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Conveniently Synthesized Butterfly-Shaped Bitriphenylenes and their Application in Solution-Processed Organic Field-Effect Transistor Devices

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Dedication ((optional))

Abstract: Various *π*-extended new bitriphenylene derivatives (both conformationally-free and conformation-locked) have been facile synthesized Scholl successfully via oxidative а cyclodehydrogenation method in good to excellent yields. Their optical properties in solution and film states reveal possibility for selfordering. The molecular packing in solid-state demonstrates favourable π - π stacking as well as weak intermolecular interactions leading to face-to-face or slipped-stack arrangements. Besides, these butterfly-shaped large bitriphenylenes display near-UV absorption, excellent photochemical, thermal, and electrochemical stabilities. The all-organic anneal-free transparent FETs fabricated from solutionprocessable bitriphenylenes showcase significant improvement (ca. 4 orders of magnitude higher) in charge transporting abilities (μ_h : from ca. 10⁻⁷ to 10⁻³ cm²/(Vs)) when compared to model triphenylene. The fabricated FETs unveil excellent air stability (> 1 year under atmospheric conditions) highlighting the utility of these novel linklocked triphenylene skeletons in organic electronics.

Introduction

Solution-processable π -conjugated organic semiconductors (for example: polycyclic aromatic hydrocarbons, PAHs) are of immense interest in recent days, especially, due to their profound application in low-cost, large-area flexible organic electronic

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devices, such as, organic field-effect transistors (OFETs), organic solar cells (OSCs), organic light emitting diodes (OLEDs).^[1] Under this category, soft and self-organizing large and rigid disc-like aromatics^[2] surrounded by long flexible chains have demonstrated high promise due to their inherent capability to (i) columnar behaviour promote packing (columnar mesophases/superstructures) by easily aligning themselves, (ii) thereby favour a large area m-orbital overlap between the adjacent molecules facilitating one dimensional (1D) migration of charge carriers,^[3] (iii) offer solution/melt-processability, and (iv) be able to self-repair defects that act as charge carrier traps. Ultimately, various large polycyclic aromatic cores, such as, hexaperi-hexabenzocoronene, coronene, porphyrin, phthalocyanine, perylenebisimide, etc. have surfaced as high mobility liquid crystal semiconductors in the literature.^[4,5]

In relevance, triphenylene-a relatively small PAH-, despite its great exploration in the field of liquid crystals due to its beneficial 1D columnar packing behaviour, chemical and photochemical stability, tuneable optical, electronic and semiconducting properties,^[2,6,7] possesses high band gap energies ($E_g > 3.7 \text{ eV}$) and is considered a poor (hole) semiconductor.^[8] Consequently, there exists scant reports on the applicability of simple triphenylenes (for example, hexaalkoxytriphenylene HAT, hexaalkylthiotriphenylenes HATT. hexaphenyl/hexatrimethylsilylethynyltriphenylenes PETP/HTMT, hexaphenyltriphenylenes PTP, etc., Figure 1)^[9] or their π extended versions in electronic devices. For example, the average mobilities of solution-processed FET devices fabricated from π -extended hole semiconductors HHBT and HDBT are 1.4 × 10^{-4} and 2.8 × 10^{-5} cm²/(Vs),^[9b,c] respectively (Figure 1). However, the synthesis of HHBT/HDBT involve multiple steps using expensive metal-based cross-coupling reactions, and mobilities of such discotics seem to depend on annealing or substrate temperatures. Such variation in mobility is reasoned to the fluctuation of molecules within the stacks or intrastack dynamism or self-healing behavior. One of the ways to improve mobility in discotic systems is to impose intermolecular order and interaction, within the stacks or between the stacks, creating multiple charge transport pathways (e.g. 1D vs 2D). This requirement could easily be met by connecting the discotics (triphenylenes, C_{3h} symmetric) covalently, locking them to provide a large π -orbital area and peripherally incorporating groups (polar) that induce intermolecular interactions. Thus, we envisaged bitriphenylenes (C_{2v} symmetric, *link-locked*, Figure 2)

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Figure 1. Structures of triphenylenes/ $\pi\mbox{-extended}$ triphenylenes explored in the literature.

as hole-semiconductor candidates for function in FETs. To the best of our knowledge, the candidature of covalently-connected triphenylenes, i.e., bitriphenylenes (Figure 2), has not been explored yet in organic electronics, while twinned triphenylenes linked by a rigid or flexible spacer have been studied only for their LC behavior.^[10]

To perk up the semiconducting nature and to capitalize on the successful 1D self-assembling behaviour of discotic triphenylenes, we designed and synthesized bitriphenylene 1 (triphenylenes are directly-linked via a C-C bond along which free-rotation is possible) and the conformationally-rigid methylene-locked (via two C-C bonds) bitriphenylenes 2-4 (Figure 2). The designed structures are aimed at the following benefits: (i) the planar π extended nature of the methylene-locked bitriphenylenes may enhance π - π stacking and molecular ordering thereby increase transfer integrals, decrease reorganization energies leading to improved charge transport properties, (ii) the incorporation of alkyl (hexyl) chains may facilitate solution-processing of thin-film devices, and (iii) the introduction of substituents of different electronic nature onto the periphery may alter the energy gap, HOMO/LUMO energy levels as well as tune intermolecular interactions favorable for electronic applications. Herein, we have demonstrated that methylene-bridged bitriphenylenes 2-4 reveal improved optical (near-UV absorption, up to 400 nm), thermal (high thermal stability > 340 °C), and electrochemical properties (low E_q , i.e., 2.96–3.25 eV, with HOMOs lying as high as -5.32 eV), when compared to simple triphenylenes or bitriphenylene 1. Powder XRD of spin-coated films or the X-ray crystal structure analyses of 2–4 reveal significant overlap between the π -system. The reported experimental observations are further supported by theoretical calculations. The OFETs fabricated by a low-cost solution-process led to stable devices and reveal improved or

analogous charge transport characteristics (*p*-type, $0.23 \times 10^{-3} \text{ cm}^2/(\text{V.s})$) when compared to other solution-processed systems based on hole-conducting triphenylenes.^[9] Indeed, FETs based on carbon-based large PAHs (*p*-type) are of huge interest at present due to their notable structural stability.^[11]





Figure 2. Construction of bitriphenylenes via a link-lock approach (top), and the novel bitriphenylene (bottom) targets 1–4 for OFET applications.

