

Electronic Supplementary Information to Tailored anharmonic–harmonic vibrational profiles for fluorescent biomarkers

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S1 *Trans* bithiophene

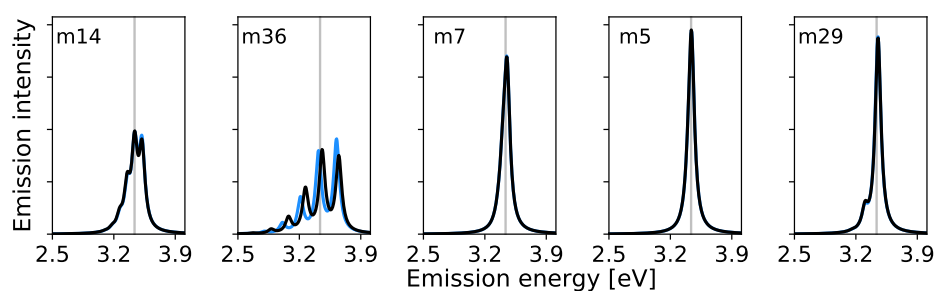


Figure S1: IMDHO-treated (blue) and VCI-treated (black) vibrational profile with a HWHM of $\gamma = 0.04$ eV for the $S_0 \leftarrow S_1$ emission for the different modes of *trans* bithiophene employing PESs from ref. [1]. The vertical transition energy is given as a vertical grey line.

S2 All-*trans* terthiophene

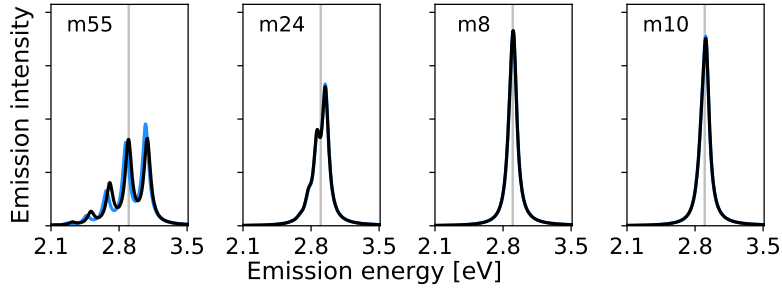


Figure S2: IMDHO-treated (blue) and VCI-treated (black) vibrational profile with a HWHM of $\gamma = 0.04$ eV for the $S_0 \leftarrow S_1$ emission for the different modes of all-*trans* terthiophene employing PESs from ref. [1]. The vertical transition energy is given as a vertical grey line.

S3 All-*trans* quaterthiophene

Table SI: Mode ranking for all-*trans* quaterthiophene using CAM-B3LYP/6-31+g(d). The most important modes with the harmonic frequency ν_i in cm^{-1} , the absolute value of the harmonic $|\Delta_i|$ and anharmonic $|\Delta_i^a|$ dimensionless displacement, the relative difference between harmonic and anharmonic displacement $\left(\frac{\Delta_i^a}{\Delta_i}\right)^2$, the resolution measure σ_i in cm^{-1} , and the effect of one-mode anharmonicity on the vibronic profile (1-mode AH).

Mode (i)	ν_i/cm^{-1}	$ \Delta_i $	$ \Delta_i^a $	$\left(\frac{\Delta_i^a}{\Delta_i}\right)^2$	σ_i/cm^{-1}	1-mode AH
74	1616	1.280	0.280	0.048	3440	moderate
9	162	1.02	0.637	0.390	168	weak
32	705	0.894	1.034	1.337	575	weak
15	333	0.693	1.439	4.315	187	weak

