Supporting Information for the manuscript

Biguanide and squaric acid as pH-dependent building blocks in crystal engineering.

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Table S1. Complete table of hydrogen bonds (Å ,°); non-classical contacts with $D\cdots A > 3.1$ Å have not been included.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
		1a		
O(1)–H(1)···O(6)	1.048(4)	1.421(4)	2.447(3)	164.6(4)
O(5)–H(5)···O(2)	1.022(4)	1.569(4)	2.568(3)	164.5(4)
N(2)–H(2) ···O(4)^{i}	1.034(4)	1.779(4)	2.742(2)	153.2(3)
N(5)–H(5B)···O(3)	1.019(4)	1.788(4)	2.743(2)	154.5(3)
N(3)–H(3B)···O(4)^{i}	1.017(4)	1.893(4)	2.789(2)	145.2(3)
N(5)–H(5A)···O(7)^{ii}	1.023(4)	1.838(4)	2.822(2)	160.5(4)
N(3)–H(3A)···O(8)^{ii}	1.014(4)	1.849(4)	2.824(2)	160.1(3)
N(4)–H(4A)···O(3)^{iii}	1.015(4)	1.900(4)	2.856(2)	155.7(4)
N(4)–H(4A) ···N(5)	1.015(4)	2.456(5)	2.9061(16)	106.1(3)
N(5)–H(5B)···N(4)	1.019(4)	2.479(4)	2.9061(16)	104.5(2)
N(4)–H(4B)···O(7)^{iv}	1.010(4)	2.068(5)	3.008(2)	154.1(4)

^{i} = -1+x,-1+y, z; ^{ii} = x,y,1+z; ^{iii} = 2-x,1-y,2-z; ^{iv} = 2-x,1-y,1-z

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
		1b		
O(5)–H(151)···O(1)^{i}	0.86(3)	1.92(4)	2.664(3)	144(4)
O(5)–H(150)···O(6)^{ii}	0.83(2)	1.87(2)	2.697(3)	177(4)
N(2)–H(20)···O(5)	0.91(2)	1.82(2)	2.717(3)	166(2)
N(5)–H(50)···O(4)	0.90(2)	1.88(3)	2.763(3)	164(2)
O(6)–H(161)···O(2)	0.85(3)	1.92(3)	2.768(3)	171(3)
O(6)–H(160)···O(2)^{iii}	0.86(3)	1.93(3)	2.783(3)	173(3)
N(3)–H(30)···O(3)	0.92(2)	1.89(2)	2.792(3)	165(2)
N(4)–H(41)···O(3)^{iv}	0.893(18)	1.942(19)	2.804(3)	162(3)
N(3)–H(31)···O(4)^{v}	0.894(19)	1.964(19)	2.833(3)	164(3)
N(5)–H(51)···O(1)^{i}	0.90(3)	1.99(3)	2.866(3)	164(2)
N(4)–H(40)···O(4)^{iii}	0.87(2)	2.04(2)	2.882(3)	162(3)
N(4)–H(40)···N(3)	0.87(2)	2.55(3)	2.932(3)	107(2)
N(3)–H(31)···N(4)	0.894(19)	2.56(3)	2.932(3)	106(2)

^{i}=2-x,1-y,-1/2+z; ^{ii}=x,1+y,z; ^{iii}=3/2-x,y,-1/2+z; ^{iv}=1-x,1-y,-1/2+z; ^{v}=-1/2+x,1-y,z.

Table S1. Complete table of hydrogen bonds (Å ,°) - continued

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
		1c		
N(7)–H(70)···O(3)^{i}	0.908(15)	1.738(16)	2.609(2)	159.9(19)
N(2)–H(20)···O(1)^{ii}	0.949(16)	1.692(16)	2.621(2)	165.3(19)
O(9)–H(109)···O(7)^{iii}	0.89(4)	2.05(3)	2.700(2)	129(3)
O(10)–H(210)···O(5)^{iv}	0.901(17)	1.825(17)	2.723(2)	175.2(18)
N(10)–H(100)···O(9)^{v}	0.880(16)	1.898(17)	2.738(3)	159(2)
N(4)–H(41)···O(8)^{iii}	0.934(18)	1.832(18)	2.759(2)	171.3(17)
N(3)–H(30)···O(10)^{vi}	0.913(16)	1.893(17)	2.764(3)	159(2)
N(5)–H(51)···O(2)^{ii}	0.935(17)	1.859(17)	2.772(2)	165(2)
N(8)–H(81)···O(5)^{iii}	0.94(2)	1.85(2)	2.777(2)	167.1(19)
N(9)–H(90)···O(6)^{vii}	0.937(19)	1.860(19)	2.792(2)	172.7(19)
N(8)–H(80)···O(4)^{i}	0.842(16)	1.981(16)	2.807(2)	166.9(16)
O(9)–H(209)···O(3)	0.876(19)	1.944(19)	2.812(3)	171(2)
N(5)–H(50)···O(7)^{vi}	0.894(16)	2.040(16)	2.871(2)	153.9(14)
N(10)–H(101)···O(6)^{iii}	0.87(2)	2.17(2)	2.876(2)	137.3(16)
O(10)–H(110)···O(1)	0.82(2)	2.14(2)	2.878(2)	151(3)
N(4)–H(40)···O(4)^{iii}	0.92(2)	2.02(2)	2.898(2)	160.7(19)
N(9)–H(91)···O(2)^{vi}	0.917(18)	2.073(17)	2.905(2)	150.2(18)
N(3)–H(31)···O(7)^{vi}	0.91(2)	2.23(2)	2.974(2)	139.5(18)
N(3)–H(31)···O(8)^{vi}	0.91(2)	2.46(3)	3.099(2)	128.1(18)
C(9)–H(9C)···N(4)	0.98	2.45	2.793(3)	100
C(10)–H(10C)···N(2)	0.98	2.38	2.785(3)	104
C(14)–H(14A)···N(7)	0.98	2.41	2.785(3)	102

^{i} = -1+x,-1+y,z; ^{ii} = -x,-1/2+y,1-z; ^{iii} = 1-x,-1/2+y,1-z; ^{iv} = 1-x,1/2+y,1-z; ^{v} = 1-x,-1/2+y,2-z;

^{vi} = x,-1+y,z; ^{vii} = x,-1+y,1+z.

