SUPPLEMENTARY INFORMATION

Conformational Switching Modulates Excited-State Pathways in a Cofacial Perylene Dimer

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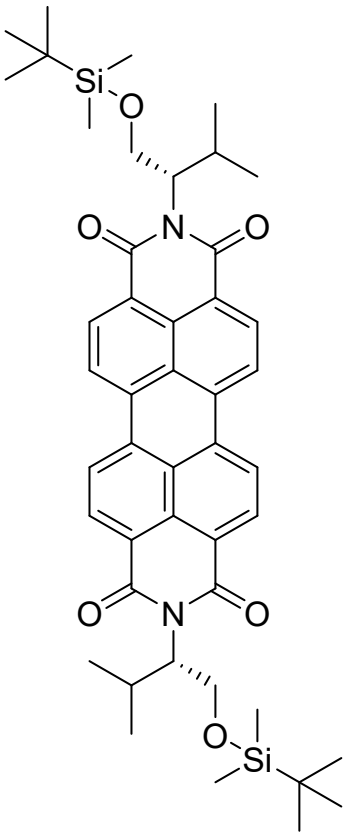


Figure S 1 Molecular structure of the **refPDI** monomer

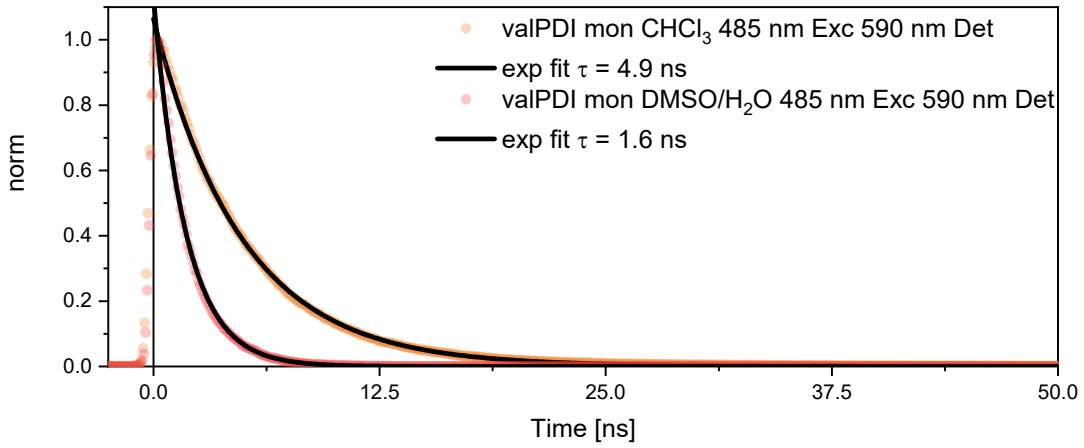
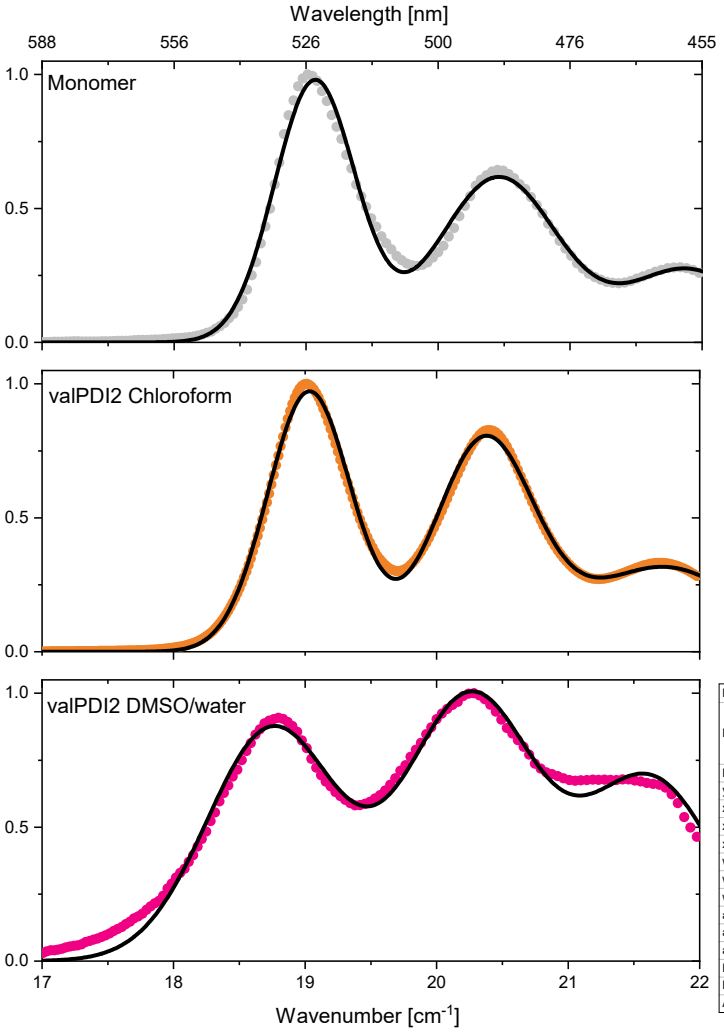


Figure S 2 ns fluorescence traces and fit (black) of **refPDI** in $CHCl_3$ (orange) and 1:1 DMSO/water (red)



Model	NewFunction1 (User)
Equation	y0 + a1 * exp(-(x-x1)^2 / (2*w1^2))+ a2 * exp(-(x-x2)^2 /(2*w2^2))+ a3 * exp(-(x-x3)^2 /(2*w3^2))
Plot	B
y0	0 ± 0
x1	19032.51199 ± 1.12009
x2	20364.36175 ± 2.52349
x3	21727.90092 ± 8.59176
w1	318.47947 ± 1.11359
w2	375.25716 ± 2.31685
w3	594.54624 ± 10.39562
a1	0.97081 ± 0.00264
a2	0.78272 ± 0.00368
a3	0.31588 ± 0.00243
Reduced Chi-Sqr	1.40889E-4
R-Square (COD)	0.99815
Adj. R-Square	0.99812

