Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Mimicking cellular phospholipid bilayer packing creates predictable crystalline molecular metal-organophosphonate macrocycles and cages.

Aysun Bulut,[b,c] Maria Maares, [a] Kaan Atak,[d] Yunus Zorlu,[c] Bünyemin Çoşut, [c] Jon Zubieta, [e] Jens Beckmann, [f] Hajo Haase,[a] Gündoğ Yücesan*[a]

[a]Lebensmittelchemie und Toxikologie, Technische Universität Berlin, Berlin, Germany

[b]Faculty of Pharmacy, Altinbas University, Istanbul, Turkey

[c]Department of Chemistry, Gebze Technical University, Kocaeli, Turkey

[d]Methods for Materials Development, Helmholtz-Zentrum Berlin, Berlin, Germany

[e] Department of Chemistry, Syracuse University, Syracuse, United States

[f] Institut für Anorganische Chemie und Kristallographie, Universität Bremen, Bremen, Germany

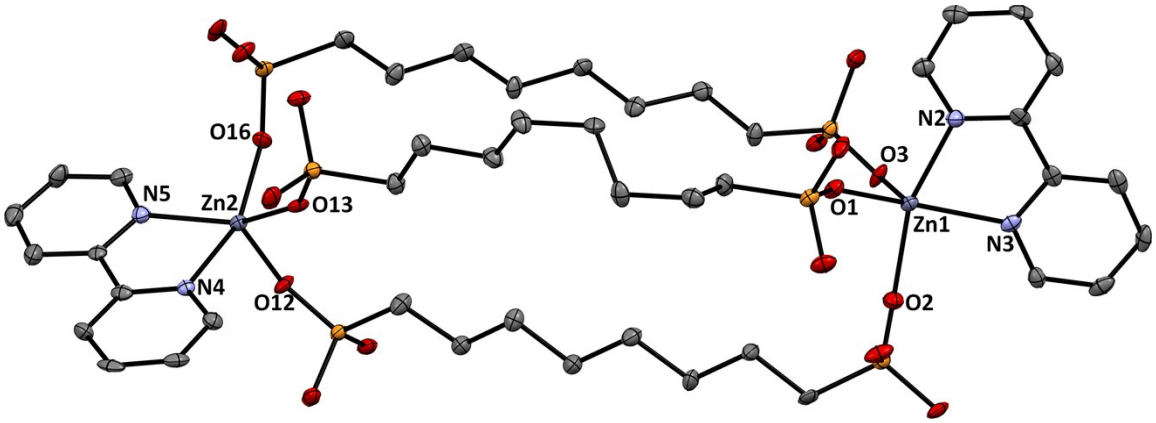


Figure S1. Coordination environment of Zn(II) atom in **1.** Displacement ellipsoids are drawn at the 50% probability level. All H-atoms are omitted for clarity.

