Supplementary Information (SI)

One- to Two-Exciton Transitions in Perylene Dimer Revealed by Two-Dimensional Electronic Spectroscopy

Giovanni Bressan,[1] Dale Green[1], Yohan Chan[1], Philip C. Bulman Page[1], Garth A. Jones[1], Stephen R. Meech[1] and Ismael A. Heisler[2,*]

[1]*School of Chemistry, Norwich Research Park, University of East Anglia, Norwich NR4 7TJ, United Kingdom*

[2]*Departamento de Física, Universidade Federal do Paraná, Caixa Postal 19044, 81531-990 Curitiba, Parana, Brazil*

*Corresponding author. Email: heisler@fisica.ufpr.br

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1) Molecular Structures of PBI M, D0 and D1

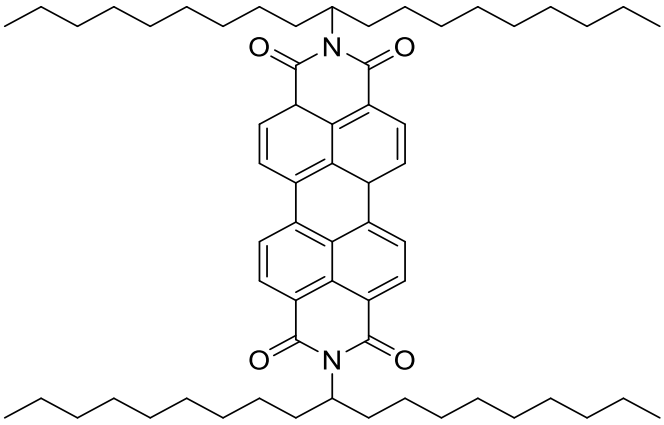

Figure S 1molecular structure of the PBI monomer M

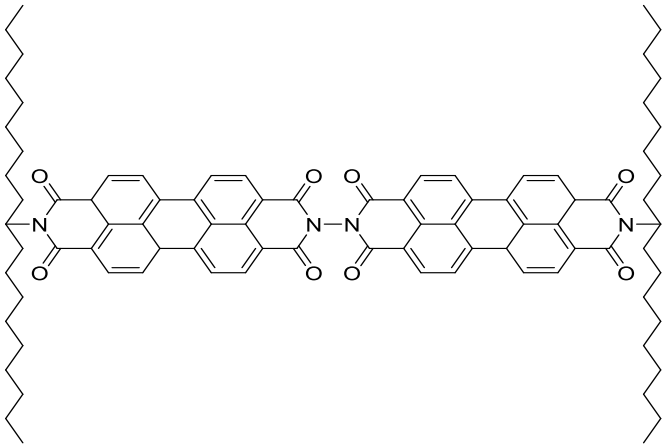

Figure S 2molecular structure of PBI D0 Dimer

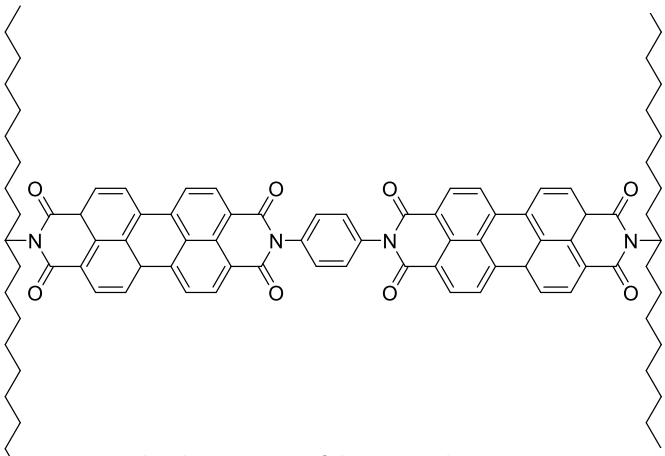

Figure S 3molecular structure of the PBI D1 dimer

2) Fluorescence spectra of PBI M, D0 and D1

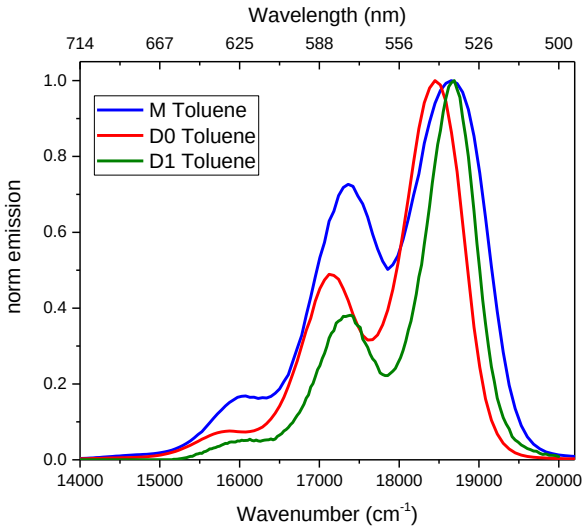

Figure S 4 Normalised fluorescence steady-state spectra of M (blue) and D0 (red) and D1 (green) in Toluene.

