Thermochromic and Aggregation Properties of Di(phenylisocyano) Rhodium(I) Diimine Complexes

Larry Tso-Lun Lo, Chi-On Ng, Hua Feng and Chi-Chiu KO*

Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, PR China.

Tel: 852-3442 6958; Fax: 852-2788 7406;
E-mail: vinccko@cityu.edu.hk

Supporting Information

The free isocyanide ligands, *4*-Cl-C_6H_4NC, *2,4,6*-Br_3-C_6H_2NC, and 2,6-$(CH_3)_2C_6H_3NC$, were prepared by the according to standard literature procedure.[1] The rhodium(I) 1,5-cyclooctadieyl diimine complexes, [Rh(bpy)(cod)]BF_4, [Rh(4,4'-$(CH_3)_2$-bpy)(cod)]BF_4 and [Rh(5,6-Br_2-phen)(cod)]BF_4, were synthesized according to literature procedure for related complex except substituted diimine ligands were used in place of the bipyridine.[2]

*General Synthetic procedure for rhodium (I) bis(phenylisocyano) diimine complexes, [Rh(N-N)(CNR)$_2$]BF$_4$ (**1** – **5**)*:

To an orange suspension of [Rh(N–N)(cod)]BF_4 (0.5 mmol) in THF (10 ml) was added in a dropwise manner, substituted phenylisocyanide (1.0 mmol) in THF (10 ml). The resulting solution was stirred at room temperature for 2 hours. After removal of the solvent by rotary evaporation, the residue was washed completely thoroughfully by copious amounts of diethyl ether to remove excess isocyanide and 1,5-cyclooctadiene ligands. Crystalline solids (red and green forms) were obtained by the slow diffusion of diethyl ether vapor into a concentrated acetone or acetonitrile solution of the complexes. The solutions of these two different colored solids or crystals gave identical ^{1}H NMR and UV-vis absorption spectra.

1: Yield: 56%. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ2.49 (s, 12H, phenyl Me), 2.65 (s, 6H, bipyridyl Me), 7.15 - 7.24 (m, 6H, phenyl H's), 7.31 (dd, 2H, J = 1.1, 5.6 Hz, 5,5'- bipyridyl H's), 8.57 (s, br, 2H, 3,3'-bipyridyl H's), 8.60 (d, 2H, J = 5.6 Hz, 6,6'- bipyridyl H's). ESI-MS: *m/z* 549 $\{M\}^+$. IR (KBr disc, ν/cm^{-1}) 1080 ν(B–F), 2082, 2136 ν(N≡C). Elemental analyses, Calcd for **1**(found) %: C 56.63 (56.67), H 4.75 (4.68), N 8.81 (9.09).

2: Yield: 54%. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ2.51 (s, 12H, Me), 7.17 - 7.28 (m, 6H, phenyl H's), 7.59 (ddd, 2H, J = 1.2, 5.5, 8.0 Hz, 4,4'- bipyridyl H's), 8.31 (td, 2H, J = 1.8, 5.5 Hz, 5,5'- bipyridyl H's), 8.69 (d, 2H, J = 8.0 Hz, 3,3'-bipyridyl H's), 8.82 (d, 2H, J = 5.5 Hz, 6,6'-bipyridyl H's). ESI-MS: *m/z* 521 $\{M\}^+$. IR (KBr disc, ν/cm^{-1}) 1080 ν(B–F), 2086, 2140 ν(N≡C). Elemental analyses, Calcd for **2** (found) %: C 55.30 (55.67), H 4.31 (4.16), N 9.21 (9.44).

3: Yield: 48%. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ2.54 (s, 12H, Me), 7.16 - 7.28 (m, 6H, phenyl H's), 8.24 (dd, 2H, J = 5.1, 8.6 Hz, 3,8-phenanthrolinyl H's), 9.06 (d, 2H, J = 8.6 Hz, 4,7-phenanthrolinyl H's), 9.27 (d, 2H, J = 5.1 Hz, 2,9-phenanthrolinyl H's). ESI-MS: *m/z* 703 $\{M\}^+$. IR (KBr disc, ν/cm^{-1}) 1080 ν(B–F), 2093, 2140 ν(N≡C). Elemental analyses, Calcd for **3**·½ MeCN (found) %: C 45.93 (45.79), H 3.17 (2.99), N 7.78 (7.52).

4: Yield: 52%. ^{1}H NMR (400 MHz, d^6-DMSO, 298K): δ7.61 – 7.77 (m, 10H, phenyl H's and 4,4'-bipyridyl H's), 8.32 (td, 2H, J = 1.6, 5.8 Hz, 5,5'-bipyridyl

H's), 8.60 (d, 2H, J = 8.0 Hz, 3,3'- bipyridyl H's), 8.95 (d, 2H, J = 5.8 Hz, 6,6'-bipyridyl H's). ESI-MS: *m/z* 533 $\{M\}^+$. IR (KBr disc, ν/cm^{-1}) 1084 ν(B–F), 2097, 2144 ν(N≡C). Elemental analyses, Calcd for 4·½ MeCN (found) %: C 46.80 (46.52), H 2.75 (2.72), N 9.82 (9.83).

