

Electronic Supplementary Information (ESI)

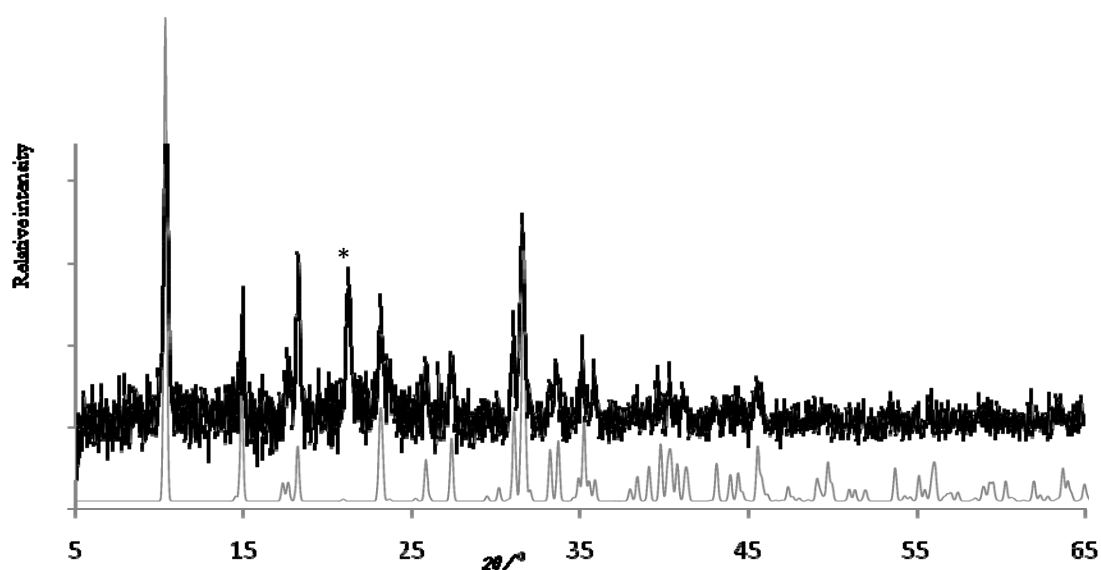


Fig. S1 Powder diffraction pattern of $\text{Bi}_5[\text{GaCl}_4]_3$ crystals synthesized from dichloromethane. Observed pattern in black and calculated peak pattern in gray. * marks the unassigned peak in the diffractogram. This peak cannot be associated with any known reactant and is viewed as a sign of impurity in the sample.

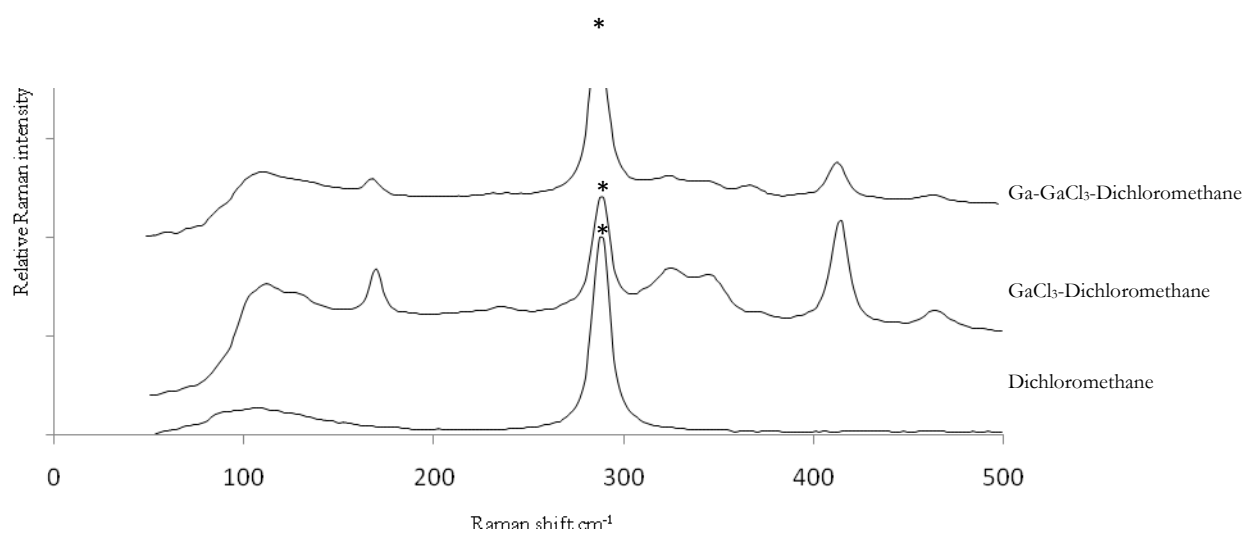


Fig. S2 Raman spectra below 500 cm^{-1} of the liquid GaCl_3 -dichloromethane and Ga-GaCl_3 -dichloromethane systems at room-temperature. Pure dichloromethane is shown for reference and the strong solvent band at 285 cm^{-1} is marked *.

