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Sensitive 1,1-dicyanovinyl push-pull dye for primary amine sensing in solution by fluorescence

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Abstract

1,1-dicyanovinyl push-pull dye **PTTCN** undergoes rapid and reversible aza-Michael addition with volatile primary aliphatic amines in solution in DMSO, yielding a highly fluorescent imine derivative. This reaction is accompanied by a dramatic colour change as well as a strong increase in fluorescence (1200-fold increase) allowing sensitive turn-on detection of primary amine in solution. In the solid state, **PTTCN** is emissive and reaction with primary amines vapours results in a shift in fluorescence and a possible ratiometric detection of primary amine. The selectivity is excellent for primary amines over secondary, tertiary and aromatic amines as well as over thiols and fluorescence spectroscopy allow to discriminate between primary and other nitrogen nucleophiles such as hydrazine and ammonia. Finally, we show as proof-of-concept that the fluorescence turn-on response can be used in response to the vapours of volatile amines released during food spoilage.

Keywords: Primary amine; Fluorescence turn-on; Ratiometric; Fluorescent Thin Film

1. Introduction

Aliphatic primary amines are organic compounds omnipresent in the pharmaceutical, cosmetics or agrochemical industry, as well as in biology and it is often necessary to be able to accurately detect trace levels in real time and

28 in different matrices. Some natural primary amines of low-molecular weight, like histamine for instance,
29 modulate essential metabolic and physiological functions in living organisms, but may also be of major health
30 concern when present in food. They thus have been identified as important markers for evaluation of food
31 quality or specific indicators for various diseases or health issues.[1-3]

32 For these reasons, many techniques have been developed so far for the qualitative and quantitative detection of
33 amines, as diverse as high performance liquid chromatography, capillary electrophoresis, gas chromatography,
34 or biosensor, to cite a few, each with its pro and cons.[4, 5] Of these, those based on chemical optical probes in
35 general and photoluminescence (PL) in particular offer definite advantages in terms of rapidity, sensitivity with
36 demonstrated limits of detection to nM, ease of handling and possibility to be used in solution or solid
37 supports.[6, 7]

38 As recently summarized in excellent reviews, various strategies exploiting the basic or nucleophilic properties of
39 amines have been reported to design chemical probes whose optical properties, whether absorption or PL,
40 change upon exposure to amines.[6] [5, 7, 8]

41 For instance, direct addition of a nucleophilic amine to a chromophore's electron-withdrawing group or
42 1,2-addition to C=C double bond conjugated with this group heavily modifies the electron delocalisation within
43 the dye molecule, therefore triggering consequent spectral changes (absorption and/or emission) and directly
44 inducing a signalling response. Thus, reversible conversion of the trifluoroacetyl group into a hemiaminal
45 function [9-11] or irreversible conversion of the tricyanovinyl group into the 1-amino-2,2-dicyanovinyl group
46 [12] results in a decrease of the electron-withdrawing strength and consequently in a blue-shift in the absorbance
47 or PL spectra. On the other hand, reversible addition of amine on aldehyde- [13-19] or ketone-containing [20]
48 chromophores gave highly fluorescent imine or iminium derivatives with usually red-shifted optical properties.

49 Dicyanovinyl group is probably one of the simplest, yet powerful, electron-withdrawing groups for this effect.
50 Aza-Michael nucleophilic addition of amine to the dicyanovinyl group is followed by the loss of a malononitrile
51 molecule to yield an imine, leading to a large spectral-shift and most often a PL turn-on response. This was
52 shown by Cheng and He who developed high sensitivity probes for primary amine vapour with polymers
53 encompassing benzylidenemalononitrile units [21] and by Shi, Dong and co-workers who described the
54 detection of amine vapours through formation of a bis-imine derivatives with a bis- dicyanovinyl based
55 probes.[22] Previously, turn-on fluorogenic probe for detecting MDMA from ecstasy tablets [23] and dual-mode
56 detection of aliphatic amines and hydrazine by PL [24] were also reported built upon a bis-diarylurea-

57 dicyanovinyl push-pull fluorophore and a dicyanovinyl-substituted oligothiophene derivative associated with
58 zinc tetraphenylporphyrin, respectively. Mohr *et al.* also described a colorimetric read-out sensor based on
59 push-pull azo dye and therefore working at wavelengths compatible with low-cost light sources and detectors.[25,
60 26] However in all these works, the end product was not characterized or simply postulated as being the 1,2
61 adduct.[26] Sathiyarayanan *et al.* reported the design of a ratiometric PL sensor for primary amine based on a
62 dicyanovinyl substituted phenanthridine derivatives and they clearly identified the end product as being the
63 corresponding imine.[27] Finally, in 2020, Burn, Show and coworkers reported two dicyanovinyl-
64 fluorene-benzothiadiazole-based fluorescent compounds, which showed rapid response to a wide range of
65 amines. Primary amines react with the dicyanovinyl by aza-Michael (1,2) addition to give the corresponding
66 imine, while PL quenching *via* photoinduced hole transfer was observed in the solid-state with other amines.[28]

67 It should be noted, however, that nucleophilic addition on dicyanovinyl based chromophores is not specific to
68 primary amines. Hydrazine indeed yields hydrazone, a much weaker electron-withdrawing group than
69 dicyanovinyl,[29] whereas thiols and cyanide give the 1,2-addition product. Here also the modification or the
70 breaking of the dye π -conjugated system leads to considerable changes in the optical properties (blue shift and
71 generally PL enhancement). Extremely sensitive and “selective” colorimetric and/or fluorescent sensors to
72 hydrazine,[30-34] cyanide,[30, 35-42] and thiols [43, 44] [36, 45] are reported. In most cases, no mention is
73 made of possible interferences from competitive amines.[25]

74 We have identified **2-((5'-(piperidin-1-yl)-[2,2'-bithiophen]-5-yl)methylene)malononitrile (PTTCN,**
75 Scheme 1), a 1,1-dicyanovinyl push-pull dye, that undergoes rapid reaction with primary amine to yield
76 fluorescent imine with emission intensities as high as 1200 times greater than the starting materials. We want to
77 present here preliminary results about its use as fluorescent probe for primary amine detection in solution and in
78 the solid state.

