Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Supporting Information for

# Molecular basis of the exciton-phonon interactions in the PE545 light-harvesting complex

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## 1. Molecular origin of quasi-harmonic modes

In the following Tables S1-S8, we report the individual rings of each bilin involved in the δ(ring), γ(ring), β(ring), υ(C-C) and υ(C-N) displacements for each mode analyzed, thus allowing identification of those expected to be strongly coupled to the excitations of the pigments. Such motions involve torsional motions δ(ring) distorting the planarity of the pyrrole rings, out of plane and in plane bendings of the rings, γ(ring) and β(ring), respectively, and υ(C-C) and υ(C-N) stretchings leading to ring breathing modes. In the 500-600 and 650-750 $cm^{-1}$ range, such motions mostly involve δ(ring), γ(ring) and β(ring) displacements. In the 950-1050 $cm^{-1}$ region, the vibrations are characterized by a mix of β(ring), υ(C-C) and υ(C-N) distortions leading to ring breathing modes. Finally, modes in the 1400-1500 $cm^{-1}$ range mostly involve υ(C-C) and υ(C-N) stretchings, again leading to ring breathing modes. The correspondence between the ring numbering and the structure of PEBs and DBVs is shown in Figure S1 and S2.

PEBs and DBVs is shown in Figure S1 and S2.

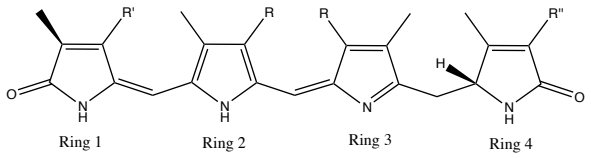


Figure S1: Correspondence between ring numbering and the structure of DBVs.

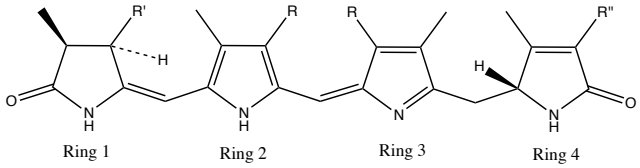


Figure S2: Correspondence between ring numbering and the structure of PEBs.

Table S1. Quasi-harmonic modes of pigment $DBV_{19A}$.

| Frequency ($cm^{-1}$) | Mode | δ(ring), γ(ring) and β (ring) |
|---|---|---|
| 493,66 | 79 | 3,4 |
| 521,93 | 80 | |
| 534,69 | 81 | 3,4 |
| 544,75 | 82 | 3,4 |
| 552,56 | 83 | 2 |
| 557,15 | 84 | 3,4 |
| 563,05 | 85 | 3,4 |
| 568,99 | 86 | |
| 573,88 | 87 | 3 |
| 576,87 | 88 | |
| 582,79 | 89 | |
| 585,11 | 90 | |
| 591,68 | 91 | |
| 594,56 | 92 | |
| 602,85 | 93 | 3,4 |
| | | δ(ring), γ(ring) and β (ring) |
| 667,26 | 102 | 2,3 |
| 677,86 | 103 | 1,2 |
| 683,33 | 104 | 3 |
| 694,92 | 105 | 1 |
| 697,02 | 106 | |
| 699,05 | 107 | |
| 711,91 | 108 | |
| 720,87 | 109 | |
| 733,33 | 110 | 1,2,3,4 |
| 738,06 | 111 | 4 |
| 756,35 | 112 | 1,2 |
| | | β (ring), ν(C-C) and ν(C-N) |
| 947,34 | 127 | 2 |
| 957,78 | 128 | 2 |
| 958,69 | 129 | 1,2 |
| 963,29 | 130 | 1 |
| 981,23 | 131 | 1 |
| 989,92 | 132 | 1,2 |
| 1005,68 | 133 | 2,3 |
| 1009,43 | 134 | 1,2,3 |
| 1028,61 | 135 | 1,2,3 |
| 1037,16 | 136 | 4 |
| 1055,17 | 137 | 1,2,3 |
| | | ν(C-C) and ν(C-N) |
| 1399,43 | 165 | 2,4 |
| 1410,20 | 166 | 1,2,3,4 |
| 1417,81 | 167 | 1,2,3,4 |
| 1426,94 | 168 | 1,2,3,4 |
| 1437,39 | 169 | 1,2,3,4 |
| 1442,27 | 170 | 1,2,3,4 |
| 1455,31 | 171 | 2,3,4 |
| 1468,32 | 172 | 1,2,3,4 |
| 1474,35 | 173 | 2,3,4 |

| | | |
|---|---|---|
| 1478,78 | 174 | 1,2,3 |
| 1483,22 | 175 | 1,2,3 |
| 1493,94 | 176 | 1,3,4 |

Table S2. Quasi-harmonic modes of pigment $DBV_{19B}$

| Frequency ($cm^{-1}$) | Mode | δ(ring), γ(ring) and β (ring) |
|---|---|---|
| 501,12 | 80 | 3,4 |
| 519,93 | 81 | 3 |
| 529,12 | 82 | 3 |
| 529,34 | 83 | 3,4 |
| 534,35 | 84 | |
| 546,37 | 85 | |
| 552,23 | 86 | 3,4 |
| 559,41 | 87 | |
| 564,00 | 88 | 1,2,3,4 |
| 567,43 | 89 | 1,2,3,4 |
| 569,37 | 90 | |
| 573,61 | 91 | |
| 578,99 | 92 | 2,3 |
| 591,10 | 93 | |
| 595,15 | 94 | |
| 604,46 | 95 | 2,3,4 |
| | | δ(ring), γ(ring) and β (ring) |
| 659,30 | 103 | 2,3,4 |
| 663,77 | 104 | 1,2,3,4 |
| 677,90 | 105 | 1,2,3,4 |
| 697,68 | 106 | 1,2,3,4 |
| 711,50 | 107 | 4 |
| 719,64 | 108 | 4 |
| 729,43 | 109 | |
| 736,25 | 110 | 1 |
| 744,67 | 111 | 1,2,3 |
| 776,86 | 112 | 1,2 |
| | | β (ring), ν(C-C) and ν(C-N) |
| 954,40 | 127 | 2,3 |
| 977,15 | 128 | 4 |
| 989,26 | 129 | 1,2,3,4 |
| 997,22 | 130 | 1,3,4 |
| 1018,10 | 131 | 2,3,4 |
| 1022,46 | 132 | 1,2,3 |
| 1030,55 | 133 | 3,4 |
| 1038,32 | 134 | 1,2,3,4 |
| 1051,51 | 135 | 2,3,4 |
| 1059,05 | 136 | 4 |
| | | ν(C-C) and ν(C-N) |
| 1401,73 | 159 | 1,4 |
| 1404,90 | 160 | 1,2,4 |
| 1421,35 | 161 | 1,2,3 |
| 1426,99 | 162 | 1,2,3,4 |
| 1438,36 | 163 | 1,2,3,4 |
| 1441,63 | 164 | 1,2,4 |
| 1462,17 | 165 | 1,3,4 |
| 1462,65 | 166 | 1,2,3,4 |
| 1469,12 | 167 | 1,2,3,4 |
| 1482,64 | 168 | 1,2,3,4 |
| 1488,28 | 169 | 1,2,3 |
| 1492,94 | 170 | 1,2,3,4 |
| 1501,85 | 171 | 1,2,3 |

