Electronic Supplementary Information for

Zinc(II) Coordination Architectures with Two Bulky Anthracene-Based Carboxylic Ligands: Crystal Structures, and Luminescent Properties

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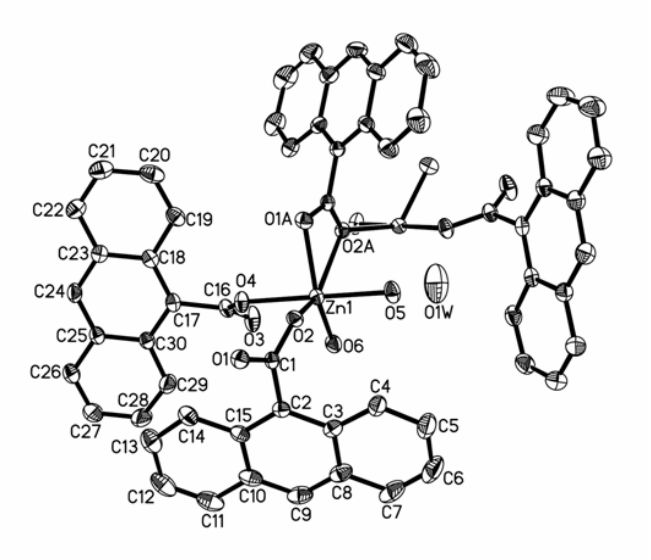
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C20
C22
C19
O1A
O2A
C23
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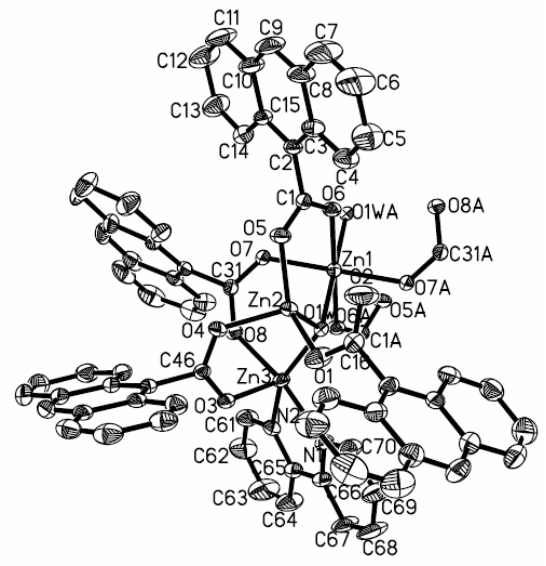
C24
C16
O4
Zn1
O5
O1W
C17
O3
O2
O6
C25
C30
O1
C1
C26
C29
C4
C28
C15
C2
C3
C5
C27
C13
C14
C6
C12
C10
C8
C7
C11
C9

(a)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C5
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C4
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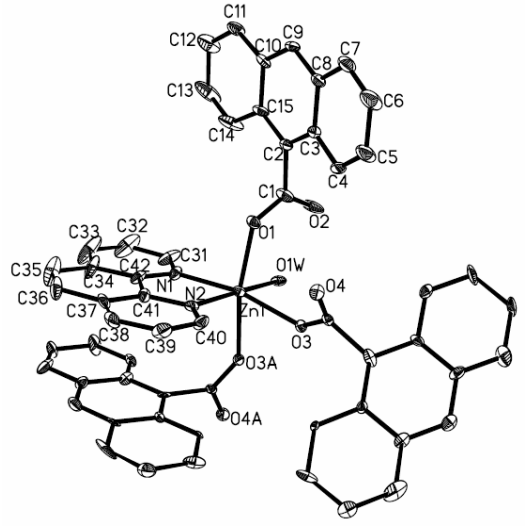
O1WA
O8A
O5
O7
C31
Zn1
C31A
O2
O7A
Zn2
O1W
O6A
O5A
O4
O8
C1A
C46
C16
Zn3
O1
O3
N2
C61
C70
C62
C65
N1
C63
C66
C69
C64
C67
C68

(b)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C12
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C13
C15
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C14
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C3
C5
C4
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O2
O1
C33
C32
C31
C35
C42
O1W
C34
N1
N2
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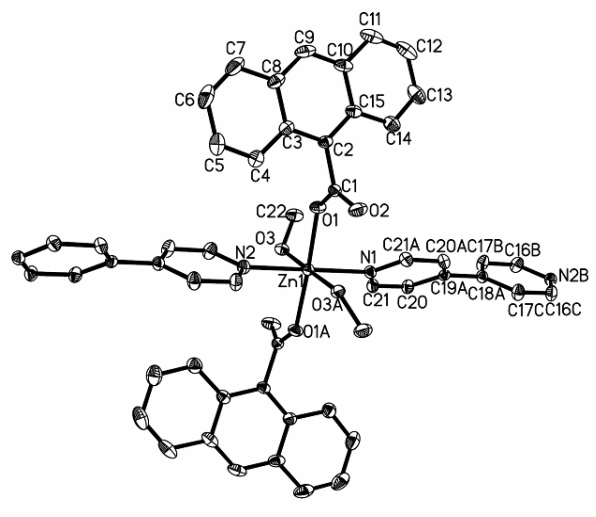
C36
Zn1
C37
C41
O3
C38
C39
C40
O3A
O4A

(c)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C9
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C3
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C5
C4
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O1
O2
O3
N2
N1
C21A
C20A
C17B
C16B
N2B
Zn1
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C20
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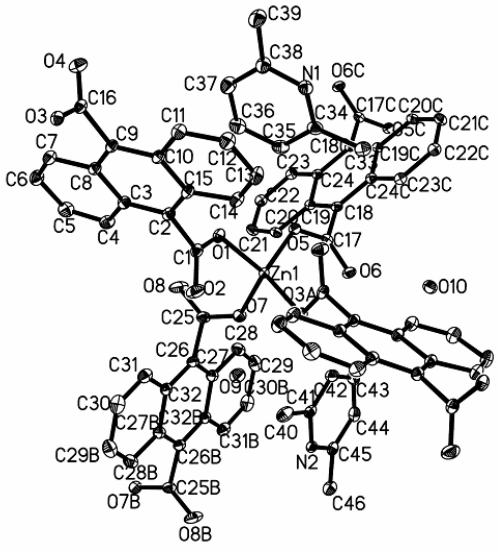
C17C
C16C
O3A
O1A

