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### Piezofluorochromic and Aggregation-Induced-Emission Compounds Containing Triphenylethylene and Tetraphenylethylene Moieties

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Abstract: New fluorescent compounds containing triphenylethylene and tetraphenylethylene moieties were synthesized, and their piezofluorochromic and aggregation-induced emission behaviors were investigated. The results show that all compounds exhibit aggregation-induced emission characteristics and only the crystalline compound possesses piezofluorochromic properties. The color, emission spectra, and mor-

### Introduction

Piezofluorochromic or piezochromic fluorescent materials are "smart" or "intelligent" materials whose fluorescence properties change in response to external pressure stimuli. As such, piezofluorochromic materials are one class of mechanoresponsive materials and have various potential applications in optical recording and pressure-sensing systems. Piezofluorochromic behavior can be achieved by changing the molecular chemical structures or altering the mode of solid-state molecular packing. It is believed that the latter change is easier than the former for affording dynamic control of the solid-state fluorescence with high efficiency and reversibility because the latter is implemented by a physical change and the former is implemented by a chemical reaction. It is well known that most chemical reactions in the

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phological structures of the one piezofluorochromic compound exhibit reversibility upon grinding and annealing (or fuming) treatments. The piezofluorochromic behaviors are caused by a

**Keywords:** emission • fluorescence • piezofluorochromism • stimuliresponsive materials • X-ray diffraction change between different modes of solid state molecular packing under external pressure. The single crystal Xray diffraction analysis reveals that the twisted conformation of the aggregation-induced emission compound leads to the formation of metastable crystal lattice with cavity which is readily destroyed under external pressure. A possible mechanism of piezofluorochromic phenomenon has been proposed.

solid state are incomplete and irreversible. Even worse, most chemical reactions often lead to loss of fluorescence ability. However, piezofluorochromic materials that are dependent on a physical change remain extremely rare.<sup>[1]</sup>

Recently, we reported some aggregation-induced emission (AIE) compounds containing a phenylvinylanthracene moiety.<sup>[2]</sup> Interestingly, four of these compounds are piezofluorochromic compounds. We realized that there exists a relationship between AIE and piezofluorochromic phenomena, and called them piezofluorochromic aggregation-induced emission (PAIE) materials as they possess both piezofluorochromism and aggregation-induced emission properties. AIE materials are an important class of luminescent materials, first reported by Tang and co-workers,<sup>[3]</sup> and exhibit many special properties, such as strong solid emission, excellent device performance and highly stimuli-sensitive fluorescence.<sup>[4]</sup> We believe that PAIE materials have the advantages of both piezofluorochromic materials and aggregation-induced emission materials and can be used more widely. To the best of our knowledge, so far there have only been five PAIE compounds (the molecular structures are shown in the Supporting Information, Scheme S1) reported in the literature. One is DBDCS reported in 2010 by Park's group,<sup>[5]</sup> and the others have been reported recently by ourselves.<sup>[2]</sup> The former contains two butoxy groups and two cyano groups in its molecular structure, which means it should not have good thermal stability properties, such as high glass-transition temperature and high decomposition temperature. However, the latter structures, which contain phenylvinylanthracene, are wholly aromatic structures with high thermal stabilities. For the former, the two-color luminescence-switching behavior was explained as an interchange between the metastable green-emitting G-phase and the thermodynamically stable blue-emitting B-phase with different modes of local dipole coupling (antiparallel and head-to-tail arrangements, respectively); the origin of this interchange was the two-directional shear-sliding capability of molecular sheets formed via intermolecular multiple C-H .....N and C-H .....O hydrogen bonds. However, for the latter compounds, there were no such hydrogen bonds in their structures. Thus, we proposed a mechanism to explain the PAIE phenomenon: destruction of the crystalline structure leads to the planarization of the molecular conformation, resulting in a red shift of photoluminescence (PL) spectrum. In our previous papers, although the change in packing structures before and after pressing was observed using wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC), single-crystal X-ray diffraction analysis for direct confirmation of the proposed mechanism was not provided because of the failure to grow single crystals of the compounds owing to their bulky molecular structures.

Herein, we reported a new series of AIE compounds containing triphenylethylene and tetraphenylethylene moieties. The compound,  $VP_3$ -(TPE)<sub>1</sub>, exhibited PAIE properties and its structure was determined by single-crystal X-ray diffraction analysis. We anticipate that this work could offer us the opportunity to elucidate the origin of the unique piezofluorochromic characteristics of AIE materials.

