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Gas and Liquid Phase Diffusivities of Isomeric Metal Complexes Derived from Multifold Ring-Closing Metatheses: Ion Mobility Mass Spectrometry Trumps DOSY NMR

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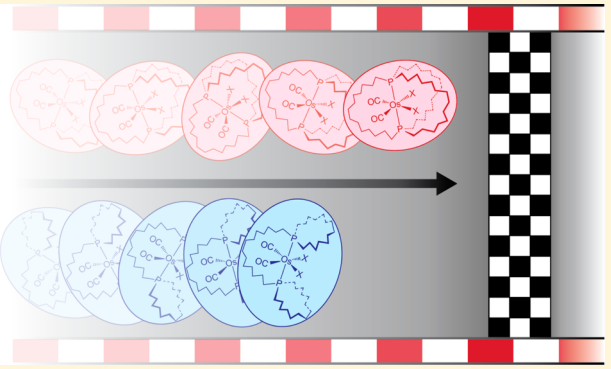
ABSTRACT: Isomeric octahedral osmium and rhenium complexes of formulas $M(CO)_y(X)_z(P((CH_2)_n)_3P)$ and $M(CO)_y(X)_z(P(CH_2)_{n-1}CH_2)((CH_2)_n)(P(CH_2)_{n-1}CH_2)$ (n/M/y/z/X = 14/Os/2/2/Cl, 14/Os/2/2/Br, 14/Re/3/1/Cl, 18/Os/2/2/Br), in which the phosphorus donor atoms occupy *trans* positions, are examined by the title techniques. The former gyroscope-like complexes are spherical or ovoid in shape, whereas the latter have phosphacycle "flaps" that increase the volume. Both types diffuse at identical rates in C_6D_6 as assayed by DOSY NMR, but ions derived from the latter exhibit up to 10% slower drift times in the gas phase by ion mobility mass spectrometry (IMMS). Thus, IMMS, which is seldom applied to isomeric organometallic or coordination compounds, provides superior differentiation.



INTRODUCTION

We have had an ongoing interest in multifold ring-closing metatheses and surveyed this growing literature in a recent review.[1] We have often sought to prepare complexes of cage-like dibridgehead diphosphines via 3-fold intramolecular *inter*ligand alkene metatheses of precursors with *trans* phosphine ligands of the formula $P((CH_2)_mCH{=}CH_2)_3$, as exemplified by **I** in Scheme 1.[2−4] The products **II** have been termed gyroscope-like, and when the spectator ligands are sufficiently small, the ML_y moieties can rotate within the methylene chains that span the two phosphorus atoms. Depending upon the coordination geometry, the minimum number of methylene groups per chain ranges from 10 to 14.

However, several types of isomeric byproducts are also possible. For example, **III**, which features two phosphacycles derived from *intra*ligand metathesis, is sometimes observed when **I** has square planar[2d] or octahedral[4b] coordination geometries. Also, a "crossed chain" variant of **II** could potentially form (**IV**), but has resisted detection to date. In any event, **III** is distinguished by its less compact shape and should obviously possess a greater molecular volume.

One way to distinguish **II** and **III** involves ^{13}C NMR spectroscopy. The former gives, in the limit of rapid ML_y rotation, $n/2$ CH_2 signals. The latter exhibits n CH_2 signals, with the $n/2$ that arise from the two phosphacycles ca. twice as intense as the $n/2$ of the *trans* spanning methylene chain. Nonetheless, for some time it proved impossible to confirm the structure of any complex of the type **III** crystallographically.[4b] Therefore, we sought to engage physical techniques that would be sensitive to the molecular shape. In this paper we report a comparison of ion mobility mass spectrometry (IMMS),[5] which is rather infrequently applied to organometallic molecules, and diffusion-ordered spectroscopy (DOSY) NMR,[6] which has become a quite common technique. Interestingly, the former method, which interrogates the gas phase conformations and collisional cross sections, proves to be more discriminating than the latter, which is employed in solution and is better known to the organometallic community.

