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Secondary hierarchical complexity in double-stranded cluster helicates covered by NNNNN type pincer ligands

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Experimental details

Materials, general methods and synthesis

All chemicals and solvents used in the syntheses were of analytical grade and used as received without further purification. ^{1}H NMR spectra were recorded on a Bruker AVANCE III 500 MHz spectrometer. FT-IR spectra were recorded on a Thermo Scientific Nicolet iS50 FTIR Spectrometer. Elemental analyses were carried out on a CE instruments EA 1110 elemental analyzer. Photoluminescence spectra were measured on a Hitachi F-7000 spectrometer.

Synthesis of $H_2^{py}PDP^{ph}$: The synthesis was performed according to a previous literature procedure.[S1] 2,6-Pyridinedicarboxaldehyde (2.6 mmol), 3-phenyl-1-(pyridine-2-yl-propan-1-one) (5.23 mmol), and 3-benzyl-5-(2-hydroxyethyl)-4-methylthiazolium chloride (1.56 mmol) were mixed under an argon atmosphere. Absolute ethanol was added and the mixture was heated to reflux. A solution of sodium *tert*-butoxide (1.56 mmol) in ethanol was added via syringe and heating was continued for 24 hours. The reaction was cooled to room temperature and ammonium acetate (15.54 mmol) was added to the mixture. The reaction mixture was heated to reflux open to air for 24 hours. The solid precipitate was collected via filtration, washed with ethanol, and dried under high vacuum to yield the desired product with Yield of 60%. X-ray quality crystals of **$H_2^{py}PDP^{ph}$** were grown from tetrahydrofuran. ^{1}H NMR (500 MHz, chloroform-d): ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.63 (d, 2H), 8.59 (d, 2H), 7.71 (m, 4H), 7.55 (d, 4H), 7.44 (t, 4H), 7.36 (t, 2H), 7.16 (m, 3H), 7.05 (d, 2H), 6.85 (d, 2H). Elemental analysis: Anal. Calc. for $C_{35}H_{25}N_5$: C 81.53, H 4.84, N 13.58%. Found: C 81.01, H 4.77, N 13.35%. Selected IR (KBr pellet, cm^{-1}): 3313(m), 3050 (w), 3025 (w), 1592 (m), 1560 (m), 1494 (s), 1466 (m), 1433 (s), 1269 (m), 1236 (m), 1152 (m), 1080(m), 1054(m), 815 (m), 759 (s), 698 (m), 637(m), 576 (w).

Synthesis of $Ag_4(^{py}PDP^{ph})_2$. Reaction of Ag_2CO_3 (232 mg, 1 mmol) and 2,2'-dithiodibenzoic acid (306 mg, 0.5 mmol) in 5 mL DMF and 1 mL aqueous ammonia (25%) under ultrasonic treatment (160W, 40 KHz, 30 min, 40 ^{o}C). The resultant solution was allowed slowly to evaporate at room temperature for two weeks to give

yellow crystals of **$Ag_4(^{py}PDP^{ph})_2$**. The crystals were isolated by filtration and dried in air. Yield: Ca. 15% based on Ag. Elemental analysis: Anal. Calc. for $C_{70}H_{46}Ag_4N_{10}$: C 57.64, H 3.18, N 9.6%. Found: C 57.83, H 3.07, N 9.42%. Selected IR (KBr pellet, cm^{-1}): 3062 (w), 3020 (w), 1593 (m), 1565 (m), 1527 (m), 1459 (s), 1427 (s), 1334 (m), 1297 (m), 1216 (m), 1154 (m), 980 (m), 810 (m), 754 (s), 631 (m), 588 (w).

