Optical Discrimination of Terpenes in Citrus Peels with a Host:Guest Sensing Array

Junyi Chen,[a] Jose L. Moreno Jr.,[a] Wen Zhang,[a] Lucas J. Gibson-Elias,[a] Ria Lian,[a] Saba Najafi,[a] Haofei Zhang,[a] Wenwan Zhong,[b]* and Richard J. Hooley[a]*

[a]*Department of Chemistry; University of California-Riverside, Riverside, CA 92521, U.S.A.* [b]*Key Laboratory of Precision and Intelligent Chemistry; Department of Chemistry, School of Chemistry and Materials Science; University of Science and Technology of China, Hefei, Anhui, 230026, P.R. China*

wenwanz@ustc.edu.cn; richard.hooley@ucr.edu

Electronic Supplementary Information

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1. General Information

Cavitands **TCC**,[1] **CHI**,[2] and fluorophores **DSMI**,[3] **DTMI**[4] and **SMITE**[5] were synthesized and characterized according to literature procedures. The dye stock solutions were prepared in DMSO (Fisher Chemical, Catalog Number: D128-1) at a concentration of 20 mM, and later diluted with water for use in experiments. (R)-(+)-Limonene, 97% stab. (Alfa Aesar L04733), Linalool, 95% (Combi-Blocks QF-3630), β-Caryophyllene, ≥ 80% (Sigma-Aldrich W225207), Sabinene, ≥ 98% (Cayman Chemical 25777), (+)-δ-Cadinene, ≥ 95% (Cayman Chemical 34444), (S)-(-)-α-Terpineol, ≥ 98% (Sigma-Aldrich 8210780005), (1S)-(-)-β-Pinene, 99% (Alfa Aesar A17818), α-Pinene, 98% (Aldrich Chemistry 147524) were utilized in the titration experiments, taking into account their respective purities. The pyrogen-, nuclease- and bacteria-free ultrapure (Type 1) water produced by Direct-Q 3 UV water purification system with Biopak polisher (Catalog Number. CDUFBI001), was used in all the experiments.

Citrus sample preparation. Citrus fruits used in this work were sourced from the University of California, Riverside campus. The fruit peels were collected and cut into small pieces. Extraction was carried out using CH_2Cl_2 (HPLC Grade, Fisher Chemical D143-1) solvent, following a peel weight (g) to CH_2Cl_2 volume (mL) ratio of 1:2. The mixture underwent sonication for approximately 2 hours, and after an incubation period of one day, the peels were filtered out. After washed by saturated NaCl (Fisher BioReagents BP358-1) solution, CH_2Cl_2 phase was separated from the water phase, and further dried by anhydrous Na_2SO_4 (Fisher Chemical S421-500). Following this, the peels were washed with saturated NaCl (Fisher BioReagents BP358-1) solution, and the CH_2Cl_2 phase was separated from the aqueous phase. It was then dried further using anhydrous Na_2SO_4 (Fisher Chemical S421-500). The extracted liquid was subsequently filtered through a 0.45μm membrane (Grand Stable Analysis Technics 2.CF2201.0001), and concentration was achieved *via* rotary evaporation at room temperature or 30 ℃, followed by a brief period of high vacuum for 5 − 10 minutes. The extraction product comprised both liquid and solid phases, which were then weighed and dissolved in 1,2-Dimethoxyethane (DME, Oakwood Chemical 098861) to create stock solutions of japonica Nagami Kumquat: 232.9 mg/mL, 'Blanco D' Oro': 381.25 mg/mL, 'Bouquet de Fleurs': 500.6 mg/mL, and Limon "variegated": 288.3 mg/mL. Sample concentration was calculated as extraction net weight divided by the total volume.

For the assessment of reproducibility and ripeness, three fruits of 'Blanco D' Oro' labeled as Oct-A, Oct-B, and Oct-C were harvested on October 27, 2023, while the other three fruits labeled as Dec-D, Dec-E, and Dec-F were harvested on December 11, 2023. All six fruits were obtained from the same tree. The

resulting sample solutions had the following concentrations, Oct-A: 239.6885 mg/mL, Oct-B: 208.835 mg/mL, Oct-C: 206.2804 mg/mL, Dec-D: 285.45 mg/mL, Dec-E: 336.56 mg/mL, Dec-F: 364.89 mg/mL.

GC-MS analysis. The stock samples in DME were diluted to 0.2 mg/mL in acetonitrile (Fisher Chemical A955-4). A gas chromatograph electron impact ionization mass spectrometer (GC-MS, Agilent Inc., 7890 GC and 5975 MSD) was used to measure diluted citrus samples. The electron impact ionization source was at 70 eV. 2 μL of each sample was programmed to be injected to a separation column (Agilent J&W DB-5MS, 30 m × 0.25 mm × 0.25 μm) with the splitless mode. The temperature of GC was set at 40 °C for 1 min, ramped up to 200 °C with a rate of 4 °C/min, held at 200 °C for 2 min, ramped to 300 °C with a rate of 30 °C/min and held at 300 °C for 2 min. The solvent delay time was set to 10 min. Compound identification was performed using the NIST 2008 mass spectral database. The corrected area was obtained from the area percent report by setting the integration parameters: initial area reject = 0, initial peak width = 0.060, shoulder detection = OFF, initial threshold = 13.0. The percentage area of total was documented in Table *S*-2. The relative areas of terpenoids *vs* limonene, expressed as a percentage, were utilized in Tables *S*-3 and *S*-4 to calculate standard deviations.

NMR measurements. Deuterated NMR solvents were obtained from Cambridge Isotope Laboratories (Andover, MA), and used without further purification. All other materials were purchased from Sigma Aldrich (St. Louis, MO) or Fisher Scientific (Fairlawn, NJ), and were used as received. NMR spectra were recorded on a Bruker Avance Neo 400 MHz NMR spectrometer. All NMR spectra were processed using MestReNova by Mestrelab. NMR experiments were done by adding 2-3 equivalents of pure terpenoid to a solution of 1 – 2.2 mM host dissolved in 500 μL of D_2O. The mixture was then sonicated for 15 minutes and let rest for 3 minutes prior to acquisition.

Fluorescence sensing measurements. The dye, host, and terpenoid/citrus sample were usually prepared at a minimum of 5× their final concentration, then sequentially added into the Tris buffer at neutral pH, accounting for dilution effects. The mixture was incubated for approximately 1 hour at room temperature, then added in the 96-well plate (Product Number 82.1581.120) with a volume = 100 μL. The fluorescence signal (F) was recorded with a BioTek Synergy H1 Hybrid Multi-Mode Microplate Reader at Fluorescence Endpoint read mode with the Ex/Em wavelengths at 460/600, 480/600 or 560/600 nm (**DSMI**), 510/600, 540/600 or 560/600 nm (**DTMI**), and 390/540 or 430/540 nm (**SMITE**), with Gain value = 100 by default. Note that all the concentrations mentioned below represent the final concentrations.

(1) Terpenoid titration. Fluorescence emission (F) curves were recorded under specific conditions. Each test solution was formulated with 0.5 μM of a fluorescent dye and 4 μM of a **TCC** or **CHI** cavitand. (R)-(+)-Limonene was tested across a concentration gradient of 0 – 5 mM (equivalent to 681.2 μg/mL) containing 0 – 0.4% DME. Other terpenoids (linalool, β-caryophyllene, sabinene, (+)-δ-cadinene, (S)-(-)-α-terpineol, (1S)-(-)-β-pinene, and α-pinene) were similarly evaluated over a concentration range of 0 – 200 μg/mL with 0 – 0.1% DME content. The final solutions were made in 20 mM Tris-HCl buffer at neutral pH. Initial preparations of the dye and cavitand solutions were at 10 times their final concentrations. The limonene stock solution was prepared at 50 mM with 4% DME, while the stock solutions of other terpenoids were prepared at 1 mg/mL with 0.5% DME. The dye, cavitand, and terpenoid were sequentially added to achieve their respective final concentrations. The F/F_0 values were calculated using F divided by the response of sensor in the absence of limonene but with the corresponding concentration of DME — F_0 which serves as the blank reference.

(2) Citrus sample titration. The fluorescence emission plots (F) were obtained by preparing solutions containing 0.5 μM dye, with 4 μM **TCC/CHI** cavitand, and a range of citrus sample concentrations spanning 0 – 0.2 mg/mL containing 0 – 0.1% DME. The final solutions were made in 20 mM Tris-HCl buffer at neutral pH. The dye and cavitand solutions were initially prepared at 10× final concentration, citrus sample solution was prepared at a concentration of 1 mg/mL containing 0.5% DME. These solutions were sequentially added to the buffer to achieve their respective final concentrations. The F/F_0 values were calculated using F divided by the response of sensor in the absence of citrus sample but with the corresponding concentration of DME — F_0 which serves as the blank reference.

(3) Fluorescence sensing array. The fluorescence assay was carried out by making the solution containing 0.5 μM fluorescent dye: **DSMI/DTMI/SMITE**, 4 μM cavitand: **TCC/CHI**, with 0.2 mg/mL citrus sample containing 0.1% DME in 20 mM Tris-HCl buffer at neutral pH. The dye, host solutions were prepared at 10× final concentration, citrus sample was prepared at 5× final concentration, and sequentially added into the buffer. F/F_0 values were calculated using F divided by the response of **host•dye** in the absence of citrus sample but with 0.1% DME (F_0).

(4) Data Analysis. The fluorescence emission and F/F_0 bar plots, as well as titration curves were generated with Origin 2021 software. All samples were measured with 3 or 5 repeats, and the average values and standard deviations were reported. 2D Principal Component Analysis (PCA) of scaled F/F_0 data along with the construction of confidence ellipses were conducted with RStudio (Version 1.2.5019), an integrated development environment (IDE) for R (version 3.6.1). Additionally, the 3D PCA plot was

generated based on the scaled raw fluorescence data obtained from the sensing array in response to the citrus sample and blank control. This was executed in Python 3.9 (64-bit) using PCA(n_components=3) and visualized through ax.scatter3D. Feature selection and classification were performed with Python 3.9 (64-bit), using StandardScaler for data standardization, Recursive Feature Elimination with Cross-Validation (RFECV) to select the optimal subset of features, Support Vector Machine (SVM) (kernel='linear') as the supervised classification estimator, RFECV(estimator=svm.SVC(kernel='linear'), step=1, cv=StratifiedKFold(n_splits=4, shuffle=True), scoring='accuracy', min_features_to_select=1). Performance metrics for the classification evaluation were calculated by using RepeatedStratifiedKFold (n_splits=4, n_repeats=3) for cross validation. The correlation heatmap of selected features was computed using pandas.DataFrame.corr(method='pearson'). PCA was applied for orthogonal linear transformation and dimensionality reduction, and SVM decision region boundary of PCA plot was generated using plot_decision_regions.

UV-Vis Absorbance. Absorbance spectra were recorded using a 1 mL solution containing 5 μM dye/40 μM cavitand, with and without 2 mg/mL citrus sample (1% DME). Control measurements utilized a 0.2 mg/mL citrus sample (0.1% DME) to ascertain its inherent absorbance peak. All solutions were prepared in a 20 mM Tris-HCl buffer at neutral pH. Baseline correction was performed by subtracting the background signal from the buffer. The UV-Vis spectra were acquired using an Agilent Cary 60 UV-Vis spectrophotometer equipped with disposable semi-micro cuvettes (Fisherbrand 14955128).

Fluorescence Emission Spectra. Emission spectra were recorded using a 400 μL solution containing 5 μM dye with or without 40 μM cavitand in 20 mM Tris-HCl buffer at neutral pH. The measurements were conducted using a Horiba PTI QM-400 fluorescence spectrophotometer equipped with a micro fluorescence quartz cuvette (Science Outlet B00GW1G80M). The scan settings were as follows: slit width = 1 nm (0.38 mm), step size = 0.5 nm, integration = 0.1 sec.

Nanoparticle Tracking Analysis (NTA). Sample solutions were prepared in a volume of 1 mL with ultrapure water followed by a degassing process of at least 30 minutes. The solutions were then infused into the measurement cell of a NanoSight NS300 (Malvern Instruments, Amesbury, United Kingdom), which is equipped with a Blue 405 nm laser, a high sensitivity sCMOS camera and a syringe pump. For each sample, 20 experiment videos of 30 seconds were captured at a frame rate of 24.9825 fps (total frame = 749), using a syringe pump speed of 50, camera level of 16, and screen gain of 1.5 at room temperature. The videos were analyzed using NTA 3.3 Dev Build 3.3.104 software (Malvern) with a detect threshold of 5 and a screen gain of 10, for the estimation of the size distribution and concentration of particles.

2. GC-MS Analysis of Citrus Varietals

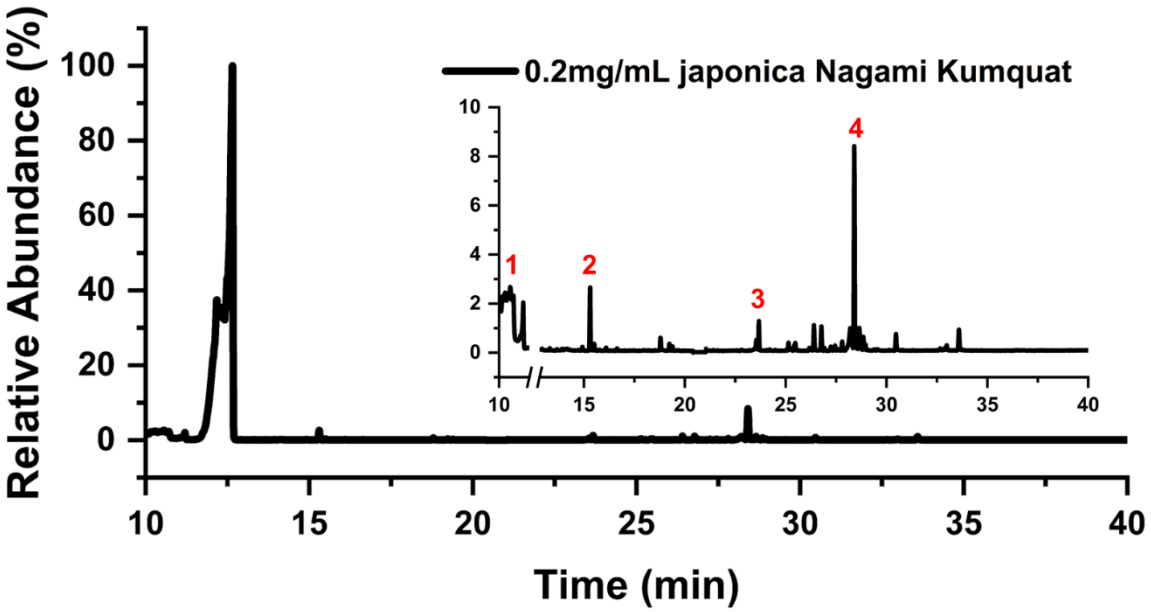

Figure *S*-1. GC-MS total ion chromatogram of 0.2 mg/mL citrus japonica, Nagami Kumquat. The inset plot has a zoomed-in view of other major peaks by excluding the limonene peak in the range of 11.5 – 12.8 min. Other major peaks are identified as follows: Peak 1: L-β-pinene, Peak 2: β-Linalool, Peak 3: δ-Elemene, and Peak 4: Germacrene D. Relative abundance percentages calculated with limonene peak abundance set at 100%.

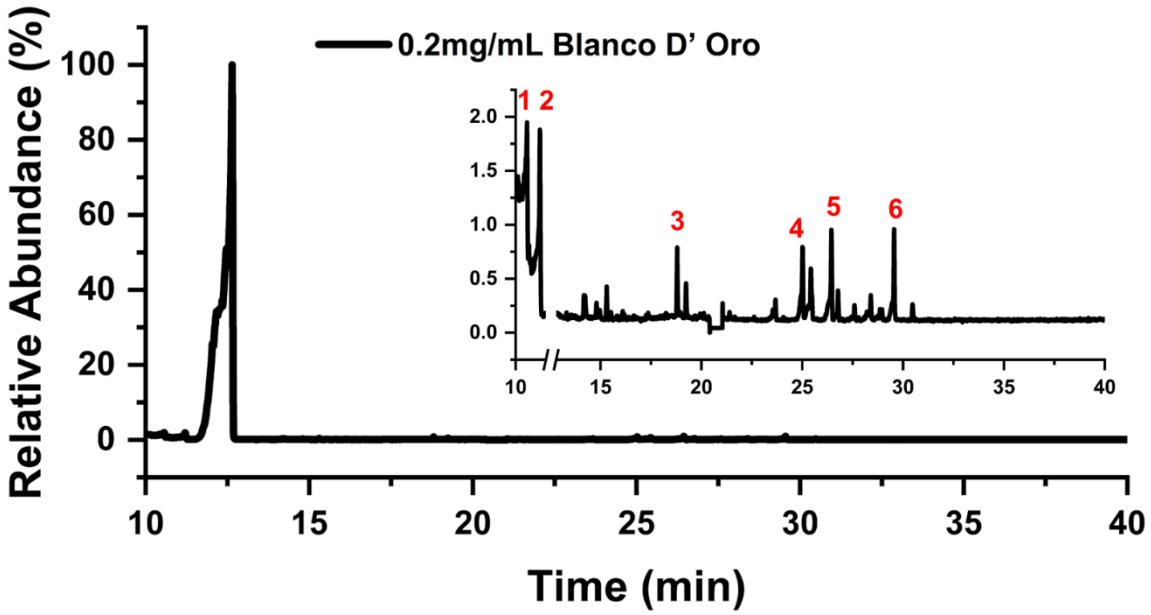

Figure *S*-2. GC-MS total ion chromatogram of 0.2 mg/mL citrus 'Blanco D' Oro'. The inset plot has a zoomed-in view of other major peaks by excluding the limonene peak in the range of 11.5 – 12.8 min. Other major peaks are identified as follows: Peak 1: Sabinene, Peak 2: L-β-pinene, Peak 3: α-Terpineol, Peak 4: Copaene, Peak 5: Caryophyllene, and Peak 6: δ-Cadinene. Relative abundance percentages calculated with limonene peak abundance set at 100%.

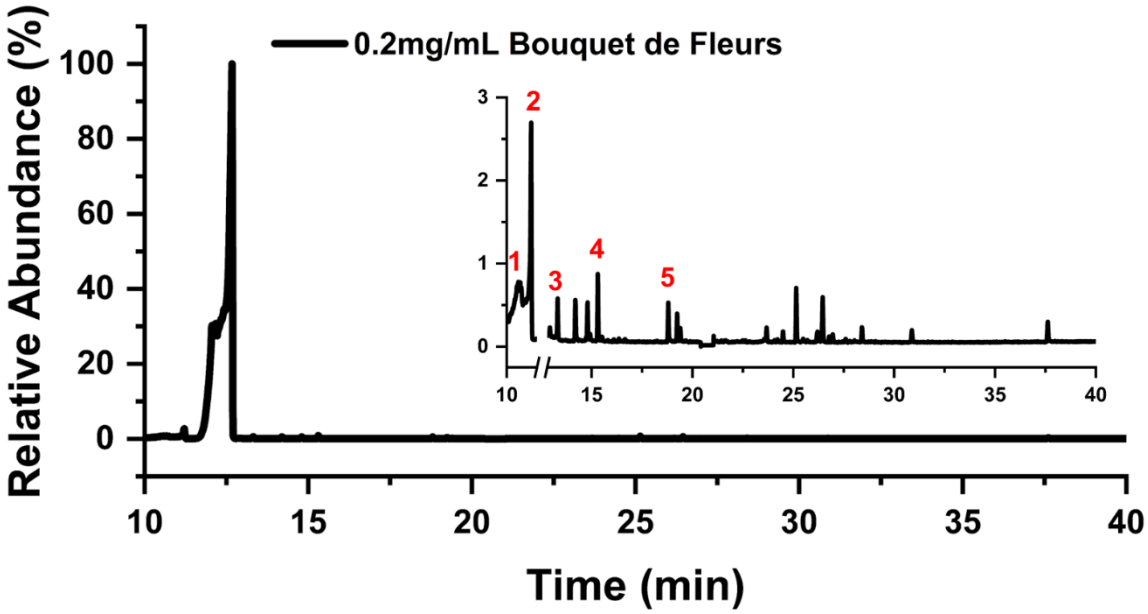

Figure *S*-3. GC-MS total ion chromatogram of 0.2 mg/mL citrus 'Bouquet de Fleurs'. The inset plot has a zoomed-in view of other major peaks by excluding the limonene peak in the range of 11.5 – 12.8 min. Other major peaks are identified as follows: Peak 1: β-Pinene, Peak 2: β-Myrcene, Peak 3: cis-β-Ocimene, Peak 4: β-Linalool, and Peak 5: α-Terpineol. Relative abundance percentages calculated with limonene peak abundance set at 100%.

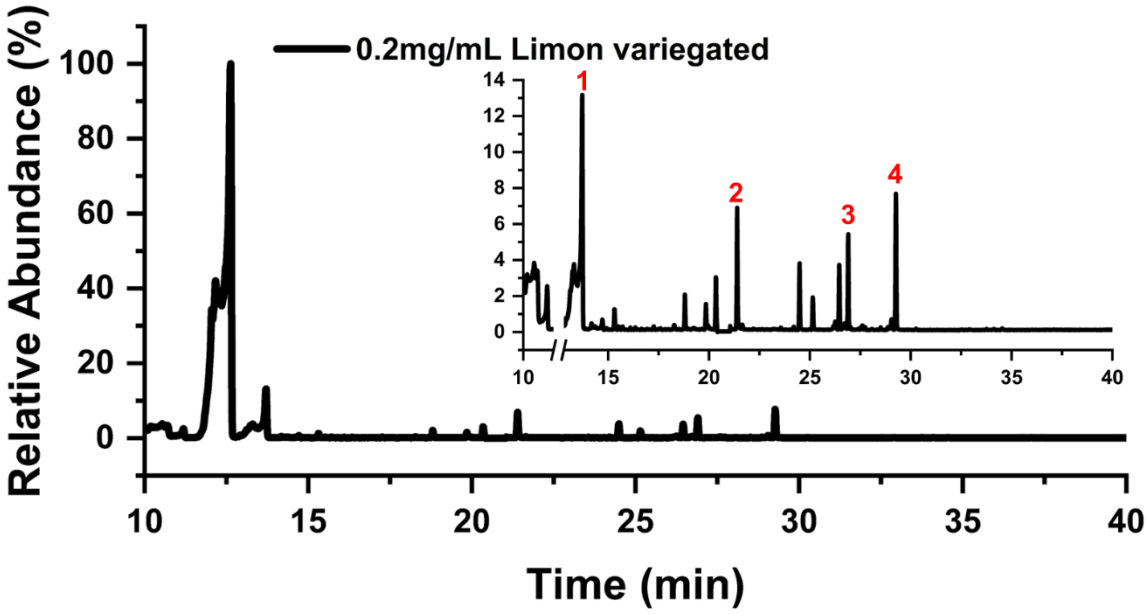

Figure *S*-4. GC-MS total ion chromatogram of 0.2 mg/mL citrus Limon "variegated". The inset plot has a zoomed-in view of other major peaks by excluding the limonene peak in the range of 11.5 – 12.8 min. Other major peaks are identified as follows: Peak 1: γ-Terpinene, Peak 2: Citral, Peak 3: α-Bergamotene, and Peak 4: β-Bisabolene. Relative abundance percentages calculated with limonene peak abundance set at 100%.

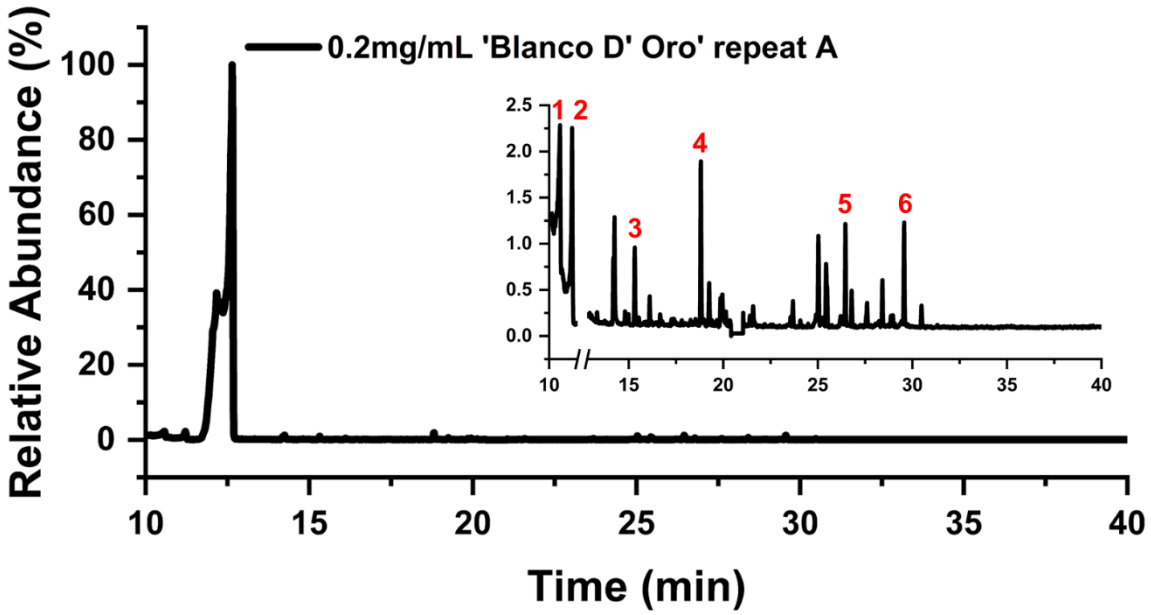

Figure *S*-5. GC-MS total ion chromatogram of 0.2 mg/mL citrus 'Blanco D' Oro' repeat Oct-A. The inset plot has a zoomed-in view of other major peaks by excluding the limonene peak in the range of 11.5 – 12.8 min. Other major peaks are identified as follows: Peak 1: Sabinene, Peak 2: L-β-pinene, Peak 3: β-Linalool, Peak 4: α-Terpineol, Peak 5: Caryophyllene, and Peak 6: δ-Cadinene. Relative abundance percentages calculated with limonene peak abundance set at 100%.

