Supplementary Information

A precise hexagonal octadecanuclear Ag macrocycle with significant luminescent properties†

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Materials and general procedures

All chemicals were commercially available and used as purchased. Ligand = 1,3,5-tris(triazol-1-ylmethyl)-2,4,6-trimethylbenzene (TTTMB) was prepared according to the literature.[1] IR data were recorded on a BRUKER TENSOR 27 spectrophotometer with KBr pellets in the region of 400–4000 cm-1.Elemental analyses (C, H and N) were carried out on a Flash EA 1112 elemental analyzer. Themogravimetric analyses were carried out with a NETZSCH STA 409 unit at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. X-ray powder diffraction measurements were recorded on a Philips X'pert PRO SUPER X-ray diffractometer using graphite monochromatized CuKα radiation (λ = 1.541874 Å). Single-crystal X-ray diffraction was performed using a Rigaku Saturn CCD diffractometer equipped with graphite monochromated MoKα radiation (λ = 0.71073 Å). The solid-state photoluminescence measurements were carried out on Edinburgh Analytical Instruments FLSP920 (Spectrofluorimeter). The photoluminescence in DMSO solution were measured at room temperature using a F-4500 HITACHI Fluorescence Spectro-135 photometer. UV-vis spectra were recorded on a SHIMADZU UV-3100 spectrophotometer.

1 J. L. Du, T. L. Hu, S. M. Zhang, Y. F. Zeng, X. H. Bu, *CrystEngComm*, 2008, ***10***, 1866–1874.

Synthesis of complex 1

A mixture of $AgNO_3$ (0.0170 g, 0.1 mmol), TTTMB (0.0363 g, 0.1 mmol), o-phthalate (0.0166 g, 0.1 mmol), and deionized water (10 mL) was sealed in a 15 mL Teflon-lined stainless steel reactor. The reactor was heated at 130 °C for 72 h and then cooled to room temperature at the rate of 5 °C /h. A large amount of light-yellow crystals of **1** were obtained (yield: 71%, based on silver). Anal. Calcd (Found) for **1**: C, 32.84 (33.12); H, 3.22 (3.80); N, 22.34 (22.39)%. IR (KBr): 3438 (m), 3085 (m), 1562(m), 1514(m), 1382(s), 1274(m), 1205(w), 1132(m), 1030(w), 1009(m), 810(w), 699(w), 677(m), 644(w).

Crystal data for 1: Crystal dimensions 0.19 × 0.18× 0.16 mm, $C_{72}H_{84}Ag_6N_{42}O_{28}$, Mr = 2633.03, trigonal, space group P6/m, a = b = 26.362(4) Å, c = 17.809(4) Å, V = 10718(3) $Å^3$, Z = 3, T = 113(2) K, λ = 0.71073Å 61090 reflections collected, 6225 unique (R_{int} = 0.0419). Final GooF = 1.023, R1 = 0.0991, wR2 = 0.3036. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by using geometrical restrains. Two of nitrate anions in **1** was treated as disorder and refined with restraints on bond lengths. For **1**, SQUEEZE was used to remove the contributions of disordered water molecules. See the CIF file for details.

