# **Supplementary Information**

# for

# Film-based Fluorescent Sensing: A "Chemical Nose" for Nicotine

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#### 1. Experimental Section

**Materials.** Phenylboronic acid derivatives (Adamas reagent, >98.0%), decaborane (United Boron, >95.0%), Pd(OAc)<sub>2</sub> (3A, 99%), and bis(diphenylphosphino)ferrocene (DPPF, Alfa Aesar, 98%) were obtained commercially. Unless stated otherwise, all other reagents were obtained from commercial sources and used without further purification. Tetrahydrofuran (THF) and diisopropylamine were distilled from metallic sodium (calcium hydride) under argon prior to use. Bis(4-bromobenzene)-*o*-carborane was synthesized and characterized according to the literature.<sup>1</sup> The cigarettes (cigarette 1: Furongwang, nicotine 1.4 mg; cigarette 2: Changsha, nicotine 1.0 mg) and E-cigarettes (E-cigarette 1: Discovery-1, nicotine 12 mg; E-cigarette 2: Discovery-2, nicotine 14 mg) were obtained commercially.

**Measurements.** <sup>1</sup>H (600 MHz), <sup>13</sup>C (150 MHz) and <sup>11</sup>B (192 MHz) NMR measurements were recorded on a Bruker AV 600 NMR spectrometer. UV-Vis spectra in solution were recorded on a Hitachi U-3900/3900H spectrophotometer at room temperature. The high-resolution mass spectra (HRMS) were acquired in atmospheric pressure chemical ionization (APCI) sources using a Bruker maXis UHR-TOF mass spectrometer. Steady state fluorescence excitation and emission spectra were obtained by using a time-correlated single photon counting fluorescence spectrometer (Edinburgh Instrument FLS920) with xenon lamp as the light source at room temperature. Fluorescence lifetimes were measured on the same system. Single-crystal X-ray diffraction was obtained using a Bruker D8 Quest single-crystal X-ray diffraction spectrometer.

**X-ray Crystallography Analyses.** Single-crystals of fluorophores F1-F4 were obtained from  $CH_2Cl_2/n$ -hexane solution. All data were collected using a Bruker APEX II CCD detector/D8 diffractometer using Cu (Ga, Mo) K $\alpha$  radiation. The data were corrected for absorption through Gaussian integration from indexing of the crystal faces. Structures were solved using the direct methods programs SHELXS-97,

and refinements were completed using the program SHELXL-97.<sup>2</sup> The crystallographic information has been deposited with Cambridge Crystallographic Data Centre, and signed to CCDC code 1917768 for F1, 1917769 for F2, 1917770 for F3 and 1917767 for F4.

General Procedure for the Synthesis of Fluorophores F1-F4: The *o*-carborane-based fluorophores were synthesized through a Suzuki coupling reaction (Scheme S1). Bis(4-bromobenzene)-*o*-carborane (454.0 mg, 1.0 mmol), phenyl-acetylene derivative (1-4, 3.0 mmol), Pd(OAc)<sub>2</sub> (112.0 mg, 0.05 mmol) and DPPF (227.0 mg, 0.05 mmol) were placed in a 10 mL Pyrex tube equipped with a magnetic stirrer. The equipment was purged with N<sub>2</sub>, followed by adding THF (10 mL) and diisopropylamine (5 mL). After refluxed for 10 h, the reaction mixture was cooled down, diluted with CHCl<sub>3</sub>, and washed with water and brine. Then, the organic layer was dried over anhydrous MgSO<sub>4</sub> and concentrated. Finally, the crude mixture was purified by silica gel column chromatography using dichloromethane/*n*-hexane as the eluent.



Scheme S1. Synthetic route of the o-carborance-based fluorophores.

**Fluorophore F1.** White powder (230 mg, 53%). <sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS, 600 MHz):  $\delta$  (ppm), 7.53 (d, J = 8.6 Hz, 4H), 7.49-7.45 (m, 4H), 7.43-7.36 (m, 8H), 7.33 (t, J=7.3 Hz, 2H), 3.14-1.99 (m, 10H). <sup>11</sup>B NMR (CDCl<sub>3</sub>, 192 MHz):  $\delta$  (ppm), -2.22, -2.88, -7.69, -10.01, -10.86. <sup>13</sup>C NMR (CDCl<sub>3</sub>/TMS, 150 MHz):  $\delta$  (ppm), 142.8, 139.2,

131.0, 129.6, 128.8, 128.0, 126.9, 126.8, 85.2. HRMS (APCI, m/z): calcd. for  $C_{26}H_{28}B_{10}$ : 450.3157, found: 450.3169.

