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ARTICLE

2,6,9,10-Tetra(*p*-dibutylaminostyryl)anthracene as a multifunctional fluorescent cruciform dye

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In this work, we have synthesized a trtradonor-capped anthracene-centered cruciform 2,6,9,10-tetra(*p*-dibutylaminostyryl)anthracene (**TDC**) and its optical properties are investigated. **TDC** is a light- and heat-stable dye and shows aggregation-enhanced emission (AEE), large and enhanced two-photon absorption cross sections (δ), fluorescence sensing selectively to transition metal ions such as Zn^{2+} and Cu^{2+}, and appreciable piezofluorochromism (PFC), which is rarely found to exist simultaneously in both cruciform and other configuration dyes. The AEE and PFC behaviours result from the existence of strongly twisted 9,10-branch, and the large and enhanced δ is ascribed to the multiple conjugation pathways and introduction of donor end-groups. **TDC** possesses non-centrosymmetric structure and semi-disjoint frontier molecular orbital, which could rationalize its fluorescence sensing selectively to Zn^{2+} and Cu^{2+}. These findings indicate further that anthracene ring is indeed a unique π-center that is different from other π-centers and can construct novel cruciforms with interesting optical properties.

Introduction

For decades, linear π-conjugated organic molecules have been the mainstay of advanced materials for optical and optoelectronic applications. Recently, higher orders, especially two-dimensional arylene-centered oligomers, have started to draw serious research interest, and some benzene-, thiophene-, anthracene-, pyrazine-, benzobisoxazole-, benzobisthiophene-centered cruciforms have been designed, synthesized and their optical and optoelectronic properties are investigated.[1–4] These new configuration materials have greatly widened the scope of molecular candidates applicable in chemosensors,[1d,1e,5] molecular switches,[6] nonlinear optical materials,[3a,3b,7] field effect transistors,[2b] and photovoltaic and electroluminescence devices.[8] We are interested in 2,6,9,10-tetra(arylvinyl)-anthracenes due to their unique π-center structure. Compared to the extensively investigated benzene-centered analogues, 2,6,9,10-tetra(arylvinyl)anthracenes have an asymmetric π-center and a strongly twisted 9,10-branch, which could render them unique aggregation behaviours and optical properties. Indeed, we have found that the donor- and/or acceptor-capped anthracene-centered cruciforms, but not the benzene-centered analogues,[7b,7c,9] show the large and the enhanced two-photon absorption (2PA) cross sections (δ),[3] and those pyridine- and/or dibutylaniline-capped anthracene- and benzene-centered cruciforms have exhibited different fluorescence sensing behaviours to metal ions.[2,10] Moreover, most donor- and/or acceptor-substituted 2,6,9,10-tetra(arylvinyl)-anthracenes could exhibit mechano-dependent stable and meta-stable solid states with the different optical properties.[11] To further understand the crucial role of π-centers and

building blocks, here we construct a tetradonor-capped anthracene-centered cruciform, 2,6,9,10-tetra(*p*-dibutylamino-styryl)anthracene (**TDC**, Scheme 1) to investigate the optical properties in both solutions and solid states. It should be noticed that tetra(*p*-dibutylaminostyryl)benzene cruciform has been found not only degrade under light irradiation but also display congruent frontier molecular orbital (FMO) feature that fail to sense metal ions.[1b–d,7b] We now report that **TDC** is not only a light- and heat-stable dye with the unique FMO structure but also exhibits at least four functions: Aggregation-enhanced emission (AEE), fluorescence sensing selectively to transition metal ions, enhanced and solvent-related δ, and appreciable piezofluorochromic (PFC) behaviour.
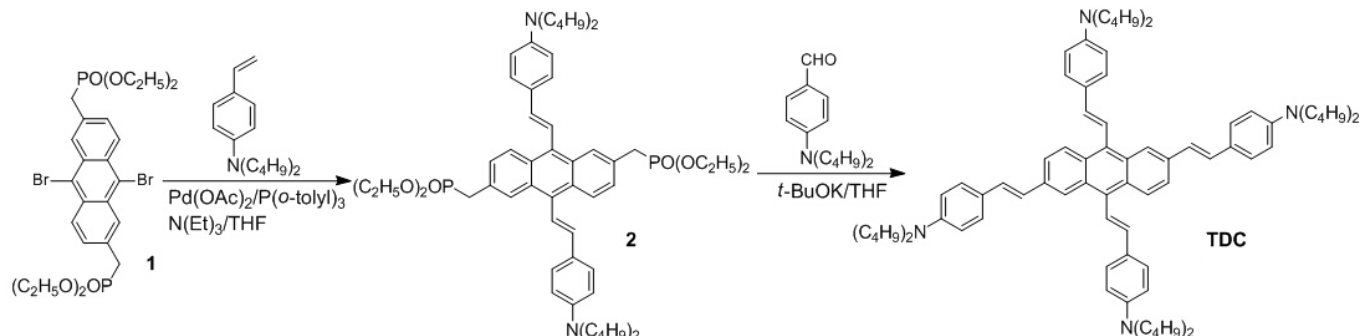
Experimental Section