Results and Discussion

Synthesis and Solubility

The general synthetic approach for the synthesis of bitriphenylenes 1 and conformationally-locked bitriphenylenes 2-4 is shown in Scheme 1. The detailed procedure for the synthesis of bitriphenylene 1 and 3-4 is described in the Supporting Information, pages S45-S50; the synthesis of 2 is reported elsewhere.^[12] We started our synthesis from the readily available biphenylene (free-rotation is possible via C-C bonds connecting the benzene rings), and fluorene (the biphenyl unit is conformationally locked via a methylene bridge through its 2,2'positions arresting free-rotation). Initially, iodination of biphenyl under I2/HIO4 in acidic conditions yielded 76% of 4,4'diiodobiphenyl.^[13a] Dibromination of fluorene using liquid bromine, afforded 2,7-dibromofluorene, in good yield (75%).[13b] The precursor compound 2,7-dibromofluorene was then subjected to dihexylation under phase transfer conditions to yield 2,7-dibromo-9,9-dihexylfluorene in excellent yields.[13c] The hexyl groups were purposefully introduced into the fluorene skeleton to improve the solution-processability of the targets in FETs. The diiodo-(5)/dibromo-(6)-derivatives were then subjected to nickelmediated Kumada-type C-C coupling^[13d] or Pd(0)-mediated twofold Suzuki coupling^[13e-i] (Step 1, Scheme 1) with excess of the 2-biphenylmagnesium corresponding bromide/2biarylpinacolboronate ester (12-13) derivatives to provide compounds 4,4'-bis(biphenyl-2"-yl)biphenyl 8 and 2,7-bis(biaryl-

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Scheme 1. General scheme for the synthesis of bitriphenylenes 1 and conformation-locked bitriphenylenes 2-4. Step 1: 2-bromobiphenyl, Ni(dppp)Cl₂, benzene, 0 C, 1 h, reflux, 3 h, 85% (for 8) or Pd(PPh₃)₄, aq. K₂CO₃, toluene:EtOH (3:1, v/v), 85 °C, 18 h, 50-78% (for 9-11); Step 2: FeCl₃, DCM, 0 °C to rt, 15 min. 85% (for 1) or DDQ/H⁺, DCM, 0 °C to rt, 15-150 min., 60-90% (for 2-4)..

2'-yl)fluorenes 9-10, respectively, in good to moderate yields. In contrast, 2,7-fluorene-bis(boronate)ester 7^[13j] was Suzukicoupled with bromotetramethoxybiphenyl 14 to offer 11. The biphenyl/biaryl units in 8-11 are now appropriately positioned for oxidative Scholl cyclization to provide the desired conformationally-locked π -extended bitriphenylene analogs. Realizing the potential of FeCl₃ in producing the chlorinated side products (especially with 9), we opted for Rathore's mild oxidative cyclization procedure (DDQ/H+, Step 2, Scheme 1) for the synthesis of 9-11 as reported by us earlier.^[14] This method gave us the desired dicyclized products 2-4 in excellent yields, without any side products.^[12] However, synthesis of 1 could be accomplished by both FeCl₃ and DDQ/H⁺ conditions. The oxidative Scholl cyclization method used in the final step for the synthesis of triphenylene derivatives is metal-free, very facile and involves organic oxidants and reagents. All the intermediates and the target bitriphenylenes 1-4 were thoroughly characterized by their melting points, infra-red, ¹H and ¹³C NMR spectroscopy, high resolution mass spectrometry techniques (see Supporting Information, pages S52-S58). All the synthesized compounds 2-4, except 1 (<0.5 mg/mL) possess remarkable solubility in common organic solvents at room temperature; for example: ~140 mg/mL (2), ~150 mg/mL (3) and ~220 mg/mL (4) in chloroform. The attachment of hexyl chains into bitriphenylenes definitely improves the solubility as expected, which may facilitate solution process of FET devices.^[15] Hence, only the methylenebridged bitriphenylenes 2-4 were opted for device studies.

Optical Properties in Solution and Film

The optical properties of 1-4 were examined in dilute chloroform solutions (ca. 1×10^{-5} M) at room temperature (Table 1). The UVvis absorption spectral profiles of 2-4 (Figure 3) display typical vibronic features similar to those observed for rigid coplanar polycyclic aromatic hydrocarbons (PAHs), unlike 1.^[16] All the bitriphenylenes exhibit relatively sharper low-energy absorption band corresponding to π - π * transition in the wavelength range 360-410 nm, besides high-energy absorptions at ca. 285 (not shown in Figure 3) and 335-345 nm. It is important to mention that the expectedly-twisted bitriphenylene 1 (calculated twist angle is ca. 40°, vide-infra), similar to simple triphenylene (λ_{max} in CH₃OH = 247, 310 nm),^[17] possesses an absorption maximum at ca. 320 nm besides a forbidden transition at ca. 370 nm; the latter is found to be prominent in the conformation-locked new C2vsymmetric bitriphenylene systems 2-4.[18] This near-UV absorption probably arises due to the extended π -conjugation (mixing of orbitals) established by the methylene bridge in 2-4, the observation which is in excellent agreement with the near-planar structure (tilt angle, ca. 1.95-3.82°) derived by X-ray structural analysis and DFT calculations (vide-infra). While the long wavelength absorption band for 2 is seen at 373-375 nm, it is slightly (ca. 10 nm) red-shifted to 383-385 nm in cases of 3-4. Such a bathochromic shift in 3-4, upon introduction of electron donating methoxy substituents (mesomeric effect) on to 2 is evident here.[19]

To gain further insights into the structural and opto-electronic properties of the synthesized bitriphenylenes **1-4**, density functional theory (DFT) and time dependent DFT (TD-DFT) calculations (for computational details, see Supporting

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Figure 3. Normalized UV-vis absorption spectra of compounds 1-4 in chloroform solution (ca. 1 \times 10 5 M).

