



# Molecular design for the highly-sensitive piezochromic fluorophores with tri-armed framework containing triphenyl-quinoline moiety



Tai-Shen Hsiao, Tai-Lin Chen, Wei-Lun Chien, Jin-Long Hong\*

Department of Materials and Optoelectronic Science, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan

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## ABSTRACT

Two tri-armed piezochromic fluorescent molecules of tris(4-(4-phenylquinolin-2-yl)phenyl)amine (TPA-3Qu) and tris(4-(6-(9H-carbazol-9-yl)-4-phenylquinolin-2-yl)phenyl)amine (TPA-3QuCz) were prepared and found to exhibit keen fluorescence responses toward compression. With the framework of a twisted, pyramidal triphenylamine (TPA) center connecting to three large quinolinecarbazole (QuCz) arms, the amorphous TPA-3QuCz exhibited a large bathochromic shift of 112 nm under gentle grinding forces, which is different from the small shift of 32 nm for TPA-3Qu under applying a relatively-large pressure of 10 MPa. Conformational transformations involving planarization of the arms were proposed to account for the observed fluorescence responses of TPA-3QuCz and TPA-3Qu towards pressure.

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## 1. Introduction

Organic fluorophores exhibiting color and fluorescence changes upon external pressure stimuli have drawn lots of attention due to their convenient tunability and high sensitivity. These piezochromic fluorescent materials have promising practical applications [1], such as mechano-sensors, security papers, data storage, and also opto-electronic devices. Most mechanisms responsible for the piezochromic fluorescence involved the changes of intermolecular stacking under external pressure stimulus [2–29]. For example, the intermolecular transformation process involved in the compression of the cyanodistyrylbenzene derivative [13] caused the corresponding fluorescent color change from blue (B-phase) to green (G-phase) due to two distinctive crystal packings with varied  $\pi$ – $\pi$  overlap. Despite the prevalent intermolecular transformation mechanism, the piezochromism of a donor–acceptor anthroquinone imide [28] system was nevertheless due to an intramolecular process, in which the single-bond linking donor and acceptor groups rotates to result in molecular planarization and therefore, the alternation on the fluorescent color. New piezochromic fluorophores with different structural frameworks are still

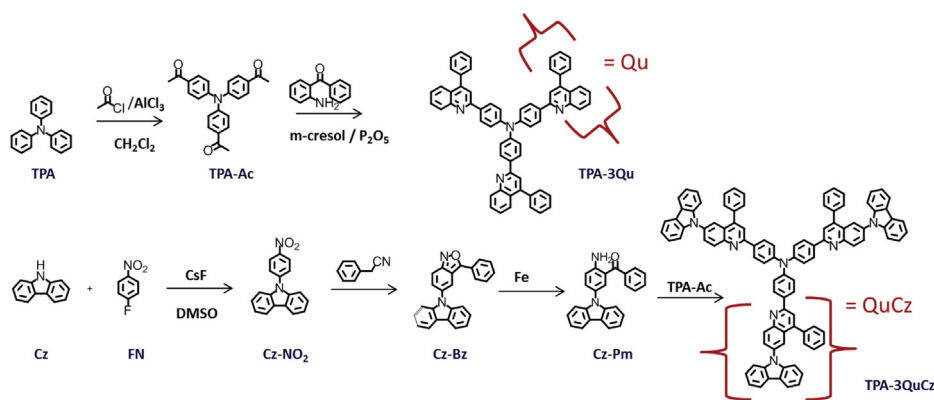
in demand and in view that new architecture provides access for the real conformational transformation responsible for the piezofluorochromism.

To have an efficient fluorescence recording system, piezochromic fluorescent materials need to have full coverage of wide emissive color spectrum under small load of pressure stimuli. Most of the conventional systems illustrated a relatively-small bathochromic shift (<50 nm) under pressure stimuli. Until now, the largest emission shift is 124 nm (from green (528 nm) to red (652 nm)) observed for bis((pyrid-2-yl)vinyl)anthracene [16]; however, such drastic fluorescence change was achieved by a large pressure load of 8 GPa. Under compression, the crystalline stacking between adjacent anthracene rings transformed into a more compact arrangement to result in the observed fluorescence red-shift.

