Supporting Information for

Mixed Solvothermal Synthesis of T*n* Cluster-Based Indium and Gallium Sulfides Using Versatile Ammonia or Amine Structure-Directing Agents

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1. Tables

Table S1. Bond valence sum (BVS) values for the In and S atoms in **1**. The BVS calculations were performed on the KDist software (Version 3.75) distributed by K. Knížek.

Atom	**BVS value**	**Atom**	**BVS value**
In1	3.23	S4	-0.79
In2	3.22	S5	-1.66
In3	3.20	S6	-1.62
In4	3.25	S7	-1.62
S1	-0.76	S8	-1.61
S2	-0.77	S9	-1.65
S3	-0.77	S10	-1.66

Table S2. Summary of alkaline metal/ammonia/ammine templated Ga-Q compounds.

Compounds	**SG**	**D**	**Reactants**	**Solvent**	**Yield**	**Ref.**
$K_8Ga_4S_{10}$	***Pnma***	0D	Ga_2S_3; 160 °C, 6 d	K_2S	NA	[1]
$[C_{10}N_4H_{26}]_{0.5}[GaS_2]$	$P2_1/n$	1D	Ga_2S_3 + S; 160 °C, 6 d	BAPP	NA	[2]
$[C_6H_8N]_2[Ga_{10}S_{16}(NC_6H_7)_2(N_2C_{12}H_{12})]$	*Pcca*	1D	Ga + S +DPE; 170 °C, 5 d	4-methylpyridine	NA	[3]
$[C_2H_8N]_2[Ga_{10}S_{16}(N_2C_{12}H_{12})(NC_2H_7)_2]$	$P3_221$	1D	Ga + S +DPE + TPP; 200 °C, 20 d	Py	NA	[4]
$[Mn(atep)]Ga_2S_4$	$P2_1/n$	1D	Ga_2S_3 + MnS + S; 180 °C, 21 d	tepa	15%	[5]
$[Mn(en)_3]_{0.5}[GaS_2]$	*Cmcm*	1D	Ga_2S_3 + $MnCl_2$ $4H_2O$ + S; 170 °C, 12 d	en	80%	[6]
$[Co(en)_3]_{0.5}[GaS_2]$	*Cmcm*	1D	Ga_2S_3 + $CoCl_2$ $6H_2O$ + S; 160 °C, 20 d	en	NA	
$[Ni(en)_3]_{0.5}[GaS_2]$	*Cmcm*	1D	Ga_2S_3 + NiS + S; 180 °C, 6 d	en	NA	
$[enH_2][Ga_4S_7(en)_2]$	$P2_1/c$	2D	Ga_2S_3 + S; 170 °C, 5 d	en	80%	
$CsGaS_2$	*C2/c*	2D	Ga2S3 + Se + CsN_3; 500℃/700℃	NA	NA	[7]
$NaGaS_2$	*C2/c*	2D	Ga + S +Na_2S; 650 °C, 5h	NA	NA	[8]
$[C_7H_{10}N]_2[Ga_{10}S_{16}(NC_7H_9)(N_2C_{12}H_{10})_{3/2}]$	$P\bar{1}$	2D	Ga + S +DPE; 200 °C, 20 d	3,5-methylpyridine	NA	[3]
$[C_5H_6N]_3[Ga_{10}S_{16}(OH)(N_2C_{13}H_{14})]$	*Pbcm*	2D	Ga + S +TMP + TPP; 200 °C, 20 d	Py	NA	[4]
UCR-18GaS-AEP	*C2/c*	3D	Ga + S; 190 °C, 6 d	AEP	86%	[9]
UCR-7GaS-TETA	$I4_1/acd$	3D	NA	NA	NA	
UCR-7GaS-TAEA	$I4_1/acd$	3D	NA	NA	NA	
UCR-7GaS-DBA	$P4_12_12$	3D	NA	NA	NA	
$[C_4NH_{12}]_6[Ga_{10}S_{18}]$	$P4_32_12$	3D	Ga + S; 170 °C, 8 d	DEA	NA	[10]
$[C_4NH_{12}]_{12}[Ga_{20}S_{35.5}(S_3)_{0.5}O]$	*C2/c*	3D	Ga + S; 190 °C, 10 d	DEA	NA	
$[Dy_2(en)_6(\mu_2\text{-}OH)_2]Ga_4S_8$	$P\bar{1}$	1D	Ga_2S_3 + $DyCl_3$+ S; 170 °C, 10 d	en	NA	[11]
$[Mn(dap)_3]_{0.5}[GaSe_2]$	*Cmcm*	1D	Ga + Mn + Se; 180 °C, 16 d	dap + H_2O	13%	[5]
$(C_4H_{11}N_2)GaSe_2$	$P2_1/c$	1D	Ga + Se; 200 °C, 8 d	piperazine + H_2O	92%	[12]
$[1,3\text{-}pdaH_2][Ga_2Se_2(Se_2)Se_3]$	$P2_1$	1D	Ga + Se; 160 °C, 6 d	1,3-pda + CH_3OH	22.4%	[13]
$[1,4\text{-}bdaH_2][Ga_2Se_3(Se_2)]$	*C2/c*	1D	Ga + Se; 160 °C, 6 d	1,4-bda + CH_3OH	9.9%	
$[Me_2NH_2]_2[Ga_2Se_2(Se_2)_2]$	$P2_1/c$	1D	Ga_2O_3 + Se; 150 °C, 5 d	DMF + $N_2H_4{\cdot}H_2O$	18.4%	
α-$[AEPH]_2[Ga_2Se_2(Se_2)_2]$	*Pn*	1D	Ga_2O_3 + Se; 120 °C, 5 d	AEP	NA	
β-$[AEPH]_2[Ga_2Se_2(Se_2)_2]$	$P2_1/c$	1D	Ga_2O_3 + Se; 170 °C, 5 d	AEP	11.9%	
$[C_6H_{16}N_2][Ga_2Se_3(Se_2)]$	*C2/c*	1D	Ga + Se; 170 °C, 10 d	trans-1,4-diaminocyclohe-xane + H_2O	NA	[14]
$[bappH_2][Ga_2Se_4]$	$P\bar{1}$	1D	Ga + Se + bapp; 170 °C, 6 d	H_2O	46%	[15]

[Mn(en)$_3$][Ga_2Se_5]	*Pbcn*	1D	Ga + Se + Mn($CH_3COO)_2$ 4H_2O + en; 170 °C, 6 d	H_2O	53%	
[H_2dap]$_2$$Ga_4Se_8$	*C2/c*	2D	Ga + Se; 170 °C, 5 d	dap + H_2O	43%	[5]
(Ph_4P)[Ga($Se_6)_2$]	$P\bar{4}$	2D	Ga + ($Ph_4P)_2Se_5$ + Se; 200 °C, 2 d	NA	60%	[15]
$RbGaSe_2$	*C2/c*	2D	GaSe + Se + RbN_3; 850℃	NA	NA	[16]
Ga_4Se_7(en)$_2$·(enH)$_2$	$P2_1/c$	2D	Ga + Se; 140 °C, 5-7 d	en	90%	[17]
($C_{13}H_{26}N_2H_2)_3$($Ga_{10}Se_{18}$)	$I\bar{4}2d$	3D	Ga_2O_3 + Se; 200 °C, 28 d	TMDP + H_2O	77%	[9]
($C_{11}H_{22}N_2H_2)_3$($Ga_{10}Se_{18}$)	$I\bar{4}m2$	3D	Ga_2O_3 + Se; 200 °C, 19 d	DPM + H_2O	84%	

Abbreviations: en = ethylenediamine; BAPP = 1,4-bis(3-aminopropyl)piperazine; DPE =1,2-di(4-pyridyl)ethylene; TPP = tetraphenylphosphonium bromide; Py = pyridine; TMP = 4,4'-Trimethylenedipyridine; TAEA = Tris(2-aminoethyl)amine; TETA = triethylenetetramine; DBA = di-n-butylamine; AEP = 1-(2-aminethyl)piperazine; DEA = diethylamine; dap = diaminopropane; 1,3-pda = 1,3-diaminopropane; 1,4-pda = 1,4-diaminopropane; TMDP = 4,4-trimethylenedipiperidine; DPM = dipiperidinomethane.

Table S3. Summary of ammonia/ammine templated In-S compounds.

