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Piezochromic luminescent and electroluminescent materials comprised of tetraphenylethene plus spirobifluorene or 9,9-diphenylfluorene

Bairong He [a], Zhengfeng Chang [a], Yibin Jiang [c], Xiaofei Xu [a], Ping Lu [e], Hoi Sing Kwok [c], Jian Zhou [a,*], Huayu Qiu [a], Zujin Zhao [a,b,**], Ben Zhong Tang [b,d,**]

[a] College of Material, Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou 310036, China
[b] State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China
[c] Center for Display Research, The Hong Kong University of Science & Technology (HKUST), Kowloon, Hong Kong, China
[d] Department of Chemistry, Division of Biomedical Engineering, Institute for Advanced Study and Institute of Molecular Functional Materials, State Key Laboratory of Molecular Neuroscience, HKUST, Kowloon, Hong Kong, China
[e] State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun 130012, China

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ABSTRACT

In this work, a series of luminogens comprised of tetraphenylethene plus spirobifluorene or 9,9-diphenylfluorene are synthesized and characterized. Whereas these luminogens are weakly fluorescent in solutions, they are highly emissive in the aggregated state, with high fluorescence quantum yields up to 99% in solid films, demonstrating aggregation-induced emission characteristics. Reversible piezochromic luminescence is observed from the solids of the luminogens. A notable emission color change from blue (445 nm) to green (503 nm) is readily realized by grinding the pristine powder of the luminogen. The blue emission is recovered by fuming the ground powder with dichloromethane vapor. The undoped electroluminescence devices using the luminogens as light-emitting layers are fabricated, affording high current efficiencies up to 7.2 cd/A.

1. Introduction

Organic solids with efficient photoluminescence (PL) are highly desired because of their practical applications in organic light-emitting diodes (OLEDs), organic lasers, non-linear optics, fluorescent sensors, etc [1]. Recently, intense research activities are attracted by the piezochromic luminescent organic solids that respond to external stimulus, such as mechanical stress, organic vapor, temperature, etc [2]. The piezochromic luminescence is mainly caused by the morphology transition between crystalline and amorphous states, or between different crystalline states, without provoking structural damage of the molecule [3–5]. This interesting emission property allows the organic solids to be used in mechano-sensors, optical data storage, security papers, etc [6]. The high emission efficiency of the solid is of particular importance to generate vivid emission color change under external stimulation. However, many chromophores that show good emissions in solutions suffer from emission-quenching in the solid state, which limits their practical utility. To address this issue, creation of luminogens by adopting building blocks that possess aggregation-induced emission (AIE) [7] characteristics is a facile and effective approach. The integration of AIE-active units with various conventional chromophores or diverse functional groups can generate efficient solid-state luminescent materials with specific property, and thus, great potential in environmental, scientific and technological aspects [8].

Tetraphenylethene (TPE) is a typical AIE-active molecule. Currently, it becomes the subject of numerous investigations because of not only its remarkable AIE attribute, but also its simple molecular structure that allows facile preparation and chemical modification [9]. The propeller-like conformation of TPE avoids tight packing of the molecules in the aggregated state, which

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* Corresponding author. Tel.: +86 571 28867898; fax: +86 571 28867899.
** Corresponding authors.
E-mail addresses: zhoujian@hznu.edu.cn (J. Zhou), zujinzhao@gmail.com (Z. Zhao), tangbenz@ust.hk (B.Z. Tang).

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alleviates intermolecular π–π interaction and thus emission quenching. Therefore, solids of TPE derivatives can fluoresce strongly, enabling them to serve as efficient host light emitters for OLEDs [10,11]. In addition, the loose packing also offers opportunity for the molecules to form metastable morphology, which induces stimuli-responsive emission behavior [12]. To enrich efficient solid-state emitters for piezochromic study as well as for the application in OLEDs, in this work, a series of luminogens with AIE characteristics are prepared based on TPE and fluorene derivatives. Highly luminescent solids of the adducts of TPE and fluorene derivatives are obtained. The piezochromic luminescent and electroluminescent properties of the adducts are investigated and delineated.

