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Article

# Ruthenium(II) Bipyridyl Complexes with C<sup>^</sup>C\* Cyclometalated **Mesoionic Carbene Ligands**

Johannes Soellner,<sup>†</sup> Ivana Císařová,<sup>‡</sup> and Thomas Strassner<sup>\*,†</sup>

<sup>†</sup>Physikalische Organische Chemie, Technische Universität Dresden, 01069 Dresden, Germany

<sup>‡</sup>Department of Inorganic Chemistry, Faculty of Science, Charles University Prague, 128 43 Praha 2, Czech Republic

**S** Supporting Information

ABSTRACT: The synthesis of four 2,2'-bipyridyl ruthenium(II) complexes with cyclometalating mesoionic 1,2,3-triazolylidene ligands via their respective p-cymene ruthenium(II) precursors is presented. Solid-state structures confirm the formation of the proposed complexes, which were characterized by UV/vis and electrochemical experiments as well as time-dependent DFT calculations including NTO analysis. The title motif shows improved photophysical properties compared to structurally related ruthenium(II) complexes with C^C\* cyclometalating imidazole-based N-heterocyclic carbene ligands. Due to their electronic properties, the presented dyes are promising candidates for an application in dye-sensitized solar cells.



# INTRODUCTION

In the last two decades, the global power output increased by nearly 40%, according to the quinquennial energy statistics released by the United Nations.<sup>1</sup> Managing the balancing act of stilling the ever-increasing hunger for energy while adjusting its generation to become more climate friendly is one of the dominating challenges of the 21st century. An obvious free and "renewable" alternative to fossil fuels as a source of energy is, among others, the sun. It is not surprising that solar energy accounted for approximately 38% of the global power capacity that was commissioned in 2017, even surpassing fossil fuels in that respect.<sup>2</sup> Current photovoltaic technologies still rely heavily on inorganic materials, which are expensive to prepare and process. Problems also arise from their toxicity and low natural abundance, for example, in the case of CdTe.<sup>3</sup> Dyesensitized solar cells (DSSCs) with organometallic dyes can avoid those problems but are still lagging behind in terms of efficiency compared to established inorganic materials.<sup>3</sup> Generally, DSSCs consist of a transparent conductive substrate that is coated with a semiconductor such as  $TiO_2$  to which the sensitizing dye is adsorbed. Upon excitation of the dye by sunlight, an electron is injected into the conduction band of the semiconductor. This process is commonly referred to as charge separation, since the electron is transported to the conduction band while the hole remains at the dye. Subsequently, the oxidized sensitizer molecule needs to be regenerated, which is usually achieved by the triiodide/iodine redox couple. The latter is in turn regenerated by the counter electrode. In order to function efficiently, each part of the DSSC needs to be carefully optimized and compatible with the other components. This challenge has been addressed in depth in a number of reviews.<sup>3,4</sup>

The efficiency of the solar cell depends on the charge separation step, and therefore the sensitizer molecule, to a

significant extent. Up to now, the most prominent and efficient sensitizing molecules are the N3,5 N719,6 and N7497 ("black dye") molecules, reaching cell efficiencies >10%. They are based upon ruthenium(II) complexes bearing carboxy functionalized polypyridyl as well as thiocyanate ligands. However, rhodanide ligands are labile, due to their monodentate nature, and contribute to decomposition processes of the dye.<sup>8</sup> A promising strategy to replace thiocyanates is the use of cyclometalating phenylpyridine ligands, which was studied by van Koten,<sup>9</sup> Grätzel,<sup>10</sup> and Berlinguette<sup>11</sup> (Figure 1, I) among others.<sup>12</sup> Following initial studies by Li<sup>13</sup> and Chung,<sup>14</sup> Barnard and co-workers<sup>15</sup> then introduced a charge-neutral imidazole based N-heterocyclic carbene (NHC) ligand to ruthenium bis-2,2-bipyridyl complexes (Figure 1, II). At the same time, structurally related tridentate ligands using 1,2,3-triazolylidenes were studied by Schubert and Berlinguette.<sup>16</sup> These  $C^*N^*C^*$  pincer type ligands carry an N-donating pyridine bridge, which is bound to the backbone of the 1,2,3-triazole moiety. Shortly after, the group of Albrecht presented ruthenium(II) complexes with the analogous bidentate ligands.<sup>17</sup> Especially the groups of Berlinguette and Schubert discussed the effect of the mesoionic carbene (MIC) donors on the photophysical properties of the resulting ruthenium(II) complexes. The higher  $\sigma$ -donor strength compared to classical NHCs enables an efficient destabilization of <sup>3</sup>MC states, which in turn leads to longer excited state lifetimes.<sup>16a,b</sup> The most recent developments, which were introduced simultaneously by our group and the group of Nazeeruddin, feature C^C\* cyclometalating ligands based on imidazolinylidenes as analogs to phenylpyridines (Figure 1, III).<sup>18</sup> A common goal of these ligand modifications

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Figure 1. Recent development of bis-2,2'-bipyridyl ruthenium(II) complexes with cyclometalating ligands.

is to fine-tune the energy levels of the frontier molecular orbitals (FMOs), particularly of the highest occupied molecular orbital (HOMO). This is done to tailor the absorption properties and correctly set the redox potentials of the dye. Thereby, it can interact optimally with the adjacent parts of the DSSC.<sup>3</sup> In that respect, cyclometalated ruthenium-(II) complexes with carbene ligands gave promising results.<sup>13,16,17,19</sup>

Herein, we report the synthesis of four ruthenium(II) complexes bearing mesoionic,  $C^{C*}$  cyclometalating 1,2,3-triazolylidene ligands. This novel class of sensitizing molecules is investigated concerning their applicability in DSSCs by UV/ vis and electrochemical experiments, as well as density functional theory (DFT) calculations. The mesoionic ligands form complexes with superior spectroscopic properties compared to their imidazolinylidene analogs as well as to related C\*^N ligated ruthenium complexes.

## RESULTS AND DISCUSSION

Synthesis and Characterization. Aryl-1,2,3-triazole ligand platforms for C<sup>^</sup>C\* cyclometalation are readily available from substituted anilines (Scheme 1). The employed procedure involves the in situ formation of the respective aryldiazonium salt, which is then reacted with sodium azide to give the intermediate arylazide. Aryl-1,2,3-triazoles 1a-d are then synthesized according to a literature procedure, which selectively introduces a methyl group to the 4-position of the heterocycle.<sup>20</sup> Syntheses of the ligand precursors are concluded by quarternization of 1a-d using methyl iodide to yield the respective 1-aryl-3,4-dimethyl-1H-1,2,3-triazolium iodides 2ad. Due to the selective blocking of one backbone position in the 1,2,3-triazole motif, silver(I)-oxide will selectively deprotonate 2a-d and form the mesoionic carbene, as desired, adjacent to the aryl moiety. In analogy to a recently published procedure<sup>15,17,21</sup> by our group, addition of [Ru(p-cymene)- $Cl_2$  leads to a transmetalation of the N-heterocyclic ligand to ruthenium and subsequent cyclometalation into the N-aryl fragment.<sup>22</sup> The analytically pure Ru *p*-cymene complexes 3ad are isolated by flash chromatography of THF solutions of the complexes over basic aluminum oxide and subsequent precipitation by addition of *n*-pentane. The formation of the





<sup>*a*</sup>Reagents and conditions: (i) NaNO<sub>2</sub>, H<sub>2</sub>O/HCl, 0 °C; (ii) NaN<sub>3</sub>, 0 °C to room temperature; (iii) CH<sub>3</sub>CH<sub>2</sub>CHO, *m*CPBA, pyrrolidine, THF, 50 °C; (iv) MeI, THF, 110 °C; (v) Ag<sub>2</sub>O, [Ru(*p*-cymene)Cl<sub>2</sub>]<sub>2</sub>, DCM, 45 °C; (vi) 2,2'-bipyridine, NH<sub>4</sub>PF<sub>6</sub>, DMSO, 140 °C.

Ru(II) p-cymene complexes is visible in the proton NMR spectra by the appearance of the characteristic septet of the isopropyl group. The yellow to orange compounds are readily soluble in polar solvents, such as dimethyl sulfoxide, acetonitrile, tetrahydrofuran, dichloromethane, and chloroform, but tend to decompose in solution within hours or days. This can be attributed to the lability of the *p*-cymene ligand, which is utilized in the following reaction step: the syntheses of the title complexes is achieved by stirring the compounds 3ad with 2,2'-bipyridine in DMSO solution at elevated temperatures. The reaction is carried out under the exclusion of light to avoid side reactions induced by the excitation of the molecule. After precipitation of residual 2,2'-bipyridine by addition of water, the cationic ruthenium complexes can be precipitated from the aqueous solution as their respective hexafluorophosphate salts by the addition of NH<sub>4</sub>PF<sub>6</sub>. The workup of the crude product is again achieved by flash chromatography of a dichloromethane solution of the complexes over basic aluminum oxide. Isolation of the analytically pure complexes 4a-d is accomplished by subsequent crystallization from dichloromethane/diethyl ether mixtures.

The compounds form solids of a dark purple to black color and deep purple solutions in polar solvents like acetonitrile, DMSO, dichloromethane, and chloroform. At low concentrations, the solutions of 4a and 4b appear violet, while 4c and 4d show a violet to red color. In contrast to the *p*-cymene complexes, the tris(bidentate) ruthenium complexes 4a-d are stable in solution over the course of days and weeks without any apparent decomposition.

Single-crystals of all complexes 4a-d suitable for X-ray diffraction experiments could be obtained by slow evaporation of solutions in water/acetone mixtures (Figures 2–5). Upon crystallization, the ruthenium complexes form dark rhomboid shaped blocks, which have a tendency to shatter when removed from the mother liquor. This can be attributed to evaporation of cocrystallized solvent molecules. Complexes 4a and 4b



Figure 2. ORTEP3 illustration of the crystal structure of compound 4a. Thermal ellipsoids drawn at 50% probability; H atoms and counterion omitted for clarity.



Figure 3. ORTEP3 illustration of the crystal structure of compound 4b. Thermal ellipsoids drawn at 50% probability; H atoms, cocrystallized  $H_2O$ , and disordered counterion omitted for clarity.

crystallize in the monoclinic space groups  $P2_1/n$  (4a) and C2/c (4b), while 4c and 4d display a triclinic symmetry in the space group  $P\overline{1}$ . All structures show the presence of a racemic mixture of the respective  $\Lambda$  and  $\Delta$  enantiomers of the ruthenium(II) complexes.

All complexes 4a-d show slightly distorted octahedral coordination geometries around the ruthenium center. This distortion is mainly a result of the formation of five-membered metallacycles by the 2,2'-bipyridines as well as the cyclometalating ligands. For example, the C^C\* bite angle C1–Ru1–C6 ranges from 79.1° to 79.8° in all complexes (Table 1) and thereby deviates from the ideal value by approximately 11°. The cyclometalating ligand itself remains almost perfectly planar in all solid-state structures. The corresponding dihedral C1–N1–C5–C6 displays values from 0.2(3)° for 4a to -2.8(2)° in 4b. Also, due to the bisheteroleptic nature of the title complexes, the ruthenium–nitrogen bond lengths are a valuable probe to assess the donor strength of the C^C\* cyclometalating ligand. Compared to Ru1–N5/Ru1–N6, the bond lengths for Ru1–N4 and Ru1–N7 show a significant



**Figure 4.** ORTEP3 illustration of the crystal structure of compound **4c**. Thermal ellipsoids drawn at 50% probability; H atoms, disordered acetone, and counterion omitted for clarity.



**Figure 5.** ORTEP3 illustration of the crystal structure of compound **4d**. Thermal ellipsoids drawn at 50% probability; H atoms and counterion omitted for clarity.

Table 1. Selected Bond Lengths [Å] and Angles [deg] for the Crystal Structures of 4a-d

|             | 4a       | 4b         | 4c         | 4d        |
|-------------|----------|------------|------------|-----------|
| Ru1-C1      | 2.030(2) | 2.0385(17) | 2.0369(15) | 2.032(3)  |
| Ru1-C6      | 2.060(2) | 2.0626(17) | 2.0673(15) | 2.054(3)  |
| Ru1–N4      | 2.104(2) | 2.1064(15) | 2.1045(13) | 2.105(3)  |
| Ru1-N5      | 2.060(2) | 2.0577(14) | 2.0609(12) | 2.053(2)  |
| Ru1–N6      | 2.047(2) | 2.0529(15) | 2.0555(12) | 2.055(2)  |
| Ru1-N7      | 2.089(2) | 2.0957(14) | 2.0916(12) | 2.096(2)  |
| C1-Ru1-C6   | 79.15(9) | 79.62(7)   | 79.78(6)   | 79.80(10) |
| C1-N1-C5-C6 | 0.1(3)   | -2.8(2)    | 0.76(19)   | -1.8(3)   |

elongation by 0.03–0.05 Å displaying a distinct trans influence by the carbon donors (Table 1). This effect is strongest for the Ru1–N4 bond trans to the anionic aryl ligand. These findings are in good agreement with data reported on other transition metal complexes bearing  $C^{C*}$  cyclometalating ligands.<sup>18</sup> Generally, the highlighted bond lengths do not exhibit any significant dependency on the substitution pattern of the ligands.

