RESEARCH FRONT

CSIRO PUBLISHING

Full Paper

www.publish.csiro.au/journals/ajc

*Aust. J. Chem.* **2011**, *64*, 153–159

# Photo-induced Energy Transfer in a $T_h$-Symmetrical Hexakis-adduct of $C_{60}$ Substituted with π-Conjugated Oligomers

*Julien Iehl,[A] Michel Holler,[A] Jean-François Nierengarten,[A,E] K. Yoosaf,[B]*
*Joanna M. Malicka,[B] Nicola Armaroli,[B,E] Jean-Marc Strub,[C]*
*Alain Van Dorsselaer,[C,E] and Béatrice Delavaux-Nicot[D,E]*

[A]Laboratoire de Chimie des Matériaux Moléculaires, Université de Strasbourg et CNRS (UMR 7509), Ecole Européenne de Chimie, Polymères et Matériaux (ECPM), 25 rue Becquerel, 67087 Strasbourg Cedex 2, France.

[B]Molecular Photoscience Group, Istituto per la Sintesi Organica e la Fotoreattività (ISOF), Consiglio Nazionale delle Ricerche (CNR), via P. Gobetti 101, 40129 Bologna, Italy.

[C]Laboratoire de Spectrométrie de Masse Bio-organique, Institut Pluridisciplinaire Hubert Curien (IPHC), Ecole Européenne de Chimie, Polymères et Matériaux (ECPM), Université de Strasbourg et CNRS (UMR 7178), 25 rue Becquerel, 67087 Strasbourg Cedex 2, France.

[D]Laboratoire de Chimie de Coordination (LCC), CNRS, Université de Toulouse (UPS, INP), 205 route de Narbonne, 31077 Toulouse Cedex 4, France.

[E]Corresponding authors. Email: nierengarten@chimie.u-strasbg.fr, armaroli@isof.cnr.it, vandors@chimie.u-strasbg.fr, Beatrice.Delavaux-Nicot@lcc-toulouse.fr

A stilbene derivative bearing a terminal alkyne unit has been prepared and grafted onto a $T_h$-symmetrical $C_{60}$ hexakis-adduct building block under alkyne/azide copper mediated Huisgen 1,3-dipolar cycloaddition conditions. The photophysical properties of the resulting fullerene derivative surrounded by 12 conjugated oligomers have been investigated. Upon excitation of the peripheral chromophores, an efficient intramolecular energy transfer to the $C_{60}$ core has been evidenced.

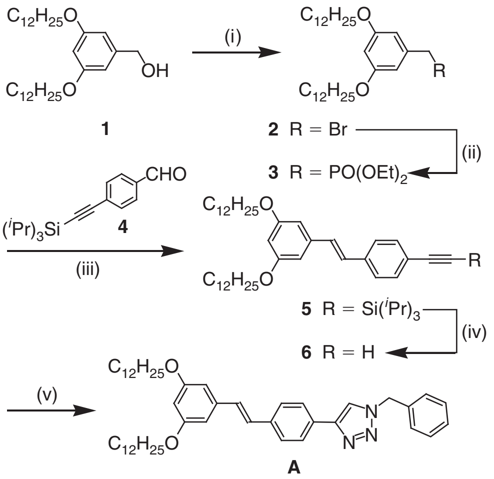
Manuscript received: 30 August 2010.
Manuscript accepted: 15 October 2010.

## Introduction

Fullerene-based photoactive molecular devices resulting from the conjugation of energy and/or electron donors with $C_{60}$ have received considerable attention in the past decade.[1] Whereas most of the hybrid compounds described so far have been constructed with mono- and bis-functionalized fullerene derivatives, related photoactive systems based on $T_h$-symmetrical hexakis-adducts of $C_{60}$ have been much scarcely considered.[2,3] This is mainly related with the difficulties associated to the synthesis of such fullerene derivatives.[4,5] The $T_h$-symmetrical octahedral addition pattern of fullerene hexakis-adducts is however attractive for the preparation of unique photoactive systems. On the one hand, its unique three-dimensional compact structure allows for the design of molecular systems with multiple copies of chromophores in a restricted space. However, the hexa-substituted fullerene core is still an excellent energy acceptor despite the high degree of addition on the $C_{60}$ framework.[2] Therefore, fullerene hexakis-adducts are potentially interesting building blocks for the preparation of light-harvesting devices.[6,7]

Fullerene hexakis-adducts are typically prepared by the one-pot reaction of $C_{60}$ with malonates under conditions initially developed by Hirsch[4] and further improved by Sun.[5] These reaction conditions are efficient when starting from relatively simple malonates but structurally more complicated hexakis-adducts are generally obtained in very low yields. Indeed, the synthesis of functionalized fullerene hexakis-adduct derivatives from the corresponding malonates is difficult, thus limiting their accessibility and therefore their applications. As part of this research, we have recently developed efficient synthetic methodologies for the preparation of structurally complex hexa-substituted fullerene derivatives.[8] They are based on the post-functionalization of easily accessible fullerene hexakis-adduct building blocks.[8–10] For this purpose, the copper mediated Huisgen 1,3-dipolar cycloaddition of azides with alkynes resulting in 1,2,3-triazoles[11] was found to be a particularly interesting tool, as it allows for the incorporation of almost any functional groups around the fullerene core. For example, fullerene hexakis-adducts bearing peripheral sugar moieties have been easily prepared by grafting unprotected

10.1071/CH10319 0004-9425/11/020153



**Scheme 1.** Reagents and conditions: (i) TMSBr, $CHCl_3$, 0°C; (ii) $P(OEt)_3$, 150°C; (iii) *t*-BuOK, THF, 0 to 25°C; (iv) TBAF, THF, 0°C; (v) benzyl azide, $CuSO_4{\cdot}5H_2O$, sodium ascorbate, $CH_2Cl_2/H_2O$, 25°C.

sugar derivatives onto the fullerene core.[12] In this paper, we now show that this synthetic approach is perfectly suited for the synthesis of photoactive fullerene hexa-adducts. In particular, 12 conjugated oligomers have been attached to the $C_{60}$ core leading to a molecular device with light harvesting properties.

