Introduction of methyl groups on vinylene segments of phenylene vinylene systems: synthesis and properties†

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A facile synthetic route towards phenylene vinylene systems with methyl substituents at the vinyl linkages is demonstrated through palladium catalyzed Heck coupling of 1,4-diisopropenylbenzene with aryl bromides. The coupling leads to a series of model compounds that feature, in some cases, direct access to a *trans*-configuration at the double bonds. The oxidative stability of these systems is surprisingly unaffected by the presence of allylic C-H bonds in the methyl substituents. The methyl substituents modulate the electronic properties of the phenylene vinylene systems by inducing a significant twist to the conjugated backbone. The study suggests that the introduction of methyl groups at vinylene sites is a viable alternative to functionalising and tuning the properties of phenylene vinylene systems.

Introduction

Phenylene vinylene oligomers and the corresponding polymers (PPVs) have been extensively investigated over the past decade as they exhibit favorable properties such as electroluminescence,[1–4] photoconductivity,[5] charge transport[6] and nonlinear optical behavior.[7] To date, a large pool of work is devoted to improving the electronic properties, color purity and processibility of these materials *via* the introduction of functional or solubilizing groups on the phenyl rings and the vinyl linkages of the phenylene vinylene backbone. On the other hand, the color stability of these systems has also been vastly improved through appropriate substitutions at the vinyl sites to reduce the double bond's susceptibility towards photooxidation.[8–11] For example, the introduction of cyano or trifluoromethyl moieties has been found to reduce the probability of oxygen attack on double bonds during excitation.[12–14] Bulky moieties such as phenyl groups have also been introduced at vinyl sites to provide steric protection against the attack of oxygen.[15]

A natural extension of this strategy would be to introduce alkyl groups at the vinyl linkages as this should, in principle, improve solubility and offer an additional parameter for electronic- and color-tuning of the phenylene vinylene system. However, there have been very few reports of systems having such alkyl substitutions. This is primarily due to synthetic difficulty, as conventional coupling procedures for phenylene vinylene systems (such as Horner–Wadsworth–Emmons,[7,16] Siegrist,[17] Heck,[18,19] Suzuki-Miyaura[20] and McMurray[21–25] coupling) either do not offer the possibility of alkyl addition at the vinyl site, or when they do, give rise to products consisting of largely inseparable mixtures of *cis*- and *trans*-stereoisomers[19,24] or only the *cis*-isomers.[25]

In this contribution, we demonstrate the viability of introducing methyl substituents at the vinyl linkages of phenylene vinylene through successful one-step synthesis and isolation of a series of methyl-substituted diisopropenylbenzenes **1–6** using the Heck coupling reaction of arylbromides with the stable and commercially available 1,4-diisopropenylbenzene **7**. We use 2D NOESY NMR experiments to confirm the *trans*,*trans*′-configuration at the vinyl linkage for selected products. We show that the oxidative stabilities of these model compounds are not affected by the presence of the methyl groups, that are in an allylic position. This is particularly interesting as it is contrary to the common assumption that allylic C-H bonds are highly susceptible to oxidation and should be avoided in polymer semiconductors. We also explore the effects of the methyl groups on the geometries and electronic properties of the model oligomers *via* experimental and theoretical modeling.

Results and discussion

Synthesis

The synthesis of alkyl substituted phenylene vinylenes was previously studied using Mukaiyama–McMurray coupling of alkyl phenyl ketones, but the reactions were not amenable to hetero-coupling, and gave mixtures of *cis*- and *trans*-stereoisomers that were difficult to separate.[24] A separate study using the Heck reaction also yielded a mixture of *cis*- and *trans*-isomers and/or internal and external olefins.[19] Here, we employed Heck coupling of 1,4-diisopropenylbenzene **7** with two molar equivalents of a range of bromoarenes **8–13**, and successfully obtained oligomers **1–6**, as shown in Table 1. Compound **7** is an excellent starting material to work with as it is a stable, inexpensive and pure commercially available crystalline solid,[26] as opposed to its 1,4-divinylbenzene analogue which is a very reactive, expensive liquid available only in 85% purity.[27] Reactions were performed

