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A water-soluble, bay-functionalized perylenediimide derivative – correlating aggregation and excited state dynamics†

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The aggregation and the photophysics of a water soluble perylenediimide (PDI) derivative that features two bromine substituents in the bay positions has been probed. Non-fluorescent aggregates were found to be present at concentrations of 1.0×10^{-5} M. *In situ* small-angle X-ray scattering (SAXS) measurements and complementary molecular modeling showed the presence of PDI aggregates. In their singlet excited states, the PDI aggregates are characterized by distinct transient fingerprints and rapid deactivation, as revealed by pump–probe experiments on the femto-, pico-, nano-, and microsecond timescales. The product of this deactivation is a PDI triplet excited state. The efficiency of the triplet formation depends on the concentration, and hence on the degree of aggregation. Notably, for PDI concentrations in the range of the critical micelle concentration, the efficiency of intersystem crossing is close to zero. In short, we have demonstrated, for the first time, aggregation-induced formation of triplet excited states for PDI derivatives.

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Introduction

Ordering and/or self-assembly of organic building blocks on the molecular scale is of utmost importance for their use in advanced molecular technologies.^{1–3} Being able to control the structure–property relationships is essential for creating self-structured, multifunctional materials.^{4,5} For stacks and other aggregate structures, early work showed that the electronic structure of both ground and the excited states is largely governed by the mutual orientation of the individual building blocks and their dipole moments.^{6–9} The impact of the aggregate structure, both on key electronic parameters such as the

fluorescence quantum yield and Stokes shift, and on the nature and lifetime of photoexcited states is most notable.^{10,11} Rylenes and their derivatives are versatile model systems that allow us to proceed far beyond just establishing the mentioned structure–property relationships.^{12,13} Perylene diimide derivatives (PDI) stand out among this class of molecules, both in terms of their photophysics and their aggregation properties.^{5,14,15} In the case of PDIs, covalent model systems have helped to shed light on the influence of geometric parameters, such as center-to-center distances or slip-stacked arrangements, and on the excited state processes that lead to changes in the photophysics, including charge transfer, charge separation, and excimer formation.^{16–20}

The fate of PDIs in their excited states is dominated by singlet excited states with fluorescence quantum yields close to unity.^{21,22} As a result, the quantum yields of intersystem crossing (ISC) processes are poor and PDI-centered triplet excited states are only accessible through sensitization, the presence of heavy metal ions,^{23–26} charge recombination,^{27,28} or singlet fission.^{29,30} In a recent study, Würthner and coworkers showed that the population of triplet excited states depends on solvent polarity because they arise as photoproducts of charge transfer and/or charge separation.³¹ Comprehensive transient-absorption studies examining the influence of aggregation on the occurrence of triplet excited states are rare.^{32,33}

We have now investigated the formation of aggregates of a brominated water soluble PDI derivative (1). Water is known to

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be the optimal medium for inducing aggregation.^{15,34} We focus on how bay substitution with halogens affects the ISC yield through potential heavy atom effects and/or a twist in the perylene core.

Results and discussion

The synthesis of PDI derivative **1** has been described previously.^{30,31,36} We first performed concentration-dependent assays of **1** by steady-state spectroscopies over a broad concentration range (from 7.3×10^{-7} to 5×10^{-4} M). Normalized absorption spectra of **1** in this concentration regime are shown in Fig. 1 and the corresponding extinction spectra are given in the ESI (Fig. S1†).

Three prominent maxima at 395, 498, and 532 nm dominate the visible region of the absorption spectrum of **1**. An additional maximum arises in the ultraviolet region and is assigned to excitation into higher-lying singlet excited states (Fig. S1†). We conclude a strong concentration dependence from the changes in Fig. 1. At concentrations of 1×10^{-5} M and lower, the bathochromic maximum is more intense than the hypsochromic maximum, whereas the reverse is the case at concentrations higher than 1×10^{-5} M (Fig. S2†). An additional red shift, from 532 to 537 nm, and an overall broadening of the absorption features accompanies these changes. From the changes in the absorption spectra, we deduce significant changes in the intermolecular PDI interactions, from monomers to aggregates. We consider the 500 nm absorption maximum in the high concentration regime to be evidence for the presence of H-type aggregates. In contrast, the low concentration regime is governed by monomers of **1**.^{14,15,35,37}

Small angle X-ray scattering (SAXS) measurements confirmed the formation of aggregates at 1.2×10^{-4} M. As seen in Fig. 2, the scattering pattern is dominated by a low- q contribution with a slope of q^{-3} . This is characteristic of macroscopic aggregation.^{38,43} We deduce a minimum aggregate size of $D_{\max} > \pi/q_{\min} \approx 26$ nm from the experimental low-angle resolution limit.³⁹

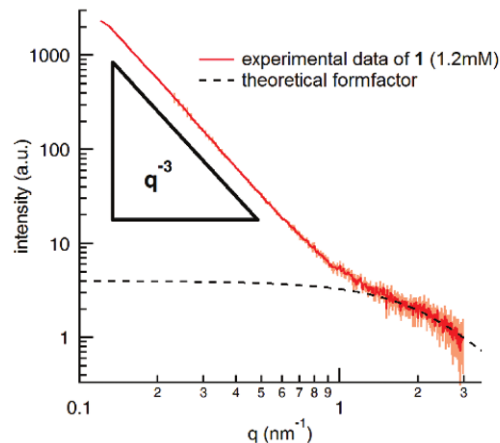


Fig. 2 SAXS data of **1** at 1.2×10^{-4} M. The low- q intensity increase compared to the form factor scattering of a single molecule is characteristic for aggregation.

Molecular-dynamics (MD) simulations and density-functional theory (DFT) calculations were carried out in order to obtain intermolecular details not available from the SAXS measurements. Initial force-field optimizations in the gas phase showed the arrangement in one dimensional (1D) helical stacks to be the lowest in energy for **1**. These initial results formed the basis for DFT (PBE0⁴⁶/cc-pVDZ⁴⁷) geometry optimizations used sequentially to build up aggregates of **1** up to the pentamer in simulated aqueous solutions using the polarizable continuum model.⁴⁸ The results are shown in Fig. 3 and the ESI (Fig. S3–S6†). The MD simulations used a 20mer and explicit water to demonstrate the stability of large aggregates in aqueous solution and to investigate their dynamics, as shown in Fig. S7 and S8 of the ESI.† Time dependent DFT (TD-DFT)⁴⁹ and AM1⁵⁰ semiempirical configuration interaction singles (CIS) were used to study the absorption characteristics of optimized and MD geometries.

