



Star-shaped ethynylpyrimidine with long alkoxy side chains: synthesis, fluorescence and 2D self-assembling

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ABSTRACT

In this contribution, we describe the synthesis of a star shaped ethynylpyrimidine having long alkoxy side chains using Suzuki cross-coupling reactions. This compound presents interesting blue light emission fluorescence as well as self-assembling properties on graphite: a chiral system is obtained starting from a nonchiral molecule. This preliminary work indicates that pyrimidine derivatives could be good candidates for the development of novel functional organic materials.

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1. Introduction

Introducing heteroaryl moieties into π -extended systems is a way to modify and sometimes enhance useful properties of advanced 'electro-optic' materials,¹ heteroaromatics being particularly useful where electron transport is necessary.

In this context, over the past decade, the synthesis of pyrimidine derivatives has received intensive research interest with applications as organic materials in various fields such as calamitic² and discotic³ liquid crystals, n -type semi-conductors⁴, fluorescence⁵ or organic light emitting devices (OLEDs) for display and lighting.⁶ Indeed, due to its aromaticity, to its strong electron-withdrawing character, to its high dipolar interaction and to its pH sensibility, pyrimidine presents the requested characteristics in order to be incorporated in organic material in view of such applications.

On one hand, and in addition to their liquid crystal 3D self-assembling, judiciously substituted pyrimidine star-shaped derivatives could present also 2D self-assembling properties.⁷ On the other hand, similar systems based on specific benzene, pyridine or triazine cored stilbenoid compounds were described⁸ and present promising applications as molecular sieves.⁹ In this latter example, the authors devised a marking/tracking procedure to achieve direct visual discrimination of individual molecules in a self-assembled layer based on respective carbon/nitrogen contrast in high resolution scanning tunneling microscopy (STM) imaging.

The marking mechanism consists just in the minimal substitution of one carbon atom by a nitrogen atom in the central conjugated core.¹⁰

Consequently, it is interesting to compare the 2D self-assembling properties of an equivalent star-shaped molecule with a pyrimidine core. The two nitrogen atoms of the pyrimidine ring are expected to alter the chemical affinity of the final host system for specific guest molecules.

As a first step towards the above molecular designs (e.g., such as compound **A**), 2,4,6-tris(phenylethynyl)pyrimidine substituted by long alkoxy chains (compound **1**, Fig. 1), which offers a possible route towards the synthesis of the compound **A**, through reduction of the C–C triple bond shows interesting electronic and self-organization properties by itself. The aim of this Letter is to describe the synthesis, fluorescence and self-assembling properties of 2,4,6-tris(phenylethynyl)pyrimidine substituted by long alkoxy chains.

2. Results and discussion

The best method for the synthesis of 2,4,6-trialkynylpyrimidine consists in carrying out Suzuki cross-coupling reaction with potassium alkynyltrifluoroborates on 2,4,6-trichloropyrimidine.¹¹ For the synthesis of the arm of the molecule, we have chosen to start from commercially available 3,4-dihydroxybenzaldehyde, and the ethynyl part will be introduced by the Corey–Fuchs method.¹² The first step consists in a Williamson reaction to form the long alkoxy chains, the second step is the action of carbon tetrabromide with triphenylphosphine on the aldehyde to access to dibromoal-

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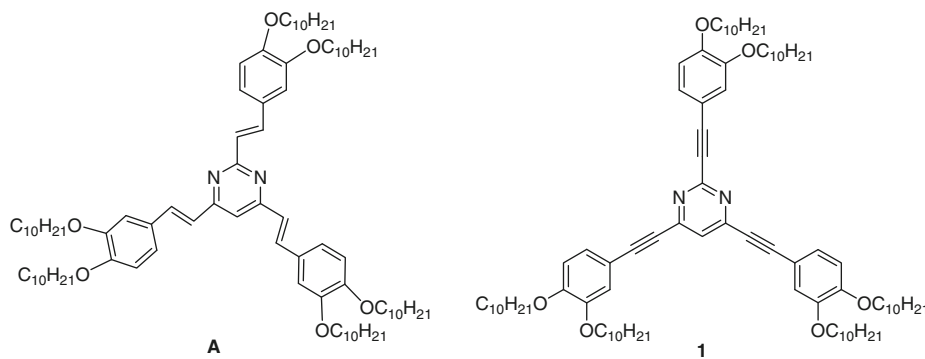