2. Experimental

2.1. General

THF was distilled from sodium benzophenone ketyl under dry nitrogen immediately prior to use. Compounds **2** and **4** were prepared by the methods in the literature [13]. All other chemicals and reagents were purchased from Aldrich or J&K Scientific Ltd. and used as received without further purification. ^{1}H and ^{13}C NMR spectra were measured on a Bruker AV 400 spectrometer in deuterated chloroform using tetramethylsilane (TMS; $\delta = 0$) as internal reference. High resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 mass spectrometer operating in MALDI-TOF mode. Elementary analysis was performed on Vario EL III. UV spectra were measured on a Shimadzu UV-2450 spectrophotometer. PL spectra were recorded on a Perkin–Elmer LS 55 spectrofluorometer.

2.2. Device fabrication and measurements

The devices were fabricated on 80 nm-ITO coated glass with a sheet resistance of 25 Ω/□. Prior to loading into the pretreatment chamber, the ITO-coated glass was soaked in ultrasonic detergent for 30 min, followed by spraying with de-ionized water for 10 min, soaking in ultrasonic de-ionized water for 30 min, and oven-baking for 1 h. The cleaned samples were treated by perfluoromethane plasma with a power of 100 W, gas flow of 50 sccm, and pressure of 0.2 Torr for 10 s in the pretreatment chamber. The samples were transferred to the organic chamber with a base pressure of 7×10^{-7} Torr for the deposition of NPB, emitter, and TPBi, which served as hole-transport, light-emitting, and electron-transport layers, respectively. The samples were then transferred to the metal chamber for cathode deposition which composed of lithium fluoride (LiF) capped with aluminum (Al). The light-emitting area was 4 mm^2. The current density-voltage characteristics of the devices were measured by a HP4145B semiconductor parameter analyzer. The forward direction photons emitted from the devices were detected by a calibrated UDT PIN-25D silicon photodiode. The luminance and external quantum efficiencies of the devices were inferred from the photocurrent of the photodiode. The electroluminescence spectra were obtained by a PR650 spectrophotometer. All measurements were carried out under air at room temperature without device encapsulation.

2.3. Synthesis

2.3.1. 9,9-Diphenyl-2,7-bis(4-(1,2,2-triphenylvinyl)phenyl)fluorene ((TPE)$_2$PF)

A mixture of **2** (0.83 g, 2.2 mmol), **5** (0.48 g, 1 mmol), Pd(PPh$_3$)$_4$ (0.11 g, 0.1 mmol), and K$_2$CO$_3$ (1.1 g, 8.0 mmol) in toluene/ethanol/water (100 mL, 8/1/1 v/v/v) was heated to reflux for 12 h under nitrogen. Then the reaction mixture was cooled to room temperature and poured into water. The organic layer was extracted with dichloromethane, and the combined organic layers were washed with a saturated brine solution and water, and dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography using hexane/dichloromethane as eluent. White solid of (TPE)$_2$PF was obtained in 56% yield. ^{1}H NMR (400 MHz, CDCl$_3$), δ (TMS, ppm): 7.67 (d, 2H, $J = 7.2$ Hz), 7.49–7.45 (m, 4H), 7.22–6.95 (m, 48H). ^{13}C NMR (100 MHz, CDCl$_3$), δ (TMS, ppm): 152.2, 145.9, 143.8, 143.7, 142.8, 141.1, 140.5, 140.1, 139.0, 138.8, 131.8, 131.5, 131.4, 128.3, 127.8, 127.7, 126.7, 126.6, 126.5, 126.2, 124.5, 120.5, 65.7. HRMS (MALDI-TOF): *m/z* 978.4228 (M$^+$, calcd 978.4226). Anal. Calcd for C$_{77}$H$_{54}$: C, 94.44; H, 5.56. Found: C, 94.33 H, 5.52.

