Organic semiconductors based on small molecules with thermally or photochemically removable groups

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Solution processable organic semiconducting small molecules are desirable for the manufacture of low-cost, large-area electronic products on flexible substrates. This article provides an overview of recent progress in OFETs based on solution processable small molecules that can be converted to insoluble organic semiconducting materials on films by thermal or photochemical removal of leaving groups after fabrication of the film.

1 Introduction

Organic semiconductors have emerged as an important class of new materials with applications, for example, in organic light emitting diodes (OLEDs), organic photovoltaics (OPVs), organic field effect transistors (OFETs), and sensor materials.[1–6] Recent progress in this field has been remarkable, and televisions based on OLEDs are now in industrial production. On the other hand, other applications of organic semiconductors such as OFETs or solar cells are still far from practical realization, for the device efficiency of organic materials in such applications is poor compared to those of Si-based devices. However, organic materials have their own advantages such as low-cost, large-area and/or low temperature device fabrication based on solution processes. Such processes offer the possibility of depositing materials from solution, enabling patterning by, *e.g.*, ink jet printing.[7] The OFET devices consist of deposited conductors (gate, source, and drain electrodes), an insulator (SiO_2 or plastics) and organic semiconductors. The thin-film transistor works as a switch between on and off states. When a bias is applied to the gate electrode, the gate is biased negatively or positively to induce hole or electron transport, respectively, in the organic semiconductor layers. This movement of holes or electrons is termed p-channel or n-channel transport, respectively. In order for OFETs to be used in driving circuits for display applications, they need to exhibit high carrier output, good switching speed, and high contrast between the on and off states. These characteristics are related to several important parameters, namely, charge-carrier field effect mobility (μ), threshold voltage (V_{th}), sub-threshold voltage (S), and on/off current ratio (I_{ON}/I_{OFF}). In OFETs, the device performance is affected by factors such as grain size, depth of grain boundary, contact resistance between organic semiconductors and electrodes, and the interface between insulators and organic semiconductors. Annealing processes, surface treatment of the dielectric layer, and variation of the deposition rate have been widely used to control the molecular order of the active thin film layer. Thus, the mobility of pentacene OFETs has been improved dramatically and now it exceeds that of amorphous SiH.[4]

Advances in OFET technology have typically focused on development of organic materials with high charge carrier mobility or solution processability. Solution processability is key to realizing low-cost, large-area electronic products on flexible substrates. In order to form OFETs from solution, the materials have to be soluble and be able to form uniform, large-area films, in which semiconducting materials are well ordered. There are three classes of solution processable organic semiconductors: type A, polymeric semiconductors; type B, small molecules with solubilizing groups; and type C, small

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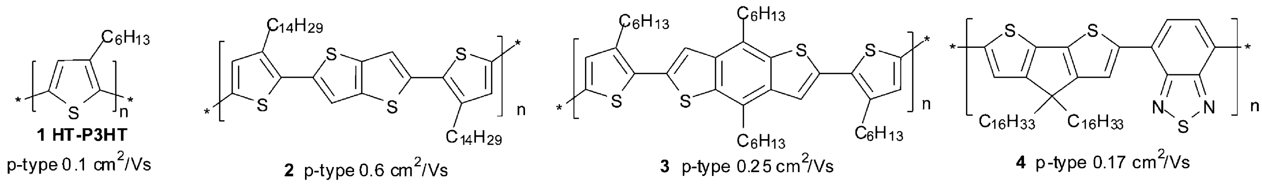


1 **HT-P3HT** p-type 0.1 cm^2/Vs

2 p-type 0.6 cm^2/Vs

3 p-type 0.25 cm^2/Vs

4 p-type 0.17 cm^2/Vs

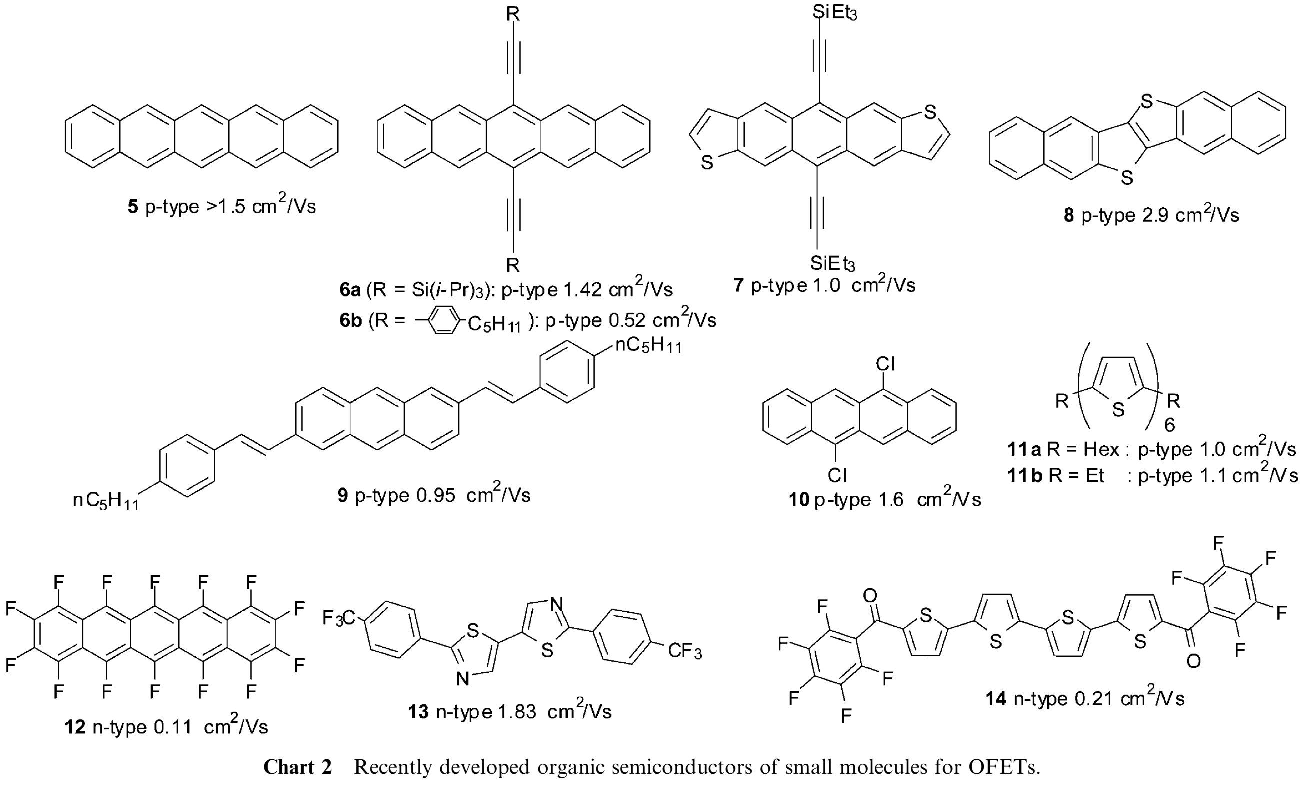
Chart 1 Recently developed polymer semiconductors for OFETs.

molecules with thermally or photochemically removable groups.

In general, polymeric materials are suitable for use in a solution process, because they tend to form amorphous thin films in most cases. For example, conjugated polymers have been extensively studied as OLED materials but their carrier mobilities are too low to be applicable to OFETs. Recently, polymeric materials **1–4**, which have a microcrystalline morphology with strong π–π interaction have been prepared to increase the carrier mobility in OFETs, as shown in Chart 1. The mobilities of the polymer OFETs are now >0.1 cm^2 V^{-1} s^{-1}.[8–11]

However, the efficiency of polymeric materials as semiconductors is still lower than that of small molecules such as **5–14** in Chart 2.[2–6,12–30] Small molecules afford polycrystalline thin films by vacuum deposition, which results in a reliable and efficient OFET. Vacuum deposited pentacene (**5**), a typical semiconducting small molecule, affords an OFET with very high mobility of >1.5 cm^2 V^{-1} s^{-1}.[14–19] For high carrier mobility, π-orbital overlap between adjacent molecules is important. The majority of unsubstituted acenes crystallize in herringbone structures, in which molecules minimize π-orbital repulsion by adopting an edge-to-face arrangement, forming a two-dimensional layer. If the face-to-face arrangement can be attained by the introduction of substituents, carrier mobilities will be improved compared to the corresponding unsubstituted (and insoluble) acenes. The introduction of substituents, however, frequently lowers performance below that of their insoluble, vacuum-deposited counterparts, because (1) substituents inhibit π–π stacking of molecules and therefore inhibit charge transfer between molecules; and (2) solubilizing groups often consist of insulating hydrocarbons, which can lower the overall conductivity of materials.[2] So far only a few films prepared from solutions of substituted acenes have been reported to show mobilities higher than 0.1 cm^2 V^{-1} s^{-1}, as shown in Chart 2.[3,20–23] Now it is a challenge to develop small molecules which exhibit high mobility and are suitable for a solution process.

In this paper, we report our strategy to develop small molecules of type C, rendered soluble by the presence of solubilizing groups, which are removed after spin-coating or printing by a thermal or photochemical process. Compared to thin films of type A or B, thin films of type C are ideal for device fabrication, for such semiconductors become insoluble after conversion from precursor films. Thus, development of type C semiconductors, whose OFETs display good performance such as high mobility (>1 cm^2 V^{-1} s^{-1}), high on/off



5 p-type >1.5 cm^2/Vs

6a (R = Si(i-Pr)$_3$): p-type 1.42 cm^2/Vs

6b (R = C$_5$H$_{11}$): p-type 0.52 cm^2/Vs

7 p-type 1.0 cm^2/Vs

8 p-type 2.9 cm^2/Vs

9 p-type 0.95 cm^2/Vs

10 p-type 1.6 cm^2/Vs

11a R = Hex : p-type 1.0 cm^2/Vs

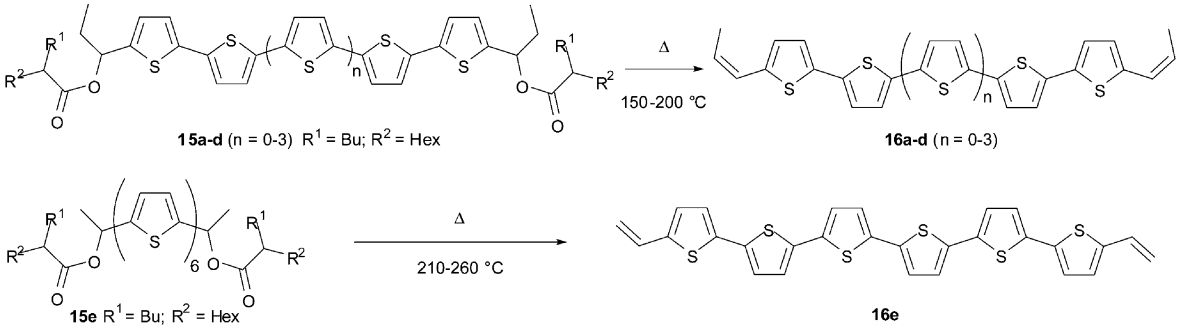
11b R = Et : p-type 1.1 cm^2/Vs

12 n-type 0.11 cm^2/Vs

13 n-type 1.83 cm^2/Vs

14 n-type 0.21 cm^2/Vs

Chart 2 Recently developed organic semiconductors of small molecules for OFETs.



