Organic Semiconductors

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Atef S. Iskander

Organic semiconductors have been attracting increasing attention owing to their fascinating properties such as low-cost, flexible, large-area, and lightweight. The rapid growth in the interest given to π-conjugated materials is boosted by the promising performances and diverse range of applications in electronic devices. In addition, their characteristics have great potentials as a platform for exploring new avenues of inventive applications. This article highlights some aspects regarding their nature, electronic device structure, physical properties, and their synthetic approaches.

1. Introduction

Since the mid-twentieth century, the landscape of electronics has been dominated by inorganic materials such as silicon (Si) and germanium (Ge). They are characterized by their outstanding semiconductor properties, and are widely used in numerous applications of solid state electronics such as memory chips, solar cells, transistors, and LEDs (GaAs, InGaAs). However, these inorganic materials suffer from many drawbacks in terms of the difficulty in processing, costly, and not viable for large area applications. Since the beginning of the 21st century, organic semiconductors are rapidly becoming important materials for the manufacture of electronics, and are seen as a potential replacement for their inorganic counterparts. Indeed, the development of electronic devices is significantly influenced by progress in organic semiconductors. Owing to their attractive features in terms of easily processing, easily modified by chemical synthesis, cheap, and ideally suited for area applications, industrial interest focuses on utility and development of organic semiconductors. These organic materials paved the way for enormous progress in the field of electronics leading to a rich variety of novel applications such as organic light-emitting devices (OLEDs) for both displays[1] and solid state lighting[2,3], organic field-effect transistors (OFETs)[4], or organic photovoltaic cells (OPVCs)[5].

2. Organic semiconductor materials

The art of synthesizing an organic semiconducting material is largely based on the construction of π-conjugated systems that lead to the desirable properties for the fabrication of electronic devices. π-conju-

gated systems are hydrocarbon compounds with alternating single and double bonds which they envisaged as the cornerstones of organic semiconductors. They are characterized by their fascinating optical and electronic properties. Owing to the weak π-bonding of these materials, the lowest electronic excitations of conjugated molecules are the π-π* transitions with an energy gap in the range of 1-3 eV leading to light absorption or emission in the visible spectral range. Thus, the inclusion of π-conjugated systems facilitates the delocalization of orbital wavefunctions. Furthermore, the elaboration of these systems by introducing electron withdrawing groups or donating groups could enhance hole or electron transport.

In a general sense, most contemporary organic optoelectronics are layered semiconductor devices that the emissive layer is a crystalline or amorphous thin-film of organic π-conjugated molecule. The emissive layer is sandwiched between two electrodes, one or both of which are transparent. Other layers of organic materials are often incorporated into organic electronic devices to facilitate the transport of electrons and holes through the device (Figure 1).

In order to form thin film, the employed process depends on the nature of organic materials whether are small molecules or polymers. Small molecules are usually deposited from the gas phase by sublimation or evaporation, whereas polymers can only be processed from solution, e.g., by spin-coating or printing techniques.
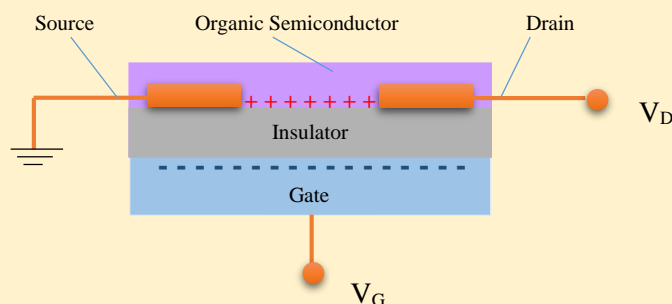

Figure 1. Schematic illustration of organic optoelectronic devices.

3. Basic properties of organic semiconductors

An understanding of the optical properties and charge carrier transport in organic semiconductors is important for designing electronic devices and for understanding their function and performance.

3.1 Optical properties

Organic semiconductors are characterized by the existence of well-defined spin states (singlet and triplet). Absorption of a photon leads to the excitation from the ground state S_o to the first excited singlet state S_1. The lifetimes of the S_1 state are in the range of few nanosecond, so leading to

a rapid decay of the excitation energy to the S_o ground state via fluorescence, or non-radiative transition, or intersystem crossing to the triplet state T_1 followed by decaying via phosphorescence or non-radiative (Scheme 1). As a consequence of relative triplet decay, the exciton production efficiency in OLEDs is limited to 25%. Enhancing the exciton production efficiency can be achieved by utilization of thermally activated delayed fluorescence molecules as assistant dopants that permit efficient transfer of all electrically generated singlet and triplet excitons from the assistant dopants to the fluorescent emitters[6] or by incorporating heavy atoms such as platinum (Pt) or iridium (Ir).
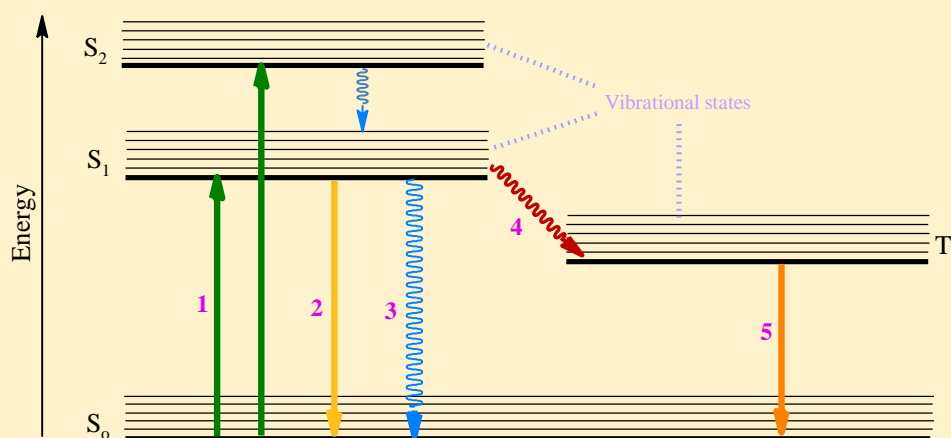
Scheme 1. Energy level scheme of an organic molecule, **1**: Absorption of light ($h\nu$), **2**: Fluorescence ($h\nu_f$), **3**: Internal conversion (IC), **4**: Intersystem crossing (ISC), 5: Phosphorescence ($h\nu_F$).

