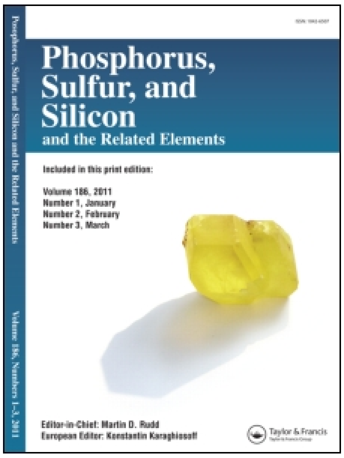

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FLUORENE COMPOUNDS WITH INTRAMOLECULAR CHARGE TRANSFER CONTAINING DITHIOLYLIDENE AND SELENATHIOLYLIDENE SUBSTITUENTS

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Abstract Condensation of polynitrofluorenes with dithiolium and selenathiolium salts in DMF leads to 9–substituted fluorenes with intramolecular charge transfer (ICT); spectral investigations show that ICT energies and intensities of ICT bands in electron absorption spectra depend substantially on heteroatom location but display very few dependence on the heteroatom nature (S or Se)

Recently it has been shown that fluorene acceptors with intramolecular charge transfer (ICT) can efficiently sensitize the photoconductivity in their ICT spectral region[1] that can be used for elaboration of photoconductive materials with selective spectral zones of sensitivity.

Herein we report the synthesis of new electron acceptors of a fluorene series **2**–**4** containing 1,2–dithiol–3–ylidene, 1,3–dithiol–2–ylidene, and 1,3–selenathiol–2–ylidene fragments by condensation of polynitrofluorenes **1**[2] with dithiolium or selenathiolium salts[3] (Scheme 1) and on spectral studies of ICT in the compounds under investigation.

Synthesized 9–substituted polynitrofluorenes **2**–**4** are stable deeply–coloured (from dark–violet to black), high–melting, scarcely soluble in most organic solvents compounds.† The presence of both acceptor fluorene and donor heterocycle moieties in the molecules of compounds **2**–**4** results in intramolecular charge transfer (which can be presented as a contribute of dipolar structures, see Scheme 1) which causes intensive light absorption in the visible spectrum region.

Two ICT bands (i.e. λ^1_{ICT} and λ^2_{ICT}) are observed for all the compounds(Table 1). Heteroatom nature (S or Se) has no apparent influence on the location of ICT bands and the ratio of their intensities (compounds **3d**, **4d**). At the same time, a change in the position of sulfur atoms from 1,3– to 1,2– (from **3d** to **2d**) causes a batochromic shift of both ICT bands, with the shift of a short-wave band (67 nm) being more pronounced than that of a long-wave one (34 nm) which brings about a decrease in the difference in the electron transition energies $h\nu^1_{ICT} - h\nu^2_{ICT}$. Moreover, the ratio of their intensities also changes dramatically. Thus, in compounds **3**, **4** it is the short-wave absorption band, λ^1_{ICT}, that is more intensive ($A^1_{ICT}/A^2_{ICT} \sim 2$), whereas in compounds **2** it is the long-wave one, λ^2_{ICT} ($A^1_{ICT}/A^2_{ICT} \sim 0.7$).

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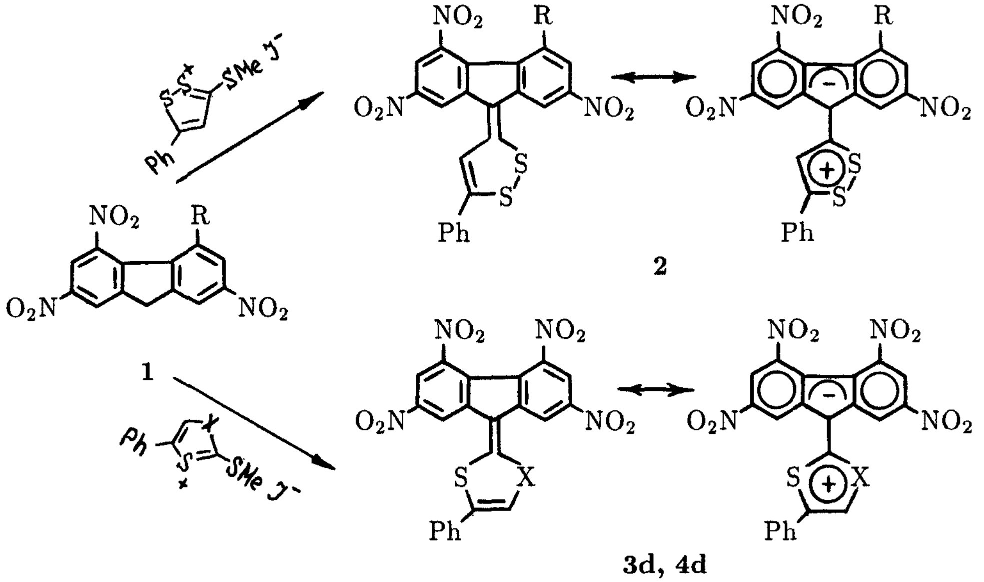
† Satisfactoty elemental analysis and IR–spectra were obtained for all new compounds. The melting points are the following (^oC): 315–317 (**2a**), >360 (**2b**, **2d**), 346–348 dec. (**2c**), 357–360 dec. (**3d**), 342–344 dec. (**4d**).

