

Light Intensity Effects on Photoinduced Charge Separation Parameters in a Molecular Triad Based on an Iridium(III) Bis(terpyridine) Unit

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The effect of photon flux on the yield and lifetime of charge separation over the extreme components of a D-Ir-A triad, where D is a triphenyl amine electron donor, A is a naphthalene bis(imide) electron acceptor and Ir is an Ir^{III} bis(terpyridine) complex, has been investigated. In usual laboratory conditions, with nanosecond and picosecond laser pulses in the 4–8 mJ range, biphotonic processes take place. Biphotonic products and their evolution

can introduce complications in reaction mechanisms and their interpretation but can also drastically reduce the yield and the lifetime of the charge-separated state. In the present case, after discussion of several possible mechanisms, the process detrimental to charge separation is ascribed to absorption of a photon by the photogenerated charge-separated state D⁺-Ir-A⁻.

Introduction

The process of converting light energy into chemical energy by synthetic molecular objects, irrespective of the level of complexity and of similarity with the natural system, is generally referred to as artificial photosynthesis. In an oversimplified view, which has become common and therefore accepted in the scientific community over the last decade, this research field includes the study of simple tetra-, tri-, and even bicomponent systems which, upon light absorption, are able to yield charge-separated (CS) states, thus mimicking the primary processes occurring in the reaction centers of bacteria and green plants. There are several differences between the natural system and the artificial ones studied in the laboratories, such as the level of complexity, the physical status, the active-species concentration, and the illumination conditions. The importance of light intensity on the outcome of early events in natural photosynthesis had not escaped biophysicists and biochemists working in the field.^[1–3] However, to our knowledge this aspect has never been clearly addressed in synthetic arrays mimicking charge separation. Herein, we address the issue of light intensity on artificial arrays by examining and discussing the effect of photon flux on charge separation and recombination in a synthetic molecular triad recently studied in our laboratories.^[4] When a multicomponent system designed to achieve charge separation is studied, the final proof of success (or failure) is provided by 1) the yield, and 2) the lifetime of the charge-separated state. Owing to the metastable nature of CS states and to their generally nonemissive nature, these determinations require time-resolved absorption spectroscopy studies that are based on lasers able to deliver light pulses at high intensity. The experimental conditions that laser sources provide are, in terms of photon intensity, many orders of magnitude different from the natural ones, whereas the photoactive component is

generally present at lower concentration than in the natural case. In these conditions, multiphotonic interactions can easily take place, and their final products might or might not be the same as those of monophotonic processes occurring at low photon flux and high concentration regimes typical of natural systems. The importance of multiphotonic absorption is testified to by the intense scientific activity in the rapidly developing field of nonlinear optical (NLO) properties connected to applications in the fields of three-dimensional microfabrication, photodynamic therapy, optical power limiting, optical data storage, two-photon fluorescence microscopy, bioimaging and more.^[5]

Going back to our specific aim, we take into consideration only the intensity-dependent processes of significance in multicomponent synthetic arrays designed to convert light into chemical energy. Without pretending to be exhaustive, the following cases can be considered: 1) simultaneous multiphoton absorption by a single chromophore; 2) consecutive multiphoton absorption by a single chromophore, and 3) single-photon absorption by several different chromophores of the arrays. Two-photon phenomena are the most probable events and we will limit discussion to this case. The first case listed above

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refers to absorption of two photons by the same unit at the same time, which, through a virtual state, leads to a level whose energy corresponds to the overall energy absorbed, that is, two 800 nm photons would lead to a level of energy of about 3 eV, corresponding to the absorption of a photon of 400 nm. This type of event has a very low cross-section, requires an extremely high photon flux, and, because of the low cross section, can favorably compete with monophotonic absorption only when no chromophore of the array has a significant absorbance at the wavelength used for excitation.^[6,7] If we exclude the systems designed for NLO applications mentioned above, this is almost never the case for photoactive systems that are specially designed to display high absorption coefficients at the excitation wavelength, and therefore this possibility will not be considered. The second case, sequential bi-photonic absorption, consists in the absorption of a further photon by an excited species or its reaction product (e.g. a radical) and is a highly probable event, provided that the intermediate state lives long enough to intercept a second photon from the laser pulse. This type of process is rather common for solutes exposed to nanosecond lasers converted to long-lived states such as triplets or radicals.^[8] Depending on whether the absorbing species is a radical or a triplet excited state, the product will be an excited radical or a higher triplet excited state. Both can internally convert and rapidly yield the starting state again, but they could also display some reactivity, yielding new products. Photoionization in this case can be a rather common outcome.^[9–11] The last type of two-photon event, that is, two single-photon absorptions by two different chromophores of an array, is the most common whenever more than one unit can absorb the excitation wavelength. If the components of the assembly are weakly coupled from an electronic viewpoint, the two units absorb independently according to their molar absorption coefficients, leading to an excited state, but there is a finite possibility (depending on the solution concentration and the photon flux) that the two absorbing chromophores are resident in the same multicomponent array. They could further react with the usual, independent reactivity, but more often a reaction between excited states can efficiently compete. Very often this type of reactivity leads to annihilation of the excited states.^[12] When the originally produced excited states succeed in reacting independently, intramolecular reactions can involve their longer-lived products.

