

Rigid and planar π -conjugated molecules leading to long-lived intramolecular charge-transfer states exhibiting thermally activated delayed fluorescence

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Abstract

Intramolecular charge transfer (ICT) is a fundamental chemical process whereby excitation moves charge from an electron donor to an electron acceptor within the same molecule. Thermally activated delayed fluorescence (TADF) exploits the ICT property to harvest triplet excited states, leading to extensive optoelectronic applications, including OLEDs. However, the highly twisted conformation of TADF molecules results in limited device lifetimes. Rigid molecules offer increased stability, yet their typical planarity and π -conjugated structures impede ICT. Herein, we introduce a new paradigm for achieving dispersion-free triplet harvesting in ICT molecules. Using fused indolocarbazole-phthalimide molecules, we demonstrate remarkably stable co-planar ICT states, yielding blue/green-TADF with good photoluminescence quantum yield and a small singlet-triplet energy gap (ΔE_{ST}) <50 meV. The formation of ICT is dictated by the bonding connectivity between the donor and acceptor fragments, leading to excited-state conjugation breaking stabilising the planar ICT excited state, revealing a new criteria for designing efficient TADF materials.

Introduction

Significant progress has been made in the field of luminescent materials having efficient ambient triplet harvesting for applications in organic light-emitting diodes (OLEDs), bio-imaging and photo-catalysis.¹⁻³ In this regard, triplet harvesting *via* thermally activated delayed

fluorescence (TADF) has emerged as a challenger technology to the incumbent room-temperature phosphorescence in OLEDs.^{1,4-6} The efficiency of TADF relies in part on minimizing the energy gap between the lowest excited singlet and triplet states. This is usually achieved using donor-acceptor charge-transfer chromophores, where orthogonally oriented D and A units, *i.e.* twisted D-A molecules,^{1,6-9} minimises the electron exchange energy and therefore the splitting between the lowest excited singlet and triplet states, provided they exhibit the same spatial symmetry.¹⁰ Different strategies have also been used to realize this objective, including spiro-linked D and A,¹¹⁻¹² arranging D and A in spatial proximity to achieve through-space charge transfer,¹³⁻¹⁴ or forming molecular exciplexes.¹⁵⁻¹⁶ One of the primary concerns with twisted D-A molecules is stability during device operation, as TADF OLED lifetimes are as yet very limited.¹⁷ To achieve high stability in an OLED, it is believed that all rotationally flexible tertiary N-C bonds must be removed from all molecules including TADF molecules as these are the weakest chemical bonds present in their structure and therefore prone to degradation.¹⁸⁻¹⁹ It is hoped that spiro-type TADF emitters,²⁰ especially used in hyperfluorescence,²¹⁻²³ could overcome this, as recently demonstrated by Stavrou et al.,²³ but as yet they also have not demonstrated great lifetime improvement. Fully rigid structures should result in far more stable molecules, offering high rates of fluorescence and short CT lifetimes with negligible energy dispersion.²⁴⁻²⁶ The latter is very large in the flexible twisted D-A molecules because of distributions of the twist angles which result in long-lived TADF components detrimental to OLED operational lifetime.²⁷ However, the main obstacle to exploiting a fully rigid D-A molecular structure is the inherent planarity and conjugation which is believed to make intramolecular charge transfer (ICT) improbable.⁷⁻¹⁰ There has been a significant amount of work developing the short-range charge transfer associated with the multi-resonance (MR-TADF) approach.²⁸⁻³¹ However, while this has achieved exciting results, it represents an entirely new framework³⁰ with a limited chemical space due to molecular design restrictions required to achieve MR-TADF. In addition, to date, these emitters often exhibit slow rates of reverse intersystem crossing (rISC) and therefore, are useful only as hyperfluorescence end-acceptors where typically D-A TADF emitters act as FRET (Förster Resonance Energy Transfer) sensitizers.^{17,22,23}

With the objective of achieving desirable rigidity, low CT dispersion energies and high fluorescence rates, our research explored an unconventional pathway of utilising rigidly planar D-A molecules that give unexpected ambient triplet harvesting. Previously, a few rigidified aminobenzonitriles have shown ICT states without the need of a large-amplitude rotational motion required to form a twisted conformation.³² However, the stability of these co-planar

ICT states depend on the energy gap and coupling between the low-lying singlet states, and ICT emission is observed only in highly polar solvents, albeit no triplet contribution has ever been reported.³³⁻³⁵ To the best of our knowledge, a fully-conjugated, co-planar and rigidified donor-acceptor chromophore giving strong ICT emission involving both singlet (prompt fluorescence) and triplet excited state (TADF) in non-polar environments has not been observed. Rajamalli et al. proposed a D-A-D system showing TADF which they claimed was planarized through hydrogen bonding between D and A.³⁶ Subsequently, Chen et al.³⁷ and He et al.³⁸ invoked similar D-A hydrogen bonding schemes in HMAT-TRZ and ICZ-TRZ, respectively for potential TADF design strategy. However, both these derivatives show large ΔE_{ST} (>0.43 eV) and do not show any TADF in dilute non-polar zeonex films, hinting towards triplet-triplet annihilation (TTA)^{37,39} or weak exciplex derived³⁸ TADF when doped in appropriate hosts at high doping concentrations. Notably, detailed potential energy surface analysis combined with experimental time-resolved spectroscopy studies on several model ‘intramolecular H-bond’ containing D-A molecules by Hempe et al.⁴⁰ and Bergmann et al.⁴¹ suggested that such D-A hydrogen bonds are unlikely to form and drive the rISC process.

To approach this seemingly intractable problem, we have developed a new molecular design utilizing a fused carbazole (indolocarbazole, ICz)⁴² in combination with a phthalimide⁴³ (PI) acceptor unit, in fully planar rigid molecular structures (ICz-PI; Figure 1) giving efficient TADF. In the context of triplet harvesting, phthalimides are particularly useful as they give efficient $\pi-\pi^*$ and $n-\pi^*$ intersystem crossing.⁴³ In addition, they are relatively weak donors and acceptors with significantly high triplet energies, ideal for blue-emitting charge-transfer systems.^{24,43} Furthermore, two isomers of ICz-PI which differ in the position of N-C and C-C bonds connecting the donor-acceptor fragments, exhibit very different excited state behaviour and photophysics. Most importantly, these emitters show stable ICT states and triplet harvesting properties both in solution and doped solid films with good photoluminescence quantum yields. We propose a mechanism that explains how conjugation is broken in the excited state of these ICz-PI molecules such that planar ICT states are stabilised to give long CT prompt lifetimes of >30 ns and persistent TADF. Our observations break new ground in showing that it is possible; (i) to stabilise ICT states in a fully-planar conjugated rigidified molecule and (ii) to achieve TADF without orthogonal D-A or highly spatially separated D and A units.