Figure 1.

cene **3**. Then 2 equiv of *n*-BuLi are added leading to the alkyne **4**. The corresponding potassium phenylalkynyltrifluoroborate **5** was obtained by metallation of **4** with *n*-BuLi followed by the action of triisopropyl borate and subsequent treatment with KHF₂ (Scheme 1).¹³

The potassium alkynyltrifluoroborate **5** was then used in cross-coupling reaction with 2,4,6-trichloropyrimidine. It should be noted that the tricoupled product cannot be obtained in one step. Indeed, when 5 equiv of **5** were used, only the dicoupled product **6** was obtained, which could be probably due to the steric hindrance induced by the long alkoxy chains. However, when a further coupling reaction was performed with **6** and five other equivalents of **5**, the expected trisubstituted product **1** is obtained with a moderate yield (Scheme 2).¹⁴

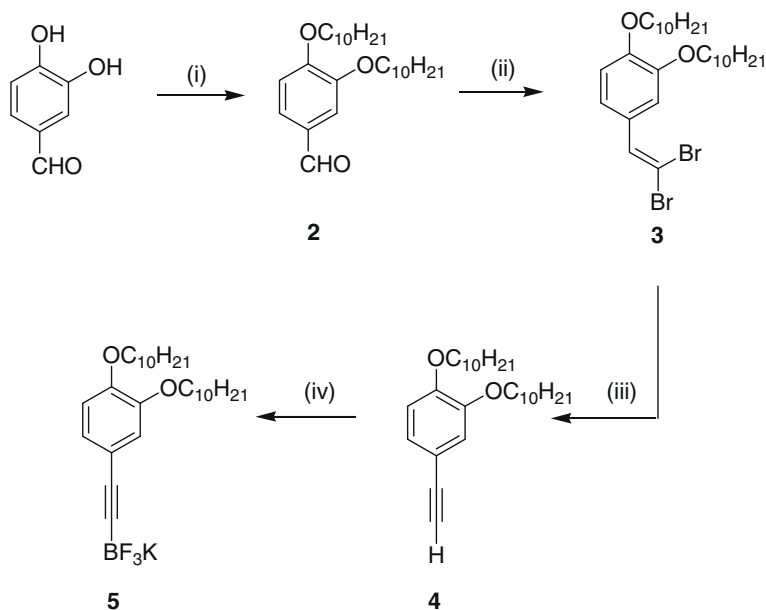
The UV absorption and fluorescence emission spectra of **1** are given in Figure 2. Compound **1** exhibits an absorption maximum at 377 nm and a structureless emission peak at 476 nm. The relative fluorescence quantum yield (Φ_F) of **1** was measured to be 0.25 using Harmane (β -carboline derivative) as a reference.¹⁵

Based on the peak position on the UV spectrum, chemically stable compound **1** appears well suited for emission of blue light with a relatively high quantum yield.

