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Chromophoric Ruthenium Complexes



Synthesis and Properties of Acridine and Acridinium Dye Functionalized Bis(terpyridine) Ruthenium(II) Complexes

Jens Eberhard,*^[a] Katrin Peuntinger,^[c] Roland Fröhlich,^[b] Dirk M. Guldi,^[c] and Jochen Mattay*^[a]

Abstract: We present first principle studies on the rational design of an acridine/*N*-methylacridinium dye (Acr/MeAcr⁺) substituted terpyridine ligand to investigate if these chromophores can act as triplet-energy storage units in bis(terpyridine) ruthenium(II) complexes. We studied the influence of the dye form

(Acr/MeAcr⁺) as well as the interconnecting linker unit (none, 4-phenyl, or 5-thien-2-yl) and investigated these aspects by steady-state/time-resolved spectroscopy, cyclic voltammetry, X-ray structure analysis, and DFT calculations.

1. Introduction

Bis(terpyridine)ruthenium(II) complexes – $[Ru(tpy)_2]^{2+}$ – constitute an important class of metal to ligand charge transfer (MLCT) dyes due to the very efficient population of their triplet excited state (³MLCT) after excitation.^[1] For a given $[Ru(tpy)_2]^{2+}$ complex the luminescence lifetime is often the primary benchmark regarding its suitability for photosensitizing applications.^[1c,2] However, most of the simple $[Ru(tpy)_2]^{2+}$ complexes are non-luminescent at room temperature indicating a fast relaxation dynamics. To this end, rapid deactivation of the ³MLCT state by metal-centered triplet (³MC) states, close in energy to the ³MLCT state, is inferred.^[1e,3] In this regard, it is important to internalize that the effective energy gap (ΔE) between the states is governed by the activation barrier and not the difference in zero-zero energy (E_{00})^[1c] of the states minima on the potential energy hypersurface.

Tremendous efforts have been made to improve this crucial bottleneck in the photophysical properties of $[Ru(tpy)_2]^{2+}$ as summarized in several reviews.^[1c,4] Briefly, potential alternatives include extending π -conjugation through introducing electron withdrawing groups (EWGs),^[5] on one hand, and the more general approach of changing the field strength, i.e. by structural changes of the ligands, on the other hand. The latter is meant to realize a more octahedral coordination environment, which

[a]	Organische Chemie I, Fakultät für Chemie, Universität Bielefeld,
	Universitätsstr. 25, 33501 Bielefeld, Germany
	E-mail: mattay@uni-bielefeld.de
	http://www.uni-bielefeld.de/chemie/emeriti/oc1-mattay/
[b]	Röntgenstrukturanalyse, Organisch-Chemisches Institut,
	Westfälische Wilhelms-Universität Münster,
	Corrensstr. 40, 48149 Münster, Germany
	in a construction of the c

 [c] Physikalische Chemie I, Department of Chemistry and Pharmacy and Interdisciplinary Center for Molecular Materials, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany

Supporting information and ORCID(s) from the author(s) for this article are

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successively separates the energy levels and increases the activation barrier of crossing to the ³MC state, respectively.^[1c,6]

A less intuitive alternative is the use of organic dyes that feature a matching triplet level leading to the so-called multichromophore approach depicted in Scheme 1.^[4,7]



Scheme 1. Simplified Jabłoński diagram for systems with at least one additional ligand-centred triplet (^{3}LC) state in energetic proximity to the $^{3}MLCT$ state of interest.

The natural choice of anthracene (Ant) – the prototype polycyclic aromatic hydrocarbon – as storage unit was subject of detailed studies but the approach was unsuccessful for the $[Ru(tpy)_2]^{2+}$ complex due to the lower lying triplet excited state of anthracene (³Ant).^[8] A breakthrough in terms of the rational linker design was the work by Hanan et al.^[4,7d,7e] They maximized the π -conjugation through the terpyridine building block and subsequent lowered the energy of the ³MLCT state to match the ³Ant state. Despite the great success with pyrimidyl-(pm) or triazinyl-type of linkers in these designs, the synthetic efforts are cumbersome.^[7d,7e] Synthetically more accessible are imidazolyl-based systems, as published by Baitalik et al., ranging from lophine-based terpyridine assemblies to multichromophoric designs by use of rigidified imidazolyl-connected anthraquinone or pyrene units.^[9]

Considering our own interest in photochemistry of functional dyes and the availability of terpyridine building blocks,^[10] we thought it would be reasonable to evaluate the multi-

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chromophore approach with the highly interesting class of 10-methylacridinium dyes (MeAcr⁺).^[11]

Acridinium dyes attract considerable interest for their subtle substituent-dependent charge transfer (CT) state. This renders acridinium compounds attractive for basic studies on charge separation (CS).^[12] 9-Arylacridinium dyes were put in the spotlight by the contrary opinion between Fukuzumi and Benniston et al.^[13] Thus, several acridinium dyes, such as MeAcr⁺,^[14] 9-Phenyl-MeAcr⁺,^[15] and especially 9-Mesity-MeAcr^{+[16]} and derivatives thereof^[17] were extensively studied in photocatalytic (redox-)applications and are currently experiencing a renaissance due to availability of cheap but powerful LED light sources.^[18]

The basic photophysical properties of 9-arylacridinium dyes are well-known and their lowest triplet excited state level (T_1) is generally found between 1.9–2.0 eV.^[12a,19] A good photophysical understanding exists also for acridine derivatives with, for example, triplet excited states at energies comparable to those of MeAcr⁺ derivatives (e.g. 1.88–1.95 eV).^[19,20]

Furthermore, the acridinium core is known for its reactive 9position, which has been explored in the context of pseudobase formation^[21] and switchability, i.e. in supramolecular systems.^[22]

In regard to the cationic nature of the MeAcr⁺ dyes, studies of quaternized pyridine acceptor units, such as methylviologen (MV^{2+}) in particular, are relevant to this work.^[1e,23] For instance the methylene bridged heteroleptic [Ru(ttpy)(ttpy-MV)]⁴⁺ system had a charge-separated (CS) state at ca. 1.63 eV which extends the overall excited state lifetime to 600 ns at 200 K.^[1e,23a]

In addition to the aforementioned findings, our concept of testing Acr/MeAcr⁺ dyes in terms of multichromophic behaviour is based on several incentives: On one hand, some of the design principles towards long-lived photosensitizers are fulfilled, namely i) π -conjugating through the linker, ii) triplet excited state energy matching relative to the ³MLCT level of π -extended [Ru(tpy)₂]²⁺ complexes (cf. [Ru(ttpy)₂]²⁺ E_{00} (77 K) 1.98 eV),^[2,24] and iii) placing an EWG by methylation of the acridine moiety to yield the electrophilic acridinium ion but with a potential drawback of photoinduced electron transfer (p-e⁻T).

To characterize the influence of the cationic dye form, we also synthesized complexes **1** and **4** with an acridine unit (Scheme 2). These complexes are not only meant references due to the similar triplet level of acridines (see above), but also to shed light on possible p-e⁻T phenomena.^[25] Notably, in a conjugated assembly of the building blocks the electronic properties and/or triplet levels of the assembly might be altered in comparison to the isolated building blocks.

On the other hand, as the linker-design might be crucial for success, we focused on a thiophene unit as easy-to-implement interconnecting group. The thienyl-group is known to contribute favorably to the photophysical properties of $[Ru(tpy)_2]^{2+}$ derivatives: Albeit being electron-rich it increases the room temperature (RT) luminescence lifetime.^[26] A notable disadvantage of this spacer is the lower redox potential of the Ru^{III}/Ru^{II} couple due to the electron donating character of the thienyl moiety





1: $n = 0 R = - [Ru(AT)_2][PF_6]_2$ **2**: $n = 0 R = CH_3 [Ru(MeAT)_2][PF_6]_4$ **3**: $n = 1 R = CH_3 [Ru(MeAPhT)_2][PF_6]_4$ **4**: $R = - [Ru(ATT)_2][PF_6]_2$ **5**: $R = CH_3 [Ru(MeATT)_2][PF_6]_4$

Scheme 2. Structures of compounds 1-5 and labeling scheme for ^1H NMR spectroscopic assignments.

(see **28**, Table 2).^[26] The geometric properties, viz. the conjugated character of the thienyl-group, was consequently verified by reviewing the available X-ray structure data on thienyl-terpyridines,^[27] literature description about its unique properties,^[26,28] and own DFT calculations (see computational section).

Last but not least the smaller homologic systems are of high importance to this work, namely 4'-pyridyl and 4'-pyridinium terpyridines (py/py⁺-tpy) with their corresponding metal ion complexes, such as, Fe,^[29] Ru^[29b,29d,30] and Os.^[29b,30b] Therefore, 4'-py/py⁺-tpy complexes can be seen as a well investigated subcategory in the field of terpyridine complexes. The potentially water-soluble 4-py⁺-tpy complexes were focus for further research and also investigated by DFT calculations.^[30d,31] In respect to these reports, our study should be regarded as the next logical step towards the larger N-heterocyclic homologues. We investigated some of these complexes for the suitability to act as sensitizer for singlet oxygen previously,^[32] while the synthesis and a more in-depth analysis of the ruthenium(II) complexes is reported here.

2. Results and Discussion

2.1. Synthesis

The synthesis for the different ligands was either straight forward, i.e. for AT ligand **8** (Scheme 3) or relied on aldehyde pro-







Scheme 4. Synthetic route to ligands 19 and 20.

tection/deprotections step, starting from commercial available 4-bromobenzaldehyde (9) and thiophene-2-carbaldehyde (10), to enable the well documented reactions of metalated linker blocks, such as, 11 and 12, with electrophilic acridin-9-one derivatives or 10-alkyl-9-aridinium salts as a key feature of all synthetic routes presented here (Scheme 4).^[12a,15b,21e,22,33] The acetal-protected intermediates were obtained in good yields (13, 84 %; 14, 68 %–99 %) while deprotection was possible with excellent yields due to simple work-up (yield 90 %–93 %).

For the synthesis of the non-methylated but thienyl-linked ligand ATT **24**, a slightly different approach was necessary by

use of a MEM-protected 9-acridone (**22**) as electrophile (Scheme 5). Up on acidic work up, necessary to achieve elimination of water of the formed 9-acridinol intermediate, the MEMand the acetal protecting groups were cleaved in an one-pot procedure leading directly to the desired acridine-carbaldehyde **23**.

