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Crystal Structures and Triboluminescence Based on Trifluoromethyl and Pentafluorosulfanyl Substituted Asymmetric N-Phenyl Imide Compounds

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Supporting Information

ABSTRACT: A series of asymmetric *N*-phenyl imides with trifluoromethyl and pentafluorosulfanyl substituents at the terminal phenyl position have been prepared. They are colorless both in solution and the solid state, and they show blue emission in the solid state. X-ray crystal structure analysis of trifluoromethyl and pentafluorosulfanyl substituted derivatives revealed highly ordered noncentrosymmetric molecular arrangements with large net-dipole moments related to the piezoelectric behavior. XRD measurements of the powders afforded intense sharp reflection peaks, indicating formation of the lamellar ordering. By grinding with a spatula, their solids showed vivid blue triboluminescence.



KEYWORDS: crystal structure analysis, triboluminescence, imide compounds, piezoelectric properties, trifluoromethyl groups

INTRODUCTION

Light emission caused by mechanical stress (force) in solid materials is known as triboluminescence (TL) (sometimes called mechanoluminescence). TL has a long history¹⁻³ and has recently been applied to real-time sensors of mechanical stress and structural damage⁴ and a resource of X-ray.⁵ As typical TL materials, inorganic solids⁶ containing lanthanoids such as europium and their complexes^{7–9} are known. Although organic compounds such as a lump of sugar,¹⁰ coumarin,¹¹ *N*-isopropylcarbazole,¹² 9-anthracenecarboxylic acid and the esters,¹³ and hexaphenylcarbodiphosphorane¹⁴ also show TL, the number is limited, and the efficiency is generally low. The TL mechanism still remains unclear, and further studies have been desired. To make progress in this field, a discovery of a new series of compounds affording vivid TL and the study on the relationship between structure and properties are especially important. According to previous reports, TL is closely related to piezoelectric properties of solids.^{1,2,7} Dipolar structures and noncentrosymmetric molecular arrangements in crystals are necessary to achieve the piezoelectric properties. However, it is generally difficult to obtain noncentrosymmetric organic crystals systematically. Bearing this in mind, we have paid attention to asymmetric N-phenyl type imides (Chart 1)^{15,16} for the following reasons. First, imide derivatives are excellent acceptors and very popular components in organic electronics.¹⁷ Investigation of physical properties and crystal structures based on simple N-phenyl imides are useful for the applications. Second, the imide derivatives have a dipole moment, and the

Chart 1. Chemical Structures of Asymmetric N-Phenyl Imide Compounds



dipolar structures are readily constructed by introducing substituents. When suitable *N*-phenyl imides are arranged with noncentrosymmetric space groups in crystals, they are expected to show piezoelectric properties leading to TL. Third, imide derivatives and the polymers have generally high chemical and thermal stabilities, mechanical toughness, and flame resistance.¹⁸ Moreover, various derivatives are easily obtained by simple synthetic methods. We have now prepared asymmetric *N*-phenyl imides **1** and **2** with trifluoromethyl¹⁹ and pentafluorosulfanyl²⁰ groups and succeeded in achieving TL behavior. The physical properties, crystal structures, and vivid TL properties are presented here.

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EXPERIMENTAL SECTION

Materials and Instrumentations. Tetrakis(triphenylphosphine)palladium(0), n-butyllithium in n-hexane, trimethyl borate, THF, DMF, phthalic anhydride, and 4-bromoaniline were purchased from Kanto Chemicals and used without further purification. 2,3-Naphthalene dicarboxylic anhydride, 4-aminobenzotrifluoride, and 4bromobenzotrifluoride were purchased from Tokyo Kasei Co. and used without further purification.

Imide derivatives 1 and 2 were synthesized by a simple condensation reaction of carboxylic anhydrides with the corresponding aromatic amines in high yields (77–85%). Imides 1a,²¹ 1c,²² 1e,²³ and $1f^{24}$ are known compounds. For the preparation of imides 1d and 2b, 4-(4-trifluoromethylphenyl)aniline was prepared by the Suzuki coupling reaction of 4-(trifluoromethyl)phenylboronic acid with 4bromoaniline.²⁵ All these imide derivatives were purified by sublimation. Experimental data were added for comparison.

