



Assembly of twisted luminescent architectures based on acenaphtho[1,2-k]fluoranthene derivatives

Journal:	<i>ChemComm</i>
Manuscript ID:	CC-COM-01-2015-000476.R1
Article Type:	Communication
Date Submitted by the Author:	03-Feb-2015
Complete List of Authors:	Han, Liang; Jilin University, State Key Laboratory of Supramolecular Structure and Materials Zhang, Yuewei; Jilin University, State Key Laboratory of Supramolecular Structure and Materials Chen, Weiping; Jilin University, State Key Laboratory of Supramolecular Structure and Materials Cheng, Xiao; Jilin University, State Key Laboratory of Supramolecular Structure and Materials Ye, Kaiqi; State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Zhang, Jingying; Jilin University, State Key Laboratory of Supramolecular Structure and Materials Wang, Yue; Jilin University,

COMMUNICATION

Assembly of twisted luminescent architectures based on acenaphtho[1,2-k]fluoranthene derivatives

Cite this: DOI: 10.1039/x0xx00000x

Liang Han, Yuewei Zhang, Weiping Chen, Xiao Cheng, Kaiqing Ye, JIngying Zhang* and Yue Wang*

Received 00th January 2015,

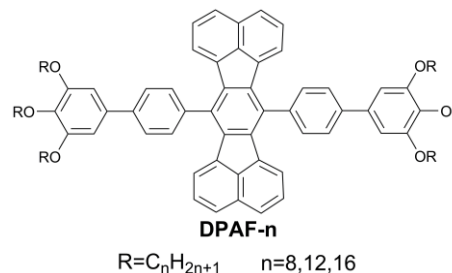
Accepted 00th January 2015

DOI: 10.1039/x0xx00000x

www.rsc.org/

Acenaphtho[1,2-k]fluoranthene derivatives **DPAF-n** as new building blocks for one-dimensional (1D) structure assembly are developed and employed to fabricate luminescent twisted nano/micro-wires; and **DPAF** rigid core attached by flexible alkyl chains with suitable length is critical for the formation of twisted architecture.

Among the attractive one-dimensional (1D) architectures, twisted and helical nano/micro-wires and ribbons based on organic functional molecules are the most representative candidates for a better understanding of some life substances and fabrication of optoelectronic devices.¹ Generally, the twisted and helical nano/micro-structures were constructed by assembling the molecules with chiral groups such as peptides,² sugar-based derivatives,³ π -conjugant oligomers⁴ and so on.⁵ Fabrication based on chiral building blocks is a popular and efficient approach to achieve twisted and helical wires and ribbons. Nevertheless, assembling achiral organic molecules into twisted and helical nano/micro-structures has become a hot topic in supramolecular chemistry area recently. The achiral molecules such as phthalocyanines,⁶ perylene bisimides,⁷ quinacridones⁸ and so on⁹ have been employed as building blocks to fabricate twisted and helical structures by intermolecular hydrogen bonding and π - π stacking interactions. These organic functional molecules with extended π -conjugated aromatic systems endow their assembly systems with unique catalysis,¹⁰ biomaterials¹¹ and optoelectronic¹² properties. Therefore,

Fig. 1 Molecular structures of **DPAF-n**.

it is still an important issue to develop new building blocks for the construction of twisted or helical structures with desired characteristics.

7,14-diphenylacenaphtho[1,2-k]fluoranthene (**DPAF**) is an extended and fused-ring molecule composed of five- and six-membered π -conjugation systems. The special structural characteristic suggested that **DPAF** based molecules have promising luminescent and semiconducting properties.¹³ Therefore, **DPAF** is considered to be a desirable building block to construct functional molecules for supramolecular assembly. In this communication three molecules **DPAF-n** ($n = 8, 12, 16$) (Fig. 1) were designed and synthesized by introducing two phenyl groups with alkyl chains to **DPAF** skeleton. **DPAF-n** molecules possess the unique molecular structure and functional characteristics as the following: (i) cross type geometry constructed by a p-quinquephenyl and acenaphtho[1,2-k]fluoranthene moieties that form the rigid core; (ii) the distinctive and large π -conjugated system suggesting in the promising emission and semiconducting properties; (iii) the **DPAF-n** structure features with rigid central core and flexible side alkyl chains allowing the performance of supramolecular assembly. **DPAF-n** molecules, which are remarkably different from the reported organic molecules for the assembly of twisted or helical structures,⁶⁻⁹ represent a new classical

State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, P.R.China. E-mails: zhangjingy@jlu.edu.cn (J. Zhang); yuewang@jlu.edu.cn (Y. Wang); Fax: +86-431-85193421; Tel: +86-431-85168484.

