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Chapter

Hexachlorinated Boron(III) Subphthalocyanine as Acceptor for Organic Photovoltaics: A Brief Overview

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Abstract

A boron(III) complex of peripherally hexachlorinated subphthalocyanine, Cl_6SubPc is a very promising small-molecule acceptor for application in organic photovoltaics. In this chapter the recent experimental results in the field are compared, and a critical review is given of the published works on the solar cells with the planar or bulk heterojunction architectures. The thin film properties of Cl_6SubPc are also considered. The approaches to the further modification of the molecular structure of boron(III) subphthalocyanine-type compounds for the enhancement of their photoelectrical properties are discussed.

Keywords: boron(III) subphthalocyanines, acceptors, organic electronics

1. Introduction

Recent achievements in the synthetic chemistry of subphthalocyanine-type compounds have led to an appearance of numerous molecular structures in a variety of shapes with markedly different redox and optical properties [1–3] and durability. However, only a few of those structures deserve the close attention of engineers involved in organic electronics.

The thin film electronic devices utilizing both subphthalocyanines and diverse phthalocyanine-type compounds are traditionally classified as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic photovoltaic cells (OPVC) [1, 4–7]. Of course, these fascinating heterocyclic molecules find their way into other areas of application such as resistive memory or molecular switches [8, 9], but those are incomparably inferior to the above three types of thin film devices in terms of practical achievements.

The light-emitting properties of conventional phthalocyanines in the undoped films do not appear to be very promising, so they are included in the OLED scheme mostly as the charge transporting components [1, 4, 10, 11]. Plint et al., who are continuing a long-term research in this field, proposed two SubPc derivatives as dopant emitters for an (8-hydroxyquinolinato)$_3$Al matrix to obtain the white light from a standard multilayer OLED made by the high-vacuum sublimation technique [12]. Also worth mentioning here is the earlier work of Torres' group [13], in which the solution-processable OLED structures incorporating variously substituted SubPcs were fabricated and tested.

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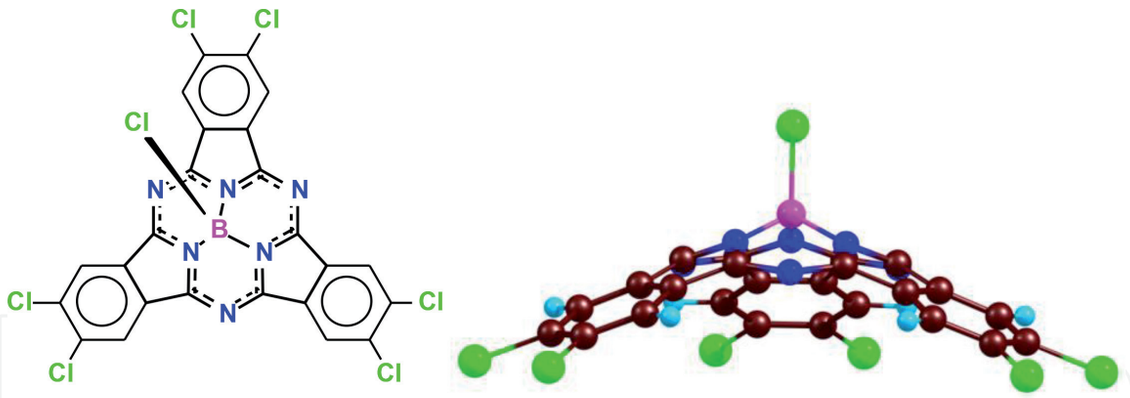


Figure 1.
Cl_6SubPc molecule: the planar chemical structure with π-conjugation (left) and the computed 3D structure illustrating the conical geometry (right). Green balls show chlorine atoms, one in the axial position (extraligand) and six on the periphery of the benzene rings.

As to the applications in OFETs, the readers should turn to the review in Ref. [14]. In short, the charge carrier mobilities measured using the standard transistor geometry in subphthalocyanine films are lower than in the films of four-leaf phthalocyanines that are capable of forming highly ordered structures in the channel. A noteworthy work was published more than 10 years ago by Yasuda and Tsutsui [15] who observed sign inversion (from N- to P-) in the majority charge carriers when transferring the SubPc-based OFETs with gold S/D electrodes from the glove box to ambient air. This adds intrigue to the current discussion of whether SubPc acts as a P- or N-type layer in the junction with another molecular material: a possible reason for that may be the unintentional doping from the adjacent layers or the unevenness of fabrication/measurement conditions for different prototypes.

