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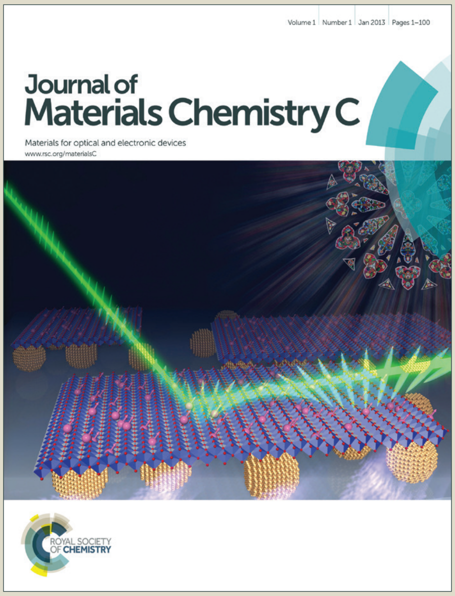

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ARTICLE

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Influence of cyano groups on the properties of piezofluorochromic aggregation-induced emission enhancement compounds derived from tetraphenylvinyl-capped ethane†

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Three tetraphenylvinyl-capped ethane derivatives, with 0, 1, and 2 cyano groups at the ethane moiety, namely, biTPE, biTPE-CN, and TPE-CN, respectively, were synthesized and characterized via photoluminescence, ultraviolet-visible absorption, wide-angle X-ray diffraction, fluorescence lifetime, and other techniques. Results indicate that the compounds possess piezofluorochromic properties and exhibit aggregation-induced emission enhancement. The distinct piezofluorochromic properties of all three compounds were reversible upon grinding and fuming. Introduction of cyano groups to the molecular structures of the derivatives significantly enhanced their piezofluorochromic activity. The relationship between structure and property was studied in detail. The results obtained will be of great help in understanding the piezofluorochromic mechanism and designing new piezofluorochromic materials.

Introduction

Stimuli-responsive fluorescent materials are a class of “smart” materials with fluorescent colors or intensities that can change in response to external stimuli, such as pressure, pH value, viscosity, temperature, light, biomolecules, metal ions, and so on. These materials have drawn considerable attention because of their promising potential applications in optical recording, fluorescent switches, and security inks.[1–13] Newly developed piezofluorochromic materials that show remarkable color and emission changes in the solid state as a result of external pressure or mechanical grinding, also called mechanofluorochromic materials, have been widely investigated over the last few years.[14–36] Reversible piezofluorochromic behavior can generally be achieved by converting the molecular packing mode in the solid state.[37]

However, considering the effects of aggregation-induced quenching occurring in most luminogenic materials, the availability of piezofluorochromic materials based on changes in physical molecular packing mode is quite limited. In 2001, aggregation-induced emission (AIE) was reported by Tang’s group.[38] The following year, Park’s group reported AIE-enhanced (AIEE) materials, which are similar to AIE materials.[39] Since then, AIE materials have attracted considerable research attention because of their potential applications in various fields, such as organic light-emitting devices and chemosensors.[40–42] Besides their fluorescent emission enhancement properties, AIE materials possess mechanical force stimulus–response properties. In 2005, Tang’s group reported that several AIE compounds possess bright–dark switching properties between their crystalline and amorphous states.[43] This unusual crystallization-induced emission enhancement effect allows the emission of these materials to be repeatedly switched between dark and bright states by fuming–heating or heating–cooling. In 2010, Park’s group reported the piezofluorochromism of a cyano-distyrylbenzene derivative that is also an AIE compound.[44] However, the relationship between the molecular structures of the AIE compound and its piezofluorochromic nature was not clearly understood then. Almost within the same year, our group synthesized and reported several new piezofluorochromic

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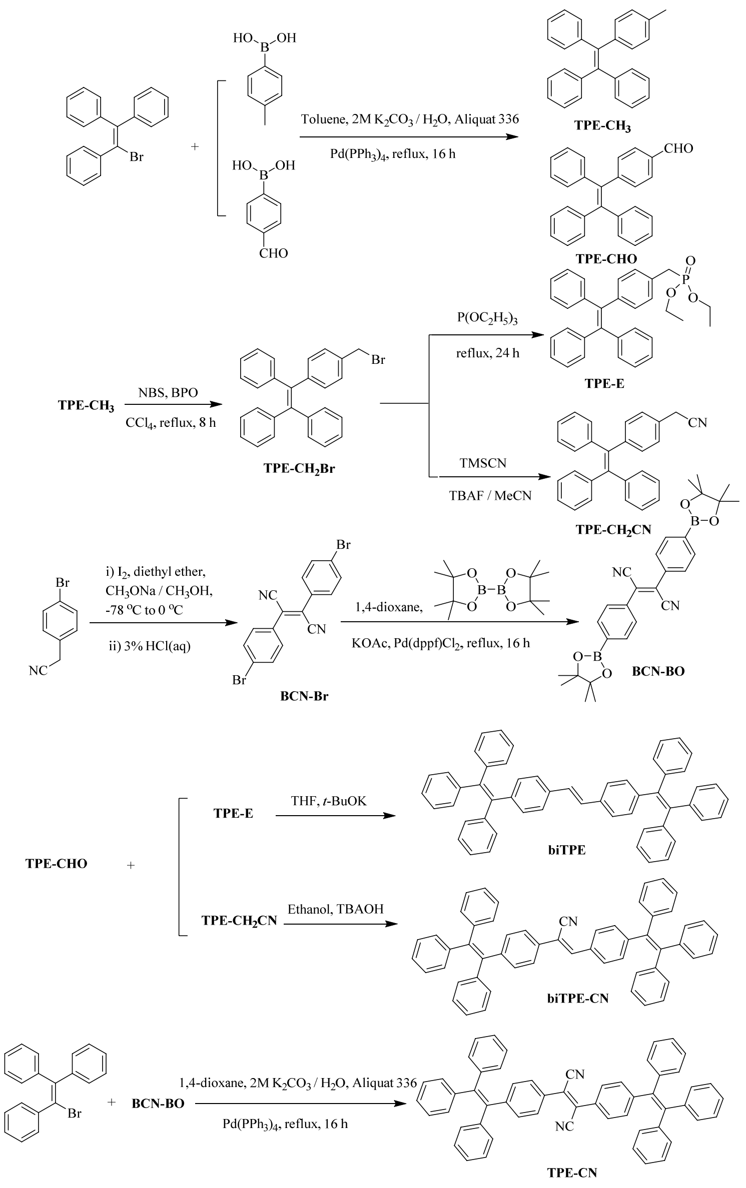
compounds with AIE natures. We further proposed that piezofluorochromism is a common property of most AIE compounds and denoted these compounds as piezofluorochromic AIE (PAIE) materials.[45–50] The discovery of PAIE as a common property allows new opportunities for designing and synthesizing other piezofluorochromic materials. Recently, some studies on the relationship between molecular structure and piezofluorochromism have been reported by Yang's group.[51-54]

