Supporting information for

Platinum CCC-NHC Benzimidazolyl Pincer Complexes: Synthesis, Characterization, Photostability, and Theoretical Investigation of a Blue-Green Emitter

Aron J. Huckaba,[†] Bei Cao,[†] T. Keith Hollis,*[,†] Henry U. Valle,[†] John T. Kelly,[†] Nathan I. Hammer,[†] Allen G. Oliver[+], Charles Edwin Webster[‡]

[†]*Department of Chemistry and Biochemistry, The University of Mississippi, University, Mississippi, 38677, United States.*

[+]*Department of Chemistry and Biochemistry, University of Notre Dame, 246B Nieuwland Hall, Notre Dame, Indiana 46556, United States.*

[‡] *Department of Chemistry, The University of Memphis, Memphis, Tennessee, 38152, United States.*

*To whom correspondence should be addressed.

E-mail: hollis@olemiss.edu

Tel: 1-662-915-5337

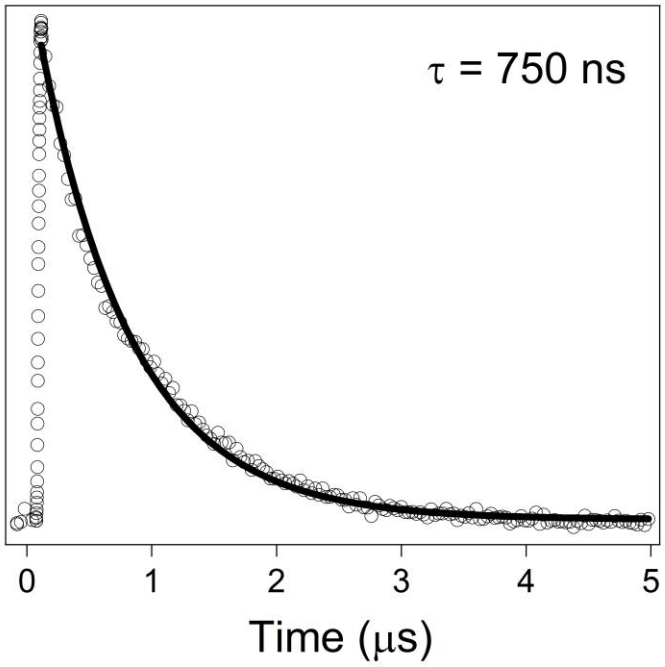
Photophysical Data

Table S1. Photophysical Properties of Pt complex **3** in CH_2Cl_2.

λ_{abs}/nm ($\varepsilon/10^{-3}$ M^{-1} cm^{-1})	λ_{em} (rel intens)[a,b]	λ_{em} (rel intens)[a,c]	τ_{rad}[b,d]
250 (9.9), 278 (7.3), 290 (7.0), 304 (7.5), 360 (1.6), 374 (2.9)	476 (100), 505.5 (60), 539.5 (20)	478 (100), 506 (85.5), 543 (38), 590 (17)	750 ns

[a]: irradiated with 371 nm light. [b]:In CH_2Cl_2. [c]: Solid State [d]: Irradiated with 355 nm light.

Figure S1. Excited state lifetime measurement of **3**.[a]



[a]: In CH_2Cl_2, Irradiated with 355 nm light.

X-Ray Crystallography Data

CRYSTAL SUMMARY

Crystal data for C28 H33 Cl N4 Pt Si2; M_r = 712.30; Triclinic; space group P -1; *a* = 7.790(3) Å; *b* = 13.294(5) Å; *c* = 13.442(5) Å; α = 81.618(4)°; β = 87.580(4)°; γ = 86.480(4)°; V = 1373.7(9) Å^3; Z = 2; T = 99(2) K; λ(Mo-Kα) = 0.71073 Å; μ(Mo-Kα) = 5.317 mm^{-1}; d_{calc} = 1.722g.cm^{-3}; 15194 reflections collected; 5569 unique (R_{int} = 0.0517); giving R_1 = 0.0268, wR_2 = 0.0674 for 5301 data with [I>2σ(I)] and R_1 = 0.0286, wR_2 = 0.0693 for all 5569 data. Residual electron density (e$^-$.Å^{-3}) max/min: 1.191/-0.798.

An arbitrary sphere of data were collected on a plate-like crystal, having approximate dimensions of 0.203 × 0.183 × 0.127 mm, on a Bruker APEX-II diffractometer using a combination of ω- and φ-scans of 0.5°. Data were corrected for absorption and polarization effects and analyzed for space group determination. The structure was solved by direct methods and expanded routinely. The model was refined by full-matrix least-squares analysis of F^2 against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Thermal parameters for the hydrogens were tied to the isotropic thermal parameter of the atom to which they are bonded (1.5 × for methyl, 1.2 × for all others).

REFERENCES

Bruker AXS. (2008). *APEX-2*. Bruker-Nonius AXS, Madison, Wisconsin, USA.

G. M. Sheldrick, *Acta Cryst.*, **2008**, *A64*, 112.

Table S1. Crystal data and structure refinement for complex **3** (CCDC 924676).

