[HMIM][Br_9]: a Room-temperature Ionic Liquid Based on a Polybromide Anion

Supporting Information

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([HMIM] = 1-hexyl-3-methylimidazolium)

1. Raman spectrum

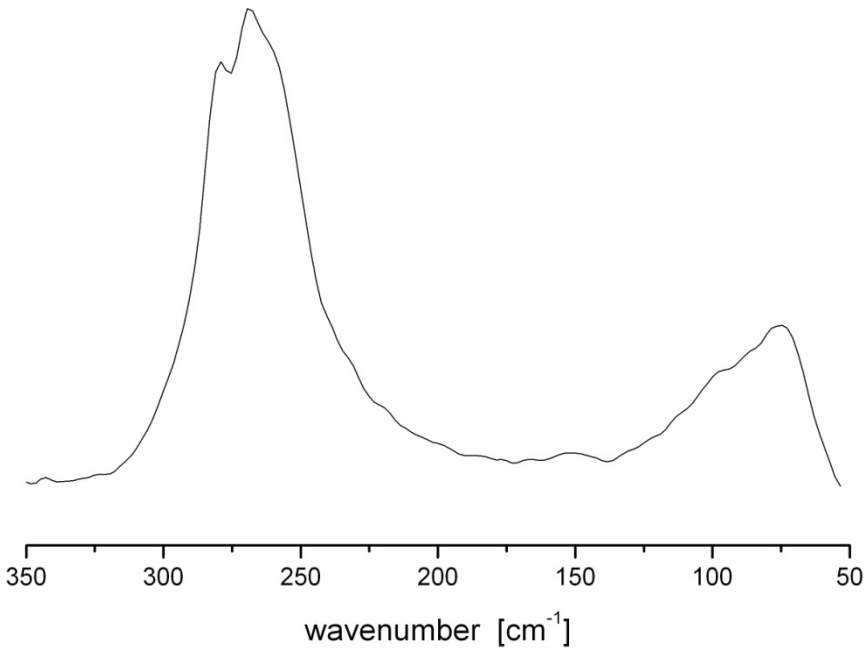

Fig. S1. Experimental Raman spectrum of [HMIM][Br_9].

2. Conductivity

Table S1. Electrical Conductivity of [HMIM][Br_9].

T (K)	Conductivity (mS cm^{-1})
285.95	36.5
290.15	41.9
294.55	47.1
298.75	52.1
302.75	57.3
307.05	62.7
310.45	67.5
314.55	72.7
318.25	77.9
321.75	83.0
324.85	88.0
328.95	93.6
333.65	98.5

3. NMR spectra

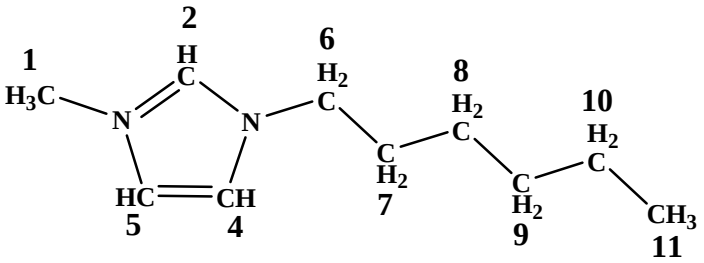

Table S2. Comparison of the ^{1}H NMR of [HMIM][Br_9] and [HMIM]Br^-.

	^{1}H: δ ([HMIM][Br_9])	^{1}H: δ ([HMIM]Br^-)	$\Delta\delta$
2	8.43	10.8	2.4
5	7.44	9.03	1.6
4	7.42	8.95	1.5
6	4.27	5.0	0.7
1	4.07	4.7	0.6
7	2.00	2.4	0.4
8–10	1.38	1.7	0.3
11	0.90	1.2	0.3

