Supporting Information

Multistimuli-responsive Materials Based on Zinc(II) Complex with High-contrast and Multicolor Switching

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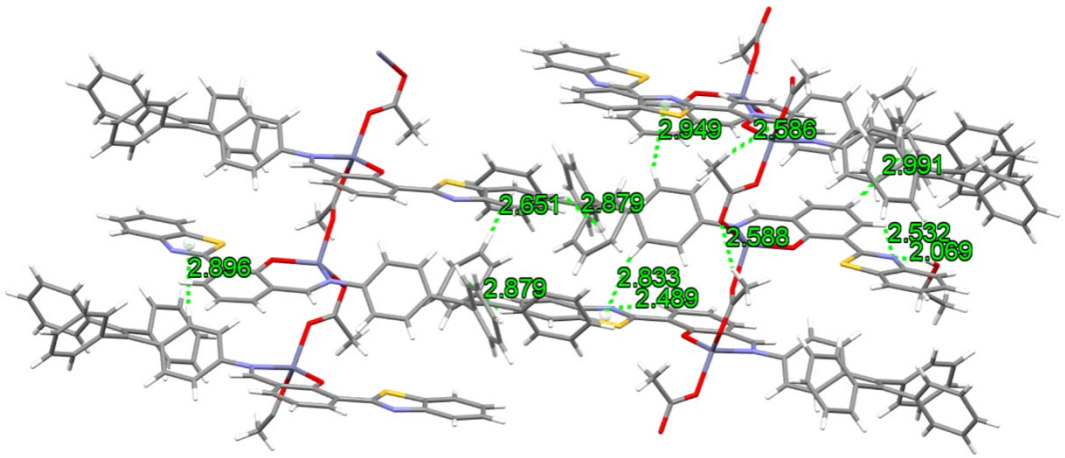

Fig. S1 Multiple intramolecular and intermolecular interactions in complex **1**.

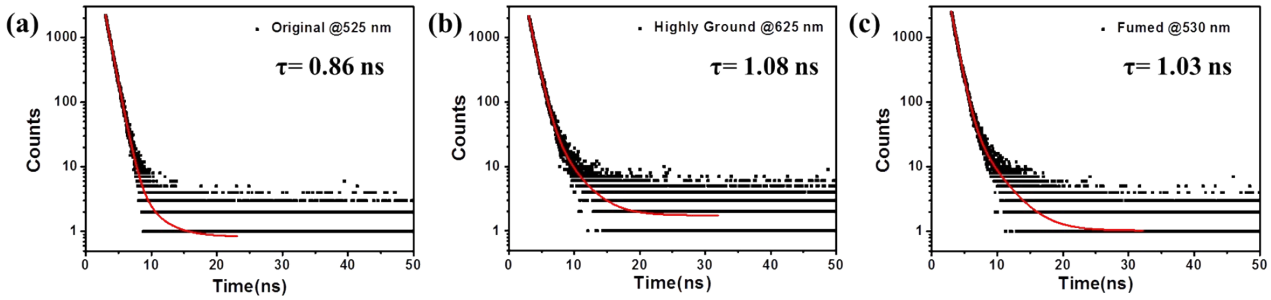

Fig. S2 Fluorescence decay curves and fit results of complex **1** in different states: (a) Original sample monitored at 525 nm. (b) Highly ground sample monitored at 625 nm. (c) Fumed sample monitored at 530 nm.

