Qiang Zhang, Tian Huang, Xing He, Zhuo-Ran Zhao and Xin Zhao*

Synthesis and properties of dicarbazolyltriphenylethylene-substituted fluorene derivatives exhibiting aggregation-induced emission enhancement

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Abstract: Two novel dicarbazolyltriphenylethylene-substituted fluorene derivatives **DctF** and **Dct$_2$F** were synthesized by the Wittig-Horner and Suzuki coupling reactions. It was reasoned that introducing linear alkyl chains into the fluorene structure could facilitate the deposition of high-quality films by an economical and simple process. The thin solid films of **DctF** and **Dct$_2$F** show strongly enhanced emissions in comparison to their dilute solutions, which indicate the aggregation-induced emission enhancement (AIEE). Their decomposition temperatures (T_d) exceed 400°C and the glass transition temperature (T_g) of **DctF** is 105°C. The maximum fluorescence emission wavelengths are in the region of 458–469 nm.

Keywords: aggregation; carbazole; emission; fluorene; Suzuki coupling.

Introduction

Organic luminescent materials have attracted considerable attention in the field of science and technology due to their applications as bioimaging agents [1], chemical sensors [2, 3], and organic light-emitting diodes (OLEDs) [4, 5]. Generally, organic luminophores are fluorescent in dilute solutions. However, the light emission of many organic fluorescent molecules is partially or totally quenched in the aggregate or solid state owing to the formation of excimers through π-π interactions [6]. The aggregation-caused quenching (ACQ) effect greatly limits practical applications of the luminophores because most of them are normally used as thin solid films, especially in OLEDs [7, 8]. To overcome this intractable problem, a successful exploration was pioneered by Tang's group in 2001 and a series of aromatic siloles were synthesized. These compounds show a unique intense emission in the aggregate state and a slight emission in the solution state [9]. Then, Park and co-workers reported aggregation-induced emission enhancement (AIEE). They found that 1-cyano-*trans*-1,2-bis-(4-methylbiphenyl)ethylene (CN-MBE) nanoparticles exhibit strong fluorescence emission in comparison to weak fluorescence of CN-MBE in solution [10]. Since these pioneering works, various organic molecules with AIEE properties, such as aromatic silole derivatives, tetraphenylethylene (TPE), and other aryl-substituted diene derivatives have been developed [11–16]. However, some problems still exist. For example, silole-based compounds are complicated and difficult to prepare, and photoisomerization of TPE-based compounds often occurs [17]. Moreover, the solubility of many highly conjugated organic luminescent materials is normally quite low, which complicates their practical applications for the fabrication of electroluminescent devices through spin-coating or ink-jet printing processes [18]. Thus, it is highly desirable to develop compounds with improved AIEE properties.

The glass transition temperature (T_g) of organic materials is very important for the stability and lifetime of devices. If a device is heated above the T_g of the organic luminophore, performance degradation often occurs. Due to high T_g temperatures and AIEE effects, carbazole-based compounds have been attractive candidates for the design of OLEDs [19–21]. Fluorene has also been widely used as a building block to form many emissive materials because of its high thermal stability, high quantum yield of photoluminescence, and improved hole-injection ability, compared to other blue chromophores [22, 23].

Inspired by these attractive features, we tried to develop novel compounds incorporating the carbazole and fluorene moieties in the molecule. Herein, two new dicarbazolyltriphenylethylene-substituted fluorene derivatives

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***Corresponding author: Xin Zhao,** Jiangsu Key Laboratory of Environmental Functional Materials, College of Chemistry, Biology and Material Engineering, Suzhou University of Science and Technology, Suzhou 215009, China, e-mail: zhaoxinsz@126.com
Qiang Zhang, Tian Huang, Xing He and Zhuo-Ran Zhao: Jiangsu Key Laboratory of Environmental Functional Materials, College of Chemistry, Biology and Material Engineering, Suzhou University of Science and Technology, Suzhou 215009, China

were designed and synthesized in high yields via the classical Wittig-Horner and Suzuki coupling routes. To improve the solubility, linear alkyl chains were introduced into the molecular structure. This feature facilitates the deposition of high-quality films using an economical and simple solution process. The photophysical, thermal, AIEE, and electrochemical properties were evaluated. These molecules are potential materials for blue-light emitters in OLEDs.

