

# **SELF-ASSEMBLING POLYCYCLIC AROMATIC HYDROCARBONS TO ORDERED NANO- TO MICRO- STRUCTURES IN THE GAS PHASE**

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## **Abstract**

We report the fabrication of nano- to micro- structures from polycyclic aromatic hydrocarbons (PAHs) without derivatizing these molecules by directly self-assembling them in the gas phase with a thermal evaporation process. Eighteen PAHs, ranging from three to ten fused rings, were selected for proof-of-concept studies and all of these PAHs self assembled to ordered nano- to micro-structures and each PAH has its unique morphology under appropriate conditions.

## **1. Introduction**

Nanostructures of polycyclic aromatic hydrocarbon (PAH) derivatives are potential candidates for improving the performance of nanoelectronics, optoelectronics, and photovoltaic cells [1, 4-6, 8, 13, 15, 16]. In general,

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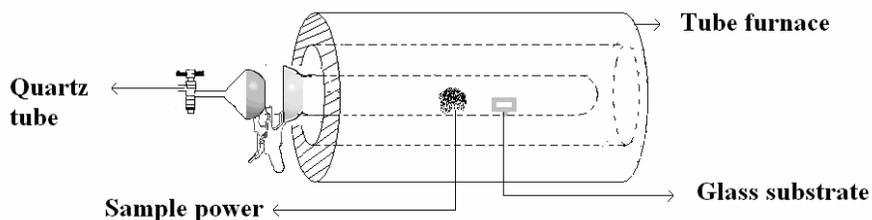
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these nanostructures are prepared in solutions by means of self-assembling processes, which are driven by strong  $\pi$ - $\pi$  interactions of PAH derivatives. Since most of PAHs have low solubilities in any solvents, a typical self-assembling process involves introducing side chains to increase the solubility [9, 10, 17, 20, 21]. However, the side chains may affect the properties of the nanoassembly. In this work, we report the fabrication nano- to micro- structures from PAHs without derivatizing these molecules, which may find wide applications in the electronic and energy fields.

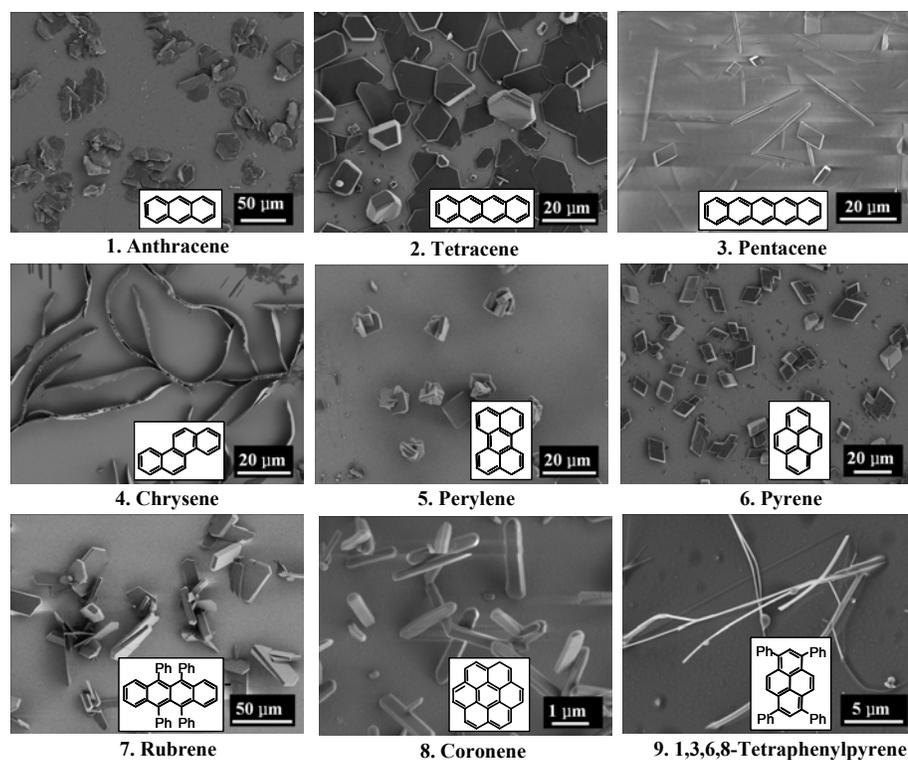
Our approach is to directly self assemble PAHs in the gas phase with a modified thermal evaporation process to avoid the solubility and side chain issues. The thermal evaporation method is a well known technique for preparing 3D nanostructures from inorganic materials or for growing a thin film of substances, including PAHs, on substrates [3]. In the recent years, the thermal evaporation method has been used to self assemble 2D monolayers of PAH derivatives on substrates for electronic applications [2, 7, 11, 14, 18, 19]; however, few reports have demonstrated the formation of 3D nanostructures from PAHs with the thermal evaporation method [12].