Identification code	UMCBAH75A
Empirical formula	$C_{28}H_{33}ClN_4PtSi_2$
Formula weight	712.30
Temperature	99(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 7.790(3) Å α = 81.618(4)°
	b = 13.294(5) Å β = 87.580(4)°
	c = 13.442(5) Å γ = 86.480(4)°
Volume	1373.7(9) $Å^3$
Z	2
Density (calculated)	1.722 $g.cm^{-3}$
Absorption coefficient (μ)	5.317 mm^{-1}
F(000)	704
Crystal color, habit	Yellow, Plate
Crystal size	0.203 × 0.183 × 0.127 mm^3
θ range for data collection	1.532 to 26.511°
Index ranges	-9 ≤ h ≤ 9, -16 ≤ k ≤ 16, -15 ≤ l ≤ 16
Reflections collected	15194
Independent reflections	5569 [R_{int} = 0.0517]
Completeness to θ = 25.242°	99.2 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5569 / 0 / 325
Goodness-of-fit on F^2	1.049

Final R indices [I>2σ(I)]	R_1 = 0.0268, wR_2 = 0.0674
R indices (all data)	R_1 = 0.0286, wR_2 = 0.0693
Extinction coefficient	n/a
Largest diff. peak and hole	1.191 and -0.798 $e^{-}.Å^{-3}$

Table S2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for complex **3**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Pt(1)	0.27713(2)	0.71310(2)	0.45758(2)	0.011(1)
Cl(1)	0.28720(12)	0.88543(6)	0.37160(6)	0.019(1)
Si(1)	0.23146(14)	0.81616(8)	0.10407(7)	0.017(1)
N(1)	0.4133(3)	0.6325(2)	0.65208(19)	0.012(1)
C(1)	0.3568(4)	0.5447(2)	0.6152(2)	0.013(1)
N(2)	0.4512(4)	0.7960(2)	0.6386(2)	0.014(1)
C(2)	0.3673(4)	0.4443(3)	0.6612(2)	0.015(1)
Si(2)	0.24900(13)	0.97863(7)	0.66015(7)	0.017(1)
N(3)	0.1590(4)	0.5407(2)	0.37649(19)	0.012(1)
C(3)	0.3030(4)	0.3701(2)	0.6107(2)	0.016(1)
N(4)	0.0938(4)	0.6699(2)	0.2617(2)	0.013(1)
C(4)	0.2301(4)	0.3953(3)	0.5159(2)	0.014(1)
C(5)	0.2244(4)	0.4968(3)	0.4722(2)	0.012(1)
C(6)	0.2830(4)	0.5721(3)	0.5218(2)	0.013(1)
C(7)	0.3881(4)	0.7246(2)	0.5899(2)	0.011(1)
C(8)	0.4936(4)	0.6459(3)	0.7398(2)	0.015(1)
C(9)	0.5193(4)	0.7495(3)	0.7306(2)	0.014(1)
C(10)	0.6026(4)	0.7925(3)	0.8030(3)	0.019(1)
C(11)	0.6531(5)	0.7267(3)	0.8879(3)	0.023(1)
C(12)	0.6232(5)	0.6230(3)	0.8991(3)	0.023(1)
C(13)	0.5433(5)	0.5799(3)	0.8259(2)	0.020(1)
C(14)	0.1672(4)	0.6449(3)	0.3523(2)	0.013(1)
C(15)	0.0383(4)	0.5824(2)	0.2277(2)	0.013(1)

C(16)	0.0793(4)	0.5003(3)	0.3017(2)	0.014(1)
C(17)	0.0365(4)	0.4013(3)	0.2907(2)	0.015(1)
C(18)	-0.0479(5)	0.3905(3)	0.2041(2)	0.019(1)
C(19)	-0.0886(5)	0.4737(3)	0.1304(2)	0.018(1)
C(20)	-0.0471(5)	0.5714(3)	0.1414(2)	0.018(1)
C(21)	0.0651(5)	0.7731(3)	0.2084(2)	0.017(1)
C(22)	0.2227(5)	0.9582(3)	0.0890(3)	0.025(1)
C(23)	0.1775(6)	0.7718(3)	-0.0165(3)	0.027(1)
C(24)	0.4489(5)	0.7608(3)	0.1435(3)	0.026(1)
C(25)	0.4405(5)	0.9059(3)	0.6051(2)	0.015(1)
C(26)	0.0621(5)	0.8953(3)	0.6733(3)	0.028(1)
C(27)	0.2074(5)	1.0970(3)	0.5699(3)	0.023(1)
C(28)	0.3004(5)	1.0122(3)	0.7860(3)	0.026(1)
H(2A)	0.4167	0.4262	0.7252	0.018
H(3A)	0.3089	0.3011	0.6416	0.020
H(4A)	0.1861	0.3445	0.4826	0.017
H(10A)	0.6235	0.8629	0.7946	0.023
H(11A)	0.7092	0.7527	0.9394	0.028
H(12A)	0.6585	0.5805	0.9586	0.028
H(13A)	0.5236	0.5093	0.8340	0.023
H(17A)	0.0640	0.3445	0.3401	0.019
H(18A)	-0.0791	0.3247	0.1945	0.022
H(19A)	-0.1454	0.4629	0.0720	0.022
H(20A)	-0.0757	0.6282	0.0923	0.021
H(21B)	0.0618	0.8211	0.2583	0.021
H(21A)	-0.0496	0.7784	0.1784	0.021
H(22A)	0.3065	0.9840	0.0365	0.038
H(22B)	0.2500	0.9802	0.1528	0.038

