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Two-dimensional oligoarylenes: synthesis and structure–properties relationships

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Abstract—A novel series of two-dimensional π -conjugated oligoarylenes has been synthesized by a divergent approach using Pd-catalysed Suzuki cross-coupling of tetraiodophenylbenzene and arylboronic acid as a key step. It has been shown that the 'X-branched' structure can provide a useful platform to construct amorphous molecular materials as it can enhance the morphological and thermal stability as well as to facilitate solubility and processibility of a material when compared to those of the corresponding linear oligomers. The diphenylamino end-capped two-dimensional oligoarylenes were found useful as a hole transporting/emitting layer for light emitting applications. © 2005 Elsevier Ltd. All rights reserved.

1. Introduction

Conjugated molecular materials¹ such as low molar mass molecules and oligomers have continuously drawn considerable attentions for their potential applications in nextgeneration electronic and opto-electronic devices such as organic light-emitting diodes (OLEDs)² and field effect transistors³ as well as in the emerging photonic technologies such as plastic laser⁴ and three-dimensional optical storage⁵ in the past few years. Tremendous progress has already been made in understanding and optimising the electronic and optical properties of linear π -conjugated molecules or oligomers.⁶ Recently, there is a great interest to increase the structural or spatial dimensions of π -conjugated molecules in order to tune and acquire more favourable physical i.e. morphological and functional properties of a material. For instance, various novel structures of π -conjugated molecules such as star-burst molecules,⁸ tetrahedral-arranged chromophores,⁹ spiro-linked oligomers¹⁰ and dendritic macromolecules¹¹ have been designed and synthesized in order to prevent molecular aggregation and facilitate amorphous glass formation of electroluminescent materials, which would enhance the fluorescence efficiency and stability of OLEDs as well as induce the formation of morphologically stable glassy states of

photonic molecular materials, which could prevent light scattering caused by grain boundaries in optical waveguides. On the other hand, we have shown that acentrically oriented donor-acceptor oligophenylenes built onto the calix[4]arene framework exhibits fluorescence enhancement.¹² Over the last few years, we have been investigating the structural factors that would enhance the technologically useful functional and material properties of oligomers¹³ and macromolecules¹⁴ as they are essential towards a rational design and an optimization of functional organic and polymeric materials. Moving along the same direction, we report herein a facile synthesis and structure-properties of a novel series of two-dimensional π -conjugated oligoarylenes as morphologically stable amorphous molecular materials based on the 'X-branched' structure in which π -conjugated arylene moieties extend around 1,2,4,5-positions of an aromatic core, 4-9. Their optical, electronic and thermal properties were characterized and compared with the corresponding linear oligomer, 4'-9'. Furthermore, the electroluminescent properties of 5- and 9-based OLEDs were investigated. The use of tetra-substituted benzene as a platform for the construction of two-dimensional π -conjugated systems has been reported; however, most of the systems employed ethynyl linkages between the benzene core and the conjugated arms.¹⁵

2. Results and discussion

We found that palladium catalysed Suzuki cross coupling

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Scheme 1. Synthesis of two-dimensional oligoarylenes, 4–9. Reagents and conditions: (i) Ph–B–(OH)₂, 5 mol% Pd(OAc)₂–2P(o-tol)₃, K₂CO₃, toluene–methanol, 75 °C, overnight; (ii) I₂, HIO₄, H₂SO₄, HOAc, CCI₄, 80 °C, 6 h; (iii) Ar–B–(OH)₂, 5 mol% Pd(OAc)₂–2P(o-tol)₃, K₂CO₃, toluene–methanol, 75 °C, 6–12 h.

was particularly versatile for the facile divergent synthesis of two-dimensional π -conjugated oligoarylenes and their linear counterparts. The general scheme for the syntheses of two-dimensional oligoarylenes, **4–9** is outlined in Scheme 1. Cross coupling of 1,2,4,5-tetrabromobenzene, 1 and phenylboronic acid in the presence of catalytic Pd(OAc)₂: 2 $P(o-tol)_3$ complex afforded tetraphenylbenzene, 2 in excellent yields. Iodination of 2 using HIO_4/I_2 also gave tetraiodophenylbenzene, 3 in excellent yields. Cross coupling of 3 and the corresponding arylboronic acid, which was generally prepared by lithium-bromide exchange of the aryl bromide at -78 °C followed by the reaction with trimethyl borate at room temperature and subsequently acid hydrolysis, afforded the desired twodimensional oligophenylenes, 4-8 in good to excellent yields. It is worth mentioning that direct cross coupling of 1 with the corresponding biphenylboronic acids afforded either two-dimensional oligophenylene in a low yield (i.e., 4 in 42% yield) or no desired product (i.e., 5). This is likely due to the steric crowdedness imposed by the proximate assembled biphenyl units. Nevertheless, cross coupling of 1 and 9,9-bis(n-butyl)-2-diphenylamino-7fluorenylboronic acid afforded **9** under typical conditions in a good yield (77%). Using the same divergent approach, the corresponding linear oligomers, 4'-9' were also synthesized as shown in Scheme 2. All the new twodimensional oligoarylenes were fully characterized by ¹H NMR, ¹³C NMR, MS, and elemental analyses or HRMS and found to be in good agreement with the expected structures.

