Electronic Supplementary Information (ESI)

Side chain effect on solid-state emission behaviours and mechanofluorochromic activities of 10H-phenothiazinylbenzo[d]imidazoles

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Materials and instruments

All the reagents were analytically pure and some chemicals were further purified by recrystallization or distillation. Melting points were determined by an OptiMelt automatic melting point system. The $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra were obtained on a Bruker Avance II DMX 400 spectrometer with DMSO-d$_6$ or CDCl$_3$ as the solvent. The absorption spectra were measured on a Shimadzu UV 3600 UV-Vis-NIR spectrometer, and the fluorescence spectra were acquired on a Perkin-Elmer LS55 spectrophotometer. The quantum yields were measured with quinine sulfate in 0.1 M sulfuric acid solution ($\Phi_f$=0.55) as the reference. The crystallographic data were determined on a Bruker Gemini Ultra diffractometer with a CCD counter. The powder X-ray diffraction patterns were recorded on DX2700 with Cu-K$_\alpha$ radiation operating at 40 kV and 40 mA by a 0.3°/min scanning rate. Differential scanning calorimetry curves were obtained on a Waters TA Q20 instrument. ML spectrum are recorded on an optical fiber spectrometer with the fiber in 1000 µm diameter and 200-1100 nm acceptable wavelength range.

Synthesis of the intermediates and the titled BIMP compounds

At 0°C, 4-cyanoaniline (12 mmol, 1.42 g) in anhydrous THF (15 mL) was slowly dropped into the mixture of 2-fluoronitrobenzene (10 mmol, 1.41 g) and t-BuOK (12 mmol, 1.34 g) in anhydrous THF (15 mL). The resulted mixture was stirred at 0°C for another 1h and then at room temperature overnight. Water (100 mL) was added and the solution was extracted with ethyl acetate (2×15 mL). The combined organic layers were dried over anhydrous Na$_2$SO$_4$ and then filtrated. The solvent was removed from the filtrate under reduced pressure and the residue was purified by silica gel column chromatography using petroleum ether/CH$_2$Cl$_2$ mixture as the eluent, producing 1 as orange solid.

4-(2-nitrophenylamino)benzonitrile (1): 77% yield; m.p. 182.3-183.9 °C; $^1$H NMR(400 MHz, CDCl$_3$) δ(ppm): 6.99(dt, $J_1$=2.0 Hz, $J_2$=6.8 Hz, 1H), 7.33(d, $J$=8.8 Hz, 2H), 7.46-7.54(m, 2H), 7.66(d, $J$=8.8 Hz, 2H), 8.22(dd, $J_1$=1.2 Hz, $J_2$=8.8 Hz, 1H), 9.43(s, 1H); $^{13}$C NMR(100 MHz, CDCl$_3$) δ(ppm): 106.86, 117.35, 118.78, 120.23, 121.21, 126.91, 133.86, 135.63, 135.69, 139.50, 143.78.
At room temperature, hydrazine hydrate (80%wt, 20 mmol) was added into the suspension of 1 (5 mmol) and palladium absorbed on carbon powder (10%wt, 0.25 mmol) in EtOH (15 mL). The resulted mixture was heated at 80°C for 8 h and then cooled to room temperature. After filtration, the filtrate was diluted with water (100 mL) and extracted with EtOAc (2×15 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc mixture as the eluent, producing 2 as greyish white solid.

4-(2-aminophenylamino)benzonitrile (2): 88% yield; m.p. 159.4-161.2°C; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 3.83 (s, br, 2H), 5.72 (s, 1H), 6.72 (dt, J₁=8.8 Hz, J₂=2.0 Hz, 2H), 6.83 (td, J₁=7.6 Hz, J₂=1.2 Hz, 1H), 6.87 (d, J=7.6 Hz, 1H), 7.15 (d, J=7.6 Hz, 2H), 7.47 (dt, J₁=8.8 Hz, J₂=2.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 100.61, 113.99, 116.41, 119.19, 120.14, 125.19, 127.03, 127.77, 133.77, 143.00, 149.59.

