ChemPubSoc Europe
DOI: 10.1002/open.201500064
Open Access ChemistryOPEN Communications

Synthesis of Arylamine Tribenzopentaphenes and Investigation of their Hole Mobility

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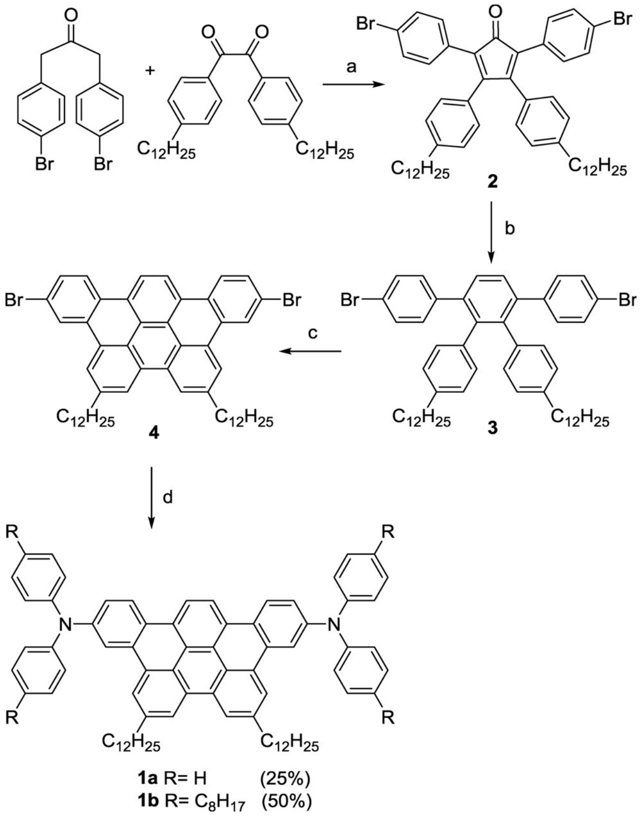
We report the versatile synthesis of two tribenzo[*fj,ij,rst*]pentaphene (TBP) derivatives bearing two diarylamine substituents attached at the opposite ends of the aromatic core. Field effect transistor (FET) devices of the bis-diarylamine-TBP compounds were fabricated using spin coating under different concentrations, spin speed, and solvent conditions. Emission spectra and surface investigation by atomic force microscopy (AFM) reveal the formation of aggregates induced by the strong π–π stacking of the aromatic core leading to island features, and thus, unexpected low hole mobilities. The synthetic strategy we show herein, however, offers the possibility to decorate the TBP core structure with various charge-carrier peripheral groups and optimized alkyl chains, which should improve the crystalline property of their thin films upon deposition, leading consequently to a better hole transport mobility.

A wide variety of one- and two-dimensional highly π-conjugated aromatic molecules have been thoroughly studied as potential organic semiconductors.[1–4] Among these conjugated compounds, polycondensed aromatic hydrocarbons with reduced symmetries are finding increasing interest, such as 1,4-diphenyl triphenylene-based derivatives whose macrocyclic[5] and polymeric[6] derivatives have shown superior electroluminescent properties.[7] We have recently disclosed the synthesis of some derivatives based on the larger aromatic core tribenzo[*fj,ij,rst*]pentaphene (TBP), whose trapezoidal structure offers some major advantages over other polycondensed aromatic hydrocarbons, most notably 1) their versatile synthesis and 2) the easy access to many possible functionalization sites.[8]

Recently, TBP derivatives with alkoxy side chains have shown better efficiency and photoconductive properties in organic photovoltaic devices than the more symmetrical hexagonal disc-shaped hexa-*peri*-hexabenzocoronene.[9,10] In order to increase hole transport efficiency of TBP, we have synthesized the arylamine tribenzo[*fj,ij,rst*]pentaphene derivative **1** with two nitrogen-containing groups attached at the opposite ends of the aromatic core. Scheme 1 summarizes the few reaction steps towards the target aryl amine pentaphene derivatives; 4,4′-didodecylbenzil was prepared from the oxidation of 4,4′-didodecyltolane[11,12] in presence of iodine and dimethyl sulfoxide (DMSO) (see Supporting Information for synthetic details).[13] The double Knoevenagel condensation reaction between the benzil and 1,3-bis(4-bromophenyl)acetone[14] in refluxing diphenyl ether[13] affords the tetraarylcyclopentadienone moiety **2** in 55% yield. This latter undergoes a [4+2] Diels–Alder cycloaddition reaction with phenylvinyl sulfoxide[15] in refluxing toluene yielding, via subsequent spontaneous de-



