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Survey of Enhanced, Thermally Stable, and Soluble Second-Order Nonlinear Optical Azo Chromophores

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A series of mono- and bisazo dyes were synthesized to obtain soluble, thermally stable, and enhanced second-order nonlinear optical chromophores (NLOphores). To prepare good sol-gel films, the most important factor was the solubility of NLOphores. Those azo NLOphores showing sufficient solubility were further classified into three groups: non-nitro-containing, nitro-containing, and fluorine-containing derivatives. Though non-nitro-containing NLOphores showed high solubility, their second-order nonlinearity was low. Nitro-containing NLOphores showed a rather high T_d and a medium nonlinearity. Fluorine-containing NLOphores, especially perfluoroalkylsulfonyl derivatives, showed high nonlinearity and a rather low T_d.

Sol-gel films doped or chemically bonded with NLOphores for electro-optic (E-O) materials have attracted much attention due to their excellent temporal stability.[1] Normally, enhanced second-order nonlinearity, good solubility (processability), and highly thermostability are important factors for the NLOphores. For the molecular design of enhanced second-order NLOphores, those compounds having high hyperpolarizability (β) and large dipole moment (μ) are very important.[2] Since sol–gel films are normally prepared from tetraethoxysilane (TEOS), good solubility of NLOphores in organic solvents, such as ethanol and 2-propanol, is required. In order to increase the solubility of organic compounds, the introduction of long alkyl chains,[3] fluorine-containing groups,[4] bulky substituents[5] into the molecules has been reported. *N*-Aryl derivatives have been reported to show not only high hyperpolarizability, but also improved thermostability compared with that of *N*-alkyl derivatives.[6] Push–pull type azo dyes have been proposed as NLOphores. Therefore, it is of importance and interest to examine these properties of azo compounds. We report here the survey of soluble and enhanced second-order azo NLOphores having high thermostability.

Experimental

Instruments. A thermal analysis was performed with a Rigaku Thermoflex TAS 200 TG 8101G apparatus. NMR spectra were recorded on a JEOL α-400 spectrometer. Mass spectra were taken on a Shimadzu QP-1000 spectrometer. UV-vis absorption spectra were measured with a Shimadzu UV-160A spectrometer.

Materials. Aniline (**1a**), 4-nitroaniline (**1b**), 4-nitro-1-naphthylamine (**1c**), 2,4-dinitroaniline (**1d**), 2-methyl-4-nitroaniline (**1e**), 4-nitro-2-(trifluoromethyl)aniline (**1f**), 2-amino-5-nitrothiazole (**1j**), 2-amino-6-nitrobenzothiazole (**1k**), 2-amino-5-[(4-nitrophenyl)sulfonyl]thiazole (**1l**), 2-aminoazobenzene (**4a**), iodobenzene, and triphenylamine were purchased from Tokyo Kasei Co., Ltd. 4-(Trifluoromethylsulfonyl)aniline (**1h**) was purchased from JRD Fluorochemicals Ltd. 4-(Perfluorobutyl)aniline (**1g**),[7] 4-(perfluorohexylsulfonyl)aniline (**1i**),[8] 4-nitronitrosobenzene (**8**),[9] 4-nitro-2-(trifluoromethyl)nitrosobenzene (**9**),[9] and pentafluoronitrosobenzene (**10**)[10] were prepared as described in the literature. 4-Phenylazo-1-naphthylamine (**4′a**) was obtained by a diazotization-coupling reaction.

Synthesis of Monoazo NLOphores (2b, 2c, 3b, 3d, 3e, 3f, 3g, 3h, 3i, 3j, 3k, and 3l). To conc. sulfuric acid (6 cm^3) was added sodium nitrite (0.69 g, 10.0 mmol). The mixture was heated to 70 °C and cooled to 0 °C. To the mixture was added a propionic acid–acetic acid–DMF mixed solution (2.5 cm^3 : 12.5 cm^3 : 10 cm^3) of an aromatic amine **1** (10.0 mmol), and the mixture was stirred at 0 °C for 2 h. To the mixture was added a DMF solution (50 cm^3) of diphenylamine (1.69 g, 10.0 mmol) or triphenylamine (2.45 g, 10.0 mmol), and stirred at 0 °C to room temperature overnight. After the reaction was completed, the mixture was neutralized with aqueous sodium hydroxide. The resulting precipitate was filtered, purified by silica-gel column chromatography (**2c**, **3b**, **3d**, **3e**, **3f**, **3j**: toluene, **3g**: C_6H_{14}; **3i**: C_6H_{14} : $CH_3C_6H_5$ = 2 : 1, **2b**, **3k**, **3l**: CH_2Cl_2, **3h**: C_6H_{14} : $CH_3COOC_2H_5$ = 1 : 2), and recrystallized (**2b**, **2c**, **3b**, **3d**, **3e**, **3f**, **3g**, **3h**, **3i**, **3j**, **3l**: C_6H_{14}, **3k**: $CH_3C_6H_5$). The physical and spectral data are shown below.

4-(4-Nitrophenylazo)diphenylamine (2b): Mp 163.9 °C (lit[11] 157.5–158.0 °C).

