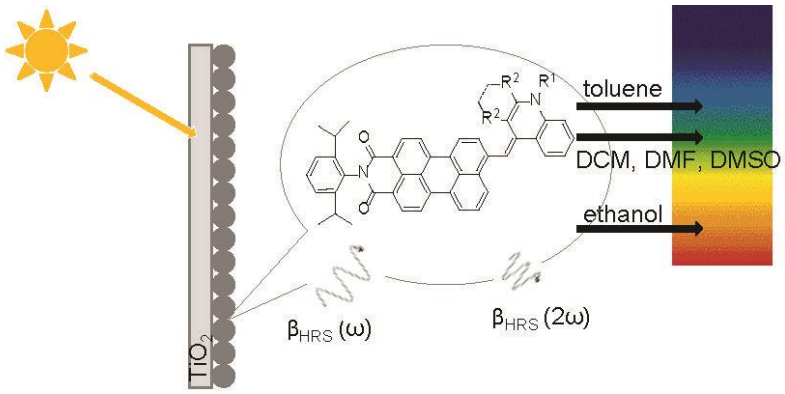
## Abstracts of the reviewed publications in English[1]

**23.** Vasilev, A., De Mey, K., Asselberghs, I., Clays, K., Champagne, B, Angelova, S., Spassova, M., Li, C., Müllen, K., "Enhanced Intramolecular Charge Transfer in New Type Donor-Acceptor Substituted Perylenes", *J. Phys. Chem. C*, 116(43) (**2012**) 22711-22719.

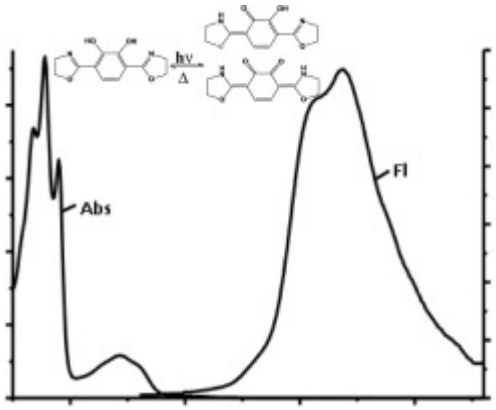
*Abstract:* Here we report the facile synthesis and physical characterization of new type N-(2,6-diisopropylphenyl)-3,4-perylenedicarboximides (PMI) with alkyl-substituted quinoline-4(1H)-ylidenemethyl or acridine-9(10H)-ylidenemethyl units as strong donors in the 9-position. When compared to parent PMI, these perylene dyes, 9-((1-methylquinoline-4(1H)-ylidene)methyl)-PMI, 9-((1-benzylquinoline-4(1H)ylidene)methyl)-PMI, 9-((1-heptylquinoline-4(1H)-ylidene)-methyl)-PMI, and 9-((10-methylacridine-9(10H)-ylidene)methyl)-PMI, show a pronounced bathochromic shift of their electronic absorption with solvatochromism because of their intramolecular charge transfer. The solvatochromic behavior of these dyes is further confirmed by second-order nonlinear optical experiments. Remarkably high second-order nonlinear optical values ($\beta_{HRS}$ up to $1300 \pm 50\times10^{-30}$ esu at 880 nm in dichloromethane) are obtained by femtosecond hyper-Rayleigh scattering. The one-step synthesis together with the spectroscopic, solvatochromic, and nonlinear optical characteristics qualify these new types of perylene dyes as promising candidates for solvent polarity probes, photovoltaics, or nonlinear optical applications.




**24.** Enchev, V., Markova, N., Stoyanova, M., Petrov, P., Rogozherov, M., Kuchukova, N., Timtcheva, I., Monev, V., Angelova, S., Spassova, M.. "Excited state proton transfer in 3,6-bis(4,5-dihydroxyoxazo-2-yl)benzene-1,2-diol", *Chem. Phys. Lett.* 563 (**2013**) 43-49.