### **Results and Discussion**

The target compounds, triphenylethene combined with different numbers of tetraphenylethene groups, were synthesized by palladium-catalyzed Suzuki-coupling reactions of

#### Abstract in Chinese:

本文合成了三个同时含三苯乙烯和四苯乙烯的新型发光化合物并对它们的 聚集诱导发光和压致变色发光行为进行了研究。结果表明,这些化合物均具 有聚集诱导发光性质,但只有具有结晶性的一个化合物表现出压致变色发光 行为。在进行研磨或退火(或溶剂诱导)处理时,样品的颜色、发光光谱以及 聚集态结构均表现出很好的可逆转变。压致变色发光行为产生的原因被认为 是在外力的作用下聚集态结构发生了改变所造成的。单晶衍射分析数据表 明,分子在晶体结构中比在单分子状态具有更加扭曲的空间构象,存在较大 的扭曲应力。在晶体结构中,弱的分子间作用力和扭曲构象导致分子不能进 行规整堆砌而使晶体结构存在大量的缺陷。上述结构特点导致晶体结构很容 易被外力破坏而产生压致变色发光现象。 triphenylethylene bromides with tetraphenylethylene boronic acid in moderate yields (54%-61%; Scheme 1). The triphenylethylene bromide, VP<sub>3</sub>-Br<sub>2</sub>, was synthesized through a Wittig-Horner reaction of the ylide reagent diethyl benzylphosphonate with 4,4'-dibromobenzophenone, whilst VP<sub>3</sub>-Br and VP<sub>3</sub>-Br<sub>3</sub> were synthesized under the same conditions from the reactions of diethyl 4-bromobenzylphosphonate with benzophenone and 4,4'-dibromobenzophenone, respectively. 4-(1,2,2-Triphenylvinyl)phenylboronic acid (TPE-B) was synthesized from diphenylmethane in three steps.<sup>[6]</sup> The hydroxy intermediate, TPE(OH)-Br, was not purified further and was used directly in the next step. After the dehydration reaction of TPE(OH)-Br in the presence of para-toluenesulfonic acid, the bromide intermediate TPE-Br was obtained. TPE-B was then prepared from TPE-Br by lithiation with *n*-butyllithium and boronation with trimethylborate. The products were purified by column chromatography on silica gel using dichloromethane/n-hexane as the eluent. Their molecular structures were confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, high-resolution mass spectrometry (HRMS), Fourier-transform infrared spectroscopy (FT-IR), and elemental analysis (EA).

To determine whether or not these compounds are AIEactive, the UV/Vis absorption and PL emission behaviors of their diluted mixtures were studied in a mixture of water/ tetrahydrofuran with different water fractions. Because the compounds were insoluble in water, increasing the water fraction in the mixed solvent could thus change their existing forms from a solution state in the pure tetrahydrofuran to the aggregated particles in the mixtures with high water content, which results in changes in the UV and PL spectra.

The absorption spectra of  $VP_3$ -(TPE)<sub>1</sub> in the water/tetrahydrofuran mixtures are shown in Figure 1. The UV/Vis spectra for the other compounds are provided in the Supporting Information, Figure S1. The spectral profile was virtually unchanged, even when a water fraction of up to circa 60% was added to the tetrahydrofuran solution. When the water fraction was increased further, the entire spectrum started to rise. The increase in absorbance in the entire spectral region was caused by the Mie effect<sup>[7]</sup> of the nanoaggregate suspensions in the solvent mixtures. The result showed



Figure 1. UV absorption spectra of  $VP_3$ -(TPE)<sub>1</sub> in water/THF mixtures with different volume fractions of water. THF = tetrahydrofuran.

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Scheme 1. Synthetic routes for the compounds.

that the  $VP_3$ -(TPE)<sub>1</sub> molecules started to markedly aggregate when the mixture contained circa 70% of water.

