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# **Small Organic Molecules in Modern Technology**

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## ***List of abbreviations***

Bn

Da – Dalton – unit of molecular mass

DSSC – Dye sensitized solar cells

D- $\pi$ -A – Donor- $\pi$ -system-Acceptor (Section 2.1).

Et

FDA – Food and Drug Administration – Principal authority of drug

FET – Field effect transistor – a transistor directed by the electric field.

FLP – Frustrated Lewis Pair (Section 2.3)

HOMO – Highest occupied molecular orbital

HTM – Hole transporting material

ICT – Intramolecular charge transfer

<sup>i</sup>Pr

LED – Light emitting diode

LUMO – Lowest unoccupied molecular orbital

MALDI – Matrix assisted

Me

Mes

NMR

NOE

NOESy

OFET

OSC

Ph

Ro5

ROESy

SET

<sup>t</sup>Bu

TCNQ

TPA

# 1. Introduction

## *1.1. Definition of the small molecule*

Following text deals with the core term “small molecules”. This term, although widely used in different connotations, does not have one universal definition. The need to sort the molecules to small, medium and large has occurred in parallel in multiple areas of chemistry, material science and life sciences. Each one of them seems to follow its definitions for its own purposes until today. The differences between the definitions can be subtle or principal. To make the matters worse, even within particular branches of science the borders between the terms small, medium and large molecules are somewhat blurred and full of exemptions.<sup>1–3</sup> A molecule can fall into category “small molecules” in some circumstances whereas in other circumstances it can be classified as “medium” one. In this situation, this publication provides its own definition which sourcing from the variety of definitions given elsewhere as their superposition of a kind.<sup>4</sup> Yet, before giving such definition, it is always useful to defend it with the underlying survey, from which it arrived.

If one tries to sort the “magnitude” of the molecule to small, medium and big molecules, several measurable and easily obtainable parameters come to mind. Molecular weight, number of atoms, repetitiveness of structure come to mind, to name some.<sup>5</sup> Yet, neither of the parameters is without a pitfall connected to its use, when too mechanistic. Molecular weight, is a good parameter do quantify the “magnitude” of a molecule of organic nature (containing predominantly carbon, nitrogen, oxygen and hydrogen), yet it has some limits when a heavy atom is present in the structure.  $M_w = 1000$  Da can

mean more than 80 carbon atoms, yet less than 10 atoms of palladium or less than 5 atoms of Bismuth. A problem of the same nature emerges when the number of atoms is used as a parameter. Other parameters such as surface or volume of electronic cloud, standardized diameters etc. have their own difficulties as they are hard to obtain, highly dependent on computational and/or spectral method used for their determination and usually can comparably characterize only the molecules of similar nature or geometry. For its relative simplicity, widespread use and the highest degree of universality, the molecular weight is indeed used the most among all the discussed parameters. And, therefore, this parameter will be discussed the most as a matter of “magnitude” of molecule, the other aforementioned parameters will be taken in account only when the method requires it.

The first scientific discipline which started to sort the molecules to small, medium and large (polymeric) is arguably analytical chemistry. In this area, the determination of magnitude of molecule and its subsequent classification depends highly on the analytical method used and its instrumental as well as practical limitations.<sup>6</sup> The separation methods are probably among the first who have started this classification. Various separation methods are used and in some cases even designed to analyse molecules of various magnitude. Some methods, such as size-exclusion chromatography<sup>7</sup> or mass resolution liquid chromatography<sup>8</sup> have a primary goal to discriminate certain molecules of particular MW and separate them. Small molecules are usually those who are suitable for gas chromatography, which are usually considered up to 600 Da, certainly not more than 1000 Da.<sup>9</sup> Medium size molecules are considered those who fall into the interval 600 (1000) Da to 10 000 Da and large molecules are considered bigger than 10 kDa. A specific term for separation methods is



“large molecule” which are molecules with molecular weight exceeding approx. 30 kDa<sup>10</sup> often mixed up with a term macromolecule or polymer as most of such big molecules are indeed some kind of polymers.<sup>11</sup>

Mass spectrometry, often used with the separation methods, term small molecule and classification of the molecular magnitude differs by the ionization technique as well as the type of detector. Concerning the ionization techniques, it can be usually said that hard ionization techniques (especially electron ionization) are more suitable for small molecules. Therefore, the term small molecule may be defined by the maximum suitable molecular weight for an ionization method designed to preferably target small molecules. Electron ionization itself allows ionization of the molecules not larger than 2000 Da (when rich in halogens and/or containing a heavy metal(s) as a central as a central atom(s) in coordination complex), which is often taken as a limit the term “small molecule” according to mass spectrometry.<sup>12</sup> More usually, though, the limit of 600 Da, which is considered to be limit for In MALDI (matrix assisted laser desorption/ionization) small molecules are considered not bigger than 500 Da, except of special cases, such as halogen (especially bromine and iodine) rich compounds.<sup>13</sup> Another view on this topic from the standpoint of mass spectrometry offers the capability of particular types of detectors. There are detectors capable of detecting only small and medium sized molecules and detectors specially constructed for detection large molecules and polymers (such as Orbitrap®, TOF detectors, etc.). This discussion, though, does not usually interfere in the divisions of magnitude of molecules. So this point of view remains mentioned in this text without further elaboration.

Another division on small, medium and big (large) size molecules can be seen in NMR spectroscopy. Nuclear Overhauser Effect (NOE)<sup>14</sup> and its exploitation in several spectroscopies (NOESy, ROESy).<sup>15</sup> This effect can acquire positive, negative values or close to zero values in dependence on the rotation correlation time ( $\tau_c$ ), which is basically the time which is necessary for a molecule to rotate one radian along its axis. This time depends on the properties of the environment (solvent, temperature, hydrostatic and atmospheric pressure), more importantly it is under the constant external conditions function of molecular weight of given molecule. Under normal experimental conditions and in common NMR spectrometry solvents, NOE can sort the molecules by their molecular weight to small molecules (having positive value of NOE) up to 700 or 800 Da, medium sized molecules (having NOE close to or equal to zero) between 700 (800) Da and 1200 (1500) Da and large molecules (having negative value of NOE, usually bigger in absolute value than small molecules) over 1200 (1500) Da.<sup>14,16</sup>

Special chapter is the definition of “small molecule” in pharmacology and pharmaceutical chemistry. The most general definition according to a general pharmacology is that a “small” molecule is small enough to be absorbed from the intestines or generally from the digestive system and small enough to penetrate some other biological barriers in human body (blood-brain, blood-air, blood-ocular).<sup>17</sup> Usually small molecules in this sense correspond to a Lipinski’s rule of five (Ro5),<sup>18</sup> which operates with molecular weight 500 Da, which can be after meeting some other conditions raised up to 900 – 1000 Da. The Ro5 predicts well the “small” character of a molecule from the biological/pharmacological standpoint. This rule is included in official definition of small molecule by the Nature family of scientific journals,<sup>19</sup>

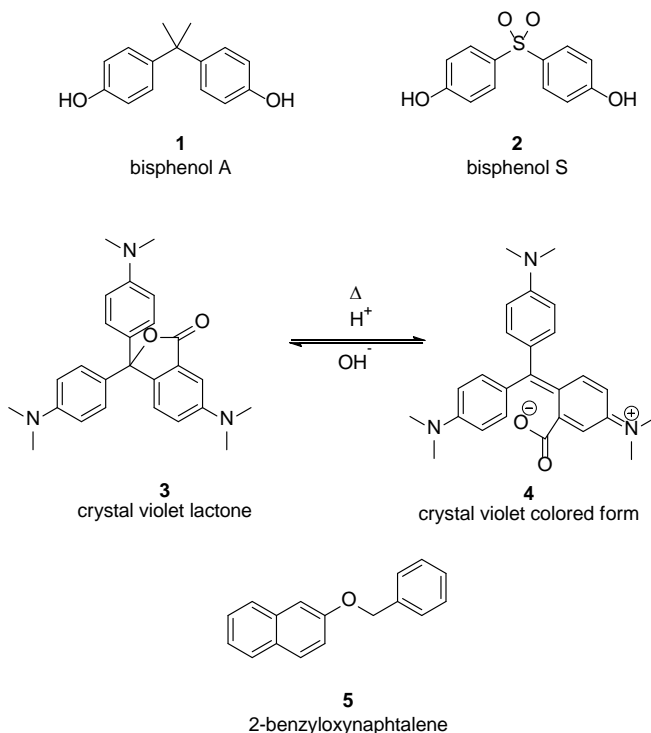
although over there the definition is adjusted by capping the molecular weight of a molecule to 800 Da.

The construction of definition used in this publication is, as it was aforementioned, trying to synthesize and superpose the definitions touched above. In further text, *organic molecules not larger than 1000 Da with not more than 100 atoms where a repetitive structure is not repeated more than three times* will be considered as “small molecules”. Physiological peptides, oligosaccharides and (exceeding  $n = 3$ ) and low molecular mechanically interlocked molecular systems (rotaxanes, catenanes, etc.) otherwise corresponding with the definition will not be considered as small molecules as these types of molecules usually fall into a category of their own.

### *1.2. Small molecules as an omnipresent entity in everyday life*

Despite the recent successes of polymers,<sup>20</sup> carbon-based materials,<sup>21–23</sup> biologics, nanoparticles, etc., small organic molecules are still the most common chemical entity used as everyday chemicals. The traditional industrial and technological branches, such as food industry, cosmetic industry, pharmaceutical industry, still use them in a growing scale. In the E-code chemicals used as food additives more than a half of singular E-items are small organic molecules (followed by inorganics and elements, and biopolymers),<sup>24</sup> most of the white cloths and fabrics, paper and plastics contain optical brighteners most of which are also often small molecules.<sup>25</sup> As of 2019 more new drugs and therapeutics newly successfully registered in FDA were also small organic molecules. Small molecules can be found as dyes and pigments not only as food additives, but also in inks, for example of printed newspapers.

But it is not only old or obsolete technology, such as food technology, newspaper and book print, etc. In fact, small organic molecules play an important role as for example dyes or pigments in digital photographs<sup>26</sup>. Alignment layer of LCD screens in everything starting with calculators and digital watches up to the smartphones and LCD televisions is formed by long but small organic molecules.<sup>27</sup> Even if principal material of a technological product (e. g. plastic) bear a number of additives such as emollients and plasticizers are present in the mass. Relatively recent technology of thermo-paper print uses bisphenol A or bisphenol S (**1**, **2**; Figure 1) as thermo-developers, leuco-dyes just like crystal violet lactone (**3**, Figure 1) as colorants and other small organic molecules as such as 2-benzyloxynaphtalene (**5**, Figure 1) as sensitizers. In an ordinary receipt obtained by shopping groceries, or as a document coming from ATM-machine whole palette of small organic molecules is present. The nature of small organic molecules has a majority of detergents.



**Figure 1** Small organic molecules used in thermo-paper print

Small organic molecules, therefore, are met in everyday life in almost any instance. We interact with them by dressing clothes, in making laundry, washing dishes, eating food or shopping and by using smartphones, laptops, etc. In fact, the number of small organic molecules, industrially produced and technologically relevant tends to increase with an increasing impact of technology to our lives. This, of course, raises significant concerns. The arguable benefits of these compounds are traded off with undeniable problems. The residues of small molecular drugs in the environments can potentially harm individual species or whole ecosystems. Some of dyes and pigments designed and fabricated to be durable structures not capable of

undergoing a significant change in their technological application pose a challenge towards their liquidation and or recycling.

Either way, small organic molecules as a part of modern technology undeniably belong to our lives and play an important role. Although other types of materials, such as polymers, nanoparticles, carbon-based materials, biologics (not only in strictly medicinal point of view), polymers etc. sometimes compete with their use, usually are aforementioned materials more or less complementary to the small molecules, moreover their use often creates a need for further use of small molecules. Therefore, as far as they are sometimes considered less prospective and less future-promising, the usage of small molecules will increase in foreseeable future and they are important to be known and studied.

### *1.3. Scope of the publication*

The aim of this publication is not, and cannot be, to describe all the small molecules present in modern technologies. As it is indicated above, their quantity exceeds any possibilities of a text like this one, moreover the use of small molecules in modern technology is ever-changing and in there is a big risk that the information given in the text would be outdated in the moment of its edition.

This publication lists the most promising and most remarkable small organic molecules in modern technology. Prospective and futuristic technologies such as organic semiconductor technologies (OLED, OFET, solar cells), optoelectronic properties (modulation of laser wavelengths), storage of information and hydrogen technologies (e. g. fuel cells) and technological

medicine are discussed. The main focus of this text is to discuss predominantly the design structure-property relationship in the small molecules, to reveal some aspects of their design making them suitable for technological purposes.

Certain branches of contemporary technology, such as small molecular drugs, detergents, (photo)catalysts (e. g. used in various chemical industrial processes) and other compounds not primarily related to the area of modern especially semiconductor technology.

## 2. Remarks on design, synthesis and retrosynthesis of technologically promising small organic molecules

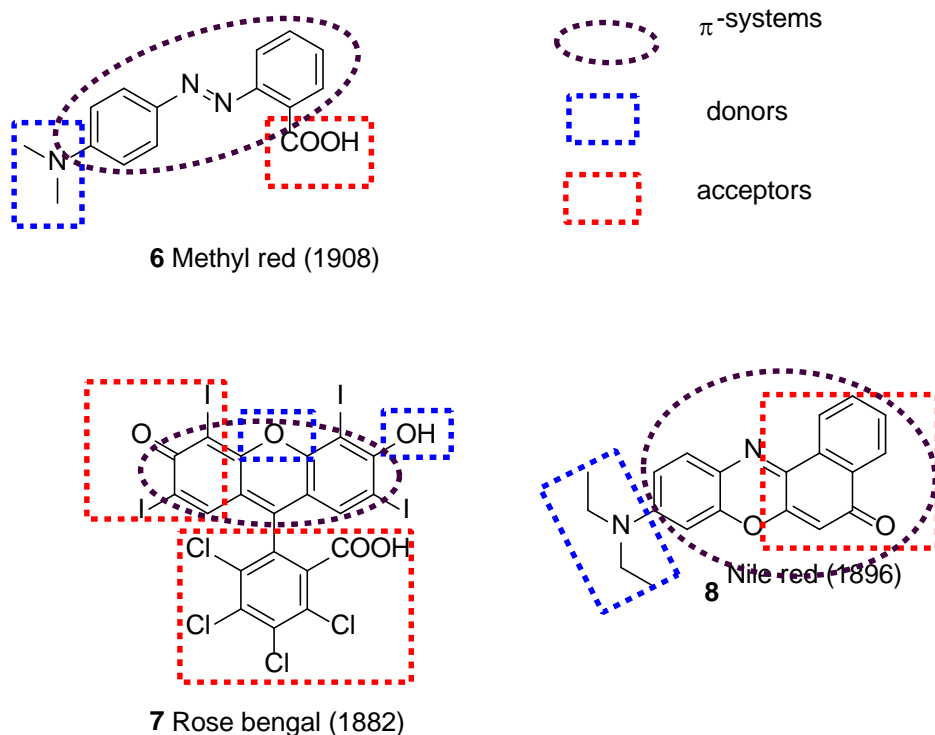
Concerning the scope of the publication (Section 1.3.), three molecular designs were picked up as the most promising and the most potentially useful in variety of future technological applications. The first one is push-pull design already having a tremendous impact on design and synthesis novel small molecular materials as dyes, pigments, optical brighteners, but especially in various semiconductor, (non)linear optical and other applications. The increased need of data storage increases a demand of molecular design capable of transforming information. Small molecules appear to have a promising role in data storage (section 2.2). (Non)linear optics and optoelectronics (Section 2.1 and Section 2.4), solar cells and other semiconductor applications, fuel cells and other high tech and high added-value applications are another branches where small molecules are playing and probably will play a significant role. Several molecular designs, such as push-pull design (Section 2.1) and frustrated Lewis pair design (Section 2.3) appear to have the most success among them. Following section identifies and deals with these types of design adding a commentary on their (retro)synthesis and on their design.