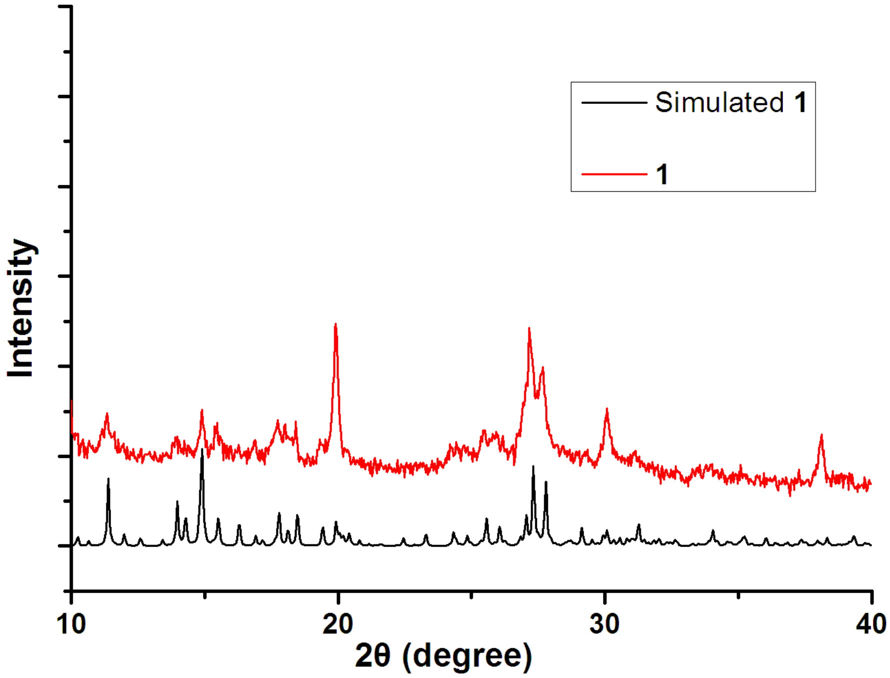

Fig. S1. PXRD patterns of **1** simulated from X-ray single-crystal data (bottom), and experiment data (top).

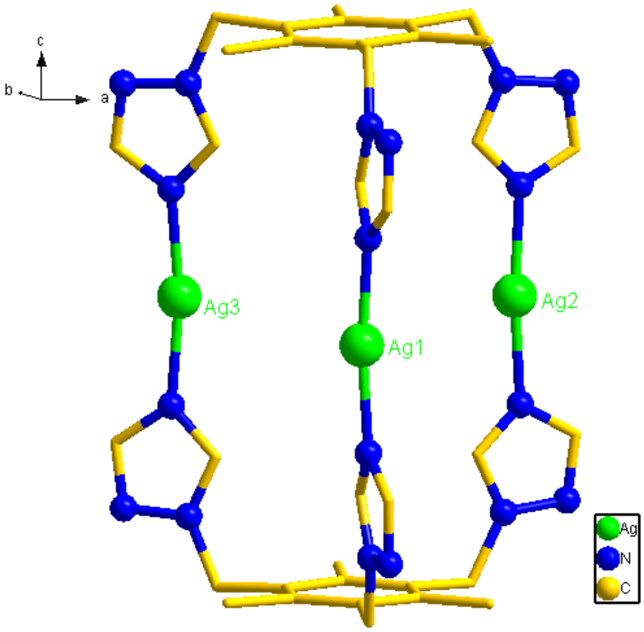

Fig. S2 Trinuclear building unit $Ag_3(TTTMB)_2$. Hydrogen atoms are omitted for clarity.

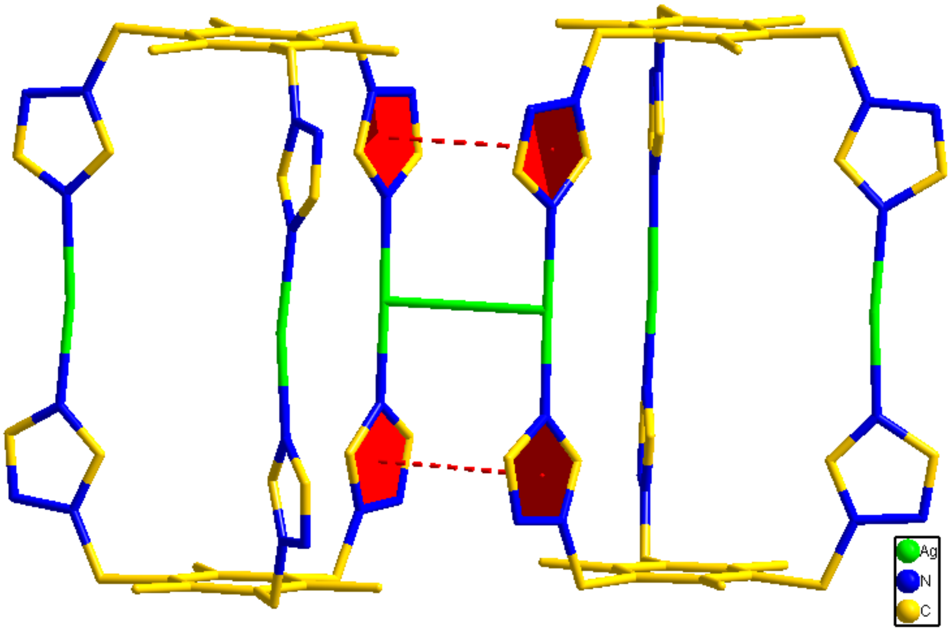

Fig. S3 π-π stacking interactions in **1**. Hydrogen atoms are omitted for clarity.

