

Supplementary Information

Broadband Emission in Hybrid Organic-Inorganic Halides of Group 12 Metals

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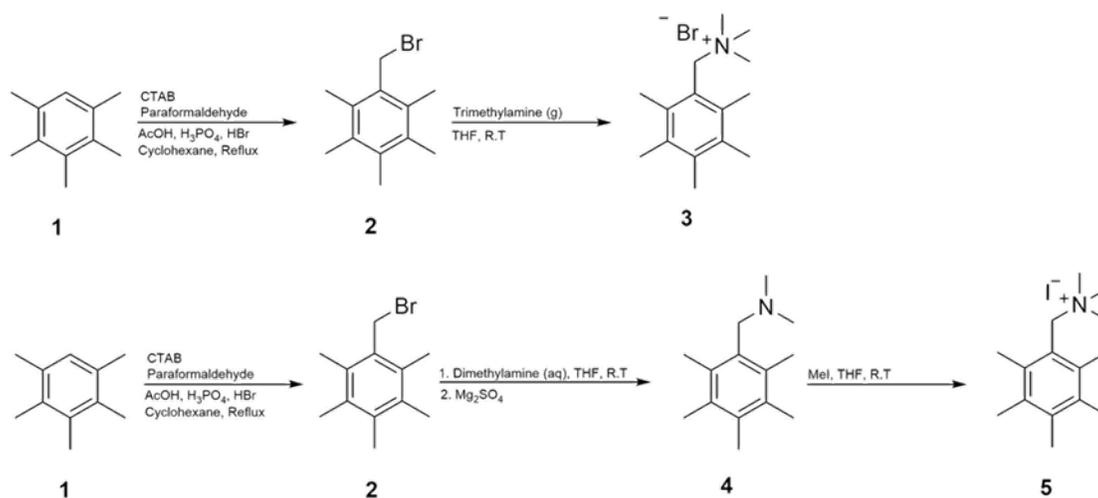
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Synthesis of trimethyl(2,3,4,5,6-pentamethylbenzyl)ammonium bromide and iodide salts



Scheme S1. Syntheses of the bromide ((R)Br, **3**) and iodide ((R)I, **5**) salts used in the formation of the target hybrid organic-inorganic compounds.

Synthesis of 1-(bromomethyl)-2,3,4,5,6-pentamethylbenzene (2): A three necked round bottom flask fitted with a reflux condenser was charged with 2.00 g (13.5 mmol) pentamethylbenzene (**1**), 0.626 g (20.8 mmol) paraformaldehyde, 0.226 g (0.620 mmol) cetyltrimethylammonium bromide (CTAB), cyclohexane (20 mL), acetic acid (10 mL), and phosphoric acid (0.5 mL). The reaction mixture was stirred vigorously (magnetic) and 10 mL of 48% hydrobromic acid was added using a dropping funnel attached to a side arm of the flask. The mixture was heated to 80 °C for 24 hours. The reaction mixture was cooled using an ice bath, diluted with 20 mL of water, transferred to an Erlenmeyer flask, and extracted three times with dichloromethane using a separatory funnel. The combined organic layers were dried over Mg₂SO₄, which was removed by vacuum filtration, and the filtrate was concentrated under reduced pressure to give product **2** in 94% yield as a white

polycrystalline solid. The $^1\text{H-NMR}$ spectrum of **2** matched that reported in the literature (Figure S1).¹

Synthesis of trimethyl (2,3,4,5,6-pentamethylbenzyl) ammonium bromide ((R)Br, 3): A round bottom flask was charged with 1.00 g (4.10 mmol) bromide **2** and THF (50 mL). The reaction flask was sealed with a rubber septum and an excess of trimethylamine gas was introduced into the reaction flask through a cannula needle. The reaction mixture was stirred magnetically overnight at room temperature. The white solid that formed was collected by gentle vacuum filtration and dried under reduced pressure. Product **3** was obtained in 89% yield as the monohydrate; mp 219-220 °C (lit mp 221-222 °C). $^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 2.24 (s, 6H, CH_3), 2.28 (s, 3H, CH_3), 2.45 (s, 6H, CH_3), 3.37 (s, 9H, N-CH_3), 5.04 (s, 2H, $\text{CH}_2\text{-N}$) (Figure S2).²

