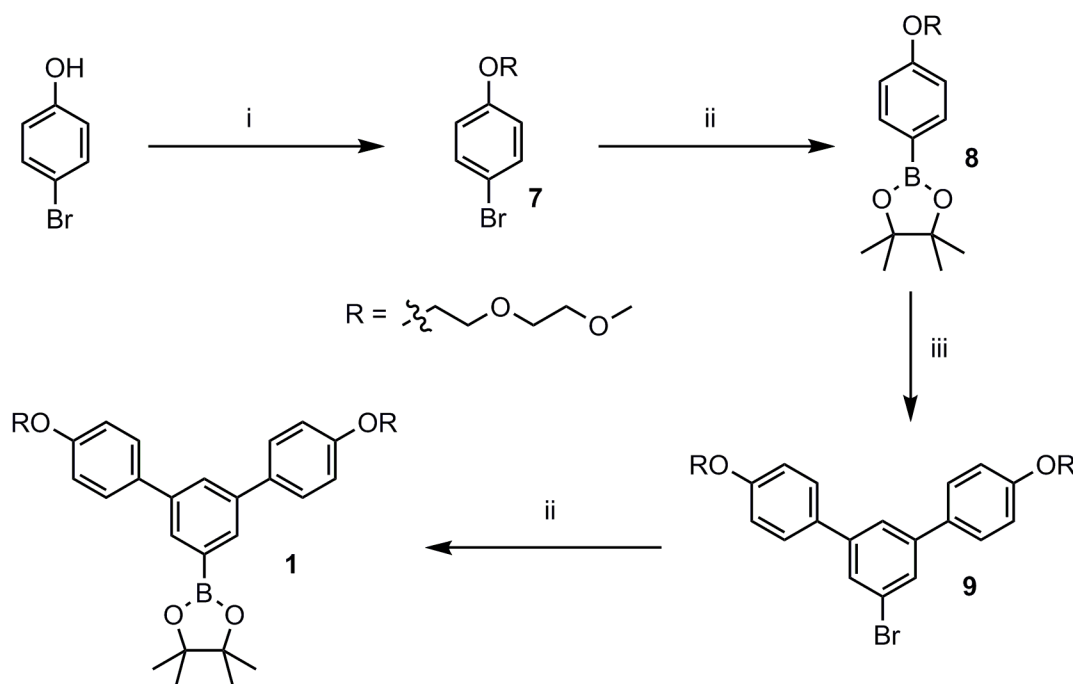


Supporting information for “Quantitative real time sensing reveals enhanced sensitivity of polar dendrimer thin films for plastic explosive taggants”

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Synthesis of dendron precursor 1 and characterising data for precursors



Scheme S1 Synthesis of dendron precursor **1**. *Conditions and reagents:* (i) NaOH, EtOH, 0.9 eq. 1-bromo-2-(2-methoxyethoxy)ethane, reflux, 83%. (ii) *n*-BuLi, THF, 2-*iso*-propoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, -78 °C-rt, Ar. *Yields:* **1** 83%, **8** 64%. (iii) Pd(PPh₃)₄, PhMe, *tert*-BuOH, aq. K₂CO₃, 100 °C, N₂, 61%.

2-{4-[2-(2-Methoxyethoxy)ethoxy]phenyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8)

7¹ (4.50 g, 16.4 mmol) was dissolved in anhydrous tetrahydrofuran (35 cm³) under argon and the resulting solution was cooled in a dry ice/acetone bath. A solution of *n*-butyl lithium in hexanes (1.6 M, 12.3 cm³) was added dropwise over 3 min and the mixture was stirred whilst cooled for a further 20 min. 2-*iso*-propoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6.7 cm³, 33 mmol) was added and the mixture was stirred with dry ice/acetone bath cooling for a further

