Taking Up the Cyanine Challenge with Quantum Tools: Supporting Information

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S1 Expanded Tables

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Table S-1: Vertical transition energies to the lowest excited-state calculated with various wavefunction models for model cyanines. All values are in eV. For methods implying the selection of an active space, the values obtained with the optimal active space as selected in the original works are reported.

Method	Geometry	Basis set	**CN3**	**CN5**	**CN7**	**CN9**	**CN11**	Ref.
Multi-reference wavefunction approaches								
DMC	MP2/cc-pVQZ	T'+ [a]	7.38	5.03	3.83	3.09	2.62	1
CAS-SCF	B3LYP/6-31G(d,p)	ANO(4s3p2d/3s1p)	7.73	4.85	3.55	2.70	2.16	2
CAS-SCF	MP2/cc-pVQZ	ANO-L-VTZP	7.56	5.32	3.91	3.13	2.39	1
CAS-PT2	B3LYP/6-31G(d,p)	ANO(4s3p2d/3s1p)	6.50	4.28	3.18	2.52	2.11	2
CAS-PT2	MP2/cc-pVQZ	ANO-L-VTZP	6.99	4.46	3.30	2.59	2.10	1
CAS-PT2 (IPEA shift)	MP2/cc-pVQZ	ANO-L-VTZP	7.19	4.69	3.52	2.81	2.46	1
Single-reference wavefunction approaches								
ADC(2)	MP2/cc-pVQZ	*aug*-cc-pVTZ		4.64	3.46	2.78	2.32	3
CIS	B3LYP/6-31G(d,p)	6-31G(d)	8.91	6.07	4.74	3.94	3.41	2
CIS	MP2/cc-pVQZ	TZVP		6.08	4.77	3.98	3.45	4
CIS(D)	MP2/cc-pVQZ	TZVP		4.85	3.65	2.95	2.48	4
CC2	MP2/cc-pVQZ	ANO-L-VTZP	7.26	4.97	3.79	3.10	2.64	1
CCSD	MP2/cc-pVQZ	ANO-L-VTZP	7.29	4.98	3.81	3.11		1
CC3	MP2/cc-pVQZ	Extrapolated	7.16	4.84	3.65	2.96	2.53	1
GW/BSE	PBE0/cc-pVQZ	*aug*-cc-pVTZ		4.80	3.63	2.96	2.48	5
HF (RPA)	MP2/cc-pVQZ	TZVP		5.79	4.51	3.75	3.23	4
Semi-empirical approaches								
PPP	–	–	5.87	3.91	3.04	2.50	2.12	6,7
ZINDO/S	B3LYP/6-31+G(d)	–	6.36	4.29	3.42	2.87	2.48	7

[a] cc-pVTZ for C and N, cc-pVDZ for H augmented by *s*, *p* and *d* diffuse functions.

Table S-2: Vertical transition energies to the lowest excited-state calculated with various DFT-based models for model cyanines. All values are in eV and are obtained at the TD-DFT level except when noted (TDA: Tamm-Dancoff Approximation).

