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_2 ($^1\Delta_g$) generation†‡

Jens Eberhard,^{*a} Katrin Peuntinger,^b Susann Rath,^a Beate Neumann,^c Hans-Georg Stammer,^c Dirk M. Guldi^b and Jochen Mattay^{*a}

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 $Ru(bpy)_3^{2+}$ 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 ($[Zn(MeATT)_2][PF_6]_4$) 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

www.rsc.org/pps

Introduction

Photosensitizers (PSs) are a common need in the field of photochemistry and -biology^{1,2} and the underlying photo-physical and molecular mechanisms are well understood.^{3–6}

In the last few years the development of specifically designed PS dyes has become particularly important for use in dye-sensitized solar cells⁷ (DSSC), light upconversion by triplet-triplet annihilation (TTA),⁸ or – more generally seen – in the study of charge separation in order to mimic the natural photosynthetic reaction cascade.⁹ 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).⁹ Progress has also been made in employing less precious metals¹⁰ in polypyridine complexes for such applications (e.g. Zn^{II} ¹¹ or $Cu^{I,12,13}$ sensitizers, $Co^{II/III}$ electrolytes¹⁴ or a combination of them¹⁵), as most of the porphyrin and phthalocyanine dyes show favorable properties with more abundant metals (e.g. Zn^{II}).¹⁶ It should also be mentioned that metal ion free sensitizers have been studied widely in the last decade due to DSSC application.¹⁷

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.¹⁸ 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 dyes¹⁸ for photodynamic therapy¹⁹ (PDT).

The photosensitized production of O_2 ($^1\Delta_g$) by triplet energy transfer is unarguably one of the main applications.²⁰ 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,^{7b} one can ask the same for PSs in order to facilitate, for instance, an environmentally friendly production of chemicals by sunlight (viz. “green” photochemistry²¹) in large area solar collectors.²² Such

^aOrganische Chemie I, Fakultät für Chemie, Universität Bielefeld, Universitätsstr. 25, 33501 Bielefeld, Germany. E-mail: mattay@uni-bielefeld.de, jens.eberhard@uni-bielefeld.de; Tel: +49 521 106 2072

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

^cAbteilung für Röntgenstrukturanalyse, Fakultät für Chemie, Universität Bielefeld, Universitätsstr. 25, 33501 Bielefeld, Germany

†This article is dedicated to the memory of Professor Nicholas J. Turro (1938–2012).

‡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_2 ($^1\Delta_g$) 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_0 , T_1), MO and spin density plots. See DOI: 10.1039/c3pp50349f

techniques can be easily adopted for O_2 ($^1\Delta_g$)-mediated photo-oxidations, for example of (–)-citronellol in rose oxide synthesis or 1,5-dihydroxynaphthalene (DHN) to Juglone²³ and subsequent photo-Friedel–Crafts acylation.²⁴ Similarly, the use of such techniques in solar water disinfection by photogenerated O_2 ($^1\Delta_g$) has been reported.²⁵ 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.²⁶

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

Correspondingly, there is a need for new 3PS s 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^{33,34} and other purely organic examples (*e.g.* coumarins³⁵) 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^{III} complexes for the photooxidation of DHN³⁶ – stimulated by the seminal work of Selke and Thompson *et al.*³⁷ about the efficient O_2 ($^1\Delta_g$) sensitization capability of platinum group metal complexes. In this regard, Wilkinson and Abdel-Shafi *et al.*³⁸ examined $[Ru(bpy)_3]^{2+}$ and derivatives in detail for their capabilities over ten years ago and some Ir^{III} and Rh^I complexes more recently.³⁹

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,^{40,41} but also by attachment of multiple chromophores with a matching triplet level.⁴²

The choice of a suitable chromophore for such purposes is *a priori* difficult and certain limitations apply as summarized by Zhao *et al.*,¹⁸ *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 T_1 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^{III} and Pt^{II} complexes and was also used to evaluate photo-oxidation 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 $[Ru(tpy)_2]^{2+}$ system⁴⁴ and a perylenebisimide (PBI) dye on C^N-cyclometalated Ir^{III} complexes.^{43b} For O_2 ($^1\Delta_g$) 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_2 ($^1\Delta_g$) quantum yield (Φ_Δ) was evaluated.^{43b}

One might ask why not more of the promising – multichromophoric or otherwise improved – bis(terpyridine) systems have been analyzed for their suitability as 3PS , as there is a good background of data on the well-known O_2 ($^1\Delta_g$) sensitizer $[Ru(bpy)_3]^{2+}$ and similar complexes.^{27,38,45,46} However, we could only find a few reports dealing with Φ_Δ of $[Ru(tpy)_2]^{2+}$ complexes.^{47,48}

In part the apparent absence of such reports can be attributed to the popular choice of anthracene^{42a} and pyrene^{49,50} dye in multichromophore approaches because of their suitable matching triplet levels. An early seminal work on anthracene-substituted terpyridine ligands by Maestri *et al.*⁵¹ mentioned O_2 ($^1\Delta_g$) generation for a homoleptic bis(terpyridine) complex of Ru^{II} , which in turn degraded the anthracene moiety due to *endo*-peroxide formation. Very recently, this reaction was employed as a switch for the $[Ru(bpy)_3]^{2+}$ luminescence.⁵²

First principle studies for 9-acridine and 10-methyl-9-acridinium-substituted homoleptic bis(terpyridine) complexes of Ru^{II} have been reported elsewhere.⁵³ For these systems it turned out that a multichromophoric benefit, *i.e.* 3MLCT 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 long-lived dark state, which was quenchable by O_2 ($^3\Sigma_g^-$). Pristine acridine is a known 3PS sensitizer^{18,54} although it is only applicable in the blue spectral region (lowest energy abs. at λ_{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^{II} complexes and their Zn^{II} counterparts (Scheme 1). The synthesis and photophysical properties of these new Zn^{II} complexes will be reported here. For comparison, we included also acridinium systems in this study because such dyes are lively discussed⁵⁵ 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 ¹H NMR spectroscopic assignments.

the ESI.[‡] The synthesis of the ligands and complexes 3–5 has been reported elsewhere.⁵³

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 × 1 × 1 μm, HYJ Sympho[®]) 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 FluoroLog 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 × 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][PF₆]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 NH₄PF₆ 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 × 20 mL) and diethyl ether (3 × 20 mL) and was left to dry in air overnight. The yellow solid was dissolved and flushed down by using MeCN (4 × 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–CH₂Cl₂ (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. C₆₄H₄ON₈S₂ZnP₂F₁₂·3H₂O requires C, 55.12; H, 3.32; N, 8.04; S, 4.60. λ_{max}(MeCN)/nm 387 sh. (ε × 10³/M⁻¹ cm⁻¹, 32.4), 361 sh. (44.5), 347 (54.4), 284 (49.0), 252 (216). IR (ATR) ν_{max}/cm⁻¹ 3065, 1609, 1600 (s), 1552, 1476, 1458, 1425, 1404, 1251, 1026, 1015, 832 (vs, PF₆⁻), 789, 758, 691, 657, 555 (s). ¹H NMR (500 MHz, MeCN-d₃) δ 9.04 (4 H, s, H^{B3',5'}), 8.70 (4 H, dt, *J* 8.0 1.1, H^{A3}), 8.44 (2 H, d, *J* 3.7, H^{C4}), 8.31 (4 H, dt, *J* 8.8, 1.1, H^{E4}), 8.12 (4 H, dt, *J* 8.8, 1.1, H^{E1}), 7.97 (4 H, td, *J* 7.8, 1.5, H^{A4}), 7.93 (4 H, ddd, *J* 8.8, 6.5, 1.3, H^{E3}), 7.69 (4 H, ddd, *J* 8.8, 6.5, 1.3, H^{E2}), 7.66 (2 H, d, *J* 3.7, H^{C3}), 7.50 (4 H, dt, *J* 5.5 1.2, H^{A6}), 7.23 (4 H, ddd, *J* 7.2, 5.5, 1.2, H^{A5}). ¹³C{¹H} NMR (151 MHz, CD₃NO₂–CD₂Cl₂ 4 : 1 v/v) δ 152.5 (C^{A2o,B2',6'}), 151.4 (C^{C2o,C5}), 151.0 (C^{A2o,B2',6'}), 150.2 (C^{A6}), 149.9 (C^{DE4'}), 143.6 (C^{A4}), 143.4 (C^{B4'}), 143.3 (C^{C2o,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'}). ¹⁹F NMR (282 MHz, MeCN-d₃) δ 72.3 (d, *J*_{F,P} 708, PF₆⁻) MS (ESI) not stable, see main text.

