Electronic Supplementary Material (ESI) for Dalton Transactions.

Stable and Color Tunable Emission Properties Based on Non-Cyclometalated Gold(III) Complexes

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Table of Contents

Crystal structure determination of 1

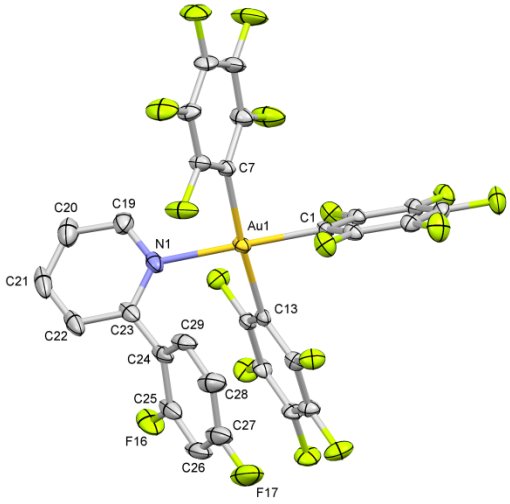

Figure S1a. The molecular structure of **1**, with displacement ellipsoids drawn at the 30% probability level. The solvent molecule and all H atoms are omitted.

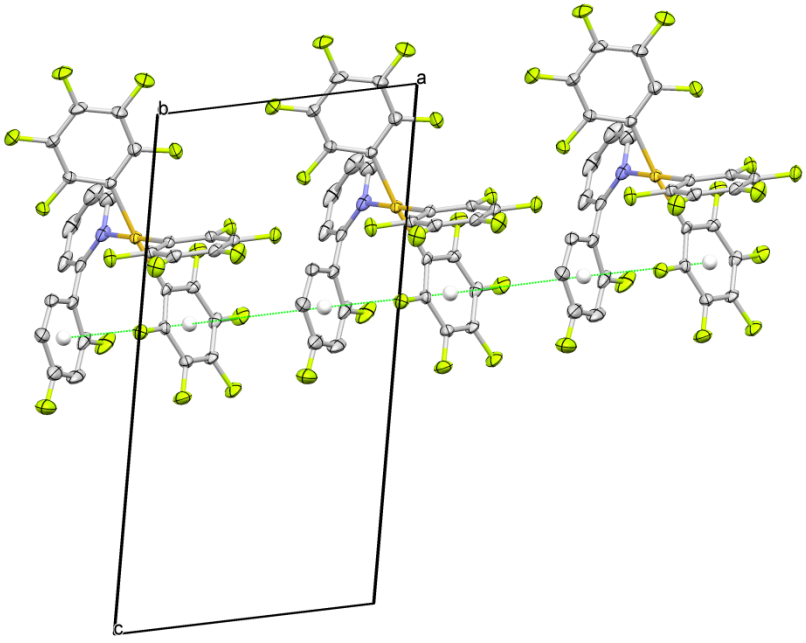

Figure S1b. A view along the *b* axis of the crystal packing of **1** showing π...π interactions as green dashed lines.

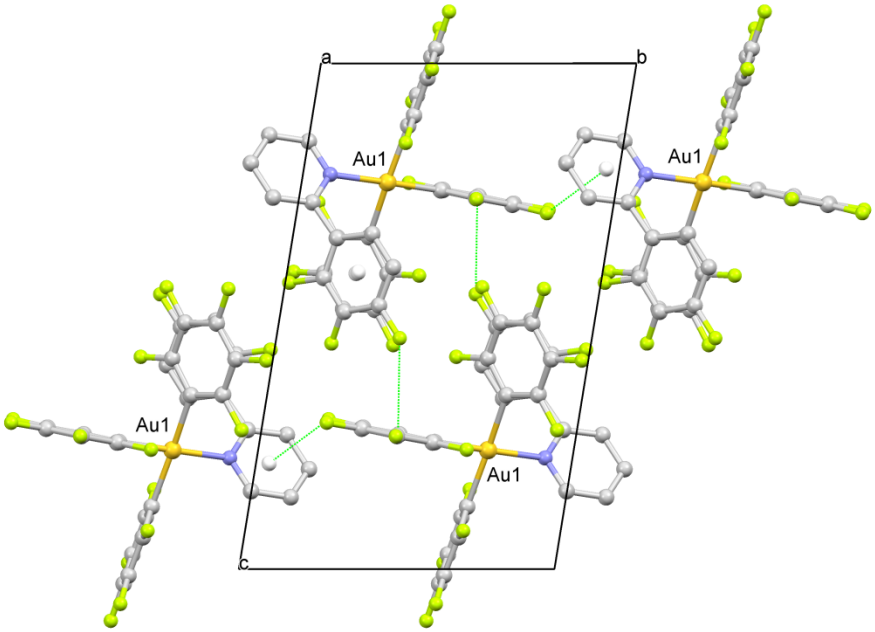

Figure S1c. A view along the *a* axis of the crystal packing of **1** showing C—F…π interactions as green dashed lines.

Table S1. Crystal data and structure refinement for 1.

CCDC number	1024826
Empirical formula	$C_{59}H_{16}Au_2Cl_2F_{34}N_2$
Formula weight	1863.57
Temperature/K	183(1)
Crystal system	triclinic
Space group	P-1
a/Å	8.4911(4)
b/Å	10.3695(4)
c/Å	17.1054(11)
α/°	98.487(4)
β/°	100.945(5)
γ/°	92.939(4)
Volume/Å^3	1457.63(13)
Z	1
ρ_{calc}g/cm^3	2.123
μ/mm^{-1}	5.271
F(000)	882.0
Crystal size/mm^3	0.33 × 0.26 × 0.13
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.81 to 56.558
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -22 ≤ l ≤ 22
Reflections collected	22202
Independent reflections	7227 [R_{int} = 0.0495, R_{sigma} = 0.0530]
Data/restraints/parameters	7227/39/470
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0349, wR_2 = 0.0731
Final R indexes [all data]	R_1 = 0.0448, wR_2 = 0.0775
Largest diff. peak/hole / e Å^{-3}	1.35/-0.88

Table S2. Bond Lengths for 1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Au1	C1	2.017(4)	C14	C15	1.378(6)
Au1	C7	2.078(4)	C14	F11	1.346(5)
Au1	C13	2.071(4)	C15	C16	1.374(6)
Au1	N1	2.113(4)	C15	F12	1.335(5)
C1	C2	1.377(6)	C16	C17	1.358(7)
C1	C6	1.360(5)	C16	F13	1.340(5)
C2	C3	1.380(6)	C17	C18	1.388(6)
C2	F1	1.343(5)	C17	F14	1.344(5)
C3	C4	1.366(6)	C18	F15	1.353(5)
C3	F2	1.352(5)	C19	C20	1.369(7)
C4	C5	1.374(6)	C19	N1	1.338(7)
C4	F3	1.332(5)	C20	C21	1.356(9)
C5	C6	1.374(6)	C21	C22	1.393(9)
C5	F4	1.344(5)	C22	C23	1.368(7)
C6	F5	1.351(4)	C23	C24	1.483(8)
C7	C8	1.381(6)	C23	N1	1.358(6)
C7	C12	1.359(6)	C24	C25	1.394(7)
C8	C9	1.384(7)	C24	C29	1.388(8)
C8	F6	1.352(5)	C25	C26	1.367(9)
C9	C10	1.368(7)	C25	F16	1.356(7)
C9	F7	1.340(5)	C26	C27	1.376(10)
C10	C11	1.371(7)	C27	C28	1.365(8)
C10	F8	1.340(5)	C27	F17	1.347(8)
C11	C12	1.375(6)	C28	C29	1.374(8)
C11	F9	1.340(5)	C30	Cl1	1.755(9)
C12	F10	1.355(5)	C30	Cl2A	1.753(9)
C13	C14	1.371(6)	C30	Cl2B	1.743(9)
C13	C18	1.391(6)	Cl1	Cl1[1]	1.486(11)

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

Table S3. Bond Angles for 1.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C1	Au1	C7	88.89(16)	C14	C13	C18	116.3(4)
C1	Au1	C13	87.15(16)	C18	C13	Au1	119.2(3)
C1	Au1	N1	177.55(15)	C13	C14	C15	122.8(4)
C7	Au1	N1	92.59(16)	F11	C14	C13	119.2(4)
C13	Au1	C7	174.61(15)	F11	C14	C15	117.9(4)
C13	Au1	N1	91.24(15)	C16	C15	C14	119.1(4)
C2	C1	Au1	120.9(3)	F12	C15	C14	120.8(4)
C6	C1	Au1	121.3(3)	F12	C15	C16	120.1(4)
C6	C1	C2	117.7(4)	C17	C16	C15	120.5(4)
C1	C2	C3	120.7(4)	F13	C16	C15	119.4(4)
F1	C2	C1	120.9(4)	F13	C16	C17	120.0(4)
F1	C2	C3	118.4(4)	C16	C17	C18	119.4(4)
C4	C3	C2	120.5(4)	F14	C17	C16	120.9(4)
F2	C3	C2	120.5(4)	F14	C17	C18	119.7(4)
F2	C3	C4	119.0(4)	C17	C18	C13	121.9(4)
C3	C4	C5	119.2(4)	F15	C18	C13	120.1(4)
F3	C4	C3	120.7(4)	F15	C18	C17	118.1(4)
F3	C4	C5	120.0(4)	N1	C19	C20	122.9(6)
C6	C5	C4	119.4(4)	C21	C20	C19	119.3(7)
F4	C5	C4	119.4(4)	C20	C21	C22	118.6(6)
F4	C5	C6	121.2(4)	C23	C22	C21	120.2(6)
C1	C6	C5	122.4(4)	C22	C23	C24	120.8(5)

F5	C6	C1	119.8(4)	N1	C23	C22	120.6(6)
F5	C6	C5	117.8(4)	N1	C23	C24	118.6(4)
C8	C7	Au1	120.9(3)	C25	C24	C23	121.3(5)
C12	C7	Au1	124.7(3)	C29	C24	C23	122.5(5)
C12	C7	C8	114.4(4)	C29	C24	C25	116.1(6)
C7	C8	C9	123.4(5)	C26	C25	C24	123.7(6)
F6	C8	C7	120.1(4)	F16	C25	C24	117.3(6)
F6	C8	C9	116.5(4)	F16	C25	C26	119.0(6)
C10	C9	C8	119.4(4)	C25	C26	C27	117.1(6)
F7	C9	C8	120.8(5)	C28	C27	C26	122.3(7)
F7	C9	C10	119.8(5)	F17	C27	C26	118.6(6)
C9	C10	C11	119.2(5)	F17	C27	C28	119.1(7)
F8	C10	C9	121.0(5)	C27	C28	C29	119.0(7)
F8	C10	C11	119.9(5)	C28	C29	C24	121.8(5)
C10	C11	C12	119.0(4)	C19	N1	Au1	116.9(3)
F9	C11	C10	119.1(4)	C19	N1	C23	118.5(5)
F9	C11	C12	121.9(4)	C23	N1	Au1	124.3(4)
C7	C12	C11	124.7(4)	Cl2A	C30	Cl1	106.9(7)
F10	C12	C7	119.5(4)	Cl2B	C30	Cl1	111.1(9)
F10	C12	C11	115.8(4)	Cl1[1]	Cl1	C30	163.2(7)
C14	C13	Au1	124.4(3)				

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

Crystal structure determination of 2.

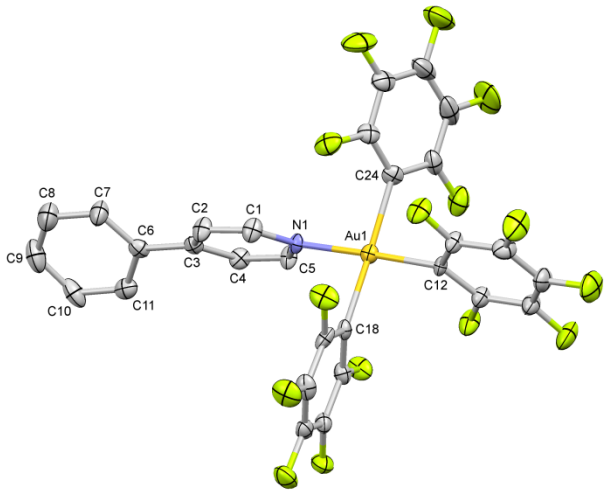

Figure S2a. The molecular structure of **2**, with displacement ellipsoids drawn at the 30% probability level (only one of the two crystallographically independent molecules is presented). All H atoms are omitted for clarity.

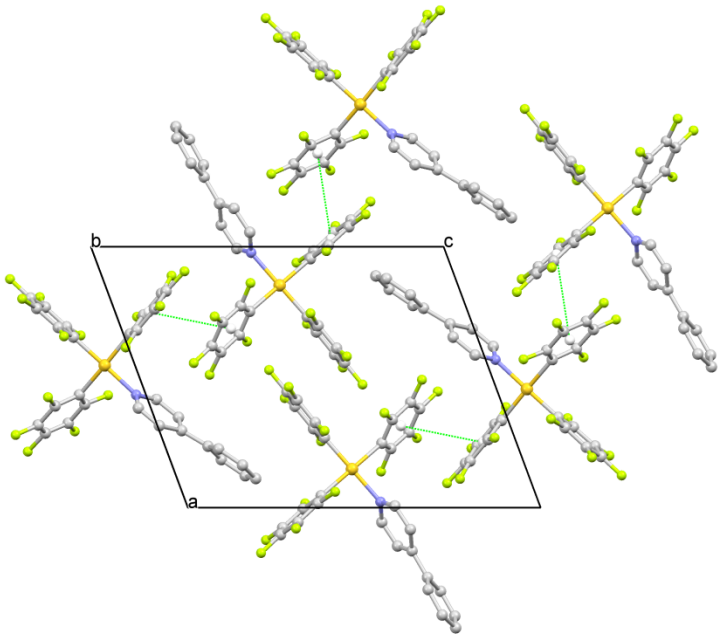

Figure S2b. A view along the *b* axis of the crystal packing of **2** showing π...π interactions as green dashed lines.

Table S4. Crystal data and structure refinement for 2.

