

Supplementary information

Luminescent N-arylphthalimidino derivatives 2- and 4-(1-oxo-1H-2,3-dihydroisoindol-2-yl)benzoic acid: examples of a new class of reaction induced crystallization for organic compound

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Materials and measurements

All chemicals and solvents, except the chemically pure *ortho*-phthalaldehyde (OPA), were of analytical pure and used as received without further purification. Thin-layer chromatography (TLC) analyses were performed with silica gel plates (250 mm) and flash chromatography (FC) was conducted over silica gel (200-300 mesh), both of which were obtained from the Qingdao Ocean Chemicals. Melting point of compound **1** was determined with a Beijing Taike XT-4 microscopy melting point apparatus and is uncorrected. Elemental analyses (C, H, N) were carried out with a Vario EL III elemental analyzer. Infrared spectra were recorded in the range of (4000–400) cm^{-1} on a Nicolet Magna 750 FT-IR spectrometer. ^1H NMR spectra were obtained at room temperature on Varian INOVA-400 spectrometer, and the chemical shift scale (ppm) is based on internal standard tetramethylsilane. LC-MS analyses were performed with a Waters Micromass ZQ-4000 mass spectrometer.

Preparation

Compound **1** and **2** were prepared adopting the same procedure. Ortho-phthalaldehyde (OPA) (0.2799 g, 2 mmol) was added to a stirred solution of o/p-aminobenzoic acid (0.2728 g, 2 mmol) in EtOH (30 mL). The reaction proceeded with gradual color change from yellow to brown upon refluxing for 3 h at about 90 °C. After the completion of reaction (TLC), the resulting solution was cooled to room temperature followed by concentration under reduced pressure. The residual crude product was purified by FC on silica gel using the mixture of AcOEt/MeOH (4:1) as the eluent to give compound **1** and **2** as yellow solid. Yields (based on OPA): 0.279 g of **1** (1.1 mmol, yield: 56%) and 0.251 g of **2** (1.0 mmol, yield: 51%). Crystals suitable for X-ray diffraction analysis were obtained as following method: o/p-aminobenzoic acid (0.253 g, 1.0 mmol) and CuCl (0.099 g, 1.0 mmol; for CuBr: 0.143 g, 1.0 mmol) were added to a 1:2 H₂O/EtOH solution (18 mL) in a Teflon-lined stainless steel reactor under the nitrogen atmosphere. The mixture was heated at 130 °C for 3 days followed by cooled to room temperature step by step. After filtration, the concurrent filtrate and air were sealed and was allowed to stand at room temperature. The block colorless crystals were formed after a period of 3 weeks. The same single crystals can also be obtained by the similar procedure but using the prepared **1** or **2** as precursor straight. Anal. Calcd. for C₁₅H₁₁NO₃ (%): C, 71.14; N, 5.53; H, 4.38. Found for **1**: C, 71.01; N, 5.49; H, 4.43. Found for **2**: C, 69.76; N, 5.38; H, 4.49. Mp for **1**: 132–134 °C; Mp for **2**: 176–177 °C. IR for **1** (KBr, cm⁻¹): 3417 (m), 3045 (m), 2920 (m), 2744 (m), 2565 (m), 1718 (vs), 1643 (vs), 1601 (s), 1493 (s), 1454 (s), 1410 (s), 1334 (m), 1302 (m), 1232 (s), 1200 (s), 1176 (s), 1144 (m), 1111 (m), 1061 (m), 1016 (w), 955(w), 916 (w), 891 (w), 746 (s), 698 (m), 681 (m), 631 (m), 575 (w), 486 (w) cm⁻¹. IR for **2** (KBr, cm⁻¹): 3444 (m), 3047 (w), 2929 (m), 1697 (vs), 1605 (s), 1514 (s), 1452 (s), 1423 (s), 1371 (s), 1336 (w), 1304 (m), 1273 (s), 1219 (m), 1178 (s), 1149 (m), 1103 (s), 1065 (w), 1030 (m), 947 (w), 858 (m), 766 (s), 731 (s), 683 (m), 580 (w), 482 (w) cm⁻¹. NMR for **1** (acetone-d₆, 400 MHz): δ 4.95 (s, 2H, ArCH₂N), 7.49 (td, *J* = 7.6, 0.8 Hz, 1H, Ar-H₆), 7.55 (q, *J* = 4 Hz, 1H, Ar-H₁₂), 7.58 (dd, *J* = 8, 1.2 Hz, 1H, Ar-H₄), 7.63–7.68 (overlapped, 2H, Ar-H₅, 7),

