

SUPPLEMENTARY MATERIAL

**An Excited State Coupled Cluster Study on Indigo Dyes**

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## S1. Solvation Parameters

In Tab. S1, we gather the settings that were used for the CPCM solvation model used in the present study. Most of the values were set to the defaults used in the ORCA program package [1], except for the dielectric constants of xylene and TCE (sourced from Jacquemin *et al.* [2] and the refractive index of TCE [3]. The refractive index of xylene was set to ORCA’s default for toluene.

**Table S1.** Settings used for the dielectric constant  $\epsilon$  and refractive index  $\eta$  in this study.

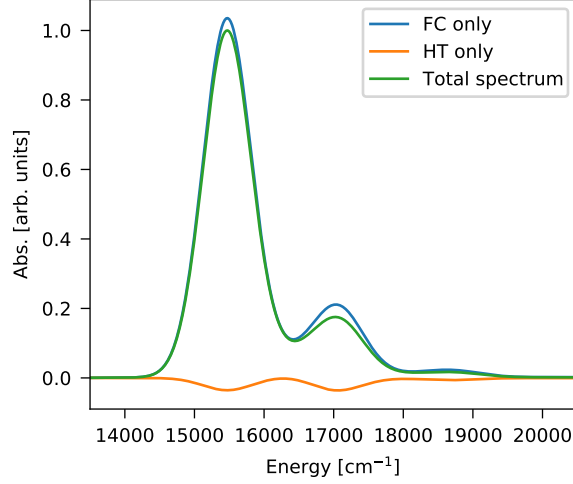
Solvent	$\epsilon$	$\eta$
Xylene	2.27	1.497
CHCl <sub>3</sub>	4.9	1.45
TCE	8.2	1.4922
EtOH	24.3	1.361
Benzene	2.28	1.501
CCl <sub>4</sub>	2.24	1.466
DMSO	47.2	1.479

## S2. Herzberg-Teller Effects from DFT

Computing Herzberg-Teller effects is significantly more expensive than the zeroth-order Franck-Condon results. To assess their magnitude on indigoid systems, we computed their effect on 6,6'-dibromoindigo in DMSO (Fig. S1).

We note that the spectrum in Fig. S1 does not contain the energetic shift computed from STEOM as do all other plotted spectra in this study, but is exclusively computed at the B3LYP-D3(BJ)-CPCM/def2-TZVP level of theory.

Fig. S1 shows that the first-order Herzberg-Teller effects are minor in that they are more than one order of magnitude smaller than the Franck-Condon results. Additionally, they also do not change the overall shape of the spectrum. Consequently, we did not include them in our results and other computed spectra.



**Figure S1.** Contributions of the Franck-Condon and Herzberg-Teller effects to the total spectrum of 6,6'-dibromoindigo in DMSO.

### S3. Brief Overview of the fic-MRCC Implementation

The fic-MRCC implementation we used in this study is to be published at the time of writing [4].

The *ansatz* can be written as

$$|\Psi\rangle = e^{\hat{T}} |0\rangle, \quad (1)$$

where  $|0\rangle$  denotes the CASSCF reference wave function. The cluster operator is given as (active indices denoted by  $t, u, v$ )

$$\begin{aligned} \hat{T} = & \frac{1}{2} t_{ab}^{ij} \hat{E}_i^a \hat{E}_j^b + t_{ab}^{it} \hat{E}_i^a \hat{E}_t^b + \frac{1}{2} t_{ab}^{tu} \hat{E}_t^a \hat{E}_u^b + t_{at}^{ij} \hat{E}_i^a \hat{E}_j^t + t_{au}^{it} \hat{E}_i^a \hat{E}_t^u \\ & + t_{ua}^{it} \hat{E}_i^u \hat{E}_t^a + t_{av}^{tu} \hat{E}_t^a \hat{E}_u^v + \frac{1}{2} t_{tu}^{ij} \hat{E}_i^t \hat{E}_j^u + t_{uv}^{it} \hat{E}_i^u \hat{E}_t^v. \end{aligned} \quad (2)$$

The similarity-transformed Hamiltonian is defined as in single-reference CC theory,

although we truncate it at second order [5],

$$\bar{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}}, \quad (3)$$

$$\approx \hat{H} + [\hat{H}, \hat{T}] + \frac{1}{2} [[\hat{H}, \hat{T}], \hat{T}]. \quad (4)$$

The energy and residual equations are consequently written as

$$\bar{H} |0\rangle = E |0\rangle, \quad (5)$$

$$r_P = \langle \tilde{\Phi}_P | \bar{H} |0\rangle \stackrel{!}{=} 0, \quad (6)$$

where  $\tilde{\Phi}_P$  denotes a contravariant, excited internally contracted function as discussed in Ref. [6]. The orthogonalization scheme to remove linear dependencies in the excitation manifold is also identical to that of Ref. [6].

