# Two-step dielectric anomalies coupled with structural phase transitions in co-crystal of 1,4-diazabicyclo[2.2.2]octane and 4, 4'-biphenol

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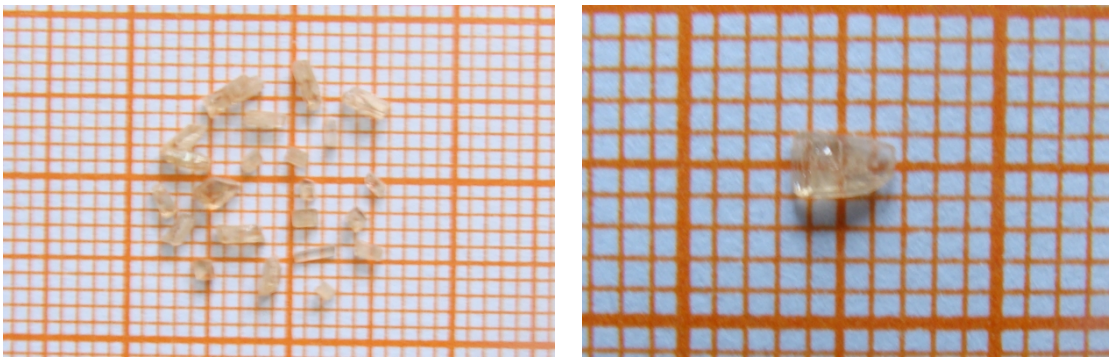


Figure S1 Colorless crystals of **1** (left) and one crystal selected for the dielectric constant measurement (right, which dimensions are 3.0×2.0×1.5 $mm^3$).

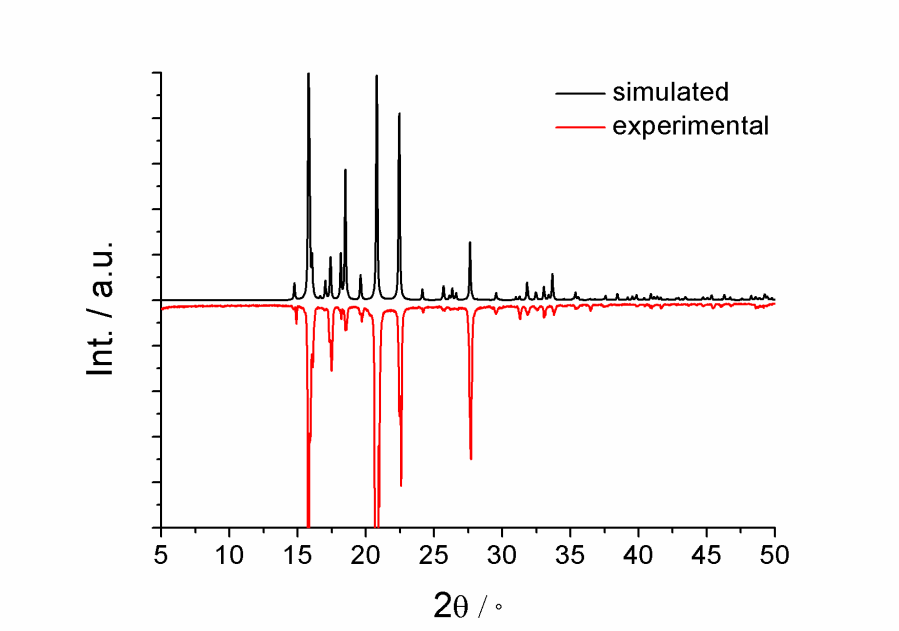



Figure S2 PXRD plots of **1** at ambient temperature (red line: experimental profile and black line: simulated profile).

