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### Article

# When Donors Turn into Acceptors: Ground and Excited State Properties of Fe<sup>II</sup> Complexes with Amine-Substituted Tridentate Bisimidazole-2-ylidene Pyridine Ligands

Yannik Vukadinovic, Lukas Burkhardt, Ayla Päpcke, Anabel Miletic, Lorena Fritsch, Björn Altenburger, Roland Schoch, Adam Neuba, Stefan Lochbrunner, and Matthias Bauer\*



**ABSTRACT:** In search of new ligand motifs for photoactive iron(II) complexes with long-lived MLCT states, a series of six complexes with tridentate amine-functionalized bis-*n*-heterocyclic carbene (NHC)-pyr-idine ligands is presented. In the homoleptic complexes imidazole-, methylimidazole-, or benzimidazole-2-ylidene, NHC donors are employed in combination with pyridine, functionalized in the 4-position by dimethylamine or dibenzylamine. The effects of these different functionalities on the electronic structure of the complexes are examined through detailed ground state characterization by NMR, single crystal X-ray diffraction, as well as electrochemical and spectroscopic methods. The net influence of these different functionalities on orbital—orbital and electrostatic ligand—iron interactions is investigated thoroughly by density functional theory, and changes in the excited state behavior and lifetimes



are finally examined by ultrafast optical spectroscopy. Great deviations of the initially expected effects by substitution in 4-position on the photochemical properties are observed, together with a significantly increased  $\pi$ -acceptor interaction strength in the benzimidazole-2-ylidene functionalized complexes.

# INTRODUCTION

Replacing noble metals, such as ruthenium and iridium, by Earth abundant transition metal (TM) complexes as photoactive compounds has been one of the most challenging quests in the field of sustainable chemistry over the last years.<sup>1-4</sup> Because of their photophysical features, noble metals combine stability with efficiency for a wide range of applications. Considering their low abundancy and high costs, the need for more abundant, inexpensive, and biocompatible metals is obvious. A promising candidate is iron, which however opens new challenges. The much smaller ligand field splitting of iron in its complexes leads to a very fast, nonemissive deactivation of the desired metal-to-ligand charge transfer  $(^{1,3}MLCT)$  states into photochemically inactive metal-centered (<sup>3,5</sup>MC) states.<sup>5,6</sup> Current efforts focus on the design of octahedral coordinated iron(II) complexes with an increased ligand field splitting  $\Delta_0$ in order to destabilize the <sup>3,5</sup>MC states.<sup>7-10</sup> Over the last few years, the use of bi- and tridentate pyridyl-N-heterocyclic carbene (NHC) ligands proved to be a promising strategy to stabilize <sup>1,3</sup>MLCT states while simultaneously destabilizing  $^{3,5}\text{MC}$  states, due to the  $\pi\text{-accepting}$  pyridine and  $\sigma\text{-donating}$  NHC moiety (Figure 1).  $^{11-15}$  The choice of the NHC functionality affects the  $\sigma$ -donor properties, which is discussed controversially.<sup>16</sup> For Au-complexes, the difference of the  $\sigma$ donating properties of several NHC was shown to be negligibly



**Figure 1.** Schematic representation of the effect of electron accepting and electron donating substituents in the pyridine backbone on the energy of the  $d\pi$  (HOMO, bonding interaction between Fe t<sub>2g</sub>-like and ligand  $\pi^*$  orbitals, Fe t<sub>2g</sub>-like centered) and  $d\pi^*$  orbitals (LUMO, antibonding interaction between Fe t<sub>2g</sub>-like and ligand  $\pi^*$  orbitals, ligand  $\pi^*$  centered). L-A: ligand with acceptor group in the 4-position of the pyridine, L-D: ligand with donor group in the 4-position of the pyridine, (L-D)(L-A): Heteroleptic complex with one donor and one acceptor group in the 4-position.

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small.<sup>17</sup> This influence was shown to be much more pronounced in ruthenium or molybdenum complexes.<sup>18,19</sup> Many efforts focus on the modifications of this structural motif by varying the number of NHC and pyridyl functions and substituting the backbone.<sup>11,20-27</sup> Investigations on the influence of substituents at the pyridine ring by Gros and Sundström.<sup>21,28,29</sup> were limited so far to electron withdrawing functions. Substituting the ligands backbone changes the electrostatic environment around the iron center. Depending on the present ligand and substituent, this effect can lead to significant stabilization or destabilization of all orbitals relative to the unsubstituted complex as shown by Jakubikova et al.<sup>30,31</sup> for polypyridine and cyclometalated Fe<sup>II</sup> complexes. The substitution of the central pyridine in the 4-position by an electron withdrawing group stabilizes all orbital energies relative to the individual unsubstituted complex. However, antibonding metal-ligand interactions are stabilized to a larger extent than their bonding counterparts. This means, for example, that the ligand  $\pi^*$ -centered orbitals and the unoccupied metal  $d\pi^*$  orbitals (LUMO, antibonding interaction between metal  $t_{2g}$ -like and ligand  $\pi^*$  orbitals) are more stabilized than the metal t2g-like centered occupied  $d\pi$  orbitals (HOMO, bonding interaction between metal t2g-like and ligand  $\pi^*$  orbitals).<sup>32</sup> In contrast, it has been observed that electron donating groups destabilize all orbital energies relative to the parent complex with unsubstituted ligands, but here the bonding metal-ligand interactions  $(d\pi)$  are more destabilized than the antibonding counterparts ( $d\pi^*$ , see Figure 1). Therefore, both strategies are in principle able to decrease the  $d\pi - d\pi^*$  gap, as has been shown for a series of ruthenium(II) complexes, where the two strategies lead to a redshift of the <sup>3</sup>MLCT emission, i.e., a stabilization of the <sup>3</sup>MLCT states.<sup>32</sup> These approaches therefore offer the chance to tune the energy of MC and MLCT states also in iron(II) complexes. The combination of both strategies, constructing a heteroleptic push-pull complex, combines both strategies, leading to an even smaller theoretical  $d\pi - d\pi^*$  or HOMO-LUMO gap (see Figure 1).<sup>33</sup>

In this study, the effect of electron donating substituents by incorporation of dimethylamine and dibenzylamine substituents in the 4-position of 2,6-bis[imidazol-2-ylidene]pyridine ligand scaffolds used for the preparation of homoleptic Fe<sup>II</sup> complexes is investigated. Imidazole-2-ylidene, methylimidazole-2-ylidene, and benzimidazole-2-ylidene are applied as NHC donors (see Scheme 1, ligands L1–L6 and resulting complexes  $Fe(L1)_2$ – $Fe(L6)_2$ ). The well-known complex [Fe(2,6-bis[imidazol-2-ylidene]pyridine]\_2]<sup>2+,11,34</sup> Fe(L7)<sub>2</sub>, shown in Scheme 2, serves as an unfunctionalized reference.

#### Scheme 1. Schematic Structure of Ligands L1-L6







Thorough characterization by means of cyclic voltammetry, UV/vis, single crystal analysis, and ab initio calculations, reveals an increase in  $\pi$ -acceptor interaction strength between the Fe  $t_{2g}$  and ligand  $\pi^*$  orbitals of the resulting complexes through the amine substitution, while the acceptor strength of the isolated ligands is decreasing. Additionally, a significant  $\pi$ -acceptor ability of the benzimidazole-2-ylidene fragment in this series (L3 and L6) is observed and correlated to the excited state behavior.

#### RESULTS AND DISCUSSION

Ligand synthesis is described in the Experimental Section. The preparation of the homoleptic Fe<sup>II</sup> complexes employs the synthetic route shown in Scheme 2 and is similar to the reference complex. Complex synthesis required the addition of 2 equiv of LiHMDS to a solution of 1 equiv of the NHC-ligand in dry THF at -10 °C, to deprotonate the ligand. Successive complexation was achieved by dropwise addition of 0.5 equiv of a Fe-precursor solution in dry THF at -10 °C. The solution was then allowed to stir at r.t. for another 12 h. After solvent removal and filtration, the crude complex was precipitated by addition to a saturated solution of potassium hexafluorophosphate in water. Purification by column chromatography yielded the final complexes in good yields of 65-80% as yellow  $(Fe(L1)_2, Fe(L2)_2, Fe(L4)_2, Fe(L5)_2)$  to red powders  $(Fe(L3)_2, Fe(L6)_2)$ , which is a first indication for a difference in the electronic structure of the benzimidazole complexes, compared to the remaining complexes  $(Fe(L1)_2, Fe(L2)_2, Fe(L2)_2)$  $Fe(L4)_2$ ,  $Fe(L5)_2$ ). Single crystals of  $Fe(L1)_2 - Fe(L6)_2$ suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into an acetonitrile (MeCN) solution of the complexes.

All compounds are characterized by a distorted octahedral symmetry. The crystal structure of complex  $Fe(L1)_2$  is shown in Figure 2, and the crystal structures of the complexes  $Fe(L1)_2-Fe(L6)_2$  are given in the Supporting Information (Figures S1–S6). The rigid tridentate ligand scaffold causes a significant distortion of all four NHC functions out of the equatorial plane, which is a well-known effect in this type of complexes.<sup>35</sup> The Fe-NHC bond length decreases in the series  $Fe(L2)_2 > Fe(L5)_2 > Fe(L1)_2 > Fe(L4)_2 > Fe(L6)_2 > Fe(L3)_2$ , which is in line with the formally expected donor strength<sup>12,34,36</sup> of the different NHC ligands (Table 1) and the observed carbene <sup>13</sup>C NMR shifts  $\delta_{C(NHC)}$  of the respective isolated NHC ligands (see Experimental Section). Herein, the benzimidazole-2-ylidene-complexes ( $Fe(L3)_2$  and  $Fe(L6)_2$ ) reveal the shortest Fe–C bond distances due to its strongest  $\sigma$ -

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Figure 2. Single crystal structure of  $Fe(L1)_2$  drawn with anisotropic displacement ellipsoids at a 50% probability level. Hydrogen atoms and counterions are omitted for clarity.