† Electronic Supplementary Information (ESI) available: Synthetic procedures and characterization data; additional emission spectra, XRD patterns, crystal data, fluorescence microscopy, FESEM images and CCDC 1043332. For crystallographic data in CIF; See DOI: 10.1039/c000000x/

building block for the fabrication of functional nano- and micro-materials.

DPAF-n were synthesized by Suzuki cross-coupling reactions between 7,14-Bis[4-bromophenyl]acenaphtho[1,2-k]-fluoranthene and 3,4,5-trialkylxyphenylboronic acid (Scheme S1, ESI†). To investigate the assembly properties of **DPAF-n** molecules, the phase transfer method based on a variety of binary solvents systems was employed. **DPAF-n** samples were dissolved in good solvents such as dioxane, chloroform, toluene and tetrahydrofuran. Then the **DPAF-n** solution was added into test tubes, and sequentially poor solvent such as methanol, ethanol and isopropanol was carefully covered on top surface of **DPAF-n** solution. Slow diffusion of poor solvent into **DPAF-n** solutions resulted in 1D nano or micro-materials with luminescent characteristic in the interlayer between good and poor solvent phases.

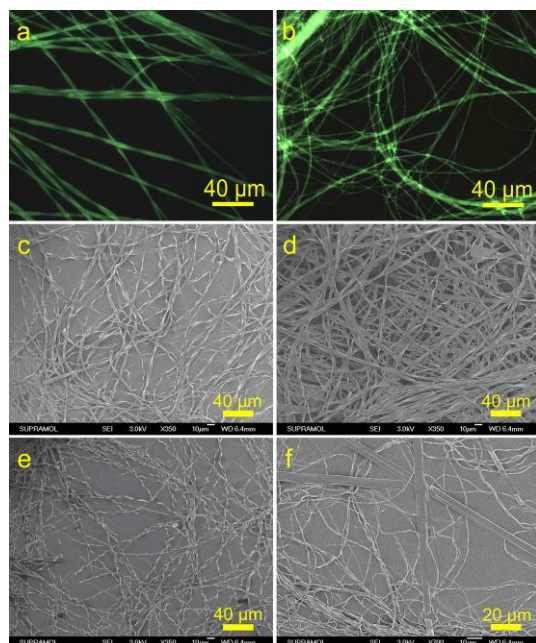


Fig. 2 Fluorescence microscopy and FESEM images of **DPAF-12** microstructures prepared by phase transfer method from ethanol and dioxane solutions in different concentrations: (a, c) 1 mg mL⁻¹; (d) 0.5 mg mL⁻¹; (b, e) 0.1 mg mL⁻¹; (f) 0.05 mg mL⁻¹.

Well distributed microwires with twisted morphology based on **DPAF-12** were obtained in the interlayer between dioxane solution of **DPAF-12** (1 mg mL⁻¹) and ethanol (Fig. 2a and 2c). The twisted microwires were as long as several micrometres. Their width and pitch are 2~3 μm and 30~40 μm, respectively, as demonstrated by fluorescence microscopy and FESEM (field emission scanning electron microscopy) images. Both of right- and left-handed twisted wires have been obtained and twisted samples were racemic mixtures in this study, which was attributed to the absence of chiral center in the molecules. The morphologies of the twisted wires displayed obviously concentration dependent characteristic. Upon decreasing the concentration of the **DPAF-12** dioxane solution, the width and the pitch of the generated twisted microwires reduced successively (Fig. 2b, 2d and 2e). When the concentration reached to

0.05 mg mL⁻¹, the twisted microwires formed accompanied by a few straight needle-like crystalline wires (Fig. 2f).

