

Double Molecular Antenna Pyrene – Bridge - Fullerene C₆₀

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Abstract: C₆₀ pyrene anthrylvinylene triads were synthesized with good yields by an *O*-alkylation reaction of pyrene anthracene chloride derivatives and functionalized fullerene C₆₀. The presence of lateral butoxy chains imparts good solubility. The NMR data indicate the formation of only the *trans* isomers. After C₆₀ cyclopropanation, the UV-Vis spectra show the pyrene electronic transition with an absorption band extending from 400 to 800 nm due to the combination of the π - π electronic transition of the anthrylvinylene moiety and the C₆₀ band, regardless the extension of the anthrylvinylene moiety. However, the emission is almost mirror-like with respect to the absorption bands of pyrene, suggesting that the HOMO and LUMO are more localized on this substituent. All the obtained compounds were characterized by ¹H and ¹³C NMR, FTIR, UV-Vis, fluorescence spectroscopy, MALDI-TOF, Electrospray or FAB+ mass spectrometry, and elemental analysis.

Keywords: Molecular antennas, molecular rods, pyrene, anthracene, fullerene.

INTRODUCTION

In recent years, organic nanomaterials have inspired growing research efforts due to the great diversity of available organic π -conjugated macromolecules, [1-6] their good thermal and chemical stability [7] and electrical conductivity [8]. In addition, the flexibility in nanomaterial synthesis and their interesting size-dependent optical properties make these materials attractive candidates for scientific and industrial applications [9]. The π -conjugated molecules most intensively studied are the poly(arylenevinylene)s, in particular poly(p-phenylenevinylene)s (PPV). Several reports on PPV bearing different aromatic chromophores can be found in literature. Among them, anthracene gives particular optical properties for oligomers or poly(anthrylvinylene) [10]. Particularly, the emission properties of *trans*-(9-anthryl) ethylenes or anthryl styryl derivatives were demonstrated to be affected by geometric distortion around the single bonds [10, 11]. Recently, the photovoltaic properties have been reported for anthrylvinylene blended with fullerene [12]. In other works, pyrene or its derivatives have also been widely used as a fluorescence probe molecule due to the strong fluorescence and electron donor effect [13-15]. From the above, pyrene-anthrylvinylene are expected to be interesting dyads with electron donor character. On the contrary, fullerene C₆₀

is known to be a strong electron-acceptor group, usually used for solar cells based on conjugated molecules. Energy transfer from fullerene to either mixed or covalently attached conjugated oligophenylenevinylene (OPV) has been widely reported [16].

In continuation of our efforts to obtain novel oligophenylenevinylene structures for optoelectronic devices [17], in the present work we report on the synthesis and optical properties in solution of two novel C₆₀-pyrene-anthrylvinylene triads. Pyrene-containing anthracene and 4-styryl anthracene units were chosen as donor groups and fullerene C₆₀ as acceptor.

EXPERIMENTAL SECTION

Materials and Methodology

Solvents and reagents were purchased as reagent grade and used without further purification. Acetone was distilled over calcium chloride. Tetrahydrofuran (THF) was distilled from sodium and benzophenone. Column chromatography (CC) was performed on Merck silica gel 60Å (70-230 mesh). ¹H and ¹³C NMR were recorded on a Varian Unity-300 MHz with tetramethylsilane (TMS) as an internal reference. Infrared (IR) spectra were measured on a Nicolet FT-SSX spectrophotometer. Elemental analysis was determined by Galbraith Laboratories, INC Knoxville. FAB+ mass spectra were taken on a JEOL JMS AX505 HA instrument. Matrix-assisted laser desorption/ionization were taken with a Tof-Spec spectrometer. The UV-Vis absorption spectra were obtained with a Shimadzu 2401 PC spectrophotometer. A

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Perkin-Elmer LS-50 spectrofluorimeter was used for acquiring the fluorescence spectra, after exciting at 10 nm under the absorption lower energy peak. Quantum yields were calculated according to the formula (reported in ref. [22]). Quinine sulfate in H₂SO₄ 1N solutions were used as standard.

Compounds 1 and 4 were Obtained Following the Methodology Reported in Reference [18]

Synthesis of Alcohols 2 and 5

0.3 g (0.92 mmol) of 97 % lithium aluminum hydride (LiAlH₄) was dissolved in 10 mL of dry THF. To this emulsion, 0.4 g or 0.8 g (0.92 mmol) of 1 or 4 dissolved in 15 mL of dry THF were added dropwise using an addition funnel. The reaction was carried at 0 °C for 4 h. After this time, 10 mL of water were added and the reaction mixture was filtered in Celite®. The solvent was evaporated and the residue was dissolved in dichloromethane. The resulting solution was dried with sodium sulfate, filtered and the product was vacuum dried, and purified by CC (Al₂O₃, hexane).

(E)-10-[2-(1-Pyrenyl)ethenyl]-9-anthracenemethanol (2)

Yellow solid, mp >300°C, yield 0.39 g (0.90 mmol) 98 %. FTIR (pellet, KBr, cm⁻¹): 3393, 2912, 1594, 1439, 1356, 1106, 1046, 961, 846, 757. UV-vis (CHCl₃, nm) λ_{max}: 551, 396, 350, 260. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 3.90 (t, 1H, *J* = 7.2 Hz, OH), 5.61 (d, 2H, *J* = 5.1 Hz, CH₂-OH), 7.48 (d, 1H, *J* = 14.9 Hz, =CH), 7.49 (d, 1H, *J* = 8.6 Hz, Ar-H), 7.52 (d, 1H, *J* = 13.7 Hz, =CH), 7.54 (d, 1H, *J* = 8.6 Hz, Ar-H), 7.99 (d, 1H, *J* = 7.6 Hz, Ar-H), 8.03 (d, 1H, *J* = 2.5 Hz, Ar-H), 8.10 (d, 1H, *J* = 4.7 Hz, Ar-H), 8.14 (d, 1H, *J* = 3.3 Hz, Ar-H), 8.18-8.28 (m, 4H, Ar-H), 8.34 (d, 1H, *J* = 8.3 Hz, Ar-H), 8.49 (d, 1H, *J* = 9.3 Hz, Ar-H), 8.53 (m, 2H, Ar-H), 8.57 (m, 2H, Ar-H), 8.75 (d, 1H, *J* = 8.1 Hz, Ar-H). ¹³C NMR: (CDCl₃, 75 MHz), δ (ppm): 57.3 (CH₂-OH), 124.03 (HC_{Ar}), 124.8 (HC_{Ar}), 126.0 (=CH), 126.0 (C_{Ar}), 126.2 (HC_{Ar}), 126.4 (=CH), 127.0 (HC_{Ar}), 127.6 (HC_{Ar}), 128.4 (HC_{Ar}), 128.4 (C_{Ar}), 128.7 (HC_{Ar}), 129.6 (HC_{Ar}), 130.9 (C_{ipso}), 131.4 (C_{ipso}). EI-MS (*m/z*): 434 (M). Calc. for C₃₃H₂₂O: C 91.21; H 5.10 %. Found C, 91.19; H, 5.14 %.

