Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Ultra-low-temperature reversible thermochromism and contactless bacterial sensing by chalcone-functionalized polydiacetylene

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Contents

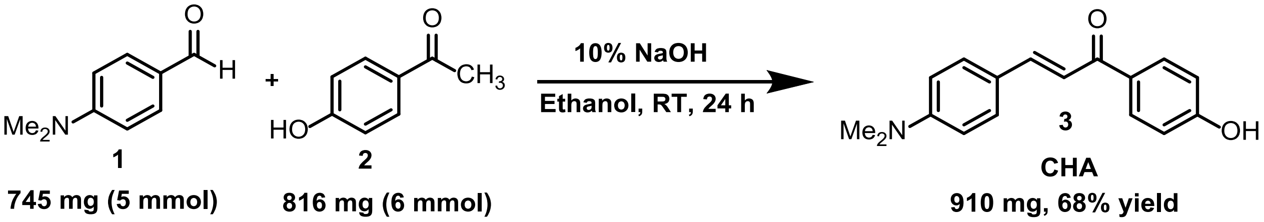
1. General methods. Flash chromatography was performed using silica gel (230−400 mesh) as the stationary phase. NMR spectra were recorded on Bruker DPX 400 instruments. The Chemical shifts, given in ppm, are relative to the residual solvent peaks. Ultraviolet–visible (UV–vis) spectra were recorded on an Evolution 220 UV–visible spectrometer (Thermo Scientific, Madison, WI). Fluorescence spectroscopy measurements were carried out using a Fluorolog spectrophotometer (HORIBA Scientific, Irvine, CA). Scanning electron microscopy (SEM) images were recorded on a JEOL JSM-7400F scanning electron microscope (JEOL Ltd, Tokyo, Japan) operated and analyzed using the instrument software. Fourier-transform infrared spectroscopy (FTIR) measurements were performed on a Thermo Scientific Nicolet 6700 spectrometer in ATR mode. Raman Measurements were performed on a LabRam HR-high resolution analytical Raman (Horiba JobinYvon, France). High resolution mass spectrometer

(HRMS) measurements were performed on a Thermo Scientific high resolution mass spectrometer in ESI mode.

2. Synthesis.

2.1 General Procedure for the synthesis of chalcone derivative (CHA).

This reaction was carried out according to a literature method as described below.[1]

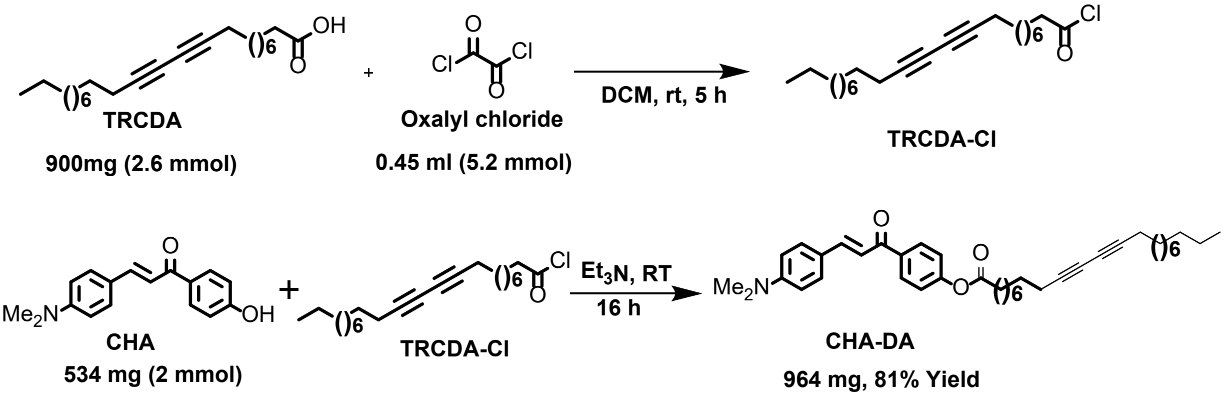


A solution of ethanol (10 ml) and 10% sodium hydroxide (5 ml) were taken in a round bottomed flask then 4-(dimethylamino)benzaldehyde **1** (745 mg, 5 mmol), 1-(4-hydroxyphenyl)ethan-1-one (816 mg, 6 mmol) was added in to the solution then the reaction mixture was stirred at rt for 24 hours. After the reaction, aq. HCl solution was added to quench the reaction and the aqueous layer was extracted with EA (50 mL × 3). The combined organic layers were washed with brine (50 mL ×1), dried over anhydrous Na_2SO_4 and concentrated. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel (Petroleum Ether/Ethyl acetate) to get the desired product **CHA** in 910 mg (68% yield).

