

Chemistry—A Structurally Based Science: My Journey from the Beauty in Fullerene Chemistry to Supramolecular Material Chemistry

Hsiu-Fu Hsu

Department of Chemistry, Tamkang University, Taiwan

'Chemistry is an art.' As a college student, I could not really apprehend how chemistry is an art as told by a physical chemistry professor. As a research assistant at National Tsin-Hua University, fascinated by the colorful nature of organometallic compounds, I was involved in metal cluster organometallic chemistry and then I found that the beauty of the molecular structures of metal cluster compounds impressed me more. 'Chemistry is an art' has then seeded in my early career of research. As chemistry being recognized as a structurally based science, designs of molecular structures have always attracted me initially to get through the resulting beautiful science behind these beautiful molecules.

With the pleasant encounter of metal cluster chemistry, I then started my PhD journey to deeply appreciate metal cluster chemistry from Prof. John R. Shapley, one of the most well-known metal cluster chemists, at University of Illinois at Urbana-Champaign. John offered many projects to choose from and metal cluster fullerene chemistry stood out in my mind. To me the project was so attractive due to the following reasons. First of all, little was known then about fullerene organometallic chemistry, not to mention fullerene metal cluster chemistry. Exploring new scientific territory has always been an important attribute for scientists. Secondly, the project's high potential in catalysis applications is promising. Thirdly, the difficulty to

achieve the project is challenging since it was yet succeeded though some former group members and many other groups worldwide had tried. The last and most important reason behind the pick was the beauty of the molecular structures.¹ In sum, the great challenge and the beauty of the project caught my strong attention and drive me through all the bad and good times in my PhD career.

The reasons behind my pick had helped me going through the tough times for my first three PhD years, full of frustrations. It turned out the three years was not a waste but had improved my experimental skill and perseverance toward chemistry research. The key to the successful identification of the first triple dihapto bonding mode of a hexagon of C₆₀ to a Ru₃ cluster unit, Ru₃(CO)₉(μ₃-η², η², η²-C₆₀),² was later found to be the realization of the very low yield and difficulty of identification on thin layer chromatography of the product. Previous to this publication, C₆₀ was suggested to be aromatic and the suggestion led to many attempts trying to achieve the coordination of C₆₀ through a C₆ ring to a single metal center. However, later, C₆₀ was realized to react primarily as an electron-deficient alkene and sometimes as a diene. The C=C π bonds were recognized to be more localized than delocalized through the cage. However, the triple dihapto coordination mode of a hexagon in C₆₀ could not be achieved until my publication in 1996 (Figure 1). A

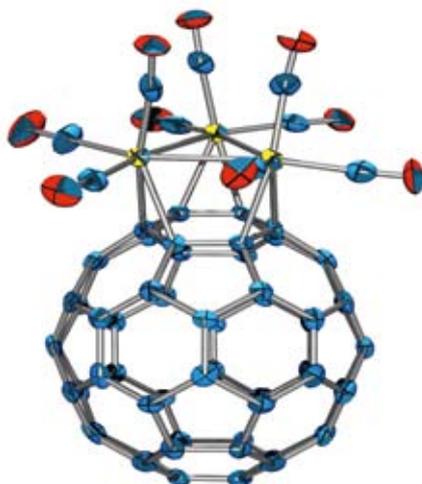


Figure 1. The first C₆ ring coordinated C₆₀ complex: the single crystal molecular structure of Ru₃(CO)₉C₆₀. Red, O; blue, C; yellow, Ru.

$\text{Ru}_3(\text{CO})_9$ unit was successfully face-capped onto the arene-like C_{60} cage. The significance of the new finding was highlighted by Chemical & Engineering News (C&EN) of American Chemical Society in the same year. A couple years later, the results were included in books including some major inorganic and organometallic chemistry textbooks. In 2010, Wikipedia presented the result under the topic of fullerene ligand.

With the success and understanding of the attributes of fullerene metal cluster compounds, other related compounds were synthesized and investigated. Phosphines were incorporated onto the ruthenium cluster in Ru_3C_{60} for improving the solubility and tuning the steric/electronic properties. The CO ligands were found to exhibit site exchange behaviors in the C_{60} and C_{70} derivatives.³ The Ru_3 unit was also used to cap the hexagon closest to the pole of C_{70} (Figure 2).⁴ Moreover, the structure of one of the isomers of two Ru_3 units capping two hexagons in one C_{70} cage was determined. Larger metal clusters were also successfully capped onto C_{60} with the help of phosphine incorporation to improve solubility for characterization.⁵ These results initiated the fullerene metal cluster chemistry and thereafter more than a hundred publications on this subject by other groups have been reported.