Compounds	**SG**	**D**	**Reactants**	**Solvent**	**Yield**	**Ref.**
($Ph_4P)_4In_2S_{27}$	$P\bar{1}$	0D	$InCl_3$ + K_2S_5; 110 °C, 10 d	Ph_4PCl + CH_3OH	58%	[18]
($Ph_4P)_2$[$In_2S_{14}]_{0.5}$[$In_2S_{16}]_{0.5}$	$P\bar{1}$	0D	$InCl_3$ + K_2S_5; RT, 2d	Ph_4PCl + DMF	48%	
[In(en)$_2$S]$_2$·2Cl	$P2_1/n$	0D	In + S; 190 °C, 5 d	en + CH_2Cl_2	40%	[19]
[Mg(en)$_3$][In_2S_4]	*Cmcm*	1D	In + S + Mg; 190 °C, 10 d	en	80%	
[$C_{10}N_4H_{26}]_{0.5}$[InS_2]	$P2_1/n$	1D	In + S; 145 °C, 5 d	BAPP	NA	[2]
[Ni(dien)$_2]_{0.5}$[InS_2]	*C2/c*	1D	In_2S_3 + Ni + S; 157 °C, 6 d	dien + H_2O	31%	[20]
[Ni(dap)$_3]_{0.5}$[InS_2]	*Cmcm*	1D	In_2S_3 + Ni + S; 157 °C, 6 d	dap + H_2O	47%	
[Ni(tepa)]$_2$[In_4S_7(SH)$_2$]·H_2O	$P2_1/c$	1D	In_2S_3 + Ni + S 157 °C, 6 d	tepa + H_2O	25%	
{[Ni(dach)$_3$][In_2S_4]3H_2O}$_n$	*C2/c*	1D	In + Ni + L-cysteine + (BMIm)Br; 160, °C, 9 d	dach + H_2O	35%	[21]
[Fe(phen)$_3]_4$[$H_4In_{20}S_{38}$]Hphen 3·HDMA·8H_2O	P_1	1D	In +Fe + Na_2S +phen; 140, °C, 18 d	DMF + H_2O	30%	[22]
[Ni(phen)$_3]_4$[$H_4In_{20}S_{38}$] ·2Hphen·2HDMA·3H_2O	*C2/c*	1D	In +Ni + Na_2S +phen; 140, °C, 32 d	DMF + H_2O	21%	
[Ni(phen)$_3]_4$[$In_{20}S_{37}$]·6Hphen·4H_2O	*C2/c*	2D	In +Ni + Na_2S +phen; 140, °C, 24 d	DMF + H_2O	32%	
[Fe(phen)$_3]_4$[$In_{20}S_{37}$]·6Hphen·4H_2O	*C2/c*	2D	In +Fe + Na_2S +phen; 140, °C, 24 d	DMF + H_2O	41%	
[$In_8S_{13}(S_3)_{1/2}$(SH)][$In_4S_6(S_3)_{1/2}$(SH)] ($TMDPH_2)_5$ (HCF-1)	$P3_1c$	2D	In + S; 150 °C, 5 d	TETA + TMDP + H_2O	65%	[23]
[($C_3H_7)_2NH_2]_3In_6S_{11}H$	$P2_1/c$	2D	In + S; 180 °C, 5 d	DPA	NA	[24]
[$CH_3CH_2NH_3]_6In_6S_{12}$	$P2_1/n$	2D	$InCl_3$ + TTCA; 160 °C, 4 d	EA + EtOH	46.1%	[25]
[$CH_3CH_2NH_3]_6In_8S_{15}$	$P2_1/n$	2D	In + S; 140 °C, 4 d	EA + EtOH	54%	[26]
[($CH_3CH_2)_2NH_2]_6In_{10}S_{18}$	$I4_1/amd$	2D	In + S; 180 °C, 7 d	DEA + H_2O	NA	[27]
[$C_6H_{16}N]_4In_4S_{10}H_4$	*C2/c*	0D	In + S; 180 °C, 5 d	DPA	NA	
[$C_{13}H_{14}N_2]_4In_9S_{17}$	$P2_1/c$	2D	In + S; 180 °C, 5 d	TMDP	NA	
[($CH_3CH_2)_2NH_2]_6In_{10}S_{18}$	$P4_32_12$	3D	In + S; 180 °C, 7 d	DEA	NA	
UCR-7InS-AEP ([$In_{10}S_{18}]^{6-}$)	$P4_1/acd$	3D	NA	NA	NA	[9]
[($CH_3)_2NH_2]_6In_{10}S_{18}$	*Pbca*	3D	In + S; 180 °C, 7 d	DMA	NA	[28]
$In_{10}S_{18}$(HPP)$_6$($H_2O)_{15}$	$I\bar{4}3m$	3D	In + S; 135 °C	HPP	10%	[29]
$In_{10}S_{18}$(DPM)$_3$($H_2O)_7$	$I\bar{4}m2$	3D	In + S; 135 °C	DPM	50%	
$In_{10}S_{18}$($C_6H_{12}NH_2)_6$(C_6H_{12}NH)($H_2O)_5$	$I\bar{4}2d$	3D	In + S; 150 °C, 4 d	C_6H_{12}NH + H_2O	43%	[30]
[$In_{33}S_{56}$]($C_{13}H_{26}N_2H_2)_{6.5}$	*R*32	3D	NA	NA	NA	[31]
($In_{34}S_{54}$)($In_{10}S_{18}$)($C_{11}H_{24}N_2)_6$	$I4_1/a$	3D	In + S + $CdCl_2$·2.5H_2O; 190 °C, 6 d	DPM	50%	[32]
[$In_{10}S_{18}$]($H_2O)_4$($C_6H_{18}N_4H_2)_{1.5}$ ($C_6H_{18}N_4H_3$)	$P4_12_12$	3D	In + S; 170 °C, 5 d	TETA + Py + H_2O	91%	[33]
(H_2DAH)$_3In_{10}S_{18}$·6H_2O	$I\bar{4}m2$	3D	In + S; 170 °C, 4 d	DAH + H_2O	41%	[34]

$(H_2DAH)_3In_{10}S_{18}$	*I*$\bar{4}$2*d*	3D	In + S; 170 °C, 8 d	DAH + H_2O	58%	
SCIF-1 ($[In_{10}S_{16}(IM)_2]^{4-}$)	*Pbca*	3D	$In(NO_3)_3$ • xH_2O + Li_2S + imidazole + 2-amino-1-butanol + DBU; 150 °C, 12 d	NA	NA	[35]
SCIF-2 ($[In_{10}S_{16}(2\text{-MIM})_2]^{4-}$)	*C*2/*c*	3D	$In(NO_3)_3$ • xH_2O + Li_2S + 2-methylimidazole + 2-amino-1-butanol + DBU; 150 °C, 12 d	NA	NA	
SCIF-3 ($[In_{10}S_{16}(2\text{-EIM})_2]^{4-}$)	*I*$\bar{4}$2*d*	3D	$In(NO_3)_3$ • xH_2O + Li_2S + 2-ethylimidazole + 2-amino-1-butanol + DBU; 150 °C, 12 d	NA	NA	
SCIF-4 ($[In_{10}S_{16}(4\text{-MIM})_2]^{4-}$)	*Pbca*	3D	$In(NO_3)_3$ • xH_2O + Li_2S + 4-methylimidazole + 2-amino-1-butanol + DBU; 150 °C, 12 d	NA	NA	
SCIF-5 ($[In_{10}S_{16}(BIM)_2]^{4-}$)	$P2_12_12_1$	3D	$In(NO_3)_3$ • xH_2O + Li_2S + Benzimidazole+ 2-amino-1-butanol + DBU; 150 °C, 12 d	NA	NA	
SCIF-6 ($[In_{10}S_{16}(MBIM)_2]^{4-}$)	*Pbca*	3D	$In(NO_3)_3$ • xH_2O + Li_2S + 5-methylbenzimidazole + 2-amino-1-butanol + DBU; 150 °C, 12 d	NA	NA	
SCIF-7 ($[In_{10}S_{16}(DMBIM)_2]^{4-}$)	*Pbca*	3D	$In(NO_3)_3$ • xH_2O + Li_2S + 5,6-dimethylbenzimidazole + 2-amino-1-butanol + DBU; 150 °C, 12 d	NA	NA	
OCF-31 ($[In_8S_{15}]^{6-}$)	$P2_12_12_1$	3D	In + S +BIM + hexamethyleneimine	H_2O	NA	

Abbreviations: en = ethylenediamine; dien = diethylenetriamine; dap = diaminopropane; tepa = tetraethylenepentamine; Ph_4PCl = tetraphenylphosphonium chloride; CH_3OH = methanol; EtOH = ethanol; DMF = Dimethylformamide; phen = 1,10-phenanthroline; dach = 1,2-diaminocyclohexane; TETA = triethylenetetramine; TMAP = 4,4′-trimethylenedipiperidine; DEA = diethylamine; TTCA = trithiocyanuric acid; EA = ethylamine; TMDP = 4,4-trimethylenedipiperidine; DPA = dipropylamine; DMA = dimethylamine; BPP = 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine; DPM = dipiperidinomethane; $C_6H_{12}NH$ = hexamethyleneimine; TMDP = 4,4-trimethylenedipiperidine; BAPP = 1,4-bis(3-aminopropyl)piperazine; Py = pyridine; DBU = 1,8-diazabicyclo[5.4.0]-7-undecene; BIM = benzimidazole.

