Electronic Supplementary Information

Complexes and salts of the nitrogen-rich triazole-tetrazole hybrid ligand with alkali and alkaline earth metal cations: experimental and theoretical findings

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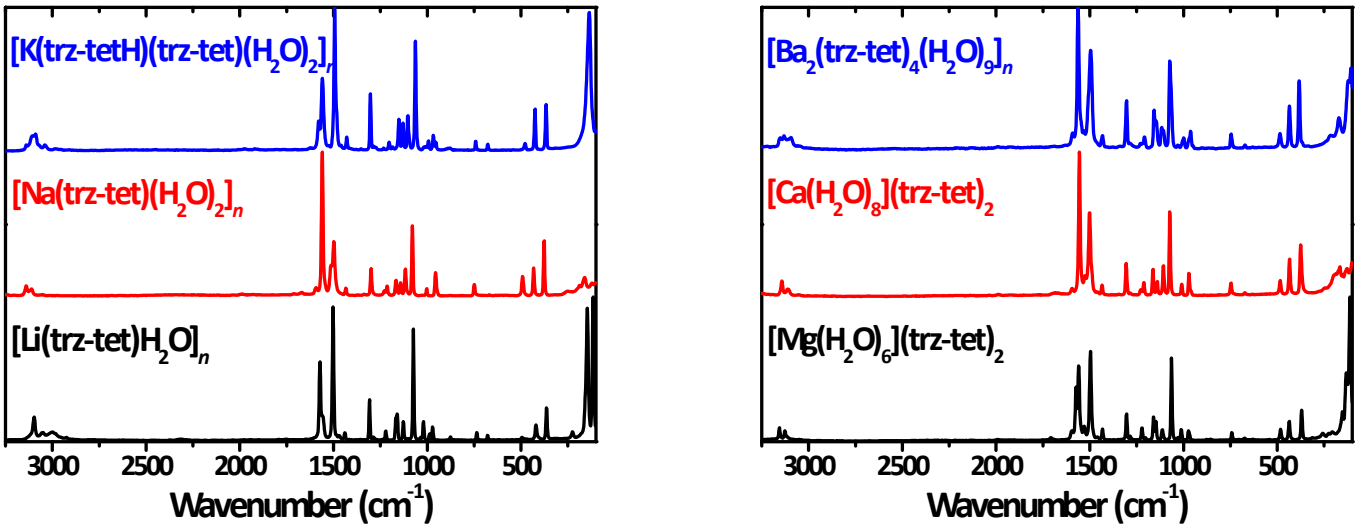


Fig. S1 Raman spectra of alkali and alkaline earth metal compounds of **trz-tetH**.

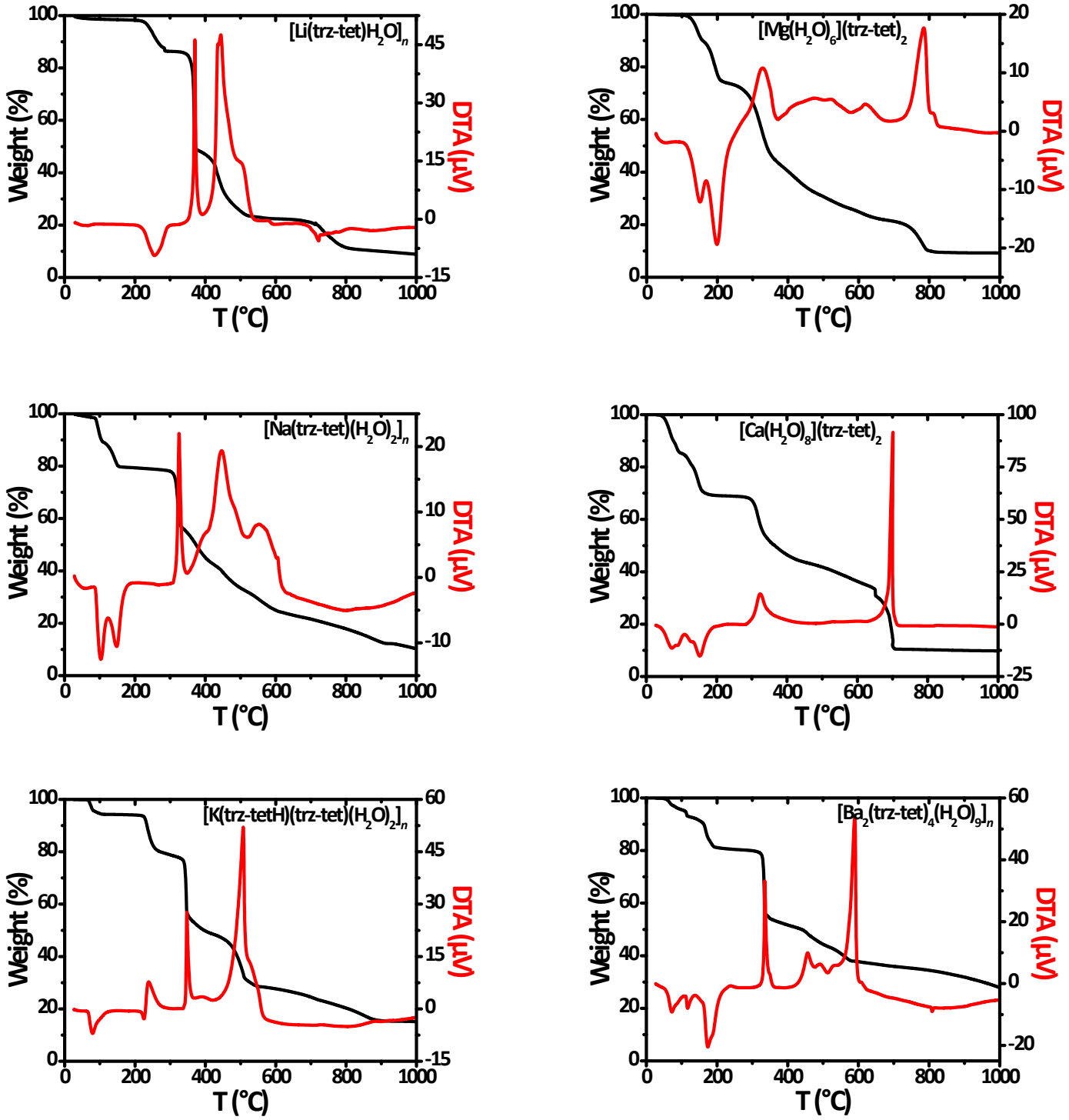


Fig. S2 Simultaneous TGA/DTA of alkali and alkaline earth metal compounds of **trz-tetH** performed in a dynamic air atmosphere.