(E,E,E)-10-[2-[2,5-Dibutoxy-4-[2-[10-[2-(1-pyrenyl)ethenyl]-9-anthracenyl]ethenyl]phenyl]ethenyl]-9-anthracenemethanol (5)

Yellow solid, yield 0.25 g (0.31 mmol) 34 %. FTIR (pellet, KBr, cm⁻¹): 3414, 2926, 2860, 1497, 1200, 1031, 842, 754. UV-vis (CHCl₃, nm) λ_{max}: 437, 364, 263. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 0.95 (m, 6H, CH₃), 1.60 (m, 4H, CH₂), 1.84 (m, 4H, CH₂), 3.71 (t, 1H, *J* = 7.4 Hz, OH), 4.19 (t, 4H, *J* = 5.8 Hz, CH₂-O), 5.74 (s, 2H, CH₂-OH), 6.84 (d, 1H, *J* = 16.5 Hz, =CH), 7.35 (d, 1H, *J* = 16.8 Hz, =CH), 7.37 (d, 1H, *J* = 16.5 Hz, =CH), 7.39 (d, 1H, *J* = 16.8 Hz, =CH), 7.45 (d, 1H, *J* = 16.8 Hz, =CH), 7.49-7.57 (m, 6H, Ar-H), 8.04 (d, 1H, *J* = 16.2 Hz, =CH), 8.05-8.13 (m, 5H, Ar-H), 8.19 (m, 6H, Ar-H), 8.32 (d, 2H, *J* = 7.8 Hz, Ar-H), 8.44 (dd, 1H, Ar-H), 8.48-8.60 (m, 5H, Ar-H), 8.67 (d, 2H, *J* = 8.1 Hz, Ar-H). ¹³C NMR: (CDCl₃, 75 MHz), δ (ppm): 13.8 (CH₃), 19.4 (CH₂), 31.6 (CH₂), 61.8 (CH₂-OH), 69.2 (CH₂-O), 111.3 (HC_{Ar}), 123.1 (HC_{Ar}), 123.8 (HC_{Ar}), 124.1 (C_{ipso}), 125.1 (HC_{Ar}), 125.1 (HC_{Ar}), 125.2 (HC_{Ar}), 125.4 (=CH), 125.9 (=CH), 126.0 (C_{Ar}), 126.3 (C_{Ar}), 126.5 (=CH), 126.7 (HC_{Ar}), 127.2 (C_{Ar}), 127.5 (=CH), 127.8 (HC_{Ar}), 128.5 (=CH), 129.7 (C_{Ar}), 129.8 (C_{Ar}), 130.1 (C_{Ar}), 131.0 (C_{Ar}),

131.2 (C_{Ar}), 131.2 (C_{Ar}), 131.6 (C_{Ar}), 132.8 (C_{ipso}), 133.3 (C_{ipso}), 133.7 (C_{ipso}), 134.9 (C_{ipso}), 151.3 (HC_{Ar}-O). EI-MS (*m/z*): 882. Calc. for C₆₅H₅₄O₃: C 88.40; H 6.16 %. Found C, 88.42; H, 6.14 %.

Synthesis of Chlorides 3 and 6

0.3 g or 0.6 g (0.69 mmol) of 2 or 5, pyridine 0.05 ml (0.7 mmol) and 0.04 ml (0.7 mmol) of SOCl₂ were dissolved in 50 mL of dry CH₂Cl₂, and then this mixture was cooled to -10° C. The reaction was carried out in nitrogen atmosphere in ice bath for 7 h. After this period, the solvent was evaporated and the resulting oil was dry supported and purified in a silica gel (60-240 pore size) column using a mixture of hexane-dichloromethane 2:1 as eluent

(E)-9-Chloromethyl-10-[2-(1-pyrenyl)ethenyl]anthracene (3)

Ambar oil, yield 0.21 g, 0.46 mmol (68 %). FTIR (pellet, KBr, cm⁻¹): 2927, 1728, 1678, 1462, 1438, 1281, 1177, 1118, 1029, 722, 695. UV-vis (CHCl₃, nm) λ_{max}: 397, 364, 344, 330, 254. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 4.09 (s, 2H, CH₂-Cl), 6.74-6.81 (br, 4H, Ar-H, =CH), 7.09 (m, 3H, Ar-H), 7.50-7.64 (br, 3H, Ar-H), 7.88 (dd, 2H, *J* = 2.7, *J* = 8.8 Hz, Ar-H), 8.01-8.37 (m, 6H, Ar-H), 8.52 (d, 1H, *J* = 8.7 Hz, Ar-H). ¹³C NMR: (CDCl₃, 75 MHz), δ (ppm): 61.7 (CH₂-Cl), 122 (HC_{Ar}), 123.0 (HC_{Ar}), 123.6 (HC_{Ar}), 125 (C_{Ar}), 125.1 (HC_{Ar}), 125.5 (=CH), 125.8 (HC_{Ar}), 126.1 (HC_{Ar}), 127.1 (=CH), 127.3 (HC_{Ar}), 127.7 (HC_{Ar}), 128.0 (HC_{Ar}), 128.6 (C_{Ar}), 129.5 (HC_{Ar}), 131.44 (C_{ipso}), 144.9 (C_{ipso}). EI-MS (*m/z*): 452 (M). Calc. for C₃₃H₂₁Cl: C 87.50; H 4.67 %. Found C, 87.47; H, 4.57 %.