H(22C)	0.1068	0.9851	0.0700	0.038
H(23A)	0.1817	0.6972	-0.0072	0.040
H(23B)	0.2610	0.7965	-0.0697	0.040
H(23C)	0.0617	0.7986	-0.0356	0.040
H(24A)	0.4486	0.6863	0.1533	0.039
H(24B)	0.4766	0.7838	0.2067	0.039
H(24C)	0.5353	0.7833	0.0912	0.039
H(25A)	0.4348	0.9177	0.5308	0.018
H(25B)	0.5477	0.9345	0.6229	0.018
H(26A)	-0.0385	0.9312	0.7009	0.042
H(26B)	0.0908	0.8325	0.7188	0.042
H(26C)	0.0360	0.8784	0.6072	0.042
H(27A)	0.1103	1.1375	0.5954	0.035
H(27B)	0.1798	1.0791	0.5044	0.035
H(27C)	0.3101	1.1369	0.5622	0.035
H(28A)	0.2001	1.0484	0.8136	0.038
H(28B)	0.3982	1.0560	0.7783	0.038
H(28C)	0.3296	0.9498	0.8319	0.038

Table S3. Anisotropic displacement parameters ($Å^2$) for complex **3**.

The anisotropic displacement factor exponent takes the form:

$-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt(1)	0.0136(1)	0.0083(1)	0.0100(1)	-0.0022(1)	0.0003(1)	-0.0007(1)
Cl(1)	0.0299(5)	0.0116(4)	0.0164(4)	-0.0009(3)	-0.0050(3)	-0.0052(3)
Si(1)	0.0251(5)	0.0129(5)	0.0120(4)	-0.0014(4)	-0.0027(4)	-0.0026(4)
N(1)	0.0137(14)	0.0119(14)	0.0112(12)	-0.0022(10)	-0.0019(10)	0.0009(11)
C(1)	0.0133(16)	0.0140(17)	0.0121(15)	-0.0034(12)	0.0031(12)	-0.0013(13)
N(2)	0.0175(15)	0.0119(15)	0.0130(13)	-0.0054(11)	0.0009(11)	-0.0013(11)
C(2)	0.0138(17)	0.0173(18)	0.0132(15)	-0.0013(13)	0.0003(12)	0.0018(13)
Si(2)	0.0224(5)	0.0118(5)	0.0159(4)	-0.0026(4)	0.0013(4)	-0.0003(4)
N(3)	0.0171(15)	0.0086(13)	0.0109(13)	-0.0018(10)	0.0006(10)	-0.0012(11)
C(3)	0.0194(18)	0.0063(16)	0.0220(16)	0.0010(13)	0.0016(13)	0.0025(13)
N(4)	0.0179(15)	0.0108(15)	0.0113(13)	-0.0032(11)	-0.0005(10)	-0.0027(11)
C(4)	0.0125(16)	0.0137(17)	0.0173(15)	-0.0070(13)	0.0014(12)	-0.0009(13)
C(5)	0.0145(16)	0.0114(16)	0.0104(14)	-0.0013(12)	0.0029(12)	0.0002(13)
C(6)	0.0098(16)	0.0142(17)	0.0143(15)	-0.0057(13)	0.0019(12)	0.0000(13)
C(7)	0.0087(15)	0.0092(16)	0.0157(15)	-0.0045(12)	0.0036(11)	-0.0022(12)
C(8)	0.0121(17)	0.0213(19)	0.0131(15)	-0.0070(13)	0.0037(12)	-0.0006(13)
C(9)	0.0136(16)	0.0170(17)	0.0135(15)	-0.0047(13)	0.0016(12)	0.0005(13)
C(10)	0.0162(18)	0.0211(19)	0.0215(17)	-0.0078(15)	-0.0035(13)	0.0010(14)
C(11)	0.0218(19)	0.030(2)	0.0206(17)	-0.0104(15)	-0.0079(14)	0.0050(16)
C(12)	0.023(2)	0.029(2)	0.0172(16)	-0.0009(15)	-0.0044(14)	0.0065(16)
C(13)	0.0198(19)	0.0187(19)	0.0193(17)	-0.0012(14)	-0.0015(13)	0.0031(14)

