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Template-Assisted Benzannulation Route to Pentacene and Tetracene Derivatives and its Application to Construct Amphiphilic Acenes That Self-Assemble into Helical Wires

Bikash Pal, Chun-Hsiung Chang, Cian-Jhe Zeng, and Chih-Hsiu Lin*

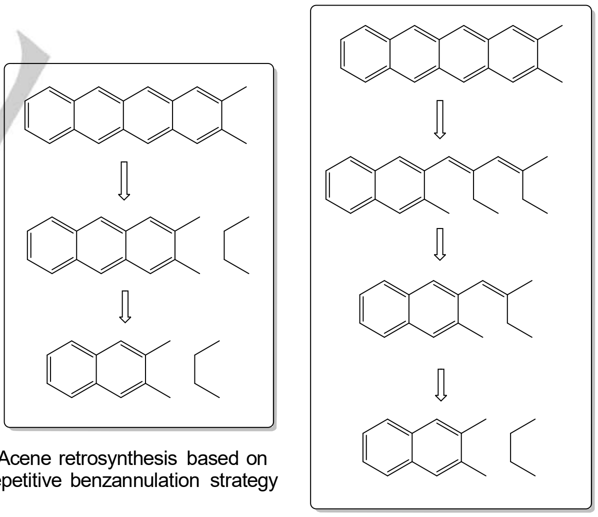
Abstract: Pentacene is one of the most versatile organic semiconductors. New synthetic strategies to construct the pentacene skeleton are imperative to produce pentacene derivatives with appropriate solubility, stability, and optoelectronic properties for various applications. This paper describes a template-directed approach to pentacene derivatives. In the retrosynthesis, the acene skeleton is viewed as a laddered double strand polyene instead of the more intuitive linearly fused hexagons. Based on this vision, the template strand of polyene is constructed with Wittig olefination, whereas the second strand is accomplished with Knoevenagel condensation to produce pentacene and tetracene derivatives. The synthetic scheme is flexible enough to generate an array of acene derivatives with substitution patterns that are hitherto difficult to access. Amphiphilic pentacene and tetracene derivatives were also synthesized by the template strategy. One pentacene based amphiphilic rod-coil molecule undergoes self-assembly to form helical wire structures that were visualized with TEM.

Introduction

In the pursuit of organic electronic material,[1] the linearly fused pentacene skeleton has been proven one of the most privileged structural motifs.[2] Pentacene derivatives have shown great promise as the semiconducting components in many devices. Parallel to this emerging endeavor, the synthetic effort towards organic conjugated systems in general also experienced a recent renaissance. Innovative methodologies are invented and refined to deliver target compounds in practical scale for physical studies or device fabrications.[3] In the present study, we wish to report a conceptually novel synthetic strategy towards pentacene and tetracene skeletons via template-directed benzannulation. Regioselective installation of various functional groups onto the acene skeletons was achieved with the new methodology.

On surveying the literature, retrosynthetic plans towards acene homologues rely heavily on stepwise benzannulation strategies. Notable examples include the Diels-Alder approaches,[4] the double aldol condensation approach,[5] the zirconocene mediated cyclization,[6] and the iterative elongation tactic based on Wittig-Knoevenagel benzannulation.[7] An alternative approach is the "precursor route" where the acene skeleton is established only in the last step from a precursor molecule via photochemical or thermolytic extrusion reactions.[8] Despite their wide applications, neither protocol is particularly effective towards multiply substituted acene derivatives. An innovated synthetic strategy that combines the merits of benzannulation and precursor approaches could potentially open access to a wider scope of acene structures. The template-directed multiple benzannulation approach to tetracene and pentacene structures described in this article is an attempt towards this direction.

This intuition to adopt the stepwise benzannulation approach is the result of viewing the acene skeleton as a linear array of fused benzene rings. However, acene can also be viewed as double strand polyenes. In fact, computational studies have long recognized that the electronic structures of high acene derivatives resemble those of double strand ladder polyenes.[9] Taking a hint from such different perspective, we propose an alternative retrosynthetic approach to acene skeleton perceiving acene as a double strand laddered polyene instead of the linear array of fused benzene rings. The most prominent path to construct double strand systems, exemplified by DNA synthesis in biological systems, is to pre-form one strand as the template to assemble the second strand. To employ this principle to acene synthesis, the template polyene formed first must carry the building blocks for the second strand. The second strand can then be assembled with the first strand as its template (scheme 1). The benzannulation and precursor routes are merged in this template approach since the acene skeletons are accomplished only in the last step from non-acene precursors via multiple benzannulation.



Acene retrosynthesis based on repetitive benzannulation strategy

Acene retrosynthesis based on template directed strategy

Scheme 1: Two distinct acene synthesis strategies based on repetitive benzannulation and template-directed construction of double strand polyene.

