Synthesis and Spectroscopic and NLO Properties of “Push-Pull” Structures Incorporating the Inductive Electron-Withdrawing Pentafluorophenyl Group

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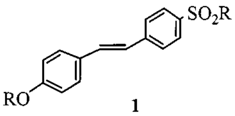
A series of "push-pull" molecules, each incorporating a pentafluorophenyl ring as an inductive accepting group, has been synthesised. The NLO properties of these compounds were measured in solution by EFISH (operating at 1907 nm) and in the solid state by the Kurtz powder technique (at 1907 nm). Values of $\mu\beta$, the product of the molecule dipole moment and its first-order hyperpolarizability, of up to 200×10^{-48} esu were obtained.

Introduction

Over recent decades, the study of organic materials with nonlinear optical properties has received growing attention thanks to their potential usefulness in the creation of integrated electro-optic and photonic devices.[1] As an example, second-order nonlinear organic materials are able to double the frequency of an incident laser light (a phenomenon also known as Second-Harmonic Generation, SHG), a property that finds applications in the development of new optical data-storage systems.[2−4] The core constituent of these second-order organic materials is usually a chromophore, typically a “push-pull” molecule: a conjugated π-electron system terminated by an electron donor and an electron acceptor group. The second-order nonlinear behaviour (expressed by the first-order hyperpolarizability β) in molecules can be increased and optimised by manipulation of the length and nature of the conjugated π-electron systems and the donor/acceptor strengths of end groups.[5] To be useful in real applications, however, such structures have to satisfy requisites of transparency[6] and thermal stability,[7] which are in turn to some extent incompatible with the structural parameters responsible for high or optimal first-order hyperpolarizability. Furthermore, the information density in optical data-storage systems is inversely proportional to the laser frequency; a higher density can thus be achieved by shortening the wavelength of the laser employed. Particularly appealing from this point of view are NLO organic materials able to operate with near infrared lasers (820−880 nm GaAs, AlGaAs diode lasers or Ti:sapphire lasers). However, the β value partially depends on the inverse square of the energy gap between ground and excited states,[5] and so the identification of organic chromophores that display a good trade-off between nonlinearity and full transparency both at 820−880 nm and at over 410 nm[8] still remains a big open challenge both for synthetic chemists and for materials scientists today.

Among the huge number of “push-pull” structures already synthesised and investigated,[9] the 4-alkoxy-4′-alkylsulfonyl-*trans*-stilbenes **1**[10] and the 4-alkoxy-2′,3′,4′,5′,6′-pentafluoro-*trans*-stilbenes **2**[11] represent some examples of chromophores that in part satisfy the requisites described above, as they are transparent over 410 nm, with λ_{max} = 335 and 326 nm and $\beta = 10$ and 15×10^{-30} esu (with a 1064 nm laser), respectively (Figure 1).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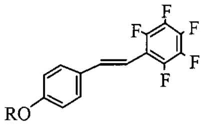
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Figure 1. “Push-pull” structures with inductive acceptors

The presence of inductive electron-withdrawing alkylsulfonyl groups in **1** and fluorine atoms in **2** is the peculiar feature that differentiates these structures from most other “push-pull” structures, in which essentially mesomeric donors and/or acceptors are normally used. In addition, compounds **2** clearly have better transparency/nonlinear behaviour trade-offs in comparison with **1** ($\beta = 15$ vs. 10×10^{-30}esu; λ_{max} = 326 nm vs. 335 nm).

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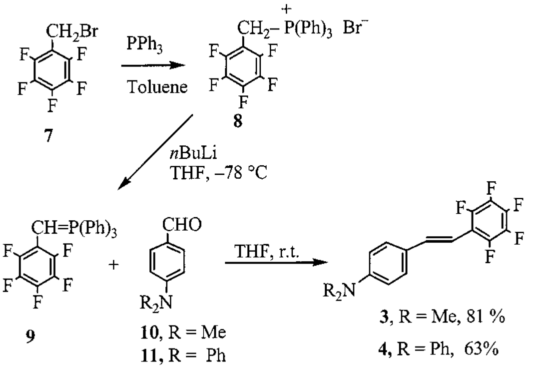
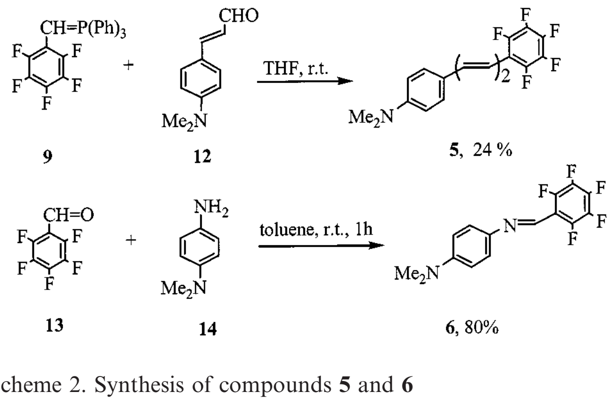
Results and Discussion