C(14)	0.0125(16)	0.0145(17)	0.0119(15)	-0.0009(13)	0.0018(12)	0.0004(13)
C(15)	0.0141(16)	0.0102(16)	0.0145(15)	-0.0041(12)	0.0024(12)	-0.0040(12)
C(16)	0.0132(17)	0.0152(17)	0.0128(15)	-0.0048(13)	0.0034(12)	-0.0010(13)
C(17)	0.0166(17)	0.0137(17)	0.0163(15)	-0.0038(13)	0.0039(12)	-0.0022(13)
C(18)	0.0226(19)	0.0161(18)	0.0195(17)	-0.0084(14)	0.0012(13)	-0.0048(14)
C(19)	0.0228(19)	0.0213(19)	0.0122(15)	-0.0073(13)	-0.0005(12)	-0.0046(14)
C(20)	0.0204(18)	0.0178(18)	0.0149(15)	-0.0028(13)	-0.0017(13)	-0.0004(14)
C(21)	0.0260(19)	0.0119(17)	0.0151(16)	-0.0046(13)	-0.0034(13)	-0.0010(14)
C(22)	0.037(2)	0.0169(19)	0.0217(18)	0.0012(14)	-0.0029(15)	-0.0073(16)
C(23)	0.036(2)	0.031(2)	0.0163(17)	-0.0065(16)	-0.0008(15)	-0.0108(18)
C(24)	0.031(2)	0.024(2)	0.0219(18)	-0.0025(15)	-0.0019(15)	0.0050(17)
C(25)	0.0183(18)	0.0130(17)	0.0139(15)	-0.0040(13)	0.0004(12)	-0.0030(13)
C(26)	0.022(2)	0.020(2)	0.039(2)	0.0006(16)	0.0024(16)	-0.0030(16)
C(27)	0.030(2)	0.0147(19)	0.0227(18)	-0.0012(15)	0.0046(15)	0.0030(15)
C(28)	0.033(2)	0.026(2)	0.0181(17)	-0.0072(15)	0.0023(15)	0.0045(17)

Table S4. Bond lengths [Å] for complex **3**.

atom-atom	distance	atom-atom	distance
Pt(1)-C(6)	1.944(3)	Pt(1)-C(14)	2.032(3)
Pt(1)-C(7)	2.039(3)	Pt(1)-Cl(1)	2.4152(12)
Si(1)-C(22)	1.868(4)	Si(1)-C(24)	1.871(4)
Si(1)-C(23)	1.875(4)	Si(1)-C(21)	1.918(4)
N(1)-C(7)	1.386(4)	N(1)-C(8)	1.397(4)
N(1)-C(1)	1.433(4)	C(1)-C(2)	1.386(5)
C(1)-C(6)	1.393(4)	N(2)-C(7)	1.355(4)
N(2)-C(9)	1.409(4)	N(2)-C(25)	1.464(4)
C(2)-C(3)	1.403(5)	Si(2)-C(27)	1.863(4)
Si(2)-C(26)	1.870(4)	Si(2)-C(28)	1.877(4)
Si(2)-C(25)	1.910(4)	N(3)-C(14)	1.380(4)
N(3)-C(16)	1.392(4)	N(3)-C(5)	1.433(4)
C(3)-C(4)	1.405(5)	N(4)-C(14)	1.356(4)
N(4)-C(15)	1.407(4)	N(4)-C(21)	1.461(4)
C(4)-C(5)	1.390(5)	C(5)-C(6)	1.391(5)
C(8)-C(9)	1.392(5)	C(8)-C(13)	1.399(5)
C(9)-C(10)	1.398(5)	C(10)-C(11)	1.387(5)
C(11)-C(12)	1.398(5)	C(12)-C(13)	1.395(5)
C(15)-C(20)	1.391(5)	C(15)-C(16)	1.397(5)
C(16)-C(17)	1.407(5)	C(17)-C(18)	1.391(5)
C(18)-C(19)	1.403(5)	C(19)-C(20)	1.387(5)

Table S5. Bond angles [°] for complex **3**.

atom-atom-atom	angle	atom-atom-atom	angle
C(6)-Pt(1)-C(14)	78.72(13)	C(6)-Pt(1)-C(7)	78.96(13)
C(14)-Pt(1)-C(7)	157.68(14)	C(6)-Pt(1)-Cl(1)	176.19(9)
C(14)-Pt(1)-Cl(1)	100.77(10)	C(7)-Pt(1)-Cl(1)	101.53(9)
C(22)-Si(1)-C(24)	111.18(19)	C(22)-Si(1)-C(23)	110.45(19)
C(24)-Si(1)-C(23)	109.58(19)	C(22)-Si(1)-C(21)	106.46(17)
C(24)-Si(1)-C(21)	108.76(17)	C(23)-Si(1)-C(21)	110.35(18)
C(7)-N(1)-C(8)	110.9(3)	C(7)-N(1)-C(1)	116.1(3)
C(8)-N(1)-C(1)	133.0(3)	C(2)-C(1)-C(6)	121.3(3)
C(2)-C(1)-N(1)	128.1(3)	C(6)-C(1)-N(1)	110.6(3)
C(7)-N(2)-C(9)	109.9(3)	C(7)-N(2)-C(25)	125.7(3)
C(9)-N(2)-C(25)	124.3(3)	C(1)-C(2)-C(3)	118.3(3)
C(27)-Si(2)-C(26)	111.86(19)	C(27)-Si(2)-C(28)	109.81(18)
C(26)-Si(2)-C(28)	110.12(18)	C(27)-Si(2)-C(25)	106.47(16)
C(26)-Si(2)-C(25)	107.86(17)	C(28)-Si(2)-C(25)	110.64(17)
C(14)-N(3)-C(16)	110.8(3)	C(14)-N(3)-C(5)	116.1(3)
C(16)-N(3)-C(5)	133.0(3)	C(2)-C(3)-C(4)	121.7(3)
C(14)-N(4)-C(15)	110.5(3)	C(14)-N(4)-C(21)	125.6(3)
C(15)-N(4)-C(21)	123.8(3)	C(5)-C(4)-C(3)	117.9(3)
C(4)-C(5)-C(6)	121.4(3)	C(4)-C(5)-N(3)	128.3(3)
C(6)-C(5)-N(3)	110.3(3)	C(5)-C(6)-C(1)	119.3(3)
C(5)-C(6)-Pt(1)	120.4(2)	C(1)-C(6)-Pt(1)	120.2(2)
N(2)-C(7)-N(1)	106.1(3)	N(2)-C(7)-Pt(1)	139.8(2)
N(1)-C(7)-Pt(1)	114.1(2)	C(9)-C(8)-N(1)	105.5(3)
C(9)-C(8)-C(13)	120.8(3)	N(1)-C(8)-C(13)	133.7(3)

