

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/230712092>

# Octupolar Derivatives Functionalized with Superacceptor Peripheral Groups: Synthesis and Evaluation of the Electron-Withdrawing Ability of Potent Unusual Groups

ARTICLE in CHEMISTRY - A EUROPEAN JOURNAL · SEPTEMBER 2012

Impact Factor: 5.73 · DOI: 10.1002/chem.201103460 · Source: PubMed

---

CITATIONS

13

---

READS

14

7 AUTHORS, INCLUDING:



Cédric Rouxel

Université de Rennes 1

17 PUBLICATIONS 184 CITATIONS

SEE PROFILE



Olivier Mongin

Université de Rennes 1

122 PUBLICATIONS 2,984 CITATIONS

SEE PROFILE



Emmanuel Magnier

Université de Versailles Saint-Quentin

64 PUBLICATIONS 1,221 CITATIONS

SEE PROFILE

# Octupolar Derivatives Functionalized with Superacceptor Peripheral Groups: Synthesis and Evaluation of the Electron-Withdrawing Ability of Potent Unusual Groups

Cédric Rouxel,<sup>[c]</sup> Céline Le Droumaguet,<sup>[c]</sup> Yohan Macé,<sup>[b]</sup> Sophie Clift,<sup>[b]</sup> Olivier Mongin,<sup>[c, d]</sup> Emmanuel Magnier,<sup>\*,[b]</sup> and Mireille Blanchard-Desce<sup>\*,[a, c]</sup>

**Abstract:** Novel tripodal derivatives with a triphenylamine core and that bear “superacidifiers” (i.e., fluorinated sulfoximinyl blocks) or novel sulfiliminyl moieties as peripheral groups were synthesized. These new chromophores show strong absorption in the near-UV region and emission in the visible region. The fluorinated sulfoximinyl moieties were found to behave as potent auxochromic and electron-withdrawing (EW) groups, thus leading to redshifted absorption and emission. These moieties promote a core-to-periphery intramolecular charge transfer (ctp-ICT) transition, the energy of which was found to be correlated to their EW strength. In this study, we

provide evidence of a linear correlation between the Hammett constant ( $\sigma_p$ ) values and the electronic gap between the ground and first excited state of the three-branched derivatives. This in turn was used to derive  $\sigma_p$  values of fluorinated sulfoximinyl moieties. These EWGs show unprecedentedly high  $\sigma_p$  values, up to 1.45 relative to 0.8 for NO<sub>2</sub>. Also, by using this method, the sulfiliminyl moiety was shown to exhibit similar EW strength as NO<sub>2</sub>, while promoting improved transparency and

solubility. Finally, the superior EW strength of the fluorinated sulfoximine peripheral moieties was shown to induce significant enhancement of the two-photon absorption responses in the red near-IR region of the three-branched derivatives relative to similar octupoles that bear more usual strong EW groups. These characteristics (improved nonlinear responses or transparency) open new routes for the design of nonlinear optical (NLO) chromophores for optical limiting or electro-optical modulation. Such building blocks could also be of interest for optoelectronic applications, including the development of solar cells.

**Keywords:** charge transfer • chromophores • fluorinated substituents • sulfilimines • sulfoximines

## Introduction


The unrivalled properties induced by the presence of fluorine atoms into molecules has allowed considerable progress in the life sciences (medicinal and agro-chemistry), energy, as well as materials chemistry.<sup>[1]</sup> Furthermore, the electron-withdrawing properties of fluorine-containing moieties as well the improved transparency brought about by replacing CH groups by CF groups (as illustrated in polymeric optical fibers) has attracted considerable attention in the field of optoelectronics materials. In particular, fluorinated moieties have been used in several nonlinear optical (NLO) organic chromophores (NLO-phores) both for second-order effects (to give push–pull chromophores with large hyperpolarizability  $\beta$ )<sup>[2]</sup> and third-order effects (including two-photon absorption).<sup>[2a,3]</sup> Sulfoxides and, to a greater extent, sulfones are well known as excellent electron-withdrawing groups (EWG)<sup>[4]</sup> and have proven to be of great interest for the design of push–pull chromophores and NLO-phores while ensuring suitable transparency, which is of high interest for applications such as electro-optical modulation<sup>[2b,5]</sup> or optical limitation.<sup>[6]</sup> By taking advantage of the increase in EW ability induced by the replacement of alkyl substituents by fluorinated ones, we have shown previously that dipolar and oc-

[a] Dr. M. Blanchard-Desce  
Univ. Bordeaux, Institut des Sciences Moléculaires  
CNRS UMR 5255, 351 Cours de la Libération  
33405 Talence Cedex (France)  
Fax: (+33) 5-40-00-66-32  
E-mail: m.blanchard-desce@ism.u-bordeaux1.fr

[b] Y. Macé, S. Clift, Dr. E. Magnier  
Institut Lavoisier de Versailles (ILV)  
CNRS UMR 8180, Université de Versailles  
St Quentin en Yvelines, 45 avenue des Etats-Unis  
78035 Versailles Cedex (France)  
Fax: (+33) 1-39-25-44-52  
E-mail: magnier@chimie.uvsq.fr

[c] Dr. C. Rouxel, Dr. C. Le Droumaguet, Dr. O. Mongin,  
Dr. M. Blanchard-Desce  
Chimie et Photonique Moléculaires  
CNRS UMR 6510, Université de Rennes 1  
Campus de Beaulieu, 35042 Rennes Cedex (France)

[d] Dr. O. Mongin  
Institut des Sciences Chimiques de Rennes  
CNRS UMR 6226, Université de Rennes 1  
Campus de Beaulieu, 35042 Rennes Cedex (France)

 Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.201103460>.

tupolar derivatives with perfluorinated sulfone moieties as EWGs exhibit large third-order NLO responses, combined with redshifted emission and strongly environmental-dependent fluorescence.<sup>[3c,d,7]</sup> Following this route and with the aim of further improving the core-to-periphery intramolecular charge transfer (ctp-ICT) properties, we wish to report here the synthesis and characterization of three-branched derivatives that bear “superacidifiers”<sup>[8]</sup> based on fluorinated sulfoximines as EW peripheral groups. In addition, we explore the potentialities of fluorinated sulfilimine moieties as original EWGs for the elaboration of ctp-ICT derivatives. The experimental investigation of the auxochromic and fluorochromic characteristics of these nonclassical substituents is reported. By means of a comprehensive study of their spectroscopic (NMR and optical) properties, we describe correlations that allow us to derive the unknown Hammett constant ( $\sigma_p$ ) values of the fluorinated EWGs. The studies reveal unprecedentedly high  $\sigma_p$  values for fluorinated sulfoximinyl moieties and determine the EW ability of an original sulfiliminyl moiety, which is shown to be as strong as  $\text{NO}_2$  but leads to improved transparency.

## Results and Discussion

**Design:** Three-branched triphenylamine-cored octupolar chromophores exhibit an intense absorption band in the visible region, which is related to a ctp-ICT transition. They also show highly polarity-sensitive emission due to the localization of the excitation on a single branch prior to emission, thus giving rise to polar emissive excited states.<sup>[3d]</sup> This behavior has led to the design of biphotonic fluorescent polarity probes.<sup>[3c]</sup> For biological imaging, it is highly desirable to shift both absorption (by using two-photon excitation, for instance) and emission in the visible towards the red region to reduce toxicity and to allow imaging at increased depth (in relation to reduced scattering and absorption by endogenous chromophores). We have shown in an earlier study that an efficient strategy to redshift both absorption and emission and to enhance both the optical responses (hyperchromic shift) and the medium sensitivity consists of increasing the electron-withdrawing strength of the peripheral groups.<sup>[3d]</sup> We herein explore the potential of fluorinated superacidifiers as “superacceptors” building blocks. We stress that the use of such moieties in the molecular NLO domain remains largely untouched, although potentialities for improving the NLO response(s)/transparency trade-off are quite attractive.

To ensure photostability and rigidity (to limit nonradiative decay processes), we have selected phenyleneethynylene (PE) connectors. An already described three-branched triphenylamine-cored octupolar compound that bears nitro end groups<sup>[9]</sup> will be used as a model chromophore (Figure 1), since the nitro moiety is the standard prototype of strong EWGs. The nitro group ( $\text{NO}_2$ ) is well known as an auxochromic substituent that promotes significant redshift and increases the intensity of the low-energy absorption

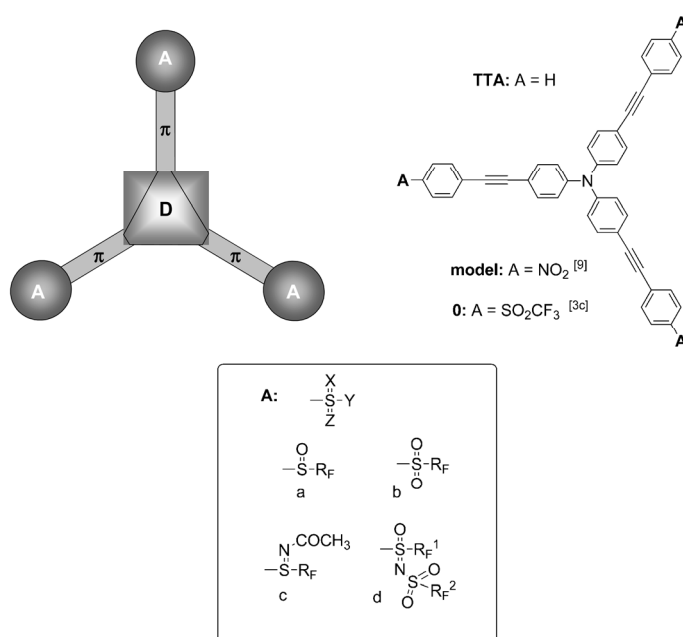
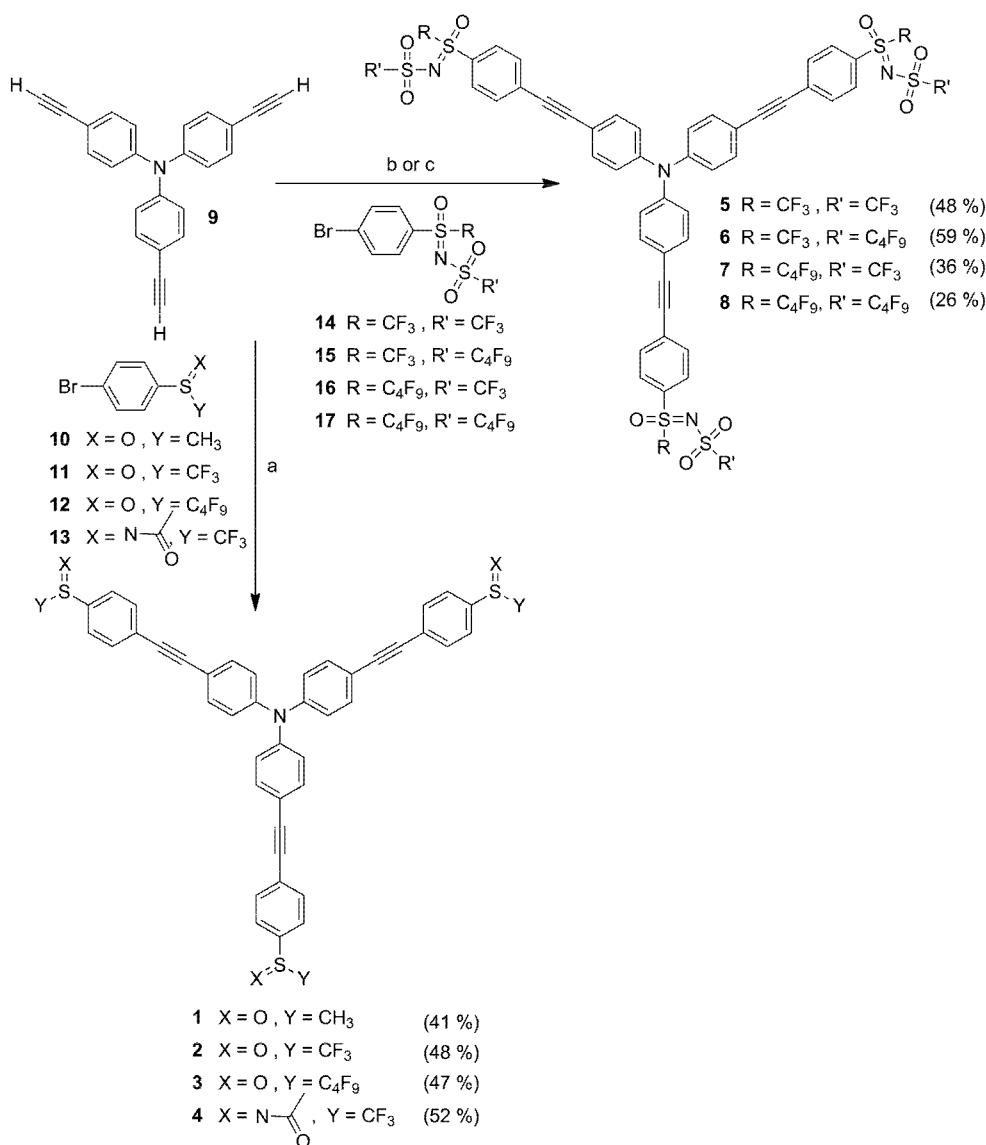