2.3.2. 1,2-Bis(4-(9,9-diphenyl-9H-fluoren-2-yl)phenyl)-1,2-diphenylethene (TPE(PF)$_2$)

Pale green solid; yield 55%. ^{1}H NMR (400 MHz, CDCl$_3$), δ (TMS, ppm): 7.78–7.75 (m, 4H), 7.59–7.54 (m, 4H), 7.40–7.21 (m, 30H), 7.12–7.03 (m, 14H). ^{13}C NMR (100 MHz, CDCl$_3$), δ (TMS, ppm): 151.8, 151.5, 145.9, 143.8, 142.9, 140.6, 140.1, 139.8, 139.3, 138.9, 131.8, 131.4, 128.3, 128.2, 127.9, 127.7, 127.6, 126.7, 126.6, 126.5, 126.2, 125.6, 124.5, 120.4, 120.2, 68.0, 65.6. HRMS (MALDI-TOF): *m/z* 964.5 (M$^+$, calcd 964.4069). Anal. Calcd for C$_{76}$H$_{52}$: C, 94.57; H, 5.43. Found: C, 94.26; H, 5.35.

2.3.3. 2,7-Bis[4-(1,2,2-triphenylvinyl)phenyl]-9,9′-spirobifluorene ((TPE)$_2$SF)

Green solid; yield 41%. The NMR signals are too weak due to the poor solubility of (TPE)$_2$SF. HRMS (MALDI-TOF): *m/z* 976.4080 (M$^+$, calcd 976.4069). Anal. Calcd for C$_{77}$H$_{52}$: C, 94.64; H, 5.36. Found: C, 94.46; H, 5.28.

2.3.4. 1,2-Bis[4-(9,9′-spirobifluorene-7-yl)phenyl]-1,2-diphenylethene (TPE(SF)$_2$)

Green solid; yield 45%. ^{1}H NMR (400 MHz, CDCl$_3$), δ (TMS, ppm): 7.83 (d, 8H, $J = 7.6$ Hz), 7.56–7.53 (m, 2H), 7.37–7.33 (m, 6H), 7.15–7.02 (m, 16H), 6.96–6.88 (m, 10H), 6.74–6.69 (m, 6H). ^{13}C NMR (100 MHz, CDCl$_3$), δ (TMS, ppm): 149.3, 149.2, 148.7, 143.8, 142.7, 141.8, 141.4, 141.0, 140.4, 140.3, 138.6, 131.7, 131.6, 131.4, 131.3, 127.9, 127.7, 127.6, 126.7, 126.5, 126.4, 126.2, 126.0, 124.1, 124.0, 122.3, 120.2, 120.0, 68.0, 66.0. HRMS (MALDI-TOF): *m/z* 960.3771 (M$^+$, calcd 960.3756). Anal. Calcd for C$_{76}$H$_{48}$: C, 94.97; H, 5.03. Found: C, 94.78; H, 5.01.

