SUPPORTING INFORMATION

Reactions of Noble-Metal Oxides in Ionic Liquids Near Room Temperature

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Content

1. Analytical Equipment

Single-crystal X-ray structure analysis. For single crystal structure analysis, suitable crystals of $[(C_8H_{14}N_2)_2Hg][CuCl_3]$ were selected, covered by inert-oil (perfluoropolyalkylether, ABCR), and placed on a plastic loop. Data collection was performed at 213 K on an IPDS II image-plate diffractometer (Stoe, Darmstadt) using Mo-K_α radiation (λ = 0.71073 Å, graphite monochromator). Suitable crystals of $(C_6H_{10}N_2)AuCl$ and $(C_6H_{10}N_2)AgI$ were selected and the data collection was performed at 180 K on an Stoe StadiVari Diffractometer with Euler geometry (Stoe, Darmstadt) using Mo-K_α radiation (λ = 0.71073 Å, graphite monochromator). Data collection for the compounds $(C_8H_{14}N_2)CuCl$, $[(C_8H_{14}N_2)_2Hg][AgCl_3]$, and $[EMIm][Ag_2I_2Cl]$ were performed at 180 K on an Stoe StadiVari diffractometer with Euler geometry (Stoe, Darmstadt) using Ga-Kα radiation (λ = 1.34013 Å, graded multilayer mirror as the monochromator). Data reduction and multi-scan absorption correction were conducted by the X-AREA software package (version 1.75).[S1] Space group determination based on systematic absence of reflections was performed by XPREP. Using Olex2,[S2] the structure was solved with the ShelXS[S3] structure solution program using Direct Methods and refined with the ShelXL[S4] refinement package using least-squares minimization. All non-hydrogen atoms were refined anisotropically. Detailed information on crystal data and structure refinement are listed in Table 1. DIAMOND was used for all illustrations.[S5] Further details of the crystal structure investigation may be obtained from the joint CCDC/FIZ Karlsruhe deposition service on quoting the depository number CSD-No. 2104796-2104800.

Fourier-transform infrared (FT-IR) spectroscopy. Spectra of the title compounds were recorded on a Bruker Vertex 70 FT-IR spectrometer. The samples were measured as pellets in KBr. Thus, 300 mg of dried KBr and 1 mg of the sample were carefully pestled together and pressed to a thin pellet.

Thermogravimetry (TG) was carried out on a Netzsch STA 449 F3 Jupiter device applying α-Al_2O_3 as crucible material and reference. Buoyancy effects were corrected by baseline subtraction of a blank measurement. The samples were measured under dried nitrogen up to 1000 °C with a heating rate of 5 K/min. The Netzsch software PROTEUS Thermal Analysis (Version 5.2.1) was used for graphical evaluation.

Excitation and emission spectra were recorded using a photoluminescence spectrometer Horiba Jobin Yvon Spex Fluorolog 3, equipped with a 450 W Xenon lamp, double

monochromator for excitation and emission, an integrating sphere (Ulbricht sphere) and a photomultiplier as the detector. The determination of the quantum yield was performed according to *Friend et al.*.[S6] First of all, the diffuse reflection of the sample was determined under excitation conditions. Thereafter, the emission was measured at this excitation wavelength. Integration over the reflected and emitted photons by use of the Ulbricht sphere results in the absolute quantum yield. Corrections were made regarding the spectral power of the excitation source, the reflection behavior of the Ulbricht sphere and the sensitivity of the detector.

2. Structural Details and Unit Cells

Details of the single-crystal structure analysis are summarized in Tables S1 and S2. The unit cells of the title compounds are displayed in Figures S1-S6.

Table S1. Crystallographic data and refinement details of the title compounds **1-3**.