(E,E,E)-9-Chloromethyl-10-[2-[2,5-dibutoxy-4-[2-[10-[2-(1-pyrenyl)ethenyl]-9-anthracenyl]ethenyl]phenyl]ethenyl]anthracene (6)

Ambar oil, yield 0.17 g, 0.18 mmol (27 %). FTIR (pellet, KBr, cm⁻¹): 2926, 2860, 1486, 1190, 1032, 835, 728. UV-vis (CHCl₃, nm) λ_{max}: 433, 367, 262. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 0.92 (m, 6H, CH₃), 1.41 (m, 4H, CH₂), 1.66 (m, 4H, CH₂), 4.23 (t, 4H, *J* = 6.3 Hz, CH₂-O), 4.71 (s, 2H, CH₂-Cl), 6.76 (d, 1H, *J* = 16.5 Hz, =CH), 7.45 (d, 1H, *J* = 16.8 Hz, =CH), 7.32 (d, 1H, *J* = 16.5 Hz, =CH), 7.34 (d, 1H, *J* = 16.8 Hz, =CH), 7.42 (d, 1H, *J* = 16.8 Hz, =CH), 7.45-7.53 (br, 6H, Ar-H), 8.00 (d, 1H, *J* = 16.2 Hz, =CH), 8.02-8.19 (br, 11H, Ar-H), 8.32 (d, 2H, *J* = 7.8 Hz, Ar-H), 8.38 (dd, 1H, *J* = 2.3 and 7.6 Hz, Ar-H), 8.44-8.58 (m, 5H, Ar-H), 8.67 (d, 2H, *J* = 8.1 Hz, Ar-H). ¹³C NMR: (CDCl₃, 75 MHz), δ (ppm): 13.3 (CH₃), 19.2 (CH₂), 32.2 (CH₂), 54.6 (CH₂-Cl), 68.6 (CH₂-O), 110.7 (HC_{Ar}), 122.1 (HC_{Ar}), 123.5 (HC_{Ar}), 123.8 (C_{ipso}), 124.4 (HC_{Ar}), 125.0 (HC_{Ar}), 125.2 (HC_{Ar}), 125.3 (=CH), 125.6 (=CH), 126.0 (C_{Ar}), 126.4 (C_{Ar}), 126.6 (=CH), 126.7 (HC_{Ar}), 127.0 (C_{Ar}), 127.3 (=CH), 127.8 (HC_{Ar}), 128.1 (=CH), 129.4 (C_{Ar}), 129.8 (C_{Ar}), 130.2 (C_{Ar}), 131.0 (C_{Ar}), 131.3 (C_{Ar}), 131.4 (C_{Ar}), 131.5 (C_{Ar}), 131.7 (C_{Ar}), 131.8 (C_{Ar}), 132.4 (C_{ipso}), 133.0 (C_{ipso}), 133.6 (C_{ipso}), 134.7 (C_{ipso}), 152.1 (C_{Ar}-O). EI-MS (*m/z*): 900 (M). Calc. for C₆₅H₅₃ClO₂: C 86.59; H 5.93 %. Found C, 86.59; H, 5.90 %.

Compound 7 was Obtained in Agreement with the Reference [14]

Synthesis of Ethers 8 and 9

A mixture of the biphenol-functionalized fullerene 7 (0.1 g, 1 mmol), potassium carbonate (0.3 g, 0.32 mmol), and KI

(1g, 0.006 mmol) in dry acetone (20 ml) was heated to reflux and stirred vigorously in nitrogen atmosphere for 20 min. The compounds 3 or 6 (0.1 g or 0.18 g, 0.2 mmol) dissolved in dry acetone (40 ml) were added dropwise and the reaction was continued for 7 days. The mixture was cooled and the precipitate was filtered. The filtrate was evaporated to dryness under reduced pressure. The residue dissolved in diethyl ether was washed with an aqueous solution of 5% Na₂CO₃ (3 times). The organic layer was dried and evaporated to dryness and purified by CC in CH₂Cl₂-methanol 9/1.

Compound 8

Brown solid, yield 0.16 g, 0.09 mmol. (94 %). FTIR (pellet, KBr, cm⁻¹): 2923, 2854, 1742, 1654, 1451, 1223, 1168, 1102, 1013, 965, 804, 747. UV-vis (CHCl₃, nm) λ_{max}: 348, 331, 278. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 4.10 (s, 4H, CH₂-O), 6.71 (d, 4H, *J* = 9 Hz, Ar-H), 7.04 (d, 4H, *J* = 9 Hz, Ar-H), 7.47 (d, 2H, *J* = 15.9 Hz, =CH), 7.48 (d, 4H, *J* = 8.4 Hz, Ar-H), 7.52 (m, 3H, Ar-H), 7.54 (d, 4H, *J* = 8.1 Hz, Ar-H), 7.63 (m, 8H, Ar-H), 7.70 (d, 2H, *J* = 15.9 Hz, =CH), 7.96-8.11 (br, 15H, Ar-H). ¹³C NMR: (CDCl₃, 75 MHz), δ (ppm): 61.1 (C), 71.7 (CH₂-O), 81.2 (C₆₀), 115.8 (HC_{Ar}), 124.0 (HC_{Ar}), 124.3 (HC_{Ar}), 124.8 (HC_{Ar}), 126.0 (=CH), 126.1 (C_{Ar}), 126.2 (HC_{Ar}), 126.6 (=CH), 127.2 (HC_{Ar}), 127.3 (C₆₀), 128.2 (HC_{Ar}), 128.3 (C_{Ar}), 128.5 (HC_{Ar}), 129.1 (C₆₀), 129.6 (HC_{Ar}), 129.7 (C₆₀), 130.2 (C_{ipso}), 130.3 (C_{ipso}), 131.3 (C_{ipso}), 131.4 (HC_{Ar}), 136.9 (C₆₀), 140.0 (C₆₀) 141.6 (C₆₀), 142.0 (C₆₀), 142.2 (C₆₀), 142.3 (C₆₀), 143.4 (C₆₀), 143.7 (C₆₀), 144.0 (C₆₀), 144.2 (C₆₀), 144.4 (C₆₀), 144.6 (C₆₀), 148.0 (C₆₀). FAB-MS (*m/z*): 1750 (M). Calc. for C₁₃₉H₅₀O₂: C 95.30; H 2.88 %. Found C, 95.30; H, 2.85 %.

