The role of conformational heterogeneity in the excited state dynamics of linked diketopyrrolopyrrole dimers

Electronic Supplementary Information

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Contents

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S1 Synthesis

S1.1 General

All reactions were performed in oven-dried glassware under nitrogen or argon. Unless stated otherwise all chemicals and solvents were purchased from Sigma-Aldrich or Merck and used as received. Analytical thin layer chromatography (TLC) was carried out using aluminium backed 0.2mm thick Merck Kieselgel Silica gel 60 GF254. All compounds were visible or visualised under UV 254nm or developed using iodine. Purification steps were conducted using recrystallisation or manual column chromatography with Merck Silica gel. Nu magnetic resonance (NMR) spectra 1H and 13C nuclei were recorded at ambient temperature (25°C) using a 400 MHz spectrometer operating at 400MHz and 101MHz respectively. All 1H and 13C NMR were obtained using CDCl3 or d6-DMSO. The 1H NMR chemical shifts (δ) are expressed in ppm relative to the residual CHCl3 (7.26 ppm) and residual DMSO (2.50 ppm), followed in brackets by multiplicity (s: singlet, d:doublet, t:triplet, m: multiplet, dd: doublet of doublet, dt :doublet of triplets), coupling constant (J) given in Hertz (Hz). Proton-decoupled 13C NMR chemical shift was reported as chemical shift (ppm), and were similarly referenced to the centre peaks of solvent used: CDCl3 (77.1 ppm) and d6-DMSO (39.52 ppm)

S1.2 Synthesis of 2-Hexyl-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione.

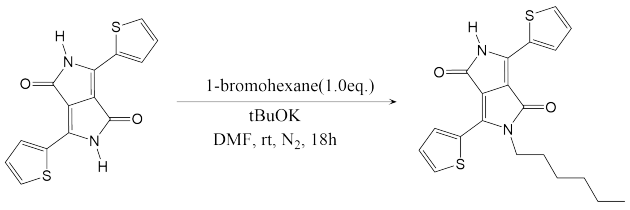

Fig. S1 Synthesis procedure for DPP dimer precursor chromophore unit.

To a stirred solution of 3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (1.0 g, 3.33 mmol) in anhydrous DMF (10mL) was added potassium tert-butoxide (1.16 g, 10.36 mmol) slowly at room temperature. The resulting dark purple solution was stirred for 1h and then 1-bromohexane (0.55 g, 3.33 mmol) was added drop-wise. After stirring the reaction mixture overnight, DMF was removed in vacuo and the crude product was dissolved in chloroform(30mL) and washed with water (2×20 mL), dried over MgSO4, filtered, then recrystallised (DCM: Petroleum ester), leaving the pure product as a crimson crystal, 0.706 g, 55% yield. 1H NMR (400 MHz, CDCl3): δ 8.89 (d, J = 3.9 Hz, 1H, Ar-H), 8.75 (s, 1H, N-H), 8.35 (d, J = 3.6 Hz, 1H, Ar-H), 7.67 (d, J = 5.0 Hz, 1H, Ar-H), 7.61 (d, J = 4.9 Hz, 1H, Ar-H), 7.35 – 7.29 (m, 1H, Ar-H), 7.25 – 7.22 (m, 1H, Ar-H), 4.12 – 4.04 (m, 2H, NCH2), 1.76 (dt, J = 15.5, 7.7 Hz, 2H, CH2), 1.42 (d, J = 7.4 Hz, 2H, CH2), 1.33 (dd, J = 8.8, 5.2 Hz, 4H, CH2), 0.94 – 0.83 (m, 3H, CH3).

S1.3 Synthesis of 5,5'-(Pentane-1,5-diyl)bis(2-hexyl-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione).

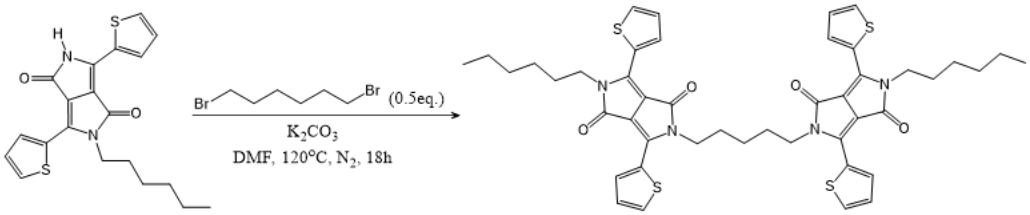

Fig. S2 Synthesis procedure for c5-linked DPP dimer.

2-Hexyl-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (0.2 g, 0.158 mmol), K2CO3 (0.143 g, 1.036 mmol), and a catalytic amount of 18-crown-6 were dissolved in anhydrous DMF (15 mL). A solution of 1,5-dibromopentane (0.054 g, 0.235 mmol) in 2mL DMF was then added to the mixture drop-wise, and the mixture was stirred at 120 °C overnight. The reaction mixture was cooled and concentrated in vacuo. The crude product was dissolved in chloroform (15 mL) and washed with water (20 mL), dried over MgSO4, and then purified on silica gel (DCM: Ethyl acetate) to give

the pure product as a purple solid, 0.082g, 32% yield. 1H NMR (400 MHz, CDCl3): δ 8.90 (d, J = 3.8 Hz, 4H, Ar-H), 7.62 (dd, J = 10.2, 4.9 Hz, 4H, Ar-H), 7.31 – 7.26 (m, 4H, Ar-H), 4.07 (dd, J = 16.1, 10.0 Hz, 8H, NCH2), 1.83 (dd, J = 15.1, 7.7 Hz, 4H, CH2), 1.73 (dd, J = 15.5, 7.9 Hz, 4H, CH2), 1.41 (d, J = 7.4 Hz, 4H, CH2), 1.37 – 1.25 (m, 10H, CH2), 0.88 (t, J = 6.7 Hz, 6H, CH3). 13C-NMR (101 MHz, CDCl3): δ 161.37, 140.08, 139.96, 135.36, 130.21, 130.21, 128.45, 42.28, 42.78, 31.34, 29.87, 29.23, 26.48, 24.42, 22.21, 13.97.

S1.4 Synthesis of 5,5'-[1,2-phenylenedi(methylene)]bis(2-hexyl-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione.

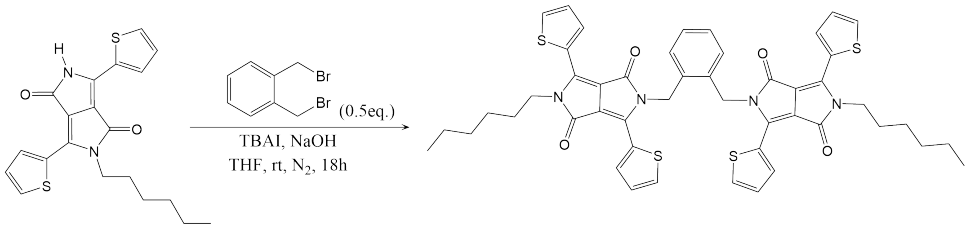

Fig. S3 Synthesis procedure for ortho-xylyl linked DPP dimer.

