Supporting Information

Mimic Uracil-Uracil base pairing: self-assembly and single crystal structure

*Menglei Zhang,[a] Zhongkui Li,[a] Yanhong Zhu,[a, b] Li Yan,[a, c] Xue Zhong,[a] Yijie Zhang,[a] Ziyao Li,[a] Yixiang Bai[a] and Hui Li[a,]**

[a] *Key Laboratory of Cluster Science of Ministry of Education, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 100081, P. R. China.*
[b] *North China University of Science and Technology, School of Pharmacy, Tangshan, Hebei, 063210, P. R. China.*
[c] *Analytical and Test Center, Beijing institute of Technology, Liangxiang Campus, Liangxiang East Road, Beijing 102488, P. R. China.*

*E-mail: *lihui@bit.edu.cn*

Content

1. Physical Properties

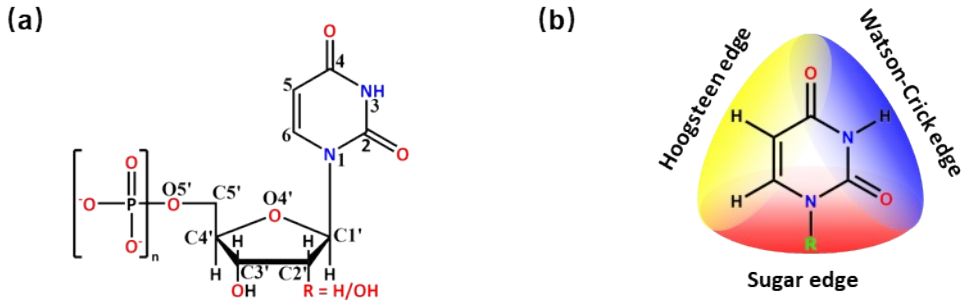

Figure S1. (a) structure of Na_2dUMP/Na_2UMP (Na_2dUMP = 2'-deoxyuridine 5'-monophosphate disodium salt; Na_2UMP = uridine 5'-monophosphate disodium salt); (b) the Waston-Crick edge, the Hoogsteen edge, and the sugar edge of the uracil base.

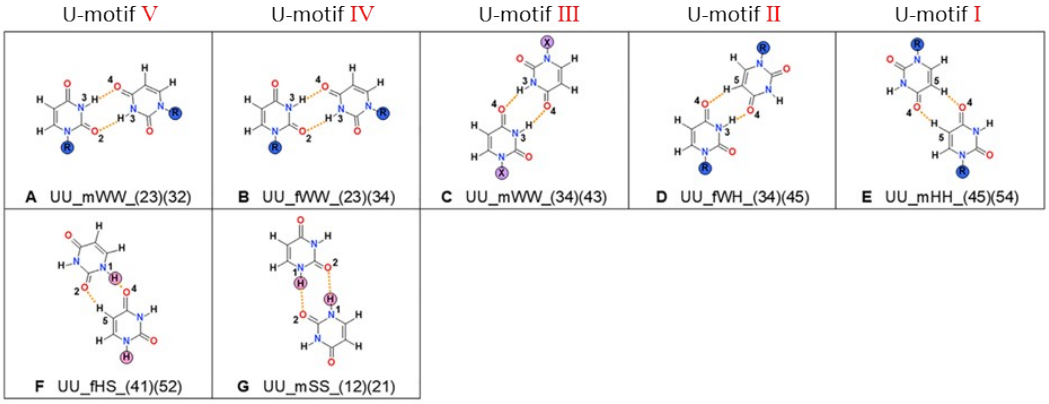

Figure S2. Seven kinds of uracil - uracil base interaction mode have been reported by M. K. Cabaj, and they are renamed as U-motif I, U-motif II, U-motif III, U-motif IV, and U-motif V.[1]

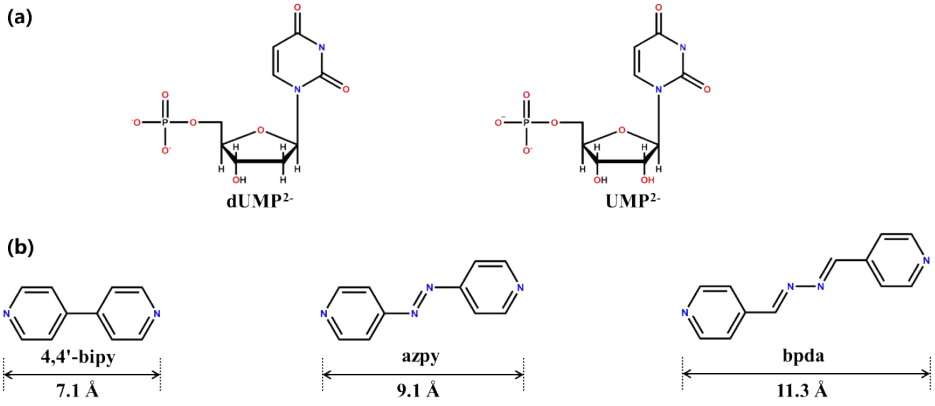

Figure S3. the chemical structure of (a) nucleotide ligands ($dUMP^{2-}$ and UMP^{2-}) and (b) auxiliary ligand (bipy, azpy and bpda) used in this article.

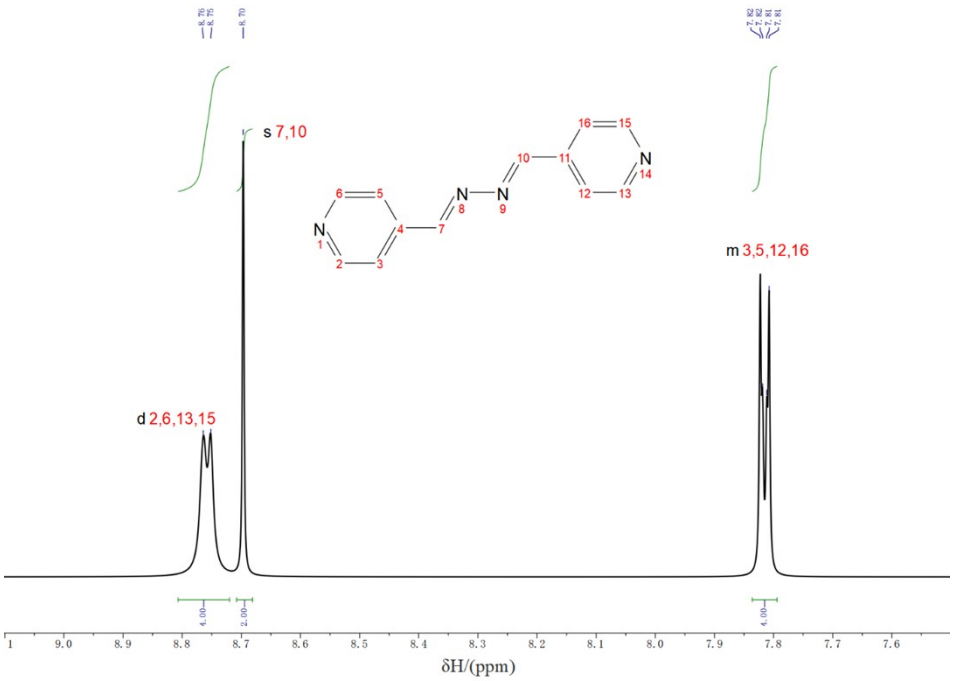

Figure S4. ^{1}H-NMR spectra of bpda in DMSO-d_6 (400 MHz, 298K).

2. Crystallographic Data

The CCDC number of **1**, **2**, **3**, **4**, and **5** are 2288977, 2288978, 2288979, 2288980, and 2288981, respectively.

Table S1. Crystallographic Data for **1**, **2**, and **3**.

Complex	**1**	**2**	**3**
Formula	$C_{19}H_{29}CoN_4O_{13}P$	$C_{58}H_{82}Co_2N_{20}O_{30}P_2$	$C_{33}H_{63}Co_2N_9O_{32}P_2$
M (mol^{-1})	611.36	1719.23	1277.72
T (K)	296.15	296.15	296.15
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1$	$P2_1$	$P1$
a ($Å$)	7.9718(5)	11.700(2)	6.7824(6)
b ($Å$)	14.0812(9)	31.930(6)	13.8721(12)
c ($Å$)	11.5373(8)	11.774(2)	15.7504(14)
α (°)	90	90	68.453(3)
β (°)	95.204(2)	106.376(7)	89.860(3)
γ (°)	90	90	80.963(3)
V ($Å^3$)	1289.75(15)	4220.1(13)	1358.8(2)
Z	2	2	1
ρ_{calc} (g/cm^3)	1.574	1.353	1.561
μ (mm^{-1})	0.800	0.518	0.771
F(000)	634.0	1788.0	664.0
2θ range (°)	3.544 to 63.138	3.606 to 50.662	3.202 to 60.718
Index ranges	$-10 \le h \le 11$ $-20 \le k \le 19$ $-15 \le l \le 16$	$-14 \le h \le 14$ $-38 \le k \le 38$ $-14 \le l \le 14$	$-9 \le h \le 9$ $-19 \le k \le 19$ $-21 \le l \le 22$
Reflections collected	17788	41264	18386
Independent reflections	7654	15105	14757
Data/restraints/paramet	7654/1/354	15105/48/1041	14757/35/732
R_{int}	0.0297	0.0467	0.0250
GOF on F^2	0.977	1.021	1.018
R_1/wR_2 [I>=2σ (I)]	0.0333/0.0630	0.0534/0.1351	0.0644/0.1550
R_1/wR_2 [all data]	0.0436/0.0665	0.063/0.1402	0.1054/0.1780
Peak/hole ($e\ Å^{-3}$)	0.47/-0.30	0.90/-0.33	1.46/-0.58
Flack parameter	0.012(11)	0.082(19)	0.03(2)

Table S2. Crystallographic Data for **4** and **5**.

Complex	**4**	**5**
Formula	$C_{30}H_{50}Co_2N_8O_{27}P_2$	$C_{27}H_{35}CdN_8O_{14}P$
M (mol^{-1})	1134.58	839.00
T (K)	296.15	296.15
Crystal system	Triclinic	orthothombic
Space group	$P1$	$C222_1$
a ($Å$)	6.9314(10)	10.7744(4)
b ($Å$)	13.624(2)	25.5061(11)
c ($Å$)	15.739(2)	31.6431(12)
α (°)	115.138(4)	90
β (°)	93.184(4)	90
γ (°)	96.631(5)	90
V ($Å^3$)	1327.5(3)	8695.9(6)
Z	1	8
ρ_{calc} (g/cm^3)	1.419	1.282
μ (mm^{-1})	0.772	0.601
F(000)	586.0	3424.0
2θ range (°)	3.342 to 49.998	2.574 to 54.268
Index ranges	$-8 \le h \le 8$ $-16 \le k \le 16$ $-18 \le l \le 18$	$-13 \le h \le 13$ $-32 \le k \le 32$ $-40 \le l \le 40$
Reflections collected	9661	49298
Independent reflections	8552	9610
Data/restraints/parameters	8552/466/584	9610/118/486
R_{int}	0.0409	0.0503
GOF on F^2	1.019	1.032
R_1/wR_2 [I>=2σ (I)]	0.0821/0.1723	0.0407/0.0922
R_1/wR_2 [all data]	0.1442/0.2002	0.0601/0.0994
Peak/hole ($e\ Å^{-3}$)	0.95/-0.91	0.99/-0.95
Flack parameter	0.11(5)	0.000(9)

3. Selected Bond Distances, Bond Angles, and Hydrogen Bond for Complexes 1-5.

Table S3. Selected bond distances (Å) for complex **1**.

Atom-Atom	Length(Å)	Atom-Atom	Length(Å)	Atom-Atom	Length(Å)
Co1-O1	2.1175(19)	Co1-O3	2.0939(19)	Co1-N1[1]	2.192(2)
Co1-O2	2.071(2)	Co1-O4	2.0429(18)	Co1-N2	2.219(2)

Symmetry mode: [1]+X,+Y,-1+Z

Table S4. Selected bond angles (°) for complex **1**.

Atom-Atom-Atom	Bond length(Å)	Atom-Atom-Atom	Bond length(Å)	Atom-Atom-Atom	Bond length(Å)
O1-Co1-N1[1]	89.83(9)	O2-Co1-N2	88.08(9)	O4-Co1-O2	177.29(8)
O1-Co1-N2	89.39(9)	O3-Co1-O1	177.31(8)	O4-Co1-O3	90.64(7)
O2-Co1-O1	89.63(8)	O3-Co1-N1[1]	92.37(9)	O4-Co1-N1[1]	91.59(8)
O2-Co1-O3	88.78(9)	O3-Co1-N2	88.39(9)	O4-Co1-N2	89.26(8)
O2-Co1-N1[1]	91.08(9)	O4-Co1-O1	90.84(8)	N1[1]-Co1-N2	178.86(13)

Symmetry mode: [1]+X,+Y,-1+Z

Table S5. The hydrogen bonds in complex **1**.