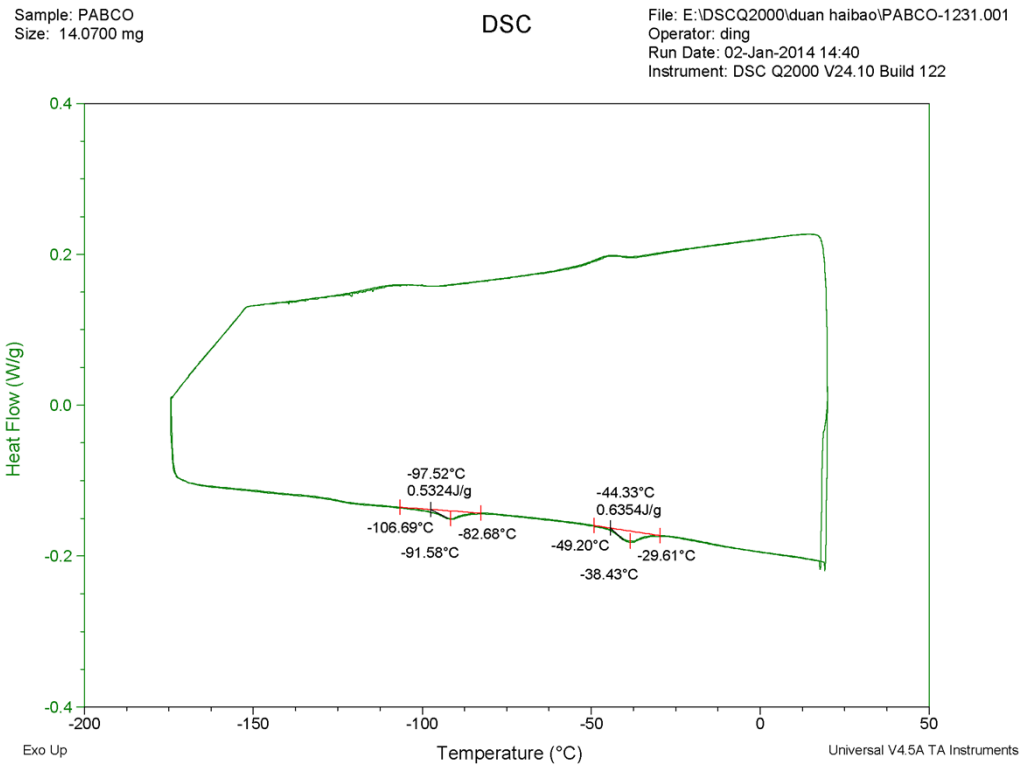



Figure S3 DSC plot of **1**.

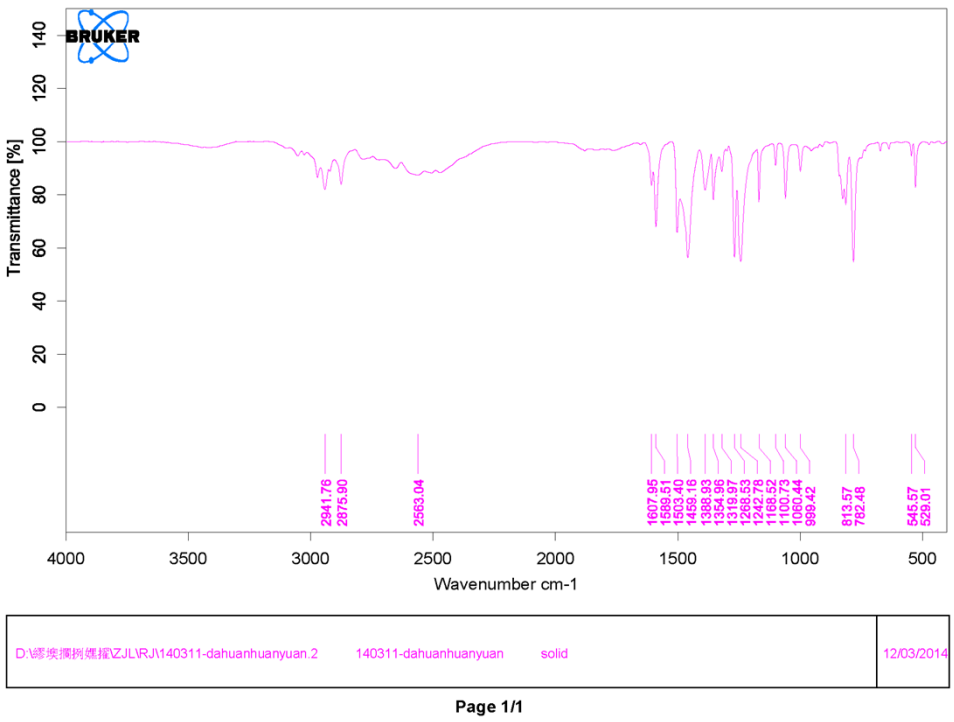



Figure S4 IR spectrum of **1**.