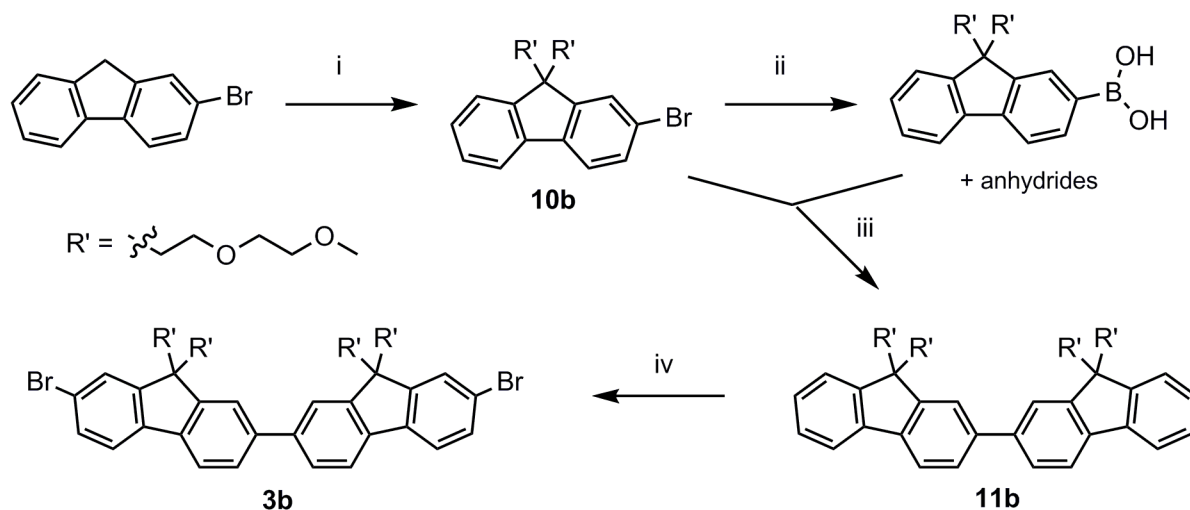
10 min. The mixture was allowed to warm to room temperature and was stirred for 19 h. The mixture was quenched with water (50 cm³), diluted with diethyl ether (100 cm³) and the layers were separated. The aqueous layer was extracted with diethyl ether (3 × 30 cm³) and the combined organics were washed with water (2 × 20 cm³) and brine (30 cm³). The aqueous layer was further extracted with diethyl ether (6 × 30 cm³) these organics were washed with brine (30 cm³) before all of the organics were combined. The organics were dried over anhydrous magnesium sulphate and filtered. The magnesium sulfate was washed with additional diethyl ether and the filtered organics combined before the volatiles were removed *in vacuo*. The volatile by-products were removed from the crude residue by short-path distillation using a kügelrohr distillation apparatus at 0.4 mbar and 120 °C to yield **8** as a yellow oil (3.63 g, 64%). Found: C, 63.2; H, 8.6; C₁₇H₂₇O₅B requires C, 63.4; H, 8.5. λ_{max} (CH₂Cl₂/nm): 241 (log ε/dm³ mol⁻¹ cm⁻¹ 4.38), 262sh (3.36) 270 (3.36), 273sh (3.34), 280 (3.26), 288sh (2.82) and 296sh (2.54). δ_H (500 MHz, CDCl₃): 1.32 (12H, s, ArB[OC(CH₃)₂]₂), 3.38 (3H, s, ArOC₂H₄OC₂H₄OCH₃), 3.56-3.58 (2H, m, ArOC₂H₄OCH₂CH₂OMe), 3.71-3.72 (2H, m, ArOC₂H₄OCH₂CH₂OMe), 3.85-3.87 (2H, m, ArOCH₂CH₂OC₂H₄OMe), 4.15-4.17 (2H, m, ArOCH₂CH₂OC₂H₄OMe), 6.90 and 7.73 (4H, AA'BB', PhH). δ_C (125 MHz, CDCl₃): 24.8, 59.0, 67.1, 69.7, 70.7, 71.9, 83.5, 113.9, 136.4, 161.3; *m/z* [ESI] anal. calcd. for C₁₇H₂₇BO₅: 321.2 (25%), 322.2 (100%), 323.2 (9%). Found 344.2 (23%, M + Na⁺), 345.2 (100%, M + Na⁺), 346.2 (16%, M + Na⁺), 360.1 (7%, M + K⁺), 361.1 (47%, M + K⁺) and 362.1 (11%, M + K⁺).

