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Short Note

4-(2-(5-(2-(*tert*-Butoxycarbonyl)hydrazinecarbonyl)-2-methylthiophen-3-yl)cyclopent-1-enyl)-5-methylthiophene-2-carboxylic Acid

Marija Matković

Division of Organic Chemistry and Biochemistry, Laboratory for Biomolecular Interactions and Spectroscopy, Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia; marija.matkovic@irb.hr

Abstract: Diarylethene (DAE) molecular photoswitches draw attention as building units in the preparation of diverse photoactive molecules. An interesting class of these molecules are photoactive peptides. A way to build DAE moiety into peptides/peptidomimetics is via DAE amino acids, an example of which has been demonstrated in bioactive cyclic peptides, wherein the DAE Fmoc-amino acid was prepared and used. Herein, the preparation of DAE Boc-amino acid is presented using a modified method of synthesis. This contribution to the DAE amino acid collection could be useful in the further enhancement of diversity in designing different routes to photoactive peptides.

Keywords: molecular photoswitches; diarylethene amino acids; photoactive peptides

1. Introduction

Since peptide molecules are the protagonists of numerous bio-interactions, the idea of making peptides/peptidomimetics with light controllable molecular structures is an ongoing challenge that will hopefully lead to new smart drugs [1]. Further, photosensitive peptides are interesting as building units in light-sensitive supramolecular systems, which could have different applications as smart materials [2].

For photosensitive peptide synthesis, the most intuitive solution is to incorporate a photo-controllable amino acid into the peptide backbone, moving the research focus to the synthesis of amino acids with a photosensitive moiety.

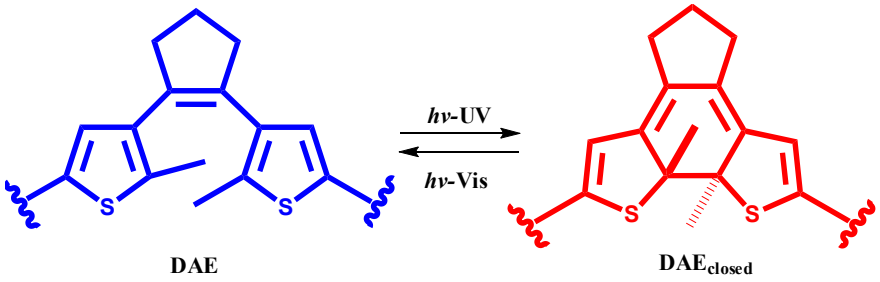
Herein, the so-called photochromic moieties, defined by the possibility of light-induced switching to another isomer or chemical species [3], become interesting, as these structural changes are spectacular enough to impact the potential peptide conformation, thereby influencing its bioactivity and/or ability to self-assemble. One of the photochromic moieties drawing considerable attention is the diarylethene (DAE) family moiety, namely the diarylethene (DAE) molecular photoswitch [4–7]. Its applicability as a functional photoswitch (Scheme 1) lies on a quality line [5] (p. 12175): it is a P-type or thermally irreversible photochromic moiety, the "back and forth" switch process is fast and has a respectable iteration limit number, and finally, it also operates in the solid state.

It is shown that the DEA molecular photoswitch can impact the bioactivity of peptides or peptidomimetics. This was achieved by incorporating the DAE Fmoc-protected hydrazino-amino acid into a gramicidin S analogue, allowing the bioactivity to be regulated using UV/Vis light [8]; the bioactivity of a DAE *bis*-pyrene diamide targeting DNA/RNA and BSA was shown to be susceptible to light control [9].