In view of electronic absorption spectra, the absorption bands/maxima of the two-dimensional oligoarylenes are generally structureless and blue shifted (<12 nm) relative to the corresponding linear oligomer. (Fig. 1) This indicates that the two-dimensional oligoarylenes are less planar than the linear oligomers in their electronic ground state.¹⁶ In contrast to the linear analogues, the fluorescence spectra of the two-dimensional oligoarylenes are also less structured but slightly red shifted (0–16 nm) indicating that the non-planarity does not improve in a great extent even in the excited state.¹³ As found from the PM3-optimized geometry of two-dimensional oligoarylenes¹⁷ that the severe distortion from planarity arises from the proximate extended π -conjugated aryl arms around the central aromatic core



Scheme 2. Synthesis of linear oligoarylenes, 4'-9'. Reagents and conditions: (i) Ph–B–(OH)₂, 5 mol% Pd(OAc)₂–2P(o-tol)₃, K₂CO₃, toluene–methanol, 75 °C, overnight; (ii) I₂, HIO₄, H₂SO₄, HOAc, CCl₄, 80 °C, 6 h; (iii) Ar–B–(OH)₂, 5 mol% Pd(OAc)₂–2P(o-tol)₃, K₂CO₃, toluene–methanol, 75 °C, 6–12 h.

and the torsion angles between the aryl arm and the aromatic core is ~80° (Fig. 2). Such a twisting from planarity in both ground- and excited-states leads to a decrease in the fluorescence quantum yields of these two-dimensional π -conjugated molecules (41–90%) as compared to those of the corresponding linear counterparts (63–99%). On the other hand, the fluorescence lifetimes of the two-dimensional oligoarylenes and their corresponding linear oligomers are very similar which are in the nanosecond timescale (Table 1) indicating that emission comes from the singlet excited states.

The redox properties of these oligoarylenes were studied by cyclic voltametry, which was carried out in a three-electrode cell set-up with 0.1 M of Bu₄NPF₄ as a supporting electrolyte in CH₂Cl₂. All the potentials reported are referenced to Fc/Fc⁺ standard and the results are tabulated in Table 1. The diphenylamino endcapped two-dimensional oligoarylenes 5 and 9, exhibit a reversible four-electron anodic redox couples with $E_{1/2}=0.45$ and 0.32 V, respectively corresponding to the arylamino oxidation (Fig. 3); on the other hand; other oligoarylenes exhibit an irreversible oxidation at comparatively high potentials (0.84-1.46 V), corresponding to the generation of radical cation on the oligoarylenes. No reduction peak was observed for all the two-dimensional oligoarylenes in the CV under the same experimental conditions. In spite of the severe twisting around the core, the two-dimensional oligoarylenes exhibit relatively smaller oxidation potential than their linear analogous (Table 1), consistent with the fluorescence results, suggesting a slight improvement in π -electron delocalization in this two-dimensional π -conjugated structure. The superior solubility in common organic solvents of the two-dimensional oligoarylenes is prominent when compared with those of the linear analogues. For instance, the solubility of the linear oligomer 4' is so low that the CV measurement is not possible.

The thermal property and the morphological stability of these oligoarylenes were investigated by TGA and DSC analyses, respectively. In general, the two-dimensional oligoarylenes exhibit a higher thermal stability and most of the two-dimensional oligoarylenes also exhibit a high glass transition, T_g when compared with those of the linear counterparts. This suggests that the non-planar conformation of this branched structure can be used to induce or further stabilize morphologically stable glass formation (Table 1).