Scheme 1

current ratio ($>10^5$), low V_{th}, and good durability, is a goal worth pursuing. After mentioning thiophene derivatives and acene compounds, we discuss in detail the OFET properties of spun-cast films of porphyrin and phthalocyanine derivatives created using this method.

2 Thiophene derivatives

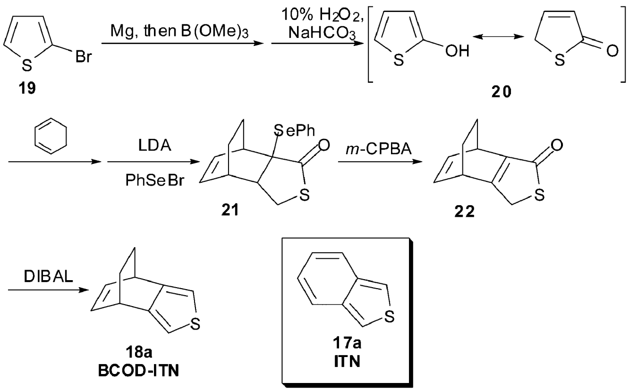
2.1 Solution processable thiophene oligomers

Thiophene polymers and oligomers are among the most promising organic semiconductors.[2,12,13,31–37] As described in the introduction, polythiophenes have been thoroughly studied as solution processable materials for OFETs, organic photovoltaics (OPVs), and so on (Chart 1).[31] Thiophene oligomers, particularly α,ω-dihexyl- and α,ω-diethylsexithiophenes (**11a** and **11b**), have also been reported to exhibit carrier mobilities as high as 1.0 cm^2 V^{-1} s^{-1} (Chart 2), but due to their limited solubility they require vacuum deposition to form thin films.[27] Since there have been many reports on solution processable oligothiophenes and their applications in OFETs, OPVs, and so on,[2,12,13,32–37] we will only focus on a series of oligothiophenes containing thermally removable solubilizing groups.

Fréchet and co-workers have reported thiophene oligomers (tetramer to heptamer: **15a–e**) with branched secondary esters at the α- and ω-positions of the oligomers, as shown in Scheme 1.[38–41] After spin-casting films from chloroform onto SiO_2, the solubilizing groups could be removed *via* an ester thermolysis reaction by heating to give thiophene oligomers, **16a–e**. The reported carrier mobilities were 0.02–0.06 cm^2 V^{-1} s^{-1}.

2.2 Isothianaphthene oligomers

Isothianaphthene (**17a**: **ITN**) is an important unit of polyisothianaphthene, a well-known low-band-gap conducting polymer.[42–44] Because of its *o*-benzoquinodimethane structure, **ITN** is unstable due to its high reactivity at the 1- and 3-positions,[45] and there have been limited reports on the synthesis of poly- and oligo-**ITN** compounds.[42–44,46–55] In 2002, Ono and co-workers reported a bicyclo[2.2.2]octadiene(BCOD)-ring fused thiophene, namely 4,7-dihydro-4,7-ethano-2-benzo[*c*]thiophene (**18a**: **BCOD-ITN**), as a synthon of 1,3-unsubstituted **ITN** (**17a**),[56] according to the synthetic scheme shown in Scheme 2. Compound **18a** was prepared from 2-bromothiophene (**19**) in 6 steps. Ono and co-workers have reported the synthesis of the **ITN** oligomers **17a–c** (*n* = 1–3), α,ω-diformyl **ITN** oligomers **25a–c** (*n* = 1–3), and the α,ω-dicyano **ITN** dimer **27** from their corresponding BCOD-fused precursors, **18a–c** (*n* = 1–3), **26a–c** (*n* = 1–3), and **28**, respectively, as shown in Scheme 3. A retro-Diels–Alder reaction was carried out at 270–280 °C for 10–15 min. The reactivity was relatively low compared to that of BCOD-fused pyrrole. The UV-Vis absorption spectra of the precursors, **26a–c** and **28**, and ITN oligomers, **25a–c** and **27**, are shown in Fig. 1.[57] The absorption spectra of the ITN oligomers showed a bathochromic shift of 102 nm for **25a**, 117 nm for **25b**, 150 nm for **25c**, and 118 nm for **27** compared to the corresponding precursors **26a–c** and **28**, respectively. The ITN precursors could be used as building blocks of core-modified porphyrins, as described in section 4.



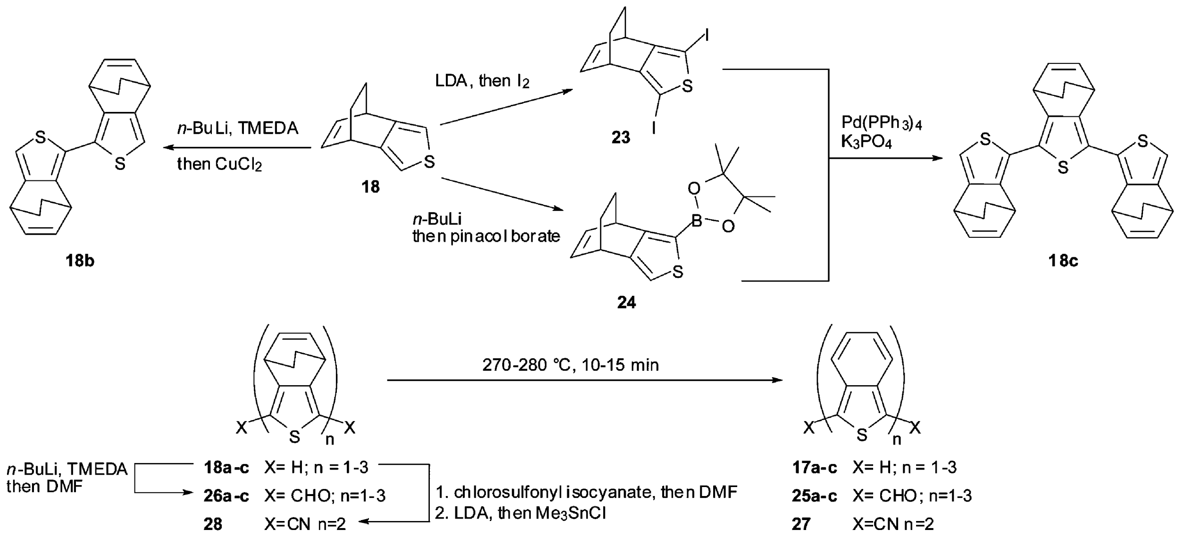
Scheme 2

3 Solution-processable acene-type semiconductors

3.1 Pentacene

Acene compounds, such as pentacene, tetracene, anthracene, and their derivatives, have attracted much attention as organic semiconductors (Chart 2).[2–5,12,13] Pentacene in particular is a promising p-type semiconductor for OFETs and OPVs, since carrier mobilities of more than 1.5 cm^2 V^{-1} s^{-1} have been reported for OFETs using vacuum-deposited pentacene[14–19] and for highly pure single-crystal OFETs.

As described in introduction, many kinds of pentacene derivatives with solubilizing groups have been reported (type B). But in order to utilize the pentacene itself, the soluble pentacene precursors, which can be easily converted to pentacene on substrates, have shown promise. Some Diels–Alder adducts of pentacene have been utilized for this purpose.[58–68]



Scheme 3

The first precursor based on this concept, **29**, was reported by Müllen and co-workers.[58,59] The leaving group was tetrachlorobenzene and the carrier mobility was 0.1 $cm^2\ V^{-1}\ s^{-1}$. An IBM group has reported some *N*-sulfinylamide adducts of pentacenes, namely **30a** and **30b**.[60,69] The retro-Diels–Alder reaction of such adducts gave pentacene, yielding the highest mobility in a pentacene film prepared by a solution process, 0.89 $cm^2\ V^{-1}\ s^{-1}$. Recently a CO adduct, **31**, of pentacene was reported by Chow and co-workers (Table 1). The leaving group was a CO molecule and the weight loss was only 9%, but the mobility was merely 8.8×10^{-3} $cm^2\ V^{-1}\ s^{-1}$.[68] Diels–Alder adducts of pentacene with thiophosgene, **32**,[64] and azodicarboxylate diesters, **33**,[65] have also been reported as pentacene precursors (Table 1), but the mobilities of pentacene films prepared from solutions of these precursors are unknown.

Although the thermal conversion of pentacene precursors to pentacene on substrates is very promising for large-area, solution processable OFET applications, the annealing at 120–200 °C during the process restricts the range of usable substrates. By contrast, photochemical conversion of precursors to pentacene would have the advantage of conversion at ambient temperature, allowing flexible plastics to be used as substrates. Furthermore, light patterning of substrates could be possible.[70] Afzali *et al.* have reported photothermal patterning of pentacene by photopolymerization of pentacene-linked monomers, **34**, followed by a retro-Diels–Alder reaction to separate pentacene from polymers (Table 1).[61] The mobility was 0.021 $cm^2\ V^{-1}\ s^{-1}$ and I_{ON}/I_{OFF} was 2×10^5. Hamers and co-workers have reported that precursor **30b** is photopatternable in the presence of a photoacid generator (PAG), as shown in Table 1.[62] The mobility was 0.25 $cm^2\ V^{-1}\ s^{-1}$ and I_{ON}/I_{OFF} was 8×10^4. The resulting pentacene films included impurities, such as polymers or PAGs, which might have lowered their mobilities.

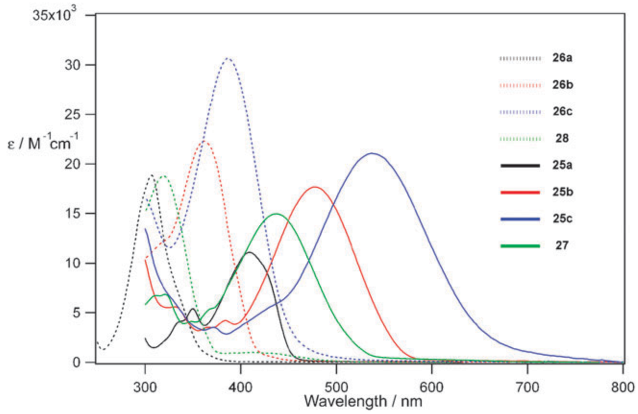
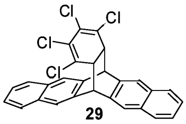
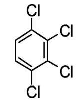
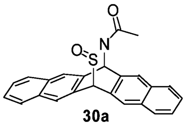
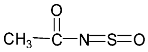
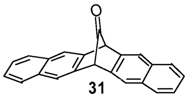
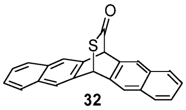
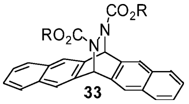
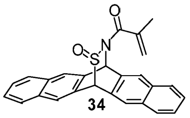
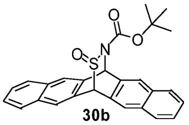
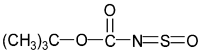
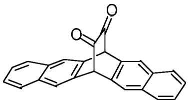


Fig. 1 UV-Vis spectra of diformyl ITN oligomers **25a–c** and dicyano ITN dimer **27** and their precursors in CH_2Cl_2.