Materials

Acetonitrile, triethylamine (N(Et)$_3$) and dichloromethane (DCM) over calcium hydride and tetrahydrofuran (THF) over metallic sodium were distilled before use. 4-pyridylaldehyde, triflates of Zn^{2+}, Cu^{2+}, Mg^{2+}, Ca^{2+}, and K^+ were commercially available from Energy Chem. Co. Ltd., China. Other solvents and reagents were analytical grade. All chemicals were used as received without further purification, unless otherwise claimed. 4-Dibutylamino-styrene was synthesized from 4-dibutylaminobenzaldehyde according to the procedure described before,[3] and 2,6-bis(diethyl-phosphorylmethyl)-9,10-dibromoanthracene (**1**) was from previous works.[3]

Measurements

^{1}H and ^{13}C NMR spectra were recorded on a Bruker–AC500 (500 MHz) spectrometer with CDCl$_3$ as solvent. The elemental analysis was performed on Perkin–Elmer 2400. Photoluminescence spectra were measured with Hitachi F-4600 spectrophotometer, and the peak wavelength of the lowest energy absorption band was used as

the excitation wavelength. Powder wide angle X-ray diffraction (PWXD) measurements were performed on a Powder X-ray Diffractometry (INCA Energy, Oxford Instruments), operating at 3 kW. Differential scanning calorimetry (DSC) experiments were carried out on a Netzsch DSC204F1 at a heating rate of 10 ^{o}C/min.

Scheme 1. Synthesis and Structure of Cruciform **TDC**.

The solution fluorescence quantum yield (Φ) was determined by the dilute solution method using rhodamine B in methanol as the reference.[12] The two-photon absorption (2PA) cross-section (δ) was measured by two-photon excitation fluorescence (2PEF) method as described by literatures.[13] The excitation light source was a mode-locked Ti:sapphire femtosecond (fs) laser (Spectra-Physics, Tsunami 3941, 700–980 nm, 80 MHz, <120 fs), which was pumped by a compact cw prolite diode laser (Spectra-Physics, Millennia Pro 5S). The fluorescence signal was recorded by a spectrofluorometer (Ocean Optics, USB2000). **TDC** was dissolved in solvent at the concentration of 1.0×10^{-4} M and the 2PEF intensity was measured at 700–850 nm using rhodamine B (1.0×10^{-4} M in methanol) as the reference.[14] The δ values of **TDC** (δ_s) could be calculated by using the equation: $\delta_s = [(S_s\Phi_r n_r^2 C_r)/(S_r\Phi_s n_s^2 C_s)]\delta_r$, where the subscripts s and r stand for the sample and reference, respectively. S and C represent the integral area of the 2PEF and the solution concentration. δ_r is the 2PA cross section of the reference molecule. The 2PEF spectra of the reference and sample were determined and collected under same measurement conditions and compared, thus the system errors and the wavelength dependence of the detectors and optics, etc. are negligible.

Piezochromic and recovering experiments: A quantity of **TDC** solid (~ 20 mg) and KBr powder (500 mg) were simply mixed in an agate mortar, and the mixed sample was pressed with IR pellet press for 1 min at room temperature under the pressure of 1500 psi. After the fluorescence color and emission spectrum was recorded, the pressed sample was put into an oven and heated for 3 min at 150 ^{o}C, and then kept for 1 min at room temperature before the measurements. The repressing experiment was same as the first pressing. The fuming experiment is to place the pressed sample into a bottle containing a little amount of dichloromethane (DCM), and the sample was put above the DCM level and kept for 1 min at room temperature. After taking the sample out a moment, the measurements were carried out.