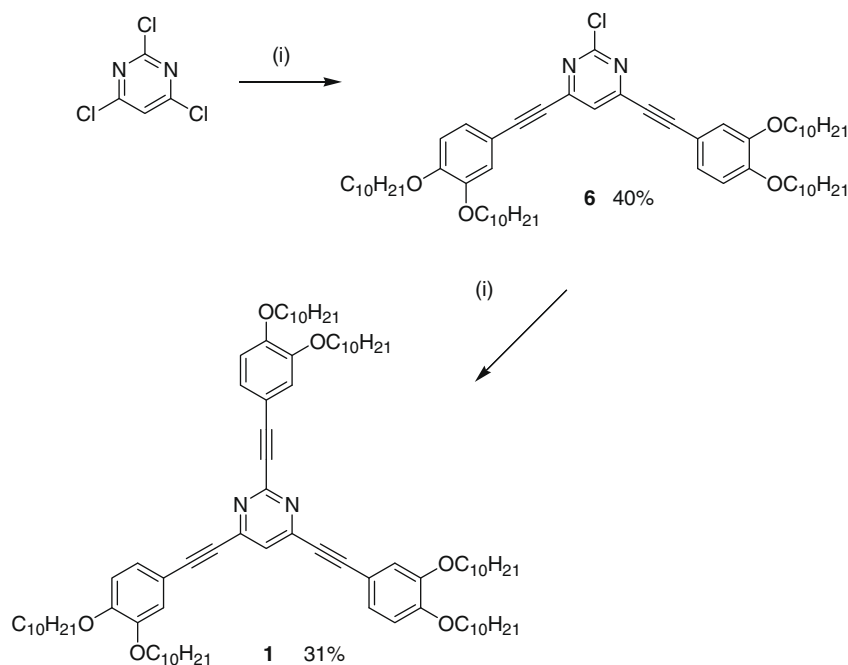
The self-organization on highly ordered pyrolytic graphite (HOPG) of compound **1** has been studied as well, using STM at

the solution-solid interface: indeed this technique permits to obtain direct-space information on the structures of spontaneously-formed self-assembled organic monolayers with a submolecular resolution.¹⁶ Such typical in situ room temperature STM images are presented in Figure 3.

Compound **1**, compared to 1,3,5-tris[*E*]-2-(3,5-didecyloxyphenyl)-ethenyl]benzene (compound **B**) as a reference material⁹ presents essentially C–C triple bonds instead of double bonds at the same location. Compound **B** is constituted of three specific molecular units designed to act as functional linking groups able to form strong surface-assisted intermolecular ‘clips’ which by interdigitation, strictly mimic the atomically precise organization of *n*-alkanes on HOPG. The ‘clip concept’ is described in details elsewhere.¹⁷ The structural difference in case of compound **1** compared with compound **B** increases the distance between alkyl chains which become less suited to form the so-called ‘clips’ of interdigitated alkyl chains. This also prevents the formation of an arrangement in exact registry with graphite. Consistently, no stable honeycomb 2D self-organization is observed for **1**: Indeed our ‘host’ system could not compensate the energetic cost of the formation of empty cavity as initially envisaged. Yet, a different 2D-self-assembly is observed, which consists in formation of dimers arranged as single domains: Dimer formation may be explained by the formation of only one clip per molecule. This may



Scheme 1. Reagents and conditions: (i) BrC₁₀H₂₁, K₂CO₃, DMF, 150 °C, 2 h, 73%; (ii) CBr₄, PPh₃, CH₂Cl₂, 15 min, 0 °C, 79%; (iii) *n*-BuLi, THF, –78 °C 1 h, 88%; (iv) 1° *n*-BuLi, THF, 78 °C 1 h, 2° B(OiPr)₃, –78 °C to –20 °C, 2 h, 3° KHF₂, H₂O, –20 °C to rt, 2 h, 80%.



Scheme 2. Reagents: (i) **5**, PdCl₂(dppf), CH₂Cl₂, Cs₂CO₃, THF, H₂O, δ , 12 h.

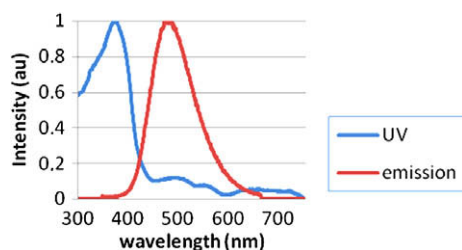


Figure 2. UV-vis absorption (blue) and fluorescence spectra (red) of **1** (excitation $\lambda = 366$ nm) in CHCl₃.

be made possible here through an ad-hoc orientation of two 3,4-substituted arms in order to exhibit two parallel alkyl chains distant of 4–5 Å. The molecular structure allows only one such pattern per molecule, which explains the formation of one single clip and then the dimer organization.