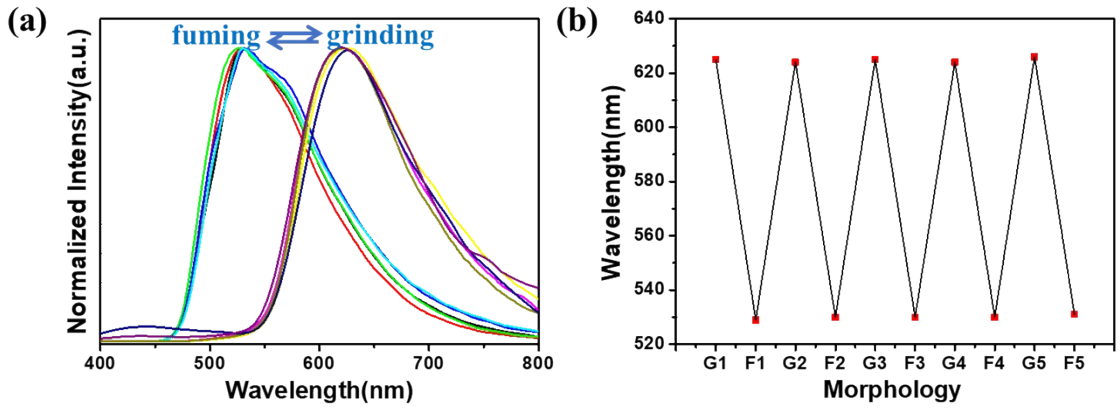

Fig. S3 (a) Emission spectra and (b) emission switching characteristics of complex **1** upon repeating the grinding and fuming processes.

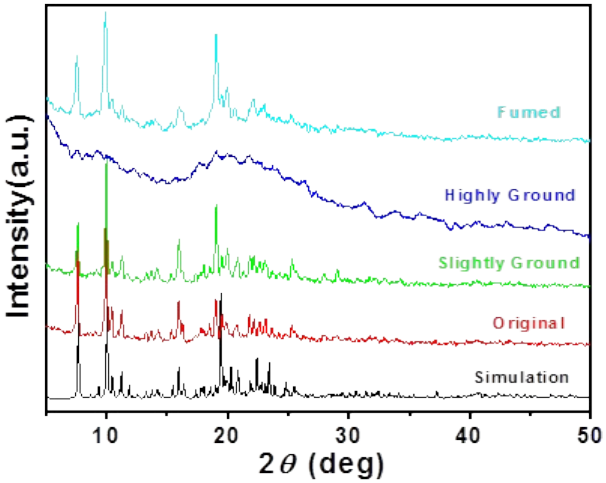

Fig. S4 PXRD patterns of the simulation of complex **1** and the samples before and after grinding, fuming under ethanol vapor.

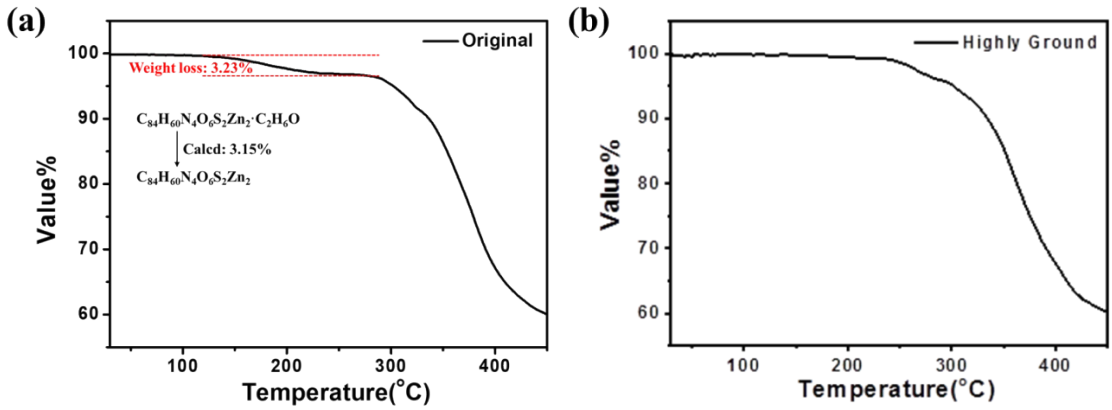

Fig. S5 TG curve of (a) Original and (b) Highly ground samples of complex **1**.