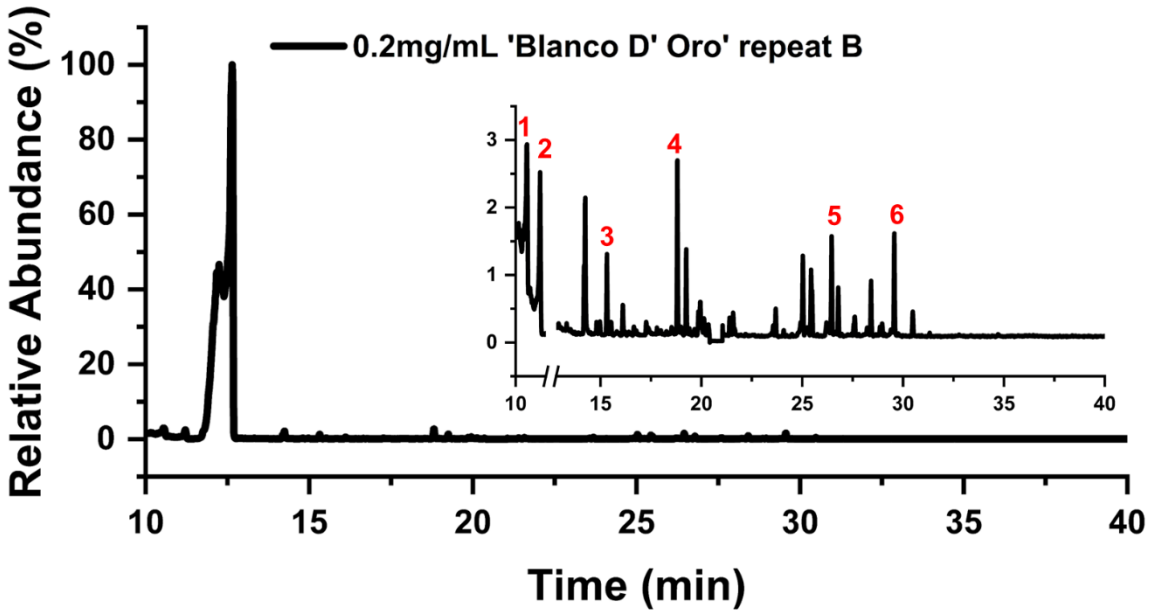

Figure *S*-6. GC-MS total ion chromatogram of 0.2 mg/mL citrus 'Blanco D' Oro' repeat Oct-B. The inset plot has a zoomed-in view of other major peaks by excluding the limonene peak in the range of 11.5 – 12.8 min. Other major peaks are identified as follows: Peak 1: Sabinene, Peak 2: L-β-pinene, Peak 3: Linalyl anthranilate, Peak 4: α-Terpineol, Peak 5: Caryophyllene, and Peak 6: δ-Cadinene. Relative abundance percentages calculated with limonene peak abundance set at 100%.

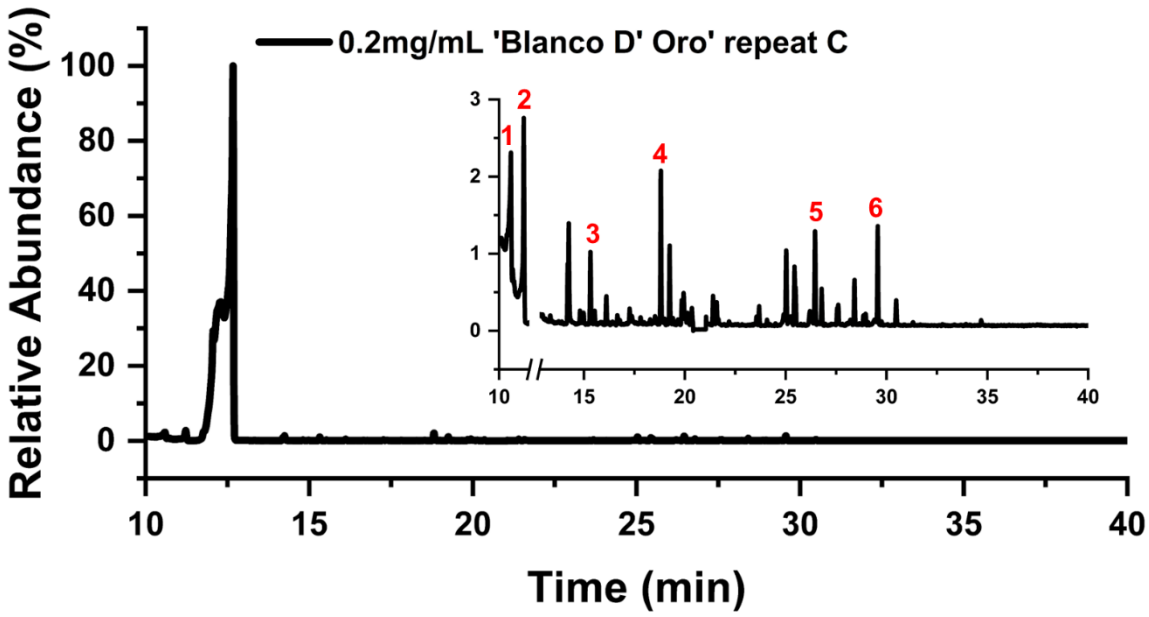

Figure *S*-7. GC-MS total ion chromatogram of 0.2 mg/mL citrus 'Blanco D' Oro' repeat Oct-C. The inset plot has a zoomed-in view of other major peaks by excluding the limonene peak in the range of 11.5 – 12.8 min. Other major peaks are identified as follows: Peak 1: Sabinene, Peak 2: L-β-pinene, Peak 3: Linalool, Peak 4: α-Terpineol, Peak 5: Caryophyllene, and Peak 6: δ-Cadinene. Relative abundance percentages calculated with limonene peak abundance set at 100%.

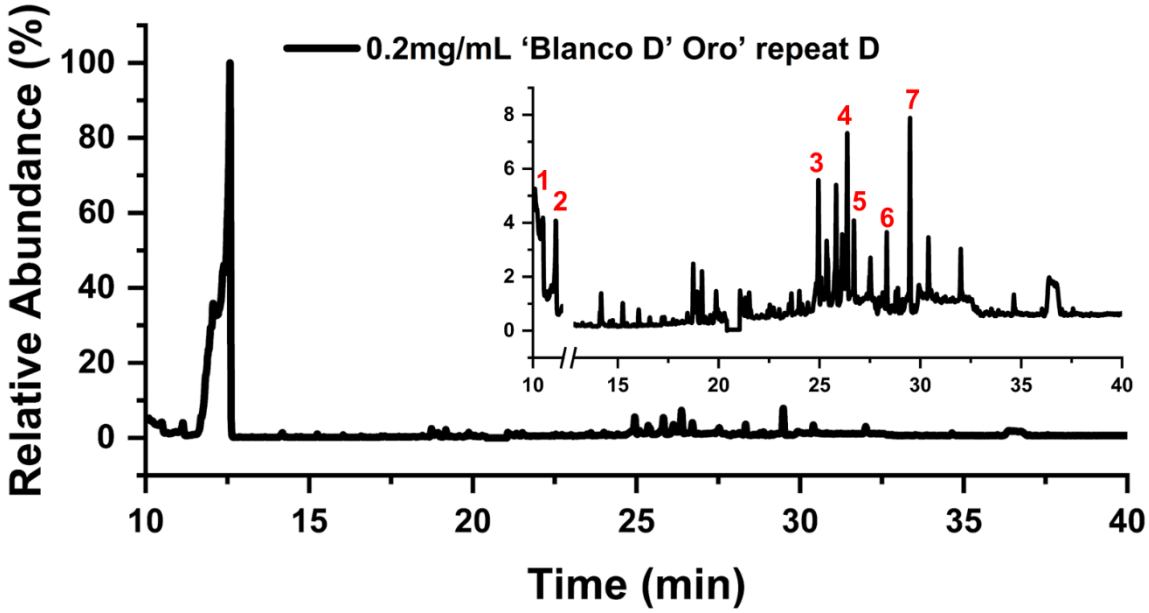

Figure *S*-8. GC-MS total ion chromatogram of 0.2 mg/mL citrus 'Blanco D' Oro' repeat Dec-D. The inset plot has a zoomed-in view of other major peaks by excluding the limonene peak in the range of 11.5 – 12.8 min. Other major peaks are identified as follows: Peak 1: Sabinene, Peak 2: β-pinene, Peak 3:

Copaene, Peak 4: Caryophyllene, Peak 5: β-Cubebene, Peak 6: Germacrene D and Peak 7: δ-Cadinene. Relative abundance percentages calculated with limonene peak abundance set at 100%.

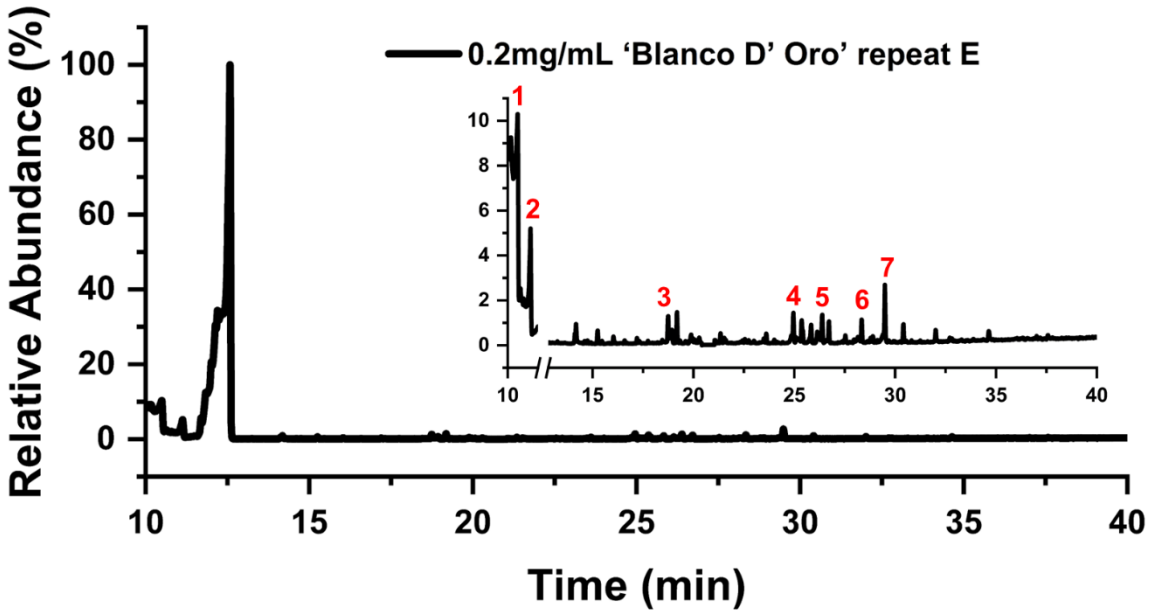

Figure *S*-9. GC-MS total ion chromatogram of 0.2 mg/mL citrus 'Blanco D' Oro' repeat Dec-E. The inset plot has a zoomed-in view of other major peaks by excluding the limonene peak in the range of 11.5 – 12.8 min. Other major peaks are identified as follows: Peak 1: Sabinene, Peak 2: β-pinene, Peak 3: α-Terpineol, Peak 4: Copaene, Peak 5: Caryophyllene, Peak 6: Germacrene D and Peak 7: β-Cadinene. Relative abundance percentages calculated with limonene peak abundance set at 100%.

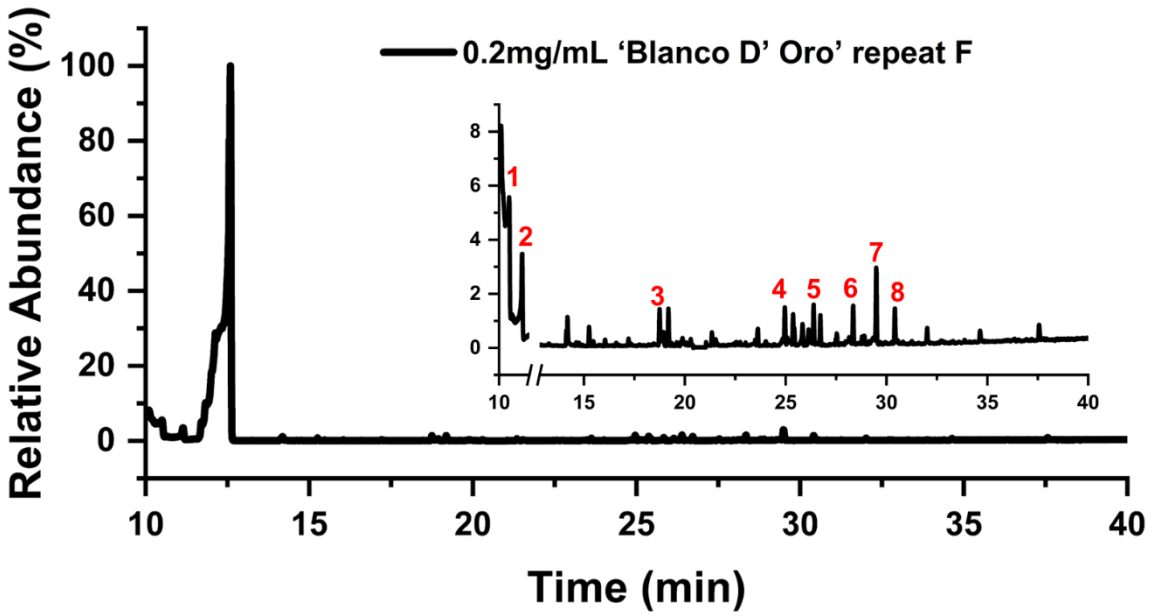

Figure *S*-10. GC-MS total ion chromatogram of 0.2 mg/mL citrus 'Blanco D' Oro' repeat Dec-F. The inset plot has a zoomed-in view of other major peaks by excluding the limonene peak in the range of 11.5 – 12.8 min. Other major peaks are identified as follows: Peak 1: Sabinene, Peak 2: β-pinene, Peak 3: α-

Terpineol, Peak 4: α-Cubebene, Peak 5: Caryophyllene, Peak 6: Germacrene D, Peak 7: δ-Cadinene, and Peak 8: Elemol. Relative abundance percentages calculated with limonene peak abundance set at 100%.

Table *S*-1. Compounds identified in citrus samples by GC-MS and their corrected area % of total.

Compound	japonica Nagami Kumquat	Blanco D' Oro	Bouquet de Fleurs	Limon variegated	Blanco D' Oro Oct-A	Blanco D' Oro Oct-B	Blanco D' Oro Oct-C
Sabinene	0.694%	0.346%			0.671%	0.651%	0.630%
β-pinene	1.207%	0.495%	0.365%	1.923%	0.591%	0.586%	0.577%
β-Myrcene			0.737%	0.448%			
Limonene	87.260%	91.704%	94.766%	79.328%	91.581%	90.359%	90.655%
γ-Terpinene				3.627%			
α-Terpinene				0.125%			
cis-β-Ocimene			0.097%				
cis-Linalool Oxide			0.084%				0.029%
1-Octanol					0.180%	0.288%	0.183%
Linalool	0.329%	0.043%	0.116%	0.153%	0.127%		0.138%
Linalyl anthranilate						0.155%	
Nonanal	0.040%			<threshold		0.033%	0.029%
trans/cis-p-Mentha-2,8-dienol	0.020%					0.054%	0.058%/0.018%
β-Citronellal							0.023%
Nerol				0.193%		0.044%	0.070%
β-Citral				0.403%			0.066%
Citral				0.789%	<threshold	0.040%	0.067%
1-Decanol						0.032%	
Geraniol acetate				0.214%			
(Z,E)-α-Famesene				0.122%			
α-Terpineol	0.070%	0.092%	0.069%	0.229%	0.265%	0.353%	0.318%
cis-Carveol						0.040%	
Decanal	0.042%	0.052%			0.079%	0.165%	0.182%
Octyl acetate	0.025%		0.029%				
δ-Elemene	0.171%	<threshold	0.031%		0.061%	0.500%	0.040%
Lavandulol, acetate	0.051%						
Copaene		0.193%					0.154%
α-Cubebene					0.151%	0.167%	
β-Cubebene	<threshold	0.107%	0.030%		0.159%		
trans-Nerolidol			0.025%				
Caryophyllene		0.232%	0.098%	0.416%	0.173%	0.214%	
α-Caryophyllene		<threshold			0.052%		
Germacrene D	1.222%	0.040%			0.075%	0.206%, 0.096%, 0.106%	0.182%, 0.075%
β-Selinene	0.144%						
γ-Elemene	0.085%		0.120%			<threshold	0.021%

α-Humulene						0.053%	
Hedycaryol	0.115%						
Seychellene							0.023%
δ-Cadinene		0.140%			0.169%	0.203%	0.198%
Osthole			0.013%				
α-Bergamotene				0.592%			
cis-α-Bisabolene				0.114%			
β-Bisabolene				0.875%			
Elemol					0.039%	0.057%	0.055%

Table *S*-2. The five repeats of citrus 'Blanco D' Oro' Oct-C sample. The peaks labelled in Figure *S*-7 were selected for analysis. Their percentage values were calculated by dividing the area of each terpenoid peak by the area of the limonene peak × 100%. The experiments were repeated 5 times, both the average values and the standard deviations derived from these five repeats.

Repeats of Oct-C	linalool	α-terpineol	caryophyllene	cadinene
1	0.1%	0.4%	1.1%	1.9%
2	0.1%	0.3%	1.2%	2.2%
3	0.2%	0.2%	0.6%	1.1%
4	0.1%	0.3%	1.2%	2.4%
5	0.1%	0.3%	1.4%	2.6%
Average: Area *vs* Limonene Area %	0.1%	0.3%	1.1%	2.0%
Standard Deviation	0.1%	0.1%	0.3%	0.5%

Table *S*-3. The five repeats of citrus 'Blanco D' Oro' Dec-F sample. The peaks labelled in Figure *S*-10 were selected for analysis. Their percentage values were calculated by dividing the area of each terpenoid peak by the area of the limonene peak × 100%. The experiments were repeated 5 times, both the average values and the standard deviations derived from these five repeats.

Repeats of Dec-F	α-terpineol	cubebene	caryophyllene	germacrene D	cadinene	elemol
1	0.2%	0.4%	0.6%	0.7%	1.6%	0.7%
2	0.2%	0.5%	0.7%	0.7%	1.4%	0.5%
3	0.2%	0.4%	0.6%	0.7%	1.2%	0.5%
4	0.2%	0.5%	0.8%	0.9%	1.6%	0.7%
5	0.2%	0.6%	0.8%	0.8%	1.4%	0.6%
Average: Area *vs* Limonene Area %	0.2%	0.5%	0.7%	0.8%	1.4%	0.6%
Standard Deviation	0.0%	0.1%	0.1%	0.1%	0.2%	0.1%

3. NMR Measurements of Terpene and Cavitand Interactions

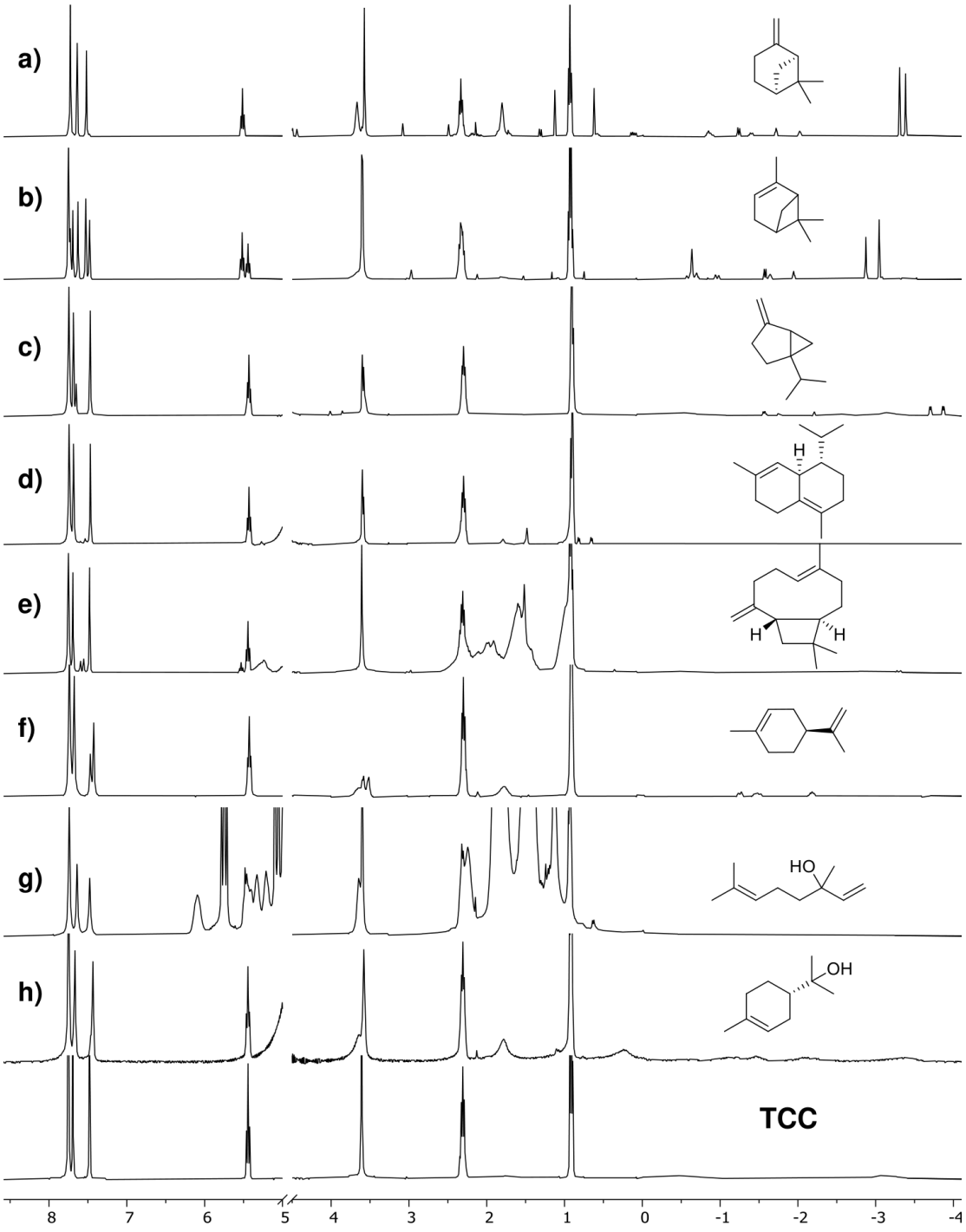

Figure *S*-11. ^{1}H-NMR spectra (400 MHz, 25 °C, D_2O) of 2.2 mM **TCC** and mixtures of **TCC** + Terpene. The bottom spectrum depicts free **TCC**, while the spectra above are of **TCC** with a) (1S)-(-)-β-pinene, b) α-pinene, c) sabinene, d) (+)-(δ)-cadinene, e) β-caryophyllene, f) (R)-(+)-limonene, g) linalool, h) (S)-(-)-α-terpineol. The structure of each corresponding terpene guest is found to the right of each spectrum.

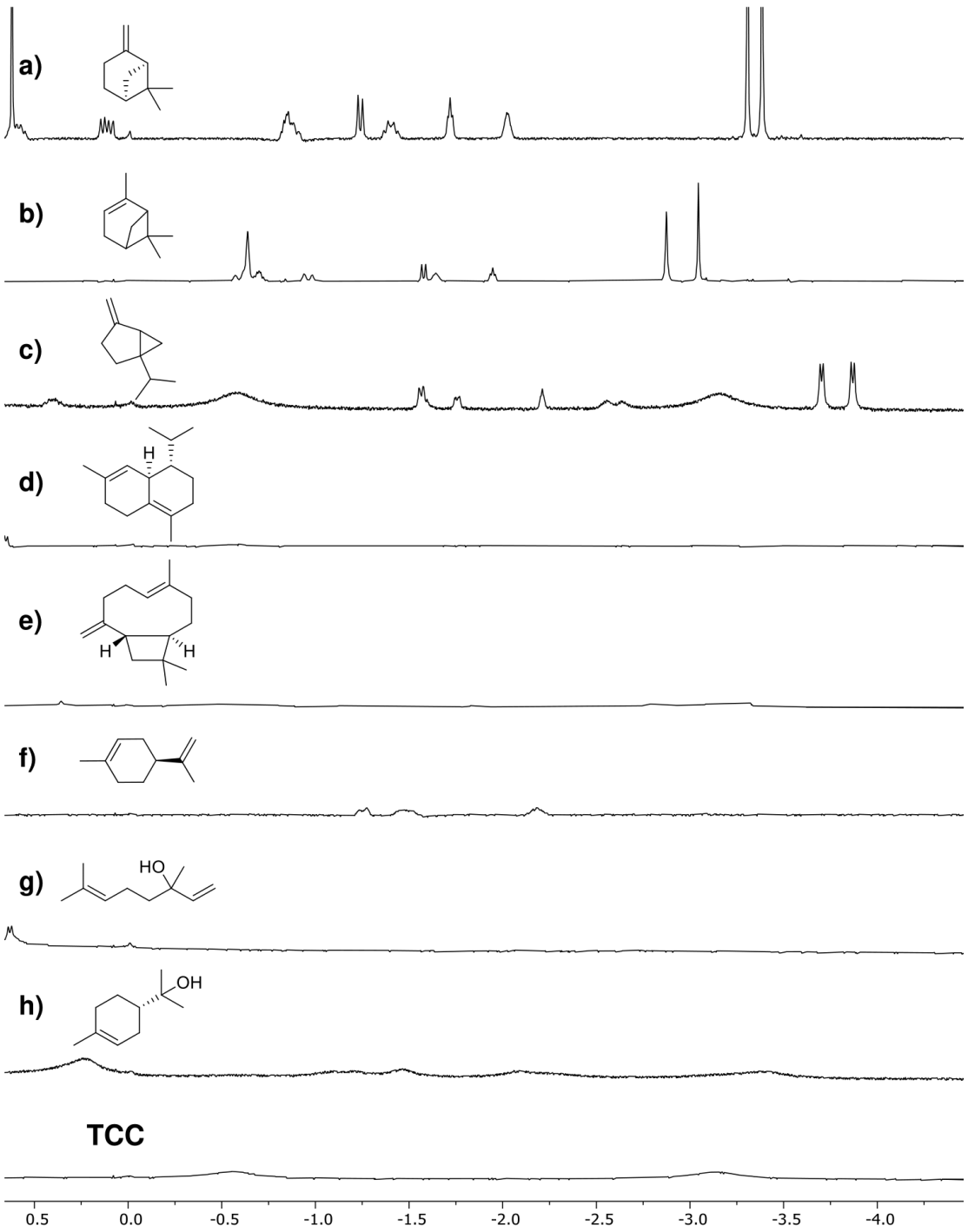

Figure *S*-12. ^{1}H-NMR spectra (400 MHz, 25 °C, D_2O) of 2.2 mM **TCC** and mixtures of **TCC** + Terpene, magnified to better designate bound guest protons. The bottom spectrum depicts free **TCC**, while the spectra above are of **TCC** with a) (1S)-(-)-β-pinene, b) α-pinene, c) sabinene, d) (+)-(δ)-cadinene, e) β-caryophyllene, f) (R)-(+)-limonene, g) linalool, h) (S)-(-)-α-terpineol. The structure of each corresponding terpene guest is found to the left of each spectrum.