Results and Discussion

A model study was carried out with the simple 2,3-anthracene diester **5** as the target. Due to their efficiency in olefin synthesis, Wittig-Horner reaction and Knoevenagel condensation are

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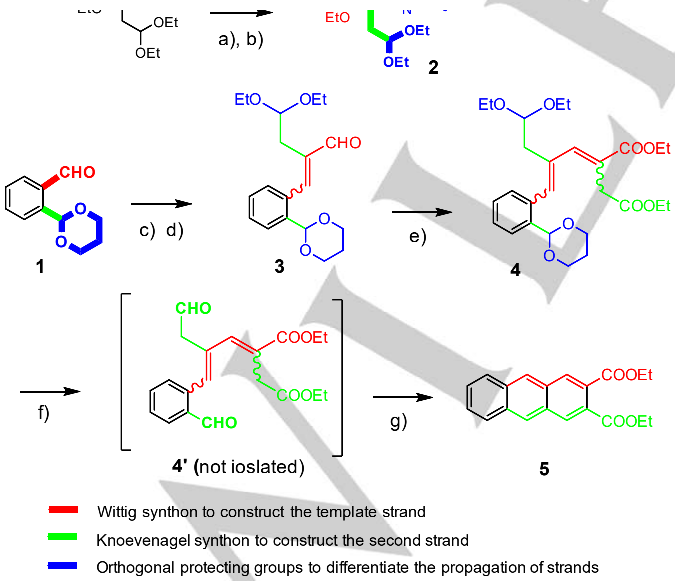
chosen to construct the two strands of polyene in the two stages. Since both reactions require aldehyde as their electrophilic components, the aldehyde groups for constructing the second strand must be protected until the first strand is accomplished. The fulfillment of this template synthesis concept is depicted in Scheme 2 in which the template strand (including its Wittig synthons) are depicted in red, the second strand in green, and the two sets of orthogonal protecting groups in blue. According to the analysis, the starting compound should be a semi-protected phthalaldehyde (as 1,3-dioxane acetal) as **1**.[10] The elongation unit **2** carries an imine based Wittig-Horner reagent[11] to construct the first strand and a masked aldehyde (protected as diethyl acetal) as the building block of the second strand. (This compound was synthesized via formylation of diethyl (3,3-diethoxypropyl)phosphonate followed by imine formation.)[12] Wittig-Horner reaction between **2** and **1** furnished the imine intermediate which was immediately hydrolyzed to aldehyde **3** in oxalic acid, whose acidity is weak enough to preserve the acetal groups intact. The unmasked aldehyde then underwent another Wittig reaction (diethyl maleate/PEt_3, according to the modification reported by McCombie and Townsend)[13] to give **4**. The diene moiety in **4** is the template strand. The acetal protecting groups were hydrolyzed at this stage. The two liberated aldehyde groups then underwent double Knoevenagel cyclization (DBU) to accomplish the anthracene skeleton.

When compared to other known benzannulation strategies, the new template-directed synthesis is not the most step-economical. However, this preliminary model study reveals several advantages of the template strategy. First, several steps are operationally simple protection-deprotection reactions that proceed with nearly quantitative yields. Secondly, all aldehyde groups for the annulation are introduced with the right redox state. No cumbersome functional group transformation reactions are required. The good yield of the last two steps (83 percent for two deprotection and two cyclization steps) indicates this methodology should be applicable to synthesize longer acene derivatives.



Scheme 2: Synthesis of diethyl 2,3-anthracene diester via template strategy-the model reaction. Reagents and conditions: (a) (i) LDA, THF, -78ºC, 1 h; (ii) ethyl formate, -78ºC, 1 h, 76 % (over two steps); (b) MeOH, cyclohexylamine, 0ºC to r.t., 3 h, 96 %; (c) (i) NaH, **2,** THF, 0ºC, 1 h, (ii) reflux, 2h; (d) CH_2Cl_2/THF (4/1), oxalic acid, 0ºC to r.t., 2 h, 74 % (over two steps); (e) (i) toluene, diethyl maleate, PEt_3, 0ºC to r.t., 30 min., (ii) **3,** reflux, 25 h, 80 %; (f) CH_2Cl_2/ $CH_3COOH/H_2O/CF_3COOH$ (2:2:1:1), r.t., 24 h; (g) CH_2Cl_2, M. S. (4 Å), DBU, r.t., 30 min., 83 % (over two steps).