Single-crystal X-ray structure determination

Single crystals of **$H_2{}^{py}PDP^{ph}$** and **$Ag_4(^{py}PDP^{ph})_2$** with appropriate dimensions were chosen under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) before being mounted on a glass fiber for data collection. Data collection was performed on a Agilent Gemini/Xcalibur single-crystal diffractometer equipped with a graphite-monochromated Mo Kα radiation source (λ = 0.71073 Å). Data reductions were performed using the CrysAlisPro software.[S2] The structure was solved using the charge-flipping algorithm, as implemented in the program SUPERFLIP[S3] and refined by full-matrix least-squares techniques against F_o^2 using the SHELXL program[S4] through the OLEX2 interface.[S5] Hydrogen atoms at carbon were generated geometrically and refined with isotropic temperature factors. The structure was examined using the Addsym subroutine of PLATON[S6] to ensure that no additional symmetry could be applied to the models. Selected crystallographic data are summarized in **Table S1**. More details on crystallographic information are available at the Cambridge Crystallographic Data Centre with CCDC numbers of 2250233 (**$H_2{}^{py}PDP^{ph}$**) and 2250234 (**$Ag_4(^{py}PDP^{ph})_2$**).

Computational details

Full geometry optimizations of **$Ag_4(^{py}PDP^{ph})_2$** was performed by density functional theory (DFT) calculations using the ORCA 4.0 version program package[S7] with the BP86 functional[S8] and the all-electron Def2-SVP set from EMSL Basis Set Exchange Library.[S9] The input coordinates were obtained from the X-ray single crystal structure data. Their optimized geometries were characterized as a minimum by vibrational analysis.

[Fig. S1-Fig. S7] & [Table S1-Table S2]

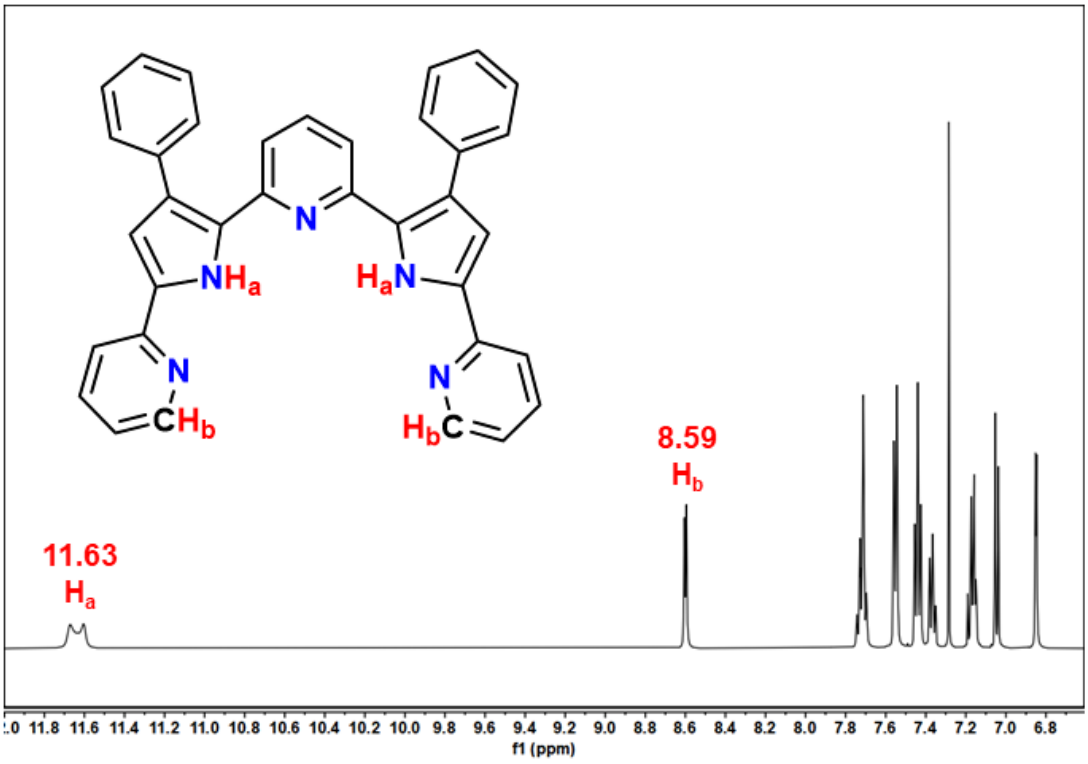

Fig. S1 ^{1}H NMR spectrum of $\mathbf{H_2^{py}PDP^{ph}}$.

