Optical Properties of Disilane-Bridged Donor−Acceptor Architectures: Strong Effect of Substituents on Fluorescence and Nonlinear Optical Properties

Masaki Shimada,[†] Yoshinori Yamanoi,*[,†] Tomonori Matsushita,[‡] Takashi Kondo,[‡] Eiji Nishibori,[§] Akari Hatakeyama,[∥] Kunihisa Sugimoto,[⊥] and Hiroshi Nishihara*[,†]

[†]Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

[‡]Department of Materials Engineering, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

[§]Division of Physics, Faculty of Pure and Applied Sciences, Tsukuba Research Center for Interdisciplinary Materials Science (TIMS), and Center for Integrated Research in Fundamental Science and Engineering (CiRfSE), University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8571, Japan

[∥]Department of Advanced Materials Science, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa-shi, Chiba 277-8561, Japan

[⊥]Japan Synchrotron Radiation Research Institute (JASRI), 1-1-1 Koto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan

Ⓢ *Supporting Information*

ABSTRACT: A series of disilane-bridged donor−acceptor architectures **1−9** containing strong electron-donating and -withdrawing substituents were designed and synthesized in acceptable yields. The substituents substantially affected the fluorescence and nonlinear optical properties of the compounds. In the solid state, the compounds showed purple−blue fluorescence (λ_{em} = 360−420 nm) with high quantum yields (up to 0.81). Compound **3**, which had *p*-*N,N*-dimethylamino and *o*-cyano substituents, exhibited optical second harmonic generation (activity 2.9 times that of urea, calculated molecular hyperpolarizability $\beta = 1.6 \times 10^{-30}$ esu) in the powder state. Density functional theory calculations for the ground and excited states indicated that both the locally excited state and the intramolecular charge transfer excited state make important contributions to the luminescence behavior.

In recent years, push−pull chromophores have been extensively studied because of their promise as light-emitting and nonlinear optical (NLO) materials.[1] A typical organic push−pull chromophore consists of an electron donor and electron acceptor connected by a π-conjugated spacer.[2] To show good photophysical properties, the compounds must absorb in the visible region. The development of bright organic emitters and nonlinear optical devices with transparency remains a synthetic challenge. Cunjugation of Si−Si σ orbital and aryl π orbital is less well studied, although materials with σ−π conjugation display photoluminescence (PL) or electron-transporting properties. Mignani,[3] Hadziioannou and van Hutten,[4] and Hiratsuka[5] have independently described the synthesis of unsymmetrical disilanes; however, no systematic study of the relationship between the chemical structures and physical properties of these compounds has been published. Systematically designed disilanes with electron-donating and electron-accepting substituents are suitable models for studying push−pull chemistry

because of their chemical versatility, which allows easy modification of the optical parameters through the introduction of donor−acceptor (D−A) substituents.

In the course of our study on the synthetic use of hydrosilanes, we described a variety of examples of transition-metal-catalyzed arylation of hydrosilanes with aryl iodides.[6] A convenient synthesis of disilane-bridged D−A compounds **1−9** is reported in Scheme 1. The introduction of suitable substituents

Scheme 1. Molecular Structures of the Unsymmetrical 1,2-Diaryldisilane Derivatives Containing Electron-Donating and -Withdrawing Groups Used in This Study
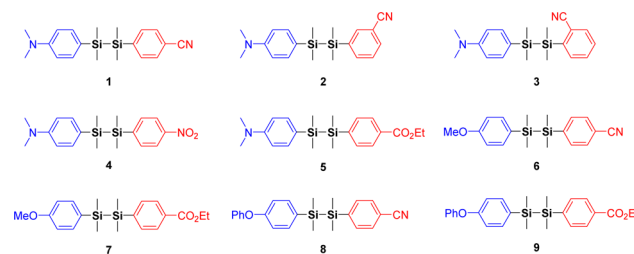
significantly altered the photophysical properties and enhanced the PL quantum yield. Importantly, unsymmetrical disilane **3**, which absorbed solely in the UV region, displayed nonlinear optical properties. Computational studies were also performed to support and provide further insight into the experimental findings.