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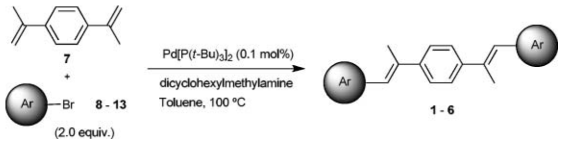
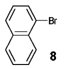
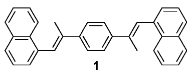
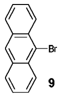
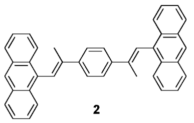
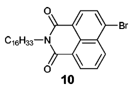
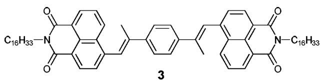
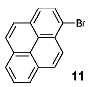
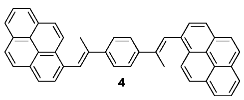
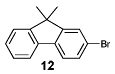
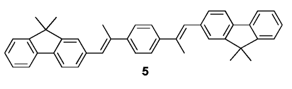
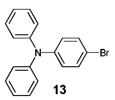
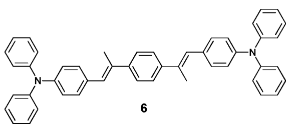
Table 1 Synthesis of diisopropenylbenzene derivatives **1–6** *via* Heck reaction of 1,4-diisopropenylbenzene **7** with bromoarenes **8–13**



Entry	Ar–Br	Product	Yield
1	 **8**	 **1**	66
2	 **9**	 **2**	71
3	 **10**	 **3**	28
4	 **11**	 **4**	8
5	 **12**	 **5**	14
6	 **13**	 **6**	22

in toluene at 100 °C using bis(tri-*t*-butylphosphine)palladium(0) [$Pd[P(tBu)_3]_2$] (1.0 mol%) as catalyst and dicyclohexylmethylamine as base/HBr scavenger.[28] The reactions were monitored by thin layer chromatography, gas chromatography mass spectrometry (GCMS) and matrix assisted laser desorption ionization-time-of-flight (MALDI-TOF) spectrometry.

We observed markedly different degrees of coupling for the various reactions. For example, the coupling between **7** and either 1-bromonaphthlene **8** or 9-bromoanthracene **9** were found to be highly stereo- and regio-selective. The desired *trans*,*trans′*-isomers **1** and **2** were formed almost exclusively, with little or no trace of other isomers as observed in GCMS. Upon cooling the reaction mixture, both **1** and **2** were found to precipitate from their respective mixtures. Filtration of the reaction mixture followed by sequential washing of the residues with copious amounts of water and hexane furnished **1** and **2** in 66% and 71% yields respectively. The yields were satisfactory considering that they reflect the overall percentages from two individual Heck reactions.

In contrast, the coupling of **7** with monomers **10–13** was found to give products with molecular weights corresponding to mono-, di-, and tri-substituted diisopropenylbenzenes, as evidenced from MALDI-TOF and GCMS analyses. In all cases, di-substituted diisopropenylbenzenes were the major products. GCMS analysis further revealed that the di-substituted components typically consisted of four distinct stereo- and regio-isomers. We believe that the isomers correspond to the four possible permutations of double substitution, as illustrated in Fig. 1. Purification of the crude reaction mixtures by column chromatography (using a mixture of dichloromethane and hexane as the eluent) yielded fractions containing mixtures of isomers. In all cases, we suspect the desired *trans*,*trans′*-isomers could be isolated from the isomer mixtures by precipitation or recrystallisation in carefully selected solvents. The products were successfully isolated in high purity in yields of 28% (**3**), 8% (**4**), 14% (**5**) and 22% (**6**). In order to confirm the *trans*,*trans′*-isomer we ran 2D NOESY NMR on (**6**) as it has the best solubility (see ESI). The results clearly show that the methyl hydrogens only have interactions with the hydrogens on the adjacent phenyl rings, and no interactions with the adjacent vinylene hydrogen. Although this result only confirms the *trans*,*trans′*-isomer for (**6**), we highly suspect the isolated fractions of the other compounds also have the same *trans*,*trans′*-isomer.

