## **Supporting Information**

## Detailed Structural and Spectroscopic Elucidation of Ferrocenium Coupled Nheterocyclic Carbene Gold(I) Complexes

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$\begin{array}{cccccccccccccccccccccccccccccccccccc$	compound #	[ <b>2</b> ][BF <sub>4</sub> ]	[ <b>3</b> ][BF4]3	[ <b>5</b> ][BF <sub>4</sub> ]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	CCDC	2109471	2109472	2109473
solventnoneClCH2CH2Clnoneformula $C_{46}H_{48}AuFe_2N_4Fe_2N_4Cl_2B_3F_{12}$ $C_{50}H_{48}AuBF_4Fe_4N_4$ fw, g/mol1052.401324.991212.13temperature, K173 K173 K173 K20 range, deg.2.71 – 28.293.03 – 26.392.73 – 28.40crystal systemmonoclinicmonoclinicmonoclinicspace group $P_{21/C}$ $P_{21/C}$ $C2/c$ $a, Å$ 11.798(2)14.447(2)18.112(5) $b, Å$ 23.649(4)24.404(4)12.733(4) $c, Å$ 15.577(3)14.886(2)19.212(5) $a, deg.$ 909090 $\beta, deg.$ 94.649(4)99.088(4)104.134(7) $\gamma, deg.$ 909090 $\gamma, deg.$ 909090 $\chi$ deg.909090 <td>structure code</td> <td>19SW013LT_0m</td> <td>19SW017LT_0m</td> <td>19SW014LT_0m</td>	structure code	19SW013LT_0m	19SW017LT_0m	19SW014LT_0m
formula $C_{46}H_{48}AuFe_2N_4BF_4$ $C_{48}H_{52}AuFe_2N_4Cl_2B_3F_{12}$ $C_{50}H_{48}AuBF_4Fe_4N_4$ fw, g/mol1052.401324.991212.13temperature, K173 K173 K173 Kwavelength0.710730.710730.7107320 range, deg.2.71 - 28.29 $3.03 - 26.39$ $2.73 - 28.40$ crystal systemmonoclinicmonoclinicmonoclinicspace group $P_{21/c}$ $P_{21/c}$ $C2/c$ $a, Å$ 11.798(2)14.447(2)18.112(5) $b, Å$ 23.649(4)24.404(4)12.733(4) $c, Å$ 15.577(3)14.886(2)19.212(5) $a, deg.$ 909090 $\beta, deg.$ 94.649(4)99.088(4)104.134(7) $\gamma, deg.$ 909090Volume, Å <sup>3</sup> 4333.7(14)5182.4(14)4296(2) $Z$ 444density, g/cm <sup>3</sup> 1.61291.69801.8739 $\mu, mm^{-1}$ 4.0923.5614.781crystal size0.15 x 0.25 x 0.40.05 x 0.25 x 0.260.25 x 0.25 x 0.35color, habitatyellow, needleblue, plategolden, blocklimiting indices, $h$ -15 $\leq h \leq 15$ -18 $\leq h \leq 17$ -24 $\leq h \leq 24$ limiting indices, $h$ -15 $\leq h \leq 15$ -18 $\leq h \leq 17$ -24 $\leq h \leq 24$ limiting indices, $l$ -20 $\leq l \leq 20$ -18 $\leq l \leq 18$ -25 $\leq l \leq 25$ ref. collected542416653642199independent data10721105825372 <td>solvent</td> <td>none</td> <td>ClCH<sub>2</sub>CH<sub>2</sub>Cl</td> <td>none</td>	solvent	none	ClCH <sub>2</sub> CH <sub>2</sub> Cl	none
fw, g/mol1052.401324.991212.13temperature, K173 K173 K173 Kwavelength0.710730.710730.7107320 range, deg.2.71 – 28.293.03 – 26.392.73 – 28.40crystal systemmonoclinicmonoclinicmonoclinicspace group $P_{21/c}$ $P_{21/c}$ $C2/c$ a, Å11.798(2)14.447(2)18.112(5)b, Å23.649(4)24.404(4)12.733(4)c, Å15.577(3)14.886(2)19.212(5)a, deg.909090 $\beta$ , deg.94.649(4)99.088(4)104.134(7) $\gamma$ , deg.909090Volume, ų4333.7(14)5182.4(14)4296(2)Z444density, g/cm³1.61291.69801.8739 $\mu$ , mm¹4.0923.5614.781crystal size0.15 x 0.25 x 0.40.05 x 0.25 x 0.260.25 x 0.25 x 0.35color, habitatyellow, needleblue, plategolden, blocklimiting indices, h-15 $\leq h \leq 15$ -18 $\leq h \leq 17$ -24 $\leq h \leq 24$ limiting indices, l-20 $\leq 1 \leq 20$ -18 $\leq 1 \leq 18$ -25 $\leq 1 \leq 25$ ref. collected542416653642199independent data10721105825372restraints000parameters refined529655294 $R_{int}$ 0.03920.06590.0520GooF <sup>al</sup> 1.05611.04371.0493<	formula	C46H48AuFe2N4BF4	$C_{48}H_{52}AuFe_2N_4Cl_2B_3F_{12}$	C50H48AuBF4Fe4N4
temperature, K173 K173 K173 Kwavelength0.710730.710730.7107320 range, deg.2.71 – 28.293.03 – 26.392.73 – 28.40crystal systemmonoclinicmonoclinicmonoclinicspace group $P_{21/c}$ $P_{21/c}$ $C2/c$ $a, Å$ 11.798(2)14.447(2)18.112(5) $b, Å$ 23.649(4)24.404(4)12.733(4) $c, Å$ 15.577(3)14.886(2)19.212(5) $a, deg.$ 909090 $\beta$ deg.909090 $\beta$ deg.909090Volume, Å <sup>3</sup> 4333.7(14)5182.4(14)4296(2) $Z$ 444density, g/cm <sup>3</sup> 1.61291.69801.8739 $\mu, mm^{-1}$ 4.0923.5614.781crystal size0.15 x 0.25 x 0.40.05 x 0.25 x 0.260.25 x 0.25 x 0.35color, habitatyellow, needleblue, plategolden, blocklimiting indices, $h$ $-15 \le h \le 15$ $-18 \le h \le 17$ 1limiting indices, $i$ $-20 \le l \le 20$ $-18 \le l \le 18$ $-25 \le l \le 25$ ref. collected542416653642199independent data10721105825372restraints000parameters refined529655294 $R_{int}$ 0.03920.06590.05200GooF <sup>a</sup> 1.05611.04371.0493R1, $h^c$ wR2 $^{d_c}$ 0.0571, 0.08790.0354, 0.08560.0214	fw, g/mol	1052.40	1324.99	1212.13
wavelength $0.71073$ $0.71073$ $0.71073$ $20$ range, deg. $2.71 - 28.29$ $3.03 - 26.39$ $2.73 - 28.40$ crystal systemmonoclinicmonoclinicmonoclinicspace group $P_{21/c}$ $P_{21/c}$ $C2/c$ $a, Å$ $11.798(2)$ $14.447(2)$ $18.112(5)$ $b, Å$ $23.649(4)$ $24.404(4)$ $12.733(4)$ $c, Å$ $15.577(3)$ $14.886(2)$ $19.212(5)$ $a, deg.$ $90$ $90$ $90$ $\beta, deg.$ $94.649(4)$ $99.088(4)$ $104.134(7)$ $\gamma, deg.$ $90$ $90$ $90$ Volume, Å^3 $4333.7(14)$ $5182.4(14)$ $4296(2)$ $Z$ $4$ $4$ $4$ density, g/cm <sup>3</sup> $1.6129$ $1.6980$ $1.8739$ $\mu, mm^{-1}$ $4.092$ $3.561$ $4.781$ crystal size $0.15 \times 0.25 \times 0.4$ $0.05 \times 0.25 \times 0.26$ $0.25 \times 0.25 \times 0.35$ color, habitatyellow, needleblue, plategolden, blocklimiting indices, $h$ $-15 \le h \le 15$ $-18 \le h \le 17$ $-16 \le k \le 17$ limiting indices, $l$ $-20 \le 1 \le 20$ $-18 \le 1 \le 16$ $-25 \le 1 \le 25$ ref. collected $54241$ $66536$ $42199$ independent data $10721$ $10582$ $5372$ restraints $0$ $0$ $0$ $0$ $0$ $0.0520$ $GooF^a$ $1.0561$ $1.0437$ $1.0493$ $R_{1,h^c}$ wR2 <sup>d,c</sup> $0.0374, 0.0879$ $0.0394, 0.0856$ $0.0214, 0.0578$ <t< td=""><td>temperature, K</td><td>173 K</td><td>173 K</td><td>173 K</td></t<>	temperature, K	173 K	173 K	173 K