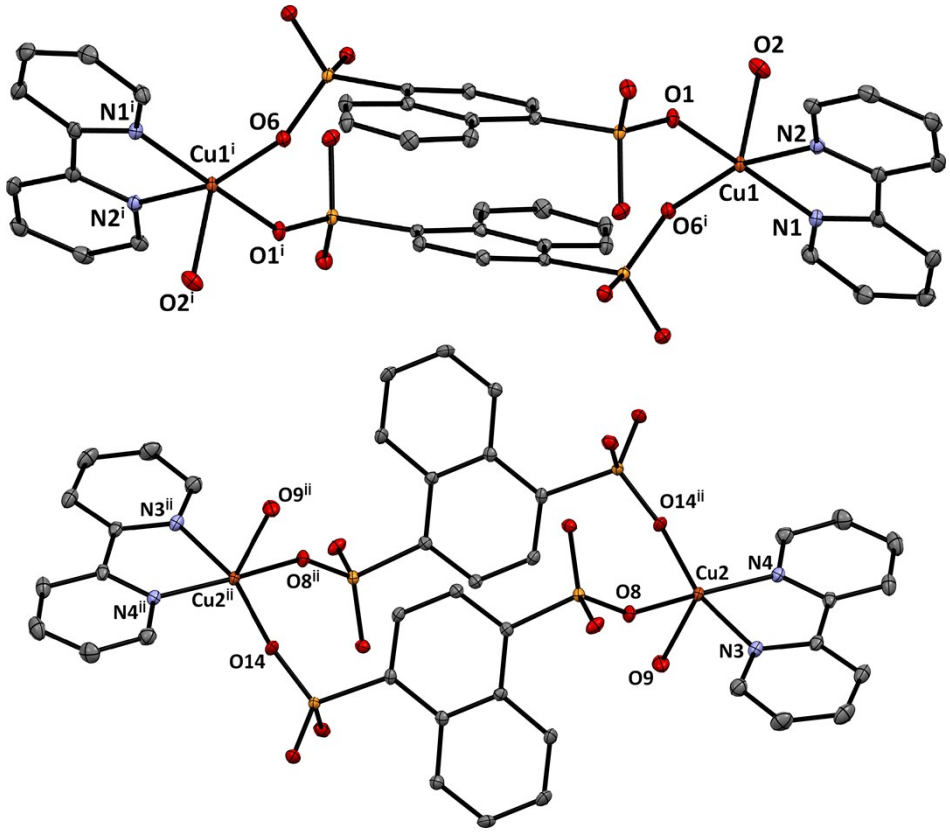


Figure S2. Coordination environment of Cu(II) atom in **2.** Displacement ellipsoids are drawn at the 50% probability level. All H-atoms and lattice water molecule are omitted for clarity. Symmetry codes: (i) −x+1, −y+1, −z+2; (ii) −x, −y+1, −z+1.