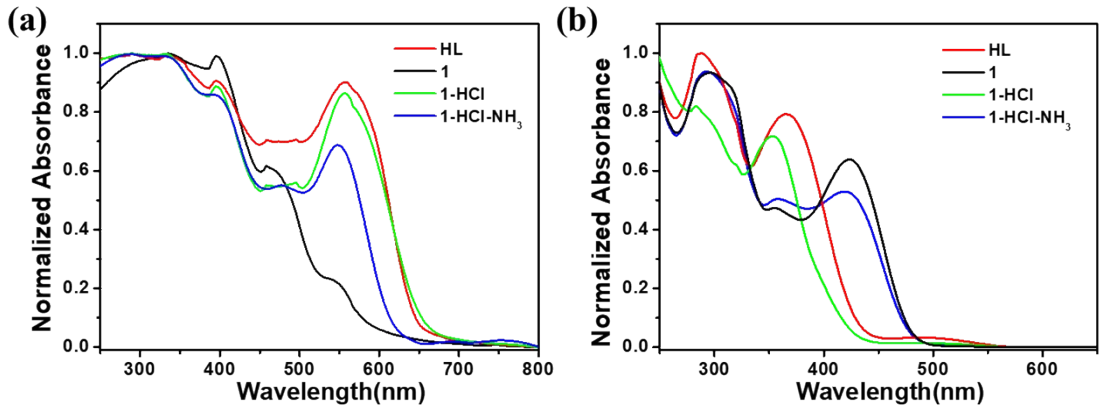

Fig. S6 UV–Vis absorption spectra of the original crystals of ligand HL, **1** before and after exposing to HCl/NH_3 vapor, (a) in solid state, (b) in THF solution.

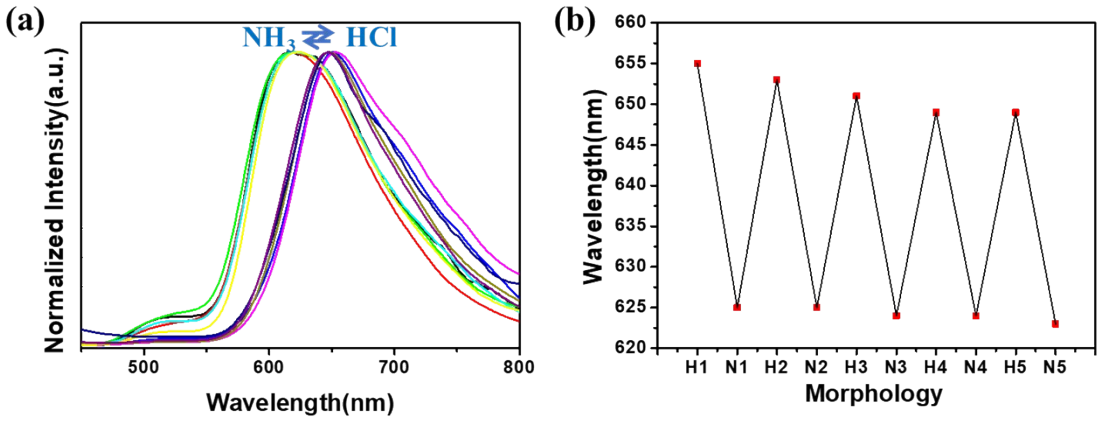

Fig. S7 (a) Emission spectra and (b) emission switching characteristics of complex **1** upon repeating the HCl–NH_3 fumigation processes.

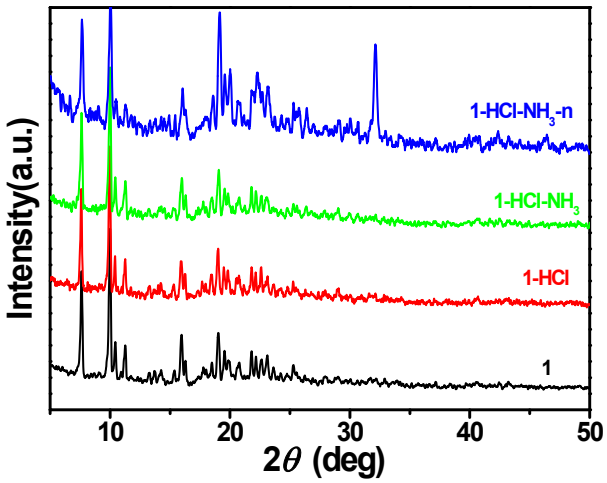

Fig. S8 PXRD patterns of complex **1** upon HCl / NH_3 fumigation processes.