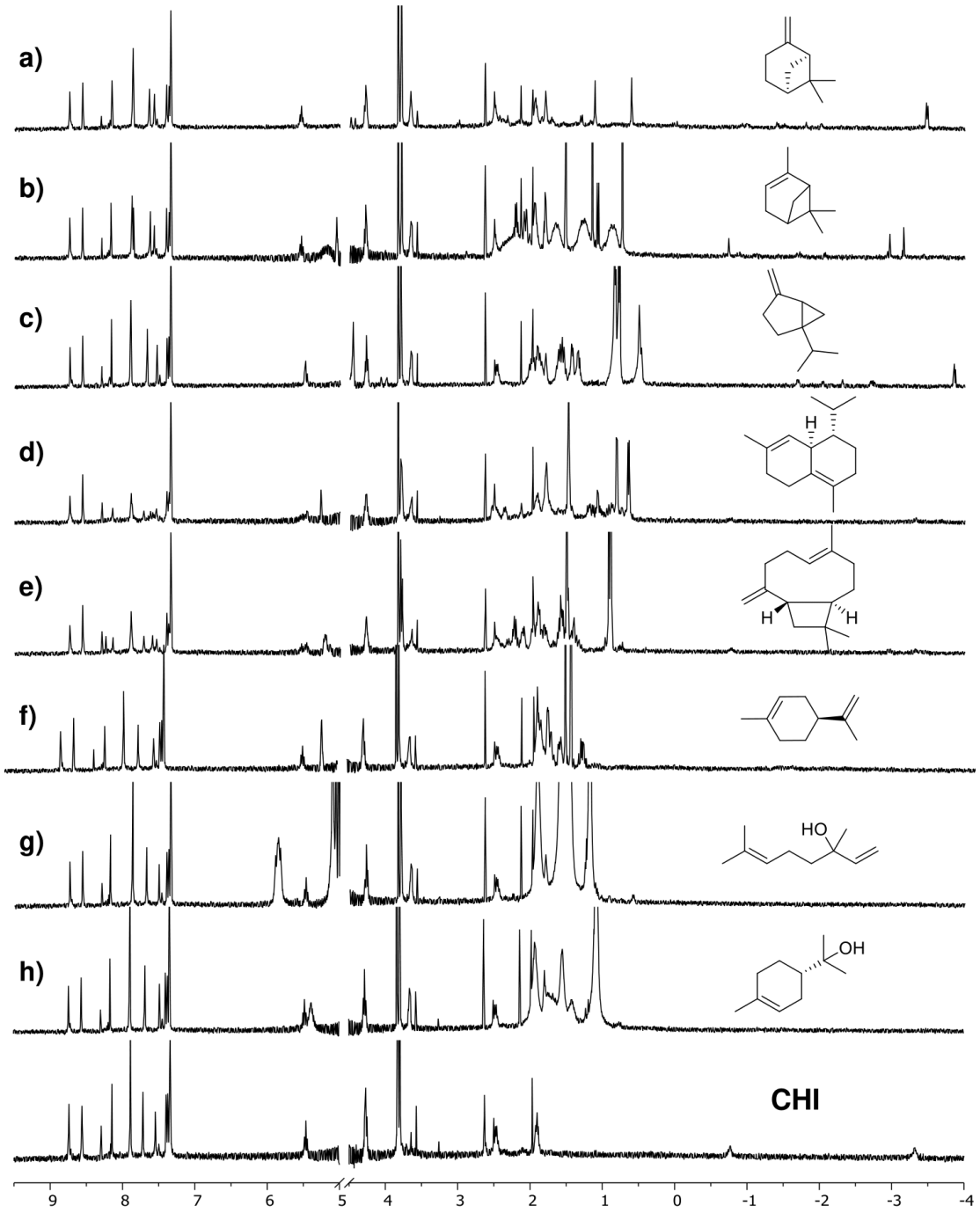

Figure *S*-13. ^{1}H-NMR spectra (400 MHz, 25 °C, D_2O) of 1 mM **CHI** and mixtures of **CHI** + Terpene. The bottom spectrum depicts free **CHI**, while the spectra above are of **CHI** with a) (1S)-(-)-β-pinene, b) α-pinene, c) sabinene, d) (+)-(δ)-cadinene, e) β-caryophyllene, f) (R)-(+)-limonene, g) linalool, h) (S)-(-)-α-terpineol. The structure of each corresponding terpene guest is found to the right of each spectrum.

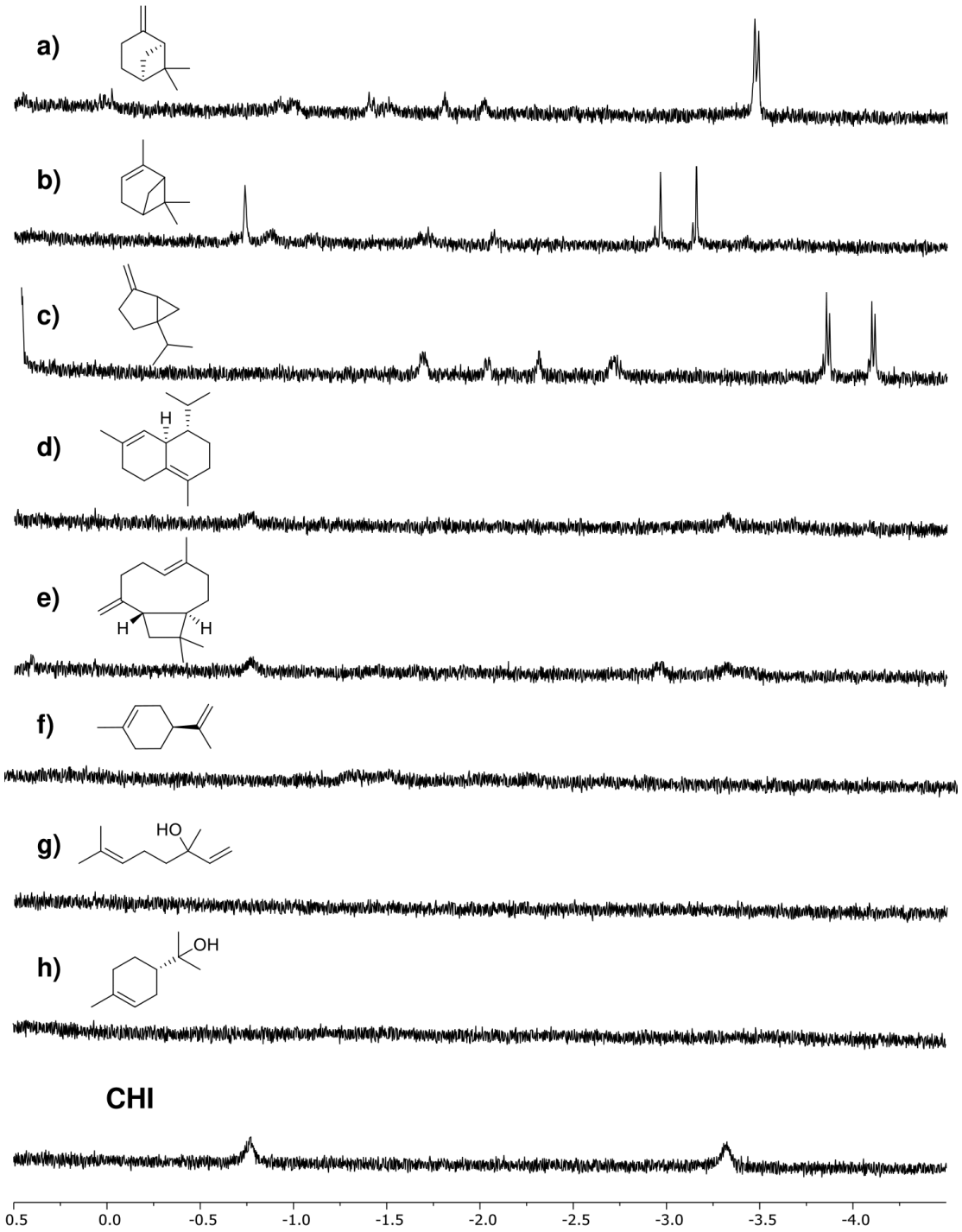

Figure *S*-14. ^{1}H-NMR spectra (400 MHz, 25 °C, D_2O) of 1 mM **CHI** and mixtures of **CHI** + Terpene, magnified to better designate bound guest protons. The bottom spectrum depicts free **CHI**, while the spectra above are of **CHI** a) (1S)-(-)-β-pinene, b) α-pinene, c) sabinene, d) (+)-(δ)-cadinene, e) β-caryophyllene, f) (R)-(+)-limonene, g) linalool, h) (S)-(-)-α-terpineol. The structure of each corresponding terpene guest is found to the right of each spectrum.

Table *S*-4. Binding affinities of added terpenes to **TCC** and **CHI** in D_2O.

Terpene	K_a (**TCC**), M^{-1}	K_a (**CHI**), M^{-1}
Limonene	*intermediate exchange*	*N/O*[b]
α-Pinene	7500	360
β-Pinene	15000	1070
Sabinene	<100[a]	420
α-Terpineol	*fast exchange*	*fast exchange*
δ-Cadinene	*N/O*	*N/O*
β-Caryophyllene	*N/O*	*N/O*
Linalool	*N/O*	*N/O*

[a]Estimated due to minimal observed free guest in the NMR spectrum; [b] N/O = no observed binding, K_a assumed to be < 5 M^{-1}, based on the sensitivity of the spectrometer.

4. Determination of Fluorescence Wavelengths

4.1 UV-Vis Absorbance

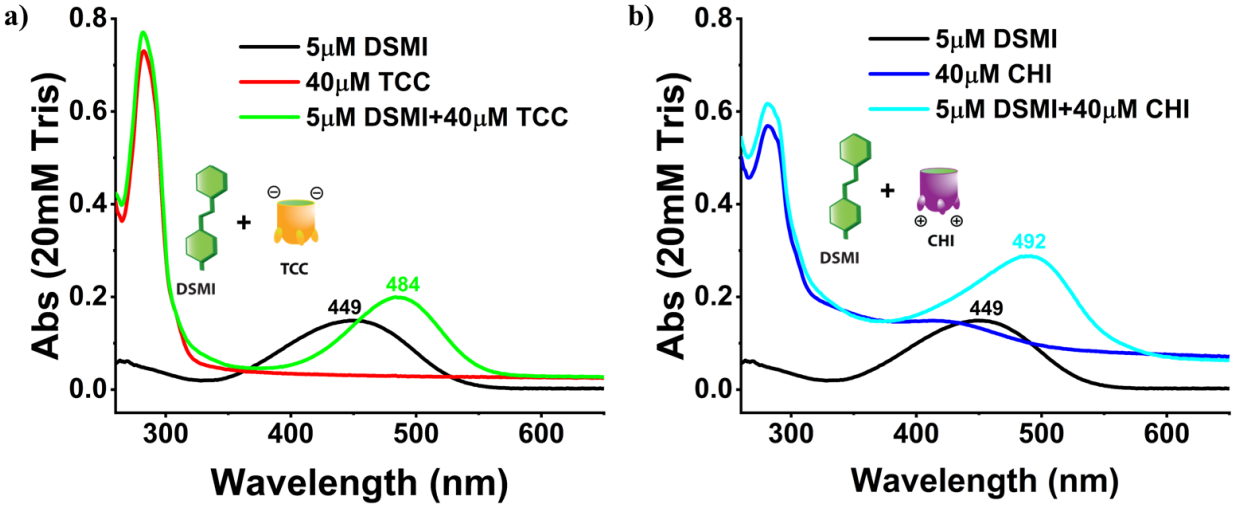

Figure *S*-15. UV-Vis spectra for 1 mL solutions of a) **DSMI, TCC, DSMI + TCC**, and b) **DSMI, CHI, DSMI + CHI**. [**DSMI**] = 5 μM, [**TCC/CHI**] = 40 μM, 20 mM Tris-HCl buffer at neutral pH, with baseline-correction.

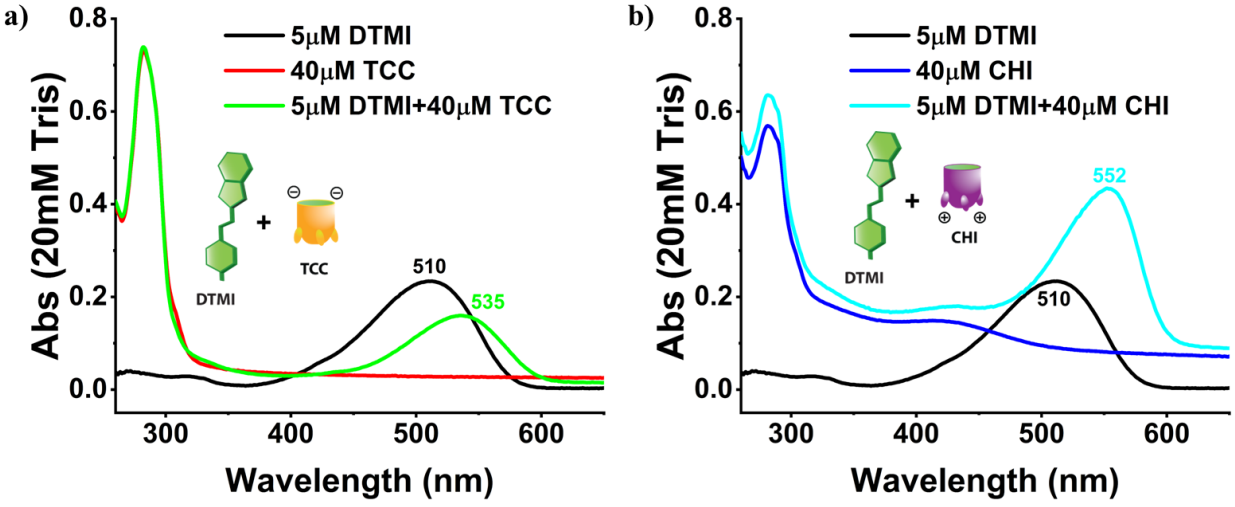

Figure *S*-16. UV-Vis spectra for 1 mL solutions of a) **DTMI, TCC, DSMI + TCC**, and b) **DTMI, CHI, DSMI + CHI**. [**DTMI**] = 5 μM, [**TCC/CHI**] = 40 μM, 20 mM Tris-HCl buffer at neutral pH, with baseline-correction.

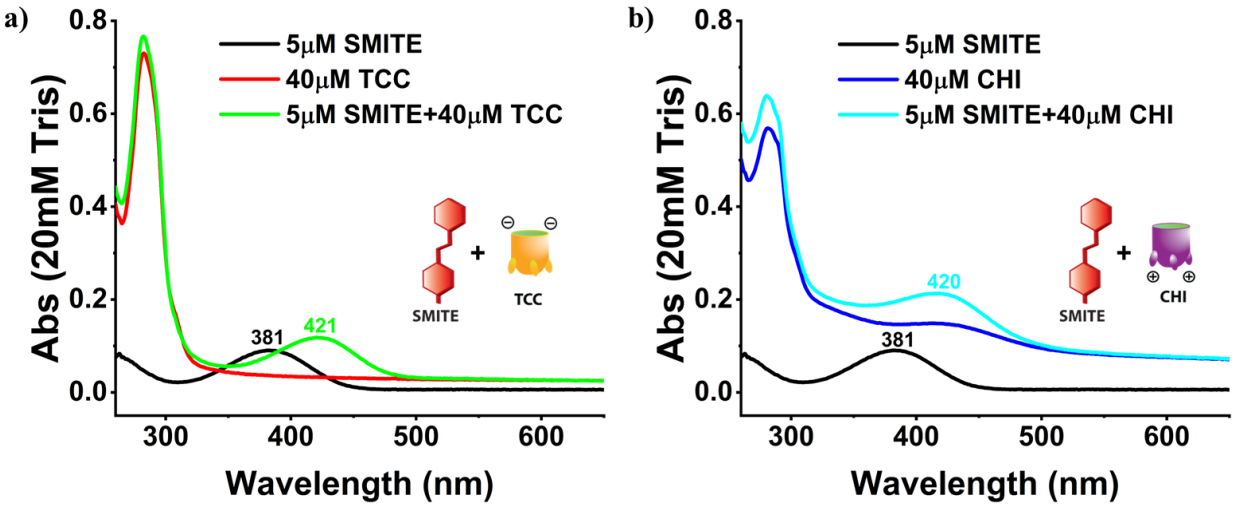

Figure *S*-17. UV-Vis spectra for 1 mL solutions of a) **SMITE, TCC, DSMI + TCC**, and b) **SMITE, CHI, DSMI + CHI**. [**SMITE**] = 5 μM, [**TCC/CHI**] = 40 μM, 20 mM Tris-HCl buffer at neutral pH, with baseline-correction.

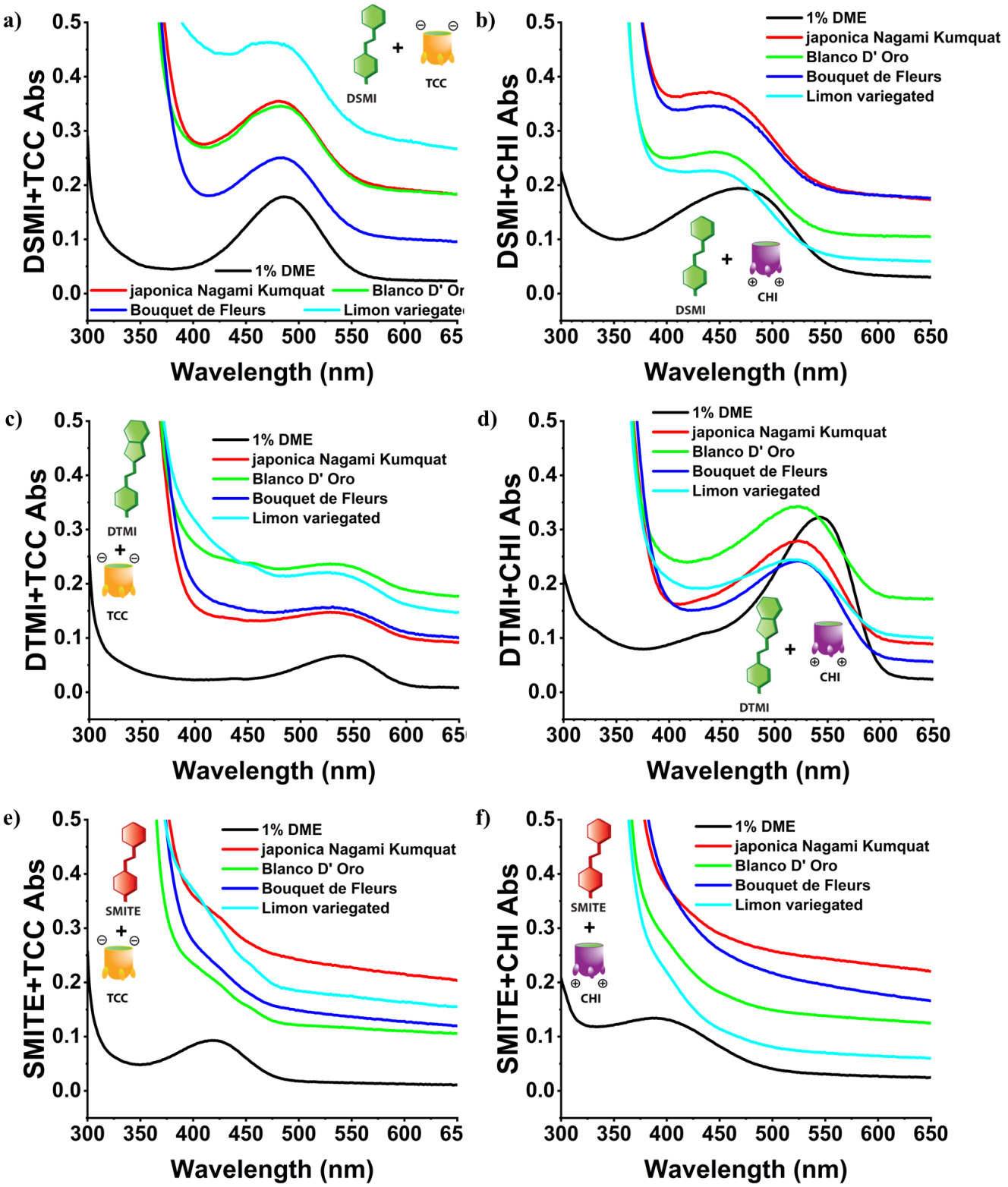

Figure *S*-18. UV-Vis spectra for 1 mL solutions of 2 mg/mL citrus sample with ~1% DME sensed by a) **DSMI** + **TCC**, b) **DSMI** + **CHI**, c) **DTMI** + **TCC**, d) **DTMI** + **CHI**, e) **SMITE** + **TCC**, and f) **SMITE**

+ CHI, baseline corrected with buffer. [**Dye**] = 5 μM, [**TCC/CHI**] = 40 μM, 20 mM Tris-HCl buffer at neutral pH.

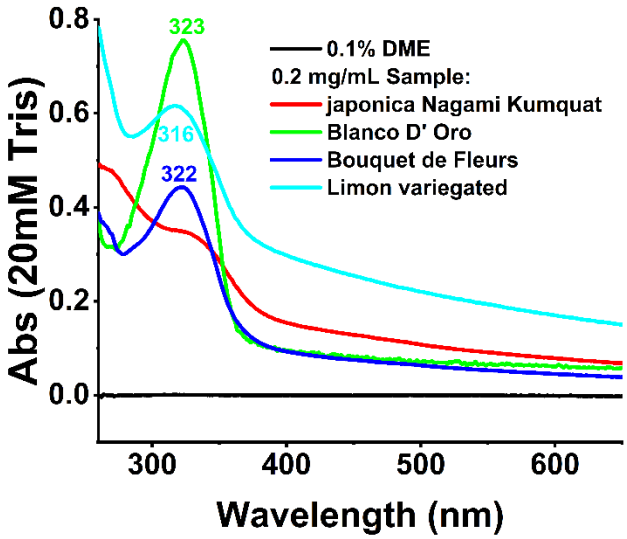

Figure *S*-19. UV-Vis spectra for 1 mL solutions of 0.2 mg/mL citrus sample with ~0.1% DME in 20 mM Tris-HCl buffer at neutral pH.

4.2 Nanoparticle Tracking Analysis

Table *S*-5. Particle mean sizes and concentrations of sample solutions: 0.2 mg/mL citrus sample with 0.1% DME in H_2O: a) japonica Nagami Kumquat, b) 'Blanco D' Oro', c) 'Bouquet de Fleurs', and d) Limon "variegated"; as well as e) 4 µM **TCC**, f) 4 µM **TCC** + 0.2 mg/mL 'Bouquet de Fleurs' citrus sample with 0.1% DME, g) 0.5µM **DSMI** + 4 µM **TCC**, and h) 0.5µM **DSMI** + 4 µM **TCC** + 0.2 mg/mL 'Bouquet de Fleurs' with 0.1% DME in H_2O, respectively. The data were measured by nanoparticle tracking analysis, and represent mean values ± standard error of 20 measurements of each sample.

