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# Tunable Silver-Containing Stationary Phases for Multidimensional Gas Chromatography

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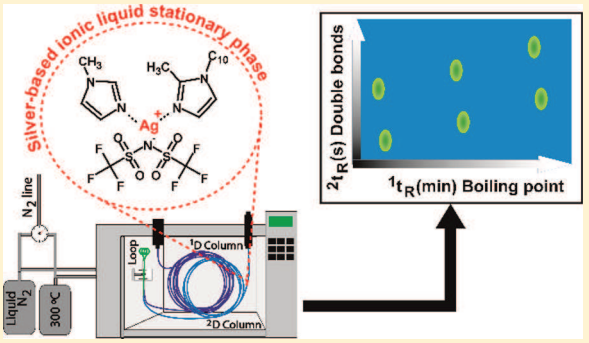
Supporting Information

**ABSTRACT:** To achieve high separation power of complex samples using multidimensional gas chromatography (MDGC), the selectivity of the employed stationary phases is crucial. The nonpolar × polar column combination remains the most popular column set used in MDGC. However, resolution of mixtures containing light analytes possessing very similar properties remains a formidable challenge. The development of stationary phases that offer unique separation mechanisms have the potential to significantly improve MDGC separations, particularly in resolving coeluting peaks in complex samples. For the first time, a stationary phase containing silver(I) ions was successfully designed and employed as a second-dimension column using comprehensive two-dimensional gas chromatography (GC × GC) for the separation of mixtures containing alkynes, dienes, terpenes, esters, aldehydes, and ketones. Compared with a widely used nonpolar and polar column set, the silver-based column exhibited superior performance by providing better chromatographic resolution of coeluting compounds. A mixture of unsaturated fatty acids was successfully separated using a GC × GC method in which the elution order in the second dimension was highly dependent on the number of double bonds within the analytes.

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Multidimensional gas chromatography, including comprehensive two-dimensional gas chromatography (GC × GC), offers high peak capacity in the analysis of complex samples that are often poorly separated in conventional one-dimensional (1D) GC.[1−5] The selection of column sets that maximize peak capacity is a major task in optimizing GC × GC methods. The nonpolar × polar column set constitutes the majority of published GC × GC methods.[6,7] However, this popular column combination does not always provide the best selectivity in the separation of structurally similar compounds that exhibit nearly identical chromatographic behavior. For example, the separation of complex samples containing paraffins, olefins, and aromatics remains a challenge using the commercially available column sets.[8]

Since the first introduction of GC × GC by Liu and Philips using the polyethylene glycol (PEG) × methyl silicone (polar × nonpolar) column combination, significant progress has been made in the development of GC stationary phases that provide specific molecular interactions and unique selectivity to separate extremely challenging samples.[9,10] For example, the dimethylpolysiloxane (HP-1) × 8% phenyl (equiv) polycarborane-siloxane (HT-8) column set was used to separate polychlorinated biphenyls and toxaphene components into groups according to the number of chlorine substituents.[11,12] Stationary phases containing liquid crystals have been shown to separate compounds according to the planarity of target analytes.[13,14] The development of cyclodextrin-based stationary phases[15] and their adaptation to 2D separations[16] have facilitated improved enantiomeric separation to determine the chiral composition of monoterpenes in Australian tea tree (*Melaleuca alternifolia*). However, choosing the appropriate second-dimension column is a challenge because it must enable fast separation and high selectivity to produce sharp peaks, satisfactory separation power, and high peak capacity.[17]

Instrumental or stationary-phase modifications are sometimes required in order to make primary columns compatible with secondary columns. For example, a column set composed of cyclodextrin × BP-20 (PEG) was reported for the enantiomeric separation of monoterpene hydrocarbons and oxygenated monoterpenes.[16] It was shown that the cyclodextrin chiral stationary phase was not suitable in the second dimension because high plate numbers and long run times are needed to obtain sufficient enantioresolution.[17] Shellie and Marriott circumvented this limitation by applying subambient-pressure (vacuum outlet) conditions at the end of the secondary column to speed up the separation.[18] Using this approach, a GC × enantio-GC method was developed using a 5% diphenyl-dimethylpolysiloxane (DB-5) × cyclodextrin

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column set. Short analyte retention times with adequate enantioresolution ($R_s \sim 1.0$) were achieved on a 1 m cyclodextrin-based second-dimension column. This example highlights that adaptation of new stationary phases with unique selectivities can further improve the separation performance of GC × GC.

