Self-assembled fullerene (C60)-pentacene superstructures for photodetectors

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Abstract
Fullerene assembling with specific donor molecules would yield multifunctional metamaterials via the collective behavior, wherein linear acenes are widely used as donor molecules to construct the charge-transfer heterojunction structure with fullerene. However, they are generally prepared by vacuum deposition due to the insoluble property of high-performance linear acenes molecules in common solvents, which makes the construction of fullerene with insoluble donor molecules still be a big challenge in the solution-processed method. To this end, chemical modification provides an effective solution-processed strategy to construct donor and acceptor systems. Here, the C60-pentacene is assembled into controllable flower-like superstructures by the surface grafting method. It is found that the nanofeatures of the microflowers could be regulated by temperature, resulting in dense flakes morphology at room temperature and loose flakes at high temperatures. Furthermore, the dense-flakes microflowers structures with less mass but better crystalline structure exhibit better optoelectronic properties. Our results reveal an effective control on the nanofeatures of the self-assembled fullerenes complex superstructures and their role for the optoelectronic performance, which may promote the exploring of fullerene superstructures as photodetectors.

KEYWORDS
fullerene-pentacene, photodetector, self-assembly, superstructures

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1 INTRODUCTION

Fullerene-base materials with unique chemical and physical properties have become one of the most extensively studied carbon nanomaterials and show promising applications in solar cells, field-effect transistors, electrochemical sensors, and photodetectors. Notably, the optoelectronic properties of fullerenes could be modulated with controlled morphologies. Therein, well-defined fullerene superstructures with tailored nanostructures present better optoelectronic performance compared with bulk materials, which were more suitable for integrating into the fabrication of sophisticated devices. For instance, fullerene nanorods demonstrated electron mobility as high as 11 cm²/V·s, whereas only 0.4 cm²/V·s were measured in fullerene film devices. In addition, fullerene C₇₀ microcubes exhibited remarkable enhancement of photoluminescence compared with pristine C₇₀ power, which was mainly attributed to the high crystallinity of the cubes.

Compared with fullerene unimolecular systems, donor–acceptor complexes based on fullerene would yield multifunctional metamaterials via the collective behavior, including a less complicated device fabrication process, superior mixture stacking, and tunable optoelectronic properties. For example, the co-crystals established via solution processes of fullerenes with porphyrin, metalloporphyrin, or sulfur-bridged annulene exhibited distinct charge transfer characteristics. In addition, linear acenes (naphthalene, anthracene, tetracene, and pentacene) were also widely used for building the charge-transfer heterojunction system with fullerene. However, they were generally prepared by vacuum deposition because most high-performance acene molecules (such as tetracene or pentacene) were insoluble in common solvents. Therefore, the construction of fullerene with insoluble donor molecules could be still a big challenge. To this end, chemical modification offers an effective approach to realize more flexibility on the type and number of functional groups on fullerene to construct fullerene superstructures.

Herein, we report a liquid–liquid interfacial precipitation (LLIP) method to manipulate the morphologies of C₆₀-pentacene superstructures. C₆₀-pentacene was synthesized by surface-grafting pentacene onto C₆₀ through the process of progressively dissolving pentacene into C₆₀/toluene solution at 110°C, as shown in Figure 1A. The nanofeature of the microflowers composed of C₆₀-pentacene was found able to be regulated by the temperatures. Loose flakes could be obtained at 110°C (fullerene (C₆₀)-pentacene microflowers, FMFs_110), whereas dense flakes (FMFs) were achieved at room temperature due to the temperature-induced differences in solubility and crystalline structure (Figure 1B). When these microflowers were used as the photodetector, the dense flakes microflower structures exhibited higher current with and without illumination, indicating more effective energy transfer between fullerene and donor molecules. These results indicate the essential of microstructure manipulation of the assembled fullerenes on the optoelectronic properties, which may bring new insights on the design of new optoelectronic devices based on fullerene superstructures.

2 EXPERIMENTAL SECTION

2.1 Materials

Pristine fullerene C₆₀ (>99.9%) was purchased from Henan Fullerene Nano New Materials Technology Co. Ltd. Pentacene (>99.999%) was obtained from Tokyo Chemical Industry Co. Ltd. Toluene (>99%), methanol (>99%), ethanol (>99%) without further purification were obtained from Aladdin Industrial Corporation.

