

## Supporting Information

### A novel 2,2':6',2''-terpyridine-based ligand and its complexes: Structures, Photophysical properties and DFT calculations to evaluate the halogen effect on the TPA

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#### 10 Structure of complexes 2, 4, 5 and 8.

**Structure of [CdLBr<sub>2</sub>]<sub>2</sub>·CHCl<sub>3</sub> (Complex 2):** Complex 2 crystallizes in the monoclinic form with space group *P2(1)/c*. As shown in **Fig. S1a**, complex 2 exhibits quite distorted trigonal bipyramidal geometry. The Cd(II) atom locates in a five coordination environment chelating with two bromine atoms and three N atoms from one ligand. Also the unit consists of two CdLBr<sub>2</sub> and one 15 chloroform. Selected bond lengths and angles are listed in **Table S1**.

From **Fig. S1a**, the weak force of C-H···Br and C-H··· $\pi$  staking interactions are widely spread in the complex to construct this super molecular structure ( $d(\text{C90-H90}\cdots\text{Br7}) = 2.811 \text{ \AA}$  and angle to be  $141.91^\circ$ ,  $d(\text{C34-H34}\cdots\pi) = 3.218 \text{ \AA}$ ).

**Fig. S2a** shows that the chloroform molecules play a significant role in forming hydrogen bonds 20 and other molecular interactions, such as: (1) C-H···Cl bonds ( $d(\text{C15-H15}\cdots\text{Cl2}) = 2.949 \text{ \AA}$  and angle to be  $134.73^\circ$ ,  $d(\text{C33-H33}\cdots\text{Cl3}) = 2.817 \text{ \AA}$  and angle to be  $177.29^\circ$ ). (2) Br···Cl bond ( $d(\text{Br8}\cdots\text{Cl3}) = 3.559 \text{ \AA}$ ).<sup>1</sup> (4) C-H···Br bond ( $d(\text{C125-H125}\cdots\text{Br2}) = 2.949 \text{ \AA}$  and angle to be  $163.40^\circ$ ). Besides the weak force of C-H···Br interactions is widely spread in the complex to construct this super molecular structure ( $d(\text{C32-H32}\cdots\text{Br8}) = 2.973 \text{ \AA}$  and angle to be  $138.57^\circ$ ).

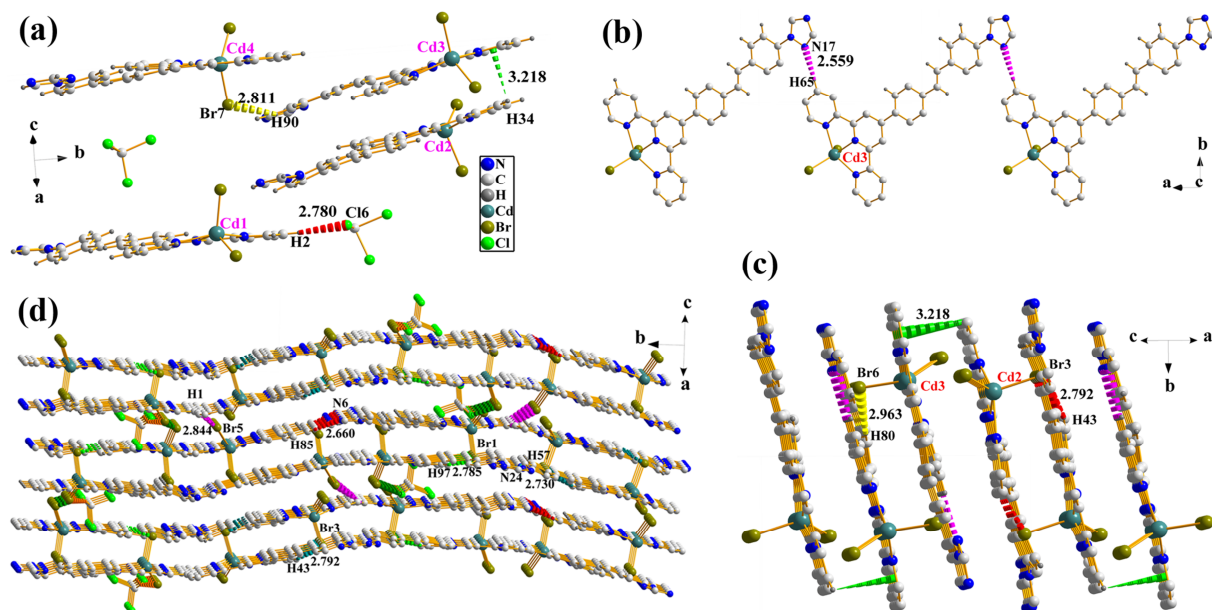
25 Also as shown in **Fig. S2b**, it is the chloroform molecules that bridged the surrounding moieties together to construct the whole supermolecular structure by forming hydrogen bonds and the other molecular interactions such as: (1) C-H···Cl bond ( $d(\text{C2-H2}\cdots\text{Cl6}) = 2.780 \text{ \AA}$  and angle to be  $173.68^\circ$ ). (2) Br···Cl bond ( $d(\text{Br5}\cdots\text{Cl6}) = 3.564 \text{ \AA}$ ).<sup>1</sup> (3) C126-Cl4··· $\pi$  staking interactions ( $d = 3.356 \text{ \AA}$ ).<sup>1</sup> (4) C-H···Br bond ( $d(\text{C126-H126}\cdots\text{Br4}) = 2.666 \text{ \AA}$  and angle to be  $150.62^\circ$ ). The 30 weak force of C-H···Br interactions is the dominant effect on the formation of the supramolecule ( $d(\text{C1-H1}\cdots\text{Br5}) = 2.844 \text{ \AA}$ , angle to be  $136.80^\circ$ ,  $d(\text{C66-H66}\cdots\text{Br6}) = 2.941 \text{ \AA}$ , angle to be  $158.04$

$^{\circ}$ ,  $d(\text{C80-H80}\cdots\text{Br6}) = 2.963 \text{ \AA}$  and angle to be  $161.52^{\circ}$ ).

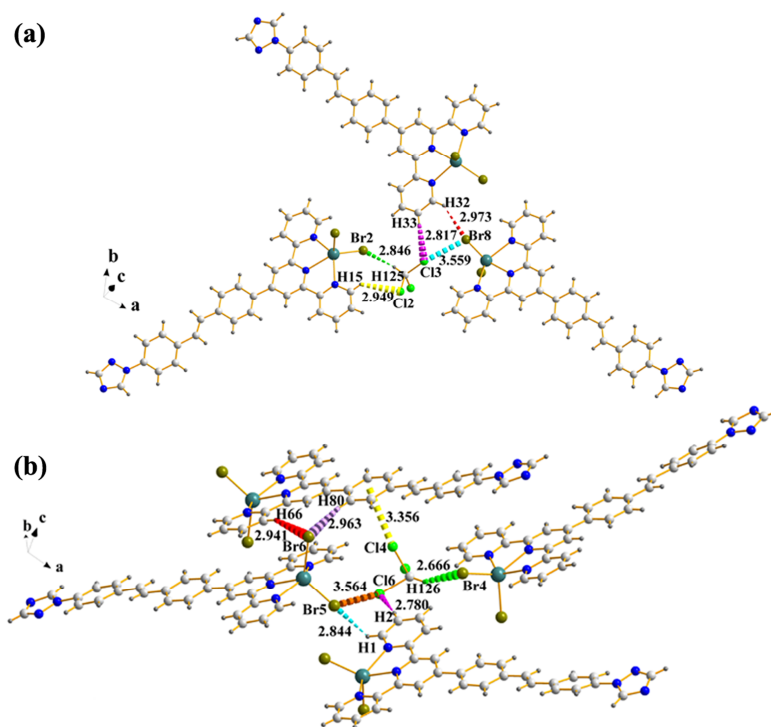
Seen along  $a$ -axis in **Fig. S1b**, the triazole ring is not directly involved in coordination, but the lone pair electrons from the N atom still have a strong Pro-e-competence, which generates a 1-D 'w' chain through C-H $\cdots$ N hydrogen bonds ( $d(\text{C65-H65}\cdots\text{N17}) = 2.559 \text{ \AA}$  and angle to be  $176.085^{\circ}$ ).