After my PhD journey cruising through fullerene chemistry, I then joined Prof. Timothy M. Swager's group at Massachusetts Institute of Technology to study liquid crystalline materials. For me, the beauty of the optical textures of liquid crystals (LCs) was irresistible. Moreover, the supramolecular correlations of LCs were beyond my imagination after focusing the molecular

structures. Tim is always full of energy on research and his research ideas then were just great to be highly appreciated by me. Against conventional wisdom on liquid crystalline compounds with rod-like or disc-like chemical structures, Tim's group discovered spherical tris-bidentate octahedral metal complexes exhibiting a propeller-like molecular geometry could pack into columns to lead to liquid crystallinity. The tris-bidentate nature provides two possible chiral senses (Δ and Λ). Excitingly, I was involved in the study of utilizing fluxionality of some octahedral coordination complexes to achieve cooperative chirality in liquid crystalline state induced by the incorporated peripheral chiral alkyl chains.⁶ The beauty of this project lies not only on the molecular structure but also the propeller columnar stacking and cooperative chiral induction.

After being an independent researcher at Tamkang University, most of my research work has been focusing on designing new liquid crystalline materials, investigating their supramolecular structure, and their potential applications. As aforementioned, compounds exhibiting liquid crystalline properties were with mainly rod-like or disc-like molecular structures. To start my own research, rod-like and disc-like molecules were designed for investigations on tuning their liquid crystalline properties for practical applications in display technologies. For rod-like compounds, symmetry breaking and rotational bulk of rigid core were utilized to enhance liquid crystallinity. The rotational bulk was realized by the rotational freedom of C-C single bonds in rigid molecular rods with naphthalene unit.

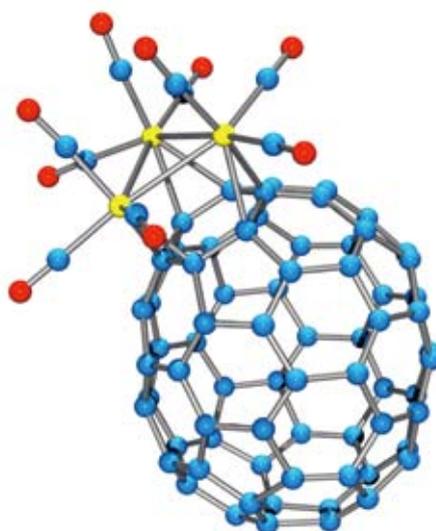


Figure 2. The first C_6 -face-capped C_{70} complex: the single crystal molecular structure of $\text{Ru}_3(\text{CO})_9\text{C}_{70}$. Red, O; blue, C; yellow, Ru.

Disc-like compounds were also investigated towards applications of optical compensating films in liquid crystal displays (LCDs) and one dimensional optoelectronic conduction.⁷ Materials showing the discotic nematic phase, the least ordered discotic phase to show a bit more ordered intermolecular packing than that of randomly packed liquids, were designed and working temperatures were tuned for practical applications through molecular design. Extrusion from disc periphery⁸ (Figure 3) and laterally-attached chain configuration⁹ (Figure 4) were employed to manipulate inter-disc interactions for resulting low melting LC materials to be used in fabrication of optical compensating films in LCDs. With the same molecular

core, materials showing molecular swirl geometry (Figure 5) were designed and the molecular swirl packing along molecular plane (Figure 6) was studied by scanning tunneling microscopy (STM).¹⁰ In liquid crystalline state, the molecular swirls exhibit highly correlated supra-structures along the molecular plane by swirl gearing interactions (Figure 7), and hence neighboring swirls are packed with the same swirl orientation sense. At the same time, the molecular swirls pack cooperatively with the same sense of swirl orientation along disc normal to lead to column formation by the strong inter-planar attractions. The two inter-disc correlations, along and perpendicular to the molecular plane, lead to highly correlated supra-structures over a large domain.

