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Graphical Abstract

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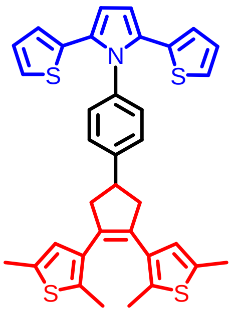

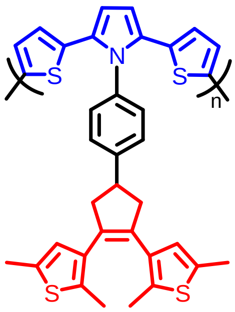

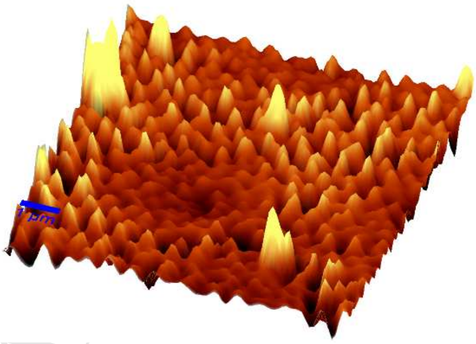

Design, synthesis, photochromism and electrochemistry of a novel material with pendant photochromic units

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Abstract

In the present work, the synthesis, photochromism and electrochemistry of a novel material **1**, *1-(4-[3,4-bis(2,5-dimethyl-3-thienyl)cyclopent-3-en-1-yl]phenyl)-2,5-di-2-thienyl-1H-pyrrole*, with pendant dithienylethene (DTE) photochromic units are described. It should be noted that the system **1** can be reversibly and efficiently switched between open (**1o**) and closed (**1c**) states by light in both solution and in the solid poly(methyl methacrylate) matrix. It is also noteworthy that the two isomers (**1o** and **1c**) of this novel system **1** can be smoothly polymerized on ITO by electrochemical means. Surprisingly, the DTE unit in **1** does not retain its photochemical switching properties after immobilization onto ITO. The morphology of the polymer film was investigated by AFM analysis. Furthermore, it was found that the polymer exhibited remarkable electrochromic features that can be switched from green in the neutral state to violet state under applied external potentials without disturbing the photochromic units.

Keywords: Dithienylethene, dithienylpyrrole, photochromic, electrochromic, thiophene.

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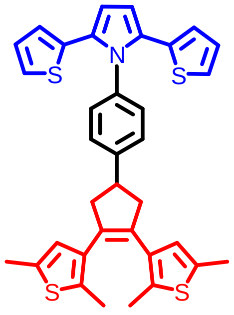
1. Introduction

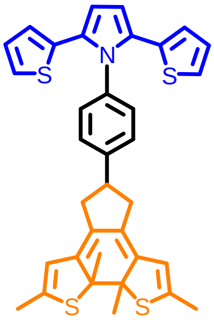
The design and synthesis of novel functional organic compounds has attracted considerable attention since they lead to a variety of advanced technological applications in the field of molecular electronics and photonics, sensors, machines and devices, light emitting diodes, photovoltaics, transistors, electrochromics, data processing and storage media.[1] Photochromic dithienylethene (DTE) derivatives are highly valuable materials due to their unique properties such as thermal stability and high fatigue resistance which are indispensable for optoelectronic applications.[2,3] However, some other properties of DTEs such as fast switching, high quantum yield and large differences between the absorption wavelengths of two isomers have also contributed to the ever increasing popularity of these compounds, which have found diverse applications as smart materials (e.g. molecular switches, optical data processing and storage devices, molecular probes, machines and imaging agents) in both bio- and nano-technological sciences as well as in materials science.[4-10] Thus, excellent molecular DTE systems, which hold great promise for applications in the field of molecular electronics and optics, have been created thus far.[11-21] Unfortunately, however, only a few photochromic conducting polymers[22-23] based on DTE systems have been reported to date.[24-27] In this context, it is a challenging task to attain novel DTE based conducting polymers.

2,5-Dithienylpyrrole (SNS) is one of the most useful core units in order to obtain materials with distinct properties.[28-34] For instance, the flavin functionalized polydithienylpyrrole (PSNS) fabricated by electrochemical methods could be used for the detection of 2,6-diamidopyridine, which is a biologically important redox-active molecule.[35] It was recently shown that a chemiluminescent PSNS functionalized with luminol appendages could be used for the detection of reactive oxygen species and blood (in forensic science).[36] Furthermore, it is noteworthy that SNS based materials can be amplified to create viable materials as molecular sensors and/or probes for the detection of metal ions.[37-39] In addition, by the help of fluorescent substituents, PSNS based polymers could exhibit both fluorescent and electrochromic properties.[40-44] It was also shown that the intrinsic properties could easily be controlled through rational design of the backbone structures.[44] Nonetheless, examples of electrochromic polymeric materials based on SNS with pendant DTE photochromic units have not been reported so far. Therefore, novel SNS based conducting polymers with pendant photochromic DTE units are welcome.

Considering the fact that both DTE and SNS units are synthetically versatile, we have designed a new molecular architecture merging these two systems; SNS with pendant DTE units (**1**, Scheme 1). Herein we wish to report the design, synthesis, photochromic features and electrochemistry of this novel molecular system. This novel photochrome **1** can be reversibly and efficiently switched between open (**1o**) and closed (**1c**) states by light in both solution and in the solid PMMA matrix. It is noteworthy that two isomers (open (**1o**) and closed (**1c**) forms) of this novel system **1** can be polymerized electrochemically. Furthermore, it was found that the polymer exhibited remarkable electrochromic features that can be switched from green color in the neutral state to violet under applied external potentials without disturbing the photochromic units.



1o

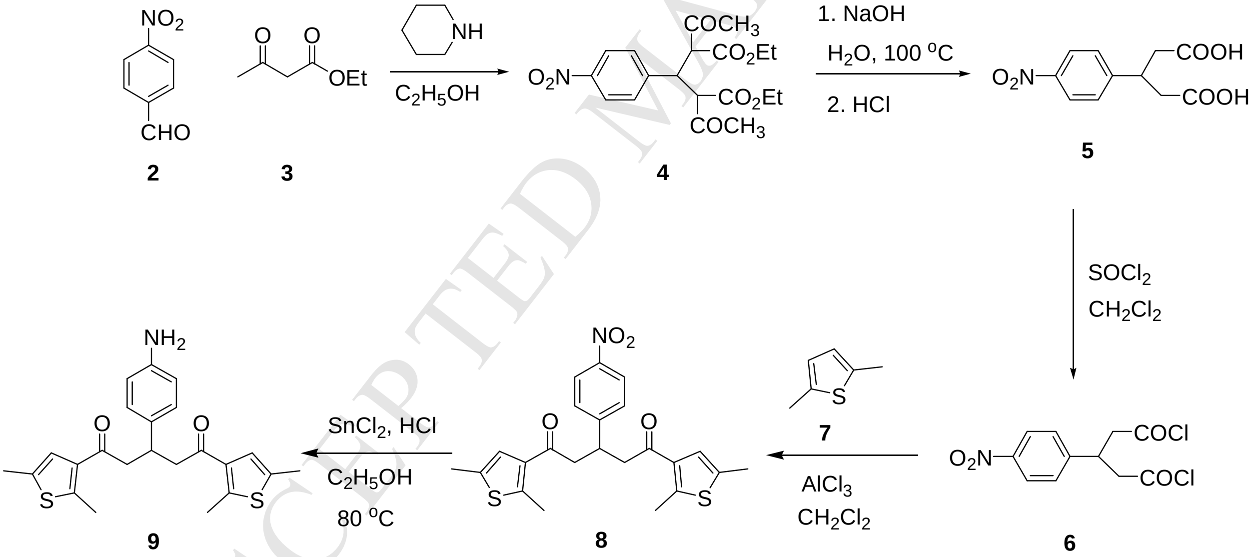


1c

Scheme 1. The structures of target compounds **1o** and **1c**.

2. Results and Discussion

The synthesis of the target compound **1** was started with a Knoevenagel type condensation reaction.[45,46] 4-Nitrobenzaldehyde (**2**) was treated with ethyl acetoacetate (**3**) in the presence of piperidine to give bisacetoacetate **4** in 75% yield (Scheme 2). Hydrolysis of **4** was carried out with NaOH to get β-arylglutaric acid **5** in a yield of 60%. β-Arylglutaric acid **5** was characterized on the basis of ^{1}H, ^{13}C NMR, and FTIR spectroscopy and elemental analysis, which firmly established the structure (see Supporting Information for ^{1}H and ^{13}C NMR spectra, Fig. S1-S2).

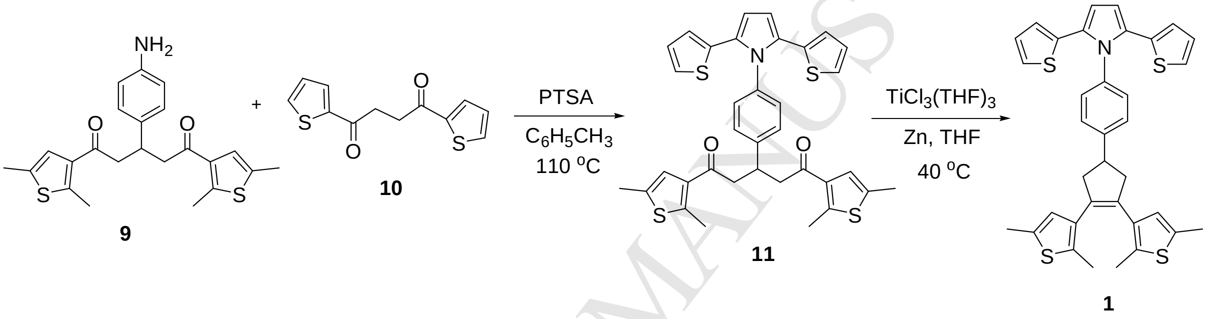


Scheme 2. Synthesis of compounds **4**-**9**.

In the next step, diacid **5** was converted to diacid chloride **6** with $SOCl_2$, which was directly used in the next step without purification (Scheme 2). At this stage, Friedel-Crafts reaction of diacid chloride **6** with 2,5-dimethylthiophene (**7**) provided **8** in a yield of 50% (see SI for spectroscopic data, Fig. S3-S5). The treatment of compound **8** with $SnCl_2$ in the presence of

HCl in refluxing ethanol resulted in the formation of the corresponding amine **9** in 90% yield (see SI for spectroscopic data).

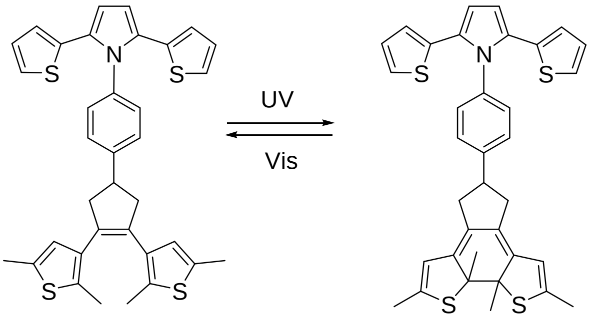
Finally, Paal-Knorr reaction of compounds **9** and **10**[41] afforded **11**, which was followed by McMurry coupling with $TiCl_3(THF)_3$ in the presence of zinc to give the target compound **1** (Scheme 3). Initial characterization of **11** and **1** was based on NMR and FTIR spectroscopic data along with the elemental and MALDI TOF mass analysis (see Supporting Information, Fig. S9-S14), which confirmed the structures.



Scheme 3. Synthesis of compounds **11** and **1**.

The absorption profile of compound **1** was examined in CH_2Cl_2 solution. The UV-Vis spectrum of **1** was characterized by broad bands between 250-400 nm (λ_{max}= 335 nm) with molar extinction coefficient (ε_m) of 18733 $M^{-1}cm^{-1}$. On the other hand, it was noted that **1** induced blue emission with a λ_{max} of 413 nm when excited at 335 nm light.

When the photochemical switching behavior of compound **1** was investigated in solution, it was found that **1** underwent efficient photochemical ring closing and opening upon irradiation with UV (365 nm) and visible (>400 nm) light, respectively (Scheme 4 and Figure 1a). The absorption changes could also be detected by the naked eye. By irradiating the colorless open isomer (**1o**) with UV light, the deep brown closed isomer (**1c**) is formed by conrotatory 6π6 electrocyclization (Figure 2a).



1o **1c**

Scheme 4. Photochemical switching of **1o**/**1c** in CH_2Cl_2 with UV (365 nm) and visible light (>400 nm).