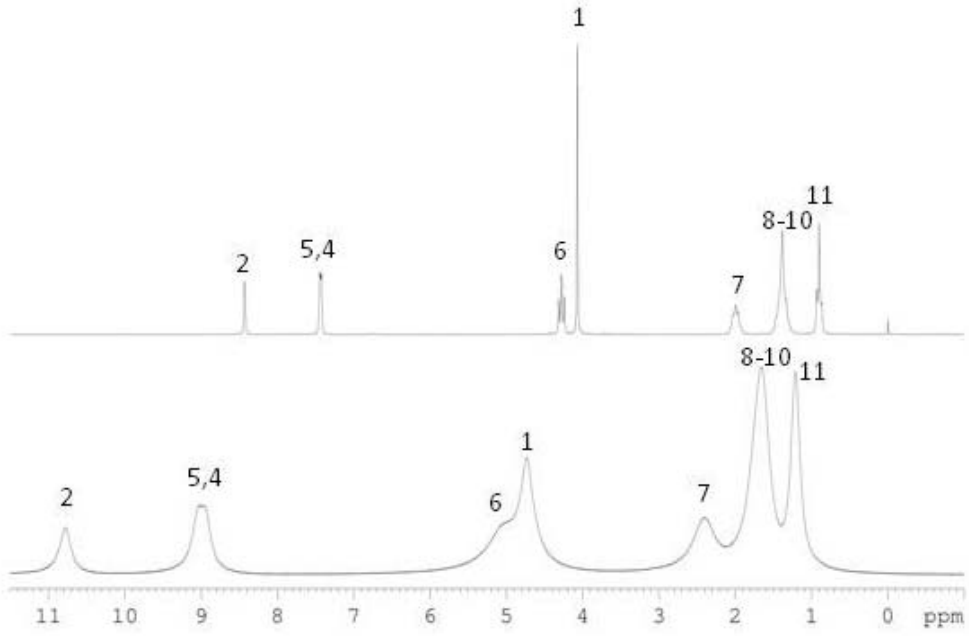

Fig. S2. ^{1}H NMR spectra of [HMIM][Br_9] (top) and [HMIM]Br^- (bottom).

4. Crystal data

Table S3. Crystal data and structure refinement for [HMIM][Br_9]

Empirical formula	$C_{10}H_{19}N_2Br_9$
Formula weight	886.46
Temperature, K	100.0
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a, Å	8.6452(5)
b, Å	16.0882(9)
c, Å	16.6066(9)
Volume, Å^3	2309.7(2)
Z	4
$\rho_{calc,}$ mg/mm^3	2.549
m, mm^{-1}	15.615
F(000), e	1632.0
Crystal size, mm^3	0.32 × 0.25 × 0.09
2Θ range for data collection	4.9 to 54.96°
Index ranges	$-9 \le h \le 11$, $-20 \le k \le 20$, $-21 \le l \le 21$
Reflections collected	22748
Independent reflections	5286 [*R*(int) = 0.0519]
Data/restraints/parameters	5286/0/192
Goodness-of-fit on F^2	1.043
Final *R* indexes [I ≥ 2σ (*I*)]	R_1 = 0.0263, wR_2 = 0.0608
Final *R* indexes [all data]	R_1 = 0.0304, wR_2 = 0.0621
Largest diff. peak / hole, e Å^{-3}	0.83 / –0.94
Flack parameter	0.05(2)

Table S4. Fractional atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for [HMIM][Br_9]. U_{eq} is defined as 1/3 of of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	U_{eq}
Br1	8716.6(6)	5370.3(3)	8101.4(3)	21.2(1)
Br2	5182.5(6)	5438.0(3)	7978.3(3)	24.60(11)
Br3	5285.9(6)	3171.6(3)	3996.8(3)	21.33(10)
Br4	5370.4(6)	6435.1(3)	3333.7(3)	25.45(11)
Br5	8381.7(5)	5148.4(3)	6348.2(3)	19.9(1)
Br6	4643.5(7)	7825.8(3)	3420.4(3)	31.59(13)
Br7	8017.3(6)	4970.0(3)	4956.7(3)	24.57(11)
Br8	2482.5(6)	5455.3(3)	7941.2(3)	27.72(12)
Br9	4336.5(7)	2063.6(3)	4776.0(3)	30.23(13)
N1	3279(5)	4014(3)	5941(2)	21.1(9)
N2	4884(5)	3296(3)	6661(2)	23.1(9)
C1	4757(6)	3781(3)	6013(3)	23.1(10)
C5	2458(6)	3674(4)	6557(3)	27.9(11)
C6	2658(7)	4530(3)	5280(3)	29.1(12)
C4	3436(6)	3224(3)	7000(3)	28.5(12)
C8	4037(7)	5870(3)	5650(3)	28.6(12)
C7	2524(7)	5451(4)	5506(4)	38.6(13)
C9	3945(7)	6797(3)	5730(4)	39.2(14)
C11	5347(8)	8153(3)	5924(3)	38.1(14)
C10	5469(8)	7230(4)	5906(4)	42.7(15)
C12	6297(7)	2883(4)	6920(3)	40.9(14)