Synthesis of N,N,2,3,4,5,6-heptamethyl-benzylamine (4): A 100 mL round bottom flask was charged with 1.00 g of **2** (4.10 mmol) and THF (50 mL). Dimethylamine was introduced by adding 1.41 g of a 40 wt% aqueous solution (0.564 g dimethylamine, 12.5 mmol) dropwise and the reaction flask was stoppered. The solution was stirred magnetically for 24 hours, the reaction was quenched by the addition of solid Mg_2SO_4 . The Mg_2SO_4 was removed by vacuum filtration, the filtrate was concentrated under reduced pressure for 24 hours to give product **4** in 86% yield a white crystalline solid. $^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 2.24 (s, 6H, CH_3), 2.26 (s, 3H, CH_3), 2.28 (s, 6H, N-CH_3), 2.33 (s, 6H, CH_3), 3.49 (s, 2H, $\text{CH}_2\text{-N}$) (Figure S3).³

Synthesis of trimethyl (2,3,4,5,6-pentamethylbenzyl) ammonium iodide ((R)I, 5): A 100 mL round bottom flask was charged with 1.00 g of **4** (4.90 mmol) and THF (20 mL). Methyl iodide

(1.39 g, 9.80 mmol) were added dropwise to the solution. The flask was stoppered, and the solution was stirred magnetically for 24 hours. Within the first 3 hours most of the product precipitated as a white solid. Solvent and excess methyl iodide were removed under reduced pressure to give product **5** in 98% yield as a white polycrystalline solid; mp 220-223 °C (lit mp 220-221 °C). ¹H NMR (CDCl₃, δ, ppm): 2.25 (s, 6H, CH₃), 2.29 (s, 3H, CH₃), 2.44 (s, 6H, CH₃), 3.34 (s, 9H, N-CH₃), 5.00 (s, 2H, CH₂-N) (Figure S4).³

