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Ultra-high thermal stability perarylated ionic liquids as gas chromatographic stationary phases for the selective separation of polyaromatic hydrocarbons and polychlorinated biphenyls

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Abstract
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Keywords
Gas chromatography, Ionic liquids, Polycyclic aromatic hydrocarbons, Polychlorinated biphenyls, Solvation parameter model

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Highlights:

- Perarylated sulfonium and phosphonium ionic liquids (ILs) exhibit high thermal stability
- Some of the ILs produced low bleed at temperatures up to 350 °C
- Perarylated cations are able to strongly interact with aromatic containing analytes
- ILs exhibited high selectivity in the separation of polyaromatic hydrocarbon isomers
- High separation selectivity in separation of polychlorinated biphenyl congeners

Ultra-high thermal stability perarylated ionic liquids as gas chromatographic stationary phases for the selective separation of polyaromatic hydrocarbons and polychlorinated biphenyls

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Abstract

Ionic liquids (ILs) are well-known in the field of separation science for their unique selectivity when used as stationary phases in gas chromatography (GC). While a significant amount of knowledge has been attained in correlating structural features of an IL to separation selectivity, developments in producing IL-based stationary phases suitable for high temperature GC studies have lagged behind. Column bleed is a result of the stationary phase undergoing volatilization /decomposition at high temperatures and is undesirable in separations coupled to GC/MS. It has been well-known that traditional classes of ILs with long alkyl side chain substituents are susceptible to Hofmann elimination at elevated temperatures. In this study, a new class of IL stationary phases containing perarylated cations exhibiting improved thermal stability are introduced. These ILs were used to prepare wall-coated open tubular columns with high column efficiency and produced very low bleed at temperatures up to 350 °C. Their unique chemical structures provide stronger π-π interactions compared to many commercially-available stationary phases. To exploit the unique interactions provided by these stationary phases, the separation of two classes of environmentally hazardous aromatic compounds, namely, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), was examined. Both classes of compounds contain structural isomers with high boiling points that are often challenging to separate. The perarylated sulfonium and phosphonium IL-based stationary phases exhibited excellent thermal stability as well as unique selectivity toward isomers of PAHs as well as toxic PCB analyte pairs.

Keywords: gas chromatography; ionic liquids; polycyclic aromatic hydrocarbons; polychlorinated biphenyls; solvation parameter model

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1. Introduction

Ionic liquids (ILs), classified as non-molecular ionic solvents, are composed of an organic cation and an inorganic/organic anion [1]. ILs possess a number of unique features such as tunable physiochemical properties, low melting points, high thermal stability, and negligible vapor pressure at ambient temperatures [2]. In the field of analytical chemistry, ILs have been widely studied in chromatographic separations, electrochemical sensing, and sample preparation [2–5]. When used as stationary phases in gas chromatography (GC), ILs exhibit unique chromatographic selectivity toward different classes of analytes that is often based on the chemical structure and combination of cations and anions [4,6].

Compared to a number of commercial stationary phases (e.g., HP-5 and SPB-50), IL-based stationary phases generally offer lower thermal stabilities, placing them at a disadvantage when high separation temperatures are required. Increased column bleed originating from thermal decomposition/volatilization of the stationary phase can lower the signal-to-noise ratio for analytes and lead to poor sensitivity [7]. To improve the chromatographic performance of the stationary phase at high temperatures, commercially-available columns are often highly crosslinked using silarylene-siloxane copolymers to prevent ion source contamination when used in mass spectrometry (MS) [8]. GC/MS compatible stationary phases provide very low bleed profiles at elevated temperatures making them highly attractive in the separation of compounds with high boiling points. To exploit the unique separation power of IL-based stationary phases in GC/MS methods, their thermal stabilities must be improved. Recent studies have shown that imidazolium/phosphonium-based ILs with aryl substituents exhibit excellent thermal stability [9]. In addition, these ILs have the potential to provide strong π-π interactions toward analytes containing aromatic functionality. These ILs represent a class of compounds that have great

potential in the separation of high molecular weight and thermally-stable organic compounds when used as stationary phases.

Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are among the more challenging high molecular weight analytes to separate by GC. PAHs are composed of multiple fused aromatic rings and the numerous isomers of these compounds are often targeted in the analysis of environmental samples [10]. They are generated primarily from the incomplete combustion of fossil fuels [11]. PCBs are a group of persistent environmental contaminants that can be found in the fatty tissues of animals and humans due to their hydrophobicity and resistance toward metabolism. Before any health and environmental restrictions were put into place, PCBs were used as fire retardants and insulating fluids in electrical capacitors leading to their widespread existence in the environment [12]. The analysis of PAHs and PCBs dates back to the early 1970s using GC with porous-layer open tubular (PLOT) and wall-coated open tubular (WCOT) columns [13,14]. Although the separation of a wide range of PAHs have been studied, certain isomers with high boiling points, such as benzo[j]fluoranthene and benzo[b]fluoranthene, are often poorly separated [15]. In the case of PCBs, the analytical challenge results from the large amount of possible congeners, where the separation of all isomers is difficult to achieve on one single column [16–18]. Due to the similar chemical and physical properties of all 209 possible congeners, co-elution is a significant challenge.

To adequately separate PAHs and PCBs, stationary phases based on polydimethylsiloxane (PDMS) containing varying amounts of dimethyl and diphenyl modification have been widely studied [19]. Shape selective stationary phases such as the C_{60} fullerene phase have been shown to exhibit better selectivity for planar PCBs. However, the high

column bleed of this stationary phase at elevated oven temperatures precluded the separation of high boiling point congeners [20]. To resolve the structural isomers for both classes of analytes, IL-based stationary phases have been explored due to their unique chromatographic selectivity [21]. Monocationic IL-based stationary phases, including 1-benzyl-3-methylimidazolium triflate and 1-(4-methoxyphenyl)imidazolium triflate, were shown to exhibit thermal stabilities up to 260 °C [22]. Dicationic ILs were subsequently developed and their thermal stabilities were found to be higher than their monocationic analogues [23]. Dicationic imidazolium IL-based stationary phases with varying linker chain lengths were further developed by Armstrong and co-workers [24]. Improved separation of the benzo[j]fluoranthene and benzo[b]fluoranthene structural isomers was observed compared to PDMS stationary phases. While dicationic imidazolium IL-based stationary phases show improved stability, they are still susceptible to decomposition at high temperatures.

Recently, it was reported that the instability of conventional IL cations (e.g., N-functionalized aromatic azaheterocycles, tetralkylphosphonium) resulted from a retro-Menschutken reaction or Hofmann elimination at elevated temperatures [25,26]. To improve the thermal stability of IL cations, sulfonium- and phosphonium-based cations with aryl moieties were reported by Davis and coworkers in an effort to suppress the thermal decomposition of conventional ILs by avoiding alkyl side chain substituents [27,28]. The removal of a hydrogen atom on the aryl substituents was found to produce unstable benzyne intermediates, hence preventing the common decomposition pathway. Therefore, sulfonium- and phosphonium-based ILs with aryl moieties hold promise as high thermal stability stationary phases that offer unique chromatographic selectivity for aromatic compounds.

In this study, six sulfonium- and phosphonium-based ILs with low melting points were designed and prepared as stationary phases for the separation of PAHs and PCBs. These IL-based stationary phases provided improved resolution of structural isomers with high boiling points from both classes of analytes compared to commercial PDMS- and IL-based stationary phases such as HP-5ms, SPB-50, and SLB-IL111. The Abraham solvation parameter model was used to study the unique solvation characteristics offered by these stationary phases. This new class of stationary phases exhibit strong π-π interactions with analytes while providing thermal stabilities ranging from 290-350 °C.

