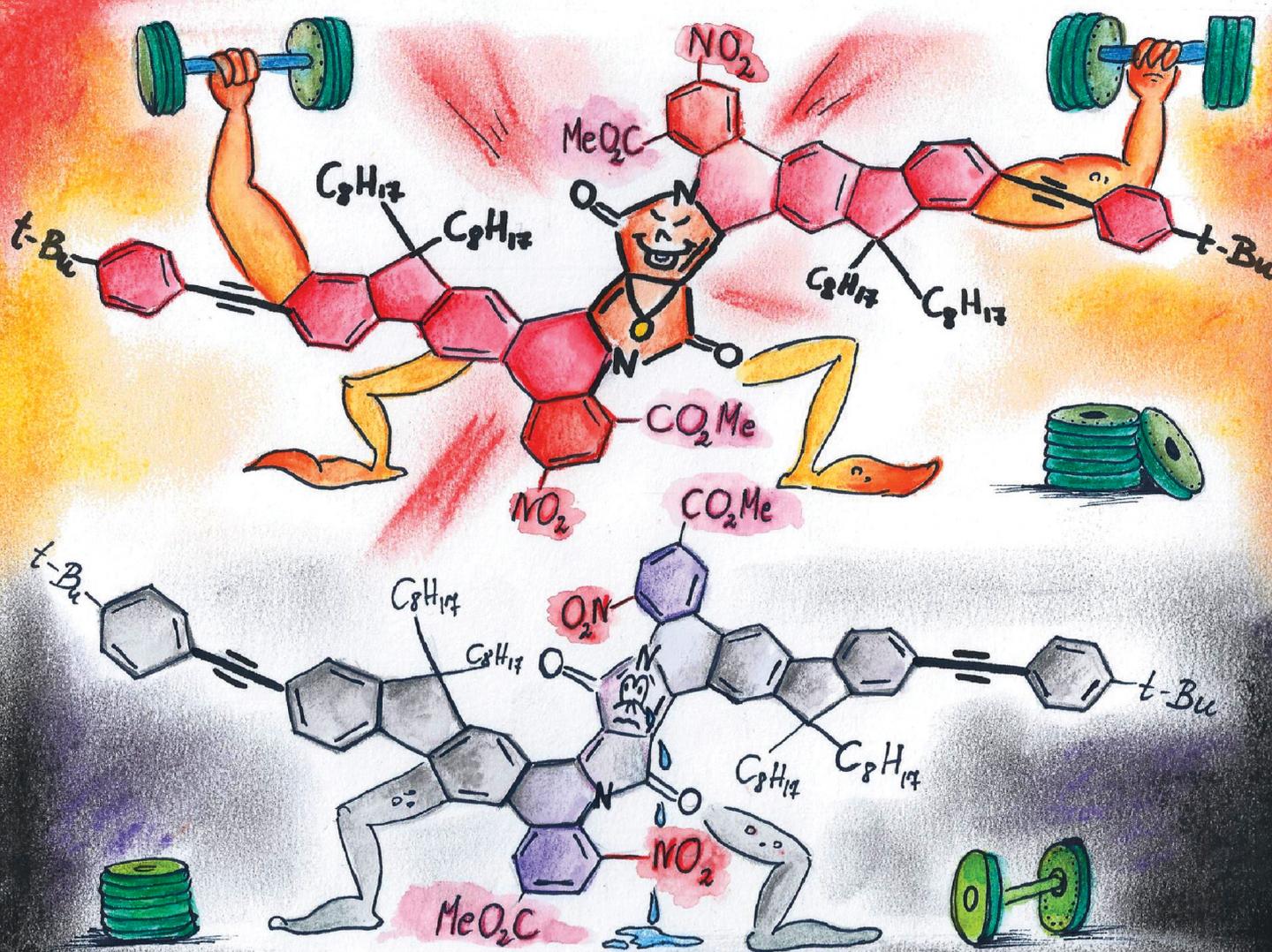


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How the nitro group position determines the emission properties of π -expanded diketopyrrolopyrroles†