In this study, tetraphenylvinyl-capped ethane derivatives, with 0, 1, and 2 cyano groups at the ethane moiety with different numbers of cyano groups were synthesized, and their AIE and piezofluorochromic properties were characterized. Piezofluorochromic activity can be significantly enhanced by introduction of cyano groups to the molecular structures of the derivatives. Structure-property relationships were studied in detail using emission and absorption spectra, wide-angle X-ray diffraction, fluorescence lifetime decay, and other techniques. The results obtained will help guide piezofluorochromic mechanism studies and enable the development of other piezofluorochromic materials in the near future.



Scheme 1. Synthetic routes for biTPE, biTPE-CN and TPE-CN.

Results and Discussion

Three tetraphenylvinyl-capped ethane derivatives possessing 0, 1, and 2 cyano groups, namely, biTPE, biTPE-CN, and TPE-CN,

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respectively, were successfully synthesized according to the routes shown in Scheme 1. The chemical structures of all compounds were characterized via nuclear magnetic resonance, mass spectrometry, and elemental analysis.

The optical properties of the derivatives were investigated using their UV-vis and photoluminescence (PL) spectra in tetrahydrofuran (THF) solution and in the solid state (Table 1). As shown in Fig. 1, the UV-vis spectra of the compounds in dilute THF solution exhibit two absorption bands corresponding to the absorption of TPE units and π-π* transitions of the conjugated π-electron system in the molecules. With increasing number of cyano groups, the maximum absorption wavelength of the corresponding compound, which is related to the π-π* transition of the conjugated π-electron system, shows red-shifts from 368 nm to 405 nm. This shift indicates that introduction of cyano groups to the molecules can reduce the electron transition energy from the ground state to the excited state. The PL spectra of the compounds both in dilute THF solution and as solid powders are shown in Fig. S1 (†ESI). Upon excitation, both biTPE and biTPE-CN are nearly non-emissive whereas TPE-CN exhibits a weak orange emission in dilute THF solution. However, all three compounds are highly emissive in their solid forms. Similar to observations from the UV-vis spectra, the maximum emission wavelengths of the compounds in THF solution and as solid powders red-shift as the number of cyano groups increases. The emission color of biTPE-CN is green, that of biTPE is blue, and that of TPE-CN is reddish-orange. To gain a better understanding of the optical properties of the three compounds, we calculated their energy levels and energy gaps (ΔE_g) by cyclic voltammetry analysis and UV-vis absorption spectroscopy (Table 1 and Fig. S2). The ΔE_g values of biTPE, biTPE-CN, and TPE-CN exhibit a decreasing tendency, which supports the hypothesis that introducing cyano groups can reduce the electron transition energy between the ground state and the excited state. Therefore, we successfully demonstrate a simple molecular design strategy to tune the PL color of TPE-capped ethane derivatives by introduction of cyano groups.

Table 1. Optical and electronic properties of the compounds

Compound	λ_{abs} ^{a} (nm)	λ_{em} ^{b} (nm)	λ_{em} ^{c} (nm)	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE_g (eV)
biTPE	301, 368	474	457	5.46	2.51	2.95
biTPE-CN	301, 383	503	491	5.63	2.85	2.78
TPE-CN	303, 405	575	517	5.74	3.22	2.52

$^{a, b}$ In THF; ^{c} Solid powder.

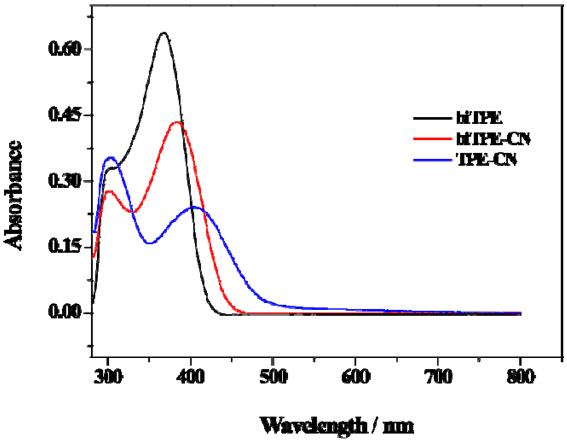

Fig. 1 UV–vis absorption spectra of biTPE, biTPE-CN, and TPE-CN in THF solution, concentration: 10 μM.

