



Short communication

Fluorinated fulvalene ruthenium compound for molecular solar thermal applications



Karl Börjesson, Anders Lennartson, Kasper Moth-Poulsen*

Department of Chemical and Biological Engineering, Chalmers University of Technology, Göteborg 412 96, Sweden

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ABSTRACT

Molecular photoswitches, i.e. molecules capable of isomerizing between two states when submitted to light stimuli, has found applications in several areas such as molecular logic, molecular electronics, and, if the two isomers differ substantially in energy, molecular solar thermal (MOST) systems. In a MOST system the photoswitchable molecule absorbs a photon where after a photoinduced isomerisation to a high energy metastable photoisomer occurs. The photon energy is thus stored within the molecule. Fulvalenediruthenium compounds, has been suggested as a candidate in MOST systems thanks to the large difference in energy between the two isomers, its relative stability, and its ability to absorb sunlight. We here present a fluorinated fulvalene ruthenium derivative and show that its processing properties is remarkably different, while having retained photoisomerization efficiency, compared to its hydrocarbon analog.

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1. Introduction

Molecular switches capable of isomerizing between two different states, when exposed to an external stimulus, such as light, have attained considerable attention during the last two decades. They have found applications in molecular logics, where the two isomers functions as on and off states [1–2]. Also in molecular electronics, they are used to switch between an on and off state. For example molecular switches have been blended with organic semiconductors in organic field effect transistors, to enable on/off switching of the electric current by light [3–5]. When blending molecules for use in molecular electronics, care has to be taken to the process parameters to obtain a good morphology of the blend. In some cases, e.g. bulk heterojunction solar cells, two non-miscible materials are used, and in other cases are miscible blends preferred. Thus, there is a need of materials with widely different process and miscibility properties.

If the two isomers are not isoenergetic, the opportunity to capture and store photon energy and perhaps more interesting solar energy arises (the molecules can still be used in other

applications) [6]. The concept is called molecular solar thermal system (MOST) and the stored energy equals the energy difference of the two isomers (Fig. 1). An energy barrier prevents relaxation from the high to low energy isomer. The theoretically maximum solar energy conversion efficiency possible for a pure MOST system is 10.6% [7], but recently it has been demonstrated that by coupling the MOST system to a photon upconversion one [8], sub-bandgap absorption is enabled, and an increase in the theoretical maximum efficiency is possible.

Several families of molecules have been proposed as candidates in molecular solar thermal storage systems: Azobenzene/stillbene isomerizes between the low energy trans form and the high energy cis form when exposed to light [9–11]. Norbornadiene perform a photochemical [2 + 2] cycloaddition when exposed to light, transforming it to the high energy isomer quadricyclane [12–17]. Fulvalenediruthenium compounds perform a rearrangement reaction, cleaving two bonds and forming two new ones [18–21]. The mechanism of this last transformation is quite intriguing. After absorbing a photon the ruthenium–ruthenium bond is broken and an internal rotation followed by a rearrangement occurs, to form the high energy isomer (Scheme 1) [22–23].

We have previously used a fulvalenediruthenium derivative, having one aliphatic carbon tail on each cyclopentadienyl ring (2, Scheme 1) [20]. The system showed only minor fatigue when repeatedly switched between the two states and energy release from the high energy state by heterogeneous catalysis was demonstrated [20]. To expand the window of process properties, we have now constructed a sister compound, having a conserved core structure but with the outer parts of the alkyl chains replaced

* Corresponding author at: Chalmers University of Technology, Chemical and Biological Engineering, Kemivägen 10, 41296 Gothenburg, Sweden.
Tel.: +46 76 199 68 55, +46 31 772 34 03.

E-mail addresses: kasper.moth-poulsen@chalmers.se, mkasper@chalmers.se (K. Moth-Poulsen).

