SUBSTITUTED DIPHENYLAMINO STYRYL BENZENES AS PROMISSIVE MATERIALS WITH TUNABLE INTENZIVE SOLID STATE FLUORESCENCE – SYNTHETIC APPROACH TO KEY INTERMEDIATE

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Introduction:

Materials, based on organic conjugated molecules, exhibiting efficient solid-state fluorescence (SSF) have been widely applied in various modern technologies [1-6]. The design of new organic solid-state fluorophores have to bear in mind intermolecular non-radiative decay processes which affect the resulting efficiency of fluorescence in the condensed phase adversely and effective reduction of these processes is essential [7].

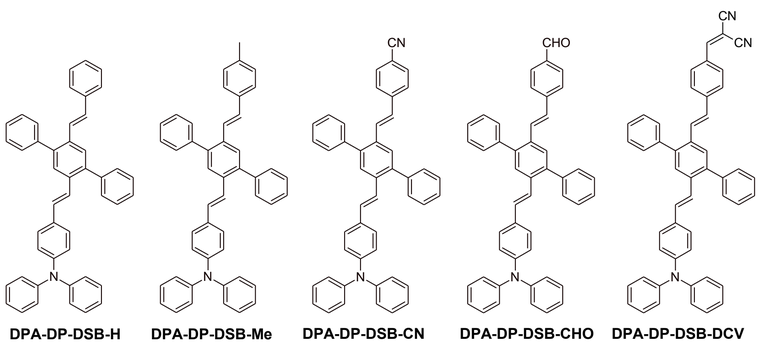
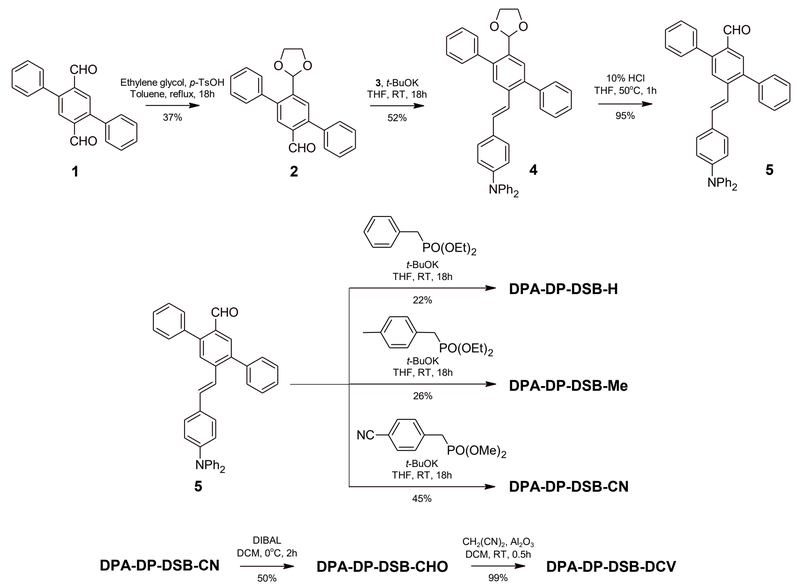


Figure. 1: Series of prepared DP-DSBs.

Synthesis of target intermediate:

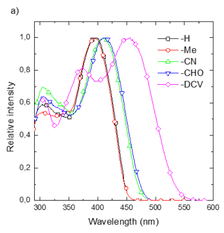


Synthesis of DPA-DP-Distyrylbenzenes.

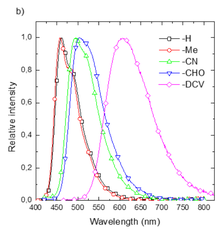
The series of all-trans push-pull end-capped side-diphenyl substituted distyrylbenzenes (DP-DSBs) was prepared by Horner–Wadsworth–Emmons coupling and the fluorescence in polar and non-polar solvents and solid-state was studied. The dependence of the excitation energies and reorganization accompanying excitation on the presence and electronic strength of an acceptor substituent were studied theoretically using time-dependent density functional theory.

Fluorescence of studied materials:

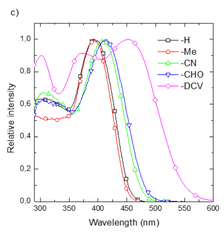
Excitation in toluene



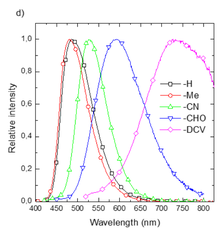
Emission in toluene



Excitation in chloroform



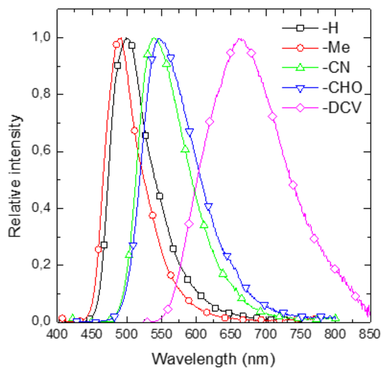
Emission in chloroform

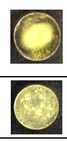
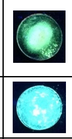
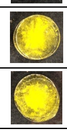
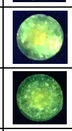