Scheme 1. Synthesis of the arylamine pentaphene derivatives. *Reagents and conditions*: a) KOH, EtOH, reflux, 1 h, 55%; b) phenylvinyl sulfoxide, toluene, reflux, 2 d, 46%; c) $FeCl_3$, CH_3NO_2, CH_2Cl_2, rt, 6 h, 76%; d) diarylamine, $Pd(OAc)_2$, NaO*t*Bu, *t*Bu_3P, reflux, 2 d, 25% (**1 a**), 50% (**1 b**).

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Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under http://dx.doi.org/10.1002/open.201500064.

carbonylation and hydrosulfinylbenzene elimination, the dibrominated tetraphenyl benzene **3** in 46 %. Cyclodehydrogenation reaction of synthon **3** with iron(III) chloride in nitromethane[16] yields the dibrominated pentaphene **4**. Buchwald–Hartwig cross-coupling reaction[17,18] of **4** with diphenyl amine derivatives gives **1 a** and **1 b** in 25 % and 50 % yield, respectively. It should be noted that the excellent stability and moderate solubility of **4** in common organic solvents offer the possibility to employ it as a key building block to synthesize a wide variety of TBP-based monomers and polymers similar to the less-extended triphenylene-based ones,[6,19] but bearing functional groups such as alkoxy groups, whose attachment prior to the cyclodehydrogenation step leads to the formation of only partially aromatized compounds.[20,21]

The two target compounds, **1 a** and **1 b**, were soluble enough to be analyzed by ^{1}H NMR, but a more useful tool for their characterization was high-resolution matrix-assisted laser desorption ionization–ion cyclotron resonance mass spectrometry (MALDI-ICR MS) using trans-2-[3-(4-t-butyl-phenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as the matrix, which reveals the high purity of the two pentaphene derivatives as shown from the measured isotopic patterns, as compared to their respective calculated ones (Figure 1).