Spectroscopic and Electrochemical Data. Absorption spectra of all complexes 4a-d were recorded in acetonitrile solution at a concentration of  $5 \times 10^{-5}$  mol/L to study their spectroscopic properties. All of the compounds show structured absorptions up to wavelengths of 650-675 nm. The slow absorption onset in the low energy range is characteristic for ruthenium-based sensitizing molecules due to low energy <sup>3</sup>MLCT transitions. All complexes show three distinct absorption maxima between 325 and 575 nm, and their position is dependent on the substitution pattern of the cyclometalating ligand. For the unsubstituted complex 4a, they can be found at approximately 380, 500, and 570 nm. The electron-donating methoxy group in 4b seems to have no impact on the absorption properties and gives an almost congruent spectrum. However, an effect of the electronic modifications in the structures is visible for 4c and 4d, which carry electron-withdrawing bromine and nitrile substitution, respectively. Here, the aforementioned absorption bands are shifted to higher energies by approximately 20 nm. The absorption maxima recorded below 325 nm, on the other hand, are identical for all presented complexes.

Compared to recently published, related molecules with imidazole based  $C^C^*$  cyclometalating ligands<sup>18</sup> the absorption spectra of **4a** and **4b** display a bathochromic shift of about 20 nm, while these of **4c** and **4d** feature absorptions at very similar energies (Figure 6). To better understand the



Figure 6. Absorption (solid) and emission (dashed) spectra for complexes 4a-d in  $5 \times 10^{-5}$  mol/L acetonitrile solutions.

transitions involved in the absorption processes, time-dependent DFT calculations using several functional/basis set combinations were employed. Among the screened methods were the GGA functionals BP86 and PBE, as well as the hybrid functionals B3LYP and PBE0 together with Pople and Ahlrichs basis sets. None of the tested combinations describes the energies of the excitations fully accurately. While the GGA functionals systematically underestimate the excitation energies, the hybrid functionals overestimate them (see ESI, Figure S1). However, the B3LYP/6-31G(d) level of theory gave the most accurate results, which are given exemplarily for complex 4a in Figure 7. According to the TD-DFT calculations, all low energy transitions are dominated by excitations from the three highest occupied molecular orbitals to the two lowest unoccupied molecular orbitals (LUMOs). While the HOMOs are clearly dominated by the metal with contributions from the cyclometalating MIC ligand, the LUMOs are almost exclusively located in the 2,2'-bipyridyl ligands (see ESI, Tables S1 and S2).

The contributions of the cyclometalating moiety to the FMOs reflect the observed bathochromic shift in the experimental absorption spectra observed for 4c and 4d, compared to 4a and 4b, which is in agreement with recently published studies.<sup>18b</sup> In order to visualize these results, the natural transition orbitals (NTOs) of the three lowest spinallowed transitions (oscillator strength >0.01) were calculated (Figure 7). The NTOs show a clear metal-to-ligand charge transfer process from the ruthenium center to the 2,2'bipyridyl ligands. This directed flow of electrons is ideal for the application of these complexes as sensitizers, since the binding of the molecules to a TiO<sub>2</sub> substrate would be achieved via carboxylate functions at the 2,2'-bipyridyl ligands. To model the impact of potential carboxylate functionalizations, we calculated the respective molecules, again, at the B3LYP/6-31G(d) level of theory. While the nature of the transitions remains unchanged in the carboxylate substituted molecule, the energies of the FMOs are stabilized noticeably and the absorption onset is red-shifted by roughly 30 nm (see ESI, Figures S2 and S3).

The high energy excitations at around 300 nm can be attributed by the NTO analysis to consist of  $\pi - \pi^*$ -transitions at the 2,2'-bipyridyl moieties. This is in accordance with their independence from substitution effects in the experimental spectra.

Upon excitation of the low-energy absorption bands ( $\lambda_{exc} = 560 \text{ nm}$ ) in deaerated acetonitrile solutions, we were able to obtain emission spectra in the near-infrared region of the electromagnetic spectrum (Figure 6). All complexes 4a-d display a single, unstructured emission band with emission maxima at 804 nm (4a), 802 nm (4b), 785 nm (4c), and 776 nm (4d) and thereby reproduce the energetic trends observed for the absorption spectra.

Cyclic voltammetry (CV) spectra of all title compounds 4ad were recorded in degassed acetonitrile solutions. The results are given in Figure 8 and Table 2 and are converted to E vs normal hydrogen electrode (NHE) for better comparison (for full spectra see ESI, Figures S4-S7). Except for the brominesubstituted complex 4c, all compounds display two reversible reduction events at approximately -1.41 V and -1.67 V (vs NHE). These events show no dependency on the substitution pattern of the cyclometalating MIC ligand, which agrees with their attribution to stepwise reductions of the 2,2'-bipyridyls that are characteristic of these ligands.<sup>18b</sup> Reversible oxidative events for Ru<sup>II</sup>/Ru<sup>III</sup> are recorded for all complexes 4a-d in the range of 0.49 to 0.68 V (vs NHE). Due to the contribution of the cyclometalating ligands to the HOMO, the electronwithdrawing substitutions in 4c and 4d result in a higher oxidation potential compared to the complexes 4a and 4b. This finding is also in agreement with the shifted absorption spectra discussed earlier. These experimentally observed trends are reproduced in the HOMO energies obtained from single point calculations with the CPCM model (solvent = acetonitrile). The DFT method underestimates the experimental values by 0.1 V for 4a and 4b, while the absolute deviation decreases for complexes 4c and 4d with electronwithdrawing substituents (Table 2).



Figure 7. Comparison of experimental and TD-DFT calculated absorption spectra (half-width at half height = 0.1 eV) of complex 4a. For selected excitations, the obtained natural transition orbitals (isoval = 0.04) are given as transitions from hole (bottom) to particle (top).



Figure 8. CV spectra of all title complexes 4a-d in acetonitrile solution vs NHE (ferrocene used as internal standard, sweep rate = 100 mV/s).

 Table 2. Electrochemical Data and Comparison with DFT

 Calculated HOMO Energies for All Title Compounds

|    | cy                        | DFT <sup>b</sup>            |                         |                    |
|----|---------------------------|-----------------------------|-------------------------|--------------------|
|    | $E_{1/2,\text{red2}}$ [V] | $E_{1/2,\mathrm{red1}}$ [V] | $E_{1/2,\text{ox}}$ [V] | $E_{\rm HOMO}$ [V] |
| 4a | -1.67                     | -1.40                       | 0.60                    | 0.50               |
| 4b | -1.68                     | -1.42                       | 0.59                    | 0.49               |
| 4c | с                         | -1.41                       | 0.66                    | 0.62               |
| 4d | -1.65                     | -1.40                       | 0.69                    | 0.68               |

<sup>*a*</sup>CVs in acetonitrile referenced internally vs Fc/Fc<sup>+</sup> and converted to *E* vs NHE by addition of 0.63 V. <sup>*b*</sup>HOMO eigenvalues converted to *E* vs NHE. <sup>*c*</sup>Irreversible event.

# CONCLUSION

We prepared four ruthenium(II) 2,2'-bipyridyl complexes with cyclometalated 1,2,3-triazolylidene ligands. The synthesis started from substituted anilines to give the respective 1,2,3-triazolium ligand precursors. The subsequently prepared ruthenium(II) *p*-cymene complexes were used as starting material in a ligand exchange reaction with 2,2'-bipyridine to

yield the title compounds as hexafluorophosphate salts. Characterization by solid-state structures confirmed the proposed binding mode of the cyclometalating ligands. In UV/vis experiments, the title compounds displayed broad absorptions with an onset between 650 and 675 nm. This corresponds to a 20 nm red-shift compared to related complexes bearing imidazole based C^C\* ligands<sup>18</sup> and a bathochromic shift of more than 100 nm with respect to known C\*^N complexes with mesoionic triazole ligands.<sup>17</sup> Time-dependent DFT calculations in combination with NTO analysis helped to assign the observed low energy transitions to MLCT processes with a directed electron transfer from the ruthenium center/cyclometalating moiety to the 2,2'-bipyridyl ligands. The contribution of the mesoionic carbene ligand to the HOMO was visualized by cyclic voltammetry, which showed a direct influence of the substitution pattern on the potential of the first oxidative event. All conducted experiments confirmed the applicability of the presented dyes as sensitizers in DSSCs.

# EXPERIMENTAL SECTION

General. All ruthenium complexes were synthesized in flame-dried glassware under argon atmosphere. Solvents of at least 99.0% purity were used in all reactions in this study. Dimethyl sulfoxide (DMSO) was dried using standard techniques, degassed using the freezepump-thaw technique, and stored over molecular sieves (4 Å). [Ru(p-cymene]Cl<sub>2</sub>]<sub>2</sub> was prepared according to a modified literature procedure. All other chemicals were obtained from common suppliers and used without further purification. <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F spectra were acquired on Bruker NMR Avance 300, Bruker DRX 500, and Bruker Avance 600 NMR spectrometers. <sup>1</sup>H and <sup>13</sup>C spectra were referenced internally (<sup>1</sup>H 7.26 ppm, <sup>13</sup>C 77.16 ppm for CDCl<sub>3</sub>; <sup>1</sup>H 2.50 ppm, <sup>13</sup>C 39.43 ppm for DMSO- $d_6$ ). <sup>19</sup>F NMR spectra were also referenced externally against trifluoromethylbenzene (-63.72 ppm vs CCl<sub>3</sub>F). Chemical shifts are given in ppm, and coupling constants J in Hz. Elemental analyses were performed by the microanalytical laboratory of our institute on a Hekatech EA 3000 Euro Vector elemental analyzer. Melting points were determined by using a Wagner and Munz PolyTherm A system and are not corrected.

**Spectroscopy.** All absorption spectra were recorded in acetonitrile solutions of the respective complexes with analyte concentrations of  $5 \times 10^{-5}$  mol/L on a PerkinElmer Lambda 365 UV/vis spectrophotometer. Prior to emission measurements, the solutions were purged with argon for 20 min. All emission spectra were obtained using a Cary Eclipse fluorescence spectrophotometer.