The similar **DPAF-12** based twisted microstructures could be also generated from other double layer solvents systems such as chloroform solution/methanol, chloroform solution/ethanol, THF solution/ethanol and chloroform solution/isopropanol with different morphologies, lengths, widths and pitches (Fig. S1, ESI†). On the other hand, by precisely regulating the composition and ratio of mixture solvent, the twisted architectures could be achieved through slow evaporation of **DPAF-12** solution (Figs. S2 and S3, ESI†).

The morphologies of the obtained microstructures are sensitive to the polarity of the chosen “poor” solvent for phase transfer methodology. In dioxane solution of **DPAF-12**/methanol system, although the twisted wires were prepared, their morphologies were not well-defined (Fig. S4, ESI†). When isopropanol was employed as the “poor” solvent, whose polarity is lower, large numbers of crystalline straight ribbons were generated in the interlayer between dioxane solution and isopropanol solvent (Fig. S5, ESI†). The fluorescence of straight needle-like ribbons showed significant blue-shifts compared with the twisted microwires that formed in dioxane solution/ethanol system. For the same organic compound that may adopt flexible molecular conformation or configuration, the different solvent media may result in various molecular packing and crystalline phases (namely polymorphs).¹⁴ The aggregated structures of organic molecules are strongly dependent of the intermolecular interactions.¹⁵ The solubility of **DPAF-12** in various solvents is different, which may induce the generation of aggregated states based on distinct intermolecular interactions. Therefore, the **DPAF-12** molecules with six long alkyl chains should take different configurations and intermolecular interaction in different solvent systems, which can result in the formation of the nano- or micro-structures with different morphologies and luminescent properties. So far, a precise mechanism for the result in this study remains unclear and some detail investigation should be performed in future.

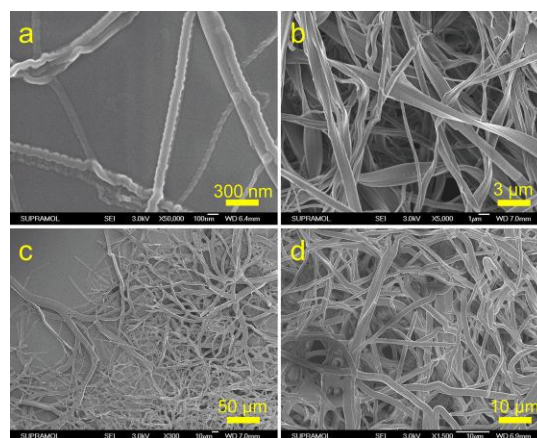


Fig. 3 FESEM images: (a) **DPAF-16** twisted nanowires prepared from chloroform solution (1 mg mL⁻¹)/methanol system; (b) **DPAF-16** microribbons prepared from chloroform solution (1 mg mL⁻¹)/ethanol system; (c) **DPAF-8** branched structures prepared from THF solution (1 mg mL⁻¹)/methanol system; (d) **DPAF-8** flat microribbons prepared from dioxane solution (1 mg mL⁻¹)/methanol system by phase transfer method.

To check the assembly properties of DPAF derivatives with different length of alkyl chains, **DPAF-16** and **DPAF-8** were used as building blocks to fabricate nano/micro-structures. Indeed, the lengths of the alkyl chains have a dramatic effect on the morphologies of the resulted architectures composed of DPAF derivatives. When compound **DPAF-16** with longer alkyl chains was employed as building blocks for molecular assembly, the individual twisted wires and twisted wire bundles were generated (Fig. 3a) in the interlayer of chloroform solution (1 mg mL⁻¹)/methanol binary solvent system. FESEM microscopy images illustrated the width and pitch of the single twisted wires was about 100 nm and several tens of nanometers, respectively, which were much smaller than those of **DPAF-12** microwires prepared by the same procedure. Under identical condition except that methanol was replaced by ethanol, most of the resulted 1D ribbons presented wider distribution in dimension and only small amount of twisted wires were observed (Fig. 3b). Carefully regulating the concentration and solvent media of **DPAF-16** in solution haven't led to the formation of well-defined twisted wires (Figs. S6-S9, ESI†).