CCDC number	1024827
Empirical formula	$C_{119}H_{43}Au_4F_{60}N_4$
Formula weight	3456.44
Temperature/K	183(1)
Crystal system	triclinic
Space group	P-1
a/Å	13.4052(8)
b/Å	13.8638(6)
c/Å	16.8973(12)
α/°	83.044(4)
β/°	68.830(6)
γ/°	80.730(4)
Volume/Å^3	2883.4(3)
Z	1
ρ_{calc}g/cm^3	1.991
μ/mm^{-1}	5.222
F(000)	1641.0
Crystal size/mm^3	0.27 × 0.15 × 0.03
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.562 to 50.7
Index ranges	-16 ≤ h ≤ 17, -17 ≤ k ≤ 18, -22 ≤ l ≤ 22
Reflections collected	33922
Independent reflections	10536 [R_{int} = 0.0665, R_{sigma} = 0.0990]
Data/restraints/parameters	10536/400/872
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0552, wR_2 = 0.1197
Final R indexes [all data]	R_1 = 0.0800, wR_2 = 0.1326
Largest diff. peak/hole / e Å^{-3}	2.27/-1.08

Table S5. Bond Lengths for 2.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.363(13)	C33	C34	1.334(14)
C1	N1	1.352(11)	C34	N2	1.335(11)
C2	C3	1.386(12)	C35A	C36A	1.3900
C3	C4	1.399(13)	C35A	C40A	1.3900
C3	C6	1.478(13)	C36A	C37A	1.3900
C4	C5	1.356(12)	C37A	C38A	1.3900
C5	N1	1.336(10)	C38A	C39A	1.3900
C6	C7	1.381(14)	C39A	C40A	1.3900
C6	C11	1.387(13)	C35B	C36B	1.3900
C7	C8	1.378(15)	C35B	C40B	1.3900
C8	C9	1.363(17)	C36B	C37B	1.3900
C9	C10	1.375(18)	C37B	C38B	1.3900
C10	C11	1.396(15)	C38B	C39B	1.3900
C12	C13	1.386(12)	C39B	C40B	1.3900
C12	C17	1.394(11)	C41	C42	1.411(12)
C12	Au1	1.990(8)	C41	C46	1.387(12)
C13	C14	1.370(13)	C41	Au2	2.050(9)
C13	F1	1.352(10)	C42	C43	1.396(14)
C14	C15	1.372(14)	C42	F16	1.353(10)
C14	F2	1.320(11)	C43	C44	1.336(13)
C15	C16	1.394(15)	C43	F17	1.309(11)
C15	F3	1.348(12)	C44	C45	1.369(13)
C16	C17	1.383(14)	C44	F18	1.355(11)
C16	F4	1.349(11)	C45	C46	1.383(13)
C17	F5	1.331(10)	C45	F19	1.334(10)
C18	C19	1.380(12)	C46	F20	1.342(10)
C18	C23	1.375(12)	C47	C48	1.380(12)
C18	Au1	2.065(9)	C47	C52	1.351(14)
C19	C20	1.375(13)	C47	Au2	2.012(9)
C19	F6	1.362(10)	C48	C49	1.380(14)
C20	C21	1.367(13)	C48	F21	1.354(11)
C20	F7	1.319(10)	C49	C50	1.377(15)
C21	C22	1.372(14)	C49	F22	1.352(11)
C21	F8	1.339(11)	C50	C51	1.367(15)
C22	C23	1.370(14)	C50	F23	1.337(11)
C22	F9	1.336(10)	C51	C52	1.369(14)
C23	F10	1.369(10)	C51	F24	1.346(12)
C24	C25	1.368(13)	C52	F25	1.355(11)
C24	C29	1.371(13)	C53	C54	1.368(14)
C24	Au1	2.081(10)	C53	C58	1.378(14)
C25	C26	1.356(15)	C53	Au2	2.040(9)
C25	F11	1.349(11)	C54	C55	1.382(17)
C26	C27	1.368(18)	C54	F26	1.383(14)
C26	F12	1.326(13)	C55	C56	1.33(2)
C27	C28	1.40(2)	C55	F27	1.331(14)
C27	F13	1.345(13)	C56	C57	1.349(19)
C28	C29	1.364(17)	C56	F28	1.387(13)
C28	F14	1.353(14)	C57	C58	1.397(15)
C29	F15	1.340(13)	C57	F29	1.326(15)
C30	C31	1.365(15)	C58	F30	1.361(12)
C30	N2	1.328(12)	N1	Au1	2.068(7)
C31	C32	1.352(15)	N2	Au2	2.069(7)
C32	C33	1.426(16)	C59	C60	1.543(5)

C32	C35A	1.477(12)	C60	C61	1.541(5)
C32	C35B	1.480(13)	C61	C61[1]	1.551(5)

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

Table S6. Bond Angles for 2.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N1	C1	C2	122.8(8)	C40A	C39A	C38A	120.0
C1	C2	C3	120.6(9)	C39A	C40A	C35A	120.0
C2	C3	C4	115.7(8)	C36B	C35B	C32	123.9(16)
C2	C3	C6	121.4(8)	C36B	C35B	C40B	120.0
C4	C3	C6	122.9(8)	C40B	C35B	C32	116.0(15)
C5	C4	C3	120.8(8)	C37B	C36B	C35B	120.0
N1	C5	C4	123.0(8)	C36B	C37B	C38B	120.0
C7	C6	C3	121.0(8)	C39B	C38B	C37B	120.0
C7	C6	C11	118.6(9)	C38B	C39B	C40B	120.0
C11	C6	C3	120.4(9)	C39B	C40B	C35B	120.0
C8	C7	C6	120.3(11)	C42	C41	Au2	121.1(6)
C9	C8	C7	121.0(12)	C46	C41	C42	114.0(8)
C8	C9	C10	120.1(12)	C46	C41	Au2	124.8(6)
C9	C10	C11	119.2(11)	C43	C42	C41	124.0(8)
C6	C11	C10	120.8(10)	F16	C42	C41	117.1(8)
C13	C12	C17	114.6(8)	F16	C42	C43	118.8(8)
C13	C12	Au1	123.8(6)	C44	C43	C42	117.4(9)
C17	C12	Au1	121.6(6)	F17	C43	C42	119.7(9)
C14	C13	C12	125.2(8)	F17	C43	C44	122.8(10)
F1	C13	C12	117.2(8)	C43	C44	C45	122.8(9)
F1	C13	C14	117.5(8)	C43	C44	F18	118.2(9)
C13	C14	C15	118.1(9)	F18	C44	C45	118.9(9)
F2	C14	C13	122.0(9)	C44	C45	C46	118.7(9)
F2	C14	C15	119.9(9)	F19	C45	C44	120.3(9)
C14	C15	C16	120.1(10)	F19	C45	C46	121.0(9)
F3	C15	C14	120.0(10)	C45	C46	C41	123.1(9)
F3	C15	C16	119.9(10)	F20	C46	C41	119.5(8)
C17	C16	C15	119.4(9)	F20	C46	C45	117.5(8)
F4	C16	C15	119.3(10)	C48	C47	Au2	121.1(7)
F4	C16	C17	121.4(10)	C52	C47	C48	116.1(9)
C16	C17	C12	122.5(8)	C52	C47	Au2	122.8(7)
F5	C17	C12	120.5(8)	C49	C48	C47	122.1(9)
F5	C17	C16	116.9(8)	F21	C48	C47	120.3(8)
C19	C18	Au1	125.0(7)	F21	C48	C49	117.7(8)
C23	C18	C19	114.5(9)	C50	C49	C48	119.3(9)
C23	C18	Au1	120.4(7)	F22	C49	C48	119.9(10)
C20	C19	C18	123.9(9)	F22	C49	C50	120.7(10)
F6	C19	C18	118.8(9)	C51	C50	C49	119.6(10)
F6	C19	C20	117.3(8)	F23	C50	C49	118.7(10)
C21	C20	C19	118.5(9)	F23	C50	C51	121.8(10)
F7	C20	C19	120.7(9)	C50	C51	C52	118.9(10)
F7	C20	C21	120.8(9)	F24	C51	C50	118.7(10)
C20	C21	C22	120.5(9)	F24	C51	C52	122.3(10)
F8	C21	C20	119.8(9)	C47	C52	C51	124.1(10)
F8	C21	C22	119.7(9)	C47	C52	F25	119.7(9)
C23	C22	C21	118.5(9)	F25	C52	C51	116.3(9)
F9	C22	C21	120.4(10)	C54	C53	C58	112.5(10)

F9	C22	C23	121.0(9)	C54	C53	Au2	126.8(9)
C22	C23	C18	124.1(9)	C58	C53	Au2	120.6(7)
F10	C23	C18	118.8(9)	C53	C54	C55	124.5(13)
F10	C23	C22	117.1(8)	C53	C54	F26	116.2(10)
C25	C24	C29	117.5(10)	C55	C54	F26	119.3(11)
C25	C24	Au1	119.7(7)	C56	C55	C54	118.4(12)
C29	C24	Au1	122.7(8)	F27	C55	C54	118.6(15)
C26	C25	C24	124.0(10)	F27	C55	C56	123.0(14)
F11	C25	C24	119.8(9)	C55	C56	C57	122.9(12)
F11	C25	C26	116.3(9)	C55	C56	F28	118.4(16)
C25	C26	C27	118.3(11)	C57	C56	F28	118.6(16)
F12	C26	C25	122.1(12)	C56	C57	C58	115.7(13)
F12	C26	C27	119.6(12)	F29	C57	C56	121.6(13)
C26	C27	C28	119.2(11)	F29	C57	C58	122.8(13)
F13	C27	C26	121.4(15)	C53	C58	C57	125.9(11)
F13	C27	C28	119.4(15)	F30	C58	C53	119.8(9)
C29	C28	C27	120.6(12)	F30	C58	C57	114.3(10)
F14	C28	C27	118.6(13)	C1	N1	Au1	120.4(6)
F14	C28	C29	120.7(15)	C5	N1	C1	116.9(7)
C28	C29	C24	120.4(12)	C5	N1	Au1	121.9(5)
F15	C29	C24	120.7(10)	C30	N2	C34	116.2(8)
F15	C29	C28	118.9(11)	C30	N2	Au2	122.8(6)
N2	C30	C31	123.0(10)	C34	N2	Au2	120.7(6)
C32	C31	C30	122.1(11)	C12	Au1	C18	90.7(3)
C31	C32	C33	114.1(10)	C12	Au1	C24	89.0(4)
C31	C32	C35A	118.1(11)	C12	Au1	N1	177.7(3)
C31	C32	C35B	125.8(11)	C18	Au1	C24	175.0(3)
C33	C32	C35A	127.6(10)	C18	Au1	N1	88.3(3)
C33	C32	C35B	118.9(10)	N1	Au1	C24	92.1(3)
C34	C33	C32	120.7(9)	C41	Au2	N2	90.7(3)
C33	C34	N2	123.8(9)	C47	Au2	C41	89.3(4)
C36A	C35A	C32	119.5(8)	C47	Au2	C53	88.6(4)
C36A	C35A	C40A	120.0	C47	Au2	N2	177.4(3)
C40A	C35A	C32	120.4(8)	C53	Au2	C41	175.1(3)
C35A	C36A	C37A	120.0	C53	Au2	N2	91.6(3)
C38A	C37A	C36A	120.0	C61	C60	C59	109.9(7)
C37A	C38A	C39A	120.0	C60	C61	C61[1]	108.8(7)

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

Crystal structure determination of 3.

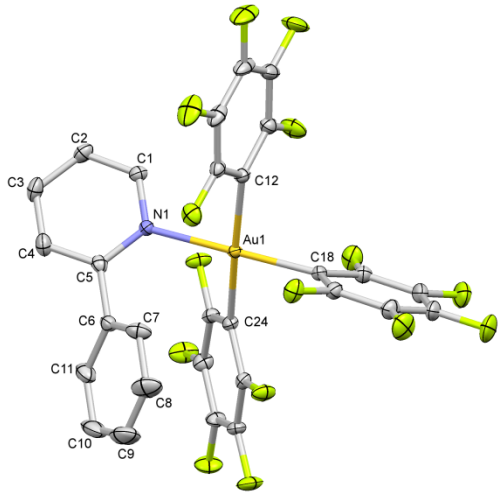

Figure S3a. The molecular structure of **3**, with displacement ellipsoids drawn at the 30% probability level. All H atoms are omitted for clarity.

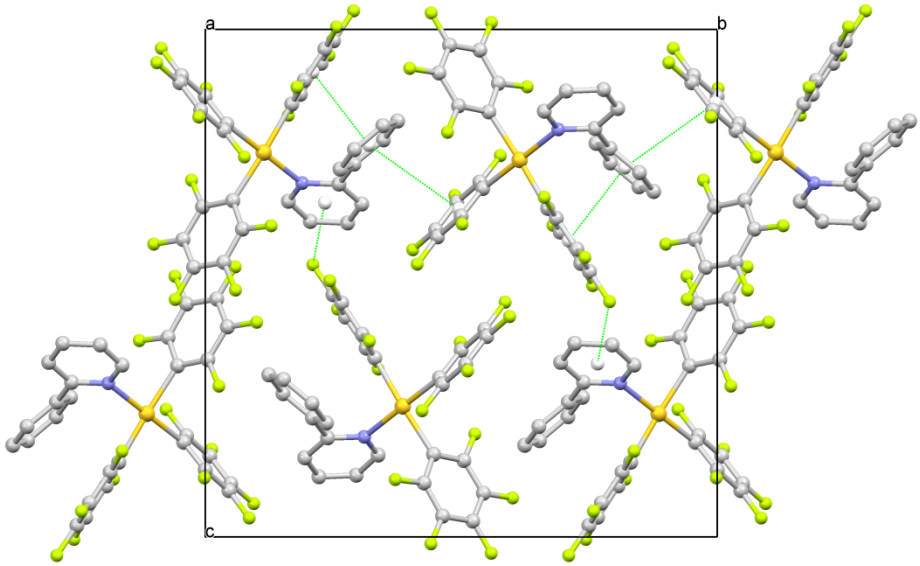

Figure S3b. A view along the *a* axis of the crystal packing of **3** showing π...π and C—F...π interactions as green dashed lines.

Table S7. Crystal data and structure refinement for 3.