Table S3. Quasi-harmonic modes of pigment $PEB_{50/61C}$

| Frequency ($cm^{-1}$) | Mode | δ(ring), γ(ring) and β (ring) |
|---|---|---|
| 511,57 | 79 | 1,2,3 |
| 517,81 | 80 | 1,2 |
| 529,18 | 81 | 1,2 |
| 539,31 | 82 | 2,3,4 |
| 548,81 | 83 | 1,2,3 |
| 556,98 | 84 | 1,3,4 |
| 563,02 | 85 | 1,2 |
| 583,20 | 86 | 1,3 |
| 595,52 | 87 | |
| 600,39 | 88 | 4 |
| | | δ(ring), γ(ring) and β (ring) |
| 660,91 | 102 | 1,2,3 |
| 666,91 | 103 | |
| 678,22 | 104 | 1,2 |
| 681,58 | 105 | 1,2,4 |
| 694,64 | 106 | 2,3,4 |
| 702,16 | 107 | 1,2,3,4 |
| 722,70 | 108 | |
| 732,69 | 109 | 1,2,3,4 |
| 752,77 | 110 | 1,2,3 |
| 757,98 | 111 | 1 |
| 765,25 | 112 | 1,2,3 |
| | | β (ring), ν(C-C) and ν(C-N) |
| 948,90 | 126 | 1,2,3,4 |
| 953,52 | 127 | 1 |
| 963,78 | 128 | 2,4 |
| 986,60 | 129 | 1,3 |
| 999,66 | 130 | 1,2 |
| 1011,51 | 131 | |
| 1014,02 | 132 | 1,2,4 |
| 1020,63 | 133 | 1,4 |
| 1031,22 | 134 | 1,4 |
| 1042,89 | 135 | 1,2 |
| 1055,20 | 136 | 1,2,3,4 |
| | | ν(C-C) and ν(C-N) |
| 1401,87 | 167 | 1,2,4 |
| 1419,33 | 168 | 1,2,4 |
| 1423,79 | 169 | 1,3,4 |
| 1441,21 | 170 | 1,2,3 |
| 1451,93 | 171 | 1,2,3,4 |
| 1472,75 | 172 | 1,2,3,4 |
| 1475,23 | 173 | 2,3 |
| 1480,75 | 174 | 1,3,4 |
| 1486,74 | 175 | 1,2,3,4 |
| 1504,22 | 176 | 1,2,3,4 |

Table S4. Quasi-harmonic modes of pigment $PEB_{50/61D}$

| Frequency ($cm^{-1}$) | Mode | δ(ring), γ(ring) and β (ring) |
|---|---|---|
| 510,23 | 79 | 1,4 |
| 517,45 | 80 | 3,4 |
| 525,94 | 81 | 2,3 |
| 530,17 | 82 | 2 |
| 543,02 | 83 | 2 |
| 551,56 | 84 | 3 |
| 556,48 | 85 | 3 |
| 568,08 | 86 | 2,3 |
| 570,12 | 87 | 2,3,4 |
| 579,56 | 88 | 1,2,3,4 |
| 582,51 | 89 | 1,2 |
| 588,46 | 90 | |
| 591,19 | 91 | 3,4 |
| 598,52 | 92 | 1,2,3 |
| | | δ(ring), γ(ring) and β (ring) |
| 663,54 | 101 | 1,4 |
| 667,51 | 102 | |
| 675,41 | 103 | 1,2 |
| 682,73 | 104 | 2 |
| 686,77 | 105 | 1,2,4 |
| 688,62 | 106 | 4 |
| 694,60 | 107 | |
| 704,72 | 108 | 2,3,4 |
| 711,11 | 109 | |
| 716,27 | 110 | 2,3,4 |
| 733,04 | 111 | 1,4 |
| 759,68 | 112 | 1,4 |
| | | β (ring), ν(C-C) and ν(C-N) |
| 942,10 | 128 | 2,3,4 |
| 971,53 | 129 | 2,4 |
| 979,21 | 130 | 2,4 |
| 994,50 | 131 | 2,3,4 |
| 1017,83 | 132 | 1 |
| 1024,10 | 133 | 1,3 |
| 1031,13 | 134 | 2,3 |
| 1039,29 | 135 | 1,2,4 |
| 1052,23 | 136 | 1,2,4 |
| | | ν(C-C) and ν(C-N) |
| 1402,27 | 166 | 1,2,3 |
| 1413,23 | 167 | 2,3,4 |
| 1416,37 | 168 | 4 |
| 1423,93 | 169 | 1,2,3,4 |
| 1427,60 | 170 | 1,4 |
| 1433,68 | 171 | 1,2,3,4 |
| 1437,55 | 172 | 1,2,4 |
| 1443,73 | 173 | 2,3,4 |
| 1452,18 | 174 | 2,3,4 |
| 1458,68 | 175 | 2,4 |
| 1460,06 | 176 | 2 |
| 1475,81 | 177 | 1,2,3,4 |
| 1482,54 | 178 | 1,2,3,4 |
| 1494,60 | 179 | 2,3,4 |
| 1496,96 | 180 | 1,3,4 |
| 1509,85 | 181 | 1,2,3,4 |

Table S5. Quasi-harmonic modes of pigment $PEB_{158C}$

| Frequency ($cm^{-1}$) | Mode | δ(ring), γ(ring) and β (ring) |
|---|---|---|
| 504,25 | 76 | 3 |
| 514,14 | 77 | 1,2,3 |
| 518,27 | 78 | 1,2 |
| 531,49 | 79 | 2,4 |
| 542,99 | 80 | |
| 546,38 | 81 | 2,3 |
| 556,06 | 82 | |
| 567,90 | 83 | |
| 572,06 | 84 | 1 |
| 576,78 | 85 | 3,4 |
| 585,64 | 86 | 1,2,3 |
| 595,54 | 87 | 1,2,3,4 |
| 602,38 | 88 | 2,4 |
| | | δ(ring), γ(ring) and β (ring) |
| 658,43 | 95 | 3 |
| 676,24 | 96 | 2,3,4 |
| 684,33 | 97 | 4 |
| 692,23 | 98 | 1,2,3 |
| 700,95 | 99 | |
| 709,95 | 100 | |
| 711,13 | 101 | 2,3,4 |
| 721,89 | 102 | 1,2,3,4 |
| 741,77 | 103 | 1,2,3,4 |
| 744,57 | 104 | 1,2,3,4 |
| 756,49 | 105 | 1,2,3,4 |
| | | β (ring), ν(C-C) and ν(C-N) |
| 954,37 | 126 | 1 |
| 959,14 | 127 | 1 |
| 966,61 | 128 | 1 |
| 977,20 | 129 | 1,2 |
| 984,21 | 130 | 1,3 |
| 998,23 | 131 | 1,3 |
| 1000,96 | 132 | 1,2,3 |
| 1029,93 | 133 | 1,2,3 |
| 1032,77 | 134 | 3 |
| 1062,44 | 135 | 2 |
| | | ν(C-C) and ν(C-N) |
| 1403,12 | 162 | 1,2,3 |
| 1406,13 | 163 | 1,3,4 |
| 1413,13 | 164 | 1,2,3 |
| 1423,01 | 165 | 1,2,3,4 |
| 1427,02 | 166 | 1,3,4 |
| 1434,66 | 167 | 1,2,3,4 |
| 1448,91 | 168 | 1,2,3,4 |
| 1454,70 | 169 | |
| 1469,46 | 170 | 2,3,4 |
| 1470,47 | 171 | 1,2,3,4 |
| 1487,23 | 172 | 2,3,4 |