After the template concept is verified, tetracene and pentacene derivatives in principle can be synthesized with a few extra elongation cycles. However, for this purpose, to carry out bidirectional template-directed benzannulation is far more step-economical. The realization of this proposal is demonstrated in Scheme 3a. 2,5-Bis(1,3-dioxan-2-yl)terephthalaldehyde (**8**) is employed as the starting compound in place of the monoaldehyde **5** in scheme 2. This compound was synthesized from known 2,5-dibromoterephthalaldehyde[14] in three steps. The two aldehyde groups were first protected as 1,3-dioxne acetal. The bromides were then converted to aldehydes with Heck coupling and ozonolysis. The subsequent steps are identical with those in Scheme 2. After a double Wittig-Horner olefination was carried out with the elongation unit **2**, the imine groups were hydrolyzed to give dialdehyde **9**. The second round of Wittig reaction (diethyl maleate and dibutyl fumarate/PEt_3) was then performed to accomplish the template strand diene in **10a** and **10b** respectively The yield to construct the template strand over three steps (four Wittig reactions overall) is 63 %. At this stage, all four acetal protecting groups were hydrolyzed. The intermediate tetra-aldehyde undergoes spontaneous cyclization to give anthracene intermediates **11a** and **11b**. A final DBU catalyzed Knoevenagel condensation effect the tetraethyl and tetrabutyl pentacene 2,3,9,10-tetracarboxylate **12a** and **12b**. The extraordinary efficiency of the template strategy is validated with the respectable 60 % yield in the final four-fold deprotection and four-fold cyclization steps.

With the template-directed synthesis of pentacene 2,3,9,10-tetraester accomplished, pentacene with other electron-withdrawing substitutions (nitrile, imide, sulfone) at these positions can also be considered. According to our previous experiences, N-alkyl pentacene 2,3,9,10-bisimide derivatives are too insoluble for purification and full characterization.[15] Yet, with the greatly enhanced synthetic efficiency, more complex solubilizing groups like 3,4,5-tris(dodecyloxyphenyl)[16] can now be incorporated to overcome the solubility problem. In Scheme 3b, the pentacene diimide **15** was synthesized from **9** with N-3,4,5-tris(dodecyloxyphenyl)maleimide replacing diethyl maleate in Scheme 3a in the Wittig reaction. With both template diene moieties in place, compound **13** underwent deprotection to liberate four aldehyde groups to furnish the pentacene skeleton. As in Scheme 3a, anthracene intermediate **14** was obtained right after the hydrolysis due to spontaneous Knoevenagel condensation. A second Knoevenagel condensation (catalyzed by DBU) furnishes the pentacene diimide **15.** The overall yield for the template-directed quadruple cyclization is 53 %.

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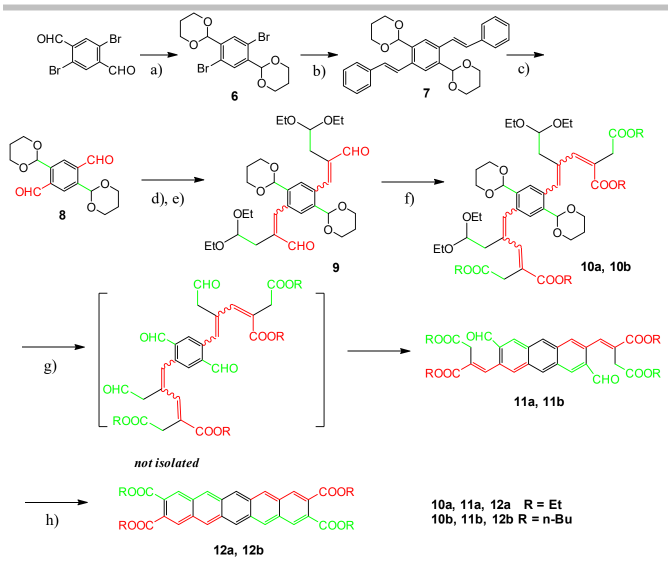
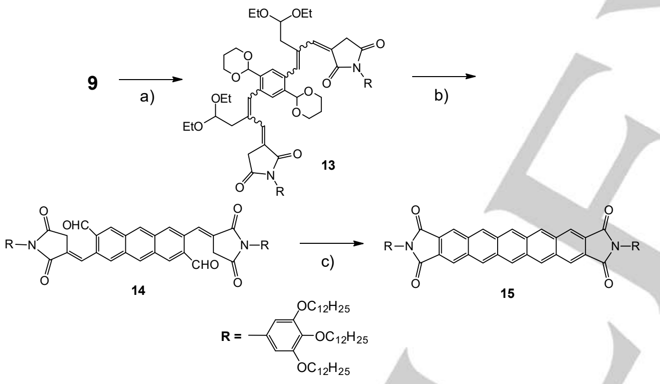
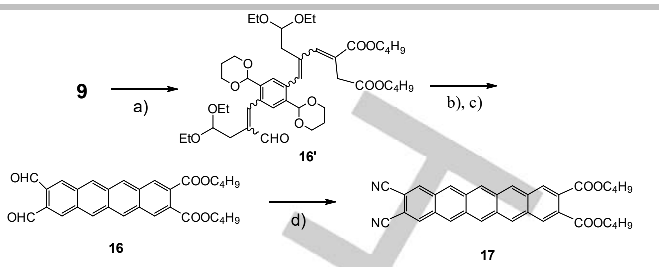