D-H-A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	∠D-H-A/°
O1-H1A…O6[1]	0.85	1.86	2.692(3)	164.2
O1-H1B…O13[2]	0.85	2	2.827(3)	162.7
O2-H2A…O5[1]	0.85	1.83	2.651(3)	159.4
O2-H2B…O11	0.85	1.96	2.722(3)	147.6
O3-H3A…O6	0.85	1.86	2.667(3)	159
O9-H9…O6[3]	0.82	2.08	2.897(3)	176.6
N4-H4…O5[4]	0.86	1.89	2.733(3)	166.3
O10-H11A…O5[5]	0.85	1.99	2.809(3)	161.7
O11-H11C…O4[5]	0.85	1.99	2.804(3)	159.0

Symmetry mode: [1]1-X, -1/2+Y, 1-Z; [2]1-X, -1/2+Y, 2-Z; [3]-1+X, +Y, +Z; [4]+X, +Y, 1+Z; [5]1+X, +Y, +Z

Table S6. Selected bond distances (Å) for complex **2**.

Atom-Atom	Length(Å)	Atom-Atom	Length(Å)	Atom-Atom	Length(Å)
Co1-O1	2.087(4)	Co1-N1	2.198(6)	Co2-O7	2.118(5)
Co1-O2	2.100(4)	Co1-N2	2.194(6)	Co2-O8	2.092(4)
Co1-O3	2.085(4)	Co2-O5	2.031(4)	Co2-N3	2.161(7)
Co1-O4	2.127(4)	Co2-O6	2.118(5)	Co2-N4	2.180(7)

Table S7. Selected bond angles (°) for complex **2**.

Atom-Atom-Atom	Bond length(Å)	Atom-Atom-Atom	Bond length(Å)	Atom-Atom-Atom	Bond length(Å)
O1-Co1-O2	94.48(17)	O3-Co1-N1	90.3(2)	O6-Co2-N3	91.8(3)
O1-Co1-O4	175.76(18)	O3-Co1-N2	95.4(2)	O6-Co2-N4	90.9(3)
O1-Co1-N1	90.2(2)	O4-Co1-N1	90.9(2)	O7-Co2-O6	87.1(2)
O1-Co1-N2	88.3(2)	O4-Co1-N2	91.0(2)	O7-Co2-N3	89.6(2)
O2-Co1-O4	89.66(17)	N2-Co1-N1	174.0(2)	O7-Co2-N4	85.8(2)
O2-Co1-N1	87.1(2)	O5-Co2-O6	85.83(19)	O8-Co2-O6	177.43(19)
O2-Co1-N2	87.3(2)	O5-Co2-O7	172.7(2)	O8-Co2-O7	90.3(2)
O3-Co1-O1	86.90(18)	O5-Co2-O8	96.67(18)	O8-Co2-N3	88.7(2)
O3-Co1-O2	177.1(2)	O5-Co2-N3	92.7(2)	O8-Co2-N4	88.4(2)
O3-Co1-O4	89.00(18)	O5-Co2-N4	92.3(2)	N3-Co2-N4	174.5(2)

Table S8. The hydrogen bonds in complex **2**.

D-H-A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	∠D-H-A/°
O1-H1A-O18[1]	0.86	1.83	2.655(6)	160.9
O1-H1B-O26[2]	0.86	2.00	2.837(7)	163.4
O3-H3A-O35	0.86	1.95	2.705(7)	145.9
O3-H3B-O27[3]	0.86	2.00	2.752(8)	145.1
O6-H6B-O33[4]	0.89	2.03	2.808(9)	145.9
O7-H7B-O16	0.85	1.88	2.716(7)	169.7
O8-H8A-O26[5]	0.88	1.87	2.714(7)	161.3
O8-H8B-O27	0.88	1.90	2.752(7)	160.9
O13-H13-O16[6]	0.82	1.97	2.685(7)	145.6
N18-H18-O23[7]	0.86	1.92	2.778(8)	174.0
O21-H21-O10[8]	0.82	1.98	2.719(7)	149.6
N20-H20A-O14[9]	0.86	2.01	2.868(8)	174.9
O25-H25A-O18[6]	0.85	1.90	2.748(8)	172.5
O25-H25B-O9	0.85	1.95	2.759(8)	160.5
O26-H26B-O9[10]	0.85	1.86	2.698(7)	169.0
O27-H27A-O28	0.85	1.90	2.651(11)	147.1
O27-H27B-N6[10]	0.85	2.09	2.845(9)	147.5
O28-H28A-O16	0.85	2.00	2.799(9)	155.4
O33-H33A-O2	0.85	2.05	2.817(7)	149.0
O35-H35A-O10	0.85	1.87	2.684(8)	161.3

Symmetry mode: [1]1+X,+Y,-1+Z; [2]3-X,-1/2+Y,-Z; [3]1+X,+Y,+Z; [4]+X,+Y,1+Z; [5]2-X,-1/2+Y,-Z; [6]+X,+Y,-1+Z; [7]2-X,1/2+Y,1-Z; [8]-1+X,+Y,+Z; [9]2-X,-1/2+Y,1-Z; [10]2-X,1/2+Y,-Z

Table S9. Selected bond distances (Å) for complex **3**.

Atom-Atom	Length(Å)	Atom-Atom	Length(Å)	Atom-Atom	Length(Å)
Co1-O1	2.110(6)	Co1-O3	2.127(6)	Co1-N1	2.213(7)
Co1-O2	2.114(6)	Co1-O4	2.048(6)	Co1-N2[1]	2.188(7)
Co2-O19	2.069(7)	Co2-O21	2.093(6)	Co2-O23	2.147(7)
Co2-O20	2.085(6)	Co2-O22	2.128(6)	Co2-O24	2.095(7)

Symmetry mode: [1]+X,+Y,-1+Z

Table S10. Selected bond angles (°) for complex **3**.

Atom-Atom-Atom	Bond length(Å)	Atom-Atom-Atom	Bond length(Å)	Atom-Atom-Atom	Bond length(Å)
O1-Co1-O2	91.5(2)	O2-Co1-N1	87.2(3)	O4-Co1-O2	175.4(3)
O1-Co1-O3	176.5(3)	O2-Co1-N2[1]	92.1(3)	O4-Co1-O3	88.7(2)
O1-Co1-N1	82.4(2)	O3-Co1-N1	101.1(3)	O4-Co1-N1	90.0(2)
O1-Co1-N2[1]	95.2(3)	O3-Co1-N2[1]	81.3(2)	O4-Co1-N2[1]	90.8(2)
O2-Co1-O3	88.3(2)	O4-Co1-O1	91.7(3)	N2[1]-Co1-N1	177.5(3)
O19-Co2-O20	89.1(3)	O20-Co2-O21	87.4(3)	O21-Co2-O23	174.2(3)
O19-Co2-O21	94.8(3)	O20-Co2-O22	172.8(3)	O21-Co2-O24	90.5(3)
O19-Co2-O22	85.3(3)	O20-Co2-O23	90.4(3)	O22-Co2-O23	94.2(3)
O19-Co2-O23	90.5(3)	O20-Co2-O24	95.6(2)	O24-Co2-O22	90.3(3)
O19-Co2-O24	173.0(4)	O21-Co2-O22	88.5(3)	O24-Co2-O23	84.3(3)

Symmetry mode: [1]+X, +Y, -1+Z

Table S11. The hydrogen bonds in complex **3**.

D-H-A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	∠D-H-A/°
O1-H1A…O13[1]	0.87	1.92	2.697(8)	149.2
O1-H1B…O5	0.87	1.95	2.758(8)	154.6
O3-H3A…O5[2]	0.87	1.86	2.653(8)	149.9
O3-H3B…O13	0.87	1.99	2.820(8)	159.4
O8-H8…O26[3]	0.82	1.9	2.698(14)	164.9
O15-H15…O8[4]	0.82	1.93	2.746(10)	176.2
O28-H28B…O2	0.85	2.05	2.789(9)	145.1
N6-H6…O17[5]	0.86	1.98	2.829(10)	170.8
N8-H8A…O10[6]	0.86	1.97	2.825(9)	172.5
O22-H22D…O12[7]	0.86	2.05	2.883(9)	164.3
O23-H23A…O25[2]	0.92	1.97	2.865(11)	164.8
O23-H23B…O28	0.92	1.98	2.857(11)	160.9
O24-H24B…O6	0.85	1.95	2.725(9)	151.3
O25-H25C…O18[1]	0.85	1.91	2.732(10)	162.4
O26-H26B…O15[1]	0.85	1.98	2.817(13)	167.1

Symmetry mode: [1]-1+X, +Y, +Z; [2]1+X, +Y, +Z; [3]-1+X, 1+Y, -1+Z; [4]1+X, -1+Y, 1+Z; [5]-1+X, +Y, -1+Z; [6]1+X, +Y, 1+Z; [7]+X, 1+Y, +Z

Table S12. Selected bond distances (Å) for complex **4**.

Atom-Atom	Length(Å)	Atom-Atom	Length(Å)	Atom-Atom	Length(Å)
Co1-O1	2.101(10)	Co1-O3	2.075(11)	Co1-N1	2.218(7)
Co1-O2	2.112(11)	Co1-O4	2.116(11)	Co1-N4[1]	2.165(15)
Co2-O21	2.080(13)	Co2-O23	2.153(12)	Co2-O25	2.074(12)
Co2-O22	2.095(12)	Co2-O24	2.055(12)	Co2-O26	2.086(12)

Symmetry mode: [1]+X, +Y, 1+Z

Table S13. Selected bond angles (°) for complex **4**.

Atom-Atom-Atom	Bond length(Å)	Atom-Atom-Atom	Bond length(Å)	Atom-Atom-Atom	Bond length(Å)
O1-Co1-O2	88.8(4)	O3-Co1-N1	89.9(4)	O24-Co2-O22	178.8(6)
O1-Co1-O4	91.8(4)	O3-Co1-N4[1]	91(2)	O24-Co2-O23	89.0(5)
O1-Co1-N1	91.2(4)	O4-Co1-N1	84.1(4)	O24-Co2-O25	93.4(5)
O1-Co1-N4[1]	88(2)	O4-Co1-N4[1]	95(2)	O24-Co2-O26	89.5(5)
O2-Co1-O4	178.4(5)	N41-Co1-N1	179(2)	O25-Co2-O21	174.3(5)
O2-Co1-N1	97.3(4)	O21-Co2-O22	90.2(5)	O25-Co2-O22	87.2(5)
O2-Co1-N4[1]	83(2)	O21-Co2-O23	84.9(5)	O25-Co2-O23	90.1(5)
O3-Co1-O1	178.5(5)	O21-Co2-O26	93.1(5)	O25-Co2-O26	92.0(5)
O3-Co1-O2	90.1(4)	O22-Co2-O23	90.0(5)	O26-Co2-O22	91.6(5)
O3-Co1-O4	89.3(5)	O24-Co2-O21	89.2(5)	O26-Co2-O23	177.5(5)

Symmetry mode: [1]+X, +Y, 1+Z

Table S14. The hydrogen bonds in complex **4**.

D-H-A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	∠D-H-A/°
O2-H2B…O5	0.91	1.87	2.714(14)	152.8
N6-H6A…O18[1]	0.86	1.83	2.680(13)	172.2
N8-H8A…O11[2]	0.86	1.97	2.814(14)	168.0
O22-H22D…O14[3]	0.89	1.84	2.701(17)	161.3
O23-H23A…O14[3]	0.88	1.84	2.674(14)	158.5
O25-H25A…O6	0.88	1.97	2.738(15)	144.2
O26-H26A…O17	0.90	2.01	2.832(18)	153.0
O27-H27B…O24	0.85	1.81	2.630(17)	162.1

Symmetry mode: [1]1+X, +Y, -1+Z; [2]-1+X, Y, 1+Z; [3]+X, -1+Y, +Z

Table S15. Selected bond distances (Å) for complex **5**.

Atom-Atom	Length(Å)	Atom-Atom	Length(Å)	Atom-Atom	Length(Å)
Cd1-O1	2.332(4)	Cd1-N1[1]	2.341(2)	Cd2-O3[1]	2.326(4)
Cd1-O1[1]	2.332(4)	Cd1-N1	2.341(2)	Cd2-O3	2.326(4)
Cd1-O2	2.305(3)	Cd2-O2	2.304(3)	Cd2-N2	2.314(6)
Cd1-O2[1]	2.305(3)	Cd2-O2[1]	2.304(3)		

Symmetry mode: [1]+X, 1-Y, 1-Z

Table S16. Selected bond angles (°) for complex **5**.