Results and Discussion

Molecular Design and Synthesis

o-ICz-PI and *p*-ICz-PI (Figure 1a) were synthesized in one-pot via a synchronous palladium-catalyzed Buchwald-Hartwig and Heck-coupling reaction pathway from previously reported bromine substituted di-*tert*-butylcarbazole and phthalimide precursors. Cz-PI (Figure 1a) was synthesized following similar conditions using unsubstituted di-*tert*-butylcarbazole via Buchwald-Hartwig coupling. 2-Ethylhexyl chains were attached to ensure good solubility of the molecules. Detailed synthetic procedures are given in the Supporting Information. All the molecules synthesized in this work were characterized by ¹H, ¹³C NMR spectroscopy and high-resolution mass spectrometry (HRMS).

Optical Properties

The optical properties of both isomers, *p*-ICz-PI and *o*-ICz-PI were measured in three solvents of varying polarity: methylcyclohexane (MCH), toluene, and dichloromethane (DCM), (Figure 1). *p*-ICz-PI has a distinct vibronic structured absorption band between 360-420 nm in all solvents and a molar extinction coefficient of 37925 Lmol⁻¹cm⁻¹ in DCM at 400 nm (Figure 1 and Supplementary Fig. 1). In contrast, the absorption of *o*-ICz-PI in this region is significantly weaker (7320 Lmol⁻¹cm⁻¹) and the first peak in the absorption band is shifted to ~330 nm (Figure 1b and Supplementary Fig. 1). This signifies a fundamentally different ground state electronic character between the two isomers, a trend observed in different solvents (Figure 1b and Supplementary Fig. 1a). The *p*-ICz-PI absorption band redshifts by only 20 nm in DCM, indicating a weak charge-transfer contribution to this otherwise strongly local transition. The reduced intensity of these transitions in *o*-ICz-PI implies stronger CT character, confirmed by the density difference plots for each molecule shown in the (Supplementary Information, Section 5). For comparison, Cz-PI, (Figure 1), the twisted D-A analogue of ICz-PI⁴⁴ has a strong absorption at 320-340 nm as seen in *o*-ICz-PI, which is attributed to the carbazole/indolocarbazole unit, and a second band at 400 nm with a longer red absorption tail (> 425 nm) than *p*-ICz-PI, characteristic of a typical twisted D-A direct charge-transfer absorption (Figure 1b and Supplementary Fig. 1a). This confirms that in *p*-ICz-PI, the 360-420 nm band is predominantly a local π - π^* transition with a weak CT character, whereas in *o*-ICz-PI the CT character is far stronger.⁴⁵ The absorption of unsubstituted PI occurs at much higher energy, ca. 3.81 eV (325 nm).⁴⁶

Upon excitation at 355 nm in MCH, *p*-ICz-PI exhibits a mirror-image emission band with small Stokes shift (11 nm), characteristic of a strongly local π - π^* transition. Increasing the solvent polarity induces spectral broadening, larger Stokes shifts (28 nm in toluene and 56

nm in dichloromethane) and loss of vibronic structure, indicating increasing charge-transfer character. However, the excited state lifetime of *p*-ICz-PI does not change substantially, suggesting a weakly mixed LE/CT excited character is retained even in DCM ($\tau_{\text{avg.}} = 5.6$ ns) and acetonitrile ($\tau_{\text{avg.}} = 8.9$ ns) as compared to MCH ($\tau_{\text{avg.}} = 6.1$ ns), see Supplementary Fig. 2a, Supplementary Table 1.

