

**Materials.** Solvents were reagent grade. Alkyl bromides and iodides (Aldrich) were used as received. Syntheses of the ammonium iodide salts have been described.<sup>1</sup> *tri*-Decylphosphine (**TDP**), *tri*-tetradecylphosphine (**TTP**), and *tri*-octadecylphosphine (**TOP**) were from CYTEC, Inc. **TOP** contained 2-3% of branched octadecyl isomers, 15 % octadecene, 8-10% toluene, and some phosphine oxides that developed over time. The other phosphines were not analyzed; all were used as received. (*Caution.* Phosphines should be handled only under oxygen-free conditions to avoid oxide formation.) The impurities were separated easily from the phosphonium salts via selective crystallization; NMR analyses indicate that the branched isomers of the salt were removed as well (*vide infra*). *tri*-Octadecylphosphine oxide was prepared as previously described:<sup>2</sup> mp 82.8-83.7°C (lit. mp 73-75°C<sup>8</sup>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 1.62 (m, 12H), 1.26 (m, 90H), 0.88 (t, *J* 6.6 Hz, 9H) ppm; <sup>31</sup>P-NMR (CDCl<sub>3</sub>) δ 49.1 ppm. Potassium ethyl xanthate, mp 210°C (dec), was synthesized according to literature procedures.<sup>3</sup> Commercial material was not suitable for our work.

**Additional instrumentation.** Ultraviolet-visible (UV-VIS) absorption spectra were recorded on a Perkin-Elmer Lambda 6 spectrometer interfaced to a 386 SX PC with Perkin-Elmer Computerized Spectrometer Software (PECSS). Infrared spectra were recorded on a Midac FT-IR spectrometer interfaced to a PC with Spectra-Calc software using pressed KBr pellets.

***tri*-Decylmethylphosphonium perchlorate (1P10ClO<sub>4</sub>)** from 25 mL (11.67 mmol) 0.467 M **1P10EX** and 2 mL (71 %, 23.6 mmol) of HClO<sub>4</sub>: 2.10 g (31.6 %), mp 40.3-43.6 °C, of a white solid at -77 °C and a transparent deformable solid at room temperature. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 2.21 (m, 6H), 1.90 (d, *J*<sub>P-CH<sub>3</sub></sub> 13.5 Hz, 3H), 1.50 (m, 12H), 1.26 (m, 36H), 0.88 (t, *J* 6.6 Hz, 9H) ppm. <sup>31</sup>P-NMR (CDCl<sub>3</sub>) δ 32.1 ppm. Anal. Calcd. for C<sub>31</sub>H<sub>66</sub>PClO<sub>4</sub>: C, 65.41; H, 11.69; Cl, 6.23. Found: C, 65.53; H, 11.75; Cl, 6.28.

***tri*-Decylmethylphosphonium hexafluorophosphate (1P10PF<sub>6</sub>)** from 25 mL (11.67 mmol) 0.467 M **1P10EX** and 2 mL (60 %, 13.6 mmol) of HPF<sub>6</sub>: 4.7 g (65.6 %), mp 55.0-56.1 °C, of a white solid. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 2.11 (m, 6H), 1.78 (d, *J*<sub>P-CH<sub>3</sub></sub> 13.5 Hz, 3H), 1.48 (m, 12H), 1.26 (m, 36H), 0.88 (t, *J* 6.6 Hz, 9H) ppm. <sup>31</sup>P-NMR (CDCl<sub>3</sub>) δ

32.0, -143.8 (septet,  $J = 713\text{ Hz}$ ) ppm.  $^{19}\text{F}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  -72.1 (d,  $J = 713\text{ Hz}$ ) ppm.

Anal. Calcd. for  $\text{C}_{31}\text{H}_{66}\text{P}_2\text{F}_6$ : C, 60.58; H, 10.82. Found: C, 60.72; H, 10.90.

**Methyl-*tri*-tetradecylphosphonium bromide (1P14Br).** In a sealed glove bag purged with nitrogen, 20 mL (40 mmol) of a 2.0 M anhyd bromomethane in *tert*-butyl methyl ether, 17.47 g (29.22 mmol) of **TTP**, and 100 mL of chloroform were stirred in an ice-bath that was allowed to melt slowly. After 1 day at room temperature, the reaction mixture was concentrated and the residual white paste was recrystallized (3x) from ethyl acetate to afford 16.58 g (79.0 %) of a white solid:  $T_{\text{K-SmA2}}$  103.5 °C,  $T_{\text{SmA2-I}}$  112.4 °C.

$^1\text{H}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  2.45 (m, 6H), 2.10 (d,  $J_{\text{P-CH}_3}$  13.2 Hz, 3H), 1.50 (m, 12H), 1.26 (m, 60H), 0.88 (t,  $J$  6.6 Hz, 9H) ppm.  $^{31}\text{P}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  32.32 ppm. Anal. Calcd. for  $\text{C}_{43}\text{H}_{90}\text{PBr}$ : C, 71.93; H, 12.63; Br, 11.13. Found: C, 72.05; H, 12.74; Br, 11.03.