2-Hexyl-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (0.05 g, 0.129 mmol), and NaOH (0.014 g, 0.259 mmol), and a catalytic amount of tetrabutylammonium iodine were dissolved in THF(5 mL) and stirred for 30 minutes. A solution of α,α'-dibromo-o-xylene(0.016 g, 0.06 mmol) in THF(2 mL) was added drop-wise and the resulting mixture stirred at room temperature overnight. After removal of the solvent in vacuo, the crude product was dissolved in chloroform (15 mL) and washed with water (20 mL), dried over MgSO4, and then purified on silica gel (DCM: Petroleum ester) to give the pure product as a pink waxy solid, 0.0292g, 26% yield. 1H NMR (400 MHz, CDCl3): δ 9.00 (d, J = 3.8 Hz, 2H, Ar-H), 8.66 (d, J = 3.8 Hz, 2H, Ar-H), 7.66 (d, J = 4.9 Hz, 2H, Ar-H), 7.54 (d, J = 4.9 Hz, 2H, Ar-H), 7.31 – 7.27 (m, 2H, Ar-H), 7.20 – 7.17 (m, 2H, Ar-H), 7.13 (dd, J = 5.6, 3.4 Hz, 2H, Ar-H), 7.06 – 7.02 (m, 2H, Ar-H), 5.42 (s, 4H, Ar-CH2-N), 4.14 – 4.07 (m, 4H, NCH2), 1.83 – 1.76 (m, 4H, CH2), 1.51 – 1.30 (m, 16H, CH2), 0.91 (t, J = 6.8 Hz, 6H, CH3). 13C NMR (101 MHz, CDCl3): δ 161.21, 135.72, 134.67, 133.27, 131.47, 131.05, 129.60, 128.60, 127.83, 124.95, 42.89, 42.35, 31.41, 29.91, 26.59, 22.57, 14.02.

S1.5 Synthesis of 5,5'-[1,3-phenylenedi(methylene)]bis(2-hexyl-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione).

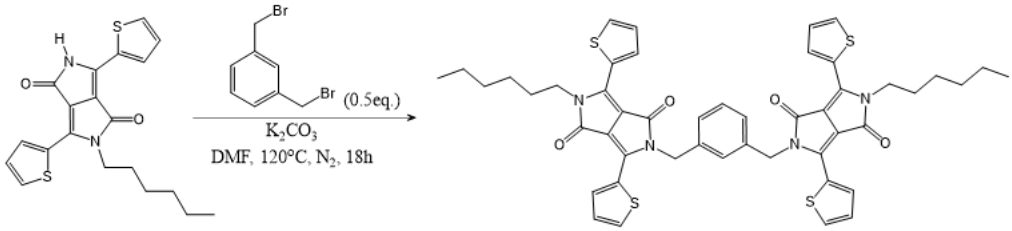

Fig. S4 Synthesis procedure for meta-xylyl linked DPP dimer.

2-Hexyl-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (0.2 g, 0.518 mmol), K2CO3 (0.143 g, 1.036 mmol), and a catalytic amount of 18-crown-6 were dissolved in anhydrous DMF (15 mL). A solution of α,α'-dibrom-m-xylene(0.062 g, 0.235 mmol) in 5mL DMF was then added to the mixture drop-wise, and the mixture was stirred at 120 °C overnight. After removal of the solvent in vacuo, the crude product was dissolved in chloroform (15 mL) and washed with water (20 mL), dried over MgSO4, and then purified on silica gel (DCM) to give the pure product as a dark red solid, 0.135 g, 37% yield. 1H NMR (400 MHz, CDCl3): δ 8.92 (d, J = 3.9 Hz, 1H, Ar-H), 8.54 (d, J = 3.8 Hz, 1H, Ar-H), 7.66 (d, J = 5.0 Hz, 1H, Ar-H), 7.37 (d, J = 4.9 Hz, 1H, Ar-H), 7.29 – 7.26 (m, 1H, Ar-H), 7.24 (s, 1H, Ar-H), 7.13 (d, J = 7.7 Hz, 1H, Ar-H), 7.07 – 7.01 (m, 2H, Ar-H), 5.28 (s, 2H, Ar-CH2-N), 4.12 – 4.01 (m, 2H, NCH2), 1.76 (dt, J = 15.5, 7.8 Hz, 2H, CH2), 1.50 – 1.28 (m, 7H, CH2), 0.89 (t, J = 6.8 Hz, 3H, CH3). 13C NMR (101 MHz, CDCl3): δ 161.21, 135.72, 134.67, 133.27, 131.47, 131.05, 129.60, 128.60, 127.83, 124.95, 42.89, 42.35, 31.41, 29.91, 26.59, 22.57, 14.02.

S1.6 Synthesis of 2,5-Dihexyl-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione.

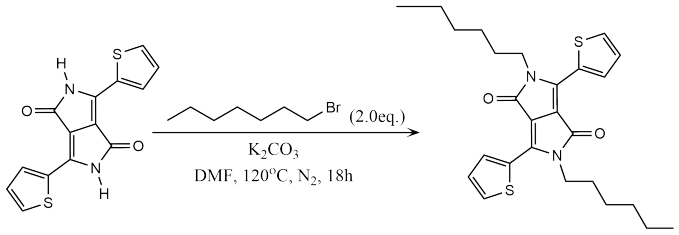

Fig. S5 Synthesis procedure for c5 model compound.

3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (1.0 g, 3.33mmol) and K2CO3 (1.38 g, 9.99mmol) were dissolved in anhydrous DMF(40 mL) and the mixture was heated at 120 °C for 30 minutes under nitrogen. 1-Bromohexane (1.03mL, 7.32mmol) was added drop-wise to the reaction mixture and the resultant solution was heated at 120 °C overnight. The reaction was cooled, and the solvent was removed in vacuo. Methanol(150 mL) was added to the crude product and stirred for 1 hour. The suspension was collected by vacuum filtration, washed with methanol and water, then recrystallised (DCM: Petroleum ester) to give the pure product as a shiny dark purple crystal, 1.67 g, yield 67%. m.p. 173.9-175.3 °C 1H NMR (400 MHz, CDCl3): δ 8.92 (d, J = 3.9 Hz, 2H, Ar-H), 7.64 (d, J = 5.0 Hz, 2H, Ar-H), 7.30 – 7.27 (m, 2H, Ar-H), 4.10 – 4.03 (m, 4H, NCH2), 1.74 (dt, J = 15.6, 7.7 Hz, 4H, CH2), 1.41 (dd, J = 14.6, 6.8 Hz, 4H, CH2), 1.37 – 1.29 (m, 8H, CH2), 0.88 (t, J = 6.9 Hz, 6H, CH3). 13C NMR (101 MHz, CDCl3): δ 161.33 (C=0), 139.99 (C-N), 135.23 (C-H), 130.64 (CH), 129.75 (CS), 128.57 (CH), 107.67 (C-CO), 42.20 (CH2), 31.39 (CH2), 29.90 (CH2), 26.53 (CH2), 22.54 (CH2), 13.99 (CH3).

S1.7 Synthesis of 2-hexyl-5-(prop-2-yn-1-yl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione.

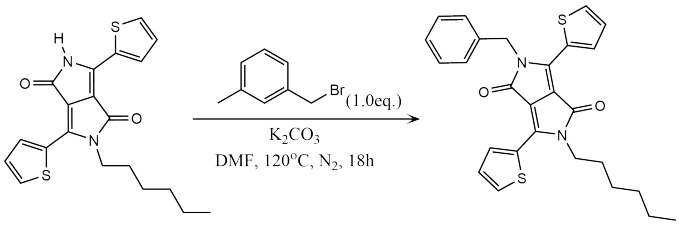

Fig. S6 Synthesis procedure for benzyl model compound.

