

JSPS Core-to-Core Meeting



Organic Electronics of Highly-Correlated Molecular Systems



McGill
UNIVERSITY



University
of Windsor

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of **GUELPH**

May 25th – 26th, 2017
McGill U., Montreal, Canada

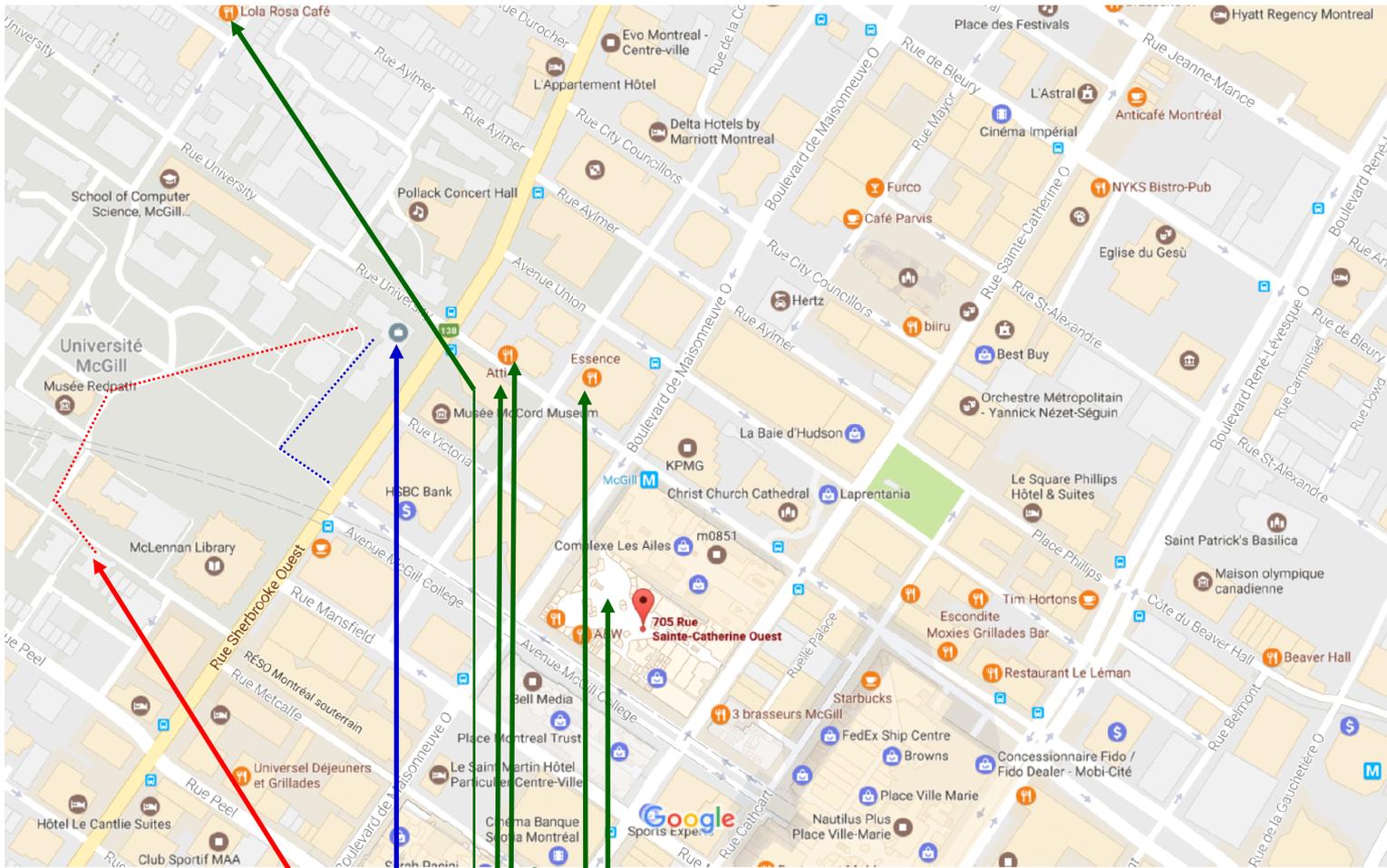
JSPS Core-to-Core Program McGill 2017

Thursday, May 25 th 2017				
Time	Speaker	Title	Institution	Duration
0930	Registration and Coffee			20
0950	Introductory Remarks			10
1000	Takayoshi Nakamura	<i>Dynamic Supramolecular Structures in the Crystalline State</i>	Hokkaido U	30
1030	Eli Zysman-Colman	<i>Photoactive Supramolecular Assemblies</i>	St-Andrews U	30
1100	Shohei Yamamoto	<i>Modulation of the Electronic and Electrochemical Properties of Metal Organic-Frameworks with Guest Introduction</i>	Nagoya U	15
1115	Chaoying Fu	<i>H-Bonding Control of Supramolecular Ordering of Diketopyrrolopyrroles</i>	McGill U	15
1130	Kentaro Tanaka	<i>Liquid Crystalline Macrocycles toward Nano Spaces in Flowable Media</i>	Nagoya U	30
1200	Tomislav Friscic	<i>Solid-state Chemistry as an Interface between Green Chemistry and Conductive Materials</i>	McGill U	30
1230	Lunch			90
1400	Kunio Awaga	<i>Chemistry and Physics of Organic Radical Crystals with Strongly-Isotropic Property</i>	Nagoya U	30
1430	John Wallis	<i>Synthesis and Properties of Functionalised BEDT-TTF and EDT-TTF Donors Including Chiral Systems</i>	Nottingham Trent U	30
1500	Yoko Tatewaki	<i>Molecular Nanocoils of Conducting Molecules with Chiral Units</i>	TUAT	20
1520	Kathryn Preuss	<i>Thiazyl Radicals as Bridging Ligands</i>	U Guelph	20
1540	Coffee Break			30
1610	Yoshiaki Shuku	<i>Crystal structure and magnetic property of triptycene triquinone radical trianion salt</i>	Nagoya	15
1625	Jaclyn Brusso	<i>A Building Block Approach to π-Conjugated Frameworks</i>	U Ottawa	30
1655	Delia Haynes	<i>The potential of dithiadiazolyls in molecular materials</i>	Stellenbosh U	20
1715	Daiki Tonouchi	<i>Current-induced mutual structure-conductivity transformation along orthogonal crystal axes in a TTF-based dimeric donor salt</i>	Nagoya U	15
1730	Jeremy Rawson	<i>Magnetism, fluorescence, photo-conductivity and charge transfer salts of the dithiadiazolyl radical, phenDTDA (phen = 9-phenanthrenyl)</i>	Windsor U	20

Conference Dinner at 18:00

JSPS Core-to-Core Program McGill 2017

Friday, May 26 th 2017				
Time	Speaker	Title	Institution	Duration
915	Takaaki Makino	<i>Synthesis of cyclic polymer via ring expansion NMP and structure characterization</i>	Nagoya U	15
930	Jean-Francois Morin	<i>Bottom-up Synthesis of Structurally Precise Graphene Nanoribbons for Organic Electronics</i>	Laval U	30
1000	Tsubasa Takei	<i>Self Assemble Structures Composed of Nonplanar π-conjugated Derivatives</i>	TUAT	15
1015	Coffee Break			30
1045	Kazuyuki Sakamoto	<i>Electronic structures of organic single crystals</i>	Chiba U	30
1115	Dima Perepichka	<i>p-Conjugated 2D Covalent Organic Frameworks</i>	McGill U	20
1135	Jun Nitta	<i>Photoelectron study of DNTT single crystal</i>	Chiba U	15
1150	Yuan Fang	<i>Polar Substituent Directed Epitaxial Growth of Two-Dimensional Porous Molecular Networks at Liquid/Solid Interfaces</i>	McGill U	15
1205	Rie Suizu	<i>Structure analysis of BDTDA/Cu(111) using a LEED I-V method</i>	Chiba U	15
1220	Lunch			85
1345	Yang Wu	<i>Covalent Organic Framework-graft-Polysulfide: A Novel Cathode for High-Energy Rechargeable Lithium Batteries</i>	Nagoya U	15
1430	Neil Robertson	<i>New Materials for Hybrid Photovoltaics</i>	U Edinburgh	30
1500	Hirofumi Yoshikawa	<i>Battery performances of chalcogen-containing organic compounds</i>	Kwansei Gakuin U	30
1530	Michio M. Matsushita	<i>Investigations on Functional Molecular Materials for "Epigenetic" Molecular Integrated Circuit</i>	Nagoya U	30
1600	Seiya Yokokura	<i>Transient Photocurrent in Photovoltaic Device Utilizing Ferroelectric layer</i>	Nagoya U	15
1615	Concluding Remarks			10



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**Banquet in Faculty Club
(3450 McTavish)**

**Lectures in OM10, basement
(801 Sherbrooke West)**

Suggested lunch options:

