Supplementary Information

Addition of $[CH(CN)_2]^-$ and $[TCNE]^{\bullet -}$ to $Ru^{VI}\equiv N$ bearing 8-quinolinolato ligands

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Experimental Section

Materials

The 8-hydroxyquinoline ligands were purchased from Acros. Malononitrile and tetracyanoethene were purchased from Aldrich. NaTCNE,[1] $[N^nBu_4][Ru(N)Cl_4]$ and $[N^nBu_4][Ru(N^{15})Cl_4]$[2] were prepared by literature procedures. All other chemicals were of reagent grade and were used without further purification.

Physical measurements

IR spectra were obtained from KBr discs by using a Bomen MB-120 FTIR spectrophotometer. UV/visible spectra were recorded on a Perkin-Elmer Lamda 19 spectrophotometer. ^{1}H NMR spectra were recorded on a Varian (300 MHz) FT NMR spectrometer. The chemical shifts (δ ppm) were reported with reference to tetramethylsilane (TMS) or residue solvent peaks.

$Ru^{VI}(N)(Q)_2Cl$ (1a). 8-hydroxyquinoline (70 mg, 0.48 mmol) was added to a solution

of $[N^nBu_4][Ru(N)Cl_4]$ (120 mg, 0.24 mmol) in methanol (8 mL), and the mixture was stirred at room temperature for 15 min. 2,6-dimethylpyridine (200 μL) was then added dropwise, resulting in the immediate formation of a dark brown microcrystalline solid. After stirring for another 30 min, the dark brown crystalline solid was filtered, washed with methanol and diethyl ether. Yield (80 mg, 76%). Calc. for $C_{18}H_{12}N_3O_2ClRu$: C, 49.3; H, 2.8; N, 9.6 %. Found: C, 49.45; H, 2.9; N, 9.4 %. λ_{max} (CH_3CN)/ nm: 237 (ε/$mol^{-1}dm^3$ cm^{-1} 14 900), 262 (19 800), 388 (2 600). ν_{max}(KBr)/cm^{-1}: 1034($Ru^{14}N$)/1009($Ru^{15}N$). δ_H (300 MHz, CD_2Cl_2): 6.72(1H, d, $^3J_{HH}$ = 7.80, Q), 7.20(1H, d, $^3J_{HH}$ = 8.10, Q), 7.40(1H, dd, $^3J_{HH}$ = 8.10, $^4J_{HH}$ =5.10, Q), 7.48(3H, m, Q), 7.63(1H, d, $^3J_{HH}$ =7.50, Q), 7.71(1H, m, Q), 7.79(1H, dd, $^3J_{HH}$ = 9, $^4J_{HH}$ = 3.9, Q), 8.47(1H, d, $^3J_{HH}$ = 8.7, Q), 8.61(1H, d, $^3J_{HH}$ = 7.5, Q), 9.25(1H, d, $^3J_{HH}$ = 3.9, Q). m/z(CH_2Cl_2): 390$[M\text{-}Cl\text{-}N]^+$, 404 $[M\text{-}Cl]^+$.

$Ru^{VI}(N)(MeQ)_2Cl$ (1b). The complex was synthesized by a similar procedure to **1a**, using 2-methyl-8-hydroxyquinoline (77 mg, 0.48 mmol). Yield (60 mg, 54%). Calc. for $C_{20}H_{16}N_3O_2ClRu$: C, 51.45; H, 3.45; N, 9.0%. Found: C, 51.6; H, 3.7; N, 8.9%. λ_{max}(CH_3CN)/nm: 237 (ε/$mol^{-1}dm^3$ cm^{-1} 22 300), 262 (28 600), 388 (3 900). ν_{max}(KBr)/cm^{-1}: 1033($Ru^{14}N$)/1009($Ru^{15}N$). δ_H (300 MHz, CD_3CN): 3.42(6H, s, 2 × CH_3), 6.37(1H, d, $^3J_{HH}$ = 7.50, Q), 7.20(1H, d, $^3J_{HH}$ = 9.00, Q), 7.28(2H, dd, $^3J_{HH}$ =

8.40, $^{4}J_{HH}$ = 5.7, Q), 7.43(2H, d, $^{3}J_{HH}$ = 7.50, Q), 7.65(1H, t, $^{3}J_{HH}$ = 7.80, Q), 7.78(1H, d, $^{3}J_{HH}$ = 8.40, Q), 8.36(1H, d, $^{3}J_{HH}$ = 8.40, Q), 8.46(1H, d, $^{3}J_{HH}$ = 8.1, Q). m/z (acetone): 418[M-Cl-N]$^{+}$, 432 [M-Cl]$^{+}$.