The direct photoconversion of precursors to pentacene was reported by our group.[71,72] A 1,2-diketone precursor (**35**) of pentacene was prepared by two routes, as shown in Scheme 4. Route A was a preparation starting from the reaction of tetraene **36** with benzyne, followed by oxidations. Route B started from the Diels–Alder reaction of pentacene with vinylenecarbonate, with subsequent deprotection and Swern oxidation. The diketone precursor of pentacene had an n–π* absorption at 460 nm and could be converted to pentacene quantitatively in solution and as a film by photoirradiation at the n–π* absorption wavelength. The leaving groups were two carbon monoxide molecules, comprising 17 wt% of the precursor molecule (Table 1). When a toluene solution of the diketone precursor was irradiated under argon, generation of pentacene and corresponding disappearance of diketone was monitored by the change in absorption spectra at the beginning of the reaction. After a while, pentacene started to precipitate because of its low solubility in toluene. The absorption spectra during the photoirradiation of the n–π* absorption of the diketone at 463 nm are shown in Fig. 2. During photoirradiation, the n–π* absorption of the diketone moiety decreased, while the typical absorption of pentacene began to be observed. After 25 min, the pentacene absorption started to decrease because it precipitated from solution. Photoconversion was also successful in a film. The UV-Vis absorption spectra of a film before and after irradiation are shown in

Table 1 Soluble precursors, their leaving groups (wt%), conversion conditions and mobilities of the resultant pentacene films

Precursor	Leaving group	wt% loss	Conditions of conversion	Mobility of film/cm^2 V^{-1} s^{-1}	Ref.
 **29**		43	180 °C	0.1	58
 **30a**	 $CH_3-\overset{O}{\overset{\|}{C}}-N{=}S{=}O$	27	130–200 °C	0.89	60
 **31**	CO	9	150 °C	8.8 × 10^{-3}	68
 **32**	SCO	18	120 °C	—	64
 **33**	$RO_2C-N{=}N-CO_2R$ (**33a**, R = Me) (**33b**, R = Et) (**33c**, R = *t*-Bu)	 35 38 45	160 °C	—	65
 **34**	Unidentified polymer	—	1, *hν*; 2, heat	0.021	61
 **30b**	 $(CH_3)_3C-O-\overset{O}{\overset{\|}{C}}-N{=}S{=}O$	37	130 °C with PAG[a]	0.25	62
 **35**	2 CO	17	*hν*	0.34	71–73

[a] PAG = photoacid generator.

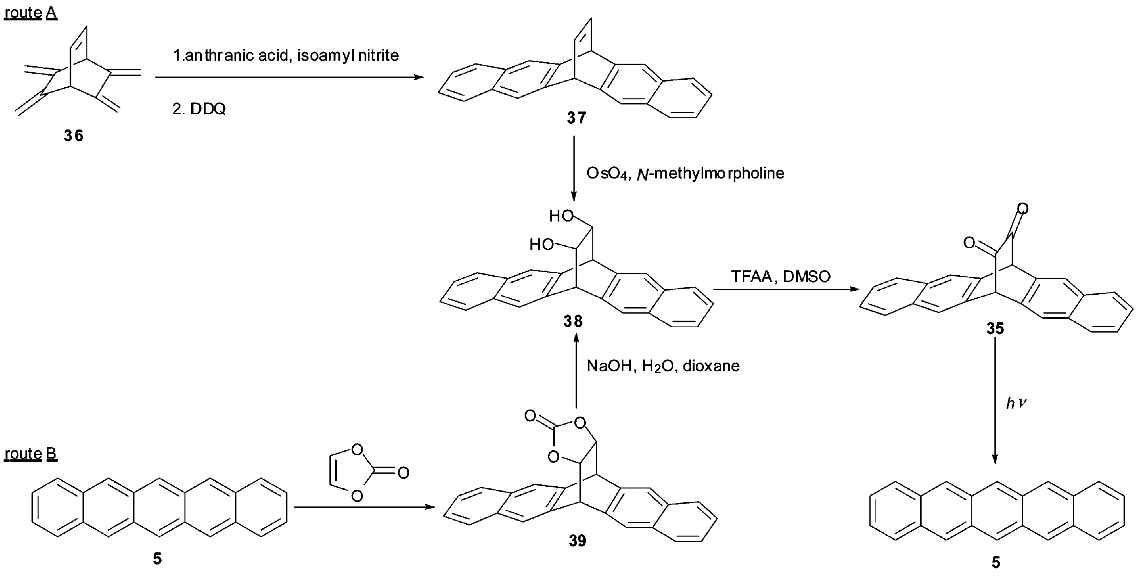
Fig. 3. The OFET performance of the pentacene film prepared by spin-coating of the precursor and subsequent photoirradiation is shown in Fig. 4. The device was fabricated as a top-contact structure on highly doped n-type SiO_2 (500 nm) after treatment with methylsilsesquioxane (MSQ). The carrier mobility of the film was 0.34 cm^2 V^{-1} s^{-1} and I_{ON}/I_{OFF} was 2 × 10^6.[73]

The n–π* absorption of the diketone precursor overlapped the π–π* absorption of pentacene, so both the precursor and pentacene absorbed radiation, and singlet oxygen was generated by energy transfer from the triplet excited state of pentacene. The reactivity of pentacene with singlet oxygen to give the 6,13-peroxide is extremely high, so device manufacture involving pentacene has to be carried out under an inert gas. Yamada *et al.* have also reported the diketone precursors[71,74,75] of air-stable 2,6-dianthrylanthracene (**40a**)[71] and 2,6-dithiophenylanthracene(**40b**).[76] The photocleavage reaction proceeded similarly under oxygen and argon when only the n–π* absorption was excited, without generating the 6,13-peroxide. The authors also succeeded in patterning using a mask during photoirradiation in air.[75] Neckers and co-workers have prepared diketone precursors of hexacene[77] and heptacene[78] (**41** and **42**), applying synthetic route A of pentacene (Scheme 4). Because of their instability towards oxygen and their low solubility in common organic solvents, hexacene and heptacene were not isolated. The photocleavage reaction was detected by MALDI-TOF mass spectra and absorption spectra in a PMMA matrix (Chart 3).

4 Porphyrins and phthalocyanines

4.1 General aspects

Porphyrin-based molecules have been extensively studied in biochemistry and their properties are well understood. For example, chlorophyll (containing Mg) is a key component in photosynthesis and heme (containing Fe) regulates oxygen transfer in hemoglobin. Development of porphyrin-based



Scheme 4

organic electronics may lead to totally biocompatible, inexpensive electronic devices. Mechanically and electrically stable phthalocyanines (Pcs) and their films are resistant to solvents and repetitive thermal stress; they are widely used as photoconductors in laser printers and as electronic materials. Organic synthesis leads to substitutions at their cores and periphery for particular applications. Comprehensive handbooks on the synthesis, structure, properties and applications of porphyrins and Pcs are available.[79] Among the many known porphyrins and related compounds, tetrabenzoporphyrins (**43**, MTBPs), MPcs (**44**), and fluorinated Pcs (**45**, F_{16}MPcs) shown in Chart 4 are particularly useful as p- or n-type semiconductors for OLEDs, OFETs and OPVs, since they accept or donate electrons easily due to their large π-electron frameworks. As they are more stable toward light and heat than acenes or oligothiophenes, they hold greater promise for practical applications in electronics.

Pcs are promising active materials for OFETs due to their stability, and have been studied widely for a long time. Among various metal complexes CuPc and NiPc show better mobility than other MPcs, but they are as low as 0.02 $cm^2\ V^{-1}\ s^{-1}$,[80] too low for use in display applications. Much effort has been expended on improving the performance of OFETs based on Pcs. Thin films obtained by a sandwich type device consisting of two kinds of Pc metal complexes displayed a mobility of 0.11 $cm^2\ V^{-1}\ s^{-1}$.[81] The mobility of an OFET based on single-crystal CuPc was 1 $cm^2\ V^{-1}\ s^{-1}$, the highest value reported so far for Pc-based OFETs.[82] Strong π-orbital overlap existed along the *b* axis of CuPc crystals.

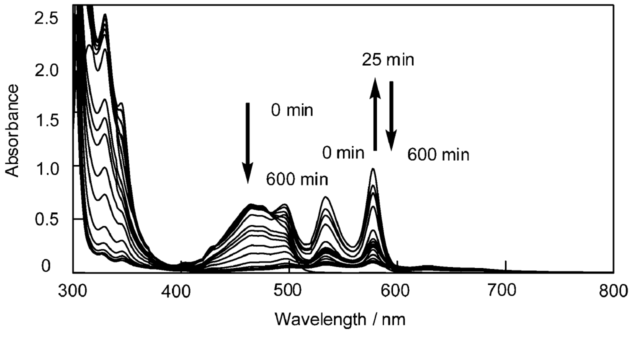


Fig. 2 The change of the absorption spectra during the photolysis (λ_{ex} = 463 nm) of α-diketone **35** in toluene under Ar atmosphere.

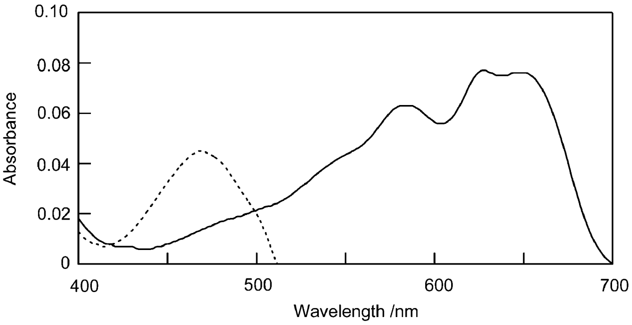


Fig. 3 Absorption spectra of a spun-cast film of α-diketone **35** before (broken line) and after (solid line) the photoirradiation by a metal halide lamp in a grove box.

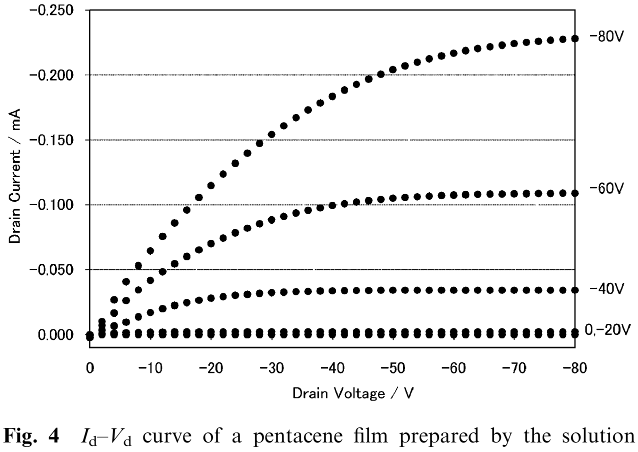


Fig. 4 I_d–V_d curve of a pentacene film prepared by the solution process of precursor **35**.