- 1) Atti (Korean restaurant)
- 2) Small food court (Thai Express & Culture)
- 3) Essence (international cuisine)
- 4) Large food court, 1st level in Eaton Centre (via McGill Subway)
- 5) Lola Rosa vegetarian café

Chemistry and Physics of Organic Radical Crystals with Strongly-Isotropic Property

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Graph theory has interpreted the cause of beauty of the diamond lattice, in terms of ‘strong isotropic property’, which is owned by only the three lattices, *i.e.* diamond, honeycomb (graphene), and K_4 lattices. It was also predicted that the K_4 carbon could be a new allotrope of carbon, in addition to diamond, graphite, graphene, fullerenes and nanotubes. While diamond has a 3D structure of the cubic $Fd\bar{3}m$ space group, consisting of tetravalent (sp^3) carbons, the K_4 carbon has a 3D chiral structure of the cubic $I4_132$ space group, consisting of trivalent (sp^2) carbons (Fig. 1(a)). In this K_4 structure, each carbon atom exists at the center of a triangle formed by the three neighboring carbon atoms, and the neighboring triangles, which share one C-C bond, are twisted with a torsion angle α ($=\pm 70.5^\circ$) of $\cos\alpha=1/3$. Since attempts to synthesize the K_4 carbon have not succeeded, it was very challenging to make this structure with delocalized π electrons. In the present work, we carried out electrochemical crystallization of the radical anion salts of a chiral molecule, (-)-NDI(naphthalene diimide)- Δ (Fig. 1(b)), using various electrolytes. X-ray crystal analysis of the obtained crystals of $(TBA)_{1.5}[(-)\text{-NDI-}\Delta]$ revealed the K_4 structure, which was formed by the unique intermolecular π overlap directed toward three directions from the triangular-shape NDI- Δ radical anions (Fig. 1(c)). This lattice was identical to the hyper-kagome lattice (Fig. 1(d)) of $S = 1/2$ Mott dimers with a 3D spin frustration. In fact, the low-temperature magnetic and heat-capacity measurements clearly revealed the formation of a spin liquid state.

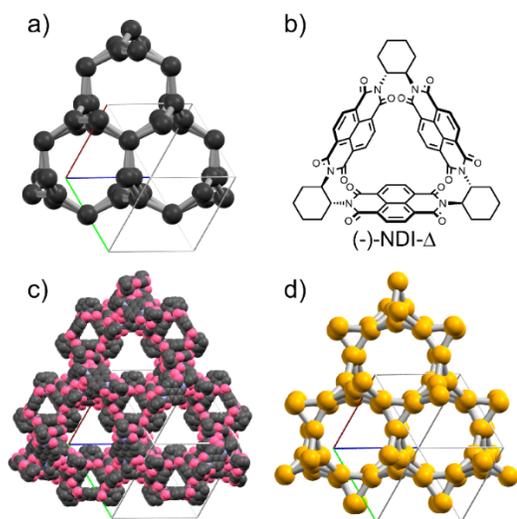


Fig. 1 Comparison of the structures of the K_4 carbon (a), the molecular structure of (-)-NDI- Δ (b), the K_4 structure of (-)-NDI- Δ (c), and the hyper-kagome lattice (d).

A Building Block Approach to π -Conjugated Frameworks

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The last 15 years has witnessed a revolution in the development of technologies associated with information processing and communications. Essential to the continuation of these technological advancements is the need for new science, and within this context one of the major fundamental challenges for the future is the development of smaller, lighter, cheaper and more efficient electronic, optical and magnetic materials. Since the use of molecular materials in organic electronics is dependent on the extent of molecular order (in addition to other factors), rational engineering of self-organizing molecular systems with multifunctional characteristics is one of the most attractive and active fields of current research. In pursuit of this goal, we have focused our attention on the design and development of heteroaromatic systems with extensive π -conjugated frameworks to investigate their photophysical properties and augment their solid-state structures such that implementation into optoelectronic devices leads to superior device performance. This presentation will focus on the synthesis, characterization and device studies of systems currently being pursued in our lab.

Polar Substituent Directed Epitaxial Growth of Two-Dimensional Porous Molecular Networks at Liquid/Solid Interfaces

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One of the important challenges in the field of two-dimensional (2D) self-assembly of organic molecules on surfaces is controlled epitaxial growth of porous molecular networks toward the longitudinal direction, forming porous multilayers on surfaces. To facilitate epitaxial growth with precise control over the interlayer geometry, point-to-point longitudinal interactions is crucial. For this purpose, we chose alkoxy-substituted dehydrobenzo[12]annulene (DBA) derivatives because of the facile formation of porous networks via van der Waals linkages between the alkyl chains and their synthetic versatility to chemical modification of the alky chains. Utilizing the advantages, we reported the formation, induction, and inversion of supramolecular chirality of the molecular networks.^{1,2} On the basis of these results, we report here the formation of bilayer films in which the interlayer geometry was controlled by interaction between the polar substituents attached to the alkyl chain.

To this end, we designed chiral DBA, cDBA-OC6(*R*)-OH and its *S* enantiomer bearing stereogenic hydroxy groups. At the interface of 1,2,4-trichlorobenzene/graphite, STM observations of cDBA-OC6(*R*)-OH and its enantiomer indicate the formation of homochiral (counterclockwise (CCW) and clockwise (CW) hexagonal forms, respectively) porous monolayer networks at low concentration (5.0×10^{-6} M). At higher concentration ($>1.0 \times 10^{-5}$ M), on the other hand, the chiral DBA forms bilayers which can be distinguished by (1) height profile (Figure 1a&b) (2) bias-dependent appearance in the STM images (Figure 1c&d). It should be emphasized that the CCW form consisting of the *R* enantiomer overlays on the domain of the same supramolecular chirality (CCW) containing the same enantiomer, indicating the bilayer formation is enantioselective.

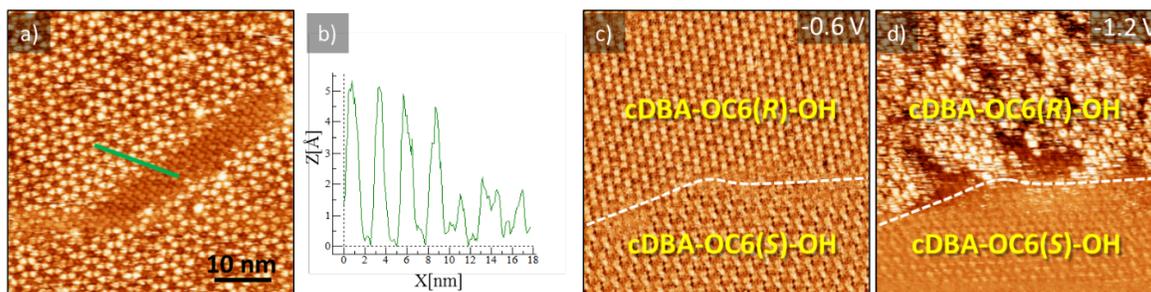
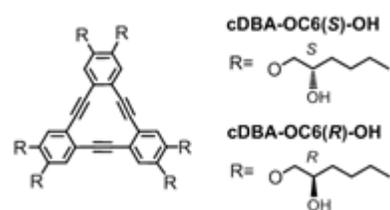


Figure 1. (a&b) STM image and height profile for cDBA-OC6(*R*)-OH at bias voltage of -0.9 V. (c&d) STM images of a mixture of *R* and *S* enantiomers at -0.6 V showing (a) monolayer domains of each enantiomer and (b) at -1.2 V showing enantioselective bilayer formation.

References

- 1 Tahara, K.; Yamaga, H.; Ghijsens, E.; Inukai, K.; Adisoejoso, J.; Blunt, M. O.; De Feyter, S.; Tobe, Y., "Control and Induction of Surface-Confined Homochiral Porous Molecular Networks", *Nat. Chem.*, Vol. 3, No. 9, (2011), pp 714-719.
- 2 Fang, Y.; Ghijsens, E.; Ivasenko, O.; Cao, H.; Noguchi, A.; Mali, K. S.; Tahara, K.; Tobe, Y.; De Feyter, S., "Dynamic Control over Supramolecular Handedness by Selecting Chiral Induction Pathways at the Solution-Solid Interface", *Nat. Chem.*, Vol. 8, No. 7, (2016), pp 711-717.