Despite the promising features of fluorinated aromatic rings as acceptor groups, their use so far seems limited to stilbenes bearing alkoxy functions only.[12] Since alkoxy functions are electron-donating groups of moderate strength with limited applications, we decided to synthesise the 4-dimethylamino-2′,3′,4′,5′,6′-pentafluoro-*trans*-stilbene (**3**), and 4-diphenylamino-2′,3′,4′,5′,6′-pentafluoro-*trans*-stilbene (**4**), in which the 4-alkoxy group is replaced by the more electron-donating dialkylamino or diarylamino groups. Through this substitution, we expected to improve markedly the second-order nonlinear responses. Compounds **3** and **4**, the synthesis of which has to the best of our knowledge never been reported before, were readily prepared in satisfactory yields by treatment of (2,3,4,5,6,-pentafluorobenzylidene)triphenylphosporane (**9**) with *para*-(dimethylamino)benzaldehyde (**10**) and *para*-(diphenylamino)benzaldehyde (**11**). The phosphorane **9** was generated in situ by treatment of the corresponding phosphonium salt **8** with *n*BuLi. In turn, **8** was prepared by treatment of commercially available pentafluorobenzyl bromide (**7**) with triphenylphosphane (Scheme 1).



Scheme 1. Synthesis of compounds **3** and **4**

In addition, we also planned the synthesis of (1*E*,3*E*)-1-[4-(dimethylamino)phenyl]-4-(2′,3′,4′,5′,6′-pentafluorophenyl)-1,3-butadiene (**5**) and *N*-[4-(dimethylamino)phenyl]-1-(2′,3′,4′,5′,6′-pentafluorophenyl)methanimine (**6**), with the aim of analysing the second order nonlinearity by increasing the π-spacer length or replacing a C−C double bond with an azomethyne functionality.



Scheme 2. Synthesis of compounds **5** and **6**

Compound **5** was synthesised similarly to compounds **3** and **4**, by treatment of **9** with *para*-(dimethylamino)cinnamaldehyde (**12**), while compound **6** was synthesised by treatment of pentafluorobenzaldehyde (**13**) with 4-(dimethylamino)aniline (**14**) in refluxing toluene (Scheme 2).

All new compounds were physically and spectroscopically characterised (see Exp. Sect.). As expected, slight upfield shifts were observed for the *ortho*- and *para*-fluorine atom resonances in **3** and **4** relative to those in **2**[13] (*ortho*-fluorine: $\delta = -144$ vs. $\delta = -143$; *para*-fluorine: $\delta = -159$ vs. $\delta = -158$), while practically no differences between **5** and **2** were observed. This was in line with the better electron-donating capabilities of the dimethylamino and diphenylamino groups, which should make the pentafluorophenyl ring more electron-rich than in the case of the methoxy-substituted one. In contrast, a downfield shift was observed in the imine derivative **6**, particularly for the *para*-fluorine signal ($\delta = -152$ vs. -158). In this derivative the fluorine resonances were close to those of a pentafluoro aromatic ring bearing an alkyl substituent, thus indicating that the imine moiety influences the fluorine resonances similarly.[14] The resonances of the quaternary carbon atom of the pentafluorophenyl ring ($\delta \approx 110$) for **3** and **5** were surprisingly shifted upfield from the usual aromatic carbon atom resonances, falling close to those of the olefinic carbon atom.

The electronic spectra of derivatives **3**−**5**, recorded in CH_2Cl_2, showed absorption bands narrower (evaluated in terms of half-height bandwidth, $\lambda_{1/2h}$) than that seen for 4-dimethylamino-4′-nitrostilbene (DANS). Narrow absorption bands indicate similar molecular geometries in the ground and excited states, while $\lambda_{1/2h}$ values represent a rough evaluation of how the absorbed energy is spread out over the vibrational levels of singlet ground (S_0) and first excited state (S_1). It was noteworthy that the substitution of the dimethylamino group with a diphenylamino moiety produced an appreciable narrowing of the absorption band ($\lambda_{1/2h} = 88$ nm vs. $\lambda_{1/2h} = 65$ nm) (Figure 2).