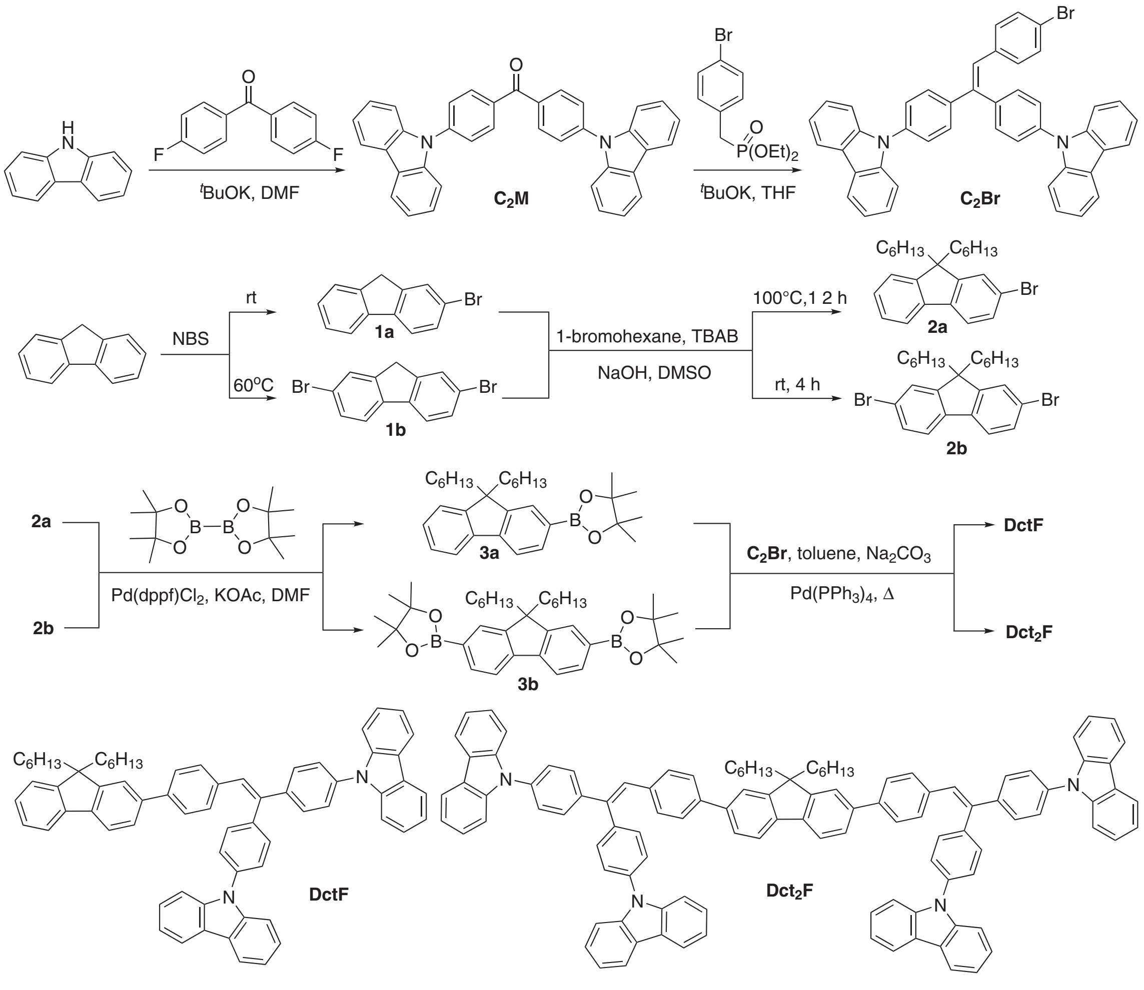
Results and discussion

Synthesis

The synthetic strategy is shown in Scheme 1. In the first step, bis(4-(9*H*-carbazol-9-yl)phenyl)methanone (**C_2M**), was obtained from carbazole and bis(4-fluorophenyl) methanone. Then, the key intermediate compound **C_2Br** was synthesized by the Wittig-Horner reaction of **C_2M** with diethyl 4-bromobenzylphosphonate. In a parallel step, the alkyl-modified fluorenes **2a**,**b** were prepared by treatment of bromofluorenes **1a,b** with 1-bromohexane in the presence of a base. Then, the borate esters **3a**,**b** were obtained by a palladium-catalyzed borylation of **2a,b**. Finally, the desired compounds **DctF** and **Dct_2F** were synthesized by the Suzuki coupling reaction of compounds **3a,b** with **C_2Br**. The structures of the target products **DctF** and **Dct_2F** were characterized and confirmed by ^1H nuclear magnetic resonance (NMR), ^{13}C NMR, mass spectroscopy (MS), and elemental analysis.