Atom-Atom-Atom	Bond length(Å)	Atom-Atom-Atom	Bond length(Å)	Atom-Atom-Atom	Bond length(Å)
O1^{1}-Cd1-O1	83.6(3)	O2^{1}-Cd1-O2	80.24(15)	O2^{1}-Cd2-O3	174.73(16)
O1-Cd1-N1	85.93(17)	O2-Cd1-N1^{1}	93.9(4)	O2-Cd2-O31	174.73(16)
O1^{1}-Cd1-N1	88.28(17)	O2^{1}-Cd1-N1	93.92(15)	O2^{1}-Cd2-O3^{1}	95.66(13)
O1^{1}-Cd1-N1^{1}	85.9(4)	O2-Cd1-N1	92.02(15)	O2^{1}-Cd2-N2	87.6(3)
O1-Cd1-N1^{1}	88.3(4)	O2^{1}-Cd1-N1^{1}	92.0(3)	O2-Cd2-N2	91.9(3)
O2-Cd1-O1	177.30(18)	N1^{1}-Cd1-N1	172.2(3)	O3^{1}-Cd2-O3	88.6(2)
O2^{1}-Cd1-O1^{1}	177.31(18)	O2-Cd2-O2^{1}	80.29(14)	N2-Cd2-O3	96.0(3)
O2-Cd1-O1^{1}	98.14(15)	O2-Cd2-O3	95.66(13)	N2-Cd2-O3^{1}	84.5(3)
O2^{1}-Cd1-O1	98.14(15)				

Symmetry mode: ^{1}+X, 1-Y, 1-Z

Table S17. The hydrogen bonds in complex **5**.

D-H-A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	∠D-H-A/°
O8-H8…O5^{1}	0.82	1.87	2.683(5)	170.0
O9-H9…O14^{1}	0.82	1.95	2.703(12)	153.1
N8-H8B…O10^{2}	0.86	1.94	2.785(5)	168.1

Symmetry mode: ^{1}-1/2+X, 3/2-Y, 1-Z; ^{2}-X, +Y, 3/2-Z

4. The IR Spectra of Complexes 1-5

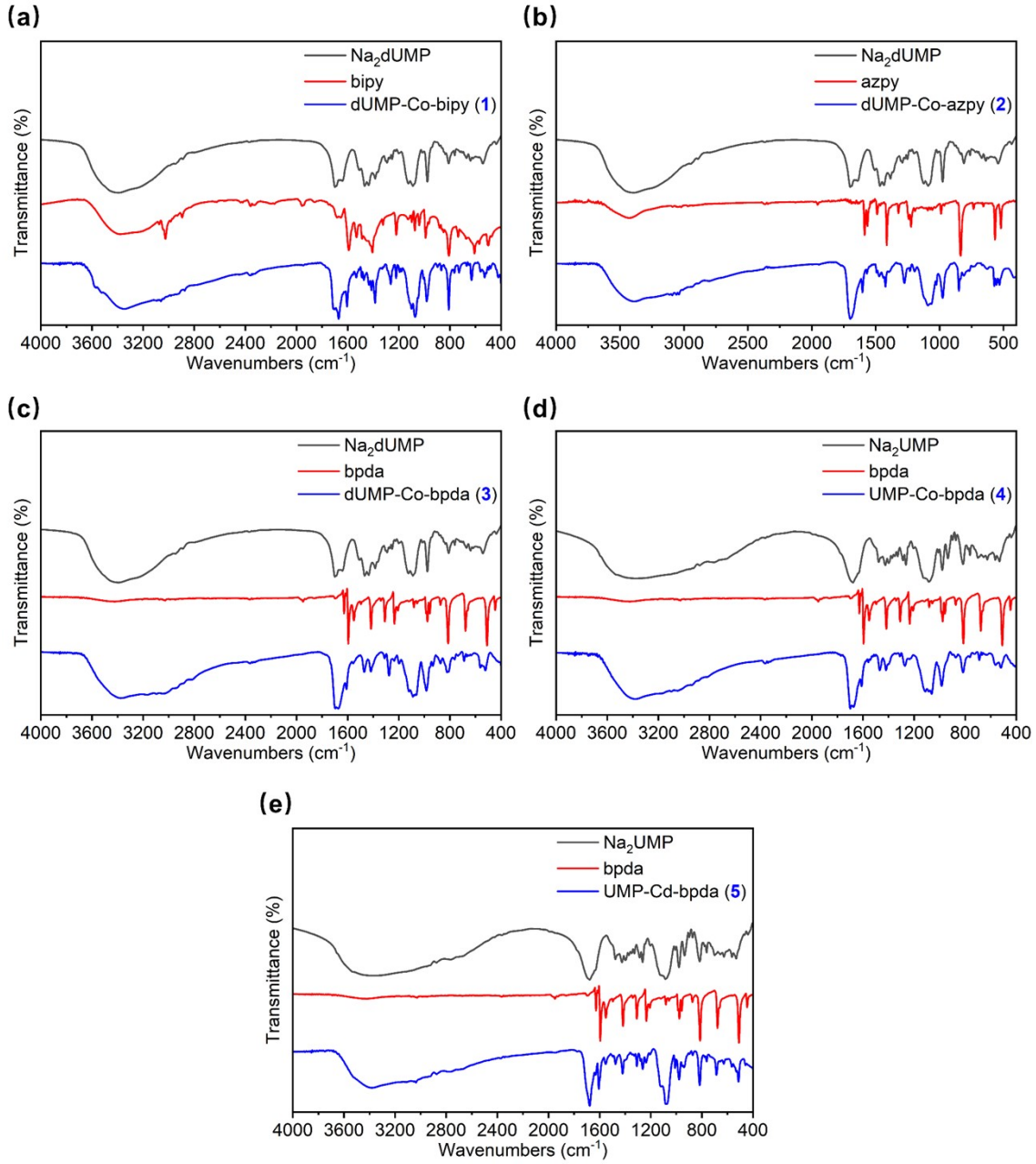

Figure S5. IR spectra of (a) **1**, (b) **2**, (c) **3**, (d) **4**, and (e) **5**. The infrared spectrum of the complexes includes not only the characteristic band of the nucleotide ligand, but also the characteristic band of the corresponding auxiliary ligand.

5. The PXRD Patterns of Complexes 1-5

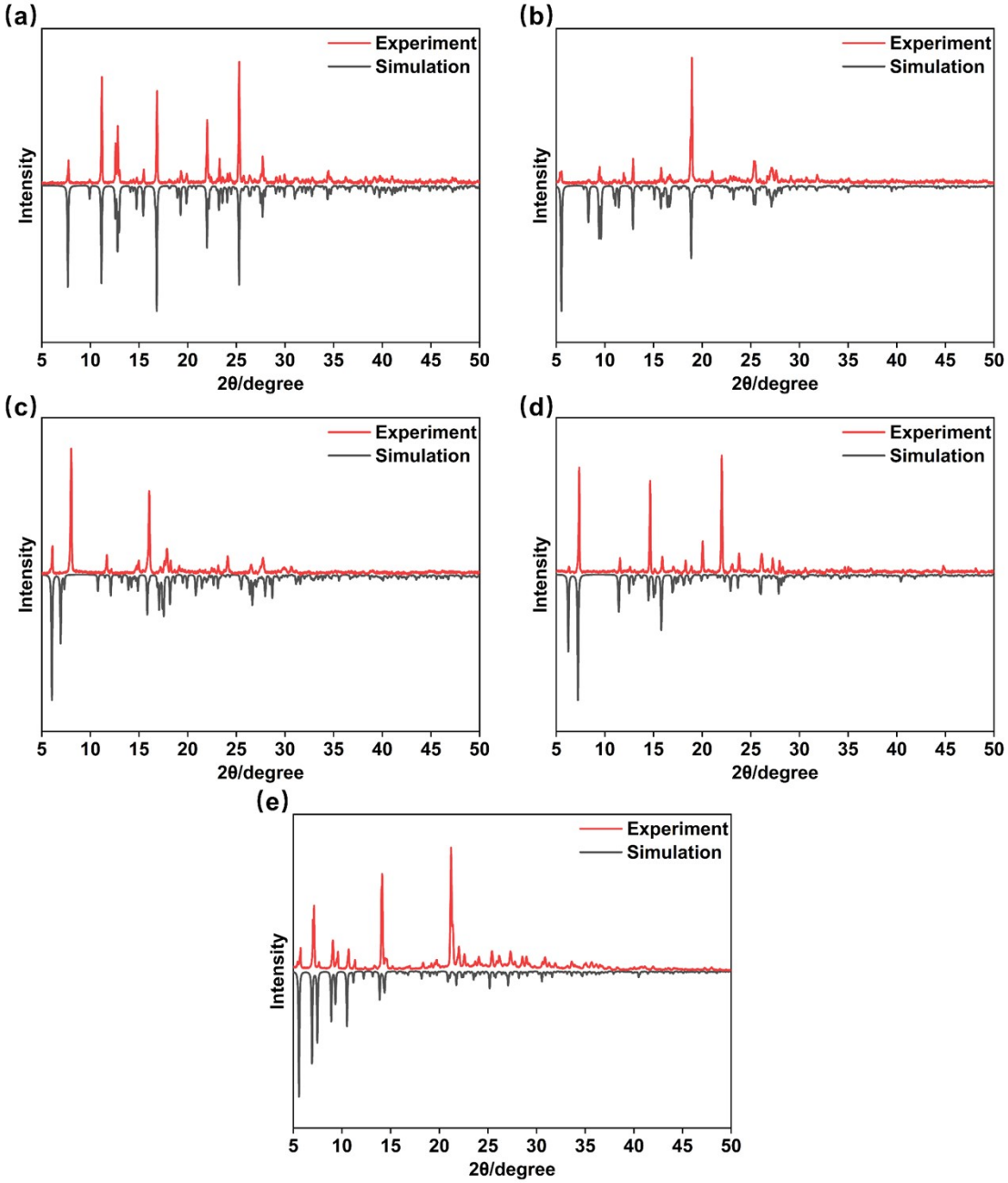

Figure S6. PXRD patterns show the comparison between the experimental values and calculated ones for (a) **1**, (b) **2**, (c) **3**, (d) **4**, and (e) **5**.

6. The thermo-Gravimetric Analysis of Complexes 1-5.

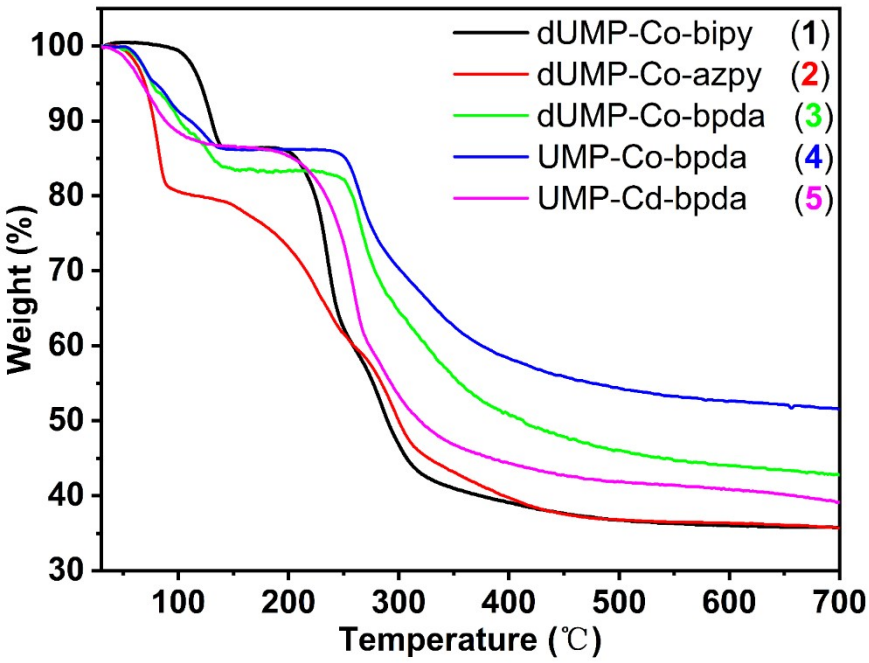

Figure S7. TG curves of **1**-**5**. The TG curves of **1**-**5** show a two-step weight loss process. The initial weight loss (**1**: obs. 13.94%, cal. 14.73%; **2**: obs. 19.66%, cal. 19.72%; **3**: obs. 16.70%, cal. 24.63%; **4**: obs. 13.74%, cal. 25.02%; **5**: obs. 15.12%, cal. 22.41%) in the temperature range 50 °C – 260 °C are assigned to the loss of guest water solvates and coordinated water molecules per formula unit. The residue of complex begins to decompose around 250 °C.

