Pillar[n]arene-Mimicking/Assisted/Participated Carbon Nanotube Materials

Subjects: Materials Science, Composites

Contributor: Zhaona Liu , Bing Li , Zhizheng Li , Huacheng Zhang

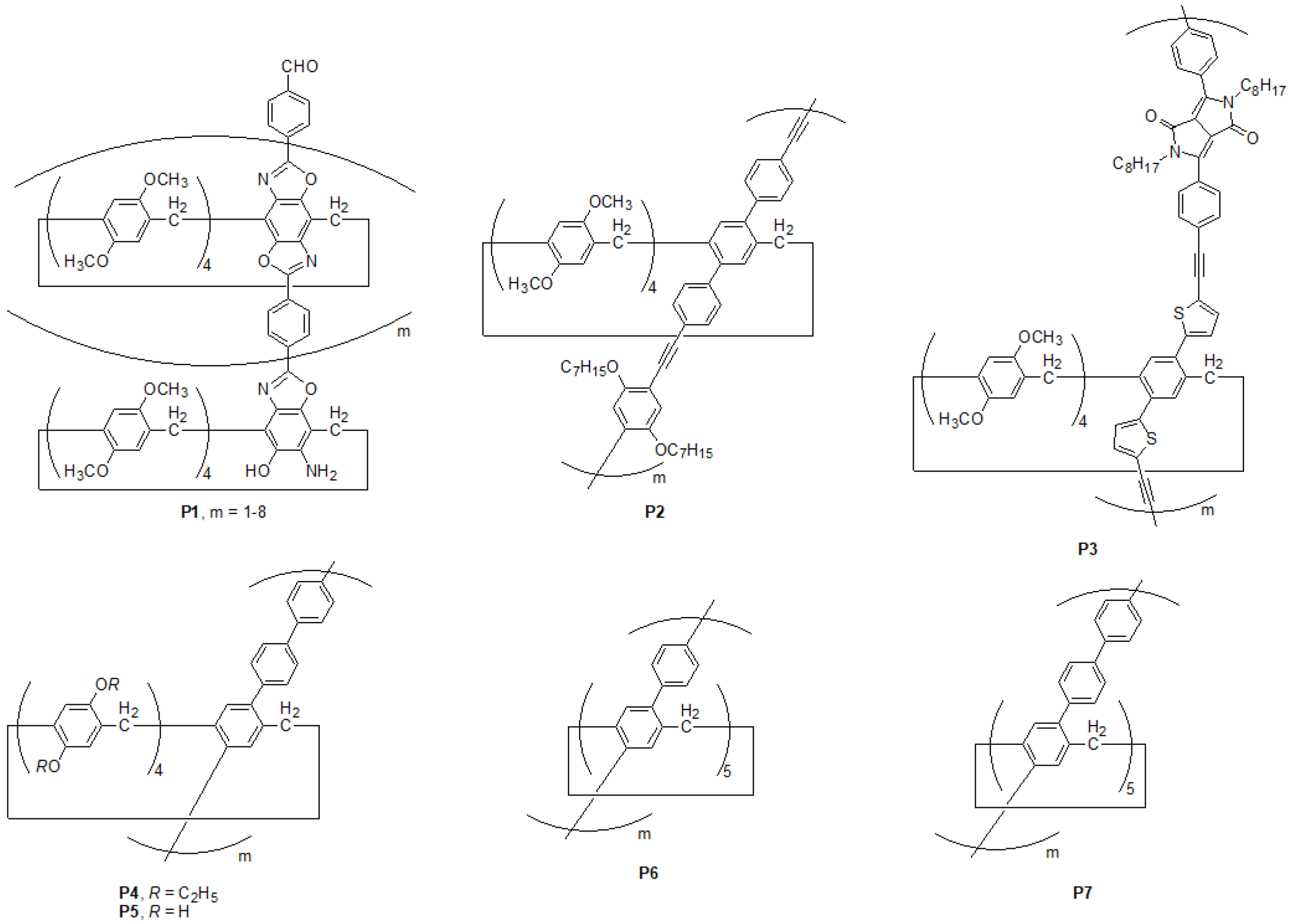
The molecular structure of pillar[n]arene could serve different roles in the fabrication of attractive carbon nanotube-based materials. Firstly, pillar[n]arene has the ability to provide the structural basis for enlarging the cylindrical pillar-like architecture by forming one-dimensional, rigid, tubular, oligomeric/polymeric structures with aromatic moieties as the linker or forming spatially “closed”, channel-like, flexible structures by perfunctionalizing with peptides and with intramolecular hydrogen bonding. Interestingly, such pillar[n]arene-based carbon nanotube-resembling structures were used as porous materials for the adsorption and separation of gas and toxic pollutants, as well as for artificial water channels and membranes. In addition to the art of organic synthesis, self-assembly based on pillar[n]arene, such as self-assembled amphiphilic molecules, is also used to promote and control the dispersion behavior of carbon nanotubes in solution. Furthermore, functionalized pillar[n]arene derivatives integrated carbon nanotubes to prepare advanced hybrid materials through supramolecular interactions, which could also incorporate various compositions such as Ag and Au nanoparticles for catalysis and sensing.

