Supplementary Information

Nonlinear optical and ferroelectric materials based on 1-benzyl-2-phenyl-1*H*-benzimidazole salts

Yong-Tao Wang,*[a] Gui-Mei Tang,[a] Chao He,[b] Shi-Chen Yan,[a] Qi-Chao Hao,[a] Long Chen,[a] Xi-Fa Long,*[b] Tian-Duo Li[a] and Seik Weng Ng*[c]

[a] Department of Chemical Engineering, Shandong Provincial Key Laboratory of Fine Chemicals, Shandong Polytechnic University, Jinan, 250353, P. R. China

[b] Fujian Institute of Research on the Structure of Mater, Chinese Academy of Science, Fuzhou, Fujian, 350002, P. R. China

[c] Department of Chemistry, University of Malaya, Kuala Lumpur, 50603, Malaysia

* Corresponding author. E-mail: ceswyt@sohu.com Fax: +086 0531 8900 0551; Tel: +086 0531 8900 0551; lxf@fjirsm.ac.cn. Fax: +086 0591 8371 4946; seikweng@um.edu.my. Fax: +060 603 7967 4193.

Experiment Section

Materials and instruments: The reagents and solvents employed were commercially available and used as received without further purification. Elemental analyses were performed on a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in range 400-4000 cm^{-1} on a Bruker Tensor27 spectrometer. Fluorescence spectra were taken using Ediburg FLS920 fluorescence spectrophotometer. Kurtz powder SHG measurements were performed on ground samples of crystalline **1-3** with a synchroscan streak camera (Hamamatsu Model C1587, 8 ps resolution) connected to a polychromator as the detector system, and an optical parametric generator (Spectra Physics, Model: OPA-800C) pumped by a mode-locked Ti: sapphire laser oscillator–amplifier system (Spectra Physics, Model: Hurricane) as the pump source. The powder second-harmonic signals were compared to that of KH_2PO_4 to determine the relative SHG efficiencies of **1-3**. The measurement of the polarization-voltage curves were carried out on the single crystals of **1-3** (single crystal approximate size 1.5 × 1.5 × 0.5 mm^3 for **1**, 1.0 × 1.0 × 0.5 mm^3 for **2**, and 1.0 × 0.5 × 0.5 mm^3 for **3**, respectively) using an aixACCT TF Analyzer 2000 system at room temperature, while the sample was covered by Ag-conducting glue on the approximate crystallographic face (010) and immerged in insulating oil.

X-ray Crystallography. Single-crystal X-ray diffraction data for salts **1-3** were collected on a Bruker CCD APEX diffractometer at room temperature with Mo Kα radiation (λ = 0.71073 Å). All the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix leastsquares methods with SHELXL.[1] All non-hydrogen atoms were located in successive difference Fourier syntheses, where they were refined with anisotropic thermal parameters on F^2. Hydrogen atoms were located at geometrically calculated positions and refined with isotropic thermal parameters. The data of the weak interactions were calculated by PLATON.[2] Crystallographic data and structural refinements for salts **1-3** are summarized in Table S1.

CCDC reference number 795444, 795443, and 795445 for **1**, **2**, and **3**, respectively. 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; or deposit@ccdc.cam.ac.uk).

Synthesis of 1-benzyl-2-phenyl-1*H*-benzimidazole (L), 1, 2, and 3

1-benzyl-2-phenyl-1*H*-benzimidazole (L). To the solution containing *o*-phenylendiamine (1.08 g, 10 mmol) in ethanol (10 ml) was added benzaldehyde (2.12 g, 20 mmol) in a 50 ml flask. After refluxing and stirring for 4 hours at 353 K, the resulting mixture was reduced under vacuum pressure. The mixture was recrystallized from ethanol, affording the production as a pale-yellow crystalline solid. Yield: 50% (1.432 g). m.p. 116-119 ^{o}C.

Salt 1. The 75% $HClO_4$ solution (0.1 mL) was added to a solution of **L** (0.142 g, 0.5 mmol) in the mixed solvents of methanol (8 mL) and water (2 mL). After two weeks, the colorless needle crystals suitable to X-ray diffraction were obtained. Yield: 0.177 g (92%); m.p. 221–225 ^{o}C; IR (KBr): 3246(w), 3180(w), 3061(w), 3034(w), 2976(m), 2920(m), 2866(m), 2825(w), 2748(w), 2632(w), 2530(w), 2357(w), 2335(w), 2027(w), 1919(w), 1624(w), 1602(m), 1556(m), 1508(m), 1479(m), 1458(s), 1429(m), 1377(w), 1361(m), 1323(m), 1303(w), 1273(w), 1126(s), 1111(s), 1045(s), 1004(w), 983(w), 939(w), 920(w), 891(w), 842(w), 817(w), 765(s), 732(m), 696(m), 623(s), 576(w), 5454(w), 478(m), 459(w); Elemental analysis calcd (%) for $C_{20}H_{17}ClN_2O_4$ (384.81): C, 62.42; H, 4.45; N, 7.28; found: C, 62.12; H, 4.47; N, 7.24.