2. Materials and methods

2.1. Materials

Naphthalene (99%), acenaphthene (99%), fluorene (98%), phenanthrene (98%), anthracene (97%), fluoranthene (98%), pyrene (98%), benzo(a)fluoranthene (99.5%), benzo(b)fluoranthene (99.9%), and benzo(k)fluoranthene (99.5%) were purchased from MilliporeSigma (Bellefonte, PA, USA). Butyraldehyde (99%), 1-chlorobutane (99%), ethyl acetate (99.5%), methyl caproate (99%), and 2-nitrophenol (99%) were purchased from Acros Organics (Morris Plains, NJ, USA). Bromoethane (98%) was purchased from Alpha Aesar (Ward Hill, MA, USA). Ethyl benzene was purchased from Eastman Kodak Company (Rochester, NJ, USA). Acetic acid (99.9%), *N*,*N*-dimethylformamide (99.9%), and toluene (99.8%) were purchased from Fisher Scientific (Pittsburgh, PA, USA). 2-chloroaniline (98%), *p*-cresol (99%), *o*-xylene (97%), *p*-xylene (99.5%), and 1-bromohexane (98%) were purchased from Fluka (Steinheim, Germany). Benzaldehyde (99%), 5-bromoacenapthene (90%), 2-nitronapthalene (85%), 1-chlorohexane (99%), 1-chlorooctane (99%), cyclohexanol (99%),

cyclohexanone (99.8%), 1-iodobutane (99%), 1-nitropropane (98%), octylaldehyde (99%), 1-pentanol (99%), 2-pentanone (99%), propionitrile (99%), 1-decanol (99%), acetophenone (99%), aniline (99.5%), benzonitrile (99%), benzyl alcohol (99%), 1-bromooctane (99%) , 1-butanol (99.8%), 1,2-dichlorobenzene (99%), dichloromethane (99.8%), 1,4-dioxane (99.5%), 1-octanol (99%), phenol (99%), pyridine (99%), pyrrole (98%), *m*-xylene (99.5%), 2-propanol (99.9%), and propionic acid (99%) were purchased from MilliporeSigma. The reagents 4-fluoroiodobenzene, Tris(4-fluorophenyl)phosphine, $Pd(OAc)_2$, potassium bis[(trifluoromethyl)sulfonyl]imide, 1,2-dichloro-4-(4-iodophenoxy)benzene, 1,4-diiodobenzene, potassium carbonate, copper(II) oxide, and 3,4-dichloro phenol were purchased from Sigma-Aldrich. A PCB calibration check solution containing 21 different congeners at a concentration of 100 µg/mL in acetone was purchased from Accustandard (New Haven, CT, USA). The chemical names and molecular structures for the PAHs and PCBs are listed in Tables S1 and S2 (see supporting information). The columns SLB-5ms (30 m × 250 µm × 0.25 µm), SPB-50 (30 m × 250 µm × 0.25 µm), and SLB-ILPAH (20 m × 180 µm × 0.05 µm) were purchased from MilliporeSigma (Bellefonte, PA, USA). The HP-5ms (30 m × 250 µm × 0.25 µm) and HP-5ms UI (30 m × 250 µm × 0.25 µm) columns were obtained from Agilent Technologies (Santa Clara, CA, USA).

2.2. Synthesis of ionic liquids

The chemical names and molecular structures of the ILs examined in this study are shown in Table 1. ILs **1**-**2** were prepared using previously reported methods [27-29]. NMR spectra were recorded on a 500 MHz JEOL spectrometer using $CDCl_3$ as a solvent at room

temperature. All chemical shifts for ^{1}H and ^{13}C NMR were reported downfield using tetramethylsilane (TMS, at d ¼ 0.00 ppm).

Synthesis of IL 3: In a 50 mL heavy wall pressure vessel with an internal thread containing a stir bar, 4-fluoroiodobenzene (1.0 equiv), tris(4-fluorophenyl)phosphine (1.0 equiv), $Pd(OAc)_2$ (1.5 mol %) and xylene (15 mL) were added under nitrogen atmosphere and reaction mixture stirred at 140 °C for 2 hours. The reaction mixture was then cooled down to room temperature and filtered to yield pure tetra(4-fluorophenyl) phosphonium iodide as a pale solid. The $[NTf_2^-]$ salt was achieved by anion exchange of $[K^+]$ $[NTf_2^-]$ (1.0 equiv) and the phosphonium salt (1.0 equiv) in water for 15 min at room temperature. The reaction mixture was then extracted three times with dichloromethane and brine solution. The combined organic extracts were dried over anhydrous Na_2SO_4, solvents were removed under reduced pressure, and pure tetra(4-fluorophenyl) phosphonium $[NTf_2^-]$ was achieved as a white solid. Pure crystals of the product were achieved by crystallization in hot ethanol. ^{1}H NMR ($CDCl_3$, 500 MHz): δH 7.65-7.61 (m, 8H), 7.42-7.39 (m, 8H); ^{13}C NMR ($CDCl^3$, 125 MHz): δC 168.0 (d), 165.9 (d), 137.1 (t), 123.3, 120.8, 118.5 (m), 115.7, 113.2, 112.5; ^{31}P NMR ($CDCl_3$, 202 MHz): δp 22.50 ppm; ^{19}FNMR ($CDCl_3$, 470 MHz): -78.96, -98.77 ppm. T_m = 137^{o}C (+/- 1.0 ^{o}C).

Synthesis of IL 4: First, 1,2-dichloro-4-(4-iodophenoxy)benzene was synthesized by mixing 1,4-diiodobenzene (1.0 equiv), potassium carbonate (2.5 equiv), copper(II) oxide (2.5 equiv), and 3,4-dichlorophenol in DMF as a solvent at 120 °C for overnight. After completion of the reaction, the pure compound was achieved by column chromatography. Then, 4-(3,4-dichlorophenoxy)phenyltriphenylphosphonium $[NTf_2^-]$ was prepared following the general procedure. ^{1}H NMR ($CDCl_3$, 500 MHz): δH 7.87-7.84 (m, 3H), 7.75-7.71 (m, 6H), 7.61-7.57 (m, 6H), 7.57-7.52 (m, 2H), 7.48-7.47 (m, 1H), 7.24-7.22 (m, 3H), 7.05-7.03 (m, 1H); ^{13}C NMR

($CDCl_3$, 125 MHz): δC 163.1, 152.7, 136.7 (d), 135.5 (d), 133.6, 131.7, 13.6 (d), 129.3, 122.7, 121.0, 120.4, 118.9, 118.8, 118.4, 117.9, 117.2, 110.5, 109.8; ^{31}P NMR ($CDCl_3$, 202 MHz): δp 23.28 ppm; ^{19}F NMR ($CDCl_3$, 470 MHz): -78.62 ppm. Tg = 3.0 ^{o}C (+/- 0.05 ^{o}C).

