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## **Strong Solid Emission and Mechanofluorochromism of Carbazole-based Terephthalate Derivatives Adjusted by Alkyl Chains**

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Three 2,5-dialkylcarbazole-substituted terephthalate derivatives, in which carbazole and ethoxylcarbonyl groups are used as electron-donating and –accepting moieties, respectively, were synthesized. Owing to the presence of steric hindrance between ethoxylcarbonyl and carbazole groups, three compounds show

- <sup>10</sup> intense blue fluorescence in both solution and solid state. The fluorescence quantum yields of compounds with octyl and hexadecyl groups in solid state exceed 95%. Single-crystal structures of three compounds were obtained and used to interpret the strong emission in solid state. More interestingly, three compounds exhibited alkyl length-dependent mechanofluorochromism. The compound with ethyl groups exhibited largest spectral shift under force stimuli, but that with hexadecyl moiety did not change its
- <sup>15</sup> emission color after grinding. Because of strong fluorescence in solution and solid, we believe that they can be used as luminescent materials and sensors.

#### Introduction

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An organic compound emitting strong fluorescence in solution and solid state is very important for its real applications as <sup>20</sup> optoelectronic materials, sensors for metal ions, anions, neutral molecules. <sup>1</sup> However, the traditional aggregation-caused quenching (ACQ) effect in solid state, owing to internal conversion, intersystem crossing, intramolecular charge transfer, intermolecular electron transfer, excimer or exciplex formation,

- <sup>25</sup> or isomerisation, results in drastically negative effects on the device performance and sensitivity of the sensors.<sup>2</sup> Tang et al. firstly introduced an effective methodology to overcome ACQ, which is called aggregation-induced emission (AIE).<sup>3</sup> The AIE active molecules are highly fluorescent in solid state, but no or <sup>30</sup> very weak emission is observed in solution state,<sup>4</sup> which limited
- their wide applications. So, organic fluorophores with strong emission in both solution and solid state should been developed. To realize the intense luminescence in solid state, several
- strategies including J-aggregation formation,<sup>5</sup> the introduction of <sup>35</sup> bulky substituent,<sup>6</sup> the formation of excimer,<sup>7</sup> and restriction of intramolecular rotation (RIR) or planarization<sup>8</sup> were developed. Generally, AIE molecules have twisted configurations and freely rotated single bonds, such as silole, tetraphenylethene, 9,10distryrylanthracene, and cyano-diphenylethene derivatives.<sup>9</sup> In
- <sup>40</sup> solution, such molecules emit weak fluorescence because of RIR. Intramolecular rotation in solid or crystal state is suppressed, and the twisted configuration leads to loose stacking, which eliminates strong  $\pi$ - $\pi$  interaction between fluorophores and then promotes strong emission. How do molecules possess intense
- <sup>45</sup> luminescence in both solution and solid state? One novel strategy is to construct molecules with twisted conformation, in which



Scheme 1. Molecular structures and photos under natural and 365 nm light.

50 free rotation of single bond is restricted. For example, Chen and co-authors designed several tetrahydro[5]helicene derivatives with rigid twisted structure, and found that they emitted strong fluorescence in solution and solid state.<sup>10</sup> Another kind of strong emissive fluorophores is 2,5- disubstituted 1,4-diaminobenzene 55 derivatives, developed by Shimizu, have been synthesized and used in organic light-emitting diodes.<sup>11</sup> Herein, we designed and synthesized three carbazole-based terephthalate derivatives (BECT, BOCT and BHCT, Scheme 1), in which carbazole and ethoxylcarbonyl groups are used as electron-donating and -60 accepting moieties, respectively. Owing to the presence of steric hindrance between ethoxylcarbonyl and carbazole groups, three compounds show intense fluorescence in both solution and solid state. Fortunately, single-crystal structures of three compounds were obtained and used to interpret the strong emission in solid 65 state. More interestingly, three compounds exhibited alkyl lengthdependent mechanofluorochromism.

