The Free Internet Journal
for Organic Chemistry

Archive for
Organic Chemistry

Paper

Arkivoc **2017**, part iii, 346-364

Design and theoretical study of D–A–π–A' organic sensitizers with [1,2,5]oxa-, thia- or selenadiazoloazine fragment

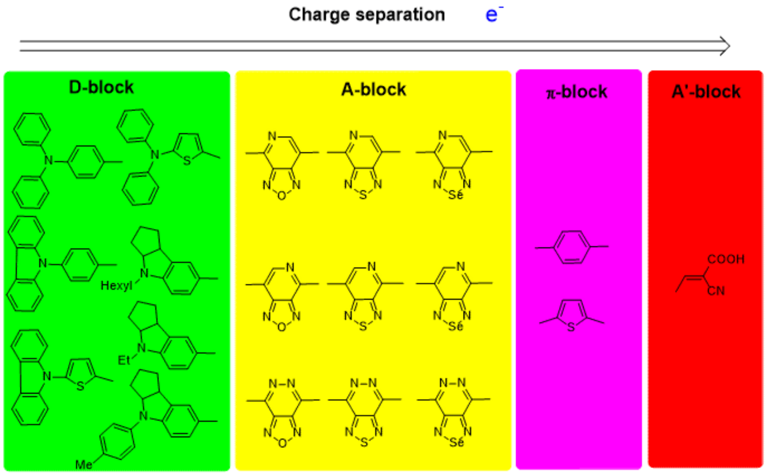
V. Potemkin,*[a] O. Bolshakov,[a] A. Safiullin,[a] A. Potemkin,[b] and M. Grishina[a]
[a]*South Ural State University, 76, pr. Lenina, Chelyabinsk, 454080, Russia*
[b]*University of Information Technologies, Mechanics and Optics, 49, Kronverkskiy prospekt, St. Petersburg, 197101, Russia*
Email: potemkinva@susu.ru

Dedicated to Professor Oleg A. Rakitin on the occasion of his 65th birthday

Received 06-20-2017 **Accepted** 08-20-2017

Abstract

A theoretical study and design of novel sensitizers based on D–A–π–A concept is fulfilled. The study shows a key role of central A-block for wavelength in UV-Vis spectra. Chalcogen of higher period as well as additional nitrogen in central A-block provide a noticeable red shift. The maximum wavelengths are observed for aliphatic/alicyclic D-blocks. The maximum oscillator strengths are observed for the planar D-block and increase along with its charge. Structure-spectral property relationships of sensitizers are studied using CRAQC (Correlation and Regression Analysis of Quantum Calculations). A method for chromophore determination is invented.



Keywords: Organic sensitizers, 1,2,5-chalcogenadiazoles, structure-spectral relationship, D-A-p-A, CRAQC

DOI: https://doi.org/10.24820/ark.5550190.p010.228

Introduction

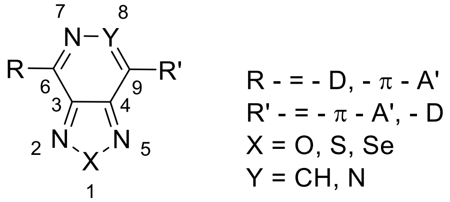
Heterocyclic chemistry of chalcogen-containing compounds is currently one of the most rapidly developing areas. It has been established that a number of structures at the boundary of organic and inorganic chemistry, characterized by a high ratio of heteroatoms (sulfur, selenium, oxygen and nitrogen) relatively to carbon has useful properties as materials with interesting optical and electrically conductive properties so 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,[5-9] anti-cancer and anti-HIV1 agents [10-13] and have drawn great interest both for industrial and academic specialists. Thus, a design of new 1,2,5-chalcogenadiazole containing molecules that determine properties useful for medicine and engineering is of a great importance. Therefore, the goal of the paper is a theoretical study of the previously unknown heterocyclic compounds containing 1,2,5-chalcogenadiazole ring which may be of interest for materials with useful properties for components of small-molecule organic solar cells (SMOSCs). The mainstream for the design of chalcogen containing heterocyclic compounds for these aims is a construction of “donor – p bridge – acceptor” (D–p–A) configuration due to their 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, cyano- and fluoro-substituted phenyl) into the p bridge (termed the D–A–p–A) configuration, displays several advantages such as regulation of the molecular energy levels, red shift in UV-Vis spectrum, and distinct improvement of photovoltaic performance along with stability. Moreover, a new “D–A–π–A” [7] concept has been proposed for designing novel organic sensitizers, in which several kinds of electron-withdrawing units are incorporated into the π bridge to tailor molecular structures and to optimize energy levels.

It has been demonstrated that the incorporated electron withdrawing additional acceptor can be treated as an ‘‘electron trap’’, showing several distinguished merits such as: 1) essentially facilitating the electron transfer from the donor to the acceptor/anchor; 2) conveniently tailoring the solar cell performance with a facile structural modification on the additional acceptor; 3) improving circuit photovoltage with the nitrogen-containing heterocyclic group; 4) conveniently tuning the molecular energy gap, and modulating the response of the light-harvesting range with the new resulting absorption band; and 5) most importantly, being capable of greatly improving the sensitizer photo-stability.[7] 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, energy levels as well as photovoltaic performances. From the quantum viewpoint the electronic and spectral properties are dependent on the energy and distribution of the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbitals so as dependent on the gap between their energies. Therefore, more specifically, our study is focused on fused [1,2,5]thiadiazolo[3,4-*c*]azine and [1,2,5]selenadiazolo[3,4-*c*]azine derivatives incorporated into D–A–π–A configuration and their comparison with the similar [1,2,5]oxadiazolo[3,4-*c*]azine 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*]azine and [1,2,5]selenadiazolo[3,4-*c*]azine derivatives is concerned with the fact that these derivatives condensed with strong electronegative rings such as pyridine or pyridazine may be used in SMOSCs due to their capability to convert light into cheap electricity.

Results and Discussion

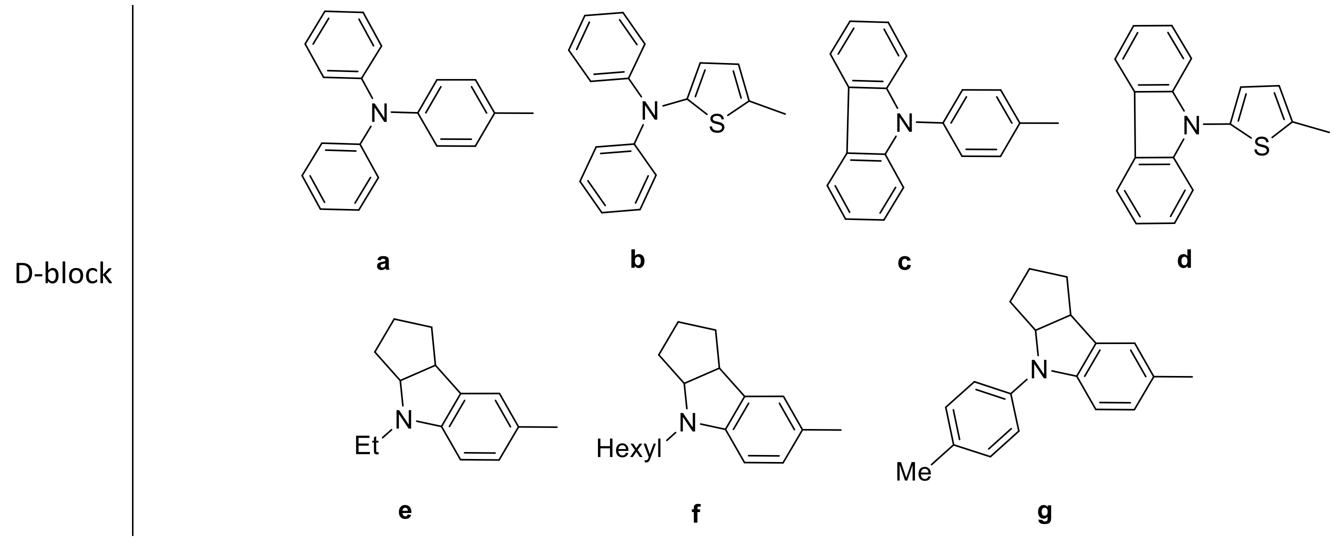
Building blocks for D–A–π–A featured organic sensitizers

