ESI

Contents

Table S1 Crystal data and structural refinement of **1**

Temperature	296 K	393 K	421 K
Chemical formula	$C_{24}H_{41}I_6N_4Pb_2$		
Wavelength (Å)	0.71073	0.71073	0.71073
CCDC numbers	1026623	1026624	1026625
Crystal system	orthorhombic	orthorhombic	triclinic
Space group	*Pbcn*	*Pbcn*	*P*-1
a (Å)	20.7859(13)	21.089(3)	8.9573(17)
b (Å)	8.8243(6)	8.9287(11)	14.924(3)
c (Å)	42.787(3)	42.348(5)	15.212(3)
α (°)	90	90	84.535(5)
β (°)	90	90	86.831(5)
γ (°)	90	90	89.177(5)
V(Å^3) / Z	7848.0(9)/8	7974.0(18)/8	2021.1(7)/2
Density (g·cm^{-3})	2.645	2.603	2.498
Abs coeff. (mm^{-1})	13.309	13.099	12.917
F(000)	5568.0	5568.0	1308.0
Data collect θ range	0.95-28.43	0.96-27.65	1.83-25.00
Index range	-26 ≤ h ≤ 27 -11 ≤ k ≤ 11 -54 ≤ l ≤ 45	-27≤ h ≤ 27 -11 ≤ k ≤ 10 -52 ≤ l ≤ 55	-10 ≤ h ≤ 10 -17 ≤ k ≤ 17 -18 ≤ l ≤ 18
Reflns collected	9697	9246	6880
Independent reflns	6322	4195	3383
Data/restraints/parameters	9697/0/327	9246/0/327	6880/389/306
Goodness-of-fit on F^2	1.069	1.006	0.953
Final R indices [I > 2σ(I)]	R_1 = 0.0489 wR_2= 0.1021	R_1 = 0.0713 wR_2 = 0.1428	R_1 = 0.0825 wR_2= 0.1953

$R_1 = \Sigma(||F_0|-|F_c||)/\Sigma|F_0|$, $wR_2 = \Sigma w(|F_0|^2-|F_c|^2)^2/\Sigma w\,(|F_0|^2)^2]^{1/2}$

Table S2 Selected bond lengths (Å) and bond angles (°) in **1** at 296, 393 and 421 K

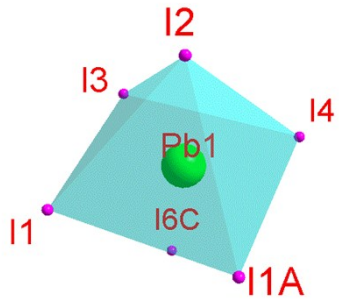
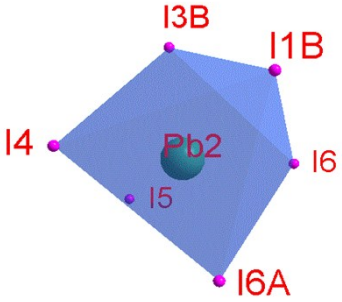
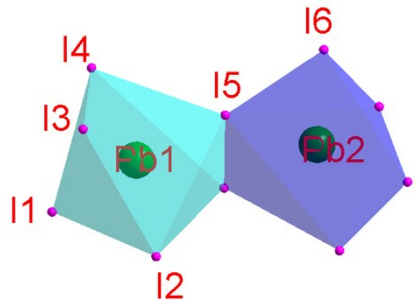
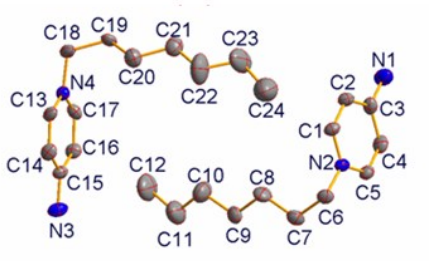
		1 (296 K)	**1** (393 K)	**1** (421 K)
	Pb1-I1	3.2650(5)	3.2451(12)	3.4150(17)
	Pb1-I2	3.0477(9)	3.0279(13)	3.066(2)
	Pb1-I3	3.1380(9)	3.2086(13)	3.023(2)
	Pb1-I4	3.1712(8)	3.0801(15)	3.331(2)
	Pb1-I6C	3.5167(9)	3.5530(8)	-
	I(2)-Pb(1)-I(3)	86.26(2)	89.20(4)	90.33(6)
	I(2)-Pb(1)-I(4)	93.87(2)	91.18(4)	104.45(5)
	I(3)-Pb(1)-I(4)	93.33(2)	91.27(4)	91.70(6)
	I(3)-Pb(1)-I(1A)	169.13(3)	177.46(4)	166.42(6)
	I(2)-Pb(1)-I(1A)	98.57(6)	102.79(3)	101.82(6)
	Pb2-I1B	3.5446(5)	3.4960(8)	3.6087(18)
	Pb2-I3B	3.0949(9)	3.1731(12)	-
	Pb2-I4	3.1955(8)	3.1376(15)	3.331(2)
	Pb2-I5	3.0416(9)	3.0340(13)	3.1379(19)
	I(5)-Pb(2)-I(3B)	88.77(2)	94.09(4)	-
	I(5)-Pb(2)-I(4)	90.89(2)	88.47(4)	90.31(6)
	I(3B)-Pb(2)-I(4)	89.83(2)	94.61(4)	-
	I(5)-Pb(2)-I(6)	88.31(2)	96.25(4)	102.72(6)
	I(4)-Pb(2)-I(6)	176.49(2)	169.44(4)	175.85(6)