Salt 2. The synthesis procedure of **2** was similar to that of **1** except that $HClO_4$ was taken place of HNO_3. Yield: 0.155 g (89%); m.p. 140–145 ^{o}C; IR (KBr): 3261(w), 3030(w), 2854(w), 2812(w), 2729(w), 2702(w), 2623(w), 2594(w), 2524(w), 2426(w), 2349(w), 1625(m), 1604(m), 1562(m), 1508(m), 1489(m), 1479(m), 1460(m), 1452(m), 1425(m), 1384(s), 1361(w), 1328(m), 1286(m), 1259(w), 1228(w), 1193(w), 1166(m), 1116(m), 1070(m), 1026(m), 1001(m), 935(w), 906(w), 881(m), 846(w), 823(m), 777(m), 761(m), 750(w), 734(m), 707(m), 694(m), 630(m), 590(w), 576(m), 561(w), 532(m), 480(m); Elemental analysis calcd (%) for $C_{20}H_{17}N_3O_3$ (347.37): C, 69.15; H, 4.93; N, 12.10; found: C, 69.48; H, 4.90; N, 12.19.

Salt 3. The synthesis procedure of **3** was similar to that of **1** except that $HClO_4$ was taken place of HCl. Yield: 0.154 g (91%); m.p. 171–175 ^{o}C; IR (KBr): 3408(w), 3373(w), 3199(br), 3039(w), 2966(w), 2920(w), 2858(w), 2812(w), 2717(m), 2673(w), 2625(m), 2569(w), 2524(w), 2160(m), 1950(w), 1919(w), 1622(s), 1600(w), 1556(s), 1508(w), 1490(w), 1477(m), 1458(s), 1429(m), 1400(m), 1361(m), 1325(m), 1284(m), 1261(s), 1230(w), 1193(w), 1166(s), 1118(m), 1070(m), 1029(m), 999(m), 941(m), 906(w), 887(s), 862(w), 817(m), 777(m), 759(s), 734(m), 709(w), 696(m), 628(m), 559(m), 528(w), 480(m), 460(m); Elemental analysis calcd (%) for $C_{20}H_{19}ClN_2O$ (338.83): C, 70.90; H, 5.65; N, 8.27; found: C, 70.62; H, 5.61; N, 8.21.

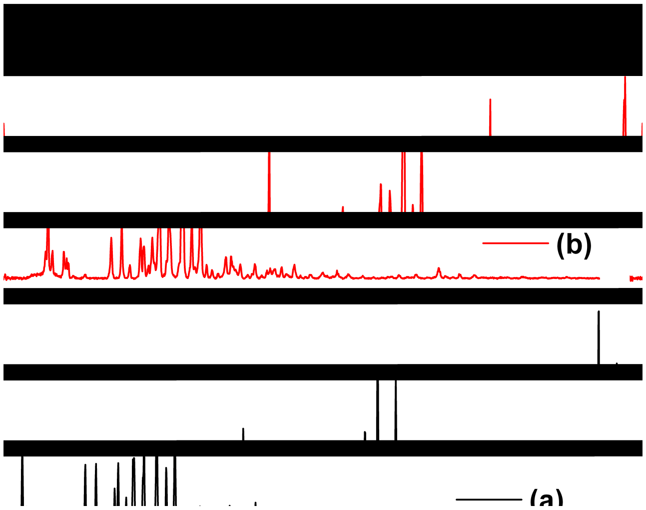


Fig. S1 X-Ray diffractometer (XRD) patterns of compound **1**: (a) simulated; (b) powdered.