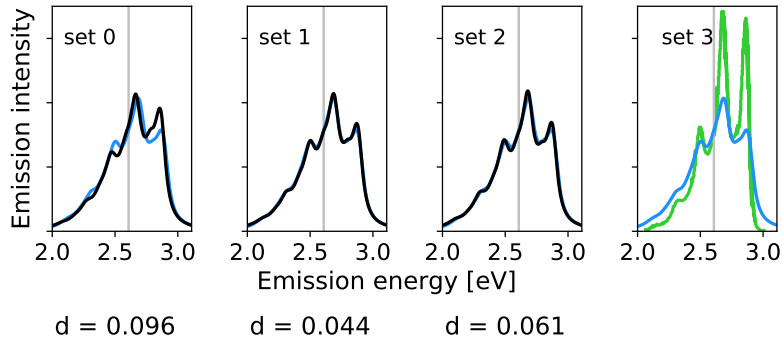


Figure S3: Hybrid VCI-in-IMDHO vibrational profiles for the $S_0 \leftarrow S_1$ emission for all-*trans* quaterthiophene for the different sets of vibrational coordinates treated by VCI (black) and that for the largest set of modes set 3 (blue) with a HWHM of $\gamma = 0.04$ eV compared to a corrected experimental spectrum of quaterthiophene at 77 K in ethanol [2] (green). The vertical transition energy is given as a vertical grey line. Within the anharmonic and hybrid models, (set 0) including 0 anharmonic mode; (set 1) including the one with most pronounced one mode anharmonicity: 74; (set 2) including two highest ranked modes: 74, 32 and (set 3) including 4 modes: 74, 9, 32, 15. The experimental spectra is shifted by 0.086 eV to get the same position of maximum as calculated spectrum. Additionally, the deviation between the shown spectra according to eq. (5) in the main text is quantified below the respective graphs.

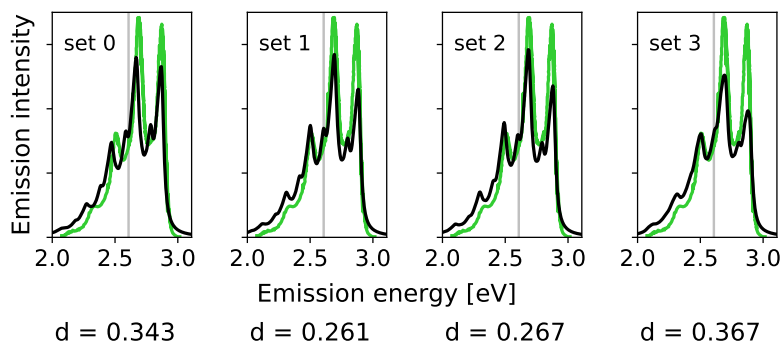


Figure S4: Hybrid VCI-in-IMDHO vibrational profiles for the $S_0 \leftarrow S_1$ emission for all-*trans* quaterthiophene for the different sets of vibrational coordinates treated by VCI (black) with a HWHM of $\gamma = 0.02$ eV compared to a corrected experimental spectrum of quaterthiophene at 77 K in ethanol [2] (green). The vertical transition energy is given as a vertical grey line. Within the anharmonic and hybrid models, (set 0) including 0 anharmonic modes; (set 1) including the one with most pronounced one mode anharmonicity: 74; (set 2) including two highest ranked modes: 74, 32 and (set 3) including 4 modes: 74, 9, 32, 15. The experimental spectra is shifted by 0.010 eV to get the same position of maximum as calculated spectrum. Additionally, the deviation between the shown spectra according to eq. (5) in the main text is quantified below the respective graphs.

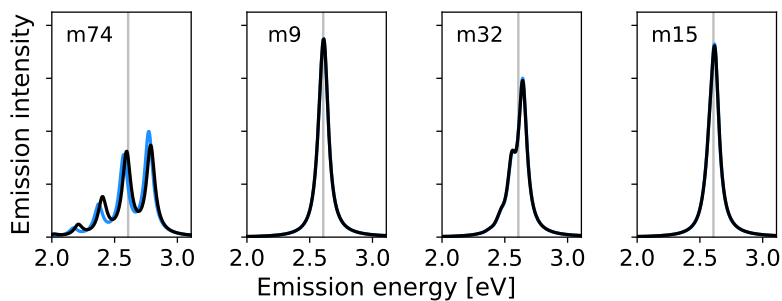


Figure S5: IMDHO treated (blue) and VCI treated (black) vibrational profile with a HWHM of $\gamma = 0.04$ eV for the $S_0 \leftarrow S_1$ emission for the different modes of all-*trans* quaterthiophene employing PESs obtained from [1]. The vertical transition energy is given as a vertical grey line.

S4 All-*trans* pentathiophene

Table SII: Mode ranking for all-*trans* pentathiophene using CAM-B3LYP/6-31+g(d). The most important modes with the harmonic frequency ν_i in cm^{-1} , the absolute value of the harmonic $|\Delta_i|$ and anharmonic $|\Delta_i^a|$ dimensionless displacement, the relative difference between harmonic and anharmonic displacement $\left(\frac{\Delta_i^a}{\Delta_i}\right)^2$, the resolution measure σ_i in cm^{-1} , and the effect of one-mode anharmonicity on the vibronic profile (1-mode AH).