To resolve complex samples containing light paraffins and olefins with similar polarity and volatility using 1D GC, alumina porous-layer open tubular (PLOT) columns are often used.[19] Although an alumina PLOT column was used in valve-based heart-cutting multidimensional GC experiments by Shellie and co-workers, this column has not been routinely employed in GC × GC because of its requirements of higher temperatures and flow rates.[1,6,20] Stationary phases that facilitate separation by argentation chromatography have potential because silver(I) ions possess unique selectivity toward unsaturated hydrocarbons.[21,22] However, the adaptation of silver-based stationary phases to GC × GC remains a challenge because of strong $\pi$-complexation between analytes and the silver-based stationary phase, which can result in slow mass transfer and wrap-around. To the best of our knowledge, no GC × GC method has been reported to date that uses an analyte-selective silver-containing stationary phase.

In this technical report, we develop the first class of silver-based stationary phases that are compatible with GC × GC separations. Using a stationary phase comprising a mixture of customized silver-based ionic liquids (ILs) and conventional imidazolium-based ILs, the $Ag^+$ concentration was tuned to facilitate chromatographic resolution of a wide variety of analytes. Additional parameters including the structural composition of the silver-based IL, the film thickness, and the column length were studied and optimized.

## EXPERIMENTAL SECTION

**Chemicals and Materials.** Bis[(trifluoromethyl)sulfonyl]-amine (99%), silver oxide (99%), dichloromethane (99.8%), acetonitrile (99.9%), 1-butylimidazole ($C_4$IM, 98%), 1-decyl-2-methylimidazole ($C_{10}$MIM, 97%), 1-chlorobutane (99%), all analytes used to evaluate the columns (see Table S1, Supporting Information), and a mixture of unsaturated fatty acids (UFA) commercially available as polyunsaturated fatty acids (PUFA No. 2, animal source) were purchased from Sigma-Aldrich (St. Louis, MO). 1-Bromooctane (98%) was obtained from Acros Organics (Morris Plains, NJ). 1-Methylimidazole (MIM, 99.0%) was purchased from Fluka (Stainheim, Germany). A SUPELCOWAX10 column (30 m, 0.20 mm i.d., 0.20 $\mu$m PEG) and untreated fused silica capillary tubing (0.25 mm i.d.) were obtained from Supelco (Bellefonte, PA). An Rtx-5MS column (30 m, 0.25 mm i.d., 0.25 $\mu$m 5% diphenyl-dimethylpolysiloxane) was purchased from Restek (Bellefonte, PA).

**Synthesis of the Silver-Based IL.** The silver-based ILs were synthesized on the basis of a previously reported procedure from the literature.[23−25] Briefly, $[(C_{10}MIM)(MIM)\text{-}Ag^+][NTf_2^-]$ was prepared through a chelation reaction performed between $[(ACN)Ag^+][NTf_2^-]$ and the MIM and $C_4$IM ligands. Silver-based ILs with other combinations of ligands were also prepared using the same procedure. The chemical structures of the silver-based ILs used in this study are shown in Figures 1a and S1. The 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide $[C_4MIM^+][NTf_2^-]$, 1-octyl-3-methylimidazolium $[C_8MIM^+][NTf_2^-]$, and 1-decyl-3-methylimidazolium $[C_{10}MIM^+][NTf_2^-]$ ILs were prepared using previously reported methods[26] and characterized by $^1$H NMR (see Figures S2−S4). A detailed description of synthetic procedures and characterization is included in the Supporting Information.