**Electrochemistry.** Cyclic voltammetry experiments were carried out using a Biologic SP-150 potentiostat in degassed, dry acetonitrile solutions, employing a platinum wire counter electrode, a glassy carbon working electrode, and a Ag/Ag<sup>+</sup> pseudo-reference electrode. All complexes were measured as 0.5 mM solutions along with 0.1 M supporting electrolyte (N(*n*-Bu)<sub>4</sub>ClO<sub>4</sub>) at a sweep rate of 100 mV/s. All measurements were internally referenced against Fc/Fc<sup>+</sup>. The obtained potentials were converted to *E* vs NHE via the redox potential of the Fc/Fc<sup>+</sup> couple vs NHE (*E* = 0.63 V).<sup>23</sup>

**Computational Details.** The Gaussian16<sup>24</sup> package was used to perform all quantum chemical calculations employing the hybrid functionals B3LYP<sup>25</sup> and PBE0,<sup>26</sup> as well as the pure functionals BP86<sup>27</sup> and PBE<sup>28</sup> together with 6-31G(d)<sup>29</sup> and def2-SVP<sup>30</sup> basis sets. Ruthenium was described by the LANL2DZ ECP and basis set.<sup>31</sup> All given structures were verified as true minima by vibrational frequency analysis and the absence of negative eigenvalues. UV/vis spectra and electronic transitions were calculated using TD-DFT methods (singlet,  $n_{\text{states}} = 50$ , CPCM, solvent = acetonitrile) as implemented in the Gaussian16 package. Conversion of energy values obtained in calculations to *E* vs NHE according to  $E_{\text{abs}} [\text{eV}] = -4.5$  eV – eU (vs NHE).<sup>32</sup> Calculated geometries were visualized with CYLview<sup>33</sup> and GaussView.<sup>34</sup>

Synthesis and Characterization. Compound 1a. Compound 1a was prepared analogously to a literature procedure.<sup>20</sup> In a 250 mL round-bottom flask, 2.794 g (30 mmol) of aniline was dissolved in 60 mL of aqueous HCl (10%) and cooled to 0 °C. Sodium nitrite (2.277 g, 33 mmol, 1.1 equiv) in 20 mL of water was added dropwise to this solution and stirred at 0  $^\circ \rm C$  for 1 h. At this temperature, 2.340 g (36 mmol, 1.2 equiv) of sodium azide was added, and the mixture was stirred at 0 °C for 4 h. The aqueous phase was extracted with diethyl ether; the combined organic phase was dried over magnesium sulfate and concentrated under reduced pressure. The residue was diluted in THF, 1.917 g (33 mmol, 1.1 equiv) of propionaldehyde and 0.866 g (30 mmol, 1 equiv) of pyrrolidine were added, and the mixture was stirred at 50 °C overnight. The solution was cooled to 0 °C; 7.855 g (33 mmol, 1.1 equiv) of 3-chloroperbenzoic acid was added in small portions and then stirred for 1 h at room temperature. All volatiles were removed in vacuo, and the product was isolated by column chromatography with an eluent mixture of isohexanes/ethyl acetate (1:1). After evaporation of all volatiles and drying in vacuo, the analytically pure product was obtained as brown solid (1.41 g, 30%). Mp 59 °C. <sup>1</sup>H NMR in CDCl<sub>3</sub> (300 MHz)  $\delta$  7.80 (s, 1H,  $CH_{arom}$ ), 7.75-7.67 (m, 2H, CH<sub>arom</sub>), 7.57-7.48 (m, 2H, CH<sub>arom</sub>), 7.47-7.39 (m, 1H, C<u>H</u><sub>arom</sub>), 2.47 (s, 3H, CC<u>H</u><sub>3</sub>). <sup>13</sup>C NMR in CDCl<sub>3</sub> (75 MHz)  $\delta$  143.8 (<u>C</u><sub>i</sub>), 137.0 (<u>C</u><sub>i</sub>), 129.9 (<u>C</u>H<sub>arom</sub>), 128.9 (<u>C</u>H<sub>arom</sub>), 120.6 (<u>C</u>H<sub>arom</sub>), 119.9 (<u>C</u>H<sub>arom</sub>), 10.7 (C<u>C</u>H<sub>3</sub>). GC-MS (EI) m/z (%) = 159 [M<sup>+</sup>, 5], 131 [M-N<sub>2</sub><sup>+</sup>, 60]. Anal. Calcd for C<sub>9</sub>H<sub>9</sub>N<sub>3</sub>: C 67.91%; H 5.70%; N 26.40%. Found: C 68.04%; H 5.95%; N 26.47%

*Compound* **1b**. Compound **1b** was prepared analogously to **1a**. 4-Methoxyaniline (3.695 g, 30 mmol) was used instead of aniline. The product was isolated by column chromatography with isohexanes/ethyl acetate (1:2) as eluent mixture (1.19 g, 21%). Mp 71 °C. <sup>1</sup>H NMR in CDCl<sub>3</sub> (300 MHz)  $\delta$  7.65 (d, *J* = 0.8 Hz, 2H, C<u>H</u><sub>triazole</sub>), 7.63–7.57 (m, 2H, C<u>H</u><sub>arom</sub>), 7.05–6.95 (m, 2H, C<u>H</u><sub>arom</sub>), 3.86 (s, 3H, OC<u>H</u><sub>3</sub>), 2.43 (s, 3H, CC<u>H</u><sub>3</sub>). <sup>13</sup>C NMR in CDCl<sub>3</sub> (75 MHz)  $\delta$  159.9 (<u>C</u><sub>i</sub>), 143.7 (<u>C</u><sub>i</sub>), 130.6 (<u>C</u><sub>i</sub>), 122.2 (<u>C</u>H<sub>arom</sub>), 119.9 (<u>C</u>H<sub>arom</sub>), 114.9 (<u>C</u>H<sub>arom</sub>), 55.7 (O<u>C</u>H<sub>3</sub>), 10.8 (C<u>C</u>H<sub>3</sub>). GC-MS (EI) *m/z* (%) = 189 (M<sup>+</sup>, 14), 161 (M – N<sub>2</sub><sup>+</sup>, 100), 146 (M – N<sub>2</sub> – Me<sup>+</sup>, 46). Anal. Calcd for C<sub>10</sub>H<sub>11</sub>N<sub>3</sub>O: C 63.48%; H 5.86%; N 22.21%. Found: C 63.77%; H 5.99%; N 21.88%.

Compound 1c. Compound 1c was prepared analogously to 1a. 4-Bromoaniline (5.161 g, 30 mmol) was used instead of aniline. The product was isolated by crystallization from a hot mixture of isohexanes and ethyl acetate (1.79 g, 25%). Mp 151 °C. <sup>1</sup>H NMR in CDCl<sub>3</sub> (300 MHz)  $\delta$  7.71 (d, J = 0.9 Hz, 1H, C<u>H<sub>trizole</sub></u>), 7.69–7.55 (m, 4H, C<u>H<sub>arom</sub></u>), 2.45 (d, J = 0.8 Hz, 3H, CC<u>H<sub>3</sub></u>). <sup>13</sup>C NMR in CDCl<sub>3</sub> (75 MHz)  $\delta$  144.2 (<u>C</u><sub>i</sub>), 136.1 (<u>C</u><sub>i</sub>), 133.0 (<u>C</u>H<sub>arom</sub>), 122.5  $\begin{array}{l} (\underline{C}_{i}), 121.9 \ (\underline{C}H_{arom}), 119.6 \ (\underline{C}H_{arom}), 10.8 \ (C\underline{C}H_{3}). \ GC-MS \ (EI) \ m/\\ z \ (\%) = 237 \ [M^{+}, 7], 208 \ [M - N_{2}^{+}, 100]. \ Anal. \ Calcd \ for \ C_{9}H_{8}BrN_{3}: \\ C \ 45.40\%; \ H \ 3.39\%; \ N \ 17.65\%. \ Found: \ C \ 45.54\%; \ H \ 3.25\%; \ N \ 17.35\%. \end{array}$ 

Compound 1d. Compound 1d was prepared analogously to 1a at a 50 mmol scale. 4-Aminobenzonitrile (5.907 g, 50 mmol) was dissolved in 100 mL of aqueous HCl (10%). Sodium nitrate (3.795 g, 55 mmol, 1.1 equiv) and sodium azide (3.901 g, 60 mmol, 1.2 equiv) were added. Later, 3.194 g (55 mmol, 1.1 equiv) of propionaldehyde, 3.556 g (50 mmol, 1 equiv) of pyrrolidine, and 13.092 g (55 mmol, 1.1 equiv) of 3-chloroperbenzoic acid were used. Purification via flash column chromatography (isohexanes/ethyl acetate, 1:2) and subsequent crystallization a from hot isohexanes/ ethyl acetate mixture vielded compound 1d (1.50 g, 16%). Mp 183 °C. <sup>1</sup>H NMR in CDCl<sub>3</sub> (300 MHz)  $\delta$  7.95–7.84 (m, 2H, CH<sub>arom</sub>), 7.87-7.77 (m, 2H, CHarom), 7.79 (s, 1H, CHtriazole), 2.46 (s, 3H,  $CCH_3$ ). <sup>13</sup>C NMR in CDCl<sub>3</sub> (75 MHz)  $\delta$  145.1 (<u>C</u><sub>i</sub>), 140.1 (<u>C</u><sub>i</sub>), 134.0 (<u>C</u>H<sub>arom</sub>), 120.4 (<u>C</u>H<sub>arom</sub>), 119.0 (<u>C</u>H<sub>arom</sub>), 117.9 (<u>C</u><sub>i</sub>), 112.1  $(\underline{C}_{i})$ , 11.0 (C<u>C</u>H<sub>3</sub>). GC-MS (EI) m/z (%) = 184 [M<sup>+</sup>, 13], 156 [M - $N_2^+$ , 43], 155 [M - N<sub>2</sub>H<sup>+</sup>, 100], 102 [M - C<sub>3</sub>H<sub>4</sub>N<sub>3</sub><sup>+</sup>, 46]. Anal. Calcd for C10H8N4: C 65.21%; H 4.38%; N 30.42%. Found: C 65.10%; H 4.34%; N 30.39%.

Compound 2a. In a sealed tube, 1.035 g (6.5 mmol) of triazole 1a and 2.279 g (13 mmol, 2 equiv) of methyl iodide were dissolved in 3 mL of THF. The mixture was stirred at 110 °C for 20 h; the precipitate was collected and washed with THF and diethyl ether. The analytically pure product was obtained as a brown solid after drying *in vacuo* (1.44 g, 74%). Mp 149 °C. <sup>1</sup>H NMR in DMSO-*d*<sub>6</sub> (600 MHz)  $\delta$  9.36 (s, 1H, C*H*<sub>triazole</sub>), 8.01–7.94 (m, 2H, C*H*<sub>phenyl</sub>), 7.78–7.69 (m, 3H, C*H*<sub>Phenyl</sub>), 4.33 (s, 3H, NC*H*<sub>3</sub>), 2.58 (s, 3H, CC*H*<sub>3</sub>). <sup>13</sup>C NMR in DMSO-*d*<sub>6</sub> (151 MHz)  $\delta$  141.4 (*C*<sub>i</sub>), 134.7 (*C*<sub>i</sub>), 131.6 (*C*H<sub>arom</sub>), 130.4 (*C*H<sub>arom</sub>), 127.0 (*C*H<sub>arom</sub>), 121.3 (*C*H<sub>arom</sub>), 37.3 (N*C*H<sub>3</sub>), 8.73 (C*C*H<sub>3</sub>). MS (ESI) *m*/*z* = 174.0 [M-I]<sup>+</sup>, 475.0 [2M-I]<sup>+</sup>. Anal. Calcd for C<sub>10</sub>H<sub>12</sub>IN<sub>3</sub>: C 39.89%; H 4.02%; N 13.95%. Found: C 40.17%; H 4.06%; N 13.81%.

Compound 2b. Compound 2b was prepared analogously to 2a. Triazole 1b (1.041 g, 5.5 mmol) and 2.342 g (16.5 mmol, 3 equiv) of methyl iodide in 3 mL of THF were used. Yield 1.15 g (63%). Mp 213 °C. <sup>1</sup>H NMR in DMSO-*d*<sub>6</sub> (600 MHz) δ 9.26 (s, 1H, C*H*<sub>arom</sub>), 7.94–7.83 (m, 2H, C*H*<sub>arom</sub>), 7.32–7.19 (m, 2H, C*H*<sub>arom</sub>), 4.29 (s, 3H, NC*H*<sub>3</sub>), 3.87 (s, 3H, OC*H*<sub>3</sub>), 2.56 (s, 3H, CC*H*<sub>3</sub>). <sup>13</sup>C NMR in DMSO-*d*<sub>6</sub> (151 MHz) δ 161.3 (<u>C</u><sub>1</sub>), 141.1 (<u>C</u><sub>1</sub>), 127.8 (<u>C</u><sub>1</sub>), 126.6 (<u>C</u>H<sub>arom</sub>), 122.9 (<u>C</u>H<sub>arom</sub>), 115.3 (<u>C</u>H<sub>arom</sub>), 55.9 (O<u>C</u>H<sub>3</sub>), 37.6 (N<u>C</u>H<sub>3</sub>), 8.6 (C<u>C</u>H<sub>3</sub>). MS (ESI) *m*/*z* = 204.0 [M – I]<sup>+</sup>, 535.0 [2M – I]<sup>+</sup>. Anal. Calcd for C<sub>11</sub>H<sub>14</sub>IN<sub>3</sub>O: C 39.90%; H 4.26%; N 12.69%. Found: C 39.89%; H 4.29%; N 12.65%.

