

Supporting Information for

One- and two-photon absorption properties of  
quadrupolar thiophene-based dyes with acceptors of  
varying strength

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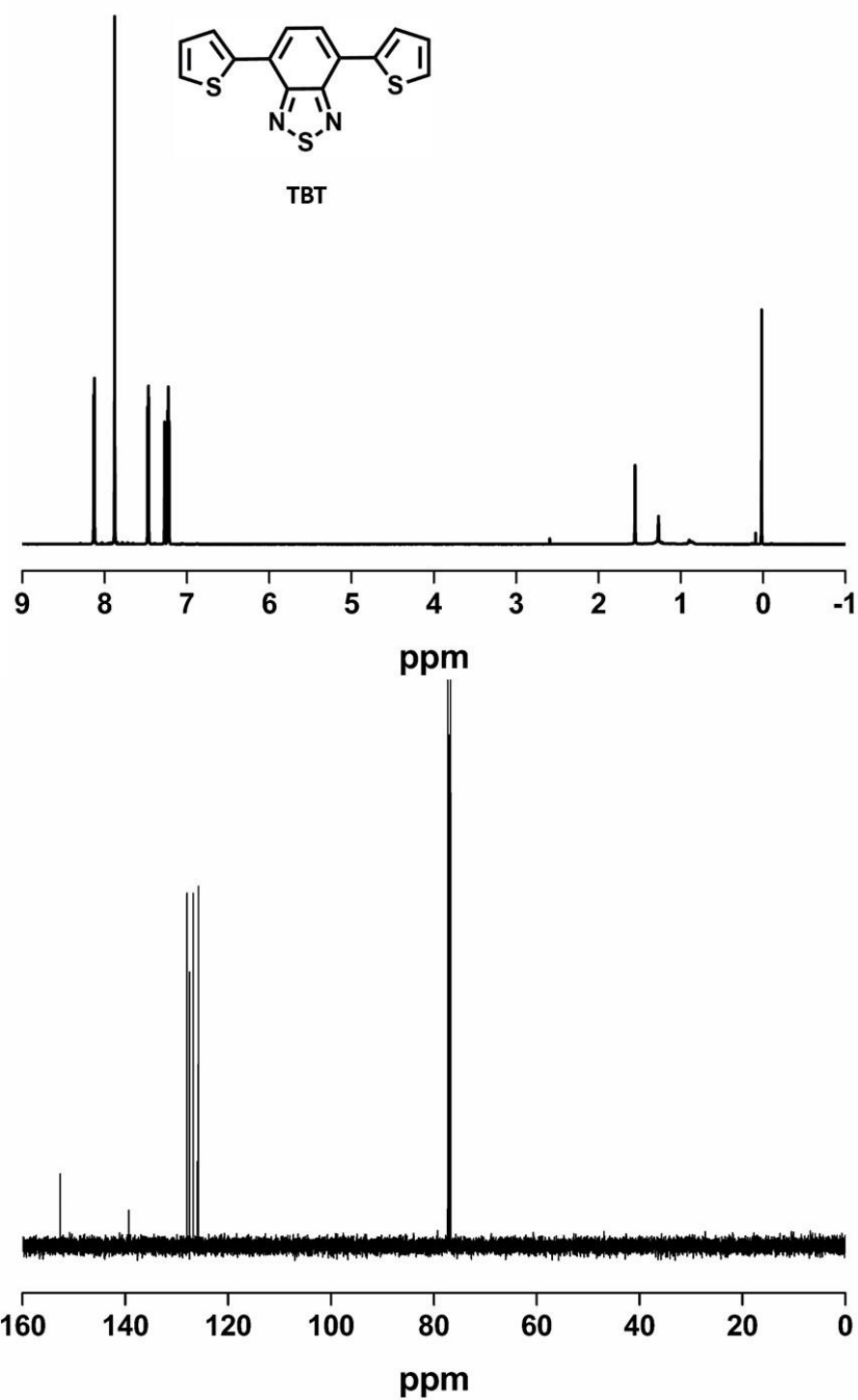
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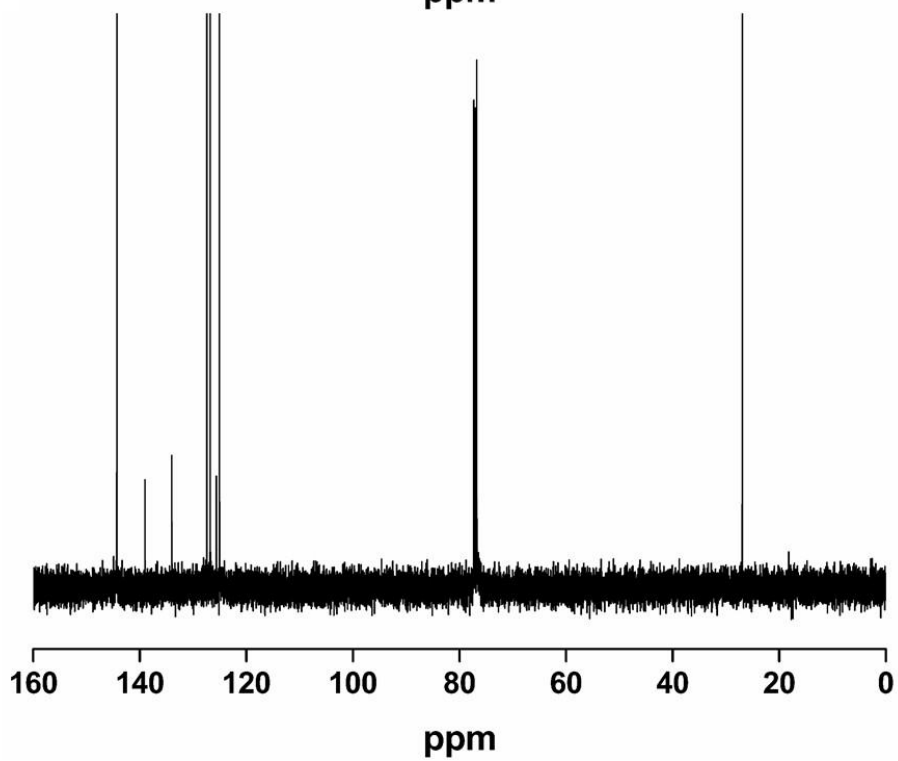
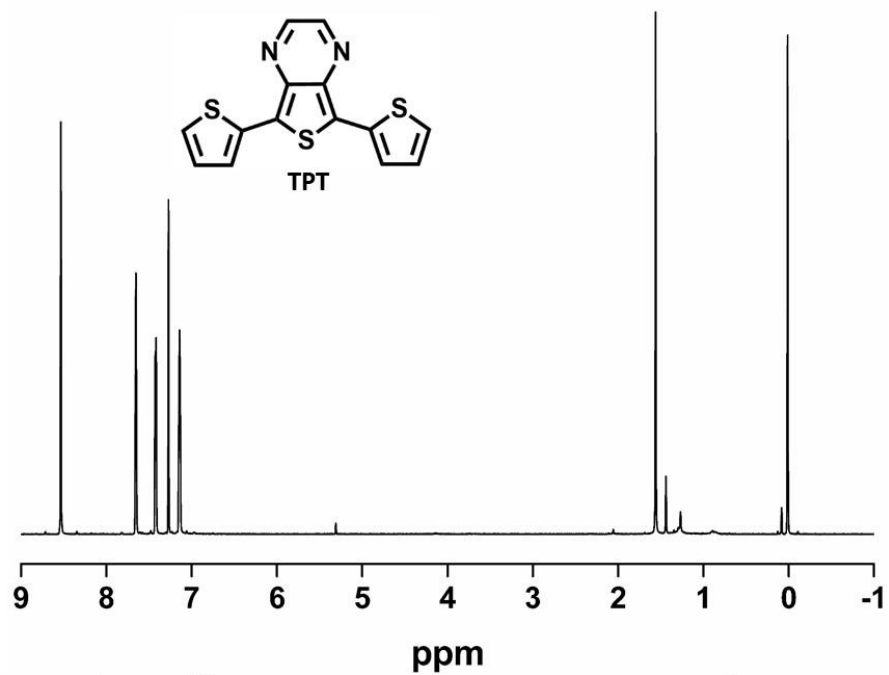
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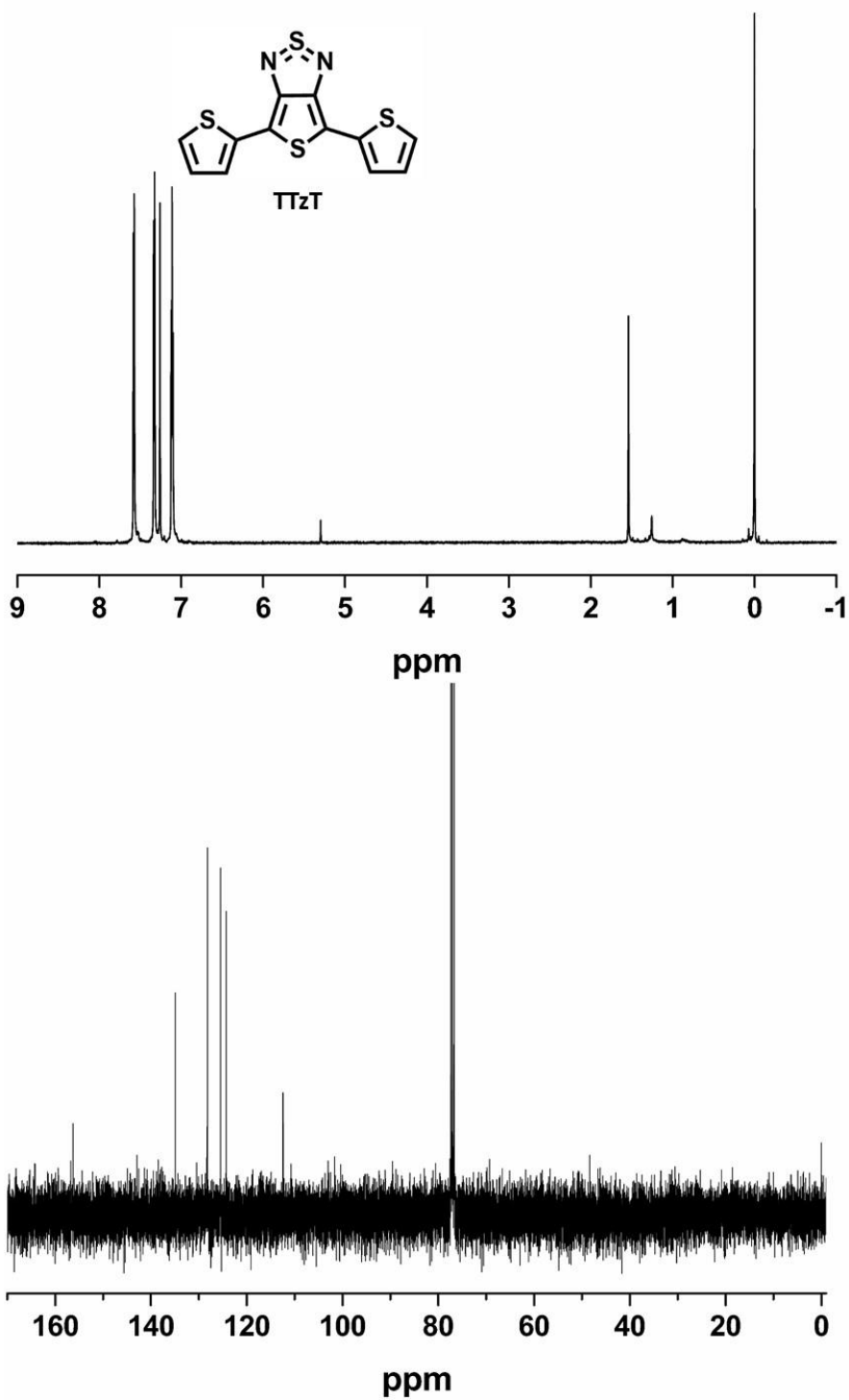
# $^1\text{H}$ AND $^{13}\text{C}$ NMR SPECTRA