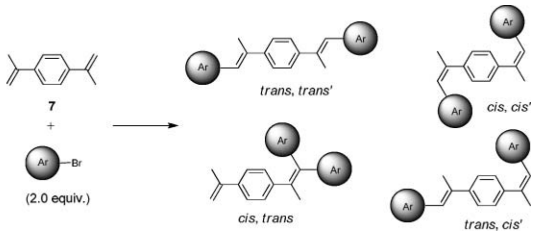


Fig. 1 The four possible stereo- and regio-isomers of di-substituted diisopropenylbenzene from Heck coupling reaction.

The marked difference in the stereo- and regio-selectivity of the Heck coupling between diisopropenylbenzene **7** and the two groups of monomers is surprising. We surmise that in the case of the bulky 9-bromoanthracene **9**, steric factors may play a part in directing the coupling for the *trans*-orientation. The relatively low solubility of **1** and **2** in toluene also suppresses further substitutions of the di-substituted products once they are formed.

Physical and optical properties

The thermal behavior and stability of the materials were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), respectively. The results are summarized in Table 2. All the materials melt above 215 °C

Table 2 Optical and physical properties of compounds **1–6**

	UV-vis				
Compound	λ_{max} (nm)[a]	Bandgap (eV)[b]	PL λ_{max} (nm)[c]	T_m (°C)[d]	T_d (°C)[d]
1	323	3.30	430	215–218	306
2	372, 391	2.92	470	300–305	380
3	379	2.78	446	59–62	428
4	356	2.97	467	234–237	390
5	342	3.13	437	248–250	353
6	362	2.97	460	243–245	362

[a] Measured in a chloroform solution. [b] Measured from the absorption onset of the UV-vis spectrum. [c] Obtained from DSC measurement. [d] Obtained from TGA measurement (temperature at 5% mass loss under nitrogen, 10 °C min^{-1} ramp rate).

with the exception of compound **3** (59–62 °C) which contains long alkyl chains. The thermal decomposition temperatures (5% mass fraction loss) of all compounds are above 350 °C, indicating that the materials have relatively high thermal stabilities.

The photophysical properties of the compounds were measured by UV-visible and fluorescence spectroscopy in chloroform solution. The compounds show strong absorption and emission in the 320–400 nm and 430–470 nm ranges, respectively (Fig. 2, Table 2). The relatively narrow ranges and high energy band gaps across the series of compounds suggest that π-conjugation in the phenylene vinylene backbones may have been attenuated as the backbones take on a more non-planar conformation to accommodate the methyl substituents. For example, the photoluminescence spectrum of compound **6** shows a single band with $\lambda_{max} = 464$ nm whereas that of the corresponding non-methyl-substituted *p*-bis(*p*-*N*,*N*-diphenylaminostyryl)benzene **14**[29] (see structure in Fig. 4) shows two red-shifted peaks at $\lambda_{max} = 470$ nm (major) and 530 nm (minor).[30] These observations are also consistent with previous reports of sterically congested stilbenes.[23]

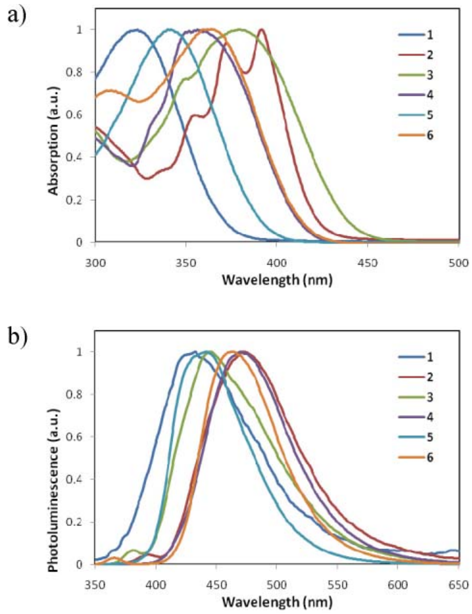


Fig. 2 (a) UV-vis absorption and (b) photoluminescence spectra of compounds **1–6** in chloroform solution.