Compound 2c. Compound 2c was prepared analogously to 2a. Triazole 1c (1.548 g, 6.5 mmol) and 1.845 g (13 mmol, 2 equiv) of methyl iodide in 5 mL THF were used. Yield 1.95 g (79%). Mp 222 °C. <sup>1</sup>H NMR in CDCl<sub>3</sub> (600 MHz) δ 9.37 (s, 1H, C<u>H<sub>triazole</sub></u>), 8.01–7.95 (m, 2H, C<u>H<sub>arom</sub></u>), 7.96–7.91 (m, 2H, C<u>H<sub>arom</sub></u>), 4.32 (s, 3H, NC<u>H<sub>3</sub></u>), 2.57 (s, 3H, CC<u>H<sub>3</sub></u>). <sup>13</sup>C NMR in CDCl<sub>3</sub> (151 MHz) δ = 141.4 (<u>C</u><sub>i</sub>), 133.9 (<u>C</u><sub>i</sub>), 133.3 (<u>C</u>H<sub>arom</sub>), 127.1 (<u>C</u>H<sub>arom</sub>), 124.7 (<u>C</u><sub>i</sub>), 123.3 (<u>C</u>H<sub>arom</sub>), 37.8 (N<u>C</u>H<sub>3</sub>), 8.6 (C<u>C</u>H<sub>3</sub>). MS (ESI) *m/z* = 252.1 [M - 1]<sup>+</sup>, 254.0 [M - 1]<sup>+</sup>, 633.0 [2M - 1]<sup>+</sup>. Anal. Calcd for C<sub>10</sub>H<sub>11</sub>BrIN<sub>3</sub>: C 31.61%; H 2.92%; N 11.06%. Found: C 31.68%; H 3.11%; N 11.00%.

Compound 2d. Compound 2d was prepared analogously to 2a. Triazole 1d (1.079 g, 5.86 mmol) and 1.680 g (11.7 mmol, 2 equiv) of methyl iodide in 4 mL of THF were used. Yield 1.51 g (79%). Mp 206 °C. <sup>1</sup>H NMR in DMSO-*d*<sub>6</sub> (300 MHz)  $\delta$  9.47 (s, 1H, C<u>H</u><sub>arom</sub>), 8.31–8.23 (m, 2H, C<u>H</u><sub>arom</sub>), 8.24–8.17 (m, 2H, C<u>H</u><sub>arom</sub>), 4.36 (s, 3H, NC<u>H</u><sub>3</sub>), 2.60 (s, 3H, CC<u>H</u><sub>3</sub>). <sup>13</sup>C NMR in DMSO-*d*<sub>6</sub> (75 MHz)  $\delta$  141.6 (<u>C</u><sub>i</sub>), 137.6 (<u>C</u><sub>i</sub>), 134.6 (<u>C</u>H<sub>arom</sub>), 127.4 (<u>C</u>H<sub>arom</sub>), 122.2 (<u>C</u>H<sub>arom</sub>), 117.5 (<u>C</u><sub>i</sub>), 114.0 (<u>C</u><sub>i</sub>), 38.0 (N<u>C</u>H<sub>3</sub>), 8.7 (C<u>C</u>H<sub>3</sub>). MS (ESI) *m*/*z* = 199.0 [M – I]<sup>+</sup>. Anal. Calcd for C 40.51%; H 3.40%; N 17.18%. Found: C 40.81%; H 3.30%; N 17.19%.

Compound 3a. In a 50 mL round-bottom flask, 0.151 g (0.5 mmol) of triazolium salt 2a and 0.064 g (0.275 mmol, 0.55 equiv) of silver(1) oxide were suspended in 15 mL of dichloromethane and

refluxed overnight under the exclusion of light. The mixture was filtered through a plug of Celite; the filtrate was transferred into a flame-dried Schlenk tube and purged with argon for 15 min. [Ru(pcymene)Cl<sub>2</sub>]<sub>2</sub> (0.153 g 0.25 mmol, 0.5 equiv) and 0.058 g (0.25 mmol, 0.5 equiv) of silver(I) oxide were added, and the reaction was stirred under argon atmosphere at room temperature for 3 days. The mixture was filtered through a plug of Celite; the filtrate was collected and concentrated to dryness. The residue was dissolved in THF and subjected to flash chromatography using basic aluminum oxide. The orange colored fraction was collected concentrated in vacuo, and the analytically pure, yellow to orange product was precipitated by addition of *n*-pentane (89 mg, 40%). Mp > 185 °C (dec.). <sup>1</sup>H NMR in CDCl<sub>3</sub> (300 MHz)  $\delta$  8.20 (dd, J = 7.4, 1.4 Hz, 1H, C<u>H</u><sub>arom/phenyl</sub>), 7.51 (dd, J = 7.6, 1.4 Hz, 1H, C<u>H</u><sub>arom/phenyl</sub>), 7.08 (td, J = 7.3, 1.4 Hz, 1H,  $C\underline{H}_{arom/phenyl}$ ), 6.98 (td, J = 7.5, 1.4 Hz, 1H,  $C\underline{H}_{arom/phenyl}$ ), 5.53  $(dd, J = 6.0, 1.3 Hz, 1H CH_{arom/cymene}), 5.45 (dd, J = 5.8, 1.2 Hz, 1H,$  $CH_{arom/cymene}$ ), 5.39 (dd, J = 5.9, 1.3 Hz, 1H,  $CH_{arom/cymene}$ ), 5.35 (dd, J = 5.8, 1.3 Hz, 1H,  $CH_{arom/cymene}$ ), 4.03 (s, 3H,  $NCH_3$ ), 2.73 (s, 3H,  $CCH_3$ , 2.28 (sept, J = 7.2 Hz, 1H,  $CH(CH_3)_2$ ), 0.92 (d, J = 6.9 Hz, 3H, CHC<u>H<sub>3</sub></u>), 0.85 (d, J = 6.9 Hz, 3H, CHC<u>H<sub>3</sub></u>). <sup>13</sup>C NMR in CDCl<sub>3</sub> (75 MHz) δ 171.1 (<u>C</u><sub>i</sub>), 166.1 (<u>C</u><sub>i</sub>), 145.0 (<u>C</u><sub>i</sub>), 142.1 (<u>C</u>H<sub>arom</sub>), 141.1  $(\underline{C}_{i})$ , 127.4  $(\underline{C}H_{arom})$ , 122.5  $(\underline{C}H_{arom})$ , 113.8  $(\underline{C}H_{arom})$ , 100.9  $(\underline{C}_{i})$ , 100.6 ( $\underline{C}_i$ ), 90.0 ( $\underline{C}H_{arom/cymene}$ ), 87.8 ( $\underline{C}H_{arom/cymene}$ ), 87.5 (<u>CH</u><sub>arom/cymene</sub>), 84.9 (<u>CH</u><sub>arom/cymene</sub>), 36.2 (N<u>C</u>H<sub>3</sub>), 31.2 (<u>C</u>H-(CH<sub>3</sub>)<sub>2</sub>), 22.9 (C<u>C</u>H<sub>3</sub>), 22.2 (C<u>C</u>H<sub>3</sub>), 19.1 (C<u>C</u>H<sub>3</sub>), 11.3 (C<u>C</u>H<sub>3</sub>). MS (ESI)  $m/z = 408.3 [M - Cl]^+, 444.2 [M + H]^+, 850.4 [2M - Cl]^+$ Cl]<sup>+</sup>. Anal. Calcd for C<sub>20</sub>H<sub>24</sub>ClN<sub>3</sub>Ru: C 54.23%; H 5.46%; N 9.49%. Found: C 54.34%; H 5.49%; N 9.41%.

Compound 3b. Compound 3b was prepared analogously to 3a at a 2.5 mmol scale. Initially, 0.828 g (2.5 mmol) of triazolium salt 2b and 0.319 g (1.38 mmol, 0.55 equiv) of silver(I) oxide were suspended in 50 mL of dichloromethane. Later, 0.765 g (1.25 mmol, 0.5 equiv) of  $[Ru(p-cymene)Cl_2]_2$  and 0.290 g (1.25 mmol, 0.5 equiv) of silver(I) oxide were added. Yield 299 mg (25%). Mp 190 °C. <sup>1</sup>H NMR in  $\text{CDCl}_3$  (300 MHz)  $\delta$  7.75 (d, J = 2.6 Hz, 1H,  $C\underline{H}_{\text{arom/phenyl}}$ ), 7.45 (d, J= 8.5 Hz, 1H,  $C\underline{H}_{arom/phenyl}$ ), 6.53 (dd, J = 8.5, 2.6 Hz, 1H,  $C\underline{H}_{arom/phenyl}$ ), 5.51 (dd, J = 5.9, 1.2 Hz, 1H,  $C\underline{H}_{arom/cymene}$ ), 5.42 (dd, J = 5.8, 1.2 Hz, 1H,  $C\underline{H}_{arom/cymene}$ ), 5.39 (dd, J = 5.9, 1.2 Hz, 1H,  $C\underline{H}_{arom/cymene}$ ), 5.35 (dd, J = 5.8, 1.2 Hz, 1H,  $C\underline{H}_{arom/cymene}$ ), 4.02 (s, 3H, NC $\underline{H}_3$ ), 3.88 (s, 3H, OC $\underline{H}_3$ ), 2.71 (s, 3H, CC $\underline{H}_3$ ), 2.29 (sept, J = 6.9 Hz, 1H, C<u>H</u>(CH<sub>3</sub>)<sub>2</sub>), 1.98 (s, 3H, CC<u>H<sub>3</sub></u>), 0.92 (d, J = 7.0 Hz, 3H,  $CCH_3$ ), 0.85 (d, J = 6.9 Hz, 3H,  $CCH_3$ ). <sup>13</sup>C NMR in  $CDCl_3$  (75 MHz)  $\delta$  169.4 ( $\underline{C}_i$ ), 167.9 ( $\underline{C}_i$ ), 157.9 ( $\underline{C}_i$ ), 140.9 ( $\underline{C}_i$ ), 139.0 ( $\underline{C}_i$ ), 126.6 (<u>C</u>H<sub>arom</sub>), 114.2 (<u>C</u>H<sub>arom</sub>), 107.9 (<u>C</u>H<sub>arom</sub>), 100.9 (<u>C</u><sub>i</sub>), 100.4  $(\underline{C}_{i})$ , 89.8  $(\underline{C}H_{arom})$ , 87.6  $(\underline{C}H_{arom})$ , 87.5  $(\underline{C}H_{arom})$ , 85.0  $(\underline{C}H_{arom})$ , 55.4 (O<u>C</u>H<sub>3</sub>), 36.0 (N<u>C</u>H<sub>3</sub>), 31.1 (<u>C</u>H(CH<sub>3</sub>)<sub>2</sub>), 22.9 (C<u>C</u>H<sub>3</sub>), 22.2  $(C\underline{CH}_3)$ , 19.1  $(C\underline{CH}_3)$ , 11.2  $(C\underline{CH}_3)$ . MS (ESI) m/z = 438.3 [M - $Cl^{+}$ , 474.2  $[M + H]^{+}$ , 491.2  $[M + NH_{4}]^{+}$ , 911.4  $[2M - Cl]^{+}$ . Anal. Calcd for C<sub>21</sub>H<sub>26</sub>ClN<sub>3</sub>ORu: C 53.33%; H 5.54%; N 8.88%. Found: C 53.41%; H 5.61%; N 8.72%.

