Synthesis of Azulene Conjugated Polymers by Cross-Coupling Reaction Catalyzed by Palladium Complexes

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Introduction

Azulene, as a non alternant aromatic hydrocarbon with a beautiful dark blue color, has been the object of most scientific research over the past few decades [1–12]. This interest was due to its unusual electronic structure and abnormal photophysical properties, including a polarized structure with a dipole of about 1.08 D [13] and unusual anti-Kasha’s S2→S0 fluorescence [14–21].

To date, azulene has received great attention in various fields of research of functional materials, such as conductive polymers, optoelectronic molecular switches, field effect transistors (OFETs), organic light-emitting diodes (OLEDs), solar cells (OSCs), nonlinear-optical (NLO) and other materials [22–33].

A number of works on the synthesis of azulene-containing polymers are described in the literature. Thus, the obtained polyazulene was first reported by the authors of the article [34]. Somewhat later new methods for obtaining polyazulene, as well as the synthesis of a number of conducting azulene containing polymers were described [35–37].

Unlike other condensed aromatic compounds, azulene exhibits abnormal fluorescence from the S2 state and only weak fluorescence from the S1→S0 [38]. This is due to a large energy gap between S1 and S2 states, and non-radiative radiation from S1 to the ground state, leading to weak S1→S0 fluorescence [39].

The structure of azulene 1 (Figure 1) can be considered as a tropylium cation condensed with an anionic pentadienyl carbocycle. The electron-sufficient cyclopentane azulene ring can rapidly undergo aromatic electrophilic substitution at C1 or C3 to form a stabilized aromatic azulene ion with 6 π-electrons [40–42]. It has been reported that the formation of tropylium structure in a number of azulene derivatives leads to interesting electrochemical and electrochromic properties [43–46]. It follows that such an available chemical transformation of azulene-containing polymers leading to the formation of stable ions can be used to regulate the general physical properties of the conjugated polymers, such as, for example, the “switching on” of fluores-
ence or a change in electrical conductivity, etc. In addition, azulene can easily lose one electron upon oxidation to form a cation radical in which the cation moiety exists as an aromatic tropylium ion. It is also known that azulene has rather low oxidizing potential and is oxidized easier, than the majority of widespread aromatic hydrocarbons [47, 48].

Thus, azulene-based conjugated polymers are expected to readily enter acid-base and redox reactions to form azulene cations/cation radicals and potentially function as effective optoelectronic materials.

![Figure 1. Polarized resonant structure of azulene 1](image)

In this paper, we report the synthesis of two fluorene-azulene π-conjugated copolymers: poly[2,7-(9,9-didodecylfluorenyl)-alt-(1',3'-azulenyl)] 3 and poly[1,3-bis(9,9-didodecylfluorene-2'-yl)azulenyl]-alt-[1'”,3’’-azulenyl] 5, via Suzuki–Miyaura cross-coupling reaction using Pd$_3$(dba)$_2$ as catalyst. This molecular construction uses both the dipole moment of the azulene unit and the feature of acquiring and losing protons in the electron donor five-membered azulene ring. The orientation of the azulene units in the conjugate copolymer 3 was random, and the attachment of the azulene units to the 2,7-fluorene unit makes the structure of the copolymer 5 more regular. The work studied the photophysical properties of the obtained copolymers, as well as their physicochemical properties in protonated states. It was shown that the synthesized copolymers 3 and 5 do not fluoresce in neutral solvents, but in acidic tetrahydrofuran, fluorescence is “switched on”.

**Experimental**

$^{1}$H and $^{13}$C NMR spectra were taken on a Jeol ECA-500 spectrometer [operating frequency 500.15 MHz ($^{1}$H) and 100.61 MHz ($^{13}$C)] in CDCl$_3$, internal standard — TMS. IR spectra were recorded on a Fourier spectrometer Avatar-360 in KBr tablets. Mass spectra were obtained on a Thermo Scientific LTQ FT Ultra spectrometer. Elemental analysis was performed on the EuroVektorEA-3000 instrument. Absorption spectra were taken on a Shimadzu UV-1800 spectrophotometer. Fluorescence spectra were recorded on an Agilent Cary Eclipse spectrofluorimeter. Thermogravimetric studies were carried out on a TGA Q500 instrument (in N$_2$ flow; heating at a rate of 10° per minute; range 20–500 °C). Differential scanning calorimetry was performed on a DSC Q2000 (in N$_2$ flow; heating at a rate of 5° per minute; range 20–300 °C). Gel permeation chromatography was performed on Agilent PL-GPC 220 (polystyrene standard; THF eluent). The melting points were determined on a Melting Point M-560 apparatus.