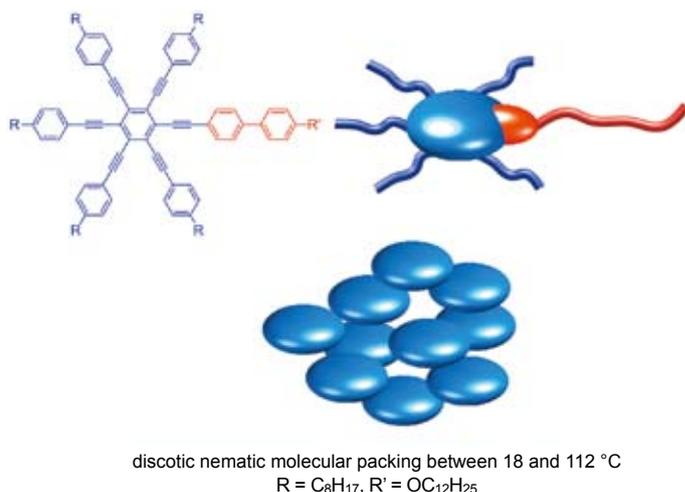


Figure 3. Room-temperature discotic nematic liquid crystals by extrusion from the disc of hexaynylbenzene. The chemical structure, schematic representations showing the extrusion of the unique sidearm, and schematic representation showing disc packing in the nematic phase.

