# Dielectric and gas adsorption/desorption properties of *x*-Li(Pc) having one-dimensional channels surrounded by $Pc^{\bullet-}$ columns

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## Contents

## Experimental details

### Synthetic procedures

**Dilithium phthalocyanine ($Li_2$(Pc)).** As published by to Barrett et al.,[1] 3.00 g (18.3 mmol) of phthalonitrile and 0.20 g (28.8 mmol) of lithium was refluxed in 1-pentanol under Ar for 0.5 h, with a color changed to deep blue. The reactant was cooled and 80 mL of toluene was added. The resulting product was filtered and extracted by acetonitrile using a Soxhlet extractor. Evaporation under reduced pressure gave 1.95 g (3.70 mmol, 80.9%) of $Li_2$(Pc).

***x*-lithium phthalocyanine (*x*-Li(Pc)).** As published by Sugimoto et al.,[2] single crystals of *x*-Li(Pc) was prepared by the electrochemical oxidation of $Li_2$(Pc) using an electrocrystallization cell equipped with a glass frit between the two compartments. Controlled potential electrolysis at approximately 0.1 V vs $Ag/Ag^+$ electrode was performed using an ALS/DY2323 potentiostat and Pt electrodes for 60 mg (0.114 mmol) of $Li_2$(Pc) with tetrabutylammonium perchlorate (supporting electrolyte) in acetonitrile. After a few days, black needle-like crystals *x*-Li(Pc) (~0.02 mg, ~18%) grew on the working Pt electrode, and were harvested by filtration.

***β*-lithium phthalocyanine (*β*-Li(Pc)).** As published by Petit et al.,[3] *β*-Li(Pc) was prepared by the electrochemical reduction of phthalonitrile using an electrocrystallization cell equipped with a glass frit between the two compartments and Pt electrodes. 1.30 g (30.14 mmol) of lithium chloride was dissolved in 45 mL of absolute ethanol, and 1.35 g (8.23 mmol) of phthalonitrile was added to the cathode side. A constant current of 66 mA (KIKUSUI PMC 250-0.25A) was applied for 1 h and the catholyte was stirred for 24 h. The filtration of the catholyte yielded black crystalline solids of *β*-Li(Pc). Further purification by the vacuum sublimation at 380 °C under ~10 Pa gave single crystals (~1.0 × 0.05 × 0.05 $mm^3$) of *β*-Li(Pc).

**Crystal structure determination**

Crystal data for *β*-Li(Pc) and *x*-Li(Pc) were collected using an automated Rigaku RAPID system with monochromated Cu-Kα radiation ($\lambda$ = 1.54187 Å). The structure was solved by a direct method using SIR-2014[4] or SHELXS-2013,[5] and refined by a full-matrix least-squares technique with SHELXL-2018/1 or SHELXL-2018/3[6] using anisotropic and isotropic thermal parameters for non-hydrogen and hydrogen atoms, respectively. In the procedure of the analyses, Yadokari-XG was used as a GUI.[7]

The crystallographic data of *β*-Li(Pc) at 300 K has been deposited at the Cambridge Crystallographic Data Centre (CCDC) as CCDC-2014942. As for x-Li(Pc) at 300 K, we performed the *SQUEEZE* procedure because measurable electron densities were observed in the one-dimensional channel, and found 7 electrons in the void, The data has been deposited as CCDC-2014943. We also refined the structure under the assumption that oxygen atoms are within the channel (CCDC-2014945, Table S1) or without considering the measurable electron densities (CCDC-2033584, Table S2). As for x-Li(Pc) at 100 K under a cooled $N_2$ gas stream on a bare single crystal, we also performed the *SQUEEZE* procedure, and found 18 electrons in the channel. The data has been deposited as CCDC-2014944. We also performed the measurement at 100 K by using a single crystal covered with oil, and found that measurable electron densities were observed at the same position to that observed at 300 K. We refined the structure under the assumption that oxygen atoms are within the channel (CCDC-2033531, Table S3). With regard to the measurement for the bare single crystal under a cooled $N_2$ gas stream of 100 K, the position of measurable electron densities in the one-dimensional channel differed from that at 300 K. Therefore, we speculated that the guest species was replaced by $N_2$ under a cooled $N_2$ gas stream at 100 K. Under the speculation, the *SQUEEZE* procedure, indicating 18 electrons in the void, implies that the occupancy of $N_2$ is 0.64. Crystal data and crystal refinement result for the bare single crystal of x-Li(Pc) at 100 K under the speculation that nitrogen molecule is within the one-dimensional channel, and those without considering the measurable electron densities are summarized in Tables S4