Melting points were obtained on a SHIMADZU DSC-60. DI mass were collected on a JEOL JMS-700 mass spectrometer. ¹H NMR and ¹³C NMR spectra were recorded on a JEOL JNM-ECP300 NMR spectrometer, and chemical shifts were referenced to tetramethylsilane (TMS). IR spectra were recorded as KBr discs on a PERKIN ELMER FT-IR Spectrometer PARAGON 1000 spectrophotometer. Elemental analyses were carried out with a LECO/CHNS-932 analyzer at the Tokyo Institute of Technology, Chemical Resources Laboratory. UV-vis spectra were recorded on a JASCO V-650 spectrophotometer. PL spectra were collected on a JASCO FP-6600 spectrometer and JASCO FP-8500 spectrometer. Photoluminescence quantum yields in the solid state were determined by using an integrating sphere (in JASCO Corporation). X-ray diffraction (XRD) measurements were carried out on a Rigaku RINT with a Cu K α source (λ = 1.541 Å). XRD patterns were obtained using Bragg-Brentano geometry with Cu K α 5 radiation as an X-ray source with an acceleration voltage of 40 kV and a beam current of 30 mA. TL spectra were measured with a polychromator-ICCD multichannel spectrophotometer system (Princeton Instruments Inc.) through a plastic optical fiber after cooling in liquid N2. The transient properties of TL were monitored by a photomultiplier connected to a storage oscilloscope (HP 54542A), where emitted light was passed through a slit (1 mm). The time resolution of the detection system was 20 ks.

N-(4-Trifluoromethylphenyl)phthalimide (1a²¹). Phthalic anhydride (920 mg, 6.21 mmol), 4-aminobenzotrifluoride (1.00 g, 6.21 mmol), and DMF (20 mL) were added to a flask, and the mixture was refluxed for 24 h. The reaction mixture was cooled to room temperature and precipitated with water. The white solid was filtered and dried. The product was purified by sublimation to give 1a (0.71 g, 77%) as a white solid. Mp 257–259 °C. MS/EI (70 eV): *m/z* 291 (M⁺, 100%). IR(KBr) ν max/cm⁻¹ 3067 (CH_{Ar}), 1787, 1722 (C=O), 1615, 1526, 700 (C=C_{Ar}), 1402, 1110 (C–N–C), 1338, 715 (CF₃). ¹H NMR (300 MHz, CDCl₃): δ 8.00 (m, 2H), 7.83 (m, 2H), 7.78 (d, 2H, *J* = 9.0 Hz), 7.65 (d, 2H, *J* = 8.1 Hz). ¹³C NMR (75 MHz, CDCl₃): δ 166.77, 134.75, 131.50, 126.44, 126.29, 126.24, 126.19, 126.14, 124.01. Anal. Calcd for C₁₅H₈F₃NO₂: C, 61.86; H, 2.77; N, 4.81. Found: C, 62.07; H, 2.72; N, 4.78.

N-(4-Pentafluorosulfanylphenyl)phthalimide (1b). Phthalic anhydride (0.34 g, 2.28 mmol), 4-aminophenylsulfurpentafluoride (0.50 g, 2.28 mmol), and DMF (15 mL) were added to a flask, and the mixture was refluxed for 24 h. The reaction mixture was cooled to room temperature and precipitated with water. The white solid was filtered and dried. The product was purified by sublimation to give 1b (0.67 g, 84%) as a white solid. Mp 219–222 °C. MS/EI (70 eV): *m/z* 349 (M⁺, 100%). IR(KBr) ν max/cm⁻¹ 3070 (CH_{Ar}), 1760, 1731 (C= O), 1514, 715 (C=C_{Ar}), 1402, 1101 (C–N–C), 821 (SF₅). ¹H NMR (300 MHz, CDCl₃): δ 7.99 (m, 2H), 7.91 (d, 2H, *J* = 9.0 Hz), 7.83 (m, 2H), 7.84 (m, 2H), 7.65 (d, 2H, *J* = 8.4 Hz). ¹³C NMR (75 MHz, CDCl₃): δ 166.60, 134.85, 131.41, 130.61, 126.96, 126.90, 126.06, 126.09. Anal. Calcd for C₁₄H₈F₅NO₂S: C, 48.14; H, 2.31; N, 4.01. Found: C, 48.21; H, 2.31; N, 3.97.