4-(4-Nitronaphthylazo)diphenylamine (2c): Mp 182.9 °C; ^{1}H NMR (DMSO-d_6) δ 6.28–6.68 (m, 5H), 6.38 (d, J = 9.0 Hz, 2H), 7.03 (t, J = 8.5 Hz, 1H), 7.10–7.21 (m, 2H), 7.29 (d, J = 9.0 Hz, 2H), 7.68 (d, J = 8.5 Hz, 1H), 7.72–7.77 (m, 1H), 8.26–8.31 (m, 1H), 8.47 (br s, 1H); EIMS (70 eV) m/z (rel intensity) 368 (M$^+$; 51), 168 (100). Anal. Found: C, 72.10; H, 4.59; N, 14.69%.

Calcd for $C_{22}H_{16}N_4O_2$: C, 71.73; H, 4.38; N, 15.21%.

4-(4-Nitrophenylazo)triphenylamine (3b): Mp 145.5 °C (lit[12] 140 °C).

4-(2,4-Dinitrophenylazo)triphenylamine (3d): Mp 203.5 °C; ^{1}H NMR (DMSO-d_6) δ 6.95 (d, J = 8.8 Hz, 2H), 7.20–7.31 (m, 6H), 7.41–7.50 (m, 4H), 7.82 (d, J = 8.8 Hz, 2H), 7.89 (d, J = 9.0 Hz, 1H), 8.58 (dd, J = 9.0 and 2.7 Hz, 1H), 8.92 (d, J = 2.7 Hz, 1H); EIMS (70 eV) m/z (rel intensity) 439 (M^+; 100), 244 (87), 167 (16).

4-(2-Methyl-4-nitrophenylazo)triphenylamine (3e): Mp 153.5 °C; ^{1}H NMR (DMSO-d_6) δ 2.71 (s, 3H), 6.98 (d, J = 9.0 Hz, 2H), 7.18–7.27 (m, 6H), 7.40–7.47 (m, 4H), 7.66 (d, J = 9.0 Hz, 1H), 7.87 (d, J = 9.0 Hz, 2H), 8.15 (dd, J = 9.0 and 2.4 Hz, 1H), 8.29 (d, J = 2.4 Hz, 1H); EIMS (70 eV) m/z (rel intensity) 408 (M^+; 100), 244 (79), 167 (11). Anal. Found: C, 73.73; H, 5.09; N, 13.71%. Calcd for $C_{25}H_{20}N_4O_2$: C, 73.51; H, 4.94; N, 13.72%.

4-[4-Nitro-2-(trifluoromethyl)phenylazo]triphenylamine (3f): Mp 208.0 °C; ^{1}H NMR (DMSO-d_6) δ 6.97 (d, J = 9.0 Hz, 2H), 7.15–7.31 (m, 6H), 7.36–7.50 (m, 4H), 7.87 (d, J = 9.0 Hz, 2H), 7.95 (d, J = 9.0 Hz, 1H), 8.59 (s, 1H), 8.61 (d, J = 9.0 Hz, 1H); ^{19}F NMR (DMSO-d_6, ext. CF_3COOH) δ 20.69 (3F); EIMS (70 eV) m/z (rel intensity) 462 (M^+; 53), 244 (100), 167 (19). Anal. Found: C, 64.60; H, 3.52; N, 12.44%. Calcd for $C_{25}H_{17}F_3N_4O_2$: C, 64.93; H, 3.71; N, 12.12%.

4-[4-(Perfluorobutyl)phenylazo]triphenylamine (3g): Oil; ^{1}H NMR (DMSO-d_6) δ 6.99 (d, J = 8.8 Hz, 2H), 7.18–7.27 (m, 6H), 7.36–7.46 (m, 4H), 7.85 (d, J = 8.8 Hz, 2H), 7.87 (d, J = 8.3 Hz, 2H), 8.00 (d, J = 8.3 Hz, 2H); ^{19}F NMR (DMSO-d_6, ext. CF_3COOH) δ −46.90 (2F), −44.02 (2F), −31.38 (2F), −2.17 (3F); EIMS (70 eV) m/z (rel intensity) 567 (M^+; 92), 244 (100), 167 (17).

4-[4-(Trifluoromethylsulfonyl)phenylazo]triphenylamine (3h): Mp 146.6 °C; ^{1}H NMR (DMSO-d_6) δ 6.97 (d, J = 7.7 Hz, 2H), 7.24–7.26 (m, 6H), 7.43–7.47 (m, 4H), 7.90 (d, J = 7.7 Hz, 2H), 8.13 (d, J = 7.7 Hz, 2H), 8.30 (d, J = 7.7 Hz, 2H); EIMS (70 eV) m/z (rel intensity) 481 (M^+; 93), 244 (100), 167 (18), 76 (15). Anal. Found: C, 62.60; H, 4.06; N, 8.40%. Calcd for $C_{25}H_{18}F_3N_3O_2S$: C, 62.36; H, 3.77; N, 8.73%.