Sample	**a) japonica Nagami Kumquat**	**b) Blanco D' Oro**	**c) Bouquet de Fleurs**	**d) Limon "variegated"**
Mean Size (nm)	194.7 ± 3.8	176.5 ± 2.0	195.0 ± 5.2	180.7 ± 4.9
Concentration (particles/ml)	$5.70 \pm 0.20 \times 10^7$	$7.75 \pm 0.21 \times 10^7$	$1.23 \pm 0.05 \times 10^7$	$7.94 \pm 0.17 \times 10^7$
Mean +/- Standard Error	**e) TCC**	**f) TCC + Bouquet de Fleurs**	**g) DSMI + TCC**	**h) DSMI+ TCC + Bouquet de Fleurs**
Mean Size (nm)	212.2 ± 22.2	183.3 ± 8.9	156.9 ± 10.5	173.2 ± 13.1
Concentration (particles/ml)	$2.69 \pm 0.22 \times 10^6$	$1.24 \pm 0.05 \times 10^7$	$2.81 \pm 0.18 \times 10^6$	$1.34 \pm 0.03 \times 10^7$

4.3 Fluorescence Emission Spectra

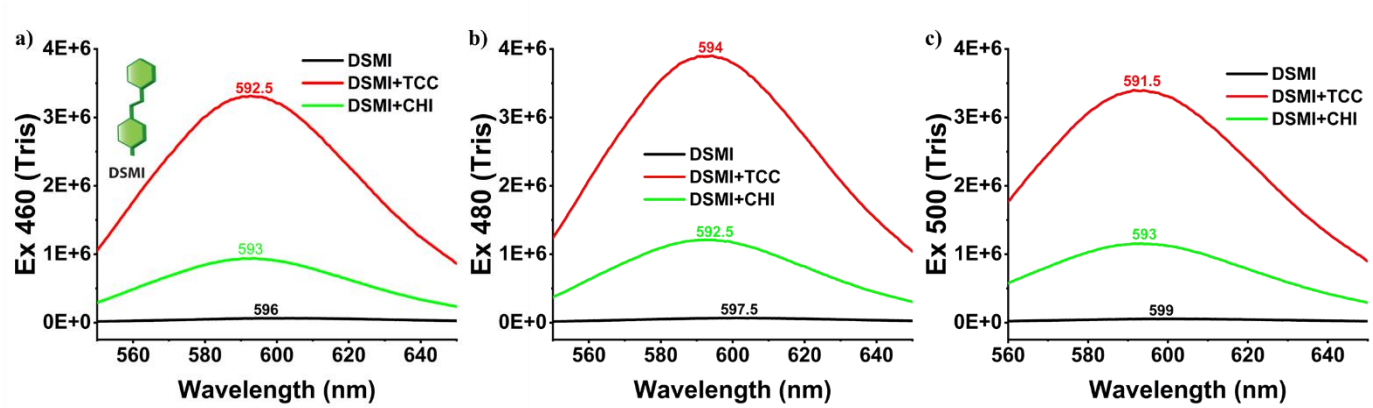

Figure *S*-20. Fluorescence emission spectra of **DSMI, DSMI + TCC**, and **DSMI + CHI** excited at a) Ex max of **DSMI** only 460 nm, b) Ex max of **DSMI + TCC** 480 nm, or c) Ex max of **DSMI + CHI** 500 nm. [**DSMI**] = 5 µM, [**TCC/CHI**] = 40 µM, 20 mM Tris-HCl buffer at neutral pH.

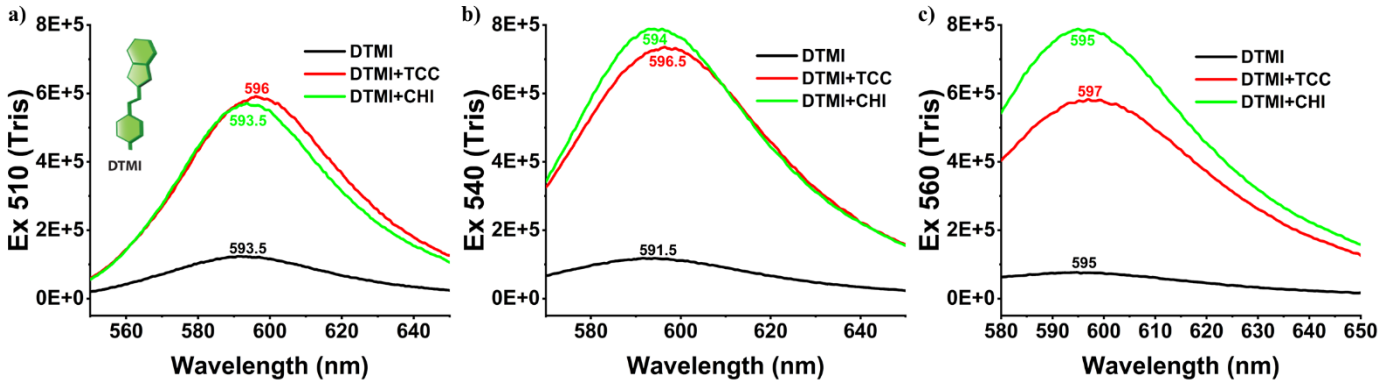

Figure *S*-21. Fluorescence emission spectra of **DTMI, DTMI + TCC**, and **DTMI + CHI** excited at a) Ex max of **DTMI** only 510 nm, b) Ex max of **DTMI + TCC** 540 nm, or c) Ex max of **DTMI + CHI** 560 nm. [**DTMI**] = 5 μM, [**TCC/CHI**] = 40 μM, 20 mM Tris-HCl buffer at neutral pH.

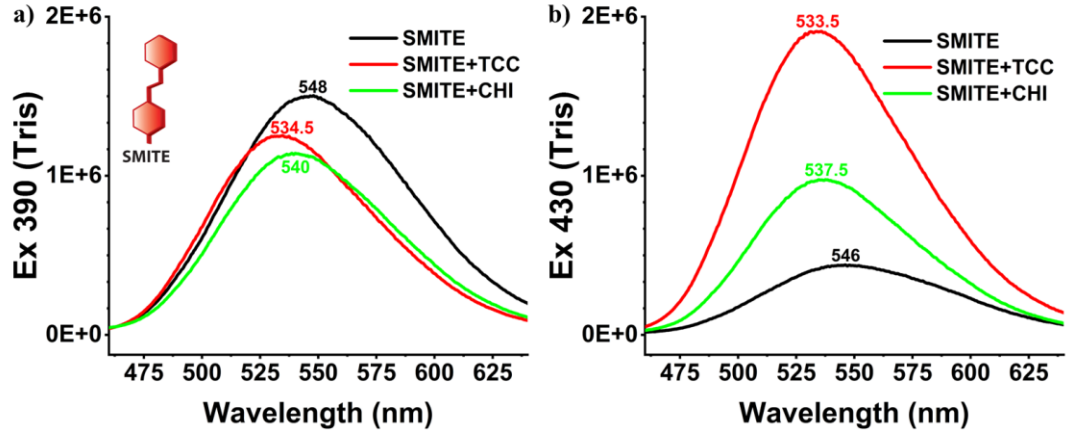

Figure *S*-22. Fluorescence emission spectra of **SMITE, SMITE + TCC**, and **SMITE + CHI** excited at a) Ex max of **SMITE** only 390 nm, or b) Ex max of **SMITE + TCC/CHI** 430 nm. [**SMITE**] = 5 μM, [**TCC/CHI**] = 40 μM, 20 mM Tris-HCl buffer at neutral pH.

5. Fluorescence Array Sensing of Citrus Varietals

The 16-element array was formed by six **DSMI** elements: **DSMI + TCC/CHI** at Ex 460, 480, 500 nm, Em 600 nm; six **DTMI** elements: **DTMI + TCC/CHI** at Ex 510, 540, 560 nm, Em 600 nm; and four **SMITE** elements: **SMITE + TCC/CHI** at Ex 390, 430 nm, Em 540 nm. Thus, each **DSMI** or **DTMI** sensor was measured at 3 wavelengths, each **SMITE** sensor was measured at 2 wavelengths. The fluorescence profile was collected by using 0.5 μM dye with 4 μM **TCC/CHI** cavitand for the sensing of 0.2 mg/ml citrus sample.

5.1 Sensing of Four Citrus Varietals

5.1.1 Bar Plots of Four Citrus Varietals

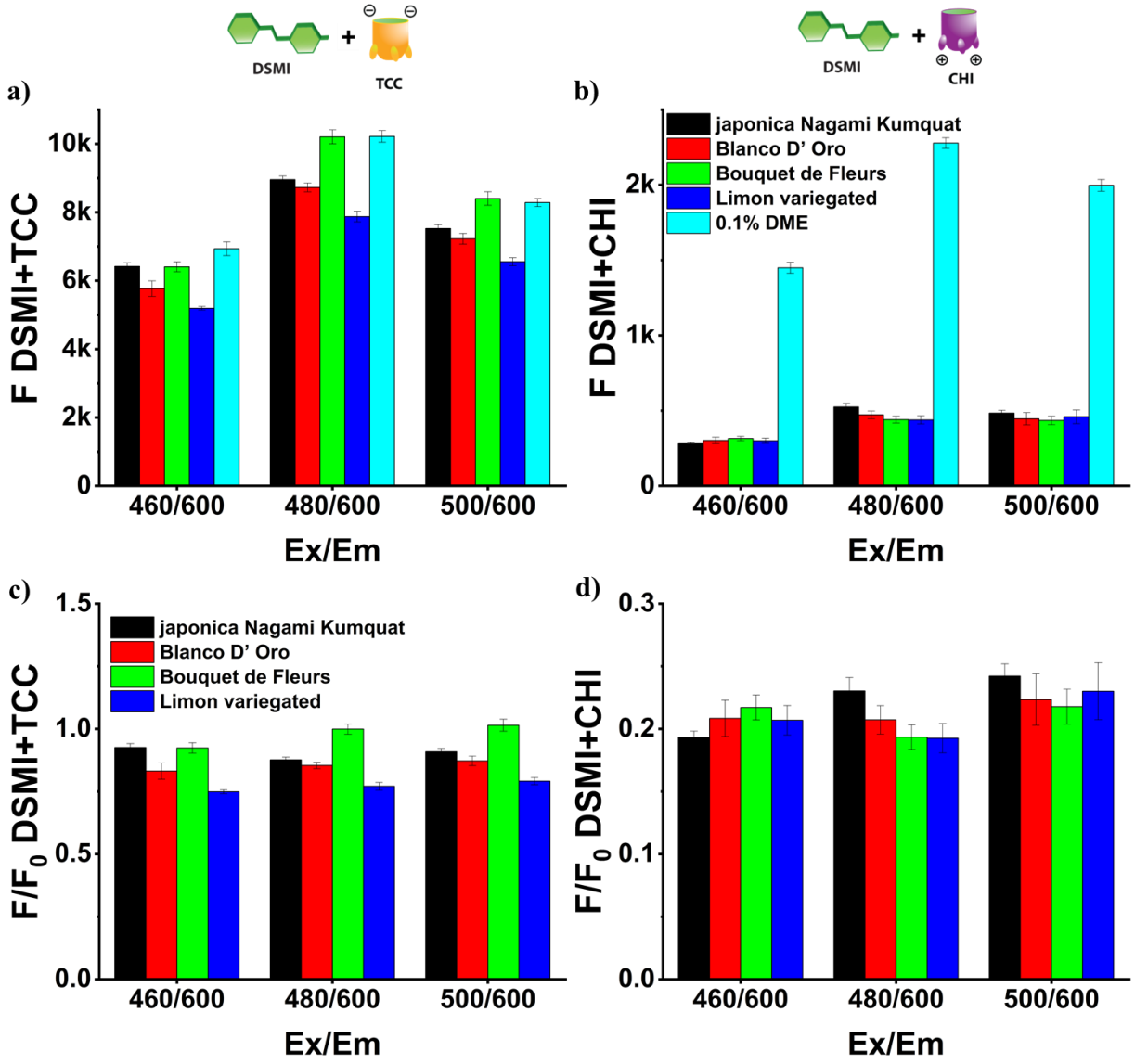

Figure *S*-23. Fluorescence emission (F) and F/F_0 bar plots of a,c) **DSMI + TCC**, and b,d) **DSMI + CHI** for sensing four citrus varietals as well as blank 0.1% DME at Ex/Em = 460/600, 480/600 and 500/600 nm. [**DSMI**] = 0.5 μM, [**TCC/CHI**] = 4 μM, [Citrus Sample] = 200 μg/mL with 0.1% DME, in 20 mM Tris-HCl buffer at neutral pH. F/F_0 values were calculated using F divided by the response of sensor element in the absence of citrus sample but with 0.1% DME (F_0).

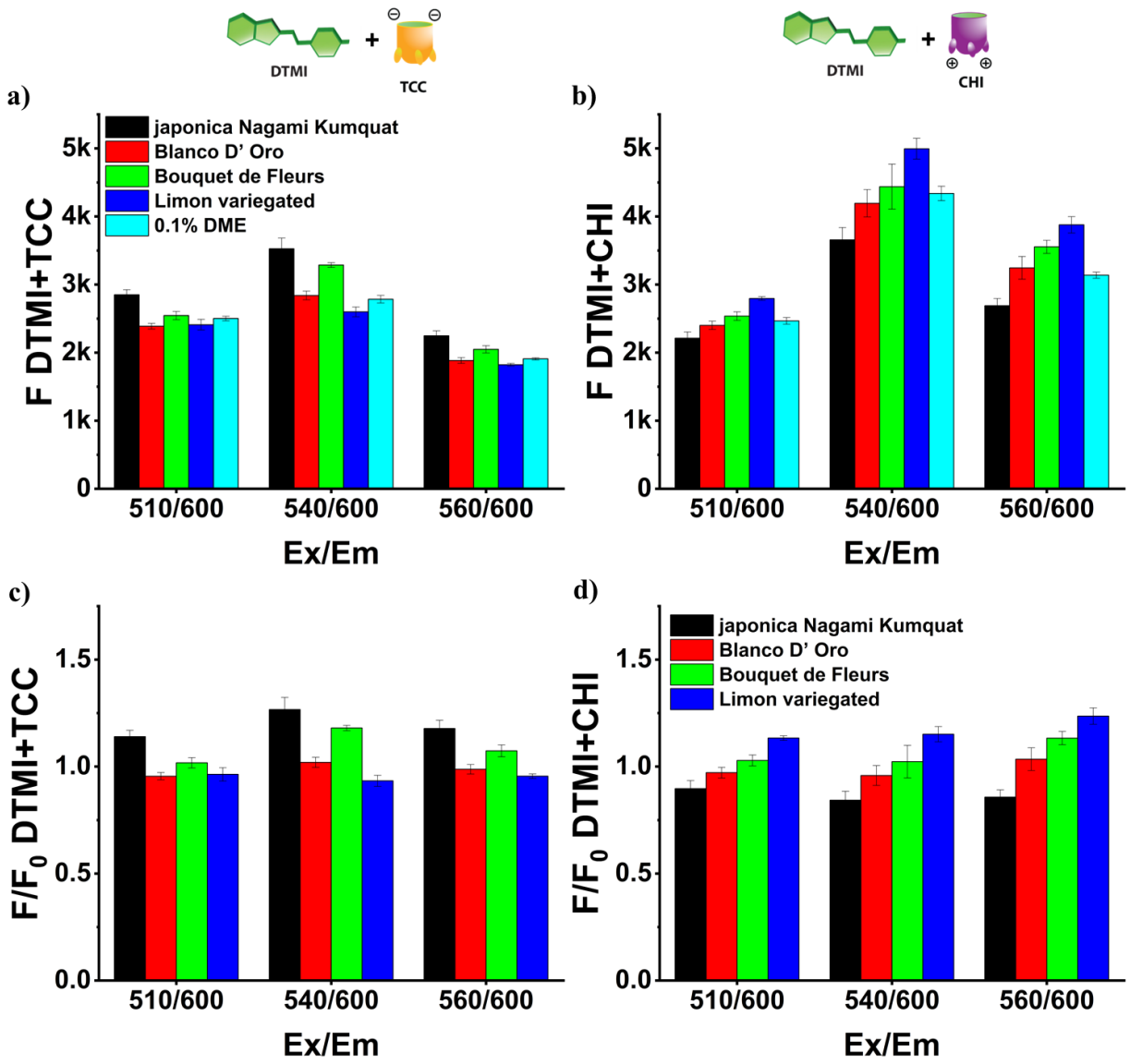

Figure *S*-24. Fluorescence emission (F) and F/F_0 bar plots of a,c) **DTMI + TCC**, and b,d) **DTMI + CHI** for sensing four citrus varietals as well as blank 0.1% DME at Ex/Em = 510/600, 540/600 and 560/600 nm. [**DTMI**] = 0.5 μM, [**TCC/CHI**] = 4 μM, [Citrus Sample] = 200 μg/mL with 0.1% DME, in 20 mM Tris-HCl buffer at neutral pH. F/F_0 values were calculated using F divided by the response of sensor element in the absence of citrus sample but with 0.1% DME (F_0).

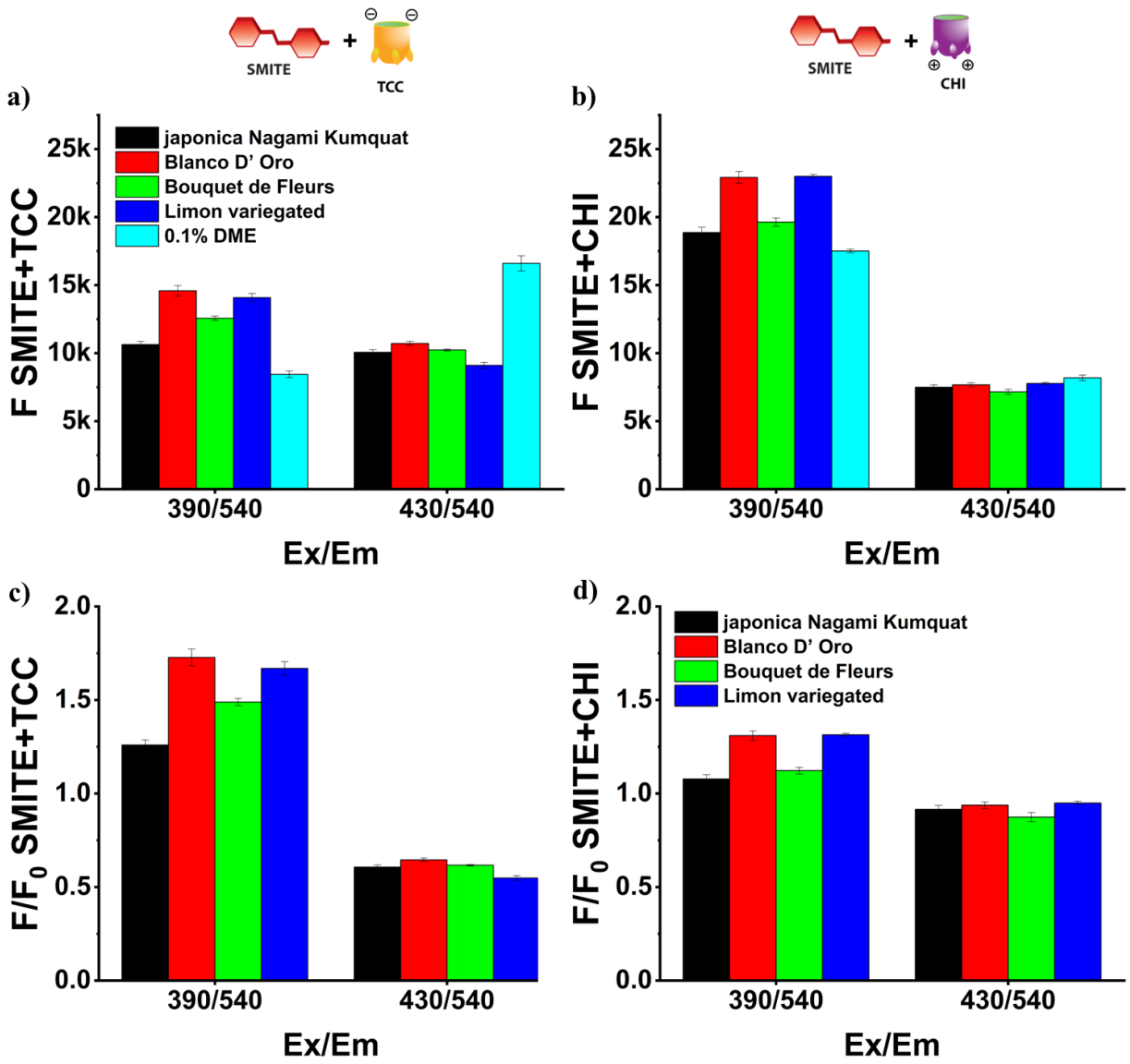

Figure *S*-25. Fluorescence emission (F) and F/F_0 bar plots of a,c) **SMITE + TCC**, and b,d) **SMITE + CHI** for sensing four citrus varietals as well as blank 0.1% DME at Ex/Em = 390/540 and 430/540 nm. [**SMITE**] = 0.5 μM, [**TCC**/**CHI**] = 4 μM, [Citrus Sample] = 200 μg/mL with 0.1% DME, in 20 mM Tris-HCl buffer at neutral pH. F/F_0 values were calculated using F divided by the response of sensor element in the absence of citrus sample but with 0.1% DME (F_0).

5.1.2 PCA and SVM-RFECV of Four Citrus Varietals

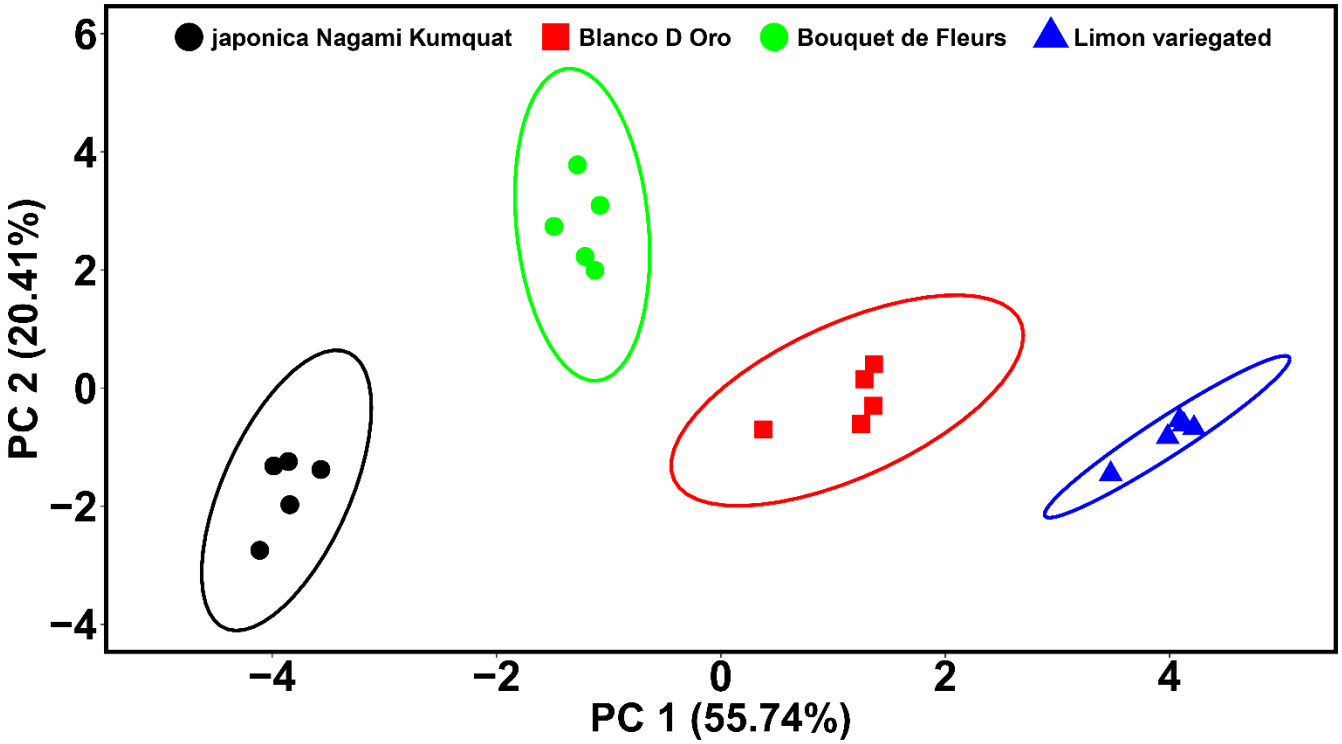

Figure *S*-26. PCA score plot of four citrus varietals obtained using the F/F_0 data of the 16-element **Host:Guest** sensor array (see bar plots in Figures *S*-23 − *S*-25): **DSMI + TCC/CHI** at all three wavelengths Ex 460, 480, 500/Em 600 nm; **DTMI + TCC/CHI** at all three wavelengths Ex 510, 540, 560/Em 600 nm; and **SMITE + TCC/CHI** at both wavelengths Ex 390, 430/Em 540 nm. **[Dye]** = 0.5 μM, **[Host]** = 4 μM, [Citrus Sample] = 0.2 mg/mL with 0.1% DME, buffer 20 mM Tris-HCl at neutral pH. The ellipses indicate 95% confidence.