**Methyl-*tri*-tetradecylphosphonium ethyl xanthate (1P14EX)** 15.50 g (21.58 mmol) of **1P14Br**, 3.68 g (22.96 mmol) potassium ethyl xanthate and 200 mL  $\text{CHCl}_3$  were stirred for 1 day, filtered, and the concentration of the yellow filtrate was adjusted to 0.1 M of **1P14EX** in  $\text{CHCl}_3$  assuming complete conversion of **1P14Br**. This solution was used to synthesize the other **1P14A**.

**Methyl-*tri*-tetradecylphosphonium chloride (1P14Cl).** The procedure described for **1P14Cl** was employed to prepare the other **1P14A**: 12 mL (1.2 mmol) of the 0.1 M **1P14EX** solution and 1 mL (12.2 mmol) conc HCl were stirred in an ice-bath that was allowed to melt slowly. After 1 day, the organic layer was washed with HPLC grade water (3X25 mL), the organic layer was concentrated to a yellow oil, and it was crystallized (3X) at 5 °C from ethyl acetate to afford 490 mg (57 %) of a white solid, mp 105.0-105.5 °C.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  2.43 (m, 6H), 2.10 (d,  $J_{\text{P-CH}_3}$  13.2 Hz, 3H), 1.50 (m, 12H), 1.26 (m, 60H), 0.88 (t,  $J$  6.6 Hz, 9H) ppm.  $^{31}\text{P}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  32.56 ppm.

**Methyl-*tri*-tetradecylphosphonium nitrate (1P14NO<sub>3</sub>)** from 40 mL (4 mmol) **1P14EX** solution and 284  $\mu\text{L}$  (70 %, 4.46 mmol) of  $\text{HNO}_3$ : 2.19 g (71.8 %) of a white amorphous solid after recrystallization (3X) from *tert*-butyl methyl ether,  $T_{\text{K-SmA2}}$  43.4 °C,  $T_{\text{SmA2-I}}$  110.4 °C.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  2.25 (m, 6H), 1.92 (d,  $J_{\text{P-CH}_3}$  13.2 Hz, 3H), 1.49 (m, 12H), 1.25 (m, 60H), 0.88 (t,  $J$  6.6 Hz, 9H) ppm.  $^{31}\text{P}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  32.4 ppm. Anal. Calcd. for  $\text{C}_{43}\text{H}_{90}\text{PNO}_3$ : C, 73.76; H, 12.96; N, 2.00. Found: C, 73.84; H, 13.01; N, 1.97.

**Methyl-*tri*-tetradecylphosphonium tetra-fluoroborate (1P14BF<sub>4</sub>)** from 40 mL (4 mmol) **1P14EX** solution and 575  $\mu$ L (48 %, 4.40 mmol) of HBF<sub>4</sub>: 2.52 g (81.8 %) of a white amorphous solid after recrystallization (3X) from ethyl acetate,  $T_{K-SmA2}$  52.6 °C,  $T_{SmA2-I}$  100.6 °C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  2.16 (m, 6H), 1.83 (d,  $J_{P-CH3}$  13.2 Hz, 3H), 1.49 (m, 12H), 1.25 (m, 60H), 0.88 (t,  $J$  6.6 Hz, 9H) ppm. <sup>31</sup>P-NMR (CDCl<sub>3</sub>)  $\delta$  32.2 ppm. <sup>19</sup>F-NMR (CDCl<sub>3</sub>)  $\delta$  -151.7 (<sup>10</sup>BF<sub>4</sub>), -151.8 (<sup>11</sup>BF<sub>4</sub>) ppm. Anal. Calcd. for C<sub>43</sub>H<sub>90</sub>PBF<sub>4</sub>: C, 71.24; H, 12.51. Found: C, 71.33; H, 12.63.

**Methyl-*tri*-tetradecylphosphonium perchlorate (1P14ClO<sub>4</sub>)** from 40 mL (4 mmol) **14P1EX** solution and 380  $\mu$ L (71 %, 4.48 mmol) of HClO<sub>4</sub>: 2.13 g (68.1 %) of a white amorphous solid after recrystallization from ethyl acetate,  $T_{K-SmA2}$  60.9 °C,  $T_{SmA2-I}$  103.2 °C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  2.18 (m, 6H), 1.87 (d,  $J_{P-CH3}$  13.2 Hz, 3H), 1.49 (m, 12H), 1.25 (m, 60H), 0.88 (t,  $J$  6.6 Hz, 9H) ppm. <sup>31</sup>P-NMR (CDCl<sub>3</sub>)  $\delta$  32.1 ppm. Anal. Calcd. for C<sub>43</sub>H<sub>90</sub>PClO<sub>4</sub>: C, 70.02; H, 12.30; Cl, 4.81. Found: C, 70.12; H, 12.33; Cl, 4.87.

