

Ultrafast Excited State Dynamics of Iridium(III) Complexes and their Changes Upon Immobilisation onto Titanium Dioxide Layers

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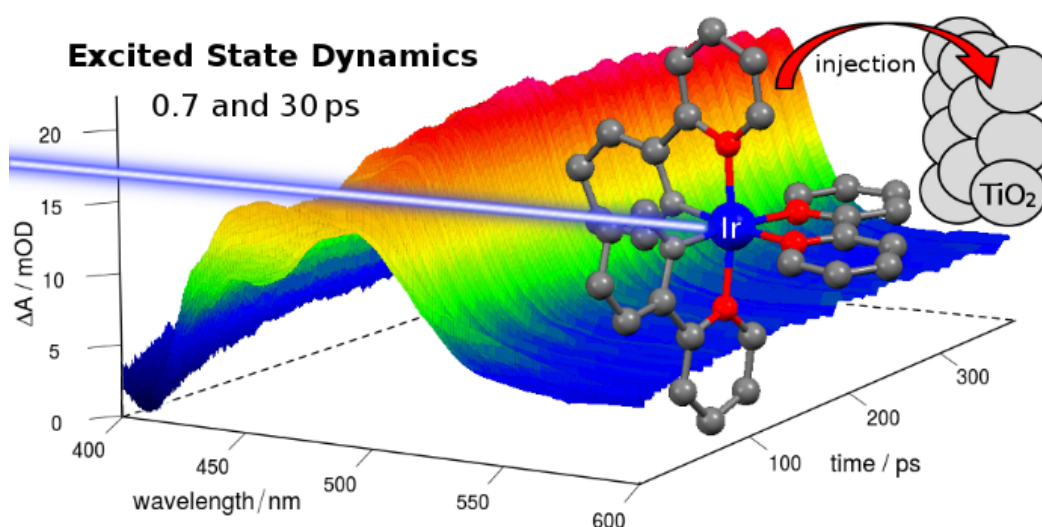
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Experimental and Synthetic Details

If not stated otherwise, all chemicals and solvents were purchased from commercial suppliers and used without further purification. For transient absorption and emission measurements spectroscopically pure acetonitrile was used as solvent (Merck, Uvasol quality).

Preparation of the iridium complexes (1 and 2). The Ir(III) complexes **1** and **2** were synthesised and characterised according to literature procedures.¹⁻⁴

For **1**, in a slightly modified procedure, a mixture of [(ppy)₂IrCl]₂ (300 mg, 279.8 µmol) and bpy (100 mg, 640.3 µmol) was dispersed in 20 mL of ethanol and heated to 100 °C in a pressure tube for 2 days. After cooling a saturated solution of ammonium hexafluorophosphate in water (550 mg, 3.37 mmol) was added forming a yellow precipitate. Filtration and thorough washing with water and diethylether followed by drying in air yielded the pure product.

Yield: 82 % (370 mg, 461.5 µmol); ¹H NMR (300 MHz, dmsO-d₆) δ = 8.89 (d, 2H, ³J = 8.4 Hz, bpy-H₃), 8.27 (m, 4H, bpy-H₄, pyb-H₆ pyridine), 7.92 (m, 6H, bpy-H₆, pyb-H₅ pyridine, pyb-H_{3'} phenyl), 7.70 (t, 2H, ³J = 6.5 Hz, bpy-H₅), 7.62 (dd, 2H, ³J = 5.7 Hz, ⁴J = 0.6 Hz, pyb-H₃ pyridine), 7.16 (t, 2H, ³J = 6.5 Hz, pyb-H₃ pyridine), 7.03 (dt, 2H, ³J = 7.4 Hz, ⁴J = 0.9 Hz, pyb-H_{4'} phenyl), 6.91 (dt, 2H, ³J = 7.4 Hz, ⁴J = 1.1 Hz, pyb-H_{5'} phenyl), 6.19 (dd, 2H, ³J = 7.5 Hz, ⁴J = 0.6 Hz, pyb-H_{6'} phenyl) ppm. HRMS (ESI-TOF in MeOH/0.1 % HCOOH in H₂O 90/10): m/z calcd. for C₃₂H₂₄IrN₄: 657.16261 [M - PF₆]⁺; found: 657.16256 (100 %) with matching isotopic pattern. ATR-IR: $\tilde{\nu}$ = 3039 (w), 1607 (w), 1582 (w), 1562 (w), 1549 (w), 1478 (w), 1445 (w), 1420 (w), 1314 (w), 1268 (w), 1248 (w), 1226 (w), 1162 (w), 1127 (w), 1107 (w), 1064 (w), 1031 (w), 898 (w), 879 (w), 835 (m), 762 (w), 754 (w), 738 (w), 728 (w), 669 (w), 630 (w), 556 (w), 470 (w), 416 (w) cm⁻¹.

Preparation of dye-sensitised TiO₂-layer (2T). Firstly, coating of TiO₂ on object slides made of soda-lime glass (Carl Roth GmbH, smoothed, in vitro diagnostic ISO8037/1) with a size of 21 mm x 26 mm x 1 mm was performed. Prior to this, the glass slides were carefully rinsed with ethanol (EtOH) and dried in air. Subsequently, a diluted suspension (ca. 0.1 ml) of a titania paste (Solaronix, Ti-Nanooxide HT, highly transparent nanocrystalline titanium dioxide paste with anatase particles of 8-10 nm) and EtOH in the ratio 1/10 (v/v) was deposited on the glass slides by drop coating. After 24 h of drying the samples were calcined in a muffle furnace (40 min, 400 °C) resulting in highly transparent TiO₂ layers. Thereafter, the slides were allowed to cool down to approximately 80 °C before dipping into a solution of complex **2** (C₃₄H₂₄F₆IrN₄O₄P, M = 889,76 g/mol, c = 1.6 mmol/l) dissolved in EtOH. After two days of dip coating the dye-sensitised TiO₂-layers (**2T**) were removed from the stock solution, washed with EtOH and dried in air. The successful sensitisation of **2** onto the titania support was evidenced by UV/vis and Raman spectroscopy (see Fig. SI1 and SI2).

