Supporting Information

for Adv. Sci., DOI: 10.1002/advs.202103402

Room Temperature Phosphorescent (RTP) Thermoplastic Elastomers with Dual and Variable RTP Emission, Photo-patternning Memory Effect, and Dynamic Deformation RTP Response

Yuefa Zhang,[†] Qikun Sun,[†] Lingtaï Yue, Yaguang Wang, Shuaiwei Cui, Haichang Zhang, Shanfeng Xue,* Wenjun Yang*
Supporting Information

Room Temperature Phosphorescent (RTP) Thermoplastic Elastomers with Dual and Variable RTP Emission, Photo-patterning Memory Effect, and Dynamic Deformation RTP Response

Yuefa Zhang,[†] Qikun Sun,[†] Lingtai Yue, Yaguang Wang, Shuaiwei Cui, Haichang Zhang, Shanfeng Xue,* Wenjun Yang*

Key Laboratory of Rubber-plastics of Ministry of Education/Shandong Province (QUST), School of Polymer Science & Engineering, Qingdao University of Science & Technology, 53-Zhengzhou Road, Qingdao, 266042, P. R. China.
E-mail: ywjph2004@qust.edu.cn, sfxue@qust.edu.cn.
Materials

Styrene–isoprene–styrene block copolymer (SIS 1125, 300 mPa·s for 25% toluene solution at 25 °C, the molecular weight is 80,000-300,000) was obtained from Yueyang Baling Huaxing Petrochemical Co., Ltd., 4-Fluorobenzonitrile and 9H-carbazole were obtained from Energy Chemical Co., Ltd.

General method

$^1$H and $^{13}$C NMR spectra was recorded on a Bruker AC500 spectrometer at 500 MHz and 125 MHz, respectively, using deuterated chloroform or deuterated dimethyl sulfoxide as the solvent and tetramethylsilane (TMS) as the internal standard. High performance liquid chromatography (HPLC) was performed on an Essentia LC-16. The running rate was 1 mL/min. X-ray diffraction (XRD) measurements were determined on a D-MAX 2500(18KW). Differential scanning calorimetry (DSC) curves were determined on a Netzsch DSC (204F1) instrument at a heating rate of 10 °C /min. Photo-fluorescence and phosphorescence emission spectra were recorded on Hitachi F-4600 spectrophotometers. Fluorescence and phosphorescence decay curves were recorded by a Hamamatsu compact fluorescence lifetime spectrometer (FLS-1000). The lifetimes ($\tau$) of the luminescence were obtained by fitting the decay curve with a multi-exponential decay function of

$$ R(t) = \sum B_i e^{-\frac{t}{\tau_i}} $$  \hspace{1cm} \text{(S1)}

where $B_i$ and $\tau_i$ represent the amplitudes and lifetimes of the individual components for multi-exponential decay profiles, respectively.

The digital photographs were captured by the FDR-AX700 4K HDR digital cameras (SONY, Japan). Photoluminescence spectra and photographs at room temperature were performed on a QE Pro spectrometer with a CCD array (Ocean Optics) as a power detector.
The Gaussian 09 program was utilized to perform the TD-DFT calculations. The ground state ($S_0$) geometry was obtained from the single crystal structure and no further geometry optimization was conducted in order to maintain the specific molecular configuration and corresponding intermolecular locations. The exciton energies of the n-th singlet ($S_n$) and n-th triplet states ($T_n$) were obtained on the corresponding ground state structure using TD-B3LYP/6-31G*. The Kohn–Sham frontier orbital analysis and spin density distributions were obtained in order to elucidate the mechanisms of possible singlet–triplet intersystem crossings (ISC). The possible $S_1$ to $T_n$ ISC channels are believed to share part of the same transition orbital compositions, and the energy levels of possible $T_n$ are considered to lie within the range of $E_{S1} \pm 0.3$ eV. Especially, the major ISC channels are mainly determined based on two elements. First, the ratio of the same transition configuration in $S_1$ and $T_n$ should be large in all the transition orbital compositions. Secondly, the energy gap between $S_1$ and the specific $T_n$ state should be small.