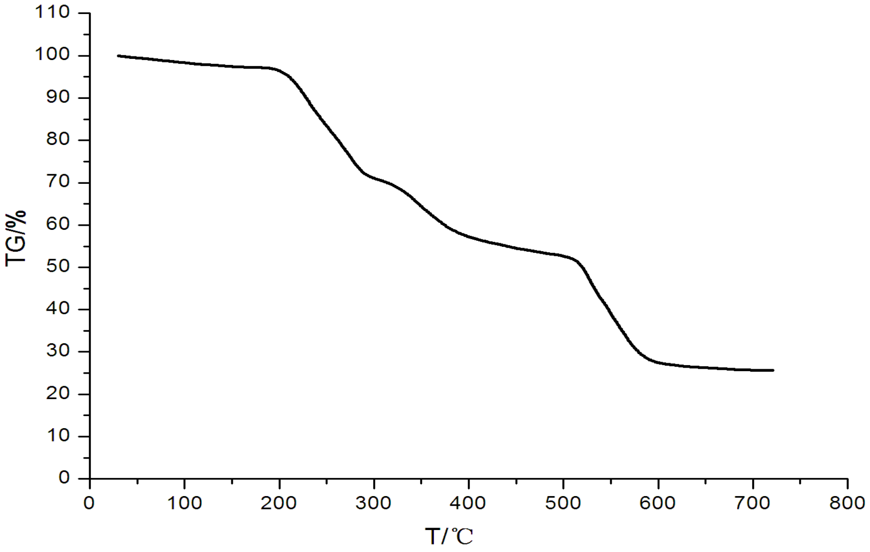

Fig. S4. TGA of **1**.

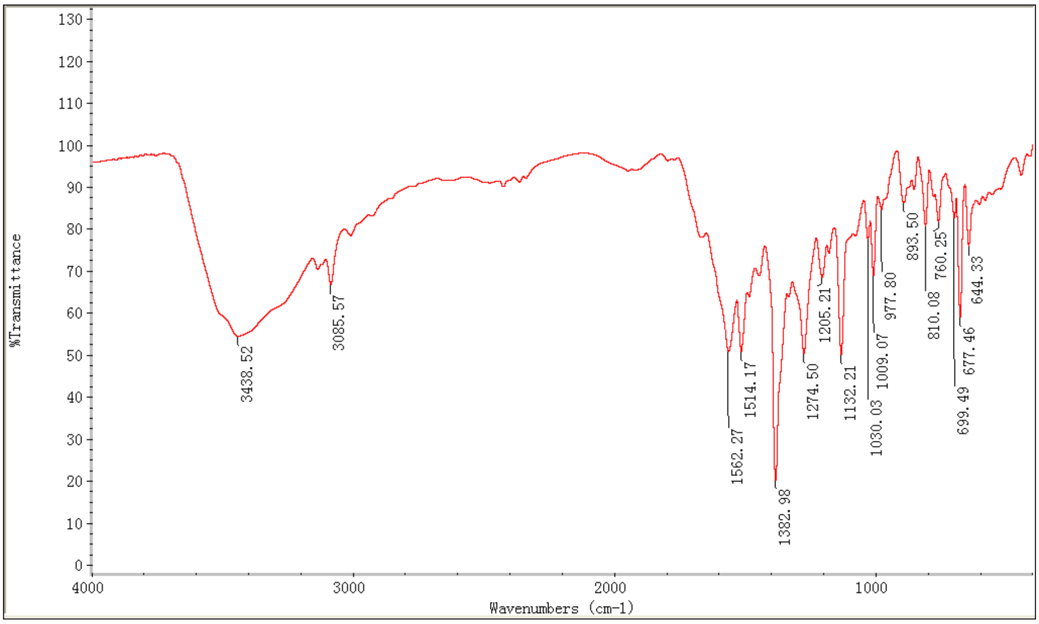

Fig. S5. IR spectra of **1**.

The origin of the unique photophysical properties derives from the $[Ag_{18}(TTTMB)_{12}]^{18+}$ or the trinuclear $[Ag_3(TTTMB)_2]^{3+}$?

Fortunately, we have obtained the trinuclear complex $[Ag_3(TTTMB)_2]^{3+}$ **2** (Fig. S6), and collected absorption and emission data of **2**. As shown in Figs. S7 and S8, we find that the photophysical properties of **2** are in nice agreement with those of the free ligand TTTMB. Therefore, we suggest the absorption/emission bands are ascribed to intraligand (IL) transition, which are different from those of **1**. So, we have determined the unique properties of **1** derive from the supramolecular unit $[Ag_{18}(TTTMB)_{12}]^{18+}$ rather than the trinuclear building unit $[Ag_3(TTTMB)_2]^{3+}$.

