Singlet Fission in Thin Films of Metallo-Supramolecular Polymer with Ditopic Thiophene-Bridged Terpyridine Ligands

Electronic Supplementary Information

David Rais, a* Jiří Pfelegera, a Miroslav Menšíka, a Alexander Zhigunova, ab Pavla Štenclová, b† Jan Svobodab, ab and Jiří Vohlidalc

a Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovského nám. 2, 162 06, Prague, Czech Republic
b Charles University, Faculty of Science, Department of Physical and Macromolecular Chemistry, Hlavova 2030, 128 40 Prague 2, Czech Republic.

Optical transitions in excimers using dipole approximation

1) Excimers model in dipole approximation
Two identical molecules A and B can form an excimer by dipole-dipole interaction if one of them is in excited state (denoted with index *) with energy $E_1$ and the other one is in the ground state (denoted with index g). Two coherent states are formed

$$|EM^+\rangle \equiv \frac{1}{\sqrt{2}}(|A^*,B_g\rangle + |A_g,B^*\rangle)$$

(1)

with energy

$$E_1 + J_1\{\cos(\theta_{12}) - 3\cos(\theta_1)\cos(\theta_2)\}$$

(2)

where

$$J_1 \equiv \frac{|\langle A^*,d^A|A_g\rangle\langle B_g|d^B|B^*\rangle|}{4\pi\varepsilon R^3}$$

(3)

and

$$|EM^-\rangle \equiv \frac{1}{\sqrt{2}}(|A^*,B_g\rangle - |A_g,B^*\rangle)$$

(4)

with energy

$$E_1 - J_1\{\cos(\theta_{12}) - 3\cos(\theta_1)\cos(\theta_2)\}$$

(5)

Here $\theta_{12}$ is angle between two transition dipole moments localized on the respective molecules A and B, and $\theta_1$, $\theta_2$ are angles between the respective transition dipole moments and the line connecting them. Thus, e.g., for the parallel non-collinear arrangement ($\uparrow\downarrow$) the splitting energy is $2J_1$ and for the collinear head-to-tail arrangement ($\rightarrow\rightarrow$) the splitting energy is $4J_1$.

The excimer states can undergo various optical transitions to higher excited states as follows:
One possible transition is into the state \( |A^*, B^* \rangle \) with energy \( 2E_1 \), corresponding to two excited identical molecules A and B close to each other. Additionally, also excimers corresponding to coherently coupled higher excited state (denoted with **) and ground state can be formed:

\[
EEM^+ \equiv \frac{1}{\sqrt{2}} (|A^{**}, B_g \rangle + |A_g, B^{**} \rangle)
\]

with energy

\[
E_2 + J_2 \{ \cos(\theta_{12}) - 3\cos(\theta_1)\cos(\theta_2) \}
\]

where \( E_2 \) is the energy of transition from \( A_g \rightarrow A^{**} \) in monomer, and

\[
J_2 \equiv \frac{(\langle A^{**} | d^A | A^* \rangle (B^* | d^B | B^{**} \rangle)}{4\pi\varepsilon R^3}
\]

and

\[
EEM^- \equiv \frac{1}{\sqrt{2}} (|A^{**}, B_g \rangle - |A_g, B^{**} \rangle)
\]

with energy

\[
E_2 - J_2 \{ \cos(\theta_{12}) - 3\cos(\theta_1)\cos(\theta_2) \}
\]

It is very important to realize that energy differences between excimers and higher excimers or two excited molecules is different from corresponding processes of isolated molecules. Consequently, if during time evolution after pump excimers are formed then probe pulses will recognize spectral shift. It concerns both the ground state bleaching as well as the excited state absorption as in excimers both ground and excited states are captured.