5: Yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ7.62 (ddd, 2H, J = 1.2, 5.6, 7.8 Hz, 4,4'-bipyridyl H's), 7.86 (s, 4H, phenyl H's), 8.34 (td, 2H, J = 1.6, 5.6 Hz, 5,5'- bipyridyl H's), 8.72 (d, 2H, J = 7.8 Hz, 3,3'-bipyridyl H's), 8.94 (d, 2H, J = 5.6 Hz, 6,6'-bipyridyl H's). ESI-MS: *m/z* 937 $\{M\}^+$. IR (KBr disc, ν/cm^{-1}) 1080 ν(B–F), 2074, 2132 ν(N≡C). Elemental analyses, Calcd for **5**·MeCN (found) %: C 29.28 (29.03), H 1.42 (1.66), N 6.57 (6.23).

1 (a) Ugi, I.; Fetzer, U.; Eholzer, U.; Knupfer, H.; Offermann, K. *Angew. Chem., Int. Ed. Eng.* **1965**, *4*, 472. (b) Obrecht, R.; Herrmann, R.; Ugi, I. *Synthesis* **1985**, *4*, 400. (c) Janza, B; Studer, A. *Org. Lett.* **2006**, *8*, 1875.

2 Ribeiro, P. E. A.; Donnici, C. L.; dos Santos, E. N. *J. Organomet. Chem.* **2006**, *691*(9), 2037.

Experimental Section

Physical Measurements and Instrumentation.

^1H NMR spectra were recorded on a Bruker AV400 (400 MHz) FT-NMR spectrometer. Chemical shifts (δ, ppm) were reported relative to tetramethylsilane (Me4Si). All positive-ion ESI mass spectra were recorded on a PE-SCIEX API 300 triple quadrupole mass spectrometer. Although the two forms (red and green forms) of these complexes can be easily distinguished visually, the simultaneous crystallizations of the two forms render these forms very difficult to separate to provide an entirely pure form with sufficient amount for elemental analysis. Since these two forms are considered to be the same complexes with different molecular packing in the crystals, finely grinded complexes containing both forms were vacuum dried before used as samples for the elemental analyses. The elemental analyses were performed on an Elementar Vario EL III Analyser. Electronic absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer with the temperature control using an Oxford Instruments cryostat (Optistat DN). Steady state emission and excitation spectra at 77 K were recorded on a Horiba Jobin Yvon Fluorolog-3-TCSPC spectrofluorometer with a diluted EtOH-MeOH (4:1 v/v) sample solution loaded in a quartz tube inside a quartz-walled Dewar flask containing liquid nitrogen. Luminescence lifetimes of the samples in 77K EtOH/MeOH (4:1) glass medium were measured using time-correlated single photon counting (TCSPC) technique on the TCSPC spectrofluorometer in a Fast MCS mode with a NanoLED-375LH excitation source, which has its excitation peak wavelength at 375 nm and pulse width shorter than 750 ps. The photon counting data were analyzed by Horiba Jobin Yvon Decay Analysis Software. The luminescence lifetimes were further validated using a conventional laser system. The excitation source for the conventional laser system was the 355-nm output (third harmonic, 8 ns) of a Spectra-Physics Quanta-Ray Q-switched GCR-150 pulsed Nd-YAG laser (10 Hz). Luminescence decay traces were recorded on a Tektronix Model TDS 620A digital oscilloscope and the lifetime (τ) determination was accomplished by the biexponential decay fitting.

Experimental details for crystal structure determination of 1 (green crystal)

Crystals (green color) suitable for X-ray diffraction studies were obtained by slow diffusion of diethyl ether vapor into an acetone solution of **1**. The crystal structure was determined on an Oxford Diffraction Gemini S Ultra X-ray single crystal diffractometer.

Crystal data for **green form of 1**: [$C_{32}H_{35}BF_4N_4O_{0.5}Rh$], formula weight = 673.36, monoclinic, C2/c (No. 15), a = 19.0965 (4) Å, b = 20.8077 (4) Å, c = 15.4552 (3) Å, α = 90°, β = 96.555(2)°, γ = 90°, V = 6101.0 (2) Å^3, Z = 8, D_c = 1.466 g cm^{-3}, $\mu(Cu–K_\alpha)$ = 4.993 mm^{-1}, F(000) = 2760, T = 173(2) K. A crystal of dimensions 0.3 × 0.2 × 0.1 mm mounted in a glass capillary was used for data collection at –100 °C on an Oxford Diffraction Gemini S Ultra X-ray single crystal diffractometer using graphite monochromatized Cu–K_α radiation (λ = 1.54178 Å).