Model	NewFunction1 (User)
Equation	y0 + a1 * exp(-(x-x1)^2 / (2*w1^2))+ a2 * exp(-(x-x2)^2 /(2*w2^2))+ a3 * exp(-(x-x3)^2 /(2*w3^2))
Plot	B
y0	0 ± 0
x1	19066.50833 ± 2.17106
x2	20457.52663 ± 5.85887
x3	21888.74751 ± 13.53151
w1	306.55288 ± 2.06036
w2	452.39107 ± 6.86258
w3	451.24517 ± 18.06153
a1	0.97481 ± 0.00504
a2	0.61585 ± 0.00465
a3	0.27175 ± 0.00508
Reduced Chi-Sqr	2.425E-4
R-Square (COD)	0.9955
Adj. R-Square	0.9954

Model	NewFunction1 (User)
Equation	y0 + a1 * exp(-(x-x1)^2 / (2*w1^2))+ a2 * exp(-(x-x2)^2 /(2*w2^2))+ a3 * exp(-(x-x3)^2 /(2*w3^2))
Plot	B
y0	0 ± 0
x1	18751.32448 ± 7.22724
x2	20260.10308 ± 8.18975
x3	21624.14783 ± 11.2698
w1	495 ± 0
w2	495 ± 0
w3	495 ± 0
a1	0.86803 ± 0.00827
a2	0.98364 ± 0.00942
a3	0.67456 ± 0.00988
Reduced Chi-Sqr	0.00154
R-Square (COD)	0.98565
Adj. R-Square	0.98544

Figure S 3 steady-state fits for Spano's excitonic coupling model

Details of the excitonic coupling calculations

The excitonic coupling strength for **valPDI$_2$** in chloroform and DMSO/water can be determined from their steady-state absorption spectra, if the Huang-Rhys factor $\lambda^2{}_{mon}$ of the reference monomer refPDI is known.[1–3] $\lambda^2{}_{mon}$ is defined as:

$$\lambda^2{}_{mon} = (R_{0-1}/R_{0-0}) \qquad \text{(S1)}$$

Where R_{0-0} and R_{0-1} are the areas of the 0-0 and 0-1 vibronic bands of its steady-state absorption spectrum (see Figure S3). $(R_{0-1}/R_{0-0}) = 0.68$ for refPDI. Equation S1 can then substituted into Equation S2 which gives the total excitonic coupling when solved for J_{Tot}:

$$R_{abs} = \left(\lambda^2{}_{mon}\right)^{-1} \left[\frac{1 - G(0,\lambda^2)e^{-\lambda^2{}_{mon} J_{Tot}/\omega_0}}{1 - G(1,\lambda^2)e^{-\lambda^2{}_{mon} J_{Tot}/\omega_0}}\right]^2 \qquad \text{(S2)}$$

Where $R_{abs} = \left(\lambda^2{}_{dim}\right)^{-1} = (R_{0-0}/R_{0-1})$ of **valPDI$_2$** in chloroform or DMSO/water and $\omega_0$is the spacing of the vibronic progression (1350 cm^{-1}). Finally, G is the vibrational function, as defined in Equation S3:

$$G\left(v_t;\lambda^2\right) = \sum_{\substack{u=0,1,.. \\ u \neq v_t}} \frac{\left(\lambda^2\right)^u}{u!(u-v_t)}, v_t \in N_0 \quad \text{(S3)}$$

The values of J_{Tot} extracted using the method outlined above are reported in the main manuscript.

The long-range Coulombic coupling for both conformers was calculated using the transition electrostatic potential method (trESP) as implemented in Multiwfn. This approach relies on point atomic charges rather than TDMs and yields more reliable estimation of coupling strengths when dipole-dipole distances are comparable or smaller to the molecular dimensions. The sum over the electrostatic interactions between transition charges of the PDI pair yields the long-range coupling J_{Coul}, as per Equation S4:

$$J_{Coul} = \frac{1}{4\pi\varepsilon_0}\sum_i\sum_j \frac{q_i^{(1)}q_j^{(2)}}{\left|r_i^{(1)} - r_j^{(2)}\right|} \quad \text{(S4)}$$

In which ε_0 is the permittivity of free space, $q_i^{(1)}$ is the transition charge of the *i*-th atom and $r_i^{(1)}$ is the position vector associated to the *i*-th charge. We used time dependent (TD-)DFT at the ω-B97XD level of theory and dgdzvp as basis set in Gaussian 16 to calculate the transition densities of the two conformers of **valPDI$_2$** populated in chloroform and DMSO/water. The transition densities were fit to atomic partial charges and the Coulomb coupling terms were calculated at the optimised ground state structures. The atomic partial charges were all rescaled by $\sqrt{2}$ as indicated in the Multiwfn manual.

The short-range couplings were calculated by using the charge transfer integral package CATNIP, the molecular orbitals (MO) coefficients were obtained by DFT calculations at the ω-B97XD/dgdzvp level of theory in Gaussian 16.

Both the long- and short-range coupling calculations required to determine transition charges or MO coefficients of each PDI chromophore. Such fragments were obtained by disconnecting the dimer structures at two opposite alpha carbons between the pair of C=O of each ligand to yield two identical "halves", followed by capping with H-atoms at the broken bonds positions to keep the S_0 multiplicity. The added H atoms were not included in the fragments used for the long-range coupling calculation in Multiwfn. Both dimer structures were geometry-optimized followed by frequency calculations to prove the existence of true minima, as determined by the absence of imaginary frequencies. All relevant coordinates are reported at the end of the present document.