I able	1.	Experimental	Bond	Length	or	$\operatorname{Fe}(L1)_2 - \operatorname{Fe}(L0)_2$

complex	Fe–N <sub>exp</sub> av <sup>b</sup>	$Fe-C_{exp}$ av <sup>b</sup>
$Fe(L1)_2$	1.920(1)	1.940(2)
$Fe(L2)_2$	1.924(4)	1.953(5)
$Fe(L3)_2$	1.907(6)	1.917(6)
$Fe(L4)_2$	1.891(8)	1.940(8)
$Fe(L5)_2$	1.905(2)	1.944(3)
$Fe(L6)_2$	1.911(5)	1.933(5)
$Fe(L7)_{2}^{27}$	1.924(3)	1.966(3)

<sup>*a*</sup>In addition, bond length of reference complex  $Fe(L7)_2$ , taken from ref 34. <sup>*b*</sup>Averaged over all binding sites.

donor potential, which is verified and discussed in the computational part.

**Electronic and Electrochemical Properties.** In order to investigate the influence of the NHCs nature and the pyridine functionalization on the electronic structure of the synthesized compounds, square wave (SW) (see Supporting Information) and cyclic voltammetry (CV) measurements were carried out

in MeCN solutions using tetrabutylammonium hexafluorophosphate,  $Bu_4NPF_6$  as supporting electrolyte (see Table 2 and Supporting Information Figures S7–S19 and Tables S7–S12). For comparison of the electrochemical behavior, we will compare the half-wave potentials in the following. All complexes show a reversible one-electron oxidation process at about 0 V versus Fc/Fc<sup>+</sup>, which is assigned to the Fe<sup>II</sup>/Fe<sup>III</sup> redox couple. The observed peak separation  $\Delta E$  range from 60 to 75 mV proves reversibility of the Fe<sup>II</sup>/Fe<sup>III</sup> redox couple and is in good agreement with related complexes.<sup>12,23</sup> Compared to the reference complex  $Fe(L7)_{2}$ , a strong reduction of the Fe<sup>2+/3+</sup> oxidation potential is observed for all complexes.<sup>20,28,34</sup> This strong reduction of the Fe<sup>II</sup> oxidation potential is explained by destabilization of the Fe 3d localized  $d\pi$  orbital energies due to the introduced amine substituents in the 4position of the pyridine. As a result, complexes  $Fe(L1)_2$  to  $Fe(L6)_2$  are easier to oxidize to their  $Fe^{3+}$  state. For the same reason, ligand localized  $d\pi^*$  orbitals are significantly destabilized compared to Fe(L7)2, shifting the ligand reduction potentials to more negative values, which thus moves out of the usable potential range for MeCN. On the other hand, a second irreversible oxidation event is observed in the case of complexes  $Fe(L1)_2 - Fe(L5)_2$  at 1.15 V, which is not present in  $Fe(L7)_2$ . It is therefore assigned to the presence of donating amines at the pyridine. The substitution in the 4position destabilizes the occupied ligand  $\pi$  orbitals significantly, shifting the according potential of ligand oxidation into the observable range of the electrochemical experiment. Fe(L6), does not show a second oxidation peak, pointing out to a weaker electrostatic destabilization through amine substitution in the 4-position of the central pyridine in this case.

Comparing the NHC motifs and the amine functionalization among each other, it is noticeable that the methylimidazole-2ylidene ligand complexes ( $Fe(L2)_2$  and  $Fe(L5)_2$ ) are characterized by stronger  $\sigma$ -donor capabilities compared to

Table 2. Experimental and Computed Electrochemical Data of Complexes Fe(L1)-Fe(L7)

complex	$E_{1/2 \text{ Ox I}} (\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}) (\text{V})^{a}$	$E_{1/2 \text{ Ox}}$ computed (Fe <sup>III</sup> / Fe <sup>II</sup> ) (V)	$E_{1/2 \text{ Ox II}} (V)^{b}$	$\lambda_{abs-max} (nm) \left[ \epsilon \left( M^{-1} \cdot cm^{-1} \right) \right]^{c}$
$Fe(L1)_2$	-0.023 (rev)	0.01	1.10 (irrev)	249 [64253]
				436 [22442]
$Fe(L2)_2$	-0.06 (rev)	-0.07	1.13 (irrev)	257 [74678]
				438 [28165]
$Fe(L3)_2$	0.18 (rev)	0.31	1.20 (irrev)	233 [90287]
				268 [63441]
				320 [28087]
				418 [23256]
$Fe(L4)_2$	0.03 (rev)	0.05	1.20 (irrev)	251 [72235]
				442 [27236]
$Fe(L5)_2$	-0.03 (rev)	-0.03	1.12 (irrev)	260 [91129]
				444 [35566]
$Fe(L6)_2$	0.12 (rev)	0.35		233 [97203]
				268 [78833]
				323 [33524]
				426 [28224]
$Fe(L7)_2$	$0.31^{34}$ (rev)	0.31		244 (34400)
				286 (31100)
				390 (9100)
				457 (15200)

"First oxidation potential. Potentials are quoted vs  $Fc/Fc^+$ . Recorded in MeCN (c = 1 mM) using  $Bu_4NPF_6$  (0.1 M) as supporting electrolyte at 400 mV·s<sup>-1</sup>. "Second oxidation potential. Potentials are quoted vs  $Fc/Fc^+$ ." (Measured in MeCN at 25 °C.

the nonmethylated complexes  $Fe(L1)_2$  and  $Fe(L4)_2$ , which is deduced from the lower oxidation potential. Considering only  $\sigma$ -donor properties, lower potentials would be expected for the benzimidazole-2-ylidene complexes  $Fe(L3)_2$  and  $Fe(L6)_2$ compared to  $Fe(L2)_2$  and  $Fe(L5)_2$  as well. This effect seems to be compensated by  $\pi$ -accepting properties of the benzimidazole-2-ylidene, since the experimental  $Fe^{2+/3+}$ potentials of complexes  $Fe(L3)_2$  and  $Fe(L6)_2$  are shifted to higher values (0.18 and 0.12 V). Such a behavior is known for complexes with a high electron density on the central transition metal,<sup>37,38</sup> but reports on NHC ligands with significant  $\pi$ -accepting properties are very rare.<sup>38-41</sup> The observations made by cyclic voltammetry are confirmed by the optical properties of the complexes, which are reflected in the UV/vis spectra of Figure 3. For all complexes, the



Figure 3. Electronic absorption spectra of complexes  $Fe(L1)_2$ - $Fe(L7)_2$  (10<sup>-5</sup> M in MeCN).

absorption spectra are composed of three main regions, which will be discussed in the following based on literature reports. Between 200 and 350 nm, intense ligand absorption is observed for all investigated complexes. The imidazole-2ylidene and methylimidazole-2-ylidene complexes  $(Fe(L1)_2)$  $Fe(L2)_{2}$ ,  $Fe(L4)_{2}$ ,  $Fe(L5)_{2}$ ) are all characterized by a broad maximum around 260 nm with a red shoulder around 280 nm. The benzimidazole-2-ylidene complexes  $(Fe(L3)_2, Fe(L6)_2)$ exhibit a distinct fine structure with five pronounced features around 240, 270, 290, and 320 nm.<sup>35,42</sup> At longer wavelengths above 350 nm, MLCT transitions are typically found.<sup>28,35</sup> Usually asymmetric MLCT features with two to three maxima are observed for Fe<sup>II</sup>(poly)-NHC-(poly)-pyridyl complexes, as it can be seen for the reference complex  $Fe(L7)_2$  in Figure 3. In the case of imidazole-2-ylidene and methylimidazole-2ylidene complexes  $(Fe(L1)_{2}, Fe(L2)_{2}, Fe(L4)_{2}, Fe(L5)_{2})$ , the splitting between the MLCT maxima decreases.<sup>28,42</sup> It is known that the bands in the range of 385-400 nm are assigned to a Fe-NHC charge transfer, whereas the MLCT band at lower energies corresponds to a Fe-pyridine charge transfer. The MLCT splitting further decreases for both benzimidazole-2-ylidene complexes  $(Fe(L3)_2 \text{ and } Fe(L6)_2)$ when compared to the reference complex  $(Fe(L7)_2)$ , resulting in one broad feature without fine structure. The MLCT maxima for both benzimidazole-2-ylidene complexes are blue-

shifted by around 20 nm compared to their imidazole-2ylidene analogues  $Fe(L1)_2$  and  $Fe(L4)_2$ . This shift agrees with literature values<sup>14</sup> and is due to the electron-accepting properties of the benzimidazole-2-ylidene ligand. Comparing the MLCT band maxima for identical NHC functionalities with different amines,  $Fe(L1)_2$  versus  $Fe(L4)_2$ ,  $Fe(L2)_2$  versus  $Fe(L5)_2$  and  $Fe(L3)_2$  versus  $Fe(L6)_2$  a slight red-shift is noticeable from the  $-NMe_2$  group  $(Fe(L1)_2 - Fe(L3)_2)$  to the  $-NBn_2$  group (Fe(L4)<sub>2</sub> $-Fe(L6)_2$  by around 6 nm. In general, it is observed that functionalization of the central pyridine ring by amine donors causes a blue shift of the MLCT transition by around 20 nm when comparing the same NHC functionalities. In turn, this means that amine donors in the backbone of the pyridine fragment destabilize the MLCT state in the Franck-Condon regime. In contrast, incorporation of -NMe<sub>2</sub> in the backbone of a Ru(II) terpyridine complex in ref 32 leads to a stabilization of the MLCT transitions in the Franck-Condon regime instead. Since all complexes  $Fe(L1)_2 - Fe(L7)_2$  lack fluorescence, a probe of the MLCT energy in its relaxed MLCT structure is not available. For this reason, transient absorption experiments were conducted to probe MLCT lifetimes, which are presented in the last section of this work.