Reference:

1. B. Korkmaz, E. A. Özeroln, Y. Gürsel, B. F. Senkal, M. Okutan, *J. Mol. Liq.* 2018**, 266,** 132-138.

2.2 General Procedure for the synthesis of chalcone attached polydiacetylene (CHA-DA)



The carboxylic acid derivative (TRCDA, 2.6 mmol, 900 mg) was dissolved in 20 mL dichloromethane (DCM) in a round-bottomed flask equipped with a magnetic stirrer. 0.45 mL of oxalyl chloride (5.2 mmol) was added to the solution and stirred for 30 min at room temperature. *N, N*-dimethylformamide (DMF) was added to the above solution in catalytic amount (2-3 drops) and stirred for 4.5 hours. The solvents and excess of oxalyl chloride were removed by rotatory evaporator under vacuum to give the corresponding acyl chloride (TRCDA-Cl). The TRCDA-Cl residue is dissolved in 10 mL DCM and used directly to the next step. In a separate flask, (E)-3-(4-(dimethylamino)phenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one (CHA, 2 mmol, 534 mg) was dissolved in DCM (10 mL) followed by the addition of triethyl amine (3 mmol, 0.417 mL). Then the acyl chloride solution (from the previous step) was added dropwise to the reaction mixture and once the addition is completed the resultant solution was stirred at room temperature for another 16 hours. Upon completion of the reaction, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel (Petroleum Ether/Ethyl acetate) to get the desired product CHA-DA in 964 mg (81% yield).

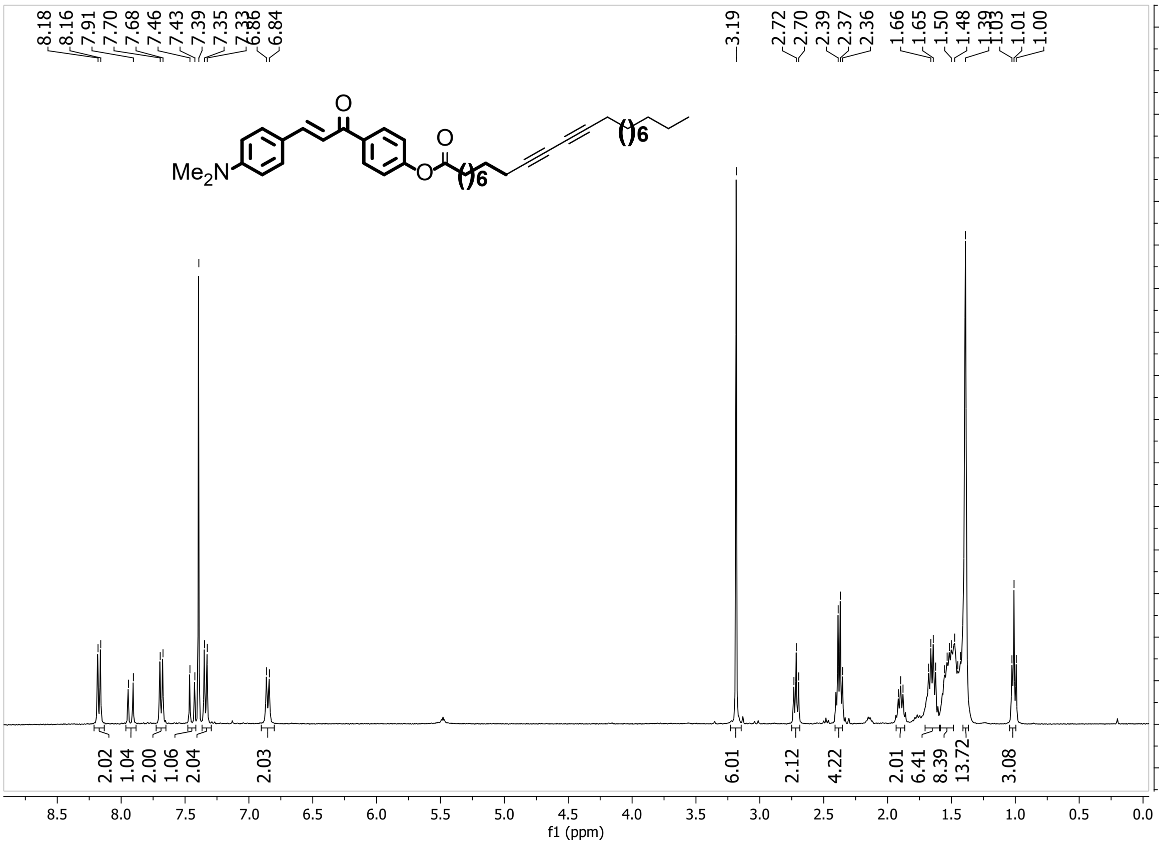
2. 3 Spectral data for the compounds CHA-DA

