# Photochemical & Photobiological Sciences

## PAPER

**Cite this:** *Photochem. Photobiol. Sci.*, 2014, **13**, 380

# A study of acridine and acridinium-substituted bis(terpyridine)zinc(II) and ruthenium(II) complexes as photosensitizers for O<sub>2</sub> ( $^{1}\Delta_{g}$ ) generation<sup>†</sup><sup>‡</sup>

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The homoleptic zinc(II) and ruthenium(II) metal complexes of bis(tridentate) 9-acridine and 10-methyl-9-acridinium-substituted terpyridines were tested for their suitability as triplet photosensitizers (PS) using the photooxidation of 1,5-dihydroxynaphthalene (DHN) to Juglone as a model reaction. Singlet oxygen  $(O_2^{-1}\Delta_g)$  generation is superior or comparable to Ru(bpy)<sub>3</sub><sup>2+</sup> for the acridine complexes, whereas the acridinium complexes are ineffective. The molecular structure of the bis(9-(5-([2,2':6',2''-terpyridin]-4'-yl)thien-2-yl)-10-methylacridinium)zinc(II) complex ([Zn(MeATT)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub>) is determined by X-ray structure analysis, whereas for other complexes DFT calculations were performed for structural parameters to obtain insights into their electronic properties.

## Received 7th October 2013, Accepted 28th November 2013 DOI: 10.1039/c3pp50349f

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## Introduction

Photosensitizers (PSs) are a common need in the field of photochemistry and -biology<sup>1,2</sup> and the underlying photophysical and molecular mechanisms are well understood.<sup>3-6</sup>

In the last few years the development of specifically designed PS dyes has become particularly important for use in dye-sensitized solar cells<sup>7</sup> (DSSC), light upconversion by triplet–triplet annihilation (TTA),<sup>8</sup> or – more generally seen – in the study of charge separation in order to mimic the natural photosynthetic reaction cascade.<sup>9</sup> Metal complexes of the polypyridine family are the backbone of such efforts next to two

multifarious research fields of their own: porphyrins and phthalocyanines.

Typical metals employed in polypyridine complexes are transition metals of the platinum group (*e.g.* Ru, Ir).<sup>9</sup> Progress has also been made in employing less precious metals<sup>10</sup> in polypyridine complexes for such applications (*e.g.* Zn<sup>II 11</sup> or Cu<sup>I 12,13</sup> sensitizers, Co<sup>II/III</sup> electrolytes<sup>14</sup> or a combination of them<sup>15</sup>), as most of the porphyrin and phthalocyanine dyes show favorable properties with more abundant metals (*e.g.* Zn<sup>II</sup>).<sup>16</sup> It should also be mentioned that metal ion free sensitizers have been studied widely in the last decade due to DSSC application.<sup>17</sup>

Nevertheless "classic" triplet sensitizers and their application remain an active research area in recent years and the progress in this field has been summarized only recently.<sup>18</sup> Advances in this field are on the one hand a "side-effect" due to the need for phosphorescent dyes in materials chemistry but also due to the need for biocompatible (water-soluble, non-toxic, *etc.*) far-red absorbing dyes<sup>18</sup> for photodynamic therapy<sup>19</sup> (PDT).

The photosensitized production of  $O_2$  ( ${}^1\Delta_g$ ) by triplet energy transfer is unarguably one of the main applications.<sup>20</sup> However, just as it is a worthwhile research goal to achieve the best possible coverage of the incident solar electromagnetic spectrum in optimization of DSSCs,<sup>7b</sup> one can ask the same for PSs in order to facilitate, for instance, an environmentally friendly production of chemicals by sunlight (*viz.* "green" photochemistry<sup>21</sup>) in large area solar collectors.<sup>22</sup> Such

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<sup>†</sup>This article is dedicated to the memory of Professor Nicholas J. Turro (1938-2012).

<sup>‡</sup>Electronic supplementary information (ESI) available: Additional views on X-ray crystal structure of 2, analytical data (full spectra) for all new compounds, exemplary UV-Vis spectra of DHN photooxidations, data of 2-methylnaphthalene and limonene irradiation experiments, O<sub>2</sub> ( $^{1}\Delta_{g}$ ) NIR emission upon irradiation of 4, transient absorption (TA) spectra of the ATT ligand and complex 2, and computational details, such as optimized geometries (S<sub>0</sub>, T<sub>1</sub>), MO and spin density plots. See DOI: 10.1039/c3pp50349f

techniques can be easily adopted for  $O_2$  ( $^1\Delta_g$ )-mediated photooxidations, for example of (–)-citronellol in rose oxide synthesis or 1,5-dihydroxynaphthalene (DHN) to Juglone<sup>23</sup> and subsequent photo-Friedel–Crafts acylation.<sup>24</sup> Similarly, the use of such techniques in solar water disinfection by photogenerated  $O_2$  ( $^1\Delta_g$ ) has been reported.<sup>25</sup> In contrast, in terms of size the advantages of microfluidic flow reactor photochemistry and the availability of efficient miniaturized light sources (LEDs, diode lasers, *etc.*) enable production processes without the need to isolate the potentially dangerous peroxide intermediates.<sup>26</sup>

The generation, application and biological impact of  $O_2$  ( ${}^{1}\Delta_g$ ) have been reviewed,<sup>2,27</sup> as well as its use with an emphasis on synthetic organic photochemistry.<sup>28-32</sup>

Correspondingly, there is a need for new <sup>3</sup>PSs as the typically employed organic dyes, such as methylene blue (MB) or rose bengal (RB), exhibit a lack of long-term stability and wavelength coverage. More recently, heavy atom-substituted BODIPY dyes<sup>33,34</sup> and other purely organic examples (*e.g.* coumarins<sup>35</sup>) were reported, mainly focused on PDT (no undesirable metal ions) or TTA upconversion applications.

Recently, Murata *et al.* reported the use of neutral and cationic C^N-cyclometalated Ir<sup>III</sup> complexes for the photooxidation of DHN<sup>36</sup> – stimulated by the seminal work of Selke and Thompson *et al.*<sup>37</sup> about the efficient O<sub>2</sub> (<sup>1</sup> $\Delta_g$ ) sensitization capability of platinum group metal complexes. In this regard, Wilkinson and Abdel-Shafi *et al.*<sup>38</sup> examined [Ru(bpy)<sub>3</sub>]<sup>2+</sup> and derivatives in detail for their capabilities over ten years ago and some Ir<sup>III</sup> and Rh<sup>I</sup> complexes more recently.<sup>39</sup>

Although polypyridine complexes of  $Ir^{III}$  have certain advantages over  $Ru^{II 9}$  (*i.e.*, no low-lying metal-centered energy levels), one should not leave aside the progress made on the parent  $Ru^{II}$  complexes in the last few years. Especially for terpyridine complexes, which lack on prolonged excited state lifetimes compared to  $[Ru(bpy)_3]^{2+}$ , rational design has lead to lifetimes in the µs-regime. This was achieved by manipulation of the terpyridine ligand itself,<sup>40,41</sup> but also by attachment of multiple chromophores with a matching triplet level.<sup>42</sup>

The choice of a suitable chromophore for such purposes is a priori difficult and certain limitations apply as summarized by Zhao et al.,<sup>18</sup> i.e., one or several chromophores tethered to the metal-coordination side with an excited singlet state higher in energy than the singlet state of interest may serve as an additional photon absorber ("antenna effect"). However, if we focus on the T1 as state of interest and consider the chromophore triplet state higher in energy but the metal ion as main cause for the intersystem crossing (ISC) then no photophysical benefit is gained in terms of triplet photophysics. This approach is therefore only appealing for compounds with an intrinsic long triplet lifetime and high ISC rates like  $[Ru(bpy)_3]^{2+}$  where the singlet state is quickly depleted by ISC. Very recently this concept has been applied to cyclometalated Ir<sup>III</sup> and Pt<sup>II</sup> complexes and was also used to evaluate photooxidation of DHN.43

More often the chromophore triplet state is lower in energy than the triplet state of interest and therefore an energy transfer may occur. In some cases the occurrence of this energy transfer might be beneficially employed, *e.g.* first principle identification of the chromophore triplet state has been reported for a BODIPY dye connected to a  $[Ru(tpy)_2]^{2^+}$  system<sup>44</sup> and a perylenebisimide (PBI) dye on C^N-cyclometalated Ir<sup>III</sup> complexes.<sup>43b</sup> For O<sub>2</sub> (<sup>1</sup> $\Delta_g$ ) sensitization purposes the localization of the triplet state is of course less important than overall light absorption, yield of triplet formation and triplet lifetime itself, and consequently the O<sub>2</sub> (<sup>1</sup> $\Delta_g$ ) quantum yield ( $\Phi_\Delta$ ) was evaluated.<sup>43b</sup>

One might ask why not more of the promising – multichromophoric or otherwise improved – bis(terpyridine) systems have been analyzed for their suitability as <sup>3</sup>PS, as there is a good background of data on the well-known O<sub>2</sub> (<sup>1</sup> $\Delta_g$ ) sensitizer [Ru(bpy)<sub>3</sub>]<sup>2+</sup> and similar complexes.<sup>27,38,45,46</sup> However, we could only find a few reports dealing with  $\Phi_{\Delta}$  of [Ru(tpy)<sub>2</sub>]<sup>2+</sup> complexes.<sup>47,48</sup>