***tri*-Octadecylphosphonium bromide (0P18Br)**. In a seal glove bag purged with nitrogen, 1.0 g (1.26 mmol) of **TOP**, 15 mL chloroform, and 5 mL (22.2 mmol) of 48 % aqueous HBr were stirred at room temperature. <sup>31</sup>P-NMR spectra of aliquots of the reaction mixture in CDCl<sub>3</sub> were used to monitor the progress of the reaction. The **TOP** peak at -31.8 ppm slowly disappeared and a new peak at 10.84 ppm appeared. After 1 d, the reaction mixture was cooled to 0 °C. A white solid, collected using a vacuum filtration apparatus packed in ice, was recrystallized (3X) from *tert*-butyl methyl ether to afford 882 mg (80 %) of a white solid, mp 103.1-106.7 °C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  7.62 (d,  $J_{P-H}$  510 Hz, 1H), 2.39 (m, 6H) 1.64 (m, 6H), 1.46 (m, 6H), 1.26 (m, 84H), 0.88 (t,  $J$  6.3 Hz, 9H) ppm. <sup>31</sup>P-NMR (CDCl<sub>3</sub>)  $\delta$  10.84 ppm.

***tri*-Octadecylphosphonium iodide (0P18I)** was prepared from 1.0 g (1.26 mmol) of **TOP**, 15 mL chloroform and 5 mL (37.9 mmol) of 57 % aqueous HI according to the procedure for **0P18Br**: 1.013 g (88 %) of a white amorphous solid,  $T_{K-SmA2}$  94.3 °C,  $T_{SmA2-I}$  109.0 °C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  7.62 (d,  $J_{P-H}$  = 510 Hz, 1H), 2.38 (m, 6H) 1.65 (m, 6H), 1.48 (m, 6H), 1.26 (m, 84H) 0.88 (t,  $J$  = 6.3 Hz, 9H) ppm. <sup>31</sup>P-NMR (CDCl<sub>3</sub>)  $\delta$  9.89 ppm. Anal. Calcd. for C<sub>54</sub>H<sub>112</sub>PI: C, 70.55; H, 12.28; I, 13.80. Found: C, 70.78; H, 12.14; I, 13.85.

**Methyl-*tri*-octadecylphosphonium bromide (1P18Br).** The other alkyl-*tri*-octadecylphosphonium halide salts were prepared at room temperature by procedures analogous to that for **1P18Br**. In a sealed glove bag purged with nitrogen, 5 mL (10 mmol) of a 2.0 M anhyd bromomethane in *tert*-butyl methyl ether, 1 g (1.26 mmol) of **TOP**, and 15 mL of chloroform were stirred in an ice-bath that was allowed to melt slowly. Progress of the reaction was monitored as above; a new peak appeared in the  $^{31}\text{P}$ -NMR spectra at 33.2 ppm. After 1 d at room temperature, the reaction mixture was cooled to 0 °C. A white solid, collected using a vacuum filtration apparatus packed in ice, was recrystallized from *tert*-butyl methyl ether to afford 1.056 g (94 %) of a white solid,  $T_{\text{K-SmA2}}$  99.4 °C,  $T_{\text{SmA2-I}}$  106.9 °C.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  2.43 (m, 6H), 2.09 (d,  $J_{\text{P-CH3}}$  13.2 Hz, 3H), 1.49 (m, 12H), 1.25 (m, 84H), 0.88 (t,  $J$  6.6 Hz, 9H) ppm.  $^{31}\text{P}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  33.21 ppm. Anal. Calcd. for  $\text{C}_{55}\text{H}_{114}\text{PBr}$ : C, 74.53; H, 12.96; Br, 9.02. Found: C, 74.44; H, 12.94; Br, 9.37.

**Ethyl-*tri*-octadecylphosphonium bromide (2P18Br)** from 3 mL (40.2 mmol) bromoethane, 10 mL  $\text{CHCl}_3$ , and 1g (1.26 mmol) **TOP**: 975 mg (86 %) of a white amorphous solid,  $T_{\text{K-SmA2}}$  94.4 °C,  $T_{\text{SmA2-I}}$  79.8 °C.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  2.61 (dq,  $J_{\text{P-CH2}}$  = 12.6 Hz,  $J_{\text{CH2-CH3}}$  = 6.9 Hz, 2H), 2.43 (m, 6H) 1.51 (m, 12H), 1.31 (t,  $J_{\text{CH2-CH3}}$  = 6.9 Hz, 3H) 1.26 (m, 84H), 0.88 (t,  $J$  = 6.6 Hz, 9H) ppm.  $^{31}\text{P}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  34.89 ppm. IR (KBr) 2920, 2851, 1470, 720  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{56}\text{H}_{116}\text{PBr}$ : C, 74.70; H, 12.98; Br, 8.87. Found: C, 74.61; H, 13.13; Br, 9.04.