Compound 3c. Compound 3c was prepared analogously to 3a at a 2.5 mmol scale. Initially, 0.950 g (2.5 mmol) of triazolium salt 2c and 0.319 g (1.38 mmol, 0.55 equiv) of silver(I) oxide were suspended in 50 mL of dichloromethane. Later, 0.765 g (1.25 mmol, 0.5 equiv) of  $[Ru(p-cymene)Cl_2]_2$  and 0.290 g (1.25 mmol, 0.5 equiv) of silver(I) oxide were added. Yield 511 mg (39%). Mp > 215  $^{\circ}$ C (dec.). <sup>1</sup>H NMR in CDCl<sub>3</sub> (300 MHz)  $\delta 8.30$  (d, J = 2.1 Hz, 1H, C<u>H</u><sub>arom/phenyl</sub>), 7.38 (d, J = 8.3 Hz, 1H,  $C\underline{H}_{arom/phenyl}$ ), 7.11 (dd, J = 8.3, 2.0 Hz, 1H,  $C\underline{H}_{arom/phenyl}$ ), 5.52 (d, J = 5.9 Hz, 1H,  $C\underline{H}_{arom/cymene}$ ), 5.48 (d, J = 5.8 Hz, 1H,  $C\underline{H}_{arom/cymene}$ ), 5.42 (d, J = 5.9 Hz, 1H,  $C\underline{H}_{arom/cymene}$ ), 5.38 (d, J = 5.9 Hz, 1H,  $CH_{arom/cymene}$ ), 4.04 (s, 3H,  $NCH_3$ ), 2.72 (s, 3H,  $CCH_3$ , 2.27 (sept, J = 7.0 Hz, 1H,  $CH(CH_3)_2$ ), 2.00 (s, 3H,  $CCH_3$ ), 0.91 (d, J = 6.9 Hz, 3H, C<u>C</u>H<sub>3</sub>), 0.84 (d, J = 6.9 Hz, 3H). <sup>13</sup>C NMR in  $\text{CDCl}_3$  (75 MHz)  $\delta$  170.8 ( $\underline{C}_i$ ), 169.2 ( $\underline{C}_i$ ), 143.9 ( $\underline{C}_i$ ), 143.7  $(\underline{C}H_{arom})$ , 141.3  $(\underline{C}_{i})$ , 125.4  $(\underline{C}H_{arom})$ , 121.1  $(\underline{C}_{i})$ , 115.0  $(\underline{C}H_{arom})$ ,  $\begin{array}{c} 101.9 \ (\underline{C}_{i}), \ 100.6 \ (\underline{C}_{i}), \ 89.7 \ (\underline{CH}_{arom}), \ 88.1 \ (\underline{CH}_{arom}), \ 87.7 \ (\underline{CH}_{arom}), \\ 85.3 \ (\underline{CH}_{arom}), \ 36.2 \ (N\underline{CH}_{3}), \ 31.2 \ (\underline{CH}(CH_{3})_{2}), \ 22.8 \ (C\underline{CH}_{3}), \ 22.3 \end{array}$  $(C\underline{C}H_3)$ , 19.1  $(C\underline{C}H_3)$ , 11.2  $(C\underline{C}H_3)$ . MS (ESI) m/z = 486.2 [M – Cl]<sup>+</sup>, 1061.1 [2M + NH<sub>4</sub>]<sup>+</sup>. Anal. Calcd for C<sub>20</sub>H<sub>23</sub>BrClN<sub>3</sub>Ru: C 46.03%; H 4.44%; N 8.05%. Found: C 46.10%; H 4.45%; N 7.97%.

Compound 3d. Compound 3d was prepared analogously to 3a at a 2.5 mmol scale. Initially, 0.815 g (2.5 mmol) of triazolium salt 2d and 0.319 g (1.38 mmol, 0.55 equiv) of silver(I) oxide were suspended in 50 mL of dichloromethane. Later, 0.765 g (1.25 mmol, 0.5 equiv) of  $[Ru(p-cymene)Cl_2]_2$  and 0.290 g (1.25 mmol, 0.5 equiv) silver(I) oxide were added. Yield 228 mg (20%). Mp > 220 °C (dec.). <sup>1</sup>H NMR in CDCl<sub>3</sub> (300 MHz)  $\delta$  8.48 (d, J = 1.6 Hz, 1H, C<u>H</u><sub>arom/phenyl</sub>), 7.56 (d, J = 8.1 Hz, 1H, C $\underline{H}_{arom/phenyl}$ ), 7.30 (dd, J = 8.1, 1.7 Hz, 1H, C $\underline{H}_{arom/phenyl}$ ), 5.56 (d, J = 6.0 Hz, 1H, C $\underline{H}_{arom/cymene}$ ), 5.52 (d, J = 5.9Hz, 1H,  $C\underline{H}_{arom/cymene}$ ), 5.45 (d, J = 5.9 Hz, 1H,  $C\underline{H}_{arom/cymene}$ ), 5.39 (d, J = 6.7 Hz, 1H,  $C\underline{H}_{arom/cymene}$ ), 4.08 (s, 3H, N<u>C</u>H<sub>3</sub>), 2.74 (s, 3H,  $C\underline{CH}_3$ , 2.27 (sept, J = 6.9 Hz, 1H,  $C\underline{H}(CH_3)_2$ ), 2.00 (s, 3H,  $C\underline{CH}_3$ ), 0.91 (d, J = 6.9 Hz, 3H, C<u>C</u>H<sub>3</sub>), 0.83 (d, J = 6.9 Hz, 3H, C<u>C</u>H<sub>3</sub>). <sup>13</sup>C NMR in CDCl<sub>3</sub> (75 MHz)  $\delta$  172.6 (<u>C</u><sub>i</sub>), 167.5 (<u>C</u><sub>i</sub>), 148.3 (<u>C</u><sub>i</sub>), 145.4 (<u>CH</u><sub>arom</sub>), 141.7 (<u>C</u><sub>i</sub>), 126.8 (<u>C</u>H<sub>arom</sub>), 120.3 (<u>C</u><sub>i</sub>), 113.8 (<u>C</u>H<sub>arom</sub>),  $(\underline{C}_{i})$ , 102.2  $(\underline{C}_{i})$ , 101.4  $(\underline{C}_{i})$ , 90.1  $(\underline{C}_{H_{arom}})$ , 88.4  $(\underline{C}_{H_{arom}})$ , 88.2  $(\underline{C}H_{arom})$ , 85.3  $(\underline{C}H_{arom})$ , 36.5  $(N\underline{C}H_3)$ , 31.2  $(\underline{C}H(CH_3)_2)$ , 22.8  $(C\underline{CH}_3)$ , 22.2  $(C\underline{CH}_3)$ , 19.1  $(C\underline{CH}_3)$ , 11.2  $(C\underline{CH}_3)$ . MS (ESI) m/z =433.3 [M - Cl]<sup>+</sup>, 496.2 [M + H]<sup>+</sup>, 486.2 [M + NH<sub>4</sub>]<sup>+</sup>, 954.2 [2M + NH<sub>4</sub>]<sup>+</sup>. Anal. Calcd for C<sub>21</sub>H<sub>23</sub>ClN<sub>4</sub>Ru: C 53.90%; H 4.95%; N 11.97%. Found: C 53.80%; H 5.12%; N 11.74%.

Compound 4a. In a flame-dried Schlenk tube, 0.133 g (0.3 mmol) of ruthenium complex **3a** and 0.103 g (0.66 mmol, 2.2 equiv) of 2,2'bipyridine were dissolved in 3 mL of DMSO. The reaction was stirred under argon atmosphere and under the exclusion of light for 20 h at 140 °C. The reaction was cooled to room temperature, 15 mL of water was added, and the mixture was stored at 8 °C overnight. The suspension was filtered through a plug of Celite, and 0.062 g (0.375 mmol, 1.25 equiv) of ammonium hexafluorophosphate in 5 mL of water was added dropwise. After storing at 8 °C overnight, the precipitate was collected, dissolved in dichloromethane, and dried over magnesium sulfate. The solution was concentrated in vacuo and subjected to flash chromatography using basic aluminum oxide. The dark violet fraction was collected anf again concentrated in vacuo, and the analytically pure product was slowly precipitated by addition of diethyl ether (133 mg, 61%). Mp > 325 °C. <sup>1</sup>H NMR in DMSO- $d_6$ (300 MHz)  $\delta$  8.66 (d, J = 5.9 Hz, 1H, C<u>H</u><sub>arom</sub>), 8.64 (d, J = 5.7 Hz, 1H, C<u>H</u><sub>arom</sub>), 8.59 (d, J = 8.2 Hz, 1H, C<u>H</u><sub>arom</sub>), 8.55 (d, J = 8.2 Hz, 1H, C<u>H</u><sub>arom</sub>), 8.18 (d, J = 5.6 Hz, 1H, C<u>H</u><sub>arom</sub>), 8.09–7.91 (m, 3H,  $CH_{arom}$ ), 7.92–7.75 (m, 3H,  $CH_{arom}$ ), 7.66 (d, J = 5.5 Hz, 1H,  $CH_{arom}$ ), 7.53 (d, J = 7.6 Hz, 1H,  $CH_{arom}$ ), 7.51–7.40 (m, 2H,  $CH_{arom}$ ), 7.33 (t, J = 6.6 Hz, 1H,  $CH_{arom}$ ), 7.28 (t, J = 6.6 Hz, 1H,  $C\underline{H}_{arom}$ ), 6.83 (t, J = 7.3 Hz, 1H,  $C\underline{H}_{arom}$ ), 6.74 (t, J = 7.1 Hz, 1H,  $C\underline{H}_{arom}$ ), 6.29 (d, J = 7.0 Hz, 1H,  $C\underline{H}_{arom}$ ), 3.99 (s, 3H,  $NC\underline{H}_{3}$ ), 1.54 (s, 3H, CC<u>H<sub>3</sub></u>). <sup>13</sup>C NMR in DMSO- $d_6$  (75 MHz)  $\delta$  177.3 (<u>C</u><sub>i</sub>), 176.5  $(\underline{C}_{i})$ , 156.9  $(\underline{C}_{i})$ , 156.2  $(\underline{C}_{i})$ , 155.2  $(2 \underline{C}_{i})$ , 153.4  $(\underline{C}H_{arom})$ , 152.9  $(\underline{C}H_{arom})$ , 148.5  $(\underline{C}H_{arom})$ , 147.8  $(\underline{C}H_{arom})$ , 147.1  $(\underline{C}_{i})$ , 141.6  $(\underline{C}_{i})$ , 136.4 (<u>C</u>H<sub>arom</sub>), 135.0 (<u>C</u>H<sub>arom</sub>), 134.5 (<u>C</u>H<sub>arom</sub>), 133.6 (<u>C</u>H<sub>arom</sub>), 132.8 (<u>C</u>H<sub>arom</sub>), 126.5 (<u>C</u>H<sub>arom</sub>), 126.4 (<u>C</u>H<sub>arom</sub>), 126.1 (2 <u>C</u>H<sub>arom</sub>), 132.8 ( $\underline{C}H_{arom}$ ), 120.5 ( $\underline{C}H_{arom}$ ), 120.1 ( $\underline{C}H_{arom}$ ), 122.9 ( $\underline{C}H_{arom}$ ), 123.3 ( $\underline{C}H_{arom}$ ), 123.2 ( $\underline{C}H_{arom}$ ), 123.0 ( $\underline{C}H_{arom}$ ), 122.9 ( $\underline{C}H_{arom}$ ), 123.9 ( $\underline{C}H_{arom}$ ), 133.9 ( $\underline{C}H_{arom}$ ), 133.9 120.6 (<u>C</u>H<sub>arom</sub>), 112.6 (<u>C</u>H<sub>arom</sub>), 35.8 (N<u>C</u>H<sub>3</sub>), 8.1 (C<u>C</u>H<sub>3</sub>). <sup>19</sup>F NMR in DMSO- $d_6$  (282 MHz)  $\delta$  -70.78 (d, J = 711.2 Hz). MS (ESI)  $m/z = 586.2 [M - PF_6]^+$ . Anal. Calcd for C<sub>30</sub>H<sub>26</sub>F<sub>6</sub>N<sub>7</sub>PRu: C 49.32%; H 3.59%; N 13.42%. Found: C 49.25%; H 3.60%; N 13.34%.

Compound 4b. Compound 4b was prepared analogously to 4a at a 0.5 mmol scale. Initially, 0.236 g (0.5 mmol) of ruthenium complex 3b and 0.172 g (1.1 mmol, 2.2 equiv) of 2,2'-bipyridine were dissolved in 4 mL of DMSO. Later, 0.103 g (0.625 mmol. 1.25 equiv) ammonium hexafluorophosphate in 5 mL of water was added. Yield 251 mg (66%). Mp > 325 °C. <sup>1</sup>H NMR in DMSO-*d*<sub>6</sub> (300 MHz)  $\delta$  8.67 (d, *J* = 5.2 Hz, 1H, *CH*<sub>arom</sub>), 8.64 (d, *J* = 5.0 Hz, 1H, *CH*<sub>arom</sub>), 8.58 (t, *J* = 8.8 Hz, 2H, *CH*<sub>arom</sub>), 8.18 (d, *J* = 5.6 Hz, 1H, *CH*<sub>arom</sub>), 8.11–8.02 (m, 1H, *CH*<sub>arom</sub>), 7.98 (tt, *J* = 7.9, 1.5 Hz, 2H, *CH*<sub>arom</sub>), 7.91–7.77 (m, 3H, *CH*<sub>arom</sub>), 7.65 (d, *J* = 5.5 Hz, 1H, *CH*<sub>arom</sub>), 7.32–7.24 (m, 1H, *CH*<sub>arom</sub>), 6.35 (d, *J* = 8.5 Hz, 1H, *CH*<sub>arom</sub>), 5.68 (s, 1H, *CH*<sub>arom</sub>), 3.97 (s, 3H, NCH<sub>3</sub>), 3.47 (s, 3H, OCH<sub>3</sub>), 1.52 (s, 3H, CCH<sub>3</sub>). <sup>13</sup>C NMR in DMSO-*d*<sub>6</sub> (75 MHz)  $\delta$  157.5 (*C*<sub>i</sub>), 156.8 (*C*<sub>i</sub>), 156.2 (*C*<sub>i</sub>), 155.4 (*C*<sub>i</sub>), 155.2 (*C*<sub>i</sub>), 153.3 (*C*H<sub>arom</sub>), 152.8 (*C*H<sub>arom</sub>), 148.6 (*C*H<sub>arom</sub>), 147.9 (*C*H<sub>arom</sub>), 141.4 (*C*<sub>i</sub>), 140.9 (*C*<sub>i</sub>), 135.0 (*C*H<sub>arom</sub>),