C(8)-C(9)-C(10)	122.6(3)	C(8)-C(9)-N(2)	107.6(3)
C(10)-C(9)-N(2)	129.8(3)	C(11)-C(10)-C(9)	116.4(3)
C(10)-C(11)-C(12)	121.3(3)	C(13)-C(12)-C(11)	122.2(3)
C(12)-C(13)-C(8)	116.6(3)	N(4)-C(14)-N(3)	106.0(3)
N(4)-C(14)-Pt(1)	139.5(3)	N(3)-C(14)-Pt(1)	114.5(2)
C(20)-C(15)-C(16)	122.5(3)	C(20)-C(15)-N(4)	130.8(3)
C(16)-C(15)-N(4)	106.6(3)	N(3)-C(16)-C(15)	106.0(3)
N(3)-C(16)-C(17)	133.4(3)	C(15)-C(16)-C(17)	120.5(3)
C(18)-C(17)-C(16)	116.8(3)	C(17)-C(18)-C(19)	122.1(3)
C(20)-C(19)-C(18)	121.1(3)	C(19)-C(20)-C(15)	117.0(3)
N(4)-C(21)-Si(1)	116.2(2)	N(2)-C(25)-Si(2)	115.1(2)

Table S6. Torsion angles [°] for complex **3**.

atom-atom-atom-atom	angle	atom-atom-atom-atom	angle
C(7)-N(1)-C(1)-C(2)	179.6(3)	C(8)-N(1)-C(1)-C(2)	0.7(6)
C(7)-N(1)-C(1)-C(6)	-1.1(4)	C(8)-N(1)-C(1)-C(6)	-180.0(3)
C(6)-C(1)-C(2)-C(3)	0.7(5)	N(1)-C(1)-C(2)-C(3)	180.0(3)
C(1)-C(2)-C(3)-C(4)	0.3(5)	C(2)-C(3)-C(4)-C(5)	0.5(5)
C(3)-C(4)-C(5)-C(6)	-2.3(5)	C(3)-C(4)-C(5)-N(3)	179.1(3)
C(14)-N(3)-C(5)-C(4)	179.1(3)	C(16)-N(3)-C(5)-C(4)	2.5(6)
C(14)-N(3)-C(5)-C(6)	0.4(4)	C(16)-N(3)-C(5)-C(6)	-176.2(3)
C(4)-C(5)-C(6)-C(1)	3.2(5)	N(3)-C(5)-C(6)-C(1)	-178.0(3)
C(4)-C(5)-C(6)-Pt(1)	178.8(2)	N(3)-C(5)-C(6)-Pt(1)	-2.3(4)
C(2)-C(1)-C(6)-C(5)	-2.4(5)	N(1)-C(1)-C(6)-C(5)	178.2(3)
C(2)-C(1)-C(6)-Pt(1)	-178.0(2)	N(1)-C(1)-C(6)-Pt(1)	2.6(4)
C(9)-N(2)-C(7)-N(1)	1.0(3)	C(25)-N(2)-C(7)-N(1)	-175.0(3)
C(9)-N(2)-C(7)-Pt(1)	-177.3(3)	C(25)-N(2)-C(7)-Pt(1)	6.7(6)
C(8)-N(1)-C(7)-N(2)	-0.4(3)	C(1)-N(1)-C(7)-N(2)	-179.5(3)
C(8)-N(1)-C(7)-Pt(1)	178.4(2)	C(1)-N(1)-C(7)-Pt(1)	-0.7(3)
C(7)-N(1)-C(8)-C(9)	-0.4(4)	C(1)-N(1)-C(8)-C(9)	178.5(3)
C(7)-N(1)-C(8)-C(13)	178.3(4)	C(1)-N(1)-C(8)-C(13)	-2.8(6)
N(1)-C(8)-C(9)-C(10)	-177.8(3)	C(13)-C(8)-C(9)-C(10)	3.3(5)
N(1)-C(8)-C(9)-N(2)	1.0(4)	C(13)-C(8)-C(9)-N(2)	-177.9(3)
C(7)-N(2)-C(9)-C(8)	-1.3(4)	C(25)-N(2)-C(9)-C(8)	174.8(3)
C(7)-N(2)-C(9)-C(10)	177.4(3)	C(25)-N(2)-C(9)-C(10)	-6.6(6)
C(8)-C(9)-C(10)-C(11)	-2.6(5)	N(2)-C(9)-C(10)-C(11)	178.9(3)
C(9)-C(10)-C(11)-C(12)	0.6(5)	C(10)-C(11)-C(12)-C(13)	0.7(6)
C(11)-C(12)-C(13)-C(8)	-0.1(5)	C(9)-C(8)-C(13)-C(12)	-1.8(5)