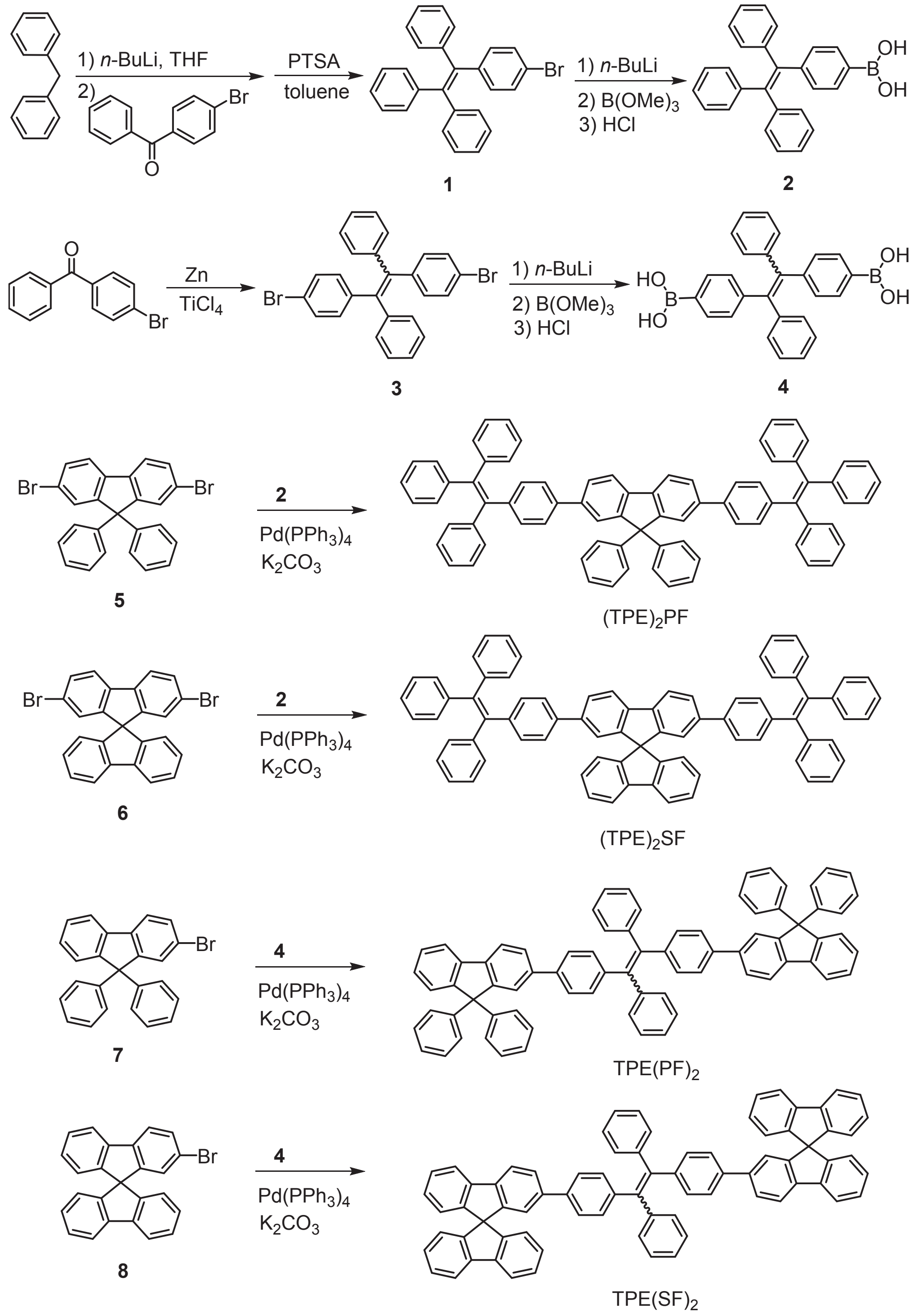
3. Results and discussion

3.1. Synthesis

Scheme 1 illustrates the synthetic routes to the luminogens comprised of TPE plus spirobifluorene or 9,9-diphenylfluorene. The detailed procedures and characterization data are given in Experimental section. Suzuki couplings of commercially available fluorene derivatives **5**–**8** with **2** or **4** generated target products in moderate yields. The structures of the final products are characterized by NMR, mass spectrometry, and elementary analysis. The solubility of (TPE)$_2$PF, TPE(PF)$_2$ and TPE(SF)$_2$ is good in common organic solvents, such as THF, dichloromethane, chloroform, etc., but (TPE)$_2$SF shows poor solubility in these solvents. All the luminogens are insoluble in water and methanol.

3.2. Optical properties

Fig. 1 shows the absorption spectra of the adducts of TPE and fluorene derivatives. The spectral profiles are varied as different fluorene derivatives incorporated. (TPE)$_2$PF and (TPE)$_2$SF show



Scheme 1. Synthetic routes to the adducts of TPE and fluorene derivatives.

close absorption maxima at 359 and 358 nm, respectively, which are longer than those of TPE(PF)$_2$ (349 nm) and TPE(SF)$_2$ (347 nm). These luminogens are almost nonfluorescent in dilute THF solutions with very weak PL signals when photoexcited. The fluorescence quantum yields (Φ_F) are low (0.4–1.7%, Table 1), measured by using 9,10-diphenylanthracene as standard. This is because the active intramolecular rotation (IMR) process of TPE units in solutions has nonradiatively deactivated the excited-state of the molecules [7,8]. In solid films, these luminogens are highly fluorescent. The PL emission peak of (TPE)$_2$PF is located at 491 nm, which is blue-shifted by 7 nm than that of TPE(PF)$_2$ (498 nm). A similar blue-shift is observed when compare the PL emissions of (TPE)$_2$SF and TPE(SF)$_2$ (Fig. 2). High Φ_F values of 96, 95 and 99% are attained from the films of (TPE)$_2$PF, TPE(PF)$_2$ and TPE(SF)$_2$, respectively, measured by integrating sphere. The Φ_F value of (TPE)$_2$SF is somewhat low (69%), possibly due to its poor solubility,

