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**Ultrafast Excited-State Dynamics of Diketopyrrolopyrrole (DPP)-Based
Materials: Static versus Diffusion-Controlled Electron Transfer Process**

Qana A. Alsulami,¹ Shawkat M. Aly,¹ Subhadip Goswami,² Erkki Alarousu,¹ Anwar
Usman,¹ Kirk S. Schanze² and Omar F. Mohammed*¹

¹Solar and Photovoltaics Engineering Research Center, Division of Physical Sciences and
Engineering, King Abdullah University of Science and Technology, Thuwal 23955-6900,
Kingdom of Saudi Arabia

²Department of Chemistry, University of Florida, P.O. Box 117200, Gainesville, Florida 32611,
United States

***Corresponding Author**

E-mail address: omar.abdelsaboer@kaust.edu.sa (O.F.M.)

ABSTRACT

Singlet-to-triplet intersystem crossing (ISC) and photoinduced electron transfer (PET) of platinum(II)-containing diketopyrrolopyrrole (DPP) oligomers in the presence and absence of tetracyanoethylene (TCNE), a strong electron-acceptor, were investigated using femtosecond and nanosecond transient absorption spectroscopy with broadband capabilities. The effect of incorporating platinum(II) in the photophysical properties of DPP molecule was evaluated by comparing the excited-state dynamics of DPP with and without Pt metal centers. Steady-state measurements reveal that platinum(II) incorporation greatly facilitates interactions between DPP-Pt(acac) and TCNE, resulting in the formation of charge transfer (CT) complexes. In the absence of TCNE, the transient absorption spectra revealed ultrafast ISC of DPP-Pt(acac) followed by a long-lived triplet state; however, in the presence of TCNE, PET from the excited DPP-Pt(acac) and from DPP to TCNE formed radical ion pairs. We measured an ultrafast PET from DPP-Pt(acac) to TCNE (i.e., a picosecond regime) that was much faster than that from DPP to TCNE (i.e., nanosecond time scale), which is a diffusion-controlled process. Our results provide clear evidence that the PET rate is eventually controlled by the platinum(II) incorporation.

INTRODUCTION

Heavy-metal complexes have been the focus of intense research activities devoted to the fields of light emitting devices,^{1,2} bioimaging,^{3,4} sensing,^{5,6} and sensitization.^{7,8} In particular, recently, a square-planar coordination of Pt(II) complexes have attracted great interest for their optical properties, which enable effective intersystem crossing (ISC) to the triplet state for many potential applications.⁹⁻¹⁷ The photophysical properties of Pt(II) complexes strongly depend on the chemical structures of the cyclometalated ligands, where the emission energies of the complexes are related to the planarity and π -conjugation of the chromophoric ligands.¹⁸ Pt(II) complexes bearing π -conjugated polymers and oligomers are established as promising for use in organic photovoltaic (OPV) applications due to their efficient light harvesting, structural versatility, and intrinsic charge-transport behavior.¹⁹⁻²¹ Specifically, extending the polymer chain or the π -conjugation of the ligand π -conjugation mostly affects the intra-ligand excited states, leading to a red shift in absorption and emission spectra, thus controlling the higher-lying metal-to-ligand charge transfer (MLCT) state and the HOMO–LUMO gap. The combination of low-energy MLCT transitions of these complexes with their long excited-state lifetimes makes them valuable for photosensitization applications.^{22,23} The effect of π -conjugation length of oligomers and the incorporation of Pt(II) as a metal center on ISC, singlet–triplet energy and triplet–triplet energy transfer, and OPV cells has been explored.^{14,24}

In solution, Pt(II) complexes interact with porphyrins, which act as electron acceptor molecules to form electron donor-acceptor (EDA) systems¹⁵ that provide valuable information about bimolecular electron transfer reactions.²⁵⁻²⁷ Vertical excitation of the EDA system, in particular, generates a substantial vibrational energy with various active modes that facilitate photoinduced electron transfer (PET) processes,^{28,29} and the rate constant of the dynamic PET mechanism is determined by diffusion of the reactants.²⁷ In contrast, the PET process is ultrafast (i.e., on the picosecond time scale) and no diffusion is needed for an entirely static quenching mechanism.²⁷ Understanding the underlying mechanisms controlling ISC and PET dynamics is therefore central to fundamental researches.¹⁷