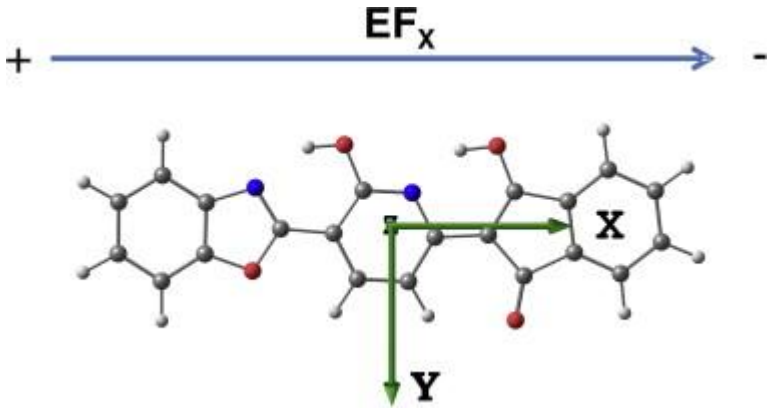
*Abstract:* A theoretical and experimental study on the absorption and fluorescence properties of a newly synthesized compound 3,6-bis(4,5-dihydroxyoxazo-2-yl)benzene-1,2-diol in ethanol is reported. Evidence suggesting intramolecular proton transfer in the excited singlet state is presented. All possible tautomeric forms are studied by means of TDDFT B3LYP/6-31G(d,p) in both the ground and the first excited singlet state. On the basis of the results obtained excited state double proton transfer in the title compound is proposed.

[1] The numbering of publications is in accordance with the candidate's complete list of scientific publications.




**25.** Enchev, V., Monev, V., Markova, N., Rogozherov, M., Angelova, S., Spassova, M., "A model system with intramolecular hydrogen bonding: effect of external electric field on the tautomeric conversion and electronic structures", *Comput. Theor. Chem.* 1006 (**2013**) 113-122.

*Abstract:* A new model tautomeric system with intramolecular hydrogen bonding is proposed. Geometry optimizations are performed at HF and MP2 levels and absorption spectra are simulated at TDDFT level. The MP2 level of theory was chosen for studying the effect of the external electric static field (EF) on the molecular electronic structure. The geometries of the tautomers as well as the transition states are fully optimized for each magnitude and for opposite directions of the applied EF. Upon variation of the electric field strength and polarity, it is possible to stabilize different tautomeric forms of the molecule. The dipole moment, HOMO–LUMO gap and the spatial distribution of the frontier orbitals are found to be sensitive to the EF strength and polarity and the different tautomeric structures are differently affected by the field. Elongation of the conjugated system providing a large number of possible tautomeric forms is also examined at HF level. Systems similar to the studied model system have potential use in the design of new molecular electronic devices.



**27.** Dikova, J., Kitova, S., Stoyanova, D., Vasilev, A., Deligeorgiev, T., Angelova, S. "New "push-pull" type merocyanine dye for application in bulk-hetrojunction organic solar cells", *Bulg. Chem. Commun.* 45(B) (**2013**) 175-180.

*Abstract:* The potentiality of our newly synthesized push-pull type merocyanine dye, labeled BMBII, for using as electron donating component in solution processed bulk heterojunction (BHJ) organic solar cells has been studied. For the purpose, soluble n-type fullerene, [6,6]-phenyl $C_{61}$ butyric acid methyl ester (PCBM), which is without alternative in the near future, is chosen as acceptor. The optical constants (n and k) of thin films obtained by spin coating from solutions in chlorbenzene of BMBII as well as of BMBII/PCBM blend are determined by spectrophotometric measurements. Further, an optical simulation of a standard BHJ cell with active layer from BMBIIdye/PCMB blend has been performed using transfer-matrix formalism. Thus, the optimum thickness of the active layer is calculated to be about 80 nm, which provides an overlapping of the total absorption with solar spectrum in a broad range between 400 and 800 nm. Finally, the maximum current density $J_{sc}$ of 13 mA.cm$^{-2}$ is determined, assuming the internal quantum efficiency, IQE, equals one. By comparing the calculated $J_{sc}$ with data for some advanced small molecular BHJ devices the perspectives for practical applications of the new merocyanine dye are discussed.

**29.** Dikova, J., Kitova, S., Stoyanova, D., Vasilev, A., Deligeorgiev, T., Angelova, S., "Optical properties of thin merocyanine dye layers for photovoltaic applications", *J. Phys. Conf. Ser.* 514 (**2014**) 01201.

*Abstract:* The potentiality was studied of our newly synthesized push-pull type merocyanine dye, labeled A1, for use as an electron donating component in solution-processed bulk heterojunction (BHJ) organic solar cells. For the purpose, a soluble n-type fullerene, [6,6]-phenyl $C_{61}$ butyric acid methyl ester (PCBM), which is currently and in the ear future without an alternative, was chosen as an acceptor. The optical constants (n and k) of thin films obtained by spin coating from solutions in chlorobenzene of A1 and of an A1/PCBM blend were determined by spectrophotometric measurements. Further, an optical simulation of a standard BHJ cell with an active layer of an A1dye/PCMB blend was performed using a transfer-matrix formalism. Thus, the optimum thickness of the active layer was calculated to be about 80 nm, which provides overlapping of the total absorption with the solar spectrum in the broad range 400 nm − 800 nm. Finally, the maximum current density, $J_{sc}$, was determined to be 13 mA.cm$^{-2}$ assuming that the internal quantum efficiency, IQE, is unity. Comparing the calculated $J_{sc}$ with data on some advanced small-molecule BHJ devices, the prospects for practical applications of the new merocyanine dye are discussed.