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	wavelength	0.71073	0.71073	0.71073
crystal systemmonoclinicmonoclinicmonoclinicspace group $P_{21/c}$ $P_{21/c}$ $C_{2/c}$ $a, \tilde{A}$ 11.798(2)14.447(2)18.112(5) $b, \tilde{A}$ 23.649(4)24.404(4)12.733(4) $c, \tilde{A}$ 15.577(3)14.886(2)19.212(5) $a, deg.$ 909090 $\beta, deg.$ 94.649(4)99.088(4)104.134(7) $\gamma, deg.$ 909090Volume, Å <sup>3</sup> 4333.7(14)5182.4(14)4296(2) $Z$ 444density, g/cm <sup>3</sup> 1.61291.69801.8739 $\mu, mm^{-1}$ 4.0923.5614.781crystal size0.15 x 0.25 x 0.40.05 x 0.25 x 0.260.25 x 0.25 x 0.35color, habitatyellow, needleblue, plategolden, blocklimiting indices, $h$ $-15 \le h \le 15$ $-18 \le h \le 17$ $-24 \le h \le 24$ limiting indices, $k$ $-31 \le k \le 31$ $-30 \le k \le 30$ $-16 \le k \le 17$ limiting indices, $l$ $-20 \le 1 \le 20$ $-18 \le 1 \le 18$ $-25 \le 1 \le 25$ ref. collected542416653642199independent data10721105825372restraints000parameters refined529655294 $R_{int}$ 0.03920.06590.0520GooF <sup>a</sup> 1.05611.04371.0493R1, <sup>b.c</sup> wR2 <sup>d.c</sup> 0.0374, 0.08790.0394, 0.08560.0214, 0.0578R1, <sup>b.c</sup> wR2 <sup>d.c</sup> 0.0571, 0.09950.0550, 0.0955 </td <td>2θ range, deg.</td> <td>2.71 - 28.29</td> <td>3.03 - 26.39</td> <td>2.73 - 28.40</td>	2θ range, deg.	2.71 - 28.29	3.03 - 26.39	2.73 - 28.40
space group $P_{21/c}$ $P_{21/c}$ $C_{2/c}$ $a, Å$ 11.798(2)14.447(2)18.112(5) $b, Å$ 23.649(4)24.404(4)12.733(4) $c, Å$ 15.577(3)14.886(2)19.212(5) $a, deg.$ 909090 $\beta, deg.$ 94.649(4)99.088(4)104.134(7) $\gamma, deg.$ 909090Volume, Å <sup>3</sup> 4333.7(14)5182.4(14)4296(2) $Z$ 444density, g/cm <sup>3</sup> 1.61291.69801.8739 $\mu, mm^{-1}$ 4.0923.5614.781crystal size0.15 x 0.25 x 0.40.05 x 0.25 x 0.260.25 x 0.25 x 0.35color, habitatyellow, needleblue, plategolden, blocklimiting indices, $h$ $-15 \le h \le 15$ $-18 \le h \le 17$ $-24 \le h \le 24$ limiting indices, $k$ $-31 \le k \le 31$ $-30 \le k \le 30$ $-16 \le k \le 17$ limiting indices, $l$ $-20 \le 1 \le 20$ $-18 \le 1 \le 18$ $-25 \le 1 \le 25$ restraints0000parameters refined529655294 $R_{int}$ 0.03920.06590.0520GooF <sup>a</sup> 1.05611.04371.0493 $R1, ^{b.c}$ wR2 <sup>d.c</sup> 0.0374, 0.08790.0394, 0.08560.0214, 0.0578 $R1, ^{b.c}$ wR2 <sup>d.c</sup> 0.0571, 0.09950.0550, 0.09550.0270, 0.0600	crystal system	monoclinic	monoclinic	monoclinic