Following the general procedure, the product **CHA-DA** was obtained as a pale yellow solid and the structure of the compound was confirmed by ^{1}H, ^{13}C NMR and **HRMS** data.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 8.7 Hz, 2H), 7.93 (d, *J* = 15.5 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.45 (d, *J* = 15.5 Hz, 1H), 7.34 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 3.19 (s, 6H), 2.72 (t, *J* = 7.5 Hz, 2H), 2.38 (d, *J* = 6.8 Hz, 4H), 1.94 – 1.87 (m, 2H), 1.65 (dd, *J* = 14.7, 7.2 Hz, 6H), 1.53 (dd, *J* = 14.0, 7.0 Hz, 8H), 1.39 (s, 13H), 1.02 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 189.3, 171.8, 145.5, 141.9, 134.6, 134.5, 130.5, 129.9, 119.0, 117.2, 112.6, 112.5, 65.4, 407, 38.0, 32.0, 29.7, 29.6, 29.4, 29.3, 29.2, 29.0, 28.9, 28.5, 28.4, 25.6, 22.8, 19.3, 14.2.

HRMS (ESI):calc. for $[(C_{40}H_{53}NO_3)H]$ (M+H) 596.4104, measured 596.4088.



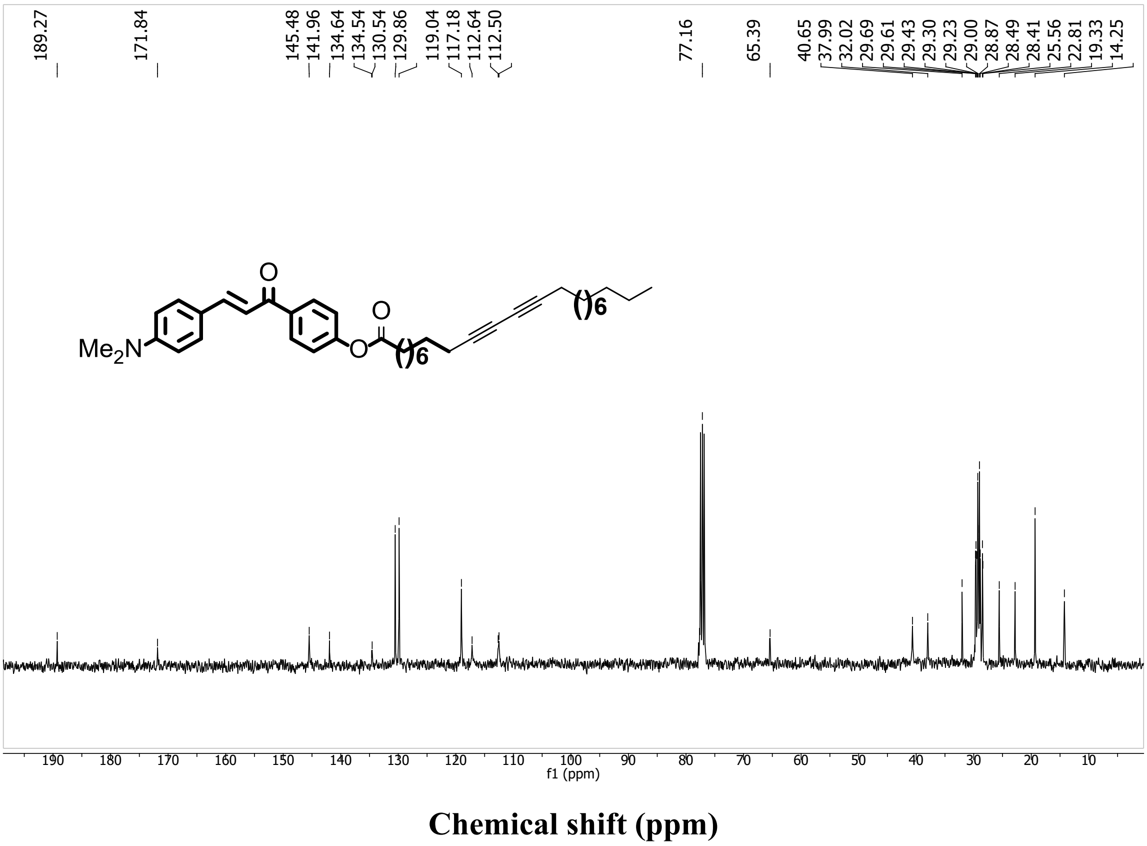


Fig.S1. ^{1}**H** and ^{13}**C NMR** Spectra for CHA-DA

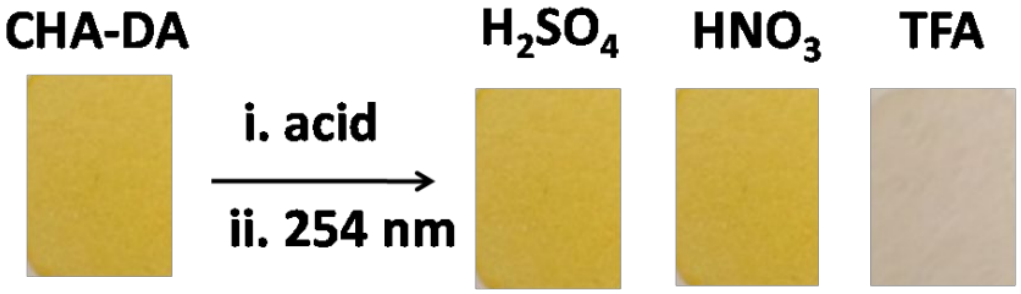


Fig.S2. Proton-induced polymerization for CHA-DA with the vapors of other acids

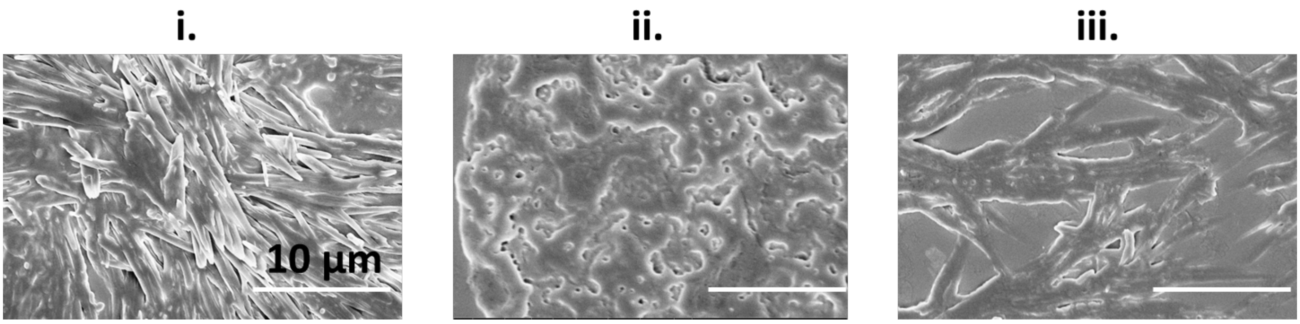


Fig.S3. i) SEM Images of Monomer (CHA-DA). ii) Monomer after exposure to HCl (CHA-DA-HCl) (iii) after polymerization (CHA-PDA-HCl).

CHA-PDA-HCl film before Cooling-Warming cycles.

CHA-PDA-HCl film after 20 Cooling-Warming cycles between 20 to -50 °C.

Fig. S4. Stability of HCl-treated Chalcone-PDA film after multiple cooling-warming cycles.

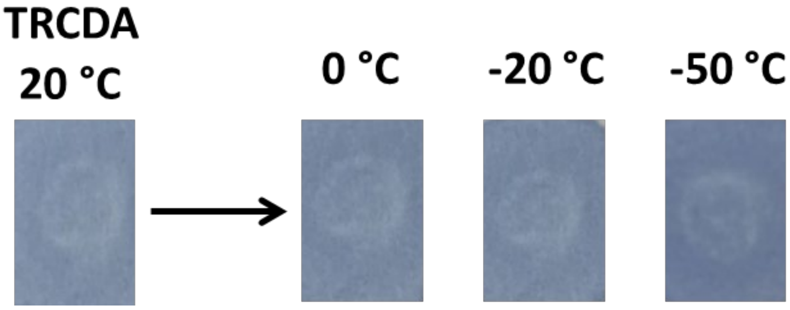


Fig. S5. Low-temperature thermochromism of simple PDA derived from 10, 12-tricosadiynoic acid.