Solid-state Chemistry as an Interface between Green Chemistry and Conductive Materials

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Metal-organic frameworks (MOFs) are a class of highly versatile advanced materials, in which open metal-organic architectures can be combined with a wide range of physicochemical properties, including catalysis, tunable porosity, luminescence, proton conduction, *etc.*¹⁻³ However, the development of MOFs into commercially viable functional materials also requires the development of materials- and energy-efficient methods for their manufacture. This presentation will outline our group's efforts in developing scalable, clean and sustainable methodologies for MOF synthesis, based on innovation in solid-state chemistry.⁴ In particular, we will describe the emergence of mechanochemical techniques for MOF synthesis, and the recent advances in understanding the underlying reaction mechanisms.⁵ We will conclude with an overview of accelerated aging⁶ – a recently introduced simple, mild technique for MOF assembly from the simplest starting materials, and describe how it can facilitate the synthesis of a class of potential proton-conducting MOF materials that could even be naturally occurring.⁷

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3. Sadakiyo, M.; Yamada, T.; Kitagawa, H. *J. Am. Chem. Soc.* **2009**, *131*, 9906.
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5. Akimbekov, Z.; Katsenis, A. D.; Nagabhushana, G. P.; Ayoub, G.; Arhangelskis, M.; Morris, A. J.; Friščić, T.; Navrotsky, A. *J. Am. Chem. Soc.* **2017**, DOI:10.1021/jacs.7b03144
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7. Huskić, I.; Pekov, I.; Krivovichev, S.; Friščić, T. *Science Adv.* **2016**, *2*, e1600621.

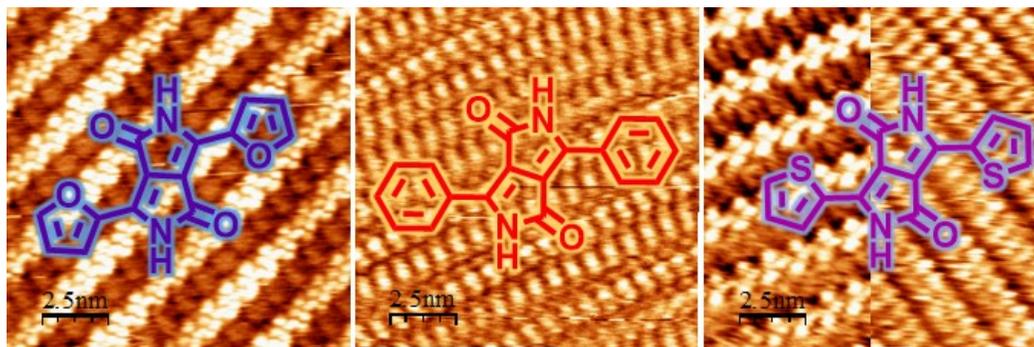
H-Bonding Control of Supramolecular Ordering of Diketopyrrolopyrroles

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Diketopyrrolopyrrole (DPP) is a widely used building block for high-mobility ambipolar semiconductors. Hydrogen bonding of N-unsubstituted DPPs has recently been identified as a tool for controlling their solid state structure and properties of semiconducting films, yet little is known about supramolecular packing of H-bonded DPP derivatives. Our work reports a comparative study of three archetypical DPP derivatives, difurylDPP (DFDPP), diphenylDPP (DPDPP), and dithienylDPP (DTDPP), at the interface and in bulk crystals.¹ Using scanning tunneling microscopy (STM) combined with X-ray crystallographic analysis, we demonstrate how the interactions of the (hetero)aromatic substituents interplay with H-bonding, causing dramatic differences in the supramolecular ordering of these structurally similar building blocks. Under all explored conditions, DPDPP exclusively forms H-bonded homoassemblies; DFDPP strongly prefers to co-assemble with alkanolic acids, through a rare lactam···carboxylic acid H-bonded complex, and DTDPP, depending on conditions, either co-assembles with alkanolic acids or self-assembles in one of two H-bonded polymorphs. One of these polymorphs suggests an out-of-plane twist of thiophene rings that form π -stacks running along the surface plane; this is unexpected considering the large energetic penalty of DTDPP deplanarization. The results are explained in terms of inter- versus intramolecular interactions, which are quantified with density functional theory calculations. This work shows that aryl substituents can strongly influence H-bonding assembly of DPP derivatives that is likely to affect their charge-transport properties.



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The potential of dithiadiazolyls in molecular materials

Delia A. Haynes^{a*}

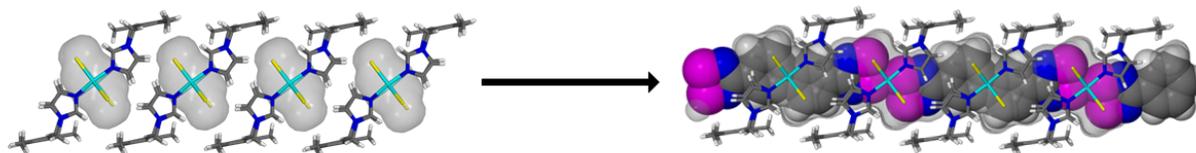
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Dithiadiazolyl radicals (DTDA) are a class of stable radicals that have been investigated for their potential as building blocks for magnetic and conducting materials.¹ DTDA tend to dimerise in the solid state, resulting in spin pairing and diamagnetic materials. We have explored the incorporation of DTDA into multi-component crystals, including co-crystals and porous materials, in order to overcome dimerisation.²

As part of this study, we have investigated the coordination of DTDA to metalloporphyrins. An interesting coordination polymer of 4-(4'-pyridyl)-1,2,3,5-dithiadiazolyl and cobalt(II) tetraphenylporphyrin has been characterised. This material has DTDA ligands in a new coordination mode. Initial investigations using EPR and UV-visible spectroscopy indicate that a number of other metalloporphyrin-DTDA complexes form in solution.

The inclusion of DTDA in metallocyclic hosts has also been investigated, and Ph-DTDA has been included in a copper-containing metallocycle. A computational study has been undertaken in order to attempt to predict whether DTDA will dimerise in the solid state.



1. see Haynes, D. A. *CrystEngComm*. **2011**, *13*, 4793-4805. and references therein.
2. Alan, C.; Haynes, D. A.; Pask, C. M. and Rawson, J. M. *CrystEngComm*. **2009**, *11*, 2048-2050; Robinson, S. W; Haynes, D. A. and Rawson, J. M. *CrystEngComm*. **2013**, *15*, 10205-10211.

Synthesis of cyclic polymer via ring expansion NMP and structure characterization

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Cyclic polymer which has cyclic topology with no edge in its structure shows unique properties in comparison with the corresponding linear polymers. For the precise measurement of the property of cyclic polymer, highly selective and efficient synthetic route is required. However, a facile and controlled preparation method for cyclic polymer has not been established. Recently, ring expansion NMP has been reported[1],[2], which features easiness and high controllability. We focused on this synthesis and tried to confirm the formation of the cyclic structure.

In previous research, we have synthesized cyclic polymer with two reactive sites. And we have obtained some proof of the ring structure by SEC-MALS and ESI-MS. But strong evidence of the cyclic structure has not been achieved. Herein, we tried preparing grafted cyclic polymer employing Huisgen reaction known as click chemistry (figure 1). The successfully obtained graft polymer was examined by AFM measurement (figure 2). Though major products were linear polymers, the structure of the polymer was clearly observed, and the formation of the cyclic structure was suggested.

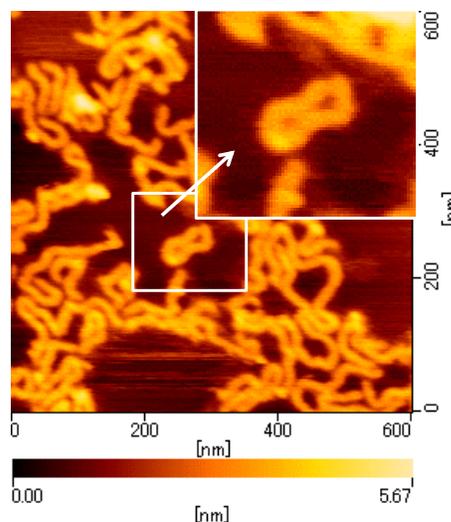


Figure 2. AFM image of the grafted polymer

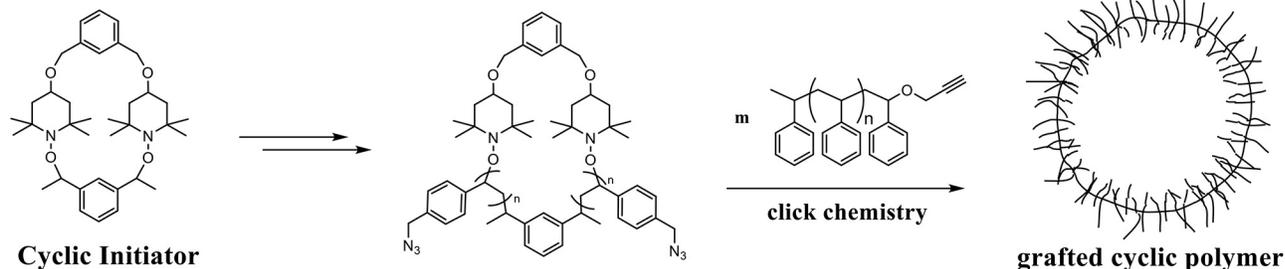


Figure 1. graft polymer synthetic scheme

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“Epigenetic” Device Preparation in an Ambipolar Organic Semiconductor Thin Film

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The phenomenon, that the channel current in FET device becomes weaker under the applied gate voltage is known as “Bias-stress Effect”. We found that the “Bias-stress Effect” of organic FET device is well suppressed at low temperature, typically below 100 K. This result could be explained in terms of the suppression of the structural relaxation of molecules in the lower temperature. Then, we tried to decrease temperature of organic FET device under applying constant V_G . As the result, the device showed the shifted threshold voltage, almost the same to the applied V_G during decreasing temperature. It becomes clearer when an ambipolar semiconducting material was used as shown in Figure 1. This result could be interpreted as the immobilization of introduced charge carrier as the floating gate. If the immobilized “frozen” charge could be regarded as “counter ion” and behaves as the dopant for the opposite sign of charge carrier, both p and n doping could be introduced as we intended. For the demonstration, we prepared a pn -junction diode within this FET device by controlling V_{DS} and V_{GS} in the cooling process. Although low temperature for freezing accumulated charge is necessary, any kinds of devices and circuits could be fabricated and reconfigured with this method on the same molecular semiconductor surface repeatedly.

