Tuning Second-Order Optical Nonlinearities in Push-Pull Benzimidazoles

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The synthesis and full characterization of new chromophores with second order optical nonlinearities containing the 2-phenyl-(5,6)-nitrobenzimidazole group is reported. Starting from 2-{4-[(4-*N*,*N*-dihydroxyethylamino)phenylazo]phenyl}-5(6)-nitrobenzimidazole, a combined theoretical and experimental approach, including theoretical computations of second order nonlinear optical activity (MNDO/AM1), X-ray structural analysis and synthetic strategies, has led to a significant optimization (more than 50%) of the NLO activity of related chromophores. The results indicate that 6-nitro-substituted compounds are more active than 5-nitro-substituted ones and that a further increase of NLO activity can be achieved by insertion of a carbon–carbon double bond between the benzimidazole and 2-phenyl rings. Calculations also suggest that an additional improvement of the nonlinearity should be expected upon functionalization of the N1 atom of the 6-nitrobenzimidazole with electron-withdrawing groups. Experimental nonlinearities (EFISH technique, $\mu\beta/10^{-48}$ esu, $\lambda = 1.907$ μm, DMF solution) between 940 and 1550 were measured.

Introduction

The study of molecular hyperpolarizabilities is a field of growing interest as it has been shown quite recently that organic compounds with high first order hyperpolarizabilities can be used as active components for electro-optical modulators capable of solving the main problem of fiber optic communication technology — the low voltage modulation at very high frequency (THz) in fiber optic communication links.[1]

The formulation of organic or hybrid (organic-inorganic) materials for applications in second order nonlinear optics (NLO) generally involves two distinct steps: first the preparation of an organic chromophore of adequate NLO activity and proper chemical functionalization (the two level model[2] provides the basic tool for designing NLO active compounds), and secondly its covalent or non-covalent insertion into a polymer or a three-dimensional network with successive (or simultaneous) polar alignment of the NLO-active segments.[3]

The choice of the chromophore is crucial because several key requirements must be satisfied.[3] Among those we can emphasise: high NLO activity, high chemical, photochemical and thermal stability, possibility of chemical functionalization (e.g. as diol or methacrylate ester) for polymerization or crosslinking, low tendency to give structured phases (crystalline or liquid-crystalline), low optical absorption in the 1.3 and 1.55 μm telecommunication bands (and corresponding second harmonic wavelengths), ease and low cost of synthesis.

In particular, chromophores bearing low aromaticity heterocycles along the conjugation path have been investigated both theoretically and experimentally and are considered as the most suitable for potential applications.[4]

Over the last few years we have systematically studied the properties of polymers containing the 2-phenyl-6-nitrobenzoxazole system in the chromophore moiety, where thermochemical stability and a fairly good NLO activity have been combined.[5] A closely related heterocycle system is 2-phenyl-(5,6)-nitrobenzimidazole (Scheme 1). Similar to benzoxazole, it shows excellent chemical and thermal stability and is relatively easy to synthesise.[6] Tautomerism is a feature of compounds containing a benzimidazole fragment due to the acid nature of the hydrogen atom bonded to nitrogen. An interesting feature of benzimidazole is the possibility of chemical functionalization at the nitrogen of the pentaatomic ring (for instance by alkylation), which removes the possibility of tautomerism (giving rise to two constitutional isomers) and introduces a new potentially useful chemical variable for the optimization of the NLO activity of the chromophore (e.g. introduction of groups with suitable electronic properties). The introduction of

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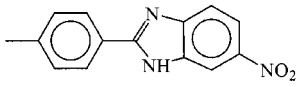
bulky lateral substituents on the chromophore is expected to positively affect the NLO performances of the material by reducing the extent of centrosymmetric dipolar coupling of the chromophores during poling.[3]



Scheme 1

In this paper we report the synthesis and characterization, including experimental (EFISH) and theoretical evaluation of second order molecular nonlinearity, of the benzimidazole chromophores shown in Scheme 2.

The chromophores are functionalized as diols and therefore they can be used as monomers in polycondensation reactions (acetylated models of **BI2** and **BIC2** have also been prepared for the X-ray structural characterization).

In spite of their potential benefits, benzimidazole compounds tailored for second order NLO applications have received little consideration up to now. We have found only two reports in the literature in which the properties of polymers based on chromophores similar to **BI2**, but based on the 5-nitro isomer rather than the 6-nitro isomer, were studied.[7] The 5-nitro isomer is the less NLO active isomer, as inferred from Kekulé conjugation schemes. Therefore, this paper is the first report on the molecular second order NLO activity of 6-nitrobenzimidazole chromophores.