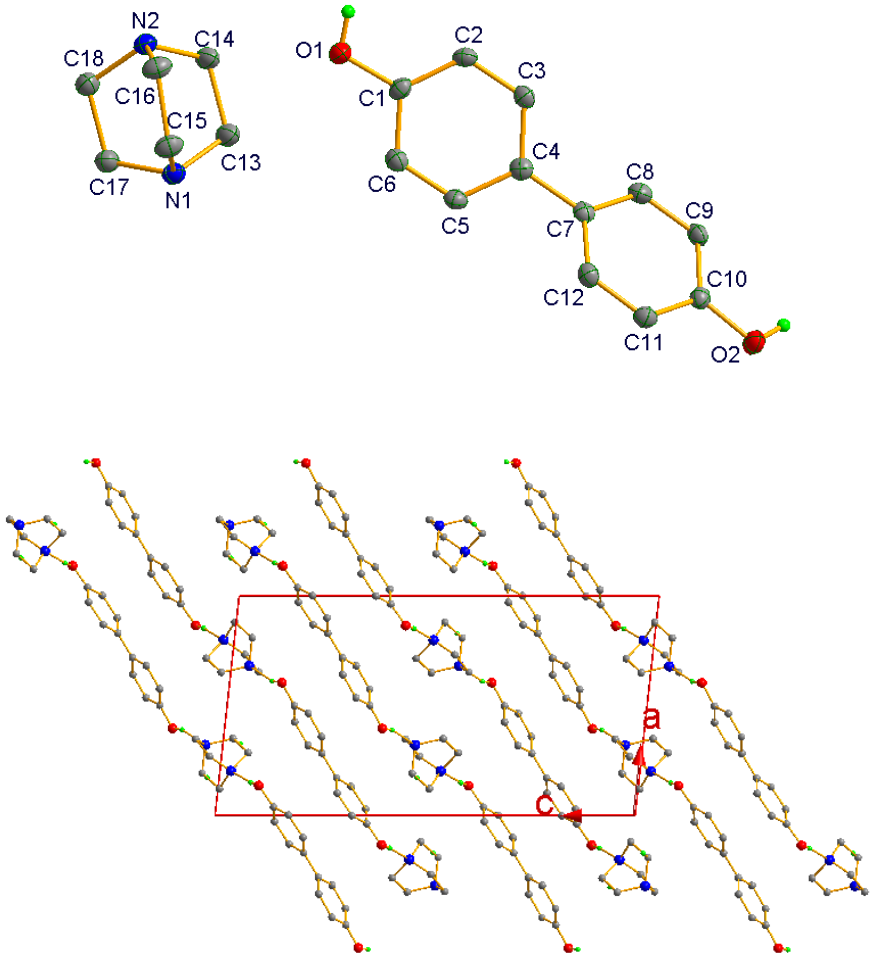
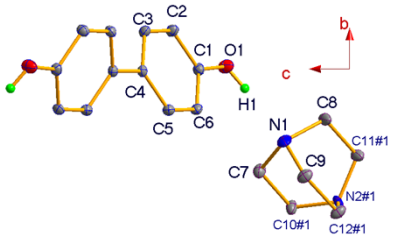


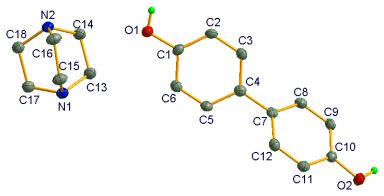

Figure S5 (a) Molecular structure of **1** with non-hydrogen atoms labeling and displacement ellipsoids at the 10% probability level in LT phase, where hydrogen atoms besides in OH groups as well as one disordered DABCO molecule are omitted for clarity (b) packing structure viewed along *b*-axis.

