Facile synthesis of a new class of aggregation-induced emission materials derived from triphenylethylene

Bingjia Xu,^a Zhenguo Chi,^{*a} Zhiyong Yang,^a Jingbo Chen,^b Shaozhi Deng,^b Haiyin Li,^a Xiaofang Li,^a Yi Zhang,^a Ningsheng Xu^b and Jiarui Xu^{*a}

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A series of new aggregation-induced emission compounds with strong blue light-emitting properties derived from triphenylethylene were facilely synthesized by a Wittig–Horner reaction of bis(4-bromophenyl)methanone with diethyl 4-bromobenzylphosphonate, followed by a Suzuki reaction with arylboronic acids. Their maximum fluorescence emission wavelengths were 452–462 nm. The glass transition temperatures ranged from 70–145 °C, and the decomposition temperatures were 360–508 °C. The unoptimized device fabricated with benzofuranyl substituted compound as emitter turned on at ~6 V, and the maximum luminance was ~1500 cd m⁻².

Introduction

Most π -conjugated organic molecules have a very high luminescence efficiency in dilute solutions, but they exhibit relatively weak or no emissions when fabricated into thin films. This is because intra- and intermolecular interactions, such as $\pi - \pi$ interactions, quench the emission process.¹ It is difficult to obtain highly emissive materials in the solid state and also to make optoelectronic devices because the organic emissive materials in the devices are normally used as thin solid films, in which aggregation is inherently accompanied with film formation.² It is thus highly desirable to develop electroluminescent materials that can emit intense light in the solid state, which is expected to overcome the aggregation quenching problem. Indeed, a few rare examples, including silole derivatives, 1,1,2,2-tetraphenylethene (TPE) derivatives and 1-cyano-trans-1,2-bis-(4-methylbiphenyl)ethylene (CN-MBE), have been recently found to show significant enhancement in their light emission upon aggregation or in the solid state.3 This intriguing phenomenon was named aggregationinduced emission (AIE) by Tang et al.^{3a} or aggregation-induced emission enhancement (AIEE) by Park et al.^{3b} Since then, AIE materials have been found to be promising emitters for the fabrication of highly efficient electroluminescent devices and stimuli-responsive materials for use in multifunctional switches.⁴ However, discoveries of AIE materials are quite limited, and most of them are silole-based compounds, which are complicated and difficult to prepare. The double bonds of TPE derivatives were synthesized by McMurry reaction with TiCl₃ (or TiCl₄) under THF reflux for 20 h.^{3h} However, the double bonds of triphenylethylene derivatives are introduced by Wittig-Horner reaction which is milder and shorter time in relation to the McMurry reaction; moreover, it is well-known that the two reactants must

^aPCFM Lab and DSAPM Lab, OFCM Institute, State Key Laboratory of Optoelectronic Materials and Technologies, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou, 510275, China. E-mail: chizhg@mail.sysu.edu.cn; xjr@mail.sysu.edu.cn; Fax: +86 20 84112222; Tel: +86 20 84111081 be the same in McMurry coupling reaction, otherwise there are various products with self- or crossed reaction.

Recently, a series of triphenylethylene carbazole derivatives with strong blue light emission, high glass transition temperature (T_g) , and AIE effect were developed in our laboratory.⁵ The twisted configuration of the three phenyl rings in triphenyl-ethylene, due to the bulky carbazole group substituents, is considered as one of the possible reasons for the AIE effect.

Here, we report a new class of triphenylethylene derivatives with strong blue light emission and AIE effect. The derivatives were easily prepared by a two-step reaction, including the Wittig–Horner and Suzuki reactions. The photophysical, thermal, AIE, electrochemical, and device properties were preliminarily evaluated.

Results and discussion

Synthesis

Our strategy for the synthesis of this new series of triphenylethylene derivatives is outlined in Scheme 1. The key precursor, 4,4',4''-(ethene-1,1,2-triyl)tris(bromobenzene)(VP₃-Br₃), was synthesized with a 87% yield from bis(4-bromophenyl)methanone with diethyl 4-bromobenzylphosphonate through the



Scheme 1 Synthetic routes to the desired compounds.

