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Research Article

Design and Theoretical Study of D–A–π–A Organic Sensitizers with [1,2,5]Thiadiazolo[3,4-*c*]pyridine, [1,2,5]Selenadiazolo[3,4-*c*]pyridine, and [1,2,5]Oxadiazolo[3,4-*c*]pyridine π Component

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The study concerns molecular design and theoretical study of novel prospective organic sensitizers based on D–A–π–A concept. A modification of the concept (DA–π–A) and new ways for design of organic sensitizers are proposed. The study shows that π-block plays a key role for the wavelength shift in UV-Vis spectra. An existence of element of higher periods in the π-block provides a noticeable bathochromic shift. The thienyl bridge in A-block provides a red shift with respect to phenyl bridge for [1,2,5]oxadiazolo[3,4-*c*]pyridines while the phenyl bridge provides a red shift with respect to thienyl bridge for [1,2,5]selenadiazolo[3,4-*c*]pyridines. The maximal wavelengths are observed for DA-blocks with aliphatic/alicyclic fragments we proposed. An influence of enthalpy of formation and polarity of DA-blocks on bathochromic shift is shown. The quantitative dependencies of wavelengths on the enthalpies and dipole moments are determined. The maximal oscillator strengths are observed for the planar DA-block. Therefore, the conditions for design of compounds possessing the maximal wavelengths and oscillator strengths are different: the latter presupposes the planar structure of DA-block while the first presupposes an existence of nonplanar aliphatic/alicyclic fragments. Thus, the further design of organic sensitizers should include some combination of these concepts.

1. Introduction

Chemistry of chalcogen-containing compounds is currently one of the most rapidly developing areas of heterocyclic chemistry. It has been established that a number of structures at the boundary of organic and inorganic chemistry, characterized by a high ratio of heteroatoms (sulfur, selenium, and nitrogen) relatively to carbon, have useful properties as materials with interesting optical and electrically conductive properties such as high biological activity [1–4]. For example, some of them containing 1,2,5-chalcogenadiazole ring are prospective high performance and low cost components of dye-sensitized solar cells [5–7], anticancer and anti-HIV1 agents [8–11], which have drawn great interest of academic and industrial specialists. Therefore, a design of new 1,2,5-chalcogenadiazole containing compounds that determine properties useful for engineering and medicine is of a great importance. Thus, the objective of the paper is a theoretical study of the previously unknown heterocyclic systems containing 1,2,5-chalcogenadiazole ring which may be of interest for specific materials with useful properties for components of small-molecule organic solar cells (SMOSCs). The mainstream for the design of chalcogen-containing heterocyclic systems SMOSCs for these aims is a construction of "donor–p bridge–acceptor" (D–p–A) configuration due to its convenient modulation of the intramolecular charge-transfer nature. Recently, it has been shown [7] that incorporation of additional electron-acceptors (such as benzothiadiazole, benzotriazole, quinoxaline, phthalimide, diketopyrrolopyrrole, thienopyrazine, thiazole, triazine, cyanovinyl, and cyano- and fluorosubstituted phenyl) into the p bridge (termed the D–A–p–A) configuration displays several advantages such

as regulation of the molecular energy levels, bathochromic shift in UV-Vis spectrum, and distinct improvement of photovoltaic performance and stability. A group from East China University of Science and Technology has proposed a novel "D–A–π–A" [7] concept for designing novel organic sensitizers, in which several kinds of electron-withdrawing units are incorporated into the π bridge to tailor molecular structures and optimize energy levels. They have systematically demonstrated that the incorporated electron-withdrawing additional acceptor can be treated as an "electron trap," showing several distinguished merits such as (i) essentially facilitating the electron transfer from the donor to the acceptor/anchor; (ii) conveniently tailoring the solar cell performance with a facile structural modification on the additional acceptor; (iii) improving circuit photovoltage with the nitrogen-containing heterocyclic group; (iv) conveniently tuning the molecular energy gap and modulating the response of the light-harvesting range with the new resulting absorption band; and (v) most importantly being capable of greatly improving the sensitizer photostability. Organic sensitizers containing additional electron-withdrawing units (or D–A–π–A dyes) are reviewed with specific concern on the relationship between molecular structures and absorption and energy levels as well as photovoltaic performances. From the quantum viewpoint the spectral and electronic properties are dependent on the energy and distribution of the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbital such as being dependent on the threshold between their energies. Therefore, more specifically, our study is focused on fused [1,2,5]thiadiazolo[3,4-*c*]pyridine and [1,2,5]selenadiazolo[3,4-*c*]pyridine derivatives incorporated into D–A–π–A configuration and their comparison with the similar [1,2,5]oxadiazolo[3,4-*c*]pyridine derivatives using DFT B3LYP calculations at the 6/311G(d,p) level of theory for the further design of new compounds with perspective properties. The specific interest to [1,2,5]thiadiazolo[3,4-*c*]pyridine and [1,2,5]selenadiazolo[3,4-*c*]pyridine derivatives is concerned with the fact that these derivatives condensed with strong electronegative rings such as pyridine or pyridazine may be used in organic solar cells due to their ability to convert light into cheap electricity.