The DFT calculations show the aggregates to consist of parallel shifted ($\theta \approx 90^\circ$) monomers along the z -axis with an inter-plane distance of 3.8 Å and twisted by $\phi = 28^\circ$. The dimerization energy was calculated in different solvent environments. The results and the exact designation of all angles are given in Fig. 3. In water, the aggregate formation is exothermic by 35 kcal mol⁻¹ per dimer interaction, resulting from the stabilization of the cationic charges by the polar environment and the hydrophobicity of the PDI core. In solvents of lower polarity (see caption of Fig. 3), Coulombic repulsion between dicationic monomers prevails over the van der Waals interaction (Fig. S9†). A further proof for the stability of the predicted helical aggregate is given by the MD simulation. Although the movement of the flexible ethyl ammonium groups around β and δ induce changes in the aggregate geometry, the linear helical shape (Fig. S7 and S8†) with a PDI to PDI twist angle ϕ of 25° is preferred. Generally, geometric parameters of the MD-derived structures are in good agreement

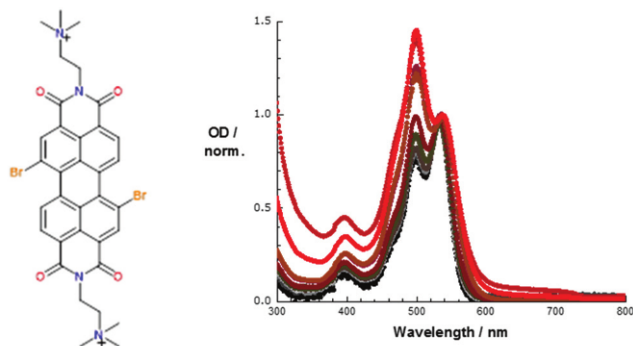


Fig. 1 Left: Molecular structure of PDI **1**. The chloride counterion is not shown. Right: Absorption spectra of **1** in water, normalized to the 535–540 nm maximum with different concentrations from 7.3×10^{-7} (grey) to 5.0×10^{-4} M (red).

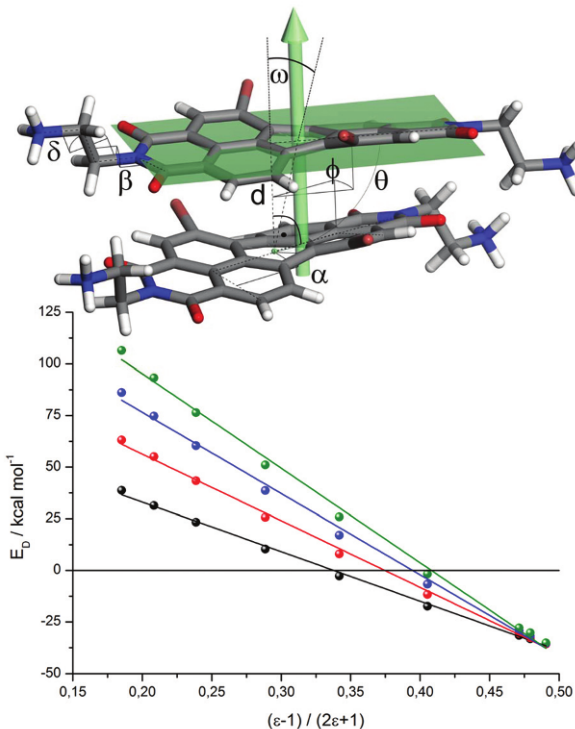


Fig. 3 Top: DFT optimized dimer geometry including the main geometric measurements – the dihedrals α , β , δ , the inter plane distance, angle and torsion (d , θ and ϕ) and the slip angle ω . Bottom: Dimerization energies of the dimer (black), trimer (red), tetramer (blue), and pentamer (green) in dependence of the Kirkwood solvent parameter. Data points from left to right resemble *n*-hexane ($\epsilon = 1.88$), 1-hexene ($\epsilon = 2.07$), toluene ($\epsilon = 2.37$), dibutylether ($\epsilon = 3.04$), diethylether ($\epsilon = 4.24$), THF ($\epsilon = 7.42$), benzonitrile ($\epsilon = 25.562$), acetonitrile ($\epsilon = 35.688$) and water ($\epsilon = 78.35$) solvation.

with the DFT study. Interestingly a group of five PDIs turned by 180° during the MD simulation, stabilizing again in the helical conformation. This indicates both flexibility and stability of the proposed structure in solvation environment. The stability, the slip angle, and the torsion in model aggregates of **1** are consistent with the steady-state spectroscopies. In particular, the slip angle ω of 14° is close to the expected value of 0° for perfect H-type aggregation. This is confirmed by vertical excitation energies calculated with TD-DFT, see Fig. S10.† The predicted vertical excitation energies for monomeric **1** are 2.31 eV (S_1) and 3.18 eV (S_2), in sound agreement with the absorption spectra. Aggregation has several effects. Firstly, the main vertical excitation is shifted to 2.50 eV. Secondly, its oscillator strength is increased significantly. Thirdly, an increase of the aggregation number leads to stabilized triplet excited states, as shown in Fig. S11.† This last result is especially important for the following discussion of the photophysics. The TD-DFT derived tendencies match the AM1 CIS results obtained for snapshots from the 20mer MD simulation. Similar the main vertical transition of the aggregates is hypsochromic shifted with respect to the monomer (Fig. S12 and S13†). Thus, the TDDFT and CIS calculations, spectroscopic data and SAXS

measurements are all consistent with H-type aggregates. The SAXS measurements suggest a length larger than 26 nm.

We also investigated the self-assembly of **1** in the solid state, on samples obtained by drop casting followed by solvent evaporation, using atomic force microscopy (AFM) and transmission electron microscopy (TEM). At a concentration of 1.2×10^{-4} M, agglomerates and aggregates of different sizes are discernable in the AFM images, as shown in Fig. S17.† Statistical analyses give an average diameter of about 30 nm, consistent with the modeling and SAXS studies. Larger amorphous and/or crystalline super-structures with diameters in the micrometer range are also observed. TEM measurements at 5×10^{-4} M reveal agglomerates and aggregates in a similar size range, as shown in Fig. S18.† Interestingly, these nanometer-sized structures are absent at 1×10^{-5} M. This concentration is significantly below the critical micelle concentration of **1**.