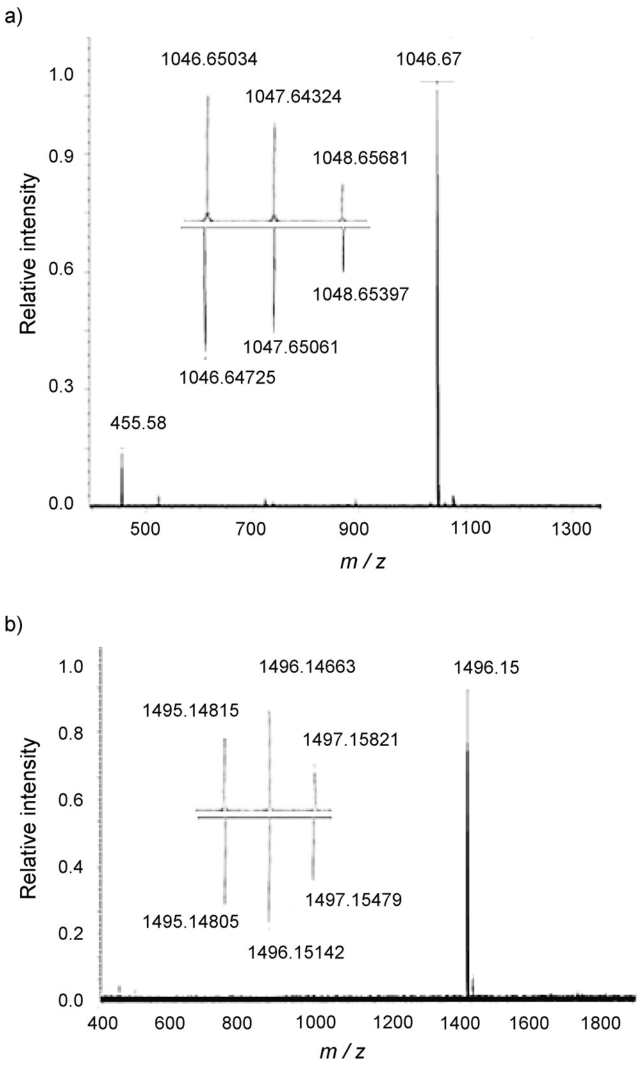

Figure 1. a) MALDI-ICR spectrum of **1 a** in DCTB; inset: measured (up) and calculated isotopic pattern (down), calculated for $C_{78}H_{82}N_2^+$. b) MALDI-ICR spectrum of **1 b** in DCTB; inset: measured (up) and calculated isotopic pattern (down), calculated for $C_{110}H_{146}N_2^+$.

The bis-diarylamine TBP derivatives **1 a** and **1 b** show strong UV/Vis absorption bands at 302 and 309 nm, respectively, which is typical for these aromatic chromophores,[8] in addition to a series of less intense bands around ~395 nm (Figure 2). The two new compounds, however, emit in the blue-green region with a slight red shift for **1 b** of ~10 nm (Figure 2) as compared to **1 a**.

It is worth mentioning that despite the very comparable absorption spectra of **1 a** and **1 b** with respect to the TBP chromophore as mentioned above, the absorption and emission spectra of the compounds we report herein are significantly red shifted from the alkyl-substituted TBP derivatives[8] by ~40 nm, which is explained by the additional conjugation due to the presence of the aryl amines as shown by density functional theory (DFT) calculations with B3LYP at the 6-31G* level (Table 1). Likewise, the 0→0 transition bands for **1 a** and **1 b** are clearly visible at 429 and 435 nm, respectively, also red shifted from the typical value of a 3,12-dialkylated TBP chromophore (~395 nm).[8]

In spite of their moderate solubility in common organic solvents, thin films of **1 a** and **1 b**, with thickness ranging typically between 30–50 nm, were made by spin-coating onto Si/SiO$_2$ substrates. In order to improve the films' smoothness and to charge optimize mobility, various solutions of **1 a** and **1 b** were prepared with different processing variables, such as the type of solvent, molar concentration, and spin speed (Table 2). All the solutions were sonicated for 30 min prior to spin-coating to reduce aggregation induced by the strong π–π stacking of the pentaphene core and to improve the molecules' solution processibility. A summary of the film roughness and field-effect transistor (FET) device performance is shown in Table 2. It is worth noting that the depict-

Table 1. DFT calculations (B3LYP at the 6-31G* level) of several TBP derivatives disubstituted at their opposite ends.

	Tribenzopentaphene (TBP) (3,12-disubstituted)						
	Parent	Diethyl	Di-NMe$_2$	NMe$_2$, NMePh	Di-NMePh	Di-NPh$_2$	Di-NTolyl$_2$
HOMO (eV)	−5.32	−5.21	−4.54	−4.59	−4.65	−4.73	−4.59
LUMO (eV)	−1.54	−1.47	−1.16	−1.23	−1.31	−1.47	−1.38
Gap	3.78	3.74	3.38	3.36	3.34	3.26	3.21
λ_{max} (nm) calcd.	362.32[a]	363.88[a]	408.61	410.67	411.32	425.87	433.29
λ_{max} (nm) exp.	—	395	—	—	—	429	435

[a] very weak transition.

