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Contorted Tetrabenzoacenes of Varied Conjugation: Charge Transport Study with Single-Crystal Field-Effect Transistors

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KEYWORDS: tetrabenzoacenes, single crystal field-effect transistor

ABSTRACT: A series of contorted and polyfused aromatic tetrabenzoacenes derivatives differing in conjugation length were synthesized and characterized. X-ray diffraction revealed the contorted molecular shape, as well as the packing arrangement of these molecules. Thus unsubstituted tetrabenzoacenes showed a shifted or perfect face-to-face π -stacking depending on their conjugation length. The single crystals of these tetrabenzoacenes were used as conducting channels in fabricating field-effect transistors (SCFETs). Tetrabenzotetracene (**TBT**) exhibited the highest measured mobility, approaching 0.81 cm²V⁻¹s⁻¹ (average 0.64 cm²V⁻¹s⁻¹) among these molecules. In contrast, theoretical calculation showed that the tetrabenzooctacene (**TBO**) crystal has a large-area, face-to-face π -packing, with the highest intermolecular coupling in the series. The lower charge mobility (average 0.32 cm²V⁻¹s⁻¹), highest 0.55 cm²V⁻¹s⁻¹) observed was rationalized as a result of possible involvement of delocalized polaron formation due to comparable electronic coupling and reorganization energy in **TBO**, as supported by the Monte Carlo simulation with such delocalized effect taken into account.

INTRODUCTION

Incorporation of organic field-effect transistors (OFETs) into organic electronic devices is being considered as the future trend in the realization of flexible electronics, like organic light-emitting diodes, memory devices, and sensors and etc.¹ An essential property for organic materials to be used in OFET as conducting channel is a high charge transport ability between neighbouring molecules. It is generally accepted that the rate of intermolecular charge transport relates to the molecular reorganization energy as well as the intermolecular transfer integral,² so that a small reorganization energy and large electronic coupling will benefit the charge mobility. Crystal engineering of organic semiconductors to improve the intermolecular π - π overlap has been an ensuing effort.³ One of the strategies is the expansion of a conjugate system to increase the possible π - π overlap. For example, the extension of fused benzene rings in linear acene was found to increase the coupling and mobility (Figure 1a)⁴, so is the extension of [1]benzothineno[3,2-b]benzothiophene derivatives (Figure 1b).⁵ Another idea is to play with substituents on the conjugate core framework to induce a face-to-face packing behaviour, which is considered to produce effective electronic coupling.⁶ For example, chlorine atoms substituted on linear acenes resulted in face-to-face packing.⁷ In the case of rubrene, the four bulky phenyl rings substituted on the periphery of tetracene backbone change the herringbone packing to co-facial herringbone packing and produced a high electronic coupling.⁸ The substitution of triisopropylsilylethynyl (TIPS) groups on the 6- and 13positions of the pentacene skeleton induces a brick-wall-type stacking.⁹ The similar idea is applied to other polycyclic aromatic systems with the choice of fitting trialkylsilylethynyl group to modulate the crystal packing.¹⁰

Journal of Materials Chemistry C

Page 2 of 17

Molecular geometry is yet another factor that influences the electronic coupling. In particular, the contorted polyaromatics have a high tendency to pack face-to-face due to self-complementarity in shape.¹¹ Thus contorted hexabenzocoronene (**cHBC**, Figure 1c) with the six annulated benzene rings twisted away from the central coronene core shows significant π - π stacking after post-deposition processing.¹² The p-type OFET mobility based on alkoxy-substituted **cHBC** thin films was about 0.02 cm² V⁻¹ s⁻¹.¹³ Contorted octabenzocircum biphenyl (**cOBCB**) is a larger π -conjugated extension of **cHBC**, which gave an OFET mobility about 0.002 cm² V⁻¹ s⁻¹.¹⁴ The 1, 2, 3, 4, 7, 8, 9, 10-tetrabenzocoronene (**TBC**) is a smaller yet contorted π -conjugated system whose single crystal gave co-facial or shifted π - π stacking, depending on the size of the substituent groups.¹⁵ A high hole-mobility of 0.7 cm² V⁻¹ s⁻¹ was obtained for symmetric tetra-chlorinated **TBC** and 1.19 cm² V⁻¹ s⁻¹ was achieved for asymmetric hexa-fluorinated **TBC** exhibited self-assembling behavior in solution to give fibrous microstructures with a space-charge limited charge mobility of 0.61 cm² V⁻¹ s⁻¹.¹⁶ Pyreno[4,5-a]coronene (**PRC**), is yet another non-planar molecule giving a perfect on-top co-facial π -stacking in its needle-like crystal. The theoretical calculation suggests a large electronic coupling of 160 meV for the co-facial dimer.¹⁷



