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

Absorption and Fluorescence Signatures of 1,2,3-Triazole Based Regioisomers : Challenging Compounds for TD-DFT †

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Synthesis:

N,N-dimethyl-4-(1-phenyl-1H-1,2,3-triazol-4-yl)aniline (da) 4-iodobenzene (386 µL, 3.45 mmol, 1.0 equiv.) was mixed with N,N-dimethyl-4-phenylacetylene (500 mg, 3.45 mmol, 1.0 equiv.) in a 20 mL scintillation vial. To the mixture were added L-proline (80 mg, 0.2 equiv.), Na_2CO_3 (150 mg, 0.4 equiv.), NaN_3 (269 mg, 1.2 equiv.), L-ascorbate acid (145 mg, 0.1 equiv.), 9:1 DMSO/H_2O (10 mL), and $CuSO_4$, $5H_2O$ (43 mg, 0.05 equiv.). The mixture was stirred overnight at 65 °C. Upon completion (monitored by TLC), the crude mixture was poured into 30 mL of dilute NH_4OH solution and stirred during 30 min. The white precipitate was isolated by filtration and washed with dilute NH_4OH, water and then with cold methanol (ATTENTION: this step is important, as copper azides are explosive when dry, and their traces should be removed before the product is dried). The crude product was dissolved in CH_2Cl_2 and subjected to a chromatography on silica gel, with CH_2Cl_2 (to remove starting materials) followed by ethyl acetate as eluent. The product was obtained as a white powder (570 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.06 (s, 1H), 7.80 (m, 4H), 7.54 (m, 2H), 7.44 (t, *J* = 7.0 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 2H), 3.01 (s, 6H, Me). ^{13}C NMR (100 MHz, $CDCl_3$) : δ 150.54, 148.93, 137.29, 129.70, 128.49, 126.86, 120.44, 118.47, 116.03, 112.59 , 40.50. Anal. found: C, 71.82; H, 5.81; N, 20.61. Calc. for $C_{16}H_{16}N_4$, 1/9 AcOEt: C, 71.96; H, 6.23; N, 20.36. m/z (Waters Q-TOF 2) 287.1269 (1 ppm) ; ($[M+Na]^+$, $C_{16}H_{16}N_4Na$ requires 287.12727).

N,N-dimethyl-4-(4-phenyl-1H-1,2,3-triazol-1-yl)aniline (dai) 4-iodo-N,N-dimethylaniline (350 mg, 1.48 mmol, 1.0 equiv.) was mixed with phenylacetylene (220 µL, 1.48 mmol, 1.0 equiv.) in a 20 mL scintillation vial. To the mixture were added L-proline (34 mg, 0.2 equiv.), Na_2CO_3 (65 mg, 0.4 equiv.), NaN_3 (115 mg, 1.2 equiv.), L-ascorbate acid (95 mg, 0.1 equiv.), 9:1 DMSO/H_2O (10 mL), and $CuSO_4 \cdot 5H_2O$ (19 mg, 0.05 equiv.). The mixture was stirred overnight at 65 °C. Upon completion (monitored by TLC), the crude mixture was poured into 30 mL of dilute NH_4OH solution and stirred during 30 min. The white precipitate was isolated by filtration and washed with dilute NH_4OH, water and then with cold methanol (ATTENTION: this step is important, as copper azides are explosive when dry, and their traces should be removed before the product is dried). The crude product was dissolved in CH_2Cl_2 and subjected to a chromatography on silica gel, with CH_2Cl_2 (remove starting materials), then ethyl acetate. The product was obtained as a white powder (191 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.07 (s, 1H), 7.91 (d, *J* = 7.2 Hz, 2H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.43 (m, 2H), 7.35 (t, *J* = 6.8 Hz, 1H), 6.79 (d, *J* = 8.7 Hz, 2H), 3.03 (s, 6H, Me). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 150.57, 130.78, 128.86, 128.85, 128.65, 128.13, 126.95, 125.77, 121.93, 112.42, 40.48. Anal. found: C, 72.56; H, 5.89; N, 20.70. $C_{16}H_{16}N_4$ Calc.: C, 72.70; H, 6.10; N, 21.20. m/z (Waters Q-TOF 2) 287.1268 (2 ppm) ; ($[M+Na]^+$, $C_{16}H_{16}N_4Na$ requires 287.12727). m/z 265.1453 (0 ppm) ; ($[M+H]^+$, $C_{16}H_{17}N_4$ requires 265.14532).