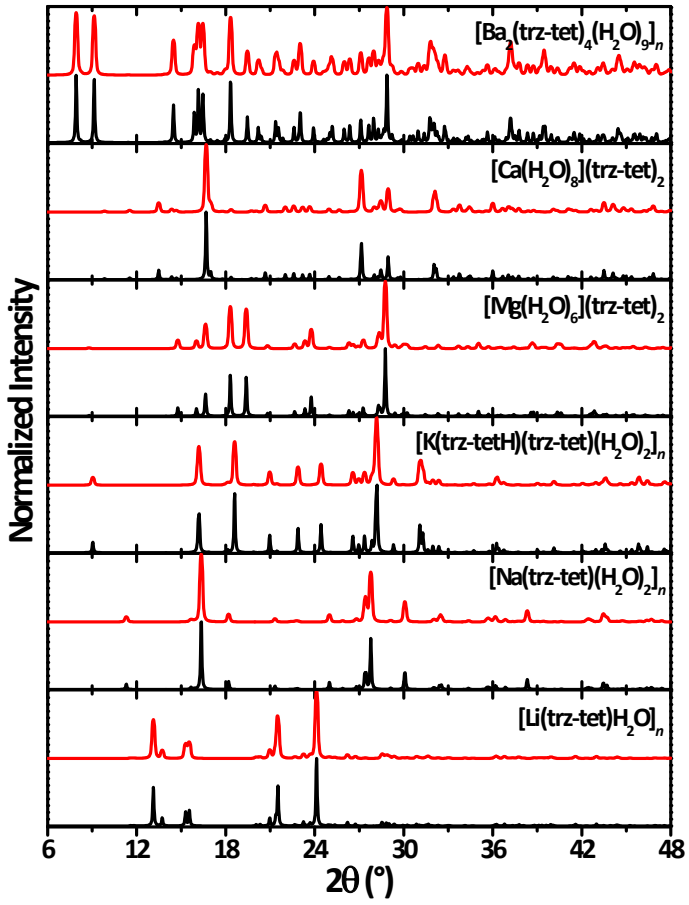
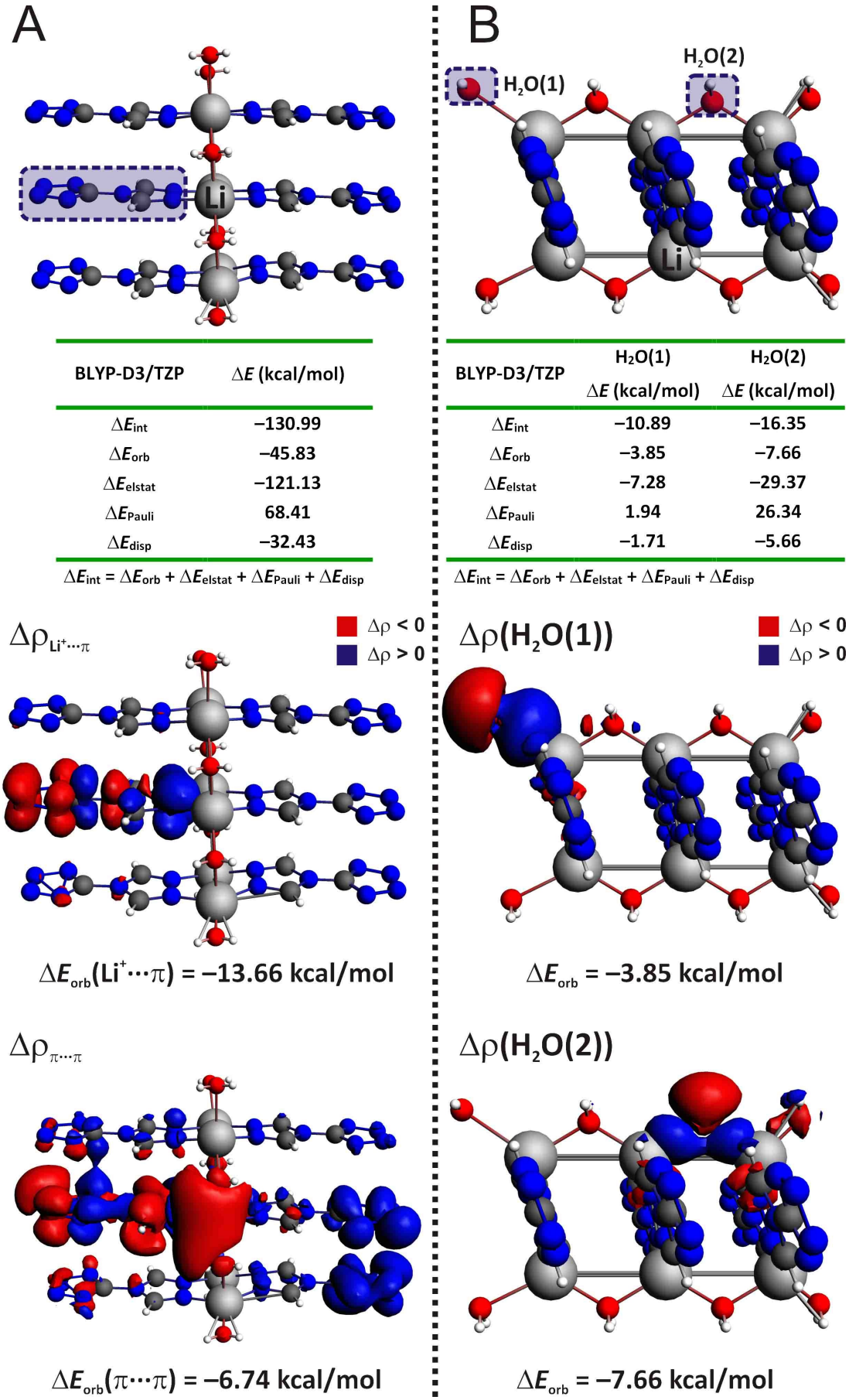


Fig. S3 Calculated (black) and experimental (red) X-ray powder diffraction patterns of the complexes described in this work.



BLYP-D3/TZP	ΔE (kcal/mol)
ΔE_{int}	–130.99
ΔE_{orb}	–45.83
ΔE_{elstat}	–121.13
ΔE_{Pauli}	68.41
ΔE_{disp}	–32.43

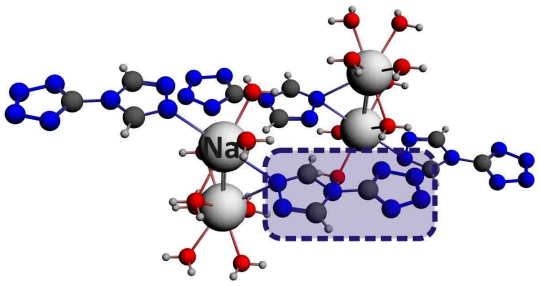
$\Delta E_{int} = \Delta E_{orb} + \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{disp}$

BLYP-D3/TZP	H2O(1) ΔE (kcal/mol)	H2O(2) ΔE (kcal/mol)
ΔE_{int}	–10.89	–16.35
ΔE_{orb}	–3.85	–7.66
ΔE_{elstat}	–7.28	–29.37
ΔE_{Pauli}	1.94	26.34
ΔE_{disp}	–1.71	–5.66

$\Delta E_{int} = \Delta E_{orb} + \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{disp}$

Fig. S4 ETS-NOCV energy decomposition results for **[Li(trz-tet)H_2O]$_n$**.

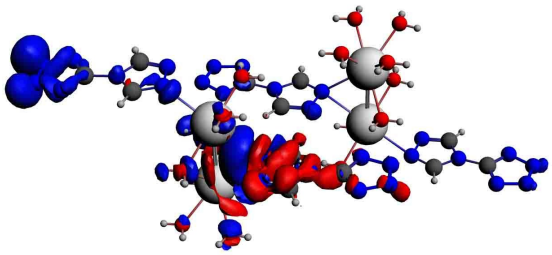
A



BLYP-D3/TZP	Δ*E* (kcal/mol)
ΔE_{int}	−134.50
ΔE_{orb}	−18.54
ΔE_{elstat}	−127.84
ΔE_{Pauli}	26.26
ΔE_{disp}	−14.38

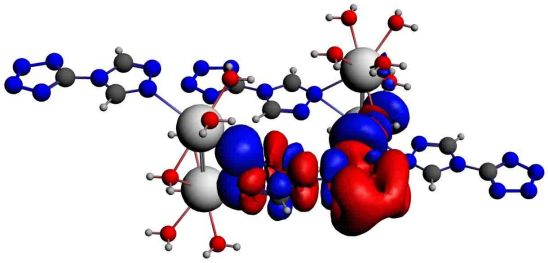
$\Delta E_{int} = \Delta E_{orb} + \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{disp}$

Δρ(1)



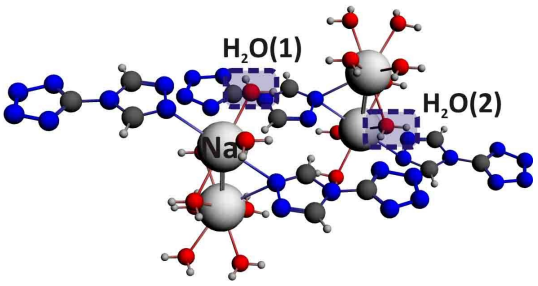
$\Delta E_{orb}(1) = -3.42$ kcal/mol

Δρ(2)



$\Delta E_{orb}(2) = -4.53$ kcal/mol

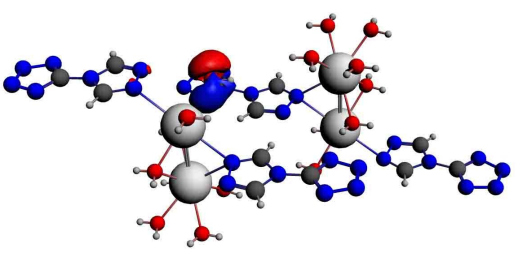
B



BLYP-D3/TZP	$H_2O(1)$ Δ*E* (kcal/mol)	$H_2O(2)$ Δ*E* (kcal/mol)
ΔE_{int}	−6.31	−25.49
ΔE_{orb}	−3.01	−11.16
ΔE_{elstat}	−9.73	−36.38
ΔE_{Pauli}	10.45	28.71
ΔE_{disp}	−4.04	−6.65

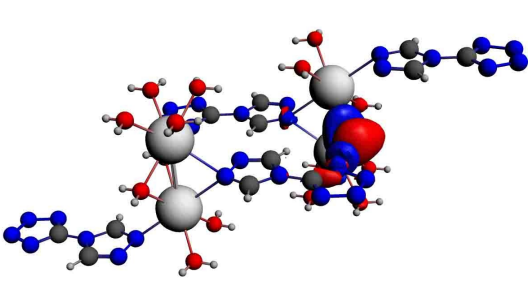
$\Delta E_{int} = \Delta E_{orb} + \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{disp}$

Δρ(H2O(1))



$\Delta E_{orb} = -3.01$ kcal/mol

Δρ(H2O(2))



$\Delta E_{orb} = -11.16$ kcal/mol

Fig. S5 ETS-NOCV energy decomposition results for **$[Na(trz\text{-}tet)(H_2O)_2]_n$**.