Computational Analysis. Unconstrained DFT optimization of all experimental investigated complexes and both unsubstituted methylimidazole and benzimidazole references  $Fe(L8)_2$ ,  $Fe(L9)_2$  were performed, and an overall good agreement of the experimentally observed bond lengths and angles is achieved as given in Table S13 of the Supporting Information. Oxidation potentials of all experimental investigated complexes  $Fe(L1)_2 - Fe(L7)_2$  were estimated as the energy differences between  $Fe^{3+}$  and  $Fe^{2+}$  states in the optimized Fe<sup>2+</sup> ground state structure (TPSSh, def2-TZVPP, D3BJ, MeCN solvation via SMD). All computed potentials were corrected by the computed  $Fe^{2+/3+}$  potential of ferrocene (4.50 eV), in analogy to the treatment of experimental data. Experimental and computational oxidation potentials are compared in Table 2 and Figure S20 of the Supporting Information. A good agreement between computed and experimental oxidation potentials with a deviation of  $\pm 0.02$ V is achieved for all complexes except for both benzimidazole compounds  $Fe(L3)_2$  and  $Fe(L6)_2$ . Here, the estimated values deviate by +0.13 V to +0.23 V from the experiment. In order to allow a more holistic view of the electronic structure of complexes  $Fe(L1)_2 - Fe(L7)_2$ , low energy features of VIS spectra (see Figure 3) were also simulated with the same series of calculations. An overall good agreement between experiment and theory is observed again for all complexes (see Supporting Information Figure S21) except the two benzimidazole compounds  $Fe(L3)_2$  and  $Fe(L6)_2$ , which are significantly red-shifted by around 1500 cm<sup>-1</sup> in the computation. The lowest energy feature is dominated in all complexes by MLCT transitions. Only in complex  $Fe(L3)_2$ metal centered states also contribute to the transitions (excited state compositions of dominating transitions are given in Supporting Information Table S14, donor and acceptor orbitals of all complexes are visualized in Supporting Information Figures S22–S30). One reason for the systematic error of the computed oxidation potentials and lowest-energy VIS-feature shifts of both benzimidazole complexes  $Fe(L3)_2$ and  $Fe(L6)_2$  might be attributed to an increased static electron correlation, which cannot be treated by DFT. For this reason, the fractional occupation number weighted densities (FOD)<sup>43</sup> were calculated and analyzed.

The FOD is obtained by performing finite-temperature DFT (FT-DFT) calculations, where the electrons in a molecule are smeared over the molecular orbitals, resulting in a fractional occupation of otherwise unoccupied molecular orbitals.<sup>44</sup> The FOD reflects the location of "hot" electrons, which are strongly correlated and chemical active. FOD plots of complexes  $Fe(L1)_2-Fe(L9)_2$  are given in Figure 4. In all complexes, a



**Figure 4.** FOD plots ( $\sigma = 0.005 \text{ e/Bohr}^3$ ) of complexes  $\text{Fe}(\text{L1})_2$ -**Fe**(L7)<sub>2</sub> (BHLYP, def2-TZVP, T = 15000 K). Static electron correlation is indicated by pink electron density. N-FOD values are given below.

significant interaction between the occupied Fe centered  $d\pi$ orbitals and empty ligand centered  $d\pi^*$  type orbitals is reflected by the FOD plots. Since the  $d\pi$  orbitals of all investigated complexes are metal centered, while  $d\pi^*$  orbitals are ligand centered, this interaction can be interpreted as backbonding of occupied Fe t<sub>2g</sub>-like ( $d\pi$ ) orbitals into empty ligand  $\pi^*$  type orbitals ( $d\pi^*$ ). Additionally, a significant contribution of the nonbonding p<sub>z</sub> orbital of the sp<sup>2</sup> amine is observed in the FOD, indicating an influence of the amine substitution on the electronic structure in this type of complexes. In contrast to the imidazole-2-ylidene Fe(L1)<sub>2</sub>/Fe(L4)<sub>2</sub>/Fe(L5)<sub>2</sub>/Fe(L8)<sub>2</sub>, all benzimidazole-2-ylidene complexes Fe(L3)<sub>2</sub>/Fe(L6)<sub>2</sub>/Fe-(L9)<sub>2</sub> exhibit a pronounced FOD located at the NHC fragment, and therefore the N FOD (number of "hot" electrons) values (Figure 4) increase by around 0.8. This reflects a significantly increased  $\pi$ -acceptor interaction character and Fe-NHC covalency of the benzimidazole-2ylidene complexes, which is in line with the shortened Fe-NHC bonds and high-field shifted <sup>13</sup>C carbene-signals. It should be mentioned here that the N FOD value is strongly influenced by the choice of the applied DFT functional. Calculations using the nonhybrid TPSS instead of BHLYP yield much smaller N FOD values without changing the trend. In the case of  $Fe(L1)_{2}$ , the values are reduced from 2.2 to 0.6 for TPSS (further information is given in Table S17 of the Supporting Information). Complexes  $Fe(L3)_2$  and  $Fe(L6)_2$  are therefore characterized by the highest degree of static electron correlation, which might be the reason for the observed difference between the DFT-computed and the experimental oxidation potentials (cf. Table 1).

Nevertheless, all dibenzylamine substituted complexes  $(Fe(L4)_2-Fe(L6)_2)$  show additional occupation of  $\pi^*$  type orbitals of the phenyl rings of the amine substituents, and therefore all N\_FOD values in the dibenzylamine series are increased by around 1.4 compared to their dimethylamine analogues  $Fe(L1)_2-Fe(L3)_2$ . In contrast, the smallest N\_FOD value of 1.9 is observed for the reference complex  $Fe(L7)_2$  with significant less visual FOD in the density plot.

This FOD analysis thus demonstrates that substitution of the pyridine fragment with an amine donor function leads to an increase in static electron correlation, especially in the case of dibenzylamine substitution, and indicates a significant  $\pi$ accepting character of the benzimidazole-2-ylidene NHC ligand in this type of complexes. This conclusion is further substantiated by ground state molecular orbitals, which were computed using the TPSSh hybrid functional together with the Ahlrichs def2-TZVPP basis set on all atoms and inclusion of MeCN solvation via SMD (frontier orbitals of all investigated complexes are depicted in Supporting Information Figures S22–S30). This choice is rationalized by the fact that MeCN is the common solvent for photochemical applications. The HOMO to HOMO-2 in  $Fe(L1)_2 - Fe(L9)_2$  reflect the  $\pi$ bonding interaction  $(d\pi)$  between iron  $t_{2g}$ -like and ligand  $\pi^*$ orbitals molecular orbitals (frontier orbitals of complex  $Fe(L1)_2$  are shown exemplarily in Figure 5, for all investigated complexes see Supporting Information Figures S22-S30). All



Figure 5.  $d\pi$  and  $d\pi^*$  orbitals of complex Fe(L1)<sub>2</sub>.

amine substituted complexes  $(Fe(L1)_2-Fe(L6)_2)$  show a significant contribution of the nonbonding  $p_z$  orbital of the sp<sup>2</sup> amine to the  $d\pi$  orbitals with z components  $(d_{xz} \text{ and } d_{yz})$  (frontier orbitals of complex  $Fe(L1)_2$  are shown exemplarily in Figure 5). This is in line with the obvious contribution of the amine nonbonding  $p_z$  orbital in the FOD plots discussed above. LUMO to LUMO+2 in complexes  $Fe(L1)_2$ ,  $Fe(L2)_2$ ,  $Fe(L4)_2$ ,  $Fe(L5)_2$  or LUMO, LUMO+2, and LUMO+3 in complexes  $Fe(L3)_2$ ,  $Fe(L6)_2$ ,  $Fe(L7)_2$ ,  $Fe(L8)_2$ , and  $Fe(L9)_2$  reflect the  $\pi$ -antibonding interaction  $(d\pi^*)$  between iron  $t_{2g}$ -like and ligand  $\pi^*$  orbitals, in agreement with the typical description of a  $\pi$ -acceptor ligand interacting with an pseudo-octahedral  $Fe^{II}$  center.