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Two complex π -expanded diketopyrrolopyrroles (EDPPs) have been prepared following a multistep but straightforward strategy. We discovered that the fate of these molecules in the excited state can be controlled by subtle differences in their structure. When NO₂ groups are located at a distant position, the quadrupolar, centrosymmetric dye exhibits strong red emission across the solvents' polarity scale. However, when NO₂ groups are adjacent to the lactam moiety, the EDPPs exhibit negligible emission even in non-polar solvents. Density functional theory (DFT) calculations indicate that the primary distinction between the two molecules lies in the structural planarity. The molecule with NO₂ groups adjacent to the lactam moiety exhibits a loss of planarity due to the coulombic repulsion between these groups. The calculations also suggest that the nitro group does not participate in the S₀ → S₁ excitation. Furthermore, for both compounds, the first two excited states (one bright and one dark) are found to be very close in energy. The change in molecular geometry affects the non-radiative deactivation of excited states, leading to the two distinct emission behaviors. Experiments in a glassy solvent at low temperatures reveal that at 77 K the photophysics of both dyes becomes the same, which proves that thermal activation is the key mechanism for the non-radiative decay of the excited state for non-emissive EDPPs.

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Introduction

The design of organic analogs of *n*-doped semiconductors benefits from electron-deficient aromatic π -conjugated molecules.¹ They can also serve as light sensitizers for photooxidation and for initiating charge transfer (CT) *via* hole transduction.² The most typical approach for decreasing the electron density is to attach electron-withdrawing substituents, and the nitro group is one of the strongest of them (Hammett constants exceeding 0.7).³ Nitro-aromatics have been widely utilized in various applications involving intramolecular charge transfer (CT),⁴ fluorescent

probes,⁵ and nonlinear optical materials.⁶ With a few exceptions, however, nitro-aromatics were historically regarded as non-emissive.⁷ The scattered examples of fluorescent nitroaromatics were regarded as a curiosity and hardly influenced the mainstream of functional dyes' chemistry. The discovery of strongly emissive nitro-aromatics in the last decade enabled a partial change of this paradigm.⁸ Several quadrupolar, centrosymmetric nitro-aromatics were discovered and investigated.⁹ This in turn led to attempts to formulate some general rules governing their strong emission.¹⁰

π -Expanded diketopyrrolopyrroles¹¹ were thought to present an ideal synthetic platform for modular access to centrosymmetric nitroaromatics. We recently reported the synthesis of a new class of π -expanded diketopyrrolopyrroles (EDPPs), which exhibit strong fluorescence in various solvents despite the presence of NO₂ groups in their structure.^{9a} The target molecules were synthesized in a two-step process which involved the *N*-arylation of DPPs followed by an intramolecular direct arylation of the aromatic rings that are present in these building blocks. This established synthetic pathway prompted us to synthesize other pigments, especially those in which the NO₂ group is in a different position. Earlier observations indicated that the position of the nitro group in relation to the π -system core has a

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profound influence on fluorescence.^{9b} Here we report how competing excited state processes decide about the fate of centrosymmetric nitro-aromatics in the excited state, by determining their emissivity. To achieve this, we first designed a suitable DPP core containing alkylated fluorene, which ensured photophysical properties in the near-infrared region and provided appropriate solubility of the final dyes.