Another peculiarity of organic semiconductor is the optical excitations "excitons", which have a considerable binding energy due to the localization on one molecule (Figure 2). The $\sigma \rightarrow \sigma^*$ transition takes place in the ultraviolet spectral range, while the lower splitting associated with π-orbitals implies $\pi \rightarrow \pi^*$ transition can take place in the visible spectral range, which this also applies to the light emission due to the transition of electron from the LUMO to HOMO. The excitons binding energy is needed to produce free charge carriers. Such extra amount of energy has impact in determining the output voltage of organic photovoltaic cells.
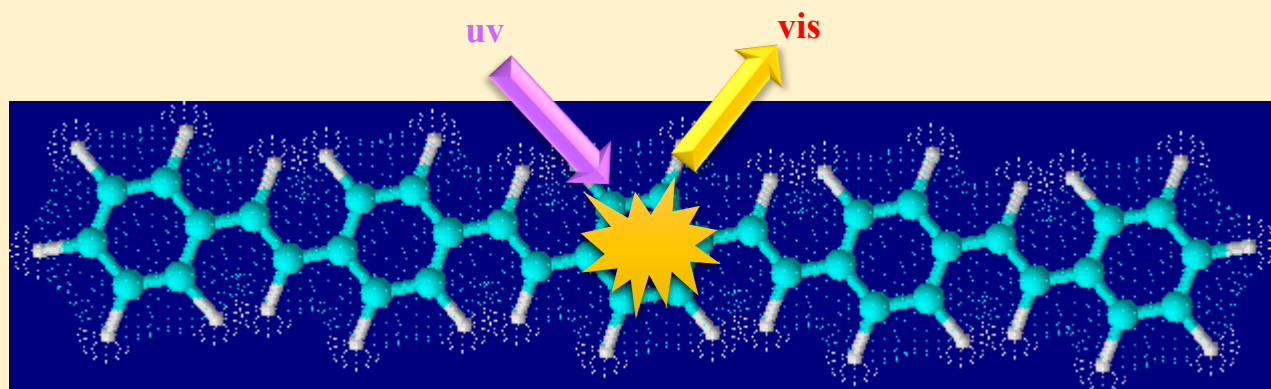
Figure 2. Illustration of emitting light from organic semiconductor materials.

3.2 Charge carrier transfer

There are two major types of organic semiconductors based on the type of majority charge carriers: p-type (holes as major charge carriers) and n-type (electrons as major charge carriers) (Figure 3). Ambipolar is another type of organic semiconductors, which has the ability to transport both electrons and holes such as carbon nanotubes[7].

The performance of electronic devices depends on the efficiency of the movement of charge carriers (electron and/or holes) within the π-conjugated materials (Figure 4). The concentration of thermally excited charge carriers in these materials is very low to produce a significant conductivity. Therefore, mobile charge carriers have to be injected either from metallic contacts or via light excitation into their layers. In this sense, an organic material is considered to be an electron or a hole transporter when its ionization energy (electron affinity) closely matches the Fermi level of the electrode material (Figure 5). To facilitate charge transport, the π-π stacking direction of π-conjugated materials should ideally be along the current flow direction. This requires the semiconductor molecules to self-assembles into certain orientation upon their vapor or solution deposition. It is also important that the thin film has large, densely packed and well-interconnected grains. The mode of charge transport is characteristic for organic semiconductors, since it is determined mostly by the extent of wave function delocalization. Most small molecules, which are high performance organic semiconductors, tend to have the long axes of the molecules oriented close to the dielectric surface with the typical grain size in the order of at least a few micrometers. In case of solution processed polymers, it is preferred for π-conjugated plane to adapt an edge-on orientation on the surface. The morphology of semiconductor film is largely dependent on the chemical and physical nature of the dielectric surface.
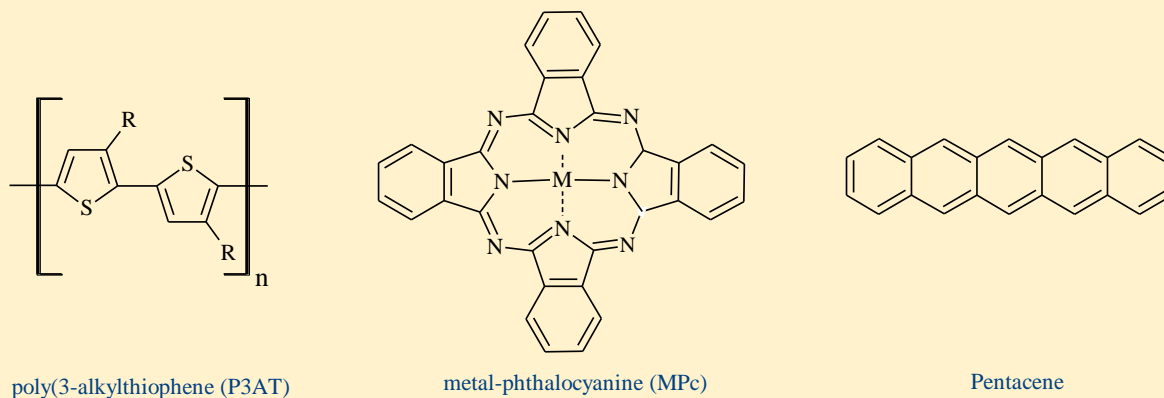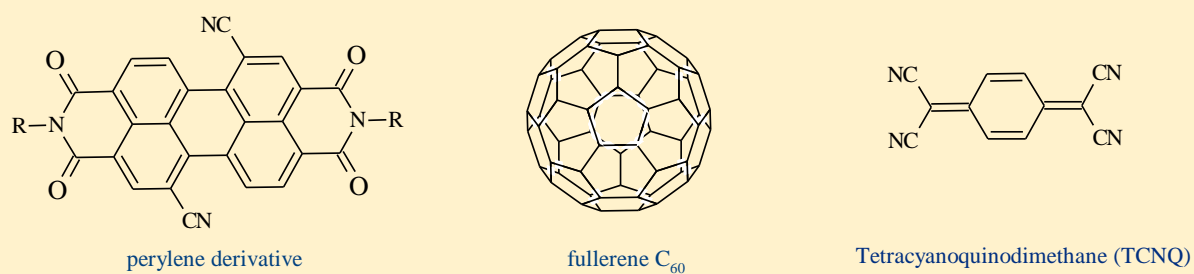
p-type organic semiconductors

