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Hydrogen Bonded Dimer Stacking Induced Emission of Amino-Benzonic Acid Compounds

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1. Experimental detail

**General.** UV-Vis absorption spectra were recorded on a SHIMADZU UV-2550 spectrophotometer and fluorescence spectra measurements were carried out with PE 55. $^1$H NMR spectra were obtained on a Bruker AVANCE 500 MHz spectrometer with tetramethylsilane as the internal standard. Mass spectra data was collected by a GC/MS mass spectrometer. The PL yields of the crystals were measured using integrating sphere connected to a PTI-C701 fluorescence spectrometer. The single crystals of compounds 1–4 suited for X-ray structural analysis were grown from slowly gas phase deposition in vacuum tube. The crystal photographs were taken by a OLYMPUS BX51 fluorescent microscope. For the laser test, the crystals were irradiated by the third harmonic (355 nm) of a Nd:YAG (yttrium-aluminum-garnet) laser at a repetition rate of 10 Hz and pulse duration of about 10 ns. The energy of the pumping laser was adjusted by using the calibrated neutral density filters. The beam was focused into a stripe whose shape is adjusted to 4×0.5 mm through using a cylindrical lens and a slit. The tip emission of the crystals was detected using a charge-coupled-device (CCD) fiber spectrograph. 2-bromobenzoic acid, aniline, p-toluidine, anhydrous sodium carbonate, cupric chloride and ethylene glycol were purchased from Beijing fine-chemicals. 4-tert-butylenzamine and 3,5-dimethylbenzenamine were purchased from Fluka. All reagents were used as received without further purification.
2-(Phenylamino)benzoic acid (1). Aniline (1.86 g, 20.0 mmol), 2-bromobenzoic acid (2.01 g, 10.0 mmol), ethylene glycol (10 mL) and anhydrous sodium carbonate (1.1 g, 10.0 mmol) were added in a reaction vessel under nitrogen gas protection and stirred until effervescence ceased. Cupric chloride (100 mg, 0.75 mmol) dissolved in water (1 mL) was added to the reaction mixture and then heated to 120 °C for 6 hours. The reaction mixture was cooled to room temperature and quenched by water. After adding charcoal, the mixture was filtered and then acidified to pH = 2 with concentrated hydrochloric acid. The precipitate was collected by filtration, washed with water and further recrystallization from acetic acid to produce 1.22 g (57%) 1 as white powder. $^1$H NMR (500 MHz, CDCl$_3$), δ (ppm): 6.76 (t, 1H, $J = 7.5$ Hz), 7.14 (t, 1H, $J = 7.0$ Hz), 7.22-7.39 (m, 6H), 8.05 (d, 1H, $J = 8$ Hz), 9.32 (broad peak, 1H). Mass (EI): 212.7 (M$^+$); Calcd for C$_{13}$H$_{11}$NO$_2$: 213.3.

2-(p-Tolylamino)benzoic acid (2). This compound was synthesized in an analogous manner to compound 1 in 48% yield. $^1$H NMR (500 MHz, CDCl$_3$), δ (ppm): 2.36 (s, 3H), 6.72 (t, 1H, $J = 7.5$ Hz), 7.12-7.19 (m, 5H), 7.32 (t, 1H, $J = 7.5$ Hz), 8.02 (d, 1H, $J = 8.3$ Hz), 9.23 (broad peak, 1H). Mass (EI): 226.8 (M$^+$); Calcd for C$_{14}$H$_{13}$NO$_2$: 227.3.

2-(4-tert-Butylphenylamino)benzoic acid (3). This compound was synthesized in an analogous manner to compound 1 in 51% yield. $^1$H NMR (500 MHz, CDCl$_3$), δ (ppm): 1.34 (s, 9H), 6.72 (t, 3H, $J = 7.5$ Hz), 7.18-7.22 (m, 3H), 7.33 (t, 1H, $J = 7.5$ Hz), 7.39 (d, 2H, $J = 8.0$ Hz), 8.02 (d, 1H, $J = 8.0$ Hz), 9.28 (broad peak, 1H). Mass (EI): 268.9 (M$^+$); Calcd for C$_{17}$H$_{19}$NO$_2$: 269.4.