$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of TBT in  $\text{CDCl}_3$



<sup>1</sup>H and <sup>13</sup>C NMR spectra of TPT in CDCl<sub>3</sub>



$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of TTzT in  $\text{CDCl}_3$

### Vibronic structure simulation.

The evaluation of the Franck-Condon (FC) vibronic progressions in electronic spectra [1-3] requires the evaluation of the Huang–Rhys (HR) factors  $S_v$  [4,5], for each vibrational mode  $v$  with frequency  $\omega_v$ .  $S_v$  is obtained from the dimensionless displacement parameters  $B_v$ , assuming the harmonic approximation and neglecting Duschinski[6] rotation:

$$B_v = \sqrt{\frac{\omega_v}{\hbar}} [\mathbf{X}_j - \mathbf{X}_i] \mathbf{M}^{1/2} \mathbf{Q}_v(j) \quad (\text{S1})$$

and hence defined as

$$S_v = \frac{1}{2} B_v^2 \quad (\text{S2})$$

where  $\mathbf{X}_{i,j}$  is the  $3N$  dimensional vector of the equilibrium Cartesian coordinates of the  $i,j$  electronic state (here the ground and excited molecular states),  $\mathbf{M}$  is the  $3N \times 3N$  diagonal matrix of atomic masses and  $\mathbf{Q}_v(j)$  is the  $3N$  dimensional vector describing the  $v$  normal coordinate of the  $j$  state in terms of mass weighted Cartesian coordinates.

From preliminary calculations carried out in vacuo it was verified that frequency changes upon excitation are not relevant and that a mirror image is retained between the absorption and emission vibronic structures. For this reason and because of the number of solvents investigated, vibronic progressions were simulated always using ground state frequencies. While this approach is approximate, and less rigorous than that discussed in recent work[7-15], it is justified by the minor changes upon excitation, computed for the active frequencies.

For each normal mode  $v$ , the Franck-Condon factor  $FC$  for a transition from a vibrational level  $m$  (of the electronic state  $i$ ) to the vibrational level  $n$  (of the electronic state  $j$ ) is [16]:

$$FC_v(m, n)^2 = e^{-S_v} S_v^{n-m} \frac{m!}{n!} \left( L_m^{(n-m)}(S_v) \right)^2 \quad (\text{S3})$$

where  $L$  is a Laguerre polynomial. The intensity  $I_v(m, n)$  of the  $m$  to  $n$  transition for the normal mode  $v$  is the  $FC$  factor, weighted for the population of the  $m$  vibrational state:

$$I_v(m, n) = FC_v(m, n)^2 \frac{\exp\left(\frac{-m\hbar\omega_v}{k_B T}\right)}{Z} \quad (\text{S4})$$

with  $k_B$  the Boltzmann constant,  $T$  the temperature and  $Z$  the partition function. The total intensity of the multimode vibrational transition, including all the active normal modes, is the simple product of the monodimensional intensities [17].

Absorption and emission spectra were simulated at  $T=300\text{K}$ . A Gaussian broadening function,  $\text{hwhm}=0.4\text{ eV}$  was superimposed to each computed intensity.

**Table S1.** Ground and lowest excited state dipole moment (Debye) of **TBT**, **TPT** and **TTzT** from CAM-B3LYP/6-31G\* level of theory in vacuo and solvent described with the PCM model.

	$\mu[S_0(tt)]$	$\mu[S_0(cc)]$	$\mu[S_1(tt)]$	$\mu[S_1(cc)]$
<b>TBT</b>				
Vacuo	0.0281	2.1689	3.3994	5.3437
CHex	0.0429	2.5552	3.6654	5.6411
CHCl <sub>3</sub>	0.0783	2.9287	3.9021	6.2303
THF	0.0962	3.0394	3.9885	6.4540
DCM	0.1023	3.1203	4.0162	6.5240
EtOH	0.1267	3.2513	4.1135	6.7788
ACN	0.1309	3.3183	4.1316	6.8246
DMF	0.1316	3.2855	4.1333	6.8308
DMSO	0.1336	3.3362	4.1417	6.8511
<b>TPT<sup>a</sup></b>				
Vacuo	0.4903	1.4078	3.3984	1.9335
CHex	0.6065	1.6082	3.7537	1.9739
CHCl <sub>3</sub>	0.7654	1.7690	4.0965	1.9672
THF	0.8342	1.8214	4.2261	1.9578
DCM	0.8578	1.8375	4.2683	1.9542
EtOH	0.9450	1.8905	4.4176	1.9317
ACN	0.9630	1.8998	4.4436	1.9284
DMF	0.9647	1.9007	4.4463	1.9281
DMSO	0.9726	1.9049	4.4594	1.9266
<b>TTzT</b>				
Vacuo	1.9903	0.0196	4.9552	3.3138
CHex	2.2952	0.0314	5.5820	3.6374
CHCl <sub>3</sub>	2.6137	0.0330	6.1568	3.8905
THF	2.7379	0.0295	6.3664	3.9734
DCM	2.7785	0.0280	6.4338	3.9991
EtOH	2.9232	0.0209	6.6682	4.0849
ACN	2.9505	0.0193	6.7118	4.1003
DMF	2.9532	0.0192	6.7160	4.1018
DMSO	2.9658	0.0184	6.7361	4.1088

<sup>a</sup> Note that for the *cc* conformer of **TPT** the ground and excited dipole moment has similar magnitude but opposite direction.

**Table S2.** Lowest four excited states of **TBT**, **TPT** and **TTzT** computed in vacuo at TD-CAM-B3LYP/6-31G\* level of theory: excitation energies (*Exc*), oscillator strength (*f*), wavefunction (*wf*, indicating coefficients and orbitals involved in the excitation).

	<i>Exc</i> / eV	<i>Exc</i> / nm	<i>f</i>	<i>wf</i> .		<i>Exc</i> / eV	<i>Exc</i> / nm	<i>f</i>	<i>wf</i>
<b>tt-TBT</b>					<b>cc-TBT</b>				
S1	2.97	418	0.429	H→L 0.70	S1	3.04	407	0.438	H→L 0.70
S2	4.40	282	0.040	H-1→L 0.62	S2	4.38	283	0.009	H-1→L 0.62
S3	4.52	274	0.434	H→L+1 0.65	S3	4.54	273	0.013	H-2→L 0.50
S4	4.53	274	0.045	H-4→L 0.44 H-2→L -0.37	S4	4.62	268	0.386	H→L+1 0.60 H-4→L 0.31
S5	4.74	262	0.083	H-3→L 0.65 H→L+1 -0.21	S5	4.62	268	0.104	H-4→L 0.50 H-6→L -0.29
<b>tt-TPT</b>					<b>cc-TPT</b>				
S1	2.55	486	0.352	H→L 0.70	S1	2.55	486	0.330	H→L 0.70
S2	3.54	350	0.002	H-4→L 0.66	S2	3.54	351	0.003	H-4→L 0.66
S3	4.20	295	0.424	H→L+1 0.68	S3	4.14	300	0.407	H→L+1 0.68
S4	4.30	288	0.071	H-5→L 0.31 H-2→L 0.23 H-1→L 0.56	S4	4.31	288	0.057	H-2→L 0.42 H-5→L -0.36 H-1→L -0.32
S5	4.40	282	0.004	H→L+2 0.39 H-1→L -0.38 H-5→L 0.35	S5	4.39	282	0.078	H-1→L 0.59 H→L+2 -0.29 H-2→L 0.15
<b>tt-TTzT</b>					<b>cc-TTzT</b>				
S1	2.08	597	0.315	H→L 0.70	S1	2.07	599	0.296	H→L 0.70
S2	4.00	310	0.499	H→L+1 0.69	S2	3.93	315	0.463	H→L+1 0.68
S3	4.04	307	0.049	H-1→L 0.68	S3	4.02	309	0.000	H→L+2 0.69
S4	4.24	292	0.004	H-2→L 0.66	S4	4.07	305	0.083	H-1→L 0.65
S5	4.30	288	0.002	H-3→L 0.70	S5	4.27	291	0.006	H-2→L 0.62



**Table S3.** Frontier orbital energies,  $E(HOMO)$  and  $E(LUMO)$ , and their energy gap,  $\Delta E(H-L)$ , of **TBT**, **TPT** and **TTzT** computed at the CAM-B3LYP/6-31G\* optimized ground state structures in vacuo and in solvent described with the PCM model.

