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Influence of C-H···π interaction on the solid–state [2+2] cycloaddition reaction of a Ag(I) coordination complex in an inorganic co-crystal

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Supporting Information

Synthesis of $[Ag_2(dppm)(4\text{-}SP)_2][Ag_2(dppm)_2]_{0.5}(BF_4)_3\cdot 2(THF)$, 1

$AgBF_4$ (19 mg, 0.1 mmol), 4-SP (18 mg, 0.1 mmol) and dppm (19 mg, 0.05 mmol) were stirred in 6 mL THF for an hour. No significant ppt was formed. Diffraction quality single crystals were obtained by diffusing either hexane or ether over this clear solution. Yield 70%. Analysis found (%): C 54.36, H 4.25, N 1.91; $C_{84}H_{82}Ag_3B_3F_{12}N_2O_2P_4$ requires C 54.26, H 4.44, N 1.51.

Synthesis of $[Ag_2(4\text{-}SP)_2(dppe)(TFA)_2]$, 3

Ag-TFA (22 mg, 0.1 mmol), 4-SP (18 mg, 0.1 mmol) and dppe (20 mg, 0.05 mmol) were stirred in 6 mL THF for 1 h. No ppt was formed. Diffraction quality single crystals were obtained by diffusing hexane over this clear solution. Yield 64%. Analysis found (%): C 56.03, H 3.46, N 2.51; $C_{56}H_{46}Ag_2F_6N_2O_4P_2$ requires C 55.93, H 3.86, N 2.33.

The NMR spectra were recorded with a Bruker ACF 300FT-NMR spectrometer with TMS as internal reference. Thermogravimetric analyses (TGA) were recorded on a TA Instrument SDT 2960 TGA Thermal Analyzer. The samples were heated at a constant rate of 5°C min^{-1} from room temperature under continuous flow nitrogen gas. Elemental analyses were performed in the Micro Analytical Laboratory, Department of Chemistry, National University of Singapore.

The UV irradiation experiments were conducted by using Luzchem photoreactor (wavelength 350 nm, Intensity ~ 1.75 mW cm^{-2}). Single crystals or crushed crystals were packed gently between two pyrex glass slides and the UV irradiations were completed by flipping the packed glass slide pairs for each sample in half of their irradiation time interval to ensure uniform irradiation. The SCSC conversion was carried out using fibre optics of MAX-150 xenon light source (150 W) of 100% intensity and wave length range 280-350 nm.

X-ray Crystallography

Intensity data of the single crystals for structure determination, were collected on a Bruker APEX diffractometer attached with a CCD detector and graphite-monochromated MoKα (λ = 0.71073 Å) radiation. Empirical absorption corrections were applied with the data using the program SADABS[1] and the crystallographic package SHELXTL[2] was used for all calculations.

Crystallographic data for 1, 2 & 3

Compounds	**1** (CCDC 934071)	**2** (CCDC 934072)	**3** (CCDC 934073)
Formula	$C_{84}H_{82}Ag_3B_3F_{12}N_2O_2P_4$	$C_{84}H_{82}Ag_3B_3F_{12}N_2O_2P_4$	$C_{56}H_{46}Ag_2F_6N_2O_4P_2$
M	1859.44	1859.44	1202.63
T (K)	100(2)	100(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal syst.	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	11.776(2)	11.9171(9)	12.550(2)
b (Å)	13.134(2)	13.1457(10)	13.733(2)
c (Å)	25.916(4)	25.686(2)	14.479(3)
α (°°)	90.704(5)	90.637(2)	90
β (°°)	91.621(5)	89.989(2)	90.245(5)
γ (°°)	100.084(5)	99.454(2)	90
Volume (Å^3)	3944.2(12)	3969.1(5)	2495.4(8)
Z	2	2	2
D_{calcd} (g/cm^3)	1.566	1.556	1.601
μ (mm^{-1})	0.896	0.891	0.921
Reflns col.	13854	13994	5718
Reflections [$I > 2\sigma$]	11683	7210	5424
Goof on F^2	1.197	1.045	1.062
Final R[$I > 2\sigma$]^a			
R1	0.0963	0.0979	0.0326
wR2^b	0.2254	0.2360	0.0836