Compound 9

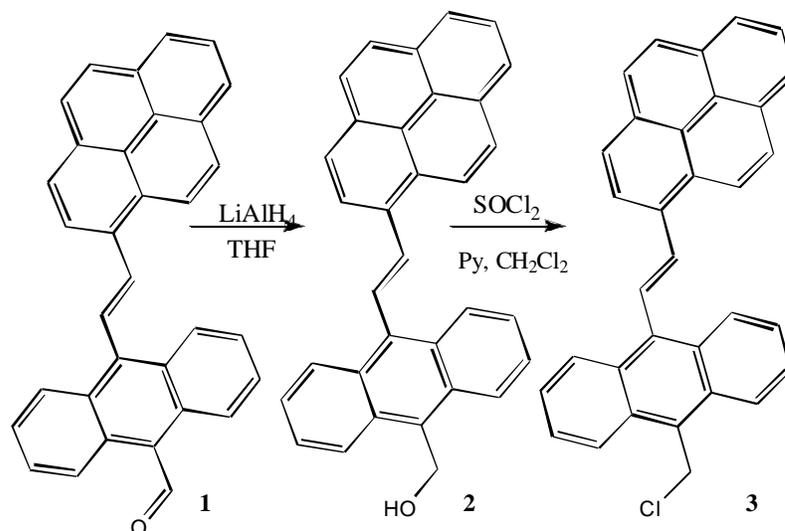
Brown oil, yield 0.27 g, 0.1 mmol. (98 %). FTIR (pellet, KBr, cm⁻¹): 2925, 2860, 1482, 1454, 1228, 1193, 1178, 1100, 1032, 963, 835, 728. UV-vis (CHCl₃, nm) λ_{max}: 346, 329. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 0.96 (m, 12H, CH₃), 1.65 (m, 8H, CH₂), 2.04 (m, 8H, Ar-H), 4.28 (s, 8H, CH₂-O), 6.72 (d, 4H, *J* = 8.1 Hz, Ar-H), 6.83 (s, 4H, *J* = 8.4 Hz, Ar-H), 7.03 (d, 2H, *J* = 15.9 Hz, =CH), 7.11-7.21 (br, 8H, Ar-H, =CH), 7.47 (d, 4H, *J* = 8.7 Hz, Ar-H), 7.49 (d, 4H, *J* = 8.1 Hz, Ar-H), 7.53 (d, 4H, *J* = 9.0 Hz, Ar-H), 7.68

(d, 2H, *J* = 15.6 Hz, =CH), 7.70 (d, 2H, *J* = 15.9 Hz, =CH), 7.74 (d, 2H, *J* = 16.5 Hz, =CH), 7.81 (m, 6H, Ar-H), 8.00-8.09 (br, 24H, Ar-H), 8.17 (d, 2H, *J* = 15.9 Hz, =CH), 8.32 (m, 4H, Ar-H), 8.38 (s, 2H, Ar-H), 8.83 (m 4H, Ar-H). ¹³C NMR: (CDCl₃, 75 MHz), δ (ppm): 14.0 (CH₃), 19.1 (CH₂), 31.8 (CH₂), 61.6 (C), 68.1 (CH₂-O), 70.2 (CH₂-O), 79.2 (C₆₀), 113.9 (HC_{Ar}), 114.5 (HC_{Ar}), 122.3 (HC_{Ar}), 123.5 (HC_{Ar}), 124.4 (HC_{Ar}), 125.1 (HC_{Ar}), 125.3 (=CH), 126.0 (=CH), 126.1 (C_{Ar}), 126.4 (C_{Ar}), 126.6 (=CH), 126.7 (HC_{Ar}), 127.1 (C₆₀), 127.2 (=CH), 127.5 (HC_{Ar}), 127.7 (=CH), 128.5 (C₆₀), 128.7 (C_{Ar}), 130.0 (C_{Ar}), 130.3 (C_{ipso}), 130.8 (C₆₀), 131.4 (HC_{Ar}), 131.5 (C_{Ar}), 131.7 (C_{Ar}), 131.9 (C_{Ar}), 132.4 (C_{ipso}), 133.3 (C_{ipso}), 134.1 (C_{ipso}), 139.0 (C₆₀), 139.7 (C₆₀), 141.8 (C₆₀), 141.9 (C₆₀), 142.1 (C₆₀), 142.7 (C₆₀), 142.8 (C₆₀), 143.3 (C₆₀), 144.2 (C₆₀), 144.3 (C₆₀), 144.5 (C₆₀), 144.7 (C₆₀), 144.9 (C₆₀), 148.7 (C₆₀), 152.5 (C_{Ar}-O). FAB-MS (*m/z*): 2649 (M). Calc. for C₂₀₃H₁₁₄O₆: C 92.04; H 4.34 %. Found C, 92.03; H, 4.32 %.

