Easy and Prompt Detection of Penicillium Rot and Conservation Status of Packaged Citrus Fruit Using an Optical Array Sensor

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Electronic Supporting Information

General experimental methods

The NMR experiments were carried out at 27 °C on a Varian UNITY Inova 500 MHz spectrometer (1H at 499.88 MHz, 13C NMR at 125.7 MHz) equipped with a pulse field gradient module (Z axis) and a tuneable 5 mm Varian inverse detection probe (ID-PFG). The chemical shift (ppm) is referred to an internal standard (the solvent itself) and the coupling constants are reported in Hz. ESI mass spectra were acquired on an API 2000-ABSciex using CH_3CN or CH_3OH (positive or negative ion mode). All chemicals were reagent grade and were used without further purification. The characterization of Hyperspectral Ultraviolet-Induced Visible Fluorescence Mapping (HUVFM) was conducted using a custom-built instrument. The analysis probe consists of a bundle of 19 Y-shaped fibres (BF19Y2HS02 sourced from Thorlabs), provided with a beam collimator (F220SMA-532 sourced from ThorLabs) separated by the box lid from the analysis point. Among the 19 fibres, 10 are Y-ends connected to the source, which is a 365 nm LED sourced from Thorlabs. The remaining 9 fibres are linked to an optical block housing bandpass filter sourced from, designed to block backscattered light from the source. Subsequently, the CCD detector (CCS100/M sourced from Thorlabs) is connected to a bundle of optical fibres arranged linearly (BFL200HS02 sourced from Thorlabs), maximizing the light collected by the sampling led. Multivariate analysis of dataset was performed by means of SIMCA-P11 (Umetrics). Dataset was centred and unity scaled.

Method of detection

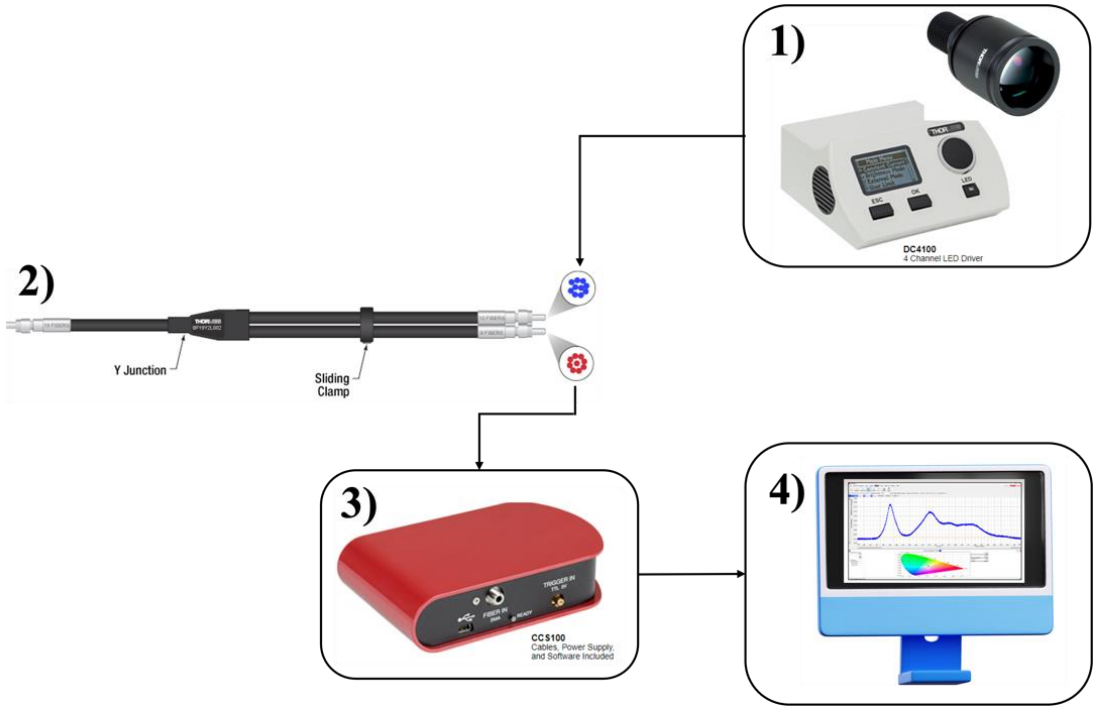

Figure S1. Schematic representation of assembled device for detection by optical fibre: 1) light source and LED driver, 2) optical fibre, 3) CCD detector and 4) computer.

Synthesis of probes

Probe **1** was bought by Merck. Probe **10** was acquired by Carlo Erba. Probes **2**, **3**, **11** and **12** were synthesized according to Santonocito et al. [1], probes **4**, **5**, **6**, **7**, **8**, **9**, **18** and **19** were obtained through synthesis proposed by Giuffrida et al. [2], probes **13** and **14** were prepared by Santonocito et al.'s method [3], probe **15** was obtained according to Tuccitto et al. [4], while probes **16**, **17** and **20** were synthesized as reported by Santonocito et al. [5-6]. Synthesis procedures as well as characterization of the probes are herein reported.

Synthesis of probe 2

To a solution of Rhodamine B (0.552 g, 1.153 mmol) and DIPEA (0.23 mL, 1.32 mmol) in 100 mL of CH_3CN at 0°C and under N_2 atmosphere, a solution of HBTU (0.5 g, 1.32 mmol) in 30 mL of CH_3CN was added. After stirring the mixture for 30 minutes at 0°C, an ice-cold solution of N-(2-hydroxyethyl)piperazine (0.162 mL, 1.32 mmol) in 15 mL of CH_3CN was added. After removal of the ice bath, the solvent was evaporated under reduced pressure. The desired compound (yield 84%) was then purified by column chromatography (silica gel, CH_2Cl_2/EtOH 95:5). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68-7.57 (m, 2H), 7.55 (m, 1H), 7.34 (m, 1H), 7.27 (d, J = 9.5 Hz, 2H), 6.96 (dd, J_1 = 9.5 Hz, J_2 = 1.8 Hz, 2H), 6.77 (d, J = 1.8 Hz, 2H), 3.62 (m, 10H), 3.41 (m, 4 H), 2.50 (t, J = 5.5 Hz, 2H), 2.39 (m, 4 H), 1.33 (t, J = 8 Hz, 12 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4, 157.7, 156.1, 155.6, 135.4, 132.2, 130.6, 130.1, 130.0, 129.8, 127.5, 114.1, 113.7, 96.2, 59.3, 57.8, 46.0, 12.5. ESI-MS *m/z* 555.4 $[M]^+$. Anal calcd for $C_{32}H_{38}ClN_3O_3$: C 70.12, H 6.99, N 7.67; found: C 69.84, H 7.17, N 7.49.

Synthesis of probe 3

To a solution of Rhodamine B (0.552 g, 1.153 mmol) and DIPEA (0.23 mL, 1.32 mmol) in 100 mL of CH_3CN at 0°C and under N_2 atmosphere, a solution of HBTU (0.5 g, 1.32 mmol) in 30 mL of CH_3CN was added. After stirring the mixture for 30 minutes at 0°C, an ice-cold solution of morpholine (0.113 mg, 1.153 mmol) in 15 mL of CH_3CN was added. After removal of the ice bath, the solvent was evaporated under reduced pressure. The desired compound (yield 80%) was then purified by column chromatography (silica gel, CH_2Cl_2/EtOH 95:5). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (m, 2H), 7.55-7.52 (m, 1H), 7.34 (m, 1H), 7.27 (d, J = 12 Hz, 2H), 6.96 (dd, J_1 = 12 Hz, J_2 = 4Hz, 2H), 6.76 (d, J = 4 Hz, 2H), 3.65–3.57 (q, J = 8Hz, 8H), 3.49 (m, 2H), 3.40 (m, 2H), 1.31 (t, J = 8Hz, 12 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.4, 157.7, 155.7, 155.6, 135.0, 132.0, 130.7, 130.3, 130.2, 130.1, 127.6, 114.2, 113.7, 96.3, 66.6, 48.0, 46.2, 42.2, 12.6 ppm. ESI-MS: *m/z* = 512.3 $[M]^+$; Anal calcd for $C_{34}H_{43}ClN_4O_3$: C, 69.08; H, 7.33; N, 9.48; found: C, 69.01; H, 7.25; N, 9.42.