All of the compounds **3**−**5** were fluorescent in CH_2Cl_2 solution, and compounds **3** and **4** showed very close maximum emission bands (457 nm vs. 458 nm), but substantially different maximum absorptions (341 nm vs. 379 nm) (Table 1). This means that **3** and **4** have the same energy difference between the S_0 ground state and the S_1/v_0 excited state (v_0 = lowest energy vibrational level), but that **4** disperses less of the absorbed energy in nonradiative vibrational relaxation processes than **3** does. Absorption spectra of the imine derivative **6** were very similar to those of **5**, indicating that the imine functionality has the same bathochromic effect as two double bonds. The thermal stabilities of these compounds were also evaluated by Differential Scanning Calorimetry (DSC). Compound **3** showed decomposition immediately above its melting point (177 °C), whereas **4** showed a sharp melting point at 102.8 °C and no decomposition up to 300 °C. This is in line with the increase in thermal stability normally observed when a

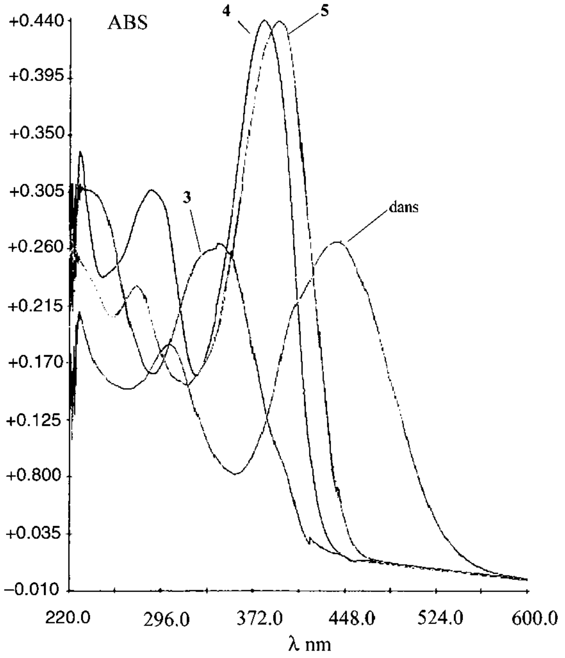


Figure 2. Absorption spectra of compounds **3−5** and DANS

dimethylamino group is replaced by a diphenylamino one.[15] The nonlinear behaviour of compounds **3−6** was evaluated in solution by EFISH, with a laser operating at 1907 nm.[16]

The values of $\mu\beta$ found were positive and in the range between 90×10^{-48} esu and 200×10^{-48} esu. In particular, compound **4** showed a $\mu\beta$ value twice that of compound **3**. This is in agreement with the presence of the same electron-withdrawing and electron-donating groups in the two compounds but with the presence of a longer π-delocalized spacer in **4**. It is known, in fact, that the length of the π-delocalized chain in push-pull molecules is a key parameter for enhancement of NLO response.[3,4] On the other hand, the behaviour observed for compounds **4** with respect to that of **3** is quite surprising. Usually, replacement of the dimethylamino donor group by a diphenylamino group, in the presence of the same π-delocalized spacer, causes a decrease in the NLO response with a concomitant increase in thermal stability. This latter was in fact higher in compound **4** than in **3**, but no significant difference was observed in the $\mu\beta$ values of the two compounds. Finally, compound **6** showed a $\mu\beta$ value slightly lower than those of **3** and **5** (+90 vs. +100 and $+110 \times 10^{-48}$ esu, respectively). This decrease can be attributed to the presence of the imine nitrogen atom in the π-spacer, causing a decrease in μ, which is, in fact, the smallest in the series (3.3 D). By taking the experimental μ values of compounds **3−6** into account, it is possible to calculate β for each compound. Given the small μ values observed for all compounds (from 3.3 D to 5.4 D, being the projection of *ortho* C−F bond dipole vector onto the molecular axis being against the direction of molecular dipole moment[12]), significant β values are obtained. These are always higher than β values observed for compounds **2**, these being in the range between $+37 \times 10^{-30}$ esu and $+21 \times 10^{-30}$ esu.

