Solution and solid-state light-induced transformations in heterometallic vanadium-ruthenium nitrosyl complex

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Abstract

The work is devoted to the preparation and photochemical investigations of the novel binuclear heterometallic complex $[\text{Ru}(\text{NO})(\text{NO}_2)_2(\mu\text{-NO}_2)(\mu\text{-CH}_3\text{COO})(\mu\text{-O})\text{VO}(\text{dbbpy})]\cdot\text{CH}_3\text{CN}$ (dbbpy - 4,4'-di-*tert*-butyl-2,2'-bipyridyl), which is obtained with quantitative yield. The structure of the complex is determined by single crystal X-ray diffraction and by DFT calculations. On the one hand, irradiation at 445 nm of an acetonitrile solution of the complex leads to a NO photo-release reaction. The light excitation induces the charge transfer from NO_2 and dbbpy ligands to the antibonding orbitals of ON-Ru-O-V chain, leading to the NO release, which is confirmed by the DFT. The quantum yield of the Ru-NO photo-cleavage is $0.57\pm0.05\%$. The products of the photolysis (NO and paramagnetic Ru^{III} complex) are confirmed by the Griess test and EPR-spectroscopy. On the other hand, the irradiation of the complex in the solid phase at 10 K results in the formation of the metastable bond isomer Ru-ON (MS1), which is detected by the infrared spectroscopy. The stretching vibration of the $\nu(\text{NO})$ band of MS1 (1750 cm^{-1}) is shifted by 150 cm^{-1} to lower energy with respect to the $\nu(\text{NO})$ band of the ground state GS (1900 cm^{-1}). The population of the MS1 is about 5%. MS1 thermally decays at 120-140 K back to the GS. Hence, this complex represents a bifunctional platform, which can release nitric oxide in solution and reversibly switch the NO ligand coordination in the solid state. It is shown, that the presence of vanadium strongly influences the photochemical properties of ruthenium nitrosyl both in the solid phase and in solution.

Keywords: ruthenium, vanadium, oxidovanadium complexes, nitrosyl, metastable states, isomerization

1. Introduction

One of the remarkable properties of nitrosyl ruthenium complexes is the ability to labilize the nitrosyl (NO) ligand under photoexcitation. Interestingly, that the outcome of NO labilization depends on the environment: in solution, light excitation of nitrosyl ruthenium leads predominantly to NO release [1], whereas in the solid state (crystal or powder) the formation of linkage isomers Ru-ON or $\text{Ru}(\eta^2\text{-(NO)})$ can be observed [2]. In some cases, both NO release and NO isomerization was observed in the solid state [3].

The NO release in solution is an appealing option for medical applications. It is known, that nitric oxide is a biological active molecule, which participates in many physiological processes, such as neurotransmission, blood pressure control, immunological responses, and antioxidant action [4–6]. The biologically relevant lifetime of the nitric oxide was estimated to be in the 0.09 - 2 s range depending on the distance from the blood vessels [7]. In this regard, ruthenium nitrosyl complexes are NO-bearing platforms enabling

phototriggered nitric oxide release, i.e. they can be applied in photodynamic therapy for targeted NO delivery. Moreover, ruthenium complexes can interact with DNA repair enzymes, thus, ruthenium nitrosyl complexes are considered as double bioactive species [8]. On the other hand, light irradiation of ruthenium nitrosyl complexes in solid phase induces the formation of metastable state isomers Ru-ON (MS1) or Ru-(η^2 -(NO)) (MS2) from the ground state Ru-NO (GS). Such isomerization is a reversible process – it is possible to drive MS1/MS2 back to the GS by heating or light irradiation [9–12]. It was shown, that the isomerization can find application in data storage based on holography technique [13].

Furthermore, the combination of ruthenium nitrosyl with a magnetic/optic/red-ox/catalytic building block leads to functional materials with photo-triggered properties. Particularly, mononuclear oxidovanadium complexes [14–18] are attractive species and can be used as building blocks for the design of bi- and polynuclear structures [19]. Oxidovanadium complexes attract considerable attention primarily due to their catalytic properties in diverse organic reactions and biological activity (insulin-enhancing effect, antidiabetic and antitumor activities) [20–24]. Complexes with V=O moiety have high activity in homo- and heterogeneous catalysis, for instance, oxidations of alkanes, alkenes, arenes, alcohols, aldehydes, ketones, and sulfur species, as well as oxidative C–C and C–O bond cleavage, carbon–carbon bond formation, deoxydehydration, haloperoxidase, cyanation, hydrogenation, dehydrogenation, ring-opening metathesis polymerization, and oxo/imido heterometathesis, etc [25–34]. Oxidovanadium complexes with N-donor heterocycle ligands show activity towards DNA cleavage upon near-IR irradiation [35–37]. In some cases, selective binding to cancer cell DNA is observed [37–41]. Thus, such complexes can be used in cancer photodynamic therapy. Furthermore, in nature, vanadium-dependent haloperoxidases (VHPO) catalyze the oxidation of halides with hydrogen peroxide [42–44], while vanadium-dependent nitrogenases are involved in nitrogen fixation [45,46].

Heterometallic complexes combining both 3d-V and 4d-Ru metals are extremely rare. According to the Cambridge Crystallographic Data Centre (CCDC), there are 6 known mixed vanadium-ruthenium complexes including only one heterometallic complex: $[L' Ru(\mu-O)(\mu-CH_3CO_2)_2 VL](PF_6)_2$, where L' and L are N,N',N'' -trimethyl-1,4,7-triazacyclononan and 1,4,7-triazacyclononane, respectively [47]. Since both metals, ruthenium and vanadium, poses biological activity, the combination of such metals in one complex can increase the biological and catalytic activity of the complex through a synergistic effect. The combination of nitrosyl photo-isomerization with a vanadium center might lead to new materials with photo-triggered properties, where the type of NO coordination affects the properties of the heterometallic complex [48].

Thus, this work is devoted to the preparation of the heterometallic complex combining nitrosyl ruthenium and oxidovanadium. The photochemical properties of the obtained complex were thoroughly studied by the combined spectroscopic (UV/vis, IR, EPR) and calculation (DFT) methods - the nitric oxide release during irradiation in solution and the formation of metastable state isomer Ru-ON (MS1) in solid state under irradiation have been investigated.

2. Materials and methods

2.1. Synthesis of $[Ru^{II}(NO)(NO_2)_2(\mu-NO_2)(\mu-CH_3COO)(\mu-O)V^VO(dbppy)]CH_3CN$ (I)

The complexes $[VO(dbppy)(H_2O)Cl_2]$ and $Na_2[Ru(NO)(NO_2)_4(OH)] \cdot 2H_2O$ were synthesized according to the methods described in [16] and [49], respectively.

A mixture of 42 mg (100 μ mol) of the complex $[VO(dbppy)(H_2O)Cl_2]$ and 41 mg (100 μ mol) of the complex $Na_2[Ru(NO)(NO_2)_4(OH)] \cdot 2H_2O$ in a 1:1 ratio was stirred in 3 ml of CH_3CN for 30 minutes with moderate heating (60°C). The initially formed brown precipitate readily dissolved during the reaction. Then the solution was filtered off from NaCl and evaporated in vacuum. As a result, a fine brown powder was obtained with a quantitative yield. Dark red crystals were obtained from a mixture of CH_3CN/CH_2Cl_2 (1/10) by the slow diffusion of hexane. IR-spectra at room temperature (KBr, cm^{-1}): 2967 (m), 1900 (vs), 1619 (m), 1585 (w), 1463 (s), 1450 (m), 1415 (s), 1326 (m), 1270 (m), 1252 (m), 1036 (m), 976 (s), 901 (w), 821 (s). UV-vis: $12400 M^{-1}cm^{-1}$ (298 nm). Elemental analysis for $C_{20}H_{28}N_6O_{11}RuV$, the calculated %: C 35.3; N 12.4; H 4.1; obtained %: C 35.0; N 12.2; H 4.2. The structure model was determined by single crystal X-ray diffraction: $P 2_1/n$; $a = 6.24 \text{ \AA}$, $b = 16.60 \text{ \AA}$, $c = 28.27 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 92.30^\circ$, $\gamma = 90^\circ$.