In the following, it will be thoroughly analyzed how different NHC and amine functionalities in the ligand backbone affect this  $\pi$ -acceptor interaction strength in the resulting complexes  $(Fe(L1)_2 - Fe(L9)_2)$ . The  $\pi$ -acceptor capability of a ligand is caused by its  $\pi^*$  electron affinity, which is determined by its  $\pi^*$ orbital eigenvalue. In general, interaction of Fe  $t_{2\sigma}$ -like orbitals with a more stable  $\pi^*$  will lead to a more stable bonding  $d\pi$ orbital. Nevertheless, the strength of the interaction between  $\pi^*$  and  $t_{2\sigma}$ -like orbitals depends not only on the electron affinity of the  $\pi^*$ , but also on the energy match and overlap of both Fe  $t_{2g}$  and  $\pi^*$  orbitals, i.e., the degree of covalency. When comparing only complexes with the same backbone functionality (see Supporting Information S21-S23), a smaller % Fe character for more stable  $d\pi$  orbitals is observed, consistent with the typical description of a stronger acceptor ligand. However, when comparing the same NHC functionality with varying substitution in the backbone, a higher % Fe character for more stable  $d\pi$  orbitals is found and vice versa, due to the superimposing electrostatic destabilizing effect on all orbitals through amine substitution.

A key aspect of this paper is the interaction strength. Detailed insights into the  $\pi$ -acceptor interaction strength of all investigated complexes are therefore provided in the following rather than discussing the ligands overall acceptor capability. For this purpose, comparative analysis of the average % Fe 3d character of the bonding  $d\pi$  interactions, in the parent (not amine functionalized) complexes  $(Fe(L7)_2 - Fe(L9)_2)$  to amine substituted complexes  $(Fe(L1)_2 - Fe(L6)_2)$  is carried out. From the amine-functionalized complexes  $Fe(L1)_2$ - $Fe(L3)_2$  (see Figure 6),  $Fe(L4)_2-Fe(L6)_2$  and  $Fe(L7)_2 Fe(L9)_2$  (see Supporting Information Figure S31–S33), the benzimidazole-2-ylidene complexes  $Fe(L3)_2$ ,  $Fe(L6)_2$ , and  $Fe(L9)_2$  exhibit a pronounced decrease of the average % Fe 3d composition of the  $d\pi$  orbitals by around 5%, which are also stabilized by roughly 0.3 eV (HOMO to HOMO-2) (see Supporting Information Figures S31-S36 and Table S15 for Loewdin Fe 3d contributions). This behavior illustrates a significant increase of the  $\pi$ -acceptor interaction strength in the complexes  $Fe(L3)_{2}$ ,  $Fe(L6)_{2}$ , and  $Fe(L9)_{2}$  compared to the imidazole  $(Fe(L1)_2, Fe(L4)_2)$  and  $Fe(L7)_2)$  and methylimidazole  $(Fe(L2)_2, Fe(L5)_2)$  and  $Fe(L8)_2)$  analogues.

In the FOD analysis, an intense interaction between Fe 3d and amine localized orbitals was observed. To shed more light on the effect of amine substitution in the 4-position of the pyridine, the imidazole complexes  $Fe(L1)_2$ ,  $Fe(L4)_2$ , and  $Fe(L7)_2$ , which only differ in the nature of the substituent  $(Fe(L1)_2: R = NMe_2, Fe(L4)_2: R = NBn_2 \text{ and } Fe(L7)_2: R = H)$  are compared in Figure 7. The amine substitution in  $Fe(L1)_2$  and  $Fe(L4)_2$  leads to a destabilization of all orbital energies relative to the unsubstituted parent complex  $Fe(L7)_2$ 



**Figure 6.** Molecular orbitals of complexes  $Fe(L1)_2 - Fe(L3)_2$  (TPSSh, D3BJ, def2-TZVPP, SMD(acetonitrile)). All orbitals with significant Fe 3d contribution are depicted in red, and the average % Fe 3d character is given for the  $d\pi$ ,  $d\pi^*$ , and  $d\sigma^*$  manifolds.



**Figure 7.** :Molecular orbitals of complexes  $Fe(L1)_2$ ,  $Fe(L4)_2$ , and  $Fe(L7)_2$  (TPSSh, D3BJ, def2-TZVPP, SMD (acetonitrile)). All orbitals with significant % Fe 3d character are shown in red, and % Fe 3d character of the  $d\pi$ ,  $d\pi^*$ , and  $d\sigma^*$  manifolds is given.

as introduced above.<sup>30,31</sup> Thus, the  $d\pi$ ,  $d\pi^*$ , and  $d\sigma^*$  orbital energies are destabilized compared to the unfunctionalized reference  $Fe(L7)_2$ . This electrostatic effect of the amine is most pronounced on the *z*-axis, affecting the  $d\pi$  orbitals with *z*character (mainly  $3d_{xz,yz}$ ) to the largest extent by destabilization. The  $d\pi$  orbital of mainly  $3d_{xy}$  character is less destabilized, leading to a much smaller splitting between the  $d\pi$  orbitals for  $Fe(L1)_2$  and  $Fe(L4)_2$  in comparison to the unsubstituted reference complex  $Fe(L7)_2$  (see Figure 7). In contrast, the opposite effect is observed for the antibonding,  $d\pi^*$  orbitals, where the z-component orbitals are less destabilized than their  $3d_{xy}$  counterpart. This effect is even more pronounced in the benzimidazole series leading to an inversed order of the  $d\pi^*$  orbitals from  $E(3d_{xy}) > E(3d_{xz,yz})$  in  $Fe(L9)_2$  to  $E(3d_{xz,yz}) > E(3d_{xy})$  in both amines  $Fe(L3)_2$  and  $Fe(L6)_2$ .

According to the discussion above, analysis of the average % Fe 3d composition of both  $d\pi$  and  $d\pi^*$  orbitals in Figure 7

shows that the donor capability of the isolated ligands in  $Fe(L1)_2$  and  $Fe(L4)_2$  is increasing and the acceptor capability is decreasing by introducing an electron pushing amine function in the 4-position of the pyridine, since the  $d\pi$  energy is significantly destabilized relative to  $Fe(L7)_2$ . Nevertheless the iron-ligand  $\pi$ -acceptor interaction strength in the complexes is increasing, since the average % Fe 3d character of the  $d\pi$  orbitals decreases to 63.1% in the case of Fe(L1), and 63.7% in the case of  $Fe(L4)_2$  compared to 69.4% in Fe(L7)<sub>2</sub> (see Figure 7 and Supporting Information Table S14). Therefore, methyl- and benzylamine introduction in 4position of the pyridine leads to a significant increase in the  $\pi$ acceptor interaction strength of the respective complexes  $(Fe(L1)_2$  and  $Fe(L4)_2)$  in the methylimidazole series  $(Fe(L1)_2, Fe(L4)_2Fe(L7)_2)$ , where substitution by dimethylamine  $(Fe(L1)_2)$  shows a more pronounced effect compared to dibenzylamine  $(Fe(L4)_2)$ . This is in contrast to the respective isolated ligands, which are stronger donors and weaker acceptors. The same effect is observed in the methylimidazole-  $(Fe(L2)_2, Fe(L5)_2Fe(L8)_2, see Supporting)$ Information Figure S35) and benzimidazole series ( $Fe(L3)_{2}$ )  $Fe(L6)_2Fe(L9)_2$ , see Supporting Information Figure S36), where the benzimidazole complexes show the largest decrease of the average % Fe 3d composition of the  $d\pi$  orbitals through amine substitution and therefore the most pronounced increase in the  $\pi$ -acceptor interaction strength of complex  $Fe(L3)_2$ . While in both, the methylimidazole and imidazole series, benzylamine substitution has the largest effect, in the benzimidazole series it is the methylamine substitution that causes the strongest  $\pi$ -acceptor interaction. The observed experimental redshift of the MLCT absorption by around 8 nm for the dibenzylamine complex  $Fe(L4)_2$  in comparison to its methylamine analogue  $Fe(L1)_2$  can therefore not be explained by an increasing  $\pi$ -acceptor interaction strength in complex  $Fe(L4)_2$  and could speculatively be assigned to a decrease of the HOMO-LUMO gap in  $Fe(L4)_2$  compared to  $Fe(L1)_2$ which is in agreement with the computational observed HOMO-LUMO gaps (for further information see Supporting Information Table S15).

So far, a large influence on the  $\pi$ -acceptor interaction strength of the resulting complexes  $(Fe(L1)_2 - Fe(L6)_2)$  by amine substitution in the 4-position of the pyridine was observed. But also, the  $\sigma$ -donor strength needs to be evaluated in this context. In analogy to the previous procedure for investigating the  $\pi$ -acceptor interaction strength, the average % Fe 3d character of the  $d\sigma^*$  orbitals is analyzed for this purpose. The average % Fe 3d character of the  $d\sigma^*$  orbitals should increase with increasing  $\sigma$ -donor interaction strength. A comparison of the average Fe 3d contributions of the d $\sigma^*$ orbitals of  $Fe(L1)_2$ ,  $Fe(L4)_2$ ,  $Fe(L7)_2$  in Figure 7 shows that the amine function in the 4-position of the pyridine ring significantly reduces the  $\sigma$ -donor interaction strength in both amine substituted complexes  $(Fe(L1)_2, Fe(L4)_2)$ , while the donor strength of both ligands L1 and L4 is increasing, since the d $\sigma^*$  orbital energy is shifting to higher energies because of the additional electrostatic destabilization through amine substitution on all orbitals.  $Fe(L4)_2$  shows the smallest average 3d contribution of the  $d\sigma^*$  orbitals in the imidazole series, and therefore, dibenzylamine substitution leads to the weakest  $\sigma$ donor interaction strength here. This is contrast to the fact that the free ligand L4 is one of the strongest donors in the series L1–L9, due to significant electrostatically destabilized  $d\sigma^*$ orbitals. This effect is also reflected by calculated <sup>3</sup>MC energies

in the Franck–Condon region of complexes  $Fe(L1)_2-Fe(L6)_2$ compared to  $Fe(L7)_2$ , which decrease by around 0.08 eV in the case of dimethylamine and around 0.07 eV for dibenzylamine in the imidazole series ( $Fe(L1)_2$ ,  $Fe(L4)_2$ ,  $Fe(L7)_2$  (for further information, see Supporting Information Table S15).

