Supplementary Information

Designing Photolabile Ruthenium Polypyridyl Crosslinkers for Hydrogel Formation and Multiplexed, Visible-light Degradation

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Experimental Procedures

Materials

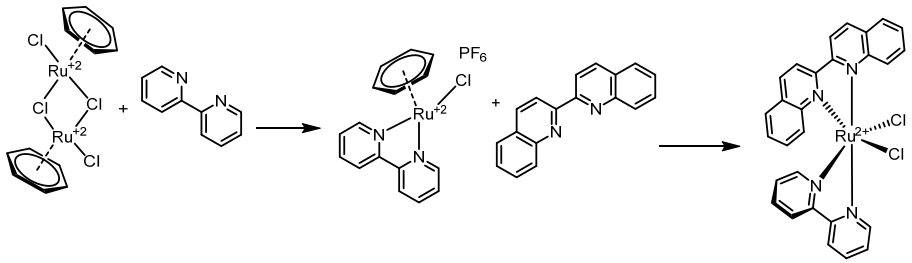
$Ru(bpy)_2Cl_2$ was purchased from Strem Chemicals; LiCl, CD_3CN, biquinoline, NH_4PF_6, $RuCl_3$, AgOTf, $AgPF_6$, and hydroquinone were purchased from Acros Organics; 4-pentynenitrile, 5-hexynenitrile, sodium ascorbate, copper sulfate and the Amberlite resins were purchased from Sigma Aldrich, and all solvents were purchased from Fisher Scientific. All chemicals were used without further purification.

Azido-PEG was purchased from PegWorks, THPTA from Click Chemistry Tools, PBS was purchased from Hyclone.

Methods

*Synthesis of Ru(bpy)$_2$(4-hexynenitrile)$_2$ (**1**)* $Ru(bpy)_2Cl_2$ (106.1 mg, 0.20 mmol) and silver triflate (AgOTf, 112 mg, 0.43 mmol) were suspended in methanol (15 mL) and stirred for 10 min. 5-hexynenitrile (178 μL, 2 mmol) was added and the reaction was heated to 50 °C for 1 h. The methanol was removed by rotary evaporation and NH_4PF_6 was added to precipitate the PF_6 salt of **1**, which was extracted using dichloromethane. The product was purified by flash chromatography on silica gel with a gradient of 1:4 acetonitrile:DCM. The nitrate salt was generated by passage through an Amberlite IRA 743 Free Base resin pre-soaked overnight in HNO_3 with methanol as the eluent; Yield: 100.6 mg, 68%. ^{1}H NMR (CD_3CN): 9.272 (d, 2H), 8.5144 (d, 2H), 8.3725 (d, 2H), 8.2741 (t, 2H), 7.9551 (t, 2H), 7.8510 (t, 2H),

7.6191 (d, 2H), 7.2636 (t, 2H), 2.7542 (m, 4H), 2.1804 (t, 2H), 2.0517 (m, 4H), 1.7048 (t, 4H). Expected Mass: 662.1462 ([**1**]$^{2+}$[NO_3^-]), observed mass: 662.1449 Da

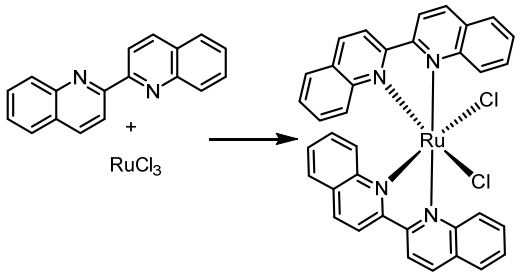


Synthesis of Ru(bpy)(biq)Cl$_2$ Bis[(benzene)dichlororuthenium] (530 mg, 1.06 mmol) and 2,2′-bipyridine (413 mg, 2.6 mmol) were added to methanol (50 mL). The solution was stirred at room temperature for 1 h, then tetrabutylammonium hexafluorophosphate (TBAPF$_6$) was added until precipitation was complete (~200 mg). The light-yellow product Ru(bz)(bpy)Cl was isolated by vacuum filtration and used without further purification for the next step (crude yield: 908 mg, 83%).

Ru(bz)(bpy)Cl[PF$_6$] (908 mg, 1.76 mmol) and LiCl (612 mg, 14.4 mmol) were suspended in DMF (7 mL) and stirred under nitrogen for 10 min. Biquinoline (433 mg, 1.70 mmol) was added, and the solution heated to 130 °C for 1 h. The reaction mixture was cooled to room temperature and added to 500 mL DI water and filtered to collect the dark green product. The precipitate was then redissolved in dichloromethane and washed 2x with water and reprecipitated from diethyl ether for the final product, Ru(bpy)(biq)Cl$_2$ (614 mg, 55% overall yield).

*Synthesis of Ru(bpy)(biq)(5-hexynenitrile)$_2$[NO$_3$]$_2$ (**2**)* The same procedure for **1** was used: Ru(bpy)(biq)Cl$_2$ (23.4 mg, 0.04 mmol), AgOTf (23 mg, 0.09 mmol), and 5-hexynenitrile (47 μL, 0.54 mmol) dissolved in methanol (10 mL), purified by silica gel chromatography (1:4 acetonitrile:DCM). Final yield: 16.6 mg, 63% yield. The water-soluble nitrate salt was generated by passage through an Amberlite IRA 743 Free Base resin presoaked in HNO_3 with methanol as the eluent. ^{1}H NMR (CD_3CN): 9.5661 (d, 1H), 8.8821 (d, 1H), 8.8529 (d, 1H), 8.4770 (s, 2H), 8.2544 (t, 2H), 8.2384 (t, 2H), 8.1190 (d, 2H), 8.0490 (t, 2H), 7.9412 (m, 4H), 7.0770 (t, 2H), 7.5757 (t, 1H), 7.4435 (d, 1H), 7.3378 (m, 3H),

7.2118 (t, 2H), 3.691 (s, 1H), 3.7054 (s, 1H), 2.9442 (t, 2H), 2.7941 (t, 2H), 2.4730 (m, 2H), 2.3016 (m, 2H). Expected mass: 734.1464 ([**2**]$^{2+}$[NO_3^-]), observed mass: 734.1473 Da



Synthesis of Ru(biq)$_2$Cl$_2$ $RuCl_3$ (207 mg, 1 mmol), hydroquinone (222 mg, 2 mmol), and LiCl (240 mg, 5 mmol) were suspended in DMF (5 mL) and stirred under nitrogen for 15 min. Biquinoline (498 mg, 1.9 mmol) was added and the reaction heated to 130 °C for 1 h. The reaction mixture was added to 500 mL DI water and product isolated following the same procedure as Ru(bpy)(biq)Cl_2. Yield: 219 mg, 33%.

*Synthesis of Ru(biq)$_2$(5-hexynenitrile)$_2$[NO$_3$]$_2$ (**3**)* Ru(biq)$_2$$Cl_2$ from previous step (100 mg, 0.15 mmol) was dissolved in 10 mL of methanol. $AgPF_6$ (105 mg, 0.4 mmol) was added, reaction was stirred at room temperature for 10 min. 5-hexynenitrile (230 μL, 2.8 mmol) was added and solution was heated to 50 °C for 1 h. Ru(biq)$_2$(5-hexynenitrile)$_2$[PF_6]$_2$ was extracted and purified as described for **1** (45.3 mg, 73%). The nitrate salt was generated using Amberlite IRA 743 Free Base resin as described for **1**. Yield: 97.9 mg, 73%. ^{1}H NMR (D_2O): 9.3868 (s, 2H), 8.7955 (d, 2H), 8.4220 (m, 6H), 8.2398 (d, 2H), 8.1253 (t, 2H), 8.1097 (s, 2H), 7.9900 (d, 2H), 7.5695 (t, 2H), 6.9401 (t, 2H), 6.8261 (d, 2H), 6.8261 (d, 2H), 3.0657 (m, 4H), 2.1894 (t, 2H), 2.0125 (m, 4H), 1.7317 (m, 4H). Expected mass: 862.2093 ([**5**]$^{2+}$[NO_3^-]), observed mass: 862.2095 Da

Synthesis of Ru(biq)$_2$(4-pentynenitrile)$_2$[NO$_3$]$_2$ was synthesized according to the protocol for **3**; with Ru(biq)$_2$(Cl)$_2$ (51 mg, 0.07 mmol), $AgPF_6$ (49 mg, 0.19 mmol), and 4-pentynenitrile (78 μL, 0.74 mmol). Yield: (45.3 mg, 73%). ^{1}H NMR (CD_3CN): 9.1485 (1H), 8.6791 (d, 2H), 8.3620 (d, 2H), 8.2986 (d, 2H), 8.2057 (s, 2H), 8.0071 (t, 2H), 8.050 (s, 2H), 7.9136 (d, 2H), 7.4970 (t, 1H), 6.8676 (t, 1H), 6.8165 (d,

2H), 2.8483 (m, 4H), 2.3369 (m, 4H), 1.8338 (t, 2H). Expected mass: 834.1779 ([**3**]$^{2+}$[NO_3^-]), observed mass: 834.1799 Da

Formation of 10 wt% PEG hydrogel

Table S1 shows the amounts of reagents used to generate a 25 uL hydrogel

	[Stock]		Amt to add (μL)	Ratio (X:RuAlkyne)
PEG	600	mg/mL	4.17	0.5:1
RuAlkyne	50	mM	9.84	1
Ascorbate	2500	mM	2.6	10:1
THPTA	1000	mM	4.92	10:1
Cu	1.5	M	3.28	10:1
MeCN			0.25	
		Total	25.00	

PEG, ascorbate, and RuAlkyne were mixed together, and the $CuSO_4$ and THPTA were mixed separately to allow the THPTA to fully coordinate the copper. The two solutions were then combined and mixed thoroughly before being allowed to gel over the course of 5-10 min. Hydrogels were then soaked in PBS to remove any excess ruthenium and copper before any experiments were done.

Figure S1 – Stability of 3 in water

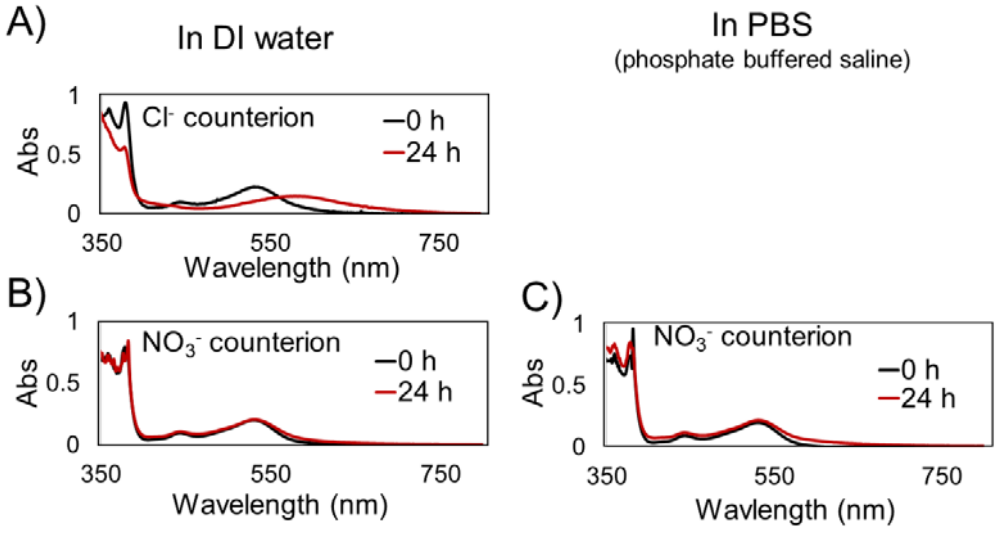
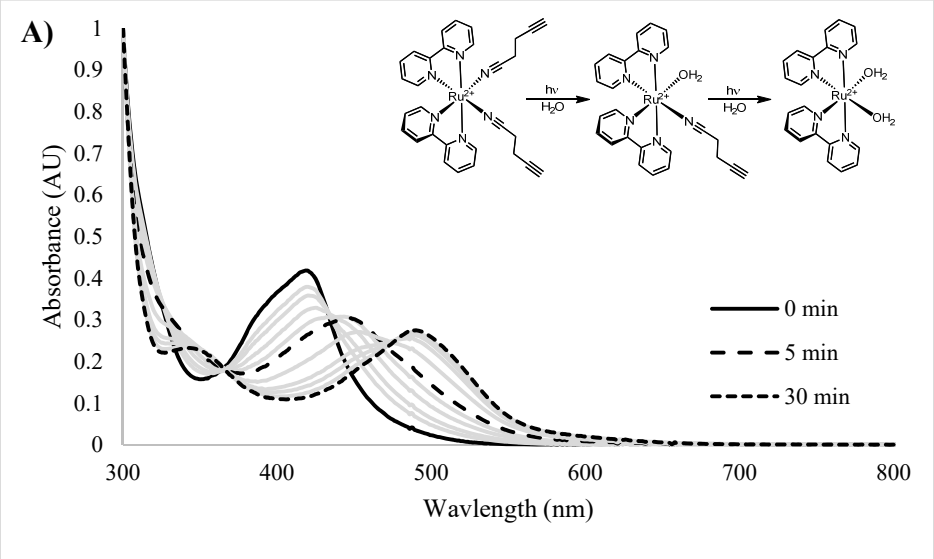


Figure S1. The NO_3^- salt of **3** was stable in both water and biologically relevant PBS. The chloride salt of the same compound showed remarkably decreased stability, perhaps owing to the protective nature of the nitrate anion.

Figure S2 – Photolysis of 1 and 2



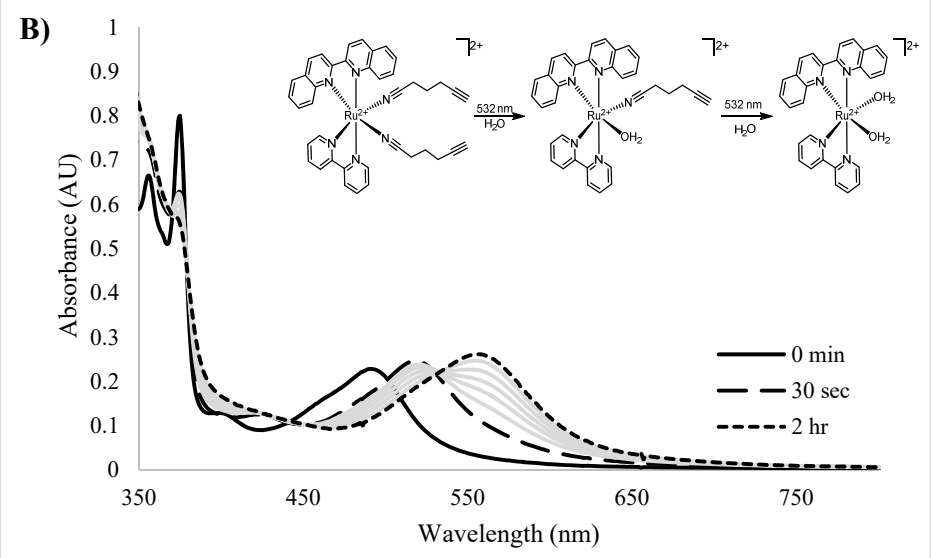


Figure S2. Photolysis of **1** and **2** in water. A) 65 μM **1** in water, irradiated with a 450 nm laser pointer (52 mW/cm^2). B) 65 μM **2** in water, irradiated with 523 nm LED (25 mW/cm^2).