Information, pages S2-S4) were carried out. The simulated optical spectra of the molecules 1–4 in chloroform are depicted in Figure S1 (page S2), and the corresponding molecular orbital contributions along with the transition states and oscillator strengths are presented in Table S1 (page S3). The theoretical results show a similar trend as those of the experiments. The absorption maximum of these bitriphenylenes range between ~280–400 nm. The low energy transitions of each molecule display $\pi \rightarrow \pi^*$ character with major contributions from HOMO \rightarrow LUMO transitions. The molecules 2–4 reveal a redshifted absorption, when compared to 1, suggesting excellent π -conjugation in conformation-locked bitriphenylenes 2-4; the twist angle calculated for 1 is ca. 40° (vide infra) which is similar to biphenyls/2,2'-binaphthyls reported in the literature (Figure S2, page S4).^[20]

As expected, the absorption maximum of bitriphenylenes 1-4 is red-shifted (ca. 4-21 nm) in films when compared to those in solution (Figure S3a,b, page S5). Besides, absorption spectrum of films (spin-coated under optimized conditions), showed a typical broadening with a residual tail-end absorption extending up to ca. 430 nm (Figure S3, page S5).^[21] This feature points to the existence of increased intermolecular π - π stacking interactions between the large *π*-extended, conformationallylocked bitriphenylenes 2-4, and suggests increased planarity of 1 in the film state.^[22] This proposal was further supported by the concentration dependent studies (UV-vis and ¹H NMR spectroscopy) of 2 and 3 in solution (Figures S3-S4, page S5-S6). When the films were annealed at 150 °C, a mild increase in the residual absorption at the tail-end (ca. 390-430 nm) of the absorption spectrum accompanied by a featureless broadening (in the range 320-365 nm) and slight bathochromic shift (ca. 1-5 nm) were noted against as-cast films. Such a characteristic phenomenon is noticed during the annealing of other large PAH films too.^[23] This highlights the effect of annealing in promoting intermolecular interactions, molecular organization and ordering in thin films of 2-4.^[23] This tendency of π -extended bitriphenylenes 2-4 to self-organize is noteworthy, and may be beneficial for solution-processed application in organic electronics. The typical absorption spectral profiles of 2 in solution and as films are displayed in Figure 4 for comparison.



Figure 4. Comparative UV-vis absorption spectra of chloroform solution, ascast film and of film annealed at 150 $^{\circ}$ C, of 2.

Photochemical and Thermal Stabilities

To check the photostability, the films/solutions of **2** were photoirradiated ($\lambda_{exc} = 250/350$ nm) for extended hours (i.e., 36–48 h) under atmospheric conditions. The UV-vis absorption spectrum as well as the ¹H NMR spectrum recorded after photoirradiation revealed no photoreaction/photodecomposition attesting to its excellent photostability (Figure S5, page S7). It should be noted that very popular semiconductors, such as, pentacene, tetracene, and fluorene, are known to undergo photooxidation in air and(or) photodimerization in presence of light limiting their application in electronics.^[24]

In order to gauge the applicability in electronic devices, thermal stabilities of compounds 1-4 were estimated by thermogravimetric (TGA) and differential scanning calorimetric (DSC) analyses under nitrogen gas (N2) atmosphere (Figure 5). All these compounds 1-4 exhibited excellent thermal stabilities (Table 1); thermal decomposition temperatures (T_d at 5% weight loss) were close to or greater than 340 °C. As may be noticed from Table 1, the highest thermal stability is owned by 1 (409 °C). The thermal stabilities are relatively higher in case of 2, when compared to 3 and 4. This may be due to the substituent methoxy groups (as rotors) in 3 and 4. The thermal stability trend follows the order: 3 < 4 < 2 < 1. DSC studies of 1-4 display both the sharp endothermic melting (T_m) and the crystallization transitions (T_c) upon several heating and cooling cycles, respectively (Table 1). On heating, 1 exhibited a reversible endothermic transition at 344 °C with a reversible T_c around 272 °C. The melting transition of compounds 2-4 show the following trend: 3 < 2 < 4. Notably, all of them possessed crystallization temperature supporting their highly crystalline nature. The above results on thermal studies reveal that bitriphenylenes 2-4 are endowed with desired virtues, i.e., high thermal stability and crystallinity, for their exploration in FETs.

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Figure 5. TGA traces of 1-4 (left) and DSC traces of 2-4 (right) under nitrogen gas atmosphere at a heating rate of 20 °C/min and 10 °C/min, respectively.

Electrochemical Properties

In addition, semiconductors must possess appropriate molecular orbital energy levels for efficient charge injection from the metal electrodes. To estimate them, the optical energy gap (E_g) values of conformationally flexible **1** and locked bitriphenylenes **2-4**, were determined from the onset of their absorption spectrum (λ_{onset} , SI, page S9). The E_g values thus estimated for their solutions and films lie in the range 3.09–3.44 eV and 2.96–3.25 eV (Table 1), respectively. The E_g trend observed in both solution and film is very similar, and the E_g values less than 3.4 eV suggest a semiconducting nature for **2-4**. A slight reduction in the energy gap observed, in case of films, may be attributed to the differences in intermolecular interaction or molecular organization (or refractive index).^[25]