Table S1. Complete table of hydrogen bonds (Å ,°) - continued

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
		1d		
O(3)–H(3A)···O(1)	0.857(16)	1.923(18)	2.7455(18)	161(2)
N(3)–H(30)···O(3)^{i}	0.894(17)	1.956(18)	2.809(2)	159.1(15)
O(3)–H(3B)···N(2)^{ii}	0.864(18)	1.997(18)	2.8517(18)	170(2)
N(5)–H(50)···O(1)	0.877(17)	2.010(18)	2.877(2)	169.8(15)
N(3)–H(31)···O(2)^{iii}	0.864(16)	2.104(16)	2.9036(17)	153.7(14)
N(4)–H(40)···O(2)^{i}	0.886(17)	2.080(18)	2.9447(18)	164.9(15)
N(4)–H(41)···O(2)^{iv}	0.877(16)	2.164(17)	2.9779(18)	154.1(14)
N(5)–H(51)···O(3)^{iii}	0.879(19)	2.368(18)	3.204(2)	159.1(19)
C(3)–H(3E)···N(2)	0.98	2.38	2.756(2)	102

^{i} = x,1+y,z; ^{ii} = 1-x,1-y,1-z; ^{iii} = -x,1-y,1-z; ^{iv} = -x,1-y,-z.

Table S1. Complete table of hydrogen bonds (Å ,°) - continued

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
		2a		
O(1)–H(1)···O(6)^{i}	0.87(2)	1.64(2)	2.496(3)	168(4)
N(6)–H(60)···O(6)^{ii}	0.91(2)	1.80(2)	2.706(3)	172(2)
N(7)–H(70)···O(8)	0.85(3)	1.91(2)	2.706(3)	155(2)
N(9)–H(90)···O(4)^{iii}	0.92(2)	1.85(2)	2.744(3)	163(2)
N(10)–H(101)···O(3)^{iv}	0.945(19)	1.857(18)	2.774(3)	163(3)
N(10)–H(100)···O(7)	0.94(2)	1.886(19)	2.810(3)	169(2)
N(8)–H(81)···O(2)^{iv}	0.92(2)	1.91(2)	2.832(3)	172(2)
O(30)–H(30C)···O(6)^{v}	0.84	2.49	2.845(8)	107
N(1)–H(10)···O(7)	0.92(2)	1.94(2)	2.846(3)	165(3)
N(5)–H(51)···O(8)^{vi}	0.93(2)	1.963(19)	2.873(3)	165(3)
N(3)–H(31)···O(5)^{vi}	0.93(2)	1.98(2)	2.892(3)	166(2)
N(3)–H(30)···O(2)^{vii}	0.93(2)	2.05(3)	2.931(3)	158(3)
N(5)–H(50)···O(4)^{iv}	0.90(2)	2.05(2)	2.946(3)	173(2)
N(4)–H(40)···O(1)^{vii}	0.90(2)	2.21(2)	2.972(3)	142(2)
N(8)–H(80)···O(5)^{ii}	0.90(2)	2.11(2)	2.978(3)	161(2)
N(4)–H(41)···N(3)	0.88(3)	2.55(2)	2.991(4)	112(2)
N(9)–H(91)···O(3)	0.91(3)	2.13(3)	3.007(3)	162(2)
O(30)–H(30C)···O(1)^{viii}	0.84	2.36	3.178(7)	163
C(10)–H(10A)···N(2)	0.95	2.32	2.894(4)	118

^{i} = 1-x,1/2+y,1/2-z; ^{ii} = x,3/2-y,1/2+z; ^{iii} = 1-x,2-y,1-z; ^{iv} = 1-x,1-y,1-z; ^{v} = -x,-1/2+y,1/2-z; ^{vi} = x,-1+y,z; ^{vii} = 1-x,-1/2+y,1/2-z; ^{viii} = -1+x,-1+y,z.

Table S1. Complete table of hydrogen bonds (Å ,°) - continued

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
		2b		
N(6)–H(160)···O(2)	0.940(18)	1.854(19)	2.766(2)	163.1(18)
N(4)–H(141)···O(4)^{i}	0.933(18)	1.879(19)	2.790(2)	164.9(18)
N(10)–H(201)···O(2)^{ii}	0.887(18)	1.936(18)	2.811(2)	168.8(18)
N(5)–H(150)···O(4)^{iii}	0.931(18)	1.929(18)	2.835(2)	163.7(16)
N(8)–H(180)···O(1)^{ii}	0.93(2)	1.94(2)	2.856(2)	167.8(18)
N(3)–H(131)···O(3)^{iii}	0.909(19)	2.025(19)	2.911(2)	164.5(17)
N(5)–H(151)···N(7)^{iv}	0.847(17)	2.079(17)	2.921(3)	173.1(17)
N(3)–H(130)···O(1)^{i}	0.880(18)	2.15(2)	2.952(2)	151.2(18)
N(4)–H(140)···O(1)^{v}	0.903(19)	2.137(19)	2.954(2)	150.2(19)
N(8)–H(181)···O(3)	0.90(2)	2.09(2)	2.968(2)	165.1(19)
N(9)–H(190)···O(3)^{vi}	0.91(2)	2.073(19)	2.973(2)	172(2)
N(8)–H(181)···N(6)	0.90(2)	2.58(2)	3.013(3)	109.9(17)
N(3)–H(130)···N(4)	0.880(18)	2.59(2)	3.013(3)	110.2(16)
N(10)–H(200)···N(2)^{iv}	0.943(19)	2.076(19)	3.018(3)	177.3(16)
N(9)–H(191)···O(2)	0.910(19)	2.50(2)	3.147(2)	128.8(17)
C(9)–H(9)···N(2)	0.95	2.34	2.923(3)	120
C(17)–H(17)···N(7)	0.95	2.57	3.081(3)	114

^{i} = -x,1-y,1-z; ^{ii} = 1+x,y,z; ^{iii} = 1-x,1-y,1-z; ^{iv} = 1-x,2-y,1-z; ^{v} = x,y,-1+z; ^{vi} = 1-x,2-y,2-z.