^bSchool of Physics and Physic Engineering, Sun Yat-sen University, Guangzhou, 510275, China

Wittig–Horner reaction. Cross-coupling of the VP₃-Br₃ with the corresponding arylboronic acids under Pd-catalyzed Suzuki conditions afforded the products VP₃-B₃, VP₃-T₃, VP₃-N₃, VP₃-(TB)₃, VP₃-(BFu)₃, VP₃-(Bt)₃, and VP₃-(TA)₃ in acceptable yields from 42% to 74%. All compounds were characterized with proton nuclear magnetic resonance (¹H NMR), carbon nuclear magnetic resonance (¹³C NMR), high-resolution mass spectroscopy (MS), and Fourier transform infrared spectroscopy (FTIR).

Thermal properties

The thermal properties of these compounds were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) and are summarized in Table 1. The DSC curves for the samples recorded during the second heating runs at a scan rate of 10 °C min⁻¹ are shown in Fig. 1 (first heating–cooling run: the compounds were heated to 300 °C and then cooled to room temperature both at 10 °C min⁻¹ rates). It can be seen that all the compounds, with the exception of VP₃-T₃, exhibited a glass transition peak. The T_g values of the compounds ranged from 70–145 °C. The T_g of the compound VP₃-(TA)₃ was the highest (145 °C) due to the bulky thianthrenyl group. All the T_g values were much higher than that of 1-methyl-1,2,3,4,5-pentaphenylsilole (MPPS, 54 °C) and 1,1,2,3,4,5-hexaphenylsilole (HPS, 65 °C), the two typical AIE-active compounds reported.⁶

The DSC curves of the phenyl substituted derivatives, VP_3 - B_3 , VP_3 - T_3 , and VP_3 - $(TB)_3$, show strong melting peaks at 198, 227

 Table 1
 Thermal properties of the compounds

	$T_{\rm g}/^{\circ}{ m C}$	$T_{\rm m}/^{\circ}{\rm C}$	$T_{\rm d}/^{\circ}{\rm C}$
VP ₃ -B ₃	70	198	361
$VP_3 - T_3$	76^a	227	376
VP_3 -(TB) ₃	119	249	376
VP ₃ -N ₃	95	N/A	427
VP_3 -(BFu) ₃	124	N/A	495
VP_3 -(Bt) ₃	134	N/A	508
VP_3 -(TA) ₃	145	N/A	494

^{*a*} Obtained from heating DSC curve of the sample prepared by quenching from its melt.



Fig. 1 DSC curves for the compounds at a scan rate of 10 $^{\circ}$ C min⁻¹ (second heating scan).

and 249 °C, respectively. However, as can be seen, the fused ring substituted derivatives, VP_3 - N_3 , VP_3 - $(BFu)_3$, VP_3 - $(Bt)_3$, and VP_3 - $(TA)_3$, have no crystallization and melting peaks but only glass transition peaks. This indicates that the presence of the fused ring units in these compounds effectively suppressed the crystallinity and resulted in very little crystal formation when it was cooled from the melting state. As such, it is expected to yield better electroluminescent properties.

It is interesting to notice that VP₃-B₃ and VP₃-(TB)₃ have cold crystallization peaks at 123 and 212 °C, respectively, while VP₃-T₃ showed no such peak. This indicates that the crystallization of compound VP₃-T₃ occurred at a very fast speed, and there existed no amorphous glassy phase after 10 °C min⁻¹ cooling from its melt. This is why there is no glass transition peak in its heating DSC curve. To try to obtain an amorphous glassy phase, the VP₃-T₃ melt was quenched by liquid nitrogen. As expected, in the first heating run, there existed a clear glass transition peak at 76 °C. However, in the second heating run, the glass transition peak could not be observed (Fig. 2). It is very interesting that there are two small cold crystallization peaks at 115 °C and 167 °C, respectively. But, the endothermic enthalpy of melting peak is obviously larger than the sum of exothermic enthalpy of



Fig. 2 DSC heating curves for VP₃-T₃ samples obtained: (1) melt quenched by liquid nitrogen; (2) after first heating run, the melt was cooled to room temperature at 10 $^{\circ}$ C min⁻¹.



Fig. 3 TGA curves of the compounds.

the two cold crystallization peaks. This result also indicates that the speed of crystallization of VP_3 - T_3 was very fast and there were large quantity of crystals formed even though the liquid nitrogen was used to freeze its melt.