To investigate their electroluminescent properties, multilayer OLEDs using the newly synthesized two-dimensional oligoarylenes bearing diphenylamino end-caps as a hole transporting/emitting layer were fabricated with a structure of ITO/two-dimensional oligoarylenes (40 nm)/PBD (40 nm)/LiF (1 nm)/Al (150 nm). The electroluminescence (EL) spectra of **5**-based devices exhibit a peak maximum at 429 nm with a narrow bandwidth and slightly blue-shifted relative to those of the linear counterparts (Fig. 4); however,



Figure 1. (a) Absorption and (b) emission spectra of two-dimensional oligoarylenes, 4–9 and linear oligoarylenes 4'-9' measured in CHCl₃.

maximum luminance and device efficiency were found to be lower than those of the linear analogous based OLEDs.¹⁸ On the other hand, although the EL spectrum of 9-based device, emitting at 550 nm, does not vary with the bias voltage, its emission maximum is ~40 nm red-shifted relative to the broad solid-state PL spectrum. Such a red shift may be due to the aggregation formation leading to the low energy trapping sites.¹⁹ To overcome the drawback, bulky or spiro-linked substituents could be introduced at the 9-position of fluorene units to suppress the aggregation formation⁸ or **9** could be used as a dopant emitter dispersing in a host matrix.^{2c} Despite such a simple two-layer structure, the luminance efficiency can reach up to 2.8 cd/A with a maximum brightness of 1700 cd/m² (Fig. 5).

3. Conclusions

In summary, a new class of two-dimensional π -conjugated oligoarylenes was first prepared and investigated. Their



4'-SCH3

Table 1. Summaries of	physical	measurements of two-dimensiona	l oligoarylenes 4-	-9 and their linear analogous $4'$ -	-9′

					-			
	$\lambda_{\max}^{\text{abs a}/\text{nm}}$ ($\varepsilon_{\max} 10^4/\text{M}^{-1} \text{ cm}^{-1}$)	λ_{\max}^{em} ^{a,b} /nm	${\Phi_{\mathrm{FL}}}^{\mathrm{a,c}}$	$ au^{ m a,d}/ m ns$	Oxid $E_{1/2}^{e}/V$	$T_{\rm g}^{\rm f}$ /°C	$T_{\rm m}^{\rm f}$ /°C	$T_{\rm dec}{}^{\rm g}/{}^{\circ}{\rm C}$
4	309 (11.8)	404	0.70	1.38	0.93(i)	178	280	394
5	349 (12.2)	433	0.48	1.34	0.45	177	301	589
6	301 (6.90)	392	0.65	1.47	1.46(i)	131	286	581
7	388 (0.38)	425	0.90	3.05	0.84(i)	No	352	571
8	302 (0.47)	394	0.47	1.36	1.20(i)	No	414	607
9	371 (13.7)	435	0.41	1.44	0.32	135	No	474
4′	319 (6.10)	384, 398	0.77	1.07	(nd)	No	187	330
5′	358 (6.38)	433	0.84	1.06	0.47	115	191	560
6′	313 (5.07)	377, 386	0.82	0.75	1.60(i)	No	234	560
7′	388 (0.22)	424	0.95	3.04	0.87(i)	No	393	542
8 ′	313 (0.58)	378	0.63	2.44	1.25(i)	No	341	487
9′	381 (8.25)	433	0.99	1.06	0.36	101	254	449

^a Measured in CHCl₃.

^b Excited at the absorption maxima.

^c Using 9,10-diphenylanthrancene ($\Phi_{360}=0.9$) as a standard.

^d Using nitrogen laser as excitation source.

^e $E_{1/2}$ versus Fc⁺/Fc estimated by CV method using platinum disc electrode as a working electrode, platinum wire as a counter electrode, and SCE as a reference electrode with an agar salt bridge connecting to the oligomer solution and all the potentials were calibrated with ferrocene, $E_{1/2}$ (Fc/Fc⁺)=0.45 V versus SCE. (i) denotes irreversible reaction and (nd) denotes not determined due to highly insoluble.

^f Determined by differential scanning calorimeter from re-melt after cooling with a heating rate of 10 °C/min under N₂.

^g Determined by thermal gravimetric analyser with a heating rate of 10 °C/min under N₂.



Figure 3. Cyclic voltammograms of 9 and 9'.

optical, electrochemical and thermal properties have been characterized and compared with those of the corresponding linear oligomers. According to the PM3 semi-empirical calculations, the twisting of the extended arylenes around the central aromatic core in the optimised geometry is substantial. However, the 'X-branched' structure can still provide improvement in π -electron delocalisation leading to slightly red-shift of emission spectra and lowering of the first oxidation potential. In addition, these two-dimensional oligoarylenes show enhancing morphological ($T_g = 131$ -178 °C) and thermal ($T_{dec} = 394-607$ °C) stabilities as well as superior solubility and processibility as compared to those of the linear counterparts. The potential use of the diphenylamino end-capped two-dimensional oligoarylenes as a hole transporting/emitting layer for OLEDs was explored and showed that OLEDs fabricated by these twodimensional luminophores exhibit a luminance efficiency up to 2.8 cd/A and a maximum brightness of 1700 cd/m^2 .