Table 1 summarises physical, spectroscopic, and nonlinear properties of the derivatives **3−6**. For purposes of comparison, the "figure of merit" *Q* (estimated by $\mu\beta_0/\lambda_{max} \times 10^{-43}$ c.g.s. units) for each compound is also reported. This figure of merit is particularly useful, since it contains: (1) the "intrinsic" (or at zero frequency) first hyperpolarizability β_0, which is a measure of the nonlinear response, (2) the dipolar moment μ in the ground state, which evaluates how easily a molecule can be oriented or poled and (3) the λ_{max}, which can be taken as a rough indicator of the transparency of the molecules. A high value of *Q* means a satisfactory compromise between these parameters.

Conclusions

In this work, we have reported on the synthesis and NLO properties of a new series of "push-pull" structures incorporating a pentafluoro aromatic ring as acceptor group. As expected, replacement of the donor alkoxy group in **2** by a dimethylamino (**3**) or a diphenylamino (**4**) moiety produces a pronounced increase in the nonlinear first order hyperpolarizability β [from 11×10^{-30} esu (estimated value at 1907 nm; see Table 1) for **2** to 23×10^{-30} esu for **3**].

Concomitantly, a useful red shift of the maximum absorption is also observed (341 nm for **3** or 379 nm for **4** vs. 326 nm of **2**), but the derivatives **3** and **4** remain transparent

Table 1. Physical, spectroscopic and nonlinear properties of **3−6**

Compound	M.p. [°C]	Abs.: λ_{max} [nm][a] ($\Delta\lambda_{1/2h}$[b])	Emiss.: λ_{max} [nm][a]	$\mu\beta$[c] (μ)	β [d] (Q[e])	Ref.
2	133	326		+35[f] (3.3)	+11 (9.2)	[12,13]
3	177[g]	341 (88)	457	+100 (4.4 D[h])	+23 (25)	this work
4	103[i]	379 (65)	458	+110 (n.d)	n.d. (23)	this work
5	188[g]	393 (72)	510	+200 (5.4 D[h])	+37 (40)	this work
6	176[g]	401 (76)	n.d.	+90 (3.3 D[j])	+21 (18)	this work

[a] Solvent CH_2Cl_2. [b] DANS has $\Delta\lambda_{1/2h} = 110$ nm and $Q = 84$.[9] [c] Solvent $CHCl_3$, values $\times 10^{-48}$esu. [d] Values $\times 10^{-30}$esu. [e] Figure of merit $Q = \mu\beta_0/\lambda_{max} \times 10^{-43}$ in c.g.s. units; $\mu\beta_0$ evaluated according to the two-state model by $\mu\beta_\lambda(1 - \lambda^2_{max}/\lambda^2)[1 - 4(\lambda^2_{max}/\lambda^2)]$, where λ is laser frequency (see ref.[12]). [f] According to the two-state model the $\mu\beta$ value for **2** was estimated at 1907 nm with: $Q\lambda_{max} \times 10^{-2}/ (1 - \lambda^2_{max}/\lambda^2)[1 - 4(\lambda^2_{max}/\lambda^2)]$ in esu, with $\lambda = 1907$ nm. [g] Melting with decomposition. [h] Measurement performed in toluene. [i] No decomposition observed up to 300 °C. [j] Measurement performed in $CHCl_3$.

above 420 nm. Particularly interesting is the narrowing effect on the maximum absorption band produced by the diphenylamino donor group, which practically cancels the observed red-shifting. Anyway, the red shift observed on going from **2** to **3** is four times smaller than the red shift observed between 4-methoxy-4′-nitrostilbene and 4-dimethylamino-4′-nitrostilbene (about 60 nm; see ref.[9]), confirming the usefulness of fluorinated aromatic ring for achieving a good trade-off between transparency and nonlinear behaviour. An increase in π-spacer length produces, as expected, an improvement of nonlinear response, with a β value that practically doubles on going from **3** (23×10^{-30} esu) to **5** (37×10^{-30} esu). The μβ value of **4** is slightly better than that of **3**. This is quite surprising, since usually, with the same spacer, the substitution of a dimethylamino group for a diphenylamino one reduces the NLO response in favour of the thermal stability. In our case, an increase in thermal stability was observed, without a decrease in NLO response. The figures of merit for derivatives **3** (25) and **4** (23) were more than twice that for **2** (9.2[12]), while those for **5** (40) were more than four times higher. These values are among the highest obtained with “push-pull” structures bearing inductive acceptors. We have also shown that the replacement of a double bond by an imine functionality produces a red shift of the maximum absorption in the electronic spectrum but does not influence the nonlinear response ($\lambda_{max} = 341$ nm and $\beta = +23$ for **3**, vs. 401 and + 21 for **6**). Another peculiar feature of “push-pull” structures bearing completely fluorinated aromatic ring is that they possess low molecule dipolar moments, since the projection of the *ortho*-C−F bond dipole vector onto the molecular axis is against the direction of molecular dipole moment.[12] This aspect should have a positive consequence on polymers doped with “push-pull” structures bearing fluorinated aromatic acceptor rings, since it would be expected that they would show a higher temporal stability of the poling.