Steady-state absorption spectroscopy. Steady-state UV/vis absorption spectra were recorded with an Analytik Jena Specord 50 spectrophotometer. The compounds **1** and **2** were dissolved in acetonitrile of spectroscopic grade and measured in a standard 1.0 cm fluorescence quartz cuvette with an optical density of 0.1 at 388 nm. The pure TiO₂ layer and the dye-sensitised TiO₂ layer (**2T**) were measured by placing a holder with the mounted glass slide into the light pass of the UV/vis absorption spectrometer.

Transient absorption measurements were performed using a regenerative Ti:sapphire amplifier laser (CPA 2001, Clark MRX) system with pulse durations of 150 fs at a repetition rate of 1 kHz. The excitation pulses centred at 388 nm were generated by frequency doubling of a fraction of the fundamental Ti:sapphire output with a BBO crystal and used without further compression. The power of the pump beam

was about 1 μJ per pulse at the sample (diameter roughly 250 μm causing an excitation of about 7 % of the molecules). Another fraction of the fundamental laser output was used to generate the 460 nm pump pulse by a noncollinear optical parametric amplifier (NOPA) where a 2 mm thick type I-BaB₂O₄ (BBO) crystal was employed. These pulses were compressed using standard fused silica prisms. The energy of the pump pulses was about 1 μJ per pulse at the sample (pulse duration 60 fs). Both excitation wavelengths (388 nm and 460 nm) passed an achromatic $\lambda/2$ -plate to adjust the polarisation relative to the probe light. The relative polarisation of the pump pulses were set to parallel, perpendicular and magic angle configuration. The absorption changes of the samples were probed over the whole visible spectral range from about 330 nm to 700 nm. Therefore, a fraction of the Ti:sapphire output was focused into a 4 mm thick calcium fluoride substrate, which was moved on an eccentric path to avoid defect formation. The fundamental 775 nm light was cut off using a high pass filter. The pump and probe beams were focused and spatially overlapped at the sample position. A standard fused silica cuvette with a layer thickness of 1 mm and a sample OD of 0.5 at the pump wavelength 388 nm was used in this setup. The compounds **1** and **2** were dissolved in acetonitrile of spectroscopic grade. The pump-probe kinetics were recorded up to a delay time of about 1500 ps. After passing the sample, the probe light was re-collimated and dispersed by a fused silica prism and spectrally resolved detected by a photo diode array with 512 pixels. The chirp of the probe light was corrected numerically during data processing by fitting the spectral-temporal appearance of the maximum of the coherent artefact signal to a polynomial and subsequent correction of the experimental time axis for this polynomial.⁵

Time-resolved emission spectroscopy. The samples were excited with femtosecond pulses at 388 nm generated as described above. The emission lifetimes were measured by a streak camera system (Streakscope C10627, Hamamatsu).

NIR micro-Raman spectroscopy. Non-resonant Raman spectra of the solid samples, excited at 785 nm, were recorded with a micro-Raman setup (LabRAM HR, Horiba JobinYvon). This setup was equipped with an Olympus BX41 microscope and a video camera. The scattered light was detected by an air-cooled CCD camera operating at 298 K. An Olympus LMPlanFL N 50 $\times$ 0.5 objective focused the laser light onto the solid samples. The grating of the spectrometer had 600 lines/mm and the validation of the wavenumber axis was done by using the Raman signal of silicon. For excitation an external diode laser (LiON Laser System) combined with a Laser Diode Controller Pilot PC 500 (SacherLasertechnik) with a wavelength of 785 nm and a power of $P_0 = 100$ mW was used. To prevent sample heating a D1 filter ($P = P_0/10$) was used.

References:

- [1] M. S. Lowry, W. R. Hudson, R. A. Pascal Jr., S. Bernhard, *J. Am. Chem. Soc.* **2004**, *126*, 14129-14135.
- [2] F. Gärtner, D. Cozzula, S. Losse, A. Boddien, G. Anilkumar, H. Junge, T. Schulz, N. Marquet, A. Spannenberg, S. Gladiali, M. Beller, *Chem. Eur. J.* **2011**, *17*, 6998-7006.
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Steady-State Absorption Spectra

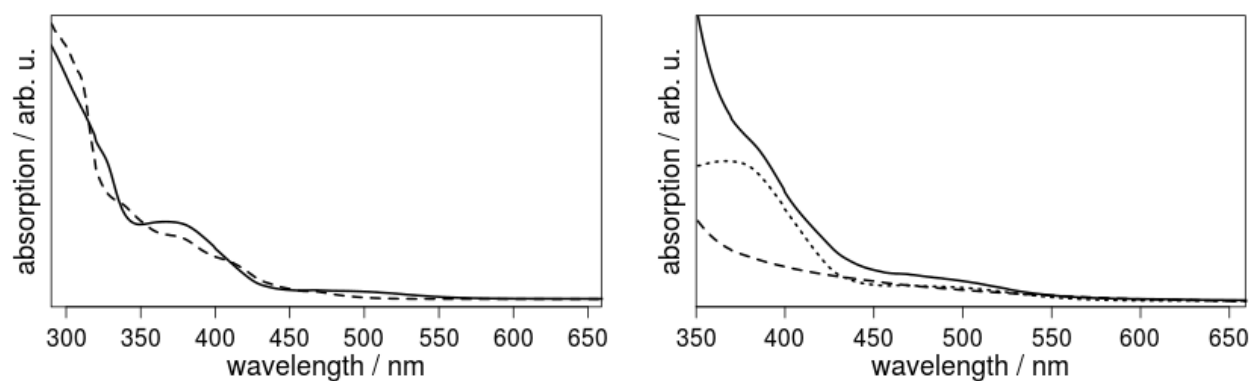


Figure S11.