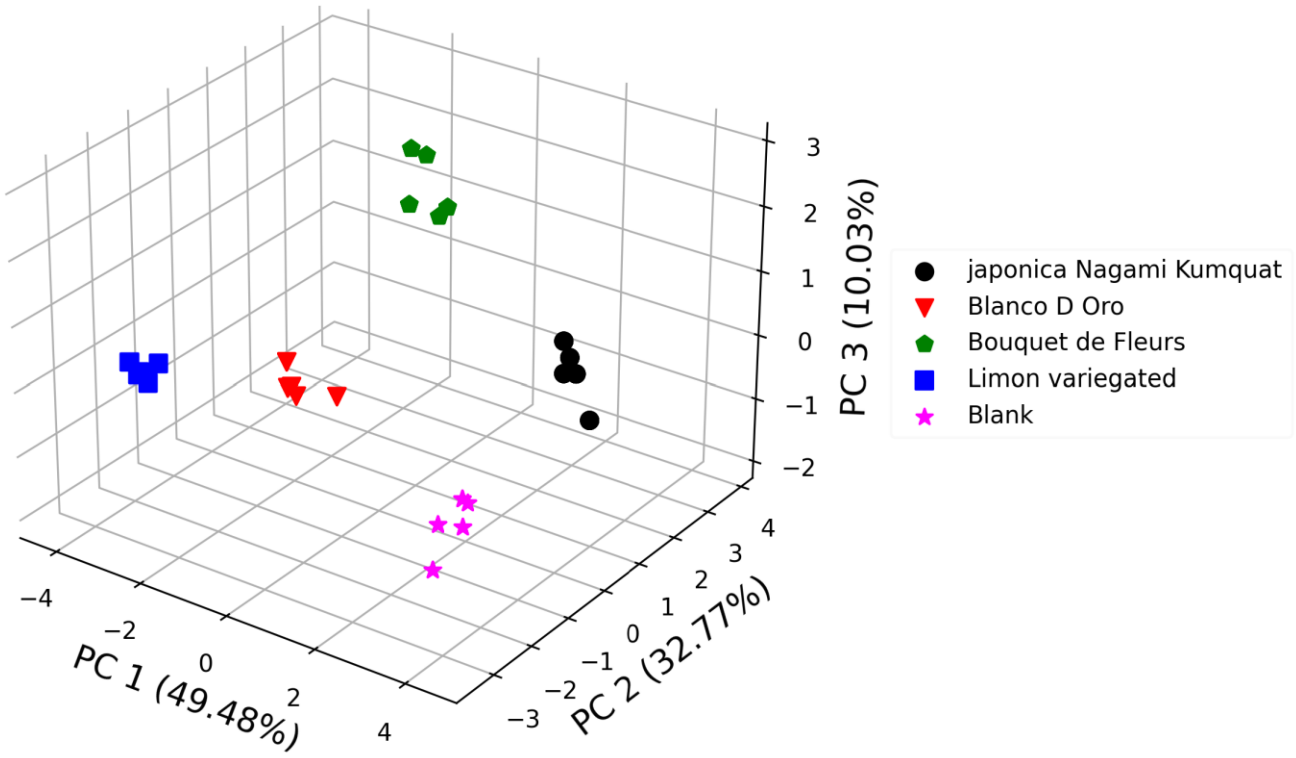

Figure *S*-27. 3D PCA plot of four citrus varietals as well as blank obtained using the raw fluorescence (F) data of the 16-element **Host:Guest** sensor array (see bar plots in Figures *S*-23 − *S*-25): **DSMI + TCC/CHI** at all three wavelengths Ex 460, 480, 500/Em 600 nm; **DTMI + TCC/CHI** at all three wavelengths Ex 510, 540, 560/Em 600 nm; and **SMITE + TCC/CHI** at both wavelengths Ex 390, 430/Em 540 nm. **[Dye]** = 0.5 μM, **[Host]** = 4 μM, [Citrus Sample] = 0.2 mg/mL with 0.1% DME, blank = 0.1% DME without extracted citrus sample, buffer 20 mM Tris-HCl at neutral pH.

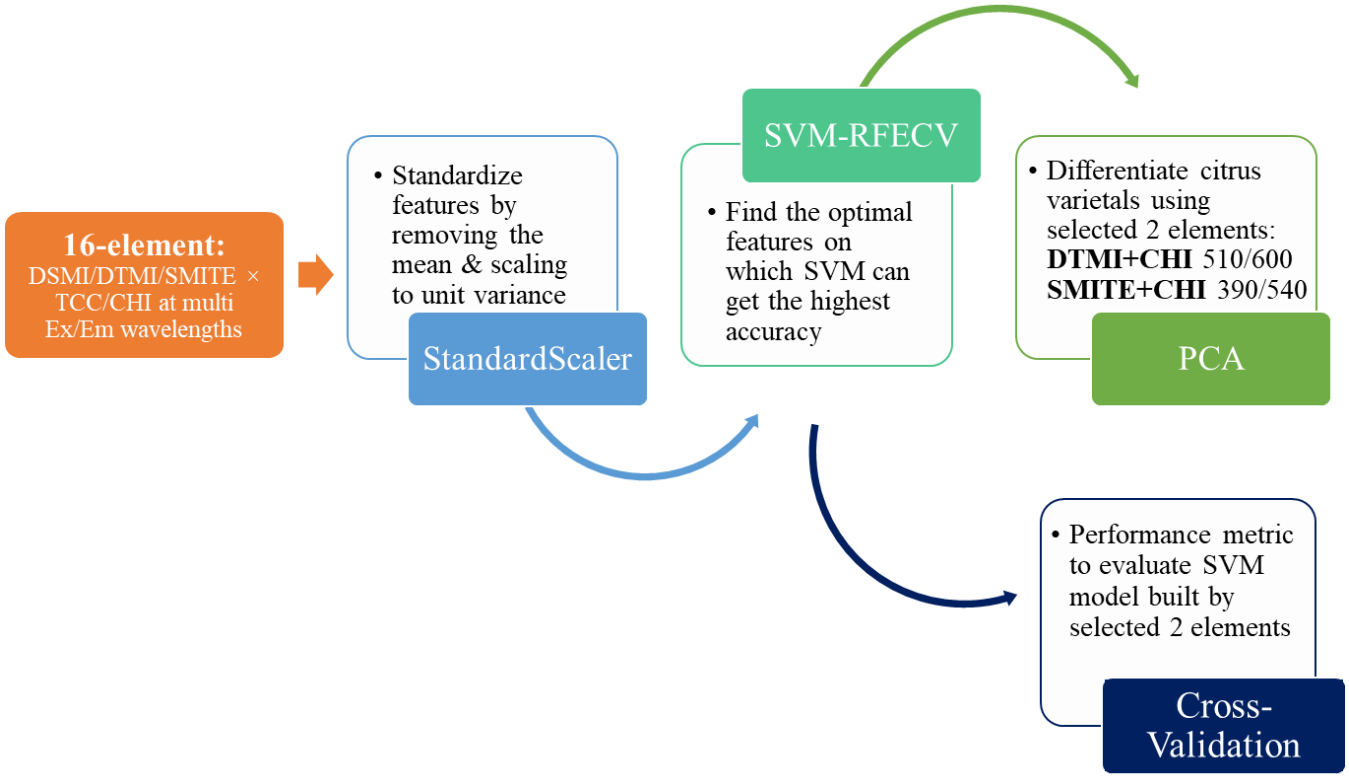

Figure S-28. Operational flowchart of the SVM-RFECV machine learning approach for feature selection.

Table *S*-6. SVM-RFECV rank list of 16-element **Host:Guest** array: **DSMI + TCC/CHI** at all three wavelengths Ex 460, 480, 500/Em 600 nm; **DTMI + TCC/CHI** at all three wavelengths Ex 510, 540, 560/Em 600 nm; and **SMITE + TCC/CHI** at both wavelengths Ex 390, 430/Em 540 nm for classification of four citrus varietals.

Dye + Host	Ex/Em (nm)	Rank	Select
DSMI + TCC	460/600	9	False
	480/600	2	False
	500/600	8	False
DSMI + CHI	460/600	14	False
	480/600	12	False
	500/600	15	False
DTMI + TCC	510/600	7	False
	540/600	5	False
	560/600	10	False
DTMI + CHI	510/600	1	True
	540/600	11	False
	560/600	6	False
SMITE + TCC	390/540	3	False
	430/540	4	False
SMITE + CHI	390/540	1	True
	430/540	13	False

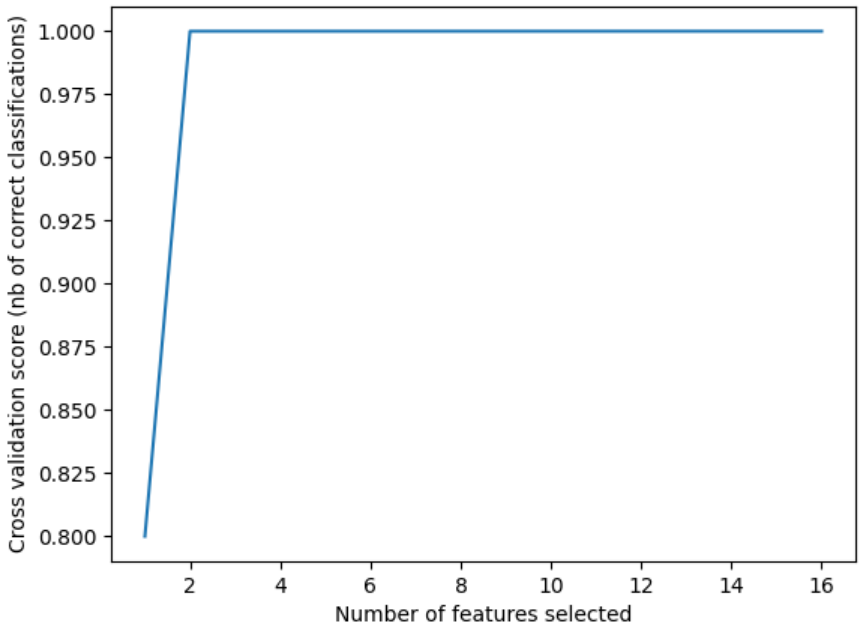

Figure *S*-29. The cross-validation scores correspond to the increasing numbers of features from the 16-element array for four citrus varietals classification.

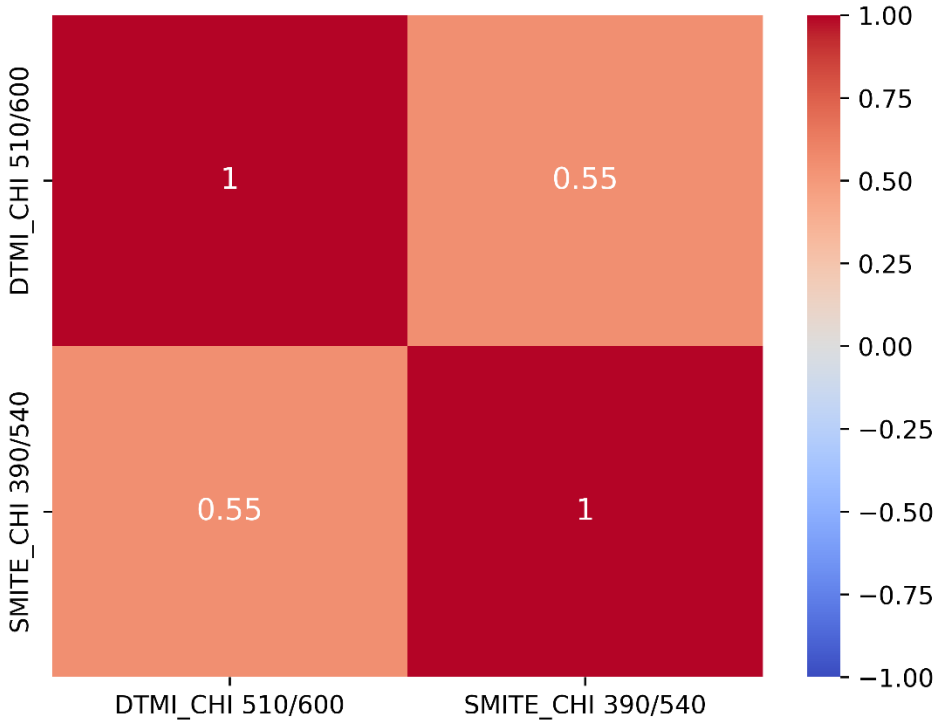

Figure *S*-30. Correlation heatmap of SVM-RFECV selected two features: **DTMI + CHI** 510/600 and **SMITE + CHI** 390/540 in the data set of four citrus varietals.

Table *S*-7. The 3-repeated 4-fold cross-validation scores of SVM-RFECV selected two elements **DTMI + CHI** 510/600 and **SMITE + CHI** 390/540 from the 16-element array, with SVM as the estimator for classification of four citrus varietals.

Evaluation Metrics	Score (standard deviation from 3 repeated running of the 4-fold cross validation)
Accuracy	1.0000 (0.0000)
Sensitivity	1.0000 (0.0000)
Specificity	1.0000 (0.0000)
Precision	1.0000 (0.0000)
F1 Score	1.0000 (0.0000)
AUC	1.0000 (0.0000)

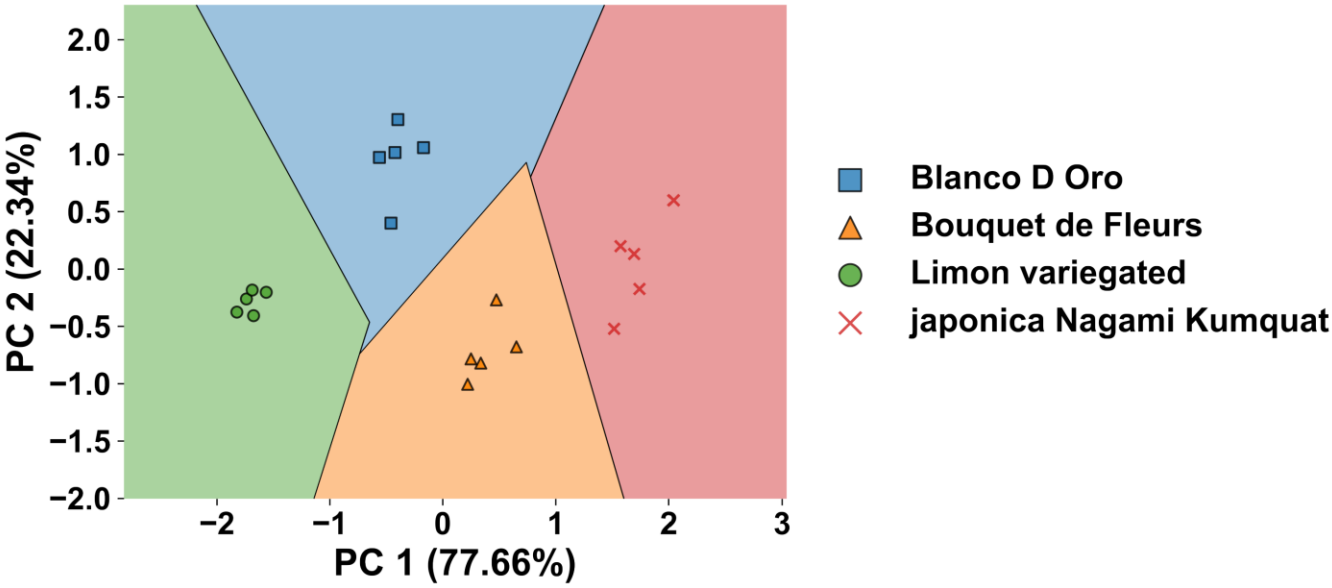

Figure *S*-31. The SVM decision region boundary plot for the classification of four citrus varietals using the PCA data of SVM-RFECV selected two elements **DTMI + CHI** 510/600 and **SMITE + CHI** 390/540 from the 16-element array.

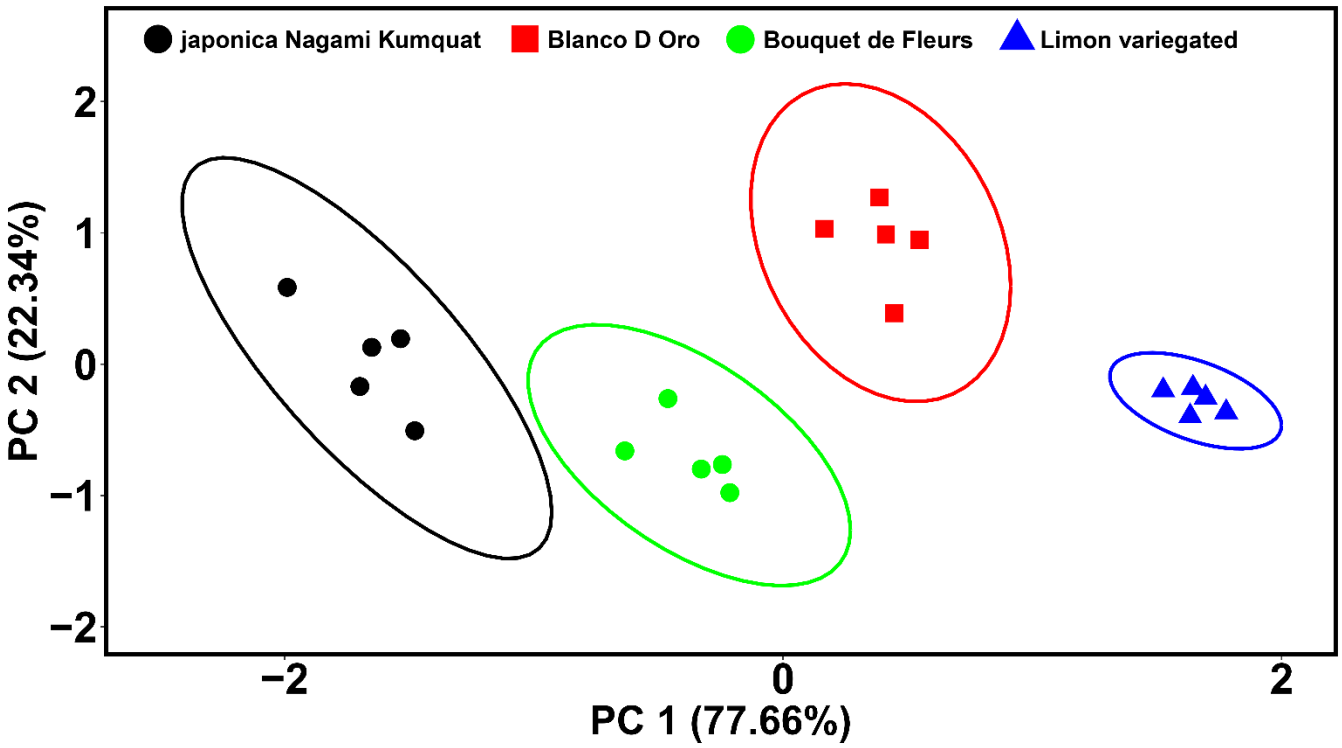

Figure *S*-32. The PCA score plot for the differentiation of four citrus varietals using the SVM-RFECV selected two elements **DTMI + CHI** 510/600 and **SMITE + CHI** 390/540 from the 16-element array. The ellipses indicate 95% confidence.

5.2 Reproducibility and Ripeness Analysis

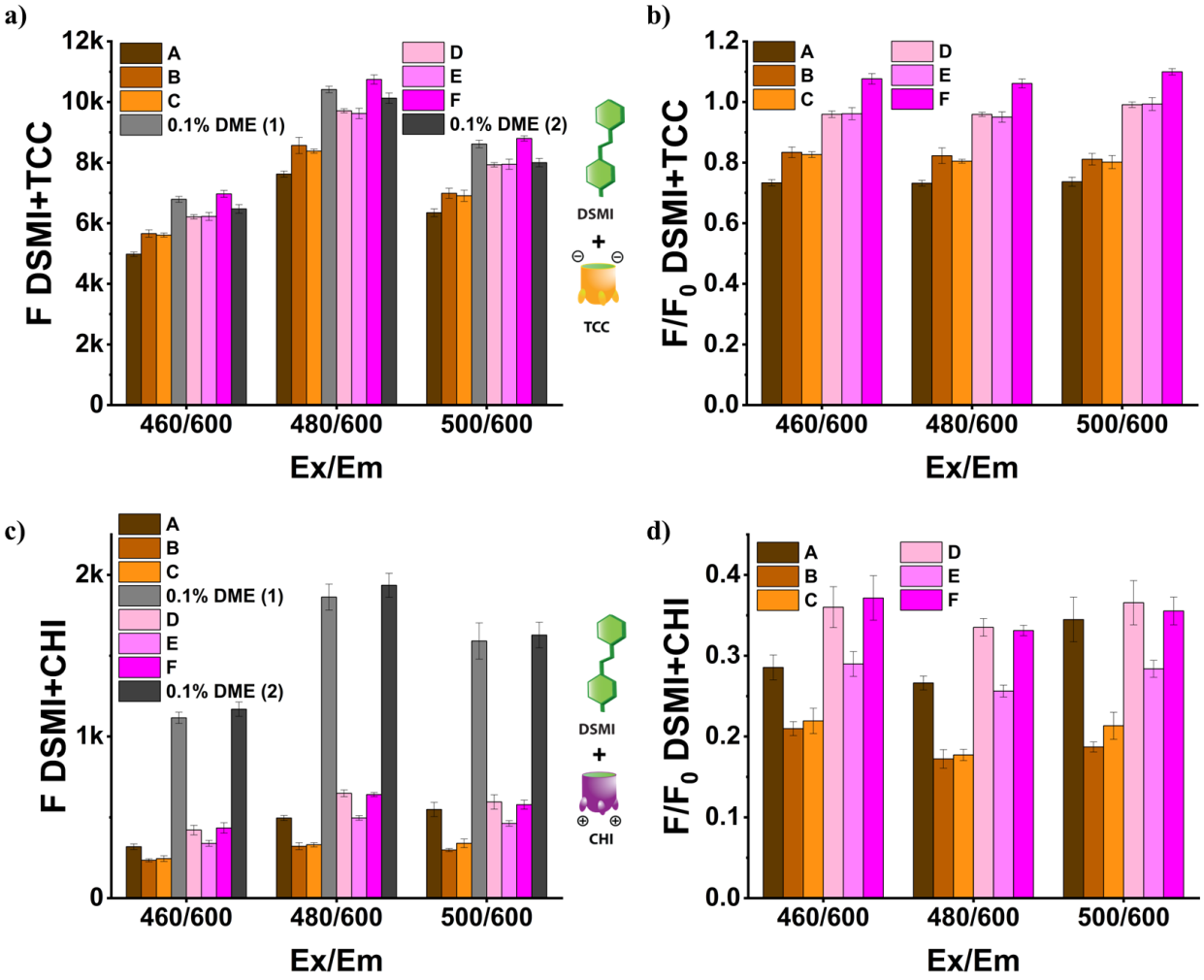

Figure *S*-33. Fluorescence emission (F) and F/F_0 bar plots of a,b) **DSMI + TCC**, and c,d) **DSMI + CHI** for sensing 'Blanco D' Oro' repeats Oct-A, B, C (harvested on October 27, 2023) and Dec-D, E, F (harvested on December 11, 2023) as well as blank 0.1% DME at Ex/Em = 460/600, 480/600 and 500/600 nm. [**DSMI**] = 0.5 μM, [**TCC/CHI**] = 4 μM, [Citrus Sample] = 200 μg/mL with 0.1% DME, in 20 mM Tris-HCl buffer at neutral pH. F/F_0 values were calculated using F divided by the response of sensor element in the absence of citrus sample but with 0.1% DME (F_0).

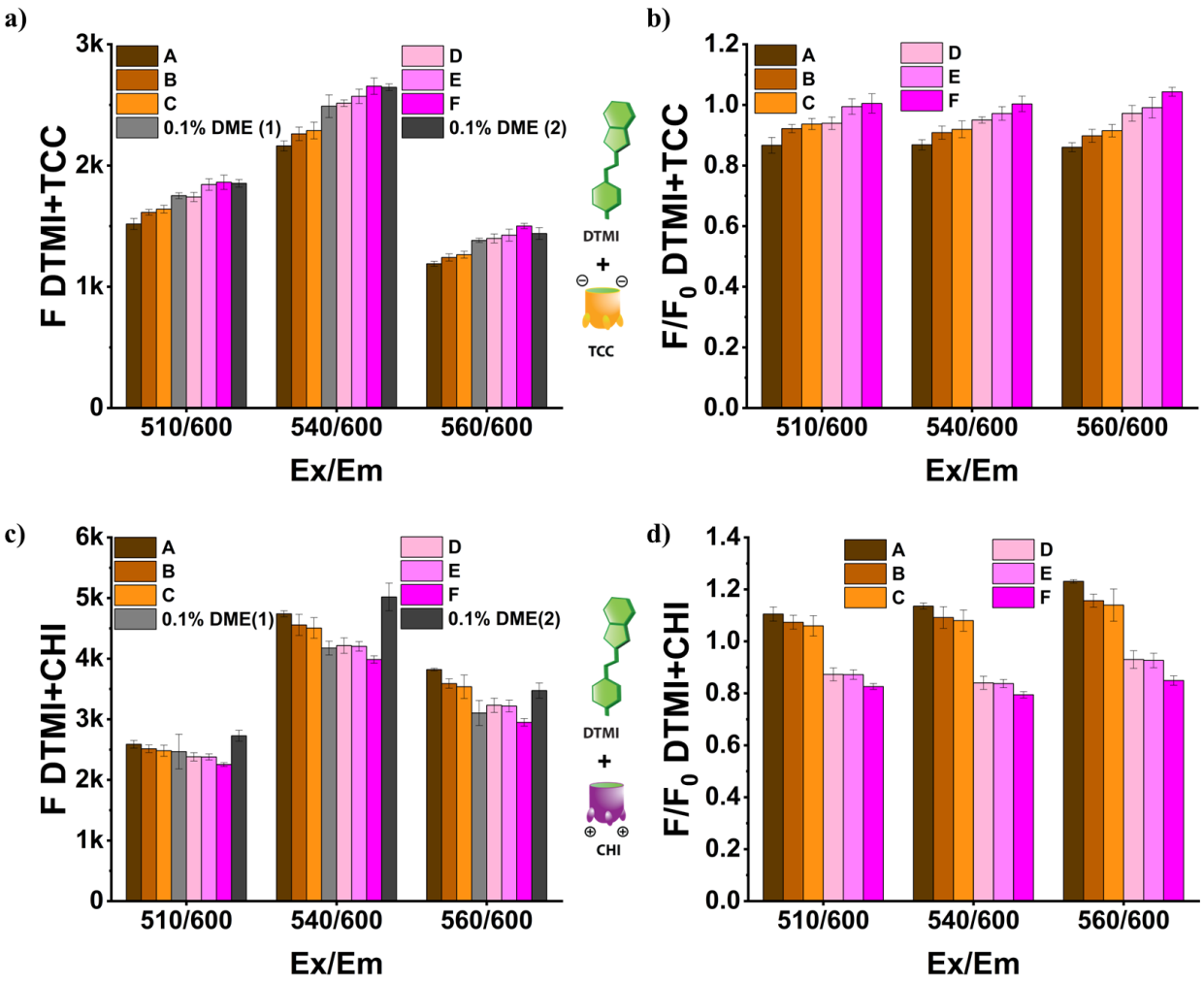

Figure *S*-34. Fluorescence emission (F) and F/F_0 bar plots of a,b) **DTMI + TCC**, and c,d) **DTMI + CHI** for sensing 'Blanco D' Oro' repeats Oct-A, B, C (harvested on October 27, 2023) and Dec-D, E, F (harvested on December 11, 2023) as well as blank 0.1% DME at Ex/Em = 510/600, 540/600 and 560/600 nm. [**DTMI**] = 0.5 μM, [**TCC/CHI**] = 4 μM, [Citrus Sample] = 200 μg/mL with 0.1% DME, in 20 mM Tris-HCl buffer at neutral pH. F/F_0 values were calculated using F divided by the response of sensor element in the absence of citrus sample but with 0.1% DME (F_0).