2) Impacts on the ground state bleaching

The ground state captured in the excimer is depleted from the absorption of the energy \( E_1 \) of the pump, however, it can contribute to the following absorption processes (excitation of the captured ground state)

\[
\langle EM^\pm | (d^A + d^B) | A^*, B^* \rangle \equiv \frac{1}{\sqrt{2}} (\langle A_g | d^A | A^* \rangle \pm \langle B_g | d^B | B^* \rangle)
\]

with energy

\[
E_1 \mp J_1 \{ \cos(\theta_{12}) - 3\cos(\theta_1)\cos(\theta_2) \}
\]

Considering the extreme packing configurations, for parallel \( \uparrow\uparrow \) and antiparallel \( \downarrow\uparrow \) orientations of transition dipole moments the transitions energy is \( E_1 - J_1 \), and for collinear arrangements \( \leftrightarrow \) and \( \rightarrow \), the allowed transition energy is \( E_1 + 2J_1 \). Depending on the packing shown above the ground state bleaching spectrum either red-shifts or blue shifts.

3) Impacts on the excited state absorption

The excited state captured in the excimer is depleted from the absorption of the energy \( E_2 - E_1 \) of the pump; however, it can contribute to the following absorption processes (excitation of the captured excited state)

\[
\langle EM^+ | (d^A + d^B) | EEM^\pm \rangle \equiv \frac{1}{2} (\langle A^* | d^A | A^{**} \rangle \pm \langle B^* | d^B | B^{**} \rangle)
\]

with energy

\[
E_2 - E_1 \mp \langle A^{**} | d^A | A^* \rangle \langle B^* | d^B | B^{**} \rangle \{ \cos(\theta_{21}^{**}) - 3\cos(\theta_1^{**})\cos(\theta_2^{**}) \}
\]

\[
\frac{4\pi\varepsilon R^3}{(\cos(\theta_{12}^{**}) - 3\cos(\theta_1^{**})\cos(\theta_2^{**}))}
\]

and
resolved ESA and GSB compared to “fully relaxed” excimers to formation. Before formation of the coherently coupled excimer, then \( N-1 \) molecules are in the ground state and both delocalized levels are equally populated. Differential spectrum of GSB measures negative absorption of one molecule peaked at energy during thermalization, \( E_2 - E_1 \pm (J_2 - J_1) \), respectively. For collinear arrangements \( \leftrightarrow \) and \( \leftarrow \), the allowed transition energies are \( E_2 - E_1 \pm 2(J_2 + J_1) \), respectively. As a result, the observed excited state absorption spectrum of an excimer is symmetrically broadened with respect to the one of excited monomer.

4) Relaxation of the excimers

Let’s assume the case of two parallel transition dipole moments. Immediately after hot excimer state formation, both delocalized levels are equally populated, 

\[ \rho_{++} = \rho_- = \frac{1}{2} \], with coherences, i.e., off-diagonal elements of density matrix, \( \rho_{+-} = 0 \) and the mean energy of excimer \( \langle H \rangle = E_1 \) of the excited monomer. During thermalization, \( \rho_{++} < \rho_- \), the coherences gradually decay, \( \rho_{+-} \to 0 \), and mean energy \( \langle H \rangle < E_1 \). For fully relaxed excimer to the bottom state \( |EM^-\rangle \), the mean energy \( \langle H \rangle = E_1 - |J_1| \), so that stable configuration increases dipole-dipole splitting \( |J_1| \) and clinches both molecules together.

As the states \( |EM^+\rangle \) and \( |EM^-\rangle \) have different sensitivity with respect to probes \( |EM^\pm\rangle \to |A^*, B^\pm\rangle \) or \( |EM^\pm\rangle \to |EM^\pm\rangle \) during thermalization process statistical weight of both excimer levels will be changed and therefore “partly coherent, relaxing” excimers will have different impacts to time-resolved ESA and GSB compared to “fully relaxed” excimers to \( |EM^-\rangle \).

We can expect some broadening of ESA in unrelaxed excimer with respect to monomer ESA. After the excimer has fully relaxed, broadening of the ESA is fixed and it corresponds just to transition \( |EM^-\rangle \to |EM^-\rangle \).