Figure 1. The three-branched triphenylamine-cored octupolar structure that contains nitro end groups (model chromophore); sulfoxide (a), sulfonyl (b), sulfiliminyl (c), and sulfoximinyl (d) EWGs.

band of  $\pi$ -conjugated and aromatic systems. This last aspect is particularly pronounced in so-called push-pull systems when  $\text{NO}_2$  is used as a (strong) EWG.<sup>[10]</sup> However, the adjunction of  $\text{NO}_2$  auxochromic groups often leads to lower fluorescence quantum yields (due to intersystem crossing in relation with low-energy  $n\text{-}\pi^*$  transitions) and also promotes a marked decrease in solubility, particularly when several nitro substituents are combined in the same molecular structure. Both of these drawbacks strongly reduce its scope for the design of fluorescent probes. In that context, our aim was to develop alternative powerful EWGs while trying to control nonradiative decay to preserve fluorescence and maintain solubility in organic environments. We have to keep in mind, however, that increased EWG strength is expected to produce a redshifted absorption and emission (due to the lowering of the lower electronic excited state), which accordingly leads to a decrease in the fluorescence quantum yield due to combined decrease of the radiative decay rate<sup>[11]</sup> and an increase in the nonradiative one. In this context, we explore here the potentialities of fluorinated sulfoximinyl<sup>[8,12]</sup> (d) as well as new fluorinated sulfiliminyl<sup>[13]</sup> (c) groups in octupolar ctp-ICT compounds (Figure 1). These EWG moieties will be compared to more classical strong EWGs such as fluorinated sulfoxides (a) and sulfonyl (b) moieties.

**Synthesis and structural characterization:** The synthesis of octupolar chromophores **1–8** was achieved by means of triple Sonogashira coupling between tris[4-(ethynylphenyl)]-amine core **9**<sup>[14]</sup> and bromo derivatives **10–17** that bear the electron-withdrawing groups (Scheme 1). Whereas sulfoxide

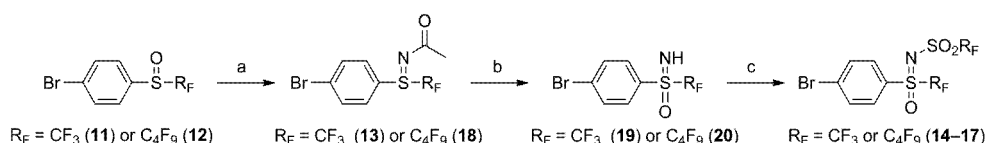


Scheme 1. a) [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>], CuI, toluene/Et<sub>3</sub>N, 40 °C, 16 h (41 % of **1**, 48 % of **2**, 47 % of **3**, 52 % of **4**); b) [Pd<sub>2</sub>(dba)<sub>3</sub>], CuI, PPh<sub>3</sub>, anhydrous toluene and Et<sub>3</sub>N, 40 °C, 5 h (48 % of **5**, 59 % of **6**, and 36 % of **7**); c) [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>], CuI, anhydrous toluene and Et<sub>3</sub>N, 40 °C, 15 h (26 % of **8**).

**10** was commercially available, molecules **11–17** were prepared according to our recent methodology.<sup>[13]</sup> We have previously disclosed a straightforward preparation of fluorinated sulfilimines. The simple treatment of sulfoxides by trifluoromethanesulfonic anhydride and a set of nitriles gave rise to a wide range of sulfilimines. These sulfur(IV) derivatives were then readily oxidized by potassium permanganate under basic conditions to produce the corresponding *NH*-sulfoximines. This methodology was a great improvement to

the seminal preparation of such compounds described by Yagupol'skii.<sup>[15]</sup> In the last step, *NH*-sulfoximines were transformed into derivatives **14** to **17** by treatment of their sodium salt form with the appropriate electrophile (Scheme 2).

To the best of our knowledge, the influence of sulfilimine and sulfoximine groups, introduced as *para* substituents of bromobenzene, has never been evaluated through palladium-coupling reactions. We were pleased to validate our



Scheme 2. Reagents and conditions: a) Tf<sub>2</sub>O, acetonitrile, –15 °C; b) KMnO<sub>4</sub>, NaOH, H<sub>2</sub>O, RT; c) NaH then TiF<sub>4</sub> or FSO<sub>2</sub>C<sub>4</sub>F<sub>9</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 40 °C.

strategy by the success of the original Sonogashira coupling reactions. Compounds **1–4** with sulfoxide or sulfilimine end groups were indeed obtained by the reaction of core **9** with bromo derivatives **10–13**, respectively, in the presence of  $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$  and CuI in toluene/ $\text{Et}_3\text{N}$ . The overall yields (in pure isolated compound) of these triple Sonogashira couplings ranged from 41 to 52 %, which corresponds to average theoretical yields of 75 to 80 % for a single coupling reaction (although this description is somewhat misleading since the reactivity of the intermediary bromides is modified by the presence of the EWGs). Compounds **5–8**, which bear sulfoximine end groups, were obtained analogously from core **9** and bromo derivatives **14–17**. On account of their pronounced sensitivity to water and nucleophilic bases, their synthesis as well as their workup and purification required strictly anhydrous conditions. In addition, in some cases, it was also necessary to replace palladium(II) with palladium(0) to reduce side reactions. Chromophores **5** and **6** were obtained in yields similar to those obtained for **1–4**, whereas **7** and **8** were obtained in lower yields (as isolated pure compounds although conversion was found to be quite good) due to their higher sensitivity to bases. This behavior nicely illustrates the strong activating effect of the sulfoximine function when a fluorinated group is attached to the sulfur atom. This property has been highlighted by recent works that describe electrophilic perfluoroalkylating reagents based on the sulfoximine function.<sup>[16]</sup> In addition, we stress that the activating effect of the electrophilic character of sulfur(IV) by fluorinated substituents is higher for sulfoximine derivatives (**d** derivatives in Figure 1) than for sulfones (**b** derivatives in Figure 1) since sulfones (such as compound **0**) were previously found to be stable in various solvents and their isolation from the Sonogashira reaction did not raise particular difficulty when using standard workup and chromatography conditions.<sup>[3c]</sup>

Compounds were characterized by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$  NMR spectroscopy, HRMS, and elemental analysis.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (Figure 2 and 3) clearly show the electron-withdrawing (EW) effect of terminal substituents on both proton and  $^{13}\text{C}$  chemical shifts. In particular, by comparing the data obtained for the synthetic octupolar derivatives with those of the tritolyamine (TTA) reference compound ( $\text{A}=\text{H}$ , Figure 1), we note that the presence of EW peripheral moieties induces deshielding of both  $\text{H}_\alpha$  and  $\text{H}_\beta$  protons and, to a lesser extent, of  $\text{H}_\alpha$  and  $\text{H}_\beta$  protons (Table 1). It also generates a marked deshielding of  $^{13}\text{C}_\alpha$ , which increases steadily following the order **1**→**8** (Table 1), whereas  $^{13}\text{C}_\beta$  is slightly shielded (Figure 3). This could be related to an intramolecular charge transfer in the ground state that generates positive or negative, respectively, charge density on corresponding carbon atoms. We observe that the influence of the different EW groups on chemical shifts is much more pronounced for  $^{13}\text{C}$  than for  $^1\text{H}$ , which is in agreement with the increased sensitivity of  $^{13}\text{C}$  chemical shifts on charge density (Table 1) and the lack (or minor contribution) of additional effects, such as magnetic anisotropy, which also influence proton chemical shifts. Hence, the difference in chemical