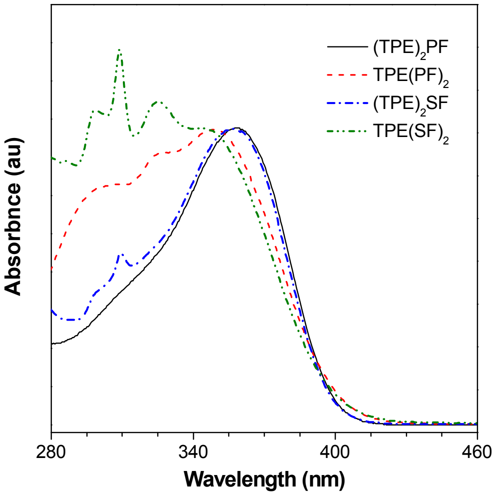


Fig. 1. Absorption spectra of the adducts of TPE and fluorene derivatives in THF solutions (10 μM).

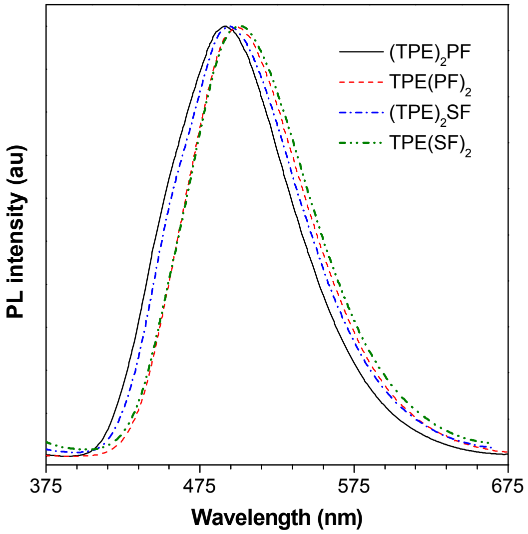


Fig. 2. PL spectra of the adducts of TPE and fluorene derivatives in solid films.

and thus, poor quality of the film prepared by drop-casting method. In comparison with the Φ_F values in solutions, the Φ_F values of the films have increased drastically, indicating that these luminogens are AIE-active.

The emission behaviors of the luminogens are further investigated in THF/water mixtures. Fig. 3 displays the PL spectra of $(TPE)_2PF$ in the mixture as an example. When a small amount of water, a nonsolvent of $(TPE)_2PF$, is added into the THF solution, the PL emission remains faint. When a large amount of water is added, the emission intensity increases swiftly. Since the dissolving capacity of the mixture with high water content becomes poor, the $(TPE)_2PF$ molecules must have aggregated. The IMR process is restricted in the condensed phase, and the radiative decay of the excited state is promoted, leading to enhancement of PL intensity. Similar emission behaviors are also recorded in other luminogens. These results demonstrate that the adducts of TPE and fluorene derivatives possess AIE characteristics indeed.

3.3. *Piezochromism*

In addition to the efficient solid-state emissions, reversible piezochromic luminescence is observed for the adducts of TPE and fluorene derivatives. Fig. 4 displays the PL spectra of $(TPE)_2PF$ in different solid states. The pristine powder of $(TPE)_2PF$ shows blue emission located at 445 nm, while the ground powder emits green light at 503 nm, representing a red-shift of 58 nm. The emission color of the ground powder is recovered to blue after fuming with dichloromethane vapor. However, the emission color is not reverted by heating method. By regrinding the fumed powder, green emission comes back again. The emission color change is so obvious that it can be readily distinguished by eyes under the illumination of a UV lamp (Fig. 5). After several cycles of the switching, the chemical structure of $(TPE)_2PF$ is not degraded, and facile and reversible emission modulation is achieved by grinding and fuming process, demonstrating the great potential of the luminogens as stimuli-responsive materials. Similar piezochromic luminescence is also found from other three luminogens.