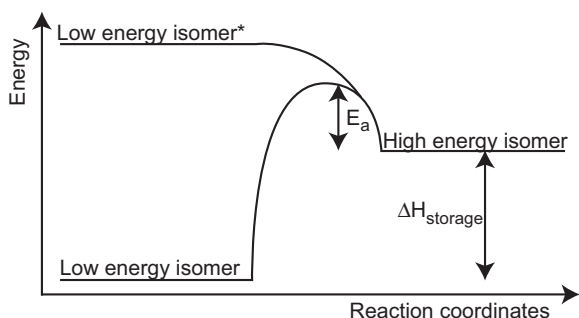


Fig. 1. Schematic picture of the concept of storing energy in photoswitchable molecules. The low energy isomer may in its electronically excited state (*) isomerize to its corresponding high energy isomer. The energy difference between the two isomers equals the storage capacity of the system ($\Delta H_{\text{storage}}$) and an energy hill (E_a) prevents fast thermal relaxation between them.

by fluorocarbon ones (**1**). We show here that, by doing this modification, the photoswitching ability is retained, while the processing properties are remarkably different.

2. Results and discussion

2.1. Synthesis

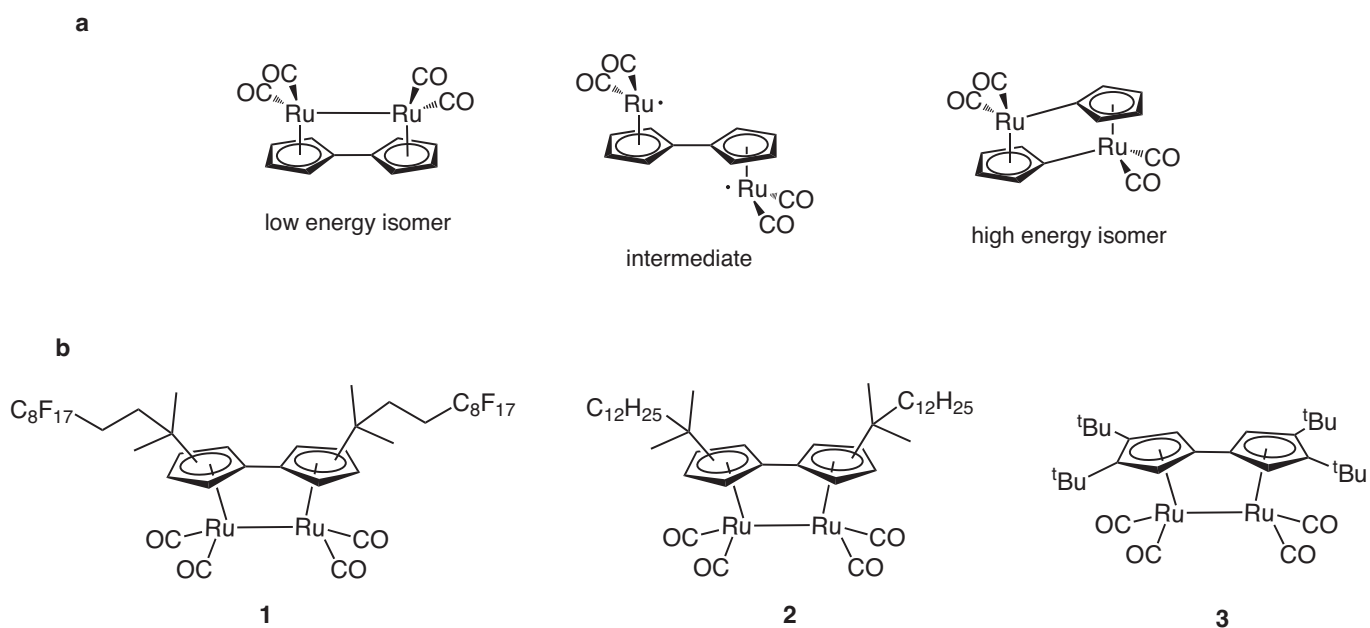
The fulvalene diruthenium compound (**1**) was synthesized using a one pot multi-step approach (Scheme 2). This methodology which was introduced by Vollhardt and coworkers [20], is less time consuming to the quite tedious six step pathway (2 % over all yield) used for making **3** [21,24–25]. Another reason for using this methodology in the synthesis is the relative instability of the intermediates. The synthesis consists of 4 steps: 1-bromo-1*H*,1*H*,2*H*,2*H*-perfluorodecane (**4**) was first treated with *tert*-butyllithium to obtain the corresponding lithium compound (**5**). 6,6-dimethylfulvene was then added to give the fulvene anion (**6**). Two anions were coupled together by use of iodine as an oxidation agent. Due to the possibility of **6** to form resonance structures, the

