# Supporting Information

## Deuterated Malonamide Synthesis for Fundamental Research on Solvent Extraction Systems

Cyril Micheau,[a] Yuki Ueda,[a] Kazuhiro Akutsu-Suyama,[b]

Damien Bourgeois,[c] and Ryuhei Motokawa[a]*

[a]Materials Sciences Research Center, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan

[b]Neutron Science and Technology Center, Comprehensive Research Organization for Science and Society (CROSS), Tokai, Ibaraki 319-1106, Japan

[c]Institut de Chimie Séparative de Marcoule, ICSM, CEA, CNRS, ENSCM, Univ Montpellier, BP 17171, Marcoule, 30207 Bagnols-sur-Cèze, France

*To whom correspondence should be addressed.

motokawa.ryuhei@jaea.go.jp (R.M.)

**CONTENTS**

**S1. $^1$H NMR data of entries 2, 3, 5–8 in the Table 1**

The $^1$H NMR spectra of entries 2, 3, 5, 6, 7, and 9 in the Table 1 were recorded using a 400 MHz NMR spectrometer (JMTC-400/54/JJ/YH, JEOL Ltd., Tokyo, Japan) at 400 MHz. The $^1$H NMR data are shown in below:

**Entry 2**: $^1$H NMR (400 MHz, $CDCl_3$, TMS, 1,4-dioxane) $\delta$ 0.82–0.91 (m, 2.48H), 1.24–1.27 (m, 5.77H), 1.47–1.53 (m, 1.41H), 3.16–3.28 (m, 1.42H), 3.43 (s, 0.18H).

**Entry 3**: $^1$H NMR (400 MHz, $CDCl_3$, TMS, 1,4-dioxane) $\delta$ 0.84–0.90 (m, 3.97H), 1.24–1.27 (m, 9.05H), 1.47–1.52 (m, 2.20H), 3.25–3.33 (m, 2.48H), 3.43 (s, 1.06H).

**Entry 5**: $^1$H NMR (400 MHz, $CDCl_3$, TMS, 1,4-dioxane) $\delta$ 0.78–0.88 (m, 8.27H), 1.22–1.29 (m, 17.7H), 1.41–1.55 (m, 4.05H), 3.12–3.27 (m, 5.56H), 3.48 (br, 0.26H).

**Entry 6**: $^1$H NMR (400 MHz, $CDCl_3$, TMS, 1,4-dioxane) $\delta$ 0.82–0.95 (m, 3.11H), 1.23–1.31 (m, 8.40H), 1.47–1.50 (m, 1.04H), 1.82–1.86 (m, 0.69H), 2.87–2.95 (m, 0.36H), 3.19–3.36 (m, 0.72H), 3.50–3.52 (m, 0.20H).

**Entry 7**: $^{1}$H NMR (400 MHz, $CDCl_3$, TMS, 1,4-dioxane) $\delta$ 0.82–0.93 (m, 2.63H), 1.15–1.30 (m, 14.3H), 1.38–1.59 (m, 2.42H), 1.75–1.86 (m, 0.82H), 2.77–3.04 (m, 0.24H), 3.19–3.39 (m, 1.12H), 3.52 (br, 0.15H).

**Entry 9**: $^{1}$H NMR (400 MHz, $CDCl_3$, TMS, 1,4-dioxane) $\delta$ 0.86–0.97 (m, 9.00H), $\delta$ 1.25–1.31 (m, 27.3H), 1.49–1.52 (m, 2.82H), 1.86 (m, 1.41H), 2.86–3.01 (m, 1.60H), 3.17–3.37 (m, 3.43H), 3.48–3.61 (m, 0.58H).