Table S1. Complete table of hydrogen bonds (Å ,°) - continued

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
		3a		
N(2)–H(120)···O(3)	0.906(15)	1.751(15)	2.6410(19)	166.5(16)
N(1)–H(110)···O(5)	0.873(17)	1.872(17)	2.711(2)	160.5(17)
N(4)–H(141)···O(1)^{i}	0.898(18)	1.874(18)	2.7358(19)	160.3(16)
O(5)–H(5A)···O(1)	0.838(18)	1.947(18)	2.7842(18)	178(2)
O(5)–H(5B)···O(1)^{ii}	0.860(18)	1.97(2)	2.8060(18)	163(2)
N(4)–H(140)···O(2)^{i}	0.936(17)	2.164(18)	2.813(2)	125.5(15)
N(3)–H(130)···O(2)^{iii}	0.899(18)	1.974(18)	2.847(2)	163(2)
N(3)–H(131)···O(4)	0.915(19)	1.974(19)	2.8856(19)	175(2)
N(5)–H(150)···O(4)^{iv}	0.907(17)	2.001(17)	2.888(2)	165.5(17)
N(5)–H(151)···O(5)^{v}	0.885(17)	2.133(17)	2.908(2)	145.9(15)
N(4)–H(141)···N(5)	0.898(18)	2.612(17)	2.951(2)	103.3(13)

^{i} = x,1/2-y,-1/2+z; ^{ii} = 2-x,-y,1-z; ^{iii} = 1+x,1/2-y,-1/2+z; ^{iv} = x,1/2-y,1/2+z; ^{v} = 2-x,1/2+y,1/2-z.

Table S1. Complete table of hydrogen bonds (Å ,°) - continued

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
		3b		
N(12)–H(112)···O(11)^{i}	0.892(16)	1.780(16)	2.651(3)	165(2)
N(7)–H(107)···O(8)	0.91(2)	1.77(2)	2.655(3)	166(3)
N(2)–H(102)···O(10)^{ii}	0.899(19)	1.797(19)	2.691(3)	173(2)
N(14)–H(214)···O(3)	0.92(2)	1.85(2)	2.717(3)	158(2)
N(9)–H(209)···O(5)^{iii}	0.93(2)	1.84(2)	2.748(3)	167(2)
N(8)–H(108)···O(6)	0.90(3)	1.91(2)	2.753(3)	157(2)
N(1)–H(101)···O(9)^{ii}	0.88(2)	1.89(2)	2.754(3)	166(2)
O(14)–H(24O)···O(9)	0.894(18)	1.879(18)	2.758(2)	168(3)
N(8)–H(208)··· O(7)	0.92(2)	1.85(2)	2.762(3)	173(3)
N(5)–H(205)··· O(14)^{iv}	0.89(3)	1.88(3)	2.764(3)	174(3)
N(11)–H(111)···O(13)	0.89(2)	1.98(2)	2.778(3)	150(2)
N(13)–H(213)···O(12)^{i}	0.91(2)	1.89(2)	2.785(3)	169(2)
N(4)–H(104)···O(1)^{v}	0.90(2)	2.06(2)	2.793(3)	138(2)
N(3)–H(203)···O(1)^{ii}	0.91(3)	2.03(2)	2.801(3)	142(2)
N(9)–H(109)···O(6)^{iii}	0.91(3)	2.18(3)	2.805(3)	126(2)
N(6)–H(106)···O(15)	0.90(2)	2.00(2)	2.811(3)	150(2)
N(13)–H(113)···O(4)^{ii}	0.92(2)	1.97(2)	2.820(3)	153(2)
N(5)–H(105)···O(2)^{vi}	0.90(3)	1.94(3)	2.823(3)	163(2)
O(13)–H(23O)···O(5)^{vii}	0.88(3)	1.96(3)	2.824(2)	168(3)
O(13)–H(13O)···O(5)	0.89(3)	1.94(3)	2.825(2)	173(3)
N(10)–H(210)···O(12)	0.89(2)	1.95(2)	2.831(3)	174(2)
O(15)–H(15O)···O(3)^{viii}	0.85(2)	1.99(2)	2.834(3)	172(3)
N(14)–H(114)···O(4)	0.91(3)	2.13(3)	2.839(3)	134(2)
N(15)–H(115)···O(10)^{ii}	0.89(2)	1.99(2)	2.853(3)	162(2)
O(14)–H(14O)···O(8)	0.859(18)	2.06(2)	2.862(2)	155(2)
N(4)–H(204)···O(2)^{v}	0.93(3)	2.06(3)	2.870(3)	146(2)
O(15)–H(25O)···O(1)^{ix}	0.85(3)	2.04(3)	2.888(3)	176(3)
N(15)–H(215)···O(4)^{ii}	0.90(2)	2.15(3)	2.952(3)	149(2)
N(15)–H(115)···N(14)	0.89(2)	2.53(2)	2.956(4)	109.9(17)

N(14)–H(214)···N(15)	0.92(2)	2.59(3)	2.956(4)	104.4(17)
N(10)–H(110)···O(13)^{x}	0.92(2)	2.25(2)	2.996(3)	138(2)
N(3)–H(103)···O(3)	0.890(19)	2.20(2)	3.004(3)	151(2)
N(4)–H(104)···N(5)	0.90(2)	2.62(3)	3.048(4)	109.8(17)
N(11)–H(111)···O(11)^{i}	0.89(2)	2.54(2)	3.066(3)	119(2)
C(31)–H(31B)···N(11)	0.98	2.42	2.880(3)	108

^{i} = 1+x,1+y,z; ^{ii} = 1+x,y,z; ^{iii} = -1+x,y,z; ^{iv} = 1-x,1-y,-z; ^{v} = 1-x,2-y,-z; ^{vi} = 2-x,2-y,-z; vii = 2-x,1-y,1-z; ^{viii} = -1+x,-1+y,z; ^{ix} = x,-1+y,z; ^{x} = 1-x,1-y,1-z.