Recently, a new class of Pt(II)(acac=acetylacetonato) complexes bearing π -conjugation-rich diketopyrrolopyrrole (DPP) oligomers have been synthesized (the chemical structures of DPP and DPP-Pt(II)(acac) are shown in Scheme 1),¹⁵ and their photophysical properties have been explored in a DMF/DCM mixture using ultrafast time-resolved absorption spectroscopy.¹⁵ Upon

interaction with a positively charged porphyrin in solution, the DPP-Pt(II)(acac) complex shows ultrafast PET and charge separation (CS) that is much faster than the ISC process. In addition, absorption of the CT state persists for a couple of nanoseconds (ns), while ground state recovery reaches a plateau (no further recovery), providing evidence for long-lived charge separation (CS) that is likely due to the dissociation of the contact radical ion pair into free ions. The long excited-state lifetime and a rapid charge recombination (CR) time makes the DPP-Pt(II)(acac) complex ideal for use in OPV applications.

Here, we continue our investigation of the bimolecular PET from DPP-Pt(II)(acac) to an electron acceptor in solution by focusing on tetracyanoethylene (TCNE) as the electron acceptor. TCNE was selected for its strong electron-accepting ability and distinctive relaxation processes, lack of spectral overlap with the donor, CT-state lifetimes in TCNE-based electron donor-acceptor systems,^{30,31} and its ability to form different complex geometries.³² Here, we predict that the DPP-Pt(II)(acac)/TCNE system can form CT complexes, thereby displaying interesting photophysical properties including ultrafast PET, rapid CS, and slow CR. In particular, incorporation of Pt(II) can control ISC and PET dynamics from the oligomer to TCNE. We evaluated the effect of incorporating Pt(II) in ISC and PET processes by comparing and analyzing the photoexcited dynamics of DPP-Pt(II)(acac)/TCNE and DPP/TCNE systems.

EXPERIMENTAL SECTION

Chemicals. DPP-Pt(II)(acac) synthesis and chemical characterization have been reported previously in detail (see Ref. 15 and 17). In this work, TCNE, dimethylformamide (DMF), and dichloromethane (DCM) were purchased from Sigma-Aldrich. TCNE was further purified by crystallization from DCM.

Steady-State Measurements. Steady-state absorption and emission spectra were recorded on a Cary5000 UV-visible spectrometer (Agilent Technologies) and a Fluoromax-4 spectrofluorometer (Horiba Scientific), respectively. The measurements were conducted in a rectangular quartz cell with a 1-cm optical path. For the DPP/TCNE system, the concentration of DPP in DMF/DCM (4:1) was held constant at 7.5 μM , while a range of 0–30.7 mM TCNE in DMF/DCM (4:1) was added successively to the solution. A similar approach was used for the DPP-Pt(II)(acac)/TCNE system, where an approximate 9.2 μM DPP-Pt(II)(acac) in a mixture of DMF and DCM(4:1) was held constant and a range of 0–30.7 mM TCNE was varied in

DMF/DCM(4:1). Fluorescence spectra were collected after excitation at 490 and 600 nm for DPP/TCNE and DPP-Pt(II)(acac)/TCNE systems, respectively.

Femtosecond Broadband Transient Absorption Spectroscopy. The detailed experimental setup of the femtosecond broadband transient absorption (TA) spectroscopy is described elsewhere.³³ Briefly, the setup employs a white-light continuum probe pulse generated by a 2-mm-thick sapphire plate and spectrally tunable pump femtosecond (fs) pulses (240–2600 nm; a few μ J energy pulses) generated in an optical parametric amplifier (Newport Spectra-Physics). The pump and probe pulses were overlapped within a 2-mm-thick cuvette cell containing $\approx$ 0.08 mM DPP or DPP-Pt(II)(acac) in DMF/DCM (4:1) solution in the presence or absence of 0.02–0.4 M TCNE. The transmitted probe light from the solution was collected and focused on a broadband UV-Vis detector to monitor change in transient absorbance (ΔA). To ensure that a fresh volume would be available for each laser shot, the sample solution was stirred constantly with a magnetic stirrer. To cover the transient spectra from a few hundred fs to μ s time delays after photoexcitation, Helios and EOS detection systems, from Ultrafast systems, with time resolutions of 120 fs and 200 ps and detection limits of 5.5 ns and 400 μ s, respectively, were employed.