Method	Geometry	Basis set	**CN3**	**CN5**	**CN7**	**CN9**	**CN11**	Ref.
Pure functionals								
BLYP	BLYP/6-311++G(d,p)	6-311G(d,p)	7.25	5.10	4.00	3.35	2.91	8
BLYP	MP2/cc-pVQZ	TZVP		5.29	4.15	3.47	3.01	4
M06-L	PBE0/cc-pVQZ	*aug*-cc-pVTZ		5.40	4.25	3.56	3.11	9
PBE	PBE/6-311++G(d,p)	6-311G(d,p)	7.56	5.25	4.12	3.44	2.99	8
PBE	PBE0/cc-pVQZ	ANO-L-VTZP	7.40	5.22	4.11	3.44	2.98	1
PBE	PBE0/cc-pVQZ	*aug*-cc-pVTZ		5.23	4.12	3.45	3.00	9
PBE	MP2/cc-pVQZ	TZVP		5.30	4.15	3.47	3.01	4
PBE (TDA)	MP2/cc-pVQZ	TZVP		6.00	4.92	4.27	3.56	4
Global hybrid functionals								
B3LYP	B3LYP/6-31+G(d)	6-31+G(d)	7.60	5.28	4.12	3.44	2.99	7
B3LYP	B3LYP/6-31G(d,p)	6-31G(d)	7.88	5.38	4.19	3.51	3.04	2
B3LYP	B3LYP/6-31G(d,p)	TZ2P	7.57	5.24	4.11	3.43	2.98	2
PBE0	PBE0/6-311++G(d,p)	6-311G(d,p)	7.70	5.34	4.17	3.49	3.02	8
PBE0	PBE0/cc-pVQZ	ANO-L-VTZP	7.62	5.33	4.18	3.50	3.03	1
PBE0	PBE0/cc-pVQZ	*aug*-cc-pVTZ		5.34	4.19	3.50	3.05	9
PBE0 (TDA)	PBE0/cc-pVQZ	ANO-L-VTZP	8.03	5.84	4.71	4.02	3.54	1
M05	PBE0/cc-pVQZ	*aug*-cc-pVTZ		5.30	4.15	3.47	3.00	9
M06	PBE0/cc-pVQZ	*aug*-cc-pVTZ		5.23	4.10	3.43	2.98	9
M06	MP2/cc-pVQZ	TZVP		5.31	4.17	3.46	3.00	4
BHHLYP (TDA)	MP2/cc-pVQZ	*aug*-cc-pVTZ		5.74	4.57	3.85	3.35	3
BHHLYP	MP2/cc-pVQZ	*aug*-cc-pVTZ		5.35	4.19	3.49	3.02	3
M08-HX	PBE0/cc-pVQZ	*aug*-cc-pVTZ		5.23	4.09	3.41	2.95	9
M05-2X	PBE0/cc-pVQZ	*aug*-cc-pVTZ		5.33	4.17	3.47	3.00	9
M06-2X	PBE0/cc-pVQZ	*aug*-cc-pVTZ		5.23	4.09	3.41	2.95	9
M06-2X	MP2/cc-pVQZ	TZVP		5.27	4.11	3.42	2.95	4
M08-SO	PBE0/cc-pVQZ	*aug*-cc-pVTZ		5.16	4.04	3.37	2.91	9
M06-HF	PBE0/cc-pVQZ	*aug*-cc-pVTZ		5.13	3.98	3.30	2.83	9
M06-HF	MP2/cc-pVQZ	TZVP		5.15	3.99	3.29	2.82	4
Range-separated hybrid functionals								
LC-BLYP	LC-BLYP/6-311++G(d,p)	6-311G(d,p)	7.47	5.19	4.05	3.37	2.90	8
CAM-B3LYP	CAM-B3LYP/6-311++G(d,p)	6-311G(d,p)	7.61	5.28	4.13	3.44	2.98	8
CAM-B3LYP	PBE0/cc-pVQZ	ANO-L-VTZP	7.55	5.26	4.12	3.44	2.97	1
LC-PBE	LC-PBE/6-311++G(d,p)	6-311G(d,p)	7.61	5.25	4.09	3.40	2.93	8
LC-PBE	HF/cc-pVQZ	TZVP		5.31	4.13	3.43	2.96	4
LC-PBE	BP86/cc-pVQZ	TZVP		5.16	4.01	3.32	2.85	4
LC-PBE	PBE/cc-pVQZ	TZVP		5.16	4.01	3.32	2.86	4
LC-PBE	PBE0/cc-pVQZ	TZVP		5.26	4.09	3.39	2.92	4
LC-PBE	LC-PBE* /cc-pVQZ	TZVP		5.30	4.12	3.42	2.94	4
LC-PBE	LC-PBE0* /cc-pVQZ	TZVP		5.33	4.15	3.44	2.96	4
LC-PBE	MP2/cc-pVQZ	TZVP		5.26	4.09	3.39	2.92	4
LC-PBE*	MP2/cc-pVQZ	TZVP		5.26	4.09	3.40	2.94	4
LC-PBE0*	MP2/cc-pVQZ	TZVP		5.37	4.19	3.49	3.02	4
Double-hybrid functionals								
B2PLYP	B3LYP/TZVP	TZV2P	7.47	5.12	3.87	3.23	2.80	10
B2PLYP	PBE0/cc-pVQZ	ANO-L-VTZP	7.30	5.05	3.92	3.25	2.80	1
Alternative schemes								
ΔSCF-BHHLYP	PBE0/TZ	TZ (STO)	7.33	4.81	3.55	2.79	2.29	11
ΔSCF-BHHLYP[a]	MP2/cc-pVQZ	*aug*-cc-pVTZ		4.87	3.72	3.06	2.62	3
ΔSCF-CAM-B3LYP[a]	MP2/cc-pVQZ	*aug*-cc-pVTZ		4.71	3.65	3.03	2.62	3
SF-BHHLYP[b]	MP2/cc-pVQZ	*aug*-cc-pVTZ		5.09	3.95	3.27	2.82	3

