Mixed ligand complexes of silver(I) supported by highly fluorinated pyrazolates, and chelating and bridging *N*-heterocycles

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Supporting information

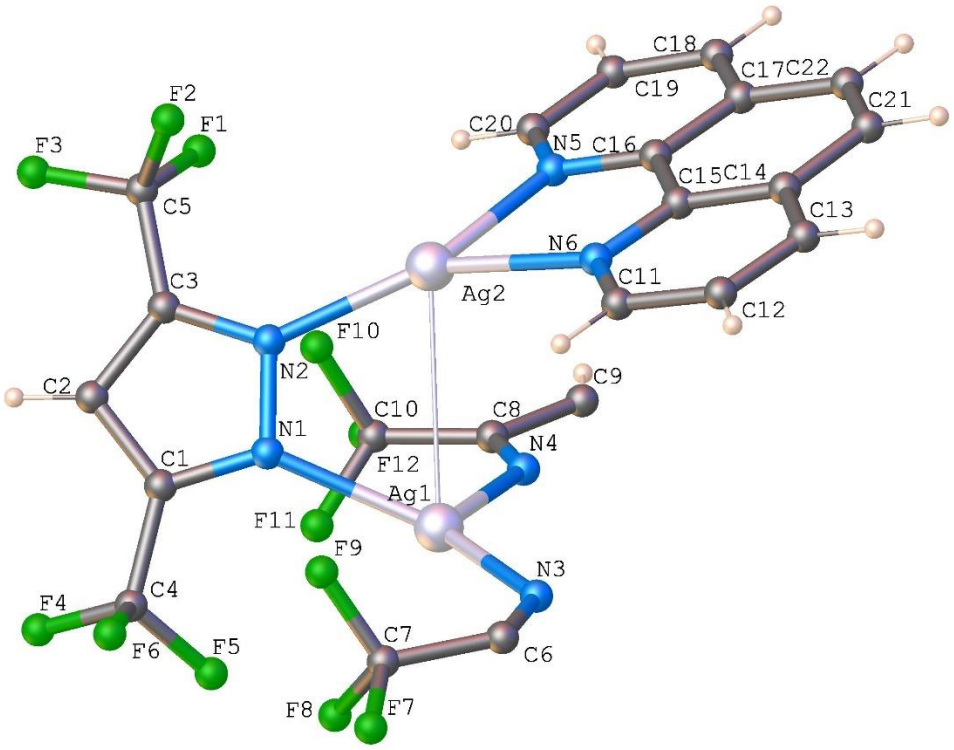


Figure S1. Atoms of $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_4(1,10\text{-phen})_2$ in the asymmetric unit.

Table S1. Crystal data and structure refinement for $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_4(1,10\text{-phen})_2$.

Empirical formula	$C_{44}H_{20}Ag_4F_{24}N_{12}$
Formula weight	1604.20
Temperature/K	100.15
Crystal system	triclinic
Space group	P-1
a/Å	9.2341(9)
b/Å	11.7296(11)
c/Å	11.7828(11)
α/°	107.2390(10)
β/°	95.6320(10)
γ/°	92.7350(10)
Volume/Å^3	1209.0(2)
Z	1
ρ_{calc}g/cm^3	2.203
μ/mm^{-1}	1.739
F(000)	772.0
Crystal size/mm^3	0.1 × 0.08 × 0.03
Radiation	MoKα (λ = 0.71073)

2Θ range for data collection/°	3.644 to 53.462
Index ranges	$-11 \leq h \leq 11$, $-14 \leq k \leq 14$, $-14 \leq l \leq 14$
Reflections collected	10688
Independent reflections	5094 [R_{int} = 0.0214, R_{sigma} = 0.0307]
Data/restraints/parameters	5094/0/379
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0315, wR_2 = 0.0763
Final R indexes [all data]	R_1 = 0.0361, wR_2 = 0.0805
Largest diff. peak/hole / e $Å^{-3}$	1.19/-0.65

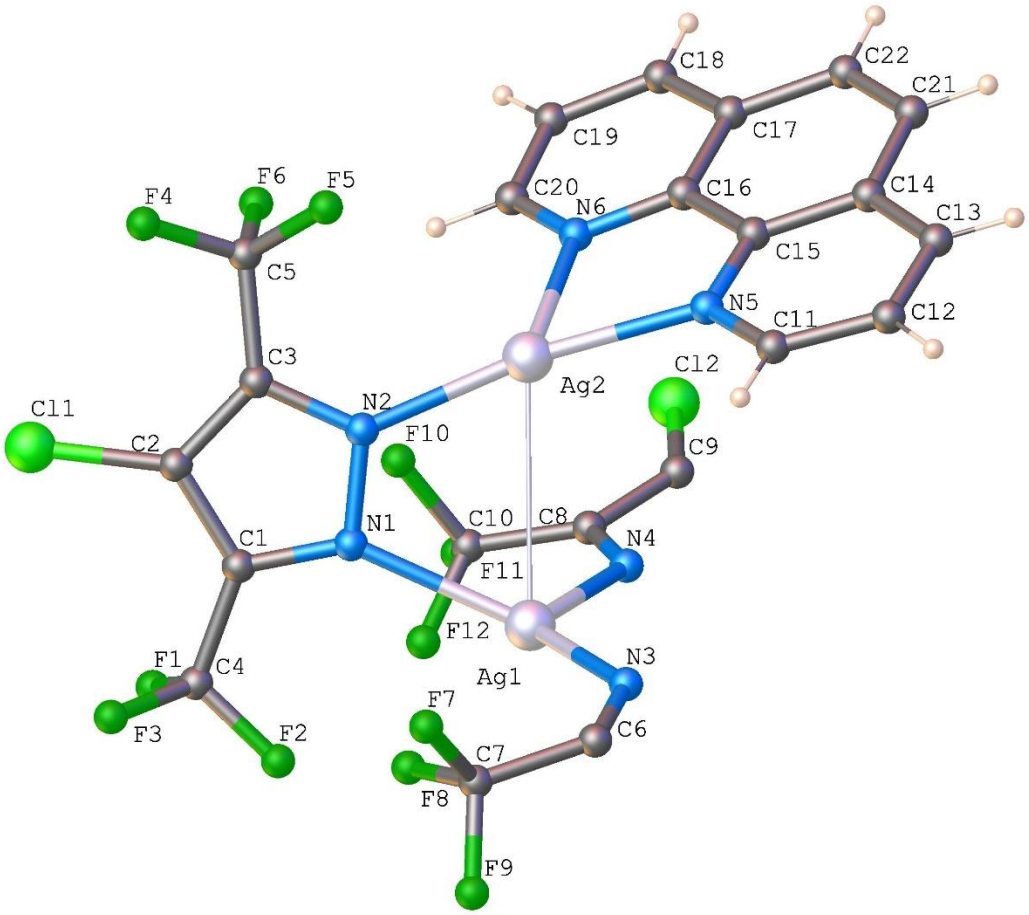


Figure S2. Atoms of {[3,5-$(CF_3)_2$Pz]Ag}$_4$(1,10-phen)$_2$ in the asymmetric unit.