The most impressive results today appear in the field of photovoltaics. We therefore will discuss SubPcs only from the viewpoint of their behavior in thin film photovoltaic cells, particularly in cells with an organic or hybrid heterojunction based on the hexachlorinated subphthalocyanine derivative Cl_6SubPc (**Figure 1**). This compound is gaining practical importance, though many other peripherally halogen-substituted SubPc derivatives have been synthesized over the last decade [1–5, 16]. To the best of our knowledge, only one hexachlorinated derivative with an extraligand other than chlorine was used in a photovoltaic cell [17]. Despite the availability of many sound publications that deal with Cl_6SubPc as the photovoltaic material, little is known about its fundamental (intrinsic) properties in a solid. In addition, we have found some inconsistencies in the discussions and speculations unsupported by the relevant experimental data.

2. Properties of Cl_6SubPc thin films

After the introduction of electron-withdrawing chlorine atoms on the periphery of a macrocycle, the Cl_6SubPc molecule behaves as the electron acceptor with respect to the molecule on the other side of the heterointerface (e.g., unsubstituted SubPc [6, 18–22]), thereby participating in the separation of the photogenerated charges. In the bulk phase, addition of chlorine atoms to the conjugated macrocycle assists in getting the electron transporting organic semiconductors [7]. Therefore, judging from its chemical formulae (**Figure 1**), Cl_6SubPc is a priori assumed to be the accept or N-type material for the organic photovoltaic cells. Perhaps, it is due to this assumption that too little effort has been made to

fundamentally characterize N-type conductivity in the Cl_6SubPc solid, except for a series of electro-physical experiments on the vacuum-deposited thin films, carried out by Beaumont et al. in [23].

The energy level alignment at SubPc/Cl_6SubPc heterojunction was recently discussed in detail [21] with the emphasis on the interface gap $E_G = E^{Donor}{}_{HOMO} - E^{Acceptor}{}_{LUMO}$ that determines the maximum achievable open-circuit voltage in a photovoltaic device with a D/A junction. The interface gap E_G of 1.95 eV was derived from soft XPS and XAS, with the use of DFT (**Table 1**) [21]. This value of E_G is much greater than what is attainable through pairing the SubPc donor with the conventional N-type acceptor C_{60}, which explains the popularity of Cl_6SubPc among the so-called "non-fullerene" acceptors for organic photovoltaics [5, 16, 17, 21, 25, 27, 30, 32, 33]. The DFT calculations on a Cl_6SubPc molecule were also performed in Refs. [6, 33], including the visualization of the most important frontier MOs. However, even in the abovementioned studies, such parameters as transport

Parameter	Value	Ref.	Comment
Sublimation temperature, °C	270–290	[24]	Greater than for many halogen$_x$SubPc
Color	Purple	[24]	In powder and in toluene solution
λ_{max}(Q), nm,	576	[25]	In chloroform
In solution	569	[24]	In toluene
	570	[26]	In dichloromethane
In sublimed film	585–590	[18, 19, 24]	Identical with SubPc
E_{opt}, eV	2.1	[20]	Link to Ref. [28]
	2.16	[27]	Not specified
	2.1	[28]	From λ_{max}(Q) in solid film
	2.19	[24]	From λ_{max}(Q) in solution
E_{act}, eV	1.38	[24]	From thermally activated conductivity in thin vacuum-deposited films
HOMO, eV[a]	6.69	[6]	From UPS
	5.9	[20, 23]	Adopted from [28]
	6.0	[21]	From XPS, XAS, and DFT
	5.8	[22]	From cyclic voltammetry
	6.06	[27]	From cyclic voltammetry
	6.0	[28, 29]	Adopted from [22]
LUMO, eV[a]	3.8	[20, 23]	Adopted from [28]
	3.9	[21]	From XPS, XAS, and DFT
	3.7	[22]	From HOMO-E_{opt} difference
	3.61	[30]	From cyclic voltammetry
	3.90	[27]	From HOMO-E_{opt} difference
	3.6	[28, 29]	From HOMO-E_{opt} difference
Charge carrier mobility μ, $cm^2\ V^{-1}\ s^{-1}$ at RT	$8 \pm 2 \times 10^{-7}$	[23]	Vertical zero-field electron mobility, from impedance spectroscopy
	8.3×10^{-6}	[27]	Blend with PTB7-Th, vertical electron mobility, from SCLC
	7.6×10^{-5}	[31]	Charge carrier mobility of the sum of holes and electrons Σ_μ, from flash-photolysis time-resolved microwave conductivity

[a] *These are actually negative, below vacuum level.*
Methods: UPS = ultraviolet photoelectron spectroscopy, XPS = X-ray photoelectron spectroscopy, XAS = X-ray absorption spectroscopy, DFT = density functional theory, SCLC = space-charge-limited current.

Table 1.
Cl_6SubPc, some experimental data.

gap, exciton binding energy E_{bi}, or diffusion lengths L_D, which are of paramount importance when constructing a heterojunction-based device [6, 34], have not been estimated[1].

