



Easy and efficient tuning of the photochromic properties of 1,2-bis[5'-methyl-2'-(2''-pyridyl)thiazolyl]perfluorocyclopentene

Marion Giraud^a, Anne Léaustic^a, Régis Guillot^a, Pei Yu^{a,*}, Francois Maurel^{b,*}, Keitaro Nakatani^c

^aICMMO, UMR 8182, Université Paris Sud 11, 91405 Orsay, France

^bITODYS, UMR 7086, Université Paris Diderot, Bâtiment Lavoisier, 15 rue Jean de Baïf, 75205 Paris, France

^cPPSM, UMR 8531, ENS Cachan, 61 avenue du Président Wilson, 94235 Cachan, France

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ABSTRACT

Photochromic properties of the tilted compound could be easily tuned by simple oxidation of the peripheral pyridine groups by mCPBA. The mono- and bis-oxidized dithiazolylethenes were found to display both solution and single crystalline state photochromisms.

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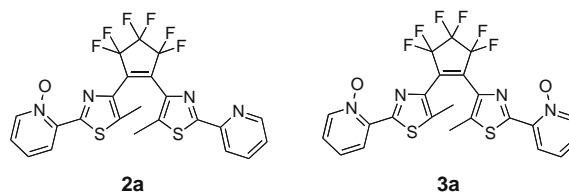
Photochromic di(heteroaryl)ethenes, notably dithienylethene-based derivatives with perfluorocyclopentene as central ethene moiety, are promising molecular switches for the development of novel photo-responsive optical and opto-electronic systems as they are known to undergo fast and fatigue-resistant photochemical reactions between two thermally stable states.¹ Moreover, their main photochromic characteristics (absorption maximum, quantum yield, thermal stability, etc.) can be tuned by playing with the nature, substitution patterns of heteroaryl groups, and with the way the two heteroaryl groups are connected to the central ethene moiety. However, the tuning of photochromic properties is often synonymous with either a multi-step post-functionalization or a total new synthesis. In this work, we report on a simple and very efficient way of tuning the photochromic features of a dithiazolylethene.

Use of photochromic di(heteroaryl)ethene-based ligands in coordination chemistry allows to access new photo-responsive coordination systems.² Dithiazolylethenes possess comparable photochromic properties to those of dithienylethenes but remain much less investigated.³ Moreover, the nitrogen atom of thiazolyl group offers an extra ligating site for potential metal coordination. As part of our ongoing effort to design new photo-responsive metal complexes,⁴ we decided to functionalize the ortho position of the pyridyl ring of 1,2-bis[5'-methyl-2'-(2''-pyridyl)thiazolyl]perfluorocyclopentene (**1a**)^{4a} in order to further enhance its ligating

capability toward metal ions. For this purpose, **1a** was allowed to react with mCPBA (meta-chloroperbenzoic acid) to activate the pyridyl ring, and two oxidation compounds were obtained: dithiazolylethene with one pyridine-oxide group (**2a**) and dithiazolylethene with two pyridine-oxide groups (**3a**)⁵ (Scheme 1). To our surprise, their photochromic properties turned out to be quite different from those of the starting **1a**.

The spectral changes of **2a** and **3a** in CHCl₃ upon UV irradiation (365 nm) are shown in Figure 1.

Under UV irradiation, the initial colorless solution of **2a** quickly turned purple-blue with appearance of a low energy band with λ_{max} at 585 nm, while that of **3a** turned deep blue with λ_{max} of its low energy band at 622 nm. The purple-blue and blue colors were stable in the dark at room temperature, but can be bleached by visible light ($\lambda > 450$ nm). The coloration and discoloration process, which corresponds to the light induced inter-conversion between the colorless open form (**2a**, **3a**) and deeply colored closed form (**2b**, **3b**) as shown in Scheme 2, could be repeated several



Scheme 1.

* Corresponding authors. Tel.: +33 1 69 15 61 83; fax: +33 1 69 15 47 54 (P.Y.).
E-mail address: yupei@icmo.u-psud.fr (P. Yu).