Figure 4. (a) Luminance-voltage-efficiency plot of 5-based OLED device. (b) EL spectra of 5-based OLEDs.



Figure 5. (a) Luminance-voltage-efficiency plot of 9-based OLED device. (b) EL and PL spectra of 9-based OLEDs.

4. Experimental

4.1. General

All the solvents were dried by the standard methods wherever needed. Thermal stabilities were determined by thermal gravimetric analyser with a heating rate of 10 °C/min under N2. The glass transitions and melting transitions were extracted from the second run DSC traces which were determined by differential scanning calorimeter with a heating rate of 10 °C/min under N₂. All the physical measurements were performed in CHCl3 including electronic absorption (UV-vis) and fluorescence spectra. The fluorescence quantum yields in chloroform were determined by dilution method using 9,10-diphenylanthrancene (λ_{exc} = 360 nm, $\Phi = 0.9$) as a standard. The fluorescence decay curves were recorded at room temperature using nitrogen laser as excitation. The lifetimes were estimated from the measured fluorescence decay using iterative fitting procedure. $E_{1/2}$ versus Fc⁺/Fc was estimated by cyclic voltammetric method using platinum disc electrode as a working electrode, platinum wire as a counter electrode, and SCE as a reference electrode with an agar salt bridge connecting to the oligomer solution dissolved in CH₂Cl₂ using 0.1 M of Bu₄NPF₆ as a supporting electrolyte with a scan rate of 100 mV/s and all the potentials were calibrated with ferrocene, $(E_{1/2}(Fc/Fc^+)=0.45 \text{ V vs SCE})$ as an external standard. The procedures for multi-layer OLED device fabrication reported previously were followed.^{11a} The device structures for 5- and 9-based OLED are ITO/5 or 7 (40 nm)/PBD (40 nm)/LiF (1 nm)/Al (150 nm).

4.1.1. 1,2,4,5-Tetraphenylbenzene 2. A mixture of 1,2,4,5-tetrabromobenzene, **1** (787 mg, 2 mmol), palladium (II) acetate (22 mg, 0.1 mmol), tri(*o*-tolyl)phosphine (61 mg, 0.2 mmol), phenylboronic acid (1.46 g, 12 mmol), toluene (30 mL), methanol (10 mL), and 2 M K₂CO₃ (8 mL) was heated at 75 °C for overnight under a nitrogen atmosphere while maintaining with good stirring. After the reaction mixture was cooled to room temperature, it was poured into water and extracted with dichloromethane (3×50 mL). The combined organic layer was dried with anhydrous Na₂SO₄ and evaporated to dryness. The crude product was further purified by silica gel column chromatography using petroleum ether–dichloromethane as eluent affording the

title compound as a white solid of 94% yield. ¹H NMR (400 MHz, CDCl₃, δ) 7.55 (s, 2H), 7.24 (s, 20H). ¹³C NMR (100 MHz, CDCl₃, δ) 140.9, 139.6, 133.0, 129.9, 128.0, 126.6. MS (FAB) *m*/*z* 382.4 (M⁺). HRMS (ESI-TOF) calcd for C₃₀H₂₂Na 405.1619, found 405.1637 (M⁺ + Na).

4.1.2. 1,2,4,5-Tetrakis(p-iodophenyl)benzene 3. A mixture of 1,2,4,5-tetraphenylbenzene, 2 (601 mg, 1.57 mmol), acetic acid (20 mL), water (1 mL), concentrated sulfuric acid (1 mL), iodine (957 mg, 3.77 mmol), iodic acid (859 mg, 3.77 mmol), and carbon tetrachloride (5 mL) was heated at 80 °C for 4 h with good magnetic stirring. After the product slurry was cooled to room temperature, it was poured into water and extracted with dichloromethane $(3 \times 50 \text{ mL})$. The combined dark purple organic layer was decolourised with sodium sulfite, washed with water, dried with anhydrous Na₂SO₄, filtered and evaporated to dryness. Purification of the crude product by recrystallization in a mixture solvent of chloroform/ethanol (v/v=4:1) afforded the title compound as a colorless crystal in 98% yield. ¹H NMR (400 MHz, CDCl₃, δ) 7.58 (d, J = 8.40 Hz, 8H), 7.38 (s, 2H), 6.90 (d, J=8.40 Hz, 8H). ¹³C NMR (100 MHz, CDCl₃, *b*) 139.7, 138.8, 137.4, 132.7, 131.6, 93.0. MS (FAB) m/z 886.1 (M⁺). HRMS (MALDI-TOF) calcd for $C_{30}H_{18}I_4$ 885.7587, found 885.7558 (M⁺).