2-Hexyl-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (0.05 g, 0.129 mmol), K2CO3 (0.259 g, 0.035 mmol), and a catalytic amount of 18-crown-6 were dissolved in anhydrous DMF (5 mL) and heated at 120 °C for 30 minutes under nitrogen. A solution of 4-methylbenzyl bromide (0.024 g, 0.129 mmol) in 2mL DMF was then added to the mixture drop-wise, and the mixture was stirred at 120 °C overnight. The reaction mixture was cooled and concentrated in vacuo. The crude product was dissolved in chloroform (15 mL) and washed with water (20 mL), dried over MgSO4, and then concentrated and purified on silica gel (DCM: Ethyl acetate) to give the pure product as a purple solid, 0.030 g, 46% yield. 1H NMR (400 MHz, CDCl3): δ 8.98 (d, J = 3.6 Hz, 1H, Ar-H), 8.64 (d, J = 3.6 Hz, 1H, Ar-H), 7.66 (d, J = 4.9 Hz, 1H, Ar-H), 7.53 (d, J = 4.9 Hz, 1H, Ar-H), 7.29 (d, J = 4.4 Hz, 1H, Ar-H), 7.19 (t, J = 6.6 Hz, 2H, Ar-H), 7.04 (d, J = 7.0 Hz, 3H, Ar-CH3), 5.31 (s, 2H, Ar-CH2-N), 4.13 – 4.07 (m, 2H, NCH2), 1.77 (dd, J = 14.9, 7.4 Hz, 2H, CH2), 1.45 (s, 2H, CH2), 1.34 (d, J = 3.3 Hz, 4H, CH2), 0.90 (d, J = 6.6 Hz, 3H, CH3). 13C NMR (101 MHz, CDCl3): δ 161.43, 136.87, 135.62, 134.60, 133.83, 130.97, 129.66, 129.40, 128.66, 128.35, 126.14, 45.11, 42.28, 31.40, 29.90, 26.55, 22.55, 21.06, 14.00.

S2 NMR

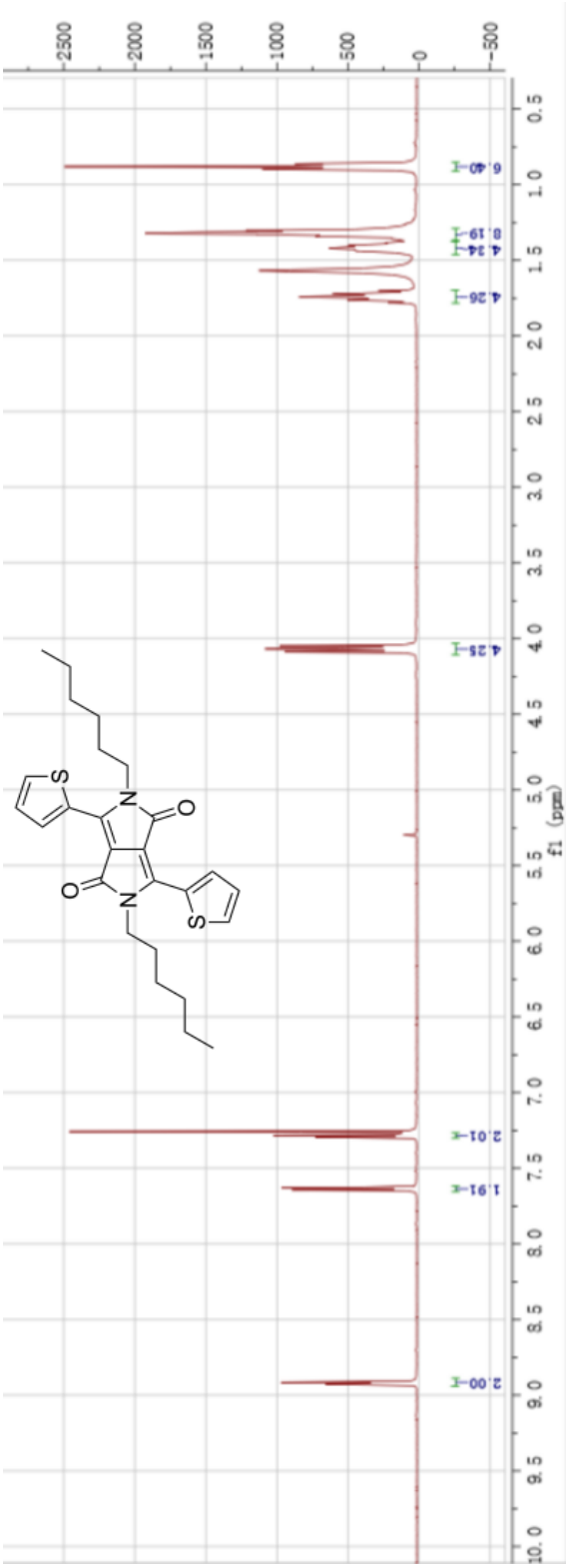

Fig. S7 1H NMR spectrum of the c6 monomer derivative. Assignments of NMR signals are given in section S1.6.

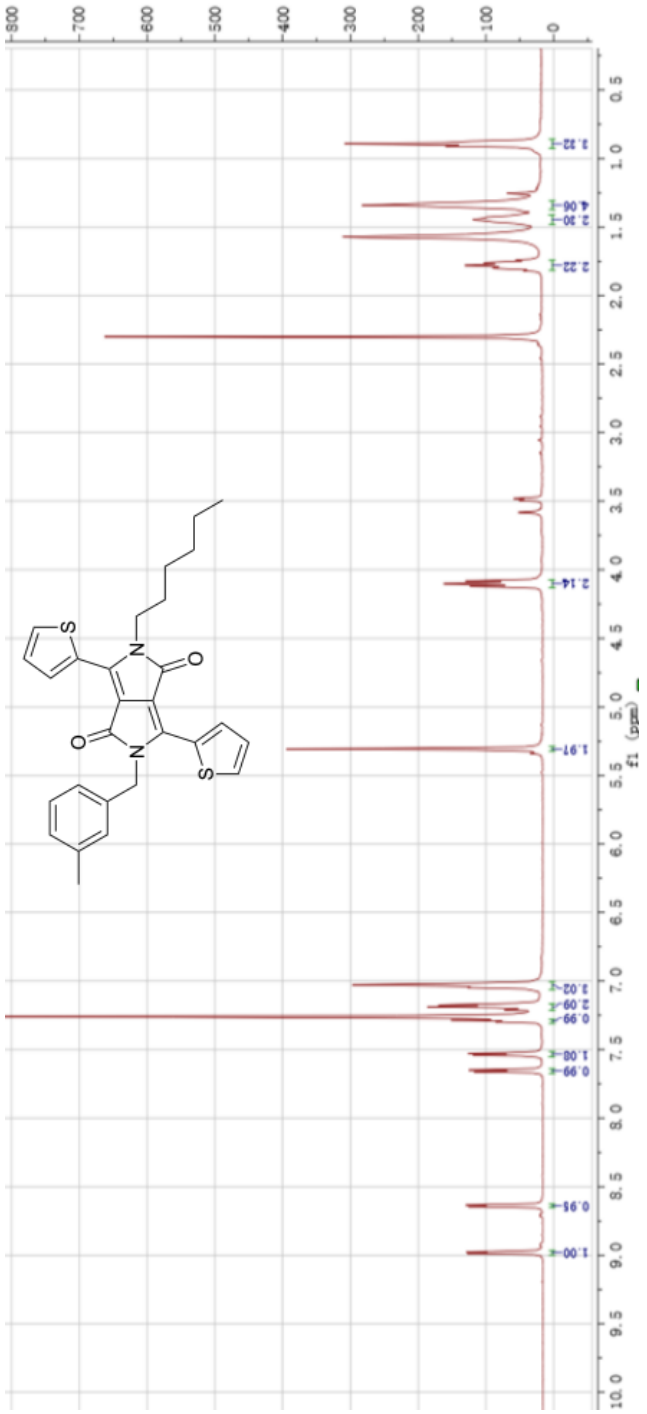

Fig. S8 1H NMR spectrum of the benzyl monomer derivative. Assignments of NMR signals are given in section S1.7.