In addition to the femtosecond TA spectroscopic measurements, to monitor the excitation dynamics in the nanosecond time scale, we conducted time-correlated single-photon counting (TCSPC) by employing a Halcyone ultrafast spectrometer (Ultrafast Systems, LLC). Halcyone is an all-in-one box using a PMT detector with a spectral range of 200–700 nm, where the instrument response function (IRF) is about $\sim$ 250 ps with a time window up to 200 μ s. This unit was integrated into the existing laser system we described above. Samples were measured in a 2-mm-thick cuvette and a magnetic stirrer was used to ensure a fresh volume of the sample.

RESULTS AND DISCUSSION

Steady-State Absorption and Emission Spectra. The absorption and fluorescence spectra of DPP-Pt(acac) with the successive addition of TCNE are shown in Fig. 1A. In the absence of TCNE, the absorption feature has two peaks at 620 and 670 nm. The absorption spectral feature of DPP-Pt(acac) is modified significantly upon the addition of TCNE: the initial 670 nm band

suffers from a successive decrease with increasing TCNE concentration and a new shoulder develops at 725 nm, indicating a ground-state interaction between DPP-Pt(acac) and TCNE likely due to the formation of a CT complex. This CT complex is expected to have a broad absorption spectrum that overlaps with the absorption of free DPP-Pt(acac). We recorded the excitation spectrum to better assign this CT band, (see the inset in Fig.1). From the recorded excitation spectrum, we anticipate the CT band to be a broad band in the 500–700 nm range with a maximum at 595 nm. Indeed TCNE, as an acceptor with modest oxidation³⁴ and reduction potentials of -0.26 V vs Ag/Ag⁺,^{35,36} has the potential for application as an acceptor to a divalent group of 10 transition-metal complexes.^{37,38} Excitation of the CT complex gives rise to an emission feature extending over the range of 640–850 nm centered at 700 nm with a vibronic shoulder at 760 nm. Successive addition of TCNE results in quenching of the DPP-Pt(acac) fluorescence, suggesting that the PET from the photoexcited DPP-Pt(acac) to the TCNE is followed by the development of a new emission band centered at 635 nm. The blue-shifted emission of the CT complex of DPP-Pt(acac)/TCNE indicates its slightly higher emission energy than that of DPP-Pt(acac). The impact of planarization of the π -electron system on the frontier orbital energy in the DPP-Pt(acac) is depicted in the literature.¹⁷ Structural changes are known to have the potential to be induced by interacting with TCNE.^{39,40} This implies that DPP-Pt(acac) and TCNE interact predominantly via static interaction, as supported by the quenching process, and leads to the expectation that less conjugation of DPP units with the two Pt(II) centers is typical of the excited state.

Fig. 1B illustrates our efforts to evaluate the effect of incorporating Pt(II). We show absorption and fluorescence of the Pt oligomer metal free (DPP) with successive addition of TCNE. In the absence of TCNE, the absorption peaks of DPP in DMF/DCM (4:1) are located at 512 and 548 nm. The absorption of DPP shows no change upon addition of TCNE; hence, formation of a CT complex is unlikely. Moreover, as discussed below, the rate of PET from the excited DPP to TCNE is very slow (on a few ns time scale), which allows us to rule out the formation of a static ground state complex. Emissions are in the range of 530–700 nm with two peaks at 564 and 607 nm. TCNE induces slight quenching (~30%) in DPP emission, which is in support of the absence of a static ground state complex. This suggests that the quenching of DPP emissions that takes places upon TCNE interaction may be caused by dynamic or diffusion controlled mechanisms. In the following, we discuss the ISC and PET from excited DPP-

Pt(acac) and DPP to TCNE. The Stern-Volmer plots are shown in Fig. 1 where the estimated quenching rate constants are found: $5.3 \times 10^{11} \text{ M}^{-1}\text{s}^{-1}$ and $1.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ for DPP-Pt(acac) and DPP, respectively. The diffusion rate of TCNE was calculated using Stokes-Einstein equation to be $7.02 \times 10^9 \text{ s}^{-1}\text{M}^{-1}$. Thus, it is clear that DPP quenching is within the diffusion limit, whereas DPP-Pt(acac) is much faster than the diffusion limit, which agrees with the anticipated mechanisms of interaction.