2. Building Blocks for D–A–π–A Featured Organic Sensitizers

Taking into account D–A–π–A concept it is necessary to select the building blocks, that is, suitable donor groups (D), acceptor groups (A), and π-fragments (π) for the design of new prospective molecules as organic sensitizers. In our study we use both traditional building blocks reviewed previously by us and by other authors and extended list of donor groups that includes some new previously unexplored fragments. Based on our recent investigations and the works of other researchers [7, 12–21] where three variants of π-fragments (π-block), [1,2,5]thiadiazolo[3,4-*c*]pyridine, [1,2,5]selenadiazolo[3,4-*c*]pyridine, and [1,2,5]oxadiazolo[3,4-*c*]pyridine, showed good characteristics, they were selected for the study. Cyanoacrylic acid as an electron-acceptor, bridged with a phenyl or thienyl fused π-block, was selected as acceptors (A-block) since it is traditionally used in that role in a number of studies (e.g., [7, 22]). Frequently, substituted amines are used as donor groups and here we are also not original in their use but our list of donor groups (D-block) includes some previously unexplored fragments. Moreover, some substituents represent fused donor and acceptor fragments at the same time and thus it is possible to invent slightly another DA–π–A concept for the design of featured organic sensitizers (where DA represents a fused indissoluble agglomerate comprising an electron donor and electron-acceptor group). Also, in order to distinguish the acceptors at the right and left side of π-block we have introduced a somewhat other designation D–A–π–A$'$ and D–A–π–A$'$. All these building blocks are shown in Scheme 1. Therefore, totally 15 building blocks named from **a** to **o** are used in this work. These building blocks allow a combinatorial design of 84 different molecules listed in Table 1.

3. The Analysis of Characteristics of the Designed Organic Sensitizers

The geometry optimization along with conformational search has been performed for each molecule listed in Table 1 at the DFT B3LYP 6-311G(d,p) level of theory. Then, the HOMO and LUMO energies, excitation energies, oscillator strengths, and wavelength for the minimal excitations have been calculated using TD SCF at the DFT B3LYP 6-311G(d,p). All these characteristics are represented in Table 1. The quantum computations were performed using GAMESS software, release May 2013 R1 [23, 24].

Statistical analysis of the calculated characteristics shows that π-block plays a key role for the quantum and spectral characteristics of the designed compounds. So, the mean value of HOMO energy of [1,2,5]oxadiazolo[3,4-*c*]pyridine derivatives is substantially lower than that for [1,2,5]thiadiazolo[3,4-*c*]pyridine and [1,2,5]selenadiazolo[3,4-*c*]pyridine derivatives (Table 2) while the HOMO energies of [1,2,5]thiadiazolo[3,4-*c*]pyridine and [1,2,5]selenadiazolo[3,4-*c*]pyridine derivatives are statistically comparable. So, it is not surprising that the presence of an element of higher periods (S, Se) in the heterocyclic π-block reduces the HOMO level which in its turn facilitates a bathochromic shift in the UV-Vis spectra. The LUMO energies behave unusually in a sequence O, S, and Se: their mean values for [1,2,5]oxadiazolo[3,4-*c*]pyridine and [1,2,5]selenadiazolo[3,4-*c*]pyridine derivatives are statistically comparable but substantially lower than that for [1,2,5]thiadiazolo[3,4-*c*]pyridine derivatives (Table 2) that should provide a red shift in the UV-Vis spectra for O and Se containing π-blocks. The intervals of HOMO and LUMO energies for [1,2,5]oxadiazolo[3,4-*c*]pyridine, [1,2,5]thiadiazolo[3,4-*c*]pyridine, and [1,2,5]selenadiazolo[3,4-*c*]pyridine derivatives are illustrated in Figure 1. Thus, a substitution of oxygen by sulfur in a π-block yields in an increase of both HOMO and LUMO levels while the substitution by selenium leads to an increase of only HOMO energy at an approximately constant LUMO energy. Therefore, a reduction of the excitation energy and correspondingly a bathochromic shift for [1,2,5]selenadiazolo[3,4-*c*]pyridine derivatives

Table 1: Quantum characteristics for designed molecules.

