Supplementary Information for

Truxene-cored π-Expanded Triarylborane Dyes as Single- and Two-Photon Fluorescent Probes for Fluoride

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1. Synthesis

Scheme S1. Synthesis of target compounds.\textsuperscript{[1,2]} (a) and (e) HIO\textsubscript{3}, I\textsubscript{2}, CH\textsubscript{3}COOH-H\textsubscript{2}SO\textsubscript{4}-H\textsubscript{2}O-CCl\textsubscript{4}, 80 °C, 4 h; (b) 2-ethynylthiophene, Pd(PPh\textsubscript{3})\textsubscript{4}, n-Bu\textsubscript{4}NF, Et\textsubscript{3}N, tetrahydrofuran (THF), reflux, 3 h; (c) and (h) dimesitylboron fluoride, n-BuLi, THF, −78 °C, 2 d; (d) 1,2-Propanediol carbonate, N-bromosuccinimide, 60 °C, 2 h; (f) diphenylamine, K\textsubscript{2}CO\textsubscript{3}, Cu (powder), 18-crown-6-ether, 1,2-dichlorobenzene, reflux, 8 h; (g) thiophen-2-yl-2-boronic acid, Pd(PPh\textsubscript{3})\textsubscript{4}, K\textsubscript{2}CO\textsubscript{3}, THF, reflux, 8 h.

2,7,12-Triiodo-5,5',10,10',15,15'-hexaethyltruxene (2). A mixture of compound 1 (1.33 g, 2.61 mmol), HIO\textsubscript{3} (0.50 g, 2.82 mmol), I\textsubscript{2} (1.00 g, 3.94 mmol), and 20 mL solvent (CH\textsubscript{3}COOH:H\textsubscript{2}SO\textsubscript{4}:H\textsubscript{2}O:CCl\textsubscript{4} = 100:5:20:8, v/v/v/v) was heated to 80 °C and stirred for 4 h at the same temperature. The mixture was then cooled to room temperature and filtered under suction. The residue was washed with water and purified by column chromatography on silica gel by using CHCl\textsubscript{3}-hexane (1:5, v/v) as the eluent to obtain compound 2 (1.98 g, 85%) as a white powder [melting point (m.p.) = 334 °C to 336 °C]. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz, ppm): δ 0.18 (s, 18 H), δ 2.04–2.11 (m, 6 H), 2.85–2.92 (m, 6 H), and 7.39–8.09 (m, 9 H). Elemental anal. calcd. for C\textsubscript{39}H\textsubscript{39}I\textsubscript{3}: C, 52.72; and H, 4.42. Found: C, 52.92; and H, 4.33. MALDI-TOF: m/z 888.0 [M\textsuperscript{+}] and 858.9 [M-29]\textsuperscript{+}.

2,7,12-tri(2-thiophenylethynyl)-5,5',10,10',15,15'-hexaethyltruxene (3). A mixture of 2 (0.50 g,
0.56 mmol), 2-ethynylthiophene (0.40 g, 3.70 mmol), Pd(PPh₃)₄ (20 mg, 0.02 mmol), n-Bu₄NF (50 mg),
THF (15 mL), and triethylamine (15 mL) was heated to reflux with stirring after being flushed with
nitrogen for 30 min. After reacting for 3 h under nitrogen, the mixture was cooled to room temperature
and poured into water (100 mL). After several times of extraction with dichloromethane (DCM, 100
mL), the organic phase was dried over MgSO₄. The solvent was removed, and the residue was purified
by column chromatography on silica gel by using DCM-hexane (1:5, v/v) as the eluent to obtain
compound 3 (0.36 g, 78%) as a yellow powder (m.p. = 286 °C to 288 °C). ^1H NMR (CDCl₃, 500 MHz,
ppm): δ 0.22–0.25 (t, J = 7.3, 18 H), 2.16–2.20 (m, 6 H), 2.96–3.00 (m, 6 H), 7.04–7.06 (m, 3 H),
7.32–7.35 (m, 6 H), 7.55–7.57 (d, J = 8.0, 3 H), 7.62 (s, 3H), and 8.31–8.32 (d, J = 8.5, 3 H). ^13C NMR
(CDCl₃, 125 MHz, ppm): δ 152.9, 145.1, 140.7, 138.5, 131.9, 129.8, 127.3, 127.2, 125.2, 124.5, 123.5,
121.0, 57.0, 29.5, and 8.6. MALDI-TOF: m/z 829.2 [M⁺]. Elemental anal. calcd. for C₅₇H₄₈S₃: C, 82.56;
H, 5.83; and S, 11.60. Found: C, 82.64; H, 6.13; and S, 11.32.

