Supporting Information

A Simple and Versatile Strategy for Realizing Bright Multicolor Mechanoluminescence

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General Information

Materials

9-*H*-carbazole (CZ), iodobenzene, CuI, K_2CO_3, *L*-Proline, 3,6-bis(4-chlorophenyl) pyrrolo[3,4-c]pyrrole-1,4(*2H,5H*)-dione, potassium tert-butoxide (*t*-BuOK), 1-Bromo-heptane and Dimethyl sulfoxide (DMSO) were obtained from Energy Chemical Ltd. Shanghai, China, and used without further purification. *N*,*N*-dimethyl-formamide (DMF) over calcium hydride were distilled before use. The other solvents were of analytical grade and are obtained commercially from available resources. PPO[1], CIDPP, BrDPP, and PDPP[2] were from our previous work.

The preparation details

We employ four polar dyes with green, yellow, orange and red emission as the dopants. The blends are prepared by adding a given amount of dopant (4~5 W%) into the stirring NPC melt at 110 ^oC and then cooled to the room temperature.

Measurements and Instruments

^1H (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded using a Bruker-AC500 spectrometer in $CDCl_3$ at 298 K and tetramethylsilane (TMS) as the internal standard. The elemental analysis was performed on Perkin-Elmer 2400. UV-visible absorption and fluorescence emission spectra were recorded on Hitachi U-4100 and Hitachi F-4600 spectrophotometers, respectively. Differential scanning calorimetry (DSC) curves were determined on a Netzsch DSC (204F1) instrument at a heating (or cooling) rate of 10 ^oC min^{-1}. Time-resolved spectra was recorded by Hamamatsu compact fluorescence lifetime spectrometer. Four given amount of polar dyes (4~5 W%) with green, yellow, orange and red emission were adding into the stirring NPC melt at 110 ^oC and then cooled to the room temperature. Mechanoluminescence (ML) spectra were collected from Acton SP2750 spectrometer with a liquid-nitrogen-cooled CCD (SPEC-10, Princeton) as a power detector.

Experimental Section

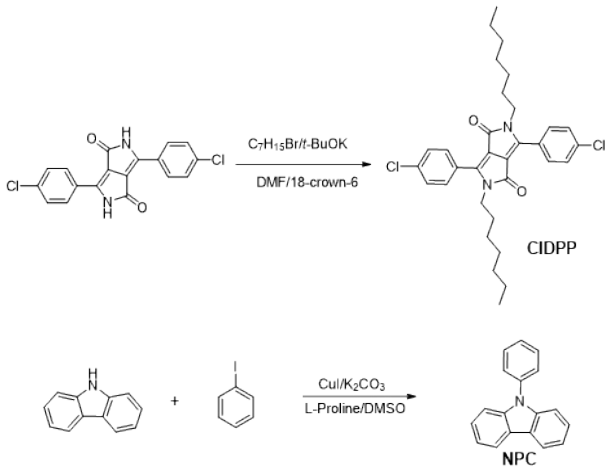
3,6-bis(4-chlorophenyl)-2-heptyl-5-hexylpyrrolo[3,4-c]pyrrole-1,4(*2H,5H*)-dione (CIDPP)

K_2CO_3 (1.2 g, 3 mmol) and 3,6-bis(4-chlorophenyl)pyrrolo[3,4-c]pyrrole-1,4(*2H,5H*)

-dione (1.0 g, 2.8 mmol) in 50 mL anhydrous DMF were stirred for 1 h at 120 °C under nitrogen atmosphere. Then 1-Bromoheptane (3.9 g, 14.0 mmol, in 5 mL DMF) was slowly added to the flask. The reaction mixture was kept for 24 h at 130 °C. The mixture was extracted with dichloromethane after being cooled to room temperature. The organic phase was dried over anhydrous $MgSO_4$, and the solvent was removed by rotary evaporation. The crude product was purified by a silica column chromatography using petroleum ether/CH_2Cl_2 (1/1, v/v) as the eluent. A yellow crystalline solid was obtained (0.91 g, yield 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.74 (m, 4H), 7.53 – 7.49 (m, 4H), 3.75 – 3.70 (m, 4H), 1.61 – 1.55 (m, 4H), 1.21 (td, J = 13.6, 12.2, 6.5 Hz, 16H), 0.84 (t, J = 6.9 Hz, 6H).

