

Optical properties of a donor–acceptor-substituted “hemi-cruciform” catechol derivative

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ABSTRACT

The optical properties of a novel catechol derivative have been studied; a very large solvatochromism of the emission spectra was observed, revealing an important low-energy intra-molecular charge-transfer. From our experiment, a chemical structure–polarizability relationship is studied according to the Lippert–Mataga correlation and compared to results obtained previously for analogous compounds. This synthetic strategy complemented with characterizations and theoretical analysis allows one to design specific charge-transfer compounds to be used as nonlinear chromophores and ligands in multifunctional complexes.

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1. Introduction

Organic molecules and related polymers [1] dedicated to applications such as electroluminescence devices (OLEDs), thin film transistors, optical storage devices, optical biosensors and solar cells are commonly based on conjugated electro-withdrawing (A) and electro-donating (D) groups linked *via* a π -conjugated system [2]. In this area, new chemosensors for the luminescent detection of relevant ions and molecules have been reported [3]. Among them, catechol derivatives displaying a pH-sensitive fluorescence emission have been proposed and described recently [4]. In order to target specific properties and applications, a better knowledge of the materials structure–property relationship would be desirable. With this goal in mind, we have recently published [5], the synthesis and optical properties of several novel 4,5-substituted-(*tert*-butyldimethylsilyl)-protected-catechols involving (D,D), (D,A) and (A,A) pairs as Z₁ and Z₂ substituents (see Fig. 1 for the general structure of this family of compounds). These molecules appeared to be promising candidates as well as for the fine-tuning of the internal charge-transfers than as potential nonlinear chromophores, luminophores and ligands within related multifunctional coordination complexes.

On one hand, the (D,D) and (A,A) combinations allow for charge-transfers (CTs) between the catecholate functions and the π -delocalized substituents in the 4th and 5th positions. On the other hand, the (D,A) substitutions favour a low-energy inter-branch CT. Since our purpose is to enhance the polarizabilities for nonlinear optical (NLO) applications, large- and low-energy intra-molecular CTs must be favoured through chemical engineering [6].

In this study, the synthesis and optical properties of a novel 4,5-[(4-phenylethynyl)-substituted]-TBDMS-protected-catecholate compound *pCat*-PECF₃-PENMe₂ are reported. The substitution with an electro-donating (NMe₂) and -withdrawing (CF₃) groups at the 4th and 5th positions, respectively, gives rise to different CT strengths and pathways within the chromophore. A correlation between the optical properties (more particularly, polarizability) and structures is suggested and complementary theoretical investigations are performed.

2. Results and discussion

2.1. Synthesis

pCat-I-PENMe₂ was prepared according to procedures already described in the literature (see Section 4 for references). 4,5-Substituted-TBDMS-protected-catechol compound *pCat*-PECF₃-PENMe₂ was obtained *via* a Sonogashira cross-coupling reaction [7], starting from commercially available 1,1-ethynyl-4-

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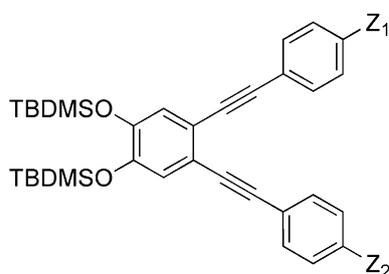


Fig. 1. General structure of the 4,5-substituted-(*tert*-butyldimethylsilyl)-protected-catechol *pCat-PEZ*₁-*PEZ*₂ compounds, Z₁, Z₂ being electro-withdrawing or -donating groups.

Table 1

Geometric data extracted from X-ray analysis. The relative orientations of aryl rings are given.

	X-ray data
C ₁₇ –C ₅ –C ₄ –C ₉ (°)	2.14
(N ₁ C ₂₄ C ₂₅)/(C ₁₀ C ₁₂ C ₁₄) (°)	5.37
(C ₉ C ₁₁ C ₁₃)/(C ₁₇ C ₁₉ C ₂₁) (°)	11.64
(C ₉ C ₁₁ C ₁₃)/(C ₂ C ₄ C ₆) (°)	11.85
(C ₁₇ C ₁₉ C ₂₁)/(C ₁ C ₃ C ₅) (°)	16.33
C ₁₅ –C ₁₆ (Å)	1.08
C ₇ –C ₈ (Å)	1.17

trifluoromethylbenzene and one equivalent of *pCat-I-PENMe*₂ (see Fig. 2).

