Electronic Supplementary Material for CrystEngComm

π-Stacking induced complexes with Z-shape motifs featuring complementary approach between electron-rich arene diamines and electron-deficient aromatic N-heterocycles

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SUPPORTING INFORMATION

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Crystal structure determination:

Reflection intensity data for complexes **1, 2 ,4 and 6** were collected at 173K on a Bruker APEX diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) using the ω technique, and those of complexes **2 and 5** were collected at 293K on a Gemini S Ultra diffractometer. All the structures were solved by direct methods and refined by full-matrix least-squares against *F2* of all data using the SHELXTL program package. Anisotropical thermal factors were assigned to non-hydrogen atoms. The positions of the hydrogen atoms were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their respective parent atoms before the final cycle of least-squares refinement. The crystal of **5** was of poor quality and had very weak high angle data. Thus, Ratio Observed/Unique Reflections was low (60%). Despite the ratio of data completeness is 0.952, the cation geometries were well defined and only the anions of BF_4^- were disorder.

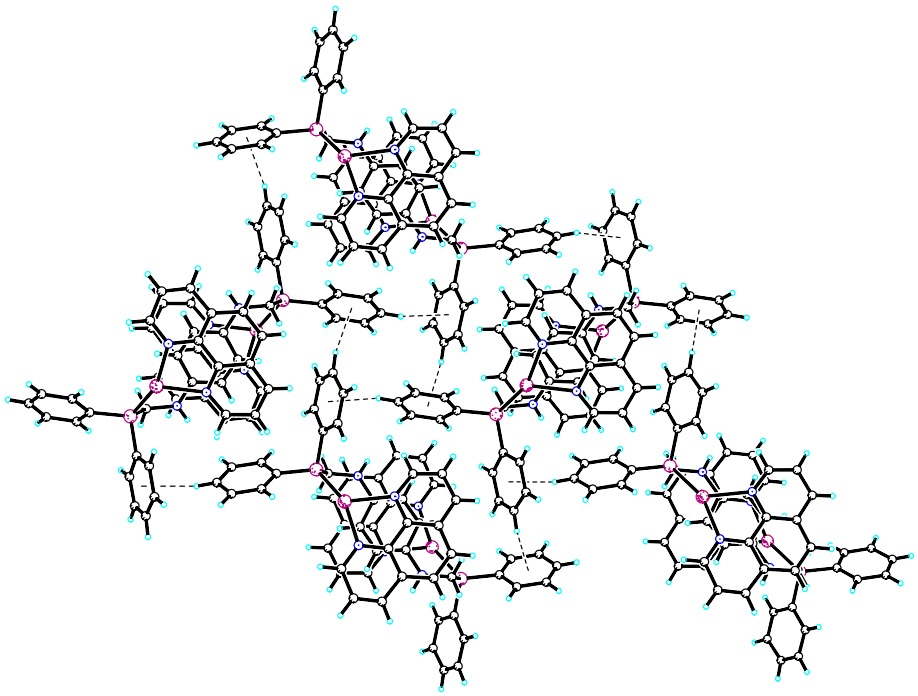


Fig. S1 View of C-H···π interaction between cations along the *bc* plane in complex **1** and complex **2**, H···$\pi_{centroid}$ = 2.84 and 3.014 Å in **1** and 2.997 and 2.863 Å in **2**.

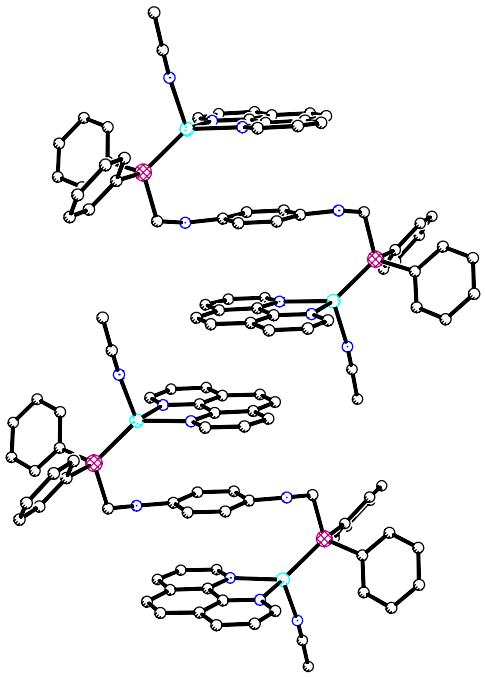


Fig. S2 View of 1-D π chain along the *a* axis, formed by π-π interaction between cations in complex **2**.