## Results and Discussion

### Synthesis

The preparation of the clickable stilbene building block **6** is depicted in Scheme 1. Compound **1** was obtained by alkylation of 3,5-dihydroxybenzyl alcohol with 1-bromododecane ($K_2CO_3$, DMF, 60°C).[13] The reaction of **1** with trimethylsilyl bromide in $CHCl_3$ followed by treatment of the resulting bromide **2** with $P(OEt)_3$ under Arbuzov conditions then gave phosphonate **3**.[14] Subsequent reaction of **3** with aldehyde **4**[15] in the presence of *t*-BuOK in THF afforded *E*-stilbene **5** in 83% yield. The Wadsworth–Emmons reaction is actually a powerful tool for the synthesis of *E*-stilbene derivatives as the *trans* olefines are selectively produced from benzylic phosphonates.[16] Indeed, the *E* stereochemistry of the double bond in stilbene **5** is confirmed by the coupling constant of ~16 Hz for the AB system corresponding to the vinylic protons in its $^1$H-NMR spectrum. Finally, treatment of **5** with tetra-*n*-butylammonium fluoride (TBAF) in THF gave terminal alkyne **6** in 86% yield. Inspection of the $^1$H NMR spectrum of **6** clearly indicates the disappearance of the TIPS-protecting group and shows the typical signal corresponding to the terminal alkyne proton at $\delta$ 3.14 ppm.

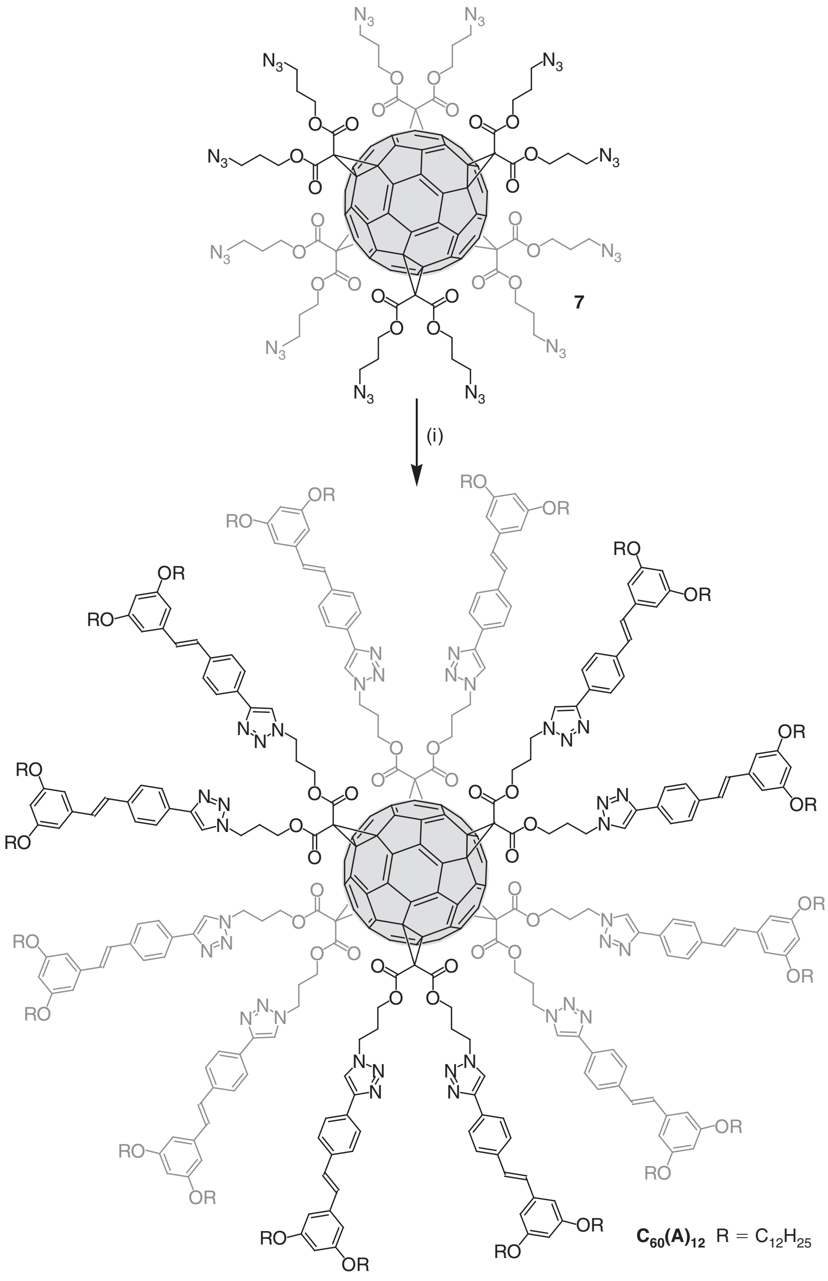
Compound **6** was then grafted on the polyazide derivative **7** (Scheme 2). Compound **7** was prepared as previously reported.[8] Owing to its high number of azide residues, this compound must be handled with special care. Upon evaporation, compound **7** has never been dried under high vacuum and the use of metallic spatula avoided. Furthermore, this compound has been always prepared on a small scale (less than 500 mg). It can also be noted that compound **7** cannot be stored as slow decomposition into insoluble polymers occurs even in solution. The latter observation is most probably the result of the slow thermolysis or photolysis of azide groups; the nitrene residues thus generated are then responsible of the intermolecular reactions leading to polymers. Upon purification, it is best to use polyazide **7** for the click reactions within the next 24 h in order to obtain good yields. A mixture of freshly prepared **7** (1 equiv.), **6** (13 equiv.), $CuSO_4{\cdot}5H_2O$ (0.1 equiv.), and sodium ascorbate (0.3 equiv.) in $CH_2Cl_2/H_2O$ was vigorously stirred at room temperature for 12 h. After workup and purification, compound $\mathbf{C_{60}(A)_{12}}$ was thus obtained in 62% yield. In addition, compound **A**, which was used as reference compound for the electrochemical and photophysical studies, was prepared under similar conditions from benzyl azide and **6** (Scheme 1).

