Electronic Supplementary Information

Exploring the Surface Chemistry of Cesium Lead Halide Perovskite Nanocrystals

Roberto Grisorio,[a,b] Milvia Elena Di Clemente,[c] Elisabetta Fanizza,[c,d] Ignazio Allegretta,[e] Davide Altamura,[f] Marinella Striccoli,[c,d] Roberto Terzano,[e] Cinzia Giannini,[f] Mihai Irimia-Vladu,[g] Gian Paolo Suranna[a,b]*

[a]*Dipartimento di Ingegneria Civile, Ambientale, del Territorio, Edile e di Chimica (DICATECh), Politecnico di Bari, Via Orabona 4, 70125 Bari, Italy.* E-mail: roberto.grisorio@poliba.it

[b]*CNR NANOTEC − Istituto di Nanotecnologia, Via Monteroni, 73100 Lecce, Italy.*

[c]*Dipartimento di Chimica, Università degli Studi di Bari " A. Moro", Via Orabona 4 , 70126 Bari, Italy.*

[d]*CNR-Istituto per i Processi Chimico Fisici, UOS Bari, Via Orabona 4 , 70126 Bari, Italy*

[e]*Dipartimento di Scienze del Suolo, della Pianta e degli Alimenti, Università degli Studi di Bari "Aldo Moro", Via G. Amendola 165/A, 70126 Bari, Italy*

[f]*Institute of Crystallography, National Research Council, via Amendola 122/O, Bari 70126, Italy*

[g]*Joanneum Research MATERIALS - Institute for Surface Technologies and Photonics, Franz-Pichler Straße 30, Weiz A-8160, Austria.*

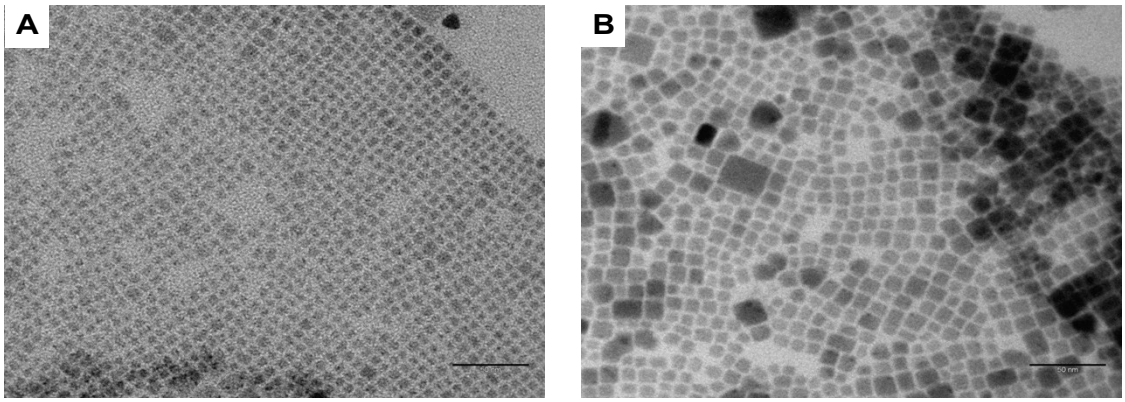

Figure S1. *TEM images of as-prepared $CsPbCl_3$ (A) and $CsPbI_3$ (B) NCs. Scale bar = 100 nm.*

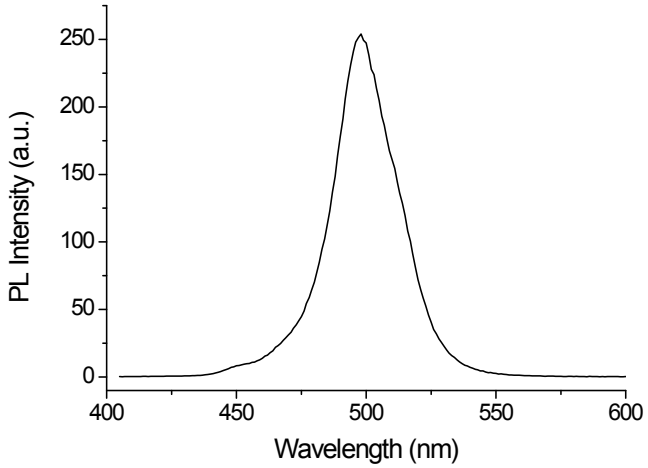

Figure S2. *PL spectrum (recorded in cyclohexane) of the supernatant recovered after the purification step for $CsPbBr_3$ NCs.*

