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Synthesis of fluorescent carboxylic acid ligands for construction of monolayers on nanostructures

Research Article

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Abstract: Two new long-chain carboxylic acids (**1**, **2**) bearing strong fluorescent group pyrene as ligands for Self-Assembled Monolayers (SAMs) have been synthesized. The multistep targeted synthesis is accomplished by use of Pyren-1-yl methylamine hydrochloride and employing simplified synthetic protocols. Compound 2 contains a chiral center purposely introduced along the atom chain in order to make it suitable for chiro-optical studies of the resulting SAMs.

Keywords: *Carboxylic acids • Fluorescent groups • Pyrene • Self-assembled monolayers (SAMs)*

1. Introduction

Self-Assembled Monolayers (SAMs) constructed by the chemisorptions of carboxylic acids on metallic or non metallic nanostructures of various shapes are reported [1]. Carboxylic acids are useful ligands (building-blocks) for the construction of monolayers on two or three dimensional metal and metal oxide surfaces especially other than gold [2-4]. Carboxylic acids are found to give stable, robust monolayers onto the surface of silver, titanium oxide, silica surface, aluminium oxide and several other substrates where the carboxylic acid group gets chemisorbed on to the surface of the substrate and anchors the molecules giving stable monolayers [5-8]. In our previous studies we reported the formation of stable self-assembled monolayers of carboxylic acids and their subsequent photopolymerization on different metal nanostructures from commercial long-chain carboxylic acids containing diacetylenic units [3,4].

As most of the work in this regards is done on construction of monolayers by use of commercially available carboxylic acids which restricts the applications of the resulting monolayers to the properties of available building-blocks. In this context the design and synthesis of new long-chain carboxylic acids as building-blocks for SAMs have been boosted. Simple, fast, and efficient synthesis methods for generation of libraries of organic compounds to be used for formation of desired monolayers, and their structure property relationship are welcomed by material chemists. In the present paper we report synthesis of two new fluorescent carboxylic acids as building-blocks for self-assembled monolayers on metallic nanostructures (such as nanoparticles, quantum dots, and nanocages). Putting strong fluorescent groups such as the polyaromatic pyrene group into the ligands for monolayers greatly extends their applications in the constructions of sensors for specific biomolecules, ions, or drug molecules. Many features make fluorescence one of the most powerful transduction mechanisms [9,10] to report the chemical recognition event. A number of fluorescence microscopy and spectroscopy techniques based on the life-time, anisotropy, or intensity of the emission of fluorescent probes have been developed over the years where quenching or enhancing of the

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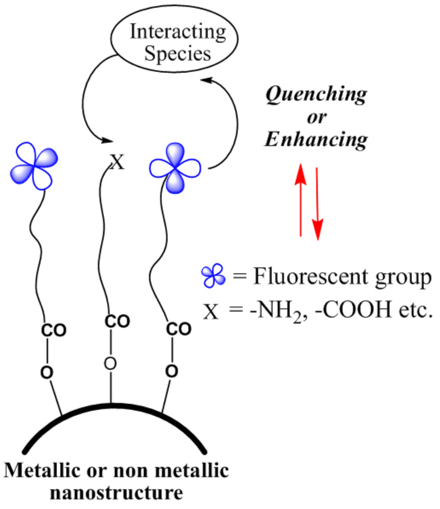


Figure 1. Fluorescent carboxylic acid monolayer anylate interactions.

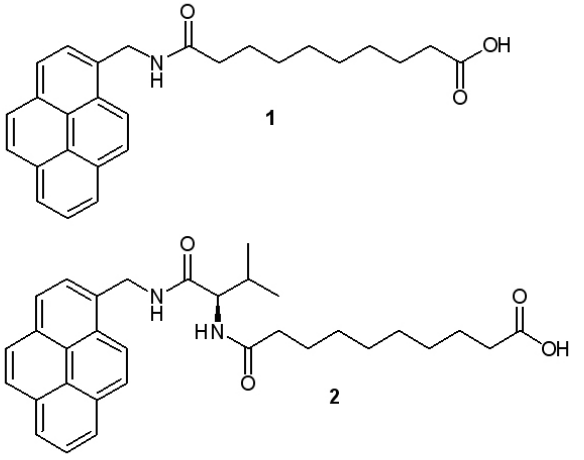


Figure 2. Newly synthesized long-chain fluorescent carboxylic acids.