Table 1 summarizes the data on some solid-state properties of Cl_6SubPc available in the literature. As expected, the most frequently discussed values are the positions of the highest occupied and lowest vacant molecular orbitals (HOMO and LUMO) since they can be used for deriving E_G and, further, for constructing the band diagrams that predict the basic photoconversion parameters of the devices employing various donor/acceptor pairs [20–23, 28–30, 35].

As seen from **Table 1**, the HOMO-LUMO values obtained by various methods/research groups fluctuate within the range of ±0.2 eV. Moreover, different numbers can be reported in the articles by the same authors ([20] *vs.* [28] or [21] *vs.* [22]). Such discrepancies are not surprising, considering the diversity of approaches/methods used for estimation [36]. Certain caution should therefore be taken when comparing the data from different sources and, especially, when relying on them in the interpretation of the device characteristics [30, 36]. For instance, in the same Ref. [30], E_G for the SubPc/Cl_6SubPc pair was calculated to be equal to 1.83 eV, i.e., the value did not coincide with that from the Ref. [21]. Importantly, the optical bandgap E_{opt} is smaller than the fundamental bandgap (the difference between the ionization potential and the electron affinity of a molecule) by the value of the electron–hole pair binding energy. Thus, the HOMO-LUMO difference obtained from the quantum chemical calculations with various levels of accuracy provides an approximation to the fundamental gap and needs to be amended before used as equivalent of E_{opt} (**Table 1**). The situation gets more complicated in a solid, where the transport of charge carriers or quasiparticles (excitons) occurs. Due to the polarization/stabilization effects, E_{bi} differs from the binding energy of electron–hole pair created within a (single) photoexcited molecule in the gas phase [36].

Cl_6SubPc sublimes in a high vacuum without noticeable decomposition, which allows one to obtain thin films on various functional substrates. The vacuum-deposited films are intensively purple colored, homogeneous, and smooth [24]. This favors their application in multilayer photovoltaic devices. However, they are electrically resistive [21, 24, 35], with the charge carrier mobility (electrons) much lower than in fullerenes (**Table 1**). In the literature, the Cl_6SubPc films are commonly treated as amorphous [21]. As recently shown, a correct choice of deposition surface and temperature contributes to the production of crystalline films of Cl_6SubPc with improved conductivity, which in turn upgrades the parameters of photovoltaic devices [24, 35]. To our knowledge, the effect of intentional or unintentional (e.g., atmospheric) doping of the Cl_6SubPc matrix on its conducting properties has not been investigated so far.

3. Fabrication of Cl_6SubPc-based heterojunctions for photovoltaic cells

Roughly, there are two types of heterojunctions with clear geometrical dissimilarity: flat heterojunction (PHJ) and bulk heterojunction (BHJ). Cl_6SubPc can be used in both—Refs. [5, 18–23, 25, 28–30, 35] and [5, 6, 27, 33], respectively. Such flexibility is accounted for by the increased, as compared to phthalocyanines, solubility of Cl_6SubPc, and subphthalocyanines in general, although a rigorous study of

[1] We have found only one source [Barito AJ. Cascade Organic Photovoltaics [thesis]. University of Michigan; 2015] unsupported by the relevant peer-reviewed journal publication, in which L_D = 4.5 nm and exciton lifetime τ = 0.53 ns are reported for the vacuum-deposited Cl_6SubPc films.

the solvation processes does not permit unambiguous attribution of conventional SubPc to the classical dyes, it is pigment-like rather [26, 37].

PHJ is prepared by sequentially depositing thin layers of donor and Cl_6SubPc. The most common A-on-D order of deposition gives a normal PHJ, assuming the cathode located on top of the device, while the D-on-A configuration with the anode on top is termed as inverted PHJ. The thickness of layers is of paramount importance, and it should be adjusted individually not only for the donor but also for Cl_6SubPc, since the experimental setup, deposition sequence, additional functional materials, etc. may vary in each research group. Thicker photoactive layers are likely to capture more incident photons and protect against leakages, but short L_D and rapidly increasing serial resistance require that the layers be kept sufficiently thin. Typical thickness of Cl_6SubPc in PHJ does not exceed few tens nanometers. Deposition process is carried out mostly via the vacuum evaporation technique, but the examples of solution-processed PHJ with subphthalocyanines are also known [38, 39].

To obtain a BHJ, a donor component and Cl_6SubPc should be dissolved in the chlorobenzene (various additives like 1,8-diiodooctane (DIO) or 1-chloronaphthalene (CN) are recommended) and then deposited using the spin-coating technique. Both the solution chemistry and post-deposition treatment of thus made blend affect the resulting device parameters [17, 27, 33].