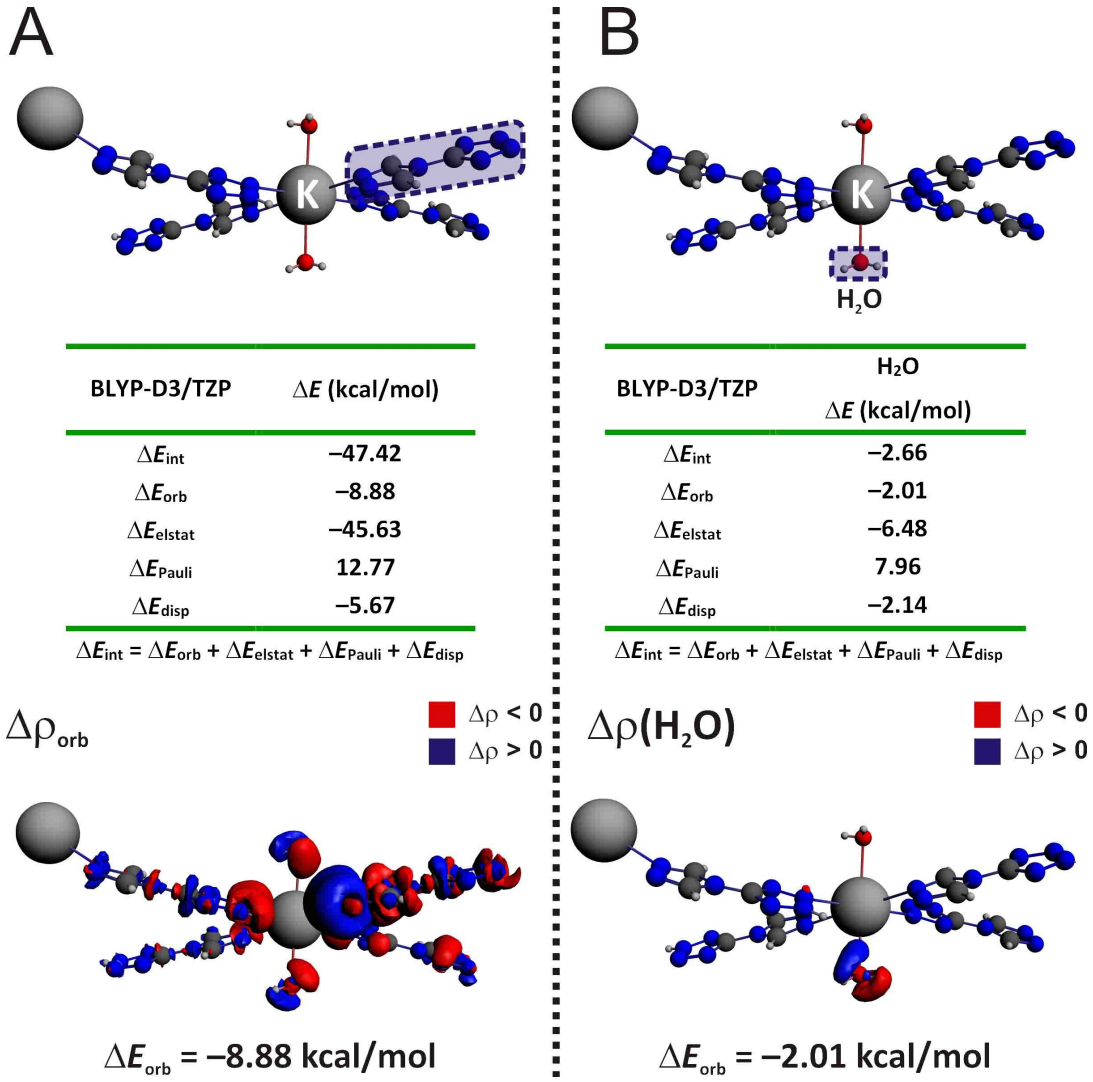
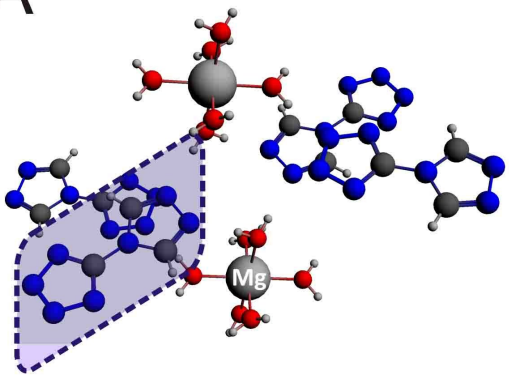


Fig. S6 ETS-NOCV energy decomposition results for **[K(trz-tetH)(trz-tet)(H$_2$O)$_2$]$_n$**.

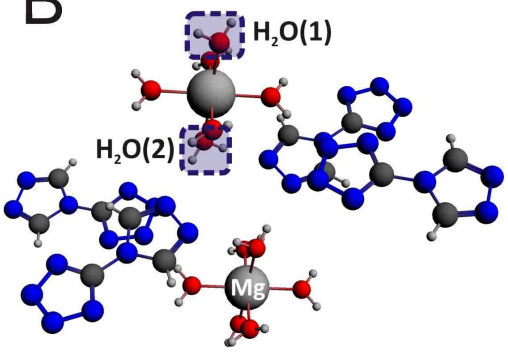
A



BLYP-D3/TZP	Δ*E* (kcal/mol)
ΔE_{int}	–91.52
ΔE_{orb}	–18.55
ΔE_{elstat}	–85.65
ΔE_{Pauli}	23.76
ΔE_{disp}	–11.08

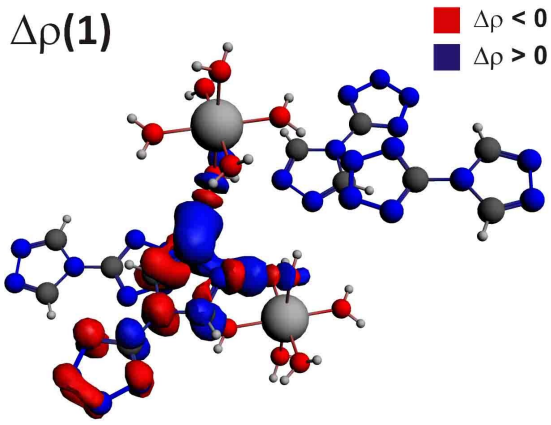
$\Delta E_{int} = \Delta E_{orb} + \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{disp}$

B

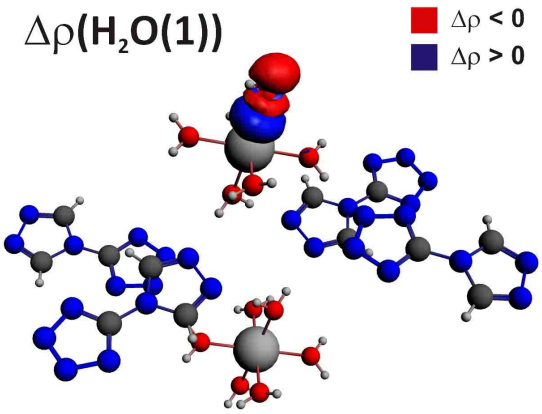


BLYP-D3/TZP	$H_2O(1)$ Δ*E* (kcal/mol)	$H_2O(2)$ Δ*E* (kcal/mol)
ΔE_{int}	–21.28	–48.32
ΔE_{orb}	–4.72	–28.17
ΔE_{elstat}	–33.43	–59.10
ΔE_{Pauli}	28.70	47.24
ΔE_{disp}	–4.53	–8.29

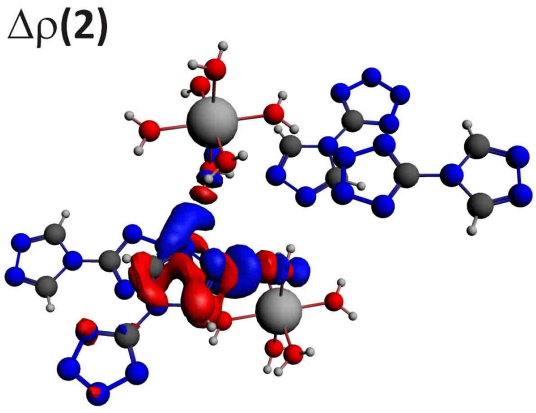
$\Delta E_{int} = \Delta E_{orb} + \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{disp}$