Complex **2** forms a 2-D structure through classical C-H $\cdots$ Br hydrogen bond interactions ( $d(\text{C80-H80}\cdots\text{Br6}) = 2.963 \text{ \AA}$ , angle to be  $161.52^{\circ}$ ,  $d(\text{C43-H43}\cdots\text{Br3}) = 2.792 \text{ \AA}$  and angle to be  $154.97^{\circ}$ ), and C-H $\cdots$  $\pi$  interactions ( $d(\text{C34-H34}\cdots\pi) = 3.218 \text{ \AA}$ ) between the neighboring dimers along  $c$ -axis (**Fig. S1c**).

10 Finally, the extended 3-D supermolecular structures are formed along the  $b$ -axis *via* C-H $\cdots$ N hydrogen bond interactions ( $d(\text{C85-H85}\cdots\text{N6}) = 2.660 \text{ \AA}$ , angle to be  $149.85^{\circ}$ ,  $d(\text{C57-H57}\cdots\text{N24}) = 2.730 \text{ \AA}$  and angle to be  $150.21^{\circ}$ ) and C-H $\cdots$ Br hydrogen bond interactions ( $d(\text{C1-H1}\cdots\text{Br5}) = 2.844 \text{ \AA}$  and angle to be  $136.80^{\circ}$ ). (**Fig. S1d**).



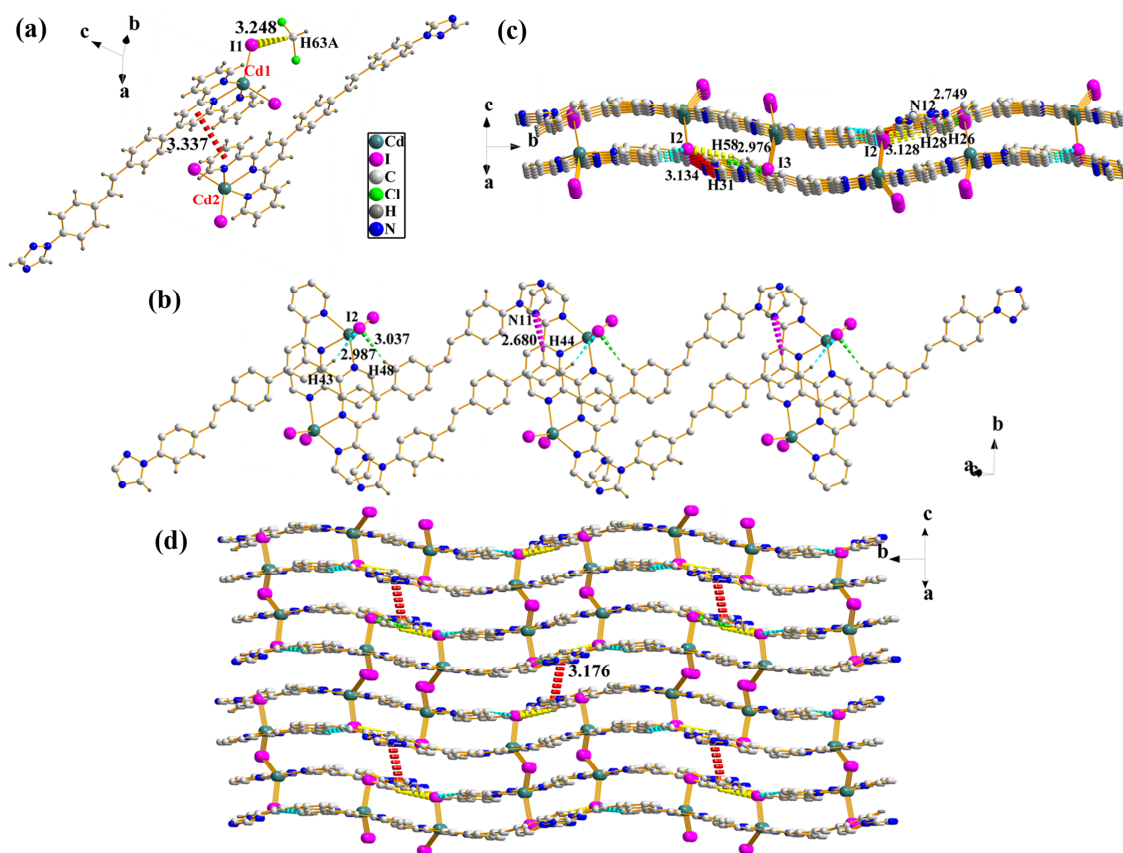
15 **Fig. S1** (a) Coordination environments of Cd with the atom numbering scheme; (b) The 1-D chain structure of complex **2** showing the C-H $\cdots$ N interactions along the  $a$ -axis; (c) The 2-D structure of complex **2** showing C-H $\cdots$ Br and C-H $\cdots$  $\pi$  interactions along the  $c$ -axis; (d) The 3-D supermolecular structure of complex **2** showing the C-H $\cdots$ N and C-H $\cdots$ Br interactions along the  $b$ -axis.



**Fig. S2** Weak interactions form solvent in complex **2**.

**Structure of  $[\text{CdLI}_2]_2 \cdot \text{CH}_2\text{Cl}_2$  (Complex 4):** Complex **4** is in distorted trigonal bipyramidal geometry as well as complex **2** (**Fig. S3**). The packing of the molecules is also very similar, except that complex **4** used  $\text{CdI}_2$  instead of  $\text{CdBr}_2$ . However, different from complex **2**, there has one dichloromethane in the unit. **Fig. S3a**, shows that the weak force of  $\text{C-H} \cdots \text{I}$  hydrogen bonds (H from free dichloromethane molecule and I from coordination compound,  $d(\text{C63-H63A} \cdots \text{I1}) = 3.248 \text{ \AA}$  and angle to be  $164.597(883)^\circ$ ) and  $\pi \cdots \pi$  staking interactions ( $d = 3.337 \text{ \AA}$ ) are widely spread in the unit.

10 Seen along the *c*-axis in **Fig. S3b**, complex **4** generates a 1-D staircase through  $\text{C-H} \cdots \text{Cl}$  hydrogen bonds ( $d(\text{C44-H44} \cdots \text{N11}) = 2.680 \text{ \AA}$ , angle to be  $172.25^\circ$ ,  $d(\text{C48-H48} \cdots \text{I2}) = 3.037 \text{ \AA}$ , angle to be  $155.77^\circ$ ,  $d(\text{C43-H43} \cdots \text{I2}) = 2.987 \text{ \AA}$  and angle to be  $160.13^\circ$ ). Contributed by another  $\text{C-H} \cdots \text{I}$  hydrogen bonds ( $d(\text{C28-H28} \cdots \text{I2}) = 3.128 \text{ \AA}$ , angle to be  $159.00^\circ$ ,  $d(\text{C31-H31} \cdots \text{I2}) = 3.134 \text{ \AA}$ , angle to be  $158.17^\circ$ ,  $d(\text{C58-H58} \cdots \text{I3}) = 2.976 \text{ \AA}$  and angle to be  $163.49^\circ$ ), a 2-D wave type structure is produced along *b*-axis (**Fig. S3c**). Finally, the extended 3-D supermolecular structures are formed along the *a*-axis via  $\pi \cdots \pi$  staking interactions with the shortest distance of  $3.176 \text{ \AA}$  (red dashed line) (**Fig. S3d**).