**Synthesis and Characterization**

*The synthetic route of laboratory-self-synthesized carbazole (LCZ).*

![Scheme S1. Synthetic route of LCZ.](image)

**9H-carbazole (LCZ).** In a 100 mL two-necked flask 2-Aminobiphenyl (2.50 g, 14.77 mmol), [Cp*IrCl]$_2$ (0.25 g, 0.31 mmol), Cu(OAc)$_2$ (0.54 g, 2.97 mmol), and PivOH (3.05 g, 29.86 mmol) in NMP (50 mL) was stirred under air at 120 °C for 3 h. After cooling, the reaction mixture was extracted with ethyl acetate, the combined organic layer dried with anhydrous MgSO$_4$, filtered and concentrated in vacuo. The crude product was purified by silica-gel column chromatography using petroleum ether/dichloromethane (5:1, v/v), yielding a white solid (1.31 g, Yield 53 %). $^1$H NMR (500 MHz, DMSO-$d_6$) δ 11.27 (s, 1H), 8.13 (d, $J$
The synthetic route of 4-(9H-carbazol-9-yl)benzonitrile (PCN/L-PCN).

**Scheme S2.** Synthetic route of PCN.

4-(9H-carbazol-9-yl)benzonitrile (PCN/L-PCN). In a 100 mL bottom, 9H-carbazole (CCZ/LCZ, 3.00 g, 17.94 mmol) and K₂CO₃ (8.22 g, 26.91 mmol) in DMSO (30 ml) was stirred at room temperature for 1 h. 4-Fluorobenzonitrile (2.61 g, 21.55 mmol) was added in the mixture and stirred at 150 °C for 12 h. The reaction mixture was poured into a large amount of ice water and stirred for additional 1 h. After the reaction mixture was extracted with ethyl acetate, the combined organic layer dried with anhydrous MgSO₄, filtered and concentrated in vacuo. The crude product was purified by silica-gel column chromatography using petroleum ether/ethyl acetate (10:1, v/v) as the eluent to give the compound as a white solid (4.09 g, Yield 85%).

**PCN:** ¹H NMR (500 MHz, Chloroform-d): δ 8.14 (d, J = 7.7 Hz, 2H), 7.92–7.86 (m, 2H), 7.75–7.70 (m, 2H), 7.49–7.38 (m, 4H), 7.33 (ddd, J = 8.0, 6.2, 1.9 Hz, 2H). ¹³C NMR (125MHz, Chloroform-d): δ 142.05, 139.87, 133.89, 127.08, 126.35, 123.98, 120.97, 120.55, 118.33, 110.45, 109.49.

**L-PCN:** ¹H NMR (500 MHz, Chloroform-d): δ 8.14 (d, J = 7.8 Hz, 2H), 7.94 – 7.88 (m, 2H), 7.78 – 7.71 (m, 2H), 7.48 – 7.41 (m, 4H), 7.34 (ddd, J = 8.0, 6.3, 1.8 Hz, 2H). ¹³C NMR (126 MHz, Chloroform-d): δ 142.08, 139.92, 133.93, 127.11, 126.39, 121.02, 120.60, 118.38, 110.50, 109.54.
Preparation of TPEx (x represents the doping mass (g) of PCN in 100 g of SIS). SIS and PCN were stirred and dissolved in chloroform at room temperature. The resulting solution was evaporated and the formed film was dried in oven at 60 °C. Then, the films were thermoplasticized on an open two-roll mill at 120 °C for 2–3 min. Finally, the thermoplasticized film was molded into 1 mm thick sample.
Supplementary Figures and Tables

**Figure S1.** a) PL Photographs of PCN crystal taken before and after removing 365 nm UV light irradiation. b) The RTP decay curve and fitted lifetimes of photo-activated PCN crystal monitored at 546 nm and excited at 365 nm.

**Figure S2.** The prompt PL and afterglow photographs of solution-processed films of PCN and SIS in chloroform after photo-activation for 10 s.
Figure S3. The delayed RTP spectra and the corresponding CIE 1931 chromaticity coordinates of photo-activated TPEx after 365 nm light excitation. A clear boundary at ca. 525 nm is observed, and the emissions before and after 525 nm are from mono-molecules and micro-crystals of PCN in SIS matrix, respectively.

Figure S4. Differential scanning calorimetric (DSC) and X-ray diffraction (XRD) curves of TPEx (x=0, 5.0, 7.0).
Figure S5. Possible ISC channels of PCN for a) a single molecule and b) three adjacent molecules.
Figure S6. (a) The prompt spectra of LCZ and CCZ crystals with 340 nm excitation under common ambient conditions. (b) The delay spectra of LCZ and CCZ crystals with 360 nm excitation under common ambient conditions. RTP afterglow photographs of LCZ (c) HPLC spectra of CCZ and LCZ monitored at the onset absorption of 346 nm with 50/50 acetonitrile (ACN)-water ratio (v/v). (d) HPLC spectra of different carbazole source monitored at the onset absorption of 346 nm with 50/50 acetonitrile (ACN)-water ratio (v/v) as the eluent reported by Liu et al. By comparing, the content of 1H-benzo[f]indole in the CCZ we used is about 0.2%.
**Figure S7.** The PL photographs of L-PCN crystal before and after removing excitation light in the dark.