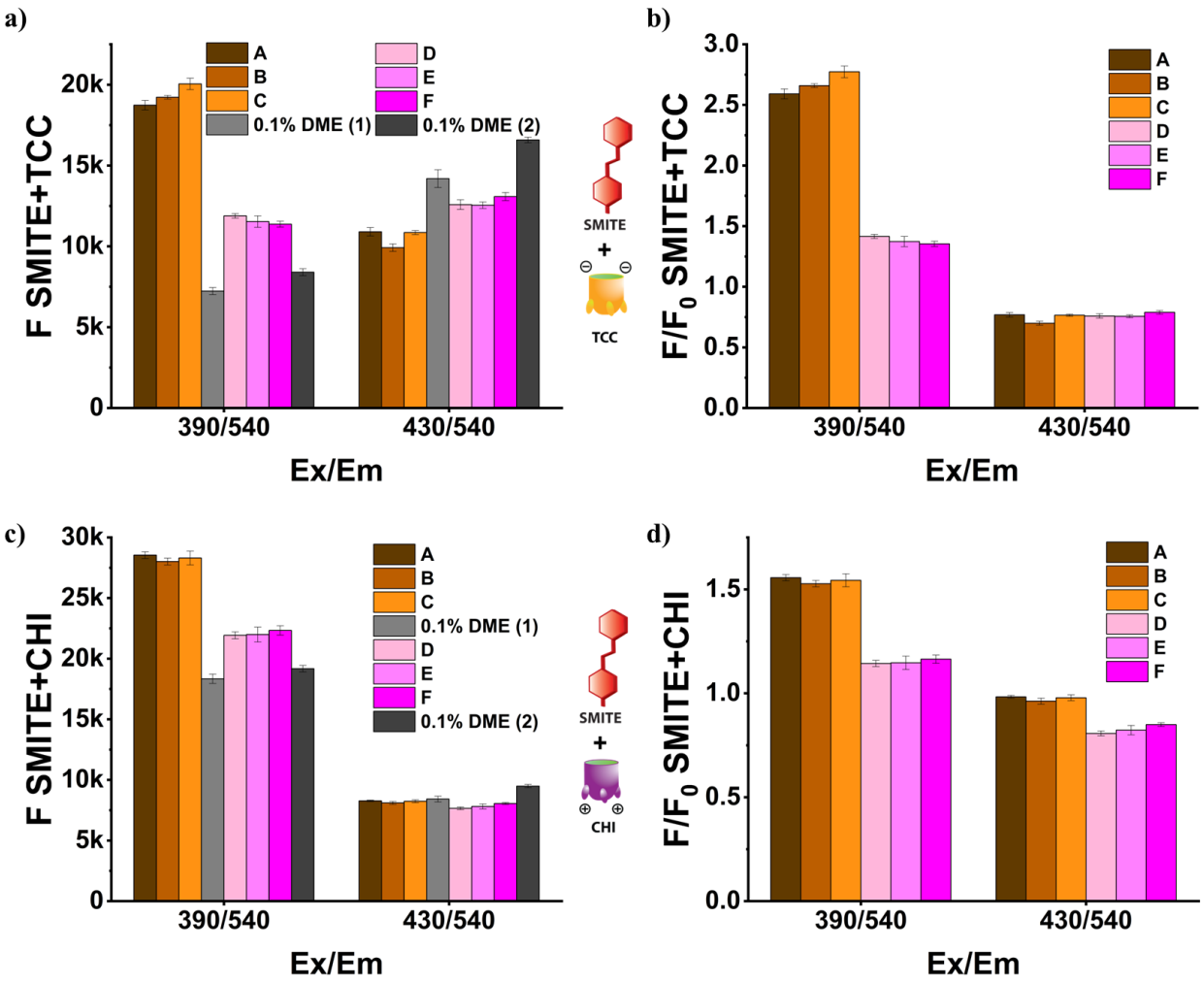

Figure *S*-35. Fluorescence emission (F) and F/F_0 bar plots of a,b) **SMITE + TCC**, and c,d) **SMITE + CHI** for sensing 'Blanco D' Oro' repeats Oct-A, B, C (harvested on October 27, 2023) and Dec-D, E, F (harvested on December 11, 2023) as well as blank 0.1% DME at Ex/Em = 390/540 and 430/540 nm. [**SMITE**] = 0.5 μM, [**TCC/CHI**] = 4 μM, [Citrus Sample] = 200 μg/mL with 0.1% DME, in 20 mM Tris-HCl buffer at neutral pH. F/F_0 values were calculated using F divided by the response of sensor element in the absence of citrus sample but with 0.1% DME (F_0).

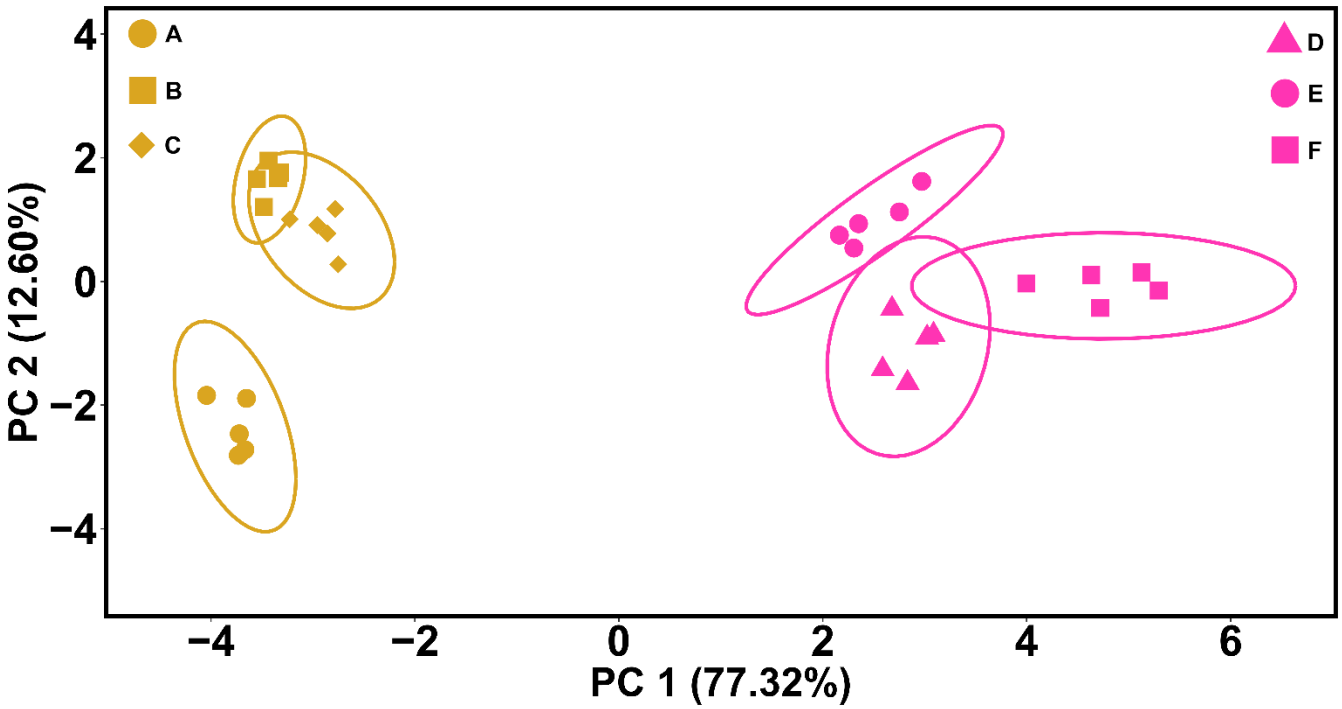

Figure *S*-36. PCA score plot of 'Blanco D' Oro' repeats Oct-A, B, C and Dec-D, E, F obtained with the F/F_0 data of 16-element **Host:Dye** sensor array (see bar plots in Figures *S*-33 − *S*-35): **DSMI + TCC/CHI** at all three wavelengths Ex 460, 480, 500/Em 600 nm; **DTMI + TCC/CHI** at all three wavelengths Ex 510, 540, 560/Em 600 nm; and **SMITE + TCC/CHI** at both wavelengths Ex 390, 430/Em 540 nm. **[Dye]** = 0.5 μM, **[Host]** = 4 μM, [Citrus Sample] = 0.2 mg/mL with 0.1% DME, buffer 20 mM Tris-HCl at neutral pH. The ellipses indicate 95% confidence.

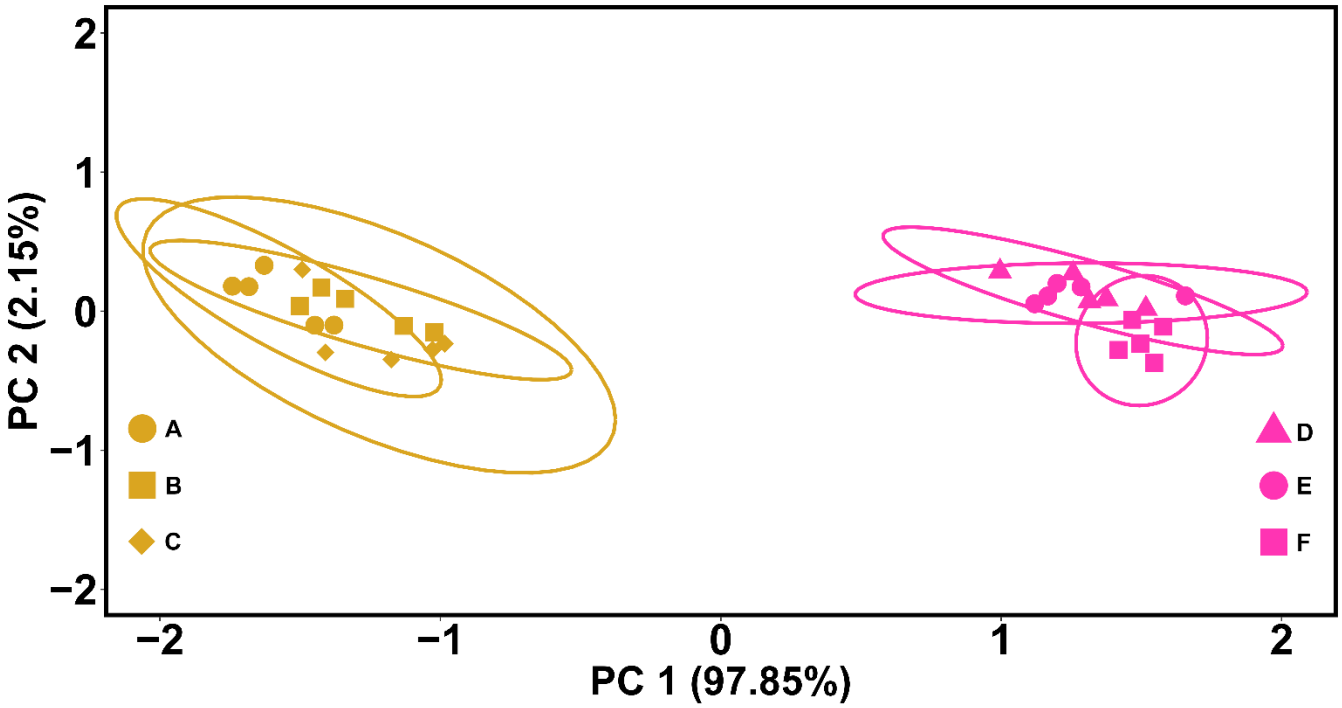

Figure *S*-37. The PCA score plot for the differentiation of 'Blanco D' Oro' repeats Oct-A, B, C and Dec-D, E, F using two elements **DTMI + CHI** 510/600 and **SMITE + CHI** 390/540 from the 16-element array. The ellipses indicate 95% confidence.

6. Fluorescence Titration Curves
6.1 Titration Curves of Limonene VS Citrus Sample

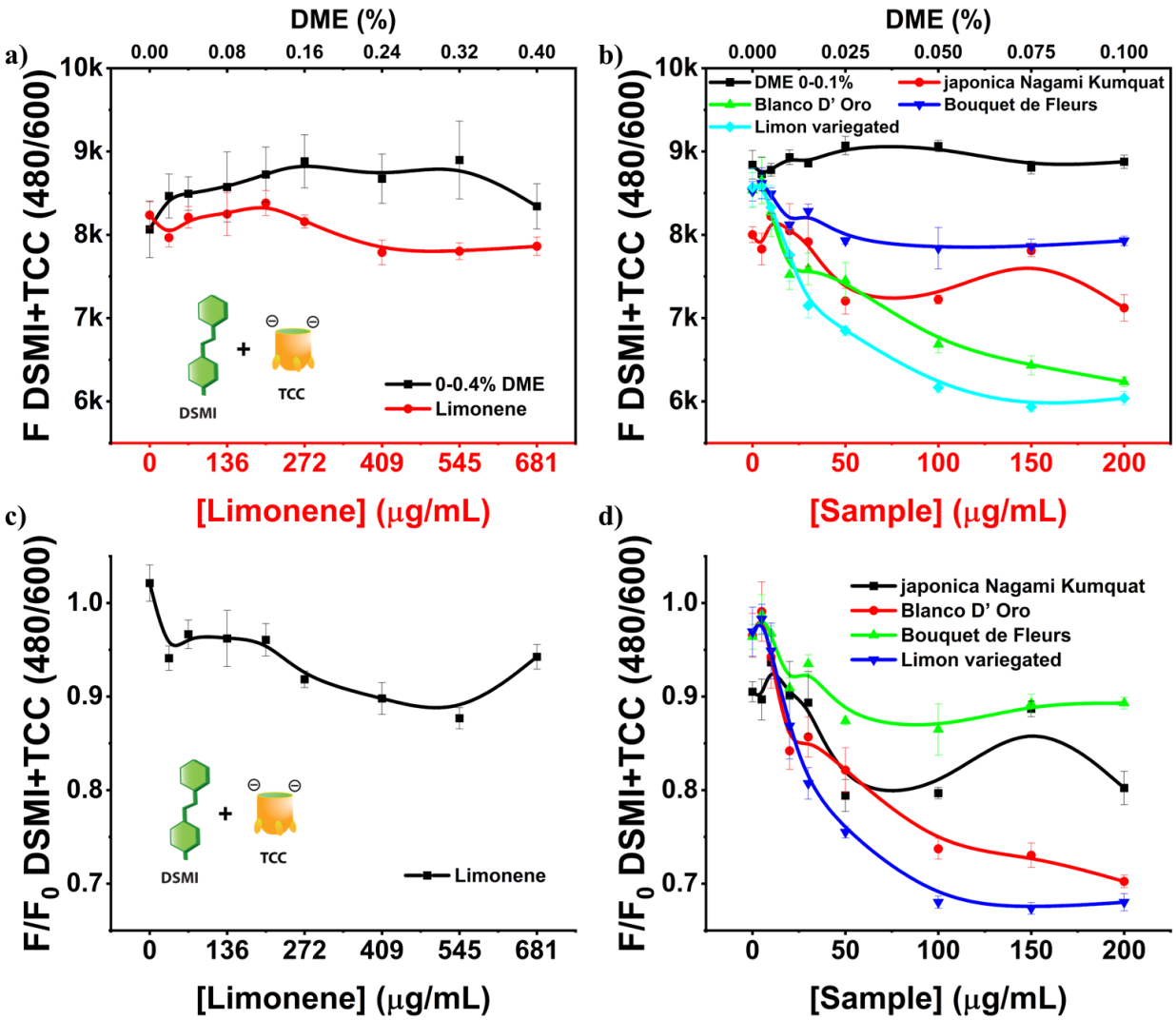

Figure S-38. Fluorescence (F) titration and F/F_0 curves of 0.5 µM **DSMI** + 4 µM **TCC** with increasing concentrations of a,c) 0 – 681 µg/mL (5 mM) limonene with 0 – 0.4% DME, or b,d) 0 – 200 µg/mL citrus sample with 0 – 0.1% DME in 20 mM Tris-HCl at neutral pH, Ex/Em = 480/600 nm. The F/F_0 values were calculated using F divided by the response of **DSMI + TCC** in the absence of limonene or sample but with the corresponding concentration of DME — F_0 which serves as the blank reference.

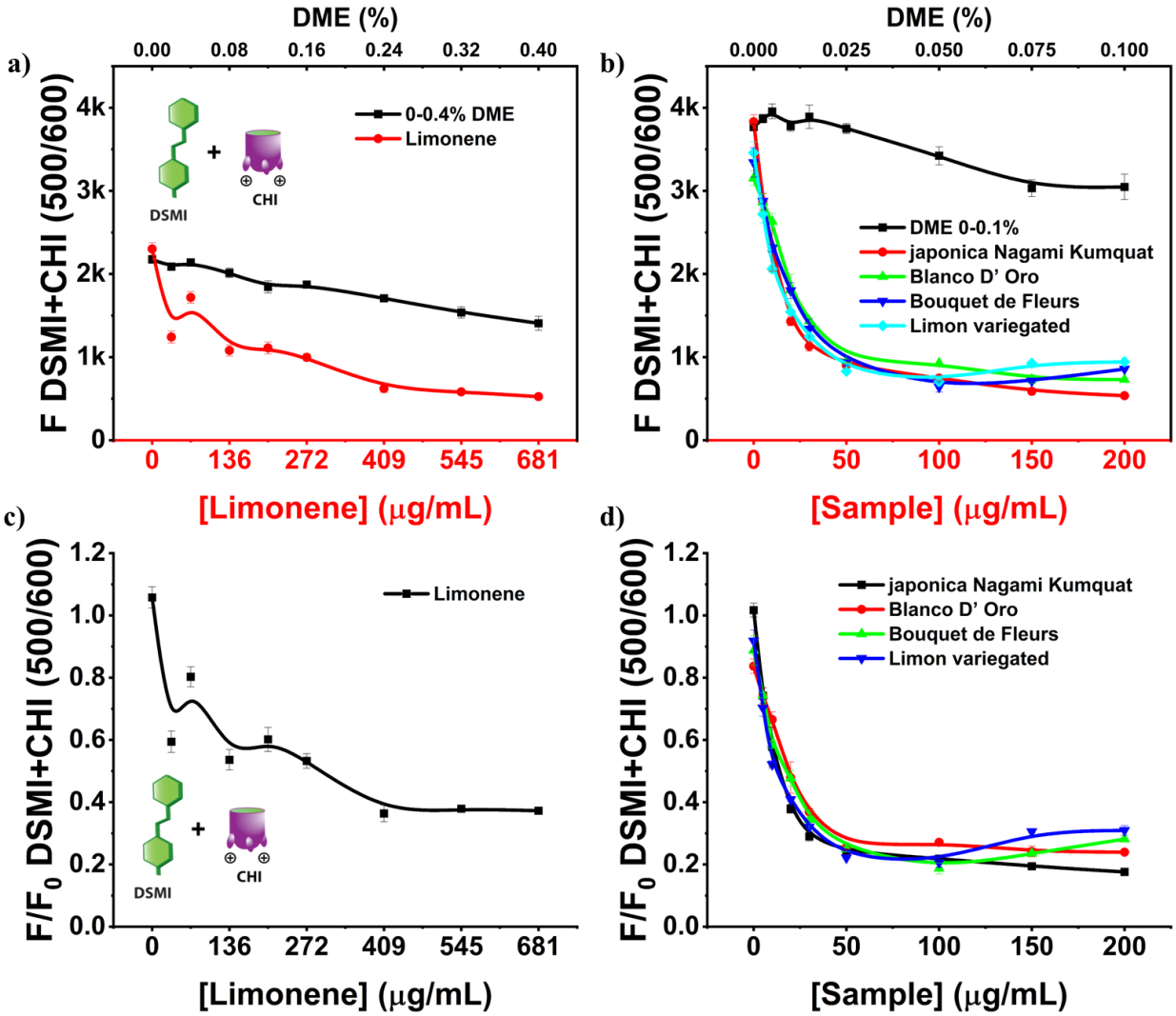

Figure *S*-39. Fluorescence (F) titration and F/F_0 curves of 0.5 μM **DSMI** + 4 μM **CHI** with increasing concentrations of a,c) 0 – 681 μg/mL (5 mM) limonene with 0 – 0.4% DME, or b,d) 0 – 200 μg/mL citrus sample with 0 – 0.1% DME in 20 mM Tris-HCl at neutral pH, Ex/Em = 500/600 nm. The F/F_0 values were calculated using F divided by the response of **DSMI** + **CHI** in the absence of limonene or sample but with the corresponding concentration of DME — F_0 which serves as the blank reference.

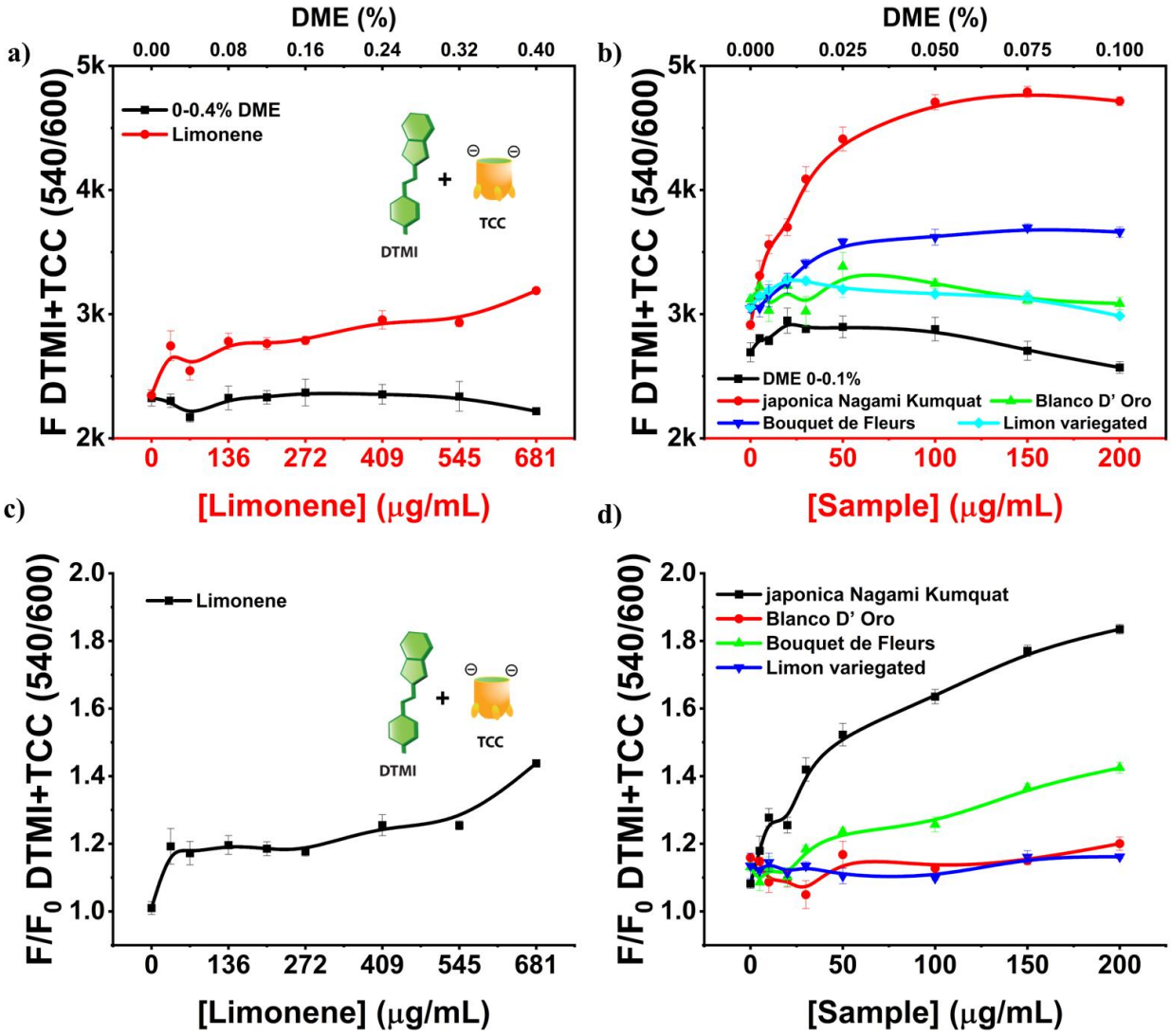

Figure *S*-40. Fluorescence (F) titration and F/F_0 curves of 0.5 μM **DTMI** + 4 μM **TCC** with increasing concentrations of a,c) 0 – 681 μg/mL (5 mM) limonene with 0 – 0.4% DME, or b,d) 0 – 200 μg/mL citrus sample with 0 – 0.1% DME in 20 mM Tris-HCl at neutral pH, Ex/Em = 540/600 nm. The F/F_0 values were calculated using F divided by the response of **DTMI + TCC** in the absence of limonene or sample but with the corresponding concentration of DME — F_0 which serves as the blank reference.