Table S1. Complete table of hydrogen bonds (Å ,°) - continued

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
		3c		
O(1)–H(1)···O(6)^{i}	0.906(16)	1.607(16)	2.5120(14)	177(3)
N(7)–H(70)···O(8)	0.892(16)	1.890(17)	2.7432(15)	159.6(18)
N(9)–H(90)···O(4)^{ii}	0.885(16)	2.042(16)	2.7865(17)	141.0(15)
N(10)–H(101)···O(7)	0.903(16)	1.902(16)	2.7940(15)	169.1(19)
N(8)–H(80)···O(2)^{iii}	0.908(15)	1.906(15)	2.8072(15)	171.3(16)
N(4)–H(40A)···O(7)^{iv}	0.899(17)	1.966(17)	2.8223(17)	158.6(17)
N(6)–H(60)···O(6)^{v}	0.887(17)	1.983(17)	2.8245(15)	158.1(17)
N(10)–H(100)···O(3)^{iii}	0.891(16)	1.964(16)	2.8424(16)	168.8(16)
N(8)–H(80A)···O(5)^{v}	0.886(16)	2.008(15)	2.8486(15)	157.8(14)
N(3)–H(30A)···O(2)^{i}	0.890(18)	2.011(18)	2.8775(17)	164.3(17)
N(9)–H(90A)···O(3)	0.889(17)	2.032(18)	2.8775(17)	158.6(17)
N(3)–H(30)···O(5)	0.895(16)	2.012(16)	2.8826(16)	164.0(16)
N(5)–H(50A)···O(8)	0.890(16)	2.023(15)	2.9019(17)	169.0(18)
N(4)–H(40)···O(5)^{i}	0.878(14)	2.118(14)	2.9646(18)	161.7(16)
N(5)–H(50)···O(4)^{ii}	0.884(16)	2.204(16)	3.0521(17)	160.8(18)
N(9)–H(90)···O(6)^{v}	0.885(16)	2.499(18)	3.1005(17)	125.8(13)
N(1)–H(10)···O(1)^{i}	0.875(17)	2.352(17)	3.1289(17)	148.0(17)
C(18)–H(18A)···N(6)	0.98	2.58	2.930(3)	101

^{i} = 1-x,1/2+y,1/2-z; ^{ii} = 1-x,2-y,1-z; ^{iii} = 1-x,1-y,1-z; ^{iv} = x,1+y,z; ^{v} = x,3/2-y,1/2+z.

Table S1. Complete table of hydrogen bonds (Å ,°) - continued

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
		3d		
N(4)–H(41)···N(1)	0.929(14)	1.923(14)	2.6541(17)	134.0(12)
N(2)–H(20)···O(1)^{i}	0.878(15)	1.912(15)	2.7602(15)	162.1(14)
N(4)–H(40)···O(2)^{ii}	0.903(13)	1.947(13)	2.8399(16)	169.7(14)
N(3)–H(30)···O(1)^{iii}	0.892(14)	1.992(14)	2.8609(16)	164.2(13)
N(3)–H(31)···O(2)^{i}	0.908(14)	2.003(14)	2.8990(16)	169.0(13)
N(5)–H(50)···O(1)^{i}	0.872(14)	2.217(15)	2.9663(18)	143.8(12)

^{i} = 1/2-x,1/2+y,1/2-z; ^{ii} = -x,2-y,-z; ^{iii} = x,1+y,z.