#### **Experimental section**

#### Measurements

(400MHz) spectrometer with CDCl<sub>3</sub> as solvent and tetramethylsilane (TMS) as the internal standard. Mass spectra were obtained with Agilent 1100 MS series and AXIMA CFR 5 MALDI-TOF (Compact) mass spectrometers. Elemental analysis was performed on a Perkin-Elmer 2400. The UV-vis absorption spectra were obtained using a Mapada UV-1800pc spectrophotometer. Photoluminescence measurements were taken on a Cary Eclipse fluorescence spectrophotometer. The 10 fluorescence quantum yields of BECT, BOCT and BHCT in solutions were measured by comparing to a standard (quinine sulfate in 1N H<sub>2</sub>SO<sub>4</sub> aqueous solution,  $\Phi_{\rm F}$ = 0.65). The excitation wavelength was 365 nm. The absolute fluorescence quantum yields were measured on an Edinburgh FLS920 steady state 15 spectrometer using an integrating sphere. Fluorescence decay experiment was measured on an Edinburgh FLS920 spectrometer equipped with an nF900 nanosecond flash lamp. The XRD patterns were obtained on an Empyrean X-ray diffraction instrument equipped with graphite-mono-chromatized CuK<sub>a</sub> <sub>20</sub> radiation ( $\lambda = 1.5418$  Å), by employing a scanning rate of 0.026° s<sup>-1</sup> in the 2 $\theta$  range from 5 to 30°. The samples were prepared by casting crystal powders, ground solid and fuming samples on glass slides at room temperature. The ground solids for steady and time-resolved fluorescence and XRD measurements were 25 obtained by simply grinding the crystals with a mortar and pestle. Single crystals were obtained in the mixture of CH<sub>2</sub>Cl<sub>2</sub> and nhexane by a slow solvent diffusion method. The molecular optimal configurations were used to obtain the frontier orbitals of BECT and BOCT by density functional theory (DFT)

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker- Avance III

<sup>30</sup> calculations at B3LYP/6-31G(d) level with the Gaussian 09W program package.

Single crystals of **BECT**, **BOCT** and **BHCT** were selected for Xray diffraction studies in a Rigaku RAXIS-RAPID diffractometer using graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073^{\circ}$ A).

<sup>35</sup> The crystals were kept at room temperature during the datacollection. The structures were solved by direct methods and refined on F<sup>2</sup> by full-matrix least-square using the SHELXTL-97 Program. The C, N, O and H atoms were easily placed from the subsequent Fourier-difference maps and refined anisotropically.



Scheme 2. Synthesis route of BECT, BOCT and BHCT.

Synthesis of BECT, BOCT and BHCT

Synthetic routes of the compounds **BECT**, **BOCT** and **BHCT** were shown in Scheme 2. The intermediate of 4<sup>12</sup>, 9, 10 and 11<sup>13</sup> <sup>45</sup> were synthesized by the reported methods. The detailed

experimental procedures were as follows: Diethyl 2,5-bis(9-ethyl-9H-carbazol-3-yl)terephthala-te (**BECT**). Toluene (10 ml) and water (10 ml) were added into a mixture of 9 (0.71g, 2.2 mmol), 4 (0.38 g, 1 mmol), K<sub>2</sub>CO<sub>3</sub> (1.5g, 11mmol) <sup>50</sup> and Pd(PPh<sub>3</sub>)<sub>4</sub> (15 mg). The reaction mixture was stirred at 90° C under N<sub>2</sub> for 24 hours. After cooled to room temperature, the solution was extracted with methylene chloride. The organic

extracts were combined, and dried over anhydrous  $Na_2SO_4$ . Upon evaporating off the solvent, the crude product was purified <sup>55</sup> by silica column with petroleum/methylene chloride (V/V = 1/2)

as the eluent to yield BECT (0.52 g, 85%) as a white powder. Elemental Analysis (%): calculated for  $C_{40}H_{36}N_2O_4$ : C, 78.92; H, 5.96; N, 4.60; found: C, 78.90; H, 5.99; N, 4.57. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  8.18 (d, J = 1.2Hz, 2H), 8.15(d, J = 7.7Hz, 60 2H), 7.98 (s, 2H), 7.43-7.53 (m, 8H), 7.26 (m, 2H), 4.45 (q, J = 1.2Hz, 2H), 8.15 (d, J = 1.2Hz, 2H)