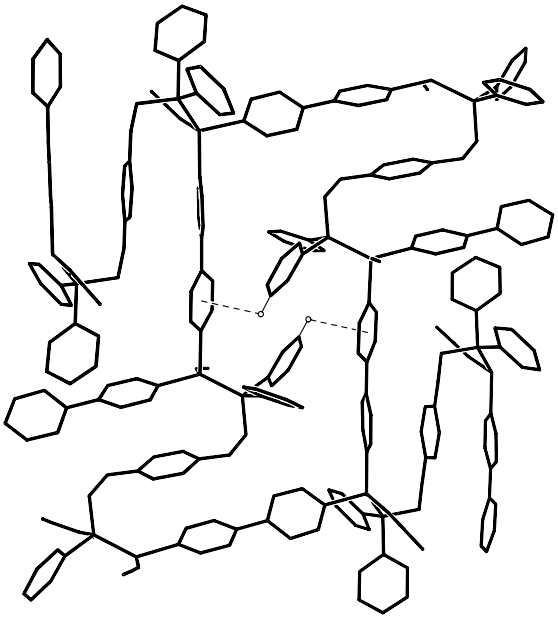


Fig. S3 Showing C-H…π weak interactions between phenyl rings attached on phosphorus atoms and uninvolved-in-π-stacking pyridyl rings in the Z-shape subunit, Ring-centroids distance: 4.454Å, dihedral angle: 25.7˚, and H···$\pi_{centroid}$: 3.057Å.

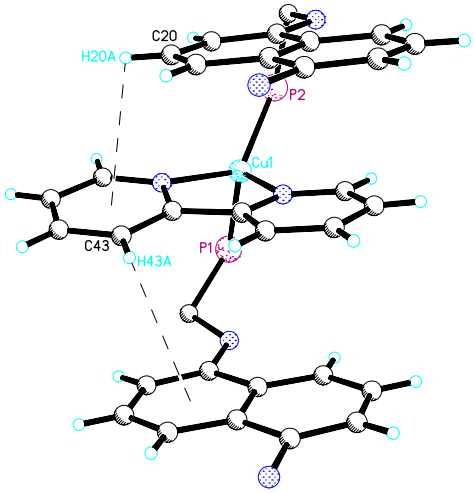
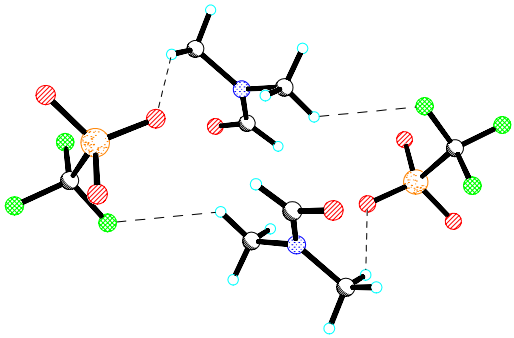
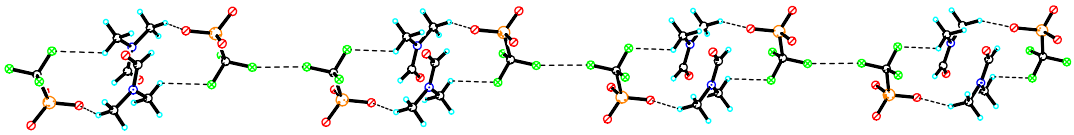


Fig. S4 C-H···π interactions between pyridyl ring and naphthalene rings in complex **5**. H20A···$\pi_{pyridyl}$ =3.237Å, H43A···π_{phenyl} = 3.372Å.