Figure S3 – Photolysis of 3 with 600 – 700 nm light

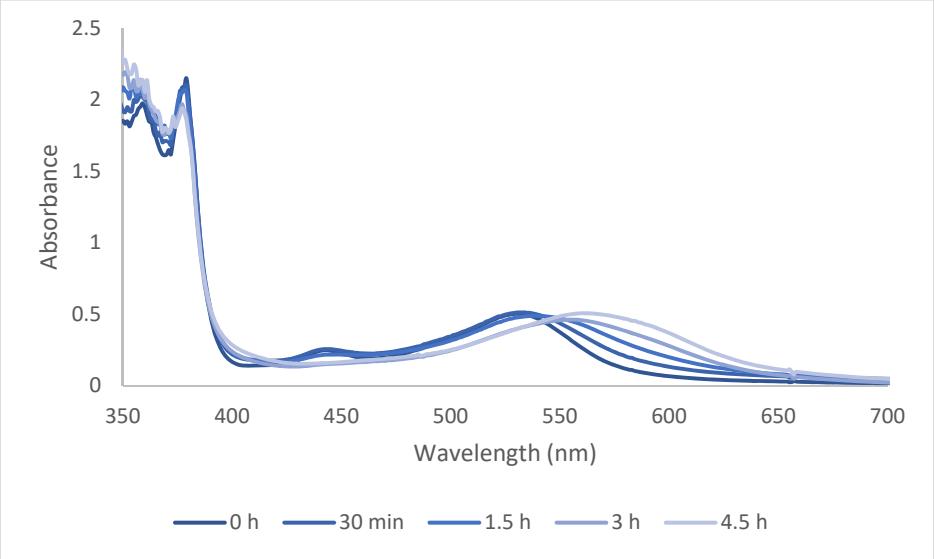


Figure S3. 80 μM solution of **3** ($Ru(biq)_2(5\text{-hexynenitrile})_2$) in water, irradiated with broadband 600 – 700 nm incandescent light (5 mW/cm^2).

Figure S4 – Kinetics traces for the determination of the quantum yield

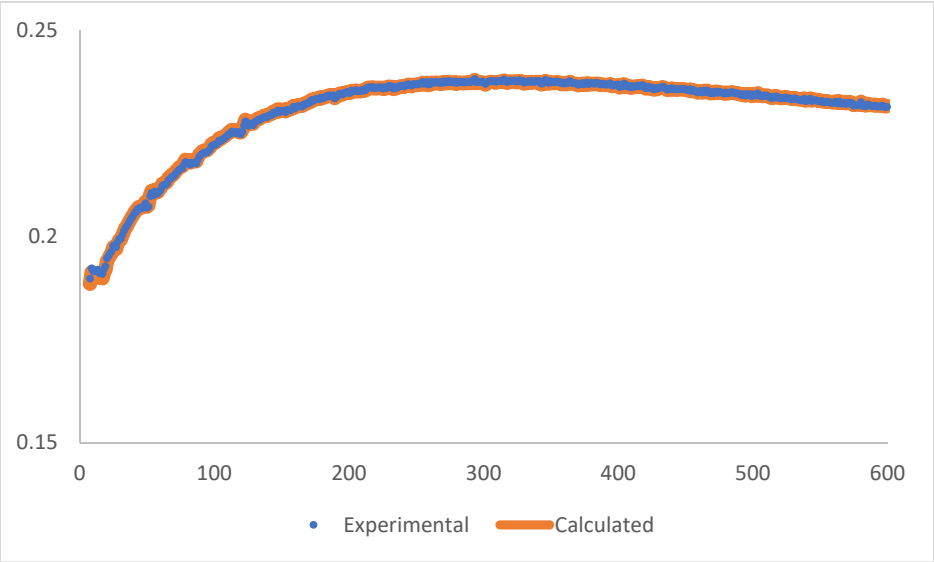


Figure S4. Kinetics trace for **3** under constant photolysis. The absorbance was measured at 565 nm throughout the experiment. The data were fit to an equation of the form

$$y = A_1 e^{-x/\tau_1} + A_2 e^{-x/\tau_2} + y_0$$

With two time constants τ_1 and τ_2 that give rate constants k_1 and k_2 according to

$$Abs@470 = \varepsilon_A [A]_0 e^{-kt} - \varepsilon_B [A]_0 e^{-kt} + \varepsilon_B [A]_0$$

The rate constants for each step for **1**-**3**:

	τ_1 (s)	k_1 (s^{-1})	τ_2 (s)	k_2 (s^{-1})
1: $Rubpy_2hexynenitrile_2$	99 ± 7	0.01004	730 ± 30	0.0014
2: $Ru(bpy)(biq)(hexynenitrile)_2$	155 ± 15	0.0068	155 ± 15	0.0068
3: $Ru(biq)_2(hexynenitrile)_2$	131 ± 6	0.0076	1034 ± 47	0.00097

Figure S5 – Crystal structure for compound 2

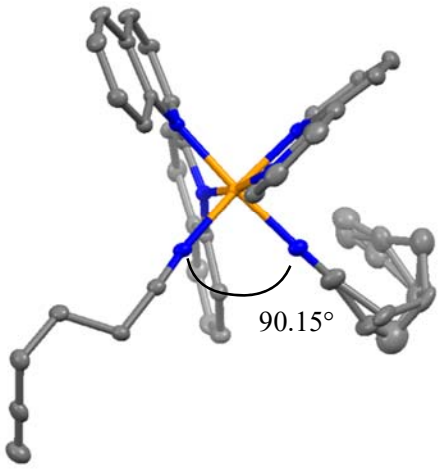


Figure S5. Crystal structure for **2** synthesized under longer, higher temperature reaction conditions. One 5-hexynenitrile ligand shows *cis* isomerization with 100% occupancy in the structure. The alkyne-biquinoline distance for the *cis*-hexyne was 3.734 Å, while the alkyne-biquinoline distance for the *trans*-hexyne was 6.809 Å. The *cis* product was observed after extended reaction times during the initial synthesis, and was irreversible.

Figure S6 – $Ru(biq)_2(4\text{-pentynenitrile})_2$

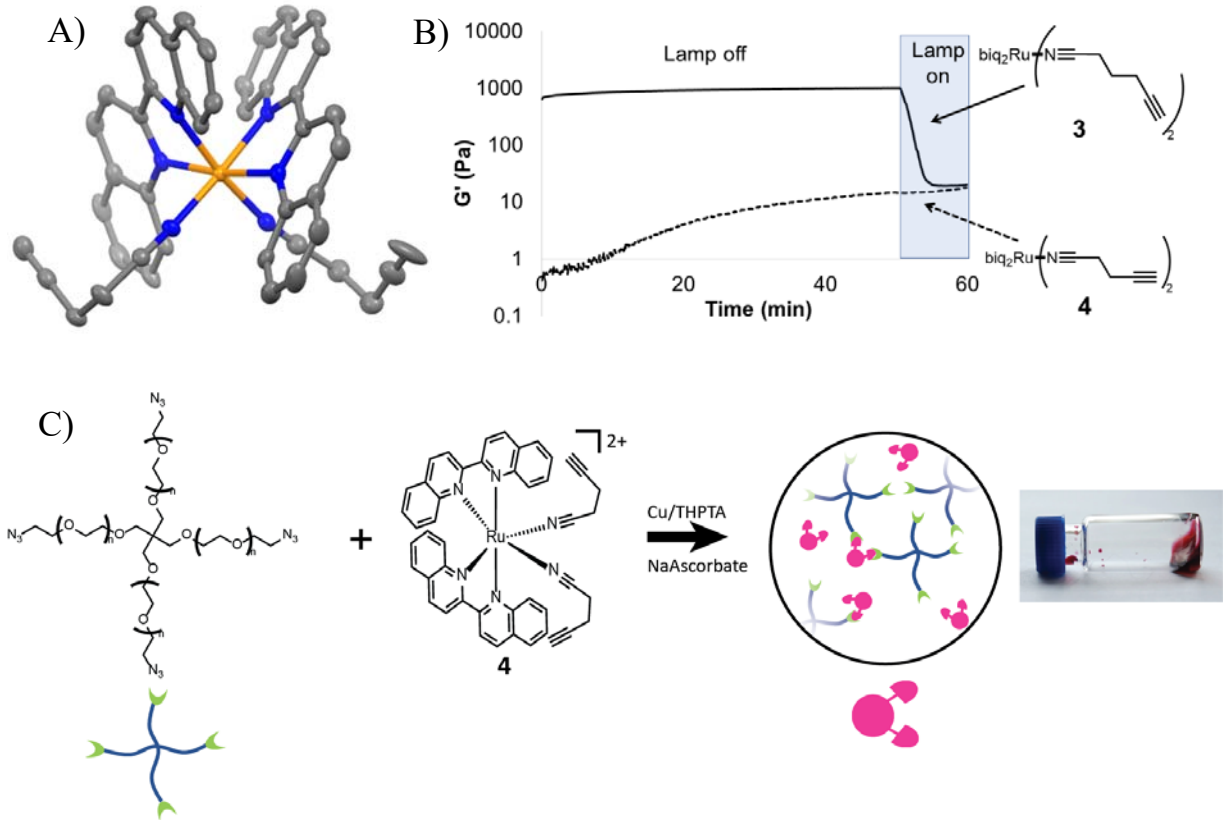


Figure S6. Shorter alkyne-bearing nitrile ligands led to poor gelation. A) $Ru(biq)_2(4\text{-pentynenitrile})_2$ was synthesized according to the same protocol as compounds **1-3**, but consistently produced *cis*-isomers that were incapable of forming a hydrogel. The alkyne-biq distances in this structure are only 3.867 and 4.030 Å. B) Rheometry of $Ru(biq)_2(4\text{-pentynenitrile})_2$ compared to compound **3**. $Ru(biq)_2(4\text{-pentynenitrile})_2$ never formed an elastic hydrogel material (C).

Figure S7 – Crystal Structure Determination of 3

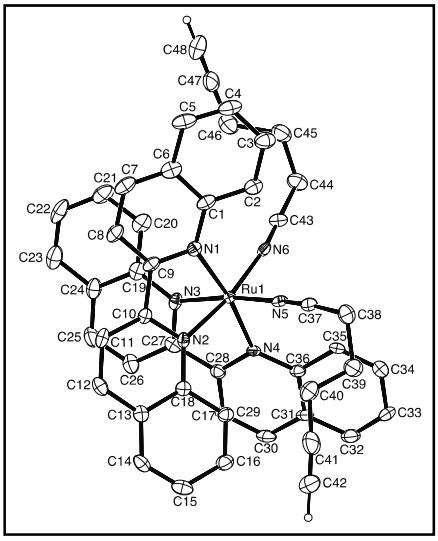


Figure S7.1. ORTEP drawing of molecule no.1 of the asymmetric unit with 50% thermal ellipsoids.

$Ru(biq)_2(5\text{-hexynenitrile})_2[PF_6]_2$, Compound **3**, $C_{48}H_{38}F_{12}N_6P_2Ru$, crystallizes in the monoclinic space group $P2_1$ (systematic absences 0k0: k=odd) with a=11.3357(9)Å, b=31.071(3)Å, c=12.8113(11)Å, β=99.628(5)°, °V=4448.7(7)Å^3, Z=4, and d_{calc}=1.627 g/cm$_3$. X-ray intensity data were collected on a Bruker APEXII [1] CCD area detector employing graphite-monochromated Mo-Kα radiation (λ=0.71073Å) at a temperature of 100K. Preliminary indexing was performed from a series of thirty-six 0.5° rotation frames with exposures of 10 seconds. A total of 2249 frames were collected with a crystal to detector distance of 54.7 mm, rotation widths of 0.5° and exposures of 30 seconds:

scan type	2θ	ω	φ	χ	Frames
ϕ	-33.00	301.86	19.62	43.59	739
ϕ	29.50	108.32	6.43	-46.47	611
ω	34.50	311.98	167.97	65.91	196
ω	-23.00	321.68	226.55	-73.06	89
ω	29.50	119.68	26.51	-76.00	99
ϕ	-33.00	308.05	27.50	57.63	510

Rotation frames were integrated using SAINT [2], producing a listing of unaveraged F^2 and $\sigma(F^2)$ values. A total of 59533 reflections were measured over the ranges $3.224 \le 2\theta \le 55.074°$, $-14 \le h \le 14$, $-40 \le k \le 40$, $-16 \le l \le 16$ yielding 19666 unique reflections (R_{int} = 0.0541). The intensity data were corrected for

Lorentz and polarization effects and for absorption using SADABS [3] (minimum and maximum transmission 0.6698, 0.7456). The structure was solved by direct methods - ShelXS-97 [4]. Refinement was by full-matrix least squares based on F^2 using SHELXL-2017 [5]. All reflections were used during refinement. The weighting scheme used was $w=1/[\sigma^2(F_o^2)+ (0.0764P)^2 + 1.3878P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0525 and wR2=0.1221 for 17036 observed reflections for which $F > 4\sigma(F)$ and R1=0.0660 and wR2=0.1322 and GOF =1.067 for all 19666 unique, non-zero reflections and 1243 variables. The maximum Δ/σ in the final cycle of least squares was 0.001 and the two most prominent peaks in the final difference Fourier were +1.63 and -0.79 e/Å^3.

Table S7.1. lists cell information, data collection parameters, and refinement data. Final positional parameters are given in Tables S7.2. Anisotropic thermal parameters are in Table S7.3. Tables S7.4. and S7.5. list bond distances and bond angles. Figure S7.1 is ORTEP representation of the molecule with 50% probability thermal ellipsoids displayed.