formed dihydrofulvalene (**7**) was a mixture of two isomers. In the final step, the dihydrofulvalene was added portion wise to a triruthenium dodecacarbonyl solution to form the final product (**1**). The reason for adding the fulvalene portion wise was to minimize possible parasitic Diels–Alder reactions by keeping the fulvalene concentration low. Compound **1** is produced as a mixture of two isomers, and attempts to separate these further failed, the challenge of separating the isomers is similar for our previously reported alkyl analogue **2** [20]. The overall yield of the three steps was 1.4 %. The yield for each step in the reaction pathway has not been determined due to the poor stability of the intermediates. A way of increasing the overall yield could perhaps be by ruthenium cyclopentadienyl dimerisation, which would circumvent the need of labile intermediates. Recent literature show on the possibility to dimerise ruthenium and rhenium cyclopentadienyl complexes in up to 50 % yield by electrochemical approaches [26–27].

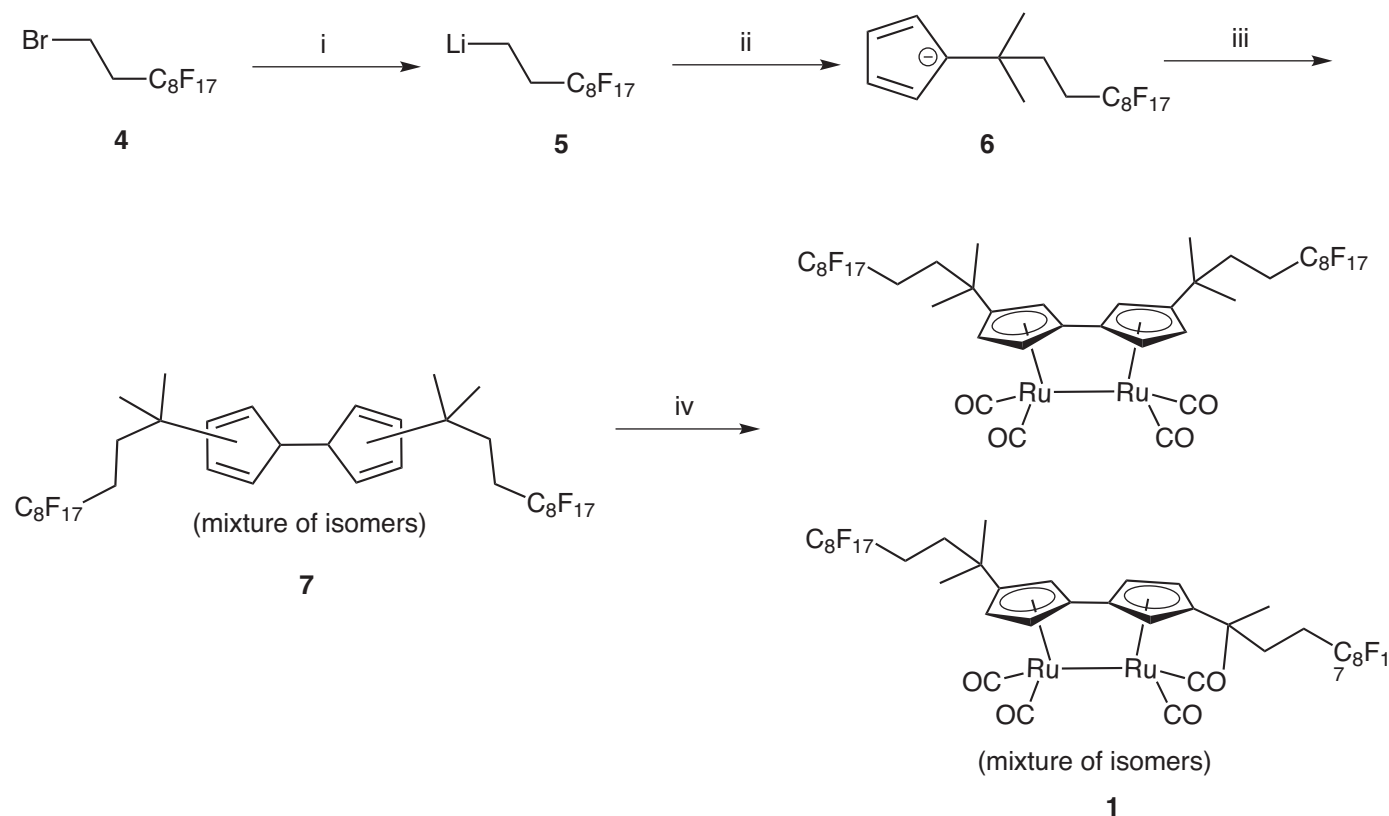
2.2. Photophysical and photochemical properties