## S2. ESI-MS data of THMA-$d_n$

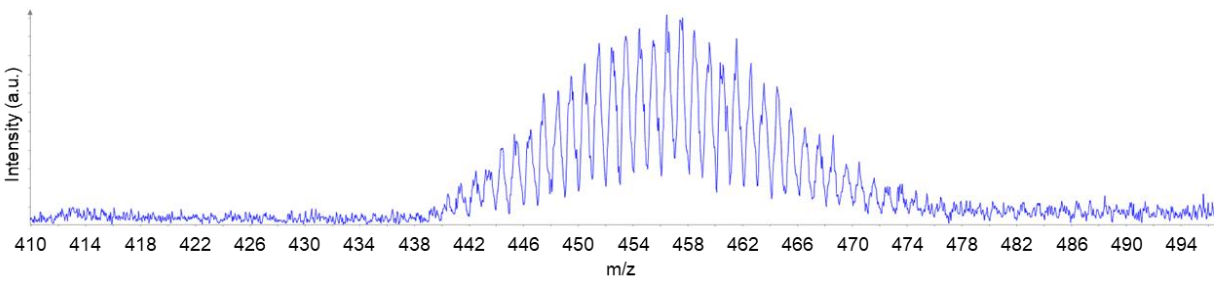


**Figure S1.** Electrospray ionization mass spectra in positive mode of THMA-*d* cation showing the mass distribution of the different isotopologues, which ranges from $d_2$–$d_{40}$. The distribution of the isotopologues is as follows ($M^+$): 0.54 %, $d_2$; 1.00 %, $d_3$; 1.00 %, $d_4$; 1.22 %, $d_5$.; 1.68 %, $d_6$ ; 2.18 %, $d_7$; 2.13 %, $d_8$; 2.68 %, $d_9$; 2.94 %, $d_{10}$; 3.36 %, $d_{11}$; 4.17 %, $d_{12}$; 4.08 %, $d_{13}$; 4.54 %, $d_{14}$; 4.99 %, $d_{15}$; 4.99 %, $d_{16}$; 4.99 %, $d_{17}$; 5.44 %, $d_{18}$; 5.44 %, $d_{19}$; 4.54 %, $d_{20}$; 4.40 %, $d_{21}$; 4.35 %, $d_{22}$; 4.04 %, $d_{23}$; 3.58 %, $d_{24}$; 3.13 %, $d_{25}$; 2.72 %, $d_{26}$; 2.54 %, $d_{27}$; 1.91 %, $d_{28}$; 1.68 %, $d_{29}$; 1.36 %, $d_{30}$; 1.27 %, $d_{31}$; 1.09 %, $d_{32}$; 1.00 %, $d_{33}$; 1.00 %, $d_{34}$; 0.95 %, $d_{35}$; 0.91 %, $d_{36}$; 0.68 %, $d_{37}$; 0.59 %, $d_{38}$; 0.44 %, $d_{39}$; 0.45 %, $d_{40}$. The deuteration ratio was estimated to be 34.6 %.