7.2Hz, 4H), 4.14 (q, J = 7.1Hz, 4H), 1.48 (t, J = 7.2 Hz, 3H), 0.95 (t, J = 7.1 Hz, 3H).  $^{13}$ C NMR (101 MHz, CDCl<sub>3</sub>, TMS):  $\delta 168.81$ , 141.12, 140.41, 139.50, 133.87, 132.12, 130.96, 126.51, 125.85, 123.04, 120.58, 120.40, 119.03, 108.62, 108.12, 61.23, 37.70, 65 13.85, 13.82. MALDI-TOF MS: m/z: calcd. for C<sub>40</sub>H<sub>36</sub>N<sub>2</sub>O<sub>4</sub>:

608.3; found: 609.6  $[M+H]^+$ . Diethyl 2,5-bis(9-octyl-9H-carbazol-3yl)terephthalate (**BOCT**). The synthesis of **BOCT** is the same as that of **BECT**. The crude product was purified by silica column with petroleum/methylene 70 chloride (V/V = 1/2) as the eluent to yield BOCT (90%) as a white powder. Elemental Analysis (%): calculated for

white powdel. Elemental Analysis (%). calculated for  $C_{52}H_{60}N_2O_4$ : C, 80.38; H, 7.78; N, 3.61; found: C, 80.39; H, 7.83; N, 3.58. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  8.17 (s, 2H), 8.15 (d, J = 7.7 Hz, 2H), 7.99 (s, 2H), 7.57 – 7.44 (m, 8H), 7.32 – 7.24 <sup>75</sup> (m, 2H), 4.37 (t, J = 7.2 Hz, 4H), 4.14 (q, J = 7.1 Hz, 4H), 2.00 –

<sup>15</sup> (m, 2H), 4.37 (t, J = 7.2 Hz, 4H), 4.14 (q, J = 7.1 Hz, 4H), 2.00 – 1.86 (m, 4H), 1.50 – 1.18 (m, 20H), 0.96 (t, J = 7.1 Hz, 6H), 0.90 (t, J = 6.6 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, TMS)  $\delta$ 168.87, 141.10, 140.89, 140.01, 133.88, 132.10, 130.91, 126.47, 125.81, 122.92, 120.50, 120.31, 118.97, 108.86, 108.35, 61.21, 43.26,

 $_{80}$  31.82, 29.43, 29.22, 29.04, 27.37, 22.63, 14.09, 13.80. MALDITOF MS: m/z: calcd. for  $C_{52}H_{60}N_2O_4$ : 776.5; found: 777.7  $[M\!+\!H]^+$ .

Diethyl 2,5-bis(9-hexadecyl-9H-carbazol-3yl)terephthalate (**BHCT**). The synthesis of **BHCT** is the same as that of **BECT**. <sup>85</sup> The crude product was purified by silica column with petroleum/methylene chloride (V/V = 1/2) as the eluent to yield **BHCT** (88%) as a white powder. Elemental Analysis (%): calculated for  $C_{68}H_{92}N_2O_4$ : C, 81.55; H, 9.26; N, 2.80; found: C, 81.51; H, 9.31; N, 2.81. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$ 

 $^{90}$  8.17 (d, J = 1.6 Hz, 2H), 8.15 (d, J = 7.7 Hz, 2H), 7.98 (s, 2H), 7.55 – 7.43 (m, 8H), 7.31 – 7.25 (m, 2H), 4.37 (t, J = 7.2 Hz, 4H), 4.13 (q, J = 7.1 Hz, 4H), 2.00 – 1.84 (m, 4H), 1.48 – 1.19 (m, 52H), 0.96 (t, J = 7.1 Hz, 6H), 0.90 (t, J = 6.8 Hz, 6H).  $^{13}$ C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.87, 141.10, 140.88, 140.00, 133.87,

 $_{95}$  132.11, 130.90, 126.47, 125.81, 122.91, 122.89, 120.50, 120.30, 118.97, 108.85, 108.35, 61.21, 43.26, 31.95, 29.72, 29.68, 29.65, 29.63, 29.57, 29.49, 29.39, 29.05, 27.39, 22.72, 14.15, 13.81. MALDI-TOF MS: m/z: calcd. for  $C_{68}H_{92}N_2O_4$ : 1000.7; found: 1001.9  $[M\!+\!H]^+$ .