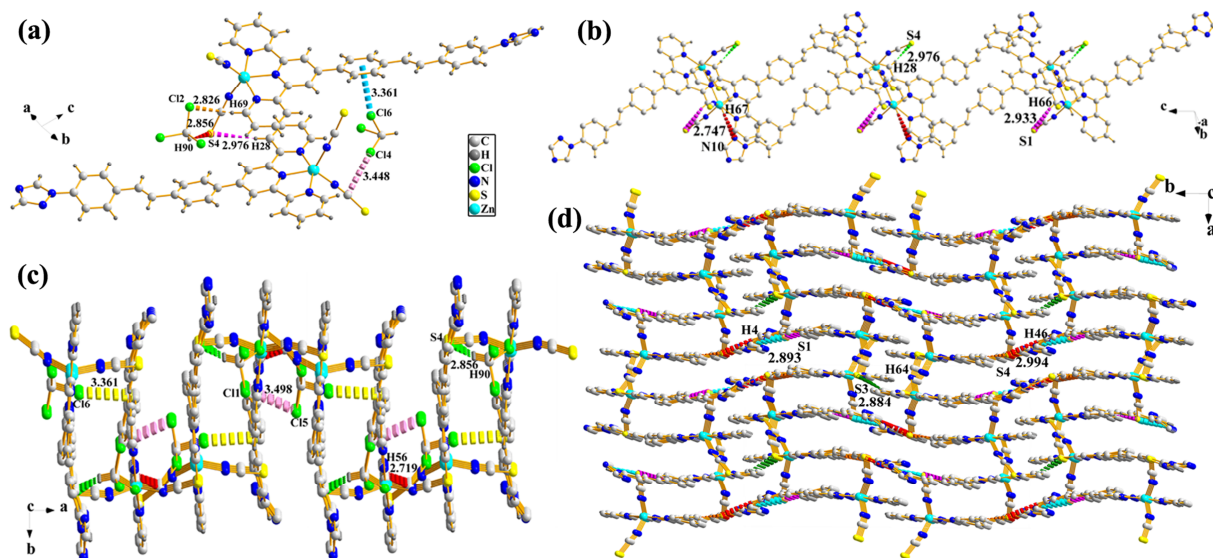
**Fig. S3** (a) Coordination environments of Cd with the atom numbering scheme; (b) The 1-D staircase structure of complex **4** showing the C–H···Cl interactions along the *c*-axis; (c) The 2-D structure of complex **4** showing the C–H···I interactions along the *b*-axis; (d) The 3-D supermolecular structure of complex **4** showing  $\pi \cdots \pi$  interactions along the *a*-axis.

**Structure of  $\text{ZnL}(\text{NCS})_2 \cdot \text{CHCl}_3$  (Complex **5**):** Complex **5** adopts the same coordination mode as complexes **2**, **3** and **4**. It crystallizes in the monoclinic form with space group  $P2(1)/n$  as shown in **Table 1**. However, different from **2**, **3** and **4**, **5** contains two  $\text{ZnL}(\text{NCS})_2$  and two chloroform molecules. From **Table S1**, it can be seen that the S–C–N bond angles are  $176.6(15)$  and  $10178.6(12)^\circ$ , i.e., the  $\text{SCN}^-$  group is almost perfectly linear. The S–C and C–N distances of 1.578 (1.611) and 1.094 (1.147) Å in  $\text{SCN}^-$  indicate a  $\pi$ -delocalization along the metal–thiocyanate chains.<sup>2</sup> This observation is consistent with the fact that the  $\text{SCN}^-$  ligand is easily polarizable ( $^-\text{S}=\text{C}\equiv\text{N}\leftrightarrow\text{S}=\text{C}=\text{N}^-$ ). Besides, with IR characterization, the absorption peak at lower wave numbers ( $2080\text{ cm}^{-1}$ ) was assigned to  $\nu(\text{N}=\text{C}=\text{S})$  of the thiocyanate in complex **5**, suggesting a 15 different binding mode in accordance with the results of X-ray analysis. **Fig. S4a** presents the functions of chloroform molecules in generating the final complex through the following interactions: (1) C–H···Cl bond ( $d(\text{C}69\text{--H}69\cdots\text{Cl}2) = 2.976\text{ \AA}$  and angle to be  $171.10^\circ$ ). (2) C–H···S bond with the distance of  $\text{C}90\text{--H}90\cdots\text{S}4$  is  $2.856\text{ \AA}$  and angle to be  $143.81^\circ$ . (3) C–Cl··· $\pi$



staging interactions ( $d(\text{C104}-\text{Cl6}\cdots\pi) = 3.361 \text{ \AA}$  and  $d(\text{C104}-\text{Cl4}\cdots\pi) = 3.448 \text{ \AA}$ ).<sup>1</sup> The weak force of  $\text{C}-\text{H}\cdots\text{S}$  within the complex constructs the supramolecule ( $d(\text{C28}-\text{H28}\cdots\text{S4}) = 2.976 \text{ \AA}$  and angle to be  $172.68^\circ$ ).

Herein, we used  $\text{Zn}(\text{SCN})_2$  instead of  $\text{CdI}_2$ , there are not only the anions, but also the metal cations are different, however, the packing of the molecules is very similar. Through  $\text{C}-\text{H}\cdots\text{N}$  ( $d(\text{C67}-\text{H67}\cdots\text{N10}) = 2.747 \text{ \AA}$  and angle to be  $173.69^\circ$ ) and  $\text{C}-\text{H}\cdots\text{S}$  hydrogen bonds ( $d(\text{C66}-\text{H66}\cdots\text{S1}) = 2.933 \text{ \AA}$  and angle to be  $168.00^\circ$ ), **5** forms into a 1-D chain along *c*-axis as seen from **Fig. S4b**. Due to an additional further  $\text{C}-\text{H}\cdots\pi$  interactions ( $d = 2.719 \text{ \AA}$ ) and  $\text{Cl}\cdots\text{Cl}$  bond interactions<sup>1</sup> ( $d(\text{Cl1}\cdots\text{Cl5}) = 3.498 \text{ \AA}$ ), a 2-D structure is produced along *a*-axis. Finally (**Fig. S4c**), 10 complex **5** forms a stable 3-D supermolecular structure through  $\text{C}-\text{H}\cdots\text{S}$  hydrogen bonds ( $d(\text{C4}-\text{H4}\cdots\text{S1}) = 2.893 \text{ \AA}$ , angle to be  $171.75^\circ$ ,  $d(\text{C64}-\text{H64}\cdots\text{S3}) = 2.884 \text{ \AA}$ , angle to be  $136.56^\circ$ ,  $d(\text{C46}-\text{H46}\cdots\text{S4}) = 2.994 \text{ \AA}$  and angle to be  $163.31^\circ$ ) along *b*-axis (**Fig. S4d**).