poly(3-alkylthiophene (P3AT)

metal-phthalocyanine (MPc)

Pentacene

n-type organic semiconductors

perylene derivative

fullerene C_{60}

Tetracyanoquinodimethane (TCNQ)

Figure 3. Molecular structure of some prototype organic semiconductors.
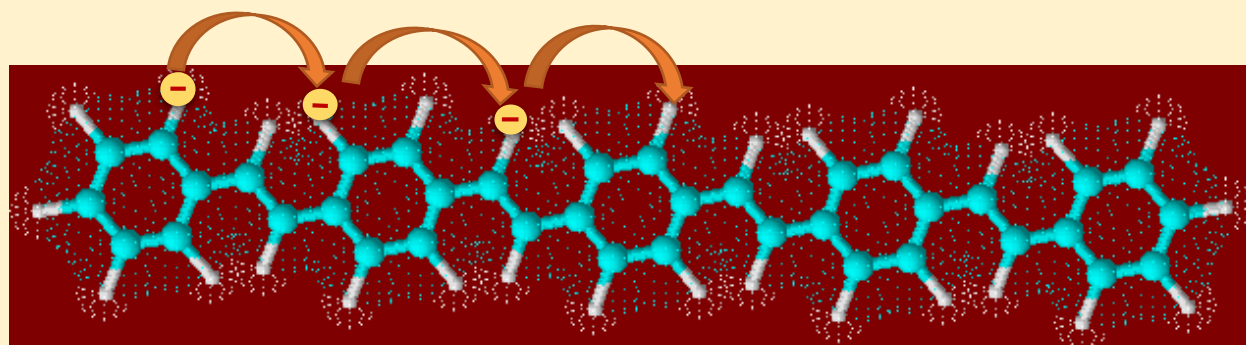
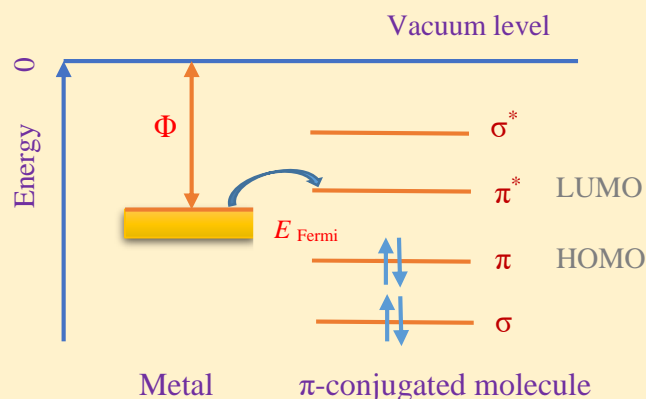**Figure 4.** Illustration of conducting charge across organic semiconductor materials.

Figure 5. Illustration of energetic positions of the orbitals in organic molecules relative to metal work functions.

4. Synthetic approaches

The chosen synthetic pathway of organic semiconductor materials and the purification are crucial for optoelectronic performance. The synthesis of small molecules is well controllable and can be purified to a high degree. In contrast, the synthesis of polymers is elaborate and can lead to the same products with some variation in optoelectronic properties. For instance, the synthesis of pendant-type polymer incorporating dioxocyclopenta[c]thiophene-based terthiophenes, as a candidate for n-type solution-processable OFET materials, was accomplished through the combination of Stille coupling reaction and palladium-catalyzed cyclopolymerization (Scheme 2)[8]. Traces of the metal catalysts may remain in the compound even after purification, which in turn can act as quenching sites to luminescence or trapping sites for charge.
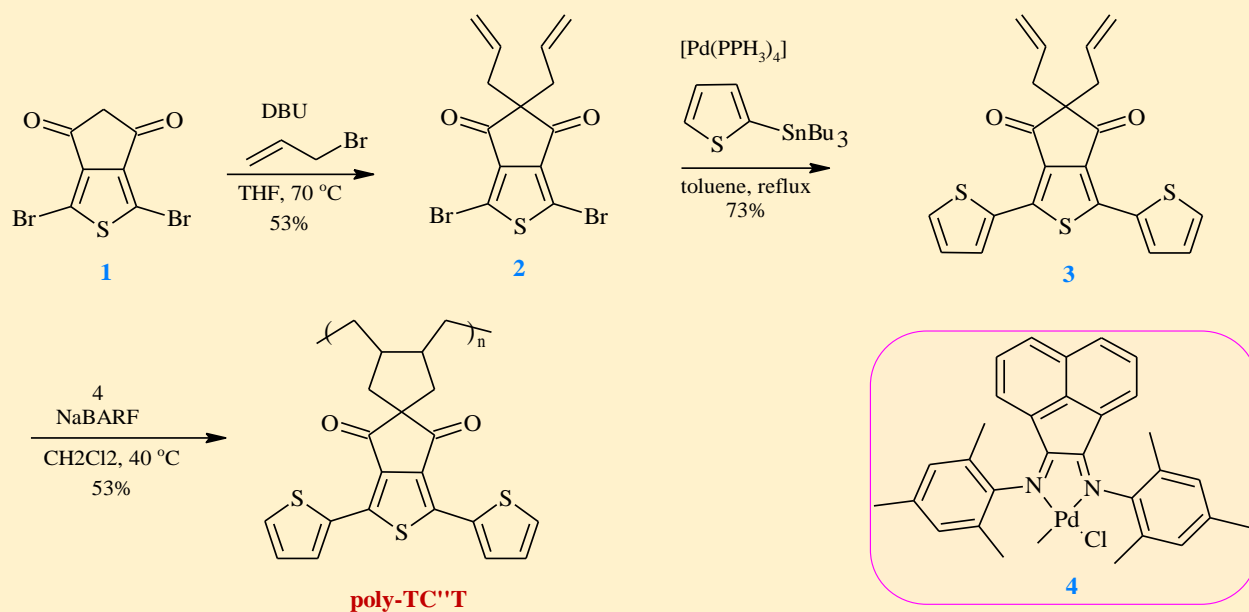
Scheme 2. Synthesis of **poly**-TC''T, BARF: $[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]^-$.