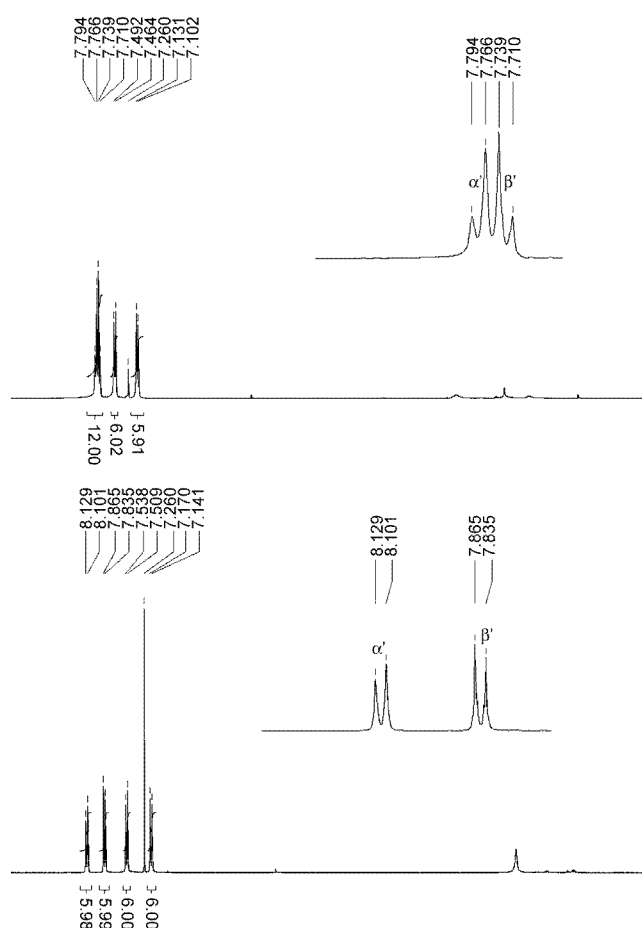


Figure 2. A)  $^1\text{H}$  NMR spectra of compound **2** in  $\text{CDCl}_3$ . B)  $^1\text{H}$  NMR spectra of compound **7** in  $\text{CDCl}_3$ .

shifts ( $\Delta\delta$ ) of acetylenic carbons  $\text{C}_\alpha$  and  $\text{C}_\beta$  provides an interesting probe for estimating the relative EW strengths of the different terminal groups and allows for a relative ranking of the series of EW moieties (including novel ones such as sulfilimines). As expected, sulfoxides were found to be the least powerful EW groups among the present series, whereas fluorinated sulfoximines behave clearly as “super-acceptors”.<sup>[8,15,17]</sup> Indeed, the  $\Delta\delta$  values for fluorinated sulfoximines (i.e., compounds **5–8**;  $\Delta\delta=10.25$  ppm) are about twice as large as those of fluorinated sulfoxides (i.e., compounds **2** and **3**) and more than ten times as large as for TTA. As anticipated from previously reported data,<sup>[15]</sup> fluorinated sulfoximinyl groups are found to behave as much stronger EWGs than prototypical  $\text{NO}_2$  groups ( $\Delta\delta=6.6$  ppm). Hence the  $^{13}\text{C}$  NMR spectroscopic study of the series of octupolar derivatives provides a sensitive way to monitor the EW strength of terminal groups and can be used as a tool to scrutinize subtle changes in the strength of an EWG.<sup>[18]</sup> For instance, the marked increase in the EW ability of the sulfoxide moieties by replacement of the hydrogen atoms of the alkyl chain with fluorine atoms is monitored by the larger  $\Delta\delta$  values (5.3 ppm for **2** as compared to 3.1 ppm for **1**, as shown in Table 1), as expected from  $\sigma_p$  values reported in the literature for SOMe and  $\text{SOCF}_3$  (0.49

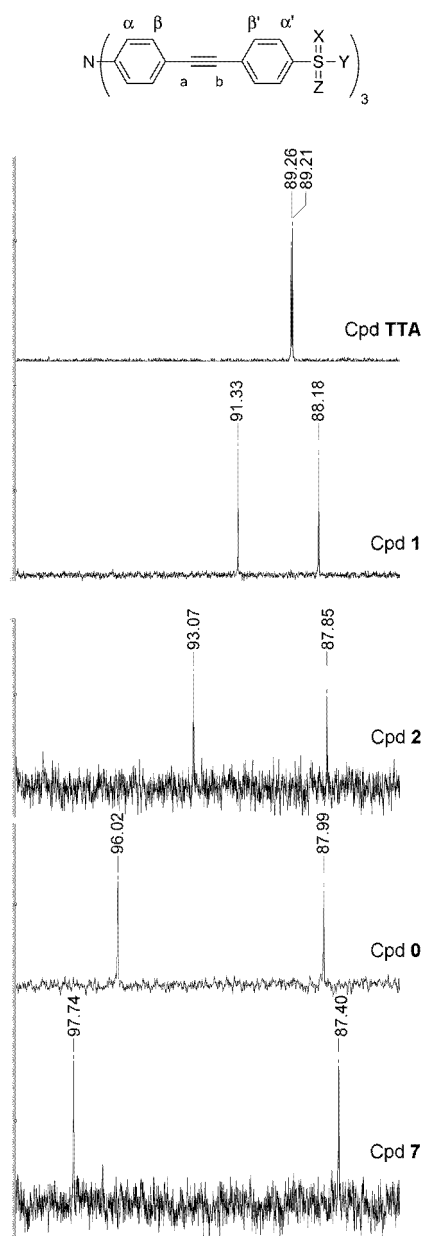


Figure 3. Inset for acetylenic carbon atoms of  $^{13}\text{C}$  NMR spectra of octupolar compounds derived from TTA (in  $\text{CDCl}_3$ ).

and 0.77, respectively) moieties. Lengthening the polyfluorinated chain allows for a slight increase in the EW strength as evidenced by the comparison of sulfoxide (**2** and **3**) and sulfoximine (**5** and **8**) derivatives. In the case of sulfoximines, this effect depends on the position of the fluorinated chain: the lengthening of  $\text{R}_\text{F}^1$  (Figure 1) allows for a slight increase in the EW strength of sulfoximinyl moieties (**5** versus **7**, and **6** versus **8**), whereas this effect is saturated for  $\text{R}_\text{F}^2$  as seen in the comparison between the (**5**; **6**) and (**7**; **8**) pairs (Table 1). However, a consequence of the slightly higher EW strength provided by  $\text{C}_4\text{F}_9$  instead of  $\text{CF}_3$  is detectable from the activation of the electrophilic reactivity of sulfur(IV), which particularly results in a high sensitivity of compounds **7** and **8** toward traces of nucleophiles (including water). This is a typical illustration of the activation of the electrophilic character of sulfur by fluorinated substituents. The NMR spectroscopic study also allowed us to estimate the EW strength of the novel partially fluorinated sulfiliminyl moiety (i.e.,  $\text{S}(\text{NAc})\text{CF}_3$ ). The measured  $\Delta\delta$  value for compound **4** ( $\Delta\delta=6.3$  ppm) is close to that of the nitro moiety and lies between the corresponding fluorinated sulfoxides ( $\Delta\delta=3.3$  ppm for compound **2**) and fluorinated sulfones ( $\Delta\delta=8.0$  ppm for compound **0**). It indicates that fluorinated sulfiliminyl moieties hold promise as EWGs for the design of chromophores for optoelectronic applications. A further gradual increase in the EW strength should be possible by lengthening the fluorinated substituent of the sulfiliminyl group and/or replacing the acetyl group by electron-withdrawing groups such as nitro, cyano, triflyl, or iminium.<sup>[19]</sup>

The NMR spectroscopic study therefore provided a useful ranking of the potent new fluorinated EWGs with respect to prototypical ones. We could also establish evidence of a linear correlation between the  $\Delta\delta$  values and the reported  $\sigma_\text{p}$  values for sulfur(II)- and sulfur(IV)-fluorinated EW moieties (Figure 4). Such a linear relationship allows one to derive the unknown Hammett constant values for fluorinated sulfoxide  $\text{SOC}_4\text{F}_9$  (0.75) and for the novel fluorinated sulfiliminyl moiety  $\text{S}(\text{NAc})\text{CF}_3$  (0.87). Finally, sulfoximine  $\text{SO}(\text{NSO}_2\text{C}_4\text{F}_9)\text{CF}_3$  was found to have a similar  $\Delta\delta$  value to  $\text{SO}(\text{NSO}_2\text{CF}_3)\text{CF}_3$ , whereas sulfoximines  $\text{SO}(\text{NSO}_2\text{CF}_3)\text{C}_4\text{F}_9$  and  $\text{SO}(\text{NSO}_2\text{C}_4\text{F}_9)\text{C}_4\text{F}_9$  were found to have slightly larger  $\sigma_\text{p}$  values (about 1.4). The low dispersion of  $\Delta\delta$  values in

Table 1. Electron-withdrawing effect on  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts for octupolar chromophores **0–8** in  $\text{CDCl}_3$ .

Cpd	EWG	$\sigma_\text{p}$	$\delta(\text{H}_\alpha)$ [ppm]	$\delta(\text{H}_\beta)$ [ppm]	$\delta(\text{H}_{\alpha'})$ [ppm]	$\delta(\text{H}_{\beta'})$ [ppm]	$\delta = \text{C}_\text{a}^\text{acetyl}/\delta = \text{C}_\text{b}^\text{acetyl}$ ( $\Delta\delta$ ) [ppm]
TTA	H	0.00 <sup>[33]</sup>	7.08	7.44	7.35	7.52	89.3/89.2 (0.1)
<b>1</b>	SOMe	0.49 <sup>[4]</sup>	7.10	7.46	7.65	7.62	91.3/88.2 (3.1)
<b>2</b>	$\text{SOCF}_3$	0.77 <sup>[15]</sup>	7.12	7.48	7.78	7.73	93.1/87.8 (5.3)
<b>3</b>	$\text{SOC}_4\text{F}_9$	— <sup>[a]</sup>	7.12	7.49	7.79	7.73	93.3/87.9 (5.4)
<b>4</b>	$\text{S}(\text{NAc})\text{CF}_3$	— <sup>[a]</sup>	7.11	7.47	7.85	7.71	93.9/87.6 (6.3)
model	$\text{NO}_2$	0.81 <sup>[33]</sup>	7.125	7.49	8.225	7.65	94.4/87.8 (6.6)
<b>0</b>	$\text{SO}_2\text{CF}_3$	1.04 <sup>[15]</sup>	7.13	7.50	8.01	7.76	95.5/87.5 (8.0)
<b>5</b>	$\text{SO}(\text{NSO}_2\text{CF}_3)\text{CF}_3$	1.39 <sup>[15]</sup>	7.20	7.57	8.15	7.89	97.5/87.3 (10.2)
<b>6</b>	$\text{SO}(\text{NSO}_2\text{C}_4\text{F}_9)\text{CF}_3$	— <sup>[a]</sup>	7.16	7.53	8.12	7.85	97.5/87.3 (10.2)
<b>7</b>	$\text{SO}(\text{NSO}_2\text{CF}_3)\text{C}_4\text{F}_9$	— <sup>[a]</sup>	7.16	7.53	8.12	7.85	97.7/87.4 (10.3)
<b>8</b>	$\text{SO}(\text{NSO}_2\text{C}_4\text{F}_9)\text{C}_4\text{F}_9$	— <sup>[a]</sup>	7.15	7.52	8.12	7.85	97.7/87.4 (10.3)

[a] Unknown.

