Supporting information

Unusual Polymeric Zn^{II}/Cd^{II} Complexes with 2,6-Diaminopurine by Synergistic Coordination of Nucleobase and Polycarboxylate Anion: Binding Behavior, Self-assembled Pattern of the Nucleobase and Luminscent Property

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Table S1. Selected bond lengths (Å) and angles (°) for 1 [a]

Zn(1)–O(7)	1.957(2)	Zn(2)–O(1)	1.967(2)
Zn(1)–O(5)	1.976(2)	Zn(2)–O(7)$^{\#2}$	1.996(2)
Zn(1)–N(9)	2.020(3)	Zn(2)–N(3)$^{\#2}$	2.076(3)
Zn(1)–O(3)$^{\#1}$	2.487(3)	Zn(2)–O(6)$^{\#2}$	2.080(2)
Zn(1)–O(4)	1.957(2)	Zn(2)–O(7)	2.317(2)
O(4)$^{\#1}$–Zn(1)–O(7)	130.49(10)	O(1)–Zn(2)–O(7)$^{\#2}$	150.28(9)
O(4)$^{\#1}$–Zn(1)–O(5)	109.60(11)	O(1)–Zn(2)–N(3)$^{\#2}$	104.14(10)
O(7)–Zn(1)–O(5)	107.70(10)	O(7)$^{\#2}$–Zn(2)–N(3)$^{\#2}$	103.10(10)
O(4)$^{\#1}$–Zn(1)–N(9)	103.34(11)	O(1)–Zn(2)–O(6)$^{\#2}$	90.46(10)
O(7)–Zn(1)–N(9)	97.01(10)	O(7)$^{\#2}$–Zn(2)–O(6)$^{\#2}$	94.93(9)
O(5)–Zn(1)–N(9)	105.15(11)	N(3)$^{\#2}$–Zn(2)–O(6)$^{\#2}$	102.81(11)
O(4)$^{\#1}$–Zn(1)–O(3)$^{\#1}$	57.42(10)	O(1)–Zn(2)–O(7)	86.03(9)
O(7)–Zn(1)–O(3)$^{\#1}$	91.68(9)	O(7)$^{\#2}$–Zn(2)–O(7)	75.40(9)
O(5)–Zn(1)–O(3)$^{\#1}$	89.93(10)	N(3)$^{\#2}$–Zn(2)–O(7)	105.50(9)
N(9)–Zn(1)–O(3)$^{\#1}$	159.27(10)	O(6)$^{\#2}$–Zn(2)–O(7)	151.48(10)

[a] Symmetry codes: #1 $-x + 3/2, -y + 3/2, -z + 1$; #2 $-x + 1, y, -z + 1/2$.

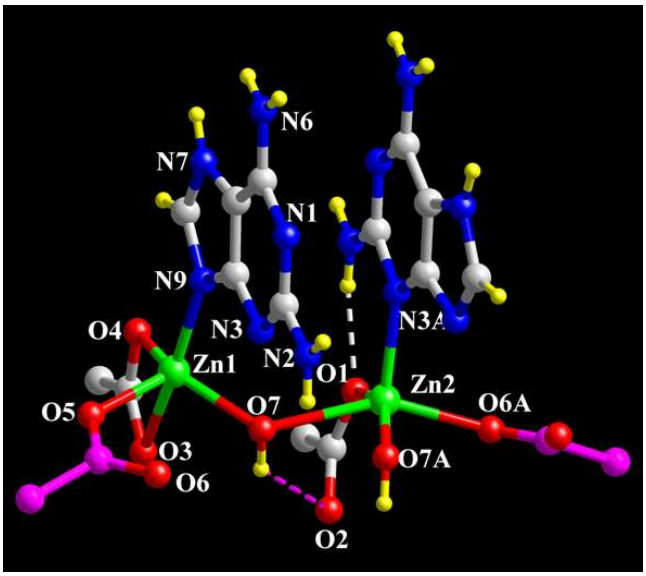

Figure S1. Local coordination environment of Zn^{II} atoms in **1.**

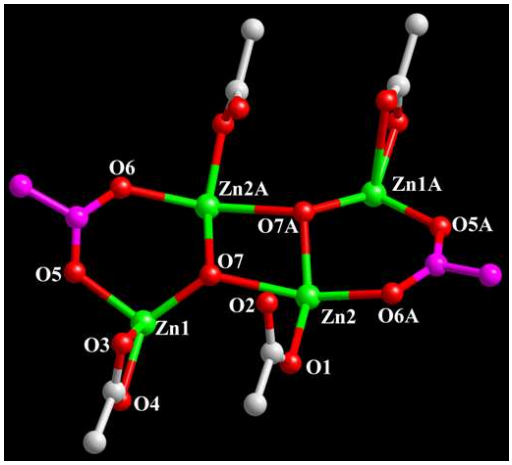

Figure S2. The connectivity of Zn^{II} ions, μ_3-OH and the carboxylate groups of tp anion within the tetranuclear subunit of **1** (Hdap nucleobase is omitted for clarity).