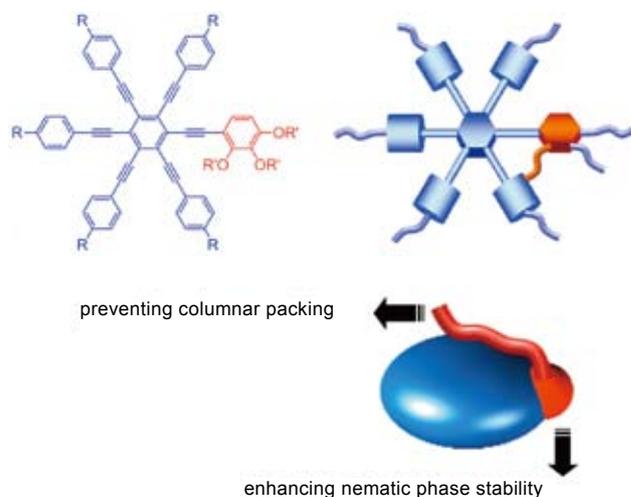
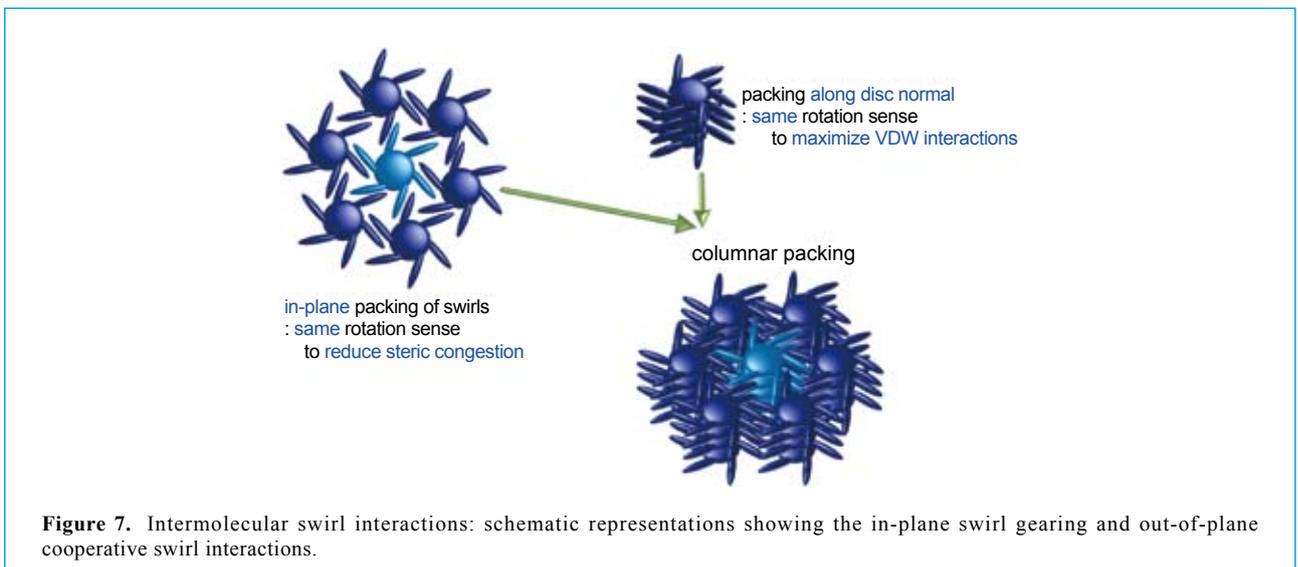
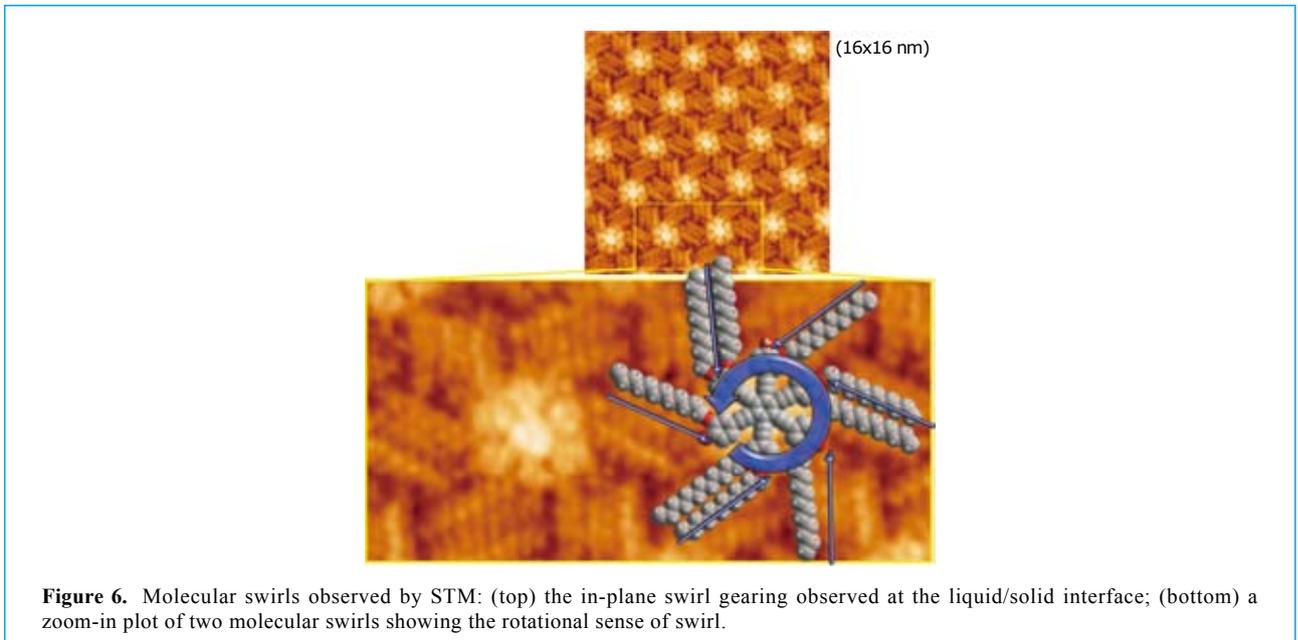
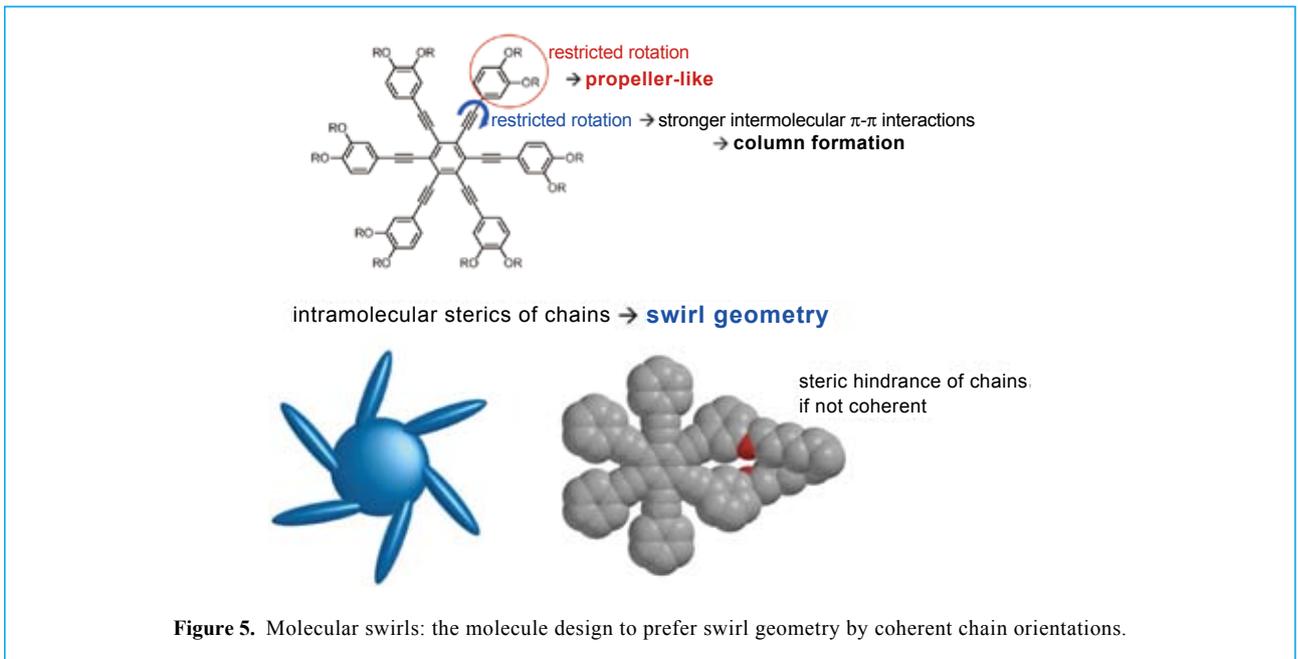