Azulene, 2,2’-(9,9-didodecyl-9H-fluorene-2,7-diyl)bis(1,3,2-dioxaborinane) (99.6 %, Pd$_2$(dba)$_3$ (99.8 %), Pd(PPh$_3$)$_3$ (99.8 %), P(o-tol)$_3$ (99 %), Et$_3$NOH (99 %), TFA (99.5 %), THF (99.9 %) as well as other reagents and solvents were purchased from Sigma-Aldrich and used without further purification. Dibromoazulene 2 was synthesized according to the literary method [49].

Poly[2,7-(9,9-didodecylfluorenyl)-alt-(1',3'-azulenyl)] (3). 17 mg (0.02 mmol) of Pd$_3$(dba)$_2$, 13 mg (0.04 mmol) of P(o-tol)$_3$ and 2 mL of tetraethylammonium hydroxide were added to a solution of 177 mg (0.62 mmol) of dibromoazulene 2 and 414 mg (0.62 mmol) of 2,2’-(9,9-didodecyl-9H-fluorene-2,7-diyl)bis(1,3,2-dioxaborinane) in 50 mL toluene under argon. The reaction mixture was stirred for 20 hours at 80 °C. After reaction completion, 100 ml of chloroform was added to the reaction flask, then washed with water in a separatory funnel. The resulting chloroform phase was concentrated in vacuo to 10 mL and added to 300 mL of methyl alcohol. The resulting precipitate was purified by various organic solvents in a Soxhlet apparatus. The product was then recovered by chloroform, precipitated from methyl alcohol, dried under vacuum. A dark orange solid was obtained. Yield 250 mg (65±0.17 %). Anal. calcd. for (C$_{30}$H$_{32}$): C 90.04; H 9.05; Found: C 89.57; H 10.38. $M_w$ = 9.5 kDa; PDI = 2.21. $^1$H NMR: $\delta$ 8.64 (m, 2H), 8.34 (m, 1H), 7.62-7.93 (m, 7H), 7.14 (m, 2H), 2.11 (m, 4H), 0.83-1.18 (m, 46H). $^{13}$C NMR: $\delta$ 151.52, 140.10, 139.63, 137.31, 137.64, 136.52, 136.51, 131.62, 129.41, 124.72, 123.64, 120.53, 55.52, 40.76, 32.54, 30.52, 29.63, 29.75, 24.55, 23.13, 14.24.

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2,7-Bis(3-bromoazulen-1-yl)-9,9-didodecyl fluorene (4). 23 mg (0.02 mmol) of Pd(PPh₃)₄ and 220 mg (0.8 mmol) of silver (I) carbonate were added to the solution of 200 mg (0.70 mmol) of bromoazulene 2 and 187 mg (0.28 mmol) of 2,2′-(9,9-didodecyl-9H-fluorene-2,7-diyl)bis(1,3,2-dioxaborinane) in 8 ml of tetrahydrofuran under argon. The reaction mixture was stirred for 16 hours at 80 °C. After reaction completion, 100 ml of water was added, then extracted with methylene chloride (3 × 50 ml). The organic phase was dried over MgSO₄, and the solvent was distilled off in vacuo. The residue was purified by silica gel column chromatography (hexane:ethyl acetate 9:1). A dark brown solid was obtained. Yield 540 mg (86 %±0.15 %). HRMS (EI): m/z [M⁺] calcd for C₉₆H₇₉Br₉ 911.8514, found 911.8521. ¹H NMR: δ 8.34 (s, 2H), 8.33 (d, J = 10.1 Hz, 2H), 7.84 (d, J = 7.7 Hz, 4H), 7.38 (s, 2H), 7.70–7.61 (m, 6H), 7.55 (d, J = 10.1 Hz, 2H), 2.10 (br.t, J = 7.0 Hz, 4H), 0.83–1.18 (m, 46H). ¹³C NMR: δ 152.03, 151.55, 144.32, 140.67, 138.71, 134.55, 127.88, 127.25, 125.26, 123.13, 120.42, 119.22, 55.67, 40.34, 31.85, 30.01, 29.25, 23.92, 22.71, 14.13. IR (ν, cm⁻¹): 2928, 2857, 1720, 1574, 1540, 1462, 1393, 1247 ± 1274.