Excited-state Dynamics of DPP-Pt(acac). To gain further insight into the excited-state dynamics of DPP-Pt(acac), time-resolved TA spectroscopy of DPP-Pt(acac) was performed in DMF/DCM(4:1) in the presence and absence of TCNE. The spectra were measured following a 560 nm laser pulse excitation. In the absence of TCNE (Fig. 2A), excitation of DPP-Pt(acac) resulted in a strong negative absorbance band corresponding to the ground state bleach (GSB) and a broad excited-state absorption (ESA) at 670–820 nm. As we reported previously, the broad ESA was assigned to the DPP-Pt(acac) triplet state as a result of ISC on a time scale of 130 ps.¹⁵

In the presence of 0.05 M TCNE, in addition to the GSB of the DPP-Pt(acac)/TCNE system, the formation of a new featureless band over the range of 700–800 nm with a shoulder at 715 nm appears rapidly after excitation (Fig. 2B). This new featureless band can be attributed to the radical cation of DPP-Pt(acac)¹⁵ in response to the PET from the excited DPP-Pt(acac) to TCNE. This band becomes more obvious in the presence of higher TCNE concentrations, as shown in Fig. 2C. This shoulder, around 715 nm, is in good agreement with that reported for the radical cation of the oligomer. Moreover, the dynamics of this band appeared to show a significant change over a 3-ns time window, which is much shorter than the triplet state lifetime that is known to have 0.16 μs .¹⁷ This new band is monitored at a very early time delay (~ 3 ps), which is in favor of an ultrafast PET mechanism. The thermodynamic feasibility of the excited-state electron transfer is estimated by the change in Gibbs free energy (ΔG^0), which is an important parameter that pertains to the driving force of electron transfer reactions.⁴¹ From the reduction potential of TCNE (-0.26 V vs Ag/Ag^+)^{35,36}, the oxidation potential, and the singlet excited-state energy of DPP-Pt(acac) ($+0.79 \text{ V}$ versus Ag/Ag^+ and 1.82 eV , respectively),^{15,17} the ΔG^0 is estimated to be -0.77 eV , indicating that PET is thermodynamically feasible.

The results shown in Fig. 3 for the kinetics of ESA and GSB at different TCNE concentrations clearly shows the rise of the triplet state of DPP-Pt(acac) in the absence of TCNE

and the ultrafast PET from the excited DPP-Pt(acac) to TCNE in the presence of an electron acceptor. The exponential fit to the ESA data shown in Fig. 3 suggests that the rate of singlet-to-triplet ($S_1 \rightarrow T_1$) ISC of DPP-Pt(acac) is ~ 130 ps, in agreement with that reported earlier.¹⁵ On the other hand, analyses of the kinetic traces collected at 740 nm in the presence of TCNE reveal the presence of two kinetic components as: $3.32 \text{ ps} \pm 0.18$ (44%) and $128.84 \text{ ps} \pm 4.08$ (56%), and $4.19 \text{ ps} \pm 0.32$ (70%) and $123.69 \text{ ps} \pm 16.21$ (30%) for 0.02 and 0.05 M TCNE, respectively. Taking into consideration the above discussed steady-state measurements and the radical cation formation in the area of TA, we can assign the fast component for the PET from the DPP-Pt(acac) to TCNE. This indicates that PET from the excited DPP-Pt(acac) to TCNE is ultrafast (i.e., 3-4 ps), similar to that of DPP-Pt(acac) to the positively charged porphyrin¹⁵ but much faster than the ISC of DPP-Pt(acac) or the PET processes in bimolecular systems without metal centers.^{32,42-46} Note that an ultrafast electron transfer that is much faster than ISC indicates that the PET reaction occurs from the singlet excited state rather than the triplet state. An ultrafast PET is evidence for a strong electronic coupling between DPP-Pt(acac) and TCNE. In addition, the longer lifetime component may be due to free DPP-Pt(acac). It is worth pointing out that the amplitude of this component should exhibit almost the same time constant while its amplitude decreases as TCNE concentration was increased.

As shown in Fig. 3B, in the absence of TCNE, the GSB is dominated by a slow component of recovery, where the time constant is much longer than the observation time window (1 ns). In the presence of TCNE, in addition to the existence of a long time component, we observed a short time component within a few hundred ps, which can be assigned to fast CR from the $\text{TCNE}^{\cdot-}$ to $\text{DPP-Pt(acac)}^{+\cdot}$. The long-lived component is due to the long-lived radical cation and the triplet state of DPP-Pt(acac).

