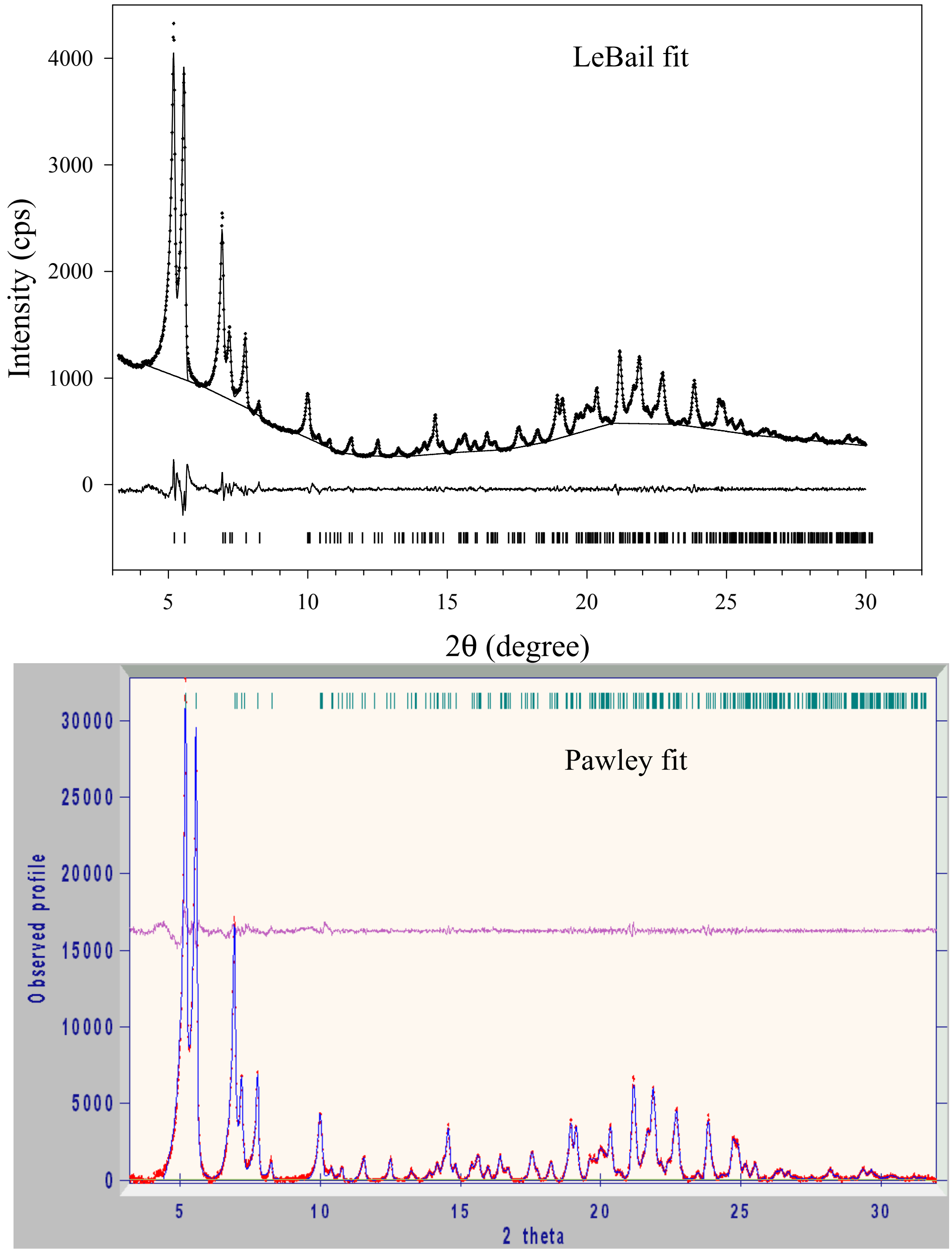
Supplementary material (ESI) for Journal of Materials Chemistry

Supporting Information (Pandian *et al.*, MS. B517976A)