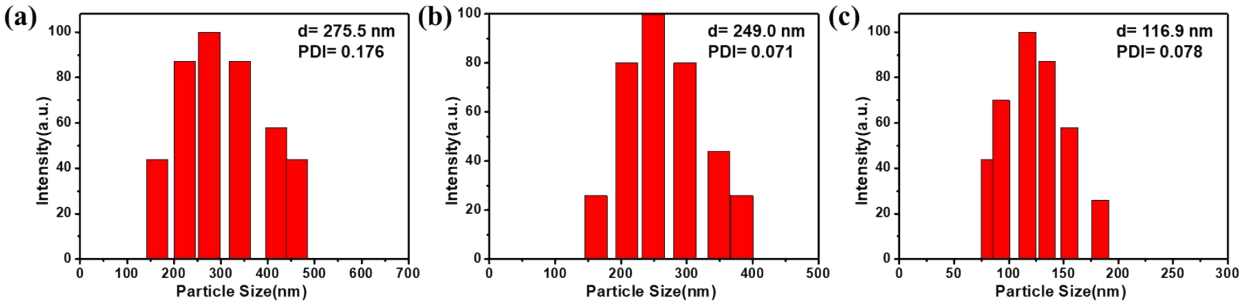

Fig. S9 DLS data of complex **1** (10 μM) in THF/H_2O: (a) 70% H_2O, (b) 80% H_2O and (c) 90% H_2O.

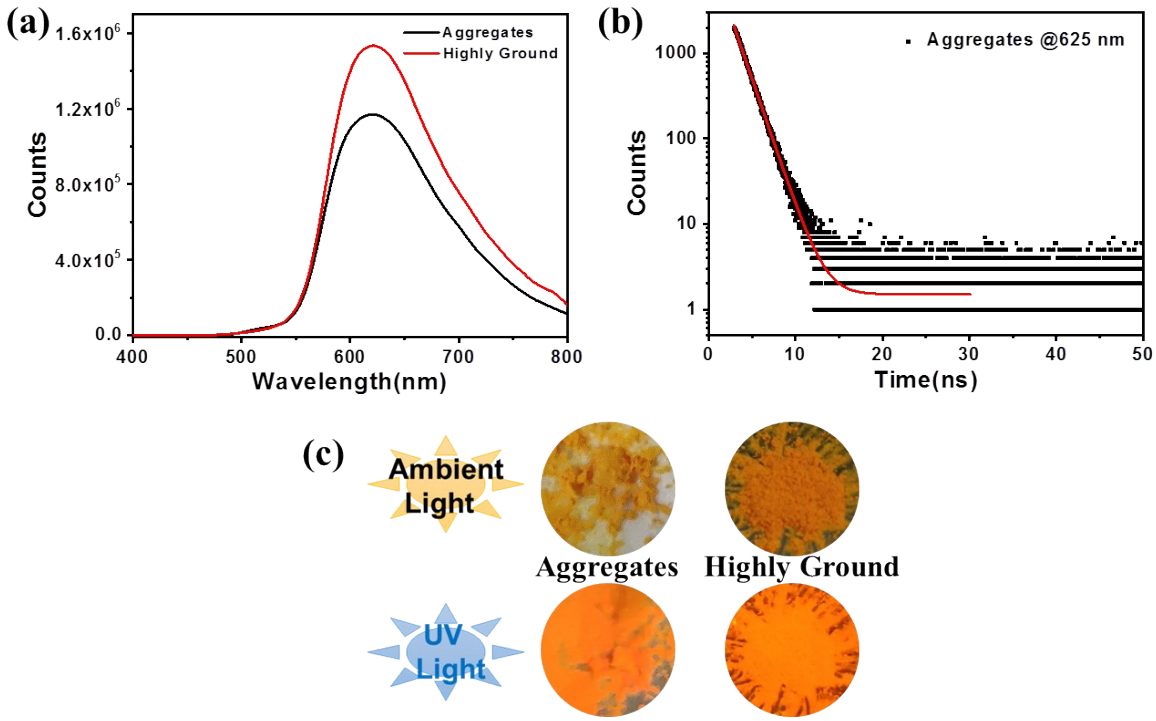

Fig. S10 (a) Emission spectra (excited at 365 nm). (b) Fluorescence decay curves and fit results. (c) Photographs under ambient light and UV (365 nm) light of the aggregates and highly ground sample of complex **1**.