Metal ion coordination to cruciform **TDC** was performed in DCM (analytical grade). 5–60 μL of triflate salt (10^{-2} M in DCM) was respectively added to DCM solutions of **TDC** (1.0×10^{-5} M, 5 mL) in a 10 mL of sample bottle via micro-syringe to afford the cruciform solution with different equiv of metal ions. The resulting solutions were capped and shaken for 1 min and transferred into a four-sided quartz spectrophotometry cuvette. The fluorescence spectra were measured at room temperature.

Preparation of aqueous nano-aggregate dispersion: An aliquot (1 mL) of stock THF solution of **TDC** with a concentration of $1.0 \times$

10^{-4} M was slowly added to a certain amount of deionized water with vigorous stirring, and concentration was kept at 1.0×10^{-5} M. These aqueous dispersions were stable during the measurement.

Synthesis

2,6-Bis(diethylphosphorylmethyl)-9,10-bis(p-dibutylamino-styryl)anthracene (2). A pressure tube containing a mixture of 4-dibutylaminostyrene (0.45 g, 1.94 mmol), 2,6-bis(diethylphos-phorylmethyl)-9,10-dibromoanthracene (0.33 g, 0.52 mmol), Pd(OAc)$_2$ (15 mg, 67 μmol), tris(o-tolyl)phosphine (0.13 g, 0.42 mmol), N(Et)$_3$ (3 mL) and THF (3 mL) was sealed under nitrogen and refluxed overnight at 80 ^{o}C. The mixture was separated by a column chromatography on silica gel using ethyl acetate/hexane (3/1) as the eluent. Yield: 0.29 g (51 %). ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.38 (d, 2H), 8.23 (s, 2H), 7.62 (d, 2H), 7.54 (d, 4H), 7.42 (d, 2H), 6.80 (d, 2H), 6.72 (d, 4H), 4.02 (m, 8H), 3.35 (m, 12H), 1.64 (m, 8H), 1.41 (m, 8H), 1.22 (m, 12H), 0.99 ppm (m, 12H). Anal. Calcd. for C$_{56}$H$_{78}$N$_2$O$_6$P$_2$: C, 71.77; H, 8.39; N, 2.99; O, 10.24; P, 6.61. Found: C, 71.84; H, 8.35; N, 3.02.

2,6,9,10-Tetra(p-dibutylaminostyryl)anthracene (TDC). Potassium tert-butoxide (0.16 g, 1.43 mmol) was added to the mixture of compound **2** (0.16 g, 0.17 mmol) and 4-dibutylaminobenzaldehyde (0.11 g, 0.47 mmol) in anhydrous THF (15 mL) at room temperature under N$_2$. The mixture was stirred overnight and then 100 mL of methanol was added. The precipitate was collected and purified by a column chromatography on silica gel using hexane/CH$_2$Cl$_2$ (2/1) as the eluent. Yield: 0.14 g (73 %). ^{1}H NMR (500MHz, CDCl$_3$): δ 8.36 (d, 2H), 8.23 (s, 2H), 7.73 (d, 2H), 7.68 (d, 2H), 7.60 (d, 4H), 7.43 (d, 4H), 7.12 (m, 4H), 6.86 (d, 2H), 6.76 (d, 4H), 6.64 (d, 4H), 3.38 (m, 8H), 3.30 (m, 8H), 1.66 (m, 8H), 1.59 (m, 8H), 1.40 (m, 16H), 0.99 ppm (m, 24H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 148.2, 147.9, 137.4, 134.7, 132.8, 130.4, 129.6, 128.9, 128.1, 128.0, 127.3, 125.2, 125.0, 124.7, 122.2, 120.3, 120.3, 111.9, 111.9, 51.2, 51.0, 31.5, 31.1, 20.7, 20.4, 14.3, 13.9 ppm. Anal. Calcd. for C$_{78}$H$_{102}$N$_4$: C, 85.50; H, 9.38; N, 5.11. Found: C, 85.41; H, 9.41; N, 5.16.