| | | |
|---|---|---|
| 1494,04 | 173 | 1,2,4 |
| 1502,91 | 174 | 1,2,3,4 |

Table S6. Quasi-harmonic modes of pigment $PEB_{82C}$

| Frequency ($cm^{-1}$) | Mode | δ(ring), γ(ring) and β (ring) |
|---|---|---|
| 507,25 | 74 | 1,2,3 |
| 516,61 | 75 | 1,2 |
| 534,31 | 76 | 3,4 |
| 541,30 | 77 | |
| 546,66 | 78 | 1 |
| 549,30 | 79 | 2,4 |
| 556,52 | 80 | 1,2,3 |
| 559,65 | 81 | |
| 577,63 | 82 | 3,4 |
| 585,73 | 83 | 1,3,4 |
| 596,32 | 84 | 1,2,3 |
| 597,12 | 85 | 1,3,4 |
| | | δ(ring), γ(ring) and β (ring) |
| 659,17 | 91 | 1,2,3,4 |
| 670,96 | 92 | 1,2,3,4 |
| 691,17 | 93 | 2 |
| 696,70 | 94 | 1,2,3 |
| 701,10 | 95 | |
| 704,24 | 96 | |
| 708,06 | 97 | 1 |
| 711,41 | 98 | |
| 725,44 | 99 | 2,3,4 |
| 732,35 | 100 | 2,3 |
| 749,93 | 101 | |
| 753,36 | 102 | 2,3,4 |
| 764,48 | 103 | 1,2,4 |
| | | β (ring), ν(C-C) and ν(C-N) |
| 947,14 | 122 | 1,3,4 |
| 962,03 | 123 | 1,4 |
| 964,13 | 124 | 1,2,3 |
| 996,12 | 125 | 1,4 |
| 1004,78 | 126 | 2,3,4 |
| 1008,34 | 127 | 1,2,3 |
| 1016,25 | 128 | 4 |
| 1033,26 | 129 | 1 |
| 1049,23 | 130 | 2,3,4 |
| | | ν(C-C) and ν(C-N) |
| 1414,09 | 163 | 1,3,4 |
| 1423,19 | 164 | 1,2,3,4 |
| 1426,92 | 165 | 1,2,3,4 |
| 1435,91 | 166 | 1 |
| 1440,30 | 167 | 1,2,3,4 |
| 1457,18 | 168 | 1,2,3,4 |
| 1468,17 | 169 | 1 |
| 1478,04 | 170 | 1,2,3,4 |
| 1493,60 | 171 | 1,2,3,4 |
| 1499,41 | 172 | 4 |
| 1507,28 | 173 | 1,2,3,4 |

Table S7. Quasi-harmonic modes of pigment $PEB_{158D}$

| Frequency ($cm^{-1}$) | Mode | δ(ring), γ(ring) and β (ring) |
|---|---|---|
| 507,90 | 75 | 3,4 |
| 512,78 | 76 | 1,2,3 |
| 521,75 | 77 | 2,3 |
| 531,92 | 78 | 1,2,3,4 |
| 534,19 | 79 | 1,3,4 |
| 555,91 | 80 | 1,2,3,4 |
| 561,69 | 81 | 1,3,4 |
| 565,78 | 82 | 1 |
| 570,99 | 83 | 3 |
| 586,22 | 84 | 1,2,3,4 |
| 590,19 | 85 | 1 |
| 595,93 | 86 | |
| 601,43 | 87 | 2 |
| | | δ(ring), γ(ring) and β (ring) |
| 662,46 | 100 | 3 |
| 681,66 | 101 | 2,3,4 |
| 690,97 | 102 | 1,3,4 |
| 693,02 | 103 | |
| 699,84 | 104 | 1,2,3,4 |
| 711,18 | 105 | 1,2,3,4 |
| 726,59 | 106 | 1,2,3,4 |
| 733,19 | 107 | 1 |
| 743,60 | 108 | 1,2,3,4 |
| 771,49 | 109 | 1,2,3 |
| | | β (ring), ν(C-C) and ν(C-N) |
| 946,49 | 124 | 1,2 |
| 975,70 | 125 | 1,2,3* |
| 979,39 | 126 | |
| 997,60 | 127 | 2 |
| 1003,23 | 128 | 2,3,4 |
| 1004,82 | 129 | 1,2,3,4 |
| 1009,66 | 130 | 1,2 |
| 1019,73 | 131 | 1,2,4 |
| 1025,28 | 132 | 1,3,4 |
| 1053,96 | 133 | 2,3,4 |
| | | ν(C-C) and ν(C-N) |
| 1400,27 | 163 | 1,2,3,4 |
| 1413,32 | 164 | 1,2,3,4 |
| 1418,70 | 165 | 2,3,4 |
| 1428,58 | 166 | 1,2,3,4 |
| 1444,91 | 167 | 3,4 |
| 1446,91 | 168 | 1,3,4 |
| 1452,29 | 169 | 1,3,4 |
| 1471,47 | 170 | 1,3 |
| 1478,99 | 171 | 1,2,3 |
| 1486,84 | 172 | 1,2,3 |
| 1502,77 | 173 | 1,3,4 |

