COVALENTLY COUPLED MULTI-DMABI CHROMOPHORES: SYNTHESIS, LINEAR AND NON-LINEAR OPTICAL PROPERTIES

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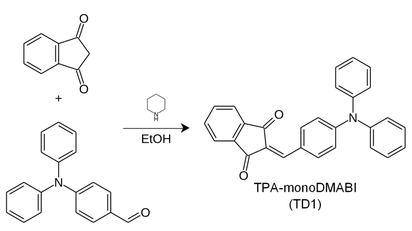
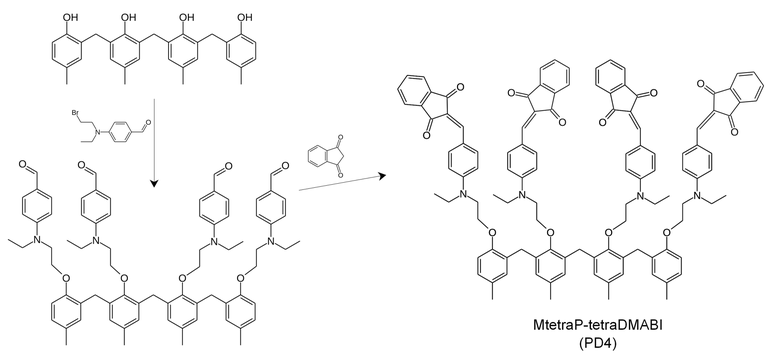
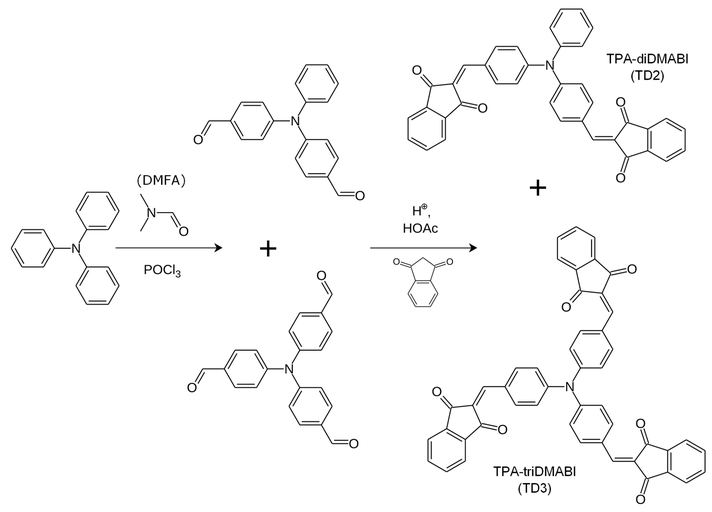
Motivation

Over last two decades there was stable interest in utilizing organic molecular materials in a wide range of non-linear optical (NLO) applications [1]. Inspired by it, our research on possible uses of DMABI chromophore possessing considerably high NLO activity [2] and all optical poling capability [3] has lasted for many years. Unfortunately DMABI also displays high levels of molecular association [4] despite its quite moderate dipole moment, what results in a significant drop of NLO activity. To overcome this, few DMABI chromophores were attached to same moiety to hinder their mutual orientation. Here we present some quantum chemical characteristics, linear and non-linear optical properties of these complex compounds.