As discussed above, all three compounds exhibit weak emission in dilute solution but strong fluorescence as solids, which reveals their nature as AIE molecules. To investigate the AIE activity of the compounds, their PL behaviors were studied in dilute mixtures of water/THF with different water fractions (f_w, the volume percentage of water in the mixtures), and the corresponding emission spectra are shown in Fig. 2. The PL behaviors of all of the compounds in water/THF remained nearly constant with increasing f_w, and the derivatives presented evident AIE or AIEE characteristics. The PL signals of the compounds in a dilute THF solution were relatively weak and remained nearly unchanged at low f_w ($f_w \leq 60\%$). This phenomenon may be attributed to intramolecular rotations of the compounds, which serve as relaxation channels for the excited state. However, the PL intensity of the compounds began to increase rapidly at $f_w > 60\%$ because of aggregation of the molecules. As f_w increases from 80% to 90%, the PL spectra exhibit decreasing intensities with red-shifted emission (Fig. 2 and Table 2); these results can be interpreted in terms of ratio changes of the two existing forms of the compounds, namely, their amorphous and crystalline phases.

Table 2. The maximum emission wavelength of the compounds with the water fractions of 80 % and 90 %

Water fraction	λ_{em} (biTPE)(nm)	λ_{em} (biTPE-CN) (nm)	λ_{em} (TPE-CN) (nm)
80 %	458	483	514
90 %	477	500	570

The morphology of aggregated TPE-CN in water/THF mixtures with f_w of 80% and 90% was observed by scanning electron

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microscopy (SEM). The SEM images in Fig. 3 evidently show two completely different aggregated forms: crystals and amorphous aggregates. TPE-CN tends to aggregate in the form of rod-shaped crystals with a diameter about 100 nm at f_w = 80% and aggregate as irregular spheres or ellipsoids at f_w = 90%. Evidently, the aggregated forms of the compounds are distinct in different water solutions.

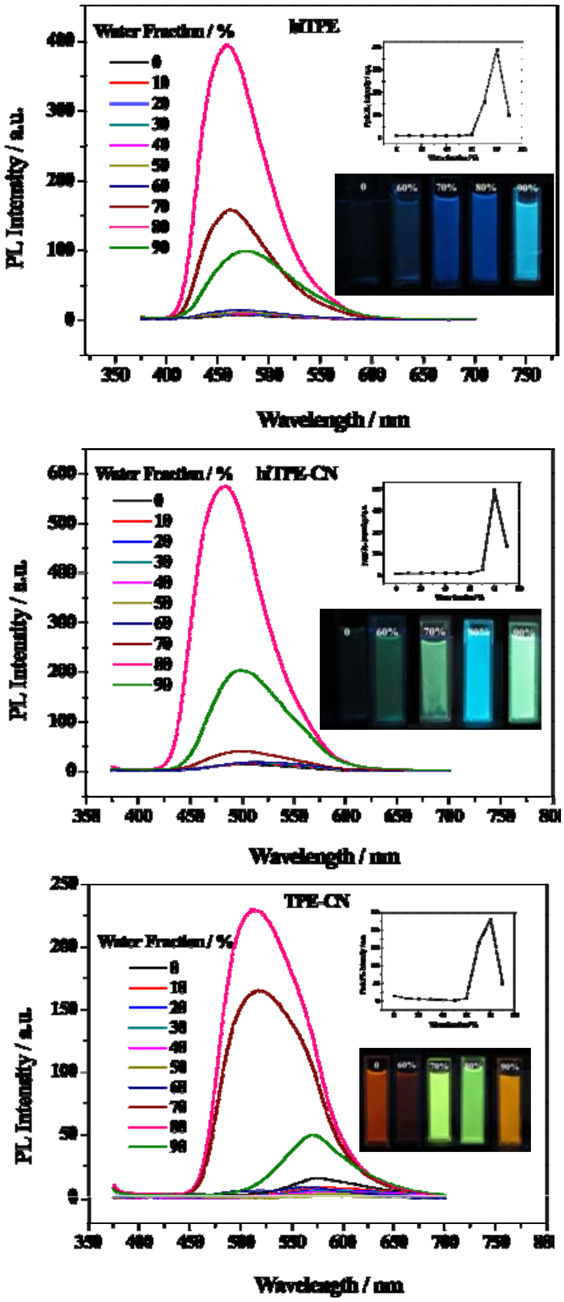

Fig. 2 PL spectra of biTPE, biTPE-CN, and TPE-CN in water/THF mixtures with different water fractions. The insets depict changes in PL peak intensity and emission images of the compounds in mixtures with different water fraction under 365 nm UV illumination.

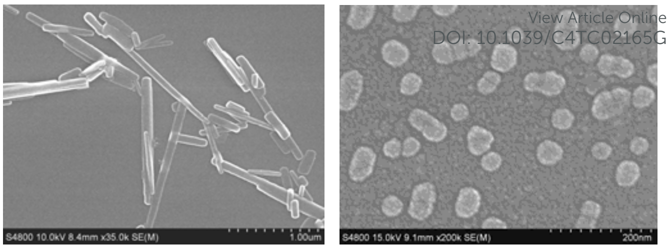

Fig. 3 SEM images of TPE-CN in water/THF mixtures with water fractions of 80 % (left) and 90 % (right).

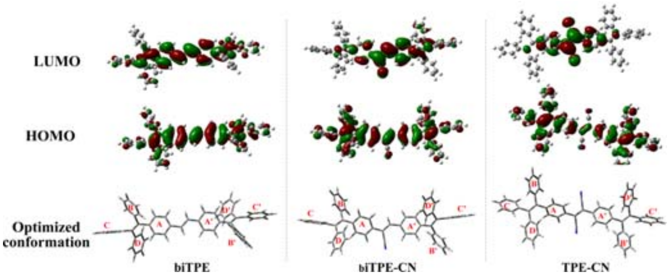

Fig. 4 Calculated spatial electron distributions of LUMOs and HOMOs, and the optimized conformation structures of the compounds.