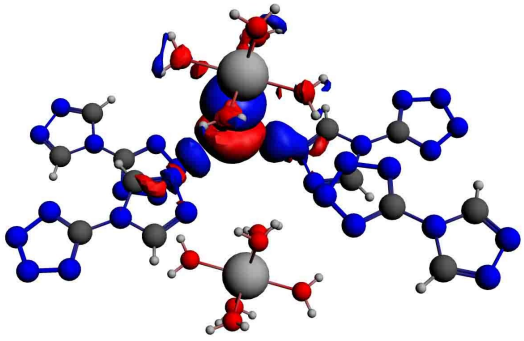
$\Delta E_{orb}(1) = -6.44$ kcal/mol



$\Delta E_{orb} = -4.72$ kcal/mol

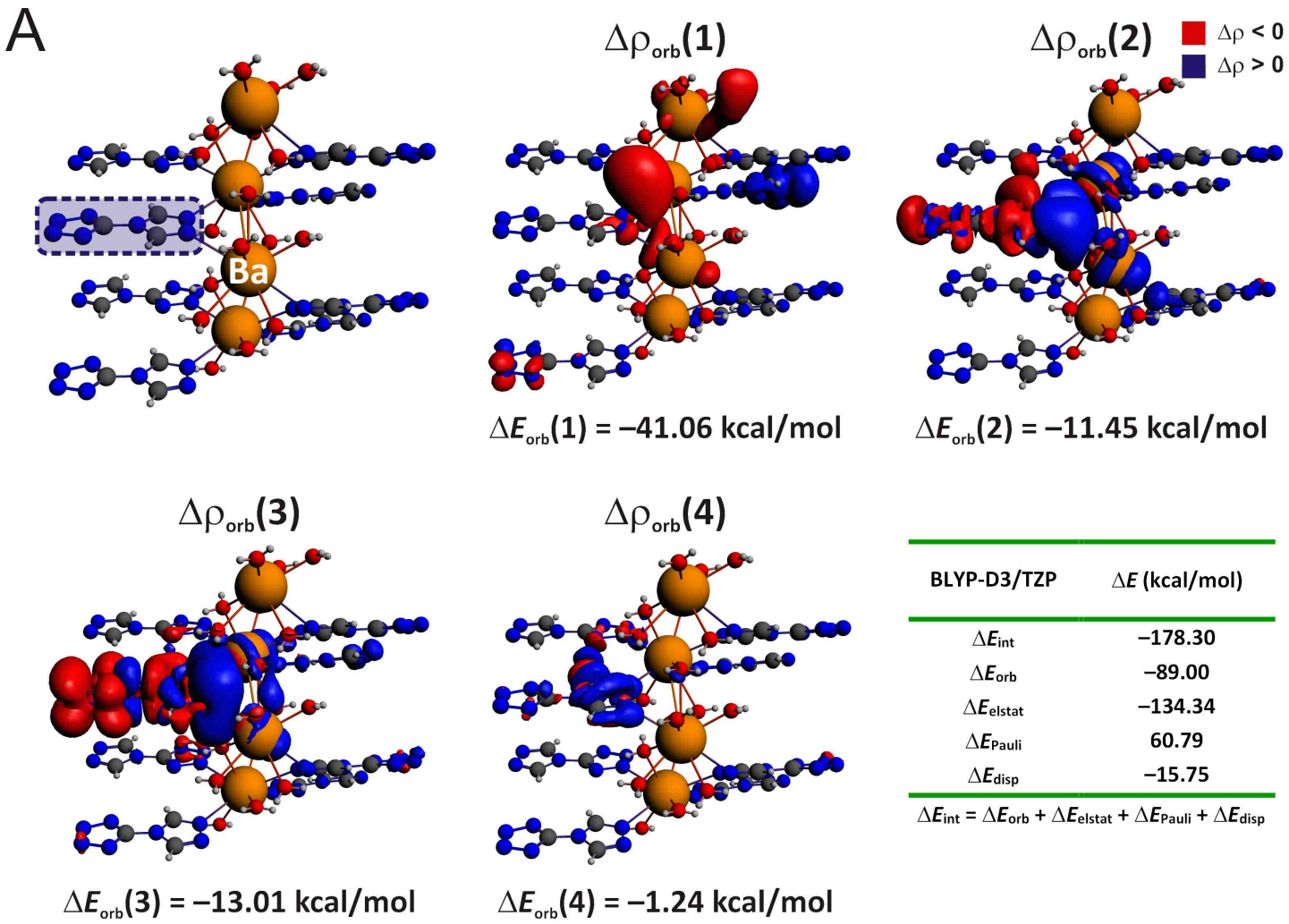


$\Delta E_{orb}(2) = -4.83$ kcal/mol



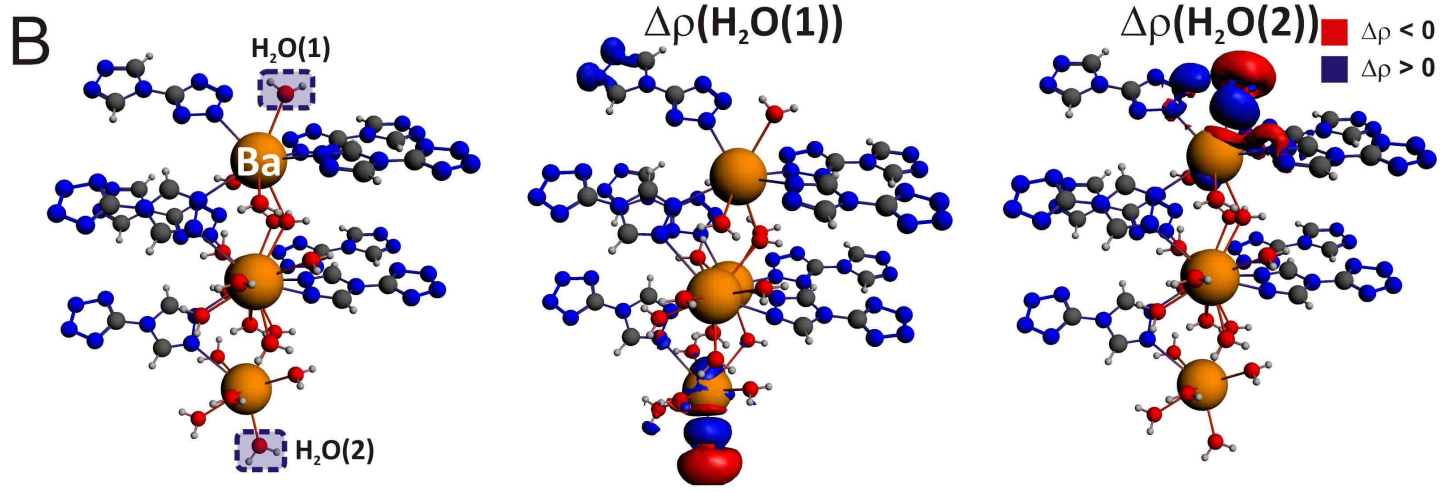
$\Delta E_{orb} = -28.17$ kcal/mol

Fig. S7 ETS-NOCV energy decomposition results for **$[Mg(H_2O)_6](trz\text{-}tet)_2$**.



BLYP-D3/TZP	ΔE (kcal/mol)
ΔE_{int}	–178.30
ΔE_{orb}	–89.00
ΔE_{elstat}	–134.34
ΔE_{Pauli}	60.79
ΔE_{disp}	–15.75

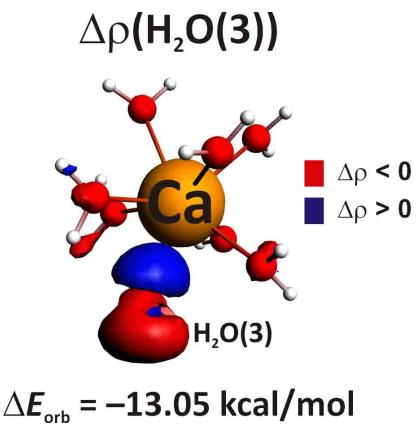
$\Delta E_{int} = \Delta E_{orb} + \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{disp}$



BLYP-D3/TZP	H2O(1) ΔE (kcal/mol)	H2O(2) ΔE (kcal/mol)
ΔE_{int}	–13.38	–14.61
ΔE_{orb}	–13.03	–7.07
ΔE_{elstat}	–31.31	–19.13
ΔE_{Pauli}	33.33	16.17
ΔE_{disp}	–2.38	–4.58

$\Delta E_{int} = \Delta E_{orb} + \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{disp}$

Fig. S8 ETS-NOCV energy decomposition results for $[Ba_2(trz\text{-}tet)_4(H_2O)_9]_n$.



BLYP-D3/TZP	$H_2O(3)$ ΔE (kcal/mol)
ΔE_{int}	–17.78
ΔE_{orb}	–13.05
ΔE_{elstat}	–33.58
ΔE_{Pauli}	35.82
ΔE_{disp}	–3.96

$\Delta E_{int} = \Delta E_{orb} + \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{disp}$

Fig. S9 ETS-NOCV energy decomposition results for **$[Ca(H_2O)_8]^{2+}$**.

Table S1 Selected bond lengths (Å) and bond angles (°) for **[Li(trz-tet)H_2O]$_n$**

Bond lengths					
N(10)–Li(1)	2.032(11)	N(3)–N(7)	1.349(7)	N(8)–C(6)	1.418(6)
N(11)–Li(1)c	2.051(11)	N(4)–N(5)	1.351(7)	N(8)–C(9)	1.359(8)
O(2)–Li(1)	1.989(11)	N(10)–N(11)	1.400(8)	N(8)–C(12)	1.367(8)
O(2)–Li(1)a	2.019(11)	N(5)–C(6)	1.326(8)	N(10)–C(9)	1.294(7)
N(3)–N(4)	1.312(8)	N(7)–C(6)	1.312(8)	N(11)–C(12)	1.309(8)
Bond angles					
Li(1)–O(2)–Li(1)a	117.9(5)	C(9)–N(10)–Li(1)	131.9(5)	N(5)–C(6)–N(7)	115.8(5)
N(10)–Li(1)–N(11)c	116.0(6)	C(12)–N(11)–Li(1)c	130.9(5)	N(5)–C(6)–N(8)	121.5(5)
N(10)–Li(1)–O(2)b	105.8(5)	N(3)–N(4)–N(5)	109.8(5)	N(7)–C(6)–N(8)	122.7(5)
O(2)–Li(1)–N(10)	106.7(5)	N(4)–N(3)–N(7)	110.2(5)	N(8)–C(9)–N(10)	110.9(5)
O(2)–Li(1)–N(11)c	108.9(5)	N(3)–N(7)–C(6)	102.3(5)	N(8)–C(12)–N(11)	110.3(5)
O(2)b–Li(1)–N(11)c	102.0(5)	N(4)–N(5)–C(6)	102.0(5)	C(6)–N(8)–C(9)	128.2(5)
O(2)–Li(1)–O(2)b	117.9(6)	N(10)–N(11)–C(12)	106.6(5)	C(6)–N(8)–C(12)	126.9(5)
N(10)–N(11)–Li(1)c	121.2(5)	N(11)–N(10)–C(9)	107.3(5)	C(9)–N(8)–C(12)	104.8(4)
N(11)–N(10)–Li(1)	120.3(5)				