Results and Discussion

Synthesis and strcture characteristics

Synthetic route and structure of **TDC** was depicted in Scheme 1. The Heck coupling of 2,6-bis(diethylphosphorylmethyl)-9,10-dibromoanthracene with 4-dibutylaminostyrene followed by

Wittig–Horner reaction with 4-dibutylaminobenzaldehyde afforded the target compound **TDC** in an overall yield of 37%, and its chemical composition and structure was confirmed by NMR spectra and elemental analysis. **TDC** was highly soluble in common organic solvents, such as THF, chloroform, DCM, toluene (PhMe), and N,N-dimethylamide (DMF). **TDC** is characterized by the asymetric π-center, strongly tiwisted 9,10-backbone, multi-conjugated pathways, and coordinatable end groups, which could confer it multi-functionality.

AEE phenomenon

Conjugated organic dyes exhibiting aggregation-induced emission effect are almost the linear and propeller molecules at present.[15] We find that **TDC**, regarded as the integrate of a highly solution-fluorescent branch 2,6-bis(*p*-dibutylaminostyryl)anthracene (Φ = 65% in THF)[16] and an almost no solution-fluorescent branch 9,10-bis(*p*-dibutylaminostyryl)anthracene (Φ = 0.8% in THF)[17] with same anthracene ring as the common π-center, shows the weak fluorescence emission in THF solution (Φ = 2.9%, Fig. 1b), implying still existence of weakening fluorescence emission effct of twisted 9,10-branch by free intramolecular torsion motion. However, when a large amount of water is added into its THF solution, obviously increased and red-shifted fluorescence emissions are observed with the Φ up to 17.6% under 90% water fraction (Fig. 1b). This could be ascribed to the restriction of intra-molecular rotation of twisted 9,10-styryl units and the probable conformation planarization to some extent in the aggregates.[17] It is noted that this aqueous Φ value (17.6%) is lower than that of 9,10-bis(*p*-dialkylaminostyryl)anthracene (Φ = 34%),[17] implying partial existence of aggregation-quenched emission effect of planar 2,6-bis(*p*-dibutylstyryl)anthracene branch. As expected, solid **TDC** is a strong red emitting material with the peak emission wavelength of 606 nm (*vide infra*). On the other hand, **TDC** exhibits good light and heat stabilities in both solution and solid state, evidenced by their unchanged emission spectra after UV light irradiation and heat treatment.
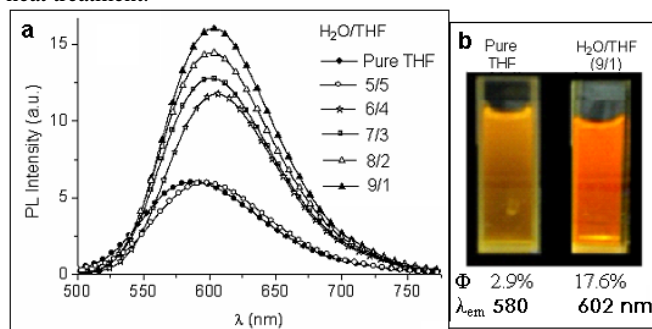

Fig. 1 The fluorescence emission (PL) spectra (a) and fluorescence images of **TDC** in H$_2$O/THF mixture (10 μM). The numbers below the images are the peak emission wavelength (λ$_{em}$) and fluorescence quantum yield (Φ), respectively.

Large and solvent-dependent 2PA activity

Donor- and/or acceptor-capped cruciforms exhibiting high degree of conjugation and multiple pathways for intramolecular electronic and photonic transfer have potential for obtaining the large and enhanced 2PA cross section (δ). However, the greatly enhanced 2PA effect occurred in the anthracene-centered but not in the benzene- or pyrazine-centered cruciforms, and the real origin of this dichotomy is not clear at present. Here we have determined the