The decomposition temperature (T_d) here is defined as the temperature at which 5% weight loss occurs during heating in nitrogen. As shown by the TGA curves presented in Fig. 3, the compounds were highly stable since they started to decompose at 361–508 °C. The T_d values of the compounds were also much higher than those of the reported AIE-active compounds MPPS (309 °C) and HPS (351 °C).¹⁰ The fused ring substituted derivatives displayed good thermal stability with T_d over 427 °C. The amounts of carbonized residues (char yield) of VP₃-(BFu)₃, VP₃-(Bt)₃, and VP₃-(TA)₃ were 22, 38, and 49%, respectively, at 900 °C in nitrogen. These are much higher than those of the nonheteroatom containing compounds: VP₃-B₃, VP₃-T₃, VP₃-(TB)₃, and VP₃-N₃. The high char yields of these compounds can be ascribed to their heterocyclic units.

Optical properties

The optical properties of the compounds in tetrahydrofuran (THF) solution and in TLC thin film were investigated by UV-vis and photoluminescence (PL) spectroscopy. As shown in Table 2, the UV maximum absorption wavelengths of the compounds were in the range of 330–345 nm. Clearly, the fused ring units had only a little influence on the maximum absorption wavelength. The maximum absorption wavelengths of VP₃-N₃ and VP₃-(TA)₃ were 331 and 330 nm, respectively. These were especially shorter than those of the three phenyl substituted derivatives: VP₃-B₃, VP₃-T₃, and VP₃-(TB)₃.

The PL spectra of the compounds showed maxima at 454–467 nm in THF solution and at 452–462 nm in solid thin film. As such, it exhibited blue light emission. In the case of a solid thin film, the maximum emission peaks of the phenyl-substituted derivatives were slightly red-shifted (1–5 nm) compared to the case of the solution. It indicates that the intermolecular interaction of the derivatives increased the planarity of the molecules in the solid state, which resulted in red-shifts of the PL spectra. On the other hand, the maximum emission peaks of the fused ring-substituted derivative films were slightly blue-shifted (3–6 nm) compared with their respective solutions. The blue-shifts could be attributed to the steric effects of the bulk fused ring

 Table 2
 Optical properties of the compounds

	λ_{\max}^{abs}/nm	λ_{\max}^{em}/nm		$arPhi_{ m FL}$ (%)	
		b	С	d	е
VP ₃ -B ₃	338	454	456	0.6	17.4
VP ₃ -T ₃	342	454	459	0.9	21.2
VP_3 -(TB) ₃	342	459	460	1.6	24.8
VP ₃ -N ₃	331	455	452	1.1	17.9
VP ₃ -(BFu) ₃	345	467	462	1.0	33.5
VP_3 -(Bt) ₃	340	462	456	1.4	35.5
VP_3 -(TA) ₃	330	457	453	1.0	17.8

^{*a*} In THF. ^{*b*} In THF. ^{*c*} TLC thin film. ^{*d*} Fluorescence quantum yields measured in THF solution. ^{*e*} Fluorescence quantum yields measured in cyclohexane solution using 9,10-diphenylanthracene as standard.

units that hindered the intermolecular interaction that tended to decrease the planarity of the molecules. This suggested that the substitution of the fused rings did not bring great changes to the conjugation of the molecular structure.

The quantum yields (Φ_{FL}) of the compounds in THF with 9,10-diphenylanthracene as the standard ($\Phi_{FL} = 90\%$) ranged from 0.6 to 1.6%. However, the Φ_{FL} determined in cyclohexane was in a range of 17.4 to 35.5%. 15- and 33-fold increases in Φ_{FL} when compared to those of THF solutions and cyclohexane solutions, respectively.

AIE properties

Almost no PL signal could be detected from a dilute solution of the compounds in tetrahydrofuran (THF). The corresponding emission spectra of compound VP₃-T₃ in aqueous THF with different water/THF ratios are shown in Fig. 4. The emission from the THF solution of VP₃-T₃ was so weak that almost no PL signal was recorded. However, a dramatic enhancement in luminescence was observed for the ~70 : 30 (v/v) water/THF mixture. While the PL intensity in THF was only 20, it was boosted to 895 in 90 : 10 (v/v) water/THF. Similar effects were



Fig. 4 PL spectra of VP_3 - T_3 in water/THF mixtures. The inset depicts the changes in PL peak intensity.



