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### Introduction

Organometallic complexes have attracted attention for a wide range of applications in photocatalysis,<sup>1-5</sup> bioimaging,<sup>6-8</sup> sensing,<sup>9,10</sup> and organic light-emitting diode (OLED) devices.<sup>11-14</sup> The spin-forbidden nature of the singlet–triplet transition often leads to slow intersystem crossing (ISC) in organic systems. However, by incorporating heavy transition metals, the ISC rate constant ( $k_{\rm ISC}$ ) can be significantly increased to typically greater than 10<sup>10</sup> s<sup>-1</sup>,<sup>15</sup> even up to 10<sup>13</sup>–10<sup>14</sup> s<sup>-1</sup> in Ru(II) complexes,<sup>16-19</sup>

## Ultrafast photophysics of *para*-substituted 2,5bis(arylethynyl) rhodacyclopentadienes: thermally activated intersystem crossing<sup>+</sup>

Zilong Guo, <sup>[b]</sup><sup>b</sup> Yaxin Wang,<sup>b</sup> Julia Heitmüller, <sup>[b]</sup><sup>a</sup> Carolin Sieck,<sup>c</sup> Andreas Prüfer,<sup>d</sup> Philipp Ralle,<sup>d</sup> Andreas Steffen, <sup>[b]</sup><sup>d</sup> Petr Henke, <sup>[b]</sup><sup>eg</sup> Peter R. Ogilby, <sup>[b]</sup>\*<sup>e</sup> Todd B. Marder, <sup>[b]</sup>\*<sup>cf</sup> Xiaonan Ma <sup>[b]</sup>\*<sup>ba</sup> and Tobias Brixner <sup>[b]</sup>\*<sup>af</sup>

2,5-Bis(phenylethynyl) rhodacyclopentadienes (RCPDs), as a type of Rh(III) complex, exhibit unusually intense fluorescence and slow intersystem crossing (ISC) due to weak metal-ligand interactions. However, details on their ultrafast photophysics and ISC dynamics are limited. In this work, electronic relaxation upon photoexcitation of two substituted RCPDs with two  $-CO_2Me$  (A-RC-A) or  $-NMe_2/-CO_2Me$  (D-RC-A) end groups are comprehensively investigated using femtosecond transient absorption spectroscopy and theoretical analysis. Upon ultraviolet and visible excitation, dephasing of vibrational coherence, charge transfer, conformation relaxation, and ISC are observed experimentally. By calculating the spin-orbit coupling, reorganization energy, and adiabatic energy gap of plausible ISC channels, semi-classical Marcus theory revealed the dominance of thermally activated ISC (S<sub>1</sub>  $\rightarrow$  T<sub>2</sub>) for both D-RC-A and A-RC-A, while S<sub>1</sub>  $\rightarrow$  T<sub>1</sub> channels are largely blocked due to high ISC barriers. With weak spin-orbit coupling, such differences in plausible ISC channels are predominately tuned by energetic parameters. Singlet oxygen sensitization studies of A-RC-A provide additional insight into the excited-state behavior of this complex.

leading to significant fluorescence quenching and enhanced phosphorescence emission. Efficient ISC can be primarily attributed to strong spin–orbit coupling (SOC) due to participation of the d-orbitals of heavy metals, which can significantly alter the photophysics due to strong metal–ligand interactions *via* metal-to-ligand charge transfer (MLCT) states that dominate electronic relaxation.<sup>20–24</sup>

Unlike complexes with ultrafast ISC, 2,5-bis(phenylethynyl) rhodacyclopentadienes (RCPDs)25-27 incorporating Rh(m) exhibit up to 69% fluorescence quantum yields ( $\Phi_{\rm f}$ ) with  $k_{\rm ISC} = 10^7 - 10^8 \, {\rm s}^{-1}$ which is several orders of magnitude slower than that in  $Ru(\pi)$ complexes.17 Intriguingly, by replacing Rh(m) with much heavier Ir(III), the corresponding iridacyclopentadienes<sup>28</sup> are still highly fluorescent. Such photophysics was attributed to weakened SOC due to low d-orbital participation in the frontier orbitals and an enlarged S<sub>1</sub>-T<sub>1</sub> energy gap ( $\Delta E_{ST}$ ).<sup>28,29</sup> Meanwhile, the T<sub>2</sub> state was reported to be an ISC destination through a thermally activated mechanism in RCPDs,28 which increased the complexity of their electronic relaxation. Investigations indicated that the fluorescence properties of RCPDs can be effectively tuned by introducing an electron donor (D) or acceptor (A) at the para-positions of the arylethynyl groups.<sup>28,30,31</sup> In particular, symmetric substitution with A/A groups ( $-CO_2Me \text{ or } -BMes_2$ ) (Mes = mesityl = 2,4,6- $Me_3C_6H_2$ ) at the *para*-positions leads to significantly higher  $\Phi_f$ than corresponding D/A (-NMe2/-CO2Me) and unsubstituted RCPDs (see Table S1<sup>†</sup>). In a simple excited-state model, enhanced



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<sup>&</sup>quot;Institut für Physikalische und Theoretische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany. E-mail: tobias.brixner@ uni-wuerzburg.de

<sup>&</sup>lt;sup>b</sup>Institute of Molecular Plus, Tianjin University, Tianjin 300072, P. R. China. E-mail: xiaonanma@tju.edu.cn

Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany. E-mail: todd.marder@uni-wuerzburg.de

<sup>&</sup>lt;sup>d</sup>Department of Chemistry and Chemical Biology, TU Dortmund University, Otto-Hahn-Str. 6, 44227 Dortmund, Germany

<sup>&</sup>lt;sup>e</sup>Department of Chemistry, Aarhus University, Aarhus DK-8000, Denmark. E-mail: progilby@chem.au.dk

<sup>&</sup>lt;sup>I</sup>Institute for Sustainable Chemistry and Catalysis with Boron (ICB), Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

<sup>\*</sup>Faculty of Science, Charles University, Hlavova 2030, 128 43 Prague 2, Czech Republic † Electronic supplementary information (ESI) available. See DOI: https://doi.org/10.1039/d4sc04306e

fluorescence emission can be attributed either to slow nonradiative relaxation of the S<sub>1</sub> state *via* dark states or suppressed ISC to the triplet state.<sup>32,33</sup> Although  $k_{\rm ISC}$  of RCPDs was determined to be  $10^7-10^8$  s<sup>-1</sup> using picosecond time-resolved infrared spectroscopy,<sup>30</sup> a full picture of their S<sub>1</sub> relaxation remains unclear. Therefore, a comprehensive picture of the photophysics of RCPDs with weak metal-ligand interactions might be helpful for future rational design of fluorescent emitters.