The energy gap (E_g) obtained in these novel bitriphenylenes **2-4** are smaller than or comparable to those of twisted **1**, π -expanded fluorenes (E_g of DTF/DSF = ca. 3.6 eV;^[26a] E_g of truxene = ca. 3.1 eV)^[26b] and triphenylene derivatives (for example, E_g of hexamethoxytriphenylene, **HMT** = ca. 3.4 eV)^[9] reported earlier. This indicates the role of methylene-bridge in extending the π -conjugation or reducing the E_g (~0.13–0.20 eV) in these novel

bitriphenylene systems. Interestingly, introduction of electron donating groups alters the E_g to an extent ~0.14–0.16 eV. On comparing 3 and 4 with HMT, one observes a significant reduction in E_{α} (up to 0.39 eV), which can be due to the *link-lock* effect in the former. The electronic effects caused (by π-extension and -OMe substituents) in the HOMO and LUMO energy levels of bitriphenylenes 2-4 were extracted from cyclic voltammetry (CV) experiments (Figure 6). Whereas bitriphenylene 2 displayed one oxidation reversibly, 3 and 4 revealed two reversible oxidations probably due to the presence of electron donating methoxy groups. The HOMO energy levels were calculated from the oxidation peak potentials (E_{ox}) derived from the differential pulse voltammograms (DPV) using the relation $E_{HOMO} = -(E_{ox} - E_{(Fc+/Fc)})$ + 4.8) eV against Fc/Fc⁺ (Figures S6 and S7, page S9). The LUMO energy levels were derived from the optical energy-gap values (E_{a} , solution) and the corresponding HOMO energy levels $(E_{LUMO} = E_{HOMO} + E_{g} \text{ eV}).^{[27]}$ The HOMO/LUMO values thus deduced are provided in Table 1. As may be noted, the HOMO energy levels of 3 and 4 are raised when compared to 2. This may be attributed to the presence of electron donating methoxy groups in the former. In contrast, the HOMO energy level of 2 is slightly increased (ca. 0.08 eV) than that of 1, which in turn is deeper (0.61 eV) than triphenylene HMT, besides lowering of its LUMO energy levels (ca. 0.12 eV).^[9,28] The above result evidently indicates that the extended π -conjugation via C–C link in **1** or the methylenebridge (lock) in 2-4 stabilizes both the HOMO/LUMO energy levels of HMT offering air-stability to bitriphenylenes.[28]

For comparison, the frontier molecular orbitals (FMOs) and energy gaps of **1-4** were calculated using DFT methods, and the results are presented in Table 2. The corresponding electron density maps of bitriphenylenes are shown in Figure 6. The calculated HOMO energy levels of **1-4** are in the range -5.40 to -6.02 eV. In all the cases, the experimental trend is observed. The HOMO energy levels of **3** (-5.47 eV) and **4** (-5.40 eV) are more destabilized than that of **2** (-5.85 eV) which again is more destabilized than **1**. This can be related to the substitution of

Molecule	λ_{max} , nm			$E_{g,d} eV$	E _{ox} /HOMO, ^e	LUMO, ^f	$T_{\rm d}/T_{\rm m}/T_{\rm c},^g$
	Abs (soln) ^a	Abs (film) ^b	Abs (film) ^c	Soln ^a /Film ^c	ev	ev	C
1	324	344, 370	345, 374	3.44/3.25	1.62/-5.84	-2.40	409/344/272
2	321, 342, 357, 375	347, 361, 379	347, 380	3.24/3.12	1.49/-5.76	-2.52	396/287/184
3	327, 346, 364, 385	353, 370, 393	359, 398	3.09/2.98	1.21/-5.48	-2.39	340/262/215
4	337, 362, 370, 383	349, 374, 398	353, 398	3.09/2.96	1.12/-5.40	-2.31	358/294/249
нмт	274 ^{<i>h</i>}	387 ^{<i>h</i>}	387 ^h	3.35/na	-5.23	-1.88	na

^{*a*} in CHCl₃ solutions. ^{*b*} as-cast. ^{*c*} annealed at 150 °C for 20 min. ^{*d*} optical energy gap derived from the onset of absorption. ^{*e*} calculated from cyclic voltammetry using DCM solutions (Bu₄NPF₆ was the supporting electrolyte) against Fc/Fc⁺. ^{*f*} calculated from the optical energy gap and HOMO energy level. ^{*g*} T_d-decomposition temperature at 5% weight loss, T_m-melting temperature, T_c-crystallization temperature. ^{*h*} in DCM solution. na: not available.

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Figure 6. Left: Cyclic voltammogram of **2-4** (1.0 mM) recorded in dichloromethane using tetrabutylammonium hexafluorophosphate as the supporting electrolyte (0.1 M). Right: Ordering of HOMO and LUMO levels of **1-4** and their respective electron density plots at B3PW91/6-31+G** level of theory.

electron donating methoxy groups in **3** and **4** as opposed to **2**, and absence of planarity in **1**. The LUMO energy levels of **1-4** are in the range -1.75 to -1.96 eV. Notably, the HOMO levels of **3** and **4** are destabilized to a greater extent than their corresponding LUMO energy levels. A closer look at the electron density plots of bitriphenylenes **1-4** reveals that the HOMOs are delocalized over the entire molecule while the LUMOs are localized on the fused central six-membered rings (Figure 6). The cyclic voltammetry and DFT results suggest that bitriphenylenes (especially **3** and **4**) described here are electron-rich and can be readily oxidized (*p*type), and their HOMO energy levels can be conveniently finetuned upto ca. -5.4 eV by attachment of –OMe groups. This enables Au (gold) to be used as source-drain electrodes for FET fabrication.