Table S2 Selected bond lengths (Å) and bond angles (°) for **[Na(trz-tet)(H_2O)$_2$]$_n$**

Bond lengths					
Na(1)–N(5)	2.6697(12)	N(5)–N(6)	1.3994(16)	N(8)–C(7)	1.3646(18)
Na(2)–N(5)	2.6697(14)	N(11)–N(12)	1.3491(17)	N(8)–C(9)	1.3570(18)
Na(1)–O(3)	2.3857(10)	N(12)–N(13)	1.3093(15)	N(8)–C(10)	1.4091(18)
Na(1)–O(4)	2.3600(10)	N(13)–N(14)	1.3552(17)	N(11)–C(10)	1.3223(17)
Na(2)–O(3)	2.3512(8)	N(5)–C(9)	1.306(2)	N(14)–C(10)	1.3247(16)
Na(2)–O(4)	2.3930(9)	N(6)–C(7)	1.295(2)		
Bond angles					
Na(1)–N(5)–Na(2)	73.96(4)	O(4)–Na(1)–N(5)a	95.16(4)	O(4)–Na(2)–O(4)b	180.00
Na(1)–O(3)–Na(2)	85.38(3)	O(3)–Na(2)–N(5)	83.90(4)	N(11)–N(12)–N(13)	109.99(11)
Na(1)–O(4)–Na(2)	85.03(3)	O(3)–Na(2)–N(5)b	96.10(4)	N(12)–N(13)–N(14)	109.55(11)
Na(1)–N(5)–N(6)	99.26(8)	O(3)b–Na(2)–N(5)b	83.90(4)	N(5)–N(6)–C(7)	106.62(12)
Na(2)–N(5)–N(6)	100.58(9)	O(4)–Na(2)–N(5)	84.97(3)	N(6)–N(5)–C(9)	107.08(12)
Na(1)–N(5)–C(9)	134.51(9)	O(4)–Na(2)–N(5)b	95.03(3)	N(12)–N(11)–C(10)	103.11(10)
Na(2)–N(5)–C(9)	133.55(9)	O(4)b–Na(2)–N(5)b	84.97(3)	N(13)–N(14)–C(10)	103.01(10)
N(5)–Na(1)–N(5)a	178.79(4)	O(3)–Na(1)–O(3)a	105.02(4)	N(5)–C(9)–N(8)	110.54(12)
N(5)–Na(1)–O(3)a	96.01(4)	O(3)–Na(1)–O(4)	77.39(3)	N(6)–C(7)–N(8)	111.16(12)
N(5)–Na(2)–O(3)b	96.10(4)	O(3)–Na(1)–O(4)a	177.22(4)	N(8)–C(10)–N(11)	121.36(11)
N(5)–Na(1)–O(4)a	95.16(4)	O(3)a–Na(1)–O(4)a	77.39(3)	N(8)–C(10)–N(14)	124.30(12)
N(5)–Na(2)–O(4)b	95.03(3)	O(4)–Na(1)–O(4)a	100.25(4)	N(11)–C(10)–N(14)	114.34(12)
N(5)–Na(2)–N(5)b	180.00	O(3)–Na(2)–O(3)b	180.00	C(7)–N(8)–C(9)	104.60(12)
O(3)–Na(1)–N(5)	83.25(4)	O(3)–Na(2)–O(4)	77.41(3)	C(7)–N(8)–C(10)	126.54(12)
O(3)–Na(1)–N(5)a	96.01(4)	O(3)–Na(2)–O(4)b	102.59(3)	C(9)–N(8)–C(10)	128.86(11)
O(4)–Na(1)–N(5)	85.62(4)				

Table S3 Selected bond lengths (Å) and bond angles (°) for **[K(trz-tetH)(trz-tet)(H_2O)$_2$]$_n$**

Bond lengths					
K(1)–N(4)	2.981(3)	N(14)–N(15)	1.394(5)	N(11)–C(10)	1.303(4)
K(1)–N(12)a	2.837(3)	N(20)–N(21)	1.351(4)	N(12)–C(13)	1.297(4)
K(1)–N(14)	2.838(3)	N(21)–N(22)	1.316(5)	N(14)–C(18)	1.300(4)
K(1)–N(21)b	2.854(3)	N(22)–N(23)	1.352(4)	N(15)–C(16)	1.304(4)
K(1)–O(2)	2.824(3)	N(6)–C(7)	1.324(4)	N(17)–C(16)	1.358(4)
K(1)–O(3)	2.736(3)	N(8)–C(7)	1.333(4)	N(17)–C(18)	1.370(4)
N(4)–N(5)	1.307(4)	N(9)–C(7)	1.402(4)	N(17)–C(19)	1.411(4)
N(4)–N(8)	1.338(4)	N(9)–C(10)	1.366(5)	N(20)–C(19)	1.319(5)
N(5)–N(6)	1.330(4)	N(9)–C(13)	1.370(4)	N(23)–C(19)	1.325(5)
N(11)–N(12)	1.393(5)				
Bond angles					
K(1)–N(4)–N(5)	125.8(2)	O(3)–K(1)–N(14)	99.08(8)	N(12)–N(11)–C(10)	107.5(3)
K(1)–N(4)–N(8)	127.1(2)	O(3)–K(1)–N(12)a	77.42(8)	N(14)–N(15)–C(16)	107.5(3)
K(1)–N(14)–N(15)	126.3(2)	O(2)–K(1)–O(3)	175.98(7)	N(15)–N(14)–C(18)	106.9(3)
N(4)–K(1)–N(12)a	76.18(9)	C(13)–N(12)–K(1)c	133.3(2)	N(6)–C(7)–N(9)	122.2(3)
N(4)–K(1)–N(14)	96.63(9)	N(4)–N(5)–N(6)	114.4(3)	N(9)–C(13)–N(12)	110.3(3)
N(14)–K(1)–N(12)a	171.90(9)	N(20)–N(21)–N(22)	109.4(3)	N(17)–C(19)–N(20)	123.2(3)
N(14)–K(1)–N(21)b	78.56(9)	N(21)–N(22)–N(23)	110.0(3)	C(7)–N(9)–C(10)	127.0(3)
O(2)–K(1)–N(4)	88.72(9)	N(5)–N(6)–C(7)	100.1(3)	C(7)–N(9)–C(13)	128.1(3)
O(2)–K(1)–N(12)a	105.73(8)	N(11)–N(12)–C(13)	107.3(3)	C(16)–N(17)–C(19)	127.2(3)
O(2)–K(1)–N(21)b	92.64(9)				

Table S4 Selected bond lengths (Å) and bond angles (°) for **$[Mg(H_2O)_6](trz\text{-}tet)_2$**

Bond lengths					
Mg(1)–O(2)	2.0945(13)	N(18)–N(19)	1.307(3)	N(14)–C(15)	1.355(2)
Mg(1)–O(3)	2.0664(14)	N(19)–N(20)	1.350(2)	N(14)–C(16)	1.409(2)
Mg(1)–O(4)	2.0367(14)	N(11)–C(15)	1.300(3)	N(17)–C(16)	1.320(2)
N(11)–N(12)	1.388(3)	N(12)–C(13)	1.295(2)	N(20)–C(16)	1.327(3)
N(17)–N(18)	1.354(2)	N(14)–C(13)	1.366(3)		
Bond angles					
O(2)–Mg(1)–O(2)a	180.00	O(3)a–Mg(1)–O(4)a	88.95(6)	N(11)–C(15)–N(14)	110.61(18)
O(2)–Mg(1)–O(3)	87.99(5)	O(4)–Mg(1)–O(4)a	180.00	N(12)–C(13)–N(14)	110.28(18)
O(2)–Mg(1)–O(3)a	92.01(5)	N(17)–N(18)–N(19)	109.52(13)	N(14)–C(16)–N(17)	122.92(18)
O(2)–Mg(1)–O(4)	91.36(5)	N(18)–N(19)–N(20)	110.51(14)	N(14)–C(16)–N(20)	122.14(16)
O(2)–Mg(1)–O(4)a	88.64(5)	N(11)–N(12)–C(13)	107.34(18)	N(17)–C(16)–N(20)	114.94(15)
O(3)–Mg(1)–O(3)a	180.00	N(12)–N(11)–C(15)	107.04(15)	C(13)–N(14)–C(15)	104.72(15)
O(3)–Mg(1)–O(4)	88.95(6)	N(18)–N(17)–C(16)	102.82(15)	C(13)–N(14)–C(16)	128.37(15)
O(3)–Mg(1)–O(4)a	91.05(6)	N(19)–N(20)–C(16)	102.21(13)	C(15)–N(14)–C(16)	126.79(16)

Table S5 Selected bond lengths (Å) and bond angles (°) for **$[Ca(H_2O)_8](trz\text{-}tet)_2$**

