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Novel 2-alkoxy- and 2-alkylthio-substituted pyrimidines containing 2-(1-methyl-1*H*-pyrrol-2-yl)vinyl moieties: optical and electrochemical properties

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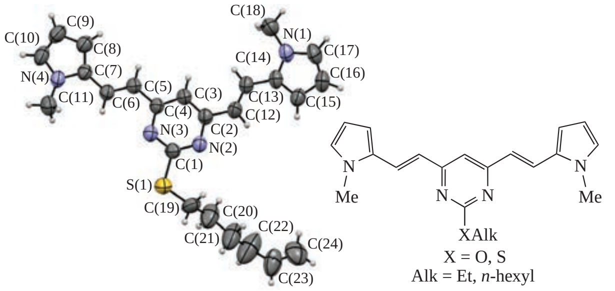
A series of novel Y-shaped dyes bearing the D–π–A–π–D fragment comprising central 2-alkoxy- or 2-alkylthio-substituted pyrimidine core and terminal 2-(1-methyl-1*H*-pyrrol-2-yl)vinyl moieties have been synthesized and studied as potential materials for the organic electronics. The obtained compounds demonstrated an efficient absorption at ~410 nm with the high molar absorption coefficient (29 790–40 620 dm^3 mol^{-1} cm^{-1}) and fluorescence emission at ~480 nm (Φ_F ~ 7.5–8.6%). Thin films of 2-ethyloxy- or 2-ethylthiopyrimidines exhibited the red-shifted photoluminescence (~600 nm).

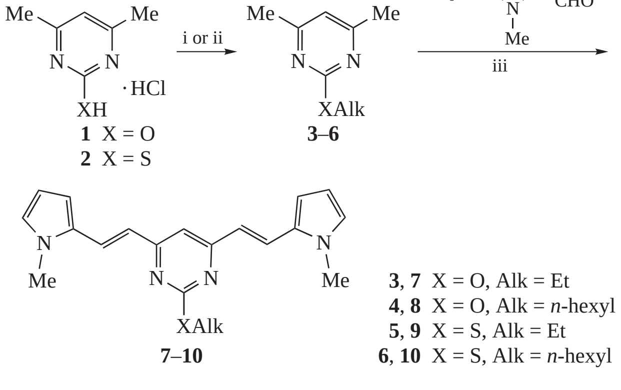


Pyrimidine as a highly electron-deficient π-system is often incorporated into the structure of small push-pull chromophores, oligomers, and polymers as their electron-withdrawing heterocyclic fragment. Its integration with the π-electron-excessive moieties through a π-conjugated bridge provides an efficient intramolecular charge transfer (ICT) upon excitation, which can in its turn induce luminescence and nonlinear properties. Thus, pyrimidine-containing chromophores of D–π–A–π–D type have found practical applications as fluorescent probes for detection of Hg^{2+} and Cu^{2+} cations,[1] as materials for pH sensors,[2–4] OLEDs[5] and OFET[6] devices, and solar cells.[7] Fluorescent pyrimidine derivatives are potential probes for the two-photon microscopy.[8] Photoluminescent properties of pyrimidines are summarized in the comprehensive review.[8]

To continue our previous studies,[9] here we report on the synthesis and characterization of Y-shaped push-pull chromophores containing the central electron-withdrawing pyrimidine core and incorporating 2-ethoxy, 2-ethylthio, 2-hexyloxy or 2-hexylthio groups and two 4,6-positioned bis(1-methyl-1*H*-pyrrol-2-yl)vinyl moieties. *N*-Methylpyrrole fragments have been embedded into the structure of target chromophores as the heterocycles possessing the powerful electron-donating ability similar to that of primary organic functionalities such as amino, dialkylamino and hydroxy groups.[10]

2-Hydroxy- and 2-mercapto-4,6-dimethylpyrimidines hydrochlorides are generally considered as useful building blocks since the two methyl groups are favorable as methylene components of the Knoevenagel condensation providing an opportunity to prepare symmetrical and asymmetrical chromophores of D–π–A–π-D or D–π–A–π–D′ types with the elongated π-conjugated chain. On the other hand, the hydroxy and mercapto groups can be readily alkylated by alkyl halides of various structure thereby increasing the solubility of resulting chromophores in common organic solvents.[9(b)–(d)]

