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ELECTRONIC SUPPLEMENTARY INFORMATION

Conformational and color polymorphism of achiral 2-methyl-3-(2-naphthalenylthio)-1,4-naphthalenedione

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Fig. ESI-1

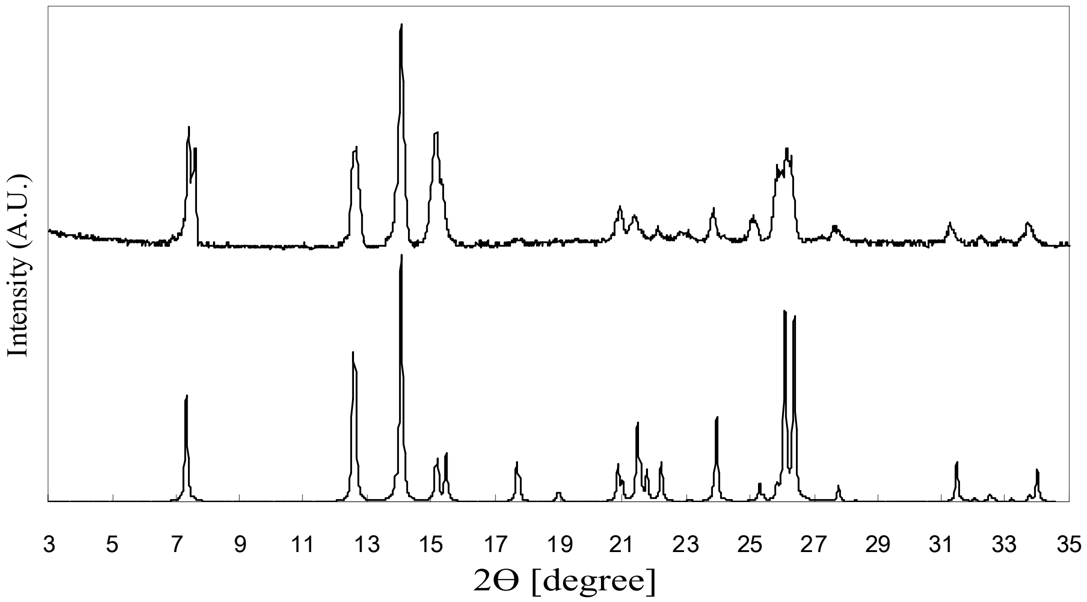

Fig. ESI-1 (a) X-ray powder diffraction pattern of crystals **IA**. (b) Simulated X-ray powder pattern of crystal **IA** calculated from crystal structure data.

Fig. ESI-2

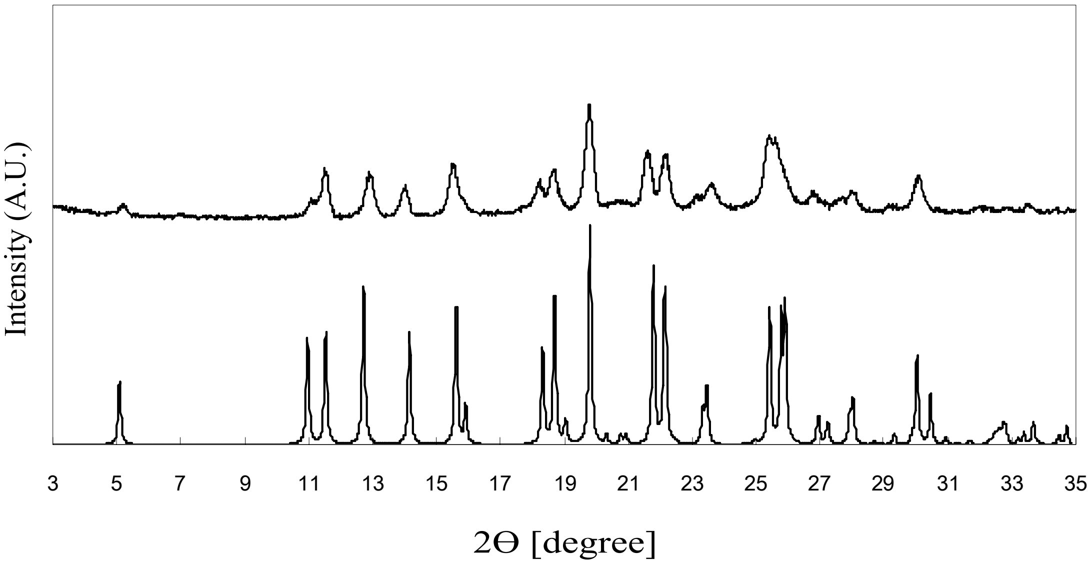

Fig. ESI-2 (a) X-ray powder diffraction pattern of crystals **IB**. (b) Simulated X-ray powder pattern of crystal **IB** calculated from crystal structure data.