79 Compound **PTTCN** and other analogues, in which the 1,1-dicyanovinyl group is connected to a strong donor
80 2-(*N*-dialkyl)-amino- or 2-(*N*-diaryl)-amino- across a 2,2'-bithiophene π -conjugated bridge conferring moderate
81 aromatic stabilization to the donor-acceptor system and therefore a high degree of conjugation between the donor
82 and acceptor end groups, were originally developed as highly polarizable chromophores for 2nd order nonlinear
83 optics.[46, 47] [48, 49] The spectroscopic properties were later studied in detail and are characteristic of such
84 donor-acceptor substituted heterocyclic compounds with a strong intramolecular charge transfer (ICT)
85 absorption band in the visible region of the spectrum, and a weak red PL that decreases in intensity as the solvent

86 polarity increases.[50, 51] The PL also increased with the viscosity, making this compound and other analogues
87 potential viscosity probes [52] and explaining the solid-state emission we observed. On the other hand, very few
88 examples of imine derivatives built on the 2-(*N*-dialkylamino or diarylamino)-2,2'-bithiophene pattern are
89 described,[53, 54] mostly chiral bichromophoric systems developed for CD exciton chirality studies or for
90 second-order NLO applications. Bereva and coworkers, nevertheless, highlighted the intense blue-green PL of
91 *N*-[[5'-(Dimethylamino)[2,2'-bithiophen]-5-yl]methylene]-cyclohexylamine and
92 *N*-[[5'-(1-Pyrrolidinyl)[2,2'-bithiophen]-5-yl]methylene]-cyclohexylamine.[53]

93

94 **2 Experimental**

95 **2.1 Materials and Methods**

96 All solvents and reagents were commercially available and used without further purification. Column
97 chromatography was carried out on silica gel (35-70 μm). ^1H and ^{13}C NMR spectra were recorded at ambient
98 temperature on a Bruker Advance 400 spectrometer operating at 400.0 MHz for proton and 101.00 MHz for
99 carbon, respectively. Chemical shifts are reported in parts per million (δ/ppm) relative to tetramethylsilane with
100 the residual solvent peaks as internal standard (2.50 and 39.5 ppm for DMSO). High-resolution mass
101 spectrometry (HRMS) were measured by ESI-TOF (Bruker Daltonics Micro TOF-Q II) at the *Centre Commun*
102 *de Spectrométrie de Masse* (UCBL, Villeurbanne, France). UV/Vis absorption spectra were measured using a
103 dual beam Jasco 670 spectrometer. Fluorescence spectra in diluted solution and in thin film were recorded on a
104 Horiba Jobin-Yvon Fluorolog-3® spectrofluorimeter equipped with red-sensitive Hamamatsu R928 PMT.
105 Spectra were reference corrected for both the excitation source light intensity variation (lamp and grating) and
106 the emission spectral response (detector and grating).

107

108 **2.2 Synthesis**

109 **2.2.1 Synthesis of 2-((5'-(piperidin-1-yl)-[2,2'-bithiophen]-5-yl)methylene)malononitrile (PTTCN)**

110 In a 20 mL microwave tube, 5-formyl-5'-piperidino-2,2'-bithiophene (**1**) (300 mg, 1.08 mmol) and
111 malononitrile (85 mg, 1.28 mmol) were dissolved in anhydrous EtOH (5 mL), followed by addition of one drop
112 of piperidine. The tube was sealed and heated at 100°C by microwave irradiation for 1 h. After cooling down to
113 room temperature, the solid was filtrated and purified by column chromatography on silica (eluent: CH_2Cl_2) to

114 afford **PTTCN** as a dark purple solid (244 mg, yield: 69%). ¹H NMR (400 MHz, DMSO-*d*₆, ppm) δ 8.38 (s, 1H),
115 7.77 (d, ³*J* = 4.3 Hz, 1H), 7.50 (d, ³*J* = 4.3 Hz, 1H), 7.29 (d, ³*J* = 4.3 Hz, 1H), 6.27 (d, ³*J* = 4.3 Hz, 1H), 3.29 (m,
116 4H), 1.61 (m, 4H), 1.82-1.43 (m, 6H). ¹³C NMR (101 MHz, DMSO-*d*₆, ppm) δ 162.9, 151.4, 150.7, 143.6, 131.0,
117 129.8, 121.5, 117.5, 115.7, 114.9, 105.6, 68.6, 50.9, 24.5, 23.0. HR-MS (ESI-QTOF) *m/z*: [M+H]⁺ calcd for
118 C₁₇H₁₆N₃S₂, 326.0786; found, 326.0770.

119 **2.2.2 Synthesis of (E)-1-(5'-(piperidin-1-yl)-[2,2'-bithiophen]-5-yl)-N-propylmethanimine (PTT-imine)**

120 Under an inert atmosphere, **1** (50.0 mg, 0.18 mmol) and n-propylamine (10.6 mg, 0.18 mmol) were dissolved
121 in CH₂Cl₂ (2 mL) and 4 Å molecular sieve (MS) was added. The mixture was heated to reflux for 2 h. MS was
122 filtered off. Evaporation under reduced pressure to dryness afforded **PTT-imine** as a yellow solid sufficiently
123 pure to be used without further purification (57 mg, yield: 99%). ¹H NMR (400 MHz, DMSO-*d*₆, ppm) δ 8.33 (s,
124 1H), 7.28 (d, *J* = 3.8 Hz, 1H), 7.06 (d, *J* = 4.0 Hz, 1H), 6.98 (d, *J* = 3.8 Hz, 1H), 6.08 (d, *J* = 4.0 Hz, 1H), 3.44 (t,
125 *J* = 6.7 Hz, 2H), 3.23-2.99 (m, 4H), 1.80-1.35 (m, 8H), 0.87 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆,
126 ppm) δ 159.5, 154.1, 140.7, 138.4, 132.1, 125.2, 120.8, 120.6, 104.6, 61.8, 51.3, 24.6, 23.7, 23.2, 11.7. HR-MS
127 (ESI-QTOF) *m/z*: [M+H]⁺ calcd for C₁₇H₂₂N₂S₂, 319.1297; found, 319.1295.

128 **2.2.3 Preparation of sol-gel film**

129 Silica-based sol preparation from methyltriethoxysilane (MTEOS): In a 2 L flask, citric acid (3.96 g, 0.02
130 mole) was dissolved in DI water (396 mL, 22 moles). Under vigorous stirring, MTEOS (400 mL, 2 moles) was
131 added to the aqueous solution. With the formation of an emulsion, the medium quickly became opaque and then
132 increasingly transparent as the ethanol was released following the hydrolysis of MTEOS. The resulting mixture
133 was heated to 45°C overnight under continuous slow stirring. The ethanol produced by the hydrolysis reaction of
134 the alkoxy silane was subsequently removed from the reaction solution at reduced pressure. The silica-based sol
135 was then extracted by adding ether which caused phase separation. The aqueous phase containing the citric acid
136 was then separated. In order to completely remove citric acid from the sol, the ethereal phase was washed several
137 times by adding water. The ether is then removed in vacuo and the resulting sol is dissolved in THF while
138 controlling the solid content (54% by mass).