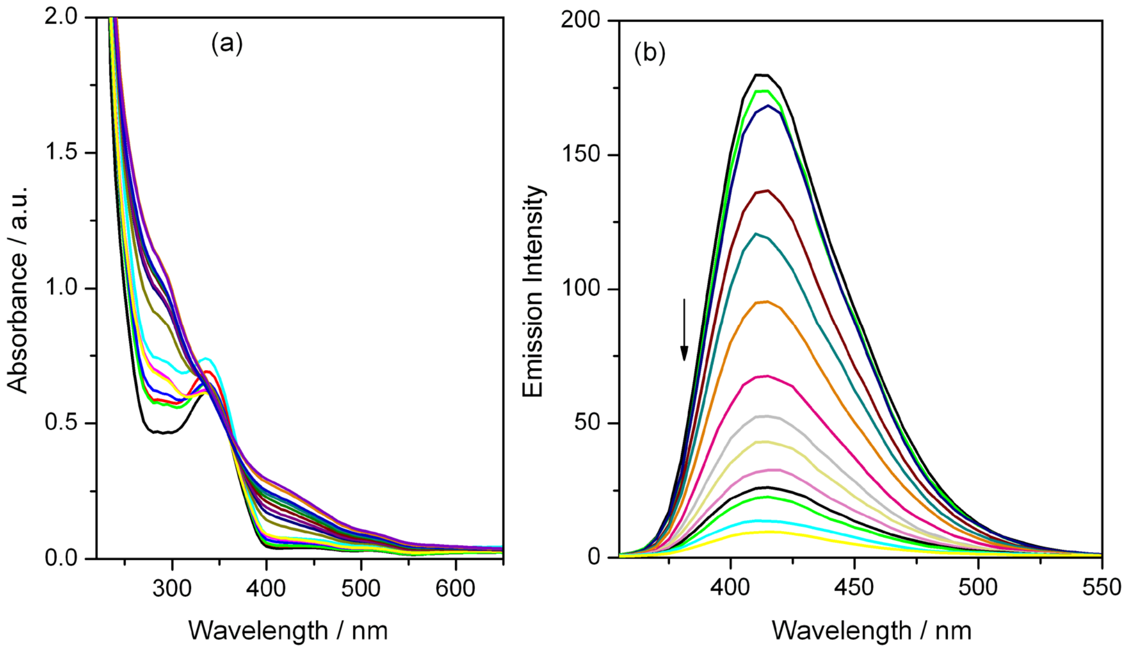


Figure 1. (a) UV/vis absorption spectra of **1** (33 µM in CH_2Cl_2) in the open (**1o**) and closed (**1c**) state upon irradiation with UV (365 nm) and visible (>400 nm) light. (b) Emission spectral changes of **1** (3.3 µM) during irradiation in CH_2Cl_2, (λ_{exc}= 335 nm).

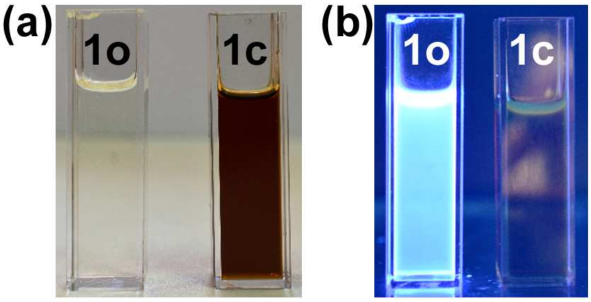


Figure 2. Compound **1** in CH_2Cl_2 before (**1o**) and after (**1c**) irradiation under (a) day light and (b) UV light (365 nm).

Figure 3a illustrates the photochromic film which was prepared by the introduction of this novel photochromic system **1o** in polymethylmetacrylate (PMMA) matrix as dopant. After the preparation of the film, it was homogeneously irradiated with UV light through a patterned mask. The color change was quite prominent on the regions that were exposed to UV light (Figure 3b). It should be noted that the system **1** can be reversibly and efficiently switched by light in both solution and in the solid poly(methyl methacrylate) (PMMA) film state (Figure 3).

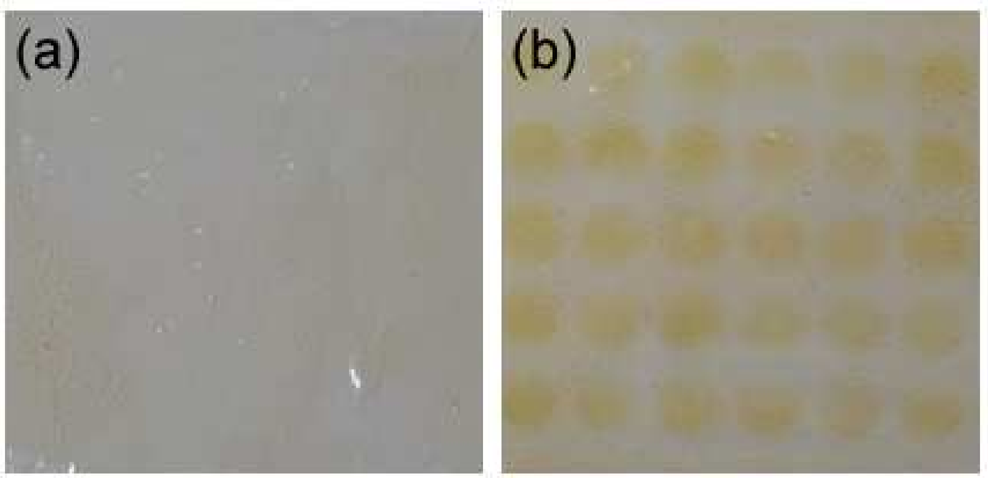


Figure 3. Images of **1** (0.25 wt.-%) in Propylene carbonate/ PMMA (2 wt.-%) matrix (a) before and (b) after irradiation.

It was also noted that compound **1** exhibited obviously different fluorescence in open and closed states under alternating irradiation of UV and visible light (Figure 2b). This is probably due to a non-radiative fluorescence-resonance energy transfer process between SNS and the closed form of the pendant DTE units, which could also be switched on and off upon irradiation (Figure 1b).

To reveal the electrochemical properties of **1o**, the redox behavior was investigated in different electrolyte solutions by cyclic voltammetry between 0.0 and 2.0 V (vs. Ag/AgCl). It was found that **1o** (3.0 x 10^{-3} M) induced multiple oxidation peaks at 0.77, 1.30, 1.56, 1.72 and 1.96 V in an electrolyte solution consisting of 0.1 M $TBAPF_6$ dissolved in a mixture of CH_3CN and CH_2Cl_2 (95:5, v/v) at a scan rate of 100 mV/s (vs. Ag/AgCl) (Figure 4a). The first peak at 0.77 V was attributed to the oxidation of SNS unit and others were probably due to the overoxidation of oligomeric species formed at 0.77 V or oxidation of DTE unit. At this stage the electropolymerization of **1o** was explored. Unfortunately, all attempts to obtain an electroactive polymer film via potentiodynamic methods were unsuccessful. Although the cyclic voltammogram in Figure 4b was promising as a characteristic signature of the formation of an electroactive polymer film on electrode surface, it was found that the product remained in the solution as a dark yellow color when the electrode was removed from the bulk solution. This was mainly attributed to the solubility and/or mechanical instability of the product under the given conditions.

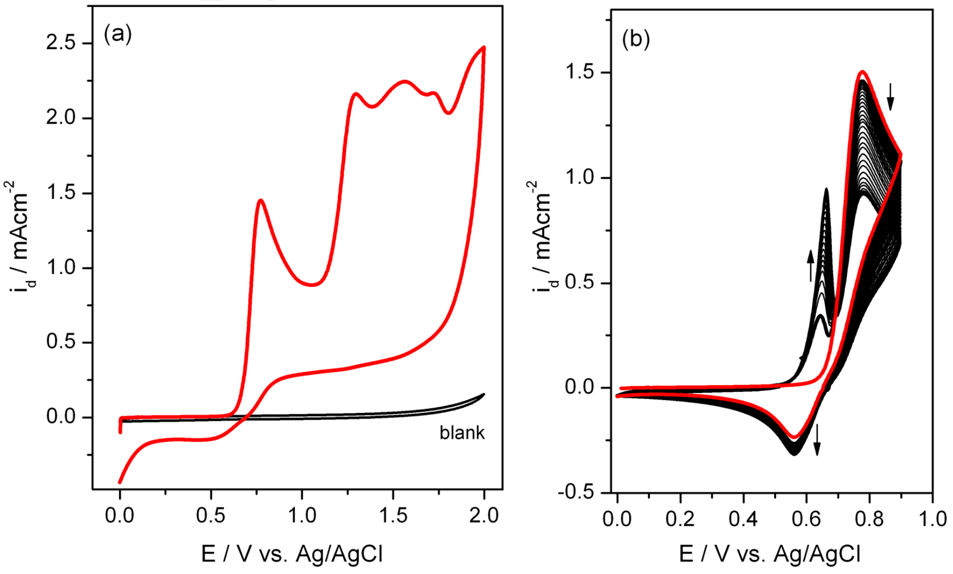


Figure 4. Cyclic voltammogram of (a) **1o** (3.0×10^{-3} M) and (b) electropolymerization in an electrolyte solution consisting of 0.1 M $TBAPF_6$ dissolved in a mixture of CH_3CN and CH_2Cl_2 solution (95:5, v/v) at a scan rate of 100 mV/s.

In order to overcome this problem, electropolymerization of **1o** was carried out in a C_2H_5OH-CH_2Cl_2 mixture (95:5, v/v) containing 0.1 M $LiClO_4$ electrolyte. During the first anodic scan, an irreversible oxidation peak at 0.72 V was observed (Figure 5a). After repetitive cycles between 0.0 V and 0.9 V, a new redox couple began to appear and its intensity was increased after each successive cycle. To our delight, a dark yellowish polymer film (**P1o**) was successfully obtained on the electrode surface when C_2H_5OH and CH_2Cl_2 mixture was used instead of CH_3CN and CH_2Cl_2 mixture (Scheme 5).

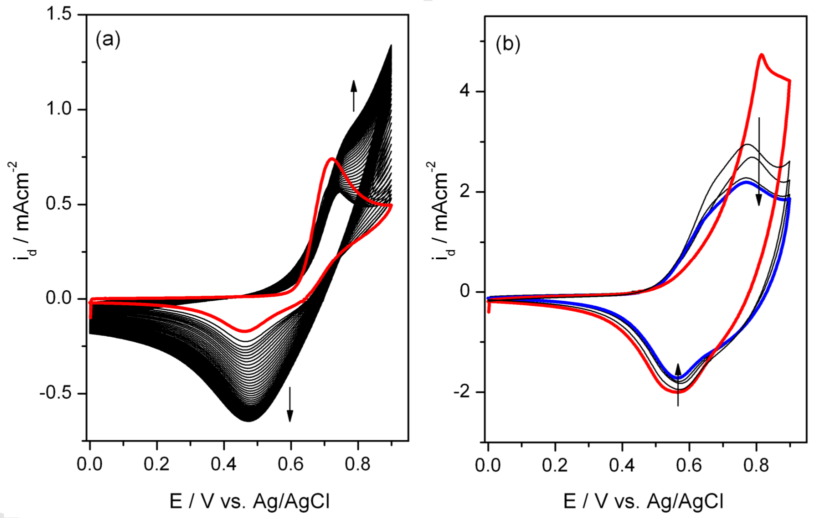
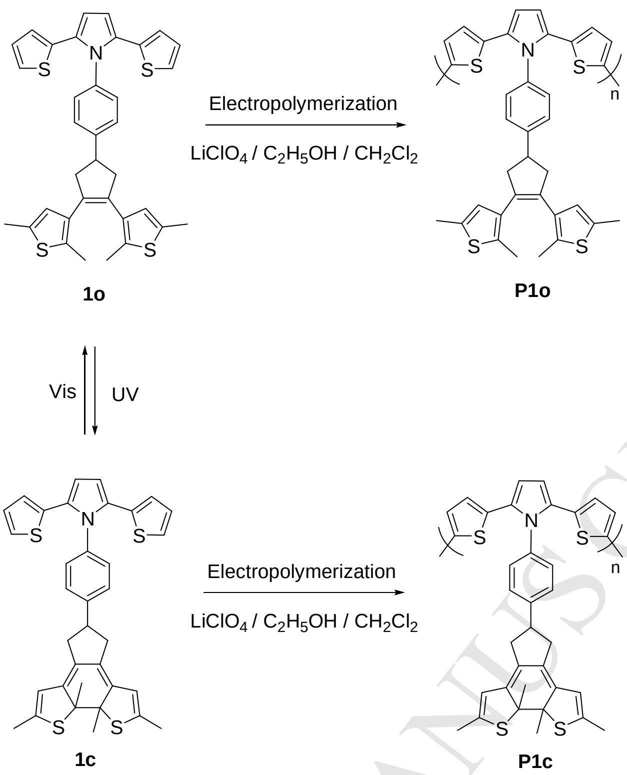


Figure 5. (a) Electropolymerization of **1o** (3.0×10^{-3} M) by potential scanning to give polymer **P1o** in an electrolyte solution consisting of 0.1 M $LiClO_4$ dissolved in C_2H_5OH and CH_2Cl_2 mixture (95:5, v/v) at a scan rate of 100 mV/s. (b) Repetitive cyclic voltammograms of **P1o** film on Pt electrode to break-in polymer film in an electrolyte solution consisting of 0.1 M $TBAPF_6$ dissolved in CH_3CN at a scan rate of 100 mV/s (vs. Ag/AgCl).