Thermal properties

The thermal properties of the compounds were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results are shown in



Scheme 1

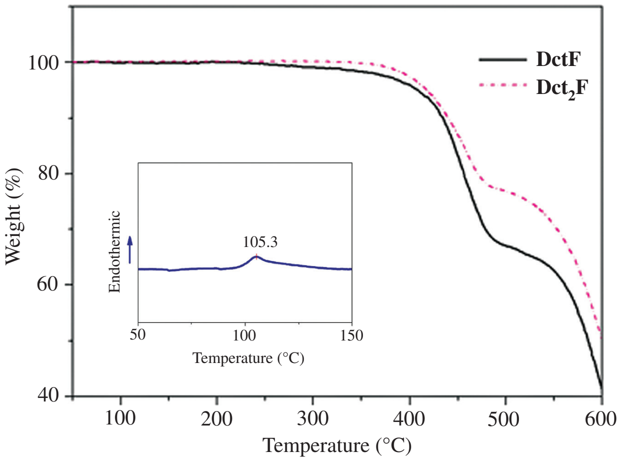


Figure 1 TGA curves of the compounds.

Figure 1. The decomposition temperatures (T_d) with 5% weight loss of **DctF** and **Dct$_2$F** are 409°C and 418°C, respectively. Interestingly, the thermal degradation of these compounds is a two-step process. It can be suggested that breakage of the C-C bonds of the alkyl chains and the C-N bonds of the carbazole moieties mainly occur during the first step of thermal degradation, followed by decomposition of the aryl rings. The T_g of **DctF** was found to be 105°C, while the T_g of **Dct2F** could not detected. Melting could not be detected even up to the T_d, presumably due to the presence of long alkyl chains and supramolecular structure, which could influence molecular tight packing in the solid state to form a highly amorphous structure. Therefore, based on the results of TGA and the DSC analysis, these compounds could form a homogeneous and stable amorphous emissive layer in OLED devices and, as such, could be useful in fabricating photoelectric devices.

The inset depicts the DSC curve of **DctF** upon the second heating run.

Photophysical properties

The optical properties of the compounds were investigated by ultraviolet-visible (UV-vis) absorption spectroscopy (UV) and photoluminescence spectroscopy (PL) in dichloromethane (DCM) and in solid film. The results are shown in Table 1. The films of **DctF** and **Dct$_2$F** were conveniently prepared by a solution-processed method, and their good solubility could be ascribed to the supramolecular steric hindrance caused by the long alkyl chains. As shown in Figure 2, the UV and PL spectra of **DctF** and **Dct$_2$F** are similar. The UV spectra show two main absorption bands. The strong absorption band in the region of 250–300 nm may correspond to the π-π^* local electron transition of the individual aromatic units, and the absorption band at longer wavelengths of 300–425 nm may be attributed to the characteristic π-π^* electron transition of the whole conjugation system. The maximum absorption wavelengths λ^{abs}_{max} appear at 343 nm for **DctF** and 342 nm for **Dct$_2$F**. The emission wavelengths λ^{abs}_{max} are at 458 nm for **DctF** and at 462 nm for **Dct$_2$F** in 1 μM DCM (Table 1). The values of λ^{em}_{max} for **DctF** and **Dct$_2$F** in DCM and in solid film exhibit a 9-nm and 7-nm redshift, respectively. The Stokes shifts of the emission bands of these compounds are similar, approximately 117 nm [24].

The quantum yields (Φ_F) of the compounds in good solvents DCM and tetrahydrofuran (THF) and poor solvent petroleum ether (PE) were determined by the standard method using quinine sulfate as the reference [25]. As can be seen from Table 1, these compounds show low fluorescence efficiency in good solvents DCM and THF, with the Φ_F values ranging from 0.09 to 0.14. By contrast, these compounds exhibit higher Φ_F values in the poor solvent PE, with the Φ_F values of **DctF** and **Dct$_2$F** of 0.41 and 0.27, respectively. The poor solvents may cause the solute molecules to form nanoaggregates [19].

Electrochemical properties

The electrochemical properties of the compounds were investigated by cyclic voltammetry (CV) in DCM containing 0.1 M tetrabutylammonium perchlorate (n-Bu_4NClO_4) as a supporting electrolyte, at a scan rate of 50 mV s^{-1} (Figure 3). The energy level parameters of **DctF** and **Dct$_2$F** are listed in Table 2. The highest occupied molecular

Table 1 Thermal and optical properties of the compounds.

Compound	T_g (°C)	T_d (°C)	λ^{abs}_{max} (nm)[a]	λ^{em}_{max} (nm)	Stokes shift (nm)[c]	Φ_F[d] DCM	Φ_F[d] THF	Φ_F[d] PE
DctF	105	409	343	458[a]/467[b]	115	0.13	0.12	0.41
Dct$_2$F	–	418	342	462[a]/469[b]	120	0.14	0.09	0.27

[a]Determined in DCM. [b]Determined in solid film. [c]Calculated from the difference of λ^{abs}_{max} and λ^{em}_{max}. [d]Fluorescence quantum yields were measured in solution using quinine sulfate (QS) as standard ($\Phi_F = 0.55$).

