Supporting information

"**Substitutient Effects on the Intermolecular Aggregation of Ag^{I}-Pyrazolato Trimers**"

By

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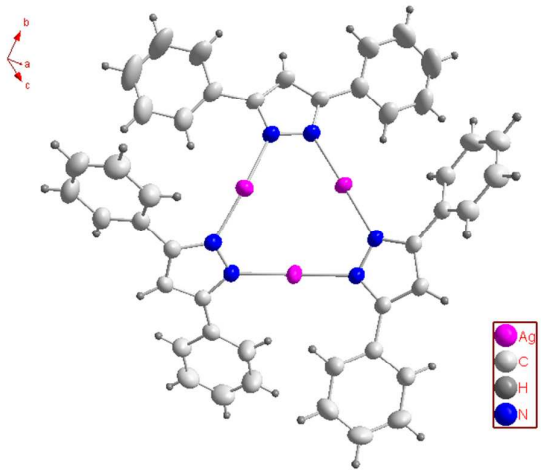

Figure S1. An ORTEP diagram of $[Ag(\mu\text{-}3,5\text{-}Ph_2pz)]_3$ (**1**).

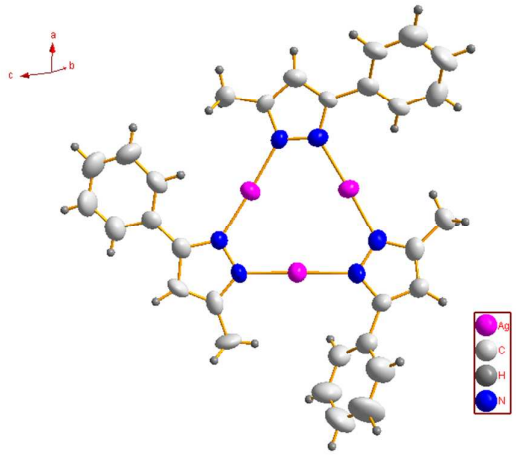

Figure S2a. An ORTEP diagram of $[Ag(\mu\text{-}3\text{-}Me\text{-}5\text{-}Ph\text{-}pz)]_3$ (**2**)

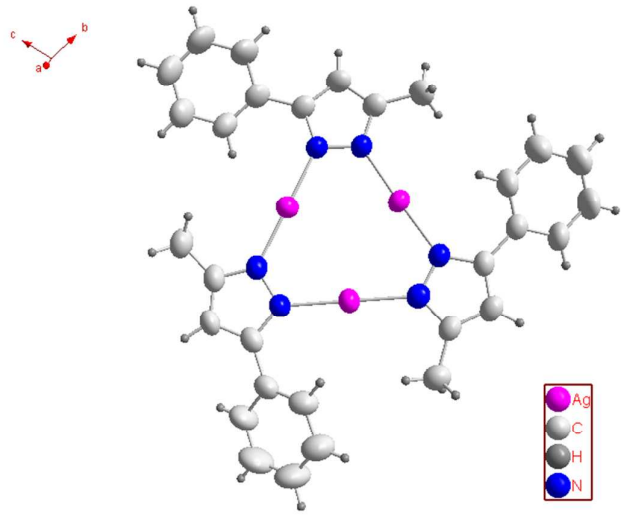

Figure S2b. An ORTEP diagram of $[Ag(\mu\text{-3-Me-5-Ph-pz})]_3$ (**2·MeOH**)