The variety of reactions following a two-photon absorption is very rich, and its occurrence under the usual experimental conditions for transient absorption spectroscopy with multicomponent systems could be rather common, if one considers that the concentrations used are of the order of 10^{-6} – 10^{-5} M, corresponding to 10^{-9} – 10^{-8} mol in 1 cm^3 , and the energy used is of the order of several (many) millijoules, corresponding to about 10^{-8} – 10^{-7} mol photons on the irradiated volume, which is generally substantially smaller than 1 cm^3 .

Whereas there is a common understanding that photon flux is an important parameter in the collection and transfer of electronic excitation energy in a so-called antenna system designed to collect and funnel light energy, and several reports discuss this parameter with respect to its rate and efficien-

cy,^[12–16] the same parameter has not received comparable attention in the wide literature on photoinduced charge separation.^[17–18] With the aim of drawing attention to this critical issue, we report and discuss herein the results of a study of the effect of photon flux on the yield and lifetime of a CS state formed in a molecular triad upon light absorption. It is shown that the photon flux parameter is crucial for efficient population of a long-lived CS state. Indeed, it is evidenced how keeping the photon flux low helps to prevent the occurrence of detrimental multiphotonic events in laboratory conditions and allows to correct parameters. Although the specific results obtained herein cannot be considered as general, it can be concluded with a degree of confidence that an improvement of the charge-separation performance of a photosynthetic device made of multicomponent arrays of strongly absorbing units (typical of most synthetic arrays) is expected at low photon flux. This finding is a fortunate outcome for practical applications, since it means that natural conditions are more favorable than laboratory conditions.

Results and Discussion

The triad D-Ir-A is shown in Figure 1 with the models D, Ir, and A of the component units. The triad is composed of a central Ir(terpy)₂³⁺ unit (terpy = terpyridine) bearing at opposite positions an aromatic amine as electron donor and an aromatic

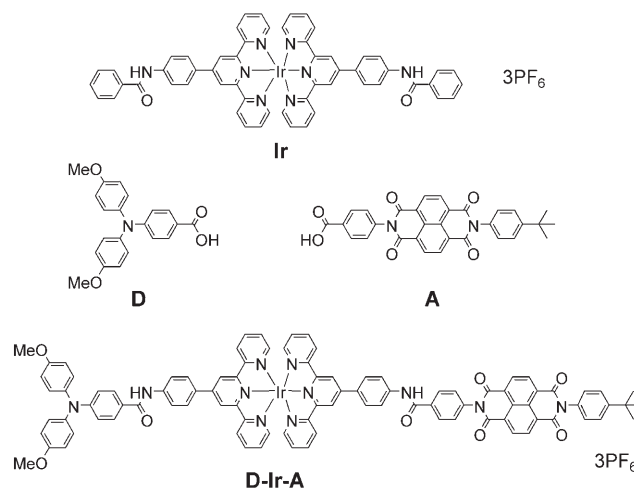


Figure 1. Triad D-Ir-A and the related reference models D, Ir, and A.

bis(imide) as electron acceptor, both of which are connected through amidophenyl spacers at the 4'-position of the terpyridine ligands.^[4]

The absorption spectra of the models, of the triad, and the spectrum resulting from the superposition of the model components are reported in Figure 2. The good additivity of the spectra points to a very modest electronic coupling of the component units, allowing the use of a localized description of the states involved in the photoinduced processes. Complete luminescence quenching of any component is detected upon excitation at 430 nm, corresponding to a selective excitation of

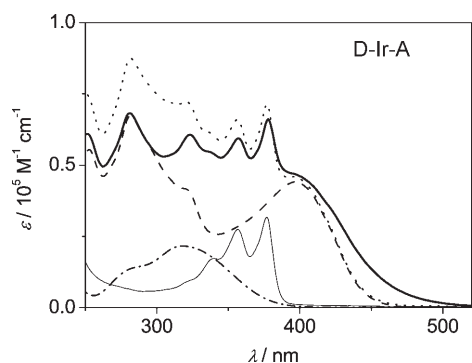


Figure 2. Absorption spectra of the model components and of the array in acetonitrile: Ir (---), D (-.-.), A (—), D-Ir-A (—), D+Ir+A (.....).

Ir. Upon excitation of the triad at 320 nm, the most favorable wavelength for D excitation where the D unit absorbs 30%, and at 357 nm, where the A unit absorbs 45% of the light, a total quenching of the luminescence of each component was detected. In Figure 3, the luminescence of the components in D-Ir-A at the three wavelengths is compared with the luminescence of the models.^[4]

The quenching was ascribed to a sequential electron transfer originating from the excited states $^1\text{D-Ir-A}$ and $\text{D-}^3\text{Ir-A}$ via the

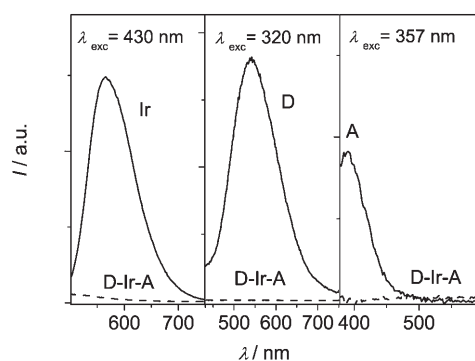


Figure 3. Luminescence spectra of the models (—) and the triad D-Ir-A (---) in air-equilibrated acetonitrile solutions following excitation at the specified wavelength; concentrations are arranged to provide the same absorption of photons in the model and in the corresponding unit in D-Ir-A. The intensity of the panels is arbitrarily scaled.