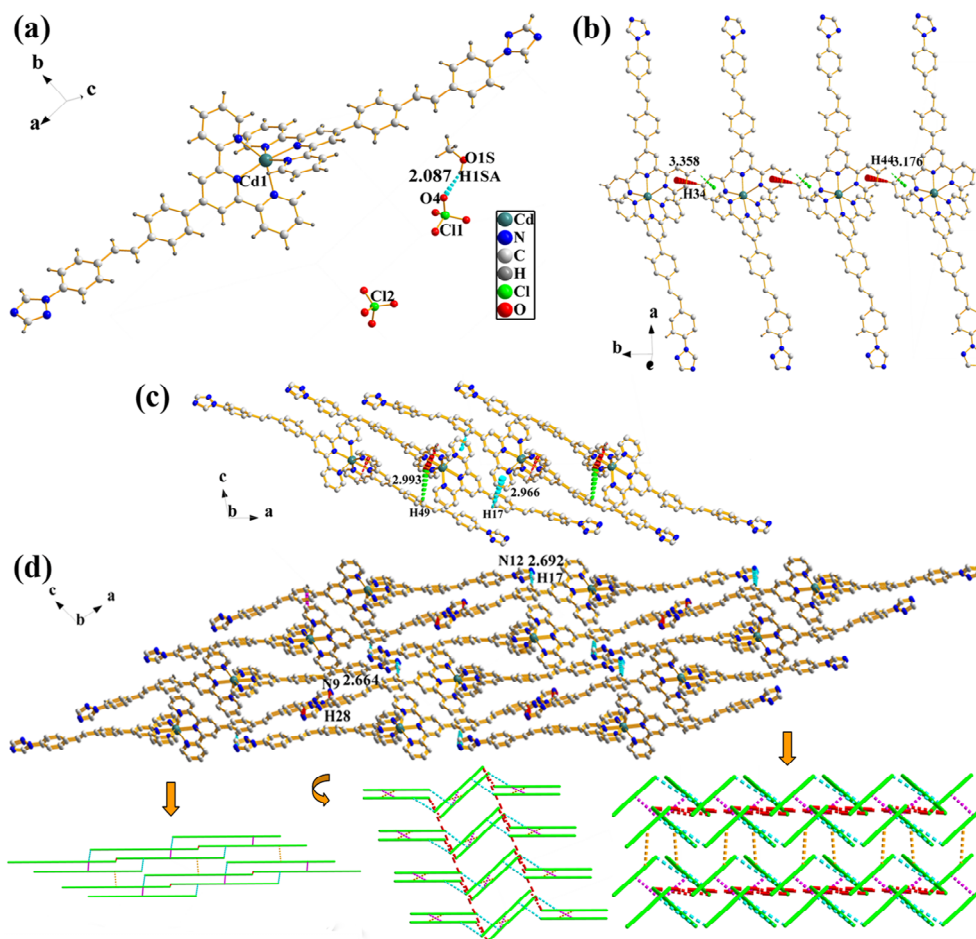


**Fig. S4** (a) Coordination environments of Zn with the atom numbering scheme and weak interactions form solvent in complex **5**; (b) The 1-D chain structure of complex **5** showing the  $\text{C}-\text{H}\cdots\text{N}$  and  $\text{C}-\text{H}\cdots\text{S}$  interactions along the *c*-axis; (c) The 2-D structure of complex **5** showing the  $\text{C}-\text{H}\cdots\pi$  and  $\text{Cl}\cdots\text{Cl}$  interactions along the *a*-axis; (d) The 3-D supermolecular structure of complex **5** showing the  $\text{C}-\text{H}\cdots\text{S}$  interactions along the *b*-axis.

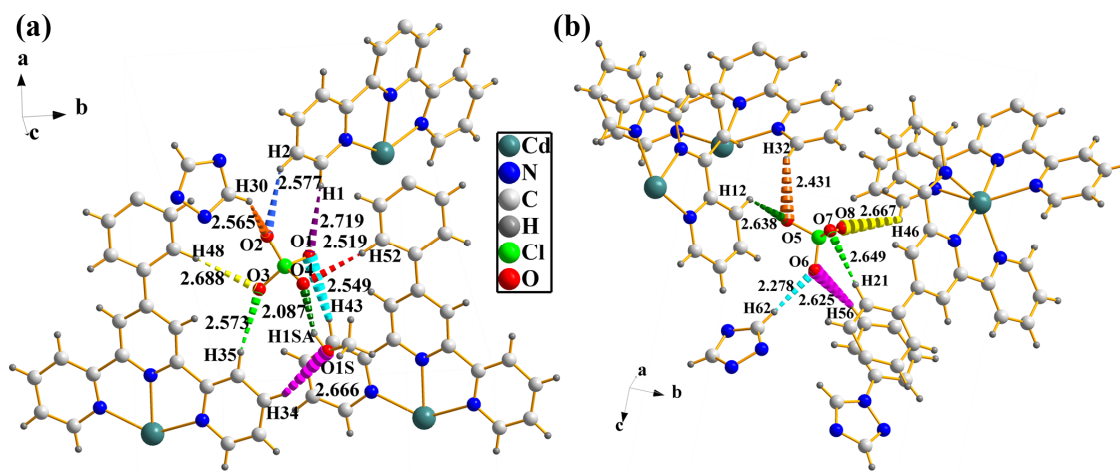
**Structure of  $[\text{CdL}_2](\text{ClO}_4)_2\cdot\text{CH}_3\text{OH}$  (Complex **8**):** Complex **8** adopts the same coordination mode as complex **7**. The  $\text{Cd}(\text{II})$  coordinates with two ligands and two perchlorate ions are free. As shown in **Fig. S5a**, the weak force of  $\text{O}-\text{H}\cdots\text{O}$  (O from free perchlorate ions and H from methanol) is widely spread in the complex to construct this super molecular structure ( $d(\text{O1S}-\text{H1SA}\cdots\text{O4}) = 2.087 \text{ \AA}$  and angle to be  $153.71^\circ$ ).

Similar to **complex 7**, the free perchlorate ions has a dominant effect indicating by the following interactions: (1)  $d(\text{C1-H1}\cdots\text{O1}) = 2.719 \text{ \AA}$  and angle to be  $161.17^\circ$ . (2)  $d(\text{C43-H43}\cdots\text{O1}) = 2.549 \text{ \AA}$  and angle to be  $171.80^\circ$ . (3)  $d(\text{C2-H2}\cdots\text{O2}) = 2.577 \text{ \AA}$  and angle to be  $137.46^\circ$ . (4)  $d(\text{C30-H30}\cdots\text{O2}) = 2.565 \text{ \AA}$  and angle to be  $138.58^\circ$ . (5)  $d(\text{C35-H35}\cdots\text{O3}) = 2.573 \text{ \AA}$  and angle to be  $147.72^\circ$ . (6)  $d(\text{C48-H48}\cdots\text{O3}) = 2.688 \text{ \AA}$  and angle to be  $175.95^\circ$ . (7)  $d(\text{C52-H52}\cdots\text{O4}) = 2.519 \text{ \AA}$  and angle to be  $173.11^\circ$ . (8)  $d(\text{O1S-H1SA}\cdots\text{O4}) = 2.087 \text{ \AA}$  and angle to be  $153.71^\circ$ . (9)  $d(\text{C12-H12}\cdots\text{O5}) = 2.638 \text{ \AA}$  and angle to be  $\text{C12-H12-O5}$  is  $127.28^\circ$ . (10)  $d(\text{C32-H32}\cdots\text{O5}) = 2.431 \text{ \AA}$  and angle to be  $141.24^\circ$ . (11)  $d(\text{C56-H56}\cdots\text{O6}) = 2.625 \text{ \AA}$  and angle to be  $126.86^\circ$ . (12)  $d(\text{C62-H62}\cdots\text{O6}) = 2.278 \text{ \AA}$  and angle to be  $172.04^\circ$ . (13)  $d(\text{C46-H46}\cdots\text{O7}) = 2.667 \text{ \AA}$  and angle to be  $123.96^\circ$ . (14)  $d(\text{C21-H21}\cdots\text{O8}) = 2.649 \text{ \AA}$  and angle to be  $168.01^\circ$ . The supramolecule was formed by the weak force of C-H $\cdots$ O hydrogen bonds (O from methanol,  $d(\text{C34-H34}\cdots\text{O1S}) = 2.666 \text{ \AA}$  and angle to be  $155.94^\circ$ ). (**Fig. S6**)