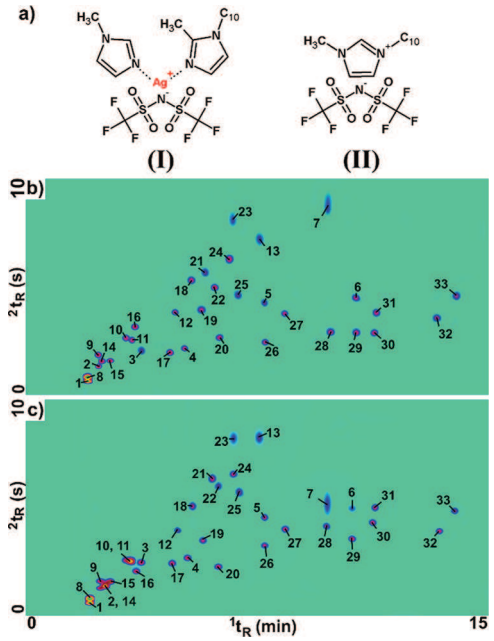


**Figure 1.** (a) Chemical structures of (I) silver-based IL ($[(C_{10}MIM)(MIM)Ag^+][NTf_2^-]$) and (II) imidazolium-based IL ($[C_{10}MIM^+][NTf_2^-]$) and (b,c) GC × GC-FID chromatograms of esters, aldehydes, and ketones obtained using the following column sets: (b) Rtx-5MS (30 m, 0.25 mm i.d., 0.25 $\mu$m) × $[(C_{10}MIM)(MIM)\text{-}Ag^+][NTf_2^-]/[C_{10}MIM^+][NTf_2^-]$ (1:30, w/w; 1.2 m, 0.25 mm i.d., 0.15 $\mu$m) and (c) Rtx-5MS (30 m, 0.25 mm i.d., 0.25 $\mu$m) × SUPELCOWAX10 (1.2 m, 0.2 mm i.d., 0.2 $\mu$m). Inlet pressure: 9.32 psi. Split ratio: 5:1. Temperature program: 40 to 44 °C at 2 °C/min, 44 to 100 °C at 5 °C/min, and 100 °C for 3 min. Modulation time: 10 s. See Table S1 for additional information on peak identification.

**Preparation of GC Columns and Probe Mixtures.** To obtain the coating solution, the silver-based IL was mixed with the conventional IL, and this mixture was dissolved in dichloromethane. Two meter segments of untreated fused silica capillary (0.25 mm i.d.) were coated by the static coating method at 40 °C. Additional details of this procedure are described in the Supporting Information. Probe mixtures were prepared by sealing 3 $\mu$L of each compound in a 20 mL headspace vial. Then, 1 $\mu$L of the headspace was injected into the GC × GC system with a split ratio of 5:1.

The UFA mixture was diluted in dichloromethane at a concentration level of 10 $\mu g\ mL^{-1}$. Then, 1 $\mu$L of the sample solution was injected into the GC × GC system with a split ratio of 100:1. The chemical structures of the UFAs are listed in Figure S5.

**Analysis by GC × GC−Flame-Ionization Detection (FID).** Two-dimensional chromatographic separations were performed on a home-built GC × GC instrument assembled on an Agilent 6890 GC (split−splitless) equipped with an FID and a two-stage cryogenic loop modulator. The first dimension employed a Rtx-5MS column (30 m, 0.25 mm i.d., 0.25 $\mu$m), and the second dimension employed a silver-based-IL column (1.2 m, 0.25 mm i.d., 0.15 $\mu$m) or a SUPELCOWAX10 column (1.2 m, 0.2 mm i.d., 0.2 $\mu$m). Hydrogen was used as the carrier gas with the inlet pressure set at 9.32 psi and a


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column flow rate of 1.2 mL $min^{-1}$. A full description of the chromatographic instrumentation is included in the Supporting Information.