Poly[1,3-bis(9′,9′-didodecylfluoren-2′-yl)azulenyl]-alt-[1′,3′-azulenyl] (5). 17 mg (0.02 mmol) of Pd₂(dba)₃, 13 mg (0.04 mmol) of P(o-tol)₃ and 2 ml of tetraethylammonium hydrogen were added to the solution of 565 mg (0.62 mmol) of compound 4 and 414 mg (0.62 mmol) of 2,2′-(9,9-didodecyl-9H-fluorene-2,7-diyl)bis(1,3,2-dioxaborinane) in 50 ml of toluene under argon. The reaction mixture was stirred for 13 hours at 80 °C. After reaction completion, 100 ml of chloroform was added to the reaction flask, then washed with water in separatory funnel. The received chloroformic phase was condensed in vacuum to 10 ml and added to 300 ml of methyl alcohol. The resulting precipitate was purified by various organic solvents in a Soxhlet apparatus. The product was then recovered by chloroform, precipitated from methyl alcohol, dried under vacuum. A dark orange solid was obtained. Yield 200 mg (60 %±0.17 %). Anal. calcd. for (CₙHₙIₙ₂): C 90.99; H 9.01; Found: C 89.88; H 8.78. Mₘ = 70.8 kDa; PDI = 2.04. ¹H NMR: δ 8.20–8.38 (m, 2H), 7.84–7.98 (m, 2H), 7.72–7.82 (m, 2H), 7.56–7.71 (m, 2H), 7.35–7.49 (m, 2H), 1.08–0.78 (m, 46H). ¹³C NMR: δ 151.55, 140.12, 139.63, 137.34, 137.67, 136.53, 131.62, 129.41, 124.73, 123.64, 120.57, 55.56, 40.72, 32.54, 30.56, 29.67, 29.72, 24.54, 23.11, 14.25.

Synthetic routes leading to azulene conjugated copolymers 3 and 5 are presented in Schemes 1 and 2. As can be seen from Scheme 1, the key compound dibromoazulene 2 was obtained according to the literature method [49]. Further, by cross-coupling Suzuki–Miyaura between dibromide 2 and 2,2′-(9,9- didodecyl-9H-fluorene-2,7-diyl)bis(1,3,2-dioxaborinane) in toluene in the presence of catalyst Pd₂(dba)₃, copolymer 3 was obtained in a good 65 % yield.

Another key molecule bis(3-bromoazulenyl)-9,9-didodecylfluorene 4 (Scheme 2) was prepared in 86 % yield by combining Suzuki dibromoazulene 2 with 2,2′-(9,9-didodecyl-9H-fluorene-2,7-diyl)bis(1,3,2-dioxaborinane) in tetrahydrofuran in the presence of tetraakis-triphenylphosphine palladium as catalyst. Similarly, the Suzuki–Miyaura reaction between 4 and 2,2′-(9,9-didodecyl-9H-fluorene-2,7-diyl)bis(1,3,2-dioxaborinane) led to the formation of polymer 5 with the most regular structure and a yield of 60 %.

The obtained azulene copolymers 3 and 5 were easily dissolved in solvents such as dichloromethane, toluene, tetrahydrofuran, ethyl acetate. The average molecular weights of the obtained copolymers were determined by gel permeation chromatography (THF eluent). Thus, the Mn values of polymers 3 and 5 were 9.5 and 70.8 kDa, respectively, and the PDI were 2.21 and 2.04, respectively.

The chemical structure and purity of copolymers 3 and 5 have been proven by NMR and mass spectrometry as well as gel permeation chromatography and elemental analysis.