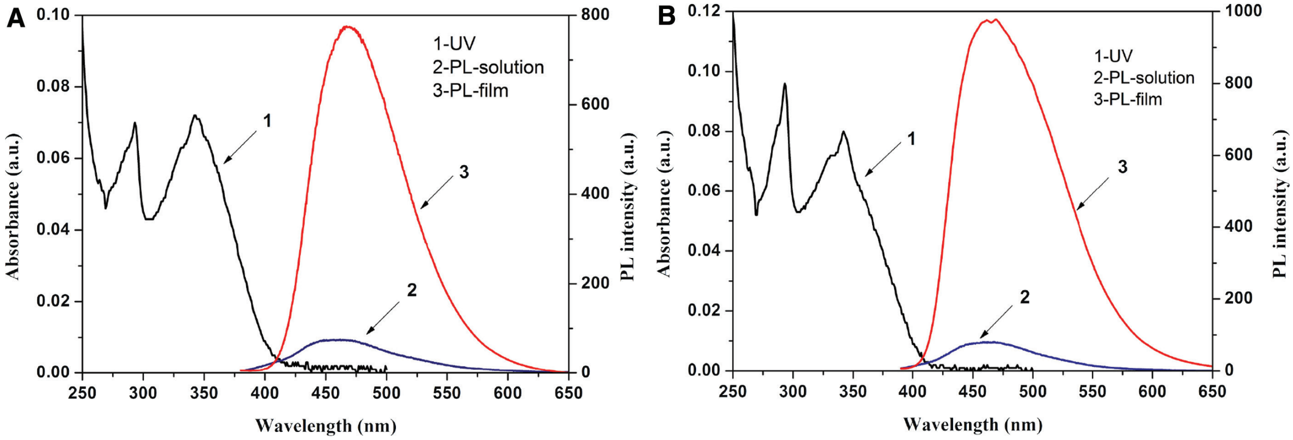


Figure 2 UV and PL spectra: **DctF** (A) and **Dct$_2$F** (B) in DCM (1 μM) and in solid film.

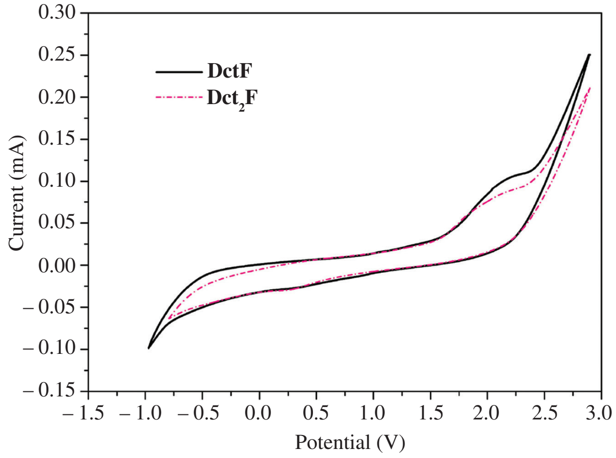


Figure 3 CV curves of the compounds in DCM.

Table 2 Electrochemical properties of the compounds.

Compd	λ_{onset} (nm)^a	E_{onset} (V)^b	E_g (eV)^c	E_{HOMO} (eV)^d	E_{LUMO} (eV)^e
DctF	417	1.44	2.97	– 6.18	– 3.21
Dct$_2$F	427	1.23	2.90	– 5.97	– 3.07

[a] The onset absorption wavelengths of the UV absorption spectra. [b] The onset oxidation potentials from the CV curves. [c] Estimated from $E_g = 1240\ \lambda_{onset}^{-1}$. [d] Calculated using the empirical equation $E_{HOMO} = -(4.74 + E_{onset})$. [e] Calculated from $E_{LUMO} = E_{HOMO} + E_g$.

orbital (HOMO) levels of **DctF** and **Dct$_2$F** are – 6.18 and – 5.97 eV, respectively. The HOMO level of **Dct$_2$F** with two dicarbazolyltriphenylethylene building blocks is higher than that of **DctF**. It can be suggested that the electron-donating substituents reduce oxidation potentials of the molecule and raise the HOMO energy level. The band gap energies of **DctF** and **Dct$_2$F** are 2.97 and 2.90 eV, respectively. Compound **Dct$_2$F** has a lower band gap energy because both its dicarbazolyltriphenylethylene building blocks are more conjugated. Therefore, both compounds might be used as hole-transporting and emissive materials in OLEDs.

AIEE properties

The compounds are soluble in common organic solvents such as THF and DCM but insoluble in water, so increasing the water fraction in the mixed solvent can change their forms from a solution in pure THF to the aggregated particles in water-THF mixtures. As shown in Figure 2, the emission of the solid film is much stronger than that in the DCM solution. The emission images of **DctF** in THF (1 μM) with different water fractions under 365 nm UV illumination at room temperature are shown in Figure 4, and the compound in high water fractions of water-THF mixtures exhibits stronger emission than that in pure THF solution. To further study the AIEE properties of the compounds, detailed PL emission behaviors of their dilute mixed solutions were evaluated.