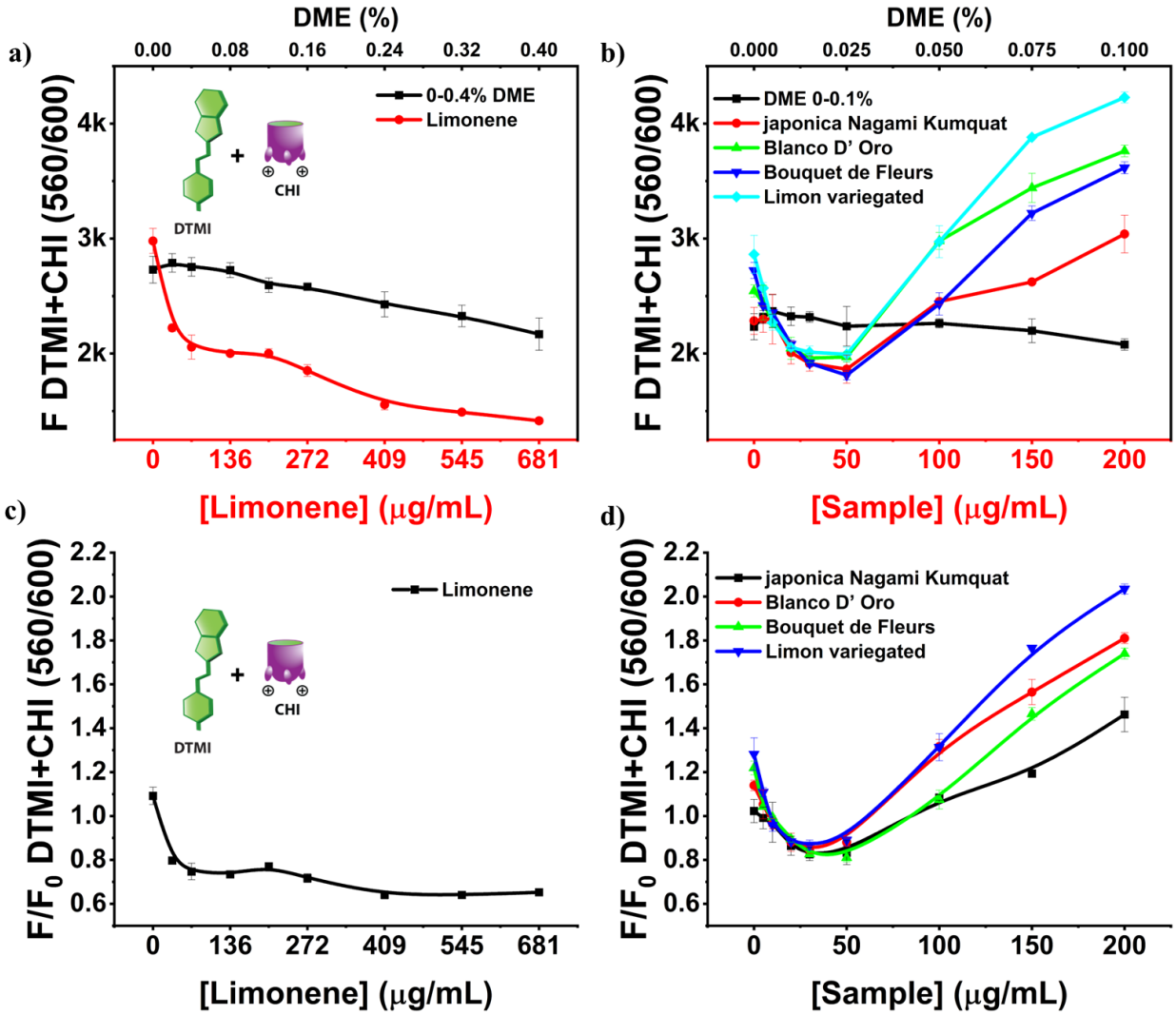

Figure *S*-41. Fluorescence (F) titration and F/F_0 curves of 0.5 μM **DTMI** + 4 μM **CHI** with increasing concentrations of a,c) 0 – 681 μg/mL (5 mM) limonene with 0 – 0.4% DME, or b,d) 0 – 200 μg/mL citrus sample with 0 – 0.1% DME in 20 mM Tris-HCl at neutral pH, Ex/Em = 560/600 nm. The F/F_0 values were calculated using F divided by the response of **DTMI** + **CHI** in the absence of limonene or sample but with the corresponding concentration of DME — F_0 which serves as the blank reference.

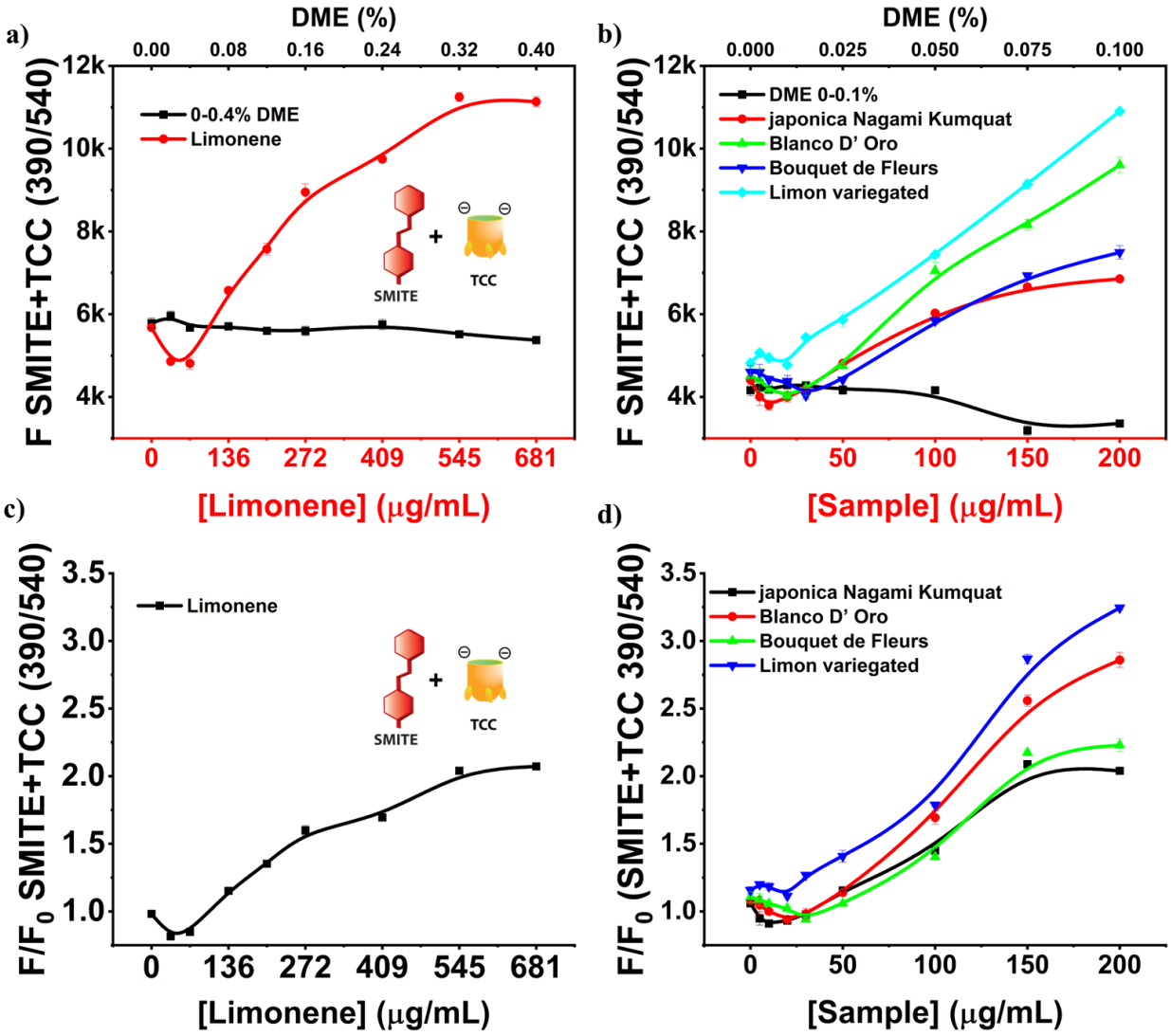

Figure *S*-42. Fluorescence (F) titration and F/F_0 curves of 0.5 μM **SMITE** + 4 μM **TCC** with increasing concentrations of a,c) 0 – 681 μg/mL (5 mM) limonene with 0 – 0.4% DME, or b,d) 0 – 200 μg/mL citrus sample with 0 – 0.1% DME in 20 mM Tris-HCl at neutral pH, Ex/Em = 390/540 nm. The F/F_0 values were calculated using F divided by the response of **SMITE + TCC** in the absence of limonene or sample but with the corresponding concentration of DME — F_0 which serves as the blank reference.

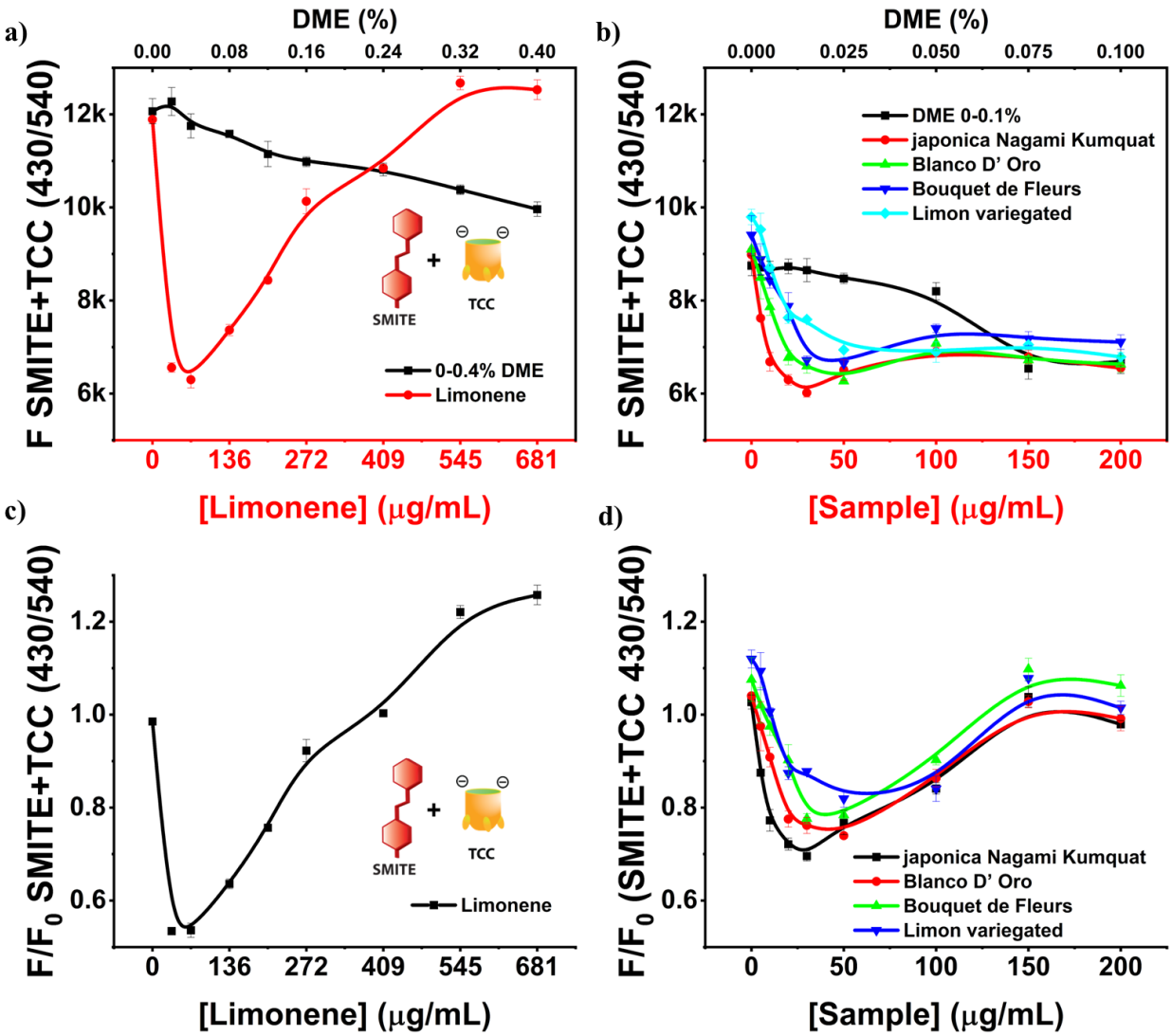

Figure *S*-43. Fluorescence (F) titration and F/F_0 curves of 0.5 μM **SMITE** + 4 μM **TCC** with increasing concentrations of a,c) 0 – 681 μg/mL (5 mM) limonene with 0 – 0.4% DME, or b,d) 0 – 200 μg/mL citrus sample with 0 – 0.1% DME in 20 mM Tris-HCl at neutral pH, Ex/Em = 430/540 nm. The F/F_0 values were calculated using F divided by the response of **SMITE + TCC** in the absence of limonene or sample but with the corresponding concentration of DME — F_0 which serves as the blank reference.

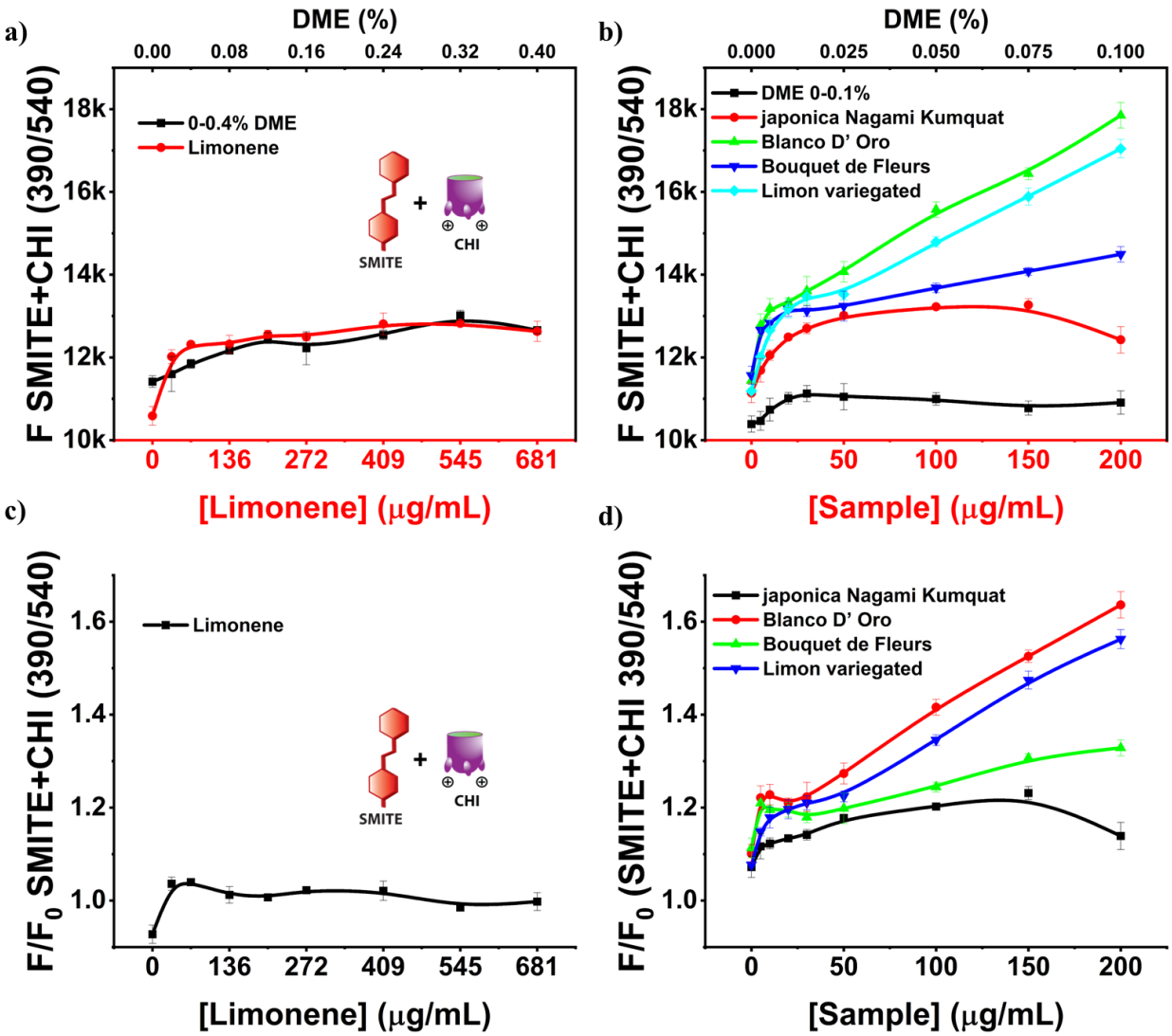

Figure *S*-44. Fluorescence (F) titration and F/F_0 curves of 0.5 µM **SMITE** + 4 µM **CHI** with increasing concentrations of a,c) 0 – 681 µg/mL (5 mM) limonene with 0 – 0.4% DME, or b,d) 0 – 200 µg/mL citrus sample with 0 – 0.1% DME in 20 mM Tris-HCl at neutral pH, Ex/Em = 390/540 nm. The F/F_0 values were calculated using F divided by the response of **SMITE + CHI** in the absence of limonene or sample but with the corresponding concentration of DME — F_0 which serves as the blank reference.

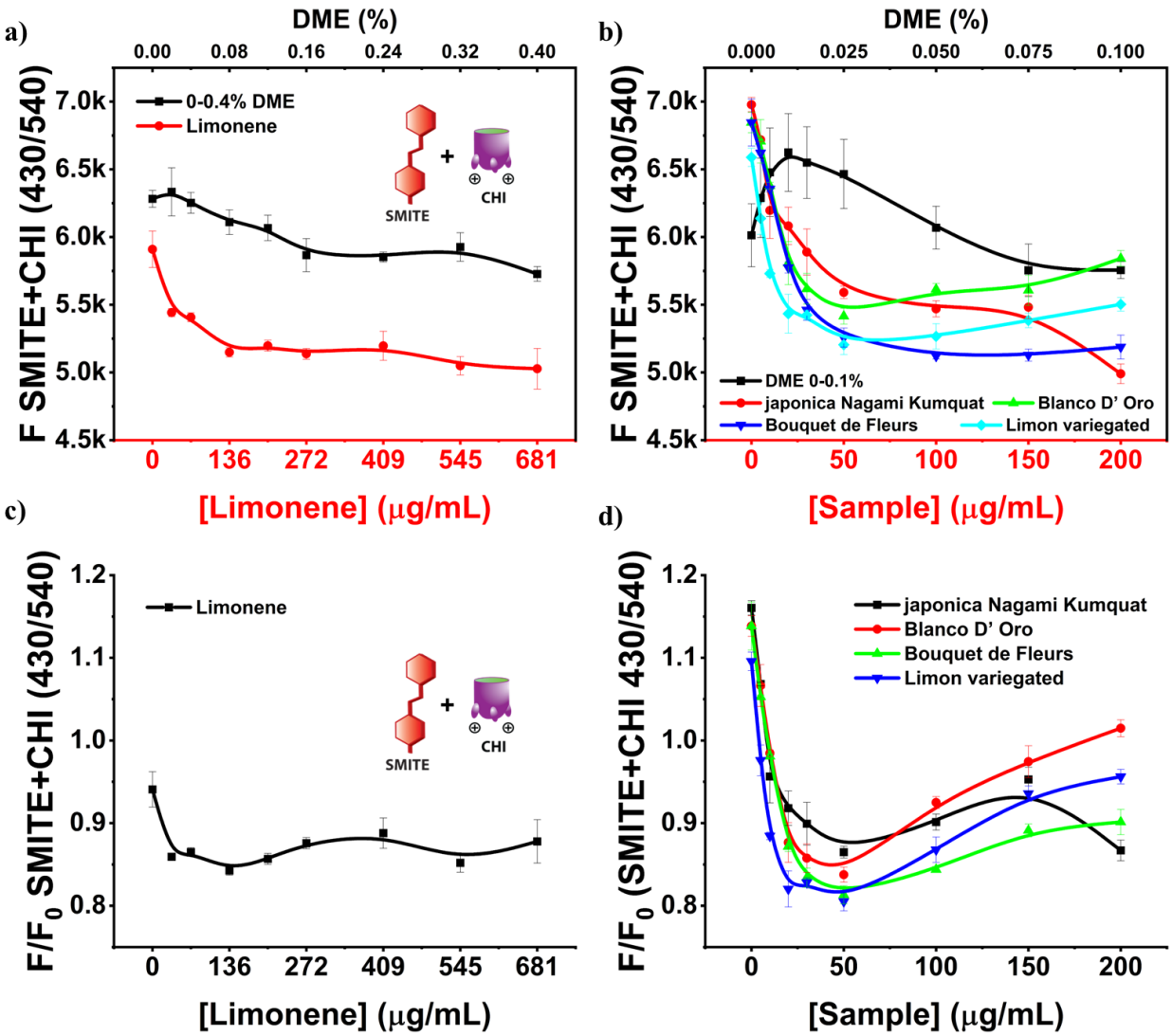

Figure S-45. Fluorescence (F) titration and F/F_0 curves of 0.5 μM **SMITE** + 4 μM **CHI** with increasing concentrations of a,c) 0 – 681 μg/mL (5 mM) limonene with 0 – 0.4% DME, or b,d) 0 – 200 μg/mL citrus sample with 0 – 0.1% DME in 20 mM Tris-HCl at neutral pH, Ex/Em = 430/540 nm. The F/F_0 values were calculated using F divided by the response of **SMITE + CHI** in the absence of limonene or sample but with the corresponding concentration of DME — F_0 which serves as the blank reference.

6.2 Fluorescence Impacts of Sample Only at Sensor Ex/Em

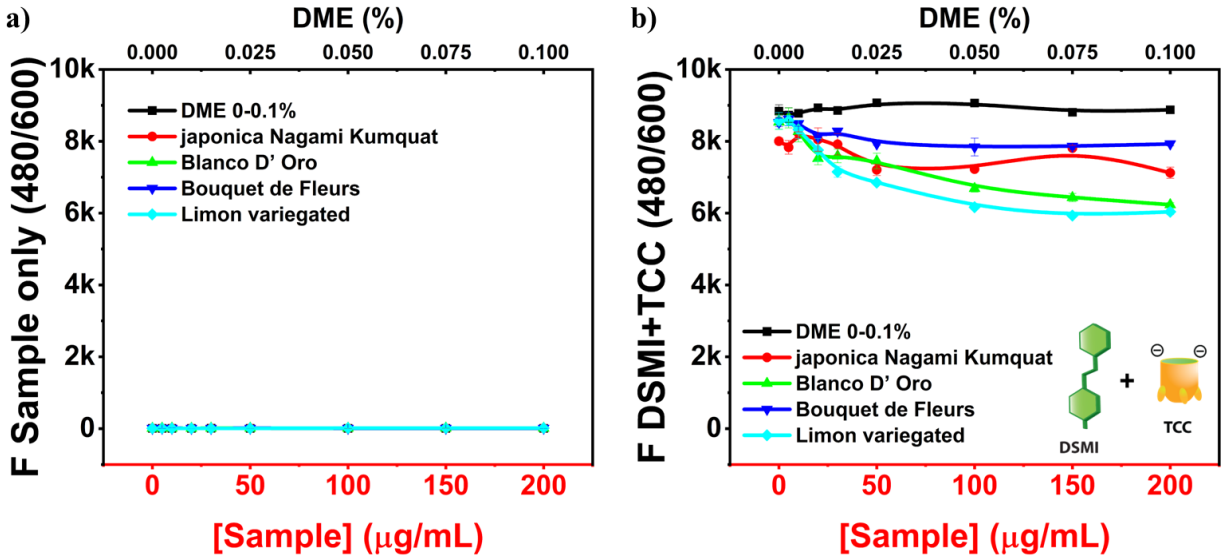

Figure *S*-46. Fluorescence (F) titration curves of a) sample only and b) sample sensed by 0.5 μM **DSMI**+ 4 μM **TCC** at Ex/Em = 480/600 nm. The range of citrus sample concentrations tested varies from 0 to 200 μg/mL with DME concentration varies from 0 to 0.1% in 20 mM Tris-HCl at neutral pH. The fluorescence impacts of sample only were measured at the Ex/Em wavelengths of **DSMI** + **TCC** 480/600 nm.

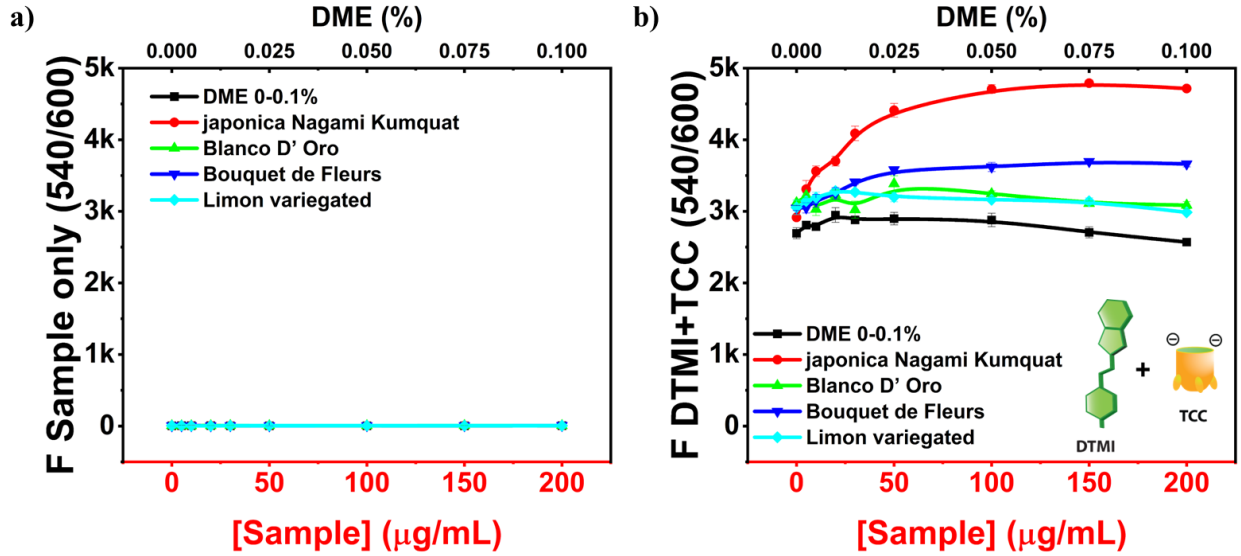

Figure *S*-47. Fluorescence titration curves of a) sample only and b) sample sensed by 0.5 μM **DTMI** + 4 μM **TCC** at Ex/Em = 540/600 nm. The range of citrus sample concentrations tested varies from 0 to 200 μg/mL with DME concentration varies from 0 to 0.1% in 20 mM Tris-HCl at neutral pH. The fluorescence impacts of sample only were measured at the Ex/Em wavelengths of **DTMI** + **TCC** 540/600 nm.