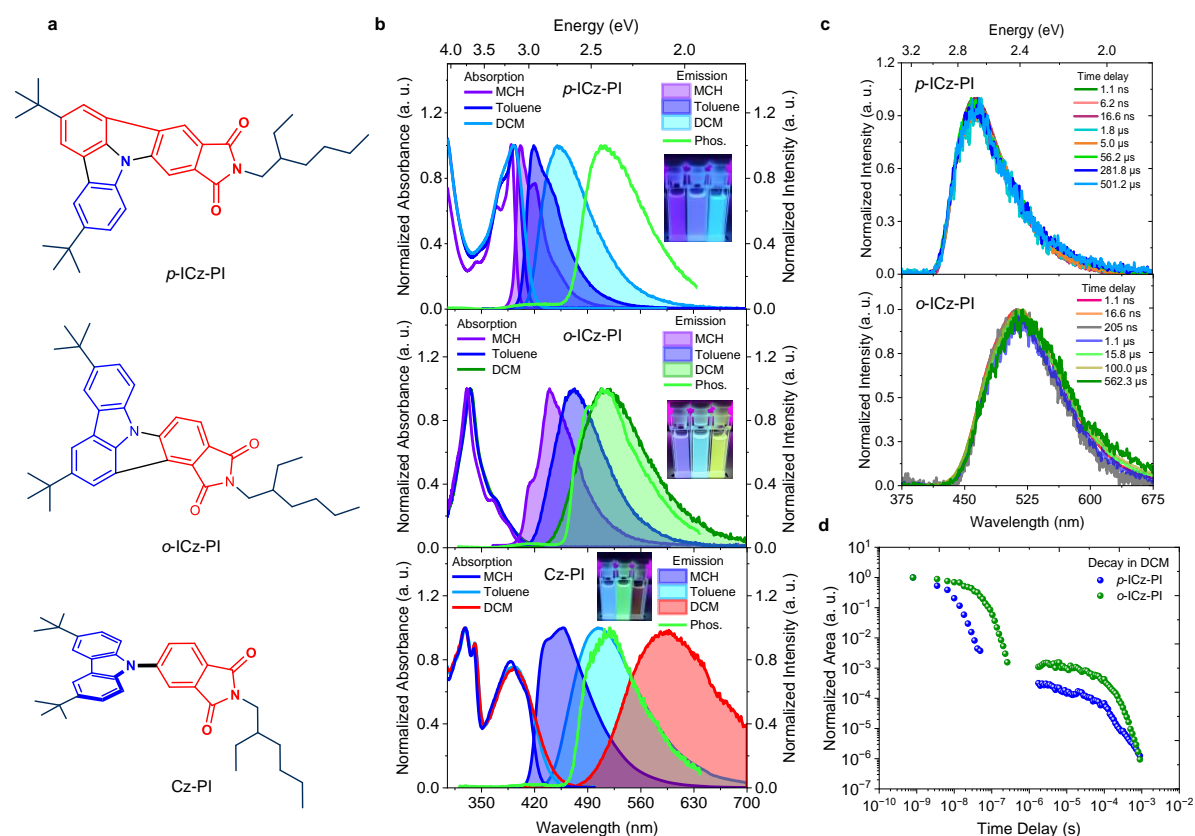


Figure 1. Absorption, fluorescence, delayed fluorescence, and phosphorescence of the investigated molecules. (a) Molecular structures of the three charge-transfer emitters (*p*-ICz-PI, *o*-ICz-PI, and Cz-PI) studied in this work. (b) Normalized absorption and steady-state emission spectra of dilute *p*-ICz-PI (top panel), *o*-ICz-PI (middle panel) and Cz-PI (bottom panel) solutions in methylcyclohexane, toluene and dichloromethane ($[c] = 2 \times 10^{-5}$ M). Inset shows the change in emission color upon changing the solvent polarity when excited at 365 nm by a UV-lamp. Phosphorescence (measured using time-gated emission at 80 K with a high time-delay of 80 ms) in 1 wt.% zeonex shown here to highlight the locally-excited nature of the T_1 state in all three molecules. (c) Time-resolved emission spectra and (d) time-resolved decay of *p*-ICz-PI and *o*-ICz-PI in degassed dichloromethane at room temperature. $\lambda_{\text{exc}} = 355$ nm, $[c] = 2 \times 10^{-5}$ M.

In comparison, ***o*-ICz-PI** has a broader featureless emission spectrum in polar solvents (Figure 1b). The Stokes shift in MCH (49 nm), toluene (81 nm) and DCM (123 nm) is substantially larger than ***p*-ICz-PI**, consistent with strong charge-transfer character. Fluorescence lifetimes confirm this with average lifetimes for ***o*-ICz-PI** increasing substantially from MCH ($\tau_{\text{avg.}} = 19.04$ ns) to DCM ($\tau_{\text{avg.}} = 35.7$ ns) (Supplementary Fig. 2b, Supplementary Table 1). Excitation of **Cz-PI** at 355 nm gives similar spectra to ***o*-ICz-PI** but with significantly larger Stokes shifts (25 nm, 95 nm and 190 nm in MCH, toluene and DCM, respectively) indicative of pure CT character of a twisted DA-TADF molecule. The longer emission wavelength observed for more polar solvents also significantly increases non-radiative decay, as expected from the energy-gap law, indicated by the marked decrease in the excited state lifetime for high polarity solvents (Supplementary Fig. 2c, Supplementary Table 1).

The respective CT and LE character of the emitting states is further highlighted by the photoluminescence quantum yields (PLQY), which are substantially lower in DCM, for ***o*-ICz-PI**, $\Phi = 0.24 (0.37) \pm 0.05$, compared to ***p*-ICz-PI**, $\Phi = 0.41 (0.47) \pm 0.05$ (figures in brackets are degassed PLQY values, Supplementary Table 2). In DCM, **Cz-PI**, has a poor PLQY in air, $\Phi \sim 0.04$; however, it increases substantially to $\Phi = 0.39 (0.61) \pm 0.05$, when measured in toluene. While the increase upon degassing is often attributed to the prevention of triplet state quenching, we note that singlet state quenching by oxygen also occurs when lifetimes are long.⁴⁷

Finally, the two ICz-PI isomers also have different phosphorescence spectra, Figure 1b (green trace). ***p*-ICz-PI** is rather structureless with onset at 2.64 eV (469 nm) whereas ***o*-ICz-PI** and **Cz-PI** are similar, having vibronically structured phosphorescence, onset at 2.70 eV (461 nm). The vibronic structure indicates that the lowest triplet state has LE character, effectively residing on the carbazole moiety.²⁴ For ***p*-ICz-PI** the lowest excited state triplet state appears to be more delocalised in character.

Triplet Harvesting in Degassed Solution State

Time-resolved emission measurements of the two ICz-PI isomers were recorded in degassed DCM. ***p*-ICz-PI** emits the same prompt (1 ns - 40 ns) and a weak delayed fluorescence (2 μ s - 1 ms) (Figure 1c-d and Supplementary Fig. 3a). In contrast, ***o*-ICz-PI** showed a more pronounced enhancement in emission intensity upon degassing (Supplementary Fig. 3b, Supplementary Table 2), indicating a larger contribution from up-conversion of triplet states in line with a smaller ΔE_{ST} of 47 meV than ***p*-ICz-PI**, 290 meV (Figure 1b). The ***o*-ICz-PI**

emission has a long-lived prompt contribution (1 ns - 250 ns) and delayed emission (1 μ s - 1 ms) component (Figure 1c-d) similar to **Cz-PI** (Supplementary Fig. 3c and 4). Time-resolved emission in MCH shows clear vibronic features for ***p*-ICz-PI**, and a shorter lifetime compared to both ***o*-ICz-PI** and **Cz-PI** (Supplementary Fig. 5). We did not observe any delayed fluorescence in MCH, presumably due to a larger ΔE_{ST} in all cases.

Ambient Triplet Harvesting in Solid Doped Films

Figure 2a shows the time-resolved emission of 1 wt.% ***p*-ICz-PI** in zeonex films. ***p*-ICz-PI** exhibit a clear prompt emission with an onset at 401 nm ($\lambda_{max.} = 434$ nm). This band red-shifts with time, which is attributed to the presence of aggregates at 1 wt.% doping, confirmed by their absence in 0.1 wt.% films (Supplementary Fig. 6). At long time-delays, >800 μ s, strong blue long-persistent emission, distinct from the phosphorescence (Figure 2b-c), is observed when the laser is turned-off. This slow DF is consistent with the relatively high $\Delta E_{ST} = 0.37$ eV in zeonex (Figure 2b and Supplementary Fig. 7).²⁶ 0.1 wt.% doped films (Supplementary Figures 6a-b), also show this delayed fluorescence confirming its monomolecular origin.