4-[4-(Perfluorohexylsulfonyl)phenylazo]triphenylamine (3i): Mp 119.3 °C; ^{1}H NMR (DMSO-d_6) δ 6.97 (d, J = 8.8 Hz, 2H), 7.19–7.31 (m, 6H), 7.40–7.48 (m, 4H), 7.89 (d, J = 8.8 Hz, 2H), 8.12 (d, J = 8.3 Hz, 2H), 8.29 (d, J = 8.3 Hz, 2H); ^{19}F NMR (DMSO-d_6, ext. CF_3COOH) δ −47.46 (2F), −44.19 (2F), −43.25 (2F), −41.46 (2F), −33.35 (2F), −3.02 (3F); EIMS (70 eV) m/z (rel intensity) 731 (M^+; 55), 348 (36), 244 (100), 167 (11). Anal. Found: C, 49.48; H, 2.77; N, 5.58%. Calcd for $C_{30}H_{18}F_{13}N_3O_2S$: C, 49.26; H, 2.48; N, 5.74%.

4-(5-Nitro-2-thiazolylazo)triphenylamine (3j): Mp 209.0 °C (lit[13] 208–209 °C).

4-(6-Nitro-2-benzothiazolylazo)triphenylamine (3k): Mp 219.4 °C (lit[13] 209–211 °C).

4-[5-(4-Nitrophenylsulfonyl)-2-thiazolylazo]triphenylamine (3l): Mp 210.8 °C; ^{1}H NMR (DMSO-d_6) δ 6.86 (d, J = 9.1 Hz, 2H), 7.29–7.38 (m, 6H), 7.43–7.55 (m, 4H), 7.86 (d, J = 9.1 Hz, 2H), 8.32 (d, J = 8.8 Hz, 2H), 8.44 (d, J = 8.8 Hz, 2H), 8.71 (s, 1H); EIMS (70 eV) m/z (rel intensity) 541 (M^+; 47), 244 (100), 167 (22). Anal. Found: C, 59.33; H, 3.64; N, 12.72%. Calcd for $C_{27}H_{19}N_5O_4S_2$: C, 59.88; H, 3.54; N, 12.93%.

Synthesis of 4-(4-Aminoarylazo)triphenylamines (2a, 3a, 5a, and 6a). To a decalin solution (5 cm^3) of 4-aminoazobenzene **4a** (1.48 g, 7.5 mmol) or 4-phenylazo-1-naphthylamine **4′a** (1.74 g, 7.5 mmol) were added iodobenzene (7.66 g, 37.5 mmol), copper powder (0.38 g, 6 mmol), and potassium hydroxide (3.5 g, 61.5 mmol), the mixture was heated at 150 °C for 8 h. After the reaction was completed, the mixture was steam-distilled. The resulting precipitate was purified by silica-gel column chromatography ($CH_3C_6H_5$) and recrystallized from hexane. The physical and spectral data are given below.

4-(Phenylazo)diphenylamine (2a): Mp 87.9 °C (lit[14] 82 °C).

4-(Phenylazo)triphenylamine (3a): Mp 113.0 °C; ^{1}H NMR (DMSO-d_6) δ 7.01 (d, J = 8.8 Hz, 2H), 7.16–7.21 (m, 6H), 7.34–7.43 (m, 4H), 7.50–7.58 (m, 3H), 7.80 (d, J = 8.8 Hz, 2H), 7.81–7.82 (m, 2H); EIMS (70 eV) m/z (rel intensity) 349 (M^+; 70), 244 (100), 167 (21), 77 (68).

***N*-Phenyl-4-(phenylazo)naphthylamine (5a):** Mp 152.0 °C (lit[15] 151 °C).

***N*,*N*-Diphenyl-4-phenylazonaphtylamine (6a):** Mp 144.3 °C; ^{1}H NMR (DMSO-d_6) δ 6.96–7.07 (m, 4H), 7.16–7.27 (m, 6H), 7.34–7.62 (m, 6H), 7.83 (d, J = 8.1 Hz, 1H), 7.98 (d, J = 8.6 Hz, 1H), 8.03–8.05 (m, 2H), 8.99 (d, J = 8.6 Hz, 1H); EIMS (70 eV) m/z (rel intensity) 399 (M^+; 100), 294 (65), 216 (22). Anal. Found: C, 84.35; H, 5.49; N, 10.30%. Calcd for $C_{28}H_{21}N_3$: C, 84.18; H, 5.30; N, 10.52%.

Synthesis of 4-(4-Aminoarylazo)triphenylamines (7b, 7e, and 7f). An ethanol solution (30 cm^3) of 4-(4-nitroarylazo)-*N*,*N*-diphenylamine **3** (1.0 mmol) and sodium sulfide (480 mg, 2.0 mmol) was refluxed for 1 h. After the reaction was completed, the solution was poured into water (200 cm^3). The product was extracted with ethyl acetate and purified by silica-gel column chromatography ($CH_3C_6H_5$). The physical and spectral data are given below.

4-(4-Aminophenylazo)triphenylamine (7b): Mp 164.0–165.0 °C; ^{1}H NMR (DMSO-d_6) δ 5.96 (s, 2H), 6.66 (d, J = 9.0 Hz, 2H), 7.01 (d, J = 9.0 Hz, 2H), 7.08–7.17 (m, 6H), 7.32–7.41 (m, 4H), 7.60 (d, J = 9.0 Hz, 2H), 7.67 (d, J = 9.0 Hz, 2H).