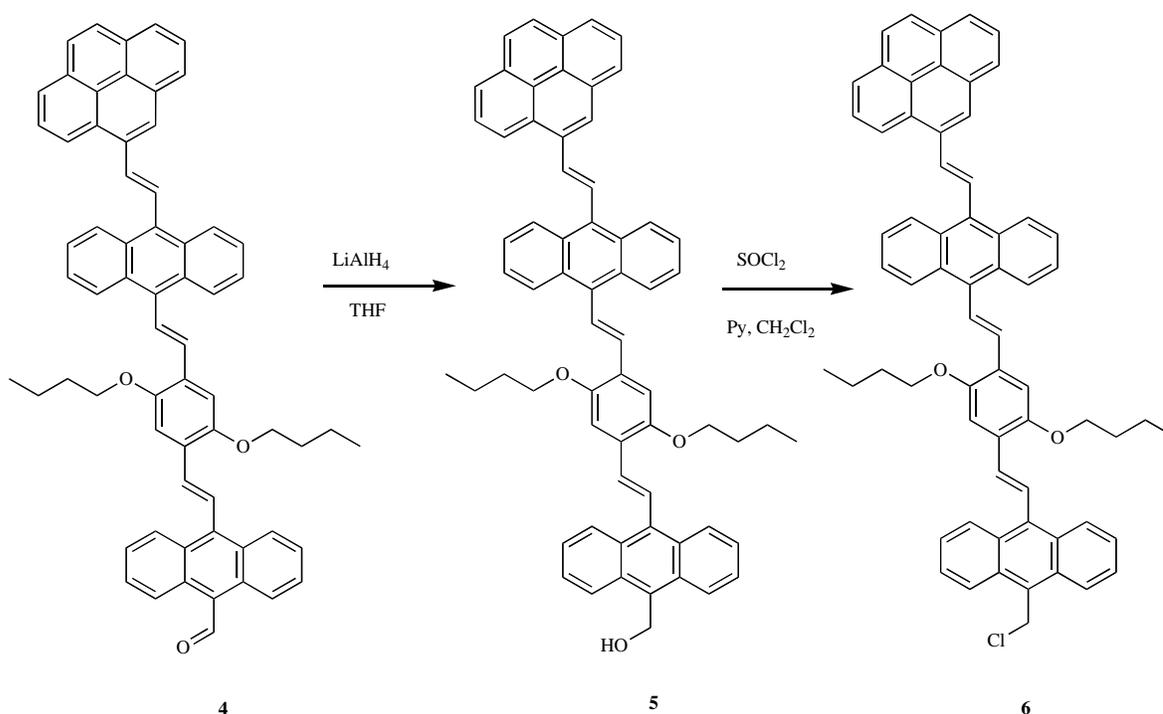
RESULTS AND DISCUSSION

The synthesis of compounds 1 and 4 were performed according to the report of Domínguez Chávez *et al.* [18], by the Horner-Wadsworth–Emmons reaction with potassium *tert*-butoxide in dry THF. The pyrene containing anthracene and 4-styryl anthracene, which have butoxy groups as solubility spacers in the main chain, imparted good solubility in polar solvents. Aldehydes 1 and 4 were reduced with LiAlH₄ in THF to give alcohols 2 and 5 in 97 and 94 % yield respectively, which were converted into chlorides 3 and 6 upon treatment with thionyl chloride and pyridine in dichloromethane (Schemes 1 and 2).

The pyrene-anthracene chloride of second oligomer derivative was obtained following a similar procedure (Scheme 2). In the ¹H NMR spectrum of the first oligomer alcohol 2 the following signals were observed; one triplet at δ_H 3.90 due to the OH group, one doublet at δ_H 5.61 assigned to the CH₂-OH group with a coupling constant *J* = 5.1 Hz, two doublets at δ_H 7.48 and at δ_H 7.52 due to the vinylic protons with coupling constants *J* = 14.9 and 13.7 Hz, respectively. Also the characteristic signals due to the pyrene and anthracene moieties at δ_H 7.49 to 8.75 ppm were observed.



Scheme 1. Synthesis of pyrene-anthracene chloride derivative.



Scheme 2. Synthesis of the pyrene-anthracene chloride derivative oligomer.

In the ^1H NMR spectrum of the second oligomer alcohol terminated **5** three signals at 0.95 to 1.83 due to the aliphatic chain were observed, at δ_{H} 4.19 one triplet due to the $\text{CH}_2\text{-O}$ groups with coupling constant $J = 5.8$ Hz, one singlet at δ_{H} 5.74 due to the $\text{CH}_2\text{-OH}$ group, five doublets at δ_{H} 6.84, 7.35, 7.37, 7.39, 7.45 and 8.04 ppm assigned to the vinylic protons with coupling constants of $J = 16.5$ and 16.8 Hz, respectively. Also were observed the characteristic signals due to the pyrene-anthracene moiety.

In the ^{13}C NMR spectrum of compound **6** the most significant resonance signals were those observed at δ_{c} 54.6 of the $\text{CH}_2\text{-Cl}$ group, at δ_{c} 68.6 of the $(\text{CH}_2\text{-O})$, and the vinylic carbons appear at δ_{c} 125.3, 125.6, 126.6, 127.3, 128.1 ppm.

The strategy used for the synthesis of the triads **8** and **9** is depicted in Scheme 3. As it is shown, it involves only one step, a *O*-alkylation between the pyrene-anthracene chlorides **3** or **6** with the functionalized fullerene C_{60} .¹⁴ The reaction was carried out in acetone and K_2CO_3 in presence of KI at reflux for 7 days and the molecular triads were obtained in good yields.

The structures of compounds **8** and **9** were confirmed by ^{13}C NMR, IR, and FAB+ mass spectrometry. In the ^{13}C NMR spectrum of compound **9** the most significant signals were those observed at δ_{c} 61.6 ppm assigned to the C of the cyclopropane group, at δ_{c} 68.1 ppm and at δ_{c} 70.2 ppm are those of the $(\text{CH}_2\text{-O})$, while that of 79.2 ppm belongs to the sp^3 carbons of the C_{60} ; 16 signals assigned to the fullerene C_{60} . The FAB mass spectrum of compound **8** is shown in Fig. (1).

Absorption and Emission Studies

Fig. (2) shows the UV-Vis spectra of compounds **3** and **6** in CHCl_3 . Two main peaks can be found at around 330 and 350 nm, in the same positions as they are observed for