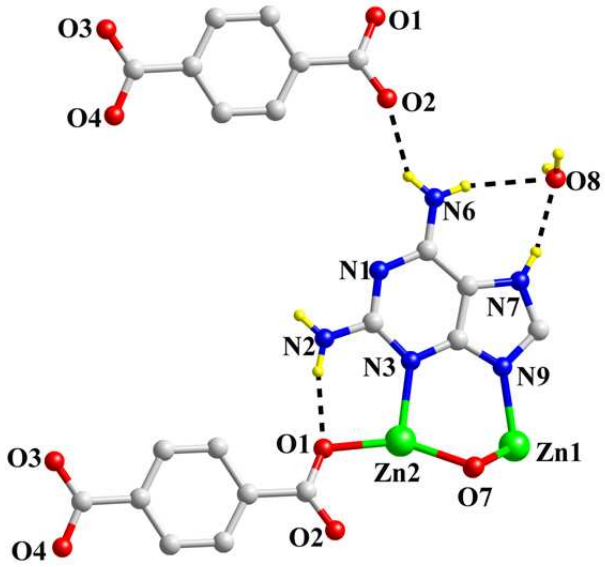

Figure S3. The hydrogen-bonding modes of the neutral Hdap nucleobase in **1**.

Table S2. Selected bond lengths (Å) and angles (°) for 2 [a]

Zn(1)–O(5)	1.9501(14)	Zn(2)–O(8)$^{\#3}$	1.9420(15)
Zn(1)–O(6)$^{\#1}$	1.9839(14)	Zn(2)–O(2)	1.9620(16)
Zn(1)–O(3)$^{\#2}$	1.9907(15)	Zn(2)–N(9)	1.9844(16)
Zn(1)–N(7)	2.0030(17)	Zn(2)–O(4)$^{\#4}$	2.0005(16)
O(5)–Zn(1)–O(6)$^{\#1}$	110.51(6)	O(8)$^{\#3}$–Zn(2)–O(2)	101.34(7)
O(5)–Zn(1)–O(3)$^{\#2}$	130.59(6)	O(8)$^{\#3}$–Zn(2)–N(9)	124.00(7)
O(6)$^{\#1}$–Zn(1)–O(3)$^{\#2}$	93.19(6)	O(2)–Zn(2)–N(9)	109.92(7)
O(5)–Zn(1)–N(7)	105.96(6)	O(8)$^{\#3}$–Zn(2)–O(4)$^{\#4}$	91.75(7)
O(6)$^{\#1}$–Zn(1)–N(7)	112.20(7)	O(2)–Zn(2)–O(4)$^{\#4}$	129.01(7)
O(3)$^{\#2}$–Zn(1)–N(7)	103.72(7)	N(9)–Zn(2)–O(4)$^{\#4}$	102.13(7)

[a] Symmetry codes: #1 $-x+2, -y, -z+1$; #2 $-x+2, -y, -z+2$; #3 $x-3/2, -y+1/2, z+1/2$; #4 $-x+1, -y, -z+2$.

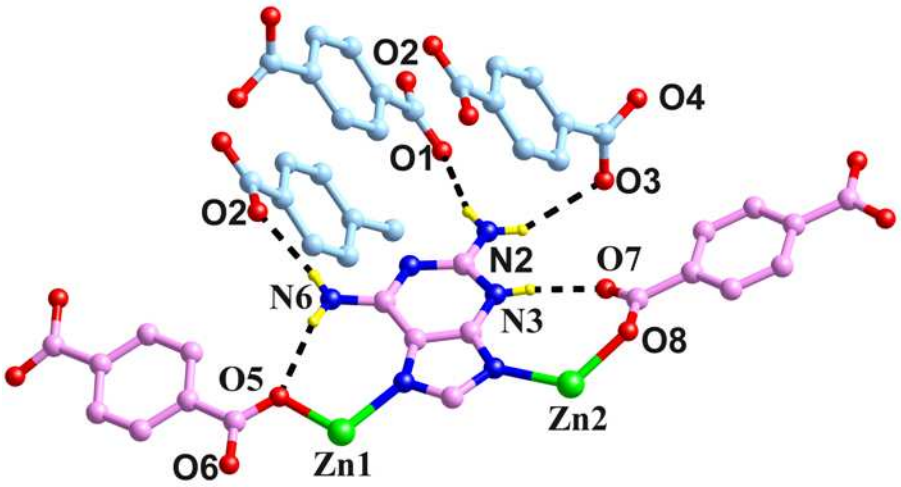

Figure S4. The hydrogen-bonding modes of the neutral Hdap nucleobase in **2**.