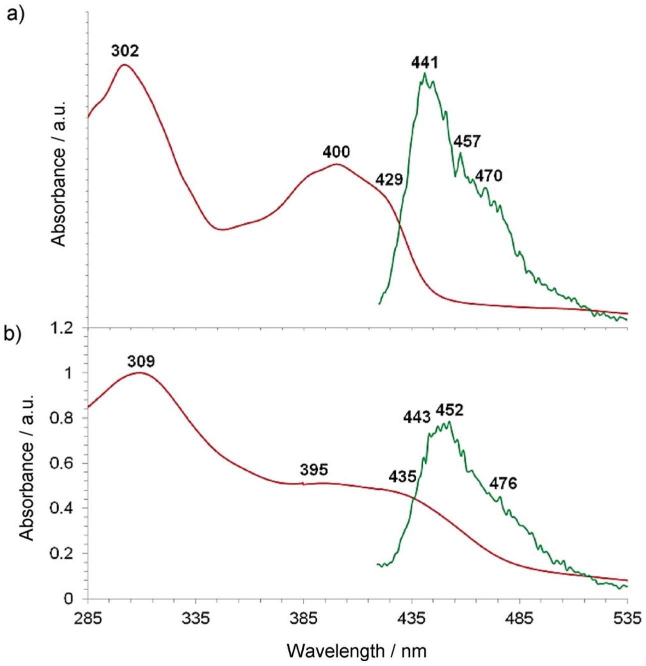

Figure 2. Normalized absorption (red) and emission (green) spectra of the tribenzopentaphene derivatives in toluene: a) emission ($c = 10^{-7}$ M, $\lambda_{ex} = 302$ nm) of **1 a**, b) emission ($c = 10^{-8}$ M, $\lambda_{ex} = 309$ nm) of **1 b**. Emission spectra were measured with a maximum intensity (internal scale) of 780 and 440, for **1 a** and **1 b**, respectively.

Table 2. Thin film spin-coating conditions, their root mean square (RMS) surface roughness, and FET mobilities.

Entry	PAH	Solv.	Conc. [10^{-4} M]	Spin speed [rpm]	RMS roughness [nm]	Mobility [$cm^2V^{-1}s^{-1}$]
1	1 a	toluene	4.5	2500	19.7	n.a.
2	1 a	toluene	4.5	4000	18.4	n.a.
3	1 b	toluene	4.5	4000	1.9	8.3×10^{-9}
4	1 a	toluene	4.5	5000	21.4	n.a.
5	1 a	toluene	2.0	4000	14.5	n.a.
6	1 b	toluene	2.0	4000	1.2	3.4×10^{-8}
7	1 a	toluene	0.5	4000	13.2	n.a.
8	1 a	DCB	2.0	4000	22.7	n.a.
9	1 b	DCB	2.0	4000	2.3	7.9×10^{-9}

n.a.: not applicable

ed results represent average values taken from four up to eight different substrates that is, more than twenty FET devices for each compound. It is worthwhile to mention that several attempts to sublime **1 a** and **1 b** under high vacuum were unsuccessful, which prevented us from employing thermal deposition known to be a much better technique to control the smoothness of thin films.[4]

None of the FET devices prepared from **1 a** showed a hole mobility, whereas **1 b** reveals a mobility of 8.3×10^{-9} $cm^2V^{-1}s^{-1}$ (Table 2, entry 3) when spin coated at 4000 rpm from a 4.5×10^{-4} M solution in toluene. This can be attributed to the island formation that takes place for **1 a** as can be seen in the atomic force microscopy (AFM) images (Figure 3). This kind of growth can be described by the Volmer–Weber growth mode, which occurs when the deposited molecules are more strongly bound to each other than to the substrate.[22] The growth of islands, and thus incomplete layers, is known to limit the transport of charge carriers and cause lower carrier mobility.[22] Given the lack of solubilizing groups for **1 a**, it is not surprising that the intermolecular interactions for **1 a** would be stronger than in **1 b**.

The mobility of **1 b** was improved by fourfold to 3.4×10^{-8} $cm^2V^{-1}s^{-1}$ when decreasing the solution concentration to 2×10^{-4} M in toluene and keeping the spin speed unchanged (Table 2, entry 6). In attempt to improve the smoothness of the films, and so the charge mobility, toluene was replaced by the more polar *o*-dichlorobenzene (DCB), which is reported to reduce aggregation for some other polycondensed aromatic hydrocarbon molecules.[23,24] However, in our hands, the surface roughness of the films increased, suggesting that *o*-di-