The structure of compounds **A** and $\mathbf{C_{60}(A)_{12}}$ was confirmed by analytical and spectroscopic data. In the $^{13}$C NMR spectra of both **A** and $\mathbf{C_{60}(A)_{12}}$, the typical signal of the sp$^2$ C atoms of the 1,2,3-triazole units[8] are detected around $\delta = 121$ and 147 ppm. The $^{13}$C NMR spectrum of fullerene hexakis-adduct $\mathbf{C_{60}(A)_{12}}$ is also in full agreement with its $T_h$-symmetrical structure and shows the expected signals for the six equivalent malonate addends. Furthermore, the three expected resonances[4,8] for the C atoms of the fullerene core are clearly observed ($\delta =$ 69.1 ppm for the sp$^3$ C atom; $\delta = 141.2$ and 145.8 ppm for the sp$^2$ C atoms). The matrix-assisted laser desorpton–ionization time-of-flight (MALDI-TOF) mass spectrum of $\mathbf{C_{60}(A)_{12}}$ is depicted in Fig. 1. The analysis of lipophilic compounds of high molecular weight such as $\mathbf{C_{60}(A)_{12}}$ is generally rather difficult due to aggregation. Furthermore, a high degree of fragmentation may prevent the observation of the expected molecular ion peak.[12] In the case of $\mathbf{C_{60}(A)_{12}}$, the expected molecular ion peak $[M+H]^+$ could be evidenced despite a high level of fragmentation. A series of typical fragments resulting from successive retro-cycloaddition reactions are observed ($[M+H-(C_{40}H_{60}O_2)_n]^+$, with $n = 1$ to 6). This fragmentation pathway is indeed classical for 1,2,3-triazole derivatives.[17] It is also worth noting that additional peaks are associated with the ones corresponding to $[M+H-(C_{40}H_{60}O_2)_n]^+$. In particular, fragments with additional loss of one or two $N_2$ residues are systematically observed as well as the sodium or potassium adducts. Finally, the retro-cycloaddition observed for $\mathbf{C_{60}(A)_{12}}$ has also been evidenced in the MALDI-TOF mass spectrum recorded for **A**. In addition to the expected molecular ion peak observed at $m/z = 706.5$, a peak is also seen at $m/z = 572$. The latter corresponds to the product of retro-cycloaddition after loss of the $PhCH_2N_3$ subunit.

In the case of $\mathbf{C_{60}(A)_{12}}$, the high level of fragmentation observed in its MALDI-TOF spectrum prevented any definitive conclusions about the monodispersity of the isolated product. In contrast, IR data confirmed that no azide (2092 cm$^{-1}$) residues remain in the final product and thus allowed us to conclude that no defected by-products are present. This was further confirmed by the stability of the prepared compound. Effectively, we have systematically observed a slow polymerization when unreacted azide subunits were still present in products prepared from **7** and alkynes. Actually, as soon as the IR spectra of the cycloaddition product revealed minor traces of azide groups (typical signal observed at ~2092 cm$^{-1}$), the material became completely insoluble after a few days of storage as in the case of building block **7** (see below).

### Electrochemistry

The electrochemical properties of $\mathbf{C_{60}(A)_{12}}$ and **A** were determined by cyclic voltammetry (CV) and Osteryoung Square Wave Voltammetry (OSWV). All the experiments were performed at room temperature in $CH_2Cl_2$ solutions containing tetra-*n*-butylammonium tetrafluoroborate (0.1 M) as supporting



**7**

**$C_{60}(A)_{12}$** R = $C_{12}H_{25}$

**Scheme 2.** Reagents and conditions: (i) **6**, $CuSO_4{\cdot}5H_2O$, sodium ascorbate, $CH_2Cl_2/H_2O$, 25°C.

electrolyte and ferrocene (Fc) as internal reference, with a Pt wire as the working electrode and a saturated calomel electrode (SCE) as a reference. Potential data for all of the compounds are collected in Table 1.

In the anodic scan, compound **A** exhibits two irreversible oxidation processes at +1.46 and +1.66 V versus SCE. Owing to its first oxidation potential, **A** appears to be a quite weak electron donor. While CV experiments were unable to detect any reduction process for **A**, OSWV revealed such a process easily at a quite high potential (−2.12 V versus SCE). In the anodic region, compound **$C_{60}(A)_{12}$** presents an irreversible peak at +1.50 V versus SCE, which can be likely attributed to the oxidation of the peripheral subunits. Under our experimental conditions, the second oxidation observed for model compound **A** could not be clearly observed for **$C_{60}(A)_{12}$**. The irreversible cathodic process seen at −1.56 V versus SCE for **$C_{60}(A)_{12}$** corresponds to a fullerene-centred process. As already shown for related hexa-substituted $C_{60}$ derivatives,[18] the high degree of addition on the fullerene cage significantly increases its LUMO energy level thus making the reduction more difficult when compared with related mono-functionalized fullerenes for which the first reduction is generally observed at −0.5 to −0.6 V versus SCE under the same experimental conditions.[19] Finally, the reduction observed in OSWV for model compound **A** is also evidenced for **$C_{60}(A)_{12}$**.

### *Photophysics*

The ground state absorption spectra of hexakis-adduct **$C_{60}(A)_{12}$** and its model compounds **A** and **$C_{60}(Ph)_{12}$**[8] in $CH_2Cl_2$ are shown in Fig. 2. The fullerene hexakis-adduct **$C_{60}(Ph)_{12}$** shows extensive absorption in the UV-Vis region and model

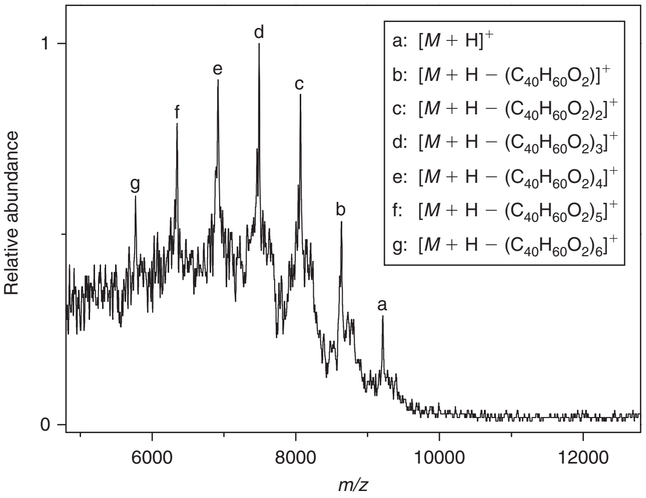


**Fig. 1.** MALDI-TOF mass spectrum of compound $\mathbf{C_{60}(A)_{12}}$ recorded in the positive mode showing the expected molecular ion peak as well as fragments resulting from successive retro-cycloaddition reactions ($[M + H - (C_{40}H_{60}O_2)_n]^+$, with n = 1 to 6).

**Table 1. Electrochemical data of A and $\mathbf{C_{60}(A)_{12}}$ determined by Osteryoung Square Wave Voltammetry (OSWV) on a Pt working electrode in $\mathbf{CH_2Cl_2 + 0.1\,M}$ $\mathbf{\textit{n}Bu_4NBF_4}$ at room temperature in the presence of ferrocene used as internal reference**[A,B]

| | Oxidation | | Reduction | |
|---|---|---|---|---|
| | $E_2$ | $E_1$ | $E_1$ | $E_2$ |
| **A** | +1.66 | +1.46 | −2.12 | |
| $\mathbf{C_{60}(A)_{12}}$ | | +1.50 | −1.56 | −2.06 |

[A] OSWV were obtained using a sweep width of 20 mV, a frequency of 10 Hz, and a step potential of 5 mV.