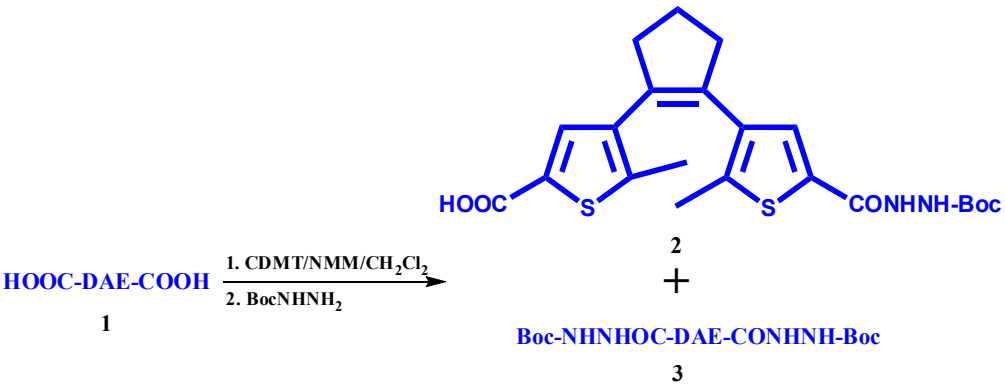
Herein, the synthesis of DAE Boc-hydrazino-amino acid [10], Figure S16, is described (Scheme 2). The amino acid can be further used in the preparation of DAE photoactive peptides on a larger scale.

Citation: Matković, M. 4-(2-(5-(2-(*tert*-Butoxycarbonyl)hydrazinecarbonyl)-2-methylthiophen-3-yl)cyclopent-1-enyl)-5-methylthiophene-2-carboxylic Acid. *Molbank* **2024**, *2024*, M1760. https://doi.org/10.3390/M1760

Received: 19 December 2023
Revised: 3 January 2024
Accepted: 4 January 2024
Published: 11 January 2024



Scheme 1. A member of the DAE family with a 2-methylthiophen ring. Upon UV irradiation, the open structure (**left**) "switches" forward to the closed structure (**right**). The "back" process is triggered using Vis light. A more detailed presentation of DAE and DAE-$_{closed}$ molecules' stereochemistry is given [11].



Scheme 2. Synthesis of Boc-amino acid (**2**) with an incorporated DAE moiety.

2. Results and Discussion

In this work, a type of DAE moiety depicted in Scheme 1 was used to synthesize a photoswitchable Boc-protected amino acid **2** (Scheme 2). Somewhat differently to the described procedure of analogous DAE Fmoc-amino acid synthesis [8], which was accomplished by coupling the starting DAE dicarboxylic acid **1** [11,12] with Fmoc-carbazate using reagent pair *N*,*N*-Diisopropylcarbodiimide (DIC)/*N*,*N*-Diisopropylethylamine (DIPEA) in dimethylformamide (DMF), in this case (Scheme 2), the starting compound DAE dicarboxylic acid **1** [Appendix B] was coupled to *tert*-Butyl-carbazate using coupling reagent pair chloro-4,6-dimethoxytriazine (CDMT)/*N*-methylmorpholine (NMM) in dry dichloromethane (CH_2Cl_2). Analogously to the described procedure [8], compound **2**, along with the by-product diamide **3,** was synthesized (Scheme 2).

In the described Fmoc-amino acid preparation [8], the target compound was further used (solid-phase synthesis) as a mixture of compounds, together with the by-product Fmoc-diamide, since, as fully protected, the diamide was not reactive. Herein, compound **2** was separated from Boc-diamide **3** by means of simple liquid–liquid extraction using organic solvent and alkaline water. This method resulted in a fairly pure target compound **2** according to ^{1}H NMR spectra (Figure S1). Using this method, compound **2** was isolated in a 36% yield, and raw diamide **3** was isolated in a 39% yield. The method herein described was performed on a scale of a few hundred mgs: 630 mg of product **2** was isolated.

Repeated trials of the method were performed. If the extraction steps were omitted, a mixture of **2** and **3** was obtained. The original procedure [8] describes the isolation of pure compounds by means of HPLC. Herein, the mixture of compounds **2**:**3** (10:4, 76 mg) was separated using preparative TLC (7% MeOH/CH_2Cl_2) to obtain fairly pure compound **2** (20 mg, Figures S3–S7).

The main features of the described DAE Fmoc- and Boc-amino acid synthesis presented herein are depicted in Table 1.

Table 1. Target DAE Fmoc- and Boc-amino acid synthesis features.