The construction of supramolecular materials based on self-assembled small molecules relies significantly on strong directional π-π stacking interaction between the cores of these molecules and microsegregation between their cores and aliphatic or hydrophilic moieties. More hierarchically organized assemblies of small molecules can be constructed by using highly directional and specific intermolecular glues, such as complementary multiple hydrogen-bonding interactions (CMHB)[9,10], which the resulting assemblies show unique functional properties.

For example, perylene 3,4:9,10-tetracarboxylic acid bisimide (PBI) is a n-type semiconductor and has an outstanding capability to form one-dimensional stacks through π-π stacking interactions in solution and in the bulk state. The introduction of aliphatic chains at the imide groups of PBI leads to oligomeric aggregates through π-π stacking interaction[11]. Further additional noncovalent interactions lead to further extended columnar assemblies in solution. The fibrous π-stacked aggregates of PBI organogelator **1** (Figure 5) have a large contact area and continuous charge-transporting pathways, which were applied to a self-sorting gel system with an oligothiophene organogelator to produce p-n heterojunctions for organic photovoltaics[12].

The application highly directional CMHB interaction in the orthogonal direction to the staking axis of π-conjugated molecules results in a more hierarchical construction of supramolecular assemblies of PBI through supramolecular polymerization (Figure 6).
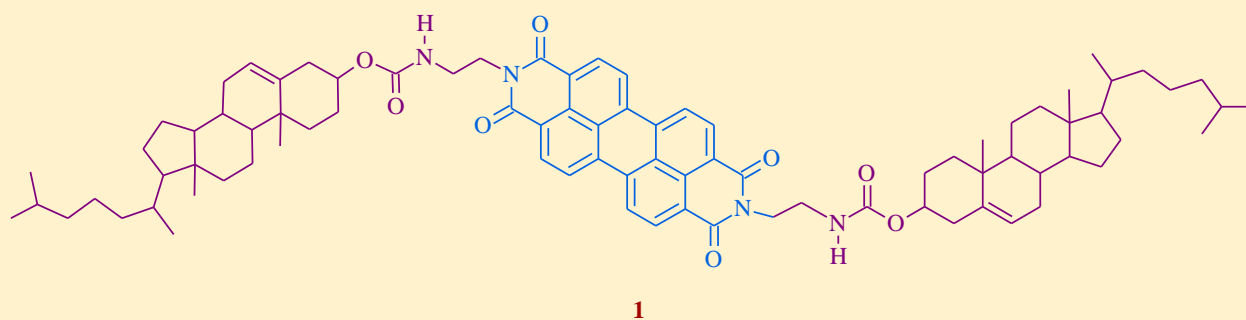

1

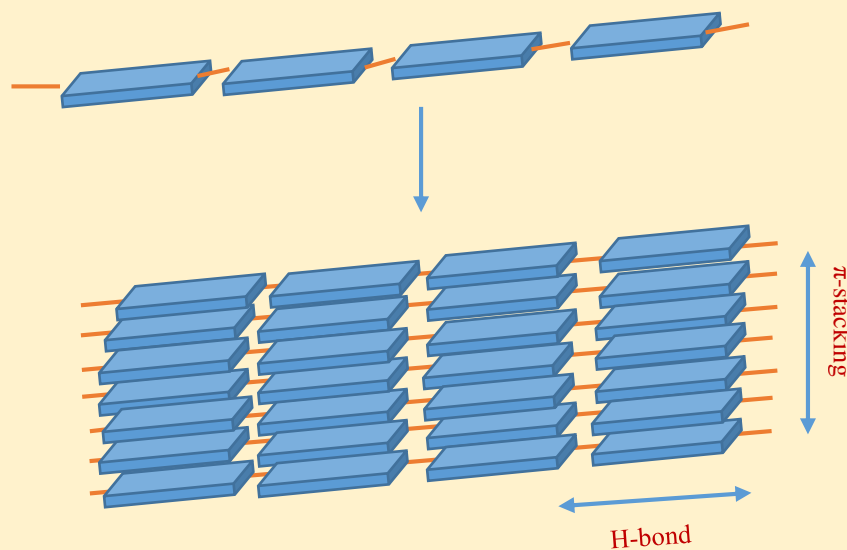**Figure 5.** Structure of amid-functionalized PBIs.