7. Supporting Information of Complexes 1-5

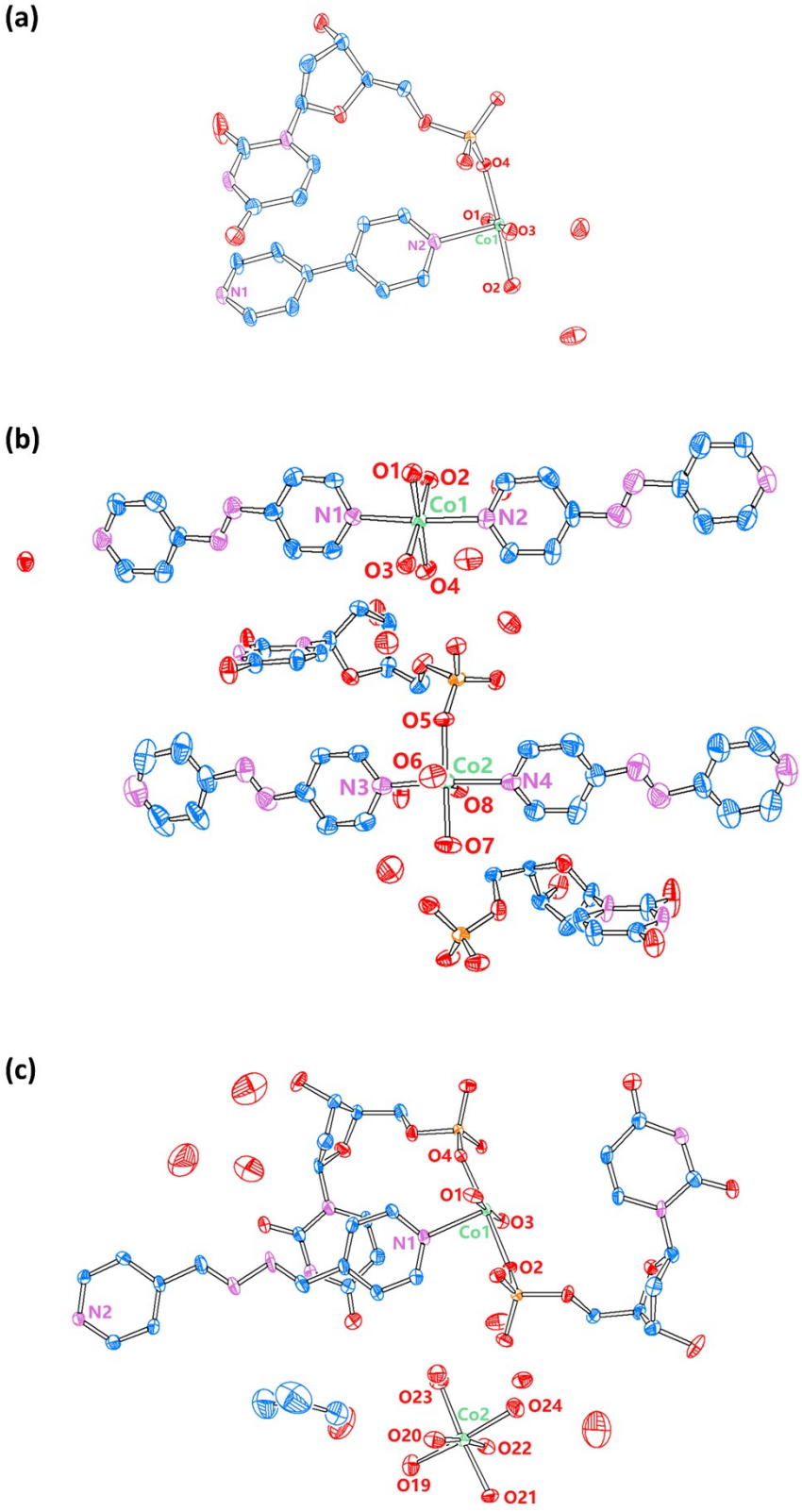

Figure S8. Oak ridge thermal ellipsoid plot (ORTEP) views of (a) **1**, (b) **2**, and (c) **3** with 50% thermal ellipsoid probability (Hydrogen atoms are removed for clearer display).

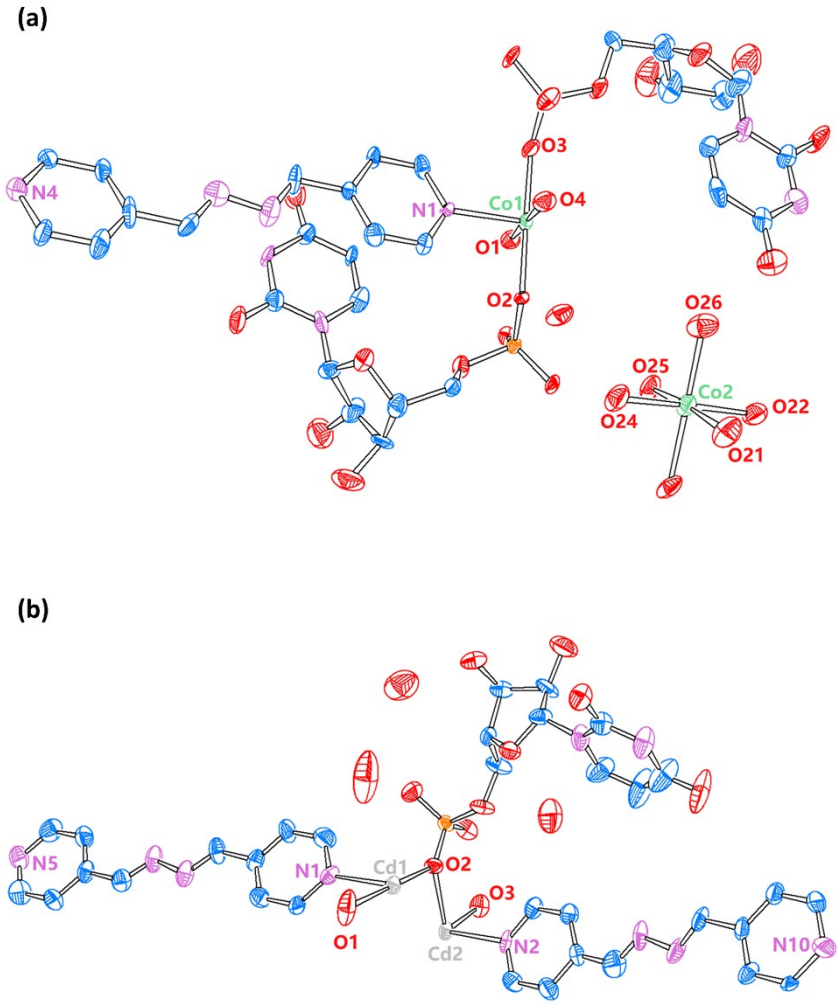

Figure S9. Oak ridge thermal ellipsoid plot (ORTEP) views of (a) **4** and (b) **5** with 50% thermal ellipsoid probability (Hydrogen atoms are removed for clearer display).

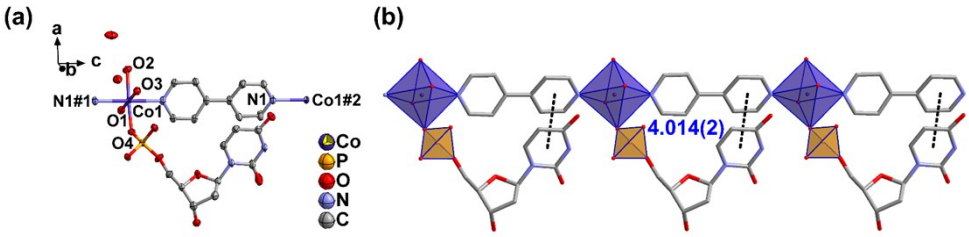

Figure S10 (a) the coordination environment diagram of **1** (hydrogen atoms have been removed for clarity). Symmetry code: #1: +X, +Y, -1+Z; #2: +X, +Y, 1+Z; (b) one-dimensional chain structure bridged by 4,4'-bipy in **1**, with a π-π stacking of 4.014(2) Å between the uracil base and the pyridine ring of auxiliary ligand.

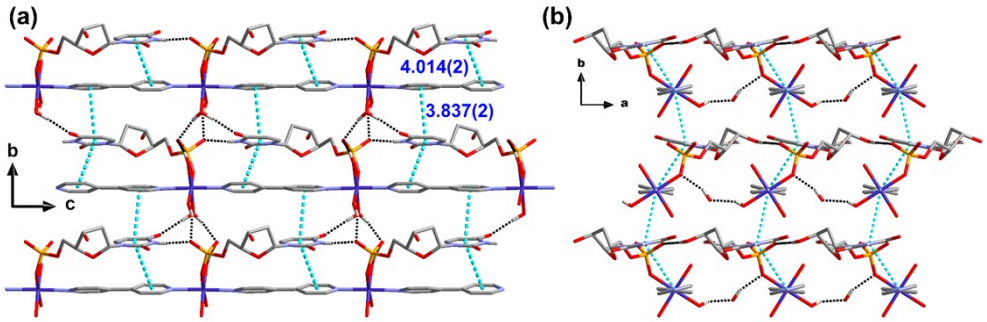

Figure S11 (a) Two-dimensional planar structure connected by hydrogen bonding (N4-H4…O5: 1.89 Å, 2.733(3) Å, 166.3°; O2-H2A…O5: 1.83 Å, 2.651(3) Å, 159.4°; O1-H1A…O6: 1.86 Å, 2.692(3) Å, 164.2°; O3-H3A…O6: 1.86 Å, 2.667(3) Å, 159.0°; O1-H1B…O13: 2.00 Å, 2.827(3) Å, 162.7°) and π-π stacking (3.837(2) Å) in **1**. (b) three-dimensional spatial structure formed by the connection of hydrogen bonding (O9-H9…O6: 2.08 Å, 2.897(3) Å, 176.6°; O2-H2B…O11: 1.96 Å, 2.722(3) Å, 147.6°; O11-H11C…O4: 1.99 Å, 2.804(3) Å, 159.0°) formed.

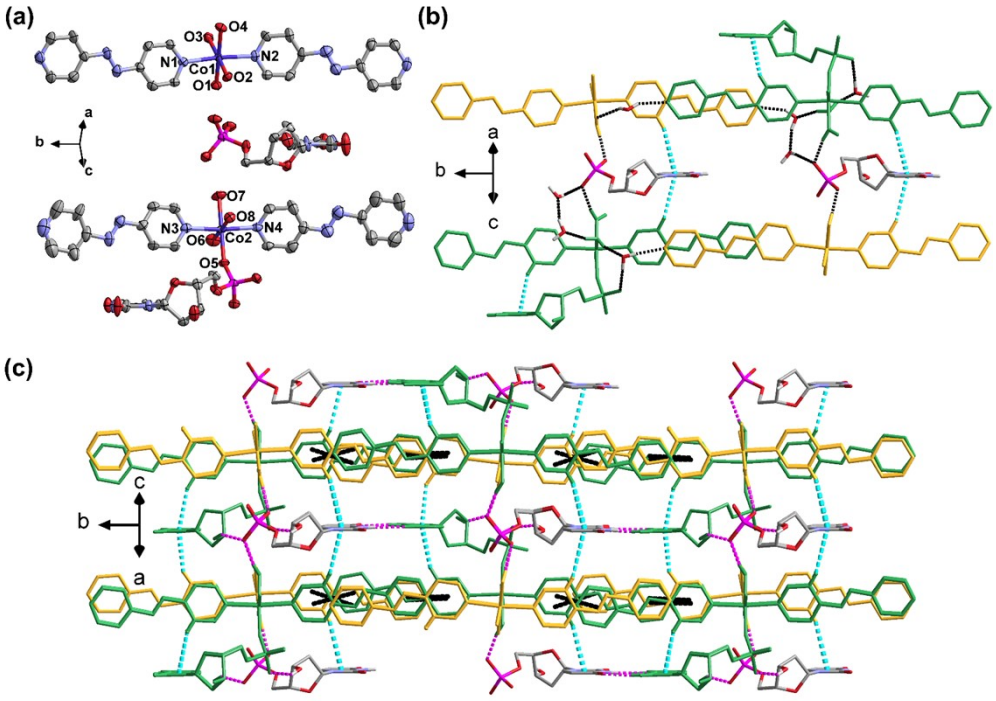

Figure S12 (a) the coordination environment diagram of **2** (hydrogen atoms have been removed for clarity); (b) one-dimensional chain structure bridged by hydrogen bonding along *b* axis in **2**; (c) three-dimensional supramolecular structure formed by face to face π-π stacking (4.123(5) Å, 4.202(6) Å, 4.342(5) Å, and 3.118(4) Å), edge to face π-π stacking (2.736(3) Å, 3.312(4) Å, 2.822(3) Å, and 3.118(4) Å), and multiple hydrogen bonding between molecules.

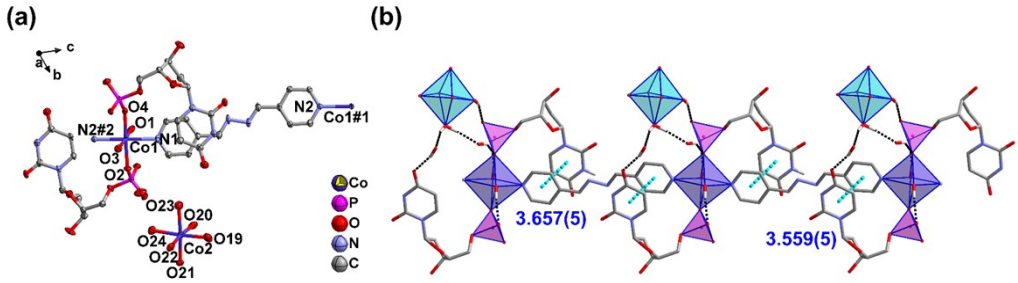

Figure S13 (a) the coordination environment diagram of **3** (partial hydrogen atoms and solvent molecule have been removed for clarity). Symmetry code: #1: +X, +Y, 1+Z; #2: +X, +Y, -1+Z; (b) one-dimensional chain structure bridged by bpda in **3**, with π-π stacking of 3.657(5) Å and 3.559(5) Å between the uracil base and the pyridine ring of auxiliary ligand. The cobalt ions with six coordinated waters are fixed to one side of the chain structure by hydrogen bonding (O23-H23A…O25: 1.97 Å, 2.865(11) Å, 164.8°; O23-H23B…O28: 1.98 Å, 2.857(11) Å, 160.9°; O24-H24B…O6: 1.95 Å, 2.725(9) Å, 151.3°; O25-H25C…O18: 1.91 Å, 2.732(10) Å, 162.4°).