Synthesis of probe 4

To a solution of 2,4-dimethy-3-ethylpyrrole (2.38 mL, 17.6 mmol) in 500 mL of dry CH_2Cl_2, 1 eq. of 2-pyridinecarboxaldehyde (0.84 mL, 8.8 mmol) was added, followed by a catalytic amount of trifluoroacetic acid (5 drops). After overnight stirring at room temperature and under nitrogen atmosphere, 1.5 eq. of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (3 g, 13.2 mmol) was added; then the mixture was stirred at room temperature and atmospheric pressure for 24 h. After the established time, the reaction was monitored by TLC

(silica gel, CH_2Cl_2 100%), then triethylamine (12 mL) and boron trifluoride diethyl etherate (14 mL) were added drop by drop and the mixture was stirred again under nitrogen atmosphere at room temperature for 2 h. The solvent is then removed under reduced pressure; the residue is solubilized in 150 mL of CH_2Cl_2 and filtered to remove the excess of DDQ. The product is isolated by column chromatography (yield 24%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.82 (d, *J* = 4.5 Hz, 1H), 7.90 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.49 (m, 2H,), 2.53 (s, 6H), 2.30 (q, *J* = 7.5 Hz, 4H), 1.21 (s, 6H), 0.98 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 155.16, 137.47, 133.18, 125.38, 124.22, 17.05, 14.55, 12.64, 11.07. ESI-MS: *m/z* 382.2 $[M+H]^+$. Anal. Calcd. For $C_{22}H_{26}BF_2N_3$: C, 69.30; H, 6.87; B, 2.84; F, 9.97; N, 11.02. Found: C, 69.15; H, 6.77; N, 10.92.

Synthesis of probe 5

To a solution of 2,4-dimethy-3-ethylpyrrole (2.38 mL, 17.6 mmol) in 500 mL of dry CH_2Cl_2, 1 eq. of 3-pyridinecarboxaldehyde (0.84 mL, 8.8 mmol) was added, followed by a catalytic amount of trifluoroacetic acid (5 drops). After overnight stirring at room temperature and under nitrogen atmosphere, 1.5 eq. of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (3 g, 13.2 mmol) was added; then the mixture was stirred at room temperature and atmospheric pressure for 6 h. After the established time, the reaction was monitored by TLC (silica gel, CH_2Cl_2 100%), then triethylamine (12 mL) and boron trifluoride diethyl etherate (14 mL) were added drop by drop and the mixture was stirred again under nitrogen atmosphere at room temperature overnight. Then, the solvent was removed under reduced pressure and the residue was redissolved in CH_2Cl_2 and filtered. The desired compound (yield 17%) was purified by column chromatography (silica gel, CH_2Cl_2 100%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.98 (t, J = 7.5 Hz, 6H), 1.28 (s, 6H), 2.30 (q, J = 7.8 Hz, 4H), 2.54 (s, 6H), 7.45 (dd, J_1 = 4.9 Hz, J_2 = 2.9 Hz, 2H), 7.64 (t of d, J_1 = 7.8 Hz, J_2 = 2.0 Hz, 1H), 8.56 (dd, J_1 = 2.0 Hz, J_2 = 1.0 Hz, 1H), 8.75 (dd, J_1 = 4.9 Hz, J_2 = 2.0 Hz, 1H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 14.76, 15.52, 16.01, 17.26, 123.12, 131.00, 131.65, 134.15, 138.89, 145.26, 150.96, 151.32, 156.35. ESI-MS: *m/z* 382.3 $[M+H]^+$. Anal. Calcd. for $C_{22}H_{26}BF_2N_3$ C, 69.30; H, 6.87; N, 11.02; found: C 69.33; H, 6.78; N, 11.01.

Synthesis of probe 6

To a solution of 2,4-dimethyl-3-ethylpyrrole (1.19 mL, 8.8 mmol) in 250 mL of dry dichloromethane, 0.42 mL of 4-pyridinecarboxaldehyde (4.4 mmol) was added, followed by a catalytic amount of trifluoroacetic acid. After overnight stirring under a nitrogen atmosphere, the mixture was concentrated to 50 mL under vacuum, and 1.5 g of 2,3-dichloro-5,6- dicyanobenzoquinone was added and stirred for 2 h. Triethylamine (6 mL) and $BF_3(OEt_2)$ (7 mL) was then added. After 2h the mixture was concentrated under a vacuum and washed with CH_2Cl_2 and water. The organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The mixture was purified by silica flash column chromatography ($CHCl_3$, 100%) to obtain probe **6** (0.40 g, 24% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.90 (d, *J* = 6.0 Hz, 2H), 7.75 (d, *J* = 6.0 Hz, 2H), 2.53 (s, 6H), 2.30 (q, *J* = 7.5 Hz, 4H), 1.27 (s, 6H), 0.98 (t, *J* = 7.5 Hz, 6H, -CH_2-CH_3). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 15.21, 15.89, 16.45, 17.01, 124.13, 130.39, 131.52, 132.12, 138.42, 144.26, 151.12, 156.81. ESI-MS: *m/z* 382.6 $[M+H]^+$. Anal. Calcd. for $C_{22}H_{26}BF_2N_3$ C, 69.30; H, 6.87; N, 11.02; found 69.29; H, 6.82; N, 10.98.

Synthesis of probe 7

To a solution of **4** (0.4 g, 1.5 mmol) in 50 mL of dry CH_3CN, 10 mL of iodoethane were added under nitrogen atmosphere. The mixture was then stirred at 45°C for 2 days, then it was monitored by TLC (neutral aluminium oxide, CH_2Cl_2 100%). Finally, the mixture was cooled to room temperature and the solvent was removed under reduced pressure. The product was purified by column chromatography (conversion 20%, yield 61%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.76 (d, *J* = 6.5 Hz, 1H), 8.67 (d of t, *J* = 7.5, 1.5 Hz, 1H), 8.56 (t of d, *J* = 7.5, 1.5 Hz, 1H), 7.96 (dd, *J* = 7.5, 1.5 Hz, 1H), 4.99 (q, *J* = 7.5 Hz, 2H), 2.58 (s, 6H), 2.33 (q, *J* = 7.5 Hz, 4H), 1.67 (t, *J* = 7.5 Hz, 3H), 1.27 (s, 6H), 1.05 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 144.96, 136.06, 135.83, 130.46, 129.58, 57.60, 55.04, 17.12, 16.69, 14.35, 13.05, 11.41. ESI-MS: *m/z* 410.3 $[M]^+$. Anal. Calcd. For $C_{24}H_{31}BF_2IN_3$: C, 53.66; H, 5.82; B, 2.01; F, 7.07; I, 23.62; N, 7.82. Found: C, 53.59; H, 5.78; N, 7.78.

Synthesis of probe 8

554 mg of **5** (1.45 mmol) were dissolved in dry CH_3CN under a nitrogen atmosphere. Then, 240 mg of dry K_2CO_3 were added and the mixture was heated at 45° C. After 10 minutes, 10 mL of iodoethane were added, and the reaction mixture was stirred for 24 h. The total conversion of the starting reagent was monitored by TLC (Al_2O_3, CH_2Cl_2). At the end of the reaction, the solvent was removed under reduced pressure, and the product **8** (yield 62%) was purified by chromatography (Al_2O_3, CH_2Cl_2/CH_3OH, from 100:0 to 90:10). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.0 (t, *J* = 7.5 Hz, 6H), 1.34 (s, 6H), 1.8 (t, *J* = 7.3 Hz, 3H), 2.32 (q, *J* = 7.5 Hz, 4H), 2.56 (s, 6H), 5.17 (q, *J* = 7.3 Hz, 2H), 8.4 (m, 2H), 8.51 (d, *J* = 3.7 Hz, 1H), 10.35 (t, *J* = 6.1 Hz, 1H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 145.23, 137.16, 136.84, 132.56, 130.55, 57.70, 54.02, 17.11, 16.15, 14.12, 13.85, 11.21. ESI-MS: *m/z* 410.3 $[M]^+$. Anal. Calcd. For $C_{24}H_{31}BF_2IN_3$: C, 53.66; H, 5.82; B, 2.01; F, 7.07; I, 23.62; N, 7.82. Found: C, 53.58; H, 5.79; N, 7.77.