pillar[n]arene carbon nanotube synthesis hybrid materials composites

1. Mimicking the Structure and Characteristics of Carbon Nanotubes by Functionalized Pillar[n]arene

1.1. Preparing Linear Pillar[n]arene-Based Oligomer/Polymer via Rigid Aromatic Bridges

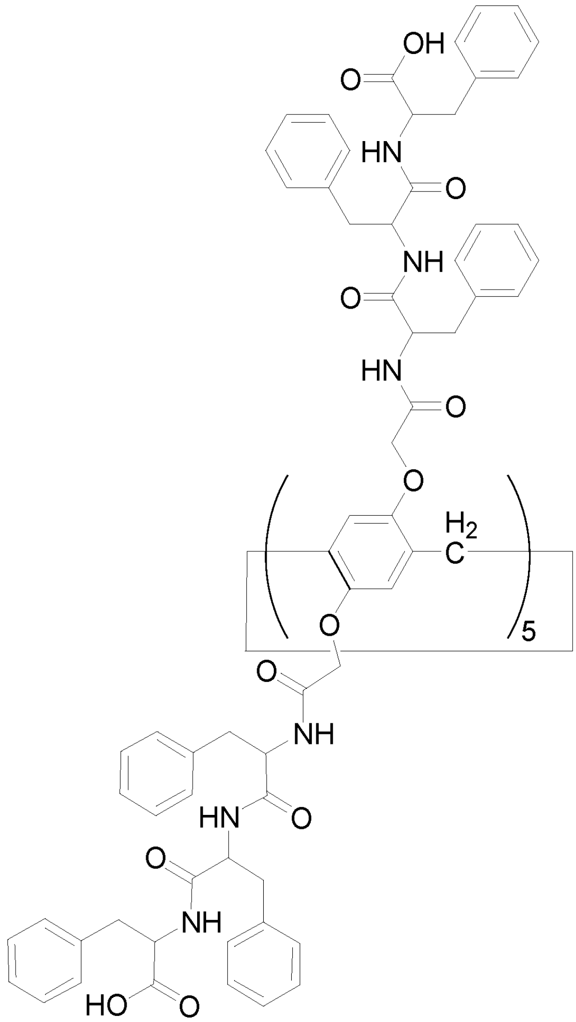
Due to the possession of rigid pillar-like molecular structures and an electron-rich cavity [1], the skeleton of functionalized pillar[n]arene was employed as previous pieces for the construction of linear oligomeric and polymeric architectures, such as **P1**–**P7** (Scheme 1), by introducing rigid aromatic bridging subunits to mimic carbon nanotubes [2][3][4][5][6]. Several classic organic syntheses such as heterocyclization and Pd-catalyzed coupling reactions [7][8][9][10] have been thoroughly employed. Particularly, those carbon nanotube-resembling linear pillar[n]arene-based porous materials have been used in diverse applications such as gas absorption [11][12], as well as the absorption and separation of toxic pollutants in water [13]. For example, **P2** exhibits a recognition towards solvent molecules such as dichloromethane [4], whereas **P3** has the ability to capture toxic pollutants such as adiponitrile [5]. In addition, **P5** can selectively absorb CO_2 rather than N_2 or methane [6], whereas **P6** and **P7** were used for separating propane gas from the simulated gas mixture of methane and propane [2].



Scheme 1. Chemical structures of pillar[5]arene-based polymers **P1**–**P7**.

1.2. Preparing Peptide-Appended Pillar[n]arene Processing Intramolecular Hydrogen Bonds

Except for introducing rigid aromatic moieties as the bridging linker for the construction of pillar[n]arene-based polymeric architectures, diverse designs and synthetic strategies were carried out for mimicking carbon nanotubes; for example [14], the peptide-appended pillar[n]arene **P8** (Scheme 2) was produced to introduce intramolecular interactions such as hydrogen bonding [15] to form “closed”, tubular, molecular architectures [16], as well as to resemble the performance of carbon nanotubes as artificial water channels [17][18] and permeable membranes [19][20][21]. It was revealed that the average single-channel osmotic water permeability [19] and the ion rejection of **P8** were greatly analogous to those of carbon nanotubes [21]. Furthermore, the pore density [22] of **P8**-based channel arrays was much higher than that of carbon nanotube-based ones [19]. It was also found that the flexible conformation of the peptide-appended pillar[n]arene was available for water permeability [20][23][24].