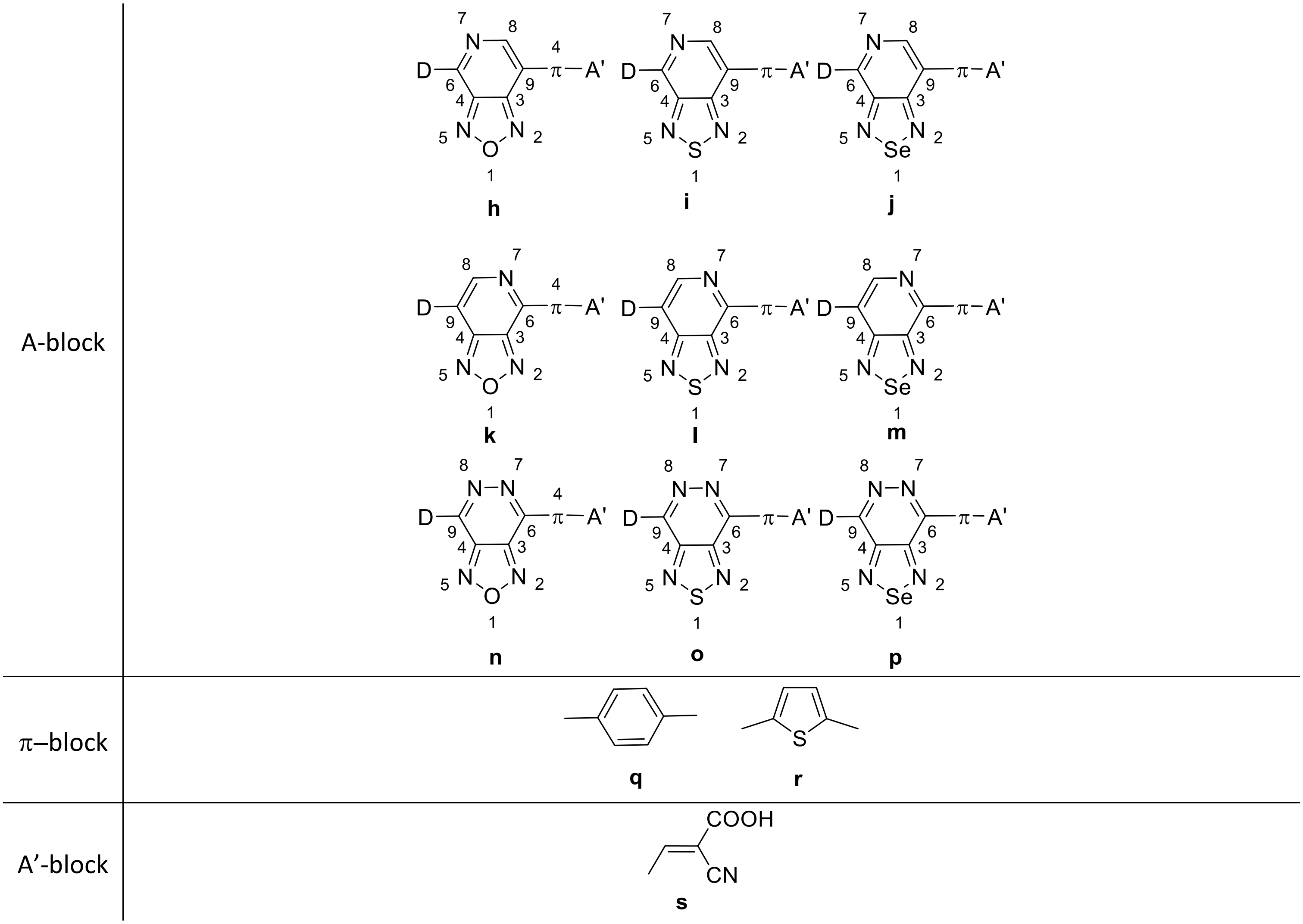
Taking into account D–A–π–A concept it is necessary to select the building blocks, i.e. suitable donor groups (D), acceptor groups (A) and π-fragments (π) for the design of new prospective molecules as organic sensitizers. In our study we use both traditional building blocks reviewed previously by us 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[7,14-24] six variants of A-fragments (A-block) which have showed good characteristics were selected for the present study: [1,2,5]thiadiazolo[3,4-*c*]pyridine, [1,2,5]selenadiazolo[3,4-*c*]pyridine, [1,2,5]oxadiazolo[3,4-*c*]pyridine, [1,2,5]thiadiazolo[3,4-*c*]pyridazine, [1,2,5]selenadiazolo[3,4-*c*]pyridazine and [1,2,5]oxadiazolo[3,4-*c*]pyridazine. The general formula for these derivatives is represented in Scheme 1.



Scheme 1. General representation of the studied organic sensitizers.

In order to distinguish the acceptors at the right and left side of π-block we have introduced a somewhat another designation D–A–π–A’. Cyanoacrylic acid was selected as acceptor (A’-block in Scheme 2), bridged with a phenyl or thienyl (π-block in Scheme 2) since they are traditionally used in that role in a number of studies (e.g., [7,24]). Substituted amines are currently used as donor groups and here we are also not original in their use but our list of donor groups (D-block) also includes some previously unexplored fragments. All these building blocks are shown in Scheme 2. Therefore, a total of 19 building blocks named from **a** to **s** are used in this work. These building blocks allow a combinatorial design of 126 different molecules listed in Table 1.





Scheme 2. Structures of considered blocks.

Table 1. Quantum characteristics for designed molecules (HOMO is the energy of highest occupied molecular orbital, eV; LUMO is the energy of 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 wave length, nm; ΔH_f is the enthalpy of formation of A-block, kcal/mole; μ is the dipole moment of A-block, D)

№	Molecule	HOMO	LUMO	Δ	E_e	OS	λ	ΔH_f	μ
1	**ahqs**	-3.5820	-0.5788	3.0032	2.6745	0.3485	464	60.6	4.33
2	**aiqs**	-3.4261	-0.5908	2.8353	2.4796	0.2441	500	60.6	4.33
3	**ajqs**	-3.4019	-0.7083	2.6936	2.4413	0.6367	508	60.6	4.33
4	**chqs**	-3.8260	-0.7660	3.0600	2.7630	0.3373	449	83.1	3.78
5	**ciqs**	-3.7245	-0.7113	3.0132	2.6852	0.2657	462	83.1	3.78
6	**cjqs**	-3.6788	-0.9251	2.7537	2.4626	0.5515	503	83.1	3.78
7	**bhqs**	-3.4868	-0.6055	2.8813	2.5785	0.4339	481	50.1	6.99
8	**biqs**	-3.3840	-0.6150	2.7690	2.4192	0.3319	512	50.1	6.99
9	**bjqs**	-3.4011	-0.7393	2.6618	2.2935	0.2642	541	50.1	6.99
10	**dhqs**	-3.6173	-0.7747	2.8427	2.6014	0.7999	477	68.6	6.39