Oxidative stability

Studies have shown that allylic C–H bonds can undergo facile proton abstraction and trigger oxidative degradation processes in organic molecules.[31,32] The introduction of methyl groups on the vinyl linkages of compounds **1–6**, and the implicit introduction of allylic protons, may therefore undermine the oxidative stabilities of these compounds. We investigated the effect of methyl substitution on photo-oxidative stability by subjecting drop-cast thin films of **6** and **14** (without allylic C–H bonds) to repeated photoluminescence measurements at an excitation wavelength of 400 nm under ambient conditions. The emission intensities of both compounds were found to decrease with each successive measurement, indicating that degradation due to photoexcitation of the films occurred during each measurement.

The intensities of the emissions, measured at wavelengths corresponding to the emission peaks, were plotted for each successive measurement relative to that of the first measurement (Fig. 3, see Supporting Information for details). The rates of degradation in compounds **6** and **14** were found to be comparable, which suggests that the degradation mechanisms in both compounds may be similar. Given that compound **14** does not contain allylic C–H bonds, this suggests that allylic hydrogens in **6** do not contribute significantly (if at all) to the degradation process of the compound, and that the degradation pathway of **6** may be independent of the additional methyl group.

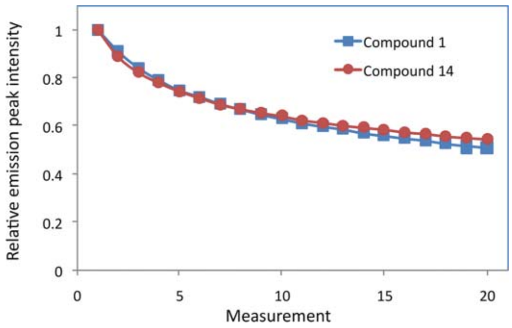


Fig. 3 Relative photoluminescence intensities of emission peaks recorded over successive photoluminescence measurements of compounds **6** (blue square) and **14** (red circle) in solid state (excitation at 400 nm). The plots show that the rates of photo-oxidative degradation of vinyl-alkylated (**6**) and non-alkylated (**14**) phenylenevinylene systems are comparable.

Theoretical study on geometry

To further investigate the effect of the methyl group on the geometries of the compounds, we performed density functional theory calculations on compound **6** and the corresponding non-substituted *p*-bis(*p*-*N*,*N*-diphenylaminostyryl)benzene **14**.[29] The geometries of **6** and **14** were fully optimized in the generalized gradient approximation with nonlocal exchange and correlation functions according to Perdew–Wang (GGA–PW91).[33] The phenylene vinylene backbone of **6** was found to be significantly twisted from planarity, with dihedral angles between the benzene rings and the double bonds ranging from 34.1° [Φ(3,4,5,6)] to 26.5° [Φ(7,8,9,10)]. In contrast, the backbone of DSA-Ph **14** was almost planar, with the largest dihedral angle found to be Φ(1′,2′,3′,4′) = 1.6° (Fig. 4a).

Analysis of the HOMO and LUMO density maps of the systems further highlighted the effects of methyl substituent on the degree of conjugation in **6**. Compared with **14**, the π-orbital contribution from the benzene rings to the HOMO frontier orbitals in **6** is reduced whereas the electron density on the double bonds is enhanced, as illustrated in Fig. 4b. The skewed distribution of electron clouds among the conjugated segments in **6** clearly illustrates an appreciable disruption in the conjugation of the system. This readily explains the wider bandgap observed in compound **6** (2.97 eV, Table 2) compared with the bandgap reported for **14** (2.70 eV).[29]