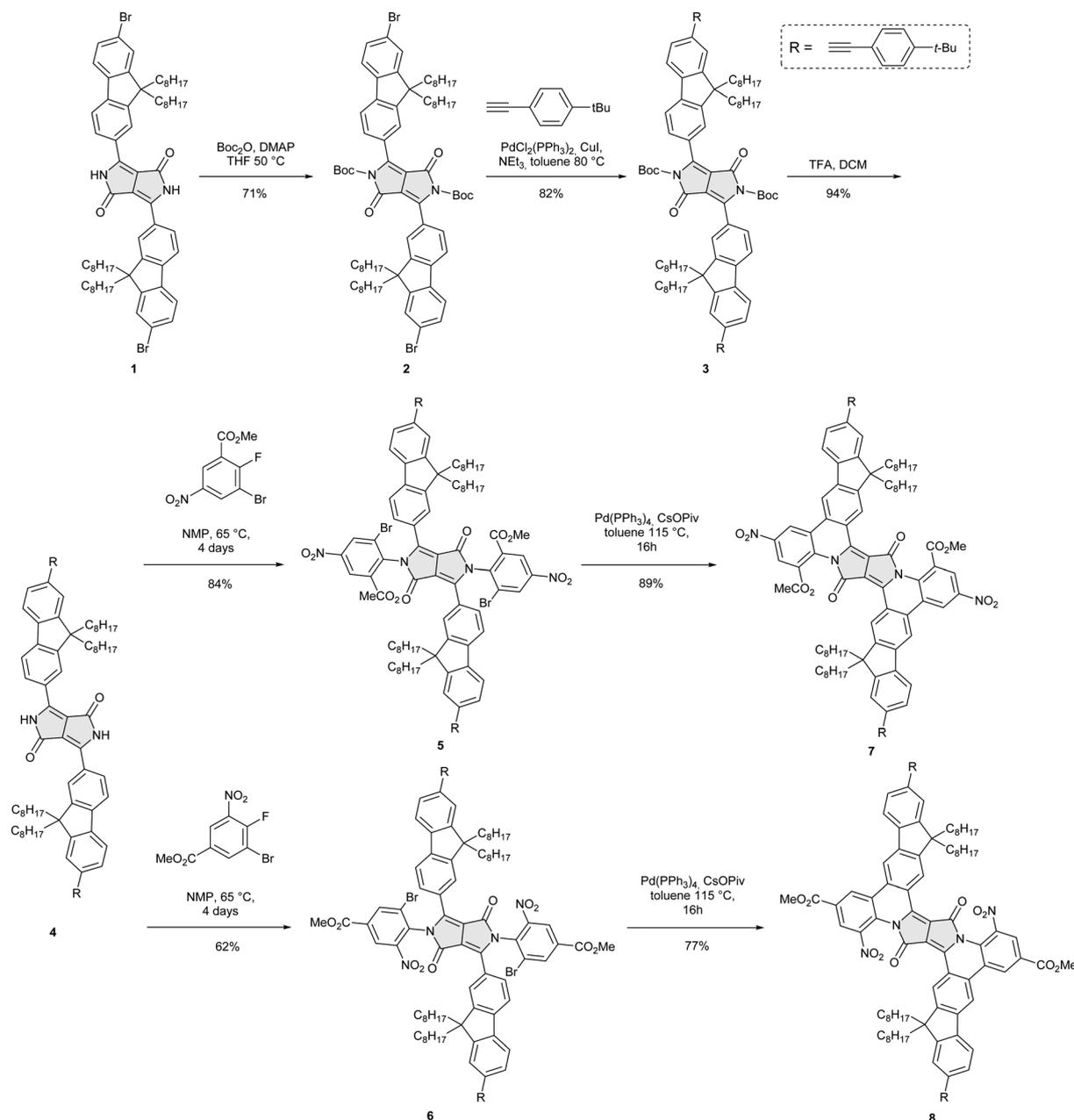
Results and discussion

Synthesis

At the outset we focused on the preparation of DPP **1** containing bromine atoms on the fluorene unit, which was achieved following

the previously reported literature procedure (Scheme 1).^{11j} The pigment was then modified by introducing an arylalkyne substituent. In order to enable the solubilization of the starting material in solvents commonly used in organic synthesis, the nitrogen atoms of the lactam core were protected with *tert*-butoxycarbonyl groups (Boc). The formed bis-Boc-DPP **2** was then subjected to Sonogashira coupling with 4-*tert*-butylphenylacetylene which resulted in the formation of DPP **3**.

It is important to note that the reaction must be carried out at a temperature equal to or below 80 °C, otherwise it leads to a mixture of products due to partial deprotection of the Boc groups of the substrate. Finally, the product of the double Sonogashira reaction *i.e.* DPP **3** was deprotected by adding



Scheme 1 The preparation of DPPs **7** and **8**.