7.70 (td, $J = 7.6, 1.2$ Hz, 1H, Ar-*H*13), 7.76 (d, $J = 7.6$ Hz, 1H, Ar-*H*14), 8.01 (dd, $J = 8.0, 1.2$ Hz, 1H, Ar-*H*11), 11.20 (s, 1H, COOH). NMR for **2**: δ 4.96 (s, 2H, ArCH₂N), 7.26–7.88 (m, 8H, Ar-*H*), 10.24 (s, 1H, COOH). ES-MS (70 eV, m/z) for **1**: 253 ([M⁺]), 235, 207, 179, 152, 133, 117, 105, 89, 77, 63, 51. ES-MS for **2** (70 eV, m/z): 253 ([M⁺]), 235, 207, 197, 169, 165, 153, 139, 127, 105, 89, 77, 65, 57.

X-ray data collection and structure determination

Single crystal X-ray intensity data of **1** and **2** were collected on a Siemens Smart CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 273 (2) K by using an ω - 2θ scan mode. Empirical absorption corrections were applied using the SADABS program. The structures were solved by the direct methods. Systematic absences of **2** indicated either space group *P*-1 or *P*1, and the structure was solved originally in *P*1. After identified the presence of a centre of inversion, the structure was converted to *P*-1 which was shown to be correct by successful refinement. The non-hydrogen atoms were generated from successive difference Fourier syntheses. The positions of H atoms in COOH and water molecule were generated from difference Fourier maps with restrained (DFIX) treatment, the positions of the other H atoms were added theoretically and riding on their parent carbon atoms before the final cycle of refinement. The final refinement was performed by full-matrix least-squares method on F^2 , with anisotropic displacement parameters for all non-hydrogen atoms. All calculations were performed using the SHELXTL program.

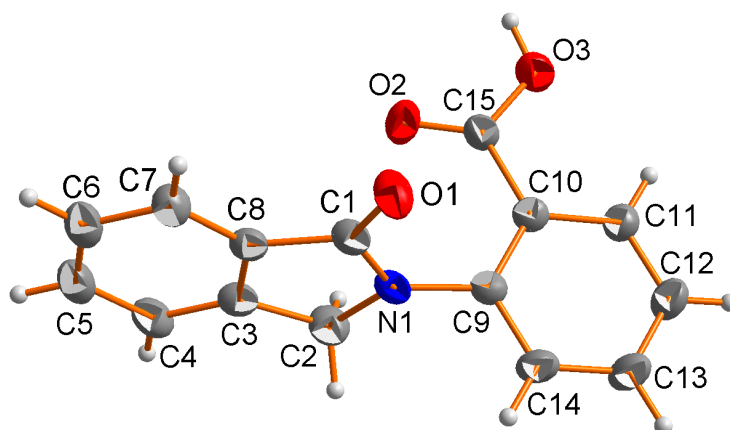


Fig. S1. Molecular structure of 2-(1-oxo-1H-2,3-dihydroisindol-2-yl)benzoic acid, with the atom-labeling scheme and probability displacement ellipsoids drawn at the 30% level.