[a] SSR variations of the ΔSCF model; [b] Spin-flip approach.

Table S-3: Vertical transition energies to the lowest excited-state calculated with various schemes (in eV) for the methylated structures (NMe_2 end groups instead of NH_2 end groups). See the caption of Tables S-1 and S-2 for more details.

Method	Geometry	Basis set	**Me-CN3**	**Me-CN5**	**Me-CN7**	**Me-CN9**	**Me-CN11**	Ref.
Multi-reference wavefunction approaches								
CAS-SCF	B3LYP/6-31G(d,p)	ANO(4s3p1d/2s)		5.97	4.04	2.63	2.07	2
CAS-PT2	B3LYP/6-31G(d,p)	ANO(4s3p1d/2s)		4.17	2.95	2.32	1.93	2
Single-reference wavefunction approaches								
CC2	MP2/cc-pVQZ	ANO-L-VTZP	6.07	4.58	3.53	2.90	2.47	1
SAC-CI	B3LYP/6-31+G(d)	6-31G(d)	5.90	4.25	3.02	2.17		12
SORCI	B3LYP/6-31+G(d)	6-31G	6.08	4.40	3.34	2.70	2.27	12
TD-DFT approaches								
BLYP	B3LYP/6-31+G(d)	6-311+G(d,p)	5.71	4.51	3.65	3.11	2.84	12
BLYP[a]	PBE0/6-311G(d,p)	6-311+G(2d,p)	5.63	4.40	3.49	2.92		13
B3LYP	B3LYP/6-31+G(d)	6-31+G(d)	6.08	4.70	3.76	3.28	2.80	12
B3LYP	B3LYP/6-31+G(d)	6-311+G(d,p)	6.02	4.66	3.73	3.17	2.79	12
B3LYP	B3LYP/6-31+G(d)	6-311+G(3df,p)	5.99	4.64	3.72	3.15	2.78	12
B3LYP[a]	PBE0/6-311G(d,p)	6-311+G(2d,p)	5.94	4.56	3.57	2.97		13
B3LYP (TDA)	B3LYP/6-31+G(d)	6-311+G(d,p)	6.46	5.14	4.23	3.68	3.30	12
PBE0	B3LYP/6-31+G(d)	6-311+G(d,p)	6.11	4.71	3.77	3.19	2.81	12
PBE0	PBE0/cc-pVQZ	ANO-L-VTZP	6.00	4.75	3.81	3.23	2.82	1
PBE0[a]	PBE0/6-311G(d,p)	6-311+G(2d,p)	6.02	4.61	3.60	3.00		13
BHHLYP	B3LYP/6-31+G(d)	6-311+G(d,p)	6.29	4.86	3.86	3.25	2.84	12
BHHLYP[a]	PBE0/6-311G(d,p)	6-311+G(2d,p)	6.32	4.77	3.71	3.07		13
CAM-B3LYP[a]	PBE0/6-311G(d,p)	6-311+G(2d,p)	6.08	4.59	3.56	2.93		13

[a] With PCM(dichloromethane) effects for both geometry and TD-DFT part.