(d)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O3
C11
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C21C
C9
C35
O5C
C7
C10
C12
C18C
C19C
C22C
C23
C33
C6
C8
C15
C13
C24
C24C
C23C
C3
C22
C5
C4
C2
C14
C20
C19
C18
C1
O1
C21
O5
C17
Zn1
O6
O8
O2
O10
O3A
C25
O7
C28
C26
C27
C29
C31
O9
C30B
C42
C43
C30
C32
C41
C27B
C32B
C31B
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C44
C29B
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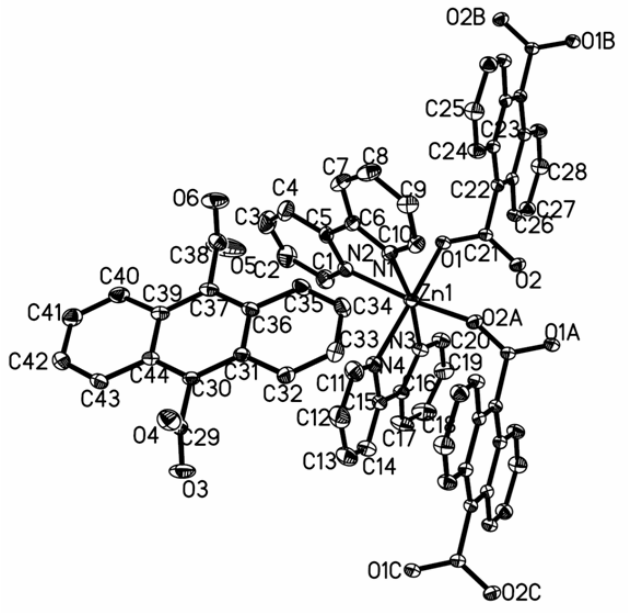
N2
C45
C28B
C25B
C46
O7B
O8B

(e)


O2B
O1B
C25
C23
C24
C7
C8
C28
C4
C9
C22
C6
C27
O6
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C10
C26
C38
O5
C2
C1
N2
N1
O1
C21
O2
C40
C39
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Zn1
C41
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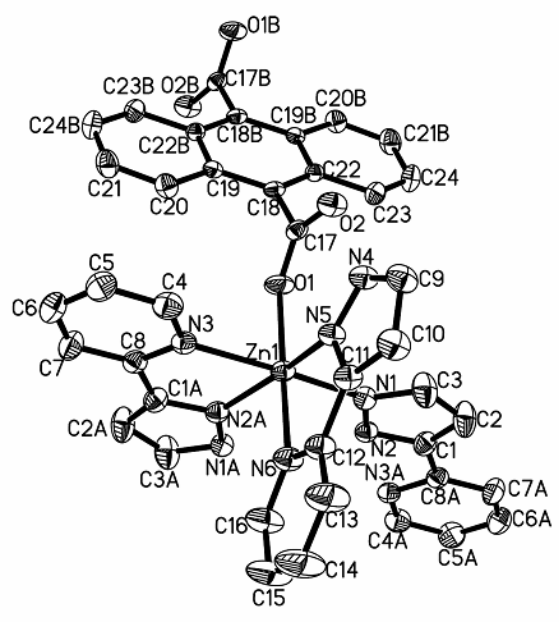
O1A
C33
N3
C20
C42
C44
C31
N4
C19
C11
C16
C43
C30
C32
C15
C12
C18
C17
O4
C29
C13
C14
O3
O1C
O2C

(f)



(g)

Fig. S1 ORTEP View of **1**-**7** with 30% thermal ellipsoid probability: a) for **1**, b) for **2** (two anthracene rings omitted for clarity), c) for **3**, d) for **4**, e) for **5**, f) for **6**, and g) for **7.** [symmetry code: for **1 A**: x, y, z. for **2, A**: 1-x, -y, 1-z. for **3 A**: x, 1/2-y, 1/2+z. for **4 A**: 2+x, 1/2-y, 1/2+z; **B**: x, 1+y, z; **C**: 2+x, 3/2-y, 1/2+z. for **5 A**: -1/2+x, y, 1/2-z; **B**: 1-x, -y, 1-z; **C**: 1-x, 1-y, 1-z. for **6 A**: 1-x, 1-y, 2-z; **B**: -x, 1-y, 2-z; **C**: 1+x, y, z. for **7 A**: 1-x, 1-y, 1-z; **B**: 1-x, 1-y, 2-z]

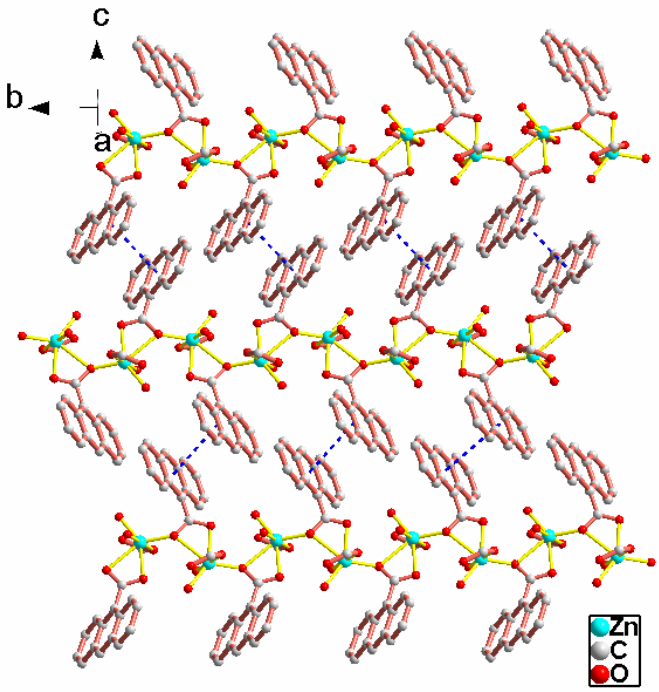


Fig. S2 View of the 2D network formed by the inter-chain π···π stacking interactions (blue dashed) in **1** (H atoms omitted for clarity).

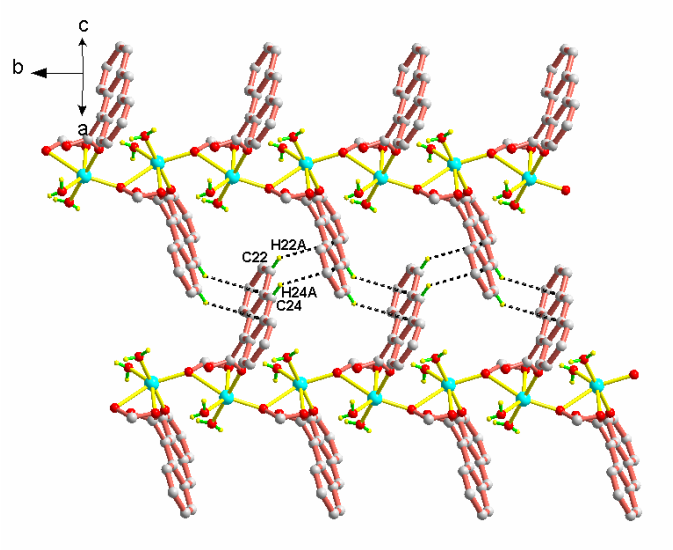


Fig. S3 View of the inter-chain C–H···π interactions (black dashed) in **1** (partial H atom omitted for clarity).

