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SHORT COMMUNICATIONS

New 2,7-Diiodo-9,9-disubstituted Fluorene Containing Tetrathiafulvalene Fragments

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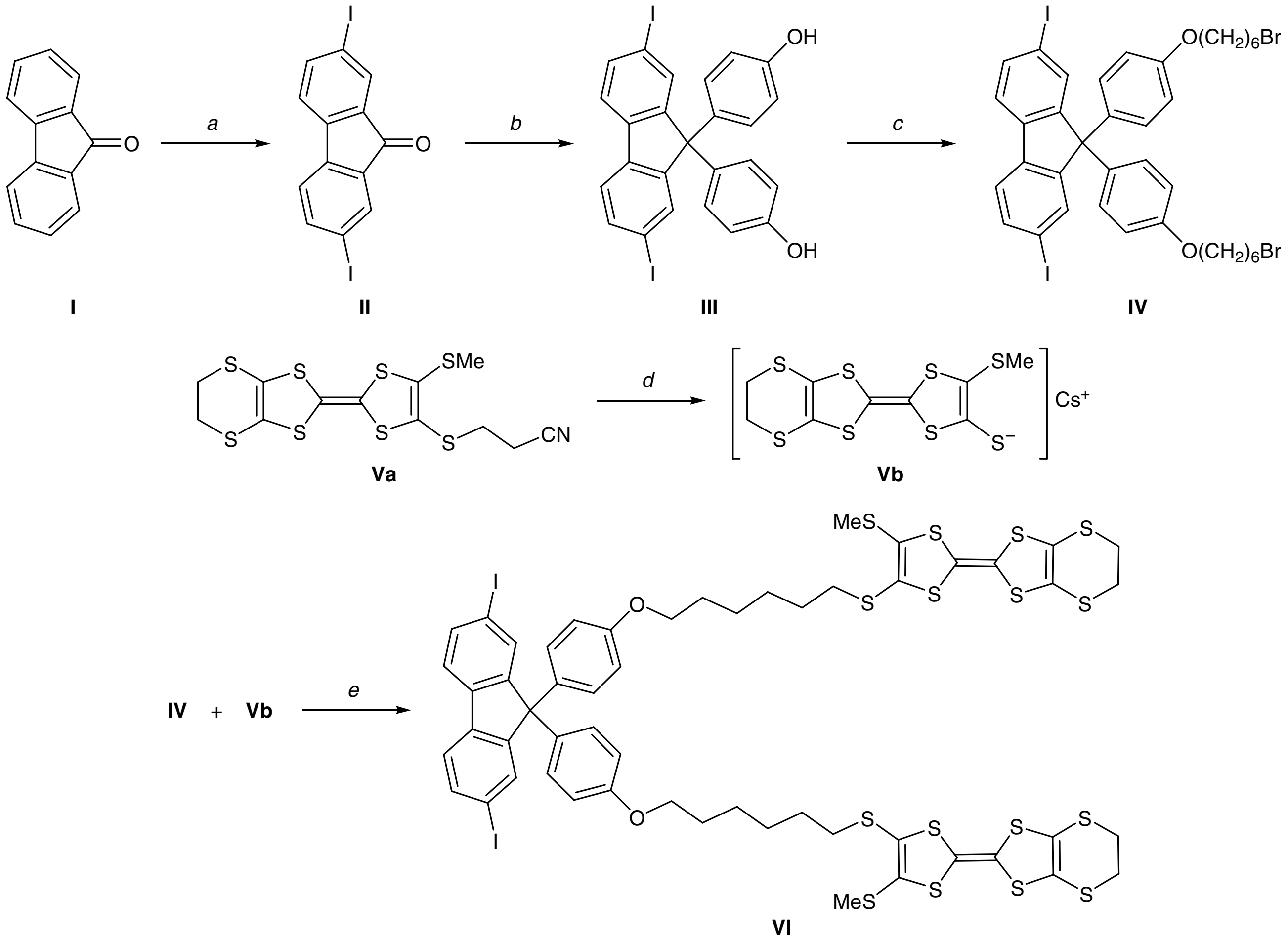
Over the past 30 years, tetrathiafulvalenes and their derivatives attract researchers' attention primary due to electroconducting and superconducting properties of radical cation salts derived therefrom [1]. On the other hand, derivatives of fluorene and carbazole attract continuously increasing interest as fragments of organic oligomers and polymers. These compounds possess such unique properties as high thermal and chemical stability and high luminescence quantum yield. Therefore, they can be used as materials for the preparation of organic light-emitting diodes (LEDs) [2, 3], field-emitting transistors (FETs) [4], and full-color polymeric display devices which are superior to liquid crystal displays (LCDs). It seems to be promising to synthesize oligomers and polymers simultaneously containing both electrically active tetrathiafulvalene moieties and substituted fluorene or carbaxole fragments and examine their optical, electrochemical, and electrophysical properties. In the recent years, fairly extensive studies have been performed on conductive thiophene-based polymers containing electrically active tetrathiafulvalene fragments (TTF) [5]. However, there are no published data on polymers derived from other TTF-containing heterocyclic monomers.