a, Å11.798(2)14.447(2)18.112(5)b, Å23.649(4)24.404(4)12.733(4)c, Å15.577(3)14.886(2)19.212(5)a, deg.909090 $\beta$ , deg.94.649(4)99.088(4)104.134(7)y, deg.909090Volume, ų4333.7(14)5182.4(14)4296(2)Z444density, g/cm³1.61291.69801.8739µ, mm⁻¹4.0923.5614.781crystal size0.15 x 0.25 x 0.40.05 x 0.25 x 0.260.25 x 0.25 x 0.35color, habitatyellow, needleblue, plategolden, blocklimiting indices, h-15 ≤ h ≤ 15-18 ≤ h ≤ 17-24 ≤ h ≤ 24limiting indices, k-31 ≤ k ≤ 31-30 ≤ k ≤ 30-16 ≤ k ≤ 17limiting indices, l-20 ≤ 1 ≤ 20-18 ≤ 1 ≤ 18-25 ≤ 1 ≤ 25ref. collected542416653642199independent data10721105825372restraints000parameters refined529655294Kint0.03920.06590.0520GooF <sup>a</sup> 1.05611.04371.0493R1, <sup>b.e</sup> wR2 <sup>d.e</sup> 0.0571, 0.09950.0394, 0.08560.0214, 0.0578	space group	$P2_{1}/c$	$P2_{1}/c$	C2/c
b, Å23.649(4)24.404(4)12.733(4)c, Å15.577(3)14.886(2)19.212(5)a, deg.909090 $\beta$ , deg.94.649(4)99.088(4)104.134(7)y, deg.909090Volume, Å <sup>3</sup> 4333.7(14)5182.4(14)4296(2)Z444density, g/cm <sup>3</sup> 1.61291.69801.8739µ, mm <sup>-1</sup> 4.0923.5614.781crystal size0.15 x 0.25 x 0.40.05 x 0.25 x 0.260.25 x 0.25 x 0.35color, habitatyellow, needleblue, plategolden, blocklimiting indices, h $-15 \le h \le 15$ $-18 \le h \le 17$ $-24 \le h \le 24$ limiting indices, l $-20 \le 1 \le 20$ $-18 \le 1 \le 18$ $-25 \le 1 \le 25$ ref. collected542416653642199independent data10721105825372restraints000parameters refined529655294Rint0.03920.06590.0520GooF <sup>a</sup> 1.05611.04371.0493R1, <sup>b,e</sup> wR2 <sup>d,e</sup> 0.0571, 0.09950.0550, 0.09550.0270, 0.0600	a, Å	11.798(2)	14.447(2)	18.112(5)
c, Å15.577(3)14.886(2)19.212(5)a, deg.909090 $\beta$ , deg.94.649(4)99.088(4)104.134(7) $\gamma$ , deg.909090Volume, ų4333.7(14)5182.4(14)4296(2)Z444density, g/cm³1.61291.69801.8739 $\mu$ , mm <sup>-1</sup> 4.0923.5614.781crystal size0.15 x 0.25 x 0.40.05 x 0.25 x 0.260.25 x 0.25 x 0.35color, habitatyellow, needleblue, plategolden, blocklimiting indices, h $-15 \le h \le 15$ $-18 \le h \le 17$ $-24 \le h \le 24$ limiting indices, k $-31 \le k \le 31$ $-30 \le k \le 30$ $-16 \le k \le 17$ limiting indices, l $-20 \le 1 \le 20$ $-18 \le 1 \le 18$ $-25 \le 1 \le 25$ ref. collected542416653642199independent data10721105825372restraints000parameters refined529655294Rint0.03920.06590.0520GooF <sup>a</sup> 1.05611.04371.0493R1, <sup>b,c</sup> wR2 <sup>d,c</sup> 0.0374, 0.08790.0394, 0.08560.0214, 0.0578R1, <sup>b,c</sup> wR2 <sup>d,e</sup> 0.0571, 0.09950.0550, 0.09550.0270, 0.0600	b, Å	23.649(4)	24.404(4)	12.733(4)
a, deg.909090 $\beta$ , deg.94.649(4)99.088(4)104.134(7) $\gamma$ , deg.909090Volume, Å <sup>3</sup> 4333.7(14)5182.4(14)4296(2)Z444density, g/cm <sup>3</sup> 1.61291.69801.8739 $\mu$ , mm <sup>-1</sup> 4.0923.5614.781crystal size0.15 x 0.25 x 0.40.05 x 0.25 x 0.260.25 x 0.25 x 0.35color, habitatyellow, needleblue, plategolden, blocklimiting indices, h $-15 \le h \le 15$ $-18 \le h \le 17$ $-24 \le h \le 24$ limiting indices, k $-31 \le k \le 31$ $-30 \le k \le 30$ $-16 \le k \le 17$ limiting indices, l $-20 \le 1 \le 20$ $-18 \le 1 \le 18$ $-25 \le 1 \le 25$ ref. collected542416653642199independent data10721105825372restraints000parameters refined529655294Rint0.03920.06590.0520GooF <sup>a</sup> 1.05611.04371.0493R1, <sup>h,e</sup> wR2 <sup>d,e</sup> 0.0571, 0.08790.0394, 0.08560.0214, 0.0578R1, <sup>h,e</sup> wR2 <sup>d,e</sup> 0.0571, 0.09950.0550, 0.09550.0270, 0.0600	<i>c</i> , Å	15.577(3)	14.886(2)	19.212(5)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	$\alpha$ , deg.	90	90	90
y, deg.909090Volume, $Å^3$ 4333.7(14)5182.4(14)4296(2)Z444density, g/cm³1.61291.69801.8739µ, mm¹4.0923.5614.781crystal size0.15 x 0.25 x 0.40.05 x 0.25 x 0.260.25 x 0.25 x 0.35color, habitatyellow, needleblue, plategolden, blocklimiting indices, h $-15 \le h \le 15$ $-18 \le h \le 17$ $-24 \le h \le 24$ limiting indices, k $-31 \le k \le 31$ $-30 \le k \le 30$ $-16 \le k \le 17$ limiting indices, l $-20 \le 1 \le 20$ $-18 \le 1 \le 18$ $-25 \le 1 \le 25$ ref. collected542416653642199independent data10721105825372restraints000parameters refined529655294R <sub>int</sub> 0.03920.06590.0520GooF <sup>a</sup> 1.05611.04371.0493R1, <sup>h,e</sup> wR2 <sup>d,e</sup> 0.0571, 0.09950.0550, 0.09550.0270, 0.0600	$\beta$ , deg.	94.649(4)	99.088(4)	104.134(7)
Volume, $Å^3$ 4333.7(14)5182.4(14)4296(2)Z444density, g/cm³1.61291.69801.8739 $\mu$ , mm¹4.0923.5614.781crystal size0.15 x 0.25 x 0.40.05 x 0.25 x 0.260.25 x 0.25 x 0.35color, habitatyellow, needleblue, plategolden, blocklimiting indices, $h$ $-15 \le h \le 15$ $-18 \le h \le 17$ $-24 \le h \le 24$ limiting indices, $k$ $-31 \le k \le 31$ $-30 \le k \le 30$ $-16 \le k \le 17$ limiting indices, $l$ $-20 \le 1 \le 20$ $-18 \le 1 \le 18$ $-25 \le 1 \le 25$ ref. collected542416653642199independent data10721105825372restraints000parameters refined529655294 $R_{int}$ 0.03920.06590.0520GooFa1.05611.04371.0493R1, <sup>b,c</sup> wR2 <sup>d,c</sup> 0.0374, 0.08790.0394, 0.08560.0214, 0.0578R1, <sup>b,e</sup> wR2 <sup>d,e</sup> 0.0571, 0.09950.0550, 0.09550.0270, 0.0600	γ, deg.	90	90	90
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Volume, Å <sup>3</sup>	4333.7(14)	5182.4(14)	4296(2)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Ζ	4	4	4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	density, g/cm <sup>3</sup>	1.6129	1.6980	1.8739
crystal size $0.15 \ge 0.25 \ge 0.4$ $0.05 \ge 0.25 \ge 0.26$ $0.25 \ge 0.25 \ge 0.35$ color, habitatyellow, needleblue, plategolden, blocklimiting indices, h $-15 \le h \le 15$ $-18 \le h \le 17$ $-24 \le h \le 24$ limiting indices, k $-31 \le k \le 31$ $-30 \le k \le 30$ $-16 \le k \le 17$ limiting indices, l $-20 \le 1 \le 20$ $-18 \le 1 \le 18$ $-25 \le 1 \le 25$ ref. collected $54241$ $66536$ $42199$ independent data $10721$ $10582$ $5372$ restraints000parameters refined $529$ $655$ $294$ Rint $0.0392$ $0.0659$ $0.0520$ GooF <sup>a</sup> $1.0561$ $1.0437$ $1.0493$ R1, <sup>b,c</sup> wR2 <sup>d,c</sup> $0.0374, 0.0879$ $0.0394, 0.0856$ $0.0214, 0.0578$ R1, <sup>b,e</sup> wR2 <sup>d,e</sup> $0.0571, 0.0995$ $0.0550, 0.0955$ $0.0270, 0.0600$	μ, mm <sup>-1</sup>	4.092	3.561	4.781