Seen along the *b*-axis in **Fig. S5b**, complex **8** generates a 1-D chain through C-H $\cdots$  $\pi$  staking interactions ( $d(\text{C34-H34}\cdots\pi) = 3.358 \text{ \AA}$  and  $d(\text{C44-H44}\cdots\pi) = 3.176 \text{ \AA}$ ). Due to an additional further C-H $\cdots$  $\pi$  staking interactions ( $d(\text{C17-H17}\cdots\pi) = 2.966 \text{ \AA}$  and  $d(\text{C49-H49}\cdots\pi) = 2.993 \text{ \AA}$ ) along *a*-axis, a 2-D structure is produced (**Fig. S5c**). Finally, complex **8** forms a stable 3-D supermolecular structure through C-H $\cdots$ N interactions ( $d(\text{C28-H28}\cdots\text{N9}) = 2.664 \text{ \AA}$  and angle to be  $132.50^\circ$ ,  $d(\text{C12-H12}\cdots\text{N17}) = 2.692 \text{ \AA}$  and angle to be  $162.63^\circ$ ) along *c*-axis (**Fig. S5d**).



**Fig. S5** (a-c) Coordination environments of Cd with the atom numbering scheme; (d) The 1-D framework of complex **8** showing C-H... $\pi$  interactions along the *b*-axis; (e) The 2-D structure of complex **8** showing C-H... $\pi$  interactions bonds along the *a*-axis; (f) The 3-D supermolecular structure of complex **8** showing the C-H...N hydrogen bond along the *c*-axis.



**Fig. S6** Weak interactions form free perchlorate ions and methanol in complex **8**.

**Table S1.** Selected Bond Lengths (Å) and Angles (°) for **2-5** and **7, 8**.

<b>[CdLBr<sub>2</sub>]<sub>2</sub>·CHCl<sub>3</sub> (2)</b>							
Cd1-N1	2.381(9)	Cd1-N2	2.394(8)	Cd1-N3	2.363(8)	Cd1-Br1	2.6640(22)
Cd1-Br2	2.4317(19)	Cd2-N7	2.408(10)	Cd2-N8	2.366(8)	Cd2-N9	2.382(9)
Cd2-Br3	2.6391(21)	Cd2-Br4	2.4173(22)	Cd3-N13	2.341(9)	Cd3-N14	2.374(8)
Cd3-N15	2.309(10)	Cd3-Br5	2.3966(24)	Cd3-Br6	2.6984(24)	Cd4-N19	2.365(9)
Cd4-N20	2.332(8)	Cd4-N21	2.376(9)	Cd4-Br7	2.6835(25)	Cd4-Br8	2.3933(24)
N1-Cd1-N2	68.3(3)	N1-Cd1-N3	135.0(3)	N2-Cd1-N3	67.9(3)	Br1-Cd1-Br2	105.26(7)
N7-Cd2-N8	68.0(3)	N7-Cd2-N9	135.7(3)	N8-Cd2-N9	69.1(3)	Br3-Cd2-Br4	104.25(8)
N13-Cd3-N14	67.3(3)	N13-Cd3-N15	135.9(3)	N14-Cd3-N15	69.2(3)	Br5-Cd3-Br6	119.95(8)
N19-Cd4-N20	68.9(3)	N19-Cd4-N21	137.8(3)	N20-Cd4-N21	69.3(3)	Br7-Cd4-Br8	123.26(8)
<b>ZnLI<sub>2</sub> (3)</b>							
Zn1-N1	2.1542(84)	Zn1-N2	2.0894(74)	Zn1-N3	2.2103(80)	Zn1-I1	2.5889(21)
Zn1-I2	2.6155(19)	N1-Zn1-N2	75.0(3)	N2-Zn1-N3	73.6(3)	N1-Zn1-N3	148.7(3)
I1-Zn1-I2	119.70(5)						
<b>[CdLI<sub>2</sub>]<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub> (4)</b>							
Cd1-N1	2.3829(55)	Cd1-N2	2.3355(41)	Cd1-N3	2.3801(51)	Cd1-I1	2.7334(9)
Cd1-I2	2.7686(10)	Cd2-N7	2.3657(54)	Cd2-N8	2.3215(50)	Cd2-N9	2.3760(52)
Cd2-I3	2.7544(10)	Cd2-I4	2.7355(10)	N1-Cd1-N2	69.08(18)	N1-Cd1-N3	137.72(19)
N2-Cd1-N3	68.78(19)	I1-Cd1-I2	112.74(2)	N7-Cd2-N8	69.74(19)	N7-Cd2-N9	137.54(19)
N8-Cd2-N9	68.4(2)	I3-Cd2-I4	125.40(3)				
<b>ZnL(NCS)<sub>2</sub>·CHCl<sub>3</sub> (5)</b>							
Zn1-N4	2.0783(92)	Zn1-N5	2.2032(83)	Zn1-N6	2.1753(100)	Zn1-N7	1.9994(86)
Zn1-N8	1.9346(140)	Zn2-N12	2.0677(93)	Zn2-N13	2.1630(87)	Zn2-N14	2.2083(82)
Zn2-N15	1.9709(162)	Zn2-N16	1.9499(98)	N7-C32	1.1276(131)	C32-S1	1.5936(108)
N8-C33	1.1184(200)	C33-S2	1.6333(159)	N15-C70	1.0936(243)	C70-S3	1.578(21)
N16-C71	1.1472(147)	C71-S4	1.6107(113)	N4-Zn1-N5	74.8(3)	N4-Zn1-N6	74.9(3)
N4-Zn1-N7	122.9(4)	N4-Zn1-N8	128.9(4)	N5-Zn1-N6	149.7(3)	N5-Zn1-N7	95.6(4)
N5-Zn1-N8	101.1(4)	N6-Zn1-N7	101.3(4)	N6-Zn1-N8	97.3(4)	N7-Zn1-N8	108.2(4)
N12-Zn1-N13	76.1(3)	N12-Zn1-N14	74.9(3)	N12-Zn1-N15	125.9(4)	N12-Zn1-N16	122.3(4)
N13-Zn1-N14	150.8(3)	N13-Zn1-N15	101.4(4)	N13-Zn1-N16	102.5(4)	N14-Zn1-N15	93.4(4)
N14-Zn1-N16	95.4(4)	N15-Zn1-N16	111.1(5)	C32-N7-Zn1	171.9(10)	N7-C32-S1	175.6(12)
C33-N8-Zn1	166.0(12)	N8-C33-S2	174.5(11)	C70-N15-Zn2	160.7(13)	N15-C70-S3	176.6(15)
C71-N16-Zn2	156.2(9)	N16-C71-S3	178.6(12)				
<b>[ZnL<sub>2</sub>]<sub>2</sub>(ClO<sub>4</sub>)<sub>4</sub>·7H<sub>2</sub>O (7)</b>							
Zn1-N1	2.183(4)	Zn1-N2	2.065(4)	Zn1-N3	2.194(4)	Zn1-N7	2.206(4)
Zn1-N8	2.064(4)	Zn1-N9	2.170(4)	Zn2-N13	2.194(4)	Zn2-N14	2.071(4)
Zn2-N15	2.187(4)	Zn2-N19	2.186(5)	Zn2-N20	2.057(4)	Zn2-N21	2.189(4)
Cl1-O1	1.366(7)	Cl1-O2	1.332(7)	Cl1-O3	1.355(9)	Cl1-O4	1.457(8)
Cl2-O5	1.390(5)	Cl2-O6	1.415(5)	Cl2-O7	1.420(5)	Cl2-O8	1.385(5)
Cl3-O9	1.361(10)	Cl3-O10	1.269(7)	Cl3-O11	1.368(9)	Cl3-O17	1.223(9)
Cl4-O12	1.316(8)	Cl4-O13	1.36(1)	Cl4-O14	1.58(2)	Cl4-O15	1.333(7)
N1-Zn1-N2	75.68(15)	N1-Zn1-N3	150.81(15)	N1-Zn1-N7	86.30(16)	N1-Zn1-N8	102.99(15)
N1-Zn1-N9	99.23(16)	N2-Zn1-N3	75.41(15)	N2-Zn1-N7	104.69(15)	N2-Zn1-N8	178.67(15)

