Supplementary information for the paper

"On the Role of Non-Covalent Interactions in the Assembly of 3D Zirconium Methyl- and Ethyl-N,N-bis phosphonates."

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Table S1. Fractional coordinates and isotropic atomic displacement factors for **1.**

Atom	x/*a*	y/*b*	z/*c*	U_{iso}x100
Zr(1)	1.0	1.0	0.0	1.7(1)
Zr(2)	0.5	1.0	0.5	2.1(1)
P(1)	0.5443(11)	0.8796(6)	0.1867(5)	2.3(2)
P(2)	1.1533(10)	0.7296(7)	0.5353(5)	2.2(2)
F(3)	0.9954(16)	0.7859(10)	-0.0491(7)	2.4(1)
O(1)	0.3055(18)	0.8710(12)	0.1217(9)	2.4(1)
O(2)	1.2529(18)	0.6115(11)	0.4385(9)	2.4(1)
O(3)	0.7036(19)	0.9727(14)	0.1179(8)	2.4(1)
O(4)	1.3514(18)	0.8210(12)	0.5657(8)	2.4(1)
O(5)	0.8859(17)	0.8625(12)	0.5049(9)	2.4(1)
O(6)	0.4429(20)	0.9321(13)	0.3218(8)	2.4(1)
N(1)	1.3096(22)	0.4654(14)	0.7261(12)	2.4(1)
C(1)	1.4738(27)	0.5297(20)	0.8010(14)	2.4(1)
C(2)	1.0721(27)	0.6050(16)	0.6720(11)	2.4(1)
C(3)	0.7790(25)	0.6696(11)	0.2183(13)	2.4(1)

Table S2. Selected bond lengths and angles for **1.**

Bond	Length/Å	Bond	Length/Å
Zr(1)-F(3)	1.956(8)	P(2)-O(2)	1.494(7)
Zr(1)-O(1)	2.09(1)	P(2)-O(4)	1.534(8)
Zr(1)-O(3)	2.038(8)	P(2)-O(5)	1.543(8)
Zr(2)-O(5)	2.016(9)	P(2)-C(2)	1.861(8)
Zr(2)-O(6)	2.121(9)	C(1)-N(1)	1.45(1)
Zr(2)-O(4)	1.984(9)	C(2)-N(1)	1.54(1)
P(1)-O(1)	1.481(8)	C(3)-N(1)	1.45(1)
P(1)-O(3)	1.463(7)	H-bonds	
P(1)-O(6)	1.600(8)	N(1)···O(2)	2.82(2)
P(1)-C(3)	1.858(8)		

Angle	Amplitude/°	Angle	Amplitude/°
F(3)-Zr(1)-O(1)	87.0(3)	O(1)-P(1)-O(3)	115.5(7)
F(3)-Zr(1)-O(1)	93.0(3)	O(1)-P(1)-O(6)	105.6(6)
F(3)-Zr(1)-O(3)	83.4(4)	O(1)-P(1)-C(3)	110.0(7)
F(3)-Zr(1)-O(3)	96.6(4)	O(2)-P(2)-O(4)	113.5(6)
O(1)-Zr(1)-O(3)	94.1(3)	O(2)-P(2)-O(5)	114.9(6)
O(1)-Zr(1)-O(3)	85.9(3)	O(2)-P(2)-C(2)	105.4(7)
O(4)-Zr(2)-O(5)	96.3(4)	C(1)-N(1)-C(2)	110.6(9)
O(4)-Zr(2)-O(5)	83.7(4)	C(1)-N(1)-C(3)	117(1)
O(4)-Zr(2)-O(6)	86.1(3)	C(2)-N(1)-C(3)	110.5(9)
O(4)-Zr(2)-O(6)	93.9(3)		

Table S3. Fractional coordinates and isotropic atomic displacement parameters for **2.**

Atom	x/*a*	y/*b*	z/*c*	U_{iso}x100
Zr(1)	0.666700	0.333300	0.13854(7)	0.92(5)
Zr(2)	1.0	0.0	0.0	1.63(8)
C(1)	0.4588(10)	-0.1068(8)	0.1012(4)	2.65(9)
C(2)	0.5490(8)	0.0024(9)	0.0860(5)	2.65(9)
N(1)	0.6509(7)	-0.0033(8)	0.0700(5)	2.65(9)
C(3)	0.7104(9)	-0.0146(9)	0.1111(5)	2.65(9)
C(4)	0.7276(8)	0.0897(8)	0.0340(5)	2.65(9)
P(1)	0.7943(3)	-0.0835(3)	0.0957(2)	2.3(1)
P(2)	0.8112(3)	0.2346(3)	0.0595(2)	2.6(1)
O(1)	0.8639(5)	-0.0584(7)	0.1441(3)	2.65(9)
O(2)	0.7172(6)	-0.2015(6)	0.0825(4)	2.65(9)
O(3)	0.8671(5)	-0.0285(5)	0.0473(2)	2.65(9)
O(4)	0.8973(6)	0.2396(5)	0.1035(3)	2.65(9)
O(5)	0.8630(6)	0.3055(6)	0.0114(3)	2.65(9)
O(6)	0.7364(7)	0.2634(7)	0.0922(3)	2.65(9)

Table S4. Selected bond lengths and angles for **2.**

Bond	Length/Å	Bond	Length/Å
Zr(1)-O(1)	2.088(6)	P(2)-O(5)	1.498(7)
Zr(1)-O(6)	2.055(6)	P(2)-O(6)	1.535(6)
Zr(2)-O(3)	2.072(5)	C(1)-C(2)	1.467(1)
P(1)-C(3)	1.898(9)	C(2)-N(1)	1.524(11)
P(1)-O(1)	1.485(6)	N(1)-C(3)	1.384(11)
P(1)-O(2)	1.492(7)	N(1)-C(4)	1.506(11)
P(1)-O(3)	1.522(6)	H-bonds	
P(2)-C(4)	1.879(9)	O(5)···N(1)	2.62(2)
P(2)-O(4)	1.610(7)	O(1)···O(4)	2.39(1)