We speculate that the lack of observations of 3D nanostructures of PAHs is due to strict conditions for the self-assembling process of PAHs, and we expect to obtain ordered nanostructures of PAHs by means of controlling the conditions, such as the evaporation temperature and the sample concentration. In our experiments, we heated PAH samples in a 10ml tube and let the PAH vapors deposit on a glass substrate 2cm away (Scheme 1). A certain amount of PAH powders were heated in a vacuum at a certain temperature for 0.5 to 1 hour. The system was then allowed to cool at room temperature. PAHs deposited on the glass substrate were collected for imaging.

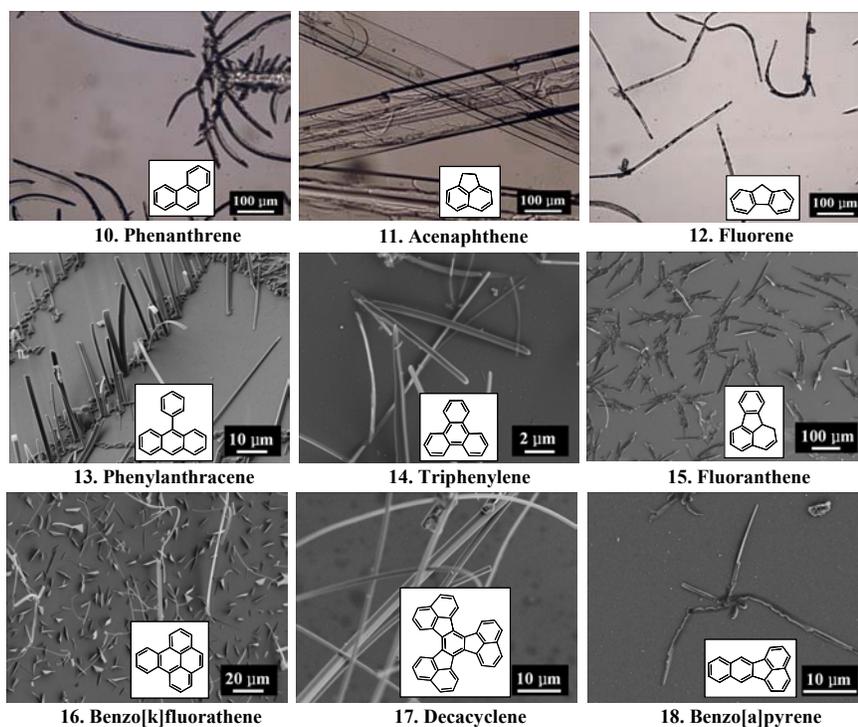


**Scheme 1.** Schematic diagram of the apparatus used in these work.

Eighteen PAHs, ranging from three to ten fused rings, were selected for proof-of-concept studies. All of these PAHs self assembled to ordered nano- to micro-structures and each PAH has its unique morphology under appropriate conditions. Figure 1 shows structures of nine PAH molecules with center of symmetry and the SEM images of the nano- or micro-structures of these PAHs prepared from thermal evaporation processed at various temperatures and with different sample concentrations. All of the PAH molecules have a center of symmetry and they favor to form two dimensional or three dimensional crystals structures except for 1,3,6,8-tetraphenylpyrene. The structures of anthracene, pyrene, rubrene, tetracene, and perylene, for examples, are irregular hexagonal plates, cubes, fused plates, irregular hexagonal tiles, and fused regular square plates, respectively. One explanation that 1,3,6,9-tetraphenylpyrene does not form 3D crystal structures is that the four phenyl groups attached on the pyrene have a large freedom to rotate, so the molecule is not precisely symmetrical. This does not apply to the four phenyl groups in rubrene because the freedom of those adjacent moieties is limited.