^{a} R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$, ^{b} wR2 = $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Structural Description of [Ag_2(4-SP)$_2$(dppe)(TFA)$_2$], 3

The dinuclear, discrete and neutral coordination complex [Ag_2(4-SP)$_2$(dppe)(TFA)$_2$], **3** (where dppe = bis(diphenyl) phosphino ethane) was obtained when dppe was used as auxiliary ligand instead of dppm. Both the Ag(I) are coordinated by one 4-SP and bridged by the dppe ligand. The coordination geometry at Ag(I) is triangular with the angles at the AgNOP core are 103.4(7)°, 114.1(5)° and 134.8(5)°, where Ag(I) occupies 0.36 Å above the NOP plane. In this compound dppe was found to adopt *transoid* form as shown in Fig. S1a. Thus the silver ions are far away to exert any argentophilic interaction. The TFA anions were found to coordinate Ag(I) in addition to balancing the charge. As there is no argentophilic interaction, 4-SP ligands are also found not to orient parallel and the shortest distance between the centres of two C=C bonds was found to be 7.31 Å. The solid state structure is stabilised by various π-π stacking interactions as shown in Fig. S1b. The pyridyl groups are found to stack parallel but oriented in opposite directions with a distance of 3.54 Å indicating significant π-π stacking interactions. On the other hand, the phenyl ring of 4-SP has partial interaction with the phenyl ring of dppe.

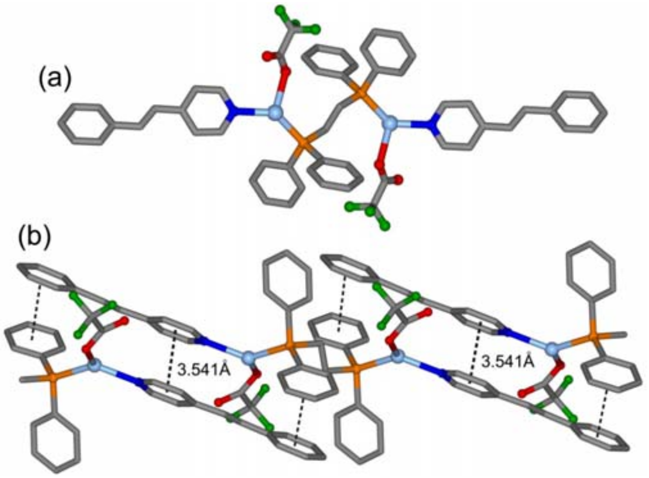

Fig. S1 (a) The structure of the discrete complex and (b) various interactions in **3**.