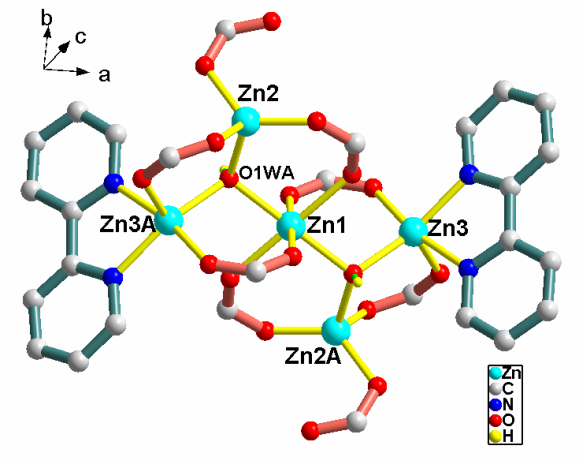


Fig. S4 View of simplified pentanuclear cluster for **2** (partial H atom and all the anthracene rings of H**L**[1] ligands omitted for clarity).

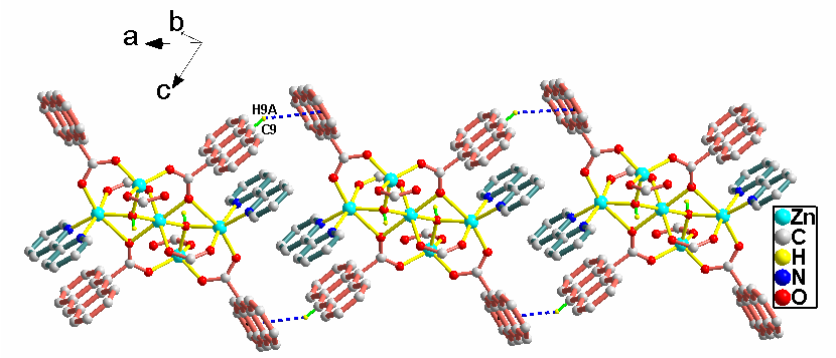


Fig. S5 View of the intermolecular C–H···π interactions between the pentanuclear units in **2** (partial H atom omitted for clarity).

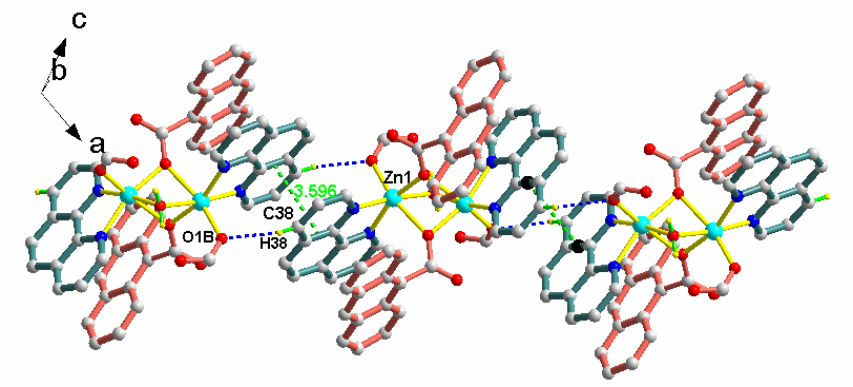


Fig. S6 View of the 1D chain formed by the intermolecular C–H···O (blue dashed) and π···π stacking (green dashed) interactions in **3** (partial H atoms and anthracene rings omitted for clarity).

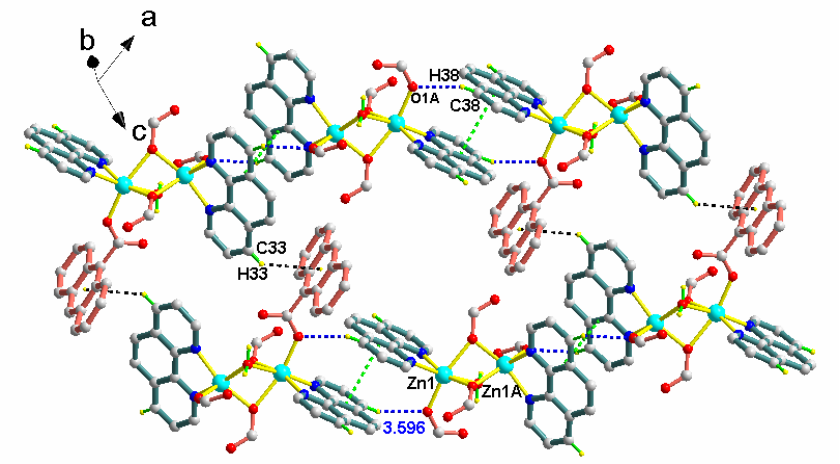


Fig. S7 View of the inter-chain C–H···π interactions (black dashed) in **3** (partial H atoms omitted for clarity).

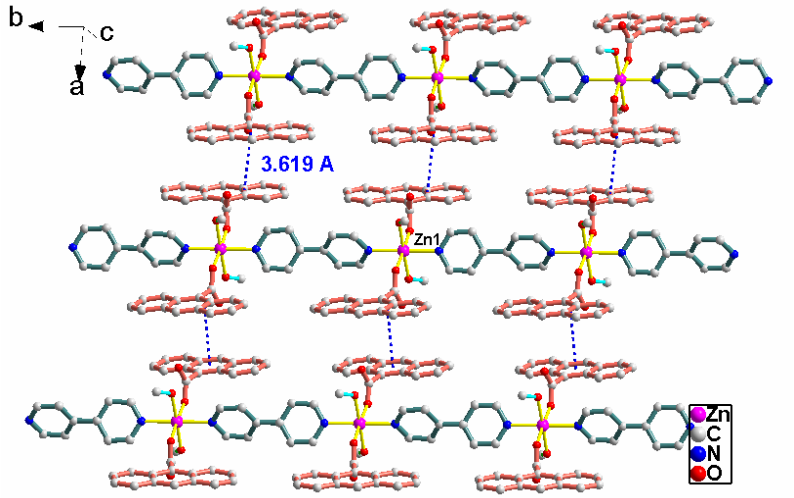


Fig. S8 View of the 2D network formed by inter-chain π···π stacking interactions (blue dashed) in **4** (H atoms omitted for clarity).