Next, **1** was photoexcited throughout the visible range and the corresponding fluorescence was monitored (see the excitation-fluorescence plot in Fig. S19†). The fluorescence, which was registered in the 550–650 nm range, was found to be independent of the excitation wavelength. This suggests the presence of only one fluorescent species. The shape of the excitation spectra, which were, for example, based on the fluorescence at 540, 560, and 650 nm, are in sound agreement with the absorption spectra in the 10^{-6} M range; see Fig. S19.† We hypothesize that only monomers of **1** fluoresce, while the corresponding aggregates do not in this concentration regime. This again is consistent with the H-type character of the aggregates. Probing the fluorescence-concentration dependence in a range similar to the absorption assays, from 7.3×10^{-7} to 1×10^{-4} M, led to subtle changes, as shown in Fig. S20 and S21.† We were careful to minimize inner filter effects by following an established protocol.⁵¹ Nonetheless, minor, but appreciable changes remained. Starting at 10^{-7} M, the fluorescence maximizes at 560 nm and is followed by a shoulder at 600 nm. From there on, a concentration increase of **1** up to 10^{-4} M leads to a blue shift of the maximum to 553 nm and a decrease in intensity relative to the 600 nm feature.

In the normalized and the differential spectra shown in Fig. 4, a sharp increase at 550 nm goes hand in hand with a decrease in the 560–700 nm range. Interestingly, the integrated fluorescence scales nearly linearly with the optical density at the excitation wavelength throughout the entire concentration range after eliminating inner filter effects, as shown in Fig. S21.†

Absorption and fluorescence are also temperature dependent (Fig. S49 and S50†). Heating, for example, a solution of **1** (1×10^{-4} M) from 298 to 360 K intensifies and shifts the bathochromic maximum from 536 to 532 nm. The ratio between optical density of hypsochromic and bathochromic maxima followed a Boltzmann distribution with an inflection point at 318 K. The minimal and maximal ratio extrapolated by this fit are 0.83 and 1.49, respectively, which is well in line with the values derived by concentration dependent measurements (Fig. S2†) at 7.3×10^{-7} and 5×10^{-4} M, respectively.

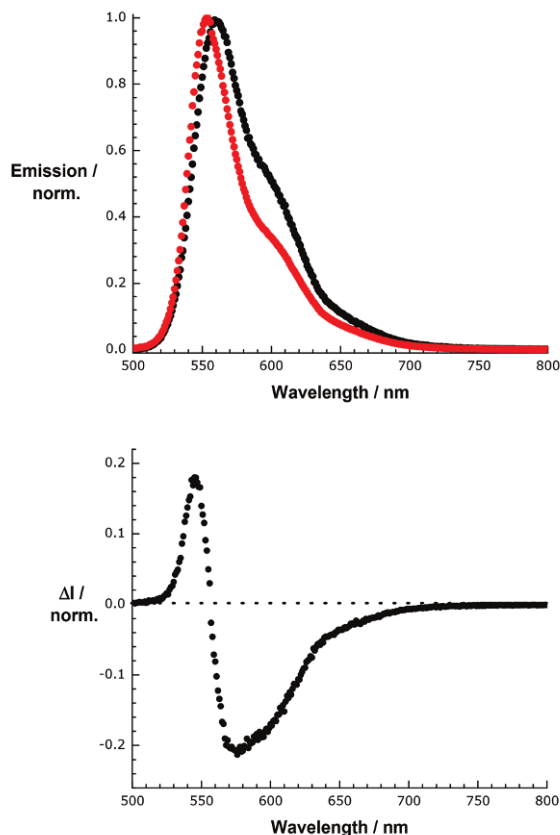


Fig. 4 Top: Normalized fluorescence spectra of **1** obtained upon 480 nm excitation in H₂O with concentrations of 7.3×10^{-7} M (black) and 1.0×10^{-4} M (red). Bottom: Differential fluorescence spectra obtained from the normalized spectra shown above.

Complementary spectroelectrochemical measurements were also performed; the fluorescence of **1** was monitored as a function of external bias. In particular, reductive potentials ranging from 0 to -500 mV were applied throughout several electrochemical cycles, revealing *quasi*-reversible behavior. This is reflected in an alternation of fluorescence attenuation and (re)intensification. Mapping the intensity changes shows that the application of reductive conditions results in an attenuation of the fluorescence, whereas re-oxidation of **1** leads to distinct changes in the fluorescence spectra in the form of an increase in the 550 to 580 nm range, as shown in Fig. 5. Overall, such an increase in fluorescence is consistent with the differential changes discussed in the context of the concentration dependence of the fluorescence, as shown by comparing Fig. 4 and 5. For a more comprehensive interpretation, additional data, such as bias-intensity profiles, *etc.* are shown in Fig. S22.†

Similar observations have been made in photoinduced charge-separation assays.^{27,28,40–42} Based on DFT calculations we can state, that reducing **1** affects the order and the orientation within the aggregates, while still keeping them intact. For that purpose reduced as well as oxidized geometries of the dimer and the trimer were optimized (Fig. S14†). The dimeri-

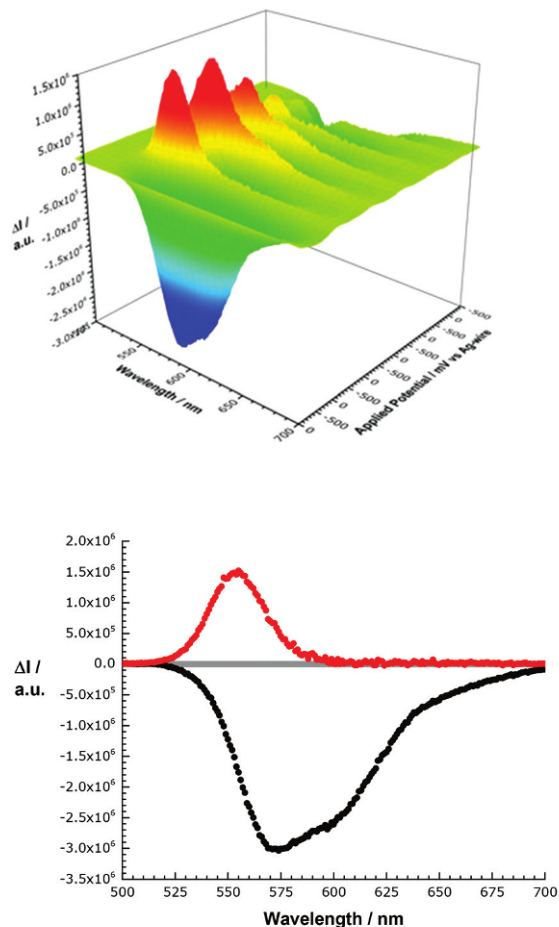


Fig. 5 Top: 3D map of the differential changes in fluorescence of **1** (1.0×10^{-4} M, H₂O, 0.05 M Na₂SO₄) throughout several spectroelectrochemical cycles (0 mV (-500 mV) -0 mV, vs. Ag-wire as quasi reference electrode). Bottom: Differential fluorescence spectra of **1** recorded at 0 mV (grey), -500 mV (black), and 0 mV (red). The spectra are taken from the first electrochemical cycle.

zation energy rises by 6 kcal mol⁻¹ for the reduced dimer, as the Coulomb repulsion is lowered when the charge of the system is decreased. Better stabilization results in higher driving force towards aggregation upon reduction and, in turn, to a lowered concentration of remaining monomer in solution. For the same reason the fully oxidized species is destabilized by 3 kcal mol⁻¹ with respect to the dimer. Interestingly inter plane distance d increase by 0.1 nm during reduction, while the twist angle ϕ and slip angle ω are lowered to 22° and 11°, meaning that the dimer anion features better H-type aggregation characteristic than the dimer. Better H-type geometry, potentially less monomer in solution and the lower oscillator strength of the anion at the excitation wavelength rationalize the decreased in emission intensity.