Table S3. Selected bond distances (Å) and angles (°) for 3 [a]

Zn(1)–O(7)	1.8908(18)	Zn(2)–O(7)	1.9616(19)
Zn(1)–O(4)$^{\#1}$	1.9717(16)	Zn(2)–O(6)$^{\#3}$	1.9623(17)
Zn(1)–N(7)	1.9841(19)	Zn(2)–O(1)	1.9971(17)
Zn(1)–O(3)$^{\#2}$	2.0214(18)	Zn(2)–N(9)$^{\#4}$	2.0181(18)
O(7)–Zn(1)–O(4)$^{\#1}$	117.19(8)	O(7)–Zn(2)–O(6)$^{\#3}$	105.37(8)
O(7)–Zn(1)–N(7)	109.30(8)	O(7)–Zn(2)–O(1)	103.18(8)
O(4)$^{\#1}$–Zn(1)–N(7)	108.08(7)	O(6)$^{\#3}$–Zn(2)–O(1)	97.27(8)
O(7)–Zn(1)–O(3)$^{\#2}$	110.95(7)	O(7)–Zn(2)–N(9)$^{\#4}$	105.02(8)
O(4)$^{\#1}$–Zn(1)–O(3)$^{\#2}$	104.03(7)	O(6)$^{\#3}$–Zn(2)–N(9)$^{\#4}$	123.19(8)
N(7)–Zn(1)–O(3)$^{\#2}$	106.71(8)	O(1)–Zn(2)–N(9)$^{\#4}$	120.54(8)

Symmetry codes: #1 $-x+1,-y+1,-z+2$; #2 $x+1, y, z$; #3 $-x+1, y+1/2, -z+3/2$; #4 $-x+2, -y+1, -z+1$.

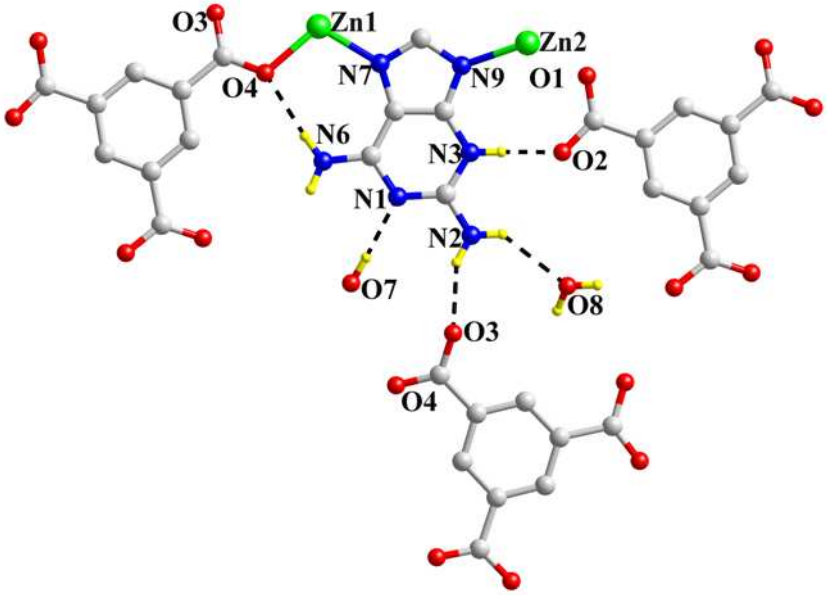

Figure S5. The hydrogen-bonding modes of the nucleobase in **3**.

