

Synthesis procedure and ^1H NMR (CDCl_3) and ^{13}C NMR (CDCl_3)

Synthesis of compounds 1a, 1b

In a 100 mL flask was placed under a positive nitrogen pressure, triphenylphosphine (1 equiv., 20 mmol, 5 g) and a solid of alkyl iodide and bromide [1 equiv., 20 mmol *i.e.*: 13 g for octadecyl iodide ($\text{C}_{18}\text{H}_{37}\text{I}$) and 11 g for octadecyl bromide] were diluted in toluene (20 mL). The stirred suspension was allowed to react for 24 h at 120 °C, and a yellow precipitate was formed. The reaction mixture was then filtered, and washed repeatedly with pentane.

Octadecyltriphenylphosphonium iodide (C18P I) **1a**. White solid, Yield = 90%, m.p. = 86 °C, T_g = 11 °C. ^1H NMR (CDCl_3): δ 0.80-0.90 (m, 3H, CH_3); 1.10-1.35 (m, 28, CH_2Me); 1.50-1.70 [m, 4H, $\text{PCH}_2(\text{CH}_2)_2$]; 3.50-3.70 (m, 2H, PCH_2); 7.70-7.90 (m, 15H, H arom). ^{13}C NMR (CDCl_3): δ 14.00 (CH_3); 22.67 (CH_2Me); 23.20; 29.37-29.66; 30.24; 31.85 (PCH_2); 118.45; 130.43; 133.70; 135.15 (P-Carom.).

Octadecyltriphenylphosphonium bromide (C18P Br⁻) **1b**. White solid, Yield = 90%, m.p. = 85 °C, T_g = 12 °C. ^1H NMR (CDCl_3): δ 0.80-0.85 (m, 3H, CH_3); 1.05-1.30 (m, 28, CH_2Me); 1.55-1.75 [m, 4H, $\text{PCH}_2(\text{CH}_2)_2$]; 3.50-3.65 (m, 2H, PCH_2); 7.70-7.85 (m, 15H, H arom). ^{13}C NMR (CDCl_3): δ 14.00 (CH_3); 22.52 (CH_2Me); 23.00; 28.90-29.66; 30.20; 32.00 (PCH_2); 118.85; 130.80; 133.50; 135.45 (P-Carom.).

* *Synthesis of octadecyltriphenylphosphonium hexafluorophosphate 1c*

Octadecyltriphenylphosphonium hexafluorophosphate ($\text{C}_{18}\text{PPF}_6^-$) **1c** was prepared by anionic exchange according to the following procedure: In a 100 mL flask, octadecyltriphenylphosphonium iodide ($\text{C}_{18}\text{P I}$) (5.000 g, 13.14 mmol, 1 equiv.) was dissolved into dichloromethane (25 mL). The mixture was stirred for 30 min at room temperature. A solution of hydrogen hexafluorophosphate (HPF_6) (3.830 g, 26.28 mmol, 2 equiv.) diluted in water (25 mL) was stirred for 30 min and added to the octadecyltriphenylphosphonium iodide solution. The stirred suspension was allowed to react for 24 h at room temperature. The reaction mixture was then introduced in a separatory funnel, and the organic layer was washed repeatedly with distilled water (4x 25 mL). The mixture was dried over anhydrous magnesium sulfate, concentrated under reduced pressure. The solvent was removed by evaporation *under vacuum*. White solid, Yield = 90%, %, m.p. =

80 °C, T_g = -2 °C. ¹H NMR (CDCl₃): δ 0.80-0.90 (m, 3H, CH₃); 1.10-1.35 (m, 28, CH₂Me); 1.45-1.70 [m, 4H, PCH₂(CH₂)₂]; 3.40-3.55 (m, 2H, PCH₂); 7.55-7.85 (m, 15H, H arom). ¹³C NMR (CDCl₃): δ 14.00 (CH₃); 22.35 (CH₂Me); 23.50; 29.12-29.74; 30.35; 31.75 (PCH₂); 118.75; 130.22; 133.50; 135.05 (P-Carom.).