RESULTS

Four pairs of octahedral complexes of the types **II**/**III**, $M(CO)_y(X)_z(P((CH_2)_n)_3P)$ and $M(CO)_y(X)_z(P(CH_2)_{n-1}CH_2)((CH_2)_n)(P(CH_2)_{n-1}CH_2)$, were selected for initial study. These were synthesized by the previously reported procedures in Scheme 2 and chromatographically separated.[4] Three pairs featured three carbon chains of 14 methylene groups: the osmium dichloride complexes **1a**/**1′a** and dibromide complexes **2a**/**2′a** and the rhenium monochloride complexes **3a**/**3′a**.[4,7] Higher homologues of **2a**/**2′a** with 18 carbon chains, **2c**/**2′c**, were similarly accessed. The crystal structures of **1a**, **2′a**, **2c**, and **3a** have been determined.[4]

IMMS is sometimes referred to as ion chromatography and separates ions based on their mobility through a neutral buffer gas (usually nitrogen or helium).[5] Ions of the same molecular mass and charge, which would give a single isotope envelope with a conventional mass spectrometer, can potentially be separated by IMMS due to differing mobilities through a gas-filled drift chamber. Provided that the sizes or shapes of the ions are

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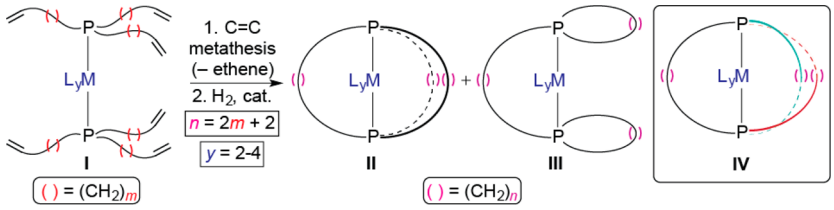
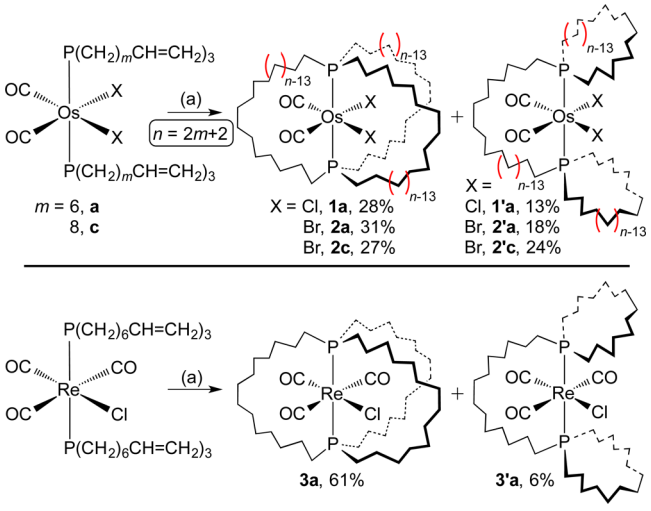
Scheme 1. Syntheses of Gyroscope-like Complexes (II) and Possible Byproducts (III, IV)



Scheme 2. Syntheses of Substrates for Ion Mobility Mass Spectrometry (IMMS) and DOSY NMR: (a) Grubbs' Catalyst (5–10 mol %), Chlorobenzene (0.0010–0.0012 M); PtO_2, H_2, THF



significantly different (and thereby the collisional cross sections), the times needed to traverse the drift chamber will vary.

IMMS data for **1a**, **1′a**, **2a,c**, **2′a,c**, **3a**, and **3′a** were recorded under standard conditions as described in the Experimental Section. For the osmium complexes, two ions $[M - X]^+$ (X = Cl, Br) and $[M + Na]^+$, were studied. For the rhenium complexes, only the $[M - Cl]^+$ ion was examined. The results are depicted in Figures 1–4. For example, the isotope envelopes for the ions $[\mathbf{1'a} - Cl]^+$ and $[\mathbf{1'a} + Na]^+$ are provided in panels A and C of Figure 1. Those for the analogous ions derived from **1a** were identical, and all agreed with the theoretical distribution. As shown in panels B and D of Figure 1, the drift times were significantly different, with the mobilities of the ions derived from **1′a** being significantly lower.