139 Preparation of doped sol-gel film: **PTTCN** (2.0 mg) dissolved in THF (1 mL) was added to the previously
140 prepared MTEOS sol (2 g, 54 wt% in THF). Once the mixing has been carried out, part of the THF (1 mL) is
141 removed under vacuum in order to obtain a viscous doped sol. The latter was spread evenly on a glass substrate
142 by centrifugation at 2000 rpm. The sol-gel film was further dried by heating at 90°C for 1 h in an oven.

143

144 **2.2.4 Preparation of PMMA thin film**

145 A solution of **PTTCN** and **PMMA** in dichloromethane (1 mg dye for 100 mg PMMA in 1 mL) was spread
146 evenly on a glass surface by spin-coating at 2000 rpm using a Karl Suss CT 62 spin-coater.

147

148 **2.3 Computational method**

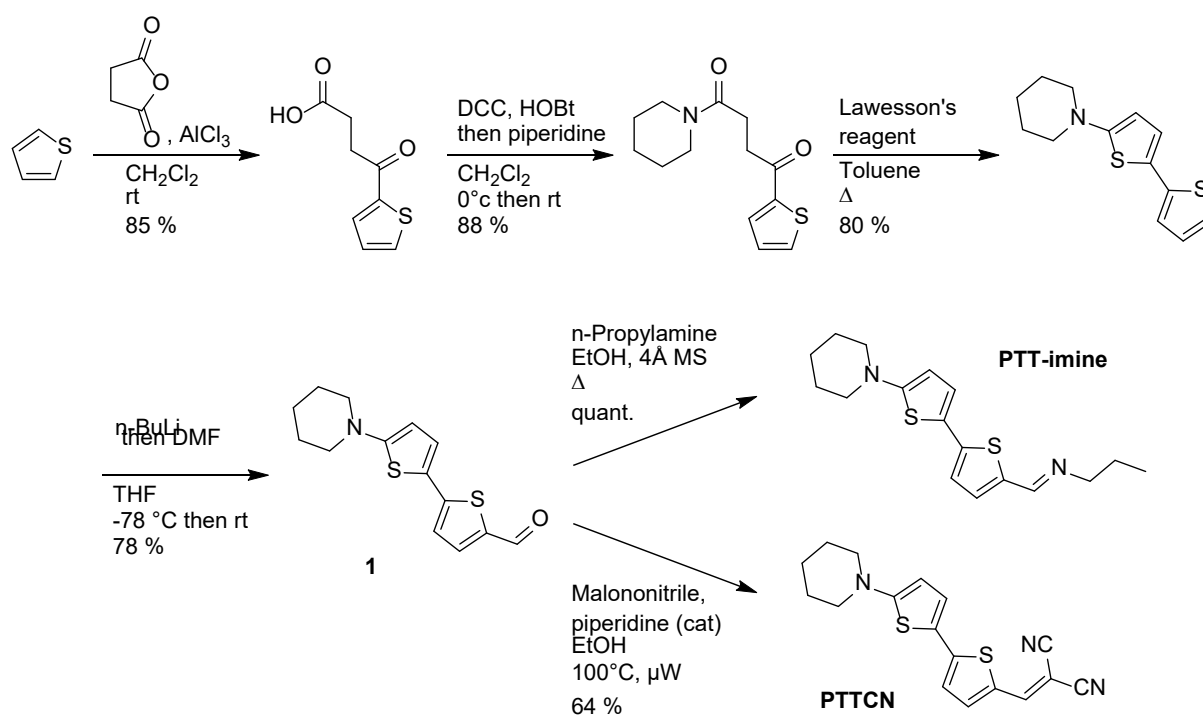
149 All calculations were performed using Gaussian package.[55] At the ground state, the structure of all the
150 compounds was optimized at the DFT/6-311G(d) level of theory using hybrid functionals PBE0.[56] Bulk
151 solvent effects (DMSO) were considered using continuum solvation model (C-PCM).[57, 58] For each
152 compound, 10 vertical excitation energies and associated excited-state densities of interest were computed at the
153 TD-DFT level with the same basis set and CAM-B3LYP functional.[59] The charge transfer transitions were
154 characterized thanks to the DCT index developed by Le Bahers et al. using the cube files generated by the
155 cubegen utility provided by the Gaussian package.[60] To simulate the colour, the trichromatic components were
156 obtained from the transmission spectra through a code developed in our group and converted into RGB ones.

157

158 **3 Results and discussion**

159 **3.1 PTTCN and PTT-imine synthesis and characterization**

160



161

162 **Scheme 1.** Synthesis of **PTTCN** and **PTT-imine**.

163

164 **PTTCN** was obtained as a dark violet powder from malononitrile and aldehyde **1** by Knoevenagel condensation.

165 **1** was prepared in five steps from thiophene, succinic anhydride and piperidine by construction of the second

166 thiophene ring by a combination of Friedel-Craft and Lawesson reactions,[61] followed by formylation by

167 α -lithiation and reaction with DMF (Scheme 1). This approach was preferred to classical bithiophene synthesis

168 using palladium catalysed coupling reaction as it gives higher yield. **PTT-imine** was in turn easily obtained from

169 **1** by reaction with n-propylamine in presence of 4 Å MS.

170 Crystals of **PTTCN**, suitable for X-ray diffraction, were grown by slow diffusion of EtOH in concentrated dye

171 solution in CHCl_3 . Crystallographic data, basic structural parameters and the X-ray crystal structure are given in

172 SI. The latter showed a quasi-planar π -delocalized system with twenty-two atoms forming the molecular mean

173 plane (maximum deviation of 0.114 Å). Only the dicyanovinylene group is slightly twisted forming a 5.7° angle

174 with the bis-thiophene entity. This is indicative of a full conjugation between the donor and the acceptor end of

175 the push-pull molecule.

176 In solution, the electronic absorption spectrum of **PTTCN** is characteristic of intramolecular charge transfer

177 (ICT) transitions in push-pull dipolar molecules with a broad absorption in the visible ($\lambda_{\text{abs}} = 575 \text{ nm}$ in DMSO,