### *2.1. Push-pull design of $\pi$ -systems*

Although push-pull design, co-presence of donor and acceptor moiety in conjugated  $\pi$ -system, has occurred and has been theoretically worked out at in the second half of 20<sup>th</sup> century and the term itself and its use begun around the turn of the centuries<sup>28</sup>, this design had been used before, especially in construction of organic dyes since the beginnings of synthetic colour-



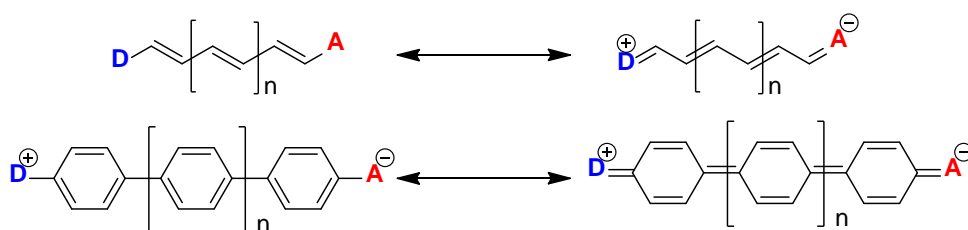
chemistry. Figure 1 shows several organic dyes firstly synthesized before 1<sup>st</sup> World War where push-pull design can be tracked and which can be called push-pull molecules even though their first creators did not probably call them this way. In most of the traditional classes of organic dyes (azo-dyes, anthraquinone dyes, etc.), there is at least one structural subclass which can fall into the category of push-pull molecules.



**Figure 2** Old organic dyes bearing the push-pull motive. In the brackets the year of first synthesis is given.

Nowadays, the push-pull design gained prominence among small organic molecules used for the photonic, semiconductor and optoelectronic purposes. Variety of uses starting as sensing dyes for various solar cells,<sup>29,30</sup> continuing the various semiconducting design, they can play the role in photocatalysis,

including those photocatalyses that are involved in CO<sub>2</sub> utilizing reactions, as chemical sensing detectors, as chromophores capable of changing/tuning laser wavelengths and in many other applications. Among one of the most interesting is that simple push-pull chromophores can be also utilized as protection agents for example for steel corrosion.<sup>31</sup> The backbone of such design is a  $\pi$ -conjugated system, often aromatic or anti-aromatic. The principal point of this molecular design is the co-presence of electron donor (push) and electron acceptor (pull) moieties (Figure 3). In such molecules, often abbreviated *D*- $\pi$ -*A* (*Donor*- $\pi$ -*linker*-*Acceptor*) systems a phenomenon described as intramolecular charge-transfer (ICT) is present.



**Figure 3** Examples of push-pull (*D*- $\pi$ -*A*) design on simple molecule models. Basic principle of ICT.

The nature of the ICT consists in the interaction between donor and acceptor through conjugation (Figure 3). Therefore, the best ICT performance in the molecule occurs the most when donor and acceptor are in the positions which allow mutual conjugation. In the most simplistic terms, ICT causes the formation of additional allowed electronic levels, where electrons can migrate or be excited. This plurality of electron levels, usually placed on the energy scale somewhere between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the non-*D*- $\pi$ -*A* system. This means *D*- $\pi$ -*A* molecules often perform lower band gap, higher Stokes shift, larger wavelength of the reddest UV/Vis absorbance maximum, they are often

colourful (going from yellow to deep violet) and they have some interesting (non)linear optic properties (they can be fluorescent, phosphorescent, etc.), some of them have even magnetic and magnetooptic capabilities, etc.

Moreover, the linear  $D-\pi-A$  systems (such as the ones shown in Figure 3) are more or less a minority of the entire family of push-pull molecules. A number of shapes and mutual positions of donors and acceptors in them is possible, synthesized and applied. The most pedagogically demonstrative is their classification by the alphabet letters. I- (linear), H-, L-, V-, X- or Y-shaped molecules can be described by their shape, most of them with some varieties in occurrence of donors and acceptors in their design.<sup>32</sup> Arguably Z- (or N-), W- (or M-), or E-shaped molecules and several other can be also spotted in literature accepting the alphabet classification paradigm, although they were not classified as such, officially. The more complex than linear shapes of push-pull systems bring even more plurality and complexity into the possible electronic levels resulting in a complex portfolio of materials applicable in wide range of optoelectronic, semiconductor and other applications. Push-pull systems are usually planar and non-planarity is considered as a limit in proper ICT.

From the orbital standpoint it can be stated that electron donors have principally effect on the energy level of highest occupied molecular orbital (HOMO), typically increasing its energy level while electron acceptors, complementarily, does decrease the energy level of electron acceptors. Yet, the situation is rarely clear and straightforward. For example, 1,3-donor-acceptor substituted benzene ring usually does have higher wavelength of reddest maximum of absorbance in the UV/Vis spectroscopy than the 1,4-donor-acceptor substituted ones. On the other hand, the absolute value of

absorbance and absorbance/concentration ratio in those maxima is usually in favour of 1,4-substituted one. This is true for 4(3)-nitroaniline<sup>33</sup> or 4(3)-hydroxybezoinitrile<sup>34</sup>, etc.

The nature and behaviour of ICT depends of a variety of parameters. The structure-properties relationships are sometimes counterintuitive and complex. The best way to simplify them is via separate evaluation of all of the three parts of push-pull molecules, the donor, the acceptor and the  $\pi$ -linker. There are several parameters to characterize the predictive effectivity and strength of a donor or an acceptor each of them has its own advantages and pitfalls. In fact, only the solution of particular  $\pi$ -skeleton with variation of *D*- and *A*-substituents by advanced quantum chemistry calculation controlled by the experimental data can provide a detailed insight into predictive effectivity and/or efficiency of particular donor and acceptor on the ICT properties. Yet, there is a need for a predictive parameter capable of anticipation the prospects of using particular acceptor for example in yet unknown small molecular skeleton.

On the other hand, simple truths, such as that molecule should be planar and donors and acceptors should be as strong as possible fails. For each purpose various forms of intramolecular charge transfer are required and intramolecular charge transfer itself can

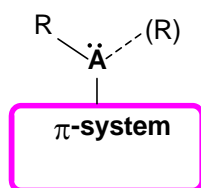
Despite the existence of more modern and more precise parameters (e. g. Pytela  $\sigma_p^i$  parameters) the Hammett equation parameters  $\sigma_p$  or  $\sigma_p^{+/-}$  appear to be the best predictive and/or easy to obtain as well as the best tabulated “single number” parameters for prediction the donor/acceptor behaviour. Avoiding the details of the Hammett equation theory the  $\sigma_p$  or  $\sigma_p^{+/-}$

parameters characterize the “willingness” of particular substituent to withdraw/donate electrons from/into the particular structure. In the most simplistic terms when  $\sigma_p$  parameter is less than 0, it means that the substituent moiety is overall electron-donating, and when the parameter is more than 0, it means the substituent moiety is overall electron-withdrawing. As a standard with  $\sigma_p = 0$  a hydrogen atom (as a substituent or moiety) is put. The absolute value of  $\sigma_p$  further characterizes the relative strength of particular donor/acceptor.

### 2.1.1. Electron donors

From basic principles of organic chemistry, both induction and mesomeric effects can affect the electron donors. As far as the *D- $\pi$ -A* systems are exclusively built on  $\pi$ -conjugated systems, the mesomeric effect is indeed more important. Hyperconjugation and electron donating effects of d-electrons are also of an importance to the construction of electron donors. Schematically, most electron donors can be projected as moieties having an atom with free electron pairs (or available d-electrons) bonded directly on the  $\pi$ -conjugated skeleton (Figure 4). Electron donors successful in recent push-pull systems can be sorted by the central donating atom. Typical donating atoms are nitrogen and oxygen, carbon based moieties can also play a role of electron donors. Among the other elements sulphur plays a dominant role. Electron donors can be also metals. In fact, alkali metals and alkaline-earth metals would be the most potent donors overall, bonds like C-M, or N-M, which would be somewhat inevitable in systems with those donors are usually weak and the molecules such as these would be chemically unstable and could not play a role in any viable technological application. Therefore, principally transition metal-based electron donors are almost exclusive as donor moieties in *D- $\pi$ -A*

molecules as the structural feature. In all of the cases of transition metals as well as in the rare cases of non-transition metals used as electron donor and/or skeletal part of a  $D\text{-}\pi\text{-A}$  molecule, the coordination complexes are used. It is worth mentioning that ferrocenyl group is the most prolific of the metal-based donors. Among the rest of the potential donor, field non-metals and metalloids, such as phosphorus, silicon, can be also used as electron donor in  $D\text{-}\pi\text{-A}$ , yet so far they are rare and their industrial and/or technological relevance is questionable.

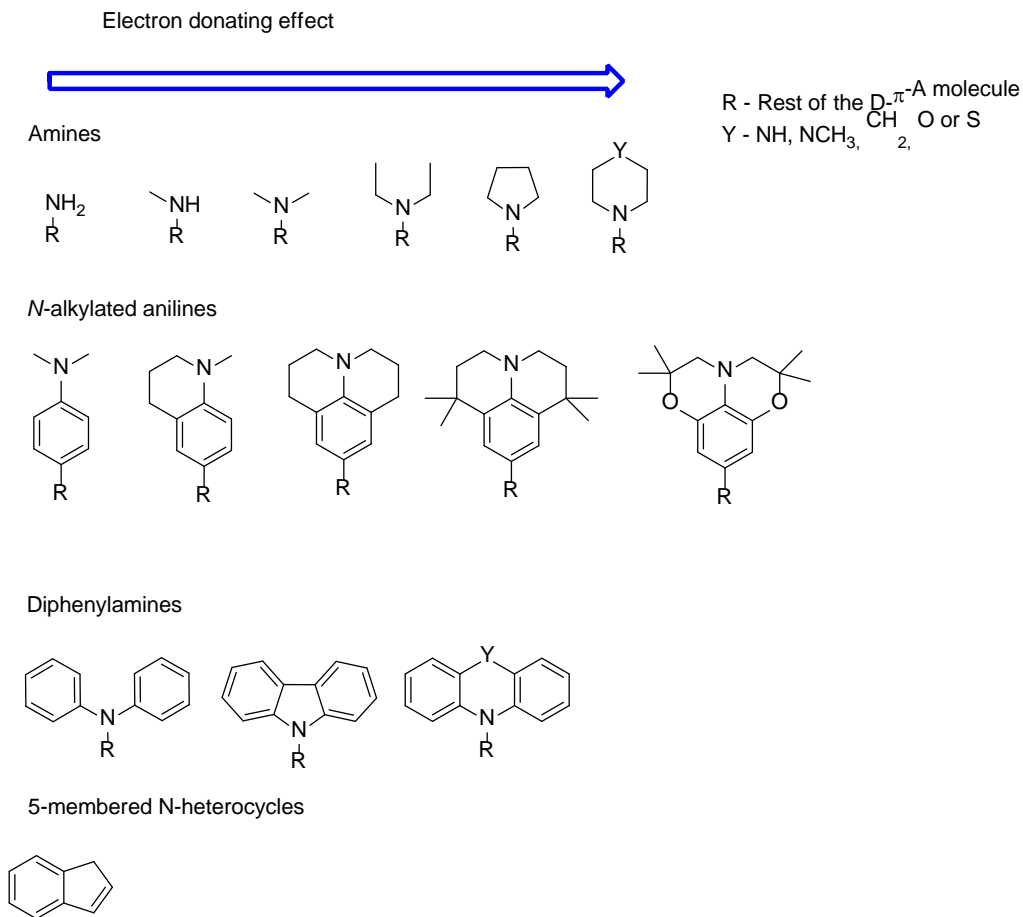


A - typically N, O, S  
R - substituent with -I effect

**Figure 4** Typical construction of electron donor.

The construction of donor part of the  $D\text{-}\pi\text{-A}$  molecule is best demonstrated on arguably the most prolific nitrogen-based donors. Amino-nitrogen with the formal oxidation state  $-III$  is the essence of virtually all nitrogen donors. The simplest nitrogen-based donor moiety is undoubtedly  $\text{-NH}_2$  ( $\sigma_p = -0.66^{33,35}$ ). This substituent is suitable for applications where the molecule can or should be compatible with aqueous environment, soluble in water or overall polar solvents. Beyond that, molecules bearing amino- or aniline- group are usually quite reactive and, therefore, incompatible with some other organic and/or inorganic components of particular system. Furthermore, organic amines and anilines are notoriously instable. A step towards better stability of electron

donor is substitution of  $\text{-NH}_2$  with alkyl, aryl or acyl substituents. Acyl substituents may adjust the stability of donor, yet they have radically negative effect on electron-donating ability ( $\sigma_p$  of *N*-acetylamino-moiety is 0.00<sup>35</sup>). Aryl moieties significantly increase a chemical stability of electron donor, while the electron-donating slightly decreasing electron donating capability (*N*-phenylamino and *N,N*-diphenylamino- groups have  $\sigma_p$  equal -0,56 and 0,22, respectively)<sup>33,35</sup>. In contrast, *N,N*-dialkyl- substituted donors have usually even bigger electron donating capacity, than the  $\text{-NH}_2$  group ( $\text{-NHMe}$   $\sigma_p = -0.70$ <sup>33,35</sup>;  $\text{NMe}_2$   $\sigma_p = -0.83$ <sup>33,35</sup>). The electron donating capacity grows slightly with the length of alkyl- chain up to the five or six C-atoms and more with the branching of alkyl chain. On the other hand bis(*tert*-butyl)amino- moiety does not bear the biggest electron donating effect because of steric-hindering effects. A locked geometry of a substituent disabling the C-N bond to rotate and change the position of free electron pair relative to a  $\pi$ -system increases the electron donating capability. The extreme example of that is a julolidin-9-yl moiety which bears incredible  $\sigma_p = -1.9$ ). Conjunction of (substituted) amino-moieties with aromatic ring (e. g. benzene), especially one of five-member electron-rich heterocycles such as thiophene or furan positioned in the line of ICT. Figure 5 provides a survey of nitrogen based electron donor groups.

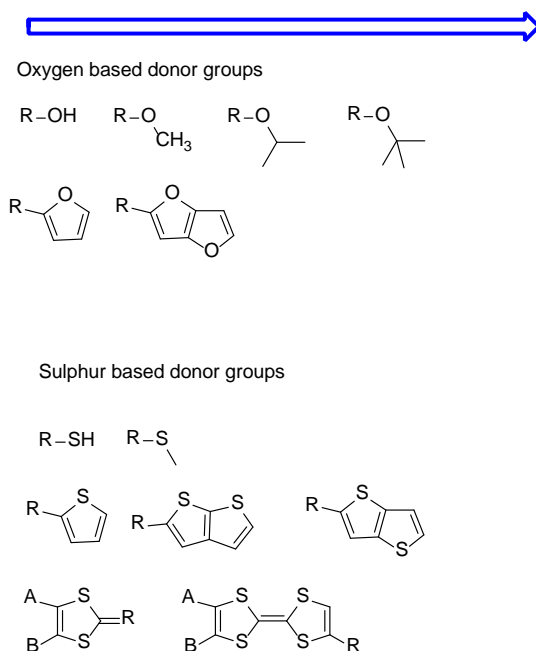


**Figure 5** Nitrogen-based electron donor groups often used in D- $\pi$ -A systems – three structural types with increasing electron donating capability.

Similar principles shown in the nitrogen-based class of donors can be tracked in the other classes of donors, especially for those based on oxygen. Sulphur and phosphorus based electron-donors are usually less potent in comparison with their oxygen and nitrogen analogues. The lower electronegativity of those elements compared with their analogues from 2<sup>nd</sup> period of the table of elements speaking in favour of better electron donating capabilities is compensated by the less convenient geometry of both 3p and



3d orbitals toward the  $\pi$ -orbitals carbon conjugated system. Contrary to that, both sulphur and phosphorus based electron donors perform very well when the polarizability of the molecule is required. The sulphur and phosphorus based donors show a bring usually a significant increase of polarity of excited state of the molecule, which can be exploited in some specific semiconductor applications. Especially sulphur based 5-membered heterocycles are prospective electron donors by themselves. Dithiafulvene or thienothiophenes<sup>36</sup> were multiply demonstrated as prospective electron donors. Figure 6 shows the non-nitrogen donor groups successfully used as electron donors in *D*- $\pi$ -*A* systems.



