effort was mounted to grow single crystals that would enable binding investi-



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Figure 3. Analytes employed in this study. NB: nitrobenzene; 2,4-DNT: 2,4-dinitrotoluene; TNT: 2,4,6-trinitrotoluene; 1-NO<sub>2</sub>Napht: 1-nitronaphtalene; DMDNB: 2,3-dimethyl-2,3-dinitrobutane; RDX: 1,3,5-trinitroper-hydro-1,3,5-triazine.

gation by means of X-ray crystallography. Further studies were then performed by using fluorescence spectroscopy in solution as well as in the solid state. The analytes tested in this study are shown in Figure 3.

The considered nitroaromatics are of widespread use amongst the commercial nitro-based explosives, either as the main components or as manufacture by-products. DMDNB is an aliphatic compound used as taggant for legally manufactured explosives; canines are particularly sensitive to this molecule, less than a part per trillion.<sup>[7c]</sup> RDX is another widespread explosive and is supposed to have a poor or nil interaction with receptors **1–6**.

#### **Results and Discussion**

**Synthesis:** The synthesis of receptors **1–5** was previously reported by our group.<sup>[8]</sup> To synthesise **1–5**, we utilised a cycloaddition reaction of an aryne<sup>[10]</sup> and anthracene. Cadogan's procedure<sup>[11a,b]</sup> utilising a haloarene and *t*BuOK in the presence of anthracene is described to yield *tert*-butyl aryl ethers as well as iptycene side-products (~2%). Revision of the method allowed for an easy three-step synthesis of **1–5** in 20–50% yield.<sup>[12]</sup> The reaction mechanism is summarised in Scheme 1. Compound **6** was prepared from pentiptycene quinone<sup>[13]</sup> and lithium phenyl acetylide.<sup>[14]</sup>

**X-ray structures:** Single crystals suitable for X-ray diffraction studies were obtained by slow evaporation of solutions of receptors **5** in benzene and **3** in nitrobenzene. **5**•C<sub>6</sub>H<sub>6</sub> crystallises in the *P*–1 space group and the unit cell contains one full and four quarter-units of **5**•C<sub>6</sub>H<sub>6</sub>, shared with neighbouring cells (Z=2).

As it is shown in Figure 4b, the dihedral angle of the thiophene rings with respect to the central plane of the iptycene is 74.7°, the two thiophenyl rings pertinent to the same 2,2'bisthiophene fragment are not perfectly coplanar, and show a plane-to-plane angle of 161°. Figure 4a and b clearly show that the benzene molecule fits into the cavity formed by the receptor. Thus, the receptor, at least in the solid state, is



Scheme 1. General synthesis of receptors 1-5.



Figure 4. Crystal structure of: a), b) 5·C<sub>6</sub>H<sub>6</sub>, and c), d) 3·C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>. Thermal ellipsoids are represented at the 50% probability level. Panels (b) and (d) show side-views of the host–guest complexes; the benzene and the nitrobenzene molecules are shown in space-fill mode. The dihedral angles,  $\phi$ , between the pendant groups and the iptycene are highlighted.

able to bind small-molecule aromatics, in an edge-to-face fashion.<sup>[7b,14]</sup>

The host-guest complex  $3 \cdot C_6 H_5 NO_2$  crystallises in the *P*-1 space group and the unit cell contains four units of the complex (*Z*=4). Figure 4c shows a similar arrangement for the complex  $3 \cdot C_6 H_5 NO_2$  to that of  $5 \cdot C_6 H_6$ ; the two benzothiophene residues lie almost perpendicular to the central benzene ring of the iptycene with a dihedral angle of 81.9° (Figure 4d). The nitrobenzene molecule fits into the cavity and also displays an edge-to-face binding mode.

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Literature on the topic of face-to-edge binding between electron-rich faces and edges of the nitroaromatics lends support to this binding mode.<sup>[15]</sup> In any case, we can expect a stronger interaction in the case of the nitrobenzene compared to the benzene guest, since the former is an electron-poor aromatic thereby more susceptible to form stronger bonds with an electron-rich walls of the iptycene receptor.

Fluorescence quenching studies: The photophysical properties of 1–6 were investigated by using UV/Vis and fluorescence spectroscopy.<sup>[16]</sup> The quantum yields of 1–5 are relatively

modest ( $\Phi_{\rm F}$ =0.10–0.20) owing to a low degree of conjugation and the presence of sulfur atoms that encourage intersystem crossing to nonradiative triplet states. Sensors **1–5** showed dramatic fluorescence quenching in the presence of nitroaromatic species compared to the very low response to nitroaliphatic materials (DMDNB).