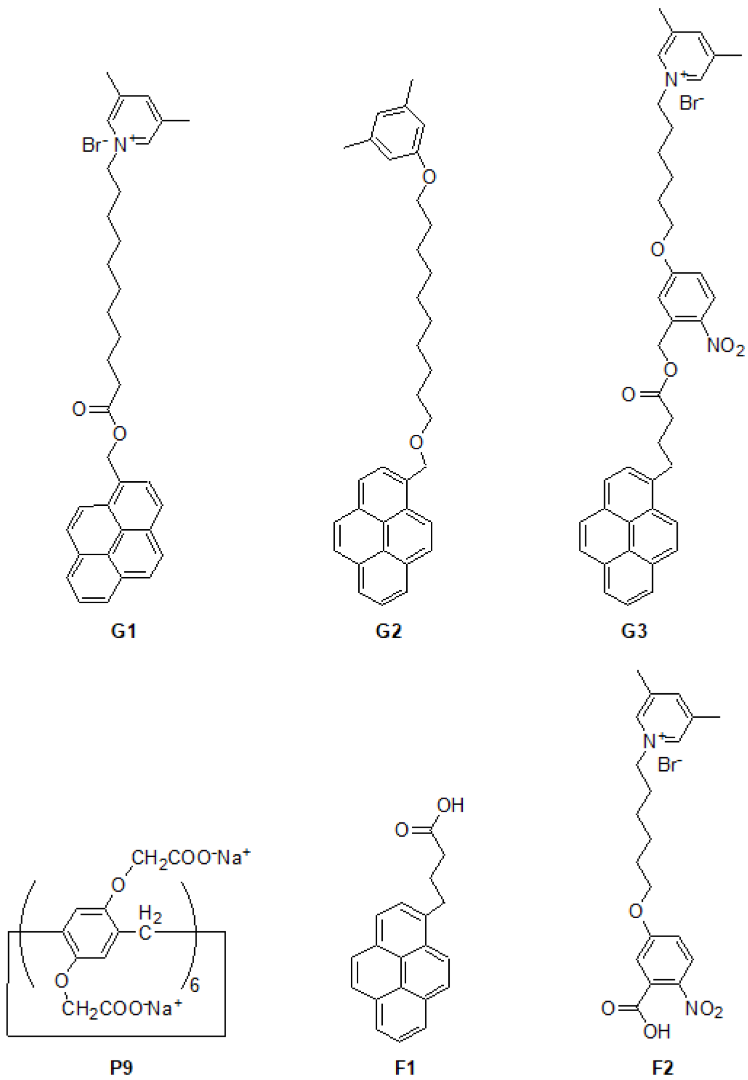


P8

Scheme 2. Chemical structures of pillar [5]arene derivative **P8** [19].

2. Dispersion of Carbon Nanotube by Using Functionalized Pillar[n]arene

Water-soluble pillar[n]arene could include hydrophobic guest molecules [25][26], producing pillar[n]arene-based self-assembled amphiphiles (PSAs) [27][28] and resembling the performance of general surfactant-dispersing carbon nanotubes [29]. For example [30], water-soluble carboxylate-perfunctionalized [31] pillar[6]arene **P9** (Scheme 3) has the ability to recognize the hydrophobic pyrene [32] derivative **G1** (Scheme 3) in the stoichiometry of 1/1, and aggregate into vesicular architectures [33] in an aqueous solution as confirmed by transmission electron microscopy (TEM) [34]. Since the water solubility of **P9** changes with the change of pH value, the morphology of **P9** ⊃ **G1**-based self-assemblies could be also controlled. In addition [30], **P9** could include another pyrene derivative **G2** (Scheme 3) with the association constant (K_a) of (8.04 ± 0.68) 10^4 M^{-1}. Additionally, the obtained amphiphilic inclusion could further disperse multi-walled carbon nanotubes well by sonication in aqueous solutions as confirmed by TEM and scanning electron microscopy (SEM). The π–π stacking interactions [35] between pyrene subunits and carbon nanotubes played a significant role in this process as confirmed by fluorescence spectroscopy [36].



Scheme 3. Chemical structures of pillar[6]arene derivative P9, guests such as pyrene derivatives **G1–G3**, as well as functional molecules **F1** and **F2** [30][37].