TFA to the pigment solution in methylene chloride. This generated free DPP **4** in the quantitative reaction yield (Scheme 1). Subsequently, *N*-arylation of DPP **4** was carried out with electron-poor aryl fluorides namely methyl 3-bromo-2-fluoro-5-nitrobenzoate and methyl 3-bromo-4-fluoro-5-nitrobenzoate, in the presence of potassium carbonate in NMP (Scheme 1). The reaction was completed after 4 days, yielding **5** and **6**, respectively. *N*-arylation of DPP **4** proceeded much slower compared to the previously described DPP bearing benzofuran units, where the reaction was completed after a few hours.^{9a} In the next step, both **5** and **6** were subjected to Pd(PPh₃)₄ in order to perform intramolecular, direct arylation in our systems. As a result we obtained good yields of two π -expandable products: **7** and **8**, both possessing 12 fused rings. The reaction was carried out overnight in dry toluene at 115 °C. Both target pigments are soluble in chlorinated and aromatic solvents, which enabled their identification using ¹H NMR and ¹³C NMR spectroscopies.

Steady-state optical absorption and emission

Absorption, emission and excitation spectra of dyes **7** and **8** have been recorded in various solvents with different polarity properties (Table 1 and Fig. 1). These spectra are characterized by an absorption band in the 500–650 nm spectral range as well as through a pronounced vibronic progression ($\approx 1520 \text{ cm}^{-1}$); however, only a slight modification in the spectral bandwidth and the position of the absorption maximum has been observed as a function of solvent polarity. Excitation and fluorescence spectra are very poorly solvent-dependent as well.

Fluorescence quantum yields (Φ_{fl}) reveal dramatically opposite behavior between dyes **7** ($\Phi_{\text{fl}} = 0.76$) and **8** ($\Phi_{\text{fl}} = 0.09$) in non-polar and slightly polar solvents (CCl₄ and toluene). At the same time a decreasing trend in the fluorescence quantum yield is observed for both compounds as the polarity of the environment is increased ($\Phi_{\text{fl}} = 0.16$ for dyes **7** and $\Phi_{\text{fl}} = 0.03$ for **8** in BZN). The virtually absent response of the emission maximum ($\lambda_{\text{em}}^{\text{max}}$) to solvent polarity for both dyes **7** and **8** indicates that the emissive excited state may be described as quadrupolar. However, the fluorescence emission quenching (for dyes **7** and **8**) as the polarity of the solvent is increased from dye **7** to **8** suggests that an additional excited state plays a key role in the deactivation pathway. Given that molar absorption coefficients are $\approx 140\,000 \text{ M}^{-1} \times \text{cm}^{-1}$ in both cases, the optical brightness for **7** reaches almost $110\,000 \text{ M}^{-1} \times \text{cm}^{-1}$ in toluene. This value should be compared from one site with optical brightness $\approx 170\,000 \text{ M}^{-1} \times \text{cm}^{-1}$ recorded for somehow

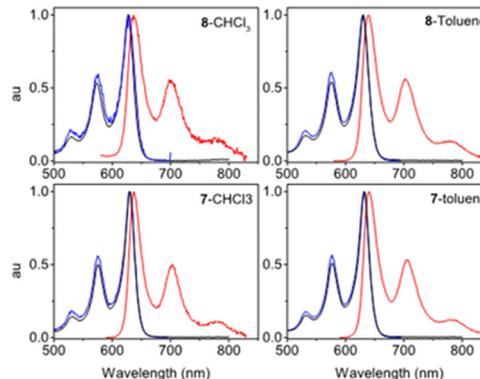


Fig. 1 Absorption, emission and excitation spectra of dyes **7** and **8** in CHCl₃ (left panels) and toluene (right panels). Spectra recorded in CCl₄, THF, CH₂Cl₂ and benzonitrile are included in the ESI.†

analogous π -expanded diketopyrrolopyrrole bearing fused fluorene units and flanking diarylamino groups.^{11j} The presence of nitro groups does not increase the fluorescence quantum yield. On the other hand it slightly decreases the molar absorption coefficient. The optical brightness of EDP **7** compared however with other described nitro-aromatics is one of the largest recorded.¹⁰

Time resolved measurements

To disentangle the mechanism leading to the fluorescence emission properties of dyes **7** and **8**, we characterized the relaxation dynamics with pump-probe spectroscopy in the UV-vis, NIR and Mid-IR spectral range.