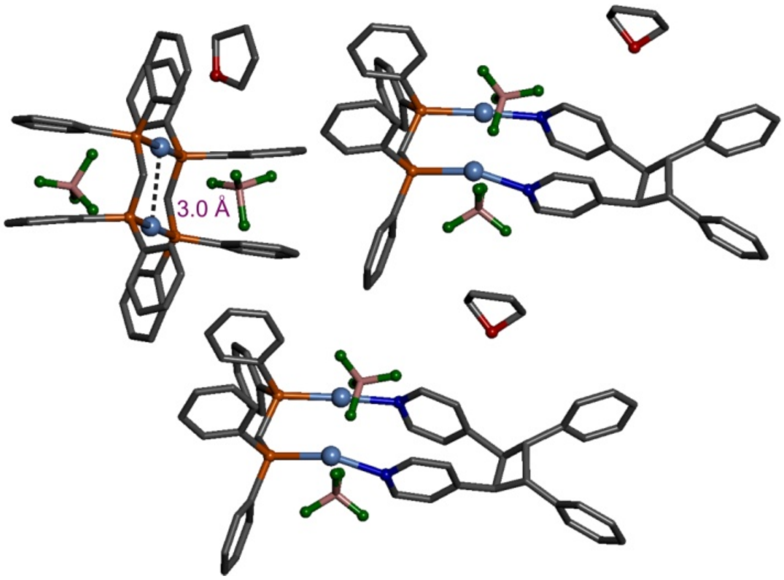

Fig. S2. Two discrete metal complex cations, $[Ag_2(dppm)(4,4'\text{-bpbpcb})]^{2+}$ and $[Ag_2(dppm)_2]^{2+}$ in the inorganic co-crystal of **2** obtained by SCSC reaction of **1**. After photodimaerization has taken place, the argentophilic interaction has been lifted from $[Ag_2(dppm)(4,4'\text{-bpbpcb})]^{2+}$ cation.

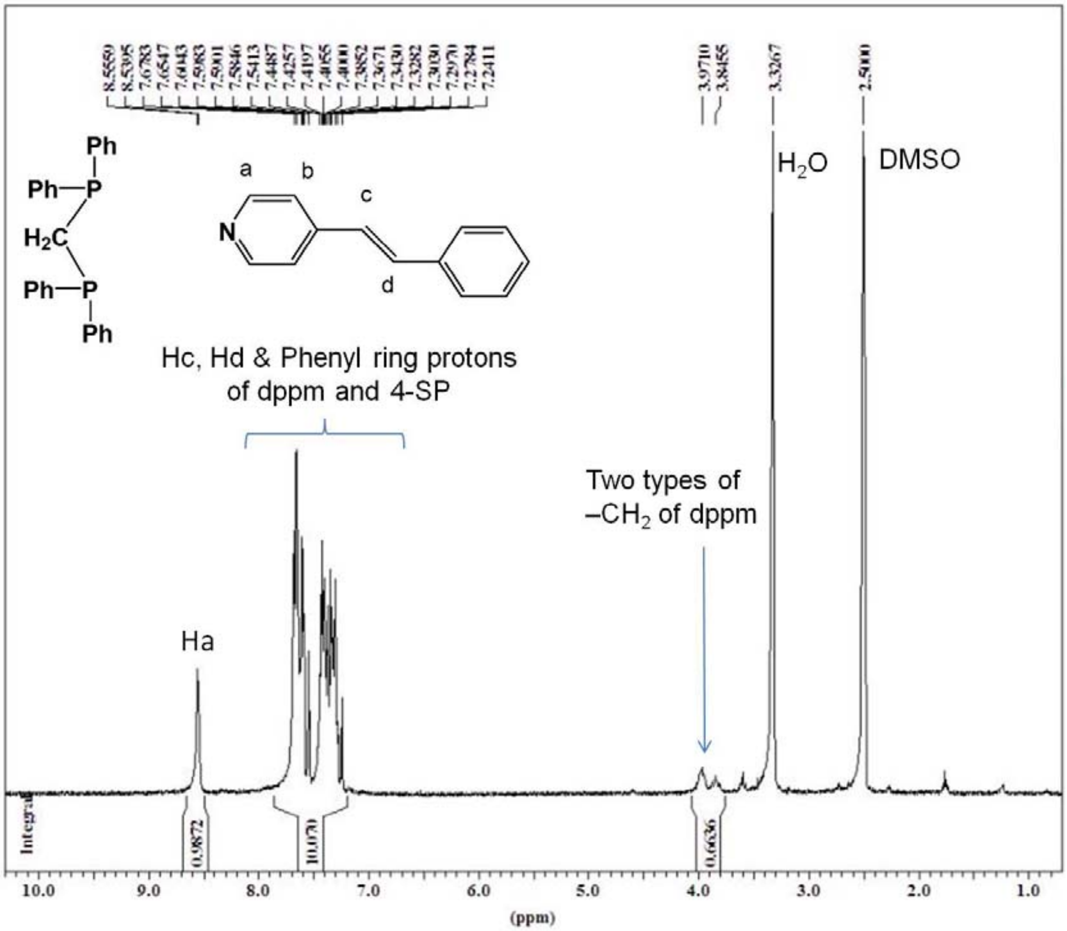

Fig. S3. ^1H NMR (300 MHz, d_6-DMSO) spectrum of **1** before UV irradiation.