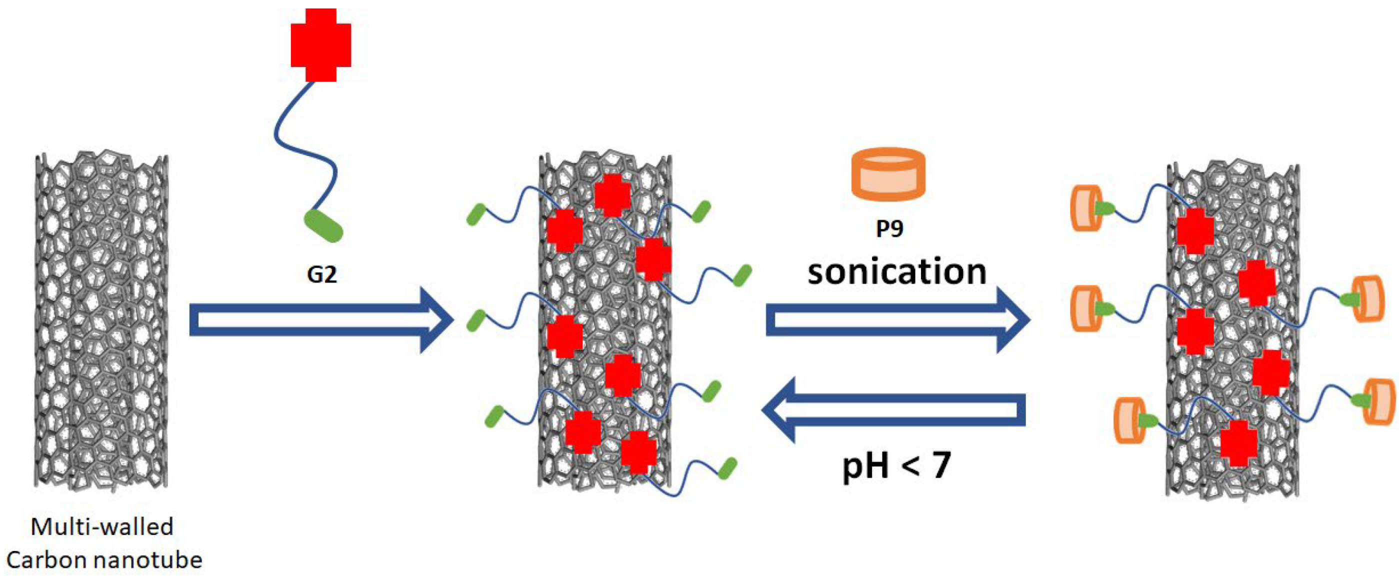
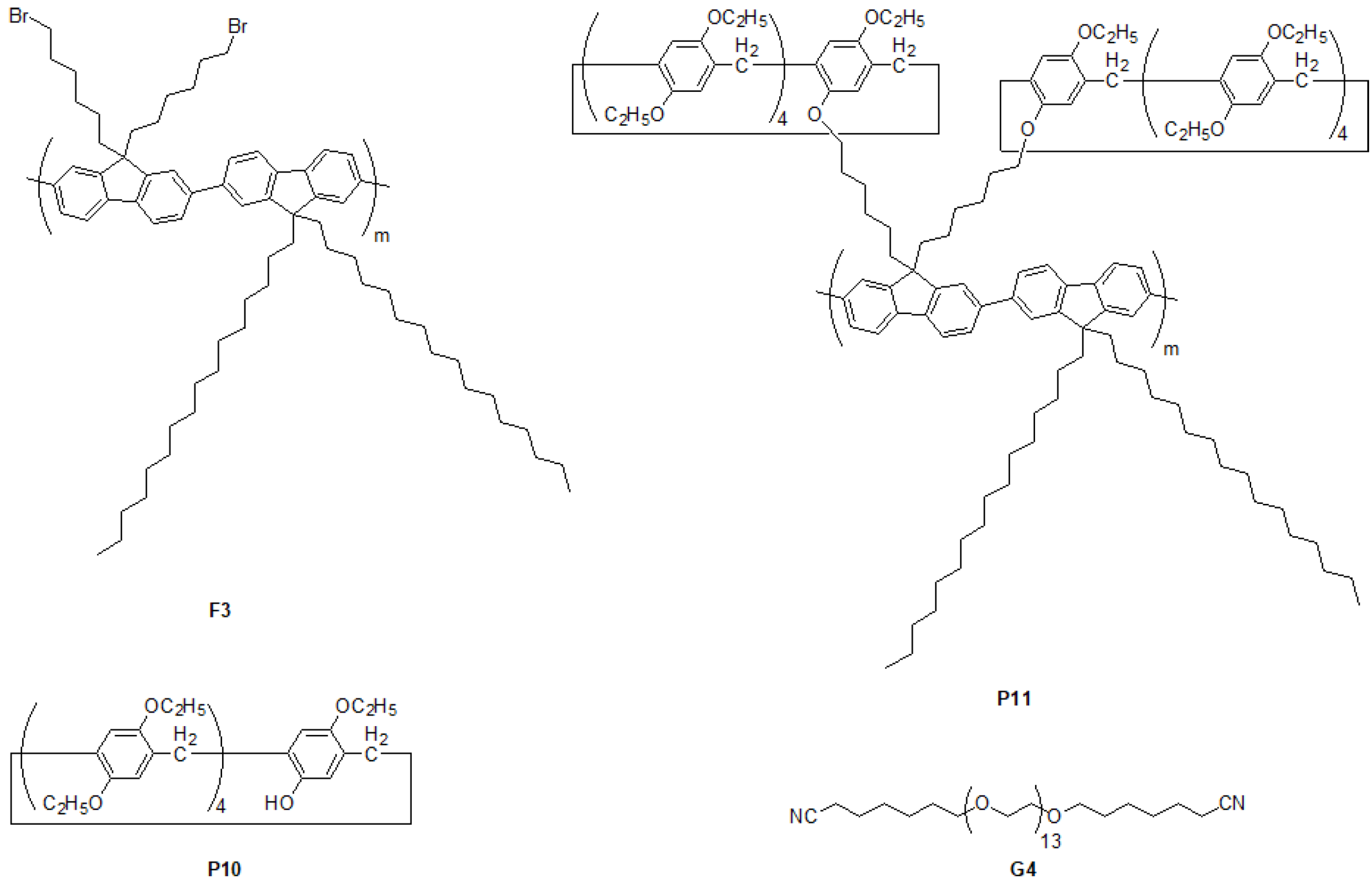


Figure 1. Illustration of dispersing multi-walled carbon nanotube by using amphiphilic host–guest inclusion **P9** ⊃ **G2** in aqueous solution [30].

Similarly [37], another pyrene derivative **G3** (Scheme 3) which is responsive to UV irradiation and degrades into **F1** and **F2** (Scheme 3) was further employed as the hydrophobic guest to be included by **P9**. Thus, the amphiphilic inclusion **P9** ⊃ **G3** was obtained and exhibited the critical aggregation concentration (CAC) [38] of 1.0 × 10^6 mol L^{-1}, which has the capacity of dispersing multi-walled carbon nanotubes in aqueous solutions as confirmed by TEM. Interestingly, the dispersion of carbon nanotubes could be controlled upon UV irradiation according to the formation/deformation of **G3**.