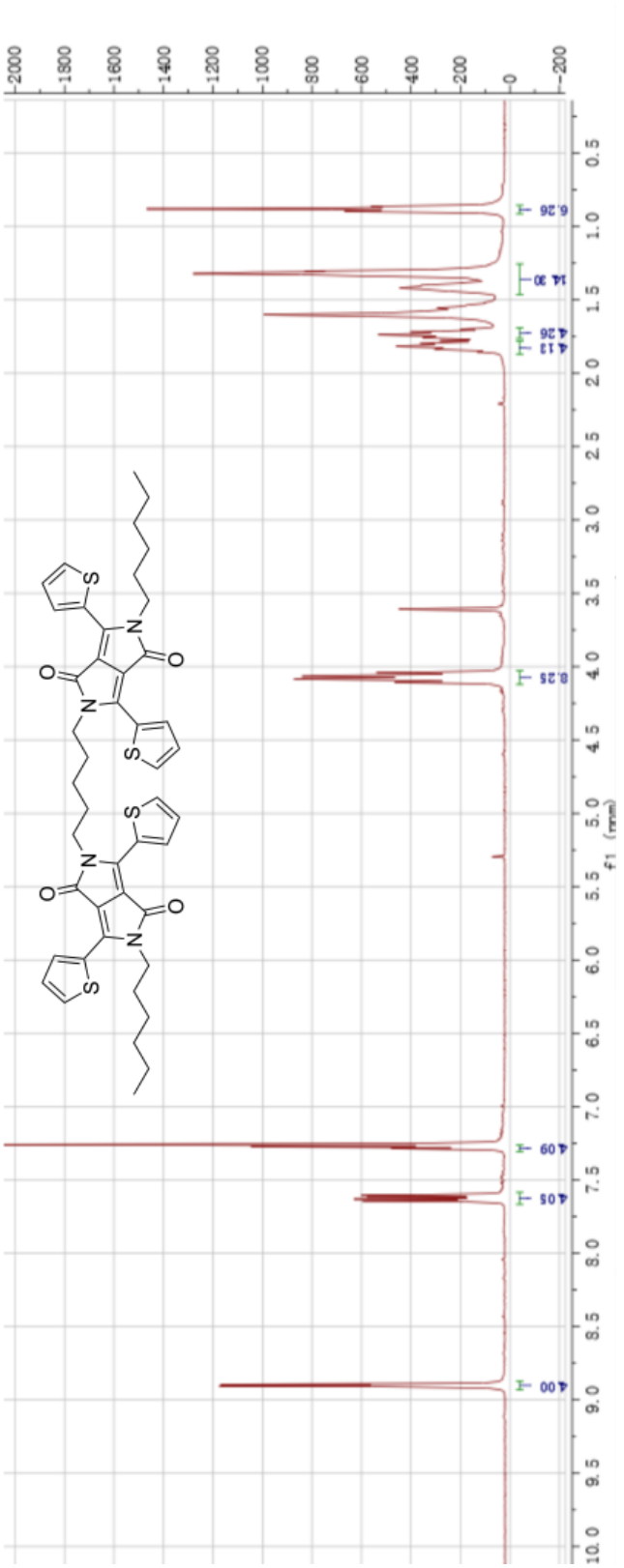

Fig. S9 1H NMR spectrum of the c5-dimer derivative. Assignments of NMR signals are given in section S1.3.

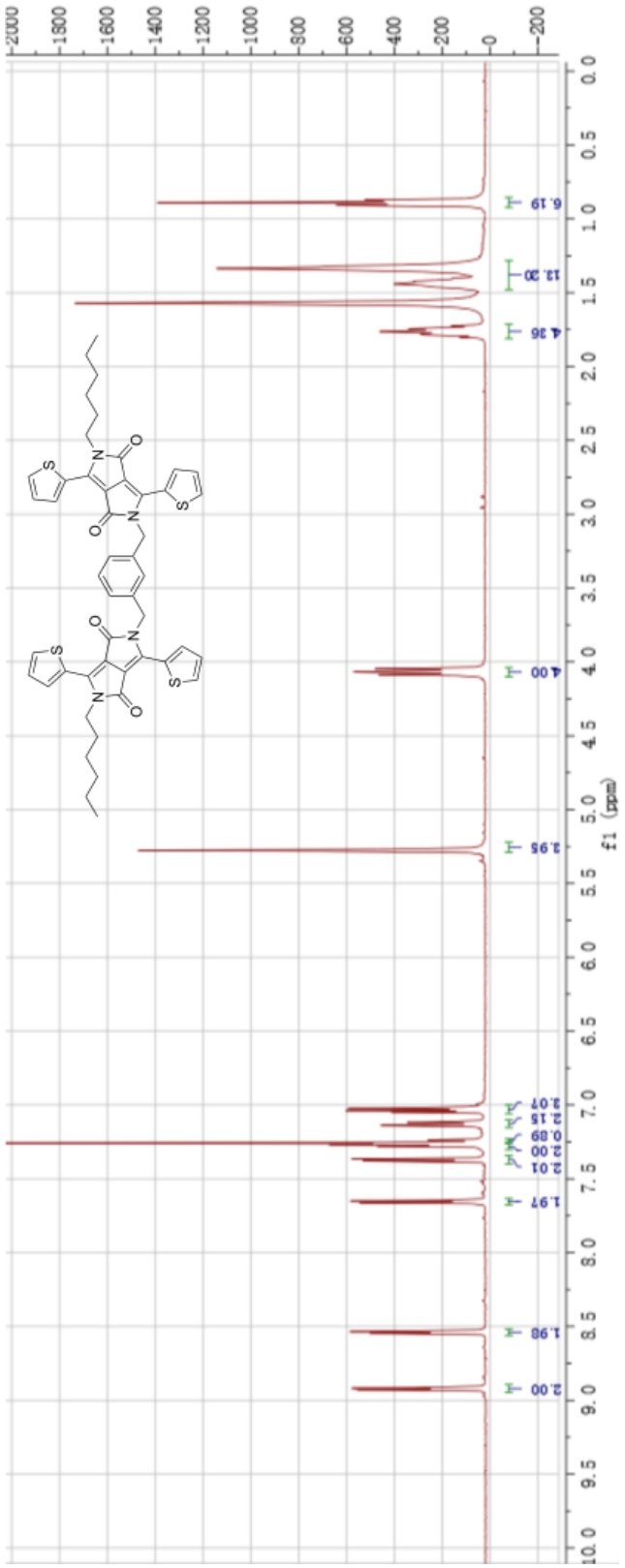

Fig. S10 1H NMR spectrum of the meta-xylyl dimer derivative. Assignments of NMR signals are given in section S1.5.