color, habitatyellow, needleblue, plategolden, blocklimiting indices, h $-15 \le h \le 15$ $-18 \le h \le 17$ $-24 \le h \le 24$ limiting indices, k $-31 \le k \le 31$ $-30 \le k \le 30$ $-16 \le k \le 17$ limiting indices, l $-20 \le 1 \le 20$ $-18 \le 1 \le 18$ $-25 \le 1 \le 25$ ref. collected $54241$ $66536$ $42199$ independent data $10721$ $10582$ $5372$ restraints000parameters refined $529$ $655$ $294$ Rint $0.0392$ $0.0659$ $0.0520$ GooF <sup>a</sup> $1.0561$ $1.0437$ $1.0493$ R1, <sup>b,c</sup> wR2 <sup>d,c</sup> $0.0374, 0.0879$ $0.0394, 0.0856$ $0.0214, 0.0578$ R1, <sup>b,e</sup> wR2 <sup>d,e</sup> $0.0571, 0.0995$ $0.0550, 0.0955$ $0.0270, 0.0600$	crystal size	0.15 x 0.25 x 0.4	0.05 x 0.25 x 0.26	0.25 x 0.25 x 0.35
limiting indices, $h$ $-15 \le h \le 15$ $-18 \le h \le 17$ $-24 \le h \le 24$ limiting indices, $k$ $-31 \le k \le 31$ $-30 \le k \le 30$ $-16 \le k \le 17$ limiting indices, $l$ $-20 \le 1 \le 20$ $-18 \le 1 \le 18$ $-25 \le 1 \le 25$ ref. collected $54241$ $66536$ $42199$ independent data $10721$ $10582$ $5372$ restraints000parameters refined $529$ $655$ $294$ Rint $0.0392$ $0.0659$ $0.0520$ GooF <sup>a</sup> $1.0561$ $1.0437$ $1.0493$ R1, $bc$ wR2 <sup>d,c</sup> $0.0374, 0.0879$ $0.0394, 0.0856$ $0.0214, 0.0578$ R1, $bc$ wR2 <sup>d,e</sup> $0.0571, 0.0995$ $0.0550, 0.0955$ $0.0270, 0.0600$	color, habitat	yellow, needle	blue, plate	golden, block
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	limiting indices, h	$-15 \le h \le 15$	$-18 \le h \le 17$	$-24 \le h \le 24$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	limiting indices, k	$-31 \le k \le 31$	$-30 \le k \le 30$	$-16 \le k \le 17$
ref. collected $54241$ $66536$ $42199$ independent data $10721$ $10582$ $5372$ restraints000parameters refined $529$ $655$ $294$ $R_{int}$ $0.0392$ $0.0659$ $0.0520$ $GooF^a$ $1.0561$ $1.0437$ $1.0493$ $R1, ^{b,c} wR2^{d,c}$ $0.0374, 0.0879$ $0.0394, 0.0856$ $0.0214, 0.0578$ $R1, ^{b,e} wR2^{d,e}$ $0.0571, 0.0995$ $0.0550, 0.0955$ $0.0270, 0.0600$	limiting indices, l	$-20 \le 1 \le 20$	$-18 \le l \le 18$	$-25 \le 1 \le 25$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	ref. collected	54241	66536	42199
restraints000parameters refined529655294 $R_{int}$ 0.03920.06590.0520GooF <sup>a</sup> 1.05611.04371.0493 $R1,^{b,c}$ wR2 <sup>d,c</sup> 0.0374, 0.08790.0394, 0.08560.0214, 0.0578 $R1,^{b,e}$ wR2 <sup>d,e</sup> 0.0571, 0.09950.0550, 0.09550.0270, 0.0600	independent data	10721	10582	5372