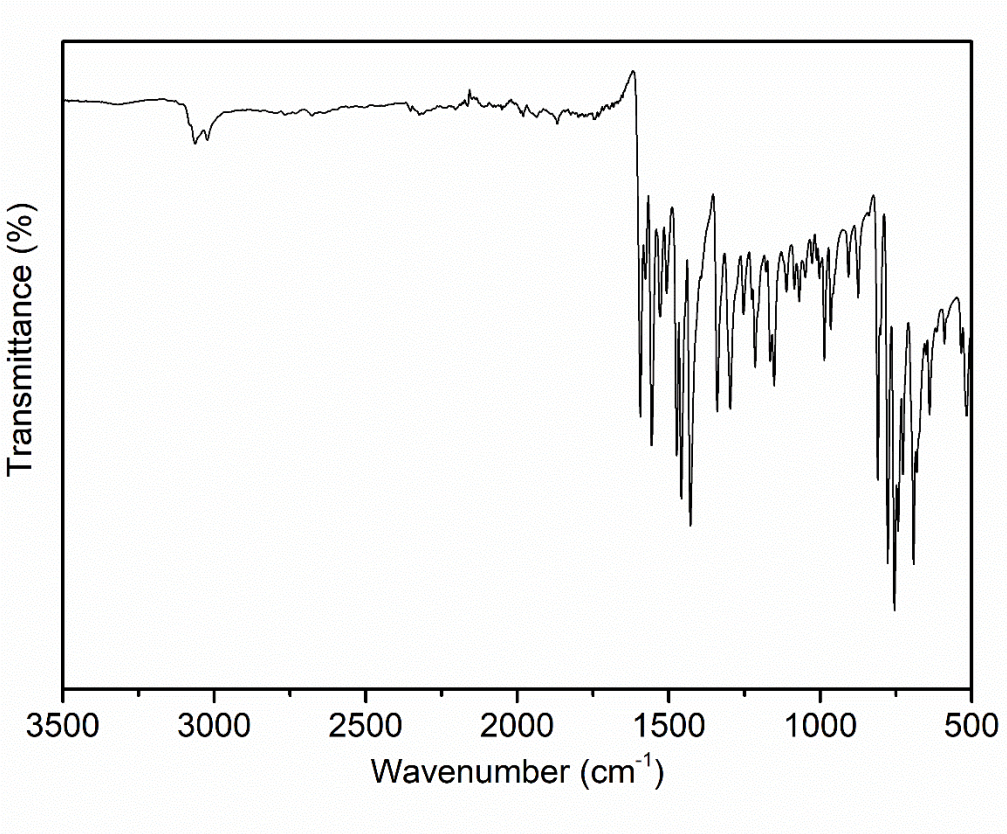

Fig. S2 FT-IR spectrum of $\mathbf{Ag_4(^{py}PDP^{ph})_2}$.