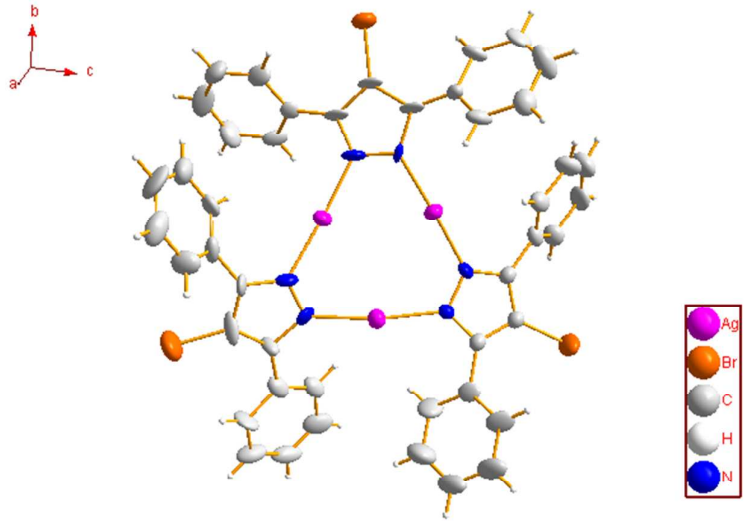

Figure S3a. An ORTEP diagram of $[Ag(\mu\text{-4-Br-3,5-Ph}_2\text{pz})]_3$ (**3**).

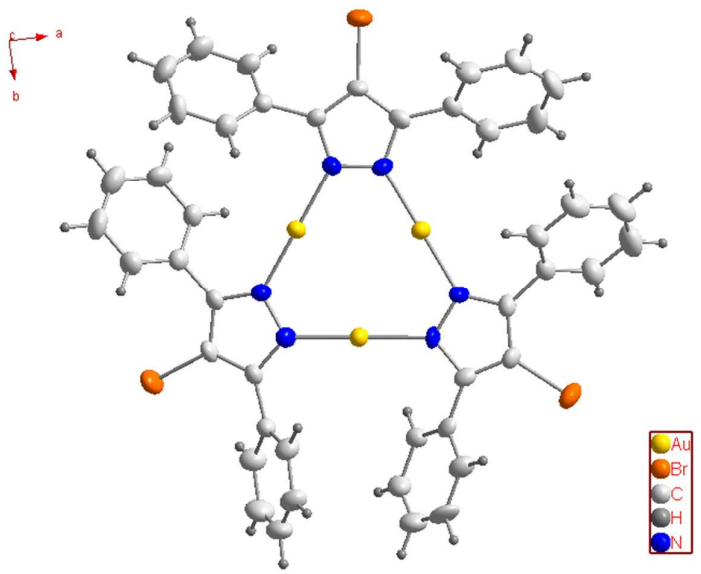

Figure S3b. An ORTEP diagram of $[Au(\mu\text{-}4\text{-}Br\text{-}3,5\text{-}Ph_2pz)]_3$ (**3-Au**).