In this work, target 2-alkoxy-4,6-bis[(*E*)-2-(1-methyl-1*H*-pyrrol-2-yl)vinyl]pyrimidines **7**, **8** and 2-alkylthio-4,6-bis[(*E*)-2-(1-methyl-1*H*-pyrrol-2-yl)vinyl]pyrimidines **9**, **10** were prepared *via* an easy-to-perform high yielding two-step process (Scheme 1). The initial 2-hydroxy- and 2-mercapto-4,6-dimethylpyrimidine hydrochlorides **1** and **2** were synthesized *via* cyclization of acetylacetone with urea or thiourea, respectively, in ethanol in the presence of conc. HCl.[11–13] Their consequent alkylation in the presence of K_2CO_3[14] or NaOH[15] (see Scheme 1) gave pyrimidines **3–6**. The key step of synthesis involved an aldol condensation between 2-substituted 4,6-dimethylpyrimidines **3–6** and *N*-methylpyrrole-2-carboxaldehyde in boiling aqueous 5 M NaOH solution in the presence of Aliquat 336 as the phase-transfer catalyst,[16] which resulted in the target perfectly stable D–π–A–π–D pyrimidines **7–10** soluble in common organic solvents. Their molecular structures were characterized by ^{1}H, ^{13}C NMR spectroscopy



3, **7** X = O, Alk = Et
4, **8** X = O, Alk = *n*-hexyl
5, **9** X = S, Alk = Et
6, **10** X = S, Alk = *n*-hexyl

Scheme 1 *Reagents and conditions:* i, AlkBr, K_2CO_3, DMF, reflux, 5 h; ii, AlkBr, NaOH, DMSO, stirring, 48 h; iii, Aliquat 336, NaOH (5 M), reflux, 6 h.

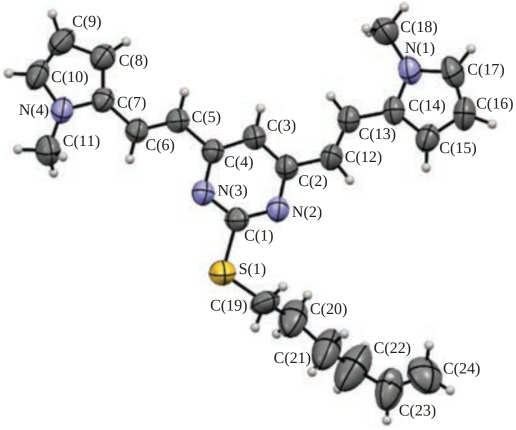


Figure 1 Molecular structure of compound **10**.

and elemental analysis.[†] The structure of compound **10** was additionally confirmed by X-ray analysis (Figures 1, S11, see Online Supplementary Materials).[‡]

Optical properties of pyrimidines **7**–**10** were investigated by UV-VIS absorption and photoluminescence spectroscopy (Figures S18–S20, Table S1). THF was chosen as the solvent in order to avoid the influence of acid traces, which are sometimes present in chloroform usually used for spectroscopic measurements. All compounds appeared to be photostable and did not undergo *cis*–*trans*-isomerization under the conditions of spectral analysis. Each of the prepared compounds demonstrated three absorption bands: two weak ones in the region of 243–316 nm (ε = 6540–11890 dm^3 mol^{-1} cm^{-1}) and an intensive one about 410–415 nm (ε = 29790–40620 dm^3 mol^{-1} cm^{-1}). The first band centered at 243 nm is ascribed to the aromatic π–π* electronic transitions in pyrimidines, the second, less intense, band centered at 285 nm corresponds to the n–π* electronic transitions involving lone pair of a nitrogen atom. The long-wavelength absorption bands (~410 nm) are the result of the intramolecular charge-transfer process occurring in the photo excited compounds; the large values of their molar absorption coefficients confirm the high efficiency ICT from the electron excessive *N*-methylpyrrol moiety to the electron-deficient pyrimidine cycle.

The obtained data have confirmed the fact that the meta-arrangement of substituents prevents an effective delocalization of the electron density along the conjugated chain. Consequently, the compounds absorb light in the UV and visible region. TDDFT calculations performed to examine the vertical singlet excitations at PBE0-D3/def2-TZVPD level in gas phase revealed that the strongest band in the absorption spectra of pyrimidines **7**–**10** correspond to S1 state with the main contribution of HOMO to LUMO (Figure S23). The calculated absorption maxima are in a good agreement with the experimental values obtained for THF solutions (Table 1). Absorption maxima of 2-alkylthio-substituted pyrimidines **9**, **10** are slightly red-shifted *vs.* those of their alkoxy analogues **7**, **8**. The same effect was observed in the emission spectra of these compounds: the emission maxima of alkylthio derivatives **9**, **10** are slightly red-shifted as well. The fluorescence quantum yields (Φ_F) were estimated and found to be about 7.5–8.6%. The optical band gap (E_g^{opt}) averaged 2.65 eV (see Table S1).