Number	Molecule	HOMO	LUMO	Δ	E_e	OS	λ	ΔH_f	μ
1	**achn**	−3.5820	−0.5788	3.0032	2.6745	0.3485	464	−39.3	4.33
2	**acin**	−3.4261	−0.5908	2.8353	2.4796	0.2441	500	−39.3	4.33
3	**acjn**	−3.4019	−0.7083	2.6936	2.4413	0.6367	508	−39.3	4.33
4	**bchn**	−3.8260	−0.7660	3.0600	2.7630	0.3373	449	−31.9	3.78
5	**bcin**	−3.7245	−0.7113	3.0132	2.6852	0.2657	462	−31.9	3.78
6	**bcjn**	−3.6788	−0.9251	2.7537	2.4626	0.5515	503	−31.9	3.78
7	**adhn**	−3.4868	−0.6055	2.8813	2.5785	0.4339	481	−30.8	6.99
8	**adin**	−3.3840	−0.6150	2.7690	2.4192	0.3319	512	−30.8	6.99
9	**adjn**	−3.4011	−0.7393	2.6618	2.2935	0.2642	541	−30.8	6.99
10	**bdhn**	−3.6173	−0.7747	2.8427	2.6014	0.7999	477	−27.5	6.39
11	**bdin**	−3.4239	−0.7382	2.6857	2.4893	1.0474	498	−27.5	6.39
12	**bdjn**	−3.4514	−0.8291	2.6224	2.4169	0.9636	513	−27.5	6.39
13	**ehn**	−3.3222	−0.4920	2.8302	2.5340	0.3073	489	−46.7	8.11
14	**ein**	−3.1606	−0.4942	2.6664	2.4837	0.6266	499	−46.7	8.11
15	**ejn**	−3.1854	−0.6183	2.5671	2.3761	0.5581	522	−46.7	8.11
16	**fhn**	−3.2915	−0.4858	2.8057	2.5328	0.3183	490	−58.1	10.31
17	**fin**	−3.1364	−0.4872	2.6493	2.4896	0.6489	498	−58.1	10.31
18	**fjn**	−3.1609	−0.6109	2.5500	2.3597	0.5664	525	−58.1	10.31
19	**ghn**	−3.3625	−0.5595	2.8030	2.5385	0.3417	488	−49.8	8.33
20	**gin**	−3.2058	−0.3076	2.8982	2.5552	0.1977	485	−49.8	8.33
21	**gjn**	−3.2395	−0.6963	2.5432	2.3112	0.5742	536	−49.8	8.33
22	**acho**	−3.5912	−0.6887	2.9025	2.5847	0.4649	480	−39.3	4.33
23	**acio**	−3.4199	−0.4885	2.9313	2.6598	0.6514	466	−39.3	4.33
24	**acjo**	−3.4413	−0.5976	2.8438	2.5671	0.5593	483	−39.3	4.33
25	**bcho**	−3.8491	−0.9134	2.9357	2.6134	0.4395	474	−31.9	3.78
26	**bcio**	−3.7531	−0.5913	3.1617	2.7906	0.2349	444	−31.9	3.78
27	**bcjo**	−3.7196	−0.8282	2.8914	2.5773	0.4885	481	−31.9	3.78
28	**adho**	−3.4974	−0.7086	2.7888	2.5091	0.5891	494	−30.8	6.99
29	**adio**	−3.3976	−0.4975	2.9001	2.5298	0.2984	490	−30.8	6.99
30	**adjo**	−3.4207	−0.6354	2.7853	2.4045	0.2494	516	−30.8	6.99
31	**bdho**	−3.5542	−0.9422	2.6120	2.4553	1.2330	505	−27.5	6.39
32	**bdio**	−3.3614	−0.7521	2.6093	2.4342	1.1429	509	−27.5	6.39
33	**bdjo**	−3.3856	−0.8307	2.5549	2.3703	1.0644	523	−27.5	6.39
34	**eho**	−3.3611	−0.6017	2.7594	2.4761	0.3877	501	−46.7	8.11
35	**eio**	−3.1911	−0.3939	2.7972	2.5873	0.5605	479	−46.7	8.11
36	**ejo**	−3.2156	−0.4997	2.7159	2.5007	0.4857	496	−46.7	8.11
37	**fho**	−3.3304	−0.6003	2.7301	2.4749	0.3953	501	−58.1	10.31
38	**fio**	−3.1702	−0.3936	2.7766	2.5758	0.5620	481	−58.1	10.31
39	**fjo**	−3.1936	−0.5029	2.6906	2.4769	0.4834	501	−58.1	10.31
40	**gho**	−3.3967	−0.6667	2.7301	2.4482	0.4004	506	−49.8	8.33
41	**gio**	−3.2504	−0.4768	2.7736	2.5473	0.5906	487	−49.8	8.33
42	**gjo**	−3.2654	−0.5736	2.6917	2.4369	0.4660	509	−49.8	8.33
43	**ackn**	−3.5863	−0.5688	3.0176	2.6694	0.2794	464	−39.3	4.33
44	**acln**	−3.4087	−0.6125	2.7962	2.5366	0.6158	489	−39.3	4.33
45	**acmn**	−3.4120	−0.7398	2.6721	2.3960	0.5374	517	−39.3	4.33
46	**bckn**	−3.8621	−0.7377	3.1245	2.8158	0.2731	440	−31.9	3.78
47	**bcln**	−3.7498	−0.4050	3.3448	2.9756	0.1498	417	−31.9	3.78
48	**bcmn**	−3.6938	−0.9177	2.7760	2.4765	0.5062	501	−31.9	3.78
49	**adkn**	−3.5553	−0.6547	2.9006	2.5500	0.2975	486	−30.8	6.99
50	**adln**	−3.4375	−0.6533	2.7842	2.3923	0.1952	518	−30.8	6.99
51	**admn**	−3.4481	−0.7790	2.6691	2.2631	0.1467	548	−30.8	6.99

Table 1: Continued.