**30.** Kitova, S., Stoyanova, D., Dikova, J., Kandinska, M., Vasilev, A., Angelova, S., "Optical modeling of bulk-heterojunction organic solar cells based on squarine dye as electron donor", *J. Phys. Conf. Ser.* 558 (**2014**) 012052.

*Abstract:* The potentiality of a squarine dye (Sq1) for using as electron donor component in bulk heterojunction organic solar cells (BHJ) has been studied from the

optical point of view. The soluble n-type fullerene, [6,6]-phenyl $C_{61}$ butyric acid methyl ester ($PC_{61}BM$), was chosen as acceptor. Optical modelling based on transfer matrix method was carried out to predict and improve photovoltaic performance of a BHJ device with blended Sq1/$PC_{61}BM$ active layer. The dependence of the absorption and the calculated maximum short circuit photocurrent ($J_{sc}^{max}$) on the thickness of the active layer ($d_{act}$), was investigated for two weight ratios of Sq1 and $PC_{61}BM$. Thus, the optimal $d_{act}$ was calculated to be about 100 nm, which provides an efficient overlapping of the total absorption with solar spectrum in the range between 580 and 900 nm. Besides, it is found that the insertion of ZnO or $C_{60}$ spacer layer shifts $J_{sc}^{max}$ peak to lower $d_{act}$ and significantly enhances $J_{sc}^{max}$ for active layers with dact < 50 nm, which is mainly due to improved light absorption by a factor of 5 to 10. Simultaneously, for $d_{act}$ < 100 nm the optical effect of inserted PEDOT:PSS hole transporting layer is negligible.

**33.** Kitova, S., Stoyanova, D, Dikova, J., Vasilev, A., Kandinska, M., Angelova, S., "Optical properties of thin films of new croconium dye for application in organic solar cells", Nanoscience & Nanotechnology: Nanostructured materials application and innovation transfer, 14 (**2015**) 71-74.

*Abstract:* The potentiality of our newly synthesized croconium dye, labeled Cr-1, for using as electron donating component in solution processed bulk heterojunction (BHJ) organic solar cells has been studied. For the purpose, soluble n-type fullerene derivative, [6,6]-phenyl $C_{61}$ butyric acid methyl ester ($PC_{61}BM$) was chosen as acceptor. The optical constants (refractive indices n and extinction coefficients k) of thin films, deposited by spin coating from methanol solutions of Cr-1 and chlorbenzene solution of $PC_{61}BM$, were determined by spectrophotometric measurements. Further, an optical simulation of a standard BHJ cell with active layer from Cr-1 dye/$PC_{61}MB$ blend was performed using transfer-matrix formalism. Thus, the optimum thickness of the active layer was calculated to be about 100 nm, which provides an overlapping of the total absorption with solar spectrum in a broad range between 350 and 900 nm. Finally, the maximum current density $J_{sc}$ of 17.9 $mA.cm^{-2}$ was determined assuming that the internal quantum efficiency equals one. By comparing the calculated $J_{sc}$ with our experimental data as well as with some advanced small molecular BHJ devices the perspectives for practical applications of the new croconium dye have been discussed.

**34.** Kitova, S., Stoyanova, D., Dikova, J., Kandinska, M., Vasilev, A., Angelova, S., Mankov, V., "Optical modeling of organic solar cell with standard and inverted structure based on squaraine dye as electron donor", *Nanoscience & Nanotechnology: Nanostructured materials application and innovation transfer*, 15(2) (**2015**) 19-23.