***tri*-Octadecylpropylphosphonium bromide (3P18Br)** from 1 mL (11.0 mmol) 1-bromopropane, 10 mL  $\text{CHCl}_3$ , and 1g (1.26 mmol) **TOP**: 752 mg (82 %) of a white amorphous solid, mp 79.6-81.9 °C.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  2.42 (m, 8H) 1.64 (m, 2H) 1.51 (m, 12H), 1.25 (m, 84H), 1.14 (t,  $J$  = 6.8 Hz, 3H) 0.88 (t,  $J$  = 6.3 Hz, 9H) ppm.  $^{31}\text{P}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  32.63 ppm.

***tetra*-Octadecylphosphonium bromide (18P18Br)** from 1 g (3.00 mmol) 1-bromooctadecane, 10 mL  $\text{CHCl}_3$ , and 1g (1.26 mmol) **TOP**: 945 mg (28 %) of a white solid, mp 92.3- 94.8 °C.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  2.44 (s, 8H), 1.60 (s, 16H), 1.25 (s, 112H), 0.87 (t,  $J$  6.3 Hz, 12H) ppm.  $^{31}\text{P}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  33.12 ppm.

**Benzyl-*tri*-octadecylphosphonium bromide (BzP18Br)** from 1.0 g (4.07 mmol)  $\alpha$ -bromotoluene 10 mL  $\text{CHCl}_3$ , and 1.0 g (1.26 mmol) **TOP**: 1.01 g (84 %) of a white

solid,  $T_{K-SmA2}$  72.1 °C,  $T_{SmA2-I}$  78.5 °C.  $^1H$ -NMR ( $CDCl_3$ )  $\delta$  7.44 - 7.36 (m, 5H), 4.24 (d,  $J$  = 15.0 Hz, 2H), 2.40 (s, 6H), 1.43 (s, 12H), 1.25 (s, 84H), 0.87 (t,  $J$  = 6.0 Hz, 9H) ppm.  $^{31}P$ -NMR ( $CDCl_3$ )  $\delta$  31.90 ppm. IR (KBr) 2954, 2920, 2852, 1472, 1453, 718  $cm^{-1}$ . UV-vis ( $CHCl_3$ )  $\lambda_{max}$  238 nm ( $\epsilon$  488).

**Methyl-tri-octadecylphosphonium iodide (1P18I)** from 3 mL (48.2 mmol) 1-iodomethane, 100 mL  $CHCl_3$ , and 10 g (12.6 mmol) **TOP**: 6.23 g (53 %) of a white amorphous solid,  $T_{K-SmA2}$  73.1 °C,  $T_{SmA2-I}$  113.5 °C.  $^1H$ -NMR ( $CDCl_3$ )  $\delta$  2.43 (m, 6H), 2.10 (d,  $J_{P-CH3}$  = 13.5, 3H) 1.51 (m, 12H), 1.24 (m, 84H), 0.88 (t,  $J$  = 6.9, 9H) ppm.  $^{31}P$ -NMR ( $CDCl_3$ )  $\delta$  31.82 ppm. Anal. Calcd. for  $C_{55}H_{114}PI$ : C, 70.77; H, 12.31; P, 3.32. Found: C, 70.68; H, 12.10; P, 3.17.

**Ethyl-tri-octadecylphosphonium iodide (2P18I)** from 0.7 mL (8.69 mmol) iodoethane, 15 mL  $CHCl_3$ , and 1g (1.26 mmol) **TOP**: 889 mg (75 %) of a white amorphous solid,  $T_{K-SmA2}$  86.8 °C,  $T_{SmA2-I}$  107.6 °C.  $^1H$ -NMR ( $CDCl_3$ )  $\delta$  2.55 (dq,  $J_{P-CH2}$  = 12.6 Hz,  $J_{CH2-CH3}$  = 6.9 Hz, 2H), 2.42 (m, 6H) 1.52 (m, 12H), 1.33 (t,  $J_{CH2-CH3}$  = 6.9 Hz, 3H), 1.26 (m, 84H), 0.88 (t,  $J$  = 6.6 Hz, 9H) ppm.  $^{31}P$ -NMR ( $CDCl_3$ )  $\delta$  34.73 ppm. Anal. Calcd. for  $C_{56}H_{116}PI$ : C, 71.00; H, 12.34; I, 13.40. Found: C, 71.25; H, 12.12; I, 13.17.

**tri-Octadecylpropylphosphonium iodide (3P18I)** from 0.5 mL (5.13 mmol) 1-iodopropane, 15 mL  $CHCl_3$ , and 1g (1.26 mmol) **TOP**: 988 mg (82 %) of a white amorphous solid, mp 86.9 - 88.7 °C.  $^1H$ -NMR ( $CDCl_3$ )  $\delta$  2.42 (m, 8H) 1.64 (m, 2H) 1.51 (m, 12H), 1.25 (m, 84H), 1.16 (t,  $J$  6.6 Hz, 3H) 0.88 (t,  $J$  6.3 Hz, 9H) ppm.  $^{31}P$ -NMR ( $CDCl_3$ )  $\delta$  32.63 ppm. Anal. Calcd. for  $C_{57}H_{118}PI$ : C, 71.21; H, 12.37; I, 13.20. Found: C, 71.41; H, 12.34; I, 13.12.