We can also expect a blue-shift of the excimer GSB signal, compared to the monomer GSB. It can be understood within the following line of reasoning: If among \( N \) molecules, one monomer is excited before formation of the coherently coupled excimer, then \( N-1 \) molecules are in the ground state and differential spectrum of GSB measures negative absorption of one molecule peaked at energy \( E_1 \). After coherent formation of the excimer, \( N-2 \) molecules are in the ground state and two states \( |EM^\pm\rangle \) are formed. Differential GSB measures negative signal of TWO molecules peaked at \( E_1 \), overlapping with one positive signal red-shifted to \( E_1 - |J_1| \) due to the transition \( |EM^+\rangle \to |A^*, B^+\rangle \).

The transition \( |EM^-\rangle \to |A^*, B^+\rangle \) is dark due to the mutually subtracted transition dipole moments. Consequently, on sub-picosecond time-scale, during the formation of hot excimer state the negative GSB is blue-shifted.

During the coherent excimer relaxation to the bottom state \( |EM^-\rangle \), that is, in delay times between 20 and 50 ps, the GSB redshifts and its intensity increases (cf. the red and magenta curves.
in Figures S1a–d). This is not given by the increasing number of excited state species, but due to the redistribution between optically active states $|EM^+\rangle$ and $|EM^-\rangle$ with respect to the probe at energy corresponding to the absorption of molecules in the ground state.

5) Excimer collisions:
Formation of excimer mutually competes with the exciton (excimer) migration, as the former induces a significant molecular reorganization. However, excimer-excimer collision is still possible due to the Förster energy transfer by dipole-dipole interaction. Principle is given by the reaction

$$|EM_A^\pm, EM_B^\pm\rangle \rightarrow |EM_A^\pm, B_g\rangle$$ \hspace{1cm} (17)

The Förster interaction energy in Fermi-Golden Rule is critically controlled by the factor

$$\langle EM_A^\pm, EM_B^\pm | d_A d_B | EEM_A^\pm, B_g\rangle = \langle EM_A^\pm | d_A | EEM_A^\pm \rangle \langle EM_B^\pm | d_B | B_g \rangle$$ \hspace{1cm} (18)

The rate of the Förster transfer will be proportional to the overlap between absorption spectrum of the process $|EM_A^\pm\rangle \rightarrow |EEM_A^\pm\rangle$ and the emission spectrum of the process $|EM_B^\pm\rangle \rightarrow |B_g\rangle$. The first one is given by the ESA spectrum of excimers, while the second one by the photoluminescence of the excimer. In the coherent regime, the bright component $|EM^+\rangle$ in the photoluminescence is active so if particular ESA and photoluminescence overlap, the Förster transfer works. Averaging over all space provides a pump intensity-dependent decay $\sim t^{-0.5}$. For relaxed excimer, $|EM^-\rangle$ is dark in the photoluminescence and the Förster transfer is blocked.

Transient absorption experiments
Here, we present the results the Transient Absorption (TA) experiments with thin films of both the metal-free T and the zinc complex PT, which are discussed in the main text. Also we present here the results of the global analyses performed on all of the TA experiments. For the experiments, we have used various pump energies $E_{ex}$, as well as various pump wavelengths $\lambda_{ex}$. For the global analysis, we have used a simple sequential 4-state model for both materials and in all pump conditions, to allow comparison of the obtained time constants and the associated spectral components.

In the case of metal-free T, we used the excitation with central wavelength $\lambda_{ex}=407$ nm, and four different total energies $E_{ex}$ in range 2000–1600 nJ. The resulting spectro-temporal transient absorption behaviour was dependent on the excitation energy, as can be seen from the plots of representative spectra (Figure S1), and the respective kinetic traces (Figure S2), recorded at probe wavelengths $\lambda_{pr}$, (429, 500, 685 and 750 nm) for which there were peaks in the TA spectra.

In the case of zinc-containig PT, we have used excitation pulses with central wavelengths $\lambda_{ex}=440$ nm and $\lambda_{ex}=332$ nm, and total energies $E_{ex}$ in range 200–1000 nJ. Similarly to the situation in T, the resulting spectro-temporal transient absorption behaviour was dependent on the excitation energy, as can be seen from the plots of representative spectra (Figure S4), and the respective kinetic traces (Figure S5), recorded at probe wavelengths $\lambda_{pr}$ (510, 669 and 759 nm) for which there were peaks in the TA spectra.