The structure was solved by direct methods employing SHELXL-97 program[3] on PC. Rh and many non-H atoms were located according to the direct methods. The positions of other non-hydrogen atoms were found after successful refinement by full-matrix least-squares using SHELXL-97 program[3] on PC. According to the SHELXL-97 program,[3] all 3581 independent reflections ($R_{\text{int}} = \Sigma|F_o^2 - F_o^2(\text{mean})| / \Sigma[F_o^2]$ = 0.0419, 2681 reflections larger than $4\sigma(F_o)$) from a total 6424 reflections were participated in the full-matrix least-squares refinement against F^2. These reflections were in the range $-19 \le h \le 20$, $-22 \le k \le 21$, $-15 \le l \le 15$ with $2\theta_{max}$ equal to 55.00°. One crystallographic asymmetric unit consists of one formula unit, including one BF_4 anion and a half diethylether. In the final stage of least-squares refinement, all non-hydrogen atoms were refined anisotropically. H atoms were generated by program SHELXL-97.[3] The positions of H atoms were calculated based on riding mode with thermal parameters equal to 1.2 times that of the associated C atoms, and participated in the calculation of final R-indices. A conventional index R_1 based on observed F values larger than $4\sigma(F_o)$ is given (corresponding to Intensity $\ge 2\sigma(I)$). $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$, $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$, The Goodness of Fit is always based on F^2: GooF = $S = \{\Sigma[w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined. The weighting scheme is: $w = 1 / [\sigma^2(F_o^2) + (\alpha P)^2 + bP]$, where P is $[2F_c^2 + \text{Max}(F_o^2,0)] / 3$. Convergence $(\Delta/\sigma)_{\text{max}}$ = 0.008 for 391 variable parameters by full-matrix least-squares refinement on F^2 reaches to R_1 = 0.0468 and wR_2 = 0.1051 with a goodness-of-fit of 0.996, the parameters a and b for weighting scheme are 0.0720 and 0.0. The final difference Fourier map shows maximum rest peaks and holes of 0.712 (near the rhodium atom) and –0.596 eÅ^{-3}, respectively.

Experimental details for crystal structure determination of 1 (red crystal)

Crystals (red crystal) suitable for X-ray diffraction studies were obtained by slow diffusion of diethyl ether vapor into an acetone solution of **1**. The crystal structure was determined on an Oxford Diffraction Gemini S Ultra X-ray single crystal diffractometer.

Crystal data for **red form of 1**: [$C_{33}H_{36}BF_4N_4ORh$], formula weight = 694.38, monoclinic, P2$_1$/c (No. 14), a = 14.7171 (5) Å, b = 13.9287 (4) Å, c = 16.6506 (5) Å, α = 90°, β = 109.209(3)°, γ = 90°, V = 3223.18 (17) Å^3, Z = 4, D_c = 1.431 g cm^{-3}, $\mu(Cu–K_\alpha)$ = 4.756 mm^{-1}, F(000) = 1424, T = 293(2) K. A crystal of dimensions 0.2 × 0.2 × 0.1 mm mounted in a glass capillary was used for data collection at 20 °C on an Oxford Diffraction Gemini S Ultra X-ray single crystal diffractometer using graphite monochromatized Cu–K$_\alpha$ radiation (λ = 1.54178 Å).

The structure was solved by direct methods employing SHELXL-97 program[3] on PC. Rh and many non-H atoms were located according to the direct methods. The positions of other non-hydrogen atoms were found after successful refinement by full-matrix least-squares using SHELXL-97 program[3] on PC. According to the SHELXL-97 program,[3] all 5498 independent reflections ($R_{\rm int} = \Sigma|F_o^2 - F_o^2({\rm mean})| / \Sigma[F_o^2]$ = 0.0193, 4669 reflections larger than $4\sigma(F_o)$) from a total 9263 reflections were participated in the full-matrix least-squares refinement against F^2. These reflections were in the range $-17 \le h \le 14$, $-16 \le k \le 16$, $-19 \le l \le 19$ with $2\theta_{max}$ equal to 67.48°. One crystallographic asymmetric unit consists of one formula unit, including one BF_4 anion and an acetone. In the final stage of least-squares refinement, all non-hydrogen atoms were refined anisotropically. H atoms were generated by program SHELXL-97.[3] The positions of H atoms were calculated based on riding mode with thermal parameters equal to 1.2 times that of the associated C atoms, and participated in the calculation of final R-indices. A conventional index R_1 based on observed F values larger than $4\sigma(F_o)$ is given (corresponding to Intensity ≥ $2\sigma(I)$). $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$, $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$, The Goodness of Fit is always based on F^2: GooF = $S = \{\Sigma[w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined. The weighting scheme is: $w = 1 / [\sigma^2(F_o^2) + (\alpha P)^2 + bP]$, where P is $[2F_c^2 + {\rm Max}(F_o^2,0)] / 3$. Convergence $(\Delta/\sigma)_{\rm max}$ = 0.003 for 405 variable parameters by full-matrix least-squares refinement on F^2 reaches to R_1 = 0.0355 and wR_2 = 0.0942 with a goodness-of-fit of 1.045, the parameters a and b for weighting scheme are 0.0614 and 1.0295. The final difference Fourier map shows maximum rest peaks and holes of 0.483 (near the rhodium atom) and –0.554 eÅ^{-3}, respectively.

3. SHELX-97, Sheldrick, G. M. (**1997**). SHELX-97: Programs for Crystal Structure Analysis (Releasse 97–2). University of Göttingen, Germany.