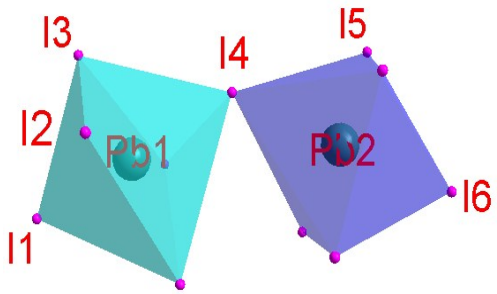
Table S3 Anisotropic and isotropic displacement parameters U_{ii} and U_{iso}(Å^2) of **1** at 296K, 393K and 421K

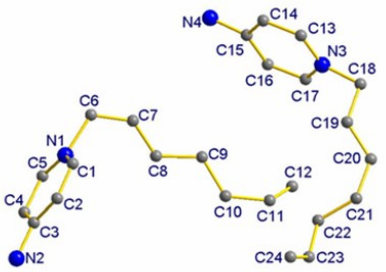




	1 at 296 K				**1** at 393 K			
Atom	U_{11}	U_{22}	U_{33}	U_{iso}	U_{11}	U_{22}	U_{33}	U_{iso}
Pb1	0.0419(2)	0.03126(19)	0.0355(2)	0.03623(11)	0.0636(5)	0.0491(3)	0.0544(4)	0.0557(2)
Pb2	0.0409(2)	0.03223(19)	0.0375(2)	0.03688(11)	0.0652(5)	0.0486(3)	0.0505(4)	0.0548(2)
I1	0.0593(5)	0.0472(4)	0.0440(4)	0.03688(11)	0.0691(8)	0.0655(6)	0.0597(7)	0.0648(3)
I2	0.0614(5)	0.0477(4)	0.0406(4)	0.0499(2)	0.1074(11)	0.0635(7)	0.0680(8)	0.0796(4)
I3	0.0525(5)	0.0520(4)	0.0517(5)	0.0521(2)	0.1072(11)	0.0553(6)	0.0827(9)	0.0818(4)
I4	0.0704(5)	0.0330(3)	0.0513(5)	0.0516(2)	0.0870(10)	0.0881(9)	0.0852(9)	0.0868(4)
I5	0.0641(5)	0.0405(4)	0.0435(4)	0.04939(19)	0.1049(11)	0.0787(7)	0.0636(8)	0.0824(4)
I6	0.0434(4)	0.0413(4)	0.0406(4)	0.04177(17)	0.0929(10)	0.0761(7)	0.0643(8)	0.0777(4)
N1	0.082(9)	0.074(8)	0.067(8)	0.074(3)	0.108(11)	0.096(10)	0.091(10)	0.098(5)
N2	0.046(6)	0.042(5)	0.035(5)	0.041(2)	0.081(7)	0.075(6)	0.069(6)	0.075(3)
N3	0.077(8)	0.056(6)	0.049(6)	0.061(3)	0.116(12)	0.127(11)	0.104(11)	0.116(5)
N4	0.042(5)	0.033(4)	0.046(5)	0.040(2)	0.090(7)	0.087(6)	0.079(7)	0.085(3)