[Zn(MeATT)₂][PF₆]₄ (2). [MeATT][PF₆] ligand (109 mg, 167 μmol) and Zn(OTf)₂ (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 NH₄PF₆ 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–

CH₂Cl₂ (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. C₆₆H₄₆N₈S₂ZnP₄F₂₄ requires C, 47.74; H, 2.79; N, 6.75; S, 3.86. $\lambda_{\max}(\text{MeCN})/\text{nm}$ 437 ($\epsilon \times 10^3/\text{M}^{-1} \text{cm}^{-1}$, 22.5), 366 (46.2), 347 (67.2), 334 (67.5), 284 (57.5), 262 (194). IR (ATR) $\tilde{\nu}_{\max}/\text{cm}^{-1}$ 3115, 1612 (s), 1575, 1553, 1478, 1426, 1273, 1250, 1028, 1015, 837 (vs, PF₆[−]), 793, 764, 557 (s). ¹H NMR (500 MHz, MeCN-d₃) δ 9.01 (4 H, s, H^{B3',5'}), 8.77 (4 H, d, *J* 7.9, H^{A3}), 8.70 (4 H, d, *J* 9.1, H^{E4}), 8.56 (2 H, d, *J* 3.8, H^{C4}), 8.48 (4 H, m, partially superimposed, H^{E3}), 8.47 (4 H, d, *J* 9.1, partially superimposed, H^{E1}), 8.21 (4 H, td, *J* 7.9, 1.4, H^{A4}), 8.03 (4 H, dd, *J* 7.8, 1.7, H^{E2}), 7.91 (4 H, dt, *J* 4.9, 1.4, H^{A6}), 7.83 (2 H, d, *J* 3.8), H^{C3}), 7.46 (4 H, ddd, *J* 7.9, 4.9, 1.4, H^{A5}), 4.92 (6 H, s, H^{D10}). ¹³C{¹H} NMR (126 MHz, MeCN-d₃) δ 153.7 (C^{D9}), 151.3 (C^{A2o.B2',6'}), 149.2 (C^{A6}), 149.1 (C^{B4'}), 148.5 (C^{A2o.B2',6'}), 144.8 (C^{C2o.C5}), 142.7 (C^{DE4'}), 142.3 (C^{A4}), 140.0 (C^{E3}), 137.4 (C^{C2o.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^{E4}), 40.2 (C^{D10}). ¹⁹F NMR (282 MHz, MeCN-d₃) δ 72.9 (d, *J*_{F,P} 707, PF₆[−]) HRMS (ESI) *m/z* 684.09337 ([M − 2 × PF₆]²⁺, calc. for C₆₆H₄₆N₈S₂⁶⁴ZnP₂F₁₂ 684.09255, Δ 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 α Atlas diffractometer. Using Olex2,⁵⁷ the structure was solved with the ShelXS⁵⁸ structure solution program using direct methods and refined with the ShelXL⁵⁸ refinement package using least squares minimisation (Table 1).

Photochemical experiments

Photochemical reactions with DHN as a substrate (1.58 ± 0.09 × 10^{−4} M, Abs. ≈ 1.2) were performed in a septum-

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 NaNO₂ 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.*³⁶ and Zhao *et al.*,⁴³ 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 O₂ (¹Δ_g) generation (Φ_{Δ}) were calculated by the usual equation⁶⁰ for relative determinations. Concentrations of all reagents and the product 5-hydroxy-1,4-naphthoquinone (Juglone) were calculated from the known molar extinction coefficients (ϵ) 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^{−1} cm^{−1} for [Ru(bpy)₃]²⁺, and 93 850 M^{−1} cm^{−1} for MB at $\lambda_{\max}$, respectively, which are both in good agreement with the values reported.^{61,62}

Irradiance was measured to 39 ± 5 mW cm^{−2} at the front side of the reaction vessel position and 28 ± 5 mW cm^{−2} 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)⁶³ revealed an average photon flux of 4.4 ± 0.1 × 10^{−7} Einstein s^{−1} (2 runs $\ddagger$) in the range of the actinometer absorbance (here: 385–500 nm). Based on some approximations (see ESI $\ddagger$) 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^{−2}) was calculated.^{63,64}

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 O₂ and irradiated in standard 5 mm (o.d.) NMR tubes or 1 cm (o.d.) Pyrex® photoirradiation tubes with a threaded septum cap.

Table 1 Crystal data and structure refinements of **2**

Composition	[Zn(MeATT) ₂][PF ₆] ₄ ·5MeCN
Formula	C ₇₆ H ₆₁ F ₂₄ N ₁₃ P ₄ S ₂ Zn
F.W./g mol ^{−1}	1865.75
Temperature/K	200.00 ± 0.10
Abs. coeff./mm ^{−1}	2.630
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>Z</i>	4
<i>a</i> /Å	38.6752 (7)
<i>b</i> /Å	8.61835 (12)
<i>c</i> /Å	24.8997 (4)
β /°	104.5408 (18)
Volume/Å ^{−3}	8033.7 (2)
Reflections coll.	28 592
Indp. Reflins.	14 124
GoF on <i>F</i> ²	1.036
Final <i>R</i> indexes (<i>I</i> ≥ 2σ(<i>I</i>))	<i>R</i> ₁ = 0.0743, <i>wR</i> ₂ 0.2044
Final <i>R</i> indexes (all data)	<i>R</i> ₁ = 0.0950, <i>wR</i> ₂ 0.2206
Disordered parts	F atoms site disordered on 2PF ₆

Computational methods

The geometries were optimized to the convergence criteria of $1 \times 10^{-5} E_h a_0^{-1}$ (*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)⁶⁵ basis sets (plus 18 electron ECP)⁶⁶ together with a CPCM solvent model for MeCN. All calculations were performed with the Gaussian 09 package⁶⁷ 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 NH₄PF₆ 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 (d¹⁰ ion).⁵¹ Some photo-physical 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 ¹H NMR spectroscopy due to characteristic shifts of the proton resonances up on complexation,⁶⁸ *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⁺ ligand and 4.92 ppm for the corresponding complex in MeCN-d₃, respectively (omitted in Fig. 1, see ESI†). Full NMR spectroscopic assignment was possible by means of 2D techniques (see ESI for spectra†) and comparison to the Ru^{II} analogs.⁵³

Furthermore, the success of the anion metathesis could be directly proven by ¹⁹F NMR spectroscopy⁶⁹ where the PF₆[−] counterion gives rise to a doublet at −72.3 ppm (*J*_{P,F} 708 Hz) *vs.* the singlet resonance of CF₃SO₃[−] at *ca.* −77 to −80 ppm.⁷⁰ The infrared spectra of **1** and **2** show only marginal differences and are dominated by the very strong absorption of the PF₆[−] ion at 834 ± 3 cm^{−1}.⁶⁹

Mass spectrometric (MS) analysis was particularly difficult for the kinetic labile Zn^{II} complexes⁷¹ compared to the corresponding Ru^{II} complexes.⁵³ High resolution MS-ESI spectra

Fig. 1 Partial ¹H NMR spectra (aromatic region) and assignment of the terpyridine proton resonances from the ligands (MeATT⁺, violet; ATT, green) and the corresponding Zn^{II} complexes (**1**, red; **2**, cyan) recorded in MeCN-d₃ solution, except for the ATT ligand which had to be recorded in CDCl₃ (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 × PF₆]²⁺ pseudo-molecular ion at *m/z* 684.09337 and a well-resolved 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 PF₆[−] 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(κ³N,N',N'') coordinated metal center are in good agreement with several structure reports for the pristine [Zn(tpy)₂]²⁺ complex,⁷² *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][PF₆]₄ × 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 ($\angle_{\text{avg.}}(\text{N}'\text{-Zn-N}') 172.9 \pm 6.1^\circ$).

Only a few $4'$ - π -extended bis(terpyridine) complexes of Zn^{II} have been reported to date,⁷³ among them *p*-biphenyl,^{73b} *p*-terphenyl^{73c} as well as *p*-phenyl-conjugates with 1,2,4-triazole^{73d} or carbazole^{73e} moieties and recently a well-comparable $4'$ -(4-pyridin-4-yl)phenyl extended complex.^{73f} However, to the best of our knowledge, no thienyl-substituted Zn^{II} 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 ($d_{\text{avg.}}(\text{Zn-N}') 2.070 \pm 0.014 \text{ \AA}$) but a similar non-linearity at this axis ($\angle_{\text{avg.}}(\text{N}'\text{-Zn-N}') 174.6 \pm 2.0^\circ$). The remaining $\text{Zn-N}'/\text{N}''$ bond lengths of the coordination sphere are elongated (*ca.* $0.11 \text{ \AA}$) and unequally distributed (*ca.* $0.01 \text{ \AA}$) between the two terpyridine ligands and can be averaged to $2.183 \pm 0.017 \text{ \AA}$. The individual angle to the main axis $\text{N}'/\text{N}''\text{-Zn-N}'$ corresponds to $75.5 \pm 0.8^\circ$.

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.*^{73f} The terpyridine fragment of **2** shows a weak interaction with the outer pyridyl-ring among one another ($d(\text{py}_{\text{ctr}}^{\text{A}} \cdots \text{py}_{\text{ctr}}^{\text{A}}) 3.709 \text{ \AA}$), which is typical for terpyridine solid state assemblies.⁷⁴ The acridinium units face each other with a considerable offset (only partial overlap at the outer ring) excluding any strong π - π interaction ($d(\text{acr}^{\text{+}}_{\text{plane}} \cdots \text{acr}^{\text{+}}_{\text{pl.}}) 3.529 \text{ \AA}$).