134.5 (<u>C</u>H<sub>arom</sub>), 133.6 (<u>C</u>H<sub>arom</sub>), 132.9 (<u>C</u>H<sub>arom</sub>), 126.5 (<u>C</u>H<sub>arom</sub>), 126.4 (<u>C</u>H<sub>arom</sub>), 126.2 (<u>C</u>H<sub>arom</sub>), 126.1 (<u>C</u>H<sub>arom</sub>), 123.2 (<u>C</u>H<sub>arom</sub>), 123.0 (<u>C</u>H<sub>arom</sub>), 122.9 (<u>C</u>H<sub>arom</sub>), 121.7 (<u>C</u>H<sub>arom</sub>), 113.1 (<u>C</u>H<sub>arom</sub>), 104.9 (<u>C</u>H<sub>arom</sub>), 54.2 (O<u>C</u>H<sub>3</sub>), 35.6 (N<u>C</u>H<sub>3</sub>), 8.04 (C<u>C</u>H<sub>3</sub>). <sup>19</sup>F NMR in DMSO-*d*<sub>6</sub> (282 MHz) δ -70.78 (d, *J* = 711.4 Hz, P<u>E</u><sub>6</sub>). MS (ESI) *m*/*z* = 616.3 [M - PF<sub>6</sub>]<sup>+</sup>. Anal. Calcd for C<sub>31</sub>H<sub>28</sub>F<sub>6</sub>N<sub>7</sub>OPRu: C 48.95%; H 3.71%; N 12.89%. Found: C 48.76%; H 3.88%; N 12.74%.

Compound 4c. Compound 4c was prepared analogously to 4a at a 0.5 mmol scale. Initially, 0.261 g (0.5 mmol) of ruthenium complex 3c and 0.172 g (1.1 mmol, 2.2 equiv) of 2,2'-bipyridine were dissolved in 5 mL of DMSO. Later, 0.103 g (0.625 mmol, 1.25 equiv) ammonium hexafluorophosphate in 5 mL of water was added. Yield 194 mg (48%). Mp > 300 °C. <sup>1</sup>H NMR in DMSO- $d_6$  (300 MHz)  $\delta$  8.68 (d, J= 3.2 Hz, 1H, C<u>H</u><sub>arom</sub>), 8.66 (d, J = 3.4 Hz, 1H, C<u>H</u><sub>arom</sub>), 8.61 (d, J = 4.4 Hz, 1H, C<u>H</u><sub>arom</sub>), 8.58 (d, J = 4.4 Hz, 1H, C<u>H</u><sub>arom</sub>), 8.15 (dd, J =5.8, 0.9 Hz, 1H, C<u>H</u><sub>arom</sub>), 8.06–7.94 (m, 3H, C<u>H</u><sub>arom</sub>), 7.92–7.80 (m, 3H, C<u>H</u><sub>arom</sub>), 7.69–7.63 (m, 1H, C<u>H</u><sub>arom</sub>), 7.53–7.43 (m, 3H, CH<sub>arom</sub>), 7.41-7.35 (m, 1H, CH<sub>arom</sub>), 7.34-7.26 (m, 1H, CH<sub>arom</sub>), 7.00 (dd, J = 8.2, 2.2 Hz, 1H,  $C\underline{H}_{arom}$ ), 6.30 (d, J = 2.1 Hz, 1H,  $C\underline{H}_{arom}$ ), 3.99 (s, 3H,  $NC\underline{H}_{3}$ ), 1.53 (s, 3H,  $CC\underline{H}_{3}$ ). <sup>13</sup>C NMR in DMSO- $d_6$  (75 MHz)  $\delta$  182.7 (<u>C</u><sub>i</sub>), 176.7 (<u>C</u><sub>i</sub>), 156.8 (<u>C</u><sub>i</sub>), 156.2 (<u>C</u><sub>i</sub>), 155.2 (<u>C</u><sub>i</sub>), 153.5 (<u>C</u>H<sub>arom</sub>), 153.1 (<u>C</u>H<sub>arom</sub>), 148.6 (<u>C</u>H<sub>arom</sub>), 148.0  $(\underline{CH}_{arom})$ , 146.4  $(\underline{C}_{i})$ , 141.9  $(\underline{C}_{i})$ , 138.1  $(\underline{CH}_{arom})$ , 135.4  $(\underline{CH}_{arom})$ , 135.0 (<u>C</u>H<sub>arom</sub>), 134.0 (<u>C</u>H<sub>arom</sub>), 133.6 (<u>C</u>H<sub>arom</sub>), 126.8 (<u>C</u>H<sub>arom</sub>), 126.5 (2  $\underline{C}H_{arom}$ ), 126.3 ( $\underline{C}H_{arom}$ ), 123.4 (2  $\underline{C}H_{arom}$ ), 123.1 (2 <u>CH</u><sub>arom</sub>), 120.5 (<u>C</u><sub>i</sub>), 114.5 (<u>C</u>H<sub>arom</sub>), 35.9 (C<u>C</u>H<sub>3</sub>), 8.1 (C<u>C</u>H<sub>3</sub>). <sup>19</sup>F NMR in DMSO- $d_6$  (282 MHz)  $\delta$  -70.78 (d, J = 711.2 Hz, P<u>F\_6</u>). MS (ESI)  $m/z = 664.2 [M - PF_6]^+$ , 666.2  $[M - PF_6]^+$ . Anal. Calcd for C<sub>30</sub>H<sub>25</sub>BrF<sub>6</sub>N<sub>7</sub>PRu: C 44.51%; H 3.11%; N 12.11%. Found: C 44.54%; H 3.03%; N 12.13%.

Compound 4d. Compound 4d was prepared analogously to 4a at a 0.35 mmol scale. Initially, 0.164 g (0.35 mmol) of ruthenium complex 3d and 0.120 g (0.77 mmol, 2.2 equiv) of 2,2'-bipyridine were dissolved in 3 mL of DMSO. Later, 0.072 g (0.438 mmol. 1.25 equiv) of ammonium hexafluorophosphate in 5 mL of water was added. Yield 251 mg (66%). Mp 229 °C. <sup>1</sup>Ĥ NMR in DMSO- $d_6$  (300 MHz)  $\delta$  8.70  $(d, J = 4.2 \text{ Hz}, 1\text{H}, \text{CH}_{arom}), 8.68 (d, J = 4.1 \text{ Hz}, 1\text{H}, \text{CH}_{arom}), 8.61 (t, J = 4.1 \text{ Hz}, 1\text{Hz}, 1\text{H}, \text{CH}_{arom}), 8.61 (t, J = 4.1 \text{ Hz}, 1\text{Hz}, 1\text{Hz}), 8.61 (t, J = 4.1 \text{ Hz}, 1\text{Hz}), 8.61 (t, J = 4.1 \text{ Hz}), 8.61 (t, J = 4.1 \text{ H$ J = 7.4 Hz, 2H, CH<sub>arom</sub>), 8.12 (d, J = 5.0 Hz, 1H, CH<sub>arom</sub>), 8.10–7.96 (m, 2H, CH<sub>arom</sub>), 7.96–7.87 (m, 2H, CH<sub>arom</sub>), 7.88–7.81 (m, 2H, CH<sub>arom</sub>), 7.70–7.64 (m, 2H, CH<sub>arom</sub>), 7.57–7.44 (m, 2H, CH<sub>arom</sub>), 7.39–7.33 (m, 1H, CH<sub>arom</sub>), 7.32–7.25 (m, 2H, CH<sub>arom</sub>), 6.54 (d, J = 1.8 Hz, 1H, CH<sub>arom</sub>), 4.03 (s, 3H, NC<u>H<sub>3</sub></u>), 1.56 (s, 3H, CC<u>H<sub>3</sub></u>). <sup>13</sup>C NMR in DMSO- $d_6$  (75 MHz)  $\delta$  180.1 (<u>C</u><sub>i</sub>), 178.8 (<u>C</u><sub>i</sub>), 156.7 (<u>C</u><sub>i</sub>), 156.1 ( $\underline{C}_i$ ), 155.1 (2  $\underline{C}_i$ ), 153.6 ( $\underline{C}H_{arom}$ ), 153.3 ( $\underline{C}H_{arom}$ ), 151.2 ( $\underline{C}_i$ ), 148.5 (<u>C</u>H<sub>arom</sub>), 148.0 (<u>C</u>H<sub>arom</sub>), 142.2 (<u>C</u><sub>i</sub>), 139.5 (<u>C</u>H<sub>arom</sub>), 135.5 (<u>C</u>H<sub>arom</sub>), 135.3 (<u>C</u>H<sub>arom</sub>), 134.2 (<u>C</u>H<sub>arom</sub>), 133.8 (<u>C</u>H<sub>arom</sub>), 126.9  $\begin{array}{c} (\underline{C}H_{arom}), 126.6 & (\underline{C}H_{arom}), 126.4 & (\underline{C}H_{arom}), 126.6 & (\underline{C}H_{arom}), 126.5 & (\underline{C}H_{arom}), 126.4 & (\underline{C}H_{arom}), 124.8 & (\underline{C}H_{arom}), 123.5 & (\underline{C}H_{arom}), 123.4 & (\underline{C}H_{arom}), 123.2 & (\underline{C}H_{arom}), 120.1 & (\underline{C}_{i}), 112.7 & (\underline{C}H_{arom}), 108.6 & (\underline{C}_{i}), 36.1 & (\underline{N}\underline{C}H_{3}), 8.1 & (\underline{C}\underline{C}H_{3}). \ ^{19}\text{F NMR in DMSO-} \end{array}$  $d_6$  (282 MHz)  $\delta$  -70.78 (d, J = 711.2 Hz,  $PE_6^-$ ). MS (ESI) m/z = 611.3 [M - PF<sub>6</sub>]<sup>+</sup>. Anal. Calcd for C<sub>31</sub>H<sub>25</sub>F<sub>6</sub>N<sub>8</sub>PRu: C 49.28%; H 3.33%; N 14.83%. Found: C 48.95%; H 3.46%; N 14.43%.

# ASSOCIATED CONTENT

# **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.8b00637.

Experimental, NMR, CV and crystallographic data as well as results of the quantum chemical calculations including TD-DFT calculated absorption spectra and FMOs (PDF)

Cartesian coordinates for all optimized structures (XYZ)

#### Accession Codes

CCDC 1851140–1851143 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*T.S.: tel, (+49)351-463-38571; fax, (+49)351-463-39679; email, thomas.strassner@chemie.tu-dresden.de.

# ORCID <sup>©</sup>

Thomas Strassner: 0000-0002-7648-457X

#### Notes

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#### REFERENCES

(1) United States Statistics Division 2015 United Nations Energy Statistics Yearbook; New York, 2017.

(2) UNEP Frankfurt School of Finance and Management; Bloomberg New Energy *Global Trends in Renewable Energy Investment*; Frankfurt/Main, 2016.

(3) Nazeeruddin, M. K.; Baranoff, E.; Grätzel, M. Dye-sensitized solar cells: A brief overview. *Sol. Energy* **2011**, *85*, 1172–1178.