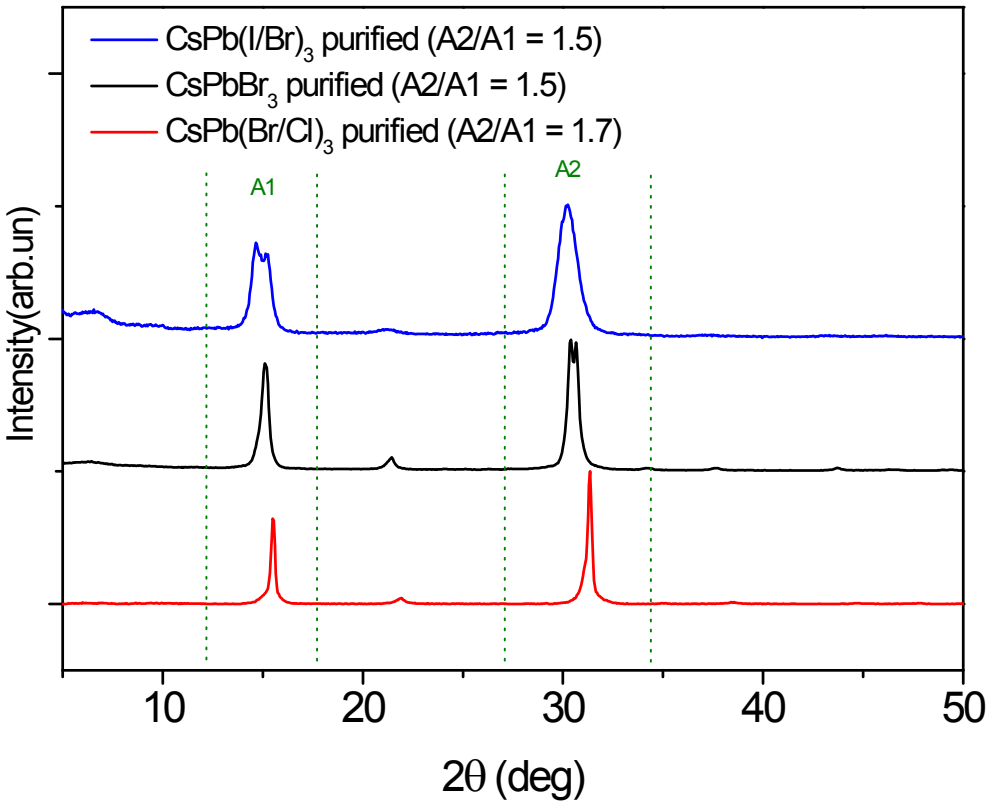

Figure S3. *XRD θ/2θ scans from purified samples, showing the intensity ratio (in the legend) between the integrated areas under the two main peaks (A1 and A2).*

Figure S4. *As-prepared (left) and purified (right) $CsPbBr_3$ NCs samples in the solid state after three weeks storage under ambient conditions and room light.*

Table S1. Element concentration (atomic %) and obtained molar ratios of the studied samples analyzed via FEG-SEM-EDX (n=3).