Figure 4. Lowering melting temperature and enhancing nematic liquid crystallinity by laterally attached chains to one sidearm of hexaynylbenzenes. The chemical structure, schematic representations showing the hindered rotation of the unique sidearm, and schematic representation showing the functions of the unique sidearm in the nematic phase.



Apart from rod-like and disc-like molecular shapes, molecular geometries in-between the two^{11,12} (Figure 8) have always intrigued scientists in the LC field. Moreover, due to the anisotropy along three coordinate axis of the molecular geometry, the molecular packing of such systems may lead to the formation of the biaxial nematic phase, the long been sought holy grail of LC research, if molecular packing along the three axis can be controlled individually. It should be noted that molecules in liquid crystalline states are with sufficient energy to tumble or rotate along some axis. The ordered molecular packing is in a dynamic equilibrium rather than being static in crystals. However, intermolecular packing is a result of multiple intermolecular interactions. Usually, only the major interactions comprehended and the

interplay of various interactions is difficult to predict and controlled. Generally, the more complicated the structure, the more complexed the intermolecular interactions. The key lies on the molecular design to bias intermolecular interactions along the three axis. Fine tuning the molecular structure to give nondegenerate molecular packing along the three axis was found to be the key for obtaining the biaxial nematic phase. Cross-like compounds were then synthesized. In single crystals, the molecular packing along the three axis are found to be nondegenerate (Figure 9). Similar molecular packing is also found in its nematic phase, identified by powder X-ray diffraction, resulting a biaxial nematic phase which has been confirmed by polarizing optical textures (Figure 10) and conoscopies.^{13,14}

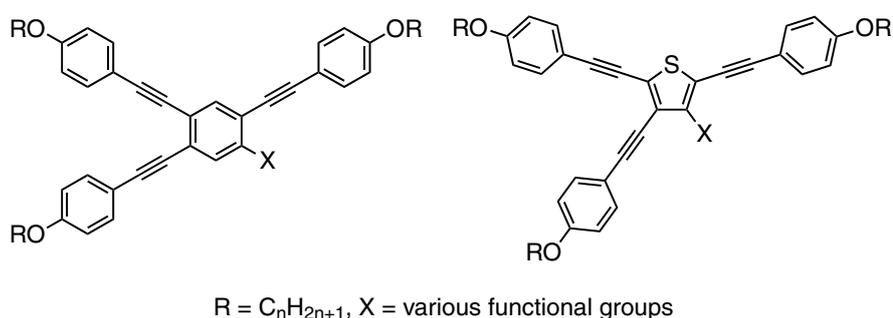


Figure 8. An unconventional molecular geometry showing liquid crystallinity: the rigid y-shaped molecules exhibiting nematic liquid crystalline phases at low melting temperatures.