1. Experimental

1.1. General methods

Crystallization solvents were purchased from Wako Pure Chemical Industry. These solvents were used directly as obtained commercially. DRS of crystals were measured with a *HITACHI U-4000 Spectrometer*. X-ray powder patterns of crystals were corrected on a *Rigaku RINT2500*. Melting points were measured on a Yanaco HK-10D. ^{1}H-NMR spectra were recorded with a Varian Mercury M300 spectrometer in chloroform-*d* using tetramethylsilane as an internal standard (300 MHz). ^{13}C-NMR spectra were recorded with a Varian Mercury M300 spectrometer in chloroform-*d* using tetramethylsilane as an internal standard (75 MHz).

1.2. Synthesis of compound 1

Although compound **1** is a commercial compound, compound **1** was synthesized following the method in literature for related compounds with some modification.[1] 2-Methyl-1,4-naphthoquinone oxide (2.0 g, 10.6 mmol) and 2-naphthalenethiol (2.0 g, 12.5 mmol) were solved to 2-propanol (150 mL). After that, 15% potassium hydroxide (0.2 mL) solution was added to 2-propanol solution. The reaction mixture was stirred at room temperature for 3h. A diethylether (300 mL) was added to reaction mixture. The combined organic layers were washed with brine, dried over Mg_2SO_4, and evaporated under vacuum to give the crude sulfide compound. Compound **1** was isolated as a solid by silica gel column chromatography (AcOEt/Hexane: 1:5) in 92% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.57 (s, 3 H), 7.25 (s, 1H), 7.38-749 (m, 2H), 7.64-7.80 (m, 2H), 7.87 (s, 2H), 7.99 (d, J = 9.0 Hz, 2H), 8.12 (d, J = 8.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.0, 126.4, 126.6, 126.7, 127.0, 127.4, 127.8, 128.0, 128.8, 129.3, 131.3,132.1, 132.1, 132.2, 132.5, 133.6, 133.7, 145.4, 149.0, 180.5, 183.0. HRMS (EI): *m/z* $[M]^+$ calcd for $C_{21}H_{14}O_2S$: 330.0715; found: 330.0767.

1.3. X-ray crystallographic study of crystal

X-ray diffraction data for single crystals were collected using *BRUKER APEX*. The crystal structures were solved by the direct method[2] and refined by full-matrix least-squares using *SHELX97*.[3] The diagrams were prepared using *PLATON*.[4] Absorption corrections were performed using *SADABS*.[5]

Nonhydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were included in the models in their calculated positions in the riding model approximation. **Crystallographic data for IA:** $C_{21}H_{14}O_2S_1$, M = 330.038, monoclinic, space group Cc, a = 22.763(3), b = 4.9872(5), c = 13.6097(15) Å, β = 95.969(2)º, V = 1536.6(3) Å^3, Z = 4, Dc = 1.428 gcm^{-3}, μ(Mo Kα) = 0.221 mm^{-1}, 6362 reflections measured, 1779 unique, final $R(F^2)$ = 0.0539 using 1538 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.0614, *Flack Parameter* = 0.4(2), T = 120(2) K. CCDC 702857. The whole molecule is disordered into two orientations. Because of this, it was necessary to restrain all the bond distances and angles to assume standard values. Also the planarity of the naphthyl ring was imposed for all four of them. **Crystallographic data for IB:** $C_{21}H_{14}O_2S_1$, M = 330.38, monoclinic, space group $P2_1$, a = 8.0141(17), b = 5.8339(12), c = 16.979(4) Å, β = 97.228(3)º, V = 787.5(3) Å^3, Z = 2, Dc = 1.3934(5) gcm^{-3}, μ(Mo Kα) = 0.215 mm^{-1}, 6936 reflections measured, 3513 unique, final $R(F^2)$ = 0.0933 using 3201 reflections with $I > 2.0\sigma(I)$, R(all data) = 0.0458, *Flack Parameter* = 0.13(7), T = 115(2) K. CCDC 702858. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; deposit@ccdc.cam.ac.uk).

1.4. Measurement of solid-state CD and absorption spectra.

The CD and absorption spectra were measured using a *Jasco J-800KCM spectrophotometer*. The solid-state samples were prepared according to the standard procedure for obtaining glassy KBr matrices.[6]

References

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