N(1)-C(8)-C(13)-C(12)	179.7(4)	C(15)-N(4)-C(14)-N(3)	0.1(4)
C(21)-N(4)-C(14)-N(3)	176.5(3)	C(15)-N(4)-C(14)-Pt(1)	-179.0(3)
C(21)-N(4)-C(14)-Pt(1)	-2.6(6)	C(16)-N(3)-C(14)-N(4)	-0.5(4)
C(5)-N(3)-C(14)-N(4)	-177.8(3)	C(16)-N(3)-C(14)-Pt(1)	178.8(2)
C(5)-N(3)-C(14)-Pt(1)	1.5(4)	C(14)-N(4)-C(15)-C(20)	178.0(3)
C(21)-N(4)-C(15)-C(20)	1.5(6)	C(14)-N(4)-C(15)-C(16)	0.3(4)
C(21)-N(4)-C(15)-C(16)	-176.1(3)	C(14)-N(3)-C(16)-C(15)	0.7(4)
C(5)-N(3)-C(16)-C(15)	177.4(3)	C(14)-N(3)-C(16)-C(17)	-178.4(4)
C(5)-N(3)-C(16)-C(17)	-1.7(6)	C(20)-C(15)-C(16)-N(3)	-178.5(3)
N(4)-C(15)-C(16)-N(3)	-0.6(4)	C(20)-C(15)-C(16)-C(17)	0.8(5)
N(4)-C(15)-C(16)-C(17)	178.7(3)	N(3)-C(16)-C(17)-C(18)	178.7(3)
C(15)-C(16)-C(17)-C(18)	-0.4(5)	C(16)-C(17)-C(18)-C(19)	0.3(5)
C(17)-C(18)-C(19)-C(20)	-0.6(5)	C(18)-C(19)-C(20)-C(15)	0.9(5)
C(16)-C(15)-C(20)-C(19)	-1.0(5)	N(4)-C(15)-C(20)-C(19)	-178.4(3)
C(14)-N(4)-C(21)-Si(1)	98.9(3)	C(15)-N(4)-C(21)-Si(1)	-85.2(4)
C(7)-N(2)-C(25)-Si(2)	94.2(3)	C(9)-N(2)-C(25)-Si(2)	-81.2(4)

Computational Data

Figure S2. Theoretical absorption spectra of complex **3**.