Reaction of $Ru^{VI}(N)Q_2Cl$ with $NCCH_2CN$

$[C_5H_{12}N][Ru^{II}\{HN=C(CN)_2\}(MeQ)_2Cl]$ (2). 1b (120 mg, 0.26 mmol) and $NCCH_2CN$ (20 mg, 0.31 mmol) were dissolved in 10 mL acetone at room temperature. Piperidine (50.8 μL, 0.52 mmol) was then slowly added to the solution with stirring, resulting in the immediate formation of a red microcrystalline solid. The red solid was filtered, washed with acetone (2 mL) and then diethyl ether (10 mL). Yield (80 mg, 50%). Calc. for $C_{28}H_{29}N_6O_2ClRu$: C, 54.4; H, 4.7; N, 13.6%. Found: C, 54.3; H, 4.7; N, 13.5%. $\lambda_{max}(CH_3CN)$/nm: 350(ε/mol^{-1}dm^3 cm^{-1} 8 300), 440(12 200), 521(9 100). ν_{max}(KBr)/cm^{-1}: 2194(CN), 3203(NH), 2956(CH), 1561. δ_H (300 MHz, CD_2Cl_2): 1.70(10H, s, CH_2), 2.68(6H, s, CH_3), 2.81(2H, s, NH), 6.73(1H, d, $^{3}J_{HH}$ = 8.70, Q), 6.93(2H, dd, $^{3}J_{HH}$ = 7.80, $^{4}J_{HH}$ = 3.30, Q), 6.98(1H, d, $^{3}J_{HH}$ = 7.50, Q), 7.19(1H, d, $^{3}J_{HH}$ = 7.50, Q), 7.35(3H, m, Q), 7.77(1H, d, $^{3}J_{HH}$ = 8.40, Q), 8.00(1H, d, $^{3}J_{HH}$ = 8.40, Q) 17.47(1H, s, N(H)=C). m/z(CH_3OH): 444, [M-Cl-(NHC(CN)$_2$)]$^{-}$, 479 [M-(NHCC(CN)$_2$)]$^{-}$, 504[M-CN-2H]$^{-}$, 531 [M-H]$^{-}$

Reaction of $Ru^{VI}(N)Q_2Cl$ with NaTCNE

$Ru^{II}Q_2(L^1)$ (3). **1a** (120 mg, 0.26 mmol) was suspended in methanol (10 mL) and NaTCNE (40 mg, 0.26 mmol) was added. The dark brown nitrido complex rapidly dissolved to give a green solution. The mixture was stirred for 12 h at room temperature, during this time the solution slowly turned red. The solvent was removed and the reddish brown residue was dissolved in CH_2Cl_2, filtered and loaded onto a neutral alumina column. Elution with dichloromethane/methanol (60:1) gave a red band which was dried to give a red solid. Recrystallization from dichloromethane/ diethyl ether gave a red crystalline solid. Yield (50 mg, 39%). Calc. for $C_{22}H_{17}N_5O_3Ru$: C, 52.8; H, 3.4; N, 14.0%. Found: C, 53.0; H, 3.5; N, 13.9%. $\lambda_{max}(CH_3CN)$/nm: 354(ε/$mol^{-1}dm^3$ cm^{-1} 6 400), 473(13 100). ν_{max}(KBr)/cm^{-1}: 2194(CN), 1561. δ_H(300 MHz, CD_2Cl_2): 3.91(3H, s, CH_3O), 6.55(1H, m, Q), 6.70(1H, d, $^3J_{HH}$ = 8.10, Q), 6.86(1H, dd, $^3J_{HH}$ = 8.10, $^4J_{HH}$ = 4.80, Q), 6.94(3H, m, Q), 7.07(1H, t, Q), 7.24(1H, dd, $^3J_{HH}$ = 8.70, $^5J_{HH}$ = 5.40, Q), 7.40(1H, t, $^3J_{HH}$ = 7.80, Q), 7.56(1H, d, $^3J_{HH}$ = 4.80, Q), 7.90(1H, d, $^3J_{HH}$ = 8.10, Q), 7.98(1H, d, $^3J_{HH}$ = 7.80, Q), 14.30(1H, s, N(H)=C), 16.60(1H, s, N(H)=C). m/z(CH_3OH): 501 $[M]^+$, 524$[M+Na]^+$