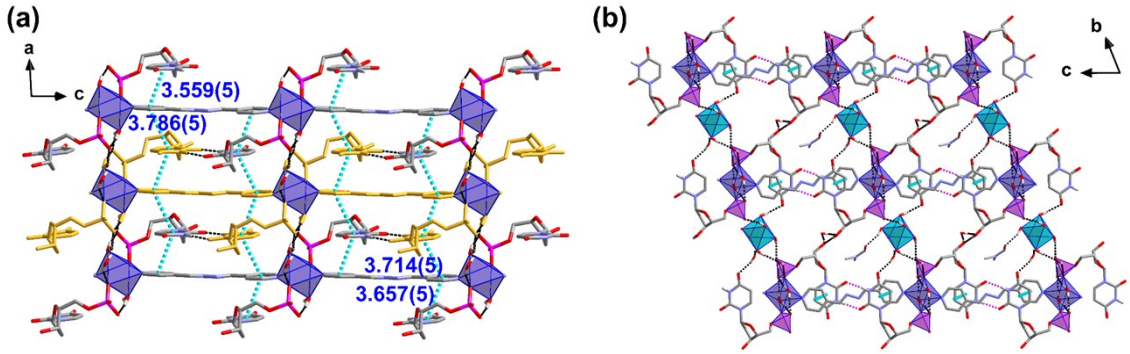

Figure S14 (a) Two-dimensional planar structure connected by hydrogen bonding (O1-H1A…O13: 1.92 Å, 2.697(8) Å, 149.2°; O3-H3B…O13: 1.99 Å, 2.820(3) Å, 159.4°; N6-H6…O17: 1.98 Å, 2.829(10) Å, 170.8°; N8-H8A…O10: 1.97 Å, 2.825(9) Å, 172.5°) and π-π stacking (3.786(5) Å and 3.714(5) Å) in **3**. (b) three-dimensional spatial structure formed by the connection of hydrogen bonding (O8-H8…O26: 1.90 Å, 2.698(14) Å, 164.9°; O15-H15…O8: 1.93 Å, 2.746(10) Å, 176.2°; O22-H22D…O12: 2.05 Å, 2.883(9) Å, 164.3°; O23-H23A…O25: 1.97 Å, 2.865(11) Å, 164.8°; O23-H23B…O28: 1.98 Å, 2.857(11) Å, 160.9°; O24-H24B…O6: 1.95 Å, 2.725(9) Å, 151.3°; O25-H25C…O18: 1.91 Å, 2.732(10) Å, 162.4°; O26-H26B…O15: 1.98 Å, 2.817(11) Å, 167.1°).

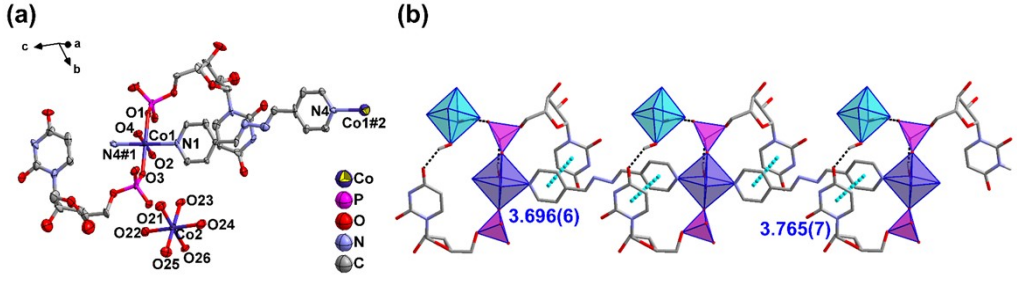

Figure S15 (a) the coordination environment diagram of **4** (partial hydrogen atoms and solvent molecule have been removed for clarity). Symmetry code: #1: +X, +Y, 1+Z; #2: +X, +Y, -1+Z; (b) one-dimensional chain structure bridged by bpda in **4**, with π-π stacking of 3.696(6) Å and 3.765(7) Å between the uracil base and the pyridine ring of auxiliary ligand. The cobalt ions with six coordinated waters are fixed to one side of the chain structure by hydrogen bonding (O2-H2B…O5: 1.85 Å, 2.703(16) Å, 154.6°; O25-H25A…O6: 1.94 Å, 2.724(15) Å, 147.5°; O26-H26A…O17: 2.01 Å, 2.827(18) Å, 149.8°).

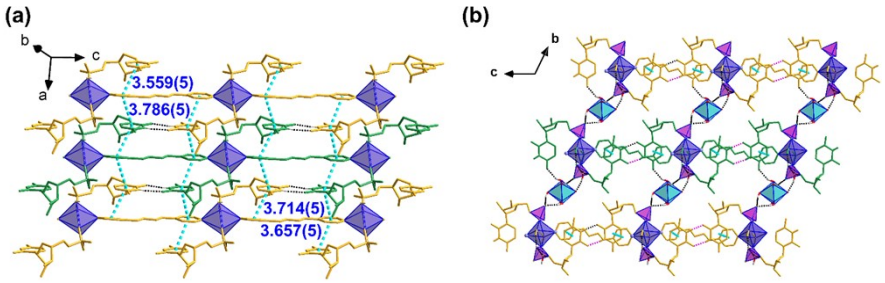

Figure S16 (a) Two-dimensional planar structure connected by hydrogen bonding (N6-H6A…O18: 1.83 Å, 2.688(13) Å, 171.8°和 N8-H8A…O11: 1.96 Å, 2.803(14) Å, 168.1°) and π-π stacking (3.786(5) Å and 3.714(5) Å) in **4**. (b) three-dimensional spatial structure formed by the connection of hydrogen bonding (O2-H2B…O5: 1.85 Å, 2.703(16) Å, 154.6°; O22-H22C…O14: 1.86 Å, 2.690(17) Å, 159.9°; O23-H23A…O14: 1.84 Å, 2.678(15) Å, 161.3°; O25-H25A…O6: 1.94 Å, 2.724(15) Å, 147.5°; O26-H26A…O17: 2.01 Å, 2.827(18) Å, 149.8°和 O27-H27B…O24: 1.79 Å, 2.616(17) Å, 162.0°).

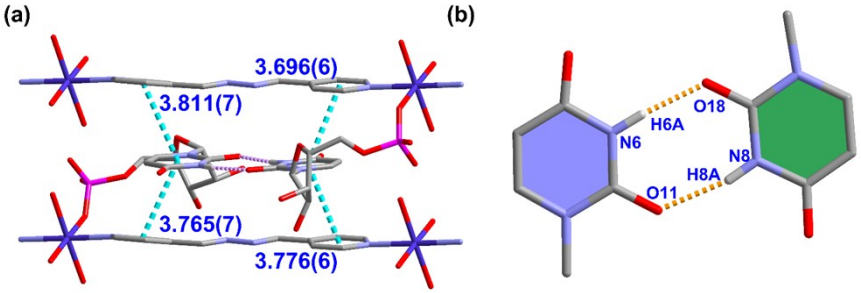

Figure S17 (a) U-motif IV structure formed by π-π stacking (3.811(7) Å, 3.696(6) Å, 3.765(7) Å and 3.776(6) Å) in **4**; (b) double hydrogen bonding in U-motif IV (N3-H3...O2: 1.83A, 2.688(13) A, 171.8° and N3-H3... O2: 1.96 Å, 2.803(14) Å, 168.1°, atom names are converted to standard nucleotide atom names).

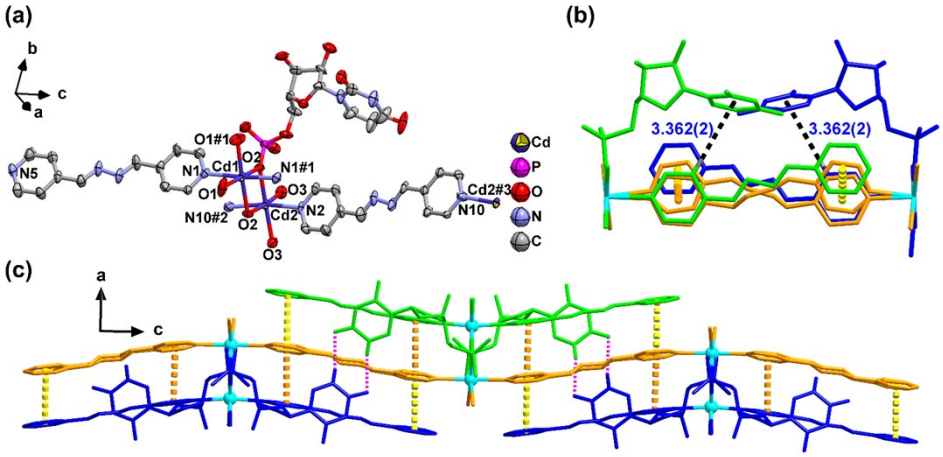

Figure S18 (a) the coordination environment diagram of **5** (partial hydrogen atoms and solvent molecule have been removed for clarity). Symmetry code: #1: +X, 1-Y, 1-Z; # 2: 1-X, 1-Y, -1/2+Z; #3: 1-X, 1-Y, 1/2+Z; (b) edge to face π-π stacking interaction 3.362(2) Å between the auxiliary ligand and uracil base in **5**; (c) one-dimensional chain structure formed in **5** by the coordination of the phosphate oxygen atom from nucleotide and the auxiliary ligand with the metal ions. Face-to-face π-π stacking interaction of 3.712(6)/3.732(6) Å (orange) and 3.729(6)/3.910(5) Å (yellow) exists between the parallel auxiliary ligand, and uracil bases are connected by double non-classical hydrogen bonds (C32-H32...O11: 2.55 Å, 3.405(6) Å, 161.2°).

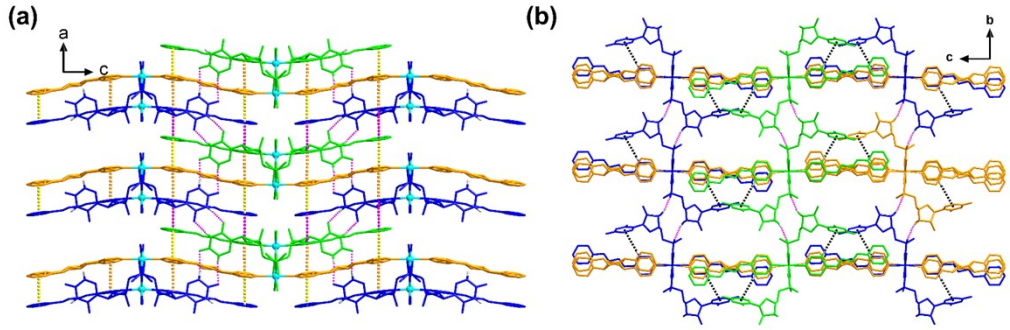

Figure S19 (a) two-dimensional structure of **5** viewed from the *b* axis. There are face to face π-π stacking interaction (3.803(3) Å) and double hydrogen bonding (N8-H8B…O10: 1.94 Å, 2.785(5) Å, 168.1°, purple) between the adjacent chains; (b) thr e two-dimensional layer structure is assembled into a three-dimensional (O8-H8... O5: 1.87 Å, 2.683(5) Å, 170.0°).

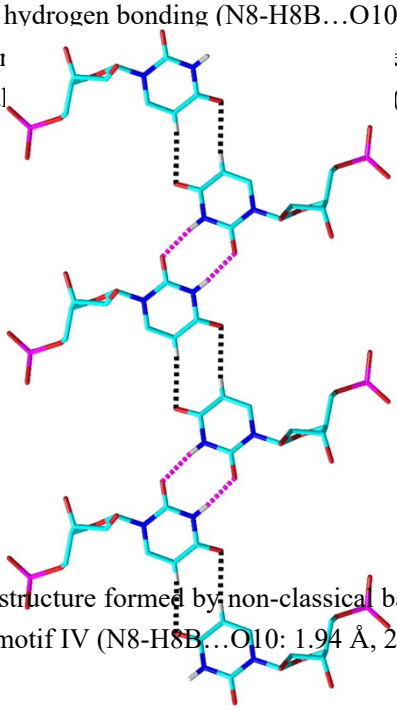

Figure S20 One-dimensional chain structure formed by non-classical base pair U-motif I (C32-H32…O11: 2.55 Å, 3.405(6) Å, 161.2°) and U-motif IV (N8-H8B…O10: 1.94 Å, 2.785(5) Å, 168.1°) in **5**;

8. DFT Calculation of U-motif

The BSSE corrected energy calculation is defined as the following formula.

$E(interaction) = E(AB) + E(BSSE) - E(A) - E(B)$

E(AB) is the energy of the complex, E(A) or E(B) represents the energy of the single compound A or B.