It is generally believed that the efficiency of power conversion (*PCE*) in the photovoltaic cells with BHJ must be greater than in the PHJ-based cells, this being due to the morphological reasons [38–40]. Quite surprisingly, in all the works dealing with both solution- and vacuum-processed BHJ with a Cl_6SubPc acceptor, the actual morphology of the photoactive layer(s) remains highly uncertain. In Ref. [6], the morphology of 20 nm thick films consisting of a co-evaporated in vacuum $SubPc_x$:Cl_6SubPc_{1-x} blend has not been elucidated. In Ref. [27], the polymer: Cl_6SubPc mixture termed as BHJ was spin-coated and annealed to obtain 75 nm thick photoactive layers (**Table 2**), but the transmission electron microscopy (TEM) images showed a homogeneous blend without a noteworthy phase separation. This led authors to a conclusion that the pure phase domains are absent. Notably, the nanocrystalline domains with high local carrier mobility of at least one of the two components of BHJ are required for efficient dissociation of the charge transfer (CT) states into free charge carriers at the D/A interface [27].

A broader morphological study in Ref. [33] included atomic force microscopy (AFM), TEM, and X-ray diffraction (XRD) measurements on the spin-coated mixtures of substituted subphthalocyanines, including Cl_6SubPc, with a polymer, also termed as BHJ. However, a thorough examination of the published images reveals that neither AFM nor TEM indicates a formation of a long-enough fibrillary structure in the films (unspecified thickness), although authors stated otherwise[2]. The XRD patterns display the changes in the intensity of a single diffraction peak corresponding to the polymeric component of the blend relative to the pure phase of the polymer (at only one D/A ratio) [33], which cannot be regarded as a proof of BHJ.

In neither of the above studies, a relevant morphological model has been developed based on the instrumental analysis. The "phase diagram" attributing the morphological changes to the composition of a binary phase [43–45] is missing as well. The well-known "mosaic" picture of the polymer: subphthalocyanine BHJ published in 2009 [38] seems to be borrowed from the sketches of the polymeric solution-made BHJ [16, 45] without being confirmed by adequate morphological analysis. Contrary to what is drawn, the authors stated at the end of the article [38] that the films stayed amorphous even for the 1:5 blend (from grazing incidence

[2] Authors claimed in the supplementary materials section that their Cl_6SubPc-based cells outperform the BHJ-based cells fabricated in Ref. [27], which is not true (**Table 2**).

Ref.	Schematic of cells*	Junction type	Parameters			
			J_{sc} (mA/cm^2)	V_{oc} (V)	*FF*	*PCE* (%)
[18, 19]	A1	PHJ	3.10	1.33	0.59	2.39
	A2		3.62	1.29	0.47	2.20
	A3		3.28	1.32	0.63	2.70
[22]	B	PHJ	3.53	1.31	0.58	2.68
[23, 28]	C1	PHJ	2.54	0.89	0.50	1.12
	C2		2.09	0.50	0.48	0.50
[30]	D1	PHJ	6.17	1.00	0.66	3.96
	D2		10.1	1.04	0.67	6.86
[25]	E1	PHJ	9.0	1.03	0.71	6.4
	E2		9.0	1.02	0.68	6.1
	E3		9.2	1.03	0.58	5.4
[28, 29]	F1	PHJ	5.72	0.60	0.56	1.89
	F2		2.13	0.44	0.57	0.52
[35]	G	PHJ	6.43	0.55	0.48	1.71
[27]	H	BHJ	10.7	0.77	0.48	4.0
[33]	K	BHJ	7.79	0.66	0.48	2.48
[41]	L	PHJ/ BHJ	8.6	0.92	56	4.46
Cells with SubNc as acceptor or donor						
[42]	M	PHJ	14.55	0.96	61	8.40
[39]	N1	BHJ	10.3	0.90	41	3.8
	N2		12.1	0.74	47	4.2