CCDC number	1024828
Empirical formula	$C_{29}H_9AuF_{15}N$
Formula weight	853.34
Temperature/K	183(1)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.9254(4)
b/Å	18.503(4)
c/Å	18.4895(11)

α/°	90
β/°	97.579(5)
γ/°	90
Volume/Å^3	2687.7(6)
Z	4
ρ_{calc}g/cm^3	2.109
μ/mm^{-1}	5.601
F(000)	1616.0
Crystal size/mm^3	0.47 × 0.31 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.634 to 61.014
Index ranges	-11 ≤ h ≤ 11, -26 ≤ k ≤ 26, -26 ≤ l ≤ 26
Reflections collected	48393
Independent reflections	8205 [R_{int} = 0.0501, R_{sigma} = 0.0318]
Data/restraints/parameters	8205/0/415
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0246, wR_2 = 0.0568
Final R indexes [all data]	R_1 = 0.0310, wR_2 = 0.0597
Largest diff. peak/hole / e Å^{-3}	1.85/-0.93

Table S8. Bond Lengths for 3.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Au1	C12	2.074(2)	C16	C17	1.372(4)
Au1	C18	2.011(2)	C16	F4	1.341(4)
Au1	C24	2.054(2)	C17	F5	1.341(3)
Au1	N1	2.109(2)	C18	C19	1.369(4)
C1	C2	1.369(4)	C18	C23	1.375(4)
C1	N1	1.353(3)	C19	C20	1.389(4)
C2	C3	1.372(4)	C19	F6	1.341(3)
C3	C4	1.365(4)	C20	C21	1.362(5)
C4	C5	1.383(4)	C20	F7	1.346(4)
C5	C6	1.476(4)	C21	C22	1.366(5)
C5	N1	1.348(3)	C21	F8	1.344(3)
C6	C7	1.390(4)	C22	C23	1.380(4)
C6	C11	1.388(4)	C22	F9	1.332(3)
C7	C8	1.375(4)	C23	F10	1.343(3)
C8	C9	1.354(6)	C24	C25	1.379(3)
C9	C10	1.363(7)	C24	C29	1.380(4)
C10	C11	1.381(5)	C25	C26	1.381(4)
C12	C13	1.372(4)	C25	F11	1.342(3)
C12	C17	1.373(4)	C26	C27	1.367(4)
C13	C14	1.377(4)	C26	F12	1.343(3)
C13	F1	1.347(4)	C27	C28	1.378(4)
C14	C15	1.365(5)	C27	F13	1.337(3)
C14	F2	1.342(4)	C28	C29	1.382(4)
C15	C16	1.371(5)	C28	F14	1.336(3)
C15	F3	1.340(3)	C29	F15	1.352(3)

Table S9. Bond Angles for 3.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C12	Au1	N1	89.19(9)	C19	C18	Au1	123.0(2)
C18	Au1	C12	90.29(10)	C19	C18	C23	116.9(2)

C18	Au1	C24	89.19(10)	C23	C18	Au1	120.0(2)
C18	Au1	N1	179.43(10)	C18	C19	C20	121.7(3)
C24	Au1	C12	175.89(10)	F6	C19	C18	120.8(2)
C24	Au1	N1	91.35(9)	F6	C19	C20	117.5(3)
N1	C1	C2	122.3(3)	C21	C20	C19	119.6(3)
C1	C2	C3	118.7(3)	F7	C20	C19	119.9(3)
C4	C3	C2	119.1(3)	F7	C20	C21	120.6(3)
C3	C4	C5	121.0(3)	C20	C21	C22	120.4(3)
C4	C5	C6	121.0(3)	F8	C21	C20	119.5(3)
N1	C5	C4	119.6(3)	F8	C21	C22	120.1(3)
N1	C5	C6	119.4(2)	C21	C22	C23	118.8(3)
C7	C6	C5	122.0(3)	F9	C22	C21	120.2(3)
C11	C6	C5	119.4(3)	F9	C22	C23	121.0(3)
C11	C6	C7	118.6(3)	C18	C23	C22	122.6(3)
C8	C7	C6	120.2(3)	F10	C23	C18	120.6(2)
C9	C8	C7	120.6(4)	F10	C23	C22	116.8(3)
C8	C9	C10	120.1(4)	C25	C24	Au1	124.46(19)
C9	C10	C11	120.6(4)	C25	C24	C29	115.7(2)
C10	C11	C6	119.8(4)	C29	C24	Au1	119.81(17)
C13	C12	Au1	119.5(2)	C24	C25	C26	122.5(2)
C13	C12	C17	115.5(2)	F11	C25	C24	120.5(2)
C17	C12	Au1	124.6(2)	F11	C25	C26	117.0(2)
C12	C13	C14	123.1(3)	C27	C26	C25	120.0(2)
F1	C13	C12	119.4(3)	F12	C26	C25	120.4(3)
F1	C13	C14	117.5(3)	F12	C26	C27	119.6(2)
C15	C14	C13	119.4(3)	C26	C27	C28	119.8(2)
F2	C14	C13	120.5(4)	F13	C27	C26	120.7(2)
F2	C14	C15	120.1(3)	F13	C27	C28	119.5(3)
C14	C15	C16	119.3(3)	C27	C28	C29	118.6(3)
F3	C15	C14	120.6(3)	F14	C28	C27	120.2(3)
F3	C15	C16	120.0(4)	F14	C28	C29	121.1(2)
C15	C16	C17	119.5(3)	C24	C29	C28	123.4(2)
F4	C16	C15	119.8(3)	F15	C29	C24	120.0(2)
F4	C16	C17	120.6(3)	F15	C29	C28	116.5(2)
C16	C17	C12	123.1(3)	C1	N1	Au1	115.97(18)
F5	C17	C12	120.3(2)	C5	N1	Au1	124.63(17)
F5	C17	C16	116.6(3)	C5	N1	C1	119.3(2)

Crystal structure determination of 4.

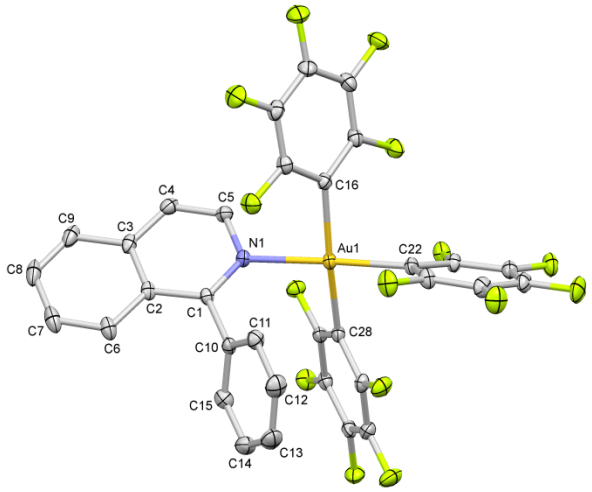

Figure S4a. The molecular structure of **4**, with displacement ellipsoids drawn at the 30% probability level. The solvent molecule and all H atoms are omitted for clarity.

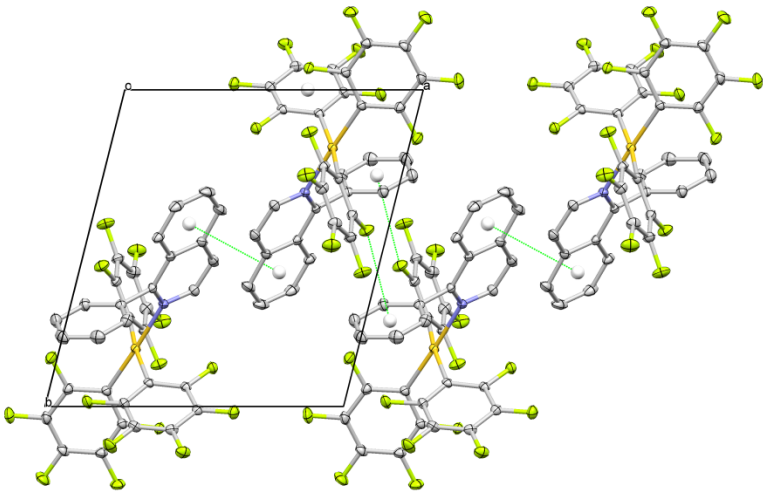

Figure S4b. A view along the *b* axis of the crystal packing of **4** showing π...π and C—F…π interactions as green dashed lines.

Table S10. Crystal data and structure refinement for 4.

CCDC number	1024829
Empirical formula	$C_{70}H_{32}Au_2F_{30}N_2O$
Formula weight	1880.91
Temperature/K	183(1)
Crystal system	triclinic
Space group	P-1
a/Å	11.2092(3)
b/Å	12.1878(3)
c/Å	12.5527(3)
α/°	104.977(2)
β/°	106.125(2)

γ/°	98.915(2)
Volume/Å^3	1543.23(7)
Z	1
ρ_{calc}g/cm^3	2.024
μ/mm^{-1}	4.889
F(000)	902.0
Crystal size/mm^3	0.47 × 0.19 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.716 to 61.012
Index ranges	-16 ≤ h ≤ 16, -17 ≤ k ≤ 17, -17 ≤ l ≤ 17
Reflections collected	27853
Independent reflections	9409 [R_{int} = 0.0378, R_{sigma} = 0.0367]
Data/restraints/parameters	9409/0/496
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0242, wR_2 = 0.0571
Final R indexes [all data]	R_1 = 0.0270, wR_2 = 0.0587
Largest diff. peak/hole / e Å^{-3}	1.33/-0.93

Table S11. Bond Lengths for 4.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.420(3)	C22	C23	1.383(3)
C1	C10	1.481(3)	C22	C27	1.379(3)
C1	N1	1.337(3)	C22	Au1	2.012(2)
C2	C3	1.424(4)	C23	C24	1.381(4)
C2	C6	1.418(3)	C23	F6	1.353(3)
C3	C4	1.400(4)	C24	C25	1.378(4)
C3	C9	1.416(4)	C24	F7	1.343(3)
C4	C5	1.355(4)	C25	C26	1.380(4)
C5	N1	1.371(3)	C25	F8	1.337(3)
C6	C7	1.359(4)	C26	C27	1.378(3)
C7	C8	1.412(5)	C26	F9	1.345(3)
C8	C9	1.356(5)	C27	F10	1.344(3)
C10	C11	1.399(3)	C28	C29	1.383(3)
C10	C15	1.392(4)	C28	C33	1.380(3)
C11	C12	1.378(4)	C28	Au1	2.059(2)
C12	C13	1.388(5)	C29	C30	1.378(3)
C13	C14	1.391(4)	C29	F11	1.351(3)
C14	C15	1.380(4)	C30	C31	1.376(4)
C16	C17	1.381(3)	C30	F12	1.343(3)
C16	C21	1.395(3)	C31	C32	1.379(4)
C16	Au1	2.077(2)	C31	F13	1.341(3)
C17	C18	1.374(4)	C32	C33	1.379(4)
C17	F1	1.352(3)	C32	F14	1.338(3)
C18	C19	1.375(4)	C33	F15	1.355(3)
C18	F2	1.349(3)	N1	Au1	2.101(2)
C19	C20	1.388(4)	O1	C34	1.424(10)
C19	F3	1.333(3)	O1	C36	1.429(12)
C20	C21	1.366(4)	C34	C35	1.482(12)
C20	F4	1.340(3)	C36	C37	1.477(12)
C21	F5	1.350(3)			

Table S12. Bond Angles for 4.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C2	C1	C10	120.8(2)	F6	C23	C22	119.7(2)
N1	C1	C2	120.9(2)	F6	C23	C24	117.5(2)
N1	C1	C10	118.3(2)	C25	C24	C23	119.3(2)
C1	C2	C3	118.7(2)	F7	C24	C23	121.0(2)
C6	C2	C1	122.4(2)	F7	C24	C25	119.7(2)
C6	C2	C3	118.9(2)	C24	C25	C26	119.2(2)
C4	C3	C2	118.0(2)	F8	C25	C24	120.5(2)
C4	C3	C9	122.7(3)	F8	C25	C26	120.3(2)
C9	C3	C2	119.3(3)	C27	C26	C25	120.1(2)
C5	C4	C3	120.1(2)	F9	C26	C25	119.1(2)
C4	C5	N1	122.4(2)	F9	C26	C27	120.8(2)
C7	C6	C2	119.9(3)	C26	C27	C22	122.2(2)
C6	C7	C8	121.4(3)	F10	C27	C22	120.0(2)
C9	C8	C7	120.2(3)	F10	C27	C26	117.8(2)
C8	C9	C3	120.4(3)	C29	C28	Au1	118.98(18)
C11	C10	C1	121.2(2)	C33	C28	C29	115.3(2)
C15	C10	C1	119.4(2)	C33	C28	Au1	125.74(18)
C15	C10	C11	119.4(2)	C30	C29	C28	123.6(2)
C12	C11	C10	120.0(3)	F11	C29	C28	120.1(2)
C11	C12	C13	120.4(3)	F11	C29	C30	116.4(2)
C12	C13	C14	119.8(3)	C31	C30	C29	118.9(2)
C15	C14	C13	120.0(3)	F12	C30	C29	121.2(2)
C14	C15	C10	120.4(3)	F12	C30	C31	119.9(2)
C17	C16	C21	114.3(2)	C30	C31	C32	120.0(2)
C17	C16	Au1	120.18(17)	F13	C31	C30	119.9(2)
C21	C16	Au1	124.68(17)	F13	C31	C32	120.2(2)
C18	C17	C16	123.6(2)	C33	C32	C31	119.0(2)
F1	C17	C16	119.8(2)	F14	C32	C31	119.4(2)
F1	C17	C18	116.6(2)	F14	C32	C33	121.5(2)
C17	C18	C19	120.1(2)	C32	C33	C28	123.3(2)
F2	C18	C17	121.3(2)	F15	C33	C28	120.3(2)
F2	C18	C19	118.6(2)	F15	C33	C32	116.4(2)
C18	C19	C20	118.6(2)	C1	N1	C5	119.9(2)
F3	C19	C18	120.8(2)	C1	N1	Au1	123.45(17)
F3	C19	C20	120.6(2)	C5	N1	Au1	116.60(15)
C21	C20	C19	119.4(2)	C16	Au1	N1	89.64(8)
F4	C20	C19	118.9(2)	C22	Au1	C16	91.12(9)
F4	C20	C21	121.6(2)	C22	Au1	C28	88.55(9)
C20	C21	C16	124.0(2)	C22	Au1	N1	176.97(8)
F5	C21	C16	119.6(2)	C28	Au1	C16	171.30(9)
F5	C21	C20	116.4(2)	C28	Au1	N1	91.15(8)
C23	C22	Au1	119.73(17)	C34	O1	C36	114.0(5)
C27	C22	C23	116.3(2)	O1	C34	C35	110.1(7)
C27	C22	Au1	123.72(18)	O1	C36	C37	109.9(7)
C24	C23	C22	122.8(2)				

Crystal structure determination of 5.