At room temperature, 10-alkyl-10H-phenothiazine-3-carbaldehyde (12 mmol) was added into the solution of 2 (10 mmol) in DMSO (20 mL) and the resulted solution was stirred at 80-100°C in an open vessel for 12-24 h. After cooled to room temperature, the solution was diluted with water (100 mL) and extracted with CH₂Cl₂ (2×15 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/CH₂Cl₂ mixture as the eluent, producing BIMP as pale to dark yellow solid or oil. All the products were recrystallized in EtOH/CH₂Cl₂ mixture to offer the corresponding solids used for all types of measurements.

4-(2-(10-methyl-10H-phenothiazin-3-yl)-1H-benzo[d]imidazol-1-yl)benzonitrile (BIMP₁): 87% yield; m.p. 227.9-229.3°C; ¹H NMR (400 MHz, DMSO-d₆) δ (ppm): 3.33 (s, 3H), 6.64 (d, J=8.4 Hz, 1H), 6.79 (dd, J₁=1.2 Hz, J₂=8.4 Hz, 1H), 6.94 (dt, J₁=1.2 Hz, J₂=7.6 Hz, 1H), 7.07 (dd, J₁=1.5 Hz, J₂=8.4 Hz, 1H), 7.10 (dd, J₁=1.2 Hz, J₂=7.6 Hz, 1H), 7.16 (dt, J₁=1.2 Hz, J₂=7.6 Hz, 1H), 7.20-7.29 (m, 2H), 7.35 (dt, J₁=1.2 Hz, J₂=6.8 Hz, 1H), 7.41-7.44 (m, 3H), 7.80 (dt, J₁=1.5 Hz, J₂=8.4 Hz, 2H), 7.86 (dt, J₁=1.2 Hz, J₂=7.6 Hz, 1H); ¹³C NMR (100 MHz, DMSO-d₆) δ (ppm): 35.45, 109.80, 112.29, 113.88, 114.40, 117.89, 120.05, 122.66, 123.09, 123.14, 123.64, 123.76, 124.05, 127.27, 127.70, 127.93, 128.06, 128.66, 133.87, 136.27, 141.03, 143.17, 144.79, 147.18, 151.46.

4-(2-(10-ethyl-10H-phenothiazin-3-yl)-1H-benzo[d]imidazol-1-yl)benzonitrile (BIMP₂): 81% yield; m.p. 198.7-200.7°C; ¹H NMR (400 MHz, DMSO-d₆) δ (ppm): 1.31 (t, J=6.8 Hz, 3H), 3.92 (q, J=6.8Hz, 2H), 7.00 (d, J=8.4 Hz, 2H), 7.06 (d, J=7.2 Hz, 1H), 7.16-7.19 (m, 2H), 7.22-7.39 (m, 5H), 7.73 (d, J=8.4 Hz, 2H), 7.81 (d, J=7.6 Hz, 1H), 8.13 (d, J=8.4 Hz, 2H); ¹³C NMR (100 MHz, DMSO-d₆) δ (ppm): 12.97, 41.73, 110.68, 111.83, 115.32, 116.21, 118.67, 119.78, 122.47, 123.20, 123.39, 123.55, 123.64, 123.92, 127.58, 127.91, 128.34, 129.11, 134.70, 136.92, 141.07, 143.17, 143.77, 146.00, 151.40.
4-(2-(10-hexyl-10H-phenothiazin-3-yl)-1H-benzo[d]imidazol-1-yl)benzonitrile (BIMP₆): 77% yield; m.p. 146.6-148.2 °C; ¹H NMR (400 MHz, DMSO-d₆) δ (ppm): 0.91(t, J=6.8 Hz, 3H), 1.33-1.45(m, 6H), 1.81(hep, J=7.2 Hz, 2H), 3.84(t, J=7.2 Hz, 2H), 6.74(d, J=8.4 Hz, 1H), 6.88(d, J=8.0 Hz, 1H), 6.97(t, J=7.2 Hz, 1H), 7.11-7.14(m, 2H), 7.19(t, J=8.0 Hz, 1H), 7.25-7.33(m, 2H), 7.39(t, J=8.0 Hz, 1H), 7.44(d, J=8.0 Hz, 1H), 7.48(d, J=8.0 Hz, 2H), 7.85(d, J=8.0 Hz, 2H), 7.90(d, J=8.0 Hz, 1H); ¹³C NMR (100 MHz, DMSO-d₆) δ (ppm): 14.01, 22.59, 26.55, 26.70, 31.42, 47.64, 109.78, 112.27, 114.72, 115.61, 116.97, 120.06, 122.94, 122.98, 123.62, 123.72, 123.98, 125.25, 127.45, 127.52, 128.06, 128.17, 128.42, 133.88, 136.29, 141.06, 143.21, 144.19, 146.76, 151.50.