Table S4. Summary of ammonia/ammine templated In-Se compounds.

Compounds	**SG**	**D**	**Reactants**	**Solvent**	**Yield**	**Ref.**
$[Ph_4P]_4In_2Se_{21}$	*P*$\bar{1}$	0D	$InCl_3$ + Na_2Se_5; RT, 2 d	Ph_4PCl + DMF	75%	[36] [37]
$(Pr_4N)_4[In_2(Se_4)_4(Se_5)]$	*P*2/*c*	0D	$InCl_3$ + Na_2Se_5; RT, 2 d	Pr_4NBr + DMF	68%	[37]
$(Et_4N)_4[In_2(Se_4)_4(Se_5)]$	*P*$\bar{1}$	0D	$InCl_3$ + Na_2Se_5; RT	Et_4NBr + DMF	72%	
$(Pr_4N)_2[In_2Se_2(Se_4)_2]$	*P*$\bar{1}$	0D	$InCl_3$ + Na_2Se_5; 110 °C, 3 d	Pr_4NBr + H_2O	80%	
$[(Ph_3P)_2N]_2[In_2Se_2(Se_4)_2]$	*P*$\bar{1}$	0D	$InCl_3$ + Na_2Se_5; 110 °C, 3 d	$[(Ph_3P)_2N]Cl$ + H_2O	60%	
$(Et_4N)_3[In_3Se_3(Se_4)_3]$	$P2_1/c$	0D	$InCl_3$ + Na_2Se_5; RT, 4 d $InCl_3$ + Na_2Se_5; 110, 3 d	Et_4NBr + CH_3CN/ Et_4NBr + H_2O	76%/85%	
$[Mn(en)_3][In_2Se_5]$	*Pbcn*	1D	In_2Se_3 + Se +$MnCl_2$; 170 °C, 6 d	en + py/thiophenol	21%	[38]
$[C_6H_{16}N_2][In_2Se_3(Se_2)]$	*C*2/*c*	1D	In + Se; 170 °C, 10 d	trans-1,4-diaminocycl-ohexane + H_2O	N_A	[39]
(bdaH)$InSe_2$	*Fdd*2	1D	In + Se; 160 °C, 6 d	bda	31.8%	[40]
$\{[Ni(phen)_3]In_2Se_5H_2O\}_n$	$P2_12_12_1$	1D	In + Ni + Se; 140 °C, 4 d	phen + din-butylamine + H_2O	31%	[41]
$\{[Fe(phen)_3]In_2Se_5H_2O\}_n$	$P2_12_12_1$	1D	In + Fe + Se; 140 °C, 4 d	phen + di-n-butylamine + H_2O	35%	
$[C_9H_{17}N_2]_3[In_5Se_{8.07}(Se_2)_{0.93}]$	$P2_1/c$	1D	In + Se + imidazole; 200 °C, 10 d	DBU + acetonitrile	NA	[42]

$[C_9H_{17}N_2]_3[In_5Se_{8.74}(Se_2)_{0.26}]$	$P\bar{1}$	1D	$InCl_3$ + Se; 200 °C, 10 d	DBU	NA	
$[C_6H_{12}N_2]_4[C_6H_{14}N_2]_3[In_{10}Se_{15}(Se_2)_3]$	$P2_1/c$	1D	In + Se; 140 °C, 10 d	DABDO + DMF	NA	
$(Ph_4P)[In(Se_6)_2]$	$P\bar{4}$	2D	In + $(Ph_4P)_2Se_5$ + Se; 200 °C, 2 d	NA	60%	[15]
$[C_7H_{10}N][In_3Se_5]$	$P2_1/c$	2D	In + Se; 185 °C, 10 d	3,5-dimethylpyridine	NA	[43]
$[C_7H_{10}N][In_3Se_5]$	$P22_12_1$	2D	In + Se; 200 °C, 10 d	2,6-dimethylpyridine	NA	
$[C_6H_{14}N_2][(C_6H_{12}N_2)_2NaIn_5Se_9]$	$C2/c$	3D	In + Se; 140 °C, 10 d	DABDO + NaOH + acetonitrile	NA	[42]
$[enH_2][NH_4][In_7Se_{12}]$	$P2_1$	3D	In + Se; 200 °C, 14 d	DABDO + H_2O	NA	
$[\mu_3\text{-}Se_4]_{3.27}\cdot[In_{49.88}Se_{95.92}]\cdot(C_5H_{12}N)_{26.0}\cdot C_2H_8N)_{42.4}$	$R\bar{3}c$	3D	In + Se; 170 °C, 5 d	PR + DMF	NA	[44]
$[In_4Se_{10}]\cdot(C_7H_{16}N)_{1.8}\cdot(C_2H_8N)_{2.2}$	*Pnma*	3D	In + Se; 170 °C, 7 d	1,4-dioxane + 3,5-DMPR + DMF	NA	
$[In_{20}Se_{39}]\cdot(C_6H_{14}N)_{12}$	$P2_1/c$	3D	In + Se; 180 °C, 6 d	H_2O + 1-MPR	NA	
$[In_{40}Se_{79}]_{38}\cdot 38H^+$-3,5-DMP	$I\bar{4}3d$	3D	In + Se; 170 °C, 5 d	3,5-DMP + ATMP	NA	[45]
$[In_{36}Se_{69}]_{30}\cdot 30H^+$-3,5-DMP	$P\bar{4}3n$	3D	In + Se; 180 °C, 7 d	3,5-dimethylpyridine + H_2O	NA	
$[C_7H_{10}N][In_9Se_{14}]$	$P6_3/m$	3D	In + Se; 200 °C, 16 d	3,5-dimethylpyridine	NA	[46]
UCR-7InSe-TETA ($[In_{10}Se_{18}]^{6-}$)	$I\bar{4}_1/acd$	3D	In + Se; 190 °C, 6 d	TETA + H_2O	33%	[47]
UCR-7InSe-PPZ ($[In_{10}Se_{18}]^{6-}$)	$I\bar{4}_1/acd$	3D	In + Se; 190 °C, 6 d	PPZ + H_2O	NA	
UCR-7InSe-DABCO ($[In_{10}Se_{18}]^{6-}$)	$I\bar{4}_1/acd$	3D	In + Se; 190 °C, 6 d	DABCO + H_2O	NA	
UCR-7InSe-AEAE ($[In_{10}Se_{18}]^{6-}$)	$P4_12_12$	3D	In + Se; 190 °C, 6 d	AEAE + H_2O	NA	
UCR-7InSe-DMAPA ($[In_{10}Se_{18}]^{6-}$)	$P4_12_12$	3D	In + Se; 190 °C, 6 d	DMAPA + H_2O	NA	
$[In_{28}Se_{54}(H_2O)_4]^{24-}\cdot 24(H^+\text{-PR})\cdot nH_2O$	$F\bar{4}_13c$	3D	In + Se; 170 °C, 7 d	PR + H_2O	NA	[48]
$(H^+\text{-DMP})_{58.26}\cdot[In_{56}Se_{113.13}]$	$P4/ncc$	3D	In + Se; 170 °C, 5 d	3,5-DMP + ATMP	NA	[49]
$(H^+\text{-MPR})_{57.94}\cdot[In_{60}Se_{118.97}]$	$C2/c$	3D	In + Se; 170 °C, 7 d	MPR + H_2O	NA	
$(NH_4)_4In_{12}Se_{20}$	$Pca2_1$	3D	In + Se; 250 °C, 2 d	NH_4OH	NA	[50]
$(NH_4)_2In_{12}Se_{19}$	$R\bar{3}$	3D	In + Se; 250 °C, 1 d	NH_4OH + H_2O	NA	
UCR-2InSe-DIPA ($[In_{33}Se_{56}]^{13-}$)	*R*32	3D	In + Se; 200 °C, 10 d	DIPA + H_2O	NA	[31]
UCR-2InSe-TETA ($[In_{33}Se_{56}]^{13-}$)	*R*32	3D	In + Se; 200 °C, 10 d	TETA + H_2O	NA	
UCR-2InSe-TAA ($[In_{33}Se_{56}]^{13-}$)	*R*32	3D	In + Se; 200 °C, 10 d	TAA + H_2O	NA	
UCR-2InSe-AEAE ($[In_{33}Se_{56}]^{13-}$)	*R*32	3D	In + Se; 200 °C, 10 d	AEAE + H_2O	NA	
UCR-2InSe-DPA ($[In_{33}Se_{56}]^{13-}$)	*R*32	3D	In + Se; 200 °C, 10 d	DPA + H_2O	NA	
UCR-2InSe-TMHD ($[In_{33}Se_{56}]^{13-}$)	*R*32	3D	In + Se; 200 °C, 10 d	TMHD + H_2O	NA	
UCR-2InSe-BAPP ($[In_{33}Se_{56}]^{13-}$)	*R*32	3D	In + Se; 200 °C, 10 d	BAPP + H_2O	NA	
UCR-2InSe-TOTD ($[In_{33}Se_{56}]^{13-}$)	*R*32	3D	In + Se; 200 °C, 10 d	TOTD + H_2O	NA	
UCR-2InSe-HMI ($[In_{33}Se_{56}]^{13-}$)	*R*32	3D	In + Se; 200 °C, 10 d	HMI + H_2O	NA	
UCR-2InSe-DAO ($[In_{33}Se_{56}]^{13-}$)	*R*32	3D	In + Se; 200 °C, 10 d	DAO + H_2O	NA	
UCR-2InSe-DMMP ($[In_{33}Se_{56}]^{13-}$)	*R*32	3D	In + Se; 200 °C, 10 d	DMMP + H_2O	NA	
UCR-2InSe-APM ($[In_{33}Se_{56}]^{13-}$)	*R*32	3D	In + Se; 200 °C, 10 d	APM + H_2O	NA	