Scheme 5. Photochemical switching and electrochemical polymerization of **1o** and **1c** states.

We were unable to determine the exact molecular weight of the polymer by gel permeation chromatography since it was insoluble in common organic solvents (CH_2Cl_2, $CHCl_3$, THF etc.). The redox properties of the polymer film **P1o** was investigated in a monomer free electrolyte solution consisting of 0.1 M $TBAPF_6$ in CH_3CN. The polymer film was cycled several times between its redox states in order to get reproducible results (see Figure 5b). After a certain number of cycles, the polymer exhibited a stable and reversible redox couple with a half wave potential of 0.69 V. Also, the peak current intensity of the redox couple increased with increasing scan rate and a linear increase in the peak currents as a function of the scan rates confirmed that the polymer **P1o** was tightly bound to the electrode surface and the redox process was non-diffusional (Figure 6).

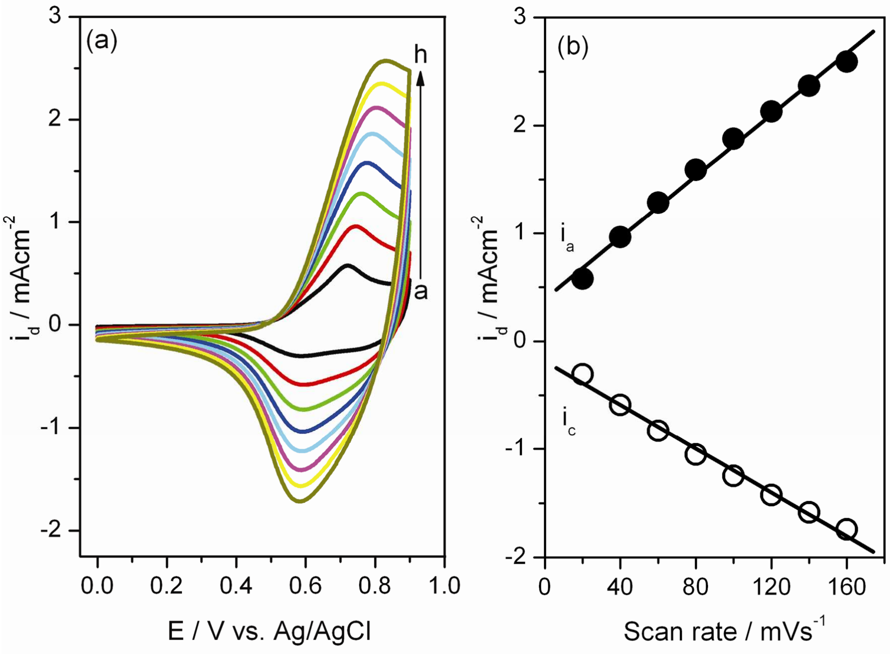


Figure 6. (a) Scan rate dependence of **P1o** on a Pt disk electrode in 0.1 M TBAH in CH_3CN at different scan rates (mVs^{-1}): a= 20; b= 40; c= 60; d= 80; e= 100; f= 120; g= 140 and h= 160. (b) Relationship of anodic (i_a) and cathodic (i_c) current peaks as a function of scan rate between neutral and oxidized states of **P1o** in 0.1 M $TBAPF_6$ in CH_3CN.

In order to elucidate the electropolymerizability of the two-isomers of compound **1** without distruption of the DTE units, electrochemical studies on the open (**1o**) and the closed (**1c**) states were extended. As expected, the formation of the polymer film **P1c** also proceeded smoothly when the closed isomer (**1c**) was subjected to polymerization (Scheme 5, Figure 7). Since peak currents of the redox couple of polymer film increased linearly as a function of scan rates, it was assumed that the corresponding polymer film **P1c** was tightly bonded to the electrode surface. These results clearly suggested that the electropolymerization of both the open (**1o**) and the closed (**1c**) states of this novel photochrome **1** can be achieved successfully without disturbing the pendant DTE units.

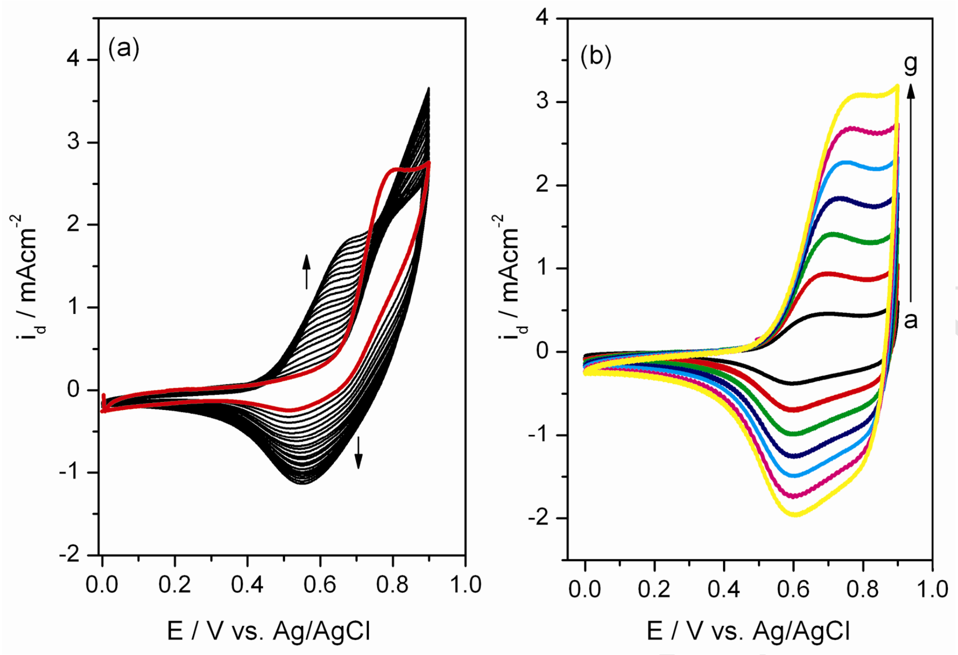


Figure 7. (a) Electropolymerization of **1c** (3.0 x 10^{-3} M) by potential scanning to give polymer **P1c** in an electrolyte solution consisting of 0.1 M $LiClO_4$ dissolved in C_2H_5OH and CH_2Cl_2 mixture (95:5, v/v) at a scan rate of 100 mV/s. The scan shown in red line is the first scan. (b) Scan rate dependence of **P1c** on a Pt disk electrode in 0.1 M TBAH in CH_3CN at different scan rates (mVs^{-1}): a= 20; b= 40; c= 60; d= 80; e= 100; f= 120 and g= 140.

It was reported that immobilization of molecules that function as switches (e.g. DTEs) might provide smart surfaces which could be controlled electrochemically or photochemically.[47-51] Indeed, it should be noted that immobilization and/or processability of the material is *sine qua non* in the context of practical and/or industrial applications, which are not accessible in solution state. Note that solution state does not always allow such applications. Keeping these facts in mind, it was envisaged that this novel photochrome **1** could also be used as an electrochromic switch due to the presence of SNS unit in the structure. In order to demonstrate the applicability of this novel photochrome **1** as electrochromicly switchable material, immobilization of **1** on ITO surface was investigated through electrochemical polymerization. Figure 8 depicts the cyclic voltammogram of **1o** during the polymerization process while the inset in Figure 8 depicts the modified **P1o**-ITO electrode, which was obtained by electropolymerization of **1o** as a mechanically stable and insoluble (CH_2Cl_2, toluene, CH_3CN) green film.

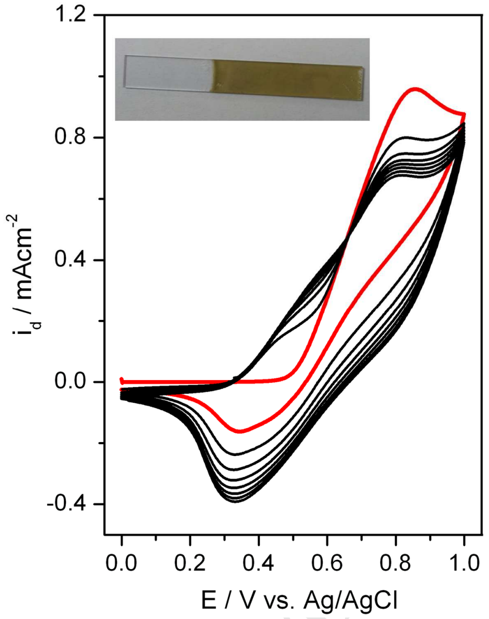


Figure 8. Electropolymerization of **1o** (1 x 10^{-5} M) by potential scanning to in an electrolyte solution consisting of 0.1 M $LiClO_4$ dissolved in C_2H_5OH-CH_2Cl_2 mixture (95:5, v/v) at a scan rate of 100 mV/s (vs. Ag/AgCl). Inset: photograph of **P1o** coated ITO electrode.

Surprisingly, DTE unit in **1** could not retain its photochemical switching properties after immobilization onto ITO. It was likely that the polymer structure was inflexible to accommodate the conformational requirements of the photoisomerization reaction. It should be noted that this was especially important in the case of DTEs since the ring-closing reaction could occur only from the *anti*-parallel conformation of the ring-open isomer.[1, 52] The morphology of the polymer film deposited on ITO was analyzed by AFM. Figure 9 demonstrates the AFM image of the **P1o** on ITO. The image unambiguously showed that the surface of the polymer film was rough.

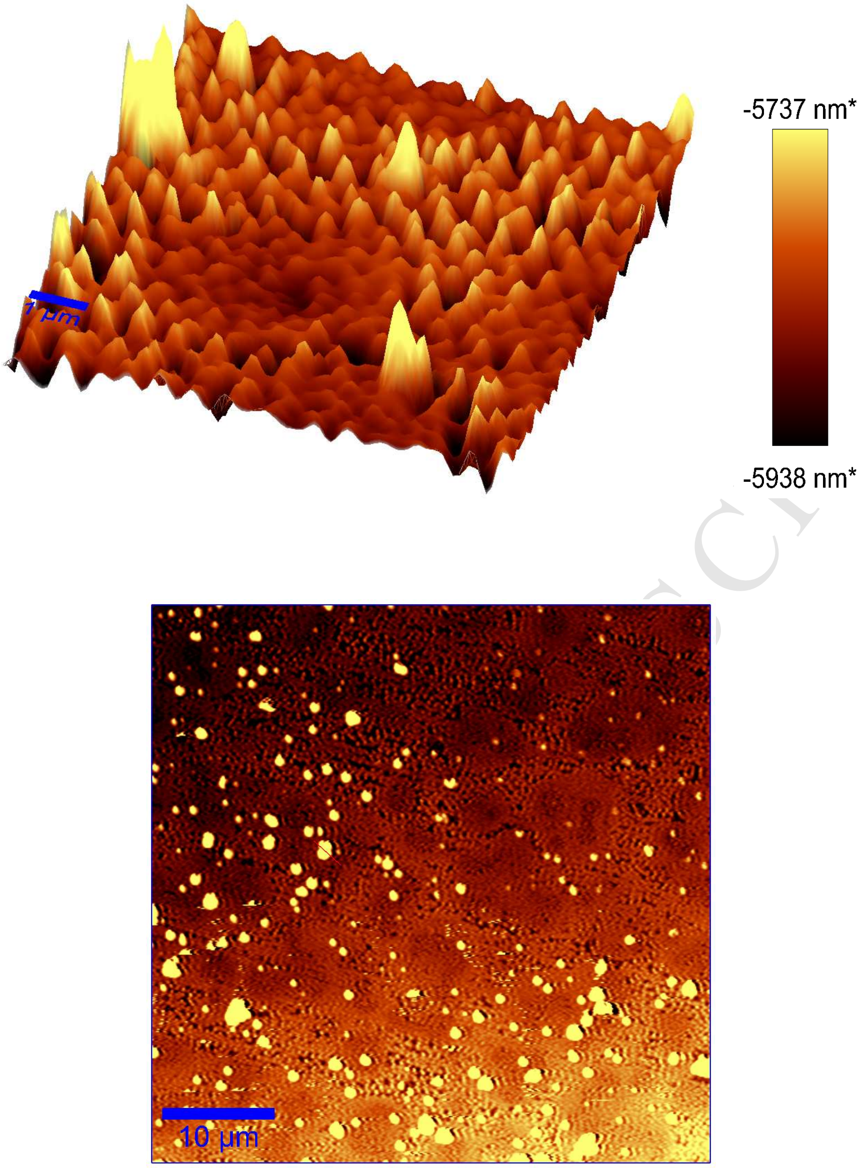


Figure 9. AFM image of **P1o** on ITO.