4-(2-(3,3-dimethylbutyl)-10H-phenothiazin-3-yl)-1H-benzo[d]imidazol-1-yl)benzonitrile (BIMP₆): 64% yield, m.p. 102.5-104.2 °C; ¹H NMR (400 MHz, DMSO-d₆) δ (ppm): 6.98(s, 9H), 1.60(dt, J₁=7.6 Hz, J₂=1.2 Hz, 2H), 3.89(dt, J₁=7.6 Hz, J₂=1.2 Hz, 2H), 6.96-7.01(m, 2H), 7.05(d, J=8.0 Hz, 1H), 7.15-7.38(m, 7H), 7.70(d, J=8.4 Hz, 2H), 7.80(d, J=7.6 Hz, 1H), 8.09(d, J=8.4 Hz, 2H), 8.35(s, 1H); ¹³C NMR (100 MHz, DMSO-d₆) δ (ppm): 29.60, 30.33, 43.63, 79.64, 110.66, 111.83, 115.70, 116.56, 118.61, 119.80, 123.42, 123.45, 123.59, 123.75, 123.90, 124.16, 127.73, 128.09, 128.29, 129.07, 129.11, 134.64, 136.92, 141.05, 143.20, 144.31, 146.57, 151.44.

4-(2-(10-phenyl-10H-phenothiazin-3-yl)-1H-benzo[d]imidazol-1-yl)benzonitrile (BIMP₆): 68% yield; m.p. 251.2-253.1 °C; ¹H NMR (400 MHz, DMSO-d₆) δ (ppm): 6.02(d, J=8.8 Hz, 1H), 6.13-6.16(m, 1H), 6.73(dd, J₁=8.8 Hz, J₂=2.0 Hz, 1H), 6.83-6.87(m, 2H), 6.99-7.01(m, 1H), 7.22(d, J=8.0 Hz, 1H), 7.27-7.31(m, 1H), 7.35-7.40(m, 4H), 7.47(d, J=8.8 Hz, 2H), 7.54(t, J=8.0Hz, 1H), 7.65(t, J=8.0 Hz, 2H), 7.83(d, J=8.0 Hz, 2H), 7.88(d, J=8.0 Hz, 1H); ¹³C NMR (100 MHz, DMSO-d₆) δ (ppm): 109.73, 112.30, 114.91, 116.10, 117.89, 119.16, 120.04, 120.43, 123.01, 123.05, 123.59, 123.69, 126.70, 127.07, 127.56, 127.87, 128.05, 128.76, 130.94, 131.05, 133.87, 136.34, 140.21, 141.07, 143.20, 143.32, 145.53, 151.29.