Table S7.1. Summary of Structure Determination of Compound 3

Empirical formula	$C_{48}H_{38}F_{12}N_6P_2Ru$
Formula weight	1089.85
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1$
a	11.3357(9)Å
b	31.071(3)Å
c	12.8113(11)Å
□	99.628(5)°
Volume	4448.7(7)Å^3
Z	4
d_{calc}	1.627 g/cm^3
□	0.519 mm^{-1}
F(000)	2200.0
Crystal size, mm	0.17 □ 0.11 □ 0.05
2□ range for data collection	3.224 - 55.074°
Index ranges	-14 ≤ h ≤ 14, -40 ≤ k ≤ 40, -16 ≤ l ≤ 16
Reflections collected	59533
Independent reflections	19666[R(int) = 0.0541]
Data/restraints/parameters	19666/73/1243
Goodness-of-fit on F^2	1.067
Final R indexes [I>=2□ (I)]	R_1 = 0.0525, wR_2 = 0.1221
Final R indexes [all data]	R_1 = 0.0660, wR_2 = 0.1322
Largest diff. peak/hole	1.63/-0.79 eÅ^{-3}
Flack parameter	0.066(10)

Table S7.2 . Refined Positional Parameters

Atom	*x*	*y*	*z*	U(eq)
Ru1	0.31093(4)	0.11876(2)	0.38528(4)	0.01455(12)
N1	0.2676(5)	0.16227(19)	0.4954(4)	0.0168(12)

N2	0.4462(5)	0.1645(2)	0.3909(4)	0.0158(12)
N3	0.4401(5)	0.08681(19)	0.4925(4)	0.0181(12)
N4	0.3828(5)	0.07563(19)	0.2872(4)	0.0150(11)
N5	0.2012(5)	0.1521(2)	0.2726(4)	0.0175(12)
N6	0.1873(5)	0.0739(2)	0.4057(4)	0.0179(12)
C1	0.1620(6)	0.1658(2)	0.5347(5)	0.0206(15)
C2	0.0537(6)	0.1498(3)	0.4762(6)	0.0222(15)
C3	-0.0503(7)	0.1527(3)	0.5166(6)	0.0302(18)
C4	-0.0509(7)	0.1703(3)	0.6170(6)	0.0311(18)
C5	0.0508(8)	0.1865(3)	0.6753(7)	0.034(2)
C6	0.1609(7)	0.1854(2)	0.6343(6)	0.0233(16)
C7	0.2667(7)	0.2030(3)	0.6896(6)	0.0296(17)
C8	0.3680(7)	0.2040(3)	0.6437(6)	0.0257(16)
C9	0.3650(6)	0.1831(2)	0.5442(5)	0.0189(14)
C10	0.4668(6)	0.1840(2)	0.4860(5)	0.0157(13)
C11	0.5748(7)	0.2049(3)	0.5247(6)	0.0230(15)
C12	0.6616(6)	0.2071(2)	0.4625(6)	0.0219(15)
C13	0.6414(6)	0.1900(2)	0.3581(5)	0.0185(14)
C14	0.7243(6)	0.1930(3)	0.2884(6)	0.0247(16)
C15	0.6975(7)	0.1774(3)	0.1881(6)	0.0265(17)
C16	0.5829(6)	0.1594(3)	0.1520(6)	0.0246(16)
C17	0.5006(6)	0.1554(2)	0.2166(5)	0.0192(15)
C18	0.5279(6)	0.1696(2)	0.3237(5)	0.0167(14)
C19	0.4596(6)	0.0892(2)	0.6029(5)	0.0211(14)
C20	0.3639(7)	0.0956(2)	0.6562(6)	0.0247(15)
C21	0.3845(8)	0.1003(3)	0.7643(6)	0.0306(17)
C22	0.4991(8)	0.0979(3)	0.8217(6)	0.035(2)
C23	0.5941(8)	0.0903(3)	0.7726(6)	0.0325(18)
C24	0.5764(7)	0.0840(3)	0.6610(6)	0.0252(16)
C25	0.6713(6)	0.0736(3)	0.6040(6)	0.0307(18)
C26	0.6472(6)	0.0659(3)	0.4991(6)	0.0258(16)
C27	0.5288(6)	0.0724(2)	0.4444(6)	0.0213(15)
C28	0.4942(6)	0.0638(2)	0.3298(5)	0.0180(14)
C29	0.5715(6)	0.0415(2)	0.2714(6)	0.0224(15)
C30	0.5323(6)	0.0327(3)	0.1676(6)	0.0240(16)
C31	0.4153(6)	0.0435(2)	0.1203(5)	0.0200(14)
C32	0.3689(6)	0.0346(3)	0.0120(6)	0.0264(16)
C33	0.2545(6)	0.0449(3)	-0.0295(5)	0.0278(17)
C34	0.1784(6)	0.0635(3)	0.0347(6)	0.0255(16)
C35	0.2200(5)	0.0724(2)	0.1386(5)	0.0195(14)
C36	0.3399(6)	0.0638(2)	0.1840(5)	0.0171(13)
C37	0.1397(6)	0.1701(3)	0.2061(5)	0.0207(15)
C38	0.0716(6)	0.1925(3)	0.1140(6)	0.0261(16)

C39	0.1485(7)	0.1978(3)	0.0271(6)	0.0320(19)
C40	0.2573(7)	0.2257(3)	0.0634(6)	0.0320(18)
C41	0.3421(8)	0.2284(4)	-0.0114(7)	0.044(2)
C42	0.4155(8)	0.2307(5)	-0.0645(7)	0.057(3)
C43	0.1239(6)	0.0488(3)	0.4301(6)	0.0228(15)
C44	0.0396(7)	0.0168(3)	0.4611(6)	0.0302(17)
C45	-0.0244(7)	0.0336(3)	0.5485(6)	0.0318(18)
C46	0.0580(7)	0.0390(4)	0.6551(7)	0.046(3)
C47	0.0041(7)	0.0613(4)	0.7351(6)	0.040(2)
C48	-0.0407(9)	0.0802(4)	0.7976(7)	0.051(3)
P1	0.86894(17)	0.05574(7)	0.15623(19)	0.0300(5)
F1	0.8935(4)	0.0436(2)	0.0405(4)	0.0455(13)
F2	0.9426(5)	0.09927(19)	0.1536(6)	0.0591(17)
F3	0.8447(4)	0.0671(2)	0.2729(5)	0.0546(16)
F4	0.7966(4)	0.01165(15)	0.1589(4)	0.0385(12)
F5	0.7487(4)	0.07959(18)	0.1050(5)	0.0504(15)
F6	0.9892(4)	0.03091(17)	0.2076(4)	0.0349(11)
P2	0.75523(18)	0.20797(8)	0.86053(16)	0.0300(5)
F7	0.7256(5)	0.1767(2)	0.7626(4)	0.0482(14)
F8	0.8409(5)	0.2346(2)	0.7989(5)	0.0523(15)
F9	0.7877(8)	0.2384(3)	0.9602(6)	0.095(3)
F10	0.6709(5)	0.1810(2)	0.9233(4)	0.0486(14)
F11	0.6433(6)	0.2373(2)	0.8102(6)	0.0700(19)
F12	0.8637(6)	0.1770(3)	0.9032(6)	0.084(2)
Ru1'	0.44114(4)	0.38239(2)	0.87854(4)	0.01936(13)
N1'	0.2945(5)	0.3407(2)	0.8678(5)	0.0229(14)
N2'	0.4701(5)	0.3405(2)	0.7609(5)	0.0216(13)
N3'	0.3585(5)	0.41924(19)	0.7520(5)	0.0178(12)
N4'	0.5779(5)	0.4230(2)	0.8494(5)	0.0188(12)
N5'	0.5308(6)	0.3429(2)	0.9904(5)	0.0287(15)
N6'	0.4013(5)	0.4270(2)	0.9843(5)	0.0219(14)
C1'	0.2160(6)	0.3343(2)	0.9382(6)	0.0229(16)
C2'	0.2451(7)	0.3486(3)	1.0431(6)	0.0294(18)
C3'	0.1658(7)	0.3425(3)	1.1128(7)	0.036(2)
C4'	0.0562(7)	0.3226(3)	1.0787(8)	0.039(2)
C5'	0.0265(7)	0.3075(3)	0.9785(7)	0.036(2)
C6'	0.1063(6)	0.3128(3)	0.9046(7)	0.0285(18)
C7'	0.0810(6)	0.2965(3)	0.8011(7)	0.0273(17)
C8'	0.1613(6)	0.3009(3)	0.7333(7)	0.0275(17)
C9'	0.2708(6)	0.3233(2)	0.7706(6)	0.0221(15)
C10'	0.3676(6)	0.3250(2)	0.7082(6)	0.0223(15)
C11'	0.3553(7)	0.3107(3)	0.6039(7)	0.0294(17)
C12'	0.4522(8)	0.3106(3)	0.5552(7)	0.0337(19)

C13'	0.5661(6)	0.3213(3)	0.6125(6)	0.0274(17)
C14'	0.6735(7)	0.3173(3)	0.5696(7)	0.0314(18)
C15'	0.7808(7)	0.3259(3)	0.6294(8)	0.037(2)
C16'	0.7872(6)	0.3382(3)	0.7360(7)	0.0290(17)
C17'	0.6861(6)	0.3430(2)	0.7806(7)	0.0255(16)
C18'	0.5743(6)	0.3356(2)	0.7178(6)	0.0236(16)
C19'	0.2395(6)	0.4193(2)	0.7113(6)	0.0244(15)
C20'	0.1527(6)	0.4150(2)	0.7781(6)	0.0239(15)
C21'	0.0363(7)	0.4110(3)	0.7375(7)	0.0332(19)
C22'	-0.0035(7)	0.4117(3)	0.6287(8)	0.039(2)
C23'	0.0770(7)	0.4192(3)	0.5632(7)	0.036(2)
C24'	0.1996(7)	0.4239(3)	0.6023(7)	0.0307(18)
C25'	0.2862(7)	0.4342(3)	0.5366(6)	0.0322(19)
C26'	0.4034(7)	0.4400(3)	0.5811(6)	0.0285(17)
C27'	0.4381(6)	0.4316(2)	0.6909(6)	0.0199(14)
C28'	0.5595(6)	0.4370(2)	0.7485(5)	0.0183(14)
C29'	0.6513(6)	0.4576(2)	0.7034(5)	0.0187(14)
C30'	0.7593(6)	0.4644(2)	0.7650(6)	0.0228(15)
C31'	0.7798(6)	0.4525(2)	0.8718(6)	0.0208(14)
C32'	0.8890(6)	0.4606(3)	0.9419(6)	0.0319(18)
C33'	0.9018(7)	0.4502(3)	1.0451(7)	0.042(2)
C34'	0.8065(7)	0.4313(3)	1.0878(6)	0.036(2)
C35'	0.7008(6)	0.4227(3)	1.0231(6)	0.0270(17)
C36'	0.6835(6)	0.4326(2)	0.9139(6)	0.0217(15)
C37'	0.5760(8)	0.3182(3)	1.0493(8)	0.042(2)
C38'	0.6325(10)	0.2885(4)	1.1330(9)	0.059(3)
C39'	0.6488(14)	0.3120(5)	1.2404(11)	0.088(5)
C40'	0.5392(14)	0.3303(4)	1.2709(9)	0.078(4)
C41'	0.4442(14)	0.2980(5)	1.2845(8)	0.069(4)
C42'	0.3712(14)	0.2706(5)	1.2956(11)	0.084(5)
C43'	0.3797(6)	0.4549(3)	1.0355(5)	0.0218(15)
C44'	0.3466(7)	0.4903(3)	1.0987(6)	0.0300(17)
C45'	0.2335(8)	0.4809(4)	1.1431(7)	0.044(2)
C46'	0.2550(9)	0.4480(4)	1.2318(7)	0.053(3)
C47'	0.1452(10)	0.4341(4)	1.2660(7)	0.058(3)
C48'	0.0560(9)	0.4199(5)	1.2881(8)	0.070(4)
P1'	0.63953(19)	0.45801(8)	0.35168(17)	0.0337(5)
F1'	0.7659(6)	0.4376(3)	0.3486(5)	0.070(2)
F2'	0.6687(6)	0.4946(2)	0.2735(5)	0.0606(16)
F3'	0.5134(5)	0.4798(2)	0.3574(5)	0.0644(18)
F4'	0.6108(6)	0.4215(2)	0.4301(5)	0.0611(17)
F5'	0.6940(5)	0.4872(2)	0.4506(5)	0.0612(17)
F6'	0.5803(7)	0.4305(2)	0.2507(5)	0.070(2)

P2'	0.0134(2)	0.28833(8)	0.39060(17)	0.0364(5)
F7'	0.1199(7)	0.3090(3)	0.3474(6)	0.091(2)
F8'	-0.0022(9)	0.2517(4)	0.3067(7)	0.112(3)
F9'	-0.0962(6)	0.2690(3)	0.4355(5)	0.072(2)
F10'	0.0329(8)	0.3229(3)	0.4826(8)	0.104(3)
F11'	0.1024(8)	0.2593(3)	0.4689(7)	0.090(2)
F12'	-0.0685(8)	0.3183(4)	0.3131(8)	0.120(3)

Table S7.3. Positional Parameters for Hydrogens in Compound 3

Atom	*x*	*y*	*z*	U(eq)
H2	0.053372	0.137043	0.408735	0.03
H3	-0.12298	0.142593	0.47608	0.04
H4	-0.123375	0.170874	0.645052	0.041
H5	0.048853	0.198585	0.743064	0.046
H7	0.268683	0.2142	0.758843	0.039
H8	0.438219	0.218222	0.677429	0.034
H11	0.587454	0.2175	0.593268	0.031
H12	0.73636	0.220072	0.489455	0.029
H14	0.800001	0.205964	0.311631	0.033
H15	0.755271	0.178677	0.142329	0.035
H16	0.563646	0.149823	0.080691	0.033
H17	0.424578	0.143076	0.190665	0.026
H20	0.28453	0.096809	0.617964	0.033
H21	0.318912	0.10518	0.80031	0.041
H22	0.511367	0.101697	0.896373	0.046
H23	0.672529	0.089257	0.812603	0.043
H25	0.751482	0.072272	0.640339	0.041
H26	0.708342	0.056152	0.46237	0.034
H29	0.649306	0.032997	0.304459	0.03
H30	0.584367	0.019176	0.126717	0.032
H32	0.418673	0.021358	-0.031478	0.035
H33	0.225297	0.039503	-0.102284	0.037
H34	0.097671	0.069828	0.005359	0.034
H35	0.167414	0.084591	0.181123	0.026
H38a	0.046396	0.221161	0.135822	0.035
H38b	-0.001195	0.175776	0.086124	0.035
H39a	0.174932	0.16906	0.006674	0.043
H39b	0.09963	0.210915	-0.036114	0.043
H40a	0.229791	0.255109	0.076703	0.043
H40b	0.300004	0.214252	0.13149	0.043
H42	0.475518	0.232507	-0.107906	0.076
H44a	0.083963	-0.009704	0.485811	0.04
H44b	-0.020517	0.009334	0.398423	0.04

H45a	-0.089591	0.013472	0.55737	0.042
H45b	-0.061276	0.061797	0.526489	0.042
H46a	0.084403	0.010195	0.682367	0.062
H46b	0.130109	0.055155	0.643638	0.062
H48	-0.076895	0.095434	0.848201	0.068
H2'	0.319526	0.362518	1.066357	0.039
H3'	0.186216	0.351851	1.184075	0.048
H4'	0.001082	0.319542	1.126571	0.052
H5'	-0.047854	0.293283	0.957413	0.048
H7'	0.007062	0.282275	0.77792	0.036
H8'	0.145201	0.289365	0.663649	0.037
H11'	0.279962	0.301126	0.567479	0.039
H12'	0.4438	0.303453	0.482247	0.045
H14'	0.669753	0.308356	0.498221	0.042
H15'	0.851816	0.32377	0.599483	0.049
H16'	0.863235	0.343329	0.778003	0.039
H17'	0.691801	0.351117	0.852793	0.034
H20'	0.177237	0.414862	0.85276	0.032
H21'	-0.020143	0.407724	0.783927	0.044
H22'	-0.08552	0.407007	0.600697	0.052
H23'	0.049558	0.42139	0.489157	0.048
H25'	0.262207	0.437099	0.462202	0.043
H26'	0.460332	0.449505	0.539549	0.038
H29'	0.637121	0.46651	0.631472	0.025
H30'	0.821723	0.477484	0.735114	0.03
H32'	0.95381	0.473535	0.915259	0.042
H33'	0.975859	0.45554	1.090058	0.056
H34'	0.816177	0.424598	1.161085	0.048
H35'	0.637521	0.409709	1.05206	0.036
H38a'	0.711157	0.278911	1.117753	0.079
H38b'	0.581383	0.262758	1.135182	0.079
H39a'	0.684184	0.29151	1.296172	0.118
H39b'	0.707162	0.335579	1.238834	0.118
H40a'	0.504711	0.351381	1.216217	0.103
H40b'	0.561698	0.346221	1.338271	0.103
H42'	0.314089	0.249077	1.30428	0.112
H44a'	0.334446	0.516503	1.054423	0.04
H44b'	0.412928	0.495929	1.157869	0.04
H45a'	0.203564	0.507877	1.170236	0.058
H45b'	0.171296	0.469911	1.085777	0.058
H46a'	0.295777	0.422636	1.207487	0.071
H46b'	0.308871	0.460646	1.292873	0.071