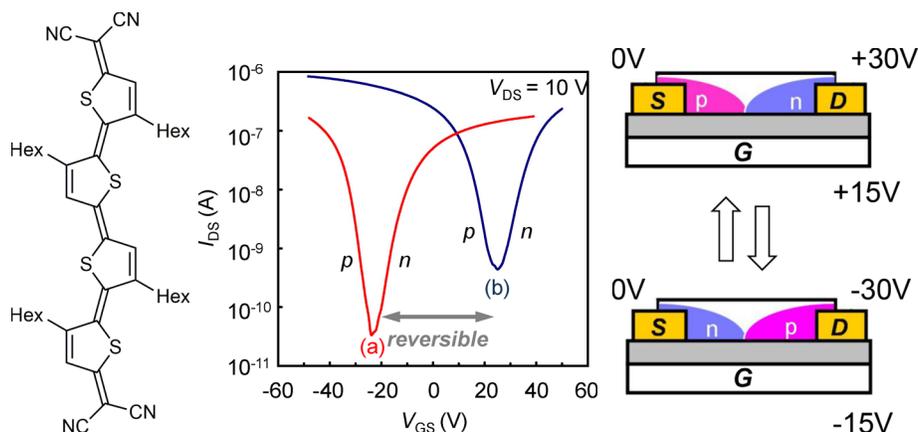


Fig.1 Molecular structure and “Epigenetic” control of the threshold voltage in an organic field effect transistor device. States (a) and (b) were prepared by keeping $V_G = -30$ V and $+30$ V during cooling processes, respectively. By controlling V_G and V_D simultaneously, rectifier could be formed and the direction could be changed in the same device.

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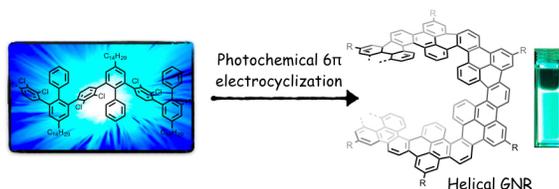
Bottom-up Synthesis of Structurally Precise Graphene Nanoribbons for Organic Electronics

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^a Département de Chimie and ^b Centre de Recherche sur les Matériaux Avancés (CERMA), 1045 Ave de la Médecine, Université Laval, Québec, QC Canada G1V0A6

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Nanographenes (NGs) and graphene nanoribbons (GNRs) are very promising materials for electronic applications. However, NGs and GNRs produced by physical methods do not allow control over size, shape and functionalization of GNRs, leading to undefined electronic and physical properties. Thus, methods to prepare such materials using the solution-phase bottom-up approach have been proposed. Yet, none of them has been proven as efficient for the introduction of electron-rich and electron-poor units on the edges of GNRs, thus limiting the modulation of their electronic properties. In this regard, our group has revisited and used a photochemical method, called the cyclodehydrochlorination reaction (CDHC), for the regioselective, mild and metal-free synthesis of NGs and GNRs from polychlorinated precursors [1,2]. Although this method is very useful for the synthesis of all-phenyl molecules, very few examples have been reported for the synthesis of heterocycle-fused NGs and GNRs. In this presentation, we will show how the CDHC reaction, a $(4n+2)\pi$ electrocyclization reaction, can be used to prepare well-defined linear and helical NGs and GNRs based on electron-rich heterocyclic motifs such as thiophene, pyrrole and ullazine. We also show how the CDHC reaction has been used to prepare ladder conjugated polymers (CLPs) with both electron-rich and electron-poor units, thus creating a permanent dipole within the polymer backbone. Carbon nanotubes wrapping and field-effect transistor (OFETs) testing of these new materials will also be presented.



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Dynamic Supramolecular Structures in the Crystalline State

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Supramolecular cations based on crown ethers are promising building blocks for constructing molecular assemblies expressing a variety of functions. We have already reported electronic functions arising from dynamic motion of supramolecular cations in the solid state. A one-dimensional stack of [15]crown-5 with lithium cation in $(\text{Li}^+)_x([\text{15}]\text{crown-5})[\text{Ni}(\text{dmit})_2]_2$ showed a lithium ion conduction in the crystal, which controlled electronic conduction in the $[\text{Ni}(\text{dmit})_2]$ column.¹ A ferroelectric transition was observed in $(m\text{-fluoroanilinium}^+)(\text{dibenzo}[18]\text{crown-6})[\text{Ni}(\text{dmit})_2]$ due to the flip-flop motion of the aryl group by applying outer electric field.²

Supramolecular rotator cations were embedded in functional anions to form multifunctional crystals. We chose $[\text{MnCr}(\text{oxalate})_3]^-$ complexes as an anion, which is known to form two-dimensional honeycomb structure exhibiting ferromagnetic transition at around 5 K, aiming at constructing multiferroic crystals. Supramolecular cations were also utilized to regulate the cation-anion assembly-structures in the solid state, which strongly affect the functions of crystals. Figure 1 shows the crystal structure of $(\text{anilinium}^+)(\text{trans-syn-trans-dicyclohexano}[18]\text{crown-6})[\text{Ni}(\text{dmit})_2]$ (**1**). The supramolecular cations formed one-dimensional columnar structure with the disorder of anilinium due to the planar conformation of the crown ether with C_{2h} symmetry.³ $[\text{Ni}(\text{dmit})_2]$ anions were inserted in the spaces between the crown ethers. In case we used a distorted supramolecular cation, $(3\text{-AP}^{2+})(\text{dibenzo}[30]\text{crown-10})$ (AP = aminopyridine) (Fig. 2), we could induce a chiral space group of the crystal, which can be used to develop chiral magnets.⁴

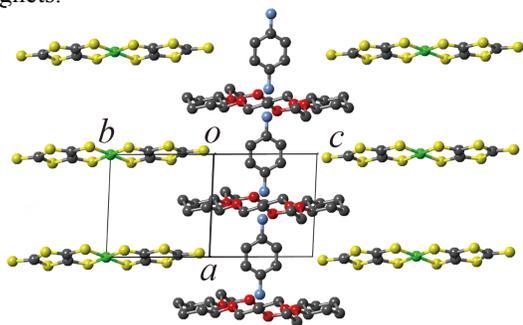


Fig. 1 Crystal structure of **1**.

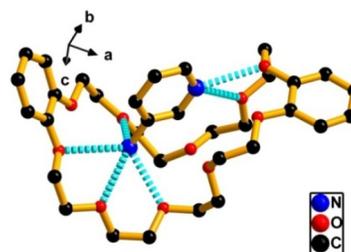


Fig. 2 Supramolecular structure.

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Photoelectron study of DNTT single crystal

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Dinaphtho [2,3-b:2',3'-f] thieno [3,2-b]-thiophene (DNTT) single crystal is a p-type organic semiconductor whose carrier mobility was reported to be $8.3 \text{ cm}^2/\text{Vs}$.¹ Based on this high mobility, the charge transport mechanism was proposed to be a band-like one,² and the theoretically obtained electronic band structure of the highest-occupied molecular orbital (HOMO) shows agreement with this transport mechanism.³ Furthermore, the anisotropic dispersion along different high symmetry direction of the Brillouin zone in the theoretical band structure suggests an anisotropic hole mobility in real space. In this paper, we report the band structure of a DNTT single crystal obtained by means of angle-resolved photoelectron spectroscopy at 300 K. The obtained negligible band dispersion shown in Fig. 1 indicates that the charge transport mechanism of DNTT cannot be a simple band-like picture. We will also discuss the carrier transport mechanism in DNTT based on the thermal vibration of molecules.