4-(2-(10-octyl-10H-phenothiazin-3-yl)-1H-benzo[d]imidazol-1-yl)benzonitrile (BIMP₆): 71% yield; m.p.143.7-145.1 °C; ¹H NMR (400 MHz, DMSO-d₆) δ (ppm): 0.91(t, J=7.2 Hz, 3H), 1.28(m, 8H), 1.45(hep, J=7.2 Hz, 2H), 1.81(hep, J=7.2 Hz, 2H), 3.83(t, J=7.2 Hz, 2H), 6.74(d, J=8.8 Hz, 1H), 6.87(d, J=8.0 Hz, 1H), 6.96(t, J=7.6 Hz, 1H),7.13(d, J=8.4 Hz, 2H), 7.19(t, J=8.4 Hz, 1H), 7.26(d, J=8.0 Hz, 1H), 7.33(m, 1H), 7.39(t, J=7.2 Hz, 1H), 7.43(d, J=2 Hz, 1H), 7.48(d, J=8.8 Hz, 2H), 7.84(d, J=8.4 Hz, 2H), 7.90(d, J=8.0 Hz, 1H); ¹³C NMR (100 MHz, DMSO-d₆) δ (ppm): 14.12, 22.63, 26.73, 26.78, 26.88, 29.18, 29.20, 31.74, 47.64, 109.78, 112.28, 114.70, 115.61, 117.90, 120.04, 122.93, 122.97, 123.61, 123.71, 123.97, 125.22, 127.44, 127.51, 128.06, 128.14, 128.42, 133.57, 136.29, 141.06, 143.20, 144.17, 146.77, 151.50.

4-(2-(10-methylheptyl)-10H-phenothiazin-3-yl)-1H-benzo[d]imidazol-1-yl)benzonitrile (BIMP₆): 78% yield; m.p.153.4-154.9 °C; ¹H NMR (400 MHz, DMSO-d₆) δ (ppm): 0.75-0.80(m, 6H), 1.17-1.38(m, 8H), 1.75-1.78(m, 1H), 3.73-3.76(m, 2H), 6.93-6.97(m, 2H), 7.03(d, J=8.4 Hz, 1H), 7.11-7.33(m, 6H), 7.39(d, J=2 Hz, 1H), 7.65(d, J=8.4 Hz, 2H), 7.76(d, J=8.0 Hz, 1H), 8.03(d, J=8.4 Hz, 2H); ¹³C NMR (100 MHz, DMSO-d₆) δ (ppm): 10.79, 14.24, 22.80, 23.74, 28.28, 30.21, 35.87, 50.72, 110.66, 111.82, 116.22, 117.12, 118.60, 119.81, 123.49, 123.53, 123.81, 123.90, 124.20, 124.95, 127.84, 128.21, 128.26, 128.99, 129.06, 134.60, 136.92, 141.06, 143.22, 144.80, 147.03, 151.52.
Table S1  Crystallographic data for BIMP$\textsubscript{1}$, BIMP$\textsubscript{2}$ and BIMP$\textsubscript{6}$