**Butyl-tri-octadecylphosphonium iodide (4P18I)** from 0.5 mL (4.07 mmol) 1-iodobutane, 15 mL  $CHCl_3$ , and 1g (1.26 mmol) **TOP**: 998 mg (81 %) of a white amorphous solid, mp 86.7 - 88.5 °C.  $^1H$ -NMR ( $CDCl_3$ )  $\delta$  2.44 (m, 8H), 1.52 (m, 16H), 1.25 (m, 84H), 1.00 (t,  $J$  6.6 Hz, 3H), 0.88 (t,  $J$  6.3 Hz, 9H) ppm.  $^{31}P$ -NMR ( $CDCl_3$ )  $\delta$  32.96 ppm. Anal. Calcd. for  $C_{58}H_{120}PI$ : C, 71.42; H, 12.40; I, 13.01. Found: C, 71.24; H, 12.29; I, 13.21.

**tri-Octadecylpentylphosphonium iodide (5P18I)** from 1 mL (7.66 mmol) 1-iodopentane, 15 mL  $CHCl_3$ , and 1g (1.26 mmol) **TOP**: 898 mg (72 %) of a white

amorphous solid, mp 82.9 - 84.9 °C.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  2.44 (m, 8H), 1.52 (m, 16H), 1.25 (m, 86H), 0.91 (t,  $J = 7.2$  Hz, 3H) 0.88 (t,  $J = 6.9$  Hz, 9H) ppm  $^{31}\text{P-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  32.96 ppm.

**Dodecyl-*tri*-octadecylphosphonium iodide (12P18I)** from 1 mL (4.96 mmol) 1-iodododecane, 15 mL  $\text{CHCl}_3$ , and 1g (1.26 mmol) **TOP**: 850 mg (80 %) of a white amorphous solid, mp 83.9 - 85.0 °C.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  2.44 (m, 8H), 1.52 (m, 16H), 1.25 (m, 100H), 0.88 (t,  $J$  6.3 Hz, 12H) ppm.  $^{31}\text{P-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  32.96 ppm.

**tetra-Octadecylphosphonium iodide (18P18I)** from 1 g (2.63 mmol) 1-iodooctadecane, 10 mL  $\text{CHCl}_3$ , and 1g (1.26 mmol) **TOP**: 945 mg (64 %) of a white solid, mp 97.6 - 99.3 °C.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  2.42 (s, 8H), 1.61 (s, 16H), 1.27 (s, 112H), 0.89 (t,  $J$  6.3 Hz, 12H) ppm.  $^{31}\text{P-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  33.02 ppm.

**Methyl-*tri*-octadecylphosphonium ethyl xanthate (1P18EX)**. A solution of 1.0 g (1.13 mmol) of **1P18Br** in 50 mL of  $\text{CHCl}_3$  was added to 1.0 g (6.32 mmol) potassium ethyl xanthate and stirred for 24 h. The yellow solution was filtered and the solvent was reduced to a yellow oil residue using a rotary evaporator. The residue was dissolved in acetone and enough hexane was added to produce a clear yellow solution. A yellow plate-like crystalline solid (752 mg, 81%) was obtained upon cooling to 0 °C,  $T_{\text{K-SmA2}}$  52.2 °C,  $T_{\text{SmA2-I}}$  59.2 °C.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  4.49 (q,  $J = 7.2$  Hz, 2H), 2.41 (m, 6H), 2.10 (d,  $J = 13.2$  Hz, 3H), 1.52 (m, 12H), 1.37 (t,  $J = 7.21$  Hz, 3H), 1.25 (m, 84H), 0.88 (t,  $J = 6.3$  Hz, 9H) ppm.  $^{31}\text{P-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  32.96 ppm.

**Methyl-*tri*-octadecylphosphonium chloride (1P18Cl)**. The procedure described for **1PCl** was employed to prepare the other anion-exchanged salts. Conc hydrochloric acid (1 mL, 12.2 mmol) was added slowly to a solution of 500 mg (0.539 mmol) **1P18EX** in 20 mL  $\text{CHCl}_3$ . The yellow solution became clear during the addition. After 1 h additional stirring, the solution was washed with HPLC grade water (5x20 mL). The cloudy organic layer was reduced to a solid residue on a rotary evaporator. Recrystallization from *tert*-butyl methyl ether (3x) afforded 454 mg (89 %) of a white solid, mp 95.5 - 97.5 °C.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  2.43 (m, 6H), 2.10 (d,  $J_{\text{P-CH}_3}$  13.2 Hz, 3H), 1.48 (m, 12H), 1.25 (m, 84H), 0.88 (t,  $J$  6.6 Hz, 9H) ppm.  $^{31}\text{P-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  33.5 ppm.