	Reagents	Isol./mg	Yield/%	Method of Isolation
Fmoc	DIC/DIPEA/DMF	-	50 [1]	HPLC
Boc	CDMT/NMM/CH_2Cl_2	630	36	Extraction/TLC

[1] It is not depicted whether the data refers to the isolated target compound.

Synthesized DAE Boc-amino acid **2** and the by-product, diamide **3**, were subjected to the photo-on and -off switch process depicted in Scheme 1. The compounds (c = 10^{-4} mol dm^{-3}, CH_3CN) were "switched-on" using UV light (254 nm) and "switched-off" by exposure to room light (Figures 1, S17 and S18).

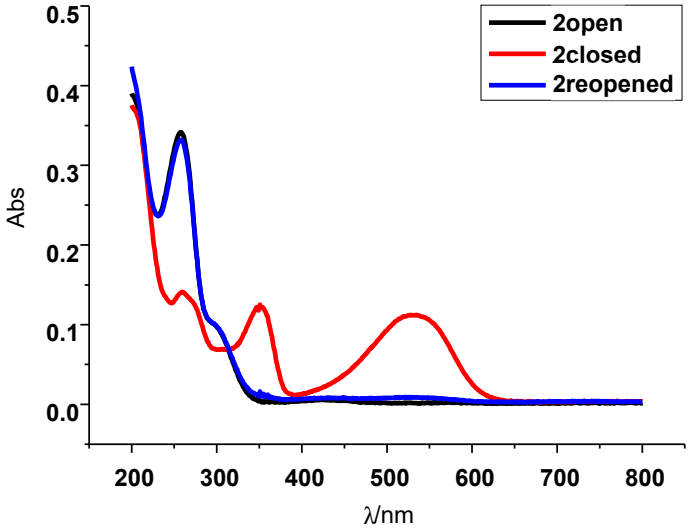


Figure 1. The photoswitch process of compound **2** (—) detected by UV–Vis absorption. The closed form (—) was induced using UV light (254 nm, 8 × 8 W, 19 s), and the reopened form (—) using visible light (room light, 1 h 47 min). The closed form has a characteristic λ_{max} in the visible light region of spectra (λ_{max} = 535 nm); (c(**2**) = 10^{-4} mol dm^{-3}, CH_3CN).

The presumed closed forms, molecules **2c** and **3c,** were obtained in an amount sufficient for NMR analysis by irradiating (254 nm) higher concentrations of **2** and **3** (4.8 and 5.8 × 10^{-4} mol dm^{-3}, respectively). The NMR spectra of open and presumed closed forms for each compound (**2** and **3** vs. **2c** and **3c**) are evidently different (Figures S23–S33), indicating an occurrence of a predicted photoproduct. The occurrence of new ^{13}C signals at 66.8 in **2c** and 68.4 in **3c** indicates the formation of a 4H-Indene ring. These signals suggest the presence of new quaternary 4 °C atoms. In both cases, there is a noticeable decrease of the thiophene ring H chemical shifts in the ^1H NMR spectra. Specifically, the chemical shifts change from 7.53 and 7.37 to 6.78 and 6.76 for **2** → **2c** ($CDCl_3$) and from 7.29 to 6.74 for **3** → **3c** ($CDCl_3$). These shifts are most likely due to the loss of aromaticity in the thiophene ring.

The method of synthesis herein presented gives a fairly pure photoswitchable DAE Boc-amino acid on a scale of a few hundred mgs. This allows, besides further Boc-solid-phase synthesis steps, further synthesis of photoswitchable peptides on a scale of a few hundred mgs in solution.

3. Materials and Methods

3.1. General

Prior to use in the coupling reaction, CH_2Cl_2 was refluxed and distilled over calcium hydride dust (CaH_2), and the collected distillate was deposited on type 4Å molecular sieves. Petroleter 40–70 °C was used. The reagents and solvents were used as supplied unless otherwise mentioned. EtOAc and CH_2Cl_2 were distilled and used as supplied. For the solid

phase extraction of preparative TLC, CH_2Cl_2 (HPLC grade) was used. The preparative plate chromatography was conducted on homemade plates (Appendix B) (Kieselgel silica gel 60 F254, 0.063–0.200 mm, Merck, KGaA, Darmstadt, Germany). Analytical plates (Kieselgel silica gel 60 F254, Merck) were used, and the spots were visualized using UV light (254 nm; see Figure S12). For the establishment of inert atmosphere gas, argon (Ar) 5.0 was used. Given yields refer to isolated amounts.