Almost no PL signals could be detected from the dilute solutions of the compounds in tetrahydrofuran. The corresponding emission spectra of compound  $VP_3$ -(TPE)<sub>1</sub> in aqueous tetrahydrofuran with different water/tetrahydrofuran ratios are shown in Figure 2 as an example (PL spectra



Figure 2. PL spectra of  $VP_3$ -(TPE)<sub>1</sub> in water/THF mixtures. The inset depicts the changes of PL peak intensity.

luminescence was observed for the approximately 70:30 (v/ v) water/tetrahydrofuran mixture. Whilst the PL intensity in tetrahydrofuran was only 4, it was boosted to circa 334 in 95:5 (v/v) water/tetrahydrofuran, enhanced about 50 times. Similar effects were observed for the other compounds. A comparison of the UV/Vis absorption and PL emission spectra showed that the abrupt broad change in the shape of the absorbance for the mixture with approximately 70% water agreed well with the sudden jump in the PL intensity; this result confirmed that the emission enhancements were induced by aggregation of the molecules. In other words, the compounds are AIE active. A photograph showing the emission of the compounds in pure tetrahydrofuran and 95:5 (v/v) water/tetrahydrofuran

of the other compounds are shown in the Supporting Infor-

mation, Figure S2). The emission from the tetrahydrofuran

solution of  $VP_3$ -(TPE)<sub>1</sub> was so weak that almost no PL

signal was recorded. However, a dramatic enhancement in

pure tetrahydrofuran and 95:5 (v/v) water/tetrahydrofuran under UV light (365 nm) at room temperature is shown in Figure 3. Clearly, tetrahydrofuran solutions of the compounds showed extremely weak fluorescence. However, the compounds in high water content water/tetrahydrofuran mixtures exhibited very strong fluorescence, thus indicating that the compounds had a strong AIE effect.



Figure 3. Emission images of the compounds in pure THF (10  $\mu$ M) and 95% water/THF solution (v/v) under UV light (365 nm) at room temperature: a) VP<sub>3</sub>-(TPE)<sub>1</sub>, b) VP<sub>3</sub>-(TPE)<sub>2</sub>, and c) VP<sub>3</sub>-(TPE)<sub>3</sub>.

The photoluminescence quantum yields ( $\Phi_{FL}$ ) were calculated for the compounds in mixtures of water and tetrahydrofuran in various proportions using 9,10-diphenylanthracene (DPA) as the standard to obtain a quantitative estimation of the AIE process. In Figure 4, the  $\Phi_{FL}$  values of the



Figure 4. Photoluminescence quantum yields  $(\Phi_{FL})$  of the compounds in water/THF mixtures with different volume fractions of water.

tetrahydrofuran solutions were very low and almost unchanged before the compound molecules started to aggregate markedly. However, the  $\Phi_{FL}$  values started to increase swiftly upon addition of a certain amount of water. The amount of water added to show the AIE effect was not the same for each compound owing to the difference in solubility. The volume fractions of water in the water/tetrahydrofuran mixtures where the  $\Phi_{FL}$  could be observed with noticeable change were 70%, 60%, and 50% for VP<sub>3</sub>-(TPE)<sub>1</sub>, VP<sub>3</sub>-(TPE)<sub>2</sub>, and VP<sub>3</sub>-(TPE)<sub>3</sub>, respectively.

Similarly, the extent of the increase was not the same for each compound. For example, when the volume fraction of water in the water/tetrahydrofuran mixture was increased to 95%, the  $\Phi_{FL}$  of VP<sub>3</sub>-(TPE)<sub>2</sub> rose to 11.2%, about 140-fold higher than that in tetrahydrofuran ( $\Phi_{FL} = 0.08\%$ ). For all the compounds, the increasing extents of  $\Phi_{FL}$  in 95% water

fractions were much higher (>50 folds) than those in the tetrahydrofuran solutions.

A decrease in photoluminescence intensity and photoluminescence  $\Phi_{FL}$  values during the addition of water was observed. This phenomenon is often observed in some compounds with AIE properties<sup>[8]</sup> and the reasons remain unclear.

The as-synthesized sample of  $VP_3$ -(TPE)<sub>1</sub>, as well as the annealed material and the fumed product with a good solvent vapor such as dichloromethane, was a white powder, and when illuminated with a 365 nm UV lamp, it emitted a strong blue light, as shown in Figure 5 (named as the B-



Figure 5.  $VP_3$ -(TPE)<sub>1</sub> taken at room temperature under natural (left) and UV light (right). Samples: (B<sub>1</sub>) as-synthesized sample; (G<sub>1</sub>) ground sample; (B<sub>2</sub>) annealed sample; (G<sub>2</sub>) re-ground sample.

form). However, the ground samples are a light-green powder and show green emission under the UV lamp (named as G-form). This result indicates that the grinding and annealing (or fuming) treatments can induce reversible interchanges in emissions (green and blue) and molecularpacking modes (G-form and B-form), exhibiting significant piezofluorochromic behaviors.