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-thienyl substituted bis(terpyridine) complexes of Ru^{II} .⁷⁵ For this series of complexes, the mean bond distance between the tpy unit and the thienyl spacer lies within $1.467 \pm 0.004 \text{ \AA}$. 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^{II} complexes show a mean bond distance for the inter-connecting bond of $1.475 \pm 0.033 \text{ \AA}$. The dihedral angle $\varphi_{\text{tpy-ph}}$ averages to $26 \pm 15^\circ$, 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 ($\varphi 8.6 \pm 9.3^\circ$) and DFT calculations ($\varphi 20.4 \pm 1.9^\circ$; both for Ru^{II}) by us.⁵³ However, in the case of the $4'$ -phenyl-tpy derived Zn^{II} complexes some examples with a nearly planar arrangement of $\varphi_{\text{tpy-ph}}$ ($1 \pm 1^\circ$) 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^{II} and Zn^{II} 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⁺ 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 $[\text{Ru}(\text{bpy})_3]^{2+}$ (orange-red) in MeCN. Part of the AM 1.5 solar spectra⁸² (right scale, 37° global tilt irradiance) is also shown in semi-transparent. Note that the scaling was arbitrarily chosen.

methylacridinium-substituted bis(terpyridine)ruthenium(II) complexes and the ligands alone have been described separately.⁵³ Briefly, acridines show local absorbance maxima at 390, 360, and 345 nm^{76,77} whereas the narrow absorption band at 365 nm and a broader second band at *ca.* 420–450 nm⁷⁸ (with $\sim 20\,000$ and $7000 \text{ M}^{-1} \text{ cm}^{-1}$, respectively) are typical for acridinium ions (see Fig. 3).⁷⁹

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 (ϵ) 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.*⁵¹ as well as for pyrenyl-substituted terpyridines more recently.⁴⁹

For the $[\text{Zn}(\text{MeATT})_2]^{4+}$ complex (**2**) the local maximum in the visible range is slightly blue shifted (437 nm) in comparison to the MeATT⁺ ligand (454 nm) but the absorption bands itself are very similar in shape (see Fig. 3). The ATT ligand and its Zn^{II} 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 ϵ values. The increase in ϵ 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,⁸⁰ which can be reasoned by the

bathochromic shift comparing pristine acridine to the AT or the ATT ligand. The slightly stronger increase in ϵ (more than twice) for the Zn^{II} complexes may also be caused by changes in intra-ligand (IL) transitions⁴⁹ due to coordination – even for “innocent” d^{10} metal ions which were studied in detail by Schubert *et al.*⁸¹

The Ru^{II} complexes show the typical broad MLCT absorption band in the 450–550 nm region. As expected,⁸⁰ the thienyl-linker caused a large increase in ϵ for **4** and **5** in comparison to the linker-free $[\text{Ru}(\text{AT})_2]^{2+}$ 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^{II} counterpart **2** (see Fig. 3).

The fluorescence quantum yields (Φ_{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^{79,83} (e.g. 9-thienyl-10-methylacridinium $\Phi_{\text{fl}} < 0.005$, $\tau \sim 100$ ps;^{79a} 9-ph- Φ_{fl} 0.063–0.005, τ 1.5 ns;^{79c,d} 9-*p*-biph- Φ_{fl} 0.020, τ 1.2 ns^{79c,d}) and as well expected for pristine and substituted acridines based on the literature data for organic solvents (e.g. 9-phenylacridine Φ_{fl} 0.080, τ 1.4 ns⁸⁴ (for MeOH)).^{84–86} For the ATT ligand and its Zn^{II} 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 $[\text{Zn}(\text{ATT})_2]^{2+}$ complex (**1**) is very similar to the spectra for the Ru^{II} counterparts reported elsewhere,⁵³ with the exception of the ¹MLCT bleaching (see Fig. 4). The major decay component

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

Compound	$\lambda_{\text{abs}} (\epsilon)$	λ_{em}	Φ_{fl}	τ/ns
ATT	387 (11.3)	589	0.017 ^a	0.73 $\pm$ 0.02 ^b 0.71 $\pm$ 0.06 ^c
MeATT ⁺	454 (8.8)	— ^d	—	n.d.
$\text{Zn}(\text{ATT})_2^{2+}$	387 (32.5)	545	0.019 ^a	0.22 $\pm$ 0.01 ^b 0.22 $\pm$ 0.05 ^c 15 800 $\pm$ 600 ^c 0.14 $\pm$ 0.02 ^d
$\text{Zn}(\text{MeATT})_2^{4+}$	457 (20.3) ^e	— ^d	—	80 $\pm$ 6 ^c
$\text{Ru}(\text{AT})_2^{2+}$	484 (21.2)	— ^d	—	0.27 $\pm$ 0.03 ^c
$\text{Ru}(\text{ATT})_2^{2+}$	504 (50.6)	— ^d	—	1090 $\pm$ 140 ^c
$\text{Ru}(\text{MeATT})_2^{4+}$	510 (47.4)	— ^d	—	0.17 $\pm$ 0.02 ^c

^a 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 Φ_{fl} 0.95, quinine disulfate in 0.05 M H_2SO_4 Φ_{fl} 0.55, fluorescein in 0.1 M NaOH Φ_{fl} 0.92 (cross-checked and within 10% of the values reported in ref. 59). ^b To compare both methods, explicit errors for τ are given, viz. determined by time correlated single photon counting (TCSPC). ^c Determined by transient absorption spectroscopy. ^d Not luminescent. ^e Shoulder (weak vibronic structure typical for acridinium ions), λ_{max} 437 (22 500 $\text{M}^{-1} \text{cm}^{-1}$). ^f Ref. 53.

Fig. 4 Upper part: differential absorption spectra (visible) obtained upon fs flash photolysis (387 nm, 200 nJ per pulse) of $[\text{Zn}(\text{ATT})_2]^{2+}$ (**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 ($15.8 \pm 0.6 \mu\text{s}$), exceeding the Ru^{II} counterpart ($1.09 \mu\text{s}$) by an order of magnitude. It was readily quenched by O_2 . Therefore, we assigned this to the formation of the intra-ligand triplet state ³IL.

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†) 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 $[\text{Zn}(\text{MeATT})_2]^{4+}$ complex (**2**) shows only a very weak transient signal (ESI†) 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 ± 17 ps).

Further insight came from fluorescence upconversion experiments following excitation at 387 nm and detection at 580 nm. For the $[\text{Zn}(\text{ATT})_2]^{2+}$ 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 $[\text{Zn}(\text{MeATT})_2]^{4+}$ 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†).

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)/LANL2DZ approach (=LACVP*).^{37,43b} 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_1).

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 ϕ 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 ϕ found experimentally on one ligand fragment might not be overrated as the rotational flexibility of the thienyl group is high (*vide supra*). The second dihedral angle (ω) 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,‡ 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^{II} series,⁵³ no metal ion influence is deducible for the first few occupied and unoccupied MOs in the Zn^{II} complexes. The individual MO plots are shown in the ESI.‡

Table 3 Comparison of selected experimentally determined structural parameters (distances (d)/Å, angles/°) with B3LYP/6-31G(d)/LANL2DZ DFT calculations for complexes **1** and **2** (and $\Delta E(\text{SCF})$ energies to S_0 /eV) as well as experimental data of some reference complexes

Parameter	$[\text{Zn}(\text{MeATT})_2]^{2+}$ (2)				$[\text{Zn}(\text{ATT})_2]^{2+}$ (1)		$[\text{Zn}(\text{R-tpy})_2]^{2+}$, 4'-R=		
	Exptl.	DFT relaxed	S_0	T_1	S_0	T_1	Ph ^{73a}	<i>p</i> -biph ^{73b}	4-pyph ^{73f}
$\Delta E(\text{SCF})$	n.a.	0.003	0	1.741	0	1.627	n.a.	n.a.	n.a.
$d(\text{N2-Zn})^a$	2.088 (3)	2.154	2.153 (1)	2.153	2.150	2.152	2.069 (4)	2.077 (3)	2.084 (4)
$d(\text{N6-Zn})^a$	2.078 (3)			2.151		2.138	2.091 (4)	2.066 (3)	2.067 (4)
$d(\text{N1-Zn})$	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)
$d(\text{N3-Zn})$	2.196 (4)						2.193 (4)	2.174 (3)	2.177 (4)
$d(\text{N5-Zn})$	2.197 (4)						2.178 (4)	2.192 (3)	2.168 (5)
$d(\text{N7-Zn})$	2.189 (4)						2.217 (4)	2.195 (3)	2.168 (5)
$d(\text{C}_{\text{tpy}}-\text{C}_{\text{spacer}})$	1.461 (6), 1.479 (6)	1.463	1.464	1.464, 1.459 ^b	1.461	1.461, 1.441 ^b	1.475 (7) ^c , 1.469 (7)	1.486 (5) ^c , 1.478 (5) ^d	1.487 (6) ^c , 1.471 (7)
$d(\text{C}_{\text{spacer}}-\text{C}_{\text{acr}})$	1.479 (6), 1.484 (6)	1.479 (1)	1.480, 1.478	1.479, 1.448 ^b	1.483 (1)	1.483, 1.398 ^b	n.a.	1.483 (5) ^d , 1.484 (5)	1.478 (6) ^d , 1.482 (7)
$d(\text{N4/8-C}_{\text{Me}})$	1.478 (6), 1.493 (6)	1.480	1.480	1.480, 1.475 ^b	n.a.	n.a.	n.a.	n.a.	n.a.
$\angle(\text{N2-Zn-N6})^a$	176.02 (15)	179.33	179.22	178.99	179.56	179.73	173.2 (2)	175.6 (1)	177.8 (2)
$\angle(\text{N2-Zn-N1})$	75.06 (13)	73.99 (1)	74.00	73.97	74.02 (1)	73.95	75.4 (1)	75.5 (1)	75.8 (2)
$\angle(\text{N2-Zn-N3})$	75.25 (13)		73.97	74.02 (1)		73.93	75.5 (1)	75.6 (1)	76.3 (2)
$\angle(\text{N6-Zn-N5})$	75.43 (14)		74.00 (1)			74.20	75.3 (1)	75.6 (1)	76.1 (2)
$\angle(\text{N6-Zn-N7})$	75.64 (14)						74.9 (1)	75.9 (1)	75.4 (2)
$\phi_{\text{tpy-spacer}}^e$	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.