**Figure S8.** The PL photographs of PCN crystal and the prompt and delayed PL spectra of the pure PCN crystal be treated under 160 °C as the films.
Figure S9. The RTP efficiencies of photo-activated TPEx measured at room temperature under 360 nm excitation.

Figure S10. The PL photographs of TPE3.5 from direct solid thermoplasticized.

Figure S11. The polarizing microscope photographs of TPEx(x=0, 2.0, 7.0).

Table S1. The singlet and triplet excited state transition configurations of the PCN from single crystal revealed by TD-DFT calculations. The matched excited states that contain the same orbital transition components of S₁ and |S₁ - Tₙ | < 0.3 eV were highlighted in red.
| n | Energy | Orbitals | Transition |
|---|--------|----------|------------|

| $S_n$ | $S_1$ | Energy (eV) | HOMO $\rightarrow$ LUMO | Energy (eV) |
|-------|-------|-------------|------------------------|-------------|
| $T_1$ | 3.7236 eV | HOMO $\rightarrow$ LUMO | 0.688 |
|       |       | HOMO-4 $\rightarrow$ LUMO+2 | 0.028 |
|       |       | HOMO-3 $\rightarrow$ LUMO | 0.220 |
|       |       | HOMO $\rightarrow$ LUMO | 0.679 |
| $T_2$ | 3.8057 eV | HOMO-5 $\rightarrow$ LUMO+5 | 0.037 |
|       |       | HOMO-2 $\rightarrow$ LUMO+1 | 0.029 |
|       |       | HOMO-1 $\rightarrow$ LUMO+1 | 0.669 |
|       |       | HOMO $\rightarrow$ LUMO+1 | 0.113 |
|       |       | HOMO $\rightarrow$ LUMO+3 | 0.069 |
| $T_3$ | 3.8935 eV | HOMO-3 $\rightarrow$ LUMO+1 | 0.020 |
|       |       | HOMO-2 $\rightarrow$ LUMO+3 | 0.034 |
|       |       | HOMO-2 $\rightarrow$ LUMO+5 | 0.028 |
|       |       | HOMO-1 $\rightarrow$ LUMO+1 | 0.103 |
|       |       | HOMO $\rightarrow$ LUMO+1 | 0.767 |
| $T_4$ | 4.4656 eV | HOMO-2 $\rightarrow$ LUMO+1 | 0.144 |
|       |       | HOMO-2 $\rightarrow$ LUMO+4 | 0.052 |
|       |       | HOMO-1 $\rightarrow$ LUMO+1 | 0.148 |
|       |       | HOMO $\rightarrow$ LUMO+2 | 0.035 |
|       |       | HOMO $\rightarrow$ LUMO+3 | 0.545 |
| $T_5$ | 4.5946 eV | HOMO-3 $\rightarrow$ LUMO+2 | 0.188 |
|       |       | HOMO $\rightarrow$ LUMO+2 | 0.688 |
|       |       | HOMO $\rightarrow$ LUMO+3 | 0.026 |
|       |       | HOMO-5 $\rightarrow$ LUMO | 0.021 |
|       |       | HOMO-4 $\rightarrow$ LUMO+2 | 0.157 |
|       |       | HOMO-3 $\rightarrow$ LUMO | 0.280 |
|       |       | HOMO-2 $\rightarrow$ LUMO+3 | 0.089 |
|       |       | HOMO-1 $\rightarrow$ LUMO+5 | 0.020 |
|       |       | HOMO $\rightarrow$ LUMO | 0.107 |
| $T_6$ | 4.6337 eV | HOMO-5 $\rightarrow$ LUMO+3 | 0.032 |
|       |       | HOMO-2 $\rightarrow$ LUMO+1 | 0.117 |
|       |       | HOMO-1 $\rightarrow$ LUMO | 0.583 |
|       |       | HOMO-1 $\rightarrow$ LUMO+3 | 0.030 |
|       |       | HOMO-1 $\rightarrow$ LUMO+4 | 0.136 |
|       |       | HOMO $\rightarrow$ LUMO+5 | 0.049 |
| $T_7$ | 4.9002 eV | HOMO-5 $\rightarrow$ LUMO+1 | 0.034 |
|       |       | HOMO-4 $\rightarrow$ LUMO | 0.059 |
|       |       | HOMO-4 $\rightarrow$ LUMO+2 | 0.490 |
|       |       | HOMO-2 $\rightarrow$ LUMO+3 | 0.071 |