^{1}H and ^{13}C NMR spectra were obtained using NMR spectrometers: AV600 (magnet 14 T, Bruker BioSpin GmbH, Rheinstetten, Germany) or AV300 (magnet 7 T, Bruker BioSpin GmbH, Rheinstetten, Germany). The NMR spectra shift was calibrated according to standard TMS or solvent residual signal.

HRMS data were collected on a high-resolution mass spectrometer//HPLC system: 6546 LC/Q-TOF//1290 Infinity II (Agilent, Santa Clara, CA, USA).

IR spectra were obtained with Perkin Elmer FT-IR UATR (Shelton, CT, USA.)

Melting points were checked on an Original Kofler Mikroheitztisch apparatus (Reichert, Wien, Austria) and were uncorrected.

The UV-Vis spectra were obtained on Varian Cary 100 Bio UV-Visible Spectrophotometer (Varian Medical Systems, Paolo Alto, CA, USA).

The photoswitch process (analysis of **2** and **3**) was induced on the compounds (**2**, **3**) in a solution (c = 10^{-4} mol dm^{-3}, CH_3CN (HPLC grade), quartz cuvette, 1 mL/1 cm) using light sources at different times: UV light/19 s (Luzchem photochemical reactor LZC-14, 254 nm, 8 × 8 W) and Vis light/1 h 47 min (room light, discharge lamps: PHILIPS master 2 × TL-D 36 W/840 and OSRAM 3 × L36 W/765). For photoswitch process (preparation of **2c** and **3c**) the differences in conditions are given in Appendix A.

Wherever possible, the procedures were performed, covering the glassware with Al foil.

For long periods, depositions of compounds are placed at +4 °C, and vials are wrapped in Al foil.

3.2. Experimental

3.2.1. Synthesis of 4-(2-(5-(2-(*tert*-Butoxycarbonyl)hydrazinecarbonyl)-2-methylthiophen-3-yl)cyclopent-1-enyl)-5-methylthiophene-2-carboxylic Acid (2)

In a two-neck glass vessel, under an atmosphere of Ar, compound **1** (1310 mg, 3.76 mmol) was suspended in dry CH_2Cl_2 (17 mL) at room temperature (20 °C). NMM (830 µL, 7.52 mmol) was added to the suspension, after which the suspension turned into a solution. The reaction solution was stirred at 500 rpm and cooled on ice. After cooling (10 min), CDMT (647 mg, 3.68 mmol) was added using a spatula in 3–4 portions for 15 min. The reaction mixture was stirred in Ar atmosphere, on ice, for 2 h. Then, another aliquot of NMM was added (830 µL, 7.52 mmol), followed by the addition of *tert*-Butyl-carbazate (487 mg, 3.68 mmol), wherein the reagent's vial was washed with dry CH_2Cl_2 (3 mL). The reaction mixture was stirred on ice for another hour and then left to spontaneously reach room temperature overnight (the water bath reached 24 °C).

The reaction mixture was poured into a separation funnel with additional CH_2Cl_2 (2 × 35 mL) and extracted with KOHaq (0.5 mol dm^{-3}, 66 mL), which produced a white suspension. To obtain good separation of the organic and water phases, diethyl ether (200 mL) and water (50 mL) were added. The layers were mixed and left to separate, which produced the organic phase O1 and the water phase.

The separated water phase was washed with CH_2Cl_2 (50 mL) and diethyl ether (100 mL). After the separation of layers, the bottom water layer was washed with additional diethyl ether (2 × 50 mL). The phases were separated, and the organic layers were combined into an organic phase (O2).