(4) (a) Baxter, J. B. Commercialization of dye sensitized solar cells: Present status and future research needs to improve efficiency, stability, and manufacturing. J. Vac. Sci. Technol., A 2012, 30, 020801-020801. (b) Bignozzi, C. A.; Argazzi, R.; Boaretto, R.; Busatto, E.; Carli, S.; Ronconi, F.; Caramori, S. The role of transition metal complexes in dye sensitized solar devices. Coord. Chem. Rev. 2013, 257, 1472-1492. (c) Bomben, P. G.; Robson, K. C. D.; Koivisto, B. D.; Berlinguette, C. P. Cyclometalated ruthenium chromophores for the dye-sensitized solar cell. Coord. Chem. Rev. 2012, 256, 1438-1450. (d) Grätzel, M. Solar Energy Conversion by Dye-Sensitized Photovoltaic Cells. Inorg. Chem. 2005, 44, 6841-6851. (e) Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. Dye-Sensitized Solar Cells. Chem. Rev. 2010, 110, 6595-6663. (f) Robertson, N. Optimizing Dyes for Dye-Sensitized Solar Cells. Angew. Chem., Int. Ed. 2006, 45, 2338-2345. (g) Ryan, M. Progress in ruthenium complexes for dye sensitised solar cells. Platinum Met. Rev. 2009, 53, 216-218. (h) Shalini, S.; Balasundaraprabhu, R.; Kumar, T. S.; Prabavathy, N.; Senthilarasu, S.; Prasanna, S. Status and outlook of sensitizers/dyes used in dye sensitized solar cells (DSSC): a review. Int. J. Energy Res. 2016, 40, 1303-1320. (i) Vougioukalakis, G. C.; Philippopoulos, A. I.; Stergiopoulos, T.; Falaras, P. Contributions to the development of ruthenium-based sensitizers for dye-sensitized solar cells. Coord. Chem. Rev. 2011, 255, 2602–2621. (j) Yanagida, S.; Yu, Y.; Manseki, K. Iodine/Iodide-Free Dye-Sensitized Solar Cells. Acc. Chem. Res. 2009, 42, 1827-1838.

(5) Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Mueller, E.; Liska, P.; Vlachopoulos, N.; Graetzel, M. Conversion of light to electricity by cis- $X_2$ bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II) charge-transfer sensitizers (X = Cl-, Br-, I-, CN-, and SCN-) on nanocrystalline titanium dioxide electrodes. *J. Am. Chem. Soc.* **1993**, *115*, 6382–6390.

(6) Nazeeruddin, M. K.; Zakeeruddin, S. M.; Humphry-Baker, R.; Jirousek, M.; Liska, P.; Vlachopoulos, N.; Shklover, V.; Fischer, C.-H.; Grätzel, M. Acid–Base Equilibria of (2,2'-Bipyridyl-4,4'-dicarboxylic acid)ruthenium(II) Complexes and the Effect of Protonation on Charge-Transfer Sensitization of Nanocrystalline Titania. *Inorg. Chem.* **1999**, *38*, 6298–6305. (7) Nazeeruddin, M. K.; Péchy, P.; Renouard, T.; Zakeeruddin, S. M.; Humphry-Baker, R.; Comte, P.; Liska, P.; Cevey, L.; Costa, E.; Shklover, V.; Spiccia, L.; Deacon, G. B.; Bignozzi, C. A.; Grätzel, M. Engineering of Efficient Panchromatic Sensitizers for Nanocrystalline TiO<sub>2</sub> -Based Solar Cells. *J. Am. Chem. Soc.* **2001**, *123*, 1613–1624.

(8) (a) Greijer Agrell, H.; Lindgren, J.; Hagfeldt, A. Degradation mechanisms in a dye-sensitized solar cell studied by UV–VIS and IR spectroscopy. *Sol. Energy* **2003**, *75*, 169–180. (b) Nguyen, H. T.; Ta, H. M.; Lund, T. Thermal thiocyanate ligand substitution kinetics of the solar cell dye N719 by acetonitrile, 3-methoxypropionitrile, and 4-tert-butylpyridine. *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 1934–1942. (c) Tuyet Nguyen, P.; Degn, R.; Thai Nguyen, H.; Lund, T. Thiocyanate ligand substitution kinetics of the solar cell dye Z-907 by 3-methoxypropionitrile and 4-tert-butylpyridine at elevated temperatures. *Sol. Energy Mater. Sol. Cells* **2009**, *93*, 1939–1945.

(9) (a) Wadman, S. H.; Kroon, J. M.; Bakker, K.; Lutz, M.; Spek, A. L.; van Klink, G. P. M.; van Koten, G. Cyclometalated ruthenium complexes for sensitizing nanocrystalline TiO<sub>2</sub> solar cells. Chem. Commun. 2007, 4, 1907-1907. (b) Wadman, S. H.; Lutz, M.; Tooke, D. M.; Spek, A. L.; Hartl, F. e.; Havenith, R. W. A.; van Klink, G. P. M.; van Koten, G. Consequences of N,C,N'- and C,N,N'-Coordination Modes on Electronic and Photophysical Properties of Cyclometalated Aryl Ruthenium(II) Complexes. Inorg. Chem. 2009, 48, 1887-1900. (c) Wadman, S. H.; van Leeuwen, Y. M.; Havenith, R. W. A.; van Klink, G. P. M.; van Koten, G. A Redox Asymmetric, Cyclometalated Ruthenium Dimer: Toward Upconversion Dyes in Dye-Sensitized TiO<sub>2</sub> Solar Cells. Organometallics 2010, 29, 5635-5645. (d) Wadman, S. H.; Kroon, J. M.; Bakker, K.; Havenith, R. W. A.; van Klink, G. P. M.; van Koten, G. Cyclometalated Organoruthenium Complexes for Application in Dye-Sensitized Solar Cells. Organometallics 2010, 29, 1569-1579.

(10) Bessho, T.; Yoneda, E.; Yum, J.; Guglielmi, M.; Tavernelli, I.; Imai, H.; Rothlisberger, U.; Nazeeruddin, M. H.; Grätzel, M. New paradigm in molecular engineering of sensitizers for solar cell applications. J. Am. Chem. Soc. **2009**, 131, 5930–5934.

(11) (a) Bomben, P. G.; Robson, K. C. D.; Sedach, P. A.; Berlinguette, C. P. On the Viability of Cyclometalated Ru(II) Complexes for Light-Harvesting Applications. Inorg. Chem. 2009, 48, 9631-9643. (b) Koivisto, B. D.; Robson, K. C. D.; Berlinguette, C. P. Systematic Manipulation of the Light-Harvesting Properties for Tridentate Cyclometalated Ruthenium(II) Complexes. Inorg. Chem. 2009, 48, 9644-9652. (c) Bomben, P. G.; Koivisto, B. D.; Berlinguette, C. P. Cyclometalated Ru Complexes of Type [Ru(II)- $(\hat{N}N)_2(\hat{C}N)$ <sup>2</sup>: Physicochemical Response to Substituents Installed on the Anionic Ligand. Inorg. Chem. 2010, 49, 4960-4971. (d) Bomben, P. G.; Gordon, T. J.; Schott, E.; Berlinguette, C. P. A trisheteroleptic cyclometalated RuII sensitizer that enables high power output in a dye-sensitized solar cell. Angew. Chem., Int. Ed. 2011, 50, 10682-10685. (e) Bomben, P. G.; Thériault, K. D.; Berlinguette, C. P. Strategies for optimizing the performance of cyclometalated ruthenium sensitizers for dye-sensitized solar cells. Eur. J. Inorg. Chem. 2011, 2011, 1806-1814. (f) Robson, K. C. D.; Sporinova, B.; Koivisto, B. D.; Schott, E.; Brown, D. G.; Berlinguette, C. P. Systematic modulation of a bichromic cyclometalated ruthenium(II) scaffold bearing a redox-active triphenylamine constituent. Inorg. Chem. 2011, 50, 6019-6028. (g) Bomben, P. G.; Borau-Garcia, J.; Berlinguette, C. P. Three is not a crowd: efficient sensitization of TiO2 by a bulky trichromic trisheteroleptic cycloruthenated dye. Chem. Commun. 2012, 48, 5599-5599. (h) Robson, K. C. D.; Bomben, P. G.; Berlinguette, C. P. Cycloruthenated sensitizers: improving the dye-sensitized solar cell with classical inorganic chemistry principles. Dalton Trans 2012, 41, 7814-7814. (i) Robson, K. C. D.; Koivisto, B. D.; Berlinguette, C. P. Derivatization of bichromic cyclometalated Ru(II) complexes with hydrophobic substituents. Inorg. Chem. 2012, 51, 1501-1507. (j) Pogozhev, D. V.; Bezdek, M. J.; Schauer, P. A.; Berlinguette, C. P. Ruthenium(II) Complexes Bearing a Naphthalimide Fragment: A Modular Dye Platform for the Dye-Sensitized Solar Cell. Inorg. Chem. 2013, 52, 3001-3006. (k) Schulze, B.; Brown, D. G.; Robson, K. C. D.; Friebe,

C.; Jäger, M.; Birckner, E.; Berlinguette, C. P.; Schubert, U. S. Cyclometalated Ruthenium(II) Complexes Featuring Tridentate Click-Derived Ligands for Dye-Sensitized Solar Cell Applications. *Chem. - Eur. J.* **2013**, *19*, 14171–14180. (l) Hu, K.; Severin, H. A.; Koivisto, B. D.; Robson, K. C. D.; Schott, E.; Arratia-Perez, R.; Meyer, G. J.; Berlinguette, C. P. Direct Spectroscopic Evidence for Constituent Heteroatoms Enhancing Charge Recombination at a  $TiO_2$ -Ruthenium Dye Interface. *J. Phys. Chem. C* **2014**, *118*, 17079–17089.

(12) (a) Kim, J.-J.; Choi, H.; Paek, S.; Kim, C.; Lim, K.; Ju, M.-J.; Kang, H. S.; Kang, M.-S.; Ko, J. A New Class of Cyclometalated Ruthenium Sensitizers of the Type ĈNN for Efficient Dye-Sensitized Solar Cells. Inorg. Chem. 2011, 50, 11340-11347. (b) Kisserwan, H.; Ghaddar, T. H. Enhancement of photocurrent in dye sensitized solar cells incorporating a cyclometalated ruthenium complex with cuprous iodide as an electrolyte additive. Dalton Trans 2011, 40, 3877-3877. (c) Singh, S. P.; Islam, A.; Yanagida, M.; Han, L. Development of a New Class of Thiocyanate-Free Cyclometalated Ruthenium(II) Complex for Sensitizing Nanocrystalline TiO2 Solar Cells. Int. J. Photoenergy 2011, 2011, 1-5. (d) Dragonetti, C.; Valore, A.; Colombo, A.; Roberto, D.; Trifiletti, V.; Manfredi, N.; Salamone, M. M.; Ruffo, R.; Abbotto, A. A new thiocyanate-free cyclometallated ruthenium complex for dye-sensitized solar cells: Beneficial effects of substitution on the cyclometallated ligand. J. Organomet. Chem. 2012, 714, 88-93. (e) Funaki, T.; Funakoshi, H.; Kitao, O.; Onozawa-Komatsuzaki, N.; Kasuga, K.; Sayama, K.; Sugihara, H. Cyclometalated Ruthenium(II) Complexes as Near-IR Sensitizers for High Efficiency Dye-Sensitized Solar Cells. Angew. Chem., Int. Ed. 2012, 51, 7528-7531. (f) Hsu, C.-W.; Ho, S.-T.; Wu, K.-L.; Chi, Y.; Liu, S.-H.; Chou, P.-T. Ru(ii) sensitizers with a tridentate heterocyclic cyclometalate for dye-sensitized solar cells. Energy Environ. Sci. 2012, 5, 7549-7549. (g) Ji, Z.; Natu, G.; Huang, Z.; Kokhan, O.; Zhang, X.; Wu, Y. Synthesis, Photophysics, and Photovoltaic Studies of Ruthenium Cyclometalated Complexes as Sensitizers for p-Type NiO Dye-Sensitized Solar Cells. J. Phys. Chem. C 2012, 116, 16854-16863. (h) Chitumalla, R. K.; Gupta, K. S. V.; Malapaka, C.; Fallahpour, R.; Islam, A.; Han, L.; Kotamarthi, B.; Singh, S. P. Thiocyanate-free cyclometalated ruthenium(ii) sensitizers for DSSC: A combined experimental and theoretical investigation. Phys. Chem. Chem. Phys. 2014, 16, 2630-2630. (i) Funaki, T.; Kusama, H.; Onozawa-Komatsuzaki, N.; Kasuga, K.; Sayama, K.; Sugihara, H. Near-IR Sensitization of Dye-Sensitized Solar Cells Using Thiocyanate-Free Cyclometalated Ruthenium(II) Complexes Having a Pyridylquinoline Ligand. Eur. J. Inorg. Chem. 2014, 2014, 1303-1311. (j) Funaki, T.; Otsuka, H.; Onozawa-Komatsuzaki, N.; Kasuga, K.; Sayama, K.; Sugihara, H. New class of NCS-free cyclometalated ruthenium(II) complexes with 6-phenylpyridine-2-carboxylate for use as near-infrared sensitizers in dye-sensitized solar cells. Inorg. Chem. Commun. 2014, 46, 137-139. (k) Hussain, M.; Islam, A.; Bedja, I.; Gupta, R. K.; Han, L.; El-Shafei, A. A comparative study of Ru(II) cyclometallated complexes versus thiocyanated heteroleptic complexes: thermodynamic force for efficient dye regeneration in dyesensitized solar cells and how low could it be? Phys. Chem. Chem. Phys. 2014, 16, 14874-14881. (1) Jäger, M.; Freitag, L.; González, L. Using computational chemistry to design Ru photosensitizers with directional charge transfer. Coord. Chem. Rev. 2015, 304-305, 146-165. (m) Shao, J.-Y.; Fu, N.; Yang, W.-W.; Zhang, C.-Y.; Zhong, Y.-W.; Lin, Y.; Yao, J. Cyclometalated ruthenium(II) complexes with bis(benzimidazolyl)benzene for dye-sensitized solar cells. RSC Adv. 2015, 5, 90001-90009. (n) Bessette, A.; Cibian, M.; Ferreira, J. G.; DiMarco, B. N.; Bélanger, F.; Désilets, D.; Meyer, G. J.; Hanan, G. S. Azadipyrromethene cyclometalation in neutral Ru II complexes: photosensitizers with extended near-infrared absorption for solar energy conversion applications. Dalton Trans 2016, 45, 10563-10576. (o) Kaneko, R.; Wu, G.; Sugawa, K.; Otsuki, J.; Islam, A.; Han, L.; Bedja, I.; Gupta, R. K. Cyclometalated ruthenium complexes with 6-(ortho-methoxyphenyl)-2,2'-bipyridine as panchromatic dyes for dye-sensitized solar cells. J. Organomet. Chem. 2017, 833, 61-70. (p) Wu, G.; Kaneko, R.; Sugawa, K.; Islam, A.; Bedja, I.; Gupta, R. K.;