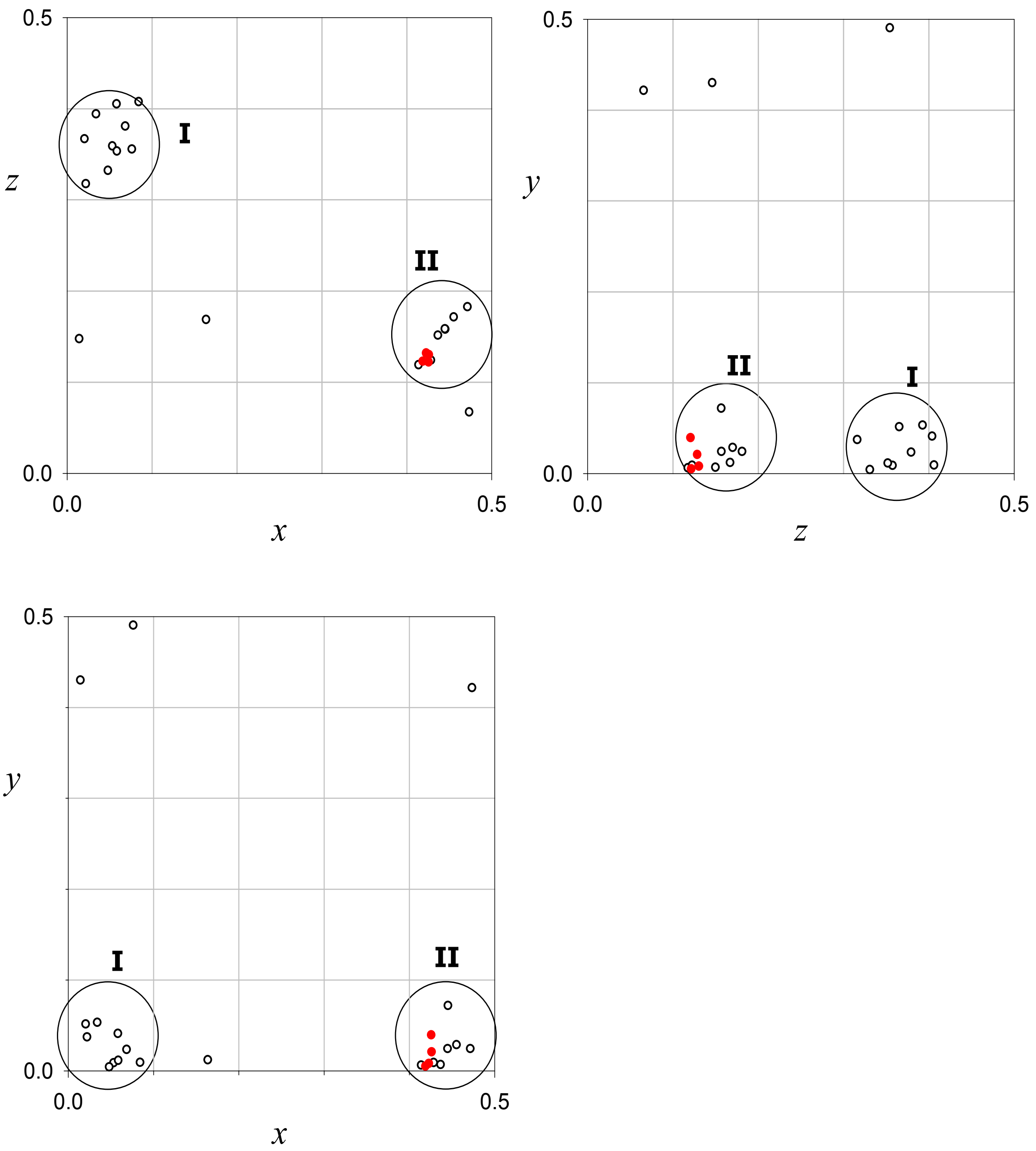
In the crystal structure analysis of LiNc-BuO powder, we have employed total of thirty eight variables; three for the naphthalocyanine (Nc) ring position, three for the ring orientation, and thirty two for the conformations of butoxy chains. Throughout the simulated annealing process of DASH, there were not found a regular conformational pattern of the butoxy chains. It is very difficult to accurately locate the butoxy chains, since they are subject to no symmetry regulation (*P*-1) and each of them has only weak X-ray scattering power. Divergent results for the conformation of the butoxy chains complicated interpretation of the DASH solutions but it could be noticed that there are favored positions and orientations of Nc ring, as displayed in S-Fig. 2. The reproducible location and orientation of the Nc ring suggests that the crystal structure of LiNc-BuO adopts one of the two molecular packing arrangements; denoted as type-I for the group centered at (0.05, 0.03, 0.37) and type-II for the group centered at (0.44, 0.02, 0.15). Further investigation using simpler model structures with shorter alkoxy chains (OPr, OEt, OMe, or OH in place of OBu) confirms the plausibility of the type-II solution which was reproducibly obtained in all the four cases. For an example the results from the LiNc-EtO model are illustrated in S-Fig. 3, in which nine solutions out of ten trials belong to type-II and have very similar locations and orientations.