**Description of the schematic (thickness of layers in nm is given in the parentheses, if specified by authors): A1 = ITO/MoO_x(5 nm)/SubPc(15)/Cl_6SubPc(20)/BCP(8)/Al, normal; A2 = ITO/BCP(8)/Cl_6SubPc(15)/SubPc(15)/MoO_x(40)/Al, inverted; A3 = ITO/MoO_x(5)/SubPc(14)/Cl_6SubPc(30)/BCP(5)/Al, optimized; B = ITO/MoO_x(5)/SubPc(10)/ Cl_6SubPc(27)/BCP(8)/Al; C1 = ITO/MoO_x(5)/Tc(60)/Cl_6SubPc(35)/BCP(8)/Al(100); C2 = ITO/MoO_x(5)/Pent(60)/Cl_6SubPc(25)/BCP(8)/Al(100); D1 = ITO/MoO_3(5)/SubNc(14)/Cl_6SubPc(8)/BCP:C_{60}(50)/Ag; D2 = ITO/PEDOT:PSS/DIP(5)/SubNc(14)/Cl_6SubPc(8)/BCP:C_{60}(50)/Ag; E1 = ITO/PEDOT:PSS/DIP(5)/SubNc(12)/Cl_6SubPc(10)/BCP:C_{60}(45)/Ag; E2 = ITO/PEDOT:PSS/DIP(5)/SubNc(12)/Cl_6SubPc(10)/C_{60}(35)/BCP(10)/Ag; E3 = ITO/PEDOT:PSS/DIP(5)/SubNc(19)/Cl_6SubPc(10)/BCP:Yb(45)/Ag; F1 = ITO/PEDOT:PSS/α6T(55, evaporated)/Cl_6SubPc (20)/BCP(10)/Ag(100); F2 = ITO/PEDOT:PSS/P3HT(55, spin-coated)/Cl_6SubPc(20)/BCP(10)/Ag(80); G = ITO/MoO_x(3)/CuI(60)/Cl_6SubPc(45)/BCP(6)/Al(100), structured; H = ITO/ZnO(40)/PTB7-Th:Cl_6SubPcCl (~75, solution)/MoO_x(10)/Ag(100); K = ITO/PEDOT:PSS(40)/PBDB-T:Cl_6SubPcCl(?, solution)/Ca(20)/Al(100); L = ITO/MoO_x(10)/DPSQ(13)/C_{60}(15)/C_{60}:ZCl:Cl_6SubPc(60,2:1:1 co-evaporated blend)/BCP(10)/Al(100); M = ITO/PEDOT:PSS(20)/α6T(60)/SubNc(12)/SubPc(18)/BCP(7)/Ag(120); N1 = ITO/MoO_3(5)/SubNc:PC_{70}BM(75,1:5 solution)/BCP(6)/Al(100); N2 = ITO/MoO_3(5)/SubNc:C_{70}(75,1:5 co-evaporated blend)/BCP(6)/Al(100).*

Donors: SubPc = unsubstituted subphthalocyanine; Tc = tetracene; Pent = pentacene; SubNc = unsubstituted subnaphthalocyanine; α6T = α-sexithiophene; P3HT = poly(3-hexylthiophene); PTB7-Th = polymer with linear formula $(C_{49}H_{57}FO_2S_6)_n$; PBDB-T = polymer with linear formula $(C_{68}H_{78}O_2S_8)_n$; DPSQ = 2,4-bis[4–(N,N-diphenylamino)–2,6-dihydroxyphenyl] squaraine.

Other device components: ITO = indium-tin oxide, In_2O_3:SnO_2; MoO_x or MoO_3 = molybdenum trioxide, usually substoichiometric; PEDOT:PSS = poly(2,3-dihydrothieno-1,4-dioxin)-poly(styrenesulfonate); BCP = bathocuproine; DIP = diindenoperylene ($C_{32}H_{16}$), CuI = cuprous iodide, ZnO = zinc oxide; ZCl = chlorinated zinc dipyrrin; PC_{70}BM = [6,6]-phenyl-C_{71}-butyric acid methyl ester.

Table 2.
Parameters of the photovoltaic cells with Cl_6SubPc as acceptor.

wide-angle X-ray scattering) and that "work is under way to improve the crystallinity of SubPc derivatives" [38].

Therefore, the researchers rely only on the fact that a film containing a mixture of two components is a BHJ. But rigorously speaking, there are certain morphological features that determine the ultrafast charge transport—the reason behind the success

of the BHJ concept in organic photovoltaics [45]. The most important of them is the formation of bicontinuous interpenetrating 3D networks of components within a D/A blend. These networks, often thought of as columnar (pipelines), comb-like, or interdigital structures, should accomplish the transport of photogenerated charge carriers to the respective electrodes. Obviously, breaking the continuity will lower the charge collection efficiency. There is ample experimental evidence of the existence of such interdigitation in the classical solution-processed polymer: fullerene blends obtained by a set of independent, complementary analytical techniques, including the secondary ion mass spectrometry (SIMS) with depth profiling [45, 46].

We have found out that the misconception about any two-component layer as being truly a BHJ rests on the analogy with few examples of the photovoltaic cells, in which the (sub)phthalocyanine is mixed with C_{60}. Vacuum-deposited SubPc:C_{60} blends are widely known in organic photovoltaics due to availability and high efficiency; they are often used as a model system in many theoretical and experimental works. However, there is only one work where their microstructure was sufficiently detailized. Pandey et al. [44] conducted a comprehensive characterization of thin films of a mixture of SubPc:C_{60}, involving XRD, TEM, optical spectroscopy, and selected area electron diffraction. At only one mixing ratio of 1:4, they found some signs of crystallinity of SubPc dispersed in the nanocrystalline C_{60} matrix, whereas other compositions resulted in amorphous films. The *PCE* of the photovoltaic cells with thus optimized composition of the photoactive layer was only 9% higher than in a similar cell, in which the composition was not optimized (1:9). Besides, the morphology characterization and photovoltaic measurements were carried out on different substrates and films of different thickness, which requires further refinement[3].