Figure 5 shows the results of the fluorimetric titration of sensor **2** with TNT. The 1,4-bis(2-thienyl)iptycene was excited at 300 nm with the emission maximum at 345 nm. Upon addition of TNT, the sensor displays a dramatic quenching of fluorescence emission. The Stern–Volmer plot shows that the quenching process is nonlinear with the increased concentration of the quencher. This supports the proposed mechanism of quenching as a result of combined dynamic and static quenching. The apparent value of the Stern–Volmer constant ( $K_{\rm SV}$ ~3.3×10<sup>3</sup> M<sup>-1</sup>) calculated from the initial linear part of the isotherm is reported in Figure 5 and in Table 1.<sup>[12,16]</sup>



Figure 5. Fluorimetric titration of sensor **2** ( $1.00 \times 10^{-5}$  M in CH<sub>2</sub>Cl<sub>2</sub>) with a standard solution of TNT (0.02 M),  $\lambda_{exc} = 300$  nm. Emission spectra before the addition of titrant and at the end of the titration are shown in bold lines. Inset: Stern–Volmer plot corresponding to that titration.

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Table 1. Values of the apparent Stern–Volmer constants recorded for receptors 1–6 and the nitro-compounds used in this study.<sup>[a]</sup>

	$K_{\mathrm{SV}}{}^{\mathrm{a}}$ [M <sup>-1</sup> ]							
analyte	1	2	3	4	5	6		
NB	$4.0 \times 10^3$ (1)	$2.2 \times 10^3$ (7)	$2.35 \times 10^3$ (2)	$1.43 \times 10^3$ (6)	91 (5)	577 (9)		
2,4-DNT	$3.57 \times 10^3$ (8)	$4.5 \times 10^3$ (1)	$3.0 \times 10^3$ (1)	$4.43 \times 10^3$ (5)	$1.29 \times 10^3$ (2)	$1.19 \times 10^3$ (3)		
TNT	$2.76 \times 10^3$ (7)	$3.3 \times 10^3$ (2)	$1.75 \times 10^3$ (4)	$1.83 \times 10^3$ (8)	$1.01 \times 10^3$ (4)	$1.33 \times 10^3$ (2)		
1-NO <sub>2</sub> Napht	$1.11 \times 10^4$ (6)	$5.10 \times 10^3$ (7)	$6.96 \times 10^3$ (7)	$6.9 \times 10^3$ (2)	$6.8 \times 10^3$ (2)	$1.34 \times 10^4$ (4)		
DMDNB	$2.3 \times 10^2$ (2)	81 (1)	167 (9)	79 (1)	17.6 (6)	38.3 (2)		

[a] Calculated from titrations performed in  $CH_2Cl_2$ ; excitation  $\lambda = 300$  nm. Fitting errors were <10%. The value in parentheses represents the standard deviation on the last digits.



Figure 6. Fluorimetric titration of sensor 1  $(1.00 \times 10^{-5} \text{ M in CH}_2\text{Cl}_2)$  with a standard solution of 2,4-DNT (0.02 M),  $\lambda_{\text{exc}} = 300 \text{ nm}$ . Emission spectra before the addition of titrant and at the end of the titration are shown in bold lines. Inset: Stern–Volmer plot pertinent to the titration.

The titration of sensor 1 with 2,4-DNT is shown in Figure 6. The behaviour of this receptor is similar to that of sensor 2 in the presence of TNT. Again, the apparent Stern–Volmer constant is reported. In Figure 7, the titration of receptor 3 with nitrobenzene is displayed. Also, in this case the receptor displays a dramatic quenching of fluorescence upon the addition of nitrobenzene.



Figure 7. Fluorescence titration of sensor **3** ( $1.00 \times 10^{-5}$  M in CH<sub>2</sub>Cl<sub>2</sub>) with a standard solution of nitrobenzene (0.02 M),  $\lambda_{exc} = 300$  nm. Emission spectra before the addition of titrant and at the end of the titration are shown in bold lines. Inset: Stern–Volmer plot pertinent to the titration.

