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Supporting Information

for

Discrimination of Saturated Alkanes and Relevant Volatile Compounds via Utilization of a Conceptual Fluorescent Sensor Array Based on Organoboron-Containing Polymers

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Experimental

Synthesis of B-1

Synthesis of bis(4-hexylphenyl)(hydroxy)borane (1). To a suspension of magnesium (16.5 mmol, 401 mg) in a solution of diisopropylaminoborane (5 mmol, 5.0 mL) in anhydrous THF (40 mL), at room temperature, was added 1-bromo-4-hexylbenzene (11 mmol, 3.2 ml). The mixture was then heated at 70°C under stirring during 20h, then cooled at 0°C and quenched with a 3M aqueous HCl solution (40 mL). The mixture was stirred for 45 minutes at room temperature. To this solution was added water (20 mL) and diethyl ether (20 mL) and the organic phase was separated. The aqueous phase was then extracted with DCM (5×30 mL). The combined organic phases were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure to afford compound 1 as a pale-yellow oil and used for the next step directly.

Synthesis of 8-((bis(4-hexylphenyl)boryl)oxy)-5,7-diiodoquinoline (B-1). To a solution of 1 (5 mmol) in 30 mL diethyl ether, was added 5,7-diiodo-8-hydroxy-quinoline (1.9848 g, 5 mmol). After 15 h of stirring at room temperature, pentane was added to complete the formation of solid B-1, the reaction mixture was then filtered over a fritted glass, washed with cold pentane and dried under high vacuum to afford pure compound B-1 as an air-stable yellow green solid. Slow evaporation of a solution of the product obtained in hexanes/CH₂Cl₂ at room temperature resulted in the formation of yellow flake crystals of X-ray quality (3.18g, 87%). ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 0.87 (t, 6H, *CH*₃, hexyl), 1.31 (m, 12H, *CH*₂*CH*₂*CH*₂, hexyl), 1.57 (m, 4H, *CH*₂, hexyl), 2.55 (m, 4H, *CH*₂, hexyl), 7.09 (d, 4H, Ar*H*), 7.34 (d, 4H, Ar*H*), 7.69 (dd, 1H, quinoline-*H*), 8.37 (m, 2H, quinoline-*H*), 8.58 (d, 1H, quinoline-*H*). ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ 14.11, 22.62, 29.15, 31.48, 31.76, 35.87 (hexyl C), 74.92, 75.66 (I-C), 124.01, 127.74, 132.00, 135.88, 141.81, 142.71, 148.64 (quinoline C), 130.17, 140.75, 160.88 (Ar C). HRMS: (m/z, [M+H]⁺): calculated: 730.1214, Found: 730.1225. Anal. Calcd (%) for B-1 (C₃₃H₃₈BI₂NO): C, 54.35; H, 5.25; N, 1.92. Found: C, 54.54; H, 5.31; N, 2.12. UV-vis (in CHCl₃): $\lambda_{max} = 424$ nm, $\varepsilon = 3.32 \times 10^3$ L/(mol·cm). Fluorescence emission (in CHCl₃) ($\lambda_{ex} = 405$ nm): $\lambda_{em} = 520$ nm. Melting point: 176-177 °C.



Synthesis of P1. To a 100 mL two-neck round-bottom flask under nitrogen atmosphere, the mixture of monomer B-1 (0.5 g, 0.69 mmol), 1,4-phenylenediboronic acid (0.1146 g, 0.69 mmol) and Pd(PPh₃)₄ (0.0399g, 0.0345 mmol) were dissolved in 15 mL tetrahydrofuran (THF). To this reaction mixture 10 mL of 1 M K₂CO₃ aqueous solution was added and stirred for 24 hours at 80 °C under nitrogen atmosphere. Reaction mixture was allowed to cool to room temperature and extracted with chloroform. The collected organic layer was dried over anhydrous MgSO₄. The solvent was removed in vacuo, and the residue was dissolved in 1 mL chloroform, then reprecipitated in methanol (200 mL); this procedure was repeated three times to afford P1 as a yellow solid (0.21 g, 56 %). ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 8.58, 8.37 (d, quinoline-*H*), 8.39 (s, quinoline-*H*), 7.69, 7.35, 7.10 (Ar*H*), 2.56, 1.58, 1.29, 0.87 (hexyl). *Mn* = 1.96 ×10⁴, *Mw* = 3.68 × 10⁴, PDI = 1.88 by GPC. UV-vis (in CHCl₃): λ_{max} = 444 nm, ε (per monomer unit) = 4.48 × 10³ L/(mol·cm). Fluorescence emission (in CHCl₃): λ_{em} = 550 nm. Fluorescence emission (film) (λ_{ex} = 405 nm): λ_{em} = 580 nm.