Table 1. Continued

№	**Molecule**	HOMO	LUMO	Δ	Ee	OS	λ	ΔHf	μ
11	**diqs**	-3.4239	-0.7382	2.6857	2.4893	1.0474	498	68.6	6.39
12	**djqs**	-3.4514	-0.8291	2.6224	2.4169	0.9636	513	68.6	6.39
13	**ehqs**	-3.3222	-0.4920	2.8302	2.5340	0.3073	489	16.6	8.11
14	**eiqs**	-3.1606	-0.4942	2.6664	2.4837	0.6266	499	16.6	8.11
15	**ejqs**	-3.1854	-0.6183	2.5671	2.3761	0.5581	522	16.6	8.11
16	**fhqs**	-3.2915	-0.4858	2.8057	2.5328	0.3183	490	-4.2	10.31
17	**fiqs**	-3.1364	-0.4872	2.6493	2.4896	0.6489	498	-4.2	10.31
18	**fjqs**	-3.1609	-0.6109	2.5500	2.3597	0.5664	525	-4.2	10.31
19	**ghqs**	-3.3625	-0.5595	2.8030	2.5385	0.3417	488	34.1	8.33
20	**giqs**	-3.2058	-0.3076	2.8982	2.5552	0.1977	485	34.1	8.33
21	**gjqs**	-3.2395	-0.6963	2.5432	2.3112	0.5742	536	34.1	8.33
22	**ahrs**	-3.5912	-0.6887	2.9025	2.5847	0.4649	480	60.6	4.33
23	**airs**	-3.4199	-0.4885	2.9313	2.6598	0.6514	466	60.6	4.33
24	**ajrs**	-3.4413	-0.5976	2.8438	2.5671	0.5593	483	60.6	4.33
25	**chrs**	-3.8491	-0.9134	2.9357	2.6134	0.4395	474	83.1	3.78
26	**cirs**	-3.7531	-0.5913	3.1617	2.7906	0.2349	444	83.1	3.78
27	**cjrs**	-3.7196	-0.8282	2.8914	2.5773	0.4885	481	83.1	3.78
28	**bhrs**	-3.4974	-0.7086	2.7888	2.5091	0.5891	494	50.1	6.99
29	**birs**	-3.3976	-0.4975	2.9001	2.5298	0.2984	490	50.1	6.99
30	**bjrs**	-3.4207	-0.6354	2.7853	2.4045	0.2494	516	50.1	6.99
31	**dhrs**	-3.5542	-0.9422	2.6120	2.4553	1.2330	505	68.6	6.39
32	**dirs**	-3.3614	-0.7521	2.6093	2.4342	1.1429	509	68.6	6.39
33	**djrs**	-3.3856	-0.8307	2.5549	2.3703	1.0644	523	68.6	6.39
34	**ehrs**	-3.3611	-0.6017	2.7594	2.4761	0.3877	501	16.6	8.11
35	**eirs**	-3.1911	-0.3939	2.7972	2.5873	0.5605	479	16.6	8.11
36	**ejrs**	-3.2156	-0.4997	2.7159	2.5007	0.4857	496	16.6	8.11
37	**fhrs**	-3.3304	-0.6003	2.7301	2.4749	0.3953	501	-4.2	10.31
38	**firs**	-3.1702	-0.3936	2.7766	2.5758	0.5620	481	-4.2	10.31
39	**fjrs**	-3.1936	-0.5029	2.6906	2.4769	0.4834	501	-4.2	10.31
40	**ghrs**	-3.3967	-0.6667	2.7301	2.4482	0.4004	506	34.1	8.33
41	**girs**	-3.2504	-0.4768	2.7736	2.5473	0.5906	487	34.1	8.33
42	**gjrs**	-3.2654	-0.5736	2.6917	2.4369	0.4660	509	34.1	8.33
43	**akqs**	-3.5863	-0.5688	3.0176	2.6694	0.2794	464	60.6	4.33
44	**alqs**	-3.4087	-0.6125	2.7962	2.5366	0.6158	489	60.6	4.33
45	**amqs**	-3.4120	-0.7398	2.6721	2.3960	0.5374	517	60.6	4.33
46	**ckqs**	-3.8621	-0.7377	3.1245	2.8158	0.2731	440	83.1	3.78
47	**clqs**	-3.7498	-0.4050	3.3448	2.9756	0.1498	417	83.1	3.78
48	**cmqs**	-3.6938	-0.9177	2.7760	2.4765	0.5062	501	83.1	3.78
49	**bkqs**	-3.5553	-0.6547	2.9006	2.5500	0.2975	486	50.1	6.99
50	**blqs**	-3.4375	-0.6533	2.7842	2.3923	0.1952	518	50.1	6.99
51	**bmqs**	-3.4481	-0.7790	2.6691	2.2631	0.1467	548	50.1	6.99

Table 1. Continued

№	Molecule	HOMO	LUMO	Δ	Ee	OS	λ	ΔHf	μ
52	**dkqs**	-3.6301	-0.9354	2.6947	2.5297	1.0599	490	68.6	6.39
53	**dlqs**	-3.4460	-0.7627	2.6833	2.4674	0.9344	502	68.6	6.39
54	**dmqs**	-3.4672	-0.8576	2.6096	2.3826	0.8454	520	68.6	6.39
55	**ekqs**	-3.3432	-0.4736	2.8696	2.5300	0.2336	490	16.6	8.11
56	**elqs**	-3.1729	-0.4986	2.6743	2.4622	0.5538	504	16.6	8.11
57	**emqs**	-3.1846	-0.6291	2.5554	2.3316	0.4831	532	16.6	8.11
58	**fkqs**	-3.3119	-0.4869	2.8250	2.4926	0.2284	497	-4.2	10.31
59	**flqs**	-3.1479	-0.4915	2.6564	2.4706	0.5824	502	-4.2	10.31
60	**fmqs**	-3.1596	-0.6221	2.5375	2.3150	0.4921	536	-4.2	10.31
61	**gkqs**	-3.3908	-0.5342	2.8565	2.5348	0.2473	489	34.1	8.33
62	**glqs**	-3.2390	-0.5717	2.6672	2.4506	0.5865	506	34.1	8.33
63	**gmqs**	-3.2477	-0.7031	2.5446	2.2884	0.503	542	34.1	8.33
64	**akrs**	-3.5999	-0.7594	2.8405	2.5826	0.7386	480	60.6	4.33
65	**alrs**	-3.4781	-0.5043	2.9738	2.5863	0.2092	479	60.6	4.33
66	**amrs**	-3.4413	-0.6612	2.7801	2.4913	0.5407	498	60.6	4.33
67	**ckrs**	-3.8673	-0.9248	2.9425	2.6152	0.3837	474	83.1	3.78
68	**clrs**	-3.7060	-0.7262	2.9798	2.6730	0.6024	464	83.1	3.78
69	**cmrs**	-3.7237	-0.8565	2.8672	2.5546	0.5159	485	83.1	3.78
70	**bkrs**	-3.5531	-0.8315	2.7216	2.4076	0.4561	515	50.1	6.99
71	**blrs**	-3.4400	-0.5862	2.8538	2.4557	0.2079	505	50.1	6.99
72	**bmrs**	-3.4544	-0.6960	2.7584	2.3414	0.1461	530	50.1	6.99
73	**dkrs**	-3.5667	-0.9566	2.6101	2.4375	1.1336	509	68.6	6.39
74	**dlrs**	-3.3761	-0.7632	2.6128	2.4218	1.047	512	68.6	6.39
75	**dmrs**	-3.3965	-0.8470	2.5495	2.3465	0.9584	528	68.6	6.39
76	**ekrs**	-3.3690	-0.6849	2.6841	2.3742	0.3321	522	16.6	8.11
77	**elrs**	-3.1957	-0.4515	2.7442	2.5179	0.5558	492	16.6	8.11
78	**emrs**	-3.2047	-0.5478	2.6569	2.4111	0.4408	514	16.6	8.11
79	**fkrs**	-3.3380	-0.6786	2.6593	2.3820	0.3464	521	-4.2	10.31
80	**flrs**	-3.1895	-0.4107	2.7788	2.4433	0.247	507	-4.2	10.31
81	**fmrs**	-3.1870	-0.5524	2.6346	2.3953	0.4685	518	-4.2	10.31
82	**gkrs**	-3.3761	-0.7646	2.6115	2.3360	0.3567	531	34.1	8.33
83	**glrs**	-3.2327	-0.5339	2.6988	2.4667	0.5582	503	34.1	8.33
84	**gmrs**	-3.2444	-0.6517	2.5927	2.3253	0.4596	533	34.1	8.33
85	**anqs**	-3.6954	-0.9327	2.7627	2.1216	0.0273	584	60.6	4.33
86	**aoqs**	-3.5115	-0.7173	2.7943	2.0430	0.0154	607	60.6	4.33
87	**apqs**	-3.5287	-1.0004	2.5282	1.8445	0.0104	672	60.6	4.33
88	**cnqs**	-3.9263	-1.1408	2.7856	2.1399	0.0018	579	83.1	3.78
89	**coqs**	-3.7898	-0.8824	2.9074	2.0455	0.0106	606	83.1	3.78
90	**cpqs**	-3.8020	-1.1473	2.6547	1.8554	0.0044	668	83.1	3.78
91	**bnqs**	-3.5874	-0.9022	2.6852	2.1332	0.0106	581	50.1	6.99
92	**boqs**	-3.4332	-0.8824	2.5508	2.0455	0.0106	606	50.1	6.99