For compound **DPAF-8** with shorter alkyl chains, non-twisted architectures were dominant in the resulted samples (Fig. 3c and d). The twisted structure was only obtained in the phase transfer system of dioxane solution (0.05 mg mL⁻¹)/methanol (Fig. S10, ESI†). It is worth noting that **DPAF-8** molecules easily assembled into flat thin emissive crystals with smooth surface (Fig. S11, ESI†) by phase transfer (chloroform solution (1 mg mL⁻¹)/methanol) or slow evaporation of dioxane solution (1 mg mL⁻¹) (Fig. S11, ESI†).

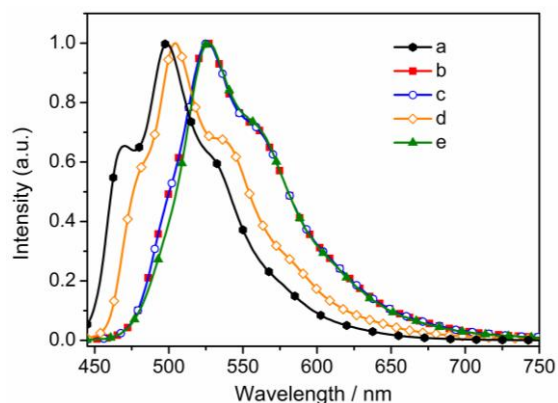


Fig. 4 Fluorescence spectra of **DPAF-12** based samples: (a) dilute solution in dioxane (0.1 mg mL⁻¹); (b) microwires prepared from dioxane solution (1 mg mL⁻¹)/methanol system by phase transfer method; (c) twisted microwires prepared from dioxane solution (1 mg mL⁻¹)/ethanol system by phase transfer method; (d) needle-like crystalline ribbons prepared from dioxane solution (1 mg mL⁻¹)/isopropanol by phase transfer method; (e) solids in powder state.

The emission spectra of **DPAF-12** samples in different states are illustrated in Fig. 4. The twisted and flexible wires prepared from dioxane solution of **DPAF-12**/methanol or ethanol systems showed very similar luminescent properties. The emission maxima (λ_{em}) at 526 nm and photoluminescent quantum yields (Φ_F) of 0.18 were recorded for the two samples. The crystal powder sample of **DPAF-12** precipitated from chloroform solution displayed very similar emission characteristic ($\lambda_{em} = 527$ nm, $\Phi_F = 0.19$) to twisted wires. The **DPAF-12** straight ribbons generated in the interlayer between

dioxane solution and isopropanol demonstrated much shorter emission maxima (504 nm) and higher photoluminescent quantum yield (0.62) compared with twisted and flexible wires. The straight ribbons' emission property was quite similar to that of **DPAF-12** dilute solution. To understand the above emission phenomena, the powder X-ray diffraction (XRD) measurements were performed (Fig. S12). The twisted and flexible wires showed similar XRD patterns to crystal powder sample, suggesting that these three samples belong to the same crystalline phase. The patterns were indexed (part of indexing peaks are marked in Fig. S12c, ESI†) and the calculated packing period distance is around 15.2 Å reflecting (100) crystal plane. For straight ribbons, the calculated packing period distance is as large as 22.213 Å. The longer packing period distance means relatively loose molecular packing, which can enhance the emission. On the contrary, the dense molecular packing can lead to self-absorption, which induced emission quenching.¹⁵ The XRD analysis results provide rational explanation for the emission behavior of the **DPAF-12** solid samples.

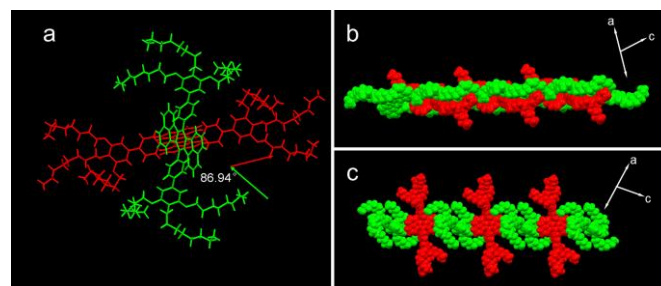


Fig. 5 Molecular packing in **DPAF-8** crystal structures: (a) view of the molecules arrangement in twisted form along the ac axial plane; (b) the molecular chains observed along [101] direction under space fill style; (c) the molecular chains observed along [101] direction under spacefill style.