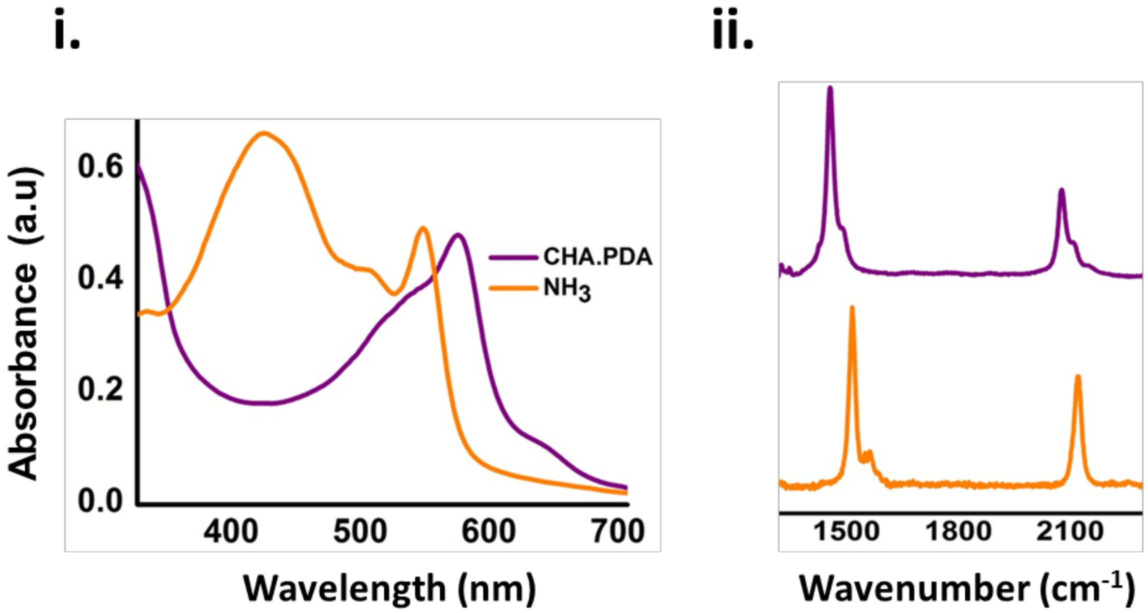


Fig. S6. i) absorption spectra of CHA-PDA before (purple line) and after (orange line) exposure to NH_3. ii) Raman spectra of CHA-PDA before (purple line) and after (orange line) exposure to NH_3.

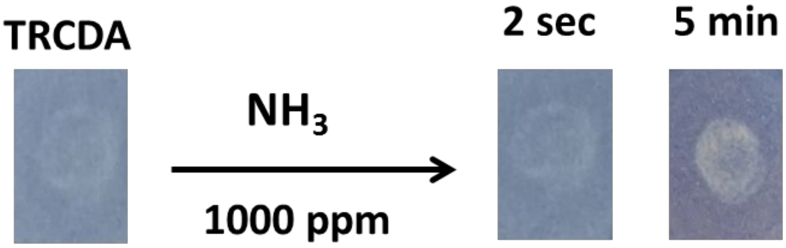


Fig. S7. Color change of simple PDA film derived from 10, 12-tricosadiynoic acid after exposure with ammonia.

