Supporting Information for:

Coordination-Induced Conformation Diversity for Pharmaceutical Polymorph Control

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 Table S1. Summary of the existing methods preparing the five polymorphs of sulfathiazole

Polymorph	Mode of	Solvent	Purity	
	Crystallization	1		
Form I	cooling	n-propanol	V, II, III, VI,I	
	cooling	amylalcohol.	III, I	
	cooling	isobutanol	pure I	
	cooling	n-butanol	pure I	
	cooling	sec-butanol	pure I	
	cooling	n-propanol	III, II	
	cooling	water	III, VI, II	
	cooling	acetone	III, II	
Form II	cooling	acetone and chloroform	III, VI, II	
	cooling	ethanol	pure II	
	cooling	nitromethane	pure II	
	cooling	methanol	pure II	
	cooling	acetonitrile	pure II	
	cooling	methanol-acetonitrile	pure II	
	evaporation	dilute ammonium	pure III	
		hydroxide		
	cooling	dilute ammonium	pure III	
		hydroxide solution		
	cooling	ethanol	II, III	
	evaporation	methanol	II, III	
Form III	cooling	water	VI, III	
	cooling	acetone-chloroform	II, VI, III	
	cooling	benzene-ethanol	never be repeated	
	cooling	isopropanol	pure III	
	cooling	aqueous ethanol	II, VI, III	
	evaporation	ethanol-water-ammonia	pure III	
	cooling	water	pure VI	
Form VI	cooling	ethanol	pure VI	
	evaporation	water	pure V	
Form V	cooling	n-propanol	I, V	

H₂N

Figure S1. The torsion angles in sulfathiazole.

	τ1	τ2		τ1	τ2
FIA	149.19	-163.63	C1B	136.51	179.95
FIB	130.19	-163.73	C1C	143.68	-172.90
FII	120.09	-167.42	C1D	97.05	178.28
FIIIA	119.74	-168.19	C2A	97.65	-169.46
FIIIB	120.89	-165.59	C2B	140.69	-169.50
FIV	120.63	-166.77	C3A	-59.84	174.75
FVA	-109.28	145.46	C3B	-119.15	174.65
FVB	111.83	-164.47	C4A	139.87	-174.00
C1A	130.19	179.57	C4B	125.49	-174.42

Table S2. The torsion angles (in degrees) of ST ligands in complexes and fivepolymorphs of ST



Figure S2. Unit cells packing of the complexes and hydrogen bonds. (a) Cu-Complex, (b) Co-Complex-I, (c) Co-Complex-II and (d) Ni-Complex.



Figure S3. Microphotographs of ST five polymorphs prepared in this work.



Figure S4. Overlay of the ligand (C2A) in Co-Complex-I (dirty violet) and four

polymorphs of ST, including FIA (blue), FIB (light blue), FII (purple), FIV (red), FVA (yellow) and FVB (light yellow)



Figure S5. Overlay of the ligand (C2B) in Co-Complex-I (dirty violet) and four polymorphs of ST, including FIA (blue), FIB (light blue), FII (purple), FIV (red), FVA (yellow) and FVB (light yellow)

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	C2A	Δ	C2B			
	N…H4A	N…H ₃ A	N•••H ₃ B	N····H₅B		
FIA	5.7Å	4.8 Å	3.0 Å	3.3 Å		
FIB	4.9 Å	5.1 Å	2.2 Å	2.7 Å		
FII	3.9 Å	3.9 Å	2.3 Å	1.7 Å		
FIV	3.9 Å	4.0 Å	2.4 Å	2.7 Å		
FVA	4.7 Å	3.8 Å	3.9 Å	4.3 Å		
FVB	3.8 Å	3.6 Å	1.8Å	1.7 Å		

Table S3. The lengths of hydrogen bonds between the water molecules of Co-Complex-I and the pyridine nitrogen of ST polymorphs in the overlay of two ligands in Co-Complex-I molecule and four polymorphs of ST



Figure S6. Overlay of the ligand (C4A) in Ni-Complex (salmon) and four polymorphs of ST, including FIA (blue), FIB (light blue), FII (purple), FIV (red), FVA (yellow) and FVB (light yellow)



Figure S7. Overlay of the ligand (C4B) in Ni-Complex (salmon) and four polymorphs of ST, including FIA (blue), FIB (light blue), FII (purple), FIV (red), FVA (yellow) and FVB (light yellow)

Table S4. The lengths of hydrogen bonds between the water molecules of Ni-Complex and the pyridine nitrogen of ST polymorphs in the overlay of two ligands in Ni-Complex molecule and four polymorphs of ST

	C4A	A	C4B		
	N····H ₅ A	N…H₂B	N…H₅B	N····H ₆ B	
FIA	3.8 Å	4.4 Å	3.4 Å	3.7 Å	
FIB	3.1 Å	3.6 Å	2.6 Å	3.4 Å	
FII	2.7 Å	3.4 Å	3.0 Å	4.1 Å	
FIV	2.6 Å	3.3 Å	2.9 Å	4.1 Å	
FVA	4.8 Å	5.5 Å	4.7 Å	4.3 Å	
FVB	2.2 Å	2.7 Å	2.4 Å	3.7Å	



Figure S8. Four bonded methanol molecules were circled in Cu-Complex



Figure S9. Overlay of the ligand (C1A) in Cu-Complex (wheat) and four polymorphs of ST, including FIA (blue), FIB (light blue), FII (purple), FIV (red), FVA (yellow) and FVB (light yellow)



Figure S10. Overlay of the ligand (C1B) in Cu-Complex (wheat) and four polymorphs of ST, including FIA (blue), FIB (light blue), FII (purple), FIV (red), FVA (yellow) and FVB (light yellow).



Figure S11. Overlay of the ligand (C1C) in Cu-Complex (wheat) and four polymorphs of ST, including FIA (blue), FIB (light blue), FII (purple), FIV (red), FVA (yellow) and FVB (light yellow).



Figure S12. Overlay of the ligand (C1D) in Cu-Complex (wheat) and four polymorphs of ST, including FIA (blue), FIB (light blue), FII (purple), FIV (red), FVA (yellow) and FVB (light yellow)

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	C1A		C1B		C1C		C1D	
	NH _{38B} -C ₃₈	NH _{37B} -C ₃₇	NH _{41A} -C ₄₁	NH _{42B} -C ₄₂	NH _{38c} -C ₃₈	NH _{37A} -C ₃₇	NH _{41C} -C ₄₁	NH _{42C} -C ₄₂
FIA	2.6 Å	2.1Å	2.0 Å	2.8 Å	2.3 Å	2.7 Å	2.9 Å	3.8 Å
FIB	2.7 Å	1.8 Å	2.0 Å	2.8 Å	2.5 Å	2.8 Å	2.5 Å	2.8 Å
FII	3.6 Å	2.8 Å	3.0 Å	3.6 Å	3.6 Å	3.8 Å	3.2 Å	2.9 Å
FIV	3.6 Å	2.7 Å	3.0 Å	3.7 Å	3.6 Å	3.8 Å	3.2 Å	2.9 Å
FVA	2.8 Å	3.1 Å	2.8 Å	3.0 Å	2.8 Å	3.0 Å	3.5 Å	5.0 Å
FVB	3.4 Å	2.7 Å	2.9 Å	3.4 Å	3.6 Å	3.5 Å	2.8 Å	2.4 Å

Table S5. The lengths of hydrogen bonds between the bonded methanol molecules of Cu-Complex and the pyridine nitrogen of ST polymorphs in the overlay of four ligands in Cu-Complex molecule and four polymorphs of ST