Table 1
Optical properties of the adducts of TPE and fluorene derivatives.

	λ_{abs} (nm)	λ_{em} (nm)		Φ_F (%)	
	Soln[a]	Aggr[b]	Film[c]	Soln[d]	Film[e]
$(TPE)_2PF$	359	498	491	0.4	96
$TPE(PF)_2$	349	502	498	1.1	95
$(TPE)_2SF$	358	496	495	0.5	69
$TPE(SF)_2$	347	503	502	1.7	99

[a] In THF solution (10 μM).
[b] Aggregates in THF/water mixture with 90% (vol%) water fraction.
[c] Film drop-casted on quartz plate.
[d] Fluorescence quantum yield (Φ_F) determined in THF solution using 9,10-diphenylanthracene ($\Phi_F = 90\%$ in cyclohexane) as standard.
[e] Fluorescence quantum yield of solid film measured by integrating sphere.

Since the light emission is closely related to the alignment of molecules in the aggregated state, the morphology of the powder is hence investigated to explain the emission switching. Fig. 6 shows the powder X-ray diffraction (XRD) patterns of pristine powder, fumed powder and reground powder. Intensive and sharp diffraction peaks are recorded from the pristine powder, revealing that it is crystalline in nature. In contrary, the profile of the ground powder lacks discernable peaks, which discloses that the ground

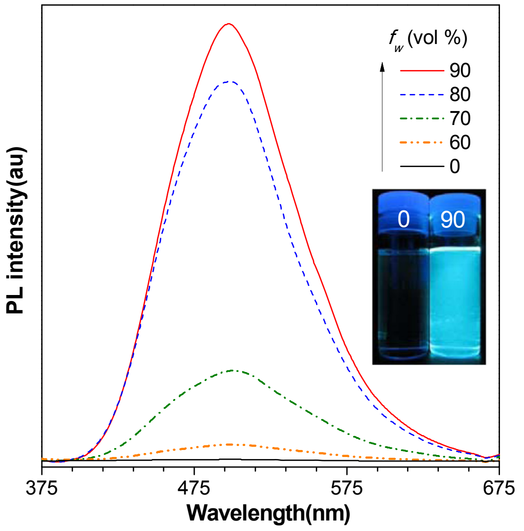


Fig. 3. PL spectra of $(TPE)_2PF$ in THF/water mixtures with various water fractions (f_w). Inset: photos of $(TPE)_2PF$ in THF/water mixtures (f_w = 0 and 90%) taken under the illumination of a UV lamp (365 nm).

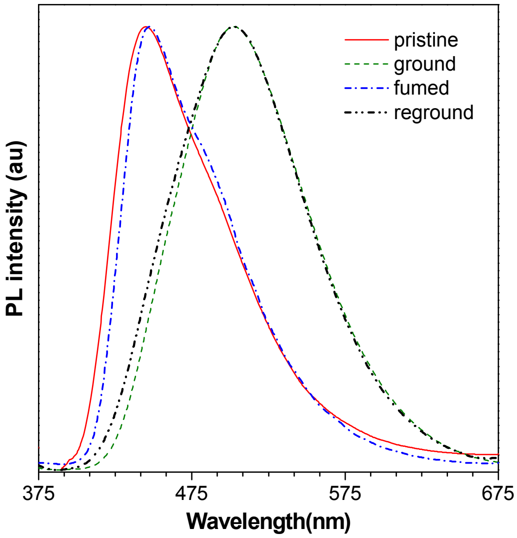


Fig. 4. PL spectra of $(TPE)_2PF$: pristine powder, ground powder, dichloromethane-fumed powder and reground powder.