Fig. S1. ADP plot of the asymmetric unit in **1b**

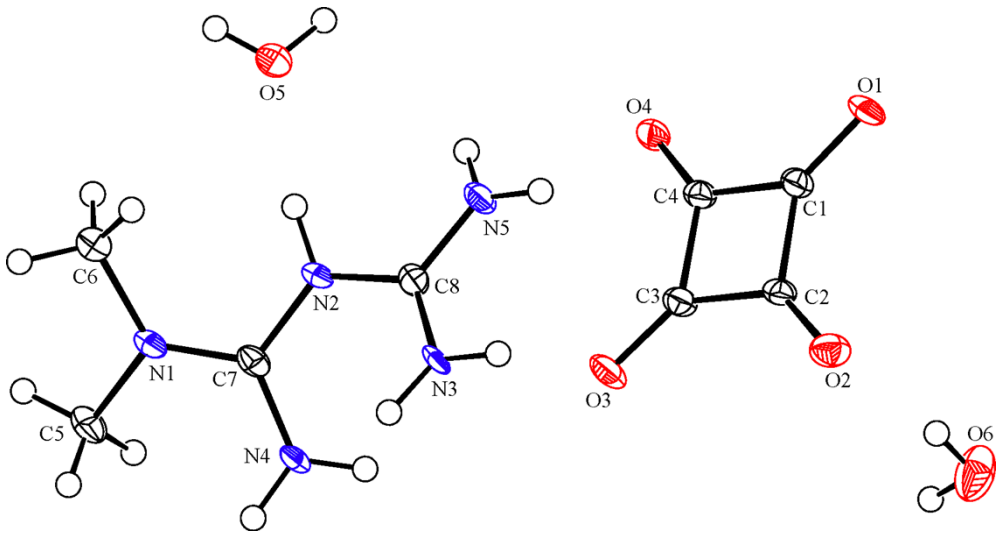

Fig. S2. ADP plot of the asymmetric unit in **1c**

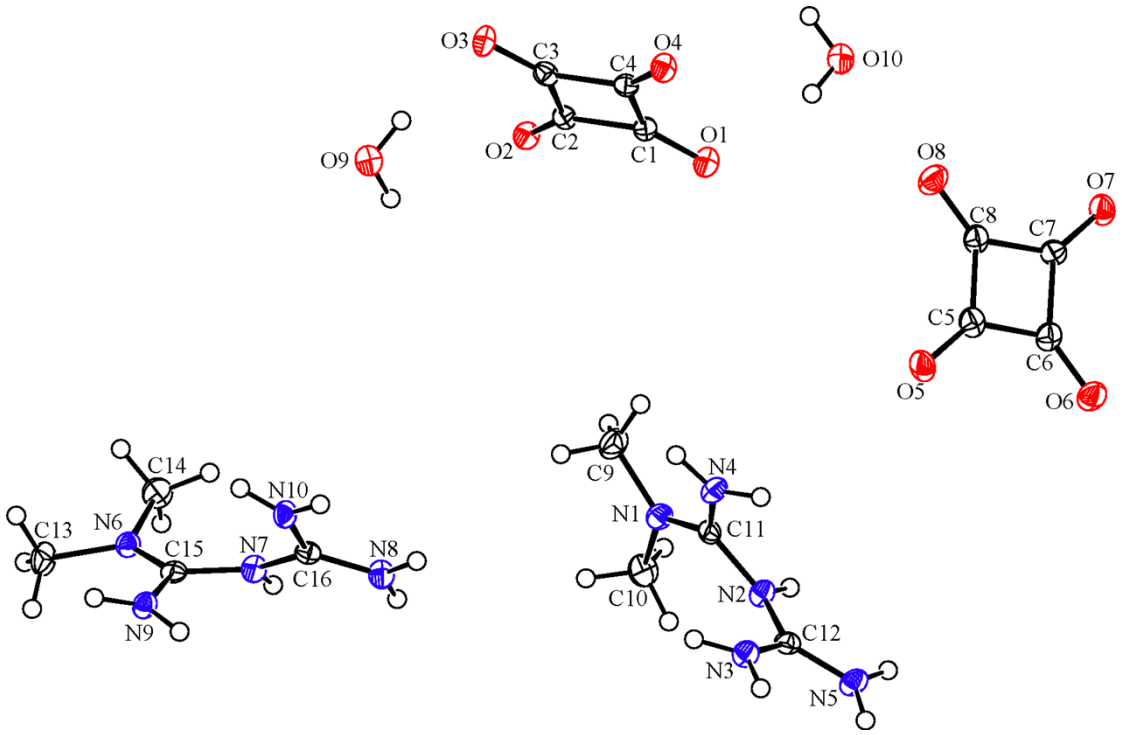

Fig. S3. ADP plot of the asymmetric unit in **1d**

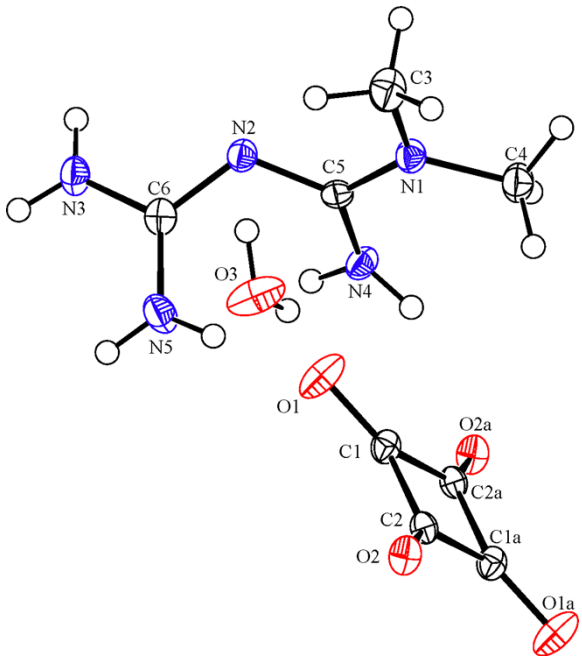