2.2. Instrumental techniques

IR spectroscopic measurements with irradiation were performed using a Nicolet 5700 FT-IR spectrometer with a resolution of $2 cm^{-1}$ in the range $400\text{--}4000 cm^{-1}$. The sample was ground, mixed with KBr and pressed into pellets. The KBr pellets were bonded by silver paste onto the cold finger of a closed-cycle cryostat (Oxford Optistat V01) and irradiated through KBr windows by LED light of different wavelengths in the range 365–405 nm and 70–200 mW optical power (Thorlabs L and LP series). The cryostat has the temperature range of 9–320 K.

UV-vis spectra were recorded on a PG Instruments T60 UV-vis single-beam spectrophotometer. UV-vis spectra of the complex were obtained in DMSO and acetonitrile in a 1 cm cell. The absorbance of the pure solvents was taken in account. The evolution of the spectra in time was monitored during perpendicular exposure by the LED at 445 nm, 100 mW.

Griess reagent was prepared as an equimolar ($5 \cdot 10^{-5}$ mole) solution of 1-naphthylamine and sulfanilamide in acetic acid/acetonitrile (1:4) mixture. The solution of the complex ($\approx 10^{-4}$ M) and Griess reagent (10^{-2} M) in acetic acid/acetonitrile (1:4) mixture was irradiated by LED 445 nm, 100 mW in a 1 cm cuvette. After the light exposure, the red area was observed at the place of the light spot.

The EPR spectra were obtained at 77 K on a Varian E-109 spectrometer operating at X-band. g-values were calculated using 2,2-diphenyl-1-picrylhydrazil (DPPH) with $g = 2.0036$ as a reference [50]. For the study of the photolysis product, on the first stage, the solution of the complex in acetonitrile (0.05 M) was irradiated at room temperature during 60 min by LED 445 nm, 100 mw, similar to UV-vis investigation. Then, the irradiated solution was cooled at 77 K and the EPR spectra was obtained.

Single-crystal X-ray diffraction data for the best crystal of **1** we have were collected using the graphite monochromatized MoK α -radiation ($\lambda=0.71073$ Å) at 150(2) K on a Bruker APEX DUO diffractometer equipped with a 4K CCD area detector. The φ - and ω -scan technique was employed to measure intensities. Absorption corrections were applied empirically using the SADABS program [51]. Structure was solved by the direct methods of the difference Fourier synthesis and further refined by the full-matrix least squares method using the SHELXTL package [52]. Atomic thermal parameters for non-hydrogen atoms were refined anisotropically. Atomic displacement parameters for some terminal carbon atoms in tert-butyl substituents and in acetonitrile solvent molecule were restrained with the ISOR command. The positions of hydrogen atoms were calculated corresponding to their geometrical conditions and refined using the riding model. Two nitro-groups were restrained with the N-O distances. The experimental and refinement details are shown in Table S1. CIF-file of the complex has been deposited into CCDC with the numbers 2027275.

2.3.DFT Computational details

The molecular geometry of [Ru(NO)(NO $_2$) $_2$ (μ -NO $_2$)(μ -CH $_3$ CO $_2$)(μ -O)VO(bpy)] was fully optimized in the acetonitrile liquid phase at the Density Functional Theory (DFT) level. All calculations were performed using the ADF-2017 program package [53–55]. The hybrid B3LYP [56–59] or VWN [56] functionals were used coupled with the triple- ζ with two polarization functions all-electron TZ2P uncontracted Slater Type Orbitals (STOs) basis set for all elements [60]. The inner shells were included in calculations. The relativistic effects were taken into account at default scalar level in Zero Order Regular Approximation (ZORA) formalism [61–63]. Solvent effects were modeled via the implicit Conductor like Screening Model (COSMO) of solvation with acetonitrile as solvent [64]. For geometry optimizations and UV-vis absorption spectrum calculations, the COSMO molecular cavity was built according to the van der Waals radii from MM3 method [65] scaled down by 1.2. The standard values for dielectric constant and refractive indexes were always assumed.

The optimized geometries were submitted to the time-dependent DFT calculations [66]. The same basis sets were used as for the optimization. The first 400/150 excited states were included in the calculation of the UV-vis absorption spectrum (VWN/B3LYP). Only singlet-singlet excitations were computed.

The convergence criteria for Self-Consistent Field were used at default 10^{-6} settings for the error of the commutator of the Fock matrix and the P-matrix, which is the density matrix in the representation of the basis functions. The rest of SCF setting were the default ones as well. The convergence criteria for geometry optimizations were set to default values of 10^{-3} Hartree for energy change, 10^{-3} Hartree Å $^{-1}$ for nuclear gradients, 10^{-2} of the Cartesian displacement, and 0.5 degree for change in angles.

3. Results and discussion

3.1.Synthesis and structure description

The oxidovanadium(IV) complex [VO(dbbpy)(H $_2$ O)Cl $_2$] was obtained from vanadium trichloride by reaction with 4,4'-di-*tert*-butyl-2,2'-bipyridine in acetonitrile in the ratio 1:1. The mixture was refluxed for 4 hours in air. The resulting solution was evaporated to dryness and was recrystallized from CH $_2$ Cl $_2$ /hexane mixture [16].

The nitrosyl ruthenium complex $\text{Na}_2[\text{Ru}(\text{NO})(\text{NO}_2)_4(\text{OH})]\cdot 2\text{H}_2\text{O}$ was obtained from ruthenium(III) chloride hydrate. Its synthesis consists of the interaction of RuCl_3 with sodium nitrite in boiling hydrochloric acid [49].

The binuclear $[\text{Ru}(\text{NO})(\text{NO}_2)_2(\mu\text{-NO}_2)(\mu\text{-CH}_3\text{COO})(\mu\text{-O})\text{VO}(\text{dbbpy})]\cdot \text{CH}_3\text{CN}$ (**I**) complex was obtained from the pre-organized ruthenium $\text{Na}_2[\text{Ru}(\text{NO})(\text{NO}_2)_4(\text{OH})]\cdot 2\text{H}_2\text{O}$ and vanadium $[\text{VO}(\text{dbbpy})(\text{H}_2\text{O})\text{Cl}_2]$ complexes (Fig. 1). The complex $[\text{VO}(\text{dbbpy})(\text{H}_2\text{O})\text{Cl}_2]$ has one facet of an octahedron formed by labile ligands, which are replaced during the reaction in acetonitrile. This approach yielded a rare example of heterometallic nitrosyl ruthenium complex in quantitative yield. The +5 oxidation state of vanadium is in agreement with the complex **I** being EPR silent in dark. Similar to the synthesis of parent vanadium(IV) complex, vanadium center was oxidized by oxygen to give vanadium(V).

Fig. 1. The scheme of synthesis of $[\text{Ru}(\text{NO})(\text{NO}_2)_2(\mu\text{-NO}_2)(\mu\text{-CH}_3\text{COO})(\mu\text{-O})\text{VO}(\text{dbbpy})]\cdot \text{CH}_3\text{CN}$ (**I**).

Single crystals of **I** were obtained by recrystallization of **I** from a mixture $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{12}$ (1:10:30 ratio). Unfortunately, no high quality crystals could be obtained. These thin-plate shaped crystals diffracted only weakly leading to rather poor diffraction data. Therefore, the structure model found for this compound exhibits rather large agreement factors *R*. Nevertheless, this crystal model shows the interesting features in this bimetallic complex, and it is supported by DFT calculations.