Anal. Calcd. for  $C_{55}H_{114}PCl$ : C, 78.46; H, 13.65; Cl, 4.21. Found: C, 78.29; H, 13.85; Cl, 4.18.

**Methyl-*tri*-octadecylphosphonium nitrate (1P18NO<sub>3</sub>)** from 500 mg (0.539 mmol) of 1P18EX, 20 mL CHCl<sub>3</sub>, and 1 mL of HNO<sub>3</sub> (69 %, 15.5 mmol): 323 mg (69 %) of a white amorphous solid,  $T_{K-SmA2}$  69.4 °C,  $T_{SmA2-I}$  107.8 °C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 2.17 (m, 6H), 1.91 (d,  $J_{P-CH3}$  13.2 Hz, 3H), 1.47 (m, 12H), 1.25 (m, 84H), 0.88 (t,  $J$  6.6 Hz, 9H) ppm. <sup>31</sup>P-NMR (CDCl<sub>3</sub>) δ 33.4 ppm. Anal. Calcd. for  $C_{55}H_{114}PNO_3$ : C, 76.06; H, 13.23; N, 1.61. Found: C, 75.92; H, 13.30; N, 1.76.

**Methyl-*tri*-octadecylphosphonium tetrafluoroborate (1P18BF<sub>4</sub>)** from 650 mg (0.701 mmol) of 1PEX, 20 mL CHCl<sub>3</sub>, and 1 mL of HBF<sub>4</sub> (48 %, 7.65 mmol): 505 mg (81 %) of a white amorphous solid,  $T_{K-SmA2}$  69.6 °C,  $T_{SmA2-I}$  105.4 °C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 2.15 (m, 6H), 1.83 (d,  $J_{P-CH3}$  13.5 Hz, 3H), 1.48 (m, 12H), 1.25 (m, 84H), 0.88 (t,  $J$  6.6 Hz, 9H) ppm. <sup>31</sup>P-NMR (CDCl<sub>3</sub>) δ 32.1 ppm. <sup>19</sup>F-NMR (CDCl<sub>3</sub>) δ -151.6 (<sup>10</sup>BF<sub>4</sub>), -151.7 (<sup>11</sup>BF<sub>4</sub>) ppm. Anal. Calcd. for  $C_{55}H_{114}PBF_4$ : C, 73.95; H, 12.86. Found: C, 73.87; H, 12.94.

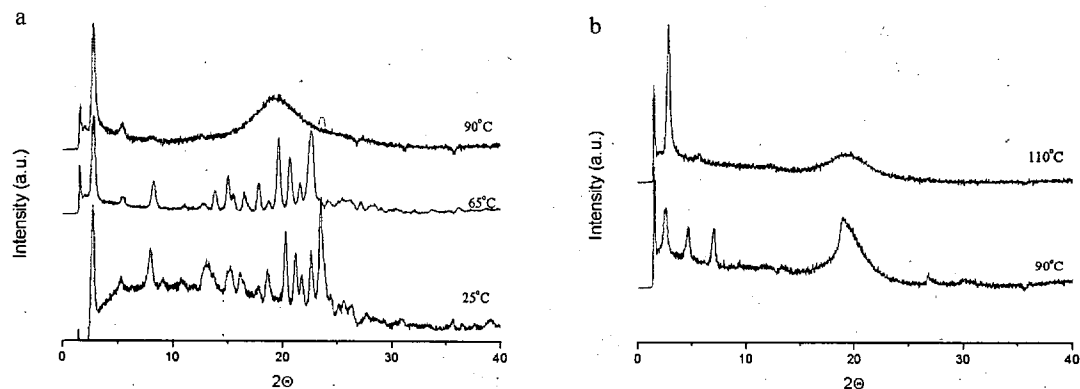
**Methyl-*tri*-octadecylphosphonium perchlorate (1P18ClO<sub>4</sub>)** from 500 mg (0.564 mmol) of 1P18EX, 25 mL CHCl<sub>3</sub>, and 1 mL of HClO<sub>4</sub> (70 %, 11.6 mmol): 358 mg (70.1%) of a white amorphous solid,  $T_{K-SmA2}$  75.4 °C,  $T_{SmA2-I}$  107.6 °C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 2.17 (m, 6H), 1.86 (d, 3H,  $J_{P-CH3}$  13.2 Hz), 1.47 (m, 12H), 1.25 (s, 84H), 0.88 (t, 9H,  $J$  6.6 Hz) ppm. <sup>31</sup>P-NMR (CDCl<sub>3</sub>) δ 33.21 ppm. Anal. Calcd. for  $C_{55}H_{114}PClO_4$ : C, 72.92; H, 12.68; Cl, 3.91. Found: C, 72.84; H, 12.77; Cl, 3.92.