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Figure 1. Structures of linear (a) linear acenes; (b)thienoacenes; contorted (c)TBC, cHBC and cOBCB; (d) PRC, TBN and Tetrabenzoacenes.

The crystal packing of **TBN** shows a partial face-to-face packing with an electronic coupling of 38.4 meV for dimer along the b-axis.¹⁸ Although **TBN** has the same twisted conformation and similar crystal packing with **PRC** mentioned above, the electronic coupling, which relates to the extent of π - π overlap, is significantly low, and this indicates a possible correlation in the size of π -conjugated skeletons with the extent of π - π overlap for contorted polyaromatics. The mobility improvement by extending π -aromatic skeleton of linear acenes (ex. tetracene, pentacene, hexacene⁴) or thienoacenes (**BTBT**, **DNTT**, **DATT**)⁵ was observed. But there is little systematic study on contorted polyaromatics as a function of conjugation length.¹⁹

In this work, we studied a series of contorted yet linear tetrabenzoacene derivatives containing tetrabenzonaphthalene (**TBN**) unit as the central core to introduce a twist in the molecule. These tetrabenzoacenes differ in their π -conjugation lengths, from naphthalene (**TBN**) to tetracene (**TBT**), hexacene (**TBH**), and octacene (**TBO**). Single crystal structures of these derivatives were determined and analysed. The physical properties, the performance of SCFETs were measured and theoretical calculation were conducted in an attempt to understand the structure/property correlation in this series of derivatives and their potential as transistor materials.

EXPERIMENTAL METHODS

All the tetrabenzoacene derivatives were synthesized in the laboratory and fully characterized by NMR, Mass and X-ray crystallography (the synthetic details are provided in Supporting Information, SI). UV-Visible spectra were recorded by using a *Jasco* V-530 double beam spectrophotometer with the sample solution prepared in dichloromethane ($\sim 10^{-5}$ M). For oxidation potential measurements, the samples were dissolved in anhydrous and degassed dichloromethane ($\sim 10^{-3}$ M) containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte. The cyclic voltammograms were recorded on a CHI 620 analyzer with glassy carbon as the working electrode, platinum wire as the counter electrode and Ag/Ag⁺ as the reference electrode respectively. The HOMO values for the solid samples were grown by vapor phase transfer method with argon or helium as the carrier gas.²⁰ The X-ray diffraction was measured on a Bruker X8APEX or Kappa APEXII X-ray diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å) and the structure was solved by SHELX 97 program.

The fabrication procedure of top-contact, top-gate SCFET device was reported earlier.¹⁵ The selected single crystal was placed on an *n*-octadecyltrichlorosilane(ODTS)-modified glass slide. Colloidal graphite was used as the source, drain and gate electrode materials. Parylene-N thin film (~2 - 4 μ m thick) was used as the insulating dielectric layer. The channel length and width of the devices depended on the crystals chosen and were determined for each crystal. The electrical characteristics of the devices were measured in ambient and in the dark by an Agilent 4156C Semiconductor Parameter Analyzer. The field-effect mobility of the OFET devices in the saturation region was calculated by using equation 1:²¹

 $I_{\text{SD,sat}} = (WC_i/2L) \,\mu_{\text{sat}}(V_{\text{G}}-V_{\text{th}})^2 \quad (1)$

where W is the channel width, L is the channel length, and C_i is the capacitance per unit area of the parylene-N gate dielectric, V_G and V_{th} are the gate-source and threshold voltage respectively.