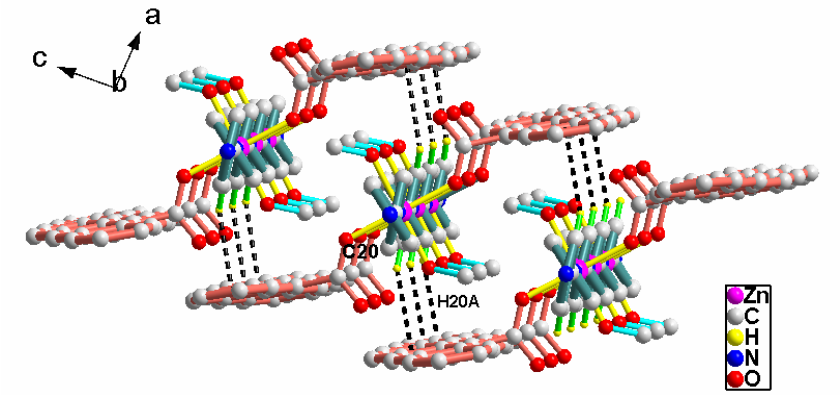


Fig. S9 View of the inter-chain C–H···π interactions (black dashed) in **4** (partial H atoms omitted for clarity).

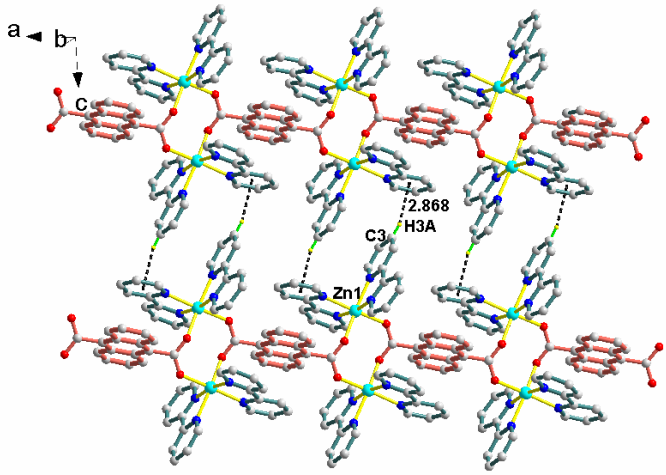


Fig. S10 View of the 2D network formed by the inter-chain C–H···π interactions (black dashed) in **6** (partial H atoms and the deprotoned HL^2 ligands omitted for clarity).

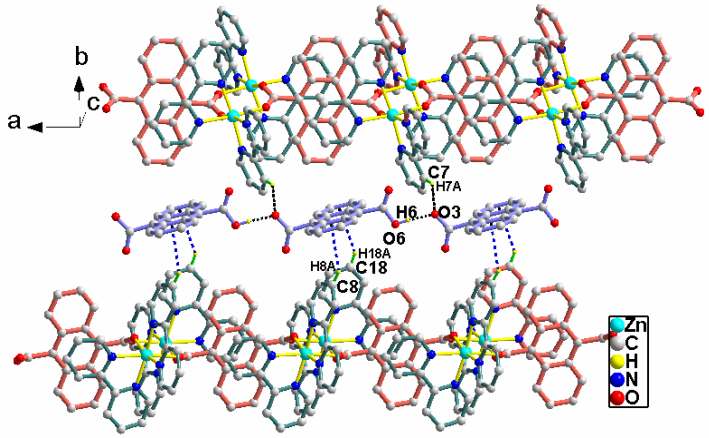


Fig. S11 View of the inter-chain C–H···π interactions (blue dashed) in **6** (partial H atoms omitted for clarity).

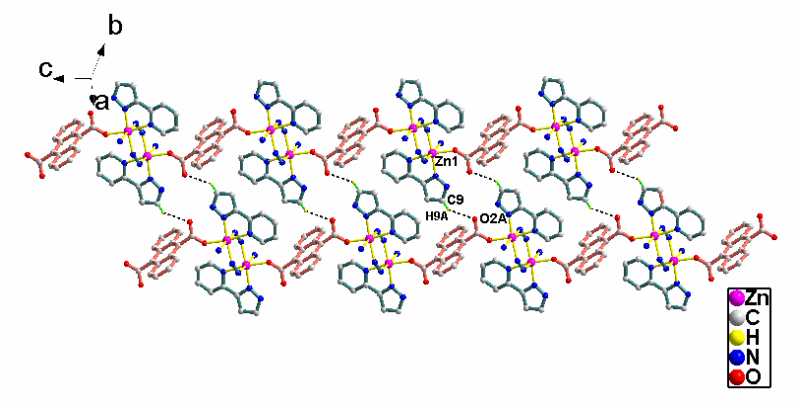


Fig. S12 View of the 2D network formed in **7** through inter-chain C–H···O H-bonding interactions (black dashed) (partial H atoms and 3-(2-pyridyl)pyrazole rings of Hpypz ligands omitted for clarity).