Table S8. Quasi-harmonic modes of pigment $PEB_{82D}$

| Frequency ($cm^{-1}$) | Mode | δ(ring), γ(ring) and β (ring) |
|---|---|---|
| 502,38 | 76 | 1,3,4 |
| 515,83 | 77 | 1,2,3,4 |
| 532,29 | 78 | 1,3,4 |
| 535,59 | 79 | 1,2 |
| 548,00 | 80 | 2 |
| 554,62 | 81 | |
| 559,38 | 82 | 3,4 |
| 562,60 | 83 | |
| 574,04 | 84 | 2,3,4 |
| 589,12 | 85 | 3 |
| 590,59 | 86 | 1,2 |
| 595,42 | 87 | 1,2 |
| | | δ(ring), γ(ring) and β (ring) |
| 662,36 | 94 | 1 |
| 664,08 | 95 | 1,2,3,4 |
| 672,91 | 96 | 1,4 |
| 684,89 | 97 | |
| 692,66 | 98 | 2,3 |
| 697,95 | 99 | |
| 706,27 | 100 | 1,2,3,4 |
| 712,72 | 101 | 1,2,3,4 |
| 720,65 | 102 | |
| 726,33 | 103 | 1,2 |
| 731,84 | 104 | 1,2,3,4 |
| 737,66 | 105 | 1,2,3 |
| 746,54 | 106 | 1,2,3,4 |
| 761,89 | 107 | 2,3 |
| | | β (ring), ν(C-C) and ν(C-N) |
| 954,36 | 126 | 1,3 |
| 975,12 | 127 | 1,3 |
| 982,89 | 128 | 2,3 |
| 994,27 | 129 | 1,3 |
| 1008,27 | 130 | 3 |
| 1014,71 | 131 | 1,2,3 |
| 1032,34 | 132 | 1,2,3,4 |
| 1042,89 | 133 | 1,2,3,4 |
| 1054,58 | 134 | 2,3,4 |
| | | ν(C-C) and ν(C-N) |
| 1405,30 | 165 | 1,2,3 |
| 1411,49 | 166 | 2,3,4 |
| 1432,37 | 167 | 1,4 |
| 1445,49 | 168 | 2,3,4 |
| 1452,28 | 169 | 1,2,3 |
| 1456,20 | 170 | 1,4 |
| 1466,07 | 171 | 1,2,3,4 |
| 1472,79 | 172 | 1,3,4 |
| 1493,30 | 173 | 1,2,3,4 |
| 1497,23 | 174 | 1,2,3,4 |
| 1500,58 | 175 | 1,3 |

## 2. Comparison of the distribution of vibrational modes found with the NMA analysis at the MM and QM levels

Figure S3 shows the distribution of normal modes computed for the pigments using the NMA analysis at the DFT B3LYP/6-31G(d) level of theory and using the classical force-field used in the MD simulation. The red/yellow bars represent the DFT/MM distribution, while the orange ones represent overlaps between the two methods.

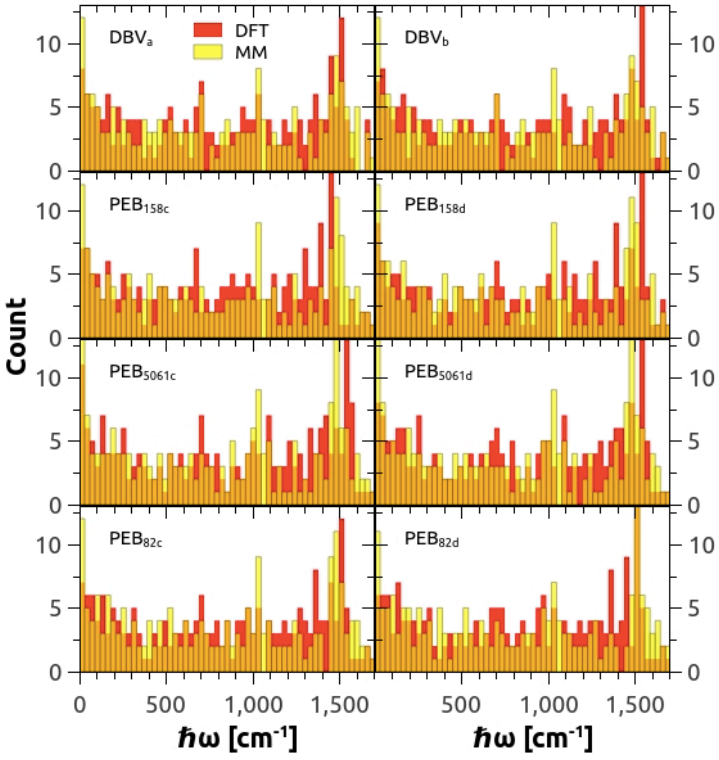


Figure S3: Comparison between QM (red) and MM (yellow) vibrational frequencies population.

## 3. Spectral densities data

$$J(\omega) = J_{continuous}(\omega) + J_{peaks}(\omega) = \frac{2\lambda}{\pi}\frac{\Omega\omega}{\omega^2+\Omega^2} + \sum_q \frac{2\lambda_q}{\pi}\frac{\nu_q\omega_q^2\omega}{\left(\omega_q^2-\omega^2\right)^2+\nu_q^2\omega^2}$$

$\lambda$ is the reorganization energy and $\Omega$ the bath cutoff frequency.

Table S9. Values used to fit the continuous part of the spectral densities for the individual pigments and their average values. Units in $cm^{-1}$.

| | λ | Ω |
|---|---|---|
| All | 75.79 | 56.82 |
| DBV | 65.57 | 16.16 |
| DBVa | 80.31 | 42.76 |
| DBVb | 85.79 | 36.82 |
| PEB_158 | 35.38 | 30.69 |
| PEB_158c | 48.59 | 25.43 |
| PEB_158d | 48.70 | 32.74 |
| PEB_5061 | 36.34 | 32.47 |
| PEB_5061c | 36.75 | 20.51 |
| PEB_5061d | 39.62 | 16.78 |
| PEB_82 | 20.00 | 31.00 |
| PEB_82c | 16.98 | 18.65 |
| PEB_82d | 23.67 | 18.98 |

Table S10. Values used to fit the damped quantum harmonic oscillators part of the spectral densities for the individual pigments and their average values. Units in $cm^{-1}$.