N2-Zn1-N9	104.04(15)	N3-Zn1-N7	97.16(16)	N3-Zn1-N8	105.91(15)	N3-Zn1-N9	91.59(15)
N7-Zn1-N8	75.13(15)	N7-Zn1-N9	151.22(15)	N8-Zn1-N9	76.11(16)	N13-Zn2-N14	75.34(16)
N13-Zn2-N15	151.20(15)	N13-Zn2-N19	90.00(16)	N13-Zn2-N20	101.46(16)	N13-Zn2-N21	97.46(16)
N14-Zn2-N15	75.89(16)	N14-Zn2-N19	105.05(16)	N14-Zn2-N20	176.62(17)	N14-Zn2-N21	103.66(16)
N15-Zn2-N19	96.15(16)	N15-Zn2-N20	107.34(15)	N15-Zn2-N21	90.55(16)	N19-Zn2-N20	75.82(16)
N19-Zn2-N21	151.29(16)	N20-Zn2-N21	75.52(16)				
<b>[CdL<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·CH<sub>3</sub>OH (8)</b>							
Cd1-N1	2.3768(31)	Cd1-N2	2.2895(32)	Cd1-N3	2.3426(30)	Cd1-N4	2.3447(32)
Cd1-N5	2.3074(33)	Cd1-N6	2.3338(32)	Cl1-O1	1.4259(34)	Cl1-O2	1.4293(45)
Cl1-O3	1.3944(45)	Cl1-O4	1.4214(37)	Cl2-O5	1.4176(44)	Cl2-O6	1.3248(58)
Cl2-O7	1.2709(109)	Cl2-O8	1.4048(96)	C1S-O1S	1.3353(150)	O1S-H1SA	0.8518(659)
C1S-H1S1	0.9610(136)	C1S-H1S2	0.9601(97)	C1S-H1S3	0.9587(117)	N1-Cd1-N2	69.58(11)
N1-Cd1-N3	139.51(11)	N1-Cd1-N4	82.53(11)	N1-Cd1-N5	103.89(11)	N1-Cd1-N6	104.46(12)
N2-Cd1-N3	70.26(11)	N2-Cd1-N4	102.17(11)	N2-Cd1-N5	170.86(10)	N2-Cd1-N6	117.23(11)
N3-Cd1-N4	110.88(11)	N3-Cd1-N5	116.59(10)	N3-Cd1-N6	89.35(11)	N4-Cd1-N5	70.1(1)
N4-Cd1-N6	140.08(11)	N5-Cd1-N6	70.08(10)	O1-Cl1-O2	108.9(2)	O1-Cl1-O3	110.8(3)
O1-Cl1-O4	109.8(2)	O2-Cl1-O3	107.6(2)	O2-Cl1-O4	111.4(3)	O3-Cl1-O4	108.3(3)
O5-Cl1-O6	111.1(3)	O5-Cl1-O7	114.9(4)	O5-Cl1-O8	106.9(3)	O6-Cl1-O7	113.2(5)
O6-Cl1-O8	101.7(6)	O7-Cl1-O8	107.9(7)	O4-H1SA-O1S	153.713(5680)	H1SA-O1S-C1S	111.(6)

**Table S2.** Photophysical properties of complexes **L** and complexes **1-8** in several of different polar solvents.

compd	Solvents	$\lambda_{\max}^{(1a)}$ [a]	$\lambda_{\max}^{(1f)}$ [b]	$\Phi$ [c]	$\Delta\nu$ [d]
<b>L</b>	THF	286, 336	408	0.468963	5252
	ethyl acetate	279, 327	404	0.549127	5829
	acetonitrile	284, 330	412	0.334894	6031
	DMF	283, 333	420	0.496245	6221
	methanol	285, 336	424	0.13953	6177
<b>1</b>	THF	286, 344	457	0.485707	7188
	ethyl acetate	284, 341	457	0.383932	7444
	acetonitrile	284, 337	414, 497	0.19454	9553
	DMF	280, 334	420	0.416786	6131
	methanol	288, 343	514	0.14775	9699
<b>2</b>	THF	286, 336	408	0.3607	5252
	ethyl acetate	283, 338	456	0.373757	7656