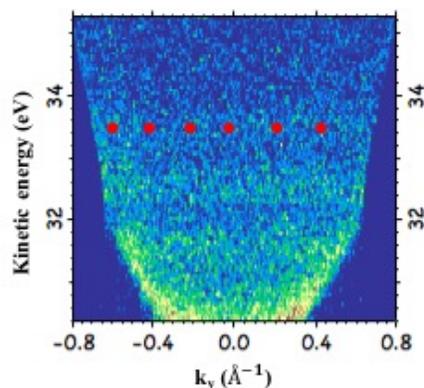


Fig.1; Valence region band structure of a DNTT single crystal along the X-M direction of the Brillouin zone.

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π -Conjugated 2D Covalent Organic Frameworks

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One-dimensional conjugated organic polymers are important optoelectronic materials with tunable properties and myriads of applications. Two-dimensional (2D) inorganic materials, such as graphene, display a spectrum of unprecedented properties that fundamentally impact the solid state physics. It would thus be intriguing to be able to combine the *tunability* of an organic polymer and 2D electron confinement in a single material – a 2D π -conjugated polymer.^[1] One possible approach to growing such materials is using flat crystalline surfaces as templates and we have been moderately successful in such on-surface polymerization.^[2] Another, potentially, better alternative is to employ self-assembly and defect correction mechanisms, through dynamic covalent polymerization. This presentation will show synthesis of covalent organic frameworks via novel Michael addition/elimination dynamic polymerization^[3] The novel properties resulting from the π -electron delocalization (conjugation) in 2D will be also be discussed.

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Coordination Complexes using Thiazyl Radical Bridging Ligands

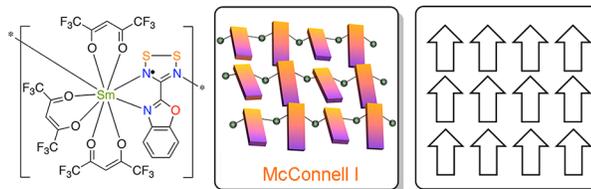
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The so-called “metal-radical approach” to designing molecule-based magnetic materials takes advantage of strong exchange coupling between the moments of a paramagnetic metal ion and the paramagnetic ligand to which it is coordinated. When transition metal ions are used, the nature of the exchange coupling can be understood and predicted based on a simple orbital-overlap model. Coupling to lanthanide metal ions is typically weak and harder to predict, but can often be rationalized based on simple superexchange arguments. Employing paramagnetic ligands to mediate magnetic coupling between metal ion moments is an attractive model for material design.

We are interested in using paramagnetic bridging ligands with varying coordination environments and varying degrees of Lewis basicity to mediate and tune the magnetic coupling between transition metal and lanthanide ions. In addition, we are interested in extending the metal-radical approach by creating paramagnetic ligands that will engage in *intermolecular* interactions. [1] Recent, unpublished work on the use of cyclic thiazyl “building blocks” as bridging paramagnetic ligands will be presented. This work includes examples of molecule-based materials that exhibit magnetic ordering, based on the design principles outlined above.



-[Sm(III)-Radical]_n- coordination polymer exhibits 3D FM ordering

[1] E. M. Fatila, A. C. Maahs, M. B. Mills, M. Rouzières, D. V. Soldatov, R. Clérac and K. E. Preuss, *Chem. Commun.*, **2016**, 52, 5414-5417.

Magnetism, fluorescence, photo-conductivity and charge transfer salts of the dithiadiazolyl radical, phenDTDA (phen = 9-phenanthrenyl)

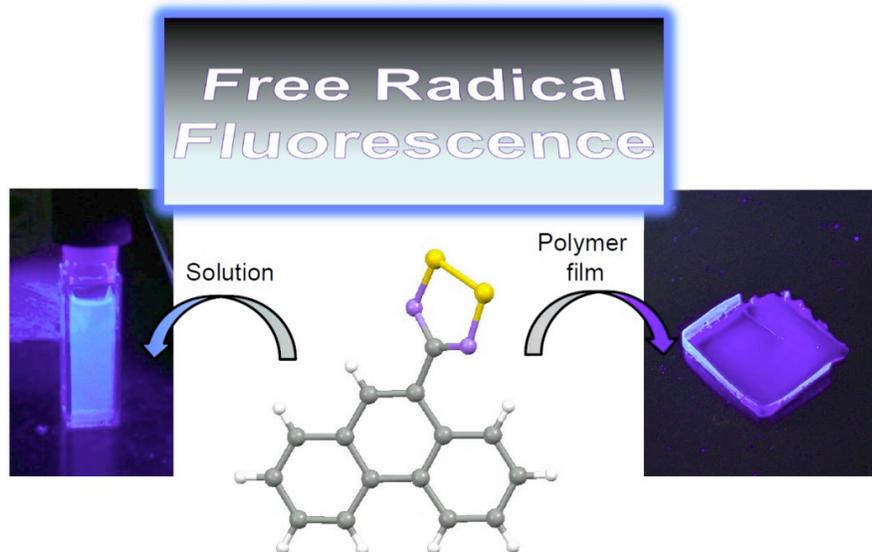
J. M. Rawson,^{*a} Y. Beldjoudi,^a I. Roman-Osorio,^a M. A. Nascimento,^a M. M. Matsushita,^b K. Awaga,^b K. Eguchi^b and D. Tonouchi^b

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Poly-aromatic hydrocarbons exhibit a range of appealing physical properties such as semi-conducting and photo-conducting behavior, fluorescence and low redox potential facilitating formation of charge transfer salts. Conversely the dithiadiazolyl (DTDA) radical is a thermally robust radical which has been used as a building block for the design of magnetic materials including *p*-NCC₆F₄DTDA and *p*-O₂NC₆F₄CNSSN. Here we describe a DTDA radical bearing the phenanthrenyl functional group (**1**) as a step towards the formation of multi-functional materials.^[1] We present results relating to the diamagnetic-paramagnetic solid state phase transition of **1** near ambient temperature, its fluorescence properties including redox-switching of fluorescence, its incorporation into polymer composites, as well as its conductivity and photoconductivity.



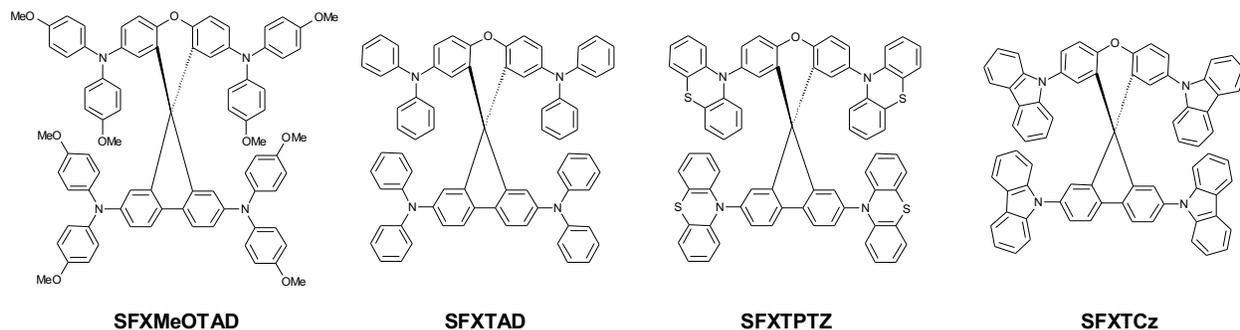
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New hole-transport materials for perovskite solar cells

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Novel hole transport materials based on cost-efficient spiro[fluorene-9,9'-xanthene] (SFX) have been recently reported by our group.¹ Namely SFX-TAD, SFX-TCz, SFX-TPTZ and SFX-MeOTAD (see figure) were fully characterized by ¹H/¹³C NMR spectroscopy, mass spectrometry, XRD and DSC. Their thermal, optical and electrochemical properties were investigated. The use of different substituents affects the highest occupied molecular orbital (HOMO) energy level proving the versatility of the central core towards the facile and low-cost preparation of spiro-hole-transport materials. Among them, we have so far studied SFX-MeOTAD in detail for application in perovskite solar cells with device architecture glass/FTO/compact TiO₂/mesoporous Al₂O₃/CH₃NH₃PbI₃-xCl_x/HTM/Au. This material shows high glass transition temperature, high solubility, purely amorphous state and HOMO level alignment almost identical to spiro-MeOTAD. We show that devices employing SFX-MeOTAD show high power conversion efficiency up to 12.4%, compared with 13.0% for spiro-MeOTAD, but with the significant advantage of more than 5 times lower cost of synthesis. Furthermore, the easy synthesis of this series has enabled us to prepare examples of varying redox potential, offering a choice of HTM tailored to other emerging perovskite solar cell materials. Herein, we will show further development of SFX-based hole transporting materials as well as new materials based on DATPA (diacetylide-triphenylamine) core, previously reported in our group.^{2,3} In particular we studied the influence of tert-butyl and different alkoxy groups on materials properties like film forming quality, energy levels, crystallinity/amorphousness, thermal stability, solubility and device performance.