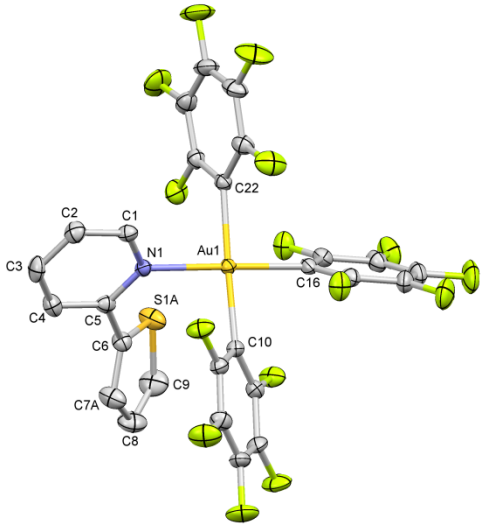

Figure S5a. The molecular structure of **5**, with displacement ellipsoids drawn at the 30% probability level. The solvent molecule, all H atoms and the minor component of the disordered thiophene are omitted.

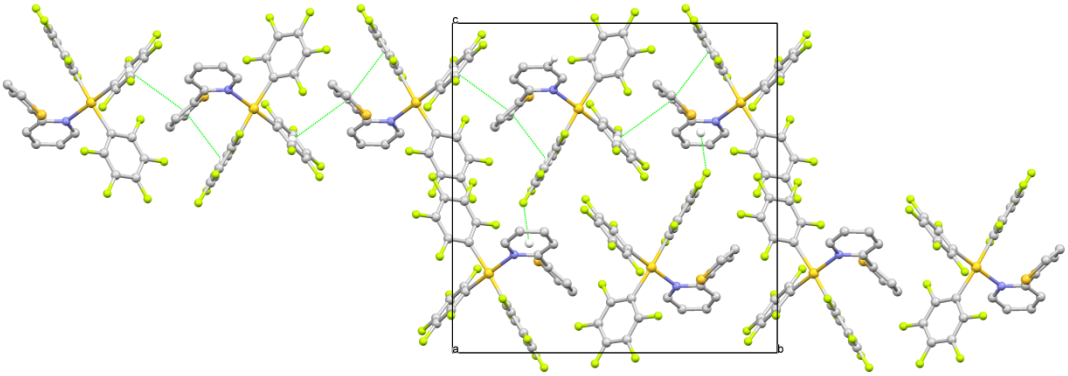

Figure S5b. A view along the *a* axis of the crystal packing of **5** showing π...π and C—F…π interactions as green dashed lines.

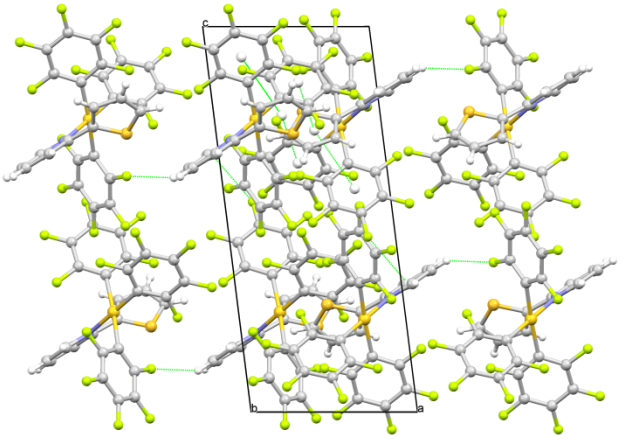

Figure S5c. A view along the *b* axis of the crystal packing of **5** showing C—H…F interactions as green dashed lines.

Table S13. Crystal data and structure refinement for 5.

CCDC number	1024830
Empirical formula	$C_{27}H_7AuF_{15}NS$
Formula weight	859.36
Temperature/K	183(1)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.9119(2)
b/Å	18.0726(4)
c/Å	18.4278(4)
α/°	90
β/°	97.163(2)
γ/°	90
Volume/Å^3	2614.40(11)
Z	4
ρ_{calc}g/cm^3	2.183
μ/mm^{-1}	5.835
F(000)	1624.0
Crystal size/mm^3	0.25 × 0.15 × 0.14
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.658 to 52.744
Index ranges	-9 ≤ h ≤ 9, -22 ≤ k ≤ 22, -23 ≤ l ≤ 23
Reflections collected	36456
Independent reflections	5337 [R_{int} = 0.0543, R_{sigma} = 0.0285]
Data/restraints/parameters	5337/2/407
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0218, wR_2 = 0.0536
Final R indexes [all data]	R_1 = 0.0241, wR_2 = 0.0549
Largest diff. peak/hole / e Å^{-3}	1.40/-0.68

Table S14. Bond Lengths for 5.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Au1	C10	2.058(3)	C13	F3	1.344(4)
Au1	C16	2.016(3)	C14	C15	1.380(4)
Au1	C22	2.069(3)	C14	F4	1.341(4)
Au1	N1	2.115(2)	C15	F5	1.351(4)
C1	C2	1.369(4)	C16	C17	1.372(4)
C1	N1	1.343(4)	C16	C21	1.374(4)
C2	C3	1.380(5)	C17	C18	1.391(5)
C3	C4	1.378(5)	C17	F6	1.341(4)
C4	C5	1.381(4)	C18	C19	1.370(5)
C5	C6	1.465(4)	C18	F7	1.349(4)
C5	N1	1.363(4)	C19	C20	1.372(5)
C6	C7A	1.379(7)	C19	F8	1.343(4)
C6	C7B	1.381(9)	C20	C21	1.377(4)
C6	S1A	1.709(3)	C20	F9	1.342(4)
C6	S1B	1.702(4)	C21	F10	1.346(4)
C7A	C8	1.423(7)	C22	C23	1.381(4)
C7B	C9	1.67(4)	C22	C27	1.380(4)
C8	C9	1.336(5)	C23	C24	1.380(5)
C8	S1B	1.520(7)	C23	F11	1.344(4)
C9	S1A	1.676(4)	C24	C25	1.372(5)
C10	C11	1.377(4)	C24	F12	1.343(4)
C10	C15	1.378(4)	C25	C26	1.370(5)
C11	C12	1.380(4)	C25	F13	1.346(4)

C11	F1	1.357(4)	C26	C27	1.377(5)
C12	C13	1.373(5)	C26	F14	1.345(4)
C12	F2	1.342(4)	C27	F15	1.348(4)
C13	C14	1.375(5)			

Table S15. Bond Angles for 5.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C10	Au1	C22	174.81(12)	F5	C15	C14	116.7(3)
C10	Au1	N1	90.28(10)	C17	C16	Au1	122.8(2)
C16	Au1	C10	89.09(12)	C17	C16	C21	117.5(3)
C16	Au1	C22	90.44(12)	C21	C16	Au1	119.7(2)
C16	Au1	N1	178.84(11)	C16	C17	C18	121.3(3)
C22	Au1	N1	90.28(11)	F6	C17	C16	121.3(3)
N1	C1	C2	122.7(3)	F6	C17	C18	117.4(3)
C1	C2	C3	118.8(3)	C19	C18	C17	119.6(3)
C4	C3	C2	119.0(3)	F7	C18	C17	120.0(3)
C3	C4	C5	120.5(3)	F7	C18	C19	120.3(3)
C4	C5	C6	120.3(3)	C18	C19	C20	120.0(3)
N1	C5	C4	119.8(3)	F8	C19	C18	119.9(3)
N1	C5	C6	119.9(3)	F8	C19	C20	120.1(3)
C5	C6	S1A	123.2(2)	C19	C20	C21	119.2(3)
C5	C6	S1B	120.5(3)	F9	C20	C19	120.0(3)
C7A	C6	C5	126.9(3)	F9	C20	C21	120.8(3)
C7A	C6	S1A	109.9(3)	C16	C21	C20	122.3(3)
C7B	C6	C5	125.3(16)	F10	C21	C16	120.6(3)
C7B	C6	S1B	113.8(16)	F10	C21	C20	117.1(3)
C6	C7A	C8	113.3(4)	C23	C22	Au1	120.4(2)
C6	C7B	C9	106(2)	C27	C22	Au1	124.1(2)
C9	C8	C7A	110.3(4)	C27	C22	C23	115.2(3)
C9	C8	S1B	124.0(4)	C24	C23	C22	123.2(3)
C8	C9	C7B	102.8(6)	F11	C23	C22	119.8(3)
C8	C9	S1A	114.7(3)	F11	C23	C24	117.0(3)
C11	C10	Au1	120.0(2)	C25	C24	C23	119.2(3)
C11	C10	C15	115.5(3)	F12	C24	C23	120.9(3)
C15	C10	Au1	124.5(2)	F12	C24	C25	119.9(3)
C10	C11	C12	123.4(3)	C26	C25	C24	119.9(3)
F1	C11	C10	119.9(3)	F13	C25	C24	120.4(3)
F1	C11	C12	116.7(3)	F13	C25	C26	119.7(3)
C13	C12	C11	118.9(3)	C25	C26	C27	119.2(3)
F2	C12	C11	121.1(3)	F14	C26	C25	120.2(3)
F2	C12	C13	119.9(3)	F14	C26	C27	120.6(3)
C12	C13	C14	119.9(3)	C26	C27	C22	123.4(3)
F3	C13	C12	119.6(3)	F15	C27	C22	119.5(3)
F3	C13	C14	120.5(3)	F15	C27	C26	117.1(3)
C13	C14	C15	119.3(3)	C1	N1	Au1	116.4(2)
F4	C14	C13	120.0(3)	C1	N1	C5	119.2(3)
F4	C14	C15	120.7(3)	C5	N1	Au1	124.2(2)
C10	C15	C14	123.0(3)	C9	S1A	C6	91.85(18)
F5	C15	C10	120.4(3)	C8	S1B	C6	93.0(3)

Crystal structure determinations: refinement details

In the crystal structure of **1**, solvent molecules of dichloromethane co-crystallized with the main Au species in a ratio 1:2. The solvent molecule is disordered over two sets of sites around a center of inversion with a site-occupancy factor of 0.5. One Cl atom is further disordered over two other positions with site-occupancy factor of 0.179(7) and 0.321(7). Some restraints/constraints had to be used to correct the geometry of the disordered components and the thermal parameters of the corresponding atoms. All non-H atoms were anisotropically refined. All hydrogen positions were calculated after each cycle of refinement using a riding model, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic H atoms, and with C—H = 0.97 Å and U_{iso}(H) = 1.2U_{eq}(C) for the methylene H atoms.

In the crystal structure of **2**, solvent molecules of hexane co-crystallized with the main Au species in a ratio 1:8. The solvent molecule lies on a center of inversion and the non-H atoms were isotropically refined with a site-occupancy factor of 0.5. Some restraints/constraints had to be used to correct the geometry of the disordered components and the thermal parameters of the corresponding atoms. All hydrogen positions were calculated after each cycle of refinement using a riding model, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic H atoms, with C—H = 0.97 Å and U_{iso}(H) = 1.2U_{eq}(C) for the methylene H atoms, and with C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C) for the methyl H atoms.

In the crystal structure of **3**, all non-H atoms were anisotropically refined and all hydrogen positions were calculated after each cycle of refinement using a riding model with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C).

In the crystal structure of **4**, solvent molecules of diethyl ether co-crystallized with the main species in a ratio 1:2. The solvent molecule lies around a center of inversion and is disordered over two sets of sites with a site-occupancy factor of 0.5. All non-H atoms were anisotropically refined. All hydrogen positions were calculated after each cycle of refinement using a riding model, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic H atoms, with C—H = 0.97 Å and U_{iso}(H) = 1.2U_{eq}(C) for the methylene H atoms, and with C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C) for the methyl H atoms.

In the crystal structure of **5**, the thiophene ligand was partially disordered over two different positions (leading to two different orientations) with site-occupancy factors of 0.189(3) and 0.811(3). Some restraints/constraints had to be used to correct the geometry of the disordered components and the thermal parameters of the corresponding atoms. All non-H atoms were anisotropically refined. All hydrogen positions were calculated after each cycle of refinement using a riding model with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C).

Shortest intra- and intermolecular interactions in the crystal structures of 1 – 5

Table S16. Shortest intra- and intermolecular interactions for 1.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C22	H22	F3[1]	0.93	2.49	3.161(6)	129.0
C29	H29	F5[2]	0.93	2.62	3.250(6)	125.2
C29	H29	F10	0.93	2.27	3.180(6)	164.3
C30	H30B	F10	0.97	2.46	3.178(12)	130.8

Y	X	Cg	d(X-Cg)/Å	Y-X-Cg/°
C3	F2	Cg1[3]	3.242(4)	138.5(3)
C27	F17	Cg2[4]	3.244(4)	135.0(4)

Cg	Cg	d(Cg-Cg)/Å	alpha/°
Cg3	Cg4	4.124(3)	12.9(3)
Cg3	Cg4[2]	4.369(3)	12.9(3)

[1]-1+X,-1+Y,+Z; [2]-1+X,+Y,+Z; [3]+X,1+Y,+Z; [4]2-X,1-Y,1-Z

Cg1 = centroid of the 6-Membered Ring (1) N(1) --> C(19) --> C(20) --> C(21) --> C(22) --> C(23)
Cg2 = centroid of the 6-Membered Ring (2) C(1) --> C(2) --> C(3) --> C(4) --> C(5) --> C(6)
Cg3 = centroid of the 6-Membered Ring (3) C(13) --> C(14) --> C(15) --> C(16) --> C(17) --> C(18)
Cg4 = centroid of the 6-Membered Ring (4) C(24) --> C(25) --> C(26) --> C(27) --> C(28) --> C(29)

Table S17. Shortest intra- and intermolecular interactions for 2.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C1	H1	F11[1]	0.93	2.34	3.145(10)	144.3
C8	H8	F15[2]	0.93	2.52	3.251(14)	136.2
C30	H30	F30[3]	0.93	2.37	3.249(12)	157.1
C31	H31	F21[3]	0.93	2.38	3.169(12)	142.9
C33	H33	F19[4]	0.93	2.55	3.236(13)	130.6
C36A	H36A	F22[3]	0.93	2.52	3.197(12)	130.3
C37A	H37A	F18[2]	0.93	2.62	3.219(11)	122.4
C38A	H38A	F10	0.93	2.41	3.207(10)	143.6

Y	X	Cg	d(X-Cg)/Å	Y-X-Cg/°
C28	F14	Cg1[5]	3.114(9)	151.0(8)
C55	F27	Cg4[6]	3.224(10)	147.3(9)
C15	F3	Cg6[5]	3.314(9)	147.4(7)

Cg	Cg	d(Cg-Cg)/Å	alpha/°
Cg6	Cg2[5]	4.223(7)	26.5(6)
Cg5	Cg3[6]	4.329(7)	29.7(6)

[1]-X,1-Y,1-Z; [2]-1+X,+Y,+Z; [3]1-X,-Y,2-Z; [4]1-X,1-Y,2-Z ; [5]1-X,1-Y,1-Z ; [6]-X,1-Y,2-Z.