As stated above, it is practically impossible to accurately determine the conformation of the butoxy chains using XRPD data, and the proposed structure model of LiNc-BuO undoubtedly contains several butoxy chains whose atomic coordinates are not correct. While it would be preferable to obtain a complete crystal structure solution extensive efforts to grow single crystals were unsuccessful. Nonetheless, we would like to emphasize that the main purpose of this work is not to fully solve the LiNc-BuO structure, but to find out the structural information that is pertinent to the observed sensor property. In that regard the location and orientation of the planar portion of the molecule plays the determining role, and we feel that the results do reliably give us accurate information on the molecular packing in LiNc-BuO. Even though the locations of the peripheral butoxy chains are not well determined, the observed molecular packing produces an open framework structure with channels running in multi-dimensions.

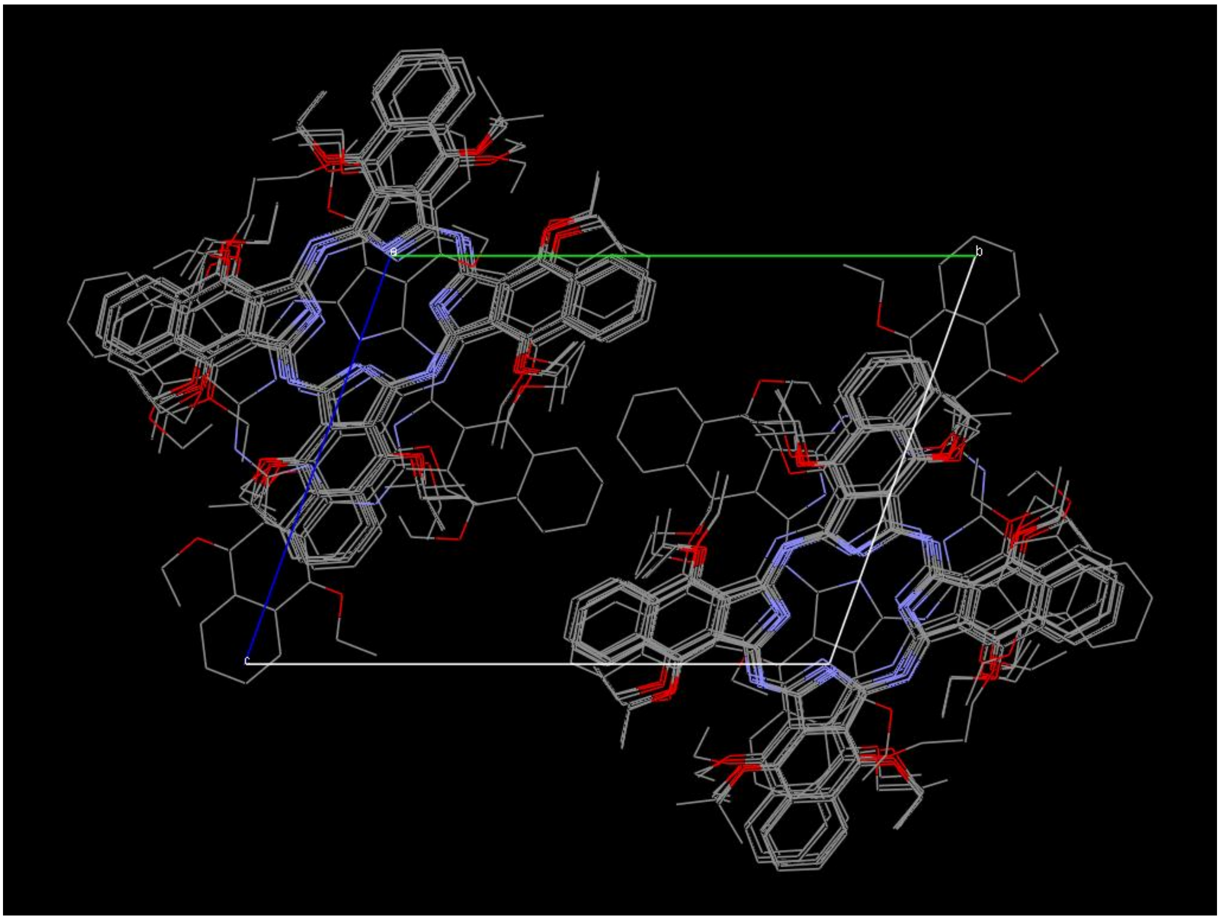
CIF file provided as supporting information