In part the apparent absence of such reports can be attributed to the popular choice of anthracene<sup>42*a*</sup> and pyrene<sup>49,50</sup> dye in multichromophore approaches because of their suitable matching triplet levels. An early seminal work on anthracenesubstituted terpyridine ligands by Maestri *et al.*<sup>51</sup> mentioned O<sub>2</sub> (<sup>1</sup> $\Delta_g$ ) generation for a homoleptic bis(terpyridine) complex of Ru<sup>II</sup>, which in turn degraded the anthracene moiety due to *endo*-peroxide formation. Very recently, this reaction was employed as a switch for the [Ru(bpy)<sub>3</sub>]<sup>2+</sup> luminescence.<sup>52</sup>

First principle studies for 9-acridine and 10-methyl-9-acridinium-substituted homoleptic bis(terpyridine) complexes of Ru<sup>II</sup> have been reported elsewhere.<sup>53</sup> For these systems it turned out that a multichromophoric benefit, *i.e.* <sup>3</sup>MLCT luminescence, could only be deduced at low temperature for both dye forms. While acridinium compounds featured short-lived components only, the acridine analogues exhibited a longlived dark state, which was quenchable by  $O_2$  ( ${}^{3}\Sigma_{g}$ ). Pristine acridine is a known <sup>3</sup>PS sensitizer<sup>18,54</sup> although it is only applicable in the blue spectral region (lowest energy abs. at  $\lambda_{max}$ 375 nm), but more importantly it cannot be decomposed by endo-peroxide formation. In the present work, we were therefore interested to evaluate the  $O_2$  ( $^1\Delta_g$ ) sensitization efficiency of the Ru<sup>II</sup> complexes and their Zn<sup>II</sup> counterparts (Scheme 1). The synthesis and photophysical properties of these new Zn<sup>II</sup> complexes will be reported here. For comparison, we included also acridinium systems in this study because such dyes are lively discussed<sup>55</sup> and may act as Type I or Type II sensitizers.56

## Experimental

### Material and methods

The manufacturer and model of the used instrumentation for routine characterization (NMR, MS, IR, mp) as well as purity and commercial sources for solvents and reagents are given in



Scheme 1 Generalized structure of photocatalysts 1–5 under study and labelling scheme for <sup>1</sup>H NMR spectroscopic assignments.

the ESI.<sup>‡</sup> The synthesis of the ligands and complexes 3-5 has been reported elsewhere.<sup>53</sup>

Steady-state UV-Vis absorption spectroscopy was performed on a Lambda 2, Lambda 40 (both Perkin Elmer) or V-630 (Jasco) double beam spectrometer using the neat solvent as a blank reference in standard PTFE-stoppered quartz cuvettes of 10 mm path length (Hellma).

Steady state fluorescence spectra were carried out using a FluoroMax 3 spectrometer (Horiba Yvon Jobin, HYJ) in the visible detection range and using a FluoroLog 3 spectrometer (HYJ) with an InGaAs detector ( $512 \times 1 \times 1 \mu$ m, HYJ Symphony®) in the NIR detection range with 180 s integration time and a slit width of 14.7 nm. Alternatively, fluorescence spectra (uncorrected) were measured with a Perkin Elmer LS 50B. Emission and excitation monochromator slit widths were both typically set to 5 nm.

Fluorescence lifetimes were determined by the time correlated single photon counting (TCSPC) technique using a Fluoro-Log 3 emission spectrometer (HYJ) equipped with an R3809U-58 MCP (Hamamatsu) and an N-403L laser diode (HYJ) with an excitation wavelength of 403 nm (<200 ps FWHM).

Femtosecond transient absorption (TA) experiments were carried out with an amplified Ti:Sapphire laser system CPA-2101 fs laser (Clark MXR; output 775 nm, 1 kHz, and 150 fs pulse width) using a transient absorption pump/probe detection system (TAPPS Helios, Ultrafast Systems). The 387 nm excitation wavelength was obtained by frequency-doubling of the fundamental wavelength in the frequency generator STORC (Clark-MXR). For excitation an energy of 200 nJ per pulse was selected.

Nanosecond transient absorption experiments were carried out with a Nd:YAG laser. The 355 nm excitation wavelength was formed by third harmonic generation. Moreover, pulse widths of less than 5 ns with energies of up to 7 mJ were selected. The optical detection was based on a pulsed Xenon lamp, a monochromator, a photomultiplier tube or a fast silicon photodiode with 1 GHz amplification and a 500 MHz digital oscilloscope. The laser power of every laser pulse was registered using a bypath with a fast silicon photodiode. The experiments were performed in a 5 mm  $\times$  10 mm quartz glass cuvette. Femtosecond fluorescence upconversion experiments were performed with the aforementioned Ti/sapphire fs laser system (Clark-MXR) which is combined with an ultrafast upconversion spectrometer system HALCYONE for detection. Emission pump pulses of 387 nm (*vide supra*) were used to stimulate the sample. With the use of a beam splitter, the fundamental wavelength of 775 nm was used as a gate pulse for sum frequency generation inside a BBO crystal. Accordingly, fluorescence kinetics were monitored at 580 nm with a time window of 0–3300 ps and a temporal resolution of 350 fs.

 $[Zn(ATT)_2][PF_6]_2$  (1). ATT ligand (56 mg, 112 µmol) and  $Zn(OTF)_2$  (20 mg, 54 µmol) were added to a solvent mixture of EtOH and THF (30 mL, 2:1 v/v) under stirring. The reaction mixture was heated to reflux for 15 min and was allowed to cool to r.t. The almost clear, golden yellow solution was filtered and an aqueous NH<sub>4</sub>PF<sub>6</sub> solution (301 mg in 20 mL) was added to the filtrate. A bright yellow suspension was formed immediately. Precipitation was completed by the addition of water (50 ml) and the suspension was filtered over a pad of Celite (ca. 2 cm). The filter pad was washed with water  $(3 \times 20 \text{ mL})$  and diethyl ether  $(3 \times 20 \text{ mL})$  and was left to dry in air overnight. The yellow solid was dissolved and flushed down by using MeCN (4  $\times$  20 mL). The volatiles of the filtrate were removed in vacuo to give pure 1 (81%, 59 mg, 44 µmol). The complex can be recrystallized from MeCN-CH<sub>2</sub>Cl<sub>2</sub> (1:1 v/v) by diethyl ether vapor diffusion (recovery 74%). Mp 327 °C (sharp). Found: C, 55.15; H, 3.21; N, 8.00; S, 4.36. C<sub>64</sub>H<sub>4</sub>ON<sub>8</sub>S<sub>2</sub>ZnP<sub>2</sub>F<sub>12</sub>·3H<sub>2</sub>O requires C, 55.12; H, 3.32; N, 8.04; S, 4.60.  $\lambda_{max}$ (MeCN)/nm 387 sh. ( $\varepsilon \times 10^3$ /M<sup>-1</sup> cm<sup>-1</sup>, 32.4), 361 sh. (44.5), 347 (54.4), 284 (49.0), 252 (216). IR (ATR)  $\tilde{\nu}_{max}/cm^{-1}$ 3065, 1609, 1600 (s), 1552, 1476, 1458, 1425, 1404, 1251, 1026, 1015, 832 (vs, PF<sub>6</sub><sup>-</sup>), 789, 758, 691, 657, 555 (s). <sup>1</sup>H NMR (500 MHz, MeCN-d<sub>3</sub>)  $\delta$  9.04 (4 H, s, H^{{\rm B3}',5'}), 8.70 (4 H, dt, J 8.0 1.1, H<sup>A3</sup>), 8.44 (2 H, d, J 3.7, H<sup>C4</sup>), 8.31 (4 H, dt, J 8.8, 1.1, H<sup>E4</sup>), 8.12 (4 H, dt, J 8.8, 1.1, H<sup>E1</sup>), 7.97 (4 H, td, J 7.8, 1.5, H<sup>A4</sup>), 7.93 (4 H, ddd, J 8.8, 6.5, 1.3, H<sup>E3</sup>), 7.69 (4 H, ddd, J 8.8, 6.5, 1.3, H<sup>E2</sup>), 7.66 (2 H, d, J 3.7, H<sup>C3</sup>), 7.50 (4 H, dt, J 5.5 1.2, H<sup>A6</sup>), 7.23 (4 H, ddd, J 7.2, 5.5, 1.2, H<sup>A5</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz,  $CD_3NO_2-CD_2Cl_2$  4:1 v/v)  $\delta$  152.5 (C<sup>A20.B2',6'</sup>), 151.4 (C<sup>C20.C5</sup>), 151.0 (C<sup>A20.B2',6'</sup>), 150.2 (C<sup>A6</sup>), 149.9 (C<sup>DE4'</sup>), 143.6 (C<sup>A4</sup>), 143.4  $(C^{B4'})$ , 143.3  $(C^{C20.C5})$ , 140.0  $(C^{D9})$ , 135.0  $(C^{C3})$ , 132.7  $(C^{E3})$ , 132.1 ( $C^{C4}$ ), 131.9 ( $C^{E4}$ ), 130.0 ( $C^{A5}$ ), 129.1 ( $C^{E2}$ ), 128.2 ( $C^{A6}$ ), 128.0 ( $C^{DE1'}$ ), 125.3 ( $C^{A3}$ ), 121.3 ( $C^{B3',5'}$ ). <sup>19</sup>F NMR (282 MHz, MeCN-d<sub>3</sub>)  $\delta$  72.3 (d,  $J_{\rm F,P}$  708, PF<sub>6</sub><sup>-</sup>) MS (ESI) not stable, see main text.