Oxidation has the opposite effect – reducing d to 3.7 Å and increasing ϕ to 32° and ω by 1°. Overall, a slightly different arrangement in the reformed aggregates is indicated by changes in the shape of the fluorescence. Therefore, we would have expected a transition state along the reaction coordinate

from the re-oxidized anion towards the dimer ground state, but neither DFT, nor semiempirical AM1 calculations gave a barrier. Based on the hypothesis that the reduced PDI core might be stabilized by interaction with the positively charged amines we created different input geometries of the reduced form by rotating around the dihedrals β and δ . Indeed, rotation of two ethyl amine groups results in a local minimum for the reduced species (Fig. S15 and S16†). Interestingly, the barrier for the recovery of initial dimer geometry after reoxidation of 14.5 kcal mol⁻¹ is significantly larger than for the forward process. Experimental attempts to overcome this barrier by heating the sample after reoxidation failed (Fig. S51†). This let us to conclude, that upon reductive conditions at least two possible reorganizations occur: one, which is barrierless, and, which forms a nearly perfect H-type aggregates with a reduced twist angle of 22° and a second one, which constitutes a trapped conformation with an increased twist angle of 40°.

The above results point to monomers of **1** in the low-concentration regime. In the higher-concentration regime, **1** likely exists predominantly as weak fluorescent aggregates.

In the next step, the influence of sodium sulfate (Na₂SO₄) and sodium dodecylbenzenesulfonate (SDBS), on the ordering/self-assembly of **1** was tested. The latter served as a surfactant, whereas the former was used to tune the ionic strength of solutions containing **1**. The addition of solid Na₂SO₄ leads to subtle differences. On the one hand, a hypsochromic change in the relative intensity ratio of the 500 and 535 nm maxima is observed. On the other hand, the fluorescence becomes less intense as the ionic strength of the solution is increased, as shown in Fig. S23.† Both observations imply ionic-strength-dependent aggregation. A somehow different picture evolves when variable weight percentages (wt%) of SDBS are present. In particular, the presence of SDBS induces a strong increase in the 535 nm intensity, which is, in addition, supported by an overall increase in absorptivity. Moreover, the absorption pattern seen in the presence of 0.5 wt% SDBS agrees with the excitation spectrum, as shown in Fig. S24.† These results suggest that the weak-fluorescent aggregates of **1** are converted into their monomers in the presence of the surface-active SDBS. Additional support for this hypothesis came from the fact that the excitation and absorption spectra of **1** in SDBS containing solutions are superimposable.

Our spectroscopic assays conducted in steady-state modes suggest an equilibrium between monomeric **1**, which dominates in the low-concentration regime, and aggregated **1**, which was observed in the high-concentration regime. In the excited state, aggregates of **1** deactivate *via* non-radiative channels. Because the fluorescence of **1** is prone to hypsochromic changes in the higher-concentration regime, the aggregates of **1** have to be, at least weakly fluorescent. This is consistent with the results of spectroelectrochemical cycles in fluorescence mode, as shown by comparing Fig. 4 and 5.

The excited state dynamics of **1** were next investigated by time-resolved pump-probe techniques. Both the pico- to the early nanosecond and the nano- to the microsecond time scale were probed. We once again used 2.5×10^{-5} , 5.0×10^{-5} ,

1.0×10^{-4} , 2.5×10^{-4} , 5.0×10^{-4} and 1.0×10^{-3} M concentrations of **1**. Upon 530 nm laser excitation and with a concentration of, for example, 2.5×10^{-5} M, the immediate formation of minima at 500 and 555 nm was observed. For **1**, the former reflects the depopulation of the ground state, while the latter relates to stimulated emission. In addition, newly developing transient absorption maxima were found at 630 and 725 nm. On the nanosecond timescale, these features transform into new maxima at 520 and 585 nm. At first glance, the excited-state fingerprints do not depend on concentration and the transient absorption spectra under the different concentrations lack any appreciable shifts, see Fig. S25–S30.† A closer look reveals, however, distinct kinetic changes as the concentration is varied. For example, the time-absorption profiles at 630 nm show a rapid and monoexponential decay within 100 ps. In contrast, in the 700–750 nm region, they are best described as a biexponential decay featuring a short-lived component similar to that found at 630 nm, and a long-lived component that exceeds the time resolution of the chosen experimental set-up, see Fig. S31.† Importantly, the relative amplitude of the short-lived component increases with concentration of **1** in the 750 nm time absorption profiles, see Fig. 6, S31, and S32.† The 500 and 750 nm kinetics suggest that the deactivation of singlet excited states in monomeric **1** repopulates the ground state directly and, as such, does not contribute to the triplet quantum yield.

Considering that the 630 nm transient lacks any concentration dependence, a tentative interpretation infers excited-state absorptions of the aggregates formed by **1**, see Fig. 6 and S32.† This excited state deactivates within 100 ps, independent of the concentration, in contrast to the relative changes in the differential absorption. It is more striking that the intensity of the 585 nm feature, which evolves within nanoseconds, displays the same concentration dependence as that at 630 nm. This relationship indicates the fast transformation of the singlet excited causes the 520 and 585 nm features. Recent studies have assigned similar transients to triplet excited states of PDIs.^{23–30}

As triplet excited states of PDIs are generally unobservable,^{23–30} we conclude that other stimuli must be at work in **1**. To this end, we consider a heavy-atom effect stemming from the two bromine substituents, an enhancement of ISC due to non-planarity of the system⁵² or a charge-transfer character in the excited state.

With the help of spectroelectrochemical reduction of **1**, the broad maximum in the 600 to 650 nm range (Fig. 7) is assignable. Overall, it matches the excited-state absorptions of aggregates of **1**. Additional TD-DFT calculations predict the most dominant transitions for the singly reduced dimer to be centered at 562 and 618 nm. The internal reorganization energy for charge separation, as they were derived from the reduced and oxidized geometries between two monomers is 0.21 eV. On the other hand, the reorganization energy within a single dimer is lowered to 0.17 eV. All of the aforementioned let us conclude that charge transfer dictates the excited states in oligomers of **1**.