3) 2DES Spectral progressions

PBI Monomer in Toluene

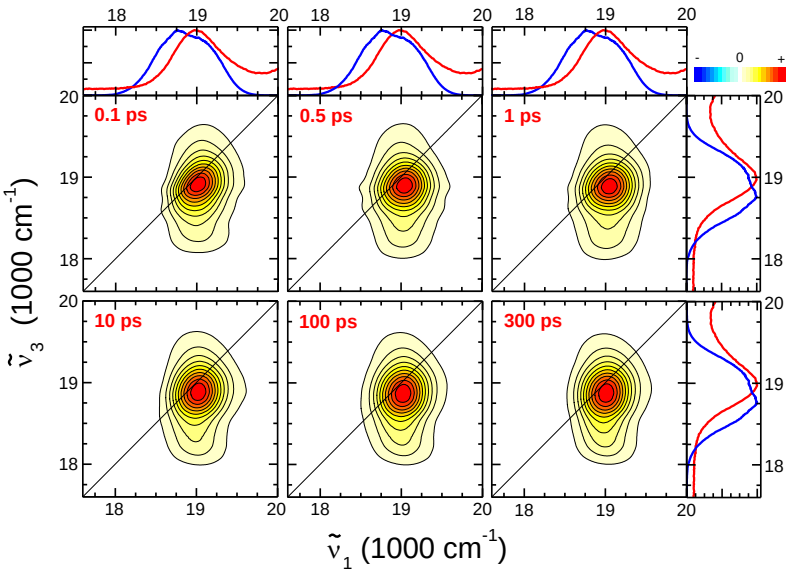

Figure S 5 Absorptive 2D-ES spectral progression for PBI M in toluene, where $\tilde{\nu}_1$ is the excitation and $\tilde{\nu}_3$ is the detection scale (in wavenumber). Each 2D graph is normalised to its positive maximum and the amplitude has 21 evenly spaced contour lines. Red number on the top left of each map indicate the population time T and in the top and right panel the steady-state absorption (red) and NOPA spectra (blue) are shown.

PBI D0 Dimer in Toluene

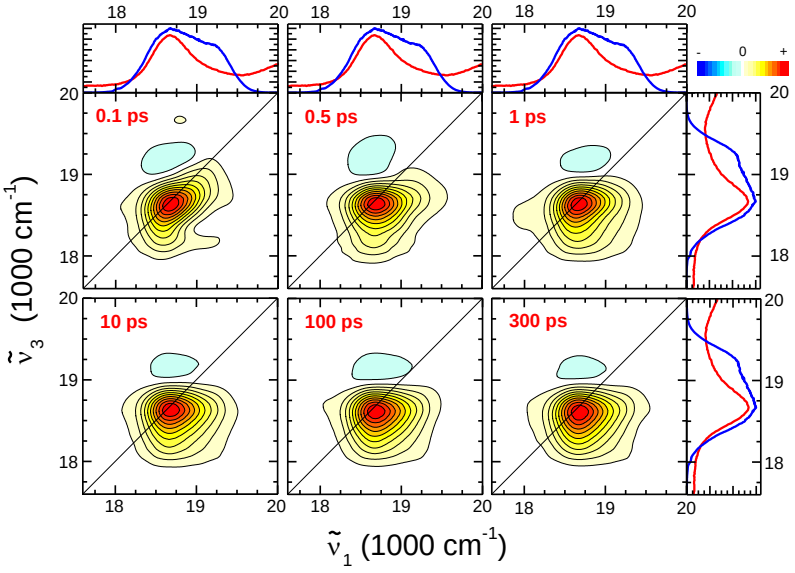

Figure S 6 Absorptive 2D-ES spectral progression for PBI D0 in toluene, where $\tilde{\nu}_1$ is the excitation and $\tilde{\nu}_3$ is the detection scale (in wavenumber). Each 2D graph is normalised to its positive maximum and the amplitude has 21 evenly spaced contour lines. Red number on the top left of each map indicate the population time T and in the top and right panel the steady-state absorption (red) and NOPA spectra (blue) are shown.