The synthetic strategies for the synthesis of 2,2':6',2"-terpyridines have been reviewed before^[1a,1b,34] Due to the facile synthesis of aldehydes we followed a Kröhnke-type approach^[35] although the isolated yield of this multi-condensation reaction is often only moderate. Terpyridines **8**, **17**, **18**, and



Scheme 5. Synthetic route to the ATT ligand (24) via aldehyde 23.





24 were isolated in 21 % - 36 % yield, which renders this step as the bottle-neck of the synthetic route. Attempts to optimize the reaction conditions for the terpyridine synthesis were unsuccessful.

The oxidation of acridanes **17** and **18** to the corresponding acridinium salts **19** and **20** was the final step of the synthetic sequence and may be considered as deprotection. Hereby, the acridane moiety served as kind of a protecting group for the highly basic conditions in Kröhnke-type condensation reactions. Otherwise nucleophiles, such as, hydroxide ions or alcohols (viz. solvent) would add to the 9-position of the acridinium moiety.

The bis(terpyridine)ruthenium(II) complexes were prepared by standard methods with $[Ru(dmso)_4Cl_2]$ as the reagent-ofchoice.^[1c,23a] The desired complexes could usually be isolated in moderate to good yields (41 % – 76 %; except **3**, 17 %).

For the synthesis of the $[Ru(MeAT)_2]^{4+}$ complex **2** we selected a "chemistry-on-the complex" approach^[7d,28,36] by *N*-methylation of **1**. Although it is known that *N*-methylation of uncomplexed py-tpy ligands can be selective,^[37] the late-stage "chemistry-on-the complex" strategy was more appealing to us. Recently, acridinone/acridine chemistry was even successfully implemented in a multi-step "chemistry-on-the complex" reaction sequence on $[Ru(bpy)_2X]^{2+}$ derivatives.^[38] The *N*-methylation of the different regioisomers of $[Ru(py-tpy)_2]^{2+}$ has been reported previously but mixtures of non-, mono-, and the desired bisalkylated product were obtained.^[29b,29c] These remarks let us consider the use of an autoclave with subsequent reaction temperatures of 110 °C (b.p. Mel 42 °C). To this end, a clean conversion was achieved and formation of any unidentified yellow byproducts^[29c] was prevented.

More detailed background information to the synthetic route and considerations thereof, respectively, are given in the Supporting Information.

The complexes were fully characterized by means of NMR and MS analysis (see Supporting Information). The success of complex formation was corroborated by ¹H NMR spectroscopy by virtue of characteristic shifts of the proton resonances upon complexation. For example, the 3'/5'-protons on the 4'-substituted tpy ligand (labeled B3') experience a downfield shift, while the 6/6''-protons (labeled A6) shift upfield. Acridinium and acridine heterocycles are easily distinguished by the general downfield shift of the signals for the MeAcr⁺ moiety (see Table S1) and the unique resonance of the methyl group usually found between 4.93–5.04 ppm.

2.2. X-ray Structure Elucidation

Crystals of the $[Ru(MeAT)_2]^{4+}$ complex (**2**) suitable for X-ray structure elucidation were grown from a MeCN solution of chromatographic purified material by slow diethyl ether vapor diffusion. Except for **2**, only crystals of poor diffraction quality were obtained.

The molecular structure of **2** is depicted in Figure 1 and selected structural parameters are compiled in Table 1. Structural parameters of **2** are compared to the published X-ray structure of $[Ru(py-tpy)_2]^{2+}$ (**29**)^[30c] and $[Ru(Et-py-tpy)_2]^{4+}$ (**30**).^[31a]



Figure 1. Structure of the $[Ru(MeAT)_2]^{4+}$ cation **2** in $[Ru(MeAT)][PF_{6]_{3,5}-}$ $[I_{3]_{0,5}-6$ MeCN with thermal ellipsoids plotted at the 33 % probability level. Important atoms are labeled while hydrogen atoms, solvent molecules, and counterions are omitted for clarity.

The primary coordination axis of **2** is identified along the N8A–Ru–N8B axis (denoted c-axis) by shorter bond lengths and almost linear coordination (177.0°) . Both parameters are in

Table 1. Comparison of selected structural parameters (distances [Å], angles \angle [°]) of complexes **2** with structural related compounds as determined by X-ray crystallography.

	[Ru(MeAT) ₂] ⁴⁺ (2)	[Ru(py-tpy) ₂] ²⁺ (29) ^[30c]	[Ru(Et-py-tpy) ₂] ⁴⁺ (30) ^[31a]	[Ru(Ant-tpy)(Cl-pm-tpy)] ²⁺ (36) ^[7e]	
c-axis ^[a]	1.973(5)	1.982(3)	1.976(3)	1.971(7)	
	1.981(5)		1.981(3)	1.977(7)	
b-axis	2.059(5)	2.082(3)	2.075(3)	2.060(8)	
	2.076(5)		2.082(3)	2.072(8)	
<i>a</i> -axis	2.053(5)	2.082(3)	2.076(4)	2.074(8)	
	2.068(6)		2.088(4)	2.090(7)	
C _{tpv} -C _{arvl}	1.483(8)	1.491(7)	1.476(6)	1.48(1) ^[b]	
	1.498(8)			1.49(1) ^[c]	
N ⁺ -C _{alkyl}	1.494(9)	-	1.49(2)	-	
	1.493(8)				
∠ c-axis	177.0(2)	180.0(1)	177.8(1)	178.1(3)	
∠b-axis	157.7(2)	157.0(1)	157.6(1)	158.2(3)	
∠a-axis	158.3(2)	157.0(1)	157.8(1)	158.8(3)	
φ	61	35	48	0 ^[b]	
	73		57	76 ^[c]	

[a] c-axis = principle coordination axis. [b] At pyrimidyl [pm] unit. [c] At 9-anthryl (Ant) unit.





agreement with the bond length and angle of 4'-py/py⁺-tpy **29** and **30**.

The nonlinearity along the coordination axis is passed to the substituents (measured as \angle N26A–Ru–N26B), which is rather pronounced in the case of **2** (163.9°), giving the overall curved topography (see Figure 2). A similar but weaker bending was also found for **29** (169.1°) and **30** (171.5°). Such a phenomenon is common for compounds without crystallographic symmetry constrains.^[31a] Severe distortions were also found for **29** in a 1-D coordination polymer with AgNO₃ (163.2°).^[39] A plausible origin was the asymmetry of anions and solvent within the lattice which seems also applicable to our case due to the mixed anion occupation in the crystal lattice.



Figure 2. Packing diagram for **2** in the unit cell. The Ru^{II} center is plotted with 33 % van der Waals radius while hydrogen atoms, solvent molecules, and counterions are omitted for clarity: a.) view along the a-axis; b.) turned 20° to emphasize perspective view.

In **2**, the four dative bond lengths are marginally shorter in comparison to **30** (0.006–0.020 Å), but the coordination angles are equal within 0.5° (see Table 1). For an in-depth discussion of the bond lengths and angles at the Ru^{II} center we refer to the comparison of DFT calculated and experimental values at a later stage.

The dihedral angle φ and the $C_{tpy}-C_{aryl}$ distance between the MeAcr⁺ moiety and the terpyridine unit agree well with examples incorporating the related 4'-(9-anthryl) residue, such as [Ru(Ant-tpy)(Cl-pm-tpy)]²⁺ (**36**).^[7e] Thus, the similar orthogonal orientation in **2** (exp. 61°/73°) due to the steric demand of the 1,8-H-atoms compared to the smaller homologous py/py⁺⁻ tpy complexes **29** and **30** does not surprise.

No noteworthy intermolecular packing features were found for **2** in regard to the X-ray packing features reported for other terpyridine metal complexes.^[31a,40] Overall, the packing in the solid state shows only weak interactions between the outer pyridyl rings (4.051 Å), but no interpenetration of the individual [Ru(MeAT)₂]⁴⁺ cations (see Figure S118).

2.3. Electrochemical Analysis

All of the ruthenium(II) terpyridine complexes were electrochemically investigated in MeCN between -2.0 and +1.5 V vs. Fc⁺/Fc. In each case, a fully reversible one-electron Ru^{III}/Ru^{II} redox process is observed in the anodic scans. The analysis of the anodic scan in electrochemical investigations is particularly important as the electron donor/acceptor-character of the 4'substituent is known to correlate with the observed potential of the Ru^{III}/Ru^{II} redox couple^[5,36a,41] and may therefore serve as an estimate for the HOMO energy.

Table 2. Electrochemical data of compounds 1–5 and some reference systems for comparison.

		$E_{1/2}$ [V] and tentative	assignment				
Compound		Ru ^{III} /Ru ^{II}	N-heterocyl. subst.	Terpyridine ligand centered reductions			Ref.
PhMeAcr ⁺		-	–0.93 (rev.)	-	-	-	this work
[Ru(AT) ₂] ²⁺	1	0.95 (rev.)	-	–1.55 (rev.)	–1.77 (rev.)	–1.83 (n.d.)	this work
[Ru(MeAT) ₂] ⁴⁺	2	1.01 (rev.)	–0.77 (rev.)	-1.14 (rev.)	–1.34 (rev.)	-1.90 (rev.)	this work
[Ru(MeAPhT) ₂] ⁴⁺	3	0.88 (rev.)	–0.89 (rev.)	n.d.	n.d.	n.d.	this work
[Ru(ATT) ₂] ²⁺	4	0.88 (rev.)	-	–1.53 (rev.)	–1.71 (rev.)	n.d.	this work
[Ru(MeATT) ₂] ⁴⁺	5	0.88 (rev.)	–0.79 (rev.)	–1.15 P _c (irrev.)	–1.24 P _c (irrev.)	n.d.	this work
[Ru(tpy) ₂] ²⁺	25	0.92 ± 0.02 (rev. ^[a])	-	-1.64 ± 0.03 (rev. ^[a])	-1.85 ± 0.08 (rev. ^[a])		[1e,29b,36a,41,46]
$[Ru(ttpy)_2]^{2+}$	27	0.87 ± 0.03 (rev. ^[a])	-	-1.64 ± 0.02 (rev. ^[a])	-1.89 ± 0.08 (rev. ^[a])	-2.34 (rev. ^[a])	[1e,2,41,46b,46c]
[Ru(th-tpy) ₂] ²⁺	28	0.83 ^b	-	–1.61 ^b	-1.82 ^[b]	-2.24	[26]
[Ru(py-tpy) ₂] ²⁺	29	0.95 (rev. ^[a])	-	-1.54 (rev. ^[a])	-1.80 (rev. ^[a])		[29b]
[Ru(Et-py-tpy) ₂] ⁴⁺	30	1.01 (rev. ^[a])	-1.09 (rev. ^[a])	–1.56 (rev. ^[a])	–1.79 (quasi-rev. ^[a])		[31a]
[Ru(Me-py-tpy) ₂] ⁴⁺	31	1.03 (rev. ^[a])	–1.06, –1.16 (rev. ^[a])	–1.56 (rev. ^[a])	-1.79 (rev. ^[a])		[29b]
$[Ru(H_3TP-tpy)_2]^{4+}$	32	> 1.22 (n.d.)	–1.16 (2 e ^{– [a]})	n.d. ^[a]	n.d. ^[a]		[41]
[Ru(H ₃ TP-ph-tpy) ₂] ⁴⁺	33	0.91 (rev. ^[a])	–1.29/-1.36 (rev. ^[a])	-1.69 (rev. ^[a])	-1.92 (rev. ^[a])		[41]
[Ru(ttpy)(ttpy-MV)] ⁴⁺	34	0.89 (rev. ^{[a]a})	–0.74 (rev. ^[a])	–1.59 (quasi-rev. ^[a])			[23a]
[Ru(Ant-pm-tpy) ₂] ²⁺	35	0.97 (rev. ^[a])	-	-1.46 (rev. ^[a])	–1.70 (irrev. ^[a])		[7d]
[Ru(tpy-HImzPy) ₂] ²⁺	37	0.96 (quasi-rev. ^[a])	-	-1.58 (quasi-rev. ^[a])	-1.81 (quasi-rev. ^[a])	–2.07 (irrev. ^[a])	[9c]