Angle	Amplitude/°	Angle	Amplitude/°
O(1)-Zr(1)-O(1)	86.9(3)	O(1)-P(1)-O(2)	118.0(5)
O(1)-Zr(1)-O(1)	86.9(3)	O(1)-P(1)-O(3)	109.5(4)
O(1)-Zr(1)-O(6)	88.4(3)	O(2)-P(1)-O(3)	108.5(5)
O(1)-Zr(1)-O(6)	93.6(3)	C(4)-P(2)-O(4)	109.2(5)
O(6)-Zr(1)-O(6)	91.3(3)	C(4)-P(2)-O(5)	106.1(5)
O(3)-Zr(2)-O(3)	90.6(3)	C(4)-P(2)-O(6)	109.1(5)
O(3)-Zr(2)-O(3)	90.6(2)	O(4)-P(2)-O(5)	114.5(4)
O(3)-Zr(2)-O(3)	89.4(2)	C(2)-N(1)-C(3)	116(1)
O(3)-Zr(2)-O(3)	89.4(2)	C(2)-N(1)-C(4)	113.3(9)
C(3)-P(1)-O(1)	102.4(5)	C(3)-N(1)-C(4)	109.5(9)
C(3)-P(1)-O(2)	108.6(5)	C(1)-C(2)-N(1)	111(1)
C(3)-P(1)-O(3)	109.5(5)		

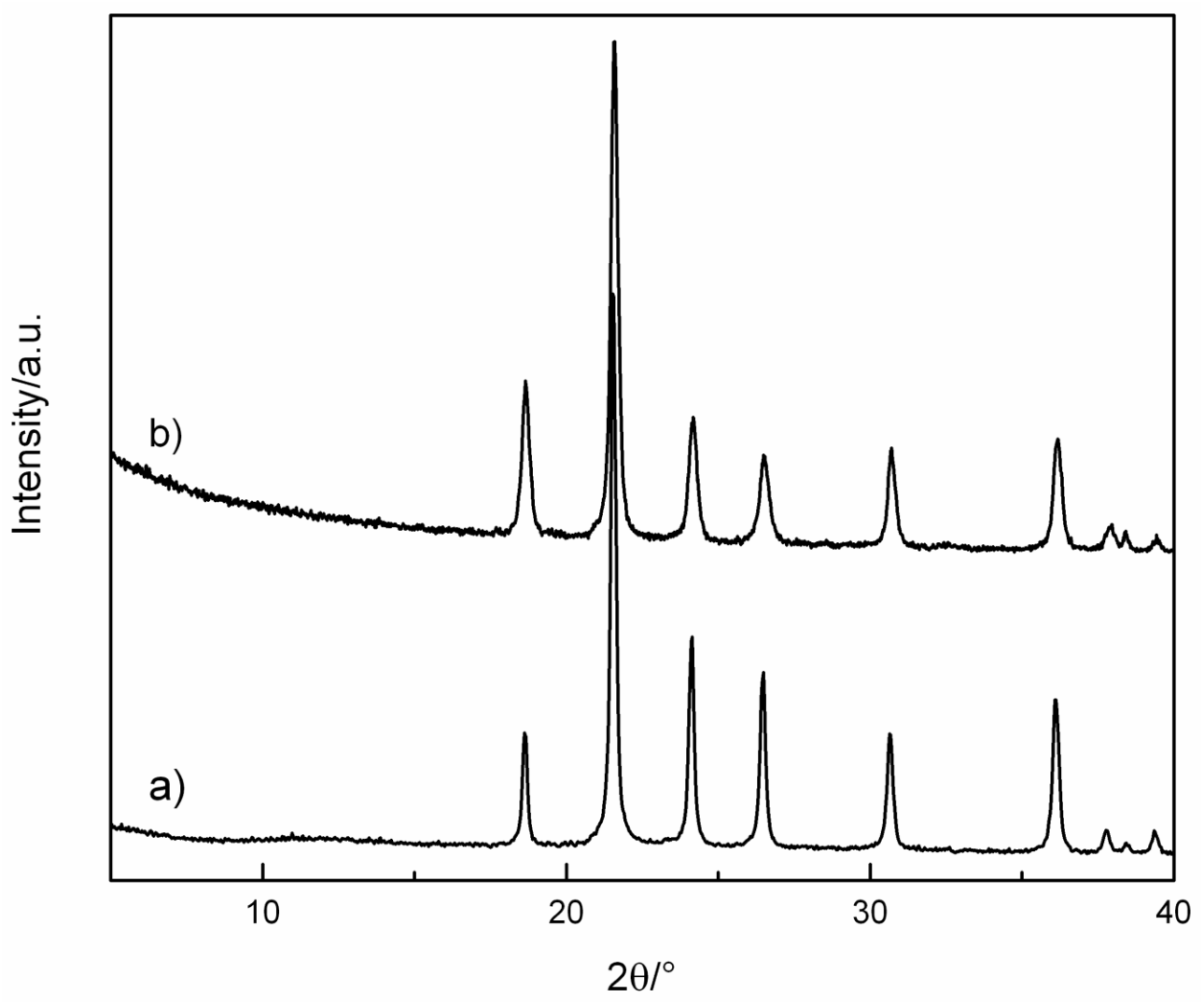

Figure 1S. XRPD patterns (Zr Pyrophosphate) of the TGA residues for **1** (a) and **2** (b).