2.2 Synthesis of fullerene-pentacene flower-like microspheres and preparation uniform films with FMFs and FMFs_110

C₆₀-pentacene was synthesized according to the previous report with less stirring time at room temperature. In brief, C₆₀ (36 mg) was dissolved in 35 ml toluene followed by sonication for 1 h. Then, the solution was transferred into a flask with the additional 13.9 mg pentacene, which was heated under stirring in an oil bath to 110°C for 3 h. The mixture solution was kept stirring for another 3 h without heating. In a typical LLIP synthesis, 2 ml of the fullerene C₆₀ solution above was added in a 10-ml glass bottle and then 5 ml methanol was quickly added by pipette, the mixture was left undisturbed at room temperature for 6 h. Finally, the supernatant (FMFs) was collected by centrifugation. FMFs_110 was fabricated with an additional process to reheat the fullerene–pentacene solution to 110°C. In case of the boiling of methanol, the system was taken out after the heating process and added methanol solvent quickly at room temperature. The as-obtained supernatants (FMFs and FMFs_110) were washed with ethanol three times and redispersed in ethanol (2 mg/ml). The suspension was gently transferred to the water surface by a syringe along the glass wall to form a film.
2.3 | Characterizations

Scanning electron microscopy (SEM; FEI Quanta 250FEG) was performed with operating voltage at 15 kV. Transmission electron microscopy (TEM) was performed by a Tecnai G220 with an operating voltage of 200 kV. The specific surface areas and pore size distributions were obtained on an automatic specific surface area analyzer (Gemini VII 2390). X-ray powder diffraction (XRD) patterns were obtained using a Bruker-AXS D8 Advance diffractometer. Raman spectra were recorded on a scattering Raman spectrometer with excitation radiation at 514 nm from an Ar+ ion. UV-Vis spectra were measured on the UV-Vis spectrophotometer (Shimadzu UV-1800). Fourier-transform infrared (FTIR) spectrometer Nicolet iS10 was applied to obtain the FTIR spectra. 1H NMR (nuclear magnetic resonance) spectrum was recorded on a Bruker NMR spectroscope.

3 | SYNTHESIS OF C₆₀-PENTACENE ADDUCT

C₆₀-pentacene was synthesized according to a reported route. Typically, pentacene powder was added in C₆₀/toluene solution followed by stirring and refluxing at 110°C. Fullerene C₆₀ have shown significant transparent violet characteristics in the toluene solvent (Figure 1C, left). However, after the reflux process, the mixture appeared with brown color, whereas the solid pentacene that originally existed at the bottom of the flask disappeared as shown in Figure 1C (right). The as-obtained solution still remained clear and transparent. A UV-Vis absorption spectrum was taken to confirm the success of grafting pentacene on fullerene in Figure 1D,E. Fullerene C₆₀ in toluene showed strong absorption peaks at 335 nm with a minor peak addressed at 407 nm. After the reflux process, the obtained
C₆₀-pentacene in toluene demonstrated a broad band between 300 and 350 nm, whereas a sharp peak centered at 437 nm and a relatively weak band at 703 nm. The weak band at about 703 nm is a strong evidence of fullerene monoadducts with pentacene. The ¹H NMR spectrum of the main products demonstrated a single methine proton absorption at 6.24 ppm which was also a typical signal of the formation of adducts as shown in Figure S1. This leads to the conclusion that with pentacene changed into two naphthalene moieties connected by a cycloaliphatic bridge, the C₆₀-pentacene adducts were obtained at 110°C in toluene. To elucidate the reaction mechanism in the solution, C₆₀ and pentacene powder were mixed and heated at 110°C under the N₂ atmosphere as shown in Figure S2. After 3 h, an appropriate amount of toluene solvent was added to remove C₆₀ and C₆₀ derivatives. Pentacene is insoluble in toluene at room temperature, however, with the temperature rising to 110°C, it was observed that the toluene solution turned into pale purple color (Figure S3), indicating that pentacene dissolved in toluene and chemically reacted with C₆₀. It should be noted that without mixing in solvents, the solid C₆₀ and pentacene powder could not react. When C₆₀ and pentacene powder were mixed and heated at 110°C under the N₂ atmosphere for 3 h, the left insoluble solid (pentacene) after the filtration by toluene (removal of C₆₀ or C₆₀ derivatives) was almost the same mass as the pentacene added in the flask (Figure S2). Thus, the heated solution provides easier accessibility for the chemical reaction between fullerene C₆₀ and pentacene.