Reduction and oxidation half-potentials $E_{1/2}$ [= ($E_{peak,cathodic} + E_{peak,anodic}$)/2] and peak separation values ($\Delta E = E_{peak,cathodic} - E_{peak,anodic}$) were obtained from square wave and cyclic voltammetry (forward scan) respectively. All data is referenced on the Fc⁺/Fc couple in MeCN with 0.1 M TBAPF₆ as supporting electrolyte at 21 ± 1 °C. Sweep rates were tested between 50–500 mV/s. Reversibility was estimated by the peak separation value ΔE compared to the Fc⁺/Fc internal reference. Conversion from/to other standard reference electrodes was achieved by the conversion tables.^[47] Values with a ±-sign are average values of the cited references and the resulting variance. Abbrv.: n.d. = not determined. [a]As stated in cited reference(s). [b]Peak separations are stated to be between 60–100 mV.





Here, the potential shifts from 0.92 V for pristine $[Ru(tpy)_2]^{2+}$ (25) to 0.95 V for 1. Upon quaternization by methylation, a distinctive shift to about 1.0 V is observed for 2. These findings are in perfect agreement with the reported data for the py/py⁺tpy complexes **30** and **31**, respectively (Table 2).^[31a]

The complexes containing a linker unit (3 - 5) possess lower oxidation potentials and compare well with the redox properties of their parent tolyl- and thienyl-terpyridine model complexes, that is, $[Ru(ttpy)_2]^{2+}$ (27) and $[Ru(th-tpy)_2]^{2+}$ (28), respectively.

This result is rather unexpected as it infers that the electrochemical perturbation – viz. the EWG character of the acridinium moiety – towards the metal center is weak. It seems that effect stemming from the Acr/MeAcr⁺ unit are counterbalanced by those from the spacer. The oxidation in **4** and **5** is after all slightly raised to 0.88 V from 0.83 V in $[Ru(th-tpy)_2]^{2+}$ (**28**). A more pronounced influence of the cationic group on the linkerterpyridine assembly was expected due to the reported data for $[Ru(H_3TP-ph-tpy)_2]^{4+}$ derivative **33**,^[41] namely an increase of about +30 mV for the Ru^{III}/Ru^{II} redox potential with respect to **27** (Table 2). Moreover, terpyridine systems containing an innocent polycyclic aromatic fragment but an electron-poor pyrimidyl^[7d,7e] (**35**, **36**) or imidazolyl linker (**37**)^[9c] perform clearly better in this regard as indicated by Ru^{III}/Ru^{II} redox processes at about 0.97 V.

From the cathodic range one may derive the influence of the metal-coordinating pyridyl-ring of the terpyridine moiety and the linker group by using the cationic acridinium moiety as a probe. The electrochemistry of MeAcr^{+[42]} and 9-PhMeAcr⁺ is well characterized: Its reduction is reported to occur at -0.92 ± 0.01 V,^[15a,21a,33a,33e,42a,42b,43,44] which conforms precisely with our reference measurements (Table 2). Correspondingly, acridinium complexes **2**, **3**, and **5** feature an additional reversible reduction at about -0.9 to -0.7 V. These are tentatively attributed to MeAcr⁺-centered reductions.^[15a,33e,42a,42b,45] [Ru(MeAT)₂]⁴⁺ (**2**) and [Ru(MeATT)₂]⁴⁺ (**5**) are 140–160 mV easier to reduce than PhMeAcr⁺. The low reduction potential of the latter was surprising as the electron-donating character of the



Figure 3. Steady exemplary CV spectra of $[Ru(AT)_2]^{2+}$ (1), $[Ru(MeAT)_2]^{4+}$ (2) and $[Ru(MeAPhT)_2]^{4+}$ (3; only to -1.35 V) vs. PhMeAcr⁺ for comparison (top). All spectra referenced to the Fc⁺/Fc couple.

thienyl-linker does not establish itself. The MeAcr⁺ reduction potential in **3**, however, is shifted less pronounced (+40 mV) to less negative potentials compared to PhMeAcr⁺ indicating again the electronically more decoupled properties of the linker group (Table 2, Figure 3).

Changes are also apparent for the terpyridine centered reductions below -1 V. For **2** the reductions are shifted by 410 mV more positive, to -1.14 and -1.34 V, compared to pristine $[\text{Ru}(\text{tpy})_2]^{2+}$ (**25**). Unfortunately no clear statements can be made for MeAcr⁺-containing complexes **3** and **5** because only poorly resolved features due to a high cathodic peak current $(I_{p,c})$ were observed at -1.15 V and -1.24 V following the first MeAcr⁺ reduction at -0.79 ± 0.01 V. It is known that acridinium ions may give irreversible peak shapes when the anionic species is formed from the radical intermediate at higher cathodic potential.^[42a] The anionic species subsequently abstracts rapidly a proton from the solvent to yield the acridane species, which may then adsorb on the electrode due to limited solubility in polar solvents.^[42a] Therefore, the potential window was limited to the reversible MeAcr⁺ reduction.

In contrast, acridine complexes **1** and **4** show the expected pattern of multiple ligand-centered reductions at -1.54 ± 0.01 , -1.76 ± 0.04 , and – if observable in the electrochemical window – at below -1.99 V.^[1e,7e,23a]

In conclusion, despite the findings for the anodic scans of complexes **1–5**, where no substantial impact of the annulated Acr/MeAcr⁺ systems was notable in terms of oxidative electrochemical properties, we concur with the reported conclusion about the quaternization effect for the cathodic scans.^[29b] Methylation affects the ligand-centered reductive processes at the terpyridine moiety to a significantly larger extent than the metal-centered oxidation processes. In general MeAcr⁺-terpyridines are even more easy to reduce than the H₃TP⁺⁻ and py⁺-tpy series and are, in turn, more comparable with the electrochemical behaviour of the methylviologen (MV²⁺) system **34**^[23a] ($E_{ox} = 0.89$, $E_{red} = -0.74$ vs. Fc⁺/Fc; see Table 2).

2.4. Analysis of Electronic Absorption Spectra

The absorption spectra of **1–5** are shown in Figure 4 while the spectra of ligands **8**, **19**, **20** and **24** are depicted in Figure 5. Absorption maxima and molar absorptivities for the complexes **1–5** as well as the corresponding ligands and some references compounds are reported in the Supporting Information. Close inspections reveals that the complexes can be arranged by an increased molar absorptivity and, furthermore, by the maximum of the MLCT transition found between 490 and 510 nm in the order [Ru(MeAT)₂]^{2+/4+} (**1**, **2**) < [Ru(MeAPhT)₂]⁴⁺ (**3**) < [Ru(MeATT)₂]^{2+/4+} (**4**, **5**) which correlates with the interconnecting linker group. In addition to the shift by the linker, complexes of the MeAcr⁺ series (**2**, **3**, **5**) show prominently a small shift (6–8 nm) of MLCT maxima (λ_{MLCT}) to lower energies concomitant with broadening at the low energy edge of the absorption compared to their Acr counterparts **1** and **4**.

The UV/Vis spectra of **1–5** are superimpositions of the typical $[Ru(tpy)_2]^{2+}$ spectra^[1a,1b] and the corresponding chromophores, that is, either the acridine or the acridinium







Figure 4. Steady state UV/Vis spectra (left axis) and uncorrected 77 K luminescence emission spectra (right axis, $\lambda_{ex.}$ at λ_{MLCT} , 10–12 μ M) of 1–5 in MeCN solution and BuCN/MeCN (9:1) glassy solvent, respectively.



Figure 5. Steady state UV/Vis spectra of the prepared ligands **8**, **19**, **20** and **24** in MeCN solution with a magnification of the S_1 and S_2 transitions shown in the inset. The spectra of acridine and PhMeAcr⁺ are included for comparison (solid grey and black lines, respectively).

unit.^[12a,12f,12e,13c,21c,21e,48] Acridinium ions have two main features in the near-UV and Vis-part of the electromagnetical spectrum: On one hand, a very narrow absorption at about 360 nm with $\varepsilon = 13000 - 20500 \text{ Lmol}^{-1} \text{ cm}^{-1}$ for the $S_0 \rightarrow S_2$ transition^[12a,12d,12e,12f,13c,21e] and, on the other hand, a broad, solvent depended and slightly vibronical-structured transition at around 425 nm for simple arene substituents with $\varepsilon = 3000-9000 \text{ Lmol}^{-1} \text{ cm}^{-1}$, for the $S_0 \rightarrow S_1$ transition. Upon substitution with a donor-type aryl-group this band shifts to lower energies by up to 50 nm and gains intensity.^[12a,12d,12e,12f,13c,21e,48a,49]

In contrast, acridines have their lowest-energy local absorption maximum at about 390 nm $(S_0 \rightarrow S_1)$ and two less pronounced transitions at about 360 nm $(S_0 \rightarrow S_2)$ and 345 nm

 $(S_0 \rightarrow S_3)$.^[19] All these features can be found in the appropriate spectra of the complexes.

Owing to the lack of a MLCT transition, the uncomplexed Acr/MeAcr⁺ ligands reveal all of the aforementioned features and compare well to UV/Vis spectra of acridine and the PhMeAcr⁺ ions, respectively (see Figure 5).