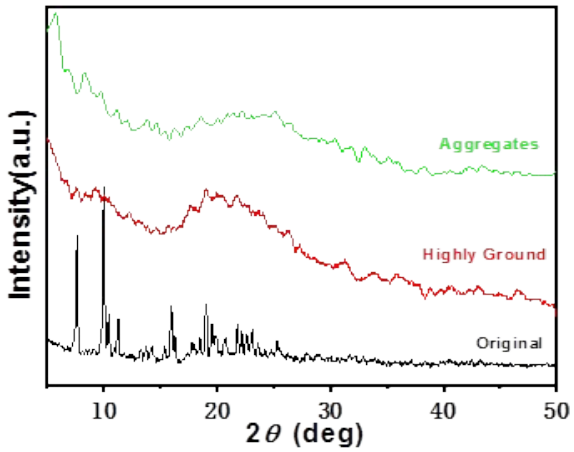

Fig. S11 PXRD patterns of original crystals, highly ground and aggregates samples of complex **1**.

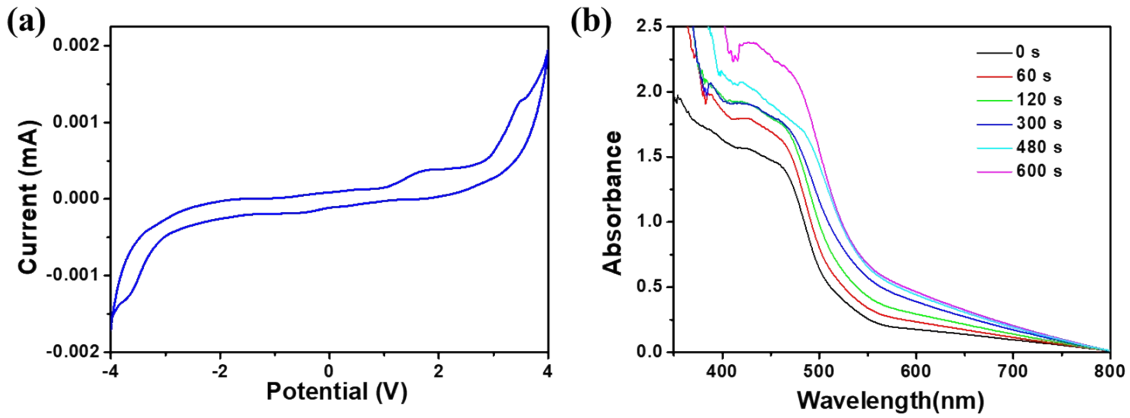

Fig. S12 (a) Cyclic voltammogram and (b) UV-Vis absorption spectra of electrochemical devices (ECD) assembled by complex **1**.

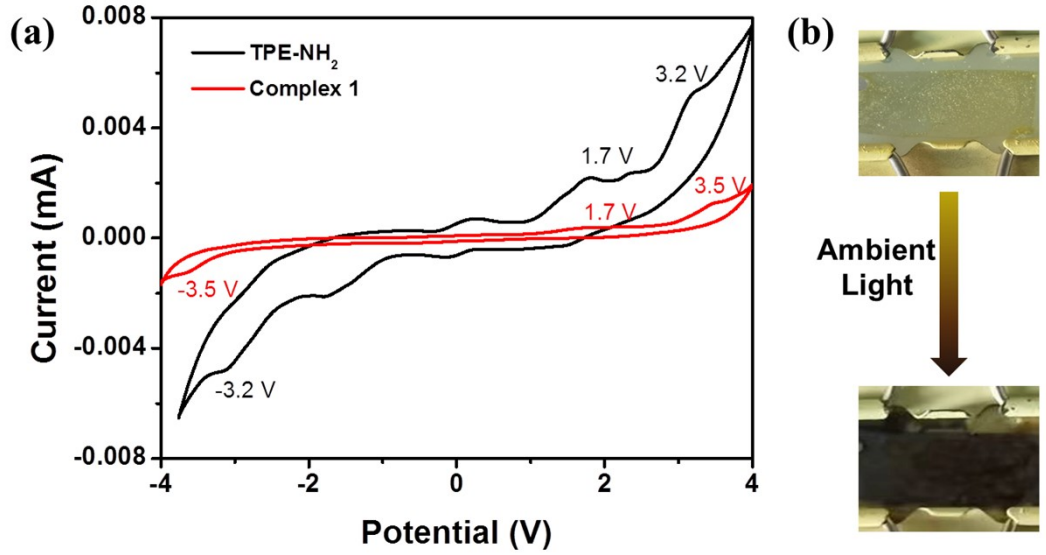

Fig. S13 (a) Cyclic voltammogram of electrochemical devices (ECD) assembled by TPE-NH_2 and complex **1**. (b) Photographs of the color changes of ECD assembled by TPE-NH_2.