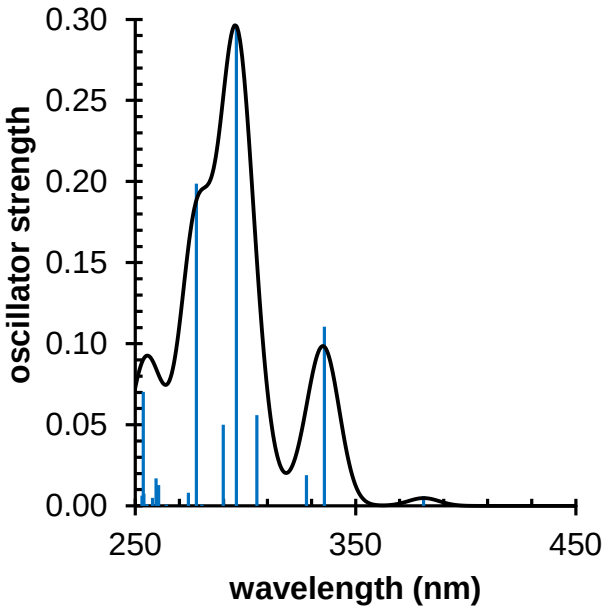


Figure S3. 3D geometry of M06-optimized ground state of complex **3.**

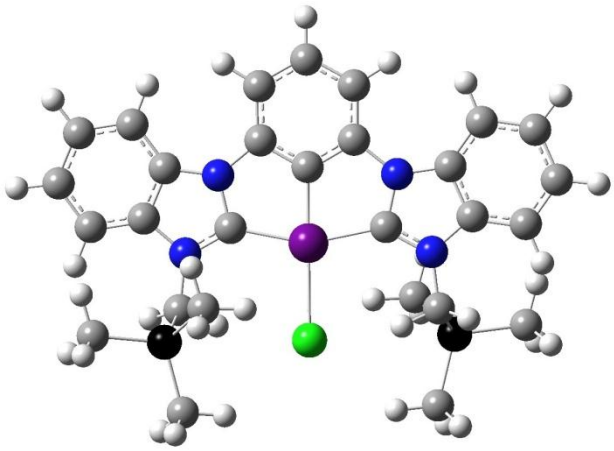


Table S7. Energetic data and Cartesian coordinates (in Angstroms) for M06-optimized S_0 of complex **3**.

```
el energy= -1446.88896252
```

```
          zpe= -1446.343228
    th energy= -1446.304663
  th enthalpy= -1446.303719
  free energy= -1446.416152

Pt,-0.0000071593,-0.0973572218,0.0002392055
Cl,-0.0004657391,-2.5804381805,0.0006704146
Si,-3.8123721797,-2.4769179288,1.1320745165
Si,3.811139263,-2.477536836,-1.1329043623
N,3.1401165079,-0.3354409284,0.5999143648
N,2.2747125838,1.6639132406,0.410288676
N,-3.1400565162,-0.3346059037,-0.6000558617
N,-2.27418882,1.664521798,-0.4101354501
C,4.1833356419,0.574295424,0.7476217204
C,5.5389077376,0.3743344574,0.984407146
H,5.9558326537,-0.6278337044,1.0747541251
C,6.3386715105,1.5058866879,1.0963053322
H,7.4057688411,1.3904712177,1.2800186166
C,5.7940859665,2.7905062011,0.976080074
H,6.4468274515,3.6576191154,1.0666984867
C,4.4374573471,2.9904970534,0.7444916523
H,4.0382705133,3.9971025208,0.6552498874
C,3.631338346,1.8598448426,0.6319025275
C,1.9796757028,0.3101588318,0.3836457196
C,1.1874138156,2.5549437203,0.2133377649
C,1.204028822,3.9472694114,0.2190366783
H,2.1140678492,4.517751568,0.3893258051
C,0.0006432118,4.6216959583,0.000146987
H,0.0007855211,5.7107640651,0.0001717555
C,-1.2029180094,3.9475929066,-0.2187704823
H,-2.1128139638,4.518318769,-0.3890131083
C,-1.1866688991,2.5552643381,-0.2131127125
C,0.0002787952,1.8636975952,0.0001166974
C,-1.9795176892,0.3106966198,-0.383407678
C,-3.6306856733,1.8608160065,-0.6322079513
C,-4.4364660476,2.9916828059,-0.7451195822
H,-4.0370384226,3.9981853208,-0.6557793015
C,-5.7930670981,2.7920445697,-0.9771836726
H,-6.4455348088,3.659336764,-1.068055385
C,-6.3379530326,1.5075706754,-1.0975668669
H,-7.4050162223,1.3924410739,-1.2816492392
C,-5.5385334311,0.375809824,-0.9853724893
H,-5.9556832005,-0.626252556,-1.075846946
C,-4.1829934235,0.5754098157,-0.7481089601
C,3.3079028034,-1.7878383315,0.5819458
H,2.3353484599,-2.2256162688,0.8467583495
H,4.0215315181,-2.0572351327,1.3750418247
C,5.6652333148,-2.2686276864,-1.391006983
H,5.9706185756,-2.7176241173,-2.3475704357
H,6.2480444483,-2.7611867092,-0.5981063069
H,5.9573744391,-1.2084824931,-1.4180554873
C,2.8808465511,-1.518343558,-2.4428856305
H,3.161139136,-0.4537952281,-2.4363898173
H,1.7957598726,-1.584562622,-2.2741845917
H,3.0985986637,-1.9117365342,-3.4461923505
C,3.3555769019,-4.2937463512,-1.1232764132
H,3.6182664462,-4.7780657915,-2.0744541112
```

```
H,2.2727544688,-4.4048112164,-0.9682594513
H,3.8718160446,-4.8379481535,-0.3192370635
C,-3.3081820155,-1.7869770674,-0.5823898537
H,-2.3355952668,-2.2249170716,-0.8468420815
H,-4.0215088985,-2.0560662239,-1.3758648288
C,-2.8820503903,-1.518682989,2.4427242142
H,-3.1005540239,-1.9121929496,3.4458220622
H,-3.1616152104,-0.4539455238,2.436376161
H,-1.7969371213,-1.5856139146,2.2744991472
C,-5.6664529848,-2.267144278,1.3895762006
H,-6.2492339741,-2.7593080097,0.5964071325
H,-5.9581003328,-1.2068659274,1.4166876253
H,-5.972370915,-2.7161424919,2.3459688261
C,-3.3577765447,-4.2933712874,1.1219961252
H,-2.2749834359,-4.404988171,0.9671762554
H,-3.8741564748,-4.8370652217,0.3177018494
H,-3.6209148003,-4.7778216179,2.0729827288
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Figure S4. 3D geometry of M06-optimized triplet state of complex **3**.

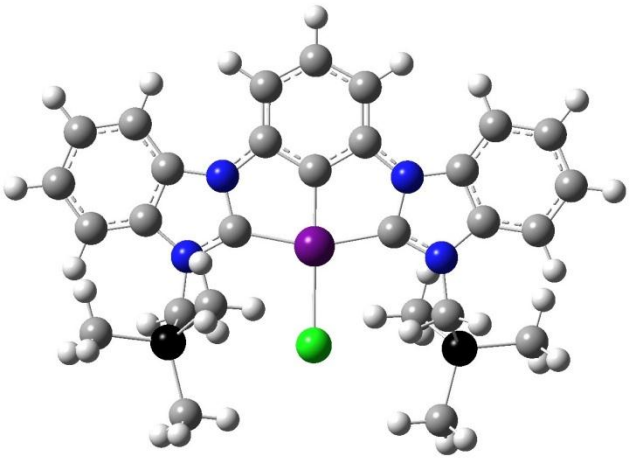

Table S8. Energetic data and Cartesian coordinates (in Angstroms) for M06-optimized T_1 of complex **3**.