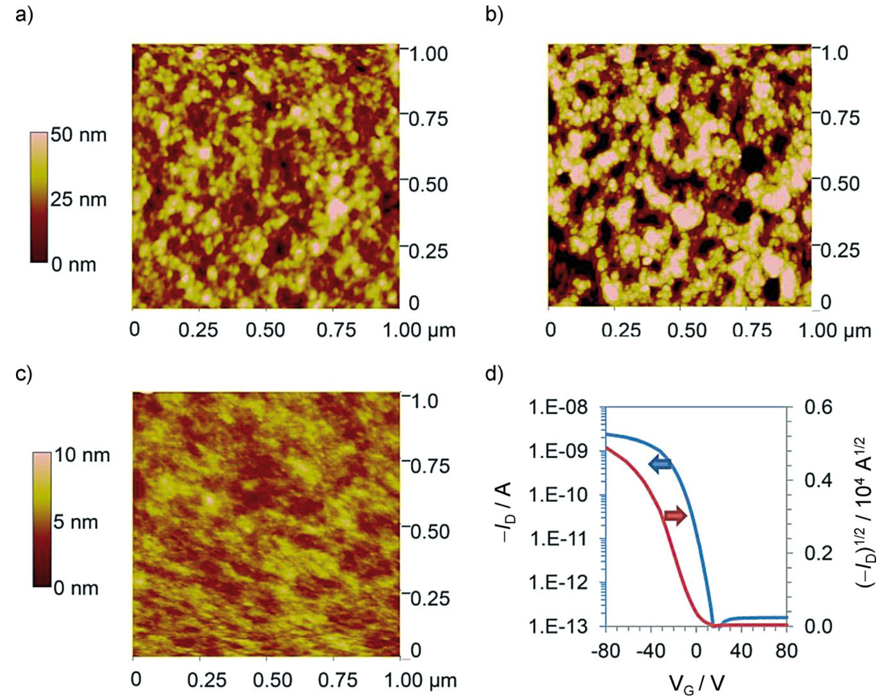

Figure 3. AFM topography image of a thin film prepared by spin-coating at 4000 rpm of a a) 0.5×10^{-4} M **1 a** in toluene b) 2×10^{-4} M **1 a** in *o*-dichlorobenzene c) 2×10^{-4} M **1 b** in toluene, and d) its transfer characteristic curves (gate-source voltage, VGS = +80 to −80 V).

chlorobenzene is not effective at decreasing aggregation for molecules **1a** and **1b** (Table 2, entries 8–9).

Figure 3b depicts the AFM investigation of the film topography of **1a** spin-coated from *o*-dichlorobenzene, showing a poor film quality with consistent island features that display an average surface roughness of ~23 nm. Replacing the solvent with toluene, altering the spin speed, and decreasing the concentration slightly improved the film quality to an average surface roughness of ~13 nm, but without detecting any mobility for their FET devices. The lack of mobility for **1a** could be explained by the small number of number alkyl chains leading to a lower solubility, and therefore, causing a more rapid aggregation that produces the island features in the solid state. The AFM investigation of thin films of **1b**, on the other hand, revealed smooth surfaces with no visible island features and an average roughness of ~2 nm (Table 2, entries 3 and 9). This later was decreased to ~1 nm when lowering the concentration of **1b** in toluene to 2×10^{-4} M (Table 2, entry 6). It should be noted that all the spin-coated films of **1a** and **1b** from *o*-dichlorobenzene show a surface roughness consistently higher than those spin-coated from toluene (see Supporting Information), implying the ineffectiveness of this solvent to improve the film quality of these two derivatives.

In conclusion, two new 3,12-disubstituted tribenzo[*fj*,*ij*,*rst*]-pentaphene derivatives bearing diaryl amine groups at their opposite ends were synthesized and their field-effect transistor (FET) devices were made by spin coating. The very low hole transport mobilities of these compounds reveal their high tendency to aggregate due to the pronounced π–π stacking interactions, as revealed from both the much reduced emission intensity and atomic force microscopy (AFM) surface investigation. This suggests the preparation of new pentaphene-based compounds bearing various charge carrier groups and optimized alkyl side chains, which should improve the thin films by crystallization, leading, consequently, to a better hole transport mobility.[1,25]

Acknowledgements

B. A. would like to thank the Kuwait Foundation for the Advancement of Sciences for supporting this work (grant number 2011-1413-02), and C. L. acknowledges the US National Science Foundation (NSF) (DMR 1407815).

Keywords: conducting materials · cross-coupling · fused-ring systems · Pi interactions · thin films

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Received: March 9, 2015