^a 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. ^b Ligand fragment with triplet localization. ^c Bond distance of $\text{C}_{\text{tpy}}-\text{C}_{\text{spacer=phenyl}}$.

^d Bond distance of $\text{C}_{\text{spacer}}-\text{C}_{\text{phenyl}}$ instead of C_{acr} . ^e Dihedral angle was measured as *cis*-torsion angle along the S–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 $\pm$ 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.†

Triplet TD-DFT calculations (in S_0 geometry approximation) suggested vertical $S_0 \rightarrow T_1$ transitions at 689/687 nm⁸⁷ (1.80 eV) for **2** and 684/680 nm⁸⁷ (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 $\Delta E(\text{SCF})$ 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/ $\pm$ 1) sets are involved. Both findings are in agreement with the transient absorption data for a ^3IL -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†) 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 (γ 158.8°, α 8.5°, β 25.2°, $\Delta(\text{C9})$ 0.34 Å, $\Delta(\text{N10})$ 0.10 Å; see ref. 88 for explanation of the parameters), as also found for the Ru^{II} counterparts by DFT calculations,⁵³ or experimentally for over-crowded acridinium ions.⁸⁸

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 π -conjugation, may also be useful for sensitization applications such as DSSCs.¹¹ In this regard, preliminary tests by the use of the *in situ* capping technique¹¹ 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^{II} complexes are roughly comparable with typical C^{N} Ir^{III} ⁸⁹ complexes or improved multichromophoric versions studied by the groups of Murata *et al.* and Zhao *et al.*^{36,43} In this regard, the $[\text{Zn}(\text{MeATT})_2]^{4+}$ complex (**2**) resembles the absorption profile of $[\text{Ru}(\text{bpy})_3]^{2+}$ quite well whereas the corresponding Ru^{II} complexes of this work exceed all examples in solar spectra coverage (see Fig. 3).

In the present case, the photooxidation reaction of DHN to Juglone²³ is used as an assay^{36,91} for the O_2 ($^1\Delta_g$) 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 (v_{init}), were calculated as reported.³⁶ 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 ($^1\Delta_g$).

Fig. 6 Plots of $\ln([DHN]_t/[DHN]_{t=0})$ vs. irradiation time (t) for the photo-oxidation 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 $[Ru(bpy)_3]^{2+}$ both exemplary also employed at a higher concentration (3.1 and 12 mol%) and *viz.* absorbance, respectively.⁹² This justifies the call for low absorbance measurements^{37c,43b} instead of comparison by mol%.

Murata *et al.*³⁶ 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 ($3811 \text{ M}^{-1} \text{ cm}^{-1}$),³⁶ 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 calculation⁶⁰ of $\Phi_{\Delta}^{\text{sens}}$. The value of $\Phi_{\Delta}^{\text{MB}}$ (~ 0.5) appears to be independent of the solvent and concentration range.^{90,93} We chose the recommended value of 0.50⁵⁴ 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.*,²⁷ and by Wilkinson and Abdel-Shafi *et al.*³⁸ as well, who reported a value of 0.57 for $\Phi_{\Delta}^{Ru(bpy)_3}$ in MeCN. Orellana and Braun *et al.* suggested 0.73 (MeOD- d_3),⁴⁵ but Tanielian *et al.* determined for $\Phi_{\Delta}^{Ru(bpy)_3}$ 0.77 (MeCN) and 0.87 (MeOH).⁹⁴ In the latter case, an incident light $\times \Phi_{\Delta}$ vs. concentration study was also performed for $[sens] > 8 \times 10^{-5} \text{ M}$. However, our sensitizer concentrations are below this threshold. There is a clear trend of lower Φ_{Δ} 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 $\Phi_{\Delta}^{Ru(bpy)_3}$ 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_{init}), quantum yield for O_2 ($^1\Delta_g$) generation (Φ_{Δ}) and yields of Juglone using complexes 1–5, the ATT ligand, and MB (=reference standard^{54,90}) as well as $Ru(bpy)_3^{2+}$ as photo-catalysts

Entry#	Compound	[sens] mol%	$k_{\text{obs}} \times 10^{-3} \text{ min}^{-1}$	$[DHN]_{t=0} \times 10^{-4} \text{ M}$	$v_{\text{init}} \times 10^{-6} \text{ M min}^{-1}$	A (at λ_{max}) a.u. (nm)	F_{area}^a (%)	$\Phi_{\Delta}^{\text{sens}}$	Yield ^b (%)
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 ± 0.1	-114 ± 1	1.51 ± 0.02	-17.4 ± 0.01	0.273 ± 0.05 (504)	282 ± 5	0.81 ± 0.01	70 ± 3
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	$Zn(AT)_2^{2+}$	2.0	−8.5	1.69	−1.46	0.112 (387)	39	0.49	16
7.2	$Zn(AT)_2^{2+}$	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

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

The observed rate constants (k_{obs}) and initial reaction velocities (v_{init}) of our data set are comparable to values reported by Zhao *et al.*⁴³ for (multichromophoric) Ir^{III} and Pt^{III} 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} 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 Φ_{Δ} was somehow different from the value reported by Murata *et al.* (0.50).³⁶ Despite the different light sources used, and in this case also solvent systems, the kinetics determined by Zhao *et al.* (k_{obs} -41.6×10^{-3} min⁻¹, v_{init} -8.32×10^{-6} M min⁻¹)^{43b} matches well to our data (Table 4, entry no. 1.2 and 1.3, respectively). The kinetic data reported by Murata *et al.*,³⁶ among them also data for MB, are almost all an order of magnitude larger (and even more for MB) as also noticed previously.⁴³ 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 (Φ_{Δ} 0.82), followed by the corresponding Zn^{II} complex (Φ_{Δ} 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 O₂ (¹Δ_g) sensitizer, *i.e.*, 0.83 ± 0.01 in MeCN and benzene,⁵⁴ and this value is nicely reflected by 4. However, acridine does not absorb significantly above 385 nm (=filter cut-off; $\epsilon < 730$ M⁻¹ cm⁻¹). 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^{II} 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 (Φ_{Δ} 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^{II} 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 O₂, in particular of the acridinium compounds as shown by Griesbeck *et al.*⁵⁶ for the lively discussed 9-mesityl-10-methyl-acridinium system,⁵⁵ we studied the reaction towards the well-known limonene⁹⁵ and 2-methylnaphthalene⁹⁶ probes as substrates. The latter can only react with the superoxide ion but

not with O₂ (¹Δ_g) and in our case, no reaction at all was noticed in MeCN saturated with O₂. However, with respect to the study of Griesbeck *et al.*,⁵⁶ 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 O₂ (¹Δ_g),⁹⁵ showed the expected product distribution of hydroperoxides as probed *via* NMR and GC (after reduction to alcohols with NaBH₄^{95d,97}) due to the Schenck ene reaction³² of the endo-cyclic double bond.

Last but not least, the typical O₂ (¹Δ_g) NIR emission at 1275 nm⁹⁸ 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^{II}) and 4 (Ru^{II}) revealed singlet oxygen (¹Δ_g) generation with quantum yields as high as 0.82. Despite the fact that 1 (Zn^{II}) 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^{II}) with the solar spectrum assists in extending the sensitization capability of the acridine building block. The acridinium containing systems 2 (Ru^{II}) and 5 (Ru^{II}) as well as the linker-free acridine-terpyridine system 3 (Ru^{II}) 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^{II} conjugates with respect to their singlet oxygen production. Notably, the design of metal complex containing conjugates carrying organic building blocks en-route towards the long-lived 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^{II} 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.