#### S4. Solvation Effects

In the main body of the text (Tab. 3), we presented the effects of a CPCM implicit solvation model on the STEOM transition energies, where CPCM was taken into account for both the geometry optimization as well as in the STEOM calculation and compared that data to all-gas-phase STEOM transition energies.

For completeness' sake, we here also give the corresponding shifts vs. the gas-phase results if we only include the indirect solvation effects on the STEOM calculation (Tab. S2). The solvated, optimized geometries are identical in these two cases. The direct solvation effects do not have a large impact on the transition energies: on average, the direct effects lead to an additional shift of  $\approx -0.03$  eV.

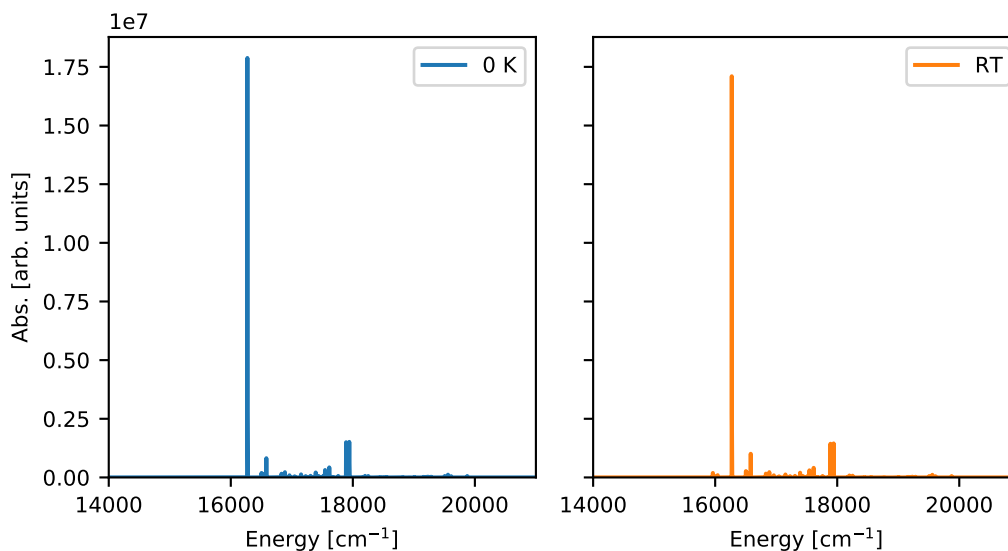
#### S5. Effect of Temperature on the Spectra

In all spectra in this study, we include the electronic ground state and the first excited electronic state. Since we also include vibrational effects to be able to compare to the experimental 0-0 transition energies, the computed spectra will show several discrete

**Table S2.** Solvation effects compared to gas-phase STEOM calculations with the ‘fast’ CPCM term omitted. Solvents sorted with increasing dielectric constant  $\epsilon$  from left to right. All values given in eV.

$\epsilon$	CCl4 2.24	Xylene 2.27	Benzene 2.28	CHCl <sub>3</sub> 4.9	TCE 8.2	EtOH 24.3	DMSO 47.2
Indigo	-0.067	-0.068	-0.068	-0.105	-0.120	-0.128	-0.131
4,4'-Bromoindigo	-0.069	-0.070	-0.070	-0.107	-0.125	-0.139	-0.143
4,4'-Chloroindigo	-0.071	-0.072	-0.072	-0.109	-0.124	-0.139	-0.144
5,5'-Bromoindigo	-0.063	-0.063	-0.063	-0.095	-0.107	-0.119	-0.122
5,5'-Chloroindigo	-0.065	-0.066	-0.066	-0.092	-0.104	-0.116	-0.120
5,5'-Nitroindigo	-0.056	-0.056	-0.048	-0.075	-0.097	-0.111	-0.113
6,6'-Bromoindigo	-0.068	-0.069	-0.069	-0.103	-0.118	-0.128	-0.135
6,6'-Chloroindigo	-0.070	-0.071	-0.071	-0.106	-0.120	-0.135	-0.138
6,6'-Nitroindigo	-0.088	-0.089	-0.089	-0.121	-0.137	-0.153	-0.157
7,7'-Bromoindigo	-0.046	-0.047	-0.047	-0.077	-0.087	-0.098	-0.101
7,7'-Chloroindigo	-0.054	-0.055	-0.055	-0.083	-0.098	-0.106	-0.108
<b>Average</b>	-0.065	-0.066	-0.065	-0.098	-0.112	-0.125	-0.128