## RESULTS AND DISCUSSION

**Optimization of Silver-Based-IL-Stationary-Phase Composition and Column Parameters.** Ionic liquids are molten salts with melting points lower than 100 °C.[27] IL-based stationary phases possess numerous properties, such as high thermal stability, low viscosity, and unique chromatographic selectivity, that make them useful in 1D GC and MDGC separations.[28−30] One of the most advantageous properties of ILs is the ability to customize unique stationary phases by judicious choice of cations or anions.

Although a silver-based-IL stationary phase [$(C_4IM)(MIM)Ag^+$][$NTf_2^-$]) was reported for the conventional 1D GC separation of unsaturated hydrocarbons,[25] its direct adaptation to GC × GC provided numerous challenges. When separations were performed using this column in the second dimension, asymmetric peaks and excessive retention of analytes were observed (see Figure S6a). Because high silver-ion concentration results in strong $\pi$-complexation toward unsaturated compounds, a stationary phase containing the neat silver-based IL was deemed to be not compatible with GC × GC separations.

To overcome the limitation presented by the neat silver-based-IL column, the selectivity and retention power of the stationary phase was tuned by dissolving the silver-based IL ([$(C_4IM)(MIM)Ag^+$][$NTf_2^-$]) in a conventional IL ([$C_{10}MIM^+$][$NTf_2^-$]) in an effort to reduce its retentive nature. As shown in Figure S6b−f, five silver-based-IL columns were prepared using mixtures of the silver-based IL and conventional IL at ratios ranging from 1:10 to 1:50 (w/w). A column containing the neat [$C_{10}MIM^+$][$NTf_2^-$] IL stationary phase was also used for comparison purposes (see Figure S6g). As the concentration of silver ions in the stationary phase was lowered, peak broadening and wrap-around in the second dimension decreased significantly (see Figure S6). However, when the stationary phase containing the lowest silver-ion concentration, [$(C_4IM)(MIM)Ag^+$][$NTf_2^-$]/[$C_{10}MIM^+$][$NTf_2^-$] 1:50 (w/w), was examined, the selectivity in the second dimension was completely lost (see Figure S6f). By comparing the second-dimension chromatographic resolution ($R$) values of selected analytes, it can be observed that higher chromatographic resolution of *n*-hexane (**1**) and 1-hexene (**2**, $R_{1,2}$ = 0.5) was obtained on the [$(C_4IM)(MIM)Ag^+$][$NTf_2^-$]/[$C_{10}MIM^+$][$NTf_2^-$] 1:20 (w/w) column, and lower peak broadening and higher chromatographic resolution of methyl 4-pentenoate (**3**), methyl pentanoate (**4**), methyl 3-pentenoate (**5**), and methyl 2,4-pentadienoate (**6**; $R_{3,4}$ = 1.2, $R_{5,6}$ = 3.3) were obtained on the [$(C_4IM)(MIM)Ag^+$][$NTf_2^-$]/[$C_{10}MIM^+$][$NTf_2^-$] 1:30 (w/w) column. Therefore, capillary columns suitable for the optimal separation of hydrocarbons and esters were prepared using stationary phases containing the silver-based IL/conventional IL at ratios of 1:20 and 1:30 (w/w), respectively.