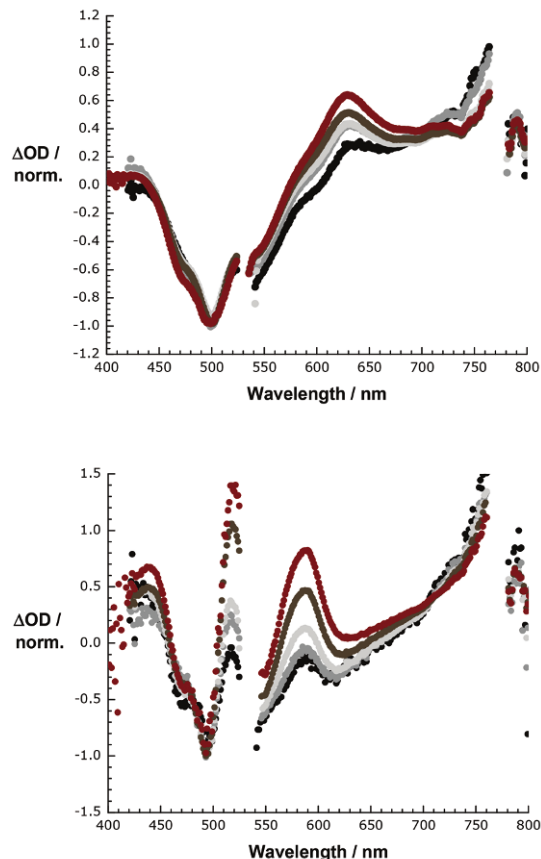


Fig. 6 Top: Differential absorption spectra of **1** in H₂O obtained upon 530 nm laser excitation at a time delay of 3 ps with concentrations of 2.5×10^{-5} (black), 5.0×10^{-5} (dark grey), 1.0×10^{-4} (grey), 2.5×10^{-4} (light brown), and 5.0×10^{-4} M (brown). Spectra are normalized to the 500 nm minimum. Bottom: Differential absorption spectra of **1** in H₂O obtained upon 530 nm laser excitation at a time delay of 3 ns with concentrations of 2.5×10^{-5} (black), 5.0×10^{-5} (dark grey), 1.0×10^{-4} (grey), 2.5×10^{-4} (light brown), and 5.0×10^{-4} M (brown). Spectra are normalized to the 495 nm minimum.

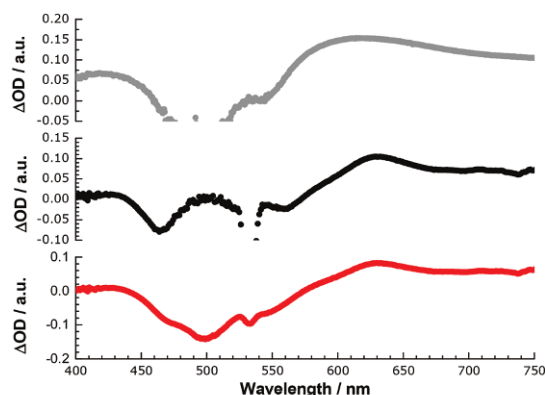


Fig. 7 Comparison of the electrochemically generated reduced form of **1** (H₂O/0.1 M Na₂SO₄/−600 mV vs. Ag-wire) (top) with the transient absorption spectra ($\lambda_{\text{ex}} = 530$ nm) at a 2 ps time delay with concentrations of 1.0×10^{-3} (middle) and 5.0×10^{-4} M (bottom).

For a planar non-brominated PDI absorption measurements support the notion of aggregate formation as the concentration is increased. The red shift of the hypsochromic maxima is, however, with 13 nm more pronounced than what is seen for **1** (Fig. S45[†]). Following 530 nm photoexcitation the transient absorption spectra (Fig. S46 and S47[†]) reveal broad excited state absorptions from 560 nm all the way to 800 nm. In contrast to **1**, the intense charge transfer feature at 630 nm is absent. Similar to **1**, a two exponential fitting function was employed to fit the time absorption profiles at 500 and 700 nm. A 344 ps component relates to the decay of the singlet excited states in the aggregates, while the monomers deactivate within several nanoseconds. Interestingly the singlet excited state lifetime is at least three time larger than what is found for **1**. More striking is, however, the lack of the 585 nm transient, which correlates with the triplet excited states. Instead, the ground state recovery at, for example, 500 nm takes place with the same kinetics parameters as the excited state deactivation. In other words, intersystem crossing is not facilitated. At first glance, ISC is absent as no heavy atom effect is operative in the non-brominated PDI. A closer look reveals that the planarity imposes significant differences in the aggregation behavior. In light of the aforementioned we cannot rule out any of the three contributions to the intersystem crossing in **1**. Considering that the non-brominated PDI lacks any appreciable charge transfer character renders it as the most probable factor to enhance ISC.

Additional transient measurements conducted on the nano- and microsecond time scales helped to document the triplet nature of the excited state through quenching experiments with molecular oxygen. 530 nm laser pulses were chosen to excite **1**. In argon-saturated solutions, the characteristic 520/580 nm features were observed at delay times as short as 20 ns. These are flanked by singlet excited-state fingerprints of monomeric **1**. In the absence of oxygen, the lifetime of the triplet excited state was determined to be 400 ns. Photoexcitation in the presence of oxygen yields the same excited-state fingerprints, but the triplet excited state lifetime was shortened, as shown in Fig. S33.[†]

The concentration dependence on the nano- and microsecond timescale and the effects on the kinetics were also examined for six different concentrations in the range from 2.5×10^{-5} to 1.0×10^{-3} M. All maxima and minima resemble the features on the shorter time scales. For example, the 520/585 nm signatures represent triplet excited states, whereas the 750 nm fingerprint originates from singlet excited-state absorptions.

Resolution of the 630 nm singlet excited-state feature of aggregated **1** is hampered by the instrumental settings, so that 420 nm was used instead. The 420 nm time absorption profiles feature a short-lived, 4 ns singlet excited state and a long-lived (350 ns) triplet excited state (Fig. S34[†]). As the concentration of **1** was increased, contributions stemming from the 300–400 ns component were found to increase. The same trend was noted for the triplet excited-state features (Fig. 8). The transient spectra of the other concentrations are summarized in Fig. S35–S38.[†]

Analyses of the ground-state recovery led to the conclusion that the effective concentration of **1** exerts no meaningful impact on the triplet excited states of **1**. Annihilation of triplets within the aggregates is a likely mechanism, so that increasing the concentration of **1** lacks any notable impact on the ground state recovery (Fig. S39†).