Sample	Element concentration (atomic %)										Molar ratios				
	Cs		Pb		Cl		Br		I		Cs	Pb	Cl	Br	I
	Conc	SD	Conc	SD	Conc	SD	Conc	SD	Conc	SD					
$CsPbI_3$	21.33	0.58	16.88	0.64	-	-	-	-	61.79	0.07	1.3	1.0	-	-	3.7
$CsPb(I/Br)_3$	23.90	0.85	17.40	0.33	-	-	34.95	1.44	23.74	0.64	1.4	1.0	-	2.0	1.4
pur. $CsPb(I/Br)_3$	24.23	0.26	18.63	0.29	-	-	48.05	0.79	9.09	0.30	1.3	1.0	-	2.6	0.5
$CsPb(Br/Cl)_3$	25.00	0.21	19.10	0.13	29.21	0.37	26.69	0.41	-	-	1.3	1.0	1.5	1.4	-
pur. $CsPb(Br/Cl)_3$	22.13	0.28	19.48	0.45	30.80	0.09	27.59	0.45	-	-	1.1	1.0	1.6	1.4	-
$CsPbBr_3$	24.16	0.77	19.99	0.20	-	-	55.85	0.85	-	-	1.2	1.0	-	2.8	-
pur. $CsPbBr_3$	25.02	0.26	19.60	0.20	-	-	55.37	0.05	-	-	1.3	1.0	-	2.8	-
$CsPbCl_3$	21.10	0.70	19.36	0.82	59.54	0.61	-	-	-	-	1.1	1.0	3.1	-	-