4-(4-Amino-2-methylphenylazo)triphenylamine (7e): Mp 60–61 °C; ^{1}H NMR ($CDCl_3$) δ 3.62 (s, 3H), 3.90 (s, 2H), 6.53 (dd, J = 8.8 and 2.4 Hz, 1H), 6.58 (d, J = 2.4 Hz, 1H), 7.05–7.16 (m, 8H), 7.27–7.31 (m, 4H), 7.62 (d, J = 8.8 Hz, 1H), 7.74 (d, J = 9.0 Hz, 2H); EIMS (70 eV) m/z (rel intensity) 378 (M^+; 100), 244 (42), 167 (14).

4-[4-Amino-2-(trifluoromethyl)phenylazo]triphenylamine (7f): Mp 134.5–135.0 °C; ^{1}H NMR (DMSO-d_6) δ 6.39 (s, 2H), 6.84 (d, J = 9.0 Hz, 1H), 7.01 (d, J = 8.8 Hz, 2H), 7.02 (s, 1H), 7.09–7.19 (m, 6H), 7.33–7.42 (m, 4H), 7.68 (d, J = 8.8 Hz, 2H), 7.71 (d, J = 9.0 Hz, 1H); ^{19}F NMR (DMSO-d_6, ext. CF_3COOH) δ 21.68 (3F); EIMS (70 eV) m/z (rel intensity) 432 (M^+; 100), 244 (92), 167 (16).

Synthesis of Bisazo NLOphores (11–15). 4-(4-Aminoarylazo)diphenylamine **7** (0.5 mmol) reacted with nitrosobenzenes (0.5 mmol) (**8**: room temperature, 5 h; **9**, **10**: 70 °C, 2 h) in acetic acid (50 cm^3). After the reaction was completed, the mixture was poured into water (300 cm^3). The product was extracted with ethyl acetate, purified by silica-gel column chromatography (**11**, **12**, **13**: $CH_3C_6H_5$, **14**: $CH_3C_6H_5$:C_6H_{14} = 1:1, **15**: C_6H_{14}) and recrystallized from a hexane–toluene mixed solution. The physical and spectral data are given below.

4-[4-(4-Nitrophenylazo)phenylazo]triphenylamine (11): Mp 241.6 °C; ^{1}H NMR ($CDCl_3$) δ 7.11 (d, J = 9.0 Hz, 2H), 7.13–7.27 (m, 6H), 7.31–7.37 (m, 4H), 7.85 (d, J = 9.0 Hz, 2H), 8.03 (d, J = 8.5 Hz, 2H), 8.07 (d, J = 9.0 Hz, 2H), 8.11 (d, J = 8.5 Hz, 2H), 8.41 (d, J = 9.0 Hz, 2H); EIMS (70 eV) m/z (rel intensity) 498 (M^+; 84), 244 (100), 167 (30). Anal. Found: C, 72.38; H, 4.66; N, 16.53%. Calcd for $C_{30}H_{22}N_6O_2$: C, 72.28; H, 4.45; N, 16.86%.

4-[2-Methyl-4-(4-nitrophenylazo)phenylazo]triphenylamine (12): Mp 221.5 °C; ^{1}H NMR ($CDCl_3$) δ 2.78 (s, 3H), 7.12 (d, J = 8.8 Hz, 2H), 7.08–7.25 (m, 6H), 7.29–7.38 (m, 4H), 7.77 (d, J = 8.7 Hz, 1H), 7.85 (d, J = 8.8 Hz, 2H), 7.89 (d, J = 8.7 Hz, 1H), 7.94 (s, 1H), 8.05 (d, J = 8.8 Hz, 2H), 8.40 (d, J = 8.8 Hz, 2H); EIMS (70 eV) m/z (rel intensity) 512 (M^+; 100), 244 (89), 167 (17). Anal. Found: C, 72.69; H, 4.84; N, 16.22%. Calcd for $C_{31}H_{24}N_6O_2$: C, 72.64; H, 4.72; N, 16.40%.

4-[4-(4-Nitrophenylazo)-2-(trifluoromethyl)phenylazo]triphenylamine (13): Mp 204.3 °C; ^{1}H NMR ($CDCl_3$) δ 7.09 (d, J = 8.8 Hz, 2H), 7.12–7.28 (m, 6H), 7.27–7.42 (m, 4H), 7.89 (d, J = 8.8 Hz, 2H), 7.99 (d, J = 8.5 Hz, 1H), 8.10 (d, J = 8.8 Hz, 2H), 8.21 (d, J = 8.5 Hz, 1H), 8.42 (d, J = 8.8 Hz, 2H), 8.43 (s, 1H); ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) δ 19.40 (3F); EIMS (70 eV) m/z (rel intensity) 566 (M^+; 16), 244 (100), 167 (15). Anal. Found: C, 65.91; H, 3.89; N, 14.82%. Calcd for $C_{31}H_{21}F_3N_6O_2$: C, 65.72; H, 3.74; N, 14.83%.