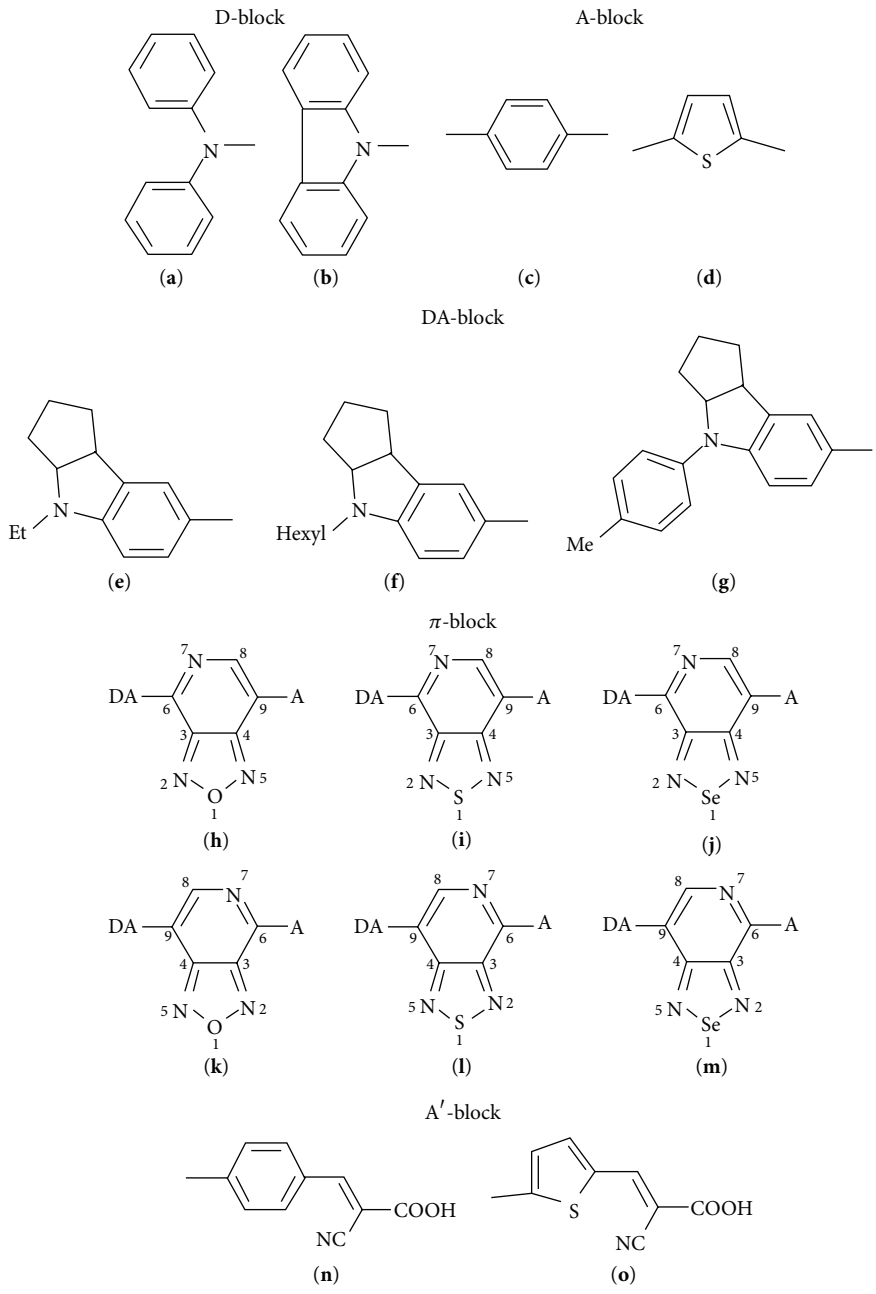
Number	Molecule	HOMO	LUMO	Δ	E_e	OS	λ	ΔH_f	μ
52	**bdkn**	−3.6301	−0.9354	2.6947	2.5297	1.0599	490	−27.5	6.39
53	**bdln**	−3.4460	−0.7627	2.6833	2.4674	0.9344	502	−27.5	6.39
54	**bdmn**	−3.4672	−0.8576	2.6096	2.3826	0.8454	520	−27.5	6.39
55	**ekn**	−3.3432	−0.4736	2.8696	2.5300	0.2336	490	−46.7	8.11
56	**eln**	−3.1729	−0.4986	2.6743	2.4622	0.5538	504	−46.7	8.11
57	**emn**	−3.1846	−0.6291	2.5554	2.3316	0.4831	532	−46.7	8.11
58	**fkn**	−3.3119	−0.4869	2.8250	2.4926	0.2284	497	−58.1	10.31
59	**fln**	−3.1479	−0.4915	2.6564	2.4706	0.5824	502	−58.1	10.31
60	**fmn**	−3.1596	−0.6221	2.5375	2.3150	0.4921	536	−58.1	10.31
61	**gkn**	−3.3908	−0.5342	2.8565	2.5348	0.2473	489	−49.8	8.33
62	**gln**	−3.2390	−0.5717	2.6672	2.4506	0.5865	506	−49.8	8.33
63	**gmn**	−3.2477	−0.7031	2.5446	2.2884	0.503	542	−49.8	8.33
64	**acko**	−3.5999	−0.7594	2.8405	2.5826	0.7386	480	−39.3	4.33
65	**aclo**	−3.4781	−0.5043	2.9738	2.5863	0.2092	479	−39.3	4.33
66	**acmo**	−3.4413	−0.6612	2.7801	2.4913	0.5407	498	−39.3	4.33
67	**bcko**	−3.8673	−0.9248	2.9425	2.6152	0.3837	474	−31.9	3.78
68	**bclo**	−3.7060	−0.7262	2.9798	2.6730	0.6024	464	−31.9	3.78
69	**bcmo**	−3.7237	−0.8565	2.8672	2.5546	0.5159	485	−31.9	3.78
70	**adko**	−3.5531	−0.8315	2.7216	2.4076	0.4561	515	−30.8	6.99
71	**adlo**	−3.4400	−0.5862	2.8538	2.4557	0.2079	505	−30.8	6.99
72	**admo**	−3.4544	−0.6960	2.7584	2.3414	0.1461	530	−30.8	6.99
73	**bdko**	−3.5667	−0.9566	2.6101	2.4375	1.1336	509	−27.5	6.39
74	**bdlo**	−3.3761	−0.7632	2.6128	2.4218	1.047	512	−27.5	6.39
75	**bdmo**	−3.3965	−0.8470	2.5495	2.3465	0.9584	528	−27.5	6.39
76	**eko**	−3.3690	−0.6849	2.6841	2.3742	0.3321	522	−46.7	8.11
77	**elo**	−3.1957	−0.4515	2.7442	2.5179	0.5558	492	−46.7	8.11
78	**emo**	−3.2047	−0.5478	2.6569	2.4111	0.4408	514	−46.7	8.11
79	**fko**	−3.3380	−0.6786	2.6593	2.3820	0.3464	521	−58.1	10.31
80	**flo**	−3.1895	−0.4107	2.7788	2.4433	0.247	507	−58.1	10.31
81	**fmo**	−3.1870	−0.5524	2.6346	2.3953	0.4685	518	−58.1	10.31
82	**gko**	−3.3761	−0.7646	2.6115	2.3360	0.3567	531	−49.8	8.33
83	**glo**	−3.2327	−0.5339	2.6988	2.4667	0.5582	503	−49.8	8.33
84	**gmo**	−3.2444	−0.6517	2.5927	2.3253	0.4596	533	−49.8	8.33