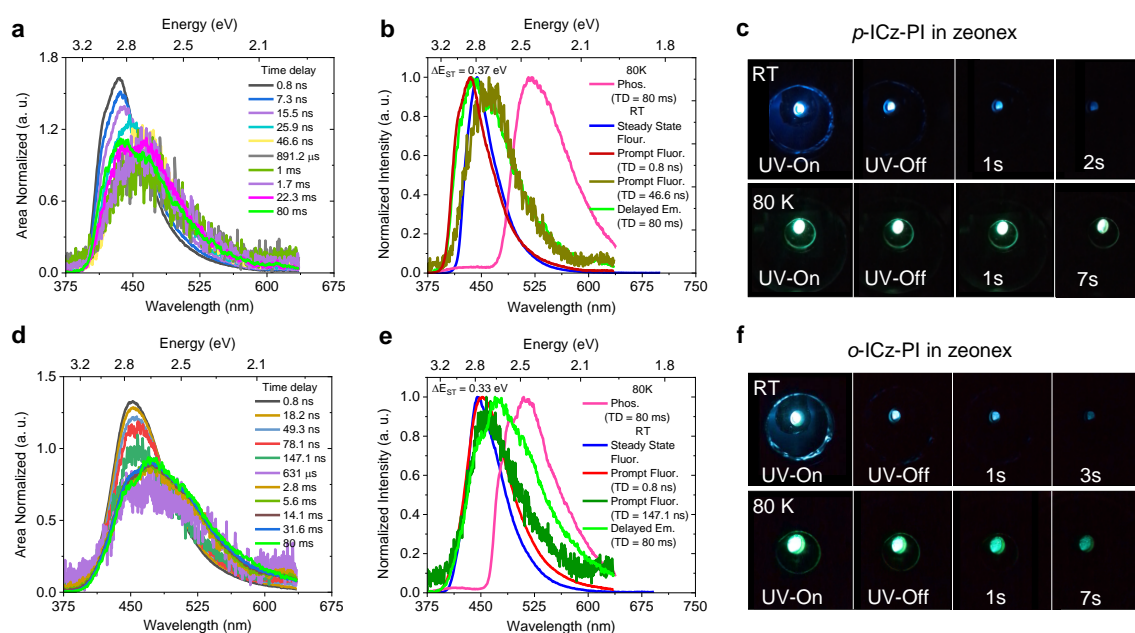


Figure 2. Triplet harvesting in solid state. (a) Time-resolved emission spectra, (b) steady-state photoluminescence (room temperature) and phosphorescence (80 K, 80 ms delay) of ***p*-ICz-PI** doped in 1 wt.% zeonex films. (d) Time-resolved emission spectra, (e) steady-state photoluminescence (room temperature) and phosphorescence (80 K, 80 ms delay) of ***o*-ICz-PI** doped in 1 wt.% zeonex films ($\lambda_{exc} = 355$ nm). Photographs of (c) ***p*-ICz-PI** and (f) ***o*-ICz-PI** doped in zeonex (1 wt.%), indicating a clear persistent emission behavior both at RT and 80 K upon excitation with a 355 nm UV source.

In contrast, 1 wt.% ***o*-ICz-PI** in zeonex film show distinctively different emission (Figure 2d). Prompt fluorescence ($\lambda_{\text{onset}} = 411$ nm and $\lambda_{\text{max}} = 451$ nm) lasts until 150 ns with no aggregate contribution. Delayed emission is seen at the same wavelengths as prompt fluorescence at time-delays >630 μ s. In addition, a new red-shifted band appears at around 516 nm. Similar emission features are also observed in 0.1 wt.% and 0.02 wt.% zeonex and neat films (Supplementary Fig. 8). Steady-state fluorescence onset in these films is independent of doping ratio, unlike the ***p*-ICz-PI** isomer (Supplementary Fig. 8a). At 80 K, at long time-delays we observe only well-structured phosphorescence onset at 461 nm, (Figure 2e and Supplementary Fig. 9). These observations suggest there is additional low levels of exciplex formation in ***o*-ICz-PI** doped zeonex films. We believe this propensity to form the exciplex state is because ***o*-ICz-PI** may well phase segregate as the zeonex films dry.

The aggregation effects on luminescence efficiency in 1 wt.% zeonex films are apparent compared to DCM solutions; ***p*-ICz-PI** which shows the largest aggregation, has a significant drop in PLQY to 0.23 ± 0.05 , ***o*-ICz-PI** showing exciplex states suffers less PLQY quenching, $\Phi = 0.17 \pm 0.05$, whereas **Cz-PI** shows a near 100-fold increase in PLQY to $\Phi = 0.43 \pm 0.05$ in zeonex film (Supplementary Table 2). This suggests that the aggregate states of ICz-PI isomers are different species. In ***p*-ICz-PI**, the aggregate not only red shifts the entire emission band but quenches PLQY by nearly a half, whereas in ***o*-ICz-PI**, the aggregate is much less pronounced and appears as a separate red emission band, i.e., a small additional exciplex contribution, that only moderately reduces PLQY. The ***o*-ICz-PI** exciplexes must be emissive, indicative of stronger donor and acceptor fragments in ***o*-ICz-PI** which can form exciplexes, whereas in ***p*-ICz-PI** they are much weaker, precluding exciplex formation. This gives key insight into the differences in electronic structure between the two isomers. **Cz-PI** clearly behaves like a typical twisted D-A TADF molecule showing much higher PLQY in non-polar zeonex films, than in highly polar solvent (Supplementary Fig. 10 and Supplementary Table 2). No exciplex emission is observed for ***o*-Cz-PI** at 80 K in the 1 wt. % zeonex films which is fully in line with the thermally activated nature of exciplex formation (Supplementary Fig. 9). Notably, a clear dispersion in the CT emission maxima is observed for **Cz-PI**, whereas, the ICz-PI isomers are completely dispersion-free as evident from their time-resolved emission characteristics, owing to their rigidified co-planar structures (Supplementary Fig. 11).

The photophysics of the ICz-PI isomers (***p*-ICz-PI** and ***o*-ICz-PI**), and **Cz-PI** in a small molecule host, [1,3-bis(*N*-carbazolyl)benzene] (mCP) was also characterised (Supplementary Fig. 12-13). The results are generally very similar to those found in zeonex but with higher DF

contribution in mCP, in line with the smaller ΔE_{ST} . These are described in the Supporting Information.