4-{4-[4-Nitro-2-(trifluoromethyl)phenylazo]-2-(trifluoromethyl)phenylazo}triphenylamine (14): Mp 270.3 °C; ^{1}H NMR ($CDCl_3$) δ 7.09 (d, J = 9.1 Hz, 2H), 7.15–7.24 (m, 6H), 7.32–7.39 (m, 4H), 7.89 (d, J = 9.1 Hz, 2H), 7.99 (d, J = 8.8 Hz, 1H), 8.01 (d, J = 8.8 Hz, 1H), 8.21 (dd, J = 8.8 and 2.1 Hz, 1H), 8.47 (d, J = 2.1 Hz, 1H), 8.54 (dd, J = 8.8 and 2.2 Hz, 1H), 8.47 (d, J = 2.2 Hz, 1H); ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) δ 19.24 (3F), 19.44 (3F); EIMS (70 eV) m/z (rel intensity) 634 (M^+; 16), 244 (100), 167 (12). Anal. Found: C, 60.79; H, 3.27; N, 13.33%. Calcd for $C_{32}H_{20}F_6N_6O_2$: C, 60.57; H, 3.18; N, 13.24%.

4-[4-Pentafluorophenylazo-2-(trifluoromethyl)phenylazo]triphenylamine (15): Mp 208.8 °C; ^{1}H NMR ($CDCl_3$) δ 7.09 (d, J = 9.0 Hz, 2H), 7.14–7.24 (m, 6H), 7.33–7.38 (m, 4H), 7.89 (d, J = 9.0 Hz, 2H), 7.98 (d, J = 8.7 Hz, 1H), 8.16 (dd, J = 8.7 and 2.0 Hz, 1H), 8.38 (d, J = 2.0 Hz, 1H); ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) δ −84.00 (2F), −73.36 (1F), −71.35 (2F), 19.36 (3F); EIMS (70 eV) m/z (rel intensity) 611 (M^+; 15), 244 (100), 167 (22). Anal. Found: C, 61.22, H, 2.96; N, 11.54%. Calcd for $C_{31}H_{17}F_8N_5$: C, 60.89; H, 2.80; N, 11.45%.

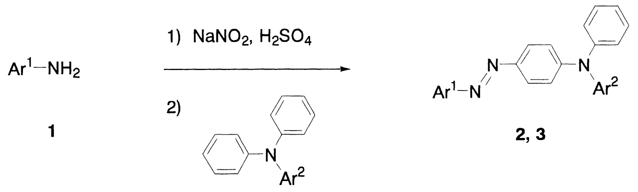
MO Calculation. Geometry optimization and a calculation of the hyperpolarizability (β) were carried out by a MOPAC98 program with the AM1 Hamiltonian.[16]

Solubility Measurement. A saturated ethanol solution of a NLOphore was prepared at 25 °C. After diluting the solution, its UV-vis absorption spectrum was measured. The solubility was calculated based on the ε value of the NLOphore at λ_{max}.

Preparation of Sol–Gel Films. A mixed solution of TEOS: tetrahydrofuran (THF):2-propanol:conc. hydrochloric acid:water: NLOphore = 1:5.8:1:1.4:4.4:0.015 in molar ratio was spin-coated (2000 rpm) on a slide glass. After drying, the film was heated at 110 °C for 10 min and then at 150 °C for 15 min.

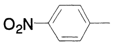
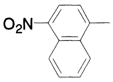
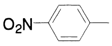
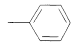
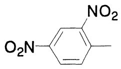
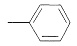
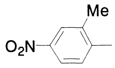
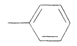
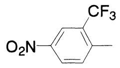
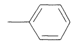
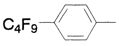
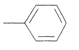
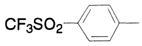
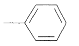
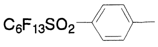
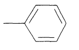
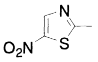
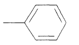
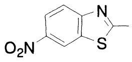
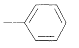
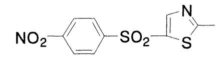
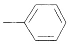
Results and Discussion

Monoazo NLOphores **2b**, **2c**, **3b**, and **3d–l** were prepared by diazotization of the starting materials **1** followed by coupling with arylamines, as shown in Scheme 1 and Table 1. Since the coupling ability of arylamines with arenediazonium salts is low, the desired products are given in low yields.



Scheme 1.

Table 1. Synthesis of NLOphores **2b**, **2c**, **3b**, and **3d–l**

Starting material		Arylamine	Product	
Compd	Ar^1	Ar^2	Compd	Yield$^{a)}$/%
1b		H	**2b**	31
1c		H	**2c**	26
1b			**3b**	18
1d			**3d**	5
1e			**3e**	17
1f			**3f**	30
1g			**3g**	28
1h			**3h**	9
1i			**3i**	21
1j			**3j**	5
1k			**3k**	5
1l			**3l**	7

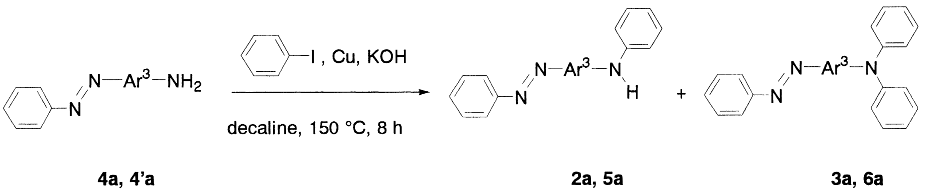
a) Isolated yields.