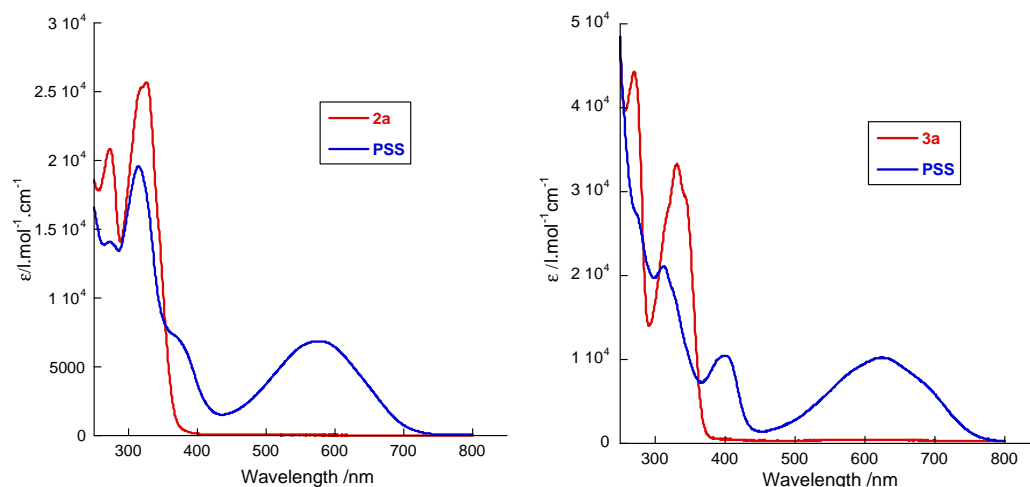
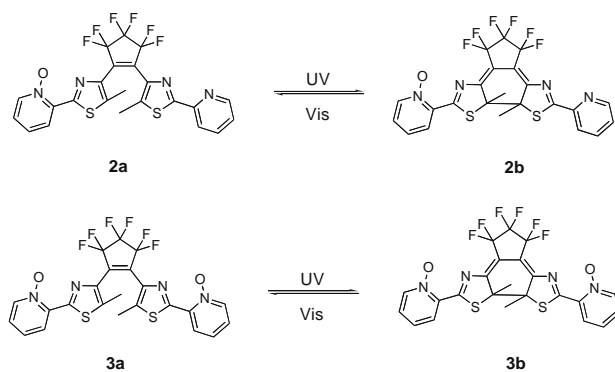


Figure 1. Electronic absorption spectra of **2a** and **3a** and their photo-stationary states (PSS) upon UV irradiation at 365 nm in CHCl_3 .



Scheme 2. Photochromic reactions of **2a** and **3a**.

times without loss of their photochromic properties. Finally, for both **2a** and **3a**, the conversion ratio in the photo-stationary state was more than 95%, as estimated by ^1H NMR.

The main photochromic properties of **2a** and **3a** as well as those reported for **1a** are gathered in Table 1.

λ_{max} of the open form of oxidized dithiazolylethene is slightly red shifted with increasing number of pyridine-oxide group, while the coefficient of molar absorption as well as the quantum yield of electrocyclization remains within the same order of magnitude. For the closed form, however, besides the 10-fold decrease of quantum yield for the discoloration (cycloreversion) observed for both **2b** and **3b** in comparison with **1b**, the most striking and naked-eye visible difference is the important and almost linear increase in the λ_{max} of the low energy band with increasing number of pyridine-oxide: ca. 40 nm red shift with each additional pyridine-oxide group.

It was reported that the oxidation of the sulfur atom of the thienyl moiety in some dithienylethene derivatives led to an important blue shift in the absorption maximum of the closed form.⁶ However, unlike the present case, the oxidation takes place on

the thienyl ring, which is directly involved in the electrocyclization. In the present case, oxidation occurs at the nitrogen atom of a peripheral pyridyl ring, which is not directly involved in the light induced electrocyclization. In order to gain a better understanding of how the formation of a single N–O bond may have such an impact on the λ_{max} of its low energy band, theoretical calculations have been performed on both the open and the closed form of these molecules.