Conc = concentration
SD = standard deviation

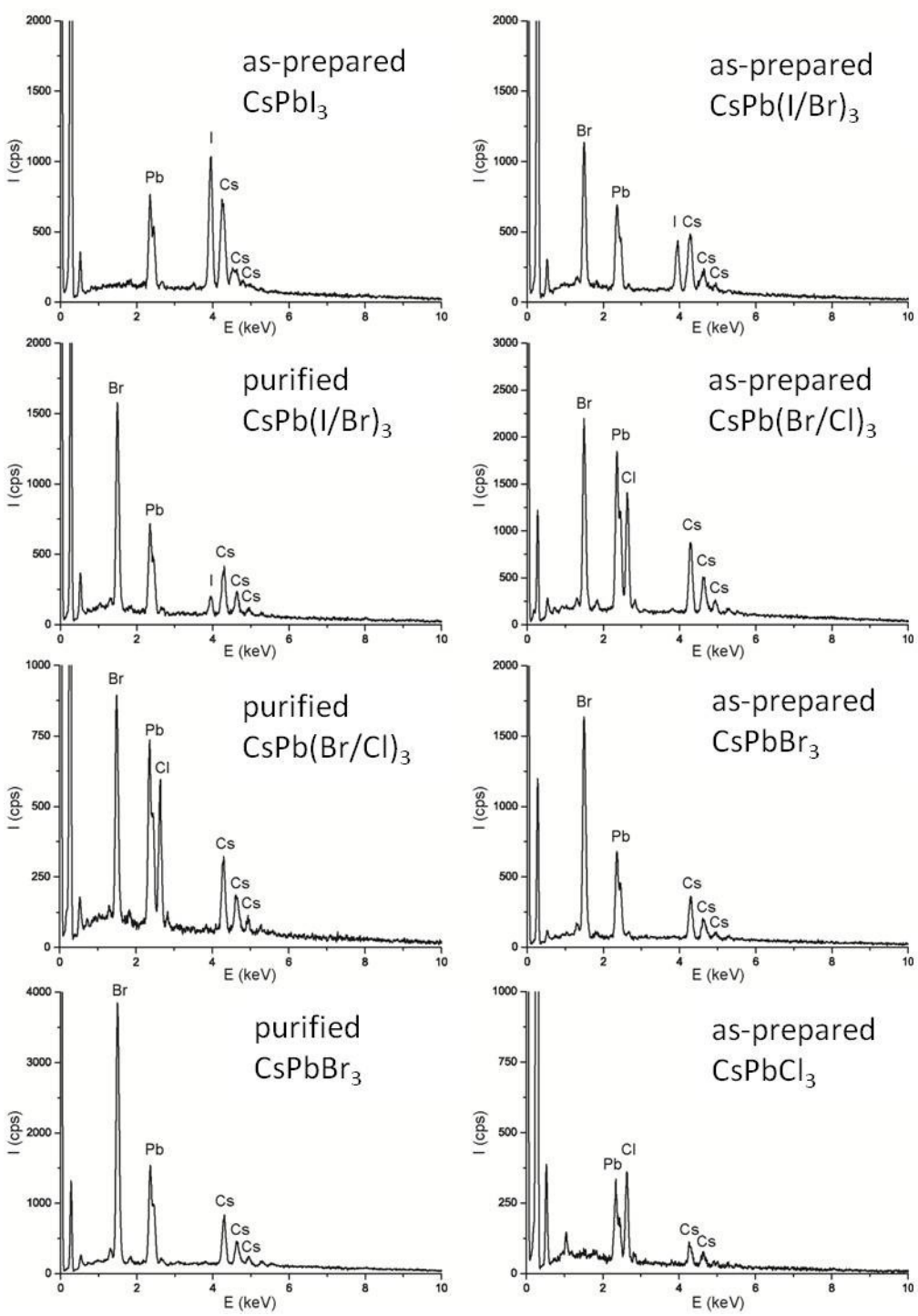

Figure S5. *EDX profiles of as-prepared and purified NCs.*

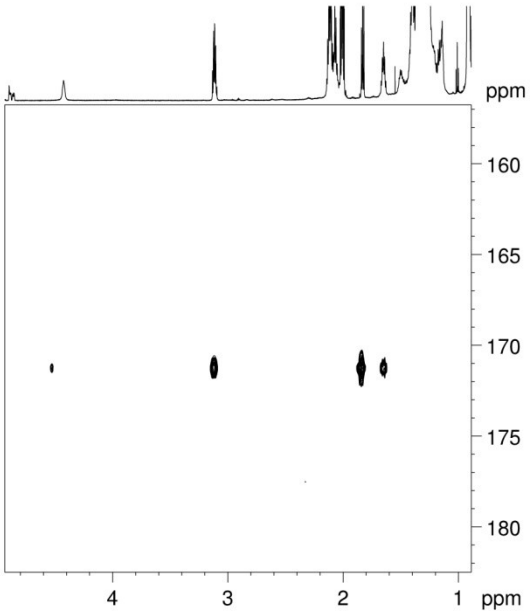

Figure S6. *HMBC spectrum in C_6D_6 of the supernatant solution containing the amide, highlighting the presence of the –CONH– group at δ = 171.8 ppm.*