Monoazo NLOphores **2a**, **3a**, **5a**, and **6a** were obtained by the N-phenylation of aminoazo precursors **4a** and **4′a**, as shown in Scheme 2 and Table 2.

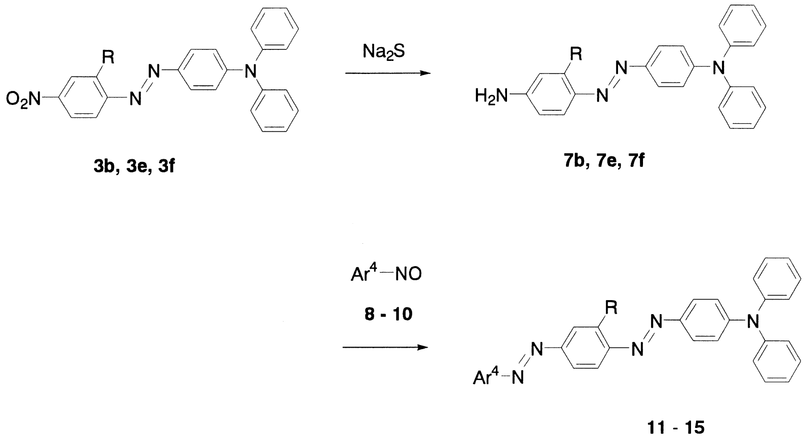
Scheme 3 shows the synthesis of bisazo NLOphores **11–15**. The monoazo nitro intermediates **3b**, **3e**, and **3f** were converted into the amino derivatives **7b**, **7e**, and **7f**, which further reacted with nitroso compounds **8–10** to provide the bisazo NLOphores **11–15** in low to good yields. The results are summarized in Table 3. These NLOphores **11–15** were not obtained by diazotization of the corresponding monoazo amino derivatives, followed by a coupling reaction with triphenylamine.

The properties of azo NLOphores **2**, **3**, **5a**, **6a**, and **11–15** are indicated in Table 4.

The structure of synthesized NLOphores can be classified into four groups: 1) less polar monoazo derivatives **2a**, **3a**, **5a**, and **6a**, 2) polar monoazo derivatives **2b**, **2c**, **3b**, and **3d–i**, 3)

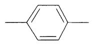
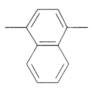


Scheme 2.



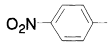
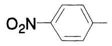
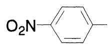
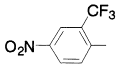
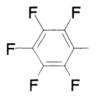
Scheme 3.

Table 2. Synthesis of NLOphores **2a**, **3a**, **5a**, and **6a**

Starting material		Product	
Compd	Ar^3	Compd	Yield$^{a)}$/%
4a		**2a** **3a**	29 26
4′a		**5a** **6a**	36 8

a) Isolated yields.

Table 3. Synthesis of NLOphores **11–15**

Starting material		Nitroso derivative		Product	
Compd	R	Compd	Ar^4	Compd	Yield$^{a)}$/%
3b	H	—	—	**7b**	74
3e	Me	—	—	**7e**	50
3f	CF_3	—	—	**7f**	60
7b	H	**8**		**11**	77
7e	Me	**8**		**12**	72
7f	CF_3	**8**		**13**	75
7f	CF_3	**9**		**14**	30
7f	CF_3	**10**		**15**	24

a) Isolated yields.

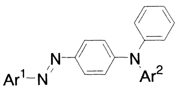
hetaryl monoazo derivatives **3j–l**, and 4) bisazo derivatives **11–15**.

The second-order nonlinearity was evaluated by calculating the $\mu\beta$ value of the molecules, where μ and β represent the dipole moment and second-order hyperpolarizability, respectively. We optimized the geometry under the constraint of the planar *trans* form for the azo NLOphores. The nonlinearity was calculated almost in the following order: hetaryl monoazo derivatives **3j–l** (580–602), bisazo derivatives **11–15** (397–920), polar monoazo derivatives **2b**, **2c**, **3b**, and **3d–i** (231–913) > less polar monoazo derivatives **2a**, **3a**, **5a**, and **6a** (3.19–24.1). It is reported that the heterocyclic compounds showed an enhanced second-order nonlinearity.[17] Interestingly, monoazo NLOphores substituted with two electron-withdrawing or perfluoroalkylsulfonyl group(s) **3d** (757), **3f** (580), **3h** (629), and **3i** (913) showed higher nonlinearity than the hetaryl monoazo derivatives **3j–l** (580–602). A bisazo NLOphore having two electron-withdrawing groups in a terminal phenyl moiety, 4-nitro-2-(trifluoromethyl)phenyl derivative **14**, showed large nonlinearity (920).