Finally, derivative **4** is emissive in the solid state, a property indispensable for the development of Organic Light-Emitting Diodes (OLEDs), and work in this area is in progress.

Experimental Section

General and Materials: 2,3,4,5,6-Pentafluorobenzyl bromide (**7**) was purchased from Aldrich Chemical Co. or readily prepared from the cheaper and commercially available 2,3,4,5,6-pentafluorobenzaldehyde (**13**; Aldrich Chemical Co. or Lancaster) by published procedures.[11] The aldehydes **10**, **11** and **12** and 4-(dimethylamino)aniline (**14**) were purchased from Aldrich Chemical Co. and were used as received. *n*BuLi (1.6 M hexane solution) was purchased from Merck Co. and titrated just before use. THF was dried by refluxing in the presence of Na/benzophenone ketyl. All manipulations were performed under an inert gas. Flash and dry chromatography were performed with Merck 60 silica gel 230−400 mesh. Melting points were measured with a Büchi 510 melting point apparatus and are uncorrected. The IR spectra were recorded with a Perkin−Elmer 1725X FT-IR spectrophotometer, the UV/Vis spectra were recorded with a Jasco V-570 UV/Vis/NIR spectrophotometer, and the NMR spectra were obtained with a Bruker AC 300. ^{19}F NMR spectra were collected using $CFCl_3$ as internal standard. The mass spectra (EI, FAB) were recorded with a VG Analytical 7070 EQ instrument. EFISH measurements were carried out in chloroform solutions at a fundamental wavelength of 1.907 μm, by using a Q-switched, mode-locked Nd^{3+}:YAG laser with a pulse duration of 15 ns at a 10 Hz repetition rate, the 1.064 μm initial wavelength of which was shifted by stimulated Raman scattering in a high-pressure hydrogen cell; χ^2 measurements were performed at a fundamental wavelength of 1.907 μm with a Q-switched, mode-locked Nd^{3+}:YAG laser, the 1.064 μm initial wavelength of which was also shifted by stimulated Raman scattering in a high-pressure hydrogen cell. A portion of this beam was directed onto capillaries containing solid samples and the scattered SHG was collected by an elliptical mirror, filtered and collected with a Hamamatsu R5108 photomultiplier tube.

General Procedure for the Preparation of Products 3, 4 and 5: The aldehydes **10**, **11** and **12** (1.2 equiv.) were added at −78 °C, under an inert gas, to a yellow tetrahydrofuran solution (25 mL) of the phosphorane **9** [generated by treating 1 mmol of **8** with 1 mmol of *n*BuLi (1 mL of 1 M hexane solution) at −78 °C for 20 min]. The mixture was allowed to react at room temperature and the progress of the reaction was monitored by TLC (eluent diethyl ether/light petroleum ether, 3:7). The reaction was practically complete after 15 h, and was then quenched by addition of 10 mL of a saturated ammonium chloride solution, and almost all the organic solvent was removed under reduced pressure. The crude oil was taken up with CH_2Cl_2 (100 mL), and the organic layer was washed twice with distilled water. The organic phase was dried with Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude reaction mixture was purified by dry flash chromatography (eluent: light petroleum ether/CH_2Cl_2, 2:8) to provide **3** (0.41 g, 81% yield), (eluent: light petroleum ether/CH_2Cl_2, 2:8) to provide **4** (0.35 g, 67% yield), (eluent: light petroleum ether/diethyl ether, 3:7) to provide **5** (0.12 g, 25% yield), together with up to 40% of unchanged aldehyde **11**.