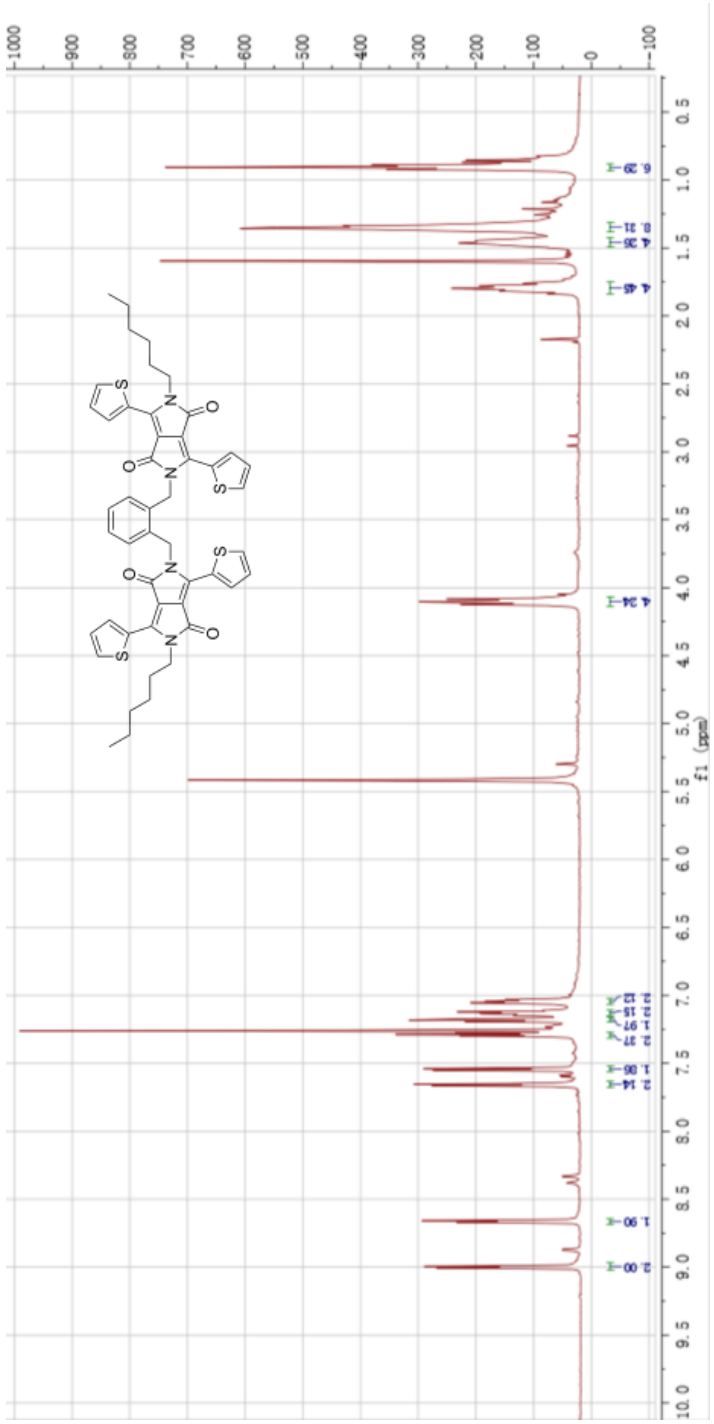

Fig. S11 1H NMR spectrum of the ortho-xylyl dimer derivative. Assignments of NMR signals are given in section S1.4.

S3 Computational Analysis

The minimum interchromophore distance for the lowest energy conformations of the dimers (as judged by the closest points between the DPP chromophore units, ignoring solubilising side-chains) was 3.67 Å for the m-xylyl dimer and 3.35 Å for the c5 dimer in DMSO and 3.55 Å for the m-xylyl dimer and 3.27 Å for the c5 dimer in toluene.

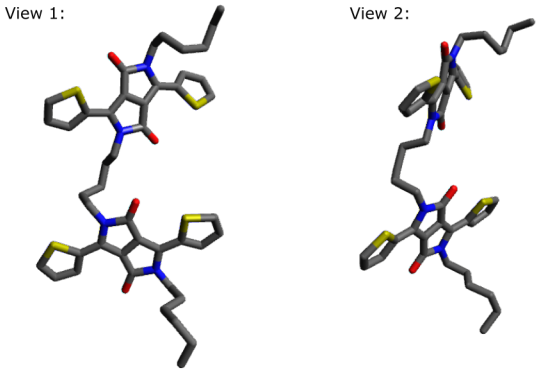

Fig. S12 Structure of the extended conformation of c5-DPP dimer calculated from two different view points. B97-3c(COSMO) level of theory.

Table S1 Full list of calculated ground-state conformations of m-xylyl - and c5- DPP dimer. Energy differences (ΔE) relative to the most stable conformer are shown (ωB97X-2-D3(BJ)/def2-TZVPP(CPCM)/B97-3c(COSMO) level of theory). Each structure is unique to the solvent continuum it is calculated in. The extended conformations such as that shown in Figure S12, are given for the c5- dimer only

Number	ΔE, kcal/mol	Boltzmann weight (T = 298.15 K)
m-xylyl dimer	DMSO	
1	0	99.9
2	4.13	0.1
3	6.62	0
4	7.00	0
m-xylyl dimer	toluene	
1	0	99.4
2	3.04	0.6
3	6.08	0
4	6.49	0
c5- dimer	DMSO	
1	0	89.0
2	1.86	3.9
3	2.08	2.7
4	2.43	1.5
5	2.70	0.9
6	3.04	0.5
7	3.09	0.5
8	3.11	0.5
9	3.32	0.3
10	3.62	0.2
11	5.01	0.0
12	5.15	0.0
Extended	74.08	0.0
c5- dimer	toluene	
1	0	71.8
2	1.00	13.2
3	1.37	7.1
4	2.04	2.3
5	2.4	1.3
6	2.57	0.9
7	2.65	0.8
8	2.65	0.8
9	2.79	0.6
10	3.04	0.4
11	3.14	0.4
12	3.29	0.3
13	4.26	0.1
14	5.45	0.0
Extended	20.36	0.0

S4 Photophysical characterisation

S4.0.1 Steady-State measurements

A strong charge-transfer band exists in the absorption spectrum of DPP arising from charge donation from the electron-rich aryl group to the electron-poor lactam core.[1] However it has also been shown that the extent of this charge shift is reduced in the excited state of DPP.[2] The reduction in polarity of the excited state explains the slight negative solvatochromism observed in benzonitrile versus toluene. All derivatives show a very slight absorption red-shift in benzonitrile, likely due to the stabilisation of the ground state charge-transfer between the aryl rings and the lactam core.

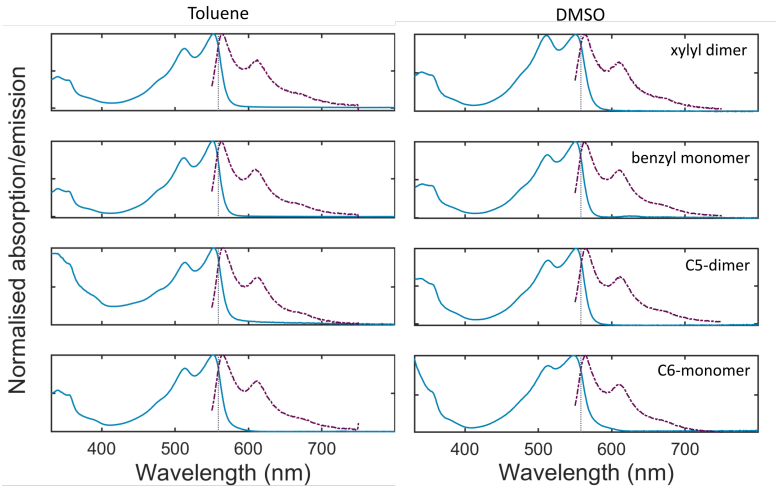

Fig. S13 Steady-state absorption and emission spectra for all monomers and dimers in toluene and DMSO.

S4.0.2 TCSPC

Each of the dimers showed different quenching behaviour in the various solvents. Figure S14 compares the fluorescence decay curves for each derivative in the three solvents studied with fit parameters given in Table S2.

Table S2 Comparison of decay times from the multiexponential fit to the fluorescence decays for all DPP derivatives. $\tau_{1,2,3} = 1/k_{1,2,3}$. B_i indicates the proportion of the total signal amplitude

		τ_{TCSPC}, (ps) (B_i%)		
Solvent	Derivative	τ_1	τ_2	τ_3
toluene	CM	5673 (100%)		
	BM	5418 (100%)		
	c5-DPP	4620 (100%)		
	o-DPP	5133 (100%)		
	m-DPP	2250 (41%)	5486 (59%)	
DMSO	CM	6138 (100%)		
	BM	6265 (100%)		
	c5-DPP	1150 (43%)	6069 (57%)	
	o-DPP	540 (85%)	5468 (15%)	
	m-DPP	884 (48%)	5830 (52%)	
bn	CM	6261 (100%)		
	BM	6067 (100%)		
	c5-DPP	1920 (89%)	5660 (11%)	
	o-DPP	922 (85%)	5213 (15%)	
	m-DPP	423 (59%)	1330 (34%)	5648 (34%)