Next, the pico- and nanosecond data were analyzed by global analysis. As a leading example, we focus on a concentration of 5×10^{-4} M to ensure the presence of aggregated **1**. A parallel model was selected and three evolution-associated spectra (EAS) were needed to describe the experimental data (Fig. S40†). Consistent with the above discussion, they are assigned to the singlet excited state deactivation in aggregates and monomers of **1** and to the triplet excited states. Importantly, contributions stemming from the triplet excited state are even significant at timescales as short as 100 ps. Turning to the nanosecond range (Fig. S41†) global analysis corroborates that the triplet excited states are not a product of intersystem crossing in monomeric **1**. The triplet excited state is present both at 1 ns and at 20 ns. Consequently, our analysis provides support for the hypothesis that the formation of triplet excited states is linked predominantly to aggregates of **1**.

In summary, we infer the formation of PDI-centered triplet excited states, but only in weak-fluorescent aggregates of **1**. Here, it is the short-lived nature of their singlet excited states that is decisive. Independent proof for our hypothesis came from addition of SDBS to convert the aggregates of **1** into their monomers at a concentration of 1.0×10^{-4} M. Signs of the monomerization of **1** include enhanced fluorescence, higher extinction coefficients and changes in the relative intensities in the absorption maxima as already demonstrated. Fig. 9 shows the differen-

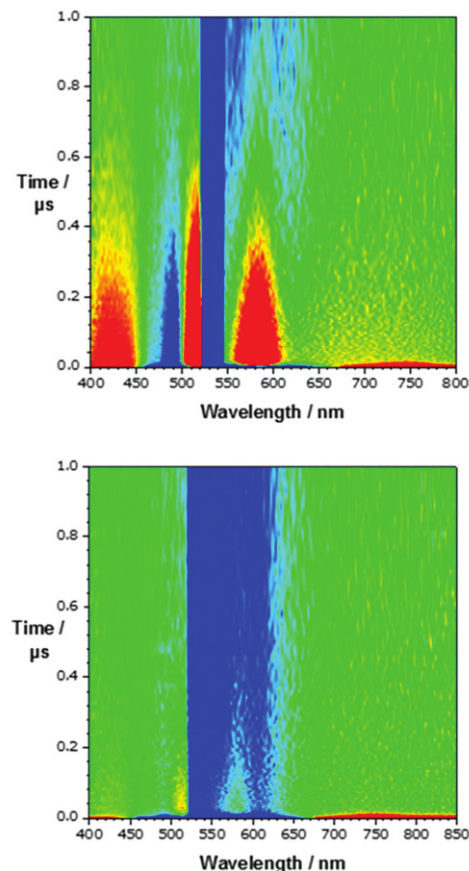


Fig. 9 Top: 2D transient absorption spectra obtained upon 530 nm excitation of **1** (1.0×10^{-4} M) with time delays between 1 ns and 1 μ s. Bottom: 2D transient absorption spectra obtained upon 530 nm excitation of **1** (1.0×10^{-4} M) in presence of 2 wt% SDBS with time delays between 1 ns and 1 μ s. The color code scales from positive differential changes (red) to negative differential changes (blue).

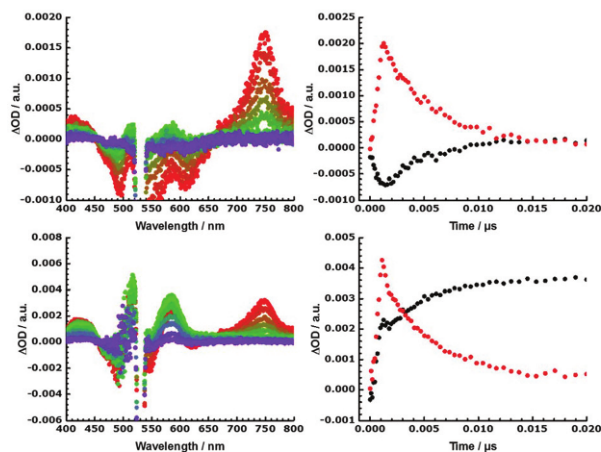


Fig. 8 Top left: Differential absorption spectra of **1** (2.5×10^{-5} M) in H_2O with different time delays from 2 (red) to 734 ns (blue) obtained upon 530 nm laser excitation. Top right: Corresponding time absorption profiles monitored at 585 (black) and 743 nm (red) monitoring the decay of the singlet excited state and the formation of triplet excited states. Bottom left: Differential absorption spectra of **1** (5×10^{-4} M) in H_2O with different time delays from 2 (red) to 734 ns (blue) obtained upon 530 nm laser excitation. Bottom right: Corresponding time absorption profiles monitored at 585 (black) and 743 nm (red) monitoring the decay of the singlet excited state and the formation of triplet excited states.

tial absorption changes formed upon photoexcitation of **1** and **1**/SDBS. The quantum efficiency for the triplet excited state formation is clearly reduced for **1**/SDBS relative to **1**. In particular, the triplet excited state features are barely visible in **1**/SDBS and the 420 nm kinetics are clearly dominated by a single deactivation process (Fig. S42†). Moreover, the relative amplitudes of the triplet and singlet excited states absorption features change from 1.87 in **1** to 0.16 in **1**/SDBS. Significant differences were also noted in the kinetics at 750 nm, which relate to singlet excited state deactivation in monomeric rather than aggregated **1** (Fig. S43†). A possible rationale infers the presence of inverted micelles. According to previous theoretical and experimental considerations, they should fluorescence and feature lifetimes in the nanosecond range.

Experimental section

Spectroscopy

UV/Vis/nIR measurements were performed using either a PerkinElmer Lambda 2 spectrometer or a Cary 5000 spectro-

meter (Varian). Emission was detected in the visible range by a Fluoromax3 spectrometer (Horiba Scientific) and in the near infrared by a Fluorolog 3 (Horiba Scientific) equipped with an InGaAs symphony as detection unit.

Transient absorption spectra on the pico- and nanosecond timescale were performed with output from CPA 2110 or CPA 2101 Ti/sapphire laser systems from Clark-MXR Inc. (775 nm, 1 kHz, 150 fs FWHM pulses). 387 nm excitation pulses were generated by second harmonic generation. For measurements with pico- and nanosecond time resolution a Helios transient absorption spectrometer was equipped. For the corresponding measurements on the microsecond time scale, a EOS transient absorption spectrometer was used. Both systems were provided by Ultrafast Systems. All measurements were carried out in 2 mm OS quartz cuvettes. Atomic force microscopy tapping mode images were recorded on a Solver Pro scanning probe microscope (NT-MDT) equipped with a Sony Exwave HAD camera optical zoom (6.5).