Table S4. Selected bond distances (Å) and angles (°) for 4 [a]

Zn(1)–O(6)$^{\#1}$	1.9599(16)	Zn(1)–O(3)	2.0861(16)
Zn(1)–O(1)$^{\#2}$	1.9767(15)	Zn(1)–O(7)	2.2675(17)
Zn(1)–N(9)	2.0524(18)		
O(6)$^{\#1}$–Zn(1)–O(1)$^{\#2}$	137.78(7)	N(9)–Zn(1)–O(3)	98.79(7)
O(6)$^{\#1}$–Zn(1)–N(9)	125.20(8)	O(6)$^{\#1}$–Zn(1)–O(7)	85.76(7)
O(1)$^{\#2}$–Zn(1)–N(9)	96.34(7)	O(1)$^{\#2}$–Zn(1)–O(7)	87.96(6)
O(6)$^{\#1}$–Zn(1)–O(3)	88.04(7)	N(9)–Zn(1)–O(7)	89.08(7)
O(1)$^{\#2}$–Zn(1)–O(3)	93.12(7)	O(3)–Zn(1)–O(7)	171.88(6)

[a] Symmetry codes: #1 $-x, -y+1, -z$; #2 $-x+1, -y+1, -z$.

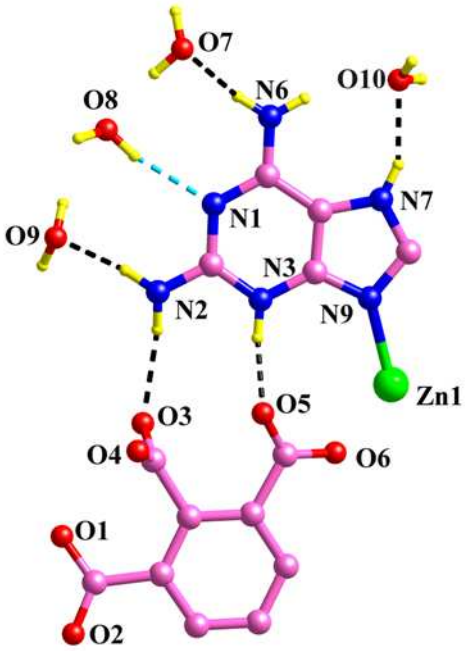

Figure S6. The hydrogen-bonding modes of the cationic H_2dap^+ nucleobase in **4**.

Table S5. Selected bond distances (Å) and angles (°) for 5 [a]

Cd(1)–N(4)$^{\#1}$	2.2980(18)	Cd(2)–N(1)	2.1816(18)
Cd(1)–N(2)	2.3313(18)	Cd(2)–N(1)$^{\#2}$	2.1816(18)
Cd(1)–O(1)	2.3352(17)	Cd(2)–O(3)$^{\#2}$	2.3767(17)
Cd(1)–O(3)$^{\#2}$	2.4074(19)	Cd(2)–O(3)	2.3768(17)
Cd(1)–O(5)	2.422(2)	Cd(2)–O(1)	2.3872(16)
Cd(1)–O(4)$^{\#2}$	2.498(2)	Cd(2)–O(1)$^{\#2}$	2.3872(16)
Cd(1)–O(2)	2.586(2)		
N(4)$^{\#1}$–Cd(1)–N(2)	104.03(7)	N(2)–Cd(1)–O(2)	89.39(7)
N(4)$^{\#1}$–Cd(1)–O(1)	148.47(6)	O(1)–Cd(1)–O(2)	52.46(6)
N(2)–Cd(1)–O(1)	87.84(6)	O(3)$^{\#2}$–Cd(1)–O(2)	126.72(6)
N(4)$^{\#1}$–Cd(1)–O(3)$^{\#2}$	128.92(6)	O(5)–Cd(1)–O(2)	79.66(8)
N(2)–Cd(1)–O(3)$^{\#2}$	100.34(6)	O(4)$^{\#2}$–Cd(1)–O(2)	177.93(7)
O(1)–Cd(1)–O(3)$^{\#2}$	75.49(6)	N(1)–Cd(2)–N(1)$^{\#2}$	180.0
N(4)$^{\#1}$–Cd(1)–O(5)	81.78(7)	N(1)–Cd(2)–O(3)$^{\#2}$	90.22(7)
N(2)–Cd(1)–O(5)	168.29(8)	N(1)$^{\#2}$–Cd(2)–O(3)$^{\#2}$	89.78(7)
O(1)–Cd(1)–O(5)	82.21(7)	N(1)–Cd(2)–O(3)	89.78(7)
O(3)$^{\#2}$–Cd(1)–O(5)	83.19(8)	N(1)$^{\#2}$–Cd(2)–O(3)	90.22(7)
N(4)$^{\#1}$–Cd(1)–O(4)$^{\#2}$	83.77(6)	O(3)$^{\#2}$–Cd(2)–O(3)	180.0
N(2)–Cd(1)–O(4)$^{\#2}$	89.00(7)	N(1)–Cd(2)–O(1)	89.54(6)
O(1)–Cd(1)–O(4)$^{\#2}$	126.16(6)	N(1)$^{\#2}$–Cd(2)–O(1)	90.46(6)
O(3)$^{\#2}$–Cd(1)–O(4)$^{\#2}$	52.38(6)	O(3)$^{\#2}$–Cd(2)–O(1)	75.11(6)
O(5)–Cd(1)–O(4)$^{\#2}$	101.84(9)	O(3)–Cd(2)–O(1)	104.89(6)
N(4)$^{\#1}$–Cd(1)–O(2)	97.88(6)	N(1)–Cd(2)–O(1)$^{\#2}$	90.46(6)
N(2)–Cd(1)–O(2)	89.39(7)	N(1)$^{\#2}$–Cd(2)–O(1)$^{\#2}$	89.54(6)
O(1)–Cd(1)–O(2)	52.46(6)	O(3)$^{\#2}$–Cd(2)–O(1)$^{\#2}$	104.89(6)
O(3)$^{\#2}$–Cd(1)–O(2)	126.72(6)	O(3)–Cd(2)–O(1)$^{\#2}$	75.11(6)
O(5)–Cd(1)–O(2)	79.66(8)	O(1)–Cd(2)–O(1)$^{\#2}$	180.0
N(4)$^{\#1}$–Cd(1)–O(2)	97.88(6)		