The quantum *ab initio* calculations were performed by a developmental version of Q-Chem program.²² The reorganization energy was calculated following the commonly used scheme in the literature,²³ at the level of B3LYP/6-31G*.²⁴ The transfer integral (*t*) between neighboring dimer pair was calculated with the directing coupling method by the LC- ω PBE scheme ($\omega = 0.2$)²⁵ and the Dunning's double- ζ basis sets.²⁶ The dimer configurations were obtained from the crystal structure, with the hydrogen coordinates optimized at the level of B3LYP/6-31G*. To see the thermal fluctuation of the electronic coupling, the configurations from molecular dynamics (MD) simulations were also sampled in the canonical ensemble (NVT) at 298 K. The MD simulation was performed using the Tinker program with the MM3 force field.²⁷ Charge-transfer rates for pairs of neighboring molecules were calculated based on Marcus theory.²⁸ The carrier transport rate at 300 K was obtained from three different approaches: (I) the Einstein relationship²⁹ where the carrier diffusion coefficient was estimated by the Marcus' charge transfer rates, together with the intermolecular distances analyzed from the crystal structure, (II) a Monte Carlo simulation ³⁰ with disorder in charge-transfer couplings derived from a molecular dynamics sampling, and (III) similar Monte Carlo simulation but with delocalized states for sites with large coupling values, similar to that described in reference.³¹

RESULTS and DISCUSSION

Synthesis.

The syntheses of various tetrabenzoacenes are shown in Scheme 1 and the key step in each is the formation of tetrabenzonaphthalene (**TBN**) moiety as the twisted core. The fluorenone-type precursors

(1, 3, 5, 7) of various conjugation lengths were commercially available or prepared in the laboratory and then underwent thesuperacid-catalyzed dehydration/cyclization to give the desired products through a pinacol rearrangement, as reported by Klumpp and Olah.³²

Scheme 1 Synthetic routes of various tetrabenzoacenes^a



^aReagent and condition: (a) $Zn/ZnCl_2$, THF/H₂O; (b) triflic acid, benzene; (c) NaOH, Ba(OH)₂, then 400°C; (d) NaOH; 20% alcoholic potash, then methanesulfonic acid, P₂O₅; (e) n-BuLi, oxygen, -78°C.

The fluorenone-type compound **3** was prepared from vacuum pyrolysis of the barium salt of 4,5phenanthrene dicarboxylic acid³³ (**2**) at 400°C through decarboxylation and cyclization, in 35 % yield.³⁴ After hydrolysis of methoxycarbonyl-substituted triphenylene **4**, cyclodehydration with Eaton's reagent led to compound **5** in 95% yield. The longest analogue **7** was prepared from compound **6** via abstraction of the bridge hydrogen at 9-position by *n*- butyllithium, followed by oxidation with oxygen.³⁵ The fluorenone derivatives was transformed to corresponding diols by pinacol coupling in the presence of zinc/zinc^{2+,36} Without further purification, these crude pinacol derivatives were dissolved in anhydrous benzene with triflic acid to yield tetrabenzoacenes smoothly in acceptable or moderate yields (45-70% for two steps). All steps were carried out in gram-scale. The final products were purified by column chromatography and vacuum-sublimation before crystal growth by vapor-phase transfer method and physical measurement.

Characterization

The **TBN** appears white, yet **TBT**, **TBH** and **TBO** appear orange. Figure 2a shows the UV-Vis absorption spectra of these compounds, except for **TBO** due to its poor solubility in common solvents. The UV-spectra of **TBN** and **TBT** conform to that reported in the literature.³⁷ The UV-spectra of **TBT** and

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TBH show a significant red-shift relative to that of **TBN**, indicating the effect of increasing π conjugation in **TBT** and **TBH** than in **TBN**. The electrochemical property of these compounds was studied by cyclic voltammetry (CV) experiment in dichloromethane solution. One oxidation peak was observed for each of these compounds, as illustrated in Figure 2b. That for **TBO** was not determined due to solubility problem. The solid state HOMO levels of these compounds were also measured by AC-2 photoelectron spectrometer. The HOMO values from both methods and the energy gaps are summarized in Table 1. The calculated frontier orbitals are shown in Figure 3. The increased conjugation length from **TBN** to **TBT** and **TBH** raises the HOMO level from 5.7 to 5.5 eV (by CV) as expected. It is interesting to note that the energy gap and HOMO values of TBT and TBH were the same, and the calculated HOMO orbitals of **TBT**, **TBH** and **TBO** were also similar. The experiments in dilute solution and calculated HOMO orbitals based on single molecule implied the analogous π -delocalized extensions of these annulated π -skeletons, that is, the HOMO orbitals do not extend to the extra rings. However, the HOMO values obtained from AC-2 for TBT, TBH and TBO were 5.5, 5.2 and 5.1 respectively, decreasing with longer extension. This different HOMO values (by AC-2) between **TBT**, **TBH** and **TBO** may imply the packing interaction can have additional influence on HOMO level in the aggregated state compare to isolated molecules.