In general, the ISC rate constant  $k_{\text{ISC}}$  between singlet (S<sub>m</sub>,  $m \ge 1$ ) and triplet (T<sub>n</sub>,  $n \ge 1$ ) excited states can be expressed *via* the Fermi golden rule,<sup>34,35</sup>

$$k_{\rm ISC} = \frac{2\pi}{\hbar} \langle \mathbf{S}_m | \hat{H}_{\rm SO} | \mathbf{T}_n \rangle^2 \rho_{\rm FC}, \qquad (1)$$

in which  $k_{\rm ISC}$  is determined by the SOC matrix element  $\langle S_m$ - $|\hat{H}_{\rm SO}|T_n\rangle$ , as well as the Franck–Condon-weighted density of states  $\rho_{\rm FC}$ , which can be described in the framework of Marcus–



Scheme 1 Chemical structures of investigated D-RC-A and A-RC-A. The Rh(III)-ligand core is illustrated in black while the peripheral groups are in gray. The phosphine ligand is  $PMe_3$ .

transient absorption (fs-TA) measurements and timedependent density-functional theory (TD-DFT) calculations. Compared with A-RC-A ( $\tau_{S_1} = 1.7 \text{ ns}$ ) substituted with two – CO<sub>2</sub>Me groups, the D-RC-A with –CO<sub>2</sub>Me/–NMe<sub>2</sub> substitution exhibits a shorter ( $\tau_{S_1} = 0.8 \text{ ns}$ ) lifetime of the S<sub>1</sub> state in toluene solution.<sup>31</sup> By resolving fs-TA data upon ultraviolet (UV) and visible excitation, the electronic relaxation channels of D-RC-A

$$\rho_{\rm FC} = \frac{1}{\sqrt{4\pi\Gamma k_{\rm B}T}} \sum_{n=0}^{\infty} \exp(-S) \frac{S^n}{n!} \times \exp\left[-\frac{\left(\Delta E_{\rm ST} + n\hbar\omega_{\rm eff} + \Gamma\right)^2}{4\Gamma k_{\rm B}T}\right].$$

Levich-Jortner theory:36-39

In a semi-classical approximation at high temperature *T*, with  $\hbar\omega_{\rm eff} \ll k_{\rm B}T$ , the Huang–Rhys factor (*S*) and effective frequency ( $\omega_{\rm eff}$ ) of internal vibrational modes can be ignored. The density  $\rho_{\rm FC}$  follows the standard Arrhenius-type equation and  $k_{\rm ISC}$  can be obtained from the Marcus-theory equation:<sup>40–43</sup>

$$k_{\rm ISC} = \frac{1}{\hbar} \left\langle S_m | \hat{H}_{\rm SO} | \mathbf{T}_n \right\rangle^2 \sqrt{\frac{\pi}{\Gamma k_{\rm B} T}} \exp\left[ -\frac{\left(\Gamma + \Delta E_{\rm ST}\right)^2}{4\Gamma k_{\rm B} T} \right].$$
(3)

Here,  $\langle \mathbf{S}_m | \hat{H}_{\rm SO} | \mathbf{T}_n \rangle$  describes the SOC matrix element,<sup>44,45</sup> while  $\Gamma$  and  $\Delta E_{\rm ST}$  represent the reorganization energy and adiabatic energy gap of the ISC ( $\mathbf{S}_m \rightarrow \mathbf{T}_n$ , m,  $n \geq 1$ ) transition, respectively. Eqn (3) has been widely employed for estimating ISC and reverse ISC rates in medium-size organic molecules and complexes.<sup>46-49</sup>

In cases of ultrafast ISC ( $k_{ISC} > 10^{12} \text{ s}^{-1}$ ) of complexes with late transition metals, extremely high  $k_{ISC}$  is observed due to a large coupling term  $\langle S_m | \hat{H}_{SO} | T_n \rangle$  up to several thousands of cm<sup>-1</sup>, which greatly amplifies the ISC rate associated with the ISC barrier ( $E_a$ ) determined by  $\Gamma$  and  $\Delta E_{ST}$ . However, RCPDs exhibit much slower ISC ( $k_{ISC} = 10^8 - 10^9 \text{ s}^{-1}$ ) due to the lack of strong metal-ligand interactions,<sup>30</sup> *i.e.*,  $\langle S_m | \hat{H}_{SO} | T_n \rangle$  in eqn (3) is expected to be small and relatively sensitive to *para*-substitution on the aryl ligand. It is hypothesized that the  $k_{ISC}$  may vary significantly with the reorganization energy and adiabatic energy gap subject to para-substitution, which determine the ISC barrier ( $E_a$ ) thermodynamically and can be discussed within the framework of Marcus theory.

In this work, two *para*-substituted 2,5- bis(arylethynyl)rhodacyclopentadiene complexes (Scheme 1) were investigated by using excitation-wavelength- $(\lambda_{ex})$ -dependent femtosecond and A-RC-A are largely revealed. Moreover, by applying semiclassical Marcus theory, we determine that ISC of both D-RC-A and A-RC-A rely on a thermally activated  $S_1 \rightarrow T_2$  transition rather than the channel that directly populates the  $T_1$  state. We also report studies of singlet oxygen,  $O_2(a^1\Delta_g)$ , sensitization by A-RC-A, which provides additional insight into the excited-state behavior of this complex.

### Results and discussion

#### Static absorption spectra

The static absorption spectra of D-RC-A and A-RC-A in THF are displayed in Fig. 1 along with the calculated vertical excitation



Fig. 1 (a and b) Static UV/visible absorption spectra of D-RC-A ((a), blue) and A-RC-A ((b), red) in THF solution  $(10^{-5} \text{ mol L}^{-1})$ , overlapped with spectra of UV (violet shaded) and visible (green shaded) excitation pulses employed in the fs-TA experiments. (c and d) TD-DFT-calculated vertical excitation energies and oscillator strengths of D-RC-A (c) and A-RC-A (d).

energies and oscillator strengths, while the corresponding calculation results are listed in Table S2.<sup>†</sup> Note that the oscillator strength (*f*) here is not referenced to the transition probability for a freely oscillating electron in a single atom, but reflects only the transition dipole moment and the energy gap between two states of the RCPDs. For both D-RC-A and A-RC-A, the pronounced absorption in the 450–550 nm region can be attributed to the S<sub>1</sub> excited state, while higher singlet (S<sub>m</sub>, m > 1) states comprise the intense absorption in the UV region. As a result, upon visible ( $\lambda_{ex} = 513$  nm) and UV ( $\lambda_{ex} = 295$  nm) optical excitation, direct population of the S<sub>1</sub> and S<sub>m</sub> states can be expected in fs-TA experiments, as described in detail below.

The observed S1 band of D-RC-A exhibits less pronounced vibronic progression than that of A-RC-A. Reduced vibronic progression might be attributed to stronger solute-solvent interaction due to excited-state charge transfer (CT) between substituted D and A groups, which was confirmed by natural transition orbital (NTO) analysis of the S<sub>1</sub> state of both RCPDs. As illustrated in Fig. S1,† A-RC-A exhibits a symmetric distribution of both hole and electron density in the S<sub>1</sub> state, indicating its locally excited (LE) nature. However, clear CT character is observed in the S<sub>1</sub> state NTOs of D-RC-A, *i.e.*, hole and electron density are asymmetrically distributed on D and A sides, respectively. A different S1 character (CT or LE) of D-RC-A and A-RC-A can also affect the corresponding S<sub>1</sub> relaxation. The initially populated S1 state undergoes rapid decay leading to the relaxed CT state, which is observed in the fs-TA signal of D-RC-A and absent for A-RC-A. Furthermore, NTO analysis on the triplet states indicates that the T1 of D-RC-A is slightly mixed with CT character like the S1 state, while the corresponding T2 state and  $T_1/T_2$  states of A-RC-A are all LE dominated.

On the other hand, NTO analysis indicates that the central Rh(m) in D-RC-A and A-RC-A is barely involved in the  $S_0 \rightarrow S_1$ ,  $S_0 \rightarrow T_1$ , and  $S_0 \rightarrow T_2$  transitions, which is consistent with previous reports on electronic transitions of RCPDs,<sup>28,31</sup> *i.e.*, the low-lying  $S_1$ ,  $T_1$ , and  $T_2$  states of RCPDs are dominated by  $\pi$ - $\pi$ \* transitions of ligands with minimal contributions of Rh(m). The photophysics indicates the weak SOC of RCPDs, which is consistent with previous reports.<sup>25–28,30,31</sup> Without pronounced metal-ligand interaction, ISC dynamics of RCPDs are largely determined by energetic parameters ( $\Gamma$  and  $\Delta E_{ST}$ ) and can thus be discussed in the framework of semi-classical Marcus theory.