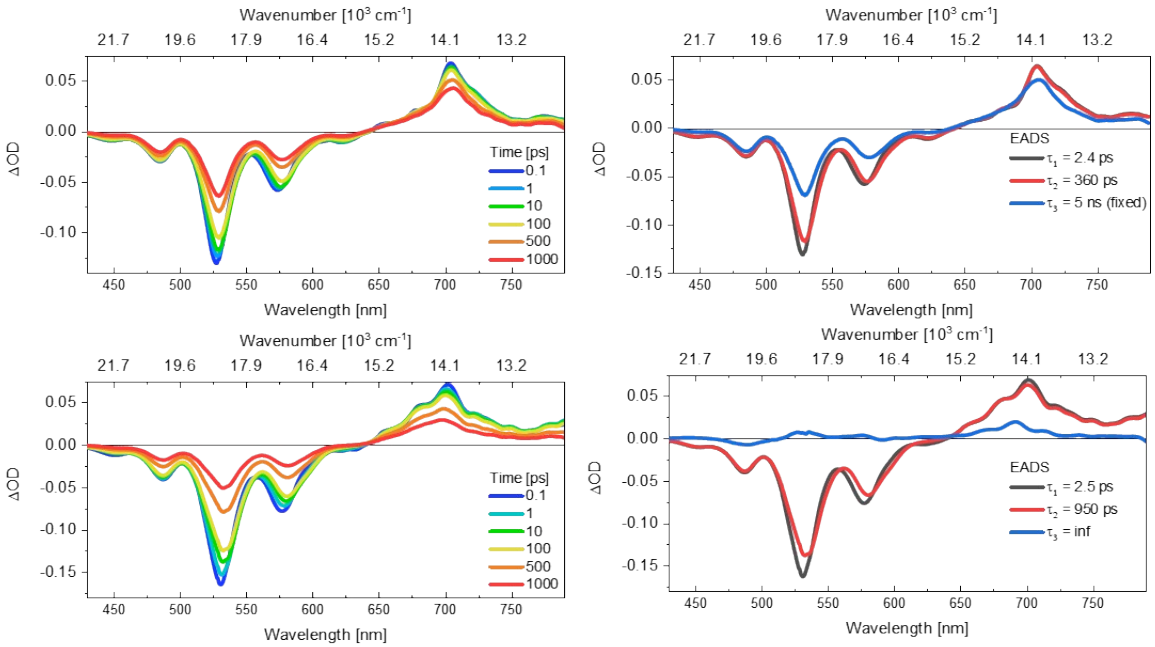
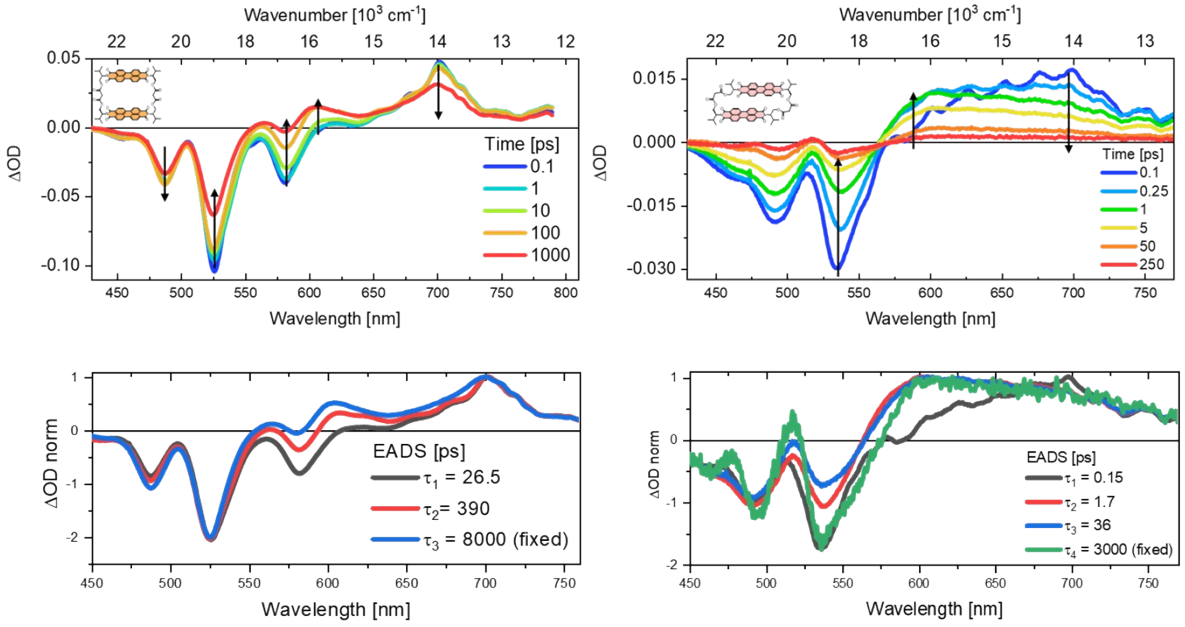


Figure S 4 fsTA spectra at selected pump probe delay times (left) and EADS from global fitting (right) of **refPDI** monomer in $CHCl_3$ (top) and DMSO/water (bottom)



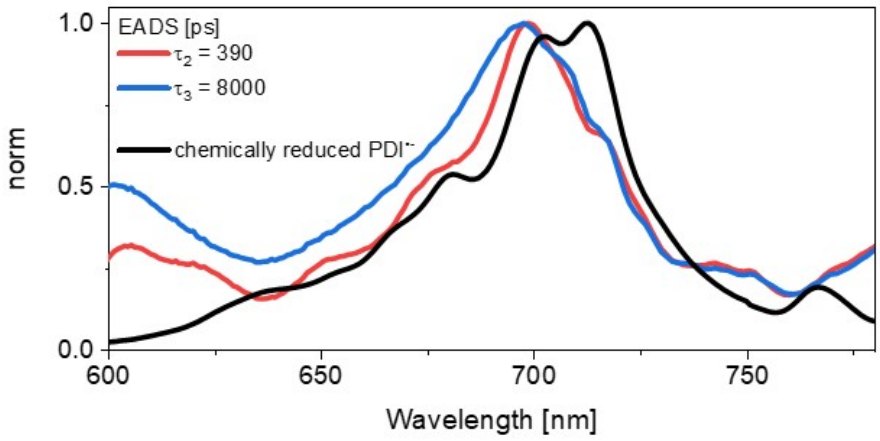


Figure S *5 (*top*)* fsTA spectra at selected pump probe delay times of **valPDI$_2$** in $CHCl_3$ (left) and DMSO/water (right).