1-Bromo-3,5-bis{4-[2-(2-methoxyethoxy)ethoxy]phenyl}benzene (9)

8 (2.67 g, 7.70 mmol) and 1,3,5-tribromobenzene (1.10 g, 3.50 mmol) were dissolved in a mixture of toluene (30 cm³) and *tert*-butanol (10 cm³). Aqueous potassium carbonate (2.0 M, 10 cm³) was added and the mixture was deoxygenated by sparging with nitrogen for 20 min. Tetrakis(triphenylphosphine)palladium(0) (0.121 g, 0.105 mmol) was added and the mixture was deoxygenated by sparging with nitrogen for 20 min. The mixture was stirred at 100 °C under nitrogen for 39 h before it was allowed to cool to room temperature. The mixture was diluted with toluene (20 cm³) and the layers were separated. The aqueous layer was extracted with toluene

($3 \times 5 \text{ cm}^3$) and the combined organics were washed with water ($2 \times 10 \text{ cm}^3$) and brine ($2 \times 10 \text{ cm}^3$). The organics were dried over anhydrous magnesium sulfate and filtered. The magnesium sulfate was washed with additional toluene and the filtered organics combined before the volatiles were removed *in vacuo*. The crude residue was separated in three stages: firstly the mixture was separated by column chromatography over silica using ethyl acetate/methanol/*n*-hexane mixtures (10:1:39-6:1:13) as eluent, secondly the mixture was further purified by column chromatography over silica using an ethyl acetate/toluene mixture (1:1) as eluent; and finally residual impurities were removed by short-path distillation using a kügelrohr distillation apparatus at 0.3 mbar and 190 °C to yield **9** as a yellow oil (1.17 g, 61%). Found: C, 61.3; H, 6.1; $\text{C}_{28}\text{H}_{33}\text{BrO}_6$ requires C, 61.7; H, 6.1. λ_{max} ($\text{CH}_2\text{Cl}_2/\text{nm}$): 270 ($\log \epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 4.86). δ_{H} (500 MHz, CDCl_3): 3.40 (6H, s, $\text{ArOC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OCH}_3$), 3.58-3.60 (4H, m, $\text{ArOC}_2\text{H}_4\text{OCH}_2\text{CH}_2\text{OMe}$), 3.72-3.74 (4H, m, $\text{ArOC}_2\text{H}_4\text{OCH}_2\text{CH}_2\text{OMe}$), 3.87-3.89 (4H, m, $\text{ArOCH}_2\text{CH}_2\text{OC}_2\text{H}_4\text{OMe}$), 4.17-4.19 (4H, m, $\text{ArOCH}_2\text{CH}_2\text{OC}_2\text{H}_4\text{OMe}$), 6.99 and 7.51 (8H, AA'BB', surface PhH), 7.60-7.61 (3H, m, overlapping branching PhH); δ_{C} (125 MHz, CDCl_3): 59.0, 67.4, 69.7, 70.7, 71.9, 114.9, 123.1, 123.8, 127.8, 128.1, 132.4, 143.1, 158.8; m/z [ESI] anal. cald. for $\text{C}_{28}\text{H}_{33}\text{O}_6\text{Br}$: 544.2 (100%), 545.2 (30%), 546.2 (97%), 547.2 (30%). Found: 567.2 (100%, $\text{M} + \text{Na}^+$), 568.2 (68%, $\text{M} + \text{Na}^+$), 569.2 (95%, $\text{M} + \text{Na}^+$), 570.2 (26%, $\text{M} + \text{Na}^+$), 583.1 (26%, $\text{M} + \text{K}^+$), 584.1 (10%, $\text{M} + \text{K}^+$), 585.1 (30%, $\text{M} + \text{K}^+$) and 586.1 (7%, $\text{M} + \text{K}^+$).