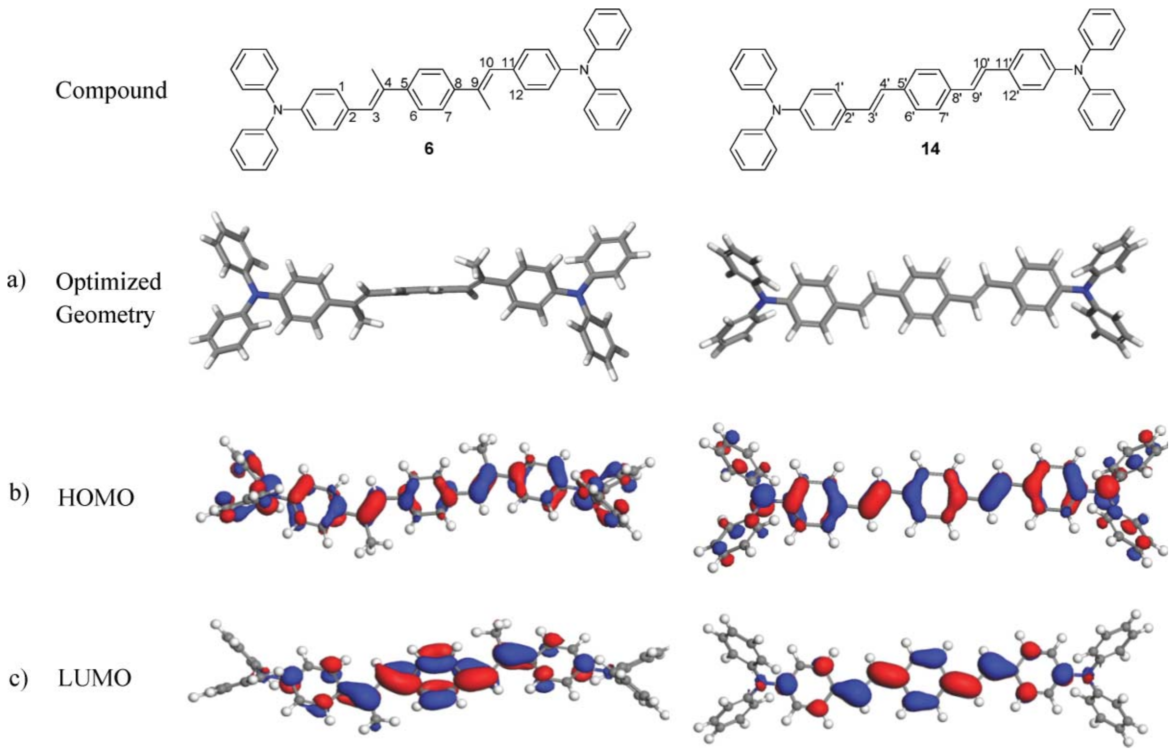


Fig. 4 The (a) optimized geometries, and (b) HOMO and (c) LUMO density maps of **6** and **14**, calculated using density functional theory in generalized gradient approximation with nonlocal exchange and correlation functions according to Perdew–Wang (GGA–PW91).

Conclusion

We have demonstrated a novel method of introducing methyl substituents at the vinylene segments in phenylene vinylene systems through a one-step Heck coupling reaction between the stable and commercially available 1,4-diisopropenylbenzene with arylbromides, while achieving the *trans*-configuration at the double bond. This method opens the door to new methods of tuning the color and electronic properties, while potentially enhancing the solubility and color stability of phenylene vinylene systems. We are currently studying these materials for potential application in organic electronic devices such as light emitting diodes (OLED), solar cells, (OPV) and thin film transistors (OTFT).