UV-vis pump-probe spectra in the 400–750 nm spectral range have been recorded with an excitation wavelength range of 525–530 nm for various solvents using the transient absorption setup described in the ESI.† All spectra show ground state bleaching plus stimulated emission signals and an excited state absorption located at 470 nm. Spectra as a function of time have been analyzed with a global fitting approach using the Glotaran program package⁹ and the unidirectional sequential model as the kinetic decaying scheme. The analysis showed that both dyes **7** and **8** contain only one main spectral component that relaxes back to the ground state (some representative transient absorption spectra are reported in Fig. S7 and S8 in the ESI.†); the additional stimulated emission increases and slight red-shift (for the $\approx 700 \text{ nm}$ band) observed in the first tens of picoseconds (Fig. S8a and b, ESI.†) have been ascribed to vibrational and structural relaxation following the new charge

Table 1 Excited state lifetimes (t) and constants (k), fluorescence quantum yields (Φ_{fl}), radiative (k_{r}) and non-radiative (k_{nr}) decay constants. Tol = toluene, THF = tetrahydrofuran, BZN = benzonitrile

	7					8				
	t (ns)	$(k_{\text{r}} + k_{\text{nr}})$ (ns ⁻¹)	Φ_{fl}	k_{r} (ns ⁻¹)	k_{nr} (ns ⁻¹)	t (ns)	$(k_{\text{r}} + k_{\text{nr}})$ (ns ⁻¹)	Φ_{fl}	k_{r} (ns ⁻¹)	k_{nr} (ns ⁻¹)
CCl ₄	3.400	0.29	0.76	0.22	0.07	0.679	1.47	0.09	0.13	1.34
Tol	3.548	0.28	0.77	0.22	0.06	0.484	2.07	0.09	0.19	1.88
CHCl ₃	0.340	1.59	0.09	0.26	2.60	0.032	31.25	0.004	0.13	31.1
THF	2.579	0.39	0.56	0.22	0.17	0.141	7.09	0.02	0.14	6.9
CH ₂ Cl ₂	0.158	6.33	0.04	0.25	6.08	0.022	45.5	0.003	0.14	45.3
BZN	0.863	1.16	0.16	0.19	0.97	0.067	14.9	0.03	0.45	14.5



distribution in the excited state. The time constants for ground state recovery are strongly solvent dependent, as suggested by fluorescence quantum yields, and are reported in Table 1.

Fluorescence lifetimes were determined by time correlated single photon counting and supported by comparison to the decay kinetics of the bleaching signal acquired with pump-probe. The agreement of the two techniques allowed the exploitation of the latter to determine the fast ground state relaxation observed for EDPP **8**. Ground state recovery dynamics allowed us to highlight that radiative decay constants are, as expected, solvent independent and very much similar for dyes **7** and **8** (see Table 1); in contrast, non-radiative processes are strongly influenced by solvent environment and by the position of nitro-groups. In more detail, the non-radiative constant increases by increasing the solvent polarity and even higher non-radiative constant (one order of magnitude larger on average) are observed when moving from compound **7** to compound **8**, suggesting that in both cases a second non-radiative decay channel is opened. UV-vis pump-probe data are fully in agreement with the presence of an additional excited state with a more pronounced charge transfer (CT) character in the relaxation pathway. The fluorescence quantum yields measured in CHCl_3 and CH_2Cl_2 do not follow the solvent polarity trend response observed for other solvents.