Figure 2. (a) Normalized UV absorption spectra; (b) plots of cyclic voltammetry of tetrabenzoacenes in dry CH_2Cl_2 with a scan rate at 0.1 V/s; (c) Thermal gravimetric analyses of tetrabenzoacenes.



Figure 3. Results of frontier molecular orbital and the calculated energy of **TBN**, **TBT**, **TBH**, and **TBO**, respectively. The calculating level is B3LYP/6-31G*, and the isovalue is 0.02 au.

Item	TBN	TBT	TBH	TBO
$E_{gap} (eV)^{a}$	3.2	2.9	2.9	
E _{HOMO} (eV) by CV	5.7	5.5	5.5	
E_{HOMO} (±0.1eV) by AC-2	5.7	5.5	5.2	5.1
Td (°C)	327	369	486	491
3	-			· - ·

Table 1. Energy levels of tetrebenzoacene derivatives

^aThe gap was estimated from the onset of their UV absorption ($E_{gap} = 1241/\lambda_{onset}$).

Thermal gravimetric analysis was performed in a nitrogen atmosphere and the decomposition temperatures (at 5% weight losses) are illustrated in Figure 2(c) and Table 1. The result showed the decomposition temperature (T_d) correlates with the molecular weight of the aromatic system in the situation where the T_d increases with increasing conjugation. Below their decomposition temperature, these compounds survived well under vacuum sublimation and during PVT crystal growth condition.

Crystal structure analyses and theoretical results

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The compounds **TBN**, **TBH**, **TBO** give needle-like or fiber-like crystals, whereas **TBT** exhibits long and flaky crystals (see ESI). The structures and crystal packing were clearly revealed by X- ray analyses and are shown in Figure 4-7. Selected crystal data are summarized in Table 2. All molecules have very similar twisted geometries. A high torsion angle between 36° and 43° was observed, depending on the conjugation length. According to the optimized structures, the two torsion angles in the molecule are the same. Yet in reality, the two torsion angles in the *fjord* regions are slightly different, which may be due to the shifted packing of neighboring molecules in the crystalline state. The degree of twist of **TBT** is the smallest in this series, and that of **TBN**, **TBH** and **TBO** are all larger than 40°.

These contorted acenes are chiral, with *P* and *M* enantiomers both present in the crystal, like other twisted molecules.^{11(a)-(c), 15(e), 18} No achiral anti-folded conformer was observed presumably due to higher strain energy. Based on the enantiomer stacking behavior in these tetrabenzoacenes, two kinds of packing models could be categorized. For **TBN**, **TBT** and **TBO**, their stackings are similar in that all crystallized in a monoclinic system, such that the same enantiomer (*P-P* or *M-M*) stacks in a column along the *b*-axis, forming π - π contacts with different overlap ratio, as seen in Fig. 4, 5 and 7. **TBO** has a perfect co-facial packing like previously reported **PRC**,¹⁷ and the π - π overlap in **TBT** packing is larger than that of **TBN**. Nevertheless, the crystal structure of **TBH** is orthorhombic and has a dense π - π stacking taking place between the *P* and *M* enantiomers and shows a complicated packing mode. The intermolecular face-to-face stacking in **TBH** crystal is not obvious.