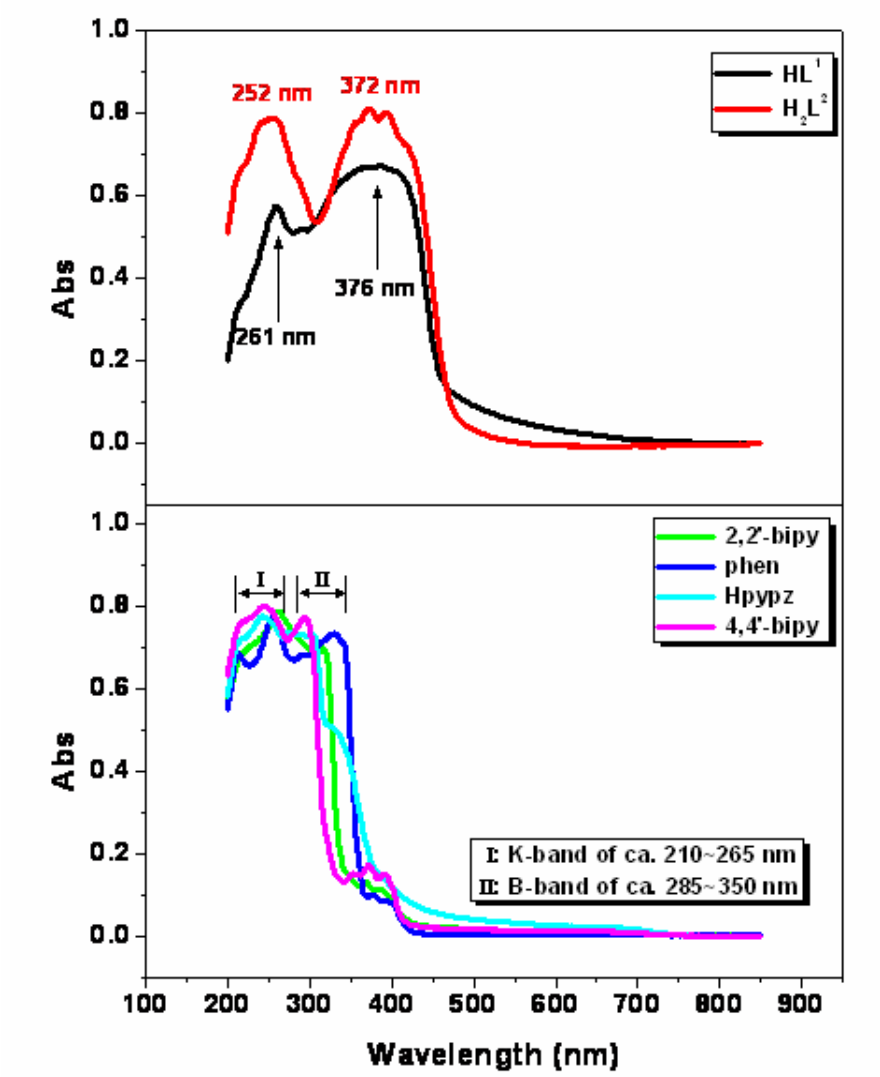
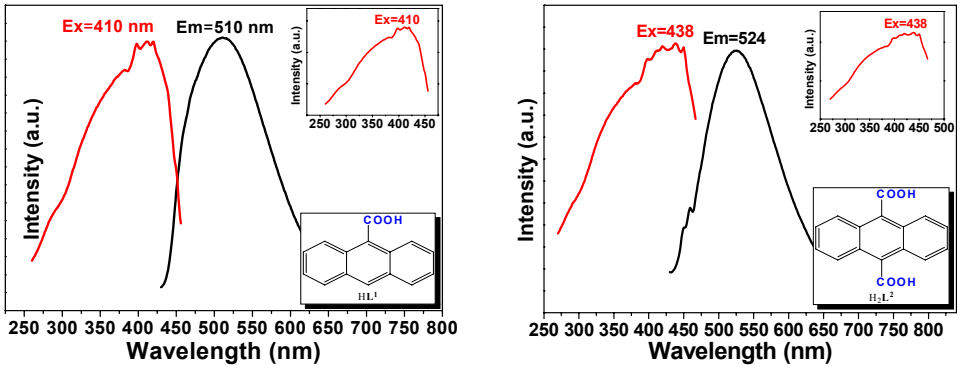
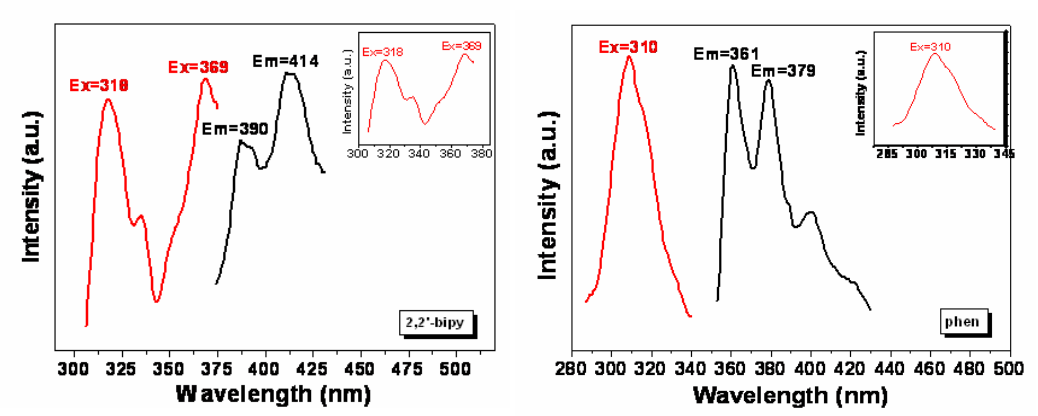


Fig. S13 Solid UV-vis absorption spectra for the free ligands H**L**^{1} and H_2**L**^{2} (top) and 2,2′-bipy, phen, Hpypz and 4,4′-bipy (bottom) at room temperature.

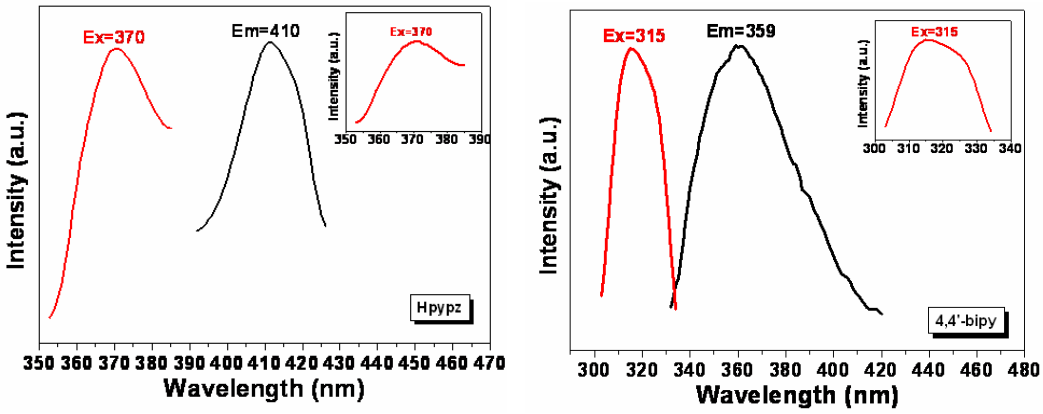


(a) (b)

Fig. S14 Excitation and emission spectra of the free ligands in the solid state at room temperature: (a) for H**L**^{1} and (b) for H_2**L**^{2} (Inset: excitation spectra of H**L**^{1} and H_2**L**^{2} only for clarity)



(a) (b)



(c) (d)

Fig. S15 Excitation and emission spectra of the free auxiliary ligands in the solid state at room temperature: (a) for 2,2′-bipy, (b) phen, (c) for Hpypz and (d) 4,4′-bipy (Inset: excitation spectra of 2,2′-bipy, phen, Hpypz and 4,4′-bipy only for clarity)