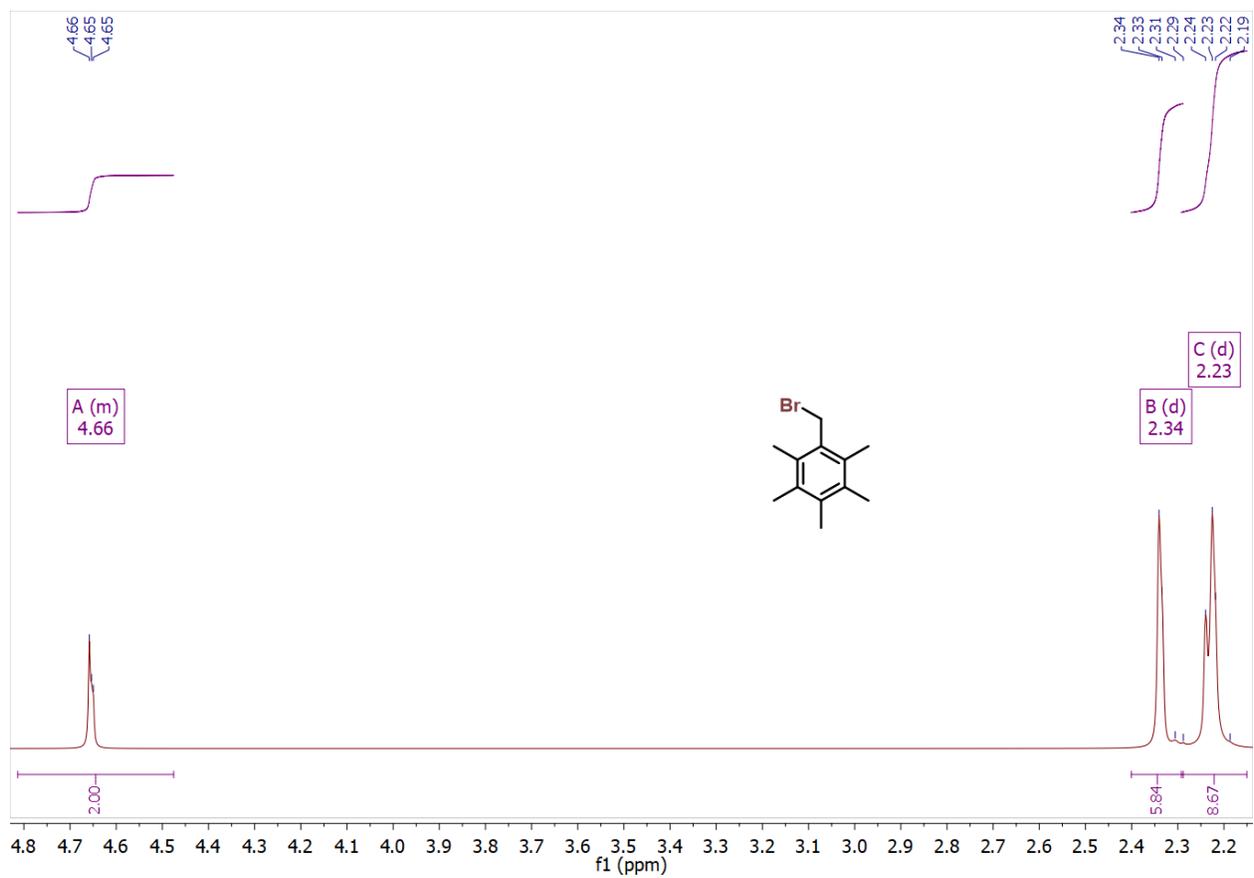


Figure S1. NMR spectrum of the 1-(bromomethyl)-2,3,4,5,6-pentamethylbenzene (**2**) precursor in CDCl₃.