Structural data: (full structural reports are provided as separate files).

Table S1. Bond lengths and inter-ring dihedral angles of **da**. Labels are given Figure S1. All calculated data use the 6-31+G(d) atomic basis set except HF geometries for which the 6-31G atomic basis set was used.[i] Distances are given in Å and angles in degrees. GS and ES label ground and excited state optimized geometries, respectively. Medium is given in parentheses (gas=gas phase, tol=toluene and THF=tetrahydrofuran).

		X-Ray		GS	GS	GS	GS	GS	ES	Δ(GS-ES)
		mol. N°	mol. N°	HF	_PBE	CAM	ωB97X	ωB97X-D	ωB97X-D	ωB97X-D
Atom1	Atom2	1	2	(gas)	(tol)	(tol)	(THF)	(THF)	(THF)	(THF)
C1	C2	1.386(3)	1.391(3)	1.385	1.391	1.39	1.392	1.392	1.386	0.006
C1	C6	1.386(2)	1.392(2)	1.388	1.395	1.392	1.393	1.393	1.414	-0.021
C2	C3	1.387(3)	1.387(2)	1.388	1.395	1.393	1.394	1.395	1.401	-0.006
C3	C4	1.382(3)	1.382(3)	1.387	1.394	1.392	1.394	1.394	1.398	-0.004
C4	C5	1.388(3)	1.392(3)	1.387	1.392	1.391	1.393	1.393	1.388	0.005
C5	C6	1.387(2)	1.381(2)	1.387	1.395	1.392	1.392	1.393	1.413	-0.020
C6	N7	1.433(2)	1.436(2)	1.416	1.417	1.423	1.427	1.424	1.379	0.045
N7	N8	1.357(2)	1.357(2)	1.346	1.343	1.342	1.337	1.342	1.412	-0.070
N7	C11	1.358(2)	1.355(2)	1.359	1.356	1.356	1.355	1.355	1.367	-0.012
N8	N9	1.321(2)	1.317(2)	1.281	1.295	1.296	1.297	1.299	1.277	0.022
N9	C10	1.372(2)	1.368(2)	1.373	1.367	1.366	1.365	1.366	1.373	-0.007
C10	C11	1.375(3)	1.383(2)	1.366	1.381	1.377	1.377	1.379	1.420	-0.041
C10	C12	1.466(3)	1.469(2)	1.462	1.461	1.467	1.471	1.467	1.409	0.058
C12	C13	1.395(2)	1.397(3)	1.393	1.400	1.397	1.398	1.399	1.427	-0.028
C12	C17	1.394(2)	1.395(2)	1.391	1.400	1.397	1.398	1.399	1.436	-0.037
C13	C14	1.387(3)	1.389(3)	1.381	1.387	1.386	1.388	1.388	1.364	0.024
C14	C15	1.404(2)	1.404(2)	1.403	1.413	1.410	1.412	1.413	1.442	-0.029
C15	C16	1.407(3)	1.413(2)	1.403	1.413	1.410	1.411	1.412	1.422	-0.010
C15	N18	1.385(2)	1.384(2)	1.384	1.378	1.384	1.385	1.382	1.356	0.026
C16	C17	1.386(3)	1.386(3)	1.382	1.387	1.387	1.389	1.388	1.378	0.010
N18	C19	1.442(3)	1.449(3)	1.452	1.446	1.450	1.452	1.451	1.457	-0.006
N18	C20	1.434(2)	1.435(3)	1.451	1.445	1.450	1.452	1.451	1.454	-0.003
		X-Ray		GS	GS	GS	GS	GS	ES	Δ(GS-ES)
dihedral	ring1ring2	mol. N°	mol. N°	HF	_PBE	CAM	ωB97X	ωB97X-D	ωB97X-D	ωB97X-D
angle		1	2	(gas)	(tol)	(tol)	(THF)	(THF)	(THF)	(THF)
C1C6N7N8	AB	-17.8(2)	21.0(2)	-30.9	-29.0	-32.8	-35.9	-36.5	-4.1	-32.4
C5C6N7C11	AB	-17.7(3)	19.9(3)	-31.4	-29.3	-32.9	-36.2	-36.8	-2.9	-33.9
N9C10C12C13	BC	15.8(3)	24.8(2)	1.8	8.4	8.4	13.9	15.8	0.6	15.2
C11C10C12C17	BC	17.2(3)	22.9(3)	2.4	9.3	9.2	14.8	16.6	0.4	16.2