H48'	-0.015815	0.408491	1.305818	0.093

Table S7.4. Bond Distances in Compound 3

Ru1-N1	2.072(6)	Ru1-N2	2.084(6)	Ru1-N3	2.084(6)
Ru1-N4	2.093(6)	Ru1-N5	2.025(6)	Ru1-N6	2.024(6)
N1-C1	1.378(9)	N1-C9	1.341(9)	N2-C10	1.346(9)
N2-C18	1.375(8)	N3-C19	1.397(9)	N3-C27	1.340(9)
N4-C28	1.341(8)	N4-C36	1.380(8)	N5-C37	1.153(9)
N6-C43	1.140(9)	C1-C2	1.418(10)	C1-C6	1.415(10)
C2-C3	1.368(10)	C3-C4	1.399(11)	C4-C5	1.362(13)
C5-C6	1.432(10)	C6-C7	1.398(12)	C7-C8	1.375(11)
C8-C9	1.425(10)	C9-C10	1.474(9)	C10-C11	1.402(10)
C11-C12	1.368(10)	C12-C13	1.422(10)	C13-C14	1.404(10)
C13-C18	1.435(9)	C14-C15	1.358(11)	C15-C16	1.420(10)
C16-C17	1.354(9)	C17-C18	1.425(10)	C19-C20	1.390(10)
C19-C24	1.416(10)	C20-C21	1.374(10)	C21-C22	1.384(12)
C22-C23	1.356(12)	C23-C24	1.423(10)	C24-C25	1.434(11)
C25-C26	1.347(11)	C26-C27	1.422(10)	C27-C28	1.480(10)
C28-C29	1.423(10)	C29-C30	1.358(10)	C30-C31	1.404(10)
C31-C32	1.427(10)	C31-C36	1.424(9)	C32-C33	1.355(11)
C33-C34	1.412(10)	C34-C35	1.365(10)	C35-C36	1.412(9)
C37-C38	1.472(10)	C38-C39	1.533(10)	C39-C40	1.516(12)
C40-C41	1.469(12)	C41-C42	1.161(13)	C43-C44	1.477(10)
C44-C45	1.525(11)	C45-C46	1.529(12)	C46-C47	1.452(14)
C47-C48	1.175(14)	P1-F1	1.599(6)	P1-F2	1.593(6)
P1-F3	1.604(6)	P1-F4	1.600(5)	P1-F5	1.593(5)
P1-F6	1.608(5)	P2-F7	1.579(6)	P2-F8	1.584(5)
P2-F9	1.581(7)	P2-F10	1.587(5)	P2-F11	1.607(7)
P2-F12	1.584(8)	Ru1'-N1'	2.094(6)	Ru1'-N2'	2.060(6)
Ru1'-N3'	2.076(6)	Ru1'-N4'	2.080(6)	Ru1'-N5'	2.027(7)
Ru1'-N6'	2.040(6)	N1'-C1'	1.383(9)	N1'-C9'	1.343(10)
N2'-C10'	1.332(9)	N2'-C18'	1.393(9)	N3'-C19'	1.362(9)
N3'-C27'	1.346(8)	N4'-C28'	1.348(9)	N4'-C36'	1.369(9)
N5'-C37'	1.137(11)	N6'-C43'	1.139(10)	C1'-C2'	1.402(11)
C1'-C6'	1.414(10)	C2'-C3'	1.382(10)	C3'-C4'	1.391(13)
C4'-C5'	1.356(14)	C5'-C6'	1.424(11)	C6'-C7'	1.404(12)
C7'-C8'	1.367(10)	C8'-C9'	1.434(10)	C9'-C10'	1.463(10)
C10'-C11'	1.393(11)	C11'-C12'	1.350(11)	C12'-C13'	1.413(11)
C13'-C14'	1.422(10)	C13'-C18'	1.410(11)	C14'-C15'	1.352(12)
C15'-C16'	1.409(12)	C16'-C17'	1.371(10)	C17'-C18'	1.402(11)
C19'-C20'	1.414(10)	C19'-C24'	1.402(11)	C20'-C21'	1.341(11)
C21'-C22'	1.391(13)	C22'-C23'	1.359(12)	C23'-C24'	1.404(11)
C24'-C25'	1.432(11)	C25'-C26'	1.367(11)	C26'-C27'	1.420(10)

C27'-C28'	1.458(10)	C28'-C29'	1.423(9)	C29'-C30'	1.357(10)
C30'-C31'	1.399(10)	C31'-C32'	1.424(10)	C31'-C36'	1.436(9)
C32'-C33'	1.346(12)	C33'-C34'	1.417(11)	C34'-C35'	1.364(11)
C35'-C36'	1.415(10)	C37'-C38'	1.476(13)	C38'-C39'	1.542(19)
C39'-C40'	1.48(2)	C40'-C41'	1.50(2)	C41'-C42'	1.21(2)
C43'-C44'	1.450(11)	C44'-C45'	1.515(11)	C45'-C46'	1.516(14)
C46'-C47'	1.453(13)	C47'-C48'	1.180(14)	P1'-F1'	1.574(6)
P1'-F2'	1.587(6)	P1'-F3'	1.595(6)	P1'-F4'	1.585(6)
P1'-F5'	1.597(6)	P1'-F6'	1.601(7)	P2'-F7'	1.549(7)
P2'-F8'	1.555(9)	P2'-F9'	1.574(6)	P2'-F10'	1.583(9)
P2'-F11'	1.582(8)	P2'-F12'	1.552(9)		

Table S7.5. Bond Angles in Compound 3

N1-Ru1-N2	77.8(2)	N1-Ru1-N3	94.7(2)	N1-Ru1-N4	170.8(2)
N2-Ru1-N4	95.7(2)	N3-Ru1-N2	82.6(2)	N3-Ru1-N4	77.9(2)
N5-Ru1-N1	88.0(2)	N5-Ru1-N2	92.1(2)	N5-Ru1-N3	173.3(2)
N5-Ru1-N4	98.8(2)	N6-Ru1-N1	96.5(2)	N6-Ru1-N2	170.7(2)
N6-Ru1-N3	90.7(2)	N6-Ru1-N4	89.1(2)	N6-Ru1-N5	95.0(2)
C1-N1-Ru1	128.4(5)	C9-N1-Ru1	111.2(4)	C9-N1-C1	119.3(6)
C10-N2-Ru1	110.7(4)	C10-N2-C18	118.8(6)	C18-N2-Ru1	128.8(5)
C19-N3-Ru1	128.1(5)	C27-N3-Ru1	110.8(4)	C27-N3-C19	118.6(6)
C28-N4-Ru1	111.4(4)	C28-N4-C36	118.3(6)	C36-N4-Ru1	129.4(4)
C37-N5-Ru1	177.9(6)	C43-N6-Ru1	171.5(6)	N1-C1-C2	120.4(6)
N1-C1-C6	120.2(7)	C6-C1-C2	119.3(6)	C3-C2-C1	120.1(7)
C2-C3-C4	120.7(8)	C5-C4-C3	121.0(7)	C4-C5-C6	120.0(7)
C1-C6-C5	118.7(7)	C7-C6-C1	119.2(7)	C7-C6-C5	122.1(7)
C8-C7-C6	119.9(7)	C7-C8-C9	118.4(7)	N1-C9-C8	122.0(6)
N1-C9-C10	115.3(6)	C8-C9-C10	122.7(7)	N2-C10-C9	114.7(6)
N2-C10-C11	122.5(6)	C11-C10-C9	122.7(6)	C12-C11-C10	119.2(6)
C11-C12-C13	120.8(6)	C12-C13-C18	116.7(6)	C14-C13-C12	123.7(7)
C14-C13-C18	119.7(6)	C15-C14-C13	120.7(7)	C14-C15-C16	119.8(7)
C17-C16-C15	121.6(7)	C16-C17-C18	119.9(7)	N2-C18-C13	121.4(6)
N2-C18-C17	120.4(6)	C17-C18-C13	118.2(6)	N3-C19-C24	120.2(6)
C20-C19-N3	120.1(6)	C20-C19-C24	119.8(7)	C21-C20-C19	119.7(7)
C20-C21-C22	121.1(8)	C23-C22-C21	120.7(7)	C22-C23-C24	120.1(8)
C19-C24-C23	118.3(7)	C19-C24-C25	118.2(7)	C23-C24-C25	123.4(7)
C26-C25-C24	120.2(7)	C25-C26-C27	118.9(7)	N3-C27-C26	122.7(7)
N3-C27-C28	115.0(6)	C26-C27-C28	122.3(6)	N4-C28-C27	115.4(6)
N4-C28-C29	122.7(6)	C29-C28-C27	121.7(6)	C30-C29-C28	118.9(6)
C29-C30-C31	120.4(6)	C30-C31-C32	122.8(6)	C30-C31-C36	118.2(6)
C36-C31-C32	119.0(6)	C33-C32-C31	120.6(6)	C32-C33-C34	120.4(7)
C35-C34-C33	120.5(7)	C34-C35-C36	121.0(6)	N4-C36-C31	121.2(6)

N4-C36-C35	120.3(6)	C35-C36-C31	118.5(6)	N5-C37-C38	173.6(7)
C37-C38-C39	110.3(6)	C40-C39-C38	111.8(7)	C41-C40-C39	114.9(7)
C42-C41-C40	175.2(9)	N6-C43-C44	178.8(8)	C43-C44-C45	112.1(7)
C44-C45-C46	113.5(7)	C47-C46-C45	114.6(7)	C48-C47-C46	178.0(11)
F1-P1-F3	179.1(4)	F1-P1-F4	89.3(3)	F1-P1-F6	89.9(3)
F2-P1-F1	90.4(3)	F2-P1-F3	90.3(3)	F2-P1-F4	179.2(3)
F2-P1-F6	90.2(3)	F3-P1-F6	89.4(3)	F4-P1-F3	90.0(3)
F4-P1-F6	89.0(3)	F5-P1-F1	89.9(3)	F5-P1-F2	90.7(3)
F5-P1-F3	90.8(3)	F5-P1-F4	90.1(3)	F5-P1-F6	179.1(3)
F7-P2-F8	89.5(3)	F7-P2-F9	178.4(5)	F7-P2-F10	90.6(3)
F7-P2-F11	89.0(4)	F7-P2-F12	87.1(4)	F8-P2-F10	179.2(4)
F8-P2-F11	90.7(3)	F8-P2-F12	89.1(4)	F9-P2-F8	90.6(4)
F9-P2-F10	89.2(4)	F9-P2-F11	92.7(5)	F9-P2-F12	91.2(5)
F10-P2-F11	90.1(3)	F12-P2-F10	90.2(4)	F12-P2-F11	176.1(5)
N2'-Ru1'-N1'	77.4(2)	N2'-Ru1'-N3'	83.3(2)	N2'-Ru1'-N4'	92.2(2)
N3'-Ru1'-N1'	92.3(2)	N3'-Ru1'-N4'	77.2(2)	N4'-Ru1'-N1'	166.1(2)
N5'-Ru1'-N1'	88.3(3)	N5'-Ru1'-N2'	90.7(3)	N5'-Ru1'-N3'	173.7(3)
N5'-Ru1'-N4'	101.2(2)	N5'-Ru1'-N6'	94.7(3)	N6'-Ru1'-N1'	101.7(2)
N6'-Ru1'-N2'	174.5(3)	N6'-Ru1'-N3'	91.3(2)	N6'-Ru1'-N4'	87.8(2)
C1'-N1'-Ru1'	129.5(6)	C9'-N1'-Ru1'	110.1(4)	C9'-N1'-C1'	119.8(6)
C10'-N2'-Ru1'	111.5(5)	C10'-N2'-C18'	119.1(6)	C18'-N2'-Ru1'	127.4(5)
C19'-N3'-Ru1'	126.0(5)	C27'-N3'-Ru1'	110.6(4)	C27'-N3'-C19'	119.7(6)
C28'-N4'-Ru1'	111.6(4)	C28'-N4'-C36'	119.2(6)	C36'-N4'-Ru1'	128.9(5)
C37'-N5'-Ru1'	174.6(8)	C43'-N6'-Ru1'	173.0(6)	N1'-C1'-C2'	120.4(7)
N1'-C1'-C6'	119.9(7)	C2'-C1'-C6'	119.7(7)	C3'-C2'-C1'	120.1(8)
C2'-C3'-C4'	120.2(8)	C5'-C4'-C3'	121.2(8)	C4'-C5'-C6'	120.3(8)
C1'-C6'-C5'	118.5(8)	C7'-C6'-C1'	119.2(7)	C7'-C6'-C5'	122.2(7)
C8'-C7'-C6'	120.8(7)	C7'-C8'-C9'	117.9(8)	N1'-C9'-C8'	122.2(6)
N1'-C9'-C10'	116.2(6)	C8'-C9'-C10'	121.4(7)	N2'-C10'-C9'	113.9(7)
N2'-C10'-C11'	122.7(6)	C11'-C10'-C9'	123.4(7)	C12'-C11'-C10'	119.0(8)
C11'-C12'-C13'	120.2(8)	C12'-C13'-C14'	123.1(7)	C18'-C13'-C12'	118.6(6)
C18'-C13'-C14'	118.3(7)	C15'-C14'-C13'	120.8(8)	C14'-C15'-C16'	119.9(7)
C17'-C16'-C15'	121.5(7)	C16'-C17'-C18'	118.8(8)	N2'-C18'-C13'	119.3(7)
N2'-C18'-C17'	120.0(7)	C17'-C18'-C13'	120.6(7)	N3'-C19'-C20'	120.9(7)
N3'-C19'-C24'	121.0(7)	C24'-C19'-C20'	118.1(7)	C21'-C20'-C19'	120.8(8)
C20'-C21'-C22'	121.4(7)	C23'-C22'-C21'	118.8(8)	C22'-C23'-C24'	121.6(8)
C19'-C24'-C23'	118.7(7)	C19'-C24'-C25'	118.0(7)	C23'-C24'-C25'	123.3(8)
C26'-C25'-C24'	119.8(7)	C25'-C26'-C27'	118.6(7)	N3'-C27'-C26'	121.8(6)
N3'-C27'-C28'	114.0(6)	C26'-C27'-C28'	124.1(6)	N4'-C28'-C27'	115.4(6)
N4'-C28'-C29'	121.9(6)	C29'-C28'-C27'	122.6(6)	C30'-C29'-C28'	118.9(6)
C29'-C30'-C31'	120.9(6)	C30'-C31'-C32'	123.7(6)	C30'-C31'-C36'	117.9(6)
C32'-C31'-C36'	118.3(6)	C33'-C32'-C31'	121.1(7)	C32'-C33'-C34'	121.0(8)
C35'-C34'-C33'	119.7(7)	C34'-C35'-C36'	121.3(7)	N4'-C36'-C31'	120.7(6)

N4'-C36'-C35'	120.8(6)	C35'-C36'-C31'	118.5(6)	N5'-C37'-C38'	175.1(11)
C37'-C38'-C39'	109.0(10)	C40'-C39'-C38'	116.0(10)	C39'-C40'-C41'	115.0(12)
C42'-C41'-C40'	177.2(15)	N6'-C43'-C44'	177.5(7)	C43'-C44'-C45'	112.2(8)
C46'-C45'-C44'	111.8(8)	C47'-C46'-C45'	112.9(9)	C48'-C47'-C46'	174.4(14)
F1'-P1'-F2'	89.2(4)	F1'-P1'-F3'	178.2(4)	F1'-P1'-F4'	90.7(4)
F1'-P1'-F5'	90.9(4)	F1'-P1'-F6'	91.4(4)	F2'-P1'-F3'	90.4(4)
F2'-P1'-F5'	90.0(4)	F2'-P1'-F6'	88.6(3)	F3'-P1'-F5'	87.3(4)
F3'-P1'-F6'	90.3(4)	F4'-P1'-F2'	179.8(5)	F4'-P1'-F3'	89.7(4)
F4'-P1'-F5'	89.8(4)	F4'-P1'-F6'	91.6(4)	F5'-P1'-F6'	177.2(4)
F7'-P2'-F8'	93.5(5)	F7'-P2'-F9'	178.0(5)	F7'-P2'-F10'	88.0(5)
F7'-P2'-F11'	90.6(5)	F7'-P2'-F12'	86.6(5)	F8'-P2'-F9'	88.1(5)
F8'-P2'-F10'	175.6(6)	F8'-P2'-F11'	90.4(6)	F9'-P2'-F10'	90.5(4)
F9'-P2'-F11'	90.5(4)	F11'-P2'-F10'	85.4(5)	F12'-P2'-F8'	90.6(6)
F12'-P2'-F9'	92.2(5)	F12'-P2'-F10'	93.6(6)	F12'-P2'-F11'	177.1(5)

This report has been created with Olex2 [6], compiled on 2018.04.18 svn.r3501 for OlexSys.