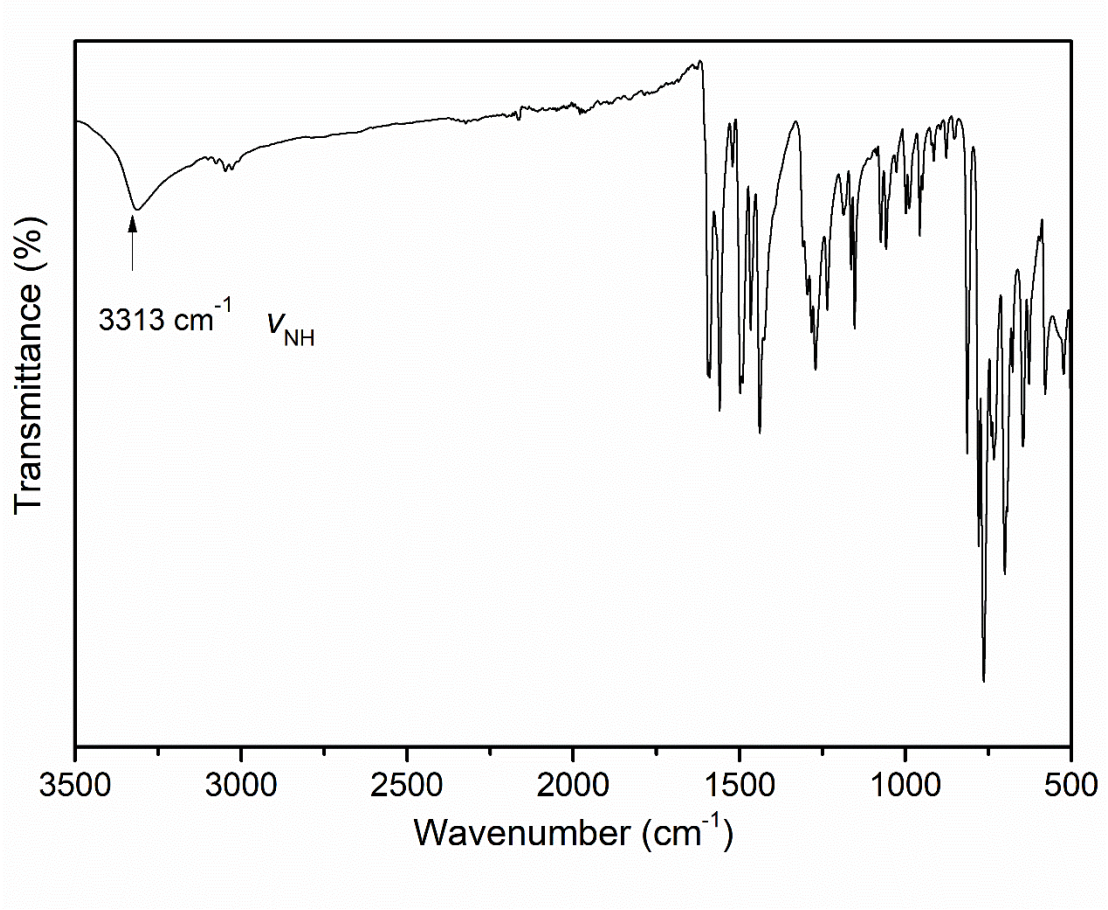

Fig. S3 FT-IR spectrum of $\mathbf{H_2^{py}PDP^{ph}}$.