Table 1. Continued

№	**Molecule**	HOMO	LUMO	Δ	Ee	OS	λ	ΔHf	μ
93	**bpqs**	-3.4636	-1.0306	2.4330	1.8332	0.0279	676	50.1	6.99
94	**dnqs**	-3.7588	-1.1821	2.5767	1.9439	0.0000	638	68.6	6.39
95	**doqs**	-3.5662	-0.9865	2.5796	1.8096	0.0000	685	68.6	6.39
96	**dpqs**	-3.5871	-1.0554	2.5318	1.8400	0.0165	674	68.6	6.39
97	**enqs**	-3.4824	-0.8329	2.6496	2.1373	0.0075	580	16.6	8.11
98	**eoqs**	-3.2890	-0.6055	2.6836	2.0375	0.0223	609	16.6	8.11
99	**epqs**	-3.3475	-0.8900	2.4575	1.7362	0.0000	714	16.6	8.11
100	**fnqs**	-3.4498	-0.8089	2.6408	2.1394	0.0343	580	-4.2	10.31
101	**foqs**	-3.2463	-0.5530	2.6933	2.0770	0.0223	597	-4.2	10.31
102	**fpqs**	-3.3217	-0.8821	2.4396	1.7367	0.0000	714	-4.2	10.31
103	**gnqs**	-3.4933	-0.9039	2.5894	2.1283	0.0429	583	34.1	8.33
104	**goqs**	-3.3491	-0.7284	2.6207	2.0432	0.0325	607	34.1	8.33
105	**gpqs**	-3.3752	-0.9675	2.4077	1.7320	0.0000	716	34.1	8.33
106	**anrs**	-3.6929	-1.0399	2.6531	2.0628	0.0485	601	60.6	4.33
107	**aors**	-3.5360	-0.8269	2.7091	1.9954	0.0358	621	60.6	4.33
108	**aprs**	-3.5716	-0.9229	2.6487	1.8674	0.0093	664	60.6	4.33
109	**cnrs**	-3.9225	-1.2656	2.6569	2.0729	0.0008	598	83.1	3.78
110	**cors**	-3.8001	-0.9931	2.8070	2.0009	0.0223	620	83.1	3.78
111	**cprs**	-3.8132	-1.1663	2.6468	1.8589	0.0099	667	83.1	3.78
112	**bnrs**	-3.5512	-0.9857	2.5655	2.0801	0.0067	596	50.1	6.99
113	**bors**	-3.4413	-0.8503	2.5911	1.9767	0.0643	627	50.1	6.99
114	**bprs**	-3.4656	-0.9585	2.5070	1.9481	0.0747	636	50.1	6.99
115	**dnrs**	-3.6891	-1.1957	2.4934	1.9951	0.0000	621	68.6	6.39
116	**dors**	-3.4963	-0.9972	2.4991	1.8606	0.0000	666	68.6	6.39
117	**dprs**	-3.5224	-1.0801	2.4423	1.8335	0.0000	676	68.6	6.39
118	**enrs**	-3.4925	-0.9797	2.5127	2.0462	0.0664	606	16.6	8.11
119	**eors**	-3.3072	-0.7265	2.5807	1.9869	0.0431	624	16.6	8.11
120	**eprs**	-3.3679	-0.8372	2.5307	1.8654	0.0064	665	16.6	8.11
121	**fnrs**	-3.4824	-1.0377	2.4447	1.9153	0.0000	647	-4.2	10.31
122	**fors**	-3.2866	-0.8408	2.4458	1.7822	0.0000	696	-4.2	10.31
123	**fprs**	-3.3494	-0.8337	2.5157	1.8679	0.0076	664	-4.2	10.31
124	**gnrs**	-3.5015	-1.0469	2.4545	2.0470	0.0841	606	34.1	8.33
125	**gors**	-3.3619	-0.8013	2.5606	2.0022	0.0024	619	34.1	8.33
126	**gprs**	-3.3951	-0.9166	2.4785	1.8602	0.0080	667	34.1	8.33

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 minimum excitations has 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.[26, 27]

Preliminary, the capability of the DFT B3LYP 6-311G(d,p) features was tested using 18 molecules with experimentally measured wavelengths[28-35] under the same conditions in dichloromethane solutions. The molecules are the benzo[1,2,5]thiadiazole derivatives which are the D–A–π–A' analogs to the molecules studied in the current paper. A good agreement between calculated and experimental wavelengths was shown. The correlation coefficient between calculated and experimental wavelengths is 0.955 and the standard error of wavelength estimation is 19 nm. Therefore, the validity of the accepted level of theory for the study of UV-Vis properties was shown.

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	2.537 ± 0.048	2.404 ± 0.032
Wavelength, nm	489.5 ± 7.9	489.7 ± 8.5	516.4 ± 6.9

Statistical analysis of the calculated characteristics shows that A-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. Analogously, the mean value of HOMO energy of [1,2,5]oxadiazolo[3,4-*d*]pyridazine derivatives is substantially lower than that for [1,2,5]thiadiazolo[3,4-*d*]pyridazine and [1,2,5]selenadiazolo[3,4-*d*]pyridazine derivatives (Table 3) while the HOMO energies of [1,2,5]thiadiazolo[3,4-*d*]pyridazine and [1,2,5]selenadiazolo[3,4-*d*]pyridazine derivatives are statistically comparable. So, it is not surprising that the presence of an element of higher periods (S, Se) in the heterocyclic A-block increases the HOMO level that in its turn facilitates a bathochromic shift in the UV-Vis spectra. The LUMO energies behave unusually in a sequence O, S, Se: their mean values for [1,2,5]oxadiazole and [1,2,5]selenadiazole derivatives are statistically comparable, but substantially lower than that for [1,2,5]thiadiazole derivatives (Tables 3, 4) both for the condensed pyridines and pyridazines that should provide a red shift in the UV-Vis spectra for O and Se containing A-blocks. Thus, a substitution of oxygen by sulfur in a A-block yields in increase of both HOMO and LUMO levels while the substitution by selenium leads to increase of only HOMO energy at an approximately constant LUMO energy. Therefore, the reduction of the excitation energy and correspondingly a bathochromic shift can be predicted certainly for [1,2,5]selenadiazole derivatives summarizing the findings on the HOMO and LUMO energies. It should be noted that the spread of energies and wavelengths for the pyridazine derivatives is more than twice greater than for the pyridine derivatives.

Table 3. Mean values and confidence intervals of quantum characteristics for [1,2,5]oxadiazolo[3,4-*d*]pyridazine (X = O, Scheme 1), [1,2,5]thiadiazolo[3,4-*d*]pyridazine (X = S) and [1,2,5]selenadiazolo[3,4-*d*]pyridazine (X = Se) derivatives

Characteristic	X = O	X = S	X = Se
HOMO energy, eV	-3.63 ± 0.16	-3.46 ± 0.17	-3.49 ± 0.16
LUMO energy, eV	-1.02 ± 0.14	-0.81 ± 0.14	-0.98 ± 0.11
Δ, eV	2.61 ± 0.11	2.64 ± 0.13	2.516 ± 0.083
Excitation energy, eV	2.069 ± 0.074	1.979 ± 0.093	1.834 ± 0.061
Wavelength, nm	600 ± 22	628 ± 31	677 ± 23
Q_{π}	-0.159 ± 0.033	-0.122 ± 0.044	-0.125 ± 0.048
Q_{DA}	0.117 ± 0.029	0.101 ± 0.032	0.106 ± 0.035
$Q_{\pi-A'}$	0.042 ± 0.015	0.021 ± 0.025	0.019 ± 0.025

Table 4. Mean values and confidence intervals of quantum characteristics for the [1,2,5]oxadiazolo-, [1,2,5]thiadiazolo-, [1,2,5]selenadiazolo- pyridine (Y = CH, Scheme 1) and pyridazine (Y = N) derivatives

Characteristic	Y = N1	Y = N2
HOMO energy, eV	-3.42 ± 0.19	-3.53 ± 0.18
LUMO energy, eV	-0.55 ± 0.15	-0.94 ± 0.15
Δ, eV	2.77 ± 0.15	2.60 ± 0.13
Excitation energy, eV	2.49 ± 0.12	1.97 ± 0.14
Wavelength, nm	499 ± 24	632 ± 45
Q_{A}	-0.111 ± 0.026	-0.185 ± 0.033
Q_{D}	0.095 ± 0.025	0.135 ± 0.028
$Q_{\pi-A'}$	0.016 ± 0.020	0.050 ± 0.015

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 smaller on average by 0.10 – 0.15 eV and the excitation energy – by 0.13 – 0.23 eV. At the same time, the [1,2,5]oxadiazolo and [1,2,5]thiadiazolo derivatives are statistically comparable in these characteristics (Tables 3, 4). Obviously, that the mean value of wavelength for selenium containing compounds is greater than that for others. The bathochromic shift for selenium containing compounds relatively to other is approximately 26 nm for the pyridine derivatives and 49 – 77 nm for the pyridazine derivatives. [1,2,5]Selenadiazolo[3,4-*d*]pyridazine derivative 105 in Table 1 (**gpqs**) possesses the maximal value of the wavelength 716 nm among the designed molecules. The minimal value of the wavelength 417 nm is observed for the [1,2,5]thiadiazolo[3,4-*c*]pyridine derivative 47 (**clqs** in Table 1).