Data	**$(C_8H_{14}N_2)CuCl$**	**$(C_8H_{14}N_2)AgI$**	**$(C_6H_{10}N_2)AuCl$**
Empirical formula	$C_8ClCuH_{14}N_2$	$AgC_8H_{14}IN_2$	$AuC_6ClH_{10}N_2$
Formula weight	237.20 g mol^{-1}	372.98 g mol^{-1}	342.58 g mol^{-1}
Crystal system	orthorhombic	monoclinic	triclinic
Space group	$P2_12_12_1$	Cc	$P\bar{1}$
Lattice parameters	a = 818.01(5) pm b = 1084.2(1) pm c = 1168.5(1) pm°	a = 1547.4(1) pm b = 658.5(1) pm c = 1237.4(1) pm β = 106.70(1)	a = 884.28(8) b = 930.20(8) c = 1068.4(1) α = 89.57(1) β = 87.39(1) γ = 82.12(7)
Cell volume	V = 1036.3(1)×10^6 pm^3	V = 1207.6(1)×10^6 pm^3	V = 869.60(13) × 10^{6}pm^3
Formula units per cell	Z = 4	Z = 4	Z = 4
Calculated density	ρ = 1.520 g cm^{-3}	ρ = 2.051 g cm^{-3}	ρ = 2.617 g cm^{-3}
Measurement limits	–8 ≤ h ≤ 10, –13 ≤ k ≤ 11, –13 ≤ l ≤ 14	–19 ≤ h ≤ 19, –8 ≤ k ≤ 8, –15 ≤ l ≤ 15	-11≤ h ≤ 11, –13 ≤ k ≤ 13, –15 ≤ l ≤ 14
2 Theta range for data collection	9.68 to 114.91°	10.39 to 118.49°	3.816 to 49.99°
Wavelength	λ(Ga-Kα) = 1.34013 Å	λ(Ga-Kα) = 1.34013 Å	λ(Mo-Kα) = 0.71073 Å
Linear absorption coefficient	μ = 12.658 mm^{-1}	μ = 22.204 mm^{-1}	μ = 17.154 mm^{-1}
Number of reflections	9949 (2132 independent)	5771 (1693 independent)	6605 (3046 independent)
Refinement methode	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Merging	R_{int} = 0.0747	R_{int} = 0.0418	R_{int} = 0.0305
Number of parameters	112	112	185
Residual electron density	0.48 to -0.43 e$^-$ 10^{-6} pm^{-3}	2.42 to -2.70 e$^-$ 10^{-6} pm^{-3}	-4.30 to 3.49 e$^-$ 10^{-6} pm^{-3}
Figures of merit	R1 ($I \geq 2\sigma_I$) = 0.0454 R1 (all data) = 0.0610 wR2 (all data) = 0.1072	R1 ($I \geq 2\sigma_I$) = 0.0750 R1 (all data) = 0.0751 wR2 (all data) = 0.1985	R1 ($I \geq 2\sigma_I$) = 0.0494 R1 (all data) = 0.0521 wR2 (all data) = 0.1407

	GooF = 0.961	GooF = 1.064	GooF = 1.089

Table S2. Crystallographic data and refinement details of the title compounds **4-6**.

Data	**$[C_8H_{14}N_2]_2[HgCuCl_3]$**	**$[C_8H_{14}N_2]_2[HgAgCl_3]$**	**[EMIm][Ag_2I_2Cl]**
Empirical formula	$C_{16}Cl_3CuH_{24}HgN_4$	$AgC_{16}Cl_3CuH_{28}HgN_4$	$AgC_6ClH_{10}I_2N_2$
Formula weight	646.90 g mol^{-1}	691.23 g mol^{-1}	616.16 g mol^{-1}
Crystal system	monoclinic	monoclinic	triclinic
Space group	*C2/c*	*C2/c*	$P\bar{1}$
Lattice parameters	*a* = 1458.4(3) pm *b* = 888.98(16) pm *c* = 1732.2(3) β = 103.4(1)°	*a* = 1420.3(1) pm *b* = 903.99(3) pm *c* = 1731.8(1) pm β = 101.1(1)	*a* = 690.28(5) *b* = 895.65(6) *c* = 1059.2(1) *α* = 85.62(1) *β* = 85.23(1) *γ* = 85.92(1)
Cell volume	V = 2184.7(7)×10^6 pm^3	V = 2182.1(1)×10^6 pm^3	V = 649.27(7) × 10^{6}pm^3
Formula units per cell	Z = 4	Z = 4	Z = 2
Calculated density	ρ = 1.967 g cm^{-3}	ρ = 2.104 g cm^{-3}	ρ = 3.152 g cm^{-3}
Measurement limits	–16 ≤ h ≤ 16, –10 ≤ k ≤ 10, –20 ≤ l ≤ 20	–10 ≤ h ≤ 17, –11 ≤ k ≤ 11, –19 ≤ l ≤ 21	-8≤ h ≤ 9, –11 ≤ k ≤ 11, –14 ≤ l ≤ 7
2 Theta range for data collection	4.83 to 48.99°	10.15 to 114.94°	3.816 to 62.764°
Wavelength	λ(Mo-Kα) = 0.71073 Å	λ(Ga-Kα) = 1.34013 Å	λ(Ga-Kα) = 1.34143 Å
Linear absorption coefficient	μ = 8.366 mm^{-1}	μ = 16.206 mm^{-1}	μ = 42.308 mm^{-1}
Number of reflections	12650 (1816 independent)	9679 (2261 independent)	7804 (3031 independent)
Refinement methode	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Merging	R_{int} = 0.0514	R_{int} = 0.0227	R_{int} = 0.0225
Number of parameters	117	117	120
Residual electron density	0.61 to -0.81 e$^-$ 10^{-6} pm^{-3}	1.23 to -1.88 e$^-$ 10^{-6} pm^{-3}	-3.106 to 1.081 e$^-$ 10^{-6} pm^{-3}
Figures of merit	R1 ($I \geq 2\sigma_I$) = 0.0252 R1 (all data) = 0.0355 wR2 (all data) = 0.0492 GooF = 0.832	R1 ($I \geq 2\sigma_I$) = 0.0239 R1 (all data) = 0.0257 wR2 (all data) = 0.0618 GooF = 1.057	R1 ($I \geq 2\sigma_I$) = 0.0462 R1 (all data) = 0.0362 wR2 (all data) = 0.1109 GooF = 1.131