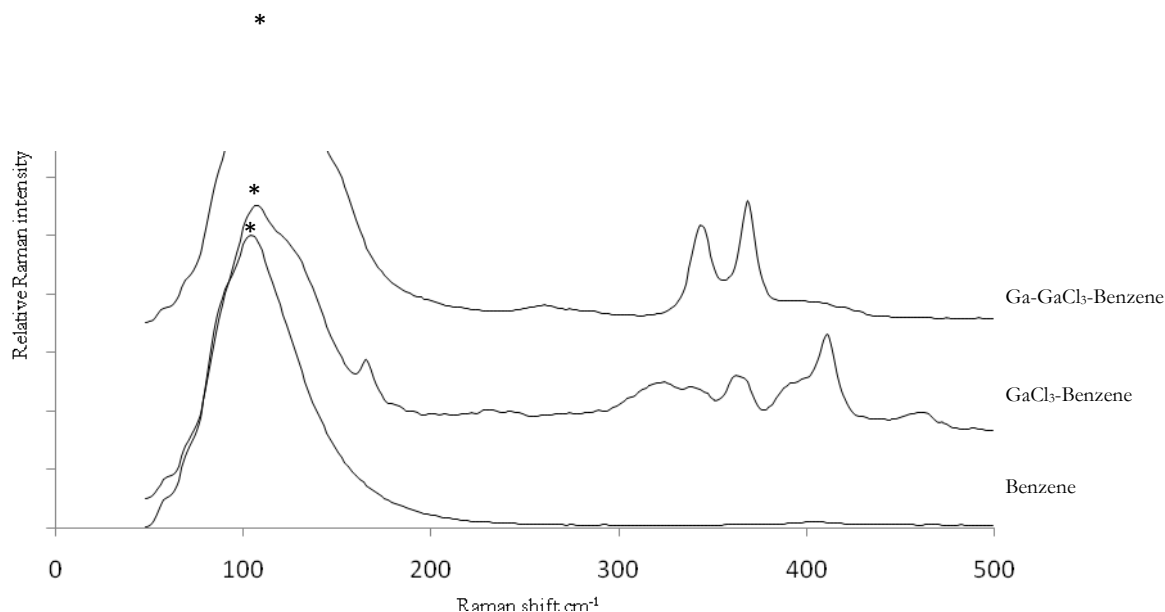


Fig. S4 Raman spectra below 500 cm^{-1} of the liquid GaCl_3 -benzene and Ga-GaCl_3 -benzene systems at room-temperature. Pure Bz is shown for reference and the strong solvent band at 112 cm^{-1} is marked *.

Table S1 Raman bands (cm^{-1}) of the dichloromethane and benzene system compared with literature data.^[9]

GaCl_3 - C_6H_6 Ref. 9a	Assignment	Ga-GaCl_3 - C_6H_6^* Ref. 9b	Assignment	Ga-GaCl_3 - C_6H_6 This work	Assignment	Ga-GaCl_3 - CH_2Cl_2 This work	Assignment
463	Ga_2Cl_6					461	Ga_2Cl_6
413	Ga_2Cl_6	418	Ga_2Cl_7^-			413	Ga_2Cl_6
393	GaCl_3	394	Ga_2Cl_7^-				
367	GaCl_3	370	Ga_2Cl_7^- and $\text{Ga}_3\text{Cl}_{10}^-$	368	Ga_2Cl_7^- and $\text{Ga}_3\text{Cl}_{10}^-$	370	GaCl_3 or Ga_2Cl_7^- and $\text{Ga}_3\text{Cl}_{10}^-$
344	Ga_2Cl_6	346	GaCl_4^-	343	GaCl_4^-	343	Ga_2Cl_6 or GaCl_4^-
Obscured	Ga_2Cl_6						
325	Ga-C	260	Ga_2Cl_7^- and/or $\text{Ga}_3\text{Cl}_{10}^-$			322	Ga-C
168	Ga_2Cl_6					168	Ga_2Cl_6
140	GaCl_3	150	GaCl_4^-				
109	Ga_2Cl_6					110	Ga_2Cl_3

*Saturated with gallium metal

Table S2 Calculated breathing mode Raman frequencies for the Bi_5^{3+} cluster together with CM, DCM, TCM and Bz benzene. For reference the experimental Raman frequency of the naked Bi_5^{3+} cluster in benzene solution is listed.^[5a]

Model system	Raman bands (cm^{-1})
Bi_5^{3+} -CM	141/154
Bi_5^{3+} -DCM	140/153
Bi_5^{3+} -TCM	154
Bi_5^{3+} -Bz	142/167
Bi_5^{3+}	139

Table S3 List of solvents used reactions; polarity and solubility of gallium(III) chloride.

Solvent	Dielectric constant (20 °C unless otherwise indicated)	Solubility	Observation
Hexane, C ₆ H ₁₄	1.890	< 50 mol %	Light yellow colored solution
n-Heptane, C ₇ H ₁₆	1.92	< 50 mol%	Light yellow colored solutions
Benzene, C ₆ H ₆	2.284	>50 mol%	Amber colored solution
Toluene, C ₇ H ₈	2.379 (25 °C)	>50 mol%	Amber colored solution
Chloroform, CHCl ₃	4.806	>50 mol%	Red/yellow solution
Tetrahydrofuran (THF), C ₄ H ₈ O	7.5 8 (25 °C)	>50 mol%	Amber colored solution, grayish solid within minutes
Dichloromethane (DCM) CH ₂ Cl ₂ ,	9.08	>50 mol%	Amber colored solution
Acetone, C ₃ H ₆ O	20.7 (25 °C)	>50 mol%	Heat release upon mixing, yellow/grayish solution
Acetonitrile, C ₂ H ₃ N	37.5	>50 mol%	Heat release upon mixing, yellow/grayish solution gel like solid within minutes
Dimethylsulfoxide, (DMSO), C ₂ H ₆ OS	46.7	>50 mol%	Heat release upon mixing, yellowish solution, gel like solid within minutes

*The polarity information (dielectric constants) found in CRC Handbook of Chemistry and Physics, 63rd edition, 1982-1983, CRC Press and in solvent supplier information.