The PL spectra of 1 μM **DctF** and **Dct$_2$F** in the water-THF mixtures with different volume fractions of water

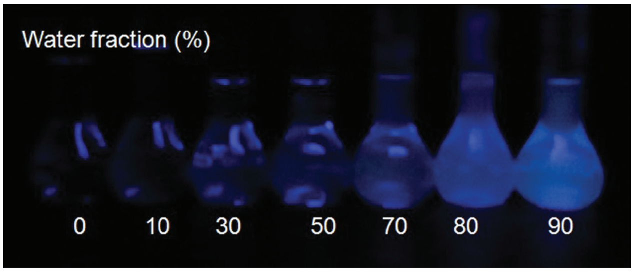


Figure 4 The emission images of **DctF** in THF (1 μM) with different water fractions under 365 nm UV illumination at room temperature.

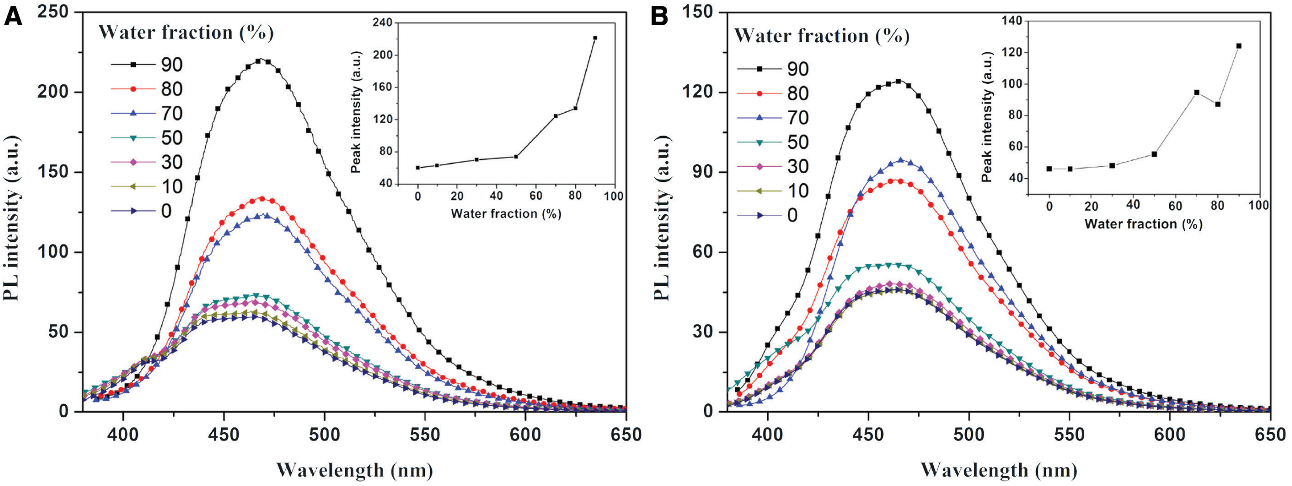


Figure 5 PL spectra of **DctF** (A) and **Dct$_2$F** (B) in THF (1 µM) with different water fractions. The inset depicts the changes in PL peak intensity.

are shown in Figure 5. **DctF** in THF exhibits weak PL intensity (~60 a.u.). However, the fluorescent intensity is significantly enhanced when the water fraction exceeds 50%. The enhancement of fluorescent intensity from 60 to 230 a.u. is observed as the volume fraction of water increases from 50% to 90%. Similar phenomena were found for **Dct$_2$F** in water-THF mixtures. The fluorescent intensity is also enhanced when the water fraction exceeds 50% and the enhancement of fluorescent intensity from 45 to 130 a.u. is observed as the volume fraction of water increases from 50% to 90%. As **DctF** and **Dct$_2$F** undergo aggregation in the system with higher water fractions, the fluorescence enhancement phenomena can be attributed to the aggregate state. Therefore, the prepared compounds were characterized as AIEE-active. The Φ_F of the compounds in the water-THF mixtures were also evaluated using quinine sulfate as the reference. The highest Φ_F of **DctF** is 0.48 when the water fraction is 90% in the mixture, which has the similar change trend with the PL intensity with a different water fraction. However, the highest Φ_F of **Dct$_2$F** is 0.30 when the water fraction is 70% in the mixture, and a further increase of the water fraction results in decrease of photoluminescent quantum yield. This phenomenon has been observed in some AIEE compounds [19, 26], and the reasons remain unclear as yet.