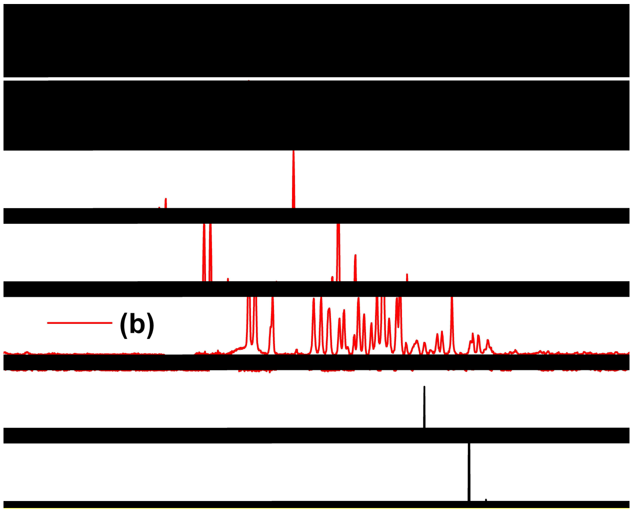


Fig. S2 XRD patterns of compound **2**: (a) simulated; (b) powdered.

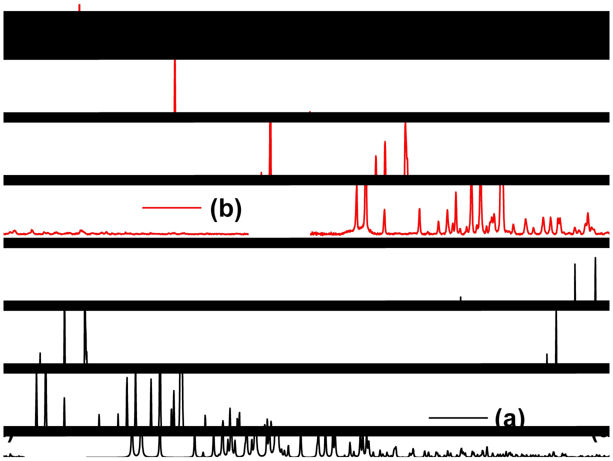


Fig. S3 XRD patterns of compound **3**: (a) simulated; (b) powdered.

Table S1 Crystallographic data and structure refinements for **1–3**

	1	**2**	**3**
chemical formula	$C_{20}H_{17}N_2,ClO_4$	$C_{20}H_{17}N_2,NO_3$	$C_{20}H_{17}N_2,H_2O,Cl$
fw	384.81	347.37	338.82
T(K)	296	293	296
λ(Mo $K\alpha$) (Å)	0.71073	0.71073	0.71073
crystal system	Triclinic	Triclinic	Triclinic
space group	$P1$ (No. 1)	$P1$ (No. 1)	$P1$ (No. 1)
a (Å)	5.7108(17)	5.707(3)	5.441(4)
b (Å)	9.011(3)	8.886(5)	8.892(6)
c (Å)	9.451(3)	9.503(5)	9.554(7)
α (degree)	70.550(3)	71.733(5)	74.542(8)
β (degree)	81.022(4)	79.378(9)	82.346(8)
γ (degree)	85.818(3)	84.199(9)	76.224(8)
V(Å^3)	452.9(2)	449.3(4)	431.5(5)
Z	1	1	1
Crystal size (mm)	0.10 × 0.10 × 0.30	0.10 × 0.10 × 0.20	0.10 × 0.10 × 0.20
μ(Mo $K\alpha$) (mm^{-1})	0.240	0.088	0.230
ρ(g·cm^{-3})	1.411	1.284	1.304
GOF	1.06	1.09	1.03
$R_1{}^a$ ($I > 2\sigma(I)$)	0.0333	0.0849	0.0325
$wR_2{}^b$ (all data)	0.0908	0.2317	0.0971
Flack	0.03(5)	-3(6)	-0.05(6)
Reflections collected	3954	2406	3741
Independent reflections	3193	1972	3005
reflections [$I > 2\sigma(I)$]	2846	1480	2817
F(000)	200	182	178