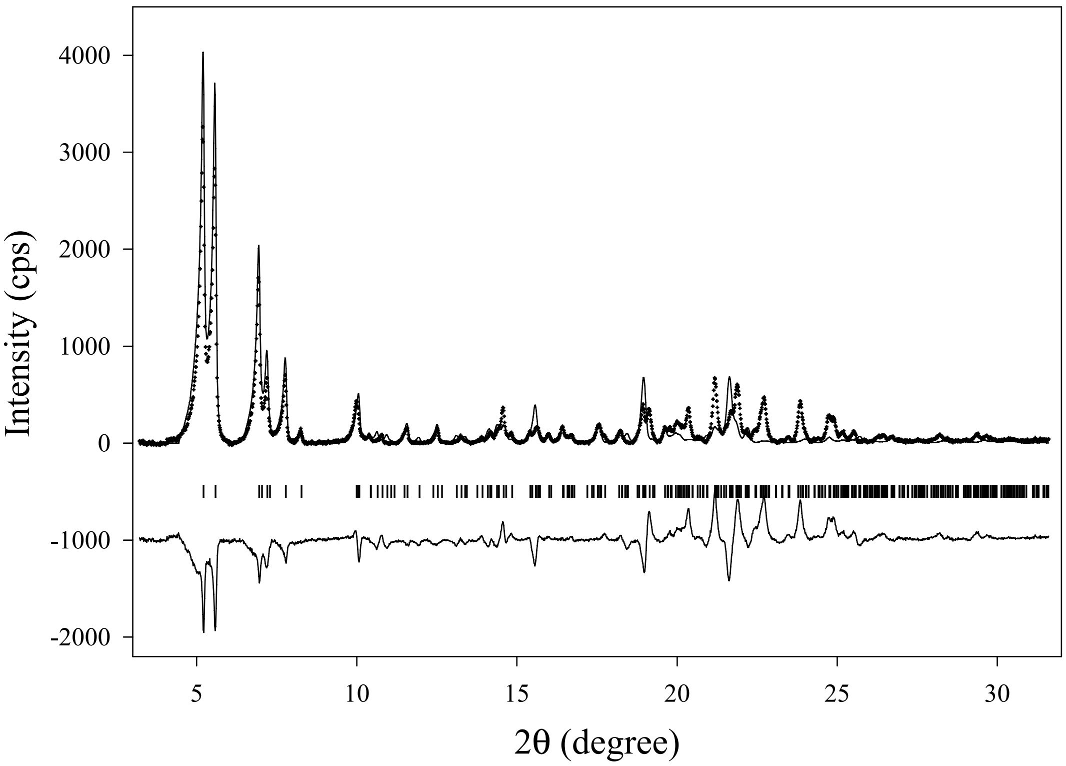
S-Fig. 1. (Top) LeBail and (bottom) Pawley fits to the XRPD pattern of LiNc-BuO. Observed (cross) and calculated data (solid line) are overlapped, and the difference pattern and expected peak positions are shown. In the LeBail fit, background is also shown.



S-Fig 2. Positional parameters obtained from initial DASH trial runs where no constraints were used. Black open circles are from trials using LiNc-BuO (20 runs with lowest χ_{pro}^2, out of 45 trials) and red filled circles are from the trials using LiNc-OH (reproducibility, 10/10), LiNc-MeO (8/10), LiNc-EtO (9/10), and LiNc-PrO (6/10). For the groups marked as I and II, average and deviations of the fractional coordinates are (0.051 ± 0.021, 0.026 ± 0.019, 0.368 ± 0.031) and (0.443 ± 0.019, 0.024 ± 0.023, 0.151 ± 0.023), respectively.



S-Fig 3. Overlapped structure solutions of LiNc-EtO obtained from ten trial runs of DASH, in which a molecular model of LiNc-EtO was determined from the XRPD data of LiNc-BuO.



S-Fig. 4. Simulated annealing refinement profile of the XRPD pattern for LiNc-BuO, between 3.2–32 °. Calculated (solid line) and observed (cross) data are overlapped. Bragg reflection positions and the difference pattern are shown at bottom.