The compounds contained a donor group on one disilane silicon atom and an acceptor group on the other. The synthesis of compounds **1−9** involved Pd-catalyzed cross-coupling reactions of hydrosilanes as a key step, which were achieved using our previously reported method (see the Supporting Information (SI)). Si−Si bond cleavage did not occur under the mild Pd-

Table 1. Photophysical Data for Disilane-Bridged Donor−Acceptor Compounds 1−9

	in CH$_2$Cl$_2$[a]					in the solid state				
compd	λ_{max}^{abs} (nm)	ε (10^4 M^{-1}cm^{-1})[b]	λ_{max}^{em} (nm)	Φ[c]	τ (ns)[d]	λ_{ex} (nm)[e]	λ_{max}^{em} (nm)	Φ[c]	τ (ns)[d]	SHG efficiency (vs urea)[f]
1	273, 304[g]	2.37, 0.78	503	0.13	29.1	331	420	0.05	13.9 (85),[h] 49.4 (15)[h]	−[i]
2	276, 306[g]	2.61, 0.51	488	0.06	37.7	331	360	0.14	3.7	−[i]
3	275, 305[g]	2.30, 0.62	501	0.10	26.3	362	411	0.13	3.9	2.9
4	276, 306,[g] 347[g]	3.11, 1.14, 0.30	−[j]	−[j]	−[j]	−[j]	−[j]	−[j]	−[j]	−[i]
5	272, 300[g]	2.79, 0.84	348, 511	0.02	3.3[k]	335	421	0.13	13.2	−[i]
6	236, 271	2.47, 1.17	462	0.21	3.9	−[l]	−[l]	−[l]	−[l]	−[l]
7	238, 270	2.62, 1.45	471	0.18	3.4	292	401	0.53	1.7	−[i]
8	240, 268[g]	2.12, 1.26	464	0.21	3.6	297	396	0.68	2.1	−[i]
9	244, 268[g]	2.53, 1.66	465	0.34	2.8	302	395	0.81	2.0	−[i]

[a]Measured in anhydrous degassed dichloromethane. [b]Molar extinction coefficient. [c]Absolute quantum yields determined using an integrating sphere system. [d]Fluorescence lifetimes detected at the maximum fluorescence wavelengths. [e]Excitation wavelength in the solid state determined by excitation spectra. [f]Measured by the powder method using a Q-switched Nd^{3+}:YAG laser (1064 nm). [g]Shoulder peak. [h]The number in parentheses is the amplitude contribution (%). [i]Not active. [j]Fluorescence was below the detection limit. [k]Detected at 511 nm. [l]Colorless oil.

catalyzed reaction conditions.[7] The analytically pure compounds were isolated in up to 41% yield and were fully characterized by ^{1}H and ^{13}C NMR spectroscopy and high-resolution mass spectrometry or elemental analysis.

The optical properties of **1−9** were investigated by UV−vis and fluorescence spectroscopy (Table 1 and Figures S1−S9 in the SI). These compounds showed absorption bands at high energies ($\lambda_{max} \approx 275$ nm for **1−5** and 240 nm for **6−9**) and weak absorption bands at low energies ($\lambda_{max} \approx 305$ nm for **1−5** and 270 nm for **6−9**) in dichloromethane. The difference between the absorption wavelengths of N,N-dimethylaminophenyl (**1−5**) and methoxyphenyl or phenoxyphenyl (**6−9**) derivatives resulted from the donor properties.

