Novel Naphthoquinone Methide Dyes for Second-order Nonlinear Optical Materials

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Naphthoquinone methide dyes show a large Pockels coefficient at 1.3 μm when poled in a polymer matrix: the second-order nonlinear hyperpolarizability (μβ) values obtained from Pockels coefficients that appear after poling in a constant electric field are (5700–7400) × 10^{-48} esu, being much higher than that of commonly used Disperse Red 1 (DR1).

Extensive efforts have been directed toward the design and synthesis of new molecular chromophores possessing large values of the first molecular hyperpolarizability (β) for use in NLO.[1,2] Poled polymers have been explored because they offer high β.[3–5] High β values might be compromised by disturbance of polar orientation of the chromophore and longer π-conjugated systems reducing non-linearity for molecular mass. Poling can overcome these problems and our strategy to obtain high-β performance poled polymer makes use of small chromophores possessing powerful donor–acceptor segments and with steric hindrance between these segments to avoid intermolecular interactions.

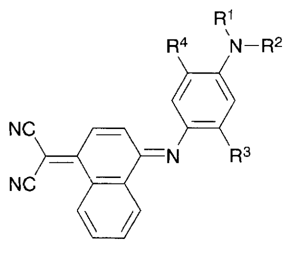
Naphthoquinone methide dyes **1**,[6] possessing a dicyanomethylene group as a powerful acceptor, could satisfy the requirements above because they are relatively small molecules (M_w 353–440) and absorb visible and near-IR light (λ_{max} *ca.* 700–800 nm) in spite of the large steric hindrance between donor and acceptor segments.[7] Moreover, if the wavelength of a laser for which a poled polymer is designed to be used is fixed at the wavelength used in telecommunications (1.3 or 1.55 μm), the wavelength of the chromophore absorption band could be located in the visible region. So far, few chromophores with such long wavelength absorptions have been investigated in this field. Thus, from the point of view of developing a new type of NLO material, this chromophore is of significant interest.

In this communication, we report the synthesis of new naphthoquinone methide dyes as NLO chromophores, the μβ values of which have been obtained from the Pockels coefficients after poling in polymer matrices in an attempt to develop materials with useful NLO properties.

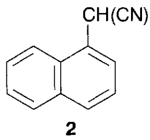
Compounds **1** have been synthesized as described previously.[6] The compound **2**, 1-naphthylmalononitrile,[8] as a coupler has been prepared *via* three steps from 1-naphthylacetonitrile. The condensation reaction of **2** with aniline derivatives in the presence of an oxidizing agent under alkaline conditions has produced the desired **1** in 15–29% yield, respectively, after purification. The structures were confirmed.[†] Poly(methylmethacrylate) (PMMA) films (2–3 μm) doped with **1** have been prepared by the spin-coating procedure onto an indium tin oxide (ITO) glass substrate from cyclopentanone. After removing residual solvent, a thin layer of gold was deposited under vacuum on to films as top electrode for poling. The samples were poled at 110 °C in a 0.5 MV cm^{-1} electric field for 10 min. After cooling, electric-field induced birefringence was measured by overlapping a 10 V_{rms} AC voltage (preventing decay of dye orientation induced by the removal of the DC poling field). The λ_{max} values of **1** in PMMA films are 728–802 nm, showing a bathochromic shift by 4–12 nm compared with those in ethyl acetate solution (see Table 1). The μβ products of **1** have been determined from their Pockels coefficients[9] as being more direct than EFISH. The relation between μβ and Pockels coefficient r_{33} is shown in eqn. (1) where n is refractive index,

$$r_{33} = \frac{2\chi^{(2)}}{n^4},\ \chi^{(2)} = \frac{Nf_\omega^2 f_0 f_0'(\mu\beta E_p)}{5kT_p} \qquad (1)$$