The results in Figures 2–4 are analogous. The isotope envelopes given in panels A and C were obtained from both isomeric complexes. Panels B and D show that the drift times for the ions derived from the spherical or ovoid gyroscope-like precursors **II** (**2a,c**, **3a**) are always shorter (up to 10%) than those derived from **III** (**2′a,c**, **3′a**), consistent with expectations based upon shape. The values are summarized in Table 1. The trend is independent of the metal (rhenium vs osmium), the nature of the ligands (chloride vs bromide), and the macrocycle size (14 vs 18 methylene groups). Thus, this technique holds particular future promise for establishing the structures of related compounds that are too poorly soluble to conveniently acquire ^{13}C NMR data and/or simply not available in sufficient quantity.

Next, DOSY ^1H NMR data were sought for a representative pair of compounds. The complexes **2c** and **2′c** were selected, in part due to the large quantity of each isomer available.[4b] As a preliminary step, ^1H NMR spectra of **2c** and **2′c** were recorded

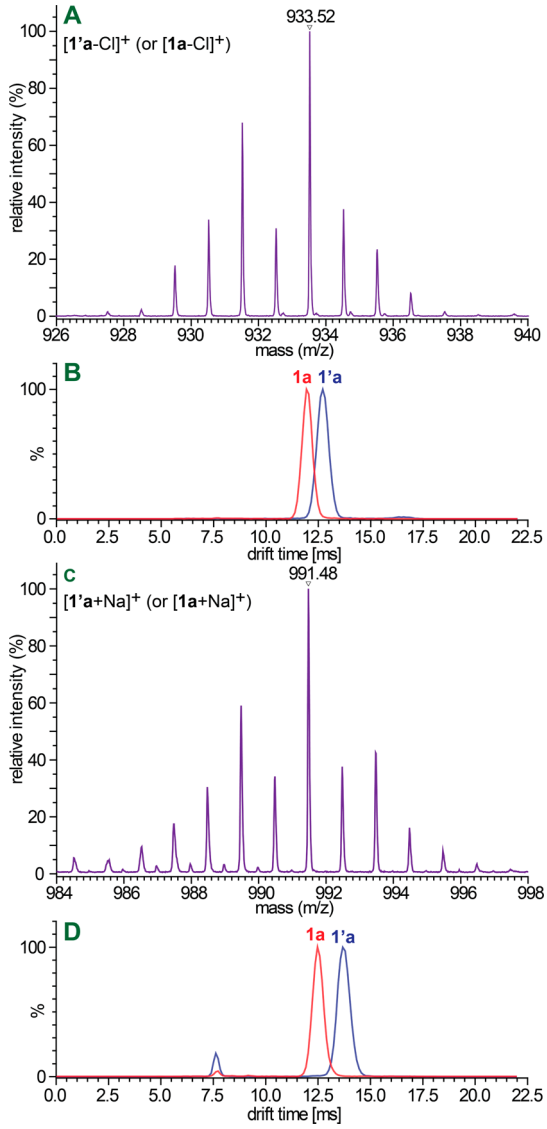


Figure 1. IMMS data for **1a** and **1′a**: Isotope envelopes (A, C) and drift times (B, D) for the ions $[M - Cl]^+$ (A, B) and $[M + Na]^+$ (C, D).

in C_6D_6. Although not a precondition, when the complexes of interest exhibit at least partially separated signals, data processing is simplified. As shown in Figure 5, this scenario is fulfilled, with **2′c** exhibiting several well-separated resonances and **2c** one (broad $PCH_2C\underline{H}_2$ signal at ca. 1.6 ppm).

Thus, DOSY ^1H NMR spectra were recorded using a 1:1 mixture of **2c** and **2′c** as described in the Experimental Section. The customary magnetic field gradient was applied along the *z* axis, and a series of spectra with increasing gradient strength were recorded (Figure 6). These exhibited the usual decay of signal intensities with increasing gradient strength. From this decay, a DOSY plot was calculated. It can easily be seen

