Electronic Supplementary Information

Quantitative Determination of $Ru(bpy)_3^{2+}$ Cation in Photochemical Reactions by Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry

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Sample/quencher mixture stability test

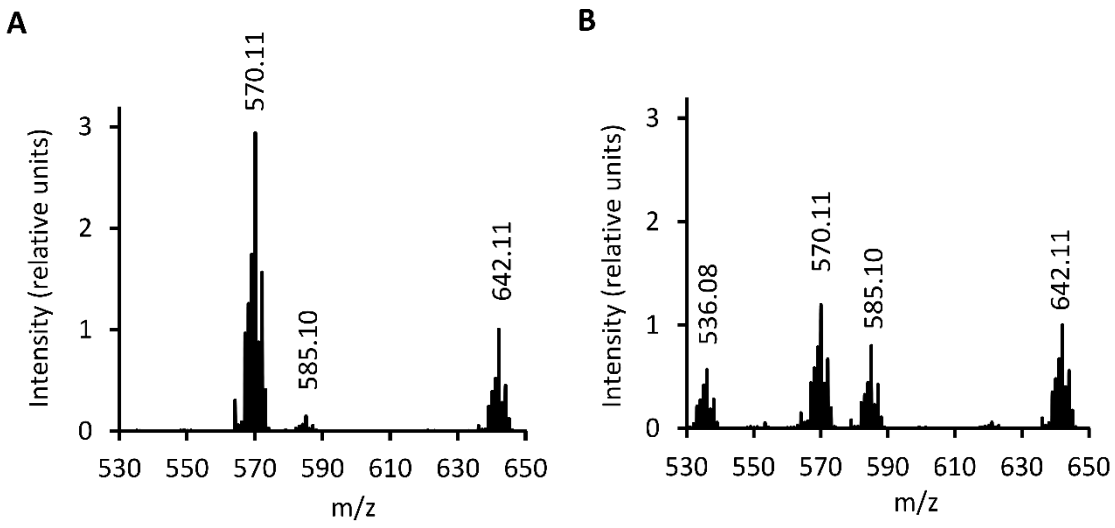

Figure S-1. MALDI spectra of the reaction mixture that was irradiated 10 minutes in the presence (A) and absence (B) of the quenching solution. Signal intensities were normalized to the peak at m/z 642.11 corresponding to the IS

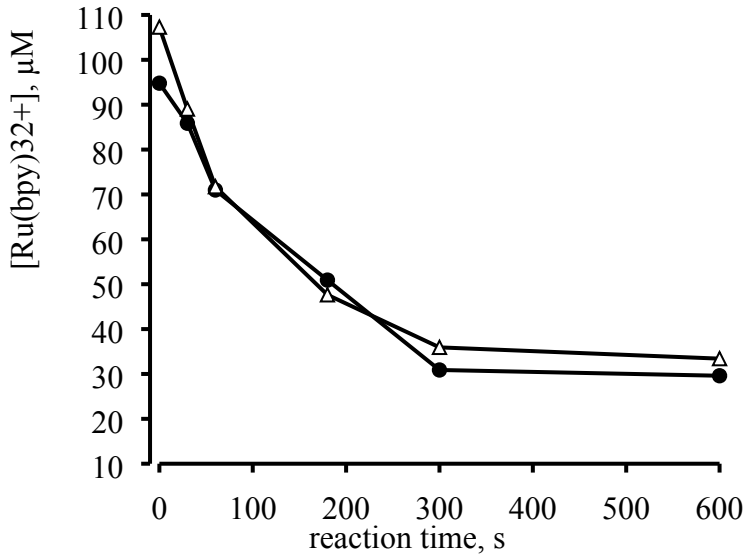

Figure S-2. Results of the MALDI MS analysis performed right after the photochemical reaction (•) and results of the MALDI MS analysis performed the next day on the same samples (Δ).