|       |       | HOMO-1 $\rightarrow$ LUMO+5 | 0.038 |
|       |       | HOMO $\rightarrow$ LUMO | 0.048 |
| $T_8$ | 4.9616 eV | HOMO-5 $\rightarrow$ LUMO+4 | 0.174 |
|       |       | HOMO-5 $\rightarrow$ LUMO+1 | 0.154 |
|       |       | HOMO-5 $\rightarrow$ LUMO+4 | 0.022 |
|       |       | HOMO-1 $\rightarrow$ LUMO+3 | 0.690 |
|       |       | HOMO-1 $\rightarrow$ LUMO+5 | 0.044 |
| $T_9$ | 4.9784 eV | HOMO-4 $\rightarrow$ LUMO+2 | 0.059 |
|       |       | HOMO $\rightarrow$ LUMO+2 | 0.030 |
|       |       | HOMO-4 $\rightarrow$ LUMO+4 | 0.055 |
|       |       | HOMO-3 $\rightarrow$ LUMO | 0.068 |
|       |       | HOMO-2 $\rightarrow$ LUMO+1 | 0.296 |
|       |       | HOMO-2 $\rightarrow$ LUMO+4 | 0.031 |
|       |       | HOMO-1 $\rightarrow$ LUMO | 0.157 |
|       |       | HOMO $\rightarrow$ LUMO | 0.022 |
|       |       | HOMO $\rightarrow$ LUMO+3 | 0.103 |
|       |       | HOMO $\rightarrow$ LUMO+5 | 0.166 |
| $T_{10}$ | 5.0988 eV | HOMO-6 $\rightarrow$ LUMO | 0.028 |
| $T_{11}$ | 5.2176 eV | HOMO-7 $\rightarrow$ LUMO | 0.036 |
| $T_{12}$ | 5.2712 eV | HOMO-8 $\rightarrow$ LUMO | 0.041 |
| T | E (eV) | Transition | Energy (eV) |
|---|---|---|---|
| T_{13} | 5.4865 | HOMO-5 -> LUMO+1 | 0.052 |
| | | HOMO-4 -> LUMO+2 | 0.145 |
| | | HOMO-3 -> LUMO | 0.245 |
| | | HOMO-2 -> LUMO+1 | 0.068 |
| | | HOMO-2 -> LUMO+3 | 0.021 |
| | | HOMO-1 -> LUMO | 0.056 |
| | | HOMO-1 -> LUMO+3 | 0.055 |
| | | HOMO-1 -> LUMO+5 | 0.075 |
| | | HOMO -> LUMO | 0.068 |
| | | HOMO -> LUMO+3 | 0.025 |
| | | HOMO -> LUMO+4 | 0.031 |
| | | HOMO -> LUMO+5 | 0.032 |
| | 5.8832 | HOMO-5 -> LUMO | 0.026 |
| | | HOMO-5 -> LUMO+1 | 0.172 |
| | | HOMO-3 -> LUMO | 0.026 |
| | | HOMO-2 -> LUMO+3 | 0.060 |
| | | HOMO-1 -> LUMO+3 | 0.102 |
| | | HOMO-1 -> LUMO+5 | 0.255 |
| | | HOMO -> LUMO+4 | 0.220 |
| | | HOMO -> LUMO+2 | 0.015 |
| T_{14} | 5.9458 | HOMO-5 -> LUMO+2 | 0.024 |
| | | HOMO-3 -> LUMO+2 | 0.516 |
| | | HOMO-1 -> LUMO+2 | 0.195 |
| | | HOMO-1 -> LUMO+4 | 0.035 |
| | | HOMO -> LUMO+2 | 0.125 |
| | 5.9863 | HOMO-5 -> LUMO+3 | 0.096 |
| | | HOMO-2 -> LUMO | 0.096 |
| | | HOMO-1 -> LUMO | 0.103 |
| | | HOMO-1 -> LUMO+2 | 0.069 |
| | | HOMO-1 -> LUMO+4 | 0.539 |
| | | HOMO-2 -> LUMO | 0.665 |
| | 6.3132 | HOMO-2 -> LUMO+1 | 0.031 |
| | | HOMO-2 -> LUMO+4 | 0.032 |
| | | HOMO-1 -> LUMO | 0.029 |
| | | HOMO-1 -> LUMO+4 | 0.077 |
| | | HOMO -> LUMO+3 | 0.110 |
| | 6.4275 | HOMO-10 -> LUMO | 0.225 |
| | | HOMO-9 -> LUMO | 0.027 |
| | | HOMO-8 -> LUMO+6 | 0.030 |
| | | HOMO-7 -> LUMO+6 | 0.130 |
| | | HOMO-6 -> LUMO | 0.101 |
| | | HOMO-3 -> LUMO | 0.035 |
| | | HOMO-3 -> LUMO+4 | 0.024 |
| | | HOMO-3 -> LUMO+7 | 0.096 |
| | | HOMO-2 -> LUMO+3 | 0.036 |
| | | HOMO -> LUMO+4 | 0.056 |
| | 6.5266 | HOMO-10 -> LUMO | 0.226 |
| | | HOMO-3 -> LUMO+1 | 0.026 |
| | | HOMO-2 -> LUMO | 0.065 |
| | | HOMO-2 -> LUMO+1 | 0.164 |
| | | HOMO-2 -> LUMO+4 | 0.022 |
| | | HOMO -> LUMO+3 | 0.032 |
| | | HOMO -> LUMO+5 | 0.526 |
| | 6.5742 | HOMO-10 -> LUMO | 0.023 |