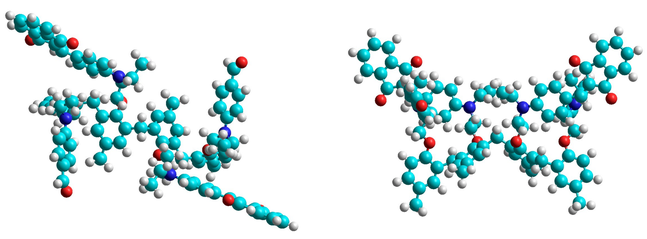
Syntheses



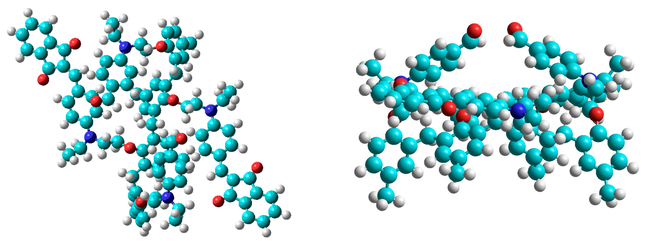




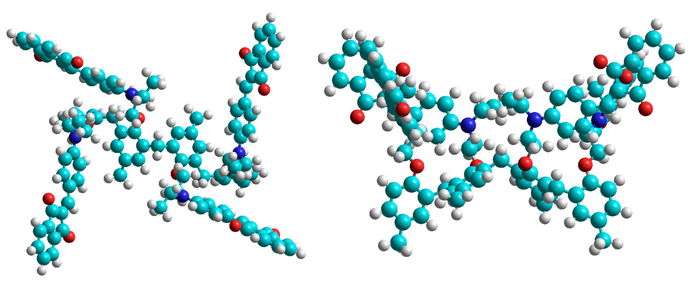
Conformations of PDs by RHF *ab initio*



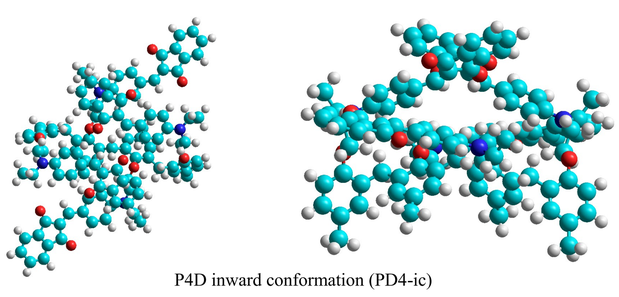
P2D 2,3 isomer outward conformation (PD2-2,3-oc)



P2D 2,3 isomer inward conformation (PD2-2,3-ic)



P4D outward conformation (PD4-oc)



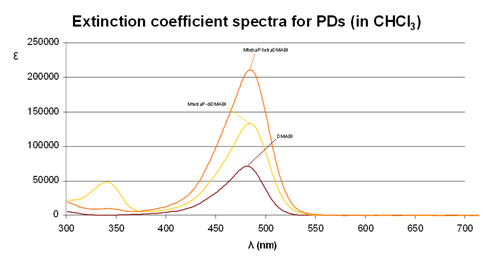
P4D inward conformation (PD4-ic)

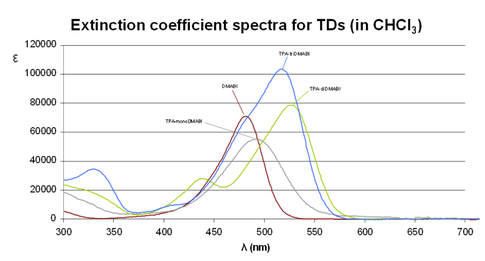
View of conformation from above Side view of conformation

Calculated properties by RHF *ab initio*

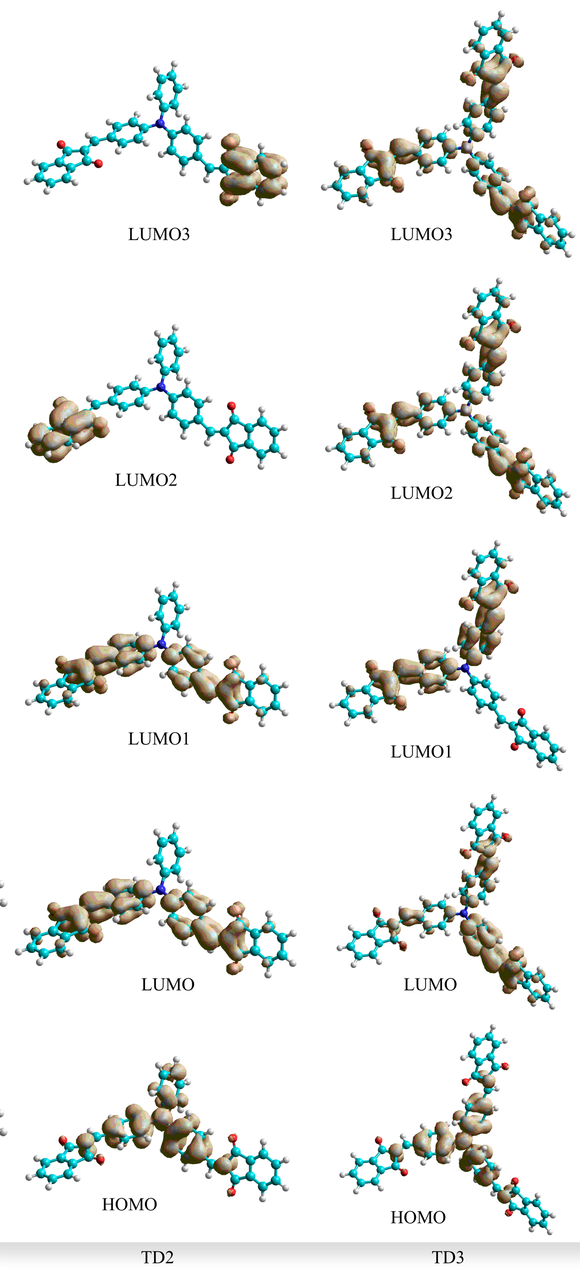
Compound	DR1	DMABI	PD2-2,3-oc	PD2-2,3-ic	PD4-oc	PD4-ic	TD1	TD2	TD3
μ, D	9.1	3.7	2.4	11.1	1.4	6.7	2.5	1.7	1.8
E, kCal/mol	-66428538	-561347.73	-2850085.54	-2850083.95	-3374723.09	-3374723.90	-800451.50	-1133509.25	-1466566.625
HOMO, eV	-7.591	-7.430	-7.625	-7.448	-7.482	-7.148	-7.324	-7.404	-7.471
LUMO, eV	1.050	1.441	1.205	1.372	1.245	1.479	1.279	0.929	0.848
β_{532}^{HRS}	36.0	22.9	26.0	18.2	34.1	34.9	31.3	34.3	37.4
β_0^{HRS}	22.4	14.0	15.5	12.2	19.8	22.0	18.6	19.7	21.5
$\frac{\beta_{532}^{HRS}}{\beta_{532}^{HRS}(\mathrm{DR1})}$	1	0.625	0.692	0.545	0.884	0.982	0.830	0.879	0.960
$\frac{\beta_{532}^{HRS}/N_{ch.}}{\beta_{532}^{HRS}(\mathrm{DMABI})}$	-	1	0.554	0.436	0.354	0.393	1.329	0.704; 0.548*	0.512; 0.398*
$\frac{\beta_0^{HRS}}{\beta_0^{HRS}(\mathrm{DR1})}$	1	0.636	0.722	0.506	0.947	0.969	0.869	0.953	1.039
$\frac{\beta_0^{HRS}/N_{ch.}}{\beta_0^{HRS}(\mathrm{DMABI})}$	-	1	0.568	0.397	0.372	0.381	1.367	0.749; 0.530*	0.544; 0.385*