To obtain further insights into the photophysical properties of the three compounds at the molecular level, quantum mechanical computations were carried out using a Gaussian 03 program. The HOMOs and LUMOs of these compounds were obtained according to the density functional method at the B3LYP/6-31G level after optimizing their structures to the lowest energy spatial conformations, as shown in Fig. 4. The HOMOs of the three compounds show similar dispersed electron cloud distributions over the entire molecules. However, variations in the electron cloud distributions of their LUMOs lead to different photophysical properties. After introduction of cyano groups to biTPE-CN and TPE-CN, most of the electron clouds of the TPE moieties transferred to the cyano groups at their LUMOs because of the strong electron-withdrawing ability of the cyano group. This observation indicates that photoinduced intramolecular charge transfers occur in the excited states of these two compounds. Thus, among the derivatives, TPE-CN, which possesses two cyano groups, emits the strongest fluorescence in THF solution. Moreover, the three compounds adopt a twisted spatial conformation at their optimized lowest energy states; this conformation disfavors close molecular packing in the solid state and leads to efficient fluorescence in this state. Dihedral angles between phenyl groups A and A’ in the three derivatives increase with increasing number of cyano groups, whereas dihedral angles between phenyl rings in TPE units (A-B, A-C, and A-D) are maintained, as demonstrated in Table S1. Introduction of cyano groups exerts little influence on the conformations of the TPE moieties but can evidently enhance the degree of molecular distortions because of steric hindrance effects. These increases in molecular distortion can cause the compounds to adopt different molecular packing modes in the solid state and may affect their macroscopic properties.

As the three compounds adopt a twisted spatial conformation in their optimized structures, assembly of the molecules into dense and closely packed structures is difficult. The crystals are easily destroyed by external pressure because of weak intermolecular interactions. This destruction may be triggered by slip deformation under external pressure. Destruction of crystalline structures may lead to molecular conformation planarization and ultimately result in red-shifting in the PL spectrum.[37] As such, the three compounds must exhibit piezofluorochromic characteristics.

Pristine or original samples of the three compounds were prepared by adding copious amounts of *n*-hexane to their dichloromethane solutions. Images of these compounds obtained at room temperature under natural and UV lights and with different sample treatments, including grinding, fuming, and regrinding, are shown in Fig. 5. As expected, the AIE compounds exhibit evident piezofluorochromic properties. The color and the emission of pristine samples showed bathochromic shifts after grinding. In addition, pristine states could be recovered by fuming the ground samples with *n*-hexane vapor, which suggests that the piezofluorochromic properties of the compounds are finely reversible. These reversible switches of both color and emission demonstrate that the compounds are promising materials for optical recording and pressure-sensing applications.

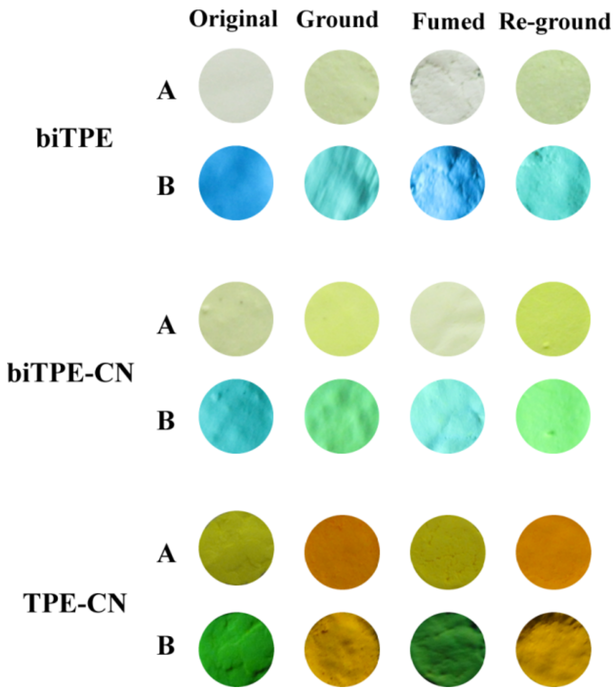

Fig. 5 Images of biTPE, biTPE-CN, and TPE-CN samples (A) taken under natural light and (B) 365 nm UV light with different processes: Original, original sample; Ground, ground sample; Fumed, fumed sample which obtained by fuming the ground sample in *n*-hexane vapor for 5 min; Re-ground, ground sample of the above fumed sample.

The detailed PL spectra of the compounds after grinding and fuming are shown in Fig. 6. After grinding, the pristine samples of biTPE, biTPE-CN, and TPE-CN exhibited red-shifts of 19, 24, and 50 nm, respectively, in their fluorescent emission spectra. The results of our previous quantum mechanical computations indicated that cyano groups can enhance the distortion degree of the molecules because of steric hindrance. Therefore, we can infer that the piezofluorochromic properties of the compounds are related to their distortion degrees; here, molecules with higher degrees of distortion display more evident piezofluorochromic properties under the stimulus of external pressure. Thus, the piezofluorochromic property of a compound can be significantly improved simply by introducing a cyano group to its molecular structure.