2.2. X-ray structure

Single crystals of *pCat-PECF*₃-*PENMe*₂ were obtained by slow evaporation of an acetonitrile solution [8]. Crystal data, refinement parameters and details of the crystallographic measurements are reported in Supporting Information (SI). On the molecular scale (Fig. 3), *pCat-PECF*₃-*PENMe*₂ exhibits a small dihedral C₁₇–C₅–C₄–C₉ angle (see Table 1). The two phenyl fragments are twisted from the catechol ring by an angle of 12° leading to a nonperfect planarity of the molecule. This particular geometry may be due to steric interactions between the hydrogen atoms of each substituted aromatic cycle.

2.3. NMR study

Characterization of the molecule by ¹H and ¹³C NMR is depicted in Section 4. Indeed, push–pull character of the compound can be visualised by using several solvents with increasing polarity (see Figure S1 in Supplementary Information and Fig. 4 for ¹H and ¹³C, respectively). In an apolar solvent such as benzene, the two central protons (H₃ and H₆) are equivalent. When increasing the polarity of the medium, the singlet observed splits into two singlets, revealing a difference in electron-density on each side of the molecule. A polar solvent stabilizes the delocalized charge making a consequent difference between the two environments of H₃ and H₆. The

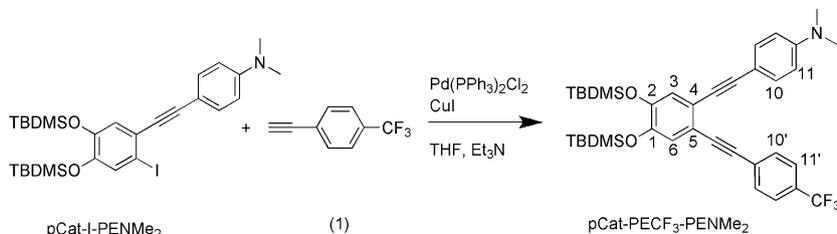


Fig. 2. Synthesis and general atom numbering also given for the NMR description (Section 4) of *pCat-PECF*₃-*PENMe*₂.

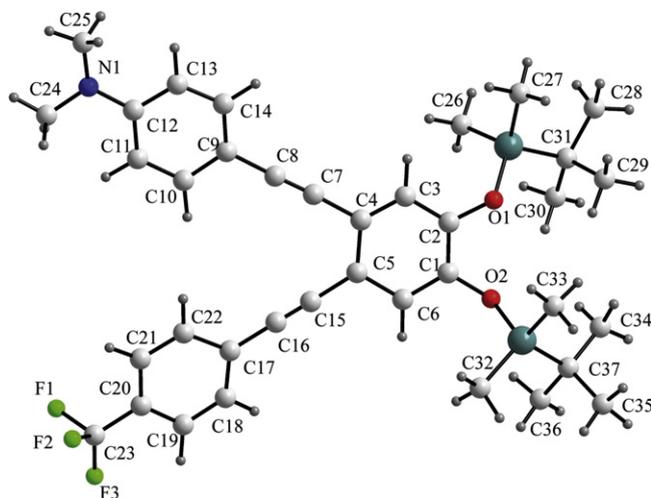


Fig. 3. X-ray structure of *pCat-PECF*₃-*PENMe*₂ (atom numbering is used in Table 1).

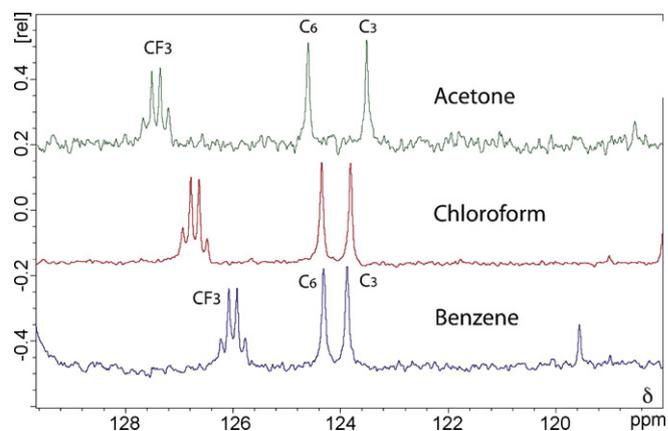


Fig. 4. ¹³C NMR spectra of *pCat-PECF*₃-*PENMe*₂ in different solvents.

phenyl bearing the CF₃ moiety exhibits a multiplet which then coalesces to a singlet in more polar solvents as shown for example in acetone (Figure S1), chemical environment difference between the two aromatic protons decreases with the charge redistribution. As shown in Fig. 4, this evolution with the environment polarity, can also be followed by ¹³C NMR and especially the larger difference in chemical shift observed between C₃ and C₆ when going from benzene to acetone.