Mode	ν_i/cm^{-1}	$ \Delta_i $	$ \Delta_i^a $	$\left(\frac{\Delta_i^a}{\Delta_i}\right)^2$	σ_i/cm^{-1}	1-mode AH
92	1600	0.960	0.164	0.029	1479	weak
91	1592	0.835	0.191	0.052	1164	weak
41	711	0.795	0.989	1.549	483	weak
18	323	0.690	1.429	4.293	180	weak

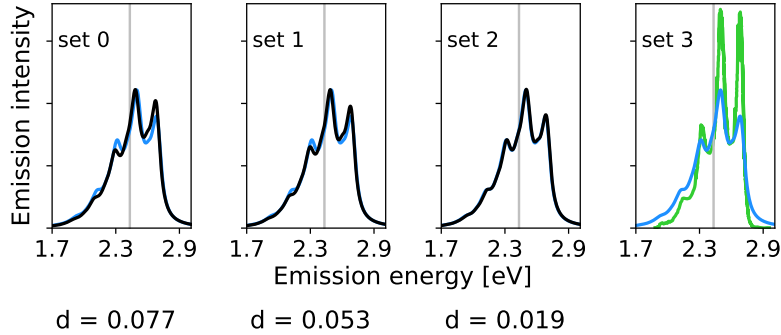


Figure S6: Hybrid VCI-in-IMDHO vibrational profiles for the $S_0 \leftarrow S_1$ emission for all-*trans* pentathiophene for the different sets of vibrational coordinates treated by VCI (black) and that for the largest set of modes set 3 (blue) with a HWHM of $\gamma = 0.04$ eV compared to a corrected experimental spectrum of pentathiophene at 77 K in ethanol [2] (green). The vertical transition energy is given as a vertical grey line. Within the anharmonic and hybrid models, (set 0) including 0 anharmonic mode, (set 1) including the highest ranked mode: 92; (set 2) including two anharmonic modes 92, 91 and (set 3) including all important modes: 92, 91, 41, 18. The experiment spectrum is shifted by 0.101 eV to get the same position of maximum as calculated spectrum. Additionally, the deviation between the shown spectra according to eq. (5) in the main text is quantified below the respective graphs.

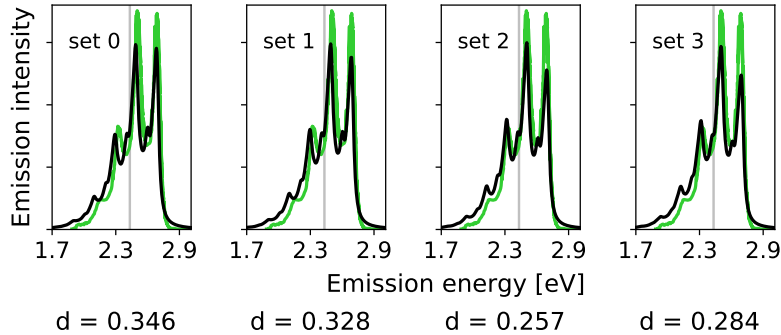


Figure S7: Hybrid VCI-in-IMDHO vibrational profiles for the $S_0 \leftarrow S_1$ emission for all-*trans* pentathiophene for the different sets of vibrational coordinates treated by VCI (black) with a HWHM of $\gamma = 0.02$ eV compared to a corrected experimental spectrum of pentathiophene at 77 K in ethanol [2] (green). The vertical transition energy is given as a vertical grey line. Within the anharmonic and hybrid models, (set 0) including 0 anharmonic mode, (set 1) including the highest ranked mode: 92; (set 2) including two anharmonic modes 92, 91 and (set 3) including all important modes: 92, 91, 41, 18. The experiment spectrum is shifted 0.005 eV to get the same position of maximum as calculated spectrum. Additionally, the deviation between the shown spectra according to eq. (5) in the main text is quantified below the respective graphs.