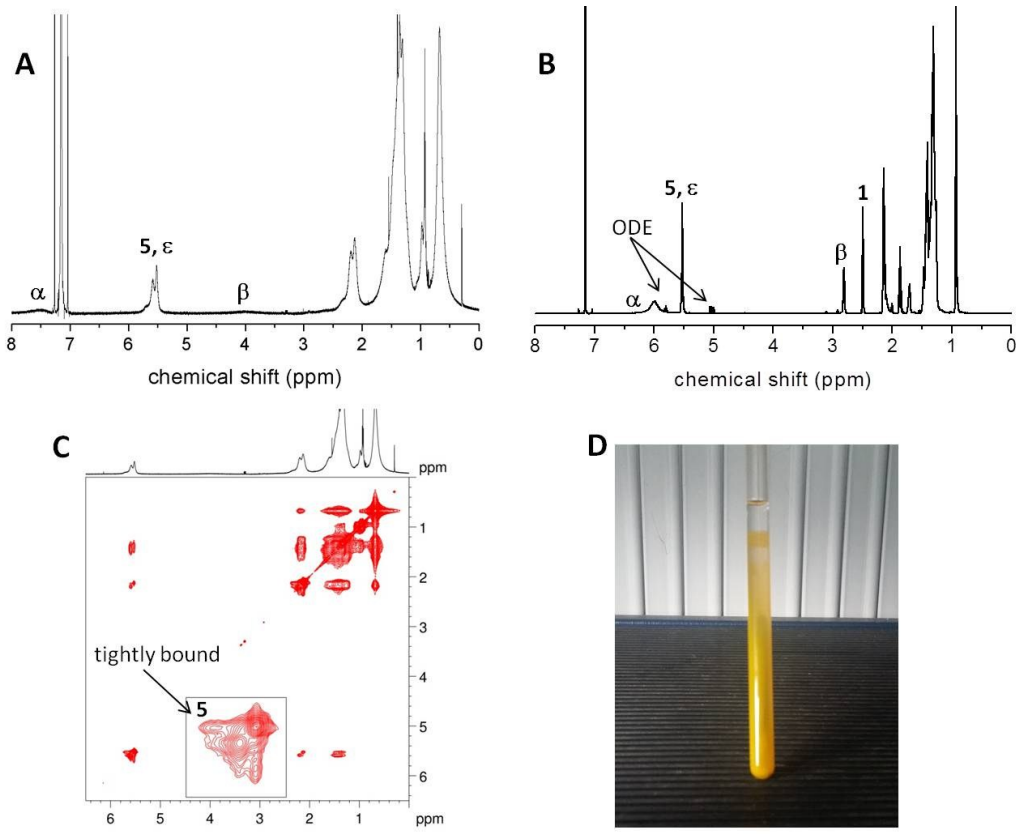

Figure S7. *(A) ^{1}H-NMR spectrum of the twice-purified $CsPbBr_3$ NCs in C_6D_6. (B) ^{1}H-NMR spectrum of the supernatant solution obtained from the relevant centrifugation in C_6D_6. (C) 2D-NOESY spectrum of twice-purified $CsPbBr_3$ NCs in C_6D_6; the inset shows an expansion of the vinylene region. (D) Picture of the same solution stored for one week in ambient conditions.*

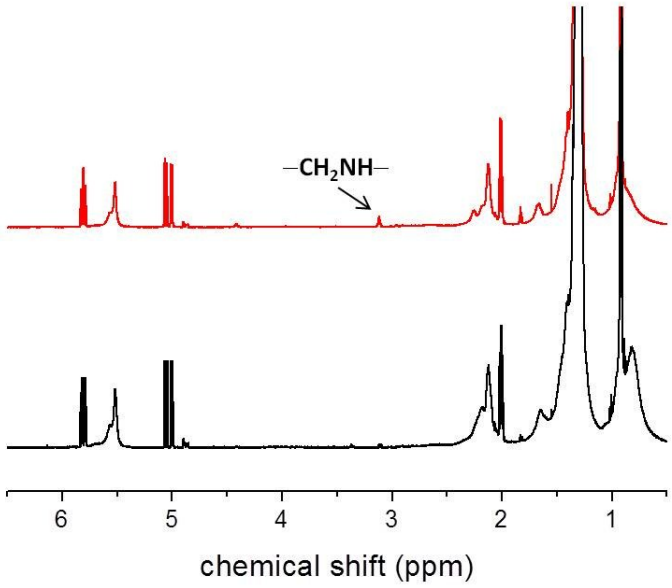

Figure S8. *^{1}H-NMR spectra of purified $CsPbBr_3$ NCs (bottom) and the relevant sample stored in ambient conditions for three weeks in C_6D_6. The arrow points to one of the typical methylene signals ($–CH_2NHCO–$) attributable to the amide presence.*