Synthesis of complex 2

A mixture of $AgClO_4$ (0.0104 g, 0.05 mmol), TTTMB (0.0181 g, 0.05 mmol), 1,3,5-benzenetricarboxylic acid (0.0105 g, 0.05 mmol), and deionized water (8 mL) was sealed in a 15 mL Teflon-lined stainless steel reactor. The reactor was heated at 130 °C for 72 h and then cooled to room temperature at the rate of 5 °C /h. The colorless crystals of **2** were obtained (yield: 34%, based on silver).

Crystal data for 2: Crystal dimensions 0.28 × 0.24× 0.21 mm, $C_{45}H_{42}Ag_3Cl_2N_{18}O_{15}$, Mr = 1469.48, Monoclinic, space group P 21/m, a = 11.978(2) Å, b = 14.054(3) Å, c= 18.062(4) Å, β=108.83(3) , V = 2877.9(10) Å^3, Z = 2, T = 293(2) K, λ = 0.71073 Å, 29147 reflections collected, 5287 unique (R_{int} = 0.0305). Final GooF = 1.178, R1 = 0.0923, wR2 = 0.2680. All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at geometrically calculated positions and refined with isotropic thermal parameter.

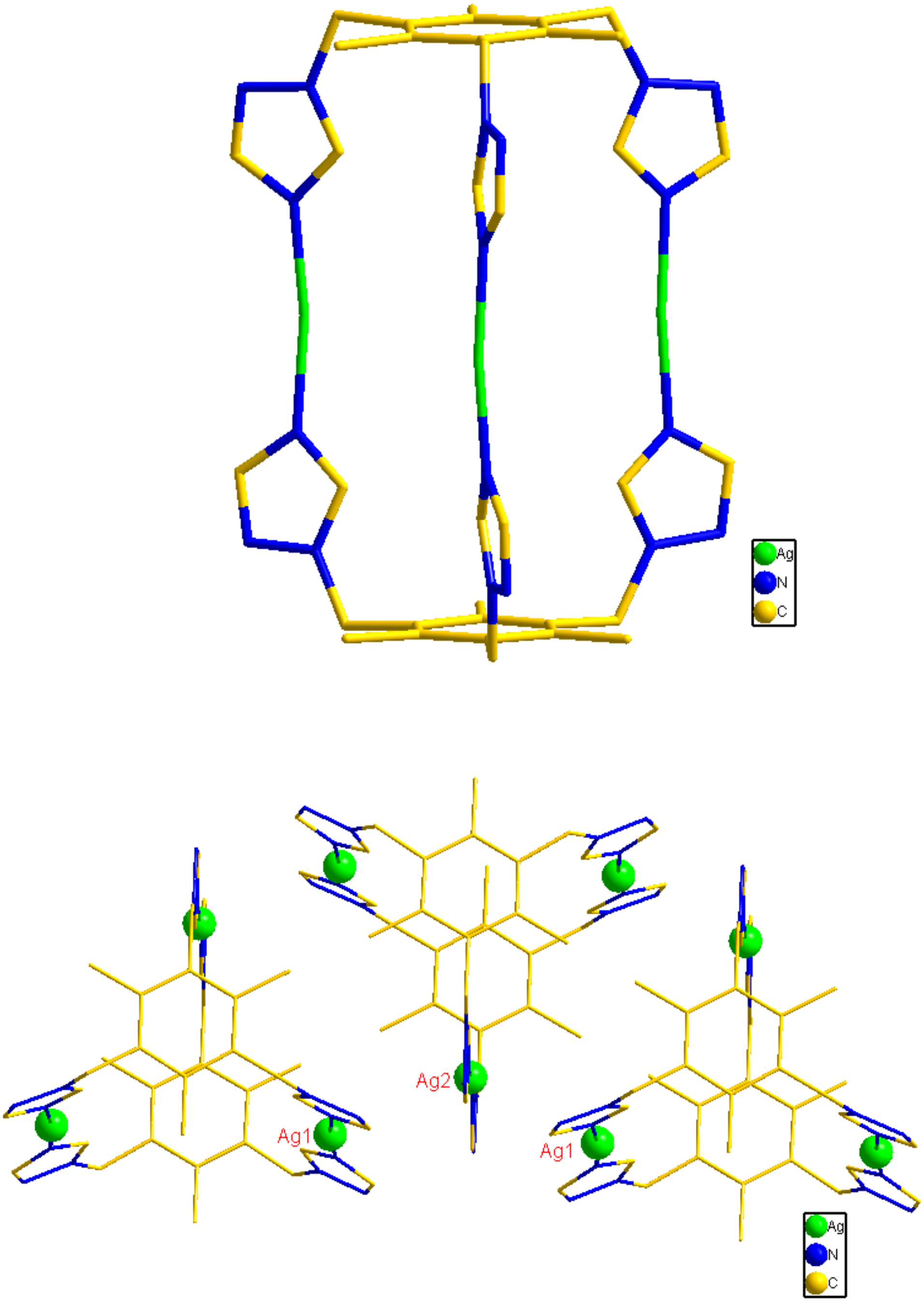

Fig. S6 (top) The structure of **2**. For clarity, the dissociative1,3,5-benzenetricarboxylic acid, the guest perchlorate anions and water molecules including H atoms have been omitted. (bottom) It shows no the Ag–Ag interactions in **2**, because the distance between the nearest Ag atoms [For Ag1–Ag2] is 5.036(16) Å. For clarity, the dissociative1,3,5-benzenetricarboxylic acid, the guest perchlorate anions and water molecules including H atoms have been omitted.

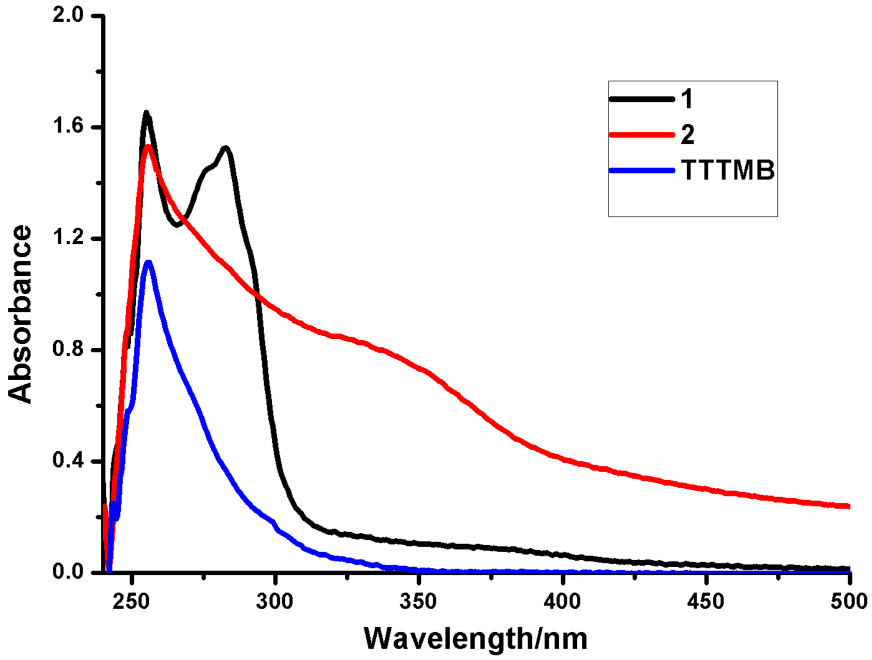

Fig. S7. UV-Vis spectral traces of **1**, **2** and **TTTMB** (2.5×10^{-4} M) in DMSO solution.

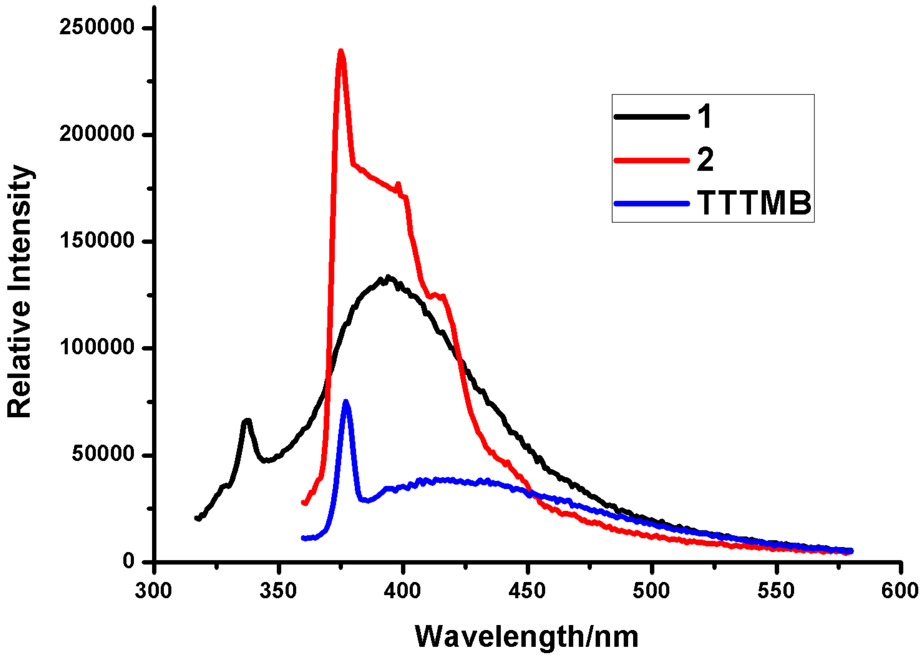

Fig. S8. Emission spectra of **1**, **2** and **TTTMB** (2.5×10^{-4} M) in DMSO solution.