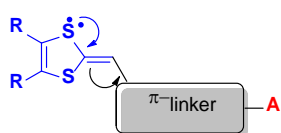
**Figure 6** Examples of non-nitrogen electron donors.

One more noteworthy effect is pro-aromatic construction of electron donors. The pro-aromatic design means that a moiety (donor in this case) is

constructed as an anti-aromatic cycle. That is to say such system bears all of the definition properties of aromatic system (planarity, ring arrangement, conjugation of  $\pi$ -bonds, charges, or free electron pairs, delocalization of electrons, suitable geometric orientation of  $\pi$ -, p- or d-orbitals perpendicular to the plane of particular ring), while having anti-aromatic number of electrons  $4n$ . Such described systems are always two electrons short of, or two electrons exceeding of an aromatic arrangement, which is energetically preferred habitually. In case of electron donors, pro-aromatic donor parts are constructed in the manner of being able to provide an electron pair to the  $\pi$ -conjugated system. The examples of donors constructed this way are given in Figure 7.

**Pro-aromatic/anti-aromatic structure ( $4n$ )**

$$4 \pi\text{-e}^- + 4 \text{ } 3p_z \text{ e}^- = 8 \text{ electrons}$$



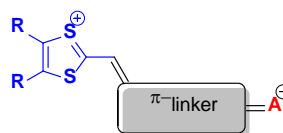
**Dithiafulvene moiety**

R = alkyl, alkyloxy or

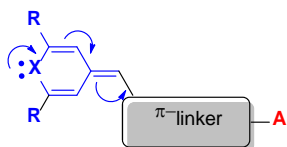
R+R = condensed benzene, or heteroarene ring

**Aromatic resonance structure ( $4n+2$ )**

$$4 \pi\text{-e}^- + 2 \text{ } 3p_z \text{ e}^- = 6 \text{ e}^-$$

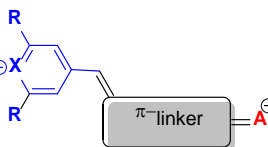


$$6 \pi\text{-e}^- + 2 \text{ } 2(3)p_z \text{ e}^- = 8 \text{ electrons}$$



**Dihydropyridine/4H(thio)pyrane moiety**

$$6 \pi\text{-e}^-$$

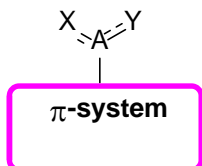


**Figure 7** Examples of pro-aromatic electron donors<sup>32,33</sup>.

### 2.1.2. Electron acceptors

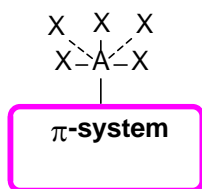
Both induction and mesomeric effects are used in construction of electron acceptors, similarly as in the case of electron donors. In fact, while I-effect of electron donors demonstrates itself in construction of electron donors as a part of them, there are multiple electron acceptors bearing only the  $-I$  effect without any mesomeric effect whatsoever. Especially fluorine containing  $-CF_3$  ( $\sigma_p = +0.54$ )  $-SF_5$  ( $\sigma_p = +0.68$ ) moieties by themselves or as a part of more complex acceptor part of the molecule demonstrated themselves as viable acceptors for multiple push-pull systems. The same holds true for ammonium and phosphonium salts as an acceptor part. With that in mind, there is still a majority of acceptors both from the standpoint of number of actual acceptors and from the standpoint of numbers of use, which exploit the negative mesomeric ( $-M$ ) effect. shows the typical acceptor design using negative induction and mesomeric effects.

"mesomeric" acceptor



A - mostly C, N, S, P  
X - electronegative atom (F, Cl, O, N)  
Y - electronegative atom (F, Cl, O, N)  
== Multiple bond (at least one of two)  
--- Optionally existing bond

"Induction" acceptor



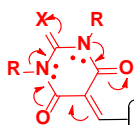
**Figure 8** Typical designs of electron acceptors.

The two most prolific acceptor groups used in the push-pull systems are undoubtedly nitro-moiety ( $-\text{NO}_2$ ;  $\sigma_p = +0.78$ ) and cyano-moiety ( $-\text{CN}$ ;  $\sigma_p = +0.66$ ). Both of them are reasonably stable groups not bringing an additional chemical instability to the molecule and both of them can be employed as a part of more complex acceptor part of the molecule. While being significantly stronger, the nitro-moiety is definitely less chemically stable than the cyano-moiety. Moreover, the chemical ways to introduce a cyano-moiety are more versatile and require less complex and chemically harsh reactions. Furthermore, the effect of cyano-moiety can be enhanced by multiple presence of cyano-moieties. 2,2-dicyanovinyl- and 2,2,3-tricyanovinyl-moieties are often used as an acceptor part, their nitro analogues are not available due to steric reasons and/or chemical availability. Moreover, nitro-groups in close vicinity interfere one with another and compromise the



**Pro-aromatic/anti-aromatic structure (4n)**

$$8 \pi\text{-e}^- + 4 \text{ } 2p_z\text{-e}^- = 12 \text{ e}^-$$

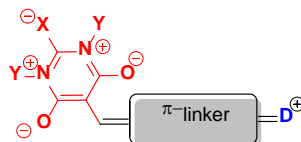


**(Thio)barbituric moiety**

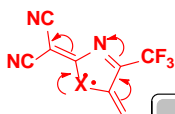
R = alkyl  
X = O, S

**Aromatic resonance structure (4n+2)**

$$6 \pi\text{-e}^-$$

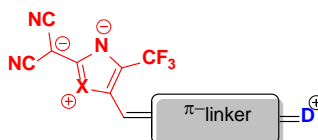


$$6 \pi\text{-e}^- + 2 \text{ } 2(3)p_z\text{-e}^- = 8 \text{ e}^-$$



**2-(Dicyanomethyloxa(thia)zoly)methyl moiety**

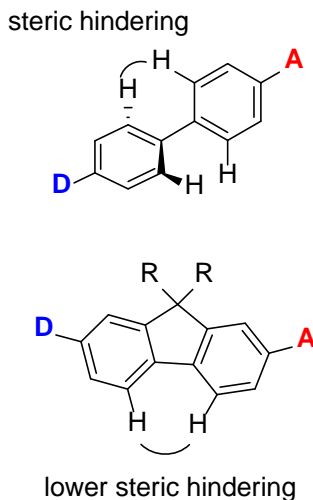
$$4 \pi\text{-e}^- + 2 \text{ } 2p_z\text{-e}^- = 6 \text{ e}^-$$



**Figure 10** Examples of pro-aromatic electron acceptors

### 2.1.3. $\pi$ -linkers

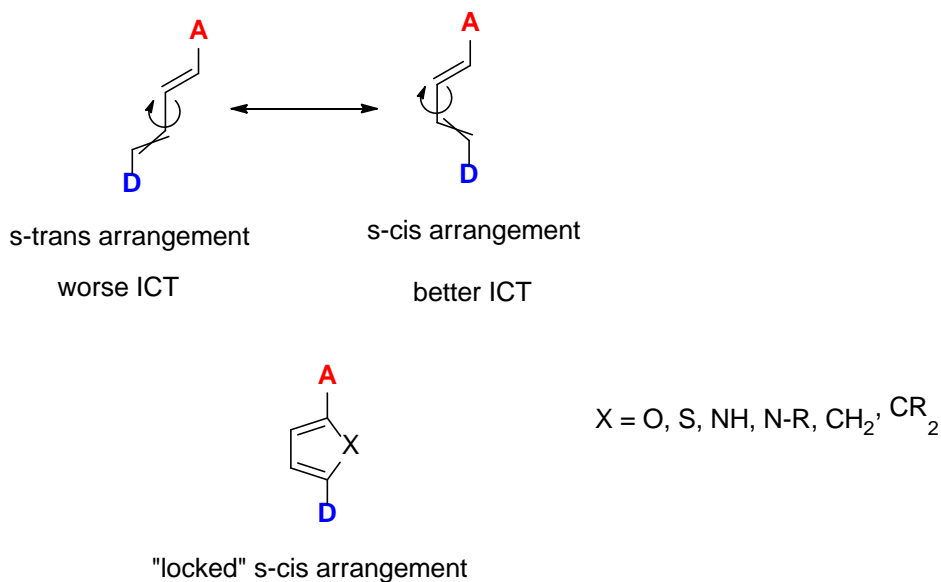
As it is multiply mentioned above, between the D- and A- part of the molecule, there should be a conjugated  $\pi$ -system. This means a system of double and/or triple C-C or C-heteroatom bonds separated by single bonds or heteroatoms capable of maintaining conjugations. As such, olefinic chains, acetylenic chains, (hetero)aromatic rings and conjugated metal complexes or combination of those are the most used backbones of the  $\pi$ -linkage. As a general rule,  $\pi$ -linkers have to be able to maintain planarity of the system and they have to provide as little obstacles as possible for ICT.<sup>37</sup>



**Figure 11** Steric arrangement of biphenyl-4,4'-diyl  $\pi$ -linker and its 2,2'-bridged analogue.

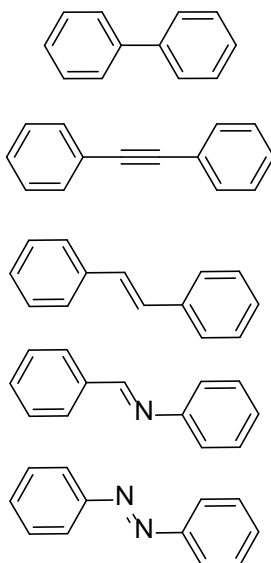
Several configurations and building principles appear to be more beneficial than others. In a conjugated sequence of double bonds *s*-cis configuration appears to provide better ICT than *s*-trans arrangement. Therefore 5-membered heteroaromatic rings especially those with sulphur, nitrogen and oxygen, as well as cyclopentadiene rings have a significant advantage compared with the simple conjugated chain of double bonds as the *s*-cis conformation is in those systems “locked” (Figure 12). Aromatic rings themselves appear to be very effective  $\pi$ -linkers, yet not all of their designs are equal. Biphenyl-4,4'-diyl linker is not planar as the *ortho*-hydrogens next to the phenyl-phenyl bond sterically prevent a perfectly *syn*-planar bonding (Figure 11) which has been multiply observed on the X-ray crystallography.<sup>32,33</sup> The substitution of a 2,2' couple of *ortho*-hydrogens with a linker, such as nitrogen, oxygen-, sulphur- or carbon-based linkers, making the linker dibenzo[b,d]heterocycle-3,7-diyl (where heterocycle means thiophene, furane), 9*H*-carbazol-2,7-diyl or 9*H*-fluoren-2,7-diyl linker can solve this

problem by significantly planarizing the  $\pi$ -linker. An insertion of acetylenic, olefinic, diazo or Ph-C=N-Ph bridge in the 1-1' linkage is another way around this problem, in fact used more often. Figure 13 demonstrates these concepts.



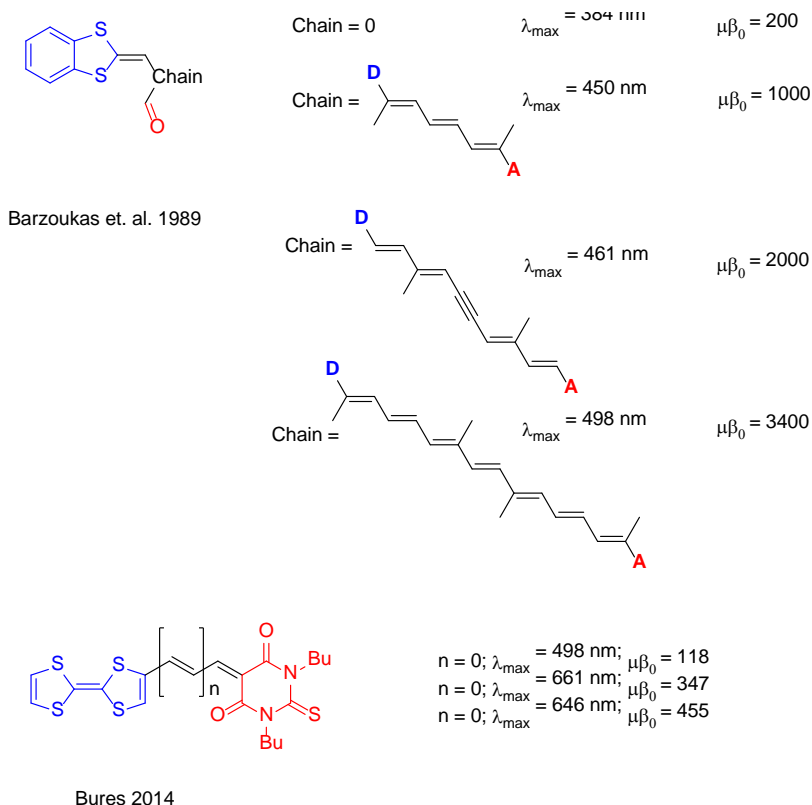
**Figure 12** "Locking" of *s-cis* butadiene arrangement.





**Figure 13** Variation of phenyl-phenyl linkage in push-pull systems

The length of the  $\pi$ -linker has a measurable impact in the ICT behaviour of push-pull systems as well. The number of  $\pi$ -bonds in the conjugation definitely decreases the energy of LUMO while having a little to no impact to HOMO energies. This results in the significant drop of band gap and, connectedly, and increase of the wavelength of the reddest maximum ( $\lambda_{\text{max}}$ ). On other words usually when both donor and acceptor part of a  $D$ - $\pi$ - $A$  system are identical the length of  $\pi$ -system (expressed in the number of  $\pi$ -bonds) would predict a significant bathochromic shift of absorption of particular  $D$ - $\pi$ - $A$  molecule, therefore lowers the energy needed for excitation of the molecule. The prolonging o  $\pi$ -system also usually means an enhancement of non-linear optical properties and the molecules on the edge of small molecule range (Section 1.1) will perform as semiconductors and/or conductors by themselves. Figure 14 demonstrates this on experimental examples.