Synthesis of P2. To a 100 mL two-neck round-bottom flask under nitrogen atmosphere, the mixture of monomer B-1 (0.5 g, 0.69 mmol), 1,4-diethynylbenzene (0.087 g, 0.69 mmol), Pd(PPh₃)₄ (0.0798g, 0.0686 mmol) and CuI (0.0131g, 0.0686 mmol) were dissolved in 14 mL toluene and 6 mL diisopropylamine, then stirred for 24 hours at 70 °C under nitrogen atmosphere. Reaction mixture was allowed to cool to room temperature and extracted with chloroform. The collected organic layer was dried over anhydrous MgSO₄. The solvent was removed in vacuo, and the residue was dissolved in 1 mL chloroform, then reprecipitated in methanol (200 mL); this procedure was repeated three times to afford P2 as a orange solid (0.31 g, 73 %). ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 8.72, 8.64, 7.99 (s, quinoline-*H*), 7.54, 7.38, 7.12, 6.99 (Ar*H*), 3.21 (alkynyl-*H*), 2.56, 1.58, 1.28, 0.87 (hexyl). *Mn* = 1.11 ×10⁴, *Mw* = 1.61 × 10⁴, PDI = 1.45 by GPC. UV-vis (in CHCl₃): λ_{max} = 332 nm, 454 nm, ε (per monomer unit) = 3.28 × 10⁴ L/(mol·cm), 8.01 × 10³ L/(mol·cm). Fluorescence emission (in CHCl₃): λ_{em} = 560 nm. Fluorescence emission (film) (λ_{ex} = 405 nm): λ_{em} = 603 nm.



Synthesis of P3. To a 100 mL two-neck round-bottom flask under nitrogen atmosphere, the mixture of monomer B-1 (0.5 g, 0.69 mmol), 2,5-diethynylthiophene (0.091 g, 0.69 mmol), Pd(PPh₃)₄ (0.0798g, 0.0686 mmol) and CuI (0.0131g, 0.0686 mmol) were dissolved in 14 mL toluene and 6 mL diisopropylamine, then stirred for 24 hours at 70 °C under nitrogen atmosphere. Reaction mixture was allowed to cool to room temperature and extracted with chloroform. The collected organic layer was dried over anhydrous MgSO₄. The solvent was removed in vacuo, and the residue was dissolved in 1 mL chloroform, then reprecipitated in methanol (200 mL); this procedure was repeated three times to afford P3 as a deep red solid (0.21 g, 51 %). ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 8.65, 8.58, 8.20 (s, quinoline-*H*), 7.75 (thienyl-H), 7.44, 7.35, 7.10 (Ar*H*), 3.41 (alkynyl-*H*), 2.55, 1.57, 1.28, 0.87 (hexyl). *Mn* = 2.16 ×10⁴, *Mw* = 3.40 × 10⁴, PDI = 1.58 by GPC. UV-vis (in CHCl₃): λ_{max} = 354 nm, 460 nm, ε (per monomer unit) = 1.07 × 10⁴ L/(mol·cm), 5.68 × 10³ L/(mol·cm). Fluorescence emission (in CHCl₃): λ_{em} = 575 nm. Fluorescence emission (film) (λ_{ex} = 405 nm): λ_{em} = 614 nm.



Synthesis of P4. To a 100 mL two-neck round-bottom flask under nitrogen atmosphere, the mixture of monomer B-1 (0.5 g, 0.69 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (0.3372 g, 0.69 mmol), Pd(PPh₃)₄ (0.040g, 0.035 mmol) were dissolved in 15 mL toluene, then stirred for 24 hours at 110 °C under nitrogen atmosphere. Reaction mixture was allowed to cool to room temperature and extracted with chloroform. The collected organic layer was dried over anhydrous MgSO₄. The solvent was removed in vacuo, and the residue was dissolved in 1 mL chloroform, then reprecipitated in methanol (200 mL); this procedure was repeated three times to afford P4 as a red solid (0.34 g, 76 %).¹H NMR (600 MHz, CDCl₃, 25 °C): δ 8.77, 8.63 (s, quinoline-*H*), 8.09, 7.62 (thienyl-H), 7.47, 7.39, 7.13 (Ar*H*), 2.56, 1.56, 1.28, 0.86