(middle) normalised evolution associated decay spectra (EADS) obtained by applying a sequential model to the fsTA data of **valPDI$_2$** in $CHCl_3$ (left) and DMSO/water (right). Data were fit in GloTarAn.[4] Global fit required 3 and 4 components -indicated in the legend- to accurately fit the data in chloroform and DMSO/water, respectively.

(bottom) comparison between ESA ($S_n \leftarrow S_1$) region of normalised EADS2 and EADS3 of **valPDI$_2$** in $CHCl_3$ (maxima at 700 nm) and steady-state absorption of the chemically reduced **refPDI** radical anion (maximum at 710 nm). The radical anion was produced adding 0.3 ml of a saturated solution of sodium dithionite ($Na_2S_2O_4$) to 3 ml of a 0.2 mM THF solution of **valPDI$_2$**

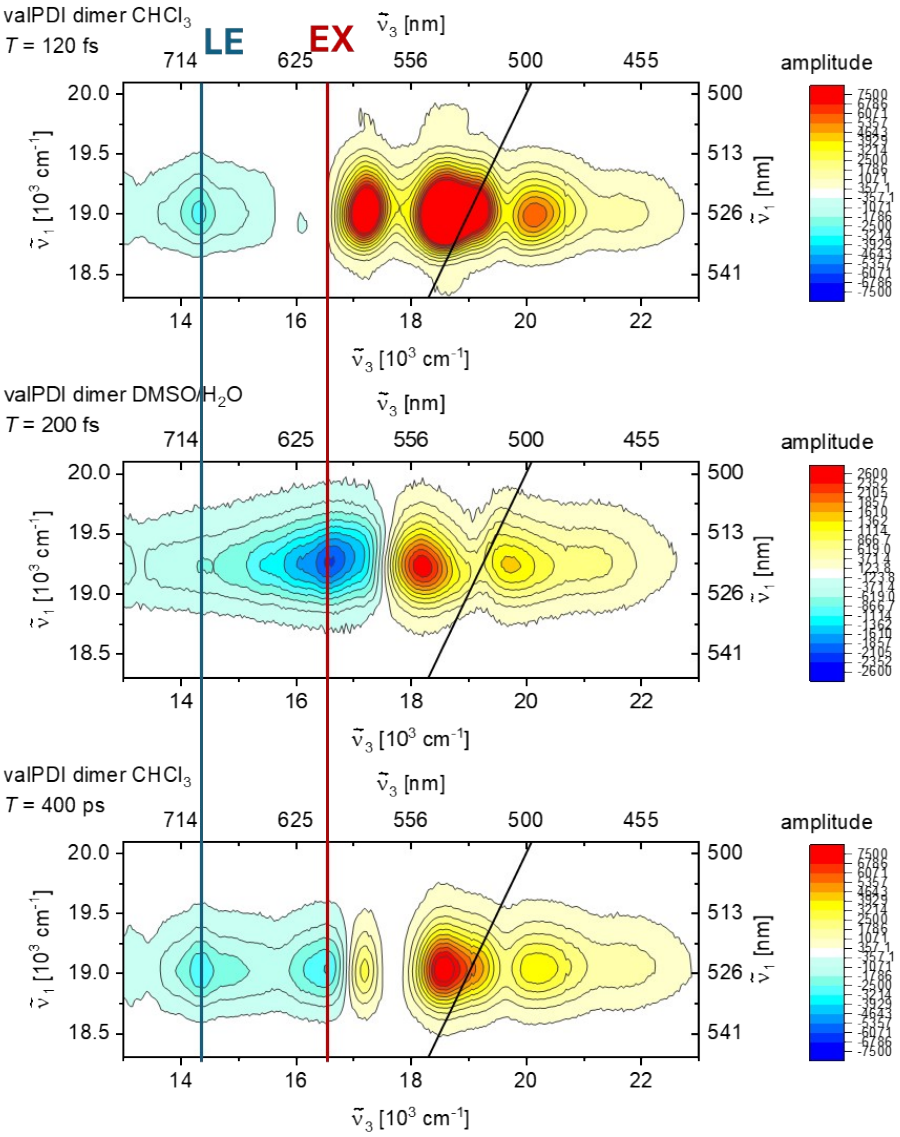


Figure S 6 Absorptive HB2DES of **valPDI$_2$** in $CHCl_3$ and DMSO/water showing the superposition of EX (red) and LE (blue) states in the open conformation.