Global analysis of the time-resolved TA spectra
To gain more insights into the microscopic mechanisms of the spectrotemporal evolutions of the TA signal following a photoexcitation of the thin solid film samples of the T and the PT, we have applied the global analysis (GA) method with sequential model to obtain a set of spectral components (the
evolution-associated differential spectra, EADS) and corresponding set of exponential decay times.\textsuperscript{1}

We are aware, that the system of linear differential equations used in the sequential model cannot describe the observed dependencies of the decay kinetics on the pump intensities (see Figures 4b,d,f in the main text). Nevertheless, the method was useful for identification of the individual spectral features, which could be assigned to particular electronic configurations of the excited state.

**Thin solid film of T**

The resulting shapes of normalized EADS together with the corresponding lifetimes $\tau_i$ obtained with the global analysis of the TA signals observed in the thin solid film of the T following the photoexcitation at $\lambda_{ex} = 407$ nm with various pulse energies are shown in Figure S3. We have used four-states in the model, as a minimum number to provide a good fit (see the Figure S2 for fit quality verification).

All of the EADS contain peak at 750 nm, and all contain also the 690 nm peak. It reflects the simultaneous decay of the two positive TA features shown in the original data (see Figure S1). The second and the third EADS, respectively, show similar shapes, with almost identical position $\lambda_{ip}$ of isosbestic point, at which $\Delta A(\lambda_{ip},t) = 0$. These two differ mostly in the steepness of the linear part of EADS curve around the IP, which is lower for the latter. The fourth EADS with lifetime in the ns time domain had the $\lambda_{ip}$ shifted towards longer wavelengths, resulting in apparent extension of the negative signal band at its red side.

From the shapes of the EADS and their lifetimes, we can form hypotheses about the physical origin of the spectral evolution of the $\Delta A(\lambda_{pr},t)$ signal. The changes in shape of EADS at the sub-picosecond lifetimes can be assigned to internal vibrational relaxation (IVR), which we reported in our previous article on dimethyl sulfoxide solutions of the T.\textsuperscript{2} The differences between the early EADS in thin film and solutions were (i) the absence of the stimulated emission signal in film, which was found in the solution and (ii) the presence of rapid drop of the GSB signal intensity, which was much slower in the solution. In case of the (i) it agreed well with the reported low intensity of photoluminescence in thin film as compared to the solution.\textsuperscript{3} It pointed us towards postulation of luminescence quenching pathway in the excited state transition model. This pathway could be caused either by formation of the triplet state\textsuperscript{4} or the excimer state\textsuperscript{5} in the solid phase. The higher rate constants, (ii), are obviously due to the mutual annihilation of excited states, which is often reported from the TA experiments with solid phase of conjugated organics.\textsuperscript{6,7} This effect is in direct consequence of high concentration of excited states, in our case up to 10 % of available absorbing chromophores at the highest pump energy of 1600 nJ, as can be inferred from the strength of $\Delta A_{GSB} \approx 0.02$ OD and the peak of thin film absorbance $A \approx 0.24$ OD.

**Thin solid film of PT**

The TA spectral features present in the thin film of the PT greatly resemble those we had found in the dimethylsulfoxide (DMSO) solutions of the free ligand T.\textsuperscript{2} The position of the ESA peak at 760 nm found in the early post-excitation delay times is red-shifted by 10 nm from its position in solution; the position of the other ESA band is apparently red-shifted by 20 nm in the thin film. Also, the position of the GSB band in thin film is red-shifted by about 50 nm. In the DMSO solution of the free ligand T, we have attributed the ESA at 750 nm to the $S_1 \rightarrow S_n$ transition within the singlet manifold, the other ESA at 650 nm with the $T_1 \rightarrow T_n$ transition within the triplet states manifold, and the time constant of $\sim 500$ ps to the intersystem crossing (ISC) process. In the DMSO solution of the PT, we could observe
the same spectral features; however the assignment of time constant to the ISC process was quite
difficult, due to mixing of the spectral features in the resulting EADS, which led us to speculate that
the simple unidirectional sequential model assumed in our global analysis was not appropriate.