PBI D1 Dimer in Toluene

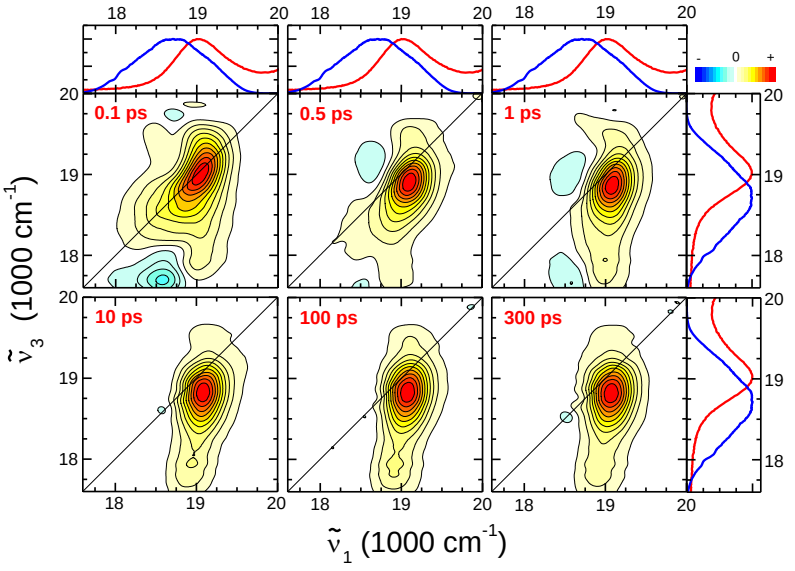

Figure S 7 Absorptive 2D-ES spectral progression for PBI D1 in toluene, where $\tilde{\nu}_1$ is the excitation and $\tilde{\nu}_3$ is the detection scale (in wavenumber). Each 2D graph is normalised to its positive maximum and the amplitude has 21 evenly spaced contour lines. Red number on the top left of each map indicate the population time T and in the top and right panel the steady-state absorption (red) and NOPA spectra (blue) are shown.

4) Double-sided Feynman diagrams for the Liouville pathways involving 1 to 2-exciton state transitions

Figure S 8 Rephasing (left) and Non Rephasing (right) double sided Feynman diagrams for the ESA pathways in a 3-level excitonically coupled PBI J-dimer.

In Figure S7 the two Feynman (Rephasing and Non Rephasing) diagrams for the ESA to a 2-exciton state are reported. The model is purely electronic and it involves transitions which couple three states: $|g\rangle$ (ground), $|e'\rangle$ (in phase, low energy, allowed 1-exciton) and $|f\rangle$ (two-exciton). Those pathways will generate a cross peak above the diagonal ($\tilde{\nu}_3 > \tilde{\nu}_1$) with negative amplitude, because of the odd number of interactions from the right.

None of these diagrams will oscillate during the population time T, because only populations in the 1 exciton state ($|e'\rangle\langle e'|$) will be created, given the proposed energy level scheme and the pulse sequence used in the 2D-ES experiment.

5) DFT calculations for M, D0 and D1, geometry optimisation and vibrational spectra

All calculations were performed with Gaussian09[1]. Molecules M, D0 and D1 were optimized with the B3LYP functional and the 6-31G* basis set. All structures were shown to be genuine minima, via a harmonic vibrational analysis (all real frequencies). Raman frequencies were also calculated, as reported below.

The optimized geometries at B3LYP/6-31G(D) for M, D0 and D1 are reported in the following tables:

M

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.876841	-2.425958	-0.000117
2	6	0	1.478326	-2.431825	-0.000103
3	6	0	0.735601	-1.249568	-0.000025
4	6	0	1.434699	0.000005	0.000003
5	6	0	2.865353	0.000010	0.000003
6	6	0	3.572998	-1.230787	-0.000055
7	6	0	-0.735596	-1.249568	0.000030
8	6	0	0.735596	1.249568	0.000027
9	6	0	-0.735601	1.249567	-0.000024
10	6	0	-1.434699	-0.000005	0.000002
11	6	0	-1.478326	2.431825	-0.000094
12	6	0	1.478312	2.431837	0.000095

