

## Push-pull fluorene acceptors with ferrocene donor moiety

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### Abstract

We report on synthesis of a series of new push-pull compounds of the type A–X–D, where A is polynitrofluorene acceptor moiety, D is donor ferrocene moiety and X is various kind of bridges between them. Electronic absorption spectra ( $\lambda_{ICT}^{max} \approx 450\text{--}700\text{ nm}$ ) and second order polarisabilities (EFISH,  $\mu\beta(0) = 100\text{--}2400 \times 10^{-48}\text{ esu}$ ) of these compounds are reported.

**Keywords:** coupling reactions, non-linear optical methods, UV-Vis-NIR absorption, frequency conversion devices

### 1. Introduction

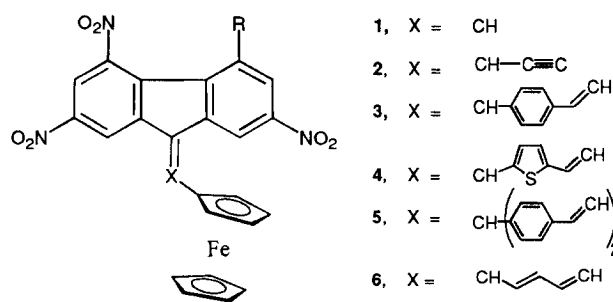
Electron acceptors of the fluorene series with intramolecular charge transfer (ICT) has been recognised for the last decade as promising candidates for photoconductive materials [1, 2], particularly as sensitizers of photothermoplastic storage media (PTSM). They exhibit substantial increasing the photosensitivity of PTSM in the ICT optical region of the acceptor. On the other hand, typical non-linear optical (NLO) chromophores for applications in optoelectronics and photonics are conjugated  $\pi$ -systems of the A–(bridge)–D type with strong acceptor (A) and donor (D) groups as terminal substituents.

Continuing our investigations of the fluorene electron acceptors with ICT from various donor moieties [2] we studied a number of fluorenes with ICT from ferrocene (Fc) as donor group, varying the length and the nature of the bridge between A and D.

### 1. Results and discussions

For the synthesis of the desired compounds a common strategy based on elaborated previously [1a, 2b] condensation of polynitrofluorenes with aldehydes was used. Compounds 1–6 display broad long-wave absorption bands between 450 and 900 nm that can be attributed to ICT transitions from the donor Fc onto acceptor fluorene moieties (Figure, Table). Ferrocene derivatives, bearing electron-withdrawing substituents conjugated to the donor moiety via  $\pi$ -electron framework have

been shown to exhibit second harmonic generation [3] although to our knowledge nitrofluorene acceptors have not been investigated in this context. It was, therefore of interest to study this property of the new push-pull molecules described in this paper. The variation of the quadratic polarisability ( $\beta$ ) was investigated using the electric field induced harmonic (EFISH) generation.



a, R=NO<sub>2</sub>; b, R=CO<sub>2</sub>Me; c, R=CO<sub>2</sub>(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>Me

A solubility problem which was encountered with tetranitroderivatives was solved by introduction of long-chain alkoxy carbonyl substituent (c) into the fluorene ring. The results of EFISH measurements are summarised in the Table. These data are consistent with previous observation [4] that for a series of homologous compounds with the same acceptor or donor unit, the dominant effect is the length of the conjugated spacer group.

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Lengthening the polyene chain generally results in a significant increase in  $\mu\beta$  values (although a saturation point is quickly reached) [4c] and compound **6b** shows substantially high level of SHG efficiency (Table). This makes nitrofluorene unit a promising candidate as an acceptor group for NLO chromophores.