N-(4-Methylphenyl)phthalimide (1c²²). Phthalic anhydride (0.92 g, 6.21 mmol), p-toluidine (0.67 g, 6.21 mmol), and DMF

(20 mL) were added to a flask, and the mixture was refluxed for 24 h. The reaction mixture was cooled to room temperature and precipitated with water. The white solid was filtered and dried. The product was purified by sublimation to give 1c (1.14 g, 78%) as a white solid. Mp 204–207 °C. MS/EI (70 eV): m/z 238 (M⁺, 100%). IR(KBr) ν max/cm⁻¹ 3040 (CH_{Ar}), 2915 (CH₃) 1747, 1714 (C=O), 1515, 722 (C=C_{Ar}), 1385, 1119 (C–N–C). ¹H NMR (300 MHz, CDCl₃): δ 7.96 (m, 4H), 7.78 (m, 4H), 2.41 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 167.41, 138.15, 134.29, 131.79, 129.76, 128.93, 126.44, 123.65, 21.18. Anal. Calcd for C₁₅H₁₁NO₂: C, 75.94; H, 4.67; N, 5.90. Found: C, 75.76; H, 4.63; N, 5.82.

N-(4'-Trifluoromethylbiphenyl)phthalimide (1d). Phthalic anhydride (1.25 g, 8.43 mmol), 4'-(trifluoromethyl)-4-biphenylamine (3)²⁵ (2.00 g, 8.43 mmol), and DMF (30 mL) were added to a flask, and the mixture was refluxed for 24 h. The reaction mixture was cooled to room temperature and precipitated with water. The white solid was filtered and dried. The product was purified by sublimation to give 2 (2.62 g, 85%) as a white solid. Mp 282–284 °C. MS/EI (70 eV): *m*/*z* 367 (M⁺, 100%). IR(KBr) ν max/cm⁻¹ 3041 (CH_{Ar}), 1790, 1731 (C=O), 1614, 1532, 713 (C=C_{Ar}), 1403, 1114 (C–N–C), 1337, 786 (CF₃). ¹H NMR (300 MHz, CDCl₃): δ 7.99 (m, 2H), 7.84 (m, 2H), 7.74 (d, 6H, *J* = 8.4 Hz), 7.58 (d, 2H, *J* = 8.4 Hz). Anal. Calcd for C₂₁H₁₂F₃NO₂: C, 68.67; H, 3.29; N, 3.81. Found: C, 68.41; H, 3.26; N, 3.78.

N-Phenylphthalimide (1e²³). Phthalic anhydride (4.00 g, 27.0 mmol), aniline (2.51 g, 27.0 mmol), and DMF (40 mL) were added to a flask, and the mixture was refluxed for 24 h. The reaction mixture was cooled to room temperature and precipitated with water. The white solid was filtered and dried. The product was purified by sublimation to give 1e (4.21 g, 70%) as a white solid. Mp 209–212 °C. IR(KBr) ν max/cm⁻¹ 3078 (CH_{Ar}), 1779, 1714 (C==O), 1594, 1505, 718 (C==C_{Ar}), 1385, 1117 (C–N–C). ¹H NMR (300 MHz, CDCl₃): δ 7.96 (m, 2H), 7.79 (m, 2H), 7.51 (d, 2H, *J* = 7.2 Hz), 7.46 (s, 1H), 7.42 (d, 2H, *J* = 6.6 Hz). ¹³C NMR (75 MHz, CDCl₃): δ 167.26, 134.38, 131.74, 131.65, 129.10, 128.09, 126.55, 123.73. Anal. Calcd for C₁₄H₉NO₂: C, 75.33; H, 4.06; N, 6.27. Found: C, 75.33; H, 3.81; N, 6.20.