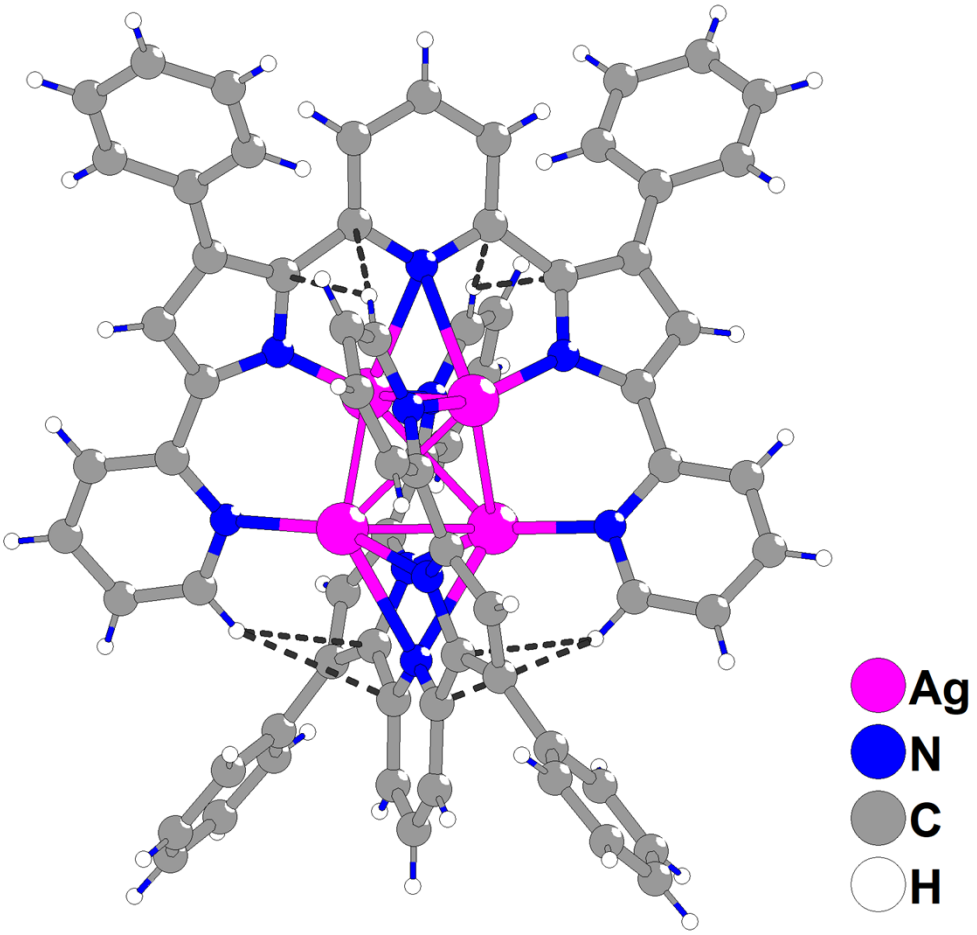

Fig. S4 Nonclassical bifurcated type C(sp^2)-H···C(sp^2) contacts are observed in the **$Ag_4(^{py}PDP^{ph})_2$** in which C-H moiety of side-arm pyridyl groups of one pincer ligand is connected to one pyrrole ring C atom and the central pyridine ring C atom from the other pincer ligand.

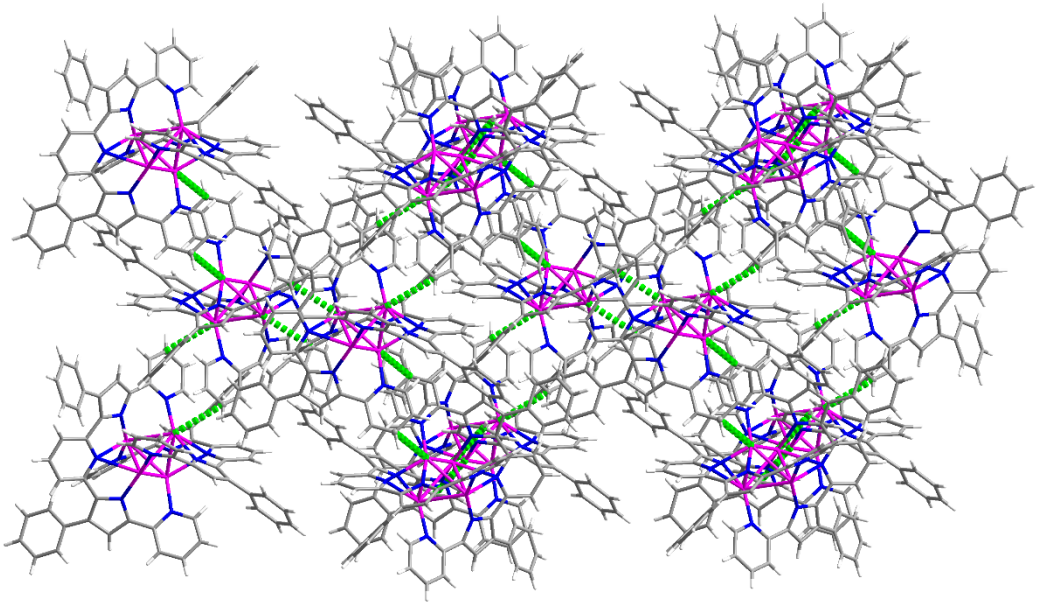

Fig. S5 $Ag^{+}\cdots\pi$ interactions (in green dotted lines) are observed in the folded sheet.