formation within a few picoseconds of a primary charge-separated state $\text{D}^+\text{-Ir}^-\text{-A}$, which rapidly transfers an electron to yield the final CS state $\text{D}^+\text{-Ir-A}^-$. This state is characterized by slow intramolecular charge recombination at ambient temperature ($\tau = 120 \mu\text{s}$) and is very insensitive to the presence of oxygen ($\tau = 100 \mu\text{s}$).^[4] An energy-level scheme with the rates of the processes leading to the CS state $\text{D}^+\text{-Ir-A}^-$ formation and decay is shown in Figure 4. This scheme was derived by a series of transient absorption determinations from the pico- to the millisecond range performed on the model components D, Ir, and A, on the dyad models D-Ir and Ir-A, and on the triad D-Ir-A using different experimental setups. A summary of the significant photophysical parameters of the models and the array can be found in Table 1.^[4,19,20] The efficiency of CS was rather

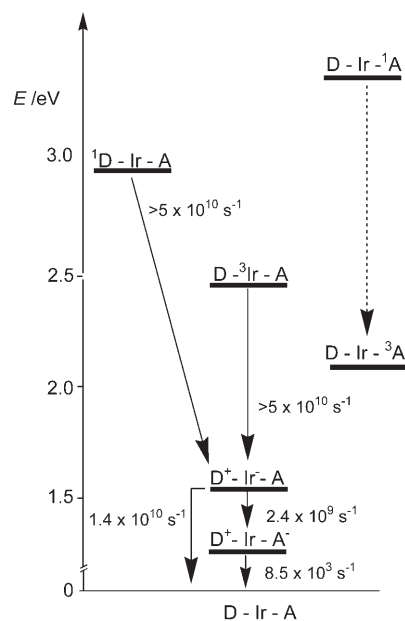


Figure 4. Energy-level scheme and reactivity of the triad D-Ir-A at low photon flux.

Table 1. Absorption and luminescence data of reaction intermediates of D-Ir-A and models at 295 K in air-equilibrated acetonitrile solutions with excitation at 355 nm.^[4]

| State | Absorption | | Luminescence | |
|--------|-----------------------------------|---------------|-----------------------------|-------------|
| | λ_{max} [nm] | τ [ns] | λ_{max} [nm] | τ [ns] |
| Ir | ^3Ir | 780 | 530 | 580 |
| | ^1A | 485, 650 | 0.05 | n.d. |
| A | ^3A | 485 | 380 ns | |
| | $\text{A}^{-[\text{a}]}$ | 475, 610 | — | |
| | ^1D | 750 | 0.490 | 540 |
| D | $\text{D}^{+[\text{a}]}$ | 760 | — | 0 |
| | $\text{D-}^3\text{Ir-A}$ | | ≤ 0.02 | |
| | $^1\text{D-Ir-A}$ | | ≤ 0.02 | |
| | $\text{D-Ir-}^3\text{A}$ | 485 | 360 | |
| D-Ir-A | $\text{D}^+\text{-Ir}^-\text{-A}$ | 765 | 0.06 | |
| | $\text{D}^+\text{-Ir-A}^-$ | 475, 610, 765 | 100×10^3 | |

[a] From chemical reduction.^[4]

low (on the order of 10%) which was due to the fast recombination reaction in the primary CS state $\text{D}^+\text{-Ir}^-\text{-A}$ ($k = 1.4 \times 10^{10} \text{ s}^{-1}$) strongly competing with the full charge separation to $\text{D}^+\text{-Ir-A}^-$ ($k = 2.4 \times 10^9 \text{ s}^{-1}$) Figure 4. Quite remarkably, charge separation in the triad occurs only upon excitation of either the D or the Ir unit, that is, from the ^1D and ^3Ir states, whereas excitation of the A unit leads very rapidly ($\tau \approx 50 \text{ ps}$) to the formation of a long-lived triplet excited state, $\text{D-Ir-}^3\text{A}$, which can only transfer electrons by intermolecular diffusive reactions. In fact, transfer of an electron from the triplet localized on an A unit to the D unit ($\text{D-Ir-}^3\text{A} \rightarrow \text{D}^+\text{-Ir-A}^-$), which would be thermodynamically feasible, is prevented by the large distance and the nature of the interposed Ir complex, which was previously

shown to display poor electron-transmission properties.^[21,22] Therefore, when energy is absorbed by the A component (D-Ir-*A is formed), the *A unit (either ¹A or ³A) displays reactivity typical of the isolated unit.

While investigating the photoreactivity of triad D-Ir-A summarized above, we noticed that variations in the intensity of the laser could produce different outcomes, as detailed below. At the wavelength used to excite the sample with both picosecond and nanosecond pulses (the third harmonic of the Nd:YAG laser, 355 nm), the components absorb with a relative probability of about 10%, 45%, and 45% for D, Ir, and A, respectively.