All of the PL spectra had a broad peak at around 480 nm in dichloromethane, except for that of **4**. The absorption spectra did not depend strongly on the solvent used, whereas the emission maxima changed significantly depending upon the solvent. The UV−vis absorption and PL spectra of representative disilane **3** in cyclohexane, dichloromethane, and acetonitrile are shown in Figure S10 and Table S5. Compound **3** showed dual fluorescence spectra with peaks around 350 nm and above 400 nm. The fluorescence peaks of **3** at around 350 nm were not shifted depending on the solvent polarity, whereas those above 400 nm showed a large red shift as the solvent polarity was increased. The emissions located at 350 nm and 400−600 nm were assigned to the locally excited (LE) emission and the intramolecular charge transfer (ICT) excited one, respectively.[8] The slope of the Lippert−Mataga plot was used to estimate the difference between the excited-state and ground-state dipole moments ($\mu_e - \mu_g$) of **3** as 20.3 D (Table S6 and Figure S11).[9,10] Fluorescence quantum yields (Φ) are shown in Table 1. The quantum yield depended on the terminal donor group and was independent of the acceptor group. The emission quantum yields of **1−5** ($\Phi = 0.02-0.13$) were lower than those of **6−9** ($\Phi = 0.18-0.34$). Subsequent investigation of the fluorescence properties of these compounds in the solid state revealed blue fluorescence (Figure 1) over a broad, unstructured emission profile with maxima at 360−420 nm. The emission maxima in the solid state were blue-shifted relative to those in the dichloromethane solutions as a result of the rigid medium. Attaching a 4-phenoxy donor group dramatically improved Φ. Compound **9** in the solid state exhibited a maximum emission band at 395 nm with a high Φ value of 0.81. This may be attributed to the twisted
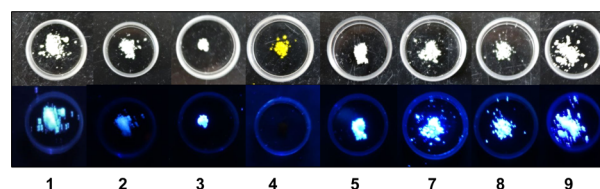

Figure 1. Photographs of (top) the appearance of **1−5** and **7−9** and (bottom) their photoluminescence in the solid state upon illumination with a 365 nm (**1−5**) or 254 nm (**7−9**) UV lamp.

4-phenoxy groups, which effectively suppress the intermolecular π−π stacking in the solid state.

To examine the photoemission dynamics, the fluorescence lifetimes (τ) of the compounds were measured. They depended on the donor and acceptor moieties (Table 1): the lifetimes achieved using the various terminal donor moieties were ranked in the order phenoxy ≤ methoxy < dimethylamino, while for the acceptor moieties, the ester group led to shorter lifetimes than the nitrile group. The τ values in the solid state were shorter than those in dichloromethane, except in the case of **5**. The fluorescence rate constant (k_f) and the nonradiative rate constant (k_{nr}) (Tables S7 and S8) observed for **1−3** and **5** were substantially smaller than those for **6−9** because of the stability of the radical cation (Me$_2$N$^{+\bullet}$) in the charge-separated state.[11]

To investigate the effect of the two terminal aromatic rings on the photophysical properties, the molecular orbitals (MOs) and transition states of **5**, **7**, and **9** were calculated using density functional theory (DFT) and time-dependent DFT (TD-DFT). Their representative frontier MOs and their energy levels are shown in Figures 2 and S15. By comparison with the transitions of the three compounds, the lowest-energy absorption band for **7** (270 nm) and **9** (268 nm) was assigned to the HOMO → LUMO transition. The fluorescence of **7** and **9** is assignable to
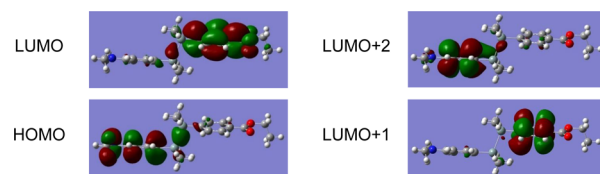

Figure 2. Selected frontier MOs for **5** calculated using DFT at the B3LYP/6-31G(d,p) level.

ICT emission via a charge-separated state, as shown by Hiratsuka et al.[5] (Tables S10 and S11). The calculated excited states of **5** indicated the HOMO → LUMO transition (the lowest excited state; 300 nm) and a combination of the HOMO → LUMO+1 (minor) and HOMO → LUMO+2 (major) transitions (second lowest excited state; 272 nm) (Table S9). Because the HOMO → LUMO+2 transition can be assigned to a π(D–A) → π*(D*–A) excitation on the donor aryl group, compound **5** has fluorescence of the D*–A state to the D–A state assignable to LE emission in addition to ICT emission (Figures 2 and S14). Thus, compound **5** has two fluorescent states and displays dual fluorescence, whereas **7** and **9** have only ICT emission.[12]

Finally, we investigated the second harmonic generation (SHG) efficiency of compounds **1**–**9** with the powder method (Figure S16).[13] This method, which uses a Q-switched Nd^{3+}:YAG laser (1064 nm), is one of the most convenient methods for screening powdered materials for NLO activity. The SHG efficiency was determined by comparison with a reference compound,[14] and the results are summarized in Table 1. Only compound **3** exhibited significant powder SHG efficiency, which was 2.9 times the intensity of urea. The molecular hyperpolarizability (β) which evaluates the second-order NLO efficiency, can be predicted from two-level models according to the literature,[1h,15,16] and that of **3** was estimated to be 1.6×10^{-30} esu, 5.0 times higher than that of urea (0.32×10^{-30} esu).[17] This result is roughly consistent with the experimental data.