Our goal is to investigate how the oxidation of pyridine units influences the conjugated structure and the optical properties of the closed form isomer by performing density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations. DFT and TD-DFT calculations using hybrid functionals have been shown to predict geometries and excitation energies in very good agreement with experimental values.⁷

The results of full-geometry optimizations, performed at the B3LYP/6-31G level of theory with GAUSSIAN 03 program package,⁸ show that the oxygen atoms attached to the pyridine unit mainly affect the geometry of the ring to which they are connected. For instance, in the closed forms, the two C–N bonds of the pyridine bearing the oxygen atom are markedly elongated with respect to the corresponding value in the non-oxidized one: the C–N bonds evolve from 1.331 Å to 1.388 Å and from 1.327 Å to 1.378 Å upon oxidation. The geometry of dithiazolylethene moiety is also slightly changed by substitution in such way that double bond lengths are elongated while single bond length are shortened, leading to a less pronounced single–double bond lengths alternation. Similar geometric deformations are obtained also for the opened forms.

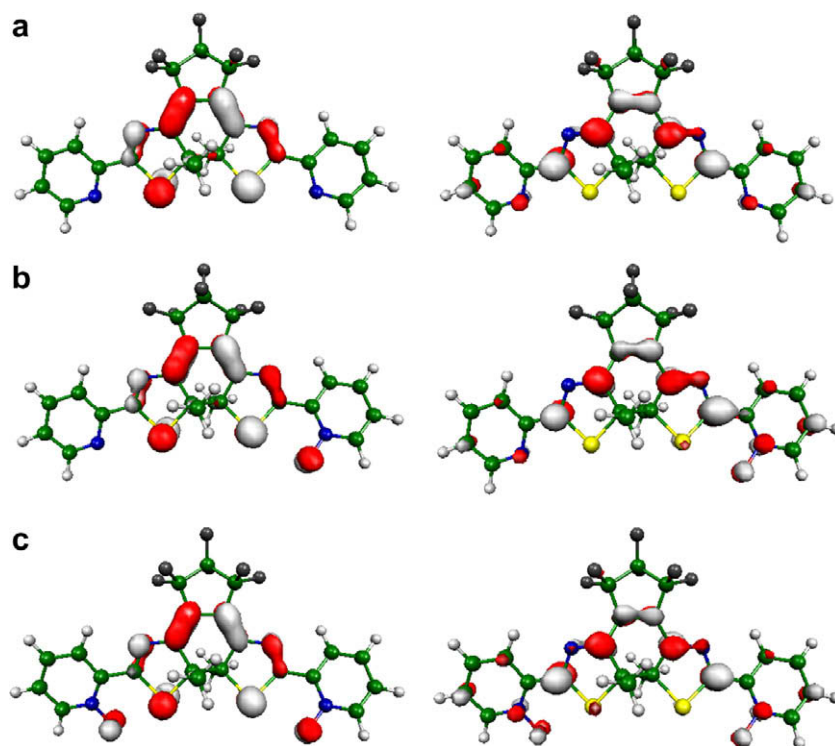
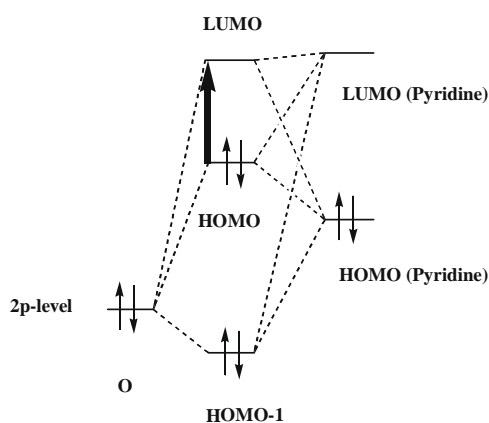
For each open and closed forms, the wavelength, the corresponding transition and the oscillator strength of the maximum absorption band provided by TD-DFT calculations are listed in Table 2. From the predicted absorption maxima of the closed forms, it is found that the calculated maxima of absorption wavelengths are in good agreement with experimental observations, thus confirming the accuracy of the B3LYP/6-31G level of theory to study the optical properties of these compounds. Furthermore, the calcula-

Table 1
UV–visible data and photochemical quantum yields in CHCl_3 of **1**, **2**, and **3**