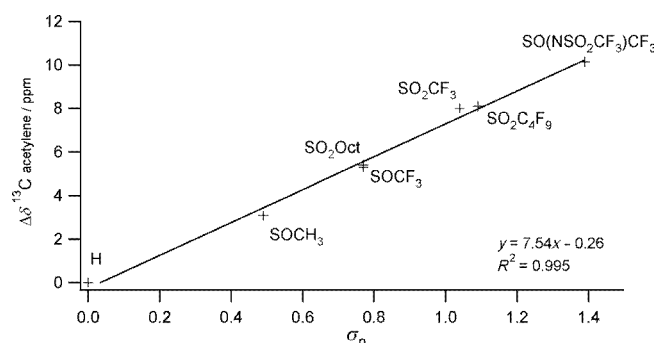


Figure 4. Linear correlation between Hammett constants ( $\sigma_p$ ) from the literature for fluorinated sulfur(II) and sulfur(IV) moieties and difference in chemical shifts ( $\Delta\delta$ ) of acetylenic carbons in octupolar derivatives.

this series indicates that NMR spectroscopic methodology is not sensitive enough to distinguish the EW strength of the various fluorinated sulfoximine groups. Complementary spectroscopic studies are thus required to yield more precise accurate  $\sigma_p$  values in that particular case (vide infra).

**Absorption and fluorescence properties:** All octupolar compounds show an intense absorption band in the near-UV-blue-visible region and emission in the visible region (Figure 5). Sulfoxides and sulfilimine derivatives (**1–4**) are violet-blue emitters, whereas sulfoximines (**5–8**) are green emitters. Absorption and fluorescence characteristics are collected in Table 2. We observed a marked bathochromic and hyperchromic shift of the low-energy absorption band as well as a significant redshifted emission upon going from fluorinated sulfones to corresponding fluorinated sulfoximine derivatives. A bathochromic and hyperchromic shift of the low-energy absorption band as well as a marked redshift of the emission is observed upon going from a fluorinated sulfone derivative (**0**) to the corresponding fluorinated sulfoximine derivatives **5** and **6** in relation to the increased EW strength of peripheral groups ( $X, Y = O, O \rightarrow X, Y = O, NSO_2R_F^2$ ). A significant increase in the Stokes shift is also noted in relation to the stronger EWG character. The same phenomenon is observed for sulfilimine derivative **4** relative

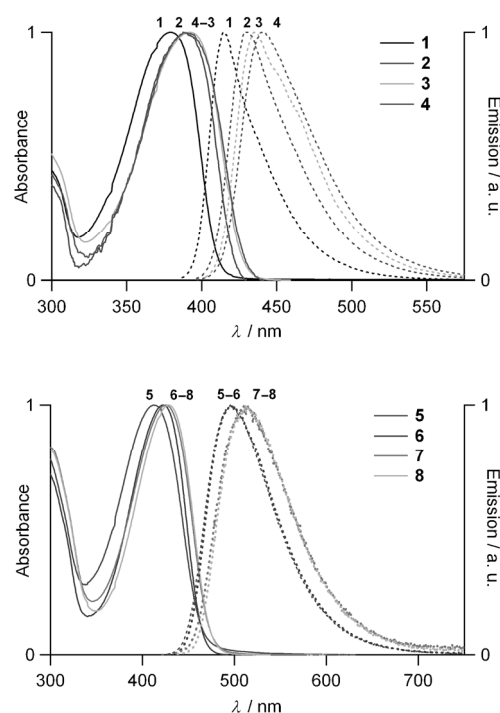


Figure 5. Normalized absorption and emission spectra of octupolar chromophores **1–4** (top) and **5–8** (bottom)

to sulfoxide derivative **2** ( $X=O \rightarrow NAc$ ), which is in agreement with the stronger EW character of the peripheral groups. In this case, however, no marked change of the absorption was observed, whereas a slight redshift of the emission as well as a decrease in the fluorescence quantum yield was observed. Hence, although being comparable to  $NO_2$  in terms of EW strength, the  $S(NAc)CF_3$  sulfiliminy group leads to improved transparency. Indeed, compound **4** was found to be 20 nm more transparent than its  $NO_2$  analogue (Table 2). This improved EWG character combined with the enlarged transparency in the visible range could be of interest for NLO applications,<sup>[2k]</sup> including optical limiting.<sup>[6]</sup>

Lengthening the fluorinated moiety also produces a bathochromic shift of the emission, the effect being stronger in

Table 2. Photophysical data for octupolar chromophores **0–8** in toluene.

Cpd	EWG	$\lambda_{abs}^{[a]}$ [nm]	$10^{-4} \epsilon^{max[b]}$ [cm <sup>-1</sup> M <sup>-1</sup> ]	FWHM <sup>[c]</sup> [cm <sup>-1</sup> ]	$\lambda_{em}^{[d]}$ [nm]	$\Phi^{[e]}$	Stokes shift <sup>[f]</sup> [cm <sup>-1</sup> ]	$E_{0-0}^{[g]}$ [eV]
TTA	H	369	7.8	3500	402	0.76	2220	3.22
<b>1</b>	SOMe	382	9.0	3500	414	0.63	2020	3.12
<b>2</b>	SOCF <sub>3</sub>	389	8.7	3700	431	0.73	2510	3.03
<b>3</b>	SOC <sub>4</sub> F <sub>9</sub>	393.5	8.8	3600	435	0.71	2420	3.00
<b>4</b>	S(NAc)CF <sub>3</sub>	390	7.2	3800	440	0.52	2910	3.00
<b>0</b>	SO <sub>2</sub> CF <sub>3</sub>	405	6.0	3700	450	0.78	2470	2.91
<b>5</b>	SO(NSO <sub>2</sub> CF <sub>3</sub> )CF <sub>3</sub>	419	8.0	3700	500	0.65	3870	2.72
<b>6</b>	SO(NSO <sub>2</sub> C <sub>4</sub> F <sub>9</sub> )CF <sub>3</sub>	422	8.1	3800	496	0.58	3540	2.72
<b>7</b>	SO(NSO <sub>2</sub> CF <sub>3</sub> )C <sub>4</sub> F <sub>9</sub>	425.5	5.1	3800	515	–	4070	2.66
<b>8</b>	SO(NSO <sub>2</sub> C <sub>4</sub> F <sub>9</sub> )C <sub>4</sub> F <sub>9</sub>	428.5	6.7	3700	516	–	3960	2.65

[a] Experimental one-photon absorption maximum. [b] Experimental molar extinction coefficient. [c] Half bandwidth. [d] Experimental one-photon emission maximum. [e] Fluorescence quantum yield determined relative to fluorescein in 0.1 N NaOH. [f] Stokes shift =  $(1/\lambda_{abs} - 1/\lambda_{em})$ . [g] Electronic gap (0–0 transition energy).

the case of sulfoximine derivatives for the fluorinated groups directly attached to the sulfur(IV) atom. We observe that fluorinated derivatives (sulfoxides **2** and **3**, sulfone **0**, and sulfoximines **5** and **6**) are good fluorescence emitters ( $\Phi = 0.6\text{--}0.8$ ),<sup>[20]</sup> as is the case of the unsubstituted derivative (TTA), but their emission is significantly redshifted (from violet to blue-green). This offers clear evidence of the influence of strong peripheral EWGs in promoting core-to-periphery intramolecular charge-transfer transitions.

As expected for ctp-ICT compounds, the fluorescence properties of octupolar derivatives **1–8** showed a marked dependency on solvent polarity (Figure 6).<sup>[21]</sup> A marked red-

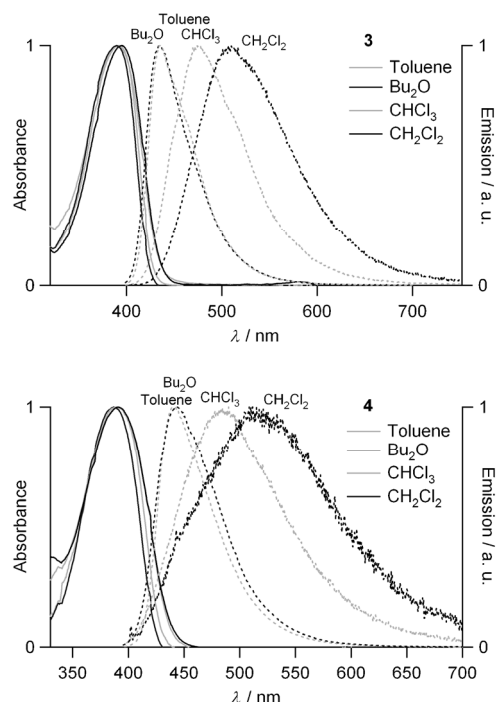


Figure 6. Solvatochromic behavior of octupolar compounds **3** (top) and **4** (bottom).

shift of the emission band was observed with increasing solvent polarity, whereas no such effect was observed for absorption. Such behavior, not observed with the unsubstituted TTA compound, provides clear evidence that highly polarized emissive excited states are produced—in agreement with excitation localization on dipolar branches after excitation prior to emission<sup>[22]</sup>—thanks to the presence of strong peripheral EWGs.

**Correlations and determination of Hammett constants:** Due to the ctp-ICT character of the  $\pi\text{--}\pi^*$  transition of octupolar derivatives **1–8**, we might expect the corresponding electronic gap (i.e., the difference in energy between relaxed ground and excited states) to be correlated to the EW ability of the peripheral groups. This assumption is secured by a series of previous works that depict the linear relationship between photophysical data and Hammett constants.<sup>[23]</sup> Indeed, Ham-

mett constants are related to ground-state properties and have been used to predict the effect of electroactive (EW or electron-releasing) substituents on chemical-reaction kinetics. The basis of this concept is a linear relationship between thermodynamic (typically acidity of benzoic acid) and kinetic data (reaction activation energy), thus leading to so-called linear free-energy relationships (LFER).<sup>[24]</sup> We can therefore assume a similar relationship between thermodynamic data and UV-visible excitation energy since electron-density shifts are involved both in covalent bond breaking and formation (reaction kinetics) and in the formation of an electronically excited state. We posit that such a correlation will be particularly relevant for intramolecular charge-transfer types of transition in which the role of electron-donating and electron-releasing substituents is crucial. To test this hypothesis, we investigated the variation of the electronic gap (Table 2) as a function of the already known  $\sigma_p$  constants for sulfonyl EWGs. We stress that it is important in doing so to derive a valid value of the electronic gap between the ground and excited state. Since the UV-visible absorption bands of the octupolar derivatives investigated in the present work are broad (due precisely to their ICT character), the exact location of the 0–0 vibronic band is not straightforward. Hence, it is important to use both absorption and emission (related to the ICT transition) characteristics to derive the electronic gap from the two mirror bands (absorption and emission). We have done so by using the data reported in the literature for octupolar derivatives that bear sulfone peripheral groups and have double-bond linkers<sup>[3d]</sup> instead of triple bond. As evidenced in Figure 7, a linear