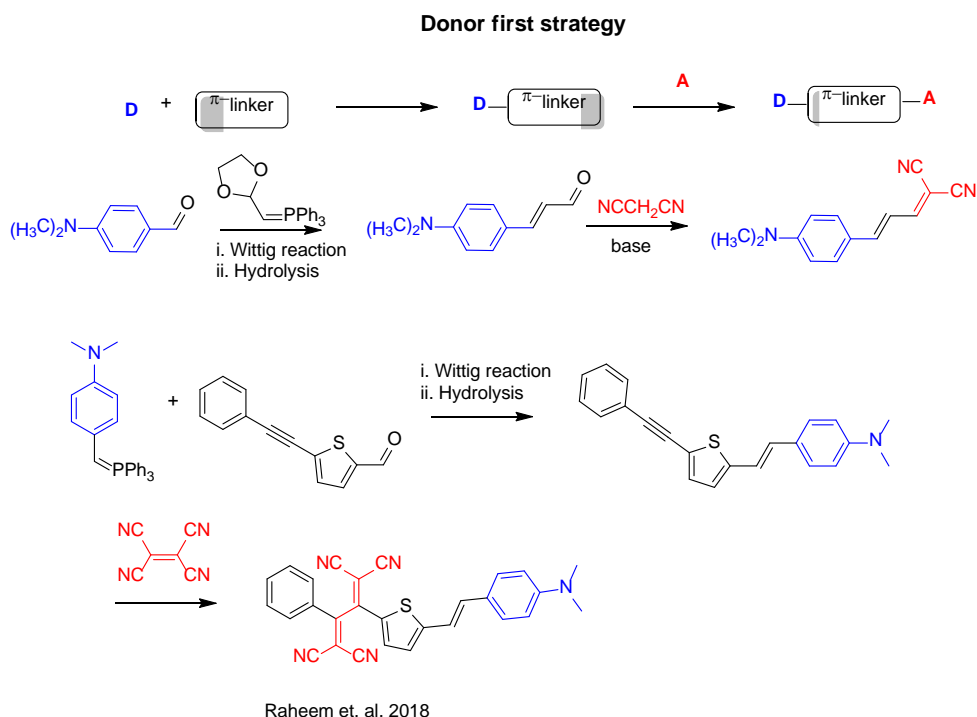


**Figure 14** Influence of the length of  $\pi$ -system on performance of push-pull system.  $\mu\beta_0$  is a product of a second order (quadratic) non-linear optical properties and is given in units ( $10^{-48}$  esu).<sup>33,38</sup>

#### 2.1.4. Construction of D- $\pi$ -A systems

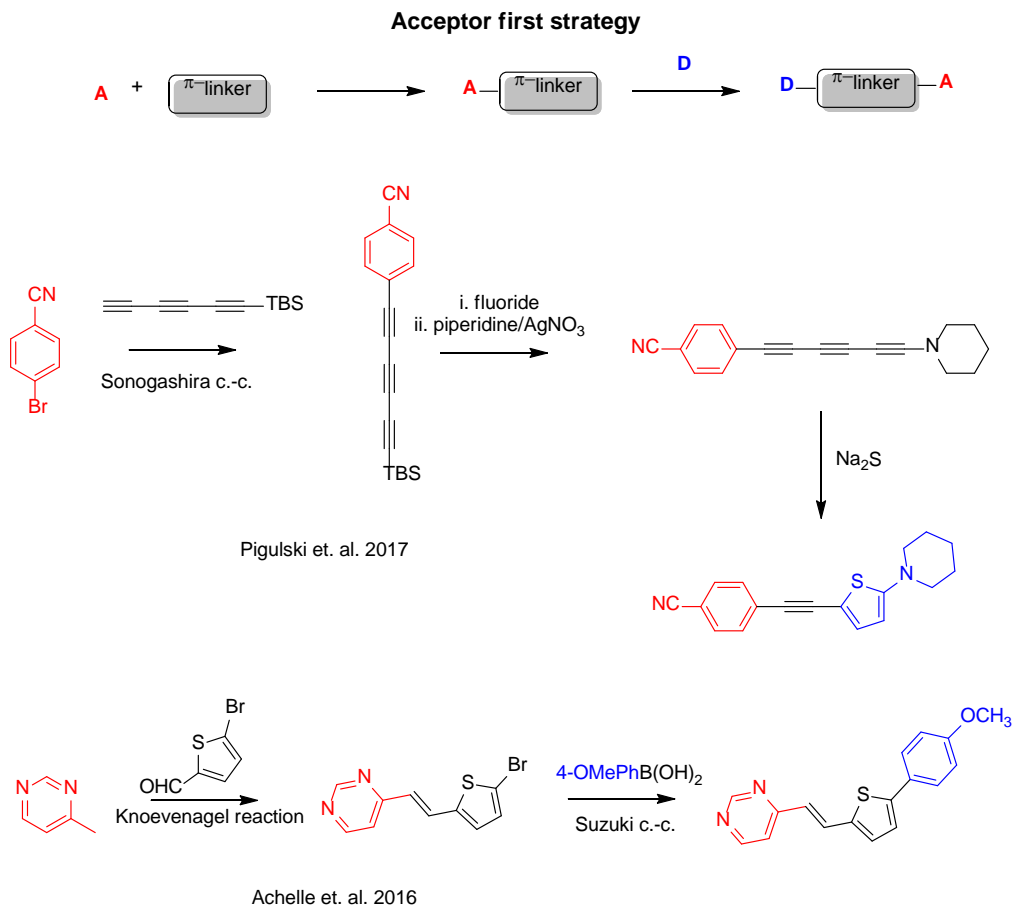
While having in hands a knowledge of construction donor, acceptor and  $\pi$ -linking part of the molecule, the remaining part is an approach to the synthesis of a D- $\pi$ -A system. In principle, four strategies are possible: (i) synthesis of a donor part with a  $\pi$ -linker at first and connection of acceptor as the last step (donor first strategy), (ii) synthesis of an acceptor part with a  $\pi$ -linker at first and connection of a donor part as the last step (acceptor first strategy), (iii)

synthesis of the donor and acceptor part in parallel each with a partial presence of  $\pi$ -linker and their connection as the last step (connection strategy), and (iv) building the  $\pi$ -linker at first and its substitution with both donors and acceptors in the last steps ( $\pi$ -linker first strategy). All of four possible strategies are used in the syntheses of *D*- $\pi$ -*A* molecules depending on the circumstances. In fact, there are multiple examples where the strategy used in particular *D*- $\pi$ -*A* system can fall somewhere between the stated categories, yet they are useful as overall demonstrative tool and will be further discussed as separate. Figures X - Y describes schematically all four of the discussed categories.



**Figure 15** Donor first strategy schematically and on literature examples.<sup>39</sup>

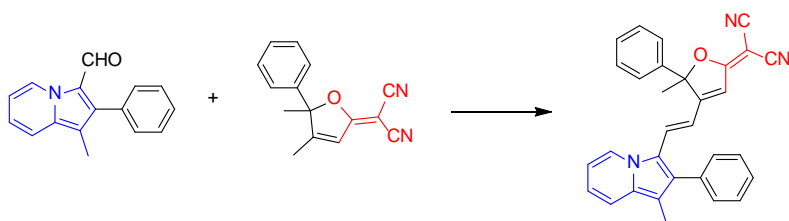
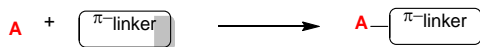
Donor first strategy (Figure 14) is among the most widely used strategies to synthesize push-pull systems. It is usually used in situations when the acceptor part of the molecule is relatively chemically simple and can be delivered into a molecule by a high-yield easy reaction. 2,2-dicyanovinyl-group can serve as one of the best examples. This group is usually introduced to the molecule by a reaction of particular aldehyde bearing a donor group and malondinitrile. In general, this reaction is reported as Knoevenagel condensation and almost quantitative yields were reported in special cases. Similarly, acceptors based on (thio)barbituric acid are suitable reactant for Knoevenagel condensation and several others. Another acceptor group usually introduced by donor first strategy is 2,2,3-tricyanovinyl-group. This group is usually added to the molecule by the reaction of electron rich molecule with tetracyanoethylene as a strong electrophile. Especially electron rich aromatic rings are perfect reactants for this reaction. 1,1,4,4-tetracyanobuta-1,3-dien-2,3-diyl acceptor bridge is usually synthesized by the reaction of tetracyanoethylene with an electron rich triple bond. The donor first strategy is also widely used when the acceptor is introducible by a cross-coupling type of reaction. Furthermore, this strategy is usually required when the donor makes a central part of multipodal and or symmetrical molecules. Triphenylamine-based chromophores are the best example of such reactions.



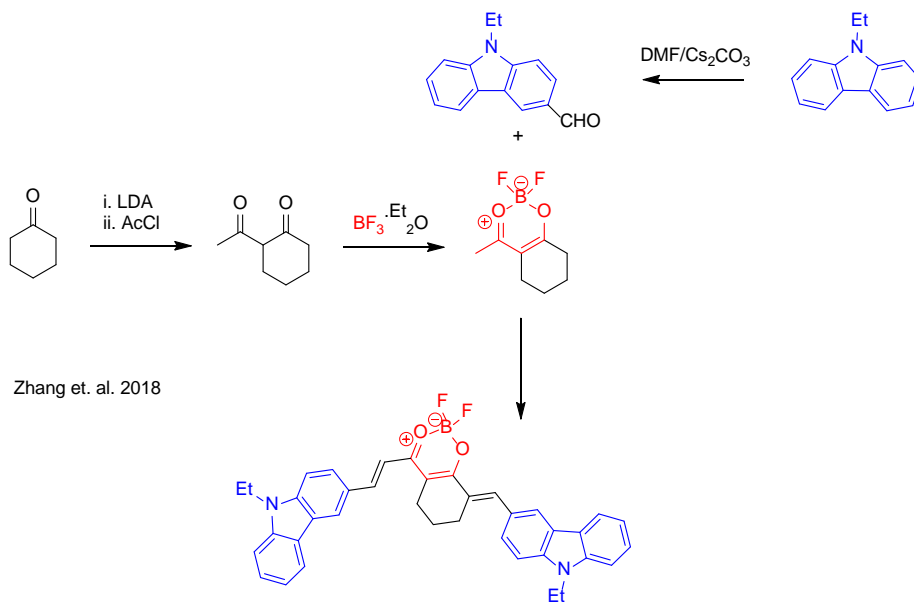
**Figure 16** Acceptor first strategy schematically and on the literature examples.<sup>40,41</sup>

Acceptor first strategy (Figure 16) is applied mostly in the cases, when molecule has can be divided in central acceptor part and preripheral acceptor parts. Molecules like indan-1,3-dione their exocyclic dicyanomethylene analogues can be the best example of this strategy as well V-shaped molecules with central quinolinizinium, bipyridinium or azacyanine acceptor core. Figure 16 shows several examples of this strategy.

### Connection strategy



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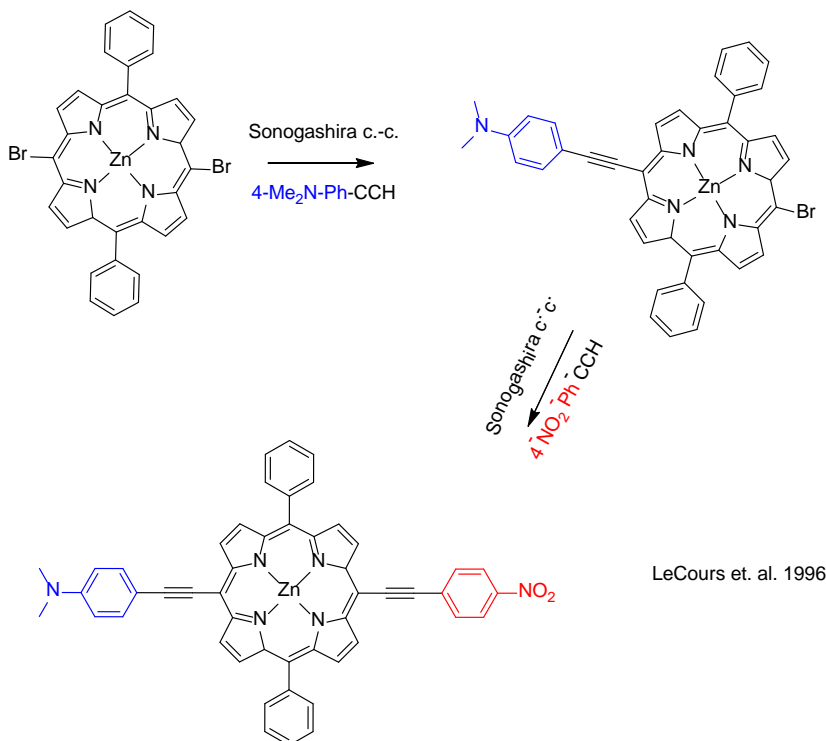
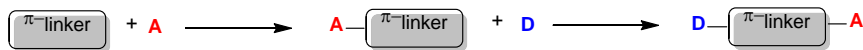


Zhang et. al. 2018

**Figure 17** Connection strategy schematically and on literature examples.<sup>42,43</sup>

The connection strategy (Figure 17) is one of most widely used strategies of synthesis the very long or, on the other hand, very small  $\pi$ -linkers. In case of the  $\pi$ -linkers consisting with no more than one bond, the simple connection between an electron donor part of the molecule and an electron acceptor part of the molecule both with comparable magnitude qualifies as the connection strategy. On the other hand, another type of connection strategy can be spotted where two parts of a  $D$ - $\pi$ - $A$  system are coupled together more or less in the middle. This is often applied when a linear  $D$ - $\pi$ - $A$  molecules are designed and synthesized. Figure 16 illustrates several examples of connection strategy from the contemporary literature.

### $\pi$ -linker first strategy



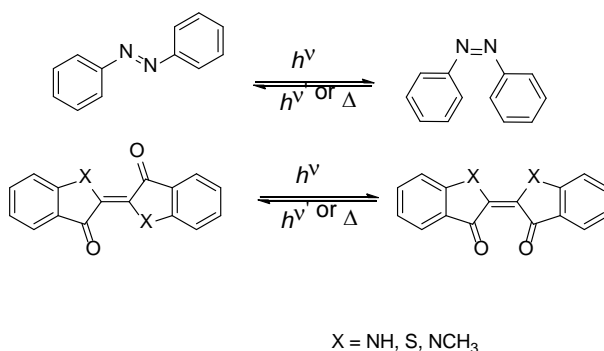
**Figure 18**  $\pi$ -linker first strategy schematically and on a literature example.<sup>44</sup>

Arguably the rarest strategy is the  $\pi$ -linker first strategy (Figure 18). This strategy is mostly used when  $\pi$ -linker is a complex multi-cyclic (hetero)aromatic system, or metal complex such as porphyrin. Figure X shows examples of syntheses of D- $\pi$ -A molecules synthesized according to this strategy.



## 2.2. Information heavy molecular design

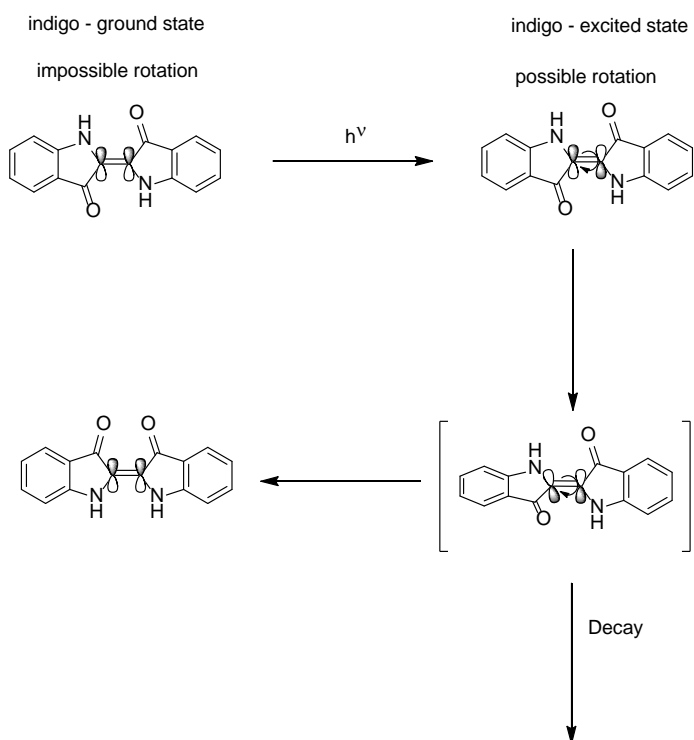
Storage of information is one of the challenges of modern technology. Small molecules appear a potential to be helpful in this field. Even relatively simple and very small molecules can carry an important information. Molecules like azobenzene and (thio)indigo exist in two isomeric structures interchangeable by the action of a (UV)-light (Figure 19). The interchange between the isomers usually also means a significant change in measurable properties such as colour (or better absorption/emission maxima of UV/visible light), electric resistance, etc. which can be exploited as a readable memory.



**Figure 19** *E/Z* switch-based equilibriums as potential carriers of information

The downside of using this types of small molecules is that the energies required for their isomerization often overlap with the energies able to promote a degradation of the molecule. In the simplest terms, the isomerization and the degradation of the molecule are very similar chemical pattern. The *trans*- isomers of both azobenzene and indigo are energetically more stable and their conversion into the less stable *cis*- isomers usually require reaching of an excited state of the molecule when the rotation along a double bon is possible. The same excited state, though, puts the molecule into

more reactive conditions therefore it can react with some chemical agents in its environment, typically water, air oxygen or carbon dioxide with can result in hydrolysis and/or oxidation or other degradation products (Figure 20).