The experimentally determined molecular structure of **I** is shown in Fig. 2. Selected bond distances are listed in Table 1. Each metal atom has a distorted octahedral environment. In the case of vanadium, the octahedral environment is defined by two N atoms from dbbpy and four O atoms from the bridging groups CH_3COO^- , NO_2^- , O^{2-} and the terminal oxo ligand. In the case of ruthenium, it is defined by four N atoms from NO_2^- and NO^+ ligands and two O atoms from the bridging CH_3COO^- and O^{2-} ligands. The metal atoms share a triangular face formed by the bridging groups CH_3COO^- , NO_2^- and O^{2-} . We propose that the bridging acetate-ion was formed during the hydrolysis of acetonitrile during the reaction. Unexpected emergence of the coordinated acetate could be explained as intricate result of interaction of coordinated nitro group with acetonitrile solvent. A reaction of that kind was not reported for acetonitrile solution of starting $[\text{Ru}(\text{NO})(\text{NO}_2)_4(\text{OH})]^{2-}$ complex, thus, we assume that the vanadium complex is involved in this transformation. In the starting vanadium complex $[\text{VO}(\text{dbbpy})(\text{H}_2\text{O})\text{Cl}_2]$, the $\text{V-O}_{\text{terminal}}$ bond length is 1.589 Å. In the binuclear complex **I** this bond is the same and equals 1.57(1) Å. The $\text{V-}\mu\text{-O}$ bond length equals 1.70(1) Å indicating the coordination of the oxo ligand, instead of hydroxo. In $[\text{VO}(\text{dbbpy})(\text{H}_2\text{O})\text{Cl}_2]$, the dbbpy ligand is symmetrically coordinated with V-N distance 2.128(3)

Å, whereas in the case of **I**, dbbpy is asymmetrically coordinated with V-N distances 2.11(1) Å and 2.17(1) Å due to the different *trans* influence of the μ_2 -oxo, and μ_2 -acetate ligands.

In order to support experimental X-Ray diffraction data, we performed quantum mechanical calculations, which provide a detailed picture of bonding and electronic structure in the studied complex. The initial structure for the calculations was based on the bonding pattern from single crystal X-ray studies. The geometry optimization was carried out at density functional theory (DFT) level with local density approximation functional (VWN) or in hybrid B3LYP functional. The basis set was TZ2P for all atoms. The solvation shell of acetonitrile was modeled as the implicit Conductor like Screening Model (COSMO). The coordination spheres are distorted octahedral for vanadium and ruthenium atoms (Table 1, Figure 2). The ruthenium atom is shifted from {N₃O} equatorial plane (nitro groups and acetate) toward the nitrosyl group in the axial position at 0.1 Å for VWN calculations (or 0.08 Å for B3LYP). The magnitude and direction of the shift is in agreement with the X-ray structural data of other known complexes [67,68]. Nitrosyl group and bridging oxo ligand occupy the axial positions. The VWN distances (1.74 (Ru-NO), 1.14 (N-O_{NO}) and 1.94 (Ru- μ -O) Å) are close to the experimental ones of related complexes [69–75], as well as the B3LYP data (1.76 (Ru-NO), 1.13 (N-O_{NO}) and 1.99 (Ru- μ -O) Å). In case of vanadium coordination sphere, the equatorial plane with dbbpy, μ_2 -oxo, and μ_2 -acetate has bond lengths varying from 1.71_O to 2.12_N Å. The axial positions are occupied by the terminal oxo and bridging nitrito groups. The vanadium-oxygen distance of the bridging nitrito ligand is noticeably elongated due to the *trans* influence of the terminal oxo ligand. This is in agreement with previous studies of VO³⁺ complexes [76–78] and our X-ray data.

Table 1

Selected computed and experimental bond distances of the studied complex.

Functional/ bond length (Å)	VWN	B3LYP	Exp.
Ru-N_{NO}	1.74	1.76	1.73(1)
N-O_{NO}	1.14	1.13	1.16(2)
avg. Ru-NO₂ (terminal)	2.04	2.10	2.21(2)
avg. ON-O (terminal)	1.23	1.23	1.14(3)
Ru-μ-NO₂	2.06	2.13	2.07(1)
V-μ-ONO	2.26	2.43	2.26(1)
O-N-(μ-O)	1.21 (1.26)	1.22 (1.26)	1.19(2) (1.31(1))
Ru(V)-OCOCH₃	2.09 (1.90)	2.14 (1.93)	2.10(1) (1.90(1))
Ru(V)-μ-O	1.94 (1.71)	1.99 (1.70)	2.00(1) (1.70(1))
V-O (terminal)	1.59	1.58	1.57(1)
V-dbbpy	2.06; 2.12	2.11; 2.18	2.10(1); 2.17(1)

Fig. 2. The structure of the complex I determined by the single crystal X-Ray diffraction.

3.2. NO release in solution

The unique feature of the metal nitrosyl complexes is the metal-to-ligand charge transfer (MLCT) from the t_{2g} -like d orbitals of d^6 ruthenium to the π^* antibonding nitrosyl orbital [79,80]. After the excitation, the relaxation of the MLCT state leads to metastable states (side-on and κO -coordination of the nitrosyl [10]) or to nitric oxide being released from the complex [1]. In the case of the studied ruthenium-vanadium complex, the MLCT transition is enhanced by antibonding interactions with bridging oxo ligand and vanadium. Thus, the electron density is transferred to the antibonding MO of ON-Ru-O-V or ON-Ru-O-V-O chains. Intense transitions promote the electron density from lone pairs in the two *trans* nitro groups or π -orbitals of the dbbpy ligand (Tables S2-S4) to the antibonding orbitals of the ON-Ru-O-V chain. These key transitions for NO labilization correspond to the 400-500 nm range of the spectrum, which causes the choice of 445 nm light source.

From the orbital point of view (Tables S2-S4), the lowest unoccupied molecular orbital (LUMO) (Fig. 3) contains atomic orbitals of nitrosyl group, ruthenium, bridging oxo ligand, and vanadium interacting in the antibonding fashion on the curved ON-Ru-O-V chain. Unoccupied orbitals involving orbitals of the whole ON-Ru-O-V-O chain are located next in energy (LUMO+1 and LUMO+2). Unoccupied orbitals with contributions of nitro, acetate, and dbbpy ligands are found at even higher energy. However, these orbitals do not play a role in the visible transitions. The nature of the highest occupied orbital (HOMO) (Fig. 3) depends on the functional choice. Oxygens' lone pairs in the two *trans* nitro groups are the HOMO-1 and HOMO for VWN and B3LYP functionals, respectively. For the VWN functional, the HOMO orbital is only 0.025 eV higher than HOMO-1 and it is constructed from the π -orbitals of the dbbpy ligand. For the B3LYP data, the occupied orbitals with

contribution from dbbpy π -system are lower in energy (HOMO-3, HOMO-4). The ruthenium t_{2g} -like d orbitals play an important role in the HOMO-2 orbital.

Fig. 3. The HOMO and LUMO orbitals by DFT calculations using VWN and B3LYP functionals.

The experimental absorption spectrum of the compound **I** in the acetonitrile solution is shown in Fig. 4. The compound **I** strongly absorbs in the UV region with the band maxima at 308 nm ($13700 \pm 500 \text{ M}^{-1} \cdot \text{cm}^{-1}$, Fig. 4). According to the DFT calculations the band corresponds to the inter- and intra-ligand transitions. Low-energy shoulder at 400-500 nm corresponds to the charge transfer from NO_2 and dbbpy ligands to the orbitals of the ON-Ru-O-V chain. The acetonitrile solution of **I** is stable in time, while a decomposition of **I** occurred in DMSO solution (Fig. S1).

Fig. 4. The absorption spectrum of the compound **I** in the acetonitrile solution.