**Fluorophore F2.** White powder (200 mg, 42%). <sup>1</sup>H NMR (DMSO- $d_6$  /TMS, 600 MHz):  $\delta$  (ppm), 9.64 (s, 2H), 7.57 (d, J = 8.7 Hz, 4H), 7.48 (d, J = 8.7 Hz, 4H), 7.43 (d, J = 8.7 Hz, 4H), 6.78 (d, J = 8.7 Hz, 4H). <sup>11</sup>B NMR (DMSO- $d_6$ , 192 MHz):  $\delta$  (ppm), -5.85, -13.24. <sup>13</sup>C NMR (DMSO- $d_6$ /TMS, 150 MHz):  $\delta$  (ppm), 157.8, 142.0, 131.1, 128.5, 127.8, 127.6, 125.7, 115.7, 86.1. HRMS (APCI, m/z): calcd. for C<sub>26</sub>H<sub>28</sub>B<sub>10</sub>O<sub>2</sub>: 481.3056, found: 481.3066.

**Fluorophore F3.** White powder (320 mg, 63%). <sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS, 600 MHz):  $\delta$  (ppm), 7.49 (d, J = 8.4 Hz, 4H), 7.41 (d, J = 8.6 Hz, 4H), 7.34 (d, J = 8.4 Hz, 4H), 6.91 (d, J = 8.7 Hz, 4H), 3.81 (s, 6H), 2.44 (s, 10H). <sup>11</sup>B NMR (CDCl<sub>3</sub>, 192 MHz):  $\delta$  (ppm), -3.1, -9.4, -10.2, -10.9. <sup>13</sup>C NMR (CDCl<sub>3</sub>/TMS, 150 MHz):  $\delta$  (ppm), 159.7, 142.3, 131.6, 131.0, 129.0, 128.0, 126.2, 114.3, 85.4, 55.3. HRMS (APCI, m/z): calcd. for C<sub>28</sub>H<sub>32</sub>B<sub>10</sub> O<sub>2</sub>: 450.3157, found: 450.3169.

**Fluorophore F4.** Faint yellow powder (310 mg, 58%). <sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS, 600 MHz):  $\delta$  (ppm), 7.45 (d, J = 8.6 Hz, 4H), 7.38 (d, J = 8.8 Hz, 4H), 7.32 (d, J = 8.6 Hz, 4H), 6.72 (d, J = 5.7 Hz, 4H), 2.96 (s, 12H). <sup>11</sup>B NMR (CDCl<sub>3</sub>, 192 MHz):  $\delta$  (ppm), - 3.2, -9.3, -10.3, -11.1. <sup>13</sup>C NMR (CDCl<sub>3</sub>/TMS, 150 MHz):  $\delta$  (ppm), 150.3, 142.36, 131.0, 128.2, 127.6, 126.7, 125.5, 112.6, 85.8, 40.4. HRMS (APCI, m/z): calcd. for C<sub>30</sub>H<sub>39</sub>B<sub>10</sub>N<sub>2</sub>: 536.4079, found: 536.4084.

## 2. Computed Photophysical Data of Compounds F1-F4

Compound	LUMO (eV)	HOMO (eV)	Eg (eV)	f
<b>F1</b>	-0.263	-7.782	7.52	0.5595
F2	-0.158	-7.295	7.14	0.5731
F3	-0.117	-7.202	7.08	0.6818
F4	-0.049	-6.457	6.41	0.6572

Table S1. Computed photophysical data of compounds F1-F4

Note: Calculated by density-functional theory (DFT) method at the level of B3LYP/6-31G(d), Eg: Energy gap; f: Oscillator strength.