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#### **Result and Discussion**

#### Photophysical properties in solution

Three compounds were synthesized by a simple Suzuki reaction (Scheme 2) in high yields. They were all characterized by <sup>1</sup>H <sup>5</sup> NMR, <sup>13</sup>C NMR, elemental analysis and mass spectroscopy. It was found that as-synthesized solids could emit intense fluorescence under 365 nm light irradiation (Scheme 1).



**Fig. 1** (a) Fluorescence of **BECT** in different solvents; (b) photos of <sup>10</sup> **BECT** solutions under 365 light irradiation.  $\lambda_{ex} = 365$  nm; (c) HOMO and LUMO distribution of **BECT** obtained after conformation optimization by quantum chemical calculation.

Firstly, the absorption and fluorescence spectra of three compounds in solutions were measured and compared. As a result, 15 they possess the similar absorption and fluorescence bands in different solvents (Fig. S10, Table S1). For example, two absorption peaks at 337 and 352 nm for **BECT** in toluene were observed. The absorption peaks of **BOCT** and **BHCT** located at 340 and 352 nm. Similar absorption peaks show that their 20 aromatic moieties have similar molecular conformations. They have also the similar emission spectra with maxima around 465 nm in toluene. Their fluorescence quantum yields (Φ) are moderate (from 0.42 to 0.49). Such high Φs relative to general AIE molecules suggests that the free rotation of single bonds in

- <sup>25</sup> compounds in our case may been suppressed.<sup>14</sup> In order to verify this hypothesis, the optimal conformation was obtained by density functional theory (DFT) calculation at B3LYP/6-31G(d) level. As shown in Fig. S11, two dihedral angles between two carbazole rings and benzene ring are large and are 52.8° and 61.2°.
- <sup>30</sup> The ester groups also stray from the plane of benzene ring, and twist angles are 22.3 ° and 33.6 °. Non-coplanar conformation should be ascribed to the steric hindrance between carbazole and ester groups. <sup>15</sup> Such enhanced steric hindrance will induce restriction of free rotation of single bond, linked carbazole and

- <sup>35</sup> central benzene ring, and then increase the radiative transition probability. In addition to the steady-state spectral measurements, time-resolved fluorescence spectra can provide more information on the excited state of fluorophores. The results suggest that the emission decay of three compounds is single exponential and
- <sup>40</sup> they have the similar fluorescence lifetimes (from 3.73 to 3.80 ns, Fig. S12, Table S1). Radiative (k<sub>r</sub>) and nonradiative (k<sub>nr</sub>) rate constants of **BECT** in cyclohexane are 0.10 and 0.16 ns<sup>-1</sup>. Larger k<sub>nr</sub> should be responsible for moderate  $\Phi$  in solution.
- When we increased the solvent polarity, three compounds exhibit 45 polarity-dependent solvatochromism of fluorescence (Fig. 1 and S10). In cyclohexane, BECT emitted blue fluorescence. Its solution had an emission peak at 463 nm. The emission maxima further shifted to 475, 484 and 521 nm in ethyl acetate, CHCl<sub>3</sub> and DMF, respectively. BOCT and BHCT have the similar 50 spectral changes. It was also found that  $\Phi$ s in different solvents except in DMF are large (from 0.35 to 0.61). Such change in fluorescence spectra indicates that the excited state has a larger dipole moment than that in ground state.<sup>16</sup> The quantum chemical calculation of BECT indicates that the HOMO state density of 55 BECT is mainly distributed at the carbazole and central benzene ring. In contrast, the electron density of the LUMO mainly locates at central benzene ring and ester groups. The stimulated transition at ca. 394 nm ascribes to the HOMO →LUMO transition. Thus, an excited state with large dipole moment will 60 emerge after light irradiation. It is in accordance with the electron
- push-pull molecular structure and suggests also that polaritydependent solvatochromism of fluorescence should be ascribed to an intramolecular charge transfer transition, be not originated from twisted intramolecular charge transfer one because that <sup>65</sup> there was not shift of fluorescence spectra when DMSO solution of **BECT** was cooled to 0 °C to from glass solid (Fig. S13).<sup>17</sup>



Fig. 2 (a) Fluorescence spectra of **BECT** in THF-water mixtures.  $\lambda_{ex} = _{70}$  365 nm.