Abbreviations: Ph_4PCl = tetraphenylphosphonium chloride; DMF = Dimethylformamide; en = ethylenediamine; Py = pyridine; bda = 1,4-butanediamine; phen = 1,10-Phenanthroline; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; DABDO = 1,4-diazabicyclo[2.2.2]octane; PR = piperidine; TETA = triethylenetetramine; PPZ = piperazine; AEAE = 2-(2-aminoethylaminoethanol); DMAPA = 3-dimethylaminopropylamine; 3,5-DMPR/3,5-DMP = 3,5-dimethylpiperidine; 1-MPR = 1-methylpiperidine; H^+-PR = protonated piperidine; ATMP = amino trimethylene phosphonic acid; MPR = 3-methylpiperidine.

2. Figures

2.1 Synthesis and Structures

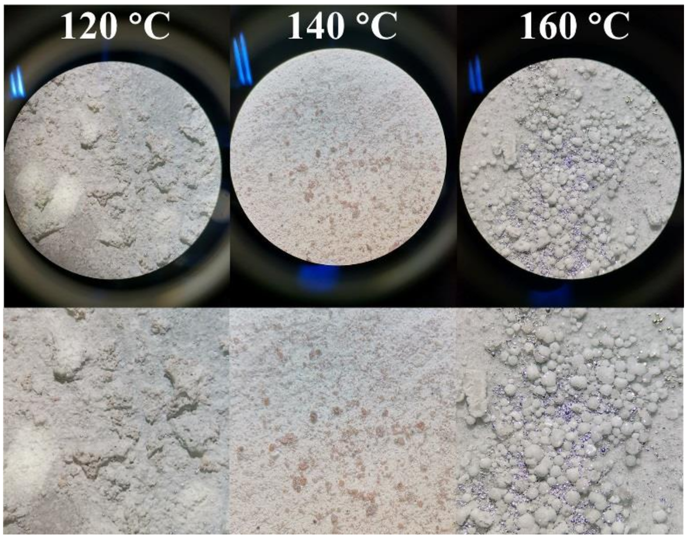


Figure S1. Photographs of the products obtained from the optimizing reactions for **2** ($N_2H_4 \cdot H_2O$:urea = 0.65:1) performed at different temperatures. Top line: products washed by distilled water; bottom line: magnified imaging of the products.

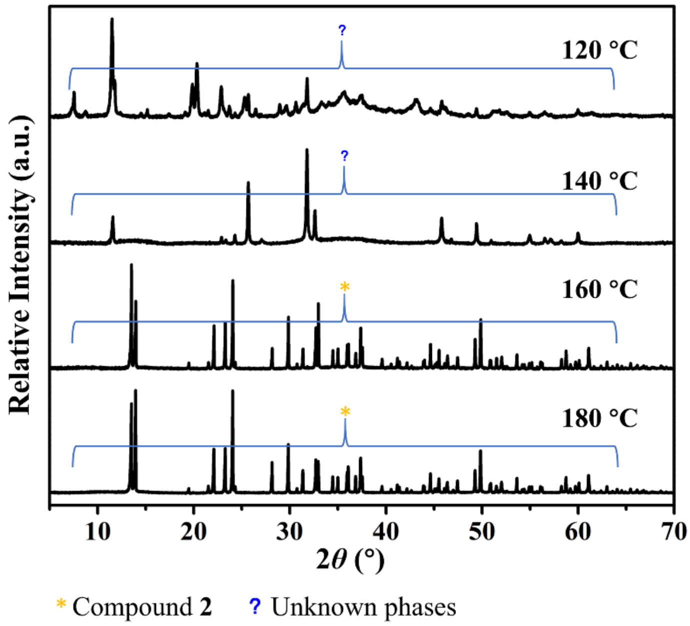


Figure S2. Powder XRD patterns of the products obtained from the optimizing reactions for **2** performed at different temperatures.

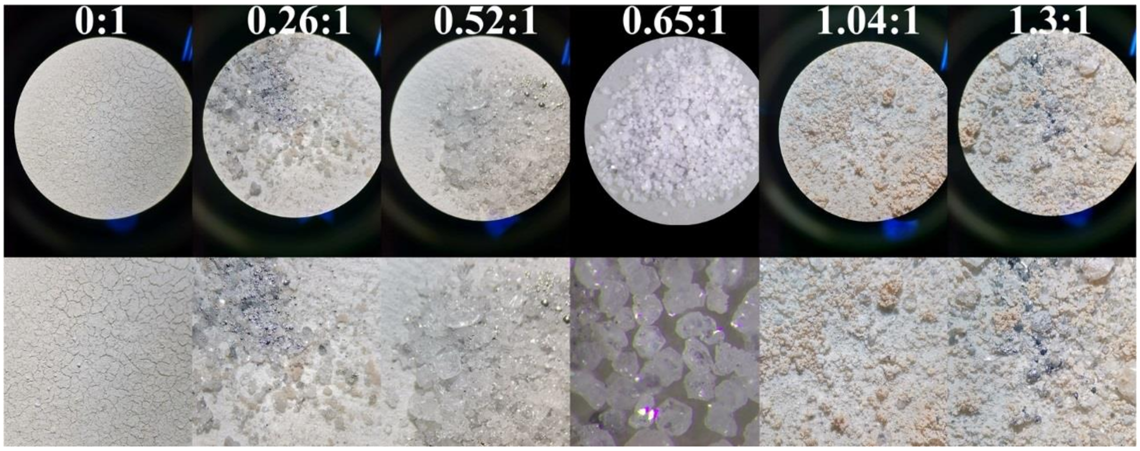


Figure S3. Photographs of the products obtained from the optimizing reactions for **2** with different $N_2H_4·H_2O$:urea molar ratios at 180 °C. Top line: products washed by distilled water; bottom line: magnified imaging of the products.

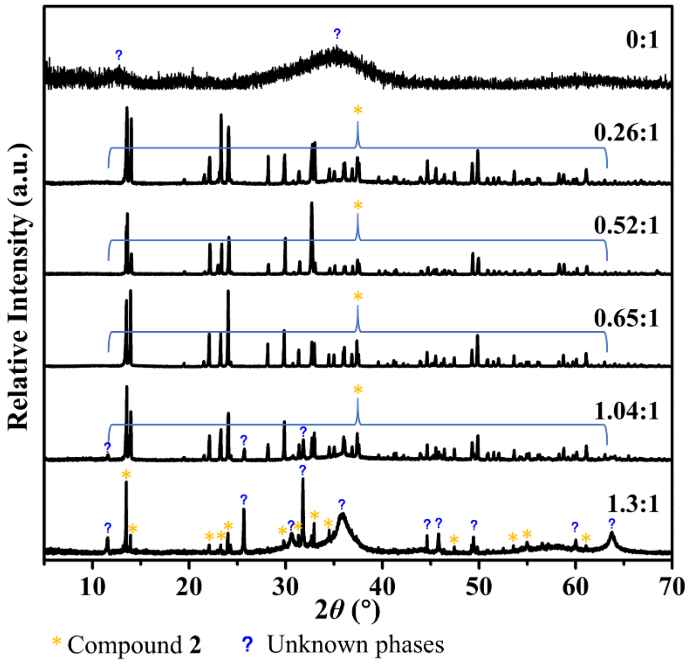


Figure S4. Powder XRD patterns of the products from optimizing reactions for **2** with different $N_2H_4·H_2O$:urea ratio at 180 °C.