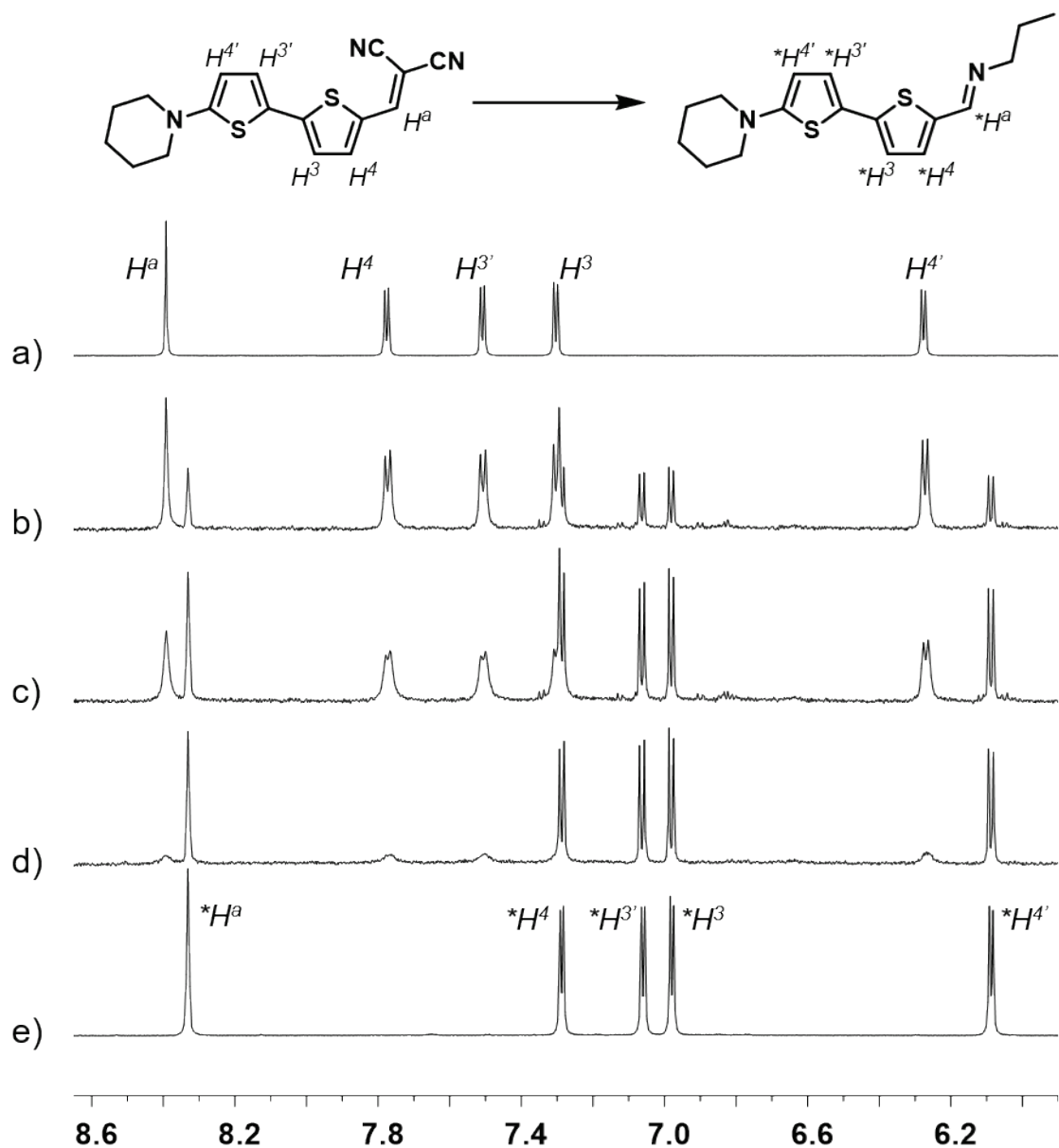
178 in good agreement with the calculated value of 509 nm, cam-B3LYP/6-311G(d)/PCM(DMSO), large molar

179 absorption coefficient values, and a small bathochromic shift in the maximum as the solvent polarity increases
180 (Figure SI 2). Upon excitation in the main absorption band PL is observed, whose peak maximum is gradually
181 red-shifted and decreases in intensity as the solvent polarity increases from toluene ($\lambda_{em} = 640$ nm, $\phi = 18$ %) to
182 DMSO where it almost vanishes ($\lambda_{em} = 695$ nm, $\phi < 1$ %). **PTTCN** also showed interesting far-red emission in
183 the solid state ($\lambda_{em} = 665$ nm, $\phi = 24$ %) easily visualized under illumination of a handheld UV lamp at 365 nm.

184 **3.2 Sensing properties in solution**

185 The reaction **PTTCN** with primary amine was first investigated by ^1H -NMR. Stepwise addition of
186 n-propylamine to a solution of **PTTCN** in $\text{-DMSO-}d_6$ immediately yielded the formation of a single new product
187 that concurs with colour change from violet to yellow along with appearing of an intense green PL that can be
188 seen under UV light. The ^1H -NMR spectrum (Figure 1) of the new product displayed similar splitting patterns
189 but significant upfield shifts for aromatic protons and the persistence of a vinylidene singlet integrating for one
190 proton at 8.33 ppm. This is in agreement with an imine structure in which the push-pull character is preserved
191 but a weaker electron-acceptor group is present. A simple nucleophilic reaction at the $\text{C}\beta$ position, as assumed by
192 Finšgar *et al.* for similar dicyanovinyl azobenzene dyes [26] or as is observed with thiols [25] and the cyanide
193 anion,[35, 42] would lead to a drastic upfield shift of the proton originally at the β -position as well as those of
194 the closest thiophene ring due to a disruption of the π -conjugation from the donor to the acceptor end. The imine
195 structure was further confirmed by mass spectrometry and the independent synthesis of **PTT-imine** from
196 aldehyde **1** and n-propylamine (Scheme 1), whose ^1H and ^{13}C NMR spectra (Figure SI 15 and SI 16) perfectly
197 match those of the new product.

198

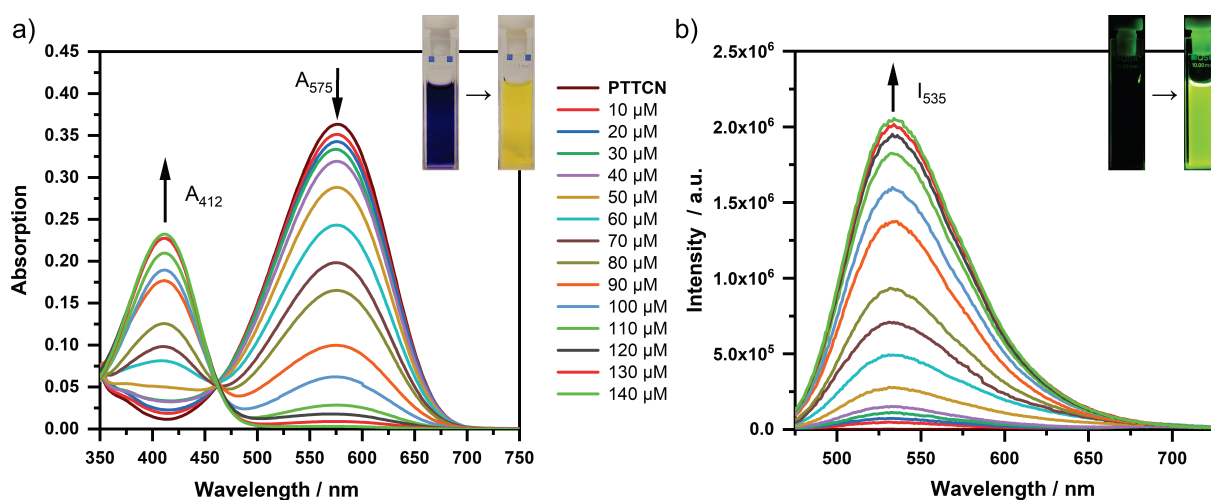


199 8.6 8.2 7.8 7.4 7.0 6.6 6.2
 200 **Figure 1.** Aromatic region of the ^1H -NMR spectra (300 MHz, DMSO- d_6) of **PTTCN** prior (a) and immediately
 201 after addition of 0.6 equiv. (b), 1.2 equiv. (c), 2.5 equiv. (d), and 4 equiv. (e) of n-propylamine.