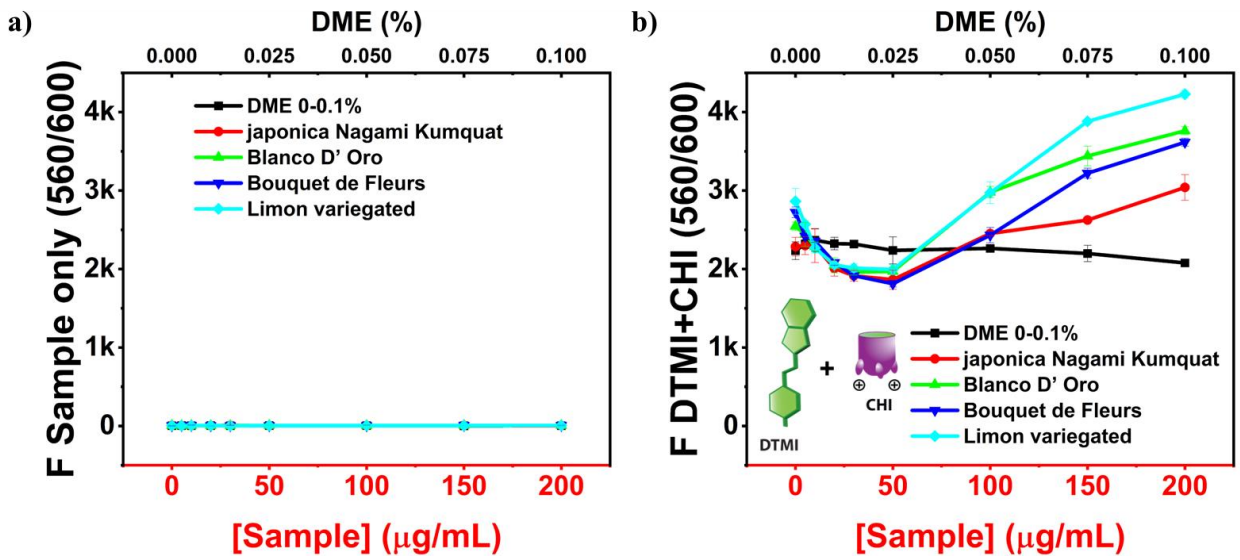

Figure *S*-48. Fluorescence titration curves of a) sample only and b) sample sensed by 0.5 μM **DTMI** + 4 μM **CHI** at Ex/Em = 560/600 nm. The range of citrus sample concentrations tested varies from 0 to 200 μg/mL with DME concentration varies from 0 to 0.1% in 20 mM Tris-HCl at neutral pH. The fluorescence impacts of sample only were measured at the Ex/Em wavelengths of **DTMI** + **CHI** 560/600 nm.

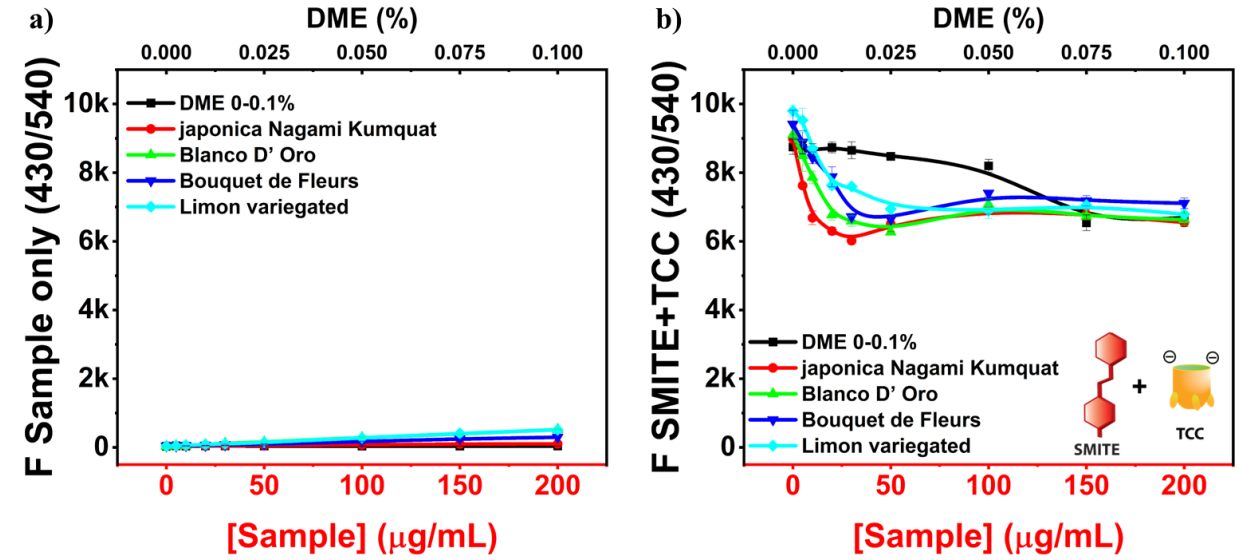

Figure *S*-49. Fluorescence titration curves of a) sample only and b) sample sensed by 0.5 μM **SMITE** + 4 μM **TCC** at Ex/Em = 430/540 nm. The range of citrus sample concentrations tested varies from 0 to 200 μg/mL with DME concentration varies from 0 to 0.1% in 20 mM Tris-HCl at neutral pH. The fluorescence impacts of sample only were measured at the Ex/Em wavelengths of **SMITE** + **TCC** 430/540 nm.

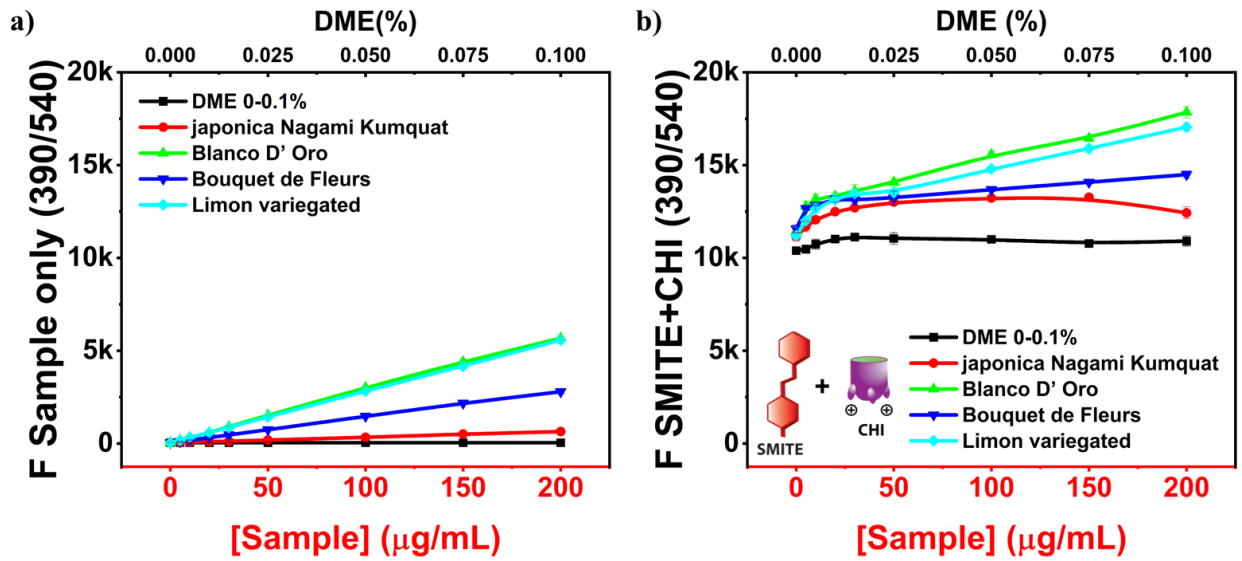

Figure *S*-50. Fluorescence titration curves of a) sample only and b) sample sensed by 0.5 μM **SMITE** + 4 μM **CHI** at Ex/Em = 390/540 nm. The range of citrus sample concentrations tested varies from 0 to 200 μg/mL with DME concentration varies from 0 to 0.1% in 20 mM Tris-HCl at neutral pH. The fluorescence impacts of sample only were measured at the Ex/Em wavelengths of **SMITE** 390/540 nm.

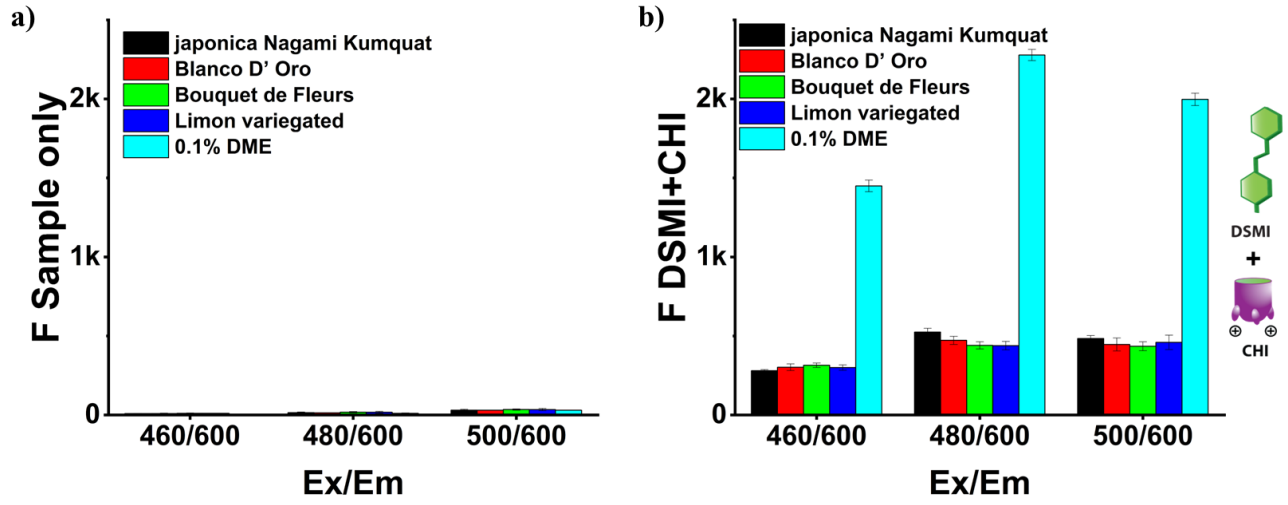

Figure *S*-51. Fluorescence bar plot of a) sample only and b) sample sensed by 0.5 μM **DSMI** + 4 μM **CHI** at Ex/Em = 460/600, 480/600 and 500/600 nm. [Citrus Sample] = 200 μg/mL with 0.1% DME, in 20 mM Tris-HCl buffer at neutral pH. The fluorescence impacts of sample only were measured at the Ex/Em wavelengths of **DSMI** 460/600, 480/600 and 500/600 nm.

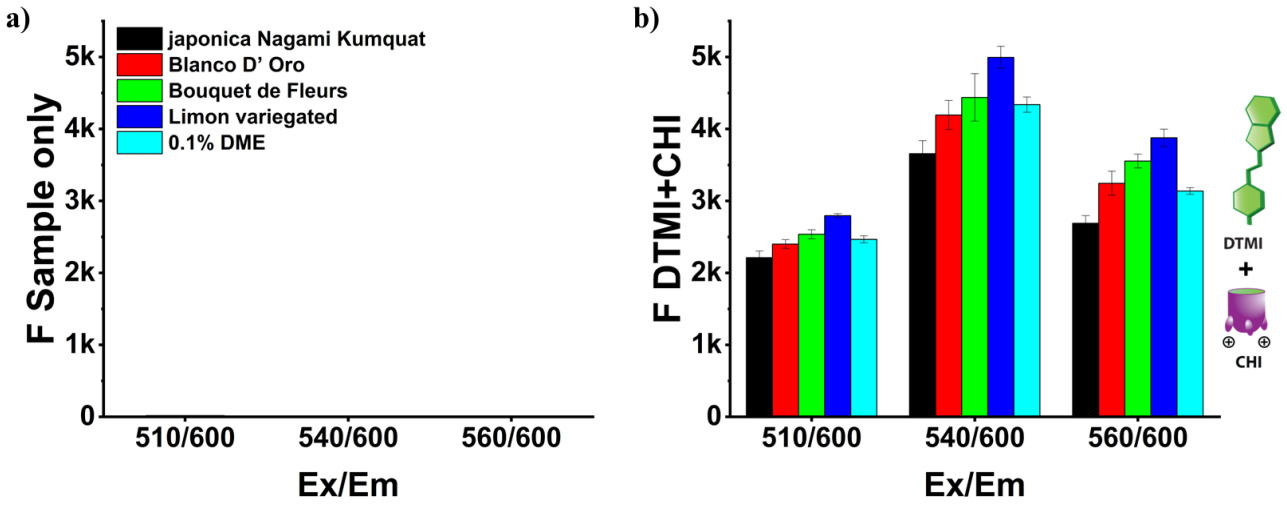

Figure *S*-52. Fluorescence bar plot of a) sample only and b) sample sensed by 0.5 μM **DTMI** + 4 μM **CHI** at Ex/Em = 510/600, 540/600 and 560/600 nm. [Citrus Sample] = 200 μg/mL with 0.1% DME, in 20 mM Tris-HCl buffer at neutral pH. The fluorescence impacts of sample only were measured at the Ex/Em wavelengths of **DTMI** 510/600, 540/600 and 560/600 nm.

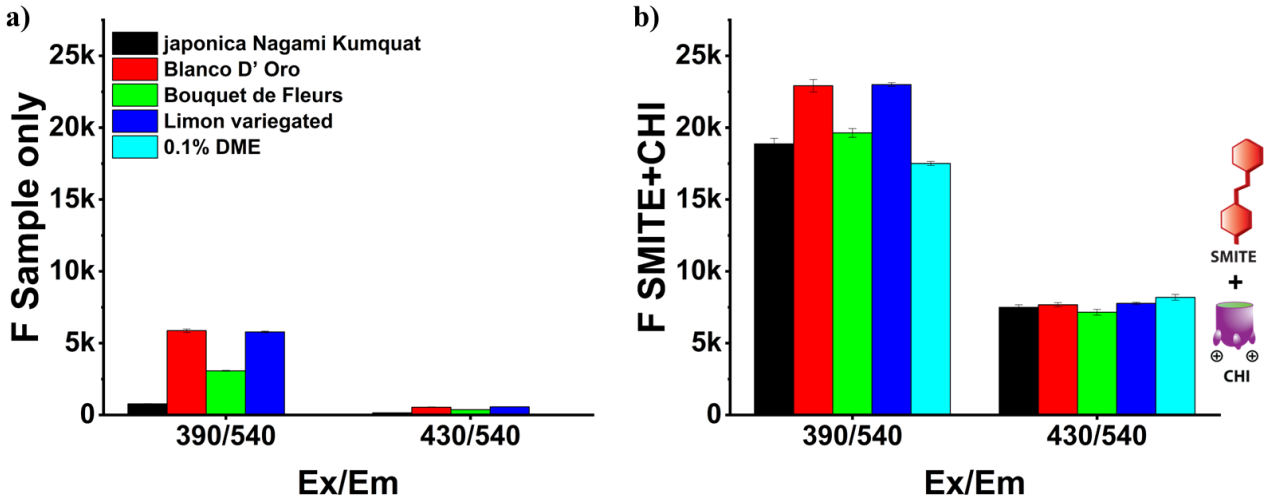

Figure *S*-53. Fluorescence bar plot of a) sample only and b) sample sensed by 0.5 μM **SMITE** + 4 μM **CHI** at Ex/Em = 390/540 and 430/540 nm. [Citrus Sample] = 200 μg/mL with 0.1% DME, in 20 mM Tris-HCl buffer at neutral pH. The fluorescence impacts of sample only were measured at the Ex/Em wavelengths of **SMITE** 390/540 and 430/540 nm.

6.3 Titration Curves of Other Terpenoids

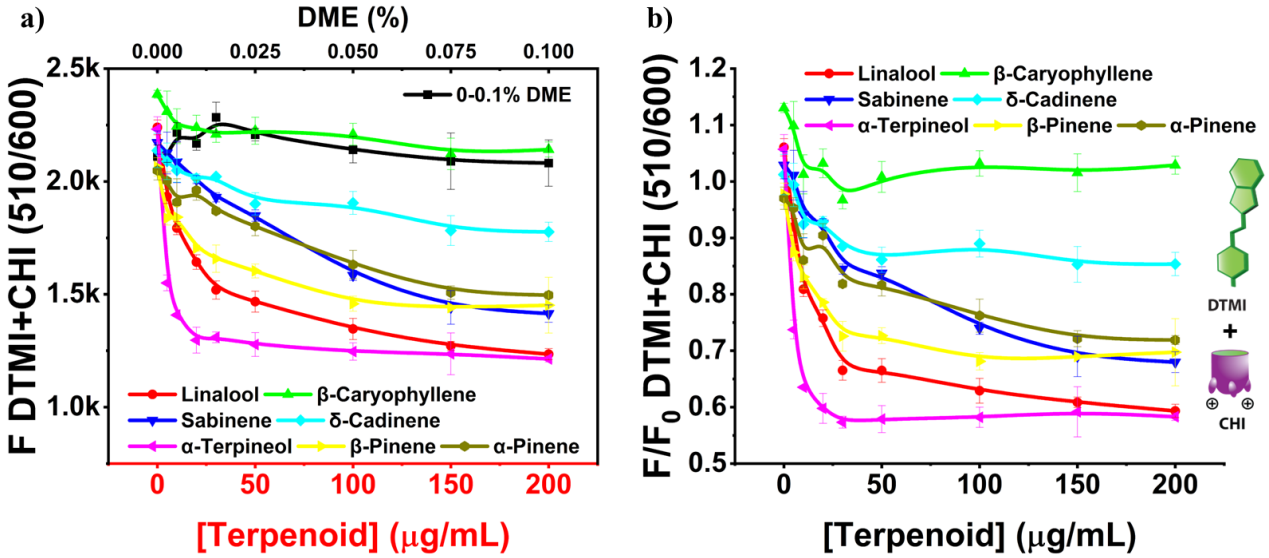

Figure *S*-54. Fluorescence (F) titration and F/F_0 curves of 0.5 μM **DTMI** + 4 μM **CHI** with increasing concentrations of 0 – 200 μg/mL terpenoid with 0 – 0.1% DME in 20 mM Tris-HCl at neutral pH, Ex/Em = 510/600 nm. **DTMI** + **CHI** 510/600 was used in terpenoid titration since it was ranked as one of the top sensors in the 16-element array. The F/F_0 values were calculated using F divided by the response of **DTMI** + **CHI** in the absence of terpenoid but with the corresponding concentration of DME — F_0 which serves as the blank reference.

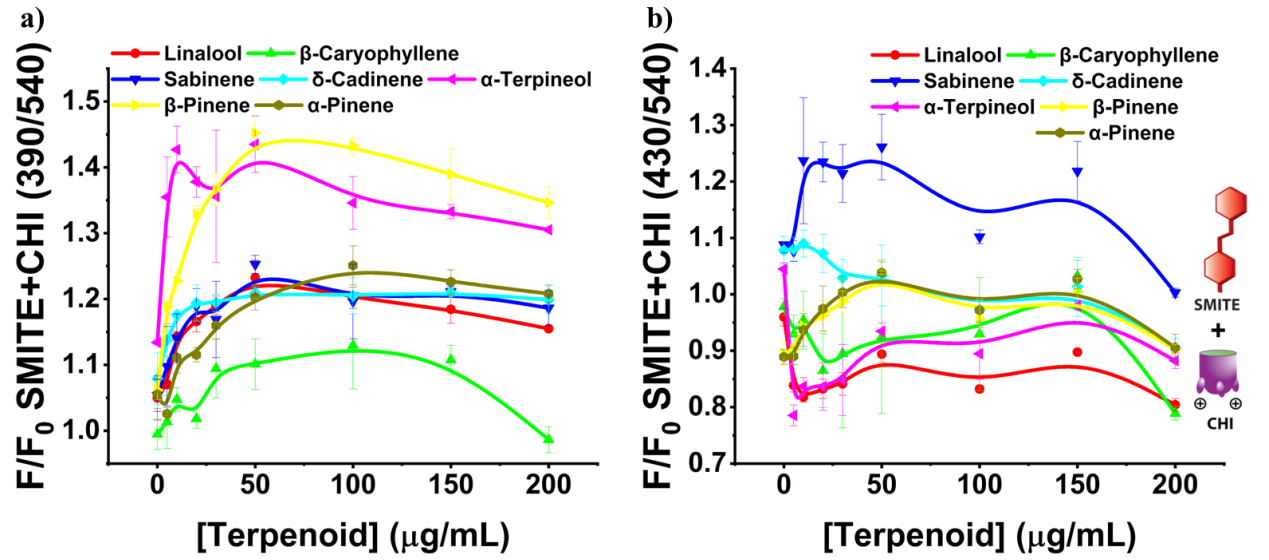

Figure *S*-55. F/F_0 titration curves of terpenoids sensed by 0.5 μM **SMITE** + 4 μM **CHI** at Ex/Em = a) 390/540 and b) 430/540 nm. The range of terpenoid concentrations tested varies from 0 to 200 μg/mL with DME concentration varies from 0 to 0.1% in 20 mM Tris-HCl at neutral pH. **SMITE** + **CHI** 390/540 was used in terpenoid titration since it was ranked as one of the top sensors in the 16-element array. The F/F_0 values were calculated using F divided by the response of sensor in the absence of terpenoid but with the corresponding concentration of DME — F_0 which serves as the blank reference.

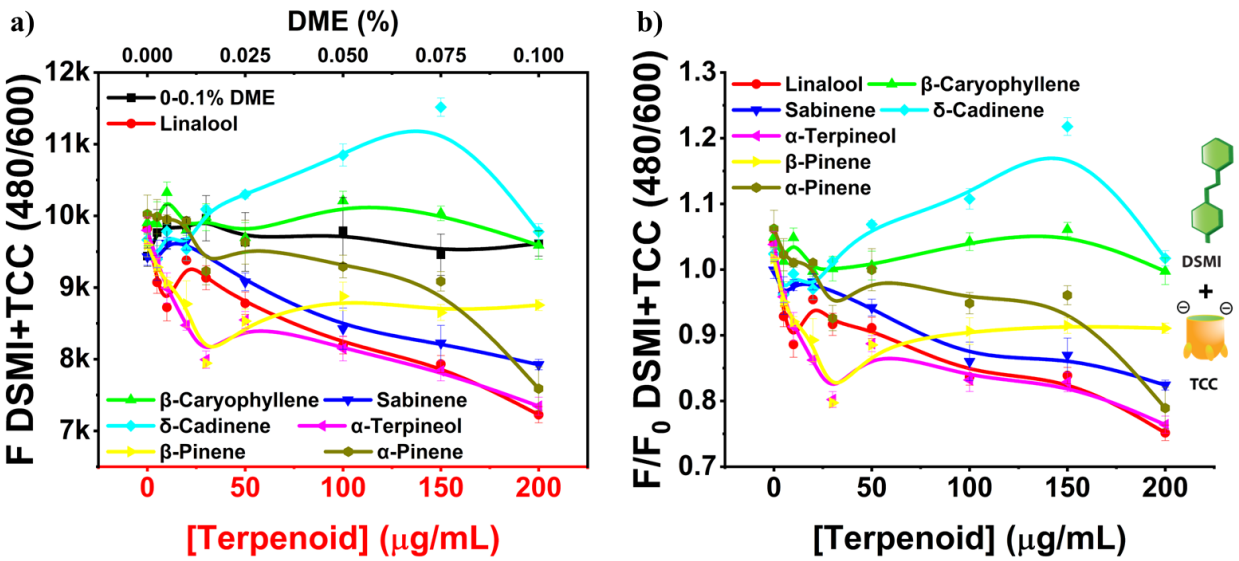

Figure *S*-56. Fluorescence (F) titration and F/F_0 curves of 0.5 µM **DSMI** + 4 µM **TCC** with increasing concentrations of 0 – 200 µg/mL terpenoid with 0 – 0.1% DME in 20 mM Tris-HCl at neutral pH, Ex/Em = 480/600 nm. **DSMI** + **TCC** 480/600 was used in terpenoid titration since it was ranked as the top second sensor in the 16-element array. The F/F_0 values were calculated using F divided by the response of **DSMI** + **TCC** in the absence of terpenoid but with the corresponding concentration of DME — F_0 which serves as the blank reference.

7. References

1. S. M. Biros, E. C. Ullrich, F. Hof, L. Trembleau and J. Rebek, Jr., *J. Am. Chem. Soc.*, 2004, **126**, 2870-2876.
2. S. Mosca, Y. Yu and J. Rebek, Jr., *Nat. Protoc.*, 2016, **11**, 1371-1387.
3. Y. Liu, M. Mettry, A. D. Gill, L. Perez, W. Zhong and R. J. Hooley, *Anal. Chem.*, 2017, **89**, 11113-11121.
4. J. Chen, B. L. Hickey, Z. Gao, A. A. P. Raz, R. J. Hooley and W. Zhong, *ACS Sens.*, 2022, **7**, 2164-2169.
5. B. L. Hickey, J. Chen, Y. Zou, A. D. Gill, W. Zhong, J. G. Millar and R. J. Hooley, *Chem. Commun.*, 2021, **57**, 13341-13344.