The as-synthesized powder of  $VP_{3}$ -(TPE)<sub>1</sub> was spread on a filter paper and a letter "M" was written on it with a metal spatula. Under the UV lamp, a green "M" is observed against the blue background (Figure 6).This result suggests that the material has the potential for application as an optical recording material.

Figure 7 shows the PL spectra of  $VP_3$ -(TPE)<sub>1</sub> after grinding and annealing treatments. The wavelength changes in solid-state emission could be repeated many times, 454 nm for the B-form and 482 nm for the G-form, indicative of an excellent reversibility in the two-way switching process. Except for the annealing treatment, the PL spectra of the Bform can be completely restored when fuming the ground sample with the vapor of a good solvent, such as dichloromethane.



Figure 6. An image taken at room temperature under 365 nm UV light: The as-synthesized powder of  $VP_3$ -(TPE)<sub>1</sub> was spread on a filter paper and a letter "M" was written with a metal spatula.



Figure 7. PL spectra of  $VP_{3^-}(TPE)_1$ : as-synthesized sample (B<sub>1</sub>); ground sample (G<sub>1</sub>); annealed sample (B<sub>2</sub>); re-ground sample (G<sub>2</sub>); re-annealed sample (B<sub>3</sub>); ground powder in dichloromethane vapor for 5 seconds (B<sub>V</sub>). Inset: repeated switching between blue and green states of the emission by cycles of grinding and annealing.

To further explore the aggregate structures of these different forms of VP<sub>3</sub>-(TPE)<sub>1</sub>, WAXD experiments were conducted (Figure 8). According to the WAXD measurements,  $VP_3$ -(TPE)<sub>1</sub> forms different molecular aggregates before and after grinding treatment. The diffraction curves of the as-synthesized, annealed, and fumed samples (B-form) display sharp, intense reflections. This result indicates that the B-form is crystalline. However, after grinding, many reflection peaks weakened or disappeared, and the diffraction curves became diffuse. But two peaks at 19.3° and 20.1° still remained. This result indicates that after grinding, most of the ordered structures have been destroyed, but the grinding sample still has some crystallinity. The WAXD results indicate that the grinding treatment leads to a change in the mode of solid-state molecular packing from high-order to low-order. From Figure 8, the B<sub>1</sub>, B<sub>2</sub>, B<sub>3</sub>, and B<sub>v</sub> curves are almost the same, which indicates that the ordered structures



Figure 8. WXRD of VP<sub>3</sub>-(TPE)<sub>1</sub> : as-synthesized sample ( $B_1$ ); ground sample ( $G_1$ ); annealed sample ( $B_2$ ); re-ground sample ( $G_2$ ); re-annealed sample ( $B_3$ ); ground powder in dichloromethane vapor for 5 seconds ( $B_V$ ).

destroyed by grinding can be restored by annealing or fuming.

The first heating DSC results are shown in Figure 9. The as-synthesized sample has a melting peak at around 216°C from the first heating run. During the second heating (see the Supporting Information, Figure S3), only a glass transition at around 90°C was observed, with no melting peak; this result indicates that it is difficult to crystallize from its melt during the cooling procedure. Interestingly, the samples after grinding reproducibly showed a cold-crystallization transition peak at around 117°C, which indicates that there is a metastable aggregation structure in the ground sample which would transfer to the more-stable state. This relatively stable aggregation structure refers to the crystal of the melting peak around 216°C. After treatment by annealing at 150°C or solvent fuming by dichloromethane for 5 seconds, the cold-crystallization transitions disappeared and the



Figure 9. DSC of VP<sub>3</sub>-(TPE)<sub>1</sub>: as-synthesized sample (B<sub>1</sub>); ground sample (G<sub>1</sub>); annealed sample (B<sub>2</sub>); re-ground sample (G<sub>2</sub>); re-annealed sample (B<sub>3</sub>); ground powder in dichloromethane vapor for 5 seconds (B<sub>V</sub>).

shapes of the two DSC curves were almost the same as that obtained from the as-synthesized sample. These results further indicate that the grinding treatment causes the change in morphology of the compound; and also that the change in morphology can easily be restored through annealing or fuming.