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Fermi surface modification induced by the adsorption of organic molecules

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Organic molecules weakly adsorbed on solid surfaces by van der Waals force slightly change the surface valence band electronic structures and thus the physical properties of surfaces. In case of phthalocyanine (Pc) compounds adsorption on In/Si(111)-($\sqrt{7}\times\sqrt{3}$), which is formed by two layers of In on Si(111) and shows superconductivity below $T_c \sim 3$ K,¹ the T_c is reported to show different changes depending on the PC, i.e., the T_c increases (decreases) with CuPc (MnPc) adsorption.² In this paper, we will present our photoemission study on CuPc adsorbed In/Si(111)-($\sqrt{7}\times\sqrt{3}$) and discuss the origin of the change in T_c based on the spin state of the adsorbate.

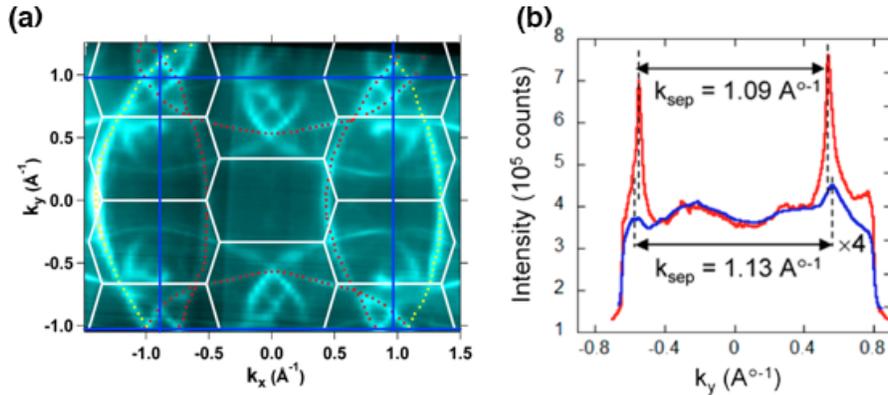


Fig. 1; (a) Fermi surface of In/Si(111)-($\sqrt{7}\times\sqrt{3}$) and (b) momentum distribution curves of the Fermi surface before (red) and after (blue) CuPc adsorption.

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Crystal Structure and Magnetic Property of Triptycene Trisquinones

Triradical Trianion Salt

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The unpaired electrons of organic radical species are attracted much attention in the field of solid state physics because of their unique magnetic, conductive and optical properties. Organic π planar molecules, in general, form strong dimers or 1D π stack columns due to its strong exchange interaction between radical species. To create 3-dimensionally π interacted crystal structures of organic radicals, we focused on triangle molecule NDI- Δ^1 (Fig a) and propeller molecule Triptycene Trisquinone (TT, Fig. b). The molecular structure of NDI- Δ and TT consist of three naphthalenetetracarboxylic diimide (NDI) moieties and three benzoquinone moiety, respectively. Notable feature of these molecules is that the π planes face toward different three directions that can realize multidimensional π - π interactions. In previous work, we have successfully obtained a unique highly isotropic 3D crystal structure, namely K_4 structure with $I4_32$ symmetry by using NDI- Δ radical anion as a building block (Fig. a).² In our present work, we revealed that reduced specie of TT forms 2D honeycomb structure reflecting its unique molecular structure. Crystal structure and physical properties of the TT triradical trianion salt will be discussed.

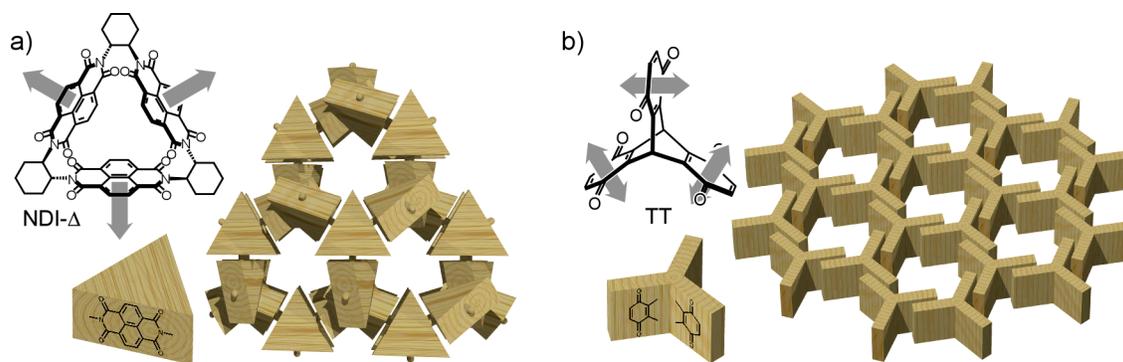


Fig. Molecular structures with the direction of π interaction and crystal packing motifs of K_4 lattice of NDI- Δ radical anion salt (a) and honey comb lattice of TT radical anion salt (b).

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Structure analysis of BDTDA/Cu(111) using a LEED I-V method

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Highly ordered molecular self-assembled 2D architectures formed on solid surfaces have recently attracted much attention in organic electronics and spintronics fields. Especially, the possibility of showing exotic electronic property such as Dirac Fermion, like graphene, motivates us to study honeycomb lattices formed by molecules with radicals. In our former study, we reported that the cyclic thiazyl diradical BDTDA (= 4,4'-bis(dithiadiazolyl),¹ see the inset of Fig. 1), forms a well-ordered 2D honeycomb network on Cu(111) due to its strong self-assembling force (Fig. 1).² In case of a free standing BDTDA layer, this structure can be regarded as “molecular graphene”, because each corner of this honeycomb lattice consists of one electron. Taking into account that a proper knowledge on the atomic structure of the honeycomb network adsorbed on Cu(111) is necessary to understand the electronic band structure, we have carried out low-energy electron diffraction (LEED) measurements. In this talk, we report the structure analysis of BDTDA/Cu(111) using a LEED I-V method.

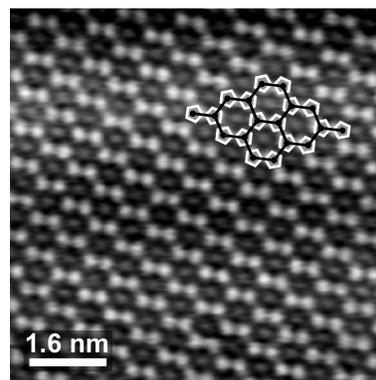
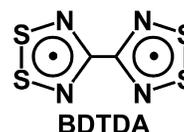


Fig. 1 Topography of the 2D BDTDA honeycomb structure on Cu(111).

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Self Assemble Structures Composed of Nonplanar π -conjugated Derivatives

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Coordination-driven self-assembly has evolved into a well-established methodology for novel metallocupramolecular structures using dative metal-ligand bonding interactions. A variety of metallocupramolecules, from two-dimensional to three-dimensional cages have been reported based on coordination-driven self-assembly. Self-assembly have wide range of applications, such as synthesis of metallocupramolecular dendrimers and uses in catalysis and sensors.

Multicomponent, selective self-assembly represents a unique assembly process in which multiple, varying components can selectively recognize and combine to generate only one discrete structure within a mixture. By mixing various molecular components that lack sufficient complementary electronic and structural information, a self-organized mixture or even disordered oligomeric species can be formed instead of one finite, discrete supramolecule. How to provide sufficient molecular information to control selective self-assembly in a multicomponent system remains a demanding issue in modern supramolecular chemistry.

In this study, we synthesized pyridine derivative to form molecular cages. Pyridine derivative was prepared by mixing compound 1 and 2. Compound 1, 2, Pd(PPh₃)₄ and K₂CO₃ dissolved in THF, EtOH and H₂O, After stirring for 20 hours, we can obtain crude products. The resultant white crystals were separated column chromatography. The characterization and physical properties of pyridine derivative will be discussed.

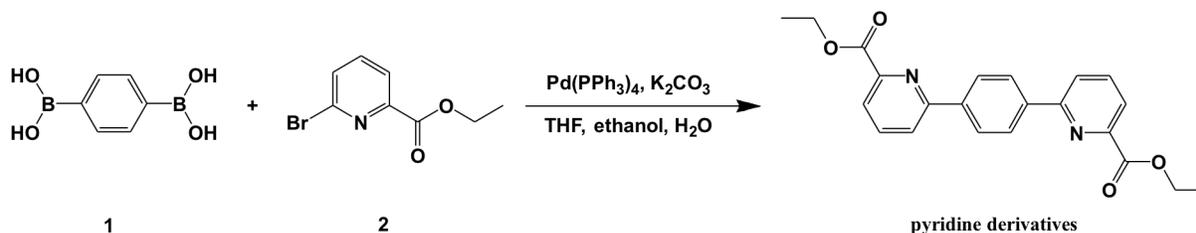


Fig.1 Scheme of pyridine derivative

Molecular Nanocoils of Conducting Molecules with Chiral Units

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Self-organization of Disc-like molecules as triphenylenes(TP), Tetrathiafulvalene(TTF), porphyrins, and phthalocyanines into columnar assemblies through their strong intermolecular π - π interaction is a highly active area of research. In recent years, many approaches have been explored in order to self-organized process and the design of molecules enabled well-defined nanostructures.