C1	0.055(4)	0.050(4)	0.051(4)	0.0520(19)	0.087(7)	0.076(7)	0.072(7)	0.078(3)
C2	0.057(4)	0.053(4)	0.051(4)	0.054(2)	0.081(8)	0.071(7)	0.074(7)	0.075(4)
C3	0.056(5)	0.052(4)	0.049(4)	0.052(2)	0.088(9)	0.078(7)	0.071(8)	0.079(4)
C4	0.058(5)	0.045(4)	0.056(4)	0.053(2)	0.085(8)	0.068(7)	0.081(8)	0.078(4)
C5	0.055(4)	0.051(4)	0.053(4)	0.0531(19)	0.089(8)	0.085(7)	0.080(7)	0.085(3)
C6	0.055(4)	0.053(4)	0.052(4)	0.054(2)	0.089(8)	0.086(7)	0.082(7)	0.086(4)
C7	0.057(5)	0.061(4)	0.058(4)	0.058(2)	0.098(8)	0.113(8)	0.092(8)	0.101(4)
C8	0.061(4)	0.066(4)	0.066(4)	0.064(2)	0.107(8)	0.124(8)	0.105(8)	0.112(4)
C9	0.064(5)	0.074(5)	0.071(5)	0.070(3)	0.125(11)	0.162(10)	0.120(10)	0.135(5)
C10	0.080(6)	0.093(6)	0.082(6)	0.085(3)	0.136(11)	0.176(11)	0.130(11)	0.147(5)
C11	0.084(7)	0.107(7)	0.090(7)	0.094(3)	0.140(12)	0.199(12)	0.129(12)	0.156(6)
C12	0.096(9)	0.125(10)	0.098(9)	0.106(5)	0.19(2)	0.26(2)	0.18(2)	0.211(10)
C13	0.053(4)	0.043(4)	0.050(4)	0.0488(18)	0.094(8)	0.090(7)	0.079(7)	0.088(4)
C14	0.054(4)	0.039(4)	0.049(4)	0.048(2)	0.093(8)	0.074(7)	0.086(8)	0.084(4)
C15	0.052(5)	0.047(4)	0.047(4)	0.049(2)	0.093(9)	0.090(8)	0.079(8)	0.088(4)
C16	0.053(4)	0.040(4)	0.051(4)	0.048(2)	0.095(8)	0.086(7)	0.073(8)	0.084(3)
C17	0.051(4)	0.048(4)	0.052(4)	0.0507(19)	0.092(8)	0.086(7)	0.087(7)	0.087(3)
C18	0.054(4)	0.049(4)	0.052(4)	0.0516(19)	0.096(8)	0.098(7)	0.087(7)	0.093(4)
C19	0.054(4))	0.058(4)	0.058(4	0.057(2)	0.103(8)	0.117(8)	0.098(8)	0.106(4)
C20	0.064(4)	0.067(4)	0.066(4)	0.066(2)	0.107(8)	0.123(8)	0.107(8)	0.112(4)
C21	0.075(6)	0.087(5)	0.078(5)	0.080(3)	0.113(10)	0.139(9)	0.113(10)	0.122(5)
C22	0.091(6)	0.107(6)	0.095(6)	0.098(3)	0.133(11)	0.162(10)	0.130(10)	0.142(5)
C23	0.091(7)	0.121(7)	0.098(7)	0.103(4)	0.136(12)	0.185(12)	0.141(12)	0.154(6)
C24	0.115(10)	0.136(10)	0.115(10)	0.122(5)	0.19(2)	0.26(2)	0.19(2)	0.217(11)