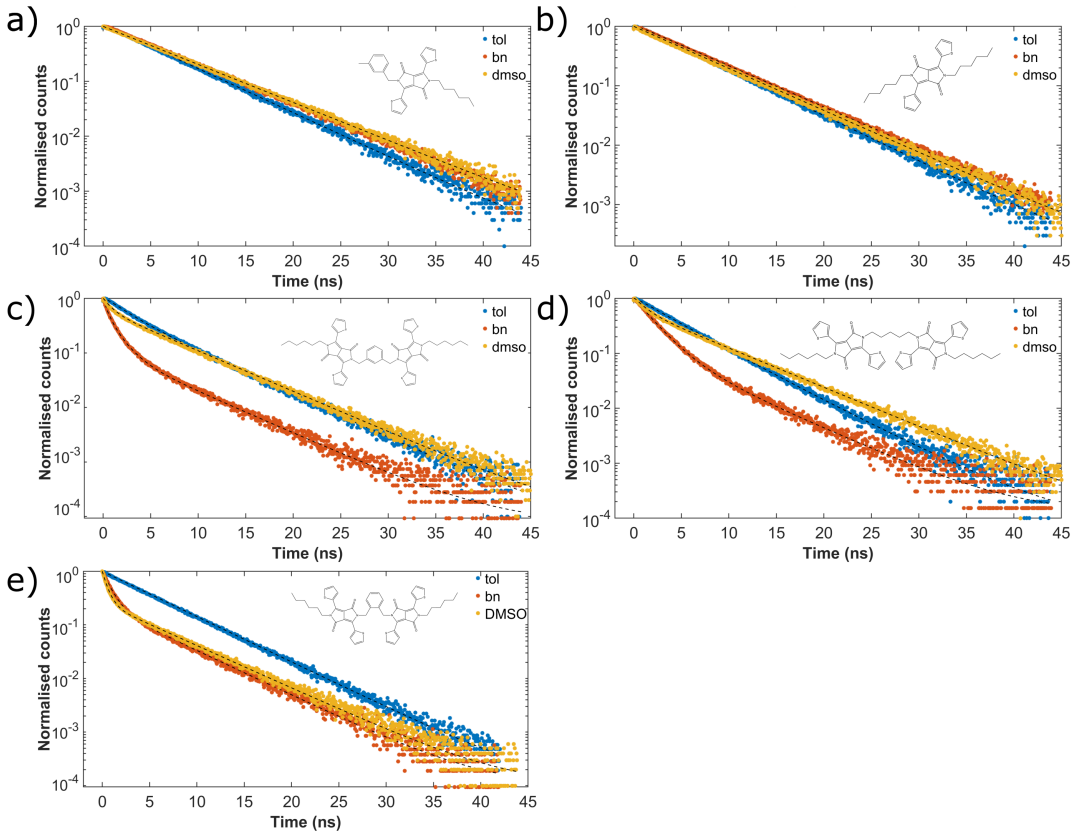

Fig. S14 Fluorescence decay curves showing the different quenching behaviour of the each DPP derivative as indicated by the structure inset, in toluene (blue), benzonitrile (red) and DMSO (yellow). Excitation wavelength was 400 nm and detection wavelength was 565 nm.

S4.0.3 TA

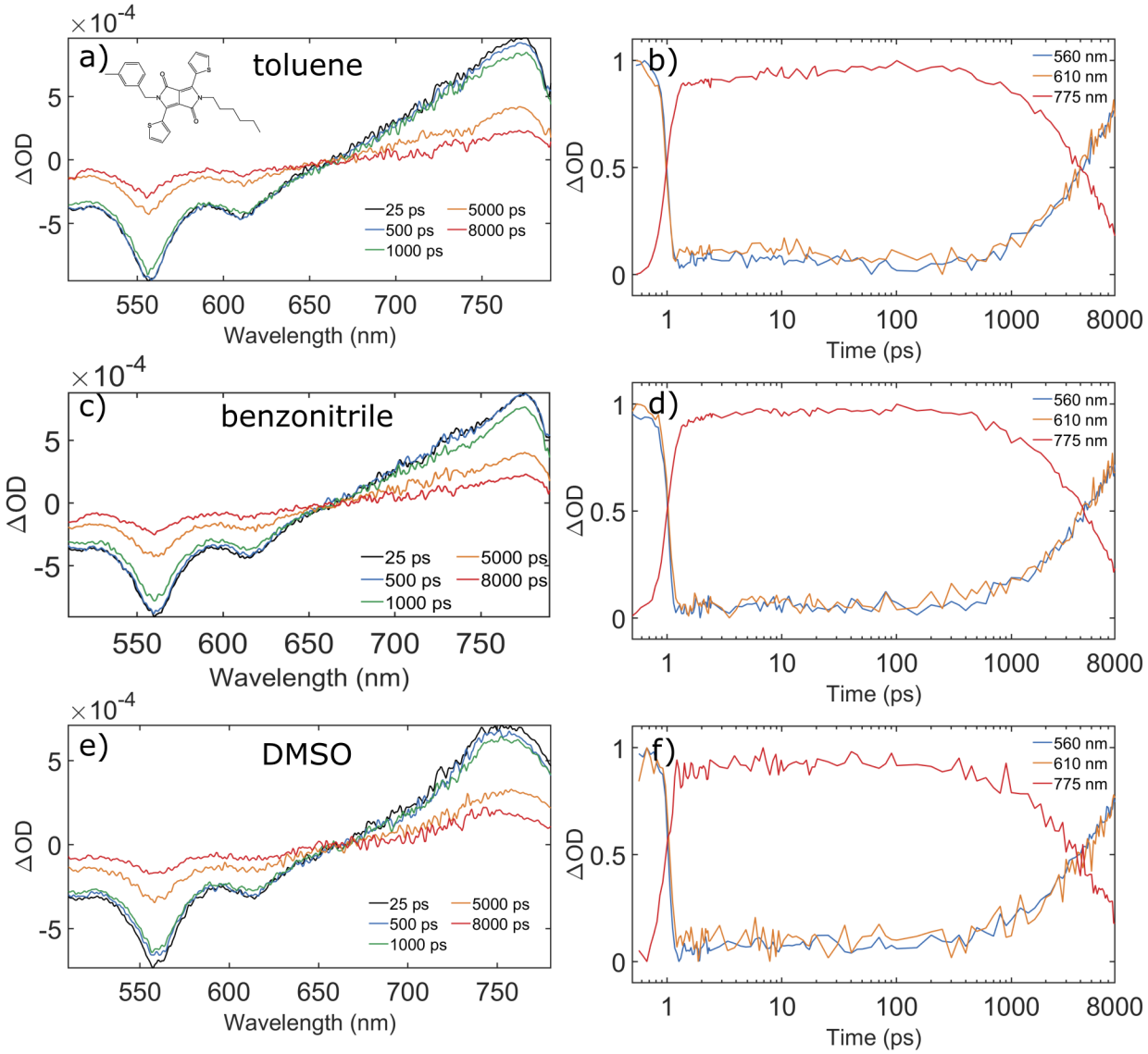

Fig. S15 Transient absorption of the benzyl model compound in the three solvents as indicated. Spectral traces at indicated pump-probe delay times (a, c, e) and temporal traces at indicated wavelengths (b, d, f).