Table S5. Anisotropic displacement parameters ($Å^2 \times 10^3$) for [HMIM][Br_9]. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka \times b \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	21.7(2)	21.4(2)	20.5(2)	–3.51(18)	–3.48(18)	0.4(2)
Br2	24.9(2)	28.1(3)	20.7(2)	–0.14(19)	0.87(18)	2.8(2)
Br3	23.9(2)	17.9(2)	22.1(2)	0.50(17)	–0.65(19)	1.7(2)
Br4	24.5(3)	25.2(3)	26.7(2)	5.1(2)	–3.5(2)	–4.1(2)
Br5	18.3(2)	17.3(2)	24.2(2)	–1.75(18)	1.40(17)	0.53(18)
Br6	31.3(3)	22.7(3)	40.7(3)	3.3(2)	–9.0(2)	–4.5(2)
Br7	31.7(3)	21.6(2)	20.4(2)	1.45(19)	4.94(19)	1.7(2)
Br8	24.5(2)	33.2(3)	25.5(2)	–6.6(2)	1.2(2)	2.8(2)
Br9	37.3(3)	20.4(3)	33.0(3)	5.5(2)	1.5(2)	–3.0(2)
N1	23(2)	20(2)	20.1(18)	–0.7(16)	–1.8(16)	3.0(17)
N2	22(2)	26(2)	20.5(18)	2.8(16)	–1.6(17)	–0.3(18)
C1	25(3)	24(3)	20(2)	4.7(19)	2(2)	–5(2)
C5	22(2)	39(3)	23(2)	–5(2)	–1(2)	–1(2)
C6	37(3)	30(3)	21(2)	3(2)	–14(2)	3(3)
C4	31(3)	32(3)	22(2)	3(2)	4(2)	–7(2)
C8	42(3)	21(3)	23(2)	2(2)	–4(2)	7(2)
C7	30(3)	38(3)	48(3)	8(3)	–4(3)	2(3)
C9	35(3)	33(3)	49(3)	18(3)	–16(3)	–7(3)
C11	47(4)	27(3)	40(3)	10(2)	–5(3)	–5(3)
C10	51(4)	35(3)	42(3)	11(3)	–10(3)	–5(3)
C12	36(3)	54(4)	33(3)	7(3)	–6(3)	11(3)

Table S6. Bond lengths for [HMIM][Br_9].

Atom	Atom	Length (Å)	Atom	Atom	Length(Å)
Br2	Br8	2.3352(7)	N2	C4	1.377(6)
Br3	Br9	2.3506(7)	N2	C12	1.456(7)
Br4	Br6	2.3285(8)	C5	C4	1.334(7)
Br5	Br7	2.3497(6)	C6	C7	1.533(8)
N1	C1	1.337(7)	C8	C7	1.491(8)
N1	C5	1.361(6)	C8	C9	1.499(7)
N1	C6	1.476(6)	C9	C10	1.519(9)
N2	C1	1.333(6)	C11	C10	1.488(8)

Table S7. Bond angles for [HMIM][Br_9].

Atom	Atom	Atom	Angle (deg)	Atom	Atom	Atom	Angle (deg)
C1	N1	C5	108.5(4)	C4	C5	N1	107.6(5)
C1	N1	C6	124.9(4)	N1	C6	C7	112.9(4)
C5	N1	C6	126.5(4)	C5	C4	N2	107.8(4)
C1	N2	C4	107.7(4)	C7	C8	C9	114.7(5)
C1	N2	C12	125.0(5)	C8	C7	C6	114.2(5)
C4	N2	C12	127.2(4)	C8	C9	C10	115.3(5)
N2	C1	N1	108.4(4)	C11	C10	C9	113.5(6)

Table S8. Hydrogen atom coordinates (Å × 10^4) and isotropic displacement parameters (Å^2 × 10^3) for [HMIM][Br_9].

Atom	*x*	*y*	*z*	U_{eq}
H1	5578	3934	5663	28
H5	1383	3745	6655	33
H6A	1623	4319	5128	35
H6B	3342	4475	4805	35
H4	3179	2911	7466	34
H8A	4742	5735	5198	34
H8B	4499	5640	6147	34
H7A	1976	5746	5067	46
H7B	1886	5500	5998	46
H9A	3208	6931	6168	47
H9B	3516	7027	5225	47
H11A	4971	8352	5402	57
H11B	6366	8393	6034	57
H11C	4621	8320	6348	57
H10A	5863	7035	6433	51
H10B	6232	7069	5491	51
H12A	6791	2617	6455	61
H12B	6046	2460	7325	61
H12C	7005	3293	7154	61