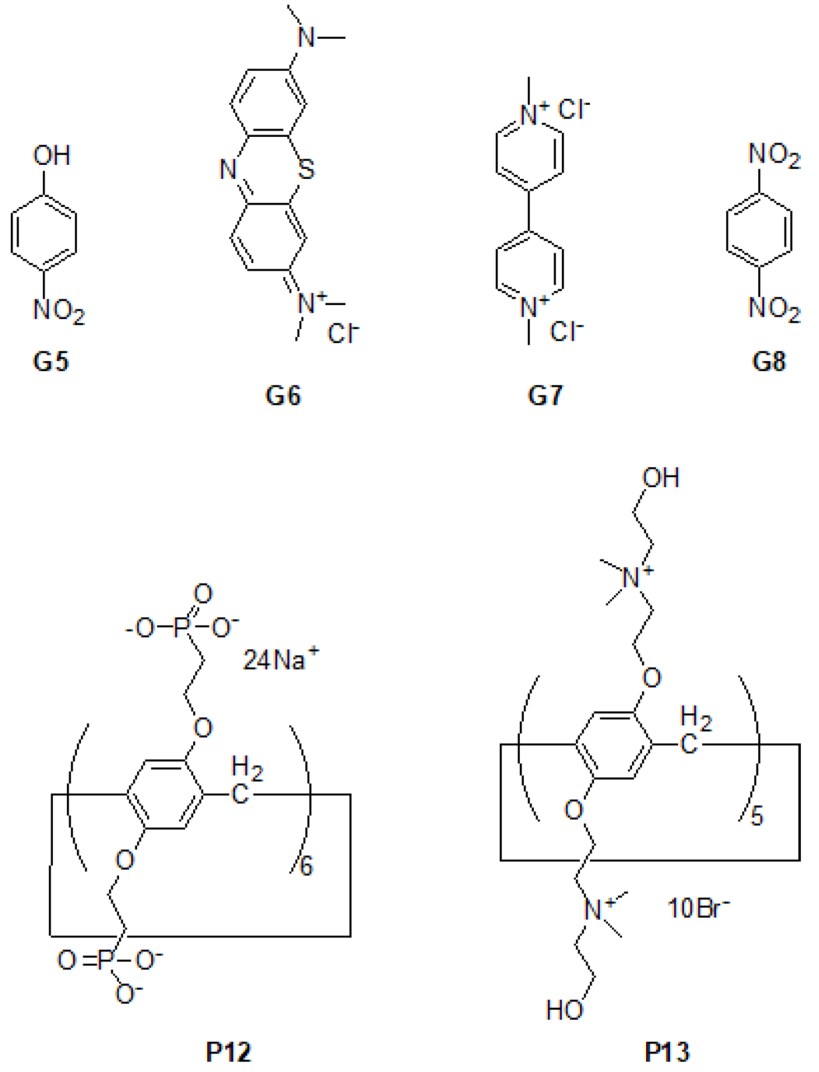
3. Decoration of Carbon Nanotube by Using Functional Pillar[n]arene

The mono-hydroxyl functionalized pillar[5]arene **P10** (Scheme 4) coupled with the alkyl bromide-modified polyfluorene **F3** (Scheme 4) via a classic nucleophilic substitution reaction led to the formation of pillar[5]arene-functionalized polymer **P11** (Scheme 4) [39]. Due to the possession of the pillar[5]arene cavity on the structural skeleton, **P11** could form a complex with a neutral poly(ethylene glycol) (PEG) derivative with two ending subunits—alkylnitrile **G4** (Scheme 4) via donor–acceptor interactions. Particularly, this obtained host–guest inclusion **P11** ⊃ **G4** not only has the capacity for properly exfoliating and dispersing single-walled carbon nanotubes in organic solvents (600 μg mL^{-1})as confirmed by ^{1}H NMR, Raman, UV–Vis–near-infrared (NIR) spectra, and thermogravimetric analysis (TGA), but also affords the preparation of pillar[5]arene-based polymer-carbon nanotube composite organogels [40][41][42] in 1,2-dichlorobenzene (40 *wt*%) via non-covalent interactions [39].



Scheme 4. Chemical structures of polymer **F3**, pillar[5]arene P10, pillar[5]arene-based polymer **P11** and PEG derivative **G4** [39].

Besides the organic and polymeric composition, diverse inorganic materials were also employed for fabricating different functional, carbon nanotube-based, hybrid materials. For example [43], the water-soluble phosphate-perfunctionalized pillar[6]arene **P12** (Scheme 5) could decorate the surface of a single-walled carbon nanotube at room temperature via π–π stacking interactions between the carbon nanotube and benzene moieties of **P12** by sonicating in aqueous solutions, as confirmed by zeta potentials and Fourier transform infrared (FTIR) spectroscopy. Particularly, Ag nanoparticles could be further well dispersed on the surface of the carbon nanotube due to the coordination environment provided by the cavity of **P12**. Thus, the obtained hybrid materials containing Ag nanoparticles, carbon nanotubes and **P12** exhibited strong catalytic activity towards a series of guest molecules such as 4-nitrophenol (**G5**, Scheme 5), methylene (**G6**, Scheme 5) and paraquat (**G7**, Scheme 5), paving the way for efficient electrochemical sensing of highly toxic herbicides.



Scheme 5. Chemical structures of pillar[6]arene P12 and pillar[5]arene **P13**, as well as guests such as **G5**–**G8** [43] [44].