202
 203 More interestingly, in the case of a volatile amine having low boiling point such as n-propylamine, ^1H NMR also
 204 evidences the reverse transformation of imine to the initial dicyanovinyl (Figure SI 4). Removal of the excess
 205 amine by evaporation under vacuum induced a colour change back to the original purple of dye **PTTCN** as well
 206 as a disappearance of the PL and the reappearing of the NMR signal of **PTTCN**. Note, however, that addition of
 207 excess malononitrile to a solution of **PTT-imine** in DMSO- d_6 immediately resulted in a colour change from
 208 yellow-green to dark red then purple, but the signals obtained are broad and the reformation of **PTTCN** could
 209 not be unambiguously demonstrated.

210 Spectroscopic studies also evidenced the interest of **PTTCN** as a primary amine fluorescent probe. The changes
 211 in the absorption and PL spectra on addition of n-octylamine (or n-propylamine) to solution of **PTTCN** in
 212 DMSO (10 μ M) are shown in Figure 2. With increasing amount of amine added, the characteristic ICT band at
 213 575 nm disappeared while the colour of the dye solution turns yellow with the concomitant appearing of a new
 214 peak with a maximum absorbance at 412 nm. The isobestic point at 462 nm indicates that a single chemical
 215 reaction takes place. Kinetic studies revealed that the reaction is first order with respect to both reactants primary
 216 amine and **PTTCN** (Figures SI 5 and SI 6).

217



218

219 **Figure 2.** Spectral changes for a solution of **PTTCN** (10 μ M) in DMSO immediately after addition of increasing
 220 amount of n-octylamine (0 to 140 μ M): (a) absorption and (b) emission spectra (λ_{ex} = 462 nm, isobestic point of
 221 the absorption spectra). Inset: solution of **PTTCN** without (left) and with (right) excess octylamine (140 μ M),
 222 daylight and under UV-light (365 nm).

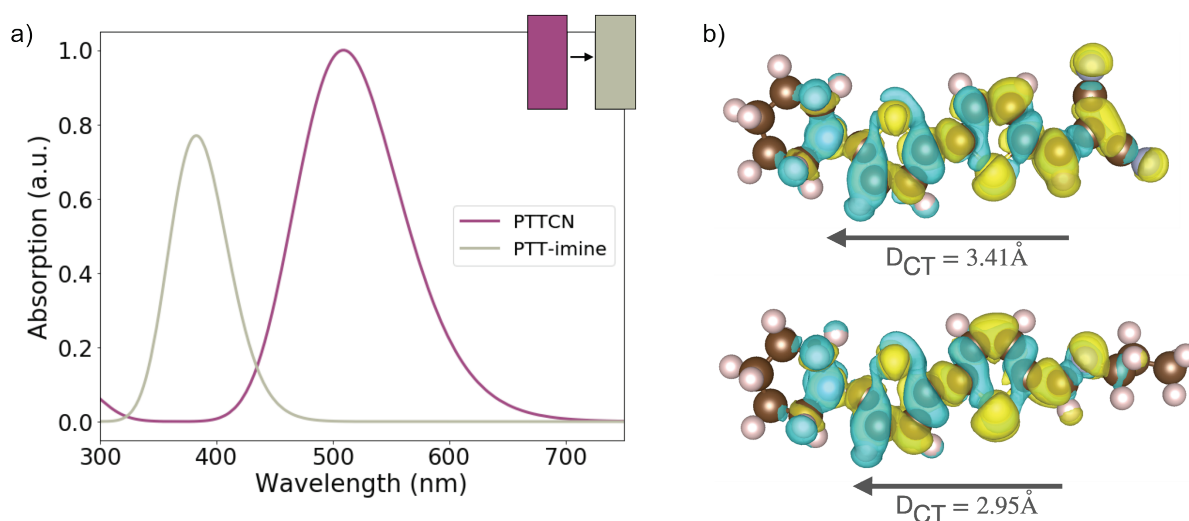
223

224 At the same time, an intense emission appeared at 535 nm that steadily increased while adding amine. At this
 225 high dye concentration (10 μ M) the reaction is fast and the fluorescence is therefore seen immediately. The
 226 quantum yield of the newly formed product reaches unity (ϕ = 0.96) whereas **PTTCN** itself is barely emissive in
 227 DMSO, a “turn-on” PL response (1160-fold emission intensity enhancement, Figure 2b) is then achieved. As
 228 shown is Figure SI 7, a theoretical limit of detection of n-octylamine was estimated to be as low as 60 nM for a
 229 dye concentration of 5 μ M. Note however that for such low concentration in amine, the reaction is much slower
 230 and the measure has to be performed 15 hours after amine addition.

231 The dramatic colour change observed when switching from dicyonovinyI to imine is clearly explained by a

232 decrease in intramolecular charge transfer and in the push-pull character. This is confirmed by DFT and TD-DFT
233 calculations on **PTTCN** and **PTT-imine**.

234 Calculations reproduced the modification of the absorption properties towards the blue range could also be
235 reproduced computationally (Figure 3-a) with a shift of the wavelength of maximum absorption from 509 nm
236 (0.28 eV difference compared to experimental value) for **PTTCN** to 383 nm (0.15 eV difference compared to
237 experimental value) for the **PTT-imine**. A fluorescence maximum at 505 nm is computed in good agreement
238 with what is observed (0.14 eV difference). The computed distance characteristic of the charge transfers under
239 absorption decreases from 3.41 Å to 2.95 Å from **PTTCN** to **PTT-imine** as illustrated on Figure 3-b, in good
240 agreement with a less efficient charge transfer.



241
242 **Figure 3.** b) Simulated absorption spectra (at CAM-B3LYP/6-311G(d) level of theory) of the two molecules in
243 DMSO along with their simulated colour (top insert). b) Representation of the difference between excited- and
244 ground-state electron densities (cyan, density increase upon transition; yellow, density decrease; isovalue of .0005)
245 as well as the CT distance (in grey) for PTTCN (top) and PTT-imine (bottom) molecules. Carbon, hydrogen, sulfur
246 and nitrogen atoms are depicted respectively by brown, white, yellow and blue spheres.