*relatively to the β of TD1

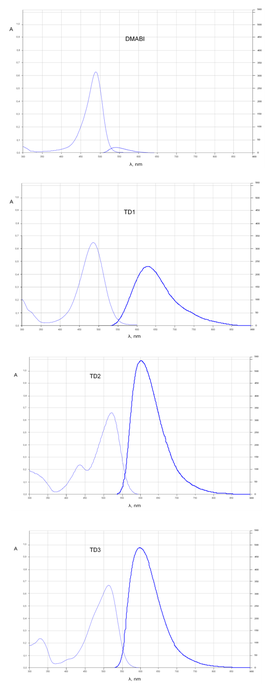




MOs by AM1



Absorbance and luminescence spectra in CH_2Cl_2



Experimental optical data

Compound		DR1	DMABI	PD2	PD4	TD1	TD2	TD3
Absorbance maximum	in $CHCl_3$	479	482	484; 342	485	492	527; 439	518; 330
	in CH_2Cl_2	n/a	489	n/a	n/a	486	521; 436	514; 329
Extinction coefficient	in $CHCl_3$	32 695	70 115	133 398; 48 125	211 283	55 263	78 758; 27 937	103 537; 34 614
	in CH_2Cl_2	n/a	79 655	n/a	n/a	53 366	78 596; 28 234	87 629; 30 808
Luminescence maximum		n/a	541	n/a	n/a	630	602	597
Luminescence intensity		n/a	22	n/a	n/a	105	545	488
β_{532}^{HRS}		805.6	980.5	2471.5	3194.7	1700.5	4036.7	5636.5
β_0^{HRS}		105.5	139.6	330.7	427.4	188.6	68.4	255.4
$\frac{\beta_{532}^{HRS}}{\beta_{532}^{HRS}(\mathrm{DR1})}$		1	1.22	3.07	3.97	2.11	5.01	7.00
$\frac{\beta_{532}^{HRS}/N_{ch.}}{\beta_{532}^{HRS}(\mathrm{DMABI})}$		-	1	1.26	0.81	1.73	2.06; 1.187*	1.92; 1.105*
$\frac{\beta_0^{HRS}}{\beta_0^{HRS}(\mathrm{DR1})}$		1	1.323	3.135	4.051	1.788	0.648	2.421
$\frac{\beta_0^{HRS}/N_{ch.}}{\beta_0^{HRS}(\mathrm{DMABI})}$		-	1	1.184	0.765	1.351	0.245; 0.181*	0.610; 0.451*

*relatively to the β of TD1

Conclusions

- Replacement of methyl groups with phenyls in amino electron donor part of DMABI causes significant increase of relative photoluminescence yield and Stokes shift. Adding more indandione units results in further enhancement of luminescence yield, but on the contrary, Stokes shift and bandwidth descents.
- Despite the general opinion that quantum chemical calculations can profoundly reflect first hyperpolarizability of a molecule, in our case of unconjugated branched molecules (PDs) values acquired experimentally by HRS show insufficient correlation with RHF *ab initio* calculated. This could imply that considering unconjugated structure as a rigid "supramolecule" is wrong. Conformational flexibility of these molecules allows attached chromophore units to act separately.
- Due to possible TPL for the case of conjugated DMABI units enhancement of HRS should be proved by further experiments.

This work is supported by the ERAF Project No. 2010/0308/2DP/2.1.1.1.0/10/APIA/VIAA/051 .

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Ieguldījums tavā nākotnē!
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