[a] Symmetry codes: #1 x, $-y + 1/2$, $z + 1/2$; #2 $-x + 1$, $-y + 1$, $-z + 1$.

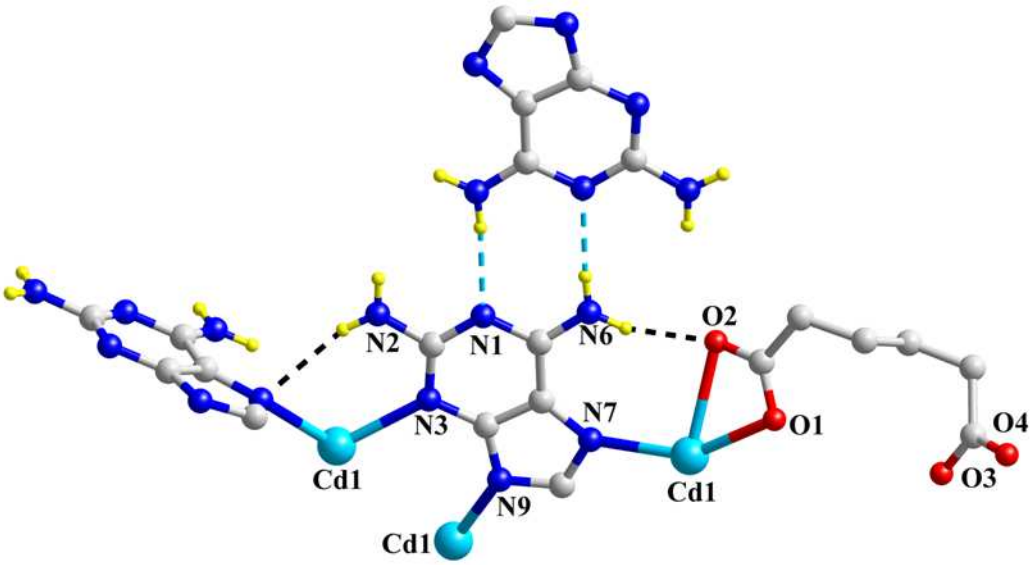

Figure S7. Hydrogen-bonding modes of the anionic dap nucleobase in **5.**

Table S6. Selected bond distances (Å) and angles (°) for 6

Cd(1)–O(4)	2.2757(17)	Cd(1)–O(1)	2.3459(17)
Cd(1)–O(8)	2.297(2)	Cd(1)–O(2)	2.4011(17)
Cd(1)–O(7)	2.3160(18)	Cd(1)–N(7)	2.3418(19)
O(4)–Cd(1)–O(8)	90.43(8)	O(8)–Cd(1)–O(2)	101.93(8)
O(4)–Cd(1)–O(7)	87.56(7)	O(7)–Cd(1)–O(2)	81.00(7)
O(8)–Cd(1)–O(7)	171.95(7)	N(7)–Cd(1)–O(2)	88.22(6)
O(4)–Cd(1)–N(7)	86.22(6)	O(1)–Cd(1)–O(2)	54.84(6)
O(8)–Cd(1)–N(7)	88.01(7)	O(7)–Cd(1)–O(1)	88.05(7)
O(7)–Cd(1)–N(7)	99.63(7)	N(7)–Cd(1)–O(1)	140.80(6)
O(4)–Cd(1)–O(1)	132.73(6)	O(4)–Cd(1)–O(2)	166.26(7)
O(8)–Cd(1)–O(1)	87.60(8)		