***N*-phenylcarbazole (NPC)**

Under nitrogen atmosphere, 9-*H*-carbazole (4.00 g, 23.9 mol) , iodobenzene (5.86 g, 28.7mmol), CuI (0.45 g, 2.39 mmol), K_2CO_3 (6.60 g, 47.8 mol) , *L*-Proline (0.276 g，2.39 mol) and DMSO (50 mL) were added to a 100 ml one-neck flask .The mixture was stirred for 36 h at 110 °C. And then cooled and extracted with CH_2Cl_2 (3×50 mL).The organic phase was dried over $MgSO_4$ and the solvent was removed via rotary evaporation. The crude product was purified by silica column chromatography using petroleum ether as the eluent to afford the pure white target compound (5.82 g, yield 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, J = 7.8 Hz, 2H), 7.65 – 7.56 (m, 4H), 7.49 (t, J = 7.2 Hz, 1H), 7.44 (d, J = 4.0 Hz, 4H), 7.32 (dt, J = 7.7, 3.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.91, 137.72, 129.86, 127.44, 125.92, 123.36, 120.30, 119.90, 109.77. MALDI-TOF MS: m/z Calcd. for $C_{18}H_{13}N$: 243.3090; found 266.3257 [M^++Na]. Anal. Calcd. for $C_{18}H_{13}N$: C, 88.86; H, 5.39; N, 5.76. Found: C, 88.84; H, 5.43; N, 5.72.



Scheme S1 The synthetic route of **CIDPP** and **NPC**.

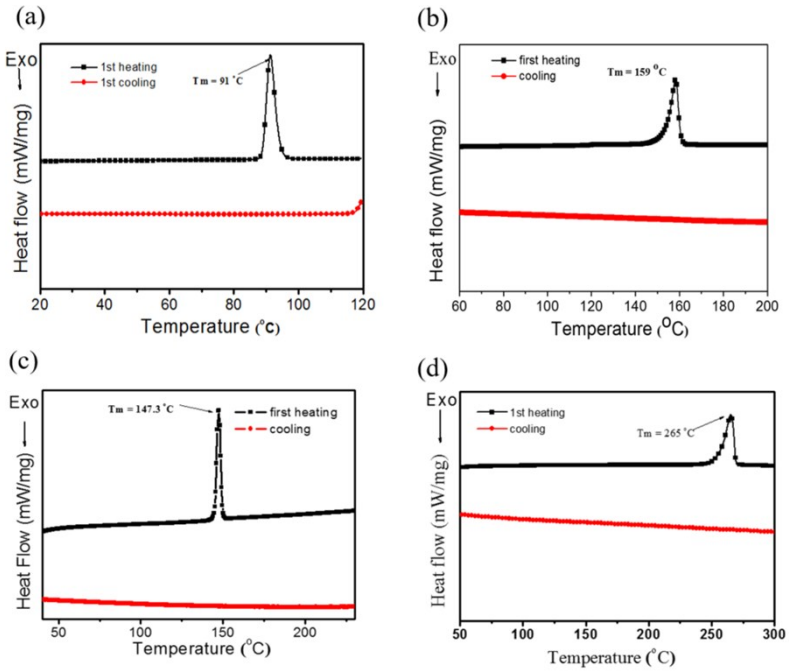


Figure S1 Differential scanning calorimetric (DSC) curves of NPC, PPO, CIDPP and PDPP solid, the DSC curves of BrDPP in reference 3.

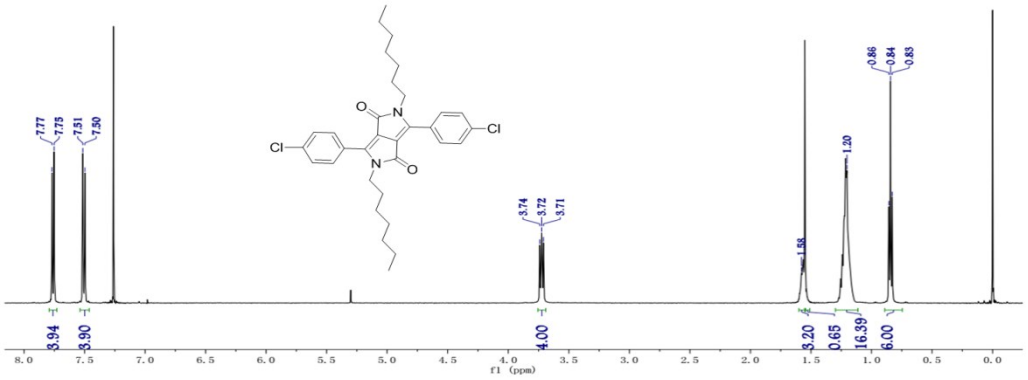


Figure S2 ^{1}H NMR spectra of CIDPP in $CDCl_3$.