2PA spectra of **TDC** in different solvents by two-photon excitation fluorescence (2PEF) method. As shown in Fig. 2, the peak δ values are 2830, 1770, and 1130 GM in toluene, tetrahydrofuran (THF), and DCM, respectively. This is an unexpected result as it is known generally that large 2PA activity is associated with the extent of intramolecular charge transfer (ICT) effect for a given molecule, and the strong ICT character commonly renders the chromophore with large δ. Fig. 3 depicts the absorption and emission spectra of **TDC** in different solvents. As expected for an excited state effect, the solvent polarity hardly affects the absorption spectra of cruciform **TDC**. However, increasing solvent polarity has led the emission spectra to gradual red shifts, which could be ascribed to its asymetric π-center and spatially separated FMO (*vide post*). This implies that the observed solvent effect on 2PA activity is not consistent with the general theoretical predictions,[18] and the disorder causes are quite complicated and many factors, such as solute-solvent interactions, changes in the chromophores geometry, and multichromophore aggregation, could all affect the 2PA allowed states and activities. Nevertheless, **TDC** has much larger δ values in the investigated three solvents and shows the enhanced δ with respect to its two branches 2,6-bis- and 9,10-bis-(p-dibutylaminostyryl)anthracenes.
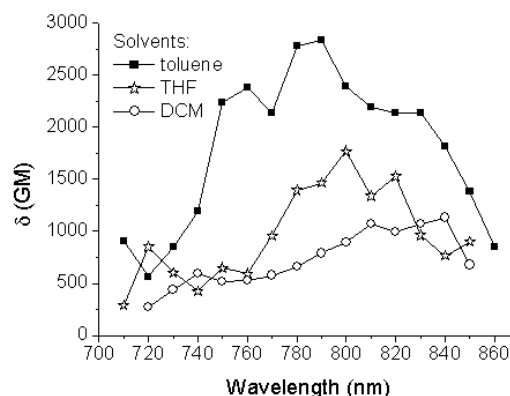

Fig. 2 Two-photon absorption spectra of **TDC** in different solvents (0.1 mM, excitation under 100 mW laser power).
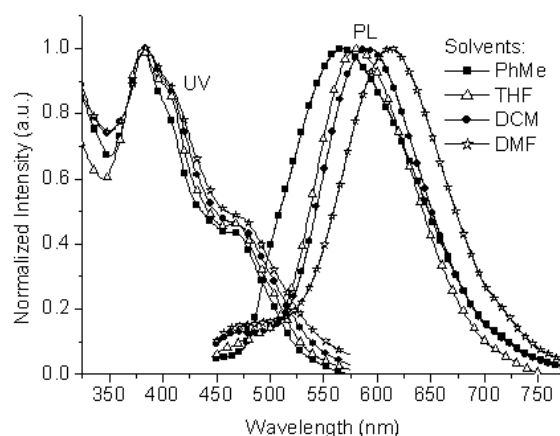

Fig. 3 The absorption and emission spectra of **TDC** in PhMe, THF, DCM, and DMF at 1.0×10^{-5} M.

Fluorescence sensing selectively to transition metal ions

Donor–acceptor-capped cruciforms have been investigated to show spatially separated FMOs, and those with coordination terminals (such as pyridine and dibutylaniline, etc.) could be used as

functional scaffolds for differential metal sensor arrays. However, tetradonor-capped cruciforms commonly show congruent FMOs and are rarely investigated. **TDC** is characteristic of an asymmetric π-center and has a semi-disjoint FMO (Fig. 4a), and its characteris is that the HOMO is almost spread out over the whole π-system, while the LUMO density is convergent and almost concentrates on the anthracene ring. This semi-disjoint FMO feature could make it show not only solvatochromism (ICT effect) but also coordination ability to some metal ions. We have examined the effect of several different physiologically-active metal cations (triflates of alkali K^+, alkaline-earth Mg^{2+} and Ca^{2+}, and transition Cu^{2+} and Zn^{2+}) on emission properties of **TDC** in dichloromethane. It is observed that Cu^{2+} and Zn^{2+}, but not K^+, Mg^{2+} and Ca^{2+}, could obviously blue-shift and enhance the fluorescence emission of cruciform **TDC** (Fig. 5), implying strong coordination abilities between **TDC** and the selected transition metal ions, and **TDC** becomes a selective sensor for some transition metal ions. This could be rationalized by qualitatively examining relative energy levels of the FMOs as the coordination happens (Fig. 4b). Upon coordination, the interaction between dibutylaniline units and metal ions will weaken the electron-donating ability of dibutylamino moieties to whole π-system, which will significantly lower the HOMO level and slightly lower the LUMO level considering the very minor distribution in the amine moieties of the LUMO electron density. The enlarged band gap could blue-shift the emission spectrum and enhance the Φ due to that the higher energy of the emitting states facilitates the radioactive pathways. The emission spectra of **TDC** solution are monotonously blue-shifted with the increase of Cu^{2+} and Zn^{2+} equiv and then remain almost unchanged at high concentrations of metal ions (Fig. 6), implying the negligible difference of the coordination capacity between 2,6- and 9,10-branches.
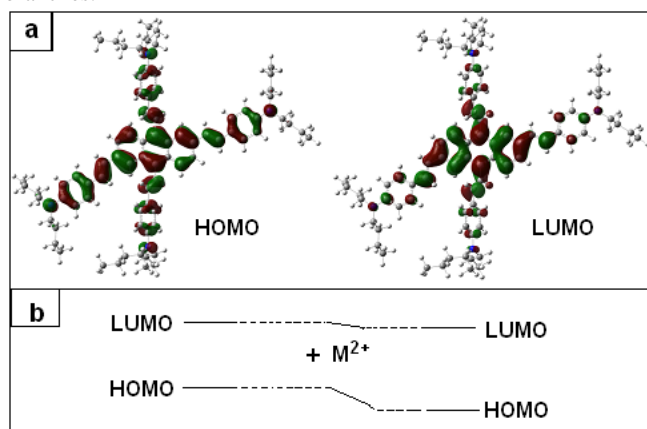