[Zn(MeATT)<sub>2</sub>][PF<sub>6</sub>]<sub>4</sub> (2). [MeATT][PF<sub>6</sub>] ligand (109 mg, 167 µmol) and Zn(OTf)<sub>2</sub> (31 mg, 84 µmol) were suspended in MeOH–MeCN (20 mL, 4:1 v/v). The orange-yellow reaction mixture was refluxed for 2 h to give a clear solution. After being cooled down to r.t. an aqueous NH<sub>4</sub>PF<sub>6</sub> solution (314 mg in 6 mL) was added and precipitation was completed by the addition of water (20 mL). The bright yellow solid was isolated by filtration (G4 glass frit), washed with water (3 × 20 mL) and left to dry overnight in air to give pure 2 (88%, 123 mg, 74 µmol). It can be recrystallized from a mixture of MeCN–

 $CH_2Cl_2$  (30 mL 2 : 1 v/v) by diethyl ether vapor diffusion (recovery 61%). Mp >270 °C (darkens), 303 °C (decomp.). Found: C, 47.47; H, 2.97; N, 6.93; S, 3.70. C<sub>66</sub>H<sub>46</sub>N<sub>8</sub>S<sub>2</sub>ZnP<sub>4</sub>F<sub>24</sub> requires C, 47.74; H, 2.79; N, 6.75; S, 3.86.  $\lambda_{max}$  (MeCN)/nm 437 ( $\varepsilon \times 10^3$ / M<sup>-1</sup> cm<sup>-1</sup>, 22.5), 366 (46.2), 347 (67.2), 334 (67.5), 284 (57.5), 262 (194). IR (ATR)  $\tilde{\nu}_{max}/cm^{-1}$  3115, 1612 (s), 1575, 1553, 1478, 1426, 1273, 1250, 1028, 1015, 837 (vvs, PF<sub>6</sub><sup>-</sup>), 793, 764, 557 (s). <sup>1</sup>H NMR (500 MHz, MeCN-d<sub>3</sub>)  $\delta$  9.01 (4 H, s, H<sup>B3',5'</sup>), 8.77 (4 H, d, J 7.9, H<sup>A3</sup>), 8.70 (4 H, d, J 9.1, H<sup>E4</sup>), 8.56 (2 H, d, J 3.8, H<sup>C4</sup>), 8.48 (4 H, m, partially superimposed, H<sup>E3</sup>), 8.47 (4 H, d, J 9.1, partially superimposed, H<sup>E1</sup>), 8.21 (4 H, td, J 7.9, 1.4, H<sup>A4</sup>), 8.03 (4 H, dd, J 7.8, 1.7, H<sup>E2</sup>), 7.91 (4 H, dt, J 4.9, 1.4, H<sup>A6</sup>), 7.83 (2 H, d, J 3.8), H<sup>C3</sup>), 7.46 (4 H, ddd, J 7.9, 4.9, 1.4, H<sup>A5</sup>), 4.92 (6 H, s, H<sup>D10</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, MeCN-d<sub>3</sub>)  $\delta$  153.7 (C<sup>D9</sup>), 151.3 (C<sup>A20.B2',6'</sup>), 149.2 (C<sup>A6</sup>), 149.1 (C<sup>B4'</sup>), 148.5 (C<sup>A20.B2',6'</sup>), 144.8 (C<sup>C20.C5</sup>), 142.7 (C<sup>DE4'</sup>), 142.3 (C<sup>A4</sup>), 140.0 (C<sup>E3</sup>), 137.4  $(C^{C20.C5})$ , 135.8  $(C^{C3})$ , 131.2  $(C^{C4})$ , 130.5  $(C^{E1})$ , 129.6  $(C^{E2})$ , 128.7 ( $C^{A5}$ ), 128.1 ( $C^{DE1'}$ ), 124.4 ( $C^{A3}$ ), 120.8 ( $C^{B3',5'}$ ), 119.8 (C<sup>E4</sup>), 40.2 (C<sup>D10</sup>), <sup>19</sup>F NMR (282 MHz, MeCN-d<sub>3</sub>) δ 72.9 (d, J<sub>EP</sub> 707,  $PF_6^{-}$ ) HRMS (ESI) m/z 684.09337 ([M - 2 ×  $PF_6$ ]<sup>2+</sup>, calc. for  $C_{66}H_{46}N_8S_2^{64}ZnP_2F_{12}$  684.09255,  $\Delta$  1.20 ppm, total of 7 resolved signals with 0.5 m/z spacing).

#### X-ray structure elucidation

Single crystals of 2 were grown by diethyl ether vapor diffusion into a MeCN solution of the complex. A suitable crystal (0.2968 mm × 0.051 mm × 0.0264 mm, orange needle) was selected and measured on an Agilent SuperNova Dual Cu K<sub>α</sub> Atlas diffractometer. Using Olex2,<sup>57</sup> the structure was solved with the ShelXS<sup>58</sup> structure solution program using direct methods and refined with the ShelXL<sup>58</sup> refinement package using least squares minimisation (Table 1).

### **Photochemical experiments**

Photochemical reactions with DHN as a substrate (1.58  $\pm$  0.09  $\times$  10<sup>-4</sup> M, Abs.  $\approx$  1.2) were performed in a septum-

Composition	[Zn(MeATT) <sub>2</sub> ][PF <sub>6</sub> ] <sub>4</sub> ·5MeCN
Formula $FW/g \text{ mol}^{-1}$	$C_{76}H_{61}F_{24}N_{13}P_4S_2Zn$
Temperature/K	$200.00 \pm 0.10$
Abs. coeff./mm <sup>-1</sup>	2.630
Crystal system	Monoclinic
Space group	$P2_1/c$
Z	4
a/A	38.6752 (7)
b/A	8.61835 (12)
c/A	24.8997 (4)
$\beta/\circ$	104.5408 (18)
Volume/A <sup>-3</sup>	8033.7 (2)
Reflections coll.	28 592
Indp. Reflns.	14 124
GoF on $F^2$	1.036
Final <i>R</i> indexes $(I \ge 2\sigma(I))$	$R_1 = 0.0743, wR_2 \ 0.2044$
Final <i>R</i> indexes (all data)	$R_1 = 0.0950, wR_2 \ 0.2206$
Disordered parts	F atoms site disordered on 2PF <sub>6</sub>

stoppered two-neck 50 ml round-bottom flask made from standard borosilicate glass, in a vigorously stirred oxygen-saturated (30 min bubbling) MeCN–MeOH solution (25 ml, 4 : 1 v/v) irradiated at a 30 cm distance by a 400 W high pressure Hg lamp (Helios Italquartz). An aqueous NaNO<sub>2</sub> solution (0.72 M) of 5 cm path length directly in front of the reaction flask served as >385 nm longpass and, particularly important, also as a heat filter. Samples were withdrawn (by syringe) in 0.5 min (initial) to 5 min time intervals. Details about the procedure can be found in the reports of Murata *et al.*<sup>36</sup> and Zhao *et al.*,<sup>43</sup> specifically, we adopted the semi-preparative mode of operation but without the stringent use of 10 mol% photocatalyst.

Experiments were performed with the absorbance maximum of the sensitizer adjusted between 0.1 and  $0.3,^{37c,43b}$ preferably lower concentrated and optically matched (vide infra). The intrinsically different absorption profiles (and small differences in optical match) were corrected by use of the intensity (also called light-harvest or absorbance) correction factor  $F_{\text{area}} = 1 - 10^{-A(\lambda) 43,7b,59}$  for 385 nm (filter cut-off) to 800 nm. The quantum yields of  $O_2$  $({}^{1}\Delta_{g})$  generation  $(\Phi_{\Delta})$  were calculated by the usual equation<sup>60</sup> for relative determinations. Concentrations of all reagents and the product 5-hydroxy-1,4-naphthoquinone (Juglone) were calculated from the known molar extinction coefficients ( $\varepsilon$ ) at  $\lambda_{max}$  (DHN and Juglone, see ref. 36; own sensitizers, see Table 2). The molar extinction coefficients of  $[Ru(bpy)_3]^{2+}$  and MB were determined for the specific solvent mixture and found to be 15 200 M<sup>-1</sup> cm<sup>-1</sup> for  $[Ru(bpy)_3]^{2+}$ , and 93 850 M<sup>-1</sup> cm<sup>-1</sup> for MB at  $\lambda_{max}$ , respectively, which are both in good agreement with the values reported.61,62

Irradiance was measured to  $39 \pm 5$  mW cm<sup>-2</sup> at the front side of the reaction vessel position and  $28 \pm 5$  mW cm<sup>-2</sup> behind (average of a 30 s measurement interval) by aid of a digital power meter (PM100, Thorlabs) equipped with a manufacturer calibrated thermal sensor (S212A, Thorlabs). Note that the large standard deviation is due to fluctuations of the lamp intensity itself as indicated by the voltmeter of the lamp power supply. Standard ferrioxalate actinometry (0.012 M)<sup>63</sup> revealed an average photon flux of  $4.4 \pm 0.1 \times 10^{-7}$  Einstein s<sup>-1</sup> (2 runs<sup>‡</sup>) in the range of the actinometer absorbance (here: 385–500 nm). Based on some approximations (see ESI<sup>‡</sup>) and correction for the normalized fraction of incident light not covered by the actinometer, *i.e.*, the 546, 577, and 579 nm Hg lines, a similar minimum value (22 ± 4 mW cm<sup>-2</sup>) was calculated.<sup>63,64</sup>

Some irradiations, such as NMR runs with (+)-limonene and 2-methylnaphthalene, were exemplary also performed with a Rayonet® photoreactor (RPR-100, Southern New England Ultraviolet Co.) equipped with 16 × 35 W low-pressure Hg lamps (RPR-4190A,  $\lambda_{max}$  419 ± 40 nm) and a merry-go-round inset. Samples were also aerated with O<sub>2</sub> and irradiated in standard 5 mm (o.d.) NMR tubes or 1 cm (o.d.) Pyrex® photoirradiation tubes with a threaded septum cap.