1 at 393 K					**1** at 421 K			
Atom	U_{11}	U_{22}	U_{33}	U_{iso}	U_{11}	U_{22}	U_{33}	U_{iso}
Pb1	0.0636(5)	0.0491(3)	0.0544(4)	0.0557(2)	0.0552(4)	0.0719(5)	0.0568(5)	0.0618(2)
Pb2	0.0652(5)	0.0486(3)	0.0505(4)	0.0548(2)	0.0582(4)	0.0670(5)	0.0742(6)	0.0668(3)
I1	0.0691(8)	0.0655(6)	0.0597(7)	0.0648(3)	0.0798(9)	0.0751(9)	0.0600(8)	0.0719(4)
I2	0.1074(11)	0.0635(7)	0.0680(8)	0.0796(4)	0.1155(13)	0.0828(11)	0.0912(11)	0.0970(5)
I3	0.1072(11)	0.0553(6)	0.0827(9)	0.0818(4)	0.0798(10)	0.1723(17)	0.0688(10)	0.1097(6)
I4	0.0870(10)	0.0881(9)	0.0852(9)	0.0868(4)	0.0877(10)	0.0873(11)	0.1271(14)	0.0995(6)
I5	0.1049(11)	0.0787(7)	0.0636(8)	0.0824(4)	0.0799(10)	0.1395(14)	0.0772(10)	0.0986(5)
I6	0.0929(10)	0.0761(7)	0.0643(8)	0.0777(4)	0.0950(12)	0.0827(11)	0.1672(18)	0.1181(7)
N1	0.108(11)	0.096(10)	0.091(10)	0.098(5)	0.132(18)	0.108(15)	0.054(12)	0.100(7)
N2	0.081(7)	0.075(6)	0.069(6)	0.075(3)	0.106(15)	0.19(2)	0.070(13)	0.122(8)
N3	0.116(12)	0.127(11)	0.104(11)	0.116(5)	0.094(13)	0.074(12)	0.095(14)	0.089(6)
N4	0.090(7)	0.087(6)	0.079(7)	0.085(3)	0.16(2)	0.079(14)	0.17(2)	0.137(9)
C1	0.087(7)	0.076(7)	0.072(7)	0.078(3)	0.085(17)	0.11(2)	0.11(2)	0.106(9)
C2	0.081(8)	0.071(7)	0.074(7)	0.075(4)	0.039(10)	0.14(2)	0.061(14)	0.080(7)

C3	0.088(9)	0.078(7)	0.071(8)	0.079(4)	0.080(15)	0.084(15)	0.073(15)	0.079(6)
C4	0.085(8)	0.068(7)	0.081(8)	0.078(4)	0.110(17)	0.114(18)	0.049(13)	0.091(7)
C5	0.089(8)	0.085(7)	0.080(7)	0.085(3)	0.080(16)	0.109(19)	0.12(2)	0.102(9)
C6	0.089(8)	0.086(7)	0.082(7)	0.086(4)	0.12(2)	0.17(3)	0.075(18)	0.124(10)
C7	0.098(8)	0.113(8)	0.092(8)	0.101(4)	0.25(4)	0.33(5)	0.13(3)	0.23(2)
C8	0.107(8)	0.124(8)	0.105(8)	0.112(4)	0.62(13)	0.50(9)	0.13(4)	0.42(5)
C9	0.125(11)	0.162(10)	0.120(10)	0.135(5)	0.22(4)	1.67(4)	0.14(4)	0.67(2)
C10	0.136(11)	0.176(11)	0.130(11)	0.147(5)	0.36(9)	1.39(13)	0.24(6)	0.64(5)
C11	0.140(12)	0.199(12)	0.129(12)	0.156(6)	0.43(12)	0.60(13)	0.40(9)	0.46(6)
C12	0.19(2)	0.26(2)	0.18(2)	0.211(10)	0.11(3)	0.27(6)	0.88(18)	0.42(6)
C13	0.094(8)	0.090(7)	0.079(7)	0.088(4)	0.098(2)	0.098(2)	0.098(2)	0.0979(19)
C14	0.093(8)	0.074(7)	0.086(8)	0.084(4)	0.1146(14)	0.1145(15)	0.1146(15)	0.1145(14)
C15	0.093(9)	0.090(8)	0.079(8)	0.088(4)	0.097(2)	0.097(2)	0.097(2)	0.0974(19)
C16	0.095(8)	0.086(7)	0.073(8)	0.084(3)	0.096(18)	0.109(19)	0.11(2)	0.104(8)
C17	0.092(8)	0.086(7)	0.087(7)	0.087(3)	0.081(15)	0.054(13)	0.13(2)	0.089(7)
C18	0.096(8)	0.098(7)	0.087(7)	0.093(4)	0.11(2)	0.14(2)	0.13(2)	0.127(10)
C19	0.103(8)	0.117(8)	0.098(8)	0.106(4)	0.34(6)	0.16(3)	0.18(4)	0.23(2)
C20	0.107(8)	0.123(8)	0.107(8)	0.112(4)	0.19(5)	0.74(14)	0.30(4)	0.42(5)
C21	0.113(10)	0.139(9)	0.113(10)	0.122(5)	0.41(8)	0.45(8)	0.24(4)	0.38(4)
C22	0.133(11)	0.162(10)	0.130(10)	0.142(5)	0.21(6)	0.10(3)	1.0(2)	0.46(7)
C23	0.136(12)	0.185(12)	0.141(12)	0.154(6)	0.32(6)	0.17(4)	0.25(5)	0.24(2)
C24	0.19(2)	0.26(2)	0.19(2)	0.217(11)	0.27(6)	0.26(6)	0.27(6)	0.27(3)