2.4. Electronic absorption spectra

In the linear absorption spectrum of *pCat-PECF*₃-*PENMe*₂, three types of bands can be observed (see Fig. 5): (i) bands pointing around 260 nm which slightly depend on the polarity solvent (see spectra, Figure S2 in SI) and is mainly attributed to π – π^* elec-

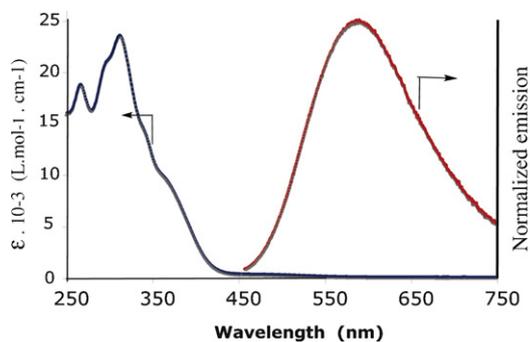


Fig. 5. Absorption and normalized emission spectra of the compound *pCat-PECF₃-PENMe₂* in DMSO.

tronic transitions centred on the aromatic rings (ii) lower energy absorption bands lying in the 280–340 nm spectral range (revealing a shoulder at higher wavelength), which may be mainly assigned to a donor–acceptor CT, and finally (iii) a broad band between 360 and 400 nm (the longest wavelength λ_{max}) ascribed to the lower energy charge-transfer between the donor (NMe₂) and the acceptor (CF₃). The low ϵ values are consistent with the less effective nonlinear-conjugated pathway followed in this charge-transfer.

The low ϵ value (Table 2) is consistent with the bent-conjugated CT pathway, confirming the influence of the nature of the substituent groups and their positions on the maximum absorption wavelengths and ϵ values. A study of the linear optical properties of this compound according to the nature of the solvent has been accomplished and the emission will be commented below in details.

2.5. Fluorescence spectroscopy

We examined fluorescence emission in solution at room temperature. Maximum absorption and emission wavelengths, Stokes shifts (defined as the loss of energy between absorption and emission of light), quantum yields and excited state lifetimes of *pCat-PECF₃-PENMe₂* compared to several other compounds of the family, are reported in Table 2. Luminescence spectra (displayed in Fig. 6) consist in broad bands centred at 400–600 nm depending on the solvent. A strong fluorescence was already observed for similar catechol substituted with two pyridine groups and the fluorescence properties were attributed to a π – π^* excited state [9]. In our case, the dependence of the maximum emission wavelength with the solvent polarity (Fig. 6) would suggest that the fluorescence properties are rather due to a CT excited state. The emission is broad, with a larger Stokes shift, a low quantum yield of 0.06 and a 5.6 ns emission lifetime.

These results suggest a large rearrangement of the electronic distribution in the excited state of this structure between the Frank–Condon excited state and the emissive excited state obtained after relaxation. This is in good agreement with the large charge redistribution from the PENMe₂ donor branch to the PECF₃ acceptor one.

Table 2

Absorption and emission properties of several protected derivatives at room temperature in THF.

Compounds	λ_{abs} (ϵ)/nm (L mol ⁻¹ cm ⁻¹)	λ_{em} (nm)	Stokes shift (cm ⁻¹)	Φ^a	τ^a (ns)	Ref.
<i>pCat-PECF₃-PENMe₂</i>	336 (31,300)	510	8050	0.06	5.6	This work
<i>pCat-PENO₂-PENMe₂</i>	338 (59,560)	420	5776	~0	2.88	3
<i>pCat-di-PEOMe</i>	290 (88,000)	320 (42,500)	3626	0.15	1.26	3
<i>pCat-di-PENMe₂</i>	322 (72,760)	415	6960	0.21	2.63	3
<i>pCat-di-PECF₃</i>	321 (20,200)	395	5900	0.14	2.03	3

^a In acetonitrile.