References

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Figure S8 – Crystal Structure Determination of Ru(biq)(bpy)(5-hexynenitrile)$_2$[PF$_6$]$_2$

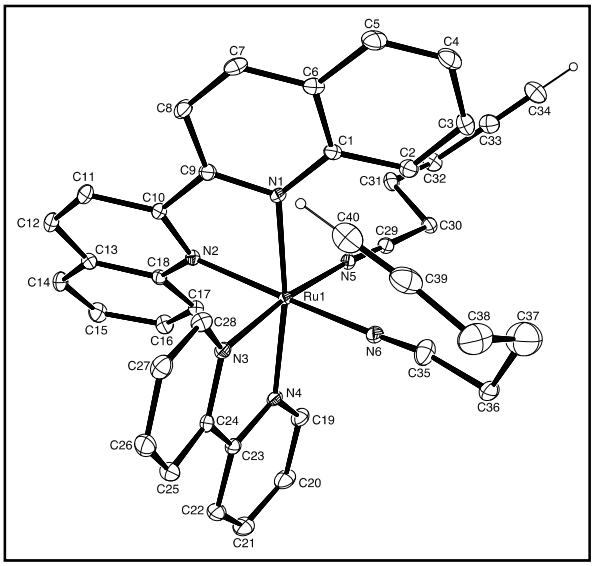

Figure S8.1. ORTEP drawing of the title compound with 50% thermal ellipsoids. This particular compound was synthesized in harsh conditions that promoted cis-alkane conformation for nitrile liagand.

Ru(biq)(bpy)(5-hexynenitrile)$_2$[PF$_6$]$_2$, $C_{44}H_{44}F_{12}N_6OP_2Ru$, crystallizes in the triclinic space group P$\bar{1}$ with a=11.4840(5)Å, b=14.0467(6)Å, c=16.5321(7)Å, □=67.166(2)°, □=83.813(2)°, □=67.008(2)°, V=2259.57(17)Å^3, Z=2, and d_{calc}=1.564 g/cm$_3$. X-ray intensity data were collected on a Bruker D8QUEST [1] CMOS area detector employing graphite-monochromated Mo-K□ radiation (□=0.71073Å) at a temperature of 100K. Preliminary indexing was performed from a series of twenty-four 0.5° rotation frames with exposures of 10 seconds. A total of 1520 frames were collected with a crystal to detector distance of 33.0 mm, rotation widths of 0.5° and exposures of 15 seconds:

scan type	2θ	ω	φ	χ	Frames
ω	7.71	201.40	288.00	54.72	304
ω	7.71	201.40	0.00	54.72	304
ω	7.71	201.40	144.00	54.72	304
ω	7.71	201.40	72.00	54.72	304
ω	7.71	201.40	216.00	54.72	304

Rotation frames were integrated using SAINT [2], producing a listing of unaveraged F^2 and □(F^2) values. A total of 66656 reflections were measured over the ranges 5.974 ≤ 2□ ≤ 55.112°, -14 ≤ h ≤ 14, -18 ≤ k ≤ 18, -21 ≤ l ≤ 21 yielding 10417 unique reflections (R_{int} = 0.0453). The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS [3] (minimum and maximum transmission 0.7183, 0.7456). The structure was solved by direct methods - ShelXT [4]. Refinement was by full-matrix least squares based on F^2 using SHELXL-2017 [5]. All reflections were used during refinement. The weighting scheme used was w=1/[□^{2}(F_o^2)+ (0.0281P)^2 + 4.8088P] where P = (F_o^2 + 2F_c^2)/3. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0426 and wR2=0.0901 for 9062 observed reflections for which F >

4□(F) and R1=0.0521 and wR2=0.0952 and GOF =1.093 for all 10417 unique, non-zero reflections and 642 variables. The maximum □/□ in the final cycle of least squares was 0.002 and the two most prominent peaks in the final difference Fourier were +0.98 and -0.92 e/Å^3.

Table S8.1. lists cell information, data collection parameters, and refinement data. Final positional parameters are given in Table S8.2. Anisotropic thermal parameters are in Table S8.3. Tables S8.4. and S8.5. list bond distances and bond angles. Figure S8.1. is an ORTEP representation of the molecule with 50% probability thermal ellipsoids displayed.

Table S8.1. Summary of Structure Determination of Ru(biq)(bpy)(5-hexynenitrile)$_2$[PF$_6$]$_2$

Empirical formula	$C_{44}H_{44}F_{12}N_6OP_2Ru$
Formula weight	1063.86
Temperature/K	100
Crystal system	triclinic
Space group	$P\bar{1}$
a	11.4840(5)Å
b	14.0467(6)Å
c	16.5321(7)Å
□	67.166(2)°
□	83.813(2)°
□	67.008(2)°
Volume	2259.57(17)Å^3
Z	2
d_{calc}	1.564 g/cm^3
□	0.510 mm^{-1}
F(000)	1080.0
Crystal size, mm	0.15 □ 0.12 □ 0.1
2□ range for data collection	5.974 - 55.112°
Index ranges	-14 ≤ h ≤ 14, -18 ≤ k ≤ 18, -21 ≤ l ≤ 21
Reflections collected	66656
Independent reflections	10417[R(int) = 0.0453]
Data/restraints/parameters	10417/168/642
Goodness-of-fit on F^2	1.093
Final R indexes [I>=2□ (I)]	R_1 = 0.0426, wR_2 = 0.0901
Final R indexes [all data]	R_1 = 0.0521, wR_2 = 0.0952
Largest diff. peak/hole	0.98/-0.92 eÅ^{-3}

Table S8.2 . Refined Positional Parameters for Ru(biq)(bpy)(5-hexynenitrile)$_2$[PF$_6$]$_2$

Atom	*x*	*y*	*z*	U(eq)
Ru1	0.66844(2)	0.70629(2)	0.81263(2)	0.01337(6)
N1	0.70557(19)	0.81355(17)	0.69402(13)	0.0144(4)
N2	0.72064(19)	0.80772(17)	0.85228(14)	0.0149(4)
N3	0.8544(2)	0.59368(17)	0.83610(14)	0.0162(4)
N4	0.6620(2)	0.59413(17)	0.93805(14)	0.0158(4)

N5	0.4802(2)	0.80034(18)	0.79776(14)	0.0171(4)
N6	0.6393(2)	0.60502(18)	0.76345(14)	0.0188(4)
C1	0.6687(2)	0.8377(2)	0.60936(16)	0.0161(5)
C2	0.5681(3)	0.8123(2)	0.59329(17)	0.0198(5)
C3	0.5312(3)	0.8372(2)	0.50909(18)	0.0231(6)
C4	0.5948(3)	0.8868(2)	0.43684(18)	0.0276(6)
C5	0.6904(3)	0.9134(2)	0.45088(18)	0.0268(6)
C6	0.7292(3)	0.8916(2)	0.53677(17)	0.0189(5)
C7	0.8230(3)	0.9239(2)	0.55301(18)	0.0231(6)
C8	0.8507(3)	0.9074(2)	0.63674(18)	0.0210(5)
C9	0.7889(2)	0.8532(2)	0.70621(17)	0.0167(5)
C10	0.8022(2)	0.8448(2)	0.79671(17)	0.0165(5)
C11	0.8843(3)	0.8833(2)	0.82135(18)	0.0223(6)
C12	0.8747(3)	0.8911(2)	0.90167(18)	0.0232(6)
C13	0.7779(2)	0.8682(2)	0.95635(17)	0.0186(5)
C14	0.7539(3)	0.8877(2)	1.03551(18)	0.0233(6)
C15	0.6540(3)	0.8711(2)	1.08385(19)	0.0247(6)
C16	0.5730(3)	0.8365(2)	1.05398(18)	0.0227(6)
C17	0.5952(2)	0.8145(2)	0.97861(17)	0.0176(5)
C18	0.6999(2)	0.8276(2)	0.92880(16)	0.0155(5)
C19	0.5596(3)	0.6004(2)	0.98689(18)	0.0223(6)
C20	0.5667(3)	0.5281(3)	1.07347(19)	0.0284(6)
C21	0.6808(3)	0.4460(3)	1.11125(18)	0.0291(7)
C22	0.7865(3)	0.4367(2)	1.06139(18)	0.0251(6)
C23	0.7744(3)	0.5115(2)	0.97476(17)	0.0180(5)
C24	0.8805(2)	0.5065(2)	0.91559(17)	0.0179(5)
C25	0.9970(3)	0.4188(2)	0.93635(19)	0.0242(6)
C26	1.0904(3)	0.4192(2)	0.8762(2)	0.0271(6)
C27	1.0646(3)	0.5072(2)	0.7957(2)	0.0251(6)
C28	0.9455(3)	0.5923(2)	0.77774(18)	0.0208(5)
C29	0.3732(3)	0.8456(2)	0.78867(17)	0.0183(5)
C30	0.2359(2)	0.9073(2)	0.77935(17)	0.0187(5)
C31	0.2038(3)	1.0186(2)	0.78892(18)	0.0213(5)
C32	0.0608(3)	1.0861(2)	0.78019(18)	0.0240(6)
C33	0.0032(3)	1.1152(2)	0.6942(2)	0.0258(6)
C34	-0.0421(3)	1.1387(3)	0.6248(2)	0.0345(7)
C35	0.6313(3)	0.5502(3)	0.7305(2)	0.0301(7)
C36	0.6253(9)	0.4629(6)	0.7032(4)	0.0337(18)
C36*	0.6103(7)	0.5054(7)	0.6677(6)	0.0353(17)
C37	0.6547(8)	0.4856(8)	0.6045(5)	0.065(2)
C37*	0.7327(5)	0.4025(5)	0.6706(4)	0.0293(12)
C38	0.7960(7)	0.4518(6)	0.5850(5)	0.0478(17)
C38*	0.8536(7)	0.4171(6)	0.6744(5)	0.0472(17)

C39	0.8444(14)	0.5383(10)	0.5753(7)	0.041(2)
C39*	0.8616(12)	0.5197(8)	0.6061(6)	0.036(2)
C40	0.891(3)	0.6014(18)	0.5704(14)	0.044(4)
C40*	0.870(3)	0.6035(15)	0.5571(12)	0.042(3)
P1	0.80039(7)	0.21270(6)	0.94623(5)	0.02430(16)
F1	0.8809(2)	0.08310(17)	0.99572(18)	0.0551(6)
F2	0.8376(2)	0.2340(2)	1.02649(14)	0.0527(6)
F3	0.7230(2)	0.34292(18)	0.90128(19)	0.0680(8)
F4	0.68097(19)	0.19316(18)	0.99772(17)	0.0547(6)
F5	0.9245(2)	0.2294(2)	0.90140(17)	0.0604(7)
F6	0.7692(3)	0.1878(3)	0.86872(17)	0.0859(10)
P2	0.21753(8)	0.72314(7)	0.62604(5)	0.02993(18)
F7	0.1116(2)	0.6955(2)	0.59540(14)	0.0535(6)
F8	0.2936(2)	0.7162(2)	0.54062(14)	0.0572(6)
F9	0.1396(2)	0.85303(19)	0.57360(18)	0.0681(8)
F10	0.14030(17)	0.73130(15)	0.71187(13)	0.0355(4)
F11	0.32290(19)	0.7490(2)	0.65955(16)	0.0515(6)
F12	0.29282(19)	0.59254(17)	0.67909(13)	0.0424(5)
O1	0.5935(2)	0.76812(19)	0.29844(15)	0.0342(5)
C41	0.3730(4)	0.8735(3)	0.2692(3)	0.0516(10)
C42	0.4725(4)	0.7596(3)	0.3051(3)	0.0484(9)
C43	0.6930(4)	0.6633(3)	0.3382(3)	0.0530(10)
C44	0.8171(4)	0.6776(3)	0.3255(3)	0.0497(10)

Table S8.3 . Positional Parameters for Hydrogens in Ru(biq)(bpy)(5-hexynenitrile)$_2$[PF_6]$_2$

Atom	***x***	***y***	***z***	**U(eq)**
H2	0.525811	0.777611	0.641211	0.024
H3	0.462245	0.821174	0.498965	0.028
H4	0.5705	0.90147	0.378729	0.033
H5	0.732169	0.947165	0.402119	0.032
H7	0.867044	0.957112	0.50567	0.028
H8	0.910977	0.932354	0.647896	0.025
H11	0.945352	0.903535	0.782439	0.027
H12	0.933013	0.911861	0.920787	0.028
H14	0.8075	0.912311	1.055253	0.028
H15	0.639252	0.883029	1.137457	0.03
H16	0.501859	0.828241	1.086579	0.027
H17	0.540101	0.790403	0.959839	0.021
H19	0.479688	0.65631	0.961079	0.027
H20	0.492821	0.535421	1.106416	0.034

H21	0.687317	0.39629	1.170729	0.035
H22	0.866431	0.379823	1.086038	0.03
H25	1.012888	0.358538	0.99175	0.029
H26	1.171215	0.359788	0.889959	0.033
H27	1.127344	0.509274	0.753385	0.03
H28	0.92768	0.652096	0.721978	0.025
H30a	0.194329	0.862546	0.82491	0.022
H30b	0.20376	0.921079	0.721009	0.022
H31a	0.245774	1.062872	0.743238	0.026
H31b	0.237221	1.004264	0.847052	0.026
H32a	0.019564	1.042335	0.826925	0.029
H32b	0.044647	1.155729	0.789338	0.029
H34	-0.07844	1.157561	0.568985	0.041
H36a	0.539716	0.460473	0.712792	0.04
H36b	0.687114	0.389038	0.74022	0.04
H36c	0.592454	0.563534	0.607567	0.042
H36d	0.536981	0.482641	0.684314	0.042
H37a	0.618877	0.444836	0.583849	0.079
H37b	0.610536	0.566367	0.569977	0.079
H37c	0.732119	0.336775	0.722646	0.035
H37d	0.730361	0.386274	0.617749	0.035
H38a	0.845491	0.381773	0.633278	0.057
H38b	0.808655	0.436998	0.530151	0.057
H38c	0.864369	0.417733	0.732796	0.057
H38d	0.924775	0.351869	0.668907	0.057
H40	0.929024	0.652214	0.566385	0.053
H40*	0.876656	0.671191	0.517471	0.051
H41a	0.391047	0.91282	0.208825	0.077
H41b	0.371985	0.914712	0.305596	0.077
H41c	0.290311	0.868364	0.269431	0.077
H42a	0.458058	0.721126	0.367301	0.058
H42b	0.469513	0.715444	0.271517	0.058
H43a	0.693176	0.611184	0.311527	0.064
H43b	0.680159	0.631226	0.401781	0.064
H44a	0.830062	0.708227	0.262468	0.075
H44b	0.885838	0.605038	0.353366	0.075
H44c	0.816633	0.729029	0.352188	0.075