Notes and references

- 1 B. I. Kruff and A. Greer, Photosensitization Reactions In Vitro and In Vivo, *Photochem. Photobiol.*, 2011, **87**, 1204–1213.
- 2 I. E. Kochevar and R. W. Redmond, in *Methods in enzymology*, ed. S. P. Colowick, N. O. Kaplan, L. Packer and H. Sies, Academic Press, San Diego and London, 2000, vol. 319, pp. 20–28.
- 3 N. J. Turro, V. Ramamurthy and J. C. Scaiano, *Principles of molecular photochemistry*, University Science Books, Sausalito, 2009.
- 4 G. J. Kavarnos and N. J. Turro, Photosensitization by reversible electron transfer: theories, experimental evidence, and examples, *Chem. Rev.*, 1986, **86**, 401–449.
- 5 G. Laustriat, Molecular mechanisms of photosensitization, *Biochimie*, 1986, **68**, 771–778.
- 6 (a) J. Mattay, Ladungstransfer und Radikationen in der Photochemie, *Angew. Chem.*, 1987, **99**, 849–870; (b) J. Mattay, Charge Transfer and Radical Ions in Photochemistry, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 825–845.
- 7 (a) A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo and H. Pettersson, Dye-Sensitized Solar Cells, *Chem. Rev.*, 2010, **110**, 6595–6663; (b) T. W. Hamann, R. A. Jensen, A. B. F. Martinson, H. van Ryswyk and J. T. Hupp, Advancing beyond current generation dye-sensitized solar cells, *Energy Environ. Sci.*, 2008, **1**, 66; (c) M. Grätzel, Dye-sensitized solar cells, *J. Photochem. Photobiol., C*, 2003, **4**, 145–153.
- 8 (a) J. Zhao, S. Ji and H. Guo, Triplet-triplet annihilation based upconversion: from triplet sensitizers and triplet acceptors to upconversion quantum yields, *RSC Adv.*, 2011, **1**, 937; (b) T. N. Singh-Rachford and F. N. Castellano, Photon upconversion based on sensitized triplet-triplet annihilation, *Coord. Chem. Rev.*, 2010, **254**, 2560–2573.
- 9 (a) L. Flamigni, J.-P. Collin and J.-P. Sauvage, Iridium Terpyridine Complexes as Functional Assembling Units in Arrays for the Conversion of Light Energy, *Acc. Chem. Res.*, 2008, **41**, 857–871; (b) E. Baranoff, J.-P. Collin, L. Flamigni and J.-P. Sauvage, From ruthenium(II) to iridium(III): 15 years of triads based on bis-terpyridine complexes, *Chem. Soc. Rev.*, 2004, **33**, 147–155.
- 10 (a) B. Bozic-Weber, E. C. Constable and C. E. Housecroft, Light harvesting with Earth abundant d-block metals: Development of sensitizers in dye-sensitized solar cells (DSCs), *Coord. Chem. Rev.*, 2013, **257**, 3089–3106; (b) C. A. Bignozzi, R. Argazzi, R. Boaretto, E. Busatto, S. Carli, F. Ronconi and S. Caramori, The role of transition metal complexes in dye sensitized solar devices, *Coord. Chem. Rev.*, 2013, **257**, 1472–1492; (c) A. S. Polo, M. K. Itokazu and N. Y. Murakami Iha, Metal complex sensitizers in dye-sensitized solar cells, *Coord. Chem. Rev.*, 2004, **248**, 1343–1361.
- 11 B. Bozic-Weber, E. C. Constable, N. Hostettler, C. E. Housecroft, R. Schmitt and E. Schönhofner, The d¹⁰ route to dye-sensitized solar cells: step-wise assembly of zinc(II) photosensitizers on TiO₂ surfaces, *Chem. Commun.*, 2012, **48**, 5727.
- 12 T. Bessho, E. C. Constable, M. Grätzel, A. Hernandez Redondo, C. E. Housecroft, W. Kylberg, M. K. Nazeeruddin, M. Neuburger and S. Schaffner, An element of surprise – efficient copper-functionalized dye-sensitized solar cells, *Chem. Commun.*, 2008, 3717.
- 13 (a) C. E. McCusker and F. N. Castellano, Orange-to-blue and red-to-green photon upconversion with a broadband absorbing copper(I) MLCT sensitizer, *Chem. Commun.*, 2013, **49**, 3537; (b) C. E. McCusker and F. N. Castellano, Design of a Long-Lifetime, Earth-Abundant, Aqueous Compatible Cu(I) Photosensitizer Using Cooperative Steric Effects, *Inorg. Chem.*, 2013, **52**, 8114–8120.
- 14 K. B. Aribia, T. Moehl, S. M. Zakeeruddin and M. Grätzel, Tridentate cobalt complexes as alternative redox couples for high-efficiency dye-sensitized solar cells, *Chem. Sci.*, 2012, **4**, 454.
- 15 B. Bozic-Weber, E. C. Constable, S. O. Fürer, C. E. Housecroft, L. J. Troxler and J. A. Zampese, Copper(I) dye-sensitized solar cells with [Co(bpy)₃]^{2+/3+} electrolyte, *Chem. Commun.*, 2013, **49**, 7222.
- 16 (a) A. Yella, H.-W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W.-G. Diau, C.-Y. Yeh, S. M. Zakeeruddin and M. Grätzel, Porphyrin-Sensitized Solar Cells with Cobalt (II/III)-Based Redox Electrolyte Exceed 12 Percent Efficiency, *Science*, 2011, **334**, 629–634; (b) M. V. Martínez-Díaz, G. d. La Torre and T. Torres, Lighting porphyrins and phthalocyanines for molecular photovoltaics, *Chem. Commun.*, 2010, **46**, 7090–7108.
- 17 (a) Y. Ooyama and Y. Harima, Molecular Designs and Syntheses of Organic Dyes for Dye-Sensitized Solar Cells, *Eur. J. Org. Chem.*, 2009, 2903–2934; (b) A. Mishra, M. K. R. Fischer and P. Bäuerle, Metallfreie organische Farbstoffe für farbstoffsensibilisierte Solarzellen – von Struktur-Eigenschafts-Beziehungen zu Designregeln, *Angew. Chem.*, 2009, **121**, 2510–2536; (c) A. Mishra, M. K. R. Fischer and P. Bäuerle, Metal-Free Organic Dyes for Dye-Sensitized Solar Cells: From Structure Property Relationships to Design Rules, *Angew. Chem., Int. Ed.*, 2009, **48**, 2474–2499.
- 18 J. Zhao, W. Wu, J. Sun and S. Guo, Triplet photosensitizers: from molecular design to applications, *Chem. Soc. Rev.*, 2013, **42**, 5323–5351.
- 19 (a) K. Plaetzer, B. Krammer, J. Berlanda, F. Berr and T. Kiesslich, Photophysics and photochemistry of photodynamic therapy: fundamental aspects, *Lasers Med. Sci.*, 2009, **24**, 259–268; (b) Á. Juarranz, P. Jaén, F. Sanz-Rodríguez, J. Cuevas and S. González, Photodynamic therapy of cancer. Basic principles and applications, *Clin. Transl. Oncol.*, 2008, **10**, 148–154; (c) A. P. Castano, T. N. Demidova and M. R. Hamblin, Mechanisms in photodynamic therapy: part one – photosensitizers, photochemistry and cellular localization, *Photodiagn. Photodyn. Ther.*, 2004, **1**, 279–293; (d) D. E. Dolmans, D. Fukumura and R. K. Jain, Photodynamic therapy for cancer, *Nat. Rev. Cancer*, 2003, **3**,