Fig. 5 The emission images of VP_3 - T_3 in pure THF (a), H_2O 90% (b), and TLC thin film (c) under UV light (365 nm) illumination at room temperature.

observed for the other compounds. The emission images of VP₃-T₃ in pure THF, 90 : 10 (v/v) water/THF, and TLC solid thin film under UV light (365 nm) illumination at room temperature are shown in Fig. 5. As can be clearly seen, the THF solution of VP₃-T₃ showed a rather weak fluorescence. However, the compound in high water fractions of water/THF mixture or in solid thin film exhibited very strong fluorescence.

The absorption spectra of VP₃-T₃ in the water/THF mixtures are shown in Fig. 6. The spectral profile was virtually unchanged when up to ~30% water was added to the THF solution. When the water fraction was further increased, the whole spectrum started to rise. The increase in the absorbance in the whole spectral region was due to light scattering of the nano-aggregates, which effectively decreased the light transmission through the mixtures.⁷ The abrupt broad change in the shape of the absorbance from 70% water fraction agreed well with the sudden jump in the PL intensity and the quantum yield shown in Fig. 4 and Table 3. These results confirm that the VP₃-T₃ molecules started to markedly aggregate when >60% of the poor solvent (water) was added to the THF solution.

In order to have a quantitative estimation of the AIE process, the photoluminescent quantum yields (Φ_{FL}) were calculated for the derivatives in mixtures of water and THF in various proportions using 9,10-diphenylanthracene (DPA) as the standard. As can be seen from Table 3, the Φ_{FL} values of the THF solutions were very low and almost unchanged when water was added up to 60% (v/v), but it started to increase swiftly upon addition of 70% (v/v) water. However, the extent of the increase was not the same for each compound. For example, when the



Fig. 6 UV absorption spectra of VP_3 - T_3 in water/THF mixtures with different volume fractions of water.

Table 3 PL quantum yields (Φ_{FL}) of the compounds in mixtures of water and THF in various proportions

H ₂ O (%)	0	10	30	50	60	70	80	90
VP ₃ -B ₃	0.6	0.6	0.6	0.6	0.7	1.1	0.8	3.8
VP ₃ -T ₃	0.9	0.9	0.9	0.9	0.9	22	17	23
$VP_3-(TB)_3$	1.6	1.5	1.7	1.7	31	35	12	23
VP ₃ -N ₃	1.0	1.0	1.1	1.3	1.4	2.7	1.9	11
VP ₃ -(BFu) ₃	1.0	1.1	1.2	1.3	1.4	5.1	3.8	19
VP_3 -(Bt) ₃	1.4	1.4	1.6	1.8	2.3	2.5	2.0	22
VP_3 - $(TA)_3$	1.1	1.0	1.0	1.0	2.2	5.3	2.4	9.3



Fig. 7 Effect of temperature on the PL relative peak intensity of the compounds and DPA in THF.

volume fraction of water in the water/THF mixture was increased to 90%, the Φ_{FL} of VP₃-T₃ rose to 23%, which was about 25-fold higher than that in THF. However, to the same water fraction, the Φ_{FL} of VP₃-B₃ was only six-fold higher than that in the THF solution. The above results indicate that the compound molecules started to aggregate markedly when the volume fraction of water reached 60%. Since water is a non-solvent of these compounds, the molecules must have aggregated in the water/THF mixtures with higher contents of water. This proves that the emissions were induced by aggregation of the derivatives.

The effect of temperature on the PL relative peak intensity of the compounds in dilute THF solutions $(10^{-5} \text{ mol } L^{-1})$ is shown in Fig. 7. It can be seen that the relative peak intensity of DPA remained almost unchanged with the temperature increased from 77 K. In contrast, all of the new compounds had dramatic decreases near the melting point of THF ($T_{\rm m} \approx 165$ K). However, the extent of the decrease was not the same for each compound. The PL peak intensities of VP₃-B₃, VP₃-T₃, VP₃- $(TB)_3$, VP_3 - N_3 , VP_3 - $(BFu)_3$, VP_3 - $(Bt)_3$, and VP_3 - $(TA)_3$ near the T_m were about 159-, 112-, 51-, 153-, 34-, 19-, and 64-fold higher than those at room temperature, respectively. The extent of the decrease seems closely related to the size of substituent because it is well known that a large substituent rotates with more difficulty than a small substituent due to steric effects. Furthermore, the AIE effects of frozen compound molecules in the solid are similar to the effects of aggregation in liquid because of the restriction on the rotation of groups. Among the three substituents, phenyl, tolylene, and *p-tert*-butylphenyl, the phenyl group was the smallest and the *p-tert*-butylphenyl group was the biggest, which results in the following decreasing order of PL peak intensities: VP₃-B₃ (159-fold), VP₃-T₃ (112-fold), VP₃-(TB)₃ (51-fold). In addition, among the fused ring substituents, the naphthyl group was the smallest, and thus the extent of the decrease in VP₃-N₃ was the highest.