Synthesis of IL 5: 4-bromophenyltriphenylphosphonium [NTf_2^-] and 4-phenoxyphenyltriphenylphosphonium [NTf_2^-] were first prepared following the general procedure. Then, an equimolar ratio of these two compounds was combined and melted to produce the desired IL. ^{1}H NMR ($CDCl_3$, 500 MHz): δ_H 7.94-790 (m, 2H), 7.86-7.84 (m, 8H), 7.76-7.71 (m, 12H), 7.64-7.55 (m, 16H), 7.48-7.41 (m, 5H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 148.08, 138.08, 135.82-135.56 (m) 134.70 (d), 134.24 (d), 133.95 (d), 130.70 (d), 129.22, 128.95 (d), 127.37, 123.64, 121.08, 118.52, 117.88, 117.25 (d), 116.97, 116.53, 116.25, 115.96, 115.73, 115.01. ^{31}P NMR ($CDCl_3$, 202 MHz): δ_p 23.98, 23.68 ppm; ^{19}F NMR ($CDCl_3$, 470 MHz): -78.60 ppm.

Tg = 2.6 ^{o}C (+/- 0.14 ^{o}C).

Synthesis of IL 6: The ILs 4-[4-(4-phenoxyphenoxy)phenoxy]phenyltriphenylphosphonium [NTf_2^-] and 4-[4-(3-fluorophenoxy)phenoxy]phenyltriphenylphosphonium [NTf_2^-] was prepared following the general procedure. Then, an equimolar ratio of these two compounds was combined and melted to result the desired IL. ^{1}H NMR ($CDCl_3$, 500 MHz): δ_H 786-7.84 (m, 6H), 7.74-7.73 (m, 12H), 7.63-7.57 (m, 12H), 7.54-7.49 (m, 4H), 7.40-7.38 (m, 1H), 7.33-7.30 (m, 2H), 7.23-7.21 (m, 4H), 7.10-7.08 (m, 3H), 7.03-7.02 (m, 2H), 6.99-6.98 (m, 2H), 6.95-6.93 (m, 2H), 6.85-6.83 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 164.5 164.4, 163.5, 162.4, 156.8, 154.8, 136.5 (t), 135.5, 134.2 (d), 130.6 (m), 129.8, 123.5, 122.2, 121.1, 120.3, 118.9-118.0 (m), 117.5, 117.3, 116.4, 112.8,

112.6, 110.1, 109.1, 108.6, 108.4, 108.3 ppm; ^{31}P NMR ($CDCl_3$, 202 MHz): δ_p 23.28, 23.24 ppm; ^{19}F NMR ($CDCl_3$, 470 MHz): -78.60, -109.38 ppm. Tg = 10.0 ^{o}C (+/- 0.03 ^{o}C).

2.3. GC column preparation

Using the static coating method, thirty-meter untreated fused silica capillaries were coated with the ILs examined in this study. The coating solution was prepared by dissolving the ILs in dichloromethane at a concentration of 0.32% (w/v) to yield an approximate film thickness of 0.20 µm. The coated columns were conditioned at 200 °C for 12 h under a constant flow of helium. The column efficiency was determined using naphthalene at 110 °C. The list of columns examined in this study and their characteristics is shown in Table 2. All columns possessed efficiencies higher than 3700 plates/meter.

2.4. Preparation of probe solute standards and chromatographic conditions

The PAH mixture was prepared by dissolving the analytes in hexane at a concentration of 0.5 mg/mL. The PAH standards were prepared in hexane at a concentration of 0.1 mg/mL. The PAH separations were performed on an Agilent 7890B gas chromatograph coupled to a flame ionization detector (GC-FID). Helium was used as the carrier gas at a flow rate of 1 mL/min. The injector and detector temperatures were held at 250 °C using a split ratio of 20:1 and an injection volume of 1 µL. The detector employed hydrogen as the makeup gas at a flow rate of 30 mL/min, while the air flow was held at 400 mL/min. The temperature program for the analysis of PAHs was optimized for each column to achieve the best separation.

The PCB mixture was diluted from the standard solution to a concentration of 8 µg/mL. Separation of the mixture was performed on an Agilent 7890B/5977A GC/MS system. Helium was employed as the carrier gas at a flow rate of 1 mL/min and all injections were performed in split mode at a split ratio of 5:1. The temperature program for the analysis of PCB mixture was

optimized for each column. For the HP-5ms UI column, the oven temperature was initially held at 125 ℃, then increased to 185 ℃ at a rate of 12 ℃/min and held for 2 min. The temperature was then ramped to 220 ℃ at a rate of 10 ℃/min with a hold time of 2 min, and finally ramped to 250 ℃ at a rate of 12 ℃/min. For the SLB-IL111 column, the oven temperature was initially held at 85 ℃, then increased to 190 ℃ at a rate of 8 ℃/min and held for 3 min. The temperature was then ramped to 235 ℃ at a rate of 8 ℃/min with a hold time of 6 min, and finally ramped to 260 ℃ at a rate of 12 ℃/min.

For IL **1**, the oven temperature was initially held at 190 ℃, then increased to 200 ℃ at a rate of 4 ℃/min and held for 5 min. The temperature was ramped to 235 ℃ at a rate of 10 ℃/min with a hold time of 5 min and finally ramped to 265 ℃ at a rate of 8 ℃/min. For IL **2**, the oven temperature was initially held at 185 ℃, then increased to 200 ℃ at a rate of 8 ℃/min with a hold time of 3 min. The temperature was then ramped to 235 ℃ at a rate of 6 ℃/min with a hold time of 10 min, and finally ramped to 265 ℃ at a rate of 10 ℃/min. For IL **3**, the oven temperature was initially held at 130 ℃, and then increased to 185 ℃ at a rate of 12 ℃/min for and held for 1 min. The temperature was then ramped to 220 ℃ at a rate of 3 ℃/min with a hold time of 2 min, and finally ramped to 265 ℃ at a rate of 12 ℃/min. For IL **4**, the oven temperature was initially held at 185 ℃, then increased to 220 ℃ at a rate of 15 ℃/min and held for 5 min. The temperature was ramped to 245℃ at a rate of 5 ℃/min with a hold time of 5 min, and finally ramped to 265 ℃ at a rate of 8 ℃/min. For IL **5**, the oven temperature was initially held at 215 ℃ for 1 min, then increased to 230 ℃ at a rate of 25 ℃/min and held for 3 min. The temperature was then ramped to 250 ℃ at a rate of 5 ℃/min with a hold time of 6 min, and finally ramped to 285 ℃ at a rate of 12 ℃/min. For IL **6**, the oven temperature was initially held at 185 ℃, then increased to 200 ℃ at a rate of 8 ℃/min and held for 3 min. The temperature

was ramped to 235 °C at a rate of 6 °C/min with a hold time of 1 min, and finally ramped to 265 °C at a rate of 10 °C/min.

For experiments involving the solvation parameter model, analytes were prepared in dichloromethane at a concentration of 1 mg/mL. All GC measurements were performed on an Agilent 7890B GC-FID instrument. Helium was used as the carrier gas at a flow rate of 1 mL/min. The injector and detector temperatures were held at 250 °C. A split ratio of 100:1 was used with an injection volume of 1 µL. The detector employed hydrogen as the makeup gas at a flow rate of 30 mL/min, while the air flow was held at 400 mL/min. A list of the 46 probe molecules along with their solute descriptors is provided in Table S3. All 46 probes were injected individually at 50, 80, and 110 ºC. Lower boiling point analytes exhibited lower retention times at higher oven temperatures, while the other analytes displayed stronger retention on the stationary phase. Therefore, not all analytes listed were subjected to the regression analysis at the three temperatures studied. Multiple linear regression analysis and statistical calculations were performed using the software Analyze-it (Leeds, UK).