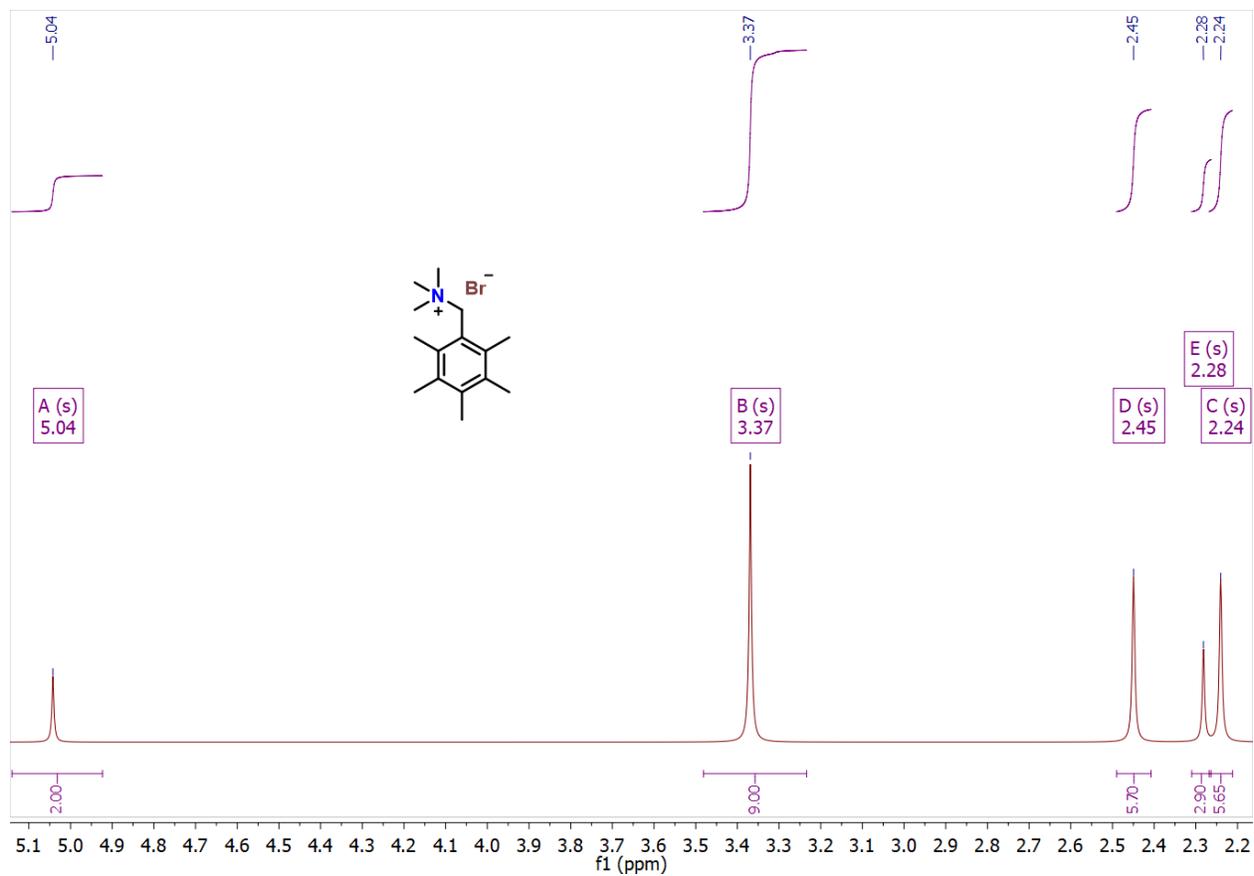


Figure S2. NMR spectrum of the trimethyl (2,3,4,5,6-pentamethylbenzyl) ammonium bromide ((R)Br, **3**) precursor in CDCl₃.