2-(3,5-Dimethylphenylamino)benzoic acid (4). This compound was synthesized in an analogous manner to compound 1 in 45% yield. $^1$H NMR (500 MHz, CDCl$_3$), δ (ppm): 2.32 (s, 6H), 6.73 (t, 1H, $J = 7.5$ Hz), 6.78 (s, 1H), 6.90 (s, 2H), 7.24 (t, 1H, $J = 8.5$ Hz), 7.35 (t, 1H, $J = 8.5$ Hz), 8.03 (d, 1H, $J = 8.0$ Hz), 9.24 (broad peak, 1H). Mass (EI): 240.9 (M$^+$); Calcd for C$_{13}$H$_{14}$NO$_2$: 241.3.
2. X-ray Crystallography

**X-Ray Crystal Structure Analysis of 1.** Single crystals of 1 suitable for X-ray crystal analysis were obtained by slow vapor deposition of 1 in a vacuum tube. Intensity data were collected at 293 K on a Rigaku R-AXIS RAPID diffractometer equipped with Mo Kα radiation ($\lambda = 0.71073$ Å). A total of 10269 reflections were measured at a maximum $2\theta$ angle of 55.0°, of which 4775 were independent reflections ($R_{int} = 0.0285$). The structures were solved with direct methods and refined with a full-matrix least-squares technique using the SHELXS v. 5.1 programs. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: C$_{13}$H$_{11}$NO$_2$; FW = 213.23, crystal size $0.57 \times 0.19 \times 0.16$ mm$^3$, Triclinic, $P\bar{1}$, $a = 8.0800(16)$ Å, $b = 9.812(2)$ Å, $c = 14.043(3)$ Å, $\alpha = 85.96(3)^{\circ}$, $\beta = 88.64(3)^{\circ}$, $\gamma = 73.45(3)^{\circ}$, $V = 1064.6(4)$ Å$^3$, $Z = 4$, $D_c = 1.330$ g cm$^{-3}$. The refinement converged to $R_1 = 0.0489$, $wR_2 = 0.1337$ ($I > 2\sigma(I)$), $GOF = 0.907$.

**X-Ray Crystal Structure Analysis of 2.** Single crystals of 2 suitable for X-ray crystal analysis were obtained by slow vapor deposition of 2 in a vacuum tube. Intensity data were collected at 293 K on a Rigaku R-AXIS RAPID diffractometer equipped with Mo Kα radiation ($\lambda = 0.71073$ Å). A total of 5927 reflections were measured at a maximum $2\theta$ angle of 55.0°, of which 2714 were independent reflections ($R_{int} = 0.0332$). The structures were solved with direct methods and refined with a full-matrix least-squares technique using the SHELXS v. 5.1 programs. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: C$_{14}$H$_{13}$NO$_2$; FW = 227.25, crystal size $0.34 \times 0.20 \times 0.11$ mm$^3$, Triclinic, $P\bar{1}$, $a = 6.4397(13)$ Å, $b = 7.3561(15)$ Å, $c = 13.882(3)$ Å, $\alpha = 93.33(3)^{\circ}$, $\beta = 91.87(3)^{\circ}$, $\gamma = 113.99(3)^{\circ}$, $V = 598.7(2)$ Å$^3$, $Z = 2$, $D_c = 1.261$ g cm$^{-3}$. The refinement converged to $R_1 = 0.0590$, $wR_2 = 0.1257$ ($I > 2\sigma(I)$), $GOF = 0.992$.