Cg1 = centroid of the 6-membered ring (1) N(2) --> C(30) --> C(31) --> C(32) --> C(33) --> C(34)
Cg2 = centroid of the 6-membered ring (2) C(41) --> C(42) --> C(43) --> C(44) --> C(45) --> C(46)
Cg3 = centroid of the 6-membered ring (3) C(53) --> C(54) --> C(55) --> C(56) --> C(57) --> C(58)
Cg4 = centroid of the 6-membered ring (4) N(1) --> C(1) --> C(2) --> C(3) --> C(4) --> C(5)
Cg5 = centroid of the 6-membered ring (5) C(18) --> C(19) --> C(20) --> C(21) --> C(22) --> C(23)
Cg6 = centroid of the 6-membered ring (6) C(24) --> C(25) --> C(26) --> C(27) --> C(28) --> C(29)

Table S18. Shortest intra- and intermolecular interactions for 3.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C2	H2	F5[1]	0.93	2.46	3.265(3)	144.3
C2	H2	F12[2]	0.93	2.57	3.240(3)	129.7
C7	H7	F5	0.93	2.31	3.241(4)	176.7

Y	X	Cg	d(X-Cg)/Å	Y-X-Cg/°
C27	F13	Cg1[3]	2.992(2)	131.98(17)
C21	F8	Cg4[4]	3.479(3)	145.83(19)

Cg	Cg	d(Cg-Cg)/Å	alpha/°
Cg2	Cg4	3.888(2)	17.12(16)
Cg2	Cg3[5]	4.108(2)	20.32(16)

[1]1+X,+Y,+Z; [2]1+X,1/2-Y,1/2+Z; [3]X,1/2-Y,-1/2+Z; [4]-X,-Y,-Z ; [5]-X,1/2+Y,1/2-Z

Cg1 = centroid of the 6-membered ring (1) N(1) --> C(1) --> C(2) --> C(3) --> C(4) --> C(5)
Cg2 = centroid of the 6-membered ring (2) C(6) --> C(7) --> C(8) --> C(9) --> C(10) --> C(11)
Cg3 = centroid of the 6-membered ring (3) C(18) --> C(19) --> C(20) --> C(21) --> C(22) --> C(23)
Cg4 = centroid of the 6-membered ring (4) C(24) --> C(25) --> C(26) --> C(27) --> C(28) --> C(29)

Table S19. Shortest intra- and intermolecular interactions for 4.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C9	H9	F13[1]	0.93	2.50	3.192(4)	131.2
C11	H11	F5	0.93	2.40	3.251(3)	152.2
C12	H12	F14[2]	0.93	2.55	3.218(4)	129.6

Y	X	Cg	d(X-Cg)/Å	Y-X-Cg/°
C21	F5	Cg3[3]	3.482(2)	133.63(14)
C25	F8	Cg4	3.407(2)	150.83(18)

Cg	Cg	d(Cg-Cg)/Å	alpha/°
Cg1	Cg1[4]	3.7820(18)	0
Cg3	Cg2	4.0573(16)	14.61(13)

[1]+X,1+Y,+Z; [2]2-X,-Y,1-Z; [3]2-X,1-Y,1-Z; [4]1-X,1-Y,1-Z

Cg1 = centroid of the 6-membered ring (1) C(2) --> C(3) --> C(9) --> C(8) --> C(7) --> C(6)
Cg2 = centroid of the 6-membered ring (2) C(28) --> C(29) --> C(30) --> C(31) --> C(32) --> C(33)
Cg3 = centroid of the 6-membered ring (3) C(10) --> C(11) --> C(12) --> C(13) --> C(14) --> C(15)
Cg4 = centroid of the 6-membered ring (4) C(16) --> C(17) --> C(18) --> C(19) --> C(20) --> C(21)

Table S20. Shortest intra- and intermolecular interactions for 5.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C2	H2	F4[1]	0.93	2.60	3.279(4)	130.1
C2	H2	F15[2]	0.93	2.43	3.263(4)	149.2
C7B	H7B	F15	0.93	2.46	3.32(3)	154.2

Y	X	Cg	d(X-Cg)/Å	Y-X-Cg/°
C13	F3	Cg3[3]	2.983(3)	136.1(2)

Cg	Cg	d(Cg-Cg)/Å	alpha/°
Cg2	Cg5[4]	3.916(7)	12.1(7)
Cg2	Cg4	3.930(7)	13.7(7)

Cg1 Cg5[4]	3.932(2)	15.21(19)
Cg1 Cg4	3.966(2)	17.35(19)

[1]1+X,1/2-Y,1/2+Z; [2]1+X,+Y,+Z; [3]X,1/2-Y,-1/2+Z; [4]1-X,-1/2+Y,3/2-Z

Cg1 = centroid of the 5-membered ring (1) S(1A) --> C(6) --> C(7A) --> C(8) --> C(9)
Cg2 = centroid of the 5-membered ring (2) C(6) --> S(1B) --> C(8) --> C(9) --> C(7B)
Cg3 = centroid of the 6-membered ring (3) N(1) --> C(1) --> C(2) --> C(3) --> C(4) --> C(5)
Cg4 = centroid of the 6-membered ring (4) C(10) --> C(11) --> C(12) --> C(13) --> C(14) --> C(15)
Cg5 = centroid of the 6-membered ring (5) C(16) --> C(17) --> C(18) --> C(19) --> C(20) --> C(21)

UV/Vis profiles of the free pyridine ligands

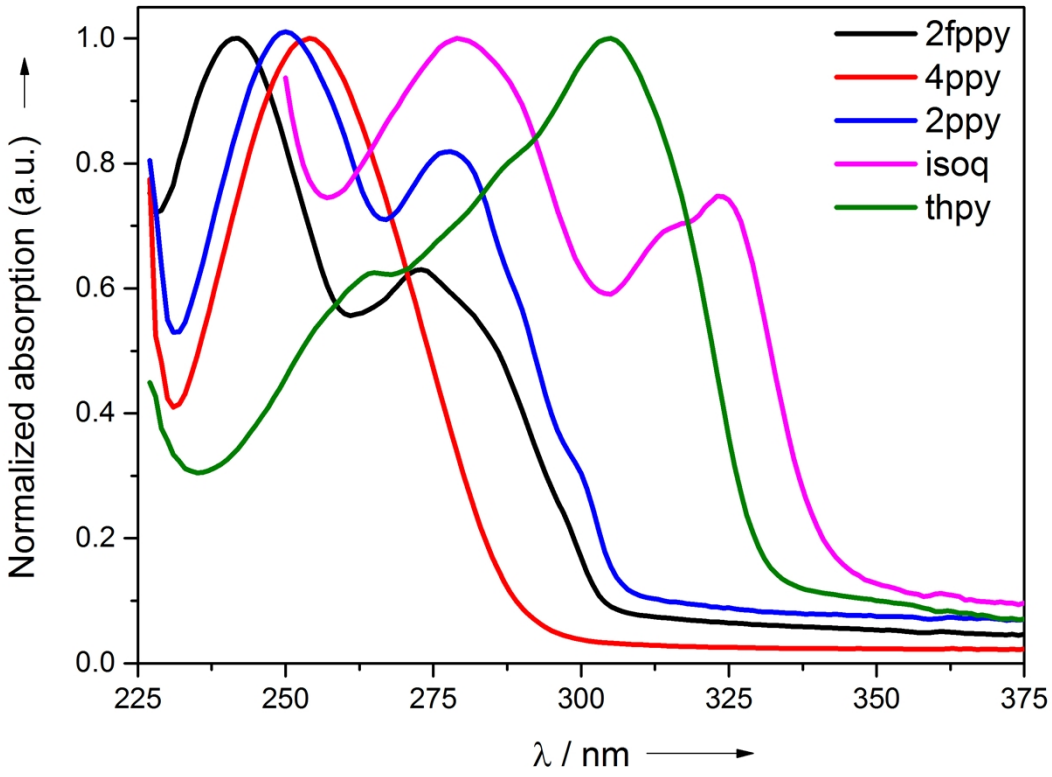

Figure S6. UV/Vis absorption spectra of the free pyridine ligands in CH_2Cl_2.

DFT calculations

Energies and cartesian coordinates of the DFT optimized ground-state structure of 1

C	0.20236900	-2.72537200	-1.86448600
H	1.04391900	-2.17961000	-2.27730300
C	-0.22681900	-3.91276400	-2.43060000
H	0.28968200	-4.31125000	-3.29739300
C	-1.32323600	-4.55675900	-1.86530600
H	-1.69247000	-5.49201100	-2.27662700
C	-1.93432100	-3.98990800	-0.75736500
H	-2.77851100	-4.47355500	-0.27829400
C	-1.45787600	-2.78642000	-0.22826400
C	-2.08910900	-2.20573200	0.97380700
C	-3.47297900	-2.02182200	1.04443800
C	-4.10934100	-1.51531200	2.16404000
H	-5.18315900	-1.36442000	2.17759500
C	-3.31778500	-1.19708800	3.25884600
C	-1.94079400	-1.36458000	3.25586800
H	-1.35738400	-1.10226500	4.13183800
C	-1.33979600	-1.86577100	2.10816100
H	-0.26561700	-2.01577300	2.09791200
C	2.24681700	-0.90447800	-0.05548800
C	3.17289000	-0.70989900	-1.07288800
C	4.49698800	-1.12500500	-0.98822700
C	4.93198900	-1.76367300	0.16686600
C	4.03811000	-1.97984100	1.20848700
C	2.72229900	-1.54890700	1.07746600
C	-1.57297500	0.59701000	-0.64628000
C	-2.28836200	1.31997900	0.29838800
C	-3.54497000	1.85612600	0.03874500
C	-4.11567900	1.67943900	-1.21628700
C	-3.42516000	0.97100100	-2.19196700
C	-2.17259300	0.44933100	-1.88991200
C	0.98158800	1.64935300	0.06179500
C	1.37766900	2.03574800	1.33502700
C	1.84646900	3.31652700	1.60288500
C	1.92758000	4.24384500	0.57070200
C	1.53887600	3.88277100	-0.71353600
C	1.07059800	2.59470200	-0.95138100
N	-0.39860700	-2.16837800	-0.79735500
F	2.79364500	-0.10441600	-2.21398500
F	5.34664300	-0.92248800	-1.99488400
F	6.19312900	-2.17241300	0.27172900
F	4.44838800	-2.59973300	2.31481800
F	1.90426200	-1.79593000	2.11747200
F	-1.78274900	1.51858800	1.52559600
F	-4.20930800	2.53108400	0.97785400
F	-5.31850300	2.18317100	-1.48057100
F	-3.96807600	0.79984900	-3.39760500
F	-1.53898900	-0.22599700	-2.86679400
F	1.31418200	1.16858200	2.35295900
F	2.21752800	3.66062000	2.83512700
F	2.37575400	5.47252600	0.81134700
F	1.61489900	4.77054300	-1.70342200
F	0.69975900	2.28818900	-2.19942800
Au	0.30248600	-0.20581400	-0.29829300
F	-4.23059200	-2.32036500	-0.02577100
F	-3.91522300	-0.71382900	4.35419100

Zero-point correction=	0.307842 (Hartree/Particle)
Thermal correction to Energy=	0.350257
Thermal correction to Enthalpy=	0.351201
Thermal correction to Gibbs Free Energy=	0.228040
Sum of electronic and zero-point Energies=	-2993.832902
Sum of electronic and thermal Energies=	-2993.790487
Sum of electronic and thermal Enthalpies=	-2993.789543
Sum of electronic and thermal Free Energies=	-2993.912705

Energies and cartesian coordinates of the DFT optimized ground-state structure of 2

C	-0.41262300	-2.06723000	0.05062300
C	-0.87697000	-2.79337000	1.13781200
C	-0.87231500	-4.18422900	1.16854900

C	-0.38820600	-4.88542200	0.07044200
C	0.08769300	-4.19200600	-1.03684400
C	0.06674800	-2.80245900	-1.02448900
C	-0.41265700	2.06723900	-0.05061200
C	-0.87701500	2.79339500	-1.13778500
C	-0.87237600	4.18425600	-1.16849000
C	-0.38827300	4.88543300	-0.07037200
C	0.08763800	4.19200000	1.03690000
C	0.06670800	2.80245300	1.02451400
C	-2.41342100	-0.00001600	-0.00002100
C	-3.13431700	-0.45138000	-1.09754500
C	-4.52470100	-0.45595300	-1.11253500
C	-5.22175800	-0.00004700	-0.00004400
C	-4.52473000	0.45587800	1.11245800
C	-3.13434500	0.45133600	1.09749100
F	-1.34510300	-2.15555200	2.22370700
F	-1.32032000	-4.84952500	2.23360100
F	-0.37304000	-6.21603400	0.08148300
F	0.55985600	-4.86463000	-2.08698700
F	0.54579000	-2.16819700	-2.11012100
F	-1.34514300	2.15559700	-2.22369300
F	-1.32039100	4.84956800	-2.23352800
F	-0.37312200	6.21604500	-0.08138600
F	0.55979500	4.86460800	2.08705400
F	0.54575800	2.16817200	2.11013200
F	-2.49775300	-0.90063600	-2.18569900
F	-5.19148100	-0.89370500	-2.17957700
F	-6.55199300	-0.00006400	-0.00005500
F	-5.19153700	0.89361500	2.17948800
F	-2.49780900	0.90060900	2.18565200
Au	-0.40538100	0.00000400	0.00000400
C	2.39159300	0.46809300	-1.05675200
C	2.39160700	-0.46805800	1.05676200
C	3.77469900	0.47761800	-1.09402100
C	3.77471400	-0.47758900	1.09400900
H	1.79993600	-0.83104900	1.89093000
C	4.50957200	0.00001500	-0.00001000
H	4.27451500	-0.83500200	1.98865300
N	1.70978300	0.00001900	0.00001000
H	1.79991200	0.83109000	-1.89091100
H	4.27448900	0.83502700	-1.98866800
C	5.98421200	0.00001600	-0.00002200
C	6.69681800	-1.04552800	0.60359000
C	6.69680400	1.04556500	-0.60364400
C	8.08795300	-1.04718500	0.59870300
H	6.16024000	-1.87874400	1.05071600
C	8.08793900	1.04723200	-0.59877300
H	6.16021400	1.87877500	-1.05076600
C	8.78697400	0.00002600	-0.00003800
H	8.62716400	-1.87132200	1.05784200
H	8.62713900	1.87137200	-1.05792100
H	9.87363200	0.00003100	-0.00004300