Synthesis of probe 9

600 mg of **6** (1.57 mmol) were dissolved in dry CH_3CN under a nitrogen atmosphere. Then, 286 mg of dry K_2CO_3 was added and the mixture was heated at 45° C. After 10 minutes, 10 mL of iodoethane were added, and the reaction mixture was stirred for 24 h. The total conversion of the starting reagent was monitored by TLC (Al_2O_3, CH_2Cl_2). At the end of the reaction, the solvent was removed under reduced pressure, and the **9** (yield 17%) was purified by column chromatography (Al_2O_3, CH_2Cl_2/CH_3OH 95/5). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 9.69 (d, *J* = 6.4 Hz, 2H), 8.05 (d, *J* = 6.1 Hz, 2H), 5.27 (q, *J* = 7.1 Hz, 2H), 2.55 (s, 6H), 2.31 (q, *J* = 7.5 Hz, 4H), 1,84 (t, *J* = 7.1 Hz, 3H), 1.34 (s, 6H), 0.99 (t, *J* = 7.5 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.2, 145.1, 136.7, 134.7, 128.9, 58.3, 53.2, 29.6, 17.1, 14.5, 13.3, 12.7. ESI-MS: *m/z* 410.3 $[M+H]^+$. Anal. Calcd. For $C_{24}H_{31}BF_2IN_3$: C, 53.66; H, 5.82; B, 2.01; F, 7.07; I, 23.62; N, 7.82. Found: C, 53.57; H, 5.78; N, 7.79.

Synthesis of probe 11

Rhodamine pentafluoro phenol[1] (407 mg, 0.632 mmol) was solubilized in 50 mL of anhydrous CH_2Cl_2 under N_2 atmosphere, then 6 eq of DIPEA (0.66 mL 3.79 mmol) and 2 eq of Di-(2-picolyl) amine (0.23 mL, 1.26 mmol) were added. The reaction was kept under stirring for 48 h at 60°C. The desired compound (263.7 mg, 55% yield) was purified by chromatographic column CH_2Cl_2 and 5% MeOH. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.55 (d, J = 3.5 Hz, 1H), 8.26 (d, J = 4 Hz, 1H), 7.88 (d, J = 7.5 Hz, 1H), 7.8 (t, J = 7.5 Hz, 1H), 7.72 (t, J = 7.5 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.48 (m, 2H), 7.34 (m, 1H), 7.27 (m, 4H), 7.19 (m, 1H), 6.97 (m, 4H), 6.67 (d, J = 7.5 Hz, 1H), 4.54 (s.br. 2H), 4.44 (s.br. 2H), 3.70 (q, J = 7.5 Hz, 8H), 1.33 (t, J = 7.5 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.5, 159.2, 157.3, 156.7, 156.4, 150.7, 149.8, 138.7, 138.2, 136.8, 133.3, 131.8, 131.4, 131.2, 131.0, 128.5, 124.2, 123.9, 123.6, 123.4, 115.2, 97.3, 55.3, 50.6, 46.8, 12.8. ESI-MS m/z 624.2 $[M+H]^+$. Anal calcd for $C_{40}H_{42}ClN_5O_2$: C, 72.77; H, 6.41; N, 10.61; found: C, 72.72; H, 6.35; N, 10.55.

Synthesis of probe 12

To a solution of Rhodamine B (501 mg, 1.13 mmol) and DIPEA (0.21 mL, 1.20 mmol) in 100 mL of CH_3CN at 0°C and under an N_2 atmosphere, was added a solution of HBTU (455 mg, 1.20 mmol) in 30 mL of CH_3CN. After stirring the mixture for 30 minutes at 0°C, an ice-cold solution of diethanolamine (0.115 mL, 1.20 mmol) in 15 mL of CH_3CN was added. The ice-bath was removed, and the solvent was removed under reduced pressure. Finally, the desired compound (yield 84%) was purified by column chromatography (silica gel, CH_2Cl_2/EtOH 9:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.82 (d, J = 8.54 Hz, 1H), 7.69-7.64 (m, 2H), 7.34 (d, J = 8.54 Hz, 1H), 7.24 (d, J = 9.76 Hz, 2H), 6.94 (dd, J_1 = 9.15 Hz, J_2 = 2.44, 2H), 6.77 (d, J = 2.44 Hz, 2H), 3.74-3.71 (m, 2H), 3.68-3.58 (m, 8H), 3.47 (m, 2H), 3.39 (m, 2H), 3.36 (m, 2H), 1.33 (t, J = 7.32 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.4, 157.8, 153.3, 155.6, 136.4, 132.1, 130.4, 130.0, 129.7, 129.3, 128.5, 113.9, 113.7, 96.1, 60.7, 59.5, 52.7, 47.9, 46.0, 38.6, 12.5. ESI-MS *m/z* 530.6 $[M+H]^+$. Anal calcd for $C_{32}H_{40}ClN_3O_4$: C, 67.89; H, 7.12; N, 7.42; found: C, 67.82; H, 7.09; N, 7.38.

Synthesis of probe 13

172 mg (0.46 mmol) of Br-NO_2-naphtalimide[7] were dissolved in 20 mL of 2-methoxyethanol under nitrogen atmosphere, and a great excess of ethanolamine was added to the solution. The reaction mixture was stirred at reflux for 36 h. Then, the solvent was removed, and probe **13** (47% yield) was obtained after purification by flash chromatography (silica gel, $CHCl_3$/CH_3OH 9:1). ^{1}H NMR (500 MHz, acetone-d_6): δ 8.43 (d, J = 8.5 Hz, 2H), 6.74 (d, J = 8.5 Hz, 2H), 6.60 (t, J = 5.0 Hz, 2H), 4.05 (q, J = 5.0 Hz, 4H), 4.01 (d, J = 7.5 Hz, 2H), 3.42 (q, J = 5.0 Hz, 4H), 2.55 (br, 2H), 2.24 (m, 1H), 0.96 (d, J = 6.5 Hz, 6H) ppm. ^{13}C NMR (125 MHz, acetone-d_6): δ 164.92, 153.87, 134.02, 133.27, 112.43, 112.33, 107.74, 60.76, 47.50, 46.90, 28.09, 20.64 ppm. ESI-MS m/z 372.3 $[M + H]^+$. Anal. calcd for $C_{20}H_{25}N_3O_4$: C, 64.67; H, 6.78; O, 17.23. Found: C, 64.61; H, 6.72; O, 17.18.

Synthesis of probe 14

1 g (3.1 mmol) of Br-NO_2-anhydride was dissolved in 90 mL of 2-methoxyethanol under nitrogen atmosphere, and 1.920 mL (18.6 mmol) of isobuthylamine was added to the solution. The reaction mixture was stirred at

reflux for 36 h. Then, the solvent was removed, and probe **14** (30% yield) was obtained after purification by flash chromatography (silica gel, $CHCl_3/CH_3OH$ 9:1). ^1H NMR (500 MHz, $CDCl_3$): δ 0.9 (d, *J* = 6.7 Hz, 6H), 1.1 (d, *J* = 6.7 Hz, 12H), 2.06 (m, 2H, CH), 2.2 (m, 1H, CH), 3.1 (d, *J* = 6.7 Hz, 4H), 4.0 (d, *J* = 6.7 Hz, 2H), 6.7 (d, *J* = 8.5 Hz, 2H), 8.4 (d, *J* = 8.5 Hz, 2H) ppm. ^{13}C NMR (125 MHz; $CDCl_3$): δ 20.3, 20.7, 27.3, 28.0, 46.7, 52.7, 107.0, 111.7, 112.4, 132.1, 133.6, 152.6, 164.8 ppm. ESI-MS m/z 396.09 $[M + H]^+$. Anal. Calcd. For $C_{24}H_{33}N_3O_2$: C, 72.88; H, 8.41; O, 8.09. Found: C, 72.81; H, 8.35; O, 8.01.