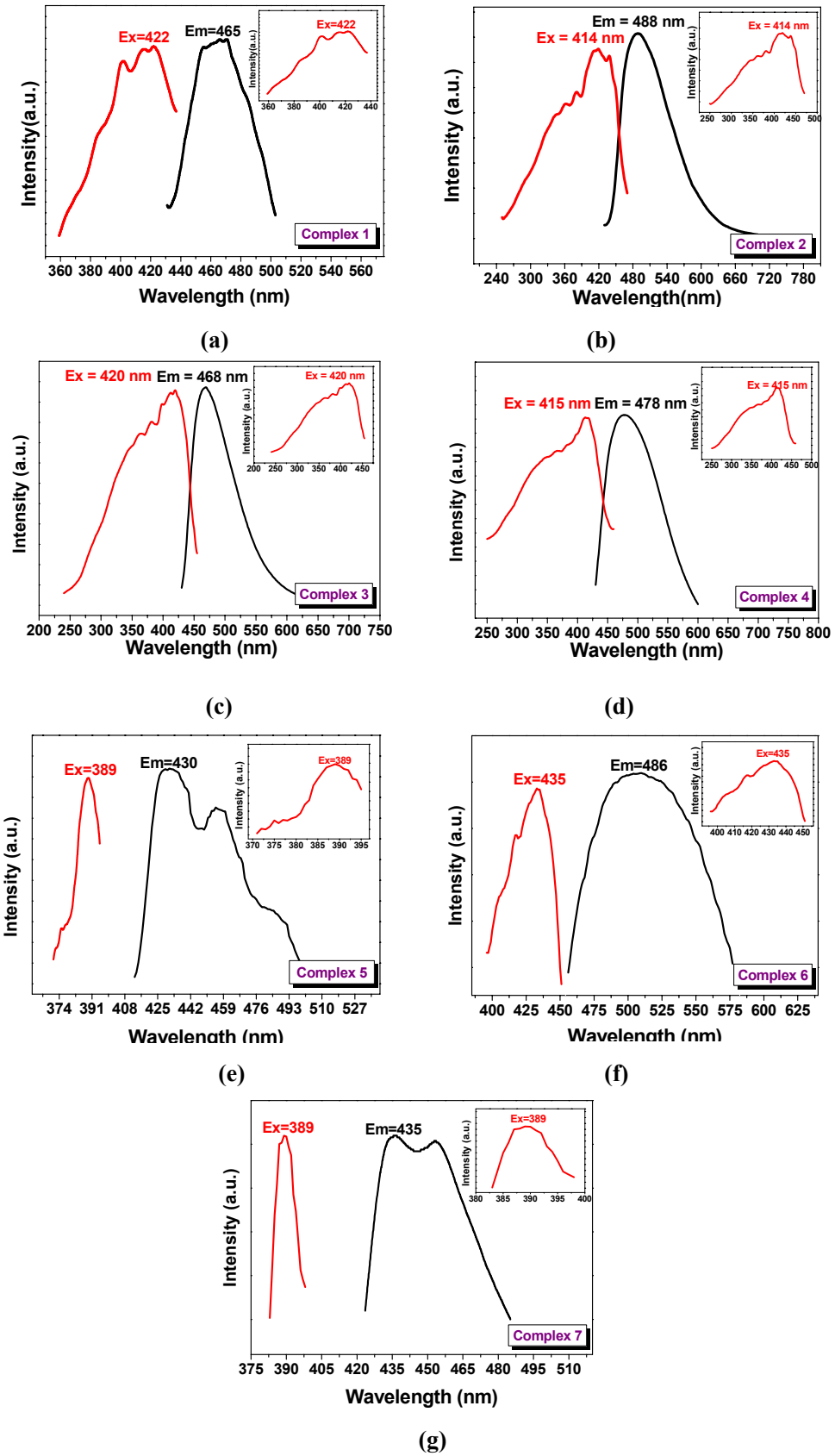


Fig. S16 Excitation and emission spectra of **1**-**7** in the solid state at room temperature: (a) for **1**, (b) for **2**, (c) for **3**, (d) for **4**, (e) for **5**, (f) for **6**, and (g) for **7** (Inset: excitation spectra of **1**-**7** only for clarity).

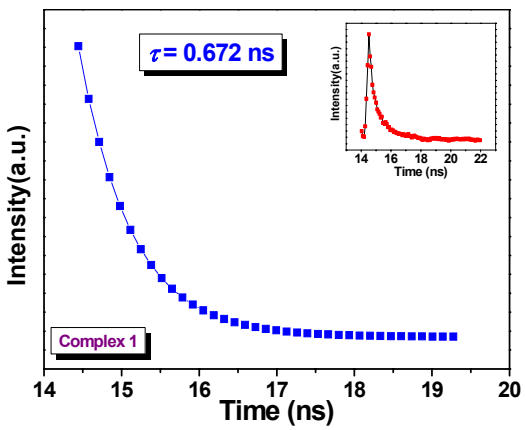
The luminescent decay curves of **1**-**7** were further obtained by femtosecond (fs) laser system at room temperature (Fig. 6 and ESI-Fig. S17). The decay curves are fitted into a single-exponential function as $I = I_0 \exp(-t/\tau)$, where I and I_0 are the luminescent intensities at times t and 0, and τ is defined as the luminescent lifetime. The lifetime τ of **1**-**7** was measured to be 0.672, 27.7, 9.13, 9.72, 0.438, 8.74, and 0.536 *n*s at the 465, 488, 468, 478, 430, 486, and 435 nm emission peaks, respectively, and much shorter than that of the emission resulted from a triplet state (> 10^{-3} s). Therefore we believe that the emissions of **1**-**7** should arise from a singlet state.[1,2] Generally, the complexes with metal-hydroxy (or oxy) clusters often have significant longer emission lifetimes than those without metal-hydroxy (or oxy) clusters.[3] Similar to the lifetime of $[Zn_4O(OAc)_6]$ (10 *n*s),[4] the lifetime of **2** is ca. 27.7 *n*s, which is significantly longer than those of other systems without metal-hydroxyl clusters and consistent with the result of its crystal structures analysis.

1 B. Valeur, *Molecular Fluorescence: Principles and Applications*, Wiley-VCH: Weinheim, 2002.

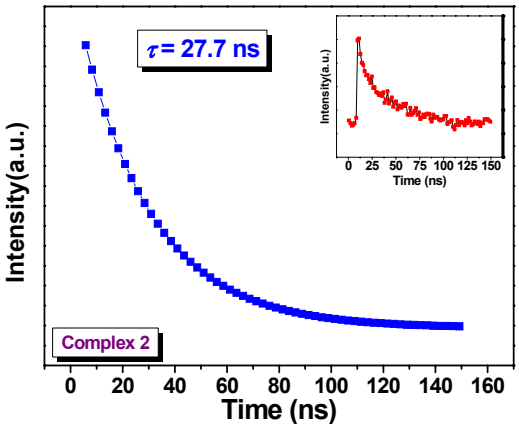
2 (*a*) G. R. Choppin and D. R. Peterman, *Coord. Chem. Rev.,* 1998, **174**, 283; (*b*) X. Pang, H. Sun, Y. Zhang, Q. Shen and H. Zhang, *Eur. J. Inorg. Chem.,* 2005, 1487.