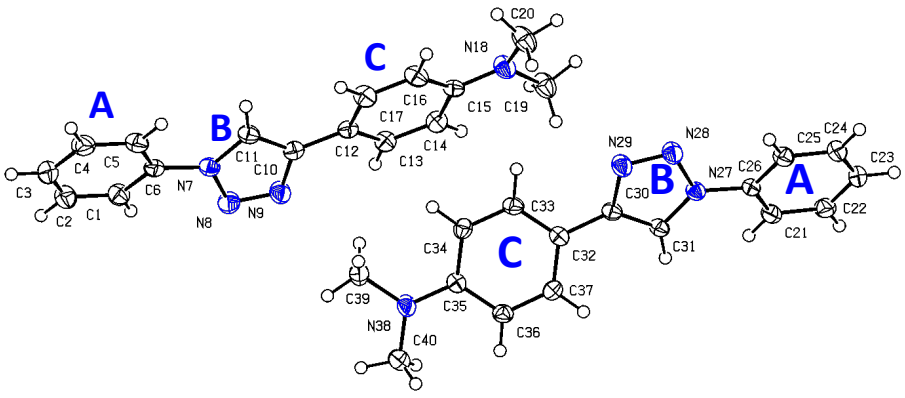


Figure S1. ORTEP representation of **da** molecules : N° 1 (top) and 2 (bottom), with atomic and ring labels.

Table S2. Bond lengths and inter-ring dihedral angles of **dai**. Labels are given Figure S2. All calculated data use the 6-31+G(d) atomic basis set except HF geometries for which the 6-31G atomic basis set was used.[ii] Distances are given in Å and angles in degrees. GS and ES label ground and excited state optimized geometries, respectively. Medium is given in parentheses (gas=gas phase, tol=toluene and THF=tetrahydrofuran).

Atom1	Atom2	X-Ray	GS HF (gas)	GS PBE (tol)	GS CAM (tol)	GS ωB97X (THF)	GS ωB97X-D (THF)	ES ωB97X-D (THF)	Δ(GS-ES) ωB97X-D (THF)
C1	C2	1.388(2)	1.386	1.392	1.39	1.392	1.392	1.39	0.002
C1	C6	1.395(2)	1.394	1.401	1.398	1.399	1.400	1.405	-0.005
C2	C3	1.393(2)	1.388	1.395	1.393	1.394	1.395	1.398	-0.003
C3	C4	1.385(2)	1.387	1.395	1.393	1.394	1.394	1.394	0.000
C4	C5	1.385(2)	1.386	1.392	1.39	1.392	1.392	1.392	0.000
C5	C6	1.396(2)	1.394	1.401	1.399	1.399	1.400	1.405	-0.005
C6	C7	1.472(2)	1.465	1.465	1.470	1.474	1.471	1.460	0.011
C7	C11	1.374(2)	1.368	1.382	1.378	1.378	1.380	1.390	-0.010
C7	N8	1.368(2)	1.370	1.363	1.363	1.363	1.363	1.361	0.002
C11	N10	1.351(2)	1.354	1.352	1.352	1.352	1.352	1.390	-0.038
N9	N10	1.354(1)	1.346	1.343	1.343	1.337	1.342	1.420	-0.078
N10	C12	1.430(2)	1.419	1.418	1.424	1.428	1.425	1.343	0.082
N8	N9	1.314(2)	1.283	1.297	1.297	1.298	1.301	1.303	-0.002
C12	C13	1.389(2)	1.384	1.393	1.390	1.391	1.391	1.438	-0.047
C12	C17	1.383(2)	1.386	1.393	1.390	1.391	1.392	1.440	-0.048
C13	C14	1.383(2)	1.838	1.388	1.387	1.388	1.388	1.367	0.021
C14	C15	1.406(2)	1.403	1.413	1.411	1.413	1.414	1.434	-0.020
C15	C16	1.406(2)	1.405	1.414	1.412	1.413	1.415	1.434	-0.019
C15	N18	1.386(2)	1.382	1.375	1.379	1.379	1.377	1.359	0.018
C16	C17	1.384(2)	1.381	1.386	1.386	1.387	1.387	1.365	0.022
N18	C19	1.440(2)	1.452	1.445	1.45	1.452	1.451	1.454	-0.003
N18	C20	1.449(2)	1.453	1.446	1.45	1.452	1.452	1.454	-0.002