a



b

Fig. S5 Showing weak interactions between $CF_3SO_3^-$ anions and DMF solvents, (a) a quadrilateral unit linked by hydrogen bond interactions and (b) a one-dimensional chain of quadrilateral linked by F···F (2.73Å) weak interactions. Hydrogen bonds: C30-H30A···F3(H30A···F3=2.551Å, C30···F3=3.60Å, ∠(CHF)=129.27°), C29-H29C···O4#1 (H29C···O4=2.499Å, C29···O4=3.351Å, ∠(CHO)=145.2°, #1= -x-1, -y, -z+1)

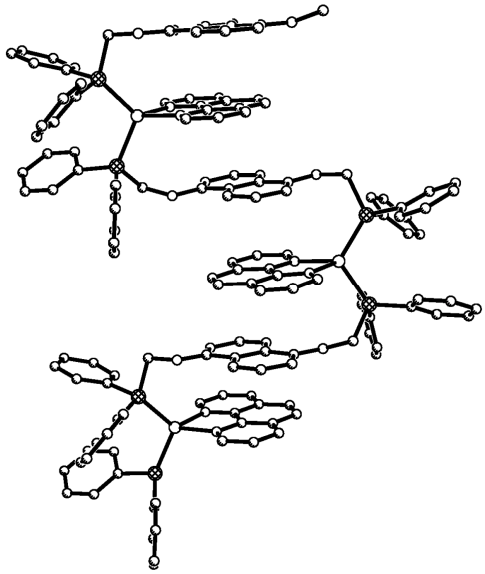


Fig. S6 The 1-D cation polymer of complex $\{[Cu(L2)(phen)](ClO_4)\cdot(DMF\}_n$. For clarity, hydrogen atoms are deleted.

Table S1 Geometric parameters of hydrogen bonds in complex 2

D-H···O	H···O (Å)	D···O (Å)	∠(DHO) (˚)
C26-H26A···O1[a](3544	2.486	3.423	168.9
C16-H16A···O2[b](4565	2.851	3.339	113
C27-H27A···O3[c](2555	2.607	3.393	140.4
C30H30A···O3[d](4465	2.827	3.329	112.6
C13-H13A···O4[d](4465	2.527	3.255	133.6
C28-H28A···O4[c](2555	2.910	3.393	112.8
C30-H30A···O5[e](1455	2.696	3.385	127.7

Symmetry Codes: (a) –x, y-0.5, -z-0.5; (b) x, -y+0.5, z-0.5; (c) –x, -y, -z; (d) x-1, -y+0.5, z-0.5; (e) x-1, y, z.

Table S2 Geometric parameters of hydrogen bonds in complex 3

D-H···O	H···O (Å)	D···O (Å)	∠(DHO) (˚)
N1-H1B···O5[a]	2.222	2.986	147.8
C24-H20A···O1[b]	2.482	3.182	132.1
C4-H4A···O2[c]	2.609	3.552	164.0
C23-H23A···O2[b]	2.681	3.552	156.3
C18-H18A···O3[d]	2.709	3.393	131.1
C28-H28B···O4[c]	2.576	3.388	142.4

Symmetry Codes: (a): x, y, z-1; (b): -x-0.5, y-0.5, -z-0.5; (c): x-0.5, -y+0.5, z-0.5; (d): -x-1, -y, -z.

Table S3 Geometric parameters of hydrogen bonds in complex 4

D-H···O	H···O (Å)	D···O (Å)	∠(DHO) (˚)
C26-H26A···O1	2.401	3.336	167.8
C13-H13A···O1[a]	2.388	3.283	156.8
C18-H18A···O2	2.617	3.228	122.5
C17-H17A···O2[b]	2.684	3.607	164.2
C6-H6A···O3[c]	2.462	3.206	131.5
C9-H9A···O3[d]	2.546	3.158	122.3
N3-H3A···O3[c]	2.583	3.131	121.2