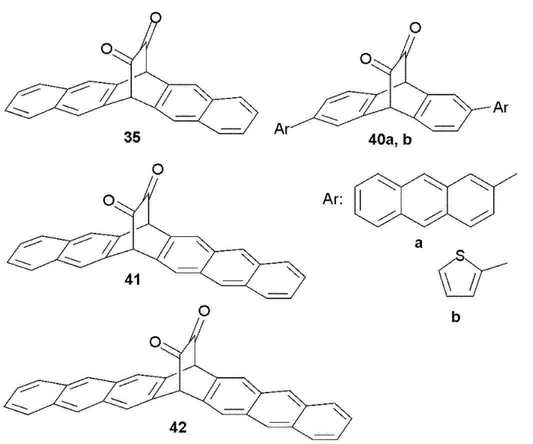


Chart 3 1,2-Diketone precursors of semiconducting acene derivatives.

Fine control of crystal structures in thin films is crucial to improving the performance of OFETs. Efforts to control Pcs and related compounds using the LB technique or discotic liquid crystals have been extensive, but the resulting mobilities were usually in the range of 10^{-3} to 10^{-4} $cm^2\ V^{-1}\ s^{-1}$.[83] A recent report of an OFET based on amphiphilic rare earth triple decker complexes with tris(Pcs), **46**, showed a remarkably high mobility of 0.24–0.60 $cm^2\ V^{-1}\ s^{-1}$ because of intramolecular π–π stacking and intermolecular *J* aggregation in the LB film, as shown in Fig. 5.[84]

Fluorinated copper phthalocyanine (**45**, $F_{16}CuPc$) is one of the few molecules exhibiting air-stable n-channel semiconducting behavior. The OFET mobility was 0.03 $cm^2\ V^{-1}\ s^{-1}$ for a thin film fabricated on SiO_2 by vapor deposition.[85]

The structure of the $F_{16}CuPc$ film on SiO_2 depended on its thickness, which could be controlled by the deposition rate and temperature.[86] This suggested that the mobility in OFETs based on Pcs could be improved by suitable choice of fabrication technique. High-performance air stable n-type OFETs based on single crystalline submicro- and nanometer ribbons of $F_{16}CuPc$ have been reported, whose mobility was 0.2 $cm^2\ V^{-1}\ s^{-1}$.[87] Such ribbons could be grown *in situ* by a physical vapor transport technique on the surface of Si/SiO_2 substrates during synthesis.

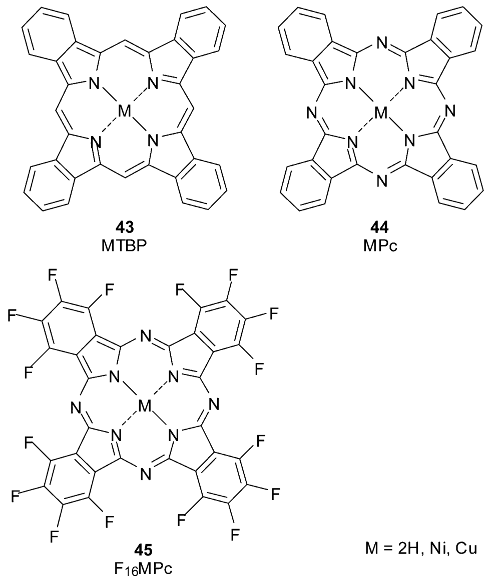


Chart 4 Benzoporphyrins (MTBPs), phthalocyanines (Pcs), and fluorinated phthalocyanines ($F_{16}MPcs$).

4.2 Synthesis of soluble precursors

As TBP and Pcs, being pigments, are generally insoluble in organic solvents, soluble precursors are required to allow their use in fabrication by solution processes. BCOD-fused porphyrins (**47**, MCPs), soluble precursors of TBPs, were prepared from BCOD-fused pyrrole **48a** in about 50% yield by a standard method ($LiAlH_4$, H^+, oxidation), as shown in Scheme 5.[88–90] As CP was soluble in organic solvents, it could be purified by column chromatography to give a pure sample (99.9%, estimated by HPLC), which was converted to pure TBP in quantitative yield by heating at 180–200 °C. Thus, insoluble TBP was prepared in a highly pure form by this thermal process. Thermal analyses (with heating at 10 °C min^{-1}) of the conversion process from CP to TBP are shown in Fig. 6. The conversion took place between 150 and 200 °C. The decrease in mass corresponded to elimination of four ethylene molecules, demonstrating quantitative conversion from 2HCP to 2HTBP. The conversion seemed to proceed in two or three steps, judging from the multiple exothermic peaks observed.

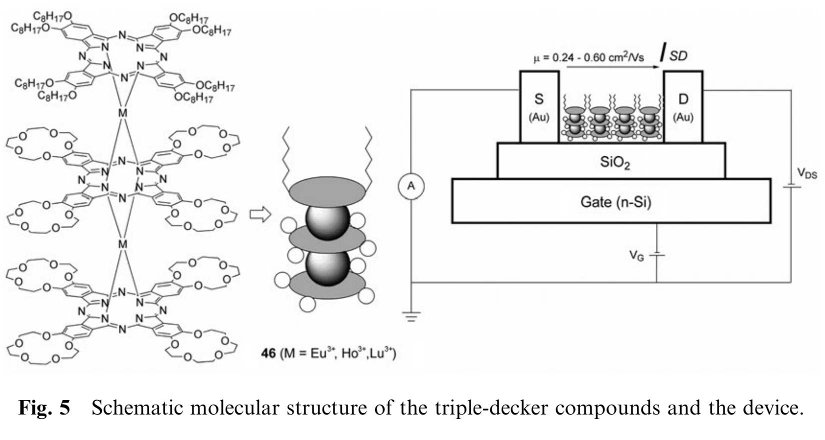
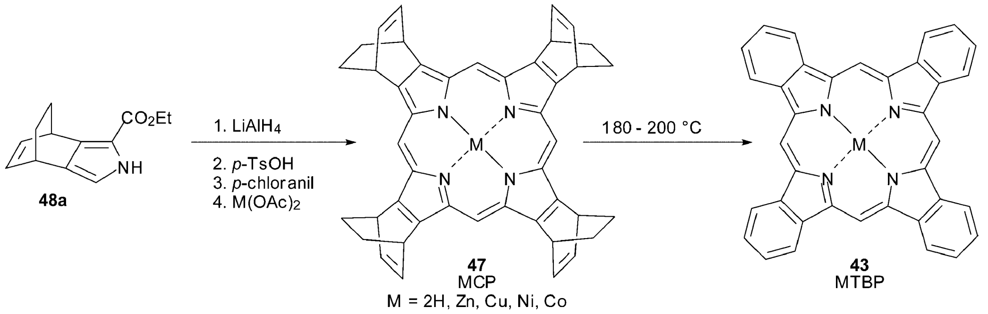


Fig. 5 Schematic molecular structure of the triple-decker compounds and the device.



Scheme 5

This strategy was very convenient for the preparation of pigments such as MTBP and MPc in a highly pure state without purification steps. The requisite BCOD-fused pyrroles were prepared by the Diels–Alder reaction of 1,3-cyclohexadiene **49** with β-(phenylsulfonyl)nitroethylene (**51a**)[91] to give adduct **52a** followed by the reaction with ethyl isocyanoacetate (Barton–Zard reaction, BZ reaction).[89,92] This process was later improved by the use of (*E*)-1,2-bis(phenylsulfonyl)ethylene (**51b**)[93] prior to the BZ reaction (Scheme 6).[94,95] (*Z*)-1,2-Bis(phenylsulfonyl)ethylene[96] was also effective for this purpose. The Diels–Alder reaction of sulfonylacetylene **53** along with a subsequent BZ reaction was the simplest way to the requisite pyrrole.[97] Combinations of 1,3-cyclohexadienes with various dienophiles and sulfonylation afforded substituted BCOD-fused pyrroles, regarded as masked isoindoles as shown in Scheme 6.[98]

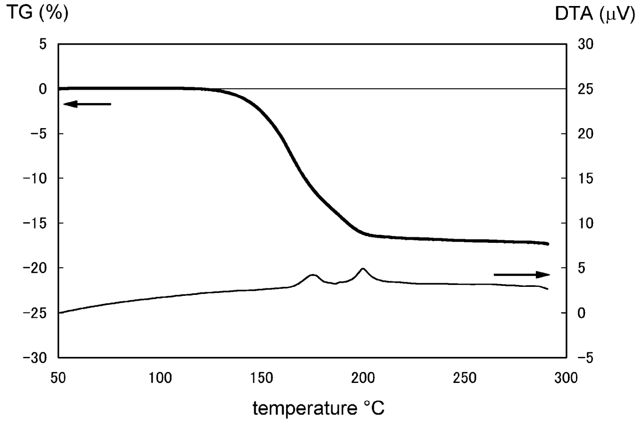
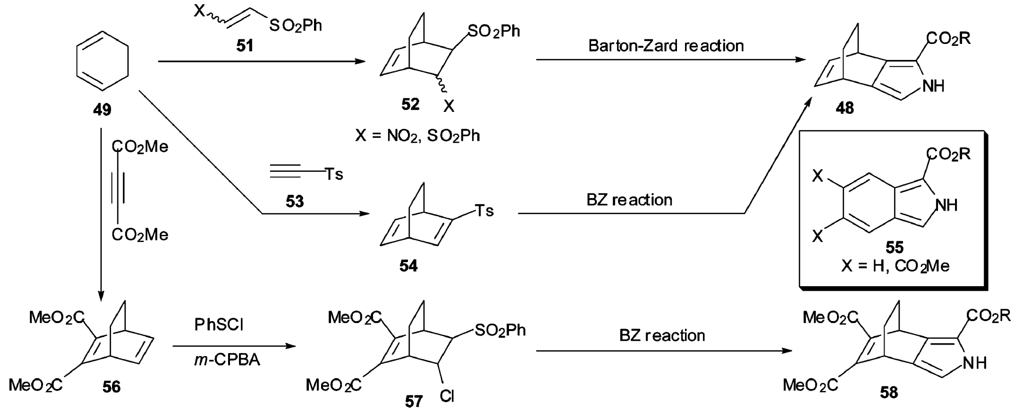


Fig. 6 Thermogravimetric analysis (left axis) and differential thermal analysis (right axis) of conversion process from CP (**47**) to TBP (**43**).