Computational studies.

To better understand the luminescent properties of **1**, the molecular orbital MO calculations[1] were employed to the dimeric unit [Ag$_3$(TTTMB)$_2$]$_2^{6+}$ of **1** and the free ligand TTTMB based on the experimental geometry. The spatial plots of the HOMO and LUMO for the dimeric unit and TTTMB together with the orbital energies are depicted in Fig. S9. The HOMO of ligand TTTMB is contributed by the π orbitals of the benzene and triazole groups, and the LUMO is mainly associated with the π* orbitals from the benzene ring. We can confirm from the figure that the emissions of TTTMB are assigned to originate from the IL [π→π*] excited states. While the HOMO and HOMO−1 of the dimeric unit [Ag$_3$(TTTMB)$_2$]$_2^{6+}$ of **1** consist mainly of the π orbitals of the benzene rings, and the LUMO and LUMO+1 are mainly associated with the Ag–Ag interactions within the complex, mixed with the Ag–N (from triazole groups) σ* orbits (Fig. S10). Therefore, we may suggest that the emission in **1** mainly originate from the ligand-to-metal–metal charge transfer (LMMCT) characters, admixed with intraligand (IL) transitions. This is essentially consistent with the experimental measurements.

It is noteworthy that compared with the ligand TTTMB (5.796 eV), the HOMO ± LUMO gap of the dimeric unit [Ag$_3$(TTTMB)$_2$]$_2^{6+}$ (4.082 eV) exhibits a significant reduction. And it is consistent with the luminescence measurements.

Calculation details: Density functional calculations were performed, employing the Gaussian 03 suite of programs,[2] at the Becke3LYP (B3LYP) level. The basis set used for C, O, N and H atoms was 6±31G while effective core potentials with a LanL2DZ basis set were employed for transition metals.

[1] (a) Keith Man-Chung Wong, Ling-Ling Hung, Wai Han Lam, Nianyong Zhu, and Vivian Wing-Wah Yam, *J. Am. Chem. Soc.*, 2007, 129, 4350-4365; (b) Shao-Liang Zheng, Jie-Peng Zhang, Xiao-Ming Chen, Zhen-Li Huang, Zhen-Yang Lin, and Wing-Tak Wong, Chem. Eur. J. 2003, 9, 3888–3896; (c) Sammual Yu-Lut Leung, Wai

Han Lam, Nianyong Zhu, and Vivian Wing-Wah Yam, *Organometallics,* 2010, 29, 5558–5569; (d) Xi Liu, Guo-Cong Guo, Ming-Lai Fu, Xue-Hui Liu, Ming-Sheng Wang, and Jin-Shun Huang, *Inorg. Chem.,* 2006, 45, 3679-3685.

[2] M. J. Frisch, et al. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

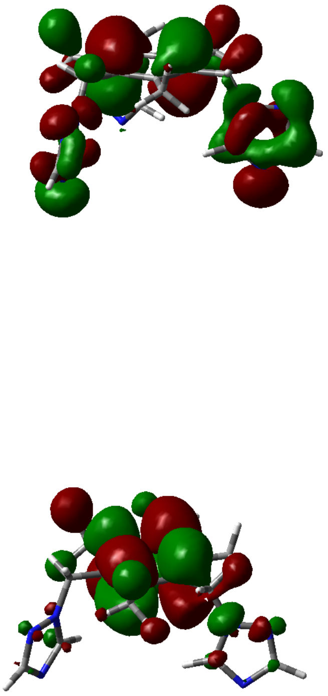

Fig. S9. TTTMB: (top) HOMO (-7.007 eV). (bottom) LUMO (-1.223 eV)