Time-resolved emission-decay behaviors of the compound sample before and after grinding were studied. The time-resolved fluorescence curves are illustrated in Figure 10. The



Figure 10. Time-resolved emission-decay curves of VP<sub>3</sub>-(TPE)<sub>1</sub>.

lifetime data were processed according to the literature method.<sup>[9]</sup> Decay in the fluorescence intensity (I) with time (t) was fitted by a double-exponential function:

$$I = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$$
(1)

where  $\tau_1$  and  $\tau_2$  are the lifetimes of shorter- and longer-lived species, respectively, and  $A_1$  and  $A_2$  are their respective amplitudes. The weighted mean lifetime ( $\langle \tau \rangle$ ) was calculated according to Equation (2):

$$<\tau>=(A_1\tau_1+A_2\tau_2)/(A_1+A_2)$$
 (2)

The lifetime data are summarized in Table 1. As can be seen from the table, there are two relaxation pathways in their fluorescence decays. This observation implies that the time-resolved PL spectra of the compound include independent emissions from the segments with different  $\pi$ -conjugation lengths because multiple lifetimes were detected. For the two samples, different pathways played different predominant roles. The excited molecules of the as-synthesized sample mainly decay through the first pathway ( $A_1$ =0.84).

Table 1. Fluorescence decay parameters of  $\mbox{VP}_3\mbox{-}(\mbox{TPE})_1$  before and after grinding.

	$\tau_1 [ns]$	$\mathbf{A}_1$	$\tau_2 [ns]$	$A_2$	$< \tau > [ns]$
Pre-grinding	1.03	0.84	2.33	0.16	1.24
Ground	1.42	0.56	2.50	0.44	1.90

However, for the ground sample, the  $A_1$  value is 0.56, showing an obvious difference. The weighted mean lifetimes  $\langle \tau \rangle$  of the as-synthesized and ground samples are 1.24 ns and 1.90 ns, respectively. This result indicates that the molecule in the G-form has a longer lifetime than that in the B-form and the change in  $\langle \tau \rangle$  is believed to be caused by a change of aggregation structure after grinding.

A single crystal of  $VP_3$ -(TPE)<sub>1</sub> was successfully grown from a tetrahydrofuran/methanol solution and its crystalline structure was determined by single-crystal X-ray diffraction analysis. The selected crystallographic data are given in the Supporting Information, Table S1.  $VP_3$ -(TPE)<sub>1</sub> crystallized in the monoclinic space group *P*21/*n*. The crystal structure of  $VP_3$ -(TPE)<sub>1</sub> shows four molecules in a crystal unit (Figure 11, bottom).



Figure 11. The molecular conformation in the single crystal with defined planes (top), and the molecular packing in a crystal unit (bottom).

The geometry of the isolated free molecule of the compound in the ground state was optimized based on B3LYP/ 6-31G calculations using the GAUSSIAN 03 package program.<sup>[10]</sup> Based on the optimized geometry, the selected dihedral angles between the aryl rings as defined in Figure 11 (top) as well as those in the single crystal were calculated and collected in Table 2. The values of the dihedral angles in the free and crystalline states are greater than 59 and 61°, respectively, thus indicating that the molecule takes a highly twisted conformation either in the free or crystalline state. The values of the dihedral angles in the single crystal are greater than those in the isolated free molecule and the difference suggests that a high twist-stress exists for the mole-

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Table 2. The dihedral angles of the selected planes of the molecule in single crystal and free molecule.

Plane	D-C	A-B	B-C	E-G	F-G
Free molecule <sup>[a]</sup>	76.2	77.2	75.7	59.2	74.8
Single crystal <sup>[b]</sup>	87.9	81.1	78.3	61.8	81.7

[a] Geometry determined from calculations using Gaussian 03; [b] Geometry determined by single-crystal X-ray diffraction.

cule in the crystalline state. Such twist stress is believed to be released when triggered by external pressure, which probably causes the loss of the long-range order of the crystal structure (i.e. destruction of the crystalline structure leads to the planarization of molecular conformation resulting in a red shift of the PL spectrum).