#### **Computational methods**

The geometries were optimized to the convergence criteria of  $1 \times 10^{-5} E_{\rm h} a_0^{-1}$  (*opt* = *tight*) by the use of a B3LYP hybrid functional with an explicit combination of 6-31G(d) (C, H, N, S) and LANL2DZ (Zn)<sup>65</sup> basis sets (plus 18 electron ECP)<sup>66</sup> together with a CPCM solvent model for MeCN. All calculations were performed with the Gaussian 09 package<sup>67</sup> without symmetry constraints and were found to be stable minima by normal mode analysis (under standard state conditions). Time-dependent density functional theory calculations (TD-DFT) were performed on the same level of theory and with the same solvent model for 150 singlet and 30 triplet transitions calculated each.

## **Results and discussion**

## Synthesis and characterization

The newly synthesized  $Zn^{II}$  complexes have been prepared by the reaction of two equivalents of the appropriate ligand with  $Zn(OTf)_2$  in water-miscible solvent mixtures and precipitated by addition of an excess aqueous  $NH_4PF_6$  solution as bright yellow solids. Further purification was usually not necessary but the complexes were routinely recrystallized once by diethyl ether vapor diffusion into a medium concentrated MeCN solution. By this technique suitable crystals could be obtained for X-ray structure analysis of 2 (see next section). In contrast to the bis(terpyridine)ruthenium(II) complexes, a color change (by visual inspection) cannot serve as an indication for complex formation as bis(terpyridine)zinc(II) complexes possess no MLCT or LMCT transitions (d<sup>10</sup> ion).<sup>51</sup> Some photophysical key parameters of the studied compounds are given in the corresponding section (*vide infra*).

The complexes may be distinguished from the pure ligand in the usual manner by <sup>1</sup>H NMR spectroscopy due to characteristic shifts of the proton resonances up on complexation,<sup>68</sup> *i.e.*, the 3'/5'-protons on the 4'-substituted tpy ligand, which thus appear as a singlet resonance, undergo a downfield shift or the pronounced upfield shift of the 6/6"-protons (Fig. 1). The 10-methylacridinium compounds of the series can also be easily assigned due to the signal of the methyl group protons at 4.74 ppm for the MeATT<sup>+</sup> ligand and 4.92 ppm for the corresponding complex in MeCN-d<sub>3</sub>, respectively (omitted in Fig. 1, see ESI<sup>‡</sup>). Full NMR spectroscopic assignment was possible by means of 2D techniques (see ESI for spectra<sup>‡</sup>) and comparison to the Ru<sup>II</sup> analogs.<sup>53</sup>

Furthermore, the success of the anion metathesis could be directly proven by <sup>19</sup>F NMR spectroscopy<sup>69</sup> where the PF<sub>6</sub><sup>-</sup> counterion gives rise to a doublet at -72.3 ppm ( $J_{\rm P,F}$  708 Hz) vs. the singlet resonance of CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> at *ca.* -77 to -80 ppm.<sup>70</sup> The infrared spectra of 1 and 2 show only marginal differences and are dominated by the very strong absorption of the PF<sub>6</sub><sup>-</sup> ion at 834 ± 3 cm<sup>-1</sup>.<sup>69</sup>

Mass spectrometric (MS) analysis was particularly difficult for the kinetic labile Zn<sup>II</sup> complexes<sup>71</sup> compared to the corresponding Ru<sup>II</sup> complexes.<sup>53</sup> High resolution MS-ESI spectra



**Fig. 1** Partial <sup>1</sup>H NMR spectra (aromatic region) and assignment of the terpyridine proton resonances from the ligands (MeATT<sup>+</sup>, violet; ATT, green) and the corresponding Zn<sup>II</sup> complexes (**1**, red; **2**, cyan) recorded in MeCN-*d*<sub>3</sub> solution, except for the ATT ligand which had to be recorded in CDCl<sub>3</sub> (crossed out signal at 7.26 ppm) due to solubility reasons.

could be obtained for 2 with a m/z peak pattern for the  $[M - 2 \times PF_6]^{2+}$  pseudo-molecular ion at m/z 684.09337 and a wellresolved isotope pattern, but the m/z 507.2 ligand signal constitutes usually the base peak in low resolution ESI spectra. For complex 1 no pseudo-molecular peak could be observed. Even with the MALDI-ToF technique and a non-protic matrix, such as DCTB,‡ loss of a ligand and substitution by a fluoride ion (or matrix molecule in case of DHB) was found as the strongest signal (see ESI‡). The fluoride ion source originates presumably from the decomposition of the  $PF_6^-$  counterion under MALDI conditions.

#### Crystallographic results

The molecular structure of the complex cation  $[Zn(MeATT)_2]^{4+}$ (2) is shown in Fig. 2. Selected bond lengths and angles are compiled in Table 3 together with selected references and DFT calculated geometries for 1 and 2.

The bond lengths and angles for the  $bis(\kappa^3 N, N', N'')$  coordinated metal center are in good agreement with several structure reports for the pristine  $[Zn(tpy)_2]^{2+}$  complex,<sup>72</sup> *i.e.*, the average distance (*d*) of the principal axis ( $d_{avg.}(Zn-N')$  2.084 ± 0.011 Å) or the corresponding angle which commonly



**Fig. 2** Structure of the  $[Zn(MeATT)_2]^{4+}$  cation (2) in  $[2][PF_6]_4 \times 5$  MeCN with thermal ellipsoids plotted at the 50% probability level. Important atoms are labeled but hydrogen atoms, solvent molecules, and counterions are omitted for clarity.

derives from the ideal 180° geometry ( $\angle_{avg.}(N'\text{-}Zn\text{-}N')$  172.9  $\pm$  6.1°).

Only a few 4'- $\pi$ -extended bis(terpyridine) complexes of  $Zn^{II}$ have been reported to date,<sup>73</sup> among them *p*-biphenyl,<sup>73b</sup> *p*-terphenyl<sup>73c</sup> as well as *p*-phenyl-conjugates with 1,2,4-triazole<sup>73d</sup> or carbazole<sup>73e</sup> moieties and recently a well-comparable 4'-(4pyridin-4-yl)phenyl extended complex.73f However, to the best of our knowledge, no thienvl-substituted Zn<sup>II</sup> complex has been reported yet, which limits the direct comparison to the phenyl-spacer. Statistical evaluation of the conjugated complexes shows a marginally shorter bond length of the principal coordination axis  $(d_{ave}(Zn-N') 2.070 \pm 0.014 \text{ Å})$  but a similar non-linearity at this axis ( $\angle_{avg.}(N'-Zn-N')$  174.6  $\pm$  2.0°). The remaining Zn-N'/N" bond lengths of the coordination sphere are elongated (ca. 0.11 Å) and unequally distributed (ca. 0.01 Å) between the two terpyridine ligands and can be averaged to 2.183  $\pm$  0.017 Å. The individual angle to the main axis N'/N"–Zn–N' corresponds to 75.5  $\pm$  0.8°.

The structural parameters of 2 fall well within all of these boundaries (see Table 3).

No remarkable packing features were found, *i.e.*, in contrast to the 4'-(4-pyridin-4-yl)phenyl extended bis(terpyridine)zinc(II) complex reported by Hayami *et al.*<sup>73f</sup> The terpyridine fragment of **2** shows a weak interaction with the outer pyridyl-ring among one another ( $d(py^{A}_{ctr.}...py^{A}_{ctr.})$  3.709 Å), which is typical for terpyridine solid state assemblies.<sup>74</sup> The acridinium units face each other with a considerable offset (only partial overlap at the outer ring) excluding any strong  $\pi$ - $\pi$  interaction ( $d(acr^+_{plane}...acr^+_{pl.})$  3.529 Å).