Electrochemical properties and electronic structure of the derivatives

It is well known that the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), which are connected to the redox potentials, are two important



Fig. 8 CV curve of VP_3 - T_3 in CH_2Cl_2 .

 Table 4
 Energy levels of the molecular orbitals and band gaps of the compounds

	HOMO/eV	LUMO/eV	$\Delta E_{\rm g}/{\rm eV}$
VP ₃ -B ₃	5.58	2.36	3.22
VP ₃ -T ₃	5.53	2.33	3.20
$VP_3-(TB)_3$	5.57	2.37	3.20
VP ₃ -N ₃	5.65	2.40	3.25
VP ₃ -(BFu) ₃	5.61	2.47	3.14
VP_3 -(Bt) ₃	5.66	2.46	3.20
VP_3 -(TA) ₃	5.54	2.25	3.29

parameters for electroluminescence materials. This is on account of their relationship with the hole-/electron-injecting ability in organic light emitting diodes (OLEDs). In order to measure the HOMO levels of the synthesized compounds, cyclic voltammetry (CV) analyses were carried out. As an example, the CV curve of VP₃-T₃ is shown in Fig. 8. The HOMO energy levels were obtained using the oxidation potential. The energy band gaps (ΔE_{g}) of the compounds were estimated from the onset wavelength of their UV absorptions. The LUMO energy levels were obtained by using the HOMO energy and the energy band gap $(\Delta E_{g} = \text{HOMO} - \text{LUMO})$. The HOMO, LUMO, and ΔE_{g} values are listed in Table 4. The ΔE_{g} values of the compounds were found to be in the range of 3.14-3.29 eV. Compounds VP₃-(BFu)₃ and VP₃-(TA)₃ exhibited the narrowest energy band gap and the widest energy band gap, respectively. The HOMO values ranged from 5.53 to 5.66 eV. Compound VP₃-T₃ had the lowest HOMO level and VP₃-(Bt)₃ had the highest HOMO level. The LUMO values ranged from 2.25 to 2.47 eV. VP₃-(TA)₃ possessed the lowest LUMO level and VP₃-(BFu)₃ possessed the highest LUMO level.

Device fabrication and electroluminescence properties

The strong blue light emission and high thermal stability of the compounds prompted us to use them to construct electroluminescence devices. As an example, a multilayer electroluminescence device, ITO/NPB/VP₃-(BFu)₃/Alq₃/LiF/Al, was fabricated using vapor deposition processes. 4,4'-Bis(1-naph-thylphenylamino)biphenyl (NPB) was used as the hole-transporting layer, and VP₃-(BFu)₃ as the emitting layer, 8-hydroxyquinoline aluminium (Alq₃) as the electron-



Fig. 9 The energy level diagram of $ITO/NPB/VP_3-(BFu)_3/Alq_3/LiF/Al$. (The energy levels except $VP_3-(BFu)_3$ were from literature.⁹)



Fig. 10 Current–voltage–luminance characteristics of the device (inset: the image was taken at 10 V voltage).

transporting layer. LiF was used between the electron-transporting layer and cathode Al to enhance electron injection, and indium-tin oxide (ITO) coated glass was used as the substrate and anode. The energy level diagram of the device is shown in Fig. 9.

The current–voltage–luminance characteristics of the unoptimized device without packaging are presented in Fig. 10. The turn-on voltage, which is defined as the voltage when the luminance is 1 cd m⁻², was 6.0 V, and a luminance of \sim 1500 cd m⁻² was obtained at 17 V.



Fig. 11 Electroluminescence spectrum of the device.

The electroluminescence (EL) spectrum of VP_3 -(BFu)₃ was shown in Fig. 11. Comparison of the EL spectrum with PL emission spectrum of the compound on TLC plate showed that the profiles of the EL band and the PL band were similar with about 12 nm red-shift for the EL peak (474 nm) compared with that of the PL peak (462 nm).