X-ray Crystal Structure Analyses

Investigation of solid-state packing arrangement of organic semiconductors is important as it can be correlated to the charge transport property in films, reasonably. Single crystals of **2-4** suitable for X-ray diffraction studies were grown by slow evaporation of their solutions of chloroform-hexane, chloroform-toluene, etc. The ball-stick model of molecular structures of bitriphenylenes **2-4**, their dimensions and molecular packing

diagrams are shown in Figure 7. As may be seen, all of them are nearly coplanar in nature; deviation from planarity calculated as the dihedral angle between the mean planes of the triphenylenes on either side of the central 5-membered ring varies from 1.95° (2) to 3.82° (3) to 3.01° (4). Interestingly, the central fluorene ring is mildly bent in all the cases (1.94° to 3.11°). The molecular packing diagrams of 2-4 clearly confirm the π - π stacking arrangement between the molecules (Figure 7). What is noteworthy is, the expanded π -system of the discotics (i.e. triphenylenes) present in bitriphenylenes 2-4 ensures strong π - π stacking interactions.^[29] The molecules of 2 (space group = $P2_1/n$, Z = 4; Table S2, pages S11-S12) arrange in a face-to-face manner (along a-axis) with a π - π stacking distance (measured between the mean planes) of 3.563 Å (Figure 7); the long molecular axis is along the crystallographic c-axis. Further, these dimers of 2 are packed in a herringbone fashion, as reported earlier.^[30] Such face-to-face interactions in a 2D π-expanded system and the sandwich herringbone-type arrangement are known to enhance the charge transport characteristics (via edgeface interactions as in pentacene/rubrene/thienoacenes), when compared to linear π -conjugated systems.^[6,30] The molecular packing diagram of 3 (space group = P-1, Z = 2; Table S3, pages S13-S14) exhibits a sandwich brick-laver arrangement with its long molecular axis oriented along the crystallographic b-axis (Figure 7). The π - π stacks of distance ca. 3.586 Å are found along the crystallographic c-axis. In addition, the molecular packing of 3 is benefited by weak C–H···O ($d_{H...O}$ = 2.678 Å and $\theta_{C-H...O}$ = 149.05°) interactions supplied by the -OMe substituents.[31] Theoretically, the observed cofacial lamellar packing is realized as the most ideal arrangement for facilitating intermolecular interactions and maximizing transfer integrals (as in 3) for an efficient 2D network charge transport.^[32] Similarly, the molecule 4 (space group = P-1, Z = 2; Table S4, pages S15-S16) exhibits dimers in a slipped- π -stack arrangement (along *a*-axis).^[30] This displaced arrangement (along the molecular long as well as the short axes, Figure 7) is probably promoted either because the additional methoxy groups (when compared to 3) in 4 occupy the available space in its curved arm-chair region preventing them to stack in a face-to-face manner, or due to the electrostatic repulsions between the cofacial electron-rich π -conjugated

Table 2. DFT calculated FMO energies, energy gaps (<i>E</i> ₉) and hole and electron reorganization energies of 1-4, and transfer integrals of 2-4.								
Molecule	HOMO ^a (eV)	LUMO ^a (eV)	E_{g}^{a} (eV)	$\lambda_{hole}{}^{b}$ (eV)	$\lambda_{\text{electron}^b}$ (eV)	$\Delta E^{b} (eV)$	V _{hole} ^c (meV)	
1	-6.02 (-5.84)	-1.86 (-2.40)	4.16 (3.44)	0.210	0.334	0.124		_
2	-5.85 (-5.76)	-1.96 (-2.52)	3.89 (3.24)	0.165	0.216	0.051	2.60	
3	-5.47 (-5.48)	-1.76 (-2.39)	3.70 (3.09)	0.204	0.246	0.042	42.35	
4	-5.40 (-5.40)	-1.75 (-2.31)	3.65 (3.09)	0.202	0.258	0.056	5.30	

^a FMOs (HOMO and LUMO) and energy gaps (E_g) were calculated in DCM medium with B3PW91/6-31+G^{**} level of theory. The experimental values are given in brackets for comparison. ^b The internal reorganization energies ($\Delta E = \lambda_{electron} - \lambda_{hole}$) were calculated using B3LYP/6-31+G^{**} level of theory. ^c The charge transfer integral values for holes (V_{hole}) were calculated using GGA-PW91 functional along with TZP basis set.

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Figure 7. Molecular structures (left), π - π stacks (middle) and unit-cell packing diagrams of **2-4** describing dimeric herringbone, brick-layer and slipped-stackarrangements (right, top to bottom) viewed along *c*-, *a*-, *c*-axes, respectively.

dimeric stacks. However, the π - π stacking distance in 4 is measured as the shortest, i.e., 3.418 Å. Besides, its molecular packing diagram highlights the presence of weak C-H···O ($d_{H \cdots O}$ = 2.560 Å and θ_{C-H-O} = 139.77°) interactions via a centrosymmetric dimeric motif favouring 2D network.^[31] Here, the molecular long axis is along the crystallographic b-axis, as in 3. A tuneability in the molecular packing arrangement from herringbone to face-to-face to slipped-stack by simple introduction of -OMe substituents on bitriphenylenes is remarkable. Indeed, the C-H···O interactions are popularly used in the design of organic solids for device applications exploiting crystal engineering strategies.^[31,33] The near-planar large molecular structure, short stacking distance, and dimeric face-toface or brick-layer or slipped-stack 2D arrangement of C2vsymmetric bitriphenylenes (as against 1D columnar arrangement of C3-symmetric triphenylenes) are the ideal characteristics desired to activate multiple charge transport pathways (vide infra). comprehend the structure-property Τo relationship of bitriphenylenes, ground state geometry optimization was performed using DFT-based calculations for 1-4 and their optimized geometries are shown in Figure S2, page S4. As expected, 1 shows a highly twisted conformation with a dihedral angle ~40°, whereas 2-4 show high degree of planarity, in agreement with the UV-vis and X-ray studies, due to the conformation rigidification by the methylene bridge. Further, to understand the packing pattern, the π - π stacking of dimers of 2-4 were optimized using DFT. The geometries of these optimized dimers, their stacking distances and binding energies are shown in Figure 8. The calculated π - π stacking distances of 2, 3 and 4 are 3.559, 3.605 and 3.495 Å, respectively. The observed results are in good agreement with the experimental data. It can be seen that the substitution of methoxy groups in 3 increases the stacking distance in the order of 0.05 Å, when compared to 2. Interestingly, the octamethoxy derivative 4 exhibits the lowest π-stacking distance between its monomers due to its slipped-stack arrangement, which is in resemblance with the X-ray analyses. The calculated binding energies of 2, 3 and 4 are -31.82, -39.51 and -53.96 kcal.mol⁻¹, respectively (Figure 8). The above results also illustrate that the incorporation of methoxy groups into large

bitriphenylenes certainly alters the stacking behaviour thereby π -orbital interactions, which consequently may influence molecular ordering and charge transport.