and S5, and deposited as 2014946 and 2033585, respectively.

**Measurements**

Dielectric measurements were performed by a two-probe AC impedance method using an impedance analyzer (HP 4194A). Electrical contacts were prepared using gold paste to attach gold wires to a compressed pellet (3 mm diameter) or a single crystal. The measurements were performed in a cryostat under vacuum using a rotary pump (~50 Pa), turbomolecular pump (~$10^{-2}$ Pa), or under $N_2$ or $O_2$ atmosphere. Gas adsorption/desorption measurements were performed by BEL SORP-max, BEL Japan Inc. The samples were heated to 373 K under vacuum (< $10^{-2}$ Pa) for 24 h prior to the measurements.

**Table S1**. Crystal data and structure refinement results for *x*-Li(Pc) at 300 K under the assumption that oxygen atoms are within the one-dimensional channel.

| | |
|---|---|
| CCDC | 2014945 |
| Chemical formula | $C_{32}H_{16}LiN_8 \cdot O_{0.35}$ |
| Formula weight | 525.77 |
| Crystal description | Black needle |
| $T$ (K) | 300 |
| Crystal system | Tetragonal |
| Space group | *P*4/*mcc* |
| $a$ (Å) | 13.8327 (13) |
| $c$ (Å) | 6.4804 (5) |
| $V$ (Å$^3$) | 1240.0 (3) |
| $Z$ | 2 |
| $d_{cal}$ (g cm$^{-3}$) | 1.408 |
| Radiation | CuKα |
| Wavelength (Å) | 1.54187 |
| $\mu$ (mm$^{-1}$) | 0.707 |
| No. of measured reflections | 13190 |
| No. of independent reflection | 627 |
| No. of observed reflections | 514 ($I > 2\sigma(I)$) |
| $R$ ($I > 2\sigma(I)$) | $R_1 = 0.0464$ |
| | $wR_2 = 0.1312$ |
| Goodness-of-fit | 1.068 |
| Parameters | 65 |

**Table S2**. Crystal data and structure refinement results for *x*-Li(Pc) at 300 K without considering the measurable electron densities in the one-dimensional channel.

| | |
|---|---|
| CCDC number | 2033584 |
| Chemical formula | $C_{32}H_{16}LiN_8$ |
| Formula weight | 519.47 |
| Crystal description | Black needle |
| $T$ (K) | 300 |
| Crystal system | Tetragonal |
| Space group | *P*4/*mcc* |
| $a$ (Å) | 13.8327 (13) |
| $c$ (Å) | 6.4804 (5) |
| $V$ (Å$^3$) | 1240.0 (3) |
| $Z$ | 2 |
| $d_{cal}$ (g cm$^{-3}$) | 1.391 |
| Radiation | CuKα |
| Wavelength (Å) | 1.54187 |
| $\mu$ (mm$^{-1}$) | 0.690 |
| No. of measured reflections | 13190 |
| No. of independent reflection | 627 |
| No. of observed reflections | 514 ($I > 2\sigma(I)$) |
| $R$ ($I > 2\sigma(I)$) | $R_1 = 0.0478$ |
| | $wR_2 = 0.1248$ |
| Goodness-of-fit | 1.041 |
| Parameters | 63 |