$Ru^{II}Q_2(L^2)$ (4). NaTCNE (40 mg, 0.26 mmol) was added to **1a** (120 mg, 0.26 mmol) dissolved in 1:1 acetone/MeOH (16 mL), the dark brown solution immediately turned

green, and the solution was further stirred for 12 h at room temperature to give a red solution. The solvent was removed and the brown red residue was dissolved in acetone, loaded onto a silica column and eluted with acetone/methanol (20:1). The reddish-purple band was collected, and recrystallization of the resulting solid from acetone/diethyl ether gave red single crystals suitable for X-ray crystallography. Yield (56 mg, 39%). Calc. for $C_{25}H_{22}N_4O_5Ru$: C, 53.7; H, 4.0; N, 10.0%. Found: C, 53.5; H, 3.75; N, 10.2%. λ_{max} (CH_3CN)/nm: 350(ε/mol^{-1}dm^3 cm^{-1} 9 300), 462(15 800), 524(14 400). ν_{max}(KBr)/cm^{-1}: 1760(CO), 1570. δ_H(300 MHz, CD_2Cl_2): 1.27(6H, s, $C(CH_3)_2$), 4.17(3H, s, CH_3O), 6.75(1H, d, $^3J_{HH}$ = 7.50, Q), 6.83(1H, d, $^3J_{HH}$ = 3.90, Q), 6.87(3H, m, Q), 6.98(1H, d, $^3J_{HH}$ = 3.90 , Q), 7.06(1H, m, Q), 7.22(1H, dd, $^3J_{HH}$ = 8.40, $^4J_{HH}$ = 5.10, Q), 7.36(1H, t, $^3J_{HH}$ = 8.10, Q), 7.48(1H, d, $^3J_{HH}$ = 4.20, Q), 7.89(1H, d, $^3J_{HH}$ = 7.80, Q), 8.01(1H, d, $^3J_{HH}$ = 8.10, Q) 16.50(1H, s, N(H)=C). m/z(CH_3OH): 561 $[M+H]^+$, 583$[M+Na]^+$.

Crystal Structure Determination.

Crystals of compound **2**, **3** and **4** were obtained for X-ray diffraction analysis. Crystal data and structure refinement details are listed in Table S1. Selected bond angles and bond lengths are given in Table S2. Crystals of suitable dimensions coated with paratone-N and mounted on a nylon cryoloop were used for X-ray diffraction analysis.

X-ray diffraction data were collected on an Oxford Diffraction Gemini S Ultra 4-circle kappa diffractometer with a 92 mm diagonal Sapphire CCD detector using monochromatized Mo-K_α radiation (λ = 0.71073 Å) or Cu-K_α radiation (λ = 1.54178 Å) at 173 K or 293K. Data collection was made with 1° oscillation step of omega (ω) and the data were processed using CrysAlis[3]. The images were interpreted and intensities were integrated using program CrysAlis. Structures were solved and refined using full-matrix least-squares based on F^2 with program SHELXS-97[4] and SHELXL-97[4] within WinGX[5]. Metal and many non-hydrogen atoms were located according to direct method. The positions of other non-hydrogen atoms were found after successful refinement using program SHELXL-97. H atoms were generated by program SHELXL-97. The positions of H atoms were calculated based on riding mode with thermal parameters equal to 1.2 times or 1.5 times that of the associated C atoms and 1.2 times that of the associated N atoms , all these were participated in the calculation of final R-indices.

Table S1. Crystal data and structure refinement details for compound **2-4**.