**Methyl-*tri*-octadecylphosphonium hexafluorophosphate (1P18PF<sub>6</sub>)** from 780 mg (0.841 mmol) of 1P18EX, 20 mL CHCl<sub>3</sub>, and 1 mL of HPF<sub>6</sub> (60%, 6.79 mmol): 380 mg (48 %) of a white solid,  $T_{K-SmA2}$  79.8 °C,  $T_{SmA2-I}$  92.3 °C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 2.12 (m, 6H), 1.80 (d,  $J_{P-CH3}$  13.5 Hz, 3H), 1.48 (m, 12H), 1.25 (s, 84H), 0.88 (t,  $J$  6.6 Hz, 9H) ppm. <sup>31</sup>P-NMR (CDCl<sub>3</sub>) δ 32.0, -143.8 (septet) ppm. <sup>19</sup>F-NMR (CDCl<sub>3</sub>) δ -72.1 ppm. Anal. Calcd. for  $C_{55}H_{114}P_2F_6$ : C, 69.43; H, 12.08. Found: C, 69.61; H, 12.25.

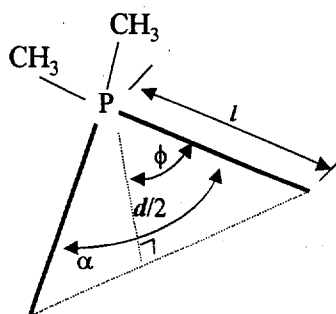
**Relationship between the SmA<sub>2</sub> phases of 1PmA and corresponding salts with *two* long chains.** The packing model proposed for SmA<sub>2</sub> phases of the *n*PmA (and *n*NmA) in Figure 5 can be extended to the smectic phases of salts with two long *n*-alkyl

chains and two methyl groups<sup>4</sup> (Supplementary Figure 2). The lamellar spacings for liquid-crystalline *di*-methyl-*di*-*n*-alkylphosphonium chloride (alkyl = octadecyl (35.6 Å), tetradecyl (28.1 Å), or decyl (21.2 Å)) are much larger than those for **1PmA** salts with chains of the same length; the height of a non-tilted triangle, defined by the phosphorus atom and the termini of the (hypothetically) extended long (tilted) chains, is greater than that of a **1PmA** tetrahedron. However, the calculated angles between chains of *di*-methyl-*di*-alkylphosphonium chlorides,  $\alpha = 92 - 93^\circ$ , are only slightly larger than those of **1PmA** salts. Chain tilting can compensate for slight differences between  $A_{3C}$  and  $A_H$ , but not for larger ones that would occur if **1PmA** were to pack like *di*-methyl-*di*-alkylphosphonium chlorides.<sup>4</sup>

In this regard, the **1PmCl** are **not** liquid-crystalline, but the corresponding *di*-methyl-*di*-alkylphosphonium chlorides are.<sup>4</sup> The cross-sectional area projected on an ionic plane by the two long alkyl chains of the *di*-methyl-*di*-alkylphosphonium chlorides,  $A_{2C}$ , is  $2 \times 21.2 / \cos(46.5^\circ) = 61.6 \text{ \AA}^2$  when the chain tilt angle  $\phi$  is  $\alpha/2$  ( $= 46.5^\circ$ ). The minimum cross-sectional area of three chains,  $3 \times 21.2 = 63.6 \text{ \AA}^2$ , occurs when they are *untilted*. Thus, the **1PmA** (and **nNmA**) cannot pack like their *di*-methyl-*di*-alkyl analogues in their liquid-crystalline phases even both are  $\text{SmA}_2$ .



**Supplementary Figure 1.** XRD patterns for 1P18I (a) and 1N18I (b) at the temperature indicated. The patterns at 110°C in (a) and 90°C in (b) are for liquid-crystalline phases.



**Supplementary Figure 2.** Average conformations of *di*-methyl-*di*-*n*-alkylphosphonium chlorides<sup>4</sup> in SmA<sub>2</sub> phases. Long alkyl chains are represented as lines.

**Supplementary Table 1.** Transition Temperatures, Enthalpies ( $\Delta H$ ) and Entropies ( $\Delta S$ ) of **nP18Br** from DSC Thermograms.