In the UV/vis spectra, a significant destabilization of the MLCT energies in the Franck-Condon region has been observed for all amine functionalized complexes compared to the reference  $Fe(L7)_2$ . This is in line with DFT calculated ground state  $d\pi - d\pi^*$  (HOMO–LUMO) gaps, which increase by around 0.2 eV and the calculated MLCT energies in the Franck-Condon region, which also increase by around 0.1 eV through amine substitution, where the dibenzylamine substituted complexes  $Fe(L4)_2 - Fe(L6)_2$  show slightly stabilized MLCT energies (by ~0.02 eV) compared to their dimethylamine analogues  $Fe(L1)_2 - Fe(L3)_2$  (see Supporting Information Figures S15 and S16). Nevertheless, these observations do not exclude a MLCT stabilization through amine substitution in the relaxed MLCT structure. Unfortunately, the complexes show no MLCT emission, which could be used to probe the MLCT energy in its a relaxed MLCT structure. For this reason, ultrafast transient absorption experiments were performed (vide infra).

To further substantiate the discussion of the complex interplay between orbital interaction and electrostatic influence, the magnitude of electrostatic destabilization in all substituted complexes is analyzed and will be compared to the influence on the Kohn–Sham (KS) orbital energies of interest. For this reason, destabilization of Fe 3p (average), Fe 1s, Fe  $d\pi^*$  (average), Fe  $d\sigma^*$  (average), and Fe  $d\pi$  (average) orbital energies of all substituted complexes  $(Fe(L1)_2 - Fe(L6)_2)$  were calculated by subtracting the (average) respective orbital energies of the appropriate unsubstituted parent complex  $(Fe(L7)_2 - Fe(L9)_2)$ . Fe 1s and 3p orbitals are used as a probe of the "pure" electrostatic destabilization, since both are metalbased and obviously nonbonding and therefore only influenced by the electrostatic destabilization, while all other bonding and antibonding interactions are naturally influenced by orbitalcovalency. The results of this approach are given in Figure 8.



**Figure 8.** Kohn–Sham (KS) orbital destabilization of Fe 1s, 3p,  $d\pi$ ,  $d\pi^*$ , and  $d\sigma^*$  orbitals of complexes  $Fe(L1)_2-Fe(L6)_2$  relative to their respective parent complex  $Fe(L7)_2-Fe(L9)_2$ . For nearly degenerate orbitals (3p,  $d\pi$ ,  $d\pi^*$ , and  $d\sigma^*$ ), average energies were used.

The destabilization of both the Fe 1s and 3p orbital energies is identical, proving the validity of the approach.  $Fe(L1)_2$  is characterized by the strongest destabilization in the investigated series by 0.38 eV, while  $Fe(L6)_2$  shows the smallest influence with a destabilization of only 0.29 eV. This observation might explain the absence of a second oxidation event in the CV of  $Fe(L6)_2$  since the  $\pi$  orbitals are not destabilized enough to be oxidized in the electrochemical window of MeCN. In general, methylamine substitution  $(Fe(L1)_2 - Fe(L3)_2)$  leads to a stronger destabilization compared to benzylamine substitution  $(Fe(L4)_2 - Fe(L6)_2)$ and imidazole and methylimidazole complexes are stronger influenced ( $Fe(L1)_{2}$ ,  $Fe(L2)_{2}$ ,  $Fe(L4)_{2}$ ,  $Fe(L5)_{2}$ ) compared to their benzimidazole analogues  $(Fe(L3)_2, Fe(L6)_2)$ . The observed covalent orbital interactions cause a deviation from the results expected according to similar Ruthenium complexes as described in the introduction.<sup>45</sup>

We observe the largest destabilization in case of the  $d\pi^*$ orbitals, but with a similar destabilization trend as observed for both nonbonding 3p and 1s orbitals, pointing out to a minor influence of orbital-covalency for all complexes. Nevertheless, the process of the average  $d\pi$  and  $d\pi^*$  destabilization over the complex series in Figure 8 clearly shows that in this case, the  $d\pi^*$  orbitals are significantly more destabilized than the  $d\pi$ orbitals. This observation can be explained by the overall observed increasing  $\pi$ -acceptor interaction strength through amine substitution, which stabilize the  $d\pi$  orbitals as discussed above. The increasing orbital interaction strength between  $\pi^*$ orbitals and Fe t<sub>2g</sub>-orbitals through amine substitution therefore prevails over the electrostatic destabilization in the case of  $d\pi$  orbitals. This is in contrast to the  $d\pi^*$  orbitals and leads to increasing HOMO-LUMO gaps and MLCT energies, consistent with an increasing acceptor interaction strength through substitution by a donor group in the 4-position of the central pyridine. One remaining important point not discussed so far is the influence on the antibonding  $d\sigma^*$  interaction. The average KS d $\sigma^*$  orbitals are 0.2 eV less destabilized compared to the  $d\pi$  orbitals, stabilizing  $\Delta_0$  and ligand field (LF) states, consistent with observation made above. In the introduction, it was proposed that antibonding iron-ligand interactions ( $d\pi^*$ and  $d\sigma^*$ ) should be less affected by the electrostatic destabilization compared to their bonding analogues (d $\pi$  and  $d\sigma$ ). This is confirmed with the results presented in Figure 8. Nevertheless, it should be mentioned that the value of 0.2 eV less destabilization of the average  $d\sigma^*$  orbital energy relative to the Fe 1s destabilization is most likely due to the additional decreasing donor interaction strength in the substituted complexes, stabilizing the  $d\sigma^*$  orbitals relative to noninteracting orbitals (e.g., 1s or 3p).

**Transient Absorption Spectroscopy.** The excited state dynamics were probed by ultrafast pump-probe spectroscopy with a time resolution of about 100 fs, using excitation pulses centered at 450 or 400 nm, depending on the absorption spectrum of the respective complex.<sup>42,46-48</sup> Transient absorption spectra of the complexes  $Fe(L1)_2-Fe(L6)_2$  in MeCN are shown for selected delay times in Figure S21 of the Supporting Information. The transient spectra of the various complexes exhibit a very similar behavior. After optical excitation, intense negative signals are detected between 380 and 480 nm that are caused by ground state bleach (GSB). The GSB mirrors nearly perfectly the ground state MLCT absorption. Positive bands are visible above 480 nm, corresponding to an excited state absorption (ESA). A second

ESA band below 380 nm is indicated but not fully visible. For complexes  $Fe(L1)_2$  and  $Fe(L3)_2$ , the ESA band below 380 nm cannot be observed because of the detection limit in the setup used in these measurements due to its more suitable excitation wavelength of 400 nm. A global fit of a sum of exponential decay components was applied to the transient absorption data of all complexes. The extracted time constants are listed in Table 3, and the decay associated amplitude spectra (DAS) are

Table 3. Time constants extracted from transient absorption spectroscopy for complexes Fe(L1)-Fe(L6)

complex	$ au_1 \ [ps]$	$ au_2$ [ps]
$Fe(L1)_2$	2.8	10.3
$Fe(L2)_2$	2.8	9.7
$Fe(L3)_2$	1.1	11.7
$Fe(L4)_2$	8.7	
$Fe(L5)_2$	2.3	9.5
Fe(L6) <sub>2</sub>	0.6	11.4

depicted in Figure 9. In general, two components are found, one with a short time constant in the few picosecond region and a dominant one with a decay time of about 10 ps. A very similar behavior was found by Haacke and Gros et al. for Fe<sup>II</sup> complexes with imidazole-2-ylidene- and benzimidazole-2ylidene-based ligands.<sup>20,28</sup> They observed dynamics, which they also characterized by two time constants. The first one of some 100 fs was assigned to the relaxation of a hot <sup>3</sup>MLCT state, directly populated by an ultrafast intersystem crossing from the <sup>1</sup>MLCT state. The second one varying between 10 and 26 ps was attributed to the <sup>3</sup>MLCT lifetime. A similar interpretation was applied by Sundström and Wärnmark et al. to the transient absorption of  $Fe(L7)_2$ .<sup>34</sup> They found again two time constants, a very short one with a lifetime of <100 fs, assigned to the ultrafast intersystem crossing from the <sup>1</sup>MLCT to the <sup>3</sup>MLCT state and one of 9 ps representing the <sup>3</sup>MLCT lifetime. In the present case, the short time constant varies between 0.6 and 2.8 ps depending on the complex, which seems to be too long for ultrafast intersystem crossing from the <sup>1</sup>MLCT to the <sup>3</sup>MLCT state. Probably this component is due to vibrational redistribution and cooling which is often reported to occur on the picosecond time scale<sup>6,49</sup> and represents the relaxation of a hot <sup>3</sup>MLCT state.<sup>20</sup> The assignment is supported by the shape of the corresponding DAS. They correlate with the slope of the DAS of the second component and have minima and maxima where this slope is particularly steep. This behavior reflects a blueshift of the transient spectra during the first picoseconds, which is expected in the case of vibrational relaxation processes. In the case of complex  $Fe(L4)_{2}$ , the fast component is not observed. Maybe it is less pronounced and hidden by the dominant decay component, which is in this case also somewhat faster than in the other compounds. The second and dominant decay component reflects the recovery of the GSB and the decay of the ESA. The time constant for all complexes is on the order of 10 ps; in line with the above cited findings it is assigned to the <sup>3</sup>MLCT lifetime. The corresponding DAS support the assignment since they show an ESA band at the long wavelength side of the bleach, which is typical for MLCT states of iron complexes.<sup>28,34,42</sup> As stated in ref 20 the absence of a 10 nm narrow ESA in the near-UV region and zero absorption in the red excludes the presence of the  ${}^{5}T_{2}$  quintuplet state. For complexes  $Fe(L4)_{2}$  and  $Fe(L6)_{2}$ 

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Figure 9. Decay associated amplitude spectra (DAS) obtained from a global fit of the transient absorption data of complexes  $Fe(L1)_2$ - $Fe(L6)_2$  and labeled by the corresponding time constants. The fastest component is depicted in black, the next faster one in red and a long living one found for  $Fe(L4)_2$  and  $Fe(L6)_2$  in blue. The cyan colored spectrum is the bleach, i.e., the scaled negative ground state absorption.

the inclusion of a third, very long-living component (>2 ns) improved the global fit significantly. However, the component is very weak compared to the others and might be caused by a slight drift of the baseline.