Compound	**2**	**3· (0.625H_2O + 0.25CH_3CH_2OH)**	**4· (0.875H_2O)**
Formula	$C_{28}H_{29}N_6O_2ClRu$	$C_{22.50}H_{19.75}N_5O_{3.88}Ru$	$C_{25}H_{23.75}N_4O_{5.88}Ru$
Formula weight	618.09	523.25	575.30
Crystal system	Triclinic	Tetragonal	Monoclinic
Space group	P-1	I-4	P2(1)/n
Unit cell dimensions a, b, c (Å) α, β, γ (deg)	a = 9.1223(5) b = 10.4936(6) c = 14.8426(9) α = 79.785(5) β = 86.546(5) γ = 72.825(5)	a = 31.5680(2) b = 31.5680(2) c = 11.1516(2)	a = 15.20680(10) b = 18.9057(2) c = 17.7568(2) β = 104.0680(10)
Cell volume ($Å^3$)	1335.90(13)	11113.0(2)	4951.88(8)
Z	2	16	8
D_{calcd} ($g/cm^{3)}$	1.537	1.251	1.543
μ (mm^{-1})	0.725	4.835	5.532
F_{000}	632.0	4236.0	2342.0
Temperature (K)	173(2)	173(2)	293(2)
Radiation	MoKα	CuKα	CuKα
λ (Å)	0.71073	1.54178	1.54178
$\theta_{min,\ max}$ (°)	3.1, 25.0	4.0, 66.9	3.4, 67.00
R_{int}	0.0614	0.0349	0.0201
R_{all}, R_{obs}	0.0761, 0.0448	0.0421, 0.0350	0.0334, 0.0259
wR_{all}, wR_{obs}	0.0732, 0.0687	0.1070, 0.1043	0.0699, 0.0679

Flack	–	-0.017(9)	–
Measured reflections: total, unique	9441, 4543	19101, 8921	26771, 8816
Goodness-of-fit on F^2	0.906	1.086	1.050

Table S2. Selected bond lengths (Å) and angles (°) of compounds **2-4**.

2			
Ru(1) – N(3)	1.903(3)	Ru(1) – N(1)	2.145(3)
N(3) – C(1)	1.344(5)	Ru(1) – N(2)	2.098(3)
N(5) – C(2)	1.150(6)	Ru(1) – O(1)	2.063(2)
N(4) – C(3)	1.149(5)	Ru(1) – O(2)	2.012(3)
C(1) – N(3) – Ru(1)	139.1(3)	C(2) – C(1) – C(3)	116.1(4)
N(4) – C(3) – C(1)	177.4(5)	N(5) – C(2) – C(1)	175.5(4)
3			
Ru(1) – N(3)	2.063(4)	Ru(1) – N(1)	2.055(5)
Ru(1) – N(4)	1.922(4)	Ru(1) – N(2)	2.037(5)
N(3) – C(20)	1.284(7)	Ru(1) – O(1)	2.056(4)
N(4) – C(21)	1.326(8)	Ru(1) – O(2)	2.085(3)
N(5) – C(22)	1.149(8)	C(21) – C(22)	1.410(7)

Ru(1) – N(3) – C(20)	114.3(4)	N(5) – C(22) – C(21)	179.7(9)
Ru(1) – N(4) – C(21)	118.6(4)	C(20) – O(3) – C(19)	116.5(5)
N(4)- Ru(1) – N(3)	78.5(2)		
4			
Ru(1) – N(3)	2.050(2)	O(5) – C(22)	1.381(4)
Ru(1) – N(4)	1.947(2)	O(5) – C(23)	1.460(3)
N(3) – C(20)	1.281(3)	Ru(1) – N(1)	2.055(2)
N(4) – C(21)	1.325(3)	Ru(1) – N(2)	2.056(2)
N(4) – C(23)	1.495(4)	Ru(1) – O(1)	2.035(2)
O(4) – C(22)	1.190(3)	Ru(1) – O(2)	2.067(2)
Ru(1) – N(3) – C(20)	115.8(2)	N(4) – C(21) – C(22)	113.1(2)
Ru(1) – N(4) – C(21)	117.4(2)	C(21) – N(4) – C(23)	107.3(2)
N(3) – Ru(1) – N(4)	78.0(1)	C(22) – O(5) – C(23)	110.5(2)
O(5) – C(23) – N(4)	103.7(2)	C(20) – O(3) – C(19)	115.9(2)
O(4) – C(22) – C(21)	133.7(3)		