With the global analysis, we have found, that to fit the TA data from the $\lambda_{ex} = 440$ nm experiment
well, a minimum of 4 decay time parameters, $\tau_i$, were necessary, thus we obtained set of four
corresponding evolution associated differential spectra (EADS) $\varepsilon(\lambda_{pr})$ (see Figure S6a–c). However,
as we expected, the resulting $\tau_i$ were dependent on the excitation pulse energy. The resulting EADS
obtained from TA experiment with given pump energy were showing large mutual similarity: Three of
four spectra were containing both of the positive ESA peaks (centered at 670 and 760 nm) with
varying proportion. Only the first EADS did not contain the peak at 670 nm. Thus, we have come to
finding that a simple unidirectional sequential model with system of linear differential kinetic
equations used in the global analysis was not appropriate.

We have arrived to similar situation, when applying the sequential global analysis to the TA data
obtained with UV pump $\lambda_{ex} = 332$ nm. Here again, the spectral features of ESA at 670 and 760 nm
were present in majority of the resulting EADS (see Figure S6d,e). Also for this pump wavelength, the
corresponding values of all $\tau_i$ were dependent on the excitation pulse energy.
Figure S1: The representative TA spectra obtained from thin film of T after photoexcitation at 407 nm. Spectra were averaged over the delay time intervals, as shown in the legend. Panels (a)–(d) show data acquired with different pump pulse total energies $E_{ex}$, as indicated in each panel.
Figure S2: Representative kinetic traces of TA signals recorded at fixed probe wavelengths in the thin film of T (the selected probe wavelengths are shown in nanometers in the legend). The red dashed lines show the traces fitted with the global analysis method. Panels (a)–(d) show data acquired with different pump pulse total energies $E_{ex}$. 
Figure S3: The results of global analyses (Evolution Associated Differential Spectra – EADS – calculated by fitting of a sequential decay model) of the TA datasets obtained after photoexcitations of the thin film of T with laser pulses of central wavelength $\lambda_{ex}=407$ nm and various energies $E_{ex}$ (shown in the respective panels). The corresponding exponential decay time constants $\tau_i$ are shown in the respective legends.
Figure S4: The representative TA spectra obtained from thin film of PT after photoexcitation by laser pulse. Spectra were averaged over the delay time intervals, as shown in the legend. Panels (a)–(c) show data acquired with pulses of central wavelength 440 nm and different pump pulse total energies $E_{ex}$, as indicated in each panel; Panels (d) and (e) show data acquired with pulses of central wavelength 332 nm.
Figure S5: Representative kinetic traces of TA signals recorded at fixed probe wavelengths in the thin film of PT (the selected probe wavelengths are shown in nanometers in the legend). The red dashed lines show the traces fitted with the global analysis method. Panels (a)–(c) show data acquired with pulses of central wavelength 440 nm and different pump pulse total energies $E_{ex}$, as indicated in each panel; Panels (d) and (e) show data acquired with pulses of central wavelength 332 nm.

vertical scales label: $\Delta A \times 10^{-3}$

probe wavelengths, $\lambda_{pr}$:
- 510 nm
- 669 nm
- 759 nm
- fitted curves
Figure S6: The results of global analysis (Evolution Associated Differential Spectra – EADS – calculated by fitting of a sequential decay model) of the TA datasets obtained after photoexcitations of the thin film of PT with laser pulses of central wavelength $\lambda_{ex}=440\,\text{nm}$ (a–c) and $\lambda_{ex}=332\,\text{nm}$ (d,e), and various energies $E_{ex}$ (shown in the respective panels). The corresponding exponential decay time constants $\tau_i$ are shown in the respective legends.
Quantum-chemical calculations

Figure S7: Electronic density contours for Highest-Occupied Molecular Orbital (left) and Lowest-Unoccupied Molecular Orbital (right) in molecule T in vacuum, as obtained from DFT calculation.

References