To figure out molecular packing and assembly characteristics of **DPAF-n** series building blocks, the single crystal structure of **DPAF-8** was investigated. In **DPAF-8** crystal the molecules adopt two different conformations, namely **S** and **I** type conformations (Fig. 5a and Fig. S13a, ESI†). For **S** type molecules, the side alkyl chains show sharp bend feature, while for **I** type molecules, the alkyl adopt relatively slight bend orientation. The **S** and **I** type molecules array alternately to form the molecular chains, which pack together to result in the architecture of crystal. Along [10 $\bar{1}$] direction, the molecules were linked together by intermolecular C-H... π interactions between alkyl chains and aromatic cores (Fig. 5b and S13c, ESI†). Along [101] direction, the molecules stack each other based on the intermolecular C-H... π interactions between adjacent molecular aromatic cores that adopt a nearly vertically packing mode (Fig. 5c and S13d, ESI†). From supramolecular point view, the **DPAF-8** molecular arrangement in crystal has obviously helical feature. Therefore, the molecular chains in Fig. 5b and 5c may pack into wires with twisted or helical characteristic. For molecules **DPAF-12** and **DPAF-16** with longer flexible alkyl chains, the twisted or helical architectures should be more easily generated based on supramolecular assembly.¹⁶ The single crystal analysis

demonstrated a possible explanation for the formation mechanism of twisted wires in this study.

In conclusion, three DPAF derivatives **DPAF-n** (n = 8, 12, 16) with identical central aromatic core and different lengths of flexible alkyl chains have been synthesized and employed as building blocks to fabricate 1D nano/micro-structures. It was demonstrated that 1D luminescent twisted wires were achieved based on **DPAF-n**. Compared with **DPAF-8** and **DPAF-16**, **DPAF-12** molecules displayed stronger twisted aggregation property and could assemble into 1D twisted structure under wide phase transfer conditions. The **DPAF-12** based wires with twisted and straight morphologies presented different emission characteristics, which were attributed to the different molecular packing in the 1D structures. The single crystal X-ray study revealed supramolecular helical structural feature in **DPAF-8** crystal, which should be the driving force to induce the formation of twisted structure in this study.

This work was supported by National Natural Science Foundation of China (91333201, 51173066 and 21221063) and Program for Chang Jiang Scholars and Innovative Research Team in University (No.IRT13018).