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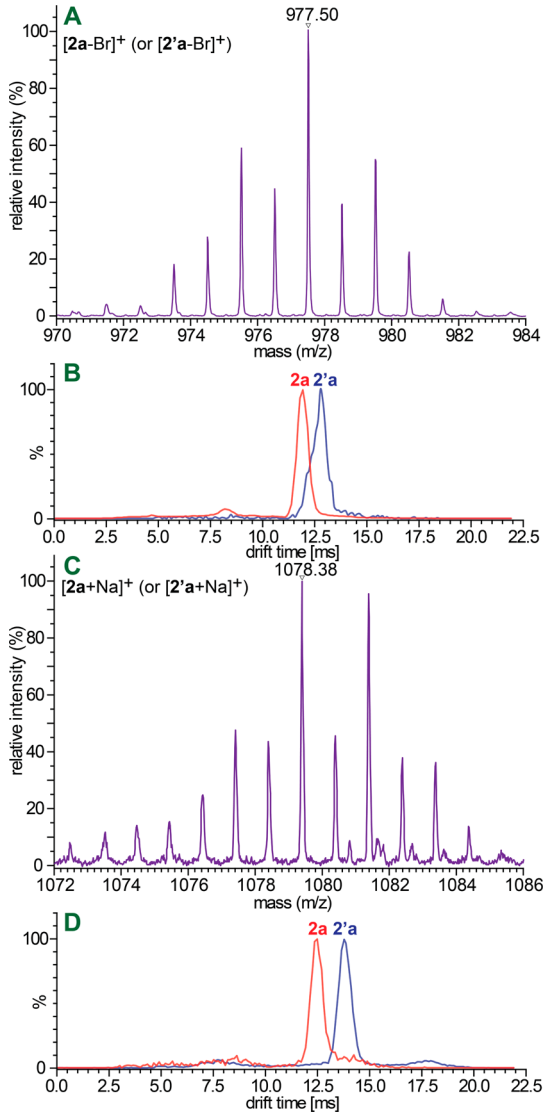

Figure 2. IMMS data for **2a** and **2′a**: Isotope envelopes (A, C) and drift times (B, D) for the ions $[M - Br]^+$ (A, B) and $[M + Na]^+$ (C, D).

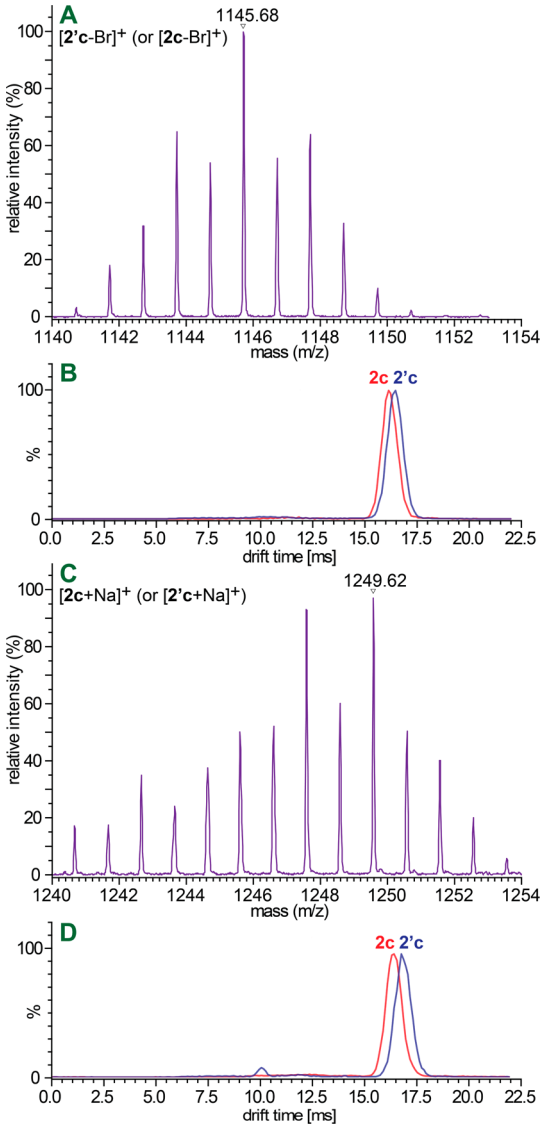

Figure 3. IMMS data for **2c** and **2′c**: Isotope envelopes (A, C) and drift times (B, D) for the ions $[M - Br]^+$ (A, B) and $[M + Na]^+$ (C, D).

from Figure 7 that the diffusion coefficients of **2c** and **2′c** are practically identical.