Table S2. Crystal data and structure refinement for {[4-Cl-3,5-$(CF_3)_2$Pz]Ag}$_4$(1,10-phen)$_2$.

Empirical formula	$C_{44}H_{16}Ag_4Cl_4F_{24}N_{12}$
Formula weight	1741.97
Temperature/K	100.15
Crystal system	triclinic
Space group	P-1
a/Å	11.2824(10)
b/Å	11.8130(10)
c/Å	11.8889(10)
α/°	115.4070(10)
β/°	109.1150(10)
γ/°	96.3290(10)
Volume/Å^3	1292.69(19)
Z	1

ρ_{calc}g/cm^3	2.238
μ/mm^{-1}	1.836
F(000)	836.0
Crystal size/mm^3	0.25 × 0.2 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.994 to 56.588
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15
Reflections collected	12785
Independent reflections	6326 [R_{int} = 0.0169, R_{sigma} = 0.0240]
Data/restraints/parameters	6326/0/397
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0290, wR_2 = 0.0746
Final R indexes [all data]	R_1 = 0.0314, wR_2 = 0.0770
Largest diff. peak/hole / e Å^{-3}	1.34/-0.63

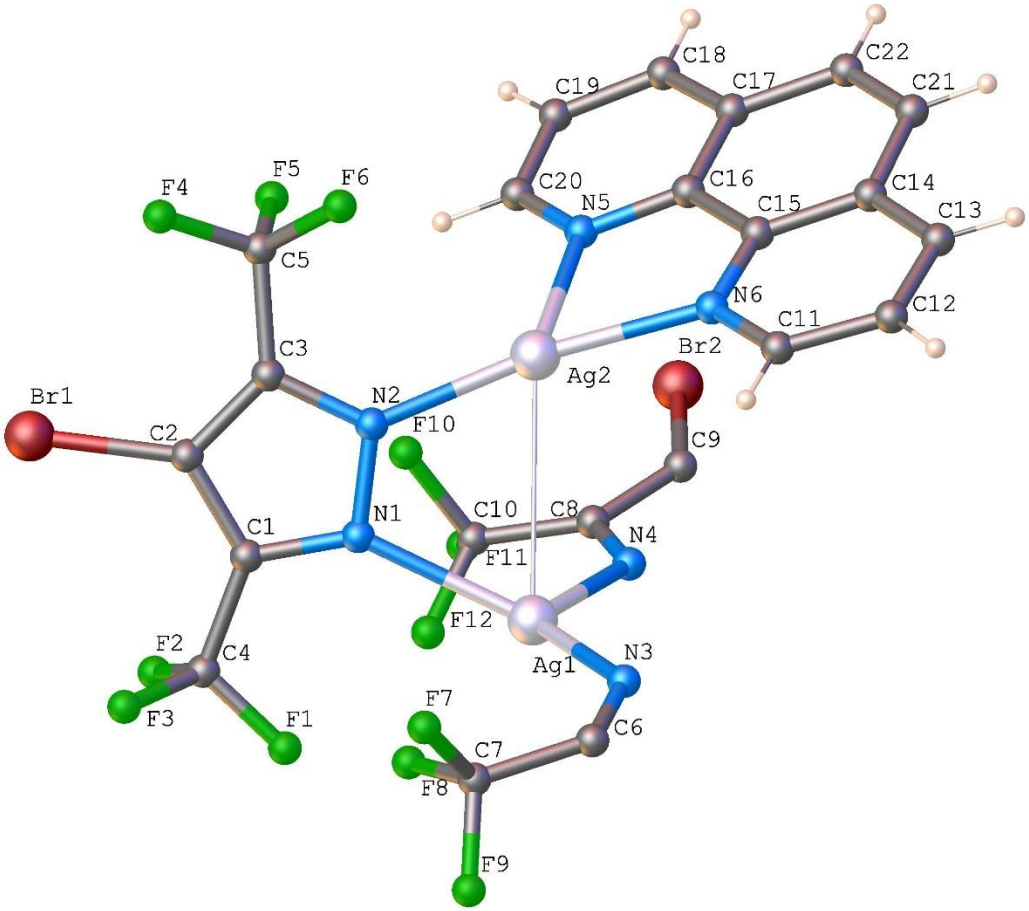


Figure S3. Atoms of $\{[4\text{-Br-3,5-}(CF_3)_2Pz]Ag\}_4(1,10\text{-phen})_2$ in the asymmetric unit.

Table S3. Crystal data and structure refinement for $\{[4\text{-Br-3,5-}(CF_3)_2Pz]Ag\}_4(1,10\text{-phen})_2$.

Empirical formula	$C_{44}H_{16}Ag_4Br_4F_{24}N_{12}$
Formula weight	1919.81
Temperature/K	100.15
Crystal system	triclinic
Space group	P-1
a/Å	11.344(2)
b/Å	11.818(2)
c/Å	11.899(2)
α/°	114.407(2)
β/°	108.836(2)
γ/°	96.696(2)
Volume/Å^3	1315.7(4)
Z	1
ρ_{calc}g/cm^3	2.423
μ/mm^{-1}	4.639
F(000)	908.0

Crystal size/mm^3	0.2 × 0.15 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.954 to 52.74
Index ranges	$-14 \leq h \leq 14$, $-14 \leq k \leq 14$, $-14 \leq l \leq 14$
Reflections collected	11283
Independent reflections	5329 [R_{int} = 0.0267, R_{sigma} = 0.0339]
Data/restraints/parameters	5329/0/397
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0378, wR_2 = 0.1028
Final R indexes [all data]	R_1 = 0.0408, wR_2 = 0.1057
Largest diff. peak/hole / e $Å^{-3}$	2.56/-1.48