Scheme 3a: Synthesis of 2,3,9,10-pentacene tetraester via bidirectional template strategy. Reagents and conditions: (a) toluene, PTSA, $HOCH_2CH_2CH_2OH$, reflux, 5 h, 96 %; (b) DMF/Et_3N (1/1) $Pd(OAc)_2$, tri(o-tolyl)phosphine, styrene, 90ºC, 16 h, 72 %; (c) CH_2Cl_2/MeOH (5/1), pyridine, O_3/O_2, -78ºC to r.t,. 1 h, Me_2S, r.t., 12 h, 85 %; (d) (i) NaH, **2**, THF, 0ºC, 1 h, (ii) reflux, 2h; (e) CH_2Cl_2/THF (4/1), oxalic acid, 0ºC to r.t., 2 h, 76 % (over two steps); (f) (i) toluene, diethyl maleate or dibutyl fumarate, PEt_3, 0ºC to r.t., 1 h, (ii) **9**, reflux, 36-48 h, 84 % or 83 %; (g) $CH_2Cl_2/CH_3COOH/H_2O/CF_3COOH$ (2:2:1:1), r.t., 24 h; (h) CH_2Cl_2, M. S. (4 Å), DBU, r.t., 30 min., 58 % or 60 % (over two steps).



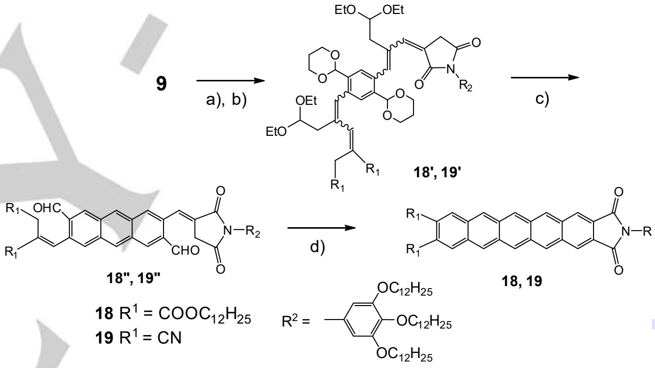
Scheme 3b: Synthesis of soluble pentacene 2,3,9,10 bisimide. Reagents and conditions: (a) (i) toluene, N-3,4,5-tris(dodecyloxyphenyl) maleimide, PEt_3, 0ºC, 1 h, (ii) **9,** reflux, 48 h, 76 %; (b) $CH_2Cl_2/CH_3COOH/H_2O/CF_3COOH$ (2:2:1:1), r.t., 24 h; (c) CH_2Cl_2, M. S. (4 Å), DBU, r.t., 30 min., 53 % (over two steps).

Pentacene derivatives with unsymmetrical substituents at terminal rings are quite rare in literature.[17] The present synthetic strategy can easily be adopted to make this class of elusive compounds. In Scheme 4a, **9** was employed in Wittig reactions with 1.3 equivalents of dibutyl fumarate and triethyl phosphine to produce **16'**. After deprotection of acetal groups and DBU catalyzed cyclization, dibutyl-8,9-diformyltetracene-2,3-dicarboxylate **16** was produced. This compound then underwent a further elongation (fumaronitrile/PEt_3/ DBU) to furnish pentacene diester dinitirle **17** in 31 % yield.



Scheme 4a: Synthesis of unsymmetrically substituted 2,3 diester-9,10 dinitrile pentacene. Reagents and conditions: (a) (i) toluene, dibutyl fumarate (1.4 eq.), PEt_3, r.t., 1 h, (ii) **9**, reflux, 36 h, 78 %; (b) $CH_2Cl_2/CH_3COOH/H_2O/CF_3COOH$ (2:2:1:1), r.t., 24 h; (c) CH_2Cl_2, M. S. (4 Å), DBU, r.t., 30 min., 62 % (over two steps); (d) CH_2Cl_2, PEt_3, fumaronitrile, 0ºC, 3 h, 31 %.

To further simplify the procedure and improve its efficiency, two consecutive Wittig reaction can be carried out on **9** using different electron deficient alkenes (dialkyl fumarate, fumaronitrile, and tris(dodecyloxyphenyl) maleimide) to produce **18'** and **19'** (Scheme 4b). The subsequent template-directed cyclization were conducted accordingly to give the pentacene imide diester **18**, and pentacene imide dinitrile **19** in practical yields (40-50%) and scale (100-200 mg).