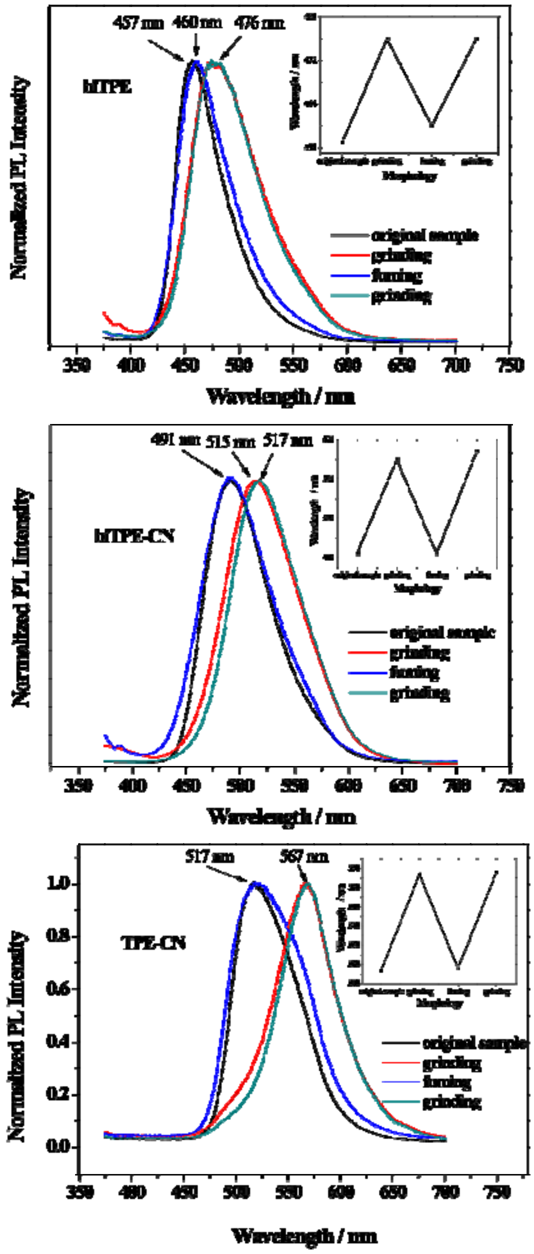

Fig. 6 Normalized PL spectra of biTPE, biTPE-CN, and TPE-CN samples. The insets depict changes on the maximum emission wavelength of the compounds.

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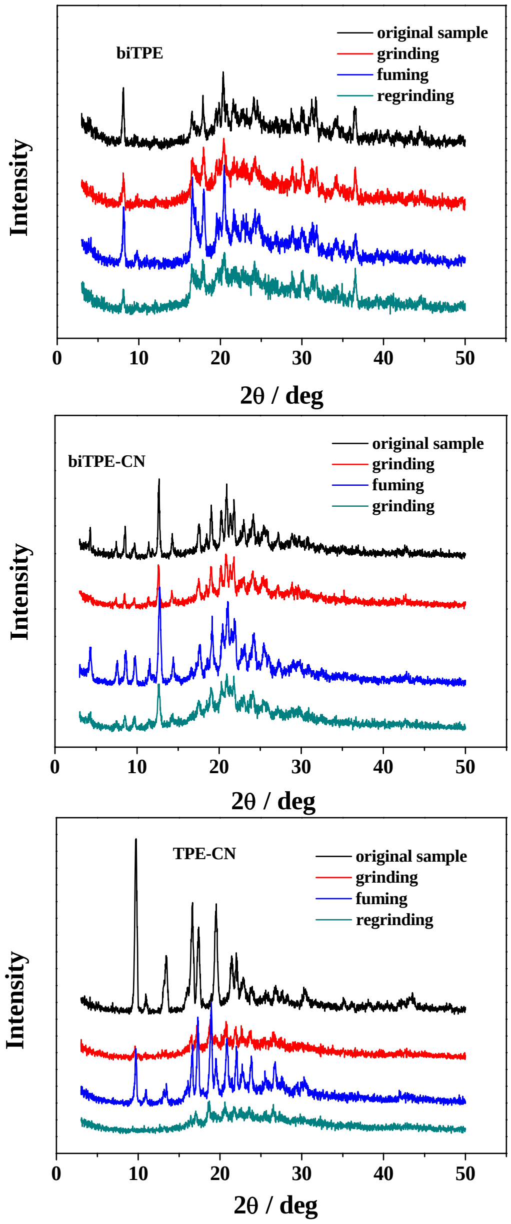

Fig. 7 WAXD curves of biTPE, biTPE-CN, and TPE-CN samples with different treatments.

To study the mechanism of piezofluorochromism, wide-angle X-ray diffraction (WAXD) measurements were carried out on the samples. The WAXD curves of the three compounds obtained after grinding and fuming are shown in Fig. 7. We can clearly observe that all of the WAXD curves of the pristine samples display sharp diffraction peaks. These diffraction peaks decrease in either number or intensity after grinding and are particularly notable on TPE-CN, which contains the largest number of cyano groups. Thus, we can conclude that the original samples exhibit relatively high degrees of order in their crystalline structures. The structural orders of the samples were destroyed to a certain degree after grinding, leading to red-shifts in their PL spectra. Either the number or intensity of diffraction peaks can be recovered by fuming the ground samples with *n*-hexane vapor; such recovery presents a reversible process with blue-shifts in PL emission. The most obvious piezofluorochromic characteristics of TPE-CN are attributed to maximum changes in degree of crystalline structure order in this sample after grinding compared with the two other samples.