Conventional ILs with different lengths of alkyl-side-chain substituents (e.g., [$C_4MIM^+$][$NTf_2^-$], [$C_8MIM^+$][$NTf_2^-$], and [$C_{10}MIM^+$][$NTf_2^-$]) as well as silver-based ILs composed of different ligands (e.g., MIM, $C_4$IM, and $C_{10}$MIM) were tested to identify the optimal stationary-phase composition. A probe mix was used to determine the resolution of selected analytes ($R_{1,2}$, *n*-hexane and 1-hexene; $R_{5,6}$, methyl 3-pentenoate and methyl 2,4-pentadienoate) to elucidate the optimal structural features for the silver-based ILs and conventional ILs. Three second-dimension columns were prepared by dissolving the [$(C_4IM)(MIM)Ag^+$][$NTf_2^-$] IL in different conventional ILs. As shown in Figure S7a, the [$C_{10}MIM^+$][$NTf_2^-$] IL used to dissolve the silver-based IL provided the best chromatographic resolution of the analyte pairs. Second-dimension columns were then prepared using different silver-based ILs composed of various ligands (e.g., [$(C_4IM)(MIM)Ag^+$][$NTf_2^-$], [$(C_{10}MIM)(MIM)Ag^+$][$NTf_2^-$], and [$(C_{10}MIM)(C_4IM)Ag^+$][$NTf_2^-$]) dissolved in the [$C_{10}MIM^+$][$NTf_2^-$] IL. As shown in Figure S7b, higher chromatographic resolution was obtained with the stationary phase consisting of [$(C_{10}MIM)(MIM)Ag^+$][$NTf_2^-$] in the [$C_{10}MIM^+$][$NTf_2^-$] IL. It was also observed that the solubility of the [$(C_{10}MIM)(MIM)Ag^+$][$NTf_2^-$] IL was higher in the [$C_{10}MIM^+$][$NTf_2^-$] IL compared with in the [$C_8MIM^+$][$NTf_2^-$] and [$C_4MIM^+$][$NTf_2^-$] ILs.

Because of strong $\pi$-complexation between analytes and the silver-based stationary phase, the film thickness and column length needed to be optimized. The effects of film thickness and column length on GC × GC separation were also investigated. As shown in Figure S8a, the silver-based-IL column with a film thickness of 0.15 $\mu$m exhibited narrower peak widths and increased chromatographic resolution compared with a column containing a 0.28 $\mu$m film thickness. Regarding the length of the second-dimension column, the 120 cm column provided the highest chromatographic resolution of methyl 3-pentenoate and methyl 2,4-pentadienoate (see Figure S8b), while minimizing wrap-around.

In the final step, the maximum allowable operating temperature (MAOT) of a 120 cm segment of the [$(C_{10}MIM)(MIM)Ag^+$][$NTf_2^-$]/[$C_{10}MIM^+$][$NTf_2^-$] 1:30 (w/w) IL stationary phase was determined. As shown in Figure S9a, the column was heated slowly in a GC oven, and an ultrasensitive flame-ionization detector was used to detect any volatilization or decomposition of the stationary phase. To further evaluate the thermal stability, the column was conditioned to different temperatures for 1 h. After each conditioning step, a mixture of methyl 2,4-pentadienoate and methyl 3-pentenoate was separated using GC × GC, and the second-dimension resolution values were compared. As shown in Figure S9, significant column bleed and loss of chromatographic resolution was observed at temperatures above 180 °C. It was also observed that the silver-based-IL column could be reused for approximately 700 injections without significant loss of chromatographic resolution or efficiency when operating below this temperature. The enhanced thermal stability of the silver-based-IL stationary phase can be attributed to the chelating ligands ($C_{10}$MIM and MIM) and the [$C_{10}MIM^+$][$NTf_2^-$] IL, which provides stability when subjected to abrupt heating cycles.[31,32]

**Separation of Analyte Mixtures Using GC × GC with a Silver-Based IL $^2$D Column.** An optimized silver-based column was prepared using a mixture of silver-based-IL ([$(C_{10}MIM)(MIM)Ag^+$][$NTf_2^-$]) and conventional IL ([$C_{10}MIM^+$][$NTf_2^-$]). As shown in Figure 1, a mixture of the following thirty-three analytes was separated using GC × GC with the Rtx-5MS and silver-based IL ([$(C_{10}MIM)(MIM)Ag^+$][$NTf_2^-$]/[$C_{10}MIM^+$][$NTf_2^-$] 1:30, w/w) column set: (**1**) propionaldehyde, (**2**) butyraldehyde, (**3**) pentanal, (**4**) hexanal, (**5**) heptanal, (**6**) octanal, (**7**) benzaldehyde, (**8**) acetone, (**9**) 2-butanone, (**10**) 2-pentanone, (**11**) 3-pentanone, (**12**) 2-hexanone, (**13**) cyclohexanone, (**14**) ethyl acetate, (**15**)