Results and Discussion

The present work is a combined experimental and theoretical approach in which synthetic strategies and calculations of first order molecular hyperpolarizabilities lead to the design of new NLO-active organic molecules with improved performances. The thermal properties of the chromophores are reported in Table 1. A fair thermal stability is observed, with decomposition temperatures close to 300 °C for all the chromophores. Measured and calculated second order nonlinearities, as well as other related quantities are reported in Table 2 and Table 3, respectively. The data in Table 2, in particular, can be compared with those of the standard chromophores *p*-nitroaniline and Dispersed Red 1, for which μβ values are 80 and 580 (1.9 μm, 10^{-48} esu), respectively.[3a]

Table 1. Thermal properties of the chromophores

	M.p. (°C)[a]	$T_{dec.}$ (°C)[b]
BI1	–	296
BI2	221	295
BIC1	–	292
BIC2	270	314

[a] Melting temperature. [b] Decomposition temperature taken as the temperature corresponding to 5% weight loss in the thermogravimetric run (10 K/min, air).

Table 2. Experimental NLO properties of chromophores

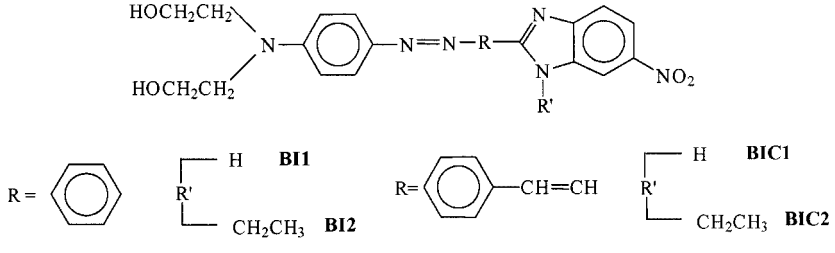
	μβ (10^{-48} esu)[a]	λ_{max} (nm)[b]	μβ(0) (10^{-48} esu)[c]
BI1	940	472	674
BI2	950	466	684
BIC1	1550	482	1074
BIC2	1400	487	968

[a] Measured by the EFISH technique in DMF at 1.907 μm. [b] Measured in DMF. [c] Extrapolated to zero frequency by the two-levels model.

Table 3. Calculated NLO properties of the chromophores

		μ (D)	β_{vec} (10^{-30} esu)	$\mu\beta_{vec}(0)$ (10^{-48} esu)
BI1	tautomer 5	11.9	38.2	454.6
	tautomer 6	10.8	48.2	520.6
BI2		10.9	44.5	485
BIC1	tautomer 5	10.9	46.4	505.8
	tautomer 6	10.9	53.9	587.0
BIC2		10.9	53.3	581.0
BICF		10.9	68.5	746.6

It is well-known that accuracy of computed hyperpolarizabilities is only achievable with very high computational costs.[8] However, in this context, reliable predictions of trends is the only thing which really matters, since the second order NLO response of all the chromophores was experimentally determined by the EFISH technique. Thus, we resorted to semiempirical methods because it has been shown by many authors[9] that low-cost semiempirical methods, in particular INDO[10] and MNDO[11] with both



Scheme 2

AM1 and PM3 parametrization, are useful in predicting reliable qualitative trends and relative magnitudes, so as to properly address synthetic modifications which improve the material's response.

Theoretical computations performed on both tautomers of **BI1** show two important structural features that could significantly affect its NLO activity. First of all, the benzimidazole and the 2-phenyl rings are not in a coplanar arrangement; the computed dihedral angle is about 32° for both the 5-nitro and 6-nitro tautomers as a consequence of the steric repulsion between the NH and *ortho*-phenyl hydrogens. Distortions from coplanarity usually decrease the molecular hyperpolarizabilities, as predicted by both the two-levels model[2] and by theoretical computations.[9a,9b,12] In the closely related case of 2-phenylbenzoxazole chromophores, theoretical computations have shown a significant decrease of β as the corresponding twist becomes greater than about 20°.[12] Secondly, according to the μβ(0) values (see Table 3), the 6-nitro tautomer of **BI1** has a significantly greater NLO activity than the 5-nitro one (about 10%), while the latter is slightly more stable than the former, the calculated energy difference being about 0.4 kcal/mol. Thus, computations suggest two ways to improve the NLO activity of this compound: removal of the tautomerism by considering only 6-nitro-substituted compounds and release of the steric hindrance by increasing the distance between the benzimidazole and 2-phenyl rings (without interrupting the π conjugation) in order to allow a more coplanar arrangement of the two rings.

With respect to the first point, we synthesized the 6-nitro-substituted **BI2** chromophore by selective alkylation of the starting nitro-phenylenediamine. In fact, since the amino group in the *para* position to the nitro group is much less nucleophilic than the amino group in the *meta* position, alkylation occurs only at the amino group in the 1-position of 5-nitro-1,2-phenylenediamine. In this paper only *N*-ethyl alkylated chromophores are described, but the synthetic procedures can be reasonably extended to more bulky alkyl groups.