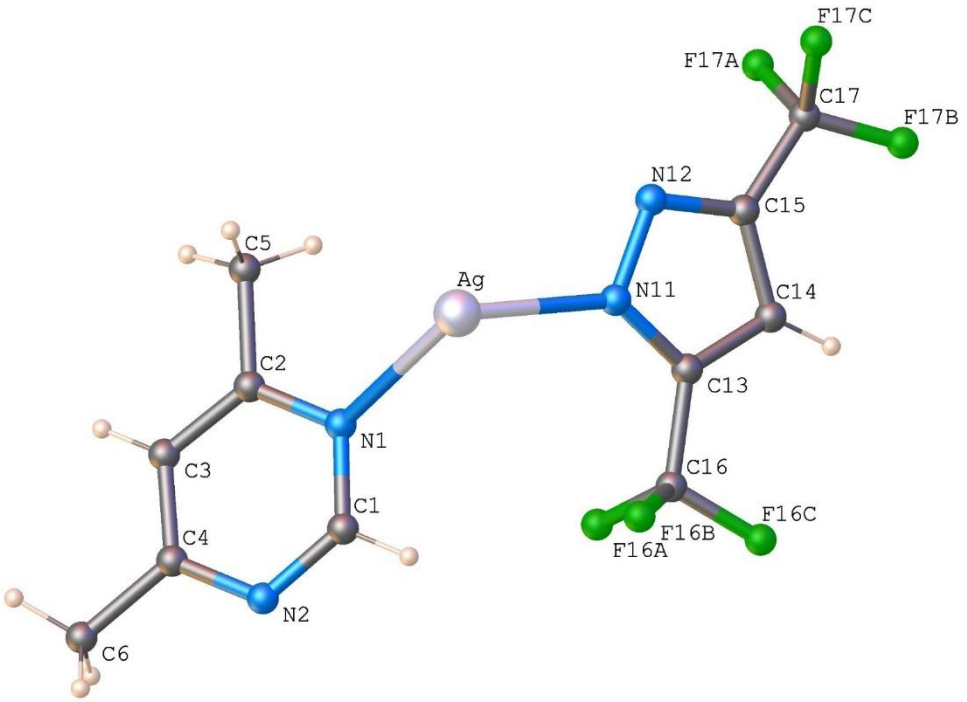


Figure S4. Atoms of $\{[3,5\text{-}(CF_3)_2Pz]Ag(4,6\text{-}Me_2\text{-}pyrm)\}_\infty$ in the asymmetric unit.

Table S4. Crystal data and structure refinement for $\{[3,5\text{-}(CF_3)_2Pz]Ag(4,6\text{-}Me_2\text{-}pyrm)\}_\infty$.

Empirical formula	$C_{22}H_{18}Ag_2F_{12}N_8$
Formula weight	838.18
Temperature/K	100.15
Crystal system	triclinic
Space group	P-1
a/Å	7.9948(16)
b/Å	9.2604(19)
c/Å	10.149(2)
α/°	95.903(3)
β/°	99.779(3)
γ/°	113.145(2)
Volume/Å^3	668.9(2)
Z	1
ρ_{calc}g/cm^3	2.081
μ/mm^{-1}	1.579
F(000)	408.0
Crystal size/mm^3	0.29 × 0.12 × 0.04
Radiation	MoKα (λ = 0.71073)

2Θ range for data collection/°	4.146 to 56.56
Index ranges	$-10 \leq h \leq 10$, $-11 \leq k \leq 12$, $-13 \leq l \leq 13$
Reflections collected	6216
Independent reflections	3176 [R_{int} = 0.0154, R_{sigma} = 0.0206]
Data/restraints/parameters	3176/0/201
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0218, wR_2 = 0.0561
Final R indexes [all data]	R_1 = 0.0226, wR_2 = 0.0568
Largest diff. peak/hole / e $Å^{-3}$	0.99/-0.68

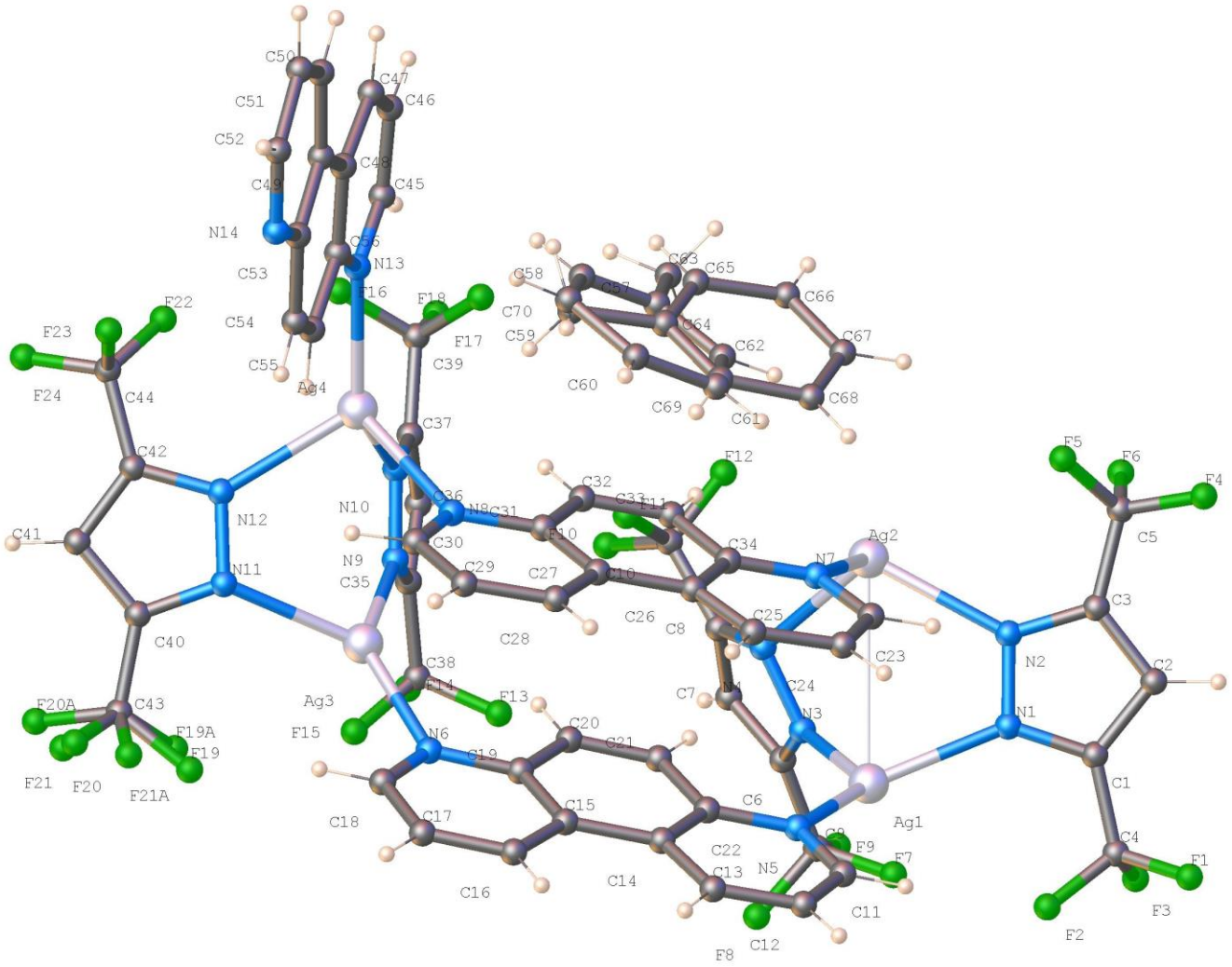


Figure S5. Atom labelling scheme of $\{[3,5\text{-}(CF_3)_2Pz]_4Ag_4(4,7\text{-phen})_3\}_\infty$ in the asymmetric unit.