Extended investigation and further optimization on the electroluminescence devices based on the new series AIE compounds are being carried out in our laboratory and will be reported in due course.

Conclusions

We have developed a new class of AIE compounds, composed of triphenylethylene derivatives. The compounds exhibit a strongly enhanced emission in the aggregated state. The derivatives are all blue light emitters, and their maximum fluorescence emission wavelengths are 452–462 nm. The glass transition temperature range is from 70 to 145 °C, and the decomposition temperatures (5% weight loss) are in the range of 360–508 °C, both of which are higher than those of the silole derivatives ever reported in the literature. The compounds were used to construct electroluminescence devices. One such device containing VP₃-(BFu)₃ exhibits a turn-on voltage of 6.0 V and a luminance of ~1500 cd m⁻². It gave a considerable performance without further optimization of the device configurations.

Experimental

All reagents and chemicals purchased from Alfa Aesar were used as received. Tetrahydrofuran (THF) was distilled from sodium/ benzophenone. Ultra-pure water was used in the experiments. All other solvents were purchased as analytical grade from Guangzhou Dongzheng Company and used without further purification. ¹H NMR and ¹³C NMR were measured on a Mercury-Plus 300 spectrometer with chemical shifts reported as ppm (in CDCl₃, TMS as internal standard). Mass spectra were measured with Thermo spectrometers (MAT95XP-HRMS). Elemental analysis was done with an Elementar Vario EL Elemental Analyzer. Fluorescence spectra were determined with a Shimadzu RF-5301PC spectrometer and the slit widths were 1.5 nm for excitation and 3 nm for emission except VP_3 -(TB)₃ (excitation: 1.5 nm, emission: 1.5 nm). The fluorescence spectra at low temperature were done with an Edinburgh Instruments Ltd spectrometer (FLSP920). The Differential scanning calorimetry (DSC) curves were obtained with a NETZSCH thermal analyzer (DSC 204) at a heating rate of 10 °C min⁻¹ under a N₂ atmosphere. Thermogravimetric analyses (TGA) were performed with a TA thermal analyzer (Q50) under a N₂ atmosphere with a heating rate of 20 °C min⁻¹. The fluorescence quantum yields (Φ_{FL}) of all the compounds in THF or THF/ water mixture were evaluated using 9,10-diphenylanthracene as the reference.8

The THF–water mixtures with different water fractions were prepared by adding Ultra-pure water slowly into the THF solution of samples under ultrasound at room temperature. For example, a 70% water fraction mixture was prepared by adding 7 mL Ultra-pure water into 3 mL of an appropriate concentration THF solution of sample in a 10 mL volumetric flask. The concentrations of all samples were adjusted to 10 μM after adding Ultra-pure water.

Cyclic voltammetry (CV) measurement was carried out on a Shanghai Chenhua electrochemical workstations CHI660C in a three-electrode cell with a Pt disk working electrode, a Ag/AgCl reference electrode, and a glassy carbon counter electrode. All CV measurements were performed under an inert argon atmosphere with supporting electrolyte of 0.1 M tetrabutylammonium perchlorate (n-Bu₄NClO₄) in dichloromethane at a scan rate of 100 mV s⁻¹ using ferrocene (Fc) as standard. The HOMO energy levels were obtained using the onset oxidation potential from the CV curves. The lowest unoccupied molecular orbital/highest occupied molecular orbital (LUMO/HOMO) energy gaps, ΔE_g , for the compounds were estimated from the onset absorption wavelength of UV-vis absorption spectra.

Synthesis of VP₃-Br₃

A solution of bis(4-bromophenyl)methanone (5.00 g, 14.7 mmol) and diethyl 4-bromobenzylphosphonate (4.50 g, 14.7 mmol) in anhydrous THF (200 mL) was stirred under an argon atmosphere at room temperature. And then potassium tert-butyloxide (1.97 g, 17.6 mmol) was added and the mixture was stirred for 2 h. The reaction mixture was concentrated and purified by silica gel column chromatography using *n*-hexane as eluent. And a white powder was obtained with the yield of 87% (6.30 g). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.42 (t, 4H), 7.25 (d, 2H), 7.10 (d, 2H), 7.00 (d, 2H), 6.85 (d, 2H), 6.83 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 141.72, 141.26, 138.48, 135.81, 132.30, 132.20, 131.57, 131.54, 131.19, 129.38, 128.20, 127.95, 122.28, 121.35; FTIR (KBr) ν (cm⁻¹): 3022 (Ar and =C-H stretching), 1610, 1587, 1484, 822, 652; MS (EI), m/z: 492 ([M - H_{1}^{+} , calcd for $C_{20}H_{13}Br_3$, 493); Anal. Calc. for $C_{20}H_{13}Br_3$: C 48.72, H 2.66, Br 48.62; found: C 48.70, H 2.68, Br 48.59%.