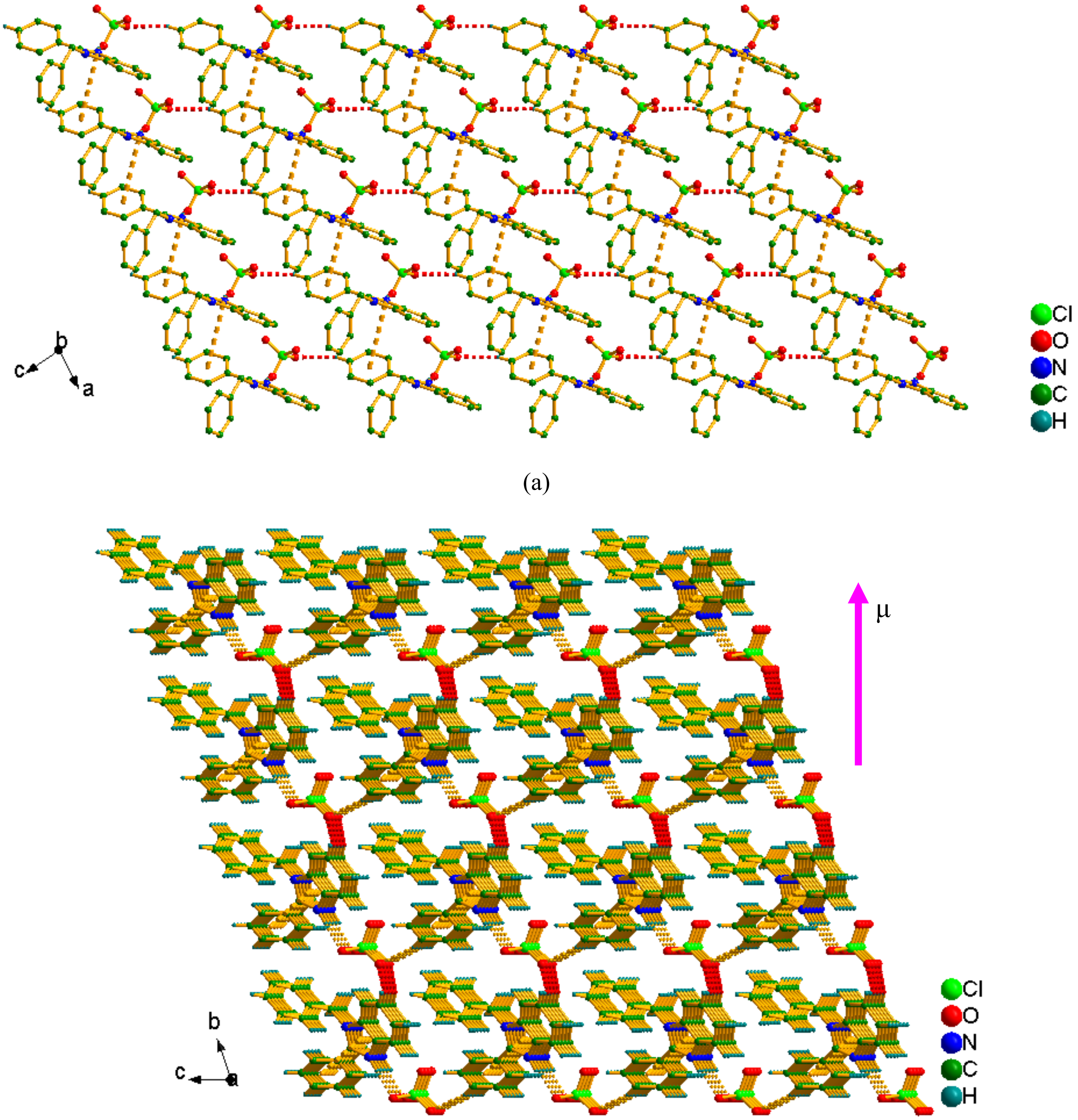
R_{int}	0.016	0.043	0.023
θ range	2.3/27.6	2.3/25.0	2.2/ 27.6
Largest peak and hole [e·Å^{-3}]	-0.14/0.20	-0.32/0.39	-0.15/0.16

[a] $R_1 = \Sigma\|F_o\| - \|F_c\|/\Sigma\|F_o\|$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$

Table S2 Hydrogen bond geometries in the crystal structures of **1-3**

Complex	D–H···A	H···A (Å)	D···A (Å)	D–H···A (°)
1^{i}				
	N1–H1···O3[a]	1.87(3)	2.801(3)	170(2)
	C11–H11A···O1[b]	2.5400	3.420(5)	158.00
	C20–H20A···N2	2.5400	2.883(3)	102.00
2^{ii}				
	N2–H2···O2	2.5100	3.140(15)	146.00
	N2–H2···O3	2.0600	2.704(13)	147.00
	C3–H3A···N1	2.5900	2.926(12)	102.00
	C18–H18A···O1[a]	2.5200	3.407(17)	160.00
3^{iii}				
	O1–H1WA···Cl1	2.41(4)	3.084(4)	151(4)
	N2–H2···O1[a]	1.72(4)	2.641(3)	175(3)
	O1–H1WB···Cl1[b]	2.22(5)	3.116(4)	165(4)
	C20–H20A···N1	2.5600	2.880(3)	101.00