| Peak | DBVa | | | DBVb | | | DBVs | | |
|---|---|---|---|---|---|---|---|---|---|
| | ωp | λp | νp | ωp | λp | νp | ωp | λp | νp |
| 1 | 89.913 | 14.533 | 54.560 | 110.255 | 32.580 | 64.920 | 95.721 | 37.619 | 77.935 |
| 2 | 180.389 | 74.394 | 95.087 | 191.999 | 55.038 | 81.963 | 186.856 | 79.085 | 105.986 |
| 3 | 276.279 | 16.997 | 37.460 | 278.474 | 12.492 | 44.806 | 277.030 | 13.496 | 38.103 |
| 4 | 323.354 | 11.536 | 56.714 | 311.386 | 15.019 | 37.716 | 314.400 | 14.433 | 47.055 |
| 5 | 386.070 | 26.036 | 83.022 | 372.476 | 23.834 | 45.225 | 374.160 | 21.540 | 52.585 |
| 6 | 458.308 | 23.030 | 85.748 | 437.176 | 40.085 | 85.368 | 440.563 | 34.066 | 84.824 |
| 7 | 552.503 | 22.243 | 65.762 | 480.738 | 8.256 | 37.834 | 483.376 | 4.975 | 35.230 |
| 8 | 618.707 | 18.109 | 97.138 | 545.722 | 10.487 | 38.739 | 550.968 | 20.779 | 56.971 |
| 9 | 680.088 | 17.236 | 46.029 | 568.148 | 7.733 | 68.075 | 596.343 | 10.804 | 65.960 |
| 10 | 727.264 | 13.613 | 86.543 | 589.208 | 15.070 | 75.044 | 663.210 | 20.199 | 58.892 |
| 11 | 815.110 | 8.817 | 47.376 | 656.698 | 20.776 | 43.160 | 709.735 | 19.988 | 89.766 |
| 12 | 894.443 | 22.991 | 58.393 | 702.316 | 10.362 | 47.795 | 815.155 | 9.407 | 57.728 |
| 13 | 942.702 | 5.751 | 36.076 | 743.064 | 4.275 | 37.584 | 895.100 | 25.727 | 64.375 |
| 14 | 972.955 | 16.565 | 37.222 | 826.493 | 16.034 | 87.260 | 971.499 | 21.800 | 50.658 |
| 15 | 1036.140 | 15.619 | 41.185 | 894.360 | 18.842 | 48.510 | 1034.780 | 16.240 | 36.142 |
| 16 | 1158.130 | 18.074 | 64.166 | 974.110 | 24.695 | 61.609 | 1151.830 | 11.913 | 53.942 |
| 17 | 1187.660 | 5.074 | 19.985 | 1033.910 | 16.400 | 31.409 | 1186.150 | 5.582 | 27.397 |
| 18 | 1241.210 | 4.961 | 24.881 | 1141.590 | 3.362 | 32.191 | 1242.260 | 5.920 | 30.112 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 19 | 1412.410 | 19.795 | 17.497 | 1173.820 | 10.670 | 63.148 | 1418.960 | 37.718 | 24.459 |
| 20 | 1423.720 | 23.924 | 18.509 | 1244.420 | 5.866 | 32.526 | 1532.700 | 57.400 | 62.046 |
| 21 | 1534.650 | 69.144 | 63.536 | 1419.690 | 28.751 | 25.191 | 1628.200 | 8.696 | 22.308 |
| 22 | 1624.300 | 6.350 | 18.949 | 1529.780 | 45.828 | 59.611 | 1696.340 | 21.172 | 24.722 |
| 23 | 1695.170 | 16.120 | 20.707 | 1631.480 | 11.048 | 23.676 | 1725.830 | 42.302 | 34.088 |
| 24 | 1724.580 | 58.299 | 37.657 | 1697.590 | 7.047 | 25.415 | 1768.580 | 17.076 | 29.955 |
| 25 | 1774.280 | 15.269 | 39.079 | 1726.030 | 6.634 | 25.448 | 1877.670 | 14.062 | 21.596 |
| 26 | 1918.450 | 50.904 | 19.361 | 1764.110 | 13.056 | 40.364 | 1918.900 | 28.971 | 17.115 |
| 27 | 1929.500 | 11.272 | 8.775 | 1875.470 | 3.710 | 22.358 | 1930.180 | 8.829 | 9.502 |
| 28 | 1992.590 | 350.994 | 24.568 | 1921.730 | 3.153 | 19.433 | 1983.920 | 79.884 | 14.306 |
| 29 | | | | 1991.560 | 51.948 | 19.297 | 1995.480 | 201.760 | 19.041 |

| Peak | PEB158c | | | PEB158d | | | PEB158s | | |
|---|---|---|---|---|---|---|---|---|---|
| | ωp | λp | νp | ωp | λp | νp | ωp | λp | νp |
| 1 | 94.272 | 59.198 | 109.625 | 82.914 | 52.908 | 71.733 | 490.792 | 9.917 | 79.069 |
| 2 | 146.139 | 4.454 | 32.038 | 160.330 | 7.990 | 61.368 | 89.954 | 67.706 | 103.090 |
| 3 | 204.693 | 7.001 | 67.129 | 218.039 | 7.569 | 56.780 | 219.693 | 32.935 | 92.919 |
| 4 | 209.638 | 37.616 | 84.960 | 276.511 | 5.355 | 27.317 | 354.202 | 14.690 | 41.967 |
| 5 | 268.175 | 2.239 | 24.167 | 315.937 | 60.790 | 178.541 | 416.997 | 8.019 | 61.362 |
| 6 | 304.593 | 23.720 | 49.118 | 317.740 | 0.841 | 15.711 | 570.482 | 8.432 | 51.254 |
| 7 | 354.511 | 13.091 | 35.064 | 350.249 | 10.769 | 41.857 | 309.016 | 20.779 | 58.662 |
| 8 | 412.005 | 9.947 | 47.902 | 498.177 | 7.542 | 71.170 | 616.634 | 17.911 | 40.442 |
| 9 | 476.525 | 10.813 | 75.314 | 577.897 | 14.329 | 66.458 | 668.727 | 1.627 | 28.385 |
| 10 | 567.559 | 6.818 | 51.567 | 617.315 | 15.381 | 32.541 | 714.039 | 11.776 | 38.638 |
| 11 | 616.052 | 16.451 | 43.391 | 716.519 | 16.169 | 37.380 | 781.753 | 6.353 | 67.435 |
| 12 | 669.163 | 4.710 | 37.469 | 818.306 | 3.881 | 44.099 | 150.947 | 4.743 | 36.640 |
| 13 | 709.797 | 7.932 | 41.223 | 877.023 | 5.093 | 31.000 | 192.179 | 4.477 | 55.762 |
| 14 | 776.159 | 6.779 | 39.276 | 943.154 | 7.129 | 25.210 | 276.206 | 7.081 | 36.267 |
| 15 | 869.593 | 6.928 | 63.173 | 958.039 | 13.312 | 80.690 | 873.261 | 7.022 | 52.236 |
| 16 | 940.069 | 25.223 | 38.469 | 1004.950 | 15.291 | 67.497 | 942.397 | 20.289 | 38.861 |
| 17 | 1005.020 | 21.043 | 38.763 | 1046.920 | 19.448 | 31.129 | 1256.570 | 1.651 | 37.507 |
| 18 | 1053.130 | 16.449 | 28.960 | 1168.530 | 4.453 | 27.098 | 1004.760 | 19.404 | 49.167 |
| 19 | 1162.900 | 6.004 | 33.861 | 1258.910 | 2.058 | 33.257 | 1050.000 | 18.030 | 31.020 |
| 20 | 1245.550 | 0.927 | 31.625 | 1397.130 | 20.481 | 48.620 | 1165.820 | 5.334 | 32.069 |
| 21 | 1372.060 | 4.733 | 27.404 | 1497.080 | 12.621 | 35.738 | 1547.410 | 12.910 | 36.081 |
| 22 | 1407.640 | 13.783 | 42.453 | 1549.200 | 18.374 | 37.195 | 1375.890 | 4.796 | 30.145 |
| 23 | 1505.080 | 17.310 | 51.283 | 1577.430 | 10.490 | 33.307 | 1404.930 | 13.939 | 41.696 |
| 24 | 1544.120 | 8.554 | 36.934 | 1677.420 | 15.263 | 49.360 | 1501.170 | 15.841 | 46.724 |
| 25 | 1573.070 | 4.803 | 22.032 | 1704.290 | 9.956 | 23.297 | 1572.360 | 5.786 | 26.036 |
| 26 | 1584.760 | 7.168 | 21.057 | 1756.950 | 5.819 | 23.276 | 1584.950 | 5.343 | 21.101 |
| 27 | 1672.580 | 9.578 | 29.692 | 1794.350 | 5.322 | 24.720 | 1674.200 | 11.695 | 39.008 |
| 28 | 1700.560 | 9.635 | 20.541 | 1850.060 | 9.585 | 15.782 | 1702.100 | 10.312 | 22.991 |
| 29 | 1756.740 | 8.006 | 26.489 | 1906.770 | 120.519 | 21.450 | 1757.160 | 7.208 | 25.882 |
| 30 | 1783.730 | 8.035 | 28.664 | 2016.300 | 12.259 | 20.109 | 1788.490 | 6.544 | 28.976 |
| 31 | 1848.350 | 9.035 | 17.010 | | | | 1849.220 | 9.343 | 16.518 |
| 32 | 1903.660 | 90.406 | 23.186 | | | | 1905.540 | 105.391 | 22.344 |
| 33 | 2013.660 | 2.194 | 15.614 | | | | 2015.840 | 7.111 | 19.051 |