(hexyl). $Mn = 1.32 \times 10^4$, $Mw = 1.54 \times 10^4$, PDI = 1.17 by GPC. UV-vis (in CHCl₃): $\lambda_{max} = 397$ nm, 506 nm, ε (per monomer unit) = 2.02×10^4 L/(mol·cm), 5.77×10^3 L/(mol·cm). Fluorescence emission (in CHCl₃): $\lambda_{em} = 615$ nm. Fluorescence emission (film) ($\lambda_{ex} = 405$ nm): $\lambda_{em} = 668$ nm.

Synthesis of monomer B-2 and polymer P5. The synthesis procedure of B-2 is the same to B-1, where 1-bromo-4-hexylbenzene was replaced by bromobenzene, and the polymer P5 is prepared using the synthesis method of P2 with B-2 as the monomer. ¹H NMR (600 MHz, CDCl₃, 25 0 C) of B-2: δ 7.24 (s, 2H, Ar*H*), 7.28 (dd, 4H, Ar*H*), 7.43 (dd, 4H, Ar*H*), 7.73 (dd, 1H, quinoline-*H*), 8.38 (s, 1H, quinoline-*H*), 8.42 (d, 1H, quinoline-*H*), 8.59 (d, 1H, quinoline-*H*). ¹H NMR (600 MHz, CDCl₃, 25 0 C) of P5: δ 8.88, 8.66 (quinoline-*H*), 8.25, 8.12, 8.06, 7.92, 7.76, 7.62, 7.49, 7.08 (Ar*H*). *Mn* = 1.44 ×10⁴, *Mw* = 1.69 × 10⁴, PDI = 1.17 by GPC.

Supplementary Figures and Tables



Figure S1. Structure of B-1 with thermal ellipsoids drawn to the 50% probability level. All hydrogen atoms have been omitted for clarity.

B-1						
B(1)–O(1)	1.551(14)	O(1)-B(1)-C(12)	110.7(10)			
B(1)–N(1)	1.663(15)	O(1)-B(1)-C(24)	110.7(10)			
B(1)–C(12)	1.615(17)	C(12)-B(1)-C(24)	117.5(9)			
B(1)–C(24)	1.599(18)	O(1)-B(1)-N(1) 98.2(8				
		C(12)-B(1)-N(1)	109.5(9)			
		C(24)-B(1)-N(1)	108.6(9)			

Table S1. Selected Bond Lengths (Å) and Angles (deg) for monomer B-1.

Data	D2		
CCDC	1581987		
formula	C ₃₃ H _{37.5} BI ₂ NO		
fw	728.75		
T/K	100(2)		
Wavelength/ Å	0.71073		
Crystal system	Monoclinic		
Space group	P2(1)/n		
a/Å	13.751(5)		
b/Å	16.557(6)		
$c/\text{\AA}$	28.155(10)		
α, deg	90		
β , deg	93.121(4)		
γ, deg	90		
$V/\text{\AA}^3$	6400(4)		
$Z, Dc/(g \text{ cm}^{-3})$	8, 1.513		
μ/mm^{-1}	1.990		
F(000)	2892		
20/deg	2.854 to 49.996		
reflns measured	64489		
reflns used (R_{int})	10974 (0.0448)		
GOF on F ²	1.316		
$F_{1}^{2} = 10 [I > 2 - (N]]$	$R_1 = 0.0732$		
Final $R\left[1 \ge 2\sigma(1)\right]$	$wR_2 = 0.1701$		
\mathcal{D} (all data)	$R_1 = 0.0888$		
r (an uata)	$wR_2 = 0.1792$		

 Table S2. Crystallographic data for monomer B-1.

Table S3. Polymerization Results

Polymer	Yield (%) ^a	Mw ^b	Mn ^b	PDI
P1	56	36800	19600	1.88
P2	73	16100	11100	1.45
Р3	51	34000	21600	1.58
P4	76	15400	13200	1.17

^a Isolated yields after reprecipitation into methanol. ^b GPC (THF), polystyrene standards.