The interconversion between acridine and acridinium species can be monitored by protonation/deprotonation studies on non-quaternized complexes such as **4**. Titration of ATT complex **4** with aliquots of acid in MeCN (Figure 6) give rise to the 260, 360, and 450 nm absorption bands. The shape of the absorption spectra and the molar absorption coefficients are in very good agreement with those seen for the quaternized variant **5**. The similarity of the methylated and the protonated complexes, as shown in Figure 6, is in good agreement with the literature.^[29a-c] Here, the aforementioned 6 – 8 nm red-shift of the MLCT transition maximum becomes also apparent. Similar observations were made for the py/py⁺-series.^[29b,30b,31a]



Figure 6. Changes in UV/Vis spectra of 5.8 μ M [Ru(ATT)₂]²⁺ (**4**) in MeCN upon titration with 0.1 μ TFA (0 to 7.5 mM, corrected for dilution). The spectra of quaternized complex **5** is included for comparison (dotted black line).

Owing to the reactivity of MeAcr⁺ to nucleophiles at the 9-position (see Introduction), complexes **3** and **5** were studied by means of titrations with sodium hydroxide (Figure 7 and Figure 8) or sodium borohydride (not shown). In all cases, about 2 equivalents nucleophile are sufficient to completely convert the complexes to the bisacridane species **3a** or **5a**, respectively, inferred from the changes in the absorption spectra. The spectral changes for this conversion are well documented in the literature.^[21d,22,50] Please note, however, that the different acridanes (e.g. –OH, –OR, –H) cannot be distinguished by absorption spectroscopy. Whereas dihydroacridanes are relatively stable (except spurious air oxidation), alkoxyacridanes and acridanols can be reverted to the Alkyl-Acr⁺ species by addition of acid, which was also ensured for the in situ formed acridanol complexes **3a** and **5a** (not shown).

In summary, the following trends were established: i) The molar absorption coefficients nearly doubled for the complexes









Figure 7. Changes in UV/Vis spectra of 9.5 μ M [Ru(MeAPhT)₂]⁴⁺ (**3**) in MeCN upon addition of increasing amounts of 1 mM aqueous NaOH solution to form bis(acridanol) complex **3a** (corrected for dilution; blue lines corresponds to \geq 2 equiv. OH⁻).

relative to the corresponding ligands. ii) All acridinium compounds show an intense absorption at 261 nm while the acridine compounds show this absorption at 251 nm. iii.) the terpyridine ligand-centered (LC_{tpy}) absorption features at about 270 – 290 nm and 300 – 350 nm (Figure 4)^[1a,1b,9c] are hardly affected by methylation as previously noted for 4'-(4-py)-tpy examples.^[29b] iv) The high intensity absorption band at 360 nm serves as an additional marker to distinguish between Acr and MeAcr⁺ compounds. v) A small shift of λ_{MLCT} to lower energies due to the quaternization of the N-heterocycle could also be

Figure 8. UV/Vis titration of 9.1 μ M [Ru(MeATT)₂]⁴⁺ (**5**) under same conditions as for complex **3** (Figure 7) to form acridanol complex **5a**.

found. This is not caused by the rise of the underlying 425 nm absorption band of the MeAcr⁺ chromophore (former S₀ \rightarrow S₁) but by a d-Ru²⁺ $\rightarrow \pi^*_{Acr+}$ MLCT transition and we will refer to this phenomenon in the TD-DFT section.

2.6. Emission Properties

While RT luminescence could not be detected in MeCN, luminescence evolved at 77 K in a butyronitrile glassy matrix for all studied complexes (see Figure 4 and Table 3). Complexes without a linker, namely **1** and **2**, emit at 664 nm (1.87 eV) while the thienyl-systems **4** and **5** emit at 672 nm (1.84 eV). The

Table 3. Compilation of luminescence data for compounds 1–5 and reference compounds at 77 K. The calculated Gibbs energy of the photoinduced electron transfer (ΔG°_{CS}) and the energy of the charge separated state (CS) is also given.

Compound		$\lambda_{em,77K.}$ [nm] (eV) ^[a]	τ [μs] ^[b,c]	CS [V]	$\Delta G^{\circ}_{CS} \ [eV]^{[d]}$	Ref.
[Ru(AT) ₂] ²⁺	1	664 (1.87)	930, 94	2.50	0.60	this work
[Ru(Me-AT) ₂] ⁴⁺	2	664 (1.87)	2020, 115	1.78	-0.10	this work
[Ru(Me-AOHT) ₂] ⁴⁺	2a	610 (2.03)	20	n.a.	n.a.	this work
[Ru(Me-APhT) ₂] ⁴⁺	3	648 (1.91)	9500, 1200	1.77	-0.14	this work
[Ru(MeA-OHPhT) ₂] ⁴⁺	3a	628 (1.98)	12	n.a.	n.a.	this work
$[Ru(ATT)_2]^{2+}$	4	672 (1.84)	1320, 111	2.41	0.56	this work
[Ru(Me-ATT) ₂] ⁴⁺	5	672 (1.84)	1430, 99	1.67	-0.18	this work
[Ru(MeA-OHTT) ₂] ²⁺	5a	659 (1.88)	13	n.a.	n.a.	this work
[Ru(MeA-HTT) ₂] ²⁺	5b	659 (1.88)	11	n.a.	n.a.	this work
[Ru(tpy) ₂] ²⁺	25	598 (2.07)	11	2.55	0.48 ^[g]	[1e,29b,36a,41,46,53]
$[Ru(ttpy)_2]^{2+}$	27	628 ^[e] (1.97)	11.0 ^[e]	2.48	0.51 ^[g]	[23a,51d,53]
$[Ru(th-tpy)_2]^{2+}$	28	656 (1.89)	16	2.44 ^[g]	0.55 ^[g]	[26]
$[Ru(py-tpy)_2]^{2+}$	29	n.a.	n.a.	2.49 ^[g]	0.60 ^[f, g]	[30b]
[Ru(Et-py-tpy) ₂] ⁴⁺	30	n.a.	n.a.	2.10 ^[g]	0.37 ^[f, g]	[31a]
$[Ru(H_3TP-tpy)_2]^{4+}$	32	622 (1.99)	10.6	> 2.44 ^[g]	> 0.45 ^[g]	[41]
[Ru(H ₃ TP-ph-tpy) ₂] ⁴⁺	33	631 (1.96)	12.1	2.20 ^[g]	0.23 ^[g]	[41]
[Ru(Ant-pm-tpy) ₂] ²⁺	35	694 (1.79)	3500	n.a.	n.a.	[7d]
[Ru(tpy-HImzPy) ₂] ²⁺	37	646 (1.92)	n.a.	2.54	0.62 ^[g]	[9c]

[a] ±3 nm for own data, independent of $\lambda_{ex.}$ [b] In BuCN/MeCN (9:1) solid matrix. Referenced to $[Ru(bpy)_3][Cl]_2 \lambda_{em.} = 580$ nm (≈ 620 nm shoulder; ratio: $\approx 1:0.23$), $\tau = 6 \pm 1$ µs (mono-exponential). [c] Composition of the amplitude; long-lived component is given first. Estimated error 15 %. [d] Calc. by use of Equation (1) with CS = $E_{Ru}^{III}_{/(II)} - E_{Iigand/ligand, reduced}$ (see Table 2); E_{00} was estimated from $\lambda_{em,max.}$ at 77 K. [e] At 90 K. [f] At 298 K. [g] Calc. from data given in the reference.



apparently electronically more decoupled **3** emits at higher energies, that is, at 648 nm (1.91 eV). The typical lower-energy vibronic shoulder of such ³MLCT emitters can only be implied by a small feature or broadening in the low energy range of the uncorrected luminescence spectra.

Initial experiments implied a dual emission behaviour for **2** – 610 and 664 nm – with different decay times. As a matter of fact, it was traceable to acridane formation (see above) in the employed solvents. Consequently, small amounts of acid ensured a uniform species present in all experiments.

Luminescence lifetimes for the complexes were obtained by fitting the decays with bi-exponential fitting functions. The lifetimes were found to be between 94–1200 μ s for the shorter lived ³MLCT component and between ca. 1 ms up to 9.5 ms for the longer lived ³LC component.

To determine the effect of the chromophores we chemically switched to the acridane compounds as established previously (see above). Indeed, in situ acridane formation, for instance for **3** to **3a**, gave rise to a different luminescence profile with a mono-exponential lifetime and emission maxima comparable to the pristine Ru(tpy)₂ complexes such $[Ru(ttpy)_2]^{2+}$ **27** (see Figure 9 and Table 3). Direct examination of the ligand triplet excited state was hampered by the lack of phosphorescence from **19** and **20** in rigid matrix at 77 K even with subsequent addition of halogenated solvents (10–20 % v/v).^[12a]



Figure 9. Luminescence decay of **1–5** in BuCN/MeCN (9:1) glassy solvent at 77 K. The left inset shows a magnification of the decay curve for **2a**, while the right inset shows an expansion for the long-lived decay of **3**.

2.7. Time-Resolved Measurements

To gather further insights into the excited state behaviour, **1**, **2**, **4**, and **5** were studied with fs and – if suitable – also with ns absorption pump-probe spectroscopy. Photoexcitation of all complexes at 387 nm leads to a bleaching of the ground state absorption in the region from 450 to 570 nm (see Figure 10 and SI). This implies the depopulation of the ¹MLCT ground state. Simultaneously with the latter, we note the formation of a new transient that spans from 550 to 800 nm (see Figure 10a). We rationalize the origin of the newly formed transient to the ³MLCT excited state.





Figure 10. a.) Differential absorption spectra upon fs flash photolysis (387 nm, 200 nJ/pulse) of **4** in deaerated MeCN with several time delays between 0.9 and 7500 ps. b.) Differential absorption spectra upon ns flash photolysis (355 nm, 6 mJ/pulse) of **4** in dearated MeCN with time delays of 0.19, 0.54, 2.2 and 4.4 μ s.