HOMO is the energy of the highest occupied molecular orbital, eV; LUMO is the energy of the lowest unoccupied molecular orbital, eV; Δ is the gap between LUMO and HOMO, eV; E_e is the excitation energy, eV; OS is the oscillator strength; λ is the wavelength, nm; ΔH_f is the enthalpy of formation of D–A- (DA-) block, kcal/mole; μ is the dipole moment of D–A- (DA-) block, D.

summarizing the findings on the HOMO and LUMO energies can be predicted certainly.

Actually, the gaps between HOMO and LUMO and correspondingly the excitation energies for the selenium containing compounds are significantly less than that for other molecules. The LUMO and HOMO difference is less on average by 0.14–0.15 eV and the excitation energy – by 0.23 eV. At the same time, the [1,2,5]oxadiazolo[3,4-*c*]pyridine and [1,2,5]thiadiazolo[3,4-*c*]pyridine derivatives are statistically comparable in these characteristics (Table 2). Obviously, the mean value of wavelength for selenium containing compounds is greater than that for others. The bathochromic shift for selenium containing compounds relative to others is approximately 26 nm. [1,2,5]Selenadiazolo[3,4-*c*]pyridine derivative 51 in Table 1 (**admn**) possesses the maximal value of the wavelength 548 nm among the designed molecules. The minimal value of the wavelength 417 nm is observed for the molecule 47 (**bcln** in Table 1).