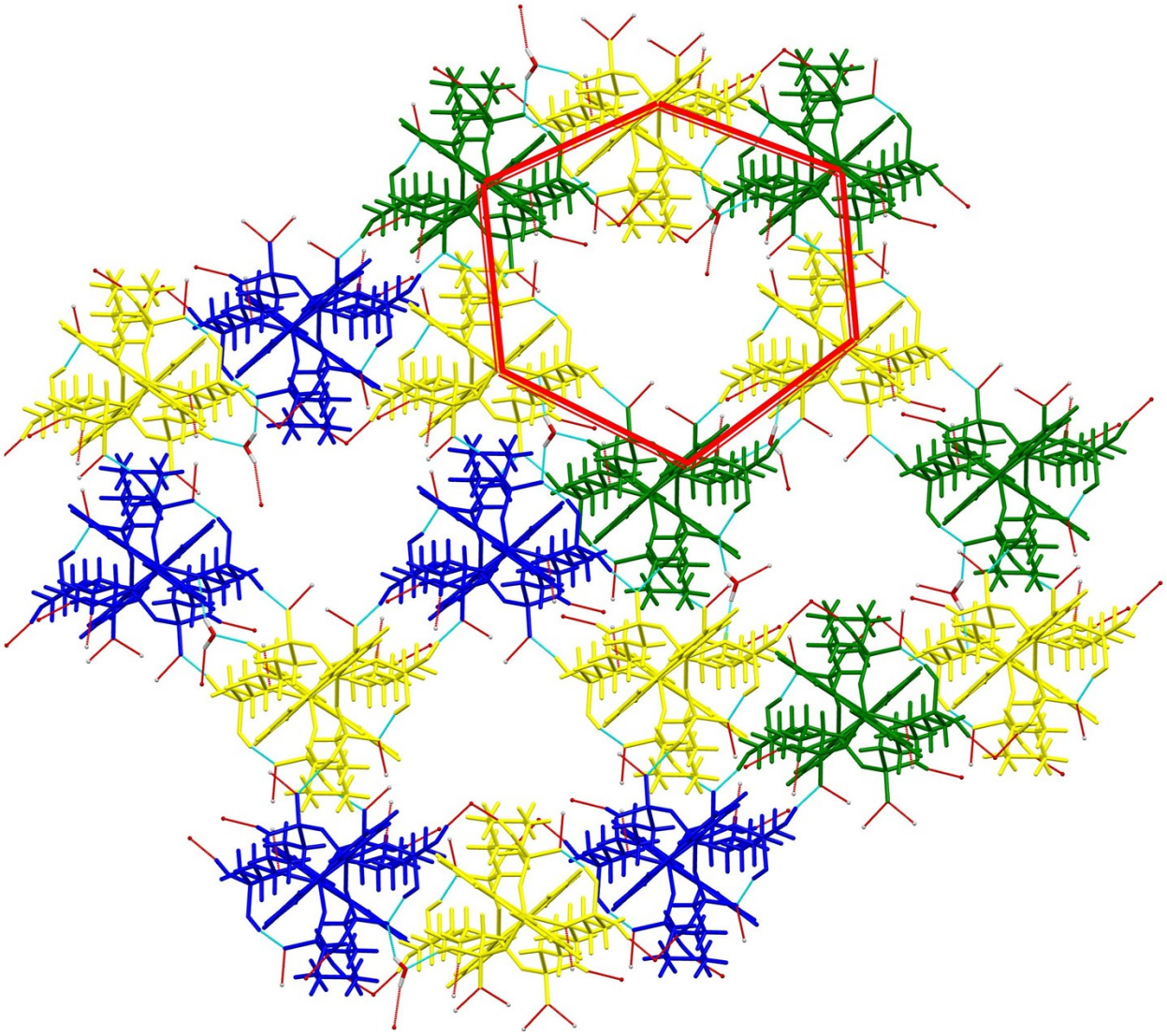


Figure S3. The hydrogen bonded 2D networks of **1**•2H_2O.

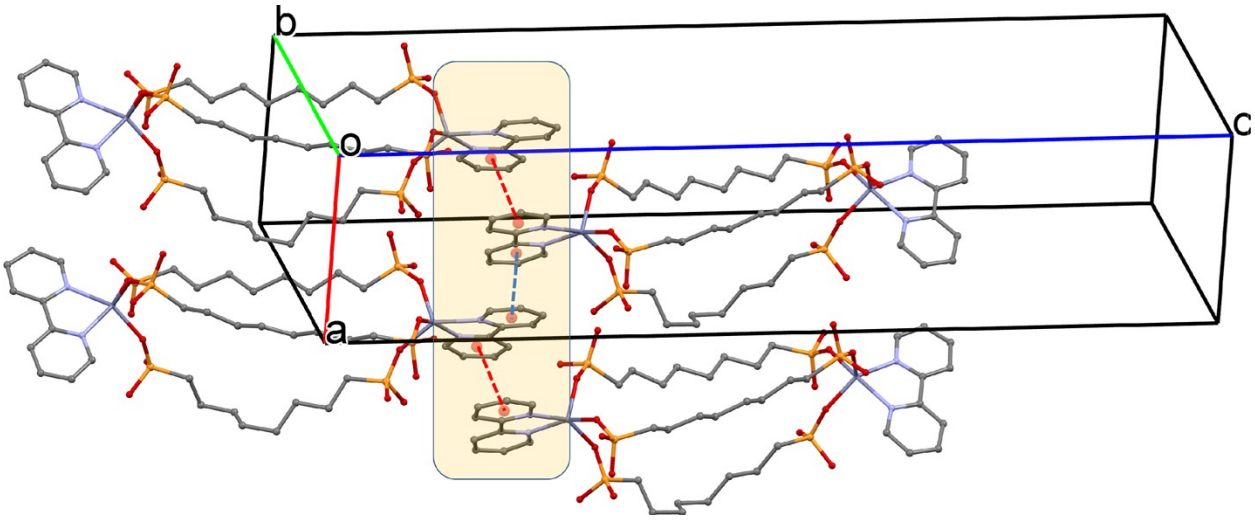
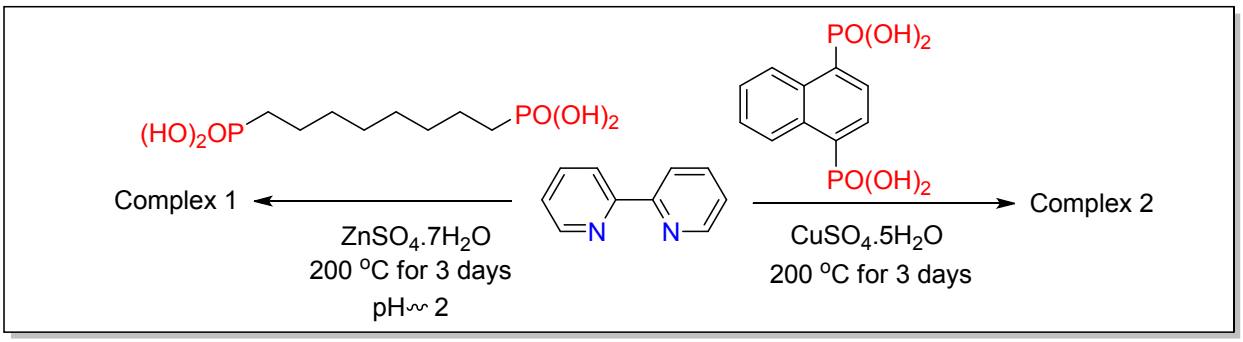