| Peak | PEB5061c | | | PEB5061d | | | PEB5061s | | |
|---|---|---|---|---|---|---|---|---|---|
| | ωp | λp | νp | ωp | λp | νp | ωp | λp | νp |
| 1 | 63.018 | 12.159 | 45.191 | 82.585 | 23.950 | 67.183 | 77.943 | 22.729 | 83.480 |
| 2 | 196.350 | 60.918 | 206.666 | 451.239 | 5.129 | 54.868 | 220.501 | 37.155 | 165.574 |
| 3 | 246.300 | 2.588 | 17.633 | 238.620 | 60.046 | 132.989 | 250.292 | 10.988 | 65.476 |
| 4 | 317.604 | 20.695 | 95.274 | 352.542 | 12.025 | 46.561 | 351.283 | 18.446 | 116.465 |
| 5 | 541.449 | 18.202 | 60.179 | 548.899 | 11.704 | 38.567 | 448.555 | 2.065 | 39.730 |
| 6 | 633.935 | 12.624 | 42.965 | 628.176 | 16.848 | 50.120 | 546.144 | 13.940 | 47.708 |
| 7 | 728.290 | 17.484 | 61.249 | 712.940 | 13.739 | 40.333 | 630.174 | 12.904 | 42.948 |
| 8 | 736.913 | 0.734 | 12.757 | 764.589 | 6.846 | 28.865 | 722.844 | 18.954 | 65.574 |
| 9 | 894.426 | 7.079 | 36.459 | 270.818 | 2.415 | 32.444 | 766.681 | 2.030 | 24.523 |
| 10 | 948.200 | 31.114 | 60.466 | 841.128 | 4.405 | 30.671 | 892.800 | 4.680 | 30.269 |
| 11 | 1043.260 | 24.787 | 29.049 | 893.600 | 5.397 | 26.642 | 162.077 | 3.693 | 34.732 |
| 12 | 1133.680 | 6.051 | 45.396 | 949.981 | 27.213 | 76.325 | 302.877 | 1.486 | 26.172 |
| 13 | 1167.070 | 5.932 | 29.307 | 1040.490 | 10.593 | 24.068 | 953.684 | 39.734 | 89.262 |
| 14 | 1756.500 | 1.268 | 10.921 | 1051.840 | 7.921 | 23.222 | 1043.780 | 22.744 | 30.474 |
| 15 | 1365.670 | 4.248 | 26.163 | 998.765 | 12.598 | 47.930 | 1126.530 | 2.636 | 34.338 |
| 16 | 1419.530 | 7.113 | 30.593 | 1186.340 | 2.416 | 24.101 | 1169.640 | 8.496 | 41.473 |
| 17 | 1491.340 | 5.633 | 37.216 | 1168.550 | 6.884 | 42.316 | 1767.940 | 5.493 | 26.468 |
| 18 | 1568.040 | 34.099 | 53.921 | 1402.460 | 8.716 | 63.684 | 1360.320 | 5.564 | 35.155 |
| 19 | 1629.170 | 27.208 | 37.913 | 1355.100 | 4.862 | 25.783 | 1419.400 | 4.504 | 30.901 |
| 20 | 1308.970 | 1.868 | 47.093 | 1115.580 | 2.552 | 32.611 | 1493.570 | 8.828 | 41.712 |
| 21 | 1704.330 | 26.246 | 24.707 | 1494.110 | 11.082 | 41.672 | 1569.950 | 28.876 | 46.554 |
| 22 | 1847.050 | 9.377 | 11.591 | 1572.210 | 24.645 | 40.823 | 1626.780 | 22.696 | 30.279 |
| 23 | 1855.800 | 16.046 | 14.449 | 1625.220 | 20.262 | 27.092 | 1395.340 | 2.536 | 58.130 |
| 24 | 1896.580 | 30.208 | 21.195 | 1664.770 | 10.002 | 23.319 | 1665.530 | 6.228 | 18.599 |
| 25 | 1997.060 | 34.051 | 21.286 | 1771.140 | 10.082 | 28.822 | 1704.140 | 24.182 | 22.482 |
| 26 | | | | 1703.810 | 22.915 | 21.486 | 1846.900 | 8.416 | 13.717 |
| 27 | | | | 1845.760 | 6.389 | 16.862 | 1855.850 | 8.307 | 12.733 |
| 28 | | | | 1855.550 | 2.084 | 8.325 | 1899.850 | 40.584 | 20.521 |
| 29 | | | | 1901.480 | 50.631 | 19.241 | 1997.580 | 19.122 | 20.929 |
| 30 | | | | 2001.120 | 4.517 | 19.235 | | | |