*Abstract:* The potential of a symmetrical n-hexyl substituted squaraine dye (Sq1) for use as electron donor component in bulk heterojunction organic solar cells (BHJ) with standard and inverted structure has been studied from optical point of view. The soluble n-type fullerene, [6,6]-phenyl-$C_{61}$-butyric acid methyl ester ($PC_{61}BM$) was chosen as acceptor. Optical modeling based on transfer matrix method was carried out to predict photovoltaic performance of a BHJ device with blended Sq1/$PC_{61}BM$ active layer. It was found out that inverted device stacks show larger calculated maximum

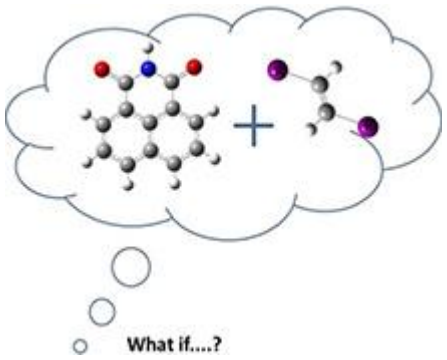
short circuit photocurrent ($J_{sc}^{max}$) compared to the standard device structure. Modeling of the optical field distribution in the different device stacks proved that this enhancement originates from an increased absorption of incident light in the active layer, and hence from the increased exciton generation rate. Besides, it is also found that the effect of the optical spacer to the increase in $J_{sc}^{max}$ is less expressed in inverted device stacks than in standard ones.

**35.** Vasilev, A., Lesev, N., Dimitrova, S., Nedelcheva-Veleva, M., Stoynov, S., Angelova, S., "Bright fluorescent dsDNA probes: novel polycationic asymmetric monomethine cyanine dyes based on thiazolopyridinequinolinium chromophore", *Color. Technol.* 131 (**2015**) 94-103.

*Abstract:* Seven tri- and tetracationic monomeric and homodimeric monomethine cyanine dyes based on thiazolo[4,5-b]pyridinium and quinolinium end groups were synthesised and characterised. The dyes were tested as fluorescent DNA intercalating probes to apply in DNA gel electrophoresis. The DNA samples stained with all dyes from the series demonstrated bright fluorescent signals. DNA fragments were successfully visualized under orange and green filters as well as under standard UV transillumination. Two of the studied dyes revealed higher sensitivity to DNA when compared with the commercial dimeric cyanine dye TOTO-1. Their sensitivity reached that of the commercial dimeric cyanine dye YOYO-1, but the emission was shifted to longer wavelengths. These qualities make the dyes suitable to apply in a wide range of medical and scientific analytical methods.

**36.** Vasilev, A.A., Baluschev, S., Cheshmedzhieva, D., Ilieva, S., Castano, O. D., Vaquero, J. J., Angelova, S.E., Landfester, K., "Assembly of New Merocyanine Chromophores with a 1,8-Naphthalimide Core by a New Method for the Synthesis of the Methine Function", *Aust. J. Chem.* 68 (**2015**) 1399-1408.

*Abstract:* A new method for the synthesis of the monomethine group using nitro as a leaving group in an SN-Ar reaction is described. A series of novel merocyanine dyes has been synthesised and their photophysical properties have been elucidated. The longest wavelength absorption occurs in the range 519–619 nm and the molar absorptivities vary with the substituents and are in the range 1000–47700 L $mol^{-1}$ $cm^{-1}$. The dyes show high chemical and photostability. One example from the series has the ability to distinguish methanol from ethanol. The introduction of a quinoid fragment into the structure leads to a pronounced intramolecular charge transfer and hence a noticeable positive solvatochromism. The structures and electronic properties of the compounds have been studied by density functional theory (DFT) and time-dependent DFT.



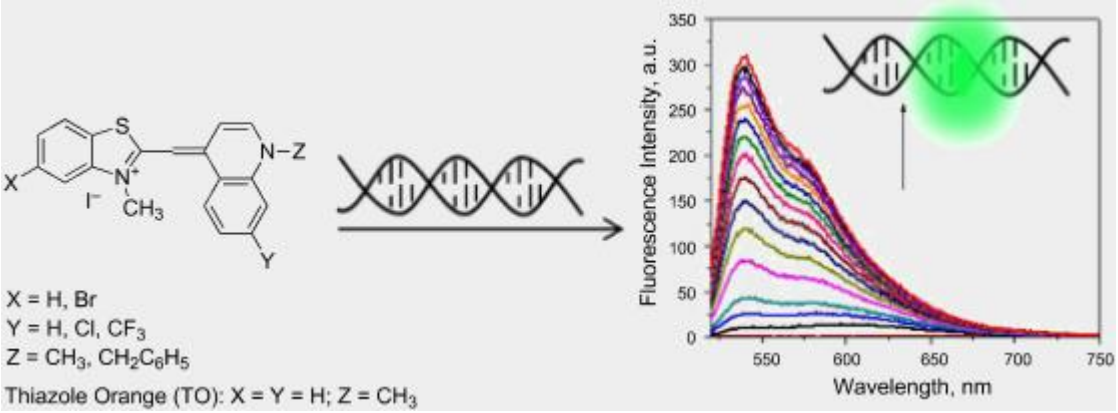

**47.** Spassova, M., Angelova, S., Kadinska, M., Vasilev, A., Kitova, S., Dikova, J., "Molecular design of electron-donor materials for fullerene-based organic solar cells", *Bulg. Chem. Commun.* 49 (G) (**2017**) 166-171.