Conclusions

Two novel dicarbazolyltriphenylethylene-substituted fluorene derivatives with AIEE properties were synthesized and characterized. Introducing linear alkyl chains into the fluorene structure highly improves the solubility in common organic solvents, which facilitates the deposition of high-quality films by a simple solution-processed method. Their T_d exceed 400°C and the T_g of **DctF** is 105°C. The excellent solubility, high thermal stability, and AIEE property of these compounds make them potential materials for the fabrication of photoelectric devices by the solution process.

Experimental

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ on a Bruker Avance III spectrometer with tetramethylsilane as the internal reference. Mass spectra were obtained using a Finnigan TSQ Advantage spectrometer. Elemental analyses (C, H, N) were measured on an Elemental Vario EL III elemental analyzer. Ultraviolet and visible (UV-vis) spectra were recorded on a Beijing Puxi TU-1901 UV-vis spectrometer. PL spectra were recorded on a Perkin Elmer LS55 spectrometer with a slit width of 4 nm for emission. DSC analysis and TGA were performed on a Perkin Elmer Pyris Diamond DSC thermal analyzer and a Beijing Henven HCT-2 thermal analyzer, respectively, with heating rate of 10 min^{-1} under nitrogen. CV measurement was carried out on a Shanghai Chenhua electrochemical workstation CHI660C with a three-electrode cell (a platinum button working electrode, an SCE reference electrode, and a platinum wire counter electrode). THF was distilled from sodium-benzophenone. All other chemicals were commercially purchased and used without further purification.

2-Bromofluorene (**1a**) and 2,7-dibromofluorene (**1b**) were prepared as previously described [27]. 2-Bromo-9,9-dihexylfluorene (**2a**), 2,7-dibromo-9,9-dihexylfluorene (**2b**), 2-(4,4,5,5-tetramethyl[1.3.2]dioxaborolan-2-yl)-9,9-dihexylfluorene (**3a**), and 2,7-bis(4,4,5,5-tetramethyl[1.3.2]dioxaborolan-2-yl)-9,9-dihexylfluorene (**3b**) were prepared as previously described [28]. Bis(4-(9*H*-carbazol-9-yl)phenyl)methanone (**C$_2$M**) and 9,9′-(4,4′-(2-(4-bromophenyl)ethene-1,1-diyl)bis(1,4-phenylene)) bis(9*H*-carbazole) (**C$_2$Br**) were prepared as previously described [29].

Synthesis of DctF

A mixture of **3a** (0.92 g, 2.0 mmol) and **C_2Br** (2.00 g, 3.0 mmol) in toluene (20 mL) and 2M aqueous Na_2CO_3 solution (10 mL) was degassed and treated with $Pd(PPh_3)_4$ (0.17 g, 0.15 mmol) under argon atmosphere. The mixture was heated under reflux with vigorous stirring for 30 h, then cooled to room temperature and treated with DCM and water. The organic layer was separated, washed with diluted HCl and brine, dried over $MgSO_4$, and concentrated. The solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography eluting with petroleum ether : DCM (6 : 1). Compound **DctF** is a yellow solid; yield 1.14 g (62%); ^{1}H NMR: δ 0.65–0.81 (m, 10H), 1.03–1.21 (m, 12H), 1.99 (t, *J* = 8.2 Hz, 4H), 7.17–7.21 (m, 1H), 7.27–7.35 (m, 9H), 7.43–7.76 (m, 22H), 8.17 (dd, *J* = 7.5, 3.8 Hz, 4H); ^{13}C NMR: δ 151.5, 151.0, 142.0, 140.9, 140.8, 140.7, 140.7, 140.7, 140.4, 139.3, 139.2, 137.2, 135.9, 132.0, 130.2, 129.2, 129.0, 127.4, 127.1, 126.8, 126.8, 126.0, 125.7, 123.6, 123.5, 122.9, 121.1, 120.4, 120.4, 120.1, 120.1, 120.0, 119.8, 109.9, 109.8, 55.2, 40.4, 31.5, 29.7, 23.8, 22.6, 14.0; ESI-MS: *m/z* 919.4 $[M+H]^+$. Anal. Calcd for $C_{69}H_{62}N_2$: C, 90.15; H, 6.80; N, 3.05; Found: C, 90.01; H, 6.91; N, 3.02.