Even for the metal-phthalocyanine complexes that tend to self-assemble (crystallize) due to a strong intermolecular interaction, a reliable experimental observation of the anticipated nanostructuring in co-evaporated blends turned out to be very problematic. As-deposited phthalocyanine: fullerene mixtures (commonly used ratio is 1:1) adopt fully amorphous structure, as witnessed via a combination of several independent analytical techniques [40, 51–55]. Again, it points to a lack of the phase separation, which is a prerequisite toward the formation of the interpenetrating D/A network typical of BHJ [45]. Only through considerable effort, by thoroughly selecting the annealing temperature, mixing ratio, or seed layer, the microscale organization of a blend can be initiated, and the pure crystalline phthalocyanine domains become visible [44, 52–54]. Unlike phthalocyanines, the SubPc molecules weakly interact in a solid, which makes their self-assembly rather difficult. As such, the formation of a well-established charge carrier percolation pathways in the SubPc:C_{60} blend will be less probable than in the phthalocyanine-based blends.

Crystallographic studies show that interactions between the neighboring Cl_6SubPc molecules in a solid are stronger than those in SubPc [23], but the formation (and observation) of a well-organized BHJ incorporating subphthalocyanine-type acceptor is still a challenging task.

[3] In mid 1990s, studies of the photoconductivity in thick films of the C_{60}-doped zinc phthalocyanine revealed the formation of a charge transfer complex that amplifies the photosensitivity of the blend [47, 48]. This was confirmed in Refs. [49, 50] using several optical methods, but later the authors sided with another model more closely associated with the BHJ, again with no morphological indications. In either way, the formation of a bimolecular CT complex means that the uniformly 1:1 mixed phase cannot be treated in terms of individual organic semiconductors any longer. Here, it is worthwhile to look further into the matter by proposing the new insights on the photoconductivity mechanisms instead of pursuing adaptation of the standard polymeric BHJ concept to the amorphous small-molecule based blends [51].

In any heterojunction type, the charge transfer across the D/A interface could also be influenced by the dipole moment of a molecule of one or both components. It bound to occur in the pyramidal subphthalocyanine molecules bearing axially attached halogen (**Figure 1**) and can further be tuned by the axial/peripheral substitution [4, 26, 56–59]. Mutual orientation of the acceptor/donor molecules at the interface affects both the dissociation distance and the local electric field during the charge transfer and separation, thus modifying the resulting V_{oc} of the device [59]. Morris et al. [59] experimentally investigated and modeled the characteristics of PHJ-based photovoltaic cells with two subphthalocyanines containing either chlorine or fluorine extraligand paired with the C_{60} acceptor. These donor molecules have nearly identical structure, except for a permanent electrical dipole, which allows the analysis of the variations in V_{oc} in terms of D/A separation width, polaron pair binding energy, and dipole orientation, other morphological factors being neglected.

Unfortunately, this interesting issue has not been given enough attention in the experiments. Theoretical considerations regarding the influence of a molecular dipole in a series of, mostly hypothetical, subphthalocyanines on the photovoltaic parameters were recently published [58]. The first-principles DFT calculations were also performed in [60] to characterize the electronic structure of the axially substituted SubPc molecules interfaced with C_{60}. A strong correlation between the experimentally measured V_{oc} and the computed CT excited state energy was found. One concluding remark hints that the dependence of these parameters on the actual interface morphology can be greater in significance than the modification of the ionization potential induced by change in the chemistry. Another prediction is that to gain a higher value of V_{oc}, the D/A interaction should be lowered, e.g., by increasing the spatial separation through the introduction of steric hindrances [60]. A fundamental theoretical study of relative arrangements of the donor and acceptor molecules was carried out by a large group of authors using the pentacene/C_{60} system as an example [61]. It was shown that the interfacial dipole originates mostly in polarization effects rather than a partial charge transfer from donor to acceptor. Next, the calculations demonstrate that the measurement of the macroscopic dipole averaged over the interface is not a representative of the local dipoles that can be induced by individual molecules at the interface. The local dipole was found to fluctuate in sign and magnitude over the interface and appears as if a sensitive probe of the relative arrangements of the pentacene and C_{60} molecules.

Note that theoretical findings are usually done under the assumption of an inert, molecularly sharp, regular, and pure PHJ (which almost never occurs in the experiments) and lack systematic verification in a representative series of the prototypical devices. For instance, the experimental evidence on the formation of a Diels-Adler adduct at the pentacene/C_{60} interface was recently found [62], thus casting doubt on the above results.

These and many other morphological issues are also addressed in the monograph, Chapter 2 in Ref. [63]. This book in general is strongly recommended for the readers interested in organic photovoltaic devices and materials.

4. Analysis of the cell performance

Table 2 summarizes the efficiency metrics for the prototypical solar cells exploiting Cl_6SubPc adopted from various sources, along with a description of the device schematics. For comparison, a few examples of the cells with subphthalocyanine are included in the last two rows. Other data collections describing the performances of variously designed photovoltaic devices based on SubPc-type compounds can also be found in Refs. [1, 4, 5, 28, 64].