For surface electrostatic potential penetration, the structure model is established based on the base in the single crystal structure. In the process of structure optimization, the position of all non-hydrogen atoms is frozen, and only the position of hydrogen atoms is optimized. At the same time, the "nosymm" instruction is added to ensure the consistency between the coordinates in the calculation process and the coordinates in the input file. The calculated parameters are: #p opt freq b3lyp/6-311g(d,p) em=gd3bj nosymm. Multiwfn and VMD programs were used to plot the surface electrostatic potentials of three U-motif structures.

Table S18 The BSSE corrected energy calculation.

	E_A/kJ·mol^{-1}	E_B/kJ·mol^{-1}	E_{BSSE}/kJ·mol^{-1}	E_{AB}/kJ·mol^{-1}	$E_{interaction}$/kJ·mol^{-1}
U-motif I	-1192708.018	-1192708.018	9.48736888	-2385446.719	-21.19565389
U-motif II	-1192708.018	-1192708.018	10.98868227	-2385457.272	-30.24775039
U-motif III	-1192708.018	-1192708.018	12.5588015	-2385472.211	-43.61590759
U-motif IV	-1192708.018	-1192708.018	11.63952345	-2385467.488	-39.81218682
U-motif V	-1192708.018	-1192708.018	12.07335728	-2385469.293	-41.1833109

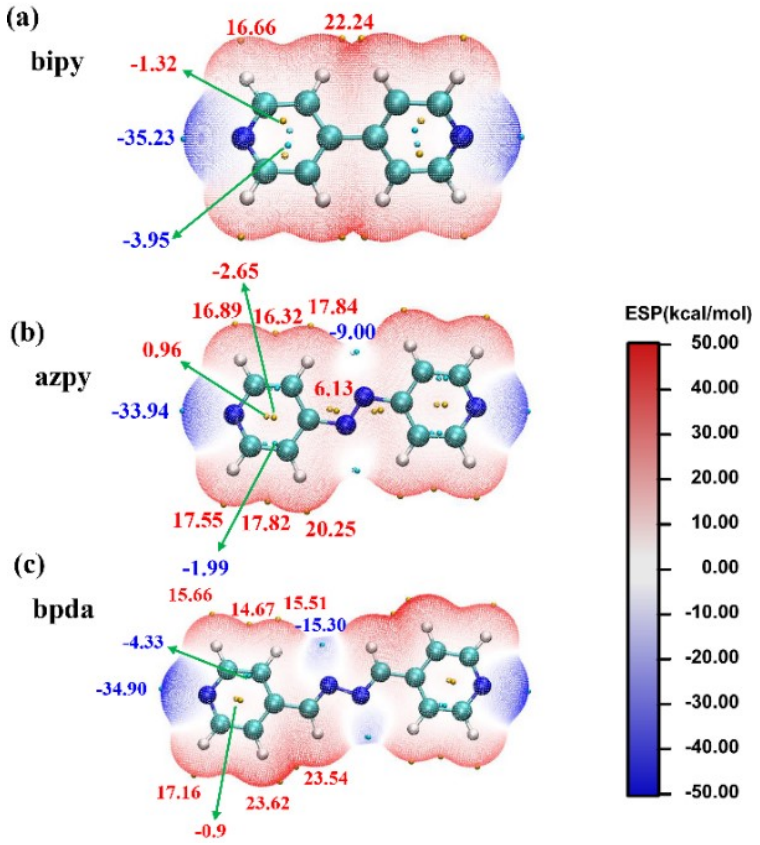

Figure S21 Surface electrostatic potential distribution of the auxiliary ligand (a) bipy, (b) azpy, and (c) bpda.

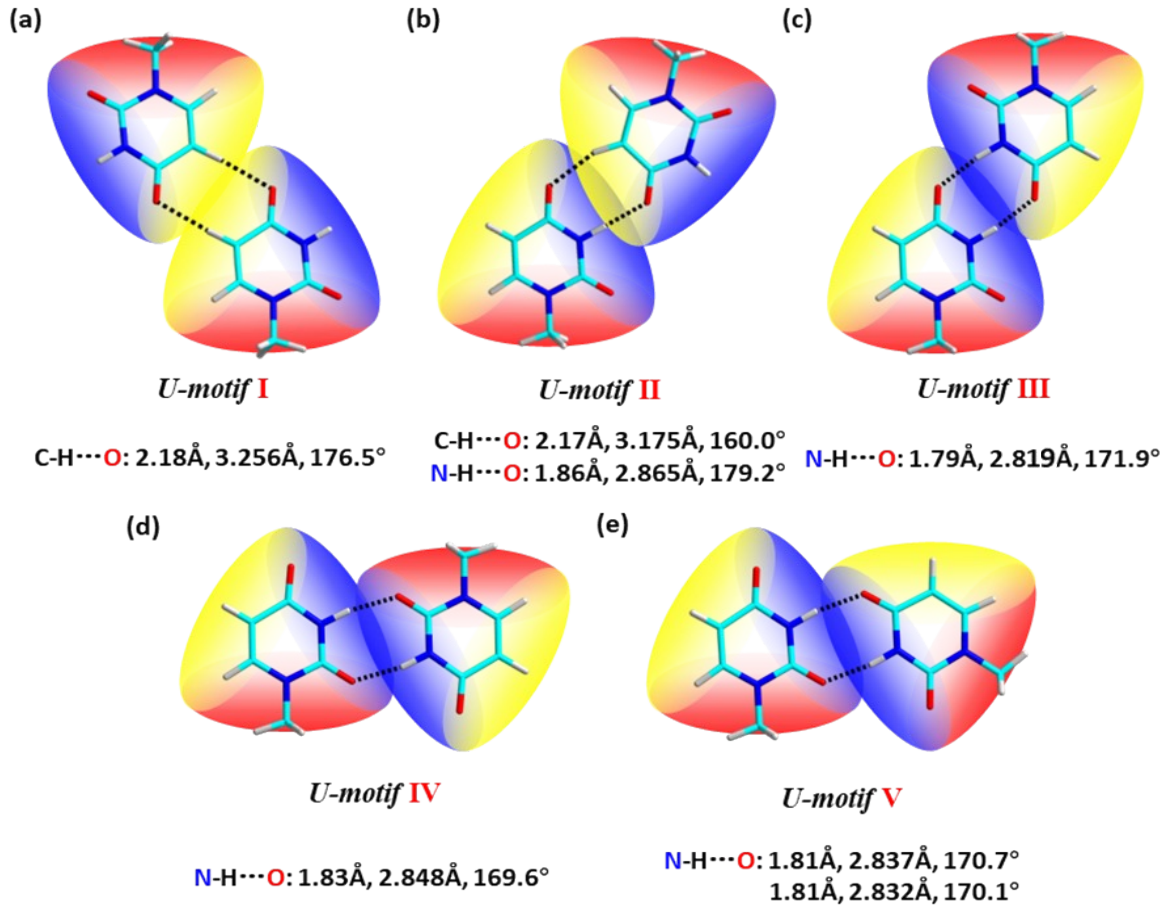

Figure S22 Optimized structure obtained by DFT calculation: (a) Structure of U-motif I; (b) Structure of U-motif II; (c) Structure of U-motif III; (d) Structure of U-motif IV; (e) Structure of U-motif V.

Table S19 Hydrogen bond data of U-motif in single crystal structure of complexes and hydrogen bond data obtained by theoretical calculation.

		D-H-A	d(H-A)/Å	d(D-A)/Å	∠D-H-A/°
Theoretical calculation	U-motif I	C5-H5…O4	2.18	3.256	176.5
	U-motif III	N3-H3…O4	1.79	2.819	171.9
	U-motif IV	N3-H3…O2	1.83	2.848	169.6
Crystal structure	U-motif III in **2**	N3-H3…O4	1.92	2.778	173.7
		N3-H3…O4	2.01	2.868	175.1
	U-motif IV in **3**	N3-H3…O2	1.98	2.829	170.8
		N3-H3…O2	1.97	2.825	172.5
	U-motif IV in **4**	N3-H3…O2	1.83	2.688	171.8
		N3-H3…O2	1.96	2.803	168.1
	U-motif I in **5**	C5-H5…O4	2.55	3.405	161.2
	U-motif IV in **5**	N3-H3…O2	1.94	2.785	168.1

Table S20 Atomic coordinate information of bipy.

Atom	Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0	0.366221	2.859106	1.0776
C	0	0.382035	1.469414	1.130004
C	0	0	0.739567	0
C	0	-0.382035	1.469414	-1.130004
C	0	-0.366221	2.859106	-1.0776
H	0	0.667662	3.439843	1.944524
H	0	0.711048	0.964508	2.029842
H	0	-0.711048	0.964509	-2.029842
H	0	-0.667662	3.439843	-1.944524
C	0	0	-0.739567	0
C	0	-0.382035	-1.469414	1.130004
C	0	0.382035	-1.469414	-1.130004
C	0	-0.366221	-2.859106	1.0776
H	0	-0.711048	-0.964508	2.029842
C	0	0.366221	-2.859106	-1.0776
H	0	0.711048	-0.964509	-2.029842
H	0	-0.667662	-3.439843	1.944524
H	0	0.667662	-3.439843	-1.944524
N	0	0	-3.559047	0
N	0	0	3.559047	0

Table S21 Atomic coordinate information of azpy.

Atom	Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0	1.255868	1.25216	0
C	0	1.256417	2.645381	0
C	0	2.481497	0.578891	0
C	0	2.481497	3.308275	0
H	0	0.316681	3.182574	0
C	0	3.641662	1.340311	0
H	0	2.507944	-0.501527	0
N	0	3.659138	2.680636	0
H	0	2.516554	4.393644	0
H	0	4.612645	0.853915	0
C	0	-1.255868	-1.25216	0
C	0	-1.256417	-2.645381	0
C	0	-2.481497	-0.578891	0
C	0	-2.481497	-3.308275	0
H	0	-0.316681	-3.182574	0
C	0	-3.641662	-1.340311	0
H	0	-2.507944	0.501527	0
N	0	-3.659138	-2.680636	0
H	0	-2.516554	-4.393644	0
H	0	-4.612645	-0.853915	0
N	0	-0.018444	0.625288	0
N	0	0.018444	-0.625288	0

Table S22 Atomic coordinate information of bpda.

Atom	Atomic Type	Coordinates (Angstroms)		
		X	Y	Z
C	0	-0.575617	1.572317	0
H	0	-1.642403	1.336	0
N	0	0.293567	0.630359	0
N	0	-0.293567	-0.630359	0
C	0	0.575617	-1.572317	0
C	0	0.181315	-2.979693	0
C	0	1.160216	-3.977498	0
C	0	-1.160216	-3.38232	0
C	0	0.762469	-5.311463	0
H	0	2.213217	-3.71983	0
C	0	-1.44716	-4.739875	0
H	0	-1.946554	-2.639577	0
N	0	-0.514001	-5.701339	0
H	0	1.505329	-6.103757	0
H	0	-2.478608	-5.079668	0
H	0	1.642403	-1.336	0
C	0	-0.181315	2.979693	0
C	0	-1.160216	3.977498	0
C	0	1.160216	3.38232	0
C	0	-0.762469	5.311463	0
H	0	-2.213217	3.71983	0
C	0	1.44716	4.739875	0
H	0	1.946554	2.639577	0
N	0	0.514001	5.701339	0
H	0	-1.505329	6.103757	0
H	0	2.478608	5.079668	0

Table S23 Atomic coordinate information of U-motif I.

Atom	Atomic Type	Coordinates (Angstroms)		
		X	Y	Z
C(Fragment=1)	0	-4.512327	-0.673739	0.003277
C(Fragment=2)	0	4.512348	0.673701	0.003066
C(Fragment=1)	0	-5.466746	1.590062	0.008863
H(Fragment=1)	0	-5.46632	2.210565	0.90743
H(Fragment=1)	0	-5.462153	2.228346	-0.877006
H(Fragment=1)	0	-6.354614	0.964325	0.001069
C(Fragment=2)	0	5.466675	-1.590139	0.008751
H(Fragment=2)	0	5.466458	-2.210545	0.907385
H(Fragment=2)	0	5.461827	-2.228519	-0.877048
H(Fragment=2)	0	6.354568	-0.96444	0.000656
N(Fragment=2)	0	4.300967	-0.706801	0.002028
C(Fragment=2)	0	2.014924	0.952719	-0.005667
C(Fragment=1)	0	-2.014895	-0.95266	-0.006243
H(Fragment=1)	0	-3.468666	-2.415803	-0.001222
H(Fragment=2)	0	3.468753	2.415806	-0.001335
C(Fragment=2)	0	3.030604	-1.235842	-0.001703
O(Fragment=2)	0	1.095087	1.755868	-0.008563
O(Fragment=1)	0	-1.095023	-1.755769	-0.009309
C(Fragment=1)	0	-3.030662	1.235862	-0.002239
C(Fragment=1)	0	-1.906286	0.493145	-0.006407
C(Fragment=2)	0	1.906256	-0.493081	-0.005612
H(Fragment=2)	0	0.926319	-0.953015	-0.008676
H(Fragment=1)	0	-0.926371	0.95312	-0.009724
N(Fragment=2)	0	3.341533	1.412319	-0.001936
N(Fragment=1)	0	-4.301003	0.706771	0.00193
N(Fragment=1)	0	-3.341484	-1.412311	-0.002019
H(Fragment=1)	0	-2.993058	2.318185	-0.002149
H(Fragment=2)	0	2.992956	-2.318163	-0.001467
O(Fragment=2)	0	5.612885	1.184696	0.007723
O(Fragment=1)	0	-5.61284	-1.184779	0.008342

Table S24 Atomic coordinate information of U-motif II.