In Table 3, we summarized the reorganization energy (λ) and interaction of important neighbors from one reference molecule in the crystal, together with the calculated electronic couplings, and the charge mobility estimated from the Einstein relationship (μ_E).²⁹ From Table 3, it is seen that the reorganization energy (λ) of **TBN** is 181 meV, and that of **TBT**, **TBH** and **TBO** is 114, 112 and 103 meV, respectively. The reorganization energy decreases by 67 meV in going from **TBN** to **TBT**. However, in going from **TBT** to **TBH** and **TBO**, the reorganization energy does not decrease much. HOMO distributions of **TBT**, **TBH** and **TBO** are very similar, that is, mostly concentrated on the "**TBT**" core of the structures. The geometry relaxation mainly occurs in the "**TBT**" portions of these three compounds, so that a similar reorganization energy is obtained.

Journal of Materials Chemistry C

The couplings for π - π stacking conformations are 75.6, 84.0 and 179 meV for **TBN**, **TBT** and **TBO**, respectively, as they are related to the degree of π - π overlap. The calculated mobility also follows the trend, with a very high mobility expected for **TBO** (17.9 cm²V⁻¹s⁻¹). On the other hand, other intercolumn couplings also exist, providing a charge-hopping network. However, such intercolumn couplings are weaker in **TBO** than those in **TBN** and **TBT**. In other words, the charge hopping network in **TBO** is essentially 1-dimensional. With higher inter-column couplings, **TBN** and **TBT** have 3dimensional charge-hopping networks. The π - π stacking offers a fast charge hopping path, and it is aligned with the crystal axis in this series. In terms of the coupling of the π - π stacking along the b-axis, **TBH** has the smallest, 41meV, compared to the other three tetrabenzoacene derivatives. Nevertheless, the charge conduction in **TBH** crystal packing can have multiple channels if one particular path is blocked. In this case, the fast charge hopping paths do not align in a single direction, as seen in Figure 6. Therefore, the contribution of these charge hopping pathways to the charge mobility will be smaller, depending on how the hopping path projected along the electric field.



Figure 4. Crystal packing of TBN by viewing along b-axis and a-axis (C-H bonds are omitted for clarity). Unit cell exhibiting long b-axis along the $(0\overline{1}0)$, short a-axis along $(\overline{1}00)$ and c-axis along (001). The crystal shown has a dimension of 0.28mm x 0.14mm x 0.08 mm.



Figure 5. Crystal packing of **TBT** by viewing along b-axis and a-axis (C-H bonds are omitted for clarity). Unit cell exhibiting long b-axis along the (010), short a-axis along (100) and c-axis along ($00\overline{1}$). The crystal shown has a dimension of 0.36 mm x 0.20 mm x 0.10 mm.



Figure 6. Crystal packing of **TBH** by viewing along b-axis and a-axis (C-H bonds are omitted for clarity). Unit cell exhibiting long b-axis along the $(0\overline{1}0)$, short axis along $(\overline{1}01)$ and c-axis along $(00\overline{1})$. The crystal shown has a dimension of 0.44 mm x 0.16 mm x 0.04 mm.



Figure 7. Crystal packing of **TBO** by viewing along b-axis and a-axis (C-H bonds are omitted for clarity)

				IJ
Compound	TBN	ТВТ	ТВН	ТВО
a (Å)	12.14	13.18	18.87	31.94
b (Å)	7.56	7.49	7.65	3.90
c (Å)	17.64	18.15	31.44	23.95
α (deg.)	90	90	90	90
β (deg.)	97.62	100.99	90	116.35
γ (deg.)	90	90	90	90
space group	$P2_1/n$	$P2_1/n$	Pbca	C2/c
Exp. and calc (in parentheses)	40.65	35.92	40.69	41.21
torsion anglo ^o	&	&	&	&
A P C D & E E C H	43.29	38.99	41.95	41.21
A-D-C-D & E-F-G-H	(43.14)	(38.85)	(41.82)	(42.25)
Exp. and calc.(in parentheses)	1.388	1.395	1.386	1.397
central C=C bond length	(1.397)	(1.400)	(1.393)	(1.392)

 Table 2. Selected structural parameters of single crystal of tetrabenzoacene derivatives