Synthesis of Dct$_2$F

This compound was prepared according to the procedure described above using **3b** (0.59 g, 1.0 mmol), **C_2Br** (2.00 g, 3.0 mmol), $[Pd(PPh_3)_4]$ (0.17 g, 0.15 mmol) in toluene (20 mL) and 2M aqueous Na_2CO_3 solution (10 mL): yellow solid (0.84 g, 56%); ^{1}H NMR: δ 0.70–0.79 (m, 10H), 1.04–1.11 (m, 12H), 2.02–2.06 (m, 4H), 7.23 (d, *J* = 6.9 Hz, 2H), 7.28–7.34 (m, 12H), 7.43–7.78 (m, 42H), 8.16–8.19 (m, 8H); ^{13}C NMR: δ 151.8, 151.7, 142.0, 140.9, 140.8, 140.7, 140.4, 140.2, 140.0, 139.3, 137.2, 135.9, 132.0, 130.2, 130.1, 129.0, 128.8, 128.8, 127.4, 127.2, 126.8, 126.8, 126.0, 125.9, 123.6, 123.5, 121.5, 121.1, 120.4, 120.4, 120.1, 120.1, 109.9, 109.8, 55.3, 40.5, 31.5, 29.7, 23.8, 22.6, 14.0; ESI-MS: *m/z* 1503.6 $[M+H]^+$. Anal. Calcd for $C_{113}H_{90}N_4$: C, 90.24; H, 6.03; N, 3.73; Found: C, 89.92; H, 6.30; N, 3.65.

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References

[1] Yang, Y. M.; Zhao, Q.; Feng, W.; Li, F. Y. Luminescent chemodosimeters for bioimaging. *Chem. Rev.* **2013**, *113*, 192–270.

[2] Xu, Z.; Yoon, J.; Spring, D. R. Fluorescent chemosensors for Zn^{2+}. *Chem. Soc. Rev.* **2010**, *39*, 1996–2006.

[3] Mahendran, V.; Pasumpon, K.; Thimmarayaperumal, S.; Thilagar, P.; Shanmugam, S. Tetraphenylethene-2-pyrone conjugate: aggregation-induced emission study and explosives sensor. *J. Org. Chem.* **2016**, *81*, 3597–3602.

[4] Yang, X. L.; Zhou, G. J.; Wong, W. Y. Functionalization of phosphorescent emitters and their host materials by main-group elements for phosphorescent organic light-emitting devices. *Chem. Soc. Rev.* **2015**, *44*, 8484–8575.

[5] Zhu, M. R.; Yang, C. L. Blue fluorescent emitters: design tactics and applications in organic light-emitting diodes. *Chem. Soc. Rev.* **2013**, *42*, 4963–4976.

[6] Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Brédas, J. L.; Lögdlund, M.; et al. Electroluminescence in conjugated polymers. *Nature* **1999**, *397*, 121–128.

[7] Li, H. Y.; Chi, Z. G.; Zhang, X. Q.; Xu, B. J.; Liu, S. W.; Zhang, Y.; Xu, J. R. New thermally state aggregation-induced emission enhancement compouns for non-doped red organic light-emitting diodes. *Chem. Commun.* **2011**, *47*, 11273–11275.

[8] Padalkar, V. S.; Seki, S. Excited-state intramolecular proton-transfer (ESIPT)-inspired solid state emitters. *Chem. Soc. Rev.* **2016**, *45*, 169–202.

[9] Luo, J.; Xie, Z. L.; Lam, J. W. Y.; Cheng, L.; Chen, H. Y.; Qiu, C. F.; Kwok, H. S.; Zhan, X. W.; Liu, Y. Q.; Zhu, D. B.; et al. Aggregation-induced emission of 1-methyl-1,2,3,4,5-pentaphenylsilole. *Chem. Commun.* **2001**, 1740–1741.

[10] An, B. K.; Kwon, S. K.; Jung, S. D.; Park, S. Y. Enhanced emission and its switching in fluorescent organic nanoparticles. *J. Am. Chem. Soc.* **2002**, *124*, 14410–14415.

[11] Chen, L.; Jiang, Y. B.; Nie, H.; Lu, P.; Sung, H. H. Y.; Williams, I. D.; Kwok, H. S.; Huang, F.; Qin, A. J.; Zhao, Z. J.; et al. Creation of bifunctional materials: improve electon-transporting ability of light emitters based on AIE-active 2,3,4,5-tetraphenylsiloles. *Adv. Funct. Mater.* **2014**, *24*, 3621–3630.

[12] Wen, J.; Huang, Z.; Hu, S.; Li, S.; Li, W. Y.; Wang, X. L. Aggregation-induced emission active tetraphenylethene-based sensor for uranyl ion detection. *J. Hazard. Mater.* **2016**, *318*, 363–370.

[13] Han, T.; Zhang, Y. J.; Feng, X.; Lin, Z. G.; Tong, B.; Shi, J. B.; Zhi, J. G.; Dong, Y. P. Reversible and hydrogen bonding-assisted piezochromic luminescence for solid-state tetraaryl-buta-1,3-diene. *Chem. Commun.* **2013**, *49*, 7049–7051.

[14] Guo, Y. X.; Feng, X.; Han, T. Y.; Wang, S.; Lin, Z. G.; Dong, Y. P.; Wang, B. Tuning the luminescence of metal-organic frameworks for detection of energetic heterocyclic compounds. *J. Am. Chem. Soc.* **2014**, *136*, 15485–15488.