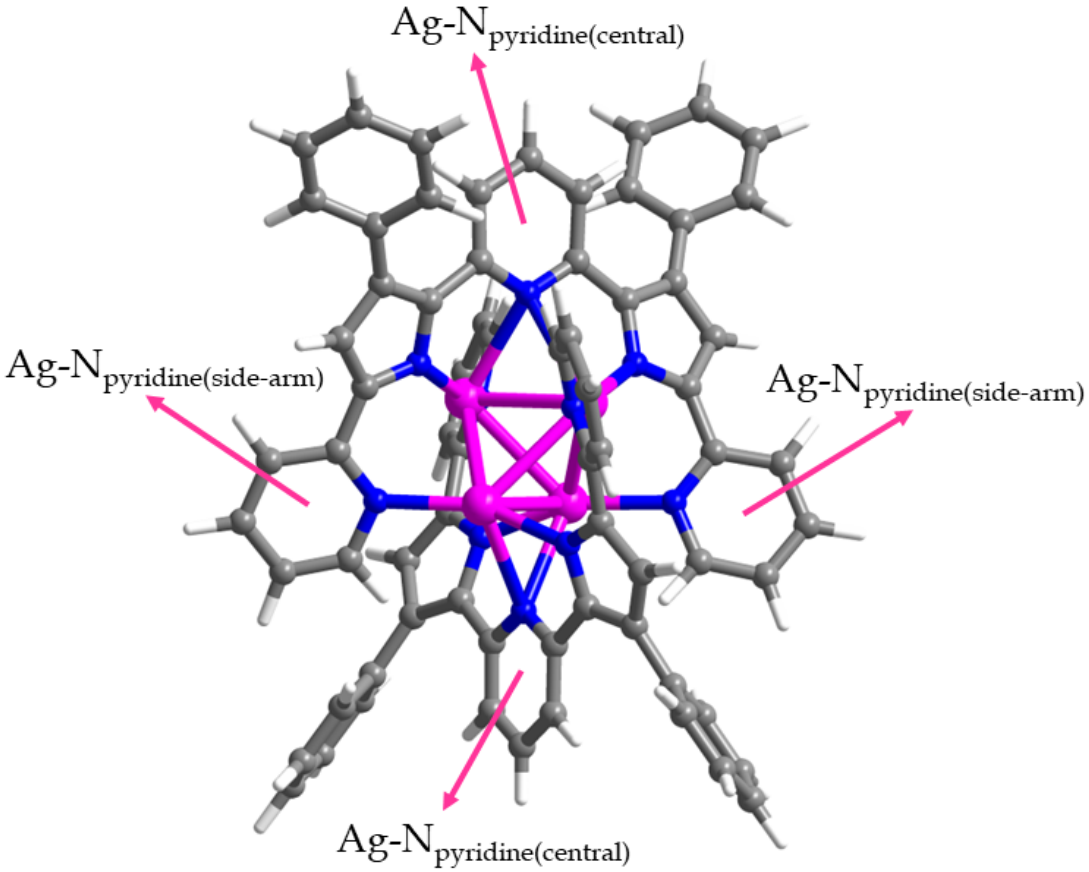

Fig. S6 DFT-optimized $\mathbf{Ag_4(^{py}PDP^{ph})_2}$. Color codes: Ag, pink; N, blue; C, grey; H, white.