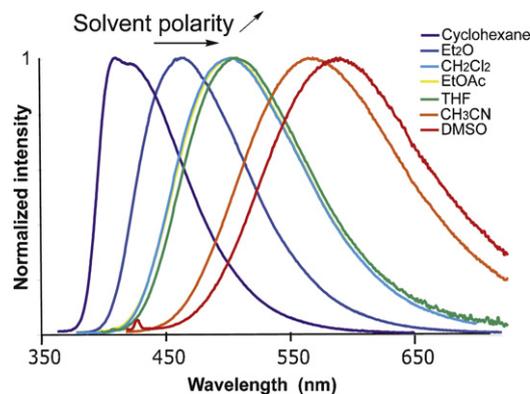


Fig. 6. Emission spectra of compound *pCat-PECF₃-PENMe₂* in several solvents, at ca. 10⁻⁶ M and 25 °C.

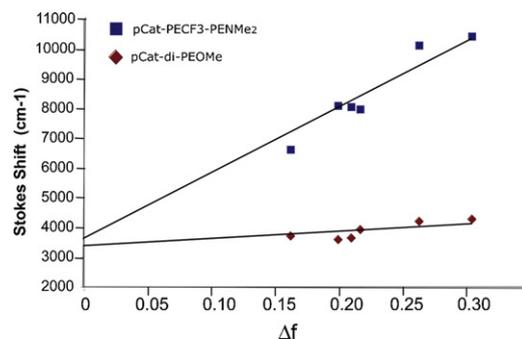


Fig. 7. Correlation of the Stokes shift and the Lippert–Mataga polarizability parameter in the seven solvents listed in Table 1, for compounds *pCat-PECF₃-PENMe₂* and *pCat-di-PEOMe* ($R^2 = 0.96$ and 0.85 , respectively).

the Stokes shift has been plotted according to the solvent orientation polarizability $\Delta f(\epsilon, n)$ (Fig. 7). The relationship between Stokes shift $\Delta\nu_{\text{ST}}$ and solvent polarity is usually given by Lippert–Mataga equation [10]. This correlation (Eq. (1)) is the most widely used equation to describe the effects of the physical properties of the solvent on the emission spectra of luminophores. It has been used here, in order to estimate the variation ($\mu_e - \mu_g$), in the dipole moment difference between the ground and the excited states (polarizability).

$$\Delta\nu_{\text{ST}} = \Delta\nu_{\text{ST}}^0 + \left[\frac{2}{(4\pi\epsilon_0)(hca^3)} \right] \times (\mu_e - \mu_g)^2 \times \Delta f(\epsilon, n) \quad (1)$$

a is the value of the Onsager cavity radius in which the fluorophore resides, h is the Planck's constant, c is the speed of light, ϵ_0 is the vacuum permittivity and $\Delta f(\epsilon, n)$ is defined as:

$$\Delta f(\epsilon, n) = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad (2)$$

where ϵ is the static dielectric constant, and n the refractive index of the solvent. The plot is linear with correlation factor $R^2 = 0.96$, suggesting that dipole–dipole interaction between the solute and

Table 3
Relative permittivity (ϵ) at 25 °C, refractive index (n) and orientational polarizability (Δf) values of solvents.

Solvents	ϵ^{25°	$n_D^{20^\circ}$	$\Delta f(\epsilon, n)$
Cyclohexane	2.0	1.426	-0.00396
Diethyl-ether	4.2	1.353	0.16223
Ethyl acetate	6.0	1.372	0.19943
THF	7.6	1.407	0.20987
Dichloromethane	8.9	1.424	0.21692
CH ₃ CN	35.9	1.344	0.30459
DMSO	46.4	1.479	0.26308

solvent are mainly responsible for the solvent-dependent fluorescence shift. On the basis of Eq. (1) and assuming that the cavity radius a is comparable for compounds previously described, the difference in the dipole moments in solution is larger for the trifluoromethyl-amino compound than for all the other ones (Table 3).

Considering the *pCat-di-PEOME* compound as a reference (due to the nearly homogenous OR-type tetra-substitution of the catechol derivative), the slope is 10 times larger for compound *pCat-PECF₃-PENMe₂* indicating a three times higher value in the difference ($\mu_{CT} - \mu_g$) (Eq. (1)).