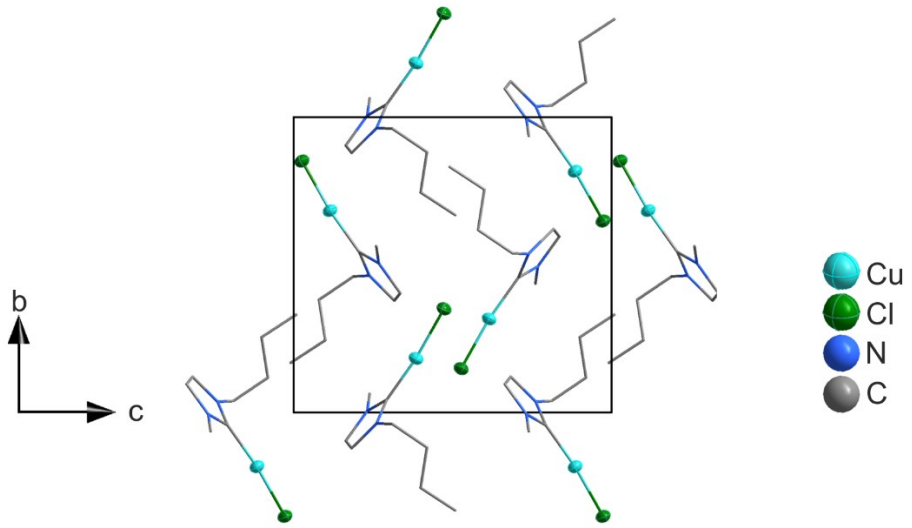

Figure S1. Unit cell of $(C_8H_{14}N_2)CuCl$ (**1**).

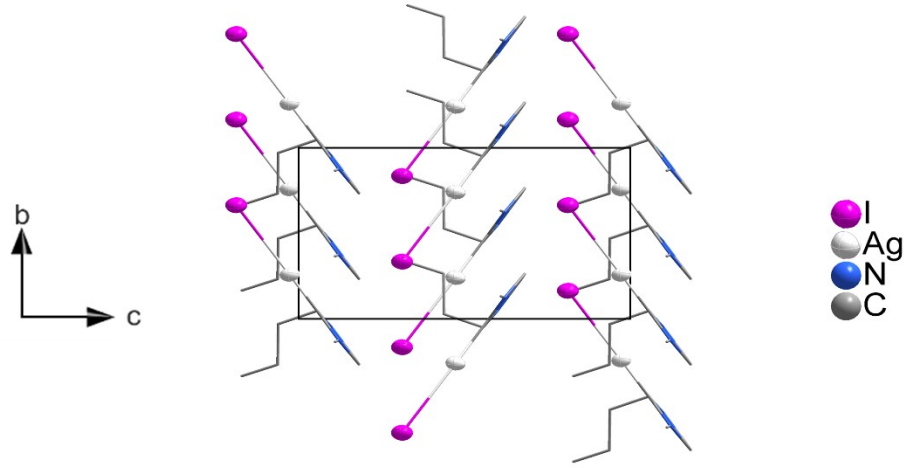

Figure S2. Unit cell of $(C_8H_{14}N_2)AgI$ (**2**).