In case of 4 short lived as well as long lived transients were observed, which did not decay on the time scale of 7.5 ns (Figure 10a). Therefore, transient absorption measurements were also performed on the microsecond time regime (Figure 10b). The depopulation of the initially prepared Franck-Condon excited state is double stage accompanied by the simultaneous formation of new short and long lived transients. The two lifetimes, which were derived from multiple wavelengths, are 4.5–6 and 300 \pm 30 ps, respectively. The short lived component is likely to be associated with the formation and relaxation dynamics of the initially populated Frank-Condon excited state, such as, linker group planarization or vibrational cooling and finally ³MLCT equilibration on the tpy ligand. Therefore, the weak transient at about 640 nm is tentatively ascribed to the formation of the reduced tpy-fragment based on evidence found for related $[Ru(tpy)_2]^{2+}$ (25) and $[Ru(ttpy)_2]^{2+}$ (27) complexes.^[1e,23a,46c,51] The longer lived component implies the subsequent triplet-energy transfer to the acridine unit, forming an extremely long lived ligand triplet state (³LC). Here, two very long lived transient features, at 420 and 700 nm, were observed (Figure 10b). The lifetime of the excited state was determined from a mono-exponential fit across the spectrum to be 1.09 ± 0.14 µs. The excited state is of triplet nature as the formed species is readily quenched by molecular oxygen (see





SI) and, as shown by us in a separate report,^[32] singlet oxygen is formed quite effectively by **4** while $[Ru(AT)_2]^{2+}$ complex **1**, without a thienyl-linker, is less efficient. The transient lifetime of this complex was determined to be 80 ns only.

The corresponding MeAcr⁺ complex **5** showed only a broad and weak transient in the visible region centred at about 660 nm and an additional broad band at about 1100 nm (see SI). The lifetime of the broad transient was determined to be 170 ± 20 ps. The spectra of the MeAcr⁺ complex **2** were very similar to **5**, but the transients were of lower intensity (see SI). Looking at the absorption time profiles, the linker-less complex [Ru(MeAT)₂]⁴⁺ (**2**) decays mono-exponentially to the ground state with 613 ± 40 ps. In both cases, the very fast recovery of the ground state implies a fast quenching as typically observed for energetic favourable *p*-e⁻T processes and subsequent back electron transfer. The Gibbs energy of *p*-e⁻T process can be calculated by using Equation (1).^[12a,51c,52]

$$\Delta G^{\circ}_{\rm CS} = F \left[E^{\circ}_{\rm Ru} \right]^{\rm III} - E^{\circ}_{\rm MeAcr/MeAcr} - E_{\rm 00} + C \tag{1}$$

where *F* is the Faraday constant; $E_{Ru}^{\circ}_{Ru}^{\parallel}_{/Ru}^{\parallel}$ and $E_{MeAcr/MeAcr}^{\circ}$ are the standard electrode potentials for a given reference electrode; E_{00} is the ³MLCT triplet energy as estimated from the luminescence maximum of the low-temperature measurements and *C* is the Coulomb correction term, which is in polar solvents like MeCN not only relative small but for charge shift processes always zero.^[12a]

In summary, *p*-e⁻T processes are energetically favourable by –0.10 to –0.14 eV for the MeAcr⁺-containing complexes **2**, **3** and **5**, whereas these processes are endergonic for Acr-substituted complexes (> 0.56 eV; see Table 3). The ΔG°_{CS} values are comparable to other terpyridine complexes. Although the Coulomb term may be be ignored in good conscience due to the presence of charge,^[12a] solvent and temperature effects concerning the E_{00} value are still neglected throughout and therefore the values shall be be considered as estimates.^[23a] For discussion of our low temperature results a study of a MV²⁺ ruthenium(II) rotaxane complex by Credi et al.^[23b] is nevertheless helpful,

where an unquenched 77 K emission was observed. The emission was attributed to the destabilization of the CS state. Similarly, no p-e⁻T quenching has been observed in frozen solvents for the tpy-prototype MV²⁺-system **34**.^[23a]

We are convinced that the competing p-e⁻T processes are frozen at 77 K for complex **2**, **3**, and **5** and the non-emissive thermal decay of the ³LC state as well as the intrinsic thermally activated decay through the ³MC state is slowed down to large extend. The existence of a non-emissive triplet state was proven for AT and ATT systems **1** and **4** by ns flash photolysis and singlet oxygen generation,^[32] both in line with the DFT findings (see below). Taken together with the DFT data, these results strongly suggest that this state is of ³LC nature as similarly deduced for the 9-anthryl case before.^[8]

While the results from time-resolved spectroscopy indicated that room temp. luminescence is unlikely to be achieved with this class of ligands, we were interested in the rationalization of the overall deactivation pathways as well as electronic features and parameters, which are inaccessible in the experiments. Similar as previously reported for the 4'-py/py⁺-tpy systems,^[31a] we focused on a computational chemistry approach as described in the following section.

2.8. Computational Modeling by DFT

2.8.1. Ground State and Optical Spectra

Terpyridine metal complexes are popular targets for density functional theory (DFT) calculations in order to gain insight in the geometrical features and the relative location of the energy levels. Several important aspects of our calculations may be briefly highlighted here while further details about the methodology are described in the Supporting Information.

The ground state structural parameters for **1–5** are well reproduced by B3LYP or PBE0 DFT calculations, which was also shown for the 4'-py/py⁺-tpy systems previously.^[30d,31a] Selected geometrical key parameters for the AT-derived complexes **1** and

Table 4. Selected structural parameters (distances [Å], angles [°]) of complexes 1 and 2 in the ground state (S_0) and for the different triplet states as obtained by calculation on the B3LYP level of theory (and PBE0 evaluation for S_{0r} respectively). For complex 2 the deviation to the experimental value as determined by X-ray structure elucidation is given as Δ_{exptl} value.

	[Ru(AT)	₂] ²⁺ (1)				[Ru(MeA	T) ₂] ⁴⁺ (2)					
Parameter	$S_0^{[a]}$	S ₀ ^[b]	³ LC ^[a]	³ MLCT ^[a]	³ MC ^[a]	S ₀ ^[a,c]	Δ_{exptl}	S0[b]	Δ_{exptl}	³ LC ^[a]	³ MLCT ^[a]	³ MC ^[a]
dist. <i>c</i> -axis	2.018	1.997	2.018,	2.018,	2.201,	2.018	0.045	1.997	0.016	2.020,	2.039,	2.202,
			2.016	2.016	2.017					2.015	2.024	2.015
dist. <i>b</i> -axis	2.127	2.096	2.128	2.128	2.163	2.127	0.074	2.096	0.037	2.126	2.131,	2.405,
											2.120	2.402
dist. <i>a</i> -axis	2.127	2.096	2.127	2.127,	2.404	2.127	0.059	2.096	0.020	2.127	2.113,	2.161,
				2.126							2.112	2.162
d.(C _{Tpy} -C _{Aryl})	1.496	1.486	1.493,	1.494,	1.493	1.497	0.014	1.488	-0.010	1.496,	1.497,	1.496
			1.467	1.467						1.477	1.462	
d.(N _{Acr} –C _{Me})	-	-	-	-	-	1.481	-0.013	1.468	-0.025	1.481,	1.481,	1.481
										1.475	1.468	
∠ <i>c</i> -axis	180.0	180.0	180.0	180.0	177.9	179.9	2.9	179.9	2.9	179.9	177.3	178.5
∠b-axis	156.6	157.4	156.6	156.4	156.2	156.6	-1.1	157.6	-0.1	156.6	157.7	138.9
∠a-axis	156.6	157.4	156.6	156.6	137.9	156.6	-1.6	157.5	-0.7	156.7	152.7	156.3
$\varphi_{(aryl-tpy)}$	89.8	69.9	51.9,	56.7,	73.4,	88.6	15.8,	83.2,	10.3,	57.4,	50.3,	78.9,
			73.0	72.6	74.3		27.5	74.4	13.3	84.1	83.0	89.0

[a] B3LYP//6-31G(d)/LANL2DZ calculation results. [b] PBE0//6-31G(d)/LANL2DZ calculation results. [c] Within 0.06 Å RMSD of a B3LYP//LANL2DZ-only calculation.





2 are composed in Table 4 (S_0 states) while data for **3–5** are compiled in the Supporting Information for reasons of space (see Table S6).

Calculated N–Ru bond lengths were always found to be in between 2.018–2.128 Å for the ground state geometry with all three axes considered. Statistical evaluation of 119 [Ru(tpy)₂]derivatives for their principal coordination axis (viz. c-axis) gave an average N–Ru bond length of 1.977 ± 0.013 Å (1 σ ; see SI). In this regard the typical overestimation of the B3LYP functional to X-ray data^[6a,54] is apparent but acceptable. In our case a direct comparison with X-ray data was only possible for complex **2** (see Table 4; Δ_{exptl} values).

In accordance with several reports^[6a,53,54] about the capabilities of the PBE0 functional in comparison to B3LYP, we found the PBE0 functional also better suitable for describing the "exact" geometry of the ground state. However, the $N_{Acr}-C_{Me}$ bond lengths are always underestimated (interestingly worse for PBE0) and the experimentally found bending along the c-axis is not covered by both functionals.

With the reproduction of structural features reasonable verified, we were interested in the electronic differences of complexes **1–5** in comparison to published data for the 4'-py/py⁺-tpy complexes.^[31,30d] For this reason we reproduced B3LYP calculations for the non-alkylated complex [Ru(py-tpy)₂]⁴⁺ (**29**) as well as [Ru(Me-py-tpy)₂]⁴⁺ (**31**) first to ensure a comparable setting.

To aid an in-depth analysis of the MOs an additional deconvolution of each MO into tpy-ligand, linker, metal atom, and 4'-substituent – either py/py⁺ or Acr/MeAcr⁺ – contributions was performed (see colour coding in Figure 11). The expected pattern of ligand based LUMOs and metal ion contribution for the HOMO levels is clearly visible. Furthermore, similar as reported,^[31] we found the HOMO and the next lower MOs (HOMO–1/–2) separated by only a small energy difference of \approx 0.1 eV for complex **31** (Figure 11, left). The MOs of the HOMO–1/–2 set itself are very close in energy (<< kT) and can be considered as degenerated. Also in accordance with previous reports,^[30d] the non-alkylated complex [Ru(py-tpy)₂]⁴⁺ (**29**) the HOMO to HOMO–1/–2 difference was even smaller (0.033 eV) while the overall frontier orbital positions were higher in energy.

With the compatibility verified, we were interested in the outcome for our Ru^{II} systems 1-5: Next to the metal-based MOs, and in contrast to the py/py+-tpy systems 29 and 31, respectively, a differentiation in almost pure terpyridine- and Acr/ MeAcr+-based MOs is prominent for complex 1-5 (Figure 11, see Figure 12 for a graphical representation). Two sets of degenerated MOs for the Acr/MeAcr⁺ chromophores are always in close proximity to the frontier orbitals. For instance, a degenerated set of MOs with π^*_{Acr} character compose the LUMO for the acridinium compounds 2, 3 and 5. Thus methylation of the acridine moiety has a pronounced effect on such systems as the Acr⁺- π^* set is decreased low enough in energy to become the LUMO set instead of the usual π^*_{tpv} MOs. This deviates notable from the py/py+-systems where these LUMOs are in principle pyridyl-based but mixed to considerable extend with terpyridine MO contribution^[31a] (own calcd.: 48 % $\pi^*_{Pv+}/44$ % π^*_{tpv} ; see Figure 11).