Pump-probe measurements evidence that ground state recovery take place at a few hundred picoseconds for dye **7** and tens of picoseconds for dye **8**.¹² This evidence suggests that both solvents may come into specific molecular interactions with dyes **7** and **8** as a result of their low but not negligible capability, to enhance the non-radiative decay¹³ and form hydrogen-bonding with molecules in the excited electronic state. It is worth mentioning that among the various solvents used to characterize the properties of excited state compounds **7** and **8**, chloroform and dichloromethane are the only ones having hydrogen bonding donor properties and are the ones where both compounds have the shortest lifetimes (no evidence of triplet state formation from pump-probe data). Due to the extended delocalization of the electron density for both dyes **7** and **8**, we expected, in analogy with formerly reported quadrupolar molecules,^{9a} NIR excited state absorptions to take place. Pump-probe measurements in the 800–910 nm spectral range have been performed for both compounds in toluene and chloroform solutions using the US-pp setup¹⁵ described in the ESI† and the global analysis results have been reported as shown in Fig. 2. In chloroform, both dyes **7** and **8** showed a broader spectral shape than in toluene as well as a slight time-dependent blue shift of the band maximum; which is practically absent in toluene. Dynamical spectral shift and spectral broadening are very common markers for the stabilization of excited states. This is due to polar and slightly polar solvents, strongly suggesting that excited state absorption involves a state characterized by a certain degree of charge separation.

Global analysis, within a two-component sequential model scheme, revealed that one main spectral component relaxes back to the ground state, with the time constant of this process being in very good agreement with that of the ground state

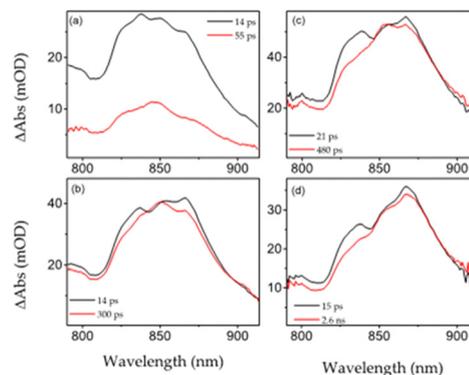


Fig. 2 Evolution associated decay spectra (EADS) of transient absorption measurements in the NIR spectral region for: **8** in CHCl_3 (a), **7** in CHCl_3 (b), **8** in toluene (c) and **7** in toluene (d).

bleaching decay. The first picosecond component has been ascribed to intramolecular structural relaxation. Transient infrared spectra (Fig. S13, ESI†) are in good agreement with the UV-vis pump-probe, showing ground state recovery on the hundred's picosecond timescale for EDPP **8** in THF.¹⁴ Additional evidence that the presence of a CT state plays the key role in determining fluorescence properties of dyes **7** and **8** has been obtained from temperature-dependent fluorescence lifetime measurements in 2Me-THF. The data are reported as shown in Fig. 3 and Fig. S10 (ESI†). Dye **7** shows no temperature dependence from 298 K to 77 K, while EDPP **8** evidences a clear increase in fluorescence lifetimes upon cooling down the solution. Broadband pump-probe measurements in the visible spectral range have been also performed in a frozen solvent and at room temperature. Results, reported in Fig. 3 and Fig. S11 and S12 of the ESI†, show no spectral shift in the first 200 ps, in net contrast to room temperature, demonstrating that in a glassy solvent, the structural relaxation is blocked.