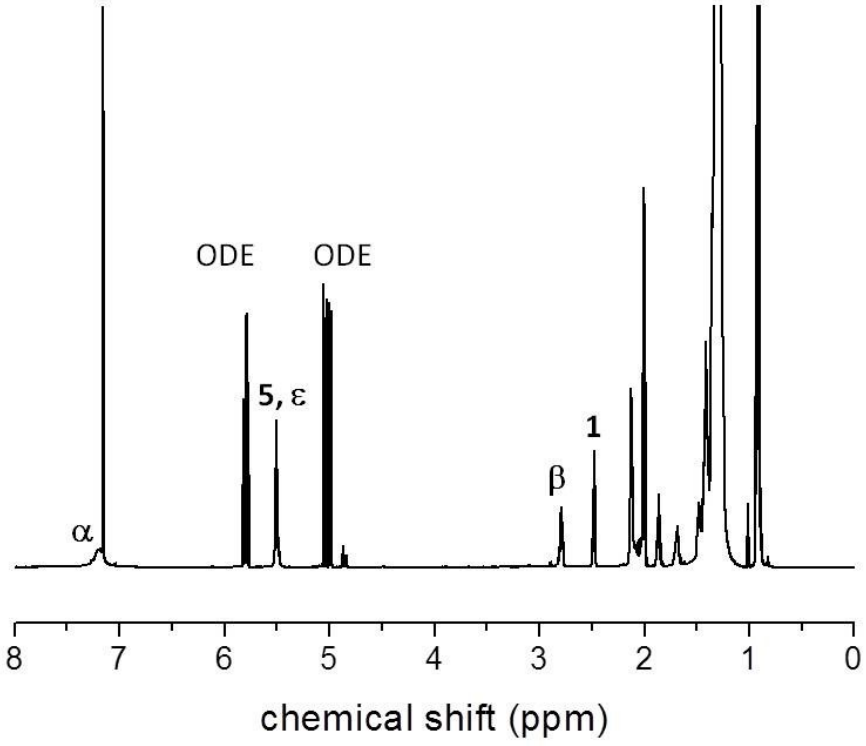

Figure S9. *^{1}H-NMR spectrum in C_6D_6 of PbI_2/OLA/OLAm/ODE mixture used for the synthesis of $CsPbI_3$ NCs immediately before the addition of cesium-oleate. No signals attributable to the amide are present.*

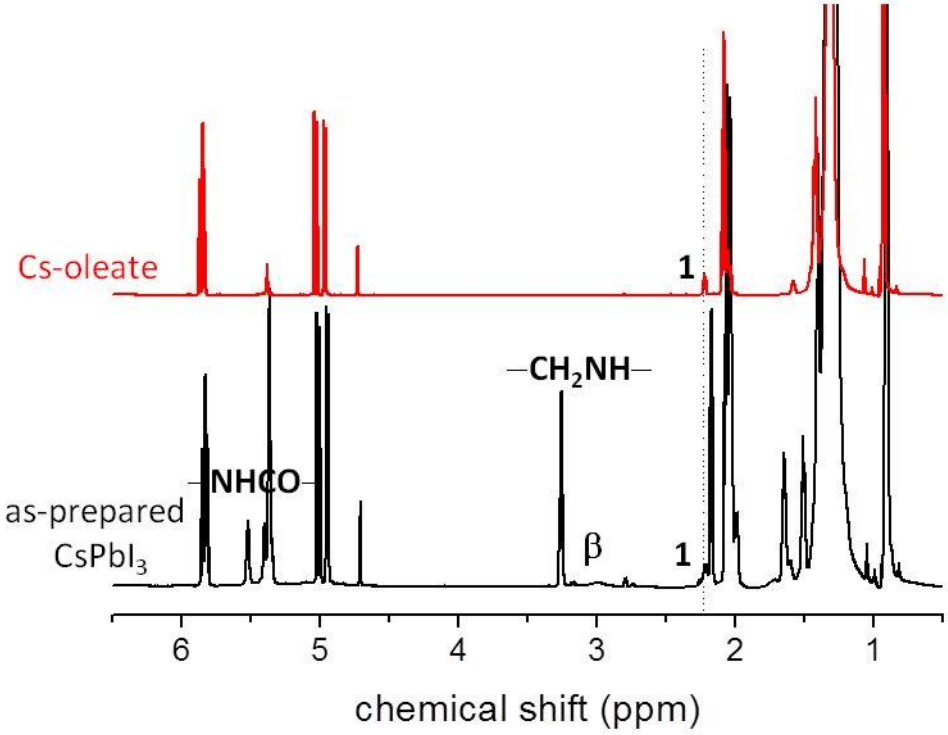

Figure S10. *Comparison between the ^{1}H-NMR spectra of as-prepared $CsPbI_3$ NCs and cesium-oleate in $CDCl_3$.*