In general, all the elucidated quantum characteristics differ significantly for pyridine and pyridazine containing compounds (Table 4). The presence of an extra nitrogen in the pyridazine containing molecules compared to pyridine containing ones reduces both HOMO and LUMO levels but the latter is decreased stronger. Then, it yields to a reduction of the LUMO-HOMO gap and in turn to an excitation energy reduction, and a red shift in UV-Vis spectra. This is not a surprise since the additional nitrogen allows an additional low energy n – π* transition. Moreover, a pyridazine ring actually is a cyclic azo compound. The majority of this class of organic substances possesses good chromophoric properties.

The analysis of the influence of π–A'-block shows that there are no overall effect on the whole set of the designed molecules but separately for [1,2,5]oxadiazolo and [1,2,5]selenadiazolo derivatives the effects were found. For [1,2,5]oxadiazolo[3,4-*c*] derivatives the π–A'-block have no significant influence on the HOMO energy, but the compounds with thienyl bridge in π–A'-block (**rs** fragment) possess less value of LUMO energy than the compounds with phenyl bridge (**qs** fragment) on average by 0.14 eV that reduces the gap between LUMO and HOMO, excitation energy and correspondingly provides a bathochromic shift in UV-Vis spectra. Actually, the mean values of the gap between LUMO and HOMO for the compounds with thienyl bridge in π–A'-block (**rs** fragment) is smaller than that for the compounds with phenyl bridge (**qs** fragment) on average by 0.14 eV, the excitation energy is smaller on average by 0.10 eV and the wavelength is greater on average by 23 nm. The mean value for the [1,2,5]selenadiazolo[3,4-*c*] derivatives with phenyl bridge is 516 nm while for the compounds with thienyl bridge the mean value is 538 nm.

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

π–A'-block have no significant influence on the HOMO and LUMO energies of [1,2,5]selenadiazolo[3,4-*c*] derivatives, but in a contrast to [1,2,5]oxadiazolo[3,4-*c*] derivatives the compounds with thienyl bridge in π–A'-block (**rs** fragment) possess greater gap between LUMO and HOMO than the compounds with phenyl bridge (**qs** fragment) on average by 0.08 eV that provides an increase of excitation energy and correspondingly provides a hypsochromic shift in UV-Vis spectra. The excitation energy greater on average by 0.07 eV and the wavelength is smaller on average by 20 nm. The mean value for the [1,2,5]selenadiazolo[3,4-*c*] derivatives with phenyl bridge is 580 nm while for the compounds with thienyl bridge the mean value is 560 nm.

No significant dependency of the HOMO and LUMO energies, the excitation energy and the wavelength on the quantum derived characteristics of D-block and on the substitution type in the A-block (**h**, **i**, **j** or **k**, **l**, **m** in Scheme 2) is observed, so the calculation of more than 500 descriptors was performed using ChemoSophia on-line software (www.chemosophia.com)[28] both for whole molecules (molecules 1 – 126 in Table 1) and for D-blocks (building blocks **a** – **g** in Scheme 2) in radical state.

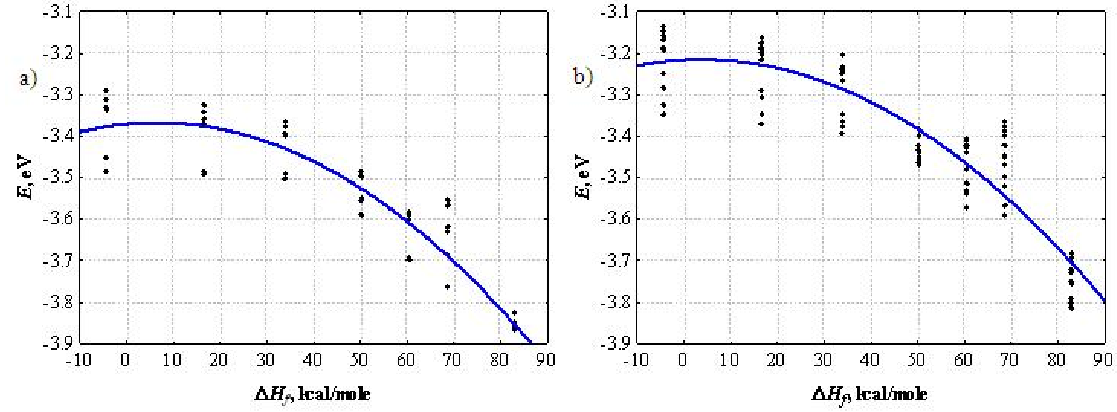


Figure 1. Relationships between ΔH_f (ChemoSophia Elastic Model) and *E* (DFT B3LYP 6-311G(d,p)): a) for [1,2,5]oxadiazolo derivatives; b) for [1,2,5]thiadiazolo[3,4-*c*] and [1,2,5]selenadiazolo derivatives.

Analysis of the descriptors showed that the HOMO energy has relationships with enthalpy of formation (ΔH_f) of D-blocks calculated within ChemoSophia Elastic Model[28] but separately for [1,2,5]oxadiazolo derivatives and for [1,2,5]thiadiazolo/[1,2,5]selenadiazolo derivatives. The enthalpies of formation for D-blocks are represented in Table 5. The relationships are shown in Fig. 1 and can be described using polynomial equation

$$E = a_0 + a_1 \Delta H_f + a_2 \Delta H_f^2 \qquad (\mathbf{1})$$

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

Table 5. Enthalpies of formation for D-blocks

D-block	ΔH_f, kcal/mole
a	60.6
b	50.1
c	83.1
d	68.6
e	16.6
f	-4.2
g	34.1

For [1,2,5]oxadiazolo derivatives the cofficients in the equation (1) are a_0 = -3.3709; a_1 = 1.071•10^{-3} and a_2 = -8.270•10^{-5}. The correlation coefficient R = 0.936; the standard deviation S = 0.036.

For [1,2,5]thiadiazolo and [1,2,5]selenadiazolo derivatives the coefficients in the equation (1) are a_0 = -3.2164; a_1 = 5.765•10^{-4} and a_2 = -7.765•10^{-5}. The correlation coefficient R = 0.918; the standard deviation S = 0.059.

Thus the values of a_0 and a_2 coefficients for [1,2,5]oxadiazolo, [1,2,5]thiadiazolo and [1,2,5]selenadiazolo derivatives coincide. So, the only difference in equations is the terms a_1 that means the slope of the curve varies by half but the curvatures for [1,2,5]thiadiazolo / [1,2,5]selenadiazolo derivatives and for [1,2,5]oxadiazolo derivatives and the beginning of the relationships are the same. Fig. 1 and equation (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 5 shows that the lower values are the characteristic feature of D-blocks (**e**, **f**, **g**) we proposed. These building blocks include alkylic and alicyclic components in their structure. Thus, the D-blocks (**e**, **f**, **g**) containing organic sensitizers should be more prospective than earlier proposed D-blocks (**a**, **c**, **b**, **d**). Actually, the **e**, **f**, **g** containing compounds possess greater HOMO energy on average 0.28 eV and LUMO energy on average 0.17 eV, smaller mean gap between LUMO and HOMO on average 0.11 eV, smaller mean excitation energy on average 0.05 eV and greater wavelength on average 11 nm than that for **a**, **c**, **b**, **d** containing compounds.

Additionally, correlations between HOMO energy and dipole moment of D–blocks calculated within ChemoSophia Elastic Model are observed. The greater polarity of the blocks provides the greater HOMO energy (the correlation coefficients 0.86, 0.86 and 0.83 for [1,2,5]oxadiazolo, [1,2,5]thiadiazolo and [1,2,5]selenadiazolo derivatives, correspondingly). The mean value of the dipole moment of **e**, **f**, **g** containing compounds (8.9 Debye) is greater than that for **a**, **c**, **b**, **d** 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 (**dhrs**) possesses the maximum value of the oscillator strength 1.233 among the designed molecules. Generally, the largest oscillator strengths are observed for the pyridine derivatives with completely planar D–

block (**c** and **d** fragments). The mean value of the oscillator strengths for the pyridine derivatives with **c** or **d** fragments is 1.02 ± 0.12 while for other pyridine derivatives, the mean value of the oscillator strengths is 0.42 ± 0.15. Moreover, the diapasons of oscillator strengths for **c** and **d** containing pyridine derivatives and for all other do not intersect. The minimal value of oscillator strength among **c** and **d** containing pyridine derivatives is 0.7999 (molecule 10 **dhqs** in Table 1) while maximal value of oscillator strength among all other molecules is 0.7386 (molecule 64, **akrs** in Table 1). The planar structure of the D–block of **c** and **d** containing molecules provides in turn the greater planarity and the minimal deviation from π-plane of the A-block for the whole **c** and **d** containing molecules. So, the standard deviation of atoms from π-plane of the A-block for the whole **c** and **d** containing pyridine derivatives is 4.94 ± 0.14 Å while for the other molecules, the standard deviation is 6.73 ± 0.42 Å. Additionally the D-block **d** contains the minimal number of electrono-poor atoms (hydrogens) among all D-blocks that provides stronger electron donor property. Therefore, it is necessary to find more planar D-blocks containing minimal number of hydrogens for the design of novel prospective organic sensitizers with the maximal oscillator strength.