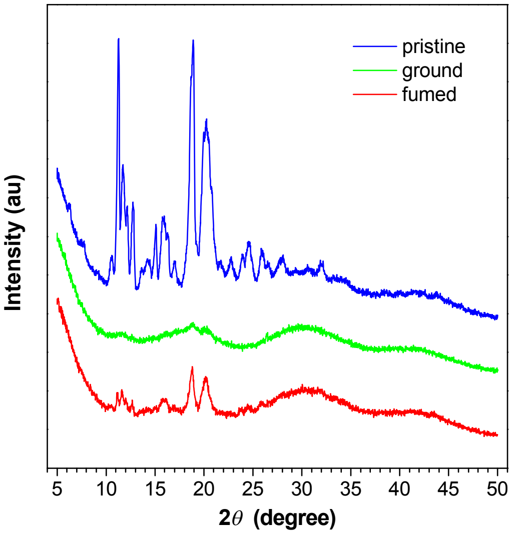


Fig. 6. XRD diffractograms of $(TPE)_2PF$: pristine powder, ground powder and dichloromethane-fumed powder.

powder is in amorphous state. The profile of fumed powder resembles that of the pristine powder, although the intensity of diffraction peaks are somewhat weak, demonstrating that the amorphous ground powder has been recovered to crystalline aggregates. These results clearly evidence that the blue to green emission color change is caused by the morphology transition from crystalline state to amorphous state, which is in good agreement with those found in other TPE derivatives [12,14,15]. In the crystalline state, the molecules adopt a twisted conformation to reduce the steric repulsion, while the external mechanical stress makes the molecules less twisted and breaks regular packing as well. The molecules in the resulting amorphous state are more planar and experience stronger intermolecular interactions, which give rise to red-shift in PL spectrum.

3.4. Electroluminescence

The application of these new luminescent materials as light emitters for electroluminescence (EL) devices is further evaluated. Multilayer undoped OLEDs with a configuration of ITO/NPB (60 nm)/emitter (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm) are fabricated. In these EL devices, the adducts of TPE and fluorene derivatives work as light-emitting layers, *N*,*N*-bis(1-naphthyl)-*N*,*N*-diphenylbenzidine (NPB) functions as a hole-transporting layer, and 2,2′,2″-(1,3,5-benzinetriyl)tris(1-phenyl-1-*H*-benzimidazole) (TPBi) serves as electron-transporting layer. The device performances are summarized in Table 2, and the characteristic curves are shown in Fig. 7. The devices of $(TPE)_2PF$, $TPE(PF)_2$, $(TPE)_2SF$ and $TPE(SF)_2$ show EL emission maxima in the range of 496–532 nm. The red-shifts observed from the EL emissions of $(TPE)_2PF$, $TPE(PF)_2$ and $TPE(SF)_2$ in comparison with their PL emissions in solid films are probably due to the microcavity effect. The device of $TPE(PF)_2$ shows the highest EL efficiencies. It is turned on at 4.6 V and affords high luminance up to 14,500 cd/m^2. The maximum current efficiency, maximum power efficiency and maximum external quantum efficiency attained by the device are 7.2 cd/A, 4.7 lm/W, and 2.6%, respectively. The devices of other luminogens also show good performances, with maximum luminance in the range of 10,500–14,500 cd/m^2 and peak current efficiencies in the range of 5.2–6.0 cd/A. These results indicate that the

Table 2
EL performances of OLEDs based on the adducts of TPE and fluorene derivatives.[a]

	EL	V_{on}	L_{max}	$\eta_{P,max}$	$\eta_{C,max}$	$\eta_{ext,max}$
	(nm)	(V)	(cd/m^2)	(lm/W)	(cd/A)	(%)
$(TPE)_2PF$	518	4.5	10,500	4.0	5.5	2.3
$TPE(PF)_2$	510	4.6	14,500	4.7	7.2	2.6
$(TPE)_2SF$	496	4.2	14,900	2.2	5.2	2.0
$TPE(SF)_2$	532	5.6	11,100	2.6	6.0	1.9

[a] Abbreviations: V_{on} = turn-on voltage at 1 cd/m^2, L_{max} = maximum luminance, $\eta_{P,max}$, $\eta_{C,max}$, and $\eta_{ext,max}$ = maximum power, current, and external quantum efficiencies, respectively.