Equilibrium equation for dimerization

$2[Rh(CNR)_2(N\text{–}N)]^+ \leftrightarrows [Rh(CNR)_2(N\text{–}N)]_2^{2+}$ equilibrium constant K

$2M \leftrightarrows D$ where M, D are the monomer and dimer, respectively.

$$K = \frac{[\mathrm{D}]}{[\mathrm{M}]^2}$$

$$[\mathrm{M}] = \pm\sqrt{[\mathrm{D}]/K} \qquad -\sqrt{[\mathrm{D}]/K} \text{ is rejected as [M] is a non-negative value}$$

$$[\mathrm{C}] = [\mathrm{M}] + 2[\mathrm{D}]$$

$$[\mathrm{C}] = \sqrt{[\mathrm{D}]/K} + 2[\mathrm{D}]$$

$$[\mathrm{C}] = \sqrt{A/K\varepsilon_D} + \frac{2A}{\varepsilon_D}$$

$$\frac{[\mathrm{C}]}{\sqrt{A}} = \frac{1}{\sqrt{K\varepsilon_D}} + \frac{2}{\varepsilon_D}\sqrt{A}$$

Where [M] and [D] are the concentration of the monomer and dimer, [C] is the total concentration of all complexes, ε_D is the extinction coefficient of dimeric form and A is the absorbance at which only the dimer form absorb, K is the equilibrium constant of the dimerization.

From the above equation, a linear relationship between [**C**]/(A)^{½} and (A)^{½} should be established for the equilibrium of the dimerization process.

Table S1. Crystal and structure determination data for the red and green crystals of **1**.

	1 (red crystal)	**1 (green crystal)**
Formula	$C_{33}H_{36}BF_4N_4ORh$	$C_{32}H_{35}BF_4N_4O_{0.5}Rh$
M_r	694.38	673.36
T / K	293(2)	173(2)
a / Å	14.7171(5)	19.0965(4)
b / Å	13.9287(4)	20.8077(4)
c / Å	16.6506(5)	15.4552(3)
α / deg	90	90
β / deg	109.209(3)	96.555(2)
γ / deg	90	90
V / Å^3	3223.18(17)	6101.0(2)
Crystal color	Red	Dark green
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	C2/c (No. 15)
Z	4	8
F(000)	1424	2760
D_c / g cm^{-3}	1.431	1.466
Crystal dimensions / mm	0.2 × 0.2 × 0.1	0.3 × 0.2 × 0.1
λ / Å (graphite monochromated, Cu– K_α)	1.54178	1.54178
Absorption coefficient / mm^{-1}	4.756	4.993
Collection range	$5.83 \le \theta \le 67.48°$ (h: –17 to 14; k: –16 to 16; l: –19 to 19)	$3.15 \le \theta \le 55.00°$ (h: –19 to 20; k: –22 to 21; l: –15 to 15)
Completeness to theta	94.8 %	93.4 %
No. of data collected	9263	6424
No. of unique data	5498	3581
No. of data used in refinement, m	4669	2681
No. of parameters refined, p	405	391
R^a	0.0355	0.0468
wR^a	0.0942	0.1051
Goodness-of-fit, S	1.045	0.996
Maximum shift, $(\Delta/\sigma)_{max}$	0.003	0.008
Residual extrema in final difference map, eÅ^{-3}	+0.483, –0.554	+0.712, –0.596

[a] $w = 1 / [\sigma^2(F_o^2) + (ap)^2 + bP]$, where $P = [2F_c^2 + \mathrm{Max}(F_o^2,0)] / 3$