As mentioned above, owing to the twisted conformation, the backbone of the molecule largely deviates from a plane and typical coplanar  $\pi$ - $\pi$  stacking becomes impossible. From Figure 11, it can be seen that the molecules are packed via weak C-H···· $\pi$  interactions in a crystal cell. This result suggests that the VP<sub>3</sub>-(TPE)<sub>1</sub> crystal has a low lattice energy. Because of the twisted conformation and weak  $\pi$ - $\pi$  interactions, the molecular packings are relatively loose and there are some defects (cavities), as shown in Figure 12. Clearly, the cavities are the most-feeble parts of the crystalline structures. The two structural features, the low lattice energy and the existence of cavities, make the crystal readily destroyable by external pressure. The destruction of the crystalline structure leads to planarization of the molecular conformation because of the release of twist



Figure 12. Molecular packing in the single crystal: wireframe (top) and space-fill representations (bottom).

stress, which is shown by the increase of molecular conjugation thus resulting in a red-shift of PL spectrum from 454 nm to 482 nm (Figure 7). This molecular mechanism may explain the piezofluorochromic behavior of this PAIE compound.

Why then do  $VP_3$ -(TPE)<sub>2</sub> and  $VP_3$ -(TPE)<sub>3</sub> not also exhibit piezofluorochromic behavior? We can get the answer from the WAXD and DSC studies of the three as-synthesized samples. As shown in Figure 13 and 14,  $VP_3$ -(TPE)<sub>2</sub> and  $VP_3$ -(TPE)<sub>3</sub> must be amorphous because there are not any



Figure 13. WAXD curves of the as-synthesized samples.



Figure 14. The first heating DSC curves of the as-synthesized samples.

sharp and intense reflections in their WAXD curves and no melting peaks in their heating DSC curves. From Figure 11 (top), it can be seen that the conformation of tetraphenylethylene moiety is highly twisted. Clearly, the higher the number of tetraphenylethylene moieties in a molecule, the harder it becomes to efficiently pack the molecules, resulting in an amorphous structure. However, for VP<sub>3</sub>-(TPE)<sub>1</sub>, there were many sharp reflection peaks in its WAXD curve and a sharp melting peak around 216 °C in its DSC curve, thereby indicating that  $VP_{3}$ - $(TPE)_{1}$  is a crystalline compound. Given that the piezofluorochromic behavior depends on a packing change from a high-order aggregation state to a low-order aggregation state, the packing structures of  $VP_{3}$ - $(TPE)_{2}$  and  $VP_{3}$ - $(TPE)_{3}$  were amorphous to begin with, and accordingly it is impossible to make further changes under external pressure; therefore, the two compounds are not PAIE-active. We can now conclude that piezofluorochromism is a general characteristic of crystalline AIE materials.

### Conclusions

A new series of aggregation-induced emission compounds containing triphenylethylene and tetraphenylethylene moieties has been synthesized. Only compound VP<sub>3</sub>-(TPE)<sub>1</sub> exhibited piezofluorochromic behavior. The spectroscopic properties and morphological structures exhibited reversible changes upon grinding and annealing (or fuming) processes. The piezofluorochromic behavior is caused by a change between two modes of solid-state molecular packing under external pressure. The twisted conformation of the aggregation-induced emission compound leads to the formation of a metastable crystal lattice with some cavities which are easily destroyed under external pressure. The planarization of molecular conformation leads to an increase in molecular conjugation and a red-shift in the PL spectrum from 454 to 482 nm. Piezofluorochromism is a general characteristic of crystalline AIE materials.