fluorescence upon interactions with the analytes can be monitored (Fig. 1). These are enormously sensitive techniques that allow even the detection of single molecules. Fluorescence does not consume analytes and no reference is required. Light can travel without physical wave-guide, facilitating enormously the technical requirements for constructions of a sensor [11]. Pyrene is preferred fluroscent precursor for putting in monolayer building-block for many reasons as it is one of the most prominent standard chromophores for probing fluorescence in relation to excimer formation. Although attached to a conducting surface, these monolayers bearing pyrene display significant fluorescence from a pyrene excited state. The SAMs obtained from pyrene derivatives are so stable that extensive washing did not result in any loss of fluorescence intensity [12-15].

2. Experimental procedure

Petroleum ether and light petroleum refer to the fractions boiling in the range of 40-60°C and 80-110°C, respectively. Solvents used as eluents were distilled prior to use. Toluene, ethanol, dichloromethane, THF, TFA, Sebacic acid, Pyren-1-yl methylamine hydrochloride, Boc-L-Valine, 2-(1H-benzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (HBTU) and benzyl bromide were extra pure commercial products and were used as received. Anhydrous methylene chloride was syringed under argon. The ^{1}H NMR and ^{13}C Spectra were recorded at 300 MHz.

2.1. Experimental procedure for synthesis of compound 1 from Scheme 1

Synthesis of diethyl sebacate (4) (Scheme 1, step *i*).

Sebacic acid (26 g, 129 mmol) was taken in a 250 mL single-neck flask, to which ethanol (63.5 mL) and concentrated sulphuric acid (5 mL) were added. The solution was then refluxed overnight. After the solvent was removed by vacuum evaporation, the residue was treated with water (200 mL) and extracted with ether three times. The ether layer was washed with 5% sodium bicarbonate and then several times with water, and dried over sodium sulphate. Evaporation of the solvent gave a dense liquid which was vacuum distilled. The product distillates out at 156-158°C at 6 mmHg as a transparent liquid: 24.8 g (75%). ^{1}H NMR ($CDCl_3$, ppm) δ = 1.22-1.29 (14H, m), 1.58-1.62 (4H, m), 2.27 (4H, t, J = 7.5), 4.11 (4H, q, J = 6).^{13}C NMR ($CDCl_3$, ppm) δ = 14.33, 25.02, 29.16, 34.40, 60.24, 173.92. Data was in accordance with reported analysis [16].

Synthesis of sebacic acid monoethyl ester (5) (Scheme 1, step *ii*).

In a two-neck round-bottom flask the side arm of which is corked, a mixture of sebacic acid (32.32 g, 160 mmol), diethyl sebacate (24 g, 93 mmol), and concentrated hydrochloric acid (4 mL, d 1.19) was added. A reflux condenser was connected to the top of the distilling flask. The flask was heated in an oil bath at 160–170°C until the mixture was completely homogeneous. The temperature of the bath was then lowered to 120–130°C, and 9.6 mL (165 mmol) of 95% ethyl alcohol was added to the solution through the condenser. The mixture was allowed to reflux for two hours. At the end of this period an additional 2 mL portion of ethyl alcohol was poured into the solution and refluxing was continued for two more hours. The oil bath was allowed to cool to about 75°C and the reaction mixture was subjected to distillation under reduced pressure, using a water pump. The temperature of the bath was increased slowly and distillation was continued until the bath temperature reached about 125°C. The bath was again cooled to 75–80°C and the distillation was continued at lower pressure, using an oil pump. The first fractions consisted of a little alcohol, water, and *n*-butyl ether. The next fraction was ethyl sebacate, bp 156–158°C at 6 mm of Hg. Ethyl hydrogen sebacate was collected at 183–187°C at 6 mm of Hg. The distillation gives product as white solid 19.1g (52%), mp = 35.6-35.9°C. ^{1}H NMR ($CDCl_3$, ppm) δ = 1.22-1.30 (11H, m), 1.58-1.62 (4H, m), 2.25-2.36 (4H, m), 4.11 (2H, q, *J* = 6).^{13}C NMR ($CDCl_3$, ppm) δ = 14.46, 24.84, 25.13, 29.18, 29.25, 34.25, 34.56, 60.44, 174.20, 180.17. Data was consistent with reported analysis [17].