Ruthenium nitrosyl complexes release coordinated nitrogen monooxide upon photolysis according to the equation:

Regardless of the ligand environment, the $\{\text{Ru}^{\text{II}}\text{NO}^+\}$ species are shown as promising NO donors [1][81]. Commonly, in the absorption spectrum the decrease in the UV-blue range and the corresponding increase of the absorption in red range after light exposure of the complexes in solutions is observed [8,50,82,83]. Since five-coordinated ruthenium complexes are not stable, the free coordination place after NO photo-release is occupied by the solvent molecule [1]. In some cases, the structures determined by the single crystal X-ray diffraction of the photo-products with the coordinated acetonitrile ligand were obtained [84,85].

The photolysis of **I** in acetonitrile solution is promoted by the 445 nm irradiation (Fig. 5). Unlike the case of decomposition of **I** in DMSO solution, the 308 nm absorption peak had no significant change through the photolysis in acetonitrile solution. The spectral differences are manifested as decrease in the ultraviolet absorption and the formation of the 388 nm band. The latter slightly loses intensity in the dark.

Fig. 5. Photolysis of the $4.35 \cdot 10^{-5}$ M solution of **I** in acetonitrile under 445 nm irradiation: blue line – before irradiation; red line – after 61 min of irradiation.

The spectral change of the freshly photolyzed solution stored in the dark resembles the nitrogen dioxide spectrum [86] (Fig. S2). This band undergoes single-exponential decay with the kinetic constant equal to $1.6 \pm 0.5 \cdot 10^{-3} \text{ s}^{-1}$. It is known, that NO_2 is in the equilibrium with N_2O_4 [87,88]. Nevertheless, reported rate constant of NO_2 disproportionation in water is significantly greater than $1.6 \pm 0.5 \cdot 10^{-3} \text{ s}^{-1}$ [89]. Hence, the assignment of the spectral evolution of the irradiated sample to the NO_2 is doubtful.

Additionally, the photolysis of the **I** in the presence of the Griess reagent (the reagent for the nitrite ion detection) was performed (Fig. S3) [90]. The oxidation of the photogenerated NO gives the nitrite ion via the quantitative reaction $4\text{NO} + \text{O}_2 + 2\text{H}_2\text{O} = 4\text{HNO}_2$ [91] or disproportionation reaction $2\text{NO}_2 + \text{H}_2\text{O} = \text{HNO}_2 + \text{HNO}_3$ [92]. The reaction of nitrite with the reagent produce the dye, characterized by the absorption band at around 500 nm (Fig. S3).

Hence, we propose the following scheme of the compound **I** photolysis:

The coordination of acetonitrile is not explicitly demonstrated, however its coordination is very likely due to previous reports and low stability of five-coordinated ruthenium species [1]. Thus, the absorbance at a given time and wavelength can be expressed as $A = \epsilon_{\text{RuNOV}} \cdot I \cdot C_{\text{RuNOV}} + \epsilon_{\text{RuV}} \cdot I \cdot (C_0 - C_{\text{RuNOV}})$. Concentrations of ruthenium complexes are derived from the photolysis equation. In the model, the quantum yield and extinction coefficients are refined by means of the least squares method to fit the experimental data. The quantum yield value is $0.57 \pm 0.05\%$.

Earlier, ruthenium nitrosyl complexes $[\text{RuNOL}_2(\text{NO}_2)_2\text{OH}]$ ($\text{L} = \text{pyridine}, \beta\text{-picoline}$) have been studied on the NO release in solution upon irradiation [8,50]. It was shown, the quantum yield of the nitric oxide release reaction was 6-20% depending on the solvent and the excitation wavelength. In the current case, the presence of vanadium sufficiently decreases the efficiency of NO photo-release, which is in an agreement with DFT calculations: the light excitation induces the charge transfer to the antibonding orbitals of ON-Ru-O-V chain, in which the presence of vanadium (LUMO occupancy is about 70%) decreases the probability of a distortion of the Ru-NO bond.

We used EPR spectroscopy to detect the paramagnetic photolysis products in the solution after light irradiation. The light exposure of the acetonitrile solution of the **I** by the 445 nm light for 60 min induce the formation of the paramagnetic species. The EPR spectrum after irradiation is presented in the Fig. 6. The spectrum presents a characteristic signal for paramagnetic Ru(III) complex with parameters $g_1 = 2.627$, $g_2 = g_3 = 2.20$ [93,94], which is consistent with the proposed photolysis scheme in which a ruthenium(III) complex with the $\{\text{V}^{\text{V}}\text{-Ru}^{\text{III}}(\text{solvent})\}$ fragment is formed. Thereby, the vacant coordination site after NO release is apparently occupied by the solvent molecule.

Fig. 6. EPR spectrum of complex **I** in acetonitrile after 60 min of 445 nm irradiation.

3.3. Photo-induced nitrosyl isomerization in solid state

The light irradiation of **I** in solution leads to the labilization of the NO^+ ligand followed by NO^0 release, whereas at temperatures below 273 K the bond isomers of nitrosyl ligand could exist. IR spectroscopy is an extremely sensitive method to verify the appearance of such isomers (MS1 or/and MS2).

The IR spectrum of complex **I** at 10 K contains bands related to the $\delta(\text{NO}_2)$ frequency vibration at 821 cm^{-1} , $\nu(\text{V-O})$ band at 973 cm^{-1} , bands of $\nu(\mu\text{-NO}_2)$ bridge ligand at 1252 , 1270 and 1585 cm^{-1} , $\nu(\text{NO}_2)$ bands at 1326 , 1416 , and 1467 cm^{-1} , $\nu(\text{C-C})$ band of dbbpy ligand at 1618 cm^{-1} and the most intense $\nu(\text{NO})$ band at 1900 cm^{-1} .

(Fig. 7 and Fig. S4). Irradiation of the complex by light in the spectral range 365–405 nm results in the formation of a new band with maximum at 1750 cm^{-1} , assigned to the $\nu(\text{NO})$ stretching vibration of the MS1 isomer and accompanied by the decrease of the $\nu(\text{NO})$ band of GS (Fig. 7). The population of MS1 is about 5%. The band exhibits a shift to lower energies compared to the GS band by 150 cm^{-1} , which is characteristic for nitrosyl ruthenium complexes [2,12,71,95–97]. The concomitant decrease of intensities of the NO_2 bands is most probably related to the nitrosyl isomerization and partial NO release (see below) (Fig. S4). The sensitivity of NO_2 bands to the change of NO linkage was shown in [68].

According to DFT calculations, the formation of bond isomers can be described as follows. After the light excitation, the excited singlet state of MLCT nature tends to undergo inter-system crossing (ISC) to the triplet MLCT of the same nature [98,99]. The triplet as well as first excited singlet states are known to have bended Ru-N-O fragment [100]. The relaxation of triplet state ends up in a point on the ground state potential energy surface, which is far from equilibrium linear geometry. From here the majority of the population relaxes to the ground state, however, a small fraction of molecules can hop to the side-on coordinated nitrosyl state (MS2). This state can be excited in a similar fashion with two different triplets as a long-living intermediate; one is O-coordinated and another is N-coordinated. The N-coordinated triplet of MS2 relaxes to GS or MS2 while the O-coordinated triplet can end up as MS2 or as O-coordinated nitrosyl with an almost linear Ru-O-N fragment (MS1). The ratio of the ground state, metastable states and generated triplets depends on the relaxation dynamics on the triplet and singlet energy surfaces, ISC process, and absorptive properties of the metastable states. The MS2 needs a special protocol to be accumulated because it absorbs excitation more readily than O- or N-coordinated nitrosyl states. On the other hand, absorptive properties of the MS1 are similar to the GS absorption; thus, the MS1 can have a decent fraction [9] or even a dominative one [10] in a solid sample.

Fig. 7. IR spectra of **I** at 10 K in GS (red line), after 10 min of 405 nm irradiation (orange line), 20 min of 405 nm irradiation (purple line) and after subsequent 5 min of 365 nm irradiation (blue line).