S2 Computational protocol for 0-0 energies

Following previous works,[14,15] we propose here an efficient approach that allowed to obtain accurate 0-0 energies for a large panel of solvated BODIPY and alike derivatives. We redirect the interested reader to these original references as well as to Ref. 16 for more details but we summarize the approach here. This protocol uses two atomic basis sets, SBS, a compact basis set for geometry optimizations and frequency calculations, and LBS, a large atomic basis set for total and transition energies. Reasonable choices for these two atomic basis sets are 6-31G(d) and 6-311+G(2d,p) as SBS and LBS, respectively. The approach also uses two variations of the well-known Polarizable Continuum Model (PCM) to model solvent effects: on the one hand, the linear-response (LR) approach[17,18] is applied for structures and vibrations whereas, on the other hand, a more refined model, either the corrected-LR (cLR)[19] or the state-specific (SS)[20] approaches, is used for both total and transition energies. The protocol presented below uses the cLR scheme, but can be straightforwardly adapted to the SS model. The equilibrium and non-equilibrium limits of the PCM approach are denoted eq and neq, respectively. Eventually, one could advocate the use of M06-2X for the DFT and TD-DFT components of the calculations. M06-2X is a global hybrid *meta*-GGA exchange-correlation functional that includes 54% of *exact* exchange.[21]

First, at the LR-PCM(eq)-TD-DFT/SBS level, one determines the optimal ground ($R_{\mathrm{SBS}}^{\mathrm{GS}}$) and excited ($R_{\mathrm{SBS}}^{\mathrm{ES}}$) state geometries. In a second step, one needs to compute the (harmonic) vibrations, at exactly the same level of theory. This gives access to the zero-point vibrational energies (ZPVE) of the two states, $E_{\mathrm{SBS}}^{\mathrm{ZPVE-GS}}$ and $E_{\mathrm{SBS}}^{\mathrm{ZPVE-ES}}$. The difference between these two values,

$$\Delta E_{\mathrm{SBS}}^{\mathrm{ZPVE}}(\mathrm{LR},\mathrm{eq}) = E_{\mathrm{SBS}}^{\mathrm{ZPVE-ES}} - E_{\mathrm{SBS}}^{\mathrm{ZPVE-GS}} \tag{S-1}$$

has to be determined. Next, using the optimal ground-state geometry one can determine the vertical absorption in gas-phase, as well as both equilibrium and non-equilibrium limits for the solvated compounds,

$$\begin{aligned}
\Delta E^{\mathrm{vert-a}}_{\mathrm{LBS}}(\mathrm{gas}) &= E^{\mathrm{ES}}_{\mathrm{LBS}}(R^{\mathrm{GS}}_{\mathrm{SBS}},\mathrm{gas}) - E^{\mathrm{GS}}_{\mathrm{LBS}}(R^{\mathrm{GS}}_{\mathrm{SBS}},\mathrm{gas}) && \text{(S-2)}\\
\Delta E^{\mathrm{vert-a}}_{\mathrm{LBS}}(\mathrm{cLR},\mathrm{neq}) &= E^{\mathrm{ES}}_{\mathrm{LBS}}(R^{\mathrm{GS}}_{\mathrm{SBS}},\mathrm{cLR},\mathrm{neq}) - E^{\mathrm{GS}}_{\mathrm{LBS}}(R^{\mathrm{GS}}_{\mathrm{SBS}},\mathrm{eq}) && \text{(S-3)}\\
\Delta E^{\mathrm{vert-a}}_{\mathrm{LBS}}(\mathrm{cLR},\mathrm{eq}) &= E^{\mathrm{ES}}_{\mathrm{LBS}}(R^{\mathrm{GS}}_{\mathrm{SBS}},\mathrm{cLR},\mathrm{eq}) - E^{\mathrm{GS}}_{\mathrm{LBS}}(R^{\mathrm{GS}}_{\mathrm{SBS}},\mathrm{eq}) && \text{(S-4)}\\
\Delta\Delta E^{\mathrm{vert-a}}_{\mathrm{LBS}} &= \Delta E^{\mathrm{vert-a}}_{\mathrm{LBS}}(\mathrm{cLR},\mathrm{neq}) - \Delta E^{\mathrm{vert-a}}_{\mathrm{LBS}}(\mathrm{cLR},\mathrm{eq}) && \text{(S-5)}
\end{aligned}$$