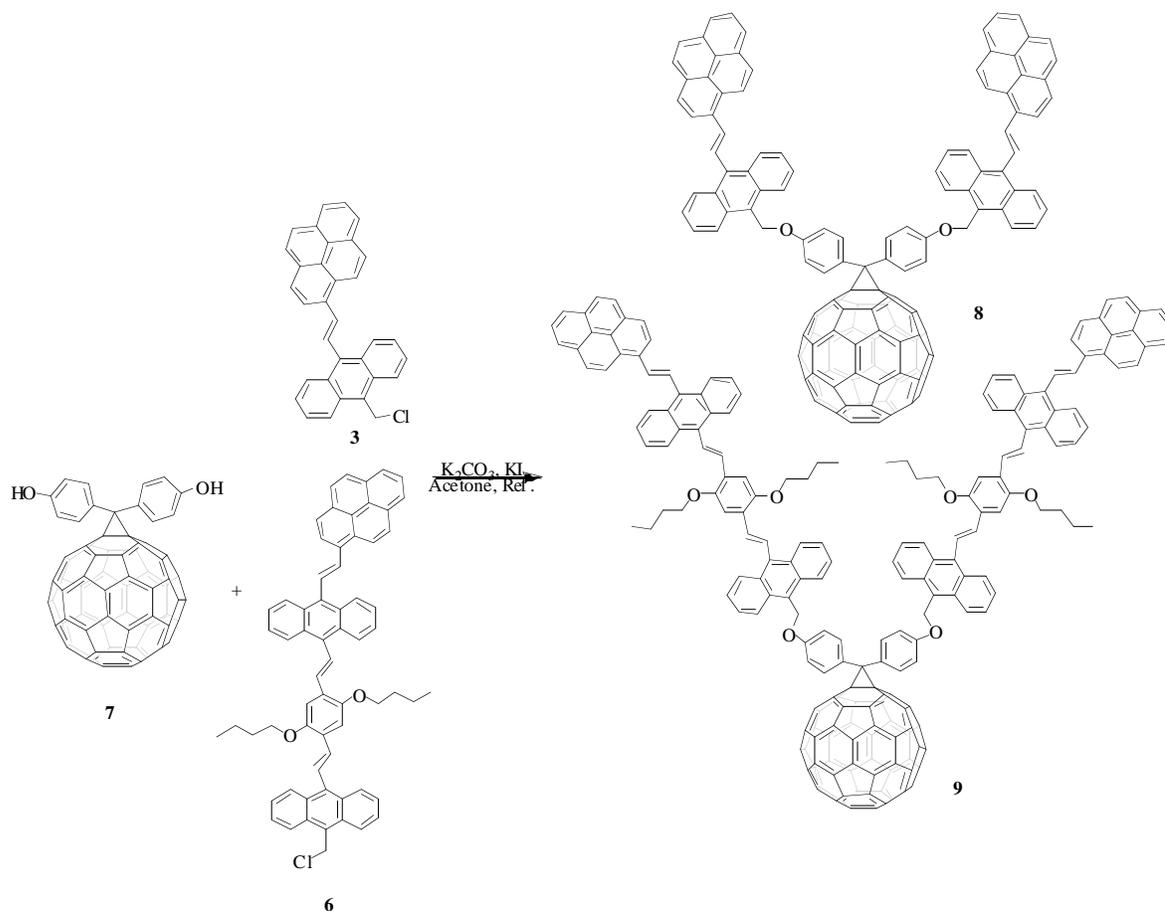
pyrene [19]. The UV absorptions from C_{60} cannot be distinguished, as they are likely overlapped by the pyrene bands. However, the absorption tail in the 500-800 nm range can be ascribed to the fullerene moiety.

The broad absorption between 400 and 500 nm is indicative of the $\pi\text{-}\pi$ electronic transitions of the anthrylvinylene segment. However, a marked peak cannot be distinguished. This result could be ascribed to the peculiar optical properties of anthrylvinylenes [10]. Fig. (3) shows the UV-Vis and fluorescence spectra of the compounds **3** and **6** in CHCl_3 . In both UV-Vis spectra, the pyrene bands can be observed in the UV region. In the visible range, an intense and sharp absorption peak due to the $\pi\text{-}\pi$ electronic transitions of the conjugated segment can be found for **3** at 438 nm. When a styryl anthracene is added compound **6**, the conjugation is expected to increase. Nevertheless, this peak markedly blue shifts to 397 nm and becomes very broad and fairly resolved.

It has been well demonstrated by several research groups that when anthracene is 9-substituted with a vinyl group, there are important interactions between the hydrogen atoms in the 1,4,5,8-positions and those of the vinyl substituent, which causes a torsion about the formal single bonds. This produces a decrease in the conjugation [10, 12]. After C_{60} cyclopropanation, the pyrene groups get closer to the anthrylvinylene moiety, as it can be observed in the AM1 ground states geometry of **8** (Fig. 4). It seems that this is the reason for the increase of steric hindrance effects.

It is worth noting that the UV-Vis spectra do not change with the change of solvent or concentration (at least, in the range detectable by our UV-Vis spectrometer), excluding intramolecular aggregation (Fig. 5).

Regarding fluorescence, for compounds **3** and **6**, the emission from the conjugated anthrylvinylene segment is



Scheme 3. Synthesis of C₆₀-pyrene-anthrylvinylene triads.

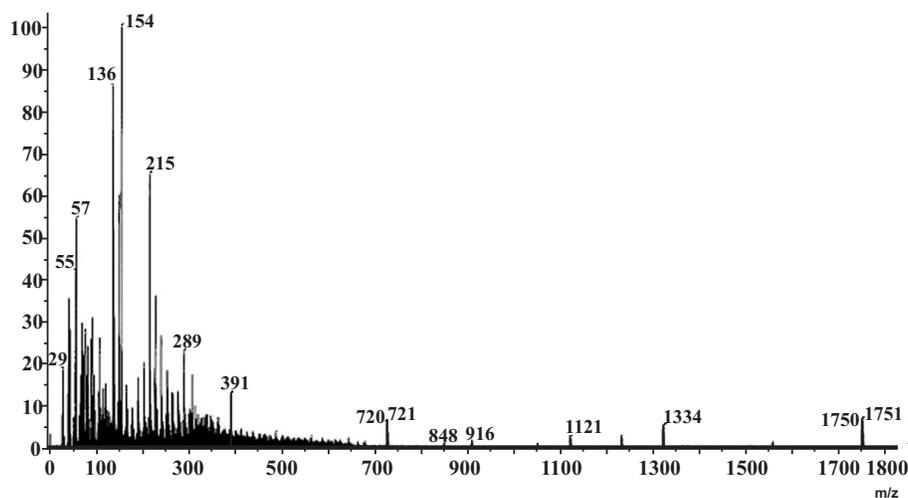


Fig. (1). FAB+ mass spectrum of the compound 8.

observed as a broad band with a maximum at 500 nm and 481 nm (Fig. 3), respectively. For the C₆₀ triads 8 and 9, for both cases of excitation on the pyrene bands (338 nm) or on the π - π^* conjugation broad absorption (385 nm), two sharp peaks are detected at 393 nm and 413 nm (Fig. 6), as for pyrene monomer emission [19, 20]. The vibronic spacing is 1230 cm⁻¹, consistent with the stretching modes of an aromatic nucleus. According to the structure and the mirror-

shape of the absorption and emission spectra, the fact that the peak wavelengths are the same as those of pyrene and that the emission peaks do not change with excitation wavelength suggests that, even if pyrene is a part of the conjugated segment through the double bonds, the HOMO and LUMO are more localized on this moiety rather than on the whole conjugated chain, independently on the extension of the latter.