The obtained water phase, a dark brown solution, was identified as basic (pH 12–14). The water phase was placed on an ice bath and acidified to pH 1 with $KHSO_4$aq (8.5 g/10 mL), which produced a very slight whitish precipitate and the appearance of an isolated dark brown rubbery semi-solid. The water phase was decanted through sinter glass. Very small

amounts of precipitate and the dark brown semi-solid were dissolved in EtOAc (100 mL). The EtOAc solution analysed on analytical TLC showed an indicative intense UV–visible spot (10% MeOH/CH_2Cl_2). The EtOAc solution was washed with 5% $NaHCO_3$ (50 mL), 0.5 mol dm^{-3} HCl (10 mL), and water (50 mL) to remove the possible residues of starting compound **1**. The organic phase was dried over anhydrous Na_2SO_4 for 3 h, filtered off, and the solvent removed under reduced pressure to produce the final product **2** at first as colourless oil in fairly good purity (Figures S1 and S2) (630 mg, 1.36 mmol, 36%).

Compound **2** was also obtained from a mixture of **2** and the by-product diamide **3** (**2**:**3** = 10:4, 76 mg, Figure S10) using two parallel preparative TLC plates eluting with 7% MeOH/CH_2Cl_2. The separated stripes on the TLC were visualized under a UV lamp (254 nm) (Figure S11). The removed two SiO_2 stripes were suspended in 7% MeOH/CH_2Cl_2 (20 and 40 mL), stirred for 25 min, and filtered through sinter glass-3 with the addition of the eluent (20 mL each portion). The solvent was removed under reduced pressure at r.t. to obtain compound **2** (Figures S3–S7 and S12). At +4 °C, the compound shows as a whitish solid (20 mg, 0.04 mmol, 43% in regard to the starting mixture). mp 162–172 °C; ^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ 7.59 (s, 1H), 7.51 (s, 1H), 2.88–2.80. (m, 4H), 2.09–2.08 (m, 2H), 2.01 (s, 3H), 1.98 (s, 3H), 1.43 (s, 9H); ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.13 (bs, 1H, NH), 7.53 (s, 1H), 7.37 (s, 1H), 6.81 (bs, 1H, NH), 2.81–2.74 (m, 4H), 2.06 (qui, J = 7.6 Hz, 2H), 1.94 (s, 3H), 1.90 (s, 3H), 1.48 (s, 9H); ^{13}C{1H, APT} NMR (150 MHz, $CDCl_3$): * δ 165.8, 161.7, 156.1, 144.4, 141.5, 137.0, 136.6, 135.8 (CH), 135.0, 134.8, 130.9 (CH), 128.8, 82.5 (C_{Boc}), 38.7 (CH_2(b,c)), 28.3 ((CH_3)$_3$), 22.9 (CH_2(a)), 15.1 (CH_3), 14.8 (CH_3); IR (ATR): ν 3261, 2926, 2852, 1663, 1460, 1246, 1156, 735 cm^{-1}; HRMS (+ESI): m/z calcd. for $[C_{22}H_{26}N_2O_5S_2]^+$: 463,1361 $[M + H]^+$, found 463,1362; R_f (7% MeOH/CH_2Cl_2): 0.35.

* Atoms Cb,c,d,e are represented by two signals (Figures S4–S6 and S22).

3.2.2. Details on by-Product **3** (Scheme 2)

The method of isolation and characterisation and spectroscopic data are available in Appendix A and Supporting Information (Figures S8–S15, S17–S19, and S21).

3.2.3. Details on Closed Forms **2c** and **3c**

The method of preparation and NMR data are available in Appendix A.2 and Supporting Information (Figures S23–S35).

4. Conclusions

The synthesis of a diarylethene (DAE) Boc-protected hydrazino-amino acid has been presented. The described procedure, with all its issues and novelties, is a contribution to the "know how" knowledge of preparing DAE building units. The information provided herein might be of good use to researchers planning to synthesize photochromic peptides with a DAE photoswitch.