Fig. 4 (a) Frontier molecular orbital plots of **TDC** calculated with B3LYP/6-31G*; (b) The energy level change upon coordination with metal ions.
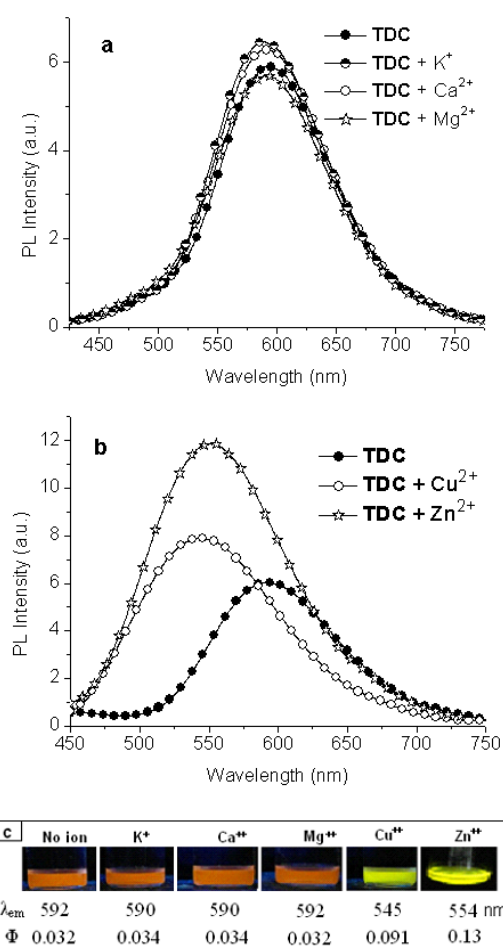

Fig. 5 Emission spectra (a,b) and fluorescence images (c) of **TDC** in dichloromethane (DCM) at 1.0×10^{-5} M upon adding 6 equiv of K^+, Ca^{2+}, Mg^{2+}, Zn^{2+} and Cu^{2+}. The numbers below the images are the peak emission wavelength (λ_{em}) and fluorescence quantum yield (Φ), respectively.
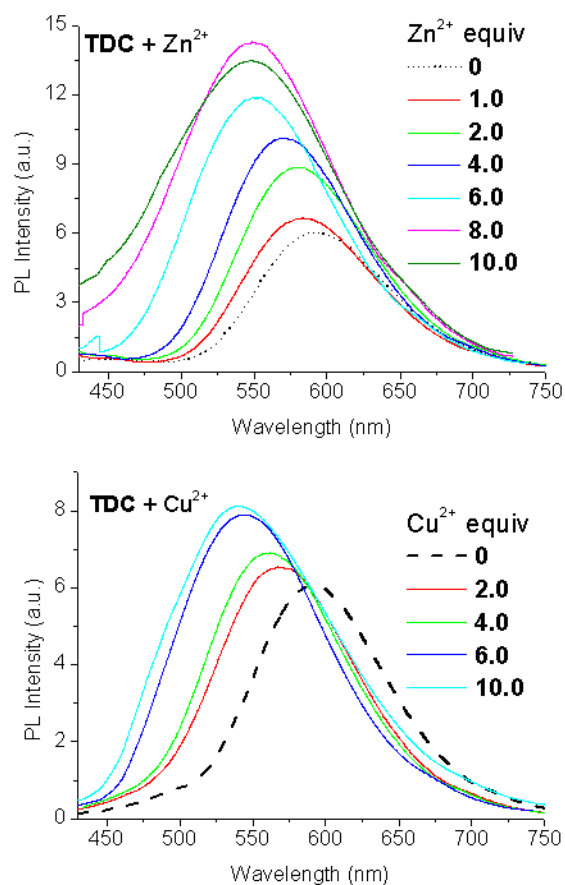
c	No ion	K^+	Ca^{++}	Mg^{++}	Cu^{++}	Zn^{++}
λ_{em}	592	590	590	592	545	554 nm
Φ	0.032	0.034	0.034	0.032	0.091	0.13