**S3. ESI-MS data of DBMA-$d_n$**

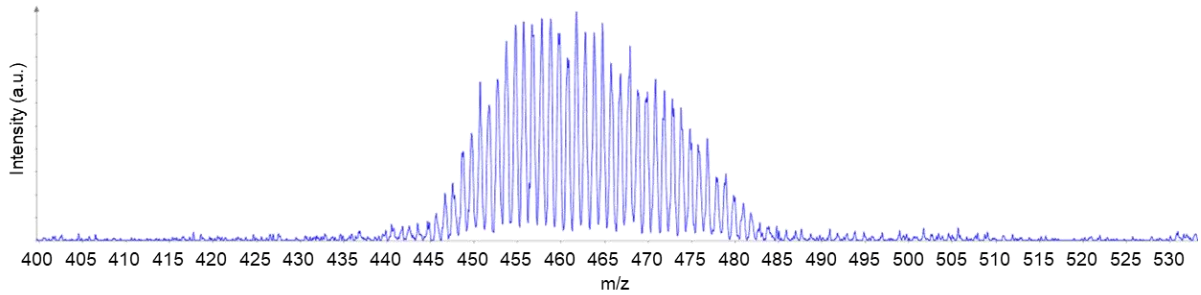


**Figure S2.** Electrospray ionization mass spectra in positive mode of DBMA-*d* cation showing the mass distribution of the different isotopologues, which ranges from $d_5$–$d_{38}$. The distribution of the isotopologues is as follows ($M^+$): $d_5$.; 0.46 %, $d_6$ ; 0.80 %, $d_7$; 1.17 %, $d_8$; 1.76 %, $d_9$; 2.13 %, $d_{10}$; 2.64 %, $d_{11}$; 2.80 %, $d_{12}$; 3.26 %, $d_{13}$; 3.89 %, $d_{14}$; 4.19 %, $d_{15}$; 4.19 %, $d_{16}$; 4.60 %, $d_{17}$; 4.19 %, $d_{18}$; 4.19 %, $d_{19}$; 4.19 %, $d_{20}$; 3.64 %, $d_{21}$; 4.19 %, $d_{22}$; 3.93 %, $d_{23}$; 3.93 %, $d_{24}$; 3.68 %, $d_{25}$; 3.43 %, $d_{26}$; 3.22 %, $d_{27}$; 3.81 %, $d_{28}$; 3.10 %, $d_{29}$; 3.14 %, $d_{30}$; 2.97 %, $d_{31}$; 2.85 %, $d_{32}$; 2.72 %, $d_{33}$; 2.51 %, $d_{34}$; 2.26 %, $d_{35}$; 2.01 %, $d_{36}$; 1.63 %, $d_{37}$; 1.30 %, $d_{38}$; 1.21 %. The deuteration ratio was estimated to be 39.6 %.

**S4. X-ray fluorescence of by-product in the deuteration of THMA-*h*$_{54}$.**

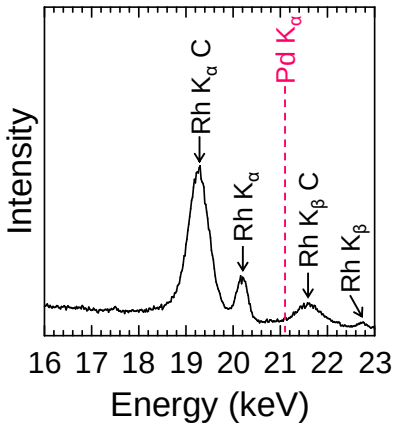


**Figure S3.** X-ray fluorescence (XRF) spectrum of the white precipitate obtained in the deuteration reaction of THMA-*h*$_{54}$, where the spectrum was recorded using a wavelength-dispersion-type XRF spectrometer (ZSX Primus II, Rigaku Corporation, Tokyo, Japan). XRF peaks of $K_\alpha$ C, $K_\alpha$, $K_\beta$ C, and $K_\beta$ of Rh were observed at 19.3, 20.2, 21.6, and 22.7 keV, respectively, whereas the XRF peak of $K_\alpha$ for Pd was not observed.

**S5. $^1$H NMR of by-product in the deuteration of THMA-*h*$_{54}$.**

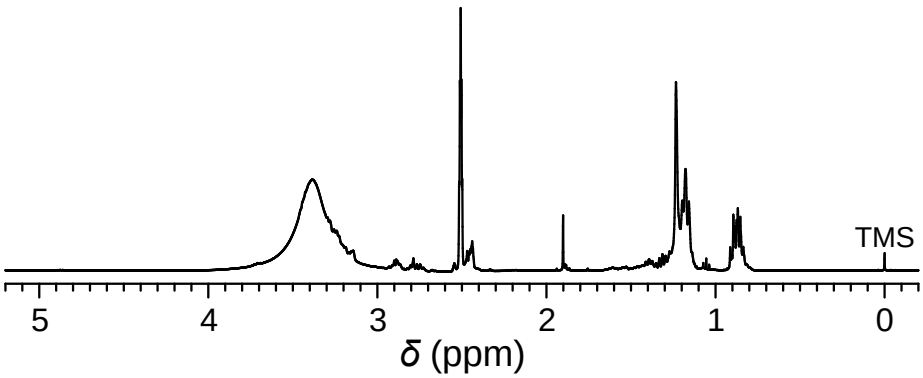


**Figure S4.** $^1$H NMR spectrum of the white precipitate, obtained in the deuteration reaction of THMA-*h*$_{54}$, in $CDCl_3$ with TMS (chemical shift reference).