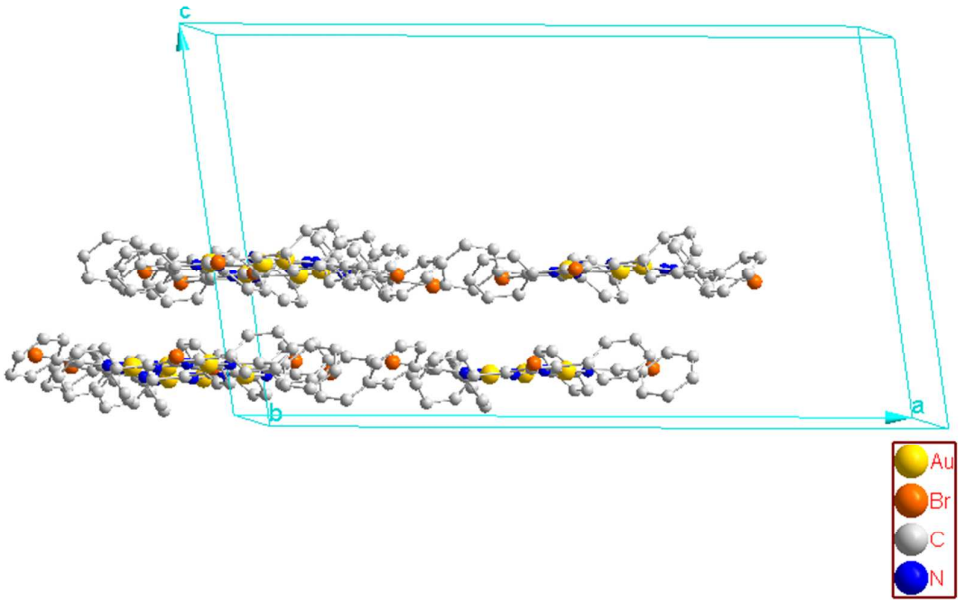

Figure S3c. A ball-and-stick representation of the packing diagram of **3-Au**, viewed along the *b*-axis.

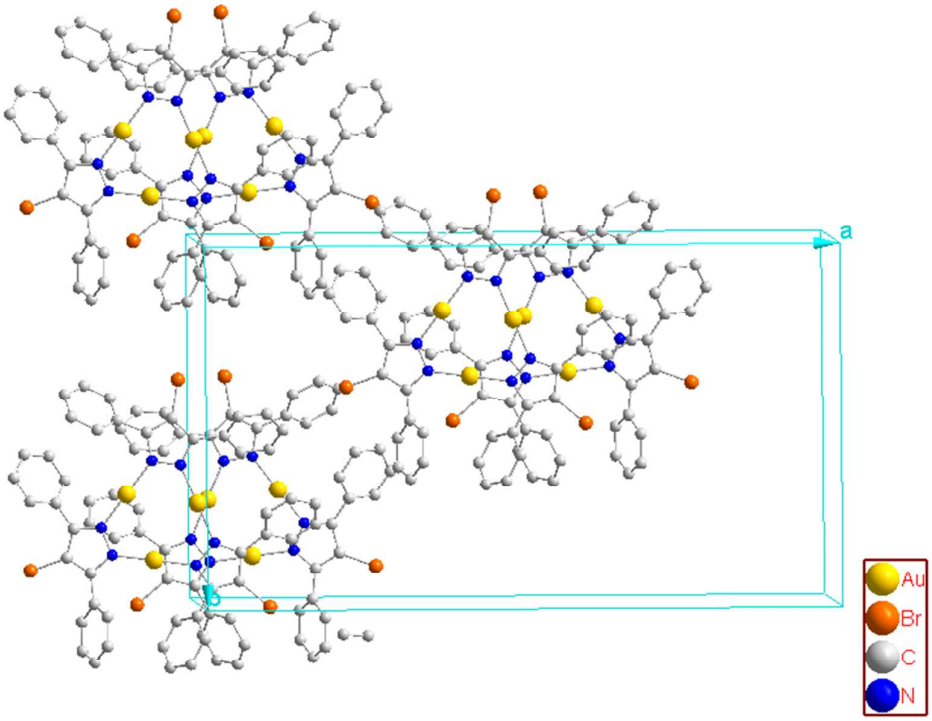

Figure S3d. A ball-and-stick representation of the packing diagram of **3-Au**, viewed along the *c*-axis.

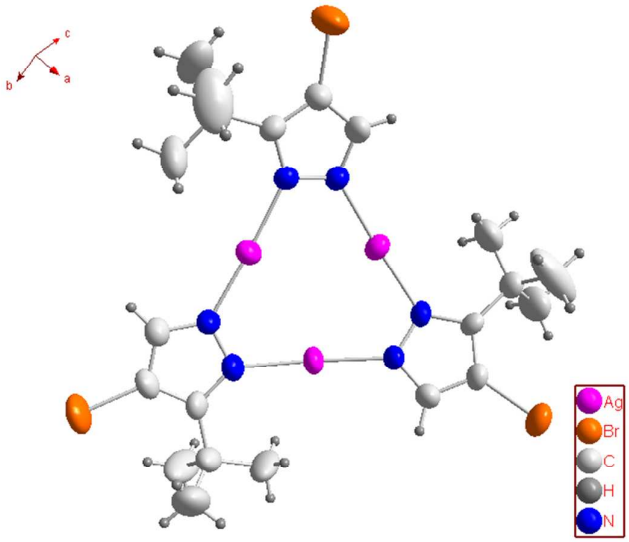

Figure S4. An ORTEP diagram of $[Ag(\mu\text{-}4\text{-}Br\text{-}3\text{-}^{t}Bupz)]_3$ (**4**).