Fig. 6 Emission spectra of **TDC** in DCM at at 1.0×10^{-5} M upon titration of Zn^{2+} and Cu^{2+}, respectively.

under UV light and gives a pressing- induced emission shift ($\Delta\lambda_{PFC}$ = $\lambda_{pressed} - \lambda_{annealed}$) of 34 nm.
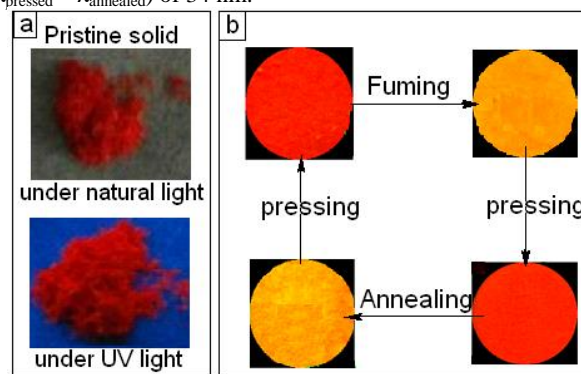

Fig. 7 Fluorescence images of **TDC** under different solid states and external stimuli.
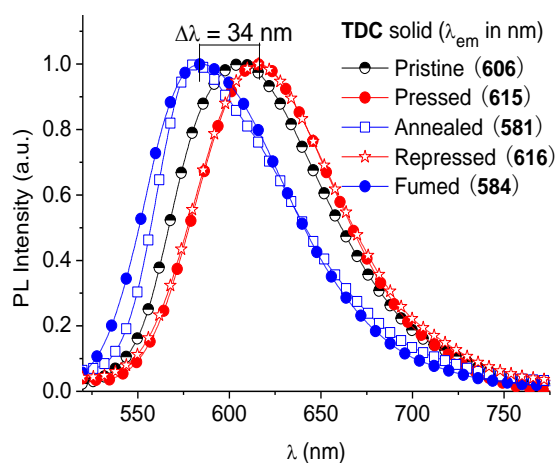

Fig 8. The normalized fluorescence emission spectra of pristine **TDC** solid and **TDC–KBr** mixture upon pressing, annealing, re-pressing and solvent-fuming.

Piezofluorochromic behaviour

In most, but not all, linear and branched 9,10-bis(arylvinyl)-anthracenes with strongly twisted conjuagted backbone, piezo-fluorochromic (PFC) phenomenon has been observed.[19] However, two branches of **TDC**, twisted 9,10-bis(*p*-dibutylaminostyryl)-anthracene and planar 2,6-bis(*p*-dibutylaminostyryl)anthracene are all non-PFC activity. To understand whether twisted 9,10-branch-containing **TDC** is a PFC dye with novel cruciform configuration, the pressing experiment on **TDC** mixed with KBr powder (for the sake of minimizing the amount of fluorophore) is carried out by using a common IR pellet press (30 s at 1500 psi). Fig. 7a shows as-prepared pure **TDC** solid images under natural light and UV light, and it is a red emitting solid with the peak emission wavelength of 606 nm. Fig. 7b shows the fluorescence colour images of the mixed sample when it is pressed, annealed, fumed, and re-pressed. It is observed that pressed sample affords a redder fluorescence colour with the peak emission wavelength of 615 nm; however, after solvent-fuming or heat-annealing the pressed sample, an orange emission colour (ca. 582 nm) is generated. Furthermore, when re-pressing the fumed or annealed sample, the fluorescence colour is again converted into the red fluorescence colour as the first pressing. Thus, **TDC** becomes a PFC material and exhibits reversible PFC behaviour. Meanwhile, the emission spectra of **TDC** sample under various external stimuli have been recorded (Fig. 8), which is comparably consistent with the corresponding fluorescence colours observed with naked eyes