As discussed above, the as-synthesized solids can emit strong fluorescence, which implies that molecular aggregation dose not induce fluorescence quenching. To study the emission property of aggregation, their emission spectra were measured in THF–water 75 mixtures (three compounds are soluble in THF and water is a poor solvent).<sup>18</sup> As shown in Fig. 2b, the THF solution of **BECT** emits strong blue fluorescence. The emission gradually quenched with addition of water and the emissive peak redshifted, which arising from the increased solvent polarity, liking in DMF. When <sup>5</sup> the water fraction increased to 80%, the emissive intensity swiftly increased, which induced by molecular aggregation because the

mixture was turbid and a redshifted absorption band with a leveloff tail was obviously observed in the 80 vol% mixture (Fig. S14). **BOCT** and **BHCT** exhibited similar spectral change in THF-<sup>10</sup> water mixture (Fig, S15). These spectral changes confirm that strong emission could be also observed in small aggregates.

 $\frac{k_{nr} (ns^{-1})}{0.14}$ 

0.0047

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Table 1. Twist angles and photophysical data of three compounds in crystals.													
	θ <sub>1</sub> (°)	$\theta_2(^{\circ})$	θ <sub>3</sub> (°)	$\theta_4$ (°)	$\theta_1 + \theta_4$ (°)	$\theta_2 + \theta_3$ (°)	$\lambda_{em} (nm)$	τ (ns)	$k_r (ns^{-1})$				
BECT	57.2	45.9	57.2	46.8	104.0	103.1	455	1.96 (37%) 4.31 (63%)	0.15				
BOCT	44.9	49.3	46.4	50.1	95.0	95.7	459	4.20 (100%)	0.23				
BHCT	30.4	52.5	30.4	52.1	82.5	82.9	469	5.78 (100%)	0.16				



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15 Fig. 3 Molecular structures and interactions between two molecules for BECT (a), BOCT (b) and BHCT (c) in their crystals. Insets are photos of crystals under 365 nm light irradiation.

To further understand the relationship between molecular structure and strong emissions in solid state, their photophysical <sup>20</sup> properties in crystal states and crystal structures were studied. **BECT** emitted strong blue fluorescence with a maximum at 455 nm (Fig. S16). Solid-state fluorescence quantum yield for **BECT** is 0.51. **BOCT** and **BHCT** have red-shifted emissive maxima at 459 and 469 nm, respectively. Their Φs in crystal state are very <sup>25</sup> high, and reach 0.98, and 0.95, respectively, which are larger than those in solutions and illustrate the characteristic aggregationinduced emission enhancement (AIEE).<sup>19</sup> The fluorescence decay of **BECT** crystals is double exponential and average lifetime is 3.44 ns (Fig. S17, Table 1). Thus, similar k<sub>r</sub> and k<sub>nr</sub> to those in <sup>30</sup> solution are obtained. Single exponential decay for **BOCT** and **BHCT** are observed and their τs increase to 4.20 and 5.78 ns. The

**BHCT** are observed and their ts increase to 4.20 and 5.78 ns. The similar  $k_rs$  to that **BECT** are evaluated, but  $k_{nr}s$  of **BOCT** and **BHCT** rapidly decrease, suggesting that larger  $\Phi s$  of **BOCT** and **BHCT** are mainly ascribe to the suppression of non-radiative transition.<sup>20</sup> Crystal structures will give more information about solid state luminescence. As shown in Fig. 3, three compounds have non-coplanar conformation in crystals. Such non-planarity caused by the steric repulsion between ester groups and carbazole

