

# Editorial for the Special Issue on Functional Organic Materials

Organic chemists are playing an increasing role in the development of new materials with combinations of properties that will underpin future technologies. This path will be full of unforeseen discoveries and phenomena that will be best unraveled by detailed structure-property studies guided by an ever expanding tool box of analytical methods and computational methods. Just as organic chemists have long looked to nature for inspiration in developing synthetic methods, the quest for making new structures that test hypotheses will inspire new reaction and process development. We are sure that those of you who currently research organic materials as well as those who aspire to join the field, will find inspiration from the truly outstanding contributions in this Special Issue of *The Journal of Organic Chemistry* on “functional organic materials”

This issue is a showcase for some spectacular examples of organic chemistry in contemporary materials research. It includes 24 (need check again before the issue is finalized) publications submitted from many different countries, including Canada, China, Germany, Japan, Poland, Singapore, Switzerland, the United Kingdom, and the United States. Contributions to this issue include novel chromophores, new synthetic methodologies, organic diradicaloids and organic semiconductors for electronic devices. The synthesis, physical properties and applications of functional organic materials are covered, reflecting the exceptional breadth of this issue.

It is remarkable that almost every article contributed to this special issue is concerned with the investigation of new  $\pi$ -systems. Research on  $\pi$ -conjugated molecular organic materials is stimulated by diverse applications in Physics and Biology. Improved organic semiconductors are required for solid-state devices, such as transistors, light-emitting diodes, sensors and photovoltaic solar cells. Chromophore engineering is also needed to create better fluorescent dyes, molecular probes and biomedical imaging agents. Advancing these applications requires new insights into molecular structure-property relationships, which, together with advances in synthetic methodology, will lead to more effective molecular designs. However, this field of research does not exist just to serve Physics and Biology. It has its own unsolved puzzles and fundamental intellectual enigmas. For example, the electronic structures of  $\pi$ -systems with substantial open-shell polyradicaloid character are still poorly understood, despite major advances over the last ten years.<sup>1</sup> Synthesis is often a bottle neck, and the development of a new synthetic route can release a flood of creativity, as illustrated by Jasti, Bertozzi and co-workers' synthesis of cycloparaphenylenes in 2008,<sup>2</sup> which has led to the invention of many fascinating curved 3D  $\pi$ -systems.

We are particularly pleased that Itami and co-workers wrote a Perspective for this issue.<sup>3</sup> They describe a quest for structurally uniform graphene nanoribbons with unique properties, such as band-gap, conductivity, carrier mobility, thermal conductivity, spin polarization, and on-off switching behavior. They show how these properties depend on structural factors, such as edge geometry, width and length. They highlight new methods for bottom-up synthesis of graphene nanoribbons, and the theoretical and experimental investigations of physical properties and applications.

They also provided an outlook on the future of graphene nanoribbons.

Novel  $\pi$ -systems offer many opportunities for creative molecular design; for example, Miyake and co-workers developed a diversity-oriented approach for the synthesis of tetrathia[8]circulenes and studied the influence of peripheral substituents on the structures and properties in both solution and solid states.<sup>4</sup> The synthesis of azulene-based BN-heteroaromatics is reported by Gao and co-workers. These compounds can be used as sensors for visual detection of fluoride ions and they undergo deboronization upon addition of trifluoroacetic acid.<sup>5</sup> Mayor and co-workers synthesized a bowl-shaped, threefold interlinked porphyrin dimer and its analogue with acetyl protected terminal thiol anchor groups for single-molecule transport experiments in mechanically controlled break junctions.<sup>6</sup> Several papers are dedicated to the preparation of new nanorings, nanohoops, nanotubes and macrocycles. In particular, Sancho-Garcia, Jasti and co-workers developed a general approach to solid-state structures mimicking carbon nanotubes, via the self-assembly of fluorinated nanohoops, which can be synthesized in a scalable, size-selective fashion.<sup>7</sup> Esser and co-workers report [2]DBP[12]CPP nanorings with [12]cycloparaphenylenes incorporating two anti-aromatic dibenzo[*a,e*]pentalene units.<sup>8</sup> Isobe and co-workers synthesized a series of cyclo-*meta*-phenylene congeners with a variation of interphenylene bridges and found that the fluorescence quantum yield increases with the number of the vinylene-bridged phenanthrenylene panels due to a reduction in the energy of the singlet excited state relative to the minimum energy conical intersection.<sup>9</sup> Other novel  $\pi$ -conjugated structures reported in this issue include an acid-responsive *N*-doped polycyclic aromatic hydrocarbon, from Gryko and co-workers.<sup>10</sup> 1,1'-Biaceanthrylene and 2,2'-biaceanthrylene with linking between five-membered rings are presented by Plunkett and co-workers.<sup>11</sup>