N is concentration of the chromophore, f_ω and f_0 are the local factors of frequency ω (light) and 0, respectively, f_0' is the local field factor of zero frequency at the poling temperature, E_p is poling electric field, k is Boltzmann's constant, and T_p is the temperature at which the molecular orientation is determined. Eqn. (1) is based on the assumption that a chromophore in a poled polymer does not aggregate: we have investigated the concentration dependence of r_{33} for naphthoquinone methide chromophore and have obtained a good linear relationship (*e.g.* see Fig. 1). The μβ values can be estimated from the slope of the straight line. The local field factor for poling electric field (E_p = 0.5 MV cm^{-1}) can be calculated from the static dielectric factor at T_p, the total value of which ($f_w^2 f_0 f_0'$) is assumed to be 7, being slightly larger than that for PMMA. T_p is also assumed to be 100 °C. These assumptions do not affect the calculation of μβ greatly and the error should be 30%. However, the error of the relative values for different samples should be less, which is good enough for the comparison of many different dyes. In



1a R^1 = Et, R^2 = CH_2CH_2OH, R^3 = Me, R^4 = H
b R^1 = R^2 = Et, R^3 = R^4 = H
c R^1 = R^2 = Et, R^3 = NHCOMe, R^3 = OMe



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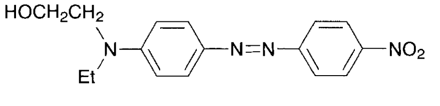

DR1

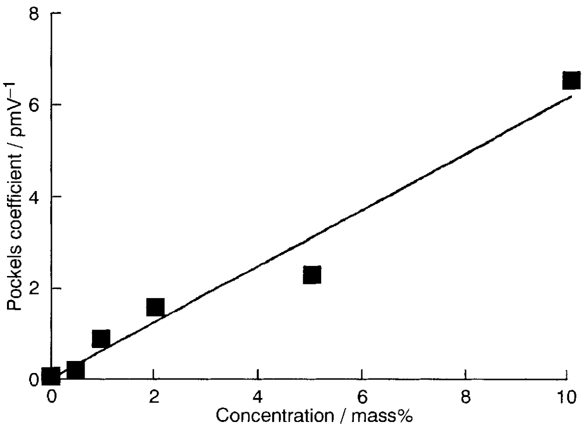

Fig. 1 Concentration dependence of Pockels coefficients for **1a** after poling in 0.5 MV cm^{-1} electric field in PMMA

order to estimate the accuracy for the measurement, the μβ value of well-known Disperse Red 1 (DR1) has been obtained ($\mu\beta = 825 \times 10^{-48}$ esu measured at 1.31 μm), which is fairly consistent with that ($\mu\beta = 1080 \times 10^{-48}$ esu) derived from the EFISH method. In Table 1, obtained μβ values of **1** as well as DR1 are summarized. Compounds **1** have μβ values of (5700–7400) × 10^{-48} esu, being much higher than that of DR1, while increments of the molecular masses of these dyes are small, suggesting that the compounds **1** could be of interest in the context of efficient NLO chromophores. Why have naphthoquinone methide-type chromophores produced dramatic enhancement of nonlinear responses? The origin of the nonlinearity can be discussed on the basis of the model of the two-level system, see eqn. (2)[10] where f is oscillator strength,

$$\mu\beta = \frac{e^2h^2}{2m} f \Delta\mu\cdot\mu \frac{1}{hc} \frac{2(3\nu_{eg}^2 - \nu_o^2)}{\nu_{eg}(\nu_{eg}^2 - \nu_0^2)} \qquad (2)$$

$\Delta\mu$ is the difference in dipole moment between ground and excited states, μ is the ground state dipole moment, ν_{eg} is a transition frequency, and ν is laser frequency. The μβ product should be influenced by four parts, *i.e.* μ, f, $\Delta\mu$, and the dispersion term $[2(3\nu_{eg}^2 - \nu^2)/\nu_{eg}(\nu_{eg}^2 - \nu^2)]$. On the basis of our measurements, the nonlineality of the naphthoquinone methide-type chromophore is compared with that of DR1 as shown in Table 2. Whereas f and $\Delta\mu$ are less than that of DR1, the ratio of the dispersion term between **1a** and DR1 is calculated to be 6.4 from the spectroscopic data, indicating that enhancement in the dispersion term is the main cause of the large μβ for the naphthoquinone methide dyes. Another important factor for obtaining a large μβ is a small intermolecular interaction between chromophores: the concentration dependence of Pockels coefficient using **1a** after poling in 0.5 MV cm^{-1} electric field shows a good linear relationship (see Fig. 1), also indicating that the intermolecular interaction is quite small, which may be attributable to the non-planar structure of the dye.