Isotopic patterns of the $Ru(bpy)_3^+$ and $Ru(phen)_3^+$ signals

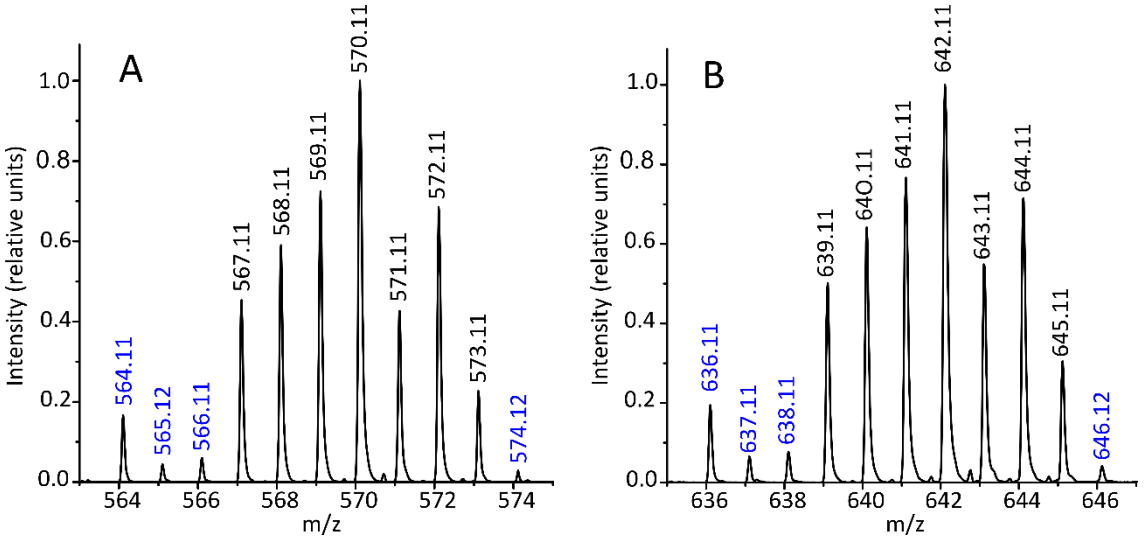

*Figure S-3. Isotopic patterns of the $Ru(bpy)_3^+$ (**A**) and $Ru(phen)_3^+$ (**B**) signals. A ratio of the area under the most intensive $Ru(bpy)_3^+$ peak (m/z 570.11) to the area under the most intensive $Ru(phen)_3^+$ peak (m/z 642.11) was used as an analytical signal in this work. Additionally, within-day reproducibility, accuracy, and linearity were calculated, when a ratio of the area under the seven most intensive $Ru(bpy)_3^+$ peaks (m/z 567.11, 568.11, 569.11, 570.11, 571.11, 572.11, and 573.11) to the area under the seven most intensive $Ru(phen)_3^+$ peaks (m/z 639.11, 640.11, 641.11, 642.11, 643.11, 644.11, and 645.11) was used as an analytical signal (Tabel S-2). However, this "seven peaks" approach did not give any improvement and was not applied for other calculations in this work.*

Assay validation

Table S-1. Within-day reproducibility, accuracy, and linearity using S_{570}/S_{642} as an analytical signal.

$[Ru(bpy)_3^{2+}]$ (μM)	1		2		3		4		5	
	RSD (%)	accuracy (% error)	RSD (%)	accuracy (% error)	RSD (%)	accuracy (% error)	RSD (%)	accuracy (% error)	RSD (%)	accuracy (% error)
90	15.4	3.2	8.7	3.4	2.0	11.6	4.0	7.9	5.7	12.4
50	2.5	2.8	8.5	4.4	6.4	2.3	7.4	12.3	4.8	6.3
15	7.6	0.1	6.8	6.1	7.4	2.6	8.6	4.0	6.7	9.9
R^2	0.990		0.968		0.997		0.992		0.972	

Table S-2. Within-day reproducibility, accuracy, and linearity using (S_{567} + S_{568} + S_{569} + S_{570} + S_{571} + S_{572} + S_{573})/(S_{639} + S_{640} + S_{641} + S_{642} + S_{643} + S_{644} + S_{645}) as an analytical signal.

$[Ru(bpy)_3^{2+}]$ (μM)	1		2		3		4		5	
	RSD (%)	accuracy (% error)	RSD (%)	accuracy (% error)	RSD (%)	accuracy (% error)	RSD (%)	accuracy (% error)	RSD (%)	accuracy (% error)
90	16.3	3.6	10.9	4.8	2.3	16.6	2.6	4.3	8.5	6.8
50	3.9	5.6	9.0	6.4	5.8	6.7	8.7	15.3	4.6	6.4
15	8.6	4.9	9.3	8.1	5.8	4.4	10.1	4.4	9.0	10.9
R^2	0.990		0.955		0.993		0.988		0.952	

Table S-3. Between-day reproducibility, accuracy, and linearity S_{570}/S_{642} as an analytical signal.