Synthesis of brominated bifluorene core **3b** and characterising data for precursors



Scheme S2 Synthesis of bifluorene core precursor **3b**. *Conditions and reagents:* (i) aq. NaOH, PhMe, 3 eq. 1-bromo-2-(2-methoxyethoxy)ethane, *n*-Bu₄NBr, 60 °C, dark, Ar, 83%. (ii) *n*-BuLi, THF, B(OMe)₃, -78 °C-rt, aq. HCl. (iii) Pd(PPh₃)₄, PhMe, *tert*-BuOH, aq. K₂CO₃, 100 °C, N₂, 73% (2 steps). (iv) 2.2 eq. Br₂, cat. I₂, CHCl₃, rt, dark, 69%.

2-Bromo-9,9-bis[2-(2-methoxyethoxy)ethyl]fluorene (**10b**)

2-Bromofluorene (2.23 g, 9.11 mmol) and tetra-*n*-butylammonium bromide (0.147 g, 0.455 mmol) were dissolved in toluene (37.5 cm³) and aqueous sodium hydroxide (50% w/w, 37.5 cm³) was added. The mixture was deoxygenated by placing *in vacuo* and purging with argon three times. Light was excluded and the mixture was stirred at 60 °C for 1 h before 1-bromo-2-(2-methoxyethoxy)ethane (3.7 cm³, 27 mmol) was added. The mixture was deoxygenated by placing *in vacuo* and purging with argon five times before light was excluded and the mixture was stirred at 60 °C for 3 d. The mixture was allowed to cool to room temperature and was diluted with toluene (20 cm³). The layers were separated and the aqueous layer was extracted with toluene (2 × 10 cm³). The combined organics were washed with water (2 × 10 cm³) and brine (2 × 10 cm³). The organics were dried over anhydrous magnesium sulfate and filtered. The magnesium sulfate was washed with additional toluene and the filtered organics combined before the volatiles were removed *in vacuo*. The residue was separated by column chromatography over silica using

ethyl acetate/*n*-hexane mixtures (3:7-2:3) as eluent to yield **10b** as a yellow oil (3.38 g, 83%). Found: C, 61.5; H, 6.7; C₂₃H₂₉BrO₄ requires C, 61.5; H, 6.5. λ_{\max} (CH₂Cl₂/nm): 232sh (log ϵ /dm³ mol⁻¹ cm⁻¹ 4.04), 268sh (4.37), 272sh (4.39), 276 (4.42), 287sh (4.23), 298 (4.03) and 309 (4.10). δ_{H} (400 MHz, CDCl₃): 2.33-2.43 (4H, m, FICH₂CH₂OC₂H₄OMe), 2.71-2.80 (4H, m, FICH₂CH₂OC₂H₄OMe), 3.14-3.22 (4H, m, FIC₂H₄OCH₂CH₂OMe), 3.28-3.30 (10H, m, overlapping FIC₂H₄OCH₂CH₂OMe and FIC₂H₄OC₂H₄OCH₃), 7.29-7.36 (2H, m, overlapping FIH), 7.37-7.42 (1H, m, FIH), 7.45 (1H, dd, $J = 8.0$ Hz, $J = 2.0$ Hz, FIH), 7.53 (1H, dd, $J = 8.0$ Hz, $J = 0.5$ Hz, FIH), 7.55 (1H, dd, $J = 2.0$ Hz, $J = 0.5$ Hz, FIH), 7.62-7.67 (1H, m, FIH). δ_{C} (100 MHz, CDCl₃): 39.5, 51.4, 58.9, 66.9, 69.9, 71.7, 119.8, 121.1, 121.2, 123.2, 126.6, 127.4, 127.8, 130.4, 139.36, 139.40, 148.5, 151.1. m/z [ESI] anal. calcd. for C₂₃H₂₉O₄Br: 448.1 (100%), 449.1 (16%), 450.1 (97%) and 451.1 (24%). Found: 471.2 (100%, M + Na⁺), 471.2 (24%, M + Na⁺), 473.1 (92%, M + Na⁺), 474.1 (21%, M + Na⁺), 487.1 (16%, M + K⁺), 488.0 (3%, M + K⁺), 489.1 (15%, M + K⁺) and 490.1 (5%, M + K⁺).