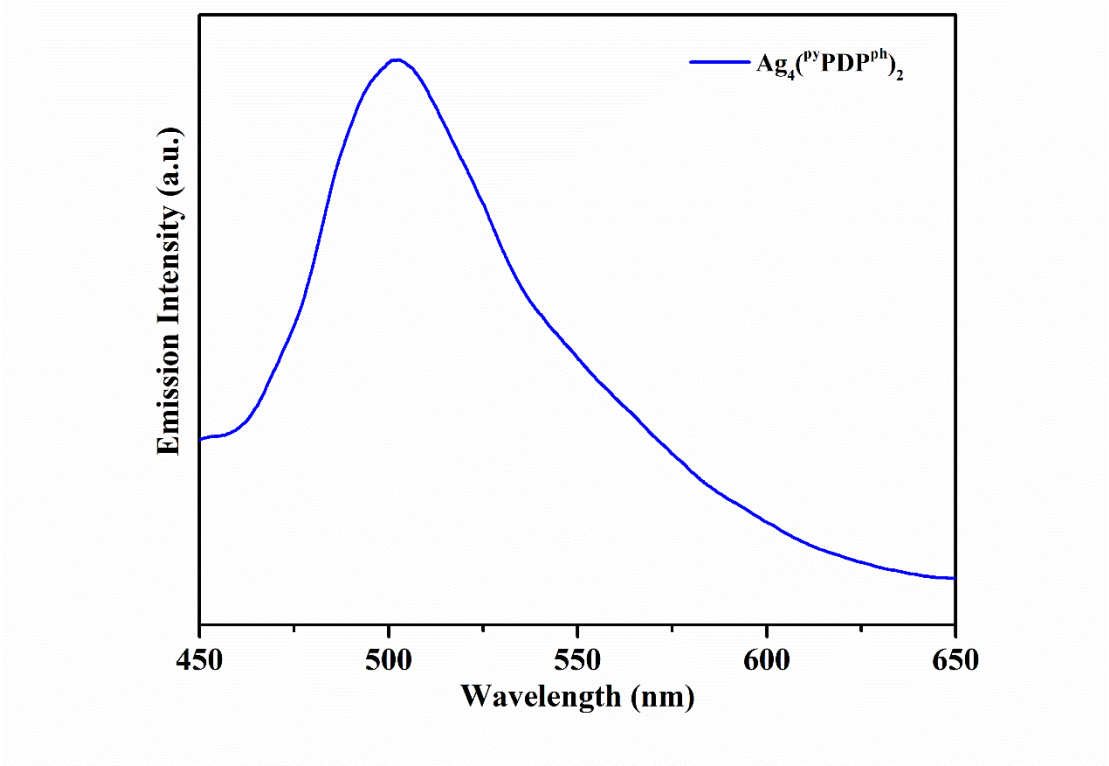

Fig. S7 Emission spectra of $\mathbf{Ag_4(^{py}PDP^{ph})_2}$ in the solid state.

Table S1 Crystallographic data and structure refinements results for $\mathbf{H_2^{py}PDP^{ph}}$ and $\mathbf{Ag_4(^{py}PDP^{ph})_2}$

	$\mathbf{H_2^{py}PDP^{ph}}$	$\mathbf{Ag_4(^{py}PDP^{ph})_2}$
Empirical formula	$C_{35}H_{27}N_5O$	$C_{70}H_{46}Ag_4N_{10}$
Formula weight	533.61	1458.685
Temperature/K	173.00	173.01(10)
Crystal system	monoclinic	tetragonal
Space group	$P2_1/n$	$I4_1/a$
a/Å	14.8674(14)	17.4174(2)
b/Å	13.0593(9)	17.4174(2)
c/Å	15.2619(12)	18.9309(3)
α/°	90	90
β/°	110.215(9)	90
γ/°	90	90
Volume/Å^3	2780.7(4)	5742.99(13)
Z	4	4
ρ_{calc}g/cm^3	1.275	1.687
μ/mm^{-1}	0.079	11.205
F(000)	1120.0	2908.1
Crystal size/mm^3	0.1 × 0.08 × 0.05	0.18 × 0.12 × 0.1
Radiation	Mo Kα (λ = 0.71073)	Cu Kα (λ = 1.54184)
2θ range for data collection/°	6.858° to 58.816°	6.9° to 152.98°
Index ranges	-17 ≤ h ≤ 18, -17 ≤ k ≤ 16, -17 ≤ l ≤ 21	-21 ≤ h ≤ 17, -21 ≤ k ≤ 15, -19 ≤ l ≤ 23
Reflections collected	14155	18744
Independent reflections	6480 [R_{int} = 0.0306, R_{sigma} = 0.0648]	2969 [R_{int} = 0.0425, R_{sigma} = 0.0230]
Data/restraints/parameters	6480/0/374	2969/0/191
Goodness-of-fit on F^2	1.025	1.081
Final R indexes [I>=2σ (I)]	R_1 = 0.0635, wR_2 = 0.1128	R_1 = 0.0282, wR_2 = 0.0683
Final R indexes [all data]	R_1 = 0.1573, wR_2 = 0.1494	R_1 = 0.0326, wR_2 = 0.0718

Table S2 Selected metric parameters for $\mathbf{Ag_4(^{py}PDP^{ph})_2}$ and the DFT-computed $\mathbf{Ag_4(^{py}PDP^{ph})_2}$.

	X-ray diffraction	DFT calculation
Ag-Ag / Å	3.0206(4)-3.0319(4)	3.0391-3.0561
$Ag\text{-}N_{pyrrole}$ / Å	2.154(2)	2.160
$Ag\text{-}N_{pyridine}$(side-arm) / Å	2.188(2)	2.204
$Ag\text{-}N_{pyridine}$(central) / Å	2.634(3)	2.689

Supplementary references

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