| Peak | PEB82c | | | PEB82d | | | PEB82s | | |
|---|---|---|---|---|---|---|---|---|---|
| | ωp | λp | νp | ωp | λp | νp | ωp | λp | νp |
| 1 | 50.224 | 21.033 | 40.443 | 87.190 | 28.433 | 110.143 | 46.839 | 10.127 | 37.860 |
| 2 | 98.690 | 8.441 | 54.790 | 267.964 | 33.152 | 209.937 | 93.680 | 0.338 | 30.620 |
| 3 | 169.875 | 13.000 | 212.050 | 265.588 | 2.411 | 21.670 | 113.029 | 26.156 | 148.256 |
| 4 | 201.899 | 2.113 | 50.294 | 280.731 | 15.874 | 36.989 | 221.430 | 12.382 | 104.168 |
| 5 | 201.899 | 2.113 | 50.294 | 338.153 | 9.830 | 58.967 | 278.883 | 23.808 | 56.814 |
| 6 | 277.428 | 27.124 | 86.871 | 526.602 | 8.015 | 32.203 | 340.030 | 12.634 | 43.903 |
| 7 | 340.033 | 13.192 | 35.262 | 597.807 | 4.730 | 35.891 | 445.174 | 3.893 | 60.442 |
| 8 | 483.113 | 13.594 | 83.926 | 628.316 | 5.760 | 54.740 | 486.685 | 3.626 | 45.440 |
| 9 | 533.084 | 7.039 | 31.957 | 656.625 | 7.622 | 32.425 | 529.245 | 7.959 | 33.279 |
| 10 | 594.575 | 2.584 | 33.484 | 719.845 | 10.997 | 40.676 | 610.526 | 9.968 | 60.289 |
| 11 | 623.206 | 6.004 | 39.839 | 464.888 | 4.078 | 86.430 | 655.807 | 8.881 | 43.301 |
| 12 | 659.490 | 7.856 | 46.759 | 824.451 | 8.348 | 36.198 | 715.745 | 11.539 | 42.812 |
| 13 | 711.208 | 12.097 | 41.336 | 881.682 | 9.017 | 41.014 | 766.551 | 0.824 | 19.123 |
| 14 | 768.180 | 2.132 | 25.268 | 926.176 | 5.544 | 29.155 | 827.372 | 7.656 | 43.074 |
| 15 | 833.964 | 6.876 | 50.587 | 980.140 | 10.452 | 36.364 | 880.392 | 6.924 | 35.511 |
| 16 | 879.498 | 4.875 | 28.935 | 1046.190 | 26.459 | 29.711 | 926.356 | 7.403 | 35.200 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 17 | 926.793 | 9.058 | 40.327 | 1276.210 | 1.675 | 28.292 | 980.785 | 11.716 | 42.043 |
| 18 | 982.821 | 14.708 | 52.929 | 1374.740 | 8.357 | 23.267 | 1046.200 | 23.626 | 29.081 |
| 19 | 1039.280 | 6.905 | 20.275 | 1402.960 | 18.084 | 43.032 | 1163.230 | 5.928 | 38.277 |
| 20 | 1050.610 | 11.999 | 23.141 | 1501.250 | 13.096 | 34.405 | 1275.880 | 1.397 | 28.874 |
| 21 | 1162.890 | 6.488 | 39.727 | 1549.630 | 20.413 | 47.540 | 1374.580 | 6.201 | 21.327 |
| 22 | 1275.360 | 1.154 | 30.446 | 1581.380 | 3.866 | 20.308 | 1400.550 | 18.671 | 42.279 |
| 23 | 1376.120 | 6.163 | 22.982 | 1659.310 | 7.940 | 56.262 | 1504.750 | 17.435 | 42.297 |
| 24 | 1400.620 | 16.478 | 37.952 | 1163.430 | 5.676 | 38.725 | 1544.590 | 9.933 | 30.486 |
| 25 | 1505.900 | 17.309 | 44.585 | 1701.620 | 11.618 | 31.820 | 1573.120 | 13.053 | 45.259 |
| 26 | 1551.630 | 22.588 | 50.580 | 1760.180 | 3.697 | 20.923 | 1643.370 | 2.516 | 20.536 |
| 27 | 1584.990 | 3.388 | 30.069 | 1794.860 | 7.741 | 29.061 | 1685.900 | 6.021 | 33.802 |
| 28 | 1644.050 | 2.811 | 31.927 | 1844.270 | 13.196 | 22.342 | 1707.420 | 8.999 | 23.352 |
| 29 | 1705.810 | 15.757 | 31.463 | 1912.000 | 59.946 | 20.951 | 1761.890 | 4.663 | 24.566 |
| 30 | 1754.540 | 1.088 | 11.722 | 2017.200 | 3.093 | 18.459 | 1797.610 | 7.773 | 30.089 |
| 31 | 1769.160 | 3.728 | 22.989 | | | | 1844.530 | 12.018 | 19.818 |
| 32 | 1803.030 | 7.571 | 30.226 | | | | 1912.860 | 90.401 | 21.065 |
| 33 | 1845.200 | 10.732 | 17.272 | | | | 2017.780 | 3.308 | 15.966 |
| 34 | 1913.290 | 120.675 | 21.031 | | | | | | |
| 35 | 2018.090 | 3.610 | 14.624 | | | | | | |

| Peaks | All pigments | | |
|---|---|---|---|
| | ωp | λp | νp |
| 1 | 199.256 | 18.144 | 93.709 |
| 2 | 207.788 | 28.316 | 327.648 |
| 3 | 289.486 | 22.122 | 82.004 |
| 4 | 355.030 | 14.789 | 79.629 |
| 5 | 471.018 | 22.203 | 162.804 |
| 6 | 547.960 | 7.935 | 48.285 |
| 7 | 601.125 | 4.209 | 70.362 |
| 8 | 622.068 | 8.874 | 55.762 |
| 9 | 663.217 | 9.148 | 74.886 |
| 10 | 718.511 | 13.213 | 59.266 |
| 11 | 821.865 | 3.801 | 51.481 |
| 12 | 881.369 | 2.253 | 34.656 |
| 13 | 904.267 | 9.630 | 91.084 |
| 14 | 962.394 | 29.823 | 97.958 |
| 15 | 1000.590 | 4.940 | 76.809 |
| 16 | 1044.610 | 17.682 | 30.975 |
| 17 | 1167.280 | 8.699 | 48.590 |
| 18 | 1246.810 | 1.164 | 26.591 |
| 19 | 1413.300 | 19.578 | 38.731 |
| 20 | 1544.360 | 52.045 | 97.948 |
| 21 | 1636.730 | 11.428 | 59.456 |
| 22 | 1701.090 | 13.782 | 27.244 |
| 23 | 1720.470 | 5.263 | 27.478 |
| 24 | 1766.690 | 19.947 | 47.127 |
| 25 | 1849.950 | 9.083 | 18.932 |
| 26 | 1903.610 | 25.040 | 24.493 |
| 27 | 1913.440 | 24.951 | 23.687 |
| 28 | 1993.040 | 48.216 | 21.889 |

## 4. Hierarchical expansion of exciton dynamics

The hierarchical expansion of exciton dynamics[1,2] for an environment described by both over and underdamped Brownian oscillators[3,4], results in the coupled differential equations

$$\begin{aligned}\partial_t\tilde{\rho}_{\boldsymbol{n}}(t) &= -[H,\tilde{\rho}_{\boldsymbol{n}}(t)] - \textstyle\sum_{i,k} n_{ik}\gamma_{ik}\tilde{\rho}_{\boldsymbol{n}}(t)\\ &-\sum_i\left(\sum_{k=1}^{\infty}\frac{c_{ik}}{\gamma_{ik}}-\sum_{k=1}^{K}\frac{c_{ik}}{\gamma_{ik}}\right)[Q_i,[Q_i,\tilde{\rho}_{\boldsymbol{n}}(t)]]\\ &-\sum_{i.k}\sqrt{(n_{ik}+1)\sqrt{|c_{ik}c_{i\bar{k}}^*|}}\left[Q_i,\tilde{\rho}_{\boldsymbol{n}_{ik}^+}(t)\right]\\ &-\textstyle\sum_{i,k}\sqrt{n_{ik}/\sqrt{|c_{ik}c_{i\bar{k}}^*|}}\left(c_{ik}Q_i\tilde{\rho}_{\boldsymbol{n}_{ik}^-}-c_{i\bar{k}}^*\tilde{\rho}_{\boldsymbol{n}_{ik}^-}Q_i\right).\end{aligned} \qquad (S1)$$