3 (*a*) G. N. Vayssilov, B. C. Gates and N. Rosch, *Angew. Chem. Int. Ed.,* 2003**, 42**, 1391; (*b*) S.-L. Zheng, J.-P. Zhang, X.-M. Chen, Z.-L. Huang, Z.-Y. Lin and W.-T. Wong, *Chem. Eur. J.,* 2003, **9**, 3888 and references therein.

4 (*a*) L. Hiltunen, M. Leskelä, M. Mäkelä and L. Niinistö, *Acta Chem. Scand., Ser. A,* 1987, **41**, 548; (*b*) H. Kunkely and A. Vogler, *J. Chem. Soc., Chem. Commun.,* 1990, 1204.



(a)



(b)

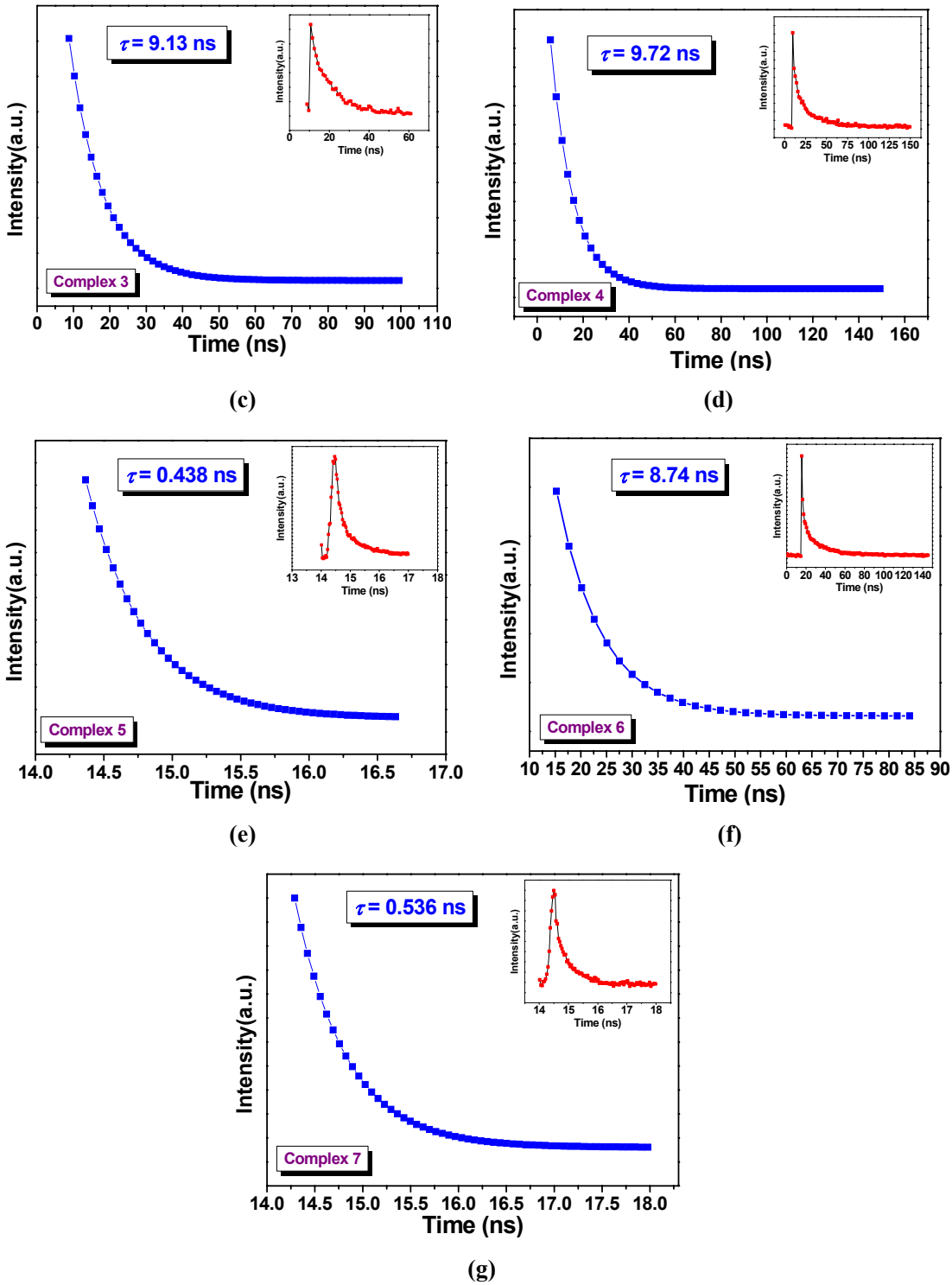
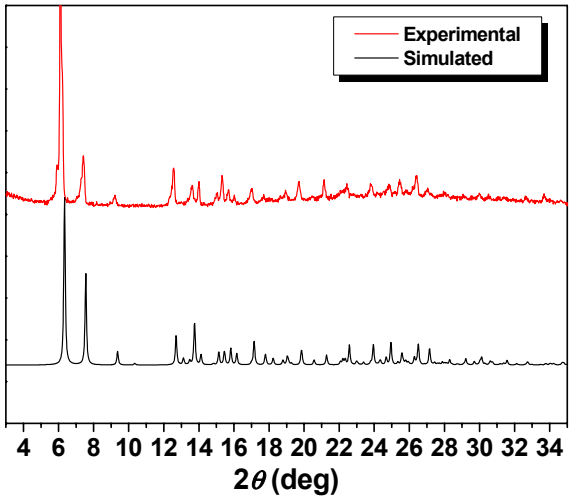
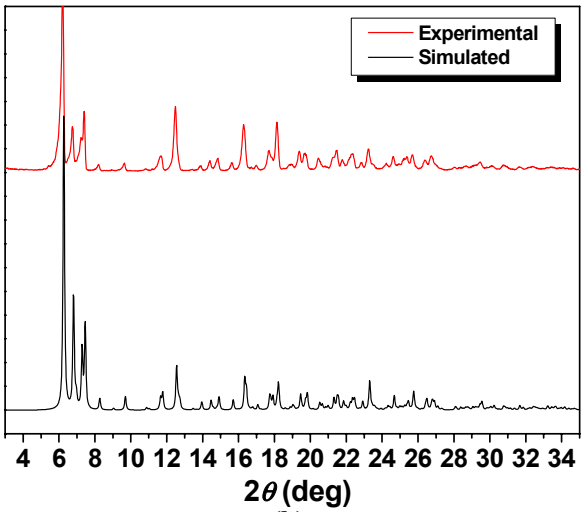