The analysis of the influence of the acceptors of A′-block shows that there are no overall effects on the whole set of the designed molecules but the effects are found separately for [1,2,5]oxadiazolo[3,4-*c*]pyridine and [1,2,5]selenadiazolo[3,4-*c*]pyridine derivatives. For [1,2,5]oxadiazolo[3,4-*c*]pyridine derivatives the A′-block has no significant influence on the HOMO energy, but the compounds with thienyl bridge in A′-block (**o** fragment) possess less value of LUMO energy than the compounds with phenyl bridge (**n** fragment) on average by 0.15 eV that reduces the gap between LUMO and HOMO and excitation energy and correspondingly provides a bathochromic shift in UV-Vis spectra. Actually,



Scheme 1: Building blocks for the design of featured organic sensitizers.

the mean values of the gap between LUMO and HOMO for the compounds with thienyl bridge in A′-block (**o** fragment) are lesser than that for the compounds with phenyl bridge (**n** fragment) on average by 0.14 eV, the excitation energy is lesser on average by 0.12 eV, and the wavelength is greater on average by 23 nm. This mean value for the [1,2,5]oxadiazolo[3,4-*c*]pyridine with thienyl bridge is 500.9 ± 9.8 nm which is comparable with the [1,2,5]selenadiazolo[3,4-*c*]pyridine derivatives (Table 2). [1,2,5]Oxadiazolo[3,4-*c*]pyridine 82 in Table 1 (**gko**) possesses the maximal value of wavelength 532 nm among the designed molecules.

There is no influence of A′-block observed on the quantum and spectral characteristics of [1,2,5]thiadiazolo[3,4-*c*]pyridine derivatives.

For [1,2,5]selenadiazolo[3,4-*c*]pyridine derivatives the A′-block has no significant influence on the HOMO and LUMO energies, but in contrast to [1,2,5]oxadiazolo[3,4-*c*]pyridine derivatives the compounds with thienyl bridge in A′-block (**o** fragment) possess greater gap between LUMO and HOMO than the compounds with phenyl bridge (**n** fragment) on average by 0.09 eV that provides an increase of excitation energy and correspondingly provides a hypsochromic shift in UV-Vis spectra. Actually, the mean values of the gap between LUMO and HOMO for the compounds with thienyl bridge in A′-block (**o** fragment) are greater than that for the compounds with phenyl bridge (**n** fragment) on average by 0.09 eV, the excitation energy is greater on average by 0.12 eV, and the wavelength is lesser on average by 16 nm.

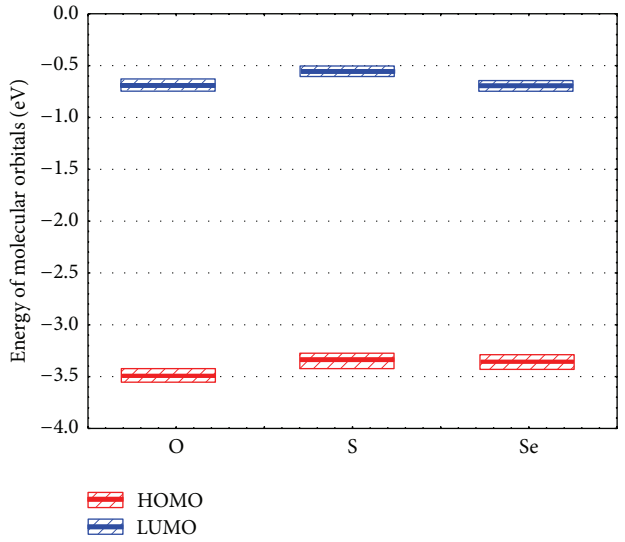


Figure 1: Orbital energies diapasons for [1,2,5]oxadiazolo[3,4-*c*]pyridine (O), [1,2,5]thiadiazolo[3,4-*c*]pyridine (S), and [1,2,5]selenadiazolo[3,4-*c*]pyridine (Se) derivatives.

Table 2: Mean values and confidence intervals of quantum characteristics for [1,2,5]oxadiazolo[3,4-*c*]pyridine (O), [1,2,5]thiadiazolo[3,4-*c*]pyridine (S), and [1,2,5]selenadiazolo[3,4-*c*]pyridine (Se) derivatives.

Characteristic	O	S	Se
HOMO energy, eV	−3.514 ± 0.068	−3.365 ± 0.071	−3.373 ± 0.068
LUMO energy, eV	−0.691 ± 0.057	−0.555 ± 0.049	−0.702 ± 0.049
Δ, eV	2.823 ± 0.051	2.812 ± 0.064	2.671 ± 0.040
Excitation energy, eV	2.537 ± 0.042	2.5374 ± 0.048	2.404 ± 0.032
Wavelength, nm	489.5 ± 7.9	489.7 ± 8.5	516.4 ± 6.9

The mean value for the [1,2,5]selenadiazolo[3,4-*c*]pyridine derivatives with phenyl bridge is 524.6 ± 8.0 nm.

No significant dependency of the HOMO and LUMO energies, the excitation energy, and the wavelength on the quantum derived characteristics of D–A- (DA-) block and on the substitution type in the π-block (**h**, **i**, and **j** or **k**, **l**, and **m** in Scheme 1) is observed, so the calculation of more than 500 descriptors was performed using ChemoSophia online software (http://www.chemosophia.com/) [25] both for whole molecules (molecules 1–84 in Table 1) and for D–A- (DA-) blocks (building blocks **a**–**g** in Scheme 1) in radical state.