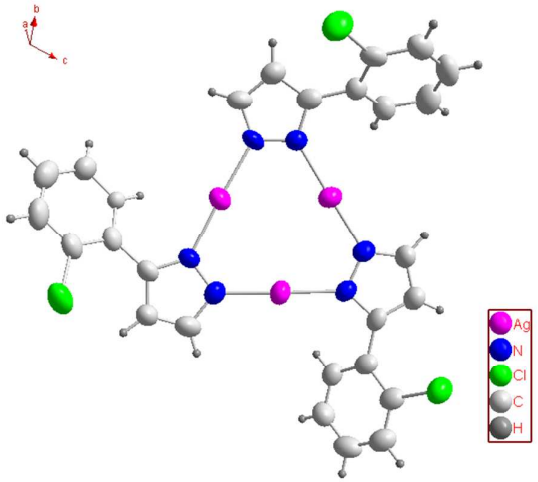

Figure S5a. An ORTEP diagram of $[Ag(\mu\text{-}3\text{-}o\text{-}Cl\text{-}Phpz)]_3$ (**5**).

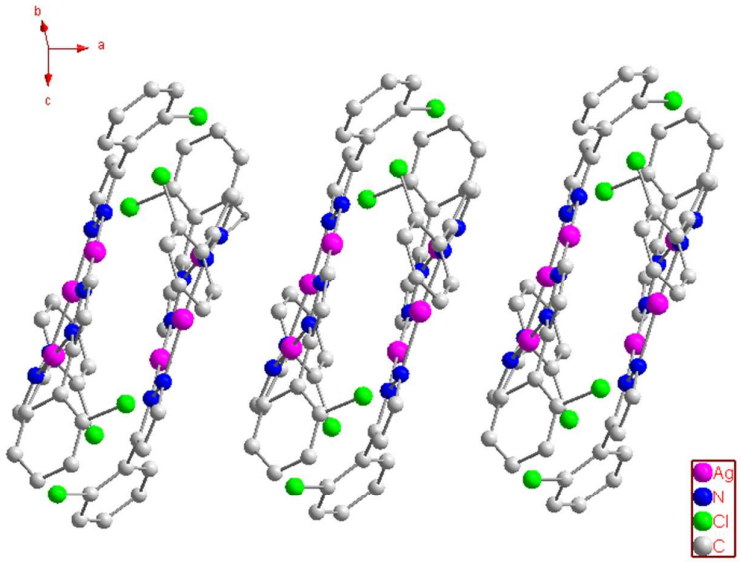

Figure S5b. A ball-and-stick representation of the packing diagram of **5**, showing pairs of trimers of S_6 symmetry stacked along the *a*-axis.