Atom	Atomic Type	Coordinates (Angstroms)		
		X	Y	Z
C(Fragment=1)	0	-4.13135	-0.869043	0.003785
C(Fragment=2)	0	4.502653	1.090475	-0.00432
C(Fragment=1)	0	-5.564383	1.110132	-0.026852
H(Fragment=1)	0	-5.547772	2.073391	0.481563
H(Fragment=1)	0	-5.896228	1.245711	-1.059351
H(Fragment=1)	0	-6.255056	0.437078	0.474613
C(Fragment=2)	0	5.52312	-1.16735	-0.008021
H(Fragment=2)	0	5.50674	-1.808014	0.87425
H(Fragment=2)	0	5.503241	-1.805912	-0.891763
H(Fragment=2)	0	6.429649	-0.564341	-0.009115
N(Fragment=2)	0	4.368289	-0.272261	-0.004581
C(Fragment=2)	0	2.098149	1.395073	0.001857
C(Fragment=1)	0	-1.641406	-0.599277	0.009204
H(Fragment=1)	0	-2.732408	-2.346481	0.007708
H(Fragment=2)	0	3.573321	3.00178	-0.001154
C(Fragment=2)	0	3.103684	-0.883065	-0.001655
O(Fragment=2)	0	1.079602	2.071986	0.004691
O(Fragment=1)	0	-0.566692	-1.186829	0.007851
C(Fragment=1)	0	-3.101647	1.31719	0.009156
C(Fragment=1)	0	-1.843373	0.833114	0.007042
H(Fragment=2)	0	1.107745	-0.435856	0.003581
H(Fragment=1)	0	-0.971042	1.473212	0.006901
N(Fragment=1)	0	-4.224932	0.52388	0.019077
N(Fragment=1)	0	-2.828664	-1.339181	0.013833
H(Fragment=1)	0	-3.299393	2.381639	0.008094
O(Fragment=1)	0	-5.099554	-1.598761	-0.014441
N(Fragment=2)	0	2.041413	-0.001574	0.00147
C(Fragment=2)	0	3.4479	1.930375	-0.001298
H(Fragment=2)	0	5.523208	1.452393	-0.006701
O(Fragment=2)	0	2.987289	-2.089696	-0.001928

Table S25 Atomic coordinate information of U-motif III.

Atom	Atomic Type	Coordinates (Angstroms) X	Y	Z
C(Fragment=2)	0	4.076133	1.382372	-0.002267
C(Fragment=1)	0	-4.076134	-1.382368	-0.003666
H(Fragment=2)	0	4.999531	1.947741	-0.003855
H(Fragment=1)	0	-4.999533	-1.947735	-0.005618
C(Fragment=2)	0	5.540902	-0.615668	0.000696
H(Fragment=2)	0	5.655421	-1.241747	0.886057
H(Fragment=2)	0	5.652945	-1.248351	-0.880236
H(Fragment=2)	0	6.303502	0.161254	-0.003263
C(Fragment=1)	0	-5.5409	0.615676	-0.001249
H(Fragment=1)	0	-5.655777	1.241709	0.884099
H(Fragment=1)	0	-5.652583	1.248405	-0.882193
H(Fragment=1)	0	-6.303501	-0.161244	-0.005559
N(Fragment=2)	0	4.225768	0.022141	-0.000026
N(Fragment=1)	0	-4.225768	-0.022137	-0.001476
C(Fragment=1)	0	-1.667271	-1.18026	-0.000811
C(Fragment=2)	0	1.667269	1.180259	-0.000351
C(Fragment=2)	0	3.114764	-0.837107	0.002406
C(Fragment=2)	0	2.869969	1.986904	-0.002548
H(Fragment=2)	0	2.768522	3.060659	-0.004374
H(Fragment=2)	0	1.057748	-0.799012	0.00298
C(Fragment=1)	0	-2.869971	-1.986903	-0.003478
H(Fragment=1)	0	-2.768525	-3.060658	-0.005269
H(Fragment=1)	0	-1.057747	0.79901	0.002784
C(Fragment=1)	0	-3.114763	0.837106	0.001406
N(Fragment=2)	0	1.893423	-0.19234	0.001906
N(Fragment=1)	0	-1.893422	0.19234	0.001371
O(Fragment=1)	0	-0.527309	-1.63784	-0.000423
O(Fragment=2)	0	0.527306	1.637839	-0.000412
O(Fragment=1)	0	-3.24761	2.041284	0.003737
O(Fragment=2)	0	3.247613	-2.041299	0.004747

Table S26 Atomic coordinate information of U-motif IV.

Atom	Atomic Type	Coordinates (Angstroms)		
		X	Y	Z
C(Fragment=2)	0	-0.38074	4.289982	-0.003579
C(Fragment=2)	0	-0.682685	1.901225	0.003828
C(Fragment=2)	0	1.602718	2.888135	-0.002779
C(Fragment=2)	0	0.96222	4.19564	-0.00554
C(Fragment=1)	0	0.682685	-1.901225	0.003828
C(Fragment=1)	0	-1.602718	-2.888135	-0.002779
C(Fragment=1)	0	-0.96222	-4.19564	-0.00554
C(Fragment=1)	0	0.38074	-4.289982	-0.003579
H(Fragment=2)	0	-0.891128	5.244505	-0.005477
H(Fragment=2)	0	1.59203	5.07172	-0.009137
H(Fragment=1)	0	-1.59203	-5.07172	-0.009137
H(Fragment=1)	0	0.891128	-5.244505	-0.005477
O(Fragment=2)	0	2.798254	2.680258	-0.00453
O(Fragment=2)	0	-1.429022	0.929088	0.007179
O(Fragment=1)	0	1.429022	-0.929088	0.007179
O(Fragment=1)	0	-2.798254	-2.680258	-0.00453
C(Fragment=1)	0	2.66434	-3.313633	0.001361
H(Fragment=1)	0	3.08426	-2.831965	-0.881934
H(Fragment=1)	0	3.083795	-2.831699	0.884674
H(Fragment=1)	0	2.920853	-4.37146	0.001569
C(Fragment=2)	0	-2.66434	3.313633	0.001361
H(Fragment=2)	0	-3.08426	2.831965	-0.881934
H(Fragment=2)	0	-3.083795	2.831699	0.884674
H(Fragment=2)	0	-2.920853	4.37146	0.001569
H(Fragment=2)	0	1.065082	0.865276	0.004249
H(Fragment=1)	0	-1.065082	-0.865276	0.004249
N(Fragment=2)	0	0.682685	1.819779	0.002364
N(Fragment=1)	0	-0.682685	-1.819779	0.002364
N(Fragment=1)	0	1.206683	-3.190692	0.001224
N(Fragment=2)	0	-1.206683	3.190692	0.001224

Table S27 Atomic coordinate information of U-motif V.

Atom	Atomic Type	Coordinates (Angstroms)		
		X	Y	Z
C(Fragment=2)	0	4.042828	-1.208513	0.000024
C(Fragment=2)	0	1.626023	-1.279841	-0.002849
C(Fragment=2)	0	2.839707	0.889044	0.001102
C(Fragment=1)	0	-1.956739	0.638094	-0.002136
C(Fragment=1)	0	-3.239454	-1.493087	0.002288
C(Fragment=1)	0	-4.449989	-0.682751	0.003879
C(Fragment=1)	0	-4.364402	0.660307	0.002491
H(Fragment=2)	0	5.023984	-1.666227	0.000636
H(Fragment=1)	0	-5.402136	-1.19035	0.006114
H(Fragment=1)	0	-5.241727	1.294288	0.003639
O(Fragment=2)	0	2.833799	2.101146	0.002312
O(Fragment=2)	0	0.544369	-1.859135	-0.004809
O(Fragment=1)	0	-0.893618	1.250529	-0.004962
O(Fragment=1)	0	-3.196706	-2.705201	0.003135
C(Fragment=1)	0	-3.090084	2.791609	-0.001977
H(Fragment=1)	0	-2.557306	3.144448	0.881391
H(Fragment=1)	0	-2.55583	3.142301	-0.885248
H(Fragment=1)	0	-4.104049	3.187542	-0.003269
H(Fragment=2)	0	0.803539	0.618806	-0.002035
H(Fragment=1)	0	-1.158652	-1.232137	-0.001877
N(Fragment=2)	0	1.69914	0.110861	-0.001042
N(Fragment=1)	0	-2.056355	-0.724902	-0.0004
N(Fragment=1)	0	-3.163602	1.331025	-0.000506
N(Fragment=2)	0	4.039197	0.160811	0.001746
C(Fragment=2)	0	2.912689	-1.945112	-0.002222
H(Fragment=2)	0	2.933247	-3.023471	-0.003478
C(Fragment=2)	0	5.274933	0.941563	0.003875
H(Fragment=2)	0	5.319607	1.578784	-0.879822
H(Fragment=2)	0	5.315367	1.58019	0.886707
H(Fragment=2)	0	6.11947	0.254671	0.006403

Table S28 Atomic coordinate information of U-motif in $[Co(dUMP)(azpy)(H_2O)_3]\cdot[Co(azpy)_2(H_2O)_4]_2\cdot(dUMP)\cdot 7H_2O$.

Part 1

Atom	Atomic Type	Coordinates (Angstroms) X	Y	Z
O	-1	2.800854	13.084898	3.572261
O	-1	0.234765	13.5585	-0.086775
N	-1	0.678871	11.420592	0.589547
N	-1	1.521277	13.273926	1.70792
H	0	1.599145	14.278887	1.786408
C	-1	1.262072	10.617721	1.523209
H	0	1.111128	9.55437	1.387126
C	-1	2.001146	11.122379	2.507703
H	0	2.477261	10.484113	3.236586
C	-1	2.143163	12.513894	2.672562
C	-1	0.777495	12.810084	0.679141
C	-1	-0.164443	10.832005	-0.460868
H	0	-1.077711	10.415879	-0.029655
H	0	-0.425359	11.623997	-1.157238
H	0	0.390265	10.049646	-0.980364

Part 2

Atom	Atomic Type	Coordinates (Angstroms) X	Y	Z
O	-1	4.248	15.7198	5.831
O	-1	1.7113	16.0218	2.0603
N	-1	3.7281	17.8362	5.0753
N	-1	2.9859	15.9244	3.9267
H	0	2.944397	14.916293	3.86962
C	-1	2.3227	16.6494	2.9662
C	-1	2.4193	18.0603	3.0821
H	0	1.926569	18.677892	2.348639
C	-1	3.0743	18.5768	4.1266
H	0	3.151046	19.64854	4.268915
C	-1	3.6699	16.4506	5.0133
C	-1	4.383	18.4943	6.215
H	0	3.638425	18.958139	6.865198
H	0	4.921225	17.728296	6.766247
H	0	5.080219	19.24849	5.848657

Table S29 Atomic coordinate information of U-motif in $\{[Co(H_2O)_6]\cdot[Co(dUMP)_2(bpda)(H_2O)_2]\cdot 7H_2O\cdot DMF\}_n$.

Part 1

Atom	Atomic Type	Coordinates (Angstroms) X	Y	Z
O	-1	2.081	9.3529	11.7092
O	-1	2.4463	12.364	8.3471
N	-1	2.2181	8.5608	9.5752
N	-1	2.2394	10.8277	9.9849
H	0	2.23051	11.5806	10.659551
C	-1	2.276	8.83	8.2355
H	0	2.281365	7.954392	7.597837
C	-1	2.3189	10.0709	7.7339
H	0	2.364041	10.268386	6.674949
C	-1	2.3431	11.1796	8.647
C	-1	2.1889	9.5712	10.4891
C	-1	2.2709	7.1612	10.0514
H	0	3.278478	6.759936	9.925914
H	0	2.00774	7.167039	11.104549
H	0	1.556932	6.561761	9.48656

Part 2

Atom	Atomic Type	Coordinates (Angstroms) X	Y	Z
O	-1	2.0367	12.7754	12.0207
N	-1	2.143	13.6092	14.1423
N	-1	2.0781	11.3064	13.7558
H	0	2.048427	10.552851	13.082331
C	-1	2.0825	12.586	13.2194
C	-1	2.1915	13.3401	15.5047
C	-1	2.1403	10.9626	15.0924
C	-1	2.1733	12.1033	15.989
H	0	2.236249	14.21822	16.136087
O	-1	2.1715	9.7914	15.4249
H	0	2.204698	11.904775	17.049327
C	-1	2.2466	14.97	13.6536
H	0	3.285736	15.31123	13.656633
H	0	1.874212	14.995083	12.633203
H	0	1.646613	15.63145	14.279731

Table S30 Atomic coordinate information of U-motif in $\{[Co(H_2O)_6]\cdot[Co(UMP)_2(bpda)(H_2O)_2]\cdot H_2O\}_n$.