Excited-state Dynamics of DPP. To evaluate the role of Pt(II), we needed to monitor the excitation dynamics of the unmetallated chromophore, DPP. Fig. 4A shows TA spectroscopy of DPP after a 560 nm laser pulse excitation in the absence TCNE. In the absence of TCNE, excitation results in a GSB below 650 nm and a broad ESA between 670 and 820 nm. The broad ESA could be assigned to the DPP singlet state, as is indicated by the very fast formation at a temporal resolution of 120 fs. Fig. 4B shows the comparison of the excitation dynamics of DPP in the presence and absence of TCNE during the early time delays. Results show that the

presence of TCNE causes a slight increase in the rates of both ESA decay and GSB recovery. The absence of ultrafast PET from the excited DPP to TCNE indicates the lack of a CT complex in the DPP/TCNE system, which is consistent with the results of steady-state absorption and fluorescence measurements. Thus, communication between DPP and TCNE in the solution is expected to take place through dynamic interactions. As can be seen in Figs. 2 and 3, a clear and fast change in the transient spectra and its dynamics are observed for the DPP-Pt(acac)/TCNE system compared to the DPP-Pt(acac) metal-free system.

To evaluate the PET from the photoexcited DPP to TCNE through dynamic interactions, we monitored the TA spectra at long time delays from sub-ns to approximately 14 ns, as shown in Fig. 5. In the absence of TCNE (Fig. 5A), DPP shows GSB at 559 nm, stimulated emission (SE) at 610 nm, and an ESA centered at 751 nm. The ESA decay, which can be safely ascribed to the depopulation of the singlet state with a time constant of 6.07 ± 0.05 ns, simultaneously with the GSB recovery, indicates the relaxation of the singlet state to the ground state. Despite that the spectral shape of the DPP/TCNE system in early time delays are similar to those of DPP, in the presence of TCNE (Fig. 5B), a new broad positive band centered at 600 nm arises in the ns time delays. This new band is most likely due to the long-lived DPP cation radical. This indicates that there is PET from the excited DPP to TCNE. We should note that the PET caused a more than 4-fold increase in the rate of ESA decay and GSB recovery of the DPP/TCNE system than those of DPP in the absence of TCNE, as indicated in Fig. 6A for DPP in the presence of 0.10 M TCNE. The dynamic nature of the interaction mechanism between DPP and TCNE is also concluded from the TCSPC measurements given in Fig. 6B. The fluorescence lifetime for DPP in absence of TCNE is clearly decreased after adding TCNE, confirming the dynamic nature of the interaction.⁴⁷ By fitting the data with a single exponential decay function, the lifetimes of DPP in the presence and absence of 0.10 M TCNE was found to be 1.52 ± 0.01 and 6.07 ± 0.05 ns, respectively. The rate of PET can be extracted from the change of fluorescence lifetime using Stern-Volmer equation: $t_0/t = 1 + K_{SV}[\text{TCNE}]$, where t_0 and t are fluorescence lifetime in absence and presence of TCNE, respectively. Accordingly, the PET rate was found to be $7.04 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ which is very close to the diffusion rate of TCNE, calculated using Stokes-Einstein equation to be $7.02 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, supporting the suggested dynamic mechanism of interaction.

Effect of Pt(II). The above observations clearly indicate the effects of incorporating Pt(II) on the excitation dynamics, ISC, and PET of DPP. We propose that the incorporation of Pt(II) increases