**Table S3**. Crystal data and structure refinement results for *x*-Li(Pc) at 100 K under the assumption that oxygen atoms are within the one-dimensional channel. The single crystal used for the measurement was covered with oil.

| | |
|---|---|
| CCDC | 2033531 |
| Chemical formula | $C_{32}H_{16}LiN_8 \cdot O_{0.35}$ |
| Formula weight | 525.77 |
| Crystal description | Black needle |
| $T$ (K) | 100 |
| Crystal system | Tetragonal |
| Space group | *P*4/*mcc* |
| $a$ (Å) | 13.8422 (3) |
| $c$ (Å) | 6.36520 (10) |
| $V$ (Å$^3$) | 1219.61 (6) |
| $Z$ | 2 |
| $d_{cal}$ (g cm$^{-3}$) | 1.458 |
| Radiation | CuKα |
| Wavelength (Å) | 1.54187 |
| $\mu$ (mm$^{-1}$) | 0.751 |
| No. of measured reflections | 12722 |
| No. of independent reflection | 623 |
| No. of observed reflections | 398 ($I > 2\sigma$ ($I$)) |
| $R$ ($I > 2\sigma$ ($I$)) | $R_1 = 0.0668$ |
| | $wR_2 = 0.1921$ |
| Goodness-of-fit | 1.106 |
| Parameters | 64 |

**Table S4**. Crystal data and structure refinement results for *x*-Li(Pc) at 100 K under the speculation that nitrogen molecules are within the one-dimensional channel. The data was collected for a bare single crystal under a cooled $N_2$ gas stream.

| | |
|---|---|
| CCDC | 2014946 |
| Chemical formula | $C_{32}H_{16}LiN_8 \cdot (N_2)_{0.64}$ |
| Formula weight | 537.40 |
| Crystal description | Black needle |
| $T$ (K) | 100 |
| Crystal system | Tetragonal |
| Space group | *P*4/*mcc* |
| $a$ (Å) | 13.8720 (10) |
| $c$ (Å) | 6.3609 (4) |
| $V$ (Å$^3$) | 1224.04 (19) |
| $Z$ | 2 |
| $d_{cal}$ (g cm$^{-3}$) | 1.458 |
| Radiation | CuKα |
| Wavelength (Å) | 1.54187 |
| $\mu$ (mm$^{-1}$) | 0.735 |
| No. of measured reflections | 12967 |
| No. of independent reflection | 624 |
| No. of observed reflections | 542 ($I > 2\sigma(I)$) |
| $R$ ($I > 2\sigma(I)$) | $R_1 = 0.0478$ |
| | $wR_2 = 0.1386$ |
| Goodness-of-fit | 1.082 |
| Parameters | 66 |

**Table S5**. Crystal data and structure refinement results for *x*-Li(Pc) at 100 K. without considering the measurable electron densities in the one-dimensional channel.

| | |
|---|---|
| CCDC number | 2033585 |
| Chemical formula | $C_{32}H_{16}LiN_8$ |
| Formula weight | 519.47 |
| Crystal description | Black needle |
| $T$ (K) | 100 |
| Crystal system | Tetragonal |
| Space group | *P*4/*mcc* |
| $a$ (Å) | 13.8720 (10) |
| $c$ (Å) | 6.3609 (4) |
| $V$ (Å$^3$) | 1224.04 (19) |
| $Z$ | 2 |
| $d_{cal}$ (g cm$^{-3}$) | 1.409 |
| Radiation | CuKα |
| Wavelength (Å) | 1.54187 |
| $\mu$ (mm$^{-1}$) | 0.699 |
| No. of measured reflections | 12967 |
| No. of independent reflection | 624 |
| No. of observed reflections | 542 ($I > 2\sigma(I)$) |
| $R$ ($I > 2\sigma(I)$) | $R_1 = 0.0866$ |
| | $wR_2 = 0.3579$ |
| Goodness-of-fit | 1.714 |
| Parameters | 63 |

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