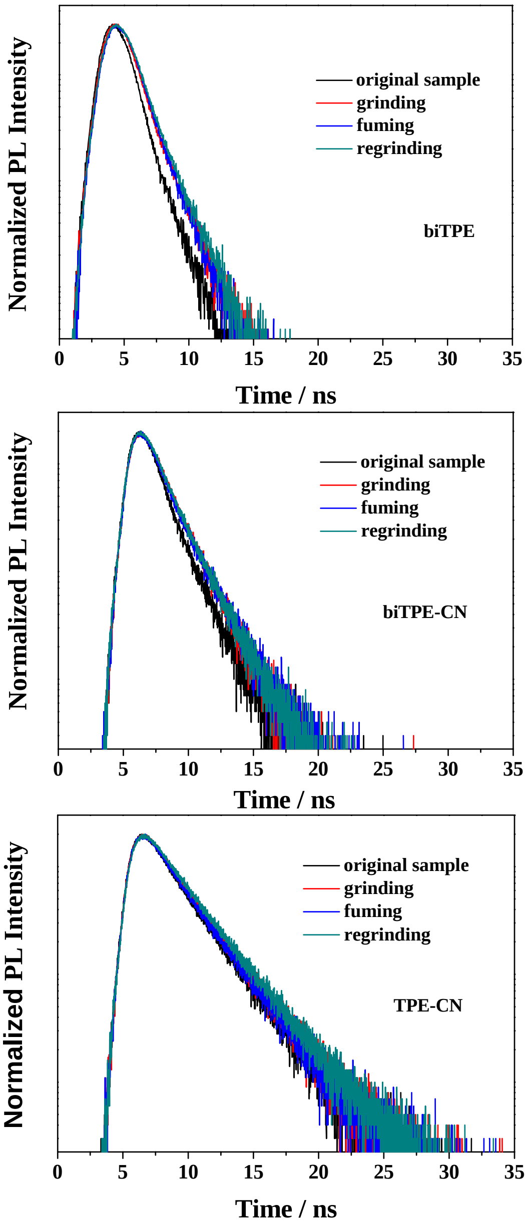

Fig. 8 Time-resolved emission decay curves of biTPE, biTPE-CN and TPE-CN samples.

The time-resolved emission decay behaviors of the compounds were further studied after grinding and fuming to understand the mechanism of piezofluorochromism. Time-resolved fluorescence curves (Fig. 8) and lifetime data (Table 3) feature two lifetimes (τ_1 and τ_2), and the weighted mean lifetimes ($<\tau>$) of the original samples increase with increasing number of cyano groups. In comparison with the pristine samples, the $<\tau>$ values of the ground samples are prolonged for approximately 0.2 ns, which indicates that

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changes in fluorescent color are accompanied by significant changes in the fluorescent lifetime of the samples. The <τ> of fumed ground samples is fairly difficult to return to original values, which is probably due to interactions between the solvent and samples.

Table 3. Solid state fluorescence lifetime data of biTPE, biTPE-CN and TPE-CN samples

Compound	Sample	τ_1 (ns)	A_1	τ_2 (ns)	A_2	<τ> (ns)
biTPE	original	0.59	85 %	1.32	15 %	0.70
	grinding	0.60	64 %	1.44	36 %	0.90
	fuming	0.68	67 %	1.39	33 %	0.91
	regrinding	0.69	64 %	1.54	36 %	1.00
biTPE-CN	original	0.72	58 %	1.62	42 %	1.09
	grinding	0.68	32 %	1.68	68 %	1.36
	fuming	0.75	49 %	1.92	51 %	1.35
	regrinding	0.75	38 %	1.76	62 %	1.37
TPE-CN	original	1.14	26 %	2.64	74 %	2.26
	grinding	1.12	17 %	2.70	83 %	2.43
	fuming	1.31	28 %	2.77	72 %	2.37
	regrinding	1.47	23 %	2.91	77 %	2.58

The relationship between the molecular aggregation state and luminescence properties of the compounds can be determined directly and definitively by single crystals, which present a highly ordered molecular packing structure. The single crystals of biTPE and biTPE-CN were grown in toluene and acetone, respectively. Two types of TPE-CN crystals showing different fluorescent emissions were also obtained in a mixture of dichloromethane and *n*-hexane (C_1, green; C_2, orange). The normalized PL spectra of biTPE, biTPE-CN, and TPE-CN crystals are shown in Fig. 9. The emission peaks of single crystals of biTPE and biTPE-CN and crystal C_1 of TPE-CN are identical to those of their pristine samples, which indicates that the corresponding pristine samples adopt molecular packing modes similar to those of the crystals in the present work. The PL emission wavelength of the TPE-CN C_2 crystal is identical to that of its ground sample, which suggests that the two TPE-CN samples present similar molecular packing modes.

The crystalline structures of biTPE and biTPE-CN were determined by single-crystal XRD analysis. X-ray crystallographic intensity data were collected and are shown in in Tables S2 and S3. As shown in Fig. 10, biTPE and biTPE-CN are packed in a head-to-head fashion to form J-aggregates. The π-π interactions in the biTPE and biTPE-CN crystals are relatively weak because of their highly twisted conformations. As the molecular structures of the compounds are similar, the crystal C_1 of TPE-CN may also be assumed to adopt J-aggregated packing.

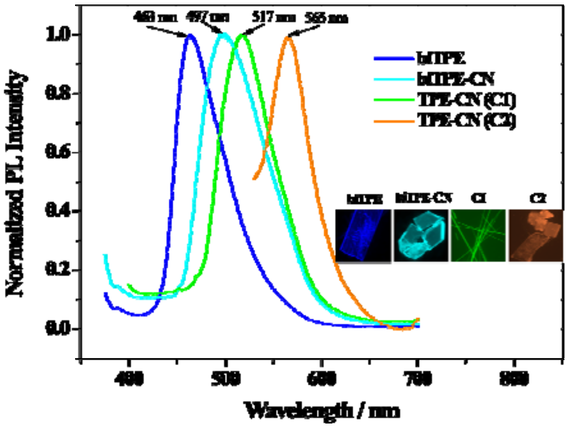

Fig. 9 Normalized PL spectra of the different crystals. The insets depict the fluorescence microscope images of the crystals.

