Electronic Supplementary Information for

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

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**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 HL¹ 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 HL² 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 HL¹ and H₂L² (top) and 2,2'-bipy, phen, Hpypz and 4,4'-bipy (bottom) at room temperature.
**Fig. S14**  Excitation and emission spectra of the free ligands in the solid state at room temperature: (a) for HL\(^1\) and (b) for H\(_2\)L\(^2\) (Inset: excitation spectra of HL\(^1\) and H\(_2\)L\(^2\) only for clarity)

**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 $\tau$ is defined as the luminescent lifetime. The lifetime $\tau$ of 1-7 was measured to be 0.672, 27.7, 9.13, 9.72, 0.438, 8.74, and 0.536 ns 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 $[\text{Zn}_4\text{O(OAc)}_6]$ (10 ns),\(^4\) the lifetime of 2 is ca. 27.7 ns, which is significantly longer than those of other systems without metal-hydroxyl clusters and consistent with the result of its crystal structures analysis.

Fig. S17  View of the luminescence decay curves: (a) for 1 ($\lambda_{\text{Em}} = 465$ nm), (b) for 4 ($\lambda_{\text{Em}} = 488$ nm), (c) for 3 ($\lambda_{\text{Em}} = 468$ nm), (d) for 4 ($\lambda_{\text{Em}} = 478$ nm), (e) for 5 ($\lambda_{\text{Em}} = 430$ nm), (f) for 6 ($\lambda_{\text{Em}} = 486$ nm), and (g) for 7 ($\lambda_{\text{Em}} = 435$ nm) (the blue lines are the fitting curves and the black-red lines inserted at the top right corner are the raw experimental curves).
**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$_3$L$^2$ ligand (for more details, please see references 8 and 22).