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Efficient Green-Red Piezofluorochromism of Bisanthracene-Modified Dibenzofulvene†

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A general approach for the synthesis of dibenzofulvene-based derivatives is demonstrated. The bisanthracene modified dibenzofulvene (F-DAn) exhibits efficient piezofluorochromic property with the fluorescence reversibly altered between green (536 nm) and red (620 nm) under external stimuli.

In recent decades, photochromism, electrochromism and piezochromism, in which the respective external stimuli are light, applied charge and pressure, have received increasing attentions due to the potential applications in sensors, smart windows, informational displays and memory devices.[1] More specifically, piezofluorochromic materials are able to undergo reversible changes in colour and fluorescence *via* mechanical grinding/ pressure without further modifying the chemical structures. Recently, molecular species, *i.e.* small organic molecules,[2] organometallics[3] and liquid crystals[4] have been shown to exhibit such piezofluorochromic properties. Within the small organic molecule category, the derivatives of stilbenes,[2a-c] dibenzofulvenes,[2d-e] fluorenones,[2f] anthracenes,[2g-i] pyrenes,[2j-k] and perylenes[2l-m] have shown evident changes in fluorescence under pressure or stress in which the emission colour is reversibly altered from blue to green; green to yellow or blue to yellow. In most reports, heteroatoms, *i.e.* N or O, are involved in these fluorophores. The heteroatoms can not only provide the sites of intermolecular C-H···X (N, O) interactions, but also contribute to the intramolecular charge transfer (ICT) that induces the red-shifting of the maximum emission peaks (λ_{em}), which is vital to construct materials with piezofluorochromism.[1f] Nevertheless, so far, it is seldom reported that the fluorescence of fluorophores can be reversibly altered between green and red emission, especially for only aromatic hydrocarbon materials without heteroatoms.

Fluorophores with aggregation-induced emission (AIE) features commonly exhibit propeller-like structures and enhanced emission owing to the restriction of the intramolecular rotation (RIR) in the solid-state.[5] AIE-active fluorophores are promising candidates for materials that exhibit piezofluorochromism thanks to their loose packing mode in the solid state.[1f] Very recently, we utilized a novel and versatile strategy to synthesize AIE-active fluorophores *via* Corey-Fuchs reaction and Suzuki coupling.[6] In this report, we demonstrate a facile synthetic pathway to dibenzofulvene derivatives to construct materials with piezofluorochromic properties without heteroatoms.

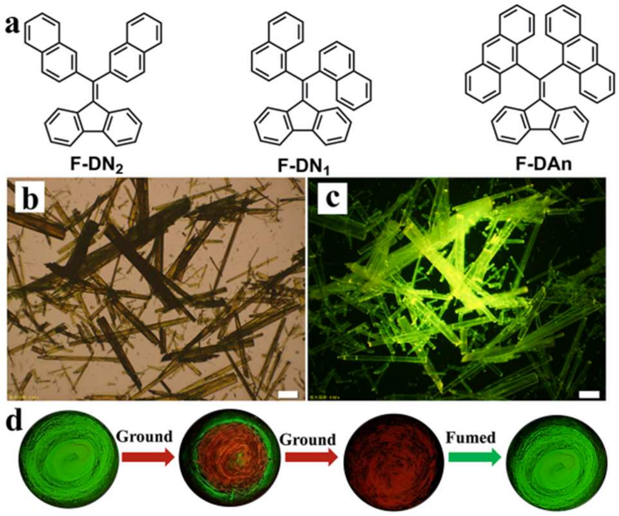

Fig. 1 (a) The structures of dibenzofulvene derivatives. Fluorescence imaging of F-DAn: (b) bright field and (c) fluorescence imaging under UV irradiation; scale bar: 200 μm; (d) photos showing the piezofluorochromism of F-DAn under alternating grinding and solvent fuming stimuli.