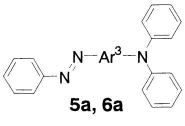
The thermostability was evaluated by measuring the decomposition temperature (T_d) of NLOphores. The typical example in the TG-DTA is shown in Fig. 1. A sharp endothermic peak corresponding to the melting point was observed at 145.5 °C, followed by an exothermic peak with decreasing weight at higher temperature. T_d is defined as shown in the figure, being 354 °C for the NLOphore **3b**.

The T_d's of other NLOphores are also indicated in Table 4. T_d was essentially in the following order: i.e., bisazo derivatives **11–15** (316–397 °C) > hetaryl monoazo derivatives **3j–l** (280–348) > polar monoazo derivatives **2b**, **2c**, **3b**, and **3d–i** (283–355) > less polar monoazo derivatives **2a**, **3a**, **5a**, and **6a** (282–332). Since the melting points of fluorine-containing monoazo derivatives **3g–i** (oil–147 °C) were rather low, their T_d's were also low. Meanwhile, the melting points of all the bisazo derivatives **11–15** were higher than 200 °C, resulting in a higher T_d (> 316).

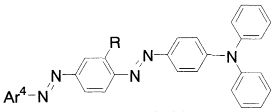
Table 4. Physical Properties of Azo NLOphores



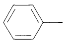
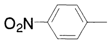
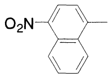
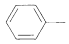
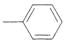
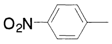
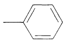
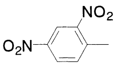
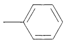
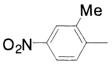
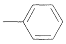
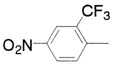
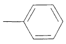
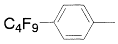
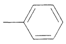
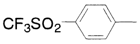
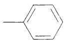
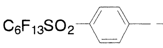
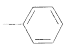
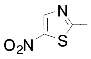
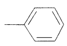
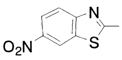
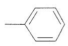
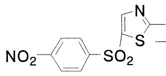
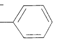
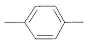
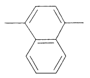
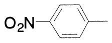
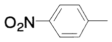
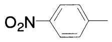
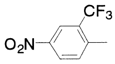
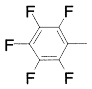
2, 3



5a, 6a



11-15

Compd	Ar¹	Ar²	Ar³	Ar⁴	R	λ_{max}[a]	ε[a]	μ[b]	β[b]	$\mu\beta$	T_d[c]	Solubility[d]
						nm		Debye	10^{-30} esu		°C	mmol dm^{-3}
2a		H	—	—	—	417	14000	1.36	17.7	24.1	288	1170
2b		H	—	—	—	474	35000	8.20	39.3	322	315	44.1
2c		H	—	—	—	491	33000	8.27	39.5	327	333	2.43
3a			—	—	—	411	16000	0.81	20.0	16.2	313	193
3b			—	—	—	474 (486[e])	17000	7.99 (5.87[e])	46.9 (54.3[e])	375	354 (393[e])	6.01
3d			—	—	—	441	18000	8.80	86.0	757	355	0.60
3e			—	—	—	473	28000	7.94	48.1	382	304	1.49
3f			—	—	—	501	29000	8.13	71.3	580	300	0.58
3g			—	—	—	441	26000	5.61	59.9	231	283	228
3h			—	—	—	472	22000	10.5	59.9	629	303	7.41
3i			—	—	—	476	31000	11.4	80.2	913	307	3.96
3j			—	—	—	567 (582[e])	33000	8.38 (6.89[e])	69.2 (68.2[e])	580	297 (295[e])	0.35
3k			—	—	—	540 (550[e])	31000	8.57 (7.21[e])	70.3 (71.8[e])	602	348 (356[e])	0.20
3l			—	—	—	545	14000	8.66	69.5	602	280	0.78
5a	—	—		—	—	455	23000	1.12	18.0	20.2	282	10.6
6a	—	—		—	—	452	13000	0.43	7.4	3.19	332	4.66
11	—	—	—		H	496	10300	7.92	68.4	541	378	0.08
12	—	—	—		Me	496	12300	8.06	66.6	537	316	0.02
13	—	—	—		CF$_3$	517	12900	7.80	85.2	665	397	0.34
14	—	—	—		CF$_3$	517	6800	8.79	104.7	920	363	0.04
15	—	—	—		CF$_3$	513	19500	4.96	80.0	397	361	0.21

a) Measured in hexane. b) Calculated by a MOPAC98-AM1 program. c) Measured by TG–DTA (10 °C min^{-1} under an air atmosphere). d) Measured in ethanol at 25°C. e) Ref. 6.