Synthesis of probe 15

555 mg (1.26 mmol) of BDPy-NH_2-NO_2[4] were dissolved in 500 mL of absolute ethanol. Palladium catalyst (175 mg of Pd on activated charcoal 10%) was added to the reaction mixture kept under vigorous stirring. Hydrogen is bubbled into the reaction mixture for 6 h, checking the reaction by TLC (CH_2Cl_2/EtOH 95:5). Then, the catalyst was filtered, and the solvent was removed under reduced pressure. The crude compound was purified by column chromatography (silica gel, CH_2Cl_2/CH_3OH 98:2) to obtain 488 mg (94% yield) of **15**. ^1H NMR (500 MHz, acetone-d_6): δ 0.96 (t, *J* = 7.5 Hz, 6H), 1.25 (s, 6H), 2.33 (q, *J* = 7.5 Hz, 4H), 2.50 (s, 6H), 7.09 (d, *J* = 8.2 Hz, 1H), 7.46 (s, 1H), 7.68 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C NMR (125 MHz, acetone-d_6): δ 153.00, 152.84, 142.12, 138.37, 132.41, 131.24, 128.29, 121.56, 16.48, 14.04, 11.78, 11.42. ESI-MS: *m/z* = 410 $[M]^-$. Anal. Calcd. For $C_{23}H_{29}BF_2N_4$: C, 67.33; H, 7.12; N, 13.65. Found: C, 67.29; H, 7.10; N, 13.62.

Synthesis of probe 16

BDPy-CH_2Cl [5] (150 mg, 0.42 mmol) was solubilized in 60 mL of dry acetonitrile; 1 eq. of KI (70 mg, 0.42 mmol), 3 eq. of K_2CO_3 (232 mg, 1.68 mmol) and 2 eq. of picolylamine (0.08 mL, 0.84 mmol) were added at room temperature and under nitrogen atmosphere. The reaction mixture was refluxed overnight and then monitored by TLC (silica gel, diethyl ether/AcOEt 6:4). The mixture was cooled at room temperature and the solvent was removed under reduced pressure. The residue was redissolved in 50 mL of CH_2Cl_2 and filtered to remove K_2CO_3, then the product (yield 40%) was isolated by column chromatography (silica gel, diethyl ether/AcOEt 6:4). ^1H NMR (500 MHz; $CDCl_3$): δ = 1.03 (t, J = 7.9 Hz, 6H), 2.38 (s, 6H), 2.41 (q, J = 7.9 Hz, 4H), 2.50 (s, 6H), 4.01 (m, 4H), 7.18 (t, J = 6.4 Hz, 1H), 7.34 (d, J = 8.2 Hz, 1H), 7.65 (t, J = 8.2 Hz, 1H), 8.55 (d, J = 6.4, 1H) ppm. ^{13}C NMR (125 MHz; $CDCl_3$) δ = 158.9, 153.4, 149.3, 138.3, 136.5, 131.8, 122.6, 55.6, 44.9, 17.1, 14.7, 12.4 ppm. ESI-MS: m/z = 422.1 $[M-H]^-$. Anal. Calcd for $C_{24}H_{31}BF_2N_4$: C, 67.93; H, 7.36; N, 13.20. Found: C, 67.87; H, 7.31; N, 13.12.

Synthesis of probe 17

Previously synthesized BDPy-CH_2Cl [6] (290 mg, 0.82 mmol) was solubilized in 60 mL of dry acetonitrile; 1 eq. of KI (136 mg, 0.82 mmol), 3 eq. of K_2CO_3 (340 mg, 2.40 mmol) and 2 eq. of ethanolamine (0.1 mL, 1.64 mmol) were added at room temperature and under nitrogen atmosphere. The reaction mixture was refluxed for 3 h until the complete conversion of the BDPy-CH_2Cl, monitored by TLC (silica gel, diethyl ether/AcOEt 6:4). The mixture was cooled at room temperature and the solvent was removed under reduced pressure. The residue

was redissolved in 50 mL of CH_2Cl_2 and filtered to remove K_2CO_3, then the product (yield 44%) was isolated by column chromatography (silica gel, diethyl ether/AcOEt 6:4). ^{1}H-NMR (500 MHz; $CDCl_3$): δ 1.05 (t, J = 7.9 Hz, 6H); 2.39 (s, 6H); 2.41 (q, J = 7.9 Hz, 4H); 2.50 (s, 6H); 2.92 (t, J = 4.9 Hz, 2H); 3.73 (t, J = 4.9 Hz, 2H); 4.01 (s, 2H) ppm. ^{13}C NMR (125 MHz; $CDCl_3$) δ 153.8 (C-CH_3 in α to N-pyr), 138.07 (C in α to CH_2-NH), 135.95 (C in α to N-pyr), 133.03 (C-CH_2-CH_3 in β to N-pyr), 131.8 (C- CH_3 in γ to N-pyr), 61.8 (CH_2-OH), 51.5 (Bdpy-CH_2-NH), 45.3 (NH-CH_2-CH_2), 29.5 (CH_3), 17.0 (CH_3), 15.0 (CH_2-CH_3), 12.6 (CH_2-CH_3) ppm. ESI-MS: *m/z* = 378.6 $[M+H]^+$. Anal. Calcd for $C_{20}H_{30}BF_2N_3O$: C, 63.67; H, 8.02; N, 11.14. Found: C, 63.61; H, 7.99; N, 11.10.

Synthesis of probe 18

1 g of benzaldehyde (9.42 mmol, 1 eq.) was dissolved in dry CH_2Cl_2 (265 mL) under nitrogen atmosphere. A catalytic amount of TFA was added and the reaction mixture was stirred at room temperature overnight under nitrogen atmosphere. The reaction was monitored by TLC (silica gel, CH_2Cl_2) following the total conversion of the starting aldehyde; then 3.21 g (14.1 mmol, 1.5 eq.) of DDQ were added. The mixture was stirred at room temperature for 20 hours, then 14 mL of triethylamine and 16 mL of $BF_3(OEt_2)$ were added. The reaction mixture was stirred overnight at room temperature. Then, the solvent was removed under reduced pressure and the mixture was redissolved in 200 ml of CH_2Cl_2 and filtered. The obtained compound (yield 72%) was purified by column chromatography (silica gel, CH_2Cl_2/*n*-hexane, 5:5). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.98 (t, J = 7.5 Hz, 6H), 1.27 (s, 6H), 2.30 (q, J =7.5 Hz, 4H), 2.53 (s, 6H), 7.27 (m, 2H), 7.47 (m, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) 150.3, 138.9, 137.8, 136.0, 135.0, 131.4, 129.8, 128.5, 128.2, 17.7, 15.0, 14.5, 11.9. ESI-MS: *m/z* = 403.22 $[M+Na]^+$. Anal. Calcd for C, 72.64; H, 7.16; N, 7.37. Found: C, 72.61; H, 7.11; N, 7.32.

Synthesis of probe 19

2 eq. of 2,4-dimethyl-3-ethylpyrrole (3.32 mL, 24.5 mmol) and 1 eq. of 4-hydroxybenzaldehyde (1.22 mL, 12.3 mmol) were dissolved in 300 mL of dry CH_2Cl_2 under nitrogen atmosphere. A catalytic amount of trifluoroacetic acid (3 drops) was added and the reaction mixture was stirred at room temperature overnight. The reaction was monitored by TLC (silica gel, CH_2Cl_2 100%) to follow the total conversion of the starting aldehyde; then 1.5 eq. of DDQ (4.19 g, 18.4 mmol) were added. The mixture was stirred at room temperature for 6 h, then 18 mL of triethylamine and 21 mL of boron trifluoride diethyl etherate were added. The reaction was stirred overnight at room temperature; then, the solvent was removed under reduced pressure and the residue was redissolved in 200 mL of CH_2Cl_2 and filtered to remove the excess of DDQ. The product (yield 22%) was purified by column chromatography (silica gel, CH_2Cl_2 100%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.95 (t, *J* = 7.5 Hz, 6H), 1.34 (s, 6H), 2.28 (q, *J* = 7.5 Hz, 4H), 2.53 (s, 6H), 5.29 (s, 1H), 6.93 (d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.48, 153.79, 140.54, 138.64, 132.97, 131.39, 129.93, 128.17, 116.29, 17.35, 14.90, 12.76, 12.12 ppm. ESI-MS: *m/z* = 419.15 $[M+Na]^+$. Anal. Calcd for C, 69.71; H, 6.87; N, 7.07. Found: C, 69.69; H, 6.81; N, 7.01.