Many organic metals and superconductors have been reported in the forms of cation radical salts and charge transfer (CT) complex using TTF based electron donor molecules. TTF molecules have a tendency to assemble in one-dimensional stacks through π - π overlaps along with stacking direction. The regular stack of partially oxidized TTF molecules provides partially filled one-dimensional π -band structures. TTF derivatives can also interact in a side by side manner through the overlap of atomic orbital of the peripheral sulfur atoms, which increases the dimensionality of the π -band structure along the transverse directions.

In this paper, we report photonic and electronic properties of molecular nanocoils composed of TTF derivatives and acceptors, with tetrafluorotetracyanoquinodimethane (F4-TCNQ). We synthesized TTF derivatives having chiral and hydrogen-bonding side chains; **R-**, **S-TTF-4UM**, **TTF-ER** and **TTF-PG**. The synthesized molecules organized into helical and nanoscopic one-dimensional assemblies by using various intermolecular interactions.

The nanocoils of (TTF derivatives) (F4-TCNQ) were fabricated on Si and quartz substrates by cast techniques. The surface morphology was examined by AFM, SEM and TEM. The nanocoils had typical dimensions of 30 nm (height) x 50 nm (width) x >10 μ m (length). The electronic and vibration spectra of (TTF derivatives) (TCNQ derivatives) in the cast film have consistent with the fully ionic ground states. The room temperature electrical conductivity (σ_{RT}) were about 10^{-4} Scm⁻¹. Next, we formed the scaffold composed of TTF derivatives, (TTF derivatives) (TCNQ derivatives), checked cytotoxicity test of 293 cell on nanocoils. 293 cells on TTF derivatives showed the activation, but these on the scaffold composed of (TTF derivatives) (TCNQ derivatives), TCNQ derivatives had the inactivation. Temperature dependent electrical conductivities and magnetic properties of (TTF derivatives) (TCNQ derivatives) will be discussed.

Current-induced mutual structure-conductivity transformation along orthogonal crystal axes in a TTF-based dimeric donor salt

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An ion-radical salt of cyclophane donor TBC3 that two TTF units are connected by four trimethylene-dithio-chain in the orthogonal orientation undergoes a structural phase transition near 170K. In this phase transition, the crystal symmetry changes from Tetragonal to Monoclinic, and magnetic susceptibility becomes almost one-half and resistibility becomes 10 times smaller in low-temperature phase. On this salt four electrodes were attached at the four corners of the crystal along the ab plane and V - I measurements were carried out along the a and b axes alternately. As a result, resistance of the current applied axis decreased while that of the other axis increased. This result suggests that the orientation of the low-resistance structure was controlled by current application.

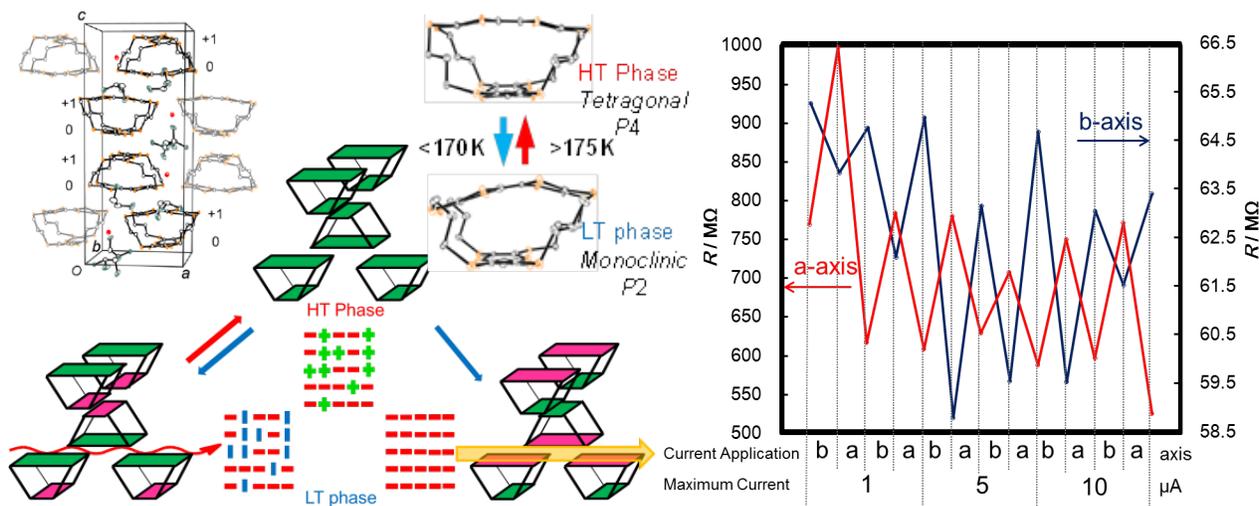


Fig.1. Crystal structure of TBC3·Br·TCE₂ (HTP) and structure change of TBC3 in the salt

Fig.2. Mutual change in the resistance of TBC3·Br·TCE₂ (LTP 170K)

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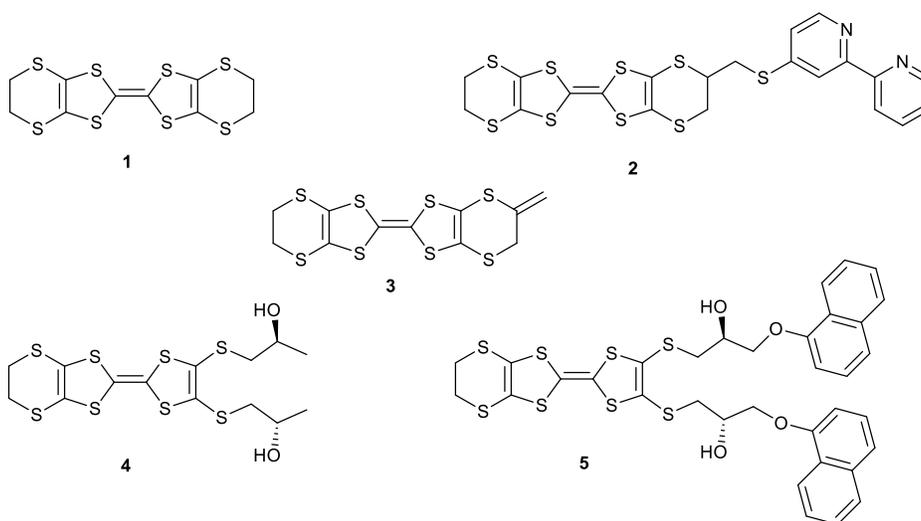
Synthesis and Properties of Organosulfur Donors Related to BEDT-TTF.

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BEDT-TTF **1** has provided a wide range of electroactive materials, including semiconductors and superconductors. The presentation will describe progress made in the synthesis of functionalised donors related to BEDT-TTF and EDT-TTF and their electrocrystallisations and diffusions with acceptors to produce conducting materials. Particular donors include molecules **2-3**. Donor **2** is of particular interest since it led to the production of a capsular 6:2 structure with Fe(II),¹ while **3** is unusual in having an *exo* methylene group.² The preparation of donors with two and three BEDT-TTF units will also be described. Emphasis will be given to the preparation of enantiopure donors, for example donors such as **4-5**, and the analysis of the crystal structures of their radical cation salts.^{3,4} An example of a BEDT-TTF salt with a chiral borate anion will also be described.⁵



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Covalent Organic Framework-*graft*-Polysulfide: A Novel Cathode for High-Energy Rechargeable Lithium Batteries

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Electrical energy storage (EES) systems play a crucial role in regulating the utilization of renewable energy resources due to the intermittent nature of renewable energy sources such as solar and wind power. Among many EES systems, rechargeable lithium batteries are the most promising system to meet the needs because of their high energy density and high energy efficiency. The capacity of lithium-ion batteries is mainly restricted by the cathode material, although lithium itself as the anode offers a gravimetric capacity of 3862 mAh g⁻¹. Organic redox-active materials are promising candidates for reliable cathode material with low cost, safety and energy density because they are heavy-metal free and can be produced from renewable sources.¹ Covalent organic frameworks (COFs) are a class of highly designable and functionalizable crystalline porous materials with desirable intrinsic properties, including large specific surface area, high stability, and low skeleton density.^{2,3} In this work, a novel covalent organic framework-*graft*-polysulfide (COF-*graft*-PS), which can be utilized as a cathode active material in lithium organic batteries, is prepared by introducing graft polymerization to the nano-channels of a covalent organic framework. The COF-*graft*-PS-based batteries show high capacity and great cycling performance. Their design characteristics and synthetic strategy open new possibilities for the preparation of novel cathode for high-energy rechargeable lithium organic batteries.