Fig. 2 shows the UV/vis absorption spectrum of **1** dissolved in chloroform. The in energy lowest lying transition is centered at 400 nm and it stretches out in the visible region to an onset around 470 nm. This transition is followed by a more intense one in the UV region located at 340 nm. This absorption spectrum is more or less superimposable to fulvalenediruthenium **2** having hydrocarbon tails located on the fulvene moieties (Fig. 2). This indicates that replacing the hydrocarbon tails to fluorocarbon ones has no or only a minor effect on the photophysics of the compound, the ability of **1** to absorb sunlight is still retained.

Fulvalenediruthenium compounds are known to be able to photoisomerize to a high energy isomer (scheme 1). The energy difference between the two isomers is 83 kJ/mol, and an energy barrier of 124 kJ/mol prevents fast backconversion of the high energy isomer [23]. The energy needed for isomerisation are thus on the same order of magnitude as a photon in the red part of the solar spectrum. The photoisomerisation can be followed either by UV/vis (seen as a decrease in absorbtivity), by IR or by NMR. In the



Scheme 1. (a) Structure of the low and high energy isomers, and a metastable intermediate of the fulvalenediruthenium core. (b) Structure of the presented compound **1**, and two sister compounds (**2** and **3** from ref [20] and [21], respectively).



Scheme 2. (i) *tert*-BuLi, Et₂O, −70 → 20 °C; (ii) 6,6-dimethylfulvene, THF, −50 → 0 → 20 °C; (iii) I₂, THF, −70 → 20 °C; (iv) Ru₃(CO)₁₂, xylenes, reflux.

NMR spectra, it is the protons at position 2 on the cyclopentadienyl moiety that has the largest change in the chemical shifts when going from the parent compound to the photoisomer. Fig. 3a show proton NMR spectra of the region where the signal of the protons at position 2 on the fulvalene moiety appear. With increasing time of irradiation a decrease of the original proton signal of the parent molecule and a concurrent buildup of a new signal, originating from the photoisomer, 1 ppm downfield of the original signal, are observed. The chemical shifts of both the parent molecule and the photoisomer are in agreement to literature values of similar compounds [18,20]. Fig. 4 show the part of the IR spectra, before and after illumination, where the carbonyl ligands of **1** absorb. A shift of 35 cm^{−1} towards higher energies for the photoisomer is observed. This indicates that the ruthenium-carbonyl binding

strength is larger for the photoisomer than for the low energy conformer of **1**.

The amount of switching events, at a certain concentration and illumination strength, is proportional to the product of the likelihood that an absorption event occurs and the photochemical quantum yield. The photochemical quantum yield can, thus, be seen as a figure of merit value of photoswitches, and it was determined using potassium ferrioxalate as a photochemical actinometer of the light source. The quantum yield for the transition between the low energy to high energy isomer was determined to be 0.2 % at 400 nm in chloroform, which is the same

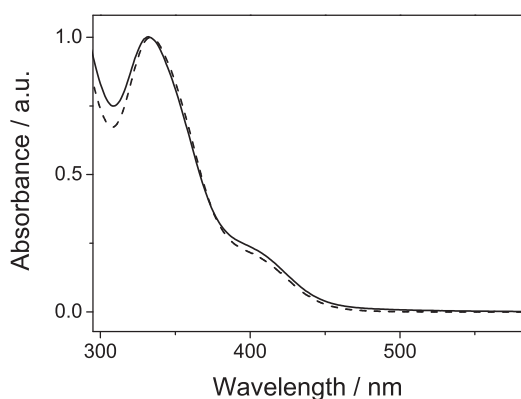


Fig. 2. Absorbance spectrum of **1** (solid line) and **2** (dashed line).