	$E(HOMO) /$ $eV$	$E(LUMO) /$ $eV$	$\Delta E(H-L)$ $/ eV$	$E(HOMO) /$ $eV$	$E(LUMO) /$ $eV$	$\Delta E(H-L)$ $/ eV$
<b>tt-TBT</b>			<b>cc-TBT</b>			
Vacuo	-6.65	-1.50	5.15	-6.66	-1.44	5.23
CHex	-6.68	-1.51	5.17	-6.70	-1.47	5.23
CHCl <sub>3</sub>	-6.71	-1.53	5.18	-6.73	-1.50	5.24
THF	-6.72	-1.54	5.18	-6.75	-1.50	5.25
DCM	-6.73	-1.55	5.18	-6.75	-1.52	5.24
EtOH	-6.74	-1.56	5.19	-6.78	-1.52	5.25
ACN	-6.75	-1.56	5.19	-6.78	-1.54	5.24
DMF	-6.75	-1.56	5.19	-6.78	-1.53	5.25
DMSO	-6.75	-1.56	5.19	-6.78	-1.54	5.24
<b>tt-TPT</b>			<b>cc-TPT</b>			
Vacuo	-6.24	-1.52	4.73	-6.25	-1.51	4.74
CHex	-6.29	-1.55	4.74	-6.29	-1.54	4.75
CHCl <sub>3</sub>	-6.34	-1.59	4.75	-6.34	-1.57	4.77
THF	-6.35	-1.60	4.75	-6.36	-1.59	4.77
DCM	-6.36	-1.61	4.75	-6.36	-1.59	4.77
EtOH	-6.38	-1.63	4.75	-6.38	-1.61	4.78
ACN	-6.39	-1.63	4.76	-6.39	-1.61	4.78
DMF	-6.39	-1.63	4.76	-6.39	-1.61	4.78
DMSO	-6.39	-1.63	4.76	-6.39	-1.61	4.78
<b>tt-TTzT</b>			<b>cc-TTzT</b>			
Vacuo	-6.09	-2.00	4.09	-6.10	-1.99	4.11
CHex	-6.12	-2.02	4.10	-6.12	-2.01	4.12
CHCl <sub>3</sub>	-6.15	-2.05	4.11	-6.15	-2.03	4.13
THF	-6.17	-2.06	4.11	-6.17	-2.04	4.13
DCM	-6.17	-2.06	4.11	-6.17	-2.04	4.13
EtOH	-6.19	-2.07	4.11	-6.19	-2.05	4.14
ACN	-6.19	-2.08	4.11	-6.19	-2.05	4.14
DMF	-6.19	-2.08	4.11	-6.19	-2.05	4.14
DMSO	-6.19	-2.08	4.11	-6.19	-2.05	4.14

**Table S4.** Experimental (*exp.*) and computed emission energies for the three dyes investigated; the computed emission energies were determined at the excited state geometry with State Specific (*SS*) or Linear response (*LR*) method. Solvent described with PCM model.

	<i>Emiss. SS (eV)</i>	<i>Emiss. LR (eV)</i>	<i>exp. (eV)</i>
<b>tt-TBT</b>			
CHex	2.22	2.26	2.31
CHCl <sub>3</sub>	2.07	2.18	2.13
THF	2.01	2.16	2.18
DCM	1.99	2.15	2.15
EtOH	1.92	2.12	2.11
ACN	1.91	2.12	2.09
DMF	1.91	2.12	2.11
DMSO	1.91	2.11	2.07
<b>tt-TPT</b>			
CHex	1.83	1.82	1.93
CHCl <sub>3</sub>	1.69	1.75	1.77
THF	1.70	1.72	1.81
DCM	1.69	1.72	1.78
EtOH	1.65	1.69	1.77
ACN	1.64	1.68	1.78
DMF	1.65	1.68	1.77
DMSO	1.64	1.68	1.76
<b>tt-TTzT</b>			
CHex	1.46	1.47	1.65
CHCl <sub>3</sub>	1.33	1.39	1.52
THF	1.28	1.36	1.53
DCM	1.27	1.35	1.50
EtOH	1.21	1.32	1.51
ACN	1.19	1.32	1.49
DMF	1.20	1.32	1.50
DMSO	1.19	1.32	1.46

**Table S5.** Total calculated Stokes Shift (*Stokes Shift tot.*), along with its vibronic component (*Stokes Shift vibr.*) and electronic component (*Stokes Shift el.*) computed with Linear Response (*Stokes Shift el.-LR*) and State Specific (*Stokes Shift el.-SS*) formalism for the three dyes investigated; calculations carried out with CAM-B3LYP/6-31G\* level of theory in vacuo and solvents described with the PCM model. Computed results to be compared with experimental (*exp.*) Stokes Shift.

	<i>Stokes Shift / eV</i>					<i>exp.</i> <sup>d</sup>
	<i>vibr.</i> <sup>a</sup>	<i>el - SS</i>	<i>el - LR</i>	<i>tot - SS</i> <sup>b</sup>	<i>tot - LR</i> <sup>c</sup>	
<b>tt-TBT</b>						
CHex	0.488	0.035	-0.001	0.523	0.487	0.467
CHCl <sub>3</sub>	0.485	0.185	0.069	0.670	0.554	0.650
THF	0.484	0.251	0.101	0.735	0.585	0.601
DCM	0.484	0.266	0.107	0.750	0.591	0.637
EtOH	0.483	0.345	0.143	0.828	0.626	0.665
ACN	0.483	0.361	0.151	0.844	0.634	0.731
DMF	0.483	0.340	0.137	0.823	0.620	0.653
DMSO	0.483	0.349	0.142	0.832	0.625	0.676
<b>tt-TPT</b>						
<u>CHex</u>	0.483	-0.014	-0.001	0.469	0.482	0.384
CHCl <sub>3</sub>	0.477	0.077	0.070	0.554	0.547	0.557
THF	0.476	0.121	0.101	0.597	0.577	0.536
DCM	0.476	0.128	0.106	0.604	0.582	0.560
EtOH	0.475	0.182	0.144	0.657	0.619	0.592
ACN	0.476	0.193	0.152	0.669	0.628	0.613
DMF	0.476	0.175	0.138	0.651	0.614	0.589
DMSO	0.476	0.181	0.142	0.657	0.618	0.576
<b>tt-TTzT</b>						
<u>CHex</u>	0.422	0.010	-0.001	0.432	0.421	0.337
CHCl <sub>3</sub>	0.423	0.134	0.074	0.557	0.497	0.469
THF	0.425	0.190	0.108	0.615	0.533	0.471
DCM	0.432	0.201	0.113	0.633	0.545	0.502
EtOH	0.431	0.270	0.153	0.701	0.584	0.500
ACN	0.432	0.285	0.161	0.717	0.593	0.544
DMF	0.432	0.265	0.147	0.697	0.579	0.505
DMSO	0.432	0.273	0.152	0.705	0.584	0.541

<sup>a</sup> Estimated from the energy difference between the maxima of absorption and emission simulated spectra (T=300K, gaussian broadening function, hwhm=0.4 eV). <sup>b</sup> Computed as the sum of *vibr.* and *el.-SS* contribution. <sup>c</sup> Computed as the sum of *vibr.* and *el.-LR* contribution. <sup>d</sup> Estimated from the energy difference between the maxima of absorption and emission experimental spectra.

**Table S6.** Computed optical properties of the first four excited states of **TBT**, **TPT** and **TTzT** (*tt* and *cc* conformers) computed in vacuo at TD CAM-B3LYP/6-31G\* level of theory: excitation energies *Exc*, oscillator strength *f* and two photon cross section  $\sigma$ .

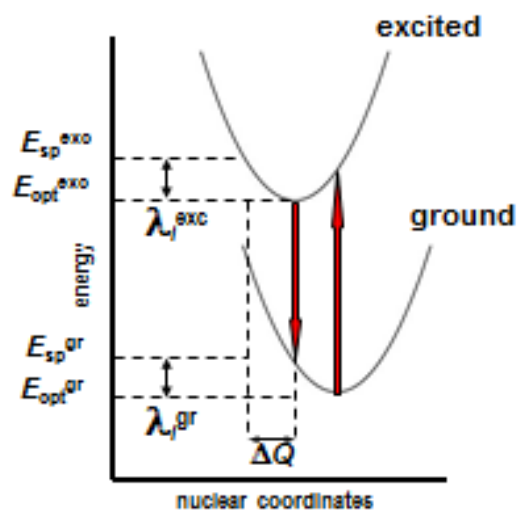
		<i>Exc</i> / eV	<i>Exc</i> / nm	<i>f</i>	$\sigma$ / GM			<i>Exc</i> / eV	<i>Exc</i> / nm	<i>f</i>	$\sigma$ / GM
<b>tt-TBT</b>						<b>cc-TBT</b>					
	S1	2.97	418	0.429	3		S1	3.04	407	0.438	2
	S2	4.40	282	0.040	528		S2	4.38	283	0.009	419
	S3	4.52	274	0.434	20		S3	4.54	273	0.013	232
	S4	4.53	274	0.045	262		S4	4.62	268	0.386	20
	S5	4.74	262	0.083	15		S5	4.62	268	0.104	17
<b>tt-TPT</b>						<b>cc-TPT</b>					
	S1	2.55	486	0.352	2		S1	2.55	486	0.330	3
	S2	3.54	350	0.002	0.03		S2	3.54	351	0.003	0.004
	S3	4.20	295	0.424	78		S3	4.14	300	0.407	72
	S4	4.30	288	0.071	851		S4	4.31	288	0.057	440
	S5	4.40	282	0.004	51		S5	4.39	282	0.078	400
<b>tt-TTzT</b>						<b>cc-TTzT</b>					
	S1	2.08	597	0.315	3		S1	2.07	599	0.296	3
	S2	4.00	310	0.499	2820		S2	3.93	315	0.463	1330
	S3	4.04	307	0.049	$5.27 \cdot 10^5$		S3	4.02	309	0.000	0.002
	S4	4.24	292	0.004	$1.20 \cdot 10^5$		S4	4.07	305	0.083	$2.47 \cdot 10^6$
	S5	4.30	288	0.002	19		S5	4.27	291	0.006	5260

**Table S7.** Dipole moments and transition dipole moments (atomic units) components ( $x, y, z$ ) related to the excited states involved in the sum over state (SOS) interpretation of 2P intensities: initial ground state  $0$ , final state  $f$  and intermediate state  $p=l$ .