We have synthesized substituted fluorene **VI** which is a complex molecular assembly including a fluorene system and two benzene rings attached to C^9 of the fluorene fragment and linked to tetrathiafulvalene moieties through eight-membered hydrocarbon bridges. Molecule **VI** contains two iodine atoms in positions *2* and *7*, which enable polymerization of this compound or its copolymerization with other aromatic or heterocyclic halogen derivatives to be performed according to Suzuki or Stille [6].

Compound **VI** was synthesized in four steps. Fluorenone **I** was halogenated with iodine in a mixture of acetic acid with carbon tetrachloride in the presence of nitric and sulfuric acids [7]; 2,7-diiodofluoren-9-one (**II**) thus obtained reacted with phenol in carbon tetrachloride in the presence of methanesulfonic acid [8] to give 9,9-bis(4-hydroxyphenyl) derivative **III** which was alkylated with 1,6-dibromohexane in acetone in alkaline medium (in a solution of potassium hydroxide in methanol). Substituted fluorene **IV** having reactive bromine atoms was then used as alkylating agent in the reaction with 2 equiv of cesium thiolate **Vb**; the latter was prepared in turn by reaction of tetrathiafulvalene **Va** with 1 equiv of $CsOH \cdot H_2O$ in DMF (Scheme 1).

Tetrathiafulvalene **Va** [9] was synthesized by cross-coupling of 4-(2-cyanoethylsulfanyl)-5-methylsulfanyl-1,3-dithiol-2-one (**VII**) [9] with 4,5-ethylenedisulfanyl-1,3-dithiole-2-thione (**VIII**) [10] (Scheme 2). Initial heterocyclic compounds **VII** and **VIII** were prepared by alkylation of zinc dithiolate complex **IX** with the corresponding alkyl halides (compound **IX** was obtained by reaction of carbon disulfide with metallic sodium in DMF [11]). 4,5-Bis(2-cyanoethylsulfanyl)-1,3-dithiol-2-thione (**X**) was converted into 4-(2-cyanoethylsulfanyl)-4-methylsulfanyl-1,3-dithiole-2-thione (**XI**) by successive treatment with 1 equiv of $CsOH \cdot H_2O$ and MeI [9, 12]. Heterocyclic compound **XI** was heated in AcOH in the presence of $Hg(OAc)_2$ to obtain oxygen derivative **VII** that was directly involved in the cross coupling to synthesize **Va**. This reaction was

Scheme 1.