Synthesis of probe 20

Previously synthesized BDPy-CH_2Cl [6] (157 mg, 0.45 mmol) was solubilized in 30 mL of dry acetonitrile; 1 eq. of KI (74 mg, 0.45 mmol), 3 eq. of K_2CO_3 (180 mg, 1.34 mmol) and 2 eq. of diethanolamine (83 μL, 0.89 mmol) were added at room temperature and under nitrogen atmosphere. The reaction mixture was refluxed for 3 h until the complete conversion of the BDPy-CH_2Cl, monitored by TLC (silica gel, diethyl ether/AcOEt 5:5). The mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was redissolved in 50 mL of CH_2Cl_2 and filtered to remove K_2CO_3, then the product (yield 16%) was isolated by column chromatography (silica gel, diethyl ether/AcOEt 5:5). ^{1}H-NMR (500 MHz; $CDCl_3$): δ 1.05 (t, J = 7.3 Hz, 6H); 2.40 (q, J = 7.3 Hz, 4H); 2.44 (s, 6H); 2.50 (s, 6H); 2.87 (t, J = 5.5 Hz, 4H); 3.60 (t, J = 5.5 Hz, 4H); 4.12 (s, 2H) ppm. ^{13}C NMR (125 MHz; $CDCl_3$) δ 153.8 (C-CH_3 in α to N-pyr), 138.07 (C in α to CH_2-NH), 135.95 (C in α to N-pyr), 133.03 (C-CH_2-CH_3 in β to N-pyr), 131.8 (C- CH_3 in γ to N-pyr), 61.8 (CH_2-OH), 51.5 (Bdpy-CH_2-NH), 45.3 (NH-CH_2-CH_2), 29.5 (CH_3), 17.0 (CH_3), 15.0 (CH_2-CH_3), 12.6 (CH_2-CH_3) ppm. ESI-MS: *m/z* = 378.6 $[M+H]^+$. Anal. Calcd for $C_{20}H_{30}BF_2N_3O$: C, 63.67; H, 8.02; N, 11.14. Found: C, 63.61; H, 7.99; N, 11.10.

Preparation of fungal inoculum

In this study, fungal inoculum was represented by conidial suspensions of the pathogen *Penicillium digitatum* prepared according to previous studies [6-7]. Briefly, *P. digitatum*, isolate P1PP0 [8], was grown on potato dextrose agar (PDA) at 25°C in the dark for seven days, until the mycelium covered at least 90% of the Petri dish and conidia were produced (Fig. S2). Then, conidia were separated from the mycelium by adding 1.00 mL of sterile distilled water (s.d.w.) to the top of the culture and gently scraping them off using a sterile inoculating loop. The obtained conidial suspension was collected with a Pasteur pipette and filtered through sterile cheesecloth. Finally, conidia were recovered by centrifugation, rinsed, resuspended in s.d.w., and their final concentration was adjusted to 10^6 conidia/mL using a hemocytometer.

Figure S2. Seven-day-old culture of *Penicillium digitatum* isolate P1PP0 grown on Potato Dextrose Agar medium at 25 °C.

Fruit inoculation and Packaging

Fruit used in this study were mature blood oranges (*Citrus* × *sinensis* (L.) Osbeck, cv. Tarocco) collected from an organically cultivated orchard. Fruits were selected based on their uniformity in rind colour (deep orange) and size (caliber 6, according to the market standard established by the Commission Delegated Regulation EU 219/428 of 12 July 2018, corresponding to 64 to 73 cm diameter). For the test, fruit were preliminarily surface-sterilized with a 1% NaClO solution for 2 min, rinsed with tap water, and air-dried at room temperature. Then, the inoculation of *P. digitatum* isolate P1PP0 was carried out as follows: the peel of each fruit was wounded, at two points, with a 2-mm-diameter plastic tip without injuring the juice sacks below the albedo; then, each wound received 20.0 µL of conidia suspension (concentration 10^6 conidia/ mL) of *P. digitatum* isolate P1PP0. Two inoculated fruits were packaged in a plastic transparent box (Volume = 3.5 L), and three arrays were face-up attached with adhesive tape on the internal part of the box lid. Contact with external environment was avoided by closing the box with parafilm; this box was labelled "inoculated". Two control fruits were inoculated with s.d.w. and packaged in a different box, which was sealed by parafilm as above described; this second box was labelled "non-inoculated".

Sensing by fluorescent array

After undergoing UV/O_3 treatment, 18 circular polyamide supports (pore size: 0.2 µm, diameter: 5 cm) were employed to drop cast 1.5 µL of each probe solution (1 mM in $CHCl_3$), and the solvent was dried at air. The initial emission (I_0) of the probes was collected through optical fibre, with excitation provided by a UV LED at 365 nm. Three arrays per box were then exposed to gaseous analytes generated inside the two boxes. Subsequently, the emission of each probe (I_{non} for "non-inoculated" and I_{in} for "inoculated") was monitored with the same method for 4 consecutive days. The entire process is witnessed by images reported in Figure S3. Day-by-day growth of *P. digitatum* in inoculated oranges can be observed in Figure S4.

Figure S3. Steps involved in sensing by fluorescent array: 1) drop casting of fluorescent probes onto polyamide solid supports; 2) array-based labels being attached on the internal part of the box lid using adhesive tape; 3) analysis of each spot emission by optical fibre.

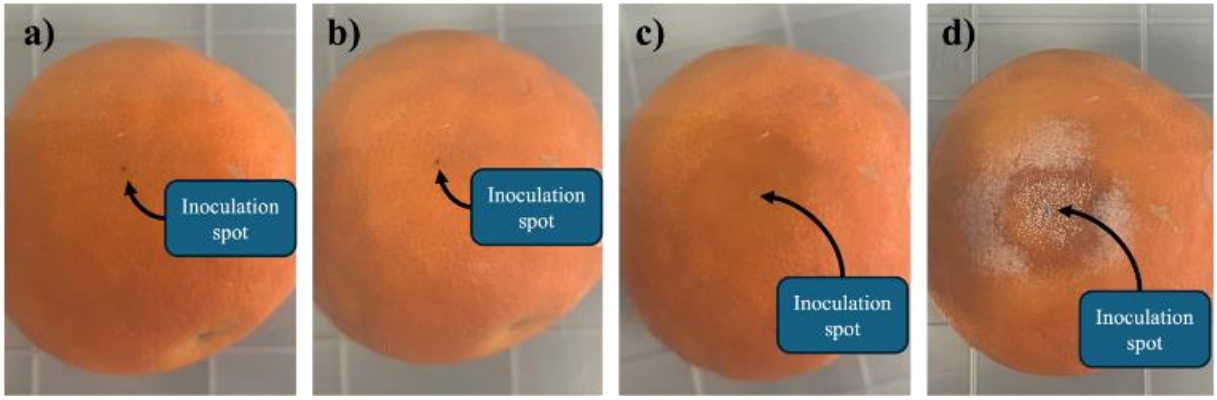

Figure S4. Day-by-day progressive growth of *Penicillium digitatum* in inoculated oranges: a) Day 1, b) Day 2, c) Day 3 and d) Day 4.

For each day, the fluorescence intensity was extrapolated from emission spectra and elaborated through subtraction of I_0, according to the formulas:

1. $\Delta I_{non} = I_{non} - I_0$, for "non-inoculated";
2. $\Delta I_{in} = I_{in} - I_0$, for "inoculated".

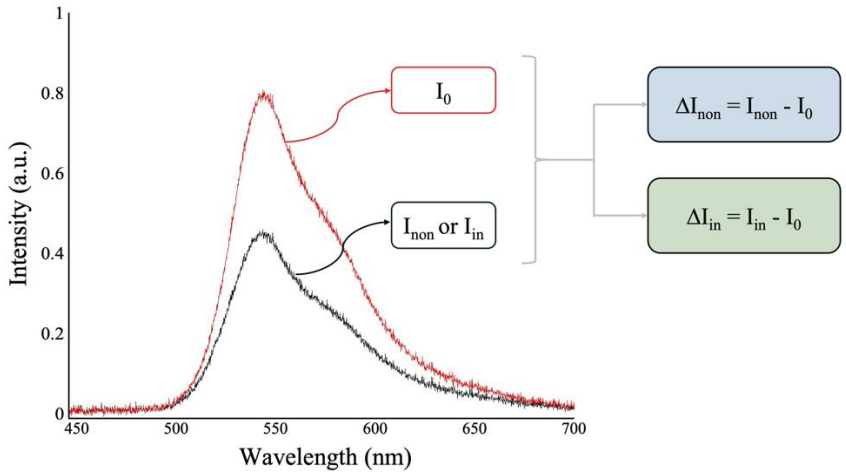

Figure S5. Extrapolation of fluorescence intensity data from emission spectra to be applied in formulas indicated on the right.