Molecule	λ_{in}	Distance ^b	p _a ^c	p_b^c	p _c ^c	Character ^d	Coupling ^e	$\mu_{\rm E}^{\rm f}$
		4.815	3.0	3.8	0.1	ΡΡ, π-π	75.64	
TBN	181	10.249	4.3	2.1	9.6	PM, parallel	28.72	0.99
		10.207	1.9	5.4	8.1	PM, parallel	11.91	
		4.927	2.7	3.7	1.2	ΡΡ, π-π	84.0	
TBT	114	8.152	2.2	3.3	6.6	РМ, СН-π	38.8	2.85
		8.579	2.2	4.2	6.6	PM, CH-π	16.9	
		6.491	0.9	0.7	6.4	РМ, π-π	41.44	
TBH	112	10.553	0.9	8.3	6.4	PM, parallel	50.57	2.81
		7.648	0.0	7.6	0.0	PP, parallel	29.28	
TBO	103	3.898	0.0	3.9	0.0	ΡΡ, π-π	178.5	17.0
	105	11.987	5.3	0.6	12	PM	13.74	17.7

Table 3. Calculated the reorganization energy and electronic coupling for hole transfer

^aReorganization Energy, in units of meV.

^bDistance (in units of Å) of the neighbor to the reference molecule, which is centered in the origin.

^cProjection of the center of the neighboring molecule to the lattice axes *a*, *b*, and *c*, in units of Å.

^dDescription of the conformation of the pair. "P" and "M" indicate the corresponding enantiomers. π - π and CH- π describe the major feature of the interaction. "Parallel" indicates that the two π fragments from the two molecules are parallel to each other, but they are shifted and there is no π orbital overlap.

^eListed are coupling of the reference molecule to the neighbor, in units of meV.

^fCharge mobility estimated from the Einstein's relationship, in the units of cm² V⁻¹ s⁻¹. For **TBN**, **TBT**, **TBH** and **TBO** we report the value for the *b*-axis.

SCFET device property

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Crystallites grown by the vapor phase transfer method were carefully examined under an optical microscope for their quality and integrity and then chosen for device fabrication. The single crystal fieldeffect transistors were prepared only along the long axis (indexed to be b-axis) in the same fashion for all compounds, as this is also the direction with significant π - π stacking and thus electronic couplings. Four to ten samples for each compound were prepared and measured in the dark under ambient condition. All of the devices exhibited typical *p*-type FET characteristics. The device characteristics are summarized in Table 4. The typical output and transfer characteristics for **TBT** are shown in Figure 8. The rests are shown in ESI, Figure S13-16.

Compound	Mobility, μ , (cm ² V ⁻¹ S ⁻¹)	Average mobility (µ _{avg})	On/off ratio	Threshold voltage (Vth, V)
TBN	0.28-0.55	0.41 ± 0.07	$10^4 - 10^5$	(-9) – (-3)
TBT	0.46-0.81	0.62 ± 0.14	$10^{5} - 10^{6}$	(0) – (-10)
TBH	0.044-0.074	0.061 ± 0.011	$10^4 - 10^5$	(-11) – (-35)
ТВО	0.11-0.55	0.32 ± 0.15	$10^2 - 10^4$	(3) - (-16)

Table 4. SCFET performance and Simulated charge mobilities of tetrabenzoacene derivatives



Figure 8. (a) Output characteristics and (b) transfer characteristics of TBT.

Simulated mobility (cm ² V ⁻¹ s ⁻¹)	TBN	TBT	TBH	ТВО
$\mu_{ m KMC}$	0.72	2.24	1.24	5.64
$\mu_{ m deloc}$	0.72	0.45	1.24	0.35

Table 5. Simulated charge mobilities of tetrabenzoacene derivatives

The SCFET devices based on tetrabenzoacenes, **TBN**, **TBT**, **TBH** and **TBO** gave on/off current ratios of 10^2 - 10^6 , and an average mobility of 0.41, 0.62, 0.061 and 0.32 cm² V⁻¹s⁻¹ respectively. Compound **TBT** exhibited the best performance among the SCFET devices, with the highest measured mobility of 0.81 cm² V⁻¹s⁻¹. In contrast to the calculation results, **TBO** has a rather moderate mobility of 0.32 cm²V⁻¹s⁻¹, and **TBH** has the lowest mobility in this series. In an attempt to understand the discrepancy, other models are being considered. Thus in Table 5 we also include simulated charge mobilities from two different Monte Carlo simulation schemes: a standard Monte Carlo simulation with delocalized states for sites with large coupling (μ_{KMC}), and a modified Monte Carlo simulation with delocalized states for sites with large coupling values (μ_{deloc}),³⁰ (additional details are in the supplementary information accompanying this work).