Table S5. Crystal data and structure refinement for $\{[3,5\text{-}(CF_3)_2Pz]_4Ag_4(4,7\text{-phen})_3\}_\infty$.

Identification code	dias46s
Empirical formula	$C_{63}H_{36}Ag_4F_{24}N_{14}$
Formula weight	1876.54
Temperature/K	100.15
Crystal system	triclinic
Space group	P-1
a/Å	12.1451(13)
b/Å	13.5207(14)
c/Å	20.327(3)

α/°	92.125(5)
β/°	96.546(6)
γ/°	103.553(11)
Volume/Å^3	3216.8(7)
Z	2
ρ_{calc}g/cm^3	1.937
μ/mm^{-1}	1.324
F(000)	1832.0
Crystal size/mm^3	0.26 × 0.15 × 0.09
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.478 to 56.55
Index ranges	-16 ≤ h ≤ 15, -17 ≤ k ≤ 17, -27 ≤ l ≤ 26
Reflections collected	30094
Independent reflections	15308 [R_{int} = 0.0293, R_{sigma} = 0.0445]
Data/restraints/parameters	15308/15/1038
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0385, wR_2 = 0.0904
Final R indexes [all data]	R_1 = 0.0497, wR_2 = 0.0973
Largest diff. peak/hole / e Å^{-3}	1.38/-0.65

Table S6. Bond Lengths for {[3,5-$(CF_3)_2$Pz]$_4$Ag$_4$(4,7-phen)$_3$}$_\infty$**.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ag1	Ag2	3.3345(6)	C1	C2	1.387(4)
Ag1	N1	2.225(2)	C1	C4	1.482(4)
Ag1	N3	2.258(3)	C2	C3	1.376(4)
Ag1	N5	2.220(3)	C3	C5	1.484(5)
Ag2	N2	2.354(3)	C6	C7	1.390(5)
Ag2	N4	2.439(3)	C6	C9	1.478(5)
Ag2	N7	2.325(3)	C7	C8	1.382(5)
Ag2	N14^1	2.315(3)	C8	C10	1.470(5)
Ag3	N6	2.235(3)	C11	C12	1.390(5)
Ag3	N9	2.235(3)	C12	C13	1.368(5)
Ag3	N11	2.287(2)	C13	C14	1.406(4)
Ag4	N8	2.502(3)	C14	C15	1.452(4)
Ag4	N10	2.279(3)	C14	C22	1.409(4)
Ag4	N12	2.355(3)	C15	C16	1.407(4)
Ag4	N13	2.277(3)	C15	C19	1.417(4)
F1	C4	1.342(3)	C16	C17	1.369(5)
F2	C4	1.336(4)	C17	C18	1.397(5)
F3	C4	1.359(4)	C19	C20	1.427(4)
F4	C5	1.340(4)	C20	C21	1.351(4)
F5	C5	1.337(4)	C21	C22	1.436(4)
F6	C5	1.346(4)	C23	C24	1.396(4)

F7	C9	1.355(4)	C24	C25	1.377(4)
F8	C9	1.343(4)	C25	C26	1.401(4)
F9	C9	1.330(4)	C26	C27	1.459(4)
F10	C10	1.327(4)	C26	C34	1.411(4)
F11	C10	1.339(5)	C27	C28	1.400(4)
F12	C10	1.332(5)	C27	C31	1.418(4)
F13	C38	1.351(4)	C28	C29	1.370(4)
F14	C38	1.344(4)	C29	C30	1.394(4)
F15	C38	1.350(5)	C31	C32	1.427(4)
F16	C39	1.353(5)	C32	C33	1.359(4)
F17	C39	1.325(4)	C33	C34	1.428(4)
F18	C39	1.356(4)	C35	C36	1.383(5)
F22	C44	1.341(4)	C35	C38	1.467(6)
F23	C44	1.343(4)	C36	C37	1.383(5)
F24	C44	1.344(4)	C37	C39	1.464(6)
F19	C43	1.347(6)	C40	C41	1.391(5)
F20	C43	1.311(6)	C40	C43	1.465(5)
F21	C43	1.367(6)	C41	C42	1.366(5)
F19A	C43	1.357(4)	C42	C44	1.483(5)
F20A	C43	1.329(5)	C45	C46	1.398(5)
F21A	C43	1.283(5)	C46	C47	1.369(5)
N1	N2	1.356(4)	C47	C48	1.405(4)
N1	C1	1.341(4)	C48	C49	1.461(5)
N2	C3	1.346(4)	C48	C56	1.411(5)
N3	N4	1.360(4)	C49	C50	1.405(5)
N3	C6	1.337(4)	C49	C53	1.415(4)
N4	C8	1.349(4)	C50	C51	1.366(5)
N5	C11	1.331(4)	C51	C52	1.399(5)
N5	C22	1.371(4)	C53	C54	1.424(5)
N6	C18	1.330(4)	C54	C55	1.349(5)
N6	C19	1.377(4)	C55	C56	1.424(4)
N7	C23	1.328(4)	C64	C65	1.347(12)
N7	C34	1.369(4)	C64	C69	1.30(3)
N8	C30	1.319(4)	C64	C70	1.47(2)
N8	C31	1.371(4)	C65	C66	1.424(13)
N9	N10	1.344(4)	C66	C67	1.375(11)
N9	C35	1.340(4)	C67	C68	1.375(10)
N10	C37	1.348(4)	C68	C69	1.40(3)
N11	N12	1.350(4)	C57	C58	1.382(13)
N11	C40	1.346(4)	C57	C62	1.397(12)
N12	C42	1.349(4)	C57	C63	1.504(12)
N13	C45	1.326(4)	C58	C59	1.38(2)
N13	C56	1.377(4)	C59	C60	1.44(2)
N14	C52	1.328(4)	C60	C61	1.39(3)