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methyl acetate, (**16**) methyl butyrate, (**17**) ethyl butyrate, (**20**) isopropyl butyrate, (**21**) methyl 4-pentenoate, (**22**) methyl pentanoate, (**23**) methyl 2,4-pentadienoate, (**24**) methyl 3-pentenoate, (**25**) methyl tiglate, (**26**) ethyl pentanoate, (**27**) isoamyl acetate, (**28**) propyl tiglate, (**29**) ethyl hexanoate, (**30**) propyl tiglate, (**31**) isopropyl tiglate, (**32**) ethyl heptanoate, and (**33**) heptyl acetate (see Table S1 for structures). To compare and benchmark the separation performance of this column set, the same mixture was analyzed using a Rtx-5MS × SUPELCOWAX10 column set, as shown in Figure 1c. The Rtx-5MS × $[(C_{10}MIM)(MIM)Ag^+][NTf_2^-]/[C_{10}MIM^+][NTf_2^-]$ 1:30 (w/w) column set provided better chromatographic resolution of analytes, especially for early eluting compounds, compared with the Rtx-5MS × SUPELCOWAX10 column set. For example, the cluster of analytes possessing low boiling points and similar polarities (e.g., butyraldehyde (**2**), 2-butanone (**9**), 2-pentanone (**10**), 3-pentanone (**11**), ethyl acetate (**14**), and methyl acetate (**15**)) was better resolved by the Rtx-5MS × silver-based-IL column set. The second-dimension chromatographic resolutions between butyraldehyde (**2**) and 2-butanone (**9**), between pentanal (**3**) and methyl butyrate (**16**), and between hexanal (**4**) and propyl 2-hexanone (**12**) were found to be 2.2, 3.8, and 6.3, respectively, using the silver-based IL and 0.9, 1.6, and 4.9 using the SUPELCOWAX10 as the second-dimension column (Table S2). When the Rtx-5MS × SUPELCOWAX10 column set is employed, the separation in the first dimension is based on the boiling point of each analyte, and the separation in the second dimension is largely based on dipolar and electron-lone-pair interactions.[33,34] In comparison, when the Rtx-5MS × silver-based-IL column set is used, the separation mechanism offered in the second dimension is strongly influenced by $\pi$-complexation between the silver ions and the double or triple bonds of the analytes. To further validate the effect of the silver IL in the second-dimension column, a column set using a neat conventional IL column (containing no $Ag^+$) was used for GC × GC separation of the analyte mixture. As shown in Figure S10, the selectivity toward the analytes in the second dimension was completely lost compared with that of the Rtx-5MS × silver-based-IL column set.

The following analyte mixture composed of alkanes, alkenes, alkynes, cycloalkanes, and terpenes was subjected to GC × GC separation using both column sets, as shown in Figure 2: (**34**) *n*-pentane, (**35**) 2,4-hexadiene, (**36**) 3-methyl-1,4-pentadiene, (**37**) 1,5-hexadiene, (**38**) 1,3-hexadiene, (**39**) 1-hexene, (**40**) *cis*-2-hexene, (**41**) 3-hexene, (**42**) *n*-hexane, (**43**) 2,3-dimethyl-1,3-butadiene, (**44**) benzene, (**45**) 2-hexyne, (**46**) 1-hexyne, (**47**) 3-hexyne, (**48**) toluene, (**49**) *n*-octane, (**50**) *m*-xylene, (**51**) *o*-xylene, (**52**) *p*-xylene, (**53**) 1,8-nonadiene, (**54**) 1-nonene, (**55**) *n*-nonane, (**56**) myrcene, (**57**) $\alpha$-terpinene, (**58**) $\gamma$-terpinene, and (**59**) terpinolene. It can be observed that the analytes were better resolved and distributed using the Rtx-5MS × silver-based-IL column set. In addition, it was found that the retention times of the analytes eluted in the second-dimension column were correlated to the number of units of unsaturation within the analyte. Nonane (**55**), 1-nonene (1 double bond, **54**), and 1,8-nonadiene (2 double bonds, **53**) eluted in 1.56, 2.25, and 3.03 s, respectively. It can also be observed that compounds with low boiling points and similar polarities (compounds **34**−**48**) were better resolved using the Rtx-5MS × silver-based-IL column set. For example, the analyte group containing 3-methyl-1,4-pentadiene (**36**), 1-hexene (**39**), 3-hexene (**41**), and *n*-hexane (**42**) were better