Fig. S4. ADP plot of the asymmetric unit in **2a**

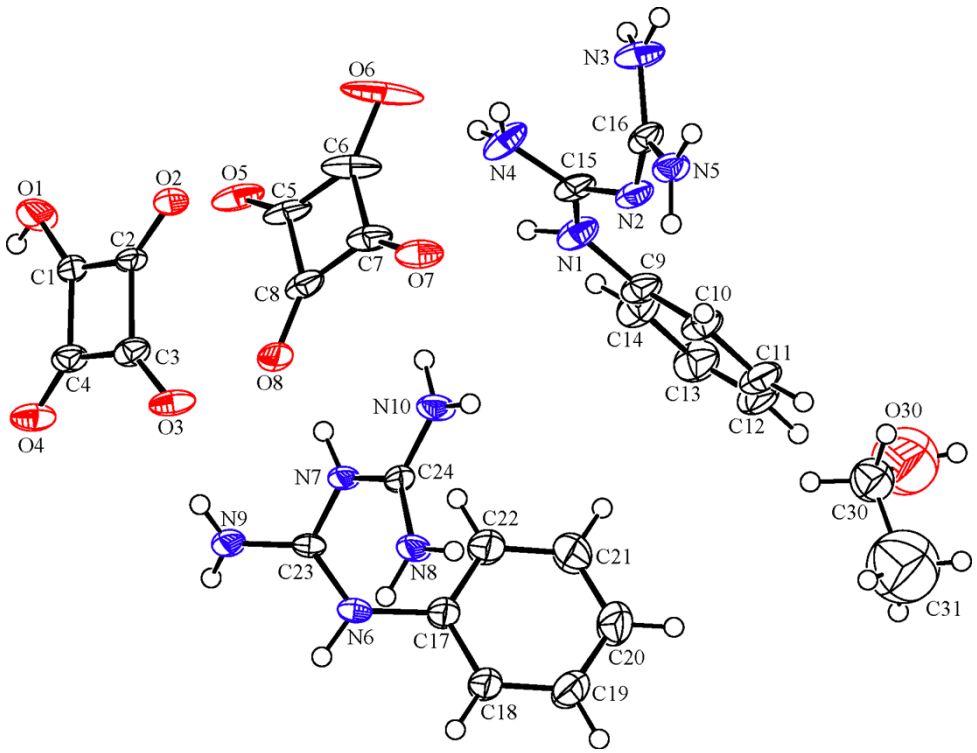

Fig. S5. ADP plot of the asymmetric unit in **2b**

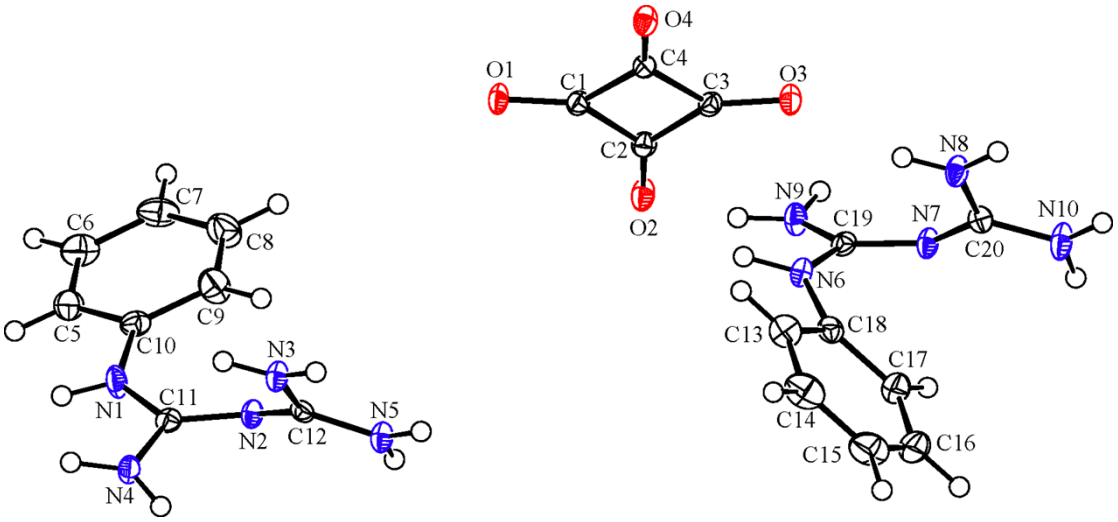

Fig. S6. ADP plot of the asymmetric unit in **3a**

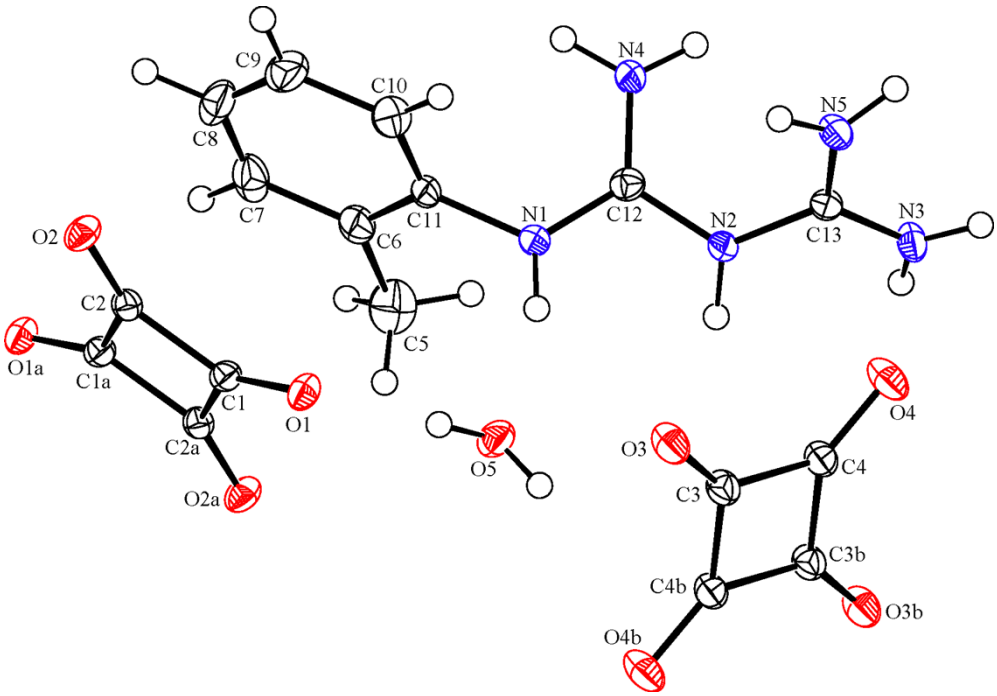

Fig. S7. ADP plot of the asymmetric unit in **3b**