Following **TBN**, **TBT** and **TBO** series, the P-P and M-M stacking offers an increased level of π - π overlap, and so is the corresponding electronic coupling values, which are 75.6, 84.0 and 178.5 meV, respectively. It is also seen that the measured mobility of **TBN** and **TBT** are quite close, with that of **TBT** being larger. Depending on the theoretical model, **TBT**'s mobility is larger than **TBN**, with simple

Einstein's relationship, or with kinetic Monte Carlo model. But **TBO** is still the highest at $5.64 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$.

In an earlier report delocalized polaron formation was suggested to form when the electronic coupling is comparable to reorganization energy so that the mobility can be diminished. It is noticed that among this series of compound, **TBO** is the only one that has a rather high electronic coupling larger than its reorganization energy (179 meV and 103 meV respectively). Thus delocalized polaron effects in the simulation (μ_{deloc}) is considered. Namely, when the sampled site has a neighboring coupling larger than the reorganization energy, the two (or more) sites are replaced by a delocalized state, which is lower in energy and the overall coupling to external sites are slightly weaker.³⁰ When this delocalized polaron is included in the kinetic Monte Carlo simulation, the mobility μ_{deloc} of **TBO** drops dramatically from 5.64 to 0.34 cm² V⁻¹s⁻¹, which appears to be close to experimental results. Similar effect is also seen on **TBT**, whose largest coupling from the crystal structure is 84 meV, pretty close to its reorganization energy of 114 meV. With a sampled disorder from a molecular dynamics simulation, a small fraction of the molecules is with coupling being larger than the reorganization energy (Figure S6 in the supplementary material). The corresponding simulated mobility is decreased from 2.24 cm² V⁻¹s⁻¹ to 0.45 cm² V⁻¹s⁻¹ when low-lying charge-delocalized state is considered. We note that the latter result is close to experimental results.

Our simulation predicted large charge mobilities for **TBH**. **TBH**'s largest electronic coupling is only about 50 meV, much smaller than the reorganization energy of 112 meV, implying that the effect of delocalized polaron does not exist. The crystal structure of **TBH** indicates several intermolecular interactions with good electronic coupling, leading to a rather isotropic connection network, which would allow easy escape should a blockage in the pathway be formed. However, the averaged and highest experimental mobility were only 0.061 and 0.074 cm² V⁻¹s⁻¹. The source of this discrepancy is not clear yet.

CONCLUSIONS

In conclusion, a series of linear contorted tetrabenzoacenes were synthesized via a convenient route using triflic acid-catalyzed rearrangement reaction of pinacol derivatives, which were prepared from benzannulated fluorenone in acceptable yields. The photo-physical properties and the calculated frontier molecular orbitals suggest that linear extension of aromatic skeletons in contorted tetrabenzoacenes did not enlarge the π -electron delocalization.

The single crystals were grown by PVT technique for X-ray analyses. For contorted tetrabenzoacenes, not only face-to-face packing exists, but other packing modes were obtained. The increased conjugated length of unsubstituted tetrabenzoacenes derivatives leads to improved intermolecular π - π overlap except for compound **TBH**, which had a slightly inferior π - π overlap but a noteworthy edge-to-face packing. Compound **TBO** showed a perfect cofacial stacking.

Among the SCFETs with these tetrabenzoacenes as the conducting channel, compound **TBT** gave the best field-effect hole-mobility of $0.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Theoretical calculation is used to rationalize the trends observed in measured mobilities with reasonable agreement, except in the case of **TBO**, whose electronic coupling is much larger than its reorganization energy. It is rationalized by the involvement of delocalized polarons, which potentially trap the charges by their lower energy state.

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There are no conflicts of interest to declare

ACKNOWLEDGMENT

Financial support from the Ministry of Science and Technology, Taiwan (Grant Number:101-2113-M-001 -006 -MY3) is gratefully acknowledged.

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Journal of Materials Chemistry C

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A series of non-planar tetrabenzo-fused acenes exhibited a hole mobility from 0.044 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ up to 0.81 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ in their single crystal field-effect transistor.