Titrations of all the sensors (1-6) with the nitroaromatics confirm that the expected recognition process is taking place. The degree of divergence from the linear collision quenching model is visualised as an upturn of the binding isotherm. The nonlinearity is presumed to be due to the increment of the contribution of the static binding. Supporting our hypothesis is the fact that this nonlinearity is much more pronounced for nitrobenzene and the least for TNT (NB  $\geq$  2,4-DNT > TNT). We presume this reflects the ability of the relatively small pentiptycene cleft to bind larger nitroaromatics, such as TNT and 2,4-DNT. Such weak binding is perhaps the reason for failure of sensors to produce hostguest crystals with TNT and 2,4-DNT. The Stern-Volmer constants for DMDNB, a common detection taggant<sup>[17]</sup> used in the legal production of explosives, are low compared to the other aromatic compounds. Naturally, DMDNB cannot form stable edge-to-face complexes with the iptycene receptor. The perfect linearity of the Stern-Volmer plot for this compound suggests a pure collisional quenching mechanism (Figure 8).



Figure 8. Combined Stern–Volmer plots for sensor **3** and the analytes used in this study. The DMDNB trace coincides with the diffusion limit for the quenching process.

From Table 1 and Figure 8 one can appreciate the difference in the Stern–Volmer constants. As expected, DMDNB shows only minor quenching activity as the absence of an aromatic ring fragment renders any interaction with receptors **1–6** impossible. Also, the high energy of its LUMO forbids any significant PET quenching. On the other hand, NB, DNT, and TNT, display Stern–Volmer constants the differences for which appear to correlate with the volume and



their corresponding fit into the pentiptycene cavity, vide supra, as well as with their LUMO energies.<sup>[3a]</sup> Furthermore, we verified our hypothesis regarding the face-to-edge binding motif by studying the interaction of RDX with receptors **2** and **3**. As expected, the  $K_{SV}$  (**2**:  $32(\pm 3) \times 10^2 \text{ M}^{-1}$ , **3**:  $16(\pm 3) \times 10^2 \text{ M}^{-1}$ ) values for RDX are consistent with a weak interaction at the limit of the diffusional quenching mechanism. We can explain the low affinity of RDX towards the receptors by the absence of an aromatic ring required for the edge-to-face interaction as well as the high LUMO energy associated with the absence of aromaticity. The stereo-electronic effects<sup>[18]</sup> of the RDX nitro-groups are assumed to prevent an effective interaction of the hydrogen atoms with the iptycene receptors.

Remarkably, the TNT quenching displayed by 1–5 suggests that the efficacy of these small-molecule sensors is comparable to, if not better than, the iptycene-based amplifying polymers ( $K_{\rm SV}=1.17\times10^3\,{\rm M}^{-1}$ ) or polysilole sensors ( $K_{\rm SV}=4.34\times10^3\,{\rm M}^{-1}$ ).<sup>[4e]</sup> In this context it is not surprising that sensor **6** shows lower Stern–Volmer constants than 1–5. The conjugation of the fluorophore to the iptycene, in fact, lowers the LUMO of the receptor and renders the electron transfer quenching less efficient.

Sensor-doped polymer films and nanofibres: One of the potential disadvantages of small-molecule sensors compared to the polymer ones is the fact that small molecules often lack good film-forming properties. In fact, sensors 1-5 appear to crystallise when deposited as films. This potential drawback is circumvented by doping the sensors into a polymeric matrix known to form good-quality films that could be applied on the surface of, for example, an optical probe. We have solution-cast the polyurethane solutions (10 % w/w) of sensors 2 and 5 in wells of a glass chip to form  $10 \mu m$  thick films (Figure 9).

The chip also comprised tetraphenylporphyrin free-base (HTPP) chosen as an internal standard, the fluorescence of which is not affected by the presence of nitroaromatics as its LUMO is below the LUMOs of the nitroaromatic compounds used in this study. The chips were exposed to vapours of nitroaromatics at equilibrium. Vapour pressures of 2,4-DNT and TNT are 180 and 10 ppb, respectively.<sup>[19]</sup> As expected, the sensor films react differently to the 2,4-DNT and TNT vapours. This is due to the different affinity of the sensor-polymer films but also due to the difference in 2,4-DNT and TNT vapour pressure. Perhaps most importantly, the fluorescence is largely recovered when the chips are reequilibrated in air without the presence of the explosives. As pointed out previously,<sup>[4]</sup> the main problem with monolithic materials is the slow response to vapours of nitroaromatics. Here too, our films required about 15 min to achieve a steady state and even longer for recovery. Although this might be offset by pumping a stream of contaminated air onto the sensor films, the results seemed to require further improvement.