The entire experiment was performed three times, using three different samples of inoculated and non-inoculated oranges, thus obtaining data from nine independent measurements. These values (reported as ΔI_{non}

and ΔI_{in}) were used as datasets processed by multivariate analysis. The tables below show the exact format of data provided to the software (descripted in General experimental methods).

Table 1. Dataset provided to the software to perform multivariate analysis for inoculates samples.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Day 1	-0.119	-0.059	-0.083	-0.215	-0.179	-0.191	-0.120	-0.171	-0.196	-0.050	-0.091	-0.104	-0.295	-0.228	-0.281	-0.268	-0.221	-0.263	-0.134	-0.168
	-0.067	-0.061	-0.022	-0.175	-0.212	-0.150	-0.102	-0.141	-0.237	-0.107	-0.074	-0.054	-0.117	-0.234	-0.273	-0.228	-0.221	-0.221	-0.131	-0.217
	-0.029	-0.044	-0.069	-0.198	-0.171	-0.164	-0.117	-0.165	-0.198	-0.052	-0.077	-0.069	-0.217	-0.284	-0.279	-0.227	-0.278	-0.216	-0.157	-0.222
	-0.075	-0.030	-0.068	-0.210	-0.165	-0.166	-0.143	-0.082	-0.141	-0.068	-0.074	-0.120	-0.248	-0.333	-0.214	-0.182	-0.230	-0.267	-0.142	-0.137
	-0.041	-0.017	-0.068	-0.223	-0.191	-0.150	-0.183	-0.136	-0.120	-0.038	-0.072	-0.079	-0.203	-0.200	-0.194	-0.213	-0.179	-0.201	-0.100	-0.146
	-0.084	-0.009	-0.010	-0.182	-0.147	-0.173	-0.198	-0.091	-0.183	-0.101	-0.108	0.005	-0.201	-0.216	-0.237	-0.149	-0.188	-0.181	-0.139	-0.146
	-0.094	-0.094	-0.065	-0.235	-0.099	-0.106	-0.132	-0.128	-0.153	0.033	-0.063	-0.089	-0.055	-0.047	-0.295	-0.149	-0.184	-0.251	-0.203	-0.187
	-0.079	-0.046	-0.032	-0.190	-0.092	-0.114	-0.212	-0.147	-0.165	0.033	-0.123	-0.063	-0.058	-0.074	-0.276	-0.163	-0.156	-0.246	-0.102	-0.181
	-0.116	-0.114	-0.111	-0.144	-0.090	-0.108	-0.134	-0.178	-0.168	0.007	-0.042	-0.085	-0.015	-0.049	-0.240	-0.083	-0.177	-0.294	-0.117	-0.191
Day 2	-0.057	-0.083	-0.074	-0.187	-0.165	-0.144	-0.128	-0.151	-0.189	-0.079	-0.161	-0.091	-0.259	-0.224	-0.231	-0.230	-0.234	-0.199	-0.130	-0.147
	-0.055	-0.053	-0.046	-0.188	-0.144	-0.106	-0.091	-0.124	-0.215	-0.060	-0.125	-0.118	-0.208	-0.217	-0.229	-0.221	-0.137	-0.215	-0.112	-0.185
	0.007	-0.056	-0.045	-0.148	-0.127	-0.120	-0.130	-0.143	-0.171	-0.110	-0.126	-0.016	-0.257	-0.258	-0.235	-0.198	-0.113	-0.206	-0.140	-0.195
	-0.085	-0.028	-0.064	-0.240	-0.156	-0.156	-0.145	-0.084	-0.158	-0.044	-0.117	-0.106	-0.235	-0.356	-0.231	-0.219	-0.251	-0.288	-0.173	-0.161
	-0.047	-0.048	-0.039	-0.275	-0.175	-0.143	-0.197	-0.113	-0.134	-0.033	-0.054	-0.073	-0.198	-0.323	-0.240	-0.249	-0.205	-0.207	-0.132	-0.159
	-0.096	0.015	-0.046	-0.220	-0.147	-0.139	-0.215	-0.096	-0.177	-0.120	-0.093	0.031	-0.229	-0.218	-0.256	-0.180	-0.222	-0.183	-0.191	-0.157
	-0.092	-0.067	-0.068	-0.235	-0.079	-0.092	-0.184	-0.062	-0.140	-0.092	-0.031	-0.050	-0.056	-0.048	-0.277	-0.123	-0.182	-0.175	-0.167	-0.184
	-0.077	-0.059	-0.031	-0.188	-0.085	-0.112	-0.219	-0.090	-0.136	-0.092	-0.095	-0.013	-0.063	-0.066	-0.251	-0.136	-0.151	-0.153	-0.073	-0.191
	-0.086	-0.104	-0.016	-0.199	-0.087	-0.094	-0.260	-0.142	-0.162	-0.118	0.006	-0.058	-0.024	-0.054	-0.217	-0.100	-0.171	-0.234	-0.150	-0.223
Day 3	-0.103	-0.070	-0.058	-0.229	-0.149	-0.174	-0.147	-0.188	-0.200	-0.074	-0.111	-0.060	-0.261	-0.215	-0.248	-0.243	-0.243	-0.150	-0.138	-0.153
	-0.113	-0.068	-0.062	-0.224	-0.200	-0.153	-0.133	-0.173	-0.256	-0.196	-0.097	-0.087	-0.280	-0.238	-0.279	-0.265	-0.261	-0.116	-0.151	-0.231
	-0.059	-0.041	-0.119	-0.238	-0.181	-0.154	-0.166	-0.167	-0.208	-0.118	-0.194	-0.101	-0.258	-0.285	-0.291	-0.245	-0.315	-0.119	-0.173	-0.209
	-0.089	-0.051	-0.091	-0.256	-0.152	-0.157	-0.160	-0.073	-0.140	-0.058	-0.086	-0.086	-0.240	-0.376	-0.198	-0.217	-0.243	-0.269	-0.157	-0.146
	-0.057	-0.019	-0.049	-0.277	-0.179	-0.201	-0.209	-0.126	-0.134	-0.065	0.025	-0.098	-0.199	-0.326	-0.208	-0.245	-0.212	-0.192	-0.129	-0.158
	-0.107	-0.001	0.012	-0.223	-0.154	-0.158	-0.224	-0.083	-0.198	-0.115	-0.112	-0.020	-0.233	-0.226	-0.248	-0.176	-0.227	-0.153	-0.176	-0.157
	-0.087	-0.071	-0.043	-0.216	-0.102	-0.065	-0.196	-0.056	-0.129	-0.149	-0.026	-0.067	-0.085	-0.042	-0.283	-0.127	-0.201	-0.133	-0.175	-0.182
	-0.066	-0.067	-0.029	-0.189	-0.089	-0.076	-0.192	-0.105	-0.136	-0.149	-0.084	-0.069	-0.108	-0.069	-0.255	-0.165	-0.165	-0.138	-0.054	-0.172
	-0.084	-0.107	0.001	-0.185	-0.065	-0.079	-0.240	-0.136	-0.159	-0.174	0.000	-0.006	-0.087	-0.052	-0.218	-0.089	-0.197	-0.247	-0.115	-0.185
Day 4	-0.209	-0.084	-0.076	-0.297	-0.211	-0.198	-0.253	-0.307	-0.289	-0.171	-0.127	-0.106	-0.287	-0.223	-0.302	-0.296	-0.308	-0.218	-0.204	-0.230
	-0.273	-0.113	-0.095	-0.283	-0.184	-0.150	-0.261	-0.320	-0.392	-0.100	-0.097	-0.106	-0.244	-0.217	-0.263	-0.215	-0.232	-0.236	-0.110	-0.252
	-0.170	-0.042	-0.069	-0.265	-0.210	-0.192	-0.227	-0.256	-0.278	-0.174	-0.159	-0.065	-0.297	-0.302	-0.314	-0.294	-0.197	-0.228	-0.220	-0.251
	-0.136	-0.075	-0.088	-0.311	-0.216	-0.203	-0.220	-0.162	-0.262	-0.121	-0.080	-0.146	-0.363	-0.398	-0.284	-0.274	-0.292	-0.191	-0.234	-0.236
	-0.116	-0.085	-0.097	-0.319	-0.247	-0.195	-0.271	-0.215	-0.209	-0.173	-0.176	-0.116	-0.232	-0.354	-0.314	-0.301	-0.253	-0.127	-0.198	-0.210
	-0.181	-0.062	-0.057	-0.265	-0.203	-0.228	-0.278	-0.179	-0.278	-0.163	-0.157	-0.035	-0.262	-0.242	-0.345	-0.229	-0.268	-0.085	-0.274	-0.221
	-0.150	-0.141	-0.126	-0.247	-0.118	-0.132	-0.241	-0.090	-0.176	-0.254	-0.136	-0.177	-0.177	-0.076	-0.318	-0.180	-0.235	-0.120	-0.198	-0.234
	-0.143	-0.127	-0.089	-0.243	-0.138	-0.142	-0.265	-0.231	-0.211	-0.254	-0.189	-0.096	-0.144	-0.090	-0.282	-0.220	-0.210	-0.122	-0.105	-0.229
	-0.118	-0.163	-0.108	-0.260	-0.157	-0.173	-0.243	-0.182	-0.212	-0.279	-0.012	-0.052	-0.100	-0.087	-0.291	-0.126	-0.221	-0.240	-0.150	-0.229