- 380–387; (e) W. M. Sharman, C. M. Allen and J. E. van Lier, Photodynamic therapeutics: basic principles and clinical applications, *Drug Discovery Today*, 1999, **4**, 507–517.
- 20 P. R. Ogilby, Singlet oxygen: there is indeed something new under the sun, *Chem. Soc. Rev.*, 2010, **39**, 3181–3209.
- 21 (a) S. Protti, D. Dondi, M. Fagnoni and A. Albini, Photochemistry in synthesis: Where, when, and why, *Pure Appl. Chem.*, 2007, **79**, 1929–1938; (b) A. Albini and M. Fagnoni, Green chemistry and photochemistry were born at the same time, *Green Chem.*, 2004, **6**, 1–6.
- 22 (a) M. Oelgemöller, C. Jung and J. Mattay, Green photochemistry: Production of fine chemicals with sunlight, *Pure Appl. Chem.*, 2007, **79**, 1939–1947; (b) J. Mattay, Von der Laborsynthese zur Solarchemie: Ein Beispiel für eine nachhaltige Chemie, *Chemie in unserer Zeit*, 2002, **36**, 98–106.
- 23 (a) O. Suchard, R. Kane, B. J. Roe, E. Zimmermann, C. Jung, P. A. Waske, J. Mattay and M. Oelgemöller, Photooxygenations of 1-naphthols: an environmentally friendly access to 1,4-naphthoquinones, *Tetrahedron*, 2006, **62**, 1467–1473; (b) M. Luiz, A. T. Soltermann, A. Biasutti and N. A. Garcia, A kinetic study on singlet molecular oxygen ($O_2 (^1\Delta_g)$) generation and quenching by dihydroxynaphthalenes, *Can. J. Chem.*, 1996, **74**, 49–54.
- 24 (a) C. Schiel, M. Oelgemöller, J. Ortner and J. Mattay, Green photochemistry: the solar-chemical 'Photo-Friedel-Crafts acylation' of quinones, *Green Chem.*, 2001, **3**, 224–228; (b) M. Oelgemöller, C. Schiel, R. Fröhlich and J. Mattay, The "Photo-Friedel-Crafts Acylation" of 1,4-Naphthoquinones, *Eur. J. Org. Chem.*, 2002, 2465; (c) L. J. Mitchell, W. Lewis and C. J. Moody, Solar photochemistry: optimisation of the photo Friedel-Crafts acylation of naphthoquinones, *Green Chem.*, 2013, **15**, 2830–2842.
- 25 (a) M. E. Jiménez-Hernández, F. Manjón, D. Garcia-Fresnadillo and G. Orellana, Solar water disinfection by singlet oxygen photogenerated with polymer-supported Ru(II) sensitizers, *Sol. Energy*, 2006, **80**, 1382–1387; (b) L. Villén, F. Manjón, D. Garcia-Fresnadillo and G. Orellana, Solar water disinfection by photocatalytic singlet oxygen production in heterogeneous medium, *Appl. Catal., B*, 2006, **69**, 1–9.
- 26 (a) E. E. Coyle and M. Oelgemöller, Micro-photochemistry: photochemistry in microstructured reactors. The new photochemistry of the future?, *Photochem. Photobiol. Sci.*, 2008, **7**, 1313–1322; (b) J.-C. Charpentier and M. Oelgemöller, Highlights of Photochemical Reactions in Microflow Reactors, *Chem. Eng. Technol.*, 2012, **35**, 1144–1152; (c) C. P. Park, R. A. Maurya, J. H. Lee and D.-P. Kim, Efficient photosensitized oxygenations in phase contact enhanced microreactors, *Lab Chip*, 2011, **11**, 1941–1945.
- 27 M. DeRosa, Photosensitized singlet oxygen and its applications, *Coord. Chem. Rev.*, 2002, **233–234**, 351–371.
- 28 N. Hoffmann, Photochemical Reactions as Key Steps in Organic Synthesis, *Chem. Rev.*, 2008, **108**, 1052–1103.
- 29 (a) M. Zamadar and A. Greer, *Handbook of Synthetic Photochemistry*, Wiley-VCH, Weinheim, 2009, pp. 353–386; (b) A. Greer, Organic chemistry of singlet oxygen, *Tetrahedron*, 2006, **62**, 10613; (c) Themed issue Organic Chemistry of Singlet Oxygen, see other reports in vol. 62, 10603–10776.
- 30 (a) E. L. Clennan, *Synthetic organic photochemistry*, Marcel Dekker, New York, 2005, vol. 12, pp. 365–390; (b) E. L. Clennan and A. Pace, Advances in singlet oxygen chemistry, *Tetrahedron*, 2005, **61**, 6665–6691; (c) E. L. Clennan, New Mechanistic and Synthetic Aspects of Singlet Oxygen Chemistry, *Tetrahedron*, 2000, **56**, 9151–9179.
- 31 (a) M. Rosaria Iesce, *Synthetic organic photochemistry*, ed. A. G. Griesbeck and J. Mattay, Marcel Dekker, New York, 2005, vol. 12, pp. 299–363; (b) M. Rosaria Iesce, F. Cermola and F. Temussi, Photooxygenation of Heterocycles, *Curr. Org. Chem.*, 2005, **9**, 109–139.
- 32 (a) M. Prein and W. Adam, Die Schenck-En-Reaktion: eine diastereoselektive Oxyfunktionalisierung mit Singulett-sauerstoff für präparative Anwendungen, *Angew. Chem.*, 1996, **108**, 519–538; (b) M. Prein and W. Adam, The Schenck Ene Reaction: Diastereoselective Oxyfunctionalization with Singlet Oxygen in Synthetic Applications, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 477–494.
- 33 A. Gorman, J. Killoran, C. O'Shea, T. Kenna, W. M. Gallagher and D. F. O'Shea, In Vitro Demonstration of the Heavy-Atom Effect for Photodynamic Therapy, *J. Am. Chem. Soc.*, 2004, **126**, 10619–10631.
- 34 N. Adarsh, M. Shanmugasundaram, R. R. Avirah and D. Ramaiah, Aza-BODIPY Derivatives: Enhanced Quantum Yields of Triplet Excited States and the Generation of Singlet Oxygen and their Role as Facile Sustainable Photooxygenation Catalysts, *Chem.-Eur. J.*, 2012, **18**, 12655–12662.
- 35 D. Huang, J. Sun, L. Ma, C. Zhang and J. Zhao, Preparation of ketocoumarins as heavy atom-free triplet photosensitizers for triplet-triplet annihilation upconversion, *Photochem. Photobiol. Sci.*, 2013, **12**, 872–882.
- 36 S.-y. Takizawa, R. Aboshi and S. Murata, Photooxidation of 1,5-dihydroxynaphthalene with iridium complexes as singlet oxygen sensitizers, *Photochem. Photobiol. Sci.*, 2011, **10**, 895–903.
- 37 (a) P. I. Djurovich, D. Murphy, M. E. Thompson, B. Hernandez, R. Gao, P. L. Hunt and M. Selke, Cyclometalated iridium and platinum complexes as singlet oxygen photosensitizers: quantum yields, quenching rates and correlation with electronic structures, *Dalton Trans.*, 2007, 3763–3770; (b) R. Gao, D. G. Ho, B. Hernandez, M. Selke, D. Murphy, P. I. Djurovich and M. E. Thompson, Bis-cyclometalated Ir(III) Complexes as Efficient Singlet Oxygen Sensitizers, *J. Am. Chem. Soc.*, 2002, **124**, 14828–14829; (c) S.-W. Lai, Y. Liu, D. Zhang, B. Wang, C.-N. Lok, C.-M. Che and M. Selke, Efficient Singlet Oxygen Generation by Luminescent 2-(2'-Thienyl)Pyridyl Cyclometalated Platinum(II) Complexes and Their Calixarene Derivatives, *Photochem. Photobiol.*, 2010, **86**, 1414–1420.
- 38 (a) A. A. Abdel-Shafi, P. D. Beer, R. J. Mortimer and F. Wilkinson, Photosensitized Generation of Singlet Oxygen

- from (Substituted Bipyridine)ruthenium(II) Complexes, *Helv. Chim. Acta*, 2001, **84**, 2784–2795; (b) A. A. Abdel-Shafi, P. D. Beer, R. J. Mortimer and F. Wilkinson, Photosensitized generation of singlet oxygen from ruthenium(II)-substituted benzoaza-crown-bipyridine complexes, *Phys. Chem. Chem. Phys.*, 2000, **2**, 3137–3144; (c) A. A. Abdel-Shafi, P. D. Beer, R. J. Mortimer and F. Wilkinson, Photosensitized Generation of Singlet Oxygen from Vinyl Linked Benzo-Crown-Ether-Bipyridyl Ruthenium(II) Complexes, *J. Phys. Chem. A*, 2000, **104**, 192–202.
- 39 A. A. Abdel-Shafi, J. L. Bourdelande and S. S. Ali, Photosensitized generation of singlet oxygen from rhenium(I) and iridium(III) complexes, *Dalton Trans.*, 2007, 2510–2516.
- 40 L. Hammarström and O. Johansson, Expanded bite angles in tridentate ligands. Improving the photophysical properties in bistridentate Ru^{II} polypyridine complexes, *Coord. Chem. Rev.*, 2010, **254**, 2546–2559.
- 41 D. G. Brown, N. Sanguantrakun, B. Schulze, U. S. Schubert and C. P. Berlinguette, Bis(tridentate) Ruthenium–Terpyridine Complexes Featuring Microsecond Excited-State Lifetimes, *J. Am. Chem. Soc.*, 2012, **134**, 12354–12357.
- 42 (a) E. A. Medlycott and G. S. Hanan, Designing tridentate ligands for ruthenium(II) complexes with prolonged room temperature luminescence lifetimes, *Chem. Soc. Rev.*, 2005, **34**, 133–142; (b) X.-y. Wang, A. Del Guerzo and R. H. Schmehl, Photophysical behavior of transition metal complexes having interacting ligand localized and metal-to-ligand charge transfer states, *J. Photochem. Photobiol., C*, 2004, **5**, 55–77.
- 43 (a) J. Sun, J. Zhao, H. Guo and W. Wu, Visible-light harvesting iridium complexes as singlet oxygen sensitizers for photooxidation of 1,5-dihydroxynaphthalene, *Chem. Commun.*, 2012, **48**, 4169–4171; (b) J. Sun, F. Zhong and J. Zhao, Observation of the long-lived triplet excited state of perylenebisimide (PBI) in C^N cyclometalated Ir(III) complexes and application in photocatalytic oxidation, *Dalton Trans.*, 2013, **42**, 9595–9605; (c) W. Wu, P. Yang, L. Ma, J. Lalevée and J. Zhao, Visible-Light Harvesting Pt(II) Complexes as Singlet Oxygen Photosensitizers for Photooxidation of 1,5-Dihydroxynaphthalene, *Eur. J. Inorg. Chem.*, 2013, **2013**, 228–231.
- 44 M. Galletta, S. Campagna, M. Quesada, G. Ulrich and R. Ziessel, The elusive phosphorescence of pyromethene-BF₂ dyes revealed in new multicomponent species containing Ru(II)–terpyridine subunits, *Chem. Commun.*, 2005, 4222–4224.
- 45 D. Garcia-Fresnadillo, Y. Georgiadou, G. Orellana, A. M. Braun and E. Oliveros, Singlet-Oxygen (¹Δ_g) Production by Ruthenium(II) complexes containing polyazahe-trocyclic ligands in methanol and in water, *Helv. Chim. Acta*, 1996, **79**, 1222–1238.
- 46 S. P. Foxon, M. A. H. Alamiry, M. G. Walker, A. J. H. M. Meijer, I. V. Sazanovich, J. A. Weinstein and J. A. Thomas, Photophysical Properties and Singlet Oxygen Production by Ruthenium(II) Complexes of Benzo[1]-dipyrido[3,2-*a*:2',3'-*c*]phenazine: Spectroscopic and TD-DFT Study, *J. Phys. Chem. A*, 2009, **113**, 12754–12762.
- 47 A. C. Benniston, V. Grossshenny, A. Harriman and R. Ziessel, Photophysical properties of closely-coupled, binuclear ruthenium(II) bis(2,2':6',2"-terpyridine) complexes, *Dalton Trans.*, 2004, 1227–1232.
- 48 H.-Y. Ding, X.-S. Wang, L.-Q. Song, J.-R. Chen, J.-H. Yu, Chao-Li and B.-W. Zhang, Aryl-modified ruthenium bis(terpyridine) complexes: Quantum yield of ¹O₂ generation and photocleavage on DNA, *J. Photochem. Photobiol., A*, 2006, **177**, 286–294.
- 49 A. D'Aléo, E. Cecchetto, L. de Cola and R. M. Williams, Metal Ion Enhanced Charge Transfer in a Terpyridine-bis-Pyrene System, *Sensors*, 2009, **9**, 3604–3626.
- 50 M. Hissler, A. Harriman, A. Khatyr and R. Ziessel, Intramolecular Triplet Energy Transfer in Pyrene–Metal Polypyridine Dyads: A Strategy for Extending the Triplet Lifetime of the Metal Complex, *Chem.–Eur. J.*, 1999, **5**, 3366–3381.
- 51 G. Albano, V. Balzani, E. C. Constable, M. Maestri and D. R. Smith, Photoinduced processes in 4'-(9-anthryl)-2,2':6',2"-terpyridine, its protonated forms and Zn(II), Ru(II) and Os(II) complexes, *Inorg. Chim. Acta*, 1998, **277**, 225–231.
- 52 Z. Ye, B. Song, Y. Yin, R. Zhang and J. Yuan, Development of singlet oxygen-responsive phosphorescent ruthenium(II) complexes, *Dalton Trans.*, 2013, **42**, 14380–14383.
- 53 J. Eberhard, K. Peuntinger, R. Fröhlich, D. M. Guldi and J. Mattay, in preparation.
- 54 F. Wilkinson, W. P. Helman and A. B. Ross, Quantum Yields for the Photosensitized Formation of the Lowest Electronically Excited Singlet State of Molecular Oxygen in Solution, *J. Phys. Chem. Ref. Data*, 1993, **22**, 113.
- 55 (a) A. C. Benniston, A. Harriman and J. W. Verhoeven, Comment: Electron-transfer reactions in the 9-mesityl-10-methylacridinium ion: impurities, triplet states and infinitely long-lived charge-shift states?, *Phys. Chem. Chem. Phys.*, 2008, **10**, 5156–5158, and references therein (b) S. Fukuzumi, H. Kotani and K. Ohkubo, Response: Why had long-lived electron-transfer states of donor-substituted 10-methylacridinium ions been overlooked? Formation of the dimer radical cations detected in the near-IR region, *Phys. Chem. Chem. Phys.*, 2008, **10**, 5159; (c) S. Fukuzumi and K. Ohkubo, Selective photocatalytic reactions with organic photocatalysts, *Chem. Sci.*, 2013, **4**, 561.
- 56 A. G. Griesbeck and M. Cho, 9-Mesityl-10-methylacridinium: An Efficient Type II and Electron-Transfer Photooxygenation Catalyst, *Org. Lett.*, 2007, **9**, 611–613.
- 57 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.
- 58 G. M. Sheldrick, A short history of SHELX, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112–122.
- 59 A. M. Brouwer, Standards for photoluminescence quantum yield measurements in solution (IUPAC Technical Report), *Pure Appl. Chem.*, 2011, **83**, 2213–2228.