The magnitude of the SHG signal obtained by the powder test is mainly governed by crystallographic factors. Single crystals of **3** (SHG-active) and **4** (SHG-inactive) for X-ray diffraction analysis were obtained by recrystallization from chloroform and acetonitrile, respectively.[18] The molecular and packing structures are shown in Figure 3. Compound **3** crystallizes in the non-

Figure 3. Crystal structures of **3** and **4**. (a) Molecular structure of **3**. (b) Packing structure of **3**. (c) Molecular structure of **4**. (d) Packing structure of **4**. Thermal ellipsoids are drawn at the 50% probability level, and H atoms have been omitted for clarity.

centrosymmetric space group *Pa* and compound **4** in the centrosymmetric space group *P2₁/c*; the crystal structure of **3** shows the twisted structure in which the two aryl groups are not parallel. The torsion angles of the Ar–Si–Si–Ar moiety (ca. 136°) and the Si–Si bond/*o*-cyanophenyl group (ca. 70°) indicate that compound **3** in crystals is distorted (Table S2). This twisted structure of **3** due to steric hindrance breaks the

symmetric crystal structure, which has D–A dipole moments since all of the molecules are oriented in the same direction. Meanwhile, the crystal structure of **4** shows that the two aryl groups are parallel and staggered in a steplike conformation. The torsion angles of the C6–Si1–Si2–C4 moiety and the Si–Si bond/*p*-nitrophenyl group were ca. 178° and ca. 90°, respectively (Table S4). The alternate directional packing ensures that the D–A dipoles avoid parallel alignments, minimizing intermolecular repulsion. Thus, these differences in the crystal packing of **3** and **4** reflect the difference in SHG activity.

In conclusion, we synthesized a series of structurally well-defined unsymmetrical disilanes **1**–**9** via Pd-catalyzed arylation of hydrosilanes with aryl iodides as a key step. The light-emitting efficiencies were improved considerably, with quantum yields of up to 0.34 in dichloromethane and 0.81 in the solid state. DFT and TD-DFT calculations supported the experimental data and provided a deeper understanding of the tuning of the photophysical properties of asymmetric disilanes.

Moreover, disilane **3** powder showed a second-order nonlinear optical response 2.9 times that of urea. The β value was calculated to be 1.6×10^{-30} esu, which is 5.0 times that of urea. The results reveal that the substituents of the donor and acceptor moieties in NLO chromophores dramatically affect their NLO properties in a properly designed system. Furthermore, these asymmetric disilanes are interesting building blocks for constructing linear and nonlinear optoelectronic materials.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Experimental details, crystallographic data for **3** and **4** (CIF), spectroscopic data, copies of ^{1}H and ^{13}C NMR spectra for the reported compounds, and additional spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors
*yamanoi@chem.s.u-tokyo.ac.jp
*nisihara@chem.s.u-tokyo.ac.jp