| | | HOMO-6 -> LUMO+1 | 0.040 |
| | | HOMO-3 -> LUMO+1 | 0.129 |
| | | HOMO-2 -> LUMO+1 | 0.023 |
| | | HOMO-2 -> LUMO+3 | 0.250 |
| \( T_{21} \) | 6.6095 eV | HOMO-2 \to\text{LUMO}+5 | 0.020 |
|-----------|-----------|----------------------|--------|
|           |           | HOMO-1 \to\text{LUMO}+5 | 0.096 |
|           |           | HOMO \to\text{LUMO}+1  | 0.037 |
|           |           | HOMO \to\text{LUMO}+4  | 0.140 |
|           |           | HOMO \to\text{LUMO}+5  | 0.044 |
|           | HOMO-10 \to\text{LUMO}+6 | 0.023 |
|           | HOMO-8 \to\text{LUMO}   | 0.119 |
|           | HOMO-7 \to\text{LUMO}   | 0.545 |
|           | HOMO-7 \to\text{LUMO}+4 | 0.024 |
|           | HOMO-7 \to\text{LUMO}+7 | 0.080 |
|           | HOMO-6 \to\text{LUMO}   | 0.025 |
|           | HOMO-3 \to\text{LUMO}+6 | 0.053 |
| \( T_{22} \) | 6.7366 eV | HOMO-6 \to\text{LUMO}+1 | 0.048 |
|           |           | HOMO-6 \to\text{LUMO}+4 | 0.038 |
|           |           | HOMO-5 \to\text{LUMO}   | 0.034 |
|           |           | HOMO-5 \to\text{LUMO}+1 | 0.027 |
|           |           | HOMO-3 \to\text{LUMO}+1 | 0.243 |
|           |           | HOMO-3 \to\text{LUMO}+4 | 0.026 |
|           |           | HOMO-2 \to\text{LUMO}+3 | 0.179 |
|           |           | HOMO-2 \to\text{LUMO}+5 | 0.104 |
|           |           | HOMO-1 \to\text{LUMO}+5 | 0.110 |
|           |           | HOMO \to\text{LUMO}+4   | 0.065 |
|           | HOMO-10 \to\text{LUMO}+6 | 0.023 |
| \( T_{23} \) | 7.0531 eV | HOMO-3 \to\text{LUMO}+6 | 0.085 |
|           |           | HOMO-2 \to\text{LUMO}+2 | 0.720 |
|           |           | HOMO \to\text{LUMO}+6   | 0.046 |
| \( T_{24} \) | 7.0601 eV | HOMO-10 \to\text{LUMO}+6 | 0.079 |
|           |           | HOMO-7 \to\text{LUMO}   | 0.071 |
|           |           | HOMO-6 \to\text{LUMO}+6 | 0.054 |
|           |           | HOMO-5 \to\text{LUMO}+6 | 0.025 |
|           |           | HOMO-3 \to\text{LUMO}+6 | 0.300 |
|           |           | HOMO-2 \to\text{LUMO}+2 | 0.209 |
|           |           | HOMO \to\text{LUMO}+6   | 0.163 |
| \( T_{25} \) | 7.1580 eV | HOMO-5 \to\text{LUMO}   | 0.594 |
|           |           | HOMO-5 \to\text{LUMO}+1 | 0.088 |
|           |           | HOMO-3 \to\text{LUMO}   | 0.033 |
|           |           | HOMO-2 \to\text{LUMO}+3 | 0.031 |
|           |           | HOMO-1 \to\text{LUMO}+3 | 0.023 |
|           |           | HOMO-1 \to\text{LUMO}+5 | 0.023 |
|           |           | HOMO-6 \to\text{LUMO}+3 | 0.044 |
|           |           | HOMO-5 \to\text{LUMO}+3 | 0.095 |
|           |           | HOMO-3 \to\text{LUMO}+3 | 0.158 |
|           |           | HOMO-2 \to\text{LUMO}   | 0.077 |
|           |           | HOMO-2 \to\text{LUMO}+1 | 0.032 |
|           |           | HOMO-2 \to\text{LUMO}+4 | 0.330 |
|           |           | HOMO-1 \to\text{LUMO}+4 | 0.022 |
|           |           | HOMO \to\text{LUMO}+3   | 0.040 |
|           |           | HOMO \to\text{LUMO}+5   | 0.068 |