Left: Absorption spectra of the Ir(III) complexes **1** (dashed) and **2** (solid) in acetonitrile solution.

Right: UV/vis absorption spectrum of the dye-sensitised TiO₂-layer **2T** (solid) in comparison to the pure TiO₂ layer (dashed) and to complex **2** (dotted) dissolved in acetonitrile. Hence, it is apparent that the absorption spectrum of the dye-sensitised TiO₂-layer **2T** is composed of the absorption of complex **2** and titania. In consequence, **2T** absorbs in the visible compared to the bare TiO₂ layer.

Raman Spectra of **2** and **2T**

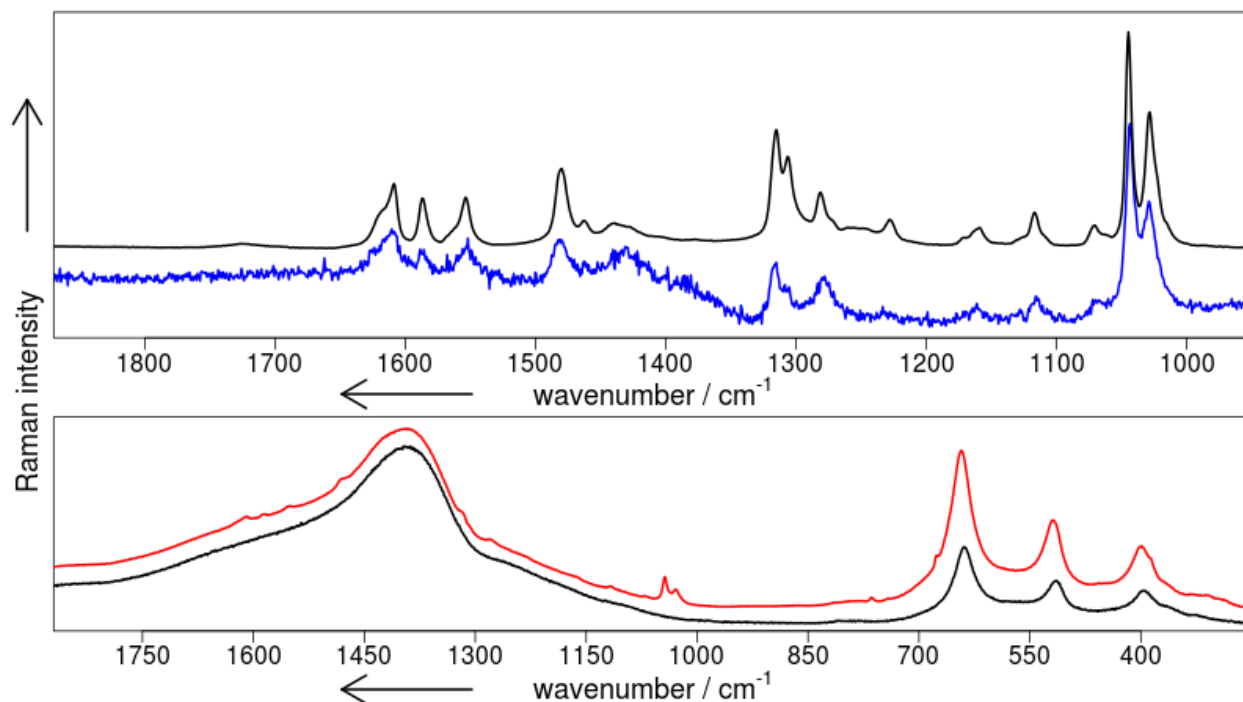


Figure S12.

Bottom: Non-resonant Raman spectrum of complex **2** sensitised on TiO₂ (**2T**, red) in comparison to the Raman spectrum of the bare TiO₂ layer (black). Both samples were excited at 784 nm.

Top: The difference Raman spectrum of these two samples (TiO₂ minus **2T**) in the range between 1850 and 950 cm⁻¹ is shown in blue. In accordance to the Raman spectrum of the pure Ir(III) complex **2** (black), the Raman bands of the difference Raman spectrum (blue) can be assigned to various ring vibration modes of the respective iridium complex. Thus, it can be concluded that complex **2** is successfully sensitised on TiO₂. However, the Raman spectra do not provide information whether **2** is covalently bound or physically adsorbed onto the titania.