This result supports a larger polarizability for compound *pCat-PECF₃-PENMe₂* as compared to the reference *pCat-di-PEOME* and a higher efficiency in nonlinear optics may be also expected, as recently reported in the literature [11]. The emission follows a mono-exponential decay in deoxygenated acetonitrile solution (recorded at 530 nm after excitation at 400 nm) and the emission lifetimes t around a few nanoseconds (see Table 2) are in good agreement with a singlet excited state emission.

The electronic properties can be traced using quantum chemical calculations. They complement the experimental analysis since a microscopic picture of the dipole orientation is available. The valence molecular orbitals HOMO and LUMO were plotted to support the electro-donor vs. -acceptor characters. These DFT calculations were conducted using the B3LYP functional and 6-311 G basis set available in the Gaussian 03 package [12]. As shown in Fig. 8, the LUMO has a strong contribution upon the CF₃ moiety. The electron flow should be oriented towards CF₃ in agreement with the substituent properties. As expected, the NMe₂ group exhibits a donor character since the HOMO is mostly localized on the electron-rich NMe₂ moiety and the intra-molecular CT direction to the LUMO can be selectively controlled. One should mention that the methoxy substituent (introduced in the calculations to replace the OTBDMS

moiety) does not seem to be involved in the CT. As compared to previously reported compounds [3], our chromophore possesses a “hemi-cruciform”-type structure, localizing the disjoint frontier molecular orbitals (FMOs) on the respective branches.

3. Conclusion

The synthesis and optical characteristics of a novel NLO target molecule have been presented following a chemical engineering route. For the described *pCat-PECF₃-PENMe₂*, a low efficiency, red-shifted bent-conjugated charge-transfer has been identified. As far as molecular polarizability is concerned, it has been shown that a fine-tuning optical properties of such molecules was possible following an optical property–structure correlation. After removal of the silyl-protecting groups, the use of this compound as ligands within complexes is currently under investigation and should lead to multifunctional coordination complexes, merging magnetic and optical properties. In the light of the chelating ability of such motif, one can anticipate low-energy metal-to-ligand and ligand-to-metal charge-transfers and efficient related nonlinear optical properties such as two-photon absorption (TPA) and related applications [14].

4. Experimental

General: All reactions were performed under anaerobic conditions in an inert atmosphere of argon using standard Schlenk-line techniques. All reagents and 4-ethynyltrifluorotoluene were purchased from commercial sources and used as received. *pCat-I-PENMe₂* was prepared according to literature procedures [13].

Instrumentation: ¹H and ¹³C NMR spectra were recorded with a Bruker AC 200 FT NMR spectrometer. Elemental analyses were obtained from the “Service Central d’Analyse de Vernaison - CNRS”. Infrared spectra were recorded in the range of 4000–200 cm⁻¹ as KBr pellets with a Mattson 3000 spectrometer. UV/vis spectra were recorded with a Jasco V-670 spectrometer using spectro-grade solvents. The steady-state emission spectra were recorded on a Photon Technology International (PTI) SE-900M spectrofluorimeter. Emission quantum yields Φ_L were determined at 25 °C in deoxygenated acetonitrile after irradiation at 335 nm and using an EtOH solution of anthracene ($\Phi_L^{Ref} = 0.27$) as a standard, according to:

$$\Phi_L^S = \frac{I_L^S(1 - 10^{-OD^{Ref}})}{I_L^{Ref}(1 - 10^{-OD^S})} \frac{n_S^2}{n_{Ref}^2} \Phi_L^{Ref}$$