Symmetry Codes: (a) x+1.5, -y-1.5, z+0.5; (b) –x+2, -y+1, -z+1; (c) x-0.5, -y+1.5, z+0.5; (d) x+0.5, -y+1.5, x+0.5

Table S4 Geometric parameters of hydrogen bonds in complex 6

D-H···O	H···O (Å)	D···O (Å)	∠(DHO) (˚)
N1-H1A···O1[a]	2.058	2.878	154.6
C29-H29A···O1	2.383	2.792	104.3
C19-H19A···O2[b]	2.667	3.384	132.6
C4-H4A···O3[c]	2.709	3.376	127.8
C15H15A···O3[d]	2.701	3.295	121.2
C16-H16A···O3[d]	2.699	3.297	121.5
C28-H28A···O3[c]	2.427	3.306	153.8
C20-H20A···O4[b]	2.529	3.396	151.8
C29-H29C···O4[e]	2.499	3.351	145.2

Symmetry Codes: (a) x-1, -y, -z+1; (b) x,, y+1, z; (c) x+1, y+1, z; (d) -x-1, -y, -z+2; (e) –x-1, -y, -z+1.

Table S5 Crystallographic Data for complexes 1, 2, 3, 4, 5 and 6

complex	**1**	**2**	**3**	**4**	**5**	**6**
formula	$C_{26}H_{22}N_4O_2Cu$	$C_{52}H_{44}N_8O_{12}Cl_2Cu_3$	$C_{56}H_{60}N_{10}O_{18}CdCu_2$	$C_{27}H_{26}N_4O_3C_{l2}CuZn$	$C_{26}H_{22}N_4O_2I_2CuHg$	$C_{26.50}H_{23}N_4O_2Cl_3CdCu$
Fw	486.02	1234.47	1400.62	654.33	940.41	711.78
Cryst syst	Monoclinic	Tetragonal	Tetragonal	Orthorhombic	Monoclinic	Monoclinic
space group	$P2_1/n$	P 4/ncc	$P\text{-}42_1c$	Pnma	$P2_1/m$	C2/c
a,Å	10.1147(15)	18.3858(10)	18.4188(11)	13.677(3)	6.6031(12)	27.620(2)
b,Å	9.0238(14)	18.3858(10)	18.4188(11)	22.383(5)	25.306(5)	14.4643(13)
c,Å	12.3071(19)	15.1821(17)	17.537(2)	= 8.6211(19)	8.5574(16)	7.2112(6)
α,°	90	90	90	90	90	90
β,°	107.377(3)	90	90	90	91.415(3)	98.941(2)
γ,°	90	90	90	90	90	90
V,$Å^3$	1072.0(3)	5132.1(7)	5949.6(9)	2639.1(10) A^3	1429.5(5)	2845.9(4)
Z	2	4	4	4,	2	4
ρ_{calcd},gm^{-3}	1.506	1.598	1.564	1.647 Mg/m^3	2.185	1.661
μ,mm^{-1}	1.051	1.408	1.143	1.955	8.296	1.807
Total no. of data	5329	36759	26316	16999	8279	16589
No. of unique data	2105	3180	5242	2828	3210	3463
No. of parameters	151	169	339	184	169	171
R_1 [I>2σ(I)]	0.0356	0.0914	0.0687	0.0391	0.0542	0.0487
wR_2 [I>2σ(I)]	0.0913	0.2450	0.1852	0.0906	0.1455	0.1283

Table S6 Selected Bonded Distances (Å) and Angles (°)