Different from the previous reports regarding the synthesis of dibenzofulvene derivatives,[2d-e] we have exploited the Corey-Fuchs reaction and subsequent Suzuki coupling[6] to afford F-DN$_1$, F-DN$_2$ and F-DAn with decent yields. The detailed synthetic route (Scheme S1) and procedures are described in ESI section, and the final compounds were characterised by NMR, MALDI-TOF-MS, and X-ray crystallography with satisfactory results. We have utilized dibenzofulvene as the core component (Fig. 1a) on the basis of the unique properties of piezochromism and the formation of unique microstructures.

Dibenzofulvene which is modified by bisanthracene units (F-DAn) exhibits self-assembly ability and efficient piezofluorochromism, which can be reversibly changed between green and red fluorescence after alternate grinding and solvent fuming process (Fig. 1d).

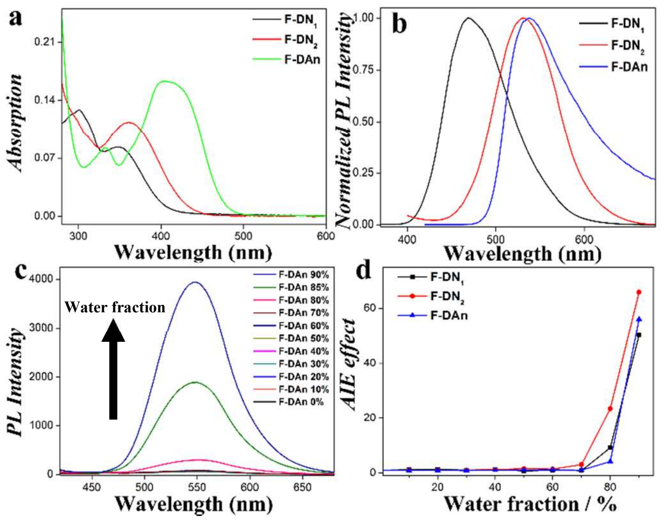

Fig. 2 (a) The UV-vis absorption spectra in THF solution (10^{-5} M) and (b) PL emission spectra in powder form of F-DN$_1$, F-DN$_2$ and F-DAn. (c) PL intensity of F-DAn in THF-water solvent mixtures (10^{-5} M) with different water content (Excitation wavelength: 405 nm). (d) The AIE-effect ($\alpha_{AIE} = I/I_0$) *vs* water fraction (%) of F-DN$_1$, F-DN$_2$ and F-DAn.

As shown in Fig. 2a, the maximum UV-vis absorption peaks (λ_{abs}) of F-DN$_1$, F-DN$_2$ and F-DAn in dilute THF solution (10^{-5} M) are located at 349 nm, 361 nm and 405 nm, respectively. The λ_{em} of F-DN$_1$, F-DN$_2$ and F-DAn in the powder form are located at 468 nm, 531 nm and 536 nm (Fig. 2b). All three compounds exhibit weak fluorescence in the 10^{-5} M THF solution. From the THF-water solvent mixture experiments (Fig. 2c and S4), we can observe that the PL intensity gradually increases as the water fraction is increased. The PL intensity of these three materials in the "aggregate" state, *i.e.* 90% water content, is dramatically enhanced. Therefore, F-DN$_1$, F-DN$_2$ and F-DAn display AIE properties. The AIE-effect (Fig. 2d), termed as $\alpha_{AIE} = I/I_0$ (I = resulting PL intensity after gradual water addition, I_0 = PL intensity in 10^{-5} M THF solution at 0% water content), of F-DN$_1$, F-DN$_2$ and F-DAn are 50.2, 62.8 and 56.0, respectively, with negligible difference in AIE-efficiency. The profile changes of PL spectra in different THF-water mixtures (Fig. S4) are probably due to the effect of morphology transition and agglomeration.[7] Generally, the AIE effect was depended on the balance of the core components (*i.e.* double bonds, silole or thiophene ring) and the periphery rotators (*i.e.* aromatic rings). As shown in the Fig. 1d, the AIE effect was found as 50.2 (F-DN$_1$); 62.8 (F-DN$_2$) and 56.0 (F-DAn), respectively. It can be envisaged that the double bond serves as the core, and the peripheral naphthalene, anthracene and fluorene can be considered as the effective rotators. Probably due to the similar volume of the peripheral rotators, the AIE effect of the associated compounds is comparable.