Electrochemistry

Cyclic Voltammetry and Square Wave Voltammetry was performed using a Methrom μ Autolab/FraIII with in cooperated impedance unit. Measurements were performed in a homemade cell ($V = 5$ ml) with a glassy carbon working electrode (3 mm diameter), a silver wire acting as pseudo reference electrode and a Pt wire serving as counter electrode. NOVA 1.10[®] from Methrom served as control software.

UV/Vis/nIR spectroelectrochemical measurements were performed in a homemade three neck cell equipped with a Pt-mesh as transparent working electrode, a Ag-wire as pseudo reference electrode and a Pt plate as counter electrode. Emission spectroelectrochemistry was conducted in a quartz cell with a optical path of 0.5 mm. A Pt mesh served as working electrode, a Pt wire served as counter and Ag-wire as pseudo reference electrode. A PGStat 101 from Methrom was used as potentiostat. The latter was controlled by the software NOVA 1.10[®] provided by Methrom.

Small angle X-ray scattering

Small angle X-ray scattering (SAXS) measurements were performed at the Austrian SAXS beamline of the electron storage ring ELETTRA using a photon energy of 8 keV.³⁸ The beamline setup was adjusted to a sample to detector distance of 763 mm to result in an accessible q -range $0.12\text{--}4\text{ nm}^{-1}$. All images were recorded using the Pilatus 1 M detector (Dectris, Switzerland). For each sample placed in a flow through cell (diameter 1.5 mm), six exposures of 20 seconds each were taken and images without radiation damage have been averaged. The q -scale was calibrated with the reference silver-behenate (d -spacing of 5.838 nm). The conversion of the images to 1D pattern was performed with the FIT2D software.⁴⁴ The data was corrected for fluctuations of the primary intensity, transmission and the corresponding background has been subtracted from each scattering pattern. The presented formfactor was calculated using the CRY SOL package.⁴⁵

Atomic force microscopy

Atomic Force Microscopy (AFM) measurements were performed using a Nanoscope V microscope (Digital Instruments Metrology Group, model MMAFMLN) in tapping mode in air at room temperature, using standard μ mash[®] SPM probe (NSC15/AIBS) with tip height 12–18 μm , cone angle $<40^\circ$ (resonant frequency 325 kHz, force constant of $\sim 40\text{ N m}^{-1}$). Image analysis has been performed with WsXM software (Nanotec Electronica S. L.).⁵ The accuracy of the AFM diameter determination was improved by tip deconvolution. Considering the diameter of AFM tip and the larger dimensions of particles, we calculated real particle diameter from formula:

$$r_c = r(\cos \theta_0 + (\cos^2 \theta_0 + (1 + \sin \theta_0)(-1 + (\tan \theta_0 / \cos \theta_0) + \tan^2 \theta_0))^{1/2})$$

where r is the particle radius, θ_0 is the mean half angle of the tip and r_c is the AFM radius of a particle, as seen in the image.⁵ For the preparation of sample surfaces the same concentration as in the SAXS experiments ($1 = 1.2 \times 10^{-4}\text{ M}$, in distilled H_2O , $\text{pH} = 7$) was used. Dispersions were spin coated and mica was used as substrate. Diameter and height distribution for aggregates of **1** was evaluated considering 5 AFM images, size $10 \times 10\text{ }\mu\text{m}$.

Transmission electron microscopy

Transmission electron microscopy (TEM) measurements were performed with a Zeiss Omega 912 microscope with an acceleration voltage of 80 kV. The samples were drop-casted on lacey carbon coated copper grids and then dried for 24 h.

Conclusions

In the current study, monomers and aggregates of PDI **1** were probed in water with particular emphasis on the excited state properties. At concentrations higher than $1 \times 10^{-5}\text{ M}$ aggregates are formed, while at concentrations lower than that monomers are predominant. Important is the fact, that the fluorescence pattern of **1** undergoes slight, but discernable changes as a function of concentration. The so formed aggregates are weak luminescing, absorbing, and almost perfect H-type in nature. Aggregates of **1** reveal upon photoexcitation singlet excited states, which are most probably excitonic, and which give rise to a distinct transient absorption maximum at 630 nm. Interestingly, this singlet excited state deactivates within approximately 100 ps. Product of this deactivation is the triplet excited state rather than the singlet ground state. Moreover, transient absorption studies, which were performed across a wide range of concentrations of **1**, evoke an even more efficient formation of triplet excited states as the concentration of **1**, and as such the degree of aggregation, increases. Formation of the triplet excited state is, however, not intrinsic to **1** as shown when photoexciting monomers of **1**, that is, at concentrations far below $1 \times 10^{-5}\text{ M}$ or through presence of surface active additives. As such, we postulate charge transfer