dihedral angle	ring1ring2	X-Ray	GS HF (gas)	GS PBE (tol)	GS CAM (tol)	GS ωB97X (THF)	GS ωB97X-D (THF)	ES ωB97X-D (THF)	Δ(GS-ES) ωB97X-D (THF)
C1C6C7N8	AB	-19.2(2)	1.3	0.3	0.5	11.8	13.3	0.0	13.3
C5C6C7C11	AB	-18.3(2)	1.9	0.9	1.0	12.4	14.0	0.0	14.0
C11N10C12C13	BC	-29.5(2)	-41.7	-36.4	-40.4	-43.9	-44.6	0.0	-44.6
N9N10C12C17	BC	-26.9(2)	-42.2	-37.1	-41.0	-44.5	-45.0	0.0	-45.0

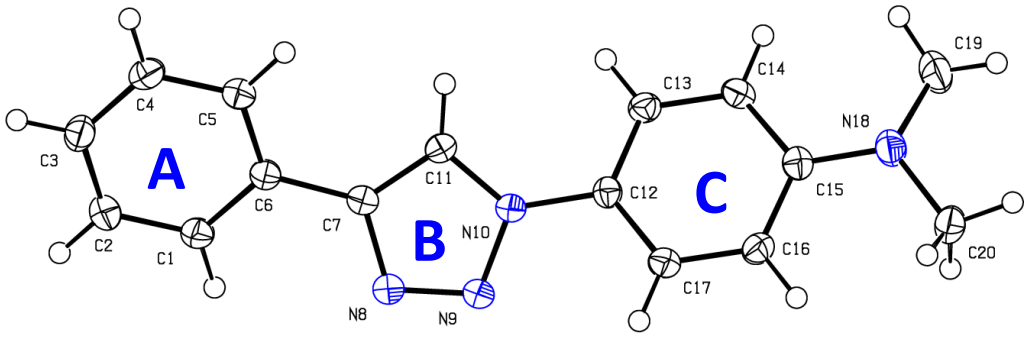


Figure S2. ORTEP representation of **dai** with atomic and ring labels.

Experimental absorption and emission spectra:

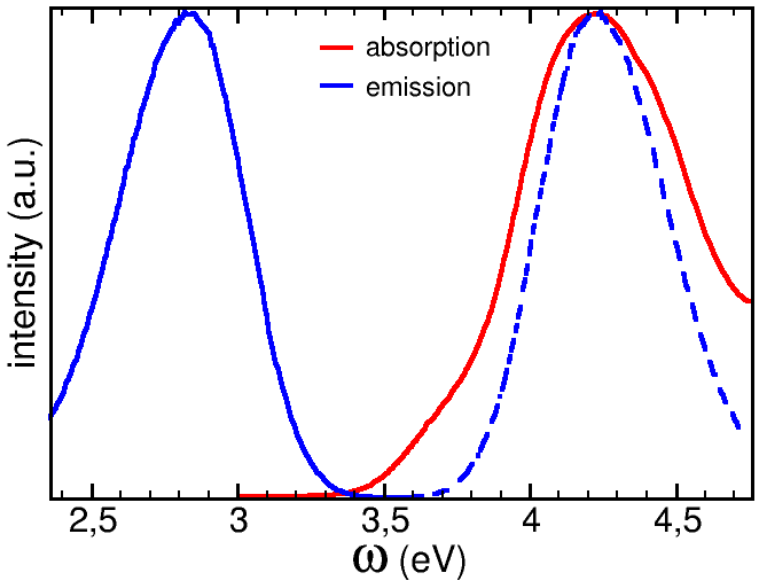


Figure S3. Normalised fluorescence (blue) and absorption (red) spectra of **da**. The dashed blue line is obtained by mirroring the fluorescence spectra so as to reveal non-mirror shapes of absorption and fluorescence spectra.