9,9,9',9'-Tetrakis[2-(2-methoxyethoxy)ethyl]-2,2'-bifluorene (11b)

10b (1.00 g, 2.23 mmol) was dissolved in anhydrous tetrahydrofuran (5 cm³) under argon and the resulting solution was cooled in a dry ice/acetone bath. A solution of *n*-butyl lithium in hexanes (1.6 M, 1.7 cm³) was added dropwise over 5 min. The mixture was allowed to stir whilst cooled for 30 min and trimethyl borate (0.50 cm³, 4.5 mmol) was added. The mixture was stirred in the dry ice/acetone bath for a further 5 min before it was allowed to warm to room temperature. After 1 h the mixture was diluted with tetrahydrofuran (10 cm³) and aqueous hydrochloric acid (3.0 M, 25 cm³) was added. The mixture was stirred at room temperature for 3 d before it was diluted with diethyl ether (30 cm³) and the layers were separated. The aqueous layer was extracted with diethyl ether (2 × 10 cm³ and 1 × 15 cm³) and brine was added to aid separation of the organic and aqueous phases. The combined organics were then washed with water (2 × 10 cm³) and brine (10 cm³) before they were dried over anhydrous magnesium sulfate and filtered. The magnesium sulfate was washed with additional diethyl ether and the filtered organics combined before the

volatiles were removed *in vacuo*. The crude product was purified by column chromatography over silica in two stages: firstly using *n*-hexane/ethyl acetate/methanol mixtures (2:3:0-0:49:1-0:19:1) as eluent and finally using *n*-hexane/ethyl acetate/methanol mixtures (2:3:0-0:1:0-0:19:1) as eluent. This purification sequence yielded a mixture of fluorenyl boronic acids and anhydrides as a colourless oil which slowly solidified to a white solid (0.722 g, 1.74 mmol of C₂₃H₃₁BO₆). This solid and 2-bromo-9,9-bis[2-(2-methoxyethoxy)ethyl]fluorene **11b** (0.870 g, 1.94 mmol) were dissolved in a mixture of toluene (30 cm³) and *tert*-butanol (10 cm³). Aqueous potassium carbonate (2.0 M, 10 cm³) was added and the mixture was deoxygenated by sparging with nitrogen for 20 min. Tetrakis(triphenylphosphine)palladium(0) (0.112 g, 0.097 mmol) was added and the mixture was deoxygenated by sparging with nitrogen for 20 min. The mixture was stirred at 100 °C under nitrogen for 3 d before it was allowed to cool to room temperature. The mixture was diluted with toluene (30 cm³), water (30 cm³) and brine (30 cm³) and the layers were separated. The aqueous layer was extracted with toluene (3 × 25 cm³) and the combined organics were washed with water (2 × 30 cm³) and water/brine mixtures (1:1, 1:3 and 0:1 v/v; 30 cm³). The organics were dried over anhydrous magnesium sulfate and filtered. The magnesium sulfate was washed with additional toluene and the filtered organics combined before the volatiles were removed *in vacuo*. The residue was separated by column chromatography over silica in two stages: firstly using ethyl acetate/*n*-hexane mixtures (4:1-1:0) as eluent and finally using ethyl acetate/toluene/methanol mixtures (4:1:0-16:3:1) as eluent to yield **3b** as a yellow oil that slowly crystallised into a yellow solid [1.123 g, 73% (2 steps)], mp = 90-92 °C. Found: C, 74.7; H, 8.1; C₄₆H₅₈O₈ requires C, 74.8; H, 7.9. λ_{max} (CH₂Cl₂/nm): 260 (log ε/dm³ mol⁻¹ cm⁻¹ 3.80), 271sh (3.89), 289sh (4.25), 304sh (4.48) and 329 (4.75). δ_H (500 MHz, CDCl₃): 2.46-2.55 (8H, m, FICH₂CH₂OC₂H₄OMe), 2.76-2.88 (8H, m, FICH₂CH₂OC₂H₄OMe), 3.19-3.25 (8H, m, ArC₂H₄OCH₂CH₂OCH₃), 3.26 (12H, s, FIC₂H₄OC₂H₄OCH₃), 3.30-3.32 (8H, m, FIC₂H₄OCH₂CH₂OMe), 7.32 (2H, ddd, *J* = 7.5 Hz, *J* = 7.5, *J* = 1.5 Hz, FIH), 7.37 (2H, ddd, *J* = 7.5 Hz, *J* = 7.5 Hz, *J* = 1.5 Hz, FIH), 7.45 (2H, br d, *J* = 7.0 Hz, FIH), 7.64 (2H, dd, *J* = 8.0 Hz, *J* = 1.5 Hz, FIH), 7.69 (2H, br d, *J* = 1.5 Hz, FIH), 7.72 (2H, br d,