Open shell singlet diradicaloids constitute a very active field of research. Ravat, Juriček and co-workers report the synthesis of a tetraphenyl derivative of a spin 1/2 graphene fragment benzo[*cd*]triangulene.<sup>12</sup> An overcrowded aromatic alkene, reported by Kubo and co-workers, shows stimuli-responsive interconversion between a closed-shell folded form and an open-shell twisted form.<sup>13</sup> Two antiaromatic constitutional isomers of pyrene-fused dicyclopenta[*a,f*]naphthalenes exhibiting moderate open-shell biradical characters and narrow energy gaps were synthesized by Liu, Feng and their co-worker.<sup>14</sup>

Several research groups report new organic semiconductors for electronic devices. For example, Miao and co-workers present the trifluoromethylation of anthraquinones for novel n-type organic semiconductors in field effect transistors (OFETs).<sup>15</sup> A series of soluble 2-substituted dinaphtho[2,3-*b*:2',3'-*f*]thieno[3,2-*b*]thiophene derivatives were synthesized by Takimiya and co-workers for solution-processed OFETs.<sup>16</sup> Perepichka and co-workers prepared a series of benzodithiophene- and indacenodithiophene-based acceptor-donor-acceptor (A-D-A) oligomers with different end groups and studied their optoelectronic properties and photovoltaic behavior through a permutation of terminal units.<sup>17</sup> Susuki, Nguyen, Yamada and co-workers have developed

a series of tetrabenzoporphyrin derivatives with multiple strongly electron-withdrawing groups, as non-fullerene acceptors in organic solar cells.<sup>18</sup> A novel building block for aggregation-induced emission luminogens, tetraphenylbenzasilole, was developed by Wang, Chen, Tang and co-workers. It exhibits efficient deep-blue emission in the aggregated state, and showed excellent result for spin-coated blue non-doped OLEDs.<sup>19</sup> Zhang, Li and co-workers report the serendipitous synthesis, properties, and non-volatile memory device applications of imidazole-fused azaacenes.<sup>20</sup>

New methodologies for synthesis of  $\pi$ -conjugated structures are also presented. Wüthner and co-workers describe the palladium-catalyzed [3 + 2] annulation of naphthalimide acceptors and thiophene donors. They used this method to prepare a series of fused D-A and A-D-A conjugated dyes, which show absorption up to the NIR region and four-fold reduction processes.<sup>21</sup> A mechanistic analysis for electrophilic aromatic coupling of hexapyrrolylbenzenes is reported by Stepień and co-workers.<sup>22</sup> Freudenberg, Bunz and co-workers report the synthesis of a series of dibenzosuberonone-fused *N*-heteroacenes, by the condensation of dibenzosuberonetriketone with substituted diamino- and tetramino-arenes.<sup>23</sup> Several other aspects of chromophore engineering are also reported in this issue. Yamaguchi, Hudson and co-workers report a series of D-A materials exhibiting thermally activated delayed fluorescence using a planarized *N*-phenylbenzimidazole acceptor.<sup>24</sup> An article by Johnson, Haley and co-workers describes the synthesis of a series of P-phenyl modified phosphorus- and nitrogen-containing phosphaquinolone heterocycles; this work reveals that slight modifications to the phosphorus center result in dramatic amplification of the fluorescence quantum yields.<sup>25</sup> A novel perylene diimide dye encapsulated by four alkylene straps is reported by Bronstein and co-workers; their experimental and computational results show that molecular encapsulation affects the photophysical properties by suppressing intermolecular  $\pi$ - $\pi$  stacking.<sup>26</sup>

We hope you enjoy reading the articles in this special issue and are similarly captivated by the beauty of the structures presented and the new physics that can only be revealed by the creation and study of new forms of matter.

## Biographies



Chunyan Chi was born in Harbin, China, in 1975. She received her bachelor degree from Qiqihar University in 1998 and master degree from Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, in 2001. She then conducted her PhD research in the Max-Planck Institute for Polymer Research with Professor Gerhard Wegner and postdoctoral work with Professor Guillermo C. Bazan in the University of California at Santa Barbara. She is now an associate professor in the Department of Chemistry, National University of Singapore. Her research interests are synthesis of extended  $\pi$ -electron systems with novel structures, aromaticity, organic diradicaloids, dyes and functional materials for organic electronics and sensors.



Harry L. Anderson completed his PhD at the University of Cambridge UK with Professor Jeremy K. M. Sanders, followed by postdoctoral work at ETH Zurich, Switzerland, with Professor François Diederich. He has led an independent research group at the University of Oxford since 1995. His interests include template-directed synthesis, multivalent cooperativity, aromaticity, photochemistry, molecular electronics and charge transport, insulated molecular wires, dyes, rotaxanes, polyyynes, cyclocarbons and  $\pi$ -conjugated porphyrin oligomers.



