Metal-free perovskites for non-linear optical materials —Supplementary Information—

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S1. STRUCTURES AND GEOMETRIES OF METAL-FREE–PEROVSKITES

Table S1 and Table S2 reports the structural parameters of the metal-free perovskites considered in this study as optimised using CRYSTAL17[1,2] as discussed in the manuscript and at the PBE0Sol-D3 level of theory.

TABLE S1. Structural parameters in Å and degrees of the fully optimised DABCO-based structures. Whenever available the relative difference from the experimental lattice constants by Ye *et al.*[3] are also reported in brackets.

MDABCO-NH_4X_3							
X	Space group	a	a_{Exp}	α	α_{Exp}	—	—
Cl	$R3$	6.482	—	83.657	—	—	—
Br	$R3$	6.692 (6.99%)	7.195	83.881 (1.16%)	84.867	—	—
I	$R3$	6.869 (5.37%)	7.259	85.298 (−0.63%)	84.767	—	—
X	Space group	a	a_{Exp}	b	b_{Exp}	c	c_{Exp}
I	$Pca2_1$	6.637 (4.28%)	6.364	10.026 (0.69%)	10.096	9.604 (1.20%)	9.490
ODABCO-NH_4X_3							
Br	$R3$	6.547 (3.17%)	6.761	89.687 (−1.74%)	88.153	—	—
I	$R3$	6.734	–	88.060	—	—	—
X	Space group	a	a_{Exp}	b	b_{Exp}	c	c_{Exp}
Cl	$Pca2_1$	12.629 (4.22%)	13.186	6.340 (4.33%)	6.627	12.506 (5.39%)	13.218
I	$Pca2_1$	13.469	—	6.720	—	13.429	—
CDABCO-NH_4X_3							
X	Space group	a	a_{Exp}	α	α_{Exp}	—	—
Br	$R3$	6.676	—	83.458	—	—	—
I	$R3$	6.780	—	84.750	—	—	—
X	Space group	a	a_{Exp}	b	b_{Exp}	c	c_{Exp}
Cl	$Pca2_1$	14.735	—	6.123	—	12.062	—

TABLE S2. Structural parameters in Å and degrees of the fully optimised R–3AQ and S–3AP-based structures. Whenever available the relative difference from the experimental lattice constants by Ye *et al.*[3] are also reported in brackets.

R–3AQ-NH_4X_3									
X	Space group	a	a_{Exp}	b	b_{Exp}	c	c_{Exp}	β	β_{Exp}
Cl	$P2_1$	6.171 (2.91%)	6.356	9.565 (5.17%)	10.087	9.0203 (4.74%)	9.469	89.589 (1.28%)	90.754
Br	$P2_1$	6.378 (3.26%)	6.593	9.869 (4.36%)	10.319	9.240 (4.43%)	9.668	89.812 (0.33%)	90.111
S–3AP-NH_4X_3									
Cl	$P2_1$	8.857 (3.05%)	9.136	8.679 (4.85%)	9.121	11.834 (5.02%)	12.459	93.339 (–1.51%)	91.950
Br	$P2_1$	9.129 (3.40%)	9.450	8.972 (4.92%)	9.436	12.398 (3.76%)	12.882	92.347(–0.80%)	91.617
I	$P2_1$	9.568	—	9.263	—	12.857	—	92.346	—

S2. OPTICAL PROPERTIES OF METAL-FREE–PEROVSKITES

Table S3 shows the diffraction index n, Δn and the acute angle 2V of the metal-free perovskites at the experimental volumes and fully relaxed as obtained with CRYSTAL17.

TABLE S3. Optical properties, including the average diffraction index n, Δn and the acute angle 2V (in degrees) of the metal-free perovskites at the experimental volumes and fully relaxed. Δn is computed following the rules described in Zhang *et al.*[4]