The heating of MS1 from 10 to 140 K induces a decrease of the $\nu(\text{NO})$ band of MS1 and an increase of the corresponding GS band, indicating the complete decay of MS1 at 120–140 K (Fig. 8). The change of absorption bands corresponds to the back MS1→GS reaction [101]. Compared to related $\text{A}_2[\text{RuNO}(\text{NO}_2)_4\text{OH}]$ ($\text{A} = \text{NH}_4^+$ and K^+) and heterometallic $[\{\text{RuNO}(\text{NO}_2)_4\text{OH}\}_2\text{Dy}_2(\text{H}_2\text{O})_2(\text{NO}_3)_2]$ complexes [102–104], where MS1 decay occurs at 190–200 K, the thermal stability of MS1 isomer of **I** is much lower (120–140 K), which is likely due to presence of vanadium. An influence of a *trans*-to-NO ligand on the thermal stability of the MS1 was shown earlier [10,67,105]. According to that, higher electronegativity of *trans*-to-NO ligand increases the thermal stability of the MS1 isomer. On the other hand, a change of the ligands in *cis*-position to NO can lead to a decrease of the MS1 thermal stability as well. For example, the MS1 decay temperature of *trans*- $[\text{RuNOPy}_4\text{OH}](\text{PF}_6)_2$ (200–220 K) is much lower compared to *trans*- $[\text{RuNO}(\text{NH}_3)_4\text{OH}]\text{Cl}_2$ (260–280 K), in which pyridines (Py) are changed to ammine ligands [2,11]. Apparently, the decrease of the MS1 thermal stability of **I** is due to low activation energy of the MS1→GS transformation [9].

Fig. 8. IR spectra of **I** after MS1 generation (405 + 365 nm irradiation) at different temperatures: 10 K (blue line), 50 K (purple line), 80 K (green line), 100 K (brown line), 120 K (orange line) and 140 K (red line).

Besides of MS1 formation after light exposure, a band at 2228 cm^{-1} has appeared. The band reflects the formation of free nitrous oxide N_2O via NO release from the complex [106]. The N_2O formation after light exposure of nitrosyl ruthenium complexes in the solid state was reported earlier [10,69,107], however the mechanism of the formation is still obscure. The possible mechanism of N_2O formation in solution could comprise the formation of $\text{M}-(\kappa^2\text{-ONNO})$ intermediates (bonding through two oxygen atoms) [108]. In this regard, MS1 formation should favor $\text{M}-(\kappa^2\text{-ONNO})$ coordination, however further investigation is needed to clarify the mechanism.

It is worth mentioning that the $GS \leftrightarrow MS1$ reaction is a reversible process, meanwhile NO release with N_2O formation is an irreversible reaction. Thus, from the difference of the area under $\nu(NO)$ of GS before and after irradiation we estimated the amount of released NO, which is 40% from initial (Fig. S4). Complex I shows thus a noticeable sensitivity to the incident light. A similar behavior was found earlier in monomeric complexes $(PyH)[Ru(NO)(NO_2)_2(ONO)Py(OH)]$ and $[Ru(NO)(NO_2)(ONO)Py_2(OH)]$, where amount of NO release was found 50 and 20% respectively [69].

4. Conclusions

In this work, the binuclear $[Ru(NO)(NO_2)_3(CH_3COO)(O)VO(dbbpy)]$ complex is obtained from the pre-organized ruthenium $Na_2[Ru(NO)(NO_2)_4(OH)] \cdot 2H_2O$ and vanadium $[VO(dbbpy)(H_2O)Cl_2]$ precursors. This approach yielded a rare example of heterometallic nitrosyl ruthenium complex in quantitative yield. The complex is characterized by the single crystal X-ray diffraction and the structure of the complex is supported by the DFT calculations.

The complex is stable in acetonitrile solution, while light irradiation of the complex solution in the blue spectral range induces NO release. According to DFT, the light irradiation at 445 nm induces the charge transfer from NO_2 and dbbpy ligands to the antibonding orbitals of ON-Ru-O-V chain, which leads to the NO release reaction. The quantum yield of the Ru-NO photo-cleavage is $0.57 \pm 0.05\%$, which is relatively low with respect to the similar monomeric ruthenium nitrosyls. This peculiarity is due to the nature of antibonding orbitals, in which the presence of vanadium decreases the probability of a breaking of the Ru-NO bond, leading to a decrease of the efficiency of NO photo-release reaction. By the Griess test and EPR-spectroscopy the products of the photolysis (NO and paramagnetic Ru^{III} complex) are confirmed. The irradiation of the complex in a solid phase at 10 K results in the formation of a metastable bond isomer Ru-ON (MS1) as detected by IR-spectroscopy. The stretching vibration of $\nu(NO)$ band of MS1 (1750 cm^{-1}) is shifted by 150 cm^{-1} to lower energy with respect to the $\nu(NO)$ band of GS (1900 cm^{-1}). The population of the MS1 is about 5%. MS1 thermally decays at 120-140 K back to the GS, which is much lower compared to related monomeric complexes, in which MS1 decays at 190-200 K. Again, this feature is likely due to the presence of vanadium in the heterometallic complex. Besides of the MS1 formation, a partial formation of nitrous oxide N_2O via NO release is confirmed, however the mechanism of the reaction is uncertain.

In conclusion, the complex I represents a bifunctional platform, which can release nitric oxide in solution and reversibly switch the NO ligand coordination in the solid state. Though partial NO release in solid state is found, the degradation of the sample can be overcome by the adjustment of optical power. It is shown, that the presence of vanadium strongly influences the photochemical properties of ruthenium nitrosyl both in the solid phase and in solution. We suggest, that since unoccupied orbitals of an almost linear ON-Ru-O-V chain are found responsible for the efficiency of the nitric oxide release, the change of the arrangement of the vanadium center towards the Ru-N-O linkage will lead to the unprecedented change in the photochemical properties in any phase.

Declaration of Competing Interest

The authors declare no competing financial interest.

Acknowledgement

We thank Russian Foundation for Basic Research Grants No. 18-03-00155 for funding. Also we thank the Federal Agency for Scientific Organizations for funding. Artem Mikhailov is grateful for financial support from the Eiffel excellence bourse program (Grant P730329G).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jphotochem.2018.12.037>.

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Solution and solid-state light-induced transformations in heterometallic vanadium-ruthenium nitrosyl complex

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Quantum yield calculation

DMSO solutions:

In the dissociative model for the DMSO dark case, the unimolecular kinetic was implemented as the reagent's concentration depends on time $C = C_0 \cdot e^{-kt}$. Total absorbance is equal to the sum of reagent (A) and products (B) absorbances:

$$A_{\text{tot}} = \varepsilon_a \cdot l \cdot C_a + \varepsilon_b \cdot l \cdot C_b \text{ (Eq. 1)}$$

Taking in account mentioned time-dependency, one can derive the following:

$$A_{\text{tot}} = \varepsilon_a \cdot l \cdot C_0 \cdot e^{-kt} + \varepsilon_b \cdot l \cdot C_0 \cdot (1 - e^{-kt}) = \varepsilon_b \cdot l \cdot C_0 + (\varepsilon_a - \varepsilon_b) \cdot l \cdot C_0 \cdot e^{-kt} \text{ (Eq. 2)}$$

The data were fitted at 283 and 318 nm where located the most pronounced changes. The best fit was achieved with the following parameters: $\varepsilon_a(318) = \varepsilon_a(283) = 12790$, $\varepsilon_b(318) = 6300$, $\varepsilon_b(283) = 18200 \text{ M}^{-1} \cdot \text{cm}^{-1}$, $k = 3.4 \pm 0.1 \cdot 10^{-4} \text{ s}^{-1}$.