Figure 11. Computed orbital energy level and MO composition for 1–5 in comparison to 29 and 31, respectively (left side) as calculated by DFT [degeneracy threshold $\Delta E_{deg.}$ set manually to 0.0256 eV (= kT) to visualise otherwise overlaid MOs]. Colour scheme of the deconvolution: ruthenium ion (red), terpyridine (blue), pyridine/-ium (bright cyan) acridine/-ium (light green), phenyl- (purple), and thienyl-linker (yellow). Configurations of the first transition with meaningful oscillator strength of TD-DFT calculations are indicated by grey lines. The circular dots mark the electrochemical determined HOMO (filled circle) and LUMO (open) obtained by the empirical interconversion relation of –4.5 eV on vacuum level \approx 0 V on NHE scale (converted from the Fc⁺/Fc standard by +0.630 V⁽⁴⁷⁾).





Figure 12. Graphical representation (isodensity contour value 0.05 e Bohr⁻³, 12 grid points Å⁻¹) of the frontier molecule orbitals for $[Ru(MeAT)_2]^{2+}$ (2).

In terms of linker influence one can state that the linker group contributes only slightly to the Acr/MeAcr⁺ MOs which justifies the overall view as an isolated terpyridine fragment connected to a 9-arylacridin/ium unit in case of complexes **4** and **5** but especially **3**.

Focussing on the metal-based orbitals the findings of previous reports^[30d,31a] can be confirmed and thereby be extended to the Acr/MeAcr⁺ class of compounds. The MOs of typical $d_{xy}/d_{xz}/d_{yz}$ shape are highly metal-based (61 – 75 %) and split in an approximately degenerated subset and a singular MO (see Figure 12 for **2**, see SI for **1** and **3**, **4**, **5**). The latter is separated by only a small energy difference (max. 0.12 eV in **4**) similarly as mentioned for the py/py⁺-tpy systems.

The e_g-type orbitals are calculated to be near the 0 eV potential energy frontier as described by other previously.^[30d] This non-degenerated set of MOs can be found at similar positions for the Acr/MeAcr⁺ class of compounds and easily identified by the 25 %–51 % metal character (Figure 11). Correspondingly, the ligand field splitting value (Δ_0) averages to 5.33 ± 0.06 eV for **1–5**.

In summary, the DFT calculated MO energies agree qualitatively well with comparable calculation for the py/py⁺ complexes and with the electrochemical determined HOMO/LUMO



energies (Figure 11). Based on the orbital analysis the MeAcr⁺ unit in **2** is clearly the best overall electron acceptor in the series as both LUMO and HOMO are lowered in energy, even surpassing the [Ru(Me-py-tpy)₂]⁴⁺ complex (**31**) theoretically. Therefore, the conclusion for the py/py⁺-tpy series could be validated, namely, that quarternization of the pendent N-heterocycle lowers the energy of the lowest lying π^* molecular orbitals, thereby increasing the electron accepting ability of the complexes.^[29c]

With the electronic structure established, it is logical to determine the possible optical transitions by TD-DFT. Starting from our own geometries we were able to reproduce the TD-DFT data for the py/py⁺-tpy systems^[31] very well with the combination of B3LYP functional and 6-31G(d)/LANDL2DZ mixed basis sets. The PBE0 functional performed worse in TD-DFT calculations with the same basis set combination (see Figure 13a, upper trace), presumably due to the low HOMO energies (see B3LYP vs. PBE0 calculated energy level diagram in the Supporting Information).^[55]



Figure 13. TD-DFT calculated transitions (coloured bars) for **2** starting with different geometries compared to the λ_{MLCT} -region of the exp. spectrum (blue, only on top, scaling $f/\epsilon = 1$ to 5×10^4). b.) λ_{MLCT} -region of the exp. spectra and calculated transitions (B3LYP) for complexes **1**, **3**, **4**, and **5** (scaling $f/\epsilon = 1$ to 2.5×10^4) for comparison. Colour coding as in Figure 4.

Thus, we decided to perform all remaining TD-DFT calculations with the B3LYP//6-31G(d)/LANDL2DZ combination on B3LYP generated geometries. The numerical data of the TD-DFT calculations for systems 1-5 as well as the py/py⁺ examples 29-31 are compiled in the Supporting Information.

More importantly, we noted systematic differences in the results by the choice of the starting geometry, namely optimized C_1 vs. C_2 symmetry vs. a PBE0 geometry. A graphical summary for complex **2** is given in Figure 13a. This let us question the





cause of these discrepancies and we assumed that the dihedral angle φ , and only subsequently the symmetry, can be made responsible. Indeed, the corresponding d-Ru²⁺ $\rightarrow \pi^*_{Acr+}$ transition becomes only active for non-orthogonal angle ranges between the Acr/MeAcr⁺ unit and the tpy fragment, which was both given for the PBE0 C_1 ($\varphi = 83.2/74.4^\circ$) and B3LYP C_2 -geometry ($\varphi = 76.8^\circ$) but not for the optimized C_1 geometries of complex **2** (see Figure 14) and **1**, respectively (see Table 5 for a compilation $\varphi_{(aryl-tpy)}$ values).



Figure 14. a.) Calculated potential energy surface (PES) for different dihedral angles φ (filled symbols) and/or ω (open symbols) on one ligand fragment of complexes **1–5**. b.) Calculated λ_{MLCT} for the d-Ru²⁺ $\rightarrow \pi^*$ Acr transition (stars) and corresponding oscillator strength (shaded bars) of the relaxed geometries for MeAcr⁺ complex **2**.

Noteworthy, all methylated systems show next to the d-Ru²⁺ $\rightarrow \pi^*$ tpy transition a second transition at lower energies due to a d-Ru²⁺ $\rightarrow \pi^*_{Acr+}$ transition (e.g, calcd. λ_{MLCT} 505 nm for **2**, 497 nm for **3**, 557 nm for **5**), assuming to be the root cause of above established red-shift and broadening of MLCT band. Moreover, the linker-extended MeAcr⁺ complexes **3** and **5** do not show the above mentioned conformation-related selection rule of the optical transition and have therefore usually high oscillator strengths for the d-Ru²⁺ $\rightarrow \pi^*_{Acr+}$ transition (see Figure 13b).

Of course this raises the question which bands are to compare with the experimentally visible MLCT transitions:

If the d-Ru²⁺ $\rightarrow \pi^*_{tpy}$ transition is chosen the predicted UV/Vis spectrum can be roughly aligned with the experimental one. Qualitatively the same trends in position and oscillator strength (as measure for the molar absorptivity) of the MLCT transition can be reproduced. The calculated bands are, however, shifted to higher energies by 0.09–0.28 eV ($\Delta \lambda = 17$ to 54 nm at these wavelengths) in comparison with the experimental results. This is a quite typical error for TD-DFT calculation of ruthenium(II) terpyridine systems.^[46a]

If, however, the d-Ru²⁺ $\rightarrow \pi^*_{Acr+}$ transition is considered, the dependency of the spectral position on dihedral angle φ needs to be addressed for proper comparison as pointed out above and also by others for conjugated terpyridine assemblies previously.^[30d,56]

For the directly connected complexes **1** and **2** the d-Ru²⁺ $\rightarrow \pi^*_{Acr+}$ transition can only considered as strong (f >> 0) at non-orthogonal angles for ω (= φ in this case). To account for the effects of the dihedral angle relaxed potential energy surface (PES) scans of ω and φ on one ligand of the complex were performed and the position of λ_{MLCT} and oscillator

Table 5. Potential energy difference (diabatic Δ -SCF [eV]) of the triplet states for complex **1–5** in respect to the S₀ state and change in geometric parameters and spin density for the different calculated triplet states.

	³ MLCT			³ LC					³ MC					
	1	2	3	1	2	3	4	5 (#1)	5 (#2)	1	2	3	4	5
Δ -SCF	1.799	1.875	2.043	1.799	1.795	1.846	1.616	1.553	1.713	1.824	1.836	1.805	1.778	1.790
Q _{Ru} ^[a]	-0.001	-0.007	-0.003	-0.001	-0.004	- 0.002	-0.002	-0.002	-0.005	0.806	0.813	0.802	0.816	0.813
RMSD ∠ _{Ru−N} ^[b]	-0.063	-1.87	-1.94	0.001	-0.015	0.003	-0.102	0.011	-0.007	-6.63	-6.57	-6.02	-6.88	-6.53
Spin on Ru ^{2+[c]}	0.84	0.86	0.86	not sigr	nificant (n.	s.)			0.15	1.72	1.76	1.76	1.49	1.76
Spin density Terpyridine fragment ^[c]	0.28 _{C4′} 0.26 _{N1′} 0.15 _{C2′} 0.15 _{C6′}	n.s	n.s	not sigr	lificant					not sigi	nificant			
Spin density on linker ^[c]	-	-	n.s.	-	-		0.31 _{C2} 0.26 _{C4}	0.17 _{C2}	0.34 _{C2} 0.25 _{C4}	-	-	not sigr	nificant	
Spin density Acr/MeAcr ⁺ fragment ^[c]	n.s.	0.43 _{C9} 0.14 _{C3} 0.14 _{C6} 0.12 _{N0}	0.40 _{C9} 0.10 _N 0.11c ₁ 0.11 _{C8} 0.11 _{C3} 0.11 _{C6}	0.56 _{C9} 0.43 _N 0.24 _{C4} 0.24 _{C5}	0.59 _{C9} 0.35 _N 0.21 _{C1} 0.21 _{C8} 0.21 _{C4} 0.21 _{C5}	0.59 _{C9} 0.39 _N 0.22 _{C1} 0.22 _{C8}	0.47 _N 0.34 _{C9} 0.20 _{C4} 0.20 _{C5}	0.49 _{C9} 0.37 _N	0.35 _N 0.32 _{C9} 0.14 _{C2} 0.14 _{C7}	not sigi	nificant			

[a] Obtained as defined by Persson et al.^[61b] Q denotes the nuclear coordinate of the ruthenium(II) ion, briefly, the sum of the geometrical change $\Sigma(\Delta dist.)$ of the six Ru–N bond lengths (in Å) relative to the S₀ conformation. [b] Denotes the root mean square deviation (RMSD) of the N–Ru–N angles (in °) of all axes calculated and referenced to a standard, e.g. O_h symmetry.^[6a] Due to the fact that bis(terpyridine) complexes generally do not show a perfect octahedral coordination geometry we chose to reference relative to the corresponding S₀ state geometry. [c] By Mulliken spin analysis (see SI for details). The numbering scheme for the spin density position is based on the IUPAC nomenclature in view as isolated fragment.