Compound 3: Pale yellow solid; m.p. 175 °C, dec. (from ethanol). IR (nujol): $\tilde{\nu} = 1001$ (ν, C−F), 959 cm^{-1} [δ, C=C (*E*)]. UV/Vis (CH_2Cl_2): $\lambda_{max} = 341$ nm ($\varepsilon = 22000$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.90 [s, 6 H, $N(CH_3)_2$], 6.65 (broad d, 2 H, $J_{ortho} = 9$ Hz, system AB-A′B′ arom.), 6.68 (d, 1 H, $J_{(E)} = 16.7$ Hz, C_6F_5−CH=C*H*−Ar), 7.28 (d, 1 H, $J_{(E)} = 16.7$ Hz, C_6F_5−C*H*=CH−Ar), 7.35 (d, 2 H, $J_{ortho} = 9$ Hz, AA′-BB′ system, arom.). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.2 (CH_3), 107.7 (Ar−*C*H=CH−C_6F_5), 110.4 (m, C_q fluorinated aromatic ring), 112.1 (CH, aromatic ring), 124.7 (C_q, aromatic ring), 128.0 (CH, aromatic ring), 137.3 (m, Ar−CH=*C*H−C_6F_5), 137.8 (bd, C−F, $^{1}J_{C-F} \approx 250$ Hz), 138.9 (bd, C−F, $^{1}J_{C-F} \approx 252$ Hz), 144.4 (bd, C−F, $^{1}J_{C-F} \approx 249$ Hz), 150.9 (C_q, aromatic ring). ^{19}F NMR ($CDCl_3$): δ = −144.13 (2 F, F_{ortho}), 159.28 (1 F, F_{para}), −164.07 (2 F, F_{meta}). MS (EI): *m*/*z* = 313 [M^{+}]. $C_{16}H_{12}F_5N$ (313.3): calcd. C 61.28, H 3.75, N 4.39; found C 61.34, H 3.86, N 4.47.

Compound 4: Bright yellow solid, m.p. 102.5 °C (from diethyl ether). IR (nujol): $\tilde{\nu} = 1004$ (ν, C−F), 966 cm^{-1} [δ, C=C (*E*)]. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon) = 379$ nm (18000). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.77 (d, 1 H, $J_{(E)} = 16.7$ Hz, C_6F_5−CH=C*H*−Ar), 6.95−7.09 (m, 6 H, C_6F_5−C*H*=CH−Ar + 5 H arom.), 7.18−7.34 (m, 9 H arom.). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 105.3 (Ar−*C*H=CH−C_6F_5), 107.6 (m, C_q fluorinated aromatic ring), 117.5 (CH, aromatic ring) 117.6 (CH, aromatic ring), 118.4 (2 CH, aromatic ring), 119.7 (2 CH, aromatic ring), 119.8 (2 CH, aromatic ring), 122.5 (CH, aromatic ring), 122.7 (CH, aromatic ring), 124.1 (2 CH, aromatic ring), 124.3 (2 CH, aromatic ring), 124.9 (C_q, aromatic ring), 131.6 (m, Ar−CH=*C*H−C_6F_5), 132.6 (bd, C−F, $^1J_{C-F} \approx$ 251 Hz), 134.2 (bd, C−F, $^1J_{C-F} \approx$ 253 Hz), 139.5 (bd, C−F, $^1J_{C-F} \approx$ 249 Hz), 142.1 (2 C_q, aromatic ring), 143.5 (C_q, aromatic ring). ^{19}F NMR ($CDCl_3$): $\delta = -143.67$ (2 F, F_{ortho}), 157.92 (1 F, F_{para}), −163.64 (2 F, F_{meta}). MS (EI): *m*/*z* = 437 [M^+]. $C_{26}H_{18}F_5N$ (437.4): calcd. C 71.39, H 3.69, N 3.20; found C 70.98, H 3.58, N 3.10.