Bond lengths					
Ca(1)–O(2)	2.4841(10)	N(17)–N(18)	1.3541(17)	N(14)–C(13)	1.367(2)
Ca(1)–O(3)	2.5494(11)	N(18)–N(19)	1.313(2)	N(14)–C(15)	1.363(2)
Ca(1)–O(4)	2.4208(12)	N(19)–N(20)	1.3519(18)	N(14)–C(16)	1.4079(17)
Ca(1)–O(5)	2.4346(10)	N(11)–C(15)	1.3036(19)	N(17)–C(16)	1.327(2)
N(11)–N(12)	1.395(2)	N(12)–C(13)	1.2991(19)	N(20)–C(16)	1.325(2)
Bond angles					
O(2)–Ca(1)–O(2)a	75.45(4)	O(3)–Ca(1)–O(4)	138.16(4)	N(11)–N(12)–C(13)	107.10(13)
O(2)–Ca(1)–O(3)	146.34(3)	O(3)–Ca(1)–O(4)a	75.88(4)	N(12)–N(11)–C(15)	107.42(14)
O(2)–Ca(1)–O(3)a	117.11(4)	O(3)–Ca(1)–O(5)	69.32(3)	N(11)–C(15)–N(14)	110.05(16)
O(2)–Ca(1)–O(4)	72.56(4)	O(4)–Ca(1)–O(4)a	144.16(4)	N(12)–C(13)–N(14)	110.37(16)
O(2)–Ca(1)–O(4)a	79.22(4)	O(4)–Ca(1)–O(5)	82.28(4)	N(14)–C(16)–N(20)	123.54(15)
O(2)–Ca(1)–O(5)	141.24(3)	O(4)–Ca(1)–O(5)a	108.18(4)	N(17)–C(16)–N(20)	114.15(12)
O(2)–Ca(1)–O(5)a	71.14(3)	O(5)–Ca(1)–O(5)a	146.45(4)	C(13)–N(14)–C(16)	126.66(14)
O(3)–Ca(1)–O(5)a	83.30(4)	N(17)–N(18)–N(19)	109.55(13)	C(15)–N(14)–C(16)	128.27(14)
O(3)–Ca(1)–O(3)a	70.97(4)	N(18)–N(19)–N(20)	109.89(12)		

Table S6 Selected bond lengths (Å) and bond angles (°) for $[Ba_2(trz\text{-}tet)_4(H_2O)_9]_n$

Bond lengths					
Ba(1)–N(11)	2.847(3)	*Ba(2B)–O(6)c	2.888(3)	N(16)–C(17)	1.358(5)
Ba(1)–N(21)	2.908(3)	N(11)–N(12)	1.314(5)	N(16)–C(20)	1.364(5)
Ba(1)–O(3)	2.852(3)	N(11)–N(15)	1.356(4)	N(18)–C(17)	1.303(5)
Ba(1)–O(4)	2.802(3)	N(12)–N(13)	1.343(4)	N(19)–C(20)	1.303(5)
Ba(1)–O(7)	2.856(3)	N(18)–N(19)	1.391(5)	N(21)–C(22)	1.296(5)
*Ba(2B)–N(25)a	2.946(3)	N(21)–N(25)	1.393(5)	N(23)–C(22)	1.359(5)
*Ba(2B)–O(3)	2.976(2)	N(27)–N(28)	1.353(4)	N(23)–C(24)	1.366(5)
*Ba(2B)–O(3)c	2.841(2)	N(28)–N(29)	1.310(5)	N(23)–C(26)	1.409(4)
*Ba(2B)–O(4)a	3.0654(7)	N(29)–N(30)	1.352(4)	N(25)–C(24)	1.289(5)
*Ba(2B)–O(5)	2.847(3)	N(13)–C(14)	1.320(4)	N(27)–C(26)	1.326(5)
*Ba(2B)–O(5)c	2.585(3)	N(15)–C(14)	1.319(5)	N(30)–C(26)	1.328(5)
*Ba(2B)–O(6)	2.553(3)	N(16)–C(14)	1.416(4)		
Bond angles					
Ba(1)–O(3)–*Ba(2B)	113.48(8)	O(7)–Ba(1)–N(21)	66.73(10)	O(6)–*Ba(2B)–O(5)c	73.55(9)
Ba(1)–O(3)–*Ba(2B)c	104.33(8)	O(7)–Ba(1)–N(21)d	144.34(10)	O(6)–*Ba(2B)–O(6)c	79.14(10)
Ba(1)–O(4)–*Ba(2B)b	99.93(6)	O(7)d–Ba(1)–N(11)d	70.10(9)	N(21)–N(25)–*Ba(2B)b	108.9(2)
*Ba(2B)–O(5)–*Ba(2B)c	10.07(2)	O(3)–Ba(1)–O(3)d	143.19(6)	C(24)–N(25)–*Ba(2B)b	137.0(2)
*Ba(2B)–O(3)–*Ba(2B)c	10.39(2)	O(3)–Ba(1)–O(4)	71.60(4)	N(11)–N(12)–N(13)	109.7(3)
*Ba(2B)b–O(4)–*Ba(2B)c	160.14(12)	O(3)–Ba(1)–O(7)	132.13(8)	N(12)–N(11)–N(15)	109.9(3)
*Ba(2B)–O(6)–*Ba(2B)c	9.04(2)	O(3)–Ba(1)–O(7)d	70.06(8)	N(27)–N(28)–N(29)	110.0(3)
Ba(1)–N(11)–N(12)	121.3(2)	O(4)–Ba(1)–O(7)	121.48(8)	N(28)–N(29)–N(30)	110.1(3)
Ba(1)–N(11)–N(15)	126.5(2)	O(7)–Ba(1)–O(7)d	117.05(11)	N(11)–N(15)–C(14)	102.3(3)
Ba(1)–N(21)–N(25)	124.8(2)	O(3)–*Ba(2B)–N(25)a	67.00(8)	N(12)–N(13)–C(14)	103.0(3)
Ba(1)–N(21)–C(22)	124.3(3)	O(4)a–*Ba(2B)–N(25)a	59.37(7)	N(18)–N(19)–C(20)	107.2(3)
N(11)–Ba(1)–N(11)d	92.22(9)	O(5)–*Ba(2B)–N(25)a	78.04(9)	N(19)–N(18)–C(17)	107.3(3)
N(11)–Ba(1)–N(21)d	132.73(10)	O(6)–*Ba(2B)–N(25)a	76.72(10)	N(21)–N(25)–C(24)	107.1(3)
N(11)–Ba(1)–N(21)	82.86(9)	O(3)–*Ba(2B)–O(3)c	65.56(7)	N(25)–N(21)–C(22)	107.3(3)
N(21)–Ba(1)–N(11)d	132.73(10)	O(3)–*Ba(2B)–O(4)a	104.71(7)	N(28)–N(27)–C(26)	102.5(3)
N(21)–Ba(1)–N(21)d	132.88(9)	O(3)–*Ba(2B)–O(5)	69.00(7)	N(29)–N(30)–C(26)	102.5(3)
N(11)–Ba(1)–O(3)d	140.11(8)	O(3)–*Ba(2B)–O(5)c	140.07(7)	N(13)–C(14)–N(15)	115.2(3)
N(21)–Ba(1)–O(3)d	83.40(9)	O(3)c–*Ba(2B)–O(5)c	74.74(7)	N(13)–C(14)–N(16)	122.3(3)
N(11)–Ba(1)–O(7)d	67.44(9)	O(3)–*Ba(2B)–O(6)c	116.01(8)	N(15)–C(14)–N(16)	122.5(3)
N(21)–Ba(1)–O(7)d	144.34(10)	O(3)–*Ba(2B)–O(6)	139.91(9)	N(16)–C(17)–N(18)	110.2(3)
N(25)a–*Ba(2B)–O(3)c	92.21(8)	O(3)c–*Ba(2B)–O(6)c	130.20(9)	N(16)–C(20)–N(19)	110.1(3)
N(25)a–*Ba(2B)–O(5)c	120.31(10)	O(4)a–*Ba(2B)–O(3)c	67.98(7)	N(21)–C(22)–N(23)	110.3(4)
N(25)a–*Ba(2B)–O(6)c	136.12(9)	O(4)a–*Ba(2B)–O(5)c	61.82(7)	N(23)–C(24)–N(25)	110.5(3)
O(3)–Ba(1)–N(11)	70.76(8)	O(4)a–*Ba(2B)–O(6)c	139.26(9)	N(23)–C(26)–N(27)	123.0(3)
O(3)–Ba(1)–N(11)d	140.11(8)	O(5)–*Ba(2B)–O(3)c	133.66(7)	N(23)–C(26)–N(30)	122.1(3)
O(3)–Ba(1)–N(21)	82.10(9)	O(5)–*Ba(2B)–O(4)a	134.39(7)	N(27)–C(26)–N(30)	114.9(3)
O(3)–Ba(1)–N(21)d	83.40(9)	O(5)–*Ba(2B)–O(5)c	148.35(7)	C(14)–N(16)–C(17)	126.0(3)

O(3)d–Ba(1)–N(11)d	70.76(8)	O(5)–*Ba(2B)–O(6)c	64.88(8)	C(14)–N(16)–C(20)	128.7(3)
O(3)d–Ba(1)–N(21)d	82.10(9)	O(5)–*Ba(2B)–O(6)	87.76(9)	C(17)–N(16)–C(20)	105.3(3)
O(4)–Ba(1)–N(11)	133.89(6)	O(5)c–*Ba(2B)–O(6)c	86.28(9)	C(22)–N(23)–C(24)	104.8(3)
O(4)–Ba(1)–N(21)	66.44(6)	O(6)–*Ba(2B)–O(3)c	134.37(9)	C(22)–N(23)–C(26)	126.7(3)
O(7)–Ba(1)–N(11)	70.10(9)	O(6)–*Ba(2B)–O(4)a	68.39(9)	C(24)–N(23)–C(26)	128.5(3)
O(7)–Ba(1)–N(11)d	67.44(9)				