Transient Photoinduced Absorption Measurements

Transient absorption measurements were performed to study the initial excited state formation dynamics for all three derivatives in degassed solution state (DCM and MCH) (Figure 3 and Supplementary Fig. 14). In MCH, **p-ICz-PI** gives an instantaneous excited state absorption (ESA) at 570 nm, followed by the emergence of an 870 nm band within 5 ps (Supplementary Fig. 15). The 870 nm ESA decays in 6.3 ns which correlates well with the fluorescence decay time of 6 ns (Supplementary Table 1), identifying this as the ESA from the emissive, highly delocalised and conjugated mixed LE/CT species. A residual ESA observed at 520-650 nm with a lifetime of 3.9 ns could potentially arise from the LE state as it is not observed in DCM. In DCM, the instantaneous 570 nm ESA band is again observed with a grow-in of ESA at 860 nm within 30 ps which decays with a lifetime of 6.7 ns (Supplementary Fig. 16), consistent with the fluorescence lifetime of 5.6 ns (Supplementary Table 1). The longer formation time could be due to the higher viscous drag of the DCM solvent shell reorganisation compared with MCH, and increased CT nature of the large delocalised mixed LE/CT excited state in DCM.⁴⁸ At the other extreme, **Cz-PI** in MCH (Supplementary Fig. 14 and 17) also has an instantaneous ESA at 560 nm followed by the emergence of a sharp ESA band at 750 nm within ca. 400 fs. This red ESA feature has a lifetime of 12.2 ns matching very closely to the fluorescence lifetime of 15.5 ns, indicating this band originates from the ICT species (Supplementary Table 1 and 3). We also observe a 10-15 nm relaxation of this state within this lifetime. This dispersion arises from dihedral angle inhomogeneity in a twisted D-A molecule, giving a broad-range of excited state lifetimes.^{49,50} In DCM, the instantaneous 560 nm band was observed to decay very rapidly within 1 ps, with the formation of an initial ICT ESA at 730 nm, that rapidly relaxes to 820 nm within ca. 1.7 ps (Figure 3 and Supplementary Fig. 18). This is consistent with the higher polarity and reorganisation of the DCM solvation shell (*vide infra*). The 820 nm ESA has a lifetime of 1.5 ns that matches the 1.5 ns fluorescence lifetime. Notably, from MCH to DCM a solvent shift of 60 nm is observed in the ICT ESA, which is less than the ca. 100 nm solvatochromic shift observed in fluorescence. The band shape and position of this red ESA is very similar to previous observations of ESA from the $^1(\text{Cz})^+$ species^{51,52} which correlates with the expected Cz donor fragment in **Cz-PI** and is indicative of a full charge transfer state. This species is not observed in **p-ICz-PI**, indicating a different (very weak) donor structure.

Finally, the fast photo-dynamics of *o*-ICz-PI has signatures consistent with both the other molecules. In MCH, instantaneous ESA at 570 nm (which we correlate with the 410 nm shoulder observed in the *o*-ICz-PI fluorescence) proceeds to rapid formation of ESA at 650 nm in 1.7 ps that slowly relaxes to 660 nm within 10 ps (Supplementary Fig. 14 and 19). This state decays with a lifetime of 14 ns, in line with the fluorescence lifetime (Supplementary Table 1). Again, we associate this ESA feature with a localised $^1(\text{Cz})^+$ donor species.^{51,52} Within ca. 1 ps, a long wavelength ESA emerges extending beyond 830 nm. This band decays in ca. 3.4 ns, indicating a different species as compared to the 660 nm ESA. In DCM (Figure 3, Supplementary Fig. 20), ESA at 670 nm emerges within 700 fs, followed by ESA at 870 nm

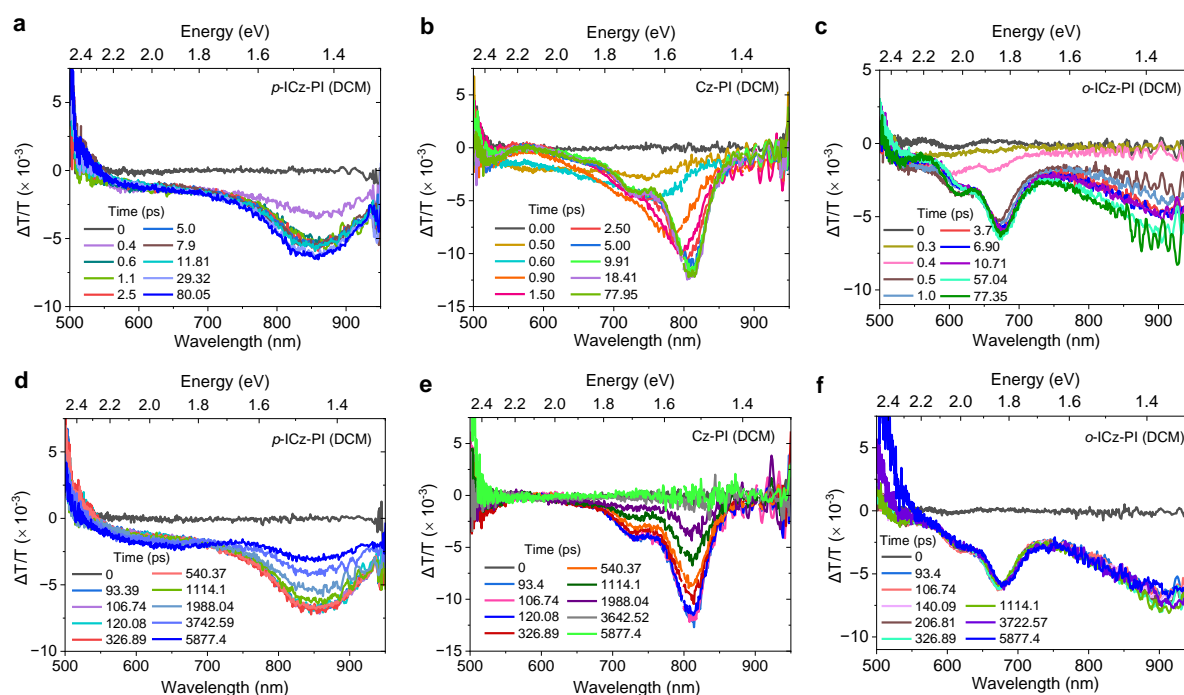


Figure 3. Early time evolution of excited state absorption spectra of *p*-ICz-PI, *o*-ICz-PI and Cz-PI measured in DCM. Excited state absorption measurements in the 0-80 ps and 0-6 ns time windows for (a and d) *p*-ICz-PI, (b and e) Cz-PI and (c and f) *o*-ICz-PI in polar DCM solutions showing the evolution of a stable CT state in *o*-ICz-PI and Cz-PI including relaxation of the CT state through solvent shell reorganisation. However, in *p*-ICz-PI very different spectral evolution shows much more locally-excited state characteristics from a large, conjugated fragment of the molecule. $\lambda_{\text{exc}} = 343 \text{ nm}$, $[c] = 1 \times 10^{-4} \text{ M}$.

over approximately 20 ps. This mirrors to some degree the behaviour of *p*-ICz-PI. The slow decay of both the 670 nm (Supplementary Fig. 20b) band and the apparent lifetime of 32 ns for the 870 nm band matches the measured 35 ns fluorescence lifetime, indicating the presence of

a long-lived ICT state. All lifetimes are collated in Supplementary Table 3. We thus ascribe the 870 nm ESA band to be from the delocalised cation species of the ***o*-ICz-PI** CT state, different to that in **Cz-PI**.