3.1 | Control the morphologies via temperature

The influence of solution temperature on C₆₀-pentacene superstructures morphologies were studied in the LLIP process. The SEM images of FMFs and FMFs_110 are shown in Figure 2A, B. Both FMFs and FMFs_110 were assembled into flower-like microspheres, but the nano-features of the microflowers were quite different. FMFs showed a dense flake morphology with a clear and smooth surface, whereas FMFs_110 had loose flakes. Further related information was provided by the scanning transmission electron microscopy images in Figure 2C, D. FMFs were composed of crisscrossed nanosheets and more solid and fewer nanosheets were observed in FMFs_110. The average diameter of FMFs was ~4.5 μm and a larger diameter of ~6.7 μm was displayed in FMFs_110 samples, as shown in Figure S4. The films composed of FMFs and FMFs_110 could be formed on the water surface, with the same area filled, the mass of FMFs_110 is four times compared with FMFs. Furthermore, as shown in Figure S5, the captured digital photo of films of FMFs and FMFs_110 displayed completely different on the macroscale, with uniform and light tawny color of FMFs, whereas FMFs_110 appeared as rugged aggregation with dark-brown color. Nitrogen

![Figure 2](image-url)
adsorption/desorption characterizations were adapted to analyze the specific surface areas and pore size distribution of FMFs and FMFs_110. As shown in Figure S6A, the isotherms of FMFs and FMFs_110 revealed type IV with an H3 hysteresis loop, indicating the mesopores and a small part of micropores. The Brunauer–Emmett–Teller (BET) surface area of FMFs and FMFs_110 are ca. 159.08 and 40.01 m²/g, respectively. The higher BET surface area of FMFs should be attributed to the dense and uniform distribution of flakes. The pores distribution curves of FMFs and FMFs_110 in Figure S6B showed mesoporous structures and centered at around 4 nm.

3.2 The analysis of molecular arrangement

High-resolution transmission electron microscopy (HR-TEM), FTIR, XRD, and UV-vis spectrum were used to further investigate the structure difference of FMFs and FMFs_110 structures. In HR-TEM images (Figure 2E,F), FMFs crystals displayed well-defined stripes with a lattice distance of 1.26 nm, whereas lattice distance of 0.86 nm was found in FMFs_110 crystals. The XRD pattern of pristine C₆₀ (pC₆₀) was assigned to the face-centered cubic (fcc) structure, showed diffraction peaks at 2θ = 10.78°, 17.64°, 20.74°, and 21.68°, which correspond, respectively, to (111), (022), (113), and (222) planes. Pentacene also demonstrated strong peaks suggesting a regular molecule arrangement. In comparison to the XRD patterns of FMFs and FMFs_110, we could find that they have similar diffraction peaks in the range of 5°–25°. However, FMFs showed strengthened diffractions at 6.75°, 12.5°, and a new peak at 25°. According to Bragg’s Law: 2d sinθ = nλ, the lattice space from peaks at 6.75° and 12.5° were well-matched with the lattice distance of 1.26 and 0.86 nm, respectively. The minimum XRD peak at 6.75° should be attributed to the naphthalene moieties derived from pentacene, whereas the peaks at 25° could be marked from pentagons. These results implied that FMFs possess a more orderly packing of C₆₀–pentacene and better crystalline structure than FMFs_110. It should be noted that neither C₆₀ nor pentacene characteristic peaks could be found in the diffraction patterns of FMFs or FMFs_110. It suggested that no C₆₀ or pentacene is involved in the crystalline formation process of FMFs and FMFs_110. The FTIR characteristic vibration peaks of pC₆₀ and pentacene were also displayed to analyze the changes in molecular vibration, as shown in Figure 3B. It seemed that the vibration of FMFs and FMFs_110 were quite similar. After the Diels–Alder reaction, the characteristic peaks of C₆₀ were retained, which indicated the rigid cages were not destroyed completely. However, the strong band at 906 cm⁻¹ (lone C–H wagging) originally present in the pentacene disappeared, which should be attributed to five benzene rings changed into two naphthalene moieties connected by a cycloaliphatic bridge. More information with the FTIR is provided in Figure S7. The Raman spectrum of pC₆₀ basically possessed eight vibrations which correspond to two A₉g and six Hg bands as shown in Figure S8. The two relatively strong bands at 495.5 and 1,464 cm⁻¹ was assigned to be A₉g(1) and A₉g(2) scattering of the C₆₀ molecule. The other six peaks as marked by black arrows at 271, 431, 709.5, 771.5, 1,421, and 1,566.5 cm⁻¹.