Acetonitrile solutions:

In order to investigate dark reaction, firstly the acetonitrile solution was irradiated for several minutes in the spectrometer. The spectral changes were monitored during irradiation, Fig. 5. After that, the solution was kept in the instrument without irradiation and the spectral evolution was monitored over 0 - 50 minutes. The model absorbance for each data point in the 350-450 nm range was calculated from equation 2 of the Supplemental Information. The unknown spectrum at infinite time was fitted as four-polynomial function and it was different for different preparatory irradiation time. The first-order kinetic constant was wavelength independent. Thus, total 4040 experimental data points were fitted using six parameters only, which were five absorptions at 350, 375, 400, 425, and 450 nm at infinite time and one kinetic constant. These parameters were adjusted to minimize sum of squared residuals. The loss of absorbance as first experimental spectrum minus modeled spectrum at infinite time was plotted in Fig. S2.

The photolysis equation of the compound I as $\{\text{RuNOV}\} + h\nu \Rightarrow \{\text{RuV}\} + \text{NO}$ can be kinetically described as:

$$-\frac{d\{\text{RuNOV}\}}{dt} = q \cdot I_{\text{abs}} \cdot \varepsilon_{\text{RuNOV}} \cdot l \cdot \{\text{RuNOV}\} / (A_{\text{total}} \cdot V_{\text{total}}) = q \cdot \varepsilon_{\text{RuNOV}} \cdot l \cdot \{\text{RuNOV}\} \cdot I \cdot (1 - 10^{-A_{\text{total}}}) / (A_{\text{total}} \cdot V_{\text{total}})$$

where q is quantum yield, $\varepsilon_{\text{RuNOV}}$ is extinction coefficient of the compound I at the excitation wavelength, l is light pass length, I_{abs} is amount of absorbed light, I is light intensity, A_{total} is total absorbance at the excitation wavelength. The term $\frac{1 - 10^{-A_{\text{total}}}}{A_{\text{total}}}$ was approximated based on the experimental data as $f(t) = a_1 \cdot e^{-b_1 t} + a_2 \cdot e^{-b_2 t} + a_3 \cdot (t - b_3)^2 - a_4 \cdot (t - b_3) + c$ with 99% accuracy which is better than numerical error of absorbance values at excitation wavelength. Solving the differential equation gives the compound I concentration:

$\{\text{RuNOV}\} = C_0 \cdot \exp(-q \cdot \varepsilon_{\text{RuNOV}} \cdot l \cdot I \cdot (t \cdot (c + a_3 \cdot b_3^2 + a_4 \cdot b_3) - t^2 \cdot (a_3 \cdot b_3 + a_4/2) + a_3 \cdot t^3/3 + a_1 \cdot (1 - e^{-b_1 t})/b_1 + a_2 \cdot (1 - e^{-b_2 t})/b_2) / V_{\text{total}})$, where C_0 is the initial concentration of the complex I. The product concentration is $\{\text{RuV}\} = C_0 - \{\text{RuNOV}\}$.

Table S1. Experimental and refinement details of the [Ru(NO)(NO₂)₂(μ-NO₂)(μ-CH₃COO)(μ-O)VO(dbbpy)]·CH₃CN.

Empirical formula	C ₂₂ H ₃₀ N ₇ O ₁₁ RuV
Formula weight	720.54
Temperature/K	150(2)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	6.2399(12)
b/Å	16.601(3)
c/Å	28.271(5)
α/°	90
β/°	92.297(6)
γ/°	90
Volume/Å ³	2926.2(9)
Z	4
ρ _{calc} /g/cm ³	1.636
μ/mm ⁻¹	0.903
F(000)	1464.0
Crystal size/mm ³	0.140 × 0.140 × 0.010
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.786 to 55.388
Index ranges	-8 ≤ h ≤ 7, -21 ≤ k ≤ 21, -35 ≤ l ≤ 36
Reflections collected	23713
Independent reflections	6761 [R _{int} = 0.0807, R _{sigma} = 0.0994]
Data/restraints/parameters	6761/58/387
Goodness-of-fit on F ²	1.163
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.1590, wR ₂ = 0.3298
Final R indexes [all data]	R ₁ = 0.1995, wR ₂ = 0.3434
Largest diff. peak/hole / e Å ⁻³	2.27/-1.82

Fig. S1. The evolution of the $2.83 \cdot 10^{-5}$ M I in DMSO. Time interval between spectra is 77 seconds. The isosbestic point is observable at 298 nm with $12,400 \pm 400 \text{ M}^{-1} \cdot \text{cm}^{-1}$ molar absorptivity. For the decomposition process, the highest degree of change occurred at 318 nm for depression and at 283 nm for suppression of the absorbance. Implemented kinetic model took in account a unimolecular decomposition reaction fitted by a single exponential term. Estimated characteristic first-order constant was $3.4 \pm 0.1 \cdot 10^{-4} \text{ s}^{-1}$.

Fig. S2. The absorbance's loss of the solution kept in the dark, which was photolysed I for 2, 5, or 10 minutes. The smoothed data is scaled gas phase absorption data of nitrogen dioxide.

Fig. S3. The photolysis of the I ($4.8 \cdot 10^{-5}$ M) in the presence of Griess reagent after 445 nm light exposure.

Fig. S4. IR spectra of **I** at room temperature (300 K) before (red line) and after 60 min 365 nm exposure at 10 K (blue line).

Table S2.

HOMO – 140, LUMO – 141. Zero energy – HOMO, shift is +6.517 eV for VWN, +7.457 eV for B3LYP

	B3LYP		VWN	
N	Energy, eV	MO	Energy, eV	MO
105			-5.116
106			-5.02
107			-4.896
108			-4.717

109			-4.607
110			-4.192
111			-4.016
112			-3.876
113	-3.816		-3.81
114	-3.652		-3.504
115	-3.605		-3.407
116	-3.48		-3.29
117	-3.416		-3.206
118	-3.248		-3.145

119	-2.773		-2.724
120	-2.709		-2.695
121	-2.37		-2.346
122	-2.212		-2.299
123	-2.194		-2.262
124	-2.003		-2.104
125	-1.795		-1.993
126	-1.616		-1.943
127	-1.565		-1.859
128	-1.526		-1.783

129	-1.421		-1.712
130	-1.391		-1.632
131	-1.383		-1.525
132	-1.334		-1.336
133	-1.189		-1.167
134	-1.09		-1.12
135	-0.977		-0.937
136	-0.802		-0.689
137	-0.537		-0.593
138	-0.459		-0.495

139	-0.025		-0.273
140	0		0
141	3.454		1.702
142	3.928		2.318
143	4.112		2.384
144	4.333		2.537
145	4.621		2.824
146	4.915		3.046
147	5.149		3.185
148	5.414		3.376

149	5.435		3.598
150	5.586		3.686
151	5.677		3.883
152	5.775		3.958
153	5.858		4.237
154	6.165		4.443
155			4.9
156			5.11
157			5.722
158			6.016

159			6.416
160			6.576

Table S3.