9-[(Pyren-1-ylmethyl)carbamoyl]nonanoic acid ethyl ester (7) (Scheme 1, step *iii*).

Sebacic acid monoethyl ester (**5**) (2 g, 8.7 mmol) and dicyclohexylcarbodiimide (1.98 g, 9.6 mmol) were taken into a two-neck flask; approximately 15 mL of dry DCM were added and the solution was kept under stirring at 0°C for 1 h. Pyren-1-yl methylamine hydrochloride (**6**) (2.36 g) was taken into a second flask, adding 75 mL of dry DCM and then triethylamine until the solution became clear. The latter solution was then added to the former one and the mixure was kept under stirring overnight at room temperature. At the end of the reaction the solution was filtered to remove urea and the solvent was taken off. The crude residue was purified by column chromatography using 1:1 petroleum ether/ethyl acetate as eluent, yielding a white solid (433 mg, 52.6%), mp 120.5-120.9°C. ^{1}H NMR ($CDCl_3$, ppm) δ = 1.21-1.26 (15H, m), 2.18-2.25 (4H, m), 4.10 (2H, q, *J* = 6), 5.16 (2H, d, *J* = 6), 5.16 (2H, d, *J* = 3), 5.75 (1H, b), 7.95-8.28 (9H, m). ^{13}C NMR ($CDCl_3$, ppm) δ = 14.48, 25.11, 29.22, 29.27, 29.32, 29.41, 34.53, 37.02, 42.25, 60.38, 123.14, 124.93, 124.98, 125.28, 125.59, 125.64, 126.35, 127.54, 127.81, 128.47, 129.29, 130.98, 131.47, 131.49, 172.86, 174.08.

9-[(Pyren-1-ylmethyl)carbamoyl]nonanoic acid (1) (Scheme 1, step *iv*) [18].

The substrate (600 mg, 1.35 mmol) was taken into a single-neck flask and 75 mL of approximately 0.5 N KOH/EtOH was added, the solution was kept under magnetic stirring at 45°C for 1.5 h. The reaction mixture was then diluted with water and acidified with 1N HCl till p*H* 2. The product separated out as a white solid which was filtered and dried. The product was recrystallized from THF/water (80:20) to obtain a white crystalline solid (390 mg, 69%), mp 163.4-163.7 °C. ^{1}H NMR ($CDCl_3$, ppm) δ = 1.22-1.28 (8H, m), 1.53-1.63 (4H, m), 2.23 (2H, t, *J* = 6), 2.28 (2H, t, *J* = 6), 5.16 (2H, d, *J* = 6), 5.76 (1H, b), 7.95-8.28 (9H, m). ^{13}C NMR ($CDCl_3$, ppm) 24.73, 25.09, 28.50, 28.94, 29.50, 34.4, 36.71, 42.0, 123.78, 124.98, 125.41, 126.34, 126.90, 131.01, 133.24, 139.0. 173.1, 179.05. Anal. found C, 78.0 H, 7.14 N, 3.37. Anal. calculated for $C_{27}H_{29}NO_3$: C, 78.04 H, 7.03 N, 3.37. Anal. found C, 78.0 H, 7.14 N, 3.37.

2.2. Experimental procedure for synthesis of compound 2 from Scheme 2

Tert-butyl 3-methyl-1-oxo-1-(pyren-1-ylmethyl-amino) butan-2-yl carbamate (9) (Scheme 2, step *i*) [19,20].