Han, L.; Otsuki, J. Effect of different auxiliary ligands and anchoring ligands on neutral thiocyanate-free ruthenium(II) dyes bearing tetrazole chromophores for dye-sensitized solar cells. *Dyes Pigm.* **2017**, *140*, 354–362.

(13) (a) Chen, H.-S.; Chang, W.-C.; Su, C.; Li, T.-Y.; Hsu, N.-M.; Tingare, Y. S.; Li, C.-Y.; Shie, J.-H.; Li, W.-R. Carbene-based ruthenium photosensitizers. *Dalton Trans* 2011, 40, 6765–6765.
(b) Chang, W.-C.; Chen, H.-S.; Li, T.-Y.; Hsu, N.-M.; Tingare, Y. S.; Li, C.-Y.; Liu, Y.-C.; Su, C.; Li, W.-R. Highly Efficient N-Heterocyclic Carbene/Pyridine-Based Ruthenium Sensitizers: Complexes for Dye-Sensitized Solar Cells. *Angew. Chem., Int. Ed.* 2010, 49, 8161–8164.
(14) Park, H. J.; Kim, K. H.; Choi, S. Y.; Kim, H. M.; Lee, W. I.; Kang, Y. K.; Chung, Y. K. Unsymmetric Ru(II) complexes with N-Heterocyclic carbene and/or terpyridine ligands: Synthesis, characterization, ground-and excited-state electronic structures and their application for DSSC sensitizers. *Inorg. Chem.* 2010, 49, 7340–7352.
(15) Barbante, G. J.; Francis, P. S.; Hogan, C. F.; Kheradmand, P. R.;

Wilson, D. J. D.; Barnard, P. J. Electrochemiluminescent Ruthenium-(II) N-Heterocyclic Carbene Complexes: a Combined Experimental and Theoretical Study. *Inorg. Chem.* **2013**, *52*, 7448–7459.

(16) (a) Schulze, B.; Escudero, D.; Friebe, C.; Siebert, R.; Görls, H.; Köhn, U.; Altuntas, E.; Baumgaertel, A.; Hager, M. D.; Winter, A.; Dietzek, B.; Popp, J.; González, L.; Schubert, U. S. A Heteroleptic Bis(tridentate) Ruthenium(II) Complex of a Click-Derived Abnormal Carbene Pincer Ligand with Potential for Photosensitzer Application. Chem. - Eur. J. 2011, 17, 5494-5498. (b) Brown, D. G.; Sanguantrakun, N.; Schulze, B.; Schubert, U. S.; Berlinguette, C. P. Bis(tridentate) ruthenium-terpyridine complexes featuring microsecond excited-state lifetimes. J. Am. Chem. Soc. 2012, 134, 12354-12357. (c) Brown, D. G.; Schauer, P. A.; Borau-Garcia, J.; Fancy, B. R.; Berlinguette, C. P. Stabilization of Ruthenium Sensitizers to TiO<sub>2</sub> Surfaces through Cooperative Anchoring Groups. J. Am. Chem. Soc. 2013, 135, 1692-1695. (d) Sinn, S.; Schulze, B.; Friebe, C.; Brown, D. G.; Jäger, M.; Altuntaş, E.; Kübel, J.; Guntner, O.; Berlinguette, C. P.; Dietzek, B.; Schubert, U. S. Physicochemical Analysis of Ruthenium(II) Sensitizers of 1,2,3-Triazole-Derived Mesoionic Carbene and Cyclometalating Ligands. Inorg. Chem. 2014, 53, 2083-2095.

(17) Leigh, V.; Ghattas, W.; Lalrempuia, R.; Müller-Bunz, H.; Pryce, M. T.; Albrecht, M. Synthesis, Photo-, and Electrochemistry of Ruthenium Bis(bipyridine) Complexes Comprising a N-heterocyclic Carbene Ligand. *Inorg. Chem.* **2013**, *52*, 5395–5402.

(18) (a) Aghazada, S.; Zimmermann, I.; Scutelnic, V.; Nazeeruddin, M. K. Synthesis and Photophysical Characterization of Cyclometalated Ruthenium Complexes with N-Heterocyclic Carbene Ligands. *Organometallics* **2017**, *36*, 2397–2403. (b) Schleicher, D.; Leopold, H.; Borrmann, H.; Strassner, T. Ruthenium(II) Bipyridyl Complexes with Cyclometalated NHC Ligands. *Inorg. Chem.* **2017**, *56*, 7217–7229.

(19) Zhang, Y.-M.; Shao, J.-Y.; Yao, C.-J.; Zhong, Y.-W. Cyclometalated ruthenium(ii) complexes with a bis-carbene CCC-pincer ligand. *Dalton Trans* **2012**, *41*, 9280–9280.

(20) Jia, Q.; Yang, G.; Chen, L.; Du, Z.; Wei, J.; Zhong, Y.; Wang, J. A Facile One-Pot Metal-Free Synthesis of 1,4-Disubstituted 1,2,3-Triazoles. *Eur. J. Inorg. Chem.* **2015**, 2015, 3435–3440.

(21) (a) Schleicher, D.; Tronnier, A.; Leopold, H.; Borrmann, H.; Strassner, T. Unusual dimer formation of cyclometalated ruthenium NHC p-cymene complexes. *Dalton Trans* **2016**, *45*, 3260–3263. (b) Le Lagadec, R.; Rubio, L.; Alexandrova, L.; Toscano, R. A.; Ivanova, E. V.; Meškys, R.; Laurinavičius, V.; Pfeffer, M.; Ryabov, A. D. Cyclometalated N,N-dimethylbenzylamine ruthenium(II) complexes [Ru(C<sub>6</sub>HR<sub>1</sub>R<sub>2</sub>R<sub>3</sub>-0-CH<sub>2</sub>NMe<sub>2</sub>)(bpy)(RCN)<sub>2</sub>]PF<sub>6</sub> for bioapplications: synthesis, characterization, crystal structures, redox properties, and reactivity toward PQQ-dependent glucose dehydrogenase. *J. Organomet. Chem.* **2004**, *689*, 4820–4832.

(22) (a) Delgado-Rebollo, M.; Canseco-Gonzalez, D.; Hollering, M.; Mueller-Bunz, H.; Albrecht, M. Synthesis and catalytic alcohol oxidation and ketone transfer hydrogenation activity of donorfunctionalized mesoionic triazolylidene ruthenium(ii) complexes. Dalton Trans 2014, 43, 4462–4473. (b) Donnelly, K. F.; Lalrempuia, R.; Muller-Bunz, H.; Albrecht, M. Regioselective Electrophilic C-H Bond Activation in Triazolylidene Metal Complexes Containing a N-Bound Phenyl Substituent. Organometallics 2012, 31, 8414–8419. (c) Ogata, K.; Inomata, S.; Fukuzawa, S.-i. Position-selective intramolecular aromatic C-H bond activation of 1,2,3-triazol-5-ylidene (tzNHC) ligands in (p-cymene)ruthenium(II) complexes. Dalton Trans 2013, 42, 2362–2365.

(23) Pavlishchuk, V. V.; Addison, A. W. Conversion constants for redox potentials measured versus different reference electrodes in acetonitrile solutions at 25°C. Inorg. Chim. Acta 2000, 298, 97-102. (24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian 16, revision B.01; Gaussian, Inc.: Wallingford, CT, 2016.

(25) (a) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. J. Phys. Chem. 1994, 98, 11623–11627. (b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. Results obtained with the correlation energy density functionals of becke and Lee, Yang and Parr. Chem. Phys. Lett. 1989, 157, 200–206. (c) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys. Rev. B: Condens. Matter Mater. Phys. 1988, 37, 785–789. (d) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. J. Chem. Phys. 1993, 98, 5648–5652.

(26) Adamo, C.; Barone, V. Toward reliable density functional methods without adjustable parameters: the PBE0 model. *J. Chem. Phys.* **1999**, *110*, 6158–6170.

(27) (a) Becke, A. D. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A: At., Mol., Opt. Phys.* **1988**, 38, 3098–3100. (b) Perdew. Erratum: Density-functional approximation for the correlation energy of the inhomogeneous electron gas. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1986**, 34, 7406. (c) Perdew, J. P. Density-functional approximation for the correlation energy of the inhomogeneous electron gas. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1986**, 33, 8822–8824.

(28) (a) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, 77, 3865–3868. (b) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple [Phys. Rev. Lett. 77, 3865 (1996)]. *Phys. Rev. Lett.* **1997**, 78, 1396–1396.

(29) (a) Hariharan, P. C.; Pople, J. A. The effect of d-functions on molecular orbital energies for hydrocarbons. *Chem. Phys. Lett.* 1972, *16*, 217–219. (b) Hariharan, P. C.; Pople, J. A. The influence of polarization functions on molecular orbital hydrogenation energies. *Theoret. Chim. Acta* 1973, *28*, 213–222. (c) Hariharan, P. C.; Pople, J. A. Accuracy of AHn equilibrium geometries by single determinant molecular orbital theory. *Mol. Phys.* 1974, *27*, 209–214. (d) Rassolov, V. A.; Pople, J. A.; Ratner, M. A.; Windus, T. L. 6-31G\* basis set for atoms K through Zn. *J. Chem. Phys.* 1998, *109*, 1223–1229. (e) Rassolov, V. A.; Ratner, M. A.; Pople, J. A.; Redfern, P. C.; Curtiss, L. A. 6-31G\* basis set for third-row atoms. *J. Comput. Chem.* 2001, *22*, 976–984. (f) Ditchfield, R.; Hehre, W. J.; Pople, J. A. Self-Consistent Molecular-Orbital Methods. IX. An Extended Gaussian-Type Basis for Molecular-Orbital Studies of Organic Molecules. *J.*

J

*Chem. Phys.* **1971**, *54*, 724–728. (g) Hehre, W. J.; Ditchfield, R.; Pople, J. A. Self-Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian-Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. *J. Chem. Phys.* **1972**, *56*, 2257–2261.

(30) Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

(31) (a) Wadt, W. R.; Hay, P. J. Ab initio effective core potentials for molecular calculations. Potentials for main group elements Na to Bi. J. Chem. Phys. **1985**, 82, 284–298. (b) Hay, P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. J. Chem. Phys. **1985**, 82, 299–310. (c) Hay, P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. J. Chem. Phys. **1985**, 82, 270–283.

(32) Lohmann, F. Notizen: Fermi-Niveau und Flachbandpotential von Molekülkristallen aromatischer Kohlenwasserstoffe. Z. Naturforsch., A: Phys. Sci. **1967**, 22, 843.

(33) Legault, C. Y. *CYLview*, 1.0.564 beta; University of Shelbrooke: Canada, 2012.

(34) Dennington, R.; Keith, T. A.; Millam, J. M. *GaussView*, version 6; Semichem Inc.: Shawnee Mission, KS, 2016.