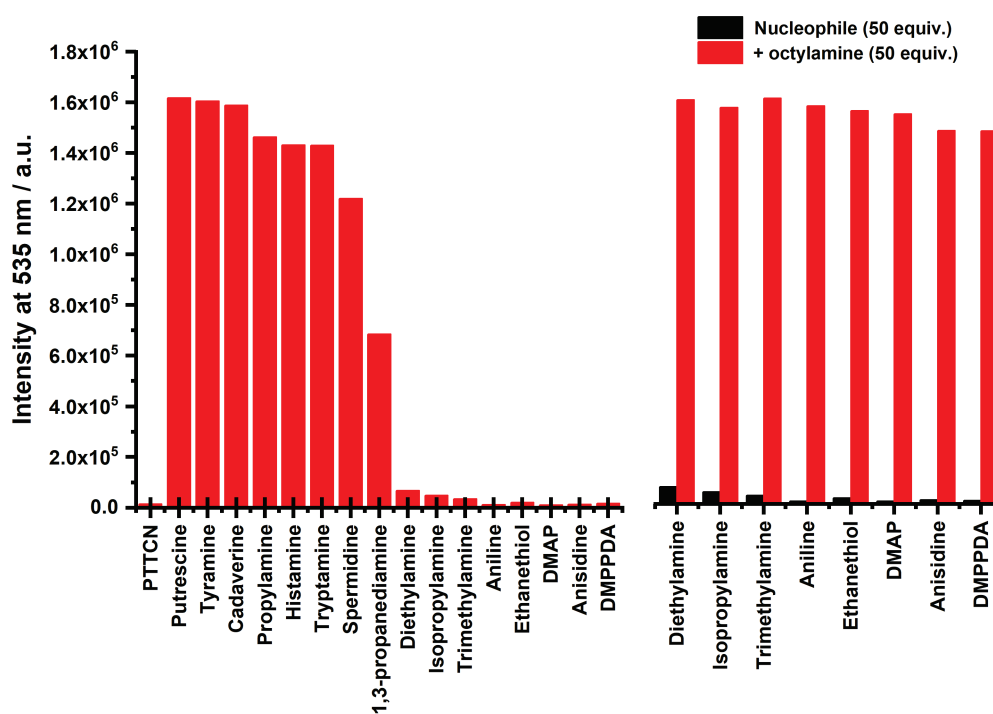
247

248 3.3 Selectivity

249 Qualitative PL-sensing studies were performed with various aliphatic amines (ammonia, putrescine, tyramine,
250 cadaverine, propylamine, histamine, tryptamine, spermidine, 1,3-diamine, diethylamine, diisopropylamine,
251 trimethylamine), aromatic amine (aniline, p-anisidine, *N,N*-dimethyl-p-phenylenediamine) and other nucleophile
252 (ethanethiol, hydrazine). Addition of secondary amine (diethylamine, diisopropylamine), tertiary amine

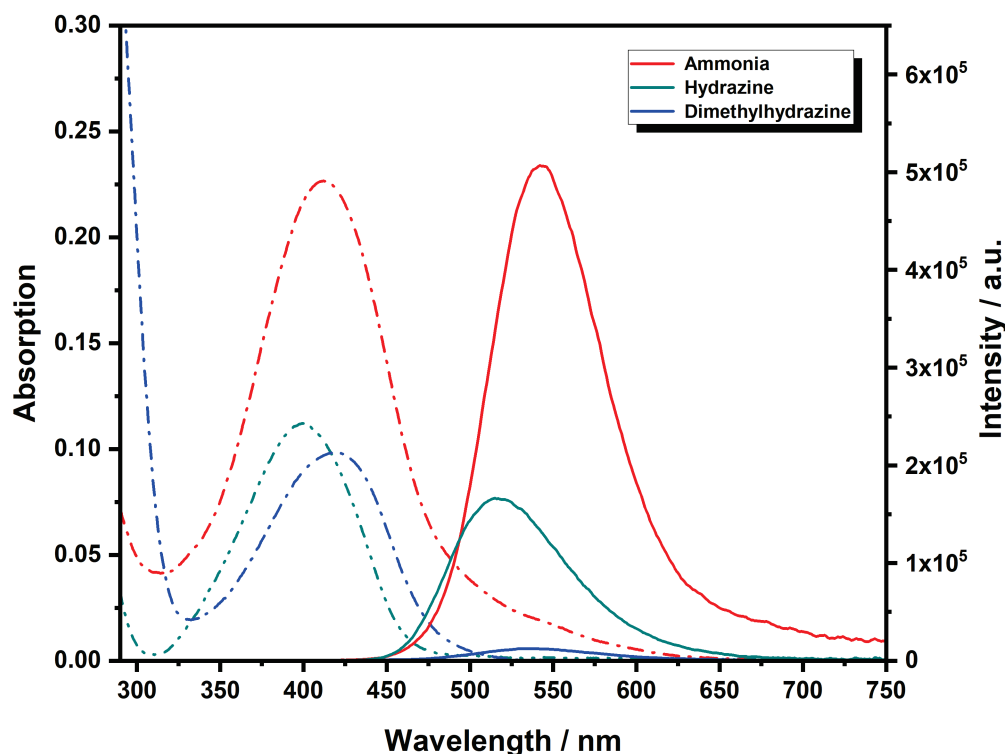
253 (trimethylamine) or thiol (ethanethiol) did not induce any colour change nor any significant change in the PL
 254 spectra of **PTTCN** in DMSO solution (Figure 4-a). The same applies when an aromatic amine is added,
 255 including electron enriched p-anisidine and N,N-dimethyl-p-phenylenediamine. However, when a primary amine
 256 (here n-propylamine, 50 equiv.) was added after addition of 50 equivalent of diethylamine, trimethylamine, or
 257 thiol, the colour immediately changed and the strong PL characteristic of the imine formation is immediately
 258 observed highlighting the selectivity for the primary amine and the absence of interference from secondary
 259 analytes (Figure 4-b).

260 On the other hands, **PTTCN** has fast PL-response to ammonia and hydrazine compounds (hydrazine or
 261 dimethylhydrazine). However, the new products obtained in these cases display slightly blue-shifted absorption
 262 and emission compared to the imine for hydrazine and red-shifted for other analytes, and are less emissive
 263 (Figure 5, Table 1), allowing to distinguish them.



264
 265 **Figure 4.** PL intensity at 535 nm ($\lambda_{exc} = 460$ nm) of 10 μ M **PTTCN** solution in DMSO with: a) different amines
 266 and nucleophiles (50 equiv); b) different amines and nucleophiles (50 equiv) then n-octylamine (50 equiv), in
 267 black the initial PL intensity before adding n-octylamine.