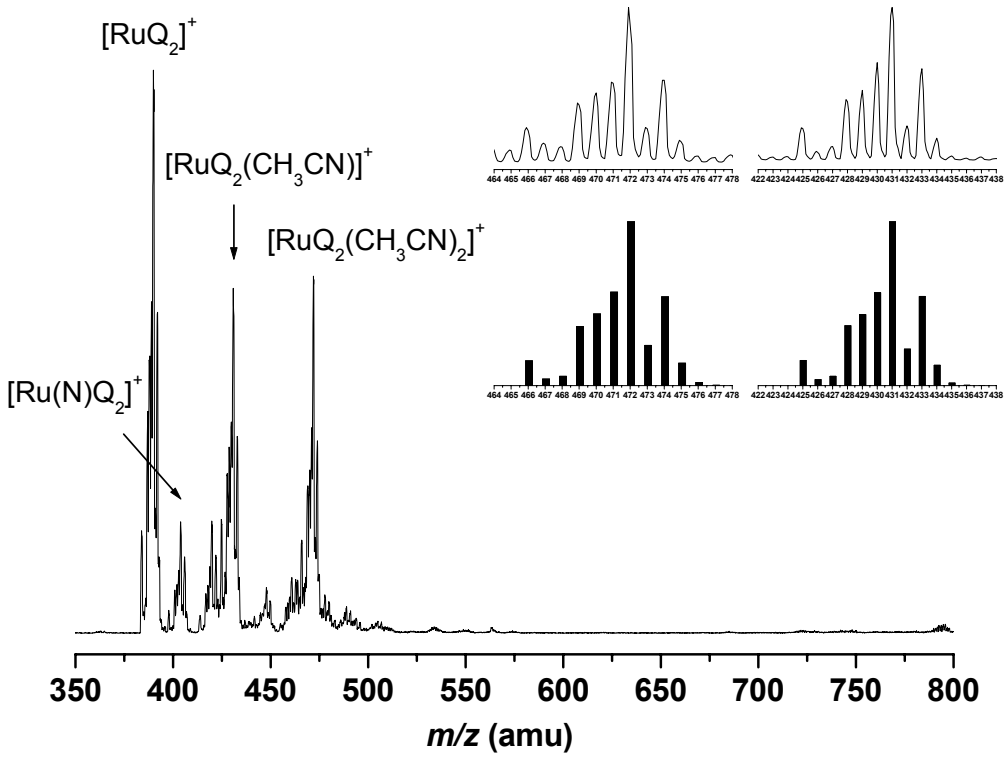

Figure S1. ESI-MS obtained at 0.5 h after the dissolution of **1a** in acetonitrile at 23 ^{0}C. Inset: isotopic pattern of peaks at m/z = 431 and 472 (top) and simulated patterns (bottom).

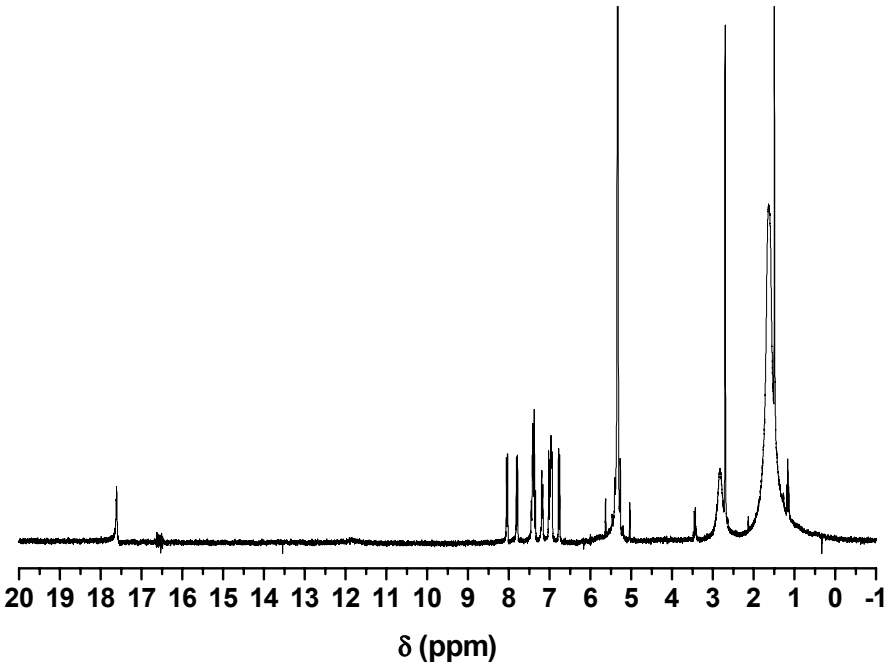

Figure S2. ^{1}H NMR spectrum of **2** in CD_2Cl_2.