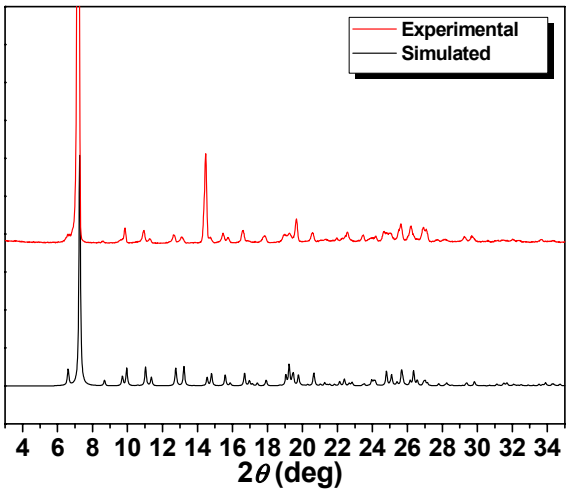
Fig. S17 View of the luminescence decay curves: (a) for **1** (λ_{Em} = 465 nm), (b) for **4** (λ_{Em} = 488 nm), (c) for **3** (λ_{Em} = 468 nm), (d) for **4** (λ_{Em} = 478 nm), (e) for **5** (λ_{Em} = 430 nm), (f) for **6** (λ_{Em} = 486 nm), and (g) for **7** (λ_{Em} = 435 nm) (the blue lines are the fitting curves and the black-red lines inserted at the top right corner are the raw experimental curves).


Experimental
Simulated
4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34
2θ (deg)

(a)


Experimental
Simulated
4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34
2θ (deg)

(b)


Experimental
Simulated
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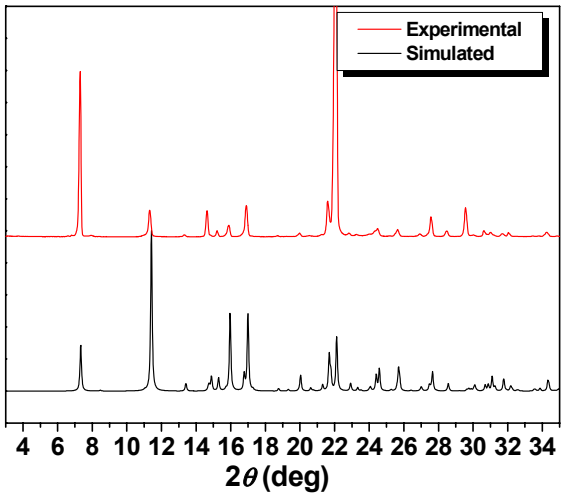
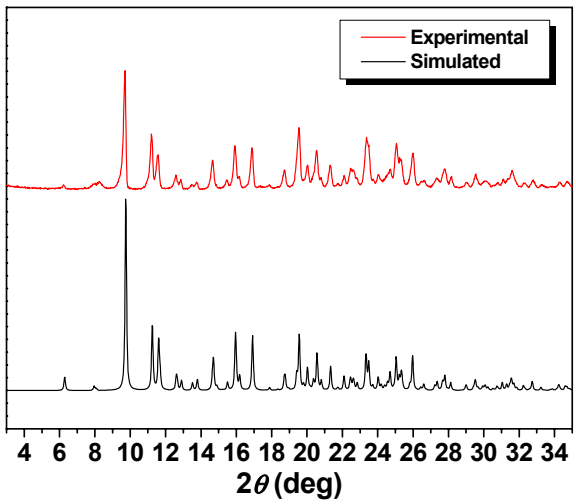
2θ (deg)

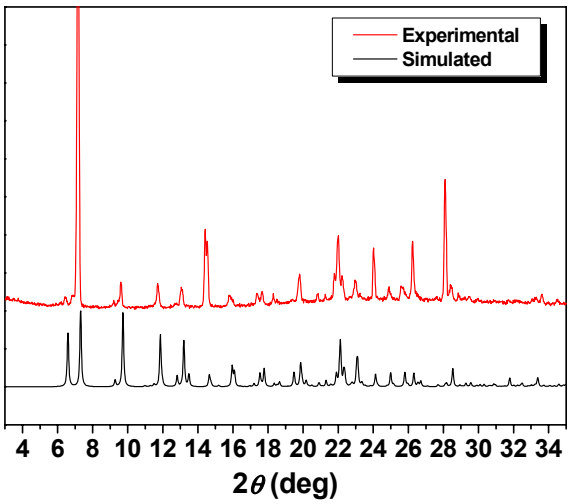
(c)


Experimental
Simulated
4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34
2θ (deg)

(d)


Experimental
Simulated
4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34
2θ (deg)

(e)


Experimental
Simulated
4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34
2θ (deg)

(f)

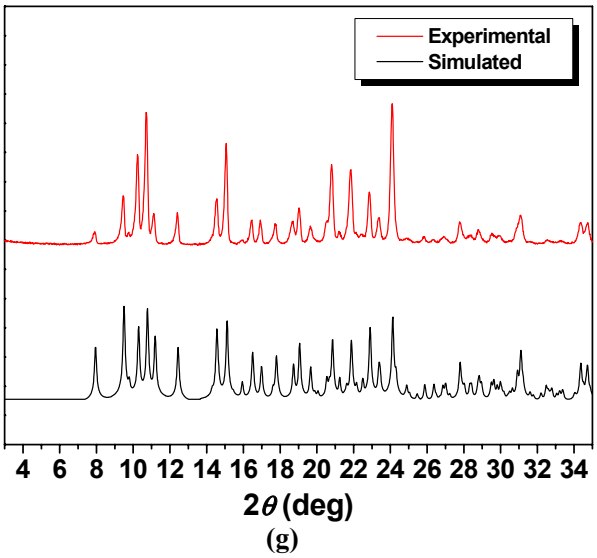
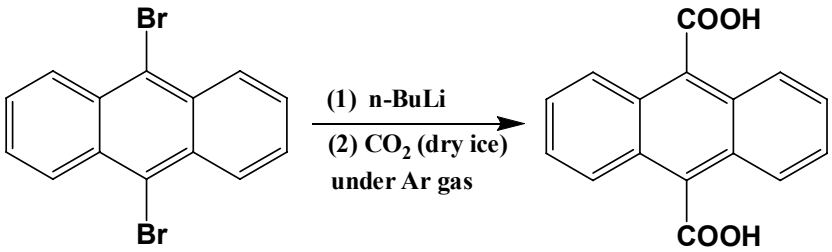


Fig. S18 X-ray powder diffraction (XRPD) patterns of (a) for **1**, (b) for **2**, (c) for **3**, (d) for **4**, (e) for **5**, (f) for **6**, and (g) for **7** measured in air, respectively.



Scheme S1 Reaction process for the synthesis of H_2L^2 ligand (for more details, please see references 8 and 22).