Table S1 Bond distances and angles of co-crystal **1** in HT, IT and LT phases




| Temperature = 296 K (HT phase) | | Temperature = 200 K (IT phase) | |
|---|---|---|---|
| O(1)-C(1) | 1.3598(16) | O(1)-C(1) | 1.352(3) |
| C(1)-C(6) | 1.3849(19) | C(1)-C(6) | 1.391(4) |
| C(1)-C(2) | 1.3849(19) | C(1)-C(2) | 1.387(3) |
| C(2)-C(3) | 1.3763(17) | C(2)-C(3) | 1.370(3) |
| C(3)-C(4) | 1.3957(18) | C(3)-C(4) | 1.397(3) |
| C(4)-C(5) | 1.3924(17) | C(4)-C(5) | 1.394(3) |
| C(4)-C(4)#1 | 1.483(2) | C(4)-C(4)#1 | 1.483(5) |
| C(5)-C(6) | 1.3816(17) | C(5)-C(6) | 1.374(3) |
| N(1)-C(7) | 1.394(18) | N(1)-C(7) | 1.41(2) |
| N(1)-C(8) | 1.422(17) | N(1)-C(8) | 1.349(14) |
| N(1)-C(9) | 1.62(2) | N(1)-C(9) | 1.67(2) |
| C(7)-C(10)#2 | 1.542(4) | C(7)-C(10)#2 | 1.540(5) |
| C(7)-C(8)#2 | 1.727(5) | C(7)-C(8)#2 | 1.788(7) |
| C(8)-C(11)#2 | 1.537(5) | C(8)-C(11)#2 | 1.542(6) |
| C(8)-C(7)#2 | 1.727(5) | C(8)-C(7)#2 | 1.788(7) |
| C(9)-C(12)#2 | 1.541(4) | C(9)-C(12)#2 | 1.556(6) |
| N(2)-C(10) | 1.40(2) | N(2)-C(10) | 1.42(2) |
| N(2)-C(11) | 1.416(19) | N(2)-C(11) | 1.365(17) |
| N(2)-C(12) | 1.61(2) | N(2)-C(12) | 1.673(19) |
| C(10)-C(7)#2 | 1.542(4) | C(10)-C(7)#2 | 1.540(5) |
| C(11)-C(8)#2 | 1.537(5) | C(11)-C(8)#2 | 1.542(6) |
| C(12)-C(9)#2 | 1.541(4) | C(12)-C(9)#2 | 1.556(6) |
| O(1)-C(1)-C(6) | 123.16(12) | O(1)-C(1)-C(6) | 118.2(2) |
| O(1)-C(1)-C(2) | 117.83(12) | O(1)-C(1)-C(2) | 123.0(2) |
| C(6)-C(1)-C(2) | 119.01(13) | C(6)-C(1)-C(2) | 118.8(3) |
| C(3)-C(2)-C(1) | 120.32(13) | C(3)-C(2)-C(1) | 120.4(2) |
| C(2)-C(3)-C(4) | 121.65(12) | C(2)-C(3)-C(4) | 121.8(2) |
| C(5)-C(4)-C(3) | 117.21(11) | C(5)-C(4)-C(3) | 116.9(2) |
| C(5)-C(4)-C(4)#1 | 121.99(8) | C(5)-C(4)-C(4)#1 | 122.22(18) |
| C(3)-C(4)-C(4)#1 | 120.81(8) | C(3)-C(4)-C(4)#1 | 120.85(16) |
| C(6)-C(5)-C(4) | 121.42(12) | C(6)-C(5)-C(4) | 121.8(2) |
| C(1)-C(6)-C(5) | 120.38(12) | C(1)-C(6)-C(5) | 120.2(2) |