All three molecules have instantaneous ESA at 560-570 nm, ascribed to the LE state of the initially photoexcited fragment. This is seen to decay faster in more polar solution. The observed long-lived ESA of the $^1(\text{Cz})^+$ species in ***o*-ICz-PI** validates the description of ***o*-ICz-PI** as a planar rigidified molecule having a remarkably stable ICT excited state. As the dynamics and ESA spectrum of ***o*-ICz-PI** show part similarities to both ***p*-ICz-PI** and **Cz-PI** we believe this fully confirms our idea that breaking of conjugation forms spatially separated D and A intramolecular fragments on ***o*-ICz-PI**, leading to a stable ICT state. These observations are also corroborated with a detailed computational study reported in the next section.

Electronic Structure Simulations

Figure 4 shows a schematic of the low-lying excited states (red = triplet and blue= singlet) of **Cz-PI**, ***o*-ICz-PI** and ***p*-ICz-PI** at the ground (S_0) and S_1 excited state geometries. The density differences associated with the transition to the lowest excited singlet states are shown on the right. As expected, the orthogonally connected **Cz-PI** shows a strong CT transition from the carbazole donor to phthalimide acceptor. Importantly, despite their structural similarity ***o*-ICz-PI** and ***p*-ICz-PI** show distinct differences in their electronic distribution which is dependent on the bonding pattern between the donor and acceptor, consistent with the experimental differences discussed above.

For ***p*-ICz-PI**, the hole is primarily localized over the single phenyl ring of the *tert*-Cz unit, with some contribution existing in the PI unit (Figure 4, Supplementary Fig. 21-26 and Supplementary Table 4-7). The electron is delocalized over the remaining fragment of the molecule that consists of both the *tert*-Cz and PI units. This configuration results in a very weak "donor" unit, contributing little CT character to the excited state, thus the emission is blue and exhibits predominantly locally-excited (LE) character. In contrast, ***o*-ICz-PI** exhibits a hole that is primarily localized over the whole ICz unit, while the electron is concentrated over the PI unit. This arrangement resembles that of **Cz-PI**, which itself shows even stronger CT character because of the 90° twist between D and A at the N-C bridging bond.

It is remarkable that with effectively 0° 'twist' *i.e.* fully planar, the D-A structure of ***o*-ICz-PI** exhibits such strong charge separation, which is consistent with the lower oscillator

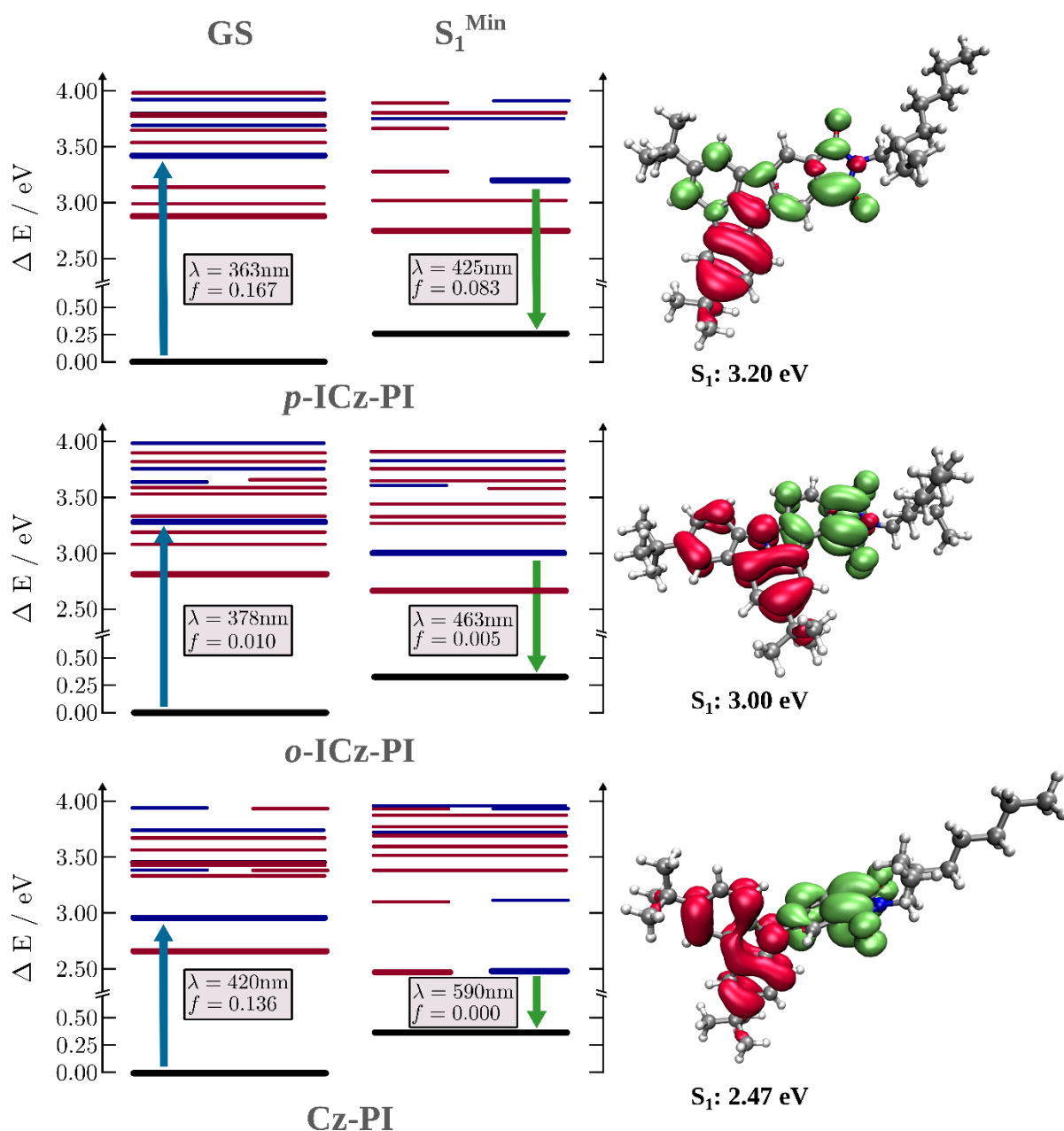


Figure 4. Theoretical energy level diagram with the difference of electronic density associated to the transition from the ground state to S_1 . Schematic of the low-lying excited states (red = triplet and blue = singlet) of *p*-ICz-PI, *o*-ICz-PI and Cz-PI at the ground and S_1 excited state geometries. The density differences associated with these transitions are shown on the right. Transition oscillator strengths are given alongside the calculated transition wavelength. All the energies are shown in Supplementary Table 4, 8 and 12.