**Table S2.** The singlet and triplet excited state transition configurations of the PCN from single crystal revealed by TD-DFT calculations. The matched excited states that contain the same orbital transition components of \( S_1 \) and \( |S_1 - T_n| < 0.3 \) eV were highlighted in red\(^2\).
| $T_n$ | $S_i$ | $E$ (eV) | $\Delta E$ (eV) |
|------|------|--------|--------------|
| $S_1$ | 3.6573 | HOMO $\rightarrow$ LUMO+1 | 0.990 |
| $T_1$ | 3.1875 | HOMO-13 $\rightarrow$ LUMO+7 | 0.021 |
| | | HOMO-10 $\rightarrow$ LUMO+1 | 0.112 |
| | | HOMO-1 $\rightarrow$ LUMO+1 | 0.788 |
| $T_2$ | 3.2256 | HOMO-15 $\rightarrow$ LUMO+4 | 0.025 |
| | | HOMO-11 $\rightarrow$ LUMO | 0.138 |
| | | HOMO-2 $\rightarrow$ LUMO | 0.761 |
| $T_3$ | 3.2404 | HOMO-12 $\rightarrow$ LUMO+8 | 0.040 |
| | | HOMO-9 $\rightarrow$ LUMO+2 | 0.123 |
| | | HOMO $\rightarrow$ LUMO+2 | 0.721 |
| | | HOMO $\rightarrow$ LUMO+5 | 0.036 |
| $T_4$ | 3.3204 | HOMO-14 $\rightarrow$ LUMO+16 | 0.026 |
| | | HOMO-7 $\rightarrow$ LUMO+6 | 0.027 |
| | | HOMO-7 $\rightarrow$ LUMO+13 | 0.022 |
| | | HOMO-4 $\rightarrow$ LUMO+4 | 0.274 |
| | | HOMO-4 $\rightarrow$ LUMO+6 | 0.377 |
| | | HOMO-4 $\rightarrow$ LUMO+7 | 0.023 |
| $T_5$ | 3.3239 | HOMO-1 $\rightarrow$ LUMO+10 | 0.111 |
| $T_6$ | 3.3249 | HOMO-17 $\rightarrow$ LUMO+15 | 0.031 |
| | | HOMO-8 $\rightarrow$ LUMO+3 | 0.048 |
| | | HOMO-8 $\rightarrow$ LUMO+12 | 0.025 |
| | | HOMO-5 $\rightarrow$ LUMO+3 | 0.661 |
| | | HOMO-2 $\rightarrow$ LUMO+3 | 0.038 |
| $T_7$ | 3.4314 | HOMO-2 $\rightarrow$ LUMO+9 | 0.119 |
| | | HOMO-6 $\rightarrow$ LUMO+5 | 0.044 |
| | | HOMO-6 $\rightarrow$ LUMO+14 | 0.020 |
| $T_8$ | 3.4742 | HOMO-17 $\rightarrow$ LUMO+15 | 0.031 |
| | | HOMO-3 $\rightarrow$ LUMO+5 | 0.043 |
| $T_9$ | 3.4952 | HOMO-6 $\rightarrow$ LUMO+11 | 0.030 |
| | | HOMO-3 $\rightarrow$ LUMO+5 | 0.039 |
| | | HOMO $\rightarrow$ LUMO+1 | 0.031 |
| | | HOMO $\rightarrow$ LUMO+2 | 0.030 |
| | | HOMO $\rightarrow$ LUMO+5 | 0.723 |
| | | HOMO $\rightarrow$ LUMO+7 | 0.060 |
| $T_{10}$ | 3.6638 | HOMO-6 $\rightarrow$ LUMO+9 | 0.033 |
| | | HOMO-8 $\rightarrow$ LUMO+3 | 0.033 |
| | | HOMO-2 $\rightarrow$ LUMO+3 | 0.843 |
| $T_{11}$ | 3.7330 | HOMO-7 $\rightarrow$ LUMO+10 | 0.033 |
| | | HOMO-1 $\rightarrow$ LUMO+4 | 0.365 |
| | | HOMO-1 $\rightarrow$ LUMO+6 | 0.465 |
| | | HOMO-1 $\rightarrow$ LUMO+7 | 0.023 |
| $T_{12}$ | 3.8293 | HOMO $\rightarrow$ LUMO+1 | 0.943 |