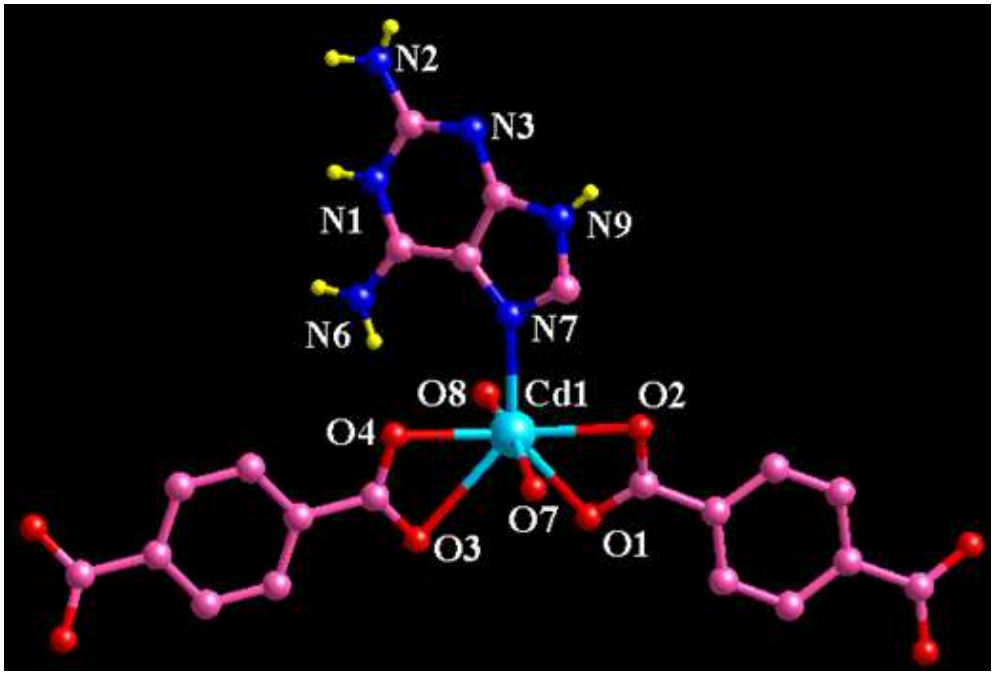

Figure S8. Local coordination environment of Cd^{II} ion in **6**.

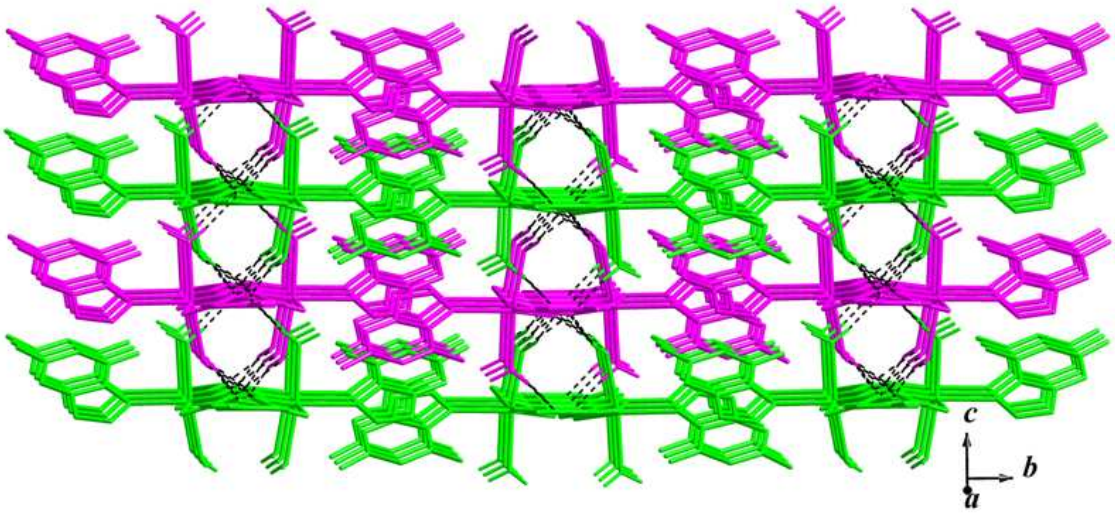

Figure S9. 3D supramolecular framework of **6** formed by intermolecular hydrogen-bonding interactions.