Boc-L-valine (Aldrich 99.9%, 1.217 g, 5.6 mmol) was taken into a 250 mL single-neck flask and 25 mL of dry DCM was added. The resulting solution was cooled to 0°C in an ice bath and 2-(1*H*-benzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (HBTU) (2.37 g, 6.16 mmol), keeping the solution under stirring at 0°C for 30 minutes. A separate solution of (pyren-1ylmethyl) amine hydrochloride (1.5 g, 5.6 mmol) in dry DCM (80 mL) was prepared by addition of triethylamine until the solution became clear. This solution was then added to the previous cooled solution containing valine and HBTU. The reaction mixture was kept under stirring overnight at room temperature. After completion of the reaction the reaction mixture was filtered, the solvent was removed to get a pinkish white residue which was then dissolved into a sufficient amount of diethyl ether: some white solid (TEA·HCl) remained undissolved, which was filtered off. The ether layer was washed three times with water, dried on anhydrous sodium sulfate. Evaporation of ether gives the crude product which was recrystallized from ethanol to give yellowish white crystals (900 mg, 38%). ^{1}H NMR ($CDCl_3$, ppm): δ = 0.89 (3H, d, *J* = 3), 0.91 (3H, d, *J* = 3), 1.33 (9H, s), 2.2 (1H, m), 3.92 (1H, dd, J_1 = 3, J_2 = 6), 5.01 (1H, b), 5.18 (2H, t, *J* = 4.5), 6.29 (1H, b), 7.95-8.26 (9H, m). ^{13}C NMR ($CDCl_3$, ppm): δ = 17.98, 19.62, 28.43, 30.87, 42.06, 60.48, 123.01, 124.91, 124.98, 125.24, 125.57, 125.61, 126.30, 127.33, 127.54, 127.78, 128.44, 129.19, 130.97, 131.01, 131.45, 131.48, 171.45.

2-Amino-3-methyl-N-(pyren-1-ylmethyl) butanamide (10) (Scheme 2, step *ii*) [21].

Compound **9** (300 mg, 0.7 mmol) was added to trifluroacetic acid (2.4 mL) kept at 0°C, and the resulting thick dark brown solution was kept under stirring for approximately 2 hours. The progress of reaction was monitored by TLC. After completion of the reaction 5% sodium bicarbonate solution was added till the solution became alkaline (p*H* 8) before extraction (three times) with ethyl acetate. The organic layer was washed with water, dried over sodium sulfate and evaporated to get the crude product as a white residue which was purified on silica gel column (1:1 hexane/ethyl acetate as eluent (145 mg, 63%). ^{1}H NMR ($CDCl_3$, ppm) 0.89 (3H, d, J = 6), 0.99 (3H, d, J = 6), 2.04 (1H, m), 3.33 (1H, b), 5.12 (1H, dd, J_1 = 6, J_2 = 12), 5.23 (1H, dd, J_1 = 6, J_2 = 6), 7.72 (1H, b), 7.97-8.31 (9H, m). ^{13}C NMR ($CDCl_3$, ppm): δ = 18.5, 31.7, 41.8, 59.9, 123.0, 123.7, 124. 9, 125.2, 125.6, 126.3, 126.6 133.3, 139.0, 171.33.

Dodecanedioic acid monobenzyl ester (11) (Scheme 2, step *iii*).

Sebacic acid (4.04 g, 20 mmol) reacted with potassium hydroxide (20 mmol) in water (10 mL), and was stirred for 1 h at room temperature. Enough toluene was added and the azeotrope was evaporated to dryness to yield 4.8 g (20 mmol) of potassium sebacate. Toluene (60 mL) was added, followed by 0.6 g (2 mmol) of tetrabutylammonium bromide (TBAB) and 4.6 mL (20 mmol) of benzyl bromide. The reaction mixture was stirred at reflux for 5 hours. Cooling of the mixture to room temperature and evaporation of solvent gave a white residue which was purified on silica gel column (2:1 hexane/ethyl acetate as eluent). Yield 7.5 g (65%), mp 39.9-40.3 °C. ^{1}H NMR ($CDCl_3$, ppm) 1.3 (8H, m), 1.65 (4H, m), 2.35 (4H, t, J = 7.2), 5.12 (2H, s), 7.29 (5H, m). ^{13}C NMR ($CDCl_3$, ppm) 24.63, 24.90, 28.94, 29.00, 33.94, 34.31, 66.05, 128.11, 128.49, 136.29, 173.55, 179.46.

Benzyl 10-[3-methyl-1-oxo-1-(pyren-1-ylmethylamino)butan-2-ylamino]-10-oxodecanoate (12) (Scheme 2, step *iv*).