The rescaled[5] auxiliary matrices $\tilde{\rho}_{\boldsymbol{n}}(t)$, are indexed by the multi-index $\boldsymbol{n}$ which has entries $n_{ik}$ and $n=\sum_{ik}n_{ik}$. $\boldsymbol{n}_{ik}^{\pm}$ is $n$ with entry $n_{ik}\to n_{ik}+1$. The reduced density matrix of the electronic system $\rho$ (with corresponding Hamiltonian $H$) is given by the operator $\tilde{\rho}_{\boldsymbol{0}}(t)$ with all $n_{ik}=0$. The operator $Q_i$ describes the coupling of the excited state of pigment $i$ to its local vibrational environment. The parameters $c_{ik}$, $c_{i\bar{k}}$ and $\gamma_{ik}$ are those appearing in an expansion of the correlation function characterizing the local environment of pigment $i$, $C_i(t)=\sum_i c_{ik}e^{-\gamma_{ik}t}$. For an underdamped ($\nu_q<2\omega_q$) Brownian oscillator this reads[6]

$$C^{BO}(t)=c_+^{BO}e^{-\gamma^+t}+c_+^{BO}e^{-\gamma^+t}+\sum_{k=1}^{K}c_k^{BO}e^{-\gamma_kt}, \qquad (S2)$$

with $c_{\pm}^{BO}=\pm i\lambda_q\frac{\omega_q^2}{2\zeta_q}\left[\cot\left(\frac{\beta\gamma^{\pm}}{2}\right)-i\right]$, $c_{ik}^{BO}=-\frac{4\,\lambda_q\omega_q^2}{\beta}\frac{\gamma_k}{(\omega_q^2+\gamma_k^2)^2-\nu_q^2\gamma_k^2}$ , $\gamma^{\pm}=\frac{\nu_q}{2}\pm i\,\zeta_q$, Matsubara frequencies $\gamma_k=2\pi k/\beta$ and shifted frequency $\zeta_q\sqrt{\omega_q^2-\nu_q^2/4}$. In equation (S1) $c_{i\bar{k}}$ refers to the coefficient of the corresponding term with complex-conjugate exponent. Here if $c_k=c_{\pm}$, $c_{\bar{k}}=c_{\mp}$ and $c_{\bar{k}}=c_k$ if the exponent is real.

In the over-damped limit ($\nu_q\gg 2\omega_q$), this reduces to the Drude form $C^D(t)=c_0^De^{\Omega_Dt}+\sum_{k=1}^{K}c_k^De^{-\gamma_kt}$ with $c_0^D=\lambda_D\Omega_D[\cot(\beta\Omega_D/2)-i]$, $c_k^D=-\frac{4\lambda_D\Omega_D}{\beta}\frac{\gamma_k}{\Omega_D^2-\gamma_k^2}$ and cut off frequency $\Omega_D=\omega_q^2/\nu_q$. When including both Brownian and Drude type components the Matsubara part of the expansions can be combined, The Matsubara

expansion is truncated at level $K$, while the hierarchy of equations itself is truncated at level $N = \sum_{ik} n_{ik}$.

## 5. Electronic and vibrational parameters

The electronic parameters for the high and low energy subunits are taken from the results of QM/MMPol calculations with site energies adjusted to better reproduce linear spectra[7]

$$H_{high} = \begin{matrix} \\ \text{PEB}_{50/60c} \\ \text{PEB}_{50/60d} \\ \text{DBV}_a \end{matrix} \begin{matrix} \begin{matrix} \text{PEB}_{50/60c} & \text{PEB}_{50/60d} & \text{DBV}_a \end{matrix} \\ \begin{pmatrix} 19450.0 & 71.7 & 2.2 \\ 71.7 & 19050.0 & -39.3 \\ 2.2 & -39.3 & 18000.0 \end{pmatrix} \end{matrix} \tag{S3}$$

$$H_{low} = \begin{matrix} \\ \text{PEB}_{82c} \\ \text{PEB}_{82d} \\ \text{DBV}_a \end{matrix} \begin{matrix} \begin{matrix} \text{PEB}_{82c} & \text{PEB}_{82d} & \text{DBV}_a \end{matrix} \\ \begin{pmatrix} 18550 & 4.0 & -11.4 \\ 4.0 & 18050 & 34.3 \\ -11.4 & 34.3 & 18000 \end{pmatrix} \end{matrix} \tag{S4}$$

For the continuous component part of the spectral density we use $\{\lambda_D, \Omega_D\} = \{36, 32\}\,\text{cm}^{-1}$ in the $\text{PEB}_{50/61}$ dimer, $\{20, 31\}\,\text{cm}^{-1}$ in the $\text{PEB}_{82}$ dimer and $\{80, 42\}\,\text{cm}^{-1}$ for the $\text{DBV}_a$. The bilins in the high energy unit are all coupled to a vibrational mode with parameters $\{\lambda_q, \omega_q, \gamma_q\} = \{17.68, 1044, 31\}\,\text{cm}^{-1}$.

In the low energy subset, the $\text{PEB}_{82}$ pair is coupled to an underdamped mode with parameters $\{\lambda_q, \omega_q, \gamma_q\} = \{8{,}529{,}33\}\,\text{cm}^{-1}$ while the $\text{DBV}_a$ is coupled to a mode with parameters $\{22, 552.5, 65.5\}\text{cm}^{-1}$.

### *References*


(1) Tanimura, Y.; Kubo, R. *J. Phys. Soc. Japan* **1989**, *58*, 101.

(2) Ishizaki, A.; Fleming, G. R. *J. Chem. Phys.* **2009**, *130*, 234111.

(3) Tanaka, M.; Tanimura, Y. *J. Phys. Soc. Japan* **2009**, *78*, 073802.

(4) Ding, J.-J.; Xu, R.-X.; Yan, Y. *J. Chem. Phys.* **2012**, *136*, 224103.

(5) Shi, Q.; Chen, L.; Nan, G.; Xu, R.-X.; Yan,Y. *J. Chem. Phys.* **2009**, *130*, 084105.

(6) Mukamel, S.; *Principles of nonlinear optical spectroscopy.* Oxford series in optical and imaging sciences **1995** (Oxford University Press)

(7) Curutchet, C.; Novoderezhkin, V. I.; Kongsted, J.; Muñoz-Losa, A.; van Grondelle, R.; Scholes, G. D.; Mennucci, B. *J. Phys. Chem. B* **2013**, *117*, 4263.