To optimise the mass exchange between the explosivescontaminated air and the sensor material, we decided to

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Figure 9. Left-hand panel: CCD images of sensor chips by using receptors 2 and 5 embedded in polyurethane and illuminated with black light, before exposure to vapours of 2,4-DNT (180 ppb),<sup>[20]</sup> TNT (10 ppb),<sup>[20]</sup> and after recovery. Within 10 min after exposure the emission of both 2 and 5 appeared to be quenched (>80%) whereas the red emission from the internal standard (tetraphenylporphyrin, HTPP) was largely unperturbed. The fluorescence is regenerated by removing the slide from the chamber. Right-hand panel: series of images, taken by using a fluorescence optical microscope, showing the polymer nanofibres mat containing sensor 5, upon exposure to 10 ppb vapours of TNT at different time intervals. RGB: image in true colours (RGB), showing both blue and red fibres. Blue: deconvolution of the blue channel showing the fibres containing only receptor 5, quenching their fluorescence after recognition of TNT. Red: red channel shows that the red fluorescent, HTPP fibres are not affected by nitroaromatics.

fashion the sensor materials into polymer nanofibre mats hoping that the use of nanofibres with a large surface area will increase the mass exchange rate from the vapour phase to the polymer. The polyurethane nanofibres were electrospun<sup>[20]</sup> from a 0.03 % (w/w) solution of the sensor in a 10 % (w/w) solution of polyurethane (Tecoflex<sup>TM</sup>). The sensor material was electrospun as long, 300–400 nm in diameter nanofibres. The blue fluorescence of nanofibre mats was imaged by using a fluorescence microscope. Once again, the red emission of the HTPP was used as an internal standard. The observable quenching of **5** (blue nanofibres, Figure 9) took place within 2–3 min, whereas the HTPP (red fibres) was not significantly quenched. Once again, the fluorescence was recovered upon re-equilibration in pure air.

The deconvolution of the RGB channels into separate red, green, and blue channels allows for integration of nonblack (i.e., non-zero) pixels (Figure 9). The ratio of blue (sensor 5)-to-red (HTPP) pixel counts serves as an output value (Table 2). The blue-to-red ratios do not change significantly between ten randomly selected sites in the mat. This confirms that one can improve the sensor performance by

Table 2. Evolution of blue/red ratio values over time.<sup>[a]</sup>

[min]	0	1	3	5
olue/red pixel	2.1835	1.8024	0.7866	0.1108

[a] Blue/red ratio values were calculated by deconvolution of the red and blue channels in the images in Figure 9 followed by integration of nonzero pixels in both the channels.

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optimising the matrix material and morphology without resynthesising the sensor moieties. It is conceivable that the blue-to-red pixel ratio can be used as a digital output in detection instruments.

#### Conclusion

In summary, we have developed simple, small-molecule sensors for aromatic nitro-compounds based on the iptycene receptor acting as the recognition moiety. Sensors 1–5 can easily be prepared on a multigram scale by a robust two-step synthetic protocol. Fluorogenic moieties attached to the benzene core of the iptycene act as signalling units, by switching off their fluorescence upon analyte recognition. Fluorimetric titration experiments revealed that the sensors 1–6 show a significant response to nitroaromatics, particularly to 2,4-DNT and TNT, and a poor response to aliphatic nitro-compounds. Thus, sensors 1–5 can be used as new, inexpensive yet sensitive compounds for the detection of explosives vapours.

Materials suitable for coating surfaces with a TNT vapour-sensitive coating were achieved simply by doping sensors **1–5** into polymer solutions. Particularly effective were nanofibre sensor mats produced by electrospinning of such sensor-doped polymer solutions. The use of polymer nanofibre mats seems to be suitable for the production of such sensor assays, as demonstrated recently by other research groups.<sup>[21a,b]</sup> Experiments with polyurethane nanofibres displayed high surface area and effective mass exchange between the sensor mat and the surrounding gas, and resulted in an effective nitroaromatic vapour recognition in 2–3 min. This confirms that the efficiency and time-line of the response may be tuned by using polymer matrices and the way these matrices are processed.

Studies employing non-equilibrium conditions, that is, pumping the contaminated headspace gas onto the sensor nanofibres expecting to dramatically improve the temporal resolution of the sensors, are in progress. Nonetheless, the use of a colour channel (red-blue) deconvolution provides a robust output signal not only for the explosives, but also as a fail-safe in case of malfunction due to, for example, nonspecific quenching or extensive contamination, which would affect both the red and blue signal levels.