Fig. S14 Photographs of complex **1**film taken under ambient light before and after fuming with HCl/NH_3 vapor.

Table S1 Crystal data and structure refinement parameters of complex **1**.

Compound	**1**
Empirical formula	$C_{86}H_{66}N_4O_7S_2Zn_2$
Formula weight	1462.28
Temperature/K	100.00(10)
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	8.9256 (3)
b/Å	19.1901 (4)
c/Å	22.0658 (7)
α/°	108.594 (2)
β/°	93.475 (3)
γ/°	94.909 (2)
Volume/Å^3	3553.58 (19)
Z	2
ρ_{calc}g/cm^3	1.367
μ/mm^{-1}	1.864
F(000)	1516.0
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	7.448 to 144.26
Index ranges	$-10 \le h \le 11$, $-16 \le k \le 23$, $-26 \le l \le 23$
Reflections collected	24940
Independent reflections	13577 [R_{int} = 0.0664, R_{sigma} = 0.0738]
Data/restraints/parameters	13557/7/914
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0583, wR_2 = 0.1518
R indices (all data)	R_1 = 0.0734, wR_2 = 0.1604
Largest diff. peak/hole (e Å^{-3})	1.13/-0.89
CCDC number	2191342

Table S2 Selected Bond Lengths (Å) and Angles (deg) of complex **1**.

Zn1—O1	1.912 (2)	Zn2—O3	1.923 (2)
Zn1—O2	1.962 (2)	Zn2—O4	1.964 (2)
Zn1—O5	1.963 (2)	Zn2—O6^{i}	1.994 (2)
O6—Zn2^{ii}	1.994 (2)	Zn2—N3	2.005 (3)
Zn1—N1	1.993 (2)		
O1—Zn1—O2	130.09 (10)	O3—Zn2—O4	104.80 (9)
O1—Zn1—O5	103.58 (9)	O3—Zn2—O6^{i}	132.15 (9)

O1—Zn1—N1	97.95 (9)	O3—Zn2—N3	96.76 (10)
O2—Zn1—O5	102.15 (9)	O4—Zn2—O6^{i}	97.42 (9)
O2—Zn1—N1	110.56 (10)	O4—Zn2—N3	116.49 (9)
O5—Zn1—N1	112.33 (10)	O6^{i}—Zn2—N3	110.38 (10)
C1—O1—Zn1	124.48 (19)	C83—O6—Zn2^{ii}	106.89 (18)
C81—O2—Zn1	109.57 (19)	C14—N1—Zn1	120.4 (2)
C41—O3—Zn2	125.3 (2)	C15—N1—Zn1	120.36 (18)
C81—O4—Zn2	128.6 (2)	C54—N3—Zn2	119.7 (2)
C83—O5—Zn1	128.9 (2)	C55—N3—Zn2	120.89 (18)

Symmetry codes: (i) x-1, y, z; (ii) x+1, y, z.

Table S3 Types of intramolecular and intermolecular interactions and corresponding distances and angles in complex **1**.

Interactions	Distances (Å)	Angles (°)
O_7-H_7···N_4	2.069	167.50
C_5-H_5···N_2	2.489	101.08
C_{45}-H_{45}···N_4	2.532	100.59
C_{82}-H_{82C}···O_6	2.588	120.87
C_{84}-H_{84A}···O_2	2.586	135.36
C_{11}-H_{11}···π(C_{69}-C_{74})	2.879	142.94
C_{17}-H_{17}···π(S_2,C_{47},N_4,C_{48},C_{53})	2.896	115.65
C_{44}-H_{44}···π(C_{62}-C_{67})	2.991	141.51
C_{57}-H_{57}···π(S_1,C_7,N_2,C_8,C_{13})	2.949	118.26
C_{59}-H_{59}···π(S_1,C_7,N_2,C_8,C_{13})	2.833	139.15
C_{73}-H_{73}···π(C_{75}-C_{80})	2.651	158.84

Table S4 The dihedral angles between different planes in complex **1**.

A/B	2.44 °
B/C	44.24 °
A/C	42.91 °
A'/B'	11.52 °
B'/C'	34.93 °
A'/C'	46.42 °