Discrimination of positional isomers by ion mobility mass spectrometry: application to organic semiconductors†

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有机半导体越来越被用于有机基的光电电子设备。由于在有机电子学中，选择性合成方法尚未得到全面控制，这使化合物有时需要通过非选择性合成路线来准备。离子迁移质谱法是区分这些混合物中的异构体的有效方法，而不是进行耗时的分析方法。离子迁移质谱法在有机电子学领域中得到了广泛的开发。

在现有的工作中，非选择性方法报道了在溶液中的2,3-二氢异茚[1,2-b]并菲的化学合成，而2,1-二氢异茚[2,1-a]并菲的化学合成却非常罕见。抗性化合物可以用于非全富勒烯有机太阳能电池中的受体，而抗性化合物在结构上具有二氢异茚[1,2-b]并菲的独特性质。在2009年，一种在一定电场中对二氢异茚并菲异构体进行检测和分离的方法被报道（方案S1，ESI†）。为了避免耗时的色谱分离方法，IMMS是一种在真空状态下对挥发性样品进行离子分离和检测的有效方法。IMMS具有良好的选择性，可以用于分离和检测具有相同元素组成的异构体。其选择性是由其在电场中的电荷性质决定的。IMMS在有机电子学中有着巨大的应用前景。
Dihydroindenofluorene isomer mixtures were diluted in acetonitrile and subsequently ionized and transferred to the gas phase of a mass spectrometer using an Electrospray Ionization (ESI) ion source. All results presented hereafter are related to radical cations that are readily produced upon ESI by the removal of one electron. The ion mobility data are represented in terms of CCS distributions determined on the basis of arrival time distributions (ATD) using a suitable calibration procedure recently developed in Mons.26 Note that each experiment described in the present paper was performed three times using different ion mobility settings (see the ESI†) to ensure the robustness of the method. The presented CCSs are mean values with standard deviations in brackets.

**Fig. 1** (A, B and C) Experimental and theoretical CCS values for 1a/1b, 2a/2b and 3a/3b radical cations. The green dots represent the location of the terphenylene core. The lengths of the substituents were theoretically extracted from the optimized geometries of each substituent, and they are also displayed. The presented CCSs are mean values with standard deviations in brackets.
The synthesis of compounds combining the bridged \( p \)-terphenylene core and two fluorene moieties through spiro-linkages yields a mixture of \textit{syn} and \textit{anti} (1a and 1b in Fig. 1A, respectively) isomers.\(^{11}\) When the isomer mixture is subjected to ion mobility experiments, a bimodal distribution (i.e., two ion families) is observed for the mass-to-charge ratio corresponding to the cation radical isomers, which might correspond to the two separated isomers, to conformers or even to contaminants. In order to assess whether the two distributions correspond to the two ionized isomers and to unambiguously assign the peaks observed in the mobilograms, the geometries of the corresponding radical cations have been optimized at the quantum-chemical level and their CCS calculated using the widely used trajectory method model, as implemented in Collidoscope\(^{27}\) (Fig. 1A). The excellent agreement between the experimental and theoretical CCS values (<3\% difference) confirms that the \textit{syn} (1a) isomer is associated with the lower CCS distribution while the \textit{anti} (1b) isomer generates the higher CCS distribution. The peak separation efficiency in ion mobility spectrometry can be quantified by associating the peak full width at half maximum values \((\delta_a, \delta_b)\) and the peak separation \((t_b - t_a)\) into a resolution parameter, \(R_s\), defined by the following equation:\(^{28}\)

\[
R_s = 1.18 \frac{t_b - t_a}{\delta_a + \delta_b}
\]

We have used here a variant of this definition by injecting the average CCS values and the width at half maximum \(\Delta CCS:\)^{28}

\[
R_s = 1.18 \frac{CCS_B - CCS_A}{\Delta CCS_A + \Delta CCS_B}
\]

For the 1a/1b isomer pair, we measured the \(R_s\), which amounted to 1.4 and reflected the small signal overlap observed in the mobilograms (see Fig. 1A). In peak separation theory, for two peaks with Gaussian distributions and the same heights/widths, a resolution of 1.5 corresponds to an overlap of less than 0.15\%.\(^{29}\)

When comparing the optimized structures of 1a/1b radical cations, the CCS difference can be clearly associated with the relative orientation of the substituents. We thus anticipate that the \(R_s\) value will be affected by the size of the substituents. Accordingly, we have next applied our IMS/quantum chemistry association to the 2a/2b\(^{30}\) and 3a/3b\(^{19}\) isomer pairs exhibiting bulkier substituents on the fluorene units (\textit{tertio}-butyl and 3,4,5-trimethoxyphenyl groups, respectively, Fig. 1B and C). The results indicate that the \textit{syn} isomer radical cations are always characterized by the smaller CCS, i.e., the more compact structures. Moreover, the \(CCS_{\text{exp}}\) increases with the substituent size, with values of 157/176 \(\text{Å}^2\), 206/234 \(\text{Å}^2\), and 288/320 \(\text{Å}^2\) for the 1a/1b, 2a/2b and 3a/3b isomer pairs, respectively. The deep correlation between the \(CCS_{\text{exp}}\) and \(CCS_{\text{th}}\) values is remarkable, leading to the straightforward identification of the isomers. As expected, the bulkier the substituent, the better is the separation efficiency, with \(R_s\) measured to be 2.3 and 2.4 for the 2a/2b and 3a/3b isomer pairs, respectively, a value which is usually associated with a baseline separation.\(^{28}\) The applicability of

\[\text{Fig. 2 } \text{Experimental and theoretical CCS values for isomers 4a/4b. The presented CCSs are mean values with the standard deviations in brackets.}\]
IMMS is not limited to fluorene substituents and to \( p \)-terphenylene backbones, as shown below by the investigation of more elaborate structures. These molecules (4a and 4b in Fig. 2) consist of an \( m \)-terphenylene core substituted by spiro-linked phenylacridine units.\(^4\) Here, the separation efficiency is less pronounced, yielding an asymmetric CCS distribution and a lower \( R_s \) factor value of 0.68 (Fig. 2). Upon Gaussian deconvolution and comparison between \( \text{CCS}_{\text{exp}} \) and \( \text{CCS}_{\text{th}} \) values, it appears that these two distributions do correspond to each regioisomer radical cation. Based on the results obtained with sterically encumbered substituents on the \( p \)-terphenylene cores, the separation efficiency is expected to be enhanced with bulkier substituents under our experimental conditions.

In summary, we have illustrated that IMMS can be advantageously used to readily detect isomers of organic semiconductors produced simultaneously in chemical reactions. This is another successful application of the IMMS technique which is here supplemented by an intimate coupling to computational chemistry allowing for the structural assignment of the IMMS signals. This original joint theoretical and experimental approach is versatile and should find application in many other research areas. The exact quantification of both isomers in the starting mixture could be estimated based on our IMMS measurements, provided that the ionization cross sections for both isomers – \( i.e. \), the mathematical relation between the ion abundance in the IMMS spectrum and the concentration in the solution phase – can be determined by a calibration procedure; this issue is beyond the scope of the present paper. Although most current commercial IMMS setups can only be exploited to detect isomers with sufficient structural differences due to the inherent instrumental resolution, we are convinced that the recent development of high resolution ion mobility instruments will reinforce the use of ion mobility technology as a routine analytical tool within the organic synthesis community to detect isomeric products and to optimize (non)-regioselective synthetic routes.

**Conflicts of interest**

There are no conflicts to declare.

**Notes and references**