#### Excitation-wavelength-dependent fs-TA

To acquire a full picture of electronic relaxation of RCPDs, we performed fs-TA experiments on D-RC-A and A-RC-A upon excitation by either UV ( $\lambda_{ex} = 295$  nm) or visible ( $\lambda_{ex} = 513$  nm) laser pulses as previously reported.<sup>50</sup> The resulting TA signal in the probe range of  $\lambda_{pr} = 320-670$  nm was recorded for delay times up to  $\Delta t = 3.8$  ns and are displayed in Fig. 2.

As shown in Fig. 2a and b, D-RC-A exhibits nearly identical fs-TA signals upon UV ( $\lambda_{ex} = 295 \text{ nm}$ ) and visible ( $\lambda_{ex} = 513 \text{ nm}$ ) excitation, respectively, in which at least three distinct bands can be distinguished. The negative band appears immediately after excitation in the  $\lambda_{pr} = 470-550 \text{ nm}$  regime and agrees with the static absorption spectrum ( $S_0 \rightarrow S_1$ ), which can be



Fig. 2 Spectro-temporal maps of  $\lambda_{ex}$ -dependent fs-TA signals of D-RC-A upon UV (a) and visible (b) excitation as well as of A-RC-A upon identical UV (c) and visible (d) excitation. The spectral signatures of ISC-generated triplet states are highlighted by white dashed lines.

attributed to the ground-state bleaching (GSB) signal. At the same time, two excited-state absorption (ESA) bands of the S<sub>1</sub> state appear in the  $\lambda_{pr} = 360-460$  nm and >550 nm regimes which, subsequently, exhibit relaxation simultaneously with the decay of the GSB band. Meanwhile, slow formation of a new positive band is observed with a center at  $\lambda_{pr} = 580$  nm, which is superimposed on the decay of the long-lived ESA band in the  $\lambda_{pr} > 550$  nm region, probably corresponding to ESA of an ISC-generated triplet state. However, the final destination (T<sub>1</sub> or T<sub>2</sub>) of the observed ISC process is difficult to identify by fs-TA data itself. Instead, ISC rates of S<sub>1</sub>  $\rightarrow$  T<sub>1</sub> and S<sub>1</sub>  $\rightarrow$  T<sub>2</sub> need to be calculated to assign the observed ISC process. Thus, we tentatively denote the triplet state generated as the T<sub>n</sub> ( $n \ge 1$ ) state.

Unlike D-RC-A, A-RC-A exhibits  $\lambda_{ex}$ -dependent relaxation behavior. Upon UV excitation, a similar fs-TA signal as that for D-RC-A was recorded for A-RC-A, although the GSB displays a double peak at  $\lambda_{pr} = 500$  nm and 535 nm, which is consistent with the pronounced vibronic progression exhibited in the static absorption spectrum. Meanwhile, triplet-state formation is also observed at  $\lambda_{pr} = 570$  nm, with a substantially slower  $k_{ISC}$ than that of D-RC-A. As shown in Fig. S2,† preliminary fitting of triplet formation dynamics of D-RC-A (at  $\lambda_{pr} = 580$  nm) and A-RC-A (at  $\lambda_{pr} = 570$  nm) indicated that the observed ISC of D-RC-A ( $\tau_{ISC}$  < 350 ps) is one order of magnitude faster than ISC of A-RC-A ( $\tau_{ISC}$  > 3.5 ns). Thus, S<sub>1</sub> state relaxation of D-RC-A might be dominated by ISC as it is much faster than radiative and non-radiative  $S_1 \rightarrow S_0$  channels. In contrast, considering the observed fluorescence lifetime ( $\sim$ 1.7 ns), the radiative and non-radiative  $S_1 \rightarrow S_0$  decay of A-RC-A might be comparable with ISC to triplet states.

Intriguingly, upon visible excitation, the triplet band of A-RC-A is absent in the fs-TA data up to the maximum delay time (3.8 ns), while the decay of ESA bands and refilling of the GSB band are still observable. In general, upon UV excitation, rapid internal conversion (IC) from initially populated  $S_m$  states leads to a vibrationally hot  $S_1$  state. Compared with the  $S_1$  state

directly populated by resonant visible excitation, excess vibrational energy of the S<sub>1</sub> state might be helpful to overcome the ISC barrier.<sup>51–54</sup> Therefore, we believe that the ISC barrier ( $E_a$ ) for A-RC-A should be higher than that for D-RC-A, which is also indicated by a slower rise of the ISC band of A-RC-A compared to that of D-RC-A upon UV excitation.

#### Ultrafast electronic relaxation

To obtain details on the electronic relaxation of the RCPDs, we performed target analysis on the corresponding  $\lambda_{ex}$ -dependent fs-TA data. On ultrafast time scales, a sequential kinetic model including several independent species was employed for all fs-TA data, while a branched scheme was considered for the decay of the relaxed (CT and structural) S<sub>1</sub> state, corresponding to competition between relaxation to the  $S_0$  state ( $S_1 \rightarrow S_0$ ) and ISC to triplet states  $(S_1 \rightarrow T_n)$ . As discussed above,  $S_1$  relaxation of D-RC-A is dominated by the  $S_1 \rightarrow T_n$  channel, for which the  $S_1$  $\rightarrow$  S<sub>0</sub> channel was correspondingly ignored in target analysis (Fig. S3<sup>†</sup>). However, for A-RC-A upon UV excitation, both the S<sub>1</sub>  $\rightarrow$  S<sub>0</sub> and S<sub>1</sub>  $\rightarrow$  T<sub>n</sub> channels were included in target analysis with a branch ratio of 0.5 (Fig. S3<sup>†</sup>). The extracted speciesassociated spectra (SAS) are displayed in Fig. 3, while the corresponding fitted time traces at selected  $\lambda_{pr}$  and the concentration evolution of each species can be found in Fig. S4 and S5,† respectively, in the ESI.†

As mentioned above, D-RC-A exhibits similar relaxation dynamics upon UV and visible excitation. Upon UV excitation, the populated  $S_m$  states undergo rapid IC with a time constant of  $\tau_1 = 206$  fs to reach the Franck–Condon region of the  $S_1$  state ( $S_m \rightarrow S_1^{\text{FC}}$ ), which is absent in the fs-TA data upon resonant visible excitation to the  $S_1$  state. The subsequent SAS exhibits a spectral depletion in the range  $\lambda_{\rm pr} = 570-670$  nm, which is consistent with fluorescence spectra of D-RC-A and can be attributed to the stimulated emission (SE) band of the S<sub>1</sub> state. Pronounced solvatochromism of D-RC-A has been reported,<sup>31</sup> implying CT character of the fluorescent bright state, which is also consistent with the NTO analysis mentioned above. Considering the observed SE signature in the SAS, we assigned the second SAS to the CT-relaxed S<sub>1</sub> state (noted as S<sub>1</sub><sup>CT</sup>), corresponding to a local minimum on the S<sub>1</sub> potential energy surface (PES). Moreover, the fitted formation time of S<sub>1</sub><sup>CT</sup> (S<sub>1</sub><sup>FC</sup>  $\rightarrow$  S<sub>1</sub><sup>CT</sup>,  $\sim$ 1 ps) is consistent with the reported formation time of the solvation-stabilized CT state of organic D-A-type chromophores in THF.<sup>55,56</sup>