Figure 6. Schematic illustration of the hierarchical organization of extended supramolecular polymers.

This strategy was employed using *N,N'*-unsubstituted PBI derivatives **1** with bulky phenoxy substituents at the 1,6,7, and 12 positions of perylene core and a series of ditopic melamines **2** with long alkyl chains (Scheme 3)[13].
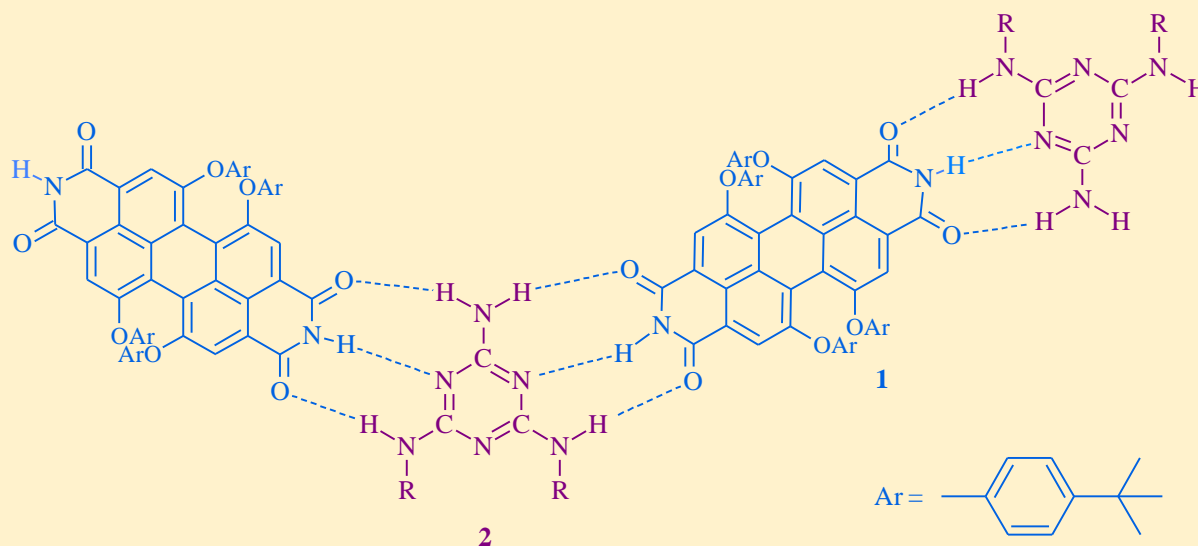
Scheme 3. Structures of PBI **1** and melamine **2**. R = *n*-C_6H_{13}.

5. Conclusion

After decades of widespread applications of inorganic materials in the field of electronics, the superior characteristics of organic semiconductors has spurred the development of their applications in electronic devices. Accordingly, new avenues of rich variety of applications are expected to follow in the near future. In turn, the remarkable expansion of their applications in optoelectronic field create a great challenge for chemists to invent the smart material and process that matches the demand of industrial interest.

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Snapshots of some topics of interest of recent notable advances in chemistry

Atef S. Iskander

Managing Director / Founder
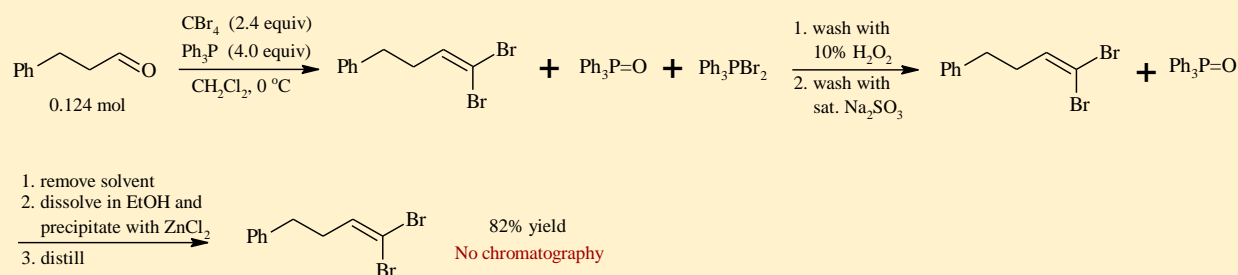
Removal of Triphenylphosphine Oxide Byproducts

An efficient method is reported to remove triphenylphosphine oxide (TPPO) byproducts in organic reactions. The method is based on the strategy that mixing $ZnCl_2$ with TPPO precipitates a TPPO-Zn complex in polar solvents.

Triphenylphosphine (TPP) reagent employs as a reductant in a range of organic reactions. In these reactions, the triphenylphosphine is transformed to triphenylphosphine oxide (TPPO). The separation of TPPO from the reaction products is often somewhat problematic, especially in polar solvents. To overcome such problems, an efficient method is demonstrated, that TPPO can be conveniently removed from reaction mixture by precipitation with $ZnCl_2$ in polar organic solvents, including EtOH, EtOAc, ^{i}PrOAc, and ^{i}PrOH with an optimal ratio at a 2:1 ratio of $ZnCl_2$ to TPPO and without need for column chromategraphy. This purification tool tolerates many common functional groups, such as alcohols, aldehydes, amides, and some nitrogen heterocycles. For example, carbazole-forming reaction, Corey-Fuchs, and the Mitsunobu reaction were examined to explore the efficiency of this method (Scheme).