Table S8.4 . Bond Distances in Ru(biq)(bpy)(5-hexynenitrile)$_2$[PF_6]$_2$, Å

Ru1-N1	2.080(2)	Ru1-N2	2.073(2)	Ru1-N3	2.068(2)

Ru1-N4	2.076(2)	Ru1-N5	2.027(2)	Ru1-N6	2.031(2)
N1-C1	1.379(3)	N1-C9	1.345(3)	N2-C10	1.348(3)
N2-C18	1.376(3)	N3-C24	1.366(3)	N3-C28	1.345(3)
N4-C19	1.346(3)	N4-C23	1.354(3)	N5-C29	1.137(3)
N6-C35	1.135(4)	C1-C2	1.412(4)	C1-C6	1.422(3)
C2-C3	1.368(4)	C3-C4	1.418(4)	C4-C5	1.357(4)
C5-C6	1.414(4)	C6-C7	1.406(4)	C7-C8	1.364(4)
C8-C9	1.404(3)	C9-C10	1.475(4)	C10-C11	1.414(4)
C11-C12	1.363(4)	C12-C13	1.412(4)	C13-C14	1.415(4)
C13-C18	1.423(4)	C14-C15	1.370(4)	C15-C16	1.408(4)
C16-C17	1.372(4)	C17-C18	1.414(3)	C19-C20	1.385(4)
C20-C21	1.369(5)	C21-C22	1.383(4)	C22-C23	1.391(4)
C23-C24	1.475(4)	C24-C25	1.381(4)	C25-C26	1.382(4)
C26-C27	1.381(4)	C27-C28	1.386(4)	C29-C30	1.464(4)
C30-C31	1.528(4)	C31-C32	1.531(4)	C32-C33	1.471(4)
C33-C34	1.182(4)	C35-C36	1.489(7)	C35-C36*	1.487(7)
C36-C37	1.561(8)	C36*-C37*	1.562(7)	C37-C38	1.540(8)
C37*-C38*	1.492(7)	C38-C39	1.473(7)	C38*-C39*	1.476(7)
C39-C40	1.177(8)	C39*-C40*	1.175(8)	P1-F1	1.591(2)
P1-F2	1.601(2)	P1-F3	1.583(2)	P1-F4	1.594(2)
P1-F5	1.593(2)	P1-F6	1.561(2)	P2-F7	1.594(2)
P2-F8	1.594(2)	P2-F9	1.595(2)	P2-F10	1.609(2)
P2-F11	1.596(2)	P2-F12	1.599(2)	O1-C42	1.429(4)
O1-C43	1.415(4)	C41-C42	1.483(5)	C43-C44	1.498(6)

Table S8.5 . Bond Angles in Ru(biq)(bpy)(5-hexynenitrile)$_2$[PF_6]$_2$, °

N2-Ru1-N1	77.82(8)	N2-Ru1-N4	96.21(8)	N3-Ru1-N1	93.25(8)
N3-Ru1-N2	88.84(8)	N3-Ru1-N4	78.78(8)	N4-Ru1-N1	170.23(8)
N5-Ru1-N1	92.79(8)	N5-Ru1-N2	95.96(8)	N5-Ru1-N3	172.97(8)
N5-Ru1-N4	95.55(8)	N5-Ru1-N6	90.15(9)	N6-Ru1-N1	96.60(8)
N6-Ru1-N2	171.88(8)	N6-Ru1-N3	85.57(9)	N6-Ru1-N4	88.49(8)
C1-N1-Ru1	129.67(16)	C9-N1-Ru1	111.12(16)	C9-N1-C1	118.8(2)
C10-N2-Ru1	110.47(16)	C10-N2-C18	118.3(2)	C18-N2-Ru1	130.53(16)
C24-N3-Ru1	115.26(17)	C28-N3-Ru1	126.14(18)	C28-N3-C24	118.2(2)
C19-N4-Ru1	126.23(18)	C19-N4-C23	118.2(2)	C23-N4-Ru1	115.47(17)
C29-N5-Ru1	174.1(2)	C35-N6-Ru1	173.6(2)	N1-C1-C2	120.6(2)
N1-C1-C6	120.3(2)	C2-C1-C6	119.0(2)	C3-C2-C1	120.4(2)
C2-C3-C4	120.6(3)	C5-C4-C3	119.8(3)	C4-C5-C6	121.2(3)
C5-C6-C1	118.8(2)	C7-C6-C1	118.7(2)	C7-C6-C5	122.5(2)
C8-C7-C6	120.0(2)	C7-C8-C9	119.0(2)	N1-C9-C8	122.7(2)
N1-C9-C10	115.2(2)	C8-C9-C10	121.9(2)	N2-C10-C9	114.4(2)

N2-C10-C11	122.3(2)	C11-C10-C9	123.0(2)	C12-C11-C10	119.2(2)
C11-C12-C13	119.8(2)	C12-C13-C14	122.3(2)	C12-C13-C18	118.3(2)
C14-C13-C18	119.4(2)	C15-C14-C13	120.4(2)	C14-C15-C16	119.9(3)
C17-C16-C15	121.1(3)	C16-C17-C18	120.1(2)	N2-C18-C13	121.0(2)
N2-C18-C17	120.1(2)	C17-C18-C13	118.8(2)	N4-C19-C20	122.3(3)
C21-C20-C19	119.6(3)	C20-C21-C22	118.9(3)	C21-C22-C23	119.3(3)
N4-C23-C22	121.7(3)	N4-C23-C24	114.9(2)	C22-C23-C24	123.4(3)
N3-C24-C23	115.1(2)	N3-C24-C25	121.5(2)	C25-C24-C23	123.4(2)
C24-C25-C26	119.7(3)	C27-C26-C25	119.1(3)	C26-C27-C28	118.9(3)
N3-C28-C27	122.6(3)	N5-C29-C30	177.1(3)	C29-C30-C31	109.9(2)
C30-C31-C32	111.9(2)	C33-C32-C31	113.2(2)	C34-C33-C32	179.4(3)
N6-C35-C36	169.9(4)	N6-C35-C36*	165.5(5)	C35-C36-C37	111.9(6)
C35-C36*-C37*	108.2(5)	C38-C37-C36	115.3(7)	C38*-C37*-C36*	114.6(5)
C39-C38-C37	112.7(9)	C39*-C38*-C37*	114.6(7)	C40-C39-C38	175.2(19)
C40*-C39*-C38*	174.6(15)	F1-P1-F2	88.48(14)	F1-P1-F4	88.19(12)
F1-P1-F5	89.90(13)	F3-P1-F1	176.73(15)	F3-P1-F2	88.27(14)
F3-P1-F4	92.00(14)	F3-P1-F5	89.70(14)	F4-P1-F2	88.75(13)
F5-P1-F2	87.60(13)	F5-P1-F4	175.92(15)	F6-P1-F1	89.53(16)
F6-P1-F2	177.71(18)	F6-P1-F3	93.72(17)	F6-P1-F4	92.33(16)
F6-P1-F5	91.26(16)	F7-P2-F8	90.60(13)	F7-P2-F9	89.51(14)
F7-P2-F10	89.52(12)	F7-P2-F11	178.38(13)	F7-P2-F12	89.47(12)
F8-P2-F9	89.80(15)	F8-P2-F10	179.50(13)	F8-P2-F11	90.77(12)
F8-P2-F12	90.90(13)	F9-P2-F10	89.72(13)	F9-P2-F11	91.36(14)
F9-P2-F12	178.77(13)	F11-P2-F10	89.12(11)	F11-P2-F12	89.64(13)
F12-P2-F10	89.58(10)	C43-O1-C42	112.4(3)	O1-C42-C41	108.9(3)
O1-C43-C44	109.6(3)				

Figure S9 – Crystal Structure Determination of $Ru(biq)_2(4\text{-pentynenitrile})_2$

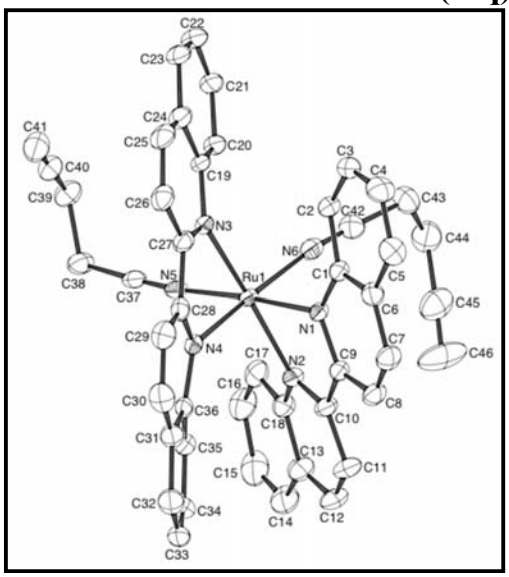

Figure S9.1. ORTEP drawing of the title compound with 50% probability thermal ellipsoids.

$Ru(biq)_2(4\text{-pentynenitrile})_2[PF_6]_2$, $C_{46}H_{34}N_6P_2F_{12}Ru$, crystallizes in the monoclinic space group $P2_1/c$ (systematic absences 0k0: k=odd and h0l: l=odd) with a=11.1852(6)Å, b=16.4112(10)Å, c=23.1159(13)Å, b=96.108(3)°, V=4219.1(4)Å^3, Z=4, and d_{calc}=1.672 g/cm^3 . X-ray intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-Ka radiation (l=0.71073 Å) at a temperature of 100(1)K. Preliminary indexing was performed from a series of thirty-six 0.5° rotation frames with exposures of 10 seconds. A total of 2400 frames were collected with a crystal to detector distance of 37.5 mm, rotation widths of 0.5° and exposures of 30 seconds:

scan type	2θ	ω	ϕ	χ	frames
ϕ	-23.00	315.83	13.08	28.88	732
ϕ	24.50	7.41	155.80	28.88	311
ϕ	22.00	321.06	56.24	41.79	132
ϕ	-23.00	328.34	49.47	79.39	725
ϕ	-23.00	334.21	38.95	73.66	500

Rotation frames were integrated using SAINT[i], producing a listing of unaveraged F^2 and $s(F^2)$ values which were then passed to the SHELXTL[ii] program package for further processing and structure solution. A total of 88028 reflections were measured over the ranges 1.52 £ q £ 27.52°, -14 £ h £ 14, -18 £ k £ 21, -29 £ l £ 30 yielding 9685 unique reflections (Rint = 0.0814). The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS[iii] (minimum and maximum transmission 0.6934, 0.7456).

The structure was solved by direct methods (SHELXS-97[iv]). Refinement was by full-matrix least squares based on F^2 using SHELXL-97.[v] All reflections were used during refinement. The weighting scheme used was $w=1/[s^2(F_o^2)+ (0.0744P)^2 + 16.0979P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0611 and wR2=0.1435 for 6260 observed reflections for which F > 4s(F) and

R1=0.1070 and wR2=0.1676 and GOF =1.016 for all 9685 unique, non-zero reflections and 623 variables.[vi] The maximum D/s in the final cycle of least squares was 0.000 and the two most prominent peaks in the final difference Fourier were +1.577 and -1.362 e/Å^3.

Table S9.1. lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Tables S9.2. and S9.3. Anisotropic thermal parameters are in Table S9.4. Tables S9.5. and S9.6. list bond distances and bond angles. Figure S9.1. is an ORTEP[vii] representation of the molecule with 50% probability thermal ellipsoids displayed.

Table S9.1. Summary of Structure Determination of $Ru(biq)_2(4\text{-pentynenitrile})_2[PF_6]_2$

Empirical formula	$C_{46}H_{34}N_6P_2F_{12}Ru$
Formula weight	1061.80
Temperature	100(1) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/c$
Cell constants:	
a	11.1852(6) Å
b	16.4112(10) Å
c	23.1159(13) Å
b	96.108(3)°
Volume	4219.1(4) Å^3
Z	4
Density (calculated)	1.672 Mg/m^3
Absorption coefficient	0.545 mm^{-1}
F(000)	2136
Crystal size	0.10 x 0.06 x 0.04 mm^3
Theta range for data collection	1.52 to 27.52°
Index ranges	-14 £ h £ 14, -18 £ k £ 21, -29 £ l £ 30
Reflections collected	88028
Independent reflections	9685 [R(int) = 0.0814]
Completeness to theta = 27.52°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6934
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9685 / 473 / 623
Goodness-of-fit on F^2	1.016

Final R indices [I>2sigma(I)]	R1 = 0.0611, wR2 = 0.1435
R indices (all data)	R1 = 0.1070, wR2 = 0.1676
Largest diff. peak and hole	1.577 and -1.362 e.Å^{-3}

Table S9.2. Refined Positional Parameters

Atom	x	y	z	U_{eq}, Å^2
Ru1	0.43347(3)	0.24845(2)	0.386782(14)	0.01759(11)
N1	0.5386(3)	0.3165(2)	0.33467(15)	0.0202(8)
N2	0.3101(4)	0.2772(2)	0.31507(16)	0.0228(8)
N3	0.5735(4)	0.2142(2)	0.44927(16)	0.0221(8)
N4	0.5071(3)	0.1486(2)	0.34806(15)	0.0203(8)
N5	0.3318(3)	0.1740(2)	0.43330(16)	0.0213(8)
N6	0.3824(4)	0.3561(3)	0.42079(17)	0.0261(9)
C1	0.6514(4)	0.3488(3)	0.34970(19)	0.0225(10)
C2	0.6937(4)	0.3641(3)	0.4083(2)	0.0248(10)
C3	0.8053(5)	0.3956(3)	0.4223(2)	0.0295(11)
C4	0.8811(5)	0.4147(4)	0.3796(2)	0.0357(13)
C5	0.8417(5)	0.4033(3)	0.3224(2)	0.0327(12)
C6	0.7248(5)	0.3707(3)	0.3055(2)	0.0266(11)
C7	0.6772(5)	0.3639(3)	0.2467(2)	0.0309(12)
C8	0.5618(5)	0.3409(3)	0.2338(2)	0.0285(11)
C9	0.4920(4)	0.3173(3)	0.27847(19)	0.0228(10)
C10	0.3645(4)	0.2971(3)	0.26754(19)	0.0245(10)
C11	0.3007(5)	0.2999(3)	0.2115(2)	0.0321(12)
C12	0.1829(5)	0.2812(4)	0.2042(2)	0.0361(13)
C13	0.1222(5)	0.2622(3)	0.2529(2)	0.0348(13)
C14	-0.0011(5)	0.2405(4)	0.2473(3)	0.0412(14)
C15	-0.0565(6)	0.2255(4)	0.2957(3)	0.0489(17)
C16	0.0058(5)	0.2361(4)	0.3518(3)	0.0398(14)
C17	0.1260(5)	0.2547(3)	0.3583(2)	0.0306(11)
C18	0.1874(5)	0.2653(3)	0.3092(2)	0.0269(11)
C19	0.5921(5)	0.2386(3)	0.50720(19)	0.0251(11)
C20	0.4991(5)	0.2756(3)	0.5341(2)	0.0281(11)
C21	0.5189(6)	0.3002(3)	0.5916(2)	0.0354(13)
C22	0.6316(6)	0.2889(4)	0.6231(2)	0.0405(14)
C23	0.7210(5)	0.2512(4)	0.5989(2)	0.0378(13)
C24	0.7050(5)	0.2234(3)	0.5401(2)	0.0301(12)
C25	0.7952(5)	0.1822(3)	0.5136(2)	0.0342(13)
C26	0.7705(5)	0.1539(3)	0.4585(2)	0.0300(11)
C27	0.6576(4)	0.1707(3)	0.4270(2)	0.0237(10)
C28	0.6235(4)	0.1368(3)	0.3686(2)	0.0228(10)
C29	0.7030(5)	0.0944(3)	0.3368(2)	0.0307(12)
C30	0.6647(5)	0.0650(3)	0.2830(2)	0.0336(12)
C31	0.5435(5)	0.0720(3)	0.2616(2)	0.0275(11)
C32	0.4958(5)	0.0430(3)	0.2058(2)	0.0330(12)
C33	0.3772(5)	0.0488(3)	0.1882(2)	0.0334(13)
C34	0.2970(5)	0.0778(3)	0.2266(2)	0.0294(11)
C35	0.3391(4)	0.1066(3)	0.2804(2)	0.0246(10)
C36	0.4634(4)	0.1102(3)	0.29740(19)	0.0201(9)
C37	0.2863(4)	0.1324(3)	0.46329(19)	0.0237(10)