In to a single neck flask compound **11** (132 mg, 0.45 mmol) was dissolved in 5 mL of dry dichloromethane, and HBTU (258 mg, 0.68 mmol) was added. The solution was cooled to 0°C and kept under stirring for 30 minutes. In to another flask compound **10** (150 mg, 0.45 mmol) was dissolved in 8 mL of dry dichloromethane and triethylamine (69 mg, 0.68 mmol) this solution was added to the initial solution and kept under stirring overnight at room temperature. After completion of the reaction the reaction mixture was filtered the solvent was removed to get the crude residue which was purified by silica gel coloumn (Hexane/ Ethyl acetate 2:1). Yield 179 mg (66%). mp 183.1-183.4°C. ^{1}H NMR ($CDCl_3$, ppm) 0.89 (3H, d, J = 3), 0.92 (3H, d, J = 3), 1.17-1.2 (8H, m), 1.46-1.5 (4H, m), 2.1-2.22 (3H, m), 2.32 (2H, t, J = 9), 4.24 (1H, dd, J_1 = 9, J_2 = 6), 5.03 (1H, dd, J_1 = 6, J_2 = 6), 5.21 (1H, dd, J_1 = 6, J_2 = 6), 6.08 (1H, d, J = 9), 6.45 (1H, b), 7.33-7.36 (5H, m), 7.92-8.21 (9H, m). ^{13}C NMR ($CDCl_3$, ppm) 18.53, 19.55, 25.08, 29.22, 34.50, 42.06, 58.73, 66.30, 122.96, 124.98, 125.54, 125.60, 126.27, 127.35, 127.52, 127.75, 128.39, 136.33, 171.20, 173.45, 173.87.

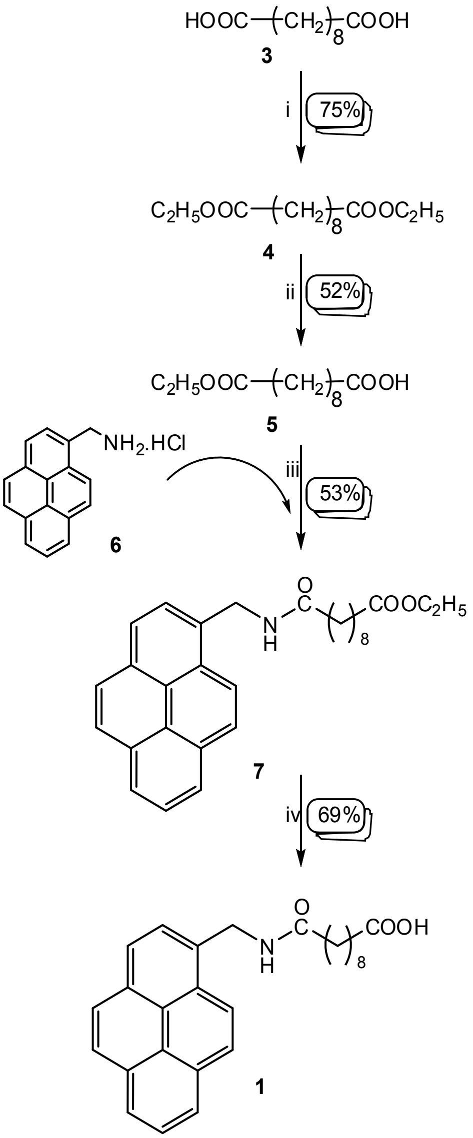
10-[3-Methyl-1-oxo-1-(pyren-1-ylmethylamino)butan-2-ylamino]-10-oxodecanoic acid (2) (Scheme 2, step *v*).

In a single-neck flask equipped with a vacuum system, compound **12** (109 mg, 0.18 mmol) was dissolved in approximately 100 mL of 1:1 THF/ethanol, followed by 101 mg of palladium on carbon (10%). The vacuum hydrogen cycles were repeated at least two times. The reaction mixture was kept stirring under hydrogen atmosphere for 25 minutes, the reaction being monitored by TLC. After disappearance of substrate, the reaction stopped. The mixture was filtered twice to remove the catalyst and concentrated to yield the crude product which was then recrystallized from ethanol to get an off-white solid (46 mg, 50%), mp 189.9-191°C. ^{1}H NMR (DMSO-D_6, ppm) 0.80 (6H, d, J = 6), 1.09-1.15 (8H, m), 1.94 (1H, m), 2.46-2.48 (4H, m), 4.12 (1H, dd, J_1 = 3, J_2 = 6), 4.98 (2H, d, J = 6), 7.85 (1H, d, J = 6), 8.00-8.28 (9H, m). 8.63 (1H, dd, J_1 = 6, J_2 = 6). ^{13}C NMR (DMSO-D_6, ppm) 18.97, 19.97, 25.17, 29.21, 34.41, 35.91, 38.12, 39.11, 39.36, 58.56, 124.01, 125.3, 125.82, 125.9, 125.91, 127.44, 127.69, 128.08, 128.75, 130.99, 131.46, 133.53, 171.80, 172.94, 175.20. Anal. calced. for $C_{32}H_{38}N_2O_4$: C, 74.68 H, 7.44 N, 5.44. Anal. found C, 74.5 H, 7.50 N, 5.39.