Figure S4. The perspective view of π-stacks between bipyridyl units in 1•2H_2O.

1. Synthesis



Scheme S1. Synthetic pathway for the preparation of complexes **1** and **2**.

2. X-ray data collection and structure refinement details for 1 and 2.

All non-hydrogen atoms were refined anisotropically using all reflections with $I > 2\sigma(I)$. Aromatic C-bound H atoms were positioned geometrically and refined using a riding mode. The H atoms of water molecules were located in a difference Fourier map and the O-H distances restrained to be 0.84 Å from O atom using DFIX command and their positions were constrained to refine on their parent O atoms with *U*iso(H) = 1.5*U*eq(O). The phosphonate H-atoms (-PO_2(OH)) were located in a difference Fourier map and the O-H distances restrained to be 0.84 Å from O atom using DFIX command and their positions were constrained to refine on their parent O atoms with *U*iso(H) = 1.5*U*eq(O). Crystallographic data and refinement details of the data collection for complexes **1** and **2** are given in Table S1. The selected bond lengths and bond angles are given in Tables S2 and S5. Geometric parameters used for the determination of the π···π interactions in **1** and **2** were shown in Tables S4 and S7. Tables S3 and S6 exhibit hydrogen-bond geometries (Å, °) for **1** and **2**. Crystal structure validations and geometrical calculations were performed using Platon software. [S1] Mercury software [S2] was used for visualization of the cif files. Additional crystallographic data with CCDC reference numbers 1451824 (for **1**) and 1563881 (for **2**) have been deposited within the Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/deposit.

Table S1. Crystal data and structure refinement details for the complex **1** and **2**.

Compound	**1**	**2**
CCDC number	1451824	1563881
Chemical formula	$C_{44}H_{76}N_4O_{20}P_6Zn_2$	$C_{40}H_{38}Cu_2N_4O_{15}P_4$
Formula weight (g. mol^{-1})	1297.64	1065.70
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	*P-1*
***a* (Å)**	8.6054 (8)	12.2401 (4)
***b* (Å)**	16.7131 (15)	12.5701 (4)
***c* (Å)**	39.418 (3)	13.4190 (5)
α(°)	90	93.658 (2)
β(°)	92.227 (2)	94.070 (2)
γ(°)	90	94.367 (2)
Crystal size (mm)	0.22 × 0.18 × 0.12	0.11 x 0.15 x 0.19
V (Å^3)	5664.9 (9)	2048.47 (12)
Z	4	2
ρ_{calcd} (g. cm^{-3})	1.521	1.728
μ (mm^{-1})	1.092	1.274
F(000)	2712	1088
θ range for data collection (°)	2.40 to 23.81	2.24 to 28.40
h/k/l	-10/10, -19/19, -46/46	-16/16, -16/16, -17/17
Reflections collected	167545	147459
Independent reflections	10064 [R(int) = 0.15]	10259 [R(int) = 0.0651]
Data/restraints/parameters	10064 / 11 / 715	10259 / 13 / 616
Goodness-of-fit on F^2	1.04	1.07
Final *R* indices [I > 2σ(I)]	R_1= 0.0695, wR_2= 0.1614	R_1 = 0.0314, wR_2 = 0.0735
***R* indices (all data)**	R_1= 0.1062, wR_2= 0.1740	R_1 = 0.0443, wR_2 = 0.0788
Largest diff. peak and hole (e.Å^{-3})	0.91 and -0.80	0.522 and -0.441

Table S2. Selected bond lengths (Å) and bond angles (°) for **1**.