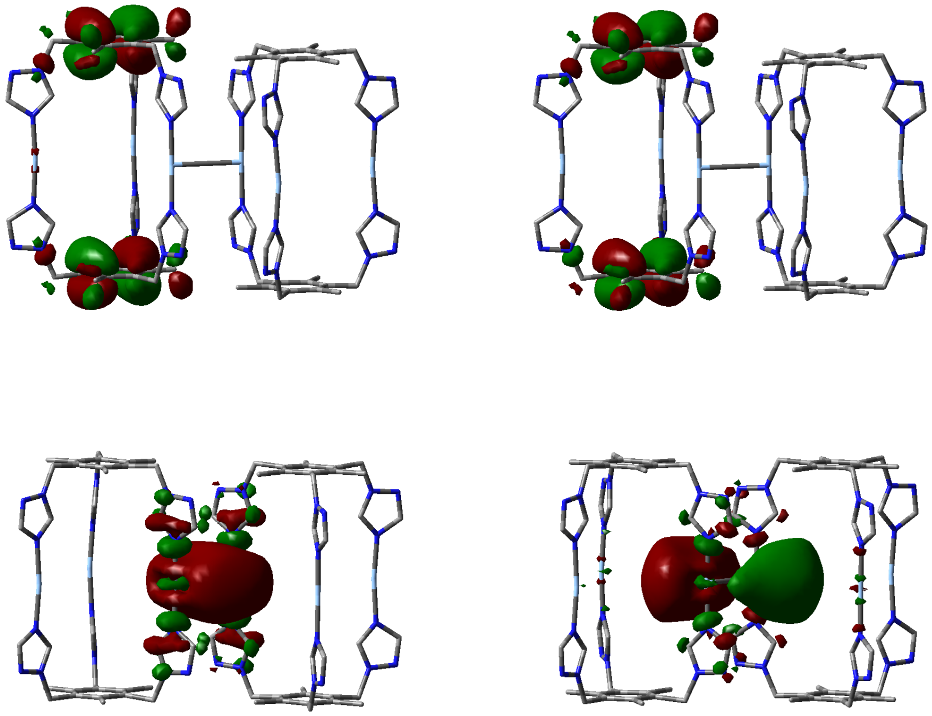

Fig. S10. $[Ag_3(TTTMB)_2]_2^{6+}$**:** (left upper) HOMO (-17.44 eV); (right upper) HOMO-1; (lower left) LUMO (-13.34 eV); (lower right) LUMO+1

UV-vis absorption spectroscopy at room temperature.

The electronic absorption spectrum of **1** shows two absorption bands at 254-256 nm and 283 nm in DMSO solution (Fig. S11). The high energy absorption bands at 254-256 nm are ascribed to intraligand (IL) transition, since free TTTMB ligand also absorbs strongly in this region. The low energy absorption bands at 283 nm are assigned as MLCT or LMCT. However, the π* levels for the TTTMB ligand (-1.223 eV, LUMO) are very high, which indicates that the π* of the TTTMB ligand is not likely to be the acceptor orbital.[1] So a MLCT excited-state assignment can be precluded. It is noted **1** exhibits an intense absorption band at 254-255 nm and a absorption shoulder at 283 nm at the concentration of 1.0×10^{-5}–2.5×10^{-4} M. However, when the concentration is up to 5.0×10^{-4} M, it shows an intense absorption band at 283 nm and a absorption shoulder at 256 nm, which is different from those of the concentration of 1.0×10^{-5}–2.5×10^{-4} M. It is mainly related to the Ag–Ag interactions within the complex. It is believed that the Ag–Ag interactions within the complex may enhance with increasing concentration, which play an important role in the low energy absorption bands. Therefore, the low energy absorption bands are assigned as LMCT, modified by the Ag–Ag interactions.

[1] V. W. W. Yam, K. K. W. Lo, *Chem. Soc. Rev.*, 1999, 323–334.

Luminescence spectroscopy at room temperature.

The photoluminescent properties of **1** at various concentrations in DMSO solution have been studied. As shown in Fig. S12, **1** exhibits interesting luminescence at 340-398 upon excitation at 290-308nm. Clear to see, there are a decrease of the intensity of the high energy emission bonds and a increase of the intensity of the low energy emission bonds with increasing concentration, except for the high energy emission bond at the concentration of 2.5×10^{-5} M. It is considered that the Ag–Ag interactions within the complex would mainly attribute to the emission with increasing concentration. Herein, the high energy emission bonds are ascribed to intraligand (IL) transition. It is because the intensity and shape of the high energy emission bonds are like those of the ligand TTTMB. The low energy emission bonds are assigned as LMCT, modified by the Ag–Ag interactions, which is suggested by MO calculations.