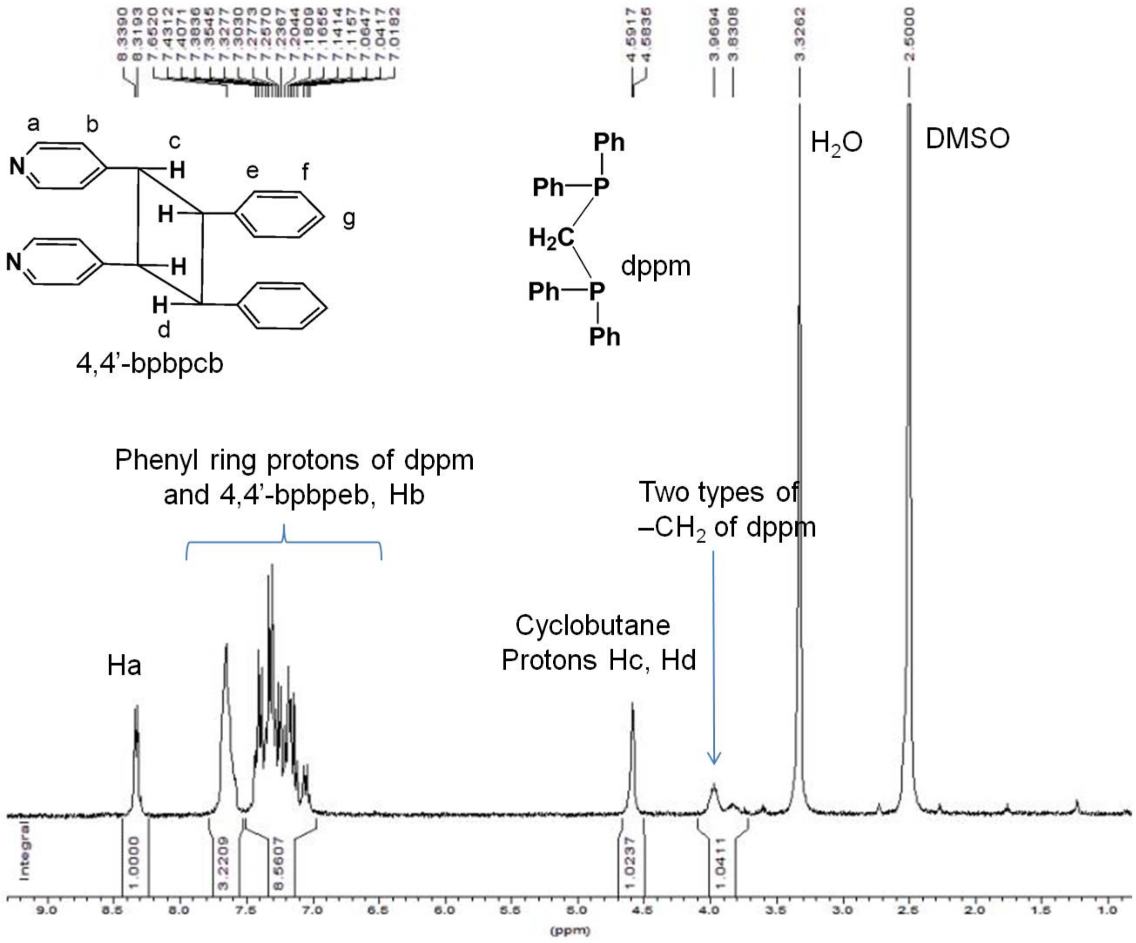

Fig. S4. ^{1}H NMR (300 MHz, d_6-DMSO) spectrum of **2**, after UV irradiation of **1**, shows that photodimerization has taken place.