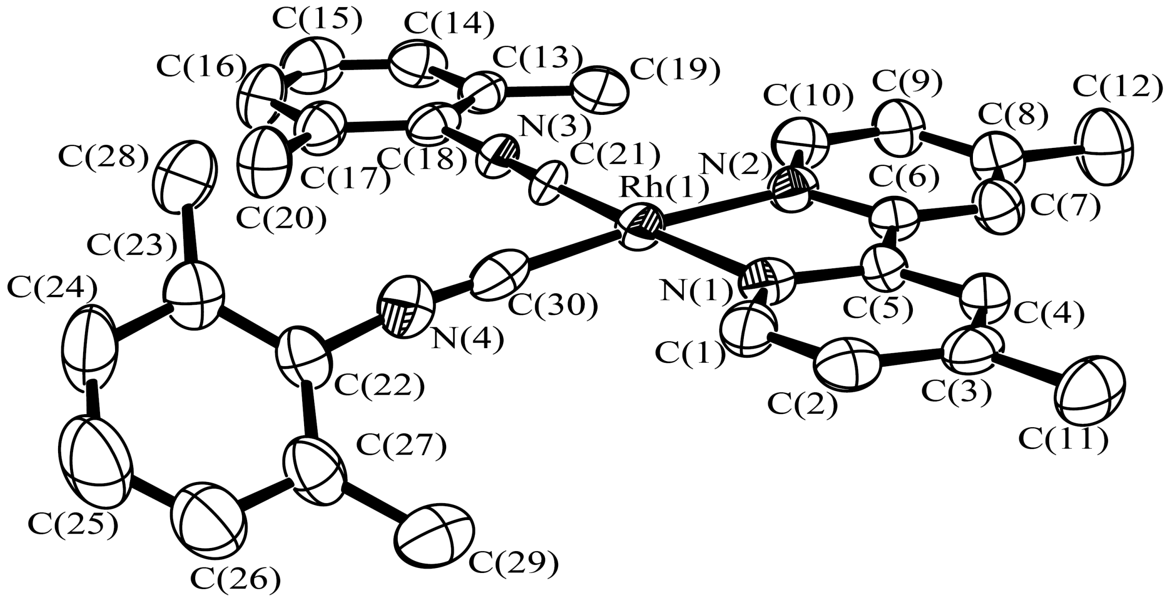


Figure S1 Ortep drawing of complex cation of **1** in green crystal with the atomic numbering scheme. Thermal ellipsoids are shown at the 50 % probability level.

Table S2 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s.) in parentheses for **1** in green crystal.

Bond distances			
Rh(1)–C(30)	1.901(3)	Rh(1)–N(1)	2.0814(18)
Rh(1)–C(21)	1.899(2)	Rh(1)–N(2)	2.0641(18)
C(21)–N(3)	1.164(3)	C(30)–N(4)	1.181(3)
C(18)–N(3)	1.402(3)	C(22)–N(4)	1.371(3)

Bond angles			
N(1)–Rh(1)–N(2)	78.12(7)	C(21)–Rh(1)–C(30)	88.72(10)
C(21)–Rh(1)–N(2)	94.47(9)	C(30)–Rh(1)–N(1)	98.45(9)
Rh(1)–C(21)–N(3)	178.4(2)	Rh(1)–C(30)–N(4)	178.0(2)
C(21)–N(3)–C(18)	175.8(2)	C(30)–N(4)–C(22)	171.9(2)

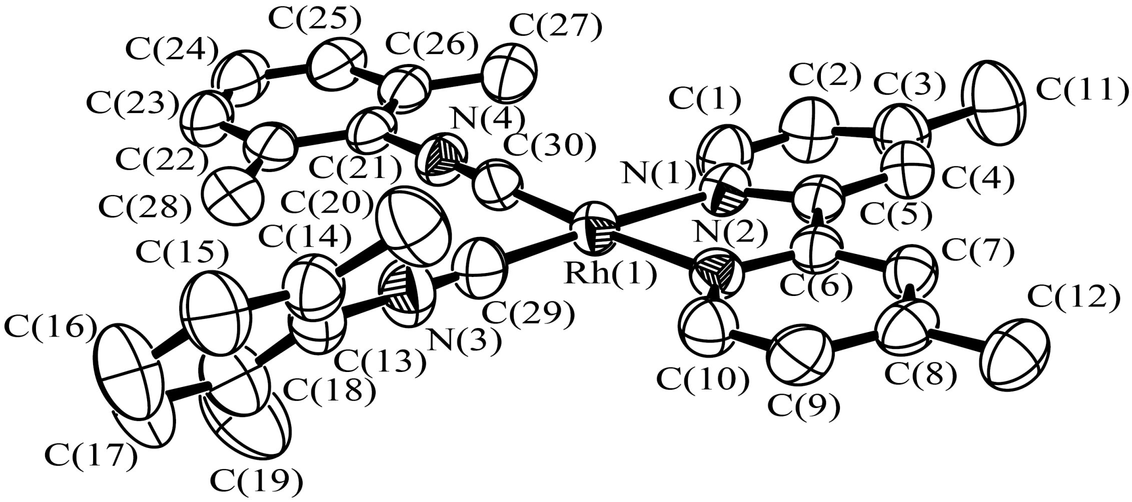


Figure S2 Ortep drawing of complex cation of **1** in red crystal with the atomic numbering scheme. Thermal ellipsoids are shown at the 50 % probability level.

Table S3 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s.) in parentheses for **1** in red crystal.

Bond distances			
Rh(1)–C(29)	1.888(4)	Rh(1)–N(1)	2.077(3)
Rh(1)–C(30)	1.899(3)	Rh(1)–N(2)	2.071(2)
C(29)–N(3)	1.164(4)	C(30)–N(4)	1.165(4)
C(13)–N(3)	1.406(4)	C(21)–N(4)	1.400(4)

Bond angles			
N(1)–Rh(1)–N(2)	78.21(9)	C(29)–Rh(1)–C(30)	88.47(13)
C(29)–Rh(1)–N(2)	96.32(12)	C(30)–Rh(1)–N(1)	97.00(11)
Rh(1)–C(29)–N(3)	178.5(3)	Rh(1)–C(30)–N(4)	179.1(3)
C(29)–N(3)–C(13)	178.0(4)	C(30)–N(4)–C(21)	176.5(3)