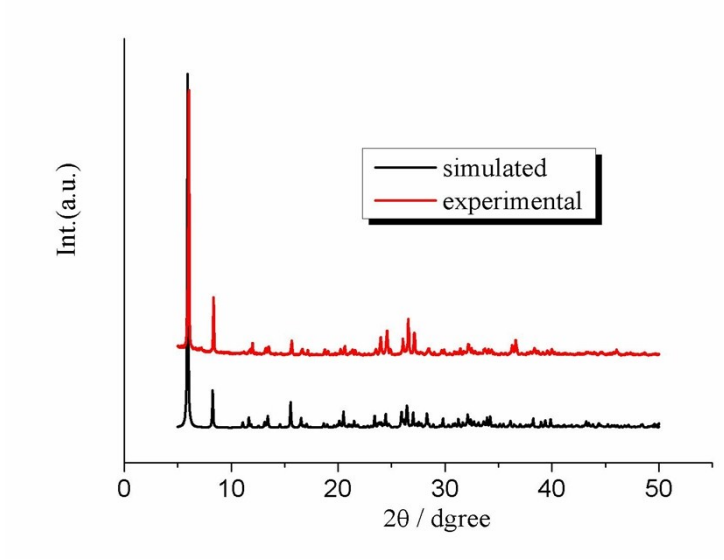


Figure S1 Powder X-ray diffraction patterns at 298 K (experimental and simulated profiles) for as-prepared sample of **1** which confirms the phase purity of the as-prepared sample.

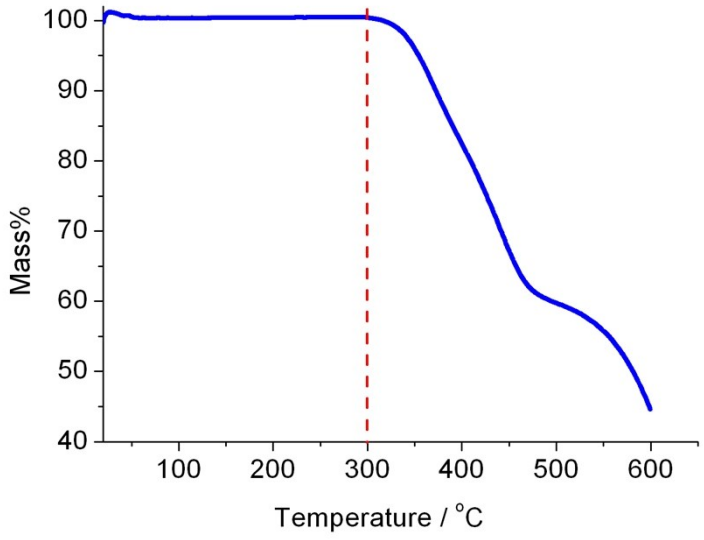


Figure S2 TGA curve for **1** (the measurements were performed under N_2 atmosphere) disclosed that **1** is thermally stable below 300 °C.