n	Transition	1st cycle				2nd cycle		$\Delta S^b$ (J/mol- T(K))
		heating		cooling		heating		
		T (°C) <sup>a</sup>	$\Delta H$ (kJ/mol)	T (°C)	$-\Delta H$ (kJ/mol)	T (°C)	$\Delta H$ (kJ/mol)	
0	K - K	-	-	-	-	41.8	1.2	-
		-	-	-	-	55.8	14.0	-
	K - I	92.4	4.0	48.2	50.1	72.7	2.3	-
		103.4	52.9	96.0	10.7	99.4	48.6	-
1	K - K	66.5	2.4	-	-	-	-	-
		83	41.3 <sup>s</sup>	70.0	66.1	82.2	62.0	183.5
	K - SmA <sub>2</sub>	94.6	8.8 <sup>s</sup>	95.3	12.0	94.5	12.1 <sup>s</sup>	32.7
		102.4	3.4	103.0	3.3	102.7	2.8 <sup>s</sup>	8.1
2	K - K	79.7	5.9	81.8	47.1	91.4	57.0	-
	K - SmA <sub>2</sub>	93.8	66.2 <sup>s</sup>	89.8	22.8	93.7	8.5	-
	SmA <sub>2</sub> - I	97.4	1.8	97.3	3.6	97.6	3.4	9.5
3	K - K	-	-	-	-	54.6	4.4	-
		-	-	-	-	64.6	-4.7	-
	K - I	79	147.8	63.7	89.6	76.7	104.8	283.2
18	K - K	-	-	-	-	87.6	49.5°	-
	K - I	94.8	201.6	83.6	185.6	94.6	129.1°	434.5
Bz <sup>c</sup>	K - K	37.1	-1.3	59.7	100.2	-	-	-
	K - SmA <sub>2</sub>	70.8	117.7	64.6	23.3	70.5	124.5	-
	SmA <sub>2</sub> - I	78.8	3.8	78.1	4.3	78.3	3.7	11.4

<sup>a</sup>Peak onset. <sup>b</sup> $\Delta S$  calculated from the average  $\Delta H$  and T based on the first cooling and second heating thermograms. <sup>c</sup>Benzyl-*tri*-octadecylphosphonium bromide. - No transition was observed; <sup>s</sup> Shoulder peak;

<sup>o</sup> Two overlapping peaks.

**Supplementary Table 2.** Transition Temperatures, Enthalpies ( $\Delta H$ ) and Entropies ( $\Delta S$ ) of **nP18I** from DSC Thermograms

n =	Transition	1st cycle				2nd cycle		$\Delta S^b$ (J/mol-T(K))
		heating	$\Delta H$	cooling	$-\Delta H$	heating	$\Delta H$	
		T (°C) <sup>a</sup>	(kJ/mol)	T (°C)	(kJ/mol)	T (°C)	(kJ/mol)	
0	K - K	-	-	76.5	33.5	-	-	-
	K - SmA <sub>2</sub>	92.5	45.4	92.2	15.6	92.1	45.5	-
	SmA <sub>2</sub> - I	111.7	2.8	111.4	2.8	110.5	2.8	7.3
1	K - K	-	-	45	16.2	48	20.2	-
	-	-	-	55.7	33.8	60.4	-11.7	-
	K - SmA <sub>2</sub>	72.1	92.9	67.6	2.8	68.7	60.6	-
	SmA <sub>2</sub> - I	112.7	3.5	112.2	3.6	112.6	3.4	9.1
2	K - K	78.6	22.5 <sup>o</sup>	72.7	29.9	82.4	2.8	-
	K - SmA <sub>2</sub>	85.3	61.7 <sup>o</sup>	77.3	24.1	84.4	49.0	-
	SmA <sub>2</sub> - I	106.9	5.1	106.4	5.5	107	5.2	14.1
3	K - K	57.4	3.7	-	-	76.5	-4.9	-
	SmA <sub>2</sub> - K	-	-	60.5	98.3	-	-	-
	I - SmA <sub>2</sub>	86.8 <sup>m</sup>	114.4	84.2	4.3	86.7 <sup>m</sup>	114.9	-
4	K - K	-	-	-	-	77	-3.1	-
	SmA <sub>2</sub> - K	-	-	64.6	94.5	-	-	-
	I - SmA <sub>2</sub>	86.3 <sup>m</sup>	106.7	71.0	4.4	85.3 <sup>m</sup>	96.3	-
5	K - K	52.6	7.2	-	-	77.2	-0.5	-
	K - I	79.9	72.1 <sup>s</sup>	68.0	61.5 <sup>s</sup>	79.2	60.1	175.5
12	K - K	-	-	-	-	68	12.2 <sup>o</sup>	-
	-	-	-	66.3	20.2	73.1	0.5 <sup>o</sup>	-
	K - I	82.4	108.4	72.6	75.4	81.7	66.3	202.3
18	K - K	-	-	-	-	92.4	5.6 <sup>o</sup>	-
	K - I	97.8	143.2 <sup>s</sup>	92.9	154.8	97.2	145.6 <sup>o</sup>	408.1

<sup>a</sup>Peak onset. <sup>b</sup> $\Delta S$  calculated from the average  $\Delta H_{\text{SmA}_2 \rightarrow \text{I}}$  and  $T_{\text{SmA}_2 \rightarrow \text{I}}$  based on the first cooling and second heating thermograms. - No transition was observed; <sup>s</sup> Shoulder peak; <sup>o</sup> Two overlapping peaks; <sup>m</sup> Melting transition.

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