The spectra registered at the end of a 35-ps laser pulse of a D-Ir-A solution (2×10^{-5} M) in acetonitrile are reported in Figure 5. The spectrum for higher energy (4 mJ) is shown in

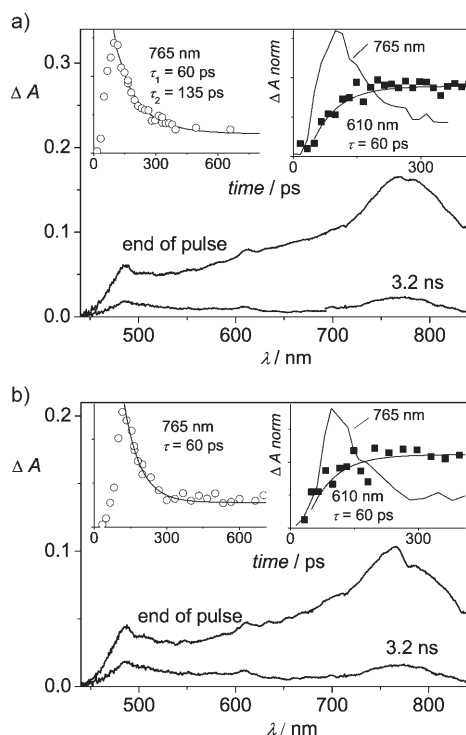


Figure 5. Transient absorption spectra detected for an air-equilibrated acetonitrile solution of D-Ir-A (2×10^{-5} M) after excitation at 355 nm with a 35-ps pulse. In the right insets, the time evolution of the absorbance at 760 nm and a derived absorbance at 610 nm (see text) are reported; in the left insets, the time profiles of the absorbance decay (○) and the related fitting (—) are shown; a) 4 mJ pulse⁻¹; b) 2.5 mJ pulse⁻¹.

Figure 5a and for lower energy (2.5 mJ) in Figure 5b. In these experimental conditions, a small portion ($\approx 1/10$) of the irradiated solution volume of ≈ 0.1 cm³ was analyzed in a collinear geometry. The number of photons incident on the irradiated volume is $\approx 1.2 \times 10^{-8}$ mol for the 4-mJ case and about half that for the 2.5-mJ case, whereas in the same volume there is 2×10^{-9} mol D-Ir-A. This means that in the higher-energy conditions the number of photons is about one order of magnitude higher than the number of (multicomponent) molecules,

whereas in the low-energy conditions there is a lower ratio of photons to molecules.

The bands of the anion A⁻ can be identified in the end-of-pulse spectrum around 480 nm and 610 nm, and the band of the cation D⁺ appears at 760 nm (Figure 5). The evolution of the D⁺ and A⁻ species was monitored at 760 nm and 610 nm, respectively; A⁻ is monitored at 610 nm because at this wavelength the superposition with the absorbance ¹A and ³A is minimized. In the left insets of Figures 5a and b (upper and lower), the decay detected at 760 nm owing mainly to the D⁺ band is reported. The decay at this wavelength can be described by a double exponential ($\tau_1 = 60$ ps and $\tau_2 = 135$ ps) at higher laser energies (upper panel of Figure 5), whereas at lower laser energy the decay is a single exponential with $\tau = 60$ ps (lower panel of Figure 5). Since the contribution of the absorption of the anion to the overall absorption in the triad at 610 nm is rather low but well characterized as a sharp maximum on a rather flat background, we chose to measure the difference between the 610 nm absorbance and the average of the absorbance measured at 600 nm and 620 nm. We define, for each time delay, $\Delta A(A^-) = \Delta A(610 \text{ nm}) - [\Delta A(600 \text{ nm}) + \Delta A(620 \text{ nm})]/2$. The time evolution of $\Delta A(A^-)$ shows a rise with a lifetime of 60 ps in both low- and high-energy conditions, in excellent agreement with the fast exponential decay measured at 760 nm (shown in arbitrary units for comparison in the right insets of Figure 5). Therefore, the high- and low-energy conditions differ for the presence of an extra decay registered at 760 nm, arising from a species with a lifetime of 135 ps. We can rule out the singlet intermediate ¹A, which is much shorter lived (50 ps), and the triplet ³A, which does not absorb above 550 nm,^[4] furthermore, these species are monophotonic products and would be present in both high- and low-energy conditions. On the contrary, the excited state of A⁻ (a doublet excited state ²A⁻), which could be formed by the absorption of a second 355 nm photon by the charge-separated state, that is, $D^+ \text{-Ir-A}^- \rightarrow D^+ \text{-Ir-}^2\text{A}^-$, could well account for this species. A⁻ is in fact reported to display a reasonable absorbance at 355 nm, and ²A⁻ has a broad absorption over the 500–800 nm range and a lifetime of 141 ps leading back to A⁻.^[23] Although this biphotonic process should not compete and interfere with the yield of the CS state (it is expected to regenerate the CS state, $D^+ \text{-Ir-}^2\text{A}^- \rightarrow D^+ \text{-Ir-A}^-$), its presence and decay complicates, in an high-energy regime, the interpretation of an intrinsically complex system.

The yield of the formation of D⁺-Ir-A⁻ is 10% (see above), and no further decay of the CS state can be detected after the time evolutions in the picosecond experiment (≈ 3.2 ns). To follow the slower time evolution of the CS state and to determine the lifetime, a flash photolysis experiment with nanosecond resolution was performed. A typical spectrum registered in the microsecond time scale after excitation by an 18-ns laser pulse in air-equilibrated solutions of D-Ir-A is shown in Figure 6; it displays the bands of the CS state, with both the A⁻ and D⁺ components. The insets show the time evolution of the main bands. The decay could be fitted by a clear monoexponential with a 100- μ s lifetime in air-equilibrated solution (120 μ s in air-free solution), independent of intensity and