*Abstract:* A set of model symmetrical and unsymmetrically substituted squaraine and croconine dyes is designed as potential electron donor component in organic photovoltaic bulk heterojunction solar cell (BHJ) where [60]PCBM fullerene is set as acceptor. Ground-state geometries and electronic structures were investigated using density functional theory (DFT) and time-dependent (TD-DFT) density functional theory at the B3LYP/6-31+G(d,p) level. The effects of the electron-rich heterocycles on these squarilium/croconium based organic dyes are studied with respect to the electronic and transport properties of the systems. The estimated HOMO-LUMO gaps of all model dyes fall in the range of the typical organic semiconductors' gap of about 2 eV. The HOMO and LUMO energy levels of the dyes are compared with respect to the acceptor's and the rigorous conditions for an effective charge transfer is discussed. The calculated high values of the oscillator strengths for all proposed dyes are indicative for large absorption coefficient. Based on the optimized molecular geometries, relative positions of the frontier orbitals, absorption maxima and transport properties we propose some of these dyes as suitable components for optoelectronic devices.

**51.** Vasilev, A., Kandinska, M., Stoyanov, S., Yordanova, S., Sucunza, D., Vaquero, J. J., Castaño, O., Baluschev, S., Angelova, S., "Halogen-containing thiazole orange analogues – new fluorogenic DNA stains", *Beilstein J. Org. Chem.* 13 (**2017**) 2902-2914.

*Abstract:* Novel asymmetric monomeric monomethine cyanine dyes 5a–d, which are analogues of the commercial dsDNA fluorescence binder thiazole orange (TO), have been synthesized. The synthesis was achieved by using a simple, efficient and environmetally benign synthetic procedure to obtain these cationic dyes in good to excellent yields. Interactions of the new derivatives of TO with dsDNA have been investigated by absorption and fluorescence spectroscopy. The longest wavelength absorption bands in the UV–vis spectra of the target compounds are in the range of 509–519 nm and these are characterized by high molar absorptivities (63000–91480 $L \cdot mol^{-1} \cdot cm^{-1}$). All investigated dyes from the series are either not fluorescent or their fluorescence is quite low, but they become strongly fluorescent after binding to dsDNA. The influence of the substituents attached to the chromophores was investigated by combination of spectroscopic (UV–vis and fluorescence spectroscopy)

and theoretical (DFT and TDDFT calculations) methods.




**56.** Kandinska, M. I., Vasilev, A. A., Videva, V. S., Angelova, S., "A novel monomeric asymmetric tricationic monomethine cyanine dye – Thiazole Orange (TO) analog: synthesis, photophysical and dsDNA binding properties", *Bulg. Chem. Commun.* 50 (J) (**2018**) 178-184.

*Abstract:* A new monomeric tricationic cyanine dye TO-3c-7Cl – analog of Thiazole Orange (TO), has been synthesized using an environmentally benign and simple method and its photophysical properties have been investigated and compared to those of the well-known nucleic acid stain TO. Dye TO-3c-7Cl has negligible intrinsic fluorescence in Tris-EDTA (TE) buffer, but in the presence of dsDNA its fluorescence intensity increases significantly. DFT and TDDFT calculations are used to compare and contrast the theoretically predicted structure and properties of the new tricationic cyanine dye and TO.

**57.** Vasilev, A., Kandinska, M., Zagraniarsky, Y., Sucunza, D., Vaquero, J. J., Castaño, O. D., Angelova, S., "Novel asymmetric azaquinolizinium monomethine cyanine dyes versus a Thiazole Orange analog: a comparison of photophysical and dsDNA binding properties", *Bulg. Chem. Commun.* 50 (J) (**2018**) 32-39.

*Abstract:* New asymmetric monomethine cyanine dyes containing an azaquinolizinium core have been synthesized using novel 4-chloropyridopyrimidinium chlorides as building blocks. The photophysical properties of the dyes have been compared to those of a novel monomeric tricationic Thiazole Orange (TO) analog. Compounds 8 and 13 have very low fluorescence in TE buffer in the absence of dsDNA, but after binding to dsDNA a dramatic increase in the fluorescence intensity was observed. Computational tools (DFT and TDDFT calculations) have been employed in studying the relationship between the chemical structure and the optical properties of the chromophores.