As seen from **Table 2**, the single-junction photovoltaic cells with Cl_6SubPc as the acceptor can generate open-circuit voltage V_{oc} in the range of 0.44–1.33 V, usually about 1 V or above. Expectedly, the decisive contribution in the resulting *PCE* makes the short-circuit current J_{sc}; its value varies several times among different devices, while fill-factor *FF* lies within a range of 0.57 ± 0.12. The reported parameters largely depend on the device scheme, adjacent functional materials, and measurement conditions used in a particular study, which make their comparison difficult. Nonetheless, there are several points to ponder on when looking at the collected data:

1. Pairing Cl_6SubPc with the congener donors, SubNc or SubPc, results in the photovoltages exceeding 1 V. This value is greater than ever reported for the analogous PHJ utilizing structurally dissimilar small-molecule acceptors, like perhalogenated phthalocyanines or perylenes. Presumably, the structural similarity of the pairing conical molecules allows them to form a more intimately bound D/A pairs at the interface. This would mean, for example, a good quality of the (less distant) physical contact at the P/N junction. Second, as discussed above, certain orientations of electrical dipole of the donor molecule relative to the intrinsic dipole of acceptor, if one exists, could favor the charge separation. Macroscopic interfacial dipole at the SubPc/Cl_6SubPc junction was found to be small (0.15 eV) in [21], but in principle its role can be significant [51, 57, 59, 61, 63][4].

2. The devices obtained entirely by the vacuum deposition techniques usually exhibit better characteristics than devices with the solution-processed heterojunction (**Table 2**). At least two reasons could be suggested, taking into account that in reality the metallic contacts and oxide buffer layers are vacuum-evaporated even in the cells referred to by the authors as "solution-processed." First, the combination of wet and dry laboratory techniques used for the growth of multilayered heterostructures incurs problems with the compatibility of materials, transfer of semi-finished samples to the evaporator and back, etc. Using the vacuum methods only, the fabrication of the entire sample can be realized within a single run without breaking the growth process, from etching of substrates to deposition of the top electrode (including characterization tools, most of which require high vacuum). Second, the simplicity and robustness of the solution-based deposition techniques are somewhat overrated in the case of BHJ based on small-molecules. This is illustrated in the preceding section that describes the difficulties in obtaining the phase-separated bicontinuous networks with SubPcs. The BHJ concept does not provide the expected benefit in efficiency and is particularly unuseful for improving V_{oc}.

3. The champion efficiency of 8.4% reported for the PHJ-based photovoltaic cells so far has been obtained for the α6T/SubNc/SubPc cascade [42], which geometrically is a sequence of vacuum-evaporated PHJs. Here, both SubNc and SubPc behave as acceptors with respect to the thiophene molecules while being donors when paired with fullerenes or halogenated subphthalocyanines (**Table 2**). The excitons freely migrate across the relatively thick layers from

[4] In Ref. [65], a complex study of the "copper phthalocyanine/C_{60}" interface by DFT, UPS, and SIMS suggests that the local net charge-induced electric field, rather than the spontaneous charge transfer across the interface, is responsible for the interface dipole, in accordance with the theoretical predictions [61]. Authors observed a sizable interface dipole of electrostatic nature (up to 0.27 eV, depending on molecular orientation with respect to the deposition surface and on the deposition sequence), which rules out the charge transfer as the origin of the interface dipole.

the wide-bandgap to the smaller-bandgap acceptor with a subsequent dissociation at the donor interface via a long-range Förster energy transfer, which is in turn a function of the relative orientation of the transition dipole moments and distance between the molecules. The mechanisms explaining why both acceptors actively contribute to the photocurrent caused an active response in the organic photovoltaic community and spawned a large number of emulations. The attempt of Bender et al. [20] to use Cl_6SubPc as the donor component of the cascade cell with the scheme "Cl_6SubPc/μ-oxo-SubPc/C_{70}" was unsuccessful, highly likely due to the wrongly cascading LUMOs (but a very small layer thickness permitted enough efficiency). The cascade cells in Refs. [25, 30], although the authors do not consider them as such, demonstrated a high photovoltaic performance (**Table 2**).

It should be noted that SubNcs hold the second position in the ranking of SubPc-type compounds after parent SubPc; their properties and optoelectronic applications deserve a separate circumstantial review.