Experimental

General

^{1}H and ^{13}C NMR data were performed on a Bruker DPX 400 MHz spectrometer with chemical shifts referenced to residual $CHCl_3$ in $CDCl_3$. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a Bruker Autoflex TOF/TOF instrument without the use of matrix. Differential scanning calorimetry (DSC) was carried out under nitrogen on a TA Instrument DSC Q100 instrument (scanning rate of 20 °C min^{-1}). Thermal gravimetric analysis (TGA) was carried out using a TA Instrument TGA Q500 instrument (heating rate of 10 °C min^{-1}). UV–vis spectra were recorded on a Shimadzu model 2501-PC. Photoluminescence (PL) spectra were measured on a Perkin-Elmer (LS50B) spectrofluorimeter. Gas chromatography-mass spectrometry (GCMS) was carried out on a Varian Chrompack 3800 gas chromatograph coupled to a Varian 4000MS mass spectrometer detector.

All commercially available materials were used as received unless otherwise noted. All reactions were carried out using Schlenk techniques in an argon or nitrogen atmosphere with anhydrous solvents. Column chromatography was carried out on silica gel [Merck Kieselgel 60 (230–400 mesh)]. TLC was performed on 0.25 mm thick plates precoated with Merck Kieselgel 60 F_{254} silica gel, and visualised by UV light (254 and 366 nm) and cerium(IV) sulfate solution.

General procedure for the synthesis of compounds 1–6

To a mixture of 1,4-diisopropenylbenzene (**7**) (1,4-di(prop-1-en-2-yl)benzene) (200 mg, 1.26 mmol, 1 equiv.), aryl bromide (2.52 mmol, 2 equiv.) and $Pd[P(t\text{-}Bu)_3]_2$ (32 mg, 63 μmol) in argon was added a degassed solution of dicyclohexylmethylamine (0.68 cm^3, 3.16 mmol, 2.5 equiv.) in toluene (15 cm^3). The resulting mixture was stirred at 100 °C for 48 hours, cooled to room temperature and quenched with distilled water (20 cm^3). For compounds **1** and **2**, precipitates were observed upon cooling of the reaction mixture. The product was obtained by filtration of the mixture followed by washing of the residue with copious amount of distilled water. For compounds **3–6**, the product was extracted into dichloromethane (3 × 30 cm^3) and the organic layer washed with dried with anhydrous $MgSO_4$ and removed *via* rotary evaporation. The product was then purified by column chromatography followed by recrystallisation in a mixture of hexane and dichloromethane.

1,4-Bis((*E*)-1-(naphthalen-1-yl)prop-1-en-2-yl)benzene (1)

Off-white solid (345 mg, 66%); mp 215–218 °C; Anal. Calcd. for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.59; H, 6.41; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.19 (6H, s, CCH_3), 7.37 (2H, s, C=CH), 7.46–7.54 (8H, m, ArH), 7.72 (4H, s, ArH), 7.82 (2H, d, J = 8.0, ArH), 7.89–7.91 (2H, m, ArH), 8.05–8.08 (2H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.8, 125.6, 125.7, 125.8, 126.2, 126.3, 126.4, 127.1, 127.7, 128.9, 132.6, 134.0, 136.1, 138.8, 142.6; MALDI-TOF-MS m/z: 410.1780; calcd for $C_{32}H_{26}$ = 410.2035.

1,4-Bis((*E*)-1-(anthracen-9-yl)prop-1-en-2-yl)benzene (2)

Yellow solid (456 mg, 70%); mp 300–305 °C; Anal. Calcd. for $C_{40}H_{30}$: C, 94.08; H, 5.92. Found: C, 94.08; H, 5.92; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.91 (6H, s, CCH_3), 7.59 (2H, s, C=CH), 7.48–7.53 (8H, m, ArH), 8.06–8.08 (8H, m, ArH), 8.20–8.22 (8H, m, ArH), 8.46 (2H, s, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.0, 124.2, 125.6, 125.9, 126.5, 126.6, 129.2, 130.2, 131.9, 133.3, 140.9, 142.2; MALDI-TOF-MS m/z: 510.2010; calcd for $C_{40}H_{30}$ = 510.2348.