Zero-point correction=	0.324385 (Hartree/Particle)
Thermal correction to Energy=	0.365200
Thermal correction to Enthalpy=	0.366144
Thermal correction to Gibbs Free Energy=	0.244787
Sum of electronic and zero-point Energies=	-2795.517460
Sum of electronic and thermal Energies=	-2795.476646
Sum of electronic and thermal Enthalpies=	-2795.475701
Sum of electronic and thermal Free Energies=	-2795.597058

Energies and cartesian coordinates of the DFT optimized ground-state structure of 3

C	0.20105000	-2.83112600	-1.65927100
H	0.97089600	-2.23061700	-2.13151100
C	-0.14163000	-4.07306400	-2.16290300
H	0.37206500	-4.45803500	-3.03741400
C	-1.14856600	-4.78979100	-1.52282400
H	-1.44534100	-5.77227200	-1.87942800
C	-1.75944400	-4.23381500	-0.40975700
H	-2.52459500	-4.77594100	0.13610700
C	-1.37650400	-2.96903000	0.05389300
C	-2.04258800	-2.39709500	1.24127600
C	-3.44093300	-2.44054200	1.32758400
H	-4.02171600	-2.84212200	0.50028000

C	-4.09083600	-1.92873200	2.44578300
H	-5.17643100	-1.94592500	2.49314600
C	-3.35116100	-1.38712000	3.49718400
H	-3.85947600	-0.98635400	4.36999700
C	-1.96044500	-1.35676900	3.42367500
H	-1.37767300	-0.93921300	4.23991200
C	-1.30569400	-1.85595800	2.30102500
H	-0.22098500	-1.84764700	2.26423600
C	2.16263000	-0.78805800	-0.06558900
C	3.01961100	-0.54889300	-1.13249800
C	4.37357500	-0.86372200	-1.10718400
C	4.91091000	-1.44275500	0.03610200
C	4.08798800	-1.70121300	1.12562300
C	2.73888100	-1.37120900	1.05380700
C	-1.79654500	0.38701500	-0.43166500
C	-2.47695600	1.11538500	0.53502000
C	-3.79959300	1.51575600	0.37992800
C	-4.47756800	1.19218600	-0.78881600
C	-3.82524700	0.47694800	-1.78566000
C	-2.50329400	0.09449500	-1.59007100
C	0.71571300	1.66715700	0.01352300
C	1.19137300	2.15184900	1.22426500
C	1.58160500	3.47627900	1.38409800
C	1.50092800	4.34774300	0.30447800
C	1.03001900	3.88833000	-0.91934700
C	0.64346400	2.55843700	-1.04889800
N	-0.39980900	-2.28591800	-0.58539100
F	2.54043500	0.00011700	-2.26451000
F	5.15564400	-0.62225400	-2.15944700
F	6.20290300	-1.75563500	0.08447400
F	4.59791000	-2.26548600	2.22044700
F	1.99181400	-1.65546700	2.13556600
F	-1.87029500	1.45564000	1.68170100
F	-4.42536100	2.20013000	1.33880700
F	-5.74563100	1.56387300	-0.95240400
F	-4.47138500	0.16709800	-2.91151100
F	-1.91391800	-0.59504200	-2.58554700
F	1.28480000	1.34225600	2.28600500
F	2.03133200	3.91546400	2.55893800
F	1.87299100	5.61727600	0.44282500
F	0.95088300	4.72256400	-1.95498300
F	0.18992300	2.15603300	-2.24155300
Au	0.15935500	-0.25032500	-0.20637400

Zero-point correction=	0.324368 (Hartree/Particle)
Thermal correction to Energy=	0.365022
Thermal correction to Enthalpy=	0.365966
Thermal correction to Gibbs Free Energy=	0.247348
Sum of electronic and zero-point Energies=	-2795.514455
Sum of electronic and thermal Energies=	-2795.473801
Sum of electronic and thermal Enthalpies=	-2795.472857
Sum of electronic and thermal Free Energies=	-2795.591475

Energies and cartesian coordinates of the DFT optimized ground-state structure of 4

C	2.64986900	0.22533500	1.43974100
C	3.59643600	-0.80791500	1.47055100
H	4.28762400	-0.93216100	0.64012800
C	3.63117900	-1.69187400	2.54419700
H	4.35459000	-2.50299600	2.55058400
C	2.73575900	-1.54224300	3.60381100
H	2.76349500	-2.23510300	4.44047900
C	1.80034900	-0.51098500	3.58150300
H	1.09659200	-0.39139700	4.40051100
C	1.75211400	0.36873700	2.50234500
H	1.02604800	1.17492100	2.49453200
C	-1.40207200	1.83602100	-0.02417500
C	-2.10681600	2.29287000	-1.13076000
C	-2.89831200	3.43543900	-1.11331400
C	-3.00428800	4.16568800	0.06408400
C	-2.31558600	3.74465800	1.19473500
C	-1.53358300	2.59624300	1.12914000
C	0.74818300	-1.68569900	-0.43600400
C	0.73870600	-2.71722200	0.49272800
C	1.43768800	-3.90413500	0.30224600
C	2.17103100	-4.08462700	-0.86395300

C	2.19360600	-3.07975900	-1.82337900
C	1.48115900	-1.90839300	-1.59345700
C	-1.98144600	-0.95656200	-0.05028100
C	-2.69835400	-1.04793300	1.13533400
C	-3.88142400	-1.77211400	1.22641700
C	-4.37272200	-2.42454700	0.10203300
C	-3.67680100	-2.34804900	-1.09797400
C	-2.49373300	-1.61911900	-1.15815400
F	-2.02598600	1.62470000	-2.29740400
F	-3.54910100	3.83812300	-2.20515000
F	-3.75402600	5.26408700	0.10639900
F	-2.40741000	4.44626800	2.32494600
F	-0.88651200	2.24796800	2.25566800
F	0.04941200	-2.59504200	1.63676500
F	1.41977800	-4.86652600	1.22654900
F	2.85000200	-5.21343300	-1.06020000
F	2.89298600	-3.25014400	-2.94714300
F	1.52887100	-0.96693500	-2.55415800
F	-2.26093300	-0.43134100	2.23970500
F	-4.54680700	-1.84446100	2.37882200
F	-5.50518900	-3.11897100	0.17453400
F	-4.14494900	-2.97315900	-2.17742800
F	-1.85134400	-1.57543500	-2.33109200
Au	-0.27287900	0.09450700	-0.17476900
C	2.61850600	1.16142500	0.29136800
C	1.47169200	2.06190300	-1.54206200
C	3.76322800	1.96243900	-0.01897300
C	2.53745700	2.81409200	-1.93831400
H	0.54169800	2.06039000	-2.09839600
C	4.92187000	1.98179900	0.80075900
C	3.72728100	2.79481600	-1.17508100
H	2.46182000	3.42907800	-2.83013700
C	6.00183600	2.76167700	0.45985900
H	4.94586600	1.38683800	1.70743100
C	4.85706000	3.57919200	-1.50714800
C	5.97494900	3.55690300	-0.70734700
H	6.88135500	2.77262300	1.09749900
H	4.82184600	4.20259900	-2.39697100
H	6.83927100	4.16338300	-0.96443600
N	1.51274000	1.24373700	-0.44781000

Zero-point correction=	0.371398 (Hartree/Particle)
Thermal correction to Energy=	0.414824
Thermal correction to Enthalpy=	0.415769
Thermal correction to Gibbs Free Energy=	0.290153
Sum of electronic and zero-point Energies=	-2948.933933
Sum of electronic and thermal Energies=	-2948.890507
Sum of electronic and thermal Enthalpies=	-2948.889563
Sum of electronic and thermal Free Energies=	-2949.015179

Energies and cartesian coordinates of the DFT optimized ground-state structure of 5

C	0.25769100	-2.77329100	-1.72775700
H	0.99091200	-2.13569900	-2.21004000
C	-0.05631200	-4.01762400	-2.24385600
H	0.43950200	-4.36732200	-3.14306000
C	-1.01094500	-4.78461600	-1.58094600
H	-1.28382100	-5.77089400	-1.94594000
C	-1.59217400	-4.28037600	-0.42895100
H	-2.30352700	-4.86682600	0.14255200
C	-1.24365400	-3.00668300	0.04234400
C	2.16441000	-0.68271500	-0.16458200
C	3.04912800	-0.19669600	-1.11959900
C	4.40886200	-0.49013400	-1.11043800
C	4.92015100	-1.30459000	-0.10742800
C	4.06718500	-1.81653200	0.86304500
C	2.71443700	-1.49910100	0.81431900
C	-1.84785600	0.33681900	-0.41127500
C	-2.54796200	1.03757100	0.56213400
C	-3.88922900	1.37921900	0.42417300
C	-4.56824100	1.02516200	-0.73482500
C	-3.89759300	0.33867400	-1.73960100
C	-2.55808900	0.01489700	-1.56019500
C	0.61574100	1.71726500	0.04166800
C	1.12120000	2.16170300	1.25586200
C	1.45169200	3.49455500	1.47115900

C	1.27814500	4.41564000	0.44510000
C	0.77569600	3.99667800	-0.78082200
C	0.45058300	2.65723300	-0.96646300
N	-0.32640400	-2.26855100	-0.62615300
F	2.60155100	0.58032600	-2.12055600
F	5.22142900	-0.00752100	-2.05072500
F	6.21693600	-1.60019700	-0.08124800
F	4.55233800	-2.60718500	1.82094000
F	1.93116400	-2.03328200	1.76668900
F	-1.94422600	1.41284600	1.70038200
F	-4.53046400	2.03835800	1.39060400
F	-5.85298600	1.34183300	-0.88237800
F	-4.54313100	0.00040100	-2.85752400
F	-1.95251400	-0.64624300	-2.56577100
F	1.29929400	1.30382000	2.26835100
F	1.93120200	3.89463900	2.64841900
F	1.59227000	5.69410600	0.63585300
F	0.60965100	4.87861100	-1.76552100
F	-0.03234100	2.29390000	-2.15986600
Au	0.14307200	-0.21428400	-0.23559800
C	-1.89594400	-2.49527100	1.24536300
C	-3.23927800	-2.60885500	1.53488400
S	-1.05107600	-1.70776800	2.53641400
C	-3.58562700	-2.03410300	2.78222500
H	-3.95565000	-3.05055100	0.84907100
C	-2.49697200	-1.51091300	3.43057900
H	-4.59385100	-2.00183100	3.18041800
H	-2.46599800	-1.01753200	4.39412800

Zero-point correction=	0.290460 (Hartree/Particle)
Thermal correction to Energy=	0.330759
Thermal correction to Enthalpy=	0.331703
Thermal correction to Gibbs Free Energy=	0.213794
Sum of electronic and zero-point Energies=	-3116.244773
Sum of electronic and thermal Energies=	-3116.204474
Sum of electronic and thermal Enthalpies=	-3116.203530
Sum of electronic and thermal Free Energies=	-3116.321440

Energies and cartesian coordinates of the DFT optimized triplet-state structure of 1

C	-0.10355200	-2.58249900	-1.97748200
H	0.97337400	-2.46328100	-2.07484800
C	-0.81532300	-3.32860100	-2.93930500
H	-0.26504100	-3.86793900	-3.70249200
C	-2.23137200	-3.20743500	-2.97640600
H	-2.79582600	-3.58807600	-3.82179300
C	-2.85813400	-2.57766000	-1.94331300
H	-3.93451800	-2.46801200	-1.93582600
C	-2.08154100	-2.12536500	-0.79014400
C	-2.57604400	-2.06344200	0.52072600
C	-3.97486500	-2.04872700	0.86749900
C	-4.43929800	-1.97073100	2.15481200
H	-5.50469600	-1.93772900	2.35489800
C	-3.50554800	-1.91228300	3.19178800
C	-2.12794300	-1.92787300	2.94826400
H	-1.43127500	-1.88338500	3.77907900
C	-1.68372800	-1.99992900	1.65085700
H	-0.61776000	-2.04408900	1.47001100
C	2.15522000	-1.13133900	-0.18274800
C	3.15620400	-0.90740700	-1.12058000
C	4.40423500	-1.51813600	-1.05718000
C	4.67910600	-2.39035000	-0.01038600
C	3.70542200	-2.64071500	0.94932300
C	2.47110300	-2.00929000	0.84462500
C	-1.42598400	0.92122300	-0.51298800
C	-2.07597900	1.50645700	0.56382400
C	-3.27654200	2.19751300	0.42920900
C	-3.85246000	2.32326900	-0.82946500
C	-3.22486800	1.75736400	-1.93326900
C	-2.02819100	1.07210100	-1.75456400
C	1.26029800	1.54931200	0.22770500
C	1.72476400	1.72579000	1.52387600
C	2.36525600	2.89306900	1.92392200
C	2.55250000	3.91864800	1.00490100
C	2.09726900	3.76827300	-0.29942200
C	1.45753400	2.59011500	-0.66987800

N	-0.67553700	-1.92550500	-0.98899700
F	2.93295200	-0.07621800	-2.15254300
F	5.33307800	-1.28128600	-1.98312700
F	5.86493400	-2.98718800	0.06911200
F	3.96347200	-3.48137200	1.95102400
F	1.56467300	-2.29245900	1.79894000
F	-1.56116000	1.41177400	1.80014400
F	-3.87996600	2.73635300	1.48924700
F	-5.00040600	2.97999400	-0.97686800
F	-3.77711200	1.87355400	-3.14150400
F	-1.46169500	0.52995600	-2.84705100
F	1.56520600	0.75906700	2.43690000
F	2.80045500	3.03565300	3.17515600
F	3.16495300	5.04055300	1.37284100
F	2.27425400	4.75147900	-1.18063500
F	1.02768400	2.48635100	-1.93248700
Au	0.33094000	-0.15002300	-0.32813100
F	-4.89726800	-2.06347200	-0.10855600
F	-3.95016200	-1.83443700	4.44619800