# 3. Crystallographic Data

Empirical formula	$C_{26}H_{28}B_{10}$
Formula weight	448.58
Temperature/K	153.01
Crystal system, Space group	Triclinic, P-1
Unit cell dimensions	a = 13.5625(6) Å
	b = 14.0717(6) Å
	c = 27.7111(11) Å
	α=100.4710(10) °
	$\beta = 99.9750(10)^{\circ}$
	$\gamma = 95.0160(10)$ °
Volume/Å <sup>3</sup>	5083.1(4)
Ζ	8
$\rho_{calc}g/cm^3$	1.172
$\mu/mm^{-1}$	0.436
<i>F</i> (000)	1872.0
Crystal size/mm <sup>3</sup>	0.5  imes 0.4  imes 0.3
Radiation	Cu Ka ( $\lambda = 1.54178$ )
2θ range for data collection/°	6.436 to 136.636
Index ranges	$-16 \le h \le 16, -16 \le k \le 16, -33 \le l \le 33$
Reflections collected	155401
Independent reflections	18518 [ $R_{int} = 0.0313$ , $R_{sigma} = 0.0156$ ]
Data/restraints/parameters	18518/0/1297
Goodness-of-fit on $F^2$	1.040
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.0412, wR_2 = 0.1029$
Final R indexes [all data]	$R_1 = 0.0426$ , $wR_2 = 0.1041$
Largest diff. peak/hole / e Å-3	0.22/-0.19

#### Table S2. Crystallographic data of F1.

Empirical formula	$C_{26}H_{28}B_{10}O_2$		
Formula weight	480.58		
Temperature/K	170.02		
Crystal system, Space group	Monoclinic, P21/c		
Unit cell dimensions	a = 28.6138(9)  Å		
	b = 11.0447(3)  Å		
	c = 40.6475(12)  Å		
	$\alpha = 90^{\circ}$		
	$\beta = 110.497(2)^{\circ}$		
	$\gamma = 90^{\circ}$		
Volume/Å <sup>3</sup>	12032.6(6)		
Ζ	16		
$\rho_{calc} g/cm3$	1.061		
μ/mm-1	0.289		
<i>F</i> (000)	4000.0		
Crystal size/mm <sup>3</sup>	0.1  imes 0.08  imes 0.05		
Radiation	Ga Ka ( $\lambda = 1.34139$ )		
$2\theta$ range for data collection/°	5.724 to 109.882		
Index ranges	$-34 \le h \le 34, -13 \le k \le 11, -49 \le l \le 49$		
Reflections collected	127138		
Independent reflections	23242 [Rint = 0.1346, Rsigma = 0.1067]		
Data/restraints/parameters	23242/38/1376		
Goodness-of-fit on F2	1.038		
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.1097, wR_2 = 0.2731$		
Final R indexes [all data]	$R1 = 0.1780$ , $wR_2 = 0.3322$		
Largest diff. peak/hole / e Å <sup>-3</sup>	0.97/-0.49		

 Table S3. Crystallographic data of F2.

Empirical formula	$C_{28}H_{32}B_{10}O_2$		
Formula weight	508.63		
Temperature/K	152.99		
Crystal system, Space group	Monoclinic, P21/c		
Unit cell dimensions	a = 14.466(4)  Å		
	b = 46.262(5)  Å		
	c = 14.325(6) Å		
	$\alpha = 90^{\circ}$		
	$\beta = 119.654(9)^{\circ}$		
	$\gamma = 90^{\circ}$		
Volume/Å <sup>3</sup>	8331(5)		
Ζ	12		
$\rho_{calc}g/cm^3$	1.217		
$\mu/\text{mm}^{-1}$	0.068		
<i>F</i> (000)	3192.0		
Crystal size/mm <sup>3</sup>	0.12  imes 0.11  imes 0.1		
Radiation	Mo Ka ( $\lambda = 0.71073$ )		
$2\theta$ range for data collection/°	4.18 to 52.97		
Index ranges	$-18 \le h \le 18, -57 \le k \le 58, -17 \le l \le 17$		
Reflections collected	182460		
Independent reflections	17167 [ $R_{int} = 0.0920$ , $R_{sigma} = 0.0576$ ]		
Data/restraints/parameters	17167/0/1087		
Goodness-of-fit on $F^2$	1.019		
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.0547, wR_2 = 0.1203$		
Final R indexes [all data]	$R_1 = 0.1043, wR_2 = 0.1410$		
Largest diff. peak/hole / e Å-3	0.23/-0.22		

 Table S4. Crystallographic data of F3.