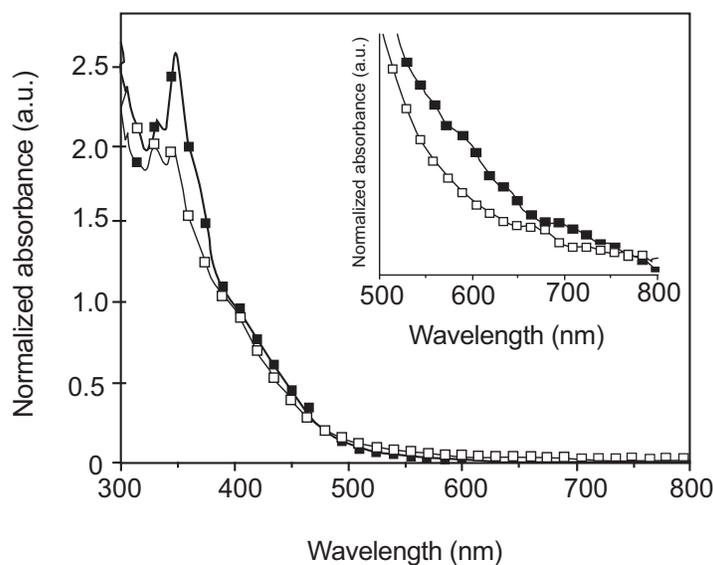


Fig. (2). UV-Vis spectra for **3** (black squares) and **6** (empty squares) in chloroform at room temperature. Inserted figure: magnification of the 500-800 nm range.

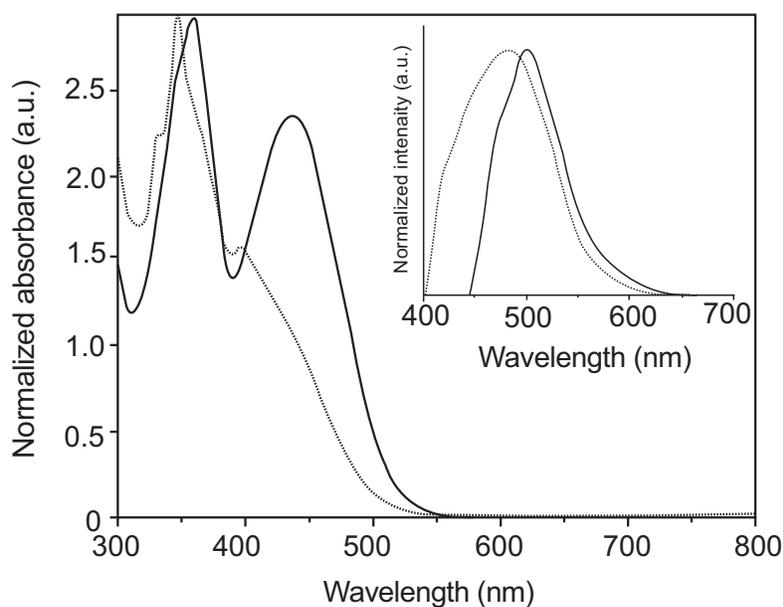


Fig. (3). UV-Vis and fluorescence (inserted) spectra of **3** (solid line) and **6** (dotted line) in chloroform at room temperature.

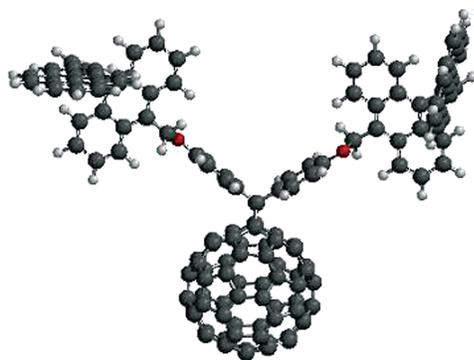


Fig. (4). AM1 ground state geometry of **8**.

When the solvent is varied (Fig. 7), the fluorescence spectra of **8** and **9** in THF and toluene do not change in shape or in position. However, a marked red shift (around 20 nm) was observed when the molecules were studied in chloroform. As chloroform has a dielectric constant value intermediate between toluene and THF, common solvent effects usually described by the Lipper equation should be discarded. Formation of internal charge transfer (ICT) state is also unlikely, because, even if the C₆₀ triads present an electron withdrawing (C₆₀) and electron donor (pyrene-anthrylvinylene) groups, the promotion of an ICT should be rather favored in polar solvents such as THF. At this moment, we can just suppose that this behavior could be due rather to specific interaction of compounds **8** and **9** with

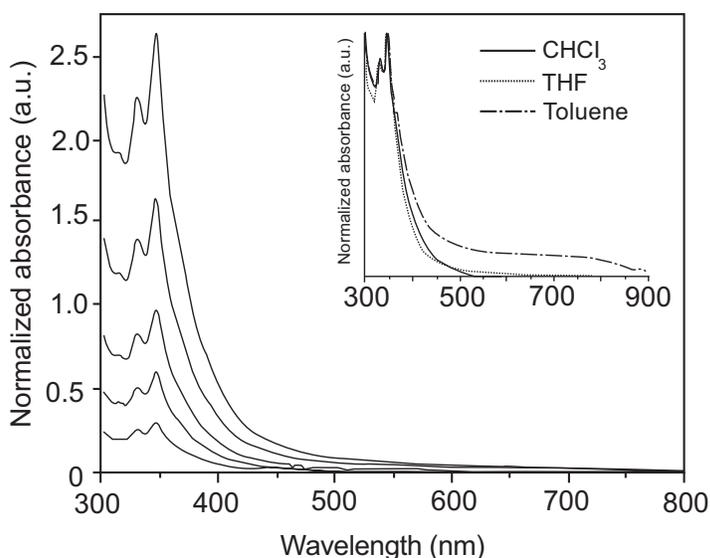


Fig. (5). UV-Vis spectra of **6** at different concentrations ($1-5 \times 10^{-7}$ mol/L) at room temperature. Inserted figure: UV-Vis-near IR spectra of **6** in different solvents at room temperature.