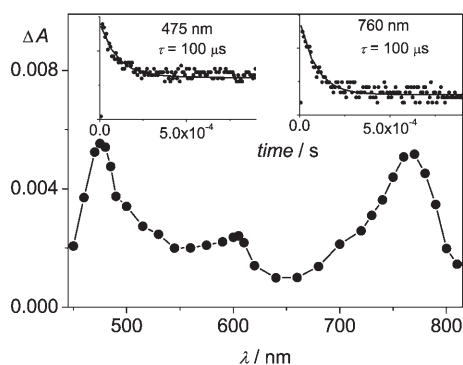


Figure 6. Typical spectrum registered at 1 μ s after the pulse in air-equilibrated acetonitrile solutions of D-Ir-A (2×10^{-5} M) excited at 355 nm (3 mJ pulse^{-1} , 18-ns pulse). In the insets, the time evolution of the CS bands at two selected wavelengths are shown.

solute concentration. This lifetime was assigned to the intramolecular recombination of D^+-Ir-A^- to the ground state D-Ir-A, and the presence of a minor component with a lifetime of tens of milliseconds was assigned to slow intermolecular reactions involving secondary products.^[4,24]

A detailed study of the laser pulse energy on the transient spectrum in the nanosecond time scale reveals that the spectral data are dependent on the laser intensity. Figure 7 shows the spectra detected at the end of the pulse and 80 ns after the end of the pulse for high (Figure 7a) and low (Figure 7b) pulse energies. At high laser energy the spectrum displays a broad band around 600–800 nm, which decays on the tens of nanoseconds time scale; this band is absent at lower laser intensity. The spectral shape is reminiscent of the 3Ir absorbance, which has a broad band with a maximum at 760–780 nm.^[4,20] The intensity effect on the decay at 760 nm is better evidenced in Figure 8, where the time profiles registered at increasing energies (1.5 mJ, 5 mJ, and 8.5 mJ) are shown for two different triad concentrations. The traces are noisy, but a clear decay of ≈ 20 ns can be observed at both concentrations at the higher energies; it disappears at $1.5 \text{ mJ pulse}^{-1}$. The decay 1) displays a short lifetime, 2) is independent of the active medium concentration, and 3) is dependent on incident light flux. This means that diffusive reaction processes can be excluded, that the nature of the process can only be intramolecular, and that it must involve the absorption of more than one photon. It should be stressed that the laser energies used here ($1\text{--}8.5 \text{ mJ pulse}^{-1}$) are well in the range of those normally used in flash photolysis experiments. The number of photons relative to the number of solute molecules can be estimated on the basis of the energy delivered and the irradiated volume. A small portion of the irradiated volume is analyzed with a 90° geometry; the analyzed volume of 0.06 cm^3 (see the Experimental Section) contains $\approx 3 \times 10^{-9}$ molecules for the $4.5 \times 10^{-5} \text{ M}$ solution (1×10^{-9} molecules for $1.8 \times 10^{-5} \text{ M}$), and the number of photons is around 3×10^{-9} per millijoule delivered. Thus, by increasing the intensity of the laser well above 1 mJ, the number of photons is much higher than the number of (multicomponent) molecules.

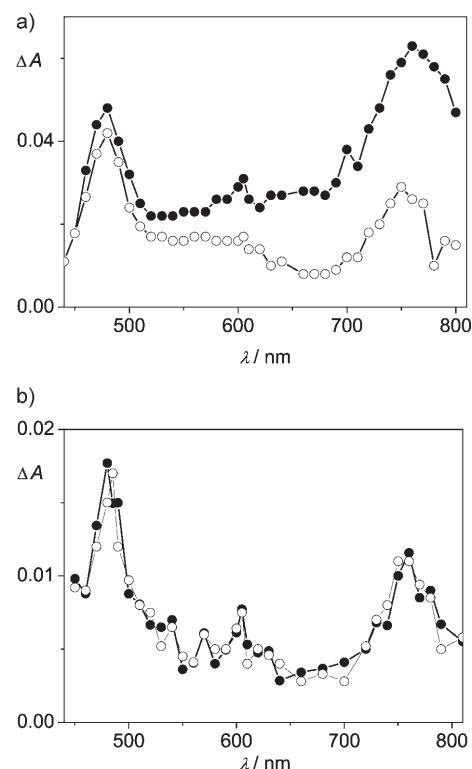


Figure 7. Transient absorption spectra of air-equilibrated acetonitrile solutions of D-Ir-A (4.5×10^{-5} M) excited at 355 nm at the end of the pulse (\bullet) and 80 ns after the end of the pulse (\circ). The laser intensity is a) $8.5 \text{ mJ pulse}^{-1}$; b) $1.2 \text{ mJ pulse}^{-1}$.

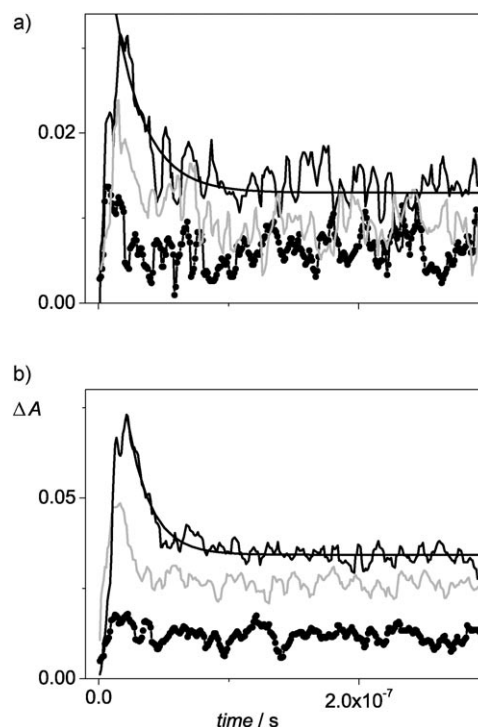


Figure 8. Decay of the absorbance registered at 760 nm for air-equilibrated acetonitrile solutions of different D-Ir-A concentrations at different excitation energies: $8.5 \text{ mJ pulse}^{-1}$ (black line), 5 mJ pulse^{-1} (grey line) and $1.5 \text{ mJ pulse}^{-1}$ (black scattered). a) $1.8 \times 10^{-5} \text{ M}$, b) $4.7 \times 10^{-5} \text{ M}$.