| | | HOMO $\rightarrow$ LUMO+5 | 0.040 |
| $T_{13}$ | 3.9764 | HOMO-10 $\rightarrow$ LUMO+7 | 0.025 |
| T  | Energy (eV) | HOMO - LUMO transitions |  
|----|-------------|-------------------------|
| T14 | 3.9796 | HOMO-4 -> LUMO+1 | 0.148  
|    |           | HOMO-1 -> LUMO+2 | 0.030  
|    |           | HOMO-1 -> LUMO+5 | 0.103  
|    |           | HOMO-1 -> LUMO+7 | 0.583  
|    |           | HOMO-10 -> LUMO+1 | 0.030  
|    |           | HOMO-4 -> LUMO+1 | 0.664  
|    |           | HOMO-1 -> LUMO+5 | 0.026  
|    |           | HOMO-1 -> LUMO+7 | 0.149  
| T15 | 4.0090 | HOMO-11 -> LUMO | 0.021  
|    |           | HOMO-11 -> LUMO+4 | 0.028  
|    |           | HOMO-2 -> LUMO+4 | 0.588  
|    |           | HOMO-2 -> LUMO+6 | 0.236  
| T16 | 4.0322 | HOMO-16 -> LUMO+7 | 0.020  
|    |           | HOMO-13 -> LUMO+7 | 0.077  
|    |           | HOMO-10 -> LUMO+1 | 0.223  
|    |           | HOMO-4 -> LUMO+1 | 0.064  
|    |           | HOMO-3 -> LUMO+1 | 0.273  
|    |           | HOMO-3 -> LUMO+2 | 0.031  
|    |           | HOMO-1 -> LUMO+1 | 0.067  
|    |           | HOMO-1 -> LUMO+13 | 0.022  
|    |           | HOMO -> LUMO+8 | 0.030  
|    |           | HOMO -> LUMO+11 | 0.027  
| T17 | 4.0401 | HOMO-13 -> LUMO+7 | 0.046  
|    |           | HOMO-10 -> LUMO+1 | 0.138  
|    |           | HOMO-4 -> LUMO+1 | 0.026  
|    |           | HOMO-3 -> LUMO+1 | 0.259  
|    |           | HOMO-3 -> LUMO+2 | 0.044  
|    |           | HOMO-3 -> LUMO+5 | 0.034  
|    |           | HOMO-1 -> LUMO+1 | 0.043  
|    |           | HOMO -> LUMO+8 | 0.177  
|    |           | HOMO -> LUMO+11 | 0.070  
| T18 | 4.0451 | HOMO-15 -> LUMO+4 | 0.095  
|    |           | HOMO-15 -> LUMO+6 | 0.052  
|    |           | HOMO-11 -> LUMO | 0.294  
|    |           | HOMO-5 -> LUMO | 0.219  
|    |           | HOMO-2 -> LUMO | 0.108  
|    |           | HOMO-2 -> LUMO+4 | 0.047  
|    |           | HOMO-2 -> LUMO+12 | 0.043  
| T19 | 4.0527 | HOMO-12 -> LUMO+8 | 0.061  
|    |           | HOMO-9 -> LUMO+2 | 0.124  
|    |           | HOMO-9 -> LUMO+8 | 0.035  
|    |           | HOMO-3 -> LUMO+1 | 0.123  
|    |           | HOMO-3 -> LUMO+2 | 0.055  
|    |           | HOMO -> LUMO+2 | 0.054  
|    |           | HOMO -> LUMO+8 | 0.431  
| T20 | 4.0658 | HOMO-12 -> LUMO+8 | 0.146  
|    |           | HOMO-9 -> LUMO+2 | 0.225  
|    |           | HOMO-6 -> LUMO+11 | 0.020  