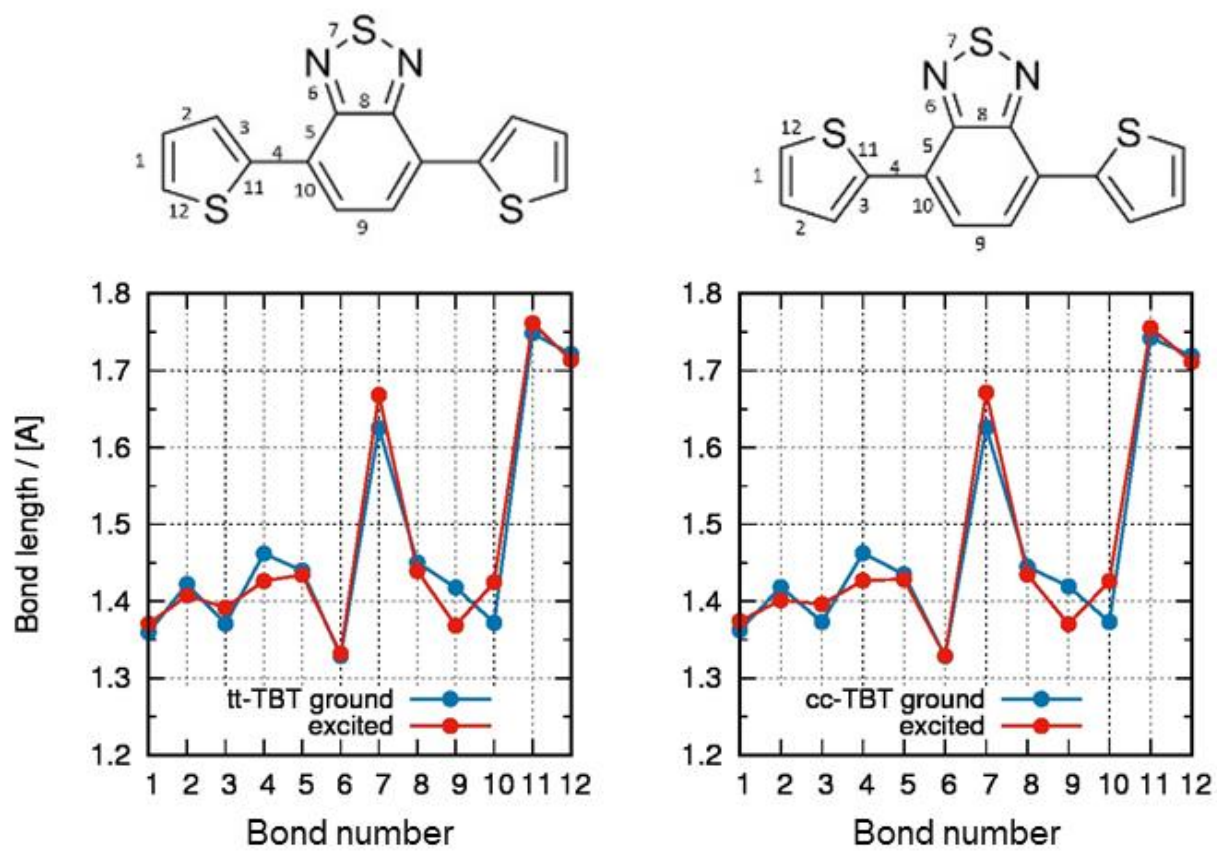
final state $f$		$\mu_{00}$	$\mu_{ff}$	$\mu_{0f}^{trs}$	$\mu_{0p}^{trs}$	$\mu_{pf}^{trs}$
<b>tt-TBT</b>						
S2	$x$	0.0000	-0.0002	0.0000	-2.4291	2.5174
	$y$	-0.0110	0.9283	-0.6067	0.0000	0.0000
	$z$	0.0009	-0.0014	0.0002	0.0001	-0.0002
S3	$x$	0.0000	-0.0002	-1.9788	-2.4291	0.0004
	$y$	-0.0110	0.8559	-0.0001	0.0000	1.0048
	$z$	0.0009	-0.0016	-0.0009	0.0001	-0.0009
S4	$x$	0.0000	0.0002	0.0003	-2.4291	1.4212
	$y$	-0.0110	0.3820	-0.6342	0.0000	-0.0003
	$z$	0.0009	-0.0011	0.0011	0.0001	0.0001
<b>tt-TPT</b>						
S2	$x$	0.0000	0.0000	-0.1599	0.0000	0.0000
	$y$	0.0000	0.0000	0.0003	2.3726	0.0000
	$z$	0.1929	0.4253	0.0000	0.0000	0.0002
S3	$x$	0.0000	0.0000	0.0000	0.0000	0.0000
	$y$	0.0000	-0.0002	-2.0286	2.3726	-0.0004
	$z$	0.1929	-1.0462	0.0000	0.0000	-1.1613
S4	$x$	0.0000	0.0000	0.0000	0.0000	-0.0001
	$y$	0.0000	0.0000	0.0000	2.3726	1.6244
	$z$	0.1929	-0.8804	-0.8197	0.0000	0.0000
<b>tt-TTzT</b>						
S2	$x$	0.0000	0.0000	0.0000	0.0000	0.0000
	$y$	0.0000	-0.0002	-2.2566	-2.4910	0.0018
	$z$	-0.7831	1.4368	0.0000	0.0000	-1.0705
S3	$x$	0.0000	0.0000	0.0000	0.0000	0.0000
	$y$	0.0000	-0.0002	0.0000	-2.4910	6.1297
	$z$	-0.7831	1.8591	-0.7044	0.0000	0.0001
S4	$x$	0.0000	0.0000	0.0000	0.0000	0.0001
	$y$	0.0000	-0.0001	0.0000	-2.4910	2.3210
	$z$	-0.7831	1.7695	-0.1916	0.0000	0.0000

**Table S8.** Computed 2P transition probability  $\delta$ , along with its components  $\delta_F$  e  $\delta_G$ , obtained from response theory (RT) and sum over states (SOS) approaches. For the latter two schemes are compared: the first including one intermediate state  $p$  ( $p=1$ ) and the second including three intermediate states  $p$  (full width half maximum 0.1 eV).

final state $f$		$\delta_F$ (GM)	$\delta_G$ (GM)	$\delta$ (GM)
<b>tt-TBT</b>				
S2	RT	6070	6260	37200
	SOS( $p=1$ )	6696	6288	38546
	SOS( $p=1,3,4$ )	7099	6433	39931
<b>tt-TPT</b>				
S4	RT	10400	10500	62700
	SOS( $p=1$ )	9947	9170	56572
	SOS( $p=1,2,3$ )	11138	10311	63519
<b>tt-TTzT</b>				
S2	RT	0.0000	60000	240000
	SOS( $p=1$ )	0.3434	53917	215668
	SOS( $p=1,3,4$ )	0.3434	54481	217926

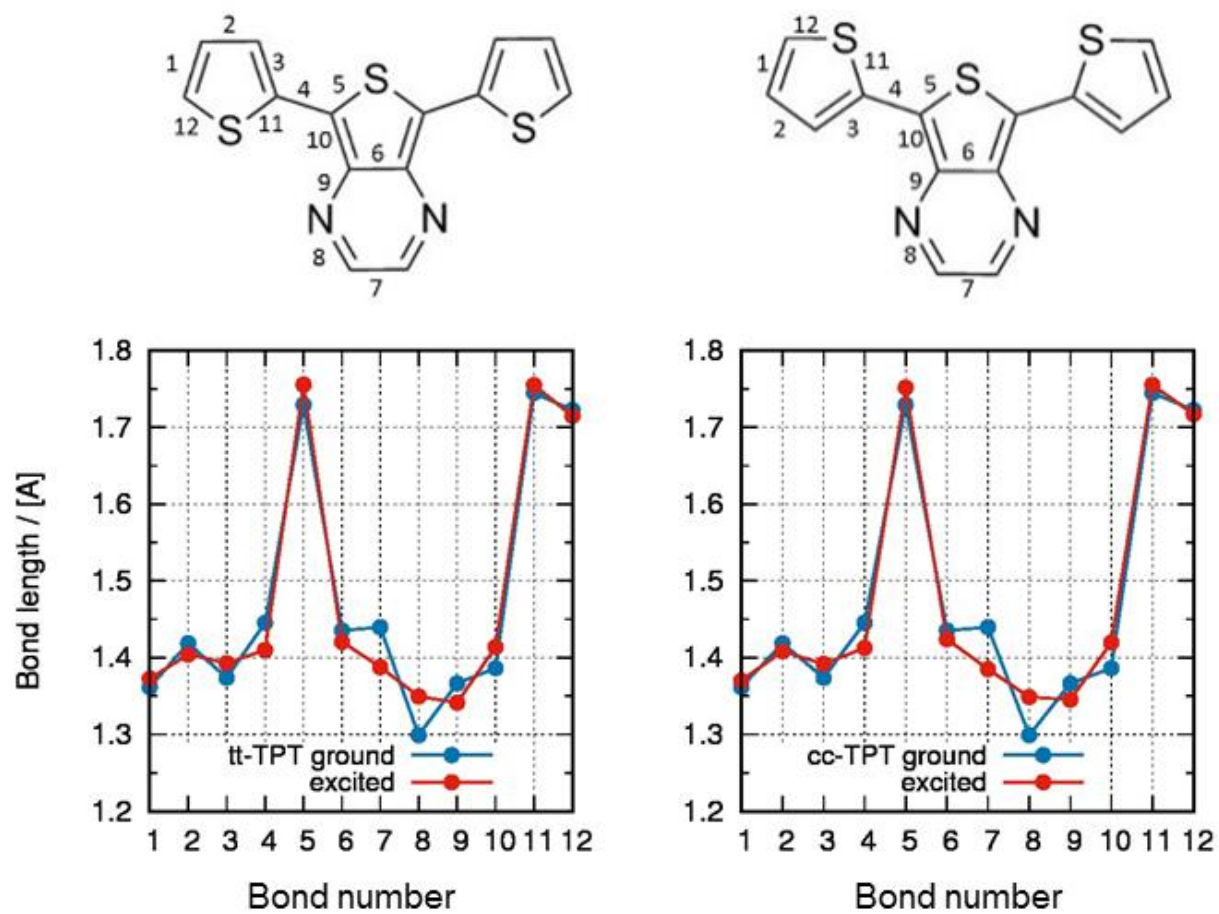


**Figure S1.** Schematic representation of the potential energy curves of ground and excited state of the chromophore and indication of the two contributions to the total internal reorganization energy  $\lambda_i$ . The total reorganization energy is determined as  $\lambda_i = \lambda_i^{gr} + \lambda_i^{exc}$