We move now to the longer-range organization of the dimers themselves as independent entities. On the **Figure 3**, six different orientations in two groups of three oriented at 60° one of the other are observed. Thus, there is epitaxy on the graphite probably due to the adsorption of the clipped parallel alkyl chains mentioned above in registry with the substrate. The axes of the domains are tilted with respect to those of graphite: two chiral domain types, enantiomer one of the other, are then observed. This phenomenon has already been reported with discotic liquid crystals¹⁸ and rod-shaped molecules.¹⁹ The molecule is then in ‘pro-chiral’ configuration, both molecules of dimer being posed on the same face.

In summary, we have synthesized a new star shaped molecule with a pyrimidine core by Suzuki cross-coupling reaction. This molecule presents interesting fluorescence properties. Interesting self-organization properties on HOPG have also been observed by STM and interpreted based on previous observation. These preliminary results confirm the clip concept proposed previously with a different molecular design.¹⁷ Moreover, with a minor modification of the molecular design of the arms of molecule **1**, the fabrica-

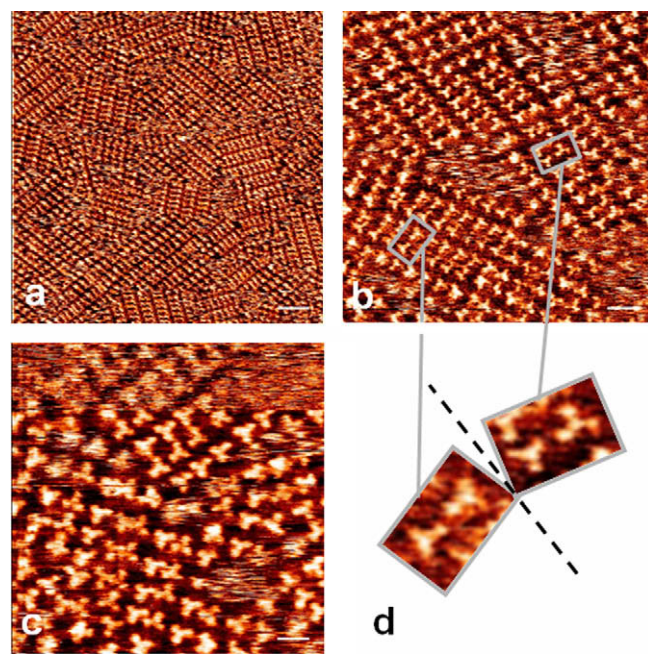


Figure 3. STM images of the monolayer of **1** on HOPG at the interface with a $\sim 10^{-2}$ mol/L solution in phenyloctane. Scan sizes: 100 × 100 nm (a), 50 × 50 nm (b) and 25 × 25 nm (c) recorded in the current (i.e., constant height) mode with a scanning rate of 40 ms per line, a sample bias of –1000 mV and a set point of 10 pA. (d) Two excerpts from image b showing the presence of mirror-symmetric domains. The symmetry line must corresponds to a mirror symmetry axis of HOPG, either $\langle 1\ 0\ 0 \rangle$ or $\langle 1\ 1\ 0 \rangle$.

tion of a honeycomb-like host matrix can be reasonably envisaged with two nitrogen atoms oriented toward the cavity, the affinity of these cavities being then modified which allows to expect a modulation of the molecular sieve properties. The next step in this series of studies will be the synthesis of compound **A**.