18
| T<sub>21</sub> | 4.0738 eV | HOMO-3 → LUMO+1 | 0.141 |
| T<sub>21</sub> | 4.0738 eV | HOMO → LUMO+2 | 0.095 |
| T<sub>21</sub> | 4.0738 eV | HOMO → LUMO+8 | 0.200 |
| T<sub>21</sub> | 4.0738 eV | HOMO → LUMO+14 | 0.037 |
| T<sub>22</sub> | 4.0998 eV | HOMO-15 → LUMO+4 | 0.031 |
| T<sub>22</sub> | 4.0998 eV | HOMO-11 → LUMO | 0.089 |
| T<sub>22</sub> | 4.0998 eV | HOMO-5 → LUMO | 0.504 |
| T<sub>22</sub> | 4.0998 eV | HOMO-5 → LUMO+3 | 0.060 |
| T<sub>22</sub> | 4.0998 eV | HOMO-4 → LUMO | 0.158 |
| T<sub>22</sub> | 4.0998 eV | HOMO-2 → LUMO | 0.024 |
| T<sub>22</sub> | 4.0998 eV | HOMO-2 → LUMO+9 | 0.040 |
| T<sub>23</sub> | 4.1142 eV | HOMO-6 → LUMO+5 | 0.035 |
| T<sub>23</sub> | 4.1142 eV | HOMO-3 → LUMO+1 | 0.180 |
| T<sub>23</sub> | 4.1142 eV | HOMO-3 → LUMO+2 | 0.161 |
| T<sub>23</sub> | 4.1142 eV | HOMO-3 → LUMO+5 | 0.171 |
| T<sub>23</sub> | 4.1142 eV | HOMO → LUMO+8 | 0.063 |
| T<sub>23</sub> | 4.1142 eV | HOMO → LUMO+11 | 0.268 |
| T<sub>24</sub> | 4.1199 eV | HOMO-2 → LUMO+1 | 0.979 |
| T<sub>25</sub> | 4.1429 eV | HOMO-8 → LUMO+3 | 0.108 |
| T<sub>25</sub> | 4.1429 eV | HOMO-8 → LUMO+12 | 0.026 |
| T<sub>25</sub> | 4.1429 eV | HOMO-5 → LUMO | 0.108 |
| T<sub>25</sub> | 4.1429 eV | HOMO-5 → LUMO+3 | 0.137 |
| T<sub>25</sub> | 4.1429 eV | HOMO-2 → LUMO+9 | 0.450 |
| T<sub>25</sub> | 4.1429 eV | HOMO-1 → LUMO+3 | 0.033 |
| T<sub>25</sub> | 4.1429 eV | HOMO-1 → LUMO+10 | 0.027 |
| T<sub>26</sub> | 4.1439 eV | HOMO-7 → LUMO+4 | 0.034 |
| T<sub>26</sub> | 4.1439 eV | HOMO-7 → LUMO+6 | 0.047 |
| T<sub>26</sub> | 4.1439 eV | HOMO-7 → LUMO+13 | 0.021 |
| T<sub>26</sub> | 4.1439 eV | HOMO-4 → LUMO+4 | 0.064 |
| T<sub>26</sub> | 4.1439 eV | HOMO-4 → LUMO+6 | 0.071 |
| T<sub>26</sub> | 4.1439 eV | HOMO-3 → LUMO+2 | 0.054 |
| T<sub>26</sub> | 4.1439 eV | HOMO-2 → LUMO+9 | 0.034 |
| T<sub>26</sub> | 4.1439 eV | HOMO-1 → LUMO+2 | 0.068 |
| T<sub>26</sub> | 4.1439 eV | HOMO-1 → LUMO+3 | 0.045 |
| T<sub>26</sub> | 4.1439 eV | HOMO-1 → LUMO+9 | 0.026 |
| T<sub>26</sub> | 4.1439 eV | HOMO-1 → LUMO+10 | 0.368 |
Figure S8. $^1$H and $^{13}$C NMR spectrum of LCZ in DMSO-$d_6$. 
Figure S9. $^1$H and $^{13}$C NMR spectrum of PCN in CDCl$_3$. 
Figure S10. $^1$H and $^{13}$C NMR spectrum of L-PCN in CDCl$_3$.

References

[1] C. J. Chen, Z. G. Chi, K. C. Chong, A. S. Batsanov, Z. Yang, Z. Mao, Z. Y. Yang, B, Liu, Nat. Mater. 2021, 20, 175.

[2] Y. Wang, Z. Zhang, L. Liu, S. Yuan, J. Ma, D. Liu, S. Xue, Q. Sun, W. Yang, J. Mater. Chem. C. 2019, 7, 9671.