Material	Space group	n		Δn		2V	
		Exp.	Relaxed	Exp.	Relaxed	Exp.	Relaxed
MDABCO-NH_4Cl_3	$R3$	1.420	1.604	0.013	0.017	3.19	4.19
MDABCO-NH_4Br_3	$R3$	1.49	1.635	0.013	0.011	0.00	0.0
MDABCO-NH_4I_3	$R3$	1.580	1.699	-0.004	0.011	0.00	4.39
ODABCO-NH_4Cl_3	$Pca2_1$	1.543	1.632	0.012	0.012	75.14	80.90
ODABCO-NH_4Br_3	$R3$	1.593	1.673	0.036	0.036	71.69	59.19
ODABCO-NH_4I_3	$R3$	1.718	1.726	0.041	0.041	67.63	57.89
CNDABCO-NH_4Cl_3	$Pca2_1$	1.569[a]	1.723	0.022	0.020	81.99	29.71
CNDABCO-NH_4Br_3	$R3$	1.581[a]	1.666	0.029	0.032	41.77	13.61
CNDABCO-NH_4I_3	$R3$	1.755[a]	1.754	0.043	0.043	6.94	6.94
R–3AQ-NH_4Cl_3	$P2_1$	1.529	1.609	-0.022	-0.007	–48.21	–68.14
R–3AQ-NH_4Br_3	$P2_1$	1.569	1.646	-0.012	-0.008	–88.52	–88.14
S–3AP-NH_4Cl_3	$P2_1$	1.512	1.586	0.023	0.023	61.04	71.53
S–3AP-NH_4Br_3	$P2_1$	1.549	1.624	-0.023	-0.023	83.38	–75.14
S–3AP-NH4-NH_4I_3	$P2_1$	1.672	1.679	-0.032	-0.032	–73.76	–74.43

[a] We imposed the experimental volume of the correspondent ODABCO-NH_4X_3 perovskites.

Table S4 and Table S5 report the dielectric constant ε, $\chi^{(1)}$, d_{ijk} components related to the $\chi^{(2)}$ and the band gap of the metal-free perovskites in conditions of experimental volume, and the fully relaxed volume, respectively.
Figure S1 **a** and **b** shows the NLO properties of the metal-free perovskites investigated at their fully relaxed volumes and lattice constants.

TABLE S4. Dielectric constant ε, $\chi^{(1)}$, d_{ijk} components related to the $\chi^{(2)}$ tensor and their norm d_{norm} (in pm/V) and band gap (in eV) of the metal-free perovskites at the experimental volumes. The geometric average of ε and $\chi^{(1)}$ in the static regime are reported.

X		ε	$\chi^{(1)}$	d_{xxx}	d_{xxy}	d_{xxz}	d_{xyy}	d_{xyz}	d_{xzz}	d_{yyy}	d_{yyz}	d_{yzz}	d_{zzz}	d_{norm}	Band gap
								MDABCO−NH_4X_3							
Cl	$R3$	2.0	1.0	1.4E−1	−4.1E−1	4.8E−2	−1.4E−1	0.0	0.0	4.1E−1	4.8E−2	0.0	−4.9E−1	7.9E−1	7.26
Br	$R3$	2.2	1.2	2.3E−1	−6.2E−1	−5.8E−2	−2.3E−1	0.0	0.0	6.2E−1	−5.8E−2	0.0	−5.8E−1	1.1	7.02
I	$R3$	2.5	1.5	−1.7E−1	1.2	4.3E−1	1.7E−1	0.0	0.0	−1.2	4.3E−1	0.0	2.1E−2	1.8	6.47
								ODABCO−NH_4X_3							
Cl	$Pca2_1$	2.4	1.4	0.0	0.0	2.3E−1	0.0	0.0	0.0	0.0	−7.6E−2	0.0	−7.6E−2	2.5E−1	7.26
Br	$R3$	2.5	1.5	1.9E−2	5.1E−1	−3.2E−1	1.5E−1	−2.9E−1	−6.9E−2	9.9E−2	−1.0E−1	−2.8E−1	−2.3E−1	7.9E−1	6.80
I	$R3$	3.0	2.0	2.7E−1	6.2E−1	−6.7E−1	−1.9E−1	−4.0E−1	1.0E−1	−8.4E−1	−4.9E−1	−2.8E−1	7.2E−3	1.5	6.08
								CNDABCO−NH_4X_3							
Cl	$Pca2_1$	2.5	1.5	0.0	0.0	6.5E−1	0.0	0.0	0.0	0.0	−1.6E−1	0.0	7.5E−2	6.8E−1	6.41
Br	$R3$	2.6	1.6	−4.5E−1	8.5E−1	2.6E−1	2.3E−1	1.2E−1	9.2E−2	−8.8E−1	3.5E−1	7.1E−2	−5.9E−1	1.5	6.38
I	$R3$	3.1	2.1	−4.5E−1	1.3	7.6E−1	4.5E−1	−1.0E−3	6.1E−4	−1.3	7.6E−1	3.8E−3	−1.4E−2	2.2	5.62
								R−3AQ−NH_4X_3							
Cl	$P2_1$	2.3	1.3	0.0	9.1E−2	0.0	0.0	6.8E−2	0.0	1.2E−2	0.0	−1.6E−1	0.0	1.9E−1	7.61
Br	$P2_1$	2.5	1.5	0.0	−7.5E−2	0.0	0.0	4.2E−3	0.0	−3.2E−1	0.0	4.0E−1	0.0	5.2E−1	7.15
								S−3AP−NH_4X_3							
Cl	$P2_1$	2.3	1.3	0.0	−2.5E−2	0.0	0.0	−4.1E−2	0.0	−1.6E−1	0.0	−1.5E−1	0.0	2.2E−1	7.48
Br	$P2_1$	2.4	1.4	0.0	−2.9E−2	0.0	0.0	−5.5E−2	0.0	−1.2E−1	0.0	−4.8E−2	0.0	1.4E−1	7.15
I	$P2_1$	2.8	1.8	0.0	−2.1E−1	0.0	0.0	−7.5E−2	0.0	−1.4E−1	0.0	2.9E−2	0.0	2.6E−1	6.55
								$LiNbO_3$							
—	$R3c$	4.4	3.4	1.7E−1	0.0	5.0	1.7E−1	0.0	0.0	0.0	5.0	0.0	1.6E1	1.8E1	5.45