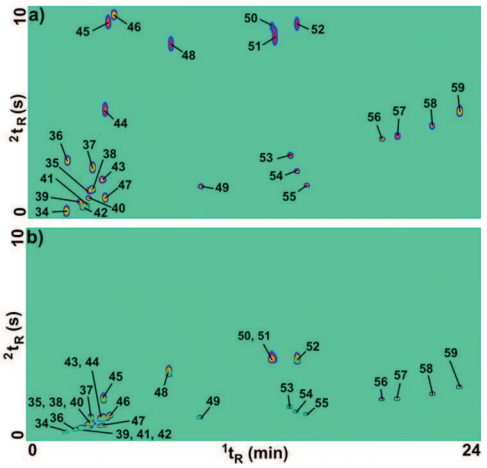


**Figure 2.** GC × GC-FID chromatograms of alkanes, alkenes, alkynes, dienes, cycloalkanes, and terpenes using the column sets (a) Rtx-5MS (30 m, 0.25 mm i.d., 0.25 $\mu$m) × $[(C_{10}MIM)(MIM)Ag^+][NTf_2^-]/[C_{10}MIM^+][NTf_2^-]$ (1:20, w/w; 0.9 m, 0.25 mm i.d., 0.15 $\mu$m) and (b) Rtx-5MS (30 m, 0.25 mm i.d., 0.25 $\mu$m) × SUPELCOWAX10 (0.9 m, 0.2 mm i.d., 0.2 $\mu$m). Inlet pressure: 9.32 psi. Split ratio: 5:1. Temperature program: 25 °C for 3 min, 25 to 44 °C at 2 °C/min, 44 to 90 °C at 5 °C/min, and 90 °C for 2.3 min. Modulation time: 10 s. See Table S1 for peak identification.

separated using the Rtx-5MS × silver-based-IL column set. The 2,4-hexadiene (**35**) and 1,3-hexadiene (**38**) pair was not separated by either column set. In addition, the probes 2,3-dimethyl-1,3-butadiene (**43**) and benzene (**44**), which coeluted on the Rtx-5MS × SUPELCOWAX10 column set, were well-separated using the Rtx-5MS × silver-based-IL column set ($R_{43,44}$ = 6.5). The analytes 2-hexyne (**45**), 1-hexyne (**46**), and 3-hexyne (**47**) exhibited a highly distinctive and interesting separation pattern. It is important to note that the 1D analysis of 1-hexyne was not possible using the neat silver-based-IL column reported by Nan et al.[25] because of its propensity of undergoing an irreversible complexation reaction with the silver-based-IL stationary phase, resulting in its tenacious retention. However, for the $[(C_{10}MIM)(MIM)Ag^+][NTf_2^-]/[C_{10}MIM^+][NTf_2^-]$ 1:20 (w/w) IL column, the strength of $\pi$-complexation was effectively tuned, allowing all alkynes to elute while being sufficient enough to provide high selectivity. As observed previously, when a neat conventional IL column was employed in the second dimension, the selectivity (compounds **34**−**59**) was completely lost (see Figure S11).