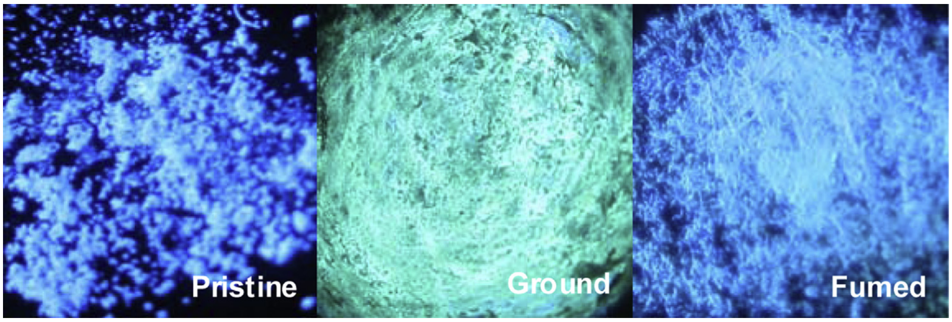


Fig. 5. Photographs of $(TPE)_2PF$: pristine powder, ground powder, and dichloromethane-fumed powder, taken under the illumination of a UV lamp (365 nm).

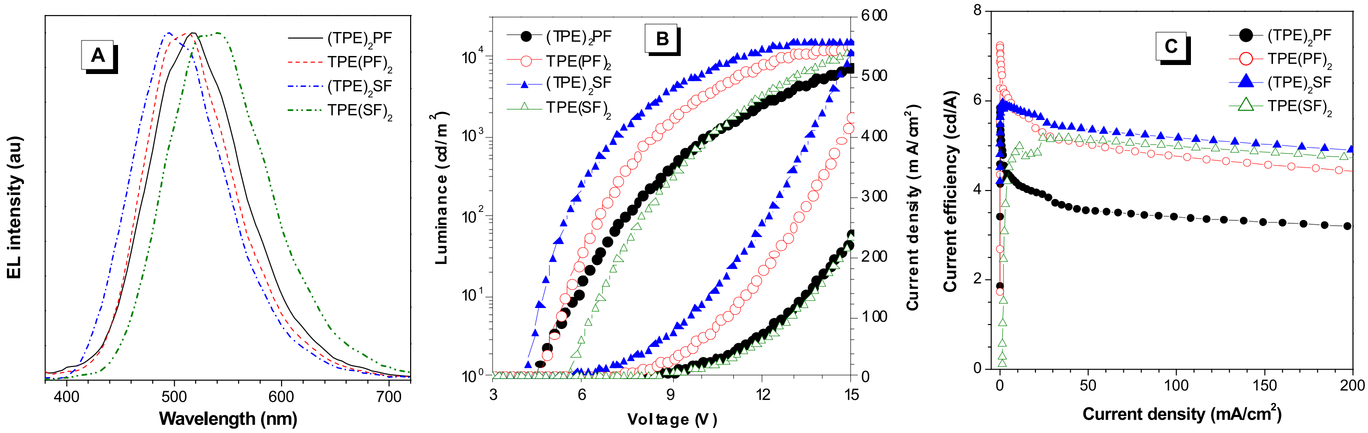


Fig. 7. (A) EL spectra, (B) changes in luminance and current density with the applied voltage and (C) current efficiency versus current density curves in multilayer devices of adducts of TPE and fluorene derivatives [ITO/NPB (60 nm)/emitter (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm)].

adducts of TPE and fluorene derivatives are good host emitters for OLEDs.

4. Conclusions

In summary, a series of luminescent materials comprised of TPE plus spirobifluorene or 9,9-diphenylfluorene are synthesized and characterized. These adducts are almost nonfluorescent in solutions but can emit strongly in aggregates or solid films, with high solid-state Φ_F values up to 99%. The piezochromic luminescent properties are studied on these adducts. Notable reversible piezochromic luminescence is observed from $(TPE)_2PF$, which shows blue light (445 nm) in crystalline state and green light (503 nm) in amorphous state. Multilayer EL devices using the adducts as host emitters are fabricated, which afford high EL efficiencies up to 7.2 cd/A. These results demonstrate that these adducts combine the merits of high solid-state emission efficiency, stimuli-responsive luminescence and efficient electroluminescence, which enable them to find an array of high-tech applications in mechano-sensors, optoelectronic devices, etc.

Acknowledgments

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