Table S7. Hydrogen bond lengths (Å) and angles (°) for **[Li(trz-tet)H_2O]$_n$**, **[Na(trz-tet)(H_2O)$_2$]$_n$**, **[K(trz-tetH)(trz-tet)(H_2O)$_2$]$_n$**, **[Mg(H_2O)$_6$](trz-tet)$_2$**, **[Ca(H_2O)$_8$](trz-tet)$_2$** and **[Ba$_2$(trz-tet)$_4$(H_2O)$_9$]$_n$**

	D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
[Li(trz-tet)H_2O]$_n$[a]	O(2)–H(2A)···N(3)$^{\#1}$	0.82	1.95	2.765(6)	174
	O(2)–H(2B)···N(4)$^{\#2}$	0.82	1.95	2.764(6)	171
[Na(trz-tet)(H_2O)$_2$]$_n$[b]	O(3)–H(3A)···N(13)$^{\#1}$	0.85(2)	2.12(2)	2.9181(16)	155.5(14)
	O(3)–H(3B)···N(14)$^{\#2}$	0.800(18)	2.084(17)	2.8585(13)	163.0(18)
	O(4)–H(4A)···N(11)$^{\#3}$	0.830(17)	2.009(17)	2.8383(14)	177.1(18)
	O(4)–H(4B)···N(12)$^{\#1}$	0.85(2)	1.98(2)	2.8116(16)	166.9(15)
[K(trz-tetH)(tet)(H_2O)$_2$]$_n$[c]	O(2)–H(2A)···N(15)$^{\#1}$	0.815(17)	1.948(19)	2.739(3)	163(3)
	O(2)–H(2B)···O(3)$^{\#2}$	0.820(19)	1.883(19)	2.700(2)	176(2)
	O(3)–H(3A)···N(11)$^{\#3}$	0.814(18)	2.010(18)	2.816(3)	171(2)
	O(3)–H(3B)···N(22)$^{\#4}$	0.814(18)	2.052(18)	2.859(3)	171(3)
	N(5)–H(5)···O(2)$^{\#5}$	0.87	1.74	2.596(3)	168
[Mg(H_2O)$_6$](trz-tet)$_2$[d]	O(2)–H(2A)···N(12)$^{\#1}$	0.82(3)	1.97(3)	2.795(2)	176(3)
	O(2)–H(2B)···N(11)$^{\#2}$	0.85(3)	2.06(3)	2.915(2)	175(3)
	O(3)–H(3A)···N(17)$^{\#3}$	0.83(3)	2.02(3)	2.849(2)	172(3)
	O(3)–H(3A)···N(18)$^{\#3}$	0.83(3)	2.62(3)	3.319(3)	142(2)
	O(3)–H(3B)···N(19)$^{\#4}$	0.86(3)	1.93(3)	2.782(2)	173(2)
	O(4)–H(4A)···N(18)$^{\#3}$	0.82(3)	1.97(3)	2.776(2)	168(3)
	O(4)–H(4B)···N(11)$^{\#5}$	0.83(3)	2.09(3)	2.905(2)	170(3)
[Ca(H_2O)$_8$](trz-tet)$_2$[e]	O(2)–H(2A)···N(11)$^{\#1}$	0.82	2.11	2.9253(16)	171
	O(2)–H(2B)···O(3)$^{\#2}$	0.82	2.11	2.9147	166
	O(3)–H(3A)···N(12)$^{\#3}$	0.82	2.05	2.8597(15)	171
	O(3)–H(3B)···N(17)	0.82	2.05	2.862(2)	168
	O(4)–H(4A)···N(20)$^{\#4}$	0.82	2.05	2.862(2)	173
	O(4)–H(4B)···N(19)$^{\#5}$	0.82	2.09	2.8997(16)	168
	O(5)–H(5A)···N(11)$^{\#6}$	0.82	2.26	2.9811(16)	146
	O(5)–H(5B)···N(18)$^{\#5}$	0.82	2.09	2.8826(16)	161
[Ba$_2$(trz-tet)$_4$(H_2O)$_9$]$_n$[f]	O(3)–H(3A)···O(7)$^{\#1}$	0.82	2.29	3.106(4)	175
	O(3)–H(3B)···N(19)$^{\#2}$	0.82	2.01	2.825(4)	172
	O(5)–H(5A)···N(13)$^{\#3}$	0.82	1.99	2.806(4)	177
	O(5)–H(5B)···N(18)$^{\#2}$	0.82	2.02	2.832(4)	172
	O(6)–H(6A)···N(12)$^{\#4}$	0.82	2.36	3.095(4)	150
	O(6)–H(6B)···N(29)$^{\#5}$	0.82	2.03	2.837(4)	168
	O(7)–H(7A)···O(7)$^{\#6}$	0.82	2.33	2.8201	119
	O(7)–H(7A)···N(12)$^{\#7}$	0.82	2.59	3.202(5)	132
	O(7)–H(7B)···N(28)$^{\#8}$	0.82	2.01	2.824(4)	170

[a] Symmetry transformations used to generate equivalent atoms: #1 x, $1 + y$, $1 + z$; #2 $1 - x$, $1 - y$, $1 - z$.

[b] Symmetry transformations used to generate equivalent atoms: #1 $1 - x$, $1/2 + y$, $1/2 - z$; #2 $-1 + x$, $1/2 - y$, $-1/2 + z$; #3 $1 - x$, $-1/2 + y$, $1/2 - z$.

[c] Symmetry transformations used to generate equivalent atoms: #1 $1 + x$, y, z; #2 $2 - x$, $-1/2 + y$, $1/2 - z$; #3 $3/2 - x$, $1 - y$, $1/2 + z$; #4 $3/2 - x$, $1 - y$, $-1/2 + z$; #5 $2 - x$, $1/2 + y$, $1/2 - z$.

[d] Symmetry transformations used to generate equivalent atoms: #1 1 + *x*, *y*, *z*; #2 1 – *x*, –*y*, – *z*; #3 1/2 + *x*, 1/2 – *y*, –1/2 + *z*; #4 –1/2 + *x*, 1/2 – *y*, –1/2 + *z*; #5 1 – *x*, –*y*, 1 – *z*.

[e] Symmetry transformations used to generate equivalent atoms: #1 3/2 – *x*, 3/2 – *y*, –*z*; #2 2 – *x*, 1 + *y*, 1/2 – *z*; #3 3/2 – *x*, 1/2 – *y*, –*z*; #4 1/2 + *x*, 1/2 + *y*, *z*; #5 2 – *x*, 1 – *y*, 1 – *z*; #6 1/2 + *x*, 1/2 – *y*, 1/2 + *z*.

[f] Symmetry transformations used to generate equivalent atoms: #1 –1 + *x*, *y*, *z*; #2 –*x*, 1 – *y*, 1 – *z*; #3 *x*, –1 + *y*, *z*; #4 1/2 – *x*, –1 + *y*, 3/2 – *z*; #5 *x*, –*y*, 1 – *z*; #6 3/2 – *x*, *y*, 3/2 – *z*; #7 1/2 – *x*, *y*, 3/2 – *z*; #8 1 – *x*, 1 – *y*, 1 – *z*.

Table S8. π···π bond lengths (Å) and angles (°) for **$[Na(trz\text{-}tet)(H_2O)_2]_n$**, **$[K(trz\text{-}tetH)(trz\text{-}tet)(H_2O)_2]_n$**, **$[Mg(H_2O)_6](trz\text{-}tet)_2$**, **$[Ca(H_2O)_8](trz\text{-}tet)_2$** and **$[Ba_2(trz\text{-}tet)_4(H_2O)_9]_n$**