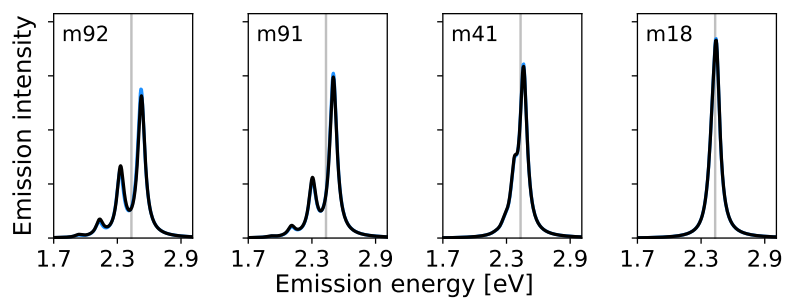


Figure S8: IMDHO treated (blue) and VCI treated (black) vibrational profile with a HWHM of $\gamma = 0.04$ eV for the $S_0 \leftarrow S_1$ emission for the different modes of all-*trans* pentathiophene using CAM-B3LYP/def2-TZVP. The vertical transition energy is given as a vertical grey line.

S5 HS84

Table SIII: Mode ranking for HS84 using CAM-B3LYP/def2-TZVP. The most important modes with the harmonic frequency ν_i in cm^{-1} , the absolute value of the harmonic $|\Delta_i|$ and anharmonic $|\Delta_i^a|$ dimensionless displacement, the relative difference between harmonic and anharmonic displacement $\left(\frac{\Delta_i^a}{\Delta_i}\right)^2$, the resolution measure σ_i in cm^{-1} , and the effect of one-mode anharmonicity on the vibronic profile (1-mode AH).

Mode	ν_i/cm^{-1}	$ \Delta_i $	$ \Delta_i^a $	$\left(\frac{\Delta_i^a}{\Delta_i}\right)^2$	σ_i/cm^{-1}	1-mode AH
133	1576	1.120	0.225	0.040	2044	weak
131	1547	0.699	0.529	0.572	879	weak
68	735	0.697	1.584	5.166	416	weak
107	1264	0.420	0.063	0.023	393	weak
126	1488	0.313	0.082	0.068	338	weak

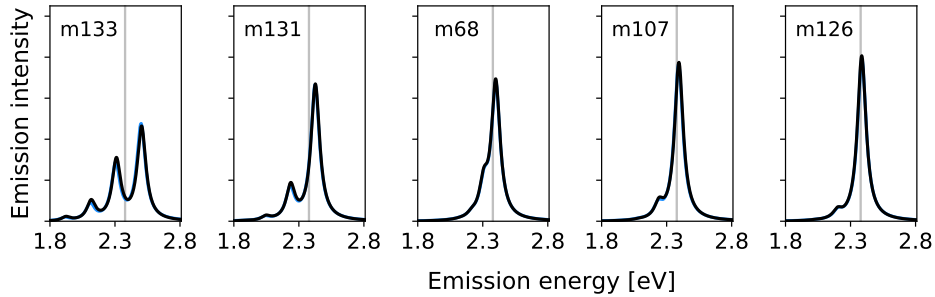


Figure S9: IMDHO treated (blue) and VCI treated (black) vibrational profile with a HWHM of $\gamma = 0.04$ eV for the $S_0 \leftarrow S_1$ emission for the different modes of HS84 using CAM-B3LYP/def2-TZVP. The vertical transition energy is given as a vertical grey line.

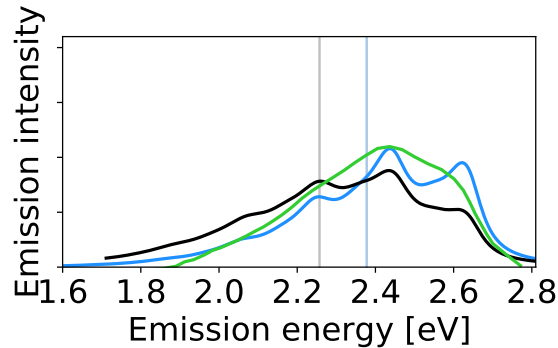


Figure S10: Calculated IMDHO harmonic emission spectra of HS84 in vacuum (blue), in water estimated with the PCM model (black) and a HWHM of $\gamma = 0.04$ eV using CAM-B3LYP/def2-TZVP compared to a corrected experimental spectrum in PBS[3] (green). The vertical transition energy in vacuum is given as a vertical grey line. The experimental and the IMDHO spectrum in solvent as well as its corresponding excitation energy (vertical blue light line) are shifted by 0.130 eV and 0.211 eV, respectively, to get the same position of maximum as IMDHO harmonic spectra in vacuum. Additionally, the deviation between the calculated spectrum in vacuum and in solvent according to eq. (5) in the main text is 0.211 and 0.343, respectively.