- $$60 \quad \Phi_{\Delta}^{\text{sens}} = \Phi_{\Delta}^{\text{std}} \times \frac{F^{\text{std}}}{F^{\text{sens}}} \times \frac{\nu_{\text{initl}}^{\text{sens}}}{\nu_{\text{initl}}^{\text{std}}}$$
- 61 (a) P. Müller and K. Brettel, $[\text{Ru}(\text{bpy})_3]^{2+}$ as a reference in transient absorption spectroscopy: differential absorption coefficients for formation of the long-lived $^3\text{MLCT}$ excited state, *Photochem. Photobiol. Sci.*, 2012, **11**, 632–636; (b) D. K. Liu, B. S. Brunschwig, C. Creutz and N. Sutin, Formation of electronically excited products in electron-transfer reactions: reaction of polypyridine complexes of cobalt (I) and ruthenium(II) in acetonitrile, *J. Am. Chem. Soc.*, 1986, **108**, 1749–1755.
- 62 (a) K. Bergmann and C. T. O'Konski, A Spectroscopic Study of Methylene Blue Monomer, Dimer, and Complexes with Montmorillonite, *J. Phys. Chem.*, 1963, **67**, 2169–2177; (b) C. Lee, Y. W. Sung and J. W. Park, Multiple Equilibria of Phenothiazine Dyes in Aqueous Cyclodextrin Solutions, *J. Phys. Chem. B*, 1999, **103**, 893–898.
- 63 M. Montalti, A. Credi, L. Prodi and T. M. Gandolfi, *Handbook of photochemistry*, CRC/Taylor & Francis, Boca Raton, 3rd edn, 2006.
- 64 D. Wöhrle, W.-D. Stohrer and M. W. Tausch, *Photochemie*, Wiley-VCH, Weinheim, 2005.
- 65 K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li and T. L. Windus, Basis Set Exchange: A Community Database for Computational Sciences, *J. Chem. Inf. Model.*, 2007, **47**, 1045–1052.
- 66 (a) P. J. Hay and W. R. Wadt, Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals, *J. Chem. Phys.*, 1985, **82**, 299–310; (b) P. J. Hay and W. R. Wadt, Ab initio effective core potentials for molecular calculations. Potentials for main group elements Na to Bi, *J. Chem. Phys.*, 1985, **82**, 284–298; (c) P. J. Hay and W. R. Wadt, Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg, *J. Chem. Phys.*, 1985, **82**, 270–283.
- 67 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. J. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09 (Revision C.1)*, 2009.
- 68 E. C. Constable, A. M. W. Cargill Thompson, D. A. Tochter and M. A. M. Daniels, Synthesis, characterisation and spectroscopic properties of ruthenium(II)-2,2':6',2''-terpyridine coordination triades, *New J. Chem.*, 1992, **16**, 855–867.
- 69 K. Mohamed and D. Padma, Spectral studies on pyridinium hexafluorophosphate, *Spectrochim. Acta, Part A*, 1985, **41**, 725–728.
- 70 (a) N. V. Ignat'ev, P. Barthen, A. Kucheryna, H. Willner and P. Sartori, A Convenient Synthesis of Triflate Anion Ionic Liquids and Their Properties, *Molecules*, 2012, **17**, 5319–5338; (b) G. J. P. Britovsek, J. England and A. J. P. White, Non-heme Iron(II) Complexes Containing Tripodal Tetradentate Nitrogen Ligands and Their Application in Alkane Oxidation Catalysis, *Inorg. Chem.*, 2005, **44**, 8125–8134.
- 71 R. Hogg and R. G. Wilkins, 57. Exchange studies of certain chelate compounds of the transitional metals. Part VIII. 2,2',2''-terpyridine complexes, *J. Chem. Soc.*, 1962, 341–350.
- 72 (a) M. A. Harvey, S. Baggio, A. Ibañez and R. Baggio, Three zinc(II) complexes presenting a ZnN_6 chromophore and with peroxodisulfate as the counter-ion, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2004, **60**, m375–m381; (b) F. Dumitru, E. Petit, A. van der Lee and M. Barboiu, Homo- and Heteroduplex Complexes Containing Terpyridine-Type Ligands and Zn^{2+} , *Eur. J. Inorg. Chem.*, 2005, **2005**, 4255–4262; (c) A. M. Goforth, M. A. Tershansy, M. D. Smith, L. Peterson, J. G. Kelley, W. J. I. DeBenedetti and H.-C. Zur Loye, Structural Diversity and Thermochromic Properties of Iodobismuthate Materials Containing d-Metal Coordination Cations: Observation of a High Symmetry $[\text{Bi}_3\text{I}_{11}]^{2-}$ Anion and of Isolated I^- Anions, *J. Am. Chem. Soc.*, 2011, **133**, 603–612.
- 73 (a) B. Maity, S. Gadadhar, T. K. Goswami, A. A. Karande and A. R. Chakravarty, Impact of metal on the DNA photocleavage activity and cytotoxicity of ferrocenyl terpyridine 3d metal complexes, *Dalton Trans.*, 2011, **40**, 11904–11913; (b) N. W. Alcock, P. R. Barker, J. M. Haider, M. J. Hannon, C. L. Painting, Z. Pikramenou, E. A. Plummer, K. Rissanen and P. Saarenketo, Red and blue luminescent metallo-supramolecular coordination polymers assembled through π - π interactions, *J. Chem. Soc., Dalton Trans.*, 2000, 1447–1462; (c) Y. H. Lee, E. Kubota, A. Fuyuhiko, S. Kawata, J. M. Harrowfield, Y. Kim and S. Hayami, Synthesis, structure and luminescence properties of Cu(II), Zn(II) and Cd(II) complexes with 4'-terphenylterpyridine, *Dalton Trans.*, 2012, **41**, 10825–10831; (d) P. Wang, Z. Li, G.-C. Lv, H.-P. Zhou, C. Hou, W.-Y. Sun and Y.-P. Tian, Zinc(II) complex with terpyridine derivative ligand as “on-off” type fluorescent probe for cobalt(II) and nickel(II) ions, *Inorg. Chem. Commun.*, 2012, **18**, 87–91; (e) X. Chen, Q. Zhou, Y. Cheng, Y. Geng, D. Ma, Z. Xie and L. Wang, Synthesis, structure and luminescence properties of zinc(II) complexes with terpyridine derivatives as ligands, *J. Lumin.*, 2007, **126**, 81–90; (f) E. Kubota, Y. H. Lee, A. Fuyuhiko, S. Kawata, J. M. Harrowfield, Y. Kim and S. Hayami, Synthesis, structure, and luminescence properties of arylpyridine-substituted terpyridine Zn(II) and Cd(II) complexes, *Polyhedron*, 2013, **52**, 435–441.