DFT calculations using VWN functional

N	Transition Energy, eV	Oscillator strength, 10^3 a.u.	Origin of the transferred electron density, weighted sum of the occupied MO	Destination of the transferred electron density, weighted sum of the occupied MO
1	1.71347	0.0391
2	1.99859	0.1850
3	2.22164	0.2814
4	2.30817	0.5378
5	2.38746	0.3777

6	2.40292	0.1043
7	2.41708	1.9290
8	2.5455	1.0540
9	2.6519	0.4587
10	2.66393	0.0998
11	2.71823	1.0170
12	2.8282	0.1188
13	2.8363	0.0536
14	2.84837	0.7903
15	2.85321	0.4501

16	2.91382	1.0380
17	2.92602	0.4158
18	2.98006	4.0040
19	3.00253	1.1710
20	3.04135	0.0263
21	3.04791	0.5007
22	3.10168	1.2700
23	3.12148	0.3191
24	3.12395	1.7100
25	3.1629	2.3240

26	3.20248	6.1640
27	3.22519	2.4640
28	3.25845	2.8850
29	3.30091	7.2760
30	3.30522	1.5700
31	3.33485	1.8990
32	3.35779	0.6567
33	3.37465	6.6350
34	3.40264	1.9960
35	3.4288	0.0595

36	3.4311	1.6890
37	3.47818	4.4030
38	3.49581	0.1731
39	3.50352	0.6918
40	3.50718	2.5610
41	3.52385	1.4740
42	3.56766	0.2099
43	3.57241	0.1837
44	3.58107	0.2364
45	3.61319	17.0800

46	3.62025	3.7100
47	3.66082	1.3040
48	3.66495	0.2857
49	3.66848	1.4770
50	3.68113	1.9130
51	3.69937	0.8175
52	3.71321	0.6818
53	3.72269	3.1150
54	3.74347	2.1020
55	3.7477	0.6063

56	3.75255	1.1120
57	3.76689	0.8562
58	3.79063	1.2600
59	3.80073	1.1430
60	3.82054	1.8460
61	3.8583	6.2920
62	3.87532	6.5890
63	3.88474	0.2443
64	3.8975	4.3700
65	3.92594	0.6206

66	3.92726	0.4194
67	3.96114	2.3220
68	3.96488	2.0860
69	3.97308	0.6956
70	3.99173	2.4580
71	3.99754	0.5430
72	4.00683	3.5610
73	4.02083	2.2990
74	4.03145	2.9430
75	4.03947	1.0040

76	4.0509	1.8520
77	4.06949	2.4350
78	4.07501	3.5760
79	4.09189	3.4030
80	4.11126	17.3000
81	4.11445	32.6700
82	4.13764	1.8810
83	4.14836	2.2550
84	4.15646	3.6900
85	4.15836	17.7700

86	4.16081	1.5390
87	4.16519	12.9900
88	4.1805	0.8220
89	4.19138	19.3600
90	4.19984	9.1600
91	4.20787	4.7700
92	4.21936	10.0400
93	4.23954	2.4150
94	4.25104	2.1750
95	4.25342	4.8840

96	4.26417	1.1900
97	4.28317	1.4010
98	4.30866	3.7690
99	4.31557	8.2490
100	4.33144	1.2790
101	4.33576	2.7060
102	4.3519	3.9690
103	4.35703	2.5900
104	4.36737	3.1130
105	4.37078	3.7020

106	4.38133	0.3936
107	4.38642	3.2920
108	4.39375	8.4270
109	4.4122	0.4537
110	4.42809	0.6103
111	4.43523	2.6310
112	4.44059	1.9310
113	4.45425	1.5520
114	4.46475	0.5480
115	4.47372	9.4660

116	4.47614	21.8700
117	4.50223	2.4860
118	4.50906	1.7150
119	4.53154	4.2940
120	4.54227	0.6143
121	4.54772	2.3430
122	4.55669	7.2610
123	4.56274	1.1540
124	4.57053	5.4230
125	4.57723	4.3300

126	4.59628	11.1200
127	4.60394	0.1766
128	4.61264	1.0800
129	4.61833	10.3300
130	4.62446	2.3480
131	4.6314	4.4820
132	4.64339	33.2700
133	4.6463	2.7030
134	4.668	7.1220
135	4.66909	2.8370

136	4.69017	3.3120
137	4.69773	5.9620
138	4.70379	6.6350
139	4.7063	3.0790
140	4.73491	11.2100
141	4.74184	8.3360
142	4.74926	1.2650
143	4.75823	6.2460
144	4.76271	0.3744
145	4.76731	6.8130

146	4.77428	7.0050
147	4.79004	2.6250
148	4.80325	3.8080
149	4.81904	6.2560
150	4.82127	31.9900
151	4.82707	8.8710
152	4.83208	3.4250
153	4.83674	19.1900
154	4.85106	7.2140
155	4.85266	2.7500

156	4.86146	5.3020
157	4.86481	17.1800
158	4.87592	27.0700
159	4.88502	1.9120
160	4.88781	10.0900
161	4.91948	5.1520
162	4.92304	4.3860
163	4.93399	2.9740
164	4.93768	3.4070
165	4.94375	3.7140

166	4.9493	7.7390
167	4.95161	0.4532
168	4.96404	1.5930
169	4.97143	6.2600
170	4.97681	4.8640
171	4.98853	6.9910
172	4.99737	7.2310
173	5.01314	2.3630
174	5.01837	17.9900
175	5.0314	10.6600

176	5.04054	12.2900
177	5.04805	1.2490
178	5.05507	4.2170
179	5.05914	5.0880
180	5.06758	10.0500
181	5.08418	14.5500
182	5.0953	7.1820
183	5.10238	7.0900
184	5.11337	4.3960
185	5.11491	8.9450

186	5.12045	16.4500
187	5.13143	11.2500
188	5.133	14.3300
189	5.1476	33.9400
190	5.15498	16.6400
191	5.16087	20.0000
192	5.16589	6.8760
193	5.17107	4.2560
194	5.1854	9.1980
195	5.19623	35.1300

196	5.20446	3.5840
197	5.21189	11.0700
198	5.21971	3.8240
199	5.22413	6.6020
200	5.23457	5.0030
201	5.24144	9.2540
202	5.24638	1.5900
203	5.25607	15.8300
204	5.26327	27.7900
205	5.27988	12.7400

206	5.28741	2.4040
207	5.28973	12.9600
208	5.3056	3.6120
209	5.31483	21.1100
210	5.32824	20.8600
211	5.33152	1.2560
212	5.34293	14.6500
213	5.34914	10.5200
214	5.3647	4.4170
215	5.3862	2.1460

216	5.39497	3.1320
217	5.39661	4.7920
218	5.40194	11.7000
219	5.41959	0.8911
220	5.42945	5.7430
221	5.43379	13.0100
222	5.45299	8.0880
223	5.45783	12.2600
224	5.46139	8.9420
225	5.46858	36.3900

226	5.47757	7.5710
227	5.48582	19.2100
228	5.49784	6.7270
229	5.50312	0.5587
230	5.51156	2.3650
231	5.51686	0.1053
232	5.51801	1.4100
233	5.52899	10.0900
234	5.54183	16.3200
235	5.55117	23.2200

236	5.56196	9.6790
237	5.5727	25.8700
238	5.58456	0.8759
239	5.58877	5.3380
240	5.59819	4.9650
241	5.60174	3.5430
242	5.60883	9.6790
243	5.61358	3.5700
244	5.61547	3.6150
245	5.62321	12.5000

246	5.62776	13.4900
247	5.63698	2.4730
248	5.64353	7.6600
249	5.65384	4.9460
250	5.6645	1.1260
251	5.67407	3.8100
252	5.67714	7.7550
253	5.6807	45.1500
254	5.68773	0.3722
255	5.70261	2.6770

256	5.70593	3.2580
257	5.7083	19.9400
258	5.71601	9.7360
259	5.72969	0.1579
260	5.7321	9.4200
261	5.74652	34.7800
262	5.76432	2.1460
263	5.76622	3.6220
264	5.77716	1.7120
265	5.78398	9.4840

266	5.78983	1.1610
267	5.79229	1.5980
268	5.7986	4.7630
269	5.80795	18.0700
270	5.81664	36.9900
271	5.82801	0.1630
272	5.83657	37.7000
273	5.838	11.3000
274	5.8482	4.9450
275	5.85404	27.1200

276	5.86551	4.0510
277	5.86778	5.5150
278	5.87831	5.3900
279	5.88293	50.9100
280	5.89113	0.5754
281	5.90734	4.7300
282	5.91813	0.5069
283	5.92774	8.8390
284	5.93757	3.8970
285	5.95242	7.4660

286	5.96015	0.3483
287	5.96742	4.9390
288	5.97237	12.4600
289	5.9789	7.3860
290	5.98538	0.8353
291	5.99154	12.6300
292	6.00288	12.7400
293	6.01198	13.1700
294	6.0163	3.0180
295	6.02349	39.4800