Carbazole-forming Reaction
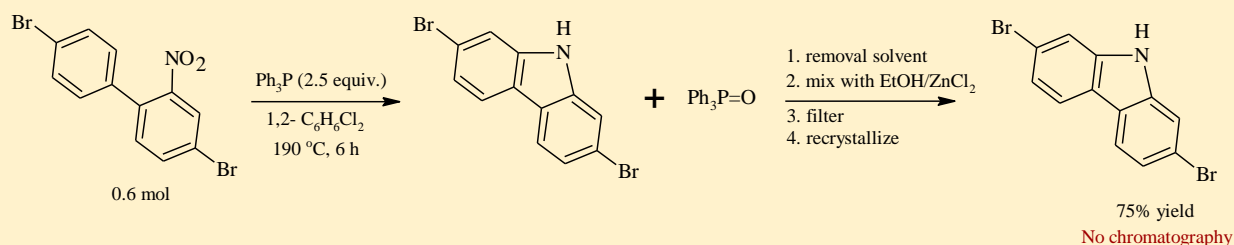
Corey-Fuchs Reaction

Mitsunobu Reaction
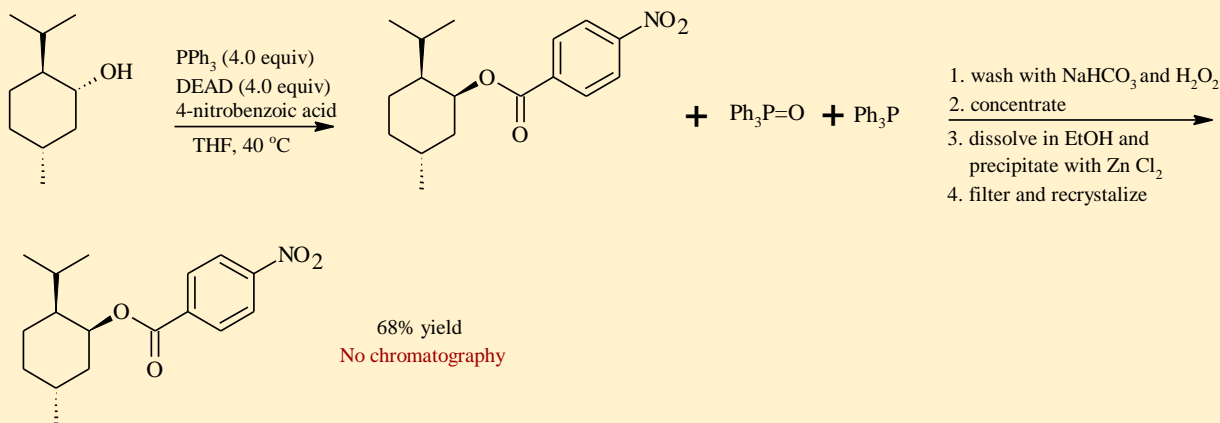
Scheme Removal of triphenyphosphin oxide by ZnCl$_2$.

This method showed its reliability in the large-scale, and will provide a substantial progress for many reactions that use triphenylphosphine as a reductant.

Review

D. C. Batesky, M. J. Goldfogel, D. J. Weix, *J. Org. Chem.,* **2017**, *82, 9931-9936.*

Improved Detection of Amino Acids in Hydrophilic Interaction Chromatography Electrospray Tandem Mass Spectrometry

A series of carboxylic acids has been investigated as additives in the HILIC ESI-MS/MS method to analyze the amino acids. With the addition of these acids to the mobile phase, the detection sensitivity and the tailing factor of acidic and basic amino acids were greatly enhanced. The oxalic acid has been found on top of the investigated acids.

Most of the analysis methods of amino acids samples do not achieve enough retention and detection sensitivity, whether they are proceeded by RP-HPLC-UV detector method, due to the nature of amino acids as amphoteric compounds, or by reversed-phase LC-MS, in which the mobile phase contains formic acid or acetic acid as a method to improve the retention value and ionization of these samples. Since most of amino acids show high polarity with low molecular weights. Therefore, derivatization has been used to improve peak shape and eliminate carryover. However, the derivatization has somewhat drawbacks such as time-consuming, reagent interference, side reactions, poor reproducibility, and derivative instability. To overcome these limitations, hydrophilic interaction chromatography (HILIC) method has been developed to analyze amino acids taking advantage of its ability to retain polar analytes and its convenience to combine with MS analysis by employing formic acid/ammonium formate or acetic acid/ammonium acetate as buffer salts to get optimized peak shapes.

In light of this, Wang and his co-workers investigated eight single acids/diacids, which contain different pKa in the range 0-5 as the mobile phase additives in the HILIC ESI-MS-MS method to analyze the amino acids. These carboxylic acid additives are: trifluoroacetic acid, oxalic acid, maleic acid, malonic acid, phthalic acid, salicylic acid, benzoic acid, and acetic acid. They showed distinct enhancement to the signal intensity and the tailing factor of acidic and basic amino acids. Among them the oxalic acid gives the highest signal intensity enhancement of aspartic acid (Asp) and glycine (Gly) and the lowest tailing factor of arginine (Arg), histidine (His) and lysine (Lys). In addition, the chromatographic shape of basic amino acids can also be improved.

The strategy of using additive acids to improve the signal intensity of acidic amino acid in ESI mass spectrometry relies on ion inhibition effect as well as the relationship between ionization influences of analytes in ESI ion-source with the property of mobile phase, such as conductivity, surface tension of solution, viscosity, and concentration of electrolytes.