Time-resolved Emission Spectra of **1** and **2** in Acetonitrile

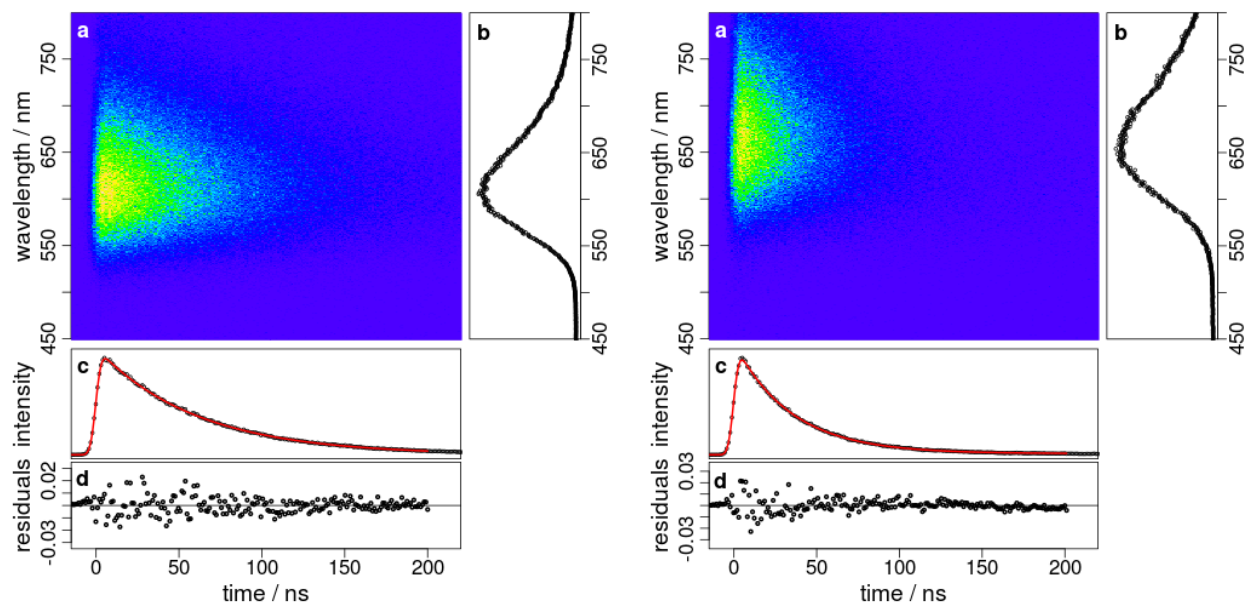


Figure S13.

- Time- and wavelength-dependent emission intensity decays of **1** (left) and **2** (right) in acetonitrile solution measured with a streak camera system,
- emission spectra obtained by summation over all times,
- time traces received by the sum over all wavelengths, where the red lines show the mono-exponentially fitted decay curves and
- residuals of the fits. The obtained lifetimes are summarised in Table S11.

Table S11. Emission maxima λ_{em} and fitted lifetimes τ_{em} of **1** and **2** in acetonitrile ($\lambda_{\text{exc}} = 388 \text{ nm}$).

complex	$\lambda_{\text{em}} / \text{nm}$	$\tau_{\text{em}} / \text{ns}$
1	610	$60.2 \pm 0.4 \text{ ns}$
2	650	$34.3 \pm 0.2 \text{ ns}$

The emission maximum of complex **2** is bathochromically shifted by 40 nm in comparison to the unsubstituted complex **1**, while the emission lifetime of **2** is much shorter than that of **1** (see Table S11). Thus, the two carboxylate anchor groups in 4,4'-position of the 2,2'-bipyridine ligand have a pronounced influence on the relaxation processes of the triplet excited states to the ground state. This behaviour is in accordance to the emission properties of related Ir(III) complexes.^{6,7}

References:

- [6] A. B. Tamayo, S. Garon, T. Sajoto, P.I. Djurovich, I. M. Tysba, R. Bau, M. E. Thompson, *Inorg. Chem.* **2005**, *44*, 8723-8732.
- [7] J. B. Waern, C. Desmarets, L.-M. Chamoreau, H. Amouri, A. Barbieri, C. Sabatini, B. Ventura, F. Barigelletti, *Inorg. Chem.* **2008**, *47*, 3340-3348.

Transient Absorption Spectra of **1** Excited at 388 nm

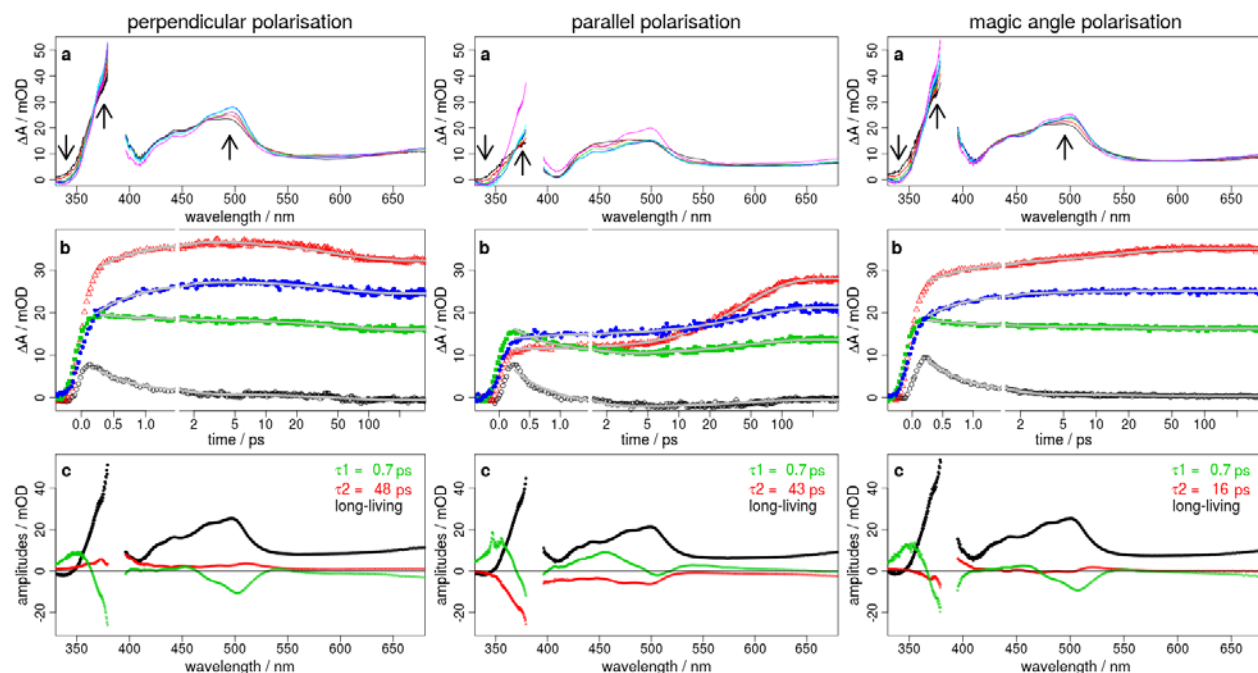


Figure S14.