13	6	0	2.876822	2.425987	0.000112
14	6	0	3.572990	1.230818	0.000058
15	1	0	3.437321	3.355054	0.000162
16	1	0	3.437343	-3.355023	-0.000174
17	6	0	-1.478312	-2.431837	0.000105
18	6	0	-2.876822	-2.425987	0.000119
19	6	0	-3.572990	-1.230818	0.000058
20	6	0	-2.865353	-0.000010	0.000001
21	1	0	-3.437322	-3.355054	0.000173
22	6	0	-2.876841	2.425958	-0.000110
23	1	0	-3.437343	3.355023	-0.000162
24	6	0	-3.572997	1.230787	-0.000054
25	1	0	0.977420	3.392304	0.000142
26	1	0	-0.977451	3.392302	-0.000142
27	1	0	0.977452	-3.392302	-0.000161
28	1	0	-0.977420	-3.392304	0.000161
29	6	0	5.055867	1.253309	0.000061
30	8	0	5.724071	2.275676	0.000102
31	6	0	5.055899	-1.253311	-0.000055
32	8	0	5.724052	-2.275704	-0.000119
33	7	0	5.666325	-0.000003	0.000007
34	1	0	6.681564	0.000081	0.000001
35	6	0	-5.055899	1.253311	-0.000056
36	6	0	-5.055867	-1.253309	0.000055
37	8	0	-5.724052	2.275704	-0.000119
38	8	0	-5.724071	-2.275676	0.000103
39	7	0	-5.666325	0.000003	0.000001
40	1	0	-6.681564	-0.000080	-0.000005

D0

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.494103	-1.707072	-1.722108
2	6	0	-4.892163	-1.711546	-1.726593
3	6	0	-5.635162	-0.879404	-0.887175
4	6	0	-4.935910	0.000066	-0.000023
5	6	0	-3.505312	0.000155	-0.000022
6	6	0	-2.797977	-0.865143	-0.872802
7	6	0	-7.106184	-0.879590	-0.887376
8	6	0	-5.635273	0.879448	0.887129
9	6	0	-7.106296	0.879467	0.887310
10	6	0	-7.805515	-0.000096	-0.000043
11	6	0	-7.849001	1.711681	1.727027
12	6	0	-4.892379	1.711684	1.726546
13	6	0	-3.494318	1.707363	1.722083
14	6	0	-2.798086	0.865523	0.872776
15	1	0	-2.934256	2.361382	2.381933
16	1	0	-2.933960	-2.361032	-2.381946
17	6	0	-7.848783	-1.711884	-1.727108
18	6	0	-9.247370	-1.707777	-1.723060

19	6	0	-9.943646	-0.866570	-0.874234
20	6	0	-9.236017	-0.000166	-0.000065
21	1	0	-9.807637	-2.361764	-2.383154
22	6	0	-9.247587	1.707432	1.722942
23	1	0	-9.807938	2.361363	2.383021
24	6	0	-9.943756	0.866165	0.874088
25	1	0	-5.392072	2.388299	2.409088
26	1	0	-7.348579	2.388046	2.409366
27	1	0	-5.391772	-2.388211	-2.409147
28	1	0	-7.348274	-2.388205	-2.409427
29	6	0	-1.318871	0.890789	0.898081
30	8	0	-0.659649	1.610656	1.624059
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35	6	0	-11.426607	-0.882466	-0.890262
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37	8	0	-12.094789	-1.602146	-1.616425
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41	6	0	1.318805	-0.897807	0.890633
42	6	0	2.798071	0.873052	-0.865177
43	6	0	2.798022	-0.872545	0.865475
44	7	0	0.691154	0.000279	0.000112
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47	6	0	4.935929	0.000158	0.000142
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51	6	0	3.494155	-1.721959	1.707279
52	6	0	4.892193	-1.726616	1.711560
53	1	0	5.391801	-2.409338	2.388062
54	6	0	5.635191	-0.887215	0.879397
55	1	0	2.934155	2.382538	-2.360701
56	1	0	2.933999	-2.381950	2.361095
57	6	0	7.106288	0.887618	-0.879211
58	6	0	7.106239	-0.887596	0.879362
59	6	0	7.805522	-0.000048	0.000037
60	6	0	7.848968	1.727505	-1.711280
61	6	0	9.236013	-0.000135	-0.000019
62	6	0	9.943716	0.874241	-0.866161
63	6	0	9.247544	1.723372	-1.707142
64	1	0	9.807895	2.383606	-2.360941
65	6	0	7.848882	-1.727601	1.711349
66	6	0	9.247459	-1.723677	1.707067
67	1	0	9.807779	-2.384035	2.360767
68	6	0	9.943674	-0.874577	0.866086
69	1	0	7.348516	2.410019	-2.387459
70	1	0	7.348402	-2.410115	2.387498
71	6	0	11.426626	-0.890656	0.881879
72	6	0	11.426668	0.890173	-0.882041
73	1	0	13.052187	-0.000516	-0.000323