During the subsequent relaxation  $(S_1^{CT} \rightarrow S_1')$  with a ~10 ps time constant, the SAS exhibit only minimal changes of spectral features, which might be explained by structural relaxation in the  $S_1$  state. In order to obtain further details on  $S_1$  relaxation, we calculated the optimized structures of both D-RC-A and A-RC-A in their  $S_1$ ,  $T_1$ , and  $T_2$  states to be compared with the  $S_0$ structure. As shown in Fig. S6 and S7,† large  $S_0 \rightarrow S_1$  twisting is observed for the peripheral phenyl and D/A groups of RCPDs, which can be quantified by the calculated twisting angles listed in Table S3.<sup>†</sup> Apart from the twisting angles, contributions of S<sub>0</sub>  $\rightarrow$  S<sub>1</sub> conformational relaxation can be generalized in reorganization energy  $(\Gamma^{S_1 \rightarrow S_0})^{.57,58}$  By summing over contributions from each vibrational mode (Fig. S8<sup>†</sup>),  $\Gamma^{S_1 \rightarrow S_0}$  of D-RC-A and A-RC-A were calculated to be 1519  $\text{cm}^{-1}$  and 1944  $\text{cm}^{-1}$ , respectively. However,  $\Gamma^{S_1 \rightarrow S_0}$  contributed by vibrational modes is not able to provide the relative contribution of each structural part of the RCPDs to conformational relaxation. Therefore, we further calculated the root-mean-square displacement (RMSD)



Fig. 3 Target-analysis-extracted species-associated spectra (SAS) of  $\lambda_{ex}$ -dependent fs-TA signals of D-RC-A upon 295 nm UV (a) and 513 nm visible (b) optical excitation, as well as SAS of A-RC-A upon identical UV (c) and visible (d) excitation. Four or five independent species were employed to reproduce the fs-TA signals.

in Cartesian coordinates of the optimized  $S_0(x_i, y_i, z_i)$  and  $S_1(x'_i, y'_i, z'_i)$  state structures,

$$\mathbf{RMSD} = \sqrt{\frac{1}{N} \sum_{i}^{N} \left[ \left( x_{i} - x_{i}^{'} \right)^{2} + \left( y_{i} - y_{i}^{'} \right)^{2} + \left( z_{i} - z_{i}^{'} \right)^{2} \right]}, \quad (4)$$

Summing over all atoms, i = 1, ..., N. The calculation leads to  $RMSD^{S_1/S_0} = 0.156$  Å for D-RC-A which is lower than that for A-RC-A (0.207 Å), consistent with the calculated  $\Gamma^{S_1 \rightarrow S_0}$ . We further calculated the relative contributions of the peripheral groups (phenyls, C≡C, and D/A, gray part in Scheme 1) and Rh(III)-ligand core (black part in Scheme 1). For D-RC-A, the RMSD<sup>S<sub>1</sub>/S<sub>0</sub></sup> was found to be dominated by twisting of the peripheral parts of the structure with  $\sim$ 90% contribution. The rotational twisting around C-C single bonds has been widely reported to be nearly barrierless,59,60 which is consistent with the observed efficient relaxation ( $S_1^{CT} \rightarrow S_1'$ , ~10 ps). Intriguingly, we found that the Rh(m)-ligand core contributes ~40% to the  $RMSD^{S_1/S_0}$  of A-RC-A *via* its own framework distortion, which is comparable with the twisting of the peripheral parts ( $\sim 60\%$ ). Compared to the rapid twisting of the peripheral groups, the distortion of the molecular framework is normally much slower due to a high potential barrier. Therefore, a two-step conformational relaxation is expected to be observed in the fs-TA data of A-RC-A, which has been widely reported in organic fluorescent systems.61-63

The extracted species  $S'_1$  corresponds to a global minimum on the  $S_1$ -state PES, which subsequently undergoes ISC leading to formation of a triplet state, featured by the rise of intense absorption centered at  $\lambda_{pr} = 580$  nm and the disappearance of SE depletion ( $\lambda_{pr} = 570-670$  nm). The formation time ( $S'_1 \rightarrow T_n$ , ~300 ps) of the triplet state corresponds to the ISC rate constant ( $k_{ISC}$ ) of D-RC-A, which is consistent with the relatively low fluorescence quantum yield ( $\Phi_f = 0.22$ ) and sub-nanosecond fluorescence lifetime ( $\tau_{S_1} = 0.8$  ns) observed in toluene solution.<sup>31</sup> Note that relaxation of the  $S_1$  state is contributed to by non-radiative decay to  $S_0$  ( $k_{RR}^S$ ), radiative decay to  $S_0$  ( $k_R^S$ ), and ISC to triplet states ( $k_{ISC}$ ). Therefore, the  $S_1$  ESA decay and GSB refilling dynamics could be largely different with formation of the triplet band, *i.e.*,  $S_1$  ESA and GSB include contributions of  $k_{\rm NR}^{\rm S}$ ,  $k_{\rm R}^{\rm S}$ , and  $k_{\rm ISC}$ , while rising of the triplet band is associated with  $k_{\rm ISC}$  only. The full picture of the electronic relaxation of the RCPDs is summarized in Fig. 4.

In the fs-TA data for A-RC-A upon UV excitation, we observed electronic relaxation that is significantly different from D-RC-A. Without a D-A structure, the CT state signature was absent in the fs-TA of A-RC-A. After excitation, rapid IC (~900 fs,  $S_m \rightarrow$  $S_1^{FC}$  is followed by two-step conformational relaxation  $(S_1^{FC} \rightarrow S_1' \rightarrow S_1'')$ , corresponding to a comparable contribution of the peripheral structure and metal-ligand core to the  $RMSD^{S_1/S_0}$ of A-RC-A. The first step  $(S_1^{FC} \rightarrow S_1', \sim 9 \text{ ps})$  exhibits a time constant similar to that of the corresponding step in D-RC-A  $(S_1^{CT} \rightarrow S_1', \sim 10 \text{ ps})$ , which was attributed to barrierless twisting of the peripheral structure. Note that the observed twisting with a  $\sim 10$  ps time constant is unobservable in our previous timeresolved IR investigation due to the limitation of low temporal resolution (10–20 ps).<sup>30</sup> The subsequent step  $(S'_1 \rightarrow S''_1, \sim 150 \text{ ps})$ accordingly corresponds to structural distortion of the Rh(m)ligand framework. Furthermore, slower triplet formation (S<sub>1</sub>"  $\rightarrow$  T<sub>n</sub>, ~3.88 ns) in A-RC-A than in D-RC-A was observed upon UV excitation, corresponding to a long-lived ( $\tau_{\rm f} = 1.7$  ns) S<sub>1</sub> state,<sup>31</sup> which is discussed in detail below. Upon  $\sim$ 25 fs visible excitation, A-RC-A exhibits largely different electronic relaxation (Fig. 3d) from the case with UV excitation (Fig. 3c). The target analysis extracted a short-lived species(noted as S<sub>1</sub><sup>\*</sup>) after excitation with a  $\sim$ 400 fs time constant. As described above, rapid IC (~900 fs,  $S_m \rightarrow S_1^{FC}$ ) was identified for A-RC-A upon UV excitation, while the observed visible-excitation-induced ~400 fs relaxation obviously cannot be assigned to IC from  $S_m$ , as the visible excitation at  $\lambda_{ex} = 513$  nm employed is resonant with the S<sub>1</sub> state of A-RC-A and, correspondingly, incapable of populating the  $S_m$  state. Moreover, as illustrated in Fig. S9,<sup>†</sup> we observed a beating behavior in the  $\lambda_{\rm pr}=400\text{-}550$  nm wavelength regime of the fs-TA data, which is observed as an oscillatory modulation in both temporal (Fig. S4<sup>†</sup>) and frequency (Fig. S9<sup>†</sup>) domains. The beating-modulated TA spectra (Fig. S9<sup>†</sup>) observed in the initial few picoseconds are highly consistent with the extracted SAS of the  $S_1^*$  species with a  $\sim 400$  fs relaxation. We therefore attribute  $S_1^*$  relaxation to dephasing of the coherent vibrational wave packet (noted as  $S_1^* \rightarrow S_1^{FC}$ ). The dephasing of  $S_1^*$  was not recognized as an independent species