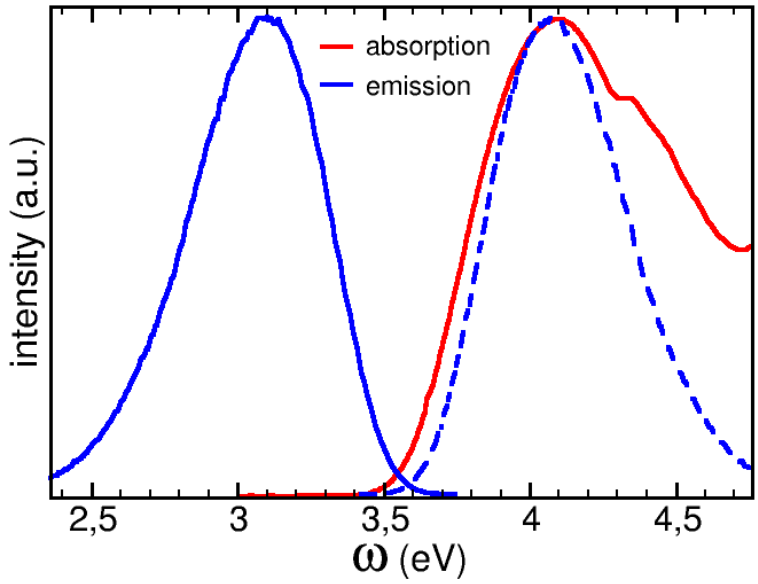


Figure S4. Normalised fluorescence (blue) and absorption (red) spectra of **dai**. The dashed blue line is obtained by mirroring the fluorescence spectra so as to reveal almost mirror shapes of absorption and fluorescence spectra.

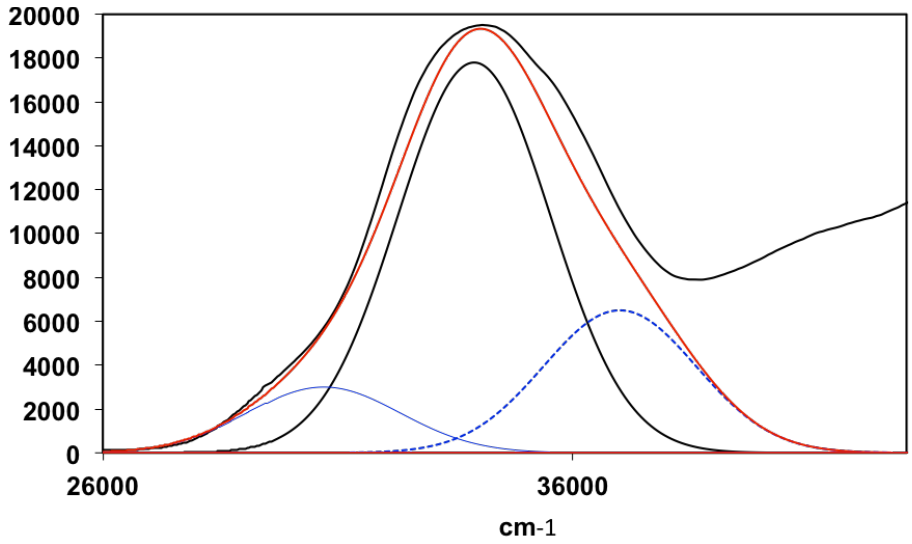


Figure S5. Tentative deconvolution of the experimental absorption spectrum of **da** recorded in THF (black line) using three Gaussian functions: $A_i \exp[-(\omega-\omega_i)^2/(\alpha^2)]$. Widths are kept constant (α=2300 cm^{-1}, *i.e.* FWHM of 0.47 eV), amplitudes and position are A_1=3000, ω_1=30700 cm^{-1}; A_2=17800, ω_2=33900 cm^{-1}; A_3=6500, ω_3=37000 cm^{-1}.