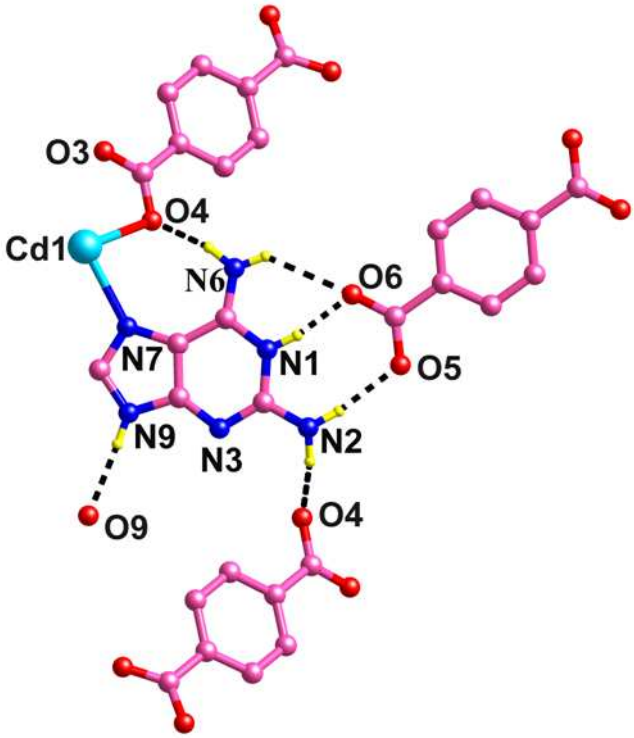

Figure S10. Hydrogen-bonding modes of the cationic H_2dap^+ nucleobase in **6**.

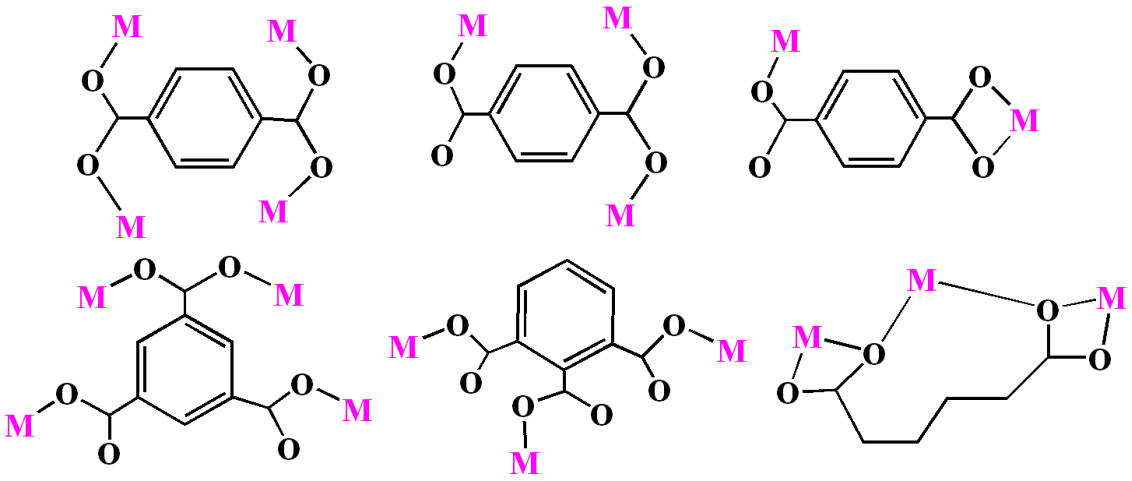

Figure S11. Coordination modes of polycarboxylate anions in complexes **1** – **6**.