Fig. 4 Electronic relaxation of D-RC-A (left two panels) and A-RC-A (right two panels) revealed by  $\lambda_{ex}$ -dependent fs-TA measurements.

in the target analysis of D-RC-A upon visible excitation, which might be associated with a less modulated spectral shape and faster  $S_1^*$  dephasing (Fig. S9†) of D-RC-A due to intense solute-solvent interactions. We further extracted beating signals by subtracting the fitted exponential components from the measured fs-TA data. The Fourier transformed power spectra of the beating signals (Fig. S10†) revealed a dominant vibrational mode at ~250 cm<sup>-1</sup> for both D-RC-A and A-RC-A. Considering that the beating frequency is independent of the 2,5-substitution, we speculate that the observed ~250 cm<sup>-1</sup> mode might originate from a distortion of the metal–ligand core.

After rapid dephasing  $(S_1^* \rightarrow S_1^{FC})$ , the  $S_1$  state of A-RC-A subsequently undergoes a two-step conformational relaxation  $(S_1^{FC} \rightarrow S_1^{'} \rightarrow S_1^{''})$  nearly identical with that of A-RC-A upon UV excitation. However, the rise of the  $T_n$  band observed in the fs-TA of A-RC-A upon UV excitation is absent upon visible excitation. Instead, we observe an isosbestic point at  $\lambda_{pr} = 530$  nm in the fs-TA data of A-RC-A upon visible excitation, indicating that the TA bands located on the blue (GSB,  $\lambda_{pr} = 430-530$  nm) and red (ESA,  $\lambda_{pr} = 530-670$  nm) sides of the isosbestic point belong to an identical process, *i.e.*, S1 relaxation. However, note that the fs-TA observation cannot fully exclude the existence of ISC of A-RC-A upon visible excitation due to the limitation of the fs-TA time window. Actually, upon visible excitation, slight spectral rising can be observed between 550 nm and 600 nm at long delays, which is consistent with the triplet band observed upon UV excitation. A plausible explanation is that visible excitation leads to an ultraslow ISC which is unobservable within our time window (3.8 ns).

By measuring the fluorescence quantum yield of A-RC-A upon UV ( $\Phi_{\rm f}^{\rm UV} = 0.29$ ) and visible ( $\Phi_{\rm f}^{\rm vis} = 0.33$ ) excitation in THF (Table S4<sup>†</sup>) and assuming an unchanged radiative decay rate constant  $(k_r)$  upon different excitation, the ISC time constant upon visible excitation was estimated to be  $\sim$ 5.75 ns (ESI,† Section S4), which is accordingly unobservable in the fs-TA with time window of 3.8 ns. We also measured the fluorescence lifetime of A-RC-A upon UV  $(\tau_{S_1}^{UV})$  and visible  $(\tau_{S_1}^{vis})$ excitation, which leads to an unchanged lifetime of ~1.6 ns (Fig. S11-S13<sup>†</sup>). However, quantitative estimation of the S<sub>1</sub> state decay (ESI,† Section S4) indicated that  $\tau_{S_1}^{vis}$  can be only <0.2 ns slower than  $\tau_{s}$ .<sup>UV</sup>, which can be easily concealed by different temporal profiles of excitation sources in the UV and visible regimes. Therefore, we believe an ultraslow ISC that is beyond our fs-TA time window leads to the absence of triplet ESA in the fs-TA of A-RC-A upon visible excitation, which corresponds to an inaccessible barrier for ISC. In the next section, we further analyze the ISC energetic diagram of D-RC-A and A-RC-A in the framework of Marcus theory to understand the fundamental mechanism that leads to the different ISC dynamics of D-RC-A and A-RC-A.

#### Marcus analysis of the ISC dynamics

As discussed above, upon identical excitation conditions, D-RC-A exhibited much faster ISC than A-RC-A, which is consistent with the reported lower  $\Phi_{\rm f}$  and shorter  $\tau_{\rm S_1}$  of D-RC-A compared to A-RC-A.<sup>31</sup> For systems with weak SOC, *i.e.*,  $\langle {\rm S}_m | \hat{H}_{\rm SO} | {\rm T}_n \rangle \ll E_{\rm a}$ , ISC can be simplified as a transition between non-adiabatic states and described by semi-classical Marcus theory.<sup>64-66</sup> As the basis for our Marcus analysis, adiabatic excitation energies of the  $S_1$  and  $T_2$  states were calculated with TD-DFT for both D-RC-A and A-RC-A, while the corresponding  $T_1$  states were calculated using unrestricted DFT (UDFT). UDFT has been reported to be reliable for calculating  $T_1$  states of organic and organometallic complexes, but is inherently not able to treat higher lying triplet states.<sup>67-69</sup>

Here, we first analyze the  $S_1 \rightarrow T_1$  channel that is regarded as the dominant ISC channel in common organic systems,<sup>70,71</sup> for which the adiabatic excitation energies of the S<sub>1</sub> and T<sub>1</sub> states are required. The ISC barrier of the  $S_1 \rightarrow T_1$  channel  $(E_a^{S_1 \rightarrow T_1})$ was estimated by a reorganization energy  $(\Gamma^{S_1 \to T_1})$  and corresponding adiabatic energy gap  $(\Delta E_{ST}^{S_1 \rightarrow T_1})$  within the framework of Marcus theory. As listed in Table 1,  $\Delta E_{ST}^{S_1 \rightarrow T_1}$  of RCPDs are comparable (0.829 eV for D-RC-A and 0.858 eV for A-RC-A) whereas D-RC-A features a higher  $\Gamma^{S_1 \rightarrow T_1}$  (0.115 eV) than A-RC-A (0.062 eV), leading to  $E_a^{S_1 \rightarrow T_1}$  for D-RC-A (1.103 eV) and A-RC-A (2.574 eV), which are comparable with the adiabatic energies of the corresponding T<sub>1</sub> states. Meanwhile, the SOC matrix elements  $\langle S_1 | \hat{H}_{SO} | T_1 \rangle$  of D-RC-A and A-RC-A were calculated to be 4.045 cm<sup>-1</sup> and 0.425 cm<sup>-1</sup>, respectively. The large ISC barrier (>1 eV) leads to virtually forbidden transitions of the  $S_1 \rightarrow T_1$  channel of D-RC-A and A-RC-A.