Scheme 4b: Simplified synthesis of unsymmetrically substituted pentacene**.** Reagents and conditions: (a) (i) toluene, N-3,4,5-tris(dodecyloxyphenyl) maleimide, PEt_3, 0ºC, 1 h, (ii) **9,** reflux, 36 h, 78 %; (b) (i) toluene, didodecyl fumarate or fumaronitrile, PEt_3, r.t. or 0ºC, 1 h, (ii) **9',** reflux, 36-48 h, 64 % or 54 %; (c) $CH_2Cl_2/CH_3COOH/H_2O/CF_3COOH$ (2:2:1:1), r.t., 24 h; (d) CH_2Cl_2, M. S. (4 Å), DBU, r.t., 30 min., 54 % or 42 % (over two steps).

Furthermore, we can take advantage of the C_{2h} symmetry of **9** to synthesize pentacene derivatives with the same symmetric property. With dodecyl-3-cyano-2-(triphenylphosphoranylidene) propanoate employed in the Wittig reaction (Scheme 4c), the template strategy opened access to pentacene 2,9-diester 3,10-dinitrile **(20),** a new class of pentacene derivatives with C_{2h} symmetry. The yield for the template directed four-fold cyclization is near 50 %. It is difficult to envision a selective synthesis of pentacene derivatives with this substitution pattern by any other methodologies hitherto available.

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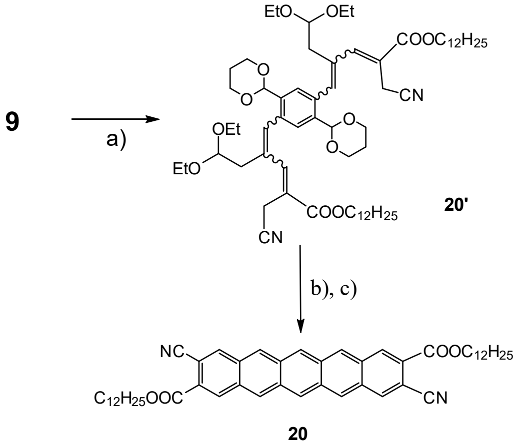
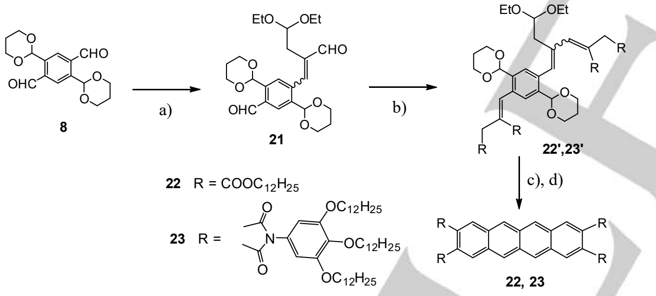


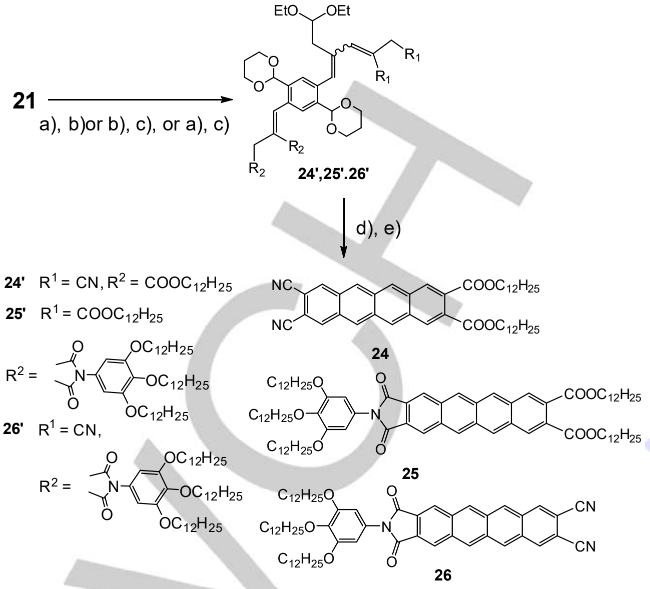
Scheme 4c: Synthesis of pentacene 2,9-diester 3,10-dinitrile with C_{2h} symmetry. Reagents and conditions: (a) toluene, dodecyl-3-cyano-2-(triphenylphosphoranylidene) propanoate,, reflux, 48 h, 73 %; (b) $CH_2Cl_2/CH_3COOH/H_2O/CF_3COOH$ (2:2:1:1), r.t., 24 h; (c) CH_2Cl_2, M. S. (4 Å), DBU, r.t., 30 min., 46 % (over two steps).