Results and Discussion

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The chemical structure and purity of copolymers 3 and 5 have been proven by NMR and mass spectrometry as well as gel permeation chromatography and elemental analysis.
Reaction conditions: (i) Pd(PPh$_3$)$_4$, Ag$_2$CO$_3$, THF, 75 °C; (ii) Pd$_2$(dba)$_3$, P(o-tol)$_3$, Et$_4$NOH, toluene, 85 °C

Scheme 2. Synthesis of π-conjugated copolymer 5

The thermal stability of copolymers 3 and 5 was investigated by nitrogen flow thermogravimetric analysis at a heating rate of 10 °C per minute. The onset of 3 and 5 decomposition (at a weight loss of 5%) was fixed at 418 °C and 432 °C, respectively, which indicates good thermal stability of the synthesized copolymers. Differential scanning calorimetry (DSC) measurements for copolymers 3 and 5 were performed at a scanning rate of 10 °C per minute. Neither endothermic nor exothermic transition was observed over the entire scanning range of 20 to 300 °C.

The absorption spectra of copolymers 3 and 5 in the UV-Vis range, including the protonated (trifluoroacetic acid doped) states are shown in Figure 2, and the corresponding data are summarized in Table 1.

In the electron absorption spectra of polymer 3 in tetrahydrofuran (THF), three absorption bands were observed with maxima at 345 ($\varepsilon = 75850$), 468 ($\varepsilon = 37120$) and 675 ($\varepsilon = 1050$) nm (Table 1). Similarly, polymer 5 showed two absorption bands of π-π * electron junction at 344 ($\varepsilon = 72500$) and 462 ($\varepsilon = 34900$) nm associated with long wave absorption at 673 ($\varepsilon = 1015$) nm. Weak absorption bands with maxima at 675 (for 3) and 673 (for 5) nm correspond to the energy transition of the $S_0 \rightarrow S_1$. 

Figure 2. UV-visible spectra of (a) 3 and (b) 5 (C=3·10$^{-5}$M in THF; addition of trifluoroacetic acid to THF)
Synthesis of Azulene Conjugated Polymers

As a result of protonation (by adding 5 %, 10 %, 15 %, 20 % trifluoroacetic acid) of copolymers 3 and 5 in THF, new absorption bands in the electron spectra with $\lambda_{\text{max}}$ at 534 nm (Table 1, Figure 2) were observed, characteristic of the 3-$\text{H}^+$ and 5-$\text{H}^+$ azulene polymers cations. Their absorption maxima showed a significant redshift of 182 nm compared to the original azulene 1 cation ($\lambda_{\text{max}}$ 352 nm [26]), due to the expansion of the π-conjugacy in the five-membered ring by fluorene fragments. In addition, isobestic points at 495 and 496 nm were observed in these spectra (Figure 2), suggesting the presence of convertible copolymers: neutral 3/5 and protonated 3-$\text{H}^+$ / 5-$\text{H}^+$.

Color changes of copolymers 3 and 5 were also observed in the study with the addition of different amounts of trifluoroacetic acid. In contrast to the dark blue color of the initial azulene 1, the solutions of copolymers 3 and 5 in tetrahydrofuran had a yellowish-green color. Addition of different concentrations of trifluoroacetic acid to the copolymer solution resulted in a color change from orange to dark green (Figure 2). Treatment of the protonated solutions of 3-$\text{H}^+$ and 5-$\text{H}^+$ polymers with triethylamine resulted in recovery of the initial state, which indicates a reversible protonation-deprotonation reaction.

It is known that, compared to colorless naphthalene (structural isomer of azulene), the color of azulene 1 is caused by weak repulsion energy between electrons on practically orthogonal HOMO and LUMO. It is also known that substitutions at the C1 or C3 atoms of azulene significantly change the electronic structure and optical properties [23]. Therefore, the color change is closely related to the change in the state of the HOMO/LUMO frontier molecular orbitals of azulene units 3 and 5 caused by protonation conditions. Thus, doping of 3 and 5 polymers with TFA led to the formation of polymeric azulenium cations, followed by a change in their color and electron spectrum.