Zero-point correction=	0.303257 (Hartree/Particle)
Thermal correction to Energy=	0.346436
Thermal correction to Enthalpy=	0.347380
Thermal correction to Gibbs Free Energy=	0.220610
Sum of electronic and zero-point Energies=	-2993.726005
Sum of electronic and thermal Energies=	-2993.682825
Sum of electronic and thermal Enthalpies=	-2993.681881
Sum of electronic and thermal Free Energies=	-2993.808651

Energies and cartesian coordinates of the DFT optimized triplet-state structure of 2

C	0.41214000	2.06808100	0.04974100
C	0.85564400	2.79157600	1.14702100
C	0.84908100	4.18231900	1.18118200
C	0.38378900	4.88562500	0.07646200
C	-0.07131500	4.19441400	-1.04069200
C	-0.04975200	2.80468900	-1.03180400
C	0.41194200	-2.06808400	-0.04954500
C	0.85815600	-2.79160900	-1.14569900
C	0.85145700	-4.18234900	-1.17992800
C	0.38317100	-4.88561600	-0.07644800
C	-0.07474400	-4.19436800	1.03953500
C	-0.05291200	-2.80464600	1.03076100
C	2.41585400	-0.00011800	0.00028600
C	3.13819000	0.44553300	-1.09868900
C	4.52861300	0.45006200	-1.11413400
C	5.22565600	-0.00025100	0.00050300
C	4.52839700	-0.45050200	1.11503100
C	3.13797700	-0.44584300	1.09937300
F	1.30425700	2.15113900	2.23977600
F	1.27689800	4.84589500	2.25611700
F	0.36708500	6.21662700	0.09042800
F	-0.52554200	4.86984400	-2.09744800
F	-0.50956500	2.17341000	-2.12674200
F	1.30973800	-2.15118500	-2.23724300
F	1.28196200	-4.84595600	-2.25377100
F	0.36626500	-6.21661500	-0.09051400
F	-0.53188900	-4.86976000	2.09505500
F	-0.51560800	-2.17332300	2.12445600
F	2.50233700	0.89024400	-2.18948800
F	5.19607600	0.88242900	-2.18348700
F	6.55630400	-0.00031500	0.00060600
F	5.19565500	-0.88292600	2.18448800
F	2.50192300	-0.89048500	2.19007900
Au	0.40500100	-0.00000500	0.00010000
C	-2.38849700	-0.46000800	-1.07470800
C	-2.38871700	0.46018500	1.07425600
C	-3.75470100	-0.47423000	-1.11841800
C	-3.75493100	0.47450000	1.11764700
H	-1.79487700	0.81726300	1.90896900
C	-4.54097500	0.00016500	-0.00047900
H	-4.22363100	0.85343100	2.01721300
N	-1.69198300	0.00007100	-0.00014700
H	-1.79448800	-0.81712500	-1.90928400
H	-4.22321600	-0.85312900	-2.01809400
C	-5.93641500	0.00021600	-0.00064600

C	-6.71723900	0.48389900	1.14523900
C	-6.71699700	-0.48341000	-1.14672000
C	-8.07936700	0.47746300	1.12987600
H	-6.20298700	0.85381600	2.02387300
C	-8.07912900	-0.47687200	-1.13168700
H	-6.20255900	-0.85336100	-2.02523000
C	-8.79991600	0.00032100	-0.00099300
H	-8.62732400	0.84207400	1.99454400
H	-8.62690200	-0.84144100	-1.99648900
H	-9.88500700	0.00036200	-0.00112400

Zero-point correction= 0.319348 (Hartree/Particle)
Thermal correction to Energy= 0.361021
Thermal correction to Enthalpy= 0.361965
Thermal correction to Gibbs Free Energy= 0.236186
Sum of electronic and zero-point Energies= -2795.413316
Sum of electronic and thermal Energies= -2795.371643
Sum of electronic and thermal Enthalpies= -2795.370698
Sum of electronic and thermal Free Energies= -2795.496478

Energies and cartesian coordinates of the DFT optimized triplet-state structure of 3

C	-0.08627400	-2.80389000	-1.66028000
H	0.95152200	-2.55347400	-1.86847600
C	-0.76492900	-3.71653400	-2.49579900
H	-0.21068800	-4.23698800	-3.26907400
C	-2.17982800	-3.78797700	-2.40835400
H	-2.75509400	-4.30589600	-3.16954500
C	-2.79391100	-3.16174700	-1.36447900
H	-3.87462100	-3.18021000	-1.27734100
C	-1.99558300	-2.51667400	-0.32644600
C	-2.43621900	-2.39820400	0.99460800
C	-3.80813700	-2.67169300	1.36037600
H	-4.52118000	-2.98225100	0.60546900
C	-4.24162900	-2.51423100	2.65485000
H	-5.28361300	-2.70613500	2.89640300
C	-3.35454000	-2.10203800	3.66832900
H	-3.70885700	-1.97349300	4.68667100
C	-2.00442400	-1.86005200	3.34880300
H	-1.31006800	-1.55613700	4.12727400
C	-1.54867200	-2.00396500	2.06082600
H	-0.49887200	-1.84345900	1.84926500
C	2.10072200	-0.98277100	-0.14018900
C	3.01107700	-0.73870400	-1.16124500
C	4.32019700	-1.20795900	-1.13705200
C	4.75293200	-1.95087000	-0.04502900
C	3.87358300	-2.21593400	0.99822000
C	2.57293400	-1.72885000	0.93085800
C	-1.70739000	0.62885000	-0.36402600
C	-2.33117600	1.26160400	0.70174300
C	-3.61051400	1.80122200	0.60862000
C	-4.29760700	1.71996700	-0.59638100
C	-3.70022600	1.10226000	-1.68905400
C	-2.42171300	0.57374600	-1.55280600
C	0.93524500	1.61249300	0.10150900
C	1.46709400	1.96173800	1.33524000
C	1.99598000	3.22424800	1.57835900
C	1.99901800	4.17104500	0.56106800
C	1.47301900	3.84794600	-0.68384900
C	0.94829300	2.57755900	-0.89665200
N	-0.65750000	-2.14937100	-0.67016200
F	2.63461100	-0.03003200	-2.23955400
F	5.15892300	-0.95803400	-2.14269400
F	6.00018400	-2.41141300	-0.00126800
F	4.28473900	-2.93303700	2.04413400
F	1.76380900	-2.01822500	1.96546800
F	-1.70988000	1.36740800	1.88642300
F	-4.18412300	2.39134700	1.65810300
F	-5.52294300	2.22950500	-0.70396500
F	-4.35944600	1.02036900	-2.84647500
F	-1.88679100	-0.02460600	-2.63259300
F	1.48441400	1.07606100	2.33949900
F	2.49926300	3.53261300	2.77318000
F	2.50325600	5.38275600	0.77870800
F	1.47356600	4.75542700	-1.65938900
F	0.44556900	2.30744300	-2.10681600

```
 Au                 0.17143900   -0.22187500   -0.23031600

Zero-point correction=                           0.319539 (Hartree/Particle)
Thermal correction to Energy=                    0.360974
Thermal correction to Enthalpy=                  0.361918
Thermal correction to Gibbs Free Energy=         0.239677
Sum of electronic and zero-point Energies=          -2795.409273
Sum of electronic and thermal Energies=             -2795.367838
Sum of electronic and thermal Enthalpies=           -2795.366894
Sum of electronic and thermal Free Energies=        -2795.489135
```

Energies and cartesian coordinates of the DFT optimized triplet-state structure of 4

```
 C                  2.64213100    0.36449600    1.50983200
 C                  3.70947200   -0.54278900    1.67489500
 H                  4.48692400   -0.59505600    0.91680900
 C                  3.74248200   -1.40950500    2.75952900
 H                  4.55919900   -2.12040700    2.85527900
 C                  2.72079600   -1.38422500    3.71126500
 H                  2.74565500   -2.06647100    4.55658900
 C                  1.65998500   -0.49057000    3.56206400
 H                  0.85901700   -0.46478600    4.29583400
 C                  1.61378400    0.36906500    2.47157400
 H                  0.79492900    1.07545900    2.38353400
 C                 -1.57197600    1.76563900    0.01833900
 C                 -2.27576600    2.20601700   -1.09519300
 C                 -3.14456300    3.29107500   -1.06852800
 C                 -3.33226100    3.97585200    0.12583900
 C                 -2.64685300    3.56905300    1.26415300
 C                 -1.78561700    2.47947400    1.18918300
 C                  0.84964200   -1.57313600   -0.41086400
 C                  0.88908200   -2.62252600    0.49739300
 C                  1.69382000   -3.74233400    0.31626000
 C                  2.48712600   -3.83587400   -0.82026400
 C                  2.46197700   -2.81329900   -1.76054200
 C                  1.64396400   -1.71111400   -1.54084600
 C                 -1.94164700   -1.06271800   -0.11425600
 C                 -2.68877100   -1.24629600    1.04133800
 C                 -3.81658800   -2.05848200    1.06792100
 C                 -4.21870400   -2.70844000   -0.09276200
 C                 -3.48998300   -2.54182700   -1.26388200
 C                 -2.36388100   -1.72534900   -1.25936700
 F                 -2.11682300    1.57918200   -2.27730900
 F                 -3.79193400    3.68158200   -2.16696500
 F                 -4.15653100    5.01902600    0.17755700
 F                 -2.81784600    4.22921800    2.40975800
 F                 -1.14522100    2.14126700    2.32214900
 F                  0.14151100   -2.58725600    1.61033700
 F                  1.71752500   -4.72289000    1.22084200
 F                  3.26712900   -4.89903600   -1.00759500
 F                  3.21807900   -2.90080600   -2.85694100
 F                  1.65042500   -0.75121800   -2.48569800
 F                 -2.33437300   -0.63657000    2.17882900
 F                 -4.51330000   -2.21791100    2.19272000
 F                 -5.29748800   -3.48704000   -0.08237000
 F                 -3.87283400   -3.16506600   -2.37764400
 F                 -1.68598100   -1.59660000   -2.40606600
 Au                -0.31469500    0.11745400   -0.14374200
 C                  2.61154200    1.27267200    0.37225800
 C                  1.35426800    2.15117600   -1.41601000
 C                  3.75149500    2.04986100   -0.01812100
 C                  2.46617100    2.87461500   -1.91508900
 H                  0.41205900    2.19300400   -1.95560900
 C                  4.92110900    2.13635100    0.74576900
 C                  3.69321400    2.83603200   -1.22059900
 H                  2.34408300    3.47383800   -2.81153000
 C                  6.05209400    2.88112500    0.29528200
 H                  4.97138400    1.64607500    1.71206300
 C                  4.81070000    3.57005200   -1.63959500
 C                  6.01067800    3.58100300   -0.88295300
 H                  6.94873800    2.88701500    0.90907700
 H                  4.74360500    4.14399400   -2.56067200
 H                  6.86887200    4.14607900   -1.23272400
 N                  1.38740400    1.39985800   -0.34309100

Zero-point correction=                           0.367062 (Hartree/Particle)
```

```
Thermal correction to Energy=                  0.411020
Thermal correction to Enthalpy=                0.411965
Thermal correction to Gibbs Free Energy=       0.283416
Sum of electronic and zero-point Energies=         -2948.844544
Sum of electronic and thermal Energies=            -2948.800586
Sum of electronic and thermal Enthalpies=          -2948.799642
Sum of electronic and thermal Free Energies=       -2948.928190
```

Energies and cartesian coordinates of the DFT optimized triplet-state structure of 5

```
 C                 -0.01497100   -2.75236100   -1.71640300
 H                  0.93410700   -2.32835900   -2.03092500
 C                 -0.62801600   -3.73863300   -2.48747400
 H                 -0.12624900   -4.11106600   -3.37360700
 C                 -1.91855500   -4.16808800   -2.12499100
 H                 -2.46156200   -4.87758100   -2.74208600
 C                 -2.47836900   -3.67691700   -0.97262800
 H                 -3.45759000   -4.01624300   -0.65533400
 C                 -1.75131700   -2.76522000   -0.13680700
 C                  2.11900200   -0.86605800   -0.14066600
 C                  2.97840100   -0.57206200   -1.19220600
 C                  4.31434900   -0.95810600   -1.21110700
 C                  4.82821600   -1.66763400   -0.13258100
 C                  4.00139100   -1.98194700    0.93923000
 C                  2.67044800   -1.57849200    0.91591500
 C                 -1.79200000    0.49919400   -0.33430400
 C                 -2.42332900    1.21663000    0.67386500
 C                 -3.72388400    1.69701000    0.55533000
 C                 -4.42993000    1.47232800   -0.61962300
 C                 -3.82754300    0.77219100   -1.65789600
 C                 -2.52783400    0.30687100   -1.49671800
 C                  0.79474000    1.64943600    0.05622000
 C                  1.33147500    2.07349000    1.26424600
 C                  1.78512600    3.37411000    1.45154600
 C                  1.70594400    4.28321100    0.40342000
 C                  1.17350600    3.88479900   -0.81657000
 C                  0.72464100    2.57771900   -0.97395800
 N                 -0.54137700   -2.23765000   -0.60598500
 F                  2.52285500    0.10370800   -2.26230800
 F                  5.10121000   -0.66149000   -2.24606700
 F                  6.10275800   -2.04973900   -0.12891700
 F                  4.49079800   -2.66882200    1.97212600
 F                  1.91706900   -1.91566300    1.97324700
 F                 -1.79049000    1.47349000    1.82953100
 F                 -4.29957300    2.36778900    1.55501800
 F                 -5.67564600    1.92350400   -0.74987200
 F                 -4.50091900    0.55395600   -2.78902100
 F                 -1.98995000   -0.36396400   -2.53144200
 F                  1.42437900    1.22716600    2.29723900
 F                  2.29358600    3.75497000    2.62315000
 F                  2.13781500    5.53077900    0.56803400
 F                  1.09524200    4.75576800   -1.82187300
 F                  0.21293600    2.23562100   -2.16182100
 Au                 0.14198500   -0.23739100   -0.19197400
 C                 -2.18602000   -2.49982700    1.15544300
 C                 -3.50431900   -2.82113300    1.72316500
 S                 -1.17732900   -1.72670000    2.37487200
 C                 -3.65281700   -2.36627300    3.00669300
 H                 -4.28600200   -3.30875700    1.15488000
 C                 -2.50540800   -1.72699500    3.51065900
 H                 -4.56485500   -2.46591400    3.58578200
 H                 -2.38394300   -1.25451600    4.47717100

Zero-point correction=                         0.286101 (Hartree/Particle)
Thermal correction to Energy=                  0.327206
Thermal correction to Enthalpy=                0.328150
Thermal correction to Gibbs Free Energy=       0.206401
Sum of electronic and zero-point Energies=         -3116.156417
Sum of electronic and thermal Energies=            -3116.115312
Sum of electronic and thermal Enthalpies=          -3116.114367
Sum of electronic and thermal Free Energies=       -3116.236117
```