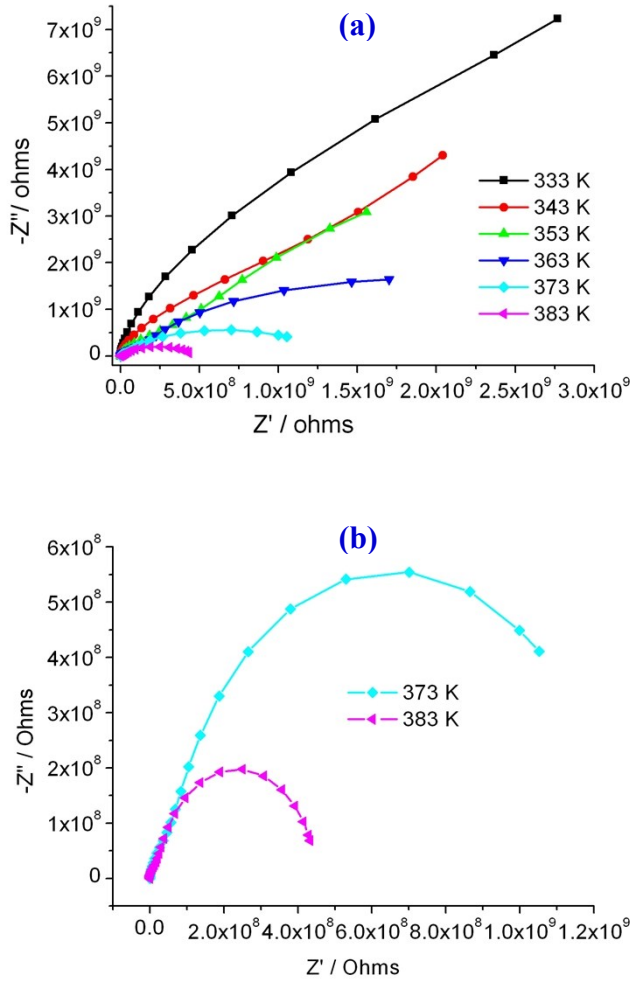


Figure S3 Complex impedance plots of **1** at selected temperatures (a) at 333, 343, 353, 363, 373 and 383 K (b) the enlarged one at 373 and 383 K.

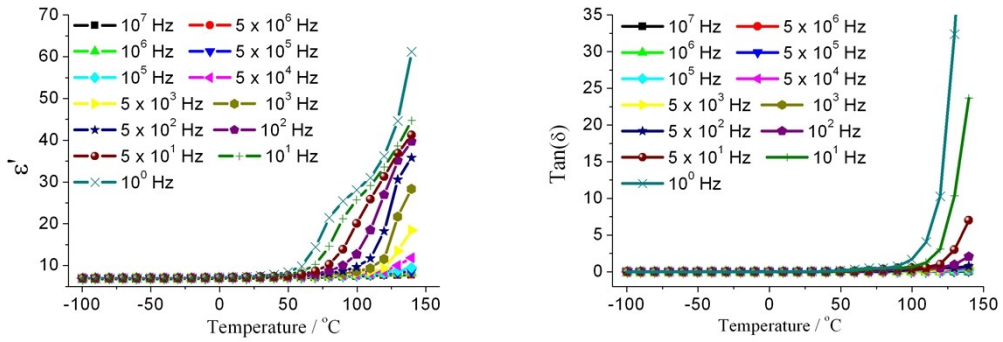


Figure S4 Variation in dielectric constant permittivity of both real and imaginary parts with temperature for **1**.