Empirical formula	$C_{30}H_{38}B_{10}N_2$
Formula weight	534.72
Temperature/K	152.99
Crystal system, Space group	Tetragonal, P4
Unit cell dimensions	a = 9.9221(5) Å
	b = 9.9221(5) Å
	c = 16.2619(8)  Å
	$\alpha = 90^{\circ}$
	$\beta = 90^{\circ}$
	$\gamma = 90^{\circ}$
Volume/Å <sup>3</sup>	1600.95(18)
Z	2
$\rho_{calc} g/cm^3$	1.109
µ/mm <sup>-1</sup>	0.435
<i>F</i> (000)	564.0
Crystal size/mm <sup>3</sup>	0.5  imes 0.4  imes 0.3
Radiation	Cu Ka ( $\lambda$ = 1.54178)
$2\theta$ range for data collection/°	8.912 to 136.542
Index ranges	$-11 \le h \le 11, -11 \le k \le 11, -19 \le l \le 19$
Reflections collected	46721
Independent reflections	2909 [ $R_{int} = 0.0327$ , $R_{sigma} = 0.0123$ ]
Data/restraints/parameters	2909/1/192
Goodness-of-fit on $F^2$	1.143
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.0667, wR_2 = 0.2079$
Final R indexes [all data]	$R_1 = 0.0668, wR_2 = 0.2080$
Largest diff. peak/hole / e Å-3	1.59/-0.29

 Table S5. Crystallographic data of F4.

# 4. Performance Comparison of Present Nicotine Sensor with the Reported Works

	Technology	Vapor/solution	DL	Device	Reference
1	Fiber optic	solution	0.074 μΜ	Yes	<i>Biosens. Bioelectron.</i> ,2017, <b>91</b> , 762
2	SERS	solution	0.0022 mg	Yes	ACS Sens., 2019, 4, 1844
3	CE-EC	solution	0.0000081 mg	No	<i>Chem. Res. Chin. Univ.</i> , 2012, <b>28</b> , 415
4	HPLC	solution	0.00007 mg	No	Int. J. Environ. Res. Public Health, 2018, <b>15</b> , 1737.
5	GC-MS	solution	0.0002 mg	No	J. Lab. Chem. Educ., 2015, 3, 37
6	Chemiresistor	vapor	No	No	Nicotine Tob. Res., 2013, 15,
7	Fluorescence	vapor/ solution	3 ppb (gaseous) 0.1 ng/cm <sup>2</sup> (aqueous)	Yes	This Work

**Table S6** Performance comparison of present nicotine sensor with the reported works.

5. Fluorescent Spectra and Photochemical Stabilities of the Films



**Figure S1.** (a) Excitation (dotted line) and emission (solid line) spectra of the films. *Note:* Ex stands for excitation, and Em means monitoring. (b) Photochemical stabilities of the films under UV light (310 nm) illumination.

6. Crystal Packing Structures of The *o*-Carborane-Based Fluorophores



**Figure S2** Crystal packing structures of the o-carborane-based fluorophores (F2 and F3), where carbon (gray), boron (pink), oxygen (red) and hydrogen (white) atoms are shown as ellipsoids at the 50% probability level. Packing structures for the fluorophore F2 (a, b) and F3 (c, d).

# 7. Fluorescence Responses of Film 1-4 to Nicotine



**Figure S3.** Relative response intensities of Film 1-4 on the exposure to saturated nicotine vapor at room temperature.

## 8. Reusability of Film 2 to Tobacco Smoke



**Figure S4.** Reusability of Film 2 to tobacco smoke at room temperature (the response tests were repeated 10 times in one day and lasted for 5 days, and the concentration of the tobacco smoke have been diluted 10 times of their saturated vapor with air).

## 9. NMR and HRMS Spectra of the Fluorophores





Figure S6. <sup>11</sup>B NMR spectrum of F1 in CDCl<sub>3</sub>.













Figure S9. <sup>1</sup>H NMR spectrum of F2 in DMSO-*d*<sub>6</sub>.



Figure S10. <sup>11</sup>B NMR spectrum of F2 in DMSO-*d*<sub>6</sub>.



Figure S11. <sup>13</sup>C NMR spectrum of F2 in DMSO-*d*<sub>6</sub>.







Figure S13. <sup>1</sup>H NMR spectrum of F3 in CDCl<sub>3</sub>.



Figure S14. <sup>11</sup>B NMR spectrum of F3 in CDCl<sub>3</sub>.



Figure S15. <sup>13</sup>C NMR spectrum of F3 in CDCl<sub>3</sub>.











Figure S18. <sup>11</sup>B NMR spectrum of F4 in CDCl<sub>3</sub>.



Figure S19. <sup>13</sup>C NMR spectrum of F4 in CDCl<sub>3</sub>.





# **10.References**

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- 2 G. M. Sheldrick, *Acta Cryst.*, 2008, **64**, 112-122.