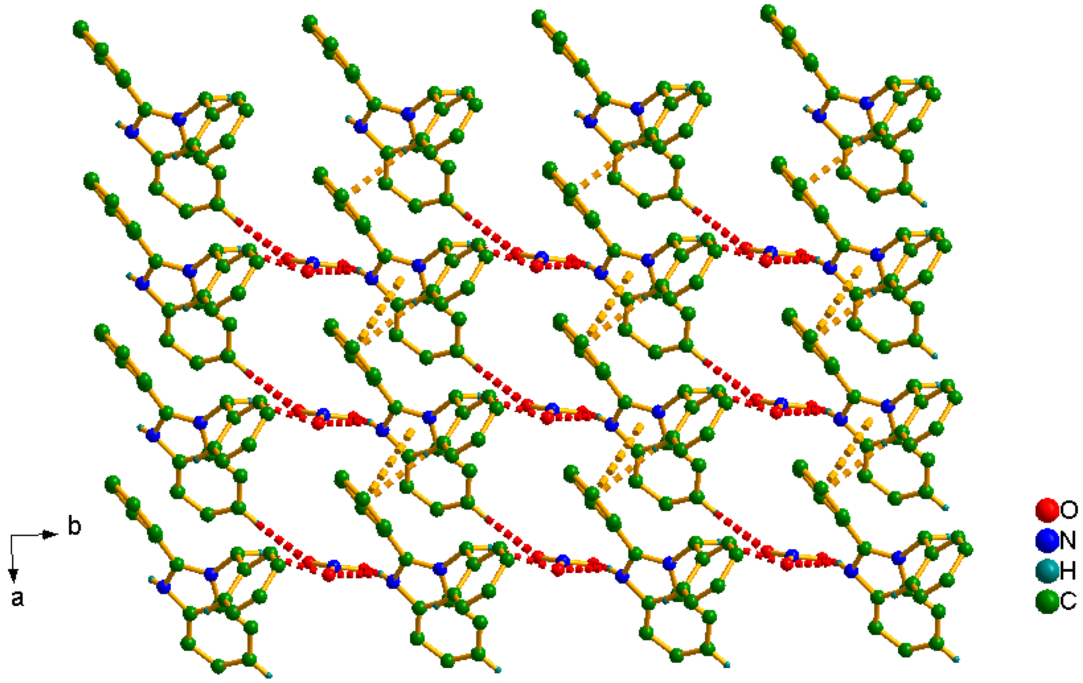
Symmetry codes: [a]x, y, -1 + z; [b]-1 + x, y, z for **1**^{i}. [a]1 + x, 1 + y, z for **2**^{ii}. [a]x, y, 1 + z; [b]-1 + x, y, z for **3**^{iii}.



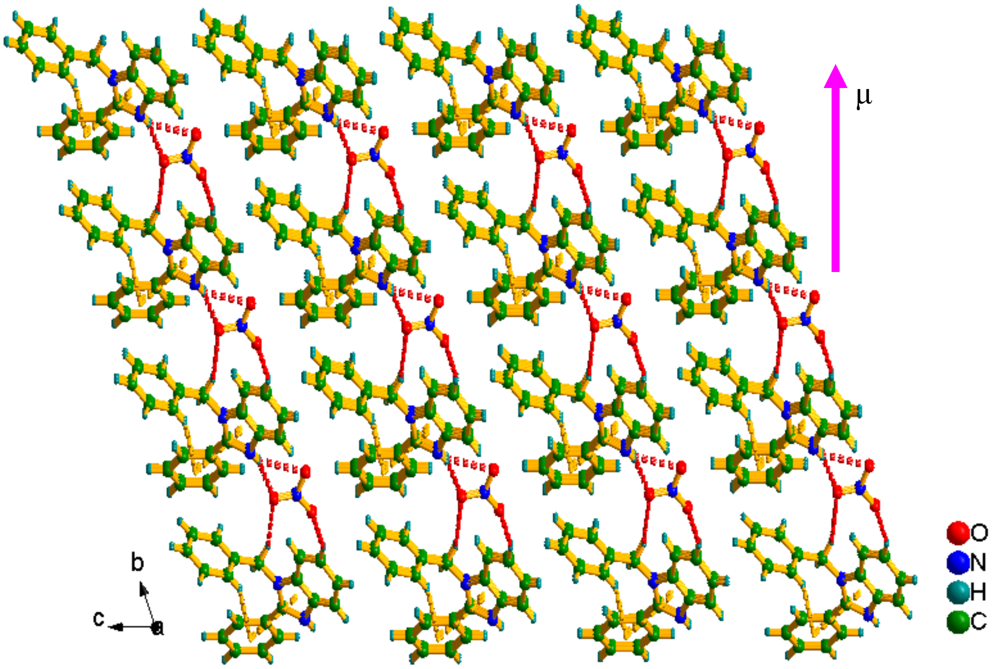
(a)

(b)

Fig. S4 (a) View point of 2D layer extending along the *b* axis in **1**. The red dash-lines and yellow ones represent hydrogen bonds and $\pi \cdots \pi$ packing interactions, respectively. (b) Packing diagram of **1** along the *a* axis. The thin yellow dashed-lines and red ones represent hydrogen bonds. The thick yellow dashed-lines stand for $\pi \cdots \pi$ packing interactions and hydrogen bonds, respectively. The purple arrow represents the direction of crystal packing polarity.