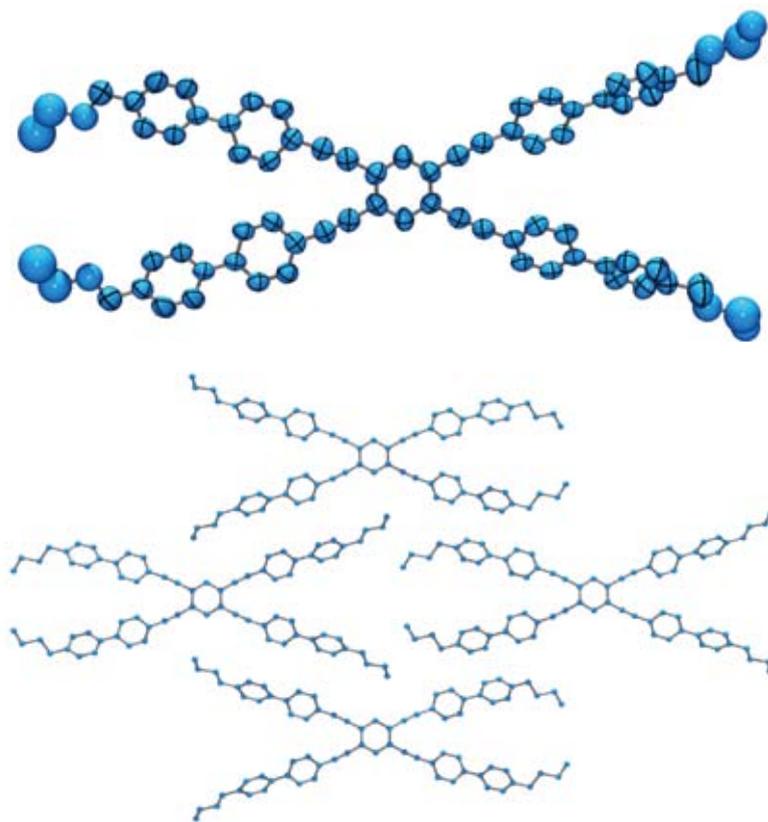


Figure 9. Cross-like molecule for optically biaxial nematic liquid crystallinity: the single crystal molecular structure (top) and the anisotropic molecular packing along the molecular plane (bottom).