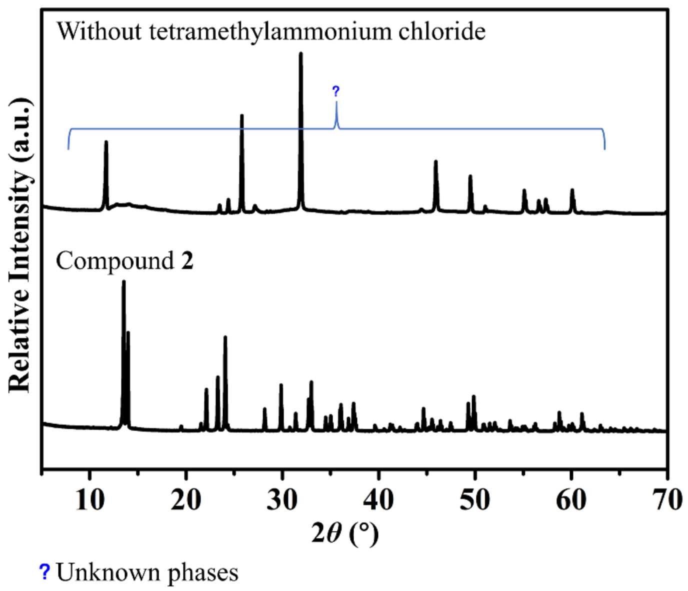


Figure S5. Powder XRD patterns of compound **2** and the product from the reaction without adding tetramethylammonium chloride.

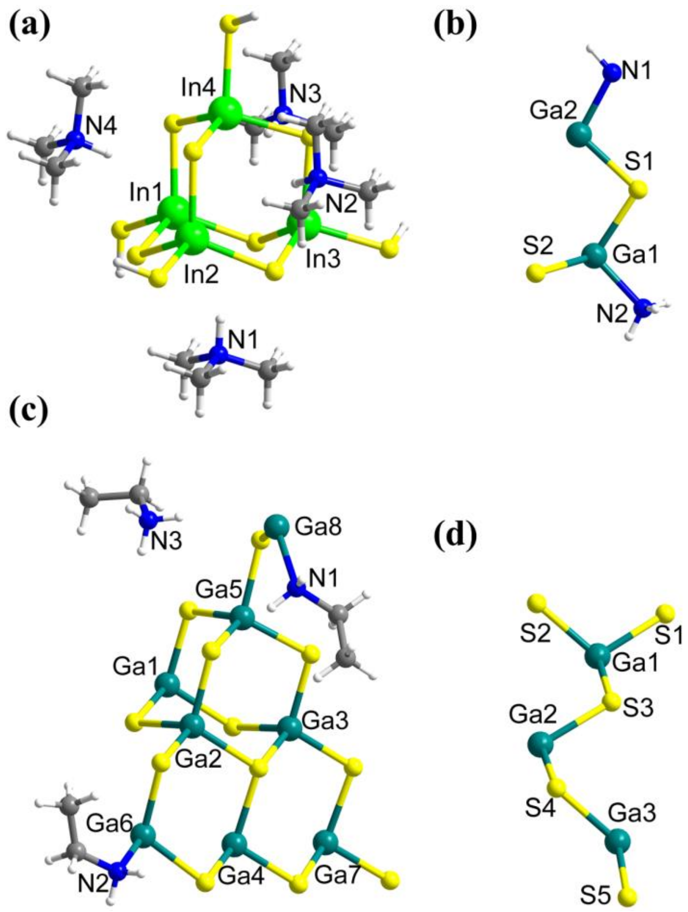


Figure S6. Asymmetric units of (a) **1**, (b) **2**, (c) **3**, and (d) **4**. Color code: In (bright green), Ga (teal), S (yellow), N (blue), C (gray), H (white). Note: some of the atoms shown in the figure are not fully occupied due to their location at special positions.

2.2 Characterizations

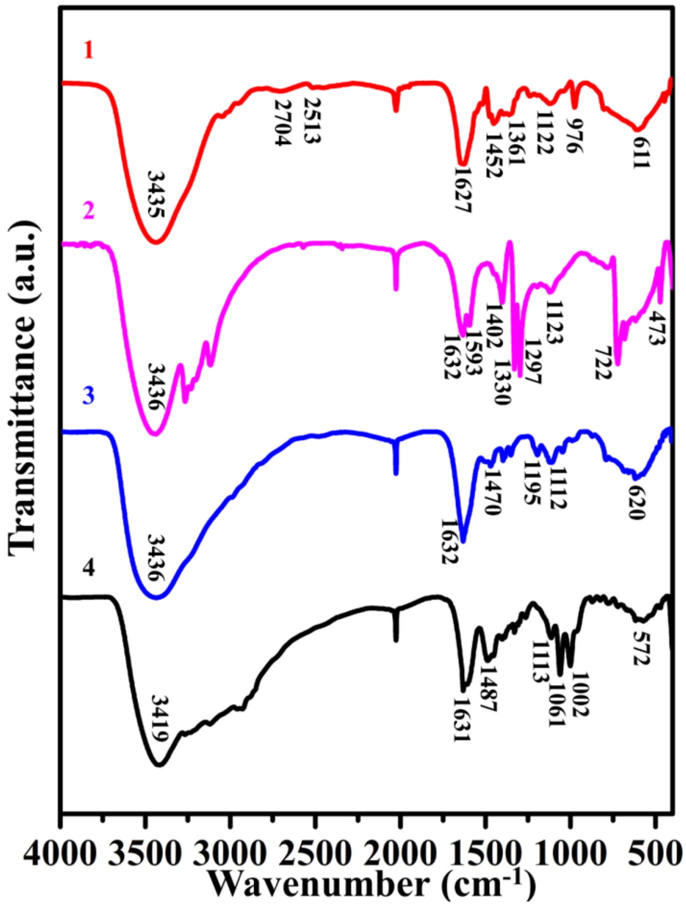
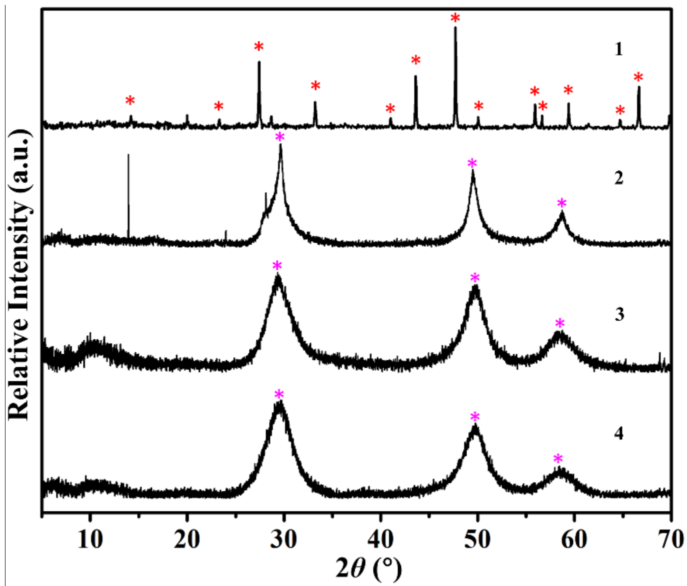


Figure S7. FTIR spectra of **1−4**.



* In_2S_3, PDF-#:65-0459 * Ga_2S_3, PDF-#:43-0916

Figure S8. Powder XRD patterns for the TG residues of **1-4**.