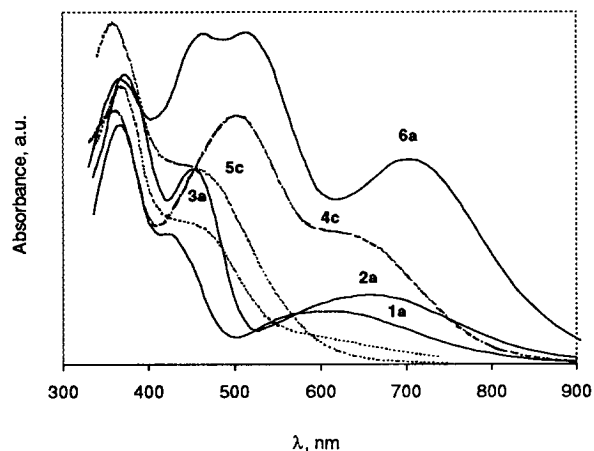


Figure. UV-Vis spectra of the investigated compounds in 1,2-dichloroethane solution.

Table. Absorption maxima ( $\lambda_{\max}$ ) in 1,2-dichloroethane solution and  $\mu\beta(0)$  values of compounds 1–6.

Compound	$\lambda_{\max} / \text{nm}$ ( $\epsilon_{\max} / \text{M}^{-1} \text{cm}^{-1}$ )	$\mu\beta(0) / 10^{-48} \text{esu}$
1a	430 (12000), 620 (4800)	100
1b	410sh, 609	
2a	451, 658	
2c	431 (13500), 616 (4600)	200±50
3a	430sh, ≈600sh	
3c	430sh, ≈600sh	800±100
4c	502 (21000), 640sh (11000)	
5c	450 (23000)	
6a <sup>a</sup>	464, 514, 706	
6b	450sh, 485sh, 660	2400±200
6c	455sh (25000), 490sh (25000), 660 (15000)	

<sup>a</sup> in acetone:  $\lambda_{\max}$  ( $\epsilon_{\max}$ ) = 461 (28000), 505 (28000), 690 (17000)

On the basis of comparison of fluorene with TCNQ acceptors and tetracyanoethylene (electron affinities or energies of intermolecular charge transfer)[5] one can conclude that polynitrofluorene-9-ylidene fragments as acceptor group is comparable to dicyanomethylene or tricyanvinyl groups but in contrast to the latest is expected to be more chemically and thermally stable which is important for trade-off design of NLO materials. Moreover, well-elaborated synthetic pathways to a wide range of fluorenes with electron-withdrawing substituents give a possibility to vary acceptor fragments in fluorene-containing NLO chromophores tuning their properties as solubility, thermal or chemical stability, spectral region of the transparency.

### 3. Experimental

All new compounds (1–6) were isolated, purified and adequately characterised by  $^1\text{H}$  NMR / mass spectra / elemental analyses. Details of the synthesis and characterisation will be published elsewhere.

EFISH generation measurement [6] have been performed in order to measure  $\mu\beta$  values of the chromophores. The experimental setup consists of a commercial (Surelite-II, "Continuum") Q-switched Nd:YAG laser ( $\lambda = 1.064 \mu\text{m}$ , 10Hz) Raman shifted to  $\lambda = 1.54 \mu\text{m}$  ( $\text{CH}_4$  at 30 atm.). Alternatively we have used an Optical parametric generator with  $1.58 \mu\text{m}$  radiation (NCPM  $\text{LiNbO}_3$ ) crystal pumped by the Nd:YAG). A special design of the EFISH cell is used to enable adjustment of the wedge angle to optimal number of SH intensity fringes. The reference signal is obtained from a quartz slab. A high speed boxcar integrator card (PCI-200, "Becker&Huckl") is used for data acquisition. Samples of each chromophore were prepared at three different concentrations in methylene chloride [typical concentration,  $c = (1-10) \times 10^{-4} \text{M}$ ] and tested using the EFISH setup. Results of  $\mu\beta$  were obtained with an experimental error of 10-15%. The EFISH analysis includes the correction to the absorption of the harmonic wave. Nonresonant hyperpolarisability values  $\mu\beta(0)$  were then deduced using the two level model approximation.

### 4. References

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