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strength was investigated (Figure 14). In our belief dihedral changes on one ligand are a more realistic approach in view of the often accounted C_1 symmetry than a pseudo- C_2 symmetric change of both ligand fragments.

As a result, a medium to high rotation barrier was calculated for the dihedral angle ω between Acr/MeAcr⁺-fragment and the 9-aryl unit by relaxed PES scans for **1**, **2** ($\omega = \varphi$) and **3** (see Figure 14a).

For the sterically more crowded compounds **1** and **2** high energies of $\Delta E_{\text{pot}} = 70-79$ kJ/mol were obtained while the sum of thermally accessible conformations around the 90° minima is quite large. This finding corroborates semiemperical calculations for 9-phenyl and 9-napth-1-yl-acridinium ions.^[12e,12f] predicting a broad angle distribution (±30°) around the ca. 90° minimum energy conformation.

Together with the wide angle range of ca. $\pm 40^{\circ}$ (equals 99.8 % Boltzmann population) a intrinsic broadening of the transition of ca. 40 nm at room temp. (see Figure 14b) is implied, whereas static TD-DFT calculation of the optimized geometry would have been absolutely misleading in the relevance of this transition. Nevertheless free rotation was still observed in NMR spectroscopy at 298 K in agreement with measurements for structural related 9-phenylanthracenes (ΔG^{\sharp} 88 kJ/mol).^[57]

For the MeAXT⁺ linker-systems 3 – 5 similar observations can be made: Thienyl-systems (X = T) **4** and **5** have a small barrier of rotation of ΔE_{pot} about 30–45 kJ/mol in regard to ω while **3** reflects the rotation barrier of a 9-phenylacridinium and -anthracene compounds (see Figure 14a). In regard to the second dihedral angle, namely φ , a large angle distribution is easily thermally accessible for the MeAXT⁺ linker-systems 3 - 5. The rotation between the tpy unit and the phenyl (X = Ph) or thienyl-linker (X = T), respectively, is clearly not hindered $(\Delta E_{\rm pot}$ <18 kJ/mol). Corresponding TD-DFT calculations show only small changes in the predicted wavelength and oscillator strength of the d-Ru²⁺ $\rightarrow \pi^*_{Acr+}$ and d-Ru²⁺ $\rightarrow \pi^*_{tpy}$ transition in depedancy of φ . For complex **3**, however, by the coincidence of having a restricted angle range for ω combined with a double minima energy landscape for φ (see Figure 14) the calculations capture the global minima of both dihedral angle populations well (S₀ φ = 70 ± 2°, ω = 36.5 ± 1° regardless of DFT functional; see Table S6). This is reflected by a a very good agreement of predicted and calculated λ_{MLCT} (calcd. 497 nm, exp. 493 nm) while usually the predicted λ_{MLCT} transition for the calculated minima conformation is red-shifted by several nanometers ($\Delta\lambda$ = 16 – 47 nm at these wavelengths; see Figure 13b).

Another aspect highlighted by the (TD)-DFT calculation was the conformation at $\approx 0^{\circ}/180^{\circ}$ angle setting for ω (or φ for **1** and **2**). Upon rotation about ω the steric stress is avoided by adopting an acridane-like ("butterfly") conformation in the high energy transition state and thereby giving up the energetically favorable planarity of Acr/MeAcr⁺ ring systems (**1**, 159°; **2**, 153°; **3**, 152°; **4**, 165°; **5**, 158°; see Figure 15).

The "butterfly" conformation in the transition state is slightly favoured for the MeAcr⁺ complexes with the energetic order 2 > 3 > 5. A similar "butterfly" shape conformation was also found experimentally on a detailed study of sterically over-





Figure 15. Structure of a forced planar conformation ($\varphi = 180^{\circ}$) for one ligand of [Ru(MeAT)₂]⁴⁺ (**2**) after relaxation ($\Delta E_{\text{pot}} + 70 \text{ kJ/mol}$).

crowded 9-(2,6-dimethoxyphenyl)-1,8-dimethoxyacridinium salts by X-ray and NMR studies (ΔG^{\ddagger} 49–83 kJ/mol).^[58] The influence of the interplanar angle on the rotation barrier of such annulated aromatic systems was pointed out in the study of 9-phenylanthracene previously.^[57] The generation of a computational artefact in our calculation seems therefore to be unlikely.

More importantly the structural similarity of this rotamer to the optimized geometry of ³LC state (see section 2.8.2) might implicit a singlet-triplet conical intersection of the two hypersurfaces nearby, and consequently opening a route for radiationless triplet relaxation, which will be discussed in further detail in the following section.

In summary, we agree with conclusions drawn by Constable et al.,^[31a] namely, the correct prediction of a red shift for the *N*-methylation is possible^[29c,30d,31] but we deduced an additional root cause next to energetical lowering of the LUMO: Thus, Acr/MeAcr⁺ systems show additional chromophore absorptions resulting in intraligand (IL) $\pi_{Acr+} \rightarrow \pi^*_{Acr+}$ -type of transitions as well as d-Ru²⁺ $\rightarrow \pi^*_{Acr+}$ MLCT transitions. In our case the latter displace the lowest energy "pure" MLCT d-Ru²⁺ $\rightarrow \pi^*_{tpy}$ -transition in all MeAcr⁺ complexes (**2**, **3**, **5**) and may therefore account for the observed red-shift as well as for the markedly broadening of the MLCT band in the titration experiments.

2.8.2. Triplet States

Geometry optimizations without symmetry restraints become particular important for the triplet states of these complexes because the unpaired electrons may localize only on one fragment of the complex (viz. C1 symmetry). Mulliken spin-density analysis of these calculations revealed that different triplet states were indeed obtained (Table 5, see Figure 16 and Figure 17 for a graphical representation).^[53,54a,59] The outcome was depending on the initial geometry. This dependency was found for other [Ru(tpy)₂]²⁺ and [Ru(bpy)₃]²⁺ systems previously.[54a,59b,60] Detailed values for the triplet geometries of complex 1 and 2 are given in Table 4 (columns ³LC, ³MC and ³MLCT) while **3** – **5** are compiled in the Supporting Information (Table S6). For a general impression the changes in bond lengths can be summarized in the parameter Q (= $\Sigma\Delta$ dist.)^[6a] and the root-mean-square deviation (RMSD) of the Ru-N coordination angles relative to the S₀ geometry which are compiled in Table 5.

The ³MC state can be easily distinguished by its dissociative character due to drastic bond elongation (Table 4; max. 2.411 Å





Figure 16. Calculated structures (B3LYP//6-31G(d)/LANL2DZ, CPCM solvent model for MeCN) for the S₀, ³LC, ³MLCT, and ³MC triplet states of [Ru(MeAT)₂]⁴⁺ (**2**) and corresponding spin density isocontour plot (purple, 0.02 e Bohr⁻³; 6 grid points Bohr⁻¹). Some structural parameters are also highlighted, viz. exceptional N–Ru bond lengths (red), 2',6'-pyridyl units out-of-plane bending (green), and parameters of the 4'-substituent (black), respectively.



Figure 17. Calculated structures (B3LYP//6-31G(d)/LANL2DZ, CPCM solvent model for MeCN) for the ${}^{3}LC$, ${}^{3}MLCT$, and ${}^{3}MC$ triplet states of [Ru(MeATT)₂]⁴⁺ (**5**) and corresponding spin density isocontour plot. Colour scheme and isocontour values as in Figure 16.



for **5**, see Table S6) on one N–Ru–N axis. For pristine $[Ru(tpy)_2]^{2+}$ (**25**), a length of 2.382 Å was calculated.^[6a,61] In view of the Q value the ³MC state manifests itself in differences of > 0.80 Å in Q and a RMSD of > 6.0° in coordination angles. Severe out of plane bending of the lateral 2',6'-pyridyl units on one ligand fragment is also noticeable (\approx 14°, see Figure 16 and Figure 17). The spin density is mainly located on the metal center (Table 5). and the values agree very well with observations described in previous publications.^[6a,61a] Structural parameters of the 4'-substituents and of the chromophore units are, however, only barely changed in the ³MC state. They resemble the S₀ geometry in most parameters (i.e. $C_{Tpy}-C_{Aryl}$ distance; see Table 4) which is in agreement with the triplet localization on the metal center.

The geometry in the ³MLCT state is more affected in this regard as both – metal center and chromophore – show moderate distortions (see Table 4 and Table 5). Despite numerous attempts no stable ³MLCT structure could be found for complex **4** and **5** due the intrinsic low dihedral angle φ between the thienyl and tpy fragment which subsequently leads only to ³LC states in optimizations.

³LC states could be found for all complexes under study and the Q and RMSD parameters are compiled in Table 5. The ³LC states of the Acr/MeAcr⁺ chromophore are of interest for energy storage as outlined in the aim of this work but on the other hand also may serve as deactivation pathway if too low in energy. Most obvious for the ³LC state are the geometrical changes of the Acr/MeAcr⁺ moiety itself, i.e. significant shorter $C_{Me}-N_{Acr}$ and $C_{Acr}-C_{Aryl}$ bond lengths. In several cases a 3LC geometry could be found which resembles the "butterfly"shape of the ground state rotamers (Figure 17, cf. Figure 15).

The calculated Δ -SCF energies of the triplet states are summarized in Table 5 while a graphical representation is depicted in Figure 18 together with the experimental determined emission maxima (see Table 6).

Most trends are captured well by this direct approach: ³MC states are predicted to be energetically close but below the ³MLCT states except for complex **1** where this level is slightly higher in energy. Furthermore the ³LC and ³MLCT state are predicted to be isoenergetic for complex **1**, therefore ideally fulfilling the requirement for an efficient multichromophoric assembly. However, as already shown in the previous section, this does not hold true experimentally.

The prediction for complex **2** is also favourable and would still enable a multichromophoric behaviour ($\Delta E = 0.080 \text{ eV} = 645 \text{ cm}^{-1}$) if *p*-e⁻T is neglected. Similarly the relative trend to higher energy emission for **3** is qualitatively correct predicted but overestimated in energy (calcd. 606 nm, exp. 648 nm). As already mentioned before, a stable ³MLCT states could not be found for complexes **4** and **5**, respectively. However, even without exact knowledge of the ³MLCT energy these systems have apparently ³LC states too low in energy to be well-suited for the multichromophore approach.