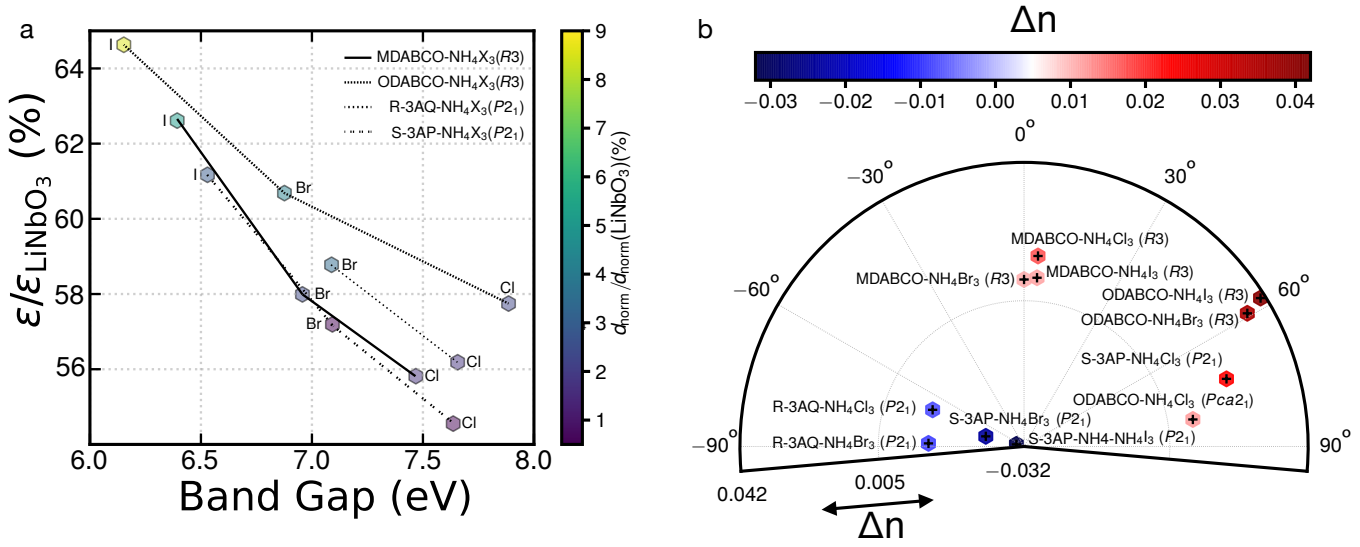

FIG. S1. **a** Computed d_{norm} (colour-bar) as function of the band gap (x-axis, eV) and average static dielectric constant (y-axis) of the metal-free perovskites at the fully relaxed volumes. The ε values computed for the metal-free perovskites are normalised against the $LiNbO_3$ ($\sim$ 4.6). Similarly, the values of d_{norm} are rescaled to that of $LiNbO_3$ ($\sim$ 17.27 pm/V). The space group of each structure is also reported. **b** Computed birefringence Δn and 2V angle of metal-free perovskites at the fully relaxed volumes. Δn is plotted on the radial axis and using the colour-bar, with red indicating positive Δn. The 2V angles provide information about the nature of the birefringence in biaxial crystals.

TABLE S5. Dielectric constant ε, $\chi^{(1)}$, d_{ijk} components related to the $\chi^{(2)}$ tensor and their norm d_{norm} (in pm/V) and band gap (in eV) of the metal-free perovskites at the fully relaxed structure. The geometric average of ε and $\chi^{(1)}$ in the static regime are reported.