(a)



(b)

Fig. S5 View point of 2D layer extending along the *c* axis in **2**. (b) Packing diagram of **2** along the *a* axis. The yellow dashed-lines and red ones represent C-H···π and hydrogen bonds interactions, respectively. The thick yellow dashed-lines stand for $\pi\cdots\pi$ packing interactions. The purple arrow stands for the direction of packing polar polarity.

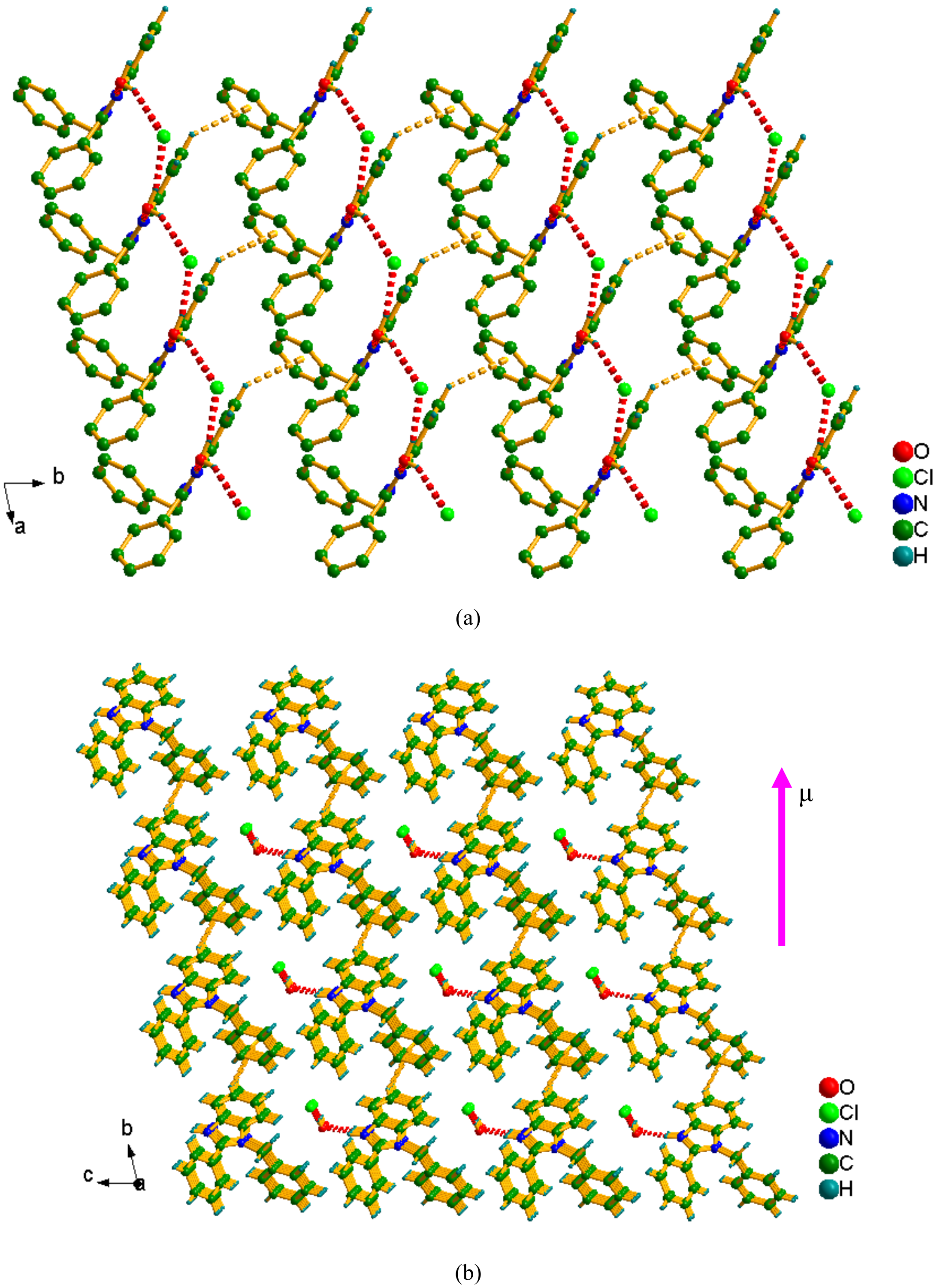
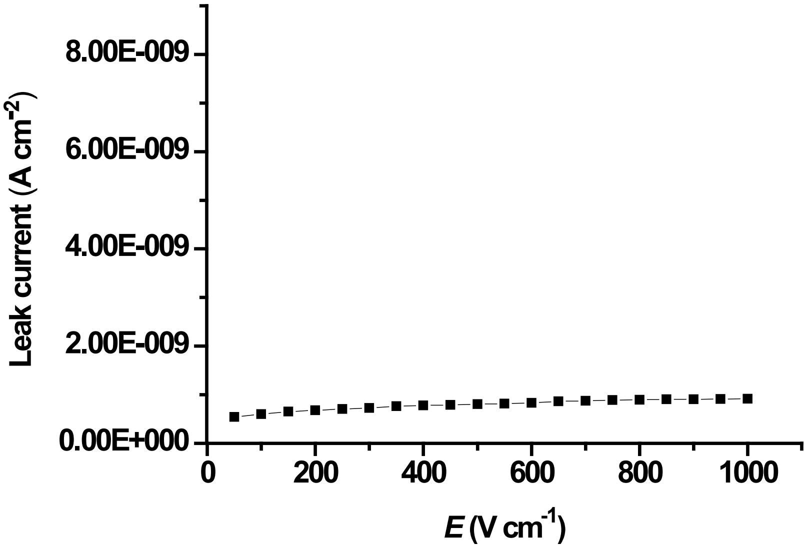
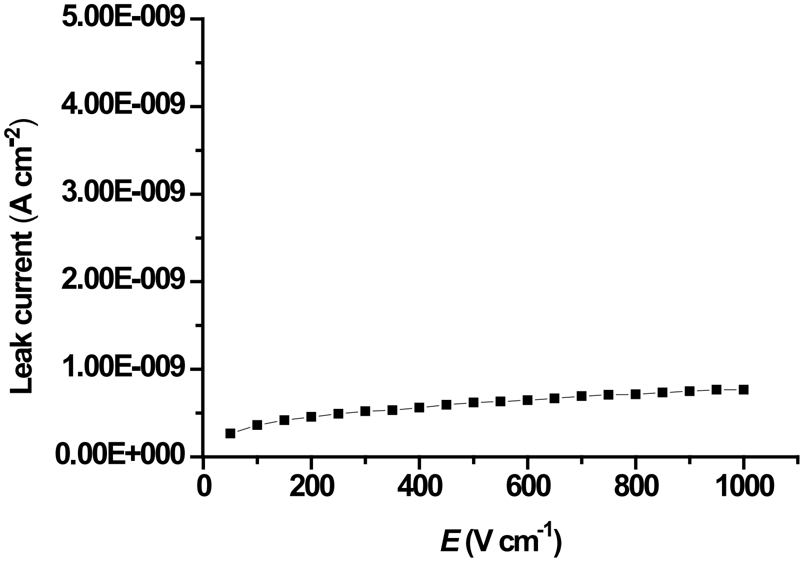