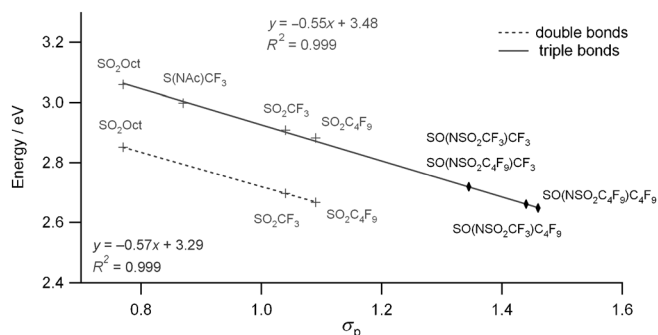


Figure 7. Linear correlations between Hammett constants ( $\sigma_p$ ) of terminal moieties and electronic gaps of octupolar derivatives built from a triphenylamine core. The + symbols represent experimental data using known  $\sigma_p$  values, whereas diamonds represent the  $\sigma_p$  values derived from the electronic gap of fluorinated sulfoximide octupoles.

correlation is indeed obtained, similar to linear free-energy relationships,<sup>[24]</sup> whereby the reaction activation energy is replaced here by the ICT transition energy. Furthermore, by using the  $\sigma_p$  values reported in the literature for the sulfone moieties and derived from the NMR spectroscopic study for the novel sulfilimine EWG (see above), a similar linear relationship is obtained for octupolar derivatives that have triple-bond linkers and bear sulfone<sup>[3c]</sup> or sulfilimine moieties (Figure 7). Interestingly the same slope (equivalent to



the Taft parameter  $\rho$  for reaction kinetics) is obtained for octupolar derivatives that have a double-bond and triple-bond connector between the triphenylamine electron-releasing core and the phenyl units that bear electron-withdrawing peripheral substituents. This too emphasizes the analogy with LFER whereby the Taft parameter is a characteristic of the type of reaction and gives information about the nature of the transition state.<sup>[24]</sup> In our case, the slope value gives information of the nature of the transition and clearly points to an ICT type of electronic transition. Hence, the ICT electronic gap—as long as it can be accurately determined as the  $E_{00}$  energy from combined absorption and emission data—represents an interesting tool for deriving  $\sigma_p$  values. As such, it provides an additional spectroscopic tool that is complementary to NMR spectroscopy, which has been used as a method for deriving Hammett values, thanks to the marked sensitivity of the chemical shifts of big nuclei (as compared to  $^1\text{H}$ ) toward electronic density.<sup>[8]</sup>

Whereas  $^{13}\text{C}$  NMR spectroscopy allows for a very precise discrimination between various sulfur(II) and sulfur(IV) derivatives (Table 1 and Figure 6), it does not allow for an acute distinction between the EW strength of the different fluorinated sulfoximine moieties (see the data for series of compounds **5–8** in Table 1). In this case, however, the dependency of the electronic gap on the EW strength is such that it allows us to distinguish between these moieties (Table 2) and to derive refined precise  $\sigma_p$  values for the different fluorinated sulfoximine moieties by using the linear correlation between EW strength and the electronic gap (Figure 7). Indeed, refined  $\sigma_p$  values larger than 1.4 are derived from the ICT electronic gap for “superacceptor” peripheral groups of octupolar compounds **7** ( $\text{SO}(\text{NSO}_2\text{CF}_3)\text{C}_4\text{F}_9$ ;  $\sigma_p = 1.44$ ) and **8** ( $\text{SO}(\text{NSO}_2\text{C}_4\text{F}_9)\text{C}_4\text{F}_9$ ;  $\sigma_p = 1.46$ ), whereas the EWGs of compounds **5** and **6** ( $\text{SO}(\text{NSO}_2\text{CF}_3)\text{CF}_3$  and  $\text{SO}(\text{NSO}_2\text{C}_4\text{F}_9)\text{CF}_3$ ) are found to have refined  $\sigma_p$  values of 1.35. This indicates that the fluorinated substituents directly linked to the sulfur(IV) atom connected to the conjugated spacer has more influence on the optical properties of the octupolar derivatives. This suggests that further increasing the EW strength of this substituent could be of interest. This also suggests that sulfur(II) moieties (such as novel sulfilimines) could likely also be further engineered to become stronger EW groups by lengthening the fluorinated chain directly connected to the sulfur(II) atom.

**Two-photon absorption:** To assess the interest in the new EWGs (fluorinated sulfoximine and sulfilimine) for the design of NLO chromophores, we investigated the two-photon absorption (TPA) response in the red near-IR (NIR) region of octupolar derivatives **5** and **4** and compared their TPA response to that of the related fluorinated sulfonyl derivative **0** that bears a typically potent EWG. Thanks to their fluorescence, their TPA

cross-sections could be measured by performing two-photon-induced fluorescence experiments in solution.<sup>[25]</sup> On the basis of an earlier theoretical study carried out by Cho and co-workers,<sup>[26]</sup> which did show some correlation between the maximum TPA cross-sections and Hammett constants of electron-donating substituents of octupolar derivatives built from a central electron-acceptor carbocation (typically inspired by prototypical crystal violet), our motivation was to investigate if such dependency is general and valid for opposite-type octupoles (i.e., those built from a central electron-donor atom, such as triphenylamine derivatives).

The TPA spectra of the selected octupolar derivatives are shown in Figure 8, whereas the maxima characteristics (position and maximum cross-sections) are collected in Table 3. We observed that the TPA spectra show typical characteris-

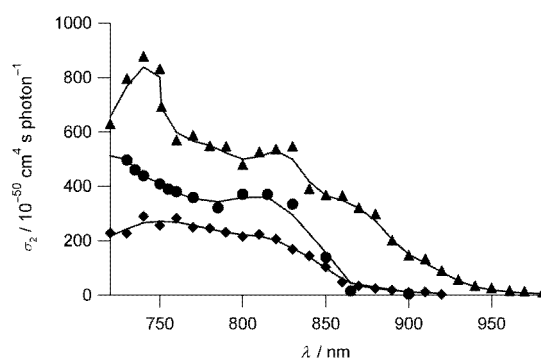


Figure 8. Two-photon absorption spectra of fluorinated sulfilimine **4** ( $\blacklozenge$ ) and sulfoximine **5** ( $\blacktriangle$ ) compared with that of related sulfonyl compound **0** ( $\bullet$ ).

tics of octupolar derivatives: a low-energy TPA band that corresponds to the lower (one-photon-allowed) excited state, which is also slightly two-photon-allowed, plus an additional stronger TPA band that peaks at higher energy and corresponds to a strongly two-photon-allowed, one-photon-forbidden excited state.<sup>[25b]</sup> The enhancement of this latter band as well as energy splitting between the two states strongly depend on the coupling between the dipolar branches.<sup>[7b,22a]</sup>

As seen in Figure 8, a major increase in the TPA bands was observed for octupole **5**, which bears fluorinated sulfoximinyl peripheral groups ( $\sigma_p = 1.35$ ), over octupole **0**, which bears fluorinated sulfonyl ( $\text{SO}_2\text{CF}_3$ ;  $\sigma_p = 1.04$ ) terminal moieties. As seen in Table 3, this leads to a maximum TPA response that is almost twice as large as that of compound **0**,

Table 3. Two-photon absorption data for selected octupolar chromophores built from a triphenylamine core and that bear novel (fluorinated sulfilimine ( $\text{S}^{\text{II}}$ ) or sulfoximine ( $\text{S}^{\text{IV}}$ )) electron-withdrawing peripheral groups.

Cpd	EWG	$\sigma_p$	$\lambda_{\text{TPA}}^{\text{max1}}$ [nm]	$\sigma_2^{\text{max1}}$ [GM]	$\lambda_{\text{TPA}}^{\text{max2}}$ [nm]	$\sigma_2^{\text{max2}}$ [GM]
<b>0</b>	$\text{SO}_2\text{CF}_3$	1.04 <sup>[15]</sup>	815	370	730	500
<b>4</b>	$\text{S}(\text{Nac})\text{CF}_3$	0.87 <sup>[a]</sup>	810	220	740	290
<b>5</b>	$\text{SO}(\text{NSO}_2\text{CF}_3)\text{CF}_3$	1.35 <sup>[a]</sup>	830	540	740	870

[a] This work.

although compound **5** is redshifted by only 15 nm. This suggests that such compounds could be of interest for the design of optical limiters for the protection of NIR sensors. This is also more than twice as large as that of the related octupole that bears dimesitylboryl peripheral moieties (375 GM at 720 nm).<sup>[27]</sup> Conversely, the novel partially fluorinated electron-withdrawing group  $\text{SNAcCF}_3$ , which has a lower  $\sigma_p$  value than fluorinated sulfonyl moiety  $\text{SO}_2\text{CF}_3$  (i.e., 0.87 instead of 1.04) and improved transparency by about 15 nm, leads to a maximum TPA cross-section that is about twice as small as octupole **0**. In that series of related compounds (i.e., octupoles with the same core and conjugated path but different EWGs), the NLO responses are thus directly correlated to the EW strength, which shows that a linear correlation between the strength of peripheral groups can also be demonstrated for octupoles built from an electron-donating core (Figure 9).<sup>[28]</sup> Such behavior can be interpreted within the framework of essential-state models.<sup>[26,29]</sup>

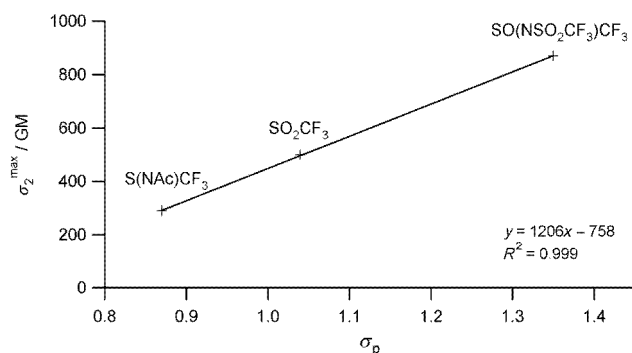


Figure 9. Linear correlation between Hammett constants ( $\sigma_p$ ) and maximum two-photon absorption cross-section ( $\sigma_2^{\text{max}}$ ) of octupolar derivatives.

Given the improved transparency and solubility that the  $\text{SNAcCF}_3$  group provides over  $\text{NO}_2$ , using such moieties as EW end groups in suitable quadrupolar derivatives could be of interest for the design of NLO-phores for optical limitation in the visible region.<sup>[6]</sup> Hence, sulfoximinyl and sulfiliminyl moieties can be considered to some extent as complementary (in terms of transparency/NLO-response tradeoff) EW building blocks for the design of NLO-phores.