For the structure description of the ligand fragment of 2 other thienyl-tpy metal ion complexes may also serve for comparison, *i.e.*, 4-bromo- and 5-bromo-2-thienvl substituted bis-(terpyridine) complexes of Ru<sup>II</sup>.<sup>75</sup> For this series of complexes, the mean bond distance between the tpy unit and the thienyl spacer lies within  $1.467 \pm 0.004$  Å. Therefore, complex 2 shows a slightly elongated bond on one ligand in the solid state assembly (see Table 3). On the other hand, the 4'-phenyl-tpy derived Zn<sup>II</sup> complexes show a mean bond distance for the inter-connecting bond of 1.475 ± 0.033 Å. The dihedral angle  $\varphi_{\rm tpy-ph}$  averages to 26 ± 15°, for these complexes whereby the large standard deviation indicates a rather rotational flexible phenyl unit. Similar indications were found for the thienyl spacer by statistical X-ray structure evaluation ( $\varphi$  8.6 ± 9.3°) and DFT calculations ( $\varphi$  20.4 ± 1.9°; both for Ru<sup>II</sup>) by us.<sup>53</sup> However, in the case of the 4'-phenyl-tpy derived Zn<sup>II</sup> complexes some examples with a nearly planar arrangement of  $\varphi_{\text{tpy-ph}}$  (1 ± 1°) on at least one ligand fragment have also been observed.73b,d

## Photophysical properties

The molar absorption spectra of the ligands and the corresponding Ru<sup>II</sup> and Zn<sup>II</sup> complexes are depicted in Fig. 3 together with the solar irradiance air mass (AM) 1.5 spectrum. Some photophysical key parameters are compiled in Table 2. The photophysical properties of the acridine and 10-



**Fig. 3** UV/Vis absorption spectra (left scale) of the ATT and MeATT<sup>+</sup> ligands, and acridine (dotted lines in shades of blue), the corresponding  $Zn^{II}$  complexes **1** and **2** (shades of green), and the  $Ru^{II}$  complexes **3**, **4**, **5** as well as  $[Ru(bpy)_3]^{2+}$  (orange-red) in MeCN. Part of the AM 1.5 solar spectra<sup>82</sup> (right scale, 37° global tilt irradiance) is also shown in semi-transparent. Note that the scaling was arbitrarily chosen.

methylacridinium-substituted bis(terpyridine)ruthenium( $\pi$ ) complexes and the ligands alone have been described separately.<sup>53</sup> Briefly, acridines show local absorbance maxima at 390, 360, and 345 nm<sup>76,77</sup> whereas the narrow absorption band at 365 nm and a broader second band at *ca.* 420–450 nm<sup>78</sup> (with ~20 000 and 7000 M<sup>-1</sup> cm<sup>-1</sup>, respectively) are typical for acridinium ions (see Fig. 3).<sup>79</sup>

The spectral signature of the  $Zn^{II}$  complexes 1 and 2 resemble largely the one of the pure ligands but with an approximately doubled molar extinction coefficient ( $\varepsilon$ ) as supposed for the formation of a homoleptic bis(terpyridine) complex. Differences are visible in the 300 to 350 nm region where pronounced absorption bands emerge in the case of 1 and 2 (see Fig. 3). These differences can be attributed to the saturation, *i.e.* by coordination or protonation, of the terpyridine nitrogen atoms and the thereby induced conformational changes. This phenomena was *i.a.* studied for the 4'-(9-anthracenyl)-terpyridine ligand in the early seminal work of Maestri *et al.*<sup>51</sup> as well as for pyrenyl-substituted terpyridines more recently.<sup>49</sup>

For the  $[Zn(MeATT)_2]^{4+}$  complex (2) the local maximum in the visible range is slightly blue shifted (437 nm) in comparison to the MeATT<sup>+</sup> ligand (454 nm) but the absorption bands itself are very similar in shape (see Fig. 3). The ATT ligand and its Zn<sup>II</sup> complex 1 show only a slight absorbance in the visible region, *viz*. the *ca.* 385 nm bands tail towards 410 and 430 nm, respectively, due to the large  $\varepsilon$  values. The increase in  $\varepsilon$  is caused by the increased conjugation as well as favorable properties of the thienyl linker, *e.g.* as shown in combination with a triphenylamine (TPA) unit,<sup>80</sup> which can be reasoned by the bathochromic shift comparing pristine acridine to the AT or the ATT ligand. The slightly stronger increase in  $\varepsilon$  (more than twice) for the Zn<sup>II</sup> complexes may also be caused by changes in intra-ligand (IL) transitions<sup>49</sup> due to coordination – even for "innocent" d<sup>10</sup> metal ions which were studied in detail by Schubert *et al.*<sup>81</sup>

The Ru<sup>II</sup> complexes show the typical broad MLCT absorption band in the 450–550 nm region. As expected,<sup>80</sup> the thienyl-linker caused a large increase in  $\varepsilon$  for 4 and 5 in comparison to the linker-free [Ru(AT)<sub>2</sub>]<sup>2+</sup> complex (3). The influence of the acridinium unit is discernible by the increased absorption in the 410–470 nm region for 5 as deduced from the Zn<sup>II</sup> counterpart 2 (see Fig. 3).

The fluorescence quantum yields ( $\Phi_{\rm fl}$ ) in MeCN, a typical example of a polar organic solvent, are low (~0.02) in all cases where fluorescence can be observed (see Table 2). This is expected for rotational unhindered acridinium ions with a donor-type arene-substituent<sup>79,83</sup> (*e.g.* 9-thienyl-10-methylacridinium  $\Phi_{\rm fl}$  < 0.005,  $\tau \sim 100$  ps;<sup>79a</sup> 9-ph- $\Phi_{\rm fl}$  0.063–0.005,  $\tau$  1.5 ns;<sup>79c,d</sup> 9-p-biph- $\Phi_{\rm fl}$  0.020,  $\tau$  1.2 ns<sup>79c,d</sup>) and as well expected for pristine and substituted acridines based on the literature data for organic solvents (*e.g.* 9-phenylacridine  $\Phi_{\rm fl}$  0.080,  $\tau$  1.4 ns<sup>84</sup> (for MeOH)).<sup>84–86</sup> For the ATT ligand and its Zn<sup>II</sup> complex fluorescence lifetimes of 0.73 and 0.22 ns were determined, respectively, corroborating the aforementioned literature.

To gain further insights into the photophysical behavior of the compounds transient absorption (TA) measurements were carried out. The signature of the TA spectrum for the  $[Zn(ATT)_2]^{2+}$  complex (1) is very similar to the spectra for the Ru<sup>II</sup> counterparts reported elsewhere,<sup>53</sup> with the exception of the <sup>1</sup>MLCT bleaching (see Fig. 4). The major decay component

**Table 2** Lowest energy absorption band maximum  $(\lambda_{abs}/nm, \varepsilon \times 10^3/M^{-1} \text{ cm}^{-1}$  in parenthesis), highest energy emission maximum  $(\lambda_{em}/nm)$ , quantum yield of fluorescence  $(\Phi_{fl})$ , and lifetime  $(\tau/ns)$  in deaerated MeCN solution at r.t

Compound	$\lambda_{\mathrm{abs}}\left(arepsilon ight)$	$\lambda_{\rm em}$	$arPhi_{ m fl}$	$\tau/\mathrm{ns}$
ATT	387 (11.3)	589	$0.017^{a}$	$0.73 \pm 0.02^b$
MeATT <sup>+</sup>	454 (8.8)	d	_	$0.71 \pm 0.06^{c}$ n.d.
$Zn(ATT)_2^{2+}$	387 (32.5)	545	$0.019^{a}$	$0.22 \pm 0.01^{b}$
				$0.22 \pm 0.05^{\circ}$ 15 800 + 600^{\circ}
Zn(MeATT) <sub>2</sub> <sup>4+</sup>	$457(20.3)^{e}$	d	_	$0.14 \pm 0.02^d$
$\operatorname{Ru}(\operatorname{AT})_2^{2+f}$	484 (21.2)	d	—	$80 \pm 6^{c}$
$\operatorname{Ru}(\operatorname{ATT})_2^{2+f}$	504 (50.6)	d	—	$0.27 \pm 0.03^{c}$
$\operatorname{Ru}(\operatorname{MeATT})_2^{4+f}$	510 (47.4)	d	_	$\frac{1090 \pm 140^c}{0.17 \pm 0.02^c}$

<sup>*a*</sup> Determined by the relative method. Error ± 0.011; average of independent determinations in both groups. Reference standard (all aerated) were 9,10-diphenylanthracene in EtOH  $\Phi_{\rm fl}$  0.95, quinine disulfate in 0.05 M H<sub>2</sub>SO<sub>4</sub>  $\Phi_{\rm fl}$  0.55, fluorescein in 0.1 M NaOH  $\Phi_{\rm fl}$  0.92 (cross-checked and within 10% of the values reported in ref. 59). <sup>*b*</sup> To compare both methods, explicit errors for  $\tau$  are given, *viz.* determined by time correlated single photon counting (TCSPC). <sup>*c*</sup> Determined by transient absorption spectroscopy. <sup>*d*</sup> Not luminescent. <sup>*e*</sup> Shoulder (weak vibronic structure typical for acridinium ions),  $\lambda_{\rm max}$  437 (22 500 M<sup>-1</sup> cm<sup>-1</sup>). <sup>*f*</sup> Ref. 53.



**Fig. 4** Upper part: differential absorption spectra (visible) obtained upon fs flash photolysis (387 nm, 200 nJ per pulse) of  $[Zn(ATT)_2]^{2+}$  (1) in deaerated MeCN with several time delays between 0.1 and 7500 ps. Lower part: differential absorption spectra (visible) obtained upon ns flash photolysis (355 nm, 6 mJ per pulse) of 1 in deaerated MeCN with time delays of 1.6 µs, 7.5 µs, 29 µs and 88 µs.

of complex 1 (225 ± 47 ps) agrees well with the fluorescence decay dynamics as determined by TCSPC. However, in TA spectra the formation of a signature with two weak but distinct maxima at 440 and 645 nm at early times is visible (1–6 ps) (see Fig. 4). At later times, *i.e.*, >150 ps, a slightly different signature emerges with two well-defined maxima at 475 and 625 nm (see Fig. 4). This transient does not decay within our time resolution of 7.5 ns. The decay of this species was subsequently determined by ns laser flash photolysis and was shown to be quite slow (15.8 ± 0.6 µs), exceeding the Ru<sup>II</sup> counterpart (1.09 µs) by an order of magnitude. It was readily quenched by O<sub>2</sub>. Therefore, we assigned this to the formation of the intra-ligand triplet state <sup>3</sup>IL.