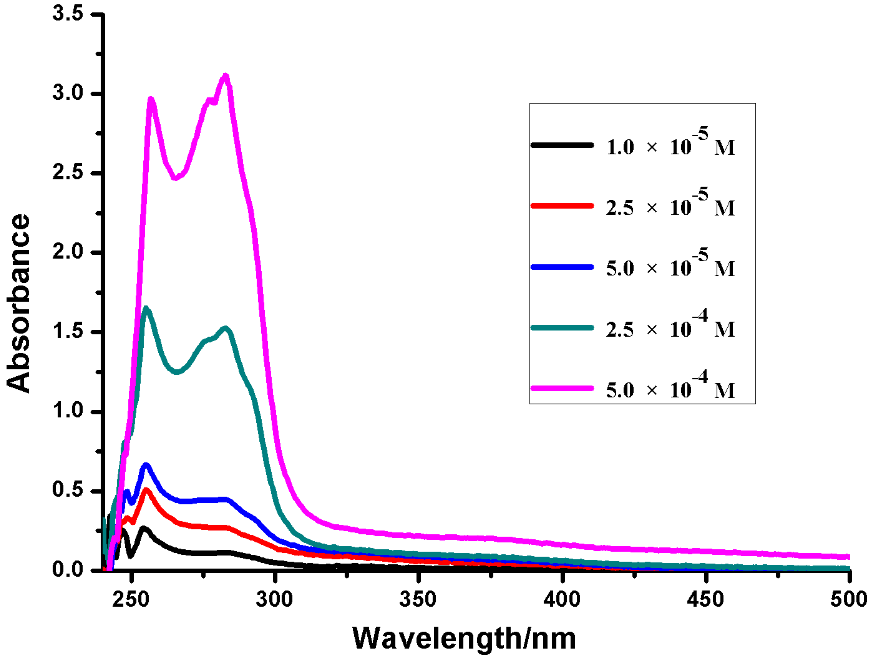

Fig. S11. UV-Vis spectral traces of **1** at various concentrations in DMSO solution.

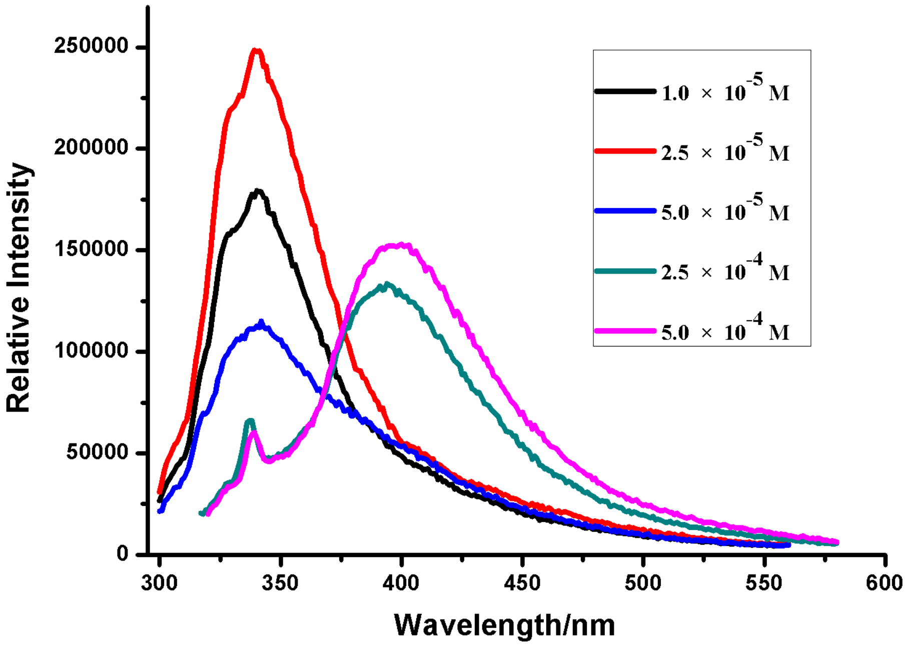

Fig. S12. Emission spectra of **1** at various concentrations in DMSO solution

Table 1 Photophysical data for **1**, **2** and TTTMB in DMSO solution

Complex	absorption λ_{max} /nm	excitation λ_{max} /nm	emission λ_{max} /nm	concentration /M
1	254, 283sh	290	340	1.0×10^{-5}
1	255, 283sh	298	340	2.5×10^{-5}
1	255, 283sh	298	347	5.0×10^{-5}
1	255, 283sh	307	394, 337sh	2.5×10^{-4}
1	283, 256sh	308	398, 339sh	5.0×10^{-4}
2	255	340	377	2.5×10^{-4}
TTTMB	255	340	377	2.5×10^{-4}