Figure 8. Geometries of optimized dimers of 2-4 and their binding energies at M06L/6-31G** level of theory.

Evaluation of Charge Transport Property by OFET Devices After probing the optical/electrical properties and possible solid-

state arrangements of butterfly-shaped bitriphenylenes 2-4, their charge transport properties were investigated by constructing OFET devices by low-cost solution-process.[34] OFET devices with bottom-gate/bottom-contact configuration were fabricated using patterned gate structure to avoid gate leakage current and parasitic effect that could lead to over-estimation of mobility. Towards application in transparent, flexible electronics and circuits,^[35] polymer dielectric (cross-linked poly(4-vinylphenol), in particular) was adopted as gate insulator. The compatibility of πexpanded semiconductors with the insulator system was tested. Aluminium was deposited and patterned using photolithography on top of cleaned boro-float glass wafer as the gate electrode. Commercially available poly(4-vinylphenol) (PVP) was crosslinked using copolymer poly(melamine-co-formaldehyde)methylated, followed by spin-coating on the patterned gate metal using our optimized recipe to provide pin-hole-free gate dielectric of thickness about 500 nm. Photolithographically-patterned gold electrodes atop cross-linked PVP layer were used as drain and source. Finally, the organic semiconductor (OSC) layer was spincoated (2-4, ca. 5.0 mg/mL, chloroform solutions) on the patterned Au (source-drain) substrates (for details, see Figure 9 and Supporting Information, pages S17-S19). Other than the ascast devices, few devices underwent a post thermal annealing at 150 °C for 20 min. The entire fabrication was carried out inside a glove-box except sample cleaning and lithography processes. Both the as-cast and annealed FETs were characterized inside a probe station under vacuum using parameter analyser. Thus, 20 FET devices of molecule 4, and 5 devices of each of molecule 2 and **3** were fabricated, for calculating the mobility (μ) and I_{on}/I_{off} ratio. The extracted parameters of the best devices of 2-4 and model compound HMT are compared in Table 3 (for average values, see: Figure S13, page S19). The output and transfer characteristics of the OFET using semiconductor 4 are shown in Figure 9.

The π -rich bitriphenylenes **2-4** exhibited a typical *p*-type accumulation characteristics, as observed by CV studies and theoretical calculations. The as-cast films of **4** (purified once by column-chromatography) showed the highest hole mobility (μ) of 0.56 × 10⁻⁴ cm²/(Vs) with a l_{on}/l_{off} ratio greater than 10⁴ at room temperature, while compounds **2**, **3** and **4** demonstrated hole mobilities of 0.71 × 10⁻⁶, 0.26 × 10⁻⁴ cm²/(Vs) and 0.55 × 10⁻⁴ cm²/(Vs), respectively, after anneal treatment. Annealing certainly

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has improved the FET performance of **2** and **3**. It is to be noted that there is no appreciable change in the performance of the device of **4** after annealing, which also reveals that the compound may be quite ordered even as-cast film. This result corroborates the effect of annealing (UV studies/AFM) in thin films. The



Figure 9. OFET device characteristics of **4**. (a) General device configuration, (b) Photograph showing array of fabricated devices on transparent glass substrate and polymer dielectric, (c) Output ($V_{DS} = -100 \text{ V}$) and (d) transfer characteristics of devices of singly purified **4** (L = 10 µm, W = 1000 µm) after annealing.

Table 3. OFET	device	characteristics	of	2–4	and	the	model	compound
HMT. ^a								10-

Molecule	At r.t. (as-c	ast film)	At 150 °C (annealed film)		
	μ (cm ² /Vs)	Ion/Ioff	μ (cm²/Vs)	Ion/Ioff	
2	nr	nr	0.71 × 10 ⁻⁶	10 ³	
3	0.78 × 10 ⁻⁶	10 ²	0.26 × 10 ⁻⁴	10 ⁴	
4	0.56 × 10 ⁻⁴	>104	0.55 × 10⁻⁴	>10 ⁴	
			0.25 × 10 ^{-4 b}	>10 ⁴ ^b	
	0.89 × 10 ⁻⁴	>10 ⁵	0.23 × 10 ^{-3 c}	>10 ⁴ ^c	
НМТ	nr	nr	0.19 × 10 ⁻⁷	27	

^a all the parameters are for devices with $L = 10 \ \mu m$, $W = 1000 \ \mu m$. ^b after one year under optimal conditions. ^c after double purification by column chromatography. r.t.: room temperature (25 °C). nr: no response.