**X-Ray Crystal Structure Analysis of 3.** Single crystals of 3 suitable for X-ray crystal
analysis were obtained by slow vapor deposition of 3 in a vacuum tube. Intensity data were collected at 293 K on a Rigaku R-AXIS RAPID diffractometer equipped with Mo K\(_\alpha\) radiation (\(\lambda = 0.71073\) Å). A total of 7326 reflections were measured at a maximum 2\(\theta\) angle of 55.0\(^\circ\), of which 3367 were independent reflections (\(R_{\text{int}} = 0.0849\)). The structures were solved with direct methods and refined with a full-matrix least-squares technique using the SHELXS v. 5.1 programs. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: C\(_{17}\)H\(_{19}\)NO\(_2\); FW = 269.33, crystal size 0.28 × 0.12 × 0.10 mm\(^3\), Triclinic, \(P-1\), \(a = 6.7328(13)\) Å, \(b = 7.8277(16)\) Å, \(c = 15.269(3)\) Å, \(\alpha = 93.68(3)\(^\circ\), \(\beta = 90.46(3)\(^\circ\), \(\gamma = 112.33(3)\(^\circ\), \(V = 742.4(3)\) Å\(^3\), \(Z = 2\), \(D_c = 1.205\) g cm\(^{-3}\). The refinement converged to \(R_1 = 0.1068\), \(wR_2 = 0.2324\) (\(I > 2\sigma(I)\)), GOF = 0.930.

X-Ray Crystal Structure Analysis of 4. Single crystals of 4 suitable for X-ray crystal analysis were obtained by slow vapor deposition of 4 in a vacuum tube. Intensity data were collected at 293 K on a Rigaku R-AXIS RAPID diffractometer equipped with Mo K\(_\alpha\) radiation (\(\lambda = 0.71073\) Å). A total of 11680 reflections were measured at a maximum 2\(\theta\) angle of 55.0\(^\circ\), of which 2776 were independent reflections (\(R_{\text{int}} = 0.0562\)). The structures were solved with direct methods and refined with a full-matrix least-squares technique using the SHELXS v. 5.1 programs. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: C\(_{15}\)H\(_{15}\)NO\(_2\); FW = 241.28, crystal size 0.20 × 0.13 × 0.09 mm\(^3\), Monoclinic, \(P21/c\), \(a = 4.0126(8)\) Å, \(b = 13.932(3)\) Å, \(c = 22.026(4)\) Å, \(\beta = 93.45(3)\(^\circ\), \(V = 1229.1(4)\) Å\(^3\), \(Z = 4\), \(D_c = 1.304\) g cm\(^{-3}\). The refinement converged to \(R_1 = 0.0545\), \(wR_2 = 0.1580\) (\(I > 2\sigma(I)\)), GOF = 1.010.
3. Photophysical Properties

The (\(\Phi_F\)) of the crystals were measured using an integrating sphere connected to PTI-C701 fluorescence spectrometer and the thin film of Aluminium tris(quinolin-8-olate) was selected as a reference. The (\(\Phi_F\)) of chloroform solutions were measured using sulfuric acid aqueous solution (0.1 M) of quinine sulfate (1 × 10^{-5} M) as reference. The concentrations of the samples were about 4.5×10^{-5} M. The slits widths and high voltage of electron-multiplier phototube of the spectrofluorimeter equipments were all set at the fixed value. The PL yields of the samples were calculated according to equation 1:

\[
Q_{ys} = Q_{yr} \times \frac{1 - 10^{-A_L}}{1 - 10^{-A_{L_r}}} \times \frac{N_s^2}{N_r^2} \times \frac{D_s}{D_r}
\]

\(Q_{ys}\) means the PL yield of the sample and \(Q_{yr}\) means the PL yield of the reference solution (0.546 here for quinine sulfate); \(A\) is the UV absorption value at the excitation wavelength (360 nm) of the fluorescence spectrum; \(L\) is the thickness of the colorimetric cylinder; \(N\) is refractive index of the solution and \(D\) is the integral value of the fluorescence spectrum area. The subscript \(r\) refers to the reference while \(s\) refers to the sample.
**Figure S1.** The narrowed band of crystal 3 under pulsed laser with power of 0.98 mJ pulse$^{-1}$
4. NMR Spectra

Figure S2. $^1$H NMR spectrum of compound 1 (500 MHz, CDCl$_3$).
**Figure S3.** $^1$H NMR spectrum of compound 2 (500 MHz, CDCl$_3$).
Figure S4. $^1$H NMR spectrum of compound 3 (500 MHz, CDCl$_3$).
Figure S5. $^1$H NMR spectrum of compound 4 (500 MHz, CDCl$_3$).
5. References