a) Transient absorption spectra of **1** in acetonitrile excited at 388 nm after 0.5 (black), 0.8 (red), 1.25 (green), 2.0 (blue), 5.0 (light blue) and 50 ps (magenta). The observed changes are marked with arrows.

b) Transient signals observed as a function of the pump-probe delay time at 345 (black), 370 (red), 460 (green) and 500 nm (blue).

c) Overlay of the obtained decay-associated spectra of the short first time constant τ_1 (green), the second time constant τ_2 (red) and the long-living component (black) of complex **1**. The long-living component belongs to the excited state absorption of the lowest triplet excited state with a lifetime in the nanosecond range (see Figure SI 3 and Table SI1).

The polarisation of the pump pulse was adjusted perpendicular (left), parallel (centre) and in magic angle (right) relative to the probe polarisation, respectively.

Transient Absorption Spectra of **1** Excited at 460 nm

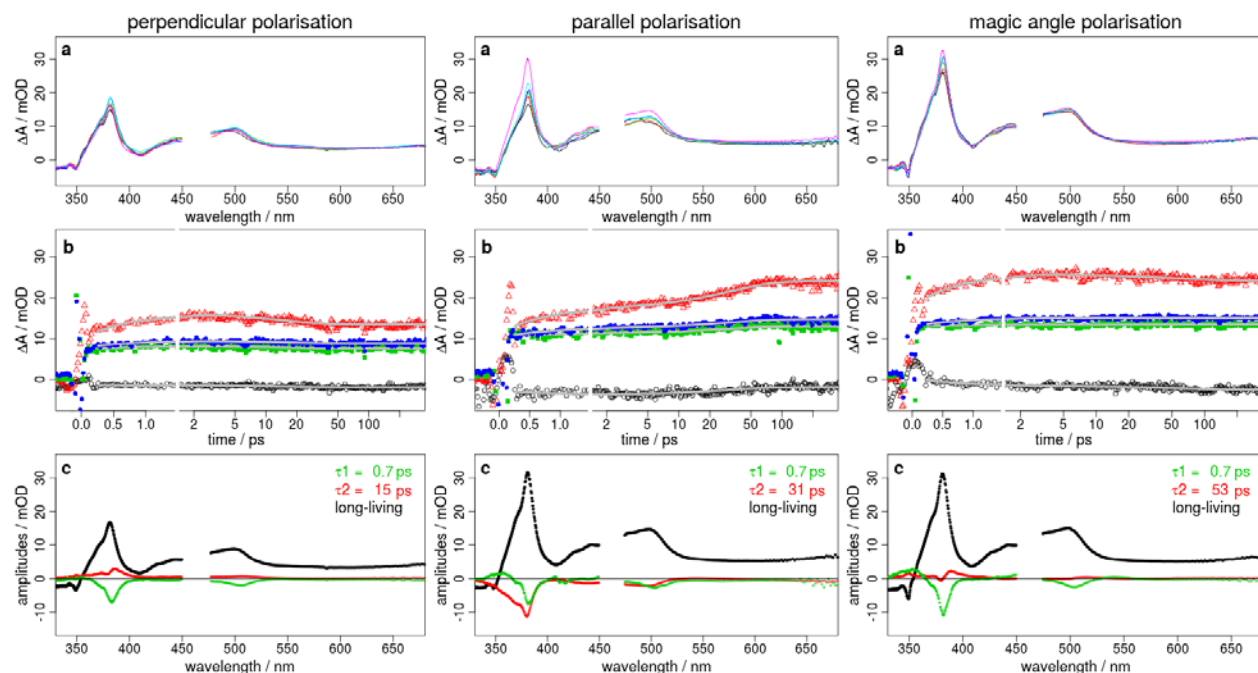


Figure S15.

a) Transient absorption spectra of **1** in acetonitrile excited at 460 nm after 0.5 (black), 0.8 (red), 1.25 (green), 2.0 (blue), 5.0 (light blue) and 50 ps (magenta).

b) Transient signals observed as a function of the pump-probe delay time at 345 (black), 385 (red), 450 (green) and 500 nm (blue).

c) Overlay of the obtained decay-associated spectra of the short first time constant τ_1 (green), the second time constant τ_2 (red) and the long-living component (black) of complex **1**. The long-living component belongs to the excited state absorption of the lowest triplet excited state with a lifetime in the nanosecond range (see Figure S13 and Table S11).

The polarisation of the pump pulse was adjusted to perpendicular (left), parallel (middle) and magic angle (right) orientation, respectively.

