†Supplementary material

Two novel six-coordinated cadmium (II) and zinc (II) complexes from carbazate β -diketonate: crystal structures, enhanced two-photon absorption and biological imaging application[†]

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[†]Dedicated to Professor Xiao-Zeng You for His 80th Birthday; [‡] These authors contributed equally to this work.

Legands

Fig. S1. The variable temperature ¹H NMR of $Zn(II)L_2(H_2O)_2$ has been measured in order to further prove the stability of the complex in DMSO.

Fig. S2.MALDI-TOF Mass spectrometry was used to further verify the stability of complex $Zn(II)L_2(H_2O)_2$ in water solution, which first dissolved in a small amount of DMF, and then diluted with water.

Fig. S3. The extended electron delocalization was confirmed by XPS from an experimental viewpoint. XPS result shows the atomic concentration sequence of O atom is $Cd(II)L_2(H_2O)_2$ (16.89) >Zn(II)L_2(H_2O)_2 (13.78) >HL (12.12) which was in accordance with the electron delocalization tendency.

Fig. S4. The abbreviated diagram of MO theory.

Fig. S5. Enlarged diagrams of the molecular orbital of HL

Fig. S6. Computation results of the Zn(II)L₂(H₂O)₂

Table S1 Crystal data and structure refinement for $Cd(II)L_2(H_2O)_2$ and $Zn(II)L_2(H_2O)_2$.

Table S2 Selected bond lengths (Å) and angles (°) for $Cd(II)L_2(H_2O)_2$ and $Zn(II)L_2(H_2O)_2$.

Table. S3. TD-DFT computational studies were performed to elucidate the electronic structures of the ground state of HL, $Cd(II)L_2(H_2O)_2$ and $Zn(II)L_2(H_2O)_2$.



Fig. S1. Variable temperature ¹H NMR spectra of $Zn(II)L_2(H_2O)_2$.



Fig. S2. MALDI-TOF mass spectra of Zn(II)L₂(H₂O)₂.



Fig. S3. XPS spectra of all the compounds



Fig. S4. The abbreviated diagram of MO theory.

Fig. S5. Enlarged diagrams of the molecular orbital of HL

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Fig. S6. Computation results of the Zn(II)L₂(H₂O)₂

 $Table \ S1 \ \ Crystal \ \ data \ and \ structure \ refinement \ for \ \ Cd(II) \\ L_2(H_2O)_2 \ and \ \ Zn(II) \\ L_2(H_2O)_2.$

Compound	$Cd(II)L_2(H_2O)_2$	$Zn(II)L_2(H_2O)_2$	
Empirical formula	C40 H38 F6 N2	C40 H38 F6 N2	
	O4 Cd	O4 Zn	
Formula weight	869.12	822.09	
Crystal system	Monoclinic	Monoclinic	
Space group	C2/c	C2/c	
Temperature (K)	293(2)	273(2)	
λ of Mo- K_{α} [Å]	0.71	0.71	
Absorption			
coefficient[mm ⁻¹]	0.06	0.06	
Unit cell dimensions	a =39.67(9) Å	a =39.08(13) Å	
	b=5.34(10) Å	b=5.27(2)Å	
	c =20.25(5)	c =20.21(6)Å	
	β=104.29(2) °	β=103.91(2)°	
V [Å ³]	4158.47(16)	4039.00(2)	
Reflections collected	15154	13298	
Reflections unique	4752	3527	
<i>R</i> _{int}	0.0321	0.0666	
R ₁	0.0646	0.0932	
wR_2	0.2065	0.2804	
Goodness of fit on F^2	1.080	1.102	

 $Table \ S2 \ Selected \ bond \ lengths \ (\text{\r{A}}) \ and \ angles \ (^{\circ}) \ for \ Cd(II) \\ L_2(H_2O)_2 \ and \ Zn(II) \\ L_2(H_2O)_2.$

$Cd(II)L_2(H_2O)_2$			
Cd(1)-O(3)	2.361(3)	O(5)-Cd(1)-O(5)#1	180.00(11)

Cd(1)-O(5)	2.227(3)	O(5)-Cd(1)-O(6)	83.37(11)
Cd(1)-O(6)	2.230(3)	O(5)-Cd(1)-O(6)#1	96.63(11)
C(22)-C(23)	1.367	O(5)-Cd(1)-O(3)#1	87.54(12)
C(23)-C(24)	1.420	O(5)-Cd(1)-O(3)	92.46(12)
C(22)-O(6)	1.279		
C(24)-O(5)	1.257		
$Zn(II)L_2(H_2O)_2$			
Zn(1)-O(1)	2.053(5)	O(2)-Zn(1)-O(2)#1	180.00(17)
Zn(1)-O(2)	2.033(5)	O(2)-Zn(1)-O(1)#1	90.19(19)
Zn(1)-O(3)	2.239(5)	O(2)-Zn(1)-O(1)	89.81(19)
C(17)-C(18)	1.424	O(2)-Zn(1)-O(3)#1	90.6(2)
C(18)-C(19)	1.323	O(2)-Zn(1)-O(3)	89.4(2)
C(19)-O(2)	1.282		
C(17)-O(1)	1.256		

Table S3 Excitation energies (*E*), corresponding wavelengths (λ), oscillator strengths (*f*) and major contributors for **HL**, **Cd(II)L**₂(**H**₂**O)**₂ and **Zn(II)L**₂(**H**₂**O)**₂ ^{*a*}. (^{*a*} Only the transitions with a calculated oscillator strength higher than 0.0010 are reported.)

	Е	λ (nm)	f	Composition	Character
	(eV)				
HL	3.48	356.27	0.0009	93(H-1)→97(L+2)(0.6101	$\pi \rightarrow \pi^*$
				2)	
	4.49	275.92	0.2032	94(H)→95 (L) (0.56918)	$n{\rightarrow}\pi^*$
	3.50	353.91	0.0011	202(H-1)→204(L)(0.5948	$\pi \rightarrow \pi^*$
$Cd(II)L_2(H_2O)_2\\$				1)	MLCT
	4.47	277.16	0.2742	202(H-1)→206(L+2)	$n \rightarrow \pi^*$
				(0.29774)	
$Zn(II)L_2(H_2O)_2$	3.95	351.00	0.0021	203(H)→204(L)(0.57055)	$\pi \rightarrow \pi^*$
					MLCT
	4.37	283.63	0.0072	203(H)→207(L+3)	$n \rightarrow \pi^*$
				(0.60174)	

According to the MO theory and the abbreviated diagram, we can clearly see that the π orbital was a distorted ellipsoid and the π * orbital was a distorted ball. Hense, from the Figure 4 in the main text, the HOMOs (H) and H-1 of HL are of π orbitals localized on the carbazole and COCHC(OH)CF₃ groups. The unoccupied molecular orbitals LUMO (L) and L+1 are of the π * orbital localized on carbazole and COCHC(OH)C₆H₅ units which was in line with the MO theory. For complexes Zn(II)L₂(H₂O)₂ as an example, the d orbitals can hardly be intuitively from the diagram, however, the computation result can be provided to prove the metal ion hybidized d,s,p-orbitals. From Fig. S6, we can clearly see that the d-orbitals of Zn (II) has highest coefficient (218.21 and 118.99).