74	8	0	0.659530	1.624363	-1.610177
75	8	0	0.659421	-1.623766	1.610423
76	8	0	12.094902	1.616242	-1.601725
77	8	0	12.094827	-1.617235	1.601079
78	7	0	12.036983	-0.000342	-0.000169

D1

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.668156	2.213497	0.980000
2	6	0	-7.066916	2.222905	0.980913
3	6	0	-7.813480	1.143692	0.503583
4	6	0	-7.116443	0.000002	-0.000004
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9	6	0	-9.284269	-1.144975	-0.501776
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11	6	0	-10.026825	-2.228624	-0.974689
12	6	0	-7.066823	-2.222893	-0.980935
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14	6	0	-4.974067	-1.117633	-0.496717
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24	6	0	-12.121414	-1.128179	-0.492787
25	1	0	-7.564988	-3.103132	-1.369050
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27	1	0	-7.565116	3.103127	1.369023
28	1	0	-9.525430	3.108328	1.359276
29	6	0	-3.490842	-1.140821	-0.513229
30	8	0	-2.858175	-2.090117	-0.946047
31	6	0	-3.490891	1.141000	0.513172
32	8	0	-2.858281	2.090347	0.945966
33	7	0	-2.834803	0.000102	-0.000023
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35	6	0	-13.604177	1.148504	0.501605
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37	8	0	-14.272859	2.085297	0.910621
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39	1	0	-15.229630	-0.000189	0.000019
40	6	0	3.490815	-1.140580	0.513451
41	6	0	3.490908	1.141049	-0.513389

42	6	0	4.974041	-1.117498	0.496795
43	6	0	4.974137	1.117818	-0.496736
44	7	0	2.834806	0.000227	-0.000058
45	6	0	5.686731	0.000129	0.000030
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47	6	0	7.116445	0.000066	0.000027
48	6	0	7.066775	-2.222839	0.980932
49	1	0	7.564928	-3.103119	1.368972
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51	6	0	5.668208	2.213564	-0.980042
52	6	0	7.066968	2.222973	-0.980879
53	1	0	7.565194	3.103208	-1.368928
54	6	0	7.813508	1.143748	-0.503544
55	1	0	5.105669	-3.060961	1.356834
56	1	0	5.105935	3.061275	-1.356761
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63	6	0	11.425234	-2.223490	0.971408
64	1	0	11.986003	-3.074873	1.342910
65	6	0	10.026977	2.228502	-0.974657
66	6	0	11.425430	2.223226	-0.971395
67	1	0	11.986274	3.074555	-1.342908
68	6	0	12.121492	1.127909	-0.492774
69	1	0	9.525226	-3.108436	1.359262
70	1	0	9.525500	3.108343	-1.359241
71	6	0	13.604203	1.148427	-0.501582
72	6	0	13.604102	-1.148887	0.501584
73	1	0	15.229633	-0.000307	-0.000012
74	8	0	2.858111	-2.089725	0.946549
75	8	0	2.858320	2.090310	-0.946397
76	8	0	14.272723	-2.085741	0.910562
77	8	0	14.272906	2.085216	-0.910574
78	7	0	14.214408	-0.000259	-0.000004
79	6	0	-1.389130	0.000135	-0.000045
80	6	0	-0.695968	-0.003923	1.209717
81	6	0	-0.696012	0.004192	-1.209819
82	6	0	0.695996	0.004812	1.209684
83	1	0	-1.242115	-0.002874	2.146560
84	6	0	0.695964	-0.004489	-1.209845
85	1	0	-1.242188	0.003118	-2.146646
86	6	0	1.389133	0.000182	-0.000098
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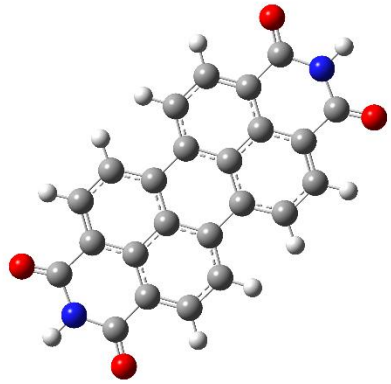
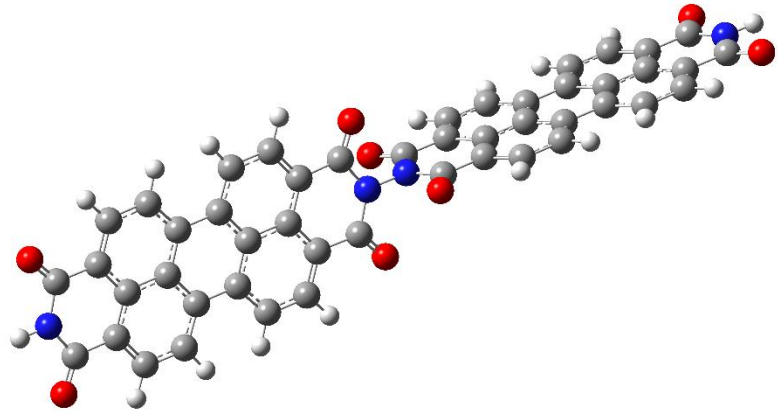
88	1	0	1.242092	-0.003920	-2.146697