Piezofluorochromism refers to the pressure-induced shortening of the intermolecular distance and the cocurrent electronic orbital overlap to result in the observed bathochromic shift. To maximize electronic orbital overlap, most piezochromic fluorescent molecules have the architecture with a large planar center connected by rotatable substituents, which undergo geometrical adjustment to result in a conformer with different fluorescent wavelengths. Instead of the normal planar central ring, piezofluorochromic TPA-3Qu and TPA-3QuCz (Scheme 1) investigated in this study possess a highly-twisted pyramidal triphenylamine (PA) center, to which two different quinoline arms (Qu and QuCz, respectively) were linked to

\* Corresponding author.

E-mail addresses: [joe79727@gmail.com](mailto:joe79727@gmail.com) (T.-S. Hsiao), [solar77411@hotmail.com](mailto:solar77411@hotmail.com) (T.-L. Chen), [jacky0149@gmail.com](mailto:jacky0149@gmail.com) (W.-L. Chien), [jihong@mail.nsysu.edu.tw](mailto:jihong@mail.nsysu.edu.tw) (J.-L. Hong).



Scheme 1. Syntheses of TPA-3Qu and TPA-3QuCz.

induce distinct fluorescence responses. Comparatively, TPA-3Qu with relatively-smaller Qu arms is crystalline material exhibiting smaller fluorescence shift of 32 nm after a pressure load of 10 MPa. The varied sensitivity in relationship to the arm structure of TPA-3QuCz and TPA-3Qu and the pressure-induced structural transformation of the arms are therefore the main focus of this study.

## 2. Experimental section

### 2.1. Instrumentations and sample preparations

The wide-angle X-ray diffraction (WAXD) was obtained with a Siemen D5000 X-ray diffractometer with a source of CuK radiations at 40 kV and 30 mA. Diffractions patterns were collected with a scan rate of  $0.1^\circ/3$  s from the  $2\theta$  ranges of 2–60°. A mass spectrum was obtained by using a BrukerDaltonicsAutoflex III MALDI-TOF mass spectrometer. Photo luminescence (PL) spectra were obtained from a LabGuide X350 FL spectrophotometer using a 450 W Xe lamp as the continuous light source.  $^1\text{H}$  NMR spectra were recorded with a VarianVXR-500 MHz FT-NMR instrument which use tetramethylsilane (TMS;  $\delta = 0$  ppm) as internal standard. The UV–vis absorption spectra were recorded with an Ocean Optics DT 1000 CE 376 spectrophotometer. Elemental analyses were performed on an Elementary Vario EL-III C, H, and N analyzer. Melting point ( $T_m$ ) of organic compound and glass transition temperature ( $T_g$ ) of oligomer were determined from a TA Q-20 differential scanning calorimeter (DSC) with a scan rate of  $10^\circ\text{C}/\text{min}$  under nitrogen. All solid samples were sealed in a hermetic pan before DSC scan.

The initial samples were placed in a mortar and were gently ground by pestle to obtain the ground samples. Powers in an IR demountable cell holder were also pressurized by a hydraulic presser to obtain pressurized pellets by desired pressure load. The sample powders were primarily heated in hotplate to the desired temperatures before immediate withdrawal to obtain air-quenched powder as the heated samples for analysis. All compressed samples were subjected to solvent annealing by placing them in a closed chamber saturated with triethylamine (TEA) vapor for 10 h to result in the solvent-annealed samples. Pellets after different treatments were then investigated by fluorescence spectrometer, WAXD and DSC.