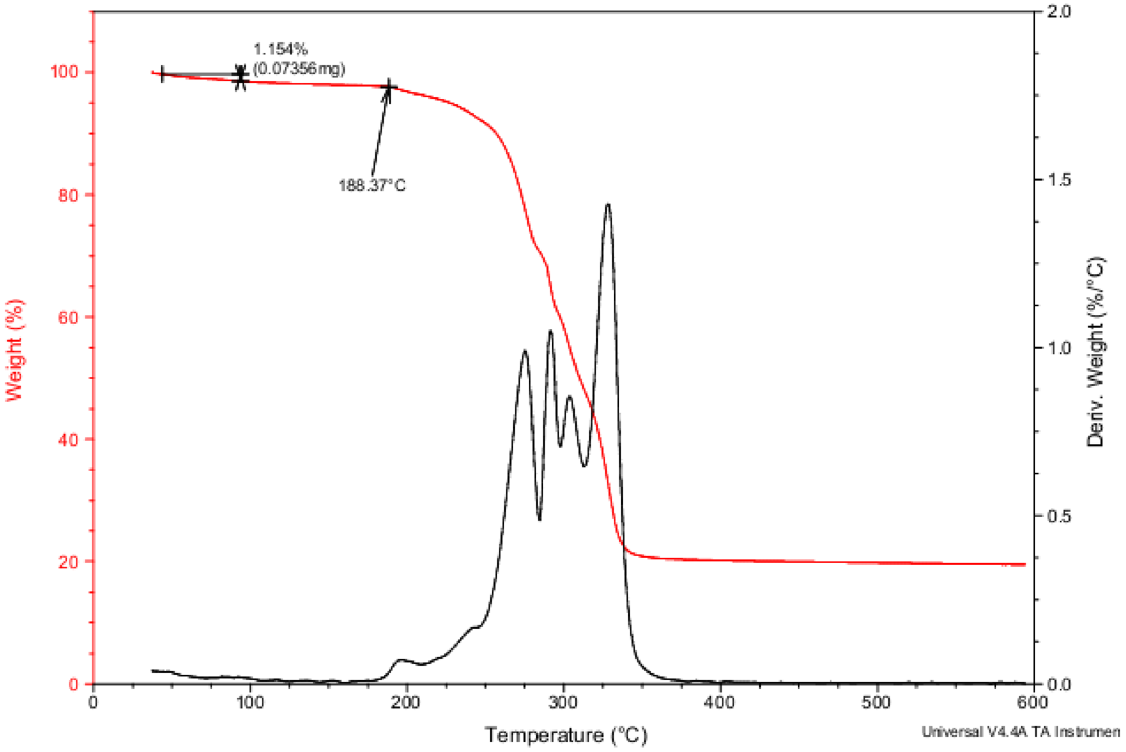

Fig. S5. TGA plot for compound **1**. The calculated weight loss for this compound is 0.77 %, where ~1.1 % weight loss was observed in TGA experiment.