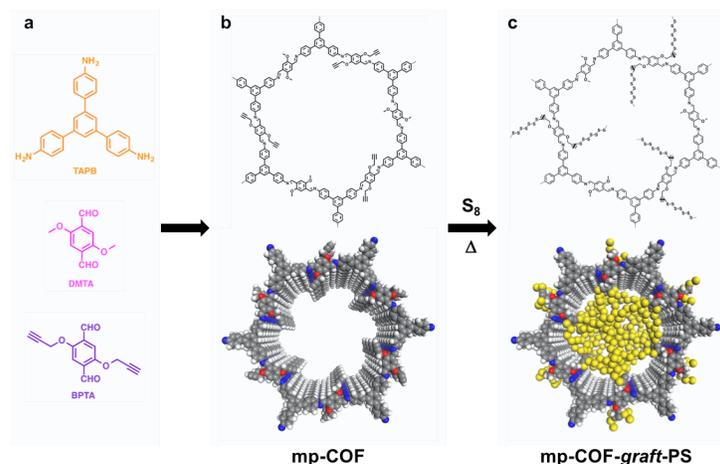


Figure 1. Schematic representation of the synthesis of mp-COF-*graft*-PS.

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Modulation of the Electronic and Electrochemical Properties of Metal Organic-Frameworks with Guest Introduction

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Metal organic-frameworks (MOFs) are widely studied for their applications. An elegant example that is reported by Fujita, *et al*, namely crystal sponge method can obtain the structure of target molecule without crystallization.¹ The molecules are inserted into the pores of crystalline porous coordination cage and the guest adsorbed crystals are analysed with single crystal X-ray diffraction analysis. Inspired by this method, we managed to insert organic donors, such as TTF, into a previously reported Mn-MOF² ($[\text{Mn}_7(2,7\text{-AQDC})_6(2,6\text{-AQDC})(\text{DMA})_6]_\infty$ with AQDC = anthraquinone dicarboxylics and DMA = N,N-dimethylacetamide) via a crystal sponge approach. The structure was determined by single crystal XRD and the formula was suggested to be $[\text{Mn}_7(2,7\text{-AQDC})_6(2,6\text{-AQDC})(\text{DMA})_6(\text{TTF})_5]_\infty$. As shown in Figure 1(c), TTF guests were categorized in three types: blue ones that are close to anthraquinones with bent structure, and space-filling red and yellow ones. Donor-acceptor interactions between TTF guest molecules and anthraquinone functional groups on the frameworks have been observed which was evidenced by solid-state diffusive reflectance method. The physical property modulation to the host frameworks is also achieved by the host-guest charge transfer interactions.

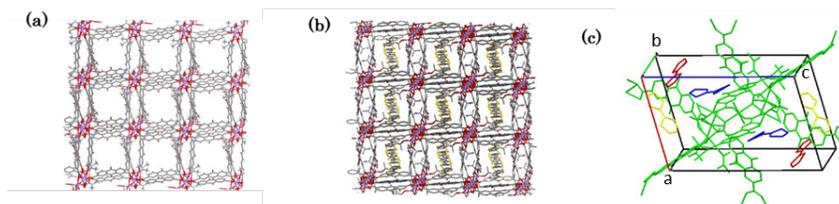


Figure 1. (a) Crystal structure of Mn-MOF, (b) crystal structure of TTF@Mn-MOF, and (c) unit cell of TTF@Mn-MOF.

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Transient Photocurrent in Photovoltaic Device Utilizing Ferroelectric layer

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Organic optoelectronic devices, such as organic photovoltaic (OPV) devices, which benefit from light weight, low cost, flexibility and a much higher internal quantum efficiency, suffer from a strong exciton binding energy. The exciton dissociation in OPVs are usually driven by the electric field generated from an electrode potential difference but it requires a field of 50–70 MVm⁻¹, which is much larger than that induced by a conventional electrode potential difference. So, it is important to increase net field in the device. In previous research, we fabricated and investigated OPVs utilizing ferroelectric layer, demonstrated that the oriented net field related to ferroelectric polarization can facilitate exciton dissociation in organic semiconductors.¹ In this study, we investigated the transient photocurrent in the device using ferroelectric layer with varying the polarization direction and magnitude of the ferroelectric layer.

First, we fabricated MFSM device structure (Figure 1), with aluminium (Al) and ITO as the electrodes, Copper phthalocyanine (CuPc) and poly(vinylidene fluoride-trifluoroethylene)(P(VDF-TrFE)) (75/25 mol%) films were chosen as the semiconductor and ferroelectric layer, respectively. The polarization direction and magnitude of the ferroelectric layer was controlled by varying the applying voltage. The correlation between the polarization of ferroelectric layer and the exciton dissociation in the semiconductor layer was investigated by measuring the photocurrent transients.

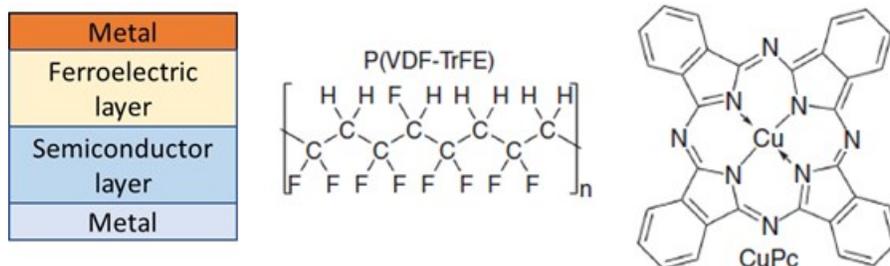


Figure 1. The structure of photovoltaic device and molecular structure of P(VDF-TrFE) and CuPc

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Battery Performances of Chalcogen-Containing Organic Compounds

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Rechargeable batteries are currently essential power sources for various applications ranging from portable electronics to the emerging large-scale applications. Chemically speaking, almost all developed cathode materials are inorganic ones, which are often costly and not so environmentally benign. Recently, to overcome such problems, organic cathode active materials have been considered as promising candidates for promoting new generations of batteries. Although significant improvements have been achieved over the past few years, organic electrode materials are not yet used in practice notably due to some recurring limitations in terms of energy densities and cycle-life performance. Among various organic materials, quinone and disulfide derivatives, which exhibit two electrons redox reactions, have attracted much attention because high specific capacities can be expected due to low-molecular weight and designability. In this work, we studied new organic materials bearing quinone and disulfide parts as cathode active materials.

Firstly, we examined the battery performance of quinone derivatives, starphene-shaped ployketon **1**, which was synthesized via three-fold cycloadditions of isobenzofuran trimer, as cathode active materials. The first discharge capacity was ca. 190 Ah/kg in the voltage range of 1.5-4.2 V at 0.1 mA/cm². This value is significantly larger than that of the theoretical one (90 Ah/kg) calculated from six electrons reduction of quinones. It is suggested that further electron reduction and electrical double layer effects were induced by aggregation of tetracenequinone. After 20 cycles, the capacity maintained more than 85 % of the initial one, which is ascribed to the insolubility of this compound into the electrolyte. This compound turned out to show a good performance as a cathode active material.

Then, disulfide-based materials were also used as cathode active materials to achieve high capacities. Herein, disulfide compounds obtained by reacting thiosulfonate S-esters with dithiols or trithiols were vulcanized by addition of elemental sulfur. For example, lithium batteries using polysulfide materials **2** consisting of 1,3,5-benzenetrithiol and 4,4'-biphenyldithiol as cathode active materials exhibited a high capacity of ca. 250 Ah/kg with a large plateau in the first discharging curve.

Finally, we focused on MOFs including disulfide parts as organic ligands since they can deliver high capacity during multiple cycles due to their stable frameworks and dual redox reactions of metal ions and ligands. Here, we used Cu-based MOF including disulfide ligands¹, although disulfides originally show poor cycle performances in spite of high capacities. As a result, the lithium batteries including Cu-based MOF showed both high capacity and stable cycle performance, which is attributed to the stable frameworks and dual redox of Cu and disulfide.

Reference

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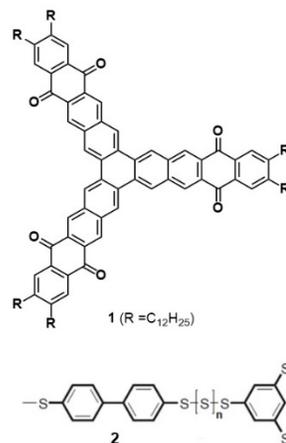


Fig. 1. Organic cathode materials used in this work

Photoactive Supramolecular Assemblies

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In this talk I will outline strategies for the supramolecular assembly and pre-organization of photoactive materials, discuss and contrast their optoelectronic properties with those of reference small molecule compounds. The motivation for this work is to (1) improve the performance of electroluminescent devices; (2) to develop selective sensors and photoredox catalysts; and (3) on a more fundamental level, to understand how the photophysical properties of the assembly can be modulated as a function of the structure of its constituent components.