**Figure 1.** Structures PAH molecules with center of symmetry and the SEM images of micro- and nano- structures of these PAHs prepared from thermal evaporation processes at various temperatures and with different sample concentrations. The numbers in the parentheses are the lengths of the bars. (1) Anthracene, 200°C, 5mg, (50μm); (2) Tetracene, 250°C, 10mg, (20μm); (3) Pentacene, 400°C, 5mg, (20μm); (4) Chrysene, 250°C, 5mg, (20μm); (5) Perylene, 250°C, 1mg, (20μm); (6) Pyrene, 190°C, 5mg, (20μm); (7) Rubrene, 350°C, 5mg, (50μm); (8) Coronene, 350°C, 5mg, (1μm); (9) 1,3,6,8- tetraphenylpyrene, 350°C, 5mg, (5μm).

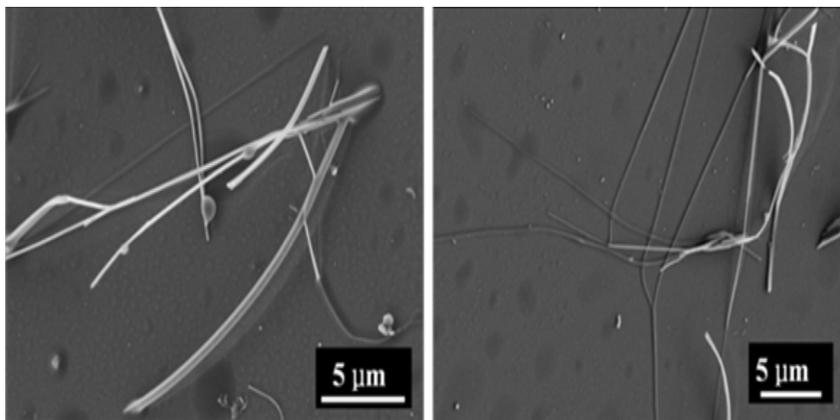


**Figure 2.** The structures of PAH molecules that do not have center of symmetry and the SEM images of micro- and nano-structures of these PAHs prepared from thermal evaporation processes at various temperatures and with different sample concentrations. The numbers in the parentheses are the lengths of the bars. B, Phenanthrene, 150°C, 5mg, (100μm); C, Acenaphthene, 150°C, 10mg, (100μm); D, Fluorene, 150°C, 1mg, (100μm); E, F, Triphenylene, 200°C, 5mg, (2μm); G, Fluoranthene, 200°C, 1mg, (100μm); H, I, J, K, 9-Phenylanthracene, 180°C, 5mg, (10μm); L, M, Benzo[a] pyrene, 150°C, 5mg, (10μm); N, O, P, Benzo[k]fluoranthene, 300°C, 1mg, (20μm); Q, R, Decacyclene, 400°C, 5mg, (10μm). The optical images, but not SEM images, of microstructures of phenanthrene, acenaphthene, and fluorene were used here because, these PAHs sublimed in high vacuum and no electron microscopy image was successfully obtained.

Figure 2 shows the structures of PAH molecules that do not have center of symmetry and the SEM images of the nano- or micro- structures of these PAHs prepared from thermal evaporation processed at various temperatures and with different sample concentrations. These PAH molecules favor the formation of one dimensional structures.