S6 1,4-diphenylbutadiene

Table SIV: Mode ranking for 1,4-diphenylbutadiene using CAM-B3LYP/def2-TZVP. The most important modes with the harmonic frequency ν_i in cm^{-1} , the absolute value of the harmonic $|\Delta_i|$ and anharmonic $|\Delta_i^a|$ dimensionless displacement, the relative difference between harmonic and anharmonic displacement $\left(\frac{\Delta_i^a}{\Delta_i}\right)^2$, the resolution measure σ_i in cm^{-1} , and the effect of one-mode anharmonicity on the vibronic profile (1-mode AH).

Mode	ν_i/cm^{-1}	$ \Delta_i $	$ \Delta_i^a $	$\left(\frac{\Delta_i^a}{\Delta_i}\right)^2$	σ_i/cm^{-1}	1-mode AH
70	1691	1.270	0.287	0.051	3452	moderate
53	1285	0.849	0.237	0.078	964	weak
69	1653	0.527	0.117	0.049	663	weak
41	1016	0.372	0.141	0.144	277	weak
60	1435	0.303	0.084	0.077	314	weak
57	1363	0.290	0.091	0.099	286	weak
64	1544	0.202	0.053	0.069	223	weak

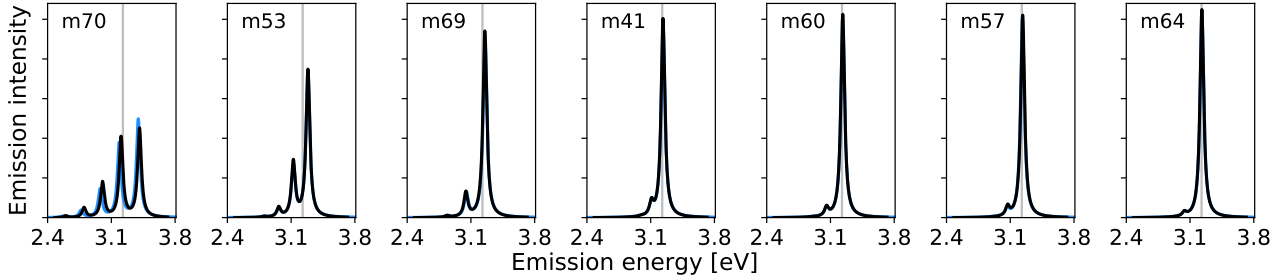


Figure S11: IMDHO treated (blue) and VCI treated (black) vibrational profile with a HWHM of $\gamma = 0.025$ eV for the $S_0 \leftarrow S_1$ emission for the different modes of 1,4-diphenylbutadiene using CAM-B3LYP/def2-TZVP. The vertical transition energy is given as a vertical grey line.

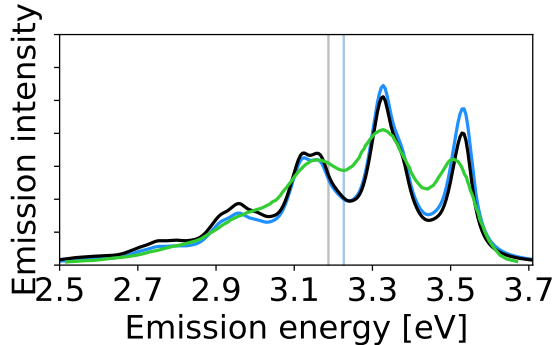


Figure S12: Calculated IMDHO harmonic emission spectra of 1,4-diphenylbutadiene in vacuum (blue), in hexane estimated with the PCM model (black) and a HWHM of $\gamma = 0.025$ eV using CAM-B3LYP/def2-TZVP compared to a corrected experimental spectrum in hexane[4, 5] (green). The vertical transition energy in vacuum is given as a vertical grey line. The experimental and the IMDHO spectrum in solvent as well as its corresponding excitation energy (vertical blue light line) are shifted by 1.527 eV and 0.196 eV, respectively, to get the same position of maximum as IMDHO harmonic spectra in vacuum. Additionally, the deviation between the calculated spectrum in vacuum and in solvent according to eq. (5) in the main text is 0.289 and 0.253, respectively.

S7 Anthracene diimide

Table SV: Mode ranking for the anthracene diimide using CAM-B3LYP/def2-TZVP. The most important modes with the harmonic frequency ν_i in cm^{-1} , the absolute value of the harmonic $|\Delta_i|$, anharmonic $|\Delta_i^a|$ dimensionless displacement, the relative difference between harmonic and anharmonic displacement $\left(\frac{\Delta_i^a}{\Delta_i}\right)^2$, the resolution measure σ_i in cm^{-1} , and the effect of one-mode anharmonicity on the vibronic profile (1-mode AH).