| | | | |
|---|---|---|---|
| C(7)-N(1)-C(8) | 116.6(10) | C(7)-N(1)-C(8) | 119.7(12) |
| C(7)-N(1)-C(9) | 103.8(10) | C(7)-N(1)-C(9) | 100.1(9) |
| C(8)-N(1)-C(9) | 103.1(11) | C(8)-N(1)-C(9) | 104.3(13) |
| N(1)-C(7)-C(10)#2 | 112.0(6) | N(1)-C(7)-C(10)#2 | 111.6(7) |
| N(1)-C(7)-C(8)#2 | 97.5(7) | N(1)-C(7)-C(8)#2 | 98.7(8) |
| C(10)#2-C(7)-C(8)#2 | 33.17(17) | C(10)#2-C(7)-C(8)#2 | 42.0(3) |
| N(1)-C(8)-C(11)#2 | 111.4(5) | N(1)-C(8)-C(11)#2 | 112.9(8) |
| N(1)-C(8)-C(7)#2 | 94.5(7) | N(1)-C(8)-C(7)#2 | 87.0(8) |
| C(11)#2-C(8)-C(7)#2 | 35.01(17) | C(11)#2-C(8)-C(7)#2 | 45.7(3) |
| C(12)#2-C(9)-N(1) | 108.6(4) | C(12)#2-C(9)-N(1) | 106.8(6) |
| C(10)-N(2)-C(11) | 114.9(13) | C(10)-N(2)-C(11) | 117.5(14) |
| C(10)-N(2)-C(12) | 104.7(10) | C(10)-N(2)-C(12) | 101.5(8) |
| C(11)-N(2)-C(12) | 103.3(12) | C(11)-N(2)-C(12) | 104.2(13) |
| N(2)-C(10)-C(7)#2 | 112.0(6) | N(2)-C(10)-C(7)#2 | 111.3(8) |
| N(2)-C(10)-C(11)#2 | 98.1(7) | N(2)-C(10)-C(11)#2 | 118.1 |
| N(2)-C(11)-C(8)#2 | 112.1(6) | N(2)-C(11)-C(8)#2 | 111.6(7) |




Temperature = 120 K (LT phase)

| | | | |
|---|---|---|---|
| N(1)-C(13) | 1.473(2) | C(16)-N(2)-C(18) | 108.07(13) |
| N(1)-C(15) | 1.473(2) | C(14)-N(2)-C(18) | 108.42(13) |
| N(1)-C(17) | 1.485(2) | O(1)-C(1)-C(6) | 117.25(14) |
| N(2)-C(16) | 1.469(2) | O(1)-C(1)-C(2) | 123.63(14) |
| N(2)-C(14) | 1.473(2) | C(6)-C(1)-C(2) | 119.12(15) |
| N(2)-C(18) | 1.481(2) | C(3)-C(2)-C(1) | 120.29(15) |
| O(1)-C(1) | 1.3614(19) | C(2)-C(3)-C(4) | 121.33(15) |
| O(2)-C(10) | 1.3584(19) | C(3)-C(4)-C(5) | 117.37(14) |
| C(1)-C(6) | 1.390(2) | C(3)-C(4)-C(7) | 122.19(14) |
| C(1)-C(2) | 1.395(2) | C(5)-C(4)-C(7) | 120.43(14) |
| C(2)-C(3) | 1.384(2) | C(6)-C(5)-C(4) | 121.64(15) |
| C(3)-C(4) | 1.399(2) | C(5)-C(6)-C(1) | 120.24(15) |
| C(4)-C(5) | 1.402(2) | C(8)-C(7)-C(12) | 117.13(15) |
| C(4)-C(7) | 1.480(2) | C(8)-C(7)-C(4) | 121.67(14) |
| C(5)-C(6) | 1.379(2) | C(12)-C(7)-C(4) | 121.18(14) |
| C(7)-C(8) | 1.394(2) | C(9)-C(8)-C(7) | 121.72(15) |
| C(7)-C(12) | 1.404(2) | C(8)-C(9)-C(10) | 120.18(15) |
| C(8)-C(9) | 1.382(2) | O(2)-C(10)-C(11) | 118.29(14) |
| C(9)-C(10) | 1.398(2) | O(2)-C(10)-C(9) | 122.72(14) |
| C(10)-C(11) | 1.390(2) | C(11)-C(10)-C(9) | 118.99(15) |
| C(11)-C(12) | 1.380(2) | C(12)-C(11)-C(10) | 120.23(15) |

| | | | |
|---|---|---|---|
| C(13)-C(14) | 1.542(2) | C(11)-C(12)-C(7) | 121.70(15) |
| C(15)-C(16) | 1.545(2) | N(1)-C(13)-C(14) | 110.31(13) |
| C(17)-C(18) | 1.544(2) | N(2)-C(14)-C(13) | 110.45(13) |
| C(13)-N(1)-C(15) | 108.63(13) | N(1)-C(15)-C(16) | 110.47(13) |
| C(13)-N(1)-C(17) | 107.83(13) | N(2)-C(16)-C(15) | 110.27(13) |
| C(15)-N(1)-C(17) | 108.34(13) | N(1)-C(17)-C(18) | 110.46(13) |
| C(16)-N(2)-C(14) | 109.02(13) | N(2)-C(18)-C(17) | 109.86(13) |