|                      | BIMP$\textsubscript{1}$ (CCDC 1919632) | BIMP$\textsubscript{2}$ (1919633) | BIMP$\textsubscript{6}$ (CCDC 1919634) |
|----------------------|----------------------------------------|----------------------------------|----------------------------------------|
| $a$                  | 7.9212(3) Å                           | 8.5519(7) Å                      | 8.6242(2) Å                           |
| $b$                  | 9.5348(3) Å                           | 10.6954(8) Å                     | 13.3809(3) Å                          |
| $c$                  | 14.0962(5) Å                          | 12.9906(11) Å                    | 11.9133(3) Å                          |
| $\alpha$             | 88.056(1)$^\circ$                     | 87.540(7)$^\circ$                | 90$^\circ$                             |
| $\beta$              | 89.137(1)$^\circ$                     | 74.165(7)$^\circ$                | 108.743(1)$^\circ$                    |
| $\gamma$             | 84.091(1)$^\circ$                     | 76.420(7)$^\circ$                | 90$^\circ$                             |
| Temperature          | 170 K                                  | 293 K                            | 170 K                                  |
| Wavelength           | 0.71073 Å                             | 0.71073 Å                        | 0.71073 Å                             |
| Volume               | 1058.31(6) Å                          | 1110.87(16) Å                    | 1301.88(5) Å                          |
| Space group          | $P\textsubscript{-1}$                 | $P\textsubscript{-1}$            | $P\textsubscript{21}$                 |
| Hall group           | $-P\textsubscript{1}$                 | $-P\textsubscript{1}$            | $P\textsubscript{2yb}$                |
| Density              | 1.351 g/cm$^3$                        | 1.329 g/cm$^3$                   | 1.277 g/cm$^3$                        |
| $Z$                  | 2                                      | 2                                | 2                                      |
| $\mu$                | 0.176 / mm                             | 0.170 / mm                       | 0.153 / mm                            |
| $F_{000}$            | 448.0                                  | 464.0                            | 528.0                                  |
| $h, k, l$ (max)      | 13, 16, 23                             | 10, 12, 15                       | 12, 19, 17                            |
| $N_{\text{ref}}$     | 10807                                  | 4069                             | 7405                                   |
| $T_{\text{min}}, T_{\text{max}}$ | 0.937, 0.981                           | 0.920, 0.934                     | 0.695, 0.746                           |
| Data completeness    | 0.987                                  | 0.998                            | 1.79/0.93                             |
| $\theta$ (max)       | 37.076                                 | 25.348                           | 30.521                                 |
| $R_{\text{reflections}}$ | 0.0466 (8253)                        | 0.0481 (2894)                    | 0.0317 (6879)                         |
| $wR^2_{\text{reflections}}$ | 0.1342 (10671)                        | 0.1262 (4059)                    | 0.0821 (7405)                         |
| $S$                  | 1.025                                  | 1.025                            | 1.037                                  |
| $N_{\text{par}}$     | 290                                    | 290                              | 335                                    |
| Flack parameter      | ----                                   | ----                             | 0.033 (0.015)                         |
Table S2  Crystallographic data for BIMP<sub>6t</sub>, BIMP<sub>8</sub> and BIMP<sub>BZ</sub>

|                  | BIMP<sub>6t</sub>·CHCl<sub>3</sub> (CCDC1919636) | BIMP<sub>8</sub> (CCDC1919635) | BIMP<sub>BZ</sub> (CCDC1919637) |
|------------------|-----------------------------------------------|-------------------------------|---------------------------------|
| **α** (°)        | 90                                            | 90                            | 87.488(1) °                     |
| **β** (°)        | 110.006(1) °                                 | 93.842(4) °                   | 70.801(1) °                     |
| **γ** (°)        | 90                                            | 90                            | 83.510(1) °                     |
| Temperature      | 170 K                                         | 273 K                         | 170 K                           |
| Wavelength       | 0.71073 Å                                     | 0.71073 Å                     | 0.71073 Å                       |
| Volume           | 3089.35(12) Å                                 | 2910.8(5) Å                   | 1190.26(8) Å                    |
| Space group      | P<sub>21/n</sub>                               | P<sub>21/n</sub>              | P·1                             |
| Hall group       | -P<sub>2yn</sub>                              | -P<sub>2yn</sub>              | -P<sub>1</sub>                  |
| Density          | 1.333 g/cm<sup>3</sup>                        | 1.206 g/cm<sup>3</sup>        | 1.374 g/cm<sup>3</sup>          |
| **Z**            | 4                                             | 4                             | 2                               |
| Mu               | 0.349 / mm                                     | 0.140 / mm                    | 0.166 / mm                      |
| **F<sub>000</sub>** | 1288.0                                         | 1120.0                        | 512.0                           |
| **h, k, l (max)** | 16, 19, 19                                     | 16, 11, 44                    | 12, 12, 15                      |
| **N<sub>ref</sub>** | 6274                                           | 8464                          | 4837                            |
| **T<sub>min</sub> - T<sub>max</sub>** | 0.689, 0.745                                   | 0.709, 0.746                  | 0.689, 0.745                    |
| Data completeness | 0.992                                          | 0.992                         | 0.989                           |
| θ (max)          | 26.386                                         | 30.056                        | 26.392                          |
| **R<sub>reflections</sub>** | 0.0441(5333)                                  | 0.1046(4654)                  | 0.0344(4418)                    |
| **wR<sup>2</sup><sub>reflections</sub>** | 0.1151(6274)                                  | 0.3696(8464)                  | 0.0916(4837)                    |
| S                | 1.038                                          | 1.278                         | 1.044                           |
| **N<sub>par</sub>** | 401                                            | 382                           | 334                             |
**Table S3**  Crystallographic data for BIMP$_{8i}$