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- Compound **3**: triphenylphosphine (1.37 g, 5.25 mmol) was added to CBr₄ (792 mg, 2.39 mmol) in anhydrous CH₂Cl₂ (17 mL) at 0 °C. Compound **2** (1.00 g, 2.39 mmol) was added and the resulting mixture was stirred at 0 °C for 10 min before the addition of H₂O (6 mL). The organic phase was separated, dried (MgSO₄) and concentrated in vacuo. The yellow slurry obtained was triturated with hexane and then Et₂O to remove Ph₃PO. The organic washings were dried (MgSO₄) and concentrated in vacuo. The residue was purified by column chromatography (silica gel, eluent petroleum ether/ethyl acetate (9:1)) to give 1.08 g (79%) of **3** as a colorless solid mp <50 °C. ¹H NMR (CDCl₃, 300 MHz): δ 0.91–0.86 (m, 6H, 2 × CH₃), 1.47–1.28 (m, 28H, 14 × CH₂), 1.83–1.78 (m, 4H, 2 × CH₂), 4.00–3.96 (m, 4H, 2 × OCH₂), 6.80 (d, *J* = 7.8 Hz, 1H, H₆), 7.06–7.02 (m, 1H, H₅), 7.19 (d, *J* = 1.7 Hz, 1H, H₂), 7.35 (s, 1H, H₁). ¹³C NMR (CDCl₃, 75 MHz): δ 14.6, 23.2, 26.5, 29.7, 29.8, 29.9 (2C), 30.1 (2C), 32.4, 69.4, 69.7, 87.3, 113.2, 114.0, 122.4, 128.2, 136.9, 149.0, 150.0. IR (KBr, cm^{−1}) 2919, 2850, 1597, 1517, 1469, 1278, 1281, 1235, 1148, 1138. Anal. Calcd for C₂₈H₄₆Br₂O₂ (512.19): C, 58.54; H, 8.07. Found: C, 58.49; H, 8.03. Compound **4**: *n*-BuLi (1.6 M, 9.66 mL, 14 mmol) was added slowly (over 1 h) to **3** (4.06 g, 7 mmol) in anhydrous THF (90 mL) cooled to −78 °C. The resulting brown solution was stirred at −78 °C for 1 h then warmed slowly to rt and stirred for a further 1 h. Saturated NH₄Cl (50 mL) was added and the mixture extracted with ether (3 × 50 mL). The combined ethereal extracts were dried (MgSO₄) and concentrated in vacuo. The residue was purified by column chromatography (silica gel, eluent petroleum ether/ethyl acetate (8:2)) to give 2.67 g (92%) of **4** as a yellow oil. ¹H NMR (CDCl₃, 300 MHz): δ 0.91 (t, *J* = 6.8 Hz, 6H, 2 × CH₃), 1.48–1.30 (m, 28H, 14 × CH₂), 1.85–1.78 (m, 4H, 2 × CH₂), 3.00 (s, 1H, H₁), 4.01–3.96 (m, 4H, 2 × OCH₂), 6.79 (d, *J* = 7.8 Hz, 1H, H₆), 7.01 (d, *J* = 1.7 Hz, 1H, H₂), 7.07 (dd, *J* = 7.8 Hz, *J* = 1.7 Hz, 1H, H₅). ¹³C NMR (CDCl₃, 75 MHz): 14.5, 23.1, 23.7, 26.4, 29.6 (2C), 29.8 (2C), 30.0, 30.1, 32.3, 32.4, 69.4, 69.5, 75.9, 84.3, 113.4, 114.5, 117.4, 125.9, 149.0, 150.4. Anal. Calcd for C₂₈H₄₆O₂ (414.35): C, 81.10; H, 11.18. Found C, 81.13; H, 11.18. Compound **5**: a solution of alkyne (1.22 g, 2.94 mmol) in 50 mL of dry THF was cooled to −78 °C under nitrogen. *n*-BuLi (1.6 M, 1 equiv) was added dropwise, and the solution was stirred for 1 h at this temperature. Triisopropylborate (1.5 equiv) was then added dropwise at −78 °C. The solution was stirred at this temperature for 1 h after which it was allowed to warm to −20 °C for 1 h. A saturated aqueous solution of potassium hydrogen difluoride (6.0 equiv) was added to the vigorously stirred solution. The resulting