Despite the electrostatic and donor/acceptor properties of the ligands discussed above, comparison of the measured lifetimes indicates that the nature of the NHC ligand part is more dominating the excited state properties than the amine substitution. The lifetime of the <sup>3</sup>MLCT state, which is determined by the fitting procedure with an uncertainty of about  $\pm 0.5$  ps, is slightly increased when going from the imidazole-2-ylidene ligands (L1, L2, L4, L5) to the benzimidazole-2-ylidene ligands (L3, L6); see Table 3. Although the difference of the obtained lifetimes is small, the observed trend could be correlated to the results of the theoretical section, since in both benzimidazole-2-ylidene complexes  $(Fe(L3)_2/Fe(L6)_2)$  the  $d\pi^*$  and  $\pi^*$  orbitals as acceptor orbitals in the MLCT excitation are significantly stabilized in contrast to imidazole-2-ylidene-  $(Fe(L1)_2/Fe (L4)_2$ ) and methylimidazole-2-ylidene complexes  $(Fe(L2)_2/$  $Fe(L5)_2$ ). Nevertheless, we have to admit that we do not know which  $d\pi^*$  or  $\pi^*$  orbital is actual the acceptor in the investigated MLCT excitation. Although this observation is in accordance with previous results, the effect is less pronounced for amine-substituted ligands.<sup>20</sup> We observed a slight increase of the <sup>3</sup>MLCT lifetime through dimethylamine substitution (Fe(L1)<sub>2</sub>,  $\tau$ (<sup>3</sup>MLCT) = 10.3 ps) in the imidazole series investigated here (Fe(L1)<sub>2</sub>, Fe(L4)<sub>2</sub>, Fe(L7)<sub>2</sub>) by 1.3 ps, while the dibenzylamine analogue showed a reduced <sup>3</sup>MLCT lifetime (Fe(L4)<sub>2</sub>,  $\tau$ (<sup>3</sup>MLCT) = 8.7 ps) compared to the unsubstituted reference (Fe(L7)<sub>2</sub>, $\tau$ (<sup>3</sup>MLCT) = 9.0 ps). Nevertheless, a significant reduction of the <sup>3</sup>MLCT lifetime through methyl- and benzyl-amine substitution is observed in the case of the benzimidazole-2-ylidene complexes.  $Fe(L3)_2$ with  $\tau({}^{3}\text{MLCT}) = 11.7$  ps and  $\text{Fe}(\text{L6})_{2}$  with  $\tau({}^{3}\text{MLCT}) = 11.4$ ps exhibit a reduction of the <sup>3</sup>MLCT lifetime by almost 5 ps compared to their unsubstituted analogue, with its lifetime of 16.4 ps.<sup>20</sup>

These results underline that the effect of substitution of the central pyridine in the 4-position in homoleptic iron(II) complexes with tridentate NHC-pyridine-NHC ligands can result in unexpected changes of the electronic structure. The

investigated set with varying NHC and amine ligands illustrates that the effect of an electron pushing amine group in the ligand backbone depends on the nature the NHC ligand. An increase of the <sup>3</sup>MLCT lifetimes through substitution in the 4-position is observed for imidazole-2-ylidene complexes, while benzimidazole-2-ylidene complexes showed a significant decrease of the <sup>3</sup>MLCT lifetime through amine substitution.

#### CONCLUSION

A detailed experimental and computational investigation of six different homoleptic iron complexes  $Fe(L1)_2-Fe(L6)_2$ , with the well-known tridentate NHC-pyridine-NHC ligand motif, employing either imidazol-2-ylidene or benzimidazol-2-ylidene NHCs in combination with various 4-amino pyridines was carried out in comparison to unsubstituted imidazole-2-ylidene  $(Fe(L7)_2)$ , methylimidazole-2-ylidene  $(Fe(L8)_2)$ , and benzimidazole-2-ylidene  $(Fe(L9)_2)$  complexes.

In such complexes, the  $\pi$ -acceptor and  $\sigma$ -donor interaction strengths are significantly affected by amine substitution in the 4-position of the central pyridine. The electrostatic destabilization through the amine in the 4-position, affects all orbitals, leading to increasing  $\sigma$ -donor capability and decreasing  $\pi$ acceptor capability of the free ligands. In the resulting complexes though, an increasing  $\pi$ -acceptor interaction strength together with a decrease in the  $\sigma$ -donor interaction strength is observed. A stronger  $\pi$ -acceptor interaction is present with dimethylamine substitution  $(Fe(L1)_2, Fe(L2)_2)$  $Fe(L3)_2$ ), while the dibenzylamine analogues ( $Fe(L4)_2$ )  $Fe(L5)_{2}$ ,  $Fe(L6)_{2}$ ) exhibit a weaker  $\sigma$ -donor interaction. From transient absorption spectroscopy, it is shown that methylamine substitution leads to extended <sup>3</sup>MLCT lifetimes in the case of imidazole-2-ylidene complexes  $(Fe(L1)_2)$  $Fe(L4)_2$ ), which is correlated to the strongest increase of the  $\pi$ -acceptor interaction strength in the ground state in the imidazole series. In contrast, <sup>3</sup>MLCT lifetimes of benzimidazole-2-ylidene complexes ( $Fe(L3)_2$ ,  $Fe(L6)_2$ ) were reduced by both methyl- and benzylamine substitution. Therefore, even changes in the nature of the NHC ligand group can reverse the observed effect on <sup>3</sup>MLCT lifetimes through amine substitution in 4-position of the central pyridine.

The results show the tremendous potential to tune the donor-acceptor properties of [Fe(bis-NHC-pyridyl)<sub>2</sub>]<sup>+2</sup>-type

complexes but also show the complexity of the interplay between electrostatic and covalent TM–ligand interactions. In this series, we observed a strong influence of changing orbital covalency through amine substitution in the 4-position of the central pyridine, canceling out the effect of the raw electrostatic destabilization, leading to increasing MLCT energies and HOMO–LUMO gaps instead, in contrast to polypyridyl ruthenium complexes. Benzimidazole-2-ylidene NHCs are an ideal choice when both  $\pi$ -accepting (stabilization of  $d\pi$ orbitals) and  $\sigma$ -donating (destabilization of  $d\sigma^*$  orbitals) effects need to be achieved.

### EXPERIMENTAL SECTION

**Quantum Chemical Calculations.** All calculations were performed with the ORCA 4.0.1 quantum chemistry package.<sup>50</sup> Unconstrained DFT optimizations of all investigated complexes were performed using the PBEh-3c method.<sup>51–53</sup>

All single-point calculations were performed using the TPSSh<sup>54</sup> hybrid functional together with the Ahlrichs def2-TZVPP<sup>55</sup> basis set on all atoms with inclusion of MeCN solvation via SMD.<sup>56</sup> Correction for dispersion interaction was included by DFT-D3 with Becke-Johnson damping (D3BJ).<sup>57–59</sup>

For all FOD calculations, the recommended combination by Grimme et al. of the BHLYP or TPSS functional together with the Ahlrichs def2-TZVP at a smear temperature of 15000 K (BHLYP) or 5000 K (TPSS) has been chosen.<sup>43,60</sup>

TDDFT singlets and triplets (15 roots) were computed using the TPSSh<sup>54</sup> and B3LYP hybrid functionals together with the Ahlrichs def2-TZVPP<sup>55</sup> basis set on all atoms with inclusion of MeCN solvation via SMD.<sup>56</sup> Correction for dispersion interaction was included by DFT-D3 with Becke-Johnson damping (D3BJ).<sup>57–59</sup>

Kohn–Sham orbitals ( $\sigma = 0.03 \text{ e/Bohr}^3$ ) and FOD plots ( $\sigma = 0.005 \text{ e/Bohr}^3$ ) were visualized with IQmol (v 2.13.0). TDDFT transitions were broadened by 1750 cm<sup>-1</sup> (fwhm) and shifted by 4268 cm-1.