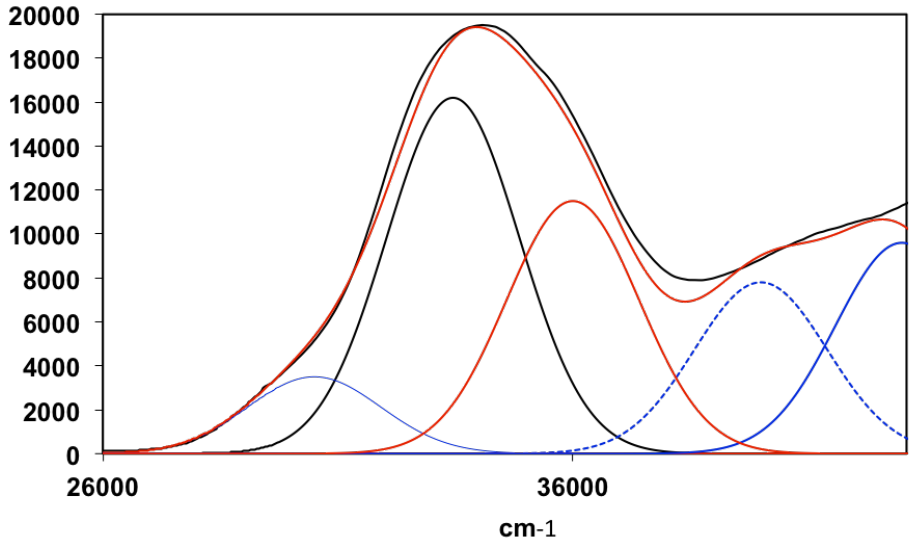


Figure S6. Tentative deconvolution of the experimental absorption spectrum of **da** recorded in THF (black line) using five Gaussian functions: $A_i \exp[-(\omega-\omega_i)^2/(\alpha^2)]$. Widths are kept constant (α=2000 cm^{-1}, *i.e.* FWHM of 0.41 eV), amplitudes and position are A_1=3500, ω_1=30500 cm^{-1}; A_2=16200, ω_2=33450 cm^{-1}; A_3=11500, ω_3=36000 cm^{-1}; A_4=7800, ω_4=40000 cm^{-1}; A_5=9600, ω_5=43000 cm^{-1}.

Comparison of Figure S3 with Figure S4 clearly reveals the non-mirror shape of the absorption spectrum of **da**. Tentative deconvolutions of the experimental absorption spectrum of **da** in THF using Gaussian functions are shown Figure S5 and S6. They lead of a splitting between the first two excited states of *ca* 0.4 eV. We underline that such a fitting procedure is relatively arbitrary and does not account for the asymmetric band shape provided by vibronic contributions. This leads us to report intervals (e.g. [0.3-0.5]) instead of a single value.

Calculated maximum of the first absorption band:

Table S3. Position of the maximum of the first absorption band ($\omega_{\max}^{abs}$) obtained after convolution of the ES data given in Table 4 and considering two Gaussians having a FWHM of 0.50 eV. Values have been calculated in gas phase and are reported in eV.

Method	**da**	**dai**
EOM-CCSD/6-31G(d)[a]	5.03	5.22
RI-CC2/SVP[b]	4.66	4.93
LC-BLYP/SVP[b]	4.78	5.01
ωB97X-D/SVP[b]	4.72	4.96
ωB97X-D/6-31G(d)[b]	4.76	5.00
ωB97X-D/6-31G(d)[b]	4.65	4.87
ωB97X-D/6-31+G(d)[c]	4.64	4.81
CAM-B3LYP/6-31+G(d)[a]	4.53	4.71
B3LYP/SVP[b]	4.61	4.30
PBE0/6-31+G(d)[a]	4.57	4.31

[a]CAM-B3LYP geometry
[b]HF geometry
[c]ωB97X-D geometry

Table S4. Position of the maximum of the first absorption band ($\omega_{\max}^{abs}$) obtained after convolution of the ES data given in Table 5 and considering two Gaussians having a FWHM of 0.50 eV. Values have been calculated using the continuum PCM model in its non-equilibrium limits and are reported in eV.