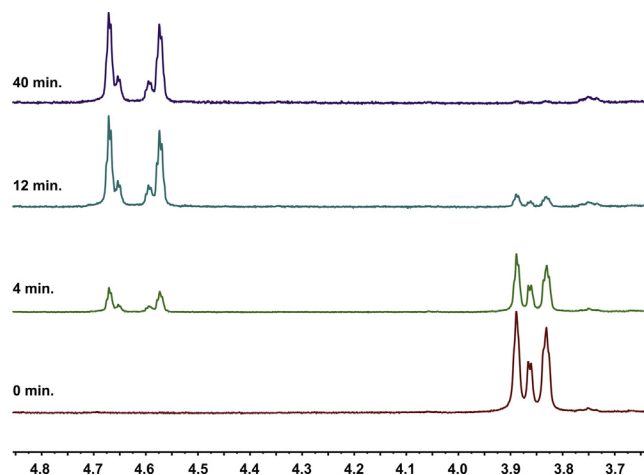


Fig. 3. Photoswitching monitored by proton NMR of the protons at position 2 of the fulvalene moiety (irradiation times are indicated in the figure).

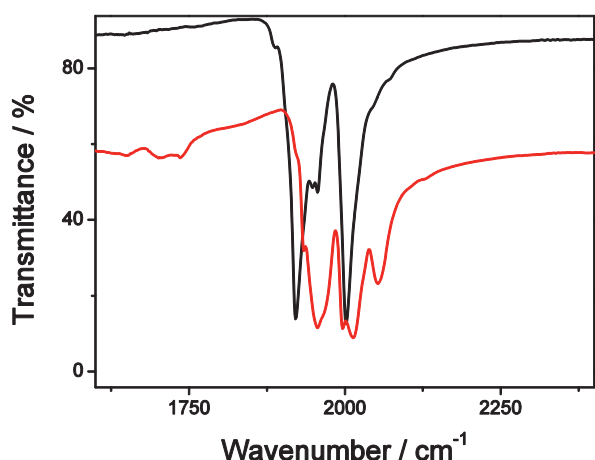


Fig. 4. Photoswitching monitored by IR of the carbonyl ligands (black: before illumination, and red: after illumination).

Table 1
Solubility and photochemical quantum yield data of fulvalenediruthenium compounds.

Compound	Solubility (mg/mL in THF)	Quantum yield (%)
1	5	0.2
2	400 ^a	0.2 ^a
3	280 ^a	n/a

^a From Ref. [20].

value as the reported value for compound **2** in toluene, showing conserved photochemistry when replacing the hydrocarbon tail with a fluorocarbon one. Furthermore, no difference in photoisomerisation quantum yield could be observed for the two isomers.

2.3. Solubility

Although the photochemistry and photophysics of **1** is similar to its hydrocarbon sister compounds **2** and **3**, the intermolecular interactions are not. Table 1 lists the solubility of compounds **1–3** in tetrahydrofuran. The lowering of the solubility of **1** compared to **2** is 2 orders of magnitude, a substantial difference. The difference in solubility can be explained by the low surface energies of fluorocarbons, which often results in both lower oil and water solubility compared to their corresponding hydrocarbons [28]. The special solubility properties of **1** make it more likely to induce phase segregation in molecular blends with a hydrocarbon material. This might be useful in switchable organic field effect transistors. A molecular switch blended with a molecular semiconductor has been shown to obtain a switchable output current and at the same time have a current mobility close to that of the pristine organic semiconductor [4].

3. Conclusions

In summary, a fulvalenediruthenium compound having fluorocarbon substituent has been synthesized. The photochemical and photophysical properties of this compound compared to the existing hydrocarbon variant are conserved. The fluorocarbon arms lowers the fulvalenediruthenium compounds miscibility with hydrocarbon substances, which makes it a suitable photo-switch for use in molecular electronics, where phase segregated blends sometimes are preferred.

4. Experimental

4.1. General

Commercially available reagents were used without further purification if not otherwise stated. All reactions were performed under Argon and solvents were dried and degassed prior to use. NMR spectra were recorded on an automated Agilent (Varian) MR400 MHz spectrometer. UV–vis spectra were measured on a Cary 5000 instrument from Varian Inc. (Agilent Technologies). IR spectra were measured on a Perkin Elmer System 2000 FT-IR.

4.2. Synthesis

4.2.1. [Bis(1,1-dimethyl-1H,1H,2H,2H-perfluorodecane)fulvalene]tetracarbonyl diruthenium (**1**).