#### **Experimental Section**

#### Materials and Measurements

Bis(4-bromophenyl)methanone, benzophenone, diethyl benzylphosphonate, diethyl 4-bromobenzylphosphonate, potassium tert-butyloxide, n-butyllithium in hexane (2.2M), diphenylmethane, tetrakis (triphenylphosphine) palladium(0), trimethylborate, para-toluenesulphonic acid, and tetrabutyl ammonium bromide (TBAB) were all purchased from Alfa Aesar and were used as received. All other reagents and solvents were purchased as analytical grade from Guangzhou Dongzheng Company (China) and used without further purification. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. Ultra-pure water was used in the experiments. VP<sub>3</sub>-Br,<sup>[11]</sup> VP<sub>3</sub>-Br<sub>3</sub><sup>[12]</sup>, and TPE-B<sup>[6]</sup> were synthesized according to literature methods. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Mercury-Plus 300 spectrometer (CDCl3 as solvent and tetramethylsilane, TMS as the internal standard). High-resolution mass spectra (HRMS) were measured on a Thermo MAT95XP-HRMS spectrometer. Elemental analyses (EA) were performed with an Elementar Vario EL elemental analyzer. FT-IR spectra were obtained on a Nicolet NEXUS 670 spectrometer (KBr pellet). UV/Vis absorption spectra (UV) were determined on a Hitachi U-3900 spectrophotometer. Fluorescence spectra (PL) were measured on a Shimadzu RF-5301PC spectrometer with a slit width of 1.5 nm for excitation and 3 nm for emission. Thermal behaviors were determined by differential scanning calorimetry (DSC) at heating and cooling rates of 10°Cmin<sup>-1</sup> under a N<sub>2</sub> atmosphere using a NETZSCH thermal analyzer (DSC 204F1). Time-resolved emissiondecay behaviors were measured on an Edinburgh Instruments Ltd spectrometer (FLSP920). Wide-angle X-ray diffraction (WAXD) measurements were performed using a Bruker X-ray diffractometer (D8 AD-VANCE, Germany) with an X-ray source of  $Cu_{K\alpha}$  ( $\lambda = 0.15406$  nm) at 40 kV and 40 mA, at a scan rate of 4° (20) min<sup>-1</sup>. Single crystals of the compound were grown from tetrahydrofuran/methanol mixtures. X-ray crystallographic intensity data were collected at 110 K using a Bruker Smart 1000 CCD diffractometer equipped with graphite monochromated Enhance (Mo) X-ray source ( $\lambda = 0.71073$  Å). The structures were solved by the direct methods following difference Fourier syntheses, and refined by the full-matrix least-squares method against  $F_0^2$  using SHELXTL software.<sup>[13]</sup> Ground samples were prepared by grinding using a pestle and mortar. Annealing experiments were done on a hot-stage with an automatic temperature-control system. The water/THF mixtures with different fractions were prepared by slowly adding distilled water into solutions of the samples in THF under sonication at room temperature. CCDC 810816 (VP<sub>3</sub>-(TPE)<sub>1</sub>) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

#### Synthesis of VP<sub>3</sub>-Br<sub>2</sub>

A solution of bis(4-bromophenyl)methanone (2.00 g, 5.8 mmol) and diethyl benzylphosphonate (1.98 g, 8.7 mmol) in anhydrous THF (40 mL) was stirred under an argon atmosphere at room temperature. Then potassium *tert*-butyloxide (1.17 g, 10.4 mmol) was added and the mixture was stirred for 4 h. The reaction mixture was concentrated and purified by column chromatography on silica gel using *n*-hexane as the eluent. White crystalline powder was obtained in a yield of 88% (2.10 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =7.42 (d, 4H), 7.14 (m, 5H), 7.02 (d, 4H), 6.92 ppm (s, 1H); FT-IR (KBr):  $\tilde{\nu}$ =3058, 3023, 1585, 1485, 1446, 822, 745, 692, 576 cm<sup>-1</sup>; HRMS (EI), *m/z*: 414 ([*M*]<sup>+</sup>, calcd for C<sub>20</sub>H<sub>14</sub>Br<sub>2</sub>, 414); Anal. calcd for C<sub>20</sub>H<sub>14</sub>Br<sub>2</sub>: C 58.00, H 3.41; found: C 57.91, H 3.48.

#### Synthesis of VP<sub>3</sub>-(TPE)<sub>1</sub>

TPE-B (0.36 g, 0.95 mmol) and VP<sub>3</sub>-Br (0.29 g; 0.86 mmol) were dissolved in toluene (30 mL), and then 2M aqueous K2CO3 solution (0.5 mL) and TBAB (0.1 g) were added. The mixture was stirred for 40 min under an argon atmosphere at room temperature. Then the [Pd-(PPh<sub>3</sub>)<sub>4</sub>] catalyst was added and the reaction mixture was stirred at 80 °C for 16 h. After cooling to room temperature, the product was concentrated and purified by column chromatography on silica gel with dichloromethane/*n*-hexane (v/v=1:10) as the eluent.  $VP_3$ -(TPE)<sub>1</sub> was obtained as a white power in 61 % yield (0.30 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta =$ 7.34-7.24 (m, 12 H), 7.20 (m, 2 H), 7.10-6.98 (m, 19 H), 6.94 ppm (s, 1 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 143.46, 143.11, 142.49, 142.34, 140.84, 140.25, 140.16, 138.43, 137.92, 136.08, 131.50, 131.14, 131.07, 130.13, 129.66, 128.45, 127.96, 127.48, 127.38, 126.22, 125.99, 125.60 ppm; FT-IR (KBr):  $\tilde{\nu} = 3023$ , 1600, 1495, 1446, 815, 760, 700 cm<sup>-1</sup>. HRMS (EI), m/z: 586 ([M]<sup>+</sup>, calcd for C<sub>46</sub>H<sub>34</sub> 586); Anal. calcd for C<sub>46</sub>H<sub>34</sub>: C 94.16, H 5.84; found: C 94.01, H 5.89.