Bond lengths (Å)					
O2—Zn1	2.038 (5)	O3—Zn1	1.955 (5)	N2—Zn1	2.127 (6)
N3—Zn1	2.163 (6)	O1—Zn1	2.004 (5)	N4—Zn2	2.140 (6)
N5—Zn2	2.141 (6)	O12—Zn2	1.945 (5)	O13—Zn2	1.969 (5)
O16—Zn2	2.049 (5)				
Bond angles (°)					
O3—Zn1—O1	103.8 (2)	O3—Zn1—O2	99.0 (2)	O1—Zn1—O2	94.0 (2)
O3—Zn1—N2	102.5 (2)	O1—Zn1—N2	91.1 (2)	O2—Zn1—N2	156.0 (2)
O3—Zn1—N3	106.6 (2)	O1—Zn1—N3	148.8 (2)	O2—Zn1—N3	88.0 (2)
N2—Zn1—N3	75.8 (2)	O12—Zn2—O13	104.7 (2)	O12—Zn2—O16	98.3 (2)
O13—Zn2—O16	94.0 (2)	O12—Zn2—N4	100.4 (2)	O13—Zn2—N4	89.4 (2)
O16—Zn2—N4	159.5 (2)	O12—Zn2—N5	109.1 (2)	O13—Zn2—N5	145.0 (2)
O16—Zn2—N5	90.1 (2)	N4—Zn2—N5	75.9 (2)		

Table S3. Hydrogen-bond geometry (Å, °) for **1**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···O2	0.93	2.55	3.068 (9)	116
C4—H4···O14^{i}	0.93	2.48	3.286 (9)	146
C7—H7···O12^{ii}	0.93	2.53	3.263 (9)	136
C9—H9···O17^{iii}	0.93	2.65	3.248 (9)	123
C10—H10···O17^{iii}	0.93	2.61	3.228 (9)	125
C11—H11···O9^{iv}	0.93	2.63	3.278 (9)	127
C14—H14···O3^{v}	0.93	2.54	3.321 (9)	142
C17—H17···O6^{vi}	0.93	2.43	3.227 (10)	144
C20—H20···O16	0.93	2.56	3.096 (9)	117
C21—H21*B*···O1	0.97	2.65	3.314 (9)	126
C35—H35*B*···O10^{vii}	0.97	2.61	3.384 (9)	137
O4—H4*A*···O19^{iii}	0.82	1.81	2.572 (8)	155
O14—H14*A*···O10^{vii}	0.82	1.78	2.576 (7)	165
O18—H18*A*···O15	0.82	1.67	2.460 (7)	161
O19—H1*W*···O15	0.84 (2)	1.93 (3)	2.694 (8)	152 (7)
O21—H3*W*···O6^{iv}	0.84 (2)	2.60 (5)	3.296 (8)	141 (6)
O21—H3*W*···O7^{iv}	0.84 (2)	1.90 (3)	2.677 (8)	153 (6)
O21—H4*W*···O2^{viii}	0.84 (2)	2.04 (3)	2.832 (8)	157 (6)
O6—H6*W*···O5^{vii}	0.83 (2)	1.79 (4)	2.574 (7)	156 (8)
O8—H8*W*···O7	0.85 (2)	1.62 (3)	2.441 (7)	164 (8)
O9—H9*W*···O10^{viii}	0.83 (2)	1.67 (3)	2.486 (7)	167 (8)
O11—H11*W*···O21	0.84 (2)	1.81 (4)	2.605 (8)	158 (8)
O17—H17*W*···O5^{ix}	0.84 (2)	1.69 (4)	2.498 (7)	158 (8)
O19—H2*W*···O16^{vii}	0.84 (2)	1.97 (2)	2.795 (8)	169 (7)

Symmetry codes: (i) x+1/2, −y+1/2, z+1/2; (ii) x−1/2, −y+1/2, z+1/2; (iii) −x+1, −y+1, −z+2; (iv) −x+1, −y, −z+2; (v) x−1/2, −y+1/2, z−1/2; (vi) x+1/2, −y+1/2, z−1/2; (vii) x−1, y, z; (viii) −x+2, −y, −z+2; (ix) −x+2, −y+1, −z+2.