In these conditions, two photons can be absorbed independently by different chromophores of the ground state D-Ir-A, and the formation of doubly excited triads $D^{-3}\text{Ir}^{-3}\text{A}$ and ${}^1\text{D}^{-3}\text{Ir}^{-3}\text{A}$ or ${}^1\text{D}^{-3}\text{Ir}^{-3}\text{A}$ should be considered. For the latter states involving ${}^1\text{D}$, even supposing a very slow reactivity, this state is not expected to survive in the nanosecond timescale because of the short lifetime of ${}^1\text{D}$ (Table 1). It is difficult to envisage some type of product of ${}^1\text{D}^{-3}\text{Ir}^{-3}\text{A}$ or ${}^1\text{D}^{-3}\text{Ir}^{-3}\text{A}$ that could live long enough to be detected in the nanosecond timescale. $D^{-3}\text{Ir}^{-3}\text{A}$ could have a longer lifetime ($\tau = 550$ and 360 ns for ${}^3\text{Ir}$ and ${}^3\text{A}$, respectively, Table 1), provided that no annihilation reaction occurs faster. The reactivity of ${}^3\text{Ir}$ toward D (Figure 4) would reduce the lifetime to few picoseconds, generating a $D^{+}\text{-Ir}^{-3}\text{A}$ state. This would very likely yield, upon electron transfer, a $D^{+}\text{-Ir}^{-}\text{A}^{-}$ state. It is, however, difficult to account for the experimental observation of a species with a broad spectrum with maximum at 760–780 nm (very likely ${}^3\text{Ir}$) and a lifetime of 20 ns.

Long-lived intermediates can be considered steady products on the timescale of the observation, and the species $D^{+}\text{-Ir}^{-}\text{A}^{-}$, which lives ≈ 100 μs in air-equilibrated samples, can be considered a good candidate for the absorption of a further photon. We know that A^{-} can absorb a photon, and D^{+} might also be able to, but upon excitation of these species we expect a rapid internal conversion to the CS ground state not interfering on the nanosecond scale (see above).^[23] Alternatively, absorption of a photon by the Ir unit is very likely (see the absorption spectra in Figure 2) and would lead to the formation of $D^{+}\text{-}{}^3\text{Ir}^{-}\text{A}^{-}$. The energy level of this state can be estimated from the energy of the CS state (1.26 eV) and of the excited state (2.43 eV) to be about 3.7 eV (Figure 9). This is a very high energy which can open several reactivity paths. The excited Ir moiety could accept an electron from A^{-} with $\Delta G^{\circ} = -2.13$ eV to yield $D^{+}\text{-Ir}^{-}\text{A}$, whereas the possibility of extraction of an electron from D^{+} to yield $\text{D-Ir}^{-}\text{A}^{-}$ seems less probable owing to the difficulty of oxidizing the Ir (tpy)₂ component.^[25,26] The hypothesis of the formation of $D^{+}\text{-Ir}^{-}\text{A}$ from $D^{+}\text{-}{}^3\text{Ir}^{-}\text{A}^{-}$ is reasonable, and because the high driving force of the reaction, according to Marcus theory, this process could be slow enough

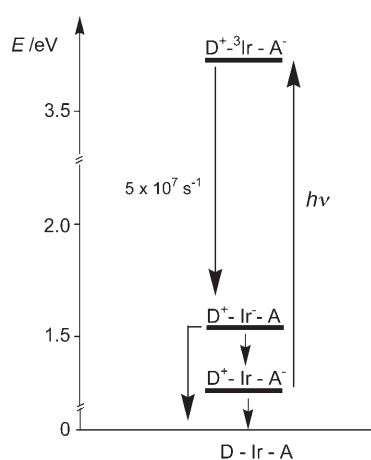


Figure 9. Energy-level scheme for D-Ir-A and reactivity of the CS state $D^{+}\text{-Ir}^{-}\text{A}^{-}$ upon absorption of a photon (high photon flux).

to take place in the nanosecond time scale.^[27] $D^{+}\text{-Ir}^{-}\text{A}$ will then decay mainly by recombination to the starting D-Ir-A, as discussed above (see Figure 4), and only about 10% will yield the CS state $D^{+}\text{-Ir}^{-}\text{A}^{-}$ again. The measured lifetime of 20 ns, corresponding to a rate $k = 5 \times 10^7 \text{ s}^{-1}$, would therefore be assigned to the rate-determining step $D^{+}\text{-}{}^3\text{Ir}^{-}\text{A}^{-} \rightarrow D^{+}\text{-Ir}^{-}\text{A}$, which starts the deactivation of the excited CS state $D^{+}\text{-}{}^3\text{Ir}^{-}\text{A}^{-}$ to the ground state. This hypothesis could explain the observations in that it agrees with the change in the optical spectra reported in Figure 7 (${}^3\text{Ir}$ has spectral features similar to those detected), and it can explain the observed 20-ns lifetime of the species and account for the reduction in the yield of the CS state at high photon flux.