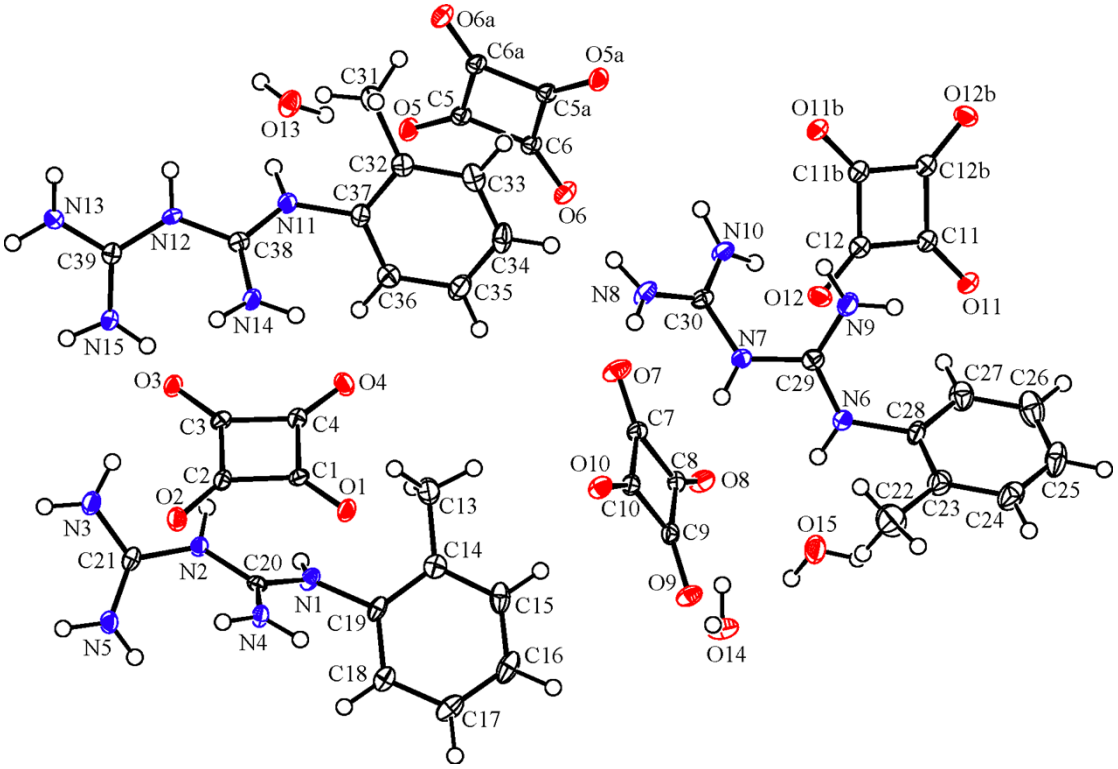

Fig. S8. ADP plot of the asymmetric unit in **3c**

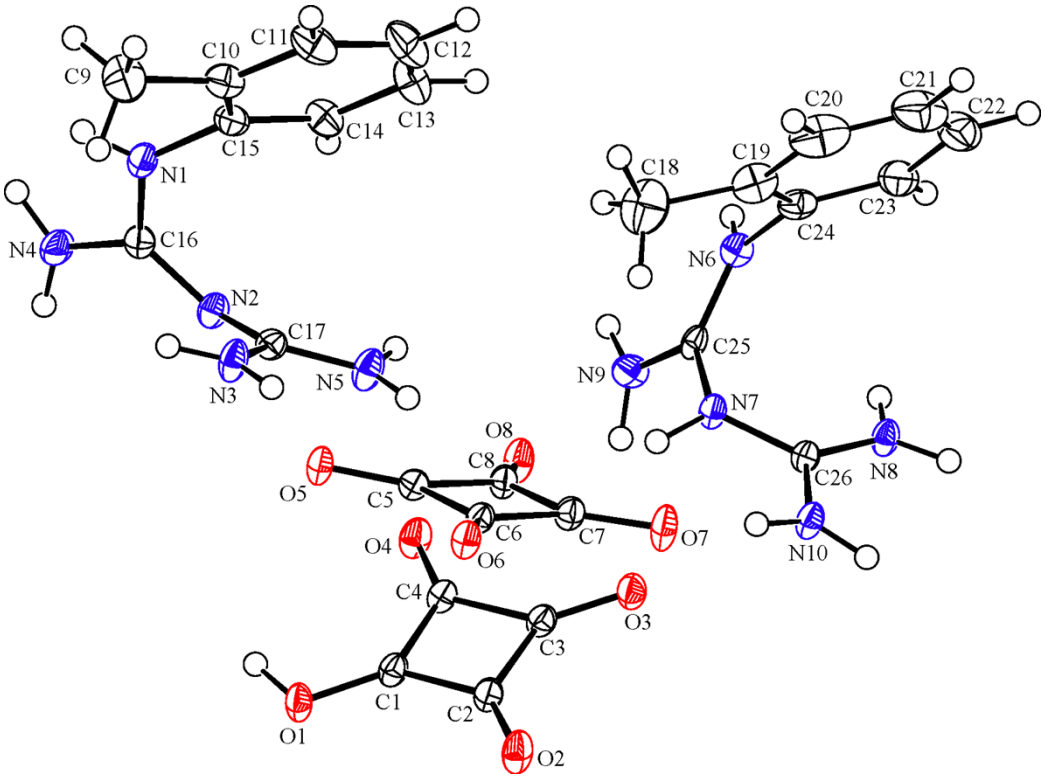

Fig. S9. ADP plot of the asymmetric unit in **3d**

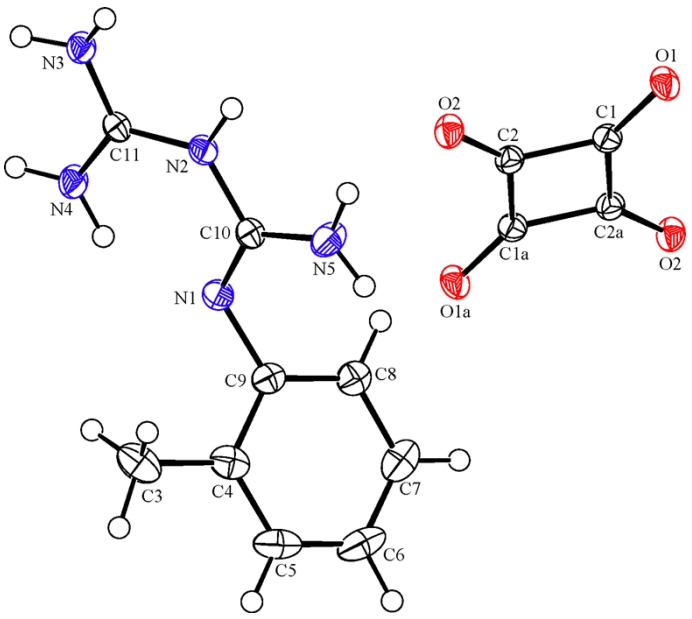

Fig. S10. Experimental and simulated powder patterns for **2a**