improved hole mobilities in the case of **4** (as-cast/annealed films) can be readily understood from (i) the alignment of its HOMO (-5.27 eV) close to the Fermi level of Au, (ii) slipped- π -stack arrangement in crystal packing diagrams, and (iii) continuous crystalline morphology and uniformity of their thin films (as confirmed by AFM, vide infra). The above result of **4** coincides with the observation from X-ray structural analyses, binding energy calculations and thin-film microstructural characterization studies (vide infra). Surprisingly, a doubly-purified (columnchromatography run twice) sample of 4, resulted in an appreciable mobility of 0.23 × 10^{-3} cm²/Vs with I_{on}/I_{off} ratio more than 10^{5} (i.e., 4-fold enhancement in mobility and one-order of magnitude higher I_{on}/I_{off} ratio as compared to that of a singly purified material or 2-fold improvement in mobility when compared to that of its ascast film) (Figure S11, page S18). Moreover, the better performance of FET devices of 3 and 4 when compared to 2 may be attributed to the role of -OMe groups in improving the HOMO and probably the molecular arrangement favourable for charge transport. It is important to state that the OFET device fabricated for the model compound HMT under the identical condition revealed a hole mobility of only $0.19 \times 10^{-7} \text{ cm}^2/(\text{Vs})$, which is three to four orders of magnitude lower than that observed for 3 and 4. Such an improved hole-transport characteristics of bitriphenylenes 3 and 4 are essentially attributed to their large, planar, extended π -conjugation, favourable π - π stacking interactions, and apt HOMO energy levels. It is remarkable that the un-encapsulated devices of 3 and 4 reveal nearly unaltered performance (reduction of mobility only by half) even after keeping the device under exposure to atmosphere for almost one year, as shown in Figure S12, page S18. Some of the salient features of the devices that project material 4 as a promising candidate are: (i) statistical observation of mobility as a function of channel lengths reveals that the change in average mobility of best-toworst device is within 15% (Figure S13, page S19), (ii) excellent stability under atmospheric condition was achieved, (iii) almost 100% yield (ratio of number of fabricated devices to the working devices) with reasonably small tolerance in mobility from device to device and batch to batch was observed, (iv) untreated polymer dielectric was used as insulator, which is compatible to flexible electronics, unlike SiO₂, and (iv) I_{or}/I_{off} ratio more than 10⁴ is good enough for use in analog-circuit applications. These aspects highlight the electronically-perturbed twinned-triphenylenes 2-4 (as against twisted 1 or discotic triphenylenes) as potential organic semiconductors, and the fabrication method adapted herein showcase the realization of low-cost flexible electronics possible with these sytems. It is to be kept in mind that not only the molecular property, but also several factors, such as, crystallinity, molecular orientation, uniformity and connectivity between the crystalline grains in thin films, device conditions and configuration, etc., are known to influence the overall device performance.

Thin-film Microstructural Characterization

To understand the performance results of OFETs, out-of-plane Xray diffraction measurements were conducted on spin-coated thin-films (device conditions) of 2-4 at room temperature and after annealing at 150 °C. The X-ray diffractograms (XRD, Figure 10) obtained for the room-temperature as-cast films of 2-4 exhibited a broad and less intense peak between $2\theta = 18$ and 38° ; no sharp features were observed between $2\theta = 4$ and 50° pointing to a poor molecular ordering/crystallinity (Figure S14, page S20). The above observation thus corroborates the no or poor performance of the as-cast devices of 2 or 3, respectively. On the other hand, annealed films (Figure 10) exhibited sharp and strong peaks at 2θ = 6.62/6.38,7.72/6.97° besides a broad peak with maximum intensity at 20 around 24.31/24.62/24.29 for 2/3/4, respectively. This definitely suggests an improved crystallinity of the films upon annealing (AFM studies, vide-infra), probably due to better molecular ordering. Therefore, it is no surprise that annealed

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devices of **2-3** performed better than the as-cast devices. It appears that the as-cast or annealed films of **4** display similar crystalline behaviour leading to comparable FET performance. The XRD pattern of the annealed thin films of **2-4**, both at lower and higher theta values, can be matched with the simulated



Figure 10. Out-of-plane XRD of the thermally annealed (150 °C) films of 2-4.

powder pattern of the bulk single crystals (Figure S14, page S20). Thus, upon comparison one may assign the broad peak observed around $2\theta = 24.3$ to 24.6° (i.e., d = 3.61-3.66 Å), in both the before- and after-annealed films of **2-4**, to the distance between the molecules that are involved in π - π stacking interaction. These d values are very much close to the π - π stacking distance calculated from the X-ray crystal structures and the calculated geometry-optimized structures. Similarly, the sharp signal(s) at lower theta values (corresponding to d = 11.45-13.8 Å), in case of annealed films, may suggest a tilted edge-on (vertical/horizontal) arrangement of molecules possible on the substrate surface, retaining π - π stacking (for more discussion, see Supporting Information, page S21).^[36]

Another important factor that usually affects the charge transport characteristics is the morphology of thin films. Hence, to understand the morphological influence in device performance thin film morphologies of the OFET devices of 2-4 were probed by tapping-mode atomic force microscopy (AFM, Figure 11). The AFM images obtained for the annealed thin films of devices 2 and 3 exhibited discontinuous larger grain sizes (ca. 50-69 nm) when compared to their continuous film morphology (ca. 5-10 nm) at room temperature. Generally, thin films of larger grain sizes contribute to increased carrier mobility, and greater discontinuity leads to poorer results. Clearly, this morphological behaviour falls in line with the observed device results of 2 and 3. Indeed, the mobilities as well as the I_{on}/I_{off} ratios are observed to be higher in the case of annealed devices of 2 and 3. In contrast, the FET device of annealed thin films of 4 under AFM revealed only minor differences in its morphology, as noticed in XRD. While films of 4 in both the conditions showcase uniform, continuous and crystalline morphology, the annealed ones appear to have slightly larger (ca. 12-19 nm) grain sizes than that in non-annealed films. This supports the observation of near identical carrier mobility values as well as high Ion/Ioff ratios for the FET devices of 4 under both annealed and non-annealed conditions. It is surprising to note that a minor variation in substitution leads to substantially different morphologies and device performances.



Figure 11. AFM height images of thin films of OFET devices of 2-4 (left to right). Top row: as-cast at room temperature; bottom row: annealed at 150 $^{\circ}$ C.