Functional (medium)	PCM Model	**da**	**dai**
PBE0 (toluene)	LR	3.66	4.11
	cLR	3.36	4.01
	SS	2.43	2.72
PBE0 (THF)	LR	4.29	4.07
	cLR	4.19	3.91
	SS	2.59	2.64
CAM-B3LYP (Toluene)	LR	4.48	4.65
	cLR	4.51	4.67
	SS	4.58	4.47
CAM-B3LYP (THF)	LR	4.52	4.65
	cLR	4.55	4.65
	SS	4.52	4.35
CAM-B3LYP (DCM)	LR	4.52	4.64
	cLR	4.56	4.65
	SS	4.53	4.33
ωB97X (THF)	LR	4.76	4.93
	cLR	4.82	4.98
	SS	4.77	4.85
ωB97X-D (THF)	LR	4.61	4.67
	cLR	4.65	4.76
	SS	4.59	4.52

Comparison between theoretical and experimental optical spectra:

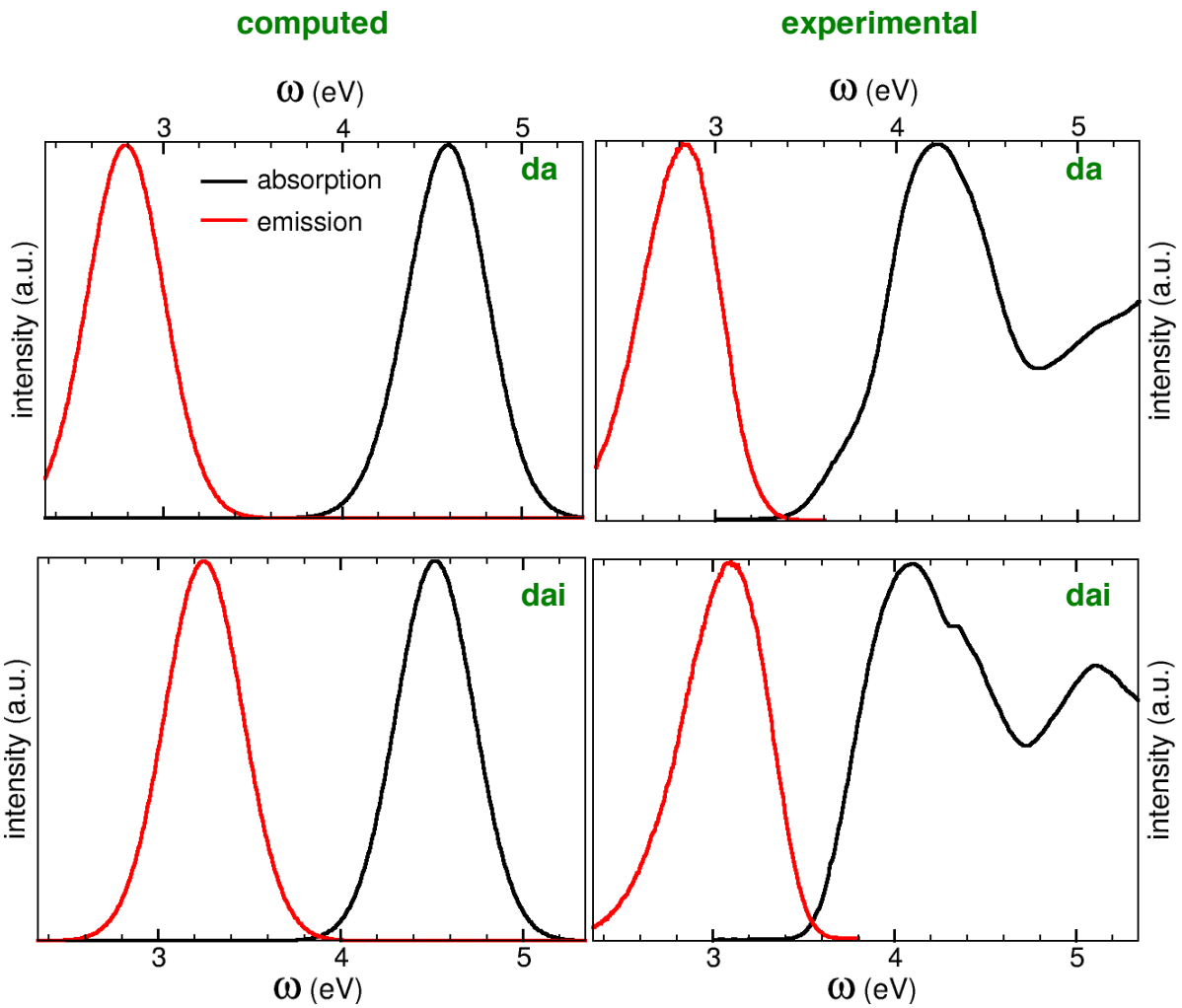
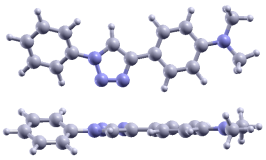
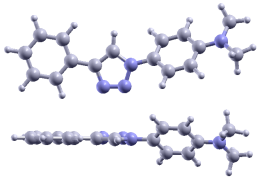
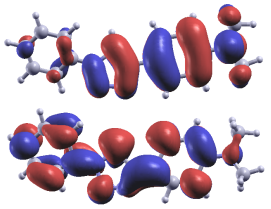
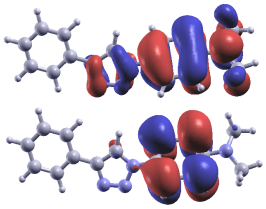
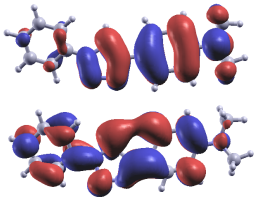
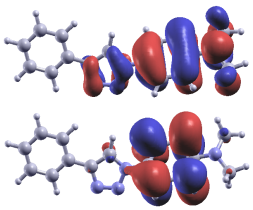
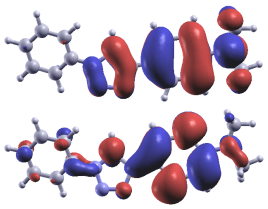
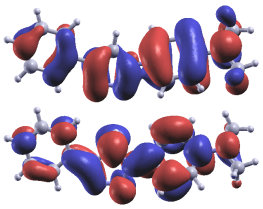
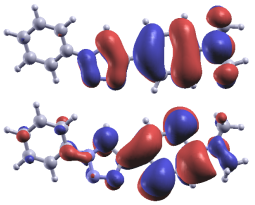
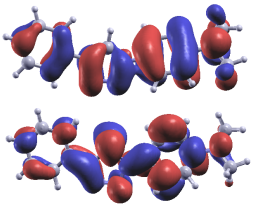