3. Results and discussion

Highly polar and thermally-stable GC stationary phases are particularly sought after in applications involving the analysis of long chain fatty acids, polycyclic aromatic sulfur heterocycles, PAHs, and PCBs [21,30–32]. Recent studies have shown that the triarylsulfonium- and tetraarylphosphonium-based ILs exhibited excellent thermal stability in that they were heated at 300 ºC for 90 days with no observable mass loss [28,29]. Perarylated ILs are highly promising to further extend the application of IL-based stationary phases for the separation of high molecular weight aromatic compounds such as PAHs and PCBs.

As shown in Table 1, six different sulfonium- and phosphonium-based ILs paired with bis[(trifluoromethyl)sulfonyl]imide ([NTf_2^-]) anions were studied. Among them, IL **1** is a sulfonium-based IL containing three phenyl substituents. ILs **2-6** are phosphonium-based ILs with different aryl moieties. ILs **3** and **4** contain halide modified aryl substituents, while ILs **5** and **6** are mixtures of phosphonium-based ILs. All ILs were prepared as stationary phases in GC columns for the evaluation of their thermal stability as well as chromatographic selectivity.

3.1 Evaluation of thermal stability of IL-based stationary phases using GC-FID

The thermal stability of ILs is often evaluated by thermogravimetric analysis (TGA). However, due to the high heating ramps that are often employed (e.g., 10-20 °C/min), it has been shown that this only measures the short-term stability of the IL [25]. Studies have shown that the maximum allowable operating temperature (MAOT) of IL-based stationary phases is approximately 100 ºC lower than what TGA experiments indicate [26]. Recently, the decomposition of GC stationary phases has been evaluated by exploiting the high sensitivity of flame ionization detection (FID). The FID approach is highly sensitive and can detect trace volatilization and/or decomposition products that may arise from the stationary phase during heating [24]. This method was used to determine the MAOT of stationary phases by evaluating the resolving power of the stationary phase after being thermally stressed at different temperatures [33].

In this study, each IL-based stationary phase was subjected to a series of heating experiments. Initially, five-meter segments of each column were conditioned to 100 ºC, 150 ºC, 200 ºC, and 250 ºC. After each conditioning step, the chromatographic performance of the stationary phase was evaluated by measuring the column efficiency based on the retention time

and peak width of naphthalene at 100 ºC, while 110 °C was used for IL **3** due to its unique retention behavior. To precisely determine the MAOT of each stationary phase, the columns were subsequently conditioned to 270 ºC, 290 ºC, 310 ºC, 330 ºC, and finally 350 ºC. The same procedure was repeated to measure the column efficiency after each heating step (see Tables S4-S9).

As shown in Tables 2 and S4, when IL **1** was conditioned from 310 to 330 ºC, a significant loss in column efficiency was observed indicating that the MAOT of the stationary phase is approximately 300 ºC. IL **2** showed an improved thermal stability with a MAOT of approximately 310 ºC, due to a drop in column efficiency being observed when the column was conditioned from 330 to 350 ºC.

The MAOT of ILs **4** and **5** was found to be approximately 350 ºC, which are the highest among the ILs examined in this study. IL **5** is comprised of a mixture of (4-bromophenyl)triphenylphosphonium and (4-phenoxyphenyl)triphenylphosphonium ILs, while IL **4** is a phosphonium-based IL with a dichlorophenoxy substituent. When both columns were conditioned from 330 to 350 ºC, the column efficiency was maintained above 2200 plates/meter indicating the very stable nature of these stationary phases. Compared to IL **5** with a MAOT of 350 ºC, IL **6** possesses a MAOT of 290 ºC (see Table S9) and is also a mixture composed of two different phosphonium-based ILs. Among the ILs examined in this study, IL **3** exhibited a particularly unique behavior. Generally, after the columns were conditioned at high oven temperatures, the retention time of the naphthalene probe molecule decreased. However, the retention time of naphthalene on the IL **3** column steadily increased. After heating at 350 °C, the retention time of naphthalene increased from 2.5 to 6.9 min with the peak width increasing from 0.08 to 1.64 min, resulting in extremely low column efficiency (see Table S6 in supporting

information). This retention behavior was observed previously by Betts, where the retention times of analytes on liquid crystal-based stationary phases increased as the columns were heated to temperatures beyond their melting points [34]. Compared to IL **3**, all other ILs exhibited excellent durability as well as high thermal stability. In total, more than 200 injections using different temperature programs were performed on each column over a 9 month period. All columns maintained column efficiencies above 2,000 plates/meter after all tests demonstrating their long-term stability.

3.2 Chromatographic selectivity of IL-based stationary phases for PAHs

The most widely used analytical methods for the determination of PAHs are GC/MS and high-performance liquid chromatography (HPLC) with fluorescence detection [35,36]. In comparison, GC/MS generally provides high sensitivity and better quantification results [32]. However, due to the presence of numerous isomers with high boiling points, the number of PAHs which can be analyzed by GC is limited by the thermal stability and selectivity of the stationary phase [37]. PDMS-based stationary phases such as HP-5ms, SLB-5ms and Rtx-5ms (bonded and highly crosslinked (5%-phenyl)-methylpolysiloxane) are most commonly used for PAH separation.

To evaluate the separation performance the stationary phases examined in this study, 12 PAHs (see Table S1) were selected and separated on the IL-based stationary phases and three commercial stationary phases, including HP-5ms, SLB-5ms, and SLB-ILPAH. As shown in Figure 1A, the 12 PAHs were separated on the HP-5ms stationary phase under optimized conditions. The SLB-5ms column, which is analogous to the HP-5ms column, provided comparable separation performance, as shown in Figures 1A and 2A. The resolution of

benzo(b)fluoranthene and benzo(k)fluoranthene was found to be 1.48 on the SLB-5ms column under optimized separation conditions and 1.46 on the HP-5ms stationary phase. The total separation time for the HP-5ms stationary phase was approximately 35 minutes, while the SLB-5ms phase required approximately 25 minutes.

The SPB-50 stationary phase is a relatively polar PDMS-based stationary phase with approximately 50% phenyl content which acts to increase its selectivity. As shown in Figure 2B, all analytes were baseline separated except for phenanthrene and anthracene (R_s = 1.07). Compared to the HP-5ms and SLB-5ms stationary phases, benzo(b)fluoranthene and benzo(k)fluoranthene were baseline separated on the SPB-50 stationary phase (R_s = 1.52). It is important to note that the separation took approximately 55 minutes, which is longer than the other stationary phases. A commercial IL-based column (SLB-ILPAH) possessing a similar chemical structure to SLB-IL59 (1,12-di(tripropylphosphonium)dodecane bis[(trifluoromethyl)sulfonyl]imide) with the only difference being the lower film thickness (d_f = 0.05 µm) was subsequently examined [7,38]. Under optimized separation conditions, all 12 PAHs were well separated within 30 minutes, as shown in Figure 1B.

The six IL-based stationary phases evaluated in this study were used for the separation of PAHs under optimized conditions. Among ILs **1**-**6**, IL **1** displayed the lowest selectivity for phenanthrene/anthracene and benzo(b)fluoranthene/benzo(k)fluoranthene, as shown in Figures S1-S4. Figures 1C and 2C show that the separation of PAHs on ILs **4** and **5**, respectively, were comparable to HP-5ms, SLB-5ms, SPB-50, and SLB-ILPAH. It is important to highlight that the IL-stationary phases are non-bonded and non-crosslinked phases and are still capable of operating at high oven temperatures (e.g., 350 °C for ILs **4** and **5**), while maintaining high column efficiency. In addition, improved selectivity for heavier PAHs such as

benzo(b)fluoranthene and benzo(k)fluoranthene was demonstrated compared to the PDMS-based stationary phases. Notably, the separation time using ILs **4** and **5** was under 30 minutes. This result highlights that IL-based stationary phases comprised of multiple aryl substituents provide unique selectivity and improved separation for heavier PAHs.