parameters refined529655294 $R_{int}$ 0.03920.06590.0520 $GooF^a$ 1.05611.04371.0493 $R1,^{b,c}$ wR2 <sup>d,c</sup> 0.0374, 0.08790.0394, 0.08560.0214, 0.0578 $R1,^{b,e}$ wR2 <sup>d,e</sup> 0.0571, 0.09950.0550, 0.09550.0270, 0.0600	restraints	0	0	0
$R_{int}$ 0.03920.06590.0520GooFa1.05611.04371.0493 $R1,^{b,c}$ wR2 <sup>d,c</sup> 0.0374, 0.08790.0394, 0.08560.0214, 0.0578 $R1,^{b,e}$ wR2 <sup>d,e</sup> 0.0571, 0.09950.0550, 0.09550.0270, 0.0600	parameters refined	529	655	294
$GooF^a$ 1.05611.04371.0493 $R1,^{b,c} wR2^{d,c}$ 0.0374, 0.08790.0394, 0.08560.0214, 0.0578 $R1,^{b,e} wR2^{d,e}$ 0.0571, 0.09950.0550, 0.09550.0270, 0.0600	Rint	0.0392	0.0659	0.0520
R1, $^{b,c}$ wR2 $^{d,c}$ 0.0374, 0.08790.0394, 0.08560.0214, 0.0578R1, $^{b,e}$ wR2 $^{d,e}$ 0.0571, 0.09950.0550, 0.09550.0270, 0.0600	GooF <sup>a</sup>	1.0561	1.0437	1.0493
R1, $^{b,e}$ wR2 $^{d,e}$ 0.0571, 0.0995 0.0550, 0.0955 0.0270, 0.0600	$R1$ , <sup><i>b,c</i></sup> w $R2^{d,c}$	0.0374, 0.0879	0.0394, 0.0856	0.0214, 0.0578
	$R1,^{b,e} wR2^{d,e}$	0.0571, 0.0995	0.0550, 0.0955	0.0270, 0.0600

Table 1. Crystallographic data for complexes  $[2][BF_4]$ ,  $[3][BF_4]_3$ ,  $[5][BF_4]$ , and  $[6][BF_4]_3$ 

 ${}^{a}\text{GooF} = \{\Sigma[W(F_{o}^{2} - F_{c}^{2})^{2}]/(n - p)\}^{1/2}, \text{ where } n = \text{number of reflections and } p \text{ is the total number of parameters refined; } {}^{b}\text{R1} = {}^{a}\text{R1} = \Sigma||F_{o}| - |F_{c}||/\Sigma|F_{o}|; {}^{c}\text{R} \text{ indices for data cut off at } I > 2\sigma(I); {}^{d}\text{wR2} = \{[\Sigmaw(Fo 2 - Fc 2) 2 / \Sigmaw(Fo 2) 2 \} 1/2; w = 1/[\sigma2 (Fo 2) + (xP) 2 + yP], \text{ where } P = (Fo 2 + 2Fc 2)/3; {}^{c}\text{R} \text{ indices for all data. } {}^{a}\text{R1} = \Sigma||F_{o}| - |F_{c}||/\Sigma|F_{o}|. {}^{b}\text{R}_{w} = \{[\Sigmaw(F_{o}^{2} - F_{c}^{2})/\Sigmaw(F_{o}^{2})^{2}\}^{1/2}; w = 1/[\sigma^{2}(F_{o}^{2}) + (xP)^{2}], \text{ where } P = (F_{o}^{2} + 2F_{c}^{2})/3.$ 



Figure S2. <sup>13</sup>C NMR spectrum of compound 1 in CDCl<sub>3</sub>.





Figure S6. <sup>13</sup>C NMR spectrum of compound 4 in CDCl<sub>3</sub>.



Figure S8. <sup>13</sup>C NMR spectrum of compound 5 in DMSO.



Figure S9. Cyclic Voltammogram of 2 with  $0.1M [N(nBu)_4]PF_6$  in DCM (1mM) as referenced to decamethylferrocene (internal standard, adjusted to SCE).



**Figure S10**. Cyclic Voltammogram of **5** with  $0.1M [N(nBu)_4]PF_6$  in DCM (1mM) as referenced to decamethylferrocene (internal standard, adjusted to SCE).



Figure S11. Electronic absorption spectra of compounds  $[2][BF_4]$  and  $[3][BF_4]_3$  recorded in Acetonitrile solvent.



**Figure S12**. Electronic absorption spectra of compounds [5][BF<sub>4</sub>] and [6][BF<sub>4</sub>]<sub>5</sub> recorded in Acetonitrile solvent.