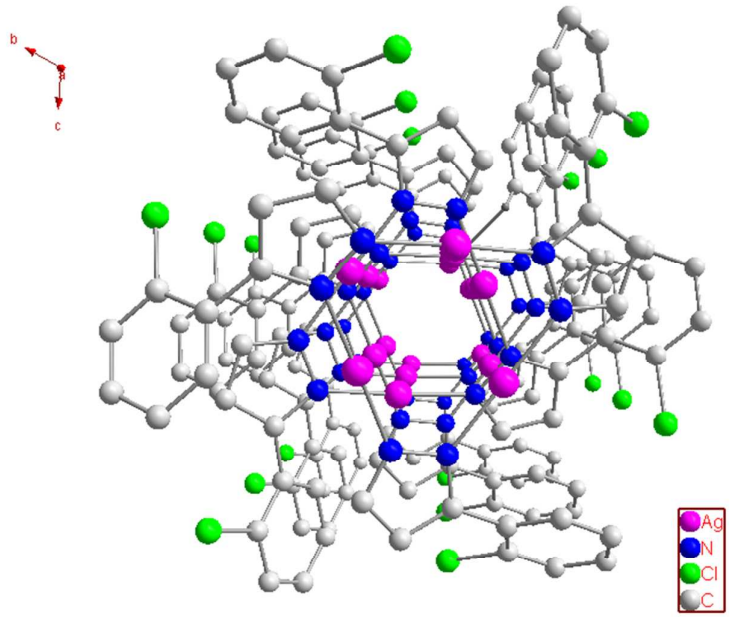

Figure S5c. A ball-and-stick representation of the packing diagram of **5**, viewed along the *a*-axis.

Table S1. Selected bond distances (Å) and bond angles(º).

1			
Ag(1)-N(1)	2.125(3)	Ag(3)-N(4)	2.109(3)
Ag(1)-N(6)	2.120(3)	Ag(1)···Ag(3)	3.3293(13)
Ag(2)-N(2)	2.120(3)	Ag(2)···Ag(3)	3.3845(14)
Ag(2)-N(3)	2.129(3)	Ag(1)···Ag(2)	3.4538(20)
Ag(3)-N(5)	2.107(3)		
N(1)-Ag(1)-N(6)	178.42(12)	N(5)-Ag(3)-N(4)	169.33(13)
N(2)-Ag(2)-N(3)	169.69(13)		
2			
Ag(1)-N(4)	2.071(10)	Ag(4)-N(7)	2.085(10)
Ag(1)-N(1)	2.083(9)	Ag(4)-N(10)	2.093(10)
Ag(2)-N(2)	2.074(10)	Ag(5)-N(9)	2.082(10)
Ag(2)-N(3)	2.094(10)	Ag(5)-N(8)	2.111(10)
Ag(3)-N(6)	2.076(10)	Ag(6)-N(11)	2.058(11)
Ag(3)-N(5)	2.085(11)	Ag(6)-N(12)	2.090(11)
Ag(1)···Ag(3)	3.2027(16)	Ag(5)···Ag(6)	3.3205(18)
Ag(1)···Ag(2)	3.3326(17)		
N(4)-Ag(1)-N(1)	176.3(4)	N(7)-Ag(4)-N(10)	174.5(4)
N(2)-Ag(2)-N(3)	177.6(4)	N(9)-Ag(5)-N(8)	178.7(4)
N(6)-Ag(3)-N(5)	176.8(4)	N(11)-Ag(6)-N(12)	175.4(4)
2·MeOH			
Ag(1)-N(1)	2.092(5)	Ag(2)-N(4)	2.091(4)
Ag(1)-N(6)	2.105(4)	Ag(3)-N(3)	2.089(4)
Ag(2)-N(5)	2.082(5)	Ag(3)-N(2)	2.090(4)
N(1)-Ag(1)-N(6)	179.69(18)	N(3)-Ag(3)-N(2)	177.72(17)
N(5)-Ag(2)-N(4)	177.18(16)		
3			
Ag(1)-N(3)	2.113(17)	Ag(4)-N(12)	2.124(14)
Ag(1)-N(2)	2.114(15)	Ag(4)-N(7)	2.132(14)
Ag(2)-N(4)	2.106(17)	Ag(5)-N(8)	2.108(15)
Ag(2)-N(5)	2.111(17)	Ag(5)-N(9)	2.118(15)
Ag(3)-N(6)	2.095(15)	Ag(6)-N(10)	2.049(15)
Ag(3)-N(1)	2.116(16)	Ag(6)-N(11)	2.087(15)
Ag(5)···Ag(6)	3.312(2)	Br(1)···Ag(4a)	3.293
Br(1)···Ag(5a)	3.544	Br(3)···Ag(4b)	3.441