## Conclusion

On the basis of comprehensive spectroscopic studies (combined NMR, absorption, and fluorescence), we have been able to determine exact  $\sigma_p$  values for closely related fluorinated sulfoximinyl moieties. These building blocks show unprecedented EW ability, as demonstrated by their unique  $\sigma_p$  values (up to 1.45 relative to 0.8 for  $\text{NO}_2$  and 1.0 for  $\text{SO}_2\text{CF}_3$ ). These moieties can thus be used not only as “superacidifiers” but also as “superacceptor” groups. This significant enhancement of EW strength leads to major TPA enhancement in octupolar derivatives (by a factor of two

relative to fluorinated sulfonyl moieties, which are known to be among the strongest neutral EWGs for NLO). Due to their unprecedented electron-withdrawing ability, these “superacceptor” moieties lead to enhanced TPA response of octupolar derivatives and should also be of interest for second-order NLO applications (such as electro-optical modulation) as well as for different optoelectronic applications, including solar cells.<sup>[30]</sup> Finally, we have also determined the EW ability of an original, partially fluorinated, sulfiliminyl moiety,  $\text{S(NAc)CF}_3$ , which was found to be close to that of the nitro moiety while providing improved transparency and solubility. This represents a promising NLO-chromic building block for an improved tradeoff between transparency, solubility, and NLO responses. In addition, subtle tuning of the EW ability could possibly be achieved by playing with the replacement of hydrogen atoms with fluorine atoms or by replacement of the acetyl moiety with some other EW moiety. This opens a new route for the design of novel fluorinated sulfiliminyl moieties with adjustable NLO/fluorescence properties. Further investigation along this direction is currently in progress.

## Experimental Section

**Synthetic procedures:** Synthetic procedures and characterization data for all octupolar chromophores are given below, and those for intermediate compounds can be found in the Supporting Information.

**Tris[4-[(4-nitrophenyl)ethynyl]phenyl]amine:** Air was removed from a solution of **9** (200 mg, 0.631 mmol) and 1-iodo-4-nitrobenzene (534 mg, 2.145 mmol, 3.4 equiv) in toluene/ $\text{Et}_3\text{N}$  (4:1; 9 mL) by blowing argon for 20 min. Then  $\text{CuI}$  (7.1 mg, 0.037 mmol) and  $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$  (26 mg, 0.037 mmol) were added, and the mixture was stirred at 40 °C for 16 h. After evaporation of the solvents, the residue was purified by column chromatography ( $\text{CH}_2\text{Cl}_2/\text{AcOEt}$  95:5) to yield the title compound (218 mg, 51 %).<sup>[9]</sup>  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.24 (d,  $J$  = 8.8 Hz, 6H), 7.66 (d,  $J$  = 8.6 Hz, 6H), 7.50 (d,  $J$  = 8.6 Hz, 6H), 7.13 ppm (d,  $J$  = 8.8 Hz, 6H);  $^{13}\text{C}$  NMR (100.62 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 147.2, 146.9, 133.3, 132.0, 130.2, 124.1, 123.5, 117.1, 94.4, 87.8 ppm.

**Tris[4-[(4-(methylsulfinyl)phenyl)ethynyl]phenyl]amine (1):** Air was removed from a solution of **9** (75 mg, 0.2363 mmol) and **10** (181 mg, 0.8271 mmol, 3.5 equiv) in toluene/ $\text{Et}_3\text{N}$  (4:1; 5 mL) by blowing argon for 20 min. Then  $\text{CuI}$  (2.7 mg, 0.0142 mmol) and  $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$  (10 mg, 0.0142 mmol) were added, and the mixture was stirred at 40 °C for 16 h. After evaporation of the solvents, the residue was purified by column chromatography ( $\text{CH}_2\text{Cl}_2/\text{AcOEt}$  98:2) to yield **1** (74 mg, 43 %).  $^1\text{H}$  NMR (300.13 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.65 and 7.62 (AA'BB',  $J(\text{A},\text{X})$  = 8.7 Hz, 12H), 7.46 and 7.10 (AA'XX',  $J(\text{A},\text{X})$  = 8.7 Hz, 12H), 2.74 ppm (s, 9H);  $^{13}\text{C}$  NMR (75.47 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 146.8, 145.1, 132.9, 132.2, 126.3, 124.0, 123.5, 117.6, 91.3, 88.2, 43.8 ppm; HRMS (ES<sup>+</sup>):  $m/z$ : calcd for  $\text{C}_{45}\text{H}_{33}\text{NO}_3\text{NaS}_3$  [ $M+\text{Na}$ ]<sup>+</sup>: 754.15148; found: 754.1514.

**Tris[4-[(4-(trifluoromethyl)sulfinyl)phenyl)ethynyl]phenyl]amine (2):** Air was removed from a solution of **9** (341 mg, 1.077 mmol) and **11** (1 g, 3.662 mmol, 3.4 equiv) in toluene/ $\text{Et}_3\text{N}$  (4:1; 16 mL) by blowing argon for 20 min. Then  $\text{CuI}$  (12 mg, 0.0646 mmol) and  $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$  (45 mg, 0.0646 mmol) were added, and the mixture was stirred at 40 °C for 16 h. After evaporation of the solvents, the residue was purified by column chromatography (heptane/ $\text{CH}_2\text{Cl}_2$  50:50) to yield **2** (463 mg, 48 %).  $^1\text{H}$  NMR (300.13 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.78 and 7.73 (AA'BB',  $J(\text{A},\text{X})$  = 8.6 Hz, 12H), 7.48 and 7.12 ppm (AA'XX',  $J(\text{A},\text{X})$  = 8.7 Hz, 12H);  $^{13}\text{C}$  NMR (75.47 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 147.1, 134.7, 133.1, 132.4, 129.1, 125.9, 124.6 (q,  $J$  = 335.4 Hz), 124.1, 117.2, 93.1, 87.8 ppm;  $^{19}\text{F}$  NMR

(282.37 MHz, CDCl<sub>3</sub>):  $\delta$  = −74.3 ppm (s, 9F; CF<sub>3</sub>); HRMS (ES<sup>+</sup>):  $m/z$ : calcd for C<sub>45</sub>H<sub>24</sub>NO<sub>3</sub>F<sub>9</sub>S<sub>3</sub> [ $M$ ]<sup>+</sup>: 893.07746; found: 893.0769.

**Tris[4-[(4-[(nonafluorobutyl)sulfonyl]phenyl)ethynyl]phenyl]amine (3):** Air was removed from a solution of **9** (200 mg, 0.63 mmol) and **12** (900 mg, 2.132 mmol, 3.4 equiv) in toluene/Et<sub>3</sub>N (4:1; 9 mL) by blowing argon for 20 min. Then CuI (7.1 mg, 0.0373 mmol) and [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (26 mg, 0.037 mmol) were added, and the mixture was stirred at 40 °C for 16 h. After evaporation of the solvents, the residue was purified by column chromatography (pentane/CH<sub>2</sub>Cl<sub>2</sub> 50:50) to yield **3** (463 mg, 47%). <sup>1</sup>H NMR (200.13 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.79 and 7.73 (AA'BB',  $J$ (A,X) = 8.7 Hz, 12H), 7.49 and 7.12 ppm (AA'XX',  $J$ (A,X) = 8.6 Hz, 12H); <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>):  $\delta$  = 147.1, 133.9, 133.2, 132.3, 129.4, 126.7, 124.1, 117.2, 93.3, 87.9 ppm; <sup>19</sup>F NMR (188 MHz, CDCl<sub>3</sub>):  $\delta$  = −126.6 (m, 6F; CF<sub>2</sub>), −122.9 (d,  $J$  = 245.3 Hz, 3F; AB system, SCF<sub>A</sub>F<sub>B</sub>), −121.6 (m, 6F; CF<sub>2</sub>), −111.7 (d, 3F; AB system, SCF<sub>A</sub>F<sub>B</sub>), −81.3 ppm (m, 9F; CF<sub>3</sub>); HRMS (ES<sup>+</sup>):  $m/z$ : calcd for C<sub>54</sub>H<sub>24</sub>NO<sub>3</sub>F<sub>27</sub>NaS<sub>3</sub> [ $M$ +Na]<sup>+</sup>: 1366.03794; found: 1366.0377.

**Tris[4-[(4-[(trifluoromethyl)-N-(acyl)sulfinimidoyl]phenyl)ethynyl]phenyl]amine (4):** Air was removed from a solution of **9** (280 mg, 0.867 mmol) and **13** (953 mg, 3.034 mmol, 3.4 equiv) in toluene/Et<sub>3</sub>N (4:1; 13 mL) by blowing argon for 20 min. Then CuI (10 mg, 0.052 mmol) and [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (37 mg, 0.052 mmol) were added, and the mixture was stirred at 40 °C for 16 h. After evaporation of the solvents, the residue was purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/EtOH 97:3) to yield **4** (459 mg, 52%). <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.85 and 7.71 (AA'XX',  $J$ (A,X) = 8.5 Hz, 12H), 7.48 and 7.11 (AA'XX',  $J$ (A,X) = 8.7 Hz, 12H), 2.24 ppm (s, 9H); <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>):  $\delta$  = 183.9, 147.1, 133.2, 132.8, 130.0, 128.6, 125.9, 124.1, 124.1 (q,  $J$  = 323.9 Hz), 93.9, 87.6, 23.9 ppm; <sup>19</sup>F NMR (282.37 MHz, CDCl<sub>3</sub>):  $\delta$  = −64.0 ppm (s, 9F; CF<sub>3</sub>); HRMS (ES<sup>+</sup>):  $m/z$ : calcd for C<sub>51</sub>H<sub>34</sub>N<sub>4</sub>O<sub>3</sub>F<sub>9</sub>S<sub>3</sub> [ $M$ +H]<sup>+</sup>: 1017.16494; found: 1017.1643.

**Tris[4-[(4-[(trifluoromethyl)-N-[(trifluoromethyl)sulfonyl]sulfonyl]phenyl)ethynyl]phenyl]amine (5):** Air was removed from a solution of **9** (49.6 mg, 0.156 mmol) and **14** (230 mg, 0.547 mmol) in anhydrous toluene/dry Et<sub>3</sub>N (5:1; 3.5 mL). Then PPh<sub>3</sub> (2.5 mg, 9.38  $\mu$ mol), CuI (1.8 mg, 9.38  $\mu$ mol), and [Pd<sub>2</sub>(dba)<sub>3</sub>] (dba = dibenzylideneacetone; 8.6 mg, 9.38  $\mu$ mol) were added. The reaction mixture was heated at 40 °C for 5 h. After removing solvents, the residue was purified by column chromatography (heptane/CH<sub>2</sub>Cl<sub>2</sub>, gradient from 60:40 to 30:70) to yield **5** (101 mg, 48%). M.p. 117–118 °C; <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.15 and 7.89 (AA'XX',  $J$ (A,X) = 8.5 Hz, 12H), 7.57 and 7.20 ppm (AA'XX',  $J$ (A,X) = 8.5 Hz, 12H); <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>):  $\delta$  = 147.5, 134.1, 133.6, 133.1, 130.6, 126.8, 124.3, 119.9 (q,  $J$  = 328.8 Hz), 118.9 (q,  $J$  = 321.5 Hz), 116.7, 97.5, 87.3 ppm; <sup>19</sup>F NMR (282.37 MHz, CDCl<sub>3</sub>):  $\delta$  = −78.4 (s, 9F; CF<sub>3</sub>), −75.2 ppm (s, 9F; CF<sub>3</sub>); HRMS (LSIMS<sup>+</sup>, mNBA):  $m/z$ : calcd for C<sub>48</sub>H<sub>24</sub>N<sub>4</sub>O<sub>9</sub>F<sub>18</sub>S<sub>6</sub> [ $M$ ]<sup>+</sup>: 1333.95802; found: 1333.9578.