**Figure 20** Schematic mechanism of E/Z switch of indigo

In general, molecules bearing an information value are not hard to find. Especially those molecules which can be switched by an addition of energy from one isomer to another. These energies usually include heat or radiation in UV or visible wavelengths. Rarely, electric current (or field), magnetic field or microwave radiation can also play a role of the source of isomerization energy. Every molecule thus capable of forming at least two tautomeric, E/Z<sup>45</sup>, open/closed ring isomers can be considered as potential carrier of an

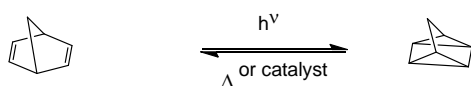
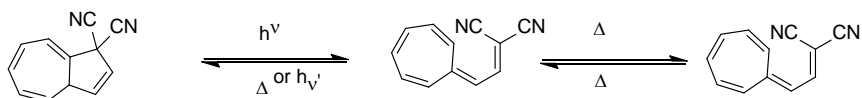
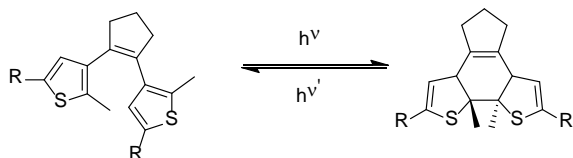
information (examples provided at Figure 20). Even R/S isomers can bear this kind of information value for example in case of sulfoxides where R/S isomers are relatively stable at room temperature, at the same time, they have relatively low barrier between R- and S- configurations (150 – 200 kJ/mol).<sup>46,47</sup> The problem is usually more with the stability and non-volatility of thus stored information. To overcome this problem special structures are designed and synthesized to be enduring enough to be capable of storing the information. Usually the E/Z isomer forming compounds are thus designed. Of them fluorinated azo-compounds are among the most prolific, others include compounds with E/Z isomers on C=C bonds for example those based on 2-substituted benzothiazole S-oxides.<sup>45</sup>

Notably, push-pull (Section 2.1) molecules are among those which can be photo-switched, especially those with double bonds in the  $\pi$ -linker. The D- $\pi$ -A design does make certain types of double bonds more prone configuration change, especially when the  $\pi$ -system is fairly short. The strength of both electron donor and electron acceptor play also the role.<sup>36,48</sup> The extreme example are molecules capable of two isomerism either by different energetic processes or by different energetic levels. This can lead in alternative reading-writing patterns and multi-level memories. Examples of such compounds are given in Figure 22. One of the most remarkable examples is the cobalt complex capable of changing open-closed ring arrangement optically and cobalt-ligand oxidation state magnetically. Applied in thin films, a very potent opto-spintronic memory device has been constructed (Figure 22).<sup>49</sup>

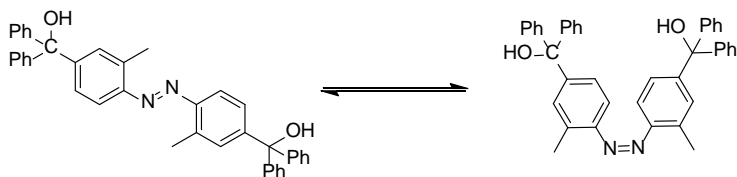
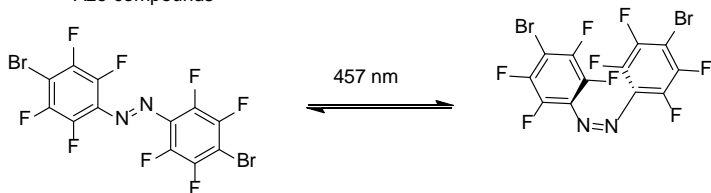
One of the best ways to exploit the photo-switching (or another energy switching) properties of molecules is an arrangement when one of the isomers has a directly measurable property which can be exploited right away. Among

these properties a capability of fluorescence is among the most important. The design of compounds capable of photo-switch to fluorescent form and leuco-form is one of the key elements of an information-heavy design.<sup>50</sup> The basic concept of this switch is to create and/or derange some form of conjugated system by the photo-switching derivatization. Thio-indigo (Figure 19 and Figure 20) is one of the compounds capable of such interchange, yet its use is often loaded with aforementioned shortcomings (*vide supra*) which can be only limitedly compensated by the relative inexpensiveness of the compound. For these purposes (otherwise called photochromism) compounds on the basis of spiropyran and chromene appear to have bigger potential.<sup>45,50–52</sup> The schematic concept as well as concrete examples of photochromism are given on Figure 23.

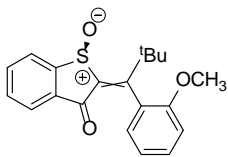
### Open-closed ring switching



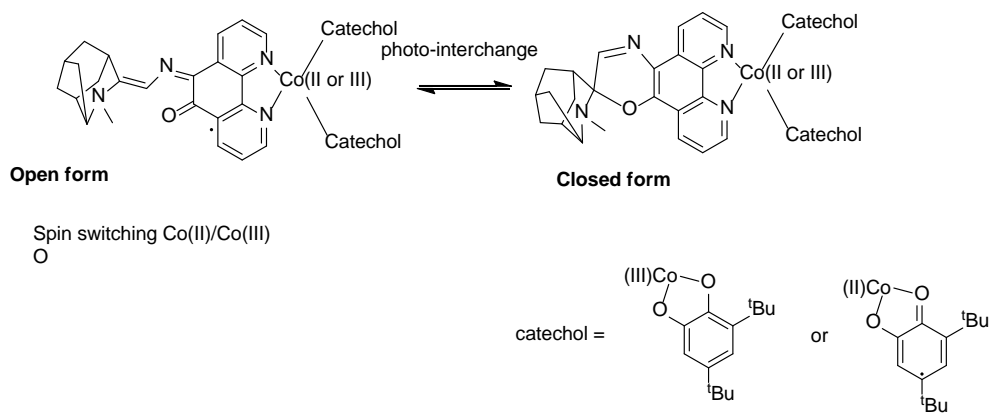
### Azo-compounds



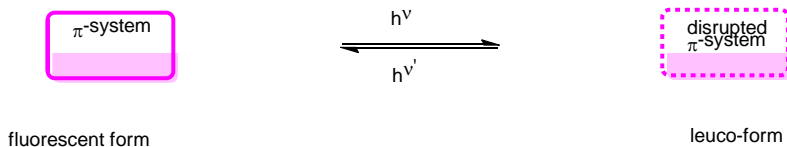
**Figure 21** Photo-switchable compounds as information carriers.<sup>45</sup>



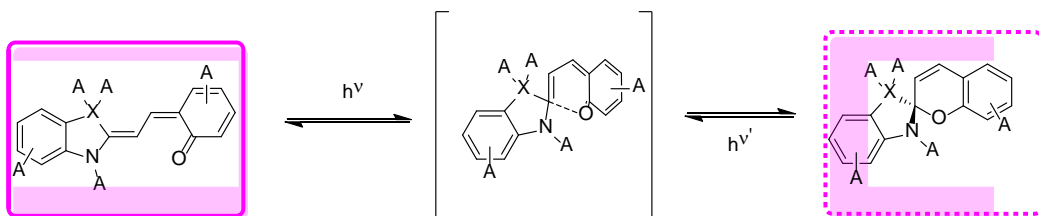
Switchable E/Z isomery  
and orientation of phenyl ring 4 possible isomers



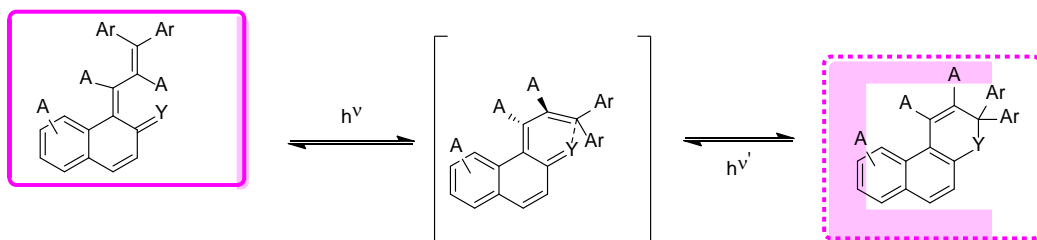
**Figure 22** Multiply switchable molecules.<sup>45,49</sup>



### Spiropyrane concept



### Spiropyrane concept



A - any substitution

Ar - Aryl- and heteroaryl substitution

X - C, less often S, O, P

Y - O, less often S

Figure 23 Two photochromic concepts in generic equilibria.<sup>45,51,52</sup>

An existence of isomers is not the only way to store an information chemically. Analogically to the molecules involved in the memory the information basis of organisms, such as DNA, RNA and several proteins and/or saccharides, there are biomimetic systems which can play a role of

memories.<sup>53</sup> As an example a device storing information in a form of peptide-like molecules<sup>54</sup> can be mentioned. Other biological and bio-mimetic small organic molecules such as saccharides, even signalling molecules (neurotransmitters) have been used in memory or memory-like experimental devices. Furthermore, combinatorial high yield very selective reactions between number of products creating unique structures when provided with specific set, such as Ugi reaction, proved themselves to be another viable mechanism of data storage.<sup>55</sup>

It is not easy to spot a common sign in the structures of information heavy design. In fact, a potential to carry an information should not be considered as a feature of a molecular design. All of the molecules do bear some kind of information and can be considered as carriers thereof. On the other hand, there are some signs which can be considered as common. A presence of some kind of chemical change or interaction is first of them. This interaction has to be, at least to a reasonable extent, reversible, yet, when made, it should be also enduring enough to carry once written information.



### 2.3. Frustrated Lewis pair (FLP) design

Hydrogen technologies are arguably the future in both energetic and chemical technology. Hydrogen as a raw material has multiple advantages. It is quite simple molecule, relatively easy to store (considering it is a gas), with predictable behaviour and with the history of more than 100 years of its industrial use. The obvious downside of using the molecule of  $H_2$  directly are safety issues coming from handling this molecule.  $H_2$  gas notoriously known for forming an explosive mixture with the air, moreover it can be stored mostly under high pressure, which brings safety handling issues as well. Therefore, hydrogen surrogates, molecules which can carry hydrogen as under less challenging conditions and deliver it into the technological application with less risks are often searched.

The problem of hydrogen surrogates always is in the contradictory nature of two needs. A good hydrogen surrogate should be able to absorb hydrogen fairly simply and should not be able to release it in transport or during the operation. Contrary to that, hydrogen should be present and releasable from it whenever necessary. Small organic and inorganic molecules such as formate,  $BH_3NH_3$  metal hydrides etc. usually limp in at least one of those requirements. Over here, there comes a niche for bigger and chemically more interesting small organic molecules such as are frustrated Lewis pairs (FLPs).

The concept and chemistry of FLPs is fairly new, sparked by the findings of a group of prof. Stephan in 2006.<sup>56</sup> A molecule 4-(bismesitylphosphanyl)-dipentafluorophenylborane was able chemically absorb a molecule of hydrogen (Figure 24) and afterwards release it by being heated. Thus “absorbed” hydrogen appeared to be activated and soon thereafter similar systems started

to be utilized in various chemical processes. The co-presence of sterically or otherwise chemically hindered (usually weak) Lewis bases and (usually strong) Lewis acids not capable of reacting with one and another can split the  $H_2$  molecule into one hydride (bonded to Lewis acid) and proton (bonded to Lewis base forming conjugated acid).

When a Lewis acid and a Lewis base are present in the same reaction mixture, they usually recombine in the reaction known as neutralization, nucleophilic (Lewis base is to large degree identical term as nucleophile) or electrophilic reactions (the same holds true for the pair Lewis acid – electrophile) or a combination thereof. Yet, certain designs of Lewis acids and Lewis bases can limit the capability of mutual recombining or make its rate as low as it is possible for another reaction to take place instead. As such, combinations of these types of mutually limitedly reactive Lewis acids and Lewis bases has been started to call “frustrated” Lewis pair as it is deprived of the possibility of reaction between a (Lewis) base and (Lewis) acid. Usually, strong Lewis acids and weak Lewis bases form this type of pair, the pair with inverse strengths (weak Lewis acid, strong Lewis base) are sometimes called “inverse FLPs”.

It is important to note that frustrated Lewis pair design, when both Lewis acid and Lewis base are a part of one molecule are, in fact, in a relation to the push-pull design. Biological  $H_2$ -equivalents (Figure 20, *vide infra*) can be viewed both as push-pull molecules and as frustrated Lewis pairs depending on a point of view. This dichotomy is not accidental. For an electronic acceptor moiety, it is typical to have the deficit of electronic density (that is why it is called electron acceptor in the first place) which is a typical sign of Lewis acid as a reagent and/or as a part of a molecule. Similarly, electron donors usually

have surplus of electronic density (that is why they “donate” electrons into the  $\pi$ -system) which again is the typical sign of a (Lewis) base. The borderline between push-pull systems and FLPs will always be arbitrary and very thin. There are some chemical moieties which do occur as both electron acceptors and Lewis acids in dependence on a particular design of the products. With that in mind, it is still useful to distinguish between those two categories. At first, push-pull systems are called almost exclusively  $\pi$ -systems, whereas in FLPs a  $\pi$ -system is not required. The main principle to distinguish these two molecular designs, though, is the final behaviour of the compound itself. Push-pull systems do sort out their electron imbalances by an intramolecular electronic interaction (ICT, Section 2.1) leading to alteration mainly the physical properties of the compound. Contrary to that FLPs manifest their electronic imbalances mainly in their reactivity. The signal reaction to even consider a compound a FLP is hetero-dissociation of a hydrogen molecule, yet there are other signal reactions which make FLPs characteristic. This also defines their industrial potential. Figure 24 demonstrates these differences.

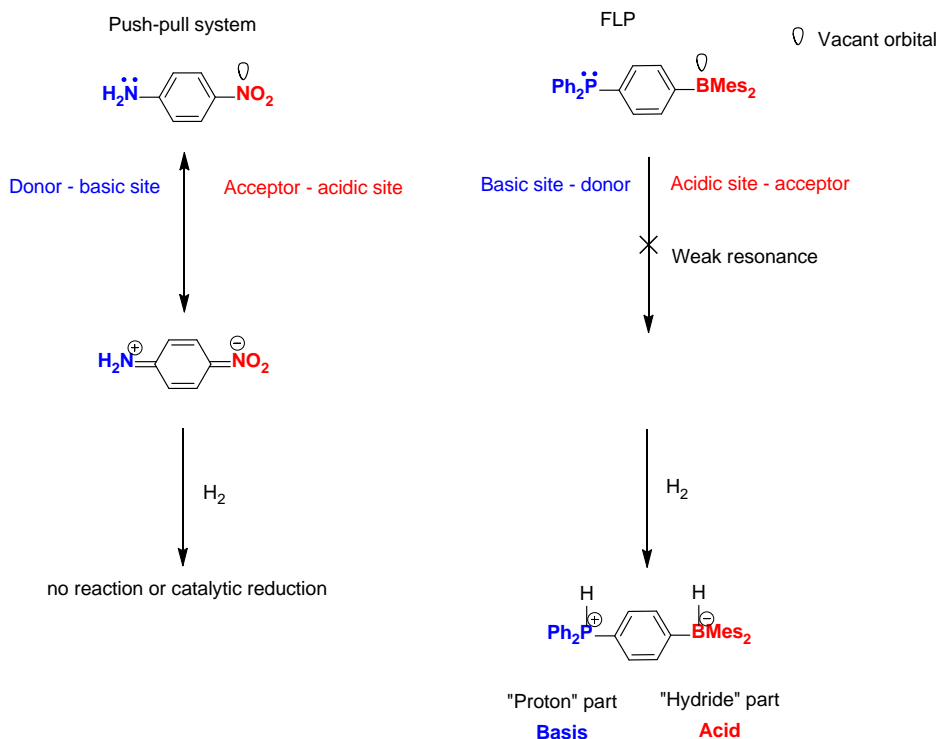


Figure 24 Comparison of similarities and differences between D- $\pi$ -A and FLP compounds.