	Cg(*I*)	Cg(*J*)	*d*[Cg(*I*)–Cg(*J*)][a]	α^a	β^a
$[Na(trz\text{-}tet)(H_2O)_2]_n$[b]	Cg(1)	Cg(2)$^{\#1}$	3.5634(7)	1.20	25.44
	Cg(1)	Cg(2)$^{\#2}$	3.5387(8)	1.39	25.08
	Cg(2)	Cg(1)$^{\#1}$	3.5634(7)	1.20	26.60
	Cg(2)	Cg(1)$^{\#2}$	3.5387(8)	1.39	24.66
	Cg(2)	Cg(2)$^{\#1}$	3.8794(8)	1.84	33.74
	Cg(2)	Cg(2)$^{\#2}$	3.9148(7)	0.00	35.27
$[K(trz\text{-}tetH)(trz\text{-}tet)(H_2O)_2]_n$[c]	Cg(1)	Cg(4)$^{\#1}$	3.5473(16)	0.77	22.57
	Cg(1)	Cg(4)$^{\#2}$	3.5464(16)	0.77	23.35
	Cg(2)	Cg(3)$^{\#1}$	3.5071(16)	0.55	22.71
	Cg(2)	Cg(3)$^{\#2}$	3.5726(16)	0.55	25.28
	Cg(3)	Cg(2)$^{\#3}$	3.5071(16)	0.55	22.21
	Cg(3)	Cg(2)$^{\#4}$	3.5727(16)	0.55	25.18
	Cg(4)	Cg(1)$^{\#3}$	3.5473(16)	0.77	22.82
	Cg(4)	Cg(1)$^{\#4}$	3.5463(16)	0.77	23.93
$[Mg(H_2O)_6](trz\text{-}tet)_2$[d]	Cg(1)	Cg(2)$^{\#1}$	3.4238(11)	1.13	20.60
	Cg(2)	Cg(1)$^{\#2}$	3.4237(11)	1.13	19.48
$[Ca(H_2O)_8](trz\text{-}tet)_2$[e]	Cg(1)	Cg(2)$^{\#1}$	3.4944(8)	6.13	23.38
	Cg(1)	Cg(2)$^{\#2}$	3.5193(8)	6.13	25.94
	Cg(2)	Cg(1)$^{\#1}$	3.5193(8)	6.13	22.88
	Cg(2)	Cg(1)$^{\#2}$	3.4944(8)	6.13	20.99
$[Ba_2(trz\text{-}tet)_4(H_2O)_9]_n$[f]	Cg(1)	Cg(4)$^{\#1}$	3.780(2)	2.9(2)	30.8
	Cg(1)	Cg(4)$^{\#2}$	3.769(2)	2.9(2)	30.8
	Cg(2)	Cg(3)$^{\#1}$	3.775(2)	4.1(2)	28.4
	Cg(2)	Cg(3)$^{\#2}$	3.742(2)	4.1(2)	34.5
	Cg(2)	Cg(4)$^{\#1}$	3.819(2)	1.7(2)	33.3
	Cg(2)	Cg(4)$^{\#2}$	3.709(2)	1.7(2)	30.5
	Cg(3)	Cg(2)$^{\#1}$	3.774(2)	4.1(2)	32.5
	Cg(3)	Cg(2)$^{\#2}$	3.743(2)	4.1(2)	32.2
	Cg(4)	Cg(1)$^{\#1}$	3.780(2)	2.9(2)	33.1
	Cg(4)	Cg(1)$^{\#2}$	3.769(2)	2.9(2)	30.0
	Cg(4)	Cg(2)$^{\#1}$	3.819(2)	1.7(2)	32.4
	Cg(4)	Cg(2)$^{\#2}$	3.709(2)	1.7(2)	30.1

[a] Cg(*I*)–Cg(*J*): distance between ring centroids; α: dihedral angle between planes Cg(*I*) and Cg(*J*); β: angle Cg(*I*) → Cg(*J*) vector and normal to plane *I*.

[b] Symmetry transformations used to generate equivalent atoms: #1 3/2 – *x*, *y*, 1 – *z*; #2 3/2 – *x*, 1/2 – *y*, 1/2 – *z*. Cg(1): N(5)–N(6)–C(7)–N(8)–C(9), Cg(2): N(11)–N(12)–N(13)–N(14)–C(10).

[c] Symmetry transformations used to generate equivalent atoms: #1 3/2 – *x*, 1 – *y*, –1/2 + *z*; #2 5/2 – *x*, 1 – *y*, –1/2 + *z*; #3 3/2 – *x*, 1 – *y*, 1/2 + *z*; #4 5/2 – *x*, 1 – *y*, 1/2 + *z*. Cg(1): N(4)–N(5)–N(6)–C(7)–N(8), Cg(2): N(9)–C(10)–N(11)–N(12)–C(13), Cg(3): N(14)–N(15)–C(16)–N(17)–C(18), Cg(4): N(20)–N(21)–N(22)–N(23)–C(19).

[d] Symmetry transformations used to generate equivalent atoms: #1 –1/2 + *x*, 1/2 – *y*, –1/2 + *z*; #2 1/2 + *x*, 1/2 – *y*, 1/2 + *z*. Cg(1): N(11)–N(12)–C(13)–N(14)–C(15), Cg(2): N(17)–N(18)–N(19)–N(20)–C(16).

[e] Symmetry transformations used to generate equivalent atoms: #1 3/2 – *x*, –1/2 + *y*, 1/2 – *z*; #2 3/2 – *x*, 1/2 + *y*, 1/2 – *z*. Cg(1): N(11)–N(12)–C(13)–N(14)–C(15), Cg(2): N(17)–N(18)–N(19)–N(20)–C(16).

[f] Symmetry transformations used to generate equivalent atoms: #1 –*x*, 1 – *y*, 1 – *z*; #2 1 – *x*, 1 – *y*, 1 – *z*. Cg(1): N(11)–N(12)–N(13)–C(14)–N(15), Cg(2): N(16)–C(17)–N(18)–N(19)–C(20), Cg(3): N(21)–N(25)–C(24)–N(23)–C(22), Cg(4): N(27)–N(28)–N(29)–N(30)–C(26).

Table S9. Experimental and optimized (periodic DFT calculations) cell parameters of the crystals of **[Li(trz-tet)H$_2$O]$_n$**, **[Na(trz-tet)(H$_2$O)$_2$]$_n$**, **[K(trz-tetH)(trz-tet)(H$_2$O)$_2$]$_n$**, **[Mg(H$_2$O)$_6$](trz-tet)$_2$**, **[Ca(H$_2$O)$_8$](trz-tet)$_2$** and **[Ba$_2$(trz-tet)$_4$(H$_2$O)$_9$]$_n$**

	[Li(trz-tet)H$_2$O]$_n$		**[Na(trz-tet)(H$_2$O)$_2$]$_n$**		**[K(trz-tetH)(trz-tet)(H$_2$O)$_2$]$_n$**		**[Mg(H$_2$O)$_6$](trz-tet)$_2$**		**[Ca(H$_2$O)$_8$](trz-tet)$_2$**		**[Ba$_2$(trz-tet)$_4$(H$_2$O)$_9$]$_n$**	
	exp	**opt**	**exp**	**opt**	**exp**	**opt**	**exp**	**opt**	**exp**	**opt**	**exp**	**opt**
a	3.434	3.969	12.994	12.708	6.710	6.956	6.707	6.797	21.535	20.604	6.577	6.735
b	9.898	8.308	10.843	10.515	10.930	10.236	20.115	18.912	6.566	6.382	10.744	10.397
c	10.611	9.295	12.846	12.397	19.560	18.785	6.724	6.714	15.712	15.281	22.344	21.464
α	115.930	107.577	90.000	89.908	90.000	89.997	90.000	90.006	90.000	90.001	90.000	90.205
β	92.170	78.452	119.421	119.343	90.000	89.999	110.850	114.181	123.301	123.126	92.554	103.652
γ	98.473	112.902	90.000	90.038	90.000	89.996	90.000	90.001	90.000	89.999	90.000	90.140

Table S10. The mean crystal cell volumes (Bohr^3) from ab-initio dynamics at different temperatures for **[Li(trz-tet)H$_2$O]$_n$**, **[Na(trz-tet)(H$_2$O)$_2$]$_n$**, **[K(trz-tetH)(trz-tet)(H$_2$O)$_2$]$_n$**, **[Mg(H$_2$O)$_6$](trz-tet)$_2$**, **[Ca(H$_2$O)$_8$](trz-tet)$_2$** and **[Ba$_2$(trz-tet)$_4$(H$_2$O)$_9$]$_n$**

T **(K)**	**[Li(trz-tet)H$_2$O]$_n$**	**[Na(trz-tet)(H$_2$O)$_2$]$_n$**	**[K(trz-tetH)(trz-tet)(H$_2$O)$_2$]$_n$**	**[Mg(H$_2$O)$_6$](trz-tet)$_2$**	**[Ca(H$_2$O)$_8$](trz-tet)$_2$**	**[Ba$_2$(trz-tet)$_4$(H$_2$O)$_9$]$_n$**
398	1905.9	10129.3	9398.2	5510.4	11786.4	10331.3
498	1907.6	10204.4	9482.9	5504.7	12019.2	10508.8
598	1981.3	10489.9	94.75.8	5689.7	12175.4	11564.3
648	1978.7	10542.1	9654.0	5627.9	12403.6	11947.1
748	2138.5	10636.6	9629.1	5947.6	13042.0	12040.4

Table S11. Interaction energies of H$_2$O and **trz-tet** moieties, and the rest of the system for **[Li(trz-tet)H$_2$O]$_n$**, **[Na(trz-tet)(H$_2$O)$_2$]$_n$**, **[K(trz-tetH)(trz-tet)(H$_2$O)$_2$]$_n$**, **[Mg(H$_2$O)$_6$](trz-tet)$_2$**, **[Ca(H$_2$O)$_8$](trz-tet)$_2$** and **[Ba$_2$(trz-tet)$_4$(H$_2$O)$_9$]$_n$**

	[Li(trz-tet)H$_2$O]$_n$	**[Na(trz-tet)(H$_2$O)$_2$]$_n$**	**[K(trz-tetH)(trz-tet)(H$_2$O)$_2$]$_n$**	**[Mg(H$_2$O)$_6$](trz-tet)$_2$**	**[Ca(H$_2$O)$_8$](trz-tet)$_2$**	**[Ba$_2$(trz-tet)$_4$(H$_2$O)$_9$]$_n$**
H$_2$O(1)	–10.89	–6.31	–2.66	–21.28	–13.99	–13.38
H$_2$O(2)	–16.35	–25.49	–2.66	–48.32	–31.13	–14.61
H$_2$O(3)[a]	–19.04	–16.31	–15.54	–35.05	–22.87	–17.96
trz-tet	–130.99	–95.75	–47.42	–91.52	–94.19	–178.30

[a] Models contain solely cation and the surrounded water species. For the example see the H$_2$O(3) model in Fig. S9.