Table 2. Dataset provided to the software to perform multivariate analysis for non-inoculates samples.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Day 1	-0.107	-0.029	-0.085	-0.194	-0.138	-0.151	-0.123	-0.140	-0.173	-0.085	-0.080	0.010	-0.224	-0.253	-0.288	-0.187	-0.169	-0.266	-0.117	-0.197
	-0.130	-0.052	-0.034	-0.160	-0.154	-0.134	-0.088	-0.162	-0.216	-0.062	-0.087	-0.103	-0.147	-0.332	-0.238	-0.204	-0.198	-0.301	-0.145	-0.171
	-0.135	-0.102	-0.057	-0.142	-0.155	-0.141	-0.090	-0.101	-0.175	-0.145	-0.043	-0.033	-0.199	-0.252	-0.289	-0.213	-0.222	-0.243	-0.185	-0.182
	-0.095	-0.045	-0.057	-0.212	-0.200	-0.200	-0.155	-0.096	-0.154	-0.035	-0.054	-0.048	-0.154	-0.180	-0.223	-0.214	-0.159	-0.281	-0.126	-0.149
	-0.063	-0.047	-0.038	-0.155	-0.138	-0.164	-0.185	-0.067	-0.141	-0.004	-0.069	-0.070	-0.139	-0.289	-0.242	-0.243	-0.196	-0.222	-0.164	-0.184
	-0.104	-0.064	-0.067	-0.211	-0.205	-0.174	-0.219	-0.099	-0.192	-0.037	-0.127	-0.075	-0.172	-0.282	-0.303	-0.159	-0.228	-0.212	-0.162	-0.163
	-0.081	-0.072	-0.045	-0.282	-0.188	-0.149	-0.165	-0.144	-0.210	-0.274	-0.063	-0.101	-0.093	-0.065	-0.308	-0.145	-0.138	-0.223	-0.165	-0.204
	-0.099	-0.053	-0.085	-0.213	-0.150	-0.151	-0.176	-0.129	-0.187	-0.214	-0.061	-0.147	-0.116	-0.044	-0.324	-0.157	-0.193	-0.207	-0.179	-0.182
	-0.053	-0.083	-0.066	-0.213	-0.181	-0.150	-0.131	-0.126	-0.192	-0.183	-0.106	-0.074	-0.072	-0.040	-0.316	-0.132	-0.201	-0.262	-0.183	-0.171
Day 2	-0.106	-0.123	-0.074	-0.199	-0.137	-0.151	-0.140	-0.128	-0.173	-0.144	-0.054	-0.005	-0.208	-0.251	-0.237	-0.181	-0.176	-0.154	-0.113	-0.180
	-0.061	-0.101	-0.024	-0.139	-0.132	-0.121	-0.103	-0.170	-0.232	-0.181	-0.097	-0.109	-0.157	-0.316	-0.210	-0.201	-0.224	-0.248	-0.120	-0.162
	-0.138	-0.031	-0.045	-0.160	-0.150	-0.126	-0.108	-0.078	-0.155	-0.109	-0.036	-0.058	-0.228	-0.240	-0.237	-0.207	-0.273	-0.162	-0.158	-0.167
	-0.073	-0.044	-0.036	-0.237	-0.203	-0.195	-0.186	-0.108	-0.163	-0.064	-0.152	-0.056	-0.179	-0.322	-0.220	-0.239	-0.227	-0.280	-0.174	-0.154
	-0.070	-0.058	-0.019	-0.210	-0.175	-0.175	-0.224	-0.083	-0.157	-0.039	-0.084	-0.107	-0.158	-0.291	-0.257	-0.267	-0.202	-0.238	-0.223	-0.181
	-0.106	-0.125	-0.045	-0.264	-0.250	-0.176	-0.227	-0.109	-0.212	-0.090	-0.117	-0.078	-0.204	-0.294	-0.296	-0.178	-0.271	-0.221	-0.195	-0.174
	-0.068	-0.056	-0.038	-0.257	-0.158	-0.133	-0.165	-0.134	-0.202	-0.272	-0.100	-0.066	-0.116	-0.061	-0.290	-0.174	-0.195	-0.125	-0.173	-0.212
	-0.087	-0.041	-0.056	-0.217	-0.112	-0.124	-0.165	-0.134	-0.169	-0.241	-0.020	-0.099	-0.145	-0.026	-0.291	-0.155	-0.211	-0.094	-0.159	-0.184
	-0.047	-0.072	-0.052	-0.196	-0.092	-0.093	-0.098	-0.097	-0.163	-0.041	-0.086	-0.088	-0.175	-0.038	-0.282	-0.134	-0.210	-0.147	-0.158	-0.160
Day 3	-0.070	-0.105	-0.109	-0.208	-0.107	-0.115	-0.129	-0.100	-0.195	-0.120	-0.100	-0.019	-0.226	-0.243	-0.255	-0.168	-0.182	-0.054	-0.077	-0.149
	-0.050	-0.075	-0.049	-0.137	-0.120	-0.110	-0.098	-0.153	-0.203	-0.134	-0.075	-0.117	-0.164	-0.318	-0.216	-0.219	-0.240	-0.211	-0.118	-0.179
	-0.104	-0.081	-0.053	-0.118	-0.136	-0.118	-0.108	-0.057	-0.152	-0.128	-0.023	-0.161	-0.222	-0.259	-0.265	-0.201	-0.260	-0.101	-0.138	-0.160
	-0.076	-0.078	-0.068	-0.242	-0.193	-0.200	-0.202	-0.102	-0.177	-0.111	-0.153	-0.068	-0.259	-0.325	-0.174	-0.244	-0.251	-0.276	-0.176	-0.156
	-0.094	-0.089	-0.056	-0.171	-0.176	-0.163	-0.252	-0.091	-0.167	-0.041	-0.163	-0.131	-0.214	-0.294	-0.240	-0.273	-0.227	-0.146	-0.230	-0.184
	-0.114	-0.100	-0.077	-0.261	-0.275	-0.185	-0.240	-0.105	-0.261	-0.083	-0.128	-0.101	-0.223	-0.297	-0.273	-0.175	-0.289	-0.169	-0.194	-0.175
	-0.035	-0.071	0.000	-0.220	-0.114	-0.055	-0.167	-0.089	-0.147	-0.124	-0.076	-0.043	-0.108	-0.057	-0.248	-0.136	-0.124	-0.082	-0.131	-0.181
	-0.069	-0.031	-0.008	-0.140	-0.068	-0.054	-0.139	-0.083	-0.133	-0.139	-0.047	-0.109	-0.147	-0.031	-0.257	-0.145	-0.191	-0.054	-0.128	-0.171
	0.015	-0.040	-0.021	-0.159	-0.076	-0.052	-0.100	-0.053	-0.132	-0.170	-0.115	-0.054	-0.174	-0.036	-0.257	-0.115	-0.174	-0.090	-0.128	-0.140
Day 4	-0.140	-0.095	-0.076	-0.243	-0.112	-0.101	-0.141	-0.112	-0.156	-0.130	-0.084	-0.072	-0.222	0.029	-0.238	-0.169	-0.186	-0.051	-0.122	-0.190
	-0.068	-0.075	-0.026	-0.157	-0.132	-0.124	-0.106	-0.179	-0.225	-0.118	-0.073	-0.123	-0.163	-0.232	-0.192	-0.208	-0.245	-0.194	-0.121	-0.158
	-0.123	-0.076	-0.077	-0.141	-0.136	-0.106	-0.114	-0.088	-0.152	-0.109	-0.014	-0.060	-0.281	-0.225	-0.209	-0.200	-0.249	-0.072	-0.135	-0.151
	-0.075	-0.095	-0.095	-0.232	-0.187	-0.174	-0.203	-0.091	-0.188	-0.088	-0.116	-0.120	-0.221	-0.338	-0.177	-0.243	-0.241	-0.125	-0.183	-0.167
	-0.106	-0.101	-0.050	-0.190	-0.150	-0.151	-0.243	-0.080	-0.172	-0.088	-0.123	-0.106	-0.215	-0.309	-0.212	-0.271	-0.219	0.070	-0.219	-0.195
	-0.124	-0.092	-0.074	-0.245	-0.297	-0.163	-0.248	-0.071	-0.212	-0.127	-0.130	-0.078	-0.226	-0.297	-0.226	-0.189	-0.287	0.081	-0.198	-0.173
	-0.087	-0.055	-0.072	-0.200	-0.121	-0.077	-0.134	-0.038	-0.091	-0.252	-0.112	-0.105	-0.164	-0.081	-0.119	-0.164	-0.127	0.085	-0.142	-0.164
	-0.069	-0.059	-0.061	-0.148	-0.068	-0.047	-0.153	0.017	-0.050	-0.267	-0.024	-0.093	-0.192	-0.034	-0.140	-0.121	-0.162	0.143	-0.168	-0.164
	-0.002	-0.053	-0.083	-0.177	-0.070	-0.081	-0.117	-0.037	-0.099	-0.299	-0.123	-0.110	-0.196	-0.050	-0.155	-0.105	-0.167	0.077	-0.144	-0.142