In view of the above facts, it was also reasonable to assume that the interconversion between parallel and antiparallel forms was not feasible within a densely-packed polymer film of **1**. Therefore, the polymer was found to be highly ordered and inflexible disallowing for conformational interconversion.

The modified ITO electrode exhibited a reversible redox couple at 0.65 V, when it was anodically scanned in a monomer-free electrolyte solution of 0.1 M $TBAPF_6$ in CH_3CN (Figure 10-inset). After constructing a simple device, the electrochromic features of the modified ITO electrode was examined by recording spectroelectrochemical behavior of the electrode under a variety of voltage pulses between 0.0 V and 0.9 V. During p-doping, the higher energy absorbance at a wavelength shorter than 500 nm (π-π* transition at 435 nm) started to decrease with an apparent new absorption band at around 650 nm, which was attributed to the formation of polaron charge (Figure 10). Upon further oxidation, the polaron charge carriers turned into the bipolaron charge carriers above 800 nm. The band gap (E_g) of the modified electrode was calculated from the onset of π-π* transition at 435 nm, and it was found to be 2.29 eV. In this process, it was assumed that charge carriers (polarons and bipolarons) were probably delocalized as the conformation of the polymer backbone on ITO was forced to be planarized to some extent. More importantly, as a result of these variations in the conformation of the polymer backbone and the absorption spectrum of the modified electrode, the color changed from green in the neutral state to violet upon doping (Figure 10). The reversibility of this process through redox cycling with full recovery of the initial state at 0.0 V unambigiously confirmed that the electrocyclic ring closure did not take place in the redox cycling of the polymer modified electrode. These results clearly indicated that the material exhibited remarkable electrochromic features that can be switched from green in the neutral state to violet state upon application of voltage pulses.

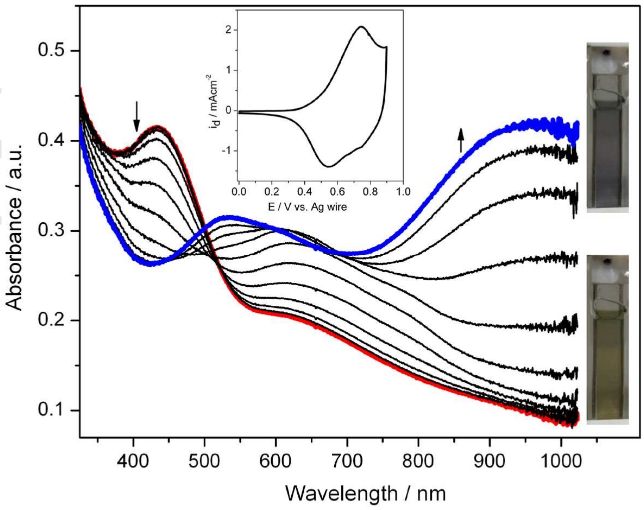


Figure 10. Electronic absorption spectra and colors of modified ITO electrode in 0.1 M TBAH-CH_3CN at various applied potentials between 0.0 V and 0.9 V. Inset: Cyclic

voltammogram of modified ITO electrode in an electrolyte solution consisting of 0.1 M $TBAPF_6$ dissolved in CH_3CN at a scan rate of 20 mV/s.

Switching time is the necessary time to change the color of the electrochromic polymer with 95 % of the full contrast (after which point the naked eyes could not sense the changes in the color) between various redox states. For this aim, a square-wave potential method was applied between 0.0 V and 0.9 V with 10 s time intervals. As depicted in Figure 11, the polymer film could be successfully switched between redox states bearing different colors in a response time of about 6.0 s for 95% of full optical switch.

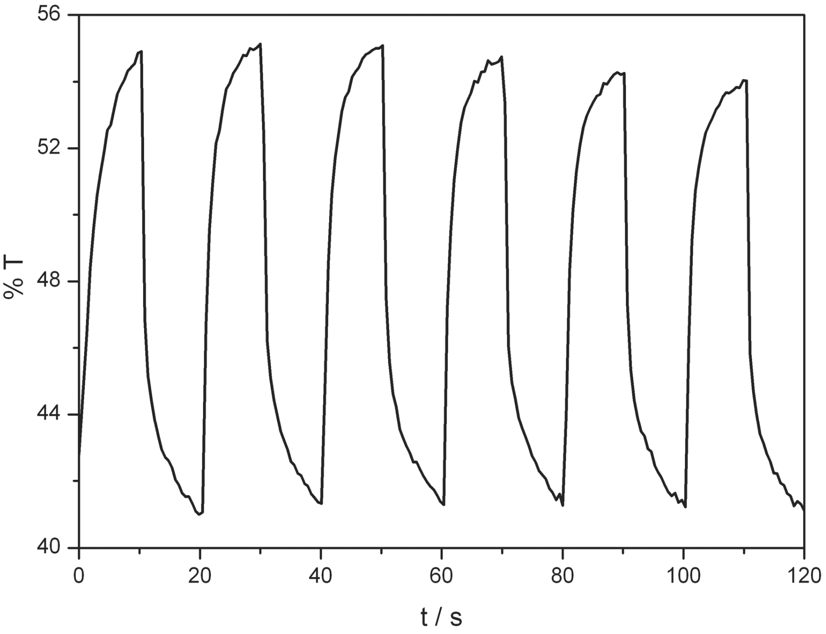


Figure 11. Chronoabsorptometry experiments for **P1o** on ITO in 0.1 M TBAH/ACN while the polymer was switched between 0.0 V and 0.9 V.

3. Conclusion

In conclusion, the synthesis, photochromism and electrochemistry of a novel material **1** with pendant DTE photochromic units are described. It should be noted that the system **1** can be reversibly and efficiently switched between open (**1o**) and closed (**1c**) states by light in both solution and in the solid PMMA matrix. It is also noteworthy that the two isomers (**1o** and **1c**) of this novel system **1** can be smoothly polymerized on ITO by electrochemical means. Surprisingly, the DTE unit in **1** does not retain its photochemical switching properties after immobilization onto ITO. On the other hand, it was found that the polymer exhibited remarkable electrochromic features that can be switched from green in the neutral state to violet state under applied external potentials without disturbing the photochromic units. Further work on the development of novel systems is currently underway in our laboratories.

4. Experimental

General Methods. All chemicals were purchased from Sigma Aldrich or Merck and used as received unless otherwise noted. FTIR spectra were recorded on a Perkin Elmer Spectrum 100 model FTIR with an attenuated total reflectance (ATR). ^{1}H (400 or 300 MHz) and ^{13}C (100 or 75 MHz) NMR spectra were recorded on a Bruker DPX-400 or Ultrashield 300 NMR Spectrometers. Combustion analyses were carried out by using a LECO CHNS-932 analyzer. Mass spectra were recorded on Waters SYNAPT MS system (TOF MS ESI$^+$) or Bruker Daltonics model MALDI TOF MS analyzer. UV-Vis and fluorescence measurements were recorded on Varian Cary 50 and Varian Cary Eclipse spectrophotometers, respectively. AFM images were collected using an atomic microscope (WITEC TS 150) in ac mode (42 N/m, 285 kHz). Data visualization was achieved using Witec Project Plus software.

0.1 M Tetrabutylammonium hexafluorophosphate (TBAH) dissolved in acetonitrile was used as electrolyte solution. A platinum button (0.02 cm^2) and a platinum wire were used as working and counter electrodes, respectively, as well as a Ag/AgCl reference electrode (calibrated externally using 10 mM solution of ferrocene/ferrocenium couple which is an internal standard calibrated to be 0.44 V in acetonitrile solution vs. Ag/AgCl). Melting points were determined on a Schorrp MPM-H2 model apparatus and are uncorrected. Column chromatography was performed on silica gel (60-200 mesh) from Merck Company. TLC was carried out on Merck 0.2 mm silica gel 60 F_{254} analytical aluminum plates. The synthesis of compound **10**[41] was carried out according to a previously published procedure.

Diethyl 2,4-diacetyl-3-(4-nitrophenyl)pentanedioate (4)

Compound **4** was synthesized according to literature method with little modification.[45-46] A mixture of 4-nitrobenzaldehyde (**2**, 0.06 mol), ethyl acetoacetate (**3**, 0.12 mol), and piperidine (2.4 mL) in 95% ethanol (60 mL) was placed in a one-neck flask and allowed to stand while stirring at room temperature until the mixture became solid (ca. 8 h). The solid was filtered, washed with 95% ethanol, and recrystallized twice from 95% ethanol to give a white powder 17.7 g (75% yield), m.p. 160-161 ^{o}C (lit. m.p. 158-160 ^{o}C)

3-(4-Nitrophenyl)pentanedioic acid (5)

4 (45 mmol) was dissolved in a mixture of distilled water (67.5 mL) and sodium hydroxide (67.5 g). The resulting mixture was refluxed vigorously for 3 h, and then cooled to room temperature and poured into water (340 mL). The resulting mixture was extracted with ether (2x100 mL). The water phase was acidified with concentrated hydrochloric acid (190 mL). The precipitated glutaric acid was removed by filtration and washed with cold water to remove sodium chloride. The acid was recrystallized from water and dried in vacuum to give a pale brown solid (6.84 g), 60% yield, m.p. 236-237 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 12.20 (s, 2H), 8.15 (d, *J* = 6.9 Hz, 2H), 7.57 (d, *J* = 6.9 Hz, 2H), 3.60-3.50 (m, 1H), 2.73 (dd, *J* = 8.1-8.1 Hz, 2H), 2.60 (dd, *J* = 8.1-8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 172.9, 152.1, 146.6, 129.4, 123.7, 39.9, 38.3; FTIR (cm^{-1}): 3209, 2983, 2933, 2907, 1696, 1607, 1515, 1402, 1347, 1311, 1286, 1250, 1220, 1186, 1162, 1118, 884, 862, 849, 753, 698. Anal. Calcd for $C_{11}H_{11}NO_6$: C, 52.18; H, 4.38; N, 5.53. Found: C, 52.16; H, 4.40; N, 5.57.

3-(4-Nitrophenyl)pentanedioyl dichloride (6)

$SOCl_2$ (0.45 mL, 6 mmol) was added to a suspension of diacid **5** (0.506 g, 2 mmol) in dry CH_2Cl_2 (20 mL) while stirring at room temperature. After 2 h, the mixture was heated under reflux overnight. The solvent was removed under reduced pressure and the diacid chloride **6** was directly used in the next step without further purification.