FIGURE 3 (A) X-ray diffraction patterns and (B) Raman spectra of (i) pristine C₆₀, (ii) pentacene, (iii) FMFs, and (iv) FMFs_110
were, respectively, related to Hg(1), Hg(2), Hg(3), Hg(4), Hg(7), and Hg(8) vibration modes. Compared with C\textsubscript{60}, the typical characteristics C–H bending centered at 1,158 and 1,178 cm\(^{-1}\), and the signals of aromatic stretching and quadrant stretching of pentacene were found in the Raman spectrum. All the characteristic peaks of \(p\)\textsubscript{C\textsubscript{60}} were found in both FMFs and FMFs\textsubscript{110}, whereas no trace of pentacene was displayed, which indicated structural damage of pentacene, which may indicate the structural disruption of pentacene and preservation of rigid fullerene structures. Moreover, there were two new peaks found in FMFs and FMFs\textsubscript{110}, which centered at 425 and 452 nm, showing the new vibration of C\textsubscript{60}-pentacene. UV-vis spectrum was also applied to analyze the accurate difference between FMFs and FMFs\textsubscript{110}. \(p\)\textsubscript{C\textsubscript{60}} displayed an original peak at 225, 256, and 328 nm in \(n\)-hexane solvent. The UV-Vis absorption spectra of FMFs and FMFs\textsubscript{110} in hexane formed a large peak between 200 and 300 nm, which was consistent with the results of C\textsubscript{60}-pentacene in toluene above. By a more detailed observation, we found that the peak of FMFs\textsubscript{110} is sharper than FMFs, and we speculated that this may be caused by the solid structure of FMFs\textsubscript{110}, as shown in Figure S9.

4 | THE FORMATION MECHANISM

To understand the effect of solvents on the morphologies adjustment of microflowers morphologies, we have carried out the assembly by using different solvent systems, including without poor solvent, and with ethanol, isopropanol, tert-butanol, and \(n\)-hexane at room temperature (Figure 4). It is found that even without assistance of poor solvent, C\textsubscript{60}-pentacenes were still inclined to form microspherical aggregates, but with solid and inhomogeneous morphology instead of flower-like morphology. For the cases of the addition of poor solvents, unless tert-butanol system, which formed the nanosheets network, the other systems of ethanol, isopropanol, \(n\)-hexane were all shown the formation of flower-like microspheres. However, the flake distribution states and densities were different compared with FMFs. These results implied that the interaction between good and poor solvents is essential to the regulation of the morphologies of fullerene nanostructures.