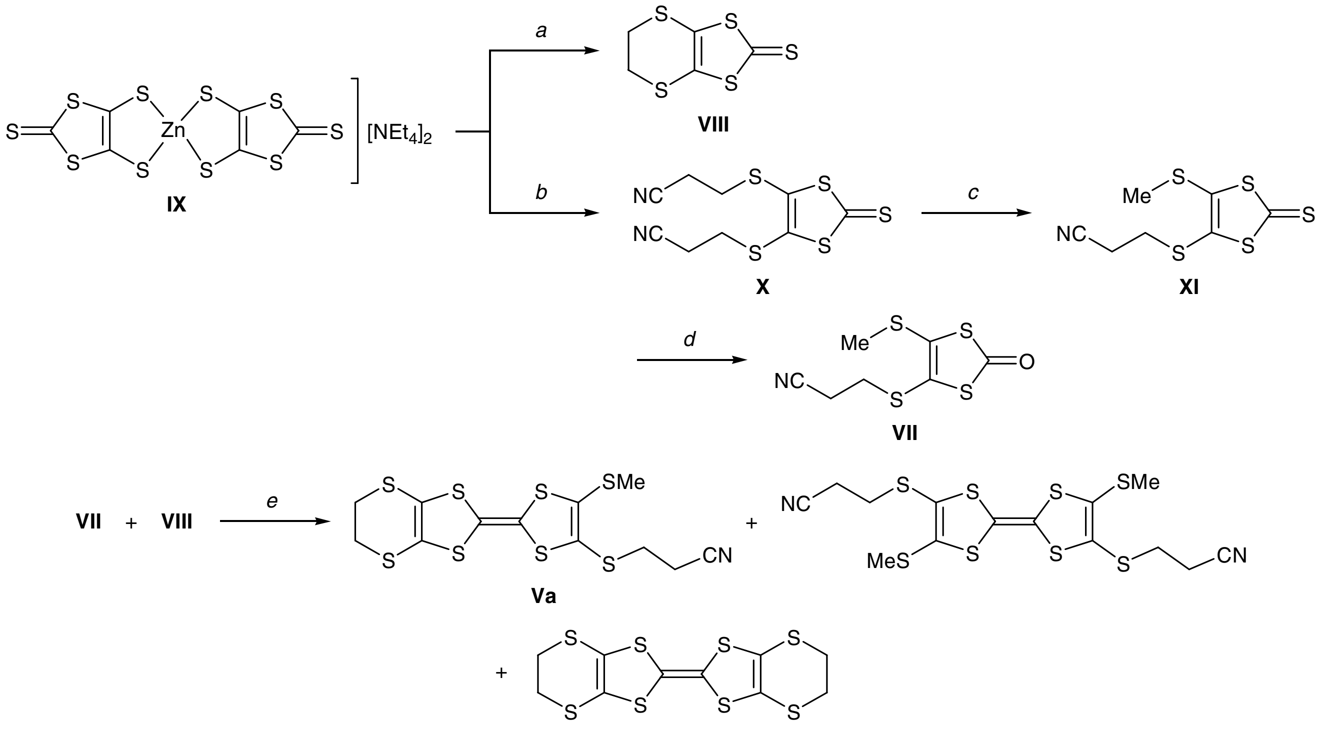
a: I_2, AcOH–CCl_4, HNO_3–H_2SO_4; *b*: phenol, $MeSO_3H$, CCl_4; *c*: 1,6-dibromohexane, KOH, MeOH, Me_2CO; *d*: DMF, $CsOH \cdot H_2O$–MeOH; *e*: 10 h, reflux.

accompanied by formation of two symmetric tetrathiafulvalenes as a result of self-coupling of 1,3-dithiol-2-one **VII** and 1,3-dithiole-2-thione **VIII**. The target cross-coupling product, tetrathiafulvalene **Va**, was isolated by either fractional crystallization from acetonitrile or column chromatography (eluent ethyl acetate–hexane, 1:2).