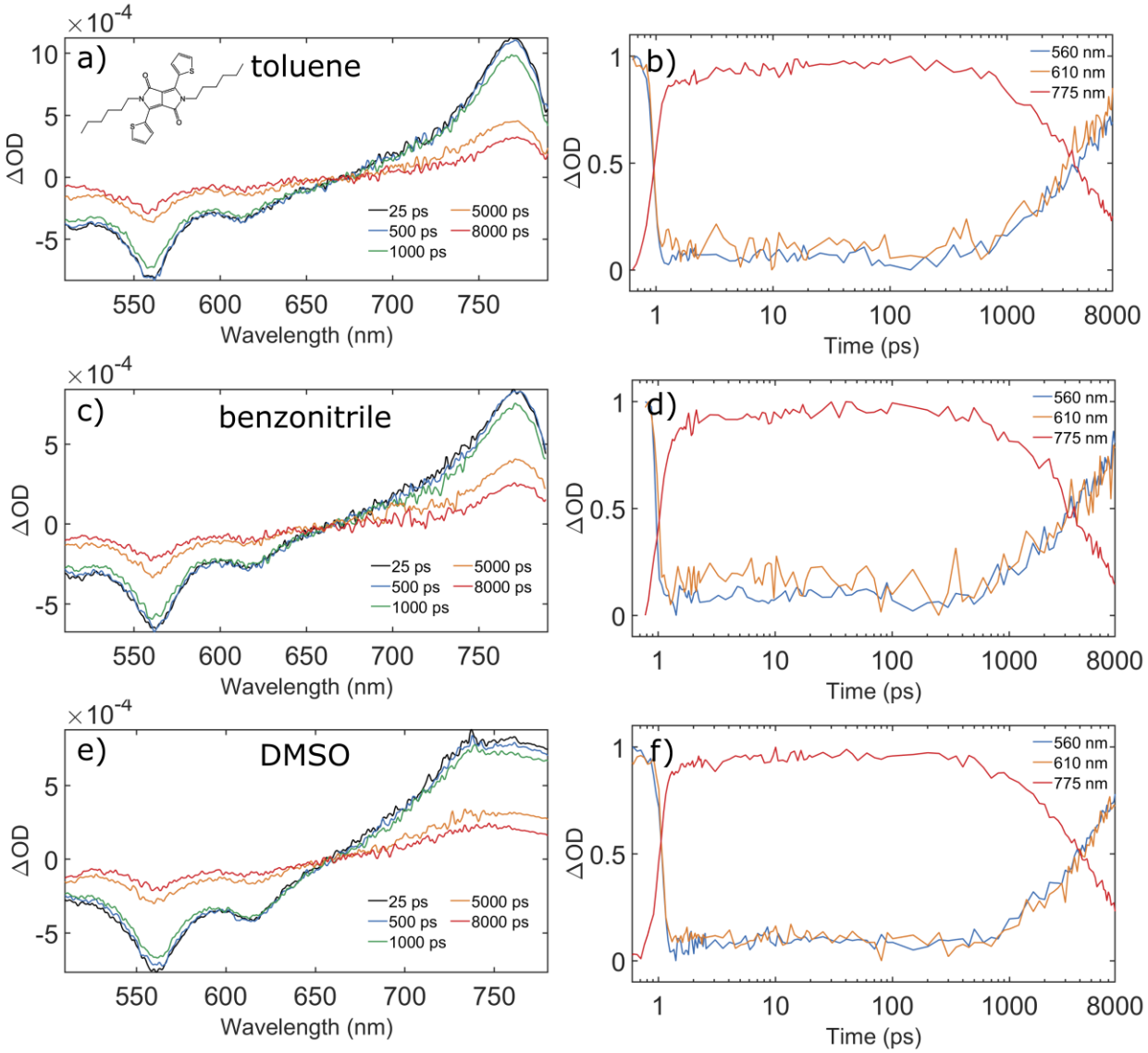

Fig. S16 Transient absorption of the C6- model compound in the three solvents as indicated. Spectral traces at indicated pump-probe delay times (a, c, e) and temporal traces at indicated wavelengths (b, d, f).

S4.0.4 Global Analysis

The transient absorption datasets for all derivatives were initially fit to a simple parallel decaying (all states simultaneously populated and then decay) or sequential (each state sequentially populated from the previous state) model with the fewest exponential terms required to achieve a good fit. For the monomers in all solvents and the o-xylyl- and c5-dimers in toluene a single exponential decay function provided an adequate fit to the datasets. For the c5-, o-xylyl and m-xylyl dimer in DMSO as well as the o-xylyl dimer in benzonitrile, a sum of 3 exponential terms was required to fit the data adequately but the model gave unrealistic evolution-associated spectra i.e. suggesting unlikely bleaches or excited state spectral features. Given the evidence for monomer-like emission from these dimers, a model was developed where two subpopulations of molecules exist with differing molecular conformations. The first relaxes radiatively to the ground state with a rate that was fixed based on the fluorescence lifetime of the model compound. The second population relaxes via a charge-separated state. The two populations are independent of each other.

Singlet population A $\rightarrow$ GS

+

Singlet population B $\rightarrow$ CS $\rightarrow$ GS

The branching ratio of the two pathways was fixed based on the pre-exponential factors of the biexponential fit to the fluorescence decays. The species associated spectra generated from this fit gave two species with singlet-like spectral features and one with an absorption in the region of the charge-separated state at 640 nm as expected.

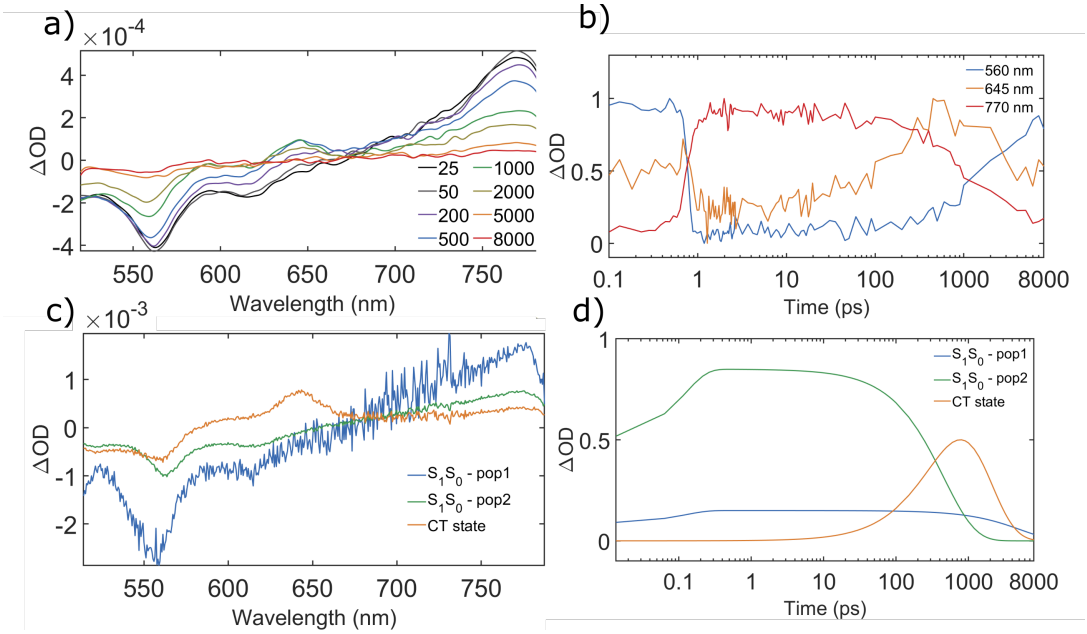

Fig. S17 a) Femtosecond-transient absorption spectra of o-DPP in benzonitrile (pump 505 nm, delays 0 - 8ns). b) Temporal absorption profiles of key transient features as labelled. c) Species associated spectra output of the global fit using the branched kinetic model described above, labelled as singlet population 1 in blue, singlet population 2 in green and CS state in yellow. d) Population kinetics of the aforementioned species.