The self-assembly fullerene derivatives super-structures were mostly driven by the interaction force of functional groups, such as hydrogen-bonding, van der
Waals force, \( \pi - \pi \) interaction or metal-coordination, and so forth. In this case, the molecular arrangement of \( C_{60} \)-pentacene was also affected by the naphthalene moieties as only fullerene nanoparticles which were demonstrated in Figure S10 would be obtained if without these moieties. However, the assembled morphologies were largely related to the solubility in solvents applied in the process. It seemed that the solubility of our \( C_{60} \)-pentacene was difficult to detect as the saturation of fullerenes in toluene is difficult to obtain. As \( C_{60} \)-pentacene has retained the original rigid structure of fullerene, we speculated that the influence of temperatures on the solubility of \( C_{60} \) in toluene may illustrate the \( C_{60} \)-pentacene in toluene. After heating at 110°C, precipitation from saturated \( C_{60} \)/toluene occurred (Figure S11), indicating the decrease of the \( C_{60} \) solubility. For the assembly process of FMFs_110, the solubility of \( C_{60} \)-pentacene in toluene was decreased when the solution is reheated to 110°C. With the addition of a poor solvent, \( C_{60} \)-pentacenes were precipitated and aggregated in a more uneven mode, which led to the formation of densely packed nanosheets and loose distributed flakes in FMFs_110 (Figure 4F). In contrast, for the assembly without the heating and at room temperature, the crystalline growth of \( C_{60} \)-pentacenes could be at a moderate rate, which facilitated the formation of a uniform flake network in FMFs (Figure 4F).

To investigate the photoconductive properties of the \( C_{60} \)-pentacene microflowers, two-terminal devices using interdigitated electrodes with 10-\( \mu \)m channel length were used to measure their photo-response properties as shown in Figure 5A. It was reported that nanosphere structures were advantageous in constructing films for devices compared with nanorods or cubes. The films of FMFs and FMFs_110 films were prepared at the air-water interface and transferred on the interdigital electrodes for optoelectronic measurement. It was found the film was almost a one-layer or two-layer structure and thus the thickness of the film was determined by the diameters of fullerene superstructures (Figure S12). The photocurrent versus voltage (\( I-V \)) curves of FMFs and FMFs_110 in the dark and under illumination (wavelengths at 266 nm with a density of 2.5 mW/cm²) were shown in Figure 5B. To confirm the significance of fullerene nanofeatures on photodetectors, fullerene microspheres with smooth and solid surfaces reported in the literature were also investigated and compared. However, these solid fullerene microspheres did not display any photocurrents indicating the significance of the hierarchical structures of FMFs and FMFs_110 for the energy transfer. From the \( I-V \) curves of FMFs and
FMFs_110 film, it was concluded that FMFs film exhibited higher currents with and without illumination than that of FMFs_110 film. Even though the FMFs_110 obtained more mass on the electrode, the dense and thinner flakes of FMFs and their better crystalline structures may help to improve the electrical conductivity. FMFs displayed an on/off ratio around 3.2 in consecutive on-off cycles (Figure 5C), whereas the ratio of FMF_110 almost the same with 3.5 (Figure 5D). It should be mentioned that the mass of FMFs_110 on interdigital electrode was four times larger than the device with FMFs film. Therefore, FMFs with less mass should show a higher response to light compared with FMFs_110. Further, the response speed of the devices was also characterized as shown in Figure S13. The rise time for FMFs and FMFs_110 film devices were extracted to 0.39 and 0.36 s, respectively. Meanwhile, the decay time for FMFs and FMFs_110 film devices were assigned to 0.37 and 0.48 s, respectively. The similar response time of film devices should be attributed to the same compounds of FMFs and FMFs_110 which were just different on nanofeatures.

6 CONCLUSIONS

Fullerene superstructures with flowerlike microstructures were generated by surface-grafting penta- cene onto the C₆₀ through the LLIP method. What’s more, the nanofeatures of the flowerlike microstructures could be well modulated by the temperature. As a result, the high heating process at 110°C produced uneven and loose flakes (FMFs_110), whereas uniform and dense flakes were obtained without heating (FMFs). The devices with FMFs film exhibited stronger photoresponse than that of FMFs_110 film. Our work presented an effective strategy for manipulating fullerene superstructures and providing insight on the role of nanofeatures of fullerene superstructures in their optoelectronic properties.