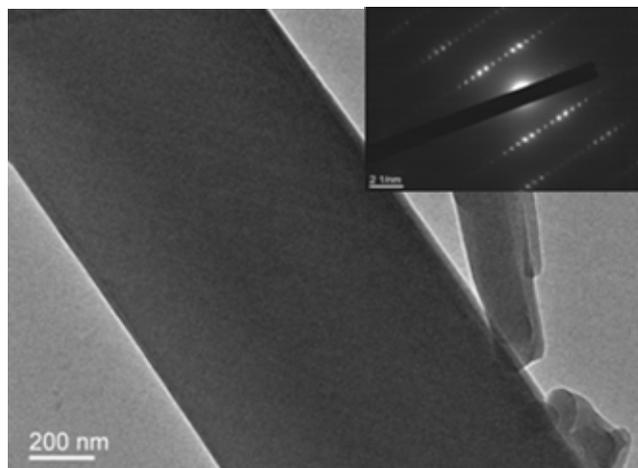
The formation of the structures is strongly related to the symmetry of the molecules. Figures 1 and 2 showed that PAH molecules with center of symmetry favor to form 2D to 3D crystal structures when prepared in the gas phase, while PAH molecules without center of symmetry favor to form 1D structures when prepared in the gas phase. These phenomena could be due to the PAH molecules with center of symmetry can form denser and more regular structures than those PAH molecules without the center of symmetry. As a result, 3D structures, such as hexagonal plates, fused regular square plates, and fused plates were obtained from PAHs with the center of symmetry. 1D structures, typically in the form of nanowires, are formed for those PAHs without the center of symmetry due to  $\pi$ - $\pi$  interaction.

As expected, the morphology and dimension of the PAH assemblies were affected by the temperature and the sample concentration in the tube. In general, when the temperature or the concentration of the samples is lower, the growth rates of the nano/microstructures decrease and the crystals are more regular and smaller, and vice versa. These phenomenas were observed for all the PAHs, we tested. For example, Figure 3 showed that the dimension of 1,3,6,8-tetraphenylpyrene nanowires assembled under two conditions varied from 50nm to 500nm.



**Figure 3.** Nanostructures of tetraphenylpyrene prepared from thermal evaporation at various temperatures and with different sample concentrations, left: 350°C, 5mg; right: 320°C, 2mg.

We are particularly interested in the nanowires of the PAHs because of their potential applications in nanoelectronic devices. The nanowires of these PAHs were dispersed onto a transmission electron microscopy (TEM) grid for structural analysis. We did not observe crystal structures from these nanowires, however, nanowires of decacyclene showed a crystalline structure (Figure 4) after an annealing process. In the annealing process, the nanowires were heated at 200°C in N<sub>2</sub> for 30min. The corresponding electron diffraction pattern (Figure 4 inset) showed diffraction spots with 20.7Å *d*-spacing in the perpendicular direction and 3.9Å *d*-spacing in the longitudinal nanowire direction, which suggested that the molecules were oriented with their long axis perpendicular to the nanowire and the  $\pi$ - $\pi$  stacking direction parallel to the nanowire. We are investigating the conversion of the morphologies of other PAH wires now.



**Figure 4.** TEM image of a nanowire of decacyclene prepared from thermal evaporation at 400°C and with 5mg sample in the tube.

In summary, self-assembling in the gas phase represents a facile approach to prepare ordered nanostructures from a large pool of PAH molecules, and possibly a mixture of two or more PAHs. We expect that heterocyclic PAHs with N, S, or O in the rings, or PAHs with OH, NH<sub>2</sub>, or C=O groups may produce more ordered structures because of extra hydrogen bonding and polar interactions. This approach can completely eliminate the effects of side chains. Particularly, the nano-assembly prepared from this method could be made in large quantities at a low cost since no PAH derivatizations are needed, which makes this approach competitive in preparing organic nanomaterials. The semiconductive and optical properties, crystal structures, and thermodynamics of these materials are under investigation. Potential applications of these nanostructures include nanoelectronics, photoelectronics, light-emitting devices, solar cells, etc.