Notes and references

- (a) A. E. Rowan and R. J. M. Nolte, *Angew. Chem., Int. Ed.*, 1998, **37**, 63-68; (b) A. R. A. Palmans and E. W. Meijer, *Angew. Chem., Int. Ed.*, 2007, **46**, 8948-8968.
- (a) J. H. Fuhrhopa and W. Helfrich, *Chem. Rev.*, 1993, **93**, 1565-1582; (b) W. Li, J. Li and M. Lee, *Chem. Commun.*, 2013, **49**, 8238-8240.
- T.-F. Lin, R.-M. Ho, C.-H. Sung and C.-S. Hsu, *Chem. Mater.*, 2008, **20**, 1404-1409.
- (a) F. D. Maria, P. Olivelli, M. Gazzano, A. Zanelli, M. Biasiucci, G. Gigli, D. Gentili, P. D'Angelo, M. Cavallini and G. Barbarella, *J. Am. Chem. Soc.*, 2011, **133**, 8654-8661; (b) M. Yamauchi, S. Kubota, T. Karatsu, A. Kitamura, A. Ajayaghosh and S. Yagai, *Chem. Commun.*, 2013, **49**, 4941-4943.
- M. Goh, M. Kyotani and K. Akagi, *J. Am. Chem. Soc.*, 2007, **129**, 8519-8527.
- (a) H. Ozawa, H. Tanaka, M. Kawao, S. Uno and K. Nakazato, *Chem. Commun.*, 2009, 7411-7413; (b) Q. Zhao, Y. Wang, Y. Qiao, X. Wang, X. Guo, Y. Yan and J. Huang, *Chem. Commun.*, 2014, **50**, 13537-13539.
- (a) D. Ke, A. Tang, C. Zhan and J. Yao, *Chem. Commun.*, 2013, **49**, 4914-4916; (b) X. Zhang, D. Görl, V. Stepanenko and F. Würthner, *Angew. Chem.*, 2014, **126**, 1294-1298; (c) Y. E, X. Ma, Y. Zhang, Y. Zhang, R. Duan, H. Ji, J. Li, Y. Che and J. Zhao, *Chem. Commun.*, 2014, **50**, 13596-13599.
- Y. Zhao, Y. Fan, X. Mu, H. Gao, J. Wang, J. Zhang, W. Yang, L. Chi and Y. Wang, *Nano. Res.*, 2009, **2**, 493-499.
- (a) T. Yamamoto, T. Fukushima, A. Kosaka, W. Jin, Y. Yamamoto, N. Ishii and T. Aida, *Angew. Chem., Int. Ed.*, 2008, **47**, 1672-1675; (b) Y. Duan, S. Yan, X. Zhou, W. Xu, H. Xu, Z. Liu, L. Zhang, C. Zhang, G. Cui and L. Yao, *Chem. Commun.*, 2014, **50**, 8335-8338; (c) H. Cao, Q. Yuan, X. Zhu, Y. P. Zhao, M. Liu, *Langmuir*, 2012, **28**, 15410-15417.
- N. Giuseppone, J.-L. Schmitt, and J.-M. Lehn, *J. Am. Chem. Soc.*, 2006, **128**, 16748-16763.
- (a) D. González-Rodríguez, J. L. J. van Dongen, M. Lutz, A. L. Spek, A. P. H. J. Schenning and E. W. Meijer, *Nat. Chem.*, 2009, **1**, 151-155; (b) G. Chen and M. Jiang, *Chem. Soc. Rev.*, 2011, **40**, 2254-2266; (c) S. Matile, A. V. Jentzsch, J. Montenegro and A. Fin, *Chem. Soc. Rev.*, 2011, **40**, 2453-2474.
- L. Chen, K. S. Mali, S. R. Puniredd, M. Baumgarten, K. Parvez, W. Pisula, S. D. Feyter and K. Mullen, *J. Am. Chem. Soc.*, 2013, **135**, 13531-13537.
- (a) E. F. Fabrizio, I. Prieto and A. J. Bard, *J. Am. Chem. Soc.*, 2000, **122**, 4996-4997; (b) M. Wehmeier, M. Wagner and K. Müllen, *Chem. Eur. J.*, 2001, **7**, 2197-2205; (c) K. Matuszák, V. Lukeš, P. Rapta, L. Dunsch, A. J. A. Aquino and H. Lischka, *Synthetic Met.*, 2007, **157**, 214-221; (d) L. Duan, D. Zhang, K. Wu, X. Huang, L. Wang and Y. Qiu, *Adv. Funct. Mater.*, 2011, **21**, 3540-3545; (e) B. F. Plummer, L. K. Steffen, T. L. Braley, W. G. Reese, K. Zych, G. Van Dyke, B. Tulle, *J. Am. Chem. Soc.*, 1993, **115**, 11542-11551.
- (a) Z. Zhang, Y. Zhang, D. Yao, H. Bi, I. Javed, Y. Fan, H. Zhang, Y. Wang, *Cryst. Growth Des.*, 2009, **9**, 5069-5076; (b) K. Wang, H. Zhang, S. Y. Chen, G. C. Yang, J. B. Zhang, W. J. Tian, Z. M. Su, Y. Wang, *Adv. Mater.* 2014, **26**, 6168-6173.
- (a) J. Wang, Y. Zhao, J. Zhang, J. Zhang, B. Yang, Y. Wang, D. Zhang, H. You and D. Ma, *J. Phys. Chem. C*, 2007, **111**, 9177-9183; (b) Y. Zhao, X. Mu, C. Bao, Y. Fan, J. Zhang and Y. Wang, *Langmuir*, 2009, **25**, 3264-3270.
- C. Dou, D. Li, H. Zhang, H. Gao, J. Zhang and Y. Wang, *Sci. China Chem.*, 2011, **54**, 641-650.