X		ε	$\chi^{(1)}$	d_{xxx}	d_{xxy}	d_{xxz}	d_{xyy}	d_{xyz}	d_{xzz}	d_{yyy}	d_{yyz}	d_{yzz}	d_{zzz}	d_{norm}	Band gap
MDABCO−NH_4X_3															
Cl	$R3$	2.6	1.6	6.8E−2	8.9E−2	–1.7E−1	–6.8E−2	0.0	0.0	–8.9E−2	–1.7E−1	0.0	–3.1E−2	2.9E−1	7.47
Br	$R3$	2.7	1.7	1.5E−1	–9.5E−3	–2.4E−1	–1.5E−1	0.0	0.0	9.5E−3	–2.4E−1	0.0	–9.7E−2	4.2E−1	6.96
I	$R3$	2.9	1.9	–2.9E−1	3.5E−1	3.8E−1	2.9E−1	0.0	0.0	–3.5E−1	3.8E−1	0.0	–2.8E−1	8.9E−1	6.39
ODABCO−NH_4X_3															
Cl	$Pca2_1$	2.7	1.7	0.0	0.0	8.3E−2	0.0	0.0	0.0	0.0	–2.4E−1	0.0	2.9E−1	3.9E−1	7.89
Br	$R3$	2.8	1.8	2.1E−1	1.9E−1	–4.2E−1	–2.6E−2	–1.9E−1	3.8E−2	–9.5E−2	–4.0E−1	–2.3E−1	3.3E−2	7.2E−1	6.88
I	$R3$	3.0	2.0	4.5E−1	6.7E−1	–5.7E−1	–1.3E−1	–4.1E−1	5.0E−2	–7.3E−1	–5.7E−1	–4.0E−1	–7.1E−2	1.5	6.15
CNDABCO−NH_4X_3															
Cl	$Pca2_1$	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Br	$R3$	2.8	1.8	–2.8E−1	3.5E−1	5.4E−1	2.7E−1	1.9E−3	–8.8E−3	–3.4E−1	5.1E−1	4.8E−3	–4.1E−1	1.1	6.39
I	$R3$	3.0	2.0	–5.3E−1	1.0	1.1	4.4E−1	–4.6E−2	–2.6E−2	–1.1	1.0	–3.1E−2	–9.1E−2	2.2	5.63
R−3AQ−NH_4X_3															
Cl	$P2_1$	2.6	1.6	0.0	–9.2E−2	0.0	0.0	7.2E−2	0.0	–9.4E−2	0.0	2.6E−1	0.0	3.0E−1	7.66
Br	$P2_1$	2.7	1.7	0.0	–7.0E−2	0.0	0.0	2.4E−2	0.0	–3.3E−1	0.0	4.7E−1	0.0	5.9E−1	7.09
S−3AP−NH_4X_3															
Cl	$P2_1$	2.5	1.5	0.0	4.3E−2	0.0	0.0	1.9E−2	0.0	–2.7E−2	0.0	–7.5E−2	0.0	9.2E−2	7.64
Br	$P2_1$	2.6	1.6	0.0	–3.9E−2	0.0	0.0	1.3E−2	0.0	–5.3E−2	0.0	7.7E−3	0.0	6.8E−2	7.09
I	$P2_1$	2.8	1.8	0.0	–2.6E−1	0.0	–3.9E−1	–5.7E−2	0.0	–9.6E−2	0.0	5.5E−2	0.0	4.9E−1	6.53
$LiNbO_3$															
—	$R3c$	4.6	3.6	–8.2E−3	0.0	3.9	8.2E−3	0.0	0.0	0.0	3.9	0.0	1.6E1	1.7E1	5.68

S3. PERFORMANCE OF DIFFERENT EXCHANGE AND CORRELATION FUNCTIONALS

Table S6 show a comparison of different DFT exchange and correlation functional on the structural parameters, such as lattice constants and angles in the MDABCO-based metal free perovskites in the space group $Pca2_1$.

TABLE S6. Performance of exchange and correlation functionals (XC) at predicting the structural parameters in Å and degrees of the MDABCO-NH_4I_3 ($Pca2_1$) structure. Whenever available the relative difference from the experimental lattice constants by Ye *et al.*[3] are also reported in brackets.

MDABCO-NH_4I_3			
XC Functional	a	b	c
PBESol	6.772 (6.41%)	10.183 (0.86%)	9.722 (2.45%)
PBESol-D3	6.629 (4.17%)	10.015 (0.80%)	9.580 (0.95%)
PBE0	6.932 (8.93%)	10.500 (4.00%)	10.027 (5.66%)
PBESol0	6.770 (6.38%)	10.197 (1.00%)	9.743 (2.67%)
PBESol0-D3	6.637 (4.28%)	10.026 (0.69%)	9.604 (1.20%)
HSE06	6.934 (8.96%)	10.495 3.95 (%)	10.027 (5.65%)

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