N14	C53	1.366(4)	C61	C62	1.49(2)		

[1]+X,-1+Y,+Z

Table S7. Bond Angles for $\{[3,5\text{-}(CF_3)_2Pz]_4Ag_4(4,7\text{-phen})_3\}_\infty$**.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Ag1	Ag2	67.34(7)	C19	C15	C14	118.7(3)
N1	Ag1	N3	101.61(9)	C17	C16	C15	119.6(3)
N3	Ag1	Ag2	64.18(7)	C16	C17	C18	119.5(3)
N5	Ag1	Ag2	112.26(6)	N6	C18	C17	123.1(3)
N5	Ag1	N1	127.66(9)	N6	C19	C15	121.7(3)
N5	Ag1	N3	126.11(9)	N6	C19	C20	118.2(3)
N2	Ag2	Ag1	61.21(7)	C15	C19	C20	120.1(3)
N2	Ag2	N4	110.79(9)	C21	C20	C19	121.3(3)
N4	Ag2	Ag1	61.68(7)	C20	C21	C22	120.4(3)
N7	Ag2	Ag1	77.92(6)	N5	C22	C14	122.1(3)
N7	Ag2	N2	98.41(9)	N5	C22	C21	117.7(3)
N7	Ag2	N4	104.62(9)	C14	C22	C21	120.2(3)
N14[1]	Ag2	Ag1	150.09(7)	N7	C23	C24	123.4(3)
N14[1]	Ag2	N2	104.04(9)	C25	C24	C23	118.8(3)
N14[1]	Ag2	N4	106.31(9)	C24	C25	C26	119.8(3)
N14[1]	Ag2	N7	131.72(9)	C25	C26	C27	123.7(3)
N6	Ag3	N11	122.13(9)	C25	C26	C34	117.6(3)
N9	Ag3	N6	138.60(9)	C34	C26	C27	118.7(3)
N9	Ag3	N11	99.20(9)	C28	C27	C26	123.5(3)
N10	Ag4	N8	97.95(9)	C28	C27	C31	117.6(3)
N10	Ag4	N12	95.51(10)	C31	C27	C26	118.9(3)
N12	Ag4	N8	96.17(9)	C29	C28	C27	120.0(3)
N13	Ag4	N8	109.48(9)	C28	C29	C30	118.5(3)
N13	Ag4	N10	134.59(10)	N8	C30	C29	124.1(3)
N13	Ag4	N12	115.90(10)	N8	C31	C27	121.7(3)
N2	N1	Ag1	112.48(18)	N8	C31	C32	118.0(3)
C1	N1	Ag1	138.8(2)	C27	C31	C32	120.2(3)
C1	N1	N2	108.1(2)	C33	C32	C31	120.8(3)
N1	N2	Ag2	117.77(18)	C32	C33	C34	120.9(3)
C3	N2	Ag2	135.0(2)	N7	C34	C26	122.3(3)
C3	N2	N1	107.0(2)	N7	C34	C33	117.2(3)
N4	N3	Ag1	113.06(19)	C26	C34	C33	120.5(3)
C6	N3	Ag1	138.2(2)	N9	C35	C36	110.8(3)
C6	N3	N4	108.4(3)	N9	C35	C38	119.9(3)
N3	N4	Ag2	106.31(17)	C36	C35	C38	129.1(3)
C8	N4	Ag2	131.9(2)	C37	C36	C35	102.6(3)

C8	N4	N3	106.6(3)	N10	C37	C36	111.2(4)
C11	N5	Ag1	119.4(2)	N10	C37	C39	119.6(3)
C11	N5	C22	118.0(3)	C36	C37	C39	129.2(3)
C22	N5	Ag1	122.65(19)	F13	C38	C35	112.9(3)
C18	N6	Ag3	117.6(2)	F14	C38	F13	106.0(3)
C18	N6	C19	118.3(3)	F14	C38	F15	106.2(3)
C19	N6	Ag3	122.7(2)	F14	C38	C35	112.1(3)
C23	N7	Ag2	117.9(2)	F15	C38	F13	105.8(3)
C23	N7	C34	118.0(3)	F15	C38	C35	113.2(3)
C34	N7	Ag2	123.13(19)	F16	C39	F18	103.5(3)
C30	N8	Ag4	117.26(19)	F16	C39	C37	113.9(3)
C30	N8	C31	117.9(3)	F17	C39	F16	107.0(4)
C31	N8	Ag4	123.8(2)	F17	C39	F18	106.1(3)
N10	N9	Ag3	119.1(2)	F17	C39	C37	112.8(4)
C35	N9	Ag3	132.4(3)	F18	C39	C37	112.8(3)
C35	N9	N10	108.3(3)	N11	C40	C41	110.2(3)
N9	N10	Ag4	116.8(2)	N11	C40	C43	120.5(3)
N9	N10	C37	107.1(3)	C41	C40	C43	129.3(3)
C37	N10	Ag4	135.6(3)	C42	C41	C40	103.4(3)
N12	N11	Ag3	114.65(19)	N12	C42	C41	111.3(3)
C40	N11	Ag3	134.4(2)	N12	C42	C44	119.8(3)
C40	N11	N12	107.9(3)	C41	C42	C44	128.9(3)
N11	N12	Ag4	119.11(19)	F19	C43	F21	94.3(7)
C42	N12	Ag4	132.6(2)	F19	C43	C40	117.9(4)
C42	N12	N11	107.2(3)	F20	C43	F19	107.6(7)
C45	N13	Ag4	120.9(2)	F20	C43	F21	96.3(7)
C45	N13	C56	117.7(3)	F20	C43	C40	122.6(5)
C56	N13	Ag4	121.3(2)	F21	C43	C40	112.4(5)
C52	N14	$Ag2^2$	119.5(2)	F19A	C43	C40	107.6(3)
C52	N14	C53	118.0(3)	F20A	C43	F19A	105.1(4)
C53	N14	$Ag2^2$	122.4(2)	F20A	C43	C40	106.7(4)
N1	C1	C2	110.4(3)	F21A	C43	F19A	109.8(4)
N1	C1	C4	120.3(3)	F21A	C43	F20A	111.9(5)
C2	C1	C4	129.2(3)	F21A	C43	C40	115.2(4)
C3	C2	C1	103.3(3)	F22	C44	F23	105.8(3)
N2	C3	C2	111.2(3)	F22	C44	F24	106.2(3)
N2	C3	C5	120.4(3)	F22	C44	C42	113.1(3)
C2	C3	C5	128.4(3)	F23	C44	F24	106.0(3)
F1	C4	F3	104.9(2)	F23	C44	C42	113.8(3)
F1	C4	C1	112.5(3)	F24	C44	C42	111.3(3)
F2	C4	F1	107.5(3)	N13	C45	C46	123.3(3)
F2	C4	F3	105.5(3)	C47	C46	C45	119.6(3)
F2	C4	C1	113.4(3)	C46	C47	C48	119.3(3)
F3	C4	C1	112.5(3)	C47	C48	C49	123.2(3)