Synthesis. General Procedure for Ligand Synthesis. The respective imidazole derivate (2.8 equiv) was slowly added to an ice-cold solution of NaH (3 equiv) in dry DMF (50 mL) under argon atmosphere. The reaction mixture was stirred at 0 °C for 1 h and then allowed to warm to r.t.. The relevant 2,6-dichloropyridine-4-amine (1 equiv) is added portion wise, and the solution was heated at 130 °C for 72 h. After being cooled to r.t., the reaction mixture was given to an ice/water mixture (500°mL) and stirred for additional 10 min. The precipitate was filtered, washed with diethyl ether (300 mL), and dried under a vacuum. Under argon atmosphere, the 2,6-bisimidazole-4-aminepyridine derivate (1 equiv) was dissolved in dry MeCN (40 mL). To the solution was added methyl iodide (4 equiv), and the reaction mixture was heated to reflux for 16 h. After being cooling to r.t., the solvent was removed under a vacuum, and the residual solid was dissolved in a minimum amount of water and added dropwise to a saturated aqueous solution of KPF<sub>6</sub>. The resulting white precipitate was filtered and dried under a vacuum. The specified synthetic regulations as well as the analytic data are given in the Supporting Information.

General Method for the Synthesis of Fe-NHC Complexes. Under an argon atmosphere the respective ligand (1 mmol) was solved in dry THF (10 mL) and cooled to -10 °C. At that temperature, LiHMDS was added to the solution which turned red instantly. A solution of FeBr<sub>2</sub> (0.5 mmol) in dry THF (5 mL) was added dropwise, and the reaction mixture was stirred at that temperature for 30 min. The reaction mixture was warmed up to r.t. and was stirred for another 12 h. Then the solvent was removed under reduced pressure, and the residue was suspended in a minimal amount of acetone. The acetone suspension was filtered and added to a saturated solution of potassium hexafluorophosphate in water resulting in precipitation of the iron(II)-NHC complexes. These crude products were purified by column chromatography (Al<sub>2</sub>O<sub>3</sub>/ MeCN). *Preparation of* [*Fe*(*BIP*<sup>NMe2</sup>)<sub>2</sub>][*PF*<sub>6</sub>]<sub>2</sub> (*Fe*(*L*1)<sub>2</sub>). Yield: 75% (0.37 mmol); yellow powder. <sup>1</sup>H NMR (500 MHz, MeCN-*d*<sub>3</sub>, 30 °C, *δ* [ppm]): 7.93 (d, 4H, CH); 6.97 (d, 4H, CH); 6.95 (s, 4H, CH); 3.24 (s, 12H, CH<sub>3</sub>); 2.63 (s, 12H, CH<sub>3</sub>) <sup>13</sup>C NMR (125 MHz, MeCN-*d*<sub>3</sub>, 30 °C, *δ* [ppm]): 203.4 (Cq(<sub>NHC</sub>)); 157.2 (Cq); 153.3 (Cq); 125.6 (CH); 115.7 (CH); 89.4 (CH); 39.8 (CH<sub>3</sub>); 34.5 (CH<sub>3</sub>). ESI-MS (*m*/*z*(%)) (MeCN): 310.12 (100) [M<sup>2+</sup>]; IR (ATR,  $\tilde{\nu}$  [cm<sup>-1</sup>]): 3185 (w), 3148 (w), 2947 (w), 1634 (w), 1568 (w), 1531 (m), 1503 (w), 1482 (w), 1466 (m), 1435 (w), 1402 (m), 1341 (m), 1262 (m), 1235 (w), 1177 (m), 1125 (w), 1085 (w), 1067 (w), 1003 (w), 987 (w), 937 (w), 865 (sh), 827 (s), 801 (s), 748 (m), 695 (s), 684 (s), 636 (w), 582 (w), 553 (s), 490 (w), 417 (w), 378 (w), 323 (w), 272 (w), 239 (w). elemental analysis: calculated for C<sub>30</sub>H<sub>36</sub>F<sub>12</sub>FeN<sub>12</sub>P<sub>2</sub>: C: 39.58; H: 3.99; N: 18.46; found: C: 39.68; H: 4.10; N: 18.43.

*Preparation of* [*Fe*(*BmlP*<sup>MMe2</sup>)<sub>2</sub>][*PF*<sub>6</sub>]<sub>2</sub> (*Fe*(*L*2)<sub>2</sub>). Yield: 75% (0.37 mmol); yellow powder. <sup>1</sup>H NMR(700 MHz, MeCN-d<sub>3</sub>, 30 °C, δ [ppm]): 7.66 (d, 4H, CH); 6.82 (s, 4H, CH); 3.22 (s, 12H, CH<sub>3</sub>); 2.47 (s, 12H, CH<sub>3</sub>); 2.08 (s, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, MeCN-d<sub>3</sub>, 30 °C, δ [ppm]): 204.4 (Cq(<sub>NHC</sub>)); 158.0 (Cq); 154.2 (Cq); 134.4 (CH); 113.3 (CH); 89.5 (CH); 40.7 (CH<sub>3</sub>); 32.1 (CH<sub>3</sub>); 9.9 (CH<sub>3</sub>). ESI-MS (*m*/*z*(%)) (MeCN): 338.15 (100) [M<sup>2+</sup>]; 821.28 (8) [M<sup>2+</sup> + PF<sub>6</sub><sup>-</sup>]. IR (ATR,  $\tilde{\nu}$  [cm<sup>-1</sup>]): 3648 (w), 3149 (w), 2931 (w), 2360 (w), 1645 (m), 1620 (m), 1539 (m), 1506 (w), 1436 (w), 1394 (m), 1336 (m), 1270 (m), 1240 (w), 1184 (w), 1166 (w), 1072 (w), 999 (w), 937 (w), 835 (s), 806 (sh), 752 (m), 698 (w), 607 (w), 555 (s), 501 (w), 410 (w), 378 (w), 349 (w). elemental analysis: calculated for C<sub>34</sub>H<sub>44</sub>F<sub>12</sub>FeN<sub>12</sub>P<sub>2</sub>: C: 42.25; H: 4.59; N: 17.39; found: C:43.24; H: 4.97; N: 17.78.

17.39; found: C:43.24; H: 4.97; N: 17.78. Preparation of  $[Fe(BBP^{NMe2})_2][PF_6]_2$  ( $Fe(L3)_2$ ). Yield: 62% (0.31 mmol); red powder. <sup>1</sup>H NMR (700 MHz, MeCN- $d_3$ , 30 °C,  $\delta$ [ppm]): 8.21 (d, 4H, CH), 7.45 (t, 4H, CH); 7.38 (t, 4H, CH); 7.36 (s, 4H, CH); 7.31 (d, 4H, CH); 3.49 (s, 12H, CH<sub>3</sub>); 2.87 (s, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, MeCN- $d_3$ , 30 °C,  $\delta$  [ppm]): 214.9 (Cq(<sub>NHC</sub>)); 158.6 (Cq); 154.7 (Cq); 139.3 (Cq); 131.9 (Cq); 125.3 (CH); 124.5 (CH); 112.5 (CH); 111.0 (CH); 91.6 (CH); 41.2 (CH<sub>3</sub>); 32.4 (CH<sub>3</sub>). ESI-MS (m/z(%)) (MeCN): 410.15 (100) [ $M^{2+}$ ]. IR (ATR,  $\tilde{\nu}$  [cm<sup>-1</sup>]): 2930 (w), 2812 (w), 1673 (w), 1640 (m), 1601 (w), 1537 (w), 1499 (m), 1463 (w), 1438 (w), 1384 (m), 1334 (sh), 1305 (m), 1231 (s), 1189 (s), 1160 (s), 1124 (s), 1092 (s), 1022 (w), 981 (s), 939 (w), 875 (w), 829 (s), 789 (s), 734 (s), 690 (m), 671 (m), 636 (w), 587 (w), 555 (s), 456 (w), 431 (m), 393 (w), 349 (w), 281 (w). elemental analysis: calculated for C<sub>46</sub>H<sub>44</sub>F<sub>12</sub>FeN<sub>12</sub>P<sub>2</sub>: C: 49.74; H: 3.99; N: 15.13; found: C: 49.51; H: 4.50; N:14.34.

Preparation of  $[Fe(BIP^{NBn2})_2][PF_6]_2$  (Fe(L4)<sub>2</sub>). Yield: 68% (0.34) mmol); yellow powder. <sup>1</sup>H NMR(500 MHz, MeCN- $d_3$ , 30 °C,  $\delta$ [ppm]): 7.58 (d, 4H, CH); 7.18 (t, 8H, CH); 7.12 (m, 12H, CH); 6.85 (s, 4H, CH); 6.71 (d, 4H, CH); 4.72 (s, 8H, CH<sub>2</sub>); 2.40 (s, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, MeCN-d<sub>3</sub>, 30 °C, δ [ppm]): 204.0 (Cq(<sub>NHC</sub>)); 157.9 (Cq); 154.6 (Cq); 137.5 (Cq); 129.7 (CH); 128.4 (CH); 127.9 (CH); 126.7 (CH); 116.5 (CH); 91.1 (CH); 54.6  $(CH_2)$ ; 35.4  $(CH_3)$ . ESI-MS(m/z(%)) (MeCN): 462.19 (100)  $[M^{2+}]$ . IR (ATR,  $\tilde{\nu}$  [cm<sup>-1</sup>]): 3168 (w), 3135 (w), 2916 (w), 2850 (w), 1729 (w), 1716 (w), 1640 (m), 1633 (m), 1603 (w), 1568 (w), 1539 (w), 1502 (m), 1480 (m), 1467 (w), 1450 (m), 1400 (m), 1343 (m), 1296 (w), 1270 (w), 1240 (m), 1255 98 (m), 1186 (w), 1155 (w), 1131 (m), 1085 (m), 1028 (w), 1000 (w), 981 (w), 945 (m), 899 (w), 837 (s), 808 (s), 728 (s), 694 (m), 616 (w), 555 (s), 485 (w), 454 (w), 408 (w), 375 (w), 349 (w), 317 (w), 265 (w), 226 (w). elemental analysis: calculated for C54H52F12FeN12P2: C: 53.39; H: 4.31; N: 13.84; found: C: 52.74; H: 4.80; N: 13.03. Preparation of  $[Fe(BmlP^{NBn2})_2][PF_6]_2$  (Fe(L5)<sub>2</sub>). Yield: 83% (0.41)