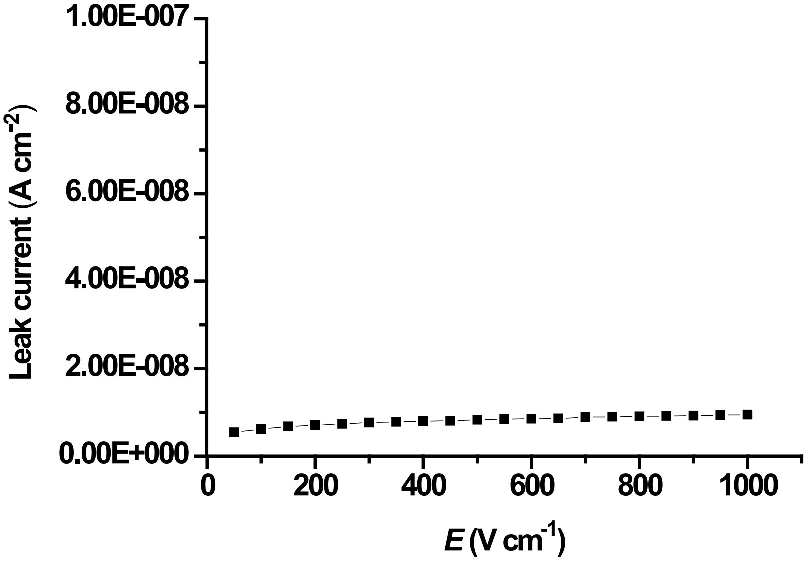
Fig. S6 (a) 2D supramolecular layer in **3** along the *c* axis. (b) Packing diagram of **3** along the *a* axis. The red dashed-lines and yellow ones stand for hydrogen bonding and C-H···π packing interactions, respectively. The purple arrow denotes the direction of packing polarity.