	$\lambda_{\text{max}}/(\text{e}/\text{M}^{-1} \text{cm}^{-1})$	$\phi_{\text{a} \rightarrow \text{b}}(\lambda_{\text{irr}}/\text{nm})$		$\lambda_{\text{max}}/(\text{e}/\text{M}^{-1} \text{cm}^{-1})$	$\phi_{\text{b} \rightarrow \text{a}}(\lambda_{\text{irr}}/\text{nm})$
2a	326 (25,694)	0.31 ± 0.01 (365)	2b	585 (8333)	0.0039 ± 0.0005 (547)
3a	331 (33,333)	0.26 ± 0.01 (365)	3b	622 (12,611)	0.0023 ± 0.0005 (547)
1a	310 (40,000)	0.17 ± 0.01 (313)	1b	545 (12,700)	0.035 ± 0.005 (547)

Table 2Optical properties of open and closed forms: λ_{\max} (S0 \rightarrow S1 transition), oscillator strength, HOMO and LUMO levels, and HLG's (HOMO and LUMO gaps)

Compound	λ_{\max} (nm)	Description	Oscillator Strength	HOMO (eV)	LUMO (eV)	HLG (eV)
<i>Open form</i>						
1a	309	HOMO \rightarrow LUMO	0.015	-6.56	-1.98	4.58
2a	346	HOMO \rightarrow LUMO	0.010	-6.19	-2.14	4.04
3a	348	HOMO \rightarrow LUMO + 1 HOMO - 4 \rightarrow LUMO + 1	0.011	-6.17	-2.15	4.01
<i>Closed form</i>						
1b	570	HOMO \rightarrow LUMO	0.021	-5.90	-3.35	2.55
2b	610	HOMO \rightarrow LUMO	0.020	-5.77	-3.40	2.36
3b	648	HOMO \rightarrow LUMO	0.019	-5.64	-3.44	2.21

**Figure 2.** HOMO (left) and LUMO (right) of closed forms of **1b** (a), **2b** (b), and **3b** (c).**Scheme 3.** Three-level model describing the nature of the frontier orbital levels of the oxidized dithiazolylenes from the interaction of the HOMO and LUMO of the pyridine group in the non-oxidized dithiazolylene and the occupied atomic orbital of oxygen atom. The large arrow illustrates the nature of the lowest energy optical transition in the oxidized dithiazolylenes.

tions clearly demonstrate that the presence of oxygen atoms in the pyridine unit of the dithiazolylene causes a strong red shift in the λ_{\max} of the closed form. For each molecule and each form, the absorption maximum originates from the promotion of one electron from the HOMO to the LUMO, which are both delocalized over the whole molecule.

The HOMO and LUMO for **1b**, **2b**, and **3b** are plotted in Figure 2. It is clear that both HOMO and LUMO of **2b** and **3b** have an antibonding nature between the p orbital of oxygen atom and frontier orbitals of molecular part of dithiazolylene. More precisely, oxidation of each pyridine unit destabilizes the HOMO level by

**Figure 3.** Photographs of **2a** (left) and **3a** (right) before and after UV irradiation at 365 nm.

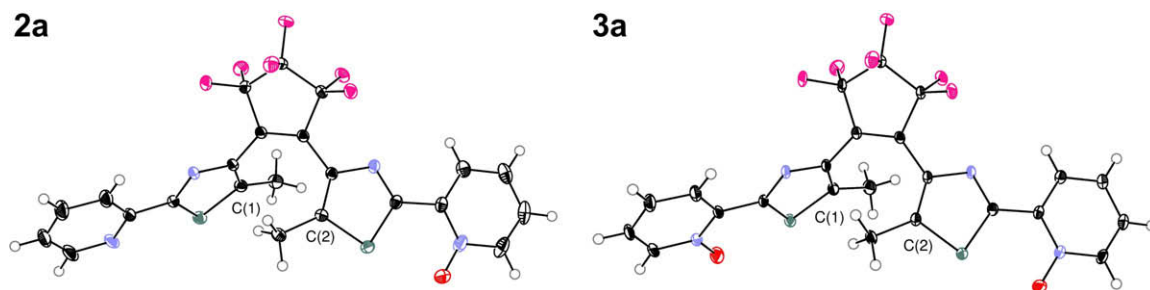


Figure 4. Molecular structures of **2a** and **3a**. Compound **2a**: Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Compound **3a**: Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

0.13 eV and stabilizes the LUMO level by 0.05 eV. Thus, the transformation of the pyridine into the corresponding pyridine oxide substantially increases the energy of HOMO but only slightly lowers the energy of LUMO.