Table S4. Geometric parameters used for the determination of the π···π interactions in **1***

Rings Cg(I)-Cg(J)[a]	Symmetry	Cg···Cg[b]	Cg(I)-Perp[c]	Cg(J)-Perp[d]	α[e]	β[f]	γ[g]
Cg(1)···Cg(4)	-1/2+x,1/2-y,1/2+z	3.815(4)	3.461(3)	3.430(3)	6.7(4)	26.0	24.9
Cg(2) ···Cg(3)	1/2+x,1/2-y,1/2+z	3.912(4)	3.437(3)	3.517(3)	7.7(4)	26.0	28.5
Cg(3)···Cg(2)	-1/2+x,1/2-y,-1/2+z	3.912(4)	3.518(3)	3.437(3)	7.7(4)	28.5	26.0
Cg(4)···Cg(1)	1/2+x,1/2-y,-1/2+z	3.816(4)	3.430(3)	3.461(3)	6.7(4)	24.9	26.0

* ($Cg\cdots Cg^b$ < 4.0 Å). [a]Cg(1), Cg(2), Cg(3), and Cg(4) represent the centroids of the six-membered aromatic rings N2-C6-C7-C8-C9-C10, N3-C1-C2-C3-C4-C5, N4-C11-C12-C13-C14-C15, and N5-C16-C17-C18-C19-C20, respectively. [b] Distance between ring centroids (Å). [c] Perpendicular distance of Cg(I) on ring J (Å). [d] Perpendicular distance of Cg(J) on ring I (Å). [e] Dihedral angle between planes I and J (°). [f] Angle between the centroid vector Cg(I)···Cg(J) vector and normal to plane I (°). [g] Angle between the centroid vector Cg(I)···Cg(J) vector and normal to plane J (°).

Table S5. Selected bond lengths (Å) and bond angles (°) for **2**.

Bond lengths (Å)			
Cu1—O1	1.9252 (15)	Cu2—O14^{ii}	1.9204 (15)
Cu1—O6^{i}	1.9463 (15)	Cu2—O8	1.9392 (15)
Cu1—N1	2.0053 (18)	Cu2—N4	2.0006 (18)
Cu1—N2	2.0104 (18)	Cu2—N3	2.0160 (18)
Cu1—O2	2.2342 (15)	Cu2—O9	2.2075 (16)
Bond angles (°)			
O1—Cu1—O6^{i}	92.52 (6)	O14^{ii}—Cu2—O8	96.47 (6)
O1—Cu1—N1	170.86 (7)	O14^{ii}—Cu2—N4	89.96 (7)
O6^{i}—Cu1—N1	92.55 (7)	O8—Cu2—N4	170.09 (7)
O1—Cu1—N2	92.40 (7)	O14^{ii}—Cu2—N3	163.94 (7)
O6^{i}—Cu1—N2	162.51 (7)	O8—Cu2—N3	91.66 (7)
N1—Cu1—N2	80.58 (7)	N4—Cu2—N3	80.34 (7)
O1—Cu1—O2	92.30 (6)	O14^{ii}—Cu2—O9	95.54 (6)
O6^{i}—Cu1—O2	102.33 (6)	O8—Cu2—O9	87.24 (6)
N1—Cu1—O2	94.04 (7)	N4—Cu2—O9	99.68 (7)
N2—Cu1—O2	94.23 (6)	N3—Cu2—O9	98.67 (7)