Compound 5: Bright yellow solid; m.p. 188 °C, dec. (from diethyl ether). IR (nujol): $\tilde{\nu}$ = 996 (ν, C−F), 978, 956 cm^{-1} [δ, C=C (*E*)]. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 392 nm (40000). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.00 [s, 6 H, $N(CH_3)_2$], 6.43 [d, 1 H, $J_{(E)}$ = 17.1 Hz, $C_6F_5-(CH{=}C\mathit{H})_2-Ar$], 6.65−6.75 (m, 4 H, 2 H system −(CH=CH)$_2$− + 2 H arom), (broad d, 2 H, J_{ortho} = 9 Hz, system AB-A′B′ arom.), 6.68 (d, 1 H, $J_{(E)}$ = 16.7 Hz $C_6F_5-CH{=}C\mathit{H}-Ar$), 7.25 (m, 1 H, $C_6F_5-(CH{=}C\mathit{H})_2-Ar$ partially covered by $CHCl_3$ signal), 7.35 (d, 2 H, J_{ortho} = 8.5 Hz, system AB-A′B′ arom.). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.7 (CH_3), 112.6 (CH, aromatic ring), 113.6 (m, C_q fluorinated aromatic ring), 113.7 (CH= 1,3-butadiene system), 125.1 (CH= 1,3-butadiene system), 125.3 (C_q, aromatic ring), 128.5 (CH, aromatic ring), 137.1 (CH= 1,3-butadiene system), 138.2 (bd, C−F, $^1J_{C-F} \approx$ 257 Hz), 139.0 (*C*H= 1,3-butadiene system), 139.6 (bd, C−F, $^1J_{C-F} \approx$ 240 Hz), 144.8 (bd, C−F, $^1J_{C-F} \approx$ 245 Hz), 150.9 (C_q, aromatic ring). ^{19}F NMR ($CDCl_3$): $\delta = -143.83$ (2 F, F_{ortho}), 158.68 (1 F, F_{para}), −163.97 (2 F, F_{meta}). $C_{18}H_{14}F_5N$ (339.3): calcd. C 63.72, H 4.16, N 4.13; found C 63.39, H 4.07, N 4.02.

Procedure for the Preparation of Product 6: A solution of 2,3,4,5,6-pentafluorobenzaldehyde (**13**; 1 mmol) and 4-(dimethylamino)aniline (**14**; 1 mmol) in toluene (10 mL) was stirred for 1 h at room temperature. The reaction solvent was removed under pressure, the crude material was taken up with cool acetone (10 mL), and the poorly soluble material, almost pure imine **6**, was collected by filtration. The imine **6** was further purified by crystallization from acetone to afford an analytically pure sample (89% yield based on purified sample).

Compound 6: Golden yellow solid; m.p. 175−176 °C, dec. (from acetone). IR (nujol): $\tilde{\nu}$ = 1651 (ν, C=N), 1001 cm^{-1} (ν, C−F). UV/Vis (CH_2Cl_2): λ_{max} (ε) = 401 nm (19000). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.01 [s, 6 H, $N(CH_3)_2$], 6.73 (bd, 2 H, J_{ortho} = 9 Hz, system AB-A′B′ arom.), 7.30 (d, 2 H, J_{ortho} = 9 Hz, system AA′-BB′ arom.), 8.58 (s, 1 H, CH=N). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.43 [$N(CH_3)_2$], 112.7 (CH, aromatic ring + C_q fluorinated aromatic ring), 122.7 (CH, aromatic ring), 137.7 (bd, C−F, $^1J_{C-F} \approx$ 250 Hz), 139.7 (C_q, non-fluorinated aromatic ring), 141.6 (bd, C−F, $^1J_{C-F} \approx$ 253 Hz), 145.9 (bd, C−F, $^1J_{C-F} \approx$ 249 Hz), 150.9 (C_q, non-fluorinated aromatic ring). ^{19}F ($CDCl_3$): $\delta = -143.07$ (2 F, F_{ortho}). 152.39 (1 F, F_{para}), −162.62 (2 F, F_{meta}). MS (EI): *m*/*z* = 313 [M^+]. $C_{15}H_{11}F_5N_2$ (314.2): calcd. C 57.11, H 3.41, N = 8.79; found C 57.33, H 3.53, N 8.91.

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[14] For example, the fluorine resonances of pentafluorobenzyl alcohol are: F_{ortho}: $\delta = -144$; F_{meta}: $\delta = -162$, F_{para}: $\delta = -154$.
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[16] An evaluation of $\chi^{(2)}$ was also performed in the solid state, by the Kurtz powder technique. Remarkably, compounds **4** and **5** showed detectable values of $\chi^{(2)}$. In particular, **4** has a second order NLO activity 0.25 times that of urea (used as standard compound), while **5** is considerably less active, with a nonlinear response 5×10^{-3} times that of urea.

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