Correlation and regression analysis of quantum calculations results

It is interesting to study the effect of each component on the overall electron structure of D–A–π–A' organic sensitizers. For this aim, the sums of Mulliken atomic charges derived from the DFT B3LYP 6-311G(d,p) computations of the whole molecules (see above item) were calculated separately for each component, i.e.

$$Q_A = \sum_{i \in A} q_i$$

$$Q_D = \sum_{j \in D} q_j$$

$$Q_{\pi-A'} = \sum_{k \in \pi-A'} q_k$$

where Q_A, Q_D and $Q_{\pi-A'}$ are the charges of A-, D- and π–A'-blocks, correspondingly; where q_i ' q_j and q_k are the Mulliken atomic charges for the atoms belonging to A-, D- and π–A'-blocks, correspondingly.

It was found that all the D-blocks are actually electron donors. No one of the D-blocks has negative charge. The charges of these blocks for all molecules are in the range 0.041 – 0.186 e. It is interesting that most of π–A'-blocks are also positively charged despite the fact that they include A'-block which is usually considered as acceptor. Only 19 of 126 compounds possess a weak negative charge in π–A'-block. The minimal value is only -0.022 e (molecule **djqs**, Table 1). The negative charges are observed only for some [1,2,5]thiadiazolo and [1,2,5]selenadiazolo derivatives. Generally, the charge of π–A'-block lies in the range -0.022 – 0.087 e (mean value is 0.027). Therefore, the π–A'-block rather donor than acceptor, contrary to traditional views. All the A-blocks are negatively charged and their charges are in the range -0.251 – -0.066 e. So, the A-blocks display distinct electron acceptor properties.

Certainly, the most electron acceptor properties are the characteristic feature of oxygen containing A-blocks (X = O, Scheme 1). The mean value of their π-blocks charges is -0.159 ± 0.034 e (Table 3). The mean values of A-, D- and π–A'-blocks charges for [1,2,5]thiadiazolo (X = S) and [1,2,5]selenadiazolo (X = Se) derivatives are comparable (see Table 3) and can be averaged. The mean value of their A-blocks charges is -0.124 ± 0.046 e. The mean value of D-blocks charge for [1,2,5]oxadiazolo derivatives is 0.117 ± 0.029 e while the mean value of D-blocks charge for [1,2,5]thiadiazolo and [1,2,5]selenadiazolo derivatives is slightly lesser and ranges 0.104 ± 0.033 e. The mean value of π–A'-blocks charge for [1,2,5]oxadiazolo derivatives is 0.041 ± 0.015 e. The mean value of π–A'-blocks charge for [1,2,5]thiadiazolo and [1,2,5]selenadiazolo derivatives is also slightly lesser and ranges 0.020 ± 0.025 e. Therefore, the oxygen containing heterocycles in the A-block pulls electron density both from D-block and from π–A'-blocks but this phenomenon is more noticeable for the D-blocks.

It should be noted that the heteroatom Y (Scheme 1) has an even greater impact on the electronic structure of the sensitizers that is not surprising, because Y is much closer to the substituents D and π–A' than heteroatom X. The charges of D-, A- and π–A'-blocks for pyridine (Y = CH) and pyridazine (Y = N) derivatives are represented in Table 4. The negative charge of A-blocks for pyridazine derivatives almost twice as much as that for pyridine derivatives. Consequently, the positive charge of D and π–A'-blocks of pyridazine derivatives significantly greater than that for pyridine derivatives.

Table 6. Correlation coefficients matrix for Mulliken partial charges of A-, π–A'-, D-blocks (Q_A, $Q_{\pi–A'}$, Q_D, correspondingly) and atoms of A-block (q_{N7}, … , q_{N5})

	q_{N7}	q_{C6}	q_{C3}	q_{C4}	q_{C9}	q_Y	q_{N2}	q_X	q_{N5}	Q_π	$Q_{\pi–A'}$	Q_{DA}
q_{N7}	1.000	-0.083	-0.181	-0.735	0.994	-0.985	0.093	-0.056	0.110	-0.776	0.710	0.550
q_{C6}	-0.083	1.000	-0.272	-0.065	-0.150	0.193	0.453	-0.455	0.451	0.013	-0.085	0.045
q_{C3}	-0.181	-0.272	1.000	0.762	-0.156	0.111	-0.433	0.388	-0.432	0.203	-0.326	-0.039
q_{C4}	-0.735	-0.065	0.762	1.000	-0.730	0.701	-0.300	0.249	-0.311	0.618	-0.611	-0.403
q_{C9}	0.994	-0.150	-0.156	-0.730	1.000	-0.989	0.079	-0.043	0.095	-0.777	0.705	0.555
q_Y	-0.985	0.193	0.111	0.701	-0.989	1.000	-0.000	-0.034	-0.018	0.770	-0.656	-0.581
q_{N2}	0.093	0.453	-0.433	-0.300	0.079	-0.000	1.000	-0.998	0.999	-0.380	0.441	0.199
q_X	-0.056	-0.455	0.388	0.249	-0.043	-0.034	-0.998	1.000	-0.997	0.357	-0.407	-0.192
q_{N5}	0.110	0.451	-0.432	-0.311	0.095	-0.018	0.999	-0.997	1.000	-0.395	0.452	0.212
Q_π	-0.776	0.013	0.203	0.618	-0.777	0.770	-0.380	0.357	-0.395	1.000	-0.719	-0.854
$Q_{\pi–A'}$	0.710	-0.085	-0.326	-0.611	0.705	-0.656	0.441	-0.407	0.452	-0.719	1.000	0.253
Q_{DA}	0.550	0.045	-0.039	-0.403	0.555	-0.581	0.199	-0.192	0.212	-0.854	0.253	1.000

It is interesting to elucidate the mutual influence of atoms within A-block and with π–A'- and D- blocks in the organic sensitizers. The correlation coefficients matrix for Mulliken partial charges of A-, π–A'-, D- blocks (Q_A, $Q_{\pi–A'}$, Q_D, correspondingly) and atoms of A-block (q_{N7}, q_{C6}, q_{C3}, q_{C4}, q_{C9}, q_Y, q_{N2}, q_X, q_{N5}) were calculated and presented in Table 6. Analyzing Table 6 it should be noted that heteroatom X has a significant influence only on the closest neighbors, i.e. atoms N2 and N5. The correlation coefficients (*R*) for the dependencies q_X – q_{N2} and q_X – q_{N5} are -0.998 and -0.997, correspondingly. Minus sign indicates that the increase in the charge of X leads to a reduction of N2 and N5 charges. The correlation coefficients of X charge dependency with the charges of other atoms and blocks are less than 0.5 that indicates a weak dependency of their charges on the charge of X heteroatom. Atom Y also has a significant effect on the closest neighbors, i.e. C9 and N7 atoms (correlation coefficients are -0.989 and -0.985, correspondingly) but its influence extends to the atom C4 (*R* = 0.701). Here we can see an alternation effect: increase in the charge of Y leads not only to a reduction of the closest neighbors

C9 and N7 charges (negative *R*) but also to an increase of the next C4 charge (positive *R*). Moreover, the charge of whole A-block also correlates with q_Y, q_{C9} and q_{N7} (*R* = 0.770, -0.777 and -0.776, correspondingly). Therefore, this fragment determines mostly the charge of A-block. Additionally, the charges of these atoms have a correlation with the π–A'-block charge (*R* = -0.656, 0.705 and 0.710). So, this fragment is responsible for electron transfer between A- and π–A'-blocks. It draws an attention that the A-block charge has a significant dependency on the D-blocks charge. The dependency is shown in Fig. 2. The figure shows that the positive charge of D-blocks is linearly related with the negative charge of A-blocks that confirms the electron donor properties of the D-blocks. The correlation coefficient for this dependency is -0.854. The dependency of A-blocks charge on the charge of π–A'-blocks is weaker (*R* = -0.719). Minus sign in the both dependencies indicates that the A-block attracts electron density from both D- and π–A'-blocks, but more strongly from the first one.