To find the Lewis pair with a limited readiness of to react between its two components, several conditions must be fulfilled. At first, the Lewis acid and the Lewis base have to be limitedly compatible from the standpoint of electronic levels. That is why usually boron-based Lewis acids and phosphorus based Lewis bases are chosen. The vacant 2p orbital of trivalent boron and the 3sp<sup>3</sup> free electron pair on trivalent phosphorus are both geometrically and energetically unfavourable to interact with one another. The incompatible electronic levels, though, are not sufficient for the slowing of the recombination/neutralization reaction. Therefore, the steric hindering and electronically active substituents have to be always a part of the design of two-component frustrated Lewis pair (FLP) design. The Lewis acids chosen as parts

of two-component FLPs are often multi-halogenated triphenylboranes such as tris(petrahaloxyphenyl)borane or tris(2,6-dihaloxyphenyl)boranes. The Lewis bases are usually phosphines, specifically those sterically hindered, such like tris(mesityl)phosphine. Figure 25 shows some examples of two-component FLPs with their potential as hydrogen carriers/extractors.<sup>57</sup>

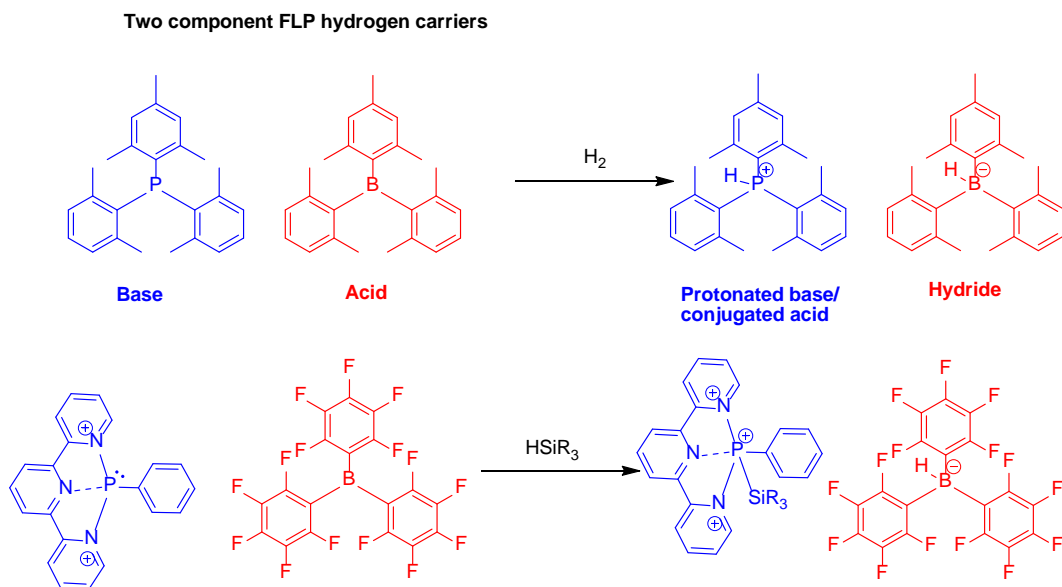
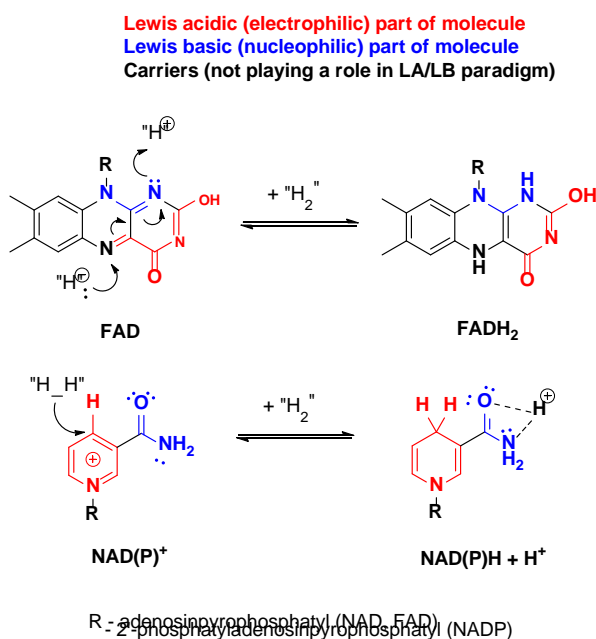


Figure 25 Two component FLP hydrogen carriers/extractors.<sup>57,58</sup>

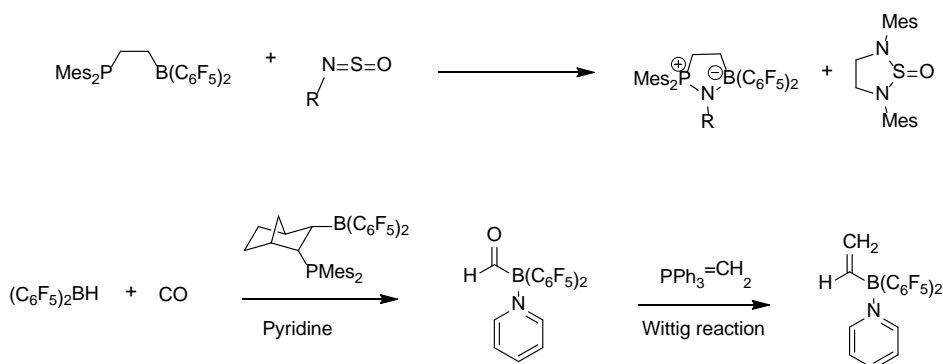
Nowadays, one-component FLPs are definitely a trend. In some cases, the border between one-component and two-(multiple-)component systems is somewhat blurred. Often times even when two parts of Lewis pair are added into a reaction mixture or another system they can transiently form one chemical entity (molecule or ion) which can but need not dissociate into other particles. As an example the mixture of tris(perfluorophenyl)borane with pyridine behaves this way.<sup>59</sup>

When speaking about FLP design itself, it is more or less considered as a one such particle (transient or not) bearing both Lewis acidic and Lewis basic moiety. The inspiration for that molecules can be taken from the nature. In biological and biochemical systems, molecules capable of bearing an equivalent of the  $H_2$ -molecule. (De)hydrogenated pairs like NAD(P)/NAD(P)H +  $H^+$  or FAD/FADH<sub>2</sub> (otherwise called as hydrogen analogues and/or carriers) active in multiple biochemical processes, most prominently in the process of cellular respiration, and more broadly in the process of ATP synthesis can be conceived as frustrated Lewis pairs by their function. Figure 10 shows their function comparable to with one-component FLP.<sup>60</sup>



**Figure 26** FAD/ $H_2$  and (NAD(P)/H+H)<sup>+</sup> biological  $H_2$  equivalents as “one-component FLPs”

Modern one-component FLPs usable for storage of hydrogen or its delivery to a reaction or to its use in fuel cells are usually molecules with a rigid organic backbone, such as benzene ring, ferrocene, imidazolium, ethylene bridge, etc. The Lewis base part usually consists of trivalent phosphorus;<sup>57</sup> trivalent nitrogen and bivalent oxygen are also prolific.<sup>61</sup> In special cases Lewis basicity can be brought by bivalent sulphur or bivalent selenium. The Lewis acid part consists predominantly of trivalent boron-based strongly Lewis acidic motives. Lewis acidity can be brought to the molecule also by a transition metal, aluminium, indium, silicon, germanium or tin, or a heavy non-transition or inner-transition metal. Some of the interesting and/or the most notable FLP molecules are presented in the Figure 27.



**Figure 27** Examples of fascinating reactivity of FLPs.<sup>57–59</sup>

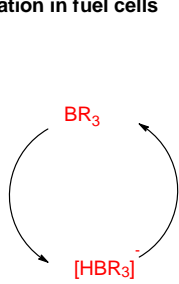
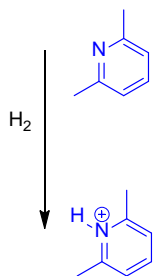
Concerning the technological applications. The impact of FLPs to the hydrogen technologies appears to be promising. The very beginning of this chemistry lead towards material capable of absorbing and controllably releasing hydrogen, which was transition metal free (and thus has limited safety and environmental concerns) and comparably expensive with the state-of-the-art transition metal technologies. From that, many other materials

having at least partially a character of FLPs occurred and are considered as promising means of H<sub>2</sub> storage or as the materials capable of extraction of H<sub>2</sub> molecule from its small molecule surrogates (such as methanol, formic acid, fatty acids, etc.).<sup>62</sup> The main prospect of utilization FLPs, though, might lay in the fuel cell technology. Capability of FLPs to activate the molecule of hydrogen itself suggest the possibility of metal free hydrogen oxidation reaction catalyst. A two component mixture of tris(*tert*-butyl)phosphine and tris(perfluorophenyl)borane appears to be active in that direction.<sup>63</sup> Remarkable results were obtained in the mixture of lutidine and acridine based Lewis acid (check Figure 26 for similarities; Figure 28). Two examples of such prospectivity of FLPs are provided at Figure 28.



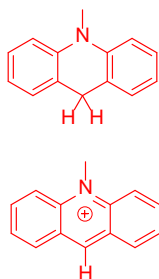
## Frustrated Lewis Pair in prospective technology

FLP mediated  $\text{H}_2$  oxidation in fuel cells

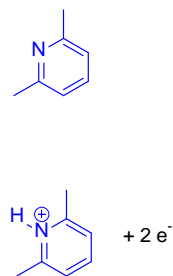


Hydride shuttle

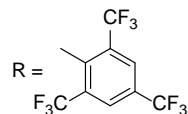
Hydride form



Lewis acid



Lawrence et. al. 2016



FLP in formic acid dehydrogenation

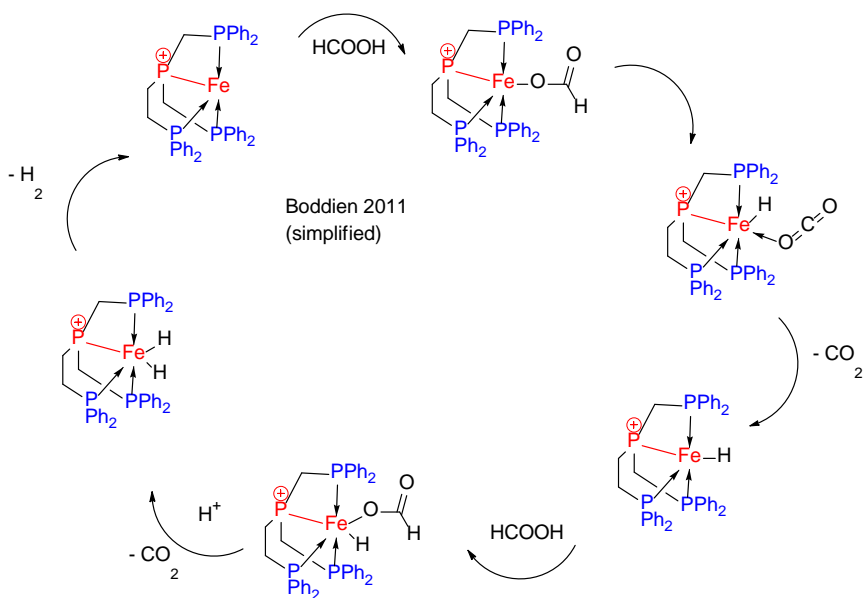
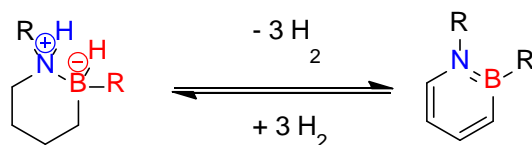


Figure 28 Prospective uses of FLPs in modern technology.<sup>64,65</sup>

As it has been suggested above, the use of such molecules need not be limited to the storage and/or safer delivery of the  $H_2$  molecule into a technological step. In fact, so far metallic hydrides appear to have several advantages with that respect. Even the prospective technologies shown in the Figure 28 may not end up in the actual application. High capacity hydrogen storage is possible in B-N compounds as a concept, especially 2-borapiperidines (Figure 29) can have tremendous capacity of  $H_2$  carrying.<sup>66</sup> If the substituents R (Figure 29) are not hydrogen but bulky substituents, preferably with electron withdrawing properties on boron and with slight electron donating activity in case of nitrogen, this concept might be viable and those absorber system (both saturated and unsaturated chemical individual) would correspond with a definition of FLP (Figure 24). Yet, as of 2021 (February) there is no literature report of existence of such compounds to the knowledge of author, only computation studies suggesting favourable energies of equilibrium were carried out.

It is necessary to mention, that FLP chemistry goes far beyond the activation of a form of hydrogen. Although, so far most of it still is the reactions concerning activating, adsorbing, extracting,  $H_2$  reducing and similar concepts.<sup>58</sup> FLPs perform similar activity towards halogens, namely in case of fluorine it may in the future open the door towards further electrophilic fluorinations which, although occurring, are due to the electronegativity of fluorine very rare. Moreover, they are typically catalysed by transition metals, especially palladium,<sup>67</sup> metal free varieties of this process are always sought and some design of already existing metal-free fluorinating agents gives optimism to these concepts.<sup>68</sup> More relevantly technologically FLPs may help with the technologically-environmental challenges, they were proven to be

able to either adsorb or react of several pollutant gasses, such as carbon monoxide, carbon dioxide, sulphur dioxide, nitrous oxide, nitric monoxide and dioxide, etc. (example given on Figure 27).<sup>57,58</sup> Conversion of those gasses into an industrial-scale material would be a great step in human industry both from technological and from environmental standpoint and the potential of FLPs in that respects seems to be yet unfulfilled.



R - substituent or H

**Figure 29** 2-Borapiperidine/2-borapyridine compounds as a high capacity  $\text{H}_2$  storage.

#### 2.4. Other useful and relevant designs

Apart of push-pull design, electron donors and acceptors in the conjugated  $\pi$ -systems can be organized in pull-pull (A- $\pi$ -A) and push-push (D- $\pi$ -D) arrangements. Those types of designs are usually required in special cases of organic semiconductor technologies. A molecule rich in electron acceptors (pull-pull) will definitely have a low LUMO level and thus will be keen to accept the electron from various sources. This, of course, will influence its reactivity and those molecules are usually fragile to various nucleophiles (reagents with access of electrons). In circumstances which do not support an occurrence of a reaction, though, those type of materials will accept electrons from various donors creating the electron-holes in the semiconductor system. Thus they will behave as n-type semiconductors. Lower energy levels of LUMO may also be

beneficial in areas such as chemical sensing and/or multiphoton (two photon or three photon) absorption.

The ability to excite its own or to acquire extraneous electrons would predestine colourful pull-pull compounds to be excellent dye sensitizers, for example, at DSSCs, yet that is not the case. Pull-pull molecules do usually suffer with reduced chemical stability. As the nucleophiles are almost omnipresent in the environment (e. g. water and airborne oxygen are, in fact, nucleophiles), their lack of chemical stability towards them often limits them in the capability of being usable. A slight change in their structure by supplementing their molecules with a weak electron donor results in an alternative molecular design push-pull-pull molecules, who appear usually very active as sensitizing dyes capable of a facile excitation and with a reasonable chemical stability (Figure 30).<sup>69</sup>

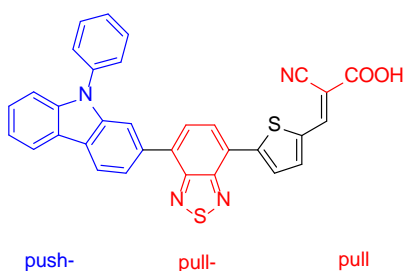


Figure 30 An example of the push-pull-pull design used as sensitizer in DSSCs.

The push-push, electron rich small organic molecules, have fairly more use in modern technologies. As stated before (vide Section 2.1.1) the occurrence of electron donors elevates the energy levels of HOMO. Thus, these molecules are very rich in electrons and usually can provide them in the sense of a reactions or an electronic process. Analogically to the push-push molecular designs they can be viewed as the p-type semiconductors providing the

electrons wherever it is energetically suitable. These properties are especially appreciated in hole transport. Somewhat counterintuitively, the hole transporters as small organic molecules have to be molecules relatively rich in electrons. This is especially because the point of hole transport is in fact a capability of providing electrons (e. g. to dye sensitizer). When HOMO level of a material is high enough to be at the energetic level comparable with LUMO of material from which a hole transport should be made this type of transport is possible and can happen.