Figure S7. Computed (left) and experimental (right) emission (red) and absorption (black) spectra of **da** (top) and **dai** (bottom) in THF. Simulated spectra have ben obtained tacking transition energies and oscillator strengths from Table 6 and 7 for the ωB97X-D functional and SS approach for the PCM model. Band shapes have been obtained using Gaussians having a FWHM of 0.50 eV. We underline that Gaussians do not introduce band asymmetry in the band-shapes; simulating such asymmetry needs to compute vibrationally resolved optical spectra that are not yet available within the PCM-SS model. Calculated absorption spectra are based on the first two excited states and do not include states relevant for the increase in absorption experimentally observed at higher energies.

Table S5. Natural transition orbitals[iii] of **da** (left) and **dai** (right) illustrating the effect of basis set for calculation in gas phase using geometries optimized at the CAM-B3LYP/6-31+G(d) level. Panels quote excited state number, associated eigenvalue, transition energy, transition wavelength and oscillator strength. Geometries and orbitals were plotted using XCrySDen.[iv]

level of theory		**da**		**dai**
geometry: CAM-B3LYP/6-31+G(d)				
level of theory		**hole** **electron**		**hole** **electron**
TD-CAM-B3LYP/6-31G(d)	<1| w=0.94 4.58 eV 271 nm f_{01}=0.52		<1| w=0.89 4.78 eV 259 nm f_{01}=0.05	
TD-CAM-B3LYP/6-31+G(d)	<1| w=0.95 4.35 eV 285 nm f_{01}=0.38		<1| w=0.91 4.61 eV 269 nm f_{01}=0.07	
TD-CAM-B3LYP/6-31G(d)	<2| w=0.88 4.84 eV 256 nm f_{02}=0.36		<2| w=0.90 4.90 eV 253 nm f_{02}=1.00	
TD-CAM-B3LYP/6-31+G(d)	<2| w=0.90 4.68 eV 265 nm f_{02}=0.41		<2| w=0.89 4.72 eV 263 nm f_{02}=0.85	

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