Tert-BuLi in pentane (6.26 mL, 1.7 M, 10 mmol) was in a dropwise fashion added to 1-bromo-1H,1H,2H,2H-perfluorodecane (2.6 g, 5 mmol) dissolved in Et₂O (17 mL) at -70°C . The mixture was stirred for 30 min at -70°C , then slowly warmed to 20°C and stirred for 1 h, recooled to -50°C , and treated with a solution of 6,6-dimethylfulvene (0.5 g, 4.7 mmol) dissolved in THF (8 mL). The reaction mixture was allowed to warm up in an ice bath (0°C) for 1 h, then left at room temperature for another 1 h, and subsequently cooled to -70°C again. I₂ (630 mg, 2.5 mmol) dissolved in THF (5 mL) was added to the reaction mixture, which then was left to react for 25 min at room temperature. The reaction mixture was then poured into a separation funnel kept under argon containing heptane (25 mL) and aq. Na₂S₂O₃ (1 w%, 25 mL). After a quick wash (the speed and handling in this step is critical) the organic phase was dried over MgSO₄, placed in a round bottom flask equipped with a septum, and cooled to -70°C . The cold solution was transferred slowly by cannula to a refluxing solution of Ru₃(CO)₁₂ (0.7 g, 1.1 mmol) in xylenes (27 mL) during 2 h. After additional 12 h at reflux, the reaction mixture was allowed to cool and the solvent was removed in vacuo. Column chromatography (petroleum ether/CH₂Cl₂, 4/1 \rightarrow 3/1, on neutral Al₂O₃) afforded the title compound as a yellow solid [34 mg, 1.4%], the isomers were inseparable by further chromatography: ¹H NMR (400 MHz, CDCl₃) δ = 5.55 (m, 2 H), 3.79 (m, 4 H), 2.10 (m, 4 H), 1.81 (m, 4 H), 1.29 (s, 3 H), 1.11 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 123.4, 91.6, 85.5, 76.5, 75.6, 34.2, 33.0, 29.1; ¹⁹F NMR (376 MHz, CDCl₃) δ = -80.8 (3 H), -114.3 (2 H), -121.7 (2 H), -121.9 (4 H), -122.7 (2 H), -123.2 (2 H), -126.1 (2 H), IR (KBr): 3125 (w), 2927 (m), 2002 (s), 1956 (s), 1921 (s), 1479 (w), 1394 (w), 1372 (m), 1332 (w), 1205 (s), 1150 (s), 1115 (m), 1074 (m), 1059 (w), 1031 (w), 958 (w), 920 (w), 841 (m), 721 (w), 704 (w), 676 (w), 654 (w), 605 (m), 563 (s), 525 (s), 459 (w) cm⁻¹.

4.2.2. Photoisomerisation of **1**.

The high energy isomer of **1** was made by irradiating **1** dissolved in chloroform for 40 min using a 150 W HQI lamp (Osram). The photoisomerisation was confirmed by NMR: ¹H NMR (400 MHz, CDCl₃) δ = 5.30 (m, 2 H), 4.66 (m, 2 H), 4.57 (m, 2 H), 2.03 (m, 4 H), 1.72 (m, 4 H), 1.22 (s, 3 H), 1.10 (s, 3 H); ¹⁹F NMR (376 MHz, CDCl₃) δ = -80.3 (3 H), -113.7 (2 H), -121.2 (2 H), -121.4 (4 H), -122.2 (2 H), -122.7 (2 H), -122.6 (2 H), IR (KBr) 2924 (m), 2854 (m), 2053 (m), 2013 (s), 1956 (s), 1459 (m), 1374 (m), 1330 (w), 1243 (s), 1151 (s), 1114 (w), 1084 (w), 1034 (w), 869 (w), 847 (w), 721 (w), 705 (m), 655 (m), 591 (w), 568 (s), 557 (m), 524 (s) cm⁻¹.

4.3. Photochemical quantum yield determination

Photoisomerization quantum yields were measured using a Spex Fluorolog 3 spectrofluorimeter (JY Horiba) as the light source with the excitation monochromator set to 400 nm (full width at half maximum = 10 nm) in all experiments. Potassium

ferrioxalate was used as a chemical actinometer to determine the photonflux of the light source [29]. Concentrations of samples dissolved in CDCl_3 were prior light exposure set so that the absorbance exceeded 2, and the amount of photoconversion was determined by NMR.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jfluchem.2014.01.012>.

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