strength of absorption for *o*-ICz-PI (Figure 4, Supplementary Fig. 27-32 and Supplementary Table 8-11), resulting in a five-fold reduction in molar absorption coefficient compared to *p*-ICz-PI (*vide infra*). The calculated $S_1 \leftarrow S_0$ oscillator strength (OS) completely reflects this,

showing significantly reduced OS for *o*-ICz-PI ($f = 0.010$), compared to *p*-ICz-PI ($f = 0.167$). Similarly, the $S_0 \leftarrow S_1$ oscillator strength decreases substantially in *o*-ICz-PI ($f = 0.005$) compared to *p*-ICz-PI ($f = 0.083$), indicating a stronger charge-transfer contribution in both the ground and excited states for *o*-ICz-PI.

To understand the stark difference between *o*-ICz-PI and *p*-ICz-PI we used the fragment orbital interaction approach that had previously characterized the competition between twisted and planar intramolecular charge transfer states in a range of D-A chromophores.⁵¹ Figure 5 shows the HOMO and LUMO molecular orbitals of *o*-ICz-PI and *p*-ICz-PI which are dominant in generating the low-lying excited states. For both isomers, the HOMO orbitals remain largely unchanged, while the LUMO orbitals exhibit a difference, becoming more localised on the acceptor for the *o*-ICz-PI. This can be explained by investigating how the LUMO is formed from each donor (Cz) and acceptor (PI) fragment. For *p*-ICz-PI, there is a bonding interaction across both bonding sites leading to a delocalisation of the LUMO across the whole molecule. In contrast, for *o*-ICz-PI there is an anti-bonding interaction across the N-C bond which enforces localisation of the LUMO onto the PI fragment increasing the CT character of the HOMO-LUMO transition. All the photophysics of the two ICz-PI isomers result from the different bonding pattern and separation of D and A fragments in the molecule.

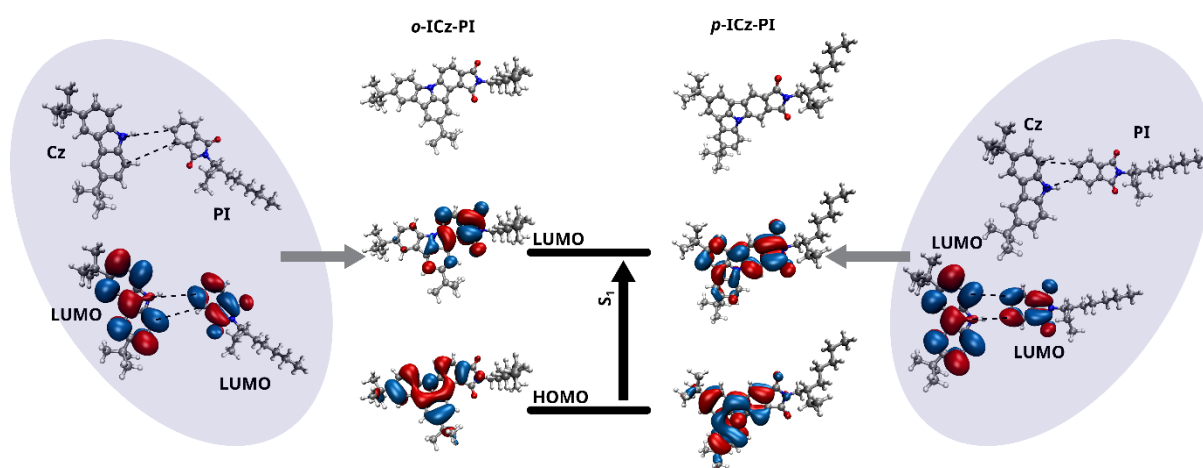


Figure 5. Orbital fragment analysis of *o*-ICz-PI and *p*-ICz-PI HOMO and LUMO levels. Fragment molecular orbital interaction for LUMOs of *o*-ICz-PI and *p*-ICz-PI. As shown in the supporting information, the S_1 state is predominantly HOMO-LUMO character. The character of the HOMO does not change between the two isomers, but the delocalisation of the LUMO is controlled by the interaction between the two fragments.

These simulations demonstrate how sensitive the molecular electronic structure can be to bonding and anti-bonding patterns and that even in a fully-rigidified, co-planar D-A molecule, the CT state can be stabilised making it possible to achieve TADF, counter to previous thinking about these photophysical phenomena. Femtosecond induced absorption measurements further reveal *o*-**ICz-PI** to have an instantaneous induced absorption at 570 nm from an initial LE state; this is a more localised state compared to that seen in *p*-**ICz-PI**, rapid formation within 700 fs of a new state that absorbs at lower energy (at 660 nm) is observed which we ascribed to the formation of the CT excited state (Figure 3 and Supplementary Fig. 14). In DCM, this state at 670 nm has much stronger intensity than in MCH, but the formation rate is slower, ascribed to inductively slow charge reorganisation due to the solvent shell inertia (Figure 3 and Supplementary Fig. 14).⁴⁸ The lifetime of the excited state is concomitant with the fluorescence lifetime measured. The induced absorption at 670 nm (in DCM) or 660 nm (in MCH) is never lost indicating a high level of electronic decoupling of the D and A fragments, independent of solvent polarity, indicating that the broken conjugation effect can fully stabilize the ICT excited state, as predicted by our calculations.