F4	C5	F6	106.3(3)	C47	C48	C56	117.8(3)
F4	C5	C3	111.4(3)	C56	C48	C49	119.0(3)
F5	C5	F4	107.2(3)	C50	C49	C48	123.0(3)
F5	C5	F6	105.6(3)	C50	C49	C53	118.1(3)
F5	C5	C3	113.4(3)	C53	C49	C48	118.9(3)
F6	C5	C3	112.4(3)	C51	C50	C49	119.3(3)
N3	C6	C7	110.7(3)	C50	C51	C52	119.3(3)
N3	C6	C9	121.3(3)	N14	C52	C51	123.4(3)
C7	C6	C9	128.0(3)	N14	C53	C49	121.9(3)
C8	C7	C6	102.8(3)	N14	C53	C54	118.4(3)
N4	C8	C7	111.5(3)	C49	C53	C54	119.7(3)
N4	C8	C10	120.4(3)	C55	C54	C53	121.2(3)
C7	C8	C10	128.0(3)	C54	C55	C56	121.3(3)
F7	C9	C6	112.1(3)	N13	C56	C48	122.3(3)
F8	C9	F7	105.8(3)	N13	C56	C55	117.9(3)
F8	C9	C6	113.3(3)	C48	C56	C55	119.8(3)
F9	C9	F7	105.8(3)	C65	C64	C70	121.9(13)
F9	C9	F8	107.1(3)	C69	C64	C65	116.4(12)
F9	C9	C6	112.2(3)	C69	C64	C70	121.6(16)
F10	C10	F11	106.3(3)	C64	C65	C66	121.7(9)
F10	C10	F12	105.6(3)	C67	C66	C65	118.7(8)
F10	C10	C8	112.5(3)	C66	C67	C68	120.2(7)
F11	C10	C8	113.3(3)	C67	C68	C69	115.6(11)
F12	C10	F11	105.8(4)	C64	C69	C68	127.3(17)
F12	C10	C8	112.8(3)	C58	C57	C62	117.7(8)
N5	C11	C12	123.2(3)	C58	C57	C63	121.3(8)
C13	C12	C11	119.4(3)	C62	C57	C63	121.0(9)
C12	C13	C14	119.5(3)	C59	C58	C57	123.8(11)
C13	C14	C15	123.1(3)	C58	C59	C60	116.9(13)
C13	C14	C22	117.7(3)	C61	C60	C59	125.2(14)
C22	C14	C15	119.2(3)	C60	C61	C62	113(2)
C16	C15	C14	123.5(3)	C57	C62	C61	123.6(15)
C16	C15	C19	117.8(3)				

[1]+X,-1+Y,+Z; [2]+X,1+Y,+Z

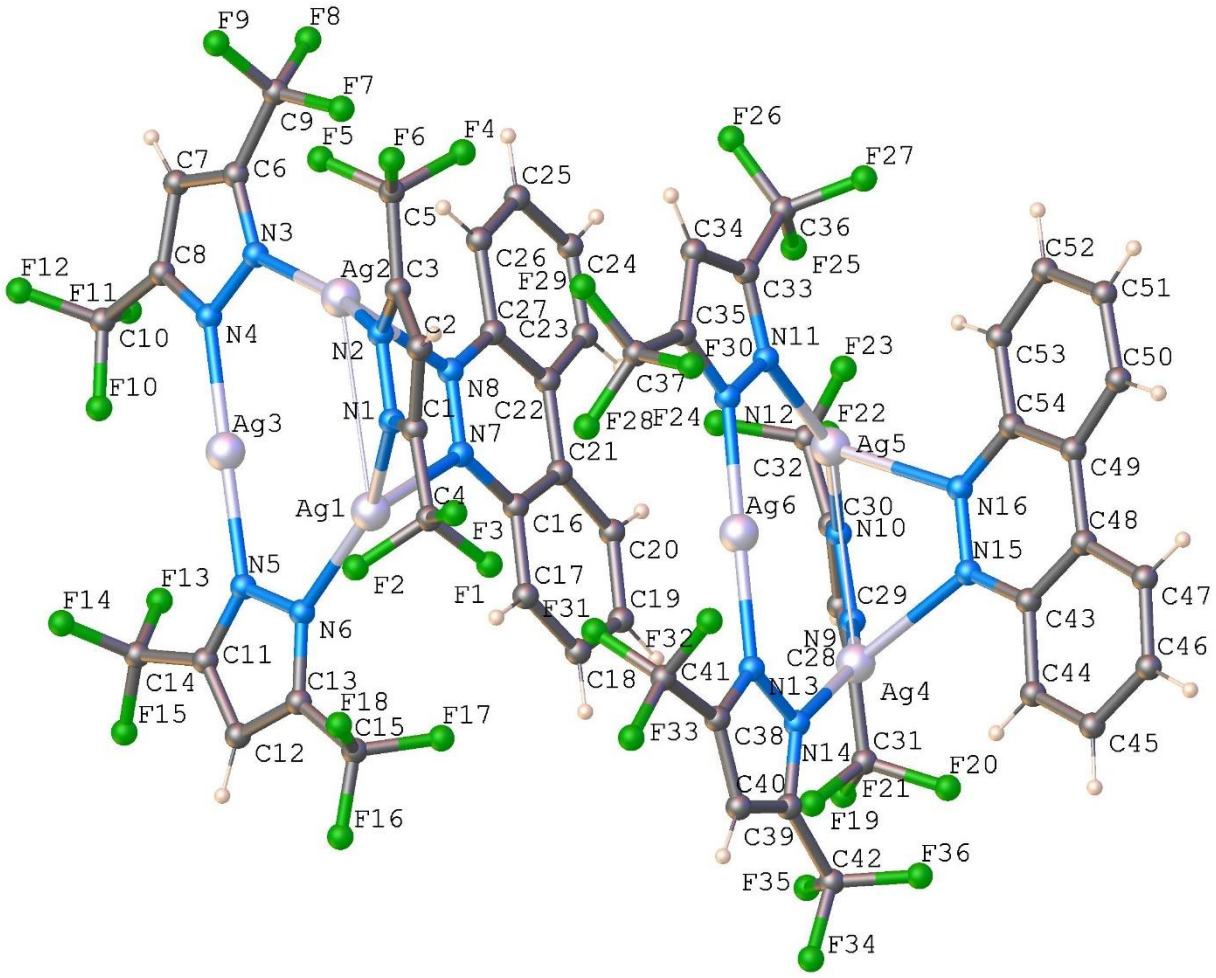
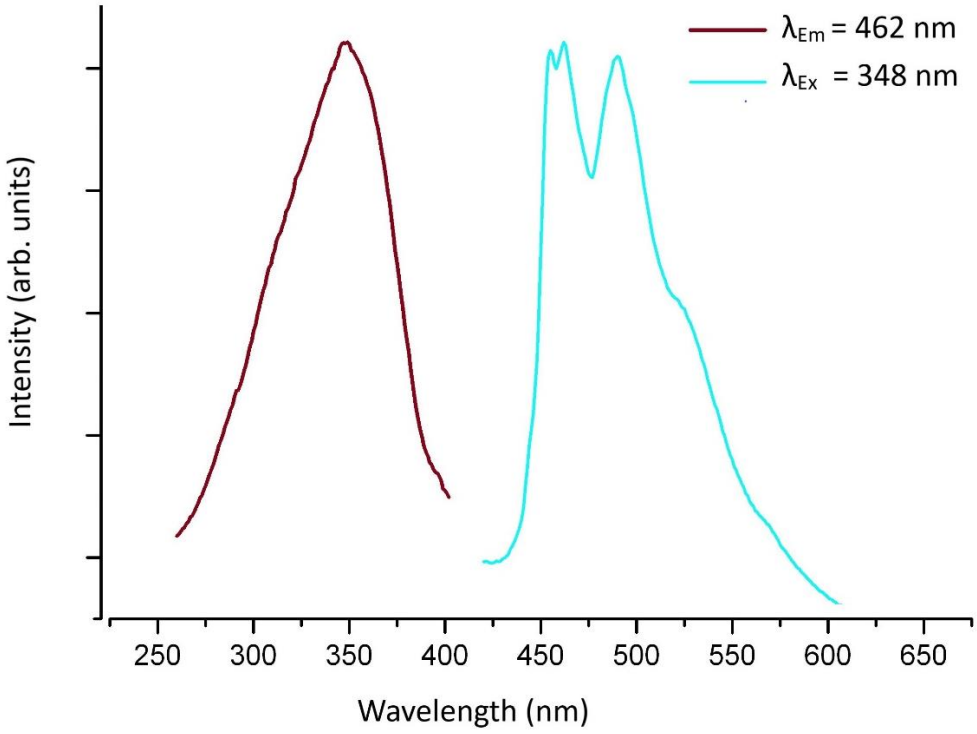