Decay-Associated Spectra, Comparison of Different Excitation Wavelengths, Complex 1

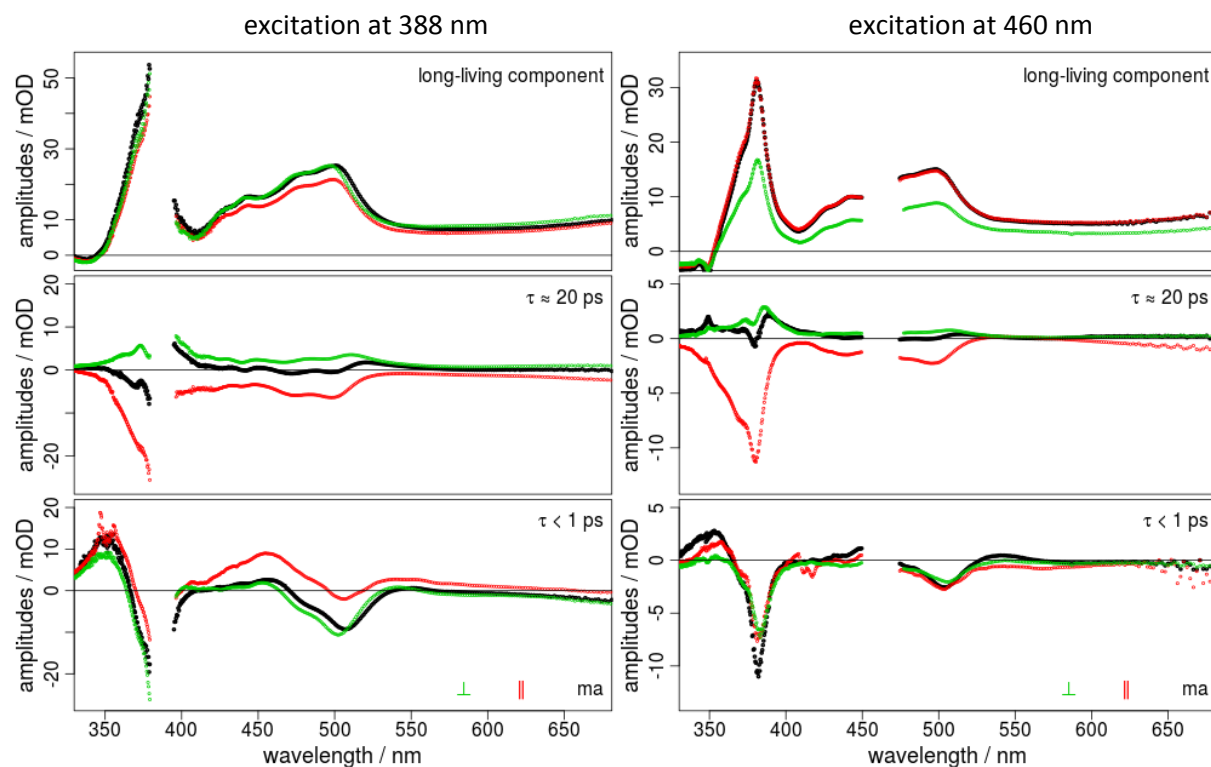


Figure S16.

Summary of the obtained decay-associated spectra of complex **1** excited at 388 (left) and 460 nm (right) with magic angle (black), parallel (red) and perpendicular (green) polarisation of the pump pulse relative to the probe. The amplitudes are shown for the long-living component (top), the second time constant (approx. 20 ps, middle) and the short time constant (0.7 ps, bottom).

Transient Absorption Spectra of **2** Excited at 388 nm

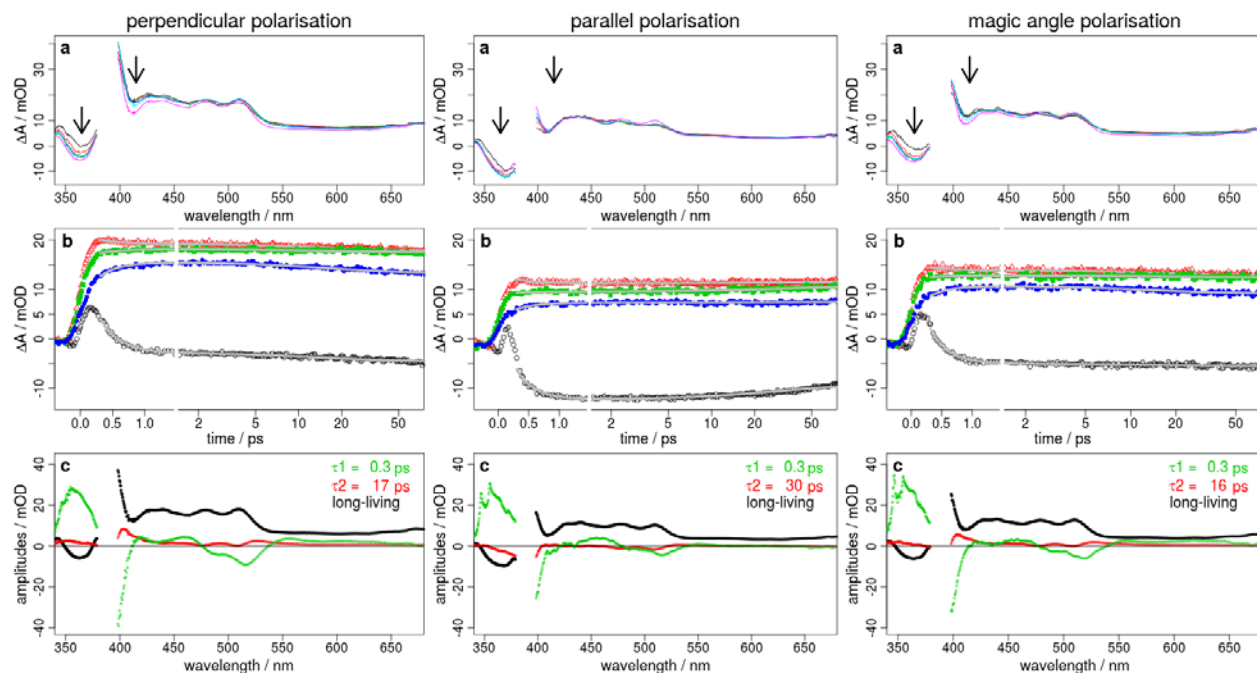


Figure S17.