Leak current (A cm^{-2})
8.00E-009
6.00E-009
4.00E-009
2.00E-009
0.00E+000
0
200
400
600
800
1000
E (V cm^{-1})

(a)

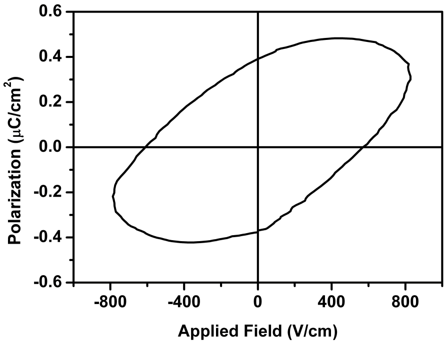

Leak current (A cm^{-2})
5.00E-009
4.00E-009
3.00E-009
2.00E-009
1.00E-009
0.00E+000
0
200
400
600
800
1000
E (V cm^{-1})

(b)

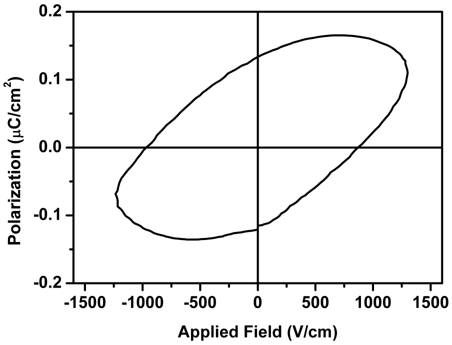


(c)

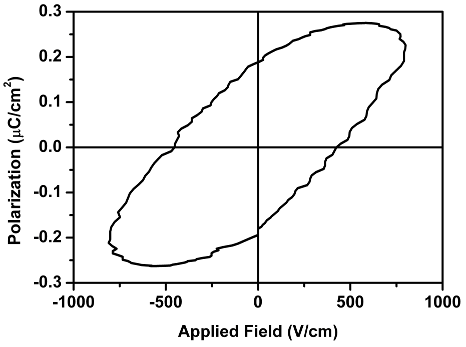
Fig. S7 Plots of leakage current in salts **1** (a), **2** (b), and **3** (c), respectively.



(a)



(b)



(c)

Fig. S8 Electric hysteresis loop of single crystal sample of **1** (a), **2** (b) and **3** (c), respectively.

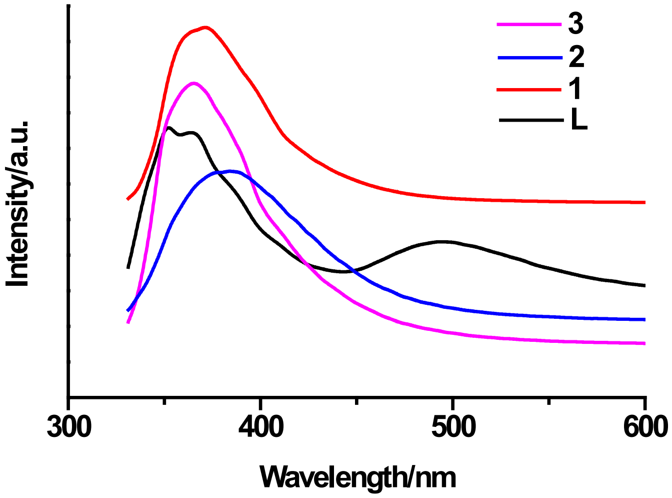


Fig. S9 Solid state fluorescent spectra for compounds **L**, **1**, **2**, and **3** at room temperature.

References

1 (*a*) G. M. Sheldrick, *SADABS*, University of Göttingen, Göttingen, Germany, 1996 and 2003; (*b*) G. M. Sheldrick, *SHELXTL NT Version 5.1. Program for Solution and Refinement of Crystal Structures*, University of Göttingen, Germany, 1997; (*c*) Bruker and AXS, *SAINT Software Reference Manual*, Madison, WI, 1998.

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