[B] Redox potential values in V versus SCE ($Fc^+/Fc$ is observed at +0.55 ± 0.01 V).

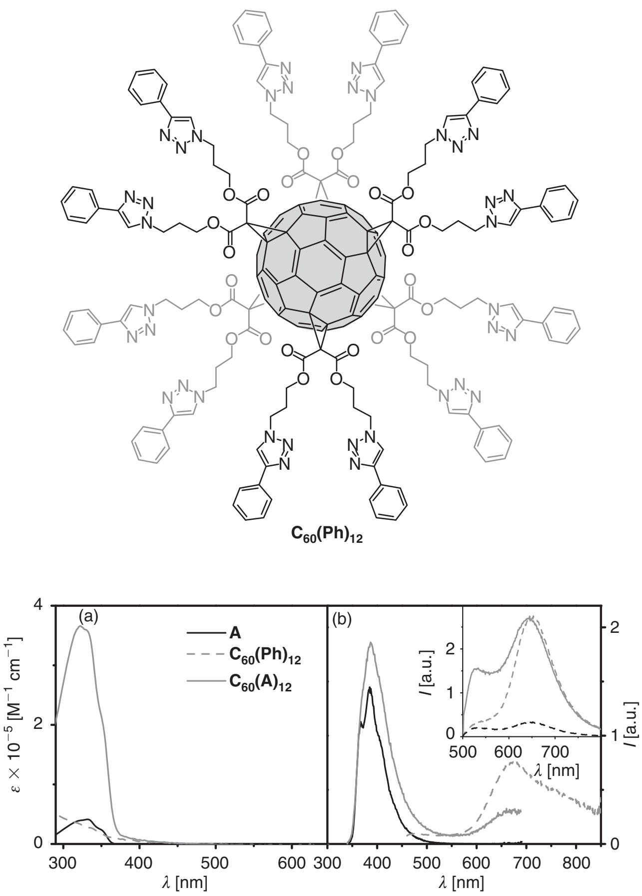


**Fig. 2.** Top: model compound $\mathbf{C_{60}(Ph)_{12}}$. Bottom: absorption (a) and emission (b) spectra of (**A**) (black), $\mathbf{C_{60}(A)_{12}}$ (grey), and $\mathbf{C_{60}(Ph)_{12}}$ (dashed grey) in $CH_2Cl_2$. Inset shows the comparison of emission spectra collected after keeping a cut-off filter at 550 nm of $\mathbf{C_{60}(A)_{12}}$ (grey) with that of $\mathbf{C_{60}(Ph)_{12}}$ having same (i) optical density at 335 nm (dashed grey) and (ii) concentration (dashed black) as that of $\mathbf{C_{60}(A)_{12}}$. Emission spectra were collected upon excitation at 335 nm.

**Table 2. Fluorescence properties of compounds A, $\mathbf{C_{60}(Ph)_{12}}$, and $\mathbf{C_{60}(A)_{12}}$ in $\mathbf{CH_2Cl_2}$**

| | $\lambda_{max}$ [nm] | $\Phi_{fl}$ | $\tau_{fl}$ [ns] |
|---|---|---|---|
| **A** | 385 | 0.4 | 1 |
| $\mathbf{C_{60}(Ph)_{12}}$ | 670 | 0.0002 | 2.7 |
| $\mathbf{C_{60}(A)_{12}}$ | 388, 670 | 0.001 (388 nm)[A]<br>0.0002 (670 nm) | 2[B] |

[A] Residual emission from the appended conjugated oligomer fragments.

[B] Determined for the emission at 670 nm after keeping a cut-off filter at 550 nm.

compound **A** has an intense absorption centred at 335 nm. Compound $\mathbf{C_{60}(A)_{12}}$ exhibits a molar absorptivity as high as 295000 $M^{-1}\,cm^{-1}$ at 335 nm owing to the presence of 12 **A** units around the central fullerene core. The emission spectra of the compounds **A**, $\mathbf{C_{60}(Ph)_{12}}$, and $\mathbf{C_{60}(A)_{12}}$ are depicted in Fig. 2, the related photophysical parameters are summarized in Table 2.

Model compound **A** is a strong fluorophore with an emission maximum around 385 nm ($\Phi_{em} = 0.4$; $\tau = 1.0$ ns). The fullerene reference compound $\mathbf{C_{60}(Ph)_{12}}$ shows a very weak fluorescence band centred around 670 nm ($\Phi_{em} = 0.0002$; $\tau = 1.7$ ns). The fluorescence spectra of model compounds recorded at 77 K ($CH_2Cl_2$) are depicted in Fig. 3. Notably, the low temperature spectrum of **A** shows a shift towards lower energy ($\lambda_{max} =$ 425 nm) as compared with 298 K. This unusual temperature trend in the fluorescence spectra is probably related to the presence of a wide range of conformers in the rigid matrix within **A** structures,[13] with emission observed predominantly from the lowest energy conformer. On the contrary, model compound $\mathbf{C_{60}(Ph)_{12}}$ showed a shift of 30 nm towards the higher energy side ($\lambda_{max} = 640$ nm).

Upon excitation of $\mathbf{C_{60}(A)_{12}}$ at 335 nm, more than 90% of the light is absorbed by the peripheral **A** subunits. The **A**-centred fluorescence intensity of $\mathbf{C_{60}(A)_{12}}$ is indeed dramatically quenched when compared with **A** (three orders of magnitude lower, Table 2) while, at the same time, a broad band above 600 nm is clearly observable. This band was further characterized by recording the emission spectrum with a cut-off filter at 550 nm and compared with that of a model compound $\mathbf{C_{60}(Ph)_{12}}$ having the same optical density at the exciting wavelength and recorded under identical conditions (Fig. 2). Notably, both samples exhibit quite similar emission profiles and comparable intensity, which is one order of magnitude higher than that of the model compound having the same concentration as that of $\mathbf{C_{60}(A)_{12}}$. These observations are consistent with the occurrence of a virtually quantitative **A** → $C_{60}$ singlet energy transfer process via the Förster mechanism, since the fluorescence

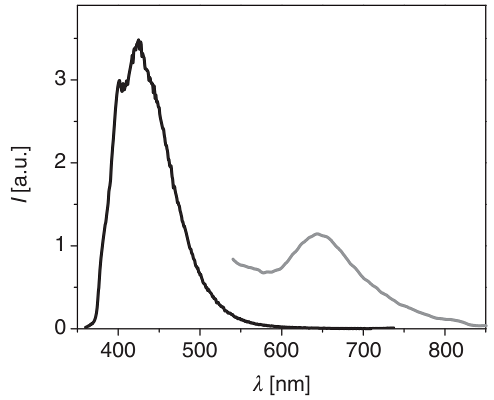


**Fig. 3.** Emission spectra of **A** (black) and $\mathbf{C_{60}(Ph)_{12}}$ (grey) in $CH_2Cl_2$ at 77 K collected after exciting at 325 nm.