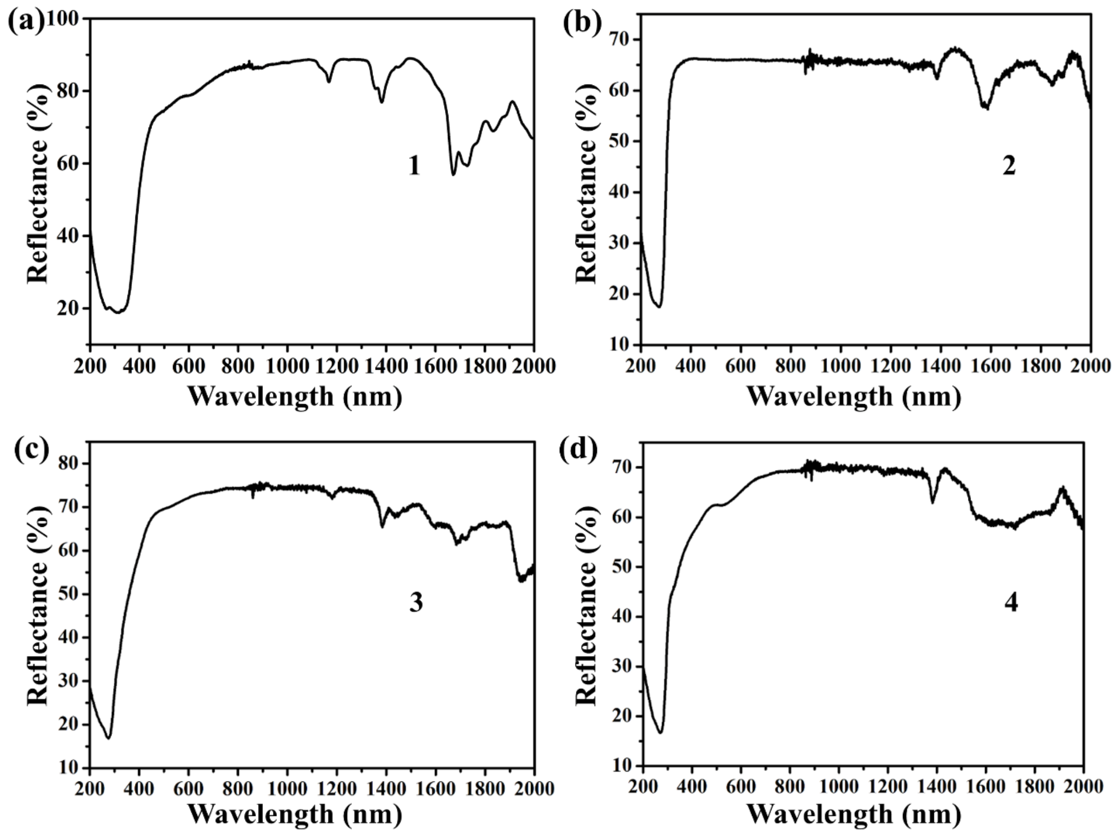


Figure S9. UV-vis reflectance spectra of compounds **1-4**.

2.3 Organic template identification for 1-4 by ^{1}H and ^{13}C NMR.

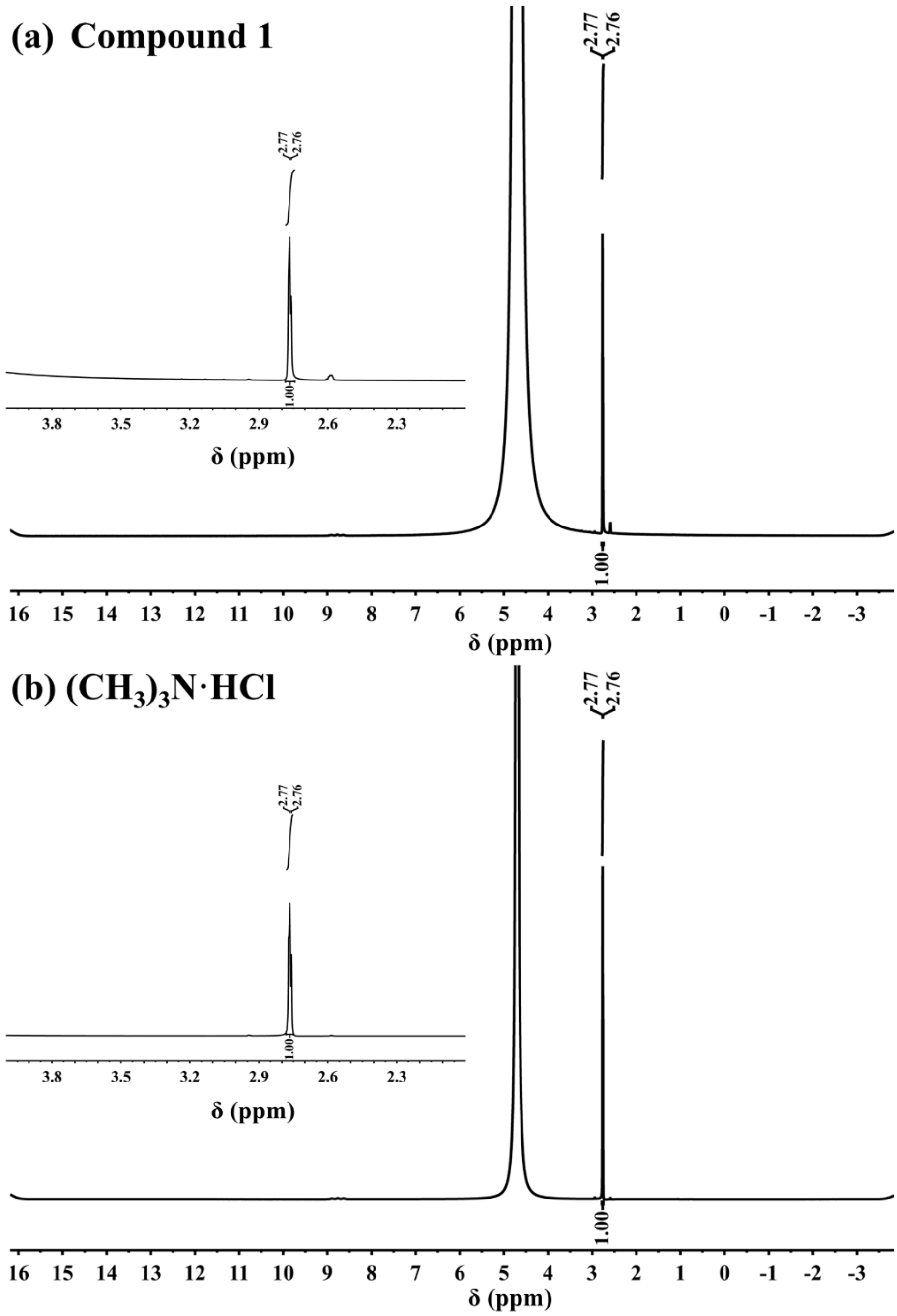


Figure S10. ^{1}H NMR spectra of **1** and $(CH_3)_3N\cdot HCl$ dissolved in mixed HCl (0.1 M)/D_2O recorded at room temperature.

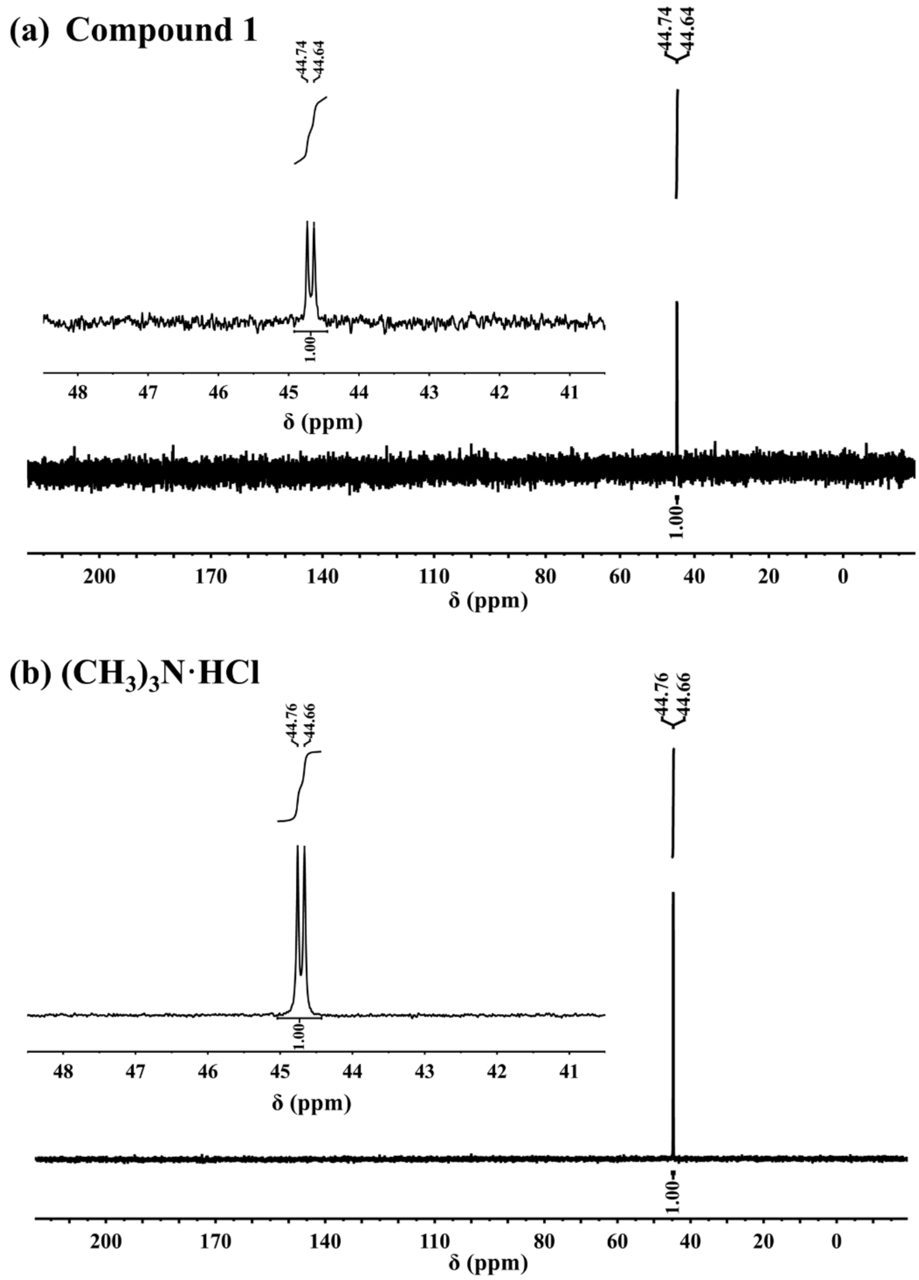


Figure S11. ^{13}C NMR spectra of **1** and $(CH_3)_3N \cdot HCl$ dissolved in mixed HCl (0.1 M)/D_2O recorded at room temperature.