**Tris[4-[(4-[(trifluoromethyl)-N-[(nonafluorobutyl)sulfonyl]sulfonyl]phenyl)ethynyl]phenyl]amine (6):** Air was removed from a solution of **9** (79 mg, 0.2506 mmol) and **15** (500 mg, 0.8769 mmol, 3.5 equiv) in toluene/Et<sub>3</sub>N (6:1; 5.8 mL) by blowing argon for 20 min. Then PPh<sub>3</sub> (4.0 mg, 0.015 mmol), CuI (3.0 mg, 0.015 mmol), and [Pd<sub>2</sub>(dba)<sub>3</sub>] (14.0 mg, 0.015 mmol) were added. The reaction mixture was heated at 40 °C for 5 h. After removal of the solvents, the residue was purified by column chromatography (heptane/CH<sub>2</sub>Cl<sub>2</sub>, gradient from 60:40 to 30:70) to yield **6** (263 mg, 59%). <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.12 and 7.85 (AA'XX',  $J$ (A,X) = 8.8 Hz, 12H), 7.53 and 7.16 ppm (AA'XX',  $J$ (A,X) = 8.8 Hz, 12H); <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>):  $\delta$  = 147.5, 134.1, 133.6, 133.1, 130.6, 128.2, 124.3, 119.9 (q,  $J$  = 328.0 Hz), 118.9 (q,  $J$  = 321.5 Hz), 116.6, 97.5, 87.3 ppm; <sup>19</sup>F NMR (282.37 MHz, CDCl<sub>3</sub>):  $\delta$  = −126.0 (m, 6F; CF<sub>2</sub>), −121.6 (m, 6F; CF<sub>2</sub>), −111.9 (m, 6F; CF<sub>2</sub>), −80.7 (m, 9F; CF<sub>3</sub>), −75.4 ppm (s, 9F; CF<sub>3</sub>); HRMS (ES<sup>+</sup>):  $m/z$ : calcd for C<sub>57</sub>H<sub>24</sub>N<sub>4</sub>O<sub>9</sub>F<sub>36</sub>S<sub>6</sub> [ $M$ ]<sup>+</sup>: 1783.92928; found: 1783.9299;  $m/z$ : calcd for C<sub>57</sub>H<sub>24</sub>N<sub>4</sub>O<sub>9</sub>F<sub>36</sub>NaS<sub>6</sub> [ $M$ +Na]<sup>+</sup>: 1806.91905; found: 1806.91926.

**Tris[4-[(4-[(trifluoromethyl)-N-[(trifluoromethyl)sulfonyl]sulfonyl]phenyl)ethynyl]phenyl]amine (7):** Air was removed from a solution of **9** (79 mg, 0.2506 mmol) and **16** (500 mg, 0.8769 mmol, 3.5 equiv) in toluene/Et<sub>3</sub>N (6:1; 5.8 mL) by blowing argon for 20 min. Then PPh<sub>3</sub> (4.0 mg, 0.015 mmol), CuI (3.0 mg, 0.015 mmol), and [Pd<sub>2</sub>(dba)<sub>3</sub>] (14.0 mg,

0.015 mmol) were added. The reaction mixture was heated at 40 °C for 5 h. After removing solvents, the residue was purified by column chromatography (heptane/CH<sub>2</sub>Cl<sub>2</sub>, gradient from 60:40 to 30:70) to yield **7** (161 mg, 36%). <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.11 and 7.85 (AA'XX',  $J$ (A,X) = 8.7 Hz, 12H), 7.52 and 7.16 ppm (AA'XX',  $J$ (A,X) = 8.7 Hz, 12H); <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>):  $\delta$  = 147.5, 134.3, 133.6, 133.0, 131.1, 128.2, 124.3, 118.8 (q,  $J$  = 320.5 Hz), 116.6, 97.7, 87.4 ppm; <sup>19</sup>F NMR (282.37 MHz, CDCl<sub>3</sub>):  $\delta$  = −125.7 (m, 6F; CF<sub>2</sub>), −119.4 (m, 6F; CF<sub>2</sub>), −110.0 (d,  $J$  = 248.3 Hz, 3F; AB system, SCF<sub>A</sub>F<sub>B</sub>), −105.3 (d, 3F; AB system, SCF<sub>A</sub>F<sub>B</sub>), −80.5 (t,  $J$  = 9.6 Hz, 9F; CF<sub>3</sub>), −78.7 ppm (s, 9F; SO<sub>2</sub>CF<sub>3</sub>).

**Tris[4-[(4-[(trifluoromethyl)-N-[(nonafluorobutyl)sulfonyl]sulfonyl]phenyl)ethynyl]phenyl]amine (8):** Air was removed from a solution of **9** (49 mg, 0.152 mmol) and **17** (366 mg, 0.508 mmol, 3.3 equiv) in toluene/Et<sub>3</sub>N (10:1; 3.3 mL) by blowing argon for 20 min. Then CuI (1.8 mg, 0.0092 mmol) and [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (6.5 mg, 0.0092 mmol) were added, and the mixture was stirred at 40 °C for 15 h. After evaporation of the solvents, the residue was purified by column chromatography (heptane/CH<sub>2</sub>Cl<sub>2</sub> 50:50) to yield **8** (89 mg, 26%). <sup>1</sup>H NMR:  $\delta$  = 8.12 and 7.85 (AA'XX',  $J$ (A,X) = 8.7 Hz, 12H), 7.52 and 7.15 ppm (AA'XX',  $J$ (A,X) = 8.7 Hz, 12H); <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>):  $\delta$  = 147.5, 134.2, 133.6, 133.0, 131.1, 128.3, 124.3, 116.7, 97.7, 87.4 ppm; <sup>19</sup>F NMR (282.37 MHz, CDCl<sub>3</sub>):  $\delta$  = −126.0 (m, 4F; CF<sub>2</sub>), −121.0 (m, 2F; CF<sub>2</sub>), −119.4 (m, 2F; CF<sub>2</sub>), −111.9 (dt,  $J$  = 76.1, 13.6 Hz, 2F; CF<sub>2</sub>), −109.7 (d,  $J$  = 243.5 Hz, 1F; AB system, SCF<sub>A</sub>F<sub>B</sub>), −105.2 (d, 1F; AB system, SCF<sub>A</sub>F<sub>B</sub>), −80.7 (t,  $J$  = 9.8 Hz, 3F; CF<sub>3</sub>), −80.5 (t,  $J$  = 9.7 Hz, 3F; CF<sub>3</sub>); HRMS (ES<sup>+</sup>):  $m/z$ : calcd for C<sub>66</sub>H<sub>24</sub>N<sub>4</sub>O<sub>9</sub>F<sub>54</sub>NaS<sub>6</sub> [ $M$ +Na]<sup>+</sup>: 2256.89975; found: 2256.8997.

**Photophysical methods:** All photophysical properties measurements have been performed with freshly prepared air-equilibrated solutions at room temperature (298 K). UV/Vis absorption spectra were recorded using a Jasco V-570 spectrophotometer. Steady-state and time-resolved fluorescence measurements were performed on dilute solutions ( $\approx 10^{-6}$  M, optical density < 0.1) contained in standard 1 cm quartz cuvettes using an Edinburgh Instruments (FLS920) spectrometer in photon-counting mode. Fully corrected emission spectra were obtained for each compound at  $\lambda_{\text{ex}} = \lambda_{\text{abs}}^{\text{max}}$  with an optical density at  $\lambda_{\text{ex}} \leq 0.1$  to minimize internal absorption. Fluorescence quantum yields were measured according to literature procedures.<sup>[31]</sup>

Two-photon absorption (TPA) measurements were conducted by investigating the two-photon-induced fluorescence in solution. Two-photon-excited fluorescence spectroscopy was performed using a mode-locked Ti:sapphire laser that generated 150 fs-wide pulses at a 76 MHz repetition rate, with a time-averaged power of several hundreds of mW (Coherent Mira 900 pumped using a 5 W Verdi). The fluorescence from the sample was collected in epifluorescence mode. The emission and the residual excitation light were removed using a barrier filter. The emission spectra were corrected for the wavelength dependence of the detection efficiency using correction factors established through the measurement of reference compounds with known fluorescence emission spectra. The emission intensities at each excitation wavelength were shown to depend quadratically on the excitation power. The two-photon emission spectra were found to correspond to those obtained with standard one-photon excitation. Absolute values for the two-photon excitation action cross-sections  $\sigma_2\Phi$  were obtained according to the method described by Xu and Webb.<sup>[25a]</sup> For the 700–980 nm excitation window,  $10^{-4}$  M fluorescein in aqueous 0.01 M NaOH was used as a reference, and corrections for the refractive index of the solvent were applied.<sup>[32]</sup>

## Acknowledgements

We thank Région Bretagne for a fellowship to C.L.D. The financial support of the Centre National de la Recherche Scientifique (CNRS) is acknowledged. We are grateful to Vincent Hugues for his assistance in TPA measurements. Y.M. thanks GlaxoSmithKline and CNRS for financial support (BDI grant), and S.C. thanks the Erasmus Program.