The fluorescence spectra of copolymers 3 and 5, including protonated (doped with trifluoroacetic acid) states are presented in Figure 3, and the corresponding data are summarized in Table 1.

![Figure 3. Fluorescence spectra of 3 and (b) 5 (C=3⋅10^-5 M in THF; when trifluoroacetic acid is added to THF). The excited wavelengths ($\lambda_{\text{ex}}$) are 295 nm](image-url)

### Table 1

<table>
<thead>
<tr>
<th>Copolymers</th>
<th>Unprotonated</th>
<th>Protonated</th>
<th>Fluorescence $^a$</th>
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<td>Absorption</td>
<td>Fluorescence</td>
<td>Absorption</td>
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<td>$\lambda_{\text{abs}}$, nm</td>
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<tr>
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Notes: $^a\lambda_{\text{ex}}$ (excitation wavelength) = 295 nm for 3 and 5. $^b$ THF/TFA = volume to volume.

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As can be seen in Figure 3, the emission bands of 3 and 5 in THF were absent in the spectra. However, upon addition of trifluoroacetic acid (i.e., 5 %, 10 %, 15 %, 20 %) copolymer 3 and 5 solutions emitted light with λ_em at 380 nm (Table 1, Figure 3). It can be seen from the fluorescence spectra that the emission intensity of the copolymers changed depending on the concentration of trifluoroacetic acid. Thus, the intensity of 3 and 5 radiation reached its highest level at a 20 % concentration of TFA. However, further increase in TFA concentration resulted in a decrease in the fluorescence intensity. This was probably due to strong self-absorption (overlap of absorption and fluorescence bands), or to the presence of unprotonated azulene fragments in the polymer chain, also leading to a decrease in radiation intensity.

As described above, the abnormal anti-Kasha fluorescence of azulene from state S_2 state instead of S_1 was caused by the large S_1-S_2 energy gap. It is obvious that under the conditions of protonation of copolymers 3 and 5 with trifluoroacetic acid, followed by the formation of azulenyl cations, there is a noticeable change in the energy levels S_1 and S_2, as well as a decrease in the gap between HOMO and LUMO. The reduction of the HOMO-LUMO energy gap is obviously effected by the following factors: 1) the presence of azulenyl cations in the system and 2) a decrease in the degree of delocalization of π-electrons in the five-membered ring of azulene.

Therefore, it can be argued that the “switching on” of fluorescence in the 3-H^+ and 5-H^+ protonated copolymers is a consequence of a significant change in the energy levels of the HOMO-LUMO frontier molecular orbitals.

**Conclusions**

Thus, two fully carbon π-conjugated azulene-based copolymers have been developed and easily synthesized by the Suzuki-Miyaura cross-coupling reaction: poly[2,7-(9,9-didodecylfluoren-yl)-alt-(1',3'-azulenyl)] 3 and poly[1,3-bis(9,9'-didodecylfluoren-2'-yl)azulenyl]-alt-[1''',3'''-azulenyl] 5.

Synthesized copolymers 3 and 5 do not fluoresce due to the presence of azulene units in the system, which suppress the emission of polymers. However, in the presence of trifluoroacetic acid, copolymers 3 and 5 became fluorescent with emission maxima (λ_em) at 380 nm. The formation of azulenyl cations in 3-H^+ and 5-H^+ copolymers, which change the electronic properties, significantly affect the fluorescence activation. It was also found that solutions of copolymers 3 and 5 in tetrahydrofuran changed color significantly upon the addition of different amounts of trifluoroacetic acid. The obtained results demonstrate that the introduction of azulene units into the conjugated polymer chain has great potential for the development of new proton functional materials.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: Nurlan Merkhatuly writing — review & editing, supervision, project administration, methodology, investigation, funding acquisition, conceptualization; Saltanat Bolatovna Abeuova writing — review & editing, supervision; Amantay Nurbaevich Iskanderov investigation, formal analysis, data curation; Saltanat Kanatovna Zhokizhanova writing — original draft, investigation, data curation; Bibizhan Bakytzhanovna Erniyazova investigation, formal analysis, data curation.

Conflicts of Interest

The authors declare no conflict of interest.

References