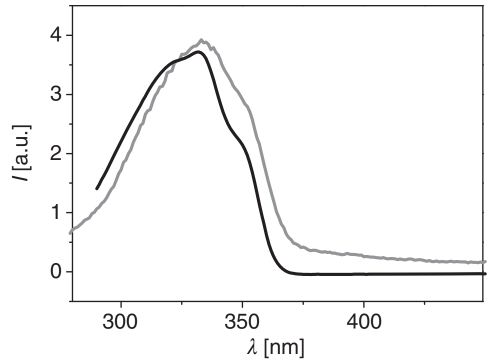


**Fig. 4.** Absorption spectrum of **A** (black) and excitation spectrum $\mathbf{C_{60}(A)_{12}}$ (grey; $\lambda_{em} = 670$ nm and cut-off filter 515 nm) in $CH_2Cl_2$.

profile of **A** (350–500 nm) overlaps with the absorption tail of the fullerene hexa-adduct core. This energy transfer mechanism was further supported by recording the excitation spectrum for $\mathbf{C_{60}(A)_{12}}$ at $\lambda_{em} = 670$ nm, which exactly matches with the absorption spectrum of model compound **A** (Fig. 4).

## Conclusion

The post-functionalization of a $T_h$-symmetric fullerene hexakis-adduct building block is a powerful synthetic strategy for the preparation of fullerene hexakis-adduct derivatives with peripheral functional groups. In this paper, we have shown that 12 π-conjugated oligomers can be efficiently grafted onto a hexa-substituted fullerene core to give core-shell ensemble $\mathbf{C_{60}(A)_{12}}$. The photophysical studies of $\mathbf{C_{60}(A)_{12}}$ revealed an efficient intramolecular energy transfer upon excitation of the peripheral chromophores. Compound $\mathbf{C_{60}(A)_{12}}$ is indeed an efficient light-harvesting device capable of channelling the light energy from the periphery to the core by efficient singlet-singlet energy transfer. This first system paves the way towards more elaborated photoactive devices in which a potent electron donating group is additionally incorporated to the system, thus allowing an electron transfer upon the initial energy transduction event to the $C_{60}$ core. This should be easily achieved by using the recently reported[9] fullerene hexakis-adduct building blocks incorporating complementary reactive centres, thus allowing the successive grafting of different functional groups. Work in this direction is currently under way in our laboratories.

## Experimental

NMR spectra were recorded on a Bruker AM 300 (300 MHz); chemical shifts ($\delta$) are reported in ppm using the solvent signal as reference and coupling constants ($J$) are given in Hz. MALDI-TOF-MS were obtained on a Bruker ULTRAFLEX TOF/TOF mass spectrometer with a dithranol matrix. Elemental analysis were performed by the analytical service at the Laboratoire de Chimie de Coordination (Toulouse, France). All reagents were used as purchased from commercial sources without further purification. Compounds **3**,[14] **4**,[15] $\mathbf{C_{60}(Ph)_{12}}$,[8] and **7**[8] were prepared according to previously reported procedures. Solvents were dried using standard techniques before use. All reactions were performed in standard glassware. Evaporation was achieved using water aspirator and drying under vacuum at $10^{-2}$ Torr. Column chromatography: silica gel 60 (230–400 mesh, 0.040–0.063 mm) was purchased from E. Merck. TLC: Precoated glass sheets with silica gel 60 $F_{254}$ (Merck), visualization by UV light. Gel permeation chromatography (GPC) was performed on Biorad, Biobeads SX-1 under the use of $CH_2Cl_2$ as eluent.

### *Compound* 5

*t*-BuOK (430 mg, 3.84 mmol) was added to a stirred solution of **3** (2.29 g, 3.84 mmol) and **4** (1.00 g, 3.49 mmol) in THF (300 mL) at 0°C. After 1 h, the mixture was allowed to slowly warm to room temperature (within 1 h), then stirred for 2 h, filtered, and evaporated. The residue was taken up with $CH_2Cl_2$, washed with $H_2O$, dried ($MgSO_4$), filtered, and evaporated. Column chromatography ($SiO_2$, cyclohexane/$CH_2Cl_2$ 9:1) yielded **5** (2.10 g, 83%) as a colourless glassy product. $\delta_H$ ($CDCl_3$) 0.89 (t, $J$ 7, 6H), 1.14 (m, 21H), 1.20–1.46 (m, 36H), 1.79 (m, 4H), 3.97 (t, $J$ 7, 4H), 6.40 (t, $J$ 2, 1H), 6.66 (d, $J$ 2, 2H), 7.03 (AB, $J$ 16, 2H), 7.43 (d, $J$ 7, 2H), 7.46 (d, $J$ 7, 2H). $\delta_C$ ($CDCl_3$) 11.3, 14.1, 18.7, 22.7, 26.1, 26.9, 29.3, 29.4, 29.45, 29.6, 29.65, 29.7, 31.9, 68.1, 91.5, 101.2, 105.2, 107.2, 122.6, 126.2, 128.2, 129.7, 132.3, 137.2, 138.9, 160.5. Anal. Calc. for $C_{49}H_{80}O_2Si$: C 80.70, H 11.06. Found: C 80.62, H 11.25%.

### *Compound* 6

A 1 M TBAF solution in THF (2.8 mL) was added to a stirred solution of **5** (2.00 g, 2.74 mmol) in dry THF (250 mL) at 0°C under argon. After 1 h, the mixture was allowed to slowly warm to room temperature (within 1 h), then stirred for 14 h and $H_2O$ (10 mL) was added. The THF was evaporated and $CH_2Cl_2$ added. The organic layer was washed with $H_2O$, dried ($MgSO_4$), and evaporated. Column chromatography ($SiO_2$, cyclohexane/$CH_2Cl_2$ 9:1) yielded **6** (1.36 g, 86%) as a colourless glassy product. $\delta_H$ ($CDCl_3$) 0.90 (t, $J$ 7, 6H), 1.20–1.50 (m, 36H), 1.80 (m, 4H), 3.14 (s, 1H), 3.98 (t, $J$ 7, 4H), 6.42 (t, $J$ 2, 1H), 6.66 (d, $J$ 2, 2H), 7.04 (AB, $J$ 16, 2H), 7.44 (d, $J$ 7, 2H), 7.48 (d, $J$ 7, 2H). $\delta_C$ ($CDCl_3$) 14.1, 22.7, 26.1, 26.9, 29.3, 29.4, 29.45, 29.55, 29.6, 29.65, 29.7, 30.2, 31.9, 68.1, 77.9, 83.7, 101.2, 105.2, 121.0, 126.3, 128.0, 130.0, 132.4, 137.2, 138.8, 160.5. Anal. Calc. for $C_{40}H_{60}O_2$: C 83.86, H 10.56. Found: C 83.65, H 10.39%.