Conclusion

In this work, we have successfully developed a novel rigidized planar charge-transfer design strategy for triplet harvesting in purely organic molecules. Importantly, these co-planar ICT states are highly sensitive to subtle differences in the bonding pattern between the donor and acceptor fragments and therefore through judicious choice of the connecting bonds, charge-transfer stabilization and access to the triplet excited state can be achieved without the need of a twisted excited geometry, previously considered essential for ICT molecules exhibiting TADF. Notably, these emitters are shown to be free of any dynamic charge-transfer state relaxation, typically associated with torsional motion between the donor-acceptor single bond leading to a dispersion of excited charge-transfer energy states and lifetimes. Consequently, development of these emitters could lead to materials with efficient triplet harvesting and highly stable charge transfer states yielding TADF with no dispersive (long-lifetime components) rISC. As recently shown, this is also essential for sensitisation in hyper fluorescent OLED applications and potential long device lifetime.²³

This work opens a new paradigm for triplet harvesters exploiting rigidly planar charge-transfer design strategies. Developing this concept should focus upon identifying suitable donor-acceptor combinations which achieve smaller singlet-triplet gaps in low polarity environments and higher mono-dispersed reverse intersystem crossing rates, both of which will improve device performance. The similarity between the behaviour of the twisted D-A TADF

emitter, **Cz-PI** and its highest performing rigidized planar variant, ***o*-ICz-PI** indicates that a large library of potential candidates based upon planarized versions of existing twisted D-A TADF emitters could be efficiently screened to identify high performing candidates. This will enable our planar rigidized charge-transfer design strategy to become a key focus for future molecular development for efficient triplet harvesting.

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Methods

Synthesis

The detailed synthetic procedures for *p*-ICz-PI, *o*-ICz-PI and Cz-PI, their chemical structure characterizations including ¹H NMR, ¹³C NMR, and high-resolution mass spectrometry can be found in Supplementary Information (Section 3) and Supplementary Figs. 39-52.

Spectroscopic methods

Steady State Measurements

Absorption, photoluminescence and excitation measurements were obtained using drop-cast films on sapphire substrates at 1 by weight for zeonex (1 wt. %) and 10 wt. % by weight (10 wt. %) for the other hosts; for the solution measurement, concentrations of 20 μM were used. A Jobin Yvon Horiba Fluorolog (double-double) spectrofluorimeter and a Shimadzu UV-vis-NIR 3600 spectrophotometer were used for emission and absorption measurements, respectively. All spectral onset energies were corrected using the Jacobian conversion of wavelengths to energies.

Time-Resolved Measurements

The time-resolved measurements were obtained using a Stanford Computer Optics 4Picos gated iCCD camera (250-950 nm) with sub-nanosecond resolution and spectrograph equipped with 300 lines/mm grating, 500 nm blaze wavelength system. For the temperature-dependent measurements, a helium-closed cycle cryopump was used, equipped with optical windows, Si thermodiode, and sample mount, attached directly to the cold head. Excitation was from the 3rd or 4th harmonic of an EKSPLA 200 ps Nd:YAG 10 Hz repetition rate laser. Time-resolved measurements were made using a variable CCD gate and delay times relative to the laser trigger, allowing emission decays to be constructed from the changes in spectrum area (normalised by gate time). TCSPC measurements were recorded with a Horiba DeltaFlex TCSPC system using a Horiba NanoLED (357 nm) and SpectraLED (330 nm) as light sources. PLQY measurements were made using a HORIBA Fluorolog-QM spectrofluorometer equipped with a high-efficiency "ECO" friendly continuous 75 W Xenon arc lamp and a HORIBA integrating sphere. The excitation wavelength used was 375 nm, and the monitored emission depended on the molecule. The spectrofluorometer specific parameters were the excitation and emission slits and exits set to 1 nm, the step size for scanning the spectra was 1 nm, and integration time was 0.1 seconds. The PLQY was then calculated using the built in Quantum Yield Calculator of the spectrofluorometer.

Transient absorption spectroscopy

The laser used in the transient absorption setup is PHAROS from Light Conversion (wavelength: 1030 nm, pulse duration: 180 fs, pulse energy: 0.6 mJ, repetition rate: 1 KHz). Part of the output is used to do third harmonic generation (THG), which produces 343 nm output. We use this 343 nm output to pump our samples and the pulse energy used is about 0.5 μ J. Another part of the output is used to pump a 2 mm sapphire plate to generate white light continuum (WLC). We use this WLC to probe the dynamics of the excited states. The polarization of the pump is vertical to the optical table, while the polarization of the probe is parallel to the optical table. The spot sizes (FW @ $1/e^2$) of the pump and probe are 270 μ m and 200 μ m, respectively. The time delay between pump and probe is controlled by a 1-meter motorized translation stage (Zaber Technologies Inc. A-LST1000AKT07G06SU), which can generate about 6 ns delay range. The pump is modulated by an optical chopper (Thorlabs Inc. MC2000B-EC) that is locked to the half frequency of the laser repetition rate to create an iterated pump on / pump off situation. The WLC goes through a spectrometer and the intensities at different wavelengths are monitored by a camera (Imaging Solutions Group LightWise LW-ELIS-1024A-1394). The camera is synchronized with the laser pulse to ensure it captures the spectrum of WLC pulse by pulse. The transient absorption spectrum at one fixed time delay is calculated by⁴⁸

$$\frac{\Delta T}{T} = \left\{ \sum_{i=1}^N \frac{\text{Spectrum}_{\text{pump on}} - \text{Spectrum}_{\text{pump off}}}{\text{Spectrum}_{\text{pump off}}} \right\} / N$$

where N is average number, in our case N=500. By changing the time delay between pump and probe, we obtain the whole transient absorption spectra.

Computational methods

All calculations were performed using the ORCA 5 quantum chemistry package.^{54,55}

Ground state and S₁ and T₁ minimum geometries were optimised using density functional (DFT) and time-dependent DFT (TD-DFT), respectively. The PBE0 functional⁵⁶ was employed throughout in conjunction with the def2-TZVP basis set⁵⁷ within the Tamm-Dancoff approximation.⁵⁸ All optimised geometries were confirmed to be minima of the potential energy surfaces by normal mode analysis. Calculations were performed in gas phase and methylcyclohexane (MCH), toluene and dichloromethane (DCM). Solvent environments described using the conductor-like polarizable continuum medium (CPCM).⁵⁹ XYZ Cartesian coordinates files are available for download as an archive.

Data availability

The data that support the plots within this paper and supplementary information and other findings of this study are available from the corresponding authors upon reasonable request.

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Author contributions

S.K. and A.P.M conceived the idea. S.K. designed the molecules, performed the synthesis and characterization under the supervision of M.R.B. S.K. and H.M.S. conducted the time-resolved photoluminescence measurements. H.M.S. performed the photoluminescence quantum yields. H.M.S., S.K. and C.L. performed the time-resolved transient absorption measurements. The quantum chemical modelling was done by J.E. and T.J.P. The preparation and editing of the manuscript were led by S. K., J. E. and A. P. M. with contributions and data interpretation from all authors. A.P.M. supervised the project.

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Ethics declarations

Competing interests

The authors declare no competing interests.

TOC graphic