Symmetry codes: (i) −x+1, −y+1, −z+2; (ii) −x, −y+1, −z+1

Table S6. Hydrogen-bond geometry (Å, °) for **2**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···O6^{i}	0.95	2.53	3.016 (3)	112
C4—H4···O13^{iii}	0.95	2.62	3.421 (3)	143
C7—H7···O12^{iii}	0.95	2.57	3.492 (3)	165
C10—H10···O1	0.95	2.47	2.994 (3)	115
C21—H21···O8	0.95	2.46	2.980 (3)	114
C27—H27···O3^{iv}	0.95	2.56	3.446 (3)	155
C30—H30···O14^{ii}	0.95	2.43	2.914 (3)	112
C33—H33···O9^{ii}	0.95	2.63	3.575 (3)	174
O2—H2*W*···O4^{v}	0.83 (2)	1.97 (2)	2.790 (2)	170 (2)
O2—H3*W*···O13^{i}	0.84 (2)	1.96 (2)	2.790 (2)	170 (2)
O3—H3*O*···O7^{i}	0.81 (2)	1.83 (2)	2.630 (2)	174 (3)
O5—H5*O*···O11^{vi}	0.84 (2)	1.76 (2)	2.603 (2)	178 (3)
O9—H9*W*···O15	0.82 (2)	1.81 (2)	2.626 (2)	175 (3)
O10—H10*O*···O7^{vii}	0.82 (2)	1.81 (2)	2.630 (2)	175 (3)
O12—H12*O*···O11^{ii}	0.81 (2)	1.80 (2)	2.611 (2)	177 (3)
O15—H15*W*···O13^{viii}	0.85 (2)	1.89 (2)	2.710 (2)	164 (2)
O15—H16*W*···O4	0.83 (2)	1.89 (2)	2.716 (2)	177 (2)

Symmetry codes: (i) −x+1, −y+1, −z+2; (ii) −x, −y+1, −z+1; (iii) x+1, y−1, z; (iv) −x+1, −y, −z+1; (v) −x+1, −y, −z+2; (vi) x, y, z+1; (vii) x, y, z−1; (viii) x, y−1, z.

Table S7. Geometric parameters used for the determination of the π···π interactions in **2**[*]

Rings Cg(I)-Cg(J)[a]	Symmetry	Cg···Cg[b]	Cg(I)-Perp[c]	Cg(J)-Perp[d]	α[e]	β[f]	γ[g]
Cg(2)···Cg(2)	2-x,-y,2-z	3.8692(13)	3.2977(9)	3.2977(9)	0.00(10)	31.5	31.5
Cg(2)···Cg(9)	1-x,-y,1-z	4.0030(13)	3.5702(9)	3.4370(9)	10.60(11)	30.8	26.9
Cg(3)···Cg(8)	1-x,-y,1-z	3.8274(13)	3.3247(8)	3.2459(9)	5.96(10)	32.0	29.7
Cg(5)···Cg(11)	x,y,z	3.7489(12)	3.2990(9)	3.5340(9)	11.62(10)	19.5	28.4

* (Cg···Cg[b] < 4.0 Å). [a]Cg(2), Cg(3), Cg(5), and Cg(11) represent the centroids of the six-membered aromatic rings N1-C1-C2-C3-C4-C5, N2-C6-C7-C8-C9-C10, C15-C16-C17-C18-C19-C20, and C35-C36-C37-C38-C39-C40, respectively. [b] Distance between ring centroids (Å). [c] Perpendicular distance of Cg(I) on ring J (Å). [d] Perpendicular distance of Cg(J) on ring I (Å). [e] Dihedral angle between planes I and J (°). [f] Angle between the centroid vector Cg(I)···Cg(J) vector and normal to plane I (°). [g] Angle between the centroid vector Cg(I)···Cg(J) vector and normal to plane J (°).

REFERENCES

(S1) Spek, A. L. Structure Validation in Chemical Crystallography. *Acta Cryst.* **2009**, *D65*, 148-155.

(S2) Macrae, C. F.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Shields, G. P.; Taylor, R.; Towler, M.; Streek, J. van de Mercury: Visualization and Analysis of Crystal Structures. *J. Appl. Cryst*. **2006**, *39*, 453-457.