Table 1 Calculated absorption maxima of S0 → S1 excitations of pyrimidines **7**–**10** obtained from the TDDFT//PBE0-D3/def2-TZVPD calculations in gas phase.

Compound	λ_{max}/nm	Oscillator strength	E/eV	Major contribution
7	406.4	1.2405	3.051	HOMO → LUMO (99%)
8	406.1	1.2312	3.053	HOMO → LUMO (99%)
9	411.1	1.1308	3.016	HOMO → LUMO (97%)
10	410.7	1.1182	3.019	HOMO → LUMO (97%)

It was interesting to compare the optical characteristics of newly synthesized pyrimidines **7**–**10** and those of reported 4,6-bis[(*E*)-2-(1-methyl-1*H*-pyrrol-2-yl)vinyl]pyrimidine.[2] The main difference between these compounds is the absence of a 2-positioned substituent in the pyrimidine ring of the latter. The data on absorption and emission of THF solutions of these compounds are very close (see Table S1). The data on absorption and emission of 4,6-bis[(*E*)-2-(1-methyl-1*H*-pyrrol-2-yl)vinyl]-pyrimidine in CH_2Cl_2 solutions (see Table S1) are rather close to the values of optical characteristics acquired for the compounds obtained in the present work. Some decrease in the fluorescence quantum yields is the result of strong electron donating effect of alkyloxy and alkylmercapto groups, which partially diminishes the electron deficiency of a pyrimidine core and, as a result, reduces the efficiency of ICT process. At the same time, the presence of aliphatic tails at C^2 position allows these dyes to form aggregates, and, consequently, the properties of an excited state become different.

Intense long wavelength absorption maxima in the UV spectra of films obtained from chlorobenzene solutions of pyrimidines **7**–**10** appear in the region of 395–416 nm, thus undergoing a very small hypsochromic shift (~6 nm) towards those of the corresponding pyrimidine solutions in THF. On the contrary, the values of absorption edges of these thin films are definitely red-shifted (~35–60 nm). The investigation of fluorescence spectra of the films has revealed that the pyrimidines containing hexyloxy or hexylthio groups (compounds **8** and **10**) do not fluoresce, while the pyrimidines bearing ethyloxy or ethylthio moieties (**7** and **9**) have demonstrated emission in the 600 nm range. The absence of fluorescence in the case of pyrimidines **8** and **10** containing the long-chain substituents is an example of aggregation-caused quenching of fluorescence (ACQ effect).[17] The formation of aggregates in solid state was also confirmed by single crystal X-ray analysis of compound **10**.

The electrochemical behavior of the synthesized chromophores containing an electroactive *N*-methylpyrrole units in their structure is of special interest. The presence of free C^5 and C$^{5'}$ positions in these heterocyclic moieties allows them to form substituted bispyrrole structures as a result of electrochemical oxidation (its mechanism has been described in detail[18]). The cyclic voltammetry method (CV) was used to obtain the electrochemical characteristics of the prepared compounds and to estimate the values of their HOMO/LUMO energy levels and electrochemical band gaps (E_g^{el}). The obtained data and experimental details are given in Online Supplementary Materials and also summarized in Table 2.

The CV curves of pyrimidines **7**–**10** (Figures S12 and S13, see Online Supplementary Materials) comprise two reversible oxidation waves derived from the redox processes in pyrrole fragments of these compounds. The CV curve shapes as well as the values of redox potentials appeared to be very similar within this group of pyrimidines (**7**–**10**). At the same time, it has been found that the HOMO levels of pyrimidines **7** and **9** (Alk = Et)

[†] For NMR and elemental analysis data, see Online Supplementary Materials.

[‡] *Crystal data for* **10**: $C_{24}H_{30}N_4S$, M = 406.58, orthorhombic, space group $Pca2_1$, a = 15.847(5), b = 16.217(5) and c = 8.899(3) Å, V = 2286.9(12) Å^3, T = 295(2) K, Z = 4, μ(MoKα) = 0.158 mm^{-1}. The final refinement parameters: R_1 = 0.0593, wR_2 = 0.1487 [for observed 2498 reflections with $I > 2\sigma(I)$]; R_1 = 0.0907, wR_2 = 0.1711 (for all independent 3801 reflections), S = 0.979. Largest diff. peak/hole: 0.190/–0.225 e Å^{-3}.