TABLE 1. UV-VIS spectral data for compounds **1** – **4**.

	Dimethylformamide				H_2SO_4
Compound	λ^1_{ICT}/nm	λ^2_{ICT}/nm	$(\hbar\nu^1_{ICT} - \hbar\nu^2_{ICT})$/eV	A^1_{ICT}/A^2_{ICT}	λ_{max}/nm
2a	500sh	587			368
2b	492	604	0.467	0.67	371
2c	498	613	0.467	0.72	370
2d	509	633	0.477	0.71	371
3d	447.5	599	0.701	2.02	360
4d	446.5	602	0.717	1.92	362
1d					367



SCHEME 1. Reactions conditions: DMF, 90–100°C, 5–20 min. Yields 70–90%. X = S (**3**), Se (**4**); R = H (**a**), COOH (**b**), COOMe (**c**), NO_2 (**d**)

So large distinction allow to hope to use this fact for developing electron or hole transport materials with various zones of electrophotosensitivity depending on acceptors' structure.

Introduction of electron-withdrawing substituents into the fluorene nucleus of compounds **2** results in a batochromic shift of both ICT bands according to an increase in their σ–constants. Quantitative estimation of the substituents effect upon the energy of the long-wave CT band using the nucleophilic σ^-–constants gives the sensitivity coefficient $\rho^- = -0.121 \pm 0.012$ eV (r –0.995).‡ Sensitivity of

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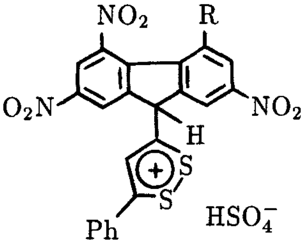
‡ $\hbar\nu^2_{ICT} = \hbar\nu^2_{ICT_0} + \rho^- \sum\sigma^-$.

ICT energy in compounds **2** to the substituents in the fluorene nucleus is between those for derivatives of 9–*bis*–(dimethylamino)methylenefluorenes ($\rho^- = -0.079 \pm 0.004$ eV, r -0.996) and 9–(α–dimethylamino)cyanomethylenefluorenes ($\rho^- = -0.176 \pm 0.010$ eV, r -0.992), (in DMF).[4]

A hypsochromic shift observed when the solvent polarity decreased§ indicates higher polarity of the excited state in the compounds under analysis as compared to the basic one.

The fact that compounds **2–4** lose colour when solved in the sulfuric acid also proves the ICT nature of the absorption bands in the visible region; long-wave absorption maxima are close to those for solutions of compounds **1** in the sulfuric acid (Table 1). This is due to the negative halochromism, i.e. when taking a proton to position 9, compounds **2–4** are converted into salts **5–7** with a dithiolium or selenathiolium unit .¶



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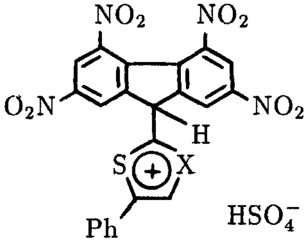

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REFERENCES

1. N.G.Kuvshinskii, N.G.Nakhodkin, N.A.Davidenko, A.M.Belonozhko, and D.D.Mysyk, *Ukr. Fiz. Zh.*, **34**, 1100 (1989).
2. Y.Abe, *J. Chem. Soc. Jap., Chem. and Ind. Chem.*, 1966 (1981); I.F. Perepichka and D.D.Mysyk, USSR Patent 862,561 (July 5, 1981); G.I.Migachev, *Zh. Vses. Khim. Ova im. D.I.Mendeleeva*, **24**, 395 (1979); (d) D.D.Mysyk and N.M.Sivchenkova, *Deposited Article, UkrNIINTI*, No 1547, 18 p., (1988).
3. A.Thuillier and J.Vialle, *Bull. Soc. Chim. France*, 1398 (1959); N.F.Haley and M.W.Fichtner, *J. Org. Chem.*, **45**, 175 (1980); A.Shafie, I.Lalezari, and F.Savabi, *Synthesis*, 764 (1977).
4. I.F.Perepichka, A.F.Popov, T.V.Artyomova, A.N.Vdovichenko, M.R.Bryce, A.S.Batsanov, J.A.K.Howard, and J.L.Megson, unpublished results.
5. M.Giffard, P.Frere, A.Gorgues, A.Riou, J.Roncali, and L.Toupet, *J. Chem. Soc., Chem. Commun.*, 944 (1993); M.Giffard, P.Alonso, J.Garin, A.Gorgues, T.P.Nguyen, P.Richomme, A.Robert, J.Roncali, and S.Uriel, *Adv. Mater., Int. Ed. Engl.*, **6**, 298 (1994).

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§ λ^1_{ICT} and λ^2_{ICT} in dioxane (nm): 435 and 572 (**3**), 434 and 573 (**4**).

¶ The reaction is reversible and upon adding water compounds **2–4** are quantitatively regenerated (See also Ref. 5).