| BIMP$_{8i}$ (CCDC1919652) |
|-----------------------------|
| $a = 7.7139(3)$ Å           |
| $b = 11.3447(4)$ Å          |
| $c = 16.7455(7)$ Å          |
| $\alpha = 100.235(1)$ °     |
| $\beta = 91.830(1)$ °       |
| $\gamma = 94.809(1)$ °      |
| Temperature                 | 170 K                      |
| Wavelength                  | 0.71073 Å                  |
| Volume                      | 1435.39(10)                |
| Space group                 | P$_{-1}$                   |
| Hall group                  | -P$_1$                     |
| Density                     | 1.223 g/cm$^3$             |
| $Z$                         | 2                          |
| $\mu$                       | 0.142 / mm                 |
| $F_{000}$                   | 560.0                      |
| $h, k, l$ (max)             | 9, 14, 21                  |
| $N_{\text{ref}}$            | 6306                       |
| $T_{\text{min}}, T_{\text{max}}$ | 0.674, 0.746             |
| Data completeness           | 0.992                      |
| $\theta$ (max)             | 27.148                     |
| $R_{\text{reflections}}$    | 0.0965(5374)               |
| $wR^2_{\text{reflections}}$ | 0.2721(6306)               |
| $S$                         | 1.063                      |
| $N_{\text{par}}$            | 373                        |
**Fig. S1** Absorption (solid lines) and emission spectra (dash lines) of BIMP$_1$ in different solvents

**Fig. S2** Absorption (solid lines) and emission spectra (dash lines) of BIMP$_8$ in different solvents
**Fig. S3**  Absorption (solid lines) and emission spectra (dash lines) of BIMP$_{6t}$ in different solvents

**Fig. S4**  Absorption (solid lines) and emission spectra (dash lines) of BIMP$_8$ in different solvents
Fig. S5  Absorption (solid lines) and emission spectra (dash lines) of BIMP$_{8i}$ in different solvents

Fig. S6  Absorption (solid lines) and emission spectra (dash lines) of BIMP$_{8z}$ in different solvents
Fig. S7  Molecular packings of BIMP$_2$ (A) and BIMP$_{Bi}$ (B)

Fig. S8  Molecular packings of BIMP$_{6t}$ (A) and BIMP$_8$ (B)
Fig. S9 PXRD patterns of BIMP$_1$ under measured and simulated conditions (A) and other conditions (B)

Fig. S10 PXRD patterns of BIMP$_2$ under measured and simulated conditions (A) and other conditions (B)

Fig. S11 PXRD patterns of BIMP$_6$ under measured and simulated conditions (A) and other conditions (B)
Fig. S12  PXRD patterns of BIMP$_{6t}$ under measured and simulated conditions (A) and other conditions (B)

Fig. S13  PXRD patterns of BIMP$_{8i}$ under measured and simulated conditions (A) and other conditions (B)

Fig. S14  PXRD patterns of BIMP$_{8}$ under measured and simulated conditions (A) and other conditions (B)
Fig. S15  PXRD patterns of BIMP_{BZ} under measured and simulated conditions (A) and other conditions (B)

Fig. S16  Solid-state emission spectra of BIMP$_1$ under different conditions (inserted: photos taken under 365 nm UV irradiation)
Fig. S17  Solid-state emission spectra of $\text{BIMP}_6$ under different conditions (inserted: photos taken under 365 nm UV irradiation)

Fig. S18  Solid-state emission spectra of $\text{BIMP}_{6t}$ under different conditions (inserted: photos taken under 365 nm UV irradiation)
Fig. S19  DSC curves of the ground BIMP samples