$[Ru(bpy)_3^{2+}]$ (μM)	day 1		day 2		day 3		day 4		day 5	
	RSD (%)	accuracy (% error)	RSD (%)	accuracy (% error)	RSD (%)	accuracy (% error)	RSD (%)	accuracy (% error)	RSD (%)	accuracy (% error)
90	7.9	14.5	5.6	9.0	15.4	3.2	6.4	8.7	3.4	3.3
50	12.3	5.1	4.5	5.9	2.5	2.8	5.4	9.7	1.8	6.7
15	9.3	1.4	5.2	4.6	7.6	0.1	6.6	1.7	4.4	13.7
R^2	0.974		0.985		0.990		0.970		0.987	

LDI mass spectra of $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$

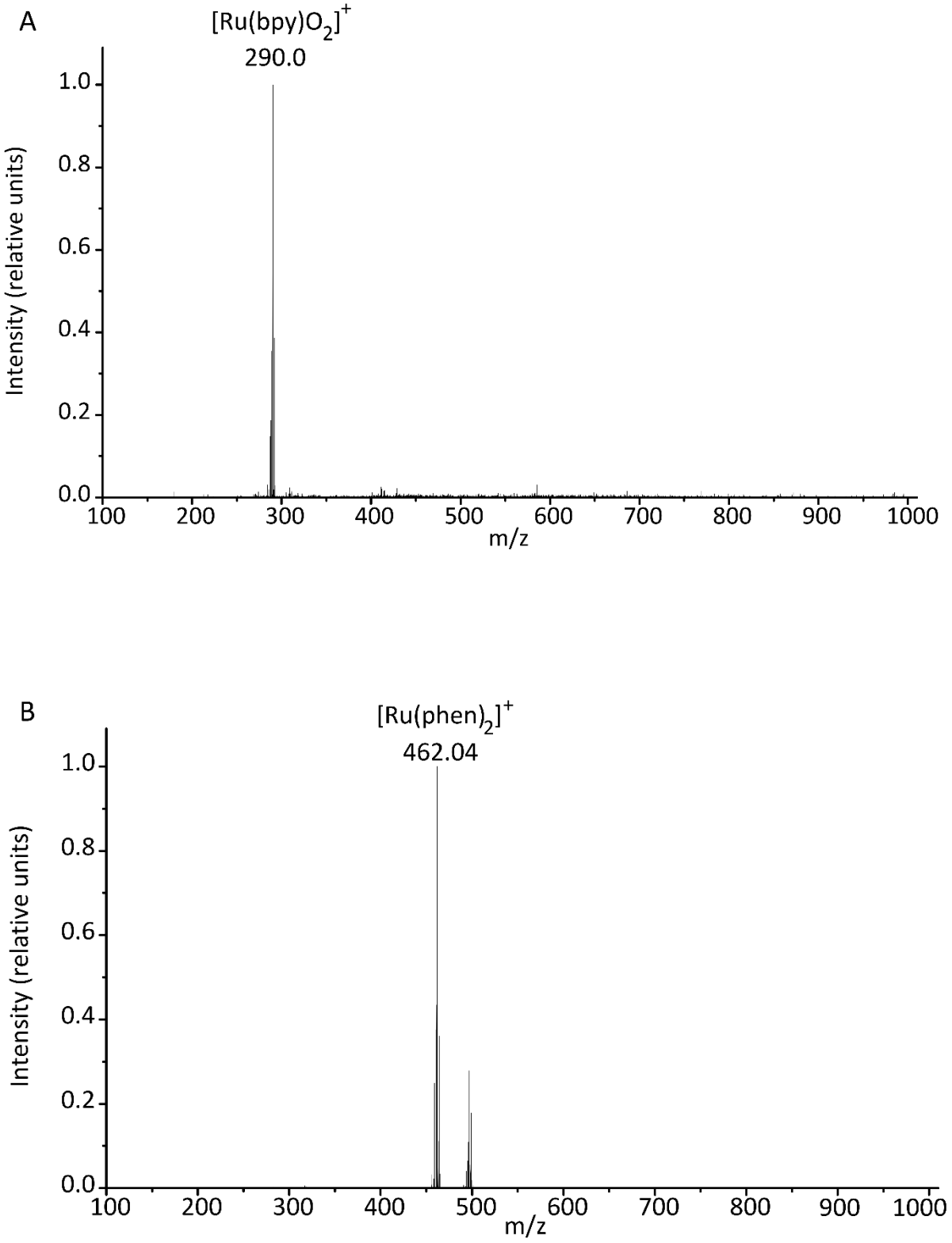

*Figure S-4. LDI mass spectra of $Ru(bpy)_3^{2+}$ (**A**) and $Ru(phen)_3^{2+}$ (**B**). Absence of the molecular peaks at m/z 570 and 642 for $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$, respectively, indicates photolysis of these complex cations.*