Table 1 Summary of the calculated and experimentally measured photophysical parameters associated with plausible ISC channels of D-RC-A and A-RC-A

	D-RC-A	A-RC-A
$S_1$ excitation energy <sup><i>a</i></sup> /eV	1.952	1.939
$T_1$ excitation energy <sup>b</sup> /eV	1.123	1.081
$T_2$ excitation energy <sup><i>a</i></sup> /eV	2.022	2.213
RMSD <sup>S<sub>1</sub>/S<sub>0</sub></sup> /Å	0.156	0.207
$RMSD^{S_1/T_1}/Å$	0.377	0.302
$RMSD^{S_1/T_2}/Å$	0.853	0.325
$\Gamma^{S_1 \rightarrow S_0}/eV$	0.188	0.241
$\Gamma^{S_1 \rightarrow T_1}/eV$	0.115	0.062
$\Gamma^{T_2 \rightarrow S_1}/eV$	0.558	0.257
$^{c}\Delta E_{\rm ST}^{\rm S_{1} \rightarrow T_{1}}/\rm eV$	0.829	0.858
$^{c}\Delta E_{\rm ST}^{\rm S_{1}\rightarrow T_{2}}/\rm eV$	-0.070	-0.274
$^{c}\Delta E_{\rm TS}^{\rm T_{2} \rightarrow S_{1}}/eV$	0.070	0.274
$\langle S_1   \hat{H}_{SO}   T_1 \rangle / cm^{-1}$	4.045	0.425
$\langle S_1   \hat{H}_{SO}   T_2 \rangle / cm^{-1}$	4.481	8.697
${}^{d}E_{a}^{S_{1} \rightarrow T_{1}}/eV$	1.103	2.574
${}^{d}E_{a}^{T_{2} \rightarrow S_{1}}/eV$	0.106	< 0.001
$e_{E_a}^{S_1 \rightarrow T_2}/eV$	0.177	0.274
$E_a^{S_1 \rightarrow T_1}/E_a^{S_1 \rightarrow T_2}$	6.325	9.387
$k_{\rm ISC}^{\rm S_1 \rightarrow T_2}$ (cal. DA)/ $k_{\rm ISC}^{\rm S_1 \rightarrow T_2}$ (cal. AA)	7.774	
$k_{\rm ISC}$ (exp.)/ps <sup>-1</sup>	1/350	1/3900
$k_{\rm ISC}$ (exp. DA)/ $k_{\rm ISC}$ (exp. AA)	11.143	

<sup>*a*</sup> Adiabatic excitation energy calculated by TD-DFT. <sup>*b*</sup> Adiabatic excitation energy calculated by UDFT. <sup>*c*</sup> Calculated by adiabatic energies of optimized geometries of corresponding electronic states, the adiabatic energy gap of an exothermic process was defined to be positive. <sup>*d*</sup> Estimated by reorganization energy and adiabatic energy gap of the corresponding transition by Marcus theory. <sup>*e*</sup> Calculated by  $E_a^{S_1 \rightarrow T_2} = E_a^{T_2 \rightarrow S_1} + \Delta E_{TS}^{T_2 \rightarrow S_1}$ .



Fig. 5 (a) Simplified energetic diagram for calculating the ISC barrier of the  $S_1 \rightarrow T_2$  transition in the framework of Marcus theory, and energy diagrams for plausible ISC channels of D-RC-A (b) and A-RC-A (c), in which both  $T_1$  and  $T_2$  states are considered.

Regarding the  $S_1 \rightarrow T_2$  channel, the calculated adiabatic energies of the S<sub>1</sub> and T<sub>2</sub> states indicate its endothermic nature with a negative  $\Delta E_{\rm ST}^{S_1 \rightarrow T_2}$  for both D-RC-A (-0.070 eV) and A-RC-A (–0.274 eV). Nevertheless, the  $S_1 \rightarrow T_2$  transition of RCPDs can still be accessible through a thermally activated mechanism as long as  $E_a^{S_1 \rightarrow T_2}$  is small enough (normally <0.2 eV), which has been observed via temperature-dependent experiments for RCPDs.<sup>28</sup> To estimate  $E_a^{S_1 \rightarrow T_2}$ , as illustrated in Fig. 5a, we calculated the reorganization energy  $(\Gamma^{T_2 \rightarrow S_1})$  and adiabatic energy gap  $(\Delta E_{TS}^{T_2 \rightarrow S_1})$  of its reverse transition  $T_2 \rightarrow S_1$ . As an exothermic process,  $E_a^{T_2 \rightarrow S_1}$  can be estimated by Marcus theory, leading to  $E_a^{T_2 \rightarrow S_1} = 0.106$  eV and <0.001 eV for D-RC-A and A-RC-A, respectively. Thus,  $E_a^{S_1 \rightarrow T_2}$  can be approximated by the sum of  $E_a^{T_2 \rightarrow S_1}$  and the adiabatic energy gap ( $\Delta E_{TS}^{T_2 \rightarrow S_1}$ ), *i.e.*, 0.177 eV and 0.274 eV for D-RC-A (Fig. 5b) and A-RC-A (Fig. 5c), respectively.

With the calculated ISC barriers and SOC matrix elements of plausible ISC channels, we can discuss the ISC dynamics of D-RC-A (Fig. 5b) and A-RC-A (Fig. 5c) in detail. For both D-RC-A and A-RC-A,  $E_a^{S_1 \rightarrow T_1}$  is substantially higher than  $E_a^{S_1 \rightarrow T_2}$  $(E_a^{S_1 \to T_1}/E_a^{S_1 \to T_2} = 6.325$  for D-RC-A and 9.387 for A-RC-A), leading to  $S_1 \rightarrow T_2$  as the dominant ISC channel of both D-RC-A and A-RC-A. Although  $S_1 \rightarrow T_2$  ISC is an endothermic process, the thermally accessible barriers ( $\sim$ 0.2 eV) lead to ISC dynamics at room temperature, which is consistent with our previously observed temperature-dependence.28 Furthermore,  $k_{\rm ISC}^{\rm S_1 
ightarrow {\rm T}_2}$  of D-RC-A were calculated to be  $\sim$ 7.7 times faster than  $k_{\rm ISC}^{\rm S_1 
ightarrow T_2}$  of A-RC-A, which is perfectly consistent with the  $\sim 11$ times faster ISC observed experimentally by fs-TA. The relatively fast ISC of D-RC-A also explains the lower  $\Phi_{\rm f}$  of D-RC-A than A-RC-A due to competition between radiative and non-radiative (including ISC) decay of the S1 state. Meanwhile, the calculated ISC barrier  $(E_a^{S_1 \rightarrow T_2})$  of D-RC-A and A-RC-A also explains the  $\lambda_{ex}$ -dependent fs-TA data of A-RC-A. For D-RC-A, the thermally accessible  $S_1 \rightarrow T_2$  channel at room temperature ( $E_a^{S_1 \rightarrow T_2}$ = 0.177 eV) leads to the observed  $\lambda_{ex}$ -independent ISC signature in the TA-data. However,  $E_a^{S_1 \rightarrow T_2}$  of A-RC-A (0.274 eV) is ~0.1 eV higher than that for the ISC channel of D-RC-A, leading to a hindered ISC  $(S_1 \rightarrow T_2)$  via a thermally activated mechanism. As discussed above, triplet ESA was consequently unobservable in the fs-TA of A-RC-A upon visible excitation due to its slow formation ( $\sim$ 5.8 ns). However, upon UV excitation, initial IC (S<sub>m</sub>  $\rightarrow$  S<sub>1</sub>) decay may lead to more population being distributed in higher vibrational levels of the S<sub>1</sub> state, leading to faster ISC that can be observed in the fs-TA data. Note that values of all ISC barriers listed in Table 1 were estimated by Marcus theory based on the TD-DFT-calculated energies of S<sub>1</sub> and T<sub>2</sub> states, and unrestricted DFT (UDFT)-calculated T<sub>1</sub> state, which can have errors up to 0.3 eV. Thus, the S<sub>1</sub>  $\rightarrow$  T<sub>2</sub> ISC barrier ( $E_a^{S_1 \rightarrow T_2}$ ) can possibly be different between D-RC-A and A-RC-A, leading to different observations in the  $\lambda_{ex}$ -dependent fs-TA data.