* *Synthesis of N-octadecyl-N'-octadecylimidazolium iodide 2c*

Three steps are necessary for the synthesis of N-octadecyl-N'-octadecylimidazolium iodide (C₁₈C₁₈Im I). The first one is the deprotonation of the imidazole ring with a solution of sodium methoxide prepared as follows: Sodium (1 equiv., 0.465 g, 20 mmol) is dissolved in dry freshly distilled methanol (10 mL) in a septum sealed, 100 mL round-bottomed, three-necked flask equipped with a condenser, a nitrogen inlet and a magnetic stirrer. Then, imidazole (1 equiv., 1.37 g, 20 mmol) and a small amount of acetonitrile (10 mL) were introduced into the solution of sodium methoxide at room temperature. After 15 min, the white suspension was formed and concentrated under reduced pressure. The dried white powder was diluted in acetonitrile and a powder of octadecyl iodide (C₁₈H₃₇I) was added under nitrogen atmosphere. The mixture was heated at 85 °C during 24 h. After the first alkylation, the same procedure was used for the second alkylation. After cooling to room temperature, the solvent was removed by evaporation *under vacuum*, and the beige solid obtained was filtered, washed repeatedly with pentane and dried. White powder, Yield = 97%, m.p. = 64 °C, T_g = 35 °C. ¹H NMR (CDCl₃): δ 0.75-0.90 (m, 6H, 2CH₃), 1.15-1.30 (m, 64H, 32 CH₂), 1.80-1.90 (m, 2H, NCH₂CH₂), 4.30 (t, 2H, CH₂N=), 7.45 (m, 1H, H arom), 7.65 (m, 1H, H arom), 9.15 [s (b), 1H, H arom]. ¹³C NMR (CDCl₃): δ 14.10 (2CH₃); 22.67 (2CH₂Me); 26.23; 28.97; 29.35-29.69; 30.24; 31.91 (CH₂); 50.10; (CH₂N=); 50.32 (CH₂N-); 121.69; 122.48 (=CN); 136.88 (N-C=N).

* *Synthesis of octadecylpyridinium iodide 3*

In a 100 mL flask was placed under a nitrogen pressure, octadecyl iodide (C₁₈H₃₇I) (10 mmol)] and distilled pyridine (1.5 equiv.). The stirred suspension was allowed to react for 24 h at room temperature. A yellow precipitate was formed. The reaction mixture was then filtered, washed repeatedly with pentane. Most of the solvent was removed *under vacuum*. Octadecylpyridinium iodide **3** was isolated after drying and fully characterized by ¹H and ¹³C NMR. White solid, Yield = 90%, m.p. = 102 °C, T_g = 44 °C. ¹H NMR (CDCl₃): δ 0.84 (t, J = 7.3 Hz, 3H, CH₃), 1.15-1.30 (m, 30H, 15 CH₂), 1.90-2.02 (m, 2H, NCH₂CH₂), 4.90 (t, J = 7.5

Hz, 2H, NCH₂), 8.05 (t, J = 7.2 Hz, 2H arom), 8.45 (t, J = 7.8 Hz, 1H, H arom), 9.35 (d, J = 5.4 Hz, 2H, H arom). ¹³C NMR (CDCl₃): δ 14.04 (CH₃); 22.58; 25.91; 28.99; 29.25-29.60; 31.81-31.84 (CH₂); 62.02 (CH₂N=); 128.57 (C=C); 144.82; 145.50 (=CN).

Thermogravimetric analysis (TGA)

Figure 1 – Effect of the anion chemical nature associated to phosphonium ionic liquids: evolution of the weight loss as a function of temperature (TGA, DTG) of the (●) C₁₈P Br⁻, (■) C₁₈P I⁻, (◆) C₁₈P PF₆⁻ (heating rate : 20 K.min⁻¹, under nitrogen atmosphere).