where E^{GS} and E^{ES} are respectively the total energies of the ground and excited states determined at the optimal ground-state geometry. $\Delta\Delta E^{\mathrm{vert-a}}_{\mathrm{LBS}}$ is the difference between non-equilibrium and equilibrium vertical absorption energies. Similarly, using the optimal excited-state geometry, one can obtain vertical fluorescence energies,

$$\begin{aligned}
\Delta E^{\mathrm{vert-f}}_{\mathrm{LBS}}(\mathrm{gas}) &= E^{\mathrm{ES}}_{\mathrm{LBS}}(R^{\mathrm{ES}}_{\mathrm{SBS}},\mathrm{gas}) - E^{\mathrm{GS}}_{\mathrm{LBS}}(R^{\mathrm{ES}}_{\mathrm{SBS}},\mathrm{gas}) && \text{(S-6)}\\
\Delta E^{\mathrm{vert-f}}_{\mathrm{LBS}}(\mathrm{cLR},\mathrm{neq}) &= E^{\mathrm{ES}}_{\mathrm{LBS}}(R^{\mathrm{ES}}_{\mathrm{SBS}},\mathrm{cLR},\mathrm{eq}) - E^{\mathrm{GS}}_{\mathrm{LBS}}(R^{\mathrm{ES}}_{\mathrm{SBS}},\mathrm{neq}) && \text{(S-7)}\\
\Delta E^{\mathrm{vert-f}}_{\mathrm{LBS}}(\mathrm{cLR},\mathrm{eq}) &= E^{\mathrm{ES}}_{\mathrm{LBS}}(R^{\mathrm{ES}}_{\mathrm{SBS}},\mathrm{cLR},\mathrm{eq}) - E^{\mathrm{GS}}_{\mathrm{LBS}}(R^{\mathrm{ES}}_{\mathrm{SBS}},\mathrm{eq}) && \text{(S-8)}\\
\Delta\Delta E^{\mathrm{vert-f}}_{\mathrm{LBS}} &= \Delta E^{\mathrm{vert-f}}_{\mathrm{LBS}}(\mathrm{cLR},\mathrm{neq}) - \Delta E^{\mathrm{vert-f}}_{\mathrm{LBS}}(\mathrm{cLR},\mathrm{eq}) && \text{(S-9)}
\end{aligned}$$

The adiabatic energy can be readily obtained from previous data,

$$\begin{aligned}
\Delta E^{\mathrm{adia}}_{\mathrm{LBS}}(\mathrm{gas}) &= E^{\mathrm{ES}}_{\mathrm{LBS}}(R^{\mathrm{ES}}_{\mathrm{SBS}},\mathrm{gas}) - E^{\mathrm{GS}}_{\mathrm{LBS}}(R^{\mathrm{GS}}_{\mathrm{SBS}},\mathrm{gas}) && \text{(S-10)}\\
\Delta E^{\mathrm{adia}}_{\mathrm{LBS}}(\mathrm{cLR},\mathrm{eq}) &= E^{\mathrm{ES}}_{\mathrm{LBS}}(R^{\mathrm{ES}}_{\mathrm{SBS}},\mathrm{cLR},\mathrm{eq}) - E^{\mathrm{GS}}_{\mathrm{LBS}}(R^{\mathrm{GS}}_{\mathrm{SBS}},\mathrm{eq}) && \text{(S-11)}
\end{aligned}$$