4,4′-(1*E*,1′*E*)-2,2′-(1,4-Phenylene)bis(prop-1-ene-2,1-diyl)bis(*N*-hexadecyl-1,8-naphthalimide) (3)

Pale green solid (350 mg, 28%); mp 59–62 °C; Anal. Calcd. for $C_{68}H_{88}N_2O_4$: C, 81.88; H, 8.89; N, 2.81. Found: C, 81.45; H, 8.73; N, 2.48; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (6H, t, J = 7.6, CH_2CH_3), 1.20–1.48 (56H, m, CH_2), 1.70–1.80 (4H, s, NCH_2CH_2), 2.22 (6H, s, CCH_3), 4.20 (4H, d, J = 7.6, NCH_2), 7.39 (2H, s, C=CH), 7.51–7.78 (8H, m, ArH), 8.40 (2H, d, J = 8.8, ArH), 8.63–8.68 (4H, m, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 18.1, 23.1, 27.6, 28.6, 29.8, 32.3, 40.9, 121.9, 123.6, 124.3, 126.7, 127.1, 128.1, 128.9, 131.0, 131.1, 131.6, 131.7, 141.6, 142.5, 142.9, 164.5, 164.7; MALDI-TOF-MS m/z: 996.6890; calcd for $C_{68}H_{88}N_2O_4$ = 996.6744.

1,4-Bis((*E*)-1-(pyren-1-yl)prop-1-en-2-yl)benzene (4)

Yellow solid (56 mg, 8%); mp 234–237 °C; Anal. Calcd. for $C_{44}H_{30}$: C, 94.59; H, 5.41. Found: C, 94.22; H, 5.78; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.26 (6H, s, CCH_3), 7.69 (2H, s, C=CH), 7.83 (4H, s, ArH), 7.00–7.04 (4H, m, ArH), 8.10–8.14 (6H, m, ArH), 8.20–8.23 (6H, m, ArH), 8.31 (2H, d, J = 8.0, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.9, 124.9, 125.2, 125.3, 125.4, 125.5, 126.3, 126.4, 126.5, 127.6, 127.7, 127.8, 129.6, 130.8, 131.5, 131.9, 133.9, 139.2, 142.7; MALDI-TOF-MS m/z: 558.1760; calcd for $C_{44}H_{30}$ = 558.2348.

1,4-Bis((*E*)-1-(9,9-dimethyl-9*H*-fluoren-2-yl)prop-1-en-2-yl)benzene (5)

Pale green solid (112 mg, 14%); mp 248–250 °C; Anal. Calcd. for $C_{42}H_{38}$: C, 92.94; H, 7.06. Found: C, 92.93; H, 7.07; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53 (12H, s, $C(CH_3)_2$), 2.39 (6H, s, CCH_3), 7.00 (2H, s, C=CH), 7.30–7.48 (8H, m, CH_2), 7.59 (4H, s, ArH), 7.74 (2H, d, J = 8.0, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.0, 27.6, 47.2, 120.1, 120.4, 123.0, 123.8, 126.3, 127.4, 127.5, 128.5, 128.6, 137.0, 137.9, 138.1, 139.4, 143.2, 154.0, 154.3; MALDI-TOF-MS m/z: 542.2780; calcd for $C_{42}H_{38}$ = 542.2974.

4,4′-(1*E*,1′*E*)-2,2′-(1,4-Phenylene)bis(prop-1-ene-2,1-diyl)bis(*N*,*N*-diphenylaniline) (6)

Pale green solid (177 mg, 22%); mp 243–245 °C; Anal. Calcd. for $C_{48}H_{40}N_2$: C, 89.40; H, 6.25; N, 4.34. Found: C, 89.53; H, 6.37; N, 4.10; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.52 (6H, s, CH_3), 6.82 (2H, s, C=CH), 7.00–7.18 (16H, m, ArH), 7.25–7.30 (12H, m, ArH), 7.52 (4H, s, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.0, 123.3, 123.7, 124.8, 126.2, 12.5, 129.7, 130.5, 133.0, 136.2, 143.2, 136.6, 148.1; MALDI-TOF-MS m/z: 644.3190; calcd for $C_{48}H_{40}N_2$ = 644.3191.

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