Timothy M. Swager is a native of Montana and completed his undergraduate studies at Montana State University in 1983. He got his start in organic materials by synthesizing and studying conducting polymers in PhD studies with Robert H. Grubbs at Caltech and in 1988 went on to do research at MIT with Mark S. Wrighton on organic transistors and photophysics. His independent career started at the University of Pennsylvania in 1990 and he then moved to MIT in 1996. His research interests are in the advancing of conducting/semiconducting polymers, new methods for materials synthesis, liquid crystals, chem/bio-sensors, materials for energy storage and conversion, separation membranes, colloids, and high strength materials.

## Reference:

- (1) Gopalakrishna, T. Y.; Zeng, W.; Lu, X.; Wu, J. From open-shell singlet diradicaloids to polyradicaloids. *Chem. Commun.* **2018**, 54, 2186–2199.
- (2) Jasti, R.; Bhattacharjee, J.; Neaton, J. B.; Bertozzi, C. R. Synthesis, characterization, and theory of [9]-, [12]-, and [18]cycloparaphenylene: Carbon nanohoop structures. *J. Am. Chem. Soc.* **2008**, 130, 17646–17647.
- (3) Yano, Y.; Mitoma, N.; Ito, H.; Itami, K. A Quest for Structurally Uniform Graphene Nanoribbons: Synthesis, Properties, and Applications. *J. Org. Chem.* **2019**, DOI: xxx (manuscript ID: jo-2019-028146).
- (4) Kato, S.; Akahori, S.; Serizawa, Y.; Lin, X.; Yamauchi, M.; Yagai, S.; Sakurai, T.; Matsuda, W.; Seki, S.; Shinokubo, H.; Miyake, Y. Systematic Synthesis of Tetrathia[8]circulenes: The Influence of Peripheral Substituents on the Structures and Properties in Solution and Solid States. *J. Org. Chem.* **2019**, DOI: 10.1021/acs.joc.9b01655.