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REFERENCES

1. Shibata K, Kubozono Y, Kanbara T, et al. Fabrication and characteristics of C₆₀ fullerene field-effect transistors. Appl Phys Lett. 2004;84:2572-2574.
2. Campoy-Quiles M, Ferenczi T, Agostinelli T, et al. Morphology evolution via self-organization and lateral and vertical diffusion in polymer: fullerene solar cell blends. Nat Mater. 2008;7:158-164.
3. Goyal RN, Gupta VK, Bachheti N, Sharma RA. Electrochemical sensor for the determination of dopamine in presence of high concentration of ascorbic acid using a fullerene-C₆₀ coated gold electrode. Electroanalysis (New York, NY). 2008;20:757-764.
4. Wei L, Yao J, Fu H. Solvent-assisted self-assembly of fullerene into single-crystal ultrathin microribbons as highly sensitive UV–visible photodetectors. ACS Nano. 2013;7:7573-7582.
5. Miyazawa KI. Synthesis of fullerene nanowhiskers using the liquid–liquid interfacial precipitation method and their mechanical, electrical and superconducting properties. Sci Technol Adv Mater. 2015;16:013502.
6. Shrestha RG, Shrestha LK, Khan AH, Kumar GS, Acharya S, Ariga K. Demonstration of ultrarapid interfacial formation of 1d fullerene nanorods with photovoltaic properties. ACS Appl Mater Interfaces. 2014;6:15597-15603.
7. Shrestha LK, Ji Q, Mori T, et al. Fullerene nanoarchitectonics: from zero to higher dimensions. Chem Asian J. 2013;8:1662-1679.
8. Shrestha LK, Shrestha RG, Yamauchi Y, et al. Nanoporous carbon tubes from fullerene crystals as the π-electron carbon source. Angew Chem Int Ed. 2015;54:951-955.
9. Krishnan V, Kasuya Y, Ji Q, et al. Vortex-aligned fullerene nanowhiskers as a scaffold for orienting cell growth. ACS Appl Mater Interfaces. 2015;7:15667-15673.
10. Bai P, Minami K, Nakanishi W, Hill JP, Ariga K, Shrestha LK. Hierarchically structured fullerene C₆₀ cube for sensing volatile aromatic solvent vapors. ACS Nano. 2016;10:6631-6637.
11. Li H, Tee BCK, Cha JJ, et al. High-mobility field-effect transistors from large-area solution-grown aligned C₆₀ single crystals. J Am Chem Soc. 2012;134:2760-2765.
12. Singh TB, Marjanović N, Matt GJ, et al. High-mobility n-channel organic field-effect transistors based on epitaxially grown C₆₀ films. Org Electron. 2005;6:105-110.
13. Park C, Yoon E, Kawano M, Joo T, Choi HC. Self-crystallization of C₇₀ cubes and remarkable enhancement of photoluminescence. Angew Chem Int Ed. 2010;49:9670-9675.
14. Borsi S, Da Ros T, Spalluto G, Prato M. Fullerene derivatives: an attractive tool for biological applications. Eur J Med Chem. 2003;38:913-923.
15. Peng Z, Hu Y, Wang J, et al. Fullerene-based in situ doping of n and Fe into a 3D cross-like hierarchical carbon composite for high-performance supercapacitors. Adv Energy Mater. 2019;9:1802928.
16. Zhang J, Xu W, Sheng P, Zhao G, Zhu D. Organic donor–acceptor complexes as novel organic semiconductors. Acc Chem Res. 2017;50:1654-1662.
17. Wakahara T, Sathish M, Miyazawa K, et al. Preparation and optical properties of fullerene/ferrocene hybrid hexagonal nanosheets and large-scale production of fullerene hexagonal nanosheets. J Am Chem Soc. 2009;131:9940-9944.
18. Wang B, Zheng S, Saha A, Bao L, Lu X, Guldi DM. Understanding charge-transfer characteristics in crystalline
nanesheets of fullerene/(metallo) porphyrin cocrys. 19. kirner sekit a, guldi dm. 25th anniversary article: 20 years of fullerene research in electron transfer chemistry. ade mater. 2014;26:1482-1493.

20. wang w, luo l, sheng p, zhang j, zhang q. multifunctional features of organic charge-transfer complexes: advances and perspectives. chem eur j. 2021;27:464-490.

21. zhang j, tan j, ma z, et al. fullerene/sulfur-bridged annulene cocrys: two-dimensional segregated heterojunctions with ambipolar transport properties and photoresponsivity. j am chem soc. 2013;135:558-561.

