# Insulator–Metal Transition Induced by Band-Filling Modulation in Molecular Mott Insulators

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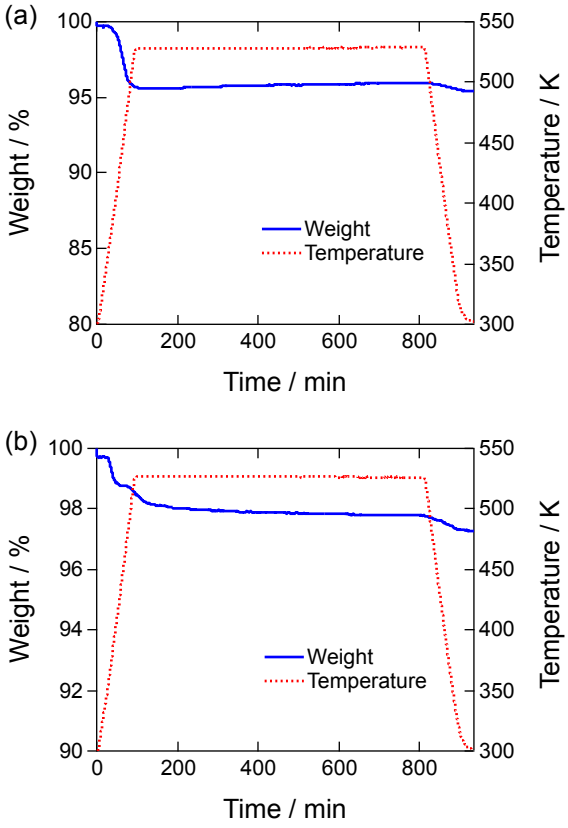


**Fig. S1** TG analysis curves of x-Li(Pc)Br$_x$ (a) and x-Li(tbp)I$_x$ (b).

**Table S1.1** Fractional coordinates, thermal parameters, and occupancy for x-Li(Pc)$Br_{0.75}$.

| | *x* | *y* | *z* | $U_{11}$/Å$^2$ | $U_{22}$/Å$^2$ | $U_{33}$/Å$^2$ | $U_{12}$/Å$^2$ | $U_{13}$/Å$^2$ | $U_{23}$/Å$^2$ | Occ. |
|---|---|---|---|---|---|---|---|---|---|---|
| Br | 0 | 0 | 0.25 | 0.0524 | 0.0524 | 0.513 | 0.0000 | 0.0000 | 0.0000 | 0.75 |
| Li | 0.5 | 0.5 | 0.5 | 0.0270 | 0.0270 | 0.0790 | 0.0000 | 0.0000 | 0.0000 | 1 |
| N1 | 0.3734(2) | 0.4395(2) | 0.5 | 0.0264 | 0.0258 | 0.0450 | 0.0004 | 0.0000 | 0.0000 | 1 |
| N2 | 0.2711(2) | 0.5810(2) | 0.5 | 0.0300 | 0.0301 | 0.0340 | 0.0015 | 0.0000 | 0.0000 | 1 |
| C1 | 0.3556(3) | 0.3431(3) | 0.5 | 0.0300 | 0.0320 | 0.0310 | −0.0023 | 0.0000 | 0.0000 | 1 |
| C2 | 0.2506(3) | 0.3253(3) | 0.5 | 0.0310 | 0.0350 | 0.0360 | −0.0054 | 0.0000 | 0.0000 | 1 |
| C3 | 0.1956(3) | 0.2420(3) | 0.5 | 0.0400 | 0.0340 | 0.0520 | −0.0050 | 0.0000 | 0.0000 | 1 |
| C4 | 0.0963(3) | 0.2526(4) | 0.5 | 0.0380 | 0.0500 | 0.0670 | −0.0160 | 0.0000 | 0.0000 | 1 |
| C5 | 0.0541(3) | 0.3429(4) | 0.5 | 0.0270 | 0.0590 | 0.0810 | −0.0080 | 0.0000 | 0.0000 | 1 |
| C6 | 0.1090(3) | 0.4268(4) | 0.5 | 0.0280 | 0.0450 | 0.0590 | −0.0013 | 0.0000 | 0.0000 | 1 |
| C7 | 0.2078(3) | 0.4156(3) | 0.5 | 0.0290 | 0.0320 | 0.0330 | −0.0042 | 0.0000 | 0.0000 | 1 |
| C8 | 0.2876(3) | 0.4855(3) | 0.5 | 0.0270 | 0.0350 | 0.0340 | 0.0007 | 0.0000 | 0.0000 | 1 |
| H3 | 0.224143 | 0.181389 | 0.5 | 0.0510[a)] | | | | | | 1 |
| H4 | 0.057389 | 0.198004 | 0.5 | 0.0620[a)] | | | | | | 1 |
| H5 | −0.012729 | 0.347608 | 0.5 | 0.0670[a)] | | | | | | 1 |
| H6 | 0.080466 | 0.487401 | 0.5 | 0.0530[a)] | | | | | | 1 |