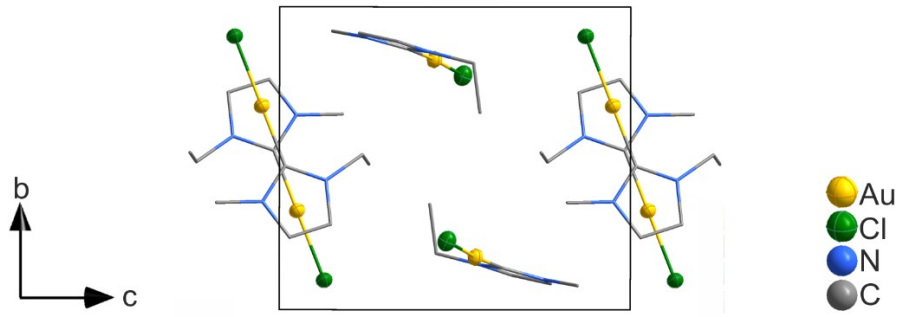

Figure S3. Unit cell of $(C_6H_{10}N_2)AuCl$ (**3**).

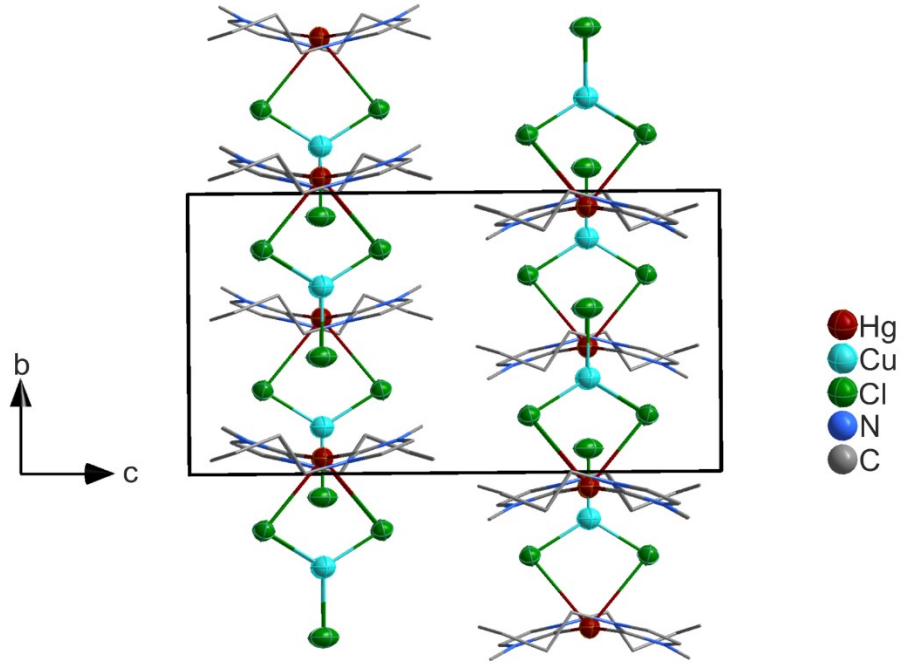

Figure S4. Unit cell of $[(C_8H_{14}N_2)_2Hg][CuCl_3]$ (**4**).