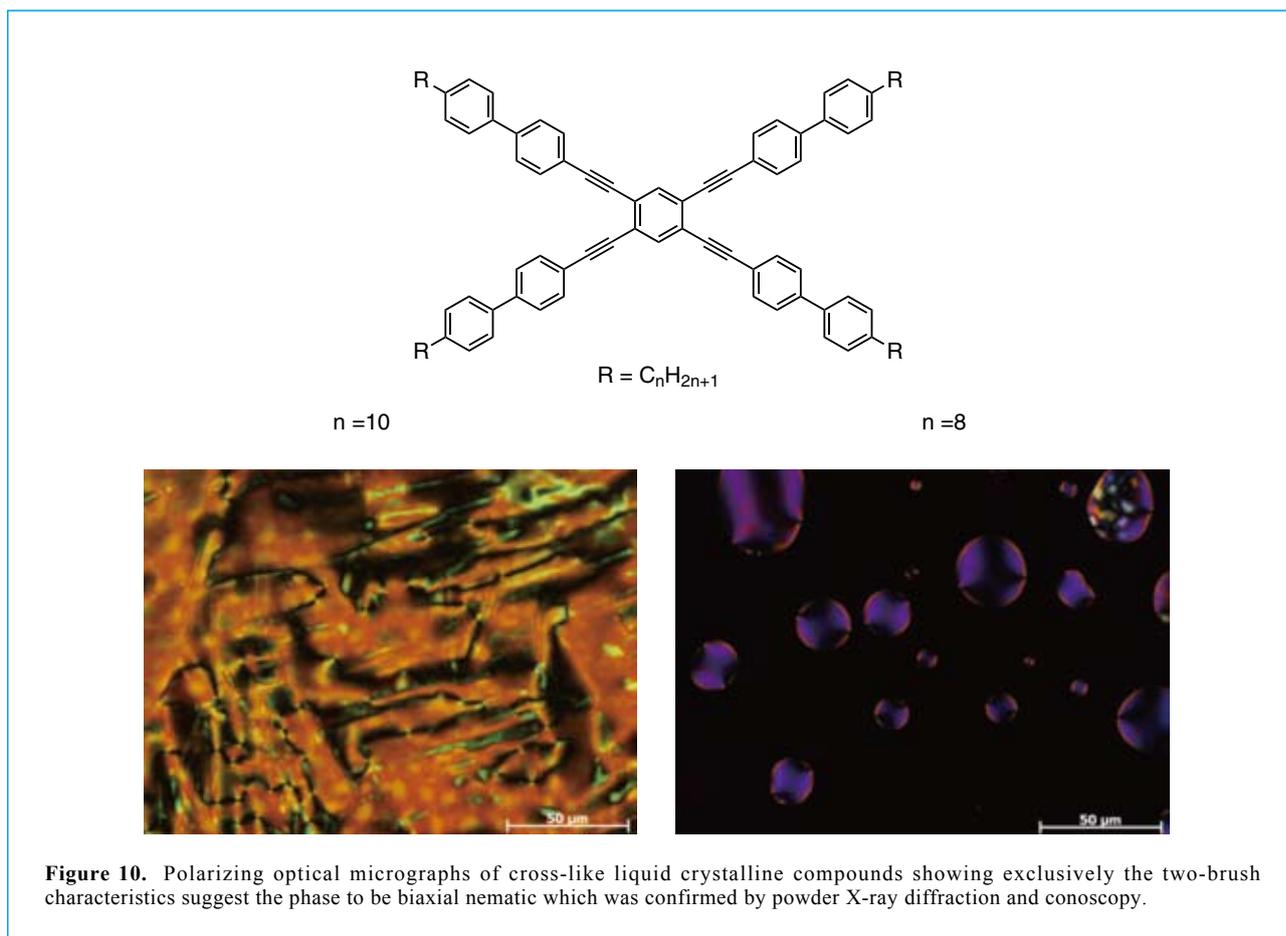


Figure 10. Polarizing optical micrographs of cross-like liquid crystalline compounds showing exclusively the two-brush characteristics suggest the phase to be biaxial nematic which was confirmed by powder X-ray diffraction and conoscopy.

Recently, my group has accidentally discovered an aggregation-induced-emission (AIE) molecular skeleton. On the way of making hexaphenylbenzene by trimerization of bisphenylalkyne, water was not excluded in the $Co_2(CO)_8$ catalyzed reaction (Figure 11). Months after taking nuclear magnetic resonance (NMR) spectra, though the molecular structure was then yet determined from the spectra, single crystals of the major product crystalized out of the solution in the NMR tube, the second accident. Moreover, the crystals are fluorescent as compared to the non-fluorescent solution. Single crystal structural determination uncovered the compound to be tetraphenyl-1,3-butadiene instead of hexaphenylbenzene.¹⁵ The beauty of this project is the switch of fluorescence of the same compound in solution and in solid.

In addition to the research work solely from my group, interesting cooperation works with other groups, domestic and international, have blossomed in recent years. Through cooperation, young students from both parties have gained a bigger scope on research. My cooperation with domestic researchers spans a wide research fields including organic chemistry, analytical chemistry, physical chemistry, supramolecular chemistry,^{16,17} polymer chemistry,¹⁸ electrical engineering,^{19,20} bioinorganic chemistry, and forestry. With long time cooperation with Prof. Long-Li Lai at National Chi-Nan University, LCs from a variety of dendrimers have been disclosed and the LC formation mechanisms of these dendrimers have been studied.²¹⁻²³ With the great assistance from Prof. Chun-hsien Chen of National Taiwan University, many high resolution STM micrographs of the dynamic molecular