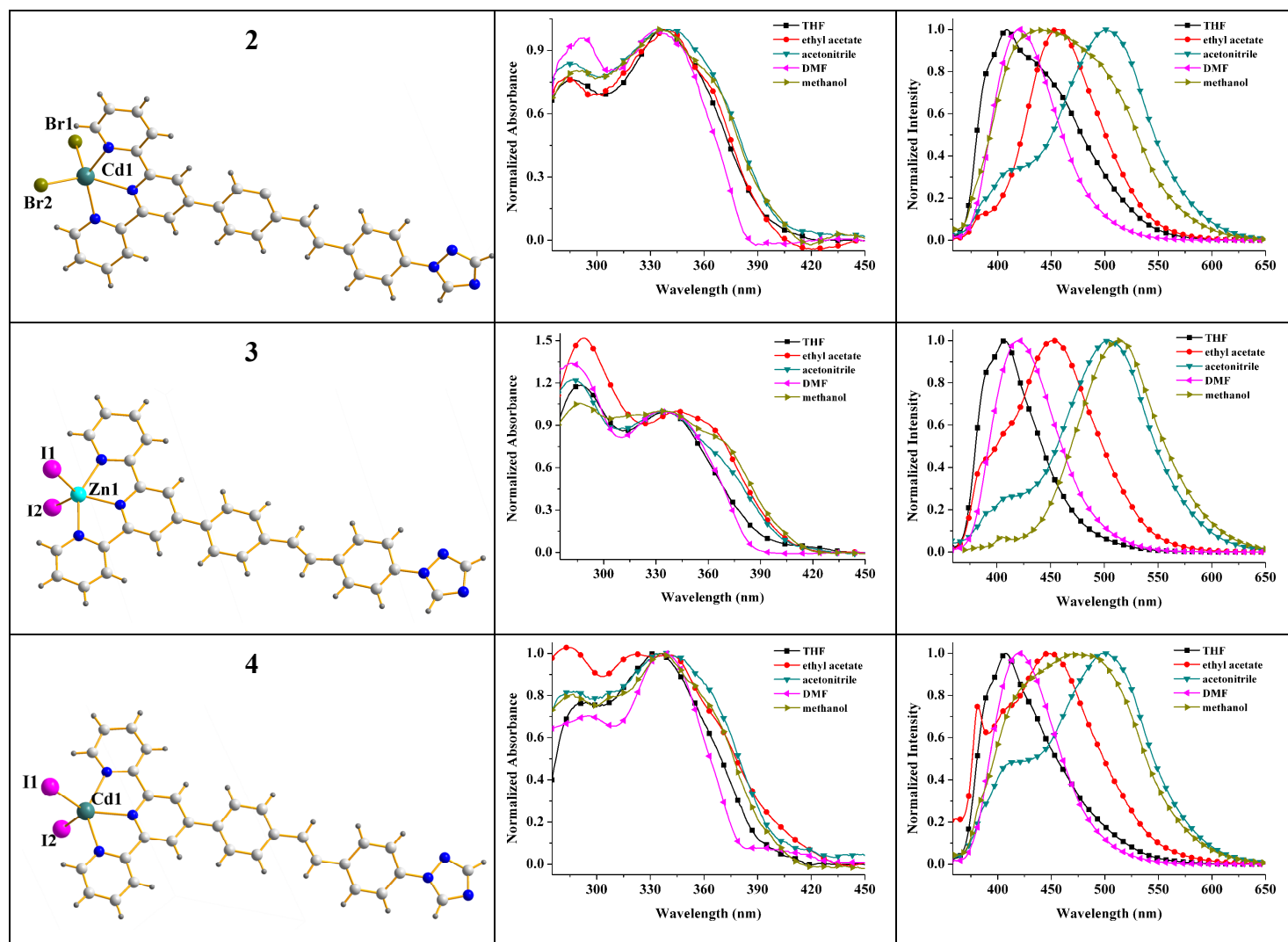
	acetonitrile	284, 339	501	0.176857	9538
	DMF	293, 333	420	0.450756	6221
	methanol	292, 334	439	0.13523	7161
	THF	287, 336	407	0.53431	5192
	ethyl acetate	289, 342	453	0.370705	7165
<b>3</b>	acetonitrile	282, 335	505	0.136296	10049
	DMF	282, 332	421	0.350207	6368
	methanol	286, 334	514	0.084818	10485
	THF	290, 335	408	0.38953	5341
	ethyl acetate	284, 342	447	0.059236	6868
<b>4</b>	acetonitrile	287, 339	501	0.172327	9538
	DMF	281, 336	419	0.605807	5896
	methanol	287, 337	474	0.166962	8577
	THF	287, 336	471	0.421251	8530
	ethyl acetate	286, 341	461	0.291445	7634
<b>5</b>	acetonitrile	287, 340	507	0.197854	9688
	DMF	284, 338	419	0.478868	5719
	methanol	286, 337	510	0.118919	10066
	THF	284, 333	408	0.477366	5520
	ethyl acetate	283, 336	406	0.440448	5131
<b>6</b>	acetonitrile	284, 336	501	0.172571	9802
	DMF	278, 335	420	0.45057	6041
	methanol	285, 339	492	0.186848	9173
	THF	282, 337	408	0.397482	5164
	ethyl acetate	285, 324	451	0.065433	8691
<b>7</b>	acetonitrile	284, 335	415	0.272793	5754
	DMF	286, 342	419	0.58932	5373
	methanol	286, 338	424	0.447704	6001
<b>8</b>	THF	283, 335	408	0.436318	5341

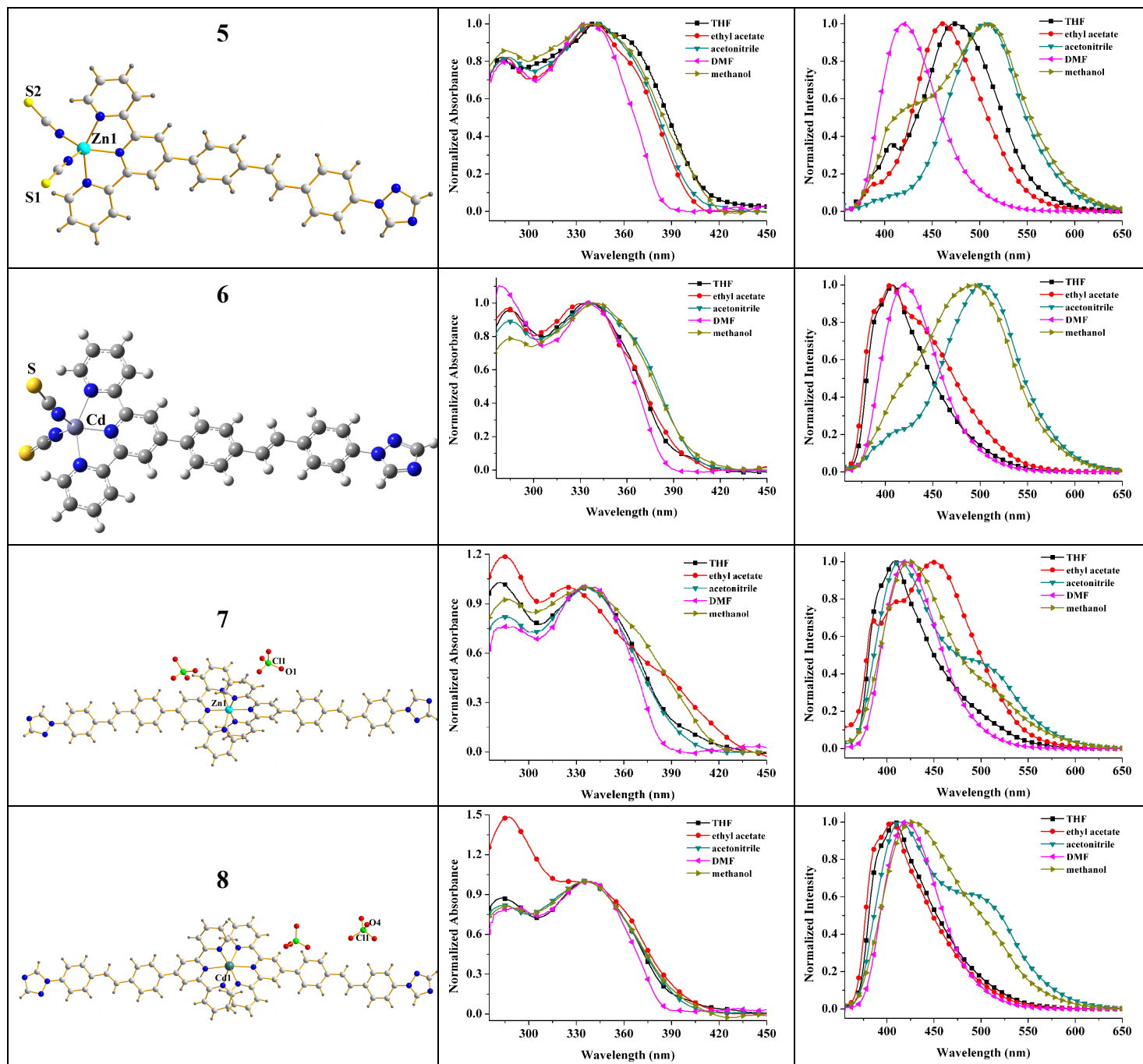
ethyl acetate	288, 326	406	0.22053	6044
acetonitrile	285, 336	415	0.275682	5666
DMF	290, 339	420	0.498042	5689
methanol	286, 335	426	0.234772	6377

[a] Peak position of the longest absorption band. [b] Peak position of SPEF, excited at the absorption maximum.