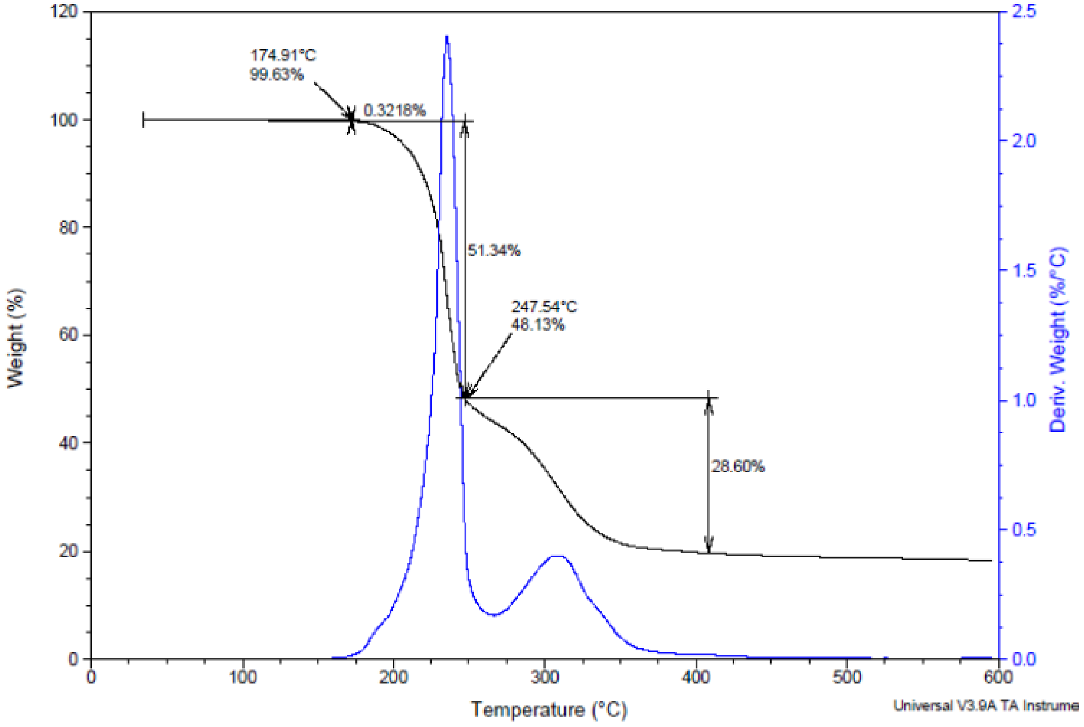

Fig. S6. TGA plot for compound **3**. No solvent loss was observed.

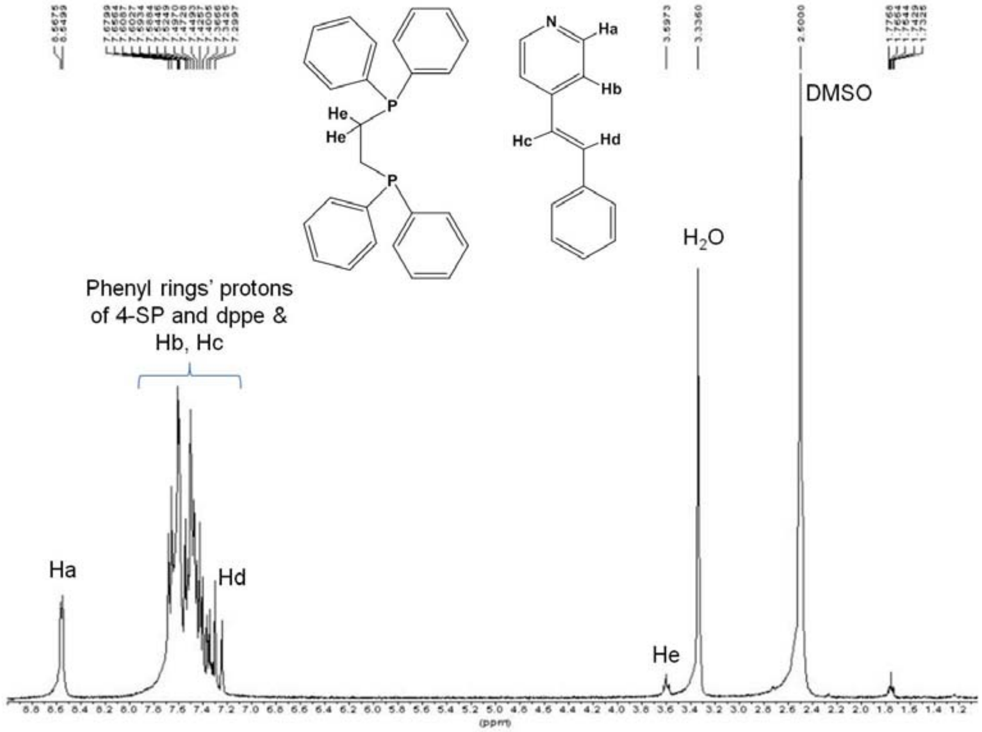

Fig. S7. ^{1}H NMR (300 MHz, d_6-DMSO) spectrum of **3**.