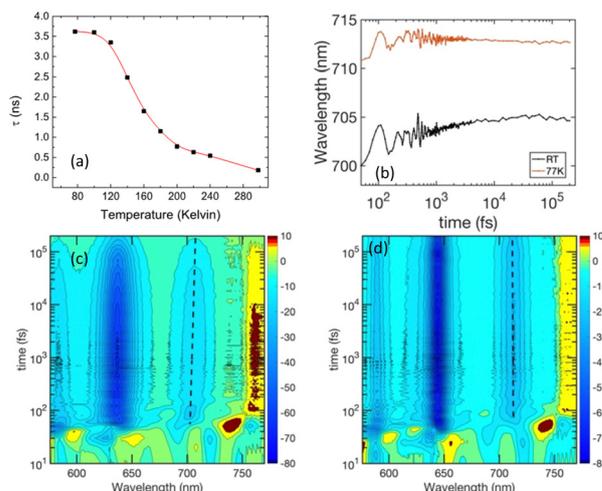


Fig. 3 Temperature dependence of the fluorescence lifetime for dye **8** in 2Me-THF solution (a). Wavelength of the minimum of the stimulated emission signal (b) from broadband pump-probe maps at room temperature (c) and 77 K (d).



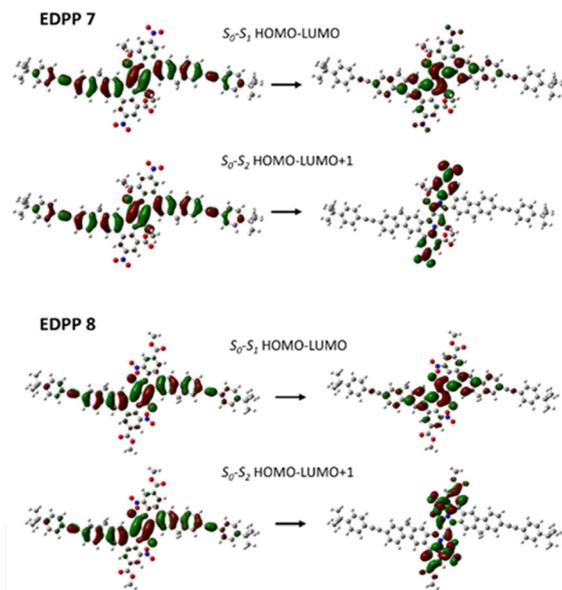


Fig. 4 The two lowest lying singlet excited states at the Franck–Condon geometry in dyes **7** and **8**. The most important Kohn–Sham molecular orbitals involved in the transitions are shown. Calculations performed at the TD-DFT level (B3LYP/6-31+G(d,p)).

These results suggest that both thermal activation and structural relaxation play key roles in the radiative and non-radiative decay mechanisms of excited states EDPPs **7** and **8**.

First principle calculations and modeling

We have performed quantum chemistry calculations for both dyes **7** and **8**. Ground state (S_0) optimized geometries have been obtained at the DFT level (B3LYP/6-31+G(d,p)), whereas the first few excited states have been calculated relying on the time-dependent DFT (TD-DFT) approach (B3LYP/6-31+G(d,p)). All the calculations have been performed in the gas phase using the Gaussian16 (Revision B.01) package.¹⁶ A fairly notable difference between the two molecules occurs already at the level of the ground state geometry, with dye **7** being planar and EDPP **8** showing a bent geometry ($\approx 160^\circ$, see Fig. S4 in the ESI[†]). TD-DFT calculations show that in dyes **7** and **8** the bright, lowest, excited state S_1 corresponds to a π - π^* (HOMO \rightarrow LUMO) transition, which involves two fluorenes and the DPP core, with almost no contribution coming from the nitro-groups (see Fig. 4). The relevant oscillator strengths are high, ranging from 1.54 for dye **8** to 1.6 for EDPP **7**. Steady-state absorption and emission spectra in Fig. 1 correspond to transitions that mainly involve S_1 . On the other hand, in both dyes **7** and **8**, the second singlet excited state S_2 corresponds to a HOMO \rightarrow LUMO+1 transition with a large involvement of the nitro-groups and a strong quadrupolar charge-transfer (CT) character (see Fig. 3). As a result, S_2 is optically dark and has no influence in the steady state spectra (see Fig. 1). At the same time, being very close in energy to S_1 in the Franck–Condon region, S_2 is involved in the solvent-dependent non-radiative processes discussed in the previous section (Fig. 5).