- (5) Xin, H.; Li, J.; Yang, X.; Gao, X. Azulene-based BN-Heteroaromatics. *J. Org. Chem.* **2019**, DOI: 10.1021/acs.joc.9b01724.
- (6) Zwick, P.; Weiland, K.; Malinčik, J.; Stefani, D.; Häussinger, D.; van der Zant, H.; Dulić, D.; Mayor, M. Mechanical Fixation by Porphyrin Fusion: Synthesis & Transport Studies of A Bicyclic Dimer. *J. Org. Chem.* **2019**, DOI: xxx (manuscript ID: jo-2019-02327c).
- (7) Van Raden, J. M.; Leonhardt, E. J.; Zakharov, L. N.; Pérez-Guardiola, A.; Pérez-Jiménez, A. J.; Marshall, C. R. Brozek, C. K.; Sancho-García, J. C.; Jasti R. Precision Nanotube Mimics via Self-Assembly of Programmed Carbon Nanohoops. *J. Org. Chem.* **2019**, DOI: 10.1021/acs.joc.9b02340.
- (8) Wassy, D.; Pfeifer, M.; Esser, B. Synthesis and Properties of Conjugated Nanorings Incorporating Dibenzo[a,e]pentalenes:[2]DBP[12]CPPs. *J. Org. Chem.* **2019**, DOI: 10.1021/acs.joc.9b01195.
- (9) Ikemoto, K.; Tokuhira, T.; Uetani, A.; Harabuchi, Y.; Sato, S.; Maeda, S.; Isobe, H. Fluorescence Enhancement of Aromatic Macrocycles by Lowering Excited Singlet State Energies. *J. Org. Chem.* **2019**, DOI: xxx (manuscript ID: jo-2019-02379s).
- (10) Sadowski, B.; Stewart, D. J.; Phillips, A. T.; Grusenmeyer, T. A.; Haley, J. E.; Cooper, T. M.; Gryko, D. T. From Dipyrrolo-naphthyridinediones to Quinazolinoindolizinoindolizino-quinazolines. *J. Org. Chem.* **2019**, DOI: 10.1021/acs.joc.9b00839.
- (11) Du, Y.; Plunkett, K. 1,1'-Biaceanthrylene and 2,2'-Biaceanthrylene: Models for Linking Larger Polycyclic Aromatic Hydrocarbons via Five-Membered Rings. *J. Org. Chem.* **2019**, DOI: 10.1021/acs.joc.9b02118.
- (12) Ravat, P.; Blacque, O.; Juriček, M. Benzo[cd]triangulene: A Spin 1/2 Graphene Fragment. *J. Org. Chem.* **2019**, DOI: 10.1021/acs.joc.9b02163.
- (13) Nishiuchi, T.; Ito, R.; Stratmann, E.; Kubo, T. Interconvertible Conformational Isomerization of an Overcrowded Tristricyclic Aromatic Ene (TAE). *J. Org. Chem.* **2019**, DOI: xxx (manuscript ID: jo-2019-02432g).
- (14) Melidonie, J.; Dmitrieva, E.; Zhang, K.; Fu, Y.; Popov, A.; Pisula, W.; Berger, R.; Liu, J.; Feng, X. Dipyrene-Fused Dicyclopenta[a,f]naphthalenes. *J. Org. Chem.* **2019**, DOI: xxx (manuscript ID: jo-2019-02626q).
- (15) Zhao, M.; Yang, X.; Tsui, G. C.; Miao, Q. Trifluoromethylation of Anthraquinones for Novel N-Type Organic Semiconductors in Field Effect Transistors. *J. Org. Chem.* **2019**, DOI: 10.1021/acs.joc.9b01263.
- (16) Kawabata, K.; Usui, S.; Takimiya, K. Synthesis of soluble dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene (DNNT) derivatives: one-step functionalization of 2-bromo-DNNT. *J. Org. Chem.* **2019**, DOI: xxx (manuscript ID: jo-2019-02585f).
- (17) Che, Y.; Zhang, Y.; Yang, Y.; Liu, C.-H.; Izquierdo, R.; Xiao, S. S.; Perepichka, D. F. Understanding the Photovoltaic Behavior of A-D-A Molecular Semiconductors through a Permutation of End Groups. *J. Org. Chem.* **2019**, DOI: 10.1021/acs.joc.9b01654.
- (18) Jeong, E.; Takahashi, K.; Rajagopal, S.; Koganezawa, T.; Hayashi, H.; Aratani, N.; Suzuki, M.; Nguyen, T.-Q.; Yamada, H. Orbital-Energy Modulation of Tetrabenzoporphyrin for Improved Open-Circuit Voltage and Application as Non-Fullerene Acceptor in Organic Solar Cells. *J. Org. Chem.* **2019**, DOI: xxx (manuscript ID: jo-2019-02386e).
- (19) Feng, W.; Su, Q.; Ma, Y.; Dzolic, Z.; Wang, Z.; Chen, S.; Tang, B. Z. Tetraphenylbenzasilole: A Novel AIE Building Block for Deep-blue Emitters with High Performance in Non-doped Spin-coating OLEDs. *J. Org. Chem.* **2019**, DOI: xxx (manuscript ID: jo-2019-02383u).
- (20) Zhao, K.; Yu, F.; Huang, Y.; Said, A. A.; Li, Y.; Zhang, Q. Unexpected Synthesis, Properties, and Non-Volatile Memory Device Application of Imidazole-fused Azaacenes. *J. Org. Chem.* **2019**, DOI: 10.1021/acs.joc.9b02156.
- (21) Shoyama, K.; Mahl, M.; Niyas, M.; Kachler, V.; Ebert, M.; Keck, C.; Würthner, F. Palladium-Catalyzed [3 + 2] Annulation of Naphthalimide Acceptors and Thiophene Donors. *J. Org. Chem.* **2019**, DOI: xxx (manuscript ID: jo-2019-02372z).
- (22) Zhylitskaya, H.; Navakouski, M.; Chmielewski, P.; Żyła-Karwowska, M.; Stępień, M. Electrophilic Aromatic Coupling of Hexapyrrolylbenzenes. A Mechanistic Analysis. *J. Org. Chem.* **2019**, DOI: xxx (manuscript ID: jo-2019-02556u).
- (23) Brosius, V.; Müller, M.; Borstelmann, J.; Rominger, F.; Freudenberg, J.; Bunz, U. Azaacenodibenzosuberones. *J. Org. Chem.* **2019**, DOI: xxx (manuscript ID: jo-2019-02756k).
- (24) Sauve, E.; Paeng, J.; Yamaguchi, S.; Hudson, Z. Donor-acceptor Materials Exhibiting Thermally Activated Delayed Fluorescence Using a Planarized N-phenylbenzimidazole Acceptor. *J. Org. Chem.* **2019**, DOI: xxx (manuscript ID: jo-2019-02283z).
- (25) Bard, J.; Bates, H.; Deng, C.-L.; Zakharov, L.; Johnson, D.; Haley, M. Amplification of the Quantum Yields of 2-λ<sup>5</sup>-Phosphaquinolin-2-ones Through Phosphorus Center Modification. *J. Org. Chem.* **2019**, DOI: 10.1021/acs.joc.9b02132.
- (26) Royackers, J.; Minotto, A.; Zeng, W.; Patel, A.; Bond, A.; Bučar, D.-K.; Cacialli, F.; Bronstein, H. Doubly Encapsulated Perylene Diimides: Effect of Molecular Encapsulation on Photo-physical Properties. *J. Org. Chem.* **2019**, DOI: xxx (manuscript ID: jo-2019-02597y).