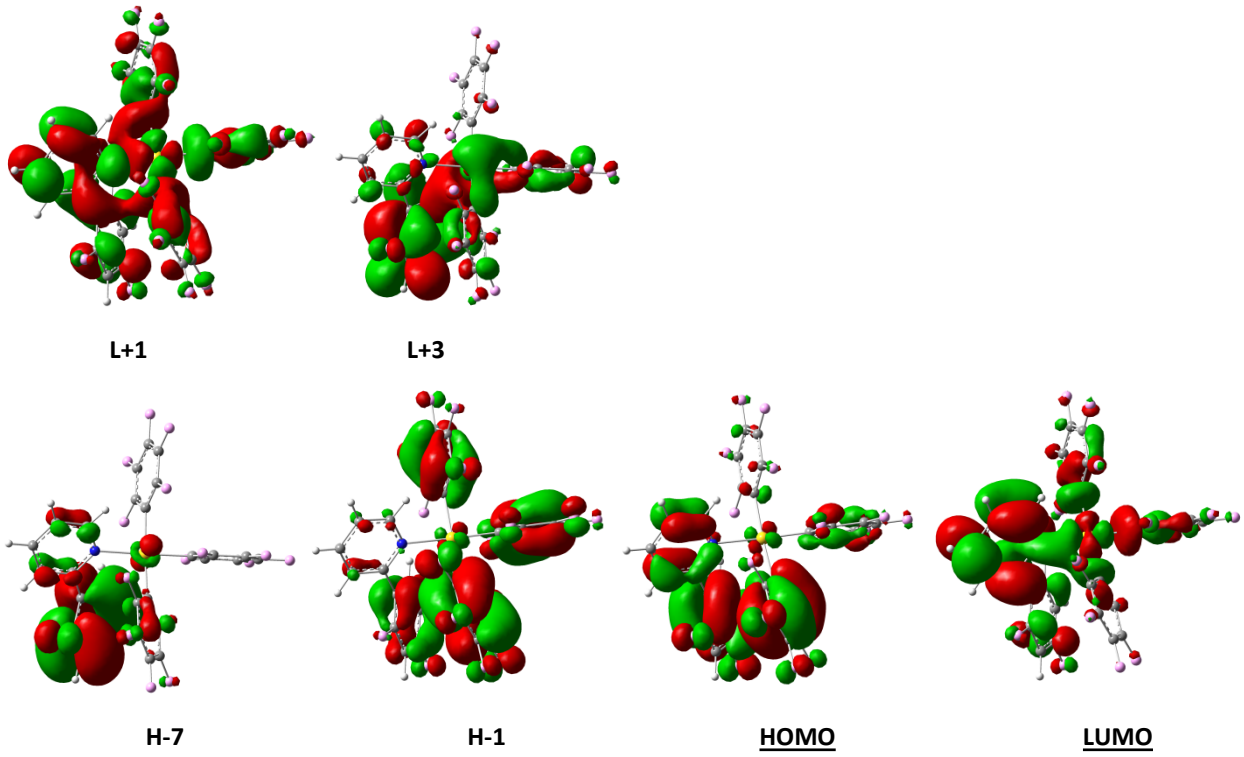

Figure S7. Spatial plots of selected frontier orbitals of the optimized ground state of **1**.

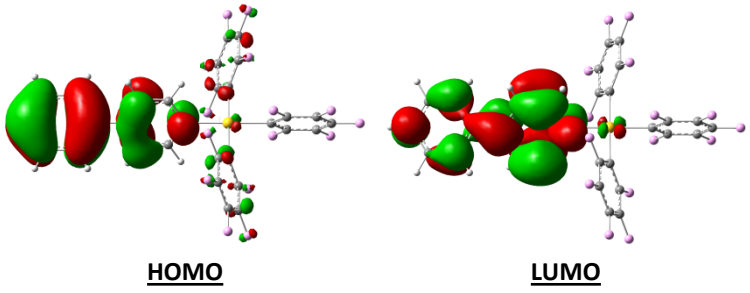

Figure S8. Spatial plots of selected frontier orbitals of the optimized ground state of **2**.

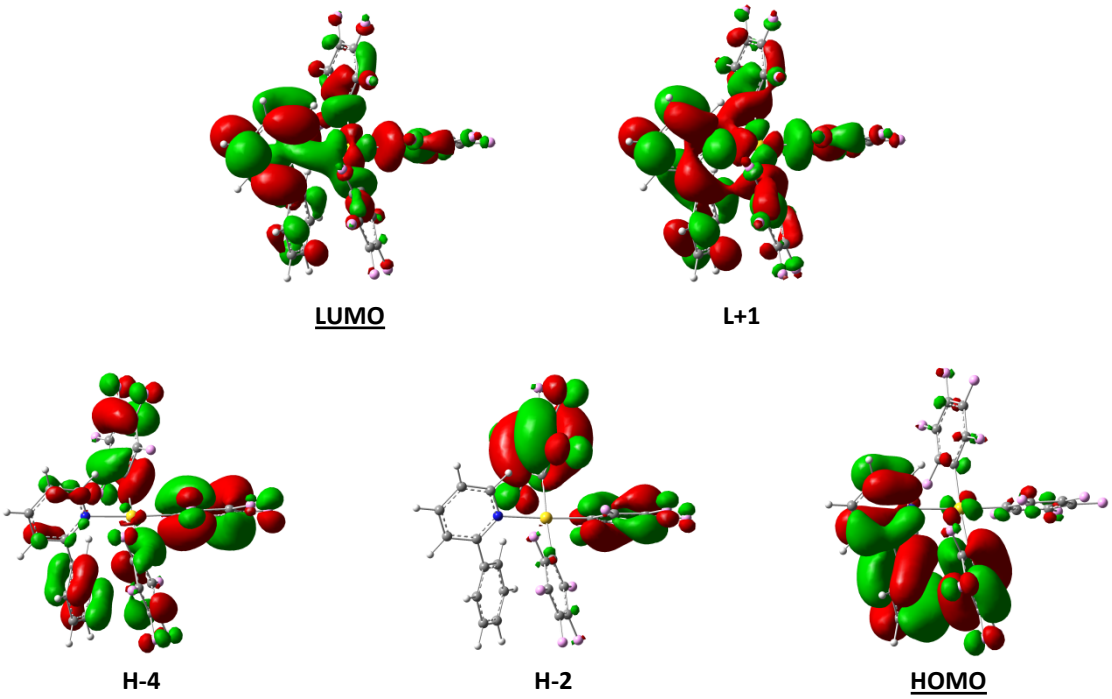

Figure S9. Spatial plots of selected frontier orbitals of the optimized ground state of **3**.

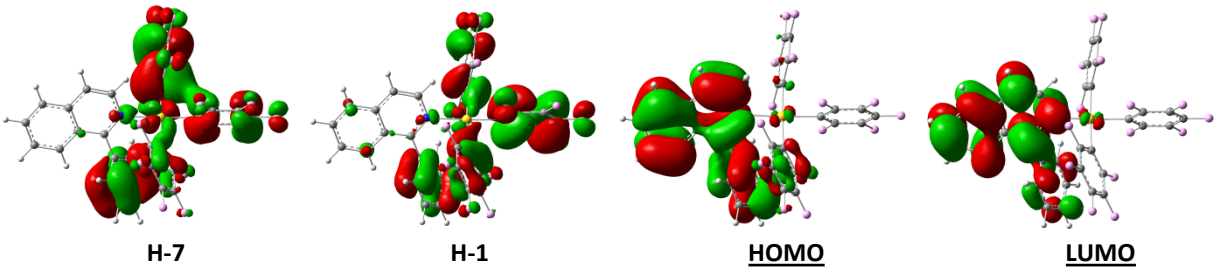

Figure S10. Spatial plots of selected frontier orbitals of the optimized ground state of **4**.

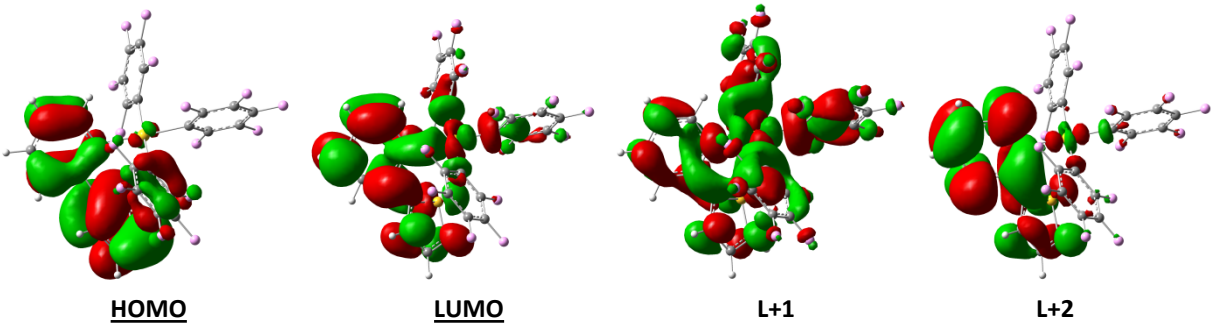

Figure S11. Spatial plots of selected frontier orbitals of the optimized ground state of **5**.

Table S21. Energy levels of a selection of frontier orbitals of the DFT optimized ground state S_0 and triplet state T_1 structures of **1** – **5**.

	MO		1	2	3	4	5
ground-state	LUMO	eV	-2.14	-2.20	-2.05	-2.30	-2.13
	HOMO	eV	-7.31	-7.39	-7.24	-7.02	-6.92
	ΔE(H-L)	eV	5.17	5.19	5.19	4.72	4.79
		nm	240	239	239	263	259
exp. abs., λmax[a]		*nm*	*277*	*279*	*281*	*335*	*317*
triplet-state	SOMO[b]	eV	-2.67	-2.63	-2.60	-2.48	-2.51
	SOMO-1	eV	-4.61	-4.81	-4.51	-4.42	-4.39

[a]recorded at room temperature in CH_2Cl_2 [b]restricted open-shell single point calculations on the optimized triplet state geometries.

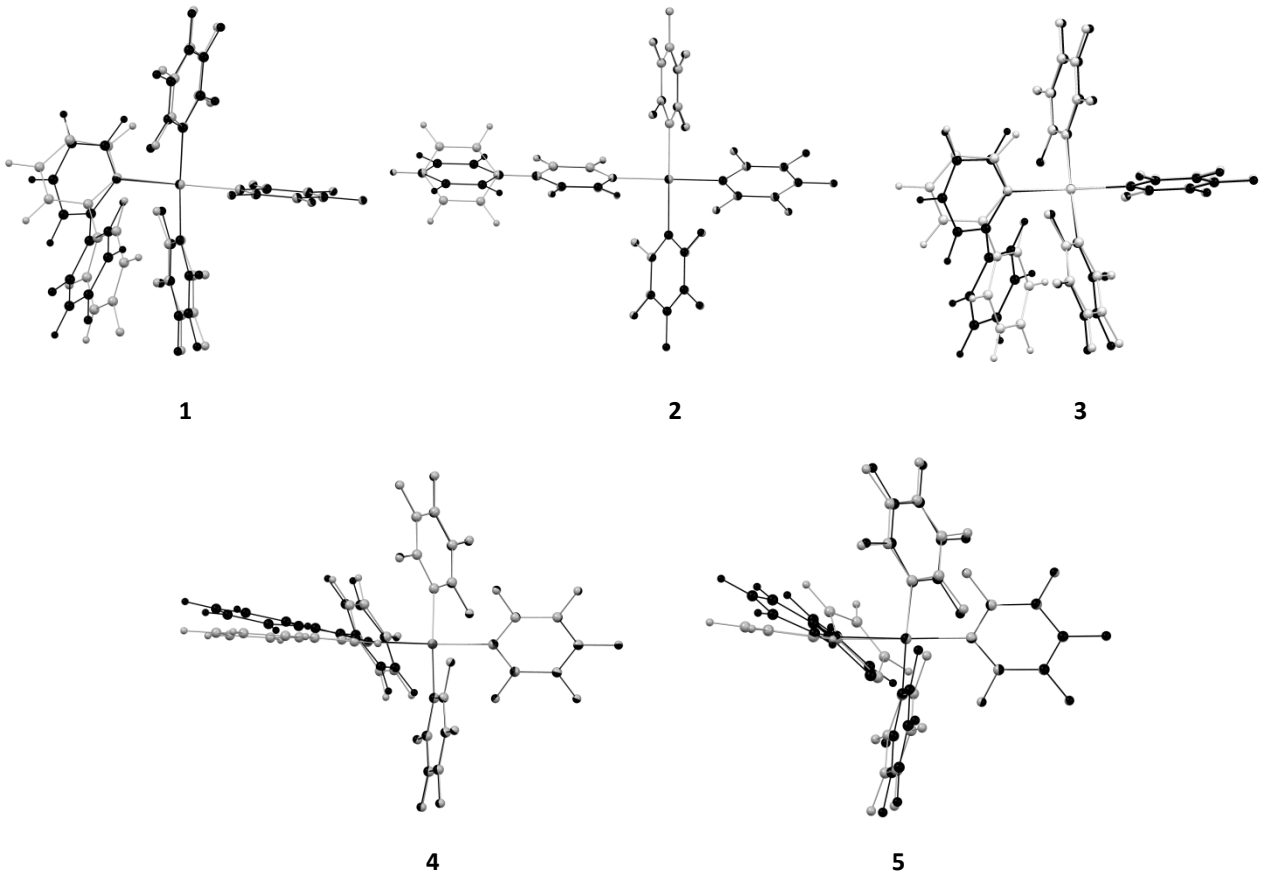

Figure S12. Overlay plots of the DFT optimized ground state (light grey) and triplet state (black) structures of **1** – **5**.