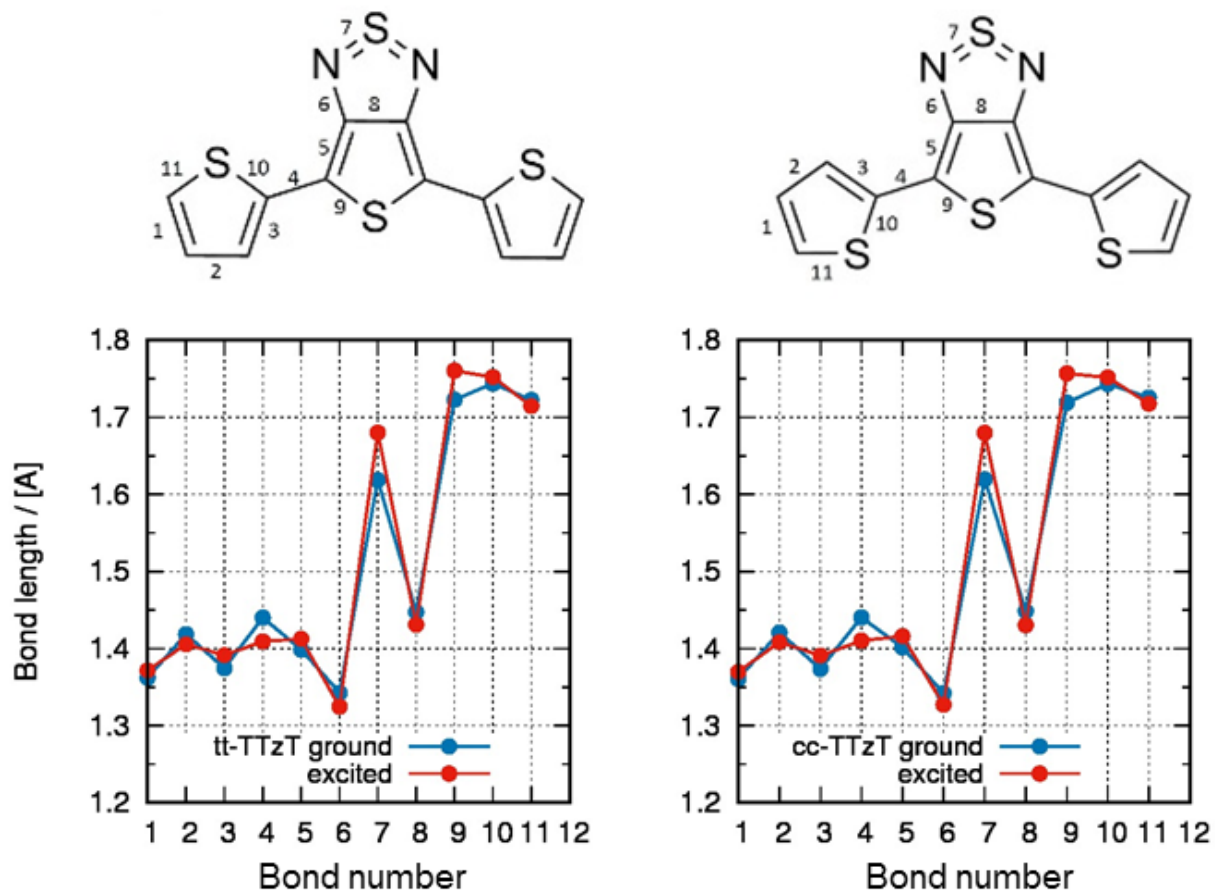


**Figure S2.** Comparison between the geometry of the ground and lowest excited state of the two conformers of **TBT**, computed at TD-CAM-B3LYP/6-31G\* in vacuo.

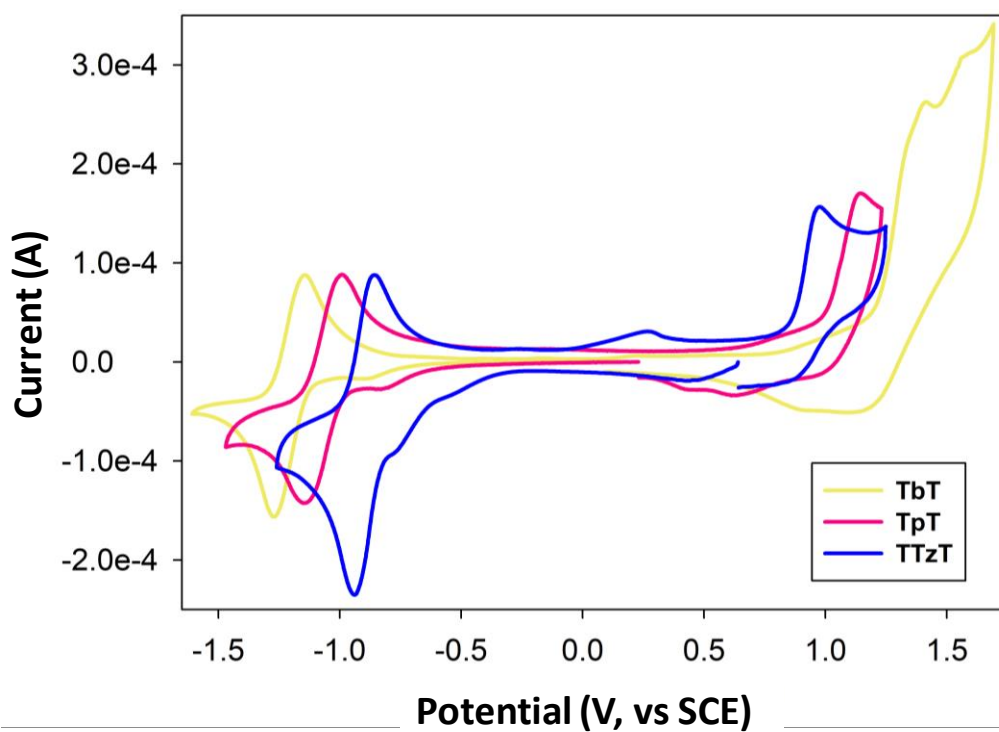




**Figure S3.** Comparison between the geometry of the ground and lowest excited state of the two conformers of TPT, computed at TD-CAM-B3LYP/6-31G\* in vacuo.

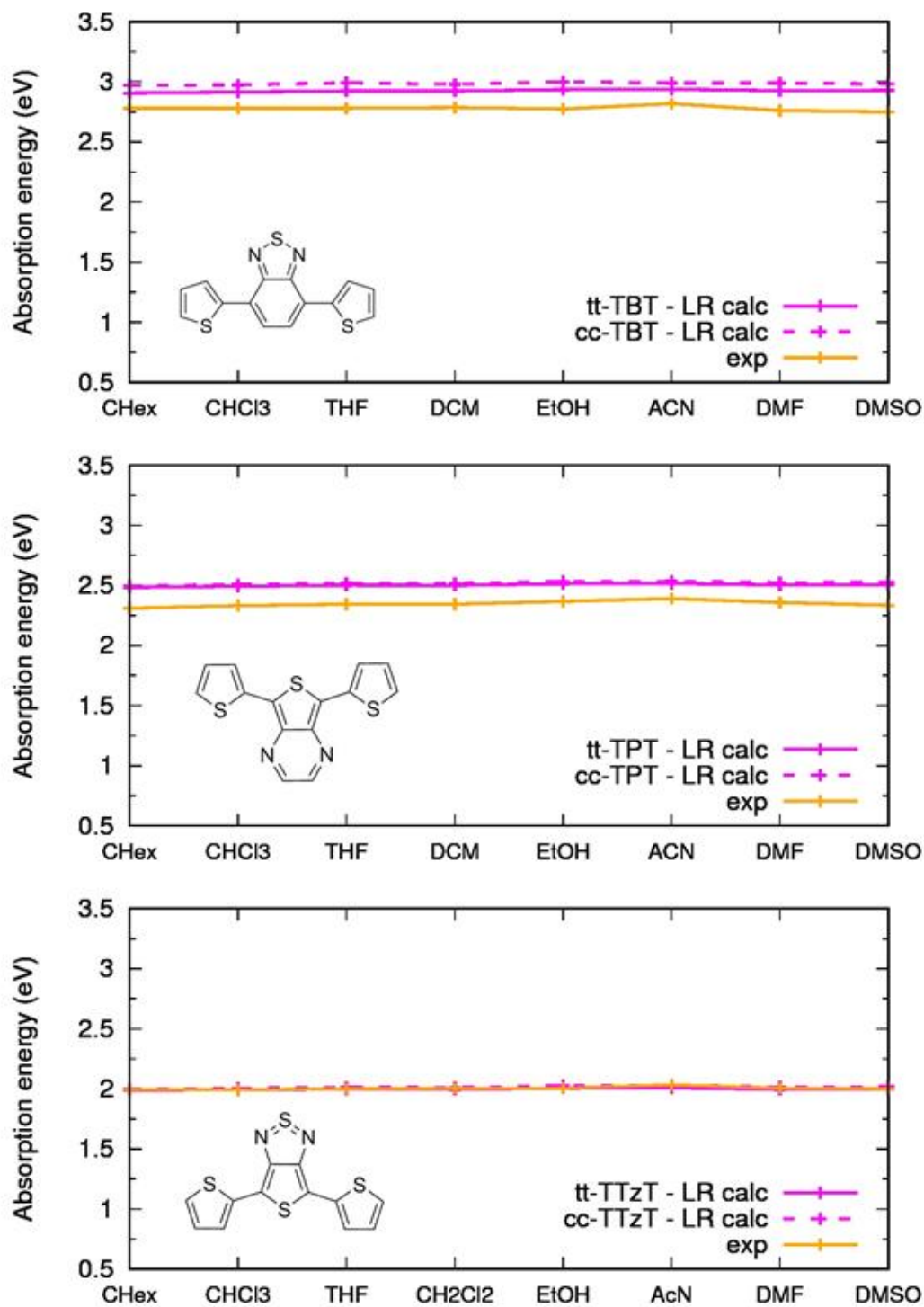


**Figure S4.** Comparison between the geometry of the ground and lowest excited state of the two conformers of TTzT, computed at TD-CAM-B3LYP/6-31G\* in vacuo.