a) thermal parameters for hydrogen atoms are $U_{eq}$.

**Table S1.2** Fractional coordinates, thermal parameters, and occupancy for x-Li(tbp)$I_{0.75}$.

| | *x* | *y* | *z* | $U_{11}$/Å$^2$ | $U_{22}$/Å$^2$ | $U_{33}$/Å$^2$ | $U_{12}$/Å$^2$ | $U_{13}$/Å$^2$ | $U_{23}$/Å$^2$ | Occ. |
|---|---|---|---|---|---|---|---|---|---|---|
| I | 0 | 0 | 0.25 | 0.0551 | 0.0551 | 0.1425 | 0.0000 | 0.0000 | 0.0000 | 0.75 |
| Li | 0.5 | 0.5 | 0.5 | 0.0450 | 0.0450 | 0.0460 | 0.0000 | 0.0000 | 0.0000 | 1 |
| N | 0.3699(3) | 0.4391(2) | 0.5 | 0.0340 | 0.0292 | 0.0320 | 0.0000 | 0.0000 | 0.0000 | 1 |
| C1 | 0.3509(3) | 0.3437(3) | 0.5 | 0.0330 | 0.0370 | 0.0290 | −0.0053 | 0.0000 | 0.0000 | 1 |
| C2 | 0.2490(3) | 0.3270(3) | 0.5 | 0.0320 | 0.0410 | 0.0300 | −0.0046 | 0.0000 | 0.0000 | 1 |
| C3 | 0.1936(4) | 0.2480(4) | 0.5 | 0.0420 | 0.0400 | 0.0510 | −0.0060 | 0.0000 | 0.0000 | 1 |
| C4 | 0.0973(4) | 0.2580(4) | 0.5 | 0.0420 | 0.0570 | 0.0770 | −0.0150 | 0.0000 | 0.0000 | 1 |
| C5 | 0.0569(4) | 0.3468(4) | 0.5 | 0.0300 | 0.0650 | 0.0820 | −0.0090 | 0.0000 | 0.0000 | 1 |
| C6 | 0.1116(3) | 0.4269(4) | 0.5 | 0.0310 | 0.0490 | 0.0590 | −0.0010 | 0.0000 | 0.0000 | 1 |
| C7 | 0.2077(3) | 0.4162(3) | 0.5 | 0.0330 | 0.0390 | 0.0300 | −0.0063 | 0.0000 | 0.0000 | 1 |
| C8 | 0.2863(3) | 0.4836(3) | 0.5 | 0.0320 | 0.0370 | 0.0300 | −0.0035 | 0.0000 | 0.0000 | 1 |
| C9 | 0.2750(3) | 0.5825(3) | 0.5 | 0.0290 | 0.0350 | 0.0340 | 0.0027 | 0.0000 | 0.0000 | 1 |
| H3 | 0.220715 | 0.188613 | 0.5 | 0.0530[a)] | | | | | | 1 |
| H4 | 0.059126 | 0.204981 | 0.5 | 0.0700[a)] | | | | | | 1 |
| H5 | −0.008150 | 0.352429 | 0.5 | 0.0710[a)] | | | | | | 1 |
| H6 | 0.084320 | 0.486260 | 0.5 | 0.0550[a)] | | | | | | 1 |

a) thermal parameters for hydrogen atoms are $U_{eq}$.