Structures:

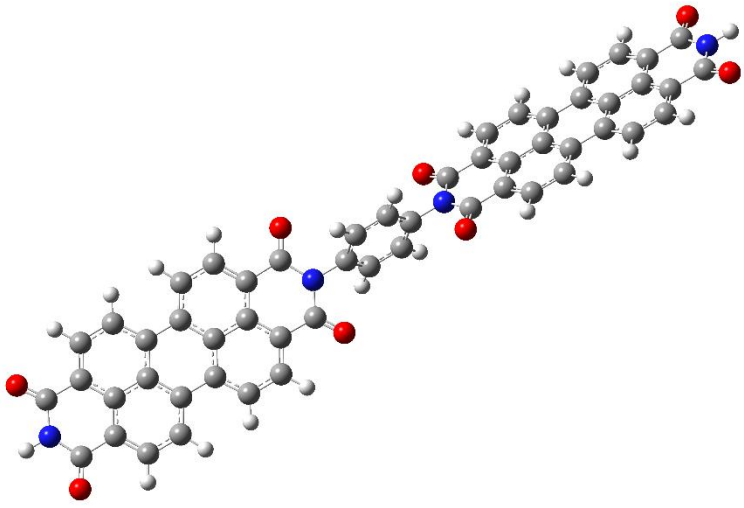
M



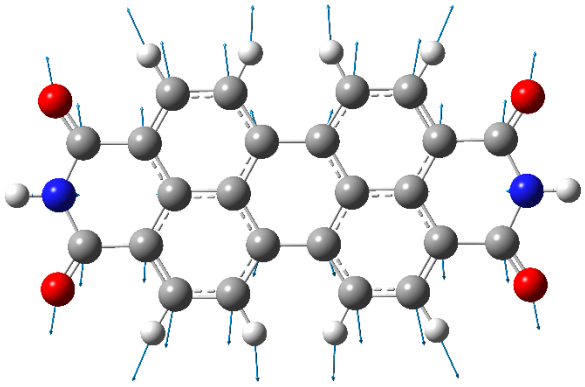
D0



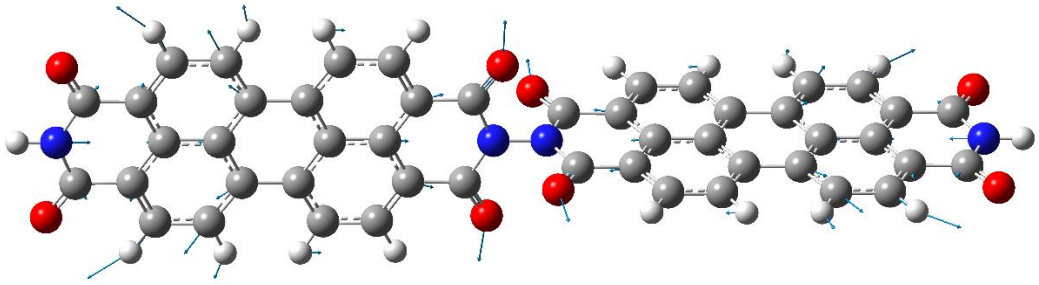
D1



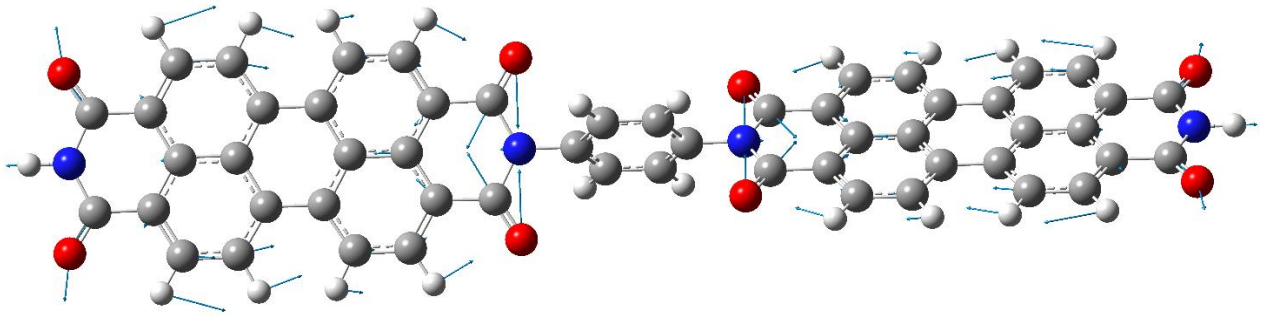
M Raman active vibrational mode at 532 cm^{-1}



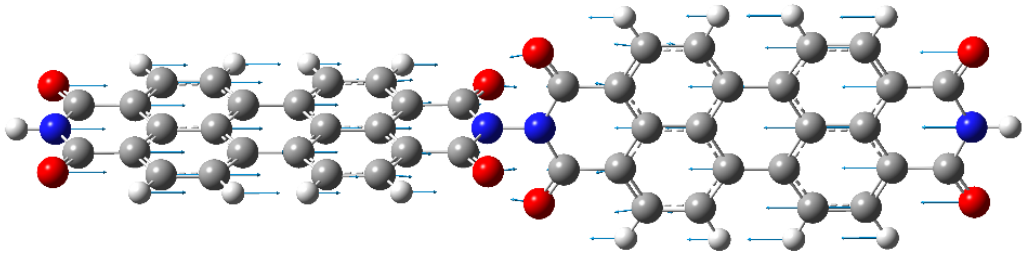
D0 Raman active vibrational mode at 550 cm^{-1}