Apart of hole transporting capabilities (further information in Section 3.1), push-push materials are used as two photon absorbers and are successful in other non-linear optical (NLO) applications both in multiphoton photonics and multiphoton emission.<sup>20,70</sup>

### 3. Organic molecules in electronics and optoelectronics

#### 3.1. Hole transporters (HTMs)

In various semiconductor applications, especially of cells of various kind (solar cells, fuel cells) an electrolyte is or would be traditionally required. The use of liquid electrolyte poses obvious technical and safety limitations, therefore is not preferred in modern technology. Therefore, solid alternatives for liquid electrolytes were always sought and required. These solid materials are usually called as it has been stated mostly in the technology of dye sensitized solar cells (DSSC), as hole transporting materials (HTMs), synonymously hole conductors or hole transporters.

Principal function of these materials is best explained on the function of a generic solar cell. Any solar cell has to consist of photo-sensitive semiconducting material capable of being excited by a quantum of (solar) light. This material usually forms the anode, as excited electrons enter the conducting band of the photosensitive material. Subsequently, when the electrons are excited up to the conducting band they are logically lacking in the valence electron levels of the material. The phenomenon of exciting electrons up to the conducting band while creating the lack of electron in the valence level of a photosensitive material is formally known as creation of a pair electron-hole. Naturally, the photosensitive materials would tend to recombine those electron levels, but it is not desired in case of cells, where a generation of electric potential is the principal goal. For a solar cell to function the holes (lacking electrons in valence levels) have to be removed away from the photosensitive material. This is called hole transport. In traditional cells and first prototypes of solar cells an electrolyte (e. g. aqueous solution of

triiodide  $I_3^-$ ) was the material that was capable of conducting the holes away (towards a cathode). In the modern, thin film and fully solid state cells this is a function of HTM.

The requirements on HTM can be implied from its function. At first HTM has to be “rich” in electrons, in other words it has to have relatively high energy of HOMO, to be able to transport the electrons back to the photosensitive material, or, using the hole convention to accept the holes from the photosensitive material. This leads to another important required property which chemical stability of electron changes, or better high degree of reversibility of the electron transfer reactions. The simplest hole transfer presumes the single-electron transition (SET) from a photosensitive material to the hole transporter. By that single-electron transfer a radical, in the case of hole transporters mostly radical-cation is created. Radicals and especially radical cations are in principle compounds very reactive and unstable. They can be stabilized by certain chemical aspects. The requirement on the hole transporter, therefore, is to be able to form a stable radical-cation (Figure 31).

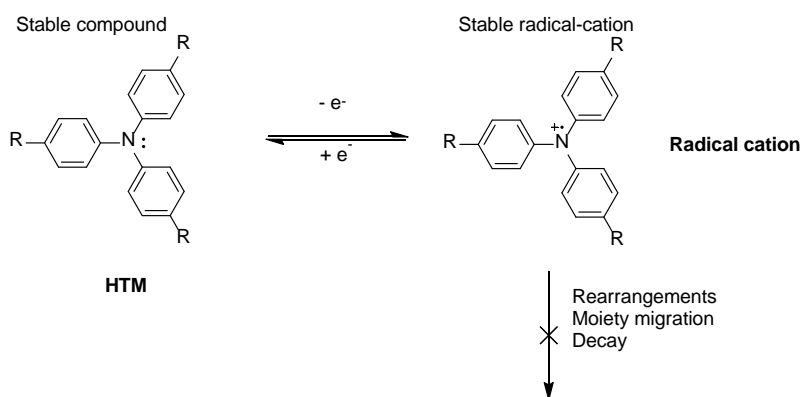


Figure 31 Principle of function of hole transporting material demonstrated on generic triphenylamine hole transporter.

In general, at least partially planar and highly symmetrical compounds with multiple  $\pi$ -conjugated systems appear to be the best design of hole transporters. Often, polycondensed aromatic rings are present and multiple C-N, C=N, or C(O)-N bonds are present. The action of those motives is schematically explained on Figure 32. Figure 33 further shows a survey of the state of the art and/or prospective compounds already successfully used as HTMs in organic solar cells (OSCs), DSSCs, heterojunction solar cellc (HJSCs), perovskite solar cells (PSC) and LED technology.

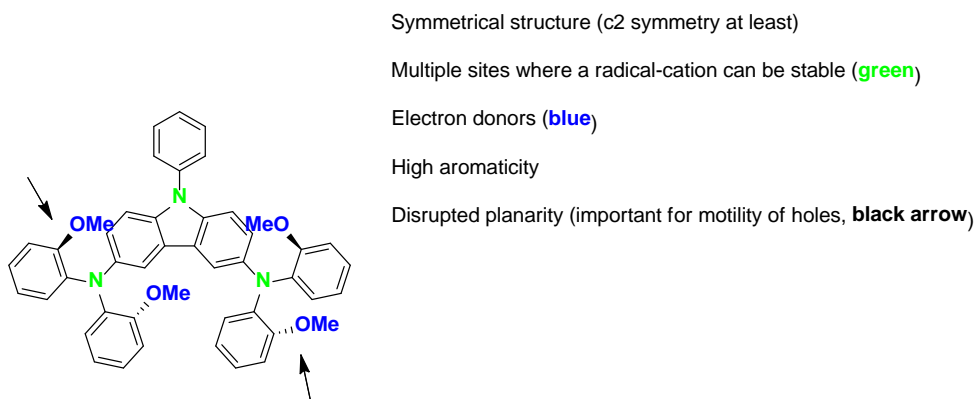
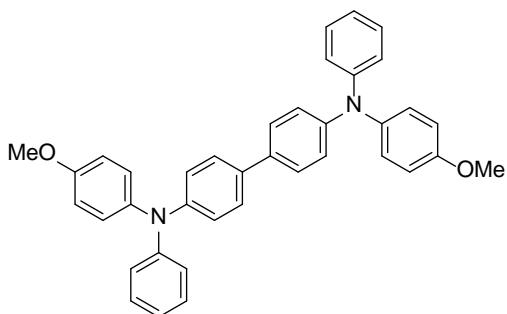
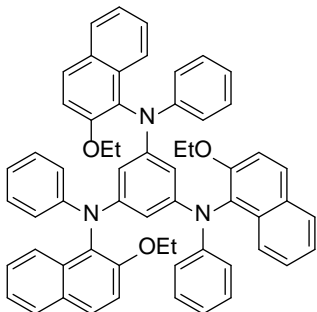


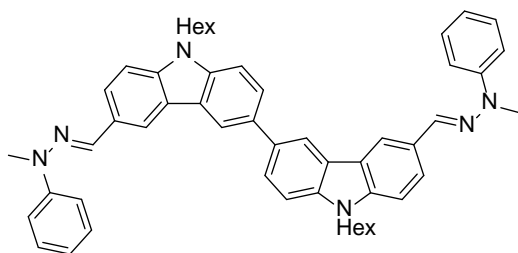
Figure 32 A typical structural signs of a hole transporter described and explained.<sup>71</sup>



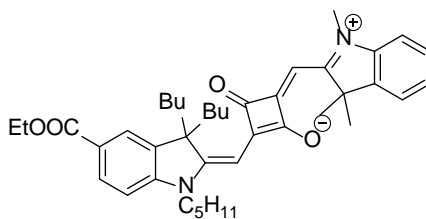
### TPA-based



### Carbazol based



### Atypical (push-pull)



### Organometallic

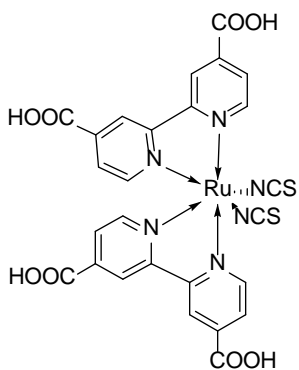


Figure 33 Examples of hole transporters.<sup>72</sup>

### 3.2. Small molecule semiconductors (especially) for OFET applications

Field effect transistors (FET) are transistors using an electric field to control a current. In typical arrangement of FET there is a source of current and the drain the space between them is usually called channel (Figure 34). The channel has historically been made of metal oxides (such devices are called MOFET and are considered becoming obsolete in modern technology) yet in with the raise of organic materials organic semiconducting channels have started to be used offering better possibilities towards thin film applications, chemical sensing and other important applications.

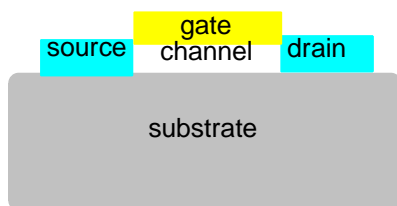


Figure 34 A general scheme of a field effect transistor.

To design a molecule of an organic semiconductor, the first obvious principle is for a molecule to have semiconducting properties. In small organic molecules, this means a plurality of  $\pi$ -bonds and high conjugation of the entire system. Therefore, a large part of the OFET semiconductors fall outside the scope of this text as the polymers and oligomers of various kind. Yet surprisingly the molecules as simple as (2,5-cyclohexadiene-1,4-diylidene)-dimalononitrile (TCNQ) or tetrathiafulvalene, both with approximately the same  $M_w = 204$  Da (Figure 34), are successful and multiply used organic semiconductors, especially for OFET devices.<sup>73</sup>

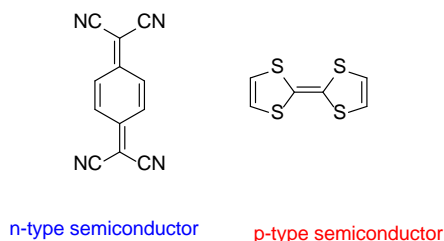


Figure 35 2,5-cyclohexadiene-1,4-diylidene)-dimalononitrile and tetrathiafulvalene.

Typical small molecule organic semiconductors, on the other hand, are molecules slightly bigger, with multiple condensed aromatic and heteroaromatic rings. Molecules with 10 or more  $\pi$ -bonds. The other requirement for such molecules. Another obvious requirement for organic semiconductors used in OFET devices is a stability towards electric field and electric current. That is usually achieved by very chemically rigid structures, again poly-condensed aromatic rings are usually a structural backbone of choice. Following that, in organic semiconductors a substitution such as donor or acceptor one is rarer and, when used, designed to increase the stability of a molecule. Aromatic C-H bonds or C-F bonds along with the alkyl- and fluoroalkyl- chains are typical sign of OFET semiconductor small molecules. Trialkyl silyl- groups are another moiety widely used in organic semiconductors, as well as cyano-moiety.<sup>74</sup>

The last structural requirement of OFET semiconductors arises from the mechanism of semiconductor properties of small organic molecules. Small-molecular organic semiconductors are usually functional as semiconductors only when organized in the molecular crystals.<sup>74</sup> Especially those which are organized on the basis of  $\pi$ - $\pi$  interactions where the electric field can influence the jump of electrons. This forms a structural demand of highly symmetrical structures capable of this kind of organization.

Like in the inorganic semiconductors, the organic semiconductors can be divided to p-type (Figure 36) and n-type (Figure) semiconductors where in p-type semiconductors where in p-type organic semiconductors an electron conductivity plays a major role, whereas in the n-type semiconductors a hole conductivity plays the most important role. Among p-type organic semiconductors a prominent role is played by a poly-condensed aromates such as tetracene, pentacene and hexacene. Interestingly enough, when the structure of aromate becomes more helical or less planar it usually ceases to be a p-type semiconductor and starts to be an n-type semiconductor. In OFET applications both p-type and n-type are used though most of the OFET channels (Figure 34), some application even have to combine those two principles.<sup>75</sup> Though, in currently made are OFETs p-type channels perform significantly better than n-type channels. Accordingly, most of the currently made OFETs, when it is possible to pick up one of the types of semiconductors, use p-type small organic semiconductors.<sup>76</sup>

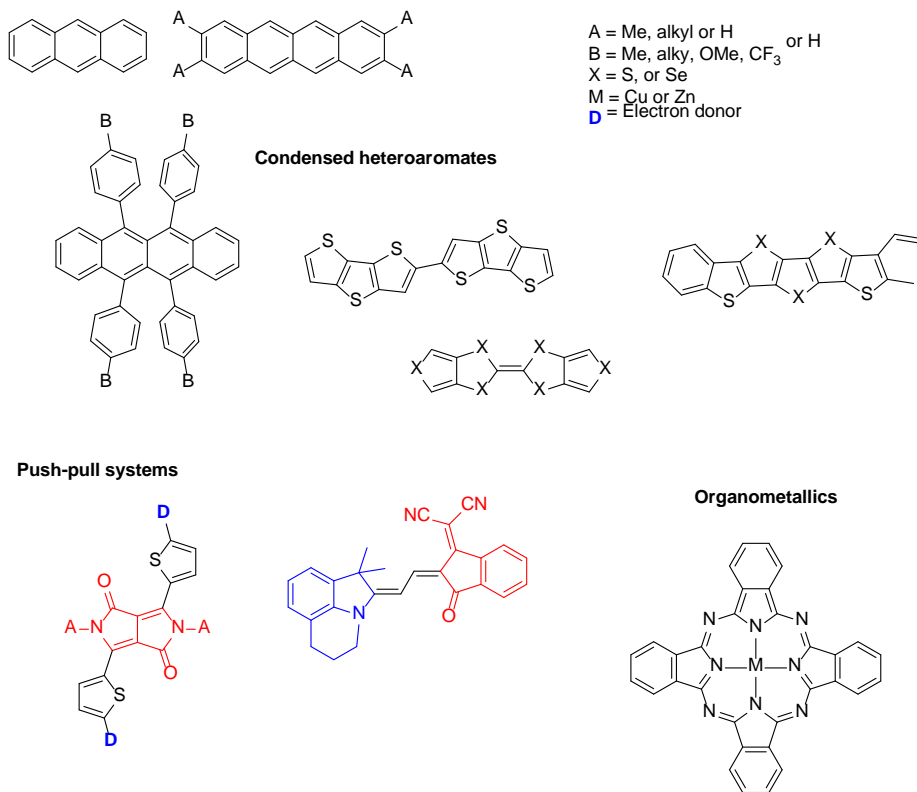
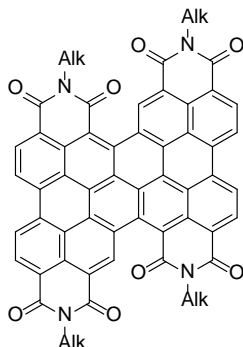
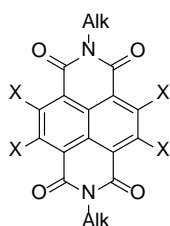


Figure 36 Examples of p-type small molecule organic semiconductors.<sup>74,77</sup>

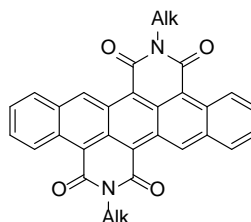
It is usually true that p-type semiconductors tend to be molecules richer in electrons and bearing more donor groups. With that stated, it is important to note that, sometimes counterintuitively, organic compounds considered to be lacking electrons appear to have also n-type semiconductor properties. Semiconducting film formed by small molecules cannot be reduced to one molecule, molecular stacking and  $\pi$ - $\pi$  interactions play an important role in both n- and p- type conductivity. Typically, viologens (Figure 38), although they are in their primary oxidation state deeply electron deficient in fact behave as the p-type semiconductors. Similarly fluorinated dithienoanthracenes<sup>78</sup> are as well expected to be more or less electron deficient. The fact of the matter is

that charge conductivity in organic semiconductors is directed by intermolecular effects, polarity and polarizability of the molecules and sometimes can be predicted only by computational chemistry.<sup>77</sup> Unsurprisingly, in case of push-pull chromophores (Section 2.1) can play the role of both p- and n- type semiconductors depending on various circumstances.