Figure S6. Atoms of {[3,5-$(CF_3)_2$Pz]Ag}$_3$(benzo[*c*]cinnoline) in the asymmetric unit.

Table S8. Crystal data and structure refinement for {[3,5-$(CF_3)_2$Pz]Ag}$_3$(benzo[*c*]cinnoline)**.**

Empirical formula	$C_{27}H_{11}Ag_3F_{18}N_8$
Formula weight	1113.05
Temperature/K	100
Crystal system	triclinic
Space group	P1
a/Å	9.771(3)
b/Å	12.915(5)
c/Å	15.031(5)

α/°	113.919(3)
β/°	91.759(4)
γ/°	107.231(4)
Volume/Å^3	1631.3(10)
Z	2
ρ_{calc}g/cm^3	2.266
μ/mm^{-1}	1.923
F(000)	1064.0
Crystal size/mm^3	0.27 × 0.24 × 0.23
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.01 to 56.592
Index ranges	$-12 \leq h \leq 12$, $-17 \leq k \leq 17$, $-19 \leq l \leq 19$
Reflections collected	15085
Independent reflections	13595 [R_{int} = 0.0307, R_{sigma} = 0.0608]
Data/restraints/parameters	13595/3/1010
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0315, wR_2 = 0.0829
Final R indexes [all data]	R_1 = 0.0318, wR_2 = 0.0833
Largest diff. peak/hole / e Å^{-3}	0.91/-0.58



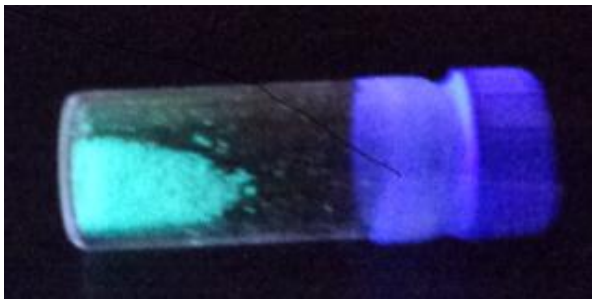


Figure S7. Room temperature emission and excitation spectra of crystalline solid samples of {[3,5-$(CF_3)_2$Pz]Ag}$_4$(1,10-phen)$_2$ showing emission bands at 455, 462, 490 nm.

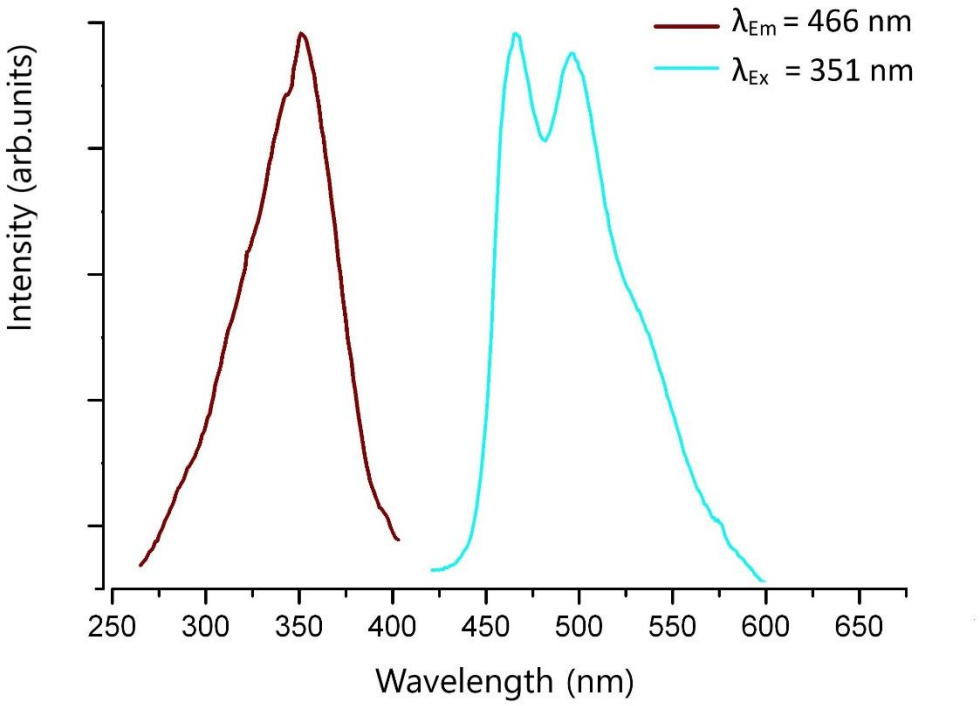


Figure S8. Room temperature emission and excitation spectra of crystalline solid samples of {[4-Cl-3,5-$(CF_3)_2$Pz]Ag}$_4$(1,10-bipy)$_2$ showing emission bands at 466 and 496 nm.