3. Results and discussion

3.1. Synthesis of 10-Oxo-10-(pyren-1-ylmethylamino) decanoic acid (1, Py-C)

The synthesis has been performed (Scheme 1) starting from commercial sebacic acid (**3**) through the synthesis of ethyl sebacate (**4**) followed by its reaction with ethanol and with excess sebacic acid to get ethyl hydrogen sebacate **5**. This monoester of the sebacic acid was then condensed with pyrene methyl amine hydrochloride (**6**) by using dicylcohexyl carbodiimide (DCC) as the condensing reagent in dry dichloromethane solvent and triethyl amine. Here triethylamine (TEA) serves not only as a mild base to catalyse the reaction but also help to neutralize the hydrochloride salt of the amine used. The condensation thus yields the intermediate ester (**7**) which upon hydrolysis with 0.5N KOH in ethanol gives the required acid (**1**) in good yields. In literature the condensation of a long-chain carboxylic acid with amine hydrochloride salts have been reported by means of an approach which involves first the conversion of the acid into an acid chloride by using thionyl chloride the same report also uses a potentially dangerous substance BOP [15]. However in the present approach we have used mild reaction conditions by choosing the appropriate

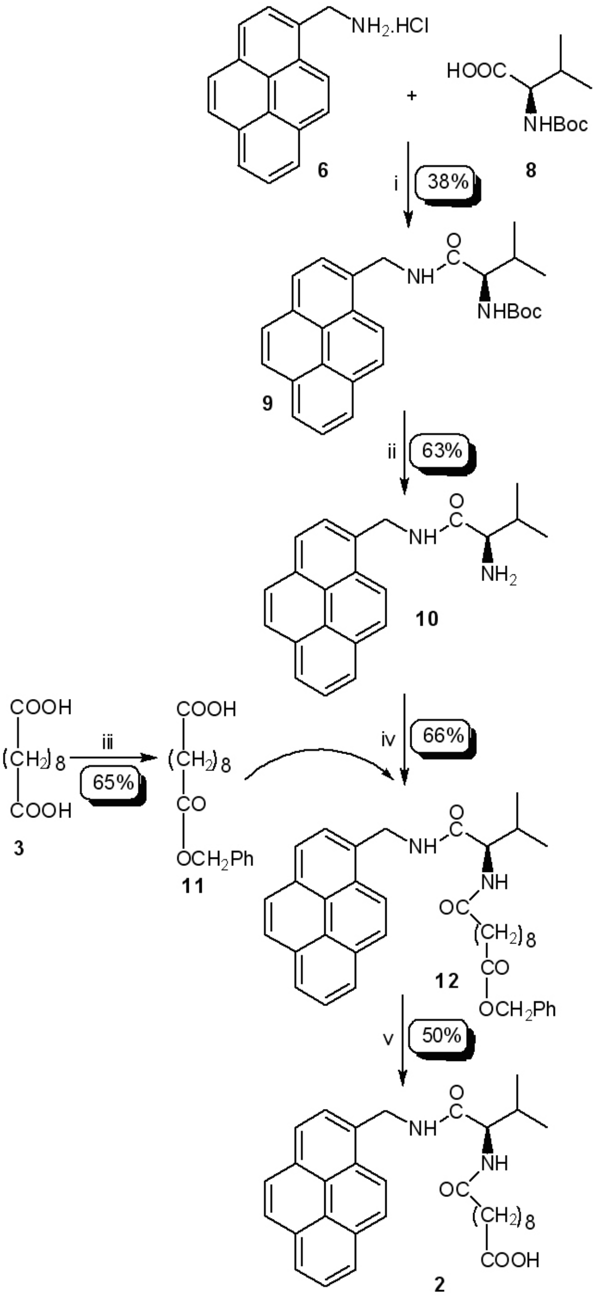


Scheme 1. Synthetic protocol for Py-C. i = EtOH, H_2SO_4; ii =Sebacic acid, EtOH, HCl; iii = DCC, DCM, TEA; iv = 0.5N KOH in Ethanol.