The signature on an early timescale observed for the ATT complex **1** is attributed to the singlet excited state. This assignment is based on a comparison with the TA spectra of the uncomplexed ATT ligand (see ESI<sup>‡</sup>) which resembles that of **1** at early timescales, *viz.* a weak maximum at *ca.* 440 nm and a second, broader one at 630 nm. This transient decays mono-exponentially within 713 ± 58 ps which coincides with the fluorescence decay (see Table 2).

The  $[Zn(MeATT)_2]^{4+}$  complex (2) shows only a very weak transient signal (ESI<sup>+</sup>) with two distinct transient absorption bands at *ca.* 495 and 670 nm, which transform into a broader

signal centered at 580 nm, which then later decays quickly (144  $\pm$  17 ps).

Further insight came from fluorescence upconversion experiments following excitation at 387 nm and detection at 580 nm. For the  $[Zn(ATT)_2]^{2+}$  complex (1) two decay lifetimes were derived. One, which is about 0.23 ± 0.08 ns, and is therefore assigned to the fluorescence lifetime, determined already by TCSPC and fs-TA and the second one of about 85 ps, which might be attributed to the ISC into the triplet state (see ns laser flash results). A similar behavior was found for the ATT ligand. This revealed basically the same decay as derived from TCSPC and fs-TA (0.70 ± 0.07 ns) but also a faster component of *ca.* 48 ps, which is attributed to the ISC due to the overall low fluorescence quantum yields. The  $[Zn(MeATT)_2]^{4+}$  complex (2) exhibits markedly shorter decay components of 4.5 ps and 26 ps, whereby the shorter component agrees well with the rise of the fs-TA signal at 580 nm (see ESI<sup>‡</sup>).

## **Computational studies**

Because no structural data could be obtained experimentally for 1, density functional theory (DFT) calculations were performed by the aid of the popular B3LYP/6-31G(d)/LANLDZ approach (=LACVP\*).<sup>37,43b</sup> The optimized structural parameters are included in Table 3. The second purpose was to obtain insight in the electronic properties of the complexes and to clarify the localization (in terms of energy as well as structure) of the lowest lying triplet state (T<sub>1</sub>).

DFT relaxation without restraints of the experimentally determined structure of complex 2 resulted in the elongation

of the N–Zn bond but further decrease of the dihedral angle  $\phi$ between the terpyridine and thienyl unit. The bond distance overestimation of 0.066 ± 0.007 Å is typical for the DFT approach at this level of theory. The higher dihedral angle  $\phi$ found experimentally on one ligand fragment might not be overrated as the rotational flexibility of the thienvl group is high (vide supra). The second dihedral angle ( $\omega$ ) between the spacer and the acridine/acridinium moiety was correctly predicted by this method. In general, the X-ray relaxation by DFT gave a structure for the complex cation within a root-mean-square deviation (RMSD) of 0.59 Å to the experimental data set. An independent computational run to find the  $S_0$  geometry (of same conformation) resulted in a geometry with a RMSD of 0.64 Å but 3 meV lower in energy. We are therefore confident that the DFT results are also acceptable for **1**.

For both compounds the MO analysis showed that the highest occupied molecule orbitals (HOMO 0/–1) as well as the lowest unoccupied MO set (LUMO 0/+1) are not degenerated (no perfect  $D_{2d}$  symmetry) but nearly isoenergetic (within 11 meV,<sup>‡</sup> artificially degenerated in Fig. 5). For the 1 the frontier orbital sets are localized mainly on the acridinium fragment with some contributions from the thienyl linker. More interesting, in this regard, is the ATT complex 2 where the LUMO set is mainly composed by terpyridine fragment contributions. As supposed, and in contrast to the DFT calculations for Ru<sup>II</sup> series,<sup>53</sup> no metal ion influence is deducible for the first few occupied and unoccupied MOs in the Zn<sup>II</sup> complexes. The individual MO plots are shown in the ESI.<sup>‡</sup>

**Table 3** Comparison of selected experimentally determined structural parameters (distances (d)/Å, angles/°) with B3LYP/6-31G(d)/LANLDZ DFT calculations for complexes 1 and 2 (and  $\Delta E$ (SCF) energies to S<sub>0</sub>/eV) as well as experimental data of some reference complexes

	$[Zn(MeATT)_2]^{2+}(2)$				$\left[\text{Zn}(\text{ATT})_2\right]^{2+}(1)$		$[Zn(R-tpy)_2]^{2+}, 4'-R=$		
Parameter	Exptl.	DFT relaxed	S <sub>0</sub>	T <sub>1</sub>	S <sub>0</sub>	T <sub>1</sub>	Ph <sup>73a</sup>	<i>p</i> -biph <sup>73b</sup>	4-pyph <sup>73f</sup>
$\Delta E(SCF)$	n.a.	0.003	0	1.741	0	1.627	n.a.	n.a.	n.a.
$d(N_2-Z_n)^a$	2.088(3)	2.154	2.153(1)	2.153	2.150	2.152	2.069(4)	2.077(3)	2.084(4)
$d(N6-Zn)^a$	2.078 (3)			2.151		2.138	2.091(4)	2.066 (3)	2.067(4)
d(N1-Zn)	2.180(4)	2.255(1)	2.255(1)	2.254(1)	2.256	2.256(1)	2.192(4)	2.185 (3)	2.181(4)
d(N3-Zn)	2.196 (4)						2.193 (4)	2.174(3)	2.177(4)
d(N5-Zn)	2.197 (4)						2.178(4)	2.192 (3)	2.168(5)
d(N7-Zn)	2.189 (4)						2.217(4)	2.195 (3)	2.168(5)
$d(C_{tpv}-C_{spacer})$	1.461 (6),	1.463	1.464	1.464,	1.461	1.461,	$1.475(7)^{c}$ ,	$1.486(5)^{c}$ ,	$1.487(6)^{c}$ ,
	1.479 (6)			$1.459^{b}$		$1.441^{b}$	1.469 (7)	1.478 (5)	1.471 (7)
$d(C_{spacer}-C_{acr})$	1.479 (6),	1.479(1)	1.480,	1.479,	1.483(1)	1.483,	n.a.	$1.483(5)^d$ ,	$1.478(6)^d$
	1.484 (6)		1.478	$1.448^{b}$		$1.398^{b}$		1.484 (5)	1.482 (7)
$d(N4/8-C_{Me})$	1.478 (6),	1.480	1.480	1.480,	n.a.	n.a.	n.a.	n.a.	n.a.
	1.493 (6)			$1.475^{b}$					
$\angle$ (N2–Zn–N6) <sup><i>a</i></sup>	176.02(15)	179.33	179.22	178.99	179.56	179.73	173.2(2)	175.6(1)	177.8(2)
∠(N2–Zn–N1)	75.06 (13)	73.99 (1)	74.00	73.97	74.02(1)	73.95	75.4(1)	75.5 (1)	75.8 (2)
∠(N2–Zn–N3)	75.25(13)		73.97	74.02(1)		73.93	75.5(1)	75.6(1)	76.3 (2)
∠(N6–Zn–N5)	75.43(14)		74.00(1)			74.20	75.3(1)	75.6(1)	76.1(2)
∠(N6–Zn–N7)	75.64(14)						74.9(1)	75.9(1)	75.4(2)
$\phi_{\mathrm{tpy-spacer}}^{e}$	20.8, 30.9	18.3, 20.4	18.4, 20.3	$17.1,^{b}_{}22.4$	14.6, 17.4	$5.2,^{b}15.6$	42.6, 31.3	16.8, 0.3	46.2, 9.4
$\omega_{\text{spacer-acr}}^{e}$	66.7, 71.3	68.9, 71.4	69.9, 71.4	$52.5,^{b}70.4$	74.9, 77.2	$10.3,^{b}77.3$	n.a.	n.a.	n.a.

<sup>*a*</sup> Principal coordination axis. For comparison with reported X-ray structures which employed a different numbering scheme care was taken to adopt the alignment accordingly, *i.e.*, lowest number to the left. <sup>*b*</sup> Ligand fragment with triplet localization. <sup>*c*</sup> Bond distance of  $C_{tpy}$ - $C_{spacer=phenyl}$ . <sup>*d*</sup> Bond distance of  $C_{spacer}$ - $C_{phenyl}$  instead of  $C_{acr}$ . <sup>*e*</sup> Dihedral angle was measured as *cis*-torsion angle along the S-C-C-C bonds. For spacer where no preferred side exists, *e.g.* phenyl, the lower angle is given.



**Fig. 5** Molecule orbital (MO) energy levels for **2** and **1** as calculated by (TD-)DFT. The lowest energy optical transitions are indicated by arrows (grey shading symbolizes size of CI coefficient) with their corresponding energy and oscillator strength (*f*). The individual contributions to the MOs from the different units of the complex are color coded as follows: tpy (blue), thienyl (orange), acridine/acridinium (green). Note that Zn contributions (cyan) are virtually not present in the selected energy range and that the degeneracy threshold was manually set to 25.6 meV = kT (298 K,  $D_{2d}$  approximation) to visualize otherwise overlapping MOs.