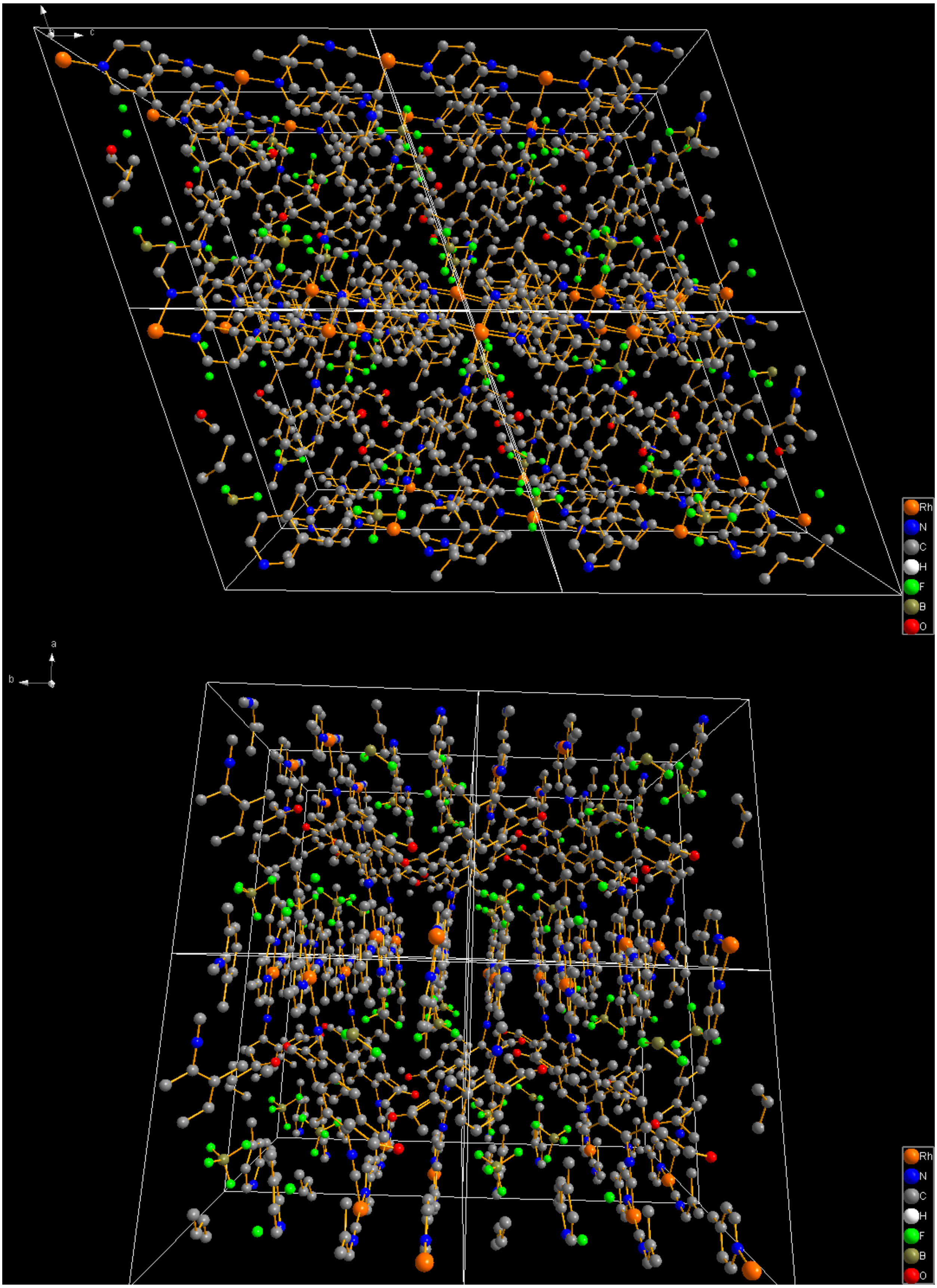


Figure S3 Perspective drawings of crystal structure of the red form of **1** in 2 × 2 × 2 supercell