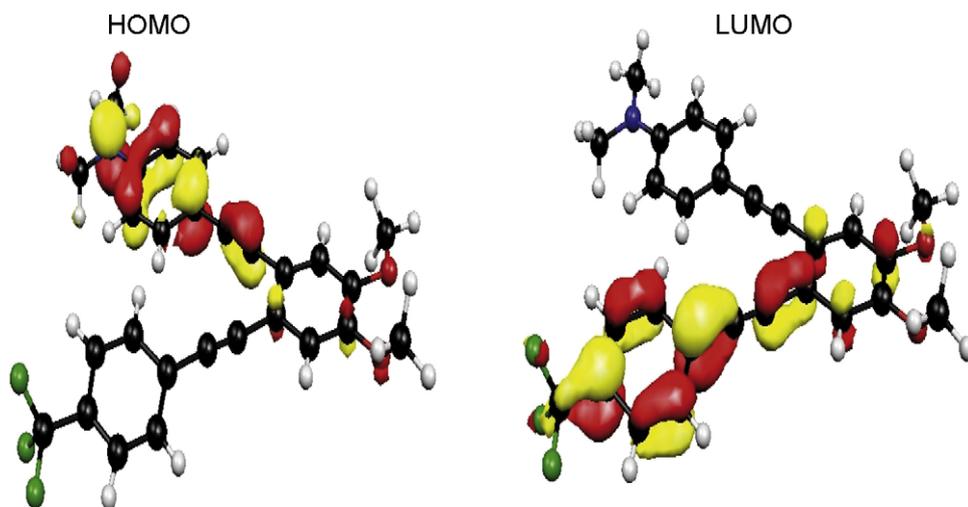


Fig. 8. HOMO and LUMO valence molecular orbital plots for compound *pCat-PECF₃-PENMe₂*.

where I_L , the emission intensity, was calculated from the spectrum area $\int I(l) dl$, OD represents the optical density at the excitation wavelength. The superscripts “S” and “Ref” refer to the sample and the standard, respectively. n is the refractive index of the solvents. The time-dependent emission experiments were performed in deoxygenated acetonitrile after excitation at $\lambda = 400$ nm obtained by the second harmonic of a Titanium: Sapphire laser (picosecond Tsunami laser spectra physics 3950-M1BB) at an 8 MHz repetition rate. Fluotime 200 from AMS technologies is used for decay acquisition. It consists of a GaAs micro-channel plate photomultiplier tube (Hamamatsu model R3809U-50) followed by a time-correlated single photon counting system from picoquant (PicoHarp300). The ultimate time resolution of the system was close to 40 ps. These measurements were recorded using the technical support from the chemistry platform “NanoBio campus” in Grenoble (France).

1,2-Bis(tert-butyl dimethylsilyloxy)-4-[2-(4-ethynylphenyl)dimethylamine],5-[2-[4-(trifluoromethyl)phenyl]ethynyl]benzene (pCat-PECF₃-PENMe₂): To a mixture of *pCat-I-PENMe₂* (330 mg, 0.54 mmol) in THF (20 mL) and Et₃N (10 mL) was added (PPh₃)₂PdCl₂ (19 mg, 0.03 mmol), CuI (10 mg, 0.05 mmol) and 4-ethynyltrifluorotoluene (0.1 mL, 0.61 mmol). The black solution was stirred during 3.5 h at 40 °C. After cooling to room temperature, the solvent was evaporated under vacuum. The remaining black solid was dissolved in CH₂Cl₂ (100 mL) and washed with 100 mL of a saturated solution of NH₄Cl in water. The organic layer was dried with MgSO₄ then, after filtration and evaporation of the solvent, the crude material was purified by flash chromatography on silica gel (CH₂Cl₂/petroleum ether, 1/3) to give 200 mg of a brown solid (57% yield). ¹H NMR (200 MHz, CDCl₃, 300 K): δ (ppm): 7.62 (m, 4H, H₁₀ and H_{10'}), 7.42 (d, 2H, ³J = 8.8 Hz, H_{11'}), 7.00 (s, 2H, H₃ and H₆), 6.66 (d, 2H, ³J = 8.8 Hz, H₁₁), 3.00 (s, 6H, NMe₂), 1.01 (s, 18H, ⁴BuSi), 0.26 (s, 12H, Me₂Si). ¹³C NMR (50 MHz, CDCl₃, 300 K): δ (ppm): 150.17, 148.08, 146.94, 132.64, 131.70, 125.26 (CF₃), 124.04 (C₆), 123.78 (C₃), 111.87, 110.20, 93.67, 91.29, 85.98, 40.22, 25.92, 18.51, -4.05. C₃₇H₄₆F₃NO₂Si₂, 0.3 CH₂Cl₂: calcd. C 66.4, H 6.9, N 2.1; found C 66.6, H 6.9, N 2.1. High resolution mass for C₃₇H₄₆F₃NO₂Si₂H⁺: 650.3 g mol⁻¹.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2010.02.012.

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