4.1.3. 1.2.4.5-Tetrakis[4'-(1-hexylsulfanyl)biphenyl-4yl]benzene 4. A mixture of 1,2,4,5-tetrakis(p-iodophenyl)benzene, 3 (443 mg, 0.5 mmol), palladium (II) acetate 0.1 mmol), tri(o-tolyl)phosphine (61 mg, (22 mg, 0.2 mmol), toluene (40 mL), methanol (20 mL), 2 M K_2CO_3 (6 mL), 4-(*n*-hexylsulfanyl)phenylboronic acid (740 mg, 3 mmol) was heated at 75 °C for overnight under a nitrogen atmosphere with good stirring. After the reaction mixture was cooled to room temperature, it was poured into water and extracted with dichloromethane $(3 \times 50 \text{ mL})$. The combined organic layer was dried with anhydrous Na₂SO₄ and evaporated to dryness. The crude product was purified by silica gel chromatography using petroleum etherdichloromethane as eluent affording a white solid with an isolated yield of 98%. ¹H NMR (400 MHz, CDCl₃, δ) 7.64 (s, 2H), 7.51 (t, J=9.60 Hz, 16H), 7.35 (t, J=7.20 Hz, 16H), 2.94 (t, J = 7.20 Hz, 8H), 1.67 (m, 8H), 1.44 (m, 8H), 1.29 (m, 16H), 0.89 (t, J=7.00 Hz, 12H). ¹³C NMR (100 MHz, CDCl₃, δ) 139.8, 139.2, 138.7, 137.9, 136.2,

130.6, 130.1, 129.3, 128.8, 127.5, 127.0, 126.7, 126.1, 33.5, 29.1, 28.5, 22.5, 14.3, 13.7. MS (FAB) m/z 1152.0 (M⁺ + 1). Anal. Calcd for C₇₈H₈₆S₄: C, 81.34; H, 7.53; S, 11.13. Found: C, 81.20; H, 7.62. Mp 280 °C.

4.1.4. 1,2,4,5-Tetrakis[(4'-diphenylamino)biphenyl-4yl]benzene 5. The synthetic procedure of 4 was followed using 4-diphenylaminophenylboronic acid (361 mg, 1.25 mmol) and 1,2,4,5-tetrakis(*p*-iodophenyl)benzene **3** (221 mg, 0.25 mmol). The pure product was separated by silica gel column chromatography using 6:1 petroleum ether–dichloromethane as eluent affording 261 mg (77%) of a milky white solid. ¹H NMR (400 MHz, CDCl₃, δ) 7.62 (s, 2H), 7.47 (d, *J*=7.20 Hz, 14H), 7.31 (d, *J*=7.20 Hz, 8H), 7.24 (t, *J*=7.20 Hz, 18H), 7.10 (d, *J*=7.60 Hz, 24H), 7.01 (t, *J*=7.00 Hz, 8H). ¹³C NMR (100 MHz, CDCl₃, δ) 147.6, 147.2, 139.5, 139.3, 138.7, 134.5, 133.0, 130.3, 129.2, 127.6, 126.1, 124.3, 124.0, 122.9. MS (FAB) *m/z* 1355.9 (M⁺). Anal. Calcd for C₁₀₂H₇₄N₄: C, 90.37; H, 5.50; N, 4.13. Found: C, 90.27; H, 5.58; N, 4.29. Mp 301 °C.

4.1.5. 1,2,4,5-Tetrakis[**4-(1-naphthyl)phenyl-1-yl**] **benzene 6.** The synthetic procedure of **4** was followed using 1-naphthylboronic acid (516 mg, 3 mmol) and 1,2,4,5-tetrakis(*p*-iodophenyl)benzene **3** (443 mg, 0.50 mmol). The pure product was separated by silica gel column chromatography using 4:1 petroleum ether–dichloromethane as eluent affording 250 mg (56%) of a white solid. ¹H NMR (400 MHz, CDCl₃, δ) 7.94 (d, *J*=8.40 Hz, 4H), 7.90 (d, *J*=8.40 Hz, 4H), 7.86 (d, *J*=6.80 Hz, 4H), 7.85 (s, 2H), 7.52 (m, 8H), 7.46 (m, 20H), 7.38 (t, *J*=7.60 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃, δ) 140.0, 139.9, 139.7, 139.2, 133.8, 133.0, 131.6, 129.9, 129.8, 128.3, 127.7, 126.9, 126.1, 125.9, 125.7, 125.4. MS (FAB) *m/z* 886.7 (M⁺ – 1). Anal. Calcd for C₇₀H₄₆: C, 94.77; H, 5.23. Found: C, 94.60; H, 5.36. Mp 286 °C.