moieties reduces the intermolecular  $\pi$ - $\pi$  interactions. No obvious

469 5.78 (100%) 0.16 0.0087 40 overlaps between aromatic rings for three compounds crystals are observed, as shown in Fig. 3. The nearest distances between two carbons of aromatic units in BOCT and BHCT crystals are 3.61 and 3.89 Å, respectively, suggesting no  $\pi$ - $\pi$  interaction. It may explain why their excited states decay via single relaxation 45 pathway. In addition, in their crystal structures, there are many kinds of intermolecular weak interactions, including  $CH \cdots \pi$ . CH···O=C and CH···O-C (Fig. S17). These weak interactions may restrict the intramolecular rotation and then block the nonradiative channel, thus making enhanced emission of BOCT 50 and BHCT.<sup>21</sup> However, a short distance of 3.53 Å between two parallel carbazole units (Fig. 2a) may allow BECT in excited state transfers energy to adjacent molecule and then its fluorescence is guenched,<sup>22</sup> which may interpret a moderate  $\Phi$ and the existence of a short fluorescence lifetime (1.96 ns) for 55 BECT crystals. Therefore, the non-coplanar molecular conformation should be responsible for the strong emission in solid state because coplanar carbazol-3-yl-vinyl based trimer and pentamer emitted weak fluorescence in solid film and gel phases. 23 Moreover, twist angles between ester groups and 60 benzene ring ( $\theta$ 1 and  $\theta$ 3) or carbazole and benzene ring ( $\theta$ 2 and 64), are alkyl chain length-dependent (Fig. S18 and Table 1). **BECT** have the largest sums of  $\theta 1$  and  $\theta 4$  or  $\theta 2$  and  $\theta 3$ . The smallest sums for BHCT are observed. It is believed that BHCT and **BECT** have best and poorest  $\pi$ -conjugated structures, 65 respectively. Therefore, longer emissive wavelengths for molecules with longer alkyl chains in crystal states were observed. MFC properties in solid state



**Fig. 4** Normalized fluorescence spectra of **BECT** (a), **BOCT** (b) and 70 **BHCT** (c) in pristine crystals and after grinding and then fuming.  $\lambda_{ex} =$ 360 nm. (d) Schematics of color changes under mechanical force and solvent fuming stimuli. Published on 12 March 2015. Downloaded by University of Pittsburgh on 12/03/2015 20:37:54.

 Table 2. Emissive peaks of solids, spectral shifts and fluorescence lifetimes of ground powders.

	$\lambda_{\text{pristine}}$	$\lambda_{\text{grind}}$	$\Delta\lambda_{\rm PFC}$ $(nm)^{\rm a}$	$\tau (ns)^b$					
BECT	455	480	25	3.07 (46%); 5.68 (54%)					
BOCT	459	474	15	3.81 (87%); 6.78 (13%)					
BHCT	469	470	1	5.77 (100%)					
<sup>a</sup> $\Delta \lambda_{PFC} = \lambda_{grinding} - \lambda_{pristine}$ , <sup>b</sup> lifetimes of ground powders.									



 $_5$  Fig. 5 XRD patterns of **BECT** (a), **BOCT** (b) and **BHCT** (c) in crystals and after grinding.

As discussed above, three compounds are non-coplanar and electronic push-pull structure, and then mechanofluorochromic (MFC) behaviours are expected.<sup>24</sup> By simply grinding the **BECT**<sup>10</sup> crystals with a mortar and pestle, a white powder with blue-green emission was obtained. When the ground powder was exposed to CH<sub>2</sub>Cl<sub>2</sub> vapor for several seconds, the fluorescence of ground powder rapidly recovered to blue (Fig. 4d). This process of fluorescence color change can be repeated many times, <sup>15</sup> suggesting an obviously reversible MFC behaviour. <sup>25</sup> After grinding, the fluorescence color of **BOCT** is also converted from blue to blue-green. However, grinding did not lead to any change in fluorescence color transformation under grinding and fuming

<sup>20</sup> stimuli. The data were listed in Table 2. Applying mechanical grinding to the **BECT** crystals resulted in a red-shift of emissive

wavelength from 455 to 480 nm (Fig. 4a), meaning a spectral shift of 25 nm. After grinding, ground **BOCT** powder has an emission peak at 474 nm, indicating a redshift of 15 nm. <sup>25</sup> However, an almost same emission peak as that of crystal sample