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) For representative reviews, see: (a) *Molecular Nonlinear Optics: Materials, Physics and Devices*; Zyss, J., Ed.; Academic Press: San Diego, CA, 1994. (b) *Nonlinear Optics of Organics and Semiconductors*; Kobayshi, K., Ed.; Springer: Tokyo, 1989. (c) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991. (d) Boyd, R. W. *Nonlinear Optics*, 3rd ed.; Academic Press: Burlington, MA, 2008. (e) Stegeman, G. I.; Stegeman, R. A. *Nonlinear Optics: Phenomena, Materials and Devices*; Wiley: Hoboken, NJ, 2012. (f) Panthi, K.; Adhikari, R. M.; Kinstle, T. H. *J. Phys. Chem. A* **2010**, *114*, 4542. (g) Kanis, D. R.; Ratner, M. A.; Marks, T. J.
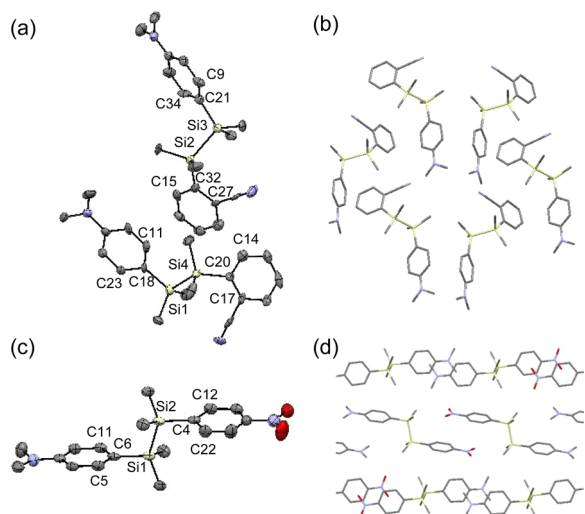
Chem. Rev. **1994**, *94*, 195. (h) Long, N. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 21.

(2) For reviews, see: (a) Grimsdale, A. C.; Cahn, K. L.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. *Chem. Rev.* **2009**, *109*, 897. (b) Liang, M.; Chen, J. *Chem. Soc. Rev.* **2013**, *42*, 3453.

(3) (a) Mignani, G.; Barzoukas, M.; Zyss, J.; Soula, G.; Balegroune, F.; Grandjean, D.; Josse, D. *Organometallics* **1991**, *10*, 3660. (b) Mignani, G.; Krämer, A.; Puccetti, G.; Ledoux, I.; Zyss, J.; Soula, G. *Organometallics* **1991**, *10*, 3656. (c) Mignani, G.; Soula, G. Organo-silicon compounds with nonlinear optical properties, their preparation, and materials and electrooptical devices containing them. PCT Int. Appl. WO 9116329 A1 19911031, 1991. (d) Soula, G.; Mignani, G. Organosilicon compounds and electrooptical devices containing them. Fr. Demande FR 2630442 A1 19900316, 1989.

(4) (a) Hissink, D.; van Hutten, P. F.; Hadziioannou, G.; van Bolhuis, F. *J. Organomet. Chem.* **1993**, *454*, 25. (b) van Hutten, P. F.; Hadziioannou, G.; Bursi, R.; Feil, D. *J. Phys. Chem.* **1996**, *100*, 85.

(5) Hiratsuka, H.; Horiuchi, H.; Takanoha, Y.; Matsumoto, H.; Yoshihara, T.; Okitsu, T.; Negishi, K.; Kyushin, S.; Matsumoto, H. *Chem. Lett.* **2007**, *36*, 1168.

(6) (a) Yamanoi, Y. *J. Org. Chem.* **2005**, *70*, 9607. (b) Yamanoi, Y.; Nishihara, H. *Tetrahedron Lett.* **2006**, *47*, 7157. (c) Yamanoi, Y.; Nishihara, H. *J. Org. Chem.* **2008**, *73*, 6671. (d) Yamanoi, Y.; Taira, T.; Sato, J.-i.; Nakamula, I.; Nishihara, H. *Org. Lett.* **2007**, *9*, 4543. (e) Yamanoi, Y.; Nishihara, H. *J. Synth. Org. Chem. Jpn.* **2009**, *67*, 778. (f) Yabusaki, Y.; Ohshima, N.; Kondo, H.; Kusamoto, T.; Yamanoi, Y.; Nishihara, H. *Chem.—Eur. J.* **2010**, *16*, 5581. (g) Lesbani, A.; Kondo, H.; Yabusaki, Y.; Nakai, M.; Yamanoi, Y.; Nishihara, H. *Chem.—Eur. J.* **2010**, *16*, 13519. (h) Kurihara, Y.; Nishikawa, M.; Yamanoi, Y.; Nishihara, H. *Chem. Commun.* **2012**, *48*, 11564. (i) Kurihara, Y.; Yamanoi, Y.; Nishihara, H. *Chem. Commun.* **2013**, *49*, 11275.