### 2.2. Synthesis

Triphenylamine (TPA), 2-aminobenzophenone, aluminum chloride, acetyl chloride, acetic acid, phosphorus pentoxide ( $\text{P}_2\text{O}_5$ ), carbazole (Cz), 1-fluoro-4-nitrobenzene (FN) and benzyl cyanide

were purchased from Aldrich Chemical Co. and used directly without further purification. THF was refluxed over sodium and benzophenone under nitrogen for more than 2 days before distillation for use. Triethylamine, dichloromethane and *m*-cresol were distilled from  $\text{CaH}_2$  under nitrogen before use.

#### 2.2.1. Synthesis of TPA-3QuCz and TPA-3Qu

TPA-3Qu and TPA-3QuCz compounds were prepared according to the procedures illustrated in the Scheme 1 and details are given below.

#### 2.2.2. 1,1',1''-(Nitrotris(benzene-4,1-diyl)) triethanone (TPA-Ac)

Triphenylamine (1 g, 4.08 mmol), anhydrous DCM (20 mL) and  $\text{AlCl}_3$  (1.69 g, 12.64 mmol) were added to a three-neck flask under nitrogen atmosphere and the whole mixtures were cooled to  $0^\circ\text{C}$  by ice-water bath. Acetyl chloride (1 g, 12.64 mmol) was then added dropwise to the stirred reaction mixture at  $0^\circ\text{C}$ . The reaction was allowed to warm to room temperature and continued for overnight. The resulting mixture was poured into ice water (125 mL), and the organic layer was collected, concentrated, and poured into a large amount of ethanol. The yellow green precipitates were collected and purified by column chromatography (EtOAc/hexane *v/v* = 1/9) to give TPA-Ac (1.45 g, yield 95%). Mp:  $160^\circ\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.55 (9H, s), 7.16 (6H, d,  $J = 8.5$  Hz), 7.9 (6H, d,  $J = 6$  Hz);  $m/z$  (EI MS) Calcd for  $\text{C}_{24}\text{H}_{21}\text{NO}_3$ , 371.15; Found, 371.11; Anal. Calcd for  $\text{C}_{24}\text{H}_{21}\text{NO}_3$ : C, 77.61; H, 5.70; N, 3.77. Found: C, 77.34; H, 5.81; N, 3.10.

#### 2.2.3. N-(4-Nitrophenyl)carbazole (Cz-NO<sub>2</sub>)

To the stirred solution mixtures of carbazole (2 g; 10 mmol) and of 4-fluoronitrobenzene (2.11 g; 15 mmol) in dried DMSO (10 mL), dried cesium fluoride (3.04 g; 20 mmol) was added at once, and the mixtures were heated at  $150^\circ\text{C}$  for 15 h under nitrogen atmosphere. The resultant products were slowly added into stirred methanol (60 mL). The precipitated yellow crystals were collected by filtration and washed thoroughly with methanol. After filtration, yellow Cz-NO<sub>2</sub> crystal (2.82 g; yield 98%) was obtained. Mp:  $210^\circ\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.33 (3H, t,  $J = 7$  Hz), 7.45 (3H, td,  $J = 6, 1$  Hz), 7.55 (2H, d,  $J = 7.8$  Hz), 7.96 (2H, dt,  $J = 13.5, 3.5$  Hz), 8.26 (2H, d,  $J = 7.5$  Hz), 8.49 (2H, dt,  $J = 9, 2.5$  Hz);  $m/z$  (EI MS) Calcd for  $\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_2$ , 288.30; Found 288.35. Anal. Calcd for  $\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_2$ : C, 74.99; H, 4.20; N, 9.72. Found: C, 74.96; H, 4.27; N, 9.85.

#### 2.2.4. 5-(9H-carbazol-9-yl)-3-phenylbenzo[c]isoxazole (Cz-Bz)

To an ice-cooled mixture of sodium hydroxide (4.68 g, 117 mmol), methanol (30 mL), and THF (50 mL), benzyl nitrile (1.27 g, 10.8 mmol) was added slowly. After stirring for 1 h, Cz-NO<sub>2</sub> (2.82 g, 9.78 mmol) was added and the whole mixtures were then

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