To expand the scope of this template-directed annulation, tetracene derivatives are the most obvious targets. The bidirectional approach in Scheme 3a and 3b cannot be directly adopted, because the tetracene does not possess a central ring to launch the elongation. However, the desymmetrization of **8** can be accomplished by using one equivalent of **2** as the limiting reagent (Scheme 5a). The following steps (hydrolysis of imine, Wittig olefination, hydrolysis of acetals, Knoevenagel cyclization) are identical as pentacene synthesis in Scheme 3a and 4a. Tetraester (86 %) and bisimide (61 %) tetracene derivatives (**22** and **23**) were produced accordingly in practical yields.

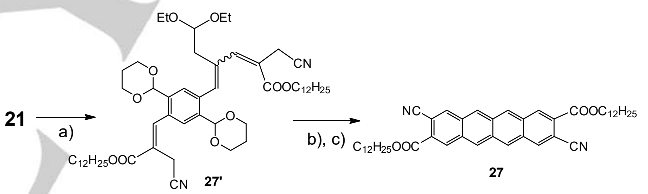


Scheme 5a: Tetracene synthesis via bidirectional template strategy. Reagents and conditions: (a) (i) NaH, **2 (1 eq.),** THF, 0ºC, 1 h, (ii) reflux, 2h; (iii) CH_2Cl_2/THF (4/1), oxalic acid, 0ºC to r.t., 2 h, 71 %; (b) (i) toluene, didodecyl fumarate or maleimide, PEt_3, r.t. or 0ºC, 1 h, (ii) **21,** reflux, 36-48 h, 74 % or 71 %; (c) $CH_2Cl_2/CH_3COOH/H_2O/CF_3COOH$ (2:2:1:1), r.t., 24 h; (d) CH_2Cl_2, M. S. (4 Å), DBU, r.t., 30 min., 86 % or 61 % (over two steps).

Tetracene diester dinitrile **24**, diester imide **25**, dinitirle imide **26**, and C_{2h} symmetric **27** tetracene derivatives were also generate in good yields (51-77% in the triple cyclization steps) with the template-directed strategy (Scheme 5b and 5c).

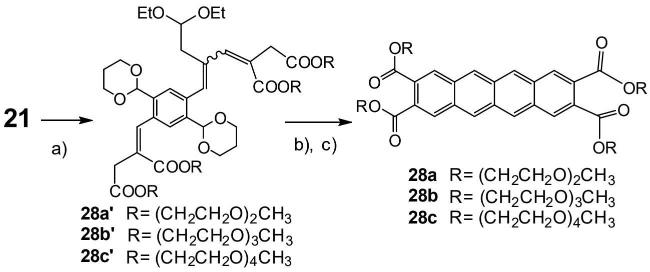


Scheme 5b: Synthesis of unsymmetrically substituted tetracene. Reagents and condition: (a) (i) toluene, fumaronitrile, PEt_3, 0ºC, 1 h, then reacts with the appropriate aldehyde, reflux, 36 h,; (b) toluene, didodecyl fumarate, PEt_3, 0ºC, 1 h, then reacts with the appropriate aldehyde**,** reflux, 36 h (c) toluene, maleimide, PEt_3, 0ºC, 1 h, then reacts with the appropriate aldehyde**,** reflux, 36 h, 64%, 69%, and 58% (over two steps) (d) $CH_2Cl_2/CH_3COOH/H_2O/CF_3COOH$ (2:2:1:1), r.t., 24 h; (e) CH_2Cl_2, M. S. (4 Å), DBU, r.t., 30 min., 77 % , 62 % and 59 % (over two steps).



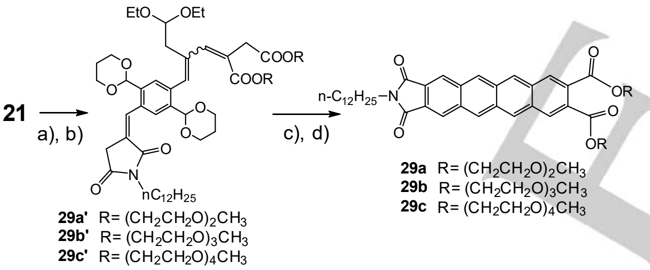
Scheme 5c: Synthesis of tetracene 2,8-diester 3,9-dinitrile with C_{2h} symmetry Reagents and conditions: (a) toluene, dodecyl-3-cyano-2-(triphenylphosphoranylidene) propanoate,, reflux, 48 h, 75 %; (b) $CH_2Cl_2/CH_3COOH/H_2O/CF_3COOH$ (2:2:1:1), r.t., 24 h; (c) CH_2Cl_2, M. S. (4 Å), DBU, r.t., 30 min., 51 % (over two steps).