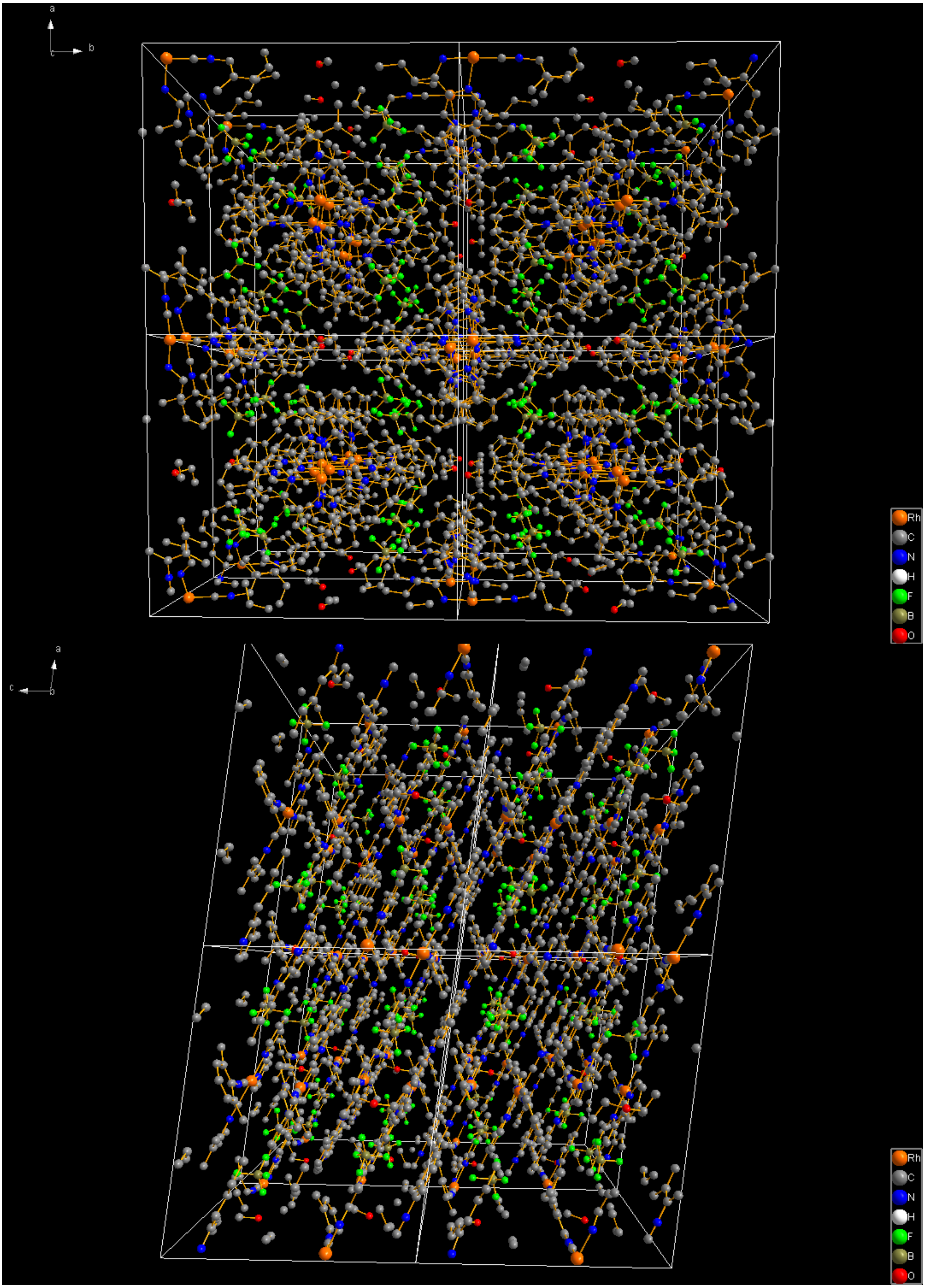


Figure S4 Perspective drawings of crystal structure of the green form of **1** in 2 × 2 × 2 supercell