The solubility was almost in the order of the dye skeleton: less polar monoazo derivatives **2a**, **3a**, **5a**, and **6a** (4.66–1170 mmol dm^{-3}) $>$ polar monoazo derivatives **2b**, **2c**, **3b**, and **3d–i** (0.58–228) $>$ hetaryl monoazo derivatives **3j–l** (0.20–0.78) $>$ bisazo derivatives **11–15** (0.02–0.34). In the polar monoazo derivatives, 4-(trifluoromethylsulfonyl)phenyl derivative **3h** (7.41) was more soluble than the 4-nitrophenyl derivative **3b** (6.01). Interestingly, short-chain perfluoroalkylsulfonyl derivatives are usually more soluble than the nitro derivative.[18] The 4-(perfluorobutyl)phenyl derivative **3g** was very soluble. The improved solubility by introducing a perfluoroalkyl group at the *p*-position in a series of dichroic bisazo dyes has also been

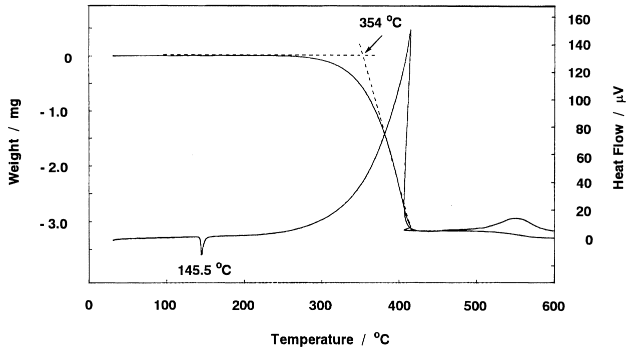


Fig. 1. TG–DTA curve of NLOphore **3b**. Measured by TG–DTA (10 °C min^{-1} under an air atmosphere).

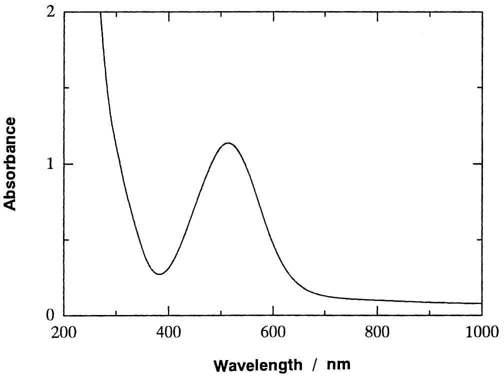


Fig. 2. UV-vis absorption spectrum of sol-gel film of **3b** prepared from TEOS.

reported.[4] In the case of bisazo derivatives **11–13**, the solubility of **13** (0.34) was larger than those of **11** (0.08) and **12** (0.02). Thus, introducing a bulky trifluoromethyl group into the central phenylene ring could improve the solubility. A similar result, that the solubility is improved by introducing bulky fluoroalkyl groups into 3,4;9,10-perylenetetracarboxydiimides, has been reported.[19]

A survey of NLOphores has been reported.[6] Unfortunately, the solubility of NLOphores was not taken into account in the paper. However, the solubility of NLOphores was the most important factor to prepare a good sol-gel film. It was found that the NLOphores were more soluble in a tetrahydrofuran (THF)–2-propanol mixed solvent than in ethanol. It was also found that the value of the solubility in ethanol at 25 °C should be larger than 2.0 mmol dm^{-3} to prepare good sol-gel films from TEOS. The solubility of NLOphores **2a**, **2b**, **2c**, **3a**, **3b**, **3g**, **3h**, **3i**, **5a**, and **6a** were larger than 2.0 mmol dm^{-3}. These NLOphores could be further classified into three groups: 1) non-nitro-containing NLOphores, **2a**, **3a**, **5a**, and **6a**, 2) nitro-containing NLOphores **2b**, **2c**, and **3b**, and 3) fluorine-containing NLOphores **3g**, **3h**, and **3i**. Non-nitro-containing NLOphores **2a**, **3a**, **5a**, and **6a** could show high solubility (4.66–1170 mmol dm^{-3}). However, their second-order nonlinearity was low (3.19–24.1). Nitro-containing NLOphores **2b**, **2c**, and **3b** showed a rather high T_d (315–354 °C) and medium nonlinearity (322–375). Fluorine-containing NLOphores **3h** and **3i** showed high nonlinearity (629 and 913). Though the solubility of the perfluorobutyl derivative **3g** was high (228), its T_d (283) and nonlinearity (231) were rather low.

A sol-gel film of NLOphore **3b** was prepared by an acid-catalyzed process as an example. The film was transparent and homogeneous, as indicated in Fig. 2. The absorption maximum (λ_max) was observed at 514 nm, being more bathochromic than that in ethanol. This can be attributed to the more polar circumstances in the sol-gel film than in ethanol.

Conclusions

We examined mono- and bisazo NLOphores having high second-order nonlinearity, high thermostability, and high solubility. The most important factor to prepare a sol-gel film from TEOS was the solubility. Several compounds showed sufficient solubility into ethanol. They were further classified into three groups: non-nitro-containing, nitro-containing, and fluorine-containing derivatives. Though non-nitro-containing NLOphores show high solubility, their second-order nonlinearity was low. Nitro-containing NLOphores showed a rather high T_d and medium nonlinearity. Fluorine-containing NLOphores, especially perfluoroalkylsulfonyl derivatives, showed high nonlinearity and a rather low T_d. The sol-gel film prepared from 4-(4-nitrophenylazo)triphenylamine was transparent and homogeneous.

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