D1 Raman active vibrational mode at 550 cm^{-1}



D0 Raman active vibrational mode at 100.36 cm^{-1}



6) FT Amplitude Maps

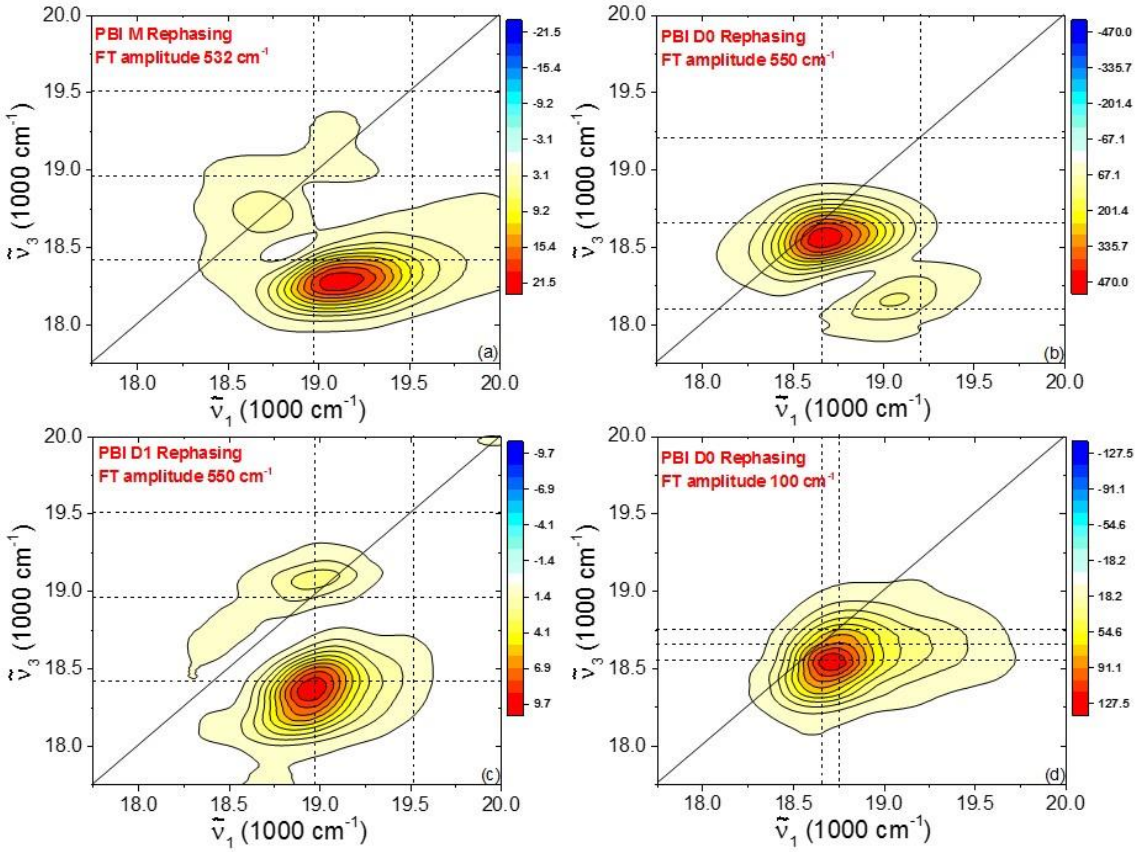


Figure S 9: Rephasing FT amplitude maps where $\tilde{\nu}_1$ is the excitation and $\tilde{\nu}_3$ is the detection scale (in wavenumber). Each 2D graph is normalised to its positive maximum and the amplitude has 21 evenly spaced contour lines. The slices of the 3D FT solid were taken at frequencies corresponding to the in-plane C-C-C bending of PBI M (a), D0 (b) and D1 (c) dimers, and at the frequency of the imide N-N stretching for D0 only (d). The position of the peaks suggests that the origin of those oscillations during the population time (T) is the presence of vibrational (ground state) and vibronic (first excited state) coherences[2].