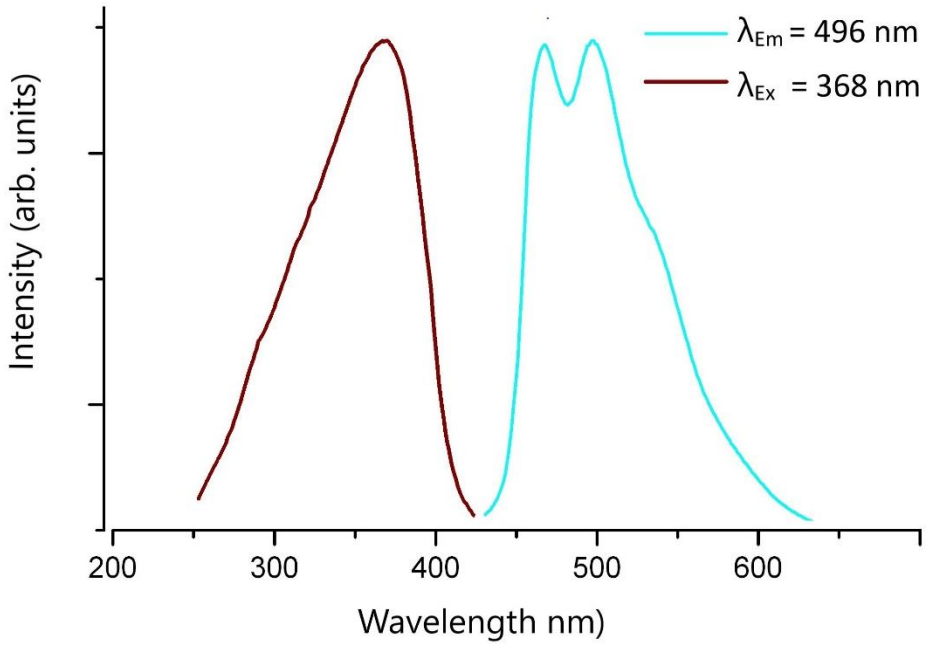


Figure S9. Room temperature emission and excitation spectra of crystalline solid samples of {[4-Br-3,5-$(CF_3)_2$Pz]Ag}$_4$(1,10-phen)$_2$ showing emission bands at 468 and 496 nm.

Computational Details

Geometry optimizations, energy decomposition analysis (EDA) and subsequent calculations were performed by using relativistic DFT methods employing the ADF code.[1] All-electron triple-ξ Slater basis set plus the double-polarization (STO-TZ2P) basis set in conjunction with the Becke-Perdew (BP86) functional were employed, within the generalized gradient approximation (GGA), with London-type dispersion interactions accounted by the pair-waise Grimme approach (BP86-D3).[2] Relativistic effects were taken into account by ZORA formalism.[3] Electronic excitations were calculated at the Time-Dependent DFT approach, by using the long-range corrected LB94 functional.

References

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2. Ehrlich, S.; Moellmann, J.; Grimme, S., Dispersion-Corrected Density Functional Theory for Aromatic Interactions in Complex Systems. *Accounts of Chemical Research* 2013, 46, 916-926.

3. Faas, S.; Snijders, J. G.; van Lenthe, J. H.; van Lenthe, E.; Baerends, E. J., The ZORA formalism applied to the Dirac-Fock equation. *Chemical Physical Letters* **1995**, 246, 632-640.

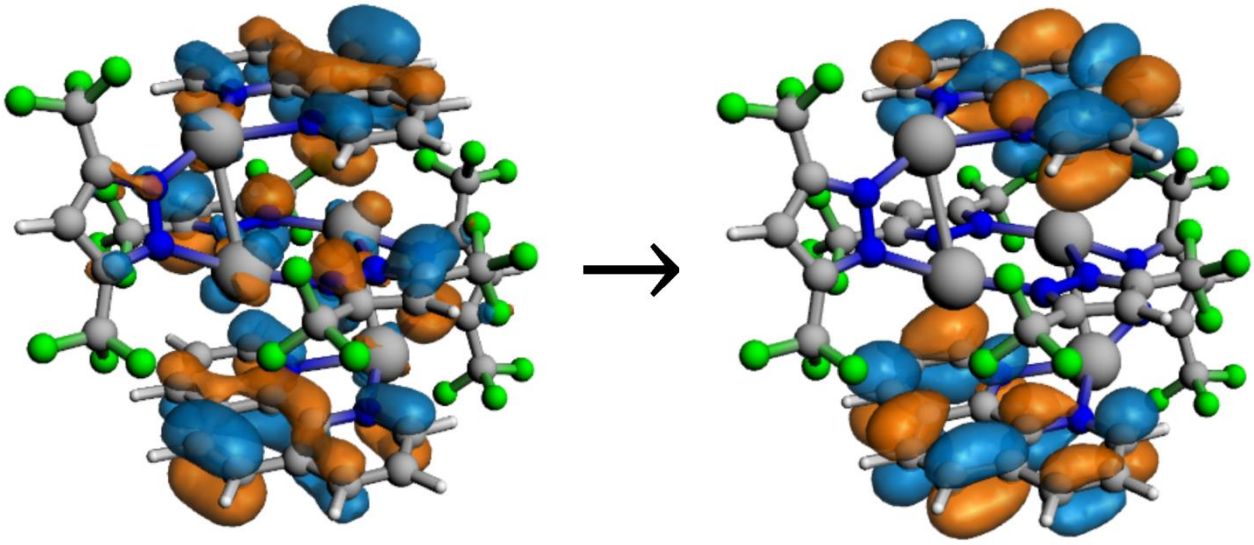

Figure S10. Relevant orbitals for the excitation transition, given for $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_4(1,10\text{-phen})_2$ (**5**) as a representative case. Showing a $\pi \rightarrow \pi^*$ phenanthroline based transition.