General procedure for the synthesis of compounds VP₃-B₃, VP₃-T₃, VP₃-N₃, VP₃-(TB)₃, VP₃-(BFu)₃, VP₃-(Bt)₃ and VP₃-(TA)₃

VP₃-Br₃ (0.30, 0.6 mmol) and the corresponding boric acid (2.8 mmol) were dissolved in toluene (30 mL), and then 2 M aqueous K₂CO₃ solution (1.5 mL) and 5 drops of Aliquat336 were added. The mixture was stirred for 45 min under an argon atmosphere at room temperature. Then the Pd(Pph₃)₄ catalyst (catalytic amount) was added and the reaction mixture was stirred at 85 °C for 16 h. After cooling to room temperature, the product was concentrated and purified by silica gel column chromatography using dichloromethane/*n*-hexane (v/v = 1/3). Yields of products: VP₃-B₃ 53%; VP₃-T₃ 56%; VP₃-N₃ 64%; VP₃-(TB)₃ 71%; VP₃-(BFu)₃ 42%; VP₃-(Bt)₃ 62%; VP₃-(TA)₃ 74%.

VP₃-B₃. ¹H NMR (300 MHz, CDCl₃) δ : 7.71–7.53 (m, 10H), 7.50–7.28 (m, 15H), 7.18 (d, 2H), 7.09 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 142.54, 142.03, 140.83, 140.78, 140.71, 140.55, 140.35, 139.54, 136.59, 131.10, 130.24, 129.02, 128.94, 128.29, 128.05, 127.58, 127.45, 127.20, 127.04, 126.86; FTIR (KBr) ν (cm⁻¹): 3029 (Ar and =C–H stretching), 1594, 1487, 1447, 845, 762,694; MS (EI), *m/z*: 484 ([M]⁺, calcd for C₃₈H₂₈, 484); Anal. Calc. for C₃₈H₂₈: C 94.18, H 5.82; found: C 94.09, H 5.86%. **VP₃-T₃.** ¹H NMR (300 MHz, CDCl₃) δ: 7.62–7.41(m, 12H), 7.41–7.25 (m, 6H), 7.25–7.22 (d, 2H), 7.19–7.11 (q, 4H), 7.03 (s, 1H), 2.39 (d, 6H), 2.36 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 142.32, 141.96, 140.42, 140.22, 139.44, 139.26, 137.97, 137.93, 137.86, 137.32, 137.19, 136.35, 131.06, 130.19, 129.72, 129.65, 128.23, 127.91, 127.32, 127.01, 126.87, 126.61, 21.54; FTIR (KBr) ν (cm⁻¹): 3029 (Ar and =C–H stretching), 2921, 2856, 1620, 1500, 1447, 1396, 810; MS (EI), *m/z*: 526 ([M]⁺, calcd for C₄₁H₃₄, 526); Anal. Calc. for C₄₁H₃₄: C 93.49, H 6.51; found: C 93.44, H 6.58%.

VP₃-N₃. ¹H NMR (300 MHz, CDCl₃) δ : 8.03–7.98 (q, 2H), 7.95–7.81 (m, 7H), 7.63–7.37 (m, 20H), 7.37–7.25 (q, 4H), 7.24 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 142.37, 140.32, 140.20, 140.04, 139.49, 136.62, 134.01, 131.75, 131.66, 130.80, 130.57, 130.29, 130.01, 129.78, 128.53, 128.38, 127.94, 127.86, 127.71, 127.22, 127.14, 126.26, 126.15, 126.00, 125.61; FTIR (KBr) ν (cm⁻¹): 3036 (Ar and =C-H stretching), 1589, 1500, 1447, 845, 800, 775; MS (EI), *m/z*: 634 ([M]⁺, calcd for C₅₀H₃₄, 634); Anal. Calc. for C₅₀H₃₄: C 94.60, H 5.40; found: C 94.57, H 5.44%.