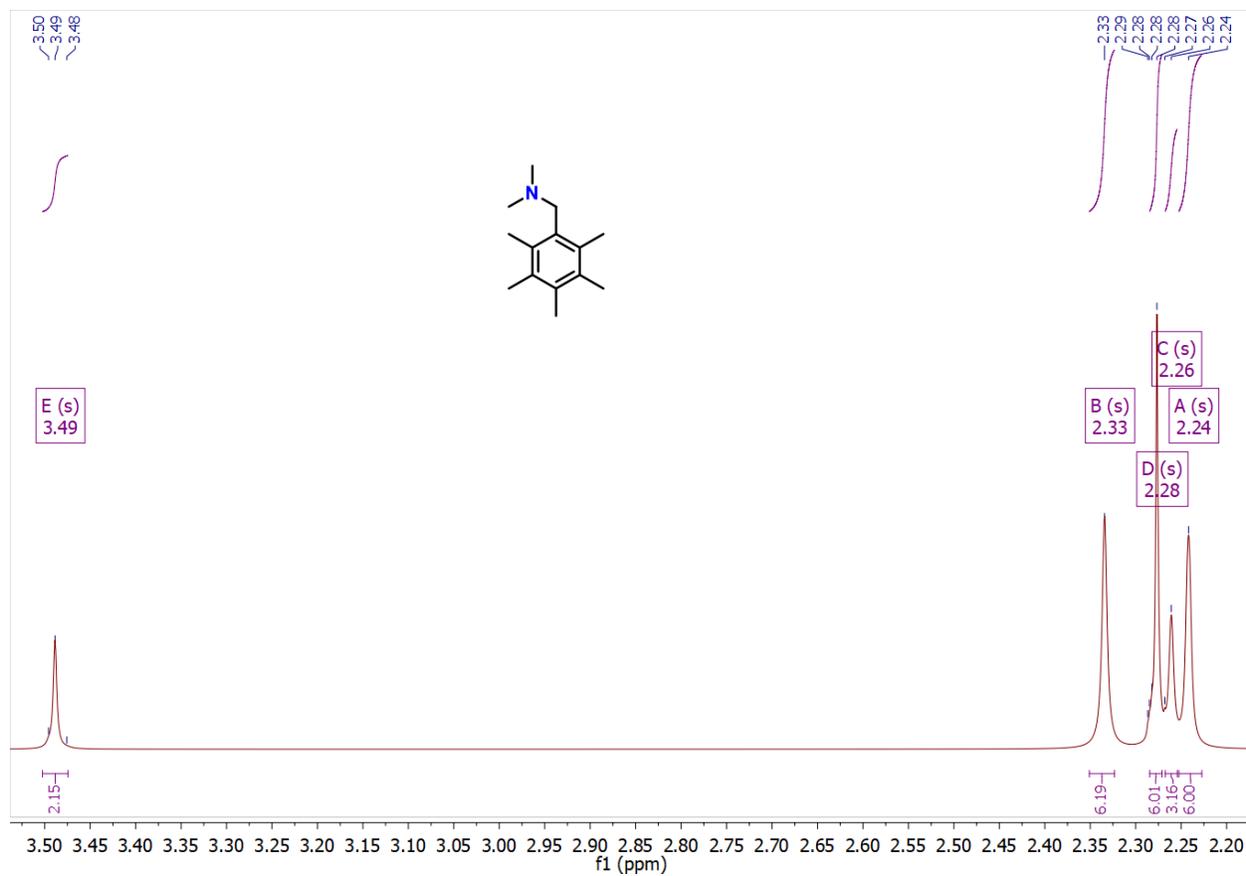


Figure S3. NMR spectrum of the N,N,2,3,4,5,6-heptamethyl-benzylamine (**4**) in CDCl₃ produced by the reaction outlined in section 2.4.