### *Compound* A

$CuSO_4{\cdot}5H_2O$ (3 mg, 0.02 mmol) was added to a mixture of **6** (100 mg, 0.175 mmol), benzyl azide (70 mg, 0.52 mmol), and sodium ascorbate (10 mg, 0.05 mmol) in $CH_2Cl_2/H_2O$ (1:1, 6 mL) at room temperature. The reaction mixture was stirred for 18 h. The organic layer was diluted with $CH_2Cl_2$, washed with water, dried ($Na_2SO_4$), filtered, and concentrated. Column chromatography ($SiO_2$, $CH_2Cl_2$) gave **A** (102 mg, 83%). $\delta_H$ ($CDCl_3$) 0.88 (t, *J* 7, 6H), 1.20–1.50 (m, 36H), 1.80 (m, 4H), 3.97 (t, *J* 7, 4H), 5.58 (s, 2H), 6.39 (t, *J* 2, 1H), 6.66 (d, *J* 2, 2H), 7.06 (AB, *J* 16, 2H), 7.30–7.45 (m, 5H), 7.54 (d, *J* 8, 2H), 7.67 (s, 1H), 7.79 (d, *J* 8, 2H). $\delta_C$ ($CDCl_3$) 14.1, 22.7, 26.1, 29.3, 29.35, 29.4, 29.55, 29.6, 29.65, 29.7, 31.9, 54.3, 68.1, 101.1, 105.1, 119.4, 125.9, 127.0, 128.1, 128.4, 128.8, 129.1, 129.2, 129.7, 134.6, 137.1, 139.1, 160.5. *m/z* 706.5 ($[M+H]^+$, 100%), 679 ($[M+H-N_2]^+$, 10), 586 ($[M+H-PhCH_2N_2]^+$, 2), 572 ($[M+H-PhCH_2N_3]^+$, 2). Anal. Calc. for $C_{47}H_{67}N_3O_2$: C 79.95, H 9.56, N 5.95. Found: C 79.57, H 9.52, N 5.89%.

### Compound $C_{60}(A)_{12}$

$CuSO_4{\cdot}5H_2O$ (2 mg, 0.011 mmol) was added to a mixture of **6** (831 mg, 1.451 mmol), **7** (260 mg, 0.111 mmol), and sodium ascorbate (7 mg, 0.033 mmol) in $CH_2Cl_2/H_2O$ (1:1, 6 mL) at room temperature. The reaction mixture was stirred for 48 h. The organic layer was diluted with $CH_2Cl_2$, washed with water, dried ($Na_2SO_4$), filtered, and concentrated. Column chromatography ($SiO_2$, $CH_2Cl_2$/MeOH 99:1) followed by GPC gave **$C_{60}(A)_{12}$** (640 mg, 62%). $\delta_H$ ($CDCl_3$) 0.89 (t, *J* 7, 72H), 1.20–1.50 (m, 432H), 1.66–1.85 (m, 48H), 2.37 (m, 24H), 3.93 (t, *J* 7, 48H), 4.40 (m, 48H), 6.38 (broad t, *J* 2, 12H), 6.62 (broad d, *J* 2, 24H), 7.00 (broad s, 24H), 7.45 (broad d, *J* 7, 24H), 7.75 (m, 36H). $\delta_C$ ($CDCl_3$) 14.0, 22.6, 26.0, 27.3, 28.9, 29.3, 29.4, 29.6, 29.65, 31.9, 45.4, 47.8, 63.7, 68.0, 69.1, 101.0, 105.0, 120.0, 125.9, 127.0, 128.2, 129.1, 129.4, 137.1, 138.9, 141.2, 145.8, 147.5, 160.4, 163.4. $\nu_{max}/cm^{-1}$ 1744 (C=O). *m/z* 9206 ($[M+H]^+$, 27%), 8633 ($[M+H-(C_{40}H_{60}O_2)_1]^+$, 52), 8060 ($[M+H-(C_{40}H_{60}O_2)_2]^+$, 83), 7488 ($[M+H-(C_{40}H_{60}O_2)_3]^+$, 100), 6915 ($[M+H-(C_{40}H_{60}O_2)_4]^+$, 90), 6342 ($[M+H-(C_{40}H_{60}O_2)_5]^+$, 75), and 5769 ($[M+H-(C_{40}H_{60}O_2)_6]^+$, 60). Anal. Calc for $C_{594}H_{792}N_{36}O_{48}$: C 77.51, H 8.67, N 5.48. Found: C 77.82, H 8.59, N 5.40%.

### Electrochemistry

The CV measurements were carried out with a potentiostat Autolab PGSTAT100. Experiments were performed at room temperature in a homemade airtight three-electrode cell connected to a vacuum/argon line. The reference electrode consisted of a SCE separated from the solution by a bridge compartment. The counter electrode was a platinum wire of $\sim 1\ cm^2$ apparent surface. The working electrode was a Pt microdisk (0.5 mm diameter). The supporting electrolyte $[nBu_4N][BF_4]$ (Fluka, 99% electrochemical grade) was used as received and simply degassed under argon. Dichloromethane was freshly distilled over $CaH_2$ before use. The solutions used during the electrochemical studies were typically $10^{-3}$ M for the compound and 0.1 M for the supporting electrolyte. Before each measurement, the solutions were degassed with bubbling Ar and the working electrode was polished with a polishing machine (Presi P230). Under these experimental conditions, $Fc^+/Fc$ is observed at $+0.55 \pm 0.01$ V.

### Photophysics

The photophysical studies were carried out in dichloromethane (Carlo Erba, spectrofluorimetric grade). Absorption spectra were recorded with a Perkin–Elmer Lambda 950 UV/vis/NIR spectrophotometer. Molar absorption values ($\varepsilon$) were calculated by applying the Lambert–Beer law to the absorbance spectra ($A_{max} < 0.7$) of the compounds.