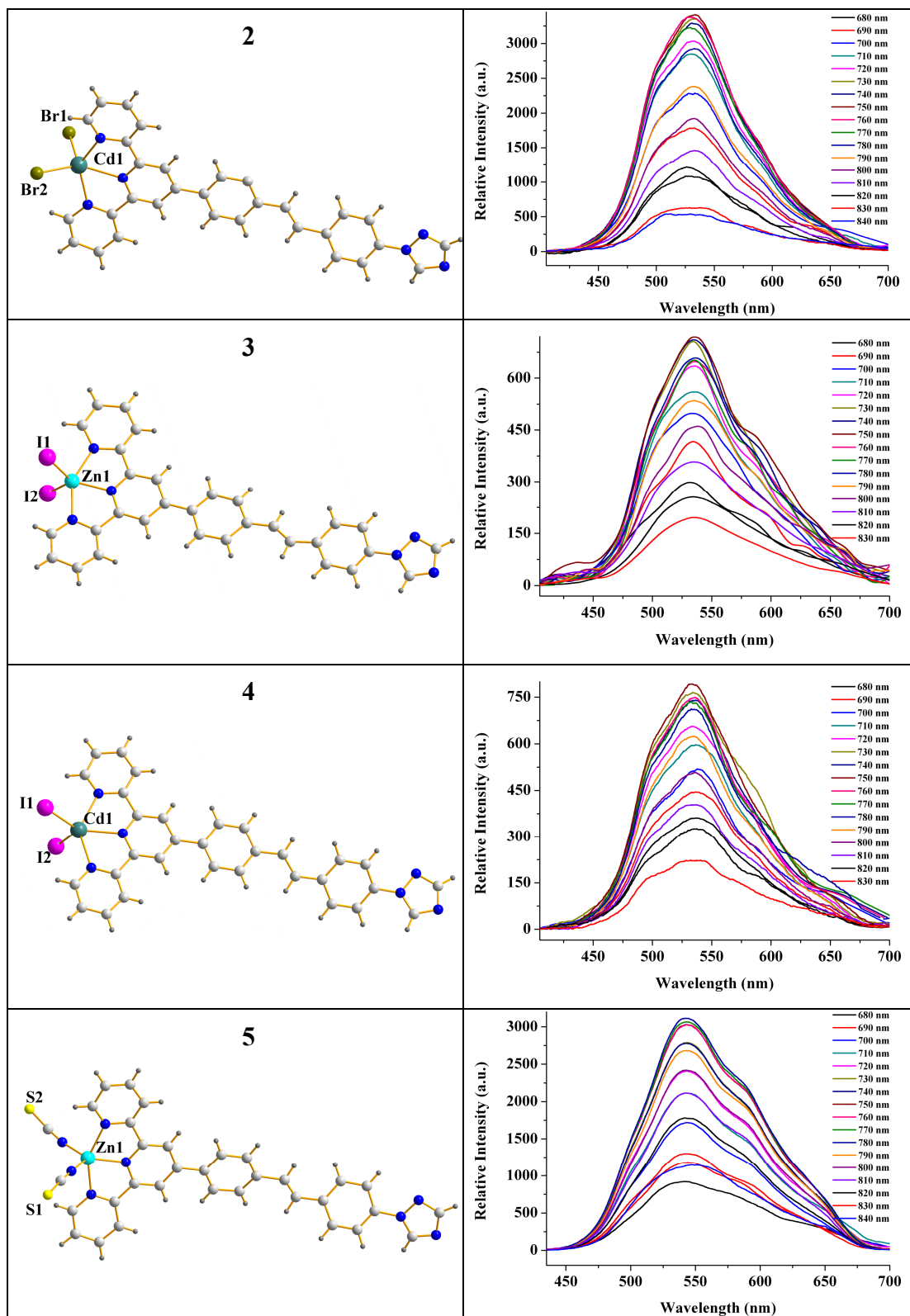
[c] Quantum yields determined by using quinine sulfate as standard. [d] Stokes' shift in  $\text{cm}^{-1}$

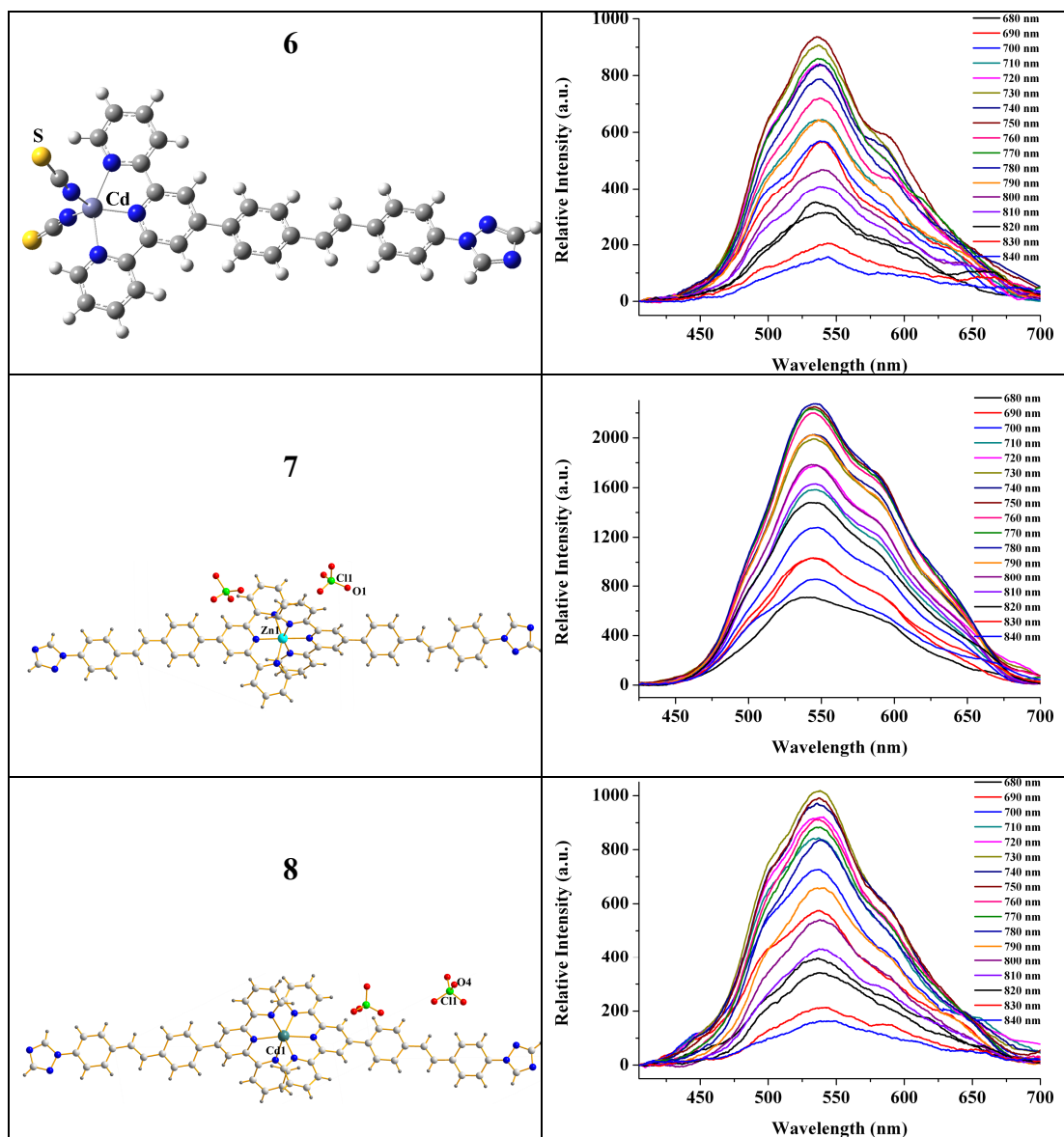
**Fig. S7** Linear absorption (left) and SPEF (right) spectra of complexes **2-8** in five organic solvents.





**Fig. S8.** The TPA spectra of complexes **2-8** in DMF under different excitation wavelengths.





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