It is proposed that the enhanced performance of oxalic acid is related to its hydrogen bond interaction between the carboxyl and amino acid. In formic acid/ammonium formate buffer mobile phase, the oxalic acid has one carboxylate anion. Electric field action of the acid can increase the stability of this carboxyl anion and the structure of this anion can subsequently reduce the polarity of amphiprotic amino acids leading to increasing the protonated of acidic amino acids and the retention time of basic amino acids (Figure).
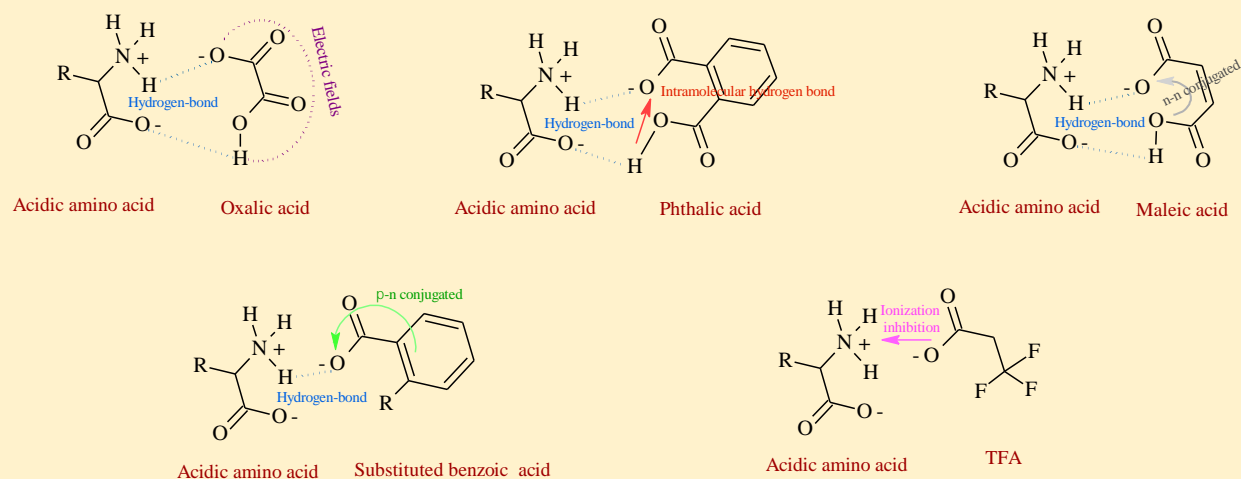

Figure proposed hydrogen bond interactions between amino acids and carboxylic acids.

The method had been applied for quantitative analysis of a range of amino acids in a pharmaceutical company and proved to be effective.
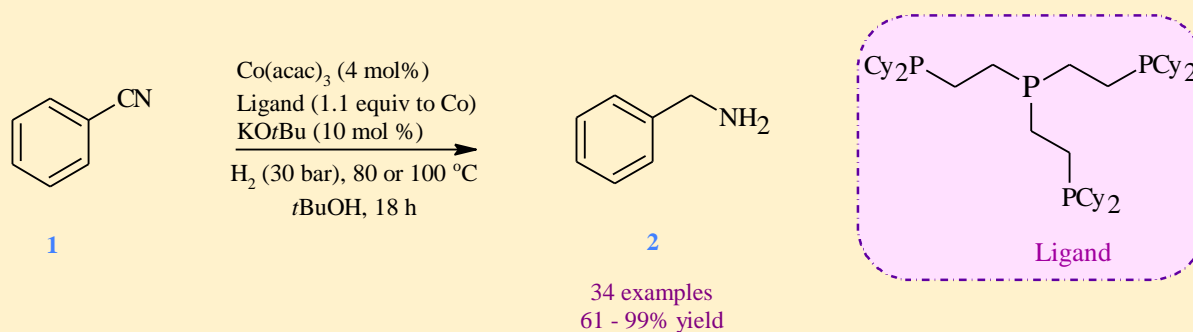
Review

D. Yin, X. Hu, D. Liu, W. Du, H. Wang, M. Guo, D. Tang, *Euro. J. MS,* **2017**, *23*, 98-104.

Selective Catalytic Hydrogenation of Nitriles to Primary Amines

A selective new procedure is described for the catalytic hydrogenation of a wide range of hetero-aromatic and aliphatic nitriles to primary amines based on an efficient cobalt/tetradentate phosphine catalyst system.

Amines are versatile building blocks in the synthesis of a wide variety of products. Most of the known synthetic methodologies of primary amines rely on the reduction of nitriles which constitue a valuable and atom-economical procedure. However, the catalysts employed to achieve nitrile reduction suffer from important limitations in terms of selectivity, toxicity, or too expensive. In this regard, Beller and co-workers adapted a strategy that based on using non-noble metal complexes in combination with non-pincer-type ligands for the catalytic hydrogenation of nitriles to primary amines.

The coblat-catalyzed hydrogenation of benzonitrile **1** to benzylamine **2** was achieved using tri[2-(dicyclohexylphosphino)ethyl]phosphine as a ligand in the presence of Co(acac)$_3$ and KOtBu and tBuOH as a solvent at 80-100 °C under 30 bar H$_2$ for 18 h (Scheme).

Scheme . Hydrogenation of benzonitrile to benzylamine.

A variety of (hetero)-aromatic and aliphatic nitriles were hydrogenation in good to excellent yields by employing in situ-generated non-noble metal system.

Review

R. Adam, C. B. Bheeter, J. R. Cabrero-Antonino, K. Junge, R. Jackstell, M. Beller, *ChemSusChem,* **2017**, *10*, 842-846.

DIPEA-promoted One-pot Process of Perfluoroalkylated Indolizinylphosphonates

An effiecient one-pot procedure is described for the synthesis of perfluoroalkylated indolizinylphosphonates *via* a three-component tandem reaction of pryidines, bromo-methyl ketones with perfluoroalkynylphosphonates.

Indolizines play a key role in synthetic and medicinal chemistry. Thus, the incorporation of a perfluoroalkyl (lipophilic) and phosphonate group into indolizine core may serve as a valuable building block for the construction of complex molecules.