Compound	λ_A^a (nm)	λ_A^b (nm)	$\varepsilon^b(\lambda_A)$ ($l \cdot mol^{-1} \cdot cm^{-1}$)	λ_F^a (nm)	λ_F^b (nm)	Φ_F^a (%)	Φ_F^b (%)	τ_f^a (ns)	τ_f^b (ns)
DPA-DP-DSB-H	396	395	49 500	461	486	84 ± 5	71 ± 3	1.27	1.53
DPA-DP-DSB-Me	395	394	54 000	458	480	85 ± 3	76 ± 9	1.24	1.54
DPA-DP-DSB-CN	409	408	39 700	494	526	86 ± 4	81 ± 4	1.49	2.01
DPA-DP-DSB-CHO	410	412	49 000	504	593	84 ± 2	60 ± 2	1.55	2.17
DPA-DP-DSB-DCV	454	460	42 300	607	731	79 ± 3	< 1	2.32	1.81

The spectroscopic and photophysical properties of the studied derivatives in toluene (a) and chloroform (b).

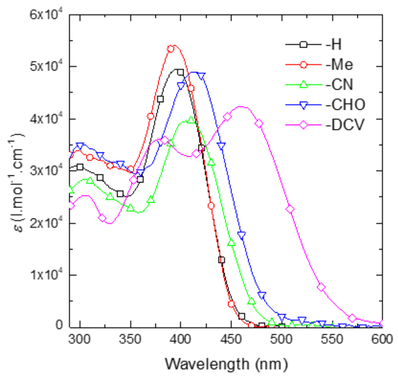
Solid-state fluorescence:



Compound	Daylight	UV lamp	λ_F	Φ_F	τ_F	B (%)
DPA-DP-DSB-H			499	15 ± 2	0.91 3.35 17.59 0.25	34 11 24 31
DPA-DP-DSB-Me			492	29 ± 4	0.73 1.54 8.17	39 58 3
DPA-DP-DSB-CN			541	39 ± 4	0.82 1.75 7.03	46 47 7
DPA-DP-DSB-CHO			545	34 ± 4	0.89 2.56 7.79	15 71 14
DPA-DP-DSB-DCV			662	5,0 ± 0,6	0.93 2.81 7.68	33 58 9

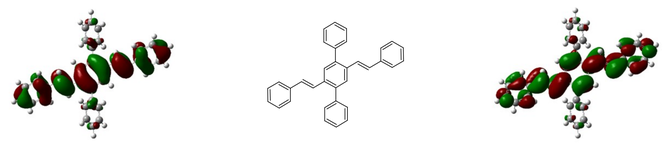
Polycrystalline samples under daylight and UV lamp.

Absorption in chloroform:

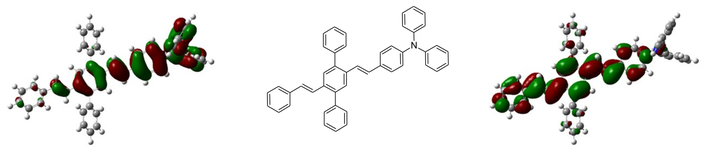


DFT Calculations:

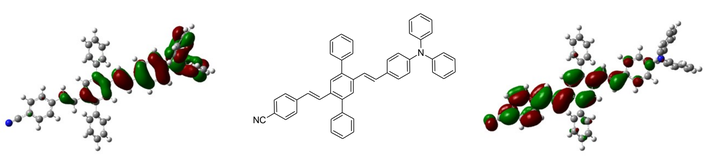
HOMO = -6.753 eV **LUMO = -0.740 eV**



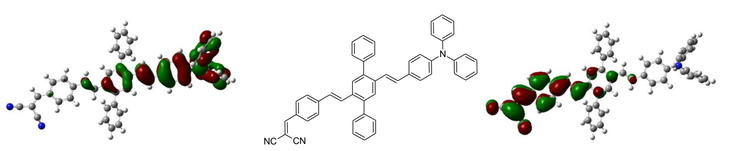
HOMO = -6.255 eV **LUMO = -0.721 eV**



HOMO = -6.372 eV **LUMO = -1.192 eV**



HOMO = -6.411 eV **LUMO = -1.995 eV**



Energy and electron density distribution of frontier MOs computed using DFT CAM-B3LYP 6-311G(d,p) in vacuum (isovalue = 0.02).

Literature:

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