DISCUSSION

With respect to metal-containing substrates, IMMS probably sees greatest use in supramolecular chemistry, as a tool for distinguishing oligomers of various lengths or ring sizes.[8] To our knowledge, there have been far fewer applications of IMMS in differentiating isomeric organometallic compounds of the same molecular formula.[9] One relevant study involves the three arene ruthenium complexes shown in Figure 8, all of which feature an η^6 ligand of formula $C_{18}H_{14}$.[10] The drift times under the conditions of measurement were 4.72, 4.17, and 4.22 ms, respectively. This nicely correlates with the footprint of the approximately two-dimensional arene ligand. As noted by a reviewer, IMMS data can be employed to calculate collisional cross sections.[11]

DOSY NMR has been widely applied to organometallic complexes. However, in our careful examination of the review literature,[6] no examples have been found where isomeric species have been differentiated. DOSY NMR studies of isomeric organic compounds have appeared,[12] but the diffusivities are usually identical, although extensive solvent optimization sometimes

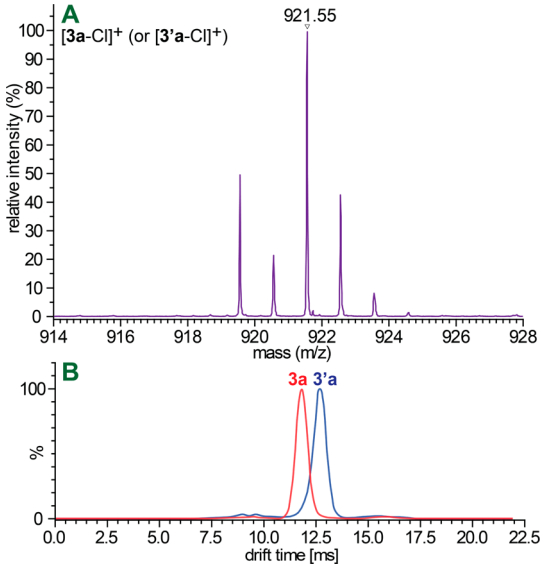

Figure 4. IMMS data for **3a** and **3′a**: Isotope envelope (A) and drift times (B) for the ions $[M - Cl]^+$.

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Table 1. Summary of Drift Times [ms] for Ions Studied

complex	$[M - X]^+$	$[M + Na]^+$
1a	11.91	12.46
1′a	12.68	13.67
2a	11.91	12.46
2′a	12.79	13.78
2c	16.10	16.43
2′c	16.43	16.76
3a	11.80	
3′a	12.68	

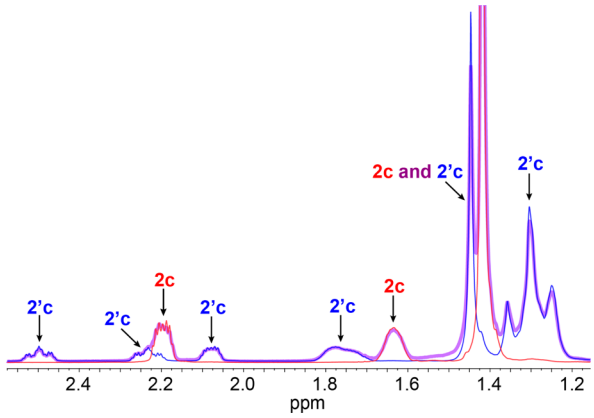

Figure 5. Overlaid ^{1}H NMR spectra (500 MHz, C_6D_6) of **2c** (red), **2′c** (blue), and a 1:1 **2c**/**2′c** mixture (purple).

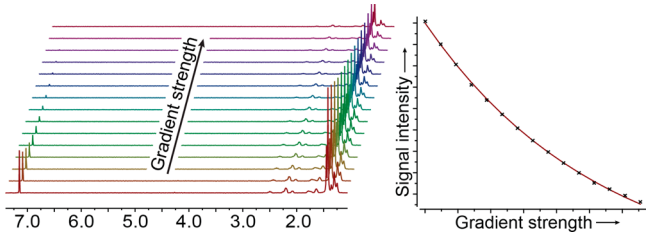

Figure 6. Stacked ^{1}H NMR spectra (500 MHz, C_6D_6, increasing gradient strength) of a 1:1 **2c**/**2′c** mixture (left); exponential fit of the signal intensities versus increasing gradient strength (right).