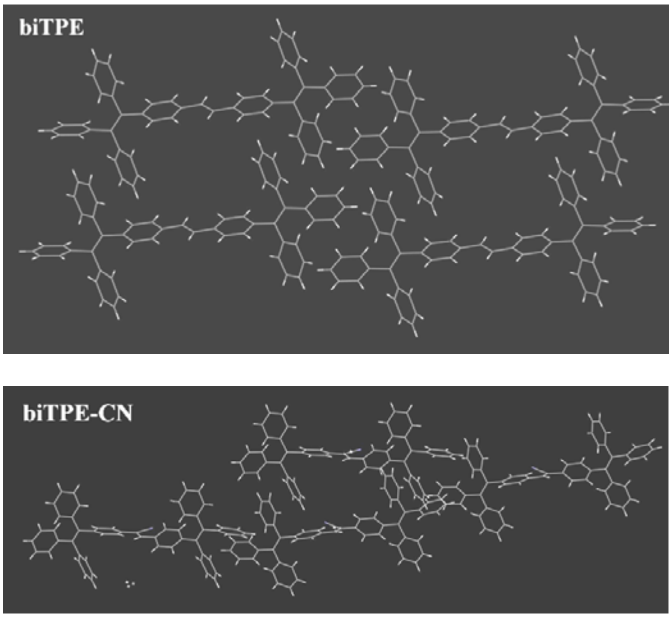

Fig. 10 Molecular packing of biTPE and biTPE-CN in their single crystal structures.

Conclusions

Three tetraphenylvinyl-capped ethane derivatives with 0, 1, and 2 cyano groups at the ethane moiety, namely, biTPE, biTPE-CN, and TPE-CN, respectively, were designed and successfully synthesized to better understand the influence of cyano groups on photophysical properties. These compounds exhibited strong AIE activities and significant cyano number-dependent piezofluorochromic properties. Spectroscopic properties and morphological structures were reversibly and repeatedly achieved upon grinding or fuming. These excellent properties indicate that the compounds are promising stimuli-responsive luminescent materials with potential applications in recording, pressure-sensing, and light-emitting. Piezofluorochromic activity was considerably enhanced by introduction of cyano groups to the molecular structures of the compound. We proposed that the twisted conformations of these compounds are a key factor influencing their piezofluorochromic activity. Structure–property relationships were studied in detail, and the results obtained can help researchers obtain a better understanding of the piezofluorochromic mechanism and develop other piezofluorochromic materials in the near future.

Experimental

General information

4-Methylphenylboronic acid, bromotriphenylethylen, 4-formylphenylboronic acid, *n*-bromosuccinimide, benzoyl peroxide, potassium tert-butoxide (t-BuOK), tetrakis(triphenyl phosphine) palladium(0), cyanotrimethylsilane, tetrabutylammonium fluoride (1 M) THF solution, 4-bromophenylacetonitrile, iodine, bis(pinacolato)diboron, tetrabutylammonium hydroxide (TBAOH), methyl trioctyl ammonium chloride, [1,1'-Bis(diphenylphosphino)ferrocene] dichloropalladium(II), and tetrabutylammonium perchlorate (electrochemical grade) were purchased from Alfa Aesar and used as received. Ultra-pure water was used in all of the experiments. All other reagents and solvents were purchased as analytical reagent-grade chemicals from Guangzhou Dongzheng Company (China) and used without further purification. Intermediates TPE-CH_3[55], TPE-CHO[45], TPE-CH_2Br[56], BCN-Br[57], and BCN-BO[58] were synthesized according to literature methods.

Proton and carbon-13 nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were measured on a Mercury-Plus 300 spectrometer [$CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard]. Mass spectra (MS) were performed on a Thermo DSQ MS spectrometer. Elemental analyses (EA) were performed with an Elementar Vario EL elemental analyzer. Ultraviolet−visible (UV−vis) absorption spectra were determined on a Hitachi U-3900 spectrophotometer. Photoluminescence (PL) spectra were measured on a Shimadzu RF-5301PC spectrometer with a slit width of 3.0 nm for both excitation and emission. Cyclic voltammetry (CV) measurement was carried out on a Shanghai Chenhua electrochemical workstation CHI660C in a three-electrode cell with a glassy carbon disk counter electrode, an Ag/AgCl reference electrode, and a Pt working electrode. All CV measurements were performed under an inert argon atmosphere with supporting electrolyte of 0.1M tetrabutyl ammonium perchlorate (*n*-Bu_4NClO_4) in dichloromethane at scan rate of 100 mV/s using ferrocene as standard. The energy gaps ΔE_g for the compounds were estimated from the absorption edges of UV-visible absorption spectra. Wide-angle X-ray diffraction (WAXD) measurements were carried out by using a Rigaku X-ray diffractometer (D/max-2200) with an X-ray source of Cu Kα(λ= 0.15406 nm) at 40 kV and 30 mA, at a scan rate of 4° (2θ) per 1 min. Time-resolved emission decay behaviors were measured on an Edinburgh Instruments spectrometer (FLSP920). Ground samples were prepared by grinding, using a mortar and pestle. The method of solvent vapor fuming treatment is filling the ground sample on a grooved glass, which was then placed it in a large beaker saturated with n-hexane vapor for 5 min at the temperature of 70 °C. The water/THF mixtures with different water fractions were prepared by slowly adding distilled water into the THF solution of samples under ultrasound at room temperature. Scanning electron microscopy (SEM) images were obtained from a Hitachi S4800 microscope operated at 15 kV. Fluorescence microscopy images were taken on a Zeiss Axio Observer A1 fluorescence microscope. X-ray crystallographic intensity data were collected by using a Bruker Smart 1000 CCD diffractometer equipped with a graphitemonochromated enhance (Mo) X-ray source. CCDC 1026011 and 1026015 contain the supplementary crystallographic data for this paper

