Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary material for

Down and Up Conversion Luminescence of the Lead-Free Organic Metal Halide Material: $(C_9H_8NO)_2\,SnCl_6\,2H_2O$

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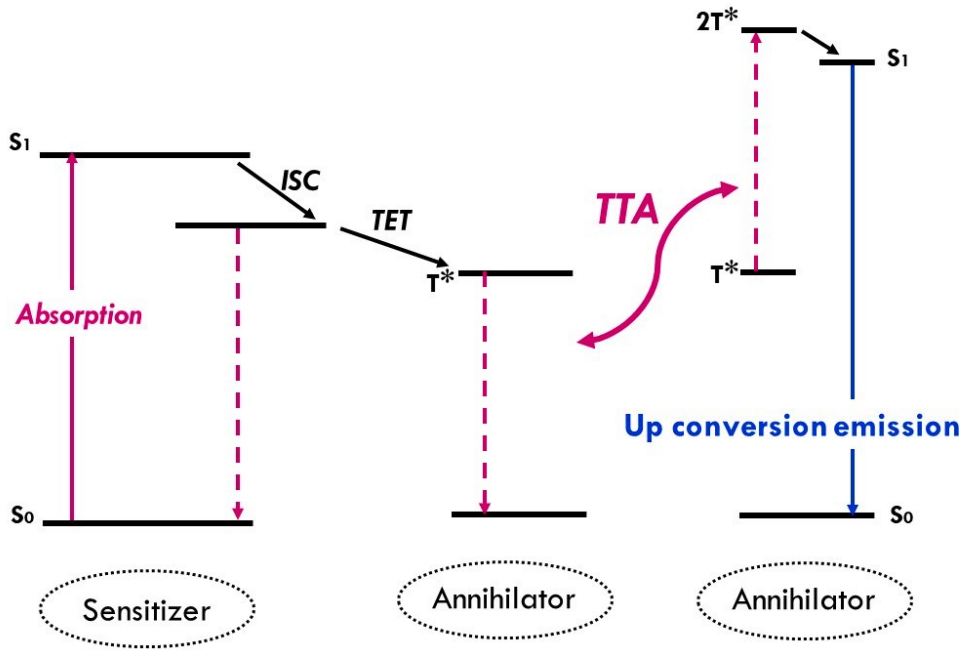

Figure S1. Schematic illustration of the triplet–triplet annihilation up conversion mechanism (TTA-UC). The triplet levels may occur with a sensitizer via intersystem crossing (ISC). It may also take place without a sensitizer via spin-orbit coupling (SOC) or via singlet–triplet fission (SF) within the annihilator.

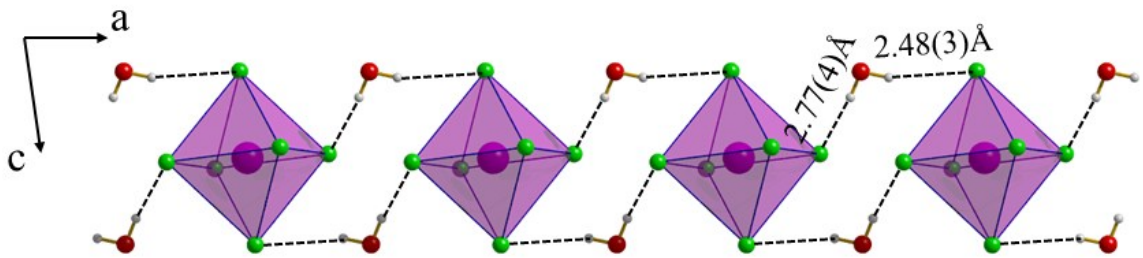

Figure S2. Packing of the $SnCl_6$ octahedra along the crystallographic axis a, indicating the shortest Cl…H-O hydrogen bonds through the lattice water molecules.

Table S1. Crystallographic data for $[HQ]_2SnCl_6.2H_2O$.

Chemical formula	$(C_9H_8NO)_2SnCl_6.2(H_2O)$
Formula weight/gmol^{-1}	659.75
Temperature (K)	100
Space group	P-1
a/Å	7.2113(5)
b/Å	9.5272(7)
c/Å	9.5104(7)
α/°	83.192(2)
β/°	79.981(2)
γ/°	71.109(2)
Volume/Å^3	607.42(8)
Z	1
Θ_{max}/°	33.249
Collected reflections	15030
Ref. independent [$F^2 > 2s(F^2)$]	4654 [4141]
μ / mm^{-1}	1.740

Tmin / Tmax	0.677 / 0.746
R_{int}	0.0286
[a]R1 [$F^2 > 2*s(F^2)$]	0.0331 [0.0261]
[a]wR2 [$F^2 > 2*s(F^2)$]	0.0635 [0.0607]
[b]Goodness-of-fit on F^2	0.991
Largest diff. peak/hole / e^- $Å^{-3}$	0.716 / -0.520

[a]*$R_1=\Sigma(Fo-Fc|/Fo)$ and $wR2= \{\Sigma[w(F_o^2-F_c^2)^2]/ \Sigma[w(F_o^2)^2]\}^{1/2}$*

[b]*$G.O.F = [(\Sigma(w(Fo^2-Fc^2))^2/(Nobs-Nvar)]^{1/2}$*

Table S2. Selected bond distances (Å) and bond angles (°).