- a) Transient absorption spectra of **2** in acetonitrile excited at 388 nm after 0.5 (black), 0.8 (red), 1.25 (green), 2.0 (blue), 5.0 (light blue) and 50 ps (magenta). The observed changes are marked with arrows.
- b) Transient signals observed as a function of the pump-probe delay time at 370 (black), 440 (red), 480 (green) and 520 nm (blue).
- c) Overlay of the obtained decay-associated spectra of the short first time constant τ_1 (0.3 ps, green), the second time constant τ_2 (16-30 ps, red) and the long living component (black). Fitted time constants are summarised in Table S12. The long-living component belongs to the excited state absorption of the lowest triplet excited state with a lifetime of 34.3 ± 0.2 ns (see Figure S13 and Table S11).

The polarisation of the pump pulse was set perpendicular (left), parallel (middle) and in magic angle (right) relative to the probe polarisation, respectively.

Transient Absorption Spectra of **2** Excited at 460 nm

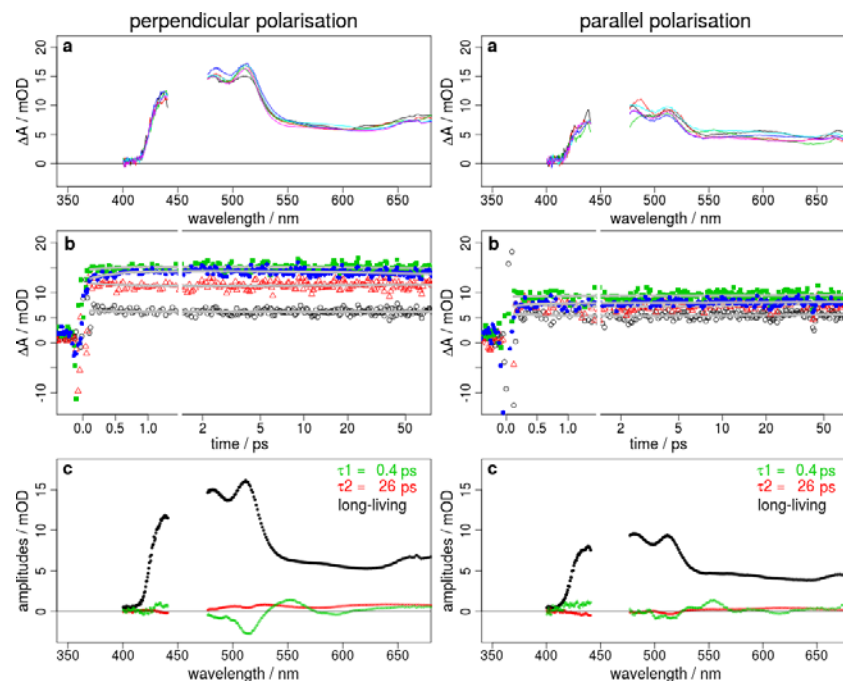


Figure S18.

a) Transient absorption spectra of **2** in acetonitrile excited at 460 nm (0.5 μJ per pulse) after 0.5 (black), 0.8 (red), 1.25 (green), 2.0 (blue), 5.0 (light blue) and 50 ps (magenta). There was no data recorded below 400 nm due to the usage of a cut-off filter.

b) Transient signals observed as a function of the pump-probe delay time at 425 (black), 440 (red), 480 (green) and 520 nm (blue).

c) Overlay of the obtained decay-associated spectra of the short first time constant τ_1 (green), the second time constant τ_2 (red) and the long-living component (black) of complex **1**. The long-living component belongs to the excited state absorption of the lowest triplet excited state with a lifetime in the nanosecond range (see Figure SI 3 and Table SI1).

The polarisation of the pump pulse was adjusted to perpendicular (left) and parallel (right) orientation, respectively.

Overview of the Fitted Time Constants under Different Conditions

Table SI2. Summary of the time constants from the nonlinear least-square fitting of the transient kinetics of **1** and **2** in acetonitrile excited at 388 and 460 nm. Differences concerning the second time constant for one complex obtained with different polarised light result from a relatively low signal to noise ratio. The transient absorption spectra and the respective fits of the kinetics can be found in figure SI4 (**1**, $\lambda_{exc} = 388$ nm), figure SI5 (**1**, $\lambda_{exc} = 460$ nm), figure SI7 (**2**, $\lambda_{exc} = 388$ nm) and figure SI8 (**2**, $\lambda_{exc} = 460$ nm).

complex	λ_{exc} / nm	polarisation	τ_1 / ps	τ_2 / ps
1	388	$\perp$	0.7	48
		$\parallel$	0.7	43
		ma	0.7	16
1	460	$\perp$	0.7	15
		$\parallel$	0.7	31
		ma	0.7	53
2	388	$\perp$	0.3	17
		$\parallel$	0.3	30
		ma	0.3	16
2	460	$\perp$	0.4	26*
		$\parallel$	0.4	26*
		ma	n.a.	n.a.