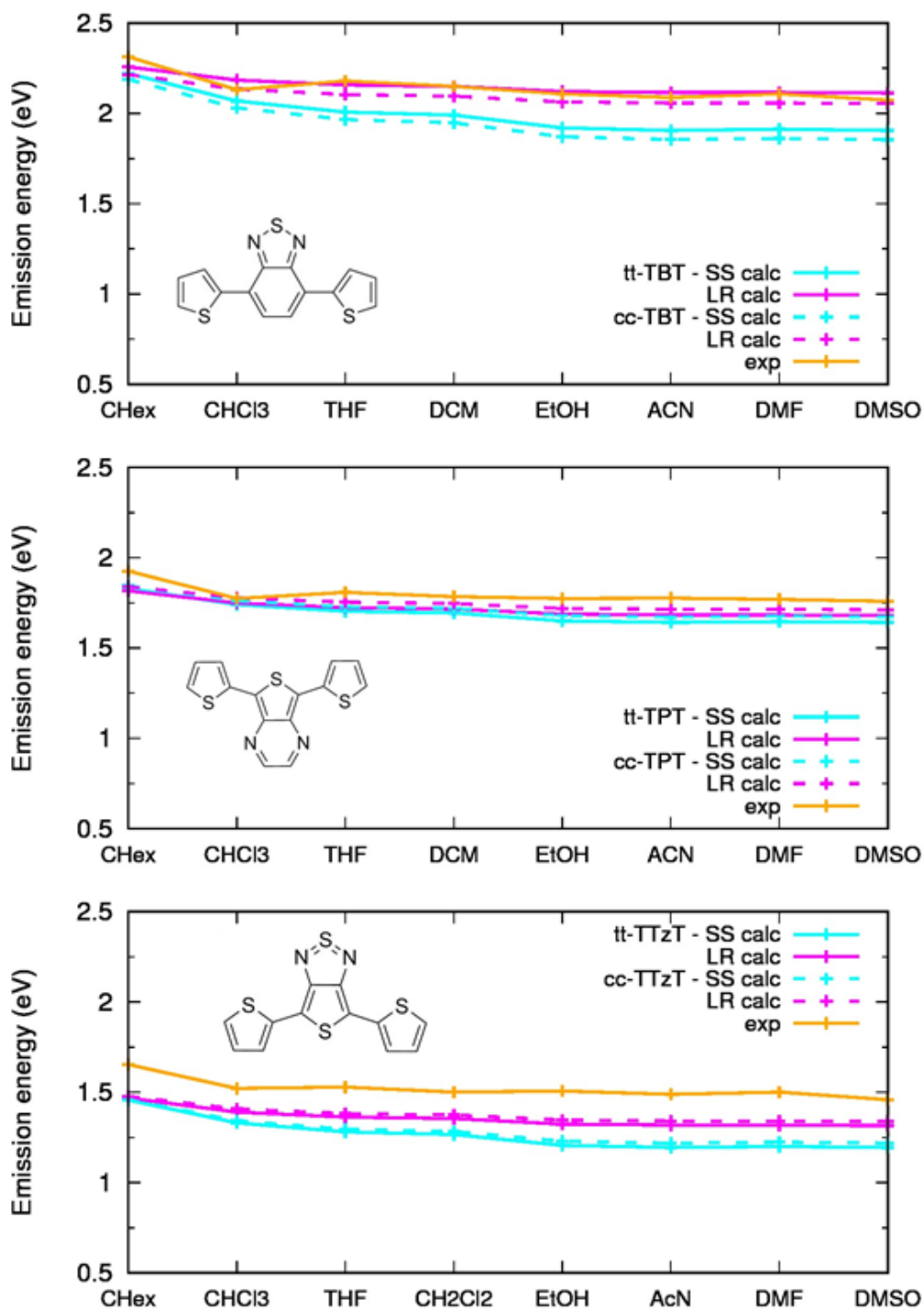


	$\Delta V$ (V)	ox (V, vs SCE)	red (V, vs SCE)
<b>TbT</b>	2.55	1.32	-1.23
<b>TpT</b>	2.21	1.14	-1.07
<b>TTzT</b>	1.95	1.04	-0.91

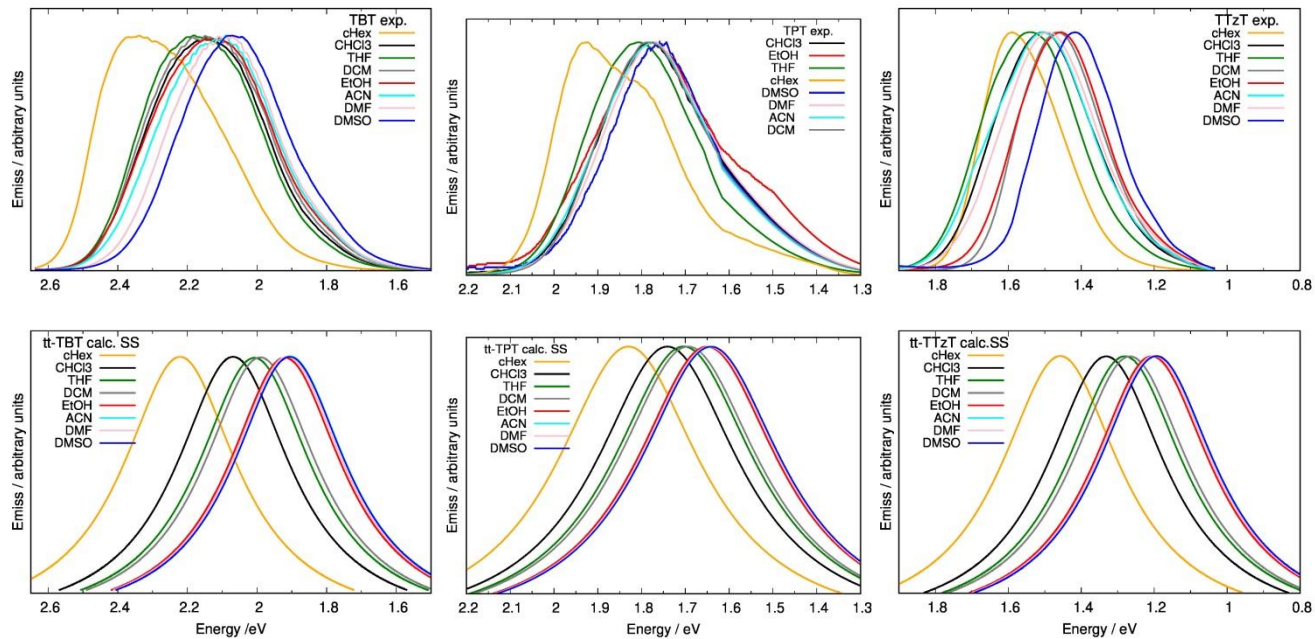
**Figure S5.** Cyclic voltammometry of **TbT** (yellow), **TpT** (red) and **TTzT** (blue) in  $\text{CH}_2\text{Cl}_2$  with  $\text{TBAPF}_6$  as electrolyte. Scan speed 0.1 V/s.



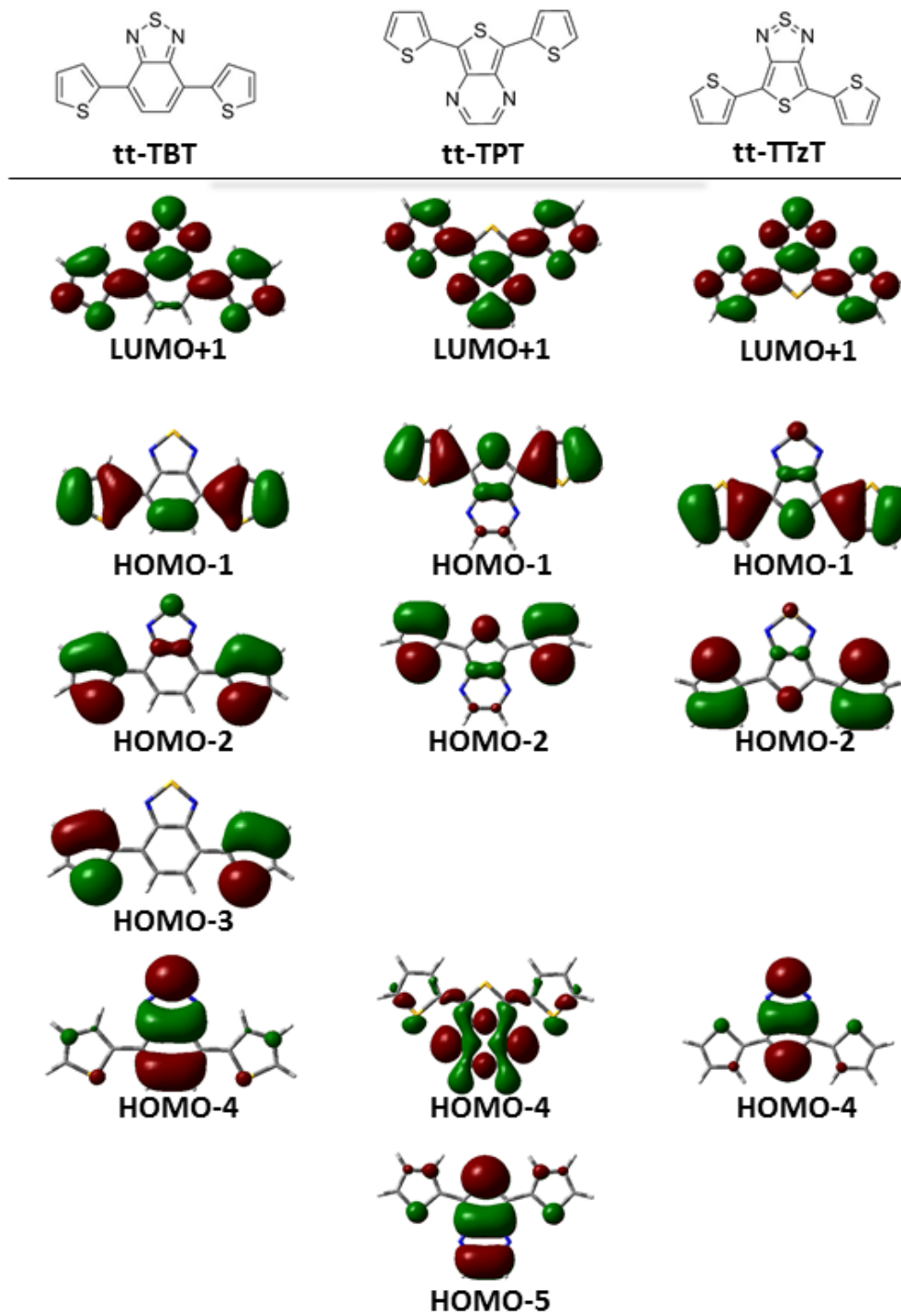
**Figure S6.** Comparison between experimental and computed absorption energies for the lowest energy absorption band, from TD-CAM-B3LYP/6-31G\* vertical excitation energy calculations. Solvent described with the PCM method.



**Figure S7.** Comparison between experimental and computed emission energies from TD-CAM-B3LYP/6-31G\* calculations at the geometry of the lowest excited state determined with the LR approach. Vertical emission energies computed with Linear Response (LR-PCM) and State Specific (SS-PCM) approaches.