Table 1 Absorption maxima, oscillator strength, μβ ($\omega = \omega + 0$) products in PMMA films at 1.31 μm

Compound	λ_{max}/nm	λ_{max}/nm[a]	μβ (10^{-48} esu)[b]
1a	752	743	6100 (3080)
1b	728	716	5700 (3040)
1c	802	798	7400 (3300)
DR1	470	—	825 (—)

[a] In ethyl acetate solution. [b] Values in parentheses represent $\mu\beta_0$, zero-frequency hyperpolarizability product, obtained from the extrapolation of the measured μβ values using the two-level model (ref. 11).

Table 2 Comparison of the spectroscopic data between **1a** and DR1

	1a	DR1
μ[a]/D	6.5	8.7
Δμ[b]/D	20	12
ν_{eg}[c]/cm^{-1}	13300	21300
f[d]	0.39	0.60
μβ (10^{-48} esu, calc.)[e]	4200	865
μβ (10^{-48} esu, obs.)	6100	825

[a] μ was obtained by measuring the concentration dependence of the dielectric constant and the refractive index of its dioxane solution: the data were analyzed according to the formula in ref. 11. [b] Δμ was obtained from the solvatochromism. [c] $\nu_{eg} = 1/\lambda_{max}$ [d] Oscillator strength. [e] From the two-level model (ref. 10).

Additionally, the incorporation of dyes into polymers as a side chain should be useful for obtaining high concentrations of the dye and for increasing the thermal stability of the poled polymers.

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Footnote

† *Data* for **1a**; mp 182–183 °C; ^{1}H NMR ($CDCl_3$) δ 1.24 (t, 3H, NCH_2CH_3), 1.69 (br, 1H, OH), 2.40 (s, 3H, Ar–CH_3), 3.87 (br. 2H, CH_2CH_2OH), 3.53 (m, 4H, NCH_2), 6.62 (d, *J* 8.8, 2.6 Hz, 1H, Ar H), 6.77 (d, *J* 2.4 Hz, 1H, Ar H), 6.69 (d, *J* 8.7 Hz, Ar H), 7.22 (d, *J* 10.2 Hz, 1H, quinoid H), 7.53 (d, *J* 10.2 Hz, 1H, quinoid H), 7.65 (m, 1H, ArH), 7.74 (m, 1H, Ar H), 8.73 (dd, *J* 7.9, 1.6 Hz, 1H, Ar H), 8.87 (dd, *J* 7.7, 1.6 Hz, 1H, Ar H); MS *m/z* 383 (M^+).

Data for **1b**; mp 140–141 °C; ^{1}H NMR ($CDCl_3$) δ 1.25 (t, 6H, NCH_2CH_3), 3.47 (q, 4H, NCH_2CH_3), 6.76 (d, *J* 9.2 Hz, 2H, Ar H), 7.10 (d, *J* 9.2 Hz, 2H, Ar H), 7.29 (d, *J* 9.8 Hz, 1H, quinoid H), 7.54 (d, *J* 10.2 Hz, 1H, quinoid H), 7.64 (m, 1H, Ar H), 7.73 (m, 1H, Ar H), 8.72 (dd, *J* 7.9, 1.6 Hz, 1H, Ar H), 8.88 (dd, *J* 7.7, 1.5 Hz, 1H, Ar H); MS *m/z* 353.

Data for **1c**: mp 193–194 °C; ^{1}H NMR ($CDCl_3$) δ 1.24 (t, 6H, NCH_2CH_3), 2.24 (s, 3H, $NHCOCH_3$), 3.46 (q, 4H, NCH_2CH_3), 3.81 (s, 3H, $ArOCH_3$), 6.50 (s, 1H, Ar H), 7.39 (d, *J* 10.2 Hz, 1H, quinoid H), 7.63 (d, *J* 10.2 Hz, 1H, quinoid H), 7.68 (m, 1H, Ar H), 7.76 (m, 1H, Ar H), 8.24 (s, 1H, Ar H), 8.54 (br., 1H, $NHCOCH_3$), 8.60 (dd, *J* 7.9, 1.6 Hz, 1H, Ar H), 8.95 (dd, *J* 8.0, 1.2 Hz, 1H, Ar H); MS *m/z* 441 ($M^+ + 2$), 426 ($M^+ + 2 -$ Me).

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