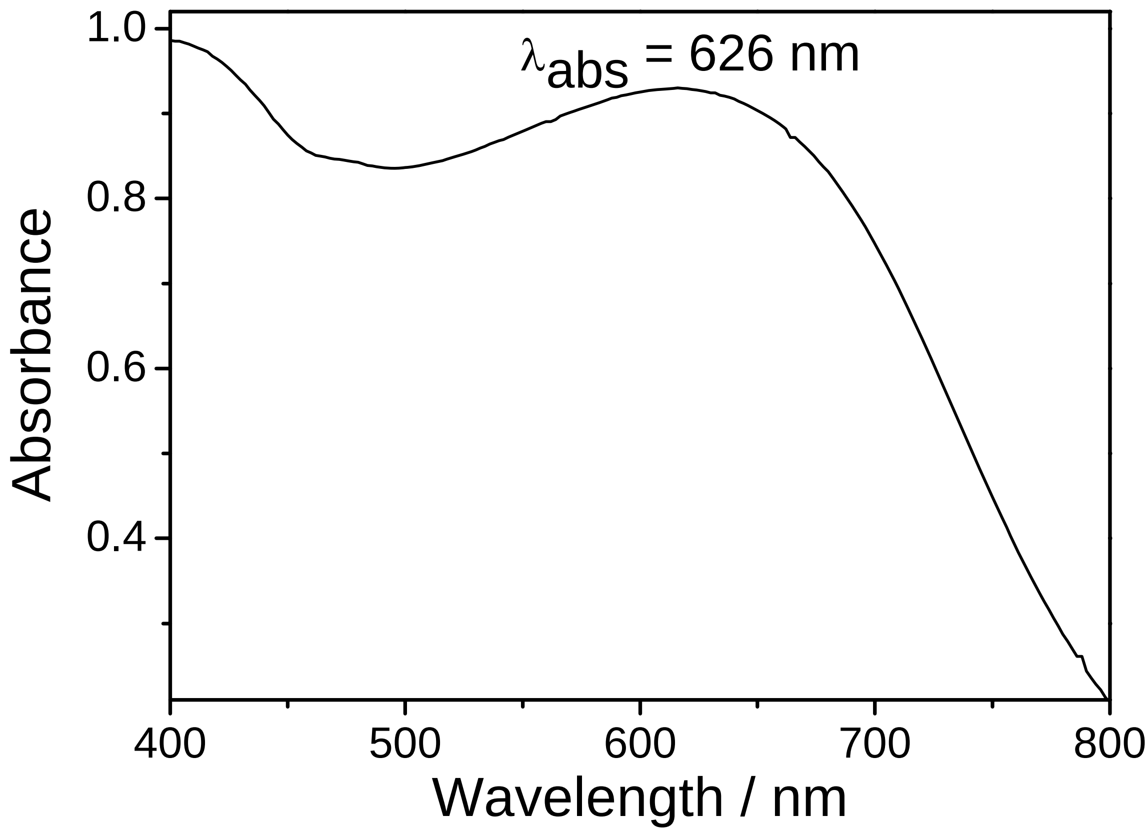
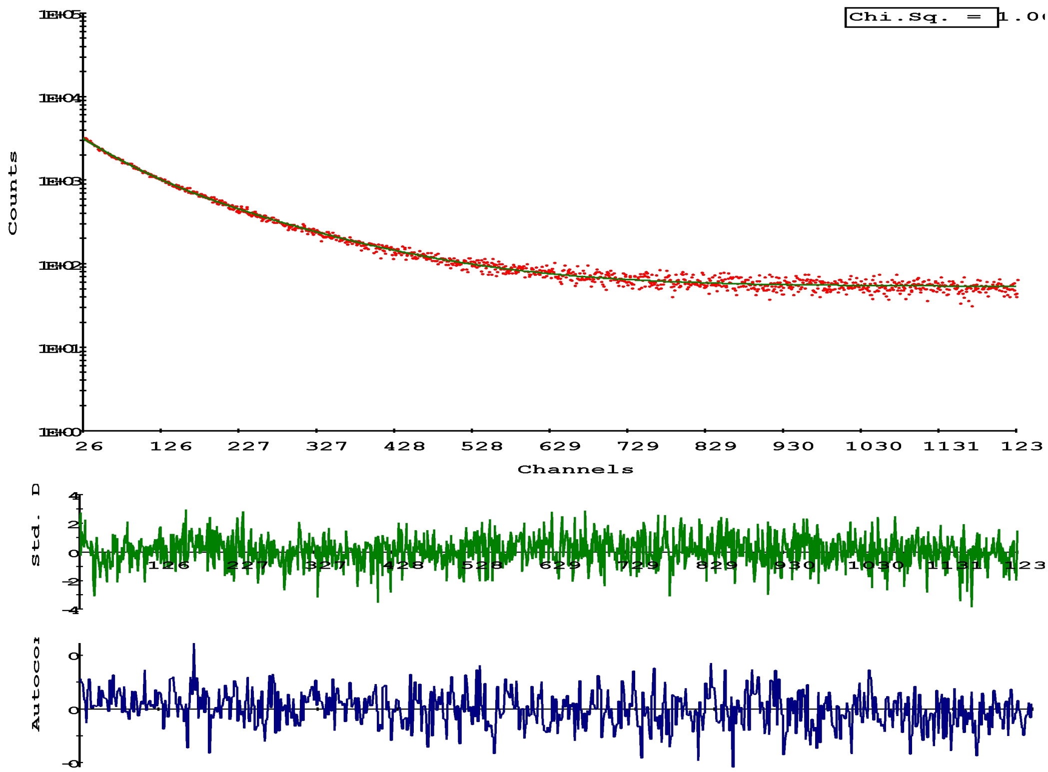


Figure S5 Solid-state reflectance spectrum of the green crystal of **5**.




```
Calculated using 2 exponentials

Prompt data : (none)
Decay data : Decay

The initial paramters are:

 Shift Value = Fixed @ 0        ch;          0              sec

 T1 Estimate = 59.46848 ch;           9.514957E-07   sec
 T2 Estimate = 237.8739 ch;           3.805983E-06   sec

 A Free
 B1 Free
 B2 Free

 Prompt and decay LO = 26     ch;     4.16E-07       sec
 Prompt and decay HI = 1231   ch;     1.9696E-05     sec

 Background on prompt = 0 (manual)
 Time calibration = 1.6E-08 sec/ch

The fitted parameters are:

 SHIFT = 0 ch

 T1    = 51.18865      ch;    8.190183E-07  sec      S.Dev = 2.727457E-08  sec
 T2    = 143.8388      ch;    2.301421E-06  sec      S.Dev = 1.623937E-08  sec
 A     = 53.44883                            S.Dev = 0.2955515
 B1    = 1638.876     [ 28.25 Rel.Ampl]      S.Dev = 14.41818
 B2    = 1481.073     [ 71.75 Rel.Ampl]      S.Dev = 6.479888
 CHISQ = 1.061188     [ 1201 degrees of freedom ]

 Chi-squared Probability =    6.90604 percent
 Durbin-Watson Parameter =   1.884806
 Negative residuals      =   47.67828 percent
 Residuals < 1 s.dev     =   68.07629 percent
 Residuals < 2 s.dev     =   94.19569 percent
 Residuals < 3 s.dev     =   99.41957 percent
 Residuals < 4 s.dev     =        100 percent
```

Figure S6 Decay analysis of TCSPC data of **5** in 77K EtOH/MeOH (4:1) glass medium.