3.3 Separation of PCB mixture on IL-based stationary phases

While a total of 209 congeners exist, some PCBs are in fact more harmful than others [39]. For example, toxic PCBs such as PCBs 28, 52, 101, 138, 153, and 180 have been found to be more persistent in environmental samples than their corresponding isomers, while PCBs 77, 81, 126, 170, and 180 are relatively less toxic but are highly bioaccumulative [40]. In this study, a mixture of 21 PCBs (see Table S2) containing PCBs 28, 52, 77, 101, 126, 138, 153, 170, and 180 were separated on all six IL-based columns. The HP-5ms UI and SLB-IL111 commercial columns were used for comparison purposes.

As shown in Figure 3A, all 21 components were separated based on their boiling points on the HP-5ms stationary phase. PCB 8, containing two chlorine substituents, possesses a boiling point of 191 ºC, while PCB 209 (with ten chlorine substituents) possesses a boiling point of approximately 466 ºC. The SLB-IL111 column displayed a unique elution order of PCBs compared to the HP-5ms column, as shown in Figure 3B.

The separation of PCBs on the six thermally-stable ILs are shown in Figures 3C-3H. Two analyte pairs (77/138 and 108/180) co-eluted on IL **1**, as shown in Figure 1C. This result indicates insufficient resolving power toward these two PCB analyte pairs. IL **2** possesses a benzoylphenyl group and does not contain any halide substituents within its chemical structure. The analyte pairs 77/138 and 108/180 were separated with a resolution of 2.23 and 1.38,

respectively, on this stationary phase (see Figure 3D and Table 3). The retention order for two analyte pairs PCB 77/138 and 180/108 was reversed on ILs **3** and **4**. As shown in Table 3, the resolution of PCB 77 and 138 analyte pair was 3.06 on IL **3** compared to that of 1.41 on IL **4**. In addition, improved resolution of PCB 108/180 analyte pair was observed on the IL **3** stationary phase compared to that of IL **4** (see Table 3). This may be due to the addition of the four fluorine substituents, hence increasing the electron density of the cation and leading to stronger π-π interactions [41].

As shown in Table 1, ILs **5** and **6** are mixture of two tetraphenylphosphonium-based ILs. IL **5** contains a bromine substituent on one cation and a phenoxy group on the other. IL **6** has a fluorophenoxyphenyl group on one cation and a phenoxyphenoxyphenyl group on the other IL cation. As shown in Figure 3G, PCBs 44 and 101 co-eluted on IL **5**, while the resolution of 44/101 was 1.43 on IL **6**. PCBs 108 and 180 were separated with a resolution of 2.88 on IL **5**, while the analyte pair co-eluted on IL **6** (see Table 3). In addition, the retention order of PCBs 77 and 138 possessing four and six chlorine substituents, respectively, was reversed on ILs **3** and **6**, as shown in Figures 3E and 3H. All six perarylated IL-based stationary phases exhibited improved resolution of analyte pairs PCB 126/128 and 108/153, compared to the commercial HP-5ms stationary phases (see Table 3).

3.4 Solvation parameter model

The Abraham solvation parameter model has been widely used to describe multiple solvation interactions between different probe molecules and stationary phases using an inverse GC approach [42,43].

$$Log\ k = c + eE + sS + aA + bB + lL \quad (1)$$

In Equation 1, *k* is the retention factor for each analyte on the high thermal stability IL stationary phases at 50 °C, 80 °C, and 110 °C. The solute descriptors (*E*, *S*, *A*, *B*, and *L*) of the 46 analytes are listed in Table S3. Each term is defined as: *E*, the excess molar refraction calculated from the solute's refractive index; *S*, the solutes dipolarity/polarizability; *A*, the solute hydrogen bond acidity; *B*, the solute hydrogen bond basicity; and *L*, the solute gas-hexadecane partition coefficient at 298 K. Multiple linear regression analysis was performed using the solute descriptors of the probe molecules and their retention factors to determine the solvation interactions. The *c* term is the intercept of the regression line. The system constants (*e*, *s*, *a*, *b*, and *l*) determine the strength of each individual interaction. Each term is defined as follows: *e*, the ability of the stationary phase to interact with analytes by non-bonding or π-π interactions; *s*, measures the dipolarity/polarizability of the stationary phase; *a*, the hydrogen bond basicity of the stationary phase; *b*, the hydrogen bond acidity of the stationary phase; and *l*, measures the dispersion forces/cavity formation of the stationary phase.

To examine the effect of aryl substituents on the solvation properties of the IL-based stationary phases, the perarylated ILs **1**-**6** were compared to the trihexyl(tetradecyl)phosphonium bis[(trifluoromethyl)sulfonyl]imide ($[P_{66614}^+][NTf_2^-]$) IL. It has been previously reported that the $[P_{66614}^+][NTf_2^-]$ IL possesses a negative *e* term value indicating little to no lone pair and π-electron interaction capability of the stationary phase [44]. In comparison, ILs **1**-**6** with multiple aryl substituents possess modest lone pair and π-electron interaction capabilities as shown in Table 4 (*e* term value ranging from 0.14 to 0.25 at 80 °C), which has been found in this study to play an important role in the separation of PAHs and PCBs. Among ILs **1**-**6**, IL **1** with the triarylsulfonium cation showed the highest capability of lone pair and π-electron interactions (*e* = 0.25 at 80 °C), while IL **2** which contains the (4-benzoylphenyl)triphenylphosphonium cation

displayed the lowest lone pair and π-electron interactions (*e* = 0.14 at 80 °C). It can be observed that the phosphonium-based ILs with halide substituents (ILs **3**-**6**) possess higher lone pair and π-electron interactions (*e* term value ranging from 0.16 to 0.22 at 80 °C) compared to IL **2** which does not contain any halide substituent. IL **2** possesses the highest polarity/polarizability among all ILs (*s* =1.80 at 80 °C), while IL **3** possesses the lowest polarity/polarizability (*s* =1.62 at 80 °C). The hydrogen bond acidity of ILs **1**-**6** range from 0.08 to 0.47 at 80 °C, while the $[P_{66614}^{+}][NTf_2^{-}]$ IL possesses a negative *b* term value. As shown in Table 4, IL **4** exhibited the highest dispersion forces (*l* = 0.63 at 80 °C), whereas IL **6** exhibited the lowest value (*l* = 0.53 at 80 °C). ILs **1**-**6** all exhibited lower dispersion forces compared to $[P_{66614}^{+}][FeCl_4^{-}]$ (*l* = 0.69 at 80 °C) and $[P_{66614}^{+}][NTf_2^{-}]$ (*l* = 0.75 at 70 °C) [44,45]. This result is likely due to the lack of multiple alkyl substituents within the cations of the perarylated ILs.