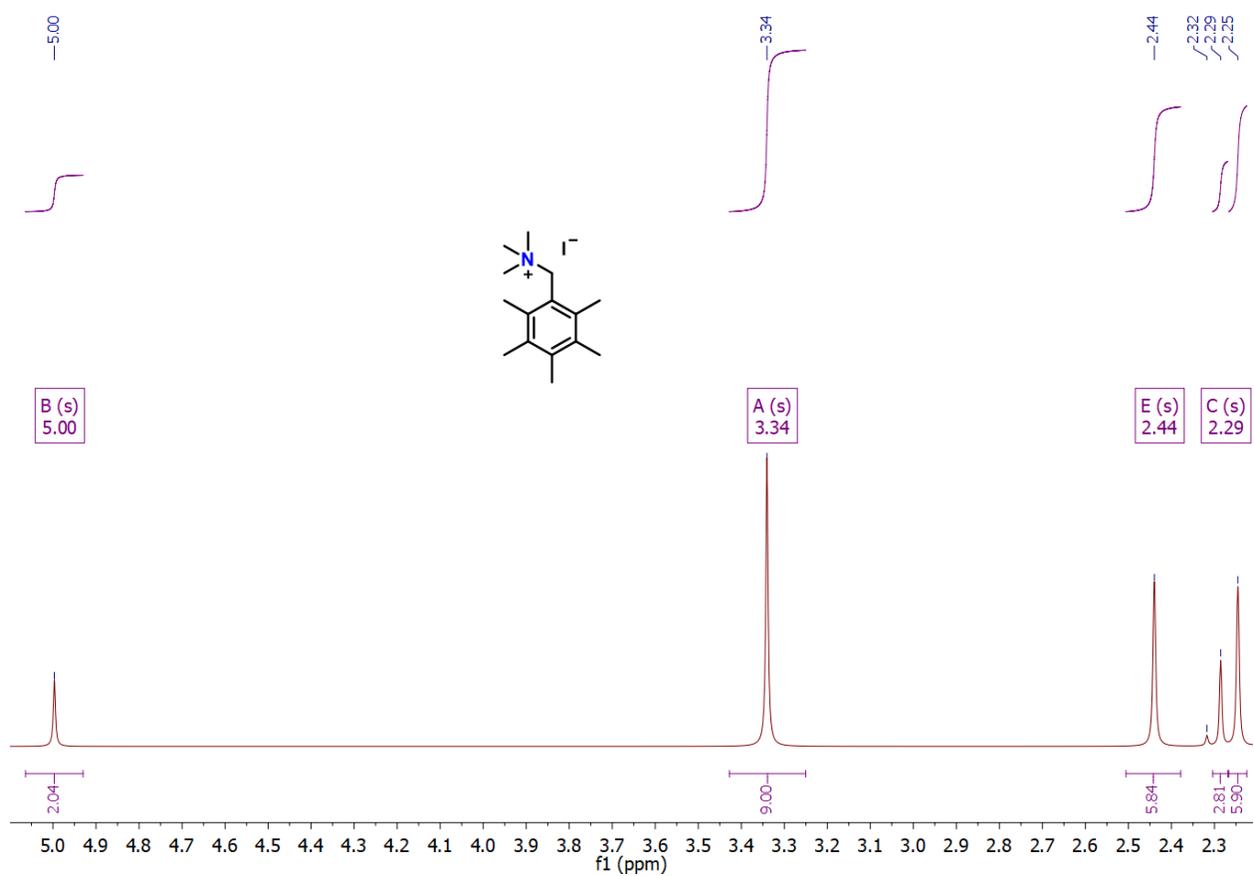


Figure S4. NMR spectrum of trimethyl (2,3,4,5,6-pentamethylbenzyl) ammonium iodide ((R)I, **5**) precursor in CDCl₃.

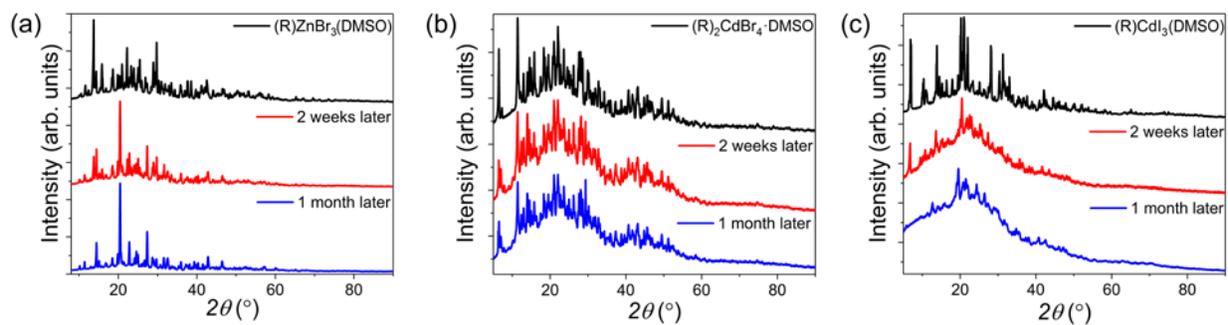


Figure S5. PXRD patterns of (a) $(R)ZnBr_3(DMSO)$, (b) $(R)_2CdBr_4 \cdot DMSO$ and (c) $(R)CdI_3(DMSO)$ samples left in ambient air for over a period of one month.