1			
Ag(1)-N(1)	2.329(8)	N(2)-Ag(1)-N(1)	73.8(3)
Ag(1)-N(2)	2.238(8)	N(2)-Ag(1)-P(1)	157.0(2)
Ag(1)-P(1)	2.337(2)	N(1)-Ag(1)-P(1)	127.4(2)
P(1)-C(11)	1.826(10)	C(11)-P(1)-C(5)	105.7(4)
P(1)-C(5)	1.835(10)	C(11)-P(1)-C(4)	104.7(5)
P(1)-C(4)	1.878(9)	C(5)-P(1)-C(4)	103.7(4)
2			
Cu(1)-N(4)	2.052(3)	N(4)-Cu(1)-N(2)	110.76(13)
Cu(1)-N(3)	2.054(3)	N(3)-Cu(1)-N(2)	80.79(12)
Cu(1)-N(2)	2.092(3)	N(4)-Cu(1)-P(1)	112.69(9)
Cu(1)-P(1)	2.1897(10)	N(3)-Cu(1)-P(1)	133.71(8)
P(1)-C(5)	1.825(3)	N(2)-Cu(1)-P(1)	116.66(9)
P(1)-C(11)	1.841(4)	C(5)-P(1)-C(11)	104.80(15)
P(1)-C(4)	1.866(4)	C(11)-P(1)-C(4)	102.44(17)
N(4)-Cu(1)-N(3)	97.64(12)	C(5)-P(1)-C(4)	101.07(17)
3			
Cu(1)-N(2)	2.017(3)	N(2)-Cu(1)-N(4)	100.54(14)
Cu(1)-N(3)#1	2.058(3)	N(3)#1-Cu(1)-N(4)	100.08(14)
Cu(1)-N(4)	2.110(4)	N(2)-Cu(1)-P(1)	133.76(11)
Cu(1)-P(1)	2.1759(11)	N(3)#1-Cu(1)-P(1)	112.58(9)
P(1)-C(5)	1.812(4)	N(4)-Cu(1)-P(1)	103.59(11)
P(1)-C(11)	1.820(4)	C(5)-P(1)-C(11)	103.98(19)
P(1)-C(4)	1.858(4)	C(5)-P(1)-C(4)	102.0(2)
N(2)-Cu(1)-N(3)#1	101.08(13)	C(11)-P(1)-C(4)	103.17(19)
#1 x+1/2, -y-1/2, z+1/2			
4			
Ag(1)-N(1)	2.279(2)	N(1)-Ag(1)-N(2)	71.91(8)
Ag(1)-P(1)	2.3529(7)	P(1)-Ag(1)-N(2)	112.49(6)
Ag(1)-N(2)	2.398(2)	N(1)-Ag(1)-O(1)	97.23(9)
Ag(1)-O(1)	2.486(2)	P(1)-Ag(1)-O(1)	104.14(8)
P(1)-C(19)	1.823(3)	N(2)-Ag(1)-O(1)	101.47(10)
P(1)-C(25)	1.834(3)	C(19)-P(1)-C(25)	106.87(11)
P(1)-C(6)	1.859(3)	C(19)-P(1)-C(6)	101.05(12)
N(1)-Ag(1)-P(1)	156.49(6)	C(25)-P(1)-C(6)	104.49(12)
5			
Cu(1)-N(4)	2.054(5)	P(2)-C(31)	1.836(6)
Cu(1)-N(3)	2.088(5)	P(2)-C(24)	1.864(6)
Cu(1)-P(2)	2.2365(18)	N(3)-Cu(1)-P(2)	128.33(17)
Cu(1)-P(1)	2.2767(19)	N(4)-Cu(1)-P(1)	113.27(15)
P(1)-C(13)	1.816(6)	N(3)-Cu(1)-P(1)	99.98(16)
P(1)-C(7)	1.821(6)	P(2)-Cu(1)-P(1)	116.38(6)
P(1)-C(6)	1.864(6)	N(4)-Cu(1)-N(3)	79.56(19)
P(2)-C(25)	1.820(6)	N(4)-Cu(1)-P(2)	113.94(16)
6			
Ag(1)-N(3)	2.251(3)	N(3)-Ag(1)-N(2)	100.69(10)
Ag(1)-N(2)	2.325(3)	N(3)-Ag(1)-P(1)	134.70(8)
Ag(1)-P(1)	2.3684(9)	N(2)-Ag(1)-P(1)	123.14(8)
P(1)-C(13)	1.822(3)	C(13)-P(1)-C(7)	103.37(15)
P(1)-C(7)	1.824(3)	C(13)-P(1)-C(6)	102.84(15)
P(1)-C(6)	1.856(3)		