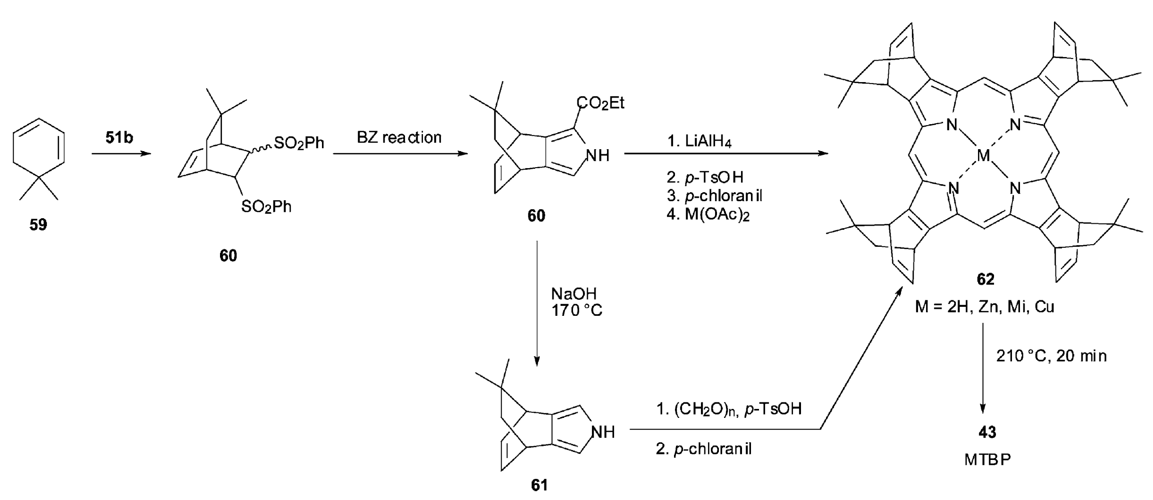
Using 5,5-dimethyl-1,3-cyclohexadiene (**59**) instead of **49**, the more soluble TBP precursor **62** was prepared, whose solubility was more than 100 times higher than that of **47** in methanol and 60 times higher in *n*-hexane (Scheme 7).[99] This higher solubility will increase the likelihood of the solution process finding industrial use because such precursors can be dissolved in non-chlorinated solvents.

Pure [2,3]naphthoporphyrin, **66**, was also prepared by the retro-Diels–Alder strategy from the precursor **65** (Scheme 8).[100] The reaction of the tripyrrane **67** with diformylheterocycles **68** afforded the corresponding heteroporphyrins **69**, which were easily converted into tetrabenzoheteroporphyrins **70** by a retro-Diels–Alder reaction, as shown in Scheme 9.[101,102] Using this procedure, heteroporphyrins **70**, carbaporphyrin **71**, and azuliporphyrin **72** could also be prepared.

The condensation of BCOD-fused tripyrrane with appropriate pyrrole dialdehydes and the subsequent retro-Diels–Alder reaction afforded acenaphthotribenzoporphyrin **74** and fluoranthene-fused TBP **76** (Scheme 10).[95] The absorptions of these new porphyrins were very intense at both Soret and Q band regions as shown in Fig. 7, where the solid lines show the UV-Vis spectra of precursors **73** and **75**, and the bold lines those of corresponding π-expanded porphyrins **74** and **76**, respectively. The absorptions of **74** and **76** covered a wide wavelength range, indicating that they were good candidates

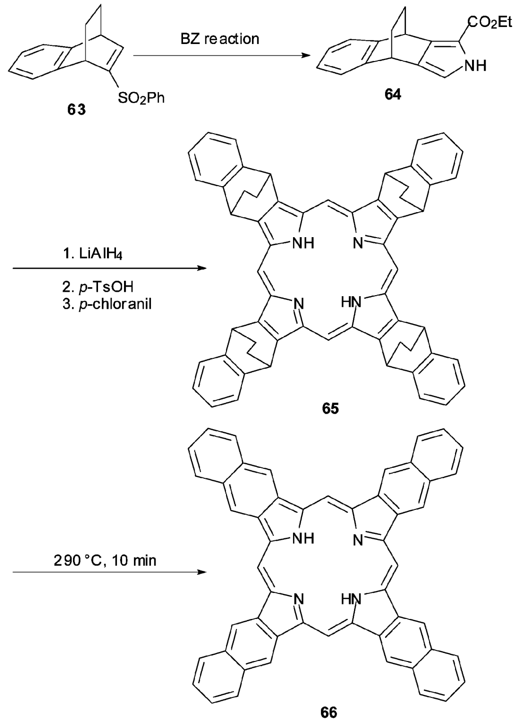


Scheme 6



Scheme 7

for use as dyes for OPVs. Yamada *et al.* have prepared 5,15-dialkynyl BCOD-fused porphyrin **79** and 5-alkenyl-15-alkynyl BCOD-fused porphyrin **80** by a [2 + 2] condensation reaction. Glaser–Hey coupling of porphyrin **82** gave butadiyne-linked BCOD-fused porphyrin dimer **83** which was converted to benzoporphyrin dimer **84** (Scheme 11). This dimer absorbed over a wide wavelength range, compared to its precursor **83**, as shown in Fig. 8.[103] The Osuka group has developed meso–meso, β–β, β–β triply linked porphyrin arrays, **85** and **86**. (Scheme 12).[104] Dibenzoporphyrin dimer **86** has an enlarged π-electronic network, and therefore exhibited extremely red-shifted absorption spectra (λ_{max} = 1150 nm) and a large two-photon absorption cross section (15 400 GM). These phenomena have shown a promise of being useful in optoelectronic applications.



Scheme 8

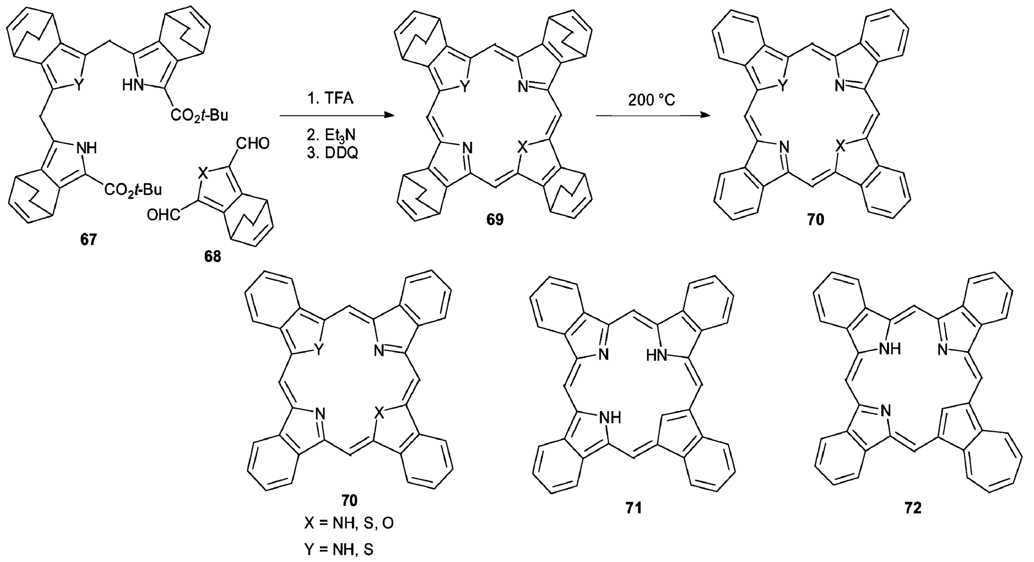
The retro-Diels–Alder strategy was extended to the synthesis of MPcs **89** and related compounds **90** as demonstrated in Scheme 13. TG analysis of an Mg complex of the BCOD-fused MPc verified the expected retro-Diels–Alder reaction with loss of 20% of the total mass, corresponding to a loss of four ethylene units and two of H_2O. This reaction initiated at 200 °C and was complete by 250 °C (Fig. 9). Thus, pure naphthalocyanine was prepared by the retro-Diels–Alder reaction of soluble precursors **87**, opening a new way to solution processable pigment semiconductors.[105] A soluble BCOD-fused tetra(pyrazino)tetraazaporphyrin **88** was prepared by the reaction of BCOD-fused dicyanopyrazine. The retro-Diels–Alder reaction of **88** gave tetra(quinoxalino)tetraazaporphyrin **90** in quantitative yield, which was a good candidate for an n-type organic semiconductor.[106]

4.3 OFETs by solution processing

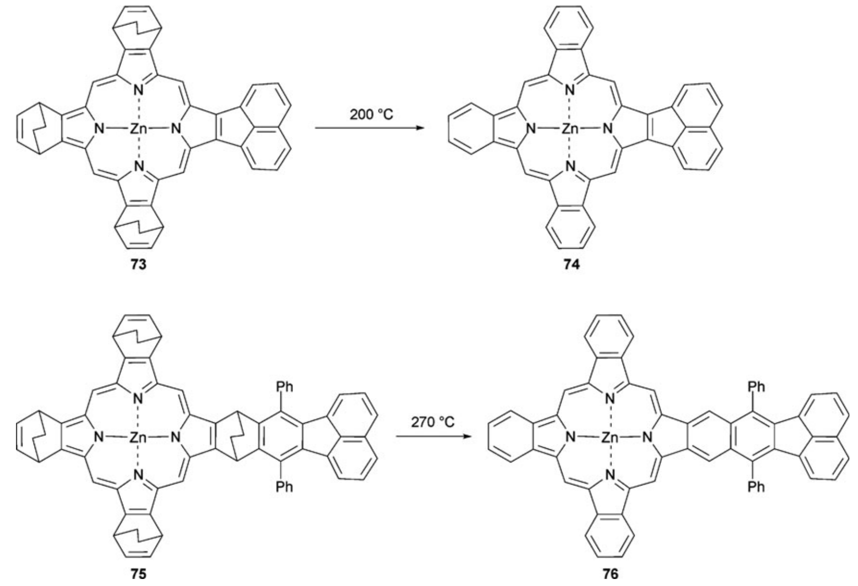
Spin-coating of 2HCP followed by heating at 210 °C afforded 2HTBP thin films, which could be used as semiconductors for OFETs (Scheme 5).

The electronic properties of the 2HTBP thin film were studied by CV, which gave E_{ox} = 0.43 V and E_{red} = −1.77 V (both *vs.* Ag/Ag$^+$), corresponding to a HOMO energy level of 5.08 eV and LUMO energy level of 2.89 eV. The HOMO–LUMO gap determined by CV data was consistent with the value of 2.2 eV estimated from the absorption spectra of this film. The proposed band structures of a 2HTBP OFET based on these values are as shown in Fig. 10. From gate-to-source in Fig. 10(a), holes accumulated at the SiO_2/TBP interface for a gate electrode biased negatively relative to the source. Similarly, from drain-to-source in Fig. 10(b), holes in the channel traveled from source to drain when the drain was biased negatively relative to the source.[107]

Scanning transmission electron microscopy (STEM) images of 2HCP and 2HTBP are shown in Fig. 11.[108] 2HCP films were amorphous, but once converted to 2HTBP, the films displayed distinct needle-shaped crystallites. Thus, polycrystalline 2HTBP thin films were readily obtained by spin-coating 2HCP and subsequent heating.