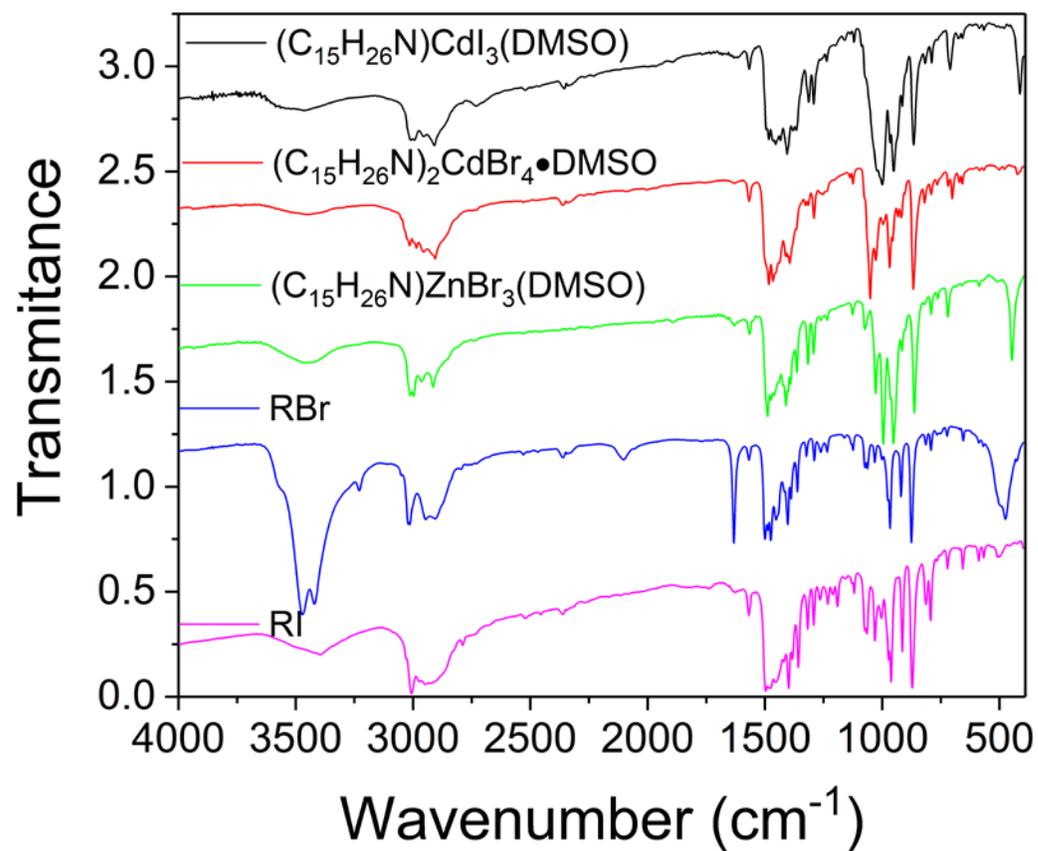


Figure S6. IR spectra of (R)ZnBr₃(DMSO), (R)₂CdBr₄•DMSO, (R)CdI₃(DMSO) and the precursor organic salts (R)Br (**3**) and (R)I (**5**).

Table S1. Selected single crystal data collection and refinement parameters for (R)ZnBr₃(DMSO), (R)₂CdBr₄·DMSO and (R)CdI₃(DMSO) at 100(2) K.

Formula	(R)ZnBr₃(DMSO)	(R)₂CdBr₄·DMSO	(R)CdI₃(DMSO)
Formula weight (g/mol)	603.59	950.90	791.59
Temperature (K)	100 (2)		
Radiation, wavelength (Å)	Mo K α , 0.71073		
Crystal system	Orthorhombic	Triclinic	Orthorhombic
Space group, <i>Z</i>	<i>P</i> 2 ₁ 2 ₁ 2, 4	<i>P</i> -1, 2	<i>P</i> 2 ₁ 2 ₁ 2, 4
<i>a</i> (Å)	8.9513(16)	8.829(7)	9.2030(10)
<i>b</i> (Å)	28.500(6)	14.244(10)	29.304(3)
<i>c</i> (Å)	8.8203(16)	15.714(11)	9.3602(11)
α , °	90	72.734(10)	90
β , °	90	89.356(10)	90
γ , °	90	89.710(10)	90
Volume (Å ³)	2250.2(7)	1887(2)	2524.3(5)
Density (ρ_{calc}) (g/cm ³)	1.782	1.674	2.083
Absorption coefficient (μ) (mm ⁻¹)	6.517	4.895	4.622
$\theta_{\text{min}} - \theta_{\text{max}}$ (°)	2.31 – 26.34	1.36 – 29.23	1.39 – 31.46
Reflections collected	34552	32253	66066
Independent reflections	4193	10050	8052
<i>R</i> ^a indices (<i>I</i> > 2 σ (<i>I</i>))	<i>R</i> ₁ = 0.0286	<i>R</i> ₁ = 0.0598	<i>R</i> ₁ = 0.0419
	<i>wR</i> ₂ = 0.0561	<i>wR</i> ₂ = 0.1622	<i>wR</i> ₂ = 0.0915
Goodness-of-fit on <i>F</i> ²	1.007	1.031	1.007
Largest diff. peak and hole (e ⁻ /Å ³)	0.344 and -0.335	1.351 and -3.429	1.320 and -0.926