Additionally, for each measurement, the nine values of fluorescence intensity were mediated to obtain a single representative value for the collected intensity. Mediated fluorescence intensity data and the corresponding emission wavelength are reported for each probe in tables 3a and 3b.

Table 3. a) Emission wavelength, fluorescence intensity before the exposure to any analyte (I_0) and after 1, 2, 3 and 4 days of exposure to inoculated oranges, each one as a mean of nine independent measurements. b) Emission wavelength, fluorescence intensity before the exposure to any analyte (I_0) and after 1, 2, 3 and 4 days of exposure to non-inoculated (healthy) oranges, each one as a mean of nine independent measurements.

a)

Probe	λmax	I_0	I_{in1}	I_{in2}	I_{in3}	I_{in4}
1	582	0.477	0.405	0.442	0.385	0.260
2	605	0.491	0.437	0.427	0.432	0.412
3	605	0.448	0.390	0.393	0.368	0.368
4	555	0.486	0.290	0.312	0.256	0.205
5	556	0.526	0.339	0.381	0.350	0.325
6	562	0.490	0.321	0.366	0.330	0.310
7	582	0.437	0.324	0.320	0.288	0.190
8	582	0.495	0.336	0.356	0.391	0.200
9	605	0.510	0.299	0.318	0.288	0.190
10	409	0.521	0.451	0.438	0.391	0.373
11	600	0.500	0.419	0.362	0.366	0.372
12	606	0.522	0.446	0.447	0.439	0.429
13	517	0.549	0.339	0.308	0.283	0.273
14	520	0.422	0.174	0.190	0.176	0.175
15	555	0.494	0.216	0.262	0.221	0.201
16	562	0.521	0.280	0.305	0.270	0.253
17	561	0.533	0.293	0.280	0.260	0.196
18	582	0.442	0.209	0.311	0.314	0.290
19	551	0.496	0.356	0.369	0.342	0.318
20	556	0.507	0.304	0.331	0.309	0.263

b)

Probe	λmax	I_0	I_{non1}	I_{non2}	I_{non3}	I_{non4}
1	582	0.540	0.416	0.438	0.465	0.429
2	605	0.514	0.453	0.429	0.427	0.432
3	605	0.493	0.434	0.445	0.423	0.433
4	555	0.481	0.316	0.315	0.326	0.300
5	556	0.548	0.399	0.408	0.427	0.421
6	562	0.506	0.364	0.373	0.392	0.495
7	582	0.459	0.358	0.341	0.347	0.339
8	582	0.504	0.370	0.379	0.401	0.378
9	605	0.527	0.339	0.341	0.344	0.349
10	409	0.530	0.433	0.385	0.402	0.411
11	600	0.478	0.407	0.415	0.412	0.420
12	606	0.519	0.477	0.462	0.420	0.434
13	517	0.538	0.348	0.340	0.334	0.316
14	520	0.439	0.160	0.171	0.166	0.297
15	555	0.477	0.206	0.249	0.232	0.264
16	562	0.536	0.335	0.340	0.340	0.344
17	561	0.550	0.354	0.326	0.323	0.324
18	582	0.483	0.213	0.296	0.361	0.378
19	551	0.519	0.370	0.389	0.408	0.393
20	556	0.506	0.323	0.336	0.344	0.340

VIP histogram

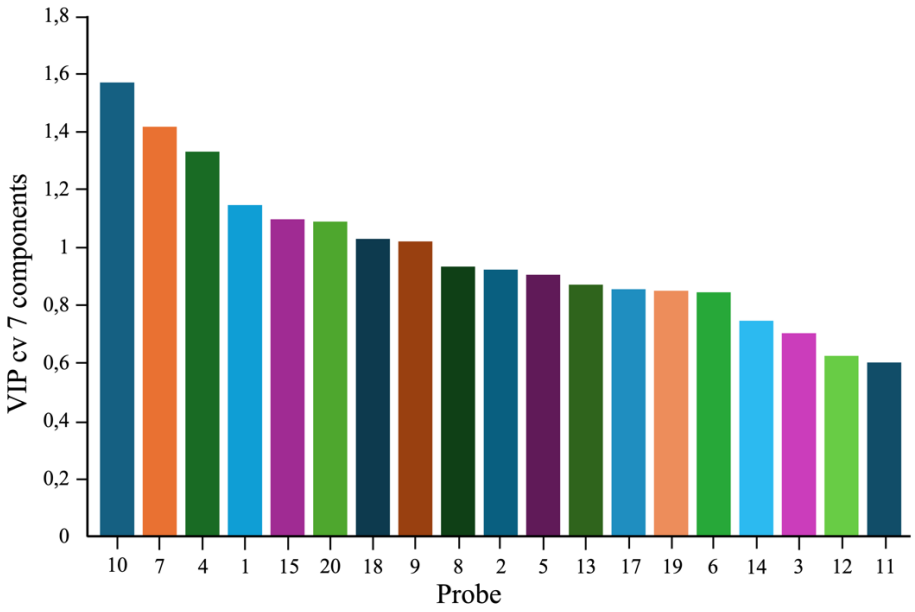

Figure S6. Ordered 7 components VIP variables cross validated. VIP is normalized so that its average square value is 1. Each coloured bar of the histogram indicates a different probe, as labelled.

Methods to assess orange quality

The table below outlines the specific minimum requirements for assessing orange quality, including the evaluation of juice content, sugar content, and the sugar/acid ratio as established by relevant regulations. It highlights how these traditional methods are limited by their destructiveness and the need to verify fruit compliance with specific minimum requirements. The developed optical array sensor, on the other hand, is a non-destructive method that assesses fruit quality solely based on emitted VOCs. This non-destructive approach enables real-time monitoring without the need for extensive compliance checks, making it particularly advantageous in practical applications.

Table S4. Comparison of traditional methods for assessing orange quality (juice content, sugar content, and sugar/acid ratio) highlighting their minimum requirements for assessing fruit quality and the advantages of the optical array sensor.

Method	Minimum Requirement for assessing fruit quality	Implication
Juice Content	30% of juice for blood orange fruit[a]	Destructive and time-consuming analyses
Sugar Content (performed by Brix Analysis)	10 g/100 ml for 'Tarocco' orange fruit[b]	
Sugar/Acid Ratio	6.5:1 for blood oranges[a] ≥ 8:1 for 'Tarocco' oranges[b]	
This study	1 orange	Non-destructive, fast, assessing the fruit quality solely on the bases of emitted VOCs

[a] values in agreement with the Commission Delegated Regulation EU 2019/428 of 12 July 2018;

[b] values in agreement with the Production Regulations of the IGP 'Red Orange of Sicily'.

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