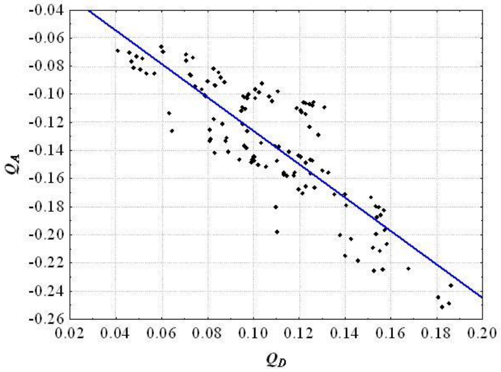


Figure 2. Dependency of A-block charge (Q_A) on the D-block charge (Q_D).

A multiple regression analysis of charges of X, Y atoms, D- and π–A'-blocks was performed for more detailed description of mutual influence of the organic sensitizers' atoms and fragments. So, the Mulliken partial charge of X heteroatom is dependent on the charges of N2, C6, N7 and N5 atoms (and vice versa their charges are dependent on the charge of X heteroatom) in accordance with the following equation.

$$q_X = -0.1073 - 1.23\cdot q_{N2} - 2.25\cdot q_{C6} + 0.207\cdot q_{N7} - 1.17\cdot q_{N5} \qquad (\mathbf{2})$$

This equation and the following equations were obtained using "Backward Stepwise" techniques. Correlation coefficient *R* = 0.9989; Standard error of estimate S = 0.0067. The terms in this equation and the following equations are arranged in descending order of their statistical significance. The equation shows that the increase of X heteroatom partial charge yields in the decrease of N2, C6 and N5 charges and in weak increase of N7 charge. Each coefficient shows an influence of each atom on X heteroatom (and conversely, an influence of X heteroatom on the atoms). So, the increase in the N2 charge by 0.1 yields in decrease of q_X by 1.23·0.1 = 0.123. So the equation shows a comparable influence of X heteroatom on neighboring N2 and N5 atoms decreasing their charge, stronger effect on C6 atom and a weak increase of N7 charge due to decrease of neighboring C6 electron density.

The dependence of q_Y is much more extensive

$$q_Y = -0.453 - 1.543\cdot q_{N7} + 1.02\cdot q_{C6} - 0.141\cdot Q_D + 0.0201\cdot q_{N5} + 0.0200\cdot q_{N2} - 3.15\cdot q_{C3} + 3.09\cdot q_{C4} \qquad (\mathbf{3})$$

R = 0.9956; S = 0.0070.

An increase of Y charge leads to decrease of the neighboring N7 charge and then to increase of the next C6 charge, decrease of the next C3 charge and increase of the next C4 charge. Thus, there is a pronounced charges alternation effect. C3 and C4 atoms are exposed to a particularly strong and almost the same influence of Y. N2 and N5 atoms are far from Y and exposed to a weak and almost the same influence of Y. There are no terms with C9 atom whose charge is apparently determined not only by Y but also by substituent R’. At the same time, some influence of Y to the D-block is observed yielding in an attraction of the electron density from the latter to Y.

π–A’-block has lesser influence (as can be seen by the lesser correlation coefficient) on the A-block which can by described by the following equation

$$Q_{\pi-A'} = 0.296 + 0.503\cdot q_{N7} + 0.075\cdot q_{N2} + 0.075\cdot q_{N5} - 0.208\cdot Q_D - 1.13\cdot q_{C6} \quad \mathbf{(4)}$$

$R = 0.866$; S = 0.012.

An increase of the electron density of π–A’-block leads to an attraction of the electron density from neighboring C6 and to an increase of all the A-block’s nitrogens electron density (a strong increase for N7 and the weak and approximately equal for N2 and N5). Moreover, π–A’-block provides some attraction of the electron density from D-block.

There is no a regularity of the influence of D-block on the atoms of A-block or on the π–A’-block of the pyridazine derivatives (Y = N, molecules 85 – 126 in Table 1) but it has a significant influence on the atoms of A-block and on the π–A’-block of pyridine derivatives (Y = CH, molecules 1 – 84 in Table 1) describing by the following equation

$$Q_D = 0.040 - 0.74\cdot q_{N7} - 0.884\cdot q_X - 1.170\cdot Q_{\pi-A'} - 1.39\cdot q_Y - 1.51\cdot q_{C6} - 1.219\cdot q_{N5} - 1.69\cdot q_{C4} - 1.31\cdot q_{C9} - 0.487\cdot q_{N2} \quad \mathbf{(5)}$$

$R = 0.9928$; S = 0.0021.

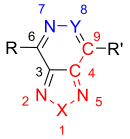
The equation shows that D-block strictly donates the electron density to the atoms of A-block and to the π–A’-block since all the terms except the free term of the equation are negative, i.e. the decrease of D-block electron density yields in the increase of N7, X, Y, C6, N5, C4, C9, N2 electron density. Moreover, D-block donates the electron density to the π–A’-block that is in agreement with the above mentioned results. Only one atom C3 has no any regularities of the influence on the charge of D-block.

More important question allowing to obtain a key for the further design of prospective organic sensitizers: how the charge characteristics of atoms and fragments are related to the energy and spectral characteristics? The regression analysis reveals no significant relationship between the HOMO energy and charges of atoms and fragments. At the same time, the regression equation for the LUMO energy shows the good statistical characteristics

$$\mathrm{LUMO} = 1.27 - 6.1\cdot q_{C9} - 50.8\cdot q_{C4} - 16.8\cdot q_{N2} - 12.01\cdot q_X + 5.35\cdot q_Y + 11.2\cdot q_{N7} - 13.2\cdot q_{N5}$$

$R = 0.943$; S = 0.070.

In accordance with the regression model an increase of the C9, C4, N2, X and N5 (red in Scheme 3) charges leads to decrease of the LUMO energy that can provide a red shift in UV-Vis spectra, while an increase of the Y and N7 (blue in Scheme 3) charges leads to increase of the LUMO energy. In accordance with Equation (3) the increase of C6, N2, N5 charge and decrease of N7 charge can be reached by increase of Y charge (i.e. using less electronegative X). The charge of π–A’-block has a contradictory impact on these atoms in accordance with other Equations (2), (4) and (5).



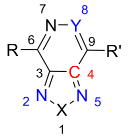
Scheme 3. Influence of atoms on LUMO energy.

In accordance with the regression model an increase of only C4 (red in Scheme 4) charge leads to decrease of excitation energy that provides the red shift in UV-Vis spectra, while an increase of the Y, N2 and N5 (blue in Scheme 4) charges leads to increase of excitation energy. It should be noted that a decrease of the N2 and N5 charge can be achieved by increase of X charge in accordance with Equation (2). Thus, the less electronegative X the less excitation energy. So, the usage of X = S or Se is preferable rather than O. In accordance with Equation (4), a The excitation energy can be described using the following regression model

$$E_e = 4.33 + 6.54 \cdot q_Y - 16.4 \cdot q_{C4} + 2.11 \cdot q_{N2} + 2.10 \cdot q_{N5}$$

R = 0.951; S = 0.088.

decrease of N2 and N5 charge can be achieved by a decrease of π–A'-block charge (i.e. using π–A'-block with the strengthened acceptor properties). Other Equations (3) and (5) show contradictory impact on these atoms.



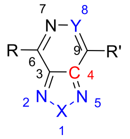
Scheme 4. Influence of atoms on the excitation energy.

The wavelength in UV-Vis spectra can be described using the following regression model

$$\lambda = 138 - 1151 \cdot q_Y + 2490 \cdot q_{C4} - 1050 \cdot q_{N5} - 1040 \cdot q_{N2} - 850 \cdot q_X$$

R = 0.959; St.Err. = 21.

In accordance with the regression model the increase of only C4 (red in Scheme 5) charge leads to the batochromic shift in UV-Vis, while an increase of the Y, N5, N2 and X charges (blue in Scheme 5) leads to decrease of wavelength. All these atoms Y, C4, N5, N2 and X determining wavelength can be confirmed as a chromophoric fragment of these organic sensitizers. It should be noted that the decrease of the Y, N5, N2 and X charges can be achieved by an increase of D-block charge in accordance with Equation (5). Thus, the increase of the donor properties of D-blocks yields in the desirable changes in the charges. In accordance with Equation (4) the decrease of N2 and N5 charge can be achieved by decreasing of π–A'-block charge (i.e. using π–A'-block with the strengthened acceptor properties). Other Equations (2) and (3) show contradictory impact on these atoms since an increase of X or Y charge yields in decrease of N2 and N5 charges.