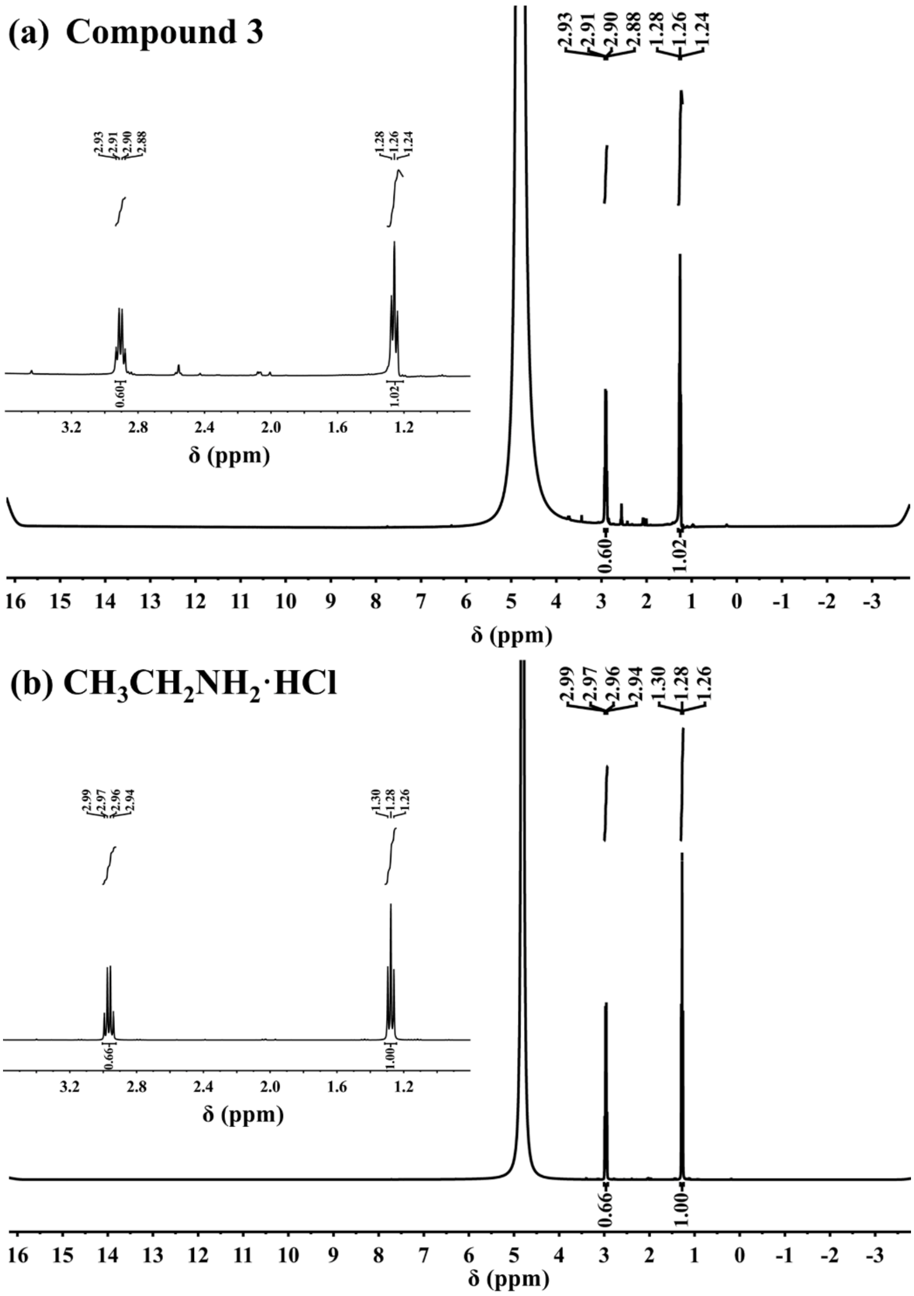


Figure S12. ^{1}H NMR spectra of **3** and $CH_3CH_2NH_2 \cdot HCl$ dissolved in $N_2H_4 \cdot H_2O$ (98%)/D_2O recorded at room temperature.

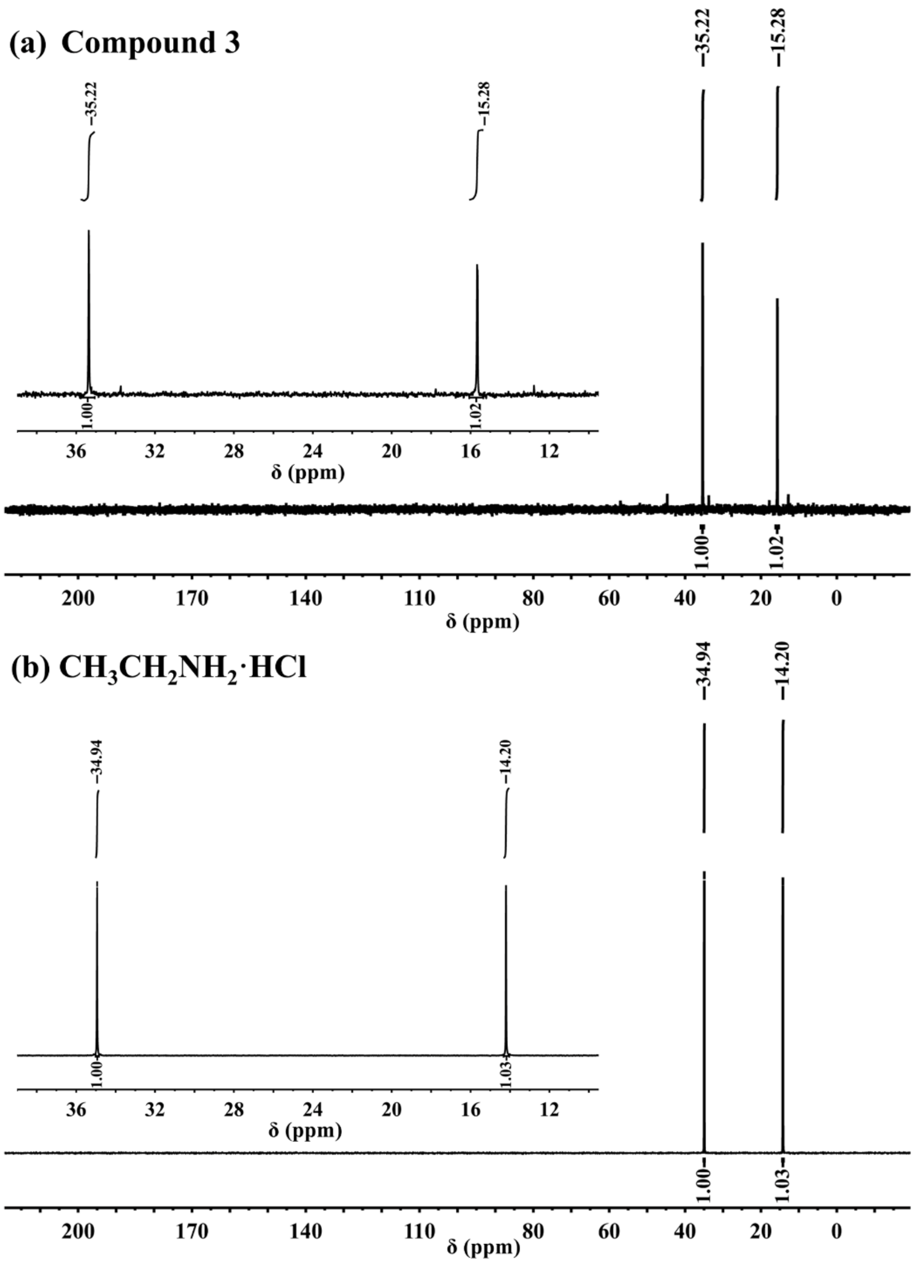


Figure S13. ^{13}C NMR spectra of **3** and $CH_3CH_2NH_2 \cdot HCl$ dissolved in $N_2H_4 \cdot H_2O$ (98%)/D_2O recorded at room temperature.