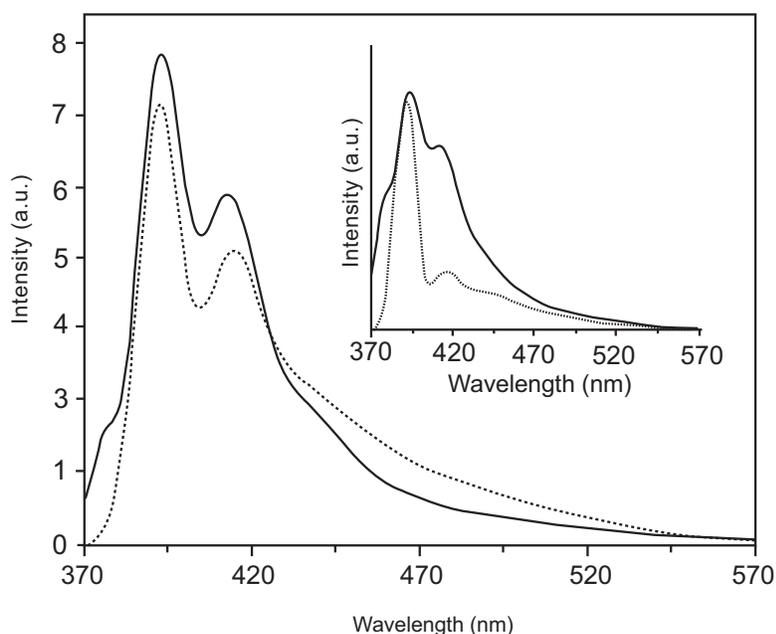


Fig. (6). Fluorescence spectra of **8** and **9** (inserted figure) in chloroform at room temperature after excitation at 338 nm (solid lines) and 385 nm (dotted lines).

CHCl₃ or to less steric hindrance between the halogenophores molecules and chloroform with respect to THF or toluene. Noticeably, as a consequence, the Stokes' shift increases passing from THF to toluene and CHCl₃, whereas the quantum yield decreases.

Under our experimental conditions, no fluorescence peaks were observed above 700 nm [21]. However, this is not sufficient to discard the emission from C₆₀. In fact, quantum yield of fullerene derivatives is very low, typically 10⁻³ and probably it is under our detector limit. Nevertheless, in general terms the fullerene derivatives have very poor fluorescence properties, which can be ascribed to energy transfer

from the pyrene-anthrylvinylene to C₆₀, as commonly observed for OPV-C₆₀ dyads or triads.

All the optical properties of the C₆₀-pyrene-anthrylvinylene triads are collected in Table 1.

CONCLUSIONS

C₆₀-pyrene-anthrylvinylene triads were synthesized with good yields by an *O*-alkylation reaction of pyrene anthracene chloride derivatives and functionalized fullerene C₆₀. The presence of lateral butoxy chains imparts good solubility. The NMR data indicate the formation of only the *trans* isomers. After C₆₀ cyclopropanation, the UV-Vis spectra show the pyrene electronic transition with an absorption band

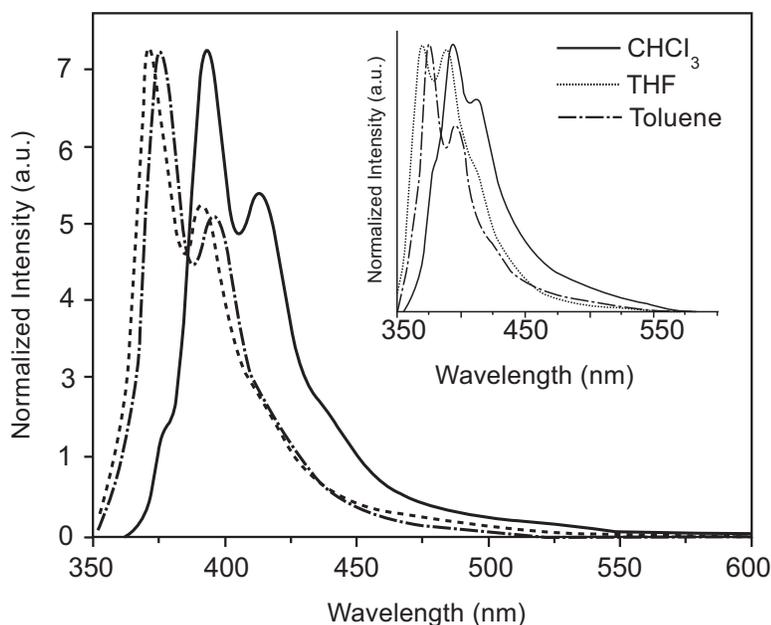


Fig. (7). Fluorescence spectra of 8 and 9 (inserted figure) in CHCl_3 , THF and toluene at room temperature.

Table 1. Optical Properties of C_{60} -pyrene-anthrylvinylene Triads in Different Solvents

| Solvent | Compound | λ_{abs} (nm) | ϵ (348 nm) ($\text{M}^{-1}\text{cm}^{-1}$) | λ_{emis} (nm) | ϕ (%) | Stokes' shift (cm^{-1}) |
|-----------------|----------|--------------------------------|--|---------------------------------|------------|---------------------------------------|
| CHCl_3 | 8 | 332, 348 | 14711 | 393, 413 | 8.6 | 3355 |
| CHCl_3 | 9 | 330, 346 | 13245 | 393, 413 | 9.7 | 3456 |
| THF | 8 | 331, 347 | 13929 | 371, 391 | 14.0 | 1864 |
| THF | 9 | 331, 346 | 28949 | 370, 389 | 15.2 | 1875 |
| Toluene | 8 | 333, 348 | 10186 | 375, 395 | 13.0 | 2069 |
| Toluene | 9 | 331, 346 | 6055 | 375, 395 | 15.9 | 2235 |

extending from 400 to 800 nm due to the combination of the π - π electronic transition of the anthrylvinylene moiety and the C_{60} band, regardless the extension of the anthrylvinylene moiety. However, the emission is almost mirror-like with respect to the absorption bands of pyrene, suggesting that the HOMO and LUMO are more localized on this substituent. Even though no emission above 700 nm was detected under our experimental conditions, this can be due to the low quantum yield values typical for C_{60} -OPV dyads or triads.

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- [21] This could probably be due to lower sensibility of our detector above 700 nm. In fact, it is worth to mention that no emission could be detected with our equipment for PCBM, which quantum yield in toluene is reported in literature to be at 712 nm equal to $0.4 \cdot 10^{-3}$ according to Sun, Y.-P.; Guduru, R.; Lawson, G. E.; Mullins, J. E.; Guo, Z.; Quinlan, J.; Bunker, C. E.; Gord, J. R. Photophysical and electron-transfer properties of mono- and multiple-functionalized fullerene derivatives. *J. Phys. Chem. B.*, **2000**, 104, 4625-4632.
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