the planarity and π -conjugation of the DPP moiety, thus reducing the HOMO–LUMO gap energy, as is evidenced by a red shift of the absorption bands (Fig. 1). The most influential role of Pt(II) is how it facilitates interactions with TCNE by forming a CT complex and enhancing electronic coupling between the DPP-Pt(acac) complex and TCNE; it is usually assumed that the electronic coupling strength increases exponentially with an inverse distance between the electron donor and acceptor.⁴⁸ The acceleration of ISC from ns to 130 ps is a central Pt(II) role in this system. Although redox properties and energy levels of singlet and triplet excited states of DPP are modified by the incorporation of Pt(II), the low reduction potential of TCNE allows electron transfer from the excited DPP-Pt(acac) or DPP to TCNE. The oxidation potentials of DPP and DPP-Pt(acac) are 0.53 and 0.28 vs Fc/Fc^+ , respectively.¹⁷ Given that the singlet excited-state energy of DPP and DPP-Pt(acac) are at the same level (1.9 and 1.8 eV, respectively), the driving force for the electron transfer (ΔG^o) from the excited DPP or DPP-Pt(acac) to TCNE are comparable on the same order of magnitude. Thus, the ultrafast PET in the case of DPP-Pt(acac) to TCNE is likely to be facilitated by the Pt centers, which may increase the planarity and π -conjugation. While interaction between DPP and TCNE appear to be diffusion controlled, as indicated by steady-state and time-resolved measurements, incorporation of Pt(II) induces the CT complex with TCNE in the ground state and facilitates ultrafast PET from DPP-Pt(acac) in the singlet excited state to TCNE.

CONCLUSION

Here, we present a detailed study of the excited-state dynamics of DPP-Pt(acac)/TCNE and DPP/TCNE systems in DMF:DCM (4:1) using time-resolved broadband transient absorption and emission spectroscopy. Results indicate that a Pt(II) center is essential to controlling the PET mechanism from the donor (DPP-Pt(acac) or DPP) to the TCNE electron acceptor. Steady-state and time-resolved data demonstrate that the most influential role of incorporated Pt(II) is to facilitate interactions between DPP-Pt(acac) with TCNE, resulting in the formation of a CT complex, which is in contrast absent from the DPP/TCNE system. Temporal evolution of TA spectra were analyzed to elucidate PET from excited DPP-Pt(acac) and DPP to TCNE. TA results show the possibility of switching the reaction mechanism from a diffusion-controlled process to a static process by incorporation of a Pt metal center into DPP.

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AUTHOR INFORMATION

Corresponding Authors

*E-mail: omar.abdelsaboor@kaust.edu.sa (O.F.M.).

Notes

The authors declare no competing financial interest.
S.M.A.: On leave from the Department of Chemistry, Assiut University, Assiut, Egypt.

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Scheme 1

Scheme 1. Chemical structures of DPP and DPP-Pt(acac)

Figure 1

Figure 1. (A) Steady-state absorption (left) and emission (right) after excitation at 600 nm of the DPP-Pt(II)(acac) complex. (B) Steady-state absorption (left) and emission (right) after excitation at 490 nm of DPP at different the indicated concentrations of TCNE. Insets are (A) excitation spectrum of DPP-Pt(acac)/TCNE recorded using $\lambda_{em}=638$ nm (left), a Stern-Volmer plot (right), and (B) a Stern-Volmer plot (right).

Figure 2

Figure 2. Transient absorption spectra (ΔA) observed at time delays from sub-ps to a few hundred ps for DPP-Pt(II)(acac) in the absence of TCNE (A), in the presence of 0.05 M TCNE(B), and in the presence of 0.4 M TCNE (C) after excitation at 560 nm.

Figure 3

Figure 3. A rescaled time profile (up to 1 ns) of ESA kinetics at 740 nm (A) and GSB at 627 nm of the DPP-Pt(II)(acac) complex in the presence and absence of TCNE (B). The solid lines represent the best fits to the obtained data.

Figure 4

Figure 4. Transient absorption spectra (ΔA) observed at time delays from sub-ps to a few ns for DPP in the absence of TCNE after excitation at 560 nm (A). A rescaled time profile (up to a few ns) of the transient absorption kinetics of an ESA at 751 nm and GSB at 613 nm for DPP in the presence and absence of 0.05 M TCNE (B). The time constants extracted from the fitting are indicated.

Figure 5

Figure 5. Transient absorption spectra (ΔA) observed at different time delays from sub-ns to approximately 14 ns for DPP in the absence of TCNE (A) and in the presence of 0.1 M TCNE after excitation at 500 nm (B).

Figure 6

Figure 6. A rescaled time profile (up to 30 ns) of the transient absorption kinetics of ESA at 748 nm and GSB at 560 nm of DPP in the presence and absence of 0.1 M TCNE after laser excitation at 500 nm (The time constants extracted from the fitting are indicated.) (A); TCSPC of DPP in the presence and absence of 0.05 and 0.1 M TCNE after laser excitation at 500 nm (The time constants extracted from the fitting are indicated) (B).

TOC graphic