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = |\sum |w(F_o^2 - F_c^2)| / \sum |w(F_o^2)||^{1/2}$, where $w = 1/|\sigma^2 F_o^2 + (AP)^2 + BP|$, with $P = (F_o^2 + 2F_c^2)/3$ and weight coefficients *A* and *B*.

Table S2. Selected interatomic distances and angles in (R)ZnBr₃(DMSO), (R)₂CdBr₄·DMSO and (R)CdI₃(DMSO) at 298(2) K.

Label	Distance (Å)	Label (°)	Angle	
<u>(R)ZnBr₃(DMSO)</u>				
Zn-	O1	2.024(5)	O1-Zn-Br1	104.61(17)
	Br1	2.3796(13)	O1-Zn-Br2	100.90(14)
	Br2	2.3820(12)	O1-Zn1-Br3	104.39(17)
	Br3	2.3951(13)	Br1-Zn1-Br3	116.19(5)
			Br2-Zn-Br3	114.07(5)
			Br1-Zn-Br2	114.30(5)
<u>(R)₂CdBr₄·DMSO</u>				
Cd-	Br1	2.6065(5)	Br1-Cd-Br4	105.105(16)
	Br2	2.6035(5)	Br1-Cd-Br3	110.057(17)
	Br3	2.5770(5)	Br4-Cd-Br3	113.073(18)
	Br4	2.5959(5)	Br1-Cd-Br2	114.355(17)
			Br4-Cd-Br2	105.954(18)
			Br3-Cd-Br2	108.321(17)
<u>(R)CdI₃(DMSO)</u>				
Cd1-	O1	2.247(7)	O1-Cd1-I3	102.5(2)
	I1	2.7283(8)	O1-Cd1-I2	102.3(2)
	I2	2.7201(8)	O1-Cd1-I1	98.97(19)
	I3	2.7305(8)	I3-Cd1-I2	118.37(3)
			I3-Cd1-I1	115.43(3)
			I2-Cd1-I1	114.98(3)

Table S3. Selected interatomic distances (Å) and angles (°) in (R)ZnBr₃(DMSO), (R)₂CdBr₄·DMSO and (R)CdI₃(DMSO) at 100(2) K.

Label	Distance	Label	Angle	
<u>(R)ZnBr₃(DMSO)</u>				
Zn-	O1	2.026(3)	O1-Zn-Br3	104.17(9)
	Br1	2.3889(8)	O1-Zn-Br1	100.82(9)
	Br2	2.3967(7)	Br3-Zn-Br1	114.20(3)
	Br3	2.3812(7)	O1-Zn1-Br2	103.86(9)
			Br3-Zn-Br2	116.59(3)
			Br1-Zn-Br2	114.54(3)
<u>(R)₂CdBr₄·DMSO</u>				
Cd-	Br1	2.571(2)	Br1-Cd-Br4	108.55(4)
	Br2	2.602(2)	Br1-Cd-Br3	112.49(5)
	Br3	2.5954(17)	Br4-Cd-Br3	105.47(5)
	Br4	2.5943(17)	Br1-Cd-Br2	110.80(3)
			Br4-Cd-Br2	114.92(6)
			Br3-Cd-Br2	104.53(4)
<u>(R)CdI₃(DMSO)</u>				
Cd1-	O1	2.262(6)	O1-Cd1-I3	100.83(16)
	I1	2.7422(8)	O1-Cd1-I2	102.28(17)
	I2	2.7421(8)	O1-Cd1-I1	99.09(15)
	I3	2.7273(8)	I3-Cd1-I2	118.29(3)
			I3-Cd1-I1	115.13(3)
			I2-Cd1-I1	116.37(3)

References

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