Figure S2. ¹H NMR spectra of monomer B-1 and polymers P1-P4.

Note: the structural identities of the polymers as produced may be quantitatively verified by assignment of the proton signals appearing in the ¹H NMR spectra. It would be no doubt that the characteristic proton signals, such as Ha and those of the whole aromatic proton signals can be assigned, of which Ha is fully isolated from the others. For the aromatic proton signals, they all appear at the low field ($\delta_p > 6.7$ ppm). Other alkyl proton signals are hard to be isolated as the solvents used for preparation and purification of the polymers may be remained. Clearly, the theoretical rations of the integrations of the three kinds of protons (methyl protons, aromatic protons belonging to the B-1 unit, aromatic protons belonging to the conjugated linker unit) for the four polymers should be 6:12:4, 6:12:4, 6:12:2 and 6:12:4, respectively, or the value of the linker is greater than that of the value depicted depending on the molecular mass of the polymers. Inspection of the data shown on the ¹H NMR traces reveals that the compositions of the polymers are roughly the expected 1:1 incorporation of the monomer to the conjugated linker.

Calculation of Molar Absorption Coefficients for B-1 and P1-P4

The molar absorption coefficients ε was calculated as equation 1:

$$\varepsilon = \frac{A}{lC} \qquad (1)$$

In this equation, A is absorbance, l is absorption path length and C is the amount concentration. The calculated molar absorption coefficients ε are shown in Table S4.

Compound	$\lambda_{\max}(nm)$	A	C (per monomer unit) 10 ⁻⁴ mol/L	<i>l</i> (cm)	ε (per monomer unit) 10 ⁴ L/(mol·cm)
B-1	424	0.091	0.274	1	0.332
P1	444	0.162	0.361	1	0.448
P2	332	1.092	0.222	1	3.28
	454	0.266	0.332	1	0.801
D2	354	0.353	0.329	1	1.07
P3	460	0.187		1	0.568
D4	397	0.628	0.312	1	2.02
P4	506	0.180		1	0.577

Table S4. Calculation of molar absorption coefficients



Figure S3. The optimized ground state structures for the model systems of ru-P1, ru-P2, ru-P3 and ru-P4, respectively.



Figure S4. Photochemical stability of monomer B-1 and polymers P1-P4 in CHCl₃ monitored at their maximum emission wavelength with 405 nm as the excitation wavelength.



Figure S5. Photochemical stability of polymers P1-P4 in film state monitored at their maximum emission wavelength with 405 nm as the excitation wavelength.



Figure S6. Fluorescence photos of compound P1-P4 before and after 6 months exposing in air, away from light and at room temperature. The pictures were obtained under UV light (365 nm).



Figure S7. Home-made sensing platform developed for VSOMs vapor detection.

Note: (1) The unit within the red box is the sensory unit, which contains a sampling structure, an optical component, and a signal amplifying and processing unit, (2) the unit within the blue box is a stationary gas supply system, (3) the unit within the yellow box is the system controller, and (4) the unit within the green box is the computer for data processing and result display. (5) the unit within the purple in the up-left corner is a sample film device.



Figure S8. Optical imagines of the prepared sensing films taken under day light and UV light (365 nm).

Note: S1, S3, S5, and S7 stand for the films with P1, P2, P3 and P4 as sensing fluorophores and silica-gel plate as a substrate, respectively, and S2, S4, S6, and S8 represent the films with glass plate as a substrate.



Figure S9. Fluorescence emission spectra of S7 in the presence of *n*-pentane saturated vapor (λ_{ex} = 467 nm) at room temperature (293 K). Inset: images of the as prepared film under UV light (365 nm) before and after treatment with *n*-pentane saturated vapor.

Compound	Vapor pressure (KPa)	In ppm (×10 ⁴)	T/K
methane	4520	4460	
ethane	3779	3730	
propane	840.9	830	
<i>n</i> -butane	208.1	205	
<i>n</i> -pentane	56.58	55.8	
<i>n</i> -hexane	16.16	16.0	
<i>n</i> -heptane	4.74	4.74 4.67	
<i>n</i> -octane	ne 1.395 1.37 ne 0.375 0.37	1.37	
<i>n</i> -nonane			
<i>n</i> -decane	0.117	0.12	203
methanol	12.97	12.8	293
toluene	2.911	2.87	
diethyl ether	59.06	58.28	
benzene	10.03	9.9	
acetone	24.65	24.3	
ethanol	5.87	5.79	
THF	18.9	18.65	
di-chloromethane (DCM)	47.4	46.78	
tri-chloromethane (TCM)	21.13	20.85	
water	2.339	0.23	

Table S5. Vapor pressure and the calculated saturated vapor pressure in ppm level of the tested VSOMs at 293 K. ¹⁻³



Figure S10. Real-time response traces of S1-S8 to saturated vapor of the tested VSOMs at room temperature (293 K).