1,5-Bis(2,5-dimethylthiophen-3-yl)-3-(4-nitrophenyl)pentane-1,5-dione (8)

A solution of the diacid chloride **6** (0.58 g, 2 mmol) and 2,5-dimethylthiophene (**7**, 0.46 mL, 4 mmol) in dry CH_2Cl_2 (15 mL) was added dropwise to a suspension of $AlCl_3$ (0.64 g, 4.8 mmol) in dry CH_2Cl_2 (5 mL) while stirring magnetically at room temperature. After addition, the reaction mixture was allowed to stand at room temperature until all the starting materials were consumed. Cold water (20 mL) was carefully added to the mixture and the organic phase was washed with saturated $NaHCO_3$ solution (100 mL), and water (100 mL), and saturated NaCl solution (100 mL), dried with $MgSO_4$, filtered, and the solvent evaporated in vacuum to yield a brown solid. The solid was purified over silica gel column eluting with $CHCl_3$ to give **8** (0.45 g) as white solid in a yield of 50%. M.p. 176-179 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 8.15 (d, *J* = 8 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.00 (s, 2H), 4.09 (p, *J* = 6.94, 1H), 3.29 (dd, *J* = 16.4-16.8 Hz, 2H, A- part of AB system), 3.18 (dd, *J* = 16.5-16.8 Hz, 2H, B- part of AB system), 2.60 (s, 6H), 2.40 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 193.4, 152.2, 148.0, 146.5, 135.4, 135.0, 128.5, 125.6, 123.7, 47.2, 36.5, 16.0, 14.9; FTIR (cm^{-1}): 2917, 2897, 2856, 1664, 1596, 1509, 1483, 1396, 1346, 1233, 1124, 1111, 1077, 973, 957, 871, 833, 822, 757, 725, 697, 683. Anal. Calcd for $C_{23}H_{23}NO_4S_2$: C, 62.56; H, 5.25; N, 3.17; S, 14.52. Found: C, 62.55; H, 5.27; N, 3.19; S, 14.56. MALDI TOF MS Calcd for $C_{23}H_{23}NO_4S_2$: 441.56, found: 442.582 $[M+H]^+$.

3-(4-Aminophenyl)-1,5-bis(2,5-dimethylthiophen-3-yl)pentane-1,5-dione (9)

A mixture of **8** (0.442 g, 1 mmol), $SnCl_2$ (0.76 g, 4 mmol) and conc. HCl (7.5 mL) in ethanol (30 mL) was heated under reflux until **8** was totally consumed. The yellow mixture was allowed to cool to room temperature and most of the solvent was removed. The product was extracted with CH_2Cl_2 (3x100 mL) after neutralization with saturated $NaHCO_3$ solution (100 mL). Organic phases were washed with water (100 mL), and saturated NaCl solution (100 mL), dried with $MgSO_4$, filtered, and the solvent was evaporated in vacuum to yield **9** (0.370 g) as yellow viscous oil in 90% yields. ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 7.03 (d, *J* = 9.1 Hz, 2H), 6.62 (d, *J* = 9.1 Hz, 2H), 7.00 (s, 2H), 3.83 (p, *J* = 7.0 Hz, 1H), 3.18 (dd, *J* = 12.1-16.1

Hz, 2H, A- part of AB system), 3.05 (dd, *J* = 20.7-11.5 Hz, 2H, B- part of AB system), 2.58 (s, 6H), 2.40 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 195.5, 147.2, 144.7, 135.6, 134.9, 134.1, 128.2, 126.0, 115.9, 48.0, 36.3, 15.0, 14.1; FTIR (cm^{-1}): 3458, 3368, 3225, 2919, 1662, 1623, 1548, 1517, 1477, 1439, 1411, 1365, 1322, 1236, 1252, 1221, 1181, 1126, 1034, 970, 951, 823, 776, 733, 701, 679. Anal. Calcd for $C_{23}H_{25}NO_2S_2$: C, 67.12; H, 6.12; N, 3.40; S, 15.58. Found: C, 67.09; H, 6.15; N, 3.43; S, 15.60. MALDI TOF MS Calcd for $C_{23}H_{25}NO_2S_2$: 411.13, found: 412.45 $[M+H]^+$.

3-(4-(2,5-Di(thiophen-2-yl)-1H-pyrrol-1-yl)phenyl)-1,5-bis(2,5-dimethylthiophen-3-yl)pentane-1,5-dione (11)

A solution of **9** (0.412 g, 1 mmol), **10** (0.25 g, 1 mmol) and p-toluenesulfonic acid (5 mg) in dry toluene (75 mL) were heated under reflux in a Dean–Stark apparatus until all the starting materials were consumed. The flask was cooled and the solvent was removed under reduced pressure. The residue was filtered through a short pad of silica gel by eluting with CH_3OH/CH_2Cl_2 (1%, v/v) to give analytically pure **11** (0.313 g) as gray solid in 50% yield. M.p. 117-119 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.30 (d, *J* = 9 Hz, 2H), 7.21 (d, *J* = 9 Hz, 2H), 7.04 (s, 2H), 6.96 (dd, *J* = 5-1 Hz, 2H), 6.74 (dd, *J* = 5-3 Hz, 2H), 6.51 (s, 2H), 6.45 (dd, *J* = 3-1 Hz, 2H), 4.04 (p, *J* = 8 Hz, 1H), 3.28 (dd, *J* = 16-7 Hz, 2H, A- part of AB system), 3.14 (dd, *J* = 16-7 Hz, 2H, B- part of AB system), 2.58 (s, 6H), 2.41 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 194.2, 147.4, 145.4, 136.7, 135.6, 135.2, 135.0, 130.1, 129.9, 128.5, 126.8, 125.9, 124.0, 123.7, 109.6, 47.9, 37.0, 15.9, 15.0; FTIR (cm^{-1}): 3101, 3071, 3035, 2952, 2921, 2893, 2851, 1665, 1544, 1511, 1476, 1412, 1366, 1229, 1221, 1127, 846, 833, 824, 768, 742, 691. Anal. Calcd for $C_{35}H_{31}NO_2S_4$: C, 67.16; H, 4.99; N, 2.24; S, 20.49. Found: C, 67.15; H, 4.97; N, 2.26; S, 20.53. MALDI TOF MS Calcd for $C_{35}H_{31}NO_2S_4$: 625,89, found: 625,69 $[M]^+$.

1-(4-[3,4-Bis(2,5-dimethyl-3-thienyl)cyclopent-3-en-1-yl]phenyl)-2,5-di-2-thienyl-1H-pyrrole (1)

A mixture of **11** (0.626 g, 1 mmol), $TiCl_3(THF)_3$ (0.742 g; 2 mmol) and Zn dust (0.163 g; 2.5 mmol) in dry THF (20 mL) was heated to 40 ^oC under inert atmosphere (N_2) for 1 h. The mixture was allowed to cool to room temperature and the solvent was removed. The product was isolated by filtering through a short pad of silica gel by eluting with n-hexane/CH_2Cl_2 (5%, v/v) as colorless liquid. Yield: 49%, 0.29 g. ^1H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.29 (d, *J* = 9 Hz, 2H), 7.16 (d, *J* = 9 Hz, 2H), 6.95 (dd, *J* = 5-1 Hz, 2H), 6.73 (dd, *J* = 5-4 Hz, 2H), 6.47-6.46 (m, 4H), 6.36 (bs, 2H), 3.63 (p, *J* = 8 Hz, 1H), 3.18 (dd, *J* = 14-8 Hz, 2H, A- part of AB system), 2.83 (dd, *J* = 14-8 Hz, 2H, B- part of AB system), 2.28 (s, 6H), 1.82 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 148.4, 136.2, 135.3, 133.0, 132.6, 130.2, 129.9, 126.8, 125.9, 123.9, 109.6, 46.4, 42.1, 15.2, 14.0; FTIR (cm^{-1}): 3103, 3069, 3040, 2915, 2852, 2734, 1721, 1673, 1563, 1511, 1430, 1413, 1378, 1350, 1323, 1299, 1264, 1223, 1198, 1140, 1105, 1072, 1044, 1015, 973, 910, 896, 843, 824, 763, 736, 689. Anal. Calcd for $C_{35}H_{31}NS_4$: C, 70.78; H, 5.26; N, 2.36; S, 21.60. Found: C, 70.75; H, 5.21; N, 2.32; S, 21.55. MALDI TOF MS Calcd for $C_{35}H_{31}NS_4$: 593,13, found: 593,117 $[M]^+$.

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Supporting Information

Copies of ^1H, ^{13}C NMR and HRMS spectra for all new compounds. This material is available free of charge via the Internet.

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Supporting Information

Design, synthesis, photochromism and electrochemistry of a novel material with pendant photochromic units

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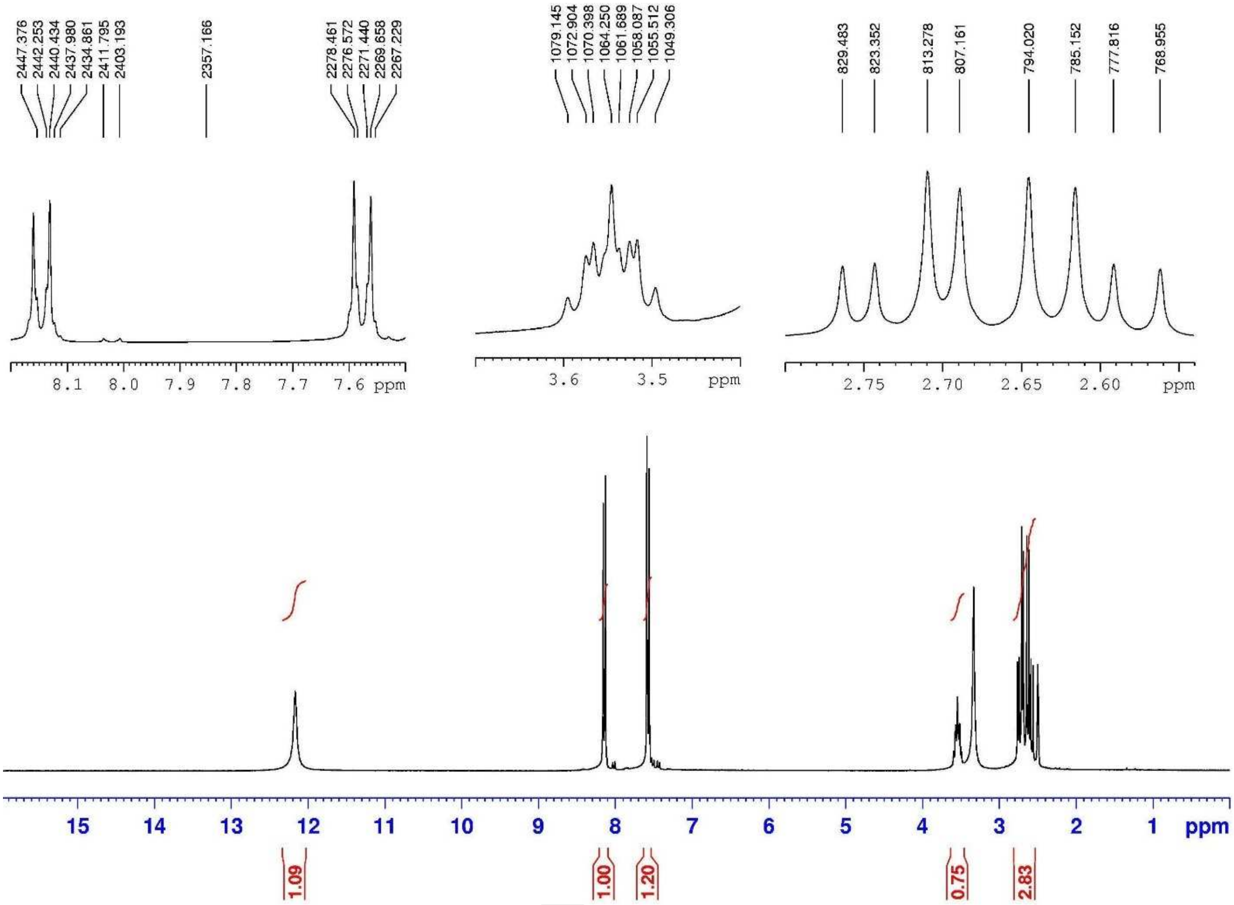


Fig. S1. ^{1}H NMR spectrum of **5** (300 MHz, DMSO-d_6).

