# **Supporting Information**

# **Pressure-Induced Emission Band Separation of Hybridized Local and Charge Transfer Excited State in a TPE-based Crystal**

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#### 1. Materials and General Methods

All the solvents and reactants were purchased from commercialized companies and used as received without further purification except for specifying otherwise.

<sup>1</sup>H NMR was recorded on the 400 MHz (Bruker ARX400) and <sup>13</sup>C NMR spectra were recorded on the Bruker 125 MHz spectrometer at room temperature with CDCl<sub>3</sub> as the solvent and tetramethylsilane (TMS) as the internal standard. ESI high resolution mass-spectra (HRMS) were acquired on a Bruker Apex IV FTMS mass spectrometer. UV-Vis spectra were acquired on the Hitachi U-4100 UV-vis spectrophotometer. Steady fluorescence spectra were performed on the Hitachi F-7000 or Edinburgh Instruments FLS920 fluorescence spectrophotometer. The calculation of quantum yield was performed on the Nanolog/FluoroLog-3-2-Ihr320 combined measurement system for infrared fluorescence equipped with an integrating sphere. Fluorescence lifetime were acquired on the Lifespec-Red Picosecond Lifetime Spectrometer ( $\lambda_{ex}$ =365nm). Differential scanning calorimetry (DSC) measurement was carried out by using TA instruments Q100 DSC. Wide angle Xraysdiffraction (WAXD) experiments were measured on a Philips X'PertPro diffractometer with a 3 kW ceramic tube as the X-ray source (Cu K $\alpha$ ) and an X'celerator detector.

Single crystal X-ray diffraction data were collected with a NONIUS KappaCCD diffractometer with graphite monochromator and Mo K $\alpha$  radiation [ $\lambda$  (MoK $\alpha$ ) = 0.71073 Å]. Structures were solved by direct methods with SHELXS-97 and refined against F2 with SHELXS-97.

High pressure experiments were performed using symmetric diamond anvil cells (DACs) at room temperature. The culet diameter of the diamond anvils was 500  $\mu$ m. The crystal was placed in the holes (diameter: ca. 170  $\mu$ m) of a T301 steel gasket, which was pre-indented to a thickness of 50 $\mu$ m. The silicon oil was used as pressure transmitting medium (PTM). A small ruby chip was inserted into the sample compartment for in situ pressure calibration according to the R1 ruby fluorescence method. The photoluminescence measurements under high pressure were performed on a QE65000 Scientific-grade spectrometer in the reflection mode. The 365 nm line of a laser with a power of 10 mW was used as the excitation source. The images of the powder under 355 nm line of a laser with a power of 10 mW were taken by putting the DAC containing the sample on a Nikon fluorescence microscope. All experiments were carried out at room temperature.

### 2. Synthesis of targeted molecule TPE=C4



Scheme S1. The synthetic route to TPE=C4.

Compound TPE-CHO was synthesized according to literature report.<sup>[1]</sup>

### TPE=C4

Butylamine (73.1 mg, 1.0 mmol) and TPE-CHO (360.4 mg, 1.0 mmol) were both placed in 50 ml round-bottomed flask. Ethanol (10 ml, HPLC grade) was then added and the solution was kept refluxing for 24h, followed by standing for another 2h at room temperature. The product was gained as a white solid after filtration. Yield: 92%.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ/ppm: 8.22 (s, 1H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.24 – 6.94 (m, 17H), 3.62 (t, *J* = 6.7 Hz, 2H), 1.98 – 1.59 (m, 2H), 1.43 (dd, *J* = 14.6, 7.3 Hz, 2H), 0.99 (t, *J* = 7.2 Hz, 3H).

<sup>13</sup>C NMR <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ/ppm: 160.56, 146.21, 143.56, 143.48, 143.45, 141.73, 140.41, 134.42, 131.63, 131.37, 131.33, 127.82, 127.75, 127.69, 127.41, 126.68, 126.59, 77.38, 77.06, 76.74, 61.52, 33.09, 20.51, 13.93.

HR-ESI-MS Calcd. For C<sub>31</sub>H<sub>29</sub>N [M+H]<sup>+</sup>: 416.23728. Found: 416.23653.



### 3. NMR spectra and HR-MS of TPE=C4









Figure S3. HR-MS spectra of TPE=C4.

# 4. Detailed data of TPE=C4 single crystal

 Table S1. Data table of TPE=C4 single crystal.

Identification code	TPE=C4
CCDC Number	1831077
Empirical formula	$C_{31} H_{29} N$
Formula weight	415.55
Temperature	273(2) K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	P 21 21 21
Unit cell dimensions	a = 9.5324(9) Å, α= 90.00°.
	b = 14.9752(14) Å, β= 90.00°.
	c = 16.6507(15) Å, γ = 90.00°.
Volume	2376.9(4) Å <sup>3</sup>
Z	4
Density (calculated)	1.161 Mg/m <sup>3</sup>
Absorption coefficient	0.066 mm <sup>-1</sup>
F(000)	888
Theta range for data collection	2.813 to 28.015°.
Index ranges	-12<=h<=12, -20<=k<=20, -
	22<=l<=21
Reflections collected	35075
Independent reflections	6023 [R(int) = 0.1104]
Final R indices [I>2sigma(I)]	R1 = 0.0619, wR2 = 0.1094
R indices (all data)	R1 = 0.1481, wR2 = 0.1381

### 5. Fluorescence decay profiles of TPE=C4



**Figure S4.** Fluorescence life time decay profiles of **TPE=C4** in original state (black) and after grinding (red).

## 6. Self-recovered property of TPE=C4



Figure S5. Optical images of original powder, ground powder and self-recovered powder.



### 7. Raman spectra during the process of decompression

**Figure S6**. Raman spectra of **TPE=C4** single crystal at different pressure when releasing at the wavenumber range of (a) 200 cm<sup>-1</sup>~1800 cm<sup>-1</sup> and (b) 2500 cm<sup>-1</sup>~3500 cm<sup>-1</sup>. Raman spectra of **TPE=C4** single crystal at 0 GPa (before compression and after release) at the wavenumber range of (c) 200 cm<sup>-1</sup>~1800 cm<sup>-1</sup> and (d) 2500 cm<sup>-1</sup>~3500 cm<sup>-1</sup>.

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