2,7-Diiodo-9*H*-fluoren-9-one (II). A solution of 4.5 g (0.025 mol) of fluorenone **I** and 6.35 g (0.025 mol) of molecular iodine in a mixture of 50 ml of glacial acetic acid and 3 ml of carbon tetrachloride (to wash off sublimed iodine) was heated to the boiling point, a mixture of 1 ml of concentrated sulfuric acid and 2 ml of fuming nitric acid was added dropwise, and the mixture was heated for 3.5 h under reflux. Some time after the addition of the acid mixture, a yellow solid separated from the reaction mixture. The mixture was cooled, and the precipitate was filtered off, washed with water until neutral washings, dried in air, and recrystallized from ethyl acetate or toluene–acetic acid (1:1). Yield 75%, yellow needles, mp 205–206°C. IR spectrum (mineral oil): ν(C=O) 1715 cm^{-1}. ^{1}H NMR spectrum, δ, ppm: 7.16 d and 7.18 d (1H each), 7.73 d and 7.76 d (1H each), 7.85 s (2H).

9,9-Bis(4-hydroxyphenyl)-2,7-diiodo-9*H*-fluorene (III). A mixture of 1.8 g (0.01 mol) of fluorenone **II**, 6.27 g (0.067 mol) of phenol, and 2.85 g (0.03 mol) of methanesulfonic acid in 20 ml of CCl_4 was heated for 40 h at 80°C under stirring. The solvent was distilled off to 1/5 of the initial volume, and the product was purified by repeated reprecipitation from acetone with water. Yield 55%, colorless crystalline substance, mp 240°C. ^{1}H NMR spectrum, δ, ppm: 6.66 d.d and 6.63 d.d (2H each), 6.92 d.d and 6.95 d.d (2H each), 7.37 d and 7.40 d (1H each), 7.58 d and 7.59 d (1H each), 7.60 d and 7.61 d (1H each).

Scheme 2.



a: $BrCH_2CH_2Br$, Me_2CO, Δ, 4–5 h; *b*: $BrCH_2CH_2CN$, Me_2CO, Δ, 3–4 h; *c*: (1) $CsOH \cdot H_2O$–MeOH, DMF; (2) MeI; *d*: $Hg(OAc)_2$–AcOH, Δ; *e*: $P(OEt)_3$.

9,9-Bis[4-(6-bromohexyloxy)phenyl]-2,7-diiodo-9*H*-fluorene (IV). Compound **III**, 2 g (3.3 mmol), was added to a solution of 0.37 g (6.6 mmol) of potassium hydroxide in 15 ml of methanol, and the resulting dark red solution of bis-phenoxide was added dropwise to a solution of 2.44 g (0.01 mol) of 1,6-dibromohexane in 15 ml of acetone. The mixture was heated until the red color disappeared, cooled, diluted with water, and extracted with diethyl ether. The extract was dried over Na_2SO_4, the solvent was removed under reduced pressure, and the residue was washed with hexane to remove excess 1,6-dibromohexane. The product was brought into further transformations without additional purification. Yield 73%, red viscous oily substance. ^1H NMR spectrum, δ, ppm: 1.32 m and 1.33 m (12H), 1.63 m and 1.73 m (4H), 3.27 t (4H), 3.76 t (4H), 6.57 d.d and 6.66 d.d (2H each), 6.89 d.d and 6.97 d.d (2H each), 7.29 d and 7.31 d (1H each), 7.50 d and 7.53 d (1H each), 7.58 s (2H).