A synthetic pathway was reported for the synthesis of indolizines bearing both perfluoroalkyl and phosphonate groups within one molecule *via* the reaction of pyridine **1** (2.0 mmol) and ω-bromoaceto-phenon **2** (2.0 mmol) with diethyl (3,3,3-trifluoroprop-1-yn-1-yl)phosphonate **3** (1 mmol), using DIPEA (1.0 mmol) as a base in THF (5 ml) at room temperature for 12 h (Scheme 1).
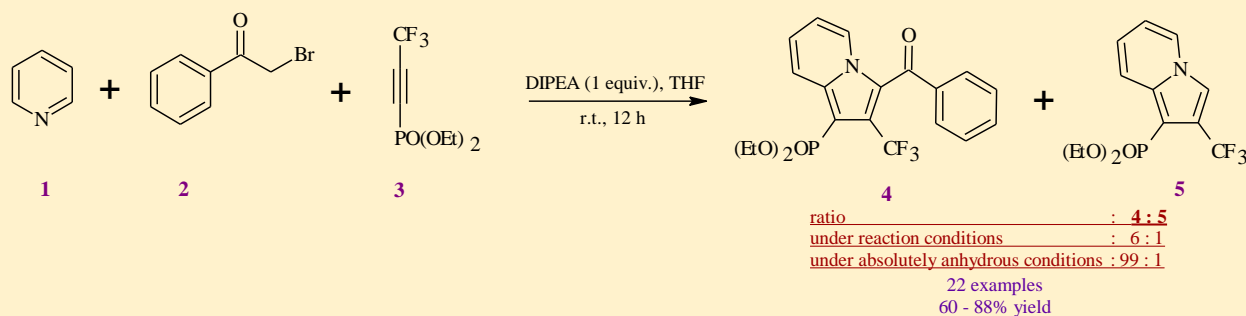
Scheme 1. The synthesis of perfluoroalkyated indolizinylphosphonates.

The authors speculated that the formation of the product **5** might be resulted from a nucleophilic addition of hydroxyl anion to ketocarbonyl group in **4** and subsequent elimination of the formed acid moiety. Hydroxyl anion was believed to be generated from moisture in the presence of base (Scheme 2).

Mechanism
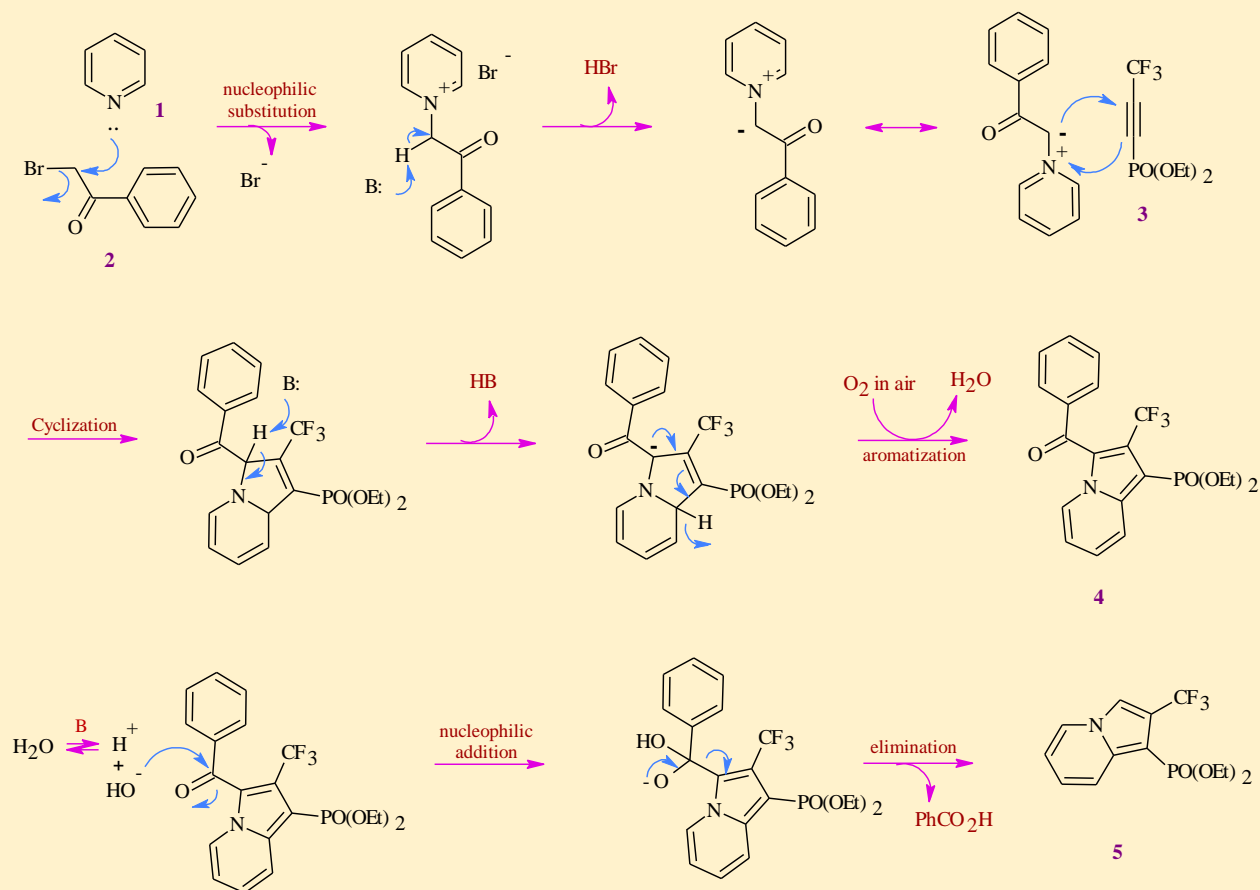
Scheme 2. The proposed mechanism for the formation of **4** and **5**.

This method is effiecnt and simple which provids the desired products with good yield and feasturs a broad substrate scope and excellent functional-group tolerance.

Review

H. Liu, D. He, Z. Sun, W. He, J. Han, J. Chen, H. Deng, M. Shao, H. Zhang, W. Cao, *Tetrahedron,* **2018**, *74,* 135-141.