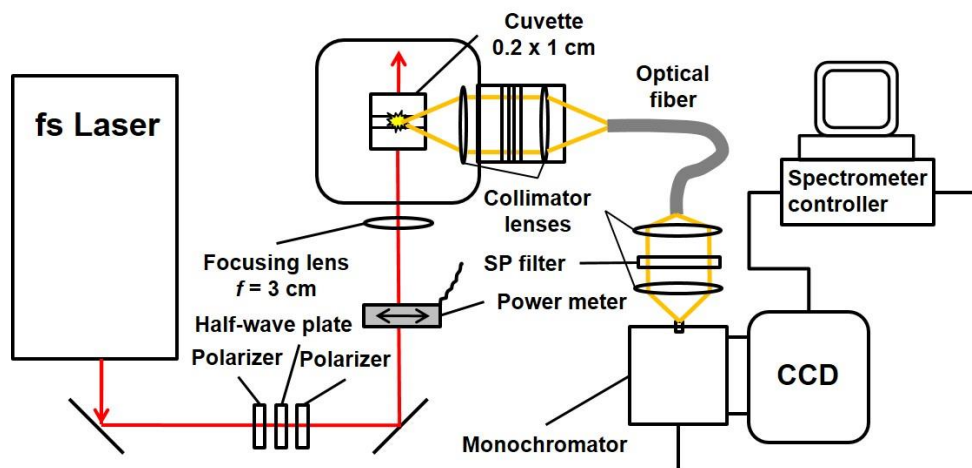


**Figure S8.** Comparison between experimental and computed emission energies from TD-CAM-B3LYP/6-31G\* calculations at the geometry of the lowest excited state determined with the LR approach. Vertical emission energies computed with the State Specific (SS-PCM) method. These figures correspond to those shown in Figs. 4-6 right except that here emission energy is in eV.



**Figure S9.** Molecular orbitals of TBT, TPT and TTzT relevant for the analysis of the lowest excited states from TD-CAM-B3LYP/6-31G\* calculations.

## Experimental apparatus for two-photon absorption spectroscopy



**Fig. S10.** Experimental apparatus for two-photon spectroscopy

The system for 2PA measurements employed in this work was based on a previously described setup [18].

The output of a tunable Ti:Sapphire laser (Chameleon Ultra II, Coherent; 80 MHz rep. rate) was passed through a half-wave plate and a polarizer for power adjustment and focused by a lens ( $f=3$  cm) in the center of a cuvette (2 mm optical path) containing the sample solution. An optical power meter (FieldMaxII-TOP, Coherent) was used to measure the incident power immediately before the cell.

The emission was collected by a convex lens (2.5 cm diameter) placed next to the cell compartment at  $90^\circ$  relative to the direction of the excitation beam and focused by another lens onto a glass fiber. At the other hand of the fiber, the light was collimated by a lens and focused onto the aperture of a monochromator. Short-pass filters were used to prevent the excitation light from reaching the detector.

The emission spectrum dispersed by the monochromator was imaged by a CCD camera (Andor iStar ICCD DH334T-18F-73). The measured signals were corrected to remove the effect of the instrument-response function (see below).

The average excitation power of ca. 50 mW was used in the experiments, i.e. well below the saturation threshold, when the plot of the emission intensity vs power started deviating from being strictly quadratic.

Deuterated solvents were used in all measurements in order to avoid absorption of the excitation light by C-H vibrational overtones [19], which may interfere with 2PA measurements.

## Calculation of two-photon absorption cross-sections



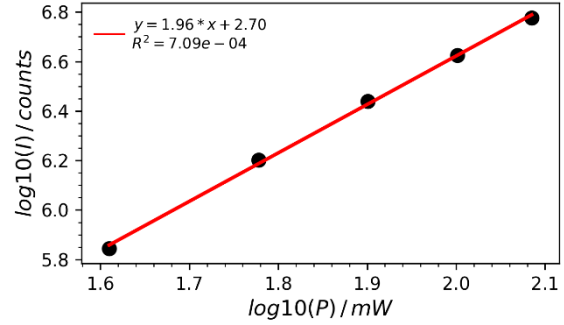
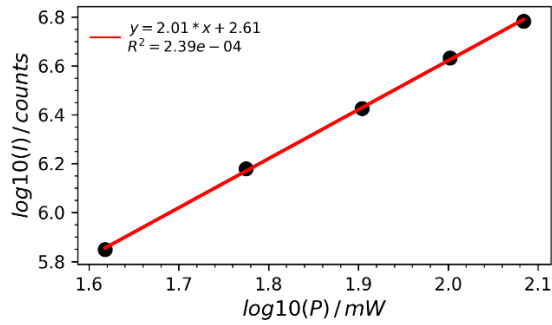
The signals of the solution of a sample and of the reference (Rhodamine B in MeOD), both with known 1P absorbance, were recorded under 1P excitation by a LED ( $\lambda_{\text{max}} = 523 \text{ nm}$ , Ledengin) in the same optical configuration as used in 2PA measurements. The relative sensitivities ( $R_{RS}$  reference/sample) of the setup were then calculated by normalizing the measured emission signals by the relative numbers of the absorbed photons, calculated by integrating the overlap between the absorption spectrum of the solution and the emission spectrum of the LED. The latter was measured using a FS920 spectrofluorometer (Edinburgh Instruments, UK), calibrated using a lamp with NIST-traceable spectral radiant flux (RS-15-50, Gamma Scientific, SN HL1956). Thus determined relative sensitivities  $R_{RS}$  included the effects of different quantum yields, solvent refractive indexes and detection efficiencies with respect to the different emission spectra.

The overall formula used for the calculation of 2PA cross-sections was:

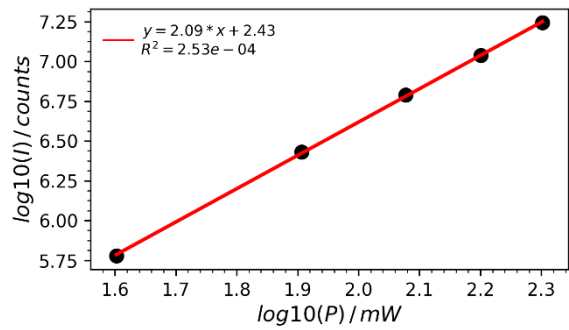
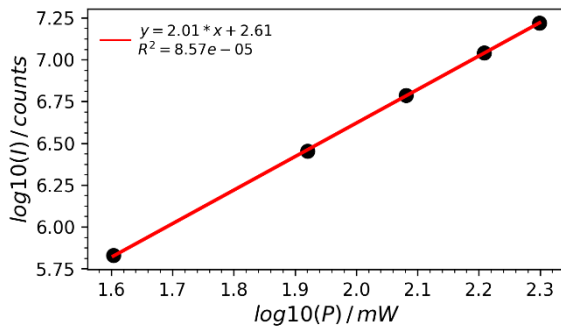
$$\sigma_S^{(2)} = \sigma_R^{(2)} \cdot \frac{I_S}{I_R} \cdot \frac{\Phi_S^2}{\Phi_R^2} \cdot \frac{c_S}{c_R} \cdot R_{RS},$$

where  $\sigma^{(2)}$  is the 2PA cross-section,  $I$  is the measured emission intensity,  $\Phi$  is the excitation photon flux,  $c$  is concentration as calculated from the absorption spectra, and indexes  $S$  and  $R$  refer to the *sample* and *reference*, respectively. The instantaneous excitation flux  $\Phi$  was calculated assuming a rectangular pulse of the duration equal to the FWHM of the actual pulse for each wavelength, as disclosed by the vendor (Coherent).

### 680 nm



### 800 nm



### 900 nm

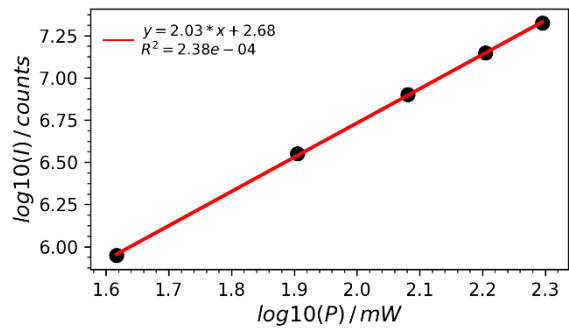
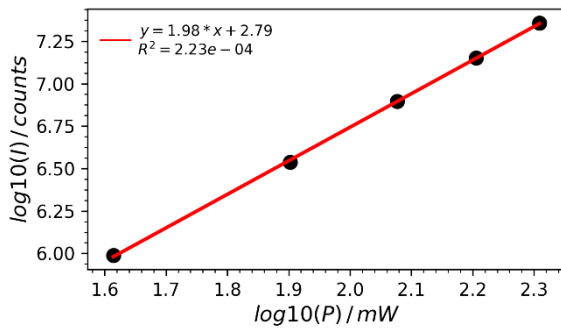
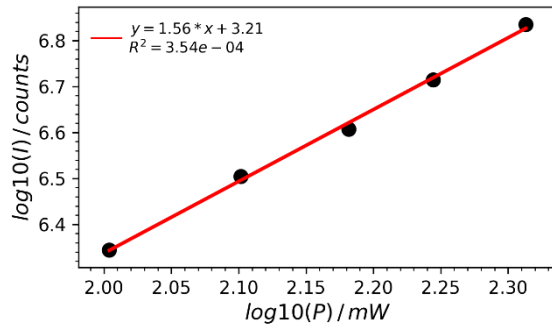
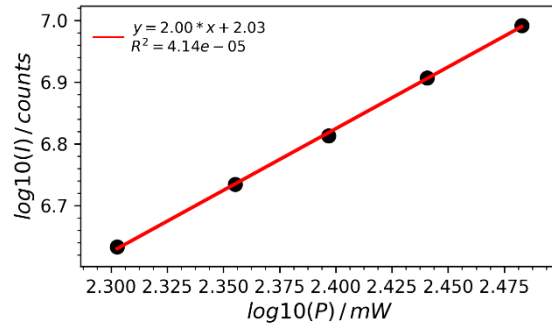
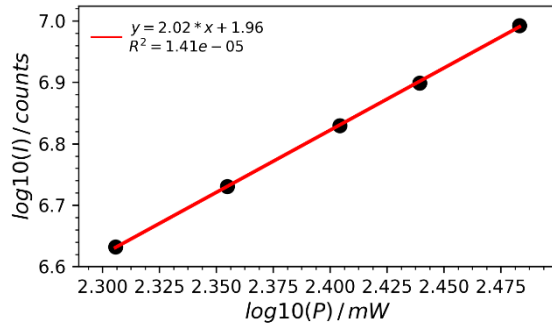


Figure S11. Power dependencies for TBT at different wavelengths.