- 74 (a) M. L. Scudder, H. A. Goodwin and I. G. Dance, Crystal supramolecular motifs: two-dimensional grids of terpy embraces in $[ML_2]^z$ complexes (L = terpy or aromatic N_3 -tridentate ligand), *New J. Chem.*, 1999, **23**, 695–705; (b) J. McMurtrie and I. G. Dance, Crystal packing in metal complexes of 4'-phenylterpyridine and related ligands: occurrence of the 2D and 1D terpy embrace arrays, *CrystEngComm*, 2009, **11**, 1141–1149; (c) J. McMurtrie and I. G. Dance, Alternative two-dimensional embrace nets formed by metal complexes of 4'-phenylterpyridine crystallised with hydrophilic anions, *CrystEngComm*, 2010, **12**, 3207–3217.
- 75 E. C. Constable, E. Figgemeier, C. E. Housecroft, S. L. Kokatam, E. A. Medlycott, M. Neuburger, S. Schaffner and J. A. Zampese, Wiring terpyridine: approaches to alkynylthienyl 2,2':6',2''-terpyridines, *Dalton Trans.*, 2008, 6752–6762.
- 76 K. Kasama, K. Kikuchi, Y. Nishida and H. Kokubun, Deactivation mechanism of excited acridine and 9-substituted acridines in water, *J. Phys. Chem.*, 1981, **85**, 4148–4153.
- 77 M. Holzapfel and C. Lambert, Photoinduced Charge Separation and Recombination in Acridine-Triarylamine-Based Redox Cascades, *J. Phys. Chem. C*, 2008, **112**, 1227–1243.
- 78 Donor groups in the 9-position shift this band to lower energies and the weak vibronic structure on this band is then lost.
- 79 (a) J. Hu, B. Xia, D. Bao, A. Ferreira, J. Wan, G. Jones II and V. I. Vullev, Long-Lived Photogenerated States of α -Oligothiophene-Acrinium Dyads Have Triplet Character, *J. Phys. Chem. A*, 2009, **113**, 3096–3107; (b) G. Jones II, D.-X. Yan, D. J. Gosztola, S. R. Greenfield and M. R. Wasielewski, Photoinduced Charge Migration in the Picosecond Regime for Thianthrene-Linked Acridinium Ions, *J. Am. Chem. Soc.*, 1999, **121**, 11016–11017; (c) G. Jones II, D.-X. Yan, S. R. Greenfield, D. J. Gosztola and M. R. Wasielewski, Anilide Linker Group as a Participant in Intramolecular Electron Transfer, *J. Phys. Chem. A*, 1997, **101**, 4939–4942; (d) H. van Willigen, G. Jones II and M. S. Farahat, Time-Resolved EPR Study of Photoexcited Triplet-State Formation in Electron-Donor-Substituted Acridinium Ions, *J. Phys. Chem.*, 1996, **100**, 3312–3316; (e) G. Jones II, M. S. Farahat, S. R. Greenfield, D. J. Gosztola and M. R. Wasielewski, Ultrafast photoinduced charge-shift reactions in electron donor-acceptor 9-arylacridinium ions, *Chem. Phys. Lett.*, 1994, **229**, 40–46.
- 80 K. C. D. Robson, B. D. Koivisto, T. J. Gordon, T. Baumgartner and C. P. Berlinguette, Triphenylamine-Modified Ruthenium(II) Terpyridine Complexes: Enhancement of Light Absorption by Conjugated Bridging Motifs, *Inorg. Chem.*, 2010, **49**, 5335–5337.
- 81 (a) M. Presselt, B. Dietzek, M. Schmitt, J. Popp, A. Winter, M. Chipper, C. Friebe and U. S. Schubert, Zinc(II) Bisterpyridine Complexes: The Influence of the Cation on the π -Conjugation between Terpyridine and the Lateral Phenyl Substituent, *J. Phys. Chem. C*, 2008, **112**, 18651–18660; (b) M. Presselt, B. Dietzek, M. Schmitt, S. Rau, A. Winter, M. Jäger, U. S. Schubert and J. Popp, A Concept to Tailor Electron Delocalization: Applying QTAIM Analysis to Phenyl-Terpyridine Compounds, *J. Phys. Chem. A*, 2010, **114**, 13163–13174.
- 82 American Society for Testing and Materials (ASTM), *ASTM G173 - 03(2012)*, <http://www.astm.org/Standards/G173.htm>
- 83 The parent acridinium ion and rotational hindered 9-aryl derivatives have usually high quantum yields of about 1.0.
- 84 K. Kikuchi, Y. Hattori, C. Sato and H. Kokubun, Deactivation mechanism of photoexcited 9-phenylacridine in methanol, *J. Phys. Chem.*, 1990, **94**, 4039–4042.
- 85 L. A. Diverdi and M. R. Topp, Subnanosecond time-resolved fluorescence of acridine in solution, *J. Phys. Chem.*, 1984, **88**, 3447–3451.
- 86 A. Kellmann, Intersystem crossing and internal conversion quantum yields of acridine in polar and nonpolar solvents, *J. Phys. Chem.*, 1977, **81**, 1195–1198.
- 87 The neglect of spin-orbit coupling and thus resulting zero oscillator strengths prevent a weighting of importance for these transitions. Most likely the nearly isoenergetic splitting is due to the unsymmetrical nature of the optimized complex geometry as found for the $S_0 \rightarrow S_n$ transitions.
- 88 B. Laleu, C. Herse, B. W. Laursen, G. Bernardinelli and J. Lacour, Bent Structure and Dynamic Stereochemistry of Chiral Acridinium Cations, *J. Org. Chem.*, 2003, **68**, 6304–6308.
- 89 Namely, $[Ir(ppy)_2(phen)]^+ < 5000 \text{ L mol}^{-1} \text{ cm}^{-1}$ at $>400 \text{ nm}$.
- 90 R. W. Redmond and J. N. Gamlin, A Compilation of Singlet Oxygen Yields from Biologically Relevant Molecules, *Photochem. Photobiol.*, 1999, **70**, 391–475.
- 91 Next to 1,3-diphenylisobenzofuran (DPBF) which can only be employed for sensitizers absorbing $>450 \text{ nm}$ (here: Ru^{II} series only). Irradiance at wavelengths below will decompose DPBF by auto-sensitization (Abs. λ_{max} 412 nm).
- 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 $\sim 3.6 \times 10^{-5} \text{ M}$, $A \approx 3.3$ in 1 cm cuvettes) vs. the low absorbing Ir^{III} complexes and recent adjustment in a similar batch procedure by Zhao *et al.*
- 93 (a) C. Tanielian and C. Wolff, Porphyrin-Sensitized Generation of Singlet Molecular Oxygen: Comparison of Steady-State and Time-Resolved Methods, *J. Phys. Chem.*, 1995, **99**, 9825–9830; (b) C. Tanielian, L. Golder and C. Wolff, Production and quenching of singlet oxygen by the sensitizer in dye-sensitized photo-oxygenations, *J. Photochem.*, 1984, **25**, 117–125.
- 94 C. Tanielian, C. Wolff and M. Esch, Singlet Oxygen Production in Water: Aggregation and Charge-Transfer Effects, *J. Phys. Chem.*, 1996, **100**, 6555–6560.
- 95 (a) G. O. Schenck, K. Gollnick, G. Buchwald, S. Schroeter and G. Ohloff, Zur chemischen und sterischen

- Selektivität der photosensibilisierten O₂-Übertragung auf (+)-Limonen und (+)-Carvomenthen, *Justus Liebigs Ann. Chem.*, 1964, **674**, 93–117; (b) K. Gollnick and G. O. Schenck, Mechanism and stereoselectivity of photosensitized oxygen transfer reactions, *Pure Appl. Chem.*, 1964, **9**, 507–526; (c) K. Gollnick and A. Schnatterer, 9,10-Dicyanoanthracene-sensitized photooxygenation of α,α' -dimethylstilbenes. Mechanism and kinetics of the competing singlet oxygen and electron transfer photooxygenation reactions, *Photochem. Photobiol.*, 1986, **43**, 365–378; (d) C. S. Foote, S. Wexler and W. Ando, Chemistry of singlet oxygen III. Product selectivity, *Tetrahedron Lett.*, 1965, **6**, 4111–4118; (e) C. S. Foote, Photosensitized oxygenations and the role of singlet oxygen, *Acc. Chem. Res.*, 1968, **1**, 104–110; (f) T. Sato and E. Murayama, The Unsensitized Photooxidation of (+)-Limonene, 1,2-Dimethylcyclohexene, and *endo*-Dicyclopentadiene, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 715–719; (g) P. Schieberle, W. Maier, J. Firl and W. Grosch, HRGC separation of hydroperoxides formed during the photosensitized oxidation of (R)-(+)-Limonene, *J. High Resolut. Chromatogr.*, 1987, **10**, 588–593; (h) V. Rapozzi, L. Beverina, P. Salice, G. A. Pagani, M. Camerin and L. E. Xodo, Photooxidation and Phototoxicity of π -Extended Squaraines, *J. Med. Chem.*, 2010, **53**, 2188–2196.
- 96 G. A. Olah and Á. Molnár, *Hydrocarbon chemistry*, Wiley-Interscience and John Wiley & Sons, Inc, Hoboken and N.J., 2nd edn, 2003.
 - 97 Actually, the hydroperoxides were also directly observable *via* GC. However, only 5 peaks were resolved on a standard HP5MS column – a phenomenon first described by Grosch *et al.* (*vide supra*) for a SE-54 column.
 - 98 A. U. Khan and M. Kasha, Direct spectroscopic observation of singlet oxygen emission at 1268 nm excited by sensitizing dyes of biological interest in liquid solution, *Proc. Natl. Acad. Sci. U. S. A.*, 1979, **76**, 6047–6049.