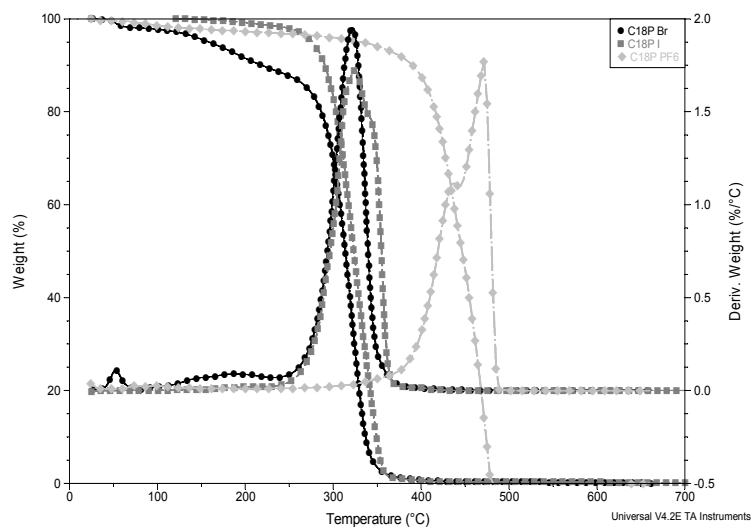
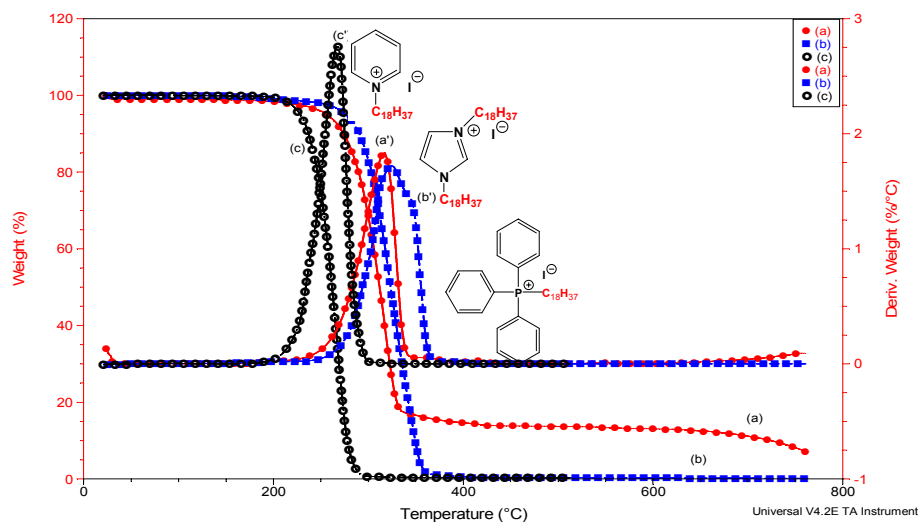
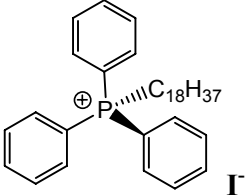
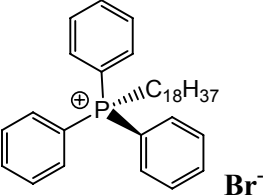
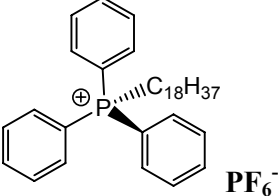
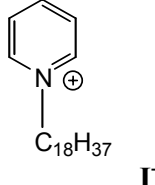
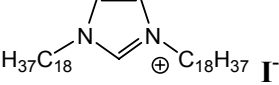


Figure 2 – Effect of the organic cation associated to iodide anion: evolution of the weight loss as a function of temperature (TGA, DTG) of the (●) $C_{18}Py I$, (●) $C_{18}C_{18}Im I$, (■) $C_{18}P PF_6^-$ (heating rate : $20 K \cdot min^{-1}$, under nitrogen atmosphere).