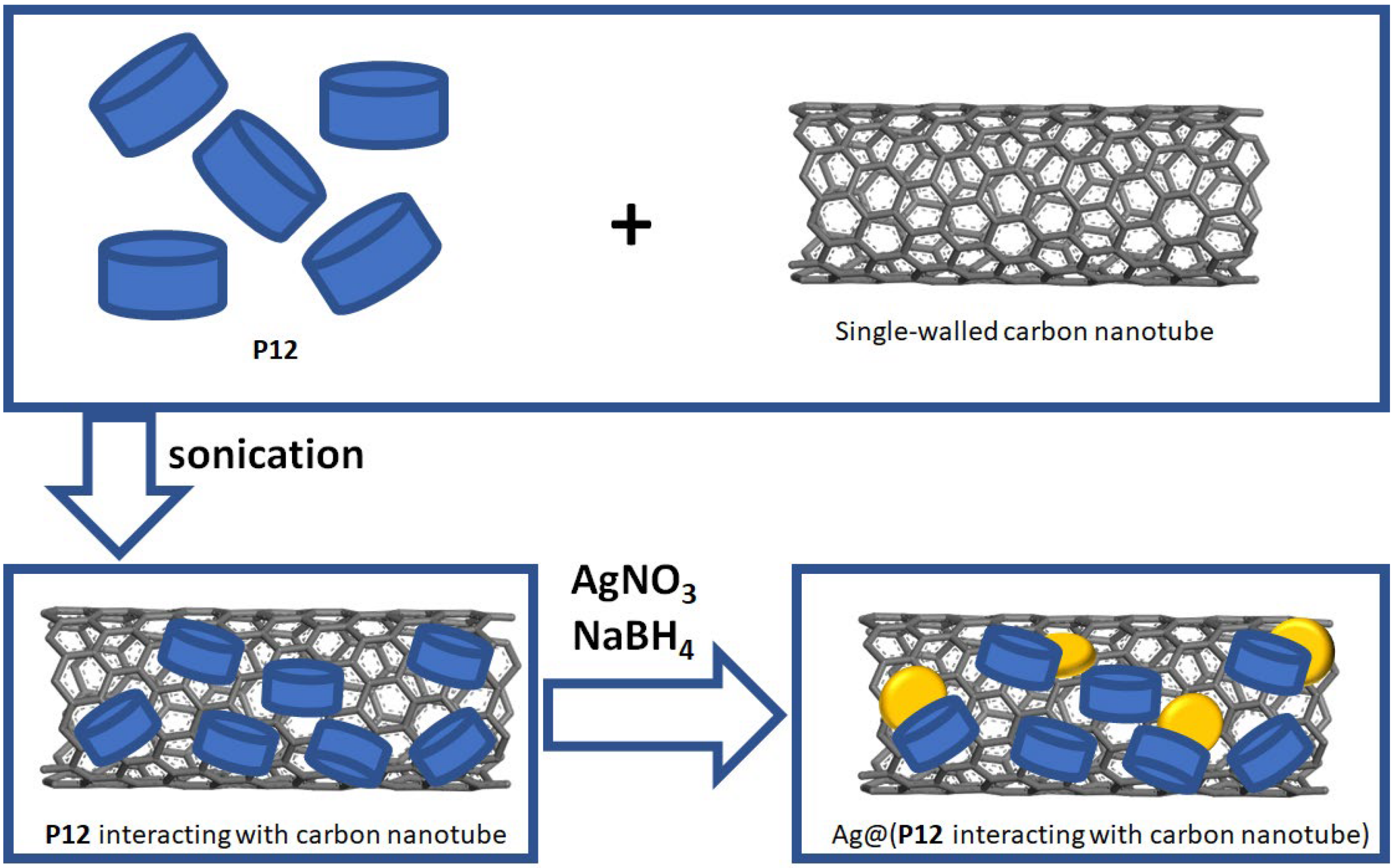


Figure 4. Illustration of the fabrication of hybrid materials Ag@(**P12** non-covalently interacting with carbon nanotubes) [43].

Except for loading Ag nanoparticles, Au nanoparticles [45][46][47] could also be introduced into carbon nanotube-based hybrid materials via the assistance of pillar[n]arene. For example, water-soluble hydroxyl pillar[5]arene **P13** (Scheme 5) was also used for dispersing single-walled carbon nanotubes in aqueous solutions via non-covalent interactions, and further assisted in promoting the formation of Au nanoparticles on the surface of carbon nanotubes, leading to the formation of hybrid materials Au@(P13 interacting with carbon nanotubes) [44]. It has been revealed that such hybrid materials had reasonable performances in catalyzing an ethanol oxidation reaction (EOR), as well as sensing *p*-dinitrobenzene (**G8**, Scheme 5) because of pillar[5]arene cavities.

References

1. Zhang, H.C.; Han, J.; Li, C. Pillararene-based conjugated porous polymers. Polym. Chem. 2021, 12, 2808–2824.
2. Talapaneni, S.N.; Kim, D.; Barin, G.; Buyukcakir, O.; Je, S.H.; Coskun, A. Pillararene based conjugated microporous polymers for propane/methane separation through host-guest complexation. Chem. Mater. 2016, 28, 4460–4466.