2-Bromo-5,5’,10,10’,15,15’-hexaethyltruxene (4). N-bromosuccinimide was added (0.35 g, 1.97
mmol) stepwise to a stirred solution of 1 (1.00 g, 1.96 mmol) in 1,2-propanediol carbonate (15 mL) at
60 °C. After reacting for 2 h at the same temperature, the mixture was cooled, poured into 100 mL water,
extracted with DCM, and then dried over magnesium sulfate. The solvent was removed, and the residue
was purified by column chromatography on silica gel by using DCM-hexane (1:5, v/v) as the eluent to obtain
the crude product 4. Recrystallization with ethanol yielded compound 4 (0.73 g, 63%) as a white
 crystal (m.p. = 232 °C to 234 °C). ^1H NMR (CDCl₃, 300 MHz, ppm): δ 0.19 (s, 18 H), 2.08 (s, 6 H),
2.86–3.03 (m, 6 H), and 7.25–8.30 (m, 11 H). TOF-MS-EI: m/z 588.0 [M⁺], 559.0 [M-29]⁺, and 510.0
[M-78]⁺.

2-Bromo-7,12-diiodo-5,5’,10,10’,15,15’-hexaethyltruxene (5). A mixture of compound 4 (0.70 g,
1.19 mmol), HIO₃ (0.11 g, 0.60 mmol), I₂ (0.30 g, 1.19 mmol), and 15 mL solvent
(CH₃COOH:H₂SO₄:H₂O:CCl₄ = 100:5:20:8, v/v/v/v) was heated to 80 °C and stirred for 4 h at the
same temperature. The mixture was then cooled to room temperature and filtered under suction. The
residue was washed with water and purified by column chromatography on silica gel by using CHCl₃-hexane (1:5, v/v) as the eluent to obtain compound 5 (0.81 g, 81%) as a white powder (m.p. = 330 °C to 332 °C). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 0.18 (s, 18 H), 2.04–2.10 (m, 6 H), 2.85–3.03 (m, 6 H), and 7.38–8.30 (m, 9 H). TOF-MS-EI: m/z 840.0 [M⁺] and 811.0 [M-29]⁺.

2-Bromo-7,12-di(N,N-diphenylamino)-5,5',10,10',15,15'-hexaethyltruxene (6). A mixture of compound 5 (0.75 g, 0.89 mmol), K₂CO₃ (1.00 g, 7.25 mmol) powder, fresh Cu (0.07 g, 1.09 mmol) powder, 18-crown-6 ether (0.15 g, 0.62 mmol), diphenylamine (0.31 g, 1.83 mmol), and 1,2-dichlorobenzene (15 mL) were heated to reflux with stirring under nitrogen atmosphere. After reacting for 8 h, the mixture was cooled to room temperature and filtered under suction. The filtrate was then condensed and purified by column chromatography on silica gel. Elution with DCM-petrol ether (1:10, v/v) yielded compound 6 (0.56 g, 69%) as a white powder (m.p. = 232 °C to 235 °C). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 0.20–0.28 (m, 18 H), 1.90–2.08 (m, 6 H), 2.81–2.94 (m, 6 H), 7.00–7.54 (m, 26 H), and 8.08–8.13 (m, 3 H). MALDI-TOF: m/z 924.8 [M⁺], 895.6 [M-29]⁺, and 844.7 [M-80]⁺.

Synthesis of 2,7-di(N,N-diphenylamino)-12-(2-thiophenyl)-hexaethyltruxene (7). A mixture of compound 6 (0.50 g, 0.54 mmol), 2-thiophene-boronic acid (0.10 g, 0.78 mmol), Pd(PPh₃)₄ (30 mg, 0.03 mmol), toluene (30 mL), ethanol (8 mL), and 2 M aqueous K₂CO₃ solution (2 mL) was heated to reflux with stirring under a nitrogen atmosphere for 24 h. The mixture was cooled to room temperature and poured into water (100 mL). After extraction with DCM, the organic phase was dried over Na₂SO₄. The solvent was removed, and the residue was purified by column chromatography on silica gel by using DCM-hexane (1:20, v/v) as the eluent to obtain compound 7 (0.16 g, 32%) (m.p. = 156 °C to 158 °C). ¹H NMR (CDCl₃, 500 MHz, ppm): δ 0.21–0.28 (m, 18 H), 1.89–2.15 (m, 6 H), 2.84–2.99 (m, 6 H), 7.02–7.67 (m, 29 H), and 8.09–8.27 (m, 3 H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ154.22, 153.67, 152.67, 147.96, 129.24, 129.05, 128.24, 128.09, 126.35, 126.04, 125.31, 124.92, 124.59, 124.21, 122.95, 122.88, 122.69, 122.27, 121.98, 119.47, 117.66, 67.98, 56.65, 29.40, 29.19, 25.63, 21.46, 8.69, 8.65, and 8.61. MALDI-TOF: m/z 927.1 [M⁺] and 898.0 [M-29]⁺.
2. Theoretical Calculation