Scheme 5. Influence of atoms on the UV-Vis spectra.

The weaker dependency was obtained for oscillator strength

$$OS = -0.62 - 8.05 \cdot q_{N7} + 3.28 \cdot Q_D - 11.4 \cdot q_{C6}$$

R = 0.849; S = 0.16.

At the same time this dependency is the best obtained for the oscillator strength. In accordance with the regression model, an increase of D-block charge leads to increase of the oscillator strength, while increase of the N7 and C6 charges leads to decrease of the oscillator strength. It should be noted that the decrease of the N7 and C6 charge along with an increase of D-block charge can be achieved by increase of the donor properties of D-block in accordance with Equation (5). Other equations show contradictory impact on these atoms and block.

This methodology performing a **C**orrelation and **R**egression **A**nalysis of **Q**uantum **C**alculations results was named CRAQC techniques.

Conclusions

Thus, a molecular design and theoretical study of novel prospective organic sensitizers based on D–A–π–A' concept has been fulfilled. Like in previous researches, it has been shown that the A-block plays a key role for the wavelength shift in UV-Vis spectra, also we have shown that a presence of an element of higher periods of the Periodic System in the A-block provides noticeable bathochromic shift. This study determines that the thienyl bridge in the π–A'-block provides 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 π-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 π–A'-block is observed for [1,2,5]thiadiazolo[3,4-*c*]pyridine derivatives. The maximal wavelengths values have been observed for D-blocks with aliphatic and alicyclic fragments we proposed. It has been shown in the study that the reduction of the enthalpy of formation and increase of polarity of D-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-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-block while the first presupposes an existence of non-planar aliphatic and/or alicyclic fragments in D-block. Thus, the next steps for the molecular design of novel prospective organic sensitizers should include some combination of these concepts. Correlation and Regression Analysis of Quantum Calculations results (CRAQC techniques) has been invented. Mutual influences of blocks, fragments and atoms in the molecules and their influence on the energy and spectral properties of organic sensitizers are studied using the CRAQC. A method for determining of chromophoric fragments has been proposed. It has been shown that the wavelengths for the elucidated organic sensitizers is determined by Y, C4, N5, N2 and X atoms while the oscillator strengths is determined by N7, C6 atoms and D-block. It allowed to pick up an additional factor – donor properties of D-block permitting to increase both wavelength and oscillator strength.

Acknowledgements

This work was supported by Act 211 Government of the Russian Federation, contract № 02.A03.21.0011, by the Russian Science Foundation (grant No. 15-13-10022) and by Ministry of Education and Science of Russian Federation (grants No. 4.7279.2017/BP, 4.9651.2017/BP, and No 4.8298.2017/BP).

References

1. Rees, C. W. *J. Heterocycl. Chem*. **1992**, *29*, 639-651.
https://doi.org/10.1002/jhet.5570290306
2. Rakitin, O. A. *Arkivoc* **2009**, 129-149.
http://dx.doi.org/10.3998/ark.5550190.0010.105
3. Rakitin, O. A. *Russ. Chem. Rev*. **2011**, *80*, 647-659.
https://doi.org/10.1070/RC2011v080n07ABEH004190
4. Konstantinova, L. S.; Knyazeva, E. A.; Rakitin, O. A. *Org. Prep. Proc. Int*. **2014**, *46*, 475-544.
https://doi.org/10.1080/00304948.2014.963454
5. Robertson, N. *Angew Chem Int. Ed. Engl.* **2006**, *45*, 2338–2345.
https://doi.org/10.1002/anie.200503083
6. Hagfeldt, A; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. *Chem. Rev.* **2010**, *110*, 6595–6663.
https://doi.org/10.1021/cr900356p
7. Wu, Y. Z.; Zhu, W. H. *Chem. Soc. Rev.* **2013**, *42*, 2039-2058.
https://doi.org/10.1039/C2CS35346F
8. Wu, Y. Z.; Zhu, W. H., Zakeeruddin, S. M.; Grätzel, M. *ACS Appl. Mater. Interfaces* **2015**, *7*, 9307-9318.
https://doi.org/10.1021/acsami.5b02475
9. Knyazeva, E. A.; Rakitin, O. A. *Russ. Chem. Rev.* **2016**, *85*, 1146-1183.
https://doi.org/10.1070/RCR4649
10. Ljichi, K.; Fujiwara, M.; Nagano, H. *Antiviral Res*. **1996**, *31*, 87-94.
https://doi.org/10.1016/0166-3542(96)00950-3
11. Rai, D.; Chen, W.; Zhan, P. *Chem. Biol. Drug Des* **2014**, *84*, 420-430.
https://doi.org/10.1111/cbdd.12328
12. Ismail, Z. H.; Ghorab, M. M.; Mohamed, E. M. A.; Aly, H. M.; El-Gaby, M. S. A. *Phosphorus Sulfur and Silicon and the Related Elements* **2008**, *183*, 2541-2554.
https://doi.org/10.1080/10426500801967815
13. Huang, X. C.; Zheng, J. S.; Chen, T. F. *et al*. *Chemical Journal of Chinese Universities* **2012**, *33*, 976-982.
14. Pushkarevsky, N. A.; Lonchakov, A. V.; Semenov, N. A. *et al. Synth. Met.* **2012**, *162*, 2267-2276.
https://doi.org/10.1016/j.synthmet.2012.10.026
15. Semenov, N. A.; Pushkarevsky, N. A.; Suturina, E. A. *et al. Inorg. Chem.* **2013**, *52*, 6654-6663.
https://doi.org/10.1021/ic400659q
16. Konstantinova, L. S.; Knyazeva, E. A.; Obruchnikova, N. V. *et al*. *Tetrahedron Lett*. **2013**, *54*, 3075-3078.
https://doi.org/10.1016/j.tetlet.2013.03.134
17. Lonchakov, A. V.; Rakitin, O. A.; Gritsan, N. P.; Zibarev, A. V. *Molecules* **2013**, *18*, 9850-9900.
https://doi.org/10.3390/molecules18089850

18. Konstantinova, L. S.; Knyazeva, E. A.; Obruchnikova, N. V. *et al*. *Tetrahedron* **2014**, *70*, 5558-5568. https://doi.org/10.1016/j.tet.2014.06.096
19. Pushkarevsky, N. A.; Semenov, N. A.; Dmitriev, A. A. *et al*. *Inorg. Chem*. **2015**, *54*, 7007-7013. https://doi.org/10.1021/acs.inorgchem.5b01033
20. Konstantinova, L. S.; Knyazeva, E. A.; Nefyodov, A. A. *et al*. *Tetrahedron Lett.* **2015**, *56*, 1107-1110. https://doi.org/10.1016/j.tetlet.2015.01.106
21. Svec, J.; Zimcik, P.; Novakova, L. *et al*. *Eur. J. Org. Chem.* **2015**, 596-604. https://doi.org/10.1002/ejoc.201403329
22. Konstantinova, L. S.; Bobkova, I. E.; Nelyubina, Y. V.; *et al*. *Eur. J. Org. Chem*. **2015**, 5585-5593. https://doi.org/10.1002/ejoc.201500742
23. Konstantinova, L. S.; Knyazeva, E. A.; Rakitin, O. A. *Molecules* **2015**, *20*, 14522-14532. https://doi.org/10.3390/molecules200814522
24. Ying, W.; Zhang, X.; Li, X, *et al*. *Tetrahedron* **2014**, *70*, 3901-3908. https://doi.org/10.1016/j.tet.2014.04.039
25. Bolshakov, O.I.; Grishina, M.A; Galushko, A. S.; Potemkin, V. A.; Rakitin, O. A. *J. Chem.* **2015**, Article ID 467593, 8 p.
26. Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J.A.; *J. Comput. Chem*. **1993**, *14*, 1347-1363.
    https://doi.org/10.1002/jcc.540141112
27. Gordon, M. S.; Schmidt, M.W. In *Theory and Applications of Computational Chemistry, the first forty years*; Dykstra, C. E.; Frenking G.; Kim, K. S.; Scuseria, G. E. Eds.; Elsevier: Amsterdam, **2005**, 1167-1189. https://doi.org/10.1016/B978-044451719-7/50084-6
28. Chemosophia s.r.o. 2015, Prague, Czech Republic http, //www.chemosophia.com. Accessed 16 Mar 2017.