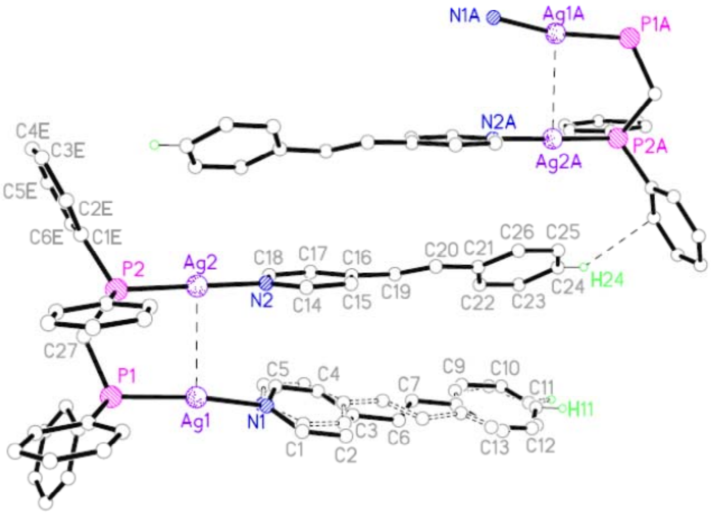

Figure S8. The details of C-H···π interactions in **1**. D(C-H), 0.95Å, D(H24···C2EA), 2.84 Å (The atoms C2E with extension A is related by symmetry, x-1, y-1, z-1), ∠C24-H24-C2EA, 146.4º, D(H24···Center of ring C1EA-C6EA), 3.04Å and ∠C24-H24-Center of ring C1EA-C6EA), 135.6º. This is comparable to average sp^2-CH/π distance, 2.70(11) Å and angle, 146.9º reported in the literature.[3]

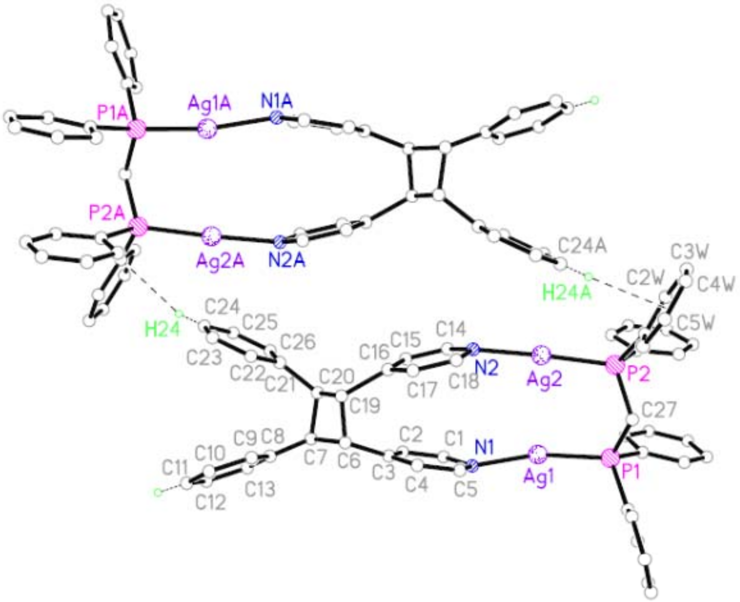

Figure S9. The details of C-H···π interactions in **2**. D(C-H), 0.95Å, D(H24···C1WA), 2.586 Å (The atoms C1W with extension A is related by symmetry, x-1, y-1, z-1), ∠C24-H24-C1WA, 151.5º, D(H24···Center of ring C1WA-C6WA), 2.495Å and ∠C24-H24-Center of ring C1WA-C6WA), 176.9º. This is comparable to average sp^2-CH/π distance, 2.70(11) Å and angle, 146.9º reported in the literature.[3] Interestingly the disordered observed in one of the 4-SP ligands for **1** was not found in **2**.

References

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2. (a) G. M. Sheldrick, *Acta Crystallogr. Sect. A,* 2008, **A64**, 112-122; (b) P. Müller, *Crystal structure refinement: a crystallographers guide to SHELXL*, Oxford University Press, 2006.

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