**Table S1.** The graphic representations of the frontier molecular orbits of N2SB.

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Table S2. The graphic representations of the frontier molecular orbitals of [N2SB-F].

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3. Calculation of association constants

The association constants of \( \text{C3B3} \) and \( \text{N2SB} \) were calculated according to a previously reported method.\(^5\)

\( \text{C3B3} \)

A THF solution of \( \text{C3B3} \) (2 mL, 10 \( \mu \)M) was placed in the cell and titrated with incremental amounts of \( \text{F}^- \) by adding a 5 \( \mu \)L THF solution of \( n\)-Bu4NF (1.8 mM), which represents a 0.45 equivalent of \( \text{C3B3} \). The absorption at 405 nm was monitored.

Fitting was conducted according to the following equations:

\[
\text{C3B3} + 3\text{F}^- \leftrightarrow \text{C3B3F}_3
\]

\[
A = k_s[\text{C3B3}] + k_p[\text{C3B3F}_3]
\]

\[
A_0 = k_s[\text{C3B3}]_0
\]

\[
[\text{C3B3}]_0 = [\text{C3B3}] + [\text{C3B3F}_3]
\]

\[
K = [\text{C3B3F}_3] / [\text{C3B3}][\text{F}^-]^3
\]

\[
\frac{A}{A_0} = \frac{1 + (k_p/k_s)K[\text{F}^-]^3}{(1 + K[\text{F}^-]^3)} \quad \rightarrow \quad (1 - \frac{A}{A_0})/\text{[F}^-]^3 = K(A/A_0) - K(k_p/k_s)
\]

The slope of the plot of \((1 - A/A_0)/[\text{F}^-]^3\) vs \(A/A_0\) indicates that the total binding constant \( K_{(\text{total})} \) of the three \( \text{F}^- \) was \( 1.3 \times 10^{14} \text{ M}^{-3} \) (Figure S1).
Figure S1. Results of fitting of absorption titration data of C3B3 with F⁻.

N2SB:

A THF solution of N2SB (2 mL, 10 μM) was placed in the cell and titrated with incremental amounts of F⁻ by adding a 5 μL THF solution of n-Bu₄NF (1.0 mM), which represents a 0.25 equivalent of N2SB. The absorption at 362 nm was monitored.

Fitting was conducted according to the following equations:

\[ \text{N2SB} + \text{F}^- \leftrightarrow \text{N2SBF} \]

\[ A = k_s [\text{N2SB}] + k_p [\text{N2SBF}] \]

\[ A_0 = k_s [\text{N2SB}]_0 \]

\[ [\text{N2SB}]_0 = [\text{N2SB}] + [\text{N2SBF}] \]

\[ K = [\text{N2SBF}] / [\text{N2SB}][\text{F}] \]

\[ A/A_0 = (1 + (k_p/k_s)K[F])/(1 + K[F]) \rightarrow (1 - A/A_0)/[\text{F}] = K(A/A_0) - K(k_p/k_s) \]

The slope of the plot of \( (1 - A/A_0)/[\text{F}] \) vs \( A/A_0 \) indicates that the binding constant \( K \) of N2SB for F⁻ was \( 3.5 \times 10^5 \text{ M}^{-1} \) (Figure S2).
**Figure S2.** Results of fitting of absorption titration data of N2SB with $\text{F}^-$.
4. $^1$H NMR and $^{13}$C NMR of C3B3 and N2SB

Figure S3. $^1$H NMR spectrum (500 MHz, CDCl$_3$) of compound C3B3.
Figure S4. $^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of compound C3B3.
Figure S5. $^1$H NMR spectrum (500 MHz, CDCl$_3$) of compound N2SB.
Figure S6. $^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of compound N2SB.
References