Differential scanning calorimetry (DSC)

| Nomenclature | structure | Melting Temperature (m.p)/ Glass transition (Tg) (°C) |
|---|--|---|
| Octadecyltriphenylphosphonium iodide $C_{18}P^+ I^-$ |  | m.p. = 86 Tg = 11 |
| Octadecyltriphenylphosphonium bromide $C_{18}P^+ Br^-$ |  | m.p. = 85 Tg = 12 |
| Octadecyltriphenylphosphonium hexafluorophosphate $C_{18}P^+ PF_6^-$ |  | m.p. = 80 Tg = -2 |
| Octadecylpyridinium iodide $C_{18}Py^+ I^-$ |  | m.p. = 102 Tg = 44 |
| N-octadecyl-N'-octadecylimidazolium iodide $C_{18}C_{18}Im^+ I^-$ |  | m.p. = 64°C Tg = 35 |

DSC curves of the PTFE/C₁₈P I⁺, Br⁻, PF₆⁻

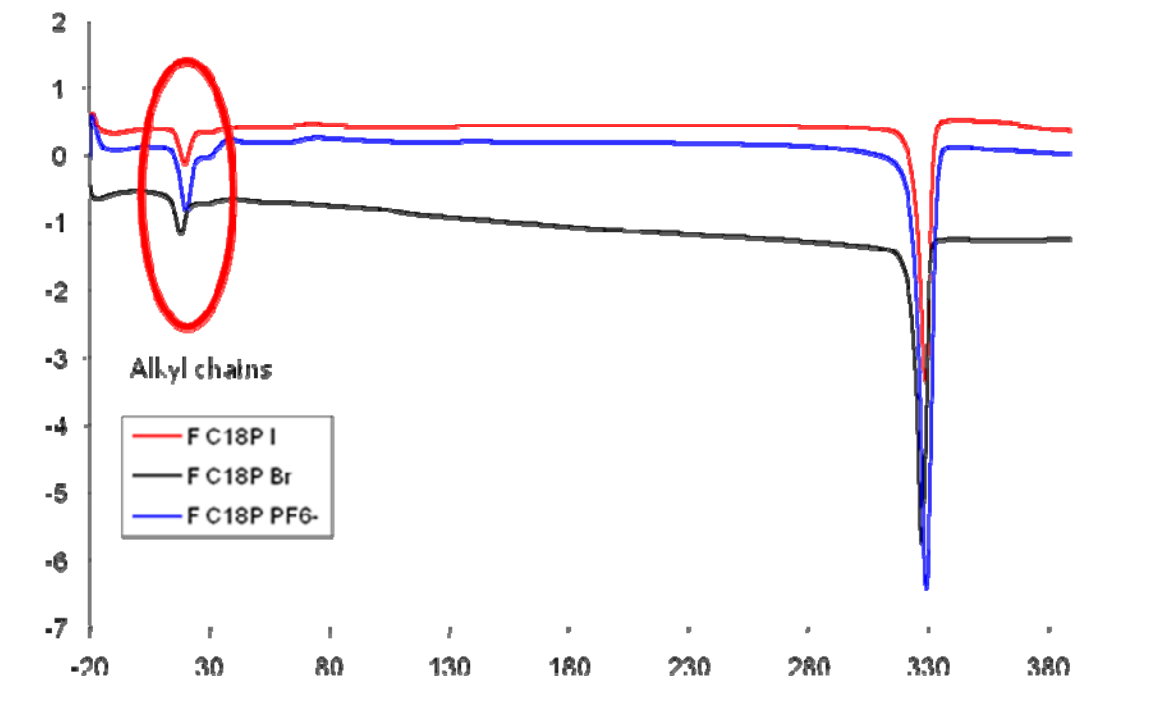


Table 1: Atomic percentage of species detected on the surface of PTFE films

X-Ray Photoelectron Spectroscopy

| Atomic % | C-F | C-C |
|--|-----|-----|
| PTFE | 59 | 30 |
| PTFE 1% C ₁₈ P I ⁺ | 97 | 3 |
| PTFE 5% C ₁₈ P I ⁺ | 93 | 5 |
| PTFE 1% C ₁₈ C ₁₈ Im I ⁺ | 88 | 12 |