Analysis of the descriptors showed that the HOMO energy has relationships with enthalpy of formation (ΔH_f) of D–A- (DA-) blocks calculated within ChemoSophia Elastic Model [25] but separately for [1,2,5]oxadiazolo[3,4-*c*]pyridine derivatives and for [1,2,5]thiadiazolo[3,4-*c*]pyridine/[1,2,5]selenadiazolo[3,4-*c*]pyridine derivatives. The enthalpies of formation for D–A- (DA-) blocks are represented in

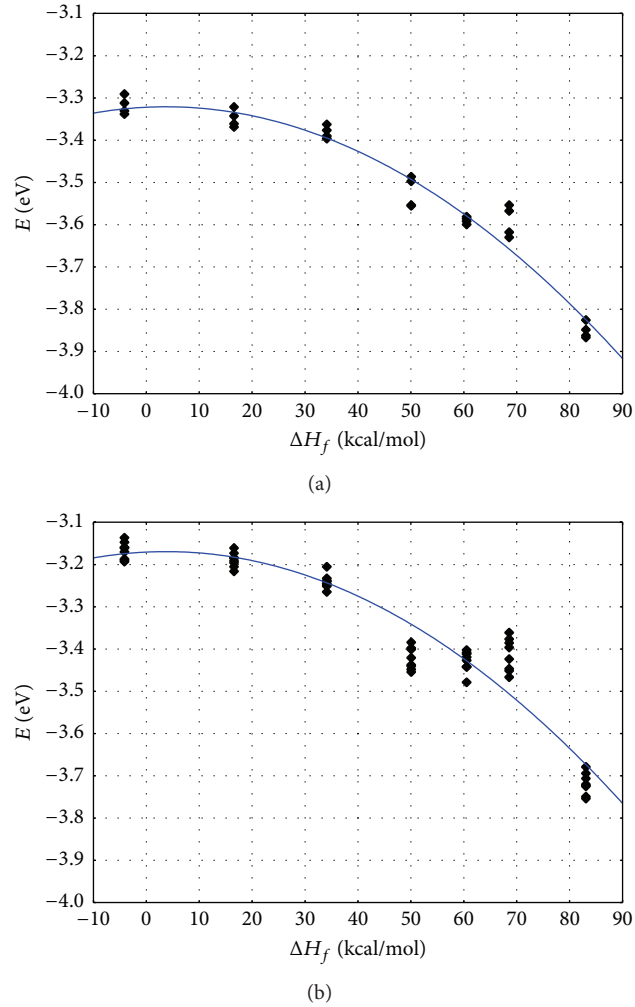


Figure 2: Relationships between ΔH_f (ChemoSophia Elastic Model) and E (DFT B3LYP 6-311G(d,p)) (a) for [1,2,5]oxadiazolo[3,4-*c*]pyridine; (b) for [1,2,5]thiadiazolo[3,4-*c*]pyridine and [1,2,5]selenadiazolo[3,4-*c*]pyridine.

Table 3. The relationships are shown in Figure 2 and can be described using the following polynomial equation:

$$E = a_0 + a_1 \Delta H_f + a_2 \Delta H_f^2, \quad (1)$$

where E is HOMO energy and a_0, a_1, and a_2 are coefficients.

The coefficients for [1,2,5]oxadiazolo[3,4-*c*]pyridine derivatives are as follows: $a_0 = -3.3220$; $a_1 = 5.915 \cdot 10^{-4}$; and $a_2 = -7.966 \cdot 10^{-4}$. The correlation coefficient $R = 0.977$; the standard deviation $S = 0.039$.

The coefficients for [1,2,5]thiadiazolo[3,4-*c*]pyridine and [1,2,5]selenadiazolo[3,4-*c*]pyridine derivatives are as follows: $a_0 = -3.1705$; $a_1 = 5.915 \cdot 10^{-4}$; and $a_2 = -7.966 \cdot 10^{-4}$. The correlation coefficient $R = 0.951$; the standard deviation $S = 0.057$.

Thus the values of a_1 and a_2 coefficients for [1,2,5]oxadiazolo[3,4-*c*]pyridine, [1,2,5]thiadiazolo[3,4-*c*]pyridine, and [1,2,5]selenadiazolo[3,4-*c*]pyridine derivatives coincide. So, the only difference in equations is the free terms a_0 which means the same form of the relationships but the curve

Table 3: Enthalpies of formation for D–A- (DA-) blocks.