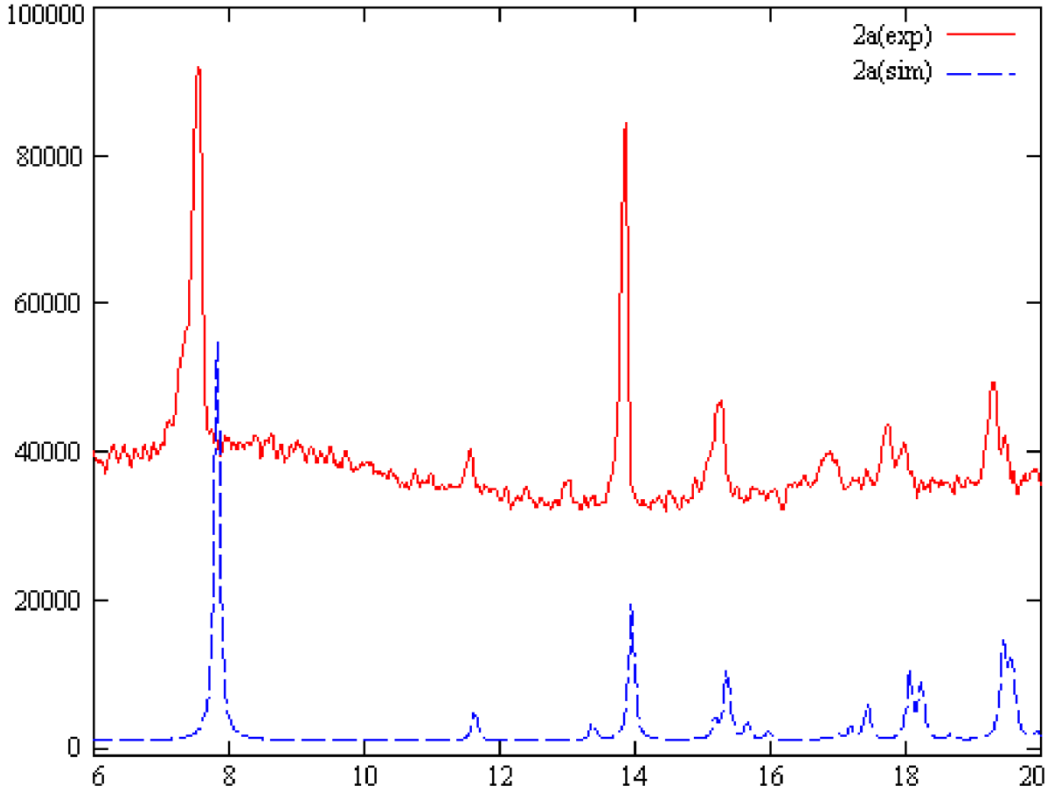

Fig. S11. Experimental and simulated powder patterns for **2b**

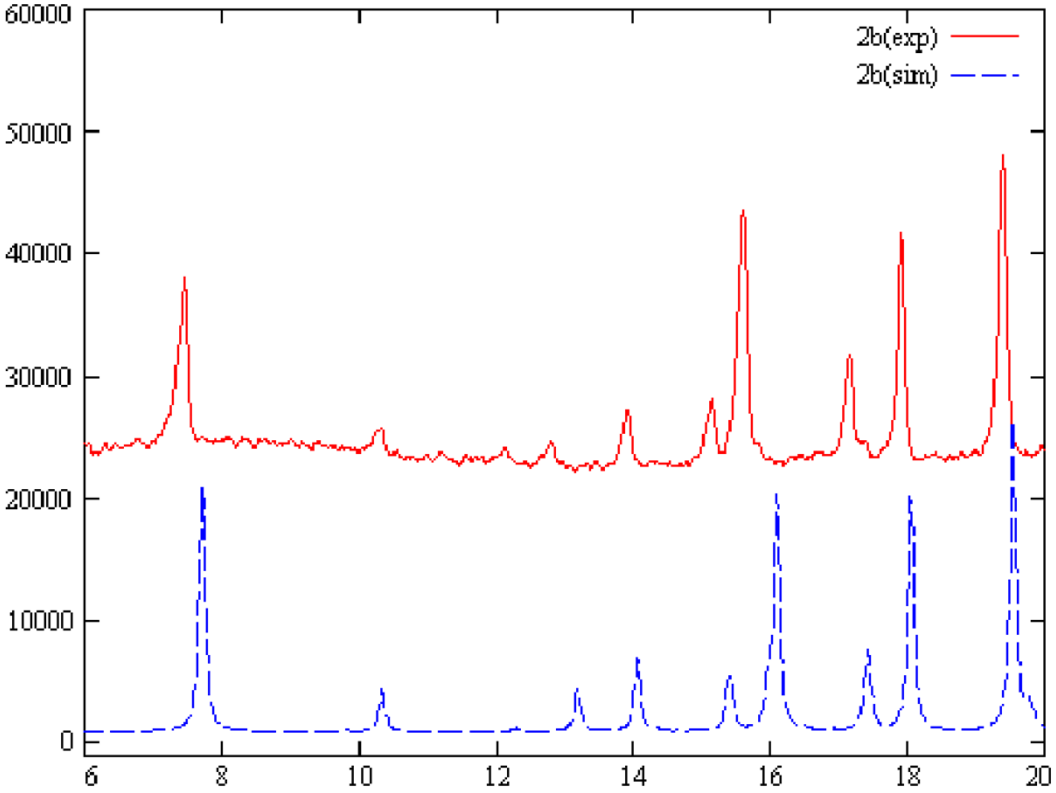

Fig. S12. Experimental and simulated powder patterns for **3c**

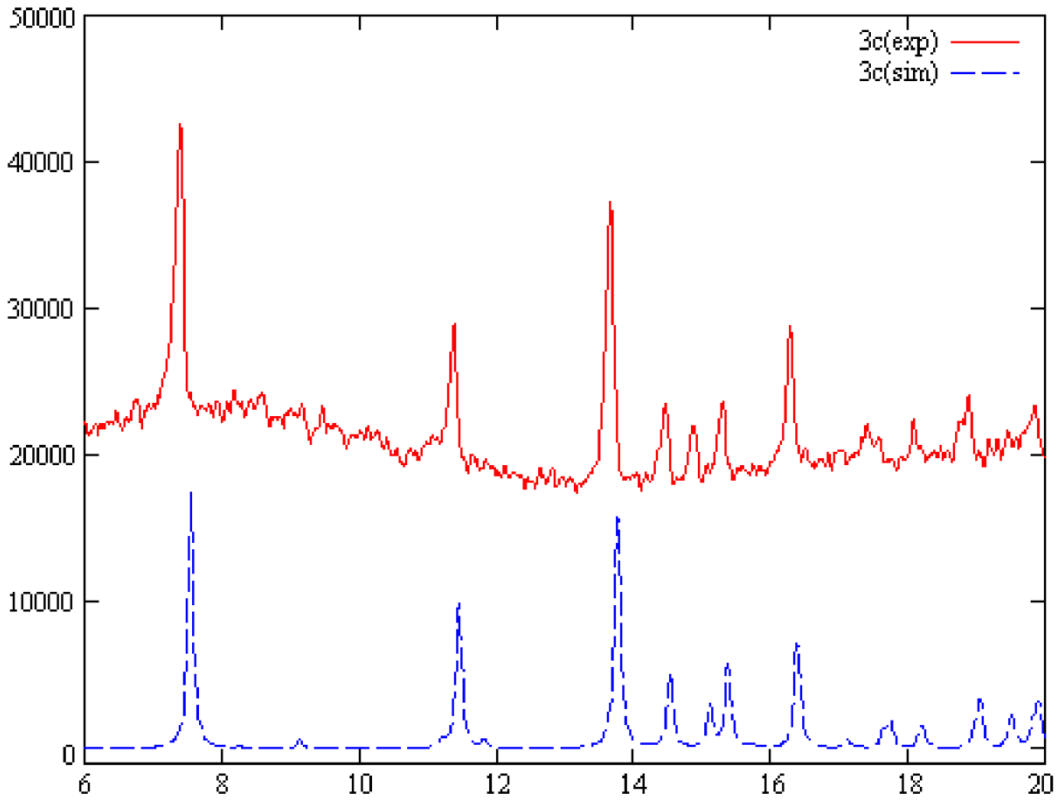

Fig. S13. Experimental and simulated powder patterns for **3d**