TD-DFT calculations predict the lowest energy transition for 2 at 473 nm with considerable oscillator strength (f 0.574) which is an overestimation of the transition energy by *ca*. 0.1 eV only, compared to the experimentally found data (Table 2). The transition is composed from the frontier orbital sets (HOMO/LUMO±0/1). The second lowest absorption of significant oscillator strength f is predicted at 350 nm (f 0.642) and corresponds to a transition from the HOMO set (0/–1) to the unoccupied second lowest MOS (+2/3) – an underestimation in energy of the typical second absorption band for acridinium compounds at 365 nm.

For **1** a pure HOMO to LUMO transition is calculated at 452 nm followed by a nearly degenerated transition at 396/394 nm from the HOMO set (0/-1) to higher unoccupied MOs (*viz.* LUMO+2/3/4). The latter transition is matching well to the experimental spectra whereas the aforementioned ILCT (acr  $\rightarrow$  tpy) transition is largely overestimated (0.46 eV). Further explicit data on the calculated transitions are compiled in the ESI.<sup>‡</sup>

Triplet TD-DFT calculations (in  $S_0$  geometry approximation) suggested vertical  $S_0 \rightarrow T_1$  transitions at 689/687 nm<sup>87</sup> (1.80 eV) for 2 and 684/680 nm<sup>87</sup> (1.82 eV) for 1, both energetically well separated (>0.62 eV) from higher energy transitions. The excitation energies are similar to the energies obtained from  $\Delta E(SCF)$  calculation for the optimized geometries (*viz.* adiabatic, see Table 3). In the case of ATT complex 1 the primary MOs involved in the  $S_0 \rightarrow T_1$  transition are the HOMO set (0/-1) and the higher unoccupied  $S_n$  states (LUMO+2/3/4) whereas for 2 only the HOMO to LUMO (0/±1) sets are involved. Both findings are in agreement with the transient absorption data for a <sup>3</sup>IL-based but differently located  $T_1$  state.

In both cases bond and angle distortions on the triplet localized ligand fragment (for geometry and spin density plots see ESI<sup>‡</sup>) are observed. This was found to be especially severe for the acridine moiety in 1 which is bent out-of-plane in "butterfly"-like fashion along the C9–N10 atom axis ( $\gamma$  158.8°,  $\alpha$  8.5°,  $\beta$  25.2°,  $\Delta$ (C9) 0.34 Å,  $\Delta$ (N10) 0.10 Å; see ref. 88 for explanation of the parameters), as also found for the Ru<sup>II</sup> counterparts by DFT calculations,<sup>53</sup> or experimentally for over-crowded acridinium ions.<sup>88</sup>

#### Photocatalytic studies

In polypyridine chemistry  $Zn^{II}$  complexes are commonly used as references to characterize the coordinated ligand without interference from MLCT transitions. As indicated in the Introduction, bathochromically-shifted highly absorbing  $Zn^{II}$  complexes, *i.e.*, by suitable dye substitution and  $\pi$ -conjugation, may also be useful for sensitization applications such as DSSCs.<sup>11</sup> In this regard, preliminary tests by the use of the *in situ* capping technique<sup>11</sup> with the ATT and MeATT ligand were discouraging and showed no noteworthy activity.

From the transient absorption data, it is evident that the acridine chromophore acts as a triplet energy sink which imposed the use as an  $O_2$  ( $^1\Delta_g$ ) sensitizer. This is especially interesting since the neat absorption data of the Zn<sup>II</sup> complexes are roughly comparable with typical C^N Ir<sup>III 89</sup> complexes or improved multichromophoric versions studied by the groups of Murata *et al.* and Zhao *et al.*<sup>36,43</sup> In this regard, the [Zn(MeATT)<sub>2</sub>]<sup>4+</sup> complex (2) resembles the absorption profile of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> quite well whereas the corresponding Ru<sup>II</sup> complexes of this work exceed all examples in solar spectra coverage (see Fig. 3).

In the present case, the photooxidation reaction of DHN to Juglone<sup>23</sup> is used as an assay<sup>36,91</sup> for the O<sub>2</sub> ( $^{1}\Delta_{g}$ ) generation efficiency by monitoring the change of the absorption of DHN at 300 nm in a MeCN–MeOH (4:1) mixed solvent system (Scheme 2).

We avoided using strictly 10 mol% due to the different intrinsic molar absorptivities of the studied compounds and highly absorbing dyes, such as MB, typically employed as a reference. The kinetic parameters, *i.e.*, the pseudo-first order rate constant ( $k_{obs}$ ) and initial reaction velocity ( $\nu_{initl}$ ), were calculated as reported.<sup>36</sup> The linearized data plots to determine  $k_{obs}$  (see Fig. 6) indicate valid pseudo-first order conditions in



Scheme 2 Photooxidation of DHN to Juglone by  $O_2$  ( $^{1}\Delta_{q}$ ).



**Fig. 6** Plots of  $\ln([DHN]_t/[DHN]_{t=0})$  vs. irradiation time (t) for the photooxidation of DHN using different sensitizers (color coding as in Fig. 3). The lines represent the least squares fit of the linear data regime. The different qualitative effective sensitizer concentrations (see Table 4 for explicit data) are indicated as follows: (-) < (---) < (...).

the time-period of the experiments (30 min) by correlation coefficient  $R_2 > 0.98$  for the least squares fit. The results are summarized in Table 4. Deviations of the DHN consumption, *viz.* violation of the pseudo-first order conditions, are visible for MB and our second standard  $[\text{Ru}(\text{bpy})_3]^{2+}$  both exemplary also employed at a higher concentration (3.1 and 12 mol%) and *viz.* absorbance, respectively.<sup>92</sup> This justifies the call for low absorbance measurements<sup>37c,43b</sup> instead of comparison by mol%.

Murata *et al.*<sup>36</sup> report non-linear behavior for the DHN consumption after about 20 min for their data set. It should also be mentioned that the product, Juglone, absorbs in the visible range and therefore is competing with incident photons. Therefore, although its molar absorption coefficient is quite low (3811  $M^{-1}$  cm<sup>-1 36</sup>), the use of early kinetics is favorable. On the other side, this limits the possibility to achieve total conversion, except for non-overlapping sensitizers like MB.

Despite the different absorption profile, we chose MB as the primary standard for the calculation<sup>60</sup> of  $\Phi_{\Delta}^{\text{sens}}$ . The value of  $\Phi_{\Delta}^{\text{MB}}$  (~0.5) appears to be independent of the solvent and concentration range.<sup>90,93</sup> We chose the recommended value of  $0.50^{54}$  and a good reproducibility of  $\Phi_{\Delta}^{\text{MB}}$  was achieved in the given concentration range for our data (see Table 4, entry set 1).

As indicated above, we used  $[Ru(bpy)_3]^{2+}$  as a cross-reference to account for the absorption profile differences in between MB and the compounds under study. However, it should not remain unmentioned here that  $[Ru(bpy)_3]^{2+}$  is somehow problematic because a more diversified data background exists in comparison to MB. This was *i.a.* summarized in the review of DeRosa et al.,<sup>27</sup> and by Wilkinson and Abdel-Shafi et al.<sup>38</sup> as well, who reported a value of 0.57 for  $\Phi_{\Delta}^{\text{Ru}(\text{bpy})3}$  in MeCN. Orellana and Braun et al. suggested 0.73 (MeOD- $d_3$ ),<sup>45</sup> but Tanielian et al. determined for  $\Phi_{\Delta}^{\text{Ru(bpy)}3}$  0.77 (MeCN) and 0.87 (MeOH).<sup>94</sup> In the latter case, an incident light  $\times \Phi_{\Delta} vs.$  concentration study was also performed for [sens] >  $8 \times 10^{-5}$  M. However, our sensitizer concentrations are below this threshold. There is a clear trend of lower  $\Phi_{\Delta}$  values at lower concentrations and light intensities as examined from the first few data points depicted by Tanielian et al.94 It is not within the scope of this work to evaluate such effects, but our (low concentration) data set reflects a value of 0.57 for  $\Phi^{\text{Ru(bpy)}_3}_{\Lambda}$  quite well.

**Table 4** Sensitizer concentration and light harvesting parameters (absorbance *A* at given wavelength and absorption area correction factor  $F_{area}$ ), pseudo-first-order kinetics parameters of DHN consumption ( $k_{obs}$ ,  $v_{initl}$ ), quantum yield for O<sub>2</sub> ( $^{1}\Delta_{g}$ ) generation ( $\Phi_{\Delta}$ ) and yields of Juglone using complexes **1–5**, the ATT ligand, and MB (=reference standard<sup>54,90</sup>) as well as Ru(bpy)<sub>3</sub><sup>2+</sup> as photo-catalysts