Synthesis

TPE-E: TPE-CH_2Br (5.00 g, 11.8 mmol) and triethyl phosphate (10 mL) were added into a 100 mL round-bottom flask. Then the mixture was stirred and refluxed for 24 h at 150 °C. After cooling to room temperature, the reaction mixture was purified by silica gel column chromatography (acetone/*n*-hexane, 1/5, v/v) to afford a white powder (4.20 g, 74 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) : 7.04-7.11 (m, 10H), 6.95-7.04 (m, 9H), 3.86-4.01 (m, 4H), 3.07 (d, 2H), 1.22 (t, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) : 143.90, 143.77, 143.72, 142.62, 141.17, 140.67, 131.68, 131.48, 129.76, 129.64, 129.44, 129.35, 127.83, 126.64, 126.58, 62.58, 62.50, 34.85, 33.03, 31.36, 16.86, 16.79; MS(EI), *m/z*: 482 ([M]$^+$, calcd for $C_{31}H_{31}O_3P$, 482).

TPE-CH_2CN: A solution of TPE-CH_2Br (3.44g, 8.08 mmol) in acetonitrile (40 mL) was stirred at room temperature. Then trimethyl cyanide (1.60 g, 16.2 mmol) and tetrabutylammonium fluoride (16.2 mL, 16.2 mmol) in THF were added and stirred for 12 h under argon atmosphere. The reaction mixture was purified by silica gel column chromatography (ethyl acetate/*n*-hexane, 1/4, v/v) to afford a white powder (1.89 g, 63 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) : 7.07-7.14 (m, 9H), 6.98-7.07 (m, 10H), 3.66 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) : 143.88, 143.58, 143.52, 141.80, 140.11, 132.19, 131.42, 127.95, 127.86, 127.47, 126.81, 126.78, 118.02, 23.70; MS(EI), *m/z*: 371 ([M]$^+$, calcd for $C_{28}H_{21}N$, 371).

biTPE: A solution of TPE-E (0.50 g, 1.04 mmol) and TPE-CHO (0.31 g, 0.87 mmol) in THF (20 mL) was stirred at room temperature. Then *t*-BuOK (0.50 g, 4.46 mmol) was added and the mixture was stirred for 12 h. After the solvent was removed under reduced pressure, the residue was recrystallized with THF/ethanol to afford a white powder (0.56 g, 93 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) : 7.19 (d, 4H), 7.07-7.14 (m, 18H), 7.01-7.07 (m, 12H), 6.98 (d, 4H), 6.91 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) : 143.90, 143.80, 143.27, 141.26, 140.79, 135.60, 131.85, 131.58, 131.52, 128.34, 127.92, 127.85, 126.67, 125.92; MS(EI), *m/z*: 688 ($[M]^+$, calcd for $C_{54}H_{40}$, 688); Anal. calcd for $C_{54}H_{40}$: C 94.15, H 5.85; found: C 94.18, H 5.82.

biTPE-CN: A solution of TPE-CH_2CN(0.50 g, 1.35 mmol) and TPE-CHO (0.49 g, 13.5 mmol) in ethanol (20 mL) was stirred at room temperature. Then tetrabutylammonium hydroxide solution (0.8 M, 5 drops) was added and the mixture was heated to reflux for 2 h. A light green solid precipitated from the system (0.81 g, 84 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.60 (d, 2H); 7.38 (s, 1H), 7.34 (d, 2H), 7.06-7.17 (m, 22H), 7.00-7.06 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 146.49, 144.96, 143.58, 143.55, 143.52, 143.46, 143.45, 143.34, 142.47, 142.10, 141.36, 141.30, 140.22, 140.09, 132.66, 132.14, 132.10, 132.02, 131.90, 131.48, 128.87, 128.04, 127.88, 126.87, 125.31, 118.29, 110.61; MS(EI), *m/z* : 713 ($[M]^+$, calcd for $C_{55}H_{39}N$, 713); Anal. calcd for $C_{55}H_{39}N$: C 92.53, H 5.51, N 1.96; found: C 92.50, H 5.53, N 1.99.

TPE-CN: A solution of BCN-BO (0.50 g, 1.04 mmol) and bromotriphenylethylene (0.77 g, 2.29 mmol) in 1, 4-dioxane (25 mL) was stirred at room temperature. 2 M potassium carbonate aqueous solution (2 mL) and aliquat 336 (10 drops) were added and the mixture was stirred for 0.5 h under an argon atmosphere. Then the $Pd(PPh_3)_4$ catalyst (catalytic amount) was added and the reaction mixture was stirred at 90 °C for 16 h. After cooling to room temperature, the reaction mixture was purified by silica gel column chromatography (dichloromethane /*n*-hexane, 1/3, v/v) to afford a light yellow powder (0.40 g, 52 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) : 7.55 (d, 4H), 7.08-7.18 (m, 22H), 6.99-7.08 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) : 147.73, 143.29, 143.15, 143.04, 139.67, 132.22, 131.47, 130.16, 128.19, 127.90, 127.27, 127.03, 124.34, 116.98; MS(EI), *m/z*: 738 ($[M]^+$, calcd for $C_{56}H_{38}N_2$, 738); Anal. calcd for $C_{56}H_{38}N_2$: C 91.03, H 5.18, N 3.79; found: C 91.00, H 5.20, N 3.81.

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Three tetraphenylvinyl-capped ethane derivatives containing different cyano group number exhibited strong AIE activities and significant cyano number-dependent piezofluorochromic properties.