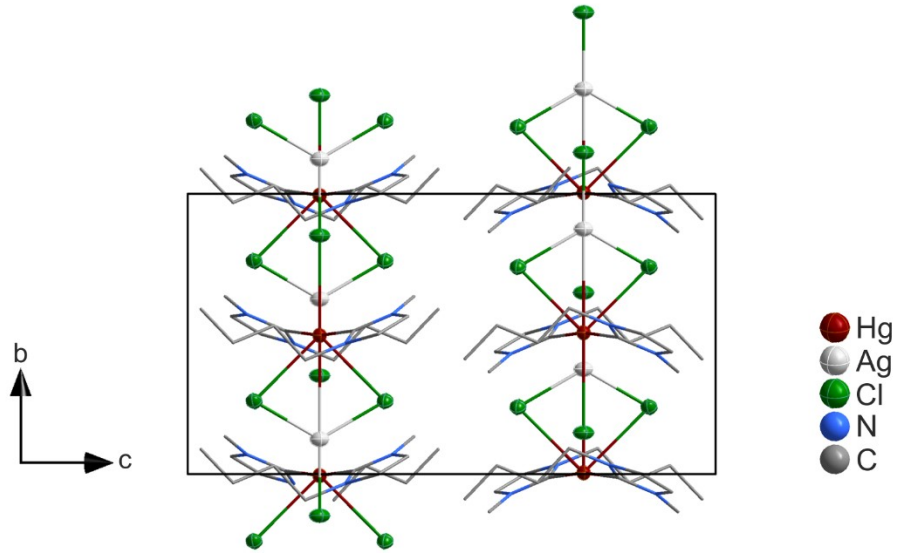

Figure S5. Unit cell of $[(C_8H_{14}N_2)_2Hg][AgCl_3]$ (**5**).

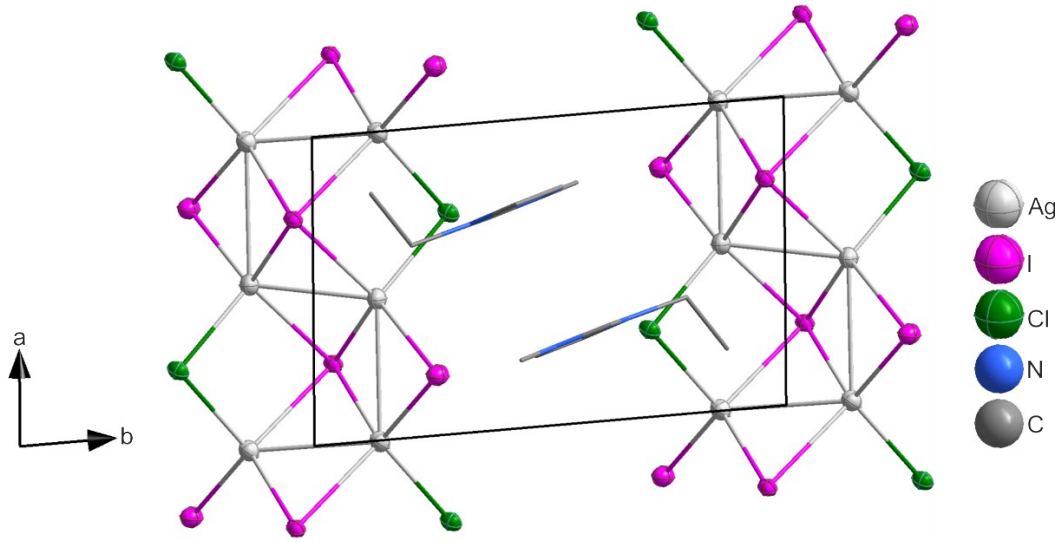

Figure S6. Unit cell of $[EMIm][Ag_2I_2Cl]$ (**6**).

3. IR spectroscopy

FT-IR spectra of the NHC compounds **1**, **3**-**5** are dominated by the imidazolium cations with characteristic vibrations of ν(C–H): 3300-2800 cm^{-1}, ν(C=N): 1650-1600 cm^{-1}, as well as the fingerprint area at 1500-500 cm^{-1}) (Figure S7).[S7] Moreover, the Hg–C stretching vibration at 720-680 cm^{-1} is observed in the spectra of **4** and **5**.[S8] Similarly, the characteristic vibrations of the $[EMIm]^+$ cation are observed for **6** (Figure S8). The absence of O–H-related vibrations at 3600-3000 cm^{-1} confirms the absence of moisture.