3. Strutt, N.L.; Zhang, H.; Schneebeli, S.T.; Stoddart, J.F. Amino-functionalized pillararene. Chem. Eur. J. 2014, 20, 10996–11004.
4. Ma, Y.J.; Chen, L.; Li, C.; Müllen, K. A fishing rod-like conjugated polymer bearing pillararenes. Chem. Commun. 2016, 52, 6662–6664.
5. Cui, W.; Tang, H.; Xu, L.X.; Wang, L.Y.; Meier, H.; Cao, D.R. Pillararene-diketopyrrolopyrrole fluorescent copolymer: A promising recognition and adsorption material for adiponitrile by selective formation of a conjugated polypseudorotaxane. Macromol. Rapid Commun. 2017, 38, 1700161.
6. Ogoshi, T.; Shimada, Y.; Akutsu, T.; Yamagishi, T. A rod-like phenolic π-conjugated polymer with pillararene units in its main chain. Polymer 2017, 128, 325–329.
7. Dennis, J.M.; White, N.A.; Liu, R.Y.; Buchwald, S.L. Pd-catalyzed C–N coupling reactions facilitated by organic bases: Mechanistic investigation leads to enhanced reactivity in the arylation of weakly binding amines. ACS Catal. 2019, 9, 3822–3830.
8. Xu, S.Q.; Kim, E.H.; Wei, A.; Negishi, E. Pd- and Ni-catalyzed cross-coupling reactions in the synthesis of organic electronic materials. Sci. Technol. Adv. Mater. 2014, 15, 044201.
9. Wang, D.; Gao, S.H. Sonogashira coupling in natural product synthesis. Org. Chem. Front. 2014, 1, 556–566.
10. Blangetti, M.; Rosso, H.; Prandi, C.; Deagostino, A.; Venturello, P. Suzuki-miyaura cross-coupling in acylation reactions, scope and recent developments. Molecules 2013, 18, 1188–1213.
11. Li, J.R.; Kuppler, R.J.; Zhou, H.C. Selective gas adsorption and separation in metal-organic frameworks. Chem. Soc. Rev. 2009, 38, 1477–1504.
12. Li, H.; Wen, C.Y.; Zhang, Y.W.; Wu, D.P.; Zhang, S.L.; Qiu, Z.J. Accelerating gas adsorption on 3D percolating carbon nanotubes. Sci. Rep. 2016, 6, 21313.
13. Gupta, V.K.; Saleh, T.A. Sorption of pollutants by porous carbon, carbon nanotubes and fullerene-an overview. Environ. Sci. Pollut. Res. 2013, 20, 2828–2843.
14. Chen, L.; Si, W.; Zhang, L.; Tang, G.F.; Li, Z.T.; Hou, J.L. Chiral selective transmembrane transport of amino acids through artificial channels. J. Am. Chem. Soc. 2013, 135, 2152–2155.
15. Hua, B.; Shao, L.; Zhang, Z.H.; Liu, J.Y.; Huang, F.H. Cooperative silver ion-pair recognition by peralkylated pillararenes. J. Am. Chem. Soc. 2019, 141, 15008–15012.
16. Zhang, H.C.; Zhao, Y.L. Chapter 9: Supramolecular assemblies from pillararenes (micellar, vesicular and tubular formations). In Pillararenes; Ogoshi, T., Ed.; The Royal Society of Chemistry: Kanazawa, Japan, 2016; pp. 208–228.

17. Strutt, N.L.; Zhang, H.; Schneebeli, S.T.; Stoddart, J.F. Functionalizing Pillararenes. Acc. Chem. Res. 2014, 47, 2631–2642.

18. Xin, P.Y.; Kong, H.Y.; Sun, Y.H.; Zhao, L.Y.; Fang, H.D.; Zhu, H.F.; Jiang, T.; Guo, J.J.; Zhang, Q.; Dong, W.P.; et al. Artificial K+ channels formed by pillararene-cyclodextrin hybrid molecules: Tuning cation selectivity and generating membrane potential. Angew. Chem. Int. Ed. 2019, 58, 2779–2784.

19. Shen, Y.x.; Si, W.; Erbakan, M.; Decker, K.; De Zorzi, R.; Saboe, P.O.; Kang, Y.J.; Majd, S.; Butler, P.J.; Walz, T.; et al. Highly permeable artificial water channels that can self-assemble into two-dimensional arrays. Proc. Natl. Acad. Sci. USA 2015, 112, 9810–9815.

20. Barden, D.R.; Vashisth, H. Water dynamics in a peptide-appended pillararene artificial channel in lipid and biomimetic membranes. Front. Chem. 2021, 9, 753635.

21. Kali, R.; Milner, S.T. Hydration shell stripping governs ion rejection in PAP water channels. Mol. Syst. Des. Eng. 2022, 7, 809–819.

22. Li, M.H.; Lou, X.Y.; Yang, Y.W. Pillararene-based molecular-scale porous materials. Chem. Commun. 2021, 57, 13429–13447.

23. Liu, Y.; Vashisth, H. Conformational dynamics and interfacial interactions of peptide-appended pillararene water channels in biomimetic membranes. Phys. Chem. Chem. Phys. 2019, 21, 22711–22721.

24. Shen, Y.x.; Song, W.; Barden, D.R.; Ren, T.; Lang, C.; Feroz, H.; Henderson, C.B.; Saboe, P.O.; Tsai, D.; Yan, H.; et al. Achieving high permeability and enhanced selectivity for angstrom-scale separations using artificial water channel membranes. Nat. Commun. 2018, 9, 2294.

25. Zhang, H.C.; Ma, X.; Nguyen, K.T.; Zeng, Y.F.; Tai, S.H.; Zhao, Y.L. Water-soluble pillararene-functionalized graphene oxide for in vitro raman and fluorescence dual-mode imaging. ChemPlusChem 2014, 79, 462–469.

26. Shurpik, D.N.; Aleksandrova, Y.I.; Mostovaya, O.A.; Nazmutdinova, V.A.; Zelenikhin, P.V.; Subakaeva, E.V.; Mukhametzyanov, T.A.; Cragg, P.J.; Stoikov, I.I. Water-soluble pillararene sulfo-derivatives self-assemble into biocompatible nanosystems to stabilize therapeutic proteins. Bioorg. Chem. 2021, 117, 105415.