Mode	ν_i/cm^{-1}	$ \Delta_i $	$ \Delta_i^a $	$\left(\frac{\Delta_i^a}{\Delta_i}\right)^2$	σ_i/cm^{-1}	1-mode AH
79	1447	0.706	0.149	0.045	833	weak
75	1398	0.642	0.133	0.043	712	weak
92	1652	0.607	0.107	0.031	785	weak
29	512	0.566	0.336	0.350	223	weak
65	1215	0.352	0.077	0.048	312	weak
81	1473	0.332	0.061	0.034	356	weak
88	1546	0.318	0.059	0.035	367	weak
89	1574	0.252	0.045	0.032	285	weak
82	1502	0.227	0.039	0.030	244	weak

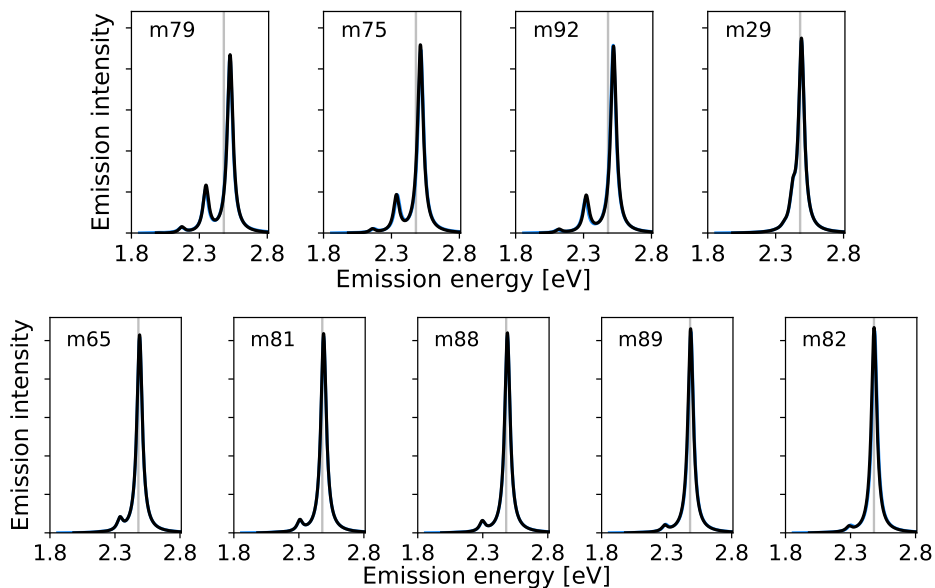


Figure S13: IMDHO treated (blue) and VCI treated (black) vibrational profile with a HWHM of $\gamma = 0.025$ eV for the $S_0 \leftarrow S_1$ emission for the different modes of anthracene diimide using CAM-B3LYP/def2-TZVP. The vertical transition energy is given as a vertical grey line.

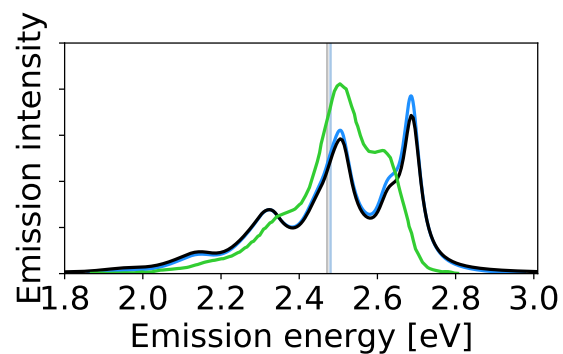


Figure S14: Calculated IMDHO harmonic emission spectra of anthracene diimide in vacuum (blue), in dichloromethane estimated with the PCM model (black) and a HWHM of $\gamma = 0.025$ eV using CAM-B3LYP/def2-TZVP compared to a corrected experimental spectrum in dichloromethane[6, 7] (green). The vertical transition energy in vacuum is given as a vertical grey line. The experimental and the IMDHO spectrum in solvent as well as its corresponding excitation energy (vertical blue light line) are shifted by 1.121 eV and 0.169 eV, respectively, to get the same position of maximum as IMDHO harmonic spectra in vacuum. Additionally, the deviation between the calculated spectrum in vacuum and in solvent according to eq. (5) in the main text is 0.489 and 0.522, respectively.

References

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