N-(4-Fluorophenyl)phthalimide (1f²⁴). Phthalic anhydride (4.00 g, 27.0 mmol), 4-fluoroaniline (3.00 g, 27.0 mmol), and DMF (40 mL) were added to a flask, and the mixture was refluxed for 24 h. The reaction mixture was cooled to room temperature and precipitated with water. The white solid was filtered and dried. The product was purified by sublimation to give 1f (4.94 g, 76%) as a white solid. Mp 183–187 °C. IR(KBr) ν max/cm⁻¹ 3062 (CH_{Ar}), 1715 (C=O), 1514, 716 (C=C_{Ar}), 1394, 1110 (C–N–C). ¹H NMR (300 MHz, CDCl₃): δ 7.95 (m, 2H), 7.80 (m, 2H), 7.43 (m, 2H), 7.20 (t, 2H, *J* = 8.5 Hz). Anal. Calcd for C₁₄H₈FNO₂: C, 69.71; H, 3.34; N, 5.81. Found: C, 70.06; H, 3.39; N, 5.76.

N-(4-Trifluoromethylphenyl)-2,3-naphthimide (2a). 2,3-Naphthalene dicarboxylic anhydride (6.14 g, 31 mmol), 4-aminobenzotrifluoride (5.00 g, 31.0 mmol), and DMF (70 mL) were added to a flask, and the mixture was refluxed for 24 h. The reaction mixture was cooled to room temperature and precipitated with water. The white solid was filtered and dried. The product was purified by sublimation to give 3 (8.60 g, 81%) as a cream-colored solid. Mp 349–351 °C. MS/EI (70 eV): *m*/*z* 341 (M⁺, 100%). IR(KBr) *v*max/cm⁻¹ 3068 (CH_{Ar}), 1788, 1714 (C=O), 1614, 1525, 725 (C=C_{Ar}), 1394, 1111 (C–N–C), 1337, 763 (CF₃). ¹H NMR (300 MHz, CDCl₃): δ 8.50 (s, 2H), 8.13 (m, 2H), 7.81 (d, 2H, *J* = 9.0 Hz), 7.77 (m, 2H), 7.71 (d, 2H, *J* = 9.0 Hz). Anal. Calcd for C₁₉H₁₀F₃NO₂: C, 66.87; H, 2.95; N, 4.10. Found: C, 66.79; H, 3.00; N, 4.20.

N-(4'-Trifluoromethylbiphenyl)-2,3-naphthimide (2b). 2,3-Naphthalene dicarboxylic anhydride (1.67 g, 8.43 mmol), 4'-(trifluoromethyl)-4-biphenylamine (3)²⁵ (2.00 g, 8.43 mmol), and DMF (40 mL) were added to a flask and the mixture was refluxed for 24 h. The reaction mixture was cooled to room temperature and precipitated with water. The white solid was filtered and dried. The product was purified by sublimation to give 3 (2.93 g, 83%) as a cream-colored solid. Mp 372–375 °C. MS/EI (70 eV): m/z 417 (M⁺, 100%). IR(KBr) ν max/cm⁻¹ 3041 (CH_{Ar}), 1787, 1714 (C=O), 1614, 1505 (C=C_{Ar}), 1398, 1133 (C–N–C), 1337, 761 (CF₃). ¹H NMR (300 MHz, CDCl₃): δ 8.50 (s, 2H), 8.13 (m, 2H), 7.74 (m, 8H), 7.64 (m, 2H). Anal. Calcd for C₂₅H₁₄F₃NO₂: C, 71.94; H, 3.38; N, 3.36. Found: C, 72.03; H, 3.26; N, 3.39.

X-ray Crystal Structure Analysis. X-ray measurements of single crystals of 1a and 1b were made on a Rigaku Saturn724 diffractometer using multilayer mirror monochromated Mo K α radiation $(\lambda = 0.71075 \text{ Å})$ at -180 °C. The structures were solved by the direct method (SIR2008) and refined by the full-matrix least-squares method on F^2 . The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. Absorption correction was applied using an empirical procedure. All calculations were performed using the CrystalStructure crystallographic software package except for refinement, which was performed using SHELXL-97.²⁶ Crystal data for 1a: C₁₅H₈F₃NO₂, M = 291.23, crystal dimensions $0.10 \times 0.08 \times 0.08$ mm, monoclinic, space group Cc, a = 27.60(2), b = 5.633(4), c = 7.961(7) Å, $\beta = 95.498(12)$, V = 1232(2) Å³, Z = 4, $D_c = 1.570$ g cm⁻³, 7566 reflections collected, 1382 independent ($R_{int} = 0.0397$), GOF = 1.089, $R_1 = 0.0615$ ($I > 2.00\sigma(I)$), $wR_2 = 0.1543$ for all reflections. Crystal data for 1b: $C_{14}H_8F_5NO_2S_7$ M = 349.27, crystal dimensions $0.10 \times 0.10 \times 0.10$ mm, orthorhombic, space group *Pna2*₁, *a* = 8.2084(8), *b* = 5.7718(6), *c* = 28.328(3) Å, *V* = 1342.1(3) Å³, Z = 4, $D_c = 1.728$ g cm⁻³, 8675 reflections collected, 2456 independent ($R_{int} = 0.0880$), GOF = 1.127, $R_1 = 0.0786$ (I > $2.00\sigma(I)$, $wR_2 = 0.2467$ for all reflections. The CCDC reference numbers are 815102 and 815103.