CCDC 1844962 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

Table 2 Comparison of empirical and calculated values of $E_{\mathrm{HOMO}}/E_{\mathrm{LUMO}}$ and $E_{\mathrm{g}}^{\mathrm{el}}$ for pyrimidines **7**–**10**.

Compound	E_{HOMO}/ eV[a]	E_{LUMO}/ eV[a]	$E_{\mathrm{g}}^{\mathrm{el}}$/ eV[b]	E_{HOMO}/ eV[c]	E_{LUMO}/ eV[c]	E_{g}/ eV[c]
7	–5.37	–3.54	1.83	–5.51	–1.94	3.57
8	–5.36	–3.54	1.82	–5.51	–1.93	3.58
9	–5.40	–3.59	1.81	–5.56	–2.00	3.56
10	–5.35	–3.56	1.79	–5.55	–1.99	3.56

[a] $E_{\mathrm{HOMO}} = -(E^{\mathrm{ox}}_{\mathrm{onset}\ vs.\ \mathrm{Ag/AgCl}} - E_{\mathrm{Fc}\ vs.\ \mathrm{Ag/AgCl}} + 4.80)$. $E_{\mathrm{LUMO}} = -(E^{\mathrm{red}}_{\mathrm{onset}\ vs.\ \mathrm{Ag/AgCl}} - E_{\mathrm{Fc}\ vs.\ \mathrm{Ag/AgCl}} + 4.80)$.[19] [b] $E_{\mathrm{g}}^{\mathrm{el}} = E_{\mathrm{HOMO}} - E_{\mathrm{LUMO}}$. [c] Calculated values.

are somewhat deeper than those of pyrimidines **8** and **10** (Alk = *n*-hexyl), while the LUMO levels remained the same for all the investigated compounds. The values of electrochemical band gaps energy ($E_{\mathrm{g}}^{\mathrm{el}}$), which was determined as the difference between HOMO and LUMO energy values, lay within 1.78–1.83 eV interval. Therefore, all the prepared compounds have the sufficiently deep-lying HOMO levels, whose values are significantly below the air oxidation threshold (*ca.* –5.27 eV) (see Table 2). This fact provides a good air stability to their molecules and increases the open circuit voltage (V_{oc}) of a solar cell made with the use of such compounds.[20]

According to the calculations, the values HOMO/LUMO energies fall in the interval from –5.51 to –5.56 eV (HOMO) and from –1.93 to –2.0 eV (LUMO). HOMO values correlate with the experimentally obtained data, while the values of LUMO level have a systematic significant deviation (Figure 2).[21]

In summary, a series of novel Y-shaped 2,4,6-trisubstituted pyrimidines containing *O*- or *S*-alkyl groups of different lengths has been synthesized in good yields (60–68%), which allows us to propose this method as the preparative one for obtaining this type of compounds. All compounds are photo- and electrochemically stable. The fluorescence of obtained films has appeared to be inherent for 2-ethyloxy- and 2-ethylthio-substituted pyrimidines (~600 nm), but in the case of 2-hexyloxy- and 2-hexylthio-substituted pyrimidines the aggregation-caused quenching of fluorescence was clearly observed. Single crystal X-ray analysis of pyrimidine containing hexylthio group has confirmed that this compound forms stacks consisting of dimers resulted from the van der Waals intermolecular attraction between hexylthio groups. The calculated absorption maxima and HOMO values are in good agreement with experimental values acquired for THF solutions. The optical characteristics of obtained compounds make them the promising candidates for further investigations as potential materials for organic electronics devices.

The instrumental studies were performed using the equipment purchased at the expense of the Program of National Research Universities of Russian Federation (program for Perm State University).

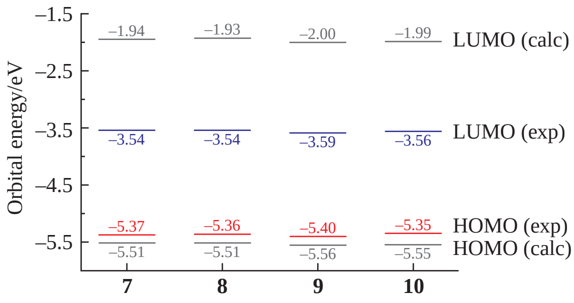


Figure 2 Frontier molecular orbital energy level diagram of pyrimidines **7**–**10**.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.01.014.

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