**Table S2** Crystal data and structure refinement results for reproduced x-Li(Pc) by chemical reduction of x-Li(Pc)$Br_x$.

| | |
|---|---|
| Chemical formula | $C_{32}H_{16}LiN_8$ |
| Formula weight | 519.47 |
| Crystal description | Black needle |
| $T$ (K) | 293 |
| Crystal system | Tetragonal |
| Space group | *P*4/*mcc* |
| $a$ (Å) | 13.8420 (5) |
| $c$ (Å) | 6.4865 (4) |
| $V$ (Å$^3$) | 1242.82 (12) |
| $Z$ | 2 |
| $d_{cal}$ (g cm$^{-3}$) | 1.388 |
| Radiation | MoKα |
| Wavelength (Å) | 0.71073 |
| $\mu$ (mm$^{-1}$) | 0.086 |
| No. of measured reflections | 4383 |
| No. of independent reflection | 802 |
| No. of observed reflections | 551 ($I > 2\sigma(I)$) |
| $R$ ($I > 2\sigma(I)$) | $R_1 = 0.0427$ |
| | $wR_2 = 0.1464$ |
| Goodness-of-fit | 0.980 |
| Parameters | 63 |

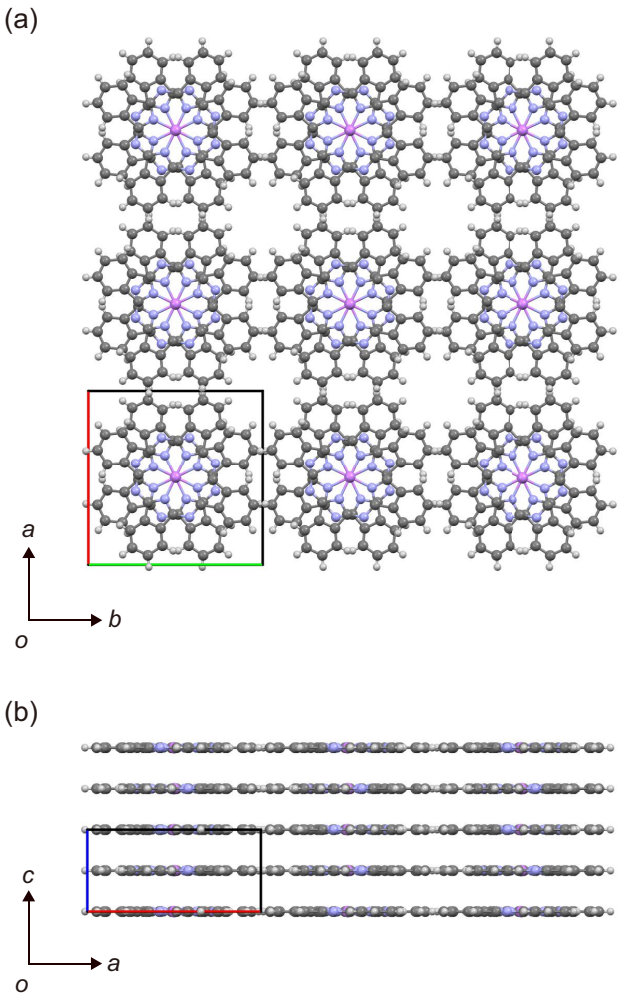


**Fig. S2** Crystal structure of reproduced x-Li(Pc) by chemical reduction of x-Li(Pc)Br$_x$ viewed along the *c*-axis (a) and the *b*-axis (b).

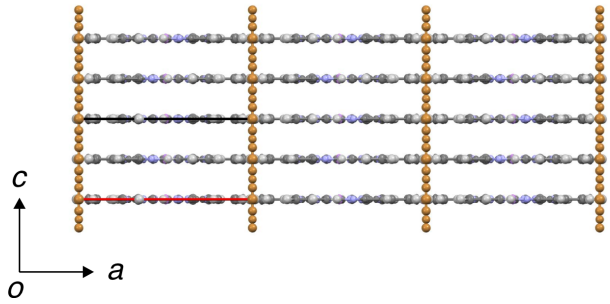


**Fig. S3** Crystal structure of x-Li(Pc)Br$_x$ employing the split-atom model for Br atoms.