Supplementary Materials: Figures S1–S10 and S13–S15: NMR spectra of **2** and **3**; Figures S11 and S12: Photos of TLC (preparative and analytical plates) of a mixture of compounds **2** and **3** and the purified target compound **2**; Figure S16: patent Markush structure similar to **2**; Figure S17: photo of solution colour for **2** and **3** in the photoswitch process; Figure S18: UV–Vis spectra of **3** (open and closed); Figures S19–S21: IR spectra and HRMS scan of isolated compounds **2** and **3**; Figure S22: molecular structures of **2** and **3**; Figure S23: ^{1}H NMR (600 MHz, CDCl3) spectrum of 2c; Figures S24–S33: NMR spectra of **2c** and **3c**; Figure S34: preparation of **2c** and **3c** followed by UV spectroscopy; Figure S35: presumed molecular structures of **2c** and **3c**; Figure S36: ^{1}H NMR spectra of **3** ($CDCl_3$) used for comparison with **3c**.

Funding: This research was conducted in the scope of a project approved and funded by the Croatian Academy of Sciences and Arts (CASA) Foundation, grant number 378 ("Photosensitive cyclic peptides…", 2019). The APC was funded by the author.

Data Availability Statement: No new data were created or analysed in this study. Data sharing is not applicable to this article.

Acknowledgments: The author expresses thanks to the head of the Laboratory for Biomolecular Interactions and Spectroscopy, I. Piantanida, for donating extra material used for experiments.

Conflicts of Interest: The author declares no conflicts of interest. The funders had no role in the design of this study, in the collection, analyses, or interpretation of data, in the writing of the manuscript, or in the decision to publish the results.

Appendix A

*Appendix A.1. Synthesis of 4-(2-(5-(2-(tert-butoxycarbonyl)hydrazinecarbonyl)-2-methylthiophen-3-yl)cyclopent-1-enyl)-2-(2-(tert-butoxycarbonyl)hydrazinecarbonyl)-5-methylthiophene (**3**)*

In continuation to the synthesis of **2** (Section 3.2.1), the organic phase O1 was washed with water (2 × 40 mL) and dried over anhydrous Na_2SO_4. After evaporation of solvent (40 °C), a yellow oil was obtained (721 mg). Concerning the O2 organic phase, additional diethyl ether (40 mL) was added and washed with water (40 mL). The obtained organic layer was dried over anhydrous Na_2SO_4. The evaporation of the solvent produced yellow oil (130 mg).

According to the TLC (10% MeOH/CH_2Cl_2), both organic phases O1 and O2 were solutions of the same, new, un-polar photosensitive raw product (yellow oil, 851 mg, 1.48 mmol, 39%) (Figures S8 and S9). The raw compound spot on the analytical TLC plate becomes dark pink under UV light (for example, see Figure S12), indicating the isolation of a photoactive compound.

An aliquot of O1 (100 mg) was purified on two TLC plates (EtOAc:petroleter = 1:1) to obtain 32 mg of more purified **3**. Product **3** was additionally purified on a TLC plate (5% MeOH/CH_2Cl_2). The product stripes were located by exposing the edge of the TLC plate (1.5–2 cm) to UV light (254 nm; see Figure S11). The obtained SiO_2 was extracted with 5% MeOH/CH_2Cl_2 and filtered through Minitip (PTFE 13/45 100/PK). The solvent was removed under reduced pressure at 25 °C to obtain compound 3 as a pale yellow solid (4 mg, 1.6%). mp 120–130 °C;^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ 9.26 (bs, 2H, NH), 7.92 (bs, 2H, NH), 7.59 (s, 2H, CH). 2.82 (t, *J* = 7.6 Hz, 4H), 2.07 (qui, *J* = 7.6 Hz, 2H), 1.96 (s, 6H), 1.43 (s, 18H); ^{13}C {1H, APT} NMR (150 MHz, $(CD_3)_2CO$): *δ* 162.8, 157.3, 142.0, 138.2, 136.4, 134.9, 131.2 (CH), 81.2 (C_{Boc}), 39.9 (CH_2(b)), 29.2 ((CH_3)$_3$), 24.2 (CH_2(a)), 15.5 (CH_3), IR (ATR): *ν* 3267, 2978, 2932, 1720, 1650, 1492, 1272, 1248, 1161, 853 cm^{-1}; HRMS (ESI): *m*/*z* calcd. for $[C_{27}H_{36}N_4O_6S_2]^+$: 577,2155 $[M + H]^+$, found 577,2154; R_f (7% MeOH/CH_2Cl_2): 0.53.