Steady-state photoluminescence spectra were recorded in right angle mode with an Edinburgh FLS920 spectrometer (continuous 450 W Xe lamp), equipped with a Peltier-cooled Hamamatsu R928 photomultiplier tube (185–850 nm). The concentration of air-equilibrated sample solutions was adjusted to obtain absorption values $A < 0.15$ at the excitation wavelength. Emission quantum yields were determined according to the approach described by Demas and Crosby,[20] using Quinine sulfate ($\Phi_{em} = 0.546$ in air-equilibrated acid water solution, 1 N $H_2SO_4$) and $[Ru(bpy)_3Cl_2]$ ($\Phi_{em} = 0.028$ in air-equilibrated water solution)[21] as standards. One cm path length square optical Suprasil Quartz (QS) cuvettes were used for measurements at RT of dilute solutions, while capillary tubes immersed in liquid nitrogen in a coldfinger quartz Dewar were used for measurements of solvent frozen glasses at 77 K.

Fluorescence lifetimes were measured with an IBH 5000F time-correlated single-photon counting device, by using pulsed NanoLED excitation source at 331 nm. Analysis of the luminescence decay profiles against time was accomplished with the Decay Analysis Software DAS6 provided by the manufacturer.

## Acknowledgements

This research was supported by the EC (contract PITN-GA-2008–215399 – FINELUMEN), the CNRS, the University of Strasbourg and the CNR (commessa PM.P04.010, MACOL). J.I. thanks the French Ministry of Research and the University of Strasbourg for his fellowship. J.M.M. thanks the Institute of Advanced Studies of the University of Bologna for her fellowship. We further thank A. Saquet for her help with the electrochemical measurements and M. Schmitt for the NMR spectra.

## References

[1] (a) For selected reviews, see: N. Martín, L. Sanchez, B. Illescas, I. Perez, *Chem. Rev.* **1998**, *98* 2527. doi:10.1021/CR9701039
(b) D. Gust, T. A. Moore, A. L. Moore, *Acc. Chem. Res.* **2001**, *34*, 40. doi:10.1021/AR9801301
(c) D. M. Guldi, *Chem. Soc. Rev.* **2002**, *31*, 22. doi:10.1039/B106962B
(d) J.-F. Nierengarten, *New J. Chem.* **2004**, *28*, 1177. doi:10.1039/B402661F
(e) H. Imahori, *J. Phys. Chem. B* **2004**, *108*, 6130. doi:10.1021/JP038036B
(f) H. Imahori, *Org. Biomol. Chem.* **2004**, *2*, 1425. doi:10.1039/B403024A
(g) J. N. Clifford, G. Accorsi, F. Cardinali, J.-F. Nierengarten, N. Armaroli, *C. R. Chim.* **2006**, *9*, 1005. doi:10.1016/J.CRCI.2005.11.010
(h) D. I. Schuster, K. Li, D. M. Guldi, *C. R. Chim.* **2006**, *9*, 892. doi:10.1016/J.CRCI.2005.11.013
(i) R. Chitta, F. D'Souza, *J. Mater. Chem.* **2008**, *18*, 1440. doi:10.1039/B717502G
(j) T. M. Figueira-Duarte, A. Gégout, J.-F. Nierengarten, *Chem. Commun.* **2007**, 109. doi:10.1039/B609383C
(k) G. Accorsi, N. Armaroli, *J. Phys. Chem. C* **2010**, *114*, 1385. doi:10.1021/JP9092699

[2] For fullerene hexakis-adducts substituted with up to six peripheral *o*-phenylenediamine or 2,9-dialkyloxyanthracene moieties, see: M. Diekers, C. Luo, D. M. Guldi, A. Hirsch, *Chemistry* **2002**, *8*, 979. doi:10.1002/1521-3765(20020215)8:4<979::AID-CHEM979>3.0.CO;2-6

[3] (a) For fullerene hexakis-adducts substituted with porphyrin derivatives, see: X. Camps, E. Dietel, A. Hirsch, S. Pyo, L. Echegoyen, S. Hackbarth, B. Röder, *Chemistry* **1999**, *5*, 2362. doi:10.1002/(SICI)1521-3765(19990802)5:8<2362::AID-CHEM2362>3.0.CO;2-5
(b) D. M. Guldi, C. Luo, M. Prato, A. Troisi, F. Zerbetto, M. Scheloske, E. Dietel, W. Bauer, A. Hirsch, *J. Am. Chem. Soc.* **2001**, *123*, 9166. doi:10.1021/JA004104L

(c) F. Rancan, M. Helmreich, A. Mölich, E. A. Ermilov, N. Jux, B. Röder, A. Hirsch, F. Böhm, *Bioconjug. Chem.* **2007**, *18*, 1078. doi:10.1021/BC0603337
(d) M. Regehly, E. A. Ermilov, M. Helmreich, A. Hirsch, N. Jux, B. Röder, *J. Phys. Chem. B* **2007**, *111*, 998. doi:10.1021/JP065626B
(e) F. Spänig, C. Kovacs, F. Hauke, K. Ohkubo, S. Fukuzumi, D. M. Guldi, A. Hirsch, *J. Am. Chem. Soc.* **2009**, *131*, 8180. doi:10.1021/JA900675T

[4] (a) A. Hirsch, I. Lamparth, T. Grösser, H. R. Karfunkel, *J. Am. Chem. Soc.* **1994**, *116*, 9385. doi:10.1021/JA00099A088
(b) A. Hirsch, O. Vostrowsky, *Eur. J. Org. Chem.* **2001**, 829. doi:10.1002/1099-0690(200103)2001:5 < 829::AID-EJOC829 > 3.0.CO;2-V

[5] (a) H. Li, A. Kitaygorodskiy, R. A. Carino, Y.-P. Sun, *Org. Lett.* **2005**, *7*, 859. doi:10.1021/OL0473851
(b) H. Li, S. A. Haque, A. Kitaygorodskiy, M. J. Meziani, M. Torres-Castillo, Y.-P. Sun, *Org. Lett.* **2006**, *8*, 5641. doi:10.1021/OL062391D

[6] (a) For reviews on light-harvesting dendrimers, see: V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni, M. Venturi, *Acc. Chem. Res.* **1998**, *31*, 26. doi:10.1021/AR950202D
(b) V. Balzani, P. Ceroni, A. Juris, M. Venturi, S. Campagna, F. Puntoriero, S. Serroni, *Coord. Chem. Rev.* **2001**, *219–221*, 545. doi:10.1016/S0010-8545(01)00351-4
(c) A. Adronov, J. M. J. Fréchet, *Chem. Commun.* **2000**, 1701. doi:10.1039/B005993P