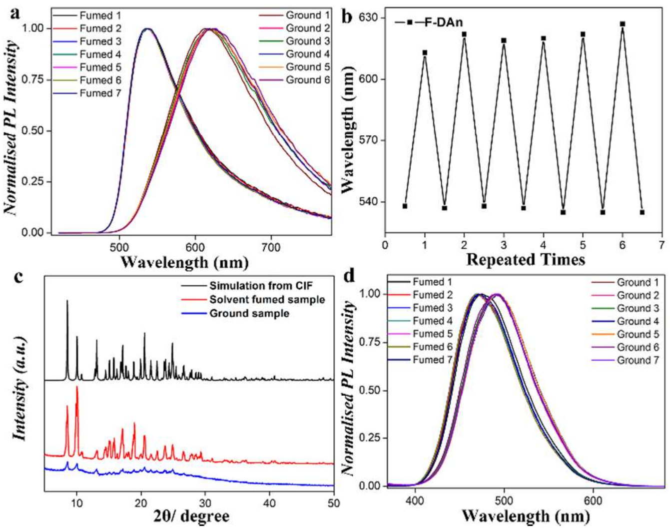

Fig. 3 (a) The PL emission spectra of fumed and ground F-DAn. (b) Cycling behaviors of the emission showing efficient reversibility. (d) Powder X-ray diffraction (PXRD) patterns of the ground and solvent fumed F-DAn samples. (d) The PL emission spectra of fumed and ground F-DN$_1$.

In addition to its AIE property, F-DAn exhibits efficient piezofluorochromism (Fig. 1d), and the fluorescence can be reversibly changed between green and red fluorescence under alternating grinding and solvent fuming procedures. To further validate this unique property, the changes in the PL spectra after grinding and subsequent solvent fuming were recorded, and the results indicate that the reversible conversions can be cycled for many times between green fluorescence (536 ± 2 nm) and red fluorescence (620 ± 7 nm) (Figure 3a and 3b). From this transformation, we have demonstrated that F-DAn is a promising piezofluorochromic material with good reversibility, large red shifts in λ_{em} (> 80 nm) and distinct emission colours associated with the fluorescence quantum yield changed from 0.63 (green state) and 0.11 (red state). Powder X-ray diffraction (PXRD) pattern of the solvent fumed F-DAn sample displays several defined peaks (Fig. 3c), indicative of the crystalline state. On the contrary, the ground F-DAn shows more ill-defined diffraction peaks with a more diffuse pattern that is more reminiscent of an amorphous material. Furthermore, the NMR spectra of ground and solvent fumed samples of F-DAn are identical to each other (Fig. S5), implying that chemical structure of F-DAn is constant before and after mechanical grind. The fluorescence lifetime of F-DAn was changed from 1.6 ns to 2.5 ns after ground (Fig. S6), probably associated with the formation of exciplex and/or the dimer.[2d, 8] It will take about 6 min for the transformation between the polycrystalline state and the amorphous state in one cycle. Therefore, the mechanism of emission changes of F-DAn before and after grinding is due to the transition between the crystalline and amorphous states, which is accompanied by intramolecular and intermolecular changes. With respects to F-DN$_1$ (Fig. 3d) and F-DN$_2$ (Fig. S7b), both of them exhibit piezofluorochromism with the changes of the λ_{em} about 20 nm *via* alternating grinding and solvent fuming operations. The changes in the λ_{em}

are accompanied again with the transformation from the crystalline state to amorphous state (Fig. S8).