*Appendix A.2. Synthesis of **2c** and **3c***

Samples of **2** and **3** (2 and 3 mg, respectively) were dissolved in acetonitrile (CH_3CN, HPLC grade, 9 mL) to obtain c(**2**) = 4.8 and c(**3**) = 5.8 × 10^{-4} mol dm^{-3}. The solutions were distributed into three fluorimetric quartz cuvettes (1 cm): 3 mL per each. For each compound, the first cuvette was used to establish irradiation conditions: each sample was irradiated in time steps, and the production of the photoproduct was followed by UV spectroscopy (Figure S34). The samples were irradiated until the ratio of peak absorbances (535, 351, and 257 nm for **2**; 528, 348, 257 for **3**) reached the ratio obtained in UV spectra in irradiating lower concentration c = 10^{-4} mol dm^{-3}, and until the upcoming saturation of the system was noticed (Figure S34a,c). The time steps were determined as 20, 40, and 60 s for **2** (a total of 2 min) and 20, 40, 60, and 20 s for **3** (a total of 2 min 20 s). The remaining cuvettes (second and third) for each compound were irradiated in one step: compound **2** for 2 min and compound **3** for 2 min 20 s. The final UV spectra of cuvettes (1.2.3.) for each compound were compared (Figure S34b,d). Having determined their equivalence, solutions of each compound were combined into a round glass vessel and evaporated (40 °C) for several minutes. For each compound, a dark pink-to-purple oily residue was obtained that was immediately scanned for ^{1}H and overnight for ^{13}C{COM}. The 2D spectra were collected in the next 48 h. (2c): ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.71 (bs, 1H, NH), 6.78 (s, 1H, CH), 6.76 (s, 1H, CH), 6.68 (bs, 1H, NH), 2.48–2.43 (m, 4H), 2.01 (s, 3H, CH_3), 1.99 (s, 3H, CH_3), 1.89 (qui, *J* = 7.4 Hz, 2H), 1.49 (s, 9H, (CH_3)$_3$); ^{13}C{^{1}H, COM} NMR (75 MHz, $CDCl_3$): see Figure S27; (3c): ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52 (bs, 2H, NH), 6.74 (s, 2H, CH), 6.60

(bs, 2H, NH), 2.45 (t, J = 7.9 Hz, 4H), 1.95 (s, 6H, CH_3), 1.89 (qui, J = 7.9 Hz, 2H), 1.49 (s, 18H, $(CH_3)_3$); $^{13}C\{^1H$, COM} NMR (150 MHz, $CDCl_3$): see Figure S33.

Appendix B

In this work, compound **1** was synthesized analogously to the procedures described [11], starting from commercially available 2-methylthiophene (98%, Sigma-Aldrich, St. Louis, MO, USA).

In the synthesis of 1,2-Bis(5-chloro-2-methylthiophen-3-yl)cyclopent-1-ene [11,13], Zn dust was activated as described [14]. Reagents Zn:$TiCl_4$ were used in a ratio of 11.1 g (169.78 mmol)/25.05 mL (228.47 mmol) with compound 1,5-Bis(5-chloro-2-methylthiophen-3-yl)pentane-1,5-dione (13.7 g, 37.92 mmol) [11,15], refluxing overnight at 85 °C under a $CaCl_2$ tube.

Prior to the synthesis of **1** (yield 93%), the THF was refluxed on Na (2 h), distilled, and deposited on Na overnight. During synthesis, partially shredded solid CO_2 was added using a spatula.

For the separation of compounds **2** and **3,** commercial plates with Kieselgel silica gel (60 F254, 0.063–0.200 mm, Merck, Darmstadt, Germany) or similar can be used as well.

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