character in densely packed aggregates of **1** to be operative in the triplet excited state formation. An enhanced heavy atom effect or a mixing of both cannot be ruled out.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- 1 J. M. Lehn, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 4763.
- 2 Z. Chen, A. Lohr, C. R. Saha-Möller and F. Würthner, *Chem. Soc. Rev.*, 2009, **38**, 564.
- 3 J. D. Badjic, A. Nelson, S. J. Cantrill, W. B. Turnbull and J. F. Stoddart, *Acc. Chem. Res.*, 2005, **38**, 723.
- 4 M. D. Watson, A. Fechtenkötter and K. Müllen, *Chem. Rev.*, 2001, **101**, 1267.
- 5 M. R. Wasielewski, *Acc. Chem. Res.*, 2009, **42**, 1910.
- 6 G. Scheibe, *Angew. Chem.*, 1937, **50**, 51.
- 7 E. E. Jelley, *Nature*, 1937, **139**, 631.
- 8 M. R. Philpott, *J. Chem. Phys.*, 1971, **55**, 2039.
- 9 M. Kasha, *Radiat. Res.*, 1963, **20**, 55.
- 10 F. Wuerthner, T. E. Kaiser and C. R. Saha-Möller, *Angew. Chem., Int. Ed.*, 2011, **50**, 3376.
- 11 F. C. Spano, *Acc. Chem. Res.*, 2010, **43**, 429.
- 12 T. Weil, T. Vosch, J. Hofkens, K. Peneva and K. Müllen, *Angew. Chem., Int. Ed.*, 2010, **49**, 9068.
- 13 S. K. Lee, Y. Zu, A. Herrmann, Y. Geerts, K. Müllen and A. J. Bard, *J. Am. Chem. Soc.*, 1999, **121**, 3513.
- 14 F. Wuerthner, D. Schmitt, C. R. Saha-Möller, B. Fimmel, S. Ogi, P. Leowanawat and D. Schmidt, *Chem. Rev.*, 2016, **116**, 962.
- 15 F. Wuerthner, *Chem. Commun.*, 2004, 1564.
- 16 J. M. Giaimo, J. V. Lockard, L. E. Sinks, A. M. Scott, T. M. Wilson and M. R. Wasielewski, *J. Phys. Chem. A*, 2008, **112**, 2322.
- 17 K. E. Brown, W. A. Salamant, L. E. Shoer, R. M. Young and M. R. Wasielewski, *J. Phys. Chem. Lett.*, 2014, **5**, 2588.
- 18 S. Herbst, B. Soberats, P. Leowanawat, M. Lehmann and F. Würthner, *Angew. Chem., Int. Ed.*, 2017, **56**, 2162–2165.
- 19 S. Ogi, V. Stepanenko, K. Sugiyasu, M. Takeuchi and F. Würthner, *J. Am. Chem. Soc.*, 2015, **137**, 3300–3307.
- 20 A. Nowak-Król, M. I. S. Röhr, D. Schmidt and F. Würthner, *Angew. Chem., Int. Ed.*, 2017, **56**, 11774.
- 21 H. Langhals, J. Karolin and L. B.-Å. Johansson, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 2919.
- 22 M. Sadrai, L. Hadel, R. R. Sauers, S. Husain, K. Krogh-Jespersen, J. D. Westbrook and G. R. Bird, *J. Phys. Chem.*, 1992, **96**, 7988.
- 23 A. A. Rachford, S. Goeb and F. N. Castellano, *J. Am. Chem. Soc.*, 2008, **130**, 2766.
- 24 F. N. Castellano, *Dalton Trans.*, 2012, **41**, 8493.
- 25 M. Schulze, A. Steffen and F. Wuerthner, *Angew. Chem., Int. Ed.*, 2015, **54**, 1570.
- 26 E. O. Danilov, A. A. Rachford, S. Goeb and F. N. Castellano, *J. Phys. Chem. A*, 2009, **113**, 5763.
- 27 L. Feng, M. Rudolf, S. Wolfrum, A. Troeger, Z. Sladina, T. Akasaka, S. Nagase, N. Martin, T. Ameri, C. J. Brabec and D. M. Guldi, *J. Am. Chem. Soc.*, 2012, **134**, 12190.
- 28 M. Rudolf, L. Feng, Z. Slanina, T. Akasaka, S. Nagase and D. M. Guldi, *J. Am. Chem. Soc.*, 2013, **135**, 11165.
- 29 S. W. Eaton, L. E. Shoer, S. D. Karlen, S. M. Dyar, E. A. Margulies, B. S. Veldkamp, C. Ramanam, D. A. Hartzler, S. Savikhin, T. J. Marks and M. R. Wasielewski, *J. Am. Chem. Soc.*, 2013, **135**, 14701.
- 30 C. M. Mauck, K. E. Brown, N. E. Horwitz and M. R. Wasielewski, *J. Phys. Chem. A*, 2015, **119**, 5587.
- 31 P. Spenst, R. M. Young, M. R. Wasielewski and F. Würthner, *Chem. Sci.*, 2016, **7**, 5428–5434.
- 32 F. Würthner, C. R. Saha-Möller, B. Fimmel, S. Ogi, P. Leowanawat and D. Schmidt, *Chem. Rev.*, 2015, **116**(3), 962–1052.
- 33 A. J. Musser, M. Maiuri, D. Brida, G. Cerullo, R. H. Friend and J. Clark, *J. Am. Chem. Soc.*, 2015, **137**, 5130.
- 34 D. Görl, X. Zhang and F. Würthner, *Angew. Chem., Int. Ed.*, 2012, **51**, 6328.
- 35 E. Tenori, A. Colusso, Z. Syrgiannis, A. Bonasera, S. Osella, A. Ostric, R. Lazzaroni, M. Meneghetti and M. Prato, *ACS Appl. Mater. Interfaces*, 2015, **7**, 28042.
- 36 F. Rigodanza, E. Tenori, A. Bonasera, Z. Syrgiannis and M. Prato, *Eur. J. Org. Chem.*, 2015, 5060.
- 37 C. D. Schmidt, C. Böttcher and A. Hirsch, *Eur. J. Org. Chem.*, 2007, 5497.
- 38 M. Burian, F. Rigodanza, H. Amenitsch, L. Almásy, I. Khalakhan, Z. Syrgiannis and M. Prato, *Chem. Phys. Lett.*, 2017, **683**, 454.
- 39 O. Glatter and O. Kratky, in *Small Angle X-ray Scattering*, Academic Press, London, 1982.
- 40 V. Strauss, J. T. Margraf, K. Dirian, Z. Syrgiannis, M. Prato, C. Wessendorf, A. Hirsch, T. Clark, A. Hirsch and D. M. Guldi, *Angew. Chem., Int. Ed.*, 2015, **54**, 8292.
- 41 M. Supur, M. E. El-Khouly, J. H. Seok, J. H. Kim, K.-Y. Kay and S. Fukuzumi, *J. Phys. Chem. C*, 2010, **114**, 10969.
- 42 R. F. Kelley, W. S. Shin, B. Ribchinsky, L. E. Sinks and M. R. Wasielewski, *J. Am. Chem. Soc.*, 2007, **129**, 3173.

- 43 H. Amenitsch, M. Rappolt, M. Kriechbaum, H. Mio, P. Laggner and S. Bernstorff, *J. Synchrotron Radiat.*, 1998, **5**, 506.
- 44 A. P. Hammersley, S. O. Svensson, M. Hanfland, A. N. Fitch and D. Hauserman, *High Pressure Res.*, 1996, **14**, 235.
- 45 D. Svergun, C. Barberato and M. H. J. Koch, *J. Appl. Crystallogr.*, 1995, **28**, 768–773.
- 46 C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158–6169.
- 47 T. H. Dunning Jr., *J. Chem. Phys.*, 1989, **90**, 1007–1023.
- 48 M. Cossi, V. Barone, R. Cammi and J. Tomasi, *Chem. Phys. Lett.*, 1996, **255**, 327–335.
- 49 G. Scalmani, M. J. Frisch, B. Mennucci, J. Tomasi, R. Cammi and V. Barone, *J. Chem. Phys.*, 2006, **124**, 1–15.
- 50 H. Kayi and T. Clark, *J. Mol. Model.*, 2009, **15**, 295.
- 51 J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Springer, US, 2006.
- 52 K. Nagarajan, A. R. Mallia, K. Muraleedharana and M. Hariharan, *Chem. Sci.*, 2017, **8**, 1776–1782.