$\perp$ = perpendicular, $\parallel$ = parallel and ma = magic angle, n.a. not available

* The contribution of the second time constant τ_2 is very little (corresponding amplitudes very small, see Figure SI8), the times are used to have comparability to all other data

Transient Absorption Spectra of the Dye-Sensitised TiO₂-Layer 2T Excited at 388 nm

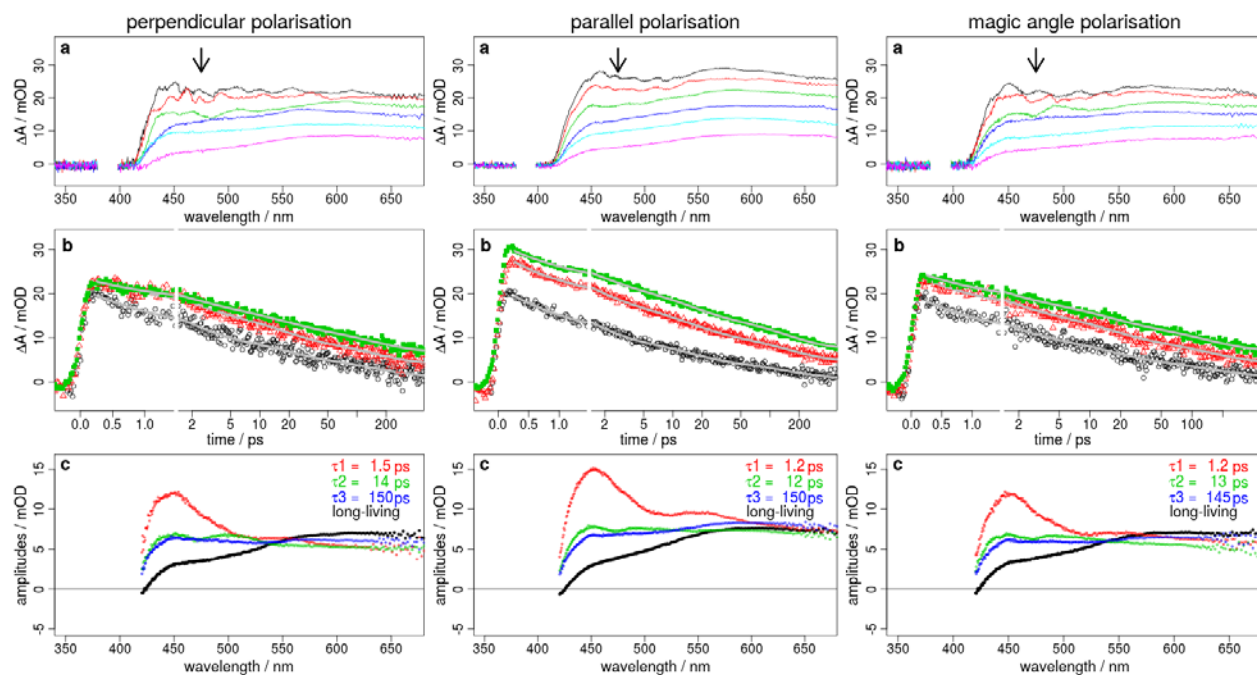


Figure S19.

a) Transient absorption spectra of **2T** excited at 388 nm after 0.5 (black), 1.0 (red), 3.0 (green), 10 (blue), 50 (light blue) and 300 ps (magenta). The observed changes are marked with an arrow in the figure. No signals below 420 nm could be detected, because a cut-off filter was used to avoid scattered light from the pump laser beam.

b) Transient signals observed as a function of the pump-probe delay time at 430 (black), 500 (red) and 600 (green).

c) Overlay of the obtained decay-associated spectra of the short first time constant τ_1 (1.2-1.5 ps, red), the second time constant τ_2 (12-14 ps, green), the third time constant τ_3 (145-150 ps, blue) and the long-living component (black).

The polarisation of the pump pulse was adjusted perpendicular (left), parallel (middle) and in magic angle (right) relative to the probe polarisation, respectively. No differences in the transient spectra and the decay associated spectra are obvious due to differently polarised light.

Comparison of Transient Spectrum of **2** with Amplitudes of Fit of **2T**

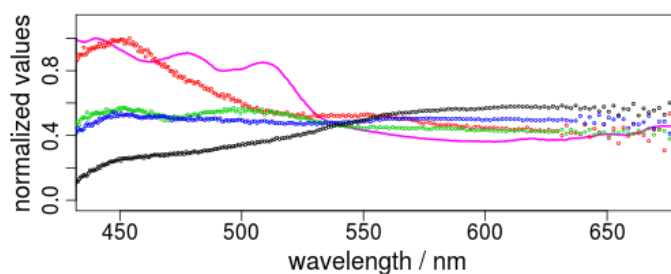


Figure S110.

Transient absorption spectrum of **2** excited at 388 nm with perpendicular polarisation of the pump pulse after 0.5 ps (magenta line). The decay-associated spectra of the short first time constant τ_1 (1.5 ps, red), the second time constant τ_2 (14 ps, green), the third time constant τ_3 (150 ps, blue) and the long-living component (black) of **2T** excited at 388 nm with a perpendicular polarised pump pulse. For better comparison the spectra are normalised. As a result, the amplitudes of the first time constant τ_1 obtained for **2T** (red) is most similar to the transient spectrum of **2** (magenta).

Calculation of the Oriental Relaxation Time τ_{or}

with

Boltzmann constant:	$k_B = 1.3806504 \cdot 10^{-23} \frac{\text{J}}{\text{K}}$
Viscosity of the solvent:	$\eta = 0.26 \cdot 10^{-3} \text{Pa s}$
Temperature:	$T = 298 \text{ K}$
Radius of molecule	$R = 0.584 \text{ nm}$
Hydrodynamic volume:	$V = \frac{4\pi}{3} (R_{\text{molecule}})^3 = 8,34 \cdot 10^{-28} \text{ m}^3$

$$\tau_{or} = \frac{V\eta}{k_B T} = 52.7 \text{ ps}$$

The radius R of the molecule was obtained from the X-ray crystal structure of $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$, CCDC number 959828.⁸

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- [8] G. E. Schneider, H. J. Bolink, E. C. Constable, C. D. Ertl, C. E. Housecroft, A. Pertegàs, J. A. Zampese, A. Kanitz, F. Kessler, S. B. Meier, *Dalton Trans.*, **2014**, 43, 1961-1964.