- [1] a) J. T. Welch, S. S. Eswarakrishnan, *Fluorine in Bioorganic Chemistry*, Wiley, New York, **1991**; b) K. L. Kirk, *J. Fluorine Chem.* **2006**, *127*, 1013–1029; c) W. K. Hagmann, *J. Med. Chem.* **2008**, *51*, 4359–4369; d) S. Purser, P. R. Moore, S. Swallow, V. Gouverneur, *Chem. Soc. Rev.* **2008**, *37*, 320–330; e) T. Hiyama, *Organofluorine Compounds: Chemistry and Applications*, Springer, Berlin, **2000**; f) P. Kirsch, *Modern Fluoroorganic Chemistry*, Wiley-VCH, Weinheim, **2004**.
- [2] a) L. T. Cheng, W. Tam, S. H. Stevenson, G. R. Meredith, G. Rikken, S. R. Marder, *J. Phys. Chem.* **1991**, *95*, 10631–10643; b) D. M. Burland, R. D. Miller, O. Reiser, R. J. Twieg, C. A. Walsh, *J. Appl. Phys.* **1992**, *71*, 410–417; c) C. R. Moylan, R. D. Miller, R. J. Twieg, K. M. Betterton, V. Y. Lee, T. J. Matray, C. Nguyen, *Chem. Mater.* **1993**, *5*, 1499–1508; d) C. R. Moylan, K. M. Betterton, R. J. Twieg, C. A. Walsh, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. B* **1994**, *8*, 69–78; e) H. Le Breton, J. F. Letard, R. Lapouyade, A. Le Calvez, R. Maleck Rassoul, E. Freysz, A. Ducasse, C. Belin, J. P. Morand, *Chem. Phys. Lett.* **1995**, *242*, 604–616; f) R. Wortmann, C. Glania, P. Kraimer, R. Matschiner, J. J. Wolff, S. Kraft, B. Treptow, E. Barbu, D. Langle, G. Gorlitz, *Chem. Eur. J.* **1997**, *3*, 1765–1773; g) X. Wu, J. Wu, Y. Liu, A. K. Y. Jen, *Chem. Commun.* **1999**, 2391–2392; h) C. H. Wang, J. N. Woodford, A. K. Y. Jen, *Chem. Phys.* **2000**, *262*, 475–487; i) J. Brunel, I. Ledoux, J. Zyss, M. Blanchard-Desce, *Chem. Commun.* **2001**, 923–924; j) A. Papagni, S. Maiorana, B. P. Del, D. Perdicchia, F. Cariati, E. Cariati, W. Marcolli, *Eur. J. Org. Chem.* **2002**, 1380–1384; k) J. Brunel, O. Mongin, A. Jutand, I. Ledoux, J. Zyss, M. Blanchard-Desce, *Chem. Mater.* **2003**, *15*, 4139–4148.
- [3] a) L. Ventelon, L. Moreaux, J. Mertz, M. Blanchard-Desce, *Chem. Commun.* **1999**, 2055–2056; b) B. Strehmel, A. M. Sarker, H. Detert, *ChemPhysChem* **2003**, *4*, 249–259; c) L. Porrès, O. Mongin, C. Katan, M. Charlot, T. Pons, J. Mertz, M. Blanchard-Desce, *Org. Lett.* **2004**, *6*, 47–50; d) C. Le Droumaguet, O. Mongin, M. H. V. Werts, M. Blanchard-Desce, *Chem. Commun.* **2005**, 2802–2804; e) S. P. McIlroy, E. Clo, L. Nikolajsen, P. K. Frederiksen, C. B. Nielsen, K. V. Mikkelsen, K. V. Gothelf, P. R. Ogilby, *J. Org. Chem.* **2005**, *70*, 1134–1146; f) H. Y. Woo, B. Liu, B. Kohler, D. Korystov, A. Mikhailovsky, G. C. Bazan, *J. Am. Chem. Soc.* **2005**, *127*, 14721–14729; g) M. Charlot, L. Porres, C. D. Entwistle, A. Beeby, T. B. Marder, M. Blanchard-Desce, *Phys. Chem. Chem. Phys.* **2005**, *7*, 600–606; h) O. Mongin, L. Porrès, M. Charlot, C. Katan, M. Blanchard-Desce, *Chem. Eur. J.* **2007**, *13*, 1481–1498.
- [4] C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.* **1991**, *91*, 165–195.
- [5] a) M. He, T. M. Leslie, J. A. Sinicropi, S. M. Garner, L. D. Reed, *Chem. Mater.* **2002**, *14*, 4669–4675; b) Y. Liao, C. A. Anderson, P. A. Sullivan, A. J. P. Akelaitis, B. H. Robinson, L. R. Dalton, *Chem. Mater.* **2006**, *18*, 1062–1067.
- [6] M. Charlot, N. Izard, O. Mongin, D. Riehl, M. Blanchard-Desce, *Chem. Phys. Lett.* **2006**, *417*, 297–302.
- [7] a) C. Katan, F. Terenziani, C. Le Droumaguet, O. Mongin, M. H. V. Werts, S. Tretiak, M. Blanchard-Desce, *Proc. SPIE Int. Soc. Opt. Eng.* **2005**, 5935, 13–27; b) F. Terenziani, C. Le Droumaguet, C. Katan, O. Mongin, M. Blanchard-Desce, *ChemPhysChem* **2007**, *8*, 723–734.
- [8] F. Terrier, E. Magnier, E. Kizilian, C. Wakselman, E. Buncel, *J. Am. Chem. Soc.* **2005**, *127*, 5563–5571.
- [9] O. P. Varnavski, J. C. Ostrowski, L. Sukhomlinova, R. J. Twieg, G. C. Bazan, T. Goodson, III, *J. Am. Chem. Soc.* **2002**, *124*, 1736–1743.
- [10] R. M. Silverstein, G. C. Basler, T. C. Morill, *Spectrometric Identification of Organic Compounds*, Wiley, New York, **1991**.
- [11] S. J. Strickler, R. A. Berg, *J. Chem. Phys.* **1962**, *37*, 814–822.
- [12] E. Magnier, C. Wakselman, *Synthesis* **2003**, 565–569.
- [13] Y. Macé, C. Urban, C. Pradet, J. Marrot, J.-C. Blazejewski, E. Magnier, *Eur. J. Org. Chem.* **2009**, 3150–3153.
- [14] F. Würthner, H.-W. Schmidt, F. Haubner, *Ger. Offen.* **1998**, DE 96–19643097.
- [15] L. M. Yagupol'skii, *J. Fluorine Chem.* **1987**, *36*, 1–28.
- [16] a) S. Noritake, N. Shibata, S. Nakamura, T. Toru, M. Shiro, *Eur. J. Org. Chem.* **2008**, 3465–3468; b) Y. Nomura, E. Tokunaga, N. Shibata, *Angew. Chem.* **2011**, *123*, 1925–1929; *Angew. Chem. Int. Ed.* **2011**, *50*, 1885–1889; c) W. Zhang, F. Wang, J. Hu, *Org. Lett.* **2009**, *11*, 2109–2112; d) W. Zhang, W. Huang, J. Hu, *Angew. Chem.* **2009**, *121*, 10042–10045; *Angew. Chem. Int. Ed.* **2009**, *48*, 9858–9861; e) C. Urban, F. Cadoret, J.-C. Blazejewski, E. Magnier, *Eur. J. Org. Chem.* **2011**, 4862–4867; f) G. K. S. Prakash, Z. Zhang, F. Wang, C. Ni, G. A. Olah, *J. Fluorine Chem.* **2011**, *132*, 792–798.
- [17] N. V. Kondratenko, V. I. Popov, O. A. Radchenko, N. V. Ignat'ev, L. M. Yagupol'skii, *Zh. Org. Khim.* **1986**, *22*, 1716–1721.
- [18] The same stands for simpler (one-branch) dipolar derivatives.
- [19] C. Urban, Y. Macé, F. Cadoret, J.-C. Blazejewski, E. Magnier, *Adv. Synth. Catal.* **2010**, *352*, 2805–2814.
- [20] In low-polarity solvents only, the yield decreased dramatically in polar solvents in relation to markedly redshifted emission.
- [21] Due to their high electrophilic reactivity, the emission of derivatives **5–8** in medium-to-high polarity solvents could not be monitored. For the same reason, reliable fluorescence quantum yield values could not be determined for compounds **7** and **8**.
- [22] a) C. Katan, F. Terenziani, O. Mongin, M. H. V. Werts, L. Porrès, T. Pons, J. Mertz, S. Tretiak, M. Blanchard-Desce, *J. Phys. Chem. A* **2005**, *109*, 3024–3037; b) F. Terenziani, C. Sissa, A. Painelli, *J. Phys. Chem. B* **2008**, *112*, 5079–5087.
- [23] a) C. S. Krämer, T. J. J. Müller, *Eur. J. Org. Chem.* **2003**, 3534–3548; b) K. P. Elango, *Transition Met. Chem.* **2004**, *29*, 125–128; c) R. Pohl, V. A. Montes, J. Shinar, P. Anzenbacher, *J. Org. Chem.* **2004**, *69*, 1723–1725; d) C.-C. Chao, M.-K. Leung, Y. O. Su, K.-Y. Chiu, T.-H. Lin, S.-J. Shieh, S.-C. Lin, *J. Org. Chem.* **2005**, *70*, 4323–4331; e) C.-H. Zhao, E. Sakuda, A. Wakamiya, S. Yamaguchi, *Chem. Eur. J.* **2009**, *15*, 10603–10612; f) L. F. M. L. Cisco, F. H. Bartoloni, D. Weiss, R. Beckert, W. J. Baader, *J. Org. Chem.* **2010**, *75*, 6574–6580; g) E. Yamaguchi, F. Shibahara, T. Murai, *J. Org. Chem.* **2011**, *76*, 6146–6158.
- [24] F. A. Carey, R. J. Sundberg, *Advanced Organic Chemistry, Part A: Structure and Mechanisms*, 3rd ed., Plenum Press, New York, **1990**.
- [25] a) C. Xu, W. W. Webb, *J. Opt. Soc. Am. B* **1996**, *13*, 481–491; b) F. Terenziani, C. Katan, E. Badaeva, S. Tretiak, M. Blanchard-Desce, *Adv. Mater.* **2008**, *20*, 4641–4678.
- [26] W.-H. Lee, H. Lee, J.-A. Kim, J.-H. Choi, M. Cho, S.-J. Jeon, B. R. Cho, *J. Am. Chem. Soc.* **2001**, *123*, 10658–10667.
- [27] J. C. Collings, S.-Y. Poon, C. Le Droumaguet, M. Charlot, C. Katan, L.-O. Pålsson, A. Beeby, J. A. Mosely, H. M. Kaiser, D. Kaufmann, W.-Y. Wong, M. Blanchard-Desce, T. B. Marder, *Chem. Eur. J.* **2009**, *15*, 198–208.
- [28] From this correlation, we can derive an estimated value of 0.94 for the Hammett constant  $\sigma_p$  of the dimesitylboryl group.
- [29] C. Sissa, V. Parthasarathy, D. Drouin-Kucma, M. H. V. Werts, M. Blanchard-Desce, F. Terenziani, *Phys. Chem. Chem. Phys.* **2010**, *12*, 11715–11727.
- [30] S. Roquet, A. Cravino, P. Leriche, O. Alévêque, P. Frère, J. Roncali, *J. Am. Chem. Soc.* **2006**, *128*, 3459–3466.
- [31] a) D. F. Eaton, *Pure Appl. Chem.* **1988**, *60*, 1107–1114; b) J. N. Demas, G. A. Crosby, *J. Phys. Chem.* **1971**, *75*, 991–1024.
- [32] M. H. V. Werts, N. Nerambourg, D. Pélégry, Y. Le Grand, M. Blanchard-Desce, *Photochem. Photobiol. Sci.* **2005**, *4*, 531–538.
- [33] O. Exner, *Correlation Analysis in Chemistry* (Eds.: N. B. Chapman, J. Shorter), Plenum Press, New York, **1978**, pp. 357–396.

Received: November 3, 2011

Revised: June 25, 2012

Published online: August 21, 2012