### **Experimental Section**

**General procedures and materials**: All synthetic manipulations were performed under dry argon atmosphere by using standard techniques. All starting materials were purchased and used as received. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Bruker DRX-300 (300 MHz) spectrometer. Emission spectra were acquired at the Edinburgh single photon counting spectrofluorimeter (FL/FS 900). The spectra in solution were obtained at room temperature by using a quartz cuvette with a path-length of 1 cm at right angle detection. The absorbance OD of all samples used for fluorescence studies were equal to or below 0.1. Fluorescence quantum yields of **1–6** were determined relative to anthracene ( $\Phi_F$ =0.27 in ethanol). The chemical shifts ( $\delta$ /ppm) are referenced to the respective solvent and splitting patterns are designed as s (singlet), d (doublet), t (triplet), m (multiplet), and br (broad). EI DIP mass spectra were recorded by using a Shimadzu QP5050A, MALDI-TOF was recorded with OmniFlex (Bruker Daltonics).

Polymer-casted sensors: Studies utilising polyurethane matrices were performed by using polymer films with incorporated sensors (2 and 5), which were prepared by casting THF solutions containing sensors 2 and 5 (0.4% w/w sensor and 0.2% w/w for HTPP films as internal standard) in Tecoflex<sup>TM</sup> and Tecoflex<sup>TM</sup>/polystyrene 2:8 (3.5% w/w) onto multi-well chips. The fluorescence quenching of the polymer films with analyte was carried out by placing the sensor chip in a tall sealed glass chamber in which the analyte vapours had been equilibrated. The equilibrium pressure of TNT at 22 °C is 10 ppb,<sup>[19]</sup> and is delivered to the sample by diffusion. The quenching of the fluorescence was estimated by placing the chamber on a UV scanner (Kodak Image Station 440CF) by using broadband UV epi-illumination centred at 365 nm. The emission in the blue region was recorded by using a blue filter (band-pass filter 380-500 nm), a red filter (long pass 580 nm). Recording blue and red fluorescence for each image allows for a direct comparison of the sensor versus internal standard (HTPP) fluorescence.

**Sensing with nanofibres**: In a typical experiment a microscope slide with electrospun fibres comprising sensor **5** and fibres comprising HTTP (internal standard) were developed in the vapour chamber. At 2, 5 and 10 min exposure the slides were removed and immediately covered with a coverslip. The images of the sensor chips were captured by using a fluorescence microscope with 365 nm epi-illumination. To prevent false positives from photobleaching every measurement was taken from a new spot on the slide. Also, control experiments show that no significant photobleaching takes place within the first 2 min of exposure to UV light.

Nanofibre fabrication: Polymer solution (10% w/w, Tecoflex<sup>TM</sup> and 0.03 % w/w, 5) was loaded into a 1 mL disposable plastic syringe. A Hamilton stainless steel needle with a 21 gauge was used. The needle was connected to a high-voltage power supply (ES30P-5W, Gamma High Voltage Research, Inc.). The polymer sensor solution was continuously dispensed by using a syringe pump (Genie Plus, Kent Scientific) at a rate of  $3\,\mu L\,min^{-1}.$  In a typical experiment a voltage of  $5\,kV$  was applied for electrospinning. The distance between the needle tip and the collector was 10 cm. The collector consists of two independent aluminium rods connected to ground and a microscope slide (75×25 mm) between them. The characterisation of the fibres was carried out by using epi-fluorescence optical microscope (DIALUX 20, Leitz/Leica) with CCD cooled colour camera (Penguin 150CL, Pixera). In a typical sensing experiment microscope slides containing electrospun fibres with 5 and fibres containing HTPP as internal standard were prepared for the TNT sensing. The slides were placed inside a sealed glass chamber in which TNT (10 ppb) and DNT vapours (180 ppb) were previously equilibrated at 23 °C. Micrographs were taken at different times during the experiment. For this we made use of an epi-fluorescence optical microscope with excitation centred at 365 nm. The RGB deconvolution and all the calculation over the images were carried out by using ImageJ.

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### CHEMISTRY

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**TNT is sensed**! Fluorescent sensors based on the iptycene recognition motif were synthesised and studied with different nitroaromatic compounds. X-ray structures confirm the establishment of edge-to-face interactions. Fluorescence studies in solution and in polymer matrices allowed the development of polymer-nanofibre sensors for the detection of nitroaromatic compounds and TNT (see figure).