*Preparation of* [*Fe*(*BmlP*<sup>NBn2</sup>)<sub>2</sub>][*PF*<sub>6</sub>]<sub>2</sub> (*Fe*(*L5*)<sub>2</sub>). Yield: 83% (0.41 mmol); yellow powder. <sup>1</sup>H NMR(500 MHz, 30 °C, MeCN-d3, δ [ppm]): 7.41 (d, 4H, CH); 7.29 (t, 8H, CH); 7.21 (d, 8H, CH); 7.20 (t, 4H, CH); 6.80 (s, 4H, CH); 4.82 (s, 8H, CH<sub>2</sub>); 2.34 (s, 12H, CH<sub>3</sub>); 1.93 (d,12H, CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, 30 °C, MeCN-d<sub>3</sub>, δ [ppm]): 204.3 (Cq(<sub>NHC</sub>)); 157.77 (Cq); 154.6 (Cq); 137.7 (Cq); 134.8 (Cq); 129.8 (CH); 128.5 (CH); 127.9 (CH); 113.3 (CH); 90.5 (CH); 55.2 (CH<sub>2</sub>); 31.0 (CH<sub>3</sub>); 9.9 (CH<sub>3</sub>).ESI-MS(*m*/*z*(%)) (MeCN): 490.21 (100) [M<sup>2+</sup>]. IR (ATR,  $\tilde{\nu}$  [cm<sup>-1</sup>]): 3141 (w), 3029

(w), 2929 (w), 2360 (w), 2323 (w), 1641 (m), 1620 (m), 1540 (w), 1506 (m), 1488 (m), 1454 (w), 1392 (m), 1348 (sh), 1332 (w), 1297 (w), 1272 (w), 1251 (w), 1209 (m), 1176 (w), 1155 (w), 1076 (w), 1027 (w), 1002 (w), 931 (w), 916 (w), 873 (w), 829 (s), 802 (s), 730 (m), 696 (m), 644 (m), 613 (w), 555 (s), 487 (w), 459 (w), 416 (w), 376 (w), 351 (w), 302 (w), 246 (w), 227 (w).elemental analysis: calculated for  $C_{58}H_{60}F_{12}FeN_{12}P_2$ : C: 54.81; H: 4.76; N: 13.22; found: C: 54.86; H: 4.86; N: 13.44.

Preparation of  $[Fe(BBP^{NBn2})_2][PF_6]_2$  (Fe(L6)<sub>2</sub>). Yield: 60% (0.30 mmol); red powder. <sup>1</sup>H NMR (700 MHz, MeCN-d3, 30 °C, δ [ppm]): 7.62 (d, 4H, CH); 7.57 (d, 4H, CH); 7.49 (t, 8H, CH); 7.35 (m, 12H, CH), 7.29 (s, 4H, CH); 7.26 (m, 4H, CH); 5.26 (s, 8H, CH<sub>2</sub>); 2.73 (s, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, MeCN-d3, 30 °C, δ [ppm]): 214.4 (Cq(<sub>NHC</sub>)); 157.6 (Cq); 154.5 (Cq); 139.2 (Cq); 137.9 (Cq); 131.6 (Cq); 130.2 (CH); 128.8 (CH); 127.9 (CH); 125.3 (CH); 124.3 (CH);111.7 (CH); 111.2 (CH); 93.3 (CH); 57.2  $(C_{(12)}H_2)$ ; 32.2  $(C_{(1)}H_3)$ . ESI-MS (m/z(%)) (MeCN): 562.22 (100) [M<sup>2+</sup>]. IR (ATR,  $\tilde{\nu}$  [cm<sup>-1</sup>]): 3060 (w), 3030 (w), 2360 (w), 2336 (w), 1640 (m), 1599 (m), 1540 (w), 1496 (m), 1452 (m), 1439 (m), 1385 (m), 1321 (m), 1293 (m), 1248 (w), 1231 (w), 1190 (m), 1138 (w), 1092 (m), 1022 (w), 939 (w), 828 (s), 791 (s), 731 (s), 696 (m), 635 (w), 585 (w), 555 (s), 546 (sh), 487 (w), 430 (m), 389 (w), 346 (w), 324 (w), 280 (w). elemental analysis: calculated for C<sub>70</sub>H<sub>60</sub>F<sub>12</sub>FeN<sub>12</sub>P<sub>2</sub>: C: 59.11; H: 4.27; N: 11.88; found: C: 59.21; H: 4.63; N: 11.69.

Transient Absorption Measurements. The transient absorption spectra of complexes  $Fe(L1)_2$  and  $Fe(L3)_2$  were recorded by pumpprobe spectroscopy with a time resolution of about 100 fs using excitation pulses at 400 nm.<sup>48</sup> For these measurements, a Ti:sapphire laser system (Spectra-Physics, Spitfire Pro) providing fundamental pulses at a center wavelength of 800 nm, and a repetition rate of 1 kHz was used. Frequency doubling of the fundamental resulted in the desired pump pulses. A white light continuum for probing was generated with a CaF<sub>2</sub> crystal. The polarizations of pump and probe were set to the magic angle, and both beams were focused into the sample resulting in overlapping spots with diameters of 104 and 74  $\mu$ m, respectively. After the sample, the probe was dispersed by a prism, and transient absorption changes were spectrally resolved recorded by an CCD array detector. The transient absorption spectra of complexes  $Fe(L2)_2$  and  $Fe(L4)_2$ -Fe(L6)<sub>2</sub> were obtained using excitation pulses at 450 nm. They were generated by means of a noncollinear optical parametric amplifier (NOPA) providing ultrashort pulses at a center wavelength of 900 nm, which were frequency doubled. The corresponding setup is pumped by a regenerative Ti:sapphire laser system (CPA 2001, Clark MXR, Inc.) operating at 775 nm and also at a repetition rate of 1 kHz. The probing was again done by a whitelight continuum; however, the spot sizes were slightly larger, i.e., 170  $\mu$ m for the pump and 130  $\mu$ m for the probe beam. The time resolution was again about 100 fs. The sample compounds were in all cases dissolved in MeCN, and the solutions were filled into 1 mm fused silica cuvettes.

Single crystal diffraction. Crystallographic data were recorded using a Bruker SMART CCD area detector equipped three-cyclediffractometer working with graphite monochromated MoK<sub>α</sub> radiation ( $\lambda = 0.71073$  Å) at 130(2) K. Structure solutions were carried out by direct methods<sup>61</sup> full matrix least-squares refinement based on F<sup>2.61</sup> All non-hydrogen atoms were refined anisotropically, and hydrogen positions were derived from geometrical reasons and afterward refined at idealized positions riding on the carbon atoms with isotropic displacement parameters  $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$  and  $d({\rm C-H}) = 0.96$  Å. The methyl groups are idealized with tetrahedral angles in a combined rotating and rigid group refinement with the 1.5fold isotropic displacement parameters of the equivalent  $U_{ij}$  of the corresponding carbon atom.

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00393.

General procedures, ligand synthesis, details of single crystal structure analysis, electrochemistry, additional computational information, additional transient absorption spectra (PDF)

# **Accession Codes**

CCDC 1950859–1950864 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**

Matthias Bauer – Department of Chemistry and Center for Sustainable Systems Design (CSSD), Paderborn University, 33098 Paderborn, Germany; o orcid.org/0000-0002-9294-6076; Email: matthias.bauer@upb.de; http:// www.chemie.upb.de/bauer

#### Authors

- Yannik Vukadinovic Department of Chemistry and Center for Sustainable Systems Design (CSSD), Paderborn University, 33098 Paderborn, Germany
- Lukas Burkhardt Department of Chemistry and Center for Sustainable Systems Design (CSSD), Paderborn University, 33098 Paderborn, Germany; Octid.org/0000-0003-0747-9811
- **Ayla Päpcke** Institute for Physics and Department of Life, Light and Matter, University of Rostock, 18051 Rostock, Germany
- Anabel Miletic Department of Chemistry and Center for Sustainable Systems Design (CSSD), Paderborn University, 33098 Paderborn, Germany
- Lorena Fritsch Department of Chemistry and Center for Sustainable Systems Design (CSSD), Paderborn University, 33098 Paderborn, Germany
- Björn Altenburger Institute for Physics and Department of Life, Light and Matter, University of Rostock, 18051 Rostock, Germany
- **Roland Schoch** Department of Chemistry and Center for Sustainable Systems Design (CSSD), Paderborn University, 33098 Paderborn, Germany
- Adam Neuba Department of Chemistry and Center for Sustainable Systems Design (CSSD), Paderborn University, 33098 Paderborn, Germany
- Stefan Lochbrunner Institute for Physics and Department of Life, Light and Matter, University of Rostock, 18051 Rostock, Germany; © orcid.org/0000-0001-9729-8277

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.0c00393

#### Notes

The authors declare no competing financial interest.

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Article

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