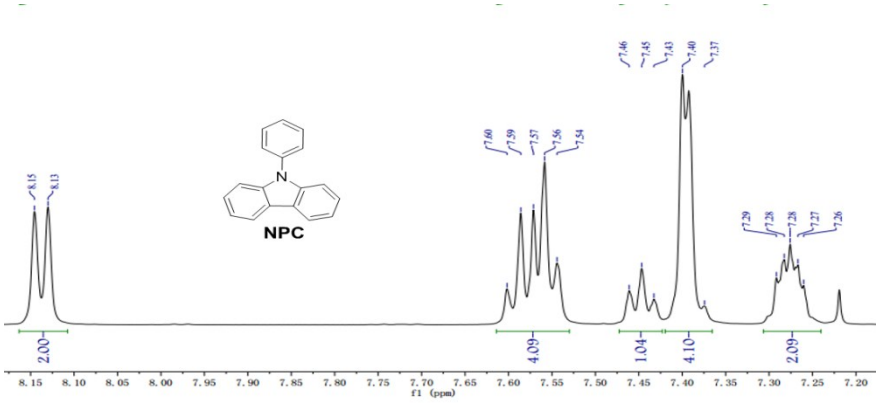


Figure S3 ^{1}H NMR spectra of NPC in $CDCl_3$.

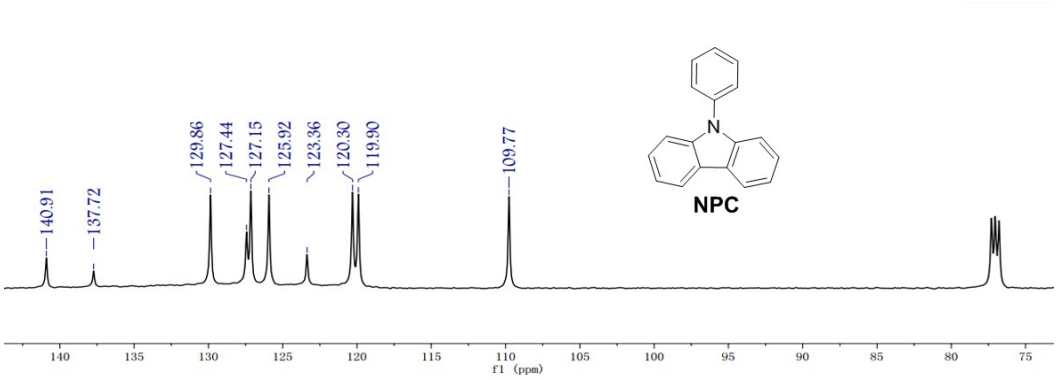


Figure S4 ^{13}C NMR spectra of NPC in $CDCl_3$.

Table S1 Single crystal structural parameters of NPC.

Compound reference	Colorless NPC crystal
Chemical formula	$C_{18}H_{13}N$
Formula weight	243.29
Crystal system	orthorhombic
a/Å	12.7887(15)
b/ Å	38.1950(19
c/ Å	10.8230(15)
α/°	90.00
β/°	90.00
γ/°	90.00
Unit cell volume/ $Å^3$	5286.6(10)
Temperature/K	296
Space group	Fdd2
Z	16
Density (calculated) /g cm^{-3}	1.223
F(000)	2048.0
Theta range for data collection	2.52 to 24.99 deg.
Index ranges	-15<=h<=15, -43<=k<=45, -12<=l<=7
Reflections measured	6523
Independent reflections	1834
Rint	0.0936
Completeness to theta = 72.13°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9852 and 0.9769
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	1834 / 1 / 173
Goodness-of-fit on F^2	0.982
Final R1 values (I> 2σ(I))	0.0427
Final wR(F^2) values (I> 2σ(I))	0.0544
Final R1values (all data)	0.1072
Final wR(F^2) values (all data)	0.0633
CCDC number	1584272

References

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(3) K. Chung, M. Kwon, B. Leung, A. Wong-Foy, M. Kim, J. Kim, S. Takayama, J. Gierschner, A. Matzger and J. Kim, ACS Cent Sci, 2015, **1**, 94.

Author Contributions

[†a] These authors contributed equally to this work.