5. Current status and perspectives

Work on design of D/A junctions with various halogen-substituted subphthalocyanines was initiated back in 2009 [64]. In the last few years it is Cl_6SubPc that has become one of the most efficient acceptors in both bilayer and blended heterojunctions. Many authors now use Cl_6SubPc as a reference when introducing their newly synthesized compounds belonging to the subphthalocyanine family in photovoltaic devices [16, 17, 24, 27, 28, 31–33, 66], as was commonly done earlier with C_{60}. However, the critical analysis of the current literature suggests that Cl_6SubPc still holds the lead among competitors. It combines availability (ease of synthesis and good yield), versatility of deposition (both wet and dry methods are available), appropriate color characteristics (position and intensity of the Q-band), and stability. Such benefits stimulate appearance of new heterojunctions designs employing this compound and steady interest in future research. For instance, such drawbacks as low charge carrier mobility in thin films can be overcome using morphology engineering [35]. Doping of the Cl_6SubPc molecular matrix with appropriate agents could be another option for improvement of the conducting properties [30]. Or vice versa, Cl_6SubPc can be doped into (mixed with) another acceptor to form a ternary blended junction [41].

Meanwhile, the search for new electron acceptors for photovoltaics among the subphthalocyanines with electron-withdrawing substituents on the periphery is underway. Two interesting approaches have been proposed last year by Torres and coworkers, who are the main newsmakers in this field. The first one consists in the synthesis of subphthalocyanines hexacyanated at the same peripheral positions as in Cl_6SubPc [31]. Unfortunately, due to the inherent instability of hexa-substituted derivatives, only slightly cyanated compounds were obtained and characterized, which have two cyano groups in only one isoindole unit, while the other two still bear two chlorines each, as in the parent Cl_6SubPc (**Figure 1**). Even for such CN_4Cl_2SubPc complex, there are indications on the increased mobility of charge carriers in vacuum-deposited films [31].

The second approach addresses the synthesis of new SubNc-type compounds with chlorines in the outer benzene rings [66]. Authors chose to directly use the dodeca-substituted derivative having four Cl atoms in each outer benzene ring, which unluckily is insoluble, whereas the entire work was targeted at making

devices with a solution-processed BHJ[5] only. In this respect another work of Bender et al. [67] is worth mentioning, in which the authors argue that due to the nature of synthesis all of the SubNcs, both commercially available or obtained using the published protocols, in fact represent a mixture of derivatives randomly chlorinated at bay position. That is, in addition to the axial chlorine, part of the molecules inevitably contains chlorine atoms attached to the inner benzene rings of the naphthalene moieties. The outer benzene rings remain always hydrogenated. The presence of 1.13–2.96 chlorines per molecule on average was estimated [67]. Curiously, chlorination of all available bay positions in this compound would yield the Cl_6SubNc compound that has not been described yet.

The electron-accepting properties of the Cl_6SubPc molecule can be further enhanced by substituting the carbon atoms not bonded to chlorine with the more electronegative nitrogen. Such subporphyrazine-type compounds are synthesized in our group [24, 68]. However, the deep-lying HOMOs often cause a decrease in the specific conductivity of the bulk material. As with many other synthetic approaches, an exact balance must be maintained between the individual properties of a molecule and the photoelectrical properties (including morphological issues) of a solid.

Eventually, the group from Kyushu University developed the SubPc-type compounds, in which two chlorines in each benzene ring are (a) replaced by the -S-(C=O)-S- semicircle, or (b) peripheral benzenes in SubPc were directly replaced with the electron-withdrawing 1,3-dithiole-2-one units [69]. The deep bowl depths and curvatures of the formed SubPc and SubPz cores (*cf*. **Figure 1**) motivated authors to investigate the bimolecular concave-convex interactions with fullerenes in the co-crystals, as a first step to the fabrication of photovoltaically active materials.

6. Conclusion

Molecular properties of the Cl_6SubPc compound, such as redox potentials and positions of the absorption bands, fluorescence quantum yield, solubility, and stability, make it a material of choice when it comes to fabrication of a small-molecule based optoelectronic device, with almost any schematic. After a proper optimization of the donor material in the P/N junction (N = Cl_6SubPc) and with corresponding device composition, the open-circuit voltages above 1.3 V can be achieved. Further progress in the power conversion efficiency is limited mostly by the density of current leaking through the illuminated device, a parameter strongly dependent on the mutual arrangement of Cl_6SubPc molecules either in a layer (for PHJ) or in the interpenetrating network (if it exists) and on the morphology of the heterointerface at the nanoscale. The questions whether the electrical dipole or symmetry of the molecule could affect the generation of charge carriers by the junction do not seem to be of serious practical importance, but are very interesting for fundamental understanding of the photovoltaic process proper.

[5] The authors claimed that SubNcs have never been tested as either donors or acceptors in solution-processed BHJ solar cells [66]. This is not correct since in 2013, Yang and coworkers have published their data on both solution-processed and vacuum-evaporated BHJ with SubNc donor (acceptor was $PC_{70}BM$ or C_{70}, respectively) [39]. The optimized devices showed promising efficiency of 4.0 and 4.4% at room temperature (**Table 2**).

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Conflict of interest

The authors declare no conflict of interest.

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