```
    el energy= -1446.78884804
          zpe= -1446.246973
    th energy= -1446.207880
  th enthalpy= -1446.206936
  free energy= -1446.320958

Pt,-0.0000978962,-0.0528390849,-0.0002742912
Cl,-0.0005133454,-2.5281862505,-0.0002588192
Si,-3.8239147393,-2.4894742832,1.1162466853
Si,3.8228631709,-2.4907516092,-1.1170408891
N,3.1508567489,-0.3149491545,0.5808567864
N,2.2894179331,1.7030747523,0.3917007144
N,-3.1511280585,-0.3138405132,-0.5815209503
N,-2.2890054711,1.7038760174,-0.3921990439
C,4.1924446501,0.593215524,0.7272774237
```

C,5.5463150294,0.3889302131,0.9642227698
H,5.9595229012,-0.6147541902,1.0525768929
C,6.355184982,1.5187125204,1.0799612853
H,7.4211787571,1.3929104802,1.264313581
C,5.8239795432,2.8042769204,0.9629206196
H,6.4802705366,3.6681938851,1.0555068222
C,4.4630694519,3.0088595813,0.7292973306
H,4.0686977397,4.0178751877,0.6416776945
C,3.6542810998,1.8860268168,0.6146028615
C,1.9752386298,0.3243890001,0.3627262676
C,1.2351210065,2.5743623203,0.2100134038
C,1.2288623641,3.9510789474,0.2095391644
H,2.1294165754,4.5391623487,0.3664192616
C,0.0007175563,4.6166577466,-0.0002316633
H,0.000910309,5.7061935059,-0.0002393615
C,-1.2276618549,3.9515103666,-0.2100054567
H,-2.1280054182,4.5399092097,-0.3669141544
C,-1.2344047141,2.5747947441,-0.2104764736
C,0.0002330855,1.8511944211,-0.0002397133
C,-1.9752949825,0.3250780907,-0.3633358739
C,-3.6538133978,1.8873087979,-0.6150390346
C,-4.4622302514,3.0104239922,-0.7295777779
H,-4.0675220819,4.0192987382,-0.6418473027
C,-5.8232163034,2.8063200284,-0.9631731604
H,-6.4792246314,3.6704650803,-1.0556405247
C,-6.3548532724,1.5209430035,-1.0803308029
H,-7.4208962185,1.3955151232,-1.2646600281
C,-5.5463550317,0.3908786175,-0.964732406
H,-5.959901959,-0.6126591245,-1.0531638311
C,-4.1924091193,0.5946891128,-0.7278200491
C,3.3197277528,-1.7644967352,0.5821934335
H,2.3501233036,-2.1996778369,0.8605421772
H,4.036464568,-2.0238873956,1.3767098618
C,5.6746003329,-2.2730242044,-1.3859851828
H,5.9797164257,-2.7376813778,-2.3352207112
H,6.2641433491,-2.7459752708,-0.5861118373
H,5.9582211917,-1.2113309815,-1.4337160385
C,2.8843976352,-1.5836692436,-2.4573093618
H,3.1364518524,-0.5123496839,-2.4659367962
H,1.79929537,-1.6718816149,-2.3021805454
H,3.1280896119,-1.9909047978,-3.449281249
C,3.390059397,-4.3128335058,-1.0574043637
H,3.6577736973,-4.8187355739,-1.9959415761
H,2.3094571124,-4.4376133135,-0.8979021231
H,3.9154927667,-4.8283045099,-0.2404223972
C,-3.3205075086,-1.7633246436,-0.5829494671
H,-2.3510578252,-2.1988373128,-0.8613112336
H,-4.0373282671,-2.0224190284,-1.3774842688
C,-2.8852488517,-1.5826566006,2.456555947
H,-3.1290838513,-1.9898301805,3.4485186588
H,-3.1370171567,-0.5112696099,2.4651798559
H,-1.8001638542,-1.6711597485,2.3014653306
C,-5.6756010513,-2.2712359404,1.3851198817
H,-6.2652418331,-2.7439628482,0.5851869943
H,-5.9589228111,-1.2094657881,1.4329126571
H,-5.9808915673,-2.7358747832,2.3343087685
C,-3.3916154546,-4.3116754361,1.0566087735

H,-2.3110373118,-4.4367518381,0.8971750667
H,-3.917136826,-4.8269833291,0.2395808533
H,-3.6595365199,-4.81752075,1.9951179348