Scheme 9



Scheme 10

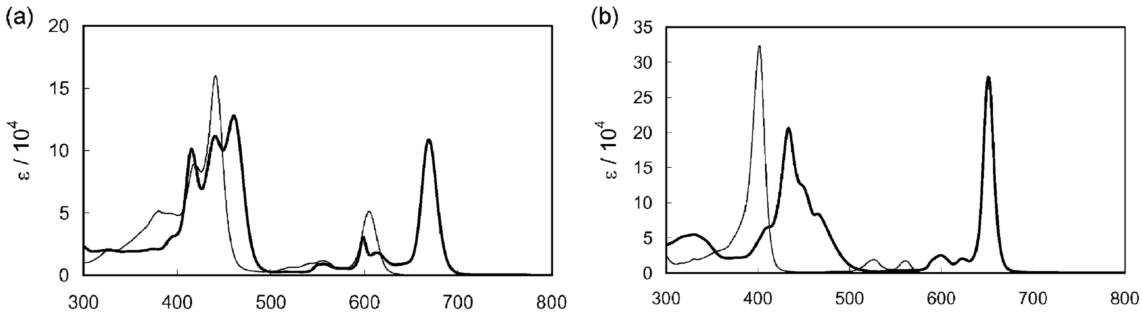
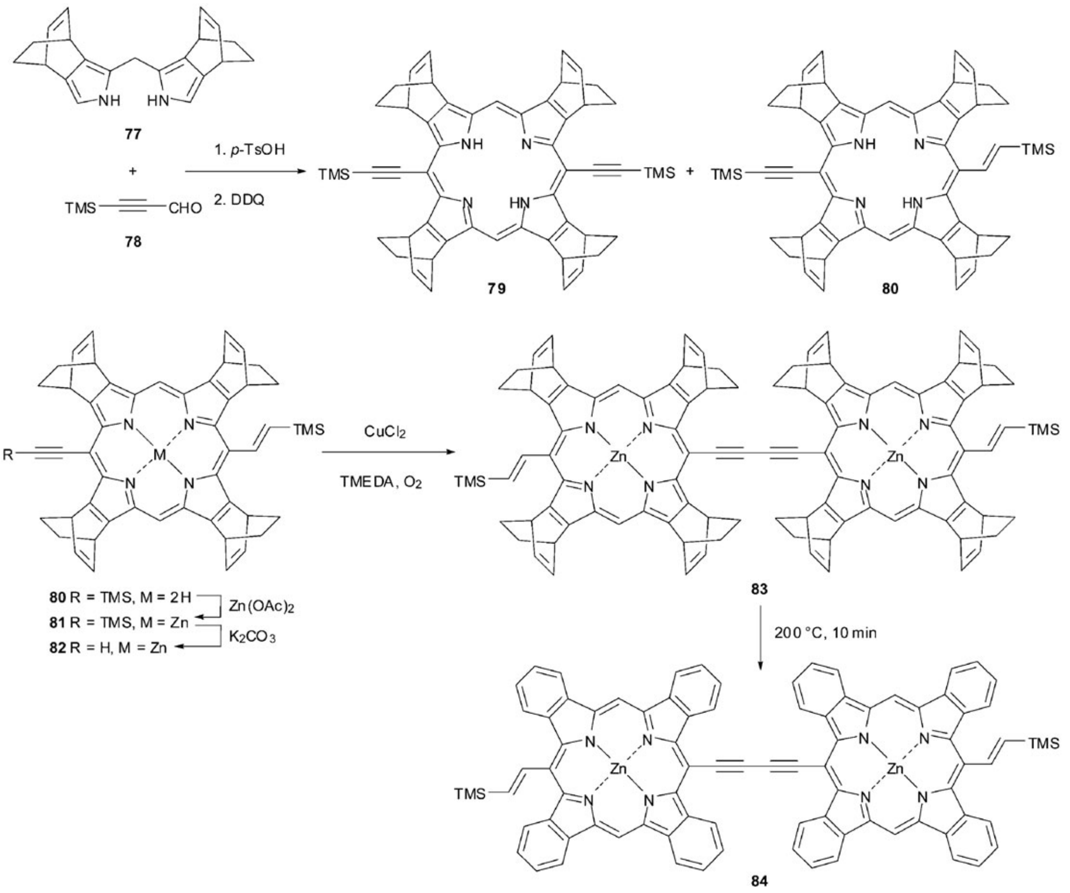


Fig. 7 UV-Vis spectra of (a) **73** (solid line) in CH_2Cl_2, **74** (bold line) in DMF, (b) **75** (solid line) in CH_2Cl_2, and **76** (bold line) in DMF.



Scheme 11

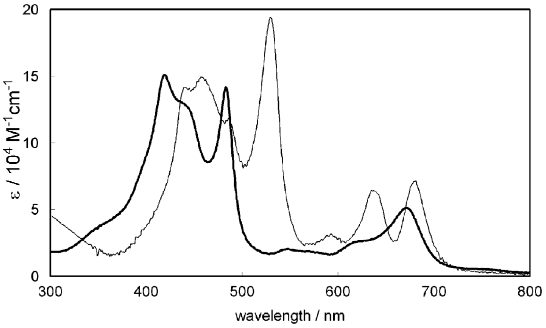
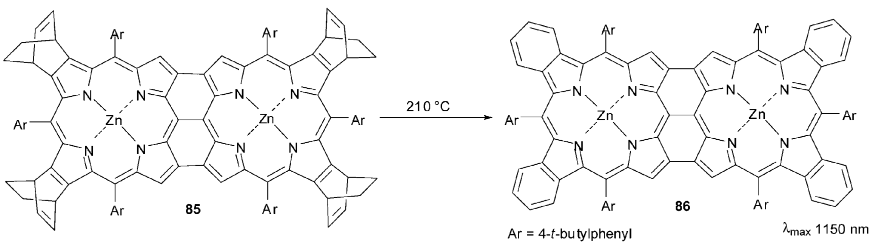
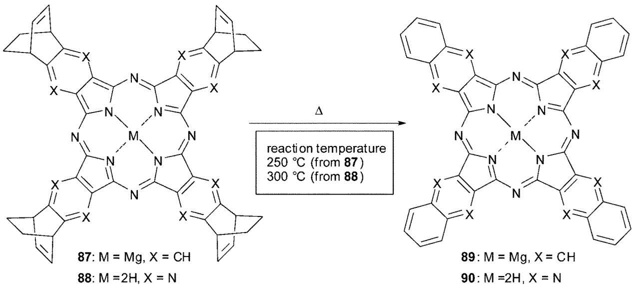


Fig. 8 UV-Vis spectra of **83** (solid line) and **84** (bold line) in DMF.

The 2HTBP OFETs were fabricated in either coplanar (bottom-contact) or staggered (top-contact) device structures. The Aramaki group first used bottom-contact devices for a TBP OFET as shown in Fig. 12.[109] Source and drain electrodes were formed by photolithography of Au (90 nm)/Cr (10 nm) on top of 300 nm thermally-grown SiO_2 on heavily doped n-type Si. The standard channel length was 10 μm and the channel width 500 μm. The semiconductor thin film was prepared by heating a spun-cast thin film of CP at 210 °C for 5 min. The *I–V* characteristics of the OFETs are shown in Fig. 13.[110] The mobility, threshold voltage, and I_{ON}/I_{OFF} were determined from the data of Fig. 13 as follows: $\mu = 0.017$ cm^2 V^{-1} s^{-1}, $V_{th} = -0.3$ V, and $I_{ON}/I_{OFF} = 1 \times 10^5$.[110] The mobility of the 2HTBP OFET was 10 times better than that of an 2HPc OFET deposited under vacuum: $\mu = 1.3 \times 10^{-3}$ cm^2 V^{-1} s^{-1} (30 °C), and 2.6×10^{-3} cm^2 V^{-1} s^{-1} (120 °C). A TBP-OFET was also fabricated by vacuum deposition at 10^{-6} Torr at various temperatures, and gave $\mu = 3 \times 10^{-4}$ cm^2 V^{-1} s^{-1} at 25 °C, 2.3×10^{-4} cm^2 V^{-1} s^{-1} at 80 °C, and 5.6×10^{-7}



Scheme 12



Scheme 13

$cm^2\ V^{-1}\ s^{-1}$ at 150 °C. These results clearly showed that spin-coated and thermally converted thin film led to better OFET performance than vacuum deposited OFETs.

An AFM image of the converted film is shown in Fig. 14.[110] The 2HCP film was amorphous and its surface quite smooth. After conversion, the surface of the film became rough with many cracks, because the thickness of the film was reduced by 20%. Therefore, this film was not suitable for a top gate device structure, because smoothness at the interface between the semiconductor and the insulator is important for OFET performance.

The mobility of the 2HTBP OFET was dependent on the channel length, as shown in Fig. 15.[110] The dependence was opposite to that of other OFETs such as pentacene OFETs, in which the semiconductor near the electrode was assumed to be inferior. In the case of 2HTBP, the grain boundary was an important factor governing mobility. Short channels had few grain boundaries, increasing mobility.

Kanicki and co-workers have studied 2HTBP OFETs using the staggered (top-contact) S/D electrodes shown in Fig. 16.[108] All processing except thermal annealing and evaporation was done in air. Compared to bottom contact S/D electrodes, this type of top contact S/D electrode avoided the problem of high contact resistance due to poor step coverage over the S/D electrodes, or poor adhesion of the metal to the organic semiconductors. Poor step coverage introduces morphological discontinuities in the organic semiconductor near the electrode. The authors discussed a possible relation between thin-film microstructure and OFET behavior in terms of non-linearity in the extraction of the device's electrical parameters. They concluded that 2HTBP formed channel regions with a degree of crystallinity higher than their organic polymer counterparts. The nature of 2HTBP was more comparable to that of micro- and poly-crystalline silicon TFTs.

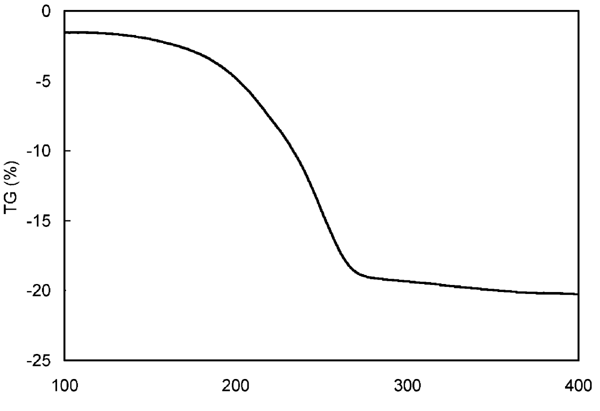


Fig. 9 Thermogravimetric analysis of conversion process from precursor **87** to naphthalocyanine **89**.