268



269

270 **Figure 5.** Absorption (dotted lines) and emission spectra (solid lines) of PTTCN upon addition of excess of
 271 ammonia, hydrazine or dimethylhydrazine (10 μ M in DMSO, $\lambda_{exc} = 400$ nm).

272

273 **Table 1.** Spectroscopic data for PTTCN and for PTTCN with addition of various N nucleophiles.

	PTTCN			+ n-propylamine			+ Ammonia			+ Hydrazine			+ N,N-dimethylhydr.		
	λ_{abs} (nm)	λ_{em} (nm)	Φ	λ_{abs} (nm)	λ_{em} (nm)	Φ	λ_{abs} (nm)	λ_{em} (nm)	Φ	λ_{abs} (nm)	λ_{em} (nm)	Φ	λ_{abs} (nm)	λ_{em} (nm)	Φ
DMSO	575	695	< 0.01	412	535	0.96	413	543	0.58	400	516	0.30	419	541	0.03
Film (sol-gel)	566	662	23	403	506	0.43	410	543	0.26	398	514	0.15	418	535	0.01
Film (PMMA)	553	656	13	404	499	0.57	nd	nd	nd	nd	nd	nd	nd	nd	nd

274

275 3.4 Primary amine vapour sensing in thin-film

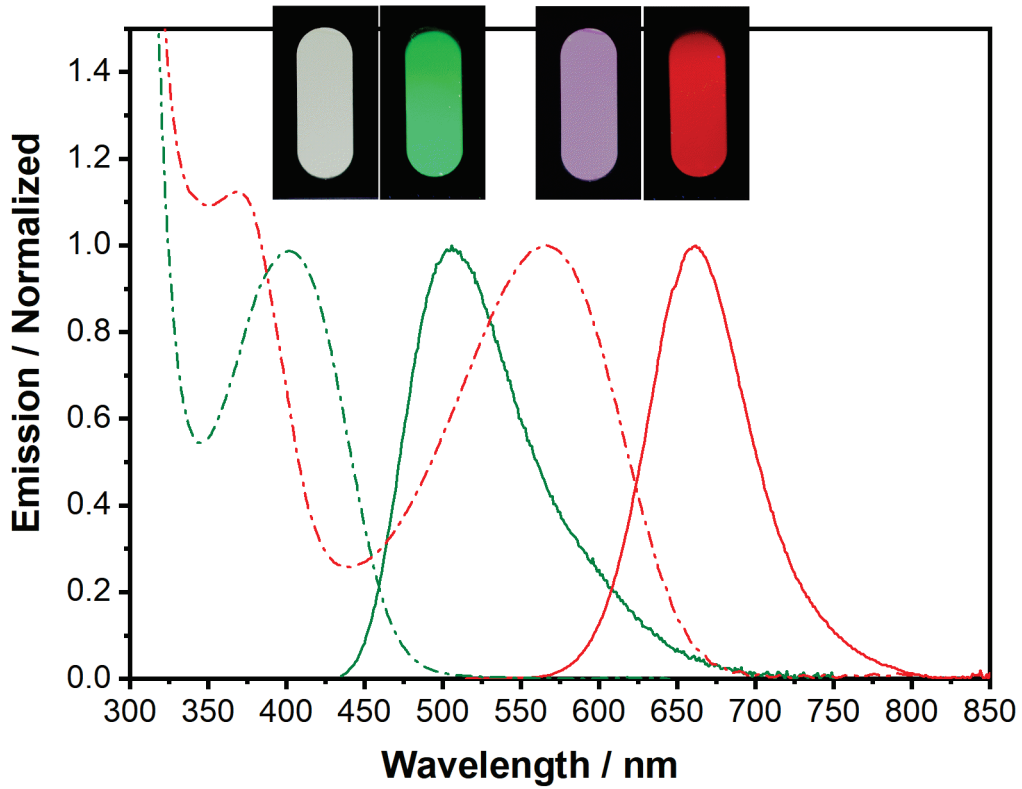
276 Having established PTTCN as a robust PL turn-on and reversible probe to detect primary amines in solution, we
 277 then investigated primary amine vapour detection by thin films of the sensing material. For this purpose,
 278 optically thin films of PTTCN in sol/gel or PMMA were obtained on glass substrate by spin-coating. The violet
 279 films displayed large absorption band at 566 nm and 553 nm respectively and showed strong far-red PL upon
 280 excitation at the absorption peak ($\lambda_{em} = 661$ nm / $\phi = 23\%$ and $\lambda_{em} = 656$ nm / $\phi = 13\%$, for sol-gel and PMMA
 281 films resp., Table 1). We then choose n-propylamine as an example for its high volatility, to test the film upon
 282 exposure to amine vapours. Exposing the sol-gel films to an atmosphere saturated with n-propylamine vapours

283 induced colour change from violet to almost colourless ($\lambda_{\text{max}} = 402 \text{ nm}$) with complete transformation in less
284 than 5 minutes. For PMMA films, the same colour change is observed ($\lambda_{\text{max}} = 403 \text{ nm}$) upon exposure to amine
285 vapour, but total conversion takes more than 20 min. The faster kinetic observed in sol-gel is probably due to the
286 more porous material in this case and therefore the greater accessibility of the dye. In the same time, for both
287 kind of films, a significant variation of emission from red to green was observed by naked eye when the films are
288 illuminated under 365 nm UV-light (Figure 6, see also SI). Upon excitation in the absorption peak strong green
289 PL signals were observed for the sol-gel and the PMMA films after exposure with amine, with maxima at
290 508 nm and 497 nm respectively. Good emission quantum yields were measured, respectively $\Phi = 57 \%$ and $\Phi =$
291 43 %. A ratiometric PL response to primary amine vapour is therefore possible when choosing the excitation
292 wavelength at 455 nm, wavelength at which the absorption of both **PTTCN** and imine are identical.

293 Similar colour changes were observed with exposure to ammonia or dimethylhydrazine vapours (Figure SI 8).
294 PLQY quantum yields in solid reflect what was observed in solution with weaker values for ammonia and
295 dimethylhydrazine than for n-propylamine. Always in agreement to what was observed in solution, no
296 fluorometric nor colourmetric responses were observed, even after 1 h, when the films were exposed to vapours
297 of secondary amine, tertiary amine, ether, ester, amide, alcohol, or thiol.

298 Unfortunately, the reversibility highlighted in solution could not easily be reproduced. Vacuum pumping of the
299 film exposed to propylamine vapour partially converts the film to its original state, but pumping for too long
300 results in severe flaking-off the films. The same observation was made when fuming malononitrile vapours after
301 amine exposure. The colour of the films reverted back to purple and the original emission partially recovered,
302 but the sample were damaged.