Entry#	Compound	[sens] mol%	$k_{\rm obs} \times 10^{-3}  {\rm min}^{-1}$	$[\mathrm{DHN}]_{t=0}\times 10^{-4}~\mathrm{M}$	$\nu_{\text{initl}} \times 10^{-6} \text{ M min}^{-1}$	A (at $\lambda_{max}$ ) a.u. (nm)	$F_{\text{area}}^{a}$ (%)	$\Phi^{ m sens}_{\Delta}$	Yield <sup>b</sup> (%)
1.1	MB	0.71	-22.7	1.68	-3.66	0.113 (655)	100	$0.50^{54,90}$	54
1.2	MB	1.4	-34.5	1.59	-5.53	0.216 (655)	174	0.42	56
1.3	MB	3.1	-90.8	1.53	-13.9	0.448 (655)	358	0.51	71
2.1	$Ru(bpy)_3^{2+}$	4.3	-30.0	1.52	-4.57	0.099 (450)	112	0.52	46
2.2	$Ru(bpy)_3^{2+}$	12	-67.4	1.53	-10.3	0.295 (450)	271	0.50	74
3	$Ru(AT)_2^{2+}$	3.5	-12.4	1.58	-1.96	0.120 (484)	172	0.15	17
4.1	$Ru(ATT)_2^{2+}$	0.97	-34.4	1.61	-5.88	0.079 (504)	91	0.82	52
$4.2^{c}$	$Ru(ATT)_2^{2+}$	$3.5\pm0.1$	$-114 \pm 1$	$1.51\pm0.02$	$-17.4\pm0.01$	$0.273 \pm 0.05 (504)$	$282\pm5$	$0.81 \pm 0.01$	$70\pm3$
5	$Ru(MeATT)_2^{4+}$	1.4	-6.44	1.64	-1.05	0.108 (510)	142	0.10	10
6	ATT	5.9	-2.5	1.59	-0.39	0.106 (387)	44	0.12	12
7.1	$Zn(ATT)_2^{2+}$	2.0	-8.5	1.69	-1.46	0.112 (387)	39	0.49	16
7.2	$Zn(ATT)_2^{2+}$	4.1	-18	1.63	-2.93	0.216 (387)	77	0.50	47
8.1	$Zn(MeATT)_2^{4+}$	1.6	-9.8	1.68	-1.66	0.061 (437)	83	0.26	8
8.2	$Zn(MeATT)_2^{4+}$	7.6	-14	1.57	-2.24	0.270 (437)	281	0.11	26

<sup>*a*</sup> Absorption correction factor  $F = 1 - 10^{-A(\lambda)} = 1 - 10^{-e(\lambda)cl}$  integrated over 385–800 nm and normalized to 100% for MB as a standard. <sup>*b*</sup> Yield of Juglone after 30 min (extrapolated if necessary) calculated from absorbance change  $\Delta(A - A_{t=0})$  at  $\lambda_{\max}$  427 nm (3811 M<sup>-1</sup> cm<sup>-1</sup>).<sup>36 c</sup> Average values of an independent determination on two different days.

The observed rate constants  $(k_{obs})$  and initial reaction velocities  $(v_{initl})$  of our data set are comparable to values reported by Zhao *et al.*<sup>43</sup> for (multichromophoric) Ir<sup>III</sup> and Pt<sup>III</sup> complexes as well as one modified  $[Ru(bpy)_3]^{2+}$  example studied by them. However, in our case the DHN consumption velocities span a wider range  $(10^{-7}-10^{-5} \text{ M min}^{-1})$ . Direct comparison is only possible in a singular case where MB was employed as a reference together with the well-known  $Ir(ppy)_3$  complex as the secondary standard. For the latter the  $arPsi_\Delta$  was somehow different from the value reported by Murata et al. (0.50).<sup>36</sup> Despite the different light sources used, and in this case also solvent systems, the kinetics determined by Zhao et al. (kobs  $-41.6 \times 10^{-3} \text{ min}^{-1}$ ,  $v_{\text{initl}} - 8.32 \times 10^{-6} \text{ M min}^{-1}$ )<sup>43b</sup> matches well to our data (Table 4, entry no. 1.2 and 1.3, respectively). The kinetic data reported by Murata et al.,<sup>36</sup> among them also data for MB, are almost all an order of magnitude larger (and even more for MB) as also noticed previously.<sup>43</sup> In this regard, we concur with the argumentation of Zhao et al.43 that this might be due to higher lamp power, concentrations, and also the different implementation method (1 cm cuvettes vs. batch) employed. Yields are generally hard to compare as different end points were used across all reports. Furthermore, as indicated before, product inhibition occurs for sensitizers absorbing in the wavelength region of Juglone.

With respect to the present work, the  $[Ru(ATT)_2]^{2+}$  complex (4) clearly stands out ( $\Phi_{\Delta}$  0.82), followed by the corresponding  $Zn^{II}$  complex ( $\Phi_{\Delta}$  0.50). As indicated in the photophysical properties section the absorption profiles are quite different. Furthermore, acridine itself is also known to be a good  $O_2$  ( $^{1}\Delta_{\alpha}$ ) sensitizer, *i.e.*,  $0.83 \pm 0.01$  in MeCN and benzene,<sup>54</sup> and this value is nicely reflected by 4. However, acridine does not absorb significantly above 385 nm (=filter cut-off;  $\varepsilon$  < 730 M<sup>-1</sup> cm<sup>-1</sup>). Therefore our strategy to use the metal fragment as "antenna" and possible ISC-enhancer for the organic dye served both purposes. In this regard, it is puzzling that the Zn<sup>II</sup> complex exhibits a lower efficiency. But this might be regarded to the cut-off filter employed which could have also affected the ATT ligand itself ( $\Phi_{\Delta}$  0.10). The latter may have a low fluorescence quantum yield indicating a possibly efficient ISC but exhibits only a short excited state lifetime and no visible triplet-triplet absorption as discussed above. The efficiency of the Zn<sup>II</sup> complex can therefore be solely attributed to its long triplet state lifetime. Complex 4, on the other hand, deactivates markedly faster (but still above 1.0 µs) which may be correlated with the metal-centered states typically thermally accessible in bis(terpyridine)ruthenium(II) complexes. All other complexes feature only very short excited state lifetime. Even the  $[Ru(AT)_2]^{2+}$  complex (3) is short-lived, despite the decent absorption profile and the acridine moiety, indicating a crucial role of the thienyl-linker.

In order to gain further insight in possible reactions with O<sub>2</sub>, in particular of the acridinium compounds as shown by Griesbeck *et al.*<sup>56</sup> for the lively discussed 9-mesityl-10-methyl-acridinium system,<sup>55</sup> we studied the reaction towards the well-known limonene<sup>95</sup> and 2-methylnaphthalene<sup>96</sup> probes as substrates. The latter can only react with the superoxide ion but

not with  $O_2$  ( ${}^1\Delta_g$ ) and in our case, no reaction at all was noticed in MeCN saturated with  $O_2$ . However, with respect to the study of Griesbeck *et al.*,<sup>56</sup> we were limited to (very) polar solvents due the two- or fourfold charge of the complexes. Exemplary studies with limonene, which is a product-specific probe to  $O_2$  ( ${}^1\Delta_g$ ),<sup>95</sup> showed the expected product distribution of hydroperoxides as probed *via* NMR and GC (after reduction to alcohols with NaBH<sub>4</sub> <sup>95d,97</sup>) due to the Schenck ene reaction<sup>32</sup> of the endo-cyclic double bond.

Last but not least, the typical  $O_2$  ( ${}^{1}\Delta_{g}$ ) NIR emission at 1275 nm<sup>98</sup> could be directly observed for the well-performing  $[Ru(ATT)_2]^{2+}$  complex 4 exemplarily probed in oxygen-saturated MeCN solution at r.t. (see ESI for spectra‡).

## Conclusions

In summary, ATT ligand-based systems 1 (Zn<sup>II</sup>) and 4 (Ru<sup>II</sup>) revealed singlet oxygen  $({}^{1}\Delta_{g})$  generation with quantum yields as high as 0.82. Despite the fact that 1 (Zn<sup>II</sup>) features only a poor overlap with the solar spectrum, efficient sensitizing evolves due to a long lived triplet excited state. In stark contrast, the good spectral overlap of 4 (Ru<sup>II</sup>) with the solar spectrum assists in extending the sensitization capability of the acridine building block. The acridinium containing systems 2 (Ru<sup>II</sup>) and 5 (Ru<sup>II</sup>) as well as the linker-free acridine-terpyridine system 3 (Ru<sup>II</sup>) are ineffective sensitizers, presumably due to their short lived excited states. From the aforementioned it seems interesting to revisit some of the highly optimized Ru<sup>II</sup> conjugates with respect to their singlet oxygen production. Notably, the design of metal complex containing conjugates carrying organic building blocks en-route towards the longlived triplet energy sinks bears great potential. Nevertheless, stability with respect to singlet oxygen and photo-degradation needs careful consideration. Such conjugates may not be of greatest interest for the area of PDT - due to the presence of metal ions - but may evolve as efficient photosensitizers in green photochemistry. Here, widely used "off-the-shelf" organic sensitizers such as MB, RB, and others lack the needed long term stability.

## Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) and the Bayerische Staatsregierung as part of the "Solar Technologies go Hybrid" initiative. The authors are grateful to Liselotte Siegfried and Dr Biljana Bozic-Weber (University of Basel) for preliminary DSSC tests of the ligands in Zn<sup>II</sup> complexes, to PD Dr Tilman Kottke (Bielefeld University) for the use of spectroscopic equipment, and to Dr Yvonne Hertle and Prof. Dr Thomas Hellweg (Bielefeld University) for the use of the 400 W high pressure Hg lamp. We furthermore thank the regional computing center of the University of Cologne (RRZK) for providing the CPU time on the DFG-funded supercomputer 'CHEOPS' and support.

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- 92 We observed a reduction of the apparent  $O_2$  ( ${}^{1}\Delta_g$ ) quantum yield if highly absorbing solutions (A > 0.7) were used under the same measurement conditions. This can be attributed to an obvious internal filter effect in this semi-preparative method of operation. It might explain also the problems encountered by Murata *et al.* for their cross-check with MB (used ~ $3.6 \times 10^{-5}$  M,  $A \approx 3.3$  in 1 cm cuvettes) *vs.* the low absorbing Ir<sup>III</sup> complexes and recent adjustment in a similar batch procedure by Zhao *et al.*
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