mixture was stirred for 1 h at −20 °C after which it was warmed to room temperature for 1 h. The solvent was removed under reduced pressure, and the resulting white solid was dried under high vacuum to remove all water. The solid was then washed with acetone and with hot acetone. The resulting organic solution was evaporated to give 1.22 g (80%) of **5** as a colorless solid. Mp >250 °C. ¹H NMR (DMSO-*d*₆, 300 MHz): δ 0.91 (t, *J* = 6.8 Hz, 6H, 2 × CH₃), 1.49–1.32 (m, 28H, 14 × CH₂), 1.82–1.72 (m, 4H, 2 × CH₂), 4.00–3.97 (m, 4H, 2 × OCH₂), 6.92–6.86 (m, 3H, H_{2,5,6}). ¹³C NMR (DMSO-*d*₆, 75 MHz) δ 14.3, 22.5, 26.0, 26.3, 28.4, 29.1, 29.2, 29.3, 29.5, 31.7, 68.5, 68.6, 90.0, 113.7, 116.5, 118.3, 124.1, 148.2, 148.4. ¹⁹F NMR (DMSO-*d*₆, 282.5 MHz) −131.9. IR (KBr, cm^{−1}) 2919, 2851, 2184, 1515, 1239, 1046.
- Compound **6**: 2,4,6-trichloropyrimidine (183 mg, 1.00 mmol), **5** (2.60 g, 5.4 mmol), PdCl₂(dppf), CH₂Cl₂ (216 mg, 0.26 mmol) and Cs₂CO₃ (5.27 g, 16.2 mmol) were mixed with THF and degassed water under Nitrogen (20:1 THF to water ratio). The solution was heated at reflux for 12 h. Then the mixture was cooled, and 10 mL of water was added to the flask. The resulting solution was then extracted with diethyl ether. The combined organic extracts were washed with 1 M HCl and brine and then dried over MgSO₄. After filtering off the solid, the solvent was removed under reduced pressure to give 375 mg (40%) of **6** as a pale yellow solid. mp = 58 °C. ¹H NMR (CDCl₃, 300 MHz): δ 0.90 (t, 12H, 4 × CH₃), 1.49–1.18 (m, 56H, 28 × CH₂), 1.89–1.81 (m, 8H, 4 × CH₂), 4.08–4.01 (m, 8H, 4 × OCH₂), 6.84 (d, *J* = 8.1 Hz, 2H, H_{Ph}), 7.12 (s, 2H, H_{Ph}), 7.21 (d, *J* = 8.1 Hz, 2H, H_{Ph}), 7.45 (s, 1H, H₅). ¹³C NMR (CDCl₃, 75 MHz): δ 13.1, 21.7, 25.0, 28.1(2C), 28.4, 28.6, 28.7, 30.9, 68.0, 68.2, 84.1, 96.8, 111.2, 111.7, 116.0, 122.0, 125.6, 147.7, 150.5, 152.1, 160.3. IR (KBr, cm^{−1}) 2818, 2850, 2212, 1557, 1514, 1469, 1268, 1243, 1128. Anal. Calcd for C₆₀H₉₁ClN₂O₄ (939.83): C, 76.68; H, 9.76; N, 2.98. Found C, 76.81; H, 9.83; N, 2.81. Compound **1**: this compound was prepared by similar procedure described for compound **6** using **6** instead of 2,4,6-trichloropyrimidine. yellow solid. mp <50 °C. ¹H NMR (CDCl₃, 300 MHz): δ 0.91 (t, 18H, 6 × CH₃), 1.49–1.18 (m, 84H, 42 × CH₂), 1.89–1.81 (m, 12H, 6 × CH₂), 4.08–4.01 (m, 12H, 6 × OCH₂), 6.90–6.85 (m, 3H, H_{Ph}), 7.15 (s, 3H, H_{Ph}), 7.24–7.21 (m, 3H, H_{Ph}), 7.48 (s, 1H, H₅). ¹³C NMR (CDCl₃, 75 MHz): δ 13.1, 21.7, 25.0, 28.1, 28.4 (2C), 28.6 (4C), 28.7, 30.9, 68.1, 68.2, 84.6, 85.9, 88.3, 95.0, 111.7, 111.8, 112.0, 116.0, 116.3, 121.9, 125.3, 125.4, 147.5, 147.7, 149.8, 150.2, 152.7. IR (KBr, cm^{−1}) 2924, 2854, 2208, 1555, 1513, 1264, 1247. Anal. Calcd for C₈₈H₁₃₆N₂O₆ (1318.03): C, 80.19; H, 10.40; N, 2.13. Found C, 80.51; H, 10.78; N, 1.89.
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