Conclusions

In the triad D-Ir-A, the effect of light intensity on the charge-separation yield and lifetime has been demonstrated; a decrease in CS lifetime from 100 μs to 20 ns and a significant reduction in yield, on the order of 90%, can occur for those arrays which absorb a second photon. The importance of the event depends on the photon flux and for multicomponent arrays made of moderately absorbing chromophores can take place in typical experimental conditions, that is, with nanosecond laser pulses of a few millijoules of energy and active medium concentrations on the order of 10^{-5} M. Care should be taken in evaluating the importance of this effect when results from laboratory conditions are extended to applications under natural illumination.

Experimental Section

The synthesis of the compounds is reported elsewhere.^[4,20] Spectrophotometric grade acetonitrile was used as purchased. Oxygen-free solutions were degassed for 10 min with a stream of argon in home-modified 10-mm fluorescence cells. A Perkin-Elmer Lambda 9 UV/Vis spectrophotometer and a Spex Fluorolog II spectrofluorimeter were used to acquire absorption and emission spectra, which were uncorrected if not otherwise specified. Transient absorption spectra and lifetimes with picosecond resolution were determined by a pump-probe apparatus with 30 ps resolution based on a Nd:YAG laser (Continuum PY10, 355 nm, 35 ps, 10 Hz) previously described and operated at energies ranging from 2.5–4 mJ pulse^{-1} .^[28] The laser was focused on a 5 mm \times 10 mm section cell in a circular spot about 5 mm in diameter. The absorbance of solutions at the excitation wavelength was $A \approx 1.2$. Nanosecond laser flash photolysis experiments were performed by a previously described system based on a Nd:YAG laser (JK Lasers, 355 nm, 18 ns pulse, 2 Hz).^[29,30] The laser was focussed on a 10 mm \times 10 mm section cell in a rectangular pattern about 10 mm wide and 3 mm high. The focused analyzing beam probed a 2 mm section of the irradiated area at a right-angle geometry close to the cell wall irradiated by the laser. The absorbance of solutions at the excitation wavelength was $A \approx 1$ or $A \approx 2.7$. The laser energy was varied between 1 mJ pulse^{-1} and 8.5 mJ pulse^{-1} . Experimental uncertainties are estimated to be within 10% for lifetime determination involving simple exponential, 20% for lifetime determinations involving multiple exponentials or more complex kinetics, 15% for quantum yields, 20% for molar absorption coefficients, and 3 nm for emission and absorption peaks.

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Keywords: charge separation · electron transfer · iridium · photochemistry · two-photon absorption