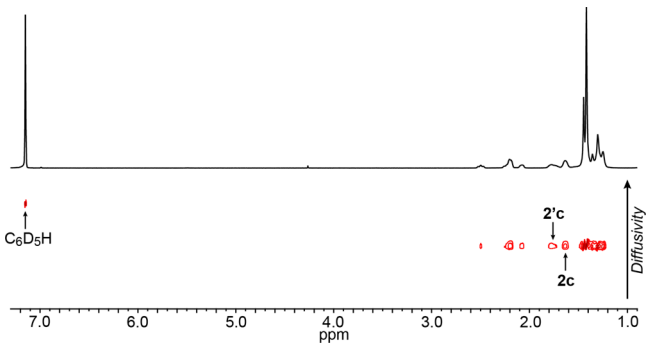

Figure 7. DOSY ^{1}H NMR plot (500 MHz, C_6D_6) of a 1:1 **2c**/**2′c** mixture showing identical diffusivities.

affords partial peak separations.[12c] Better results have been obtained in the presence of micelles, sols, and surfactants.[13]

In any case, IMMS would not likely be the first technique that would come to mind to an experimental inorganic or organometallic chemist seeking to assign structures to two complexes based upon shape. Our data represent the first comparative study showing that IMMS can deliver superior results with organometallic complexes. Furthermore, sample sizes can be orders of magnitude lower and analysis times much shorter. However, from a mechanistic standpoint, it should be emphasized that IMMS data reflect the diffusivities of *ions* in the gas phase—in the present case, either a cation derived by halide ionization or sodium cation addition—as opposed to the unaltered substrate.

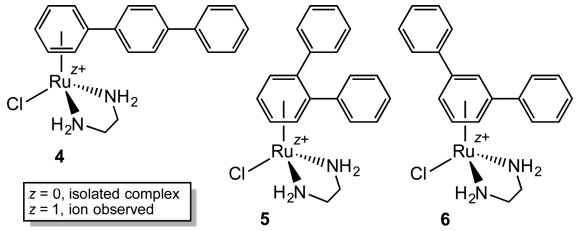

Figure 8. Isomeric arene ruthenium complexes differentiated by IMMS.

In conclusion, this work has shown that IMMS can differentiate isomeric organometallic compounds of unlike sizes or shapes with a resolution significantly greater than that of DOSY NMR spectroscopy. As such, this now-routine technique[5] deserves much wider application in the characterization of organometallic and other metal-containing molecules.

EXPERIMENTAL SECTION

Ion Mobility Mass Spectrometry.[5] Electrospray ionization ion mobility mass spectrometry (ESI-IMMS) data were acquired on a Synapt HDMS G2 mass spectrometer (Waters UK Ltd., Manchester, UK) equipped with a traveling-wave ion mobility cell maintaining 2.3 Torr of nitrogen. Samples were ca. 2×10^{-6} M in 50:50 v/v MeOH/CH_2Cl_2. Ions were formed by a nanoelectrospray source in the positive ion mode. The source temperature was 100 °C, and the capillary voltage was 1.8 kV. The cone voltage was 40 V, and the extraction voltage was 4 V. For the ion mobility experiments, the traveling wave ion mobility cell was operated at a wave velocity of 300 m/s and amplitude of 22 V.

DOSY NMR. Spectra were recorded on a Varian NMRS 500 MHz spectrometer equipped with a 5 mm ^{1}H/^{19}F/^{13}C/^{31}P quad resonance probe and a *z* gradient coil (up to 30 G/cm) using a 1:1 **2c**/**2′c** mixture (0.005 g/mL each; combined concentration 0.0082 M in C_6D_6). The probe temperature was kept at 25 °C, and the samples were allowed to equilibrate for at least 15 min. ^{1}H diffusion experiments were carried out with static samples using the convection-compensated bipolar pulse pair stimulated echo pulse sequence (Dbppste_cc).[14] The 90° pulse was 9.90 μs. The incremented gradient strength (g) was varied from 1 to 30 G/cm. The bipolar pulse gradient duration (δ) was 2 ms, and the diffusion period (Δ) was 30 ms. The number of transients per increment was 16 with a relaxation delay of 2 s. The field gradient strength was calibrated by measuring the self-diffusivity (D_s) of 10% D_2O in H_2O ($D_s = 22.7 \times 10^{-10}$ m^2 s^{-1}).[15] DOSY spectra were generated with the program MestReNova 6.0.2.[16]

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Notes

The authors declare no competing financial interest.

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