RESULTS AND DISCUSSION

X-ray Crystal Structure Analysis. Single crystals of 1a were obtained by slow evapolation of the chloroform solution. X-ray analysis revealed the twisted geometry with a dihedral angle of 57.6° between the imide and phenyl rings (Figure S1, Supporting Information). The dihedral angle is similar to those of other *N*-phenyl substituted imide derivatives.^{22,23} Interestingly, these molecules form a quite regular layer structure in the crystal as depicted in Figure 1, in which they are arranged in the



Figure 1. Crystal structures of (a) 1a viewed along the *b*-axis and (b) 1b viewed along the *b*-axis.

same direction. The molecules are packed in a herringbone manner with close contacts between the carbons of carbonyl units and the oxygens of neighboring carbonyl units (2.87 and 2.93 Å). The trifluoromethyl groups are also arranged regularly

to afford a fluorine layer. The crystal belongs to a noncentrosymmetric space group Cc, resulting in a large net-dipole moment. On the other hand, single crystals of 1b with a pentafluorosulfanyl group were obtained by slow evapolation of the chloroform/DMF solution. The dihedral angle between the imide and phenyl rings is 60.1°, which is a little larger than that in 1a due to the bulky substituent. The molecular arrangement is almost the same with that of 1a with close contacts of 2.99 and 3.02 Å between the carbonyl groups. The crystal belongs to a noncentrosymmetric space group *Pna2*₁. The crystal structure of imide 1c with a methyl group is already reported with a noncentrosymmetric space group Pna21.22 However, compared with 1a and 1b, the imide 1c takes a half-slipped herringbone packing along the molecular long axis (Figure S3, Supporting Information). In contrast, nonsubstituted phenyl and 4fluorophenyl derivatives 1e and 1f have a center of symmetry in crystals.^{23,24} This result suggests that the substituent on the phenyl ring determines the crystal structure, and the bulkiness seems important for formation of noncentrosymmetric crystals.

Optical and Electrochemical Properties. The asymmetric *N*-phenyl imides 1 and 2 are colorless in solution and the solid state. The absorption spectra in dichloromethane are described in Figure 2 and Figure S6, Supporting Information.



Figure 2. Absorption spectra of imides 1a, 1b, 1d, 2a, and 2b in CH₂Cl₂.

Reflection spectra in the solid state are also collected using integrated sphere, and broad and red-shifted peaks are shown in Figure 3 (after K-M transformation). The imides 1 and 2



Figure 3. Reflection spectra of imides 1a, 1b, 1d, 2a, and 2b in the solid state (after K-M transformation).

exhibit blue fluorescence in the solid state, and the emission maxima are summarized in Table 1. Although intensity of the solid emission is low, the photoluminescence quantum yields of compounds 1a and 1b could be determined and are described in Table 1. Values of other derivatives are less.

The cyclic voltammograms of **1** and **2** were measured to investigate their electron-accepting properties, and the potentials

Table 1. Optical and Electrochemical Data

compd	$\lambda_{\rm abs} \ ({\rm nm}) \ (\log \ \varepsilon)^a$	$\lambda_{_{\mathrm{em}}} (\mathrm{nm})^b (\Phi)$	$E_{\rm red}~(V)^c$
1a	239 (4.48), 295 (3.22)	448 (4.0%)	-1.26
1b	241 (4.51), 295 (3.23)	444 (3.3%)	-1.36^{d}
1c	230 (4.40), 293 (3.24)	505	-1.36
1d	227 (4.32), 265 (4.50)	485	-1.30
1f	294 sh.	495	-1.38
1e	295 sh.	488	-1.35
2a	265 (4.84), 361 (3.63)	456	-1.40
2b	267, 361sh.	457	-1.43