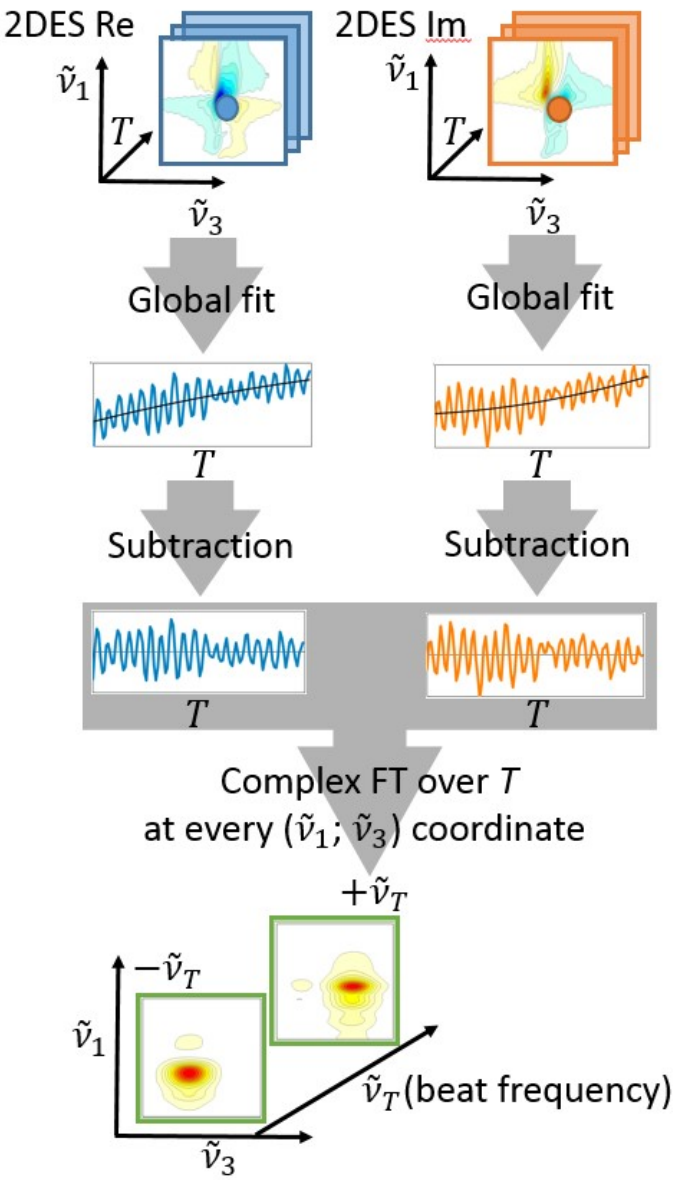


Figure S 7 Scheme of the method to extract complex valued coherent beatmaps from a HB2DES dataset. Adapted from Bressan et al.[5]

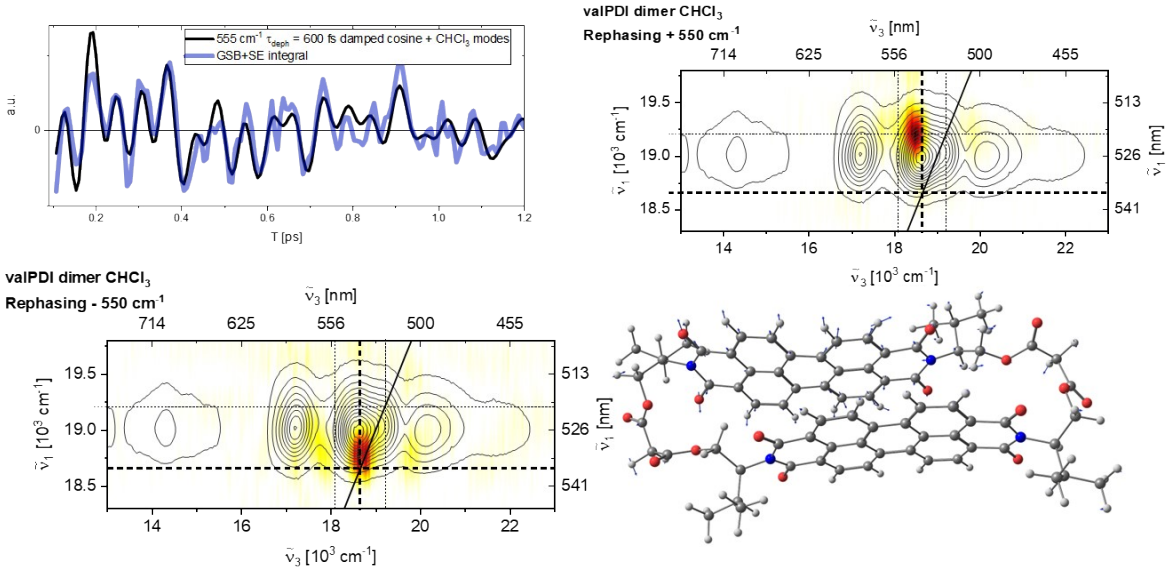


Figure S 8 Integrated oscillatory residuals (blue) in the GSB+SE region of the **valPDI$_2$** response in CHCl3. Data were fit to a sum of damped cosines at 369 cm^{-1} with fixed dephasing time of 1 ps to account for the strong $CHCl_3$ solvent response and to molecular modes at 180 and 550 cm^{-1} with 650 fs dephasing time. Rephasing positive and negative beatmaps at 550 cm^{-1} showing the pattern expected for a two electronic level displaced harmonic oscillator comprising of GSB and SE vibrational coherence.[6] Beatmaps are shown as white-yellow-red heat maps and amplitude normalized to 1. Black dashes indicate the position of the 0-0 transition; thin dashes are drawn at ± 550 cm^{-1} from the 0-0 transition. DFT structure showing the displacement vectors associated with the ring breathing at 530 cm^{-1}

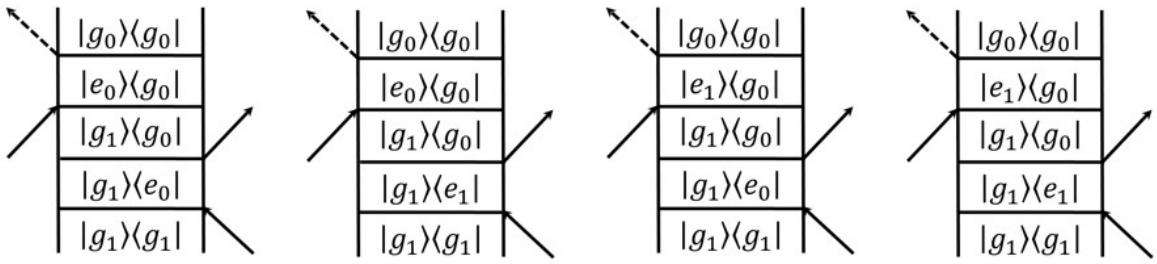


Figure S 9 Rephasing double-sided Feynman diagrams accounting for hot ground state bleach pathways oscillating at negative frequencies during *T*. g and e are the electronic ground and excited states and the subscripts indicate the number of quanta of a Raman active low frequency (below 200 cm^{-1}) molecular vibration coupled to the electronic transition.