4.1.6. 1,2,4,5-Tetrakis[4'-(9"-anthryl)phenyl-1'-yl] benzene 7. The synthetic procedure of **4** was followed using 9-anthracylboronic acid (400 mg, 1.8 mmol) and 1,2,4,5-tetrakis(*p*-iodophenyl)benzene, **3** (266 mg, 0.30 mmol). The pure product was separated by silica gel column chromatography using 4:1 petroleum ether–dichloromethane as eluent affording 250 mg (77%) of a yellow solid. ¹H NMR (400 MHz, CDCl₃, δ) 8.51 (s, 4H), 8.05 (t, *J*=8.80 Hz, 10H), 7.74 (d, *J*=8.80 Hz, 4H), 7.70 (d, *J*=8.00 Hz, 8H), 7.47 (d, *J*=8.40 Hz, 8H), 7.39 (t, *J*=7.60 Hz, 10H), 7.17 (t, *J*=8.00 Hz, 10H). MS (FAB) *m/z* 1086.5 (M⁺ – 1). Anal. Calcd for C₈₆H₅₄: C, 94.99; H, 5.01. Found: C, 94.92; H, 5.19. Mp 352 °C.

4.1.7. 1,2,4,5-Tetrakis[**4**'-(**9**"-**phenanthryl**)**phenyl-1**'-**yl**] **benzene 8.** The synthetic procedure of **4** was followed using 9-phenanthrylboronic acid (400 mg, 1.8 mmol) and 1,2,4,5-tetrakis(*p*-iodophenyl)benzene, **3** (266 mg, 0.30 mmol). The pure product was separated by silica gel column chromatography using 4:1 petroleum ether-dichloromethane as eluent affording 250 mg (77%) of a light-yellow solid. ¹H NMR (400 MHz, CDCl₃, δ) 8.78 (d, J=8.00 Hz, 4H), 8.72 (d, J=7.60 Hz, 4H), 7.97 (d, J= 8.00 Hz, 4H), 7.90 (d, J=4.80 Hz, 6H), 7.75 (s, 4H), 7.63 (m, 12H), 7.55 (d, J=2.40 Hz, 12H), 7.49 (m, 8H). ¹³C NMR (100 MHz, CDCl₃, δ) 140.1, 139.8, 139.3, 138.5,

133.1, 131.6, 131.1, 130.6, 130.0, 129.8, 128.7, 127.5, 126.9, 126.6, 126.5, 122.9, 122.5. MS (FAB) m/z 1087.5 (M⁺). Anal. Calcd for C₈₆H₅₄: C, 94.99; H, 5.01. Found: C, 95.05; H, 4.98. Mp 414 °C.

4.1.8. 1,2,4,5-Tetrakis[2'-diphenylamino-9',9'-bis(nbutyl)-7'-fluorenyl]benzene 9. To a mixture of 1,2,4,5tetrabromobenzene, 5 (76 mg, 0.19 mmol), 9,9-bis(n-butyl)-2-diphenylamino-7-fluorenylboronic acid (570 mg, 1.14 mmol), Pd(OAc)₂ (8.5 mg, 5 mol%) and tri(o-tolyl)phosphine (23 mg, 10 mol %) in a 100 mL round-flask were added toluene (10 mL), methanol (5 mL) and 2 M aqueous solution of K₂CO₃ (2.5 mL). The reaction mixture was stirred under a nitrogen atmosphere at 75 °C for overnight. After cooling to room temperature, the reaction mixture was poured into cool water and extracted with dichloromethane $(3 \times 50 \text{ mL})$. The combined organic layer was dried with anhydrous Na₂SO₄ and evaporated to dryness. The crude product was then purified by column chromatography with petroleum ether-dichloromethane (v/v=4:1) as eluent affording the desired product as a white solid (270 mg, 77% yield). ¹H NMR (400 MHz, CDCl₃, δ) 7.69 (s, 2H), 7.46 (t, J = 7.0 Hz, 8H), 7.28 (d, J = 7.6 Hz, 4H), 7.22 (t, J =7.6 Hz, 20H), 7.10 (d, J = 7.6 Hz, 16H), 7.05 (s, 4H), 6.98 (dd, J=7.2 Hz, 12H), 1.69–1.70 (m, 16H), 0.93–0.99 (m, 16H), 0.67 (t, J=7.0 Hz, 40H). ¹³C NMR (100 MHz, CDCl₃, *δ*) 152.2, 150.5, 148.0, 146.9, 140.1, 139.5, 139.2, 136.0, 133.4, 129.1, 128.8, 124.4, 123.7, 123.3, 122.4, 120.4, 119.3, 118.7, 54.8, 39.9, 26.1, 22.9, 14.0. MS (FAB) m/z 1852.8 (M⁺). HRMS (ESI-MS) calcd for C₁₃₈H₁₃₈N₄: 1853.1032 (M⁺+1). Found: 1853.0970.