22. zheng s, cuong nt, okada s, et al. solvent-mediated shape engineering of fullerene (c\textsubscript{60}) polyhedral microcrystals. chem mater. 2018;30:7146-7153.

23. zheng s, xu m, lu x. facile method toward hierarchical fullerene architectures with enhanced hydrophobicity and photoluminescence.acs appl mater interfaces. 2015;7:20285-20291.

24. zheng s, zhong j, matsuda w, et al. fullerene/cobalt porphyrin charge-transfer cocrys: excellent thermal stability and high mobility. nano res. 2018;11:1917-1927.

25. boyd pd, reed ca. fullerene-porphyrin constructs. acc chem res. 2005;38:235-242.

26. sun d, tham fs, reed ca, boyd pdw. extending supramolecular fullerene-porphyrin chemistry to pillared metal-organic frameworks. proc nail acad sci. 2002;99:5088-5092.

27. sullivan p, jones t. pentacene/fullerene (c\textsubscript{60}) heterojunction solar cells: device performance and degradation mechanisms. org electrorn. 2009:6:565-660.

28. wei l, wu y, wang l, fu h, yao j. supramolecular synthesis of fullerene/tetracene hybrid flowerlike microstructures of nanoplates via the charge-transfer interactions. j phys chem c. 2011;115:21629-21634.

29. briggs jb, miller gp. [60] fullerene--acene chemistry: a review. c r chim. 2006:9:916-927.

30. shao y, sista s, chu c-w, sievers d, yang y. enhancement of tetracene photovoltaic devices with heat treatment. appl phys lett. 2007;90:103501.

31. wu y, yin z, xiao j, et al. crystal structure and phototransistor behavior of n-substituted heptacene.acs appl mater interfaces. 2012;4:1883-1886.

32. cataldo f, garcía-herández da, manchado a. on the c\textsubscript{60} fullerene adduct with pentacene: synthesis and stability. fuller nanotub. car n. 2015;23:818-823.

33. mack j, miller gp. synthesis and characterization of a c\textsubscript{60}-pentacene monoadduct. fullerenes. fuller nanotub car n. 1997;5:607-614.

34. cataldo f, garcía-herández da, manchado a. a study on the synthesis and stability of the c\textsubscript{60} fullerene/tetracene adduct. eur chem bull. 2014;3:740-744.

35. tang q, maji s, jiang b, et al. manipulating the structural transformation of fullerene microtubes to fullerene microhorns having microscopic recognition properties.acs nano. 2019;13:14005-14012.

36. yumi hizume kt, charvet r, yamamoto y, saeki a, seki s, aida t. chiroselective assembly of a chiral porphyrin-fullerene dyad: photoconductive nanofiber with a top-class ambipolar charge-carrier mobility. j am chem soc. 2010;132:6628-6629.

37. xue p, lu r, zhao l, et al. hybrid self-assembly of a \( \pi \) gelator and fullerene derivative with photinduced electron transfer for photocurrent generation. langmuir. 2010;26(9):6669-6675.

38. shrestha lk, sathish m, hill jp, et al. alcohol-induced decomposition of olmstead's crystalline ag (i)--fullerene heterostructure yields 'bucky cubes'. j phys chem c. 2013;1:1174-1181.

39. babu ss, möhwald h, nakanishi t. recent progress in morphology control of supramolecular fullerene assemblies and its applications. chem soc rev. 2010;39:4021-4035.

40. nakanishi t, schmitt w, michinobu t, kurth dg, ariga k. hierarchical supramolecular fullerene architectures with controlled dimensionality. chem commun. 2005:48:5982-5984.

41. ho c-c, chen p-y, lin k-h, juan wt, lee wl. fabrication of monolayer of polymer/nanospheres hybrid at a water-air interface.acs appl mater interfaces. 2011;3:204-208.

42. ahmad n, bottomley a, ionaul a. optimizing refractive index sensitivity of supported silver nanocube monolayers. j phys chem c. 2012;116:185-192.

43. khanha s, utsav h, chaliyawala h, et al. systematic investigation of close-packed silica nanospheres monolayer under sintering conditions. j ear ceram soc. 2019;39:1411-1419.

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