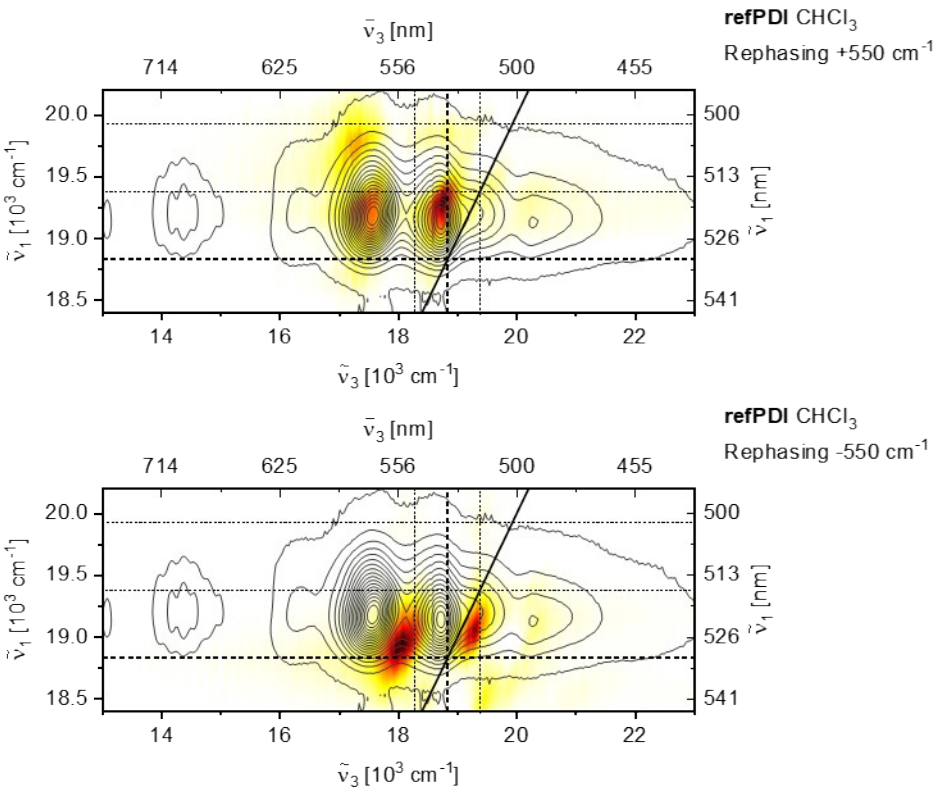
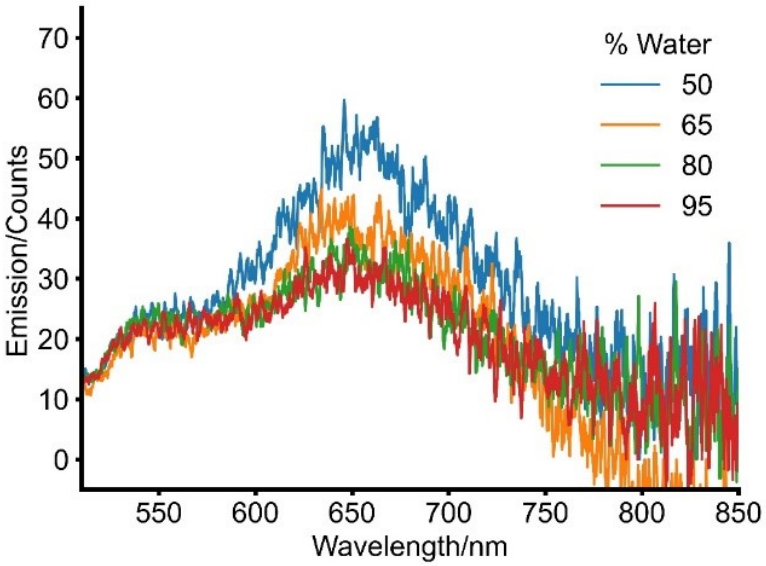


Figure S 10 Rephasing positive and negative beatmaps at 550 cm-1 of **refPDI** in $CHCl_3$ showing the pattern expected for a two electronic level displaced harmonic oscillator comprising of GSB and SE vibrational coherence. Beatmaps are shown as white-yellow-red heat maps and amplitude normalized to 1. Black dashes indicate the position of the 0-0 transition; thin dashes are drawn at ± 550 cm^{-1} from the 0-0 transition The redshifted signals at detection frequencies of~17500 (positive) and 18000 cm^{-1} (negative) are due to anharmonic coupling between the 550 cm^{-1} PDI breathing and the1350 cm^{-1} stretching mode giving rise to the strong vibronic progression evident in the absorption and emission spectra of **refPDI**. Anharmonic coupling between low frequency modes and the vinyl stretch was previously reported by us for other PDI derivatives in chlorinated solvents.[7]



Solvent ratio ($DMSO:H_2O$)	**valPDI$_2$ FQY** (%)
50:50	6.5
35:65	4
20:80	5
5:95	4

Figure S 11 Emission spectra and FQY (table) of 1 μM solutions of **valPDI$_2$** in different DMSO/water volume fraction solvent mixtures. Data were measured on an Edinburgh Instruments FLS1000 spectrometer with 0.1 nm step size and 250 ms dwell time using an a PMT-980 photomultiplier tube and an integrating sphere (for FQY measurements). All measurements were taken with 3 nm excitation bandwidth and 0.95 nm emission bandwidth and samples excited at 493 nm.