4.1.9. Bis(4-n-hexylsulfanyl-1-yl)pentaphenyl 4'. A mixture of bis(*p*-iodophenyl)benzene, 3' (443 mg, 0.5 mmol), palladium (II) acetate (22 mg, 0.1 mmol), tri(o-tolyl)phosphine (61 mg, 0.2 mmol), toluene (30 mL), methanol (15 mL), 2 M K₂CO₃ (3 mL), and 4-(n-hexylsulfanyl)phenylboronic acid (370 mg, 1.5) was heated at 75 °C for 3–4 h under a nitrogen atmosphere with good stirring. After the reaction mixture was cooled to room temperature, it was poured into water and extracted with dichloromethane $(3 \times 50 \text{ mL})$. The combined organic layer was dried with anhydrous Na₂SO₄ and evaporated to dryness. The crude product was purified by silica gel column chromatography using dichloromethane as eluent affording a white solid (256 mg) with an isolated yield of 88%. ¹H NMR (400 MHz, CDCl₃, δ) 7.67–7.21 (m, 20H), 2.97 (t, J= 7.20 Hz, 4H), 1.67-1.71 (m, 4H), 1.46-1.43 (m, 4H), 1.29-1.32 (m, 8H), 0.89 (t, J = 6.00 Hz, 6H). MS (FAB) m/z 583.9 (M^++1) . Anal. Calcd for $C_{78}H_{86}S_2$: C, 86.55; H, 7.95; S, 11.00. Found: C, 86.38; H, 8.05; S, 10.95. Mp 187 °C.

4.1.10. Bis(4-diphenylamino-1-yl)pentaphenyl 5'. The synthetic procedure of 4' was followed using 4-diphenyl-aminophenylboronic acid (1.68 g, 5.84 mmol) and bis(*p*-iodophenyl)benzene, 3' (936 mg, 1.94 mmol). The pure product was separated by silica gel column chromatography using petroleum ether–dichloromethane as gradient eluent affording 1261 mg (91%) of a milky white solid. ¹H NMR (400 MHz, CDCl₃, δ) 7.73 (d, *J*=3.60 Hz, 4H), 7.70 (d, *J*=8.40 Hz, 4H), 7.65 (d, *J*=8.40 Hz, 4H), 7.52 (d, *J*=8.40 Hz, 4H), 7.27 (t, *J*=8.40 Hz, 8H), 7.15 (m, 12H), 7.03 (t, *J*=7.40 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃, δ) 147.6,

147.3, 139.6, 139.6, 139.0, 134.4, 129.3, 127.6, 127.4, 127.3, 127.0, 124.5, 123.8, 123.0. MS (FAB) m/z 716.3 (M⁺). Anal. Calcd for C₅₄H₄₀N₂: C, 90.47; H, 5.62; N, 3.91. Found: C, 90.39; H, 5.68; N, 3.91. Mp 191 °C.

4.1.11. Bis[4'-(1"-naphthyl)phenyl-1'-yl] benzene 6'. The synthetic procedure of 4' was followed using 1-naphthylboronic acid (413 mg, 2.4 mmol) and bis(*p*-iodophenyl)benzene, 3' (386 mg, 0.80 mmol). The pure product was separated by silica gel column chromatography using 4:1 petroleum ether–dichloromethane as eluent affording 350 mg (91%) of a white solid. ¹H NMR (400 MHz, CDCl₃, δ) 8.00 (d, *J*=8.00 Hz, 2H), 7.92 (d, *J*=8.80 Hz, 2H), 7.88 (d, *J*=8.00 Hz, 2H), 7.82 (s, 4H), 7.80 (d, *J*=8.40 Hz, 4H), 7.61 (d, *J*=8.40 Hz, 4H), 7.53 (t, *J*=8.00 Hz, 2H), 7.46 (m, 6H). ¹³C NMR (100 MHz, CDCl₃, δ) 139.9, 139.8, 139.8, 139.5, 133.8, 131.6, 130.6, 128.3, 127.7, 127.5, 127.0, 126.9, 126.1, 126.0, 125.8, 125.4. MS (FAB) *m*/z 482.5 (M⁺). Anal. Calcd for C₃₈H₂₆: C, 94.57; H, 5.43. Found: C, 94.34; H, 5.48. Mp 234 °C.