‘lines’ if the linewidth is artificially set to low values, e.g.,  $1 \text{ cm}^{-1}$ . In case of the spectrum being computed at absolute zero (0 K), the transition lowest in energy corresponds to the 0-0 transition, and all others to ‘0- $n$ ’ transitions to a vibrationally excited mode  $n$  of the first excited electronic state (Fig. S2). Note that the following discussion is limited to Indigo in DMSO, without loss of generality.



**Figure S2.** Computed spectra of Indigo in DMSO. The left plot has been computed at absolute zero (0 K), whereas the right spectrum was computed at room temperature (298.15 K).

In case we compute the spectrum at a temperature higher than absolute zero, e.g.,

room temperature (298.15 K), we obtain additional transitions. These are visible in the right spectrum of Fig. S2 and correspond to  $n-0$  (and possibly  $n-m$ ) transitions where the molecule is vibrationally excited in its electronic ground state. These transitions are only available at higher-than-zero temperatures since the vibrational modes of the ground state are populated according to the Boltzmann distribution (see Sec. 2.3 of the main document). In contrast, we always see the vibrational progression of the final electronic state since the molecule can be electronically and vibrationally excited at the same time (cf. Eq. 21).

Notwithstanding, the 0-0 transition remains the by far the strongest and the  $n-0$  transitions are still fairly weak at room temperature since the vibrational ground state of the electronic ground state will still be the most populated one. Moreover, the geometric displacement to the first excited electronic state is small in this case, which also leads to a strong 0-0 transition.

## S6. Spectrum of Indigo in $\text{CHCl}_3$

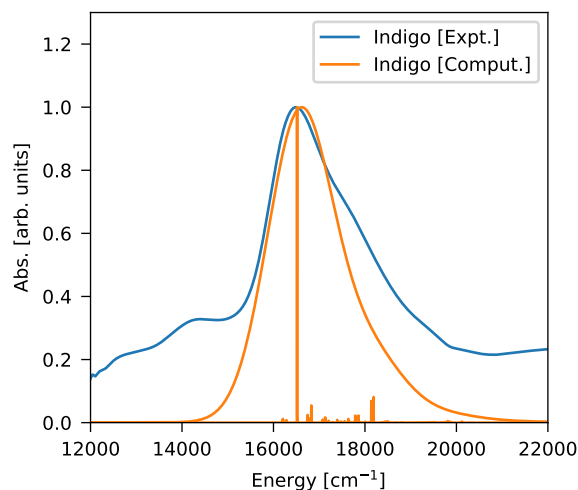
In addition to the spectra shown in the main article, we also measured the absorption spectrum of indigo in  $\text{CHCl}_3$  (Fig. S3). This commercially available sample is not as pure as the dyes measured in Fig. 4, as there are two ‘bumps’ towards lower energies and a much higher background towards higher energies. Nevertheless, the main peak of indigo is well resolved and coincides almost perfectly with our computed 0-0 transition at  $16516.0 \text{ cm}^{-1}$ . Furthermore, the left shoulder is very well reproduced after choosing an inhomogeneous linewidth of  $700 \text{ cm}^{-1}$  for the computed vibrational transitions.

## S7. Optimized Geometries

The optimized geometries are available in a zip-compressed archive.

## S8. Fundamental Mode of Indigo in DMSO

The xyz trajectory files containing the dominant fundamental modes for the spectrum of indigo in DMSO, presented in Fig. 4, are also included in the zip-compressed archive.



**Figure S3.** Normalized experimental and computed spectra of indigo in  $\text{CHCl}_3$ . The unshifted computed spectrum is presented once with an inhomogeneous line broadening of  $700\text{ cm}^{-1}$  and once with sticks to indicate the vibrational transitions.

## S9. Experimental Data

The raw experimental data for indigo and genuine Tyrian purple (both measured in  $\text{CHCl}_3$ ) is available in plain text format in the zip-compressed archive.

The experimental data has been smoothed slightly with cubic splines prior to plotting using the `scipy.interpolate.splrep` function of the SciPy [7] software package.

## References

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