^{*a*}In CH₂Cl₂. ^{*b*}Emission maxima in solids, excited at 310 nm. ^{*c*}0.1 M n-Bu₄NPF₆ in DMF, Pt electrode, V vs SCE. Half-wave potentials. ^{*d*}An irreversible wave, E_{pc} . In CH₂Cl₂, the reduction peak was observed as a reversible wave at $E_{red} = -1.43$ V.

are listed in Table 1. Almost all derivatives showed a clear reversible reduction wave in DMF (see Figure S12–S16, Supporting Information). Only in the case of imide **1b** with a pentafluorosulfanyl group was the return peak not observed in DMF. The anion radical of imide may react with the pentafluorosulfanyl group. The simple imide **1a** with an electron-withdrawing trifluoromethyl group showed the highest reduction potential in these measurements.

Triboluminescence Measurements. By grinding the powder of **1a** with a microspatula at room temperature, blue light emission was observed as shown in Figure 4a. The TL



Figure 4. TL of 1a (a) at room temperature in the dark and (b) after cooling in liquid N_2 under daylight. (c) Decay of light emission of 1a at room temperature.

could be observed by eyes in dark. The intensity of the emission was remarkably increased at low temperature. Thus, after the solid in a tube was cooled in a liquid nitrogen bath, the sample was pulled out from the bath and immediately grinded outside. The TL became strong enough to be clearly observed in daylight as depicted in Figure 4b, indicating that a radiationless deactivation process was effectively suppressed at low temperature. The blue-light was collected by a polychromator-ICCD multichannel spectrophotometer system through a plastic optical fiber outside a glass sample tube to give the spectra. The luminescence lifetime at room temperature could be monitored by a photomultiplier connected to a storage oscilloscope and estimated as an order of ten nanoseconds in Figure 4c. The TL spectrum exhibited almost the same emission maximum as the PL one as shown in Figure 5a, suggesting that the TL and



Figure 5. PL and TL spectra of (a) 1a, (b) 1b, (c) 1d, (d) 2a, and (e) 2b.

PL arise from the similar excited state. The decay of the emission also supports that the TL is fluorescence. On the other hand, sharp peaks of approximately 369 nm in Figure 5a can be ascribed to the emission of the excited nitrogen gas, which has often been observed in other TL materials.^{1–3}

Besides 1a, the other imides 1 and 2, except for 1e and 1f, exhibited TL (Table 2). The TL spectra of 1b, 1d, 2a, and 2b

 Table 2. Triboluminescence Data and Calculated Dipole

 Moments

compd	$\lambda_{\rm em} \ ({\rm nm})^a$	HOMO ^c	LUMO ^c	dipole moment (debye) ^c
1a	454	6.77	2.51	5.71
$1a^d$		7.04	2.38	5.70
1b	446	6.98	2.65	7.53
$\mathbf{1b}^d$		7.23	2.41	6.48
1c	Ь	6.17	2.24	2.06
1d	490	6.22	2.42	5.82
1e		6.38	2.28	2.53
1f		6.35	2.37	4.01
2a	436	6.66	2.28	6.84
2b	460	6.18	2.19	6.88

^{*a*}TL maxima after cooling in liquid N_2 . ^{*b*}Too weak to decide the maximum. ^{*c*}Performed using Gaussian 03 program at B3LYP/6-31G(d) levels of theory. ^{*d*}Performed using CIF files.

are depicted in Figure 5. The biphenyl derivatives **1d** and **2b** show the emission maxima at longer wavelengths than those of phenyl derivatives **1a** and **2a**. It should be noted that imides **1e** and **1f**, which did not exhibit detectable TL, have a center of symmetry in crystals.^{23,24} This fact suggests that noncentrosymmetric

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structures are necessary for the TL behavior based on these simple *N*-phenyl imides.²⁷ Although quantitative comparisons of TL have not been accomplished, the intensity was obviously dependent on the molecular and crystal structures. Thus, the TL intensity of **1c** was clearly weaker than those of other imide derivatives as described in Table 2. To investigate their electronic states, the molecular orbital calculations were carried out using the Gaussian 03 program at B3LYP/6-31G(d) levels of theory. Figure 6 depicts the calculated HOMOs and



Figure 6. (a, c) HOMO and (b, d) LUMO of imides 1a and 2a calculated using Gaussian 03 at B3LYP/6-31G(d) levels of theory.