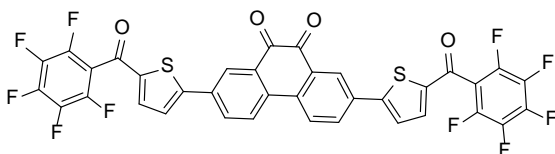
#### Polycondensed di(poly-)imides



Alk = alkyl or H  
 B = CF<sub>3</sub>  
 X = typically halogen, alkyl, perfluoroalkyl or condensed (hetero)aryl  
 M = Cu or Zn  
 D = Electron donor



#### Highly fluorinated compounds



#### Cyano containing compounds

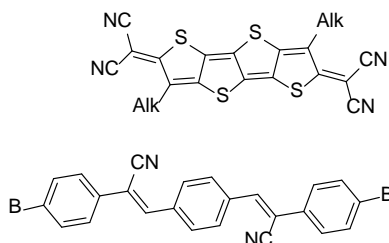


Figure 37 Examples of n-type small molecule organic semiconductors.<sup>74,79,80</sup>

The n-type semiconductors are indeed usually electron deficient structures, yet even here can be spotted some exemptions Figure 37. One of them is dibenzodithiafulvalene, which is considered to be an n-type semiconductor although most of the compounds considered chemically similar are in fact p-type semiconductors. N-type semiconductors do usually suffer problems with aerobic stability. Their LUMO should be lower than  $-4$  eV to gain at least some type of stability which, on the other hand, compromises their performance. In several applications, OFETs with both p- and n-type organic semiconductors are required, thus the research focusses on searching exceptionally stable n-type semiconductors. Polyimines (Figure 37) derived from naphthalene-1,4,5,8-tetracarboxylic acid are of the molecules with utmost stability while performing well as n-type semiconductors. Yet, even they are not capable to offer similar performance like the top tier p-type semiconductors.

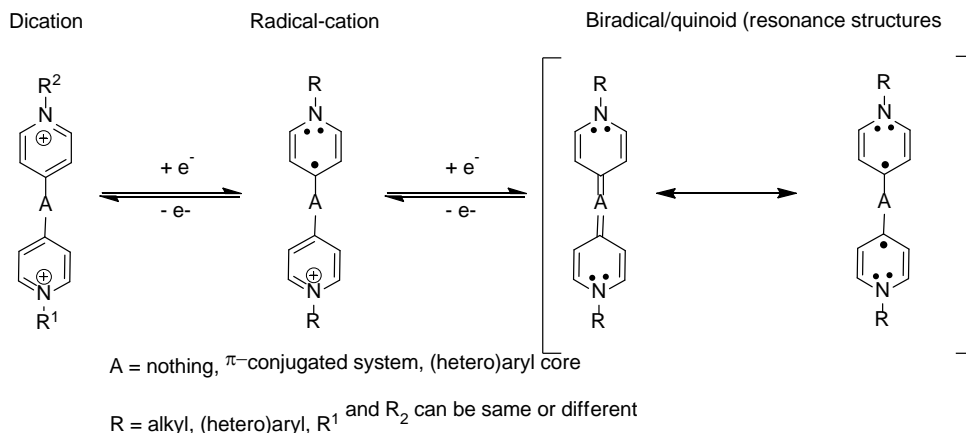
Small organic molecules as the semiconductors usually source from poly-condensed aromatic systems with variety of  $\pi$ -bonds. To predict a good semiconductor and predict a prospective p- or n- type is not as easy, as it seems (*vide supra*). Overall though, it holds true that the electron rich organic compounds are significantly likelier to be p-type semiconductors and the electron poor organic compounds regularly fall into the n-type category, as it has been aforementioned (Section 2.4), unless other effect of the crystal environment or  $\pi$ - $\pi$  stacking come to play.

### 3.3. OLED chromophores

Light emitting diodes (LEDs) are semiconductor devices in which an electric current is converted to a light. When the light emitting layer is an organic or polymeric compound they are classified as OLEDs or PLEDs (in case of polymers). LEDs, OLEDs and PLEDs play increasingly important role as light sources (especially when low radiation power and low power consumption is required), but more often as displays, control lights or indicator lights. Small organic molecules play an important role nowadays both in the electronics of this devices and, more importantly, as the actual electrochromic entity used in the devices.

Small organic molecules capable of activity in LEDs, therefore, have to have electrochromic properties. In general, electrochromic properties are achieved in an organic molecule whenever it has at least one oxidation state with luminescent properties. The textbook example of such molecules are viologens (Figure 13) which have at least two oxidation states capable of light emission.<sup>81</sup> The dication, radical-cation and biradical/quinoid oxidation states can be mutually interchangeable in dependence on the varying electric potential, whereas at least radical cation is always luminescent making the vilogens electroluminescent.





**Figure 38** General structure of viologens and principle of their electrochromism.

The electroluminescent properties, though, are not restricted to the viologens and their analogues. Several compounds with push-pull design (Section 2.1, Figure X) and with the alternative push-push and other designs as well. Notably a special class of molecules connecting the design of both properties of push-pull molecules (Section 2.1, Figure 39) and the frustrated Lewis pairs (Section 2.3) is among the most potent OLED chromophores.<sup>82</sup> The push-pull design proves especially perspective when the emitted light ought to be in the red and/or near infrared region.<sup>83</sup> Diaryl- (especially dimesityl-) boranes with triarylamino moiety in their structure can be stated as both push-pull and frustrated Lewis pair molecules in dependence on the point of view (this idea is further discussed in Section 2.3; Figure 24). But more often push-push and/or pull-pull designs are present (Figure 39 and Figure 40). In general, a reversible interchange in oxidation state(s) requires an electron-rich structure when electron conductivity is the key mechanism of electrochromism or electron poor structure when hole conductivity is such key mechanism.

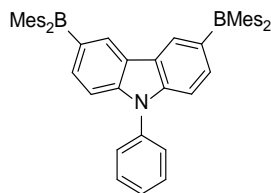


Figure 39 Electrochromic material resembling the structure of FLPs (Section 2.3).<sup>82</sup>

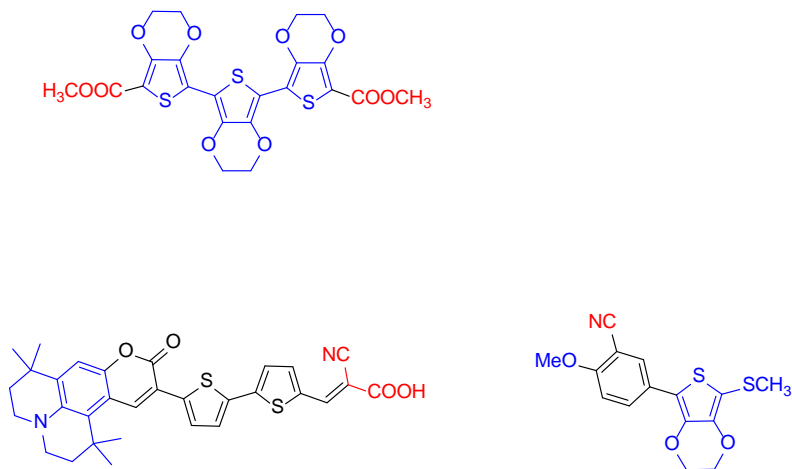


Figure 40 Examples of push-pull chromophores used as emitters in OLEDs.<sup>84,85</sup>

For an ideal OLED chromophore, the electroluminescence should be perfectly reversible. This, similarly to the problems with HTMs (Section 3.1) and organic semiconductors (Section 3.2) brings an obvious challenge towards the stability of a small organic molecules. More often than not, a single electron transfer means an opportunity for a chemical reaction, rearrangement or other structural change which usually compromise the electroluminescent properties of a device. One way around that is to connect some of the OLED chromophores into a macromolecule having repetitive small molecular motives, which brings us beyond our scope. Another strategy is to

introduce a transition metal into the molecule forming a complex. The central atom (transition metal) of the metallic complex can have the ability to buffer the electron transfers by changing its own oxidation state, minimizing the potential damage of the organic ligands. Transition metal complexes on the basis of iron, copper, ruthenium, palladium, platinum etc. are the state-of-the-art OLED electroluminescent materials nowadays. shows several most prominent organometallic electroluminescent materials used in OLED devices.

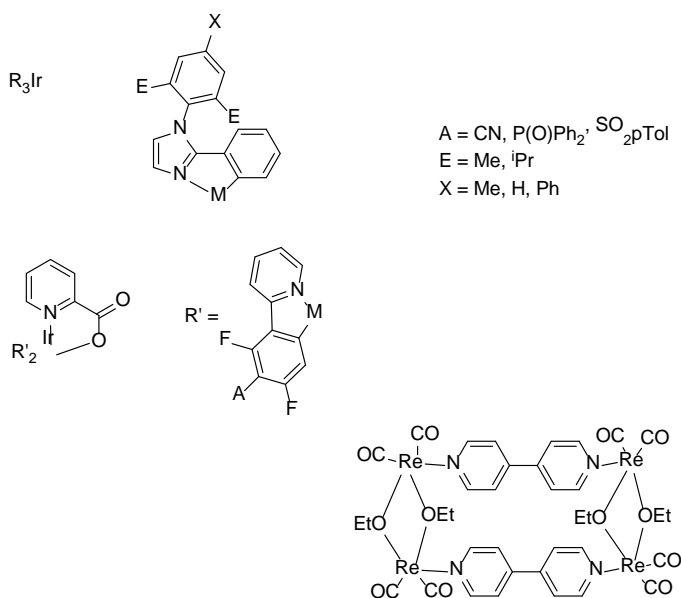


Figure 41 Examples of several potent organometallic OLED electrochromophores.<sup>86</sup>

On the other hand, a presence of transition metals carries with itself obvious questions of both safety and impact on the environment. That is why “pure” organic chromophores are usually considered safer and more suitable to be used in OLEDs. The aforementioned molecular designs such as push-pull (push-push or pull-pull) can deliver such properties, yet sometimes the stability and subsequent aging of the devices becomes more intensive problem. One

way around it is using of elements with available d-orbitals, especially the elements from the third period having available (and usually unoccupied) 3d orbitals which are energetically and geometrically suitable for interaction with typical organic  $\pi$ -bonds and orbitals usually present in the compounds with an organic backbone. And indeed sulphur, phosphorus and silicon, respectively, are among the most used heteroatoms in OLED chromophores. The presence of additional d-orbitals usually increases the stability towards oxidation and brings additional electronic levels for the (electro)excitation of electrons which has been multiply both theoretically and experimentally demonstrated to have a beneficial effect to the actual electrochromic properties. Figure 42 shows several successful OLED chromophores containing the elements from the 3<sup>rd</sup> period.

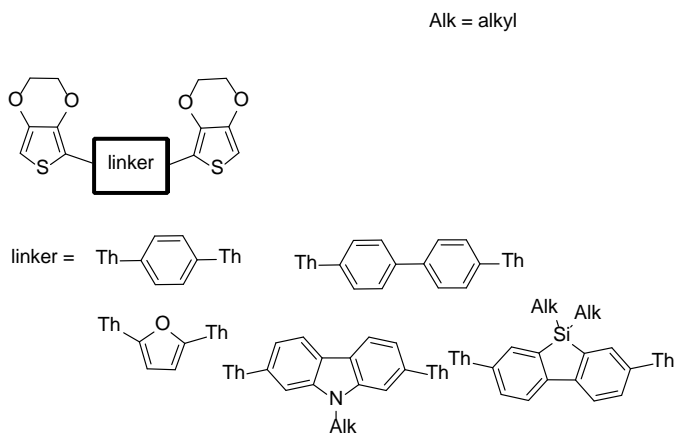


Figure 42 Thiophene-base electro-chomophores.<sup>81</sup>

For the real diodes, the simplistic theories offered above often fail and cannot deliver predictable and efficient emitters. Several advanced theories and concepts were developed due to it. One of the recent ones is “hybridized local and charge transfer” (HCLT) according to this principle local excitation<sup>87</sup>.

This leads to the design of D-A emitters partially resembling the principles of D- $\pi$ -A design, with the exception that they have, on purpose deranged planarity and level of conjugation throughout the molecule is, from the chemical standpoint, poor. Similar theories abbreviated TTA and TADF lead to other designs of molecules which do show remarkable quantum yield as LED emitters. Figure X show some LED emitters designed in accordance with these theories.

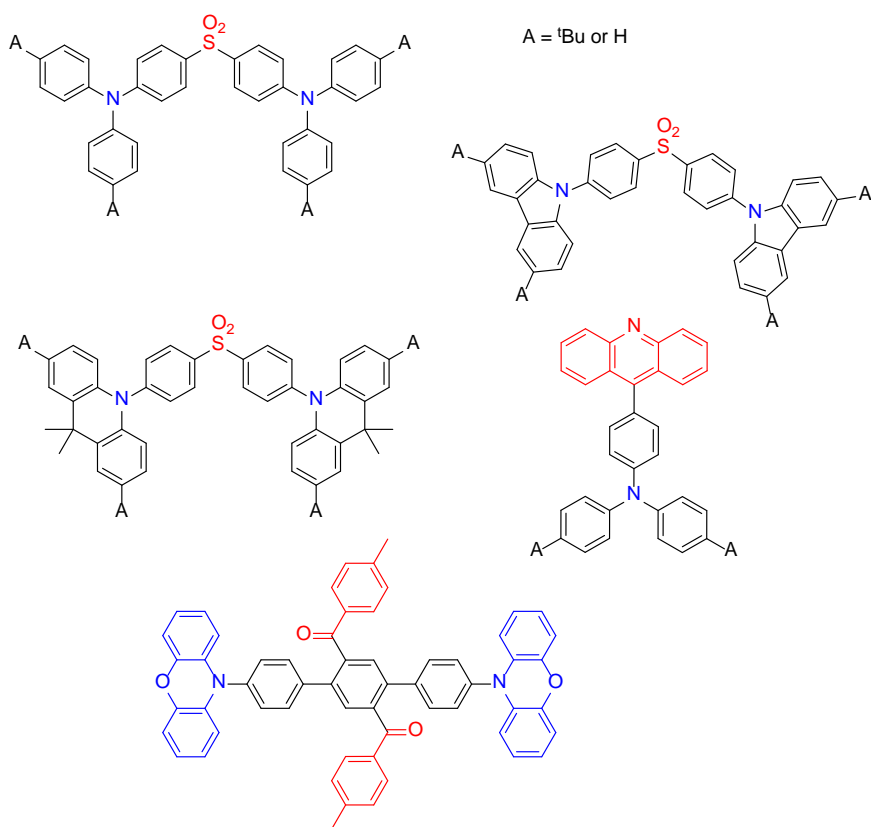


Figure 43 OLED emitters designed and synthesized according to recent structure-activity theories.<sup>86</sup>

## 4. Conclusions – the future of small organic molecules in technology

Although new sorts of materials, such as nanoparticles, carbon-based materials, inorganic materials such and polymers increase a portfolio of chemical compounds useful in various chemical and technological processes, small organic molecules, as defined in this text (Section 1.1) are not to be found as obsolete. Variety of their use in modern technologies especially those concerning various semiconductor technologies, electricity generation and data storage, etc. is tremendous and is likely to even increase. As of 2021 (year of finishing this text) at least thousand published concepts in each of the areas briefly touched by this text have been published. Additionally, at least 200 patents are contemporarily pending concerning DSSCs, BHJSCs, PSCs and other types of solar cells alone. Furthermore, at least there are approximately higher hundreds or lower thousands of those solutions currently commercially used in devices of everyday use. Displays of various kind (e. g. cell phones), memory devices, detection systems in cars and other vehicles, and some other high-tech applications use small organic molecules in variety of roles and functions.

Naturally, it would be both quite impossible, Sysiphean and counterproductive, to provide an exhaustive list of all of the concepts (not to say actual compounds) used in utilization of small molecules in modern technology. Instead of that, this text is a brief summarization of pedagogically relevant concepts and their actual projection to a chemical theory. Of course, the story here is to introduce the most basic concepts of technological, especially semiconductor design of small molecules and, hopefully, to attract

the attention to these concepts and, more hopefully to inspire may dear colleagues to start developing some of them.

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