The trends in our results can be rationalized by a simple three-level model involving the frontier molecular orbitals of the non-oxidized dithiazolyethene in its closed form and the occupied atomic orbital of the oxygen. This is illustrated in Scheme 3. The interaction between the conjugated skeleton of the dithiazolyethene and the electron-donating oxygen atom leads to an overall destabilization of the HOMO and a very weak stabilization of the LUMO. This interaction is more pronounced for the HOMO level as a consequence of its stronger interaction with the donor level, leading thus to a decrease in the HOMO–LUMO gap (HLG).

Finally, like **1a**, both **2a** and **3a** were found to display single crystalline state photochromism. Upon UV irradiation (365 nm), the colorless single crystal of **2a** turned blue, while that of **3a** changed from colorless to blue-green, as shown in Figure 3. And this process is reversible as the blue and blue-green colors could be bleached by visible light.

The crystal structures of **2a** and **3a** were determined.⁹ The ORTEP views of their molecular structures are depicted in Figure 4.

Both molecular structures are characterized by a common feature: the two methyl groups attached to the photo-reactive carbon atoms in both molecules are in trans conformation and the distance between the two reactive carbon atoms is, respectively, 3.68 Å for **2a** and 3.65 Å for **3a**. In other words, the molecular structures of both compounds fulfill the two well-established and necessary conditions to observe crystalline state photochromism.¹⁰

In conclusion, we have shown that a simple oxidation of the nitrogen atom of the peripheral pyridyl ring in 1,2-bis[5'-methyl-2'-(2''-pyridyl)thiazolyl]perfluorocyclopentene strongly impacts on its photochromic properties, leading notably to a large red shift of the low energy band in its closed form. And this red shift is linearly proportional to the number of pyridine-oxide group present in the molecule. Such a tuning of photochromic properties may be extended to other di(heteroaryl)ethene derivatives. Further transformations of **2a** and **3a** into more coordinating photochromic ligands toward metal ions are under way.

References and notes

- Reviews and some recent and selected examples: (a) Irie, M. *Chem. Rev.* **2000**, *100*, 1685–1716; (b) Matsuda, K.; Irie, M. *J. Photochem. Photobiol. C: Photochem. Rev.* **2004**, *5*, 169–182; (c) Higashiguchi, K.; Matsuda, K.; Tanifuji, N.; Irie, M. *J. Am. Chem. Soc.* **2005**, *127*, 8922–8923; (d) Odo, Y.; Matsuda, K.; Irie, M. *Chem. Eur. J.* **2006**, *12*, 4283–4288; (e) Tian, H.; Wang, S. *Chem. Commun.* **2007**, 781–792; (f) Sud, D.; Wigglesworth, T. J.; Branda, N. R. *Angew. Chem., Int. Ed.* **2007**, *46*, 8017–8019; (g) Kronemeijer, A. J.; Akerman, H. B.; Kudernac, T.; van Wees, B. J.; Feringa, B. L.; Blom, P. W. M.; de Boer, B. *Adv. Mater.* **2008**, *20*, 1467–1473; (h) Berberich, M.; Krause, A. M.; Orlandi, M.; Scandola, F.; Würthner, F. *Angew. Chem., Int. Ed.* **2008**, *47*, 6616–6619; (i) Corredor, C. C.; Huang, Z. L.; Belfield, K. D.; Morales, A. R.; Bondar, M. V. *Chem. Mater.* **2007**, *19*, 5165–5173; (j) Bossi, M.; Belov, V.; Polyakova, S.; Hell, S. W. *Angew. Chem., Int. Ed.* **2006**, *45*, 7462–