FlexAnalysis script and macro for automatic data processing

A FlexAnalysis method script for an automatic finding of m/z 570.11 ($[Ru(bpy)_3]^+$) and 642.11 ($[Ru(phen)_3]^+$) peaks in the spectrum:

```
Option Explicit
Sub Main
    UndoAllProcessing()
    Dim dRange(1) As Double
            dRange(0) = 569.8
            dRange(1) = 570.4

            {dRange(0) = 566.8}
            {dRange(1) = 573.4}
            {for the "seven peaks" approach}

    Dim ResultSpec As Spectrum
    Set ResultSpec = Spectra(1).Process(faFindPeaks, dRange)

Dim tRange(1) As Double
            tRange(0) = 641.8
            tRange(1) = 642.4

            { tRange(0) = 638.8}
            {tRange(1) = 645.8}
            {for the "seven peaks" approach}

    Dim aResultSpec As Spectrum
    Set aResultSpec = Spectra(1).Process(faFindPeaks, tRange)

    ResultSpec.Enabled = True
   aResultSpec.Enabled = True

    Save
End Sub
```

This script is based on Bruker Daltonik GmbH PMF.FAMSMethod.[1]

A FlexAnalysis macro that extracts the peak information (m/z and peak area) from the spectra and transfers it into an Excel sheet:

```
Attribute VB_Creatable = True
Attribute VB_Exposed = False
Attribute VB_GlobalNameSpace = False
Attribute VB_Name = "MassListToExcel"

'#Uses "FATools.obm"

Option Explicit
Option Base 1


Private aAnaSpec() As TAnaSpec
Private nSpectra%
Private Const sDelimiter$ = vbTab

Property Get MenuItem$
   MenuItem = "File/Export/Mass List to Excel"
End Property

Property Get EnableMenuItem As Boolean
   EnableMenuItem = Tools.GetSelectedAnaSpec(aAnaSpec) > 0
End Property
Sub Main
    Execute
End Sub

Sub Execute
    On Error GoTo Failed

   MassListToExcel

    Exit Sub

Failed:
    MsgBox Err.Description
End Sub

Private Sub MassListToExcel
   ' Transfer the mass list to Excel
   nSpectra = Tools.GetSelectedAnaSpec(aAnaSpec)
   If nSpectra = 0 Then
      Err.Raise 1,,"No spectrum selected"
   End If

   ' Open Excel application
    Dim Excel As Object
```

```
    Set Excel = OpenExcel
    '
    Dim i%
    For i = 1 To nSpectra

        Excel.Sheets(1).Activate

        Dim sName$
        sName = Replace(aAnaSpec(i).oAnalysis.Name, "\", "_")
        sName = Replace(sName, " ", "_")
        sName = Left(sName, 31)

        Dim Paster$
        Paster = "A" + CStr(3*i-2) + ":" + "A" + CStr(3*i-2)

        {Paster = "A" + CStr(15*i-14) + ":" + "A" + CStr(15*i-14)}
            {for the “seven peaks” approach}

    CopyMassListToClipboard aAnaSpec(i).oAnalysis, aAnaSpec(i).oSpectrum

            Excel.Range(Paster).Select
            Excel.Sheets(1).Paste

    Next i

    Clipboard ""
End Sub

Private Function OpenExcel As Object
    Dim ExcelApp As Object
    On Error Resume Next
    Set ExcelApp = GetObject(,"Excel.Application")
    If ExcelApp = Null Then
        Set ExcelApp = CreateObject("Excel.Application")
    End If
    ExcelApp.Visible = True
    ExcelApp.Workbooks.Add
    Set OpenExcel = ExcelApp
End Function

Private Sub CopyMassListToClipboard(oAnalysis As Analysis, oSpectrum As
Spectrum)

    Dim sName$
    sName =Replace(GetSpectrumName(oAnalysis, oSpectrum), "\1 1SRef Raw", "")
    Dim sCsv$
    sCsv =sName + vbTab

    sCsv = sCsv + "m/z" +vbTab + "Area"+ vbCrLf
```

```
        On Error Resume Next

        Dim oPeakList As MassList
        Set oPeakList = oSpectrum.MassList

        Dim i%

        For i = 1 To oPeakList.Count
            Dim oPeak As MassPeakInfo
            Dim sValue$

            Set oPeak = oPeakList(i)

            sValue = ""
            sValue = Replace(CStr(oPeak.MassToChargeValue), ",", ".")
            sCsv = sCsv  +sDelimiter + sValue + sDelimiter
            sValue = ""
            sValue = Replace(CStr(oPeak.Area), ",", ".")
            sCsv = sCsv + sValue + vbCrLf
        Next
        Clipboard sCsv
    End Sub

    Private Function GetSpectrumName(oAnalysis As Analysis, oSpectrum As
Spectrum)
        GetSpectrumName = oAnalysis.Name + " " + oSpectrum.Name
    End Function
```

This script is based on Bruker Daltonik GmbH MassListToExcel.obm.[1]

(1). Bruker Daltonik GmbH, *FlexAnalysis Scripting Manual*, *Version 3.0*, 2006.