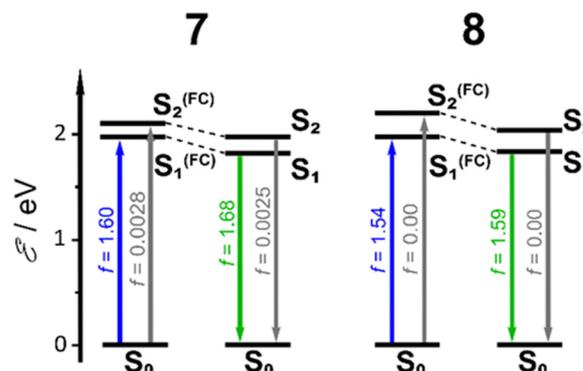


Fig. 5 Excited state energy levels obtained from TDDFT calculations in the gas phase for compounds EDPP **7** and EDPP **8**; oscillators' strength is reported in brackets.

Our recent analysis of the literature¹⁰ on fluorescent nitroaromatics has shown that there are two major scenarios of the dependence of fluorescence intensity on solvent polarity, which originates from the interplay between ISC and CT once the molecules reach their S_1 states. Indeed in most cases, the fluorescent nitroaromatics' emission strength decreases as the medium polarity increases. In the case of nitro-stilbenes however, fluorescence intensity is low in non-polar solvents and it increases in media of intermediate polarity or strong polarity.^{4,7*ij*} This is related to suppressing intersystem crossing in moderately polar solvents. Interestingly in the case of nitro-1,4-distyrylbenzenes Spalletti and co-workers claim that the structure of emissive $^1\text{ICT}^*$ state does not lose planarity even in very polar solvents and the fluorescence is not quenched in *e.g.* DMF.^{7*ij*} In other words excited state dynamics in polar media facilitates the population of a planar $^1\text{ICT}^*$ state resulting in strong emission. The emphasis on the importance of planarity bears a strong resemblance to our findings.

Conclusions

By implementing very subtle changes in the structures of two regioisomeric, quadrupolar, centrosymmetric, π -expanded diketopyrrolopyrroles, it is possible to completely alter their emissive properties. Moving nitro groups from a distant position to the sp^2 carbon atom close to the C=O bond decreases the fluorescence intensity by a factor of 10. In contrast, placing the nitro group at a distant position leads to a super strong emitter with optical brightness $\approx 110\,000\text{ M}^{-1} \times \text{cm}^{-1}$ at 635 nm. TD-DFT computations for dyes **7** and **8**, indicate, that upon excitation, these molecules reach a bright S_1 state characterized by $\pi\pi^*$ nature, with the energy of the dark S_2 state being only slightly higher than that of S_1 (Fig. 5). Unlike dye **7**, EDPP **8**, once in the bright S_1 state, undergoes a rapid internal conversion to the dark S_2 state through thermal activation.¹⁷ Photophysical studies in frozen glass provide convincing evidence that the rate constant k_{nr} for the non-emissive EDPP reaches values comparable to those of the emissive DPP below 120 K. Broadband pump-probe suggests that the thermally



activated internal conversion through the CT S₂ state is mediated by intramolecular structural relaxation. The fundamental difference between dyes **7** and **8** arises from the fact that the presence of the nitro group at the *ortho* position relative to the bridge with the DPP core, is sufficient to induce non-planarity in both the ground state and excited state conformations of dye **8**. In this context, the presence of the nitro group plays a decisive role, as the coulombic repulsion between the negative charges (with the second being the oxygen of the C=O group) results in a non-planar conformation. In the broader context, a comparison of these findings with some earlier results^{9b} points out the following: in the case of larger polarized dyes, the molecules which possess nitro groups in positions that enable a maintaining the planarity of the π -system tend to show strong fluorescence. Their excellent properties such as large optical brightness open the door for future applications in optoelectronics. Given the recent renaissance of interest in nitroaromatics this work should inspire the future design of strongly emitting fluorophores bearing NO₂ groups, with distinctive π -expanded architectures.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Data availability

All experimental details and data supporting this article are available in the ESI.†

Conflicts of interest

There are no conflicts to declare.

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