Conclusions

A new class of perarylated ILs with high thermal stability were successfully applied as GC stationary phases. These triarylsulfonium and tetraarylphosphonium IL-based stationary phases displayed unique selectivity toward PAHs and PCBs compared to a broad series of commercial stationary phases. Compared to HP-5ms, SLB-5ms, and SPB-50, ILs **4** and **5** exhibited unique selectivity and improved resolution of the benzo(b)fluoranthene and benzo(k)fluoranthene isomers possessing high boiling points. A mixture of 21 PCBs were separated with optimized conditions using the six IL-based stationary phases as well as two commercial HP-5ms UI and SLB-IL111 stationary phases. The retention order of analyte pairs such as PCBs 108/180 was reversed on the IL **3** and **5** columns, compared to the widely used HP-5ms column. The elution order of PCB 77/138 remained the same on all columns except the

SLB-IL111 and IL **3** columns. In addition, improved resolution of analyte pairs PCB 126/128 and 108/153 was observed on all six perarylated IL-based stationary phases compared to the commercial HP-5ms stationary phase. The solvation characteristics of these ILs were evaluated using the Abraham solvation parameter model. These ILs displayed high lone pair and π-electron interaction capability compared to conventional phosphonium ILs containing long alkyl chain substituents in the cation (e.g., $[P_{66614}^{+}][NTf_2^{-}]$). This new class of IL-based stationary phases are non-bonded and not crosslinked but exhibit increased MAOT and unique selectivity toward PAHs and PCBs, making them promising materials for a broad range of applications.

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Figure Legends

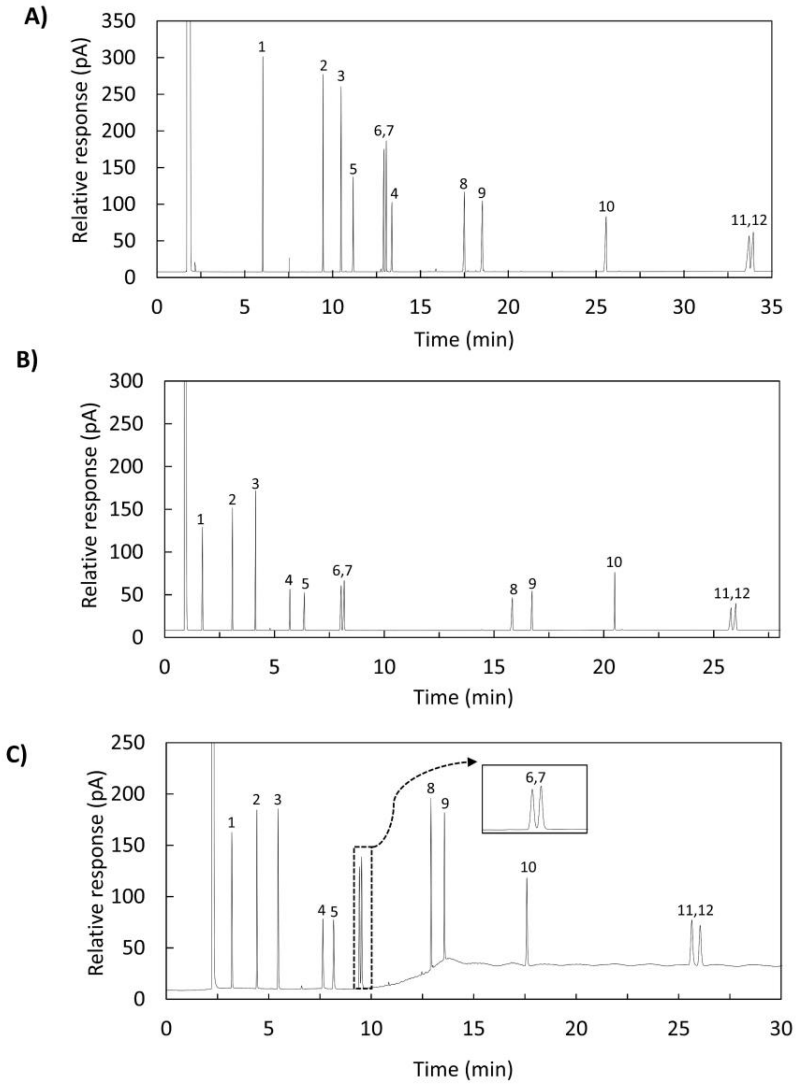


Figure 1. Chromatographic separation of PAHs on 3 different stationary phases. **A)** HP-5ms (30 m × 250 µm × 0.25 µm), **B)** SLB-ILPAH (20 m × 180 µm × 0.05 µm), **C)** IL **4** (30 m × 250 µm × 0.20 µm). Analytes: 1, naphthalene; 2, acenaphthene; 3, fluorene; 4, 5-bromoacenapthene; 5, 2-nitronapthalene; 6, phenanthrene; 7, anthracene; 8, fluoranthene; 9, pyrene; 10, benzo(a)fluoranthene; 11, benzo(b)fluoranthene and 12, benzo(k)fluoranthene. Separation conditions: **A)** initial, 95 °C for 2 min, 12 °C/min to 190 °C, 3 °C/min to 235 °C, 1.5 °C/min to 255 °C. **B)** 125-175 °C at 12 °C/min, hold for 4 min, 5 °C/min to 195 °C, hold for 3 min, 15 °C/min to 260 °C. **C)** initial, 200 °C for 1 min, 25 °C/min to 245 °C, hold for 7 min, 30 °C/min to 350 °C. Flow rate: 1 mL/min. Analyte concentration: 0.5 mg/mL.