X-ray difraction and DSC analysis

To get an insight into the PFC behaviour, wide-angle X-ray diffraction (WXD) and differential scanning calorimetry (DSC) experiments on **TDC** under different solid states are performed. WXD curves indicate that both as-prepared and ground solids show broad and featureless diffraction profiles reflecting notable amorphous features (Fig. 9). In contrast, the WXD pattern of the annealed and fumed solids display sharp multiple peaks implying microcrystalline states. This deduction could be further confirmed by DSC measurement. There is a glass transition at 137 °C and a cold-crystallization transition at 151 °C for the as-prepared solid before the isotropic melt transition (187 °C). After grinding, the glass transition is lowered to 119 °C and an additional cold-crystallization peak appears at 135 °C, implying further amorphization and weak intermolecular interactions for **TDC** solid upon grinding. This is probably the cause for the emission difference between as-prepared and ground solids. To the annealed solid, only an isotropic melt transition is observed. Above these results indicate that grinding and annealing could induce the phase transition of **TDC** solid

between crystalline and amorphous states, which should be responsible for the PFC behaviour.
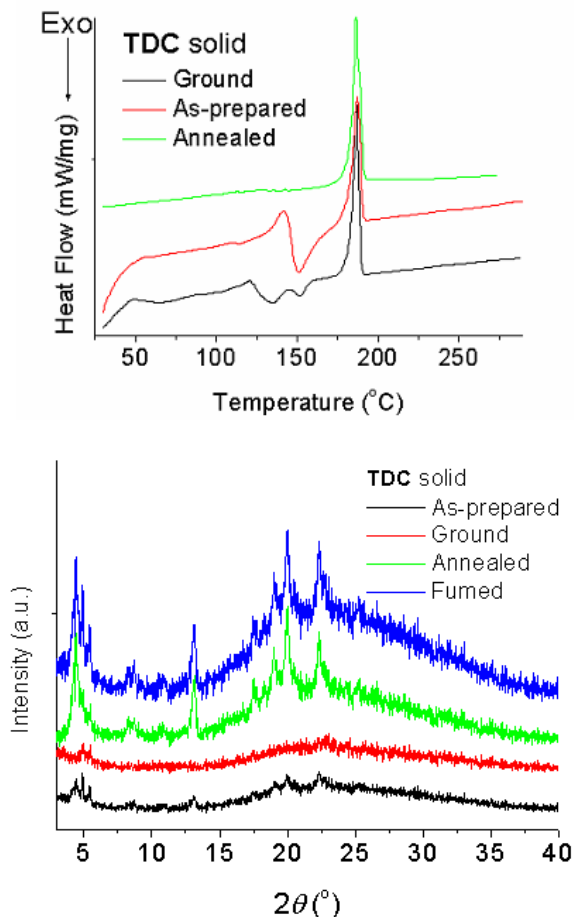

Fig. 9. WXD (a) and DSC (b) curves of **TDC** under different solid states.

Conclusions

We have synthesized a new tetradonor cruciform (**TDC**) with anthracene ring as the common π-centre and *p*-dibutylamino-styryl unit as the peripheral groups linked at 2,6,9,10-positions of anthracene to demonstrate the crucial role of π-center nature in rendering the cruciform unique optical properties. Unlike the benzene-centred analogues, **TDC** is a light- and heat-stable dye and exhibits multi-functional optical properties, such as AEE and PFC behaviours induced by twisted branch 9,10-divinylanthracene, multiple and asymmetric conjugation pathways rendered the large and solvent-dependent δ, the spatially semi-disjoint FMO and fluorescence sensing selectively to transition metal ions. WXD and DSC analyses reveal that grinding and annealing could induce the phase transition of **TDC** solid between crystalline and amorphous states, which should be responsible for the PFC behaviour.

Acknowledgements

Notes and references

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