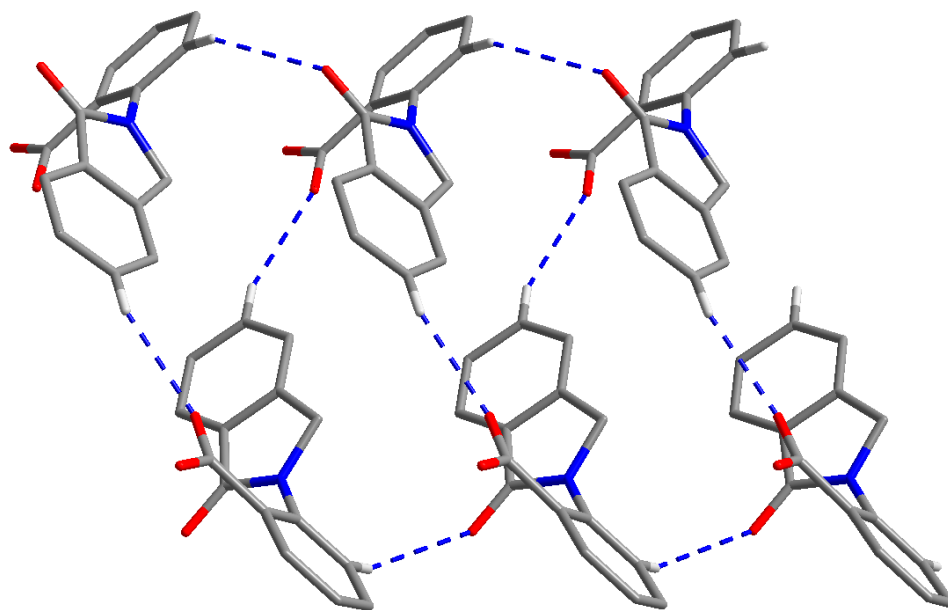


Fig. S2. A view of the helical array of molecules of 2-(1-oxo-1H-2,3-dihydroisindol-2-yl)benzoic acid along the b-axis induced by O...H-C weak interaction.

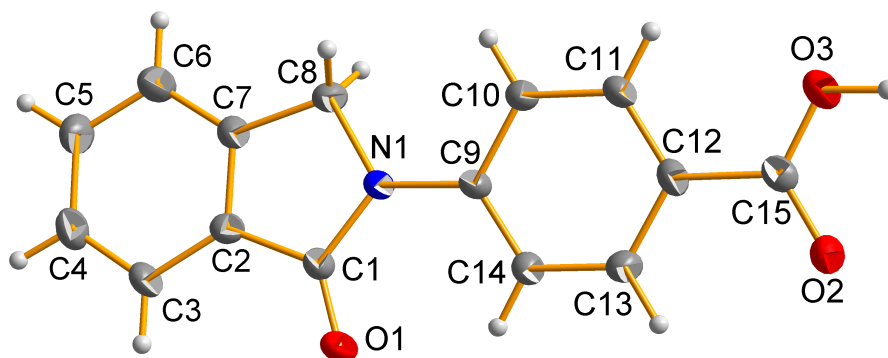


Fig. S3 Molecular structure of 4-(1-oxo-1H-2,3-dihydroisoindol-2-yl)benzoic acid, with the atom-labeling scheme and probability displacement ellipsoids drawn at the 30% level.

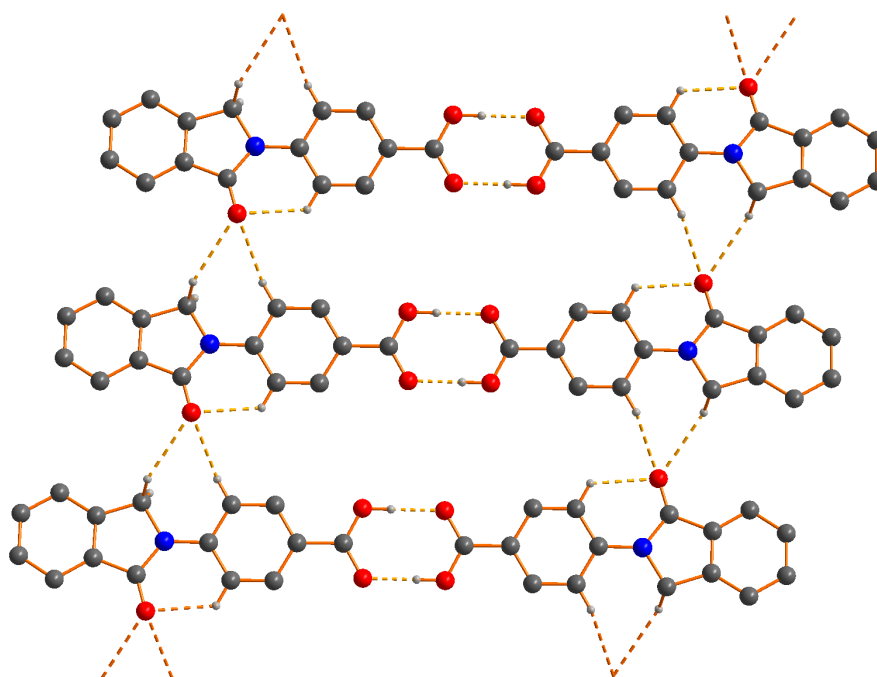


Fig. S4 The hydrogen-bond stabilized ladder-like structure along *a*-axis constructed from the hydrogen-bonded dimer of 4-(1-oxo-1H-2,3-dihydroisoindol-2-yl)benzoic acid.