- [1] W. Zinth, J. Wachtveitl, *ChemPhysChem* **2005**, *6*, 871–880, and references therein.
- [2] J. Barber, B. Andersson, *Trends Biochem. Sci.* **1992**, *17*, 61–66.
- [3] D. Mauzerall, *J. Phys. Chem.* **1976**, *80*, 2306–2309.
- [4] L. Flamigni, E. Baranoff, J.-P. Collin, J.-P. Sauvage, *Chem. Eur. J.* **2006**, *12*, 6592–6606.
- [5] See, for example: Issue on Optical Nonlinearities in Chemistry: *Chem. Rev.* **1994**, *94*, 1–278, and references therein; T.-C. Lin, S.-J. Chung, K.-S. Kim, X. Wang, G. S. He, J. Swiatkiewicz, H. E. Pudavar, P. N. Prasad, *Adv. Polym. Sci.* **2003**, *161*, 157–193, and references therein; T. K. Ahn, K. S. Kim, D. Y. Kim, S. B. Noh, N. Aratani, C. Ikeda, A. Osuka, D. Kim, *J. Am. Chem. Soc.* **2006**, *128*, 1700–1704; M. Drobizhev, Y. Stepanenko, Y. Dzenis, A. Karotki, A. Rebane, P. N. Taylor, H. L. Anderson, *J. Chem. Phys. B* **2005**, *109*, 7223–7236; A. Bhaskar, G. Ramakrishna, Z. Lu, R. Twieg, J. M. Hales, D. J. Hagan, E. Van Stryland, T. Goodson III, *J. Am. Chem. Soc.* **2006**, *128*, 11840–11849; T. E. O. Screen, J. R. G. Thorne, R. G. Denning, D. G. Bucknall, H. L. Anderson, *J. Am. Chem. Soc.* **2002**, *124*, 9712–9713; I. Asselberghs, M. J. Therien, B. J. Coe, J. A. McCleverty, K. Clays, *ACS Symp. Ser.* **2006**, *928*, 527–540; M. A. Oar, W. R. Dichtel, J. M. Serin, J. M. J. Fréchet, J. E. Rogers, J. E. Slagle, P. A. Fleitz, L.-S. Tan, T. Y. Ohulchanskyy, P. N. Prasad, *Chem. Mater.* **2006**, *18*, 3682–3692; O. Mongin, L. Porrès, M. Charlot, C. Katan, M. Blanchard-Desce, *Chem. Eur. J.* **2007**, *13*, 1481–1498; J. Arnbjerg, M. Johnsen, P. K. Frederiksen, S. E. Braslavsky, P. R. Ogilby, *J. Phys. Chem. A* **2006**, *110*, 7375–7385.
- [6] S. Dellonte, E. Gardini, F. Barigelletti, G. Orlandi, *Chem. Phys. Lett.* **1977**, *49*, 596–598.
- [7] D. W. Brousmiche, J. M. Serin, J. M. Fréchet, G. S. He, T.-C. Lin, S. J. Chung, P. N. Prasad, *J. Am. Chem. Soc.* **2003**, *125*, 1448–1449.
- [8] See, for example: U. Lachish, A. Schafferman, G. Stein, *J. Chem. Phys.* **1976**, *64*, 4205–42119.
- [9] A. Alchalal, M. Tamir, M. Ottolenghi, *J. Phys. Chem.* **1972**, *76*, 2229–2235.
- [10] R. Boch, M. K. Whittlesey, J. C. Scaiano, *J. Phys. Chem.* **1994**, *98*, 7854–7857.
- [11] S. El-Gogary, G. Grabner, *Photochem. Photobiol. Sci.* **2006**, *5*, 311–316.
- [12] See, for example: M. Gutierrez-Nava, G. Accorsi, P. Masson, N. Armaroli, J.-F. Nierengarten, *Chem. Eur. J.* **2004**, *10*, 5076–5086; G. De Belder, G. Schweitzer, S. Jordens, M. Lor, S. Mitra, J. Hofkens, S. De Feyter, M. Van der Auweraer, A. Herrmann, T. Weil, K. Müllen, F. C. De Schryver, *ChemPhysChem* **2001**, *2*, 49–55; G. Bergamini, P. Ceroni, M. Maestri, V. Balzani, S.-K. Lee, F. Vögtle, *Photochem. Photobiol. Sci.* **2004**, *3*, 898–903.
- [13] M. D. Benites, T. E. Johnson, S. Weghorn, L. Yu, P. D. Rao, J. R. Diers, S. I. Yang, C. Kirmaier, D. F. Bocian, D. Holten, J. S. Lindsey, *J. Mater. Chem.* **2002**, *12*, 65–80.
- [14] A. Morandeira, E. Vauthey, A. Schuwey, A. Gossauer, *J. Phys. Chem. A* **2004**, *108*, 5741–5751.
- [15] J. Larsen, B. Brüggemann, T. Polívka, Sundström, E. Åkesson, J. Sly, M. J. Crossley, *J. Phys. Chem. A* **2005**, *109*, 10654–10662.
- [16] E. Atas, Z. Peng, V. D. Kleiman, *J. Phys. Chem. B* **2005**, *109*, 13553–13560.
- [17] M. Andersson, L. E. Sinks, R. T. Hayes, Y. Zhao, M. Wasielewski, *Angew. Chem.* **2003**, *115*, 3247–3251; *Angew. Chem. Int. Ed.* **2003**, *42*, 3139–3143.
- [18] E. Fron, T. D. M. Bell, A. Van Vooren, G. Schweitzer, J. Cornil, D. Beljonne, P. Toele, J. Jacob, K. Müllen, J. Hofkens, M. Van der Auweraer, F. C. De Schryver, *J. Am. Chem. Soc.* **2007**, *129*, 610–619.
- [19] E. Baranoff, I. M. Dixon, J.-P. Collin, J.-P. Sauvage, B. Ventura, L. Flamigni, *Inorg. Chem.* **2004**, *43*, 3057–3066.
- [20] L. Flamigni, B. Ventura, F. Barigelletti, E. Baranoff, J.-P. Collin, J.-P. Sauvage, *Eur. J. Inorg. Chem.* **2005**, 1312–1318.
- [21] I. M. Dixon, J.-P. Collin, J.-P. Sauvage, L. Flamigni, *Inorg. Chem.* **2001**, *40*, 5507–5517.
- [22] L. Flamigni, G. Marconi, I. M. Dixon, J.-P. Collin, J.-P. Sauvage, *J. Phys. Chem. B* **2002**, *106*, 6663–6671.
- [23] D. Gosztola, M. P. Niemczyk, W. A. Svec, A. S. Lucas, M. R. Wasielewski, *J. Phys. Chem. A* **2000**, *104*, 6545–6551.
- [24] The secondary products are triad molecules bearing a single radical site, either D⁺-Ir-A or D-Ir-A⁻. In air-equilibrated conditions they were produced by a series of reactions started by singlet oxygen, formed by reaction of D-Ir³⁺A with oxygen. In air-free conditions they were formed by reactions of two D-Ir-A molecules.
- [25] J.-P. Collin, I. M. Dixon, J.-P. Sauvage, J. A. Gareth Williams, F. Barigelletti, L. Flamigni, *J. Am. Chem. Soc.* **1999**, *121*, 5009–5016.
- [26] I. M. Dixon, J.-P. Collin, J.-P. Sauvage, L. Flamigni, S. Encinas, F. Barigelletti, *Chem. Soc. Rev.* **2000**, *29*, 385–391.
- [27] R. A. Marcus, *Angew. Chem.* **1993**, *105*, 1161–1172; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1111–1121.
- [28] B. Ventura, A. Degli Esposti, B. Koszarna, D. T. Gryko, L. Flamigni, *New J. Chem.* **2005**, *29*, 1559–1566, and references therein.
- [29] L. Flamigni, *J. Chem. Soc. Faraday Trans.* **1994**, *90*, 2331–2336.
- [30] L. Flamigni, *J. Phys. Chem.* **1992**, *96*, 3331–3337.

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