27. Zhang, H.C.; Liu, Z.N.; Zhao, Y.L. Pillararene-based self-assembled amphiphiles. Chem. Soc. Rev. 2018, 47, 5491–5528.

28. Zhang, H.C.; Zhao, Y.L. Pillararene-based assemblies: Design principle, preparation and applications. Chem. Eur. J. 2013, 19, 16862–16879.

29. Cao, S.; Zhou, L.; Liu, C.; Zhang, H.C.; Zhao, Y.X.; Zhao, Y.L. Pillararene-based self-assemblies for electrochemical biosensors. Biosens. Bioelectron. 2021, 181, 113164.

30. Yu, G.C.; Xue, M.; Zhang, Z.B.; Li, J.Y.; Han, C.Y.; Huang, F.H. A water-soluble pillararene: Synthesis, host-guest chemistry, and its application in dispersion of multiwalled carbon nanotubes in water. J. Am. Chem. Soc. 2012, 134, 13248–13251.
31. Liu, Y.M.; Zhou, F.; Yang, F.; Ma, D. Carboxylated pillararene (n = 5–7) host molecules: High affinity and selective binding in water. Org. Biomol. Chem. 2019, 17, 5106–5111.
32. Billing, B.K.; Agnihotri, P.K.; Singh, N. Development of pyrene-stacked carbon nanotube-based hybrid: Measurement of NO3− ions using fluorescence spectroscopy. Analyst 2018, 143, 3343–3352.
33. Hua, Y.J.; Chen, L.; Hou, C.X.; Liu, S.B.; Pei, Z.C.; Lu, Y.C. Supramolecular vesicles based on amphiphilic pillararenes for smart nano-drug delivery. Int. J. Nanomed. 2020, 15, 5873–5899.
34. Colombo, F.; Norton, E.G.; Cocucci, E. Microscopy approaches to study extracellular vesicles. Biochim. Biophys. Acta Gen. Subj. 2021, 1865, 129752.
35. Chen, T.; Li, M.X.; Liu, J.Q. π–π stacking interaction: A nondestructive and facile means in material engineering for bioapplications. Cryst. Growth Des. 2018, 18, 2765–2783.
36. Haddad, R.; Holzinger, M.; Maaref, A.; Cosnier, S. Pyrene functionalized single-walled carbon nanotubes as precursors for high performance biosensors. Electrochim. Acta 2010, 55, 7800–7803.
37. Yang, J.; Yu, G.C.; Xia, D.Y.; Huang, F.H. A pillararene-based UV-responsive supra-amphiphile: Synthesis, self-assembly, and application in dispersion of multiwalled carbon nanotubes in water. Chem. Commun. 2014, 50, 3993–3995.
38. Novo, M.; Freire, S.; Al Soufi, W. Critical aggregation concentration for the formation of early amyloid-β (1-42) oligomers. Sci. Rep. 2018, 8, 1783.
39. Shamshoom, C.; Fong, D.; Li, K.; Kardelis, V.; Adronov, A. Pillararene-decorated single-walled carbon nanotubes. ACS Omega 2018, 3, 13935–13943.
40. Zeng, L.P.; Lin, X.X.; Li, P.; Liu, F.Q.; Guo, H.; Li, W.H. Recent advances of organogels: From fabrications and functions to applications. Prog. Org. Coat. 2021, 159, 106417.
41. Wei, T.B.; Zhao, Q.; Li, Z.H.; Dai, X.Y.; Niu, Y.B.; Yao, H.; Zhang, Y.M.; Qu, W.J.; Lin, Q. Supramolecular organogel with aggregation-induced emission for ultrasensitive detection and effective removal of Cu2+ and Hg2+ from aqueous solution. Dyes Pigm. 2021, 192, 109436.
42. Esposito, C.L.; Kirilov, P.; Roullin, V.G. Organogels, promising drug delivery systems: An update of state-of-the-art and recent applications. J. Control. Release 2018, 271, 1–20.
43. Zhao, G.F.; Gao, Z.H.; Li, H.N.; Liu, S.M.; Chen, L.J.; Zhang, R.L.; Guo, H. Controlled assembly of Ag nanoparticles on the surface of phosphate pillararene functionalized single-walled carbon

nanotube for enhanced catalysis and sensing performance. Electrochim. Acta 2019, 318, 711–719.

44. Borjigin, T.; Zhao, G.F.; Zhang, Y.H.; Liang, M.F.; Liu, B.H.; Liu, H.; Yang, X.F.; Guo, H. Control loading au nanoparticles on the surface of hydroxyl pillararene functionalized single-walled carbon nanotubes and its application in catalysis and sensing. Sustain. Energy Fuels 2019, 3, 2312–2320.
45. Liu, Z.N.; Liu, W.B.; Huang, Y.Z.; Zhang, H.C. Facile fabrication of free-standing Cu2O-Au nanocomposite on Cu foil for high performance glucose sensing. J. Alloys Compd. 2020, 848, 156532.
46. Zhu, H.T.Z.; Shangguan, L.Q.; Huang, F.H. Multi-functional pillararene-stabilized gold nanoparticles. Matter 2019, 1, 788–789.
47. Li, P.y.; Chen, Y.; Chen, C.h.; Liu, Y. Multi-charged bis(p-calixarene)/pillararene functionalized gold nanoparticles for ultra-sensitive sensing of butyrylcholinesterase. Soft Matter 2019, 15, 8197–8200.