It is important to note that most calculated energies differences are in the order of magnitude of the estimated DFT error at this level of theory. To obtain nevertheless an estimate about the quality of the calculated Δ -SCF energies for the ³MLCT state







Figure 18. Energy of the experimentally determined emission maxima (black bars with FWHM indicated as fading grey area) and the calculated Δ -SCF energies of the different triplet states (³MLCT, red; ³LC, blue; ³MC, green) for complexes **1–5**. Note that no ³MLCT states could be found for complexes **4** and **5**. The energy for the "butterfly"-like Acr/MeAcr⁺ high energy rotamer of the ground state is also indicated (dark grey). Please note the different scaling and the arising axis break for the energy scale in this area.

Table 6. Singlet–triplet energy difference in λ [nm] (eV) by Δ -SCF (= $\Delta E_{diabatic}$) calculations and by TD-DFT S₀–T₁ (= $\Delta E_{vertical}$) transition calculations.

Compound		Δ -SCF 3 MLCT a	$\Delta E_{\rm vert}{}^{\rm b}$	ΔE_{vert}^{c}	Exp.
[Ru(AT) ₂] ²⁺	1	689 (1.80)	667 (1.86)	668 (1.86)	664 (1.87)
[Ru(MeAT) ₂] ⁴⁺	2	661 (1.87)	667 (1.86)	665 (1.86)	664 (1.87)
[Ru(MeAPhT) ₂] ⁴⁺	3	606 (2.04)	657 (1.89)	649 (1.91)	648 (1.91)
[Ru(ATT) ₂] ²⁺	4	not found	680 (1.82)	672 (1.84)	672 (1.84)
[Ru(MeATT) ₂] ⁴⁺	5	not found	690 (1.80)	679 (1.83)	672 (1.84)

[a] ΔE (SCF) calculated from optimized B3LYP geometries. [b] First 30 S₀–T_n transitions calculated on B3LYP S₀ geometry. [c] Same as before but starting from PBE0 S₀ geometry. Note that the lowest energy transition provided here was always well separated from other S₀–T_n transitions (e.g. for [Ru(MeAT)²]⁴⁺ (**2**); $\Delta E = +0.432$ eV). However, no statement about oscillator strengths can be made as these transitions are spin-forbidden and spin-orbit coupling is neglected throughout by the calculations.

we performed additional TD-DFT S_0-T_1 calculations starting from the optimized S_0 B3LYP as well as PBE0 S_0 geometries. The results are compiled in Table 6 and show a quite remarkable correlation – especially for the PBE0 calculations. The good correlation presumably has two reasons: On the one hand the geometries of the emitting ³MLCT state show only moderate distortions in Q and RMSD values in comparison to the S_0 state (see Δ -SCF approach; Table 5) and on the other hand simple error cancelation due to calculation of the difference can be assumed. Therefore, a direct S_0-T_1 TD-DFT calculation, under assumption of the T_1 state to be of ³MLCT in nature, appears to be a valid choice. By this methodology the ³MLCT energies of complex **4** and **5** can be estimated to be in the range of 1.80–1.84 eV. Interestingly this holds also true for **3** which was overestimated by the Δ -SCF approach (see above).

3. Conclusions

A family of terpyridine ligands incorporating either an acridine or a methylacridinium chromophore and different linker groups (none, phenyl, thienyl) have been synthesized by different routes. Linker-extended acridinium-terpyridine ligands have been synthesized by the use of acridane intermediates as protected acridinium moieties. The desired terpyridine ligands and their ruthenium(II) complexes have been synthesized by standard methods, except for complex **2**, which was directly methylated starting from **1** by a "chemistry on the complex" approach.

The physicochemical properties were investigated by a combination of experimental and theoretical approaches. The electrochemical and absorption features of the complexes are in line with previous findings for the py/py⁺-type series (**29**– **31**^[30b,30c,31a]). To our surprise, no substantial positive impact of the introduction of the Acr/MeAcr⁺ moiety was notable while vice versa for the MeAcr⁺ complexes **2**, **3**, and **5** the reduction potential of the MeAcr⁺ was less negative.

Therefore, the well-known principle that properties of individual units must not necessary be reflected in the de novo molecular assembly holds true. This is not only eminent by contrary electrochemical expectations but also established by HOMO/LUMO and triplet calculations – especially in ligand dynamics of the ³LC states (discussed below). In this regard the chosen connectivity by use of the C-9 position to retain symmetry was unexpectedly unfortunate.

Complex 2, 3, and 5 showed in DFT calculations a lowered LUMO level of almost pure $\pi^*_{\text{Acr+}}$ MO composition. This leads to pronounced and broader MLCT transitions in electronic absorption spectra. The latter was verified by conversion of the acridine complexes 1 and 4 to the corresponding protonated compounds at low pH but also through in situ destruction of the acridinium chromophore by formation of acridanes for complex 3 and 5. By using this conversion technique in low-temperature luminescence measurements, the proposed electronic influence of the Acr/MeAcr⁺ moiety on the ruthenium(II) complex fragment could be proven. The ³MLCT emission lifetimes of 1-5 compare favorably with current benchmark systems in the milliseconds regime at 77 K.^[7d,7e] The chemical conversion to acridane derivatives reverts the emission properties solely to the corresponding Ru(tpy)₂-fragment of the complex. However, a photophysical distinction between acridine and acridinium compounds was hardly possible for 1-5 at this temperature. This is understandable by the similar triplet energies, while competitive decay mechanism, especially ³MC-mediated relaxation and p-e⁻T, are slowed down or suppressed in the rigid matrix. Time-resolved measurements on selected complexes suggest a fast formation and decay of the ³MLCT states, presumably via $p-e^{-T}$ mechanism in the case of **5** or formation of long-lived but non-emissive ³LC state in the case of **1** and **4**.

In view of our overall design principle this means that i) for complexes 1 and 2 the stabilizing effect of a conjugated





4'-substituent on the Ru(tpy)2-fragment is missing due to the steric bulk of the Acr/MeAcr⁺ units; ii) for linker-extended complexes some positive effects of the Acr/MeAcr+ fragment are counterbalanced by our choice of a conjugated linker - especially for the thienyl complexes 4 and 5; iii) in case of the $[Ru(MeAPhT)_2]^{4+}$ complex (3) theoretical and experimental data suggest an electronically more decoupled linker group, namely an isolated MeAcr⁺ chromophore and a 4'-p-tolylterpyridine ligand (ttpy). This manifests itself in an exceptional long lifetime of 9.5 ms at 77 K and a high energy ³MLCT emission compared to the other complexes. It underlines the crucial interplay of electron donor character and electronic decoupling of the 9arene substituent for acridinium dyes but also for the 4'-position in terpyridine ligands in such complexes. By this, complex 3 is heading towards a multichromophoric behaviour but the lower reduction potential of the PhMeAcr⁺ unit in the complex (-0.89 V vs. -0.93 V for PhMeAcr⁺) combined with the lack of influence towards the HOMO led this complex still be susceptible to guenching via $p - e^{-T} (\Delta G^{\circ} = -0.14 \text{ eV})$.

Another aspect highlighted by the (TD)-DFT calculations but underestimated in our design principles was the dihedral twist angle between the individual aryl fragments (φ or ω). Both are of course key parameters in view on electronic conjugation. Stabilization via increased planarization was supposed to act on the 4'-substituent of the tpy-unit once the excited state is formed. However, even in ground state steric stress at the 4'-position, induced by rotation of the Acr/MeAcr+ moiety around its C_2 axis, is avoided by adopting an acridane-like ("butterfly") conformation as transition state at low angles. The structural similarity of this rotamer to the optimized geometry of ³LC state suggest a route for radiationless triplet relaxation at similar nuclear coordinates. In turn, it underlines the importance to account for the conformational dynamics in the study of any sophisticated designed [Ru(tpy)₂]²⁺ complex. This was also important to identify the major transitions as some of these transitions were found to depend distinctly on the dihedral angles between the fragments - especially for linkerless complexes 1 and 2.

The "ordinary" non-emissive deactivation channel of $Ru(tpy)_2$ complexes into the ³MC states could not be probed experimentally but the existence of ³MC states close in energy (1.78–1.84 eV) is also implicit by the DFT calculations. As pointed out in the introduction the design goal of a multichromophoric system does not directly influence the ³MC energy level and an energetically close positioning to the ³MLCT or ³LC states must not increase the chance for fast quenching.

From all the detailed studies within this work the message can be summarized plainly: While we still assume our rational design principle is a valid choice, the electronic interplay of the assembly together with the structural dynamics of such larger annulated ring systems in terms of distortions and rotational degrees of freedom was underestimated.

Further studies, such as temperature-depended measurements^[3,51c,51d] are required as the exact nature of some of the photophysical processes could not be fully deduced due to the complicated interplay between the fragments. Therefore, two options for further work eventuates: i) The synthesis of a rotational inhibited system at the Acr/MeAcr⁺ fragment, such as a 2,6-methylphenyl spacer, seems especially appealing for the long-lived [Ru(MeAPhT)₂]⁴⁺ complex **3** to prevent the proposed deactivation channel of the ³LC state by rotation of the moiety around the C-9 position. The rotation towards the terpyridine fragment, however, shall not be hindered.^[53] ii) Under the aspect that the C-9 position as connecting point was misfortunate but "simple" acridine or acridinium dyes would still be a viable option for the multichromophore approach, it may be of interest to evaluate either different or rigidified points of attachment but also linker units, such as 1*H*-1,2,3-triazolyl, which may partially decouple the Acr/MeAcr⁺ unit while stabilizing the terpyridine fragment.^[56] Recent reports show interesting approaches towards utilizing typical acridine reactions directly on complexes.^[38]

Last but not least we do not see the occurrence of a slightly exergonic p-e⁻T process for acridinium dyes as major obstacle at first instance, as by such, switchability of long-lived luminescence by pH change might be feasible.

Experimental Section

Procedures and references for the synthesis of known compounds and detailed data on all new compounds and corresponding ruthenium(II) complexes **1–5** are given in the Supporting Information. The SI holds also detailed information regarding the instrumentation for routine characterization, electrochemistry, and photophysical measurements (absorption, transient absorption and low temp. luminescence) as well as employed computational methods and the instrument and software used to derive X-ray structure information.

CCDC 1421582 (for **2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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