Coordinates

valPDI2 in H_2O

O	14.31065	-2.84217	12.64182
O	11.52014	-7.55509	11.75193
O	17.19156	-4.50085	15.76230
O	13.98778	-8.98419	15.33146
O	16.07215	-6.77954	12.41802
O	14.98067	-9.67667	12.54505
N	15.82792	-3.62861	14.16436
O	12.66662	6.28916	19.11902
O	9.41787	2.12398	17.11630
N	12.68966	-8.32513	13.56519
O	15.99528	4.83191	21.87413
O	17.77983	-8.22625	12.79791
C	14.84400	-2.72031	13.73777
N	14.46131	5.64537	20.38974
C	16.00154	-2.54447	16.34494
C	14.54163	-1.60494	14.63993
C	11.21825	-2.26039	15.42577
C	13.58527	4.16833	18.64928
C	13.81281	1.80578	17.11757
C	14.90267	-0.38956	16.73867
N	10.54937	1.35501	18.94980
C	16.81878	-7.86382	12.15179
C	14.03290	0.63662	16.28025
C	14.45922	3.14727	19.06440
C	13.36402	-8.09327	14.76729
C	16.54950	-2.48306	17.61196
H	17.18939	-3.28266	17.95089
C	13.26507	-6.74390	15.34587
O	14.46086	-10.01852	10.36773
C	11.50292	-3.50246	14.72634

C	16.38512	-3.63184	15.44171
C	12.60263	-3.01906	17.33971
C	14.54233	1.93225	18.33056
C	12.89616	-4.25780	16.63557
C	12.80678	3.97876	17.52317
H	12.11933	4.75238	17.21936
C	10.99500	-3.77470	13.46030
H	10.40314	-3.04072	12.93997
C	16.31571	-1.38870	18.42967
H	16.77822	-1.37894	19.40233
C	11.92332	-5.99303	13.46736
C	15.53427	-0.31629	18.00901
C	13.70901	-5.24862	17.17891
H	14.19812	-5.09522	18.12615
C	12.02524	-7.31549	12.84447
C	10.41270	-1.26867	14.87386
H	10.01073	-1.38090	13.88114
C	12.58303	-9.68642	12.98049
H	12.36114	-9.48967	11.93877
C	13.70060	-0.59342	14.21638
H	13.24368	-0.66135	13.24192
C	16.29684	-8.57346	10.93338
H	17.09562	-9.17203	10.50284
H	15.96576	-7.86405	10.18037
C	15.39532	0.89661	18.79789
C	13.45761	0.50952	15.02003
H	12.81325	1.28113	14.63435
C	13.50313	5.43860	19.38802
C	15.23477	3.32675	20.22367
C	12.31130	-4.48400	15.36043
C	13.88157	-6.47466	16.55398

H	14.48457	-7.23686	17.02171
C	15.14647	-1.51685	15.90711
C	11.39404	-0.88836	17.45012
C	12.92908	2.82191	16.76562
H	12.32955	2.73919	15.87453
C	15.13902	-9.49871	11.22734
C	11.73679	-2.06805	16.73474
C	11.19811	-4.99764	12.84019
H	10.76681	-5.18758	11.87003
C	16.02903	2.29196	20.67938
H	16.61795	2.42983	21.57250
C	17.80330	-3.97912	12.71141
H	18.46848	-4.06214	13.57141
C	13.09155	-2.75852	18.61587
H	13.74889	-3.45878	19.10236
C	16.42464	-4.51195	13.13814
H	15.74911	-4.43067	12.29288
C	10.55689	0.07560	16.86203
C	12.49824	-5.74291	14.72496
C	10.09164	-0.11768	15.57478
H	9.45660	0.62869	15.12421
C	16.09509	1.09367	19.98459
H	16.74172	0.32395	20.37134
C	11.35878	-10.43827	13.53526
H	10.51737	-9.76730	13.35057
C	13.86928	-10.48963	12.98984
H	13.75402	-11.32794	12.31144
H	14.15900	-10.84212	13.96613
O	11.78109	0.61538	20.72139
O	12.40098	6.54763	22.05954
C	10.13558	1.25993	17.61060

C	11.10656	-11.70999	12.73216
H	11.12994	-11.52153	11.65959
H	10.12677	-12.11414	12.97812
H	11.84069	-12.48215	12.95651
C	15.27023	4.62405	20.90494
C	12.73569	-1.61447	19.31335
H	13.11183	-1.45252	20.31119
O	10.49694	4.52040	20.69193
C	11.87914	-0.68541	18.75488
C	16.41823	-5.97118	13.57501
H	17.37017	-6.29683	13.96881
H	15.65037	-6.15347	14.31798
C	9.88235	2.41443	19.74199
H	9.64523	3.17131	19.00242
C	17.73642	-2.51670	12.29265
H	17.06322	-2.38009	11.44701
H	18.72340	-2.17139	11.99191
H	17.40125	-1.86765	13.09900
C	14.61418	6.97895	21.02820
H	15.62483	6.95249	21.43061
C	11.39598	-10.73108	15.02734
H	12.23212	-11.37378	15.29517
H	11.46690	-9.82437	15.62166
H	10.47963	-11.24217	15.31858
C	11.42922	0.45841	19.55661
C	18.38283	-4.82253	11.58265
H	18.58362	-5.84467	11.88970
H	19.32774	-4.39545	11.25277
H	17.71167	-4.84767	10.72424
C	14.59476	8.16567	20.05430
H	13.58841	8.32513	19.68458

O	11.54127	8.58664	21.58305
C	13.73263	7.06180	22.26816
H	13.68033	8.07576	22.64543
H	14.13922	6.41695	23.03849
C	7.70836	3.03014	20.86838
H	8.12230	3.38413	21.80977
H	6.69779	2.68069	21.07047
H	7.63996	3.87572	20.18585
O	10.10433	4.67094	22.92162
C	8.53746	1.89472	20.28250
H	8.00548	1.52747	19.40281
C	10.79575	3.09881	20.74884
H	11.83690	3.01158	20.46786
H	10.67273	2.74413	21.76204
C	15.52248	7.90464	18.87432
H	16.53918	7.70474	19.21524
H	15.55654	8.77787	18.22595
H	15.20347	7.06204	18.26636
C	15.03958	9.42781	20.78629
H	14.34868	9.71796	21.57329
H	15.09268	10.25746	20.08407
H	16.02887	9.30386	21.22849
C	8.65375	0.74110	21.26632
H	9.13990	-0.12671	20.82788
H	7.65937	0.43111	21.58330
H	9.21057	1.02296	22.15801
C	11.41973	7.38949	21.72095
C	10.22519	5.17963	21.82547
C	10.10685	6.65532	21.55793
H	9.75219	6.84441	20.54852
H	9.39675	7.09307	22.25426