### 740 nm



### 750 nm



### 800 nm

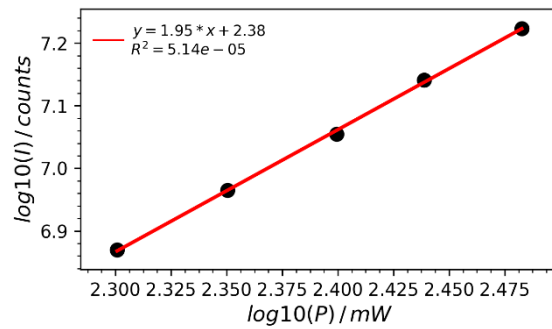
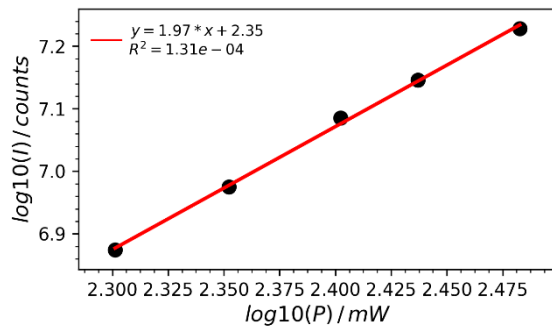


Figure S12. Power dependencies for TPT at different wavelengths.

1020 nm

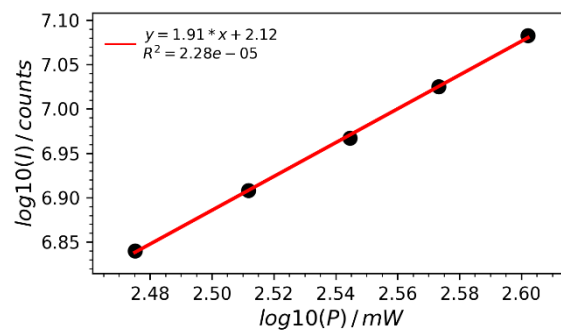
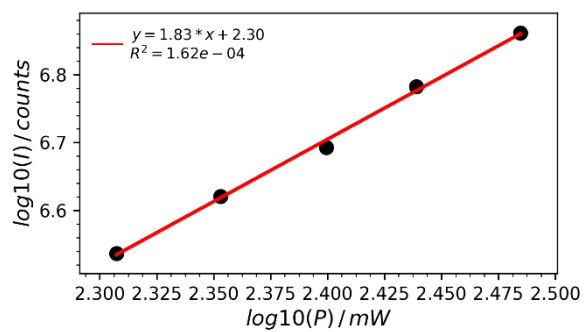
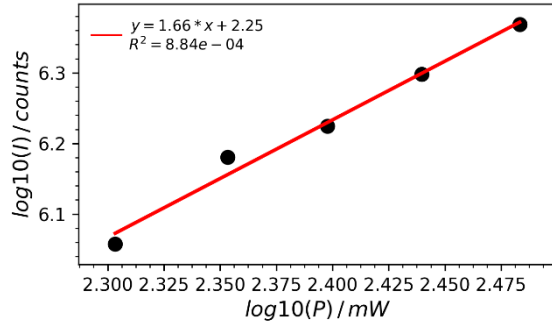
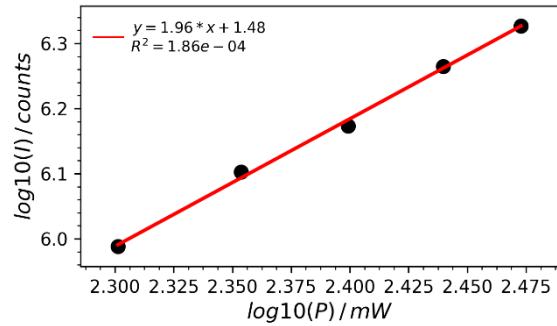
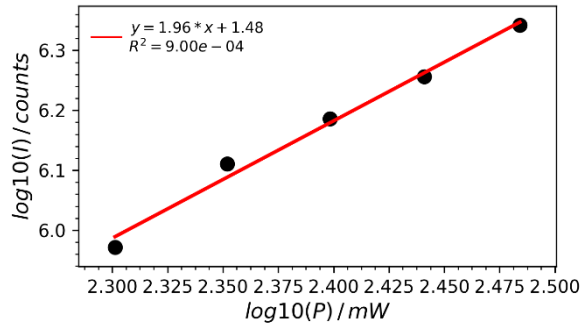


Figure S12. Continued - Power dependencies for TPT at different wavelengths.

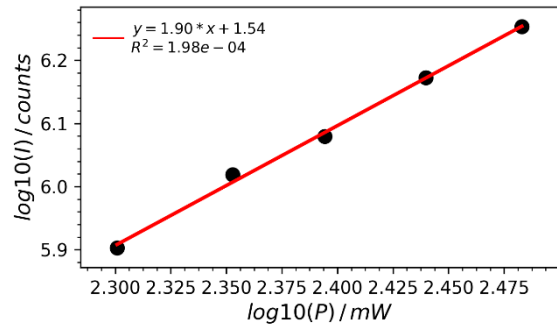
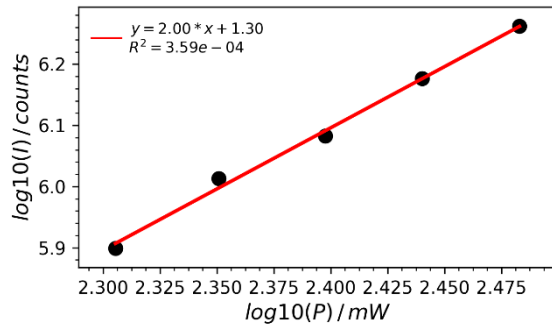
### 930 nm



### 940 nm

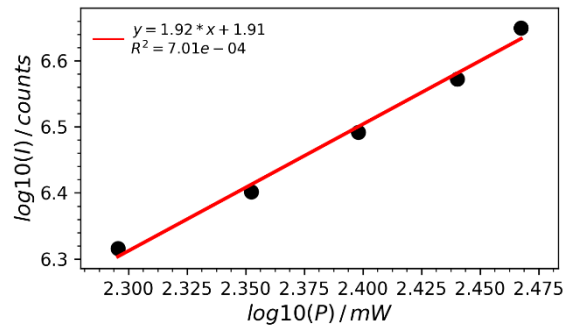
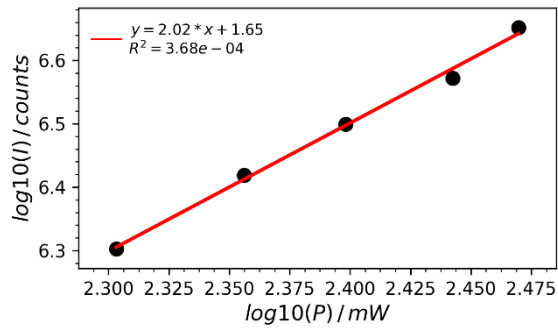


### 960 nm

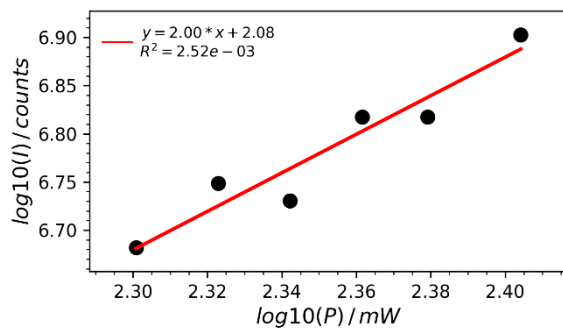


**Figure S13.** Power dependencies for TTzT at different wavelengths.

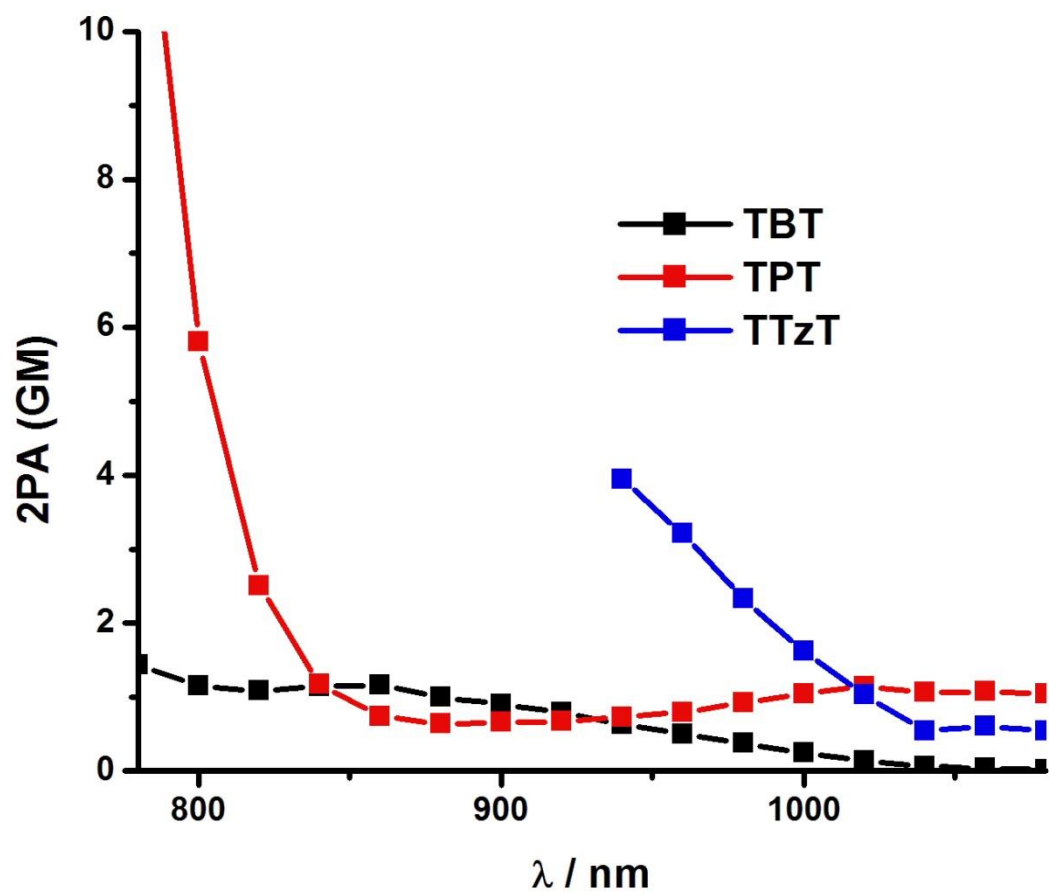
### 1000 nm



### 1080 nm



**Figure S13.** Continued - Power dependencies for TTzT at different wavelengths.



**Figure S14.** 2P absorption of TBT, TPT and TTzT in CDCl<sub>3</sub> showing, in agreement with computed results (see Table S6) the weak cross-section in the region of the S<sub>0</sub>-S<sub>1</sub> transition of TBT and TPT.

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