LUMOs, showing that the LUMOs are located on the imide parts. The dipole moments were also calculated and are summarized in Table 2. Introduction of strong electron-withdrawing substituents such as trifluoromethyl and pentafluorosulfanyl groups in **1a** and **1b** makes dipole moments larger than that of the methyl derivative **1c**. The fact that the TL intensity of **1c** was not strong suggests that the dipole moment is related to TL.

X-ray Diffraction Patterns. To investigate the molecular arrangement in the solid, X-ray diffraction (XRD) of powders was measured in reflection mode. The XRD diffraction patterns based on the powders are depicted in Figure 7. The XRD



Figure 7. XRD patterns of powders of (a) pre- and (b) postgrinding 1a, (c) pre- and (d) postgrinding 1b, and (e-h) postgrinding 1c, 1d, 2a, and 2b.

patterns of imides showed that TL little changed through grinding, although the relative peak intensity and shape changed slightly as seen in Figures 7a-d and S18-S23, Supporting Information. In addition, the patterns were also kept through sublimation. This result suggests that a phase transition did not occur through the grinding and sublimation. Sharp reflection peaks are observed in all compounds, and those in 1a, 1b, 1d, 2a, and 2b indicate the formation of the highly ordered lamella structures. The *d*-spacings obtained from the first reflection peaks were 13.97 Å for 1a, 14.02 Å for 1b, 17.52 Å for 1d, 16.29 Å for 2a, 19.45 Å for 2b. Since the molecular lengths of the imides obtained from the single-crystal X-ray analysis and the molecular orbital calculations are 11.60 Å for 1a, 12.99 Å for 1b, 16.17 Å for 1d, 14.28 for 2a, and 18.62 Å for 2b, these molecules are considered to form the lamella structures corresponding to each molecular length. On the other hand, the d-spacing of 1c with a half-slipped herringbone type packing was different from the molecular length (d-spacing: 8.53 Å, molecular length: 11.45 Å). The weak TL property of 1c may be also ascribed to the crystal structure. Trifluoromethyl and pentafluorosulfanyl substituents seem to play an important role in making the layer structures. Introduction of extended π -conjugation in imides 1d, 2a, and 2b keeps the layer structures and the strong TL, although their emission spectra are red-shifted and broadened.

CONCLUSIONS

From these experimental data, we have deduced the following mechanism for the TL observed here. When the piezoelectric crystal breaks, the crack surface is electrified. Electronic discharge at the crack surface makes the excited states of compounds and the surrounding N₂ gas resulting in the emission. The dipolar structures and noncentrosymmetric molecular arrangements in crystals are necessary to achieve the strong piezoelectric properties (space groups of Cc and $Pna2_1$ belong to the piezo- and pyro-electroric groups). These agree with the TL mechanism reported by Zink et al.¹ On the other hand, we have found the trifluoromethyl and pentafluorosulfanyl substituted asymmetric N-phenyl imides form noncentrosymmetric crystals with high possibility and demonstrated TL using imides for the first time. Although the photoluminescence quantum efficiencies of imides shown in Table 1 are not so high, the TL behavior has high durability and the TL intensity is considerably maintained, even after they are well-ground. This is attributed to the chemical and electrochemical stability of the imide derivatives. In addition, the twist conformation and herringbone-type packing are important to achieve the solid emission and the low conductivity leading to high dielectric properties.

In summary, imide derivatives with asymmetric structures were found to show vivid TL. Investigation on the relationship between the TL behavior and structure revealed that the noncentrosymmetric molecular arrangement is an important factor for TL, and the desired crystal structures were successfully obtained by using simple *N*-phenyl imides. The trifluoromethyl and pentafluorosulfanyl substituents can assist the molecules in achieving high dipole moments and the layer structures. Further studies on the TL mechanism and development of high-performance TL materials are currently under way.

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ASSOCIATED CONTENT

S Supporting Information

X-ray crystal structure analysis, UV—vis and photoluminescence spectra, CV data, molecular orbital calculations, XRD data, and decay of light emission. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

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