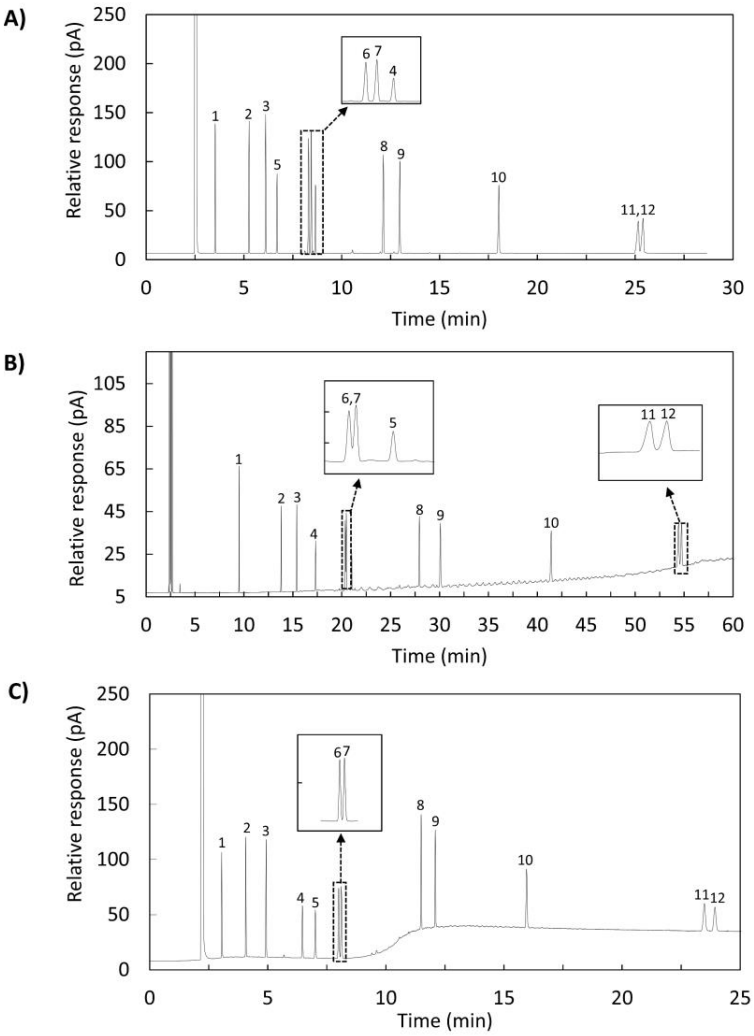


Figure 2. Chromatographic separation of PAHs on 3 different stationary phases. **A)** SLB-5ms (30 m × 250 µm × 0.25 µm), **B)** SPB-50 (30 m × 250 µm × 0.25 µm), **C)** IL **5** (30 m × 250 µm × 0.20 µm). Analytes: 1, naphthalene; 2, acenaphthene; 3, fluorene; 4, 5-bromoacenapthene; 5, 2-nitronapthalene; 6, phenanthrene; 7, anthracene; 8, fluoranthene; 9, pyrene; 10, benzo(a)fluoranthene; 11, benzo(b)fluoranthene and 12, benzo(k)fluoranthene. Separation conditions: **A)** 150-200 °C at 15 °C/min, hold for 1 min, 5 °C/min to 260 °C. **B)** 125-185 °C at 12 °C/min, held for 2 min, 10 °C/min to 220 °C, hold for 2 min, 1.5 °C/min to 250 °C. **C)** initial, 205 °C for 1 min, 25 °C/min to 260 °C, hold for 5 min, 30 °C/min to 330 °C. Flow rate: 1 mL/min. Analyte concentration: 0.5 mg/mL.

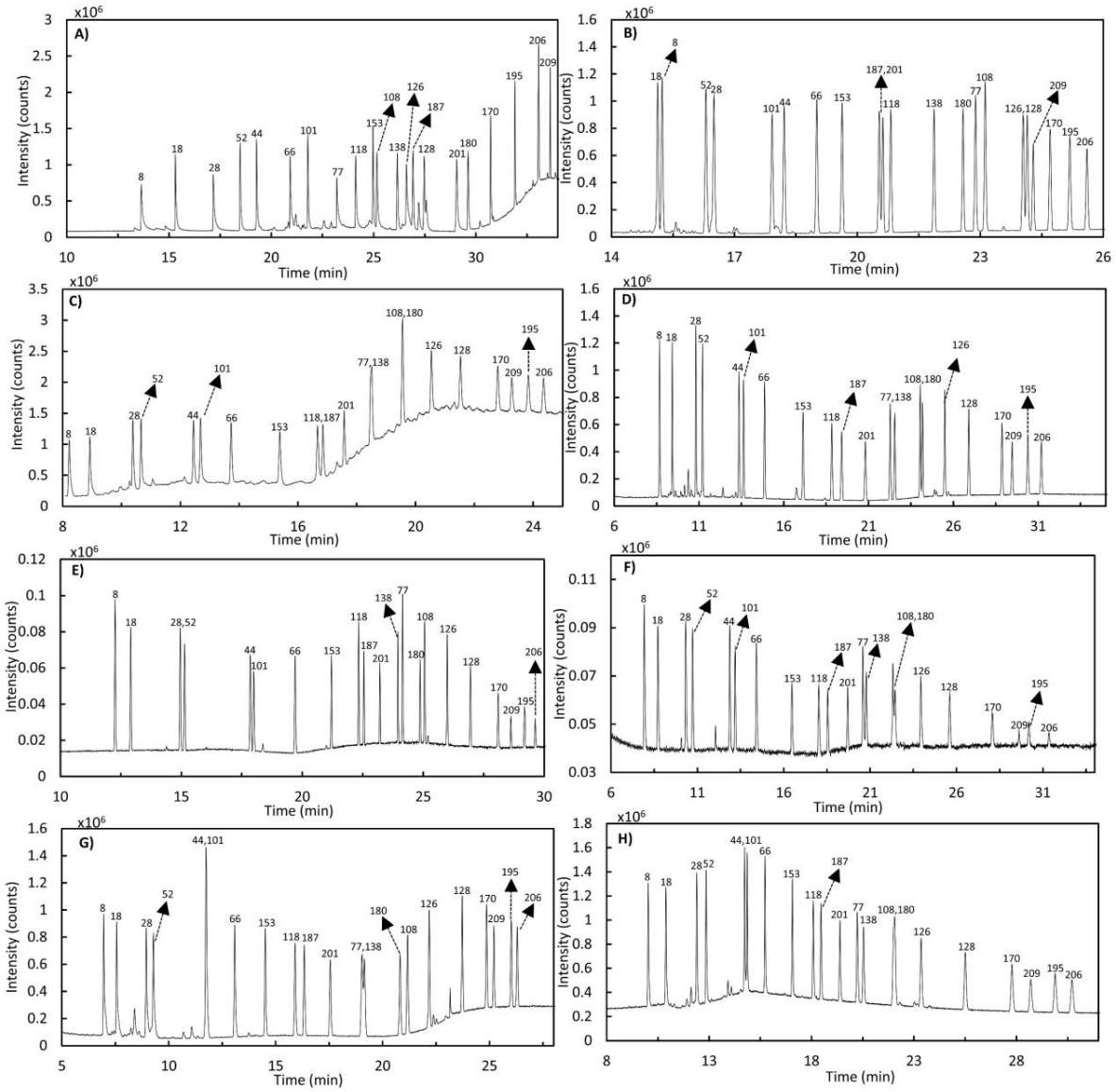


Figure 3. Chromatographic separation of 21 PCBs on eight columns. **A)** HP-5ms UI (30 m × 250 µm × 0.25 µm), **B)** SLB-IL111 (30 m × 250 µm × 0.20 µm), **C)** IL **1** (30 m × 250 µm × 0.20 µm), **D)** IL **2** (30 m × 250 µm × 0.20 µm), **E)** IL **3** (30 m × 250 µm × 0.20 µm), **F)** IL **4** (30 m × 250 µm × 0.20 µm), **G)** IL **5** (30 m × 250 µm × 0.20 µm), **H)** IL **6** (30 m × 250 µm × 0.20 µm). The temperature program was optimized for each column (see experimental section and Table S10 for each optimized temperature program). Separations were performed on an Agilent 7890B/5977A GC/MS system. Helium was used as the carrier gas at a flow rate of 1 mL/min. The injector temperatures were held at 250 °C and a split ratio of 5:1 was used. The MS was operated at 70 eV with electron ionization (EI) in SCAN mode. Refer to Table S2 for the corresponding name and chemical structure of the PCBs.

Table 1 Chemical structures of the high thermal stability ILs examined as stationary phases in this study

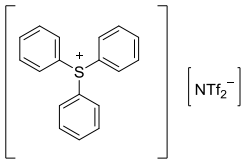
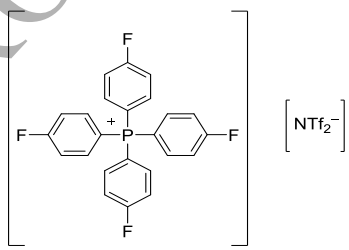
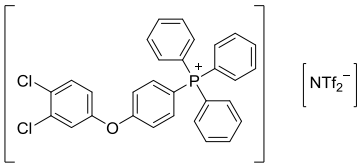
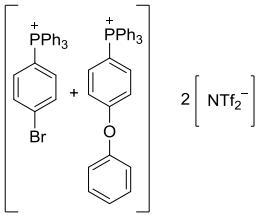
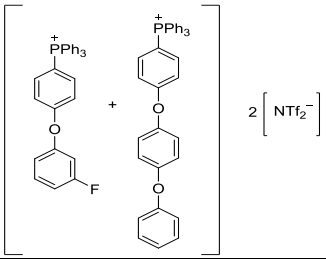
IL No.	Chemical Name of IL	Chemical Structure
1	Triphenylsulfonium bis[(trifluoromethyl)sulfonyl]imide	
2	(4-Benzoylphenyl)triphenylphosphonium bis[(trifluoromethyl)sulfonyl]imide	
3	Tetrakis(4-fluorophenyl)phosphonium bis[(trifluoromethyl)sulfonyl]imide	
4	(4-(3,4-Dichlorophenoxy)phenyl)triphenylphosphonium bis[(trifluoromethyl)sulfonyl]imide	
5	Mixture of (4-bromophenyl)triphenylphosphonium bis[(trifluoromethyl)sulfonyl]imide and (4-phenoxyphenyl)triphenylphosphonium bis[(trifluoromethyl)sulfonyl]imide	
6	Mixture of (4-(3-fluorophenoxy)phenyl)triphenylphosphonium bis[(trifluoromethyl)sulfonyl]imide and (4-(4-phenoxyphenoxy)phenyl)triphenylphosphonium bis[(trifluoromethyl)sulfonyl]imide	