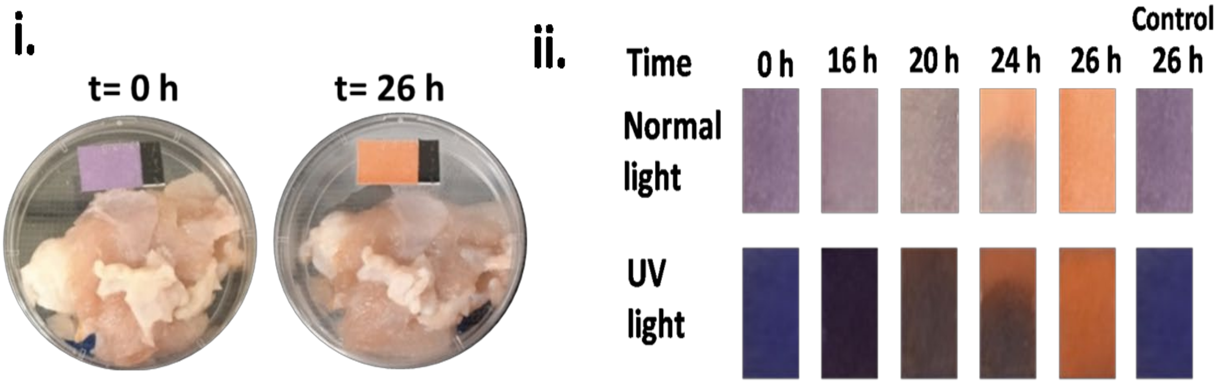


Fig. S8 i. The visible color change of the CHA-PDA film after exposure to chicken for 26 h. **ii.** The time-dependent color and fluorescence changes of the CHA-PDA film after exposure to chicken.

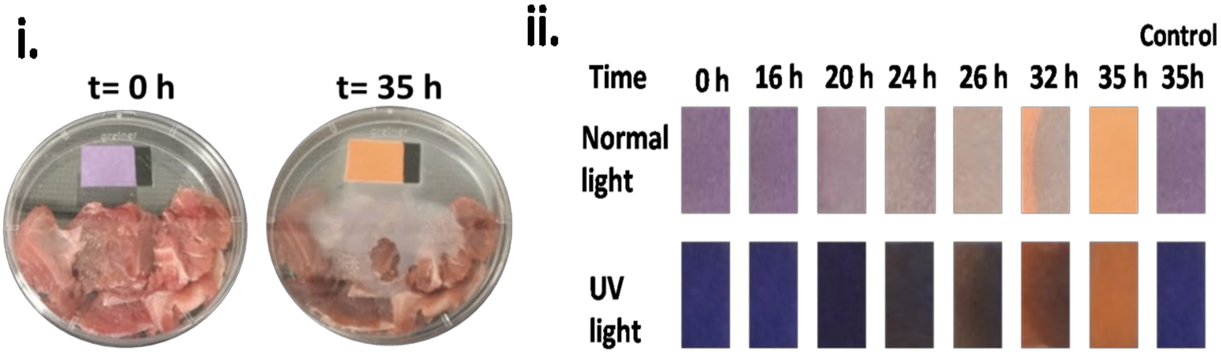


Fig. S9. i. The visible color change of the CHA-PDA film after exposure to beef for 35 h. **ii.** The time-dependent color and fluorescence changes of the CHA-PDA film after exposure to beef.

S. No	**Reference**	**Types of Sensor**	**Sensitivity with amines [Detection Limit]**	**Response time**
1.	*Macromolecular Research,* 2016, **24,** 380-384. **(Reference 11)**	Color/ fluorometric sensor based on PDA/PVA Hybrid Films.	4.3 ppm.	Amine: 2 hours Beef : 35 hours
2.	*Sensors & Actuators: B. Chemical,* 2019, **297,** 126734. **(Reference 53)**	Color/ fluorometric sensor based on Silica-reinforced PDA nanofiber	7 ppm.	Amine: 10 min Fish: 4 days.
3.	*J. Mater. Chem. C,* 2019, **7,** 1919. **(Reference 10)**	Color/ fluorometric sensor based on PDA vesicles stabilized with cellulose Nanocrystals in chitosan matrix.	Not mentioned	Amine: 10 min Beef: 24 hours.
4.	*Anal. Chem.* 2020, **92**, 1611−1617. **(Reference 52)**	Color/ fluorometric sensor based on paper coated PDA/DMPC Vesicles.	70 ppm	Amine: 10 min Fish: 40 hours.
5.	*Chem. Eur. J.* 2017*,* **23,** 3562 – 3566. **(Reference 46)**	Colorimetric sensor based on Meldrum's activated furan (MAF) Coated nylon filters.	0.5 ppm	Amine: 5 min Fish: 48 hours.
6.	**Present Work**	Paper based color/ fluorometric sensor made up of chalcone attached PDA system.	3 ppb	Amine: 1-2 sec Fish: 22 hours.

Table. S1. Comparison of various sensors used for amines and meat spoilage detection.