C38	0.2305(5)	0.0803(3)	0.5044(2)	0.0313(12)
C39	0.2850(5)	0.0935(4)	0.5673(2)	0.0337(12)
C40	0.4137(5)	0.0701(3)	0.5779(2)	0.0330(12)
C41	0.5167(6)	0.0519(4)	0.5868(3)	0.0404(14)
C42	0.3573(5)	0.4198(3)	0.4331(2)	0.0318(12)
C43	0.3270(5)	0.5043(3)	0.4459(3)	0.0382(13)
C44	0.1966(6)	0.5252(4)	0.4242(3)	0.0451(15)
C45	0.1652(6)	0.5072(4)	0.3612(3)	0.0488(16)
C46	0.1360(6)	0.4918(6)	0.3139(3)	0.071(3)
P1	0.04497(9)	-0.02662(7)	0.36058(4)	0.0273(3)
F1	-0.08338(11)	-0.03106(13)	0.33035(9)	0.0459(8)
F2	0.00683(19)	-0.07675(16)	0.41132(8)	0.0902(17)
F3	0.17331(11)	-0.02217(14)	0.39082(9)	0.0518(9)
F4	0.0831(2)	0.02352(16)	0.30985(8)	0.0783(14)
F5	0.07660(19)	-0.10509(11)	0.32988(11)	0.0767(14)
F6	0.01333(19)	0.05186(11)	0.39128(11)	0.0738(13)
P2	0.1192(3)	0.3523(2)	0.54759(15)	0.0385(10)
F7	0.0511(5)	0.4311(2)	0.5306(3)	0.066(2)
F8	0.1198(7)	0.3743(4)	0.61194(16)	0.080(2)
F9	0.1873(5)	0.2736(3)	0.5645(3)	0.082(2)
F10	0.1186(6)	0.3303(4)	0.48324(16)	0.088(2)
F11	-0.0003(4)	0.3076(3)	0.5494(3)	0.088(2)
F12	0.2387(4)	0.3971(4)	0.5458(4)	0.076(2)
P2'	0.1360(4)	0.3399(3)	0.55373(19)	0.0432(12)
F7'	0.0374(6)	0.3805(4)	0.5126(3)	0.076(2)
F8'	0.0964(8)	0.3891(6)	0.6046(3)	0.083(3)
F9'	0.2346(5)	0.2993(4)	0.5949(3)	0.059(2)
F10'	0.1755(8)	0.2907(5)	0.5029(2)	0.091(3)
F11'	0.0486(6)	0.2719(5)	0.5660(4)	0.094(3)
F12'	0.2234(7)	0.4079(4)	0.5415(4)	0.084(2)

$U_{eq}={}^{1}/_{3}[U_{11}(aa^*)^2+U_{22}(bb^*)^2+U_{33}(cc^*)^2+2U_{12}aa^*bb^*\cos\gamma+2U_{13}aa^*cc^*\cos\beta+2U_{23}bb^*cc^*\cos\alpha]$

Table S9.3. Positional Parameters for Hydrogens

Atom	x	y	z	U_{iso}, Å^2
H2	0.6451	0.3527	0.4375	0.033
H3	0.8322	0.4047	0.4612	0.039
H4	0.9579	0.4351	0.3903	0.047
H5	0.8914	0.4169	0.2940	0.043
H7	0.7250	0.3753	0.2171	0.041
H8	0.5280	0.3405	0.1953	0.038
H11	0.3401	0.3146	0.1796	0.043
H12	0.1415	0.2808	0.1671	0.048
H14	-0.0439	0.2364	0.2107	0.055
H15	-0.1361	0.2082	0.2920	0.065
H16	-0.0352	0.2304	0.3845	0.053
H17	0.1666	0.2602	0.3953	0.041
H20	0.4242	0.2836	0.5133	0.037
H21	0.4570	0.3242	0.6094	0.047
H22	0.6450	0.3078	0.6611	0.054
H23	0.7946	0.2431	0.6209	0.050
H25	0.8709	0.1744	0.5336	0.045

H26	0.8275	0.1235	0.4414	0.040
H29	0.7822	0.0863	0.3525	0.041
H30	0.7189	0.0404	0.2605	0.045
H32	0.5471	0.0198	0.1812	0.044
H33	0.3481	0.0335	0.1506	0.044
H34	0.2147	0.0773	0.2152	0.039
H35	0.2852	0.1240	0.3059	0.033
H38a	0.2407	0.0236	0.4939	0.042
H38b	0.1450	0.0916	0.5015	0.042
H39a	0.2771	0.1506	0.5771	0.045
H39b	0.2396	0.0620	0.5929	0.045
H41	0.5974	0.0377	0.5939	0.054
H43a	0.3803	0.5406	0.4277	0.051
H43b	0.3398	0.5130	0.4876	0.051
H44a	0.1435	0.4946	0.4466	0.060
H44b	0.1832	0.5827	0.4309	0.060
H46	0.1121	0.4792	0.2751	0.095

Table S9.4. Refined Thermal Parameters (U's)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru1	0.01999(18)	0.01973(18)	0.01259(16)	0.00107(15)	-0.00037(11)	0.00058(17)
N1	0.025(2)	0.019(2)	0.0158(18)	0.0021(15)	-0.0002(15)	0.0025(16)
N2	0.026(2)	0.022(2)	0.0186(18)	0.0004(15)	-0.0029(16)	0.0017(17)
N3	0.029(2)	0.020(2)	0.0169(18)	0.0037(15)	-0.0021(16)	-0.0041(17)
N4	0.026(2)	0.018(2)	0.0169(18)	0.0034(15)	0.0026(15)	-0.0003(16)
N5	0.020(2)	0.027(2)	0.0163(18)	-0.0008(16)	-0.0016(15)	-0.0045(17)
N6	0.028(2)	0.030(2)	0.0197(19)	0.0034(17)	0.0005(16)	-0.0006(19)
C1	0.027(3)	0.020(2)	0.019(2)	0.0015(18)	-0.0001(19)	0.003(2)
C2	0.030(3)	0.025(3)	0.019(2)	0.0014(19)	-0.0001(19)	0.001(2)
C3	0.036(3)	0.028(3)	0.024(2)	0.000(2)	-0.002(2)	-0.006(2)
C4	0.026(3)	0.041(3)	0.039(3)	-0.002(2)	0.000(2)	-0.011(2)
C5	0.026(3)	0.036(3)	0.038(3)	0.000(2)	0.011(2)	-0.004(2)
C6	0.031(3)	0.024(3)	0.025(2)	0.000(2)	0.005(2)	-0.002(2)
C7	0.038(3)	0.033(3)	0.022(2)	0.002(2)	0.010(2)	0.001(2)
C8	0.037(3)	0.030(3)	0.018(2)	0.002(2)	0.004(2)	0.004(2)
C9	0.031(3)	0.019(2)	0.018(2)	0.0002(18)	0.0006(19)	0.003(2)
C10	0.028(3)	0.027(3)	0.018(2)	0.0004(19)	-0.0025(19)	0.004(2)
C11	0.034(3)	0.042(3)	0.018(2)	0.001(2)	-0.004(2)	0.003(2)
C12	0.037(3)	0.042(3)	0.026(3)	0.003(2)	-0.012(2)	0.003(3)
C13	0.032(3)	0.035(3)	0.034(3)	0.003(2)	-0.011(2)	0.006(2)
C14	0.031(3)	0.041(4)	0.047(3)	0.007(3)	-0.014(2)	0.001(3)
C15	0.029(3)	0.042(4)	0.072(5)	0.015(3)	-0.011(3)	-0.003(3)
C16	0.028(3)	0.043(4)	0.048(3)	0.011(3)	0.003(2)	0.006(2)
C17	0.029(3)	0.029(3)	0.033(3)	0.005(2)	0.002(2)	0.010(2)
C18	0.028(3)	0.025(3)	0.027(2)	0.0012(19)	-0.002(2)	0.004(2)
C19	0.034(3)	0.023(3)	0.016(2)	0.0049(18)	-0.0065(18)	-0.010(2)
C20	0.038(3)	0.028(3)	0.018(2)	0.0014(19)	-0.001(2)	-0.007(2)
C21	0.057(4)	0.031(3)	0.017(2)	0.002(2)	0.000(2)	-0.013(3)
C22	0.062(4)	0.039(3)	0.018(2)	0.002(2)	-0.006(3)	-0.011(3)
C23	0.047(3)	0.037(3)	0.025(2)	0.008(3)	-0.017(2)	-0.015(3)
C24	0.032(3)	0.031(3)	0.026(2)	0.006(2)	-0.005(2)	-0.004(2)
C25	0.026(3)	0.038(3)	0.035(3)	0.012(2)	-0.013(2)	-0.003(2)
C26	0.025(3)	0.029(3)	0.035(3)	0.007(2)	-0.003(2)	0.002(2)
C27	0.024(3)	0.026(3)	0.020(2)	0.0058(19)	0.0006(19)	-0.004(2)
C28	0.023(3)	0.018(2)	0.027(2)	0.0045(19)	0.0021(19)	-0.002(2)
C29	0.024(3)	0.031(3)	0.037(3)	0.004(2)	0.006(2)	0.007(2)
C30	0.036(3)	0.030(3)	0.037(3)	-0.002(2)	0.016(2)	0.004(2)
C31	0.035(3)	0.026(3)	0.022(2)	-0.001(2)	0.009(2)	0.000(2)
C32	0.045(3)	0.031(3)	0.026(3)	-0.004(2)	0.013(2)	0.001(2)
C33	0.056(4)	0.025(3)	0.019(2)	-0.001(2)	0.002(2)	-0.008(3)
C34	0.037(3)	0.024(3)	0.027(3)	-0.004(2)	-0.002(2)	-0.001(2)
C35	0.029(3)	0.022(2)	0.022(2)	0.0008(19)	0.0001(19)	0.002(2)
C36	0.027(3)	0.016(2)	0.018(2)	0.0022(17)	0.0051(18)	-0.0008(19)
C37	0.026(3)	0.028(3)	0.016(2)	-0.0033(19)	-0.0025(18)	0.000(2)
C38	0.032(3)	0.040(3)	0.022(2)	0.002(2)	0.001(2)	-0.012(2)
C39	0.037(3)	0.041(3)	0.024(2)	0.004(2)	0.009(2)	0.001(3)
C40	0.041(3)	0.032(3)	0.025(3)	0.004(2)	0.005(2)	-0.003(3)
C41	0.040(4)	0.038(3)	0.043(3)	0.009(3)	0.001(3)	-0.001(3)

C42	0.037(3)	0.031(3)	0.027(3)	-0.002(2)	0.004(2)	-0.001(2)
C43	0.049(4)	0.028(3)	0.038(3)	-0.005(2)	0.007(3)	0.000(3)
C44	0.055(4)	0.042(4)	0.040(3)	-0.001(3)	0.013(3)	0.005(3)
C45	0.041(4)	0.065(5)	0.041(4)	0.010(3)	0.005(3)	-0.005(3)
C46	0.050(4)	0.141(8)	0.023(3)	0.009(4)	0.009(3)	-0.036(5)
P1	0.0267(7)	0.0305(7)	0.0248(6)	-0.0028(5)	0.0037(5)	0.0042(5)
F1	0.0386(19)	0.056(2)	0.0424(19)	-0.0058(16)	0.0006(15)	0.0056(16)
F2	0.056(3)	0.132(4)	0.088(3)	0.076(3)	0.031(2)	0.039(3)
F3	0.0381(19)	0.069(3)	0.047(2)	-0.0177(18)	-0.0042(15)	0.0011(17)
F4	0.056(3)	0.119(4)	0.062(3)	0.041(3)	0.012(2)	-0.011(3)
F5	0.040(2)	0.071(3)	0.118(4)	-0.056(3)	-0.001(2)	0.014(2)
F6	0.068(3)	0.066(3)	0.081(3)	-0.042(2)	-0.023(2)	0.025(2)
P2	0.0371(18)	0.053(2)	0.0251(17)	-0.0029(16)	0.0000(14)	0.0079(15)
F7	0.066(4)	0.055(4)	0.078(5)	0.012(3)	0.004(4)	0.013(3)
F8	0.102(6)	0.099(6)	0.035(3)	-0.011(3)	-0.004(3)	0.021(4)
F9	0.109(5)	0.061(3)	0.074(5)	0.002(3)	0.004(4)	0.036(4)
F10	0.130(7)	0.098(7)	0.036(3)	-0.014(3)	0.006(3)	0.014(4)
F11	0.071(4)	0.067(5)	0.126(7)	-0.004(4)	0.013(4)	-0.016(3)
F12	0.049(3)	0.094(5)	0.086(6)	0.006(4)	0.008(3)	0.002(3)
P2'	0.069(3)	0.031(2)	0.029(2)	0.0019(17)	0.003(2)	0.0073(18)
F7'	0.075(4)	0.082(5)	0.066(5)	0.009(4)	-0.018(4)	0.022(4)
F8'	0.095(7)	0.091(6)	0.065(4)	-0.023(4)	0.015(4)	0.038(4)
F9'	0.047(4)	0.076(6)	0.053(4)	0.020(4)	0.006(3)	0.011(4)
F10'	0.108(7)	0.110(7)	0.053(4)	-0.036(4)	0.003(4)	0.038(4)
F11'	0.094(5)	0.100(5)	0.078(6)	0.032(4)	-0.033(5)	-0.048(5)
F12'	0.087(4)	0.073(5)	0.089(7)	0.036(4)	0.000(5)	-0.017(4)

The form of the anisotropic displacement parameter is:

$\exp[-2\pi^2(a^{*2}U_{11}h^2+b^{*2}U_{22}k^2+c^{*2}U_{33}l^2+2b^*c^*U_{23}kl+2a^*c^*U_{13}hl+2a^*b^*U_{12}hk)]$