Last but not least, note that although the  $T_2$  state is heavily involved in the ISC dynamics of D-RC-A and A-RC-A, we believe that the observed triplet signal at  $\lambda_{pr} = 570-580$  nm in the fs-TA data must be assigned to the  $T_1$  rather than the  $T_2$  state. Spinallowed  $T_2 \rightarrow T_1$  transitions with  $\sim 1$  eV energy gaps are expected to be much faster than the corresponding  $S_1 \rightarrow T_2$  transitions, leading to limited accumulation of  $T_2$  species. Thus, the observed ESA bands should be assigned to the  $T_1$  states formed through rapid decay from the  $T_2$  state. Similarly, the ISC populated  $T_2$  states are energetically higher than the corresponding  $S_1$ states of D-RC-A and A-RC-A, leading to potential exothermic reverse ISC (RISC,  $T_2 \rightarrow S_1$ ). However, such an RISC process cannot be the dominant decay channel of the  $T_2$  state due to competition of spin-allowed internal conversion ( $T_2 \rightarrow T_1$ ).

#### Singlet oxygen sensitization

Having the above fs-TA and theoretical data in hand, we then examined the ability of photoexcited A-RC-A to sensitize singlet molecular oxygen,  $O_2(a^1\Delta_g)$ , and the associated kinetics for two reasons: (1) this would likely provide additional information on the formation of triplet states upon light irradiation, and (2) a compound which is both fluorescent and can generate  $O_2(a^1\Delta_g)$  from its triplet state could be potentially useful for

**Table 2**  $O_2(a^1\Delta_q)$  quantum yields,  $\Phi_{\Delta}$ , for A-RC-A<sup>*a*</sup>

Gas	$\Phi_{\Delta}$
2% O <sub>2</sub>	0.10
$21\% O_2$	0.18
40% O <sub>2</sub>	0.23
70% O <sub>2</sub>	0.32
100% O <sub>2</sub>	0.34

 $^a$  Errors on  $\Phi_\Delta$  are  $\pm$  10%. Data for the pertinent experiments are shown in Fig. 6.



**Fig. 6** (a) Integrated intensity of the  $O_2(a^1\Delta_g)$  phosphorescence signal upon irradiation at 417 nm, normalized by the sensitizer absorbance and the  $O_2(a^1\Delta_g)$  lifetime, plotted as a function of laser power and collected over a range of  $O_2$  concentrations for both A-RC-A and for the reference standard, phenalenone (PN), in toluene-d<sub>8</sub>. The  $O_2$  concentration is represented as the percent of  $O_2$  in the  $O_2/N_2$  gas mixture bubbled through the solution. The slopes of the linear fits are proportional to the  $O_2(a^1\Delta_g)$  quantum yield. Representative time-resolved  $O_2(a^1\Delta_g)$  phosphorescence traces used to obtain the A-RC-A data are shown in (b and c). (b) The data from 100 µs to 2000 µs were fitted by a single exponential decay function (solid lines) to obtain the lifetime of  $O_2(a^1\Delta_g)$  (i.e.,  $1/k_{\Delta}$ ). (c) Using  $k_{\Delta}$  as a fixed parameter, eqn (5) was used as a fitting function (solid lines) to obtain where  $O_2(a^1\Delta_g)$  was formed in the photosensitized reaction. (d) Plot of  $k_T$ , obtained from the fits shown in (c) for the A-RC-A data, against the concentration of dissolved oxygen. The slope,  $(1.3 \pm 0.1) \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>, is the bimolecular rate constant for oxygen quenching of the  $O_2(a^1\Delta_g)$  precursor. The intercept yields a value of ~9 µs for the lifetime of this  $O_2(a^1\Delta_g)$  precursor in the absence of oxygen. Both of these numbers are consistent with expectation for oxygen quenching of a triplet state.<sup>74,82</sup>

both bio-imaging and photodynamic therapy.<sup>72,73</sup> Moreover, using the fluorescence, one has the advantage of being able to insure that the sensitizing compound was localized at the desired location in a heterogeneous biological system.<sup>74</sup> We note that in our previous studies,<sup>28,30</sup> we found that several related complexes are capable of simultaneous fluorescence and O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) sensitization, with reasonable quantum yields for both processes, often summing to *ca.* 1.

Quantum yields of  $O_2(a^1\Delta_g)$  production,  $\Phi_{\Delta}$ , were obtained by monitoring the intensity of the 1275 nm  $O_2(a^1\Delta_g) \rightarrow O_2(X^3\Sigma_g^-)$ phosphorescence in time-resolved experiments, as described previously.<sup>75,76</sup> Experiments were performed upon irradiation of A-RC-A at 417 nm. The integrated intensity of the time-resolved  $O_2(a^1\Delta_g)$  phosphorescence signal, measured as a function of incident laser power, was normalized by the sensitizer absorbance and the  $O_2(a^1\Delta_g)$  lifetime. Although a bleaching experiment indicates that A-RC-A can react with  $O_2(a^1\Delta_g)$  (Fig. S14†), all data were recorded under conditions where A-RC-A bleaching was negligible.

We first performed experiments in toluene-h<sub>8</sub>, using a solution that had been bubbled with a gas stream containing 2% oxygen and 98% N<sub>2</sub> (the reasons for using low concentrations of oxygen will become apparent below when discussing the kinetics of the time-resolved  $O_2(a^1\Delta_g)$  phosphorescence signal). In this case, we performed one set of experiments using 1*H*-phenalenone (PN) in benzene as the reference  $O_2(a^1\Delta_g)$ 

photosensitizer ( $\Phi_{\Delta} = 0.92 \pm 0.03$ ),<sup>77,78</sup> and another using *m*tetraphenylporphyrin (TPP) in benzene as the reference photosensitizer ( $\Phi_{\Delta} = 0.66 \pm 0.08$ ).<sup>79</sup> The results yield a value of  $\Phi_{\Delta}$  for A-RC-A of 0.09  $\pm$  0.01. The pertinent data are shown in Fig. S15 and S16.<sup>†</sup>

Singlet oxygen phosphorescence data recorded upon irradiation of A-RC-A show an increase in the value of  $\Phi_{\Delta}$  with increasing oxygen concentration (Table 2). In contrast, corresponding data from the PN-sensitized production of  $O_2(a^1\Delta_g)$ do not show an increase in  $\Phi_{\Delta}$  with an increase in the oxygen concentration (Fig. 6a). These data indicate that, in the PN experiment, the lifetime of the  $O_2(a^1\Delta_g)$  precursor (*i.e.*, the PN triplet state) is sufficiently long that the entire <sup>3</sup>PN population is effectively quenched at a low oxygen concentration, which is consistent with expectation. For the A-RC-A experiment, the data indicate that the  $O_2(a^1\Delta_g)$  precursor, presumably the A-RC-A triplet state, is sufficiently short-lived that higher oxygen concentrations are needed to quench a larger fraction of the <sup>3</sup>A-RC-A population.

Given that the lifetime of the S<sub>1</sub> state of A-RC-A in oxygen-free toluene is 1.7 ns, the S<sub>1</sub> state is so short-lived that it cannot be quenched by oxygen, even in an oxygen-saturated solution at atmospheric pressure. This can be confirmed in a calculation where one accepts that the quenching will occur at the diffusion controlled limit (*i.e.*,  $k_{diff} = 3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ). As such, we infer that the O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) precursor will be the A-RC-A triplet state (*vide* 

*infra*). We then chose to obtain information about the kinetics of the  $O_2(a^1\Delta_g)$  precursor, again presumably the A-RC-A triplet state, using our time-resolved  $O_2(a^1\Delta_g)$  phosphorescence data, as described below.