Br(3)···Ag(5b)	3.454	Br(3)···Ag(6b)	3.542
Br(5)···Ag(1c)	3.472	Br(5)···Ag(2c)	3.208
Br(5)···Ag(3c)	3.567		
N(3)-Ag(1)-N(2)	176.9(7)	N(12)-Ag(4)-N(7)	170.0(6)
N(4)-Ag(2)-N(5)	177.9(7)	N(8)-Ag(5)-N(9)	176.6(7)
N(6)-Ag(3)-N(1)	176.3(7)	N(10)-Ag(6)-N(11)	175.7(7)
3-Au			
Au(1)-N(6)	1.998(6)	Au(2)-N(5)	2.002(6)
Au(1)-N(1)	2.001(6)	Au(2)-N(4)	2.008(6)
Au(3)-N(3)	2.001(6)	Au(3)-N(2)	2.016(6)
Au(1)···Au(2)	3.3479(5)	Au(1)···Au(3)	3.3681(5)
Au(2)···Au(3)	3.3792(6)		
N(6)-Au(1)-N(1)	178.8(2)	N(5)-Au(2)-N(4)	178.1(2)
N(3)-Au(3)-N(2)	179.6(3)		
4			
Ag(1)-N(6)	2.116(7)	Ag(2)-N(3)	2.133(7)
Ag(1)-N(1)	2.138(6)	Ag(2)-N(2)	2.115(6)
Ag(3)-N(4)	2.097(7)	Ag(3)-N(5)	2.130(6)
N(6)-Ag(1)-N(1)	171.7(3)	N(2)-Ag(2)-N(3)	172.3(3)
N(4)-Ag(3)-N(5)	176.7(3)		
5			
Ag(1)-N(6)	2.146(6)	Ag(2)-N(2)	2.096(7)
Ag(1)-N(1)	2.147(6)	Ag(3)-N(4)	2.117(7)
Ag(2)-N(3)	2.095(7)	Ag(3)-N(5)	2.097(7)
N(6)-Ag(1)-N(1)	177.2(3)	N(4)-Ag(3)-N(5)	178.4(3)
N(3)-Ag(2)-N(2)	176.5(3)		

Symmetry codes:

3: a) *x*, *y*-1, *z*; b) –*x*+1, *y*-1/2, -*z*+2; c) *x*-1, *y*+1, *z*.

Table S2. Selected distances(Å) of Ag···Ag and Ag···Br. Intertrimer Ag···Ag contacts of less than 3.44 Å, the sum of Bondi's van der Waals radii of Ag atoms, are listed here.

Complex	Ag···Ag(intratrimer)	Ag···Ag(intertrimer)	Br···$(Ag)_3$
$[Ag(3,5\text{-}Ph_2pz)]_3$ (**1**)	3.329(1) 3.385(1) 3.454(2)		
$\{[Ag(3\text{-}Me\text{-}5\text{-}Phpz)]_3\}_2$ (**2**)	3.333(1) 3.468(1) 3.470(2) 3.396(2) 3.422(1) 3.440(1)	3.203(1) 3.321(2)	
$[Ag(3\text{-}Me\text{-}5\text{-}Phpz)]_3$ (**2·MeOH**)	3.421(2) 3.429(2) 3.464(3)	3.419(2) 3.433(3)	
$[Ag(4\text{-}Br\text{-}3,5\text{-}Ph_2pz)]_3$ (**3**)	3.312(2) 3.425(2) 3.632(2) 3.459(2) 3.462(2) 3.566(2)		3.208(2) 3.473(2) 3.568(2) 3.249(2) 3.545(2) 3.722(2) 3.441(2) 3.454(2) 3.543(2)
$[Ag(4\text{-}Br\text{-}3\text{-}^tBupz)]_3$ (**4**)	3.382(4) 3.439(3) 3.458(2)	3.142(3)	3.567(5) 3.766(3) 3.968(3)
$[Ag(3\text{-}o\text{-}Cl\text{-}Phpz)]_3$ (**5**)	3.458(3) 3.508(3) 3.585(2)		