7) TG-FROG

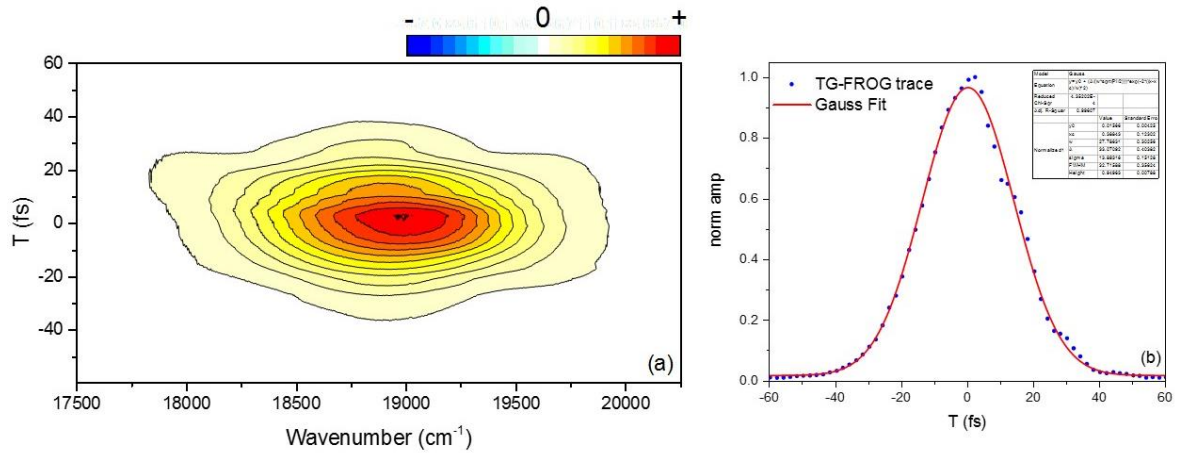


Figure S 10: Transient Grating-Frequency Resolved Optical Gating (TG-FROG) measured with cyclohexane in a 1 mm cell (a). TG-FROG trace (blue dots) at 19000 cm^{-1} and Gaussian fit (red line) (b). The FWHM extracted from the fit is 32 fs.

References

(1) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. Gaussian 09, Revision C.1. Gaussian, Inc., Wallingford CT 2009.

(2) Camargo, F. V. D. A.; Grimmelsmann, L.; Anderson, L.; Meech, S. R.; Heisler, I. A. Supplemental Material - Resolving Vibrational from Electronic Coherences in Two-Dimensional Electronic Spectroscopy : The Role of the Laser Spectrum. **2017**, *033001* (January), 1–19.