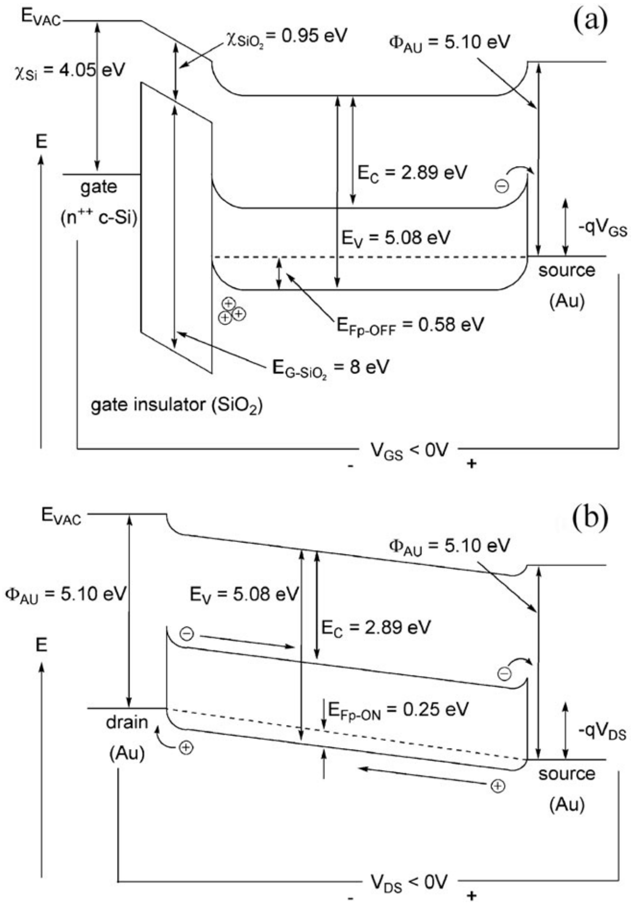


Fig. 10 Proposed energy band diagrams for a 2HTBP OFET with Au S/D electrodes. (a) Gate to source. (b) Drain to source.[104]

Many organic semiconductors, including 2HTBP, exhibit environmental drawbacks. Exposure of the 2HTBP OFET to ambient atmosphere leads to significant changes, namely, increase in overall conductivity, lower I_{ON}/I_{OFF}, and larger sub-threshold swing. However, thermal annealing under N_2 or vacuum regains most of the original performance. In order to minimize O_2 and H_2O exposure, fabrication and testing are carried out in an inert environment, or OFET devices are overcoated with impermeable materials.[111]

After conversion from a precursor thin film, 2HTBP becomes insoluble, making it ideal for post-processing steps such

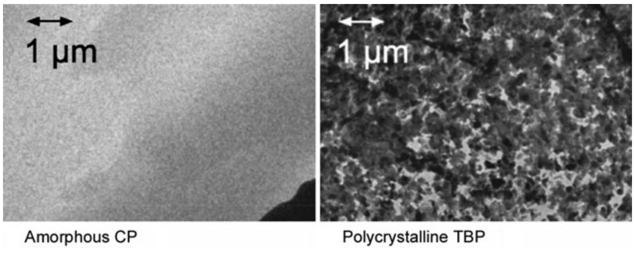


Fig. 11 A STEM bright-field image of an amorphous 2HCP precursor film and a thermally annealed, polycrystalline 2HTBP film.

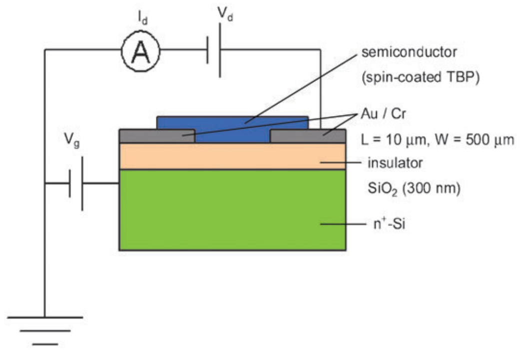


Fig. 12 A schematic view of bottom-contact device for TBP-OFET.

as metallization or encapsulation. For example, 2HTBP OFETs are coated with a soluble n-type semiconductor, [6,6]-phenyl-C_{61} butyric acid methyl ester (PCBM), as shown in Fig. 17.[112] The top coating extends the lifetime of the device in that the field-effect mobility, sub-threshold slope, and off-state current are maintained at their as-fabricated states for a long time.

OFETs incorporating metal porphyrins such as CuTBP[113] or NiTBP[114] were also fabricated by a solution process using the corresponding soluble precursors, and offered better performance than those using TBP itself. XRD patterns from drop-cast NiCP and NiTBP thin films are shown in Fig. 18, which shows that the pattern for drop-cast NiCP displayed no measurable peaks. Upon heating, numerous diffraction peaks appeared, indicative of the formation of crystal planes. XRD spectra from both drop-cast and NiTBP powder were used to define the NiTBP unit cell *via* the Pawley and Rietveld powder refinement methods combined with Pareto optimization both to match the experimental XRD spectra and to minimize the

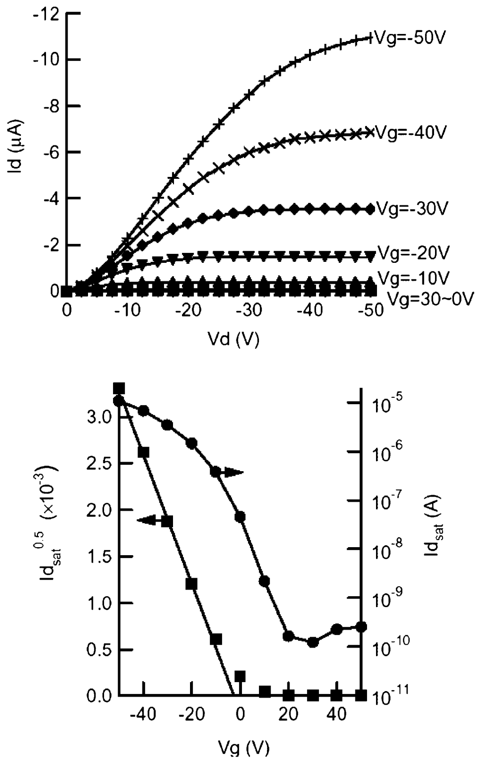


Fig. 13 I_d–V_g Characteristics of an FET using 2HTBP as a semiconductor. The channel length is 10 μm and the channel width is 500 μm.

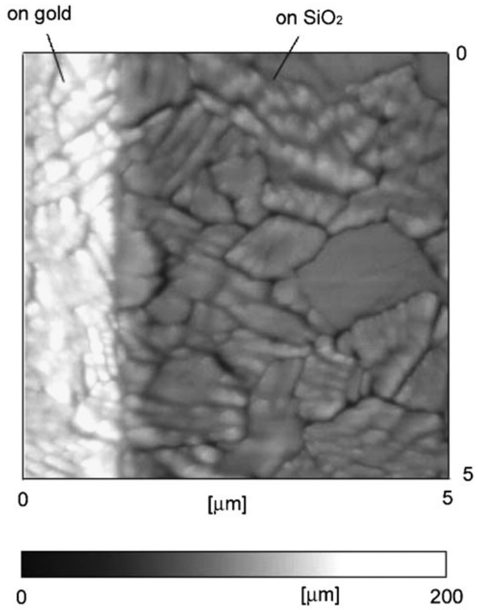


Fig. 14 AFM Image of the 2HTBP film.

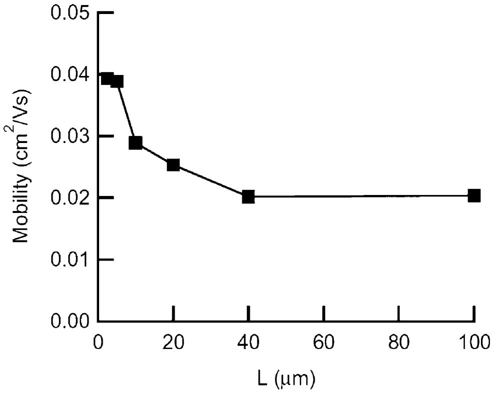


Fig. 15 Mobility of a 2HTBP OFET as a function of channel length.

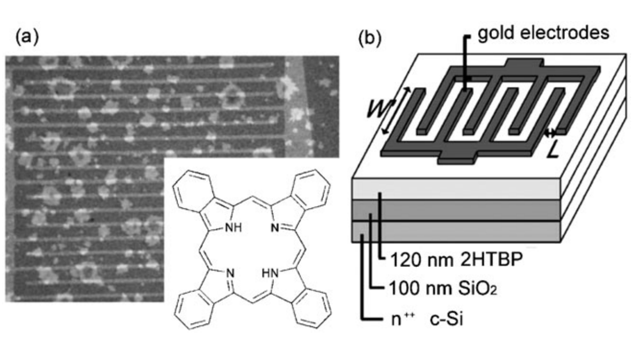


Fig. 16 (a) Top view of a 2HTBP OFET displaying the polycrystalline thin film and source and drain electrodes. The chemical structure of the TBP molecule is also shown. (b) A schematic view of the staggered source and drain electrode configuration used in this study.

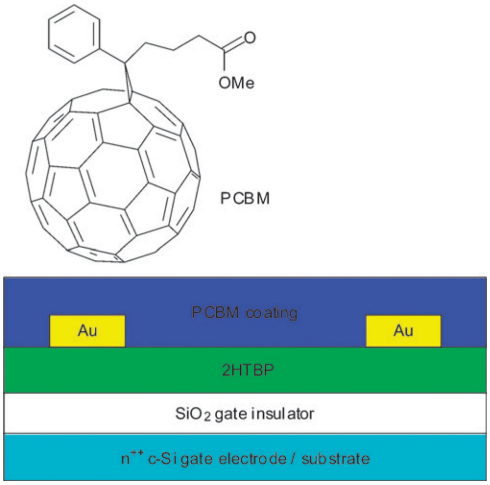


Fig. 17 A schematic view of PCBM-coated 2HTBP OFET.

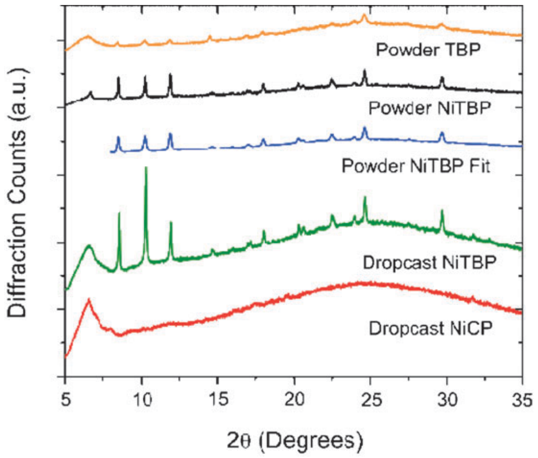


Fig. 18 XRD spectra of NiTBP and NiCP powders and thin films.

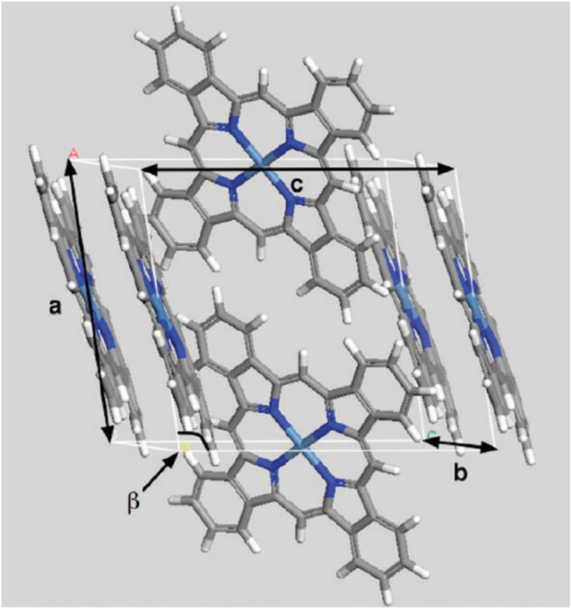


Fig. 19 Proposed molecular structure of the monoclinic NiTBP unit cell.