**Supporting information available.** Experimental procedures and additional figures.

### Reference

- [1] M. F. Calhoun, Olaya D. Sanchez, M. E. Gershenson and V. Podzorov, *Nature Mater.* 7 (2008), 84-89.
- [2] M. E. Cañas-Ventura, W. Xiao, D. Wasserfallen, K. Müllen, H. Brune, J. V. Barth and R. Fasel, *Angew. Chem. Int. Ed.* 46 (2007), 1814.
- [3] C. W. Chu, Y. Shao, V. Shrotriya and Y. Yang, *Appl. Phys. Lett.* 86 (2005), 243506.
- [4] S. A. Dibenedetto, D. L. Frattarelli, A. Facchetti, M. A. Ratner and T. J. Marks, *J. Amer. Chem. Soc.* 131 (2009), 11080-11090.
- [5] X. L. Feng, M. Y. Liu, W. Pisula, M. Takase, J. L. Li and K. Müllen, *Adv. Mater.* 20 (2008), 2684.
- [6] Y. Fogel, M. Kastler, Z. Wang, D. Andrienko, G. J. Bodwell and K. J. Müllen, *Amer. Chem. Soc.* 129 (2007), 11743-11749.
- [7] S. J. H. Griessl, M. Lackinger, F. Jamitzky, Th. Markert, M. Hietschold and W. M. Heckl, *Langmuir* 20 (2004), 9403.
- [8] M. Hietschold, M. Lackinger, S. Griessl, W. M. Heckl, T. G. Gopakumar and G. W. Flynn, *Microelect. Engineer.* 82 (2005), 207-214.
- [9] J. P. Hill, W. Jin, A. Kosaka, T. Fukushima, H. Ichihara, T. Shimomura, K. Ito, T. Hashizume, N. Ishii and T. Aida, *Science* 304 (2004), 1481.
- [10] T. Ishi-I, K. Murakami, Y. Imai and S. Mataka, *Org. Lett.* 7 (2005), 3175.
- [11] O. Ivasenko, J. M. MacLeod, K. Y. Chernichenko, E. S. Balenkova, R. V. Shpanchenko, V. G. Nenajdenko, F. Rosei and D. F. Perepichka, *Chem. Comm.* (2009), 1192-1194.
- [12] T. Kimura, H. Koizumi, H. Kinoshita and T. Ichikawa, *Jpn. J. Appl. Phys.* 46 (2007), 703.
- [13] E. W. Meijer and A. P. H. J. Schenning, *Nature* 419 (2002), 353.
- [14] A. Rouhanipour, M. Roy, X. Feng, H. J. Räder and K. M. Müllen, *Angew. Chem. Int. Ed.* 48 (2009), 4602-4604.
- [15] A. P. H. J. Schenning and E. W. Meijer, *Chem. Comm.* (2005), 3245.
- [16] L. Schmidt\_Mende, A. Fechtenkotter, K. Müllen, E. Moons, R. H. Friend and J. D. Mackenzie, *Science* 293 (2001), 1119-1122.
- [17] E. Schwartz, V. Palermo, C. E. Finlayson, Y. -S. Huang, M. B. J. Otten, A. Liscio, S. Trapani, I. Gonzalez-Valls, P. Brocorens, J. J. L. M. Cornelissen, K. Peneva, K. Müllen, F. C. Spano, A. Yartsev, S. Westenhoff, R. H. Friend, D. Beljonne, R. J. M. Nolte, P. Samori and A. E. Rowan, *Chem. Eur. J.* 15 (2009), 2536-2547.
- [18] S. Sohnchen, K. Hanel, A. Birkner, G. Witte and C. Woll, *Chem. Mater.* 17 (2005), 5297-5304.

- [19] J. A. Theobald, N. S. Oxtoby, M. A. Phillips, N. R. Champness and P. H. Beton, *Nature* 424 (2003), 1029-1031.
- [20] F. Würthner, *Chem. Comm.* (2004), 1564.
- [21] S. Xiao, J. Tang, T. Beetz, X. Guo, N. Tremblay, T. Siegrist, Y. Zhu, M. Steigerwald and C. J. Nuckolls, *Amer. Chem. Soc.* 128 (2006), 10700.
- [22] Y. S. Zhao, H. Fu, A. Peng, Y. Ma, D. Xiao and J. Yao, *Adv. Mater.* 20 (2008), 2859-2876.