condensing reagent (DCC), solvent and base (TEA) simplifying the procedure and obtaining overall similar yields.

3.2. Synthesis of 10-[3-methyl-1-oxo-1-(pyren-1-ylmethylamino) butan-2-ylamino]-10-oxodecanoic acid (2, PyC-Chiral)

The synthesis of 10-[3-methyl-1-oxo-1-(pyren-1-ylmethylamino)2-butylamino]-10-oxodecanoic acid (PyC-Chiral) (**2**) bearing a pyrene end-group and provided with a chiral center along the atom chain has been performed. The chiral center is purposely introduced in order to carry out chiro-optical studies of the monolayers fabricated from the chiral molecule. The synthesis starts from two commercially available reagents; pyrene methyl amine hydrochloride (**6**) and Boc-L-Valine (**8**). In the first step the condensation between the acid and the amine was achieved by using 2-(1H-benzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (HBTU) and TEA in dry dichloromethane to give the intermediate



Scheme 2. Synthetic protocol for PyC-Chiral. i = HBTU, TEA; DCM; ii = TFA; iii = Benzyl bromide, DCC; iv = HBTU, TEA, DCM; v = H_2, Pd on C.

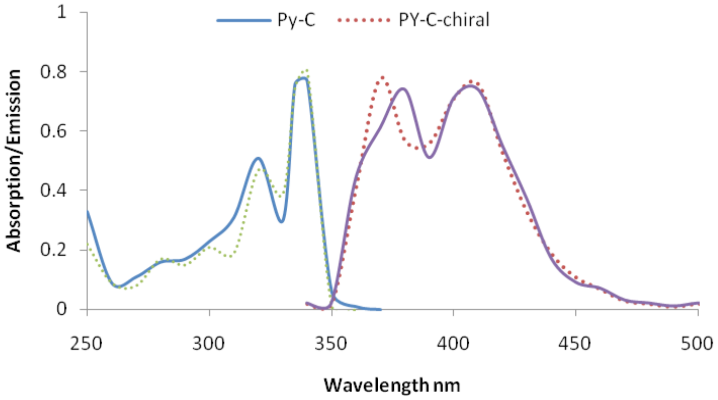


Figure 3. Normalized absorption and emission spectrum of PyC (solid line) and PyC-chiral (dotted line).

9. In addition to its high reactivity, HBTU has also been shown to fulfill the very important requirement of avoiding racemization at adjacent sites [19]. The Boc-protecting group was then removed by using trifluoroacetic acid to generate the free amine (**10**). The latter was then reacted with the monobenzyl ester of sebacic acid (**11**) by again using the HBTU, TEA, DCM protocol to get the condensation product (**12**). In the final step the deprotection of the benzyl ester was performed by using hydrogen gas and palladium on carbon (10%) as the catalyst in THF/ethanol (50:50) to get the final acid (**2**), which was then recrystallized from boiling ethanol.

Fig. 3 shows the absorption and emission spectra of the compounds PyC and PyC-Chiral. The measurements were carried out in toluene and the excitation wavelength used was 334 nm. The maximum absorption wavelength of the conjugated polyaromatic pyrene nucleus at 320 and 335 nm can be seen.

4. Conclusion

In summary new carboxylic acids with strongly fluorescent group pyrene have been synthesized. The selection of end-groups has been done with the consideration of the structure property relationship, and the requirement of the specific applications of the resulting monolayers constructed from these compounds. The synthetic strategies mentioned here can be applied to the synthesis of other similar derivatives of varying chain lengths to generate libraries of building blocks for self-assembled monolayers. The experiments of constructions of monolayers from the compounds mentioned above are underway and the results will be reported separately.

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