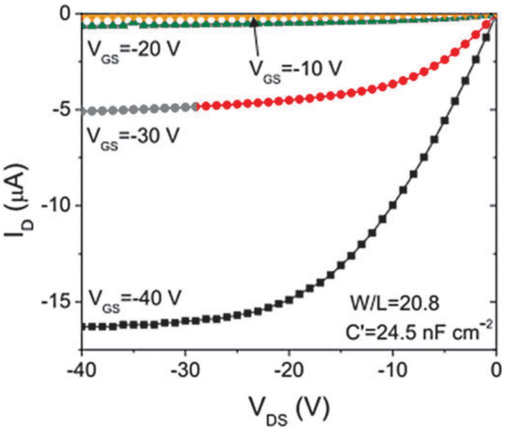


Fig. 20 Output characteristics for a NiTBP OFET.

potential energy. The unit cell was monoclinic with $P2_1/n$ symmetry (Fig. 19).

The output characteristics of NiTBP OFETs are shown in Fig. 20 from which it could be determined that the mobility of this transistor was on the order of 0.1 and 0.2 cm^2 V^{-1} s^{-1}, respectively, in the linear and saturation regimes. These were the highest values among solution processed OFETs using porphyrins or Pcs as semiconductors. OFETs based on CuTBP exhibited a similar performance with mobility 0.1 cm^2 V^{-1} s^{-1}. A polarized optical micrograph of a spun-cast CuTBP thin film is shown in Fig. 21, displaying its polycrystalline nature. The electrodes seen there were 20 μm wide, indicating that CuTBP formed domains of approximately equal size. By comparison, NiTBP formed crystals with size approaching 1 μm,[114] and TBP on the order of 2 μm in diameter.[109]

Solution processed 2HTBP OFETs were fabricated using precursor 2HCP, deposited on a thermal SiO$_2$ gate insulator patterned with nanometer-scale trenches. Thermal conversion of 2HCP to 2HTBP was enhanced by ordered TBP aggregation in the prepatterned trenches (Fig. 22). OFETs with channels parallel to trench direction growth were found to have carrier mobility approaching one order of magnitude greater than transistors fabricated with the channel oriented perpendicular to dendrite growth.[115]

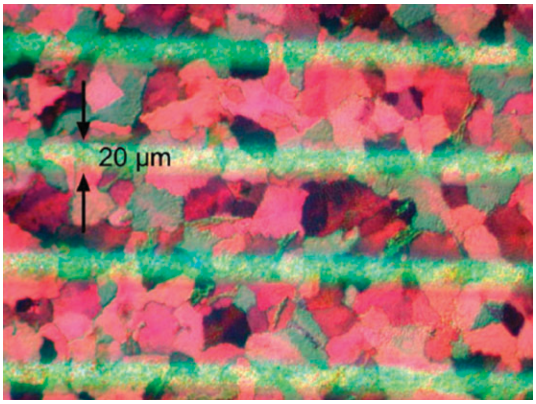


Fig. 21 Polarized optical micrograph of a continuous, spun-cast CuTBP thin-film on thermally oxidized c-Si. The electrodes in the figure are 20 μm wide.

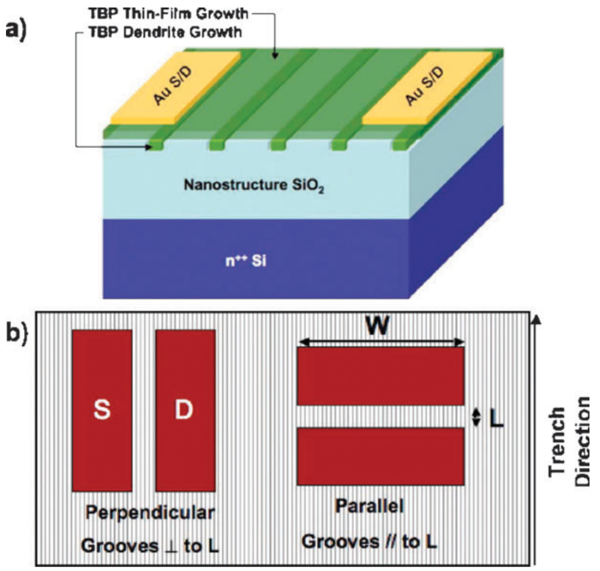


Fig. 22 (a) Schematic cross section of nanostructured TBP OFETs and (b) top view schematic of nanostructured OFETs structures.

Both fractal and micrometer-scale ordered nanorod aggregation were observed in precursor-route TBP thin films deposited on bare SiO$_2$, as shown in Fig. 23(a) and (b).[115] Thinner regions of the same film, with sparser surface coverage, displayed fractal aggregation. For a thin film with denser surface coverage, nanorod-type aggregation was predominant. Typical rod-shaped TBP aggregates were 60 nm wide and 300 nm long. AFM height micrographs of a TBP thin film are shown in Fig. 23(c) and (d). Upon thermal conversion of 2HCP, 2HTBP demonstrated preferential alignment along the trench direction.

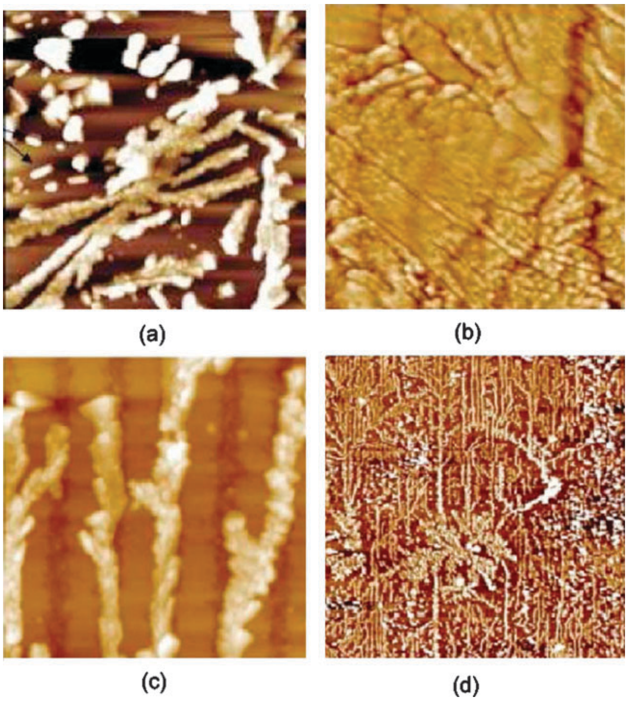


Fig. 23 AFM Height micrographs of (a) fractal aggregation of sparse, solution-processed TBP; (b) aligned domain formation in more dense TBP; (c) a close view of TBP aggregation within trenches; and (d) a wider-scale view of TBP aggregation wire formation within trenches. The axes dimensions are (a) 3 μm, (b) 2 μm, (c) 2.2 μm and (d) 25.2 μm. Samples in (c) and (d) have a trench periodicity of 450 nm and a trench depth of 10 nm.

4.4 Thin film organic solar cells

Porphyrins and Pcs tend to aggregate face-to-face through π–π stacking interactions. Therefore they are ideal for electronic conduction and have been extensively used for plastic OP V^{-1} s^{-1}.[1,116–118] Generally, vacuum deposited Pcs are used for p-type semiconductors, but porphyrins have also been investigated.[119–122] Shao and Yang have reported a heterojunction OPV fabricated by vacuum deposition of PtOEP and C$_{60}$, as ITO|PEDOT|PtOEP|C$_{60}$|BCP|Al. Its fill factor was 0.57 and power-conversion efficiency, 2.1%.[123]

Soluble precursors of 2HTBP were used not only for OFETs but also for thin film organic solar cells. Spin-coating of soluble p- and n-type semiconductors provided a simple method for fabrication of solar cells, as illustrated in Fig. 24. 2HTBP films on ITO electrodes (ITO|2HTBP) were prepared by continuous spin-coating of a soluble precursor, 2HCP, on ITO electrodes followed by thermal conversion of 2HCP to 2HTBP by simply heating the electrodes. Photocurrent generation was observed using a three-electrode system with ITO|2HTBP as a working electrode, Pt as a counter electrode, Ag/Ag$^+$ as a reference electrode, and hexyl viologen (HV) as an electron acceptor. A two-layer structure of 2HTBP and PCBM films and a three-layer structure of films of 2HTBP, a 2HTBP-PCBM mixture, and PCBM on ITO electrodes were also prepared by spin-coating. IPCE values up to 7% were obtained for the three-layer structure. Action spectra of the three-layer structure showed that overall, visible light from 380 to 700 nm could be utilized to sensitize the photocurrent generation system.[124]

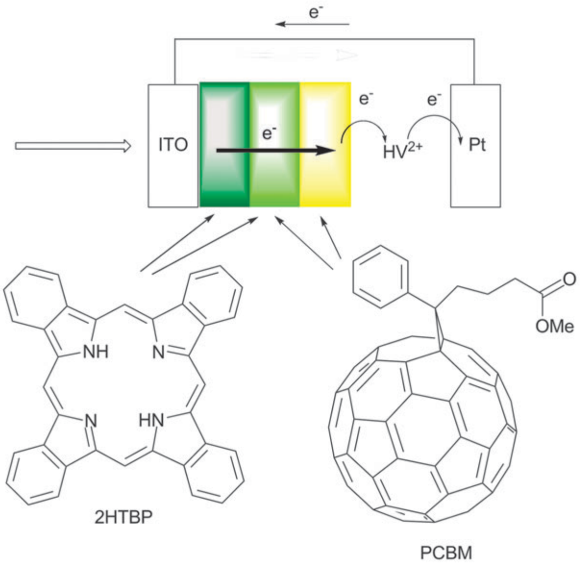


Fig. 24 Schematic diagram of photoenergy conversion system using 2HTBP and PCBM.

Very recently, OPVs based on TBP films prepared by solution processing of CP followed by thermal conversion have been reported by Sato *et al.*,[125] who prepared heterojunction and bulk heterojunction structures combining 2HTBP as a donor and fullerenes, PCBM and/or [6,6]-phenyl-C_{61} butyric acid *n*-butyl ester (PCBNB) as acceptors. In the p–n heterojunction structure, power energy conversion (η) was 2.2% and in the p–i–n structure the efficiency increased to $\eta = 3\%$.

5 Conclusion

Insoluble small molecules (pigments) such as pentacene, TBP, or Pc could be used to fabricate thin film electronics by a solution process using their soluble precursors with thermally or photochemically removable groups. This technology has advantages over the conventional vacuum deposition of small molecules and solution processes involving soluble polymers or oligomers because of its simplicity and excellent performance. This soluble precursor route also offers the possibility of developing new conducting small molecules. For example, naphthalocyanines are unstable under the conditions of vacuum deposition, leading to difficulties in device production. However, the solution process involving soluble precursors makes the construction of OFET devices under mild conditions possible. Thus, this process not only holds promise for the creation of cheap, large-area, patternable, plastic devices, but also for the development of new semiconducting small molecules.

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