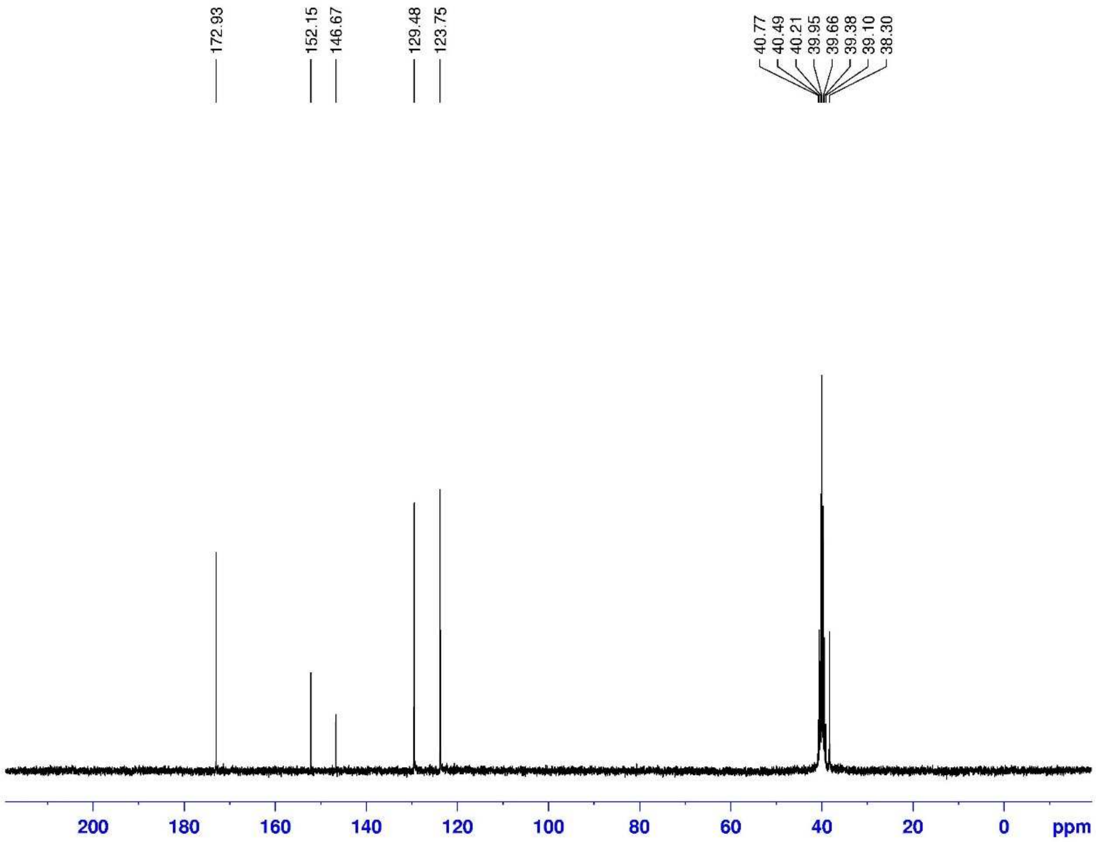


Fig. S2. ^{13}C NMR spectrum of **5** (75 MHz, DMSO-d$_6$).

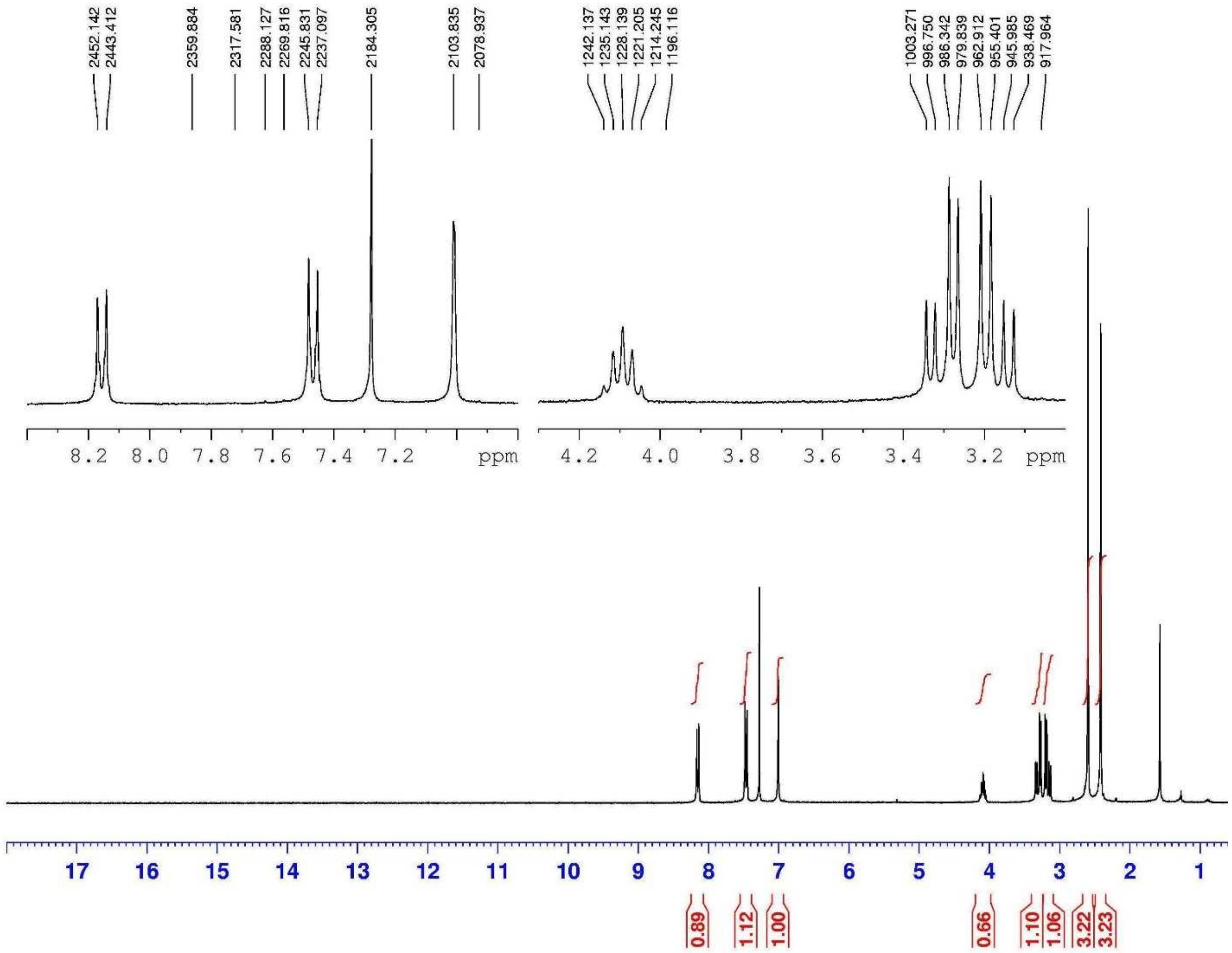
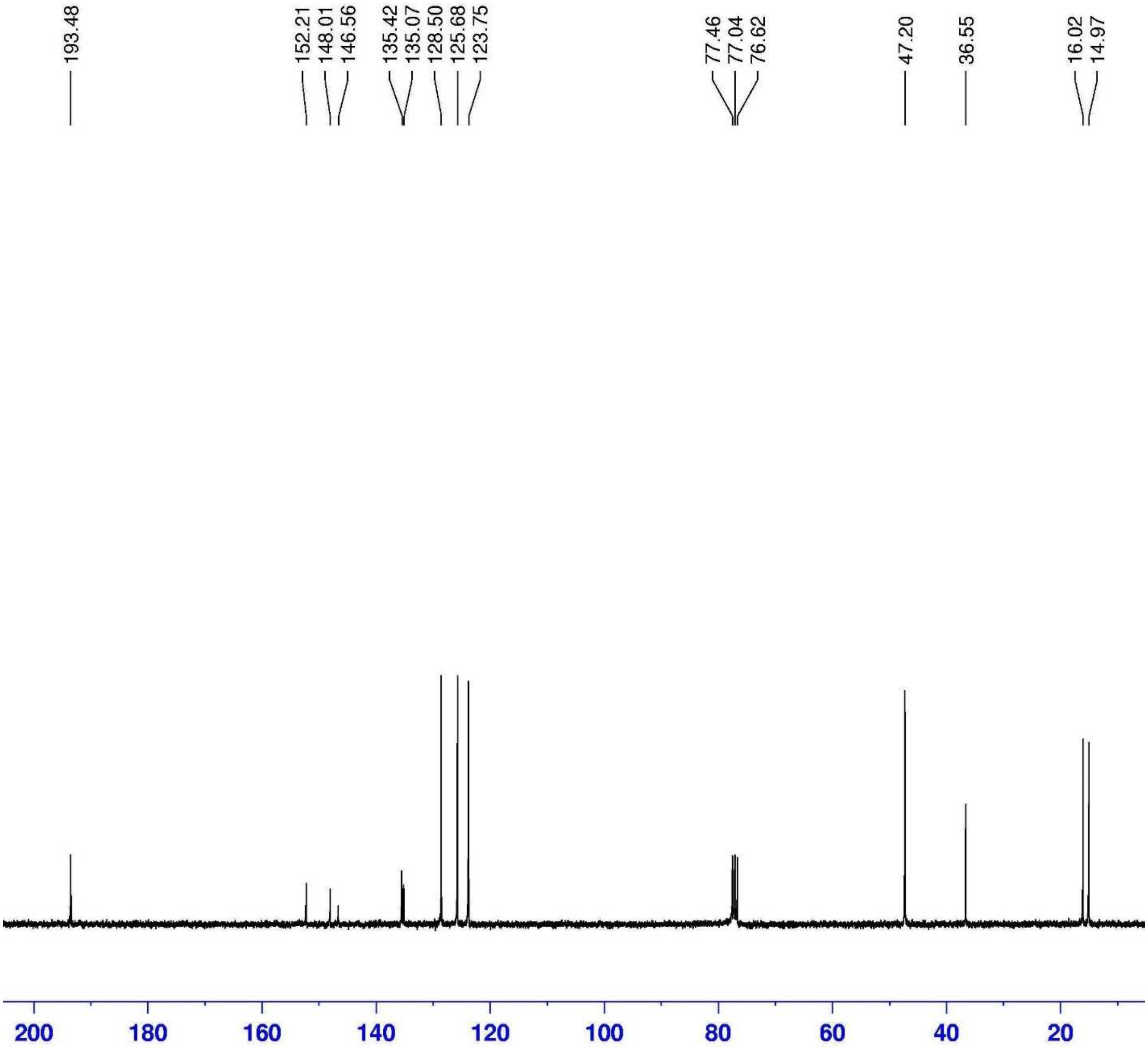


Fig. S3. ^{1}H NMR spectrum of **8** (300 MHz, $CDCl_3$).



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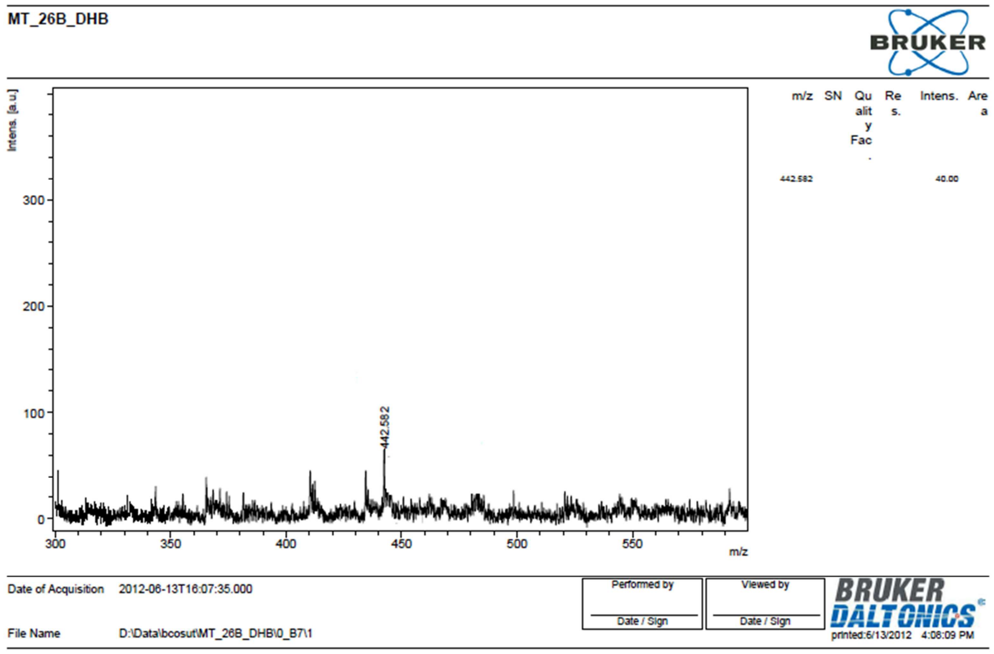

Fig. S5. MALDI TOF Mass spectrum of **8**.