$J = 7.5$ Hz, FIH), 7.76 (2H, d, $J = 8.0$ Hz, FIH). δ_{C} (125 MHz, CDCl_3): 39.8, 51.2, 58.9, 67.1, 69.9, 71.7, 119.9, 120.1, 121.5, 123.2, 126.6, 127.3, 127.4, 139.7, 140.1, 140.5, 149.1, 149.6. m/z [MALDI-TOF] anal. calcd. for $\text{C}_{46}\text{H}_{58}\text{O}_8$: 738.4 (100%), 739.4 (53%), 740.4 (16%), 741.4 (3%). Found: 738.6 (100%), 739.6 (42%), 740.6 (9%), 741.6 (2%).

Tabulated thin film quenching constants and detection limit concentrations

Analyte	K (ppm ⁻¹) 5a	K (ppm ⁻¹) 5b	K (ppm ⁻¹) 6a	K (ppm ⁻¹) 6b
DNT	5.50 ± 0.22	4.25 ± 0.17	1.31 ± 0.10	1.50 ± 0.12
DNB	10.6 ± 0.6	8.27 ± 0.35	1.89 ± 0.13	2.12 ± 0.18
pNT	0.095 ± 0.005	0.128 ± 0.008	0.061 ± 0.002	0.038 ± 0.003
NM	$(8.18 \pm 0.52) \times 10^{-5}$	$(6.56 \pm 0.19) \times 10^{-5}$	$(10.4 \pm 0.5) \times 10^{-5}$	$(15.0 \pm 0.5) \times 10^{-5}$
DMNB	0.017 ± 0.006	0.087 ± 0.001	0.033 ± 0.010	0.064 ± 0.006

Table S1 Quenching constants K for each dendrimer-analyte combination determined from least squares fitting to F_0/F versus $[Q]$ plots.

Analyte	$[Q]$ (ppm) 5a	$[Q]$ (ppm) 5b	$[Q]$ (ppm) 6a	$[Q]$ (ppm) 6b
DNT	$(1.82 \pm 0.36) \times 10^{-3}$ (1%)	$(2.35 \pm 0.47) \times 10^{-3}$ (1%)	$(7.63 \pm 1.53) \times 10^{-3}$ (4%)	$(6.67 \pm 1.33) \times 10^{-3}$ (4%)
DNB	$(0.95 \pm 0.19) \times 10^{-3}$ (3%)	$(1.21 \pm 0.24) \times 10^{-3}$ (4%)	$(5.29 \pm 1.06) \times 10^{-3}$ (18%)	$(4.72 \pm 0.94) \times 10^{-3}$ (16%)
pNT	0.105 ± 0.021 (<1%)	0.078 ± 0.016 (<1%)	0.164 ± 0.033 (<1%)	0.262 ± 0.052 (<1%)
NM	122 ± 24 (<1%)	152 ± 30 (<1%)	96 ± 19 (<1%)	67 ± 13 (<1%)
DMNB	1.40 ± 0.28 (52%)	0.76 ± 0.15 (28%)	0.75 ± 0.15 (28%)	0.52 ± 0.10 (19%)

Table S2 Detection limit concentrations for each analyte-dendrimer combination. Numbers in parentheses indicate percentage of saturated vapour concentration.

References

- (1) Yamazaki, O.; Togo, H.; Nogami, G. and Yokoyama, M., *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2519.