[7] For examples of light-harvesting systems using fullerene mono-adducts as the final energy and/or electron acceptor, see: (a) N. Armaroli, F. Barigelletti, P. Ceroni, J.-F. Eckert, J.-F. Nicoud, J.-F. Nierengarten, *Chem. Commun.* **2000**, 599. doi:10.1039/B000564I
(b) F. Langa, M. J. Gomez-Escalonilla, E. Diez-Barra, J. C. Garcia-Martinez, A. de la Hoz, J. Rodriguez-Lopez, A. Gonzalez-Cortes, V. Lopez-Arza, *Tetrahedron Lett.* **2001**, *42*, 3435. doi:10.1016/S0040-4039(01)00484-1
(c) J. L. Segura, R. Gomez, N. Martin, C. P. Luo, A. Swartz, D. M. Guldi, *Chem. Commun.* **2001**, 707. doi:10.1039/B100397F
(d) M. Schwell, N. K. Wachter, J. H. Rice, J. P. Galaup, S. Leach, R. Taylor, R. V. Bensasson, *Chem. Phys. Lett.* **2001**, *339*, 29. doi:10.1016/S0009-2614(01)00249-4
(e) G. Accorsi, N. Armaroli, J.-F. Eckert, J.-F. Nierengarten, *Tetrahedron Lett.* **2002**, *43*, 65. doi:10.1016/S0040-4039(01)02083-4
(f) N. Armaroli, G. Accorsi, J. N. Clifford, J.-F. Eckert, J.-F. Nierengarten, *Chem. Asian J.* **2006**, 564. doi:10.1002/ASIA.200600082
(g) L. Pérez, J. C. Garcia-Martinez, E. Diez-Barra, P. Atienzar, H. Garcia, J. Rodriguez-Lopez, F. Langa, *Chem. Eur. J.* **2006**, *12*, 5149. doi:10.1002/CHEM.200600207
(h) J. N. Clifford, A. Gégout, S. Zhang, R. Pereira de Freitas, M. Urbani, M. Holler, P. Ceroni, J.-F. Nierengarten, N. Armaroli, *Eur. J. Org. Chem.* **2007**, 5899. doi:10.1002/EJOC.200700689

[8] J. Iehl, R. Pereira de Freitas, B. Delavaux-Nicot, J.-F. Nierengarten, *Chem. Commun.* **2008**, 2450. doi:10.1039/B804393K

[9] (a) J. Iehl, J.-F. Nierengarten, *Chemistry* **2009**, *15*, 7306. doi:10.1002/CHEM.200901291
(b) J. Iehl, J.-F. Nierengarten, *Chem. Commun.* **2010**, *46*, 4160. doi:10.1039/C0CC00252F

[10] A similar approach has been also developed in the group of S. Bräse, see: (a) P. Pierrat, S. Vanderheiden, T. Muller, S. Bräse, *Chem. Commun.* **2009**, 1748. doi:10.1039/B900367C
(b) P. Pierrat, C. Réthoré, T. Muller, S. Bräse, *Chemistry* **2009**, *15*, 11458. doi:10.1002/CHEM.200902141

[11] (a) R. Huisgen, *Pure Appl. Chem.* **1989**, *61*, 613. doi:10.1351/PAC198961040613
(b) R. Huisgen, W. Szeimies, L. Moebius, *Chem. Ber.* **1967**, *100*, 2494. doi:10.1002/CBER.19671000806
(c) C. W. Tornøe, M. Meldal, *Proceedings of the 2nd International and 17th American Peptide Symposium, Peptides: The Waves of the Future* **2001**, p. 263 (Eds M. Lebl, R. A. Houghten) (Kluwer: San Diego, CA).
(d) V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2002**, *41*, 2596. doi:10.1002/1521-3773(20020715)41:14 < 2596::AID-ANIE2596 > 3.0.CO;2-4

[12] (a) J.-F. Nierengarten, J. Iehl, V. Oerthel, M. Holler, B. M. Illescas, A. Muñoz, N. Martín, J. Rojo, M. Sánchez-Navarro, S. Cecioni, S. Vidal, K. Buffet, M. Durka, S. P. Vincent, *Chem. Commun.* **2010**, *46*, 3860. doi:10.1039/C0CC00034E
(b) P. Compain, C. Decroocq, J. Iehl, M. Holler, D. Hazelard, T. Mena Barragán, C. Ortiz Mellet, J.-F. Nierengarten, *Angew. Chem. Int. Ed.* **2010**, *49*, 5753. doi:10.1002/ANIE.201002802

[13] J.-F. Eckert, J.-F. Nicoud, J.-F. Nierengarten, S.-G. Liu, L. Echegoyen, F. Barigelletti, N. Armaroli, L. Ouali, V. Krasnikov, G. Hadziioannou, *J. Am. Chem. Soc.* **2000**, *122*, 7467. doi:10.1021/JA9941072

[14] T. M. Figueira-Duarte, A. Gégout, J. Olivier, F. Cardinali, J.-F. Nierengarten, *Eur. J. Org. Chem.* **2009**, 3879. doi:10.1002/EJOC.200900290

[15] S. Prathapan, T. E. Johnson, J. S. Lindsey, *J. Am. Chem. Soc.* **1993**, *115*, 7519. doi:10.1021/JA00069A068

[16] J.-F. Eckert, J.-F. Nicoud, D. Guillon, J.-F. Nierengarten, *Tetrahedron Lett.* **2000**, *41*, 6411. doi:10.1016/S0040-4039(00)01095-9

[17] M. A. Fazio, O. P. Lee, D. I. Schuster, *Org. Lett.* **2008**, *10*, 4979. doi:10.1021/OL802053K

[18] F. Cardullo, P. Seiler, L. Isaacs, J.-F. Nierengarten, R. F. Haldimann, F. Diederich, T. Mordasini-Denti, W. Thiel, C. Boudon, J.-P. Gisselbrecht, M. Gross, *Helv. Chim. Acta* **1997**, *80*, 343. doi:10.1002/HLCA.19970800203

[19] R. Pereira de Freitas, J. Iehl, B. Delavaux-Nicot, J.-F. Nierengarten, *Tetrahedron* **2008**, *64*, 11409. doi:10.1016/J.TET.2008.09.047

[20] G. A. Crosby, J. N. Demas, *J. Phys. Chem.* **1971**, *75*, 991. doi:10.1021/J100678A001

[21] S. R. Meech, D. Phillips, *J. Photochem.* **1983**, *23*, 193. doi:10.1016/0047-2670(83)80061-6