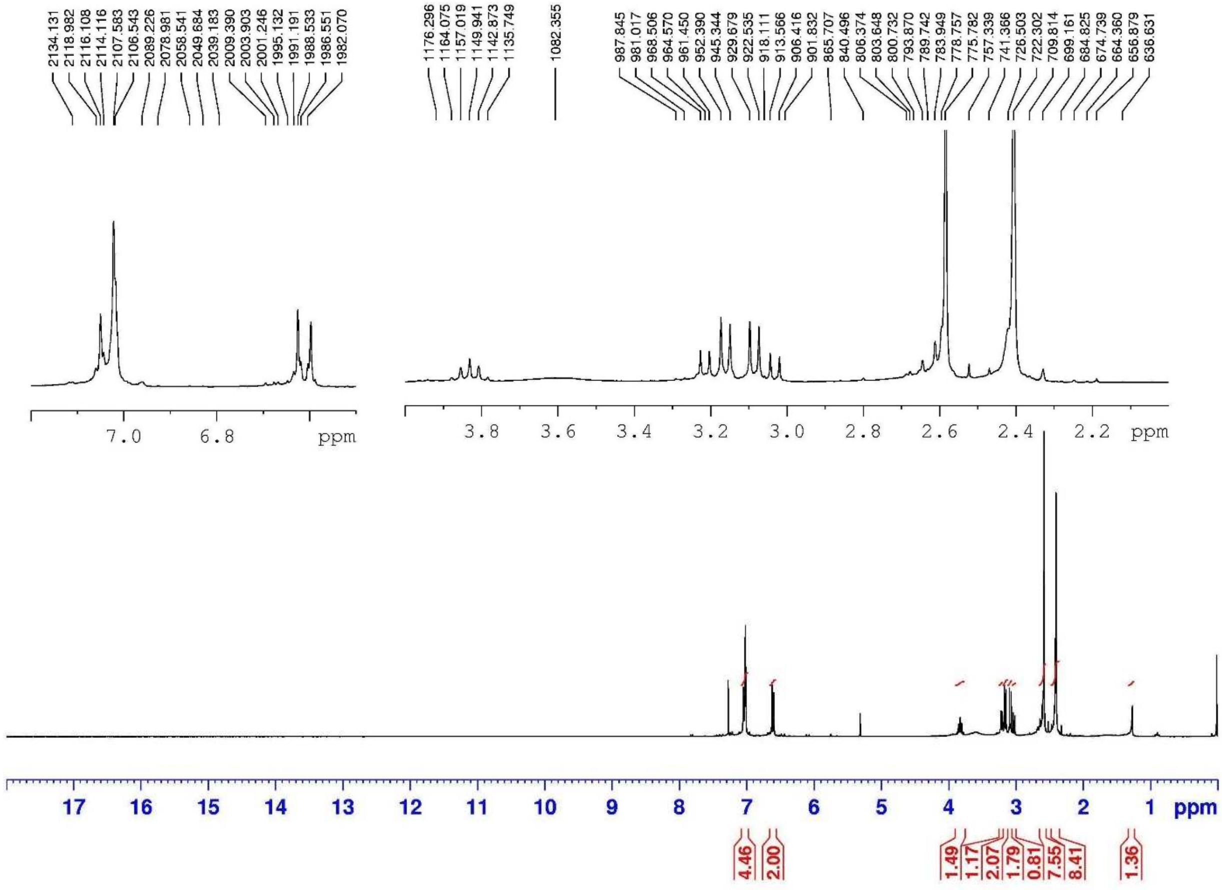

Fig. S6. ^{1}H NMR spectrum of **9** (300 MHz, CDCl$_3$).

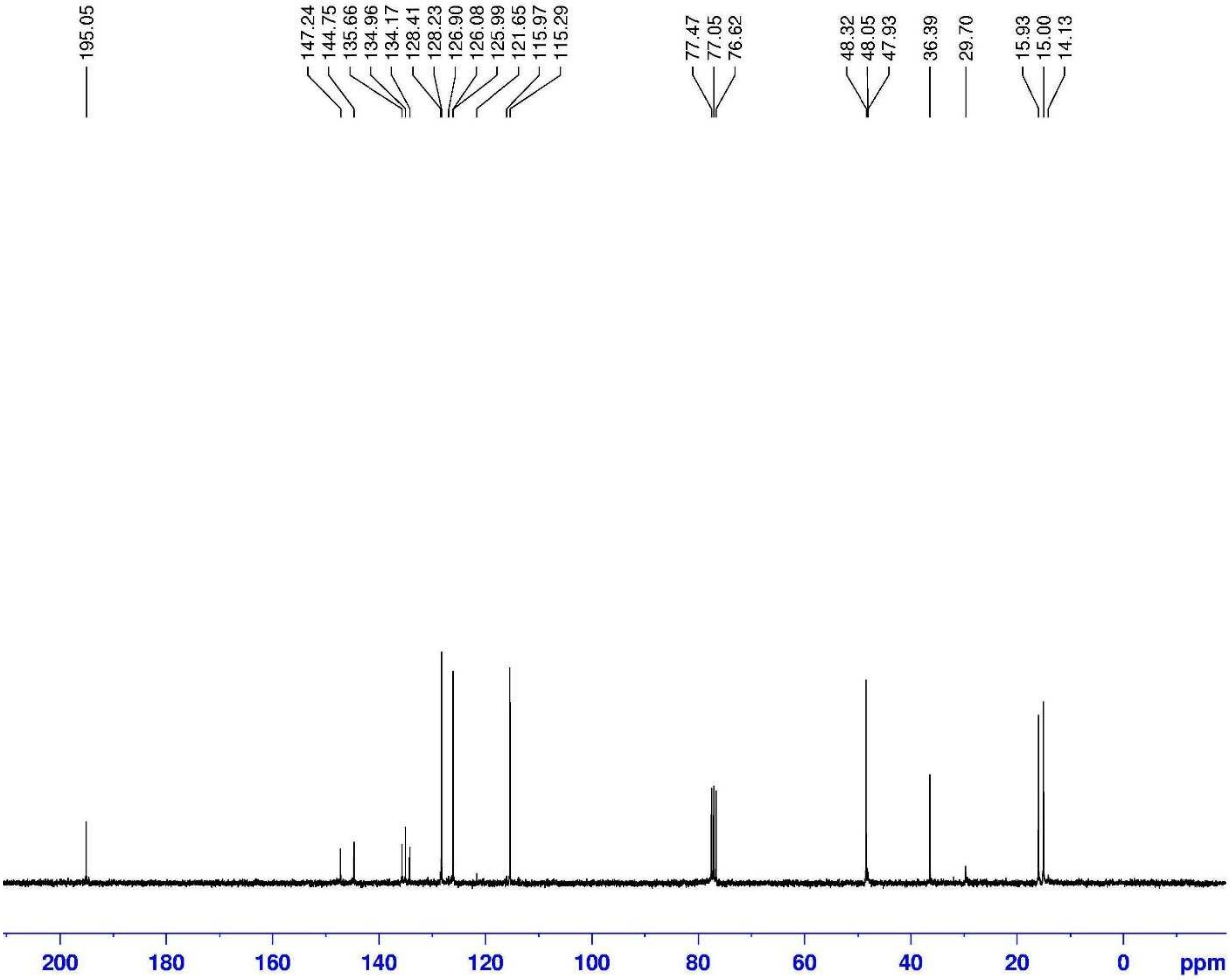

Fig. S7. ^{13}C NMR spectrum of **9** (75 MHz, $CDCl_3$).

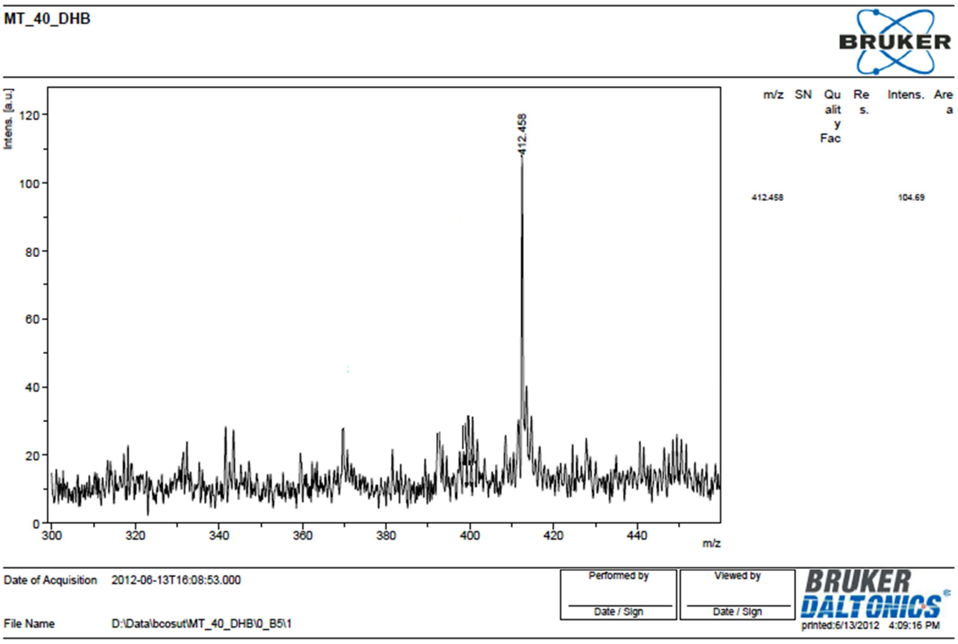

Fig. S8. MALDI TOF Mass spectrum of **9**.

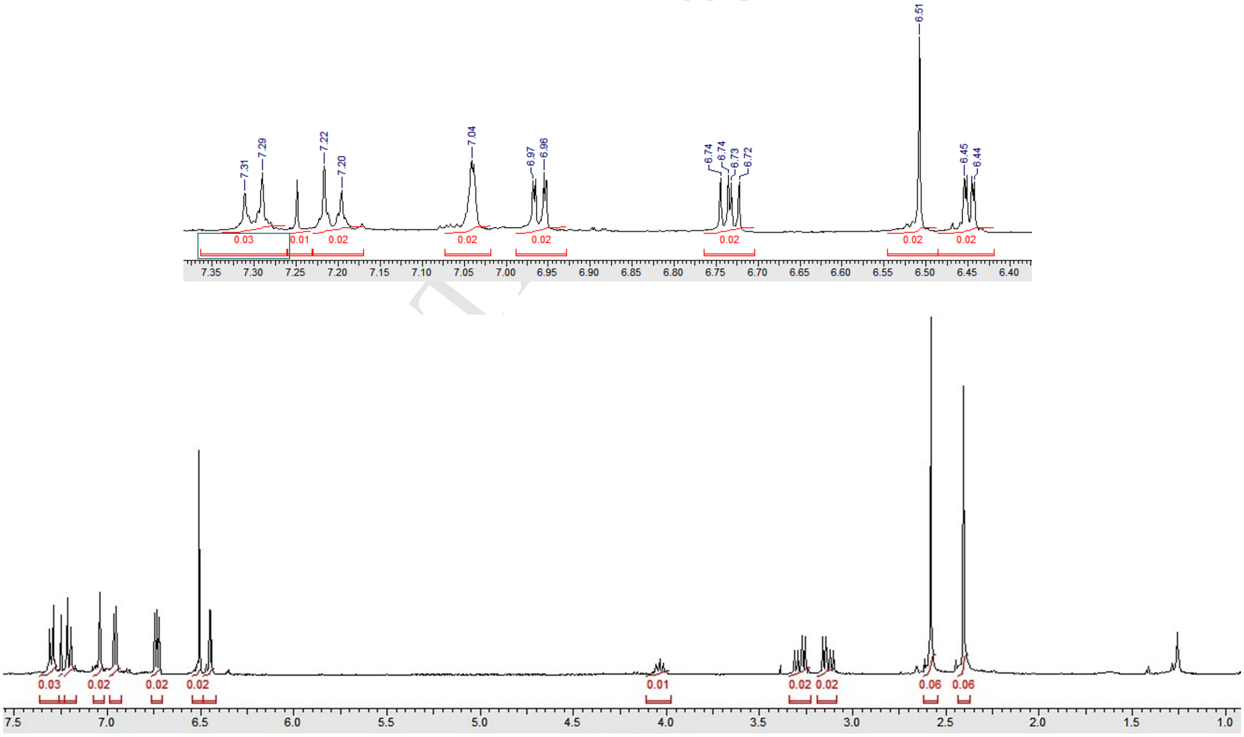

Fig. S9. ^{1}H NMR spectrum of **11** (400 MHz, $CDCl_3$).