- was found after applying mechanical grinding to the **BHCT** crystals. Based on these spectral changes, we can conclude that the length alkyl chain can regulate the MFC properties of materials.<sup>26</sup>
- <sup>30</sup> To determine different MFC behaviors, X-ray diffraction (XRD) patterns and time-resolved spectra were investigated. The crystals of **BECT** and **BOCT** show many sharp and strong peaks. The ground powders have very weak diffraction peaks (Fig. 5), suggesting the solids after grinding is amorphous. After fuming
- <sup>35</sup> by CH<sub>2</sub>Cl<sub>2</sub> vapor, sharp and strong diffraction peaks, similar to those of the crystals, appeared again. Such spectral changes suggest the reversibility of MFC behaviors for **BECT** and **BOCT** is based on the reversible phase transformation between crystal and amorphous states.<sup>27</sup>



Fig. 6 Time-resolved fluorescence spectra of (a) **BECT**, (b) **BOCT** and (a) **BHCT** in crystal and ground states.  $\lambda_{ex} = 365$  nm.

40

The fluorescence lifetimes of **BECT** and **BOCT** became longer after grinding (Table 1 and 2). For instance, ground **BECT** solid <sup>45</sup> still has two fluorescence lifetimes, but they prolong to 3.07 ns, and 5.68 ns, respectively (Fig. 6a). **BOCT** after grinding possesses two lifetimes too, and a longer  $\tau$  of 6.78 ns appears (Fig.

6b). As discussed above, longer wavelengths for **BOCT** and **BHCT** crystals were observed because of smaller twist angle sums. So, we suppose that planarity in molecular structure under mechanical force stimulus should be responsible for MFC

- <sup>5</sup> behaviors of **BECT** and **BOCT**.<sup>28</sup> Because the sums of twist angle θ1 and θ4 or θ2 and θ3 in **BECT** crystal are largest relative to those in **BOCT** crystal, meaning a poorest π-conjugation, a better π-conjugation for **BECT** is anticipated if the twist angles decrease after grinding. Therefore, ground **BECT** solids emit
- <sup>10</sup> fluorescence with longer wavelength and have a large spectral shift under force stimulus. On the other hand, we found that the (002) and (003) diffraction peaks of single crystals are stronger than those in stimulated pattern (Fig. S20), meaning oriented growth along with 001 direction. After grinding diffraction peaks is still exist and are similar to those of stimulated and fuming
- pattern (Fig. 5c), which illuminates that mechanical grinding only destroyed oriented stacking, and the molecular packing in crystal cell did not change, so MFC behaviour for **BHCT** was not observed. Time-resolved fluorescence spectra also prove it.
  <sup>20</sup> Fluorescence decay of ground **BHCT** powders is also single exponential and the lifetime is the same as crystal one (Fig. 6c). These spectral observations reveal that the length alkyl chains affect the molecular packing in crystal and then determine the
  - responsive properties to external mechanical force stimuli.

#### 25 Conclusions

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Three carbazole-based terephthalate derivatives were designed and synthesized. Due to steric hindrance, molecules adopt noncoplanar conformation and emit strong fluorescence in both solution and solid state. The fluorescence quantum yield of <sup>30</sup> compounds with two octyl and hexadecyl groups reaches 0.98 and 0.95, respectively. Moreover, compounds with ethyl and octyl groups exhibited mechanofluorochromic behaviour, but the presence of hexadecyl groups did not lead to the fluorescence change under mechanical force stimuli. The crystal structures and

<sup>35</sup> time-resolved fluorescence spectra suggest that the difference in the length of alkyl chain affect molecular packing and then determines their response to external stimuli. Because of strong fluorescence in solution and solid, we believe that they can be used as luminescent materials and sensors.

#### 40 Acknowledgements

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#### Notes and references

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† Electronic Supplementary Information (ESI) available: [NMR, MS, UV-vis, fluorescence, and time-resolved fluorescence spectra, photophysical data in solution and solid state, molecular packing in crystals. CCDC 1031692, 1031667, and 1031666 for BECT, BOCT and
 60 BHCT, respectively]. See DOI: 10.1039/b00000x/

<sup>‡</sup> Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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## Graphic Abstract



strong emssion in solution and solid state

Carbazole-based terephthalate derivatives could emit strong fluorescence in both solution and solid state, and the emission response to force stimuli in solid state could be controlled by the length of alkyl chain.