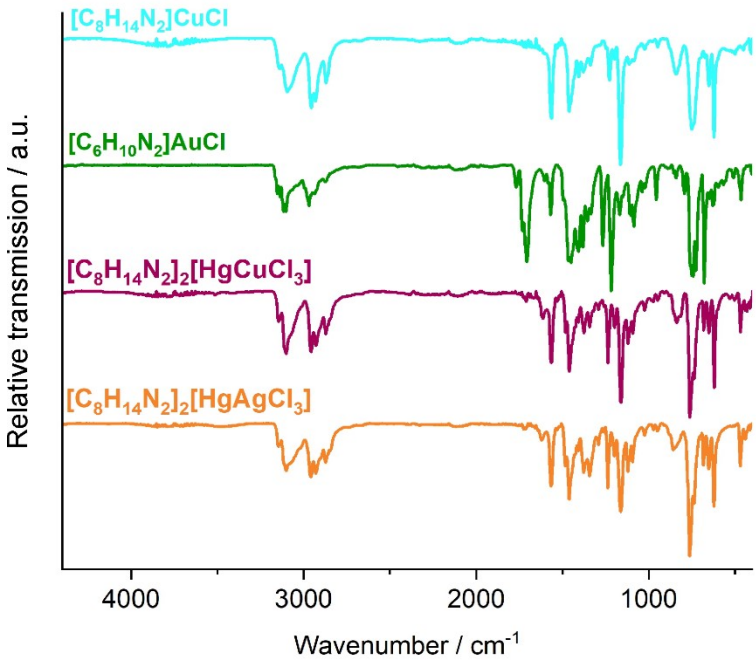

Figure S7. FT-IR spectra of $(C_8H_{14}N_2)CuCl$ (**1**), $(C_6H_{10}N_2)AuCl]$ (**3**), $[(C_8H_{14}N_2)_2Hg][CuCl_3]$ (**4**), and $[(C_8H_{14}N_2)_2Hg][AgCl_3]$ (**5**).

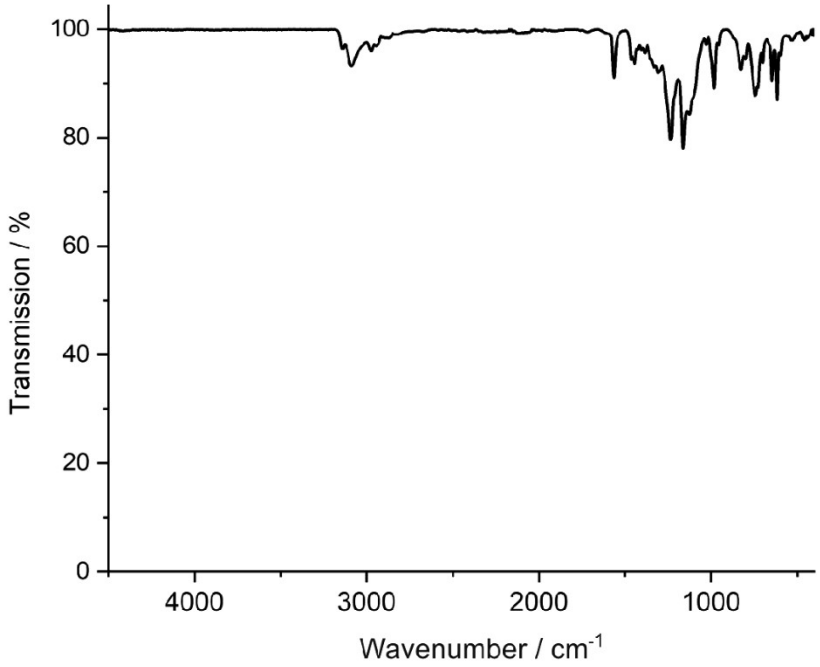

Figure S8. FT-IR spectrum of $[C_6H_{11}N_2][Ag_2I_2Cl]$ (**6**).

References

S1 X-RED32: *Data Reduction Program (Version 1.01)*, Stoe, Darmstadt 2001.

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S5 DIAMOND: *Crystal and Molecular Structure Visualization*, Crystal Impact GbR, Bonn 2016.

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S7 (a) Y. Jeon, J. Sung, C. Seo, H. Lim, H. Cheong, M. Kang, B. Moon, Y. Ouchi and D. Kim, *J. Phys. Chem. B.*, 2008, **112**, 4735-4740. (b) T. Liu, Y. Danten, J. Grondin and R. Vilar, *J. Raman Spectrosc.*, 2016, **47**, 449-456.

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