Sn-Cl1	2.4372(4)	C6-C1	1.417(2)
Sn-Cl2	2.4251(5)	C5-C7	1.415(3)
Sn-Cl3	2.4294(4)	C7-C8	1.375(3)
C1-O2	1.345(2)	C8-C9	1.392(3)
C1-C2	1.374(2)	C9-N1	1.333(2)
C2-C3	1.411(3)	N1-C6	1.370(2)
C3-C4	1.371(3)	Cl1-Sn-Cl2	89.346(15)
C4-C5	1.421(3)	Cl1-Sn-Cl3	90.327(14)
C5-C6	1.416(2)	Cl2-Sn-Cl3	90.150(16)

Table S3. Distortion parameters.

λ_{oct}[a]	0.9999
σ^2_{oct} (°²)[b]	0.2026

$\lambda_{oct} = \frac{1}{6}\sum_{i=1}^{6}(d_i/d_0)^2$ [a] is the quadratic octahedral elongation, where d_i are the six independent Sn–Cl bond lengths, d_0 is the mean Sn–Cl bond length. [b] $\sigma_{oct}^2 = \frac{1}{11}\sum_{i=1}^{12}(\alpha_i - 90)^2$ is the octahedral angle variance, where α_i are the Cl–Sn–Cl angles. [1,2]

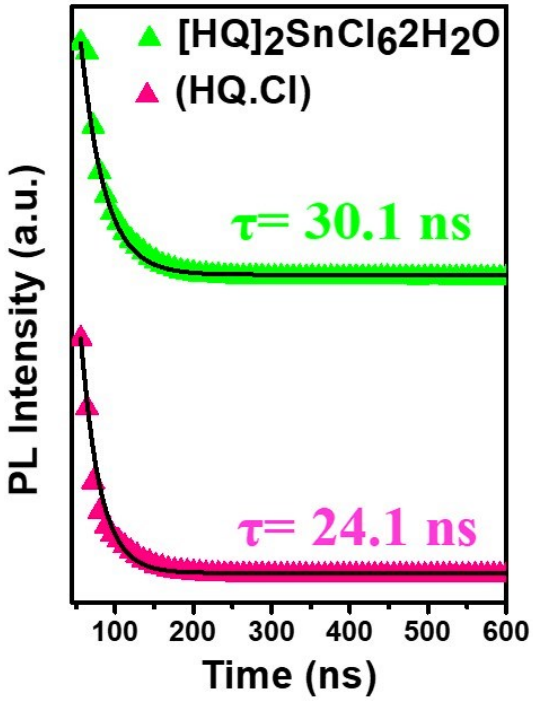

Fig. S3 Time-Resolved PL lifetime of $[HQ]_2SnCl_6.2H_2O$ and (HQ.Cl) salt under 375 nm excitation.

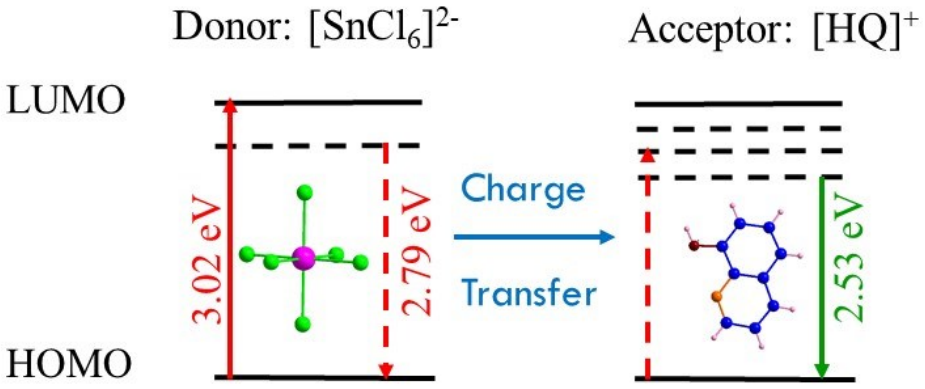

Fig. S4 Energy diagram of $[HQ]_2SnCl_6.2H_2O$ electronic structure. The HOMO and LUMO levels for $[SnCl_6]^{2-}$ dianions and $[HQ]^+$ cations are included. Red dashed arrows correspond to non-radiative transitions illustrating the conversion of inorganic excitation to organic one.

References

[1] D Cortecchia, S Neutzner, ARS Kandada, E Mosconi, D Meggiolaro, F De Angelis, C Soci and A Petrozza; *J. Am. Chem. Soc*. (2017), **139**, 39−42.

[2] K. Robinson, G. V. Gibbs, P. H. Ribbe, *Science* (1971), **172**, 567.