4.1.12. Bis[4'-(9"-anthracyl)phenyl-1'-yl]benzene 7'. The synthetic procedure of 4' was followed using 9-anthracylboronic acid (368 mg, 1.66 mmol) and bis(*p*-iodophenyl)benzene, 3' (266 mg, 0.55 mmol). The pure product was separated by silica gel column chromatography using 4:1 petroleum ether-dichloromethane as eluent affording 253 mg (79%) of a light-yellow solid. ¹H NMR (400 MHz, CDCl₃, δ) 8.52 (s, 2H), 8.06 (d, *J*=8.40 Hz, 4H), 7.90 (d, *J*=6.40 Hz, 8H), 7.77 (d, *J*=8.80 Hz, 4H), 7.54 (d, *J*=8.00 Hz, 4H), 7.48 (t, *J*=8.00 Hz, 4H), 7.38 (t, *J*=8.00 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃, δ) 139.7, 137.8, 133.2, 131.7, 131.3, 130.1, 128.3, 127.5, 126.9, 126.7, 126.6, 125.6, 125.3, 125.1. MS (FAB) *m/z* 582.5 (M⁺). Anal. Calcd for C₄₆H₃₀: C, 94.81; H, 5.19. Found: C, 95.01; H, 5.15. Mp 393 °C.

4.1.13. Bis[4'-(9"-phenanthryl)phenyl-1'-yl]benzene 8'. The synthetic procedure of 4' was followed using 9-phenanthrylboronic acid (200 mg, 0.90 mmol) and bis-(*p*-iodophenyl)benzene, 3' (145 mg, 0.30 mmol). The pure product was separated by silica gel column chromatography using 6:1 petroleum ether-dichloromethane as eluent affording 145 mg (83%) of a light-yellow solid. ¹H NMR (400 MHz, CDCl₃, δ) 8.80 (d, J=8.40 Hz, 2H), 8.74 (d, J=8.40 Hz, 2H), 8.02 (d, J=8.40 Hz, 2H), 7.92 (d, J=7.60 Hz, 2H), 7.83 (d, J=9.20 Hz, 8H), 7.75 (s, 2H), 7.65 (m, 10H), 7.57 (t, J=8.00 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃, *δ*) 139.9, 139.8, 139.7, 138.4, 135.2, 131.1, 130.9, 130.6, 128.7, 127.6, 126.9, 126.8, 126.7, 126.6, 126.5, 125.0, 123.0, 122.6. MS (FAB) m/z 583.9 (M⁺+1). Anal. Calcd for C₄₆H₃₀: C, 94.81; H, 5.19. Found: C, 94.67; H, 5.24. Mp 341 °C.

4.1.14. 1,4-Bis[2'-diphenylamino-9',9'-bis(*n*-butyl)-7'**fluorenyl]benzene** 9'. To a mixture of 1,4-dibromobenzene 1' (94 mg, 0.40 mmol), 9,9-bis(*n*-butyl)-2-diphenylamino-7-fluorenylboronic acid (470 mg, 0.96 mmol), palladium(II) acetate (11 mg, 5 mol%) and tri(*o*-tolyl)phosphine (30 mg, 10 mol%) in a 100 mL round-flask were added toluene (20 mL), methanol (10 mL) and 2 M aqueous solution of K₂CO₃ (2 mL). The reaction mixture was stirred under the atmosphere of nitrogen at 75 °C for 12 h. After cooling to

room temperature, the reaction mixture was poured into cool water and extracted with dichloromethane $(3 \times 50 \text{ mL})$. The combined organic layer was dried with anhydrous Na₂SO₄ and evaporated to dryness. The crude product was then purified by silica column chromatography using petroleum ether-dichloromethane (v/v=6:1) as eluent affording the desired product as a light-yellow solid (301 mg, 78% yield). ¹H NMR (400 MHz, CDCl₃, δ) 7.75 (s, 4H), 7.67 (d, J=7.6 Hz, 2H), 7.61-7.55 (m, 6H), 7.24 (t, J=7.8 Hz, 8H), 7.13 (d, J=7.6 Hz, 10H), 7.01 (dd, J=7.6 Hz, 6H), 1.86-1.94 (m, 8H), 1.06-1.11 (m, 8H), 0.70 (t, J = 7.6 Hz, 20H). ¹³C NMR (100 MHz, CDCl₃, δ) 152.4, 151.3, 148.0, 147.1, 140.3, 140.3, 138.7, 135.9, 129.1, 127.4, 125.8, 123.8, 123.4, 122.5, 121.2, 120.4, 119.4, 119.3, 55.0, 40.0, 26.1, 23.0, 13.9. MS (FAB) m/z 965.2 (M^+) . Anal. Calcd for $C_{72}H_{72}N_2$ (%): C, 89.58; H, 7.52; N, 2.90. Found: C, 89.38; H, 7.45; N, 3.08. Mp 254 °C.

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