Reorganization Energies and Transfer Integrals

Further, to understand the carrier transport mechanism in bitriphenylenes 1-4, the internal reorganization energies (λ_{hole} for holes and $\lambda_{\text{electron}}$ for electrons) and their energy differences (ΔE) were calculated using DFT (Supporting Information, pages S22-S23). The results are displayed in Table 2. The λ_{hole} values of 1-4 range between 0.163–0.210 eV and the $\lambda_{electron}$ values range between 0.212–0.334 eV. The fact that λ_{hole} values are lower than $\lambda_{\text{electron}}$ values (shallow LUMO levels) suggests faster hole transportation character.^[37] This is in good alignment with the FET device results which reveal p-type transport characteristics. Interestingly, the energy difference (ΔE) between hole and electron reorganization values of the conformation-locked bitriphenylenes 2-4 are lower (0.05 eV) than the twisted bitriphenylene 1 (0.124 eV). This result reiterates that the structural modification by methylene-bridge provides large extended π -conjugation and improves charge transport characteristics in 2-4, as observed by experiments.

Intermolecular electronic coupling (V_{hole}) has also been computed for bitriphenylenes 2-4. V_{hole} values for different charge transport pathways (Figure S15, page S24) were calculated using the X-ray structural data, and the results are consolidated in Table 4. From the crystal packing of 2, three different charge transport pathways, ie., face-to-face, edge-to-edge and face-to-edge orientations of molecular dimers were considered. The V_{hole} of 2 in the face-toface direction was calculated to be 2.60 meV, which is lower than the values of 3 and 4. Also, for the edge-to-edge and face-to-edge direction of 2, the transfer integrals were calculated as 1.36 and 4.31 meV, respectively. These results indicate that in 2, the charge transport occurs mainly along the face-to-edge direction of the dimers, which is in line with its XRD and discouraging FET results. For bitriphenylenes 3 and 4, due to their planar π - π stacking arrangements in the crystal lattice, only two pathways were evaluated, i.e, face-to-face and edge-to-edge orientations. In the case of 3, the V_{hole} values along the face-to-face and edgeto-edge directions were 42.35 and 2.31 meV, respectively, which are the highest among the three bitriphenylenes considered. This is in contrary to the device measurements where the as-cast 4 exhibits enhanced mobility in comparison to 3. The primary

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charge transport pathway in 3 is along the face-to-face direction. For 4, the V_{hole} values for the above two pathways were 5.30 and 0.68 meV, respectively, with face-to-face pathway having higher probability of charge transport. The reason for higher electronic coupling values for 3 than 4 may be due to the slipped-stack packing nature of 4 which minimizes the HOMO overlap between the dimers. However, we believe other factors/parameters that control the morphology of thin-film in FET devices may also play significant roles in the efficient charge transport of 4. As proposed by Marcus theory, large transfer integrals and small reorganization energies are expected to lead to high mobility.^[38,39] One must also keep in mind that transfer integrals are very sensitive to the relative positions of the neighboring molecules. That is, the intermolecular distance, shifting or tilting of the molecules in films impact carrier transport considerably. Hence, accurate theoretical predictions of charge transport properties of organic semiconductors in the film-state remain quite challenging.

Table 4. Charge transfer integrals (V_{hole}) for the molecular dimers 2-4 in different orientations obtained from X-ray crystal structure.

Molecule	Charge-transfer integrals (V _{hole}) in meV						
	Face-to-face	Edge-to-edge	Face-to-edge				
2	2.60	1.36	4.31				
3	42.35	2.31	- /				
4	5.30	0.68	- /				

Otherwise, the trends seen here with the theoretical results are comparable with the OFET device mobility measurements. It is obvious that further optimization on this skeleton and the device conditions may enroute to stable, efficient solution-processable bitriphenylenes for organic electronics. This aspect of research is presently ongoing in our laboratory.

Conclusions

The methylene-bridged conformationally-free and conformationally-rigid bitriphenylenes are synthesized using a facile and efficient Scholl oxidative cyclodehydrogenation strategy. Methylene-bridged bitriphenylenes are nearly planar, and their optical characteristics reveal similarity to that of a typical PAH system. Planarization via methylene-bridge has led to large extended π-conjugation, lowering of HOMO/LUMO energy levels and considerable reduction in optical band gap. Incorporation of electron donating substituents raises the HOMO energy levels considerably. The films of bitriphenylenes reveal excellent thermal and photochemical stabilities and tendency for molecular organization. Their solid-state structures display substituentdependent dimeric face-to-face or slipped-stack or herringbone 2D arrangement indicating a promise for charge transport behaviour. They possess good solubility in common organic solvents, facilitating low-cost solution-process fabrication of transparent organic FET devices. The average mobilities of FETs achieved from bitriphenylenes can be as high as ca. 10⁻³ cm²/(Vs) with appreciable I_{on}/I_{off} ratios (greater than 10⁵). Valuably, these FET devices reveal excellent air-stability for more than a year without much performance deterioration. Thin-film microstructural characterization studies support that the films of annealed devices are crystalline when compared to the as-cast devices. The theoretical calculations reiterate that these bitriphenylenes can be potential candidates for OFET applications. From the point of view of advantages associated with discotic small molecules such as triphenylenes, these large π -extended butterfly-shaped bitriphenylenes can be excellent candidates for cost-efficient, stable, light-weight, solution-processable and plastic/transparent electronic devices and circuits.

Experimental Section

Materials. All the reagents and solvents described in the manuscript were of high purity (Analytical Grade) and were purchased from commercial sources. They were used as received without further purification unless mentioned. The key starting materials, 4,4'-diiodobiphenyl (5),^[13a] 2,7-dibromofluorene,^[13b] 9,9-dihexyl-2,7-dibromofluorene 6,^[13c] 2-bromo-3',5-dimethoxy-1,1'-biphenyl,^[40] 2-bromo-3',4,4',5-tetramethoxy-1,1'-biphenyl (14),^[21] 2,2'(9,9'-dihexyl-9*H*-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7),^[13i] 4,4'-bis(biphenyl)biphenyl (8),^[13d] 9,9-dihexyl-2,7-bis(biphenyl-2'-yl)fluorene 9^[12] and 2,^[12] were synthesized according to the literature reported procedures and the spectra were verified. The complete experimental procedures including general aspects, analytical and characterization data of the compounds 1, 3, 4, 10, 11 and 13, their spectral traces are provided in the supporting information.

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