For the triplet-state-photosensitized production of  $O_2(a^1\Delta_g)$ in homogeneous solutions, the intensity, I(t), of the timeresolved 1275 nm  $O_2(a^1\Delta_g) \rightarrow O_2(X^3\Sigma_g^-)$  phosphorescence signal is generally modeled using a fitting function based on eqn (5)<sup>74,75,81</sup>

$$I(t) = \frac{I_{\text{tot}}}{k_{\Delta} - k_{\text{T}}} \left[ e^{-k_{\text{T}}t} - e^{-k_{\Delta}t} \right].$$
(5)

In eqn (5),  $I_{tot}$  is proportional to the total integrated intensity of  $O_2(a^1\Delta_g)$  phosphorescence,  $k_T$  is the decay rate constant for the  $O_2(a^1\Delta_{\alpha})$  precursor (*i.e.*, the reciprocal lifetime of the sensitizer triplet state) and  $k_{\Delta}$  the rate constant for  $O_2(a^1\Delta_{\alpha})$  decay (*i.e.*, the reciprocal  $O_2(a^1\Delta_{\alpha})$  lifetime). By performing the  $O_2(a^1\Delta_{\alpha})$  phosphorescence experiment in toluene- $d_8$  as opposed to toluene- $h_8$ , we take advantage of the large H/D solvent isotope effect on the  $O_2(a^1\Delta_{\alpha})$  lifetime.<sup>74</sup> In this way, we can independently characterize  $k_{\Delta}$  in a time domain where  $k_{\rm T}$  does not appreciably influence the signal (Fig. 6b). Using this value of  $k_{\Delta}$  as a fixed parameter, we can then re-fit the  $O_2(a^1\Delta_{\sigma})$  phosphorescence data in the time domains where  $k_{\rm T}$  influences the signal (Fig. 6c). We applied this procedure for experiments performed using a series of comparatively low oxygen concentrations to assess more accurately the decay rate constant of the  $O_2(a^1\Delta_{\alpha})$ precursor.

In Fig. 6d, we plot the values of  $k_{\rm T}$  thus obtained for A-RC-A against the oxygen concentration to yield the bimolecular rate constant for oxygen quenching of the  $O_2(a^1\Delta_g)$  precursor. We determined oxygen concentrations using the mole fraction of oxygen in the bubbling gas (controlled by  $O_2$  and  $N_2$  flow meters) and Henry's Law constants published by Battino, *et al.*<sup>82</sup> The value obtained for this quenching rate constant is  $(1.3 \pm 0.1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . As an independent control for this study on A-RC-A, we performed the same experiment using PN as the  $O_2(a^1\Delta_g)$  sensitizer (Fig. S17†), and the results obtained provide credence for our results on A-RC-A. Specifically, our data for the quenching of <sup>3</sup>PN by oxygen yield a rate constant of  $(2.2 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , which is consistent with published data.<sup>78</sup>

The data obtained from Fig. 6d are consistent with the following assignment: the  $O_2(a^1\Delta_g)$  precursor upon irradiation of A-RC-A is a triplet state whose lifetime in the absence of oxygen is ~9 µs.

From Fig. 6b, the values of the  $O_2(a^1\Delta_g)$  lifetime obtained (*i.e.*,  $k_{\Delta}^{-1} = 296 \pm 3 \ \mu$ s) are shorter than what is expected for the solvent-mediated deactivation of  $O_2(a^1\Delta_g)$  in toluene-d<sub>8</sub>. For the latter, we independently recorded a value of  $326 \pm 3 \ \mu$ s using PN as the sensitizer with the same batch of toluene-d<sub>8</sub> used for the A-RC-A experiments. Using eqn (6), and with the A-RC-A concentration of  $1.7 \times 10^{-5}$  M used in our experiments, we obtain a rate constant of ~1.8  $\times 10^7$  M<sup>-1</sup> s<sup>-1</sup> for the deactivation/removal of  $O_2(a^1\Delta_g)$  by A-RC-A. Given the magnitude of this rate constant, it is likely that the mechanism for A-RC-A-mediated deactivation of  $O_2(a^1\Delta_g)$  involves some charge transfer from A-RC-A to  $O_2(a^1\Delta_g)^{.74,80}$  Moreover, based on an A-

RC-A bleaching experiment (Fig. S14<sup>†</sup>), a small component of this rate constant reflects a chemical reaction between A-RC-A and  $O_2(a^1\Delta_g)$ .

$$k_{\Delta}^{\text{obs.with A-RC-A}} = k_{\Delta}^{\text{obs.without A-RC-A}} + k_{q}[\text{A-RC-A}]$$
(6)

We also considered the interesting possibility that the  $O_2(a^1\Delta_g)$  precursor might possibly be the  $T_2$  state. However, our data indicate that the  $O_2(a^1\Delta_g)$  precursor upon irradiation of A-RC-A has quite a long lifetime (~9 µs obtained from the intercept of the plot in Fig. 6d) and, as such, it must be the  $T_1$  state, as spin-allowed internal conversion from  $T_2$  to  $T_1$  is expected to be quite rapid (*vide supra*).

### Conclusions

We investigated the ultrafast photophysics and intersystem crossing (ISC) dynamics of two para-substituted 2,5-bis(phenylethynyl) RCPDs (D-RC-A and A-RC-A) using excitationwavelength-dependent fs-TA measurements and TD-DFT calculations. The electronic relaxation channels of the S1 state were revealed in detail, including charge transfer, conformational relaxation, vibrational dephasing, and ISC. By calculating the thermodynamic barrier and spin-orbit coupling, plausible ISC channels were revealed using semi-classical Marcus theory, *i.e.*, ISC is dominated by the thermally activated  $S_1 \rightarrow T_2$ channel. With weak metal-ligand interactions, the plausible ISC channels of RCPDs are largely affected by ISC barriers. Studies of the sensitization of  $O_2(a^1\Delta_{\alpha})$  by A-RC-A give quantum yields  $\Phi_{\Delta}$  of up to ~0.3 at high oxygen concentrations, consistent with the rate of ISC being competitive with that of fluorescence. The relatively long lifetime of the triplet state responsible for sensitization of  $O_2(a^1\Delta_g)$  of ~9 µs indicates that it must be T<sub>1</sub>, being formed rapidly from T<sub>2</sub>. Our work, especially the paradigm on ISC dynamics, might provide useful insight into the behavior of other fluorescent emitters.

### Data availability

The data supporting this article have been included as part of the ESI.†

### Author contributions

Zilong Guo: conceptualization, methodology, investigation, data curation, formal analysis, visualization and writing original draft; Yaxin Wang: data curation, formal analysis and validation; Julia Heitmüller: data curation and formal analysis; Carolin Sieck: investigation and data curation; Andreas Prüfer: investigation and data curation; Philipp Ralle: investigation and data curation; Andreas Steffen: conceptualization, methodology, investigation, writing – review and editing; Petr Henke: methodology, data curation, formal analysis and validation; Peter R. Ogilby: methodology, supervision, and writing – review and editing; Todd B. Marder: conceptualization, formal analysis, funding acquisition, supervision, and writing – review and editing; Xiaonan Ma: conceptualization, formal analysis, funding acquisition, supervision, and writing – review and editing; Tobias Brixner: conceptualization, formal analysis, funding acquisition, supervision, and writing – review and editing.

## Conflicts of interest

There are no conflicts to declare.

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