Table S9.5. Bond Distances, Å

Ru1-N6	2.039(4)	Ru1-N5	2.050(4)	Ru1-N4	2.079(4)
Ru1-N3	2.091(4)	Ru1-N1	2.093(4)	Ru1-N2	2.095(4)
N1-C9	1.347(6)	N1-C1	1.378(6)	N2-C10	1.351(6)
N2-C18	1.379(6)	N3-C27	1.328(6)	N3-C19	1.392(6)
N4-C28	1.351(6)	N4-C36	1.374(6)	N5-C37	1.132(6)
N6-C42	1.127(7)	C1-C2	1.410(6)	C1-C6	1.424(6)
C2-C3	1.357(7)	C3-C4	1.404(7)	C4-C5	1.362(8)
C5-C6	1.429(7)	C6-C7	1.409(7)	C7-C8	1.347(7)
C8-C9	1.413(6)	C9-C10	1.459(7)	C10-C11	1.412(6)
C11-C12	1.346(8)	C12-C13	1.408(8)	C13-C14	1.417(8)
C13-C18	1.425(7)	C14-C15	1.357(9)	C15-C16	1.415(9)
C16-C17	1.371(8)	C17-C18	1.398(7)	C19-C20	1.407(7)
C19-C24	1.425(7)	C20-C21	1.383(7)	C21-C22	1.399(8)
C22-C23	1.348(9)	C23-C24	1.426(7)	C24-C25	1.409(8)
C25-C26	1.356(7)	C26-C27	1.415(7)	C27-C28	1.472(7)
C28-C29	1.398(7)	C29-C30	1.361(8)	C30-C31	1.397(8)
C31-C32	1.426(7)	C31-C36	1.427(6)	C32-C33	1.349(8)
C33-C34	1.410(7)	C34-C35	1.368(7)	C35-C36	1.405(7)
C37-C38	1.466(7)	C38-C39	1.531(7)	C39-C40	1.485(8)
C40-C41	1.186(8)	C42-C43	1.465(8)	C43-C44	1.530(9)
C44-C45	1.489(9)	C45-C46	1.137(9)	P1-F6	1.5299
P1-F4	1.5300	P1-F5	1.5300	P1-F3	1.5300
P1-F1	1.5300	P1-F2	1.5300	P2-F7'	1.244(7)
P2-F8'	1.496(8)	P2-F12'	1.499(9)	P2-F11	1.5299
P2-F12	1.5300	P2-F9	1.5300	P2-F7	1.5301
P2-F8	1.5301	P2-F10	1.5301	P2-F11'	1.618(8)
P2-F10'	1.621(8)	P2-F9'	1.821(7)	F7-F7'	0.935(9)
F7-P2'	1.822(7)	F8-P2'	1.488(7)	F9-F9'	0.934(9)
F9-P2'	1.244(7)	F9-F10'	1.446(9)	F9-F11'	1.556(10)
F10-F10'	0.986(8)	F10-F7'	1.447(9)	F10-P2'	1.628(7)
F11-F11'	0.863(9)	F11-F7'	1.552(10)	F11-P2'	1.608(8)
F12-P2'	1.510(9)	P2'-F12'	1.5299	P2'-F8'	1.5300
P2'-F7'	1.5300	P2'-F10'	1.5300	P2'-F9'	1.5301
P2'-F11'	1.5301				

Table S9.6. Bond Angles, °

N6-Ru1-N5	96.89(16)	N6-Ru1-N4	171.36(16)	N5-Ru1-N4	91.35(15)
N6-Ru1-N3	100.73(16)	N5-Ru1-N3	83.92(15)	N4-Ru1-N3	77.51(15)
N6-Ru1-N1	87.57(15)	N5-Ru1-N1	175.32(15)	N4-Ru1-N1	84.25(15)
N3-Ru1-N1	96.64(15)	N6-Ru1-N2	85.51(16)	N5-Ru1-N2	101.18(15)
N4-Ru1-N2	95.44(15)	N3-Ru1-N2	171.49(15)	N1-Ru1-N2	77.72(15)
C9-N1-C1	119.3(4)	C9-N1-Ru1	112.1(3)	C1-N1-Ru1	128.0(3)
C10-N2-C18	119.0(4)	C10-N2-Ru1	112.5(3)	C18-N2-Ru1	127.6(3)
C27-N3-C19	119.1(4)	C27-N3-Ru1	112.7(3)	C19-N3-Ru1	127.8(3)
C28-N4-C36	118.4(4)	C28-N4-Ru1	111.9(3)	C36-N4-Ru1	127.4(3)
C37-N5-Ru1	172.6(4)	C42-N6-Ru1	171.2(4)	N1-C1-C2	121.1(4)
N1-C1-C6	119.9(4)	C2-C1-C6	119.0(5)	C3-C2-C1	120.2(5)
C2-C3-C4	121.8(5)	C5-C4-C3	119.7(5)	C4-C5-C6	120.6(5)
C7-C6-C1	119.0(5)	C7-C6-C5	122.2(5)	C1-C6-C5	118.6(4)
C8-C7-C6	119.3(5)	C7-C8-C9	120.4(5)	N1-C9-C8	121.3(5)
N1-C9-C10	115.8(4)	C8-C9-C10	122.8(4)	N2-C10-C11	121.8(5)
N2-C10-C9	115.5(4)	C11-C10-C9	122.7(4)	C12-C11-C10	120.0(5)
C11-C12-C13	120.0(5)	C12-C13-C14	122.1(5)	C12-C13-C18	118.6(5)
C14-C13-C18	119.3(5)	C15-C14-C13	119.8(6)	C14-C15-C16	120.6(6)
C17-C16-C15	120.6(6)	C16-C17-C18	120.0(5)	N2-C18-C17	120.6(4)
N2-C18-C13	120.1(5)	C17-C18-C13	119.3(5)	N3-C19-C20	120.5(4)
N3-C19-C24	119.8(5)	C20-C19-C24	119.6(4)	C21-C20-C19	120.0(5)
C20-C21-C22	120.3(6)	C23-C22-C21	120.8(5)	C22-C23-C24	121.2(5)
C25-C24-C19	119.1(5)	C25-C24-C23	123.0(5)	C19-C24-C23	117.9(5)
C26-C25-C24	119.3(5)	C25-C26-C27	119.8(5)	N3-C27-C26	122.4(4)
N3-C27-C28	115.6(4)	C26-C27-C28	121.9(5)	N4-C28-C29	121.9(4)
N4-C28-C27	114.5(4)	C29-C28-C27	123.5(5)	C30-C29-C28	120.1(5)
C29-C30-C31	119.5(5)	C30-C31-C32	123.2(5)	C30-C31-C36	118.5(4)
C32-C31-C36	118.3(5)	C33-C32-C31	120.7(5)	C32-C33-C34	120.4(5)
C35-C34-C33	120.6(5)	C34-C35-C36	120.2(5)	N4-C36-C35	120.6(4)
N4-C36-C31	120.4(4)	C35-C36-C31	119.0(4)	N5-C37-C38	177.4(5)
C37-C38-C39	112.2(4)	C40-C39-C38	113.7(4)	C41-C40-C39	179.3(7)
N6-C42-C43	176.7(6)	C42-C43-C44	112.3(5)	C45-C44-C43	113.2(5)
C46-C45-C44	176.6(7)	F6-P1-F4	90.0	F6-P1-F5	180.0
F4-P1-F5	90.0	F6-P1-F3	90.0	F4-P1-F3	90.0
F5-P1-F3	90.0	F6-P1-F1	90.0	F4-P1-F1	90.0
F5-P1-F1	90.0	F3-P1-F1	180.0	F6-P1-F2	90.0
F4-P1-F2	180.0	F5-P1-F2	90.0	F3-P1-F2	90.0
F1-P1-F2	90.0	F7'-P2-F8'	103.9(5)	F7'-P2-F12'	103.8(5)
F8'-P2-F12'	92.5(4)	F7'-P2-F11	67.1(5)	F8'-P2-F11	86.5(7)
F12'-P2-F11	170.2(5)	F7'-P2-F12	112.9(5)	F8'-P2-F12	93.5(7)
F12'-P2-F12	9.8(5)	F11-P2-F12	180.0	F7'-P2-F9	142.4(4)
F8'-P2-F9	104.0(5)	F12'-P2-F9	99.6(5)	F11-P2-F9	90.0
F12-P2-F9	90.0	F7'-P2-F7	37.6(4)	F8'-P2-F7	76.0(5)
F12'-P2-F7	80.3(5)	F11-P2-F7	90.0	F12-P2-F7	90.0
F9-P2-F7	180.0	F7'-P2-F8	118.1(5)	F8'-P2-F8	14.5(4)
F12'-P2-F8	91.4(7)	F11-P2-F8	90.0	F12-P2-F8	90.0
F9-P2-F8	90.0	F7-P2-F8	90.0	F7'-P2-F10	61.9(5)
F8'-P2-F10	165.5(4)	F12'-P2-F10	88.5(7)	F11-P2-F10	90.0
F12-P2-F10	90.0	F9-P2-F10	90.0	F7-P2-F10	90.0
F8-P2-F10	180.0	F7'-P2-F11'	97.4(5)	F8'-P2-F11'	87.9(5)

F12'-P2-F11'	158.1(5)	F11-P2-F11'	31.7(3)	F12-P2-F11'	148.3(3)
F9-P2-F11'	59.1(4)	F7-P2-F11'	120.9(4)	F8-P2-F11'	83.6(5)
F10-P2-F11'	96.4(5)	F7'-P2-F10'	97.2(4)	F8'-P2-F10'	158.1(5)
F12'-P2-F10'	87.7(5)	F11-P2-F10'	96.8(5)	F12-P2-F10'	83.2(5)
F9-P2-F10'	54.5(3)	F7-P2-F10'	125.5(3)	F8-P2-F10'	143.7(3)
F10-P2-F10'	36.3(3)	F11'-P2-F10'	83.8(3)	F7'-P2-F9'	173.2(5)
F8'-P2-F9'	80.8(3)	F12'-P2-F9'	80.7(3)	F11-P2-F9'	108.7(4)
F12-P2-F9'	71.3(4)	F9-P2-F9'	30.8(4)	F7-P2-F9'	149.2(4)
F8-P2-F9'	66.4(4)	F10-P2-F9'	113.6(4)	F11'-P2-F9'	77.7(3)
F10'-P2-F9'	77.7(3)	F7'-F7-P2	54.4(4)	F7'-F7-P2'	57.1(4)
P2-F7-P2'	2.7(2)	P2'-F8-P2	11.4(3)	F9'-F9-P2'	88.1(7)
F9'-F9-F10'	129.6(10)	P2'-F9-F10'	68.9(4)	F9'-F9-P2	92.1(6)
P2'-F9-P2	4.0(3)	F10'-F9-P2	65.9(3)	F9'-F9-F11'	118.6(9)
P2'-F9-F11'	65.2(4)	F10'-F9-F11'	92.2(4)	P2-F9-F11'	63.3(3)
F10'-F10-F7'	124.5(7)	F10'-F10-P2	76.9(4)	F7'-F10-P2	49.3(3)
F10'-F10-P2'	66.5(4)	F7'-F10-P2'	59.3(3)	P2-F10-P2'	10.4(2)
F11'-F11-P2	79.8(6)	F11'-F11-F7'	124.8(8)	P2-F11-F7'	47.6(3)
F11'-F11-P2'	69.1(5)	P2-F11-P2'	10.7(3)	F7'-F11-P2'	57.9(3)
P2'-F12-P2	11.4(3)	F9-P2'-F8	104.4(5)	F9-P2'-F12	103.2(5)
F8-P2'-F12	92.4(4)	F9-P2'-F12'	112.7(5)	F8-P2'-F12'	91.9(7)
F12-P2'-F12'	9.8(5)	F9-P2'-F8'	118.2(4)	F8-P2'-F8'	14.5(4)
F12-P2'-F8'	93.0(7)	F12'-P2'-F8'	90.0	F9-P2'-F7'	142.4(4)
F8-P2'-F7'	104.3(4)	F12-P2'-F7'	99.3(5)	F12'-P2'-F7'	90.0
F8'-P2'-F7'	90.0	F9-P2'-F10'	61.8(4)	F8-P2'-F10'	165.5(4)
F12-P2'-F10'	87.1(7)	F12'-P2'-F10'	90.0	F8'-P2'-F10'	180.0
F7'-P2'-F10'	90.0	F9-P2'-F9'	37.6(4)	F8-P2'-F9'	75.7(4)
F12-P2'-F9'	80.7(5)	F12'-P2'-F9'	90.0	F8'-P2'-F9'	90.0
F7'-P2'-F9'	180.0	F10'-P2'-F9'	90.0	F9-P2'-F11'	67.3(5)
F8-P2'-F11'	88.1(7)	F12-P2'-F11'	170.2(5)	F12'-P2'-F11'	180.0
F8'-P2'-F11'	90.0	F7'-P2'-F11'	90.0	F10'-P2'-F11'	90.0
F9'-P2'-F11'	90.0	F9-P2'-F11	97.9(5)	F8-P2'-F11	88.6(5)
F12-P2'-F11	157.9(5)	F12'-P2'-F11	148.2(3)	F8'-P2'-F11	82.7(5)
F7'-P2'-F11	59.2(3)	F10'-P2'-F11	97.3(5)	F9'-P2'-F11	120.7(3)
F11'-P2'-F11	31.8(3)	F9-P2'-F10	96.9(4)	F8-P2'-F10	158.2(5)
F12-P2'-F10	87.1(5)	F12'-P2'-F10	84.0(5)	F8'-P2'-F10	143.8(3)
F7'-P2'-F10	54.4(3)	F10'-P2'-F10	36.2(3)	F9'-P2'-F10	125.6(3)
F11'-P2'-F10	96.0(5)	F11-P2'-F10	83.9(3)	F9-P2'-F7	173.3(5)
F8-P2'-F7	81.0(3)	F12-P2'-F7	80.4(3)	F12'-P2'-F7	70.7(4)
F8'-P2'-F7	66.9(4)	F7'-P2'-F7	30.9(4)	F10'-P2'-F7	113.1(4)
F9'-P2'-F7	149.1(4)	F11'-P2'-F7	109.3(4)	F11-P2'-F7	78.0(3)
F10-P2'-F7	77.5(3)	F7-F7'-P2	88.0(7)	F7-F7'-F10	129.3(10)
P2-F7'-F10	68.8(4)	F7-F7'-P2'	92.1(6)	P2-F7'-P2'	4.1(3)
F10-F7'-P2'	66.2(3)	F7-F7'-F11	118.8(9)	P2-F7'-F11	65.3(4)
F10-F7'-F11	92.3(4)	P2'-F7'-F11	62.9(3)	P2-F8'-P2'	11.4(3)
F9-F9'-P2'	54.3(4)	F9-F9'-P2	57.1(4)	P2'-F9'-P2	2.8(2)
F10-F10'-F9	124.7(7)	F10-F10'-P2'	77.3(5)	F9-F10'-P2'	49.3(3)
F10-F10'-P2	66.8(4)	F9-F10'-P2	59.5(3)	P2'-F10'-P2	10.5(2)
F11-F11'-P2'	79.1(6)	F11-F11'-F9	124.4(8)	P2'-F11'-F9	47.5(3)
F11-F11'-P2	68.5(5)	P2'-F11'-P2	10.5(3)	F9-F11'-P2	57.6(3)
P2-F12'-P2'	11.4(3)				

[i] Bruker (2009) SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.

[ii] Bruker (2009) SHELXTL. Bruker AXS Inc., Madison, Wisconsin, USA.

[iii] Sheldrick, G.M. (2007) SADABS. University of Gottingen, Germany.

[iv] Sheldrick, G.M. (2008) Acta Cryst. A64,112-122.

[v] Sheldrick, G.M. (2008) Acta Cryst. A64,112-122.

[vi] $R1 = \Sigma||F_o| - |F_c|| / \Sigma |F_o|$

$wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{½}$

$GOF = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{½}$

where n = the number of reflections and p = the number of parameters refined.

[vii] "ORTEP-II: A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations". C.K. Johnson (1976) ORNL-5138.