D–A- (DA-) block	ΔH_f, kcal/mole
ac	60.6
bc	83.1
ad	50.1
bd	68.6
e	16.6
f	−4.2
g	34.1

for [1,2,5]thiadiazolo[3,4-*c*]pyridine and [1,2,5]selenadiazolo[3,4-*c*]pyridine derivatives lies above the curve for [1,2,5]oxadiazolo[3,4-*c*]pyridine derivatives approximately by 0.15 eV. Figure 2 and (1) show that the reduction of ΔH_f leads to increase of HOMO energy and in turn may provide a reduction of excitation energy and a bathochromic shift. Table 3 shows that the lower values are the characteristic feature of DA-blocks (**e**, **f**, and **g**) we proposed. These building blocks include alkyl and alicyclic components in their structure. Thus, the DA-blocks (**e**, **f**, and **g**) containing organic sensitizers should be more prospective than earlier proposed D–A-blocks (**ac**, **bc**, **ad**, and **bd**). Actually, the DA containing compounds possess less mean gap between LUMO and HOMO on average 0.12 eV, less mean excitation energy on average 0.07 eV, and greater wavelength on average 13 nm than D–A containing compounds.

Additionally, correlations between HOMO energy and dipole moment of D–A- (DA-) blocks calculated within ChemoSophia Elastic Model are observed. The greater polarity of the blocks provides the greater HOMO energy (the correlation coefficients 0.90, 0.88, and 0.88 for [1,2,5]oxadiazolo[3,4-*c*]pyridine, [1,2,5]thiadiazolo[3,4-*c*]pyridine, and [1,2,5]selenadiazolo[3,4-*c*]pyridine derivatives, correspondingly). The mean value of dipole moment of DA containing compounds (8.9 Debye) is greater than that for D–A containing compounds on average by 3.6 Debye.

An analysis of the oscillator strengths shows the following: [1,2,5]oxadiazolo[3,4-*c*]pyridine derivative 31 in Table 1 (**bdho**) possesses the maximal value of the oscillator strength 1.233 among the designed molecules. The minimal value of the oscillator strength 0.146 nm is observed for the molecule 72 (**admo** in Table 1). Generally, the largest oscillator strengths are observed for molecules with completely planar D–A-block (**bc** and **bd** fragments). The mean value of the oscillator strengths for the molecules with **bc** or **bd** fragments is 1.02 ± 0.12 while for other molecules the mean value of the oscillator strengths is 0.42 ± 0.15. Moreover, the diapasons of oscillator strengths for **bc** and **bd** containing molecules and for all other molecules do not intersect. The minimal value of oscillator strength among **bc** and **bd** containing molecules is 0.7999 (molecule 10 **bdhn** in Table 1) while maximal value of oscillator strength among all other molecules is 0.7386 (molecule 64, **acko**, in Table 1). The planar structure of the D–A-block of **bc** and **bd** containing molecules provides in turn the greater planarity and the minimal deviation from π-plane of the π-block for the whole **bc** and **bd** containing molecules. So, the standard deviation of atoms from π-plane of the π-block for the whole **bc** and **bd** containing molecules is 4.94 ± 0.14 Å while for the other molecules the standard deviation is 6.73 ± 0.42 Å. Additionally the D-block **b** contains the minimal number of electron-poor atoms (hydrogens) among all D- and DA-blocks which provides stronger electron donor property. Therefore, it is necessary to find more planar D–A-blocks containing minimal number of hydrogens for the design of novel prospective organic sensitizers with the maximal oscillator strength.

4. Conclusions

Thus, a molecular design and theoretical study of novel prospective organic sensitizers based on D–A–π–A concept have been fulfilled. A modification of the concept (DA–π–A) and new ways for molecular design of organic sensitizers have been proposed. As in previous researches, it has been shown that the π-block plays a key role for the wavelength shift in UV-Vis spectra; also we have shown that an existence of an element of higher periods of the Periodic System in the π-block provides a noticeable bathochromic shift. This study determines that the thienyl bridge in the A-block provides a red shift with respect to the phenyl bridge for [1,2,5]oxadiazolo[3,4-*c*]pyridine derivatives and vice versa the phenyl bridge in the A-block provides a red shift with respect to the thienyl bridge for [1,2,5]selenadiazolo[3,4-*c*]pyridine derivatives. No significant influence of the bridge in A-block was observed for [1,2,5]thiadiazolo[3,4-*c*]pyridine derivatives. The maximal values of wavelengths have been observed for DA-blocks with aliphatic and alicyclic fragments we proposed. It has been shown in the study that the enthalpy of formation reduction and increase of polarity of D–A- (DA-) blocks yields in bathochromic shift in UV-Vis spectra. The quantitative dependencies of wavelengths on the enthalpies of formation and dipole moments are determined. It has been shown that the maximal values of the oscillator strength are observed for the planar D and A components in D–A- (DA-) block. Therefore, it has been shown in this study that the conditions for the design of compounds possessing the maximal wavelength and the maximal oscillator strength are different: the latter presupposes the planar structure of D–A- (DA-) block while the first presupposes an existence of nonplanar aliphatic and/or alicyclic fragments in D–A- (DA-) block. Thus, the next steps for the molecular design of novel prospective organic sensitizers should include some combination of these concepts.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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