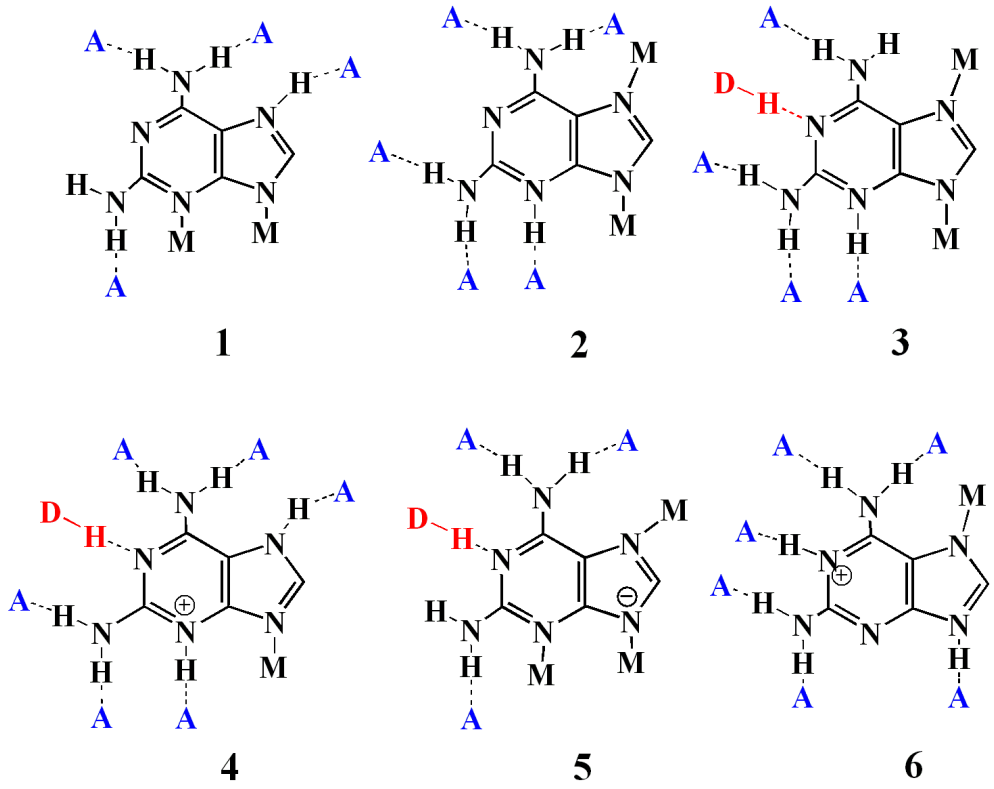

Figure S12. Hydrogen-bonding sites of 2,6-diaminopurine nucleobase in polymers **1** – **6**.

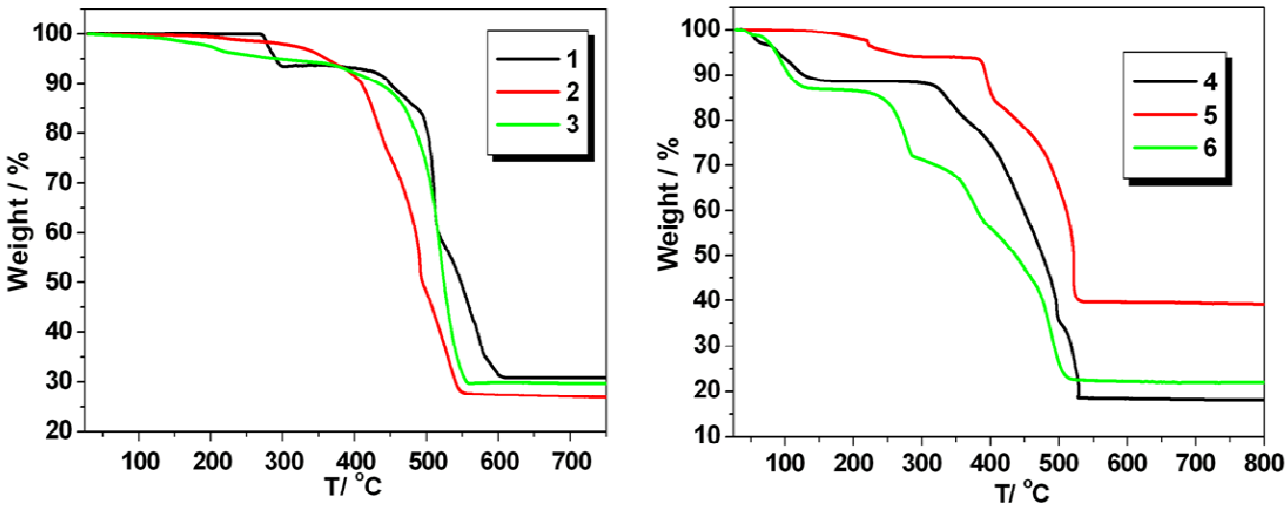

Figure S13. TG curves for **1 – 6**.