In addition to creating novel π-systems through chemical synthesis, another important objective in the current exploration of organic electronic materials is to assemble flat aromatic systems into 3-D supramolecular architectures with well-defined shapes and sizes. It is generally acknowledged that the intermolecular packing orders of chromophores can have profound influences on the charge transporting and energy transfer properties of the materials, sometimes overturn the structural effects of individual chromophores.[18] Perylene diimide based self-assembly systems are now commonly employed in sensors and photovoltaic devices.[19] Self-assembly studies of pentacene scaffold mostly focus on crystal engineering of 6,13-disubstituted derivatives.[5f, 20] For terminal substituted acenes, coil-rod anthracene and tetracene derivatives were reported to form self-assembled organic gelators which display energy transfer properties.[21] Since the template strategy opened the synthetic access to unsymmetrically substituted pentacene and tetracene derivatives, we perceived the opportunity to construct amphiphilic acene derivatives as the building blocks for new types of acene based self-assembly structures. The target molecules for such investigation are composed of rigid acene moieties substituted with hydrophilic groups at one end of the structure and hydrophobic groups on the other. To accommodate the template-directed synthetic protocol, oligo ethylene glycol esters and N-dodecyl imide are chosen as the hydrophilic and hydrophobic moieties respectively. In an attempt to fine-tune the volume ratio among aromatic rod, hydrophobic coil, and hydrophilic coil, diethylene glycol, triethylene glycol, and tetraethylene glycol are incorporated into these systems. Three 2,3,8,9-tetracene tetrakis(oligo ethylene glycol)ester (**28a, 28b,** and **28c**) were first synthesized (Scheme 6a) to test whether the oligo ethylene glycol chain is compatible with the multiple benzannulation reactions. Satisfactory yields were recorded for all three model compounds (80-83%).

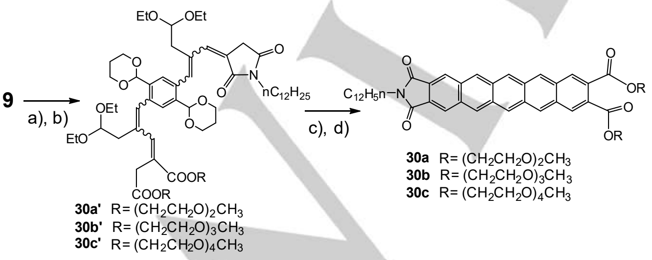


Scheme 6a: Synthesis of water soluble tetracene derivatives. Reagents and conditions: (a) (i) toluene, bis(di, tri, or tetra-ethylene glycol methyl ether) fumarate, PEt_3, r.t., 1 h (ii) **21**, reflux, 48 h, 95 %, 89 %, and 86 %; (b) CH_2Cl_2/CH_3COOH/H_2O/CF_3COOH (2:2:1:1), r.t., 24 h, 84 %, 82 %, and 80 %; (c) CH_2Cl_2, M. S. (4 Å), DBU, r.t., 30 min., 83 % , 80 %, and 81 %.

Next, amphiphilic tetracene (**29a**, **29b**, and **29c**) and pentacene (**30a**, **30b**, and **30c**) derivatives were synthesized according to the procedures in Scheme 6b and 6c. The yields for the template-directed multiple cyclization steps are comparable with those observed previously (Scheme 4b, 5b).



Scheme 6b: Synthesis of amphiphilic tetracene derivatives via bidirectional template strategy. Reagents and conditions: (a) (i) toluene, bis(di, tri, or tetra-ethylene glycol methyl ether) fumarate, PEt_3, r.t., 1 h (ii) **21,** reflux, 48 h; (b) (i) toluene, N-dodecyl maleimide, PEt_3, 0ºC, 1 h; (ii) **21'**, reflux, 48 h, 65 %, 63 %, and 64 %; (b) CH_2Cl_2/CH_3COOH /H_2O/CF_3COOH (2:2:1:1), r.t., 24 h, 87 %, 85 %, and 84 %; (c) CH_2Cl_2, M. S. (4 Å), DBU, r.t., 30 min., 85 % , 83 %, and 84 %.



Scheme 6c: Synthesis of amphiphilic pentacene derivatives via bidirectional template strategy. Reagents and conditions: (a) (i) toluene, bis(di, tri, or tetra-ethylene glycol methyl ether) fumarate, PEt_3, r.t., 1 h (ii) **9,** reflux, 48 h; (b) (i) toluene, N-dodecyl maleimide, PEt_3, 0ºC, 1 h; (ii) **9'**, reflux, 48 h, 59 %, 55 %, and 53 %; (c) CH_2Cl_2/CH_3COOH /H_2O/CF_3COOH (2:2:1:1), r.t., 24 h, 87 %, 86 %, and 82 %; (d) CH_2Cl_2, M. S. (4 Å), DBU, r.t., 30 min., 64 % , 62 %, and 61 %.