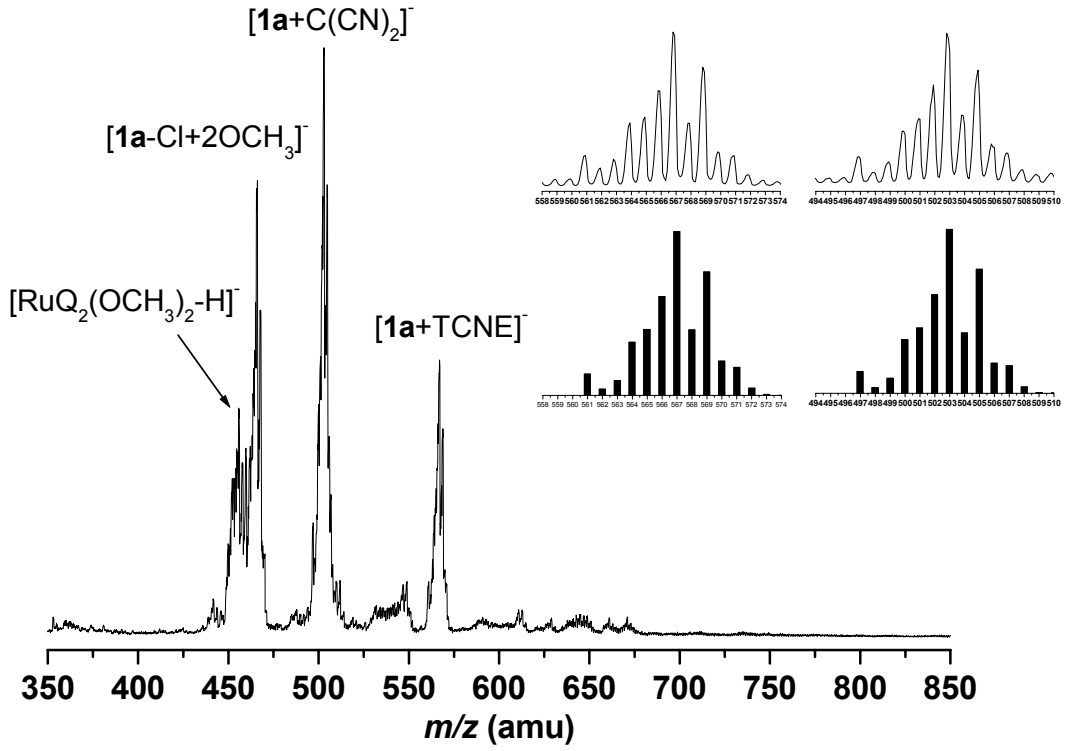

Figure S3. ESI-MS of **1a** in methanol obtained immediately after addition of NaTCNE at 0°C. Inset: isotopic patterns of peak at m/z = 566 and 502 (top) and simulated pattern (bottom).