2,7-Diiodo-9,9-bis(4-{6-[5-methylsulfanyl-2-(4,5-ethylenedisulfanyl-1,3-dithiol-2-ylidene)-1,3-dithiol-4-ylsulfanyl]hexyloxy}phenyl)-9*H*-fluorene (VI). Tetrathiafulvalene **Va**, 0.33 g (0.78 mmol), was dissolved in 10 ml of anhydrous DMF (preliminary purged with argon) on slight heating, a solution of 0.13 g (0.78 mmol) of $CsOH \cdot H_2O$ in 5 ml of anhydrous methanol was added in one portion, the mixture was stirred for 30 min, a solution of 0.36 g (0.39 mmol) of fluorene **IV** in 5 ml of DMF was added, and the mixture was heated for 10 h under reflux. It was then cooled and diluted with water, and the precipitate was filtered off, washed with a large amount of water, dried in air, and purified by chromatography on silica gel using ethyl acetate–hexane (1:2) as eluent. Yield 42%, red crystalline substance, mp 72–73°C. ^1H NMR spectrum, δ, ppm: 1.37 m and 1.4 m (12H), 1.52 m and 1.67 m (4H), 2.38 s (6H), 2.74 t (4H), 3.21 d and 3.22 d (4H each), 3.84 t (4H), 6.63 d.d and 6.71 d.d (2H each), 6.95 t (4H), 7.37 d and 7.39 d (1H each), 7.58 d and 7.61 d (2H each). Found, %: I 16.93; S 34.12. $C_{55}H_{52}I_2O_2S_{15}$. Calculated, %: I 16.79; S 33.93.

The ^1H NMR spectra were recorded on a Mercury Plus-300 spectrometer using hexamethyldisiloxane as internal reference. The IR spectra were measured on a UR-20 spectrometer.

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REFERENCES

1. Wudl, F., Smith, G.M., and Hufnagel, E.J., *J. Chem. Soc. D*, 1970, no. 21, p. 1453; Bryce, M.R., *Adv. Mater.*, 1999, vol. 11, no. 1, p. 11.
2. Kraft, A., Grimsdale, A.C., and Holmes, A.B., *Angew. Chem., Int. Ed.*, 1998, vol. 37, p. 402; Bernius, M.T., Inbasekaran, M., O'Brien, J., and Wu, N., *Adv. Mater.*, 2000, vol. 12, p. 1737; Oyston, S., Wang, Ch., Hughes, G., Batsanov, A.S., Perepichka, I.F., Bryce, M.R., Ahn, J.H., Pearson, Ch., and Petty, M.C., *J. Mater. Chem.*, 2005, vol. 15, p. 194.
3. Vannikov, A.V., *Ros. Khim. Zh.*, 2001, vol. 14, nos. 5–6, p. 41.
4. Carrol, R.L. and Gorman, Ch.B., *Angew. Chem. Int. Ed.*, 2002, vol. 41, p. 4378; Mori, T., Noda, B., Wada, H., Taguchi, T., Kambayashi, T., Ishikawa, K., and Takezoe, H., *54th Fujihara Seminar "Organic Semiconductors and Conductors: Half Century and Future Prospects,"* Aug–Sep 2005, p. 17.
5. Huchet, L., Akoudad, S., and Roncali, J., *Adv. Mater.*, 1998, vol. 10, no. 7, p. 541.
6. Hassan, J., Sevignon, M., Gazzi, C., Scholtz, E., and Lemaire, M., *Chem. Rev.*, 2002, vol. 102, p. 1359; Bellina, F., Carpita, A., and Rossi, R., *Synthesis*, 2004, no. 15, p. 2419.
7. *Sintezy iodistykh organicheskikh soedinenii* (Syntheses of Organic Iodine Compounds), Tomsk: Tomsk. Politech. Gos. Univ., 1976, p. 54.
8. Brunner, K., van Dijken, A., Borner, H., Bastiansen, J.J.A.M., Kiggen, N.M.M., and Langeveld, B.M.W., *J. Am. Chem. Soc.*, 2004, vol. 126, no. 19, p. 6035.
9. Simmonsen, K.B., Svenstrup, N., Lau, J., Simmonsen, O., Mørk, P., Kristensen, G.J., and Becher, J., *Synthesis*, 1996, no. 3, p. 407.
10. Hartke, K., Kissel, Th., Quante, J., and Matusch, R., *Chem Ber.*, 1980, vol. 113, p. 1898.
11. Steimecke, G., Sieler, J., Kirmse, R., and Hoyer, T., *Phosphorus Sulfur*, 1979, vol. 7, p. 49.
12. Svenstrup, N., Rasmussen, K.M., Hansen, T.K., and Becher, J., *Synthesis*, 1994, no. 8, p. 809.