296	6.03375	5.8260
297	6.03529	0.8796
298	6.04451	4.1370
299	6.05418	12.6700
300	6.05505	10.1400
301	6.05939	5.9340
302	6.07918	4.4010
303	6.0831	0.9282
304	6.08915	19.6600
305	6.09745	23.4100

306	6.11169	13.0200
307	6.12074	18.0200
308	6.12791	10.4200
309	6.14636	19.6700
310	6.15186	7.5200
311	6.17006	8.4000
312	6.17454	4.8320
313	6.17749	13.2300
314	6.18863	1.4550
315	6.20205	11.3900

316	6.21021	36.2000
317	6.21765	12.5000
318	6.22345	8.6210
319	6.22892	3.4180
320	6.23742	8.6750
321	6.24392	7.4580
322	6.24966	4.9620
323	6.25917	2.7220
324	6.26019	8.3980
325	6.26734	24.5100

326	6.27584	23.4700
327	6.28009	3.4350
328	6.2822	2.3570
329	6.28843	3.1500
330	6.29315	4.6090
331	6.29436	4.0870
332	6.30448	10.8600
333	6.30821	3.1730
334	6.32553	1.8460
335	6.33402	11.8400

336	6.34182	4.1600
337	6.34774	1.6060
338	6.35449	11.2000
339	6.36538	1.9950
340	6.37385	18.1300
341	6.38192	0.3723
342	6.38329	16.2200
343	6.40165	2.8990
344	6.41408	14.2200
345	6.41795	1.6900

346	6.42103	3.1870
347	6.42771	7.3370
348	6.43377	11.6700
349	6.43616	21.5800
350	6.43942	3.8130
351	6.4455	15.9800
352	6.45014	5.6410
353	6.46585	3.6460
354	6.46982	31.7800
355	6.47954	13.6600

356	6.48529	92.3600
357	6.50133	3.0060
358	6.51394	5.5270
359	6.51666	5.0800
360	6.52054	3.4400
361	6.53519	5.2070
362	6.54213	0.5940
363	6.55147	8.5860
364	6.55766	2.1540
365	6.55856	3.9250

366	6.58108	3.1710
367	6.58412	36.6100
368	6.58728	6.5390
369	6.60244	5.5460
370	6.6065	6.0630
371	6.61057	1.6230
372	6.61326	5.5110
373	6.62522	8.5920
374	6.63151	17.0200
375	6.64141	15.3700

376	6.64553	4.4650
377	6.65419	4.0340
378	6.66458	24.6800
379	6.66846	3.8150
380	6.67668	5.0190
381	6.67936	1.8150
382	6.69127	0.4689
383	6.69508	15.2100
384	6.70598	1.4570
385	6.71446	1.5830

386	6.72484	16.8300
387	6.73566	4.6590
388	6.74182	0.7458
389	6.74735	12.4200
390	6.75416	4.2530
391	6.76603	12.5400
392	6.76668	10.3100
393	6.78276	1.5270
394	6.78347	9.8890
395	6.78555	12.8400

396	6.79552	8.4450
397	6.80087	47.3400
398	6.82518	31.7700
399	6.83265	3.4070
400	6.84727	4.4730

Table S4.

DFT calculations using B3LYP functional

N	Transition Energy, eV	Oscillator strength, 10^3 a.u.	Origin of the transferred electron density, weighted sum of the occupied MO	Destination of the transferred electron density, weighted sum of the occupied MO
1	2.67786	0.4078
2	2.78304	0.0077
3	2.95455	0.4771

4	3.02389	0.6156
5	3.12507	0.0837
6	3.14237	0.9721
7	3.183	0.2292
8	3.28456	1.7370
9	3.41255	1.0750
10	3.4589	0.5025
11	3.47688	0.9552
12	3.48987	1.4830
13	3.53082	2.5650

14	3.54217	12.2500
15	3.58493	1.2090
16	3.67005	0.4375
17	3.71037	1.1170
18	3.71764	28.3100
19	3.78114	2.9140
20	3.82163	0.7424
21	3.88591	6.4600
22	3.89911	0.3882
23	3.94155	1.9430

24	3.94675	2.9390
25	3.966	17.8400
26	3.97481	1.3550
27	4.01317	3.8930
28	4.02192	1.5250
29	4.04996	0.2411
30	4.0763	1.0470
31	4.09549	0.1044
32	4.11431	0.7174
33	4.133	0.7139

34	4.14714	1.1560
35	4.17593	2.6570
36	4.21134	0.6016
37	4.22324	0.2327
38	4.24817	1.8300
39	4.25488	1.0890
40	4.28313	1.7060
41	4.29906	0.0807
42	4.31307	7.5470
43	4.32301	4.8170

44	4.33617	2.7660
45	4.36639	69.3900
46	4.36927	62.4300
47	4.40386	0.9012
48	4.41766	0.9628
49	4.43122	13.3800
50	4.44146	6.8500
51	4.47073	2.6980
52	4.47165	2.9460
53	4.50012	11.6500

54	4.52963	3.7480
55	4.55384	0.3494
56	4.5695	12.6600
57	4.57812	6.4710
58	4.59846	3.8160
59	4.60684	23.5800
60	4.61164	3.7870
61	4.63352	0.5288
62	4.64958	3.1310
63	4.68803	3.5620

64	4.70424	1.8200
65	4.72462	4.1290
66	4.73752	9.0690
67	4.74696	0.3229
68	4.75396	0.4954
69	4.76689	1.4560
70	4.77301	1.7140
71	4.78564	1.4390
72	4.79165	38.6400
73	4.81665	5.2260

74	4.82913	9.2310
75	4.85705	1.6590
76	4.8598	3.2010
77	4.88653	28.9900
78	4.89826	2.8740
79	4.90494	1.6650
80	4.90904	1.4740
81	4.93322	4.4960
82	4.93513	1.9030
83	4.94869	6.2800

84	4.96281	2.0240
85	4.97315	9.6890
86	4.98656	7.7020
87	5.00118	10.6500
88	5.00652	4.6130
89	5.02737	12.3000
90	5.04122	4.3860
91	5.05446	7.9660
92	5.07096	13.3000
93	5.07333	34.6200

94	5.08021	15.4200
95	5.08957	7.0190
96	5.09487	3.5020
97	5.12066	16.9700
98	5.12447	14.2300
99	5.13979	8.5270
100	5.15666	15.8000
101	5.16843	16.7500
102	5.17166	3.3720
103	5.1826	6.6790

104	5.19547	17.3300
105	5.19674	13.1900
106	5.2169	2.0740
107	5.22157	5.9450
108	5.22288	12.2400
109	5.23839	1.7060
110	5.24563	1.3890
111	5.25367	3.9870
112	5.26299	5.7540
113	5.27046	14.2000

114	5.27527	34.8200
115	5.28167	14.1900
116	5.29095	15.8400
117	5.30805	13.7500
118	5.31751	10.8300
119	5.32565	4.9080
120	5.33453	6.5790
121	5.34322	1.9600
122	5.35979	4.9250
123	5.36776	9.4370

124	5.38008	6.6590
125	5.38374	8.7960
126	5.39904	28.9500
127	5.40434	9.1740
128	5.40896	10.1400
129	5.4206	18.3900
130	5.43337	0.6896
131	5.45337	17.3800
132	5.4715	40.2500
133	5.48062	19.7100

134	5.50693	56.8800
135	5.51872	5.9760
136	5.52385	66.5300
137	5.54579	5.4780
138	5.55768	1.8910
139	5.5637	19.8000
140	5.57065	0.5322
141	5.57924	4.7250
142	5.58247	11.2900
143	5.59416	9.5750

144	5.60296	0.1805
145	5.61553	8.6190
146	5.62143	23.8000
147	5.63308	13.0500
148	5.63794	2.7270
149	5.65031	15.7900
150	5.66379	35.6000