- 7465; (k) Zou, Y.; Yi, T.; Xiao, S.; Li, F.; Li, C.; Gao, X.; Wu, J.; Yu, M.; Huang, C. J. *Am. Chem. Soc.* **2008**, *130*, 15750–15751; (l) Golovkova, T. A.; Kozlov, D. V.; Neckers, D. C. *J. Org. Chem.* **2005**, *70*, 5545–5549; (m) Maly, K. E.; Zhang, P.; Wand, M. D.; Buncel, E.; Lemieux, R. P. *J. Mater. Chem.* **2004**, *14*, 2806–2812; (n) Mulder, A.; Jukovic, A.; Huskens, J.; Reinhoudt, D. N. *Org. Biomol. Chem.* **2004**, *2*, 1748–1755; (o) Lim, S.-J.; Seo, J.; Park, S.-Y. *J. Am. Chem. Soc.* **2006**, *128*, 14542–14547; (p) Chen, Y.; Zeng, D. X.; Xie, N.; Dang, Y. Z. *J. Org. Chem.* **2005**, *70*, 5001–5005.
- (a) Fernandez-Acebes, A.; Lehn, J. M. *Chem. Eur. J.* **1999**, *5*, 3285–3292; (b) Frayssé, S.; Coudret, C.; Launay, J. P. *Eur. J. Inorg. Chem.* **2000**, 1581–1590; (c) Norsten, T. B.; Branda, N. R. *Adv. Mater.* **2001**, *13*, 347–349; (d) Matsuda, K.; Takayama, K.; Irie, M. *Inorg. Chem.* **2004**, *43*, 482–489; (e) Yakayama, K.; Matsuda, K.; Irie, M. *Chem. Eur. J.* **2003**, *9*, 5605–5609; (f) Tian, H.; Chen, B.; Tu, H.; Müllen, K. *Adv. Mater.* **2002**, *14*, 918–923; (g) Jukes, R. T. F.; Adamo, V.; Hartl, F.; Belsler, P.; De Cola, L. *Inorg. Chem.* **2004**, *43*, 2779–2782; (h) Belsler, P.; De Cola, L.; Hartl, F.; Adamo, V.; Bozic, B.; Chriqui, Y.; Iyer, V. M.; Jukes, R. T. F.; Kühni, J.; Querol, M.; Roma, S.; Salluce, N. *Adv. Funct. Mater.* **2006**, *16*, 195–208; (i) Lee, P. H.-M.; Ko, C.-C.; Zhu, N.; Yam, V. W.-W. *J. Am. Chem. Soc.* **2007**, *129*, 6058–6059; (j) Aubert, V.; Guerschais, V.; Ishow, E.; Hoang-Thi, K.; Ledoux, I.; Nakatani, K.; Le Bozec, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 577–580; (k) Motoyama, K.; Koike, T.; Akita, M. *Chem. Commun.* **2008**, 5812–5814; Indelli, M. T.; Carli, S.; Ghirotti, M.; Chiorboli, C.; Ravaglia, M.; Garavelli, M.; Scandola, F. *J. Am. Chem. Soc.* **2008**, *130*, 7286–7299.
- (a) Uchida, K.; Ishikawa, T.; Takeshita, T.; Irie, M. *Tetrahedron* **1998**, *54*, 6627–6638; (b) Takami, S.; Kawai, T.; Irie, M. *Eur. J. Org. Chem.* **2002**, 3796–3800; (c) Takami, S.; Kobatake, S.; Kawai, T.; Irie, M. *Chem. Lett.* **2003**, *32*, 892–893; (d) Kuroki, L.; Takami, S.; Shibata, K.; Irie, M. *Chem. Commun.* **2005**, 6005–6007; (e) Nakagawa, T.; Atsumi, K.; Nakashima, T.; Hasegawa, Y.; Kawai, T. *Chem. Lett.* **2007**, *36*, 372–373; (f) Nakashima, T.; Atsumi, K.; Kawai, T.; Nakagawa, T.; Hasegawa, Y.; Kawai, T. *Eur. J. Org. Chem.* **2007**, 3212–3218.
- (a) Giraud, M.; Léaustic, A.; Charlot, M. F.; Yu, P.; Césarino, M.; Philouze, C.; Pansu, R.; Nakatani, K.; Ishow, E. *J. New Chem.* **2005**, *29*, 439–446; (b) Giraud, M.; Léaustic, A.; Guillot, R.; Yu, P.; Lacroix, P. G.; Nakatani, K.; Pansu, R.; Maurel, F. *J. Mater. Chem.* **2007**, *17*, 4414–4425.
- Synthetic procedure and selected data for 2a and 3a:** To a solution of **1a** (198 mg, 0.38 mmol) in 5 ml of CH₂Cl₂ was added portionwise mCPBA (96 mg, 70–75%, 0.4 mmol) in ca. 5 ml of CH₂Cl₂ over 1 h. After stirring over night at room temperature, the solution was treated with aqueous Na₂CO₃ (10 ml), and aqueous phase was extracted with CH₂Cl₂ (10 ml). Combined organic phase was then washed with brine (20 ml) and dried over Na₂SO₄. After vacuum evaporation of CH₂Cl₂, residue was subjected to column chromatography (silica gel, CH₂Cl₂). Both **2a** and **3a** were isolated as a white powder in 34% and 19% yields, respectively. It has to be noted that **3a** could be obtained almost quantitatively when 1 equiv of **1a** was treated with 3 equiv of mCPBA. **Selected data for 2a:** ¹H NMR (CDCl₃, 250 MHz): δ 2.03 (s, 3H), 2.06 (s, 3H), 7.25–7.40 (m, 3H), 7.78 (t, 1H), 8.12 (d, 1H), 8.33 (d, 1H), 8.49 (d, 1H), 8.57 (d, 1H). **Elem. Anal.** Calcd for C₂₃H₁₄F₆N₄O₂: C 51.11, H 2.61, N 10.37; exp. C 50.52, H 2.53, N 10.15. **Selected data for 3a:** ¹H NMR (CDCl₃, 250 MHz): δ 2.03 (s, 3H), 7.25–7.40 (m, 2H), 8.33 (d, 1H), 8.49 (d, 1H). **Elem. Anal.** Calcd for C₂₃H₁₄F₆N₄O₂S₂: C 49.64, H 2.54, N 10.07; exp. C 49.22, H 2.23, N 9.92.
- (a) Jeong, Y.-C.; Yang, S. I.; Ahn, K.-H.; Kim, E. *Chem. Commun.* **2005**, 2503–2505; (b) Jeong, Y.-C.; Park, D. G.; Kim, E.; Ahn, K.-H.; Yang, S. I. *Chem. Commun.* **2006**, 1881–1883; (c) Fukaminato, T.; Tanaka, M.; Kuroki, L.; Irie, M. *Chem. Commun.* **2008**, 3924–3926.
- Perrier, A.; Maurel, F.; Aubard, J. J. *Photochem. Photobiol. A* **2007**, *189*, 167–176.
- Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.

Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; GAUSSIAN 03; Gaussian: Wallingford, CT, 2004.

9. CCDC 711768 and 711769 contain the supplementary crystallographic data for this Letter. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Selected data for two compounds. Compound **2a**: $C_{23}H_{14}F_6N_4OS_2$, $M = 540.50$, monoclinic, $a = 16.2695$ (10) Å, $b = 8.3528$ (5) Å, $c = 16.5567$ (9) Å, $\alpha = 90^\circ$, $\beta = 96.4100$ (10)°, $\gamma = 90^\circ$, $V = 2235.9$ (2) Å³, $T = 100$ (1) K, space group $P2_1/n$

(no. 14), $Z = 4$, $\mu(\text{Mo-K}\alpha) = 0.314$ mm⁻¹, 25351 reflections measured, 9813 unique ($R_{\text{int}} = 0.0273$), 7752 ($I > 2\sigma(I)$) which were used in all calculations. The final $R(F_2) = 0.0592$. Compound **3a**: $C_{23}H_{14}F_6N_4O_2S_2 \cdot H_2O$ $M = 574.52$, monoclinic, $a = 16.2804$ (5) Å, $b = 8.3976$ (2) Å, $c = 16.5490$ (5) Å, $\alpha = 90^\circ$, $\beta = 97.040$ (2)°, $\gamma = 90^\circ$, $V = 2245.46$ (11) Å³, $T = 100$ (1) K, space group $P2_1/n$ (no. 14), $Z = 4$, $\mu(\text{Mo-K}\alpha) = 0.325$ mm⁻¹, 23,460 reflections measured, 5457 unique ($R_{\text{int}} = 0.0349$), 4874 ($I > 2\sigma(I)$) which were used in all calculations. The final $R(F_2) = 0.0501$.

10. Morimoto, M.; Irie, M. *Chem. Commun.* **2005**, 3895–3905.