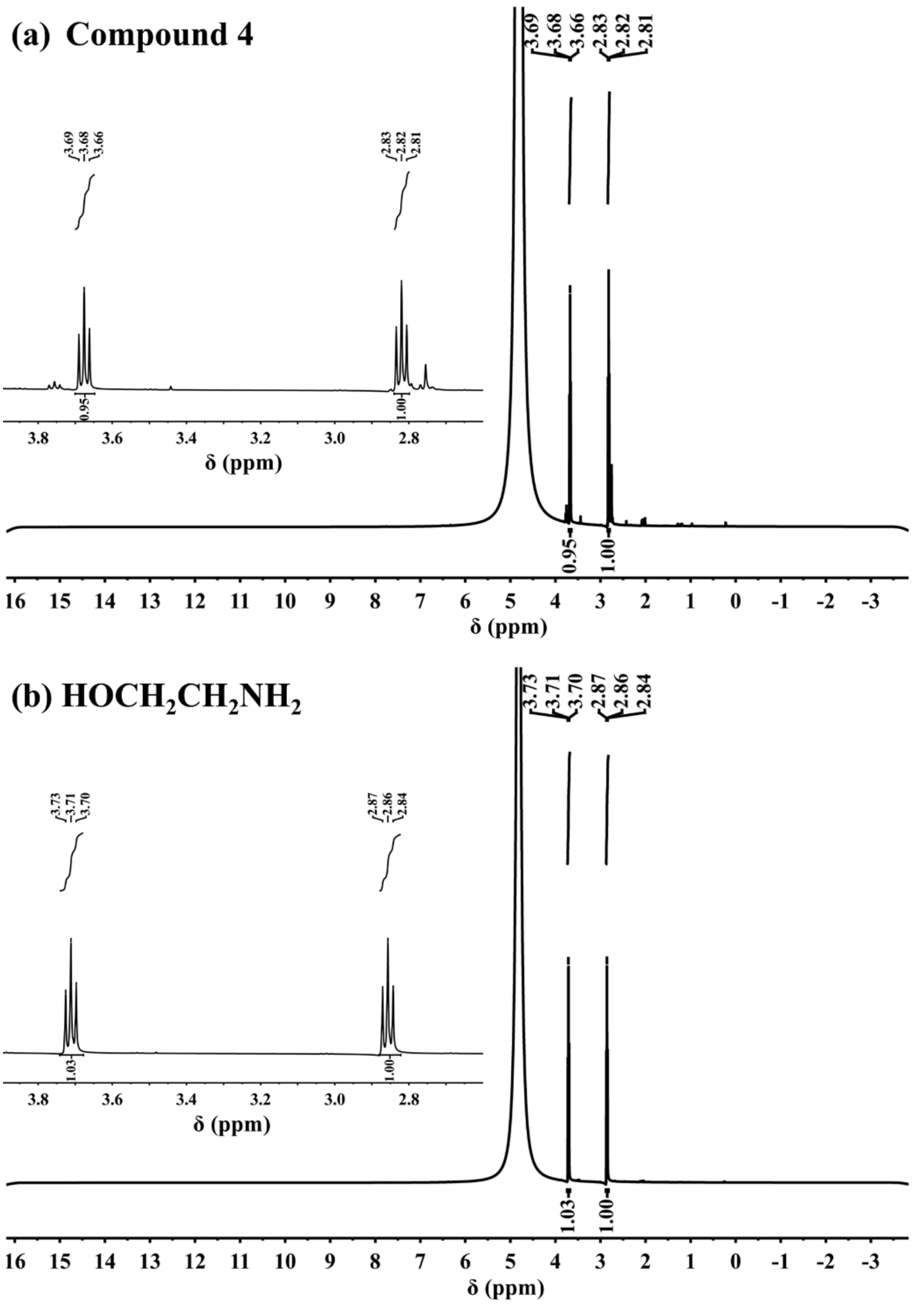


Figure S14. ^{1}H NMR spectra of **4** and $HOCH_2CH_2NH_2$ dissolved in $N_2H_4 \cdot H_2O$ (98%)/D_2O recorded at room temperature.

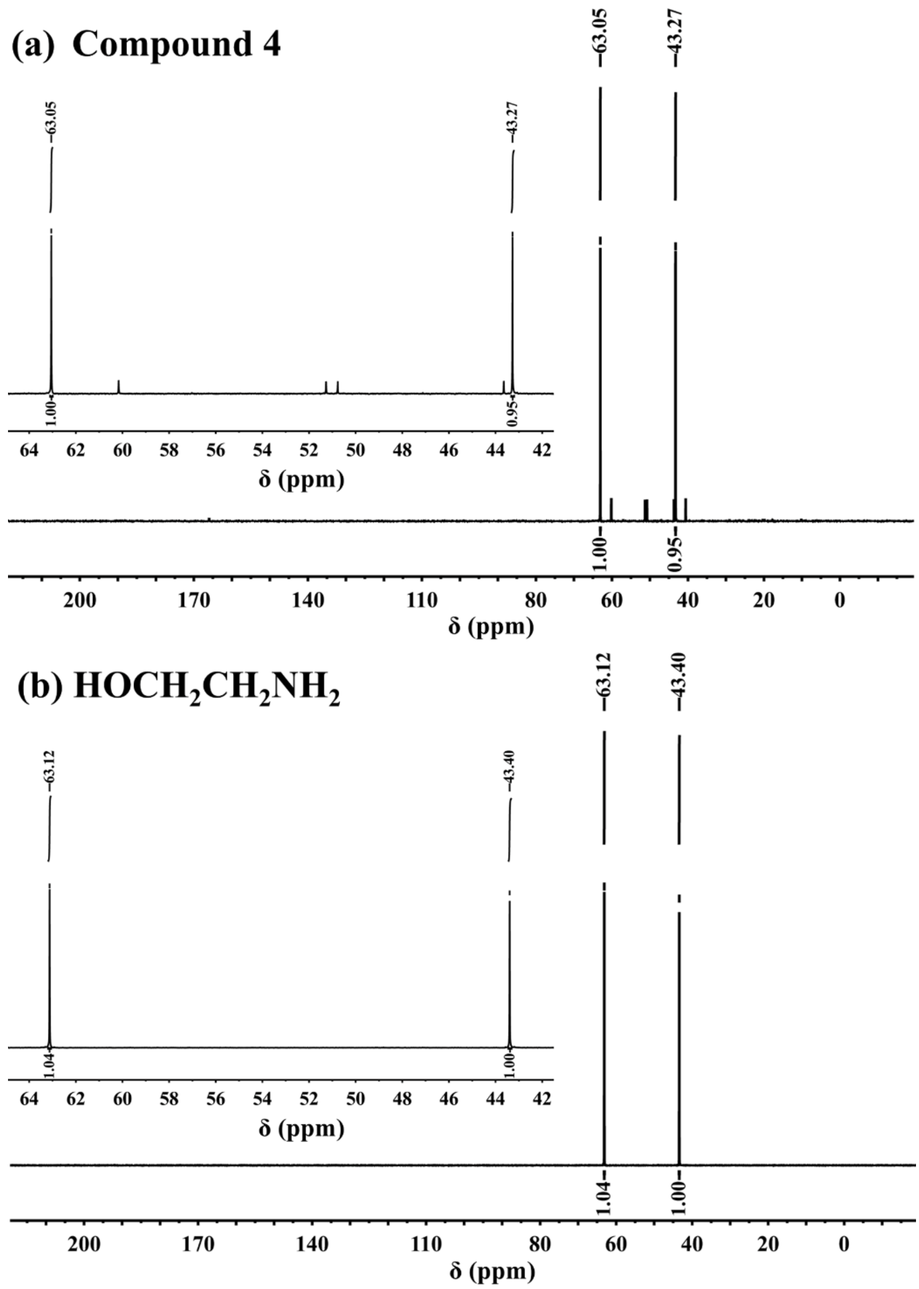


Figure S15. ^{13}C NMR spectra of **4** and $HOCH_2CH_2NH_2$ dissolved in $N_2H_4{\cdot}H_2O$ (98%)/D_2O recorded at room temperature.

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