303

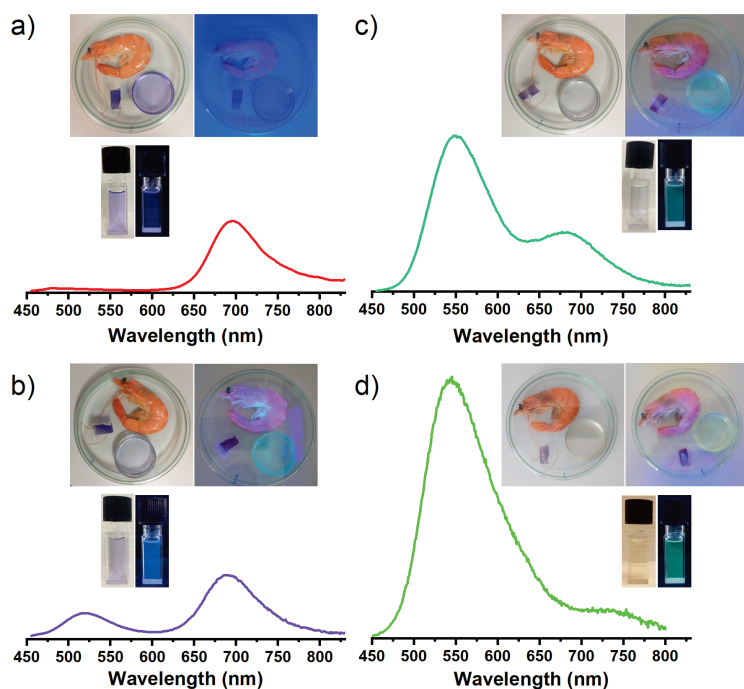


304

305 **Figure 6.** Normalized absorption (dotted line) and PL spectra (solid line) of **PTTCN** sol-gel film before (red) and
 306 after (green) exposure to n-propylamine vapour. Inset: the photography showed the film mounted in the support
 307 before (right) and after (left) exposure to n-propylamine of **PTTCN** in the absence (black) and presence (red) of
 308 saturated propylamine vapor under daylight or UV-light (365 nm).

309

310 **3.5 Tentative of monitoring seafood freshness**



311
 312 **Figure 7.** Attempt to control shrimp freshness, followed by a week: a) initial situation, b) after 24 hours, c) after 72
 313 hours, d) after 150 hours. For each time: picture of a solution (20 μM in DMSO in the small crystallizer) and of a
 314 sol-gel film on a glass substrate, placed inside the box with the whole animal, under daylight (left) and under
 315 handheld UV light (right); picture of the spectroscopic cell used for recording the fluorescence under daylight (left)
 316 and under 365nm UV-light of a portable lamp (right); and emission spectra recorded in the spectrofluorimeter –
 317 $\lambda_{\text{exc}} = 430 \text{ nm}$.

318
 319 Various volatile amine/ammonia vapours are generated during food spoilage. Using shrimps as an example,
 320 we tested whether **PTTCN** and the prepared materials can be used as fluorescent probe for monitoring seafood
 321 freshness. To do so, sol-gel spin-coated film as well as a DMSO solution of **PTTCN** (20 μM) were placed inside
 322 a packing box in which a shrimp was stored at room temperature for 1 week. A picture of the whole was taken
 323 every 24 hours and the emission spectra of the solution and films ($\lambda_{\text{exc}} = 430 \text{ nm}$) were also recorded. These data
 324 are summarised in Figure 7. Initially, only **PTTCN** emission was observed both in film and in solution (weak
 325 emission in concentrated solution, Figure 7a). Changes can be directly observed by naked eye in the solution
 326 sample. After 24 h, while the solution was still purple, indicating that **PTTCN** was still the main species in
 327 solution, a blue fluorescence emanated from the solution when viewed under 365 nm UV-light. The
 328 corresponding emission spectrum (Figure 7b) showed the appearing of a new emission band at 540 nm, in
 329 addition to the main **PTTCN** emission. This new band strongly increased in intensity after 48 and then 72 hours

330 (Figure 7b and 7c), as the solution lost its purple colour to grey, and then became almost the only detectable
331 emission after one week when the solution turned yellow (Figure 7d).

332 Unfortunately, during the same period of time, the changes to the film are not as visually spectacular. The
333 overall colour does not change and remains purple, albeit slightly faded, as does the fluorescence when viewed
334 under 365 nm UV-light, dominated by the intense red emission of **PTTCN**. It is only when the emission spectra
335 are recorded with a spectrofluorimeter, that a change is clearly seen with the appearing of a new band at 540 nm
336 in addition to the (intense) fluorescence of **PTTCN** (Fig. SI-12) when exciting at a wavelength close to the imine
337 absorption maximum ($\lambda_{\text{exc}} = 430$ nm). When PMMA films are used instead, no change both in absorption and
338 fluorescence spectra are observed. This could originate from the weak concentration of amine in the atmosphere
339 of the box reducing the kinetic of the reaction that is already slower in PMMA than in sol-gel film (see above).

340 While these film results confirm the previous observations and the formation of new emissive species, they
341 also reveal the limitation of the system. The detection of volatile amines during food spoilage could not be easily
342 followed with the naked eye, although it could be possible with the use of an appropriate measuring instrument.

343 **Conclusion**

344 In solution in DMSO or embedded in PMMA or sol-gel films, the dicyanovinyl compound **PTTCN** reacts with
345 strong nucleophilic nitrogen-containing analytes and especially primary aliphatic amine in a transformation
346 dicyanovinyl \rightarrow imine, that is reversible in nature. This transformation results in significant changes in the
347 optical properties, particularly fluorescence. **PTTCN** is only slightly emissive but displays a large emission in
348 the far-red in the solid-state, while the imine compounds formed by reaction with primary amines, on the other
349 hand, are highly emissive in both solution and in the solid state. In consequence, **PTTCN** can serve as a very
350 sensitive turn-on probe to detect primary amines in solution with a 1200-fold enhancement of the fluorescence
351 intensity during the reaction of **PTTCN** with n-propylamine. Sensitivity in the nanomolar range by fluorescence
352 monitoring was achieved and an excellent selectivity for primary amines over other amine nucleophiles was
353 evidenced both in solution and in the solid-state. We have also shown that monitoring of seafood spoilage is
354 possible with colour changes in response to the vapours released during shrimp spoilage, visible to naked-eye
355 accompanied by spectacular fluorescence enhancement over time in solution. Spin-coated films can also serve as
356 probe, highlighting the potential of **PTTCN** for low-cost amine probes, even though the response is less obvious
357 and only visible by instrumental recording.

358

359 **Declaration of Competing Interest**

360 The authors declare that they have no known competing financial interests or personal relationships that could
361 have appeared to influence the work reported in this paper.

362 **Acknowledgements**

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364 **Appendix A. Supplementary data**

365 The following is Supplementary data to this article: Experimental details, additional figures, films and
366 characterizations.

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