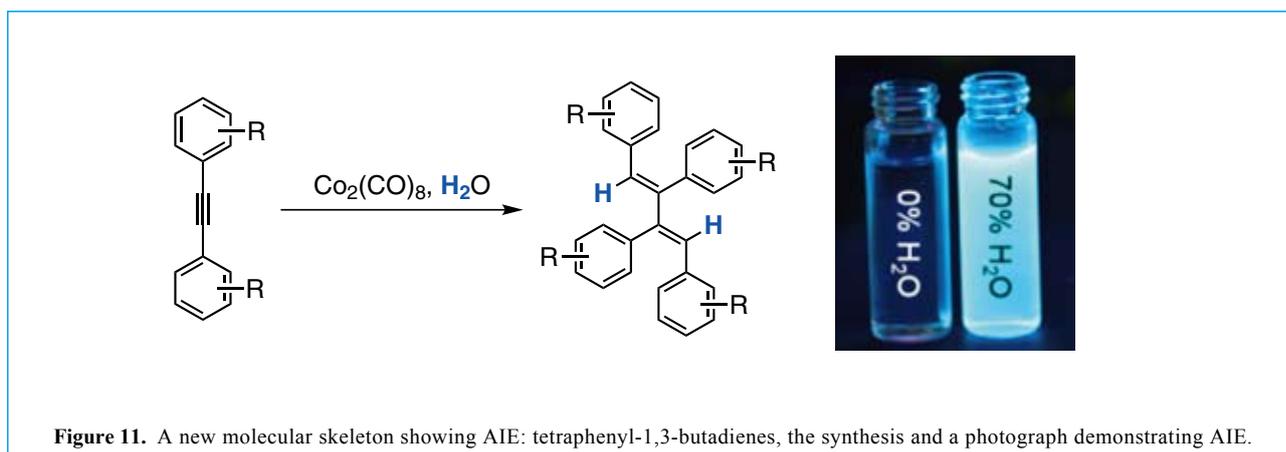


Figure 11. A new molecular skeleton showing AIE: tetraphenyl-1,3-butadienes, the synthesis and a photograph demonstrating AIE.

packing of our LC molecules at liquid/solid interface (Figure 6) have been obtained to correlate dynamic intermolecular correlations in liquid crystalline states.^{10,24,25} With Prof. Sheng-Hsien Chou, a molecular switch by an organogel was achieved.¹⁶ Phosphorescence behaviors of metallomesosens were investigated through cooperation with Prof. Yun Chi of National Tsing-Hua University and Prof. Pi-Tai Chou of National Taiwan University.²⁶ Organic nanomaterials with dynamic shape changes was investigated with Prof. Chien-Chung Cheng of National Chia-Yi University.²⁷ Recently, as the chair, I have called together a group of several scientists for an energy project. After being away from fullerene chemistry for more than fifteen years, the fullerene metal cluster chemistry comes back for this energy project.

Internationally, my group has long been involved in research cooperation with groups in Japan and France. Prof. Tohru Yamada of Keio University and I started research cooperation by student exchange first. Later, by incorporating expertise from both parties, chiral groups have been generated onto our LC systems. More importantly, the cooperation has nourished many young scientists from Japan and Taiwan. They are now involved in academic or industrial jobs in their countries. With Prof. Hsiao-Hua Yu, then at RIKEN, conjugated polymers of dioxothiophenes by direct C–H arylation has been

developed. With Prof. Michito Yoshizawa of Tokyo Institute of Technology, facile catch/release of fullerene compounds by a photo-responsive molecular tube has been disclosed.²⁸ The concept and the supra-molecular structure are again a beauty unable to resist. With Prof. Remi Chauvin of University of Toulouse, new projects are under way.

I deeply appreciate all collaborators for their kindness to let me enjoy their sciences and the beauty of their research. My group members, past and current, are acknowledged for their hard working style and their appreciation on research projects of the group. The young prospects start their young research careers from the beauty of molecules, then suffer from the originally looked easy but eventually found nontrivial chemical synthesis and property investigations, and finally comprehend the beauty of the sciences behind their projects. As some chemical providers offer various building blocks in recent years, molecular designs and chemical synthesis have been expedited, and young students can avoid some frustrations on synthesis and enjoy more of the beauty of science. I have enjoyed a lot in the journey by working with the most talented scientists by cooperation and the most promising students from my group and other interacted groups. The beauty of molecules and science behind these scientific projects lasts, and the journey towards the beauty of chemistry goes on.

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Introduction of the author:



Hsiu-Fu Hsu

Professor, Department of Chemistry, Tamkang University, Taiwan

[Education and employment] 1984-1988 B.S., National Sun Yet-Sen University; 1992-1997 Ph.D., University of Illinois at Urbana-Champaign (Supervisor: Prof. John R. Shapley); 1997-1999 postdoctoral associate, Massachusetts Institute of Technology (Supervisor: Prof. Timothy M. Swager); 1999-2003 Assistant Professor, 2003-2007 Associate Professor, 2007-present Professor, Tamkang University.

[Specialties] Organometallic Chemistry, Liquid Crystal Chemistry, Organic Synthesis, Material Chemistry