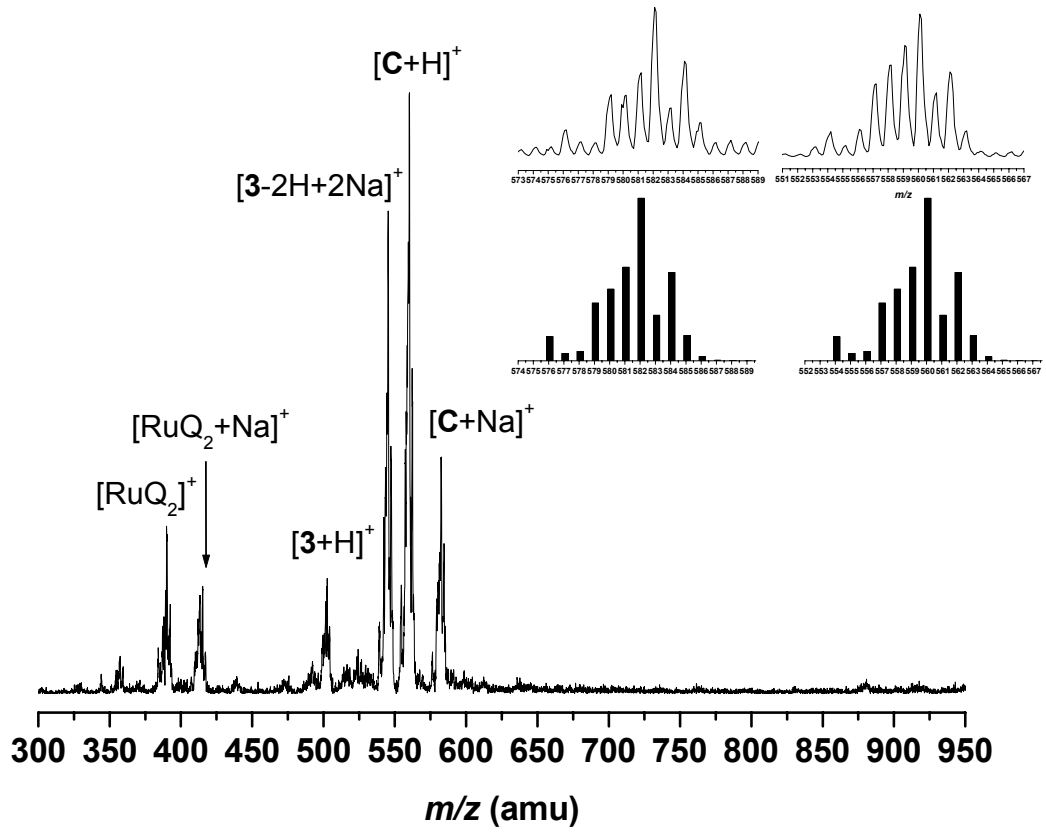

Figure S4. ESI-MS of reaction of **3** with piperidine in acetone after 24 h. Inset: isotopic pattern of peaks at m/z = 560 and 582 and simulated patterns

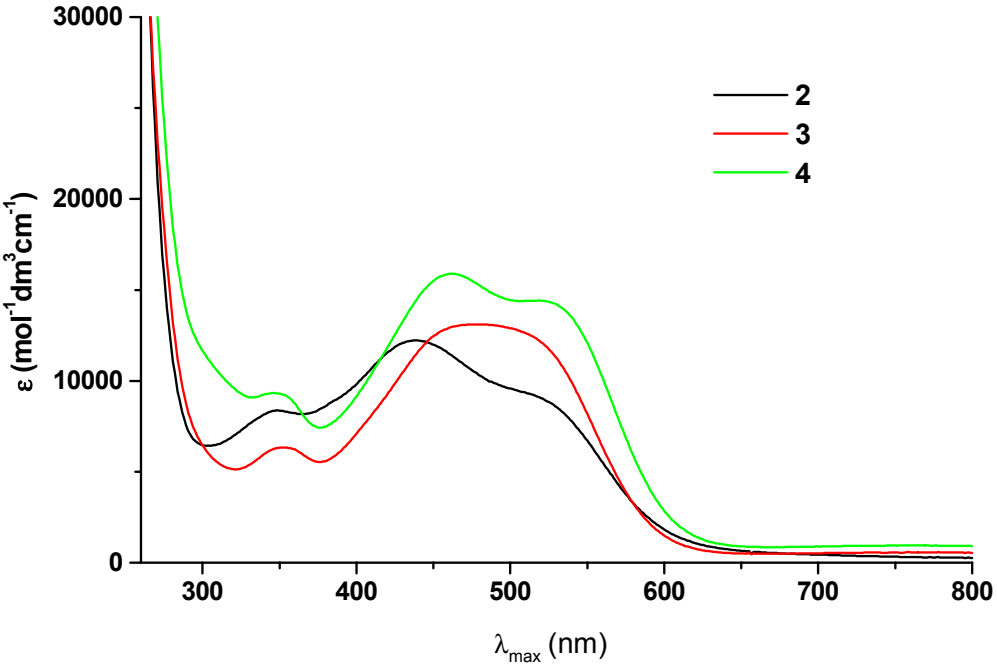

Figure S2. UV/Vis spectrum of compounds **2-4** in acetonitrile.

References:

1. Ganesan, S. V. Rosokha, J. L. K. Kochi *J. Am. Chem. Soc.* **2003**, *125*, 2559-2571.

2. W. P. Griffith, D. Pawson, *J. Chem. Soc.* **1973**, 1315. V.

3. CrysAlis, Oxford Diffraction Ltd.,Version 1.171.33.46, 2009.

4. G. M. Sheldrick *SHELXS97* and *SHELXL97*, Program for Crystal Structure Solution and Refinements; University of Göttingen: Germany, 1997.

5. L. J. Farrugia, *J. Appl. Cryst.* **1999**, 32, 837-838.