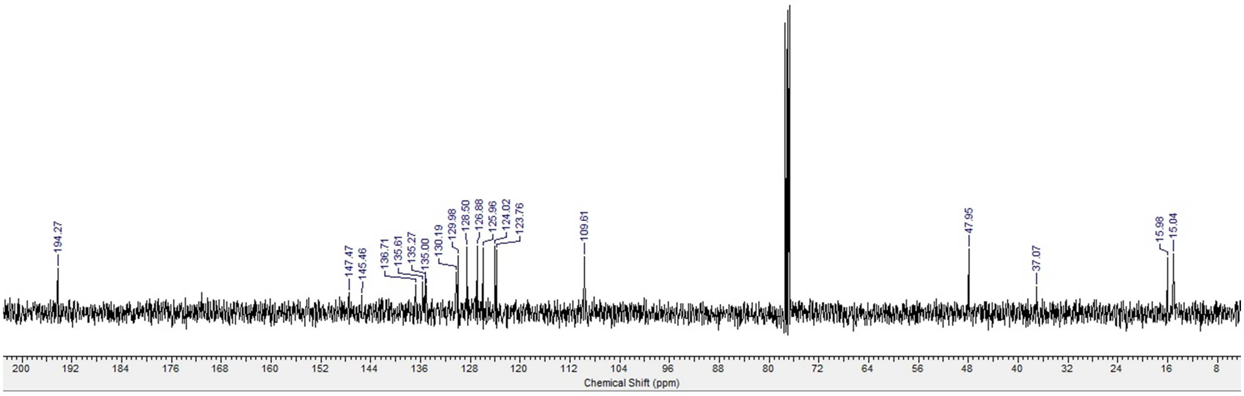

Fig. S10. ^{13}C NMR spectrum of **11** (100 MHz, $CDCl_3$).

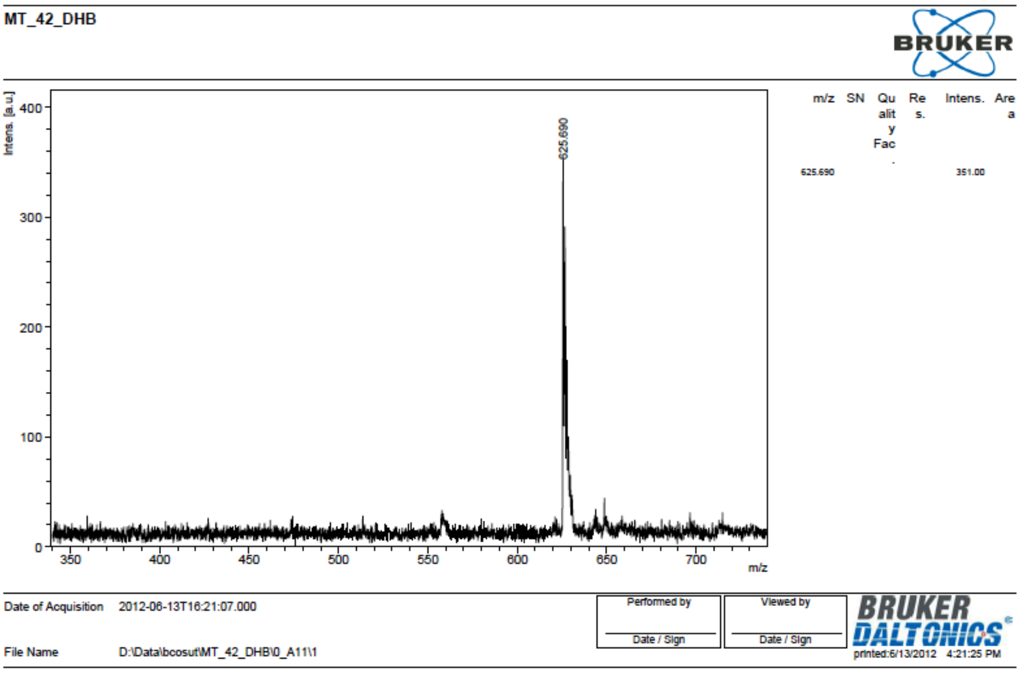

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Fig. S11. MALDI TOF Mass spectrum of **11**.

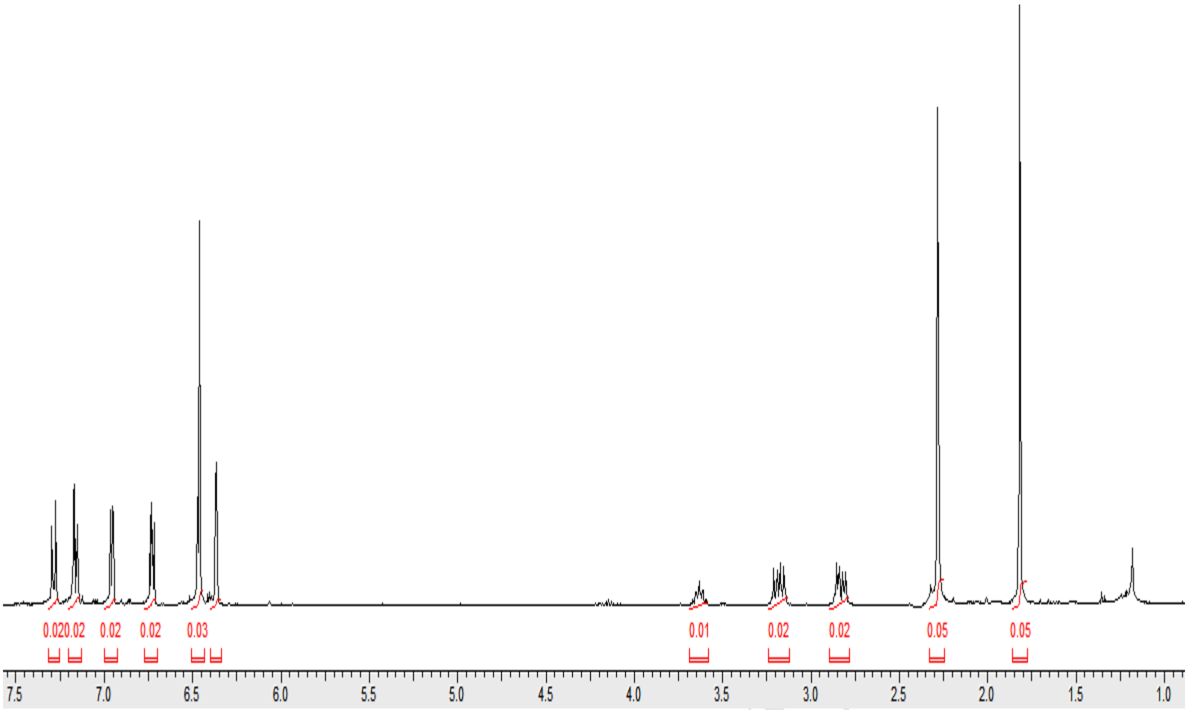


Fig. S12. ^{1}H NMR spectrum of **1** (400 MHz, CDCl$_3$).

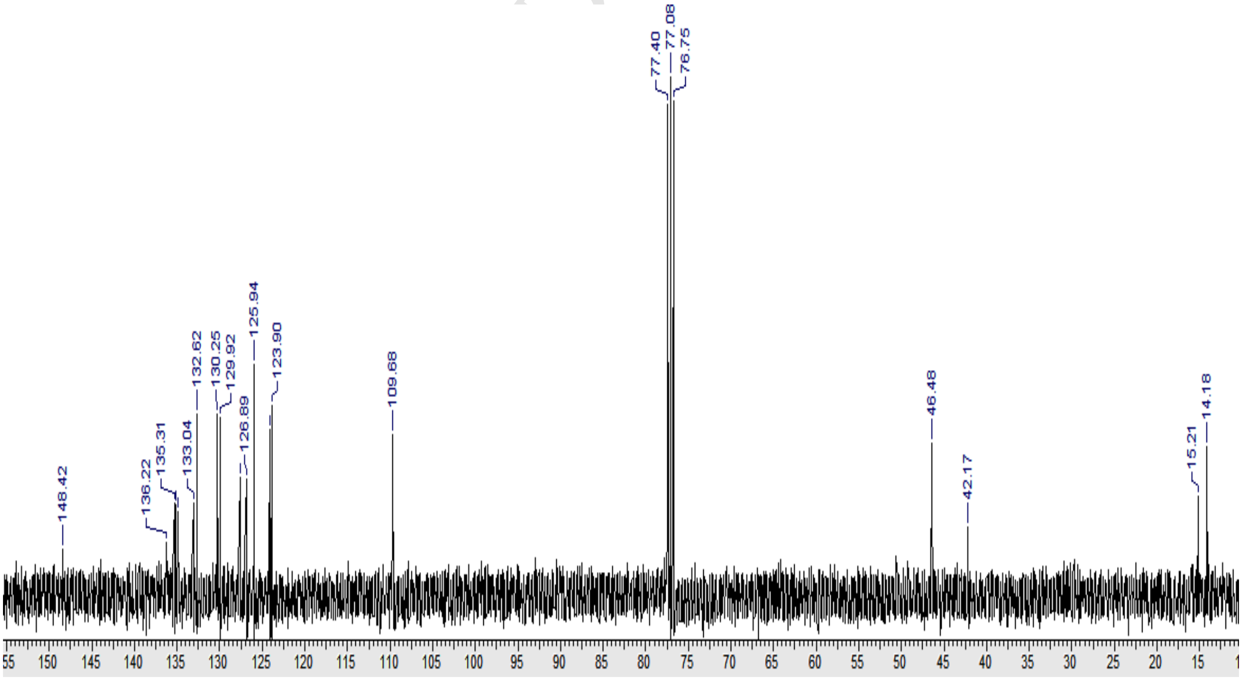
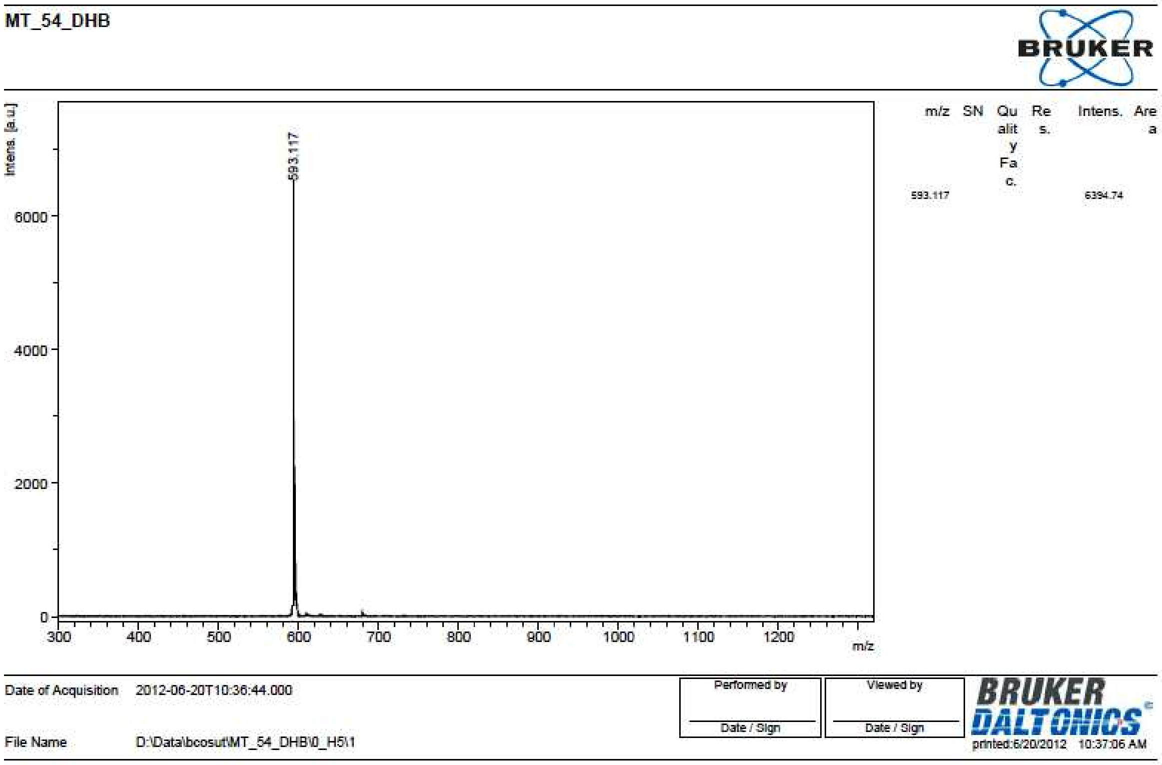


Fig. S13. ^{13}C NMR spectrum of **1** (100 MHz, CDCl$_3$).



MT_54_DHB

m/z	SN	Quality Fac.	Res.	Intens.	Area
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Date of Acquisition 2012-06-20T10:36:44.000

File Name D:\Data\bcosut\MT_54_DHB\0_H5\1

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Fig. S14. MALDI TOF Mass spectrum of **1**.