

Electronic Supporting Information for

Organic Molecules with Inverted Gaps between First Excited Singlet and Triplet States and Appreciable Fluorescence Rates

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1 Compound Numbering

To provide a unique identifier for all compounds investigated in the course of this study, every compound is assigned a unique number prefixed by the letter "S," for Supporting Information (SI). These numbers differ from the ones used in the main text. In the additional SI files, we attached a table of all compounds mentioned in the main text together with their SI numbers. In addition, there is a list of all molecules investigated with their SI numbers and their SMILES strings, as well as a PDF file containing the SI numbers of all compounds investigated together with an image of the corresponding molecular graph.

2 Supplementary Results

In this section, additional results, that did not fit into the main manuscript, are presented.

2.1 Gaussian Process Regression

Gaussian process regression was carried out using Python (version 3.6.9)¹ together with the scikit-learn package (version 0.21.2).² First, data was transformed linearly to be within the interval [0,1]. As kernel, we used a sum of the Matérn kernel with $\nu = \frac{5}{2}$ and the White kernel.

2.2 Solvatochromic Shift Calibration

Table S1 provides the data used for calibrating for the solvatochromic shift with the corresponding references. Table S2 provides the results of linear regressions carried out for that purpose. These linear regressions were used to estimate the absorption wavelength for the compounds investigated in the course of this study.

Table S1: Calibration of solvatochromic shift using experimental absorption data. The solvents used in experiment, if known, are added in parenthesis. Computations were carried out without solvent model.

Compound	Experiment	$\Delta E(S_0-S_1)$ [eV]			
		EOM-CCSD/cc-pVDZ	ADC(2)/cc-pVDZ	ω B2PLYP/def2-SVP	SA-SF-PBE50/def2-SVP
S1	1.039 ³ (hexane)	1.092	1.038	1.316	1.095
S11	1.908 ⁴ (EtOH)	1.659	1.536	1.881	1.635
S13	1.845 ⁵ (EtOH)	2.012	1.863	2.226	1.957
S46	1.974 ⁶ (hexane)	2.264	2.062	2.421	2.163
S47	1.962 ⁷ (EtOH)	1.999	1.852	2.213	1.988
S52	2.039 ⁸ (MeCN)	2.251	2.093	2.479	2.210
S53	2.335 ⁸ (MeCN)	2.526	2.333	2.755	2.518
S77	1.947 ⁸ (MeCN)	2.114	1.970	2.333	2.016
S84	2.799 ⁹ (MeCN)	2.791	2.578	3.028	2.909
S559	1.950 ¹⁰ (CHCl ₃)	2.197	1.963	2.423	2.193
S210	1.807 ⁴ (EtOH)	1.786	1.651	2.011	1.764

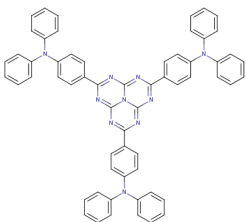
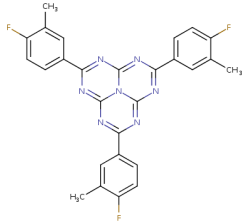
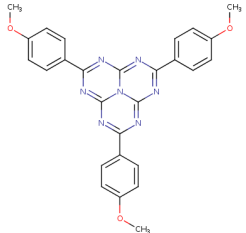
Table S2: Results of linear regression of experimental against predicted vertical S_1 excitation energies: $\Delta E(S_0-S_1)_{\text{exp}} = \text{Slope} \cdot \Delta E(S_0-S_1)_{\text{com}} + \text{Intercept}$

Method	Slope	Intercept [eV]	R ²	F	N
EOM-CCSD/cc-pVDZ	0.87(11)	0.17(22)	0.88	67	11
ADC(2)/cc-pVDZ	0.96(11)	0.13(22)	0.89	72	11
ω B2PLYP/def2-SVP	0.87(10)	-0.03(23)	0.89	74	11
SA-SF-PBE50/def2-SVP	0.85(9)	0.23(18)	0.91	93	11

2.3 Azaphenalene Derivatives from Literature

Table S3 provides the computational results for the structures of derivatives of **2** investigated in the literature. **L1** is a simplified analogue of a compound used as OLED emitter,¹¹ the six tert-butyl groups were removed to reduce computational cost and avoid prohibitively expensive computations. **L2** was also used as OLED emitter.^{12,13} **L3** was characterized both experimentally and computationally in a very recent study.¹⁴

Table S3: Results of our computational protocol for derivatives of **2** studied in the literature.

Molecule	ω B2PLYP/def2-SVP			
	$\Delta E(S_0-S_1)$ [eV]	$\Delta E(S_0-T_1)$ [eV]	$\Delta E(S_1-T_1)$ [eV]	$f_{12}(S_0-S_1)$
 <p>L1</p>	3.1490	3.0480	0.1010	0.0000
 <p>L2</p>	3.1290	3.4180	-0.2890	0.0000
 <p>L3</p>	3.1710	3.3590	-0.1880	0.0000

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