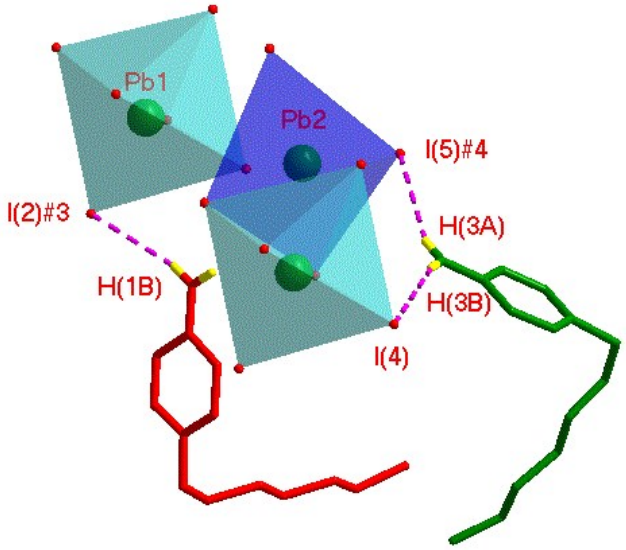


Figure S5 H-bonding interactions between the cation and the inorganic double chain for **1** in LT phase (at 296 K).

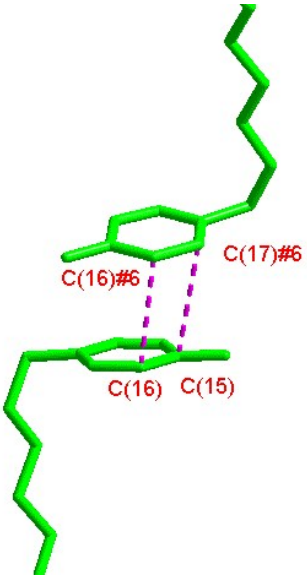


Figure S6 The π…π stacking between two adjacent pyridyl rings containing N(3) atom for **1** in HT phase (at 421 K).