#### Synthesis of VP3-(TPE)2

TPE-B (0.48 g, 1.3 mmol) and VP<sub>3</sub>-Br<sub>2</sub> (0.22 g; 0.53 mmol) were dissolved in toluene (30 mL), and then 2M aqueous K<sub>2</sub>CO<sub>3</sub> solution (0.7 mL) and TBAB (0.1 g) were added. The mixture was stirred for 40 min under an argon atmosphere at room temperature. Then the [Pd(PPh\_3)4] catalyst was added and the reaction mixture was stirred at 80°C for 16 h. After cooling to room temperature, the product was concentrated and purified by column chromatography on silica gel with dichloromethane/n-hexane (v/v=1:8) as eluent. Light green power of VP3-(TPE)2 was obtained in 60% yield (0.29 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 7.52$  (d, 2 H), 7.48 (d, 2H), 7.39 (d, 2H), 7.33 (d, 2H), 7.20 (s, 1H), 7.16-6.99 (m, 2H), 6.98 ppm (s, 1 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 143.45, 142.70, 142.58, 142.03, 141.52, 140.89, 140.25, 139.48, 139.19, 138.96, 137.98, 137.12, 131.59, 131,09, 131,52, 130.60, 129.33, 127.78, 127.51, 127.43, 126.67, 126.32, 126.24, 125.77 ppm; FT-IR (KBr):  $\tilde{\nu} = 3023$ , 1600, 1495, 1446, 817, 760, 700 cm<sup>-1</sup>; HRMS (EI), m/z: 916 ([M]<sup>+</sup>, calcd for C<sub>72</sub>H<sub>52</sub>, 916); Anal. calcd for C72H52: C 94.29, H 5.71; found: C 94.21, H 5.73.

#### Synthesis of VP<sub>3</sub>-(TPE)<sub>3</sub>

TPE-B (1.0 g, 2.7 mmol) and VP<sub>3</sub>-Br<sub>3</sub>(0.29 g, 0.59 mmol) were dissolved in toluene (30 mL), and then 2 M aqueous K<sub>2</sub>CO<sub>3</sub> solution (1.5 mL) and

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TBAB (0.1 g) were added. The mixture was stirred for 40 min under an argon atmosphere at room temperature. Then the  $[Pd(PPh_3)_4]$  catalyst was added and the reaction mixture was stirred at 80 °C for 16 h. After cooling to room temperature, the product was concentrated and purified by column chromatography on silica gel with dichloromethane/*n*-hexane (v/v=1:4) as eluent. VP<sub>3</sub>-(TPE)<sub>3</sub> was obtained as a light-green powder in 54% yield (0.40 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.53 (d, 2H), 7.48(d, 2H), 7.39 (d, 2H), 7.34 (d, 3H), 7.33–7.28 (t, 4H), 7.25 (d, 2H), 7.48(d, 2H), 7.39 (d, 2H), 7.34 (d, 3H), 7.33–7.28 (t, 4H), 7.25 (d, 2H), 7.48(d, 24.59, 142.50, 141.97, 141.53, 140.88, 140.25, 139.47, 139.26, 139.02, 138.46, 137.98, 136.08, 131.53, 131.09, 130.60, 129.71, 127.76, 127.43, 126.75, 126.24, 126.05, 125.78, 125.59 ppm; FT-IR (KBr):  $\bar{\nu}$ =3023, 1600, 1495, 1445, 817, 760, 700 cm<sup>-1</sup>; HRMS (FAB), *m*/z: 1247 ([*M*+H]<sup>+</sup>, calcd for C<sub>98</sub>H<sub>70</sub>, 1246); Anal. calcd for C<sub>98</sub>H<sub>70</sub>: C 94.34, H 5.66; found: C 94.26, H 5.62.

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