**Separation of Unsaturated Fatty Acids Using GC × GC with a Silver-Based-IL Column.** To further validate the application of the GC × GC method using a silver-based-IL column, a UFA sample was analyzed using the SUPELCOWAX10 × $[(C_{10}MIM)(MIM)Ag^+][NTf_2^-]/[C_{10}MIM^+][NTf_2^-]$ 1:30 (w/w) column set. The UFA sample is composed of long-chain fatty acids (from 14 to 22 carbons) with 0 to 6 units of unsaturation. The sample was initially separated using a conventional 1D system in order to determine the elution order of the analytes (see Figure S12a). The UFA sample (fraction from $^1t_R$ = 15 to 47 min, UFAs from C14:0 to C18:3) was subjected to GC × GC separation, as shown in Figure 3. The silver-based-IL stationary phase provided good selectivity for the analytes within the sample as evidenced by UFAs containing the same carbon chain length being well-separated. As an example, the second-


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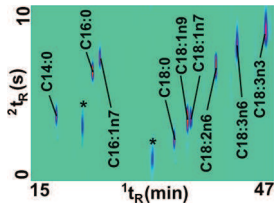


**Figure 3.** GC × GC-FID chromatogram of an unsaturated fatty acid sample obtained using the SUPELCOWAX10 (30 m, 0.25 mm i.d., 0.25 μm) × [($C_{10}$MIM)(MIM)$Ag^+$][$NTf_2^-$]/[$C_{10}MIM^+$][$NTf_2^-$] (1:30, w/w; 0.4 m, 0.25 mm i.d., 0.15 μm) column set. Inlet pressure: 9.32. Split ratio: 100:1. Temperature program: isothermal mode at 180 °C for 47 min. Modulation time: 10 s. For peak identification, refer to Figure S5. The peaks labeled with asterisks (*) refer to interfering compounds present within the purchased sample.

dimension retention times of C18:0 (0 double bond), C18:1n7 (1 double bond), C18:2n6 (2 double bonds), and C18:3n3 (3 double bonds) were found to be 2.27, 3.55, 6.48, and 8.57 s, respectively. UFAs possessing more than 20 carbon atoms were not studied because they exceeded the MAOT of the column. Overall, UFAs (from C14:0 to C18:3) were well-separated and exhibited unique retention behavior using this column set. This study is the first time in which UFAs were separated by GC × GC using an analyte-selective silver column with a retention order in the second dimension highly correlated to the number of double bonds.

In summary, a GC × GC compatible silver-based stationary phase was successfully developed. The unique chromatographic selectivity and GC × GC compatibility of the stationary phases were achieved through careful structural design and mixing of the silver-based IL and conventional ILs as well as the optimization of film thickness and column length. This study will guide the design and development of new generations of silver-based stationary phases with high thermal stability capable of providing unique selectivity for a broader range of analytes possessing similar polarities within complex samples, such as long-chain UFAs in food products and isomers of long-chain unsaturated hydrocarbons within petrochemicals. Furthermore, the approach of employing analyte-selective components within a tunable stationary phase further demonstrates the unique features offered by ILs in separation science.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.9b00472.

Detailed description of instrumentation, synthesis, and the capillary-column-coating procedure; list of probe molecules used to characterize the silver-based-IL columns; separation performance of selected pairs of analytes by GC × GC-FID using a silver-based-IL column or a SUPELCOWAX10 column as the second-dimension column; chemical structures of the silver-based ILs and conventional ILs; $^1$H NMR spectra; chemical structures of unsaturated fatty acids; GC × GC-FID chromatograms; chromatographic resolutions; evaluation of film thickness and capillary-column length for the separation of methyl 3-pentenoate and methyl 2,4-pentadienoate; thermal stability of the silver-based-IL stationary-phase column; and chromatographic resolution between methyl 2,4-pentadienoate and methyl 3-pentenoate (PDF)

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### Notes

The authors declare no competing financial interest.

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