(7) (a) Lesbani, A.; Kondo, H.; Sato, J.-i.; Yamanoi, Y.; Nishihara, H. *Chem. Commun.* **2010**, *46*, 7784. (b) Inubushi, H.; Hattori, Y.; Yamanoi, Y.; Nishihara, H. *J. Org. Chem.* **2014**, *79*, 2974.

(8) For example, see: (a) Shizuka, H.; Hiratsuka, H. *Res. Chem. Intermed.* **1992**, *18*, 131. (b) Banerji, N.; Angulo, G.; Barabanov, I.; Vauthey, E. *J. Phys. Chem. A* **2008**, *112*, 9665. (c) Steinmetz, M. G.; Yu, C.; Li, L. *J. Am. Chem. Soc.* **1994**, *116*, 932.

(9) For Lippert−Mataga plots, see: (a) Lippert, E. *Z. Naturforsch., A* **1955**, *10*, 541. (b) Lippert, E.; Moll, F. *Z. Elektrochem.* **1954**, *58*, 718. (c) Mataga, N.; Kaifu, Y.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1956**, *29*, 465. (d) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319. (e) Filarowski, A.; Kluba, M.; Cieślik-Boczula, K.; Koll, A.; Kochel, A.; Pandey, L.; De Borggraeve, W. M.; van der Auweraer, M.; Catalán, J.; Boens, N. *Photochem. Photobiol. Sci.* **2010**, *9*, 996.

(10) μ_e and μ_g are the dipole moments of the excited and ground states, respectively. The value of $\mu_e - \mu_g$ for pentamethylphenylsilane was estimated to be 8.3 D. See: Yamamoto, M.; Kudo, T.; Ishikawa, M.; Tobita, S.; Shizuka, H. *J. Phys. Chem. A* **1999**, *103*, 3144.

(11) Rettig, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 971.

(12) It is known that pentamethyldisilanes display dual fluorescence from LE states and twisted ICT states (from twisting between the Si−Si and aryl groups). But these D−A series did not contribute to them because the disilanes with OMe or OPh (**6−9**) did not display dual fluorescence. For studies of dual fluorescence of pentamethyldisilanes, see: (a) Sakurai, H.; Sugiyama, H.; Kira, M. *J. Phys. Chem.* **1990**, *94*, 1837. (b) Tajima, Y.; Ishikawa, H.; Miyazawa, T.; Kira, M.; Mikami, N. *J. Am. Chem. Soc.* **1997**, *119*, 7400. (c) Ishikawa, H.; Shimanuki, Y.; Sugiyama, M.; Tajima, Y.; Kira, M.; Mikami, N. *J. Am. Chem. Soc.* **2002**, *124*, 6220. (d) Ishikawa, H.; Sugiyama, M.; Shimanuki, Y.; Tajima, Y.; Setaka, W.; Kira, M.; Mikami, N. *J. Phys. Chem. A* **2003**, *107*, 10781. (e) Ishikawa, H.; Sugiyama, M.; Baba, I.; Kira, M.; Mikami, N. *J. Phys. Chem. A* **2005**, *109*, 8959.

(13) Kurtz, S. K.; Perry, T. T. *J. Appl. Phys.* **1968**, *39*, 3978.

(14) We measured the SHG efficiency relative to 2-(*N*-prolinol)-5-nitropyridine (PNP). The SHG efficiency of PNP is 140 times higher than that of urea. See: Twieg, R. J.; Dirk, C. W. *J. Chem. Phys.* **1986**, *85*, 3537.

(15) (a) Morley, J. O.; Docherty, V. J.; Pugh, D. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1357. (b) Docherty, V. J.; Pugh, D.; Morley, J. O. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 1179. (c) Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664. (d) Oudar, J. L. *J. Chem. Phys.* **1977**, *67*, 446.

(16) Morley estimated the hyperpolarizability of compound **4** for SHG as 14.66×10^{-30} esu with theoretical calculations. See: Morley, J. O. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3015.

(17) Ledoux, I.; Zyss, J. *J. Chem. Phys.* **1982**, *73*, 203.

(18) Crystallographic data for the structures of **3** and **4** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 1030759 and CCDC 1000485, respectively.