Preliminary self-assembly studies were carried out with these amphiphilic compounds. The compounds were dissolved in 45-50 % THF/water solution (10^{-4}~10^{-5} M). Slow evaporation of solvents allows the molecules to undergo self-assembly under mild condition. The molecular assemblies thus formed were then visualized with TEM and AFM (Figure 1). In such investigation, compound **29b**, **29c**, **30b**, and **30c** do not exhibit any visible organized structure under the microscope. However, two compounds with diethylene glycol chains (**29a** and **30a**) formed notable features under the same condition. As shown the Figure 1, the amphiphilic tetracene **29a** forms network structures composed of fibrous assembly of various diameters ranging from 30-60 nm. The result from amphiphilic pentacene derivative **30a** is more fascinating. The compound assembles into wire like nanostructures with more uniform diameter near 20 nm. From the TEM image, these nanowire assemblies are clearly helical. Furthermore, these wires bundled up to form aggregates under the assembly condition. Since the dimension of compound **30a** is about 4 nm in its extended conformation, it is quite probable that the observed wire and fiber structures are composed of folded molecular bilayer stacks as in Aida's amphiphilic hexabenzocoronene assembly.[22] However, since it is impossible to preclude pentacene derivatives undergo decomposition during the assembly process, it must be cautioned that such molecular assembly might contain some decomposition products of **30a**.

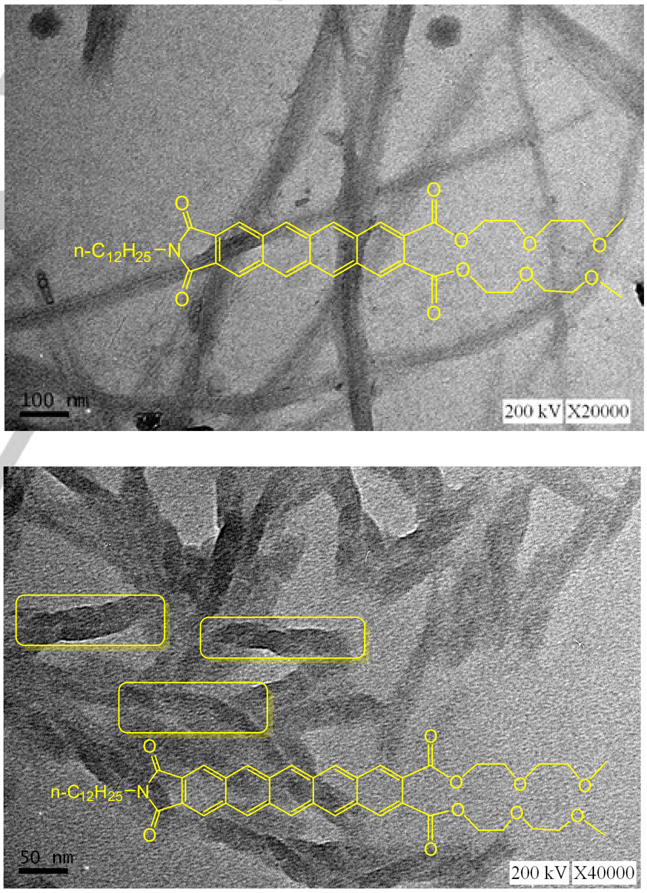


Figure 1: TEM image of amphiphilic tetracene and pentacene self-assemble (helical assemblies of **30a** are highlighted in yellow boxes)

Conclusions

In conclusion, we have developed a novel synthetic scheme to construct the acene skeletons. The new strategy adopts a distinct retrosynthetic approach by treating the acene structure as a double strand polyene instead of a linearly fused array of benzene rings. The key conceptual renovation is to pre-form the first strand of diene and use it as the template to direct the synthesis of the second diene strand. In practice, the first strand of diene was constructed with Wittig-Horner reaction while the second strand is accomplished with Knoevenagel condensation. Combining the template approach with the bidirectional growth strategy, we successfully conducted three-fold and four-fold cyclization reactions to furnish tetracene and pentacene derivatives in moderate to good yields (20-50 % over 7 steps from readily available compounds). Unsymmetrically substituted pentacene and tetracene derivatives with ester, nitrile, and imide substituents are also accessible through this strategy. Moreover, the capacity of the template strategy was showcased in the synthesis of amphiphilic acene derivative with oligo ethylene glycol ester and alkyl imide substituents at both ends of the molecules. One of these amphiphilic pentacene derivatives **30a** forms helical wire assemblies in aqueous/THF medium. This strategy should prove particularly handy when screening the physical properties of a series of compounds. It should also be applicable to the synthesis of higher acene and related polycyclic aromatic systems.

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