[15] Zhang, X. D.; Ye, J. W.; Xu, L. F.; Yang, L. J.; Feng, D.; Ning, G. L. Synthesis, crystal structures and aggregation-induced emission enhancement of aryl-substituted cyclopentadiene derivates. *J. Lumin.* **2013**, *139*, 28–34.

[16] Szłapa, A.; Kula, S. Błaszkiewicz, U.; Grucela, M.; Schab-Balcerzak, E.; Filapek, M. Simple donor-π-acceptor derivatives exhibiting aggregation-induced emission characteristics for use as emitting layer in OLED. *Dyes Pigments* **2016**, *129*, 80–89.

[17] Pan, L. X.; Luo, W. W.; Chen, M.; Liu, J. K.; Xu, L.; Hu, R. R.; Zhao, Z. J.; Qin, A. J.; Tang, B. Z. Tetraphenylpyrazine-based luminogens with aggregation-enhanced emission characteristics: preparation and property. *Chin. J. Org. Chem.* **2016**, *36*, 1316–1324.

[18] Liu, C.; He, W.; Shi, G.; Luo, H. Y.; Zhang, S.; Chi, Z. G. Synthesis and properties of a new class of aggregation-induced enhanced emission compounds: intense blue light emitting triphenylethylene derivatives. *Dyes Pigments* **2015**, *112*, 154–161.

[19] Yang, Z. Y.; Chi, Z. G.; Xu, B. J.; Li, H. Y.; Zhang, X. Q.; Li, X. F.; Liu, S. W.; Zhang, Y.; Xu, J. R. High-Tg carbazole derivetives as a new class of aggregation-induced emission enhancement materials. *J. Mater. Chem.* **2010**, *20*, 7352–7359.

[20] Kruzinauskiene, A.; Matoliukstyte, A.; Michaleviciute, A.; Grazulevicius, J. V.; Musnickas, J.; Gaidelis, V.; Jankauskas, V. Carbazolyl- and diphenylamino substituted fluorenes as hole transport materials. *Synth. Metals* **2007**, *157*, 401–406.

[21] Tomkeviciene, A.; Grazulevicius, J. V.; Dmytro, V.; Jankauskas, V.; Sini, G. Structure-properties relationship of carbazole and fluorene hybrid trimers: experimental and theoretical approaches. *Phys. Chem. Chem. Phys.* **2014**, *16*, 13932–13942.

[22] Chen, Z.; Liang, J. H.; Han, X.; Yin, J.; Yu, G. A.; Liu, S. H. Fluorene-based novel highly emissive fluorescent molecules with aggregate fluorescence change or aggregation-induced emission enhancement characteristics. *Dyes Pigments* **2015**, *112*, 59–66.

[23] Feng, X. J.; Peng, J. H.; Xu, Z.; Fang, R. R.; Zhang, H. R.; Xu, X. J.; Li, L. D.; Gao, J. H.; Wong, M. S. AIE-active fluorene derivatives for solution-processable nondoped blue organic light-emitting devices (OLEDs). *ACS Appl. Mater. Interfaces* **2015**, *7*, 28156–28165.

[24] Krotkus, S.; Kazlauskas, K.; Miasojedovas, A.; Gruodis, A.; Tomkeviciene A.; Grazulevicius, J. V.; Jursenas, S. Pyrenyl-Functionalized fluorene and carbazole derivates as blue light emitters. *J. Phys. Chem. C* **2012**, *116*, 7561–7572.

[25] Kubin, R. F.; Fletcher, A. N. Fluorescence quantum yields of some rhodamine dyes. *J. Lumin.* **1982**, *27*, 455–462.

[26] Li, H. Y.; Zhang, X. Q.; Chi, Z. G.; Xu, B. J.; Zhou, W.; Liu, S. W.; Zhang, Y.; Xu, J. R. New thermally stable piezofluorochromic aggregation-induced emission compounds. *Org. Lett.* **2011**, *13*, 556–559.

[27] Lv, H. F.; Zhang, H.; Li, M.; Shan, W. Y. Study on the synthesis of bromofluorene. *Chem. Adhesion* **2012**, *24*, 29–31.

[28] Jo, J.; Chi, C.; Höger, S.; Wegner, G.; Yoon, D. Y. Synthesis and characterization of monodisperse oligofluorenes. *Chem. Eur. J.* **2004**, *10*, 2681–2688.

[29] Zhang, X. Q.; Yang, Z. Y.; Chi, Z. G.; Chen, M. N.; Xu, B. J.; Wang, C. C.; Liu, S. W.; Zhang, Y. Xu, J. R. A multi-sensing fluorescent compound derived from cyanoacrylic acid. *J. Mater. Chem.* **2010**, *20*, 292–298.