and the same holds for best estimates of the 0-0 energies, that are obtained by adding Eqs. (S-1) and (S-11),

$$\Delta E^{0-0}_{\mathrm{BE}}(\mathrm{eq}) = \Delta E^{\mathrm{adia}}_{\mathrm{LBS}}(\mathrm{cLR},\mathrm{eq}) + \Delta E^{\mathrm{ZPVE}}_{\mathrm{SBS}}(\mathrm{LR},\mathrm{eq}) \qquad \text{(S-12)}$$

These 0-0 energies are often compared to the experimental absorption-fluorescence crossing point (AFCP). However, the measured absorption and fluorescence curves correspond to neq phenomena, and therefore, one needs to correct the previous equation thanks to the results of Eqs. (S-5) and (S-9)

$$\Delta E_{\mathrm{BE}}^{\mathrm{AFCP}}(\mathrm{neq}) \;=\; \Delta E_{\mathrm{BE}}^{0-0}(\mathrm{eq}) + \frac{1}{2}\left[\Delta\Delta E_{\mathrm{LBS}}^{\mathrm{vert-a}} + \Delta\Delta E_{\mathrm{LBS}}^{\mathrm{vert-f}}\right] \tag{S-13}$$

An explanation of the presence of the 1/2 factor can be found in Ref. 16. $\Delta E_{\mathrm{BE}}^{\mathrm{AFCP}}(\mathrm{neq})$ in Eq (S-13) constitues the theoretical best estimate of the AFCP obtained at the TD-DFT level. As explained in the Account, adiabatic TD-DFT does a poor job for cyanine and BODIPY derivatives, and it is necessary to correct these energies with the results obtained through adequate wavefunction (Ψ) theories, e.g., CC2, SOS-CIS(D) or GW/BSE. If only gas phase calculations are available, then one first need to determine the gas-phase transition energies with the selected Ψ on both $R_{\mathrm{SBS}}^{\mathrm{GS}}$ and $R_{\mathrm{SBS}}^{\mathrm{ES}}$. The adiabatic energy presents a form similar to Eq. (S-10),

$$\Delta E_{\mathrm{LBS}}^{\mathrm{adia-\Psi}}(\mathrm{gas}) \;=\; E_{\mathrm{LBS}}^{\mathrm{ES-\Psi}}(R_{\mathrm{SBS}}^{\mathrm{ES}}, \mathrm{gas}) - E_{\mathrm{LBS}}^{\mathrm{GS-\Psi}}(R_{\mathrm{SBS}}^{\mathrm{GS}}, \mathrm{gas}) \tag{S-14}$$

where $E^{\mathrm{ES-\Psi}}$ and $E^{\mathrm{GS-\Psi}}$ are respectively the wavefunction excited-state and ground-state energies determined on the (TD)-DFT geometries. For instance, if the SOS-CIS(D) method is applied, the ground-state [excited-state] energy is determined with a single-point SOS-MP2 [SOS-CIS(D)] calculation. This allows to correct the TD-DFT estimates obtained in Eq. (S-13),

$$\Delta E_{\mathrm{BE}}^{\mathrm{AFCP-\Psi}}(\mathrm{neq}) \;=\; \Delta E_{\mathrm{BE}}^{\mathrm{AFCP}}(\mathrm{neq}) + \left[\Delta E_{\mathrm{LBS}}^{\mathrm{adia-\Psi}}(\mathrm{gas}) - \Delta E_{\mathrm{LBS}}^{\mathrm{adia}}(\mathrm{gas})\right] \tag{S-15}$$

which generally well reproduce the experimental values.

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