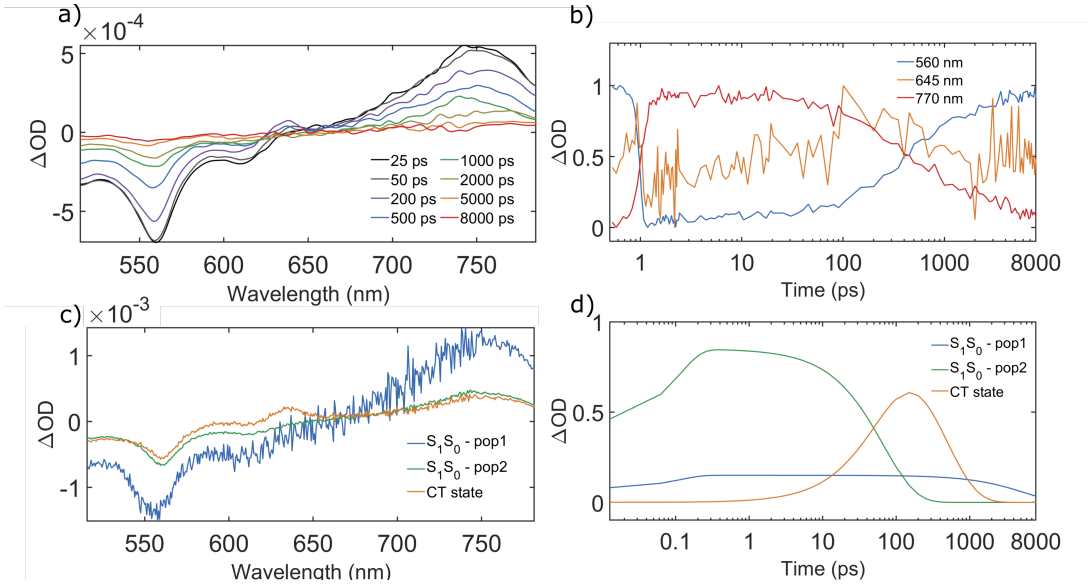

Fig. S18 a) Femtosecond-transient absorption spectra of o-DPP in dmso (pump 505 nm, delays 0 - 8ns).b) Temporal absorption profiles of key transient features as labelled. c) Species associated spectra output of the global fit using the branched kinetic model described above labelled as singlet population 1 in blue, singlet population 2 in green and CS state in yellow. d) Population kinetics of aforementioned species.

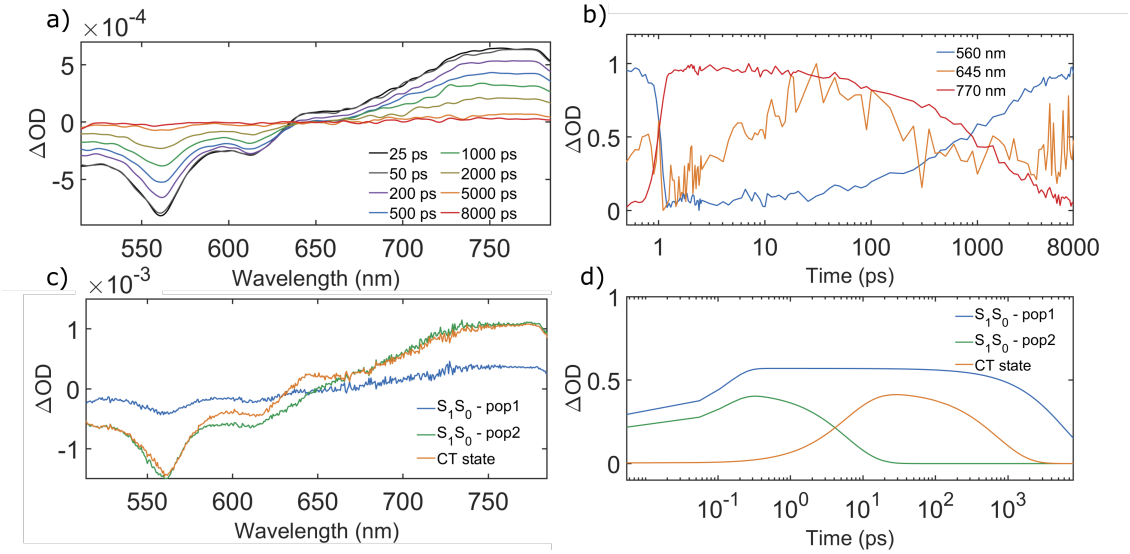

Fig. S19 a) Femtosecond-transient absorption spectra of c5-DPP in DMSO (pump 505 nm, delays 0 - 8ns).b) Temporal absorption profiles of key transient features as labelled. c) Species associated spectra output of the global fit using the branched kinetic model described above, labelled as singlet population 1 in blue, singlet population 2 in green and CS state in yellow. d) Population kinetics of aforementioned species.

S4.0.5 Spectroelectrochemistry

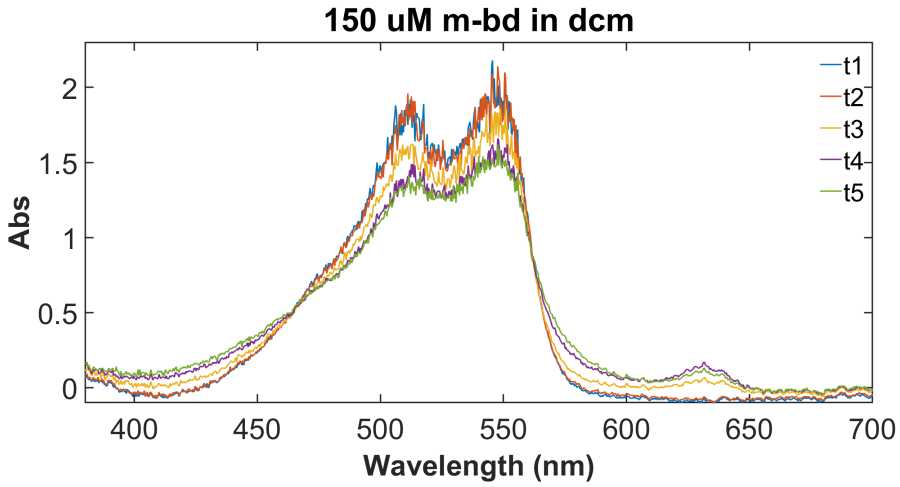

Fig. S20 Spectroelectrochemical features of the meta-xylyl DPP dimer in acetonitrile with 0.1 M $TBAPF_6$ as electrolyte. Applied voltage was fixed at -1.5 V and measurements were taken at 15 second intervals ordered from t1 to t5. The feature at 640 nm can be seen to grow in over time and is assigned to the radical anion.

S4.0.6 TRIR

In the global analysis of the transient IR spectra of the DPP model compounds, at least three exponential terms are required to fit the monomer datasets - in contrast to the transient absorption datasets for the equivalent molecules which show simple, monoexponential decay. A key difference between the two experiments is the solution concentrations. The TRIR experimental solution concentration was much higher in the transient IR experiment and therefore the possibility of forming excimer complexes is higher for these experiments. Figure S21 shows a comparison of all derivatives at 2ps pump-probe delay showing very different spectral shapes in the C6-monomer in DMSO which could be related to excimer formation. Note that the dimer solutions could be well described using the kinetic model described above and in the main text suggesting that the transient absorption and infrared data sets have very similar kinetics. Therefore we do not anticipate contributions to the transient IR signals from inter-dimer excimer formation.

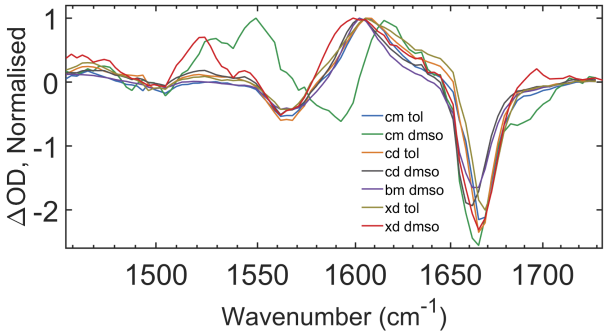

Fig. S21 Spectral traces of all DPP derivatives at 2 ps pump-probe delay in solvents as noted.

References

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