To further understand the piezofluorochromism and probe the structural features and intermolecular packing modes in these dibenzofulvene derivatives, single crystal formation *via* solution evaporation process using DCM and methanol were obtained for F-DN$_1$ and F-DAn. However, single crystal of F-DN$_2$ proved to be difficult to obtain. The ORTEP structures of F-DN$_1$ and F-DAn are shown in Fig. 4 and S9 to S10. Both of F-DN$_1$ and F-DAn reveal a propeller-like structure, which is consistent with the optimized structure obtained from DFT calculations using B3LYP/6-31G(d) basis set in Gaussian 09 program (Fig. S11). For F-DN$_1$, calculations from PLATON[9] show no classical $\pi\cdots\pi$ interactions. Two kinds of C-H$\cdots\pi$ interactions with the distances of 2.72 Å (H18$\cdots$Cg$_{C29-C34}$) and 2.94 Å (H23$\cdots$Cg$_{C19-C24}$, Cg denotes a centroid defined by some specified atoms) can be observed (Fig. 4c). With respect to F-DAn, the anthracence blades in F-DAn are perpendicular with each other, and the dihedral angles of the anthracence rings is 95.5°. Besides C-H$\cdots\pi$ interaction with the distances of 2.73 Å (H4$\cdots$Cg$_{C37-C42}$), two weak $\pi\cdots\pi$ interactions with the distances of 3.91 Å (Cg$_{C1-C6}\cdots$Cg$_{C8-14}$), and 3.99 Å (Cg$_{C30-C35}\cdots$Cg$_{C37-C42}$) are observable. As depicted in Fig. 4d and S12, F-DAn single crystals are grown prominently long the [010] axis, in which the $\pi\cdots\pi$ interactions, labeled with purple colour, are crossed. More interestingly, it seems like the whole crossed $\pi\cdots\pi$ stacks between the contiguous anthracence rings are formed into two pillars, in which the two pillars are connected with multiple C-H$\cdots\pi$ interactions (labeled with green lines). The non-contacted dibenzofulvene rings are aligned at the periphery, and separated by these anthracence pillars (Fig. S12). Probably due to the weak interactions in the crystal of F-DAn, intriguing piezofluorochromism can be observed *via* simple grinding and fuming procedures.

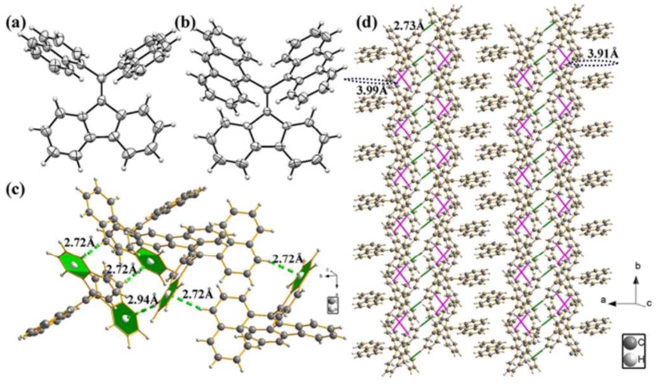

Fig. 4 The ORTEP drawings of (a) F-DN$_1$; (b) F-DAn; Part of the molecular packing mode (c) F-DN$_1$; (d) F-DAn. The C-H$\cdots\pi$ interactions are shown in the green dotted lines, and the $\pi\cdots\pi$ interactions are shown as purple dotted lines.

In conclusion, we have demonstrated a general and facile synthetic strategy to afford dibenzofulvene derivatives *via* Corey-Fuchs reaction and subsequent Suzuki coupling reactions. The weak intermolecular interactions in F-DAn are probably accountable for this piezofluorochromism with a bathochromic shift of λ_{em} (> 80 nm) reversibly altered between green and red emission under external stimuli, which is seldom reported. More importantly, we elucidate that aromatic hydrocarbon materials without any electron-withdrawing groups and heteroatoms can be served as promising candidates for piezofluorochromic materials.

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Notes and references

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† Electronic Supplementary Information (ESI) available: experimental procedures/characterisation, optical spectra, molecular simulation and crystallographic information files (CIFs) with CCDC 1010824 and 1010825. See DOI: 10.1039/c000000x/.

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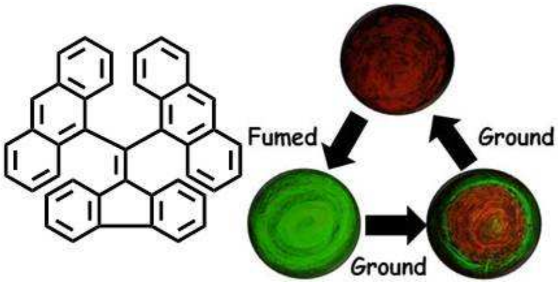

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