Part 1

Atom	Atomic Type	Coordinates (Angstroms)		
		X	Y	Z
O	-1	-0.9627	6.7488	2.2761
N	-1	-0.8365	7.8157	0.2256
C	-1	-0.8871	6.6545	0.9883
C	-1	-0.8079	7.7358	-1.1614
N	-1	-0.909	5.4135	0.364
C	-1	-0.8301	6.4957	-1.7873
H	0	-0.765296	8.675916	-1.693837
H	0	-0.951144	4.579635	0.929995
C	-1	-0.8806	5.3345	-1.0246
H	0	-0.807406	6.402006	-2.86033
O	-1	-0.8749	4.2012	-1.54
C	-1	-0.79	9.1034	1.0205
H	0	-0.735488	9.92347	0.306804
H	0	-1.68648	9.173188	1.631614
H	0	0.08517	9.087299	1.665694

Part 2

Atom	Atomic Type	Coordinates (Angstroms)		
		X	Y	Z
O	-1	-1.0267	6.092	5.77
N	-1	-1.0551	4.7071	4.0209
H	0	-0.95119	5.499413	3.406125
C	-1	-1.1233	4.8807	5.3977
H	0	-1.326248	3.942349	7.295584
C	-1	-1.1407	3.4319	3.4761
C	-1	-1.2769	3.7783	6.2314
O	-1	-1.1038	3.3168	2.2118
N	-1	-1.2945	2.3298	4.3073
C	-1	-1.3628	2.5018	5.6858
H	0	-1.482479	1.603349	6.274253
C	-1	-1.3841	0.9976	3.759
H	0	-0.56398	0.378235	4.128826
H	0	-2.339789	0.540798	4.025289
H	0	-1.314529	1.079915	2.676991

Table S31 Atomic coordinate information of U-motif in $\{[Cd_2(UMP)_2(bpda)_3(H_2O)_4]\cdot 2H_2O\}_n$.

Part 1

Atom	Atomic Type	Coordinates (Angstroms) X	Y	Z
O	-1	-5.4752	5.3976	-6.1723
O	-1	-8.7962	4.2705	-8.9939
C	-1	-6.7017	5.2123	-6.3654
N	-1	-7.1673	4.9165	-7.6401
H	0	-6.51915	4.913181	-8.412257
C	-1	-8.4937	4.546	-7.8274
C	-1	-9.3545	4.4713	-6.7381
H	0	-10.373876	4.166945	-6.912197
C	-1	-8.8889	4.7671	-5.4635
H	0	-9.502908	4.721459	-4.574938
N	-1	-7.5625	5.1376	-5.2761
C	-1	-7.1228	5.5408	-3.9748
H	0	-6.037827	5.603319	-3.988127
H	0	-7.533137	6.518452	-3.70589
H	0	-7.430676	4.802767	-3.231941

Part 2

Atom	Atomic Type	Coordinates (Angstroms) X	Y	Z
O	-1	-5.299	5.3976	-9.6487
O	-1	-1.978	4.2705	-6.827
C	-1	-4.0725	5.2123	-9.4555
N	-1	-3.6069	4.9165	-8.1809
H	0	-4.255044	4.913184	-7.408745
C	-1	-2.2805	4.546	-7.9935
C	-1	-1.4197	4.4713	-9.0828
H	0	-0.400318	4.166972	-8.908704
C	-1	-1.8853	4.7671	-10.3575
H	0	-1.27126	4.721436	-11.246046
N	-1	-3.2117	5.1376	-10.5448
C	-1	-3.6519	5.5408	-11.8469
H	0	-3.344984	4.801936	-12.589285
H	0	-4.736784	5.604341	-11.832911
H	0	-3.240457	6.517813	-12.116185

Part 3

Atom	Atomic Type	Coordinates (Angstroms) X	Y	Z
O	-1	5.2992	5.3976	-6.1723
O	-1	1.9782	4.2705	-8.9939
C	-1	4.0727	5.2123	-6.3654
N	-1	3.6071	4.9165	-7.6401
H	0	4.25525	4.913181	-8.412257
C	-1	2.2807	4.546	-7.8274
C	-1	1.4199	4.4713	-6.7381
H	0	0.400524	4.166945	-6.912197
C	-1	1.8855	4.7671	-5.4635
H	0	1.271492	4.721459	-4.574938
N	-1	3.2119	5.1376	-5.2761
C	-1	3.6516	5.5408	-3.9748
H	0	4.736573	5.603319	-3.988127
H	0	3.241263	6.518452	-3.70589

H	0	3.343724	4.802767	-3.231941

Part 4

Atom	Atomic Type	Coordinates (Angstroms) X	Y	Z
O	-1	5.4754	5.3976	-9.6487
O	-1	8.7964	4.2705	-6.827
C	-1	6.7019	5.2123	-9.4555
N	-1	7.1675	4.9165	-8.1809
H	0	6.519356	4.913184	-7.408745
C	-1	8.4939	4.546	-7.9935
C	-1	9.3547	4.4713	-9.0828
H	0	10.374082	4.166972	-8.908704
C	-1	8.8891	4.7671	-10.3575
H	0	9.50314	4.721436	-11.246046
N	-1	7.5627	5.1376	-10.5448
C	-1	7.1225	5.5408	-11.8469
H	0	7.429416	4.801936	-12.589285
H	0	6.037616	5.604341	-11.832911
H	0	7.533943	6.517813	-12.116185

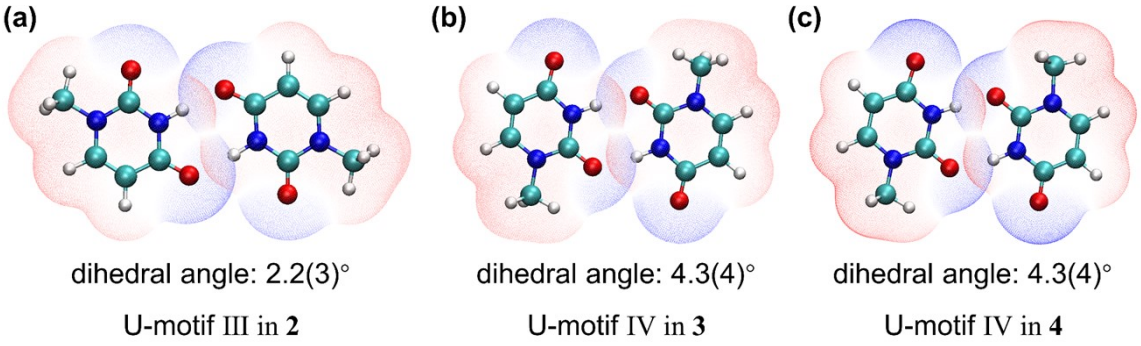

Figure S23 (a) surface electrostatic potential distribution and dihedral angle of U-motif III in **2**; (b) surface electrostatic potential distribution and dihedral angle of U-motif IV in **3**; (c) surface electrostatic potential distribution and dihedral angle of U-motif IV in **4** (red color : positive and blue color : negative).

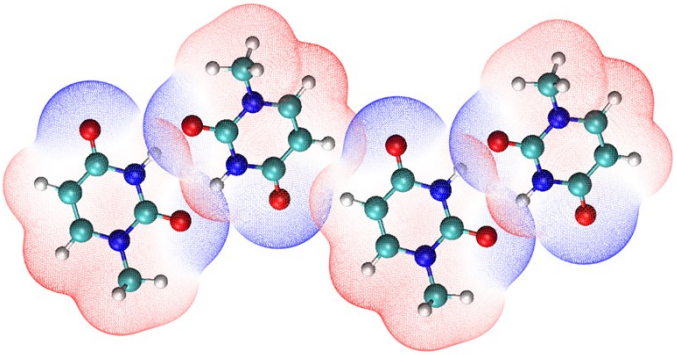

Figure S24 calculated surface electrostatic potential penetration diagram of multiple uracil-uracil full uracil-uracil base pair structure.

9. The UV/vis Absorption Spectrums of Complexes 1-5

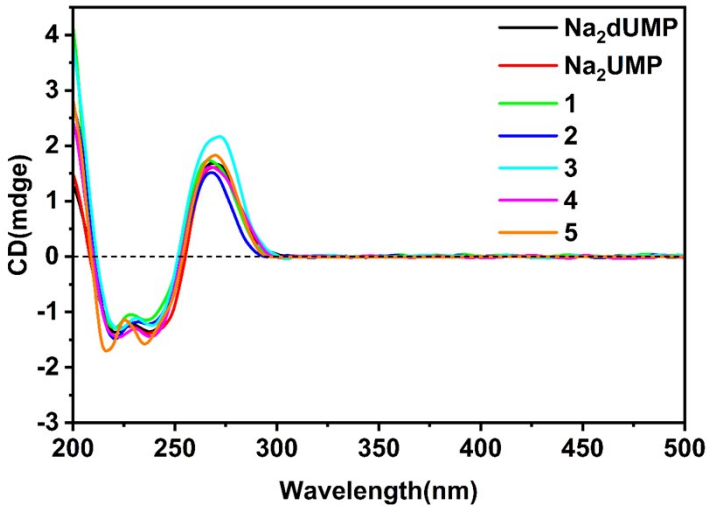

Figure S25 the CD spectra of Na_2dUMP, Na_2UMP, and **1** - **5** in solution, and the concentration of nucleotide was 2.5×10^{-5} mol/L.

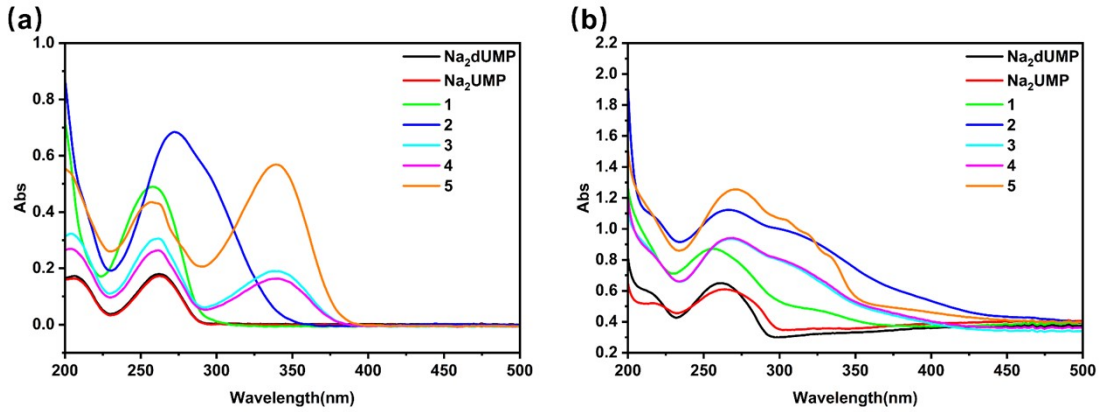

Figure S26 (a) The UV-vis spectra of Na_2dUMP, Na_2UMP, and complexes **1**-**5** in aqueous solution at room temperature, and the concentration of nucleotide was 2.5×10^{-5} mol/L; (b) the UV-vis spectra of Na_2dUMP, Na_2UMP, and complexes **1**-**5** in solid state at room temperature (Sample : KBr = 1 : 200).

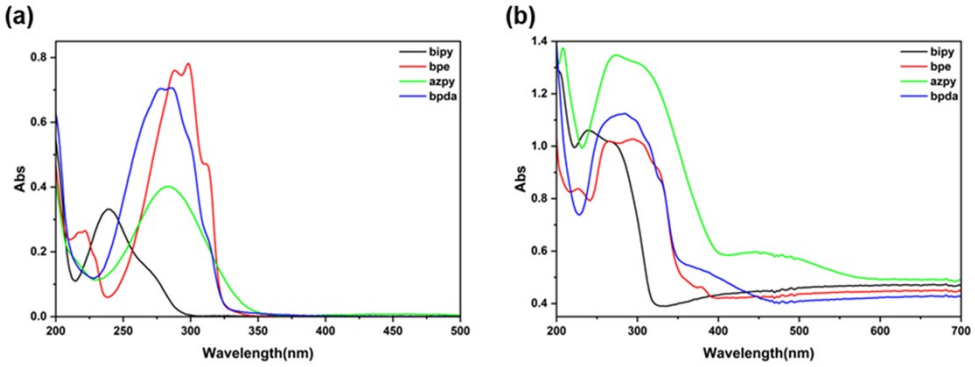

Figure S27 (a) UV-Vis absorption spectra of auxiliary ligands (bipy, bpe, azpy and bpda) in solution. The solvent of the solution was water-ethanol mixed solvent with volume ratio of 7:3, and the concentration of auxiliary ligand was 2.5×10^{-5} mol/L. (b) UV-Vis absorption spectra of auxiliary ligands (bipy, bpe, azpy and bpda) in solid state, which is performed by KBr tablet method (Sample: KBr = 1:200).

References

1. M. K. Cabaj and P. M. Dominiak, *Nucleic Acids Res.*, 2020, **48**, 8302-8319.