VP₃-(TB)₃. ¹H NMR (300 MHz, CDCl₃) δ : 7.61 (d, 4H), 7.55 (d, 4H), 7.50–7.30 (m, 14H), 7.12 (d, 2H), 7.05 (s, 1H), 1.37 (t, 18H), 1.34 (d, 9H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 150.58, 150.50, 150.40, 142.27, 141.96, 140.34, 140.10, 139.34, 139.29, 137.97, 137.88, 137.82, 136.36, 131.02, 130.18, 128.18, 127.92, 127.37, 126.97, 126.82, 126.65, 125.96, 125.88, 34.93, 31.75; FTIR (KBr) ν (cm⁻¹): 3029 (Ar and =C–H stretching), 2961, 2866, 1607, 1497, 1459, 1260, 1113, 822; MS (EI), *m/z*: 652([M]⁺, calcd for C₅₀H₅₂, 652); Anal. Calc. for C₅₀H₅₂: C 91.97, H 8.03; found: C 91.91, H 8.08%.

VP₃-(BFu)₃. ¹H NMR (300 MHz, CDCl₃) δ : 8.08–7.88 (m, 9H); 7.88–7.70 (m, 4H); 7.68–7.53 (m, 8H), 7.53–7.29 (m, 12H), 7.21 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 156.32, 153.57, 143.03, 142.41, 139.98, 137.06, 135.88, 135.02, 131.05, 130.21, 129.32, 128.86, 128.64, 128.50,128.26, 127.45, 126.92, 126.76, 125.56, 125.28, 125.18, 124.39, 123.48, 123.00, 120.90, 119.97, 119.83; FTIR (KBr) ν (cm⁻¹): 3029 (Ar and =C-H stretching), 1585, 1515, 1450, 1392, 1191, 840, 750; MS (EI), *m/z*: 754 ([M]⁺, calcd for C₅₆H₃₄O₃, 754); Anal. Calc. for C₅₆H₃₄O₃: C 89.10, H 4.54; found: C 89.12, H 4.51%.

VP₃-(Bt)₃. ¹H NMR (300 MHz, CDCl₃) δ : 8.21–8.09 (m, 6H); 7.86–7.74 (m, 7H), 7.64–7.56 (m, 6H), 7.56–7.37(m,12H), 7.28 (d, 2H), 7.21 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 142.91, 142.37, 140.13, 140.06, 139.75, 139.25, 138.83, 138.68, 138.59, 137.20, 136.89, 136.76, 136.48, 135.96, 131.14, 130.32, 128.99, 128.62, 128.44, 128.29, 128.17, 127.05, 125.36, 124.60, 122.86, 121.95, 120.77, 120.66; FTIR (KBr) ν (cm⁻¹): 3057 (Ar and =C– H stretching), 1602, 1580, 1510, 1454, 1439, 1382, 795, 745; MS (EI), *m/z*: 803 ([M]⁺, calcd for C₅₆H₃₄S₃, 803); Anal. Calc. for C₅₆H₃₄S₃: C 83.75, H 4.27, S 11.98; found: C 83.77, H 4.25, S 12.01%.

VP₃-(TA)₃. ¹H NMR (300 MHz, CDCl₃) δ : 7.60 (d, 2H), 7.38– 7.26 (m, 14H), 7.24–7.13 (m, 6H), 7.13–7.03 (q, 2H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 142.40, 142.29, 139.85, 139.72, 138.86, 137.04, 136.54, 136.47, 136.41, 136.12, 136.06, 135.71, 135.59, 135.29, 135.18, 135.13, 130.40, 130.24, 129.72, 129.40, 129.07, 128.67, 128.50, 127.95, 127.77, 127.51, 127.29; FTIR (KBr) ν (cm⁻¹): 3050(Ar and =C-H stretching), 1605, 1574, 1507, 1439, 1384, 1108, 842, 747; MS (EI), *m/z*: 899 ([M]⁺, calcd for C₅₆H₃₄S₆, 899); Anal. Calc. for C₅₆H₃₄S₆: C 74.79, H 3.81, S 21.39; found: C 74.74, H 3.86, S 21.33%.

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