Table 2 Studied IL-based stationary phases with their corresponding column dimensions, chromatographic efficiency, and thermal stability

Stationary Phase	Column Length (m)	Film Thickness (µm)	Efficiency[a] (plates/meter)	Thermal Stability[b] (°C)
IL **1**	30	0.20	3774	300
IL **2**	30	0.20	3741	310
IL **3**	30	0.20	4190	310
IL **4**	30	0.20	4154	350
IL **5**	30	0.20	4379	350
IL **6**	30	0.20	4270	290

[a] All columns were evaluated at 110 °C using naphthalene as the test probe to determine the chromatographic efficiency.
[b] Thermal stability was determined by taking 5 m segments of each column and conditioning them for one hour at each temperature from 100 to 350 °C in 50 °C increments. The efficiency of each column was tested after each conditioning step (See Tables S4-S9).

Table 3 Comparison of chromatographic selectivity and resolution for five PCB analyte pairs on six IL-based columns and two commercial columns

Stationary phase	PCB 44/101			PCB 77/138			PCB 108/180			PCB 126/128			PCB 108/153		
	EO[a]	α[b]	R_s	EO[a]	α[b]	R_s	EO[a]	α[b]	R_s	EO[a]	α[b]	R_s	EO[a]	α[b]	R_s
HP-5ms UI	44/101	1.13	32.57	77/138	1.13	29.63	108/180	1.18	49.11	126/128	1.03	8.26	153/108	1.01	2.26
SLB-IL111	101/44	1.01	3.52	138/77	1.04	13.44	180/108	1.02	7.37	126/128	1.01	1.27	153/108	1.18	45.71
IL **1**	44/101	1.02	2.69	77/138	1.00[c]	0[c]	108/180	1.00[c]	0[c]	126/128	1.04	9.80	153/108	1.27	39.05
IL **2**	44/101	1.02	2.82	77/138	1.01	2.23	108/180	1.01	1.38	126/128	1.05	11.90	153/108	1.40	60.42
IL **3**	44/101	1.01	1.66	138/77	1.01	3.06	180/108	1.01	2.89	126/128	1.03	12.66	153/108	1.18	54.75
IL **4**	44/101	1.02	2.83	77/138	1.01	1.41	108/180	1.01	1.08	126/128	1.07	11.24	153/108	1.35	46.30
IL **5**	44/101	1.00[c]	0[c]	77/138	1.01	0.97	180/108	1.04	2.88	126/128	1.07	14.94	153/108	1.46	68.64
IL **6**	44/101	1.01	1.43	77/138	1.02	2.07	108/180	1.00[c]	0[c]	126/128	1.09	13.05	153/108	1.29	36.34

[a] EO refers to the elution order of the analytes (e.g., 44/101 indicates that PCB 44 eluted before PCB 101).
[b] The selectivity (α) was calculated based on the retention factor of the second eluting analyte divided by the retention factor of the first analyte.
[c] Analyte pairs co-eluted.

Table 4 System constants of the perarylated ILs examined in this study using the solvation parameter model at three different temperatures

Stationary Phase	Temperature (°C)	System Constants								
		c	*e*	*s*	*a*	*b*	*l*	*n* [a]	R^2 [a]	*F* [a]
IL **1**	50	-3.24 (0.09)	0.20 (0.07)	1.94 (0.09)	2.10 (0.08)	0.47 (0.11)	0.93 (0.02)	37	0.99	566
	80	-3.22 (0.09)	0.25 (0.06)	1.70 (0.08)	1.78 (0.06)	0.40 (0.10)	0.54 (0.02)	31	0.99	569
	110	-3.50 (0.08)	0.16 (0.08)	1.77 (0.08)	1.55 (0.07)	0.17 (0.11)	0.53 (0.01)	30	0.99	538
IL **2**	50	-2.96 (0.10)	0.20 (0.07)	1.87 (0.10)	2.19 (0.09)	0.22 (0.13)	0.63 (0.02)	33	0.98	429
	80	-3.13 (0.09)	0.14 (0.07)	1.80 (0.08)	1.80 (0.07)	0.13 (0.10)	0.55 (0.02)	37	0.99	605
	110	-3.10 (0.09)	0.13 (0.08)	1.63 (0.10)	1.40 (0.08)	0.16 (0.11)	0.46 (0.02)	28	0.99	517
IL **3**	50	-2.43 (0.09)	0.06 (0.06)	1.52 (0.08)	1.23 (0.08)	0.64 (0.12)	0.60 (0.02)	17	0.99	443
	80	-3.24 (0.09)	0.19 (0.07)	1.62 (0.09)	1.45 (0.14)	0.47 (0.13)	0.56 (0.02)	17	0.99	493
	110	-2.94 (0.07)	0.27 (0.05)	1.42 (0.06)	1.48 (0.06)	0.31 (0.10)	0.41 (0.01)	17	0.99	518
IL **4**	50	-3.28 (0.08)	0.17 (0.06)	1.82 (0.08)	2.13 (0.08)	0.16 (0.10)	0.69 (0.02)	38	0.99	721
	80	-3.47 (0.09)	0.16 (0.07)	1.72 (0.09)	1.78 (0.07)	0.08 (0.10)	0.63 (0.02)	33	0.99	593
	110	-3.39 (0.08)	0.11 (0.07)	1.71 (0.08)	1.52 (0.07)	0.13 (0.11)	0.50 (0.02)	37	0.98	509
IL **5**	50	-3.21 (0.08)	0.21 (0.08)	1.82 (0.10)	2.07 (0.08)	0.27 (0.11)	0.68 (0.02)	37	0.98	570
	80	-3.25 (0.09)	0.22 (0.07)	1.68 (0.08)	1.73 (0.07)	0.17 (0.11)	0.59 (0.02)	33	0.99	540
	110	-3.37 (0.06)	0.20 (0.07)	1.58 (0.08)	1.44 (0.07)	0.08 (0.10)	0.53 (0.02)	34	0.99	750
IL **6**	50	-2.92 (0.07)	0.19 (0.06)	1.80 (0.08)	2.00 (0.08)	0.22 (0.10)	0.63 (0.02)	37	0.99	778
	80	-2.93 (0.08)	0.18 (0.06)	1.64 (0.08)	1.68 (0.07)	0.12 (0.10)	0.53 (0.02)	32	0.98	527
	110	-3.45 (0.05)	0.16 (0.05)	1.69 (0.06)	1.58 (0.05)	0.25 (0.08)	0.50 (0.01)	29	0.99	1197

[a] *n*, number of probe analytes subjected to multiple linear regression; R^2, correlation coefficient; *F*, Fisher coefficients.