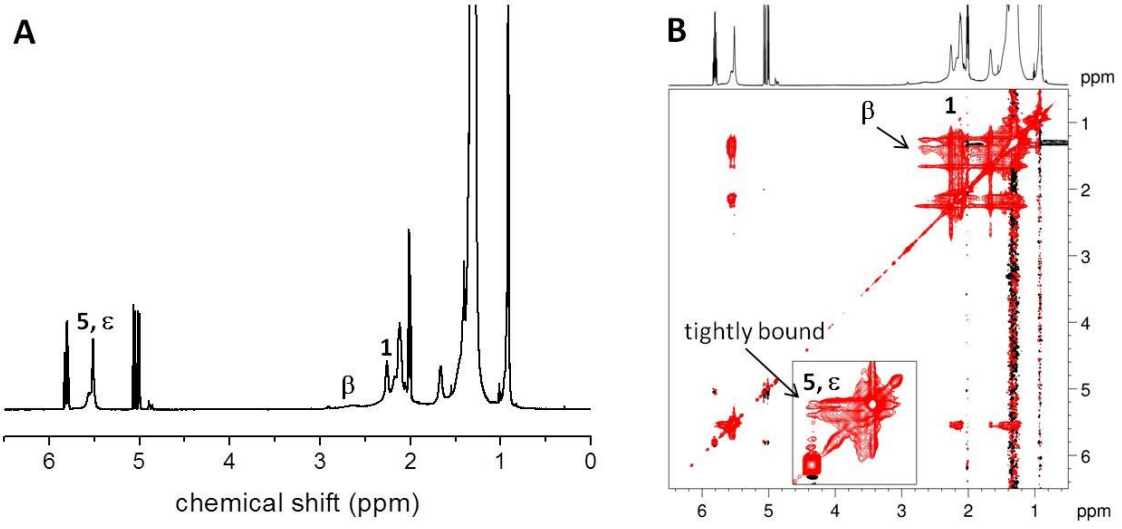

Figure S11. *(A) ^{1}H-NMR spectrum of as-prepared $CsPb(Br/Cl)_3$ NCs in C_6D_6 and (B) the relevant 2D-NOESY spectrum.*

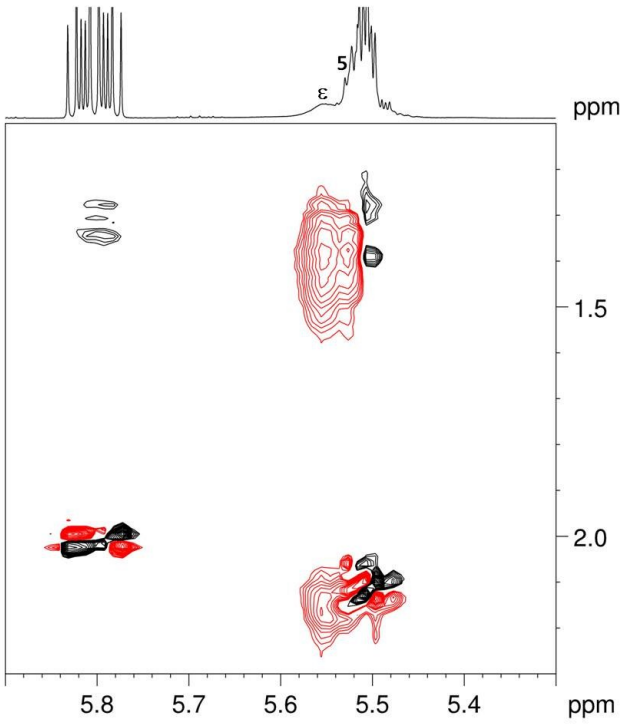

Figure S12. *Expansion of the vinylene region of the2D-NOESY spectrum of as-prepared* $CsPb(I/Br)_3$ *NCs in* C_6D_6 *evidencing the absence of tightly bound ligands.*