Note: (a) The Arabic numerals in the figure stand for different chemicals: specifically, methane (1), ethane (2), propane (3), *n*-butane (4), *n*-pentane (5), *n*-hexane (6), *n*-heptane (7), *n*-octane (8), *n*-nonane (9), *n*-decane (10), methanol (11), toluene (12), diethyl ether (13), benzene (14), acetone (15), ethanol (16), THF (17), DCM (18), TCM (19) and water (20). (b) S1, S3, S5, and S7 stand for the films with P1, P2, P3 and P4 as sensing fluorophores and silica-gel plate as a substrate, respectively, and S2, S4, S6, and S8 represent the films with glass plate as a substrate.



Figure S11. Real-time response traces of S7 to the vapor of tested VSOMs at a concentration of 1.37×10^4 ppm at room temperature (293 K).

Note: The Arabic numerals in the figure stand for different chemicals: specifically, methane (1), ethane (2), propane (3), *n*-butane (4), *n*-pentane (5), *n*-hexane (6), *n*-heptane (7), *n*-octane (8), methanol (9), toluene (10), diethyl ether (11), benzene (12), acetone (13), ethanol (14), THF (15), DCM (16), and TCM (17).

	<i>n</i> -pentane	<i>n</i> -hexane	diethyl ether	THF	ТСМ	acetone
polarity	0.00	0.06	2.90	4.20	4.40	5.40
Size (Å ³)	2.8×1.8×6.9	2.8×1.8×8.2	2.9×1.8×6.6	3.0×3.0×4.0	2.9×2.9×1.9	2.8×1.7×4.3
b. p./°C	36	69	35	66	61	57
$\lambda_{ m abs.}$	500	500	504	504	506	510
$\lambda_{ m em}$	590	595	620	624	620	630
Q. Y. /%	15.50	12.59	12.67	5.74	8.41	2.82

Table S6. Important parameters of some typical analytes and photophysical properties of P4.



Figure S12. Molecular packing modes: capped sticks (a), spacefill (b) of compound B-1 in crystal state.



Figure S13. Real-time response traces of S9 to the saturated vapor of tested VSOMs at room temperature (293 K). Inset is the pictures of the film device taken under the illumination of daylight or UV light.

Note: The Arabic numerals in the figure stand for different chemicals: specifically, methane (1), ethane (2), propane (3), *n*-butane (4), *n*-pentane (5), *n*-hexane (6), *n*-heptane (7), *n*-octane (8), *n*-nonane (9), *n*-decane (10), methanol (11), toluene (12), diethyl ether (13), benzene (14), acetone (15), ethanol (16), THF (17), DCM (18), and TCM (19).



Figure S14. Real-time sensing response curves of S9 to the same concentration $(1.37 \times 10^4 \text{ ppm})$ VSOMs vapor at room temperature (293 K). Inset is the pictures of the film device taken under the illumination of daylight or UV light.

Note: The Arabic numerals in the figure stand for different chemicals: specifically, methane (1), ethane (2), propane (3), *n*-butane (4), *n*-pentane (5), *n*-hexane (6), *n*-heptane (7), *n*-octane (8), methanol (9), toluene (10), diethyl ether (11), benzene (12), acetone (13), ethanol (14), THF (15), DCM (16), and TCM (17).



Figure S15. ¹H NMR spectrum of monomer B-1



Figure S16. ¹³C NMR spectrum of monomer B-1



Figure S17. High resolution mass spectrum of compound B-1.

Figure S18. ¹H NMR spectrum of 5,5'-bis(trimethylstannyl)-2,2'-bithiophene.

Figure S19. ¹H NMR spectrum of 2,5-diethynylthiophene

Figure S20. ¹H NMR spectrum of B-2.

Figure S21. ¹H NMR spectrum of monomer B-2 and polymer P5.

Reference

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