O	17.33779	-6.04092	18.12792
H	17.24892	-5.52079	17.31395
H	17.09888	-6.94918	17.88665
O	15.26510	-5.61936	19.88061
H	16.07750	-5.69291	19.34600
H	14.89567	-6.52033	19.90095
O	18.60287	3.81867	21.91097
H	18.61644	3.09042	22.54116
H	17.75284	4.27483	22.02816
O	19.13170	2.95412	19.38675
H	18.85539	3.29224	20.26344
H	20.08249	3.10499	19.35296
O	14.02753	0.42938	22.42520
H	13.37318	0.45427	21.71122
H	13.51627	0.10006	23.19683
O	13.55678	-6.92483	9.76862
H	13.23469	-6.52469	8.95248
H	12.76631	-7.18438	10.25895
O	12.11749	-1.41893	11.31612
H	12.82078	-1.97251	11.68636
H	12.24891	-1.42736	10.36417
O	19.38125	0.19205	18.89485
H	19.11093	1.09787	19.11765
H	19.11631	-0.37178	19.64730
O	10.85623	2.57433	13.83312
H	10.12449	2.78441	14.42272
H	10.97344	3.34070	13.26270
O	18.97320	-0.59431	16.35491
H	19.86640	-0.56801	15.99905
H	19.07335	-0.35466	17.30452
O	17.13989	1.27265	15.55890

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H	8.92385	-2.53882	18.79647
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Cl	-1.90516602904895	7.89976347321312	22.17672262357610
C	-2.48986507722188	8.61663788125817	23.68316166427738
Cl	-1.81896765836483	7.74013841929060	25.06877317731321
Cl	-2.03651898162262	10.32647602839944	23.76723824826411
H	-3.57729991222606	8.53200653763233	23.71350631202443

Cl	13.17757444656262	9.10737986600648	26.74823404573479
C	12.30991990094370	8.10761279244713	25.58066918149351
Cl	12.77428137932001	8.54868449875582	23.93516920094385
Cl	12.65904575370570	6.39720675568826	25.86732910740666
H	11.23218450204580	8.26553574731944	25.68663889040706
Cl	-0.47732734363946	2.09584391526949	23.56039657627996
C	-1.82169150299821	3.23772190743942	23.67605185717000
Cl	-1.29409436055440	4.85671311628692	23.20297977251067
Cl	-3.15782494312111	2.71562641874091	22.64351273735283
H	-2.17071191651627	3.27260943099268	24.70950538716658
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C	1.62173360760642	-1.24684332702752	20.97956470235812
Cl	0.22273745178163	-0.16443601253151	21.02757320445392
Cl	2.37060840400854	-1.32436375509388	22.58233221534899
H	2.34752699682658	-0.83465516975088	20.26993813502294
Cl	6.03559982696595	10.21633784866000	17.39509358042191
C	4.44893870650057	10.24920063359712	16.63903651066229
Cl	3.81824527375947	11.89857354810936	16.63835051506573
Cl	4.55962787503325	9.62009622432870	14.99223453833674
H	3.78147033481347	9.60997518674770	17.22025077190210
Cl	13.18298607893058	3.44802063334574	24.07862360016684
C	13.89847449175009	4.10788158024122	22.59929131655983
Cl	13.50404118949640	3.07926571319002	21.21351328085359
Cl	13.31117183938368	5.75009378121002	22.30908955140120
H	14.98292356960306	4.13564044538492	22.71699408131615
Cl	-1.37678689245007	5.68862808833851	19.90269322878435
C	-1.53079115093285	4.04296526122007	19.27328280948696
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Cl	-0.68213060845775	2.90360293532615	20.32539671324159
H	-2.58791918785083	3.77300546986228	19.24456836620345
Cl	4.95246692216806	1.24372716905738	24.43402090823974

C	5.03016665260727	2.48594387346537	25.70015854284425
Cl	3.60512295723259	2.38275098154141	26.73838025163129
Cl	6.49390456462881	2.28360276202927	26.65745786322690
H	5.05710645049257	3.47131165561707	25.22976767943605
Cl	4.20594127139493	-4.83120273126832	18.80802232761854
C	4.63595370495074	-3.12246486350169	18.64762559939433
Cl	3.40031198161514	-2.28868344549917	17.70934491335810
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H	5.59096986119444	-3.03128901422726	18.11649088389615
Cl	10.64641505726709	8.05846711731438	17.49520784428847
C	9.54640602279028	9.26653792206457	16.81361022359573
Cl	10.47216158133985	10.61529129359802	16.14830836178059
Cl	8.53951937348855	8.52607874752981	15.56639196714682
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C	7.51553680719007	12.67080524784129	19.75913718345380
Cl	5.83050412992797	13.07114859335827	19.40443562143141
Cl	8.39572034806290	12.39208293195557	18.25269262168306
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Cl	-0.14656230048438	11.33270760042838	19.41810146251213
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Cl	1.04551193610644	9.74496355519130	17.30078663336967
Cl	-1.22045457073584	8.70137764427124	18.77617696869504
H	-1.13472648477534	10.61217236229507	17.39036035752153
Cl	10.00494936010599	10.39275482491929	27.41070747690094
C	9.09943201518092	9.00002438370663	28.00217429039092
Cl	10.21026987248677	7.66378418784330	28.34060771060911
Cl	8.20934794945573	9.44043224310871	29.46570321312153
H	8.39169236379437	8.68384322252965	27.23319145863710

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