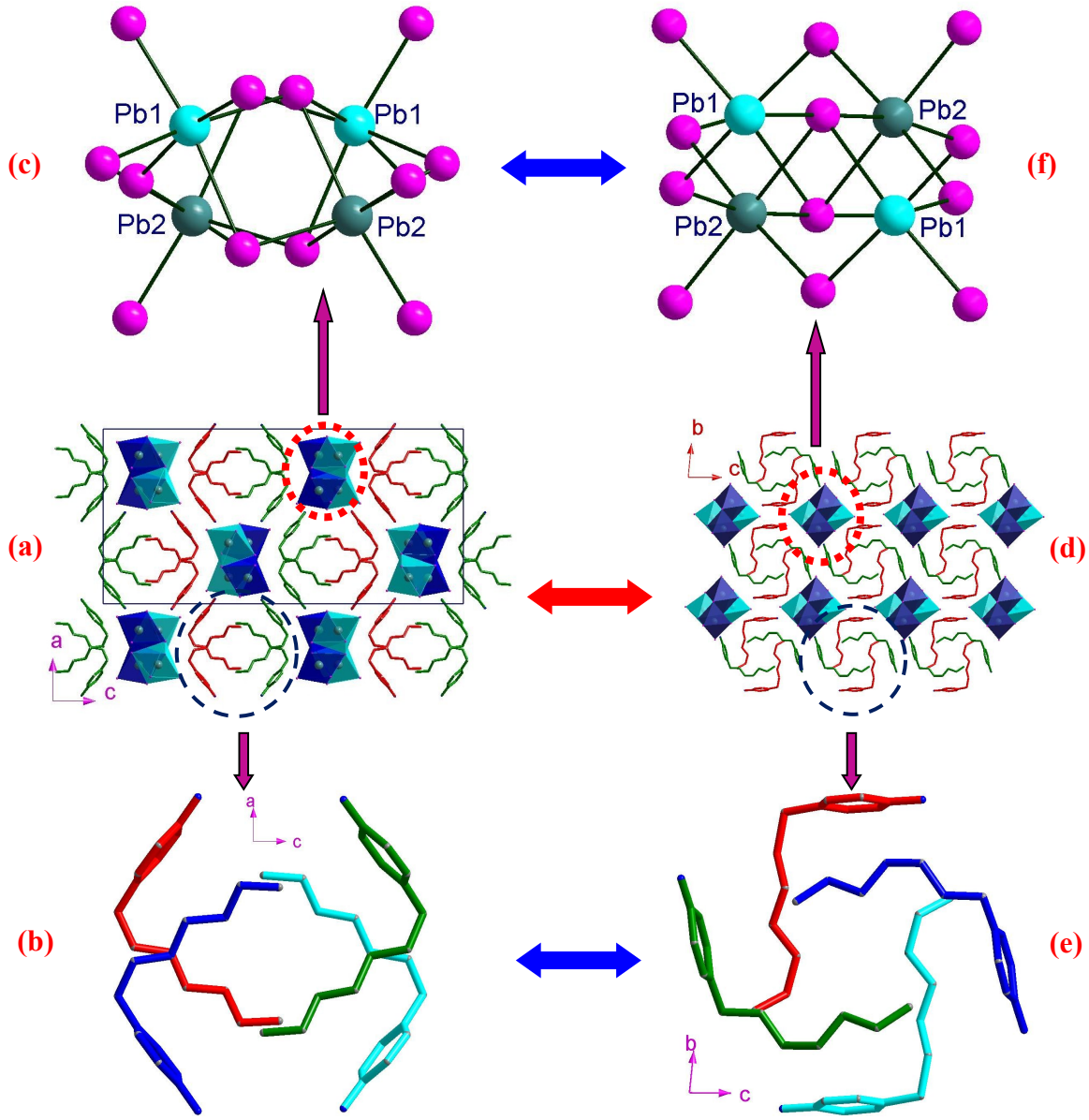


Figure S7 Illustration for the relative orientation changes between neighbouring cations in a cation arrangement as well as within an anion chain in (a, b and c) LT phase (d, e and f) HT phase viewed along the inorganic chain direction.

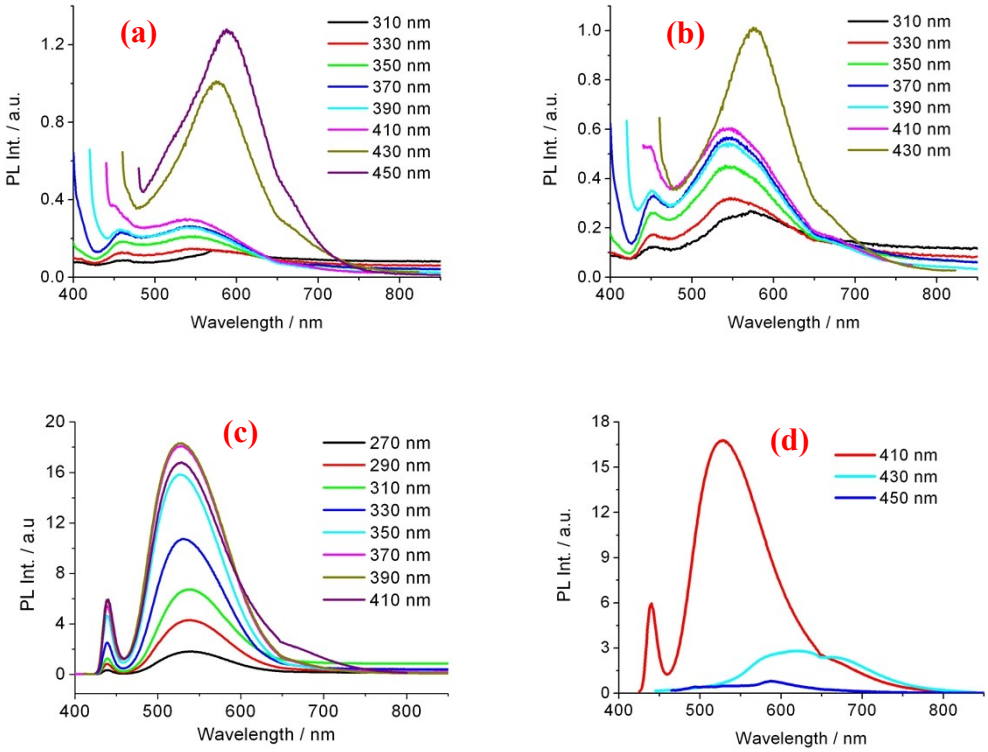


Figure 8 Solid-state PL spectra of **1** at (a) 223 K (b) 173 K (c, d) 10 K under variation of excited light.