Theoretical computations on chromophore **BI2** show that the advantage of having only the more active 6-nitro isomer is balanced by the increased dihedral angle between benzimidazole and the 2-phenyl rings (48.2° according to MNDO/AM1 full geometry optimization), due to the greater steric encumbrance of ethyl as compared to hydrogen. Nevertheless, the computed μβ(0) of **BI2** is slightly higher than the Boltzmann average of the μβ(0) of the two tautomers of **BI1** (476.9 $\cdot 10^{-48}$ esu), which is consistent with the experimental results (Table 2 and 3), thus confirming the reliability of the computational procedure adopted here in predicting how hyperpolarizability changes as the chemical structure of the chromophore is changed.

The X-ray molecular structure of the diacetate ester of **BI2** (**ACBI2**) is shown in Figure 1; selected bond lengths, bond angles and torsion angles are given in Table 4 for **ACBI2** and **ACBIC2**, together with the computed values. The computed MNDO/AM1 optimum geometries are in good agreement with the X-ray data, the bond lengths being reproduced to within 0.02 Å; only the dihedral angles

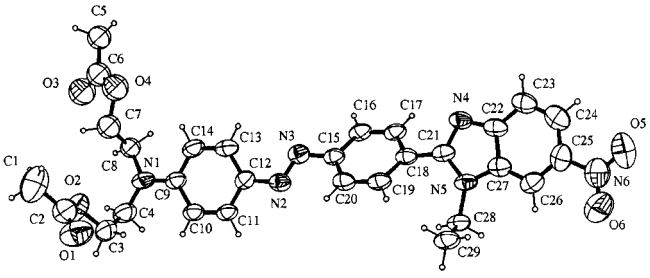


Figure 1. ORTEP drawing of **ACBI2**; thermal ellipsoids are shown at the 30% probability level

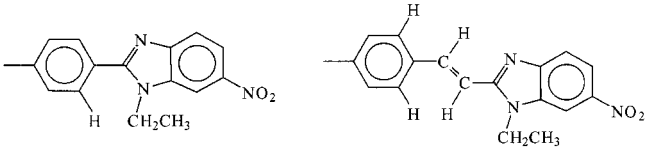
Table 4. Selected bond lengths (Å), bond angles (°) and torsion angles (°) for **ACBI2** and **ACBIC2**; calculated values for the optimized geometry of **BI2**, **BIC2** and **BICF** at the MNDO/AM1 level are also reported

	X-ray	MNDO/AM1			
	ACBI2	ACBIC2	BI2	BIC2	BICF
N1−C9	1.364(6)	1.376(4)	1.396	1.396	1.396
N2−C12	1.397(6)	1.415(4)	1.429	1.429	1.429
N2−N3	1.259(5)	1.257(4)	1.232	1.232	1.232
N3−C15	1.418(6)	1.421(4)	1.437	1.437	1.437
N4−C21	1.324(5)				
N4−C23		1.323(4)			
N5−C21	1.374(5)				
N5−C23		1.366(4)			
C8−N1−C9	118.9(5); 123.8(7)	120.2(3)			
C4−N1−C9	121.4(4)	121.8(3)	121.2	121.2	121.2
C8−N1−C4	119.0(5)	117.0(3)	117.3	117.2	117.3
C11−C12−N2−N3	162.6(4)	−176.1(3)	174.2	175.8	175.2
C12−N2−N3−C15	177.6(3)	−178.6(3)	179.1	179.3	179.2
C16−C15−N3−N2	160.7(4)	−162.9(3)	154.1	160.7	157.1
C17−C18−C21−N5	−147.0(4)		131.8		
C17−C18−C21−C22		164.9(4)		158.2	162.5
C21−C22−C23−N5		174.4(4)		162.7	180.0

referring to the orientations of some rings are slightly different, but this can probably be ascribed to packing effects.

The observed dihedral angle between the benzimidazole and 2-phenyl rings of **ACBI2** [37.5(2)°; 48.2° according to the MNDO/AM1 optimization of **BI2**] is determined by the intramolecular close contact C19···C28 (3.206 Å). A non-coplanar arrangement of the phenyl rings linked to the azo group is also observed [dihedral angle 40.3(2)° between mean planes] as a result of small torsions (<20°) around the bonds C15−N3 and C12−N2, in close agreement with the results yielded by MNDO/AM1 geometry optimization (37.4°). As we have reported for the homologous benzoxazole chromophore,[12] small torsions around these bonds, in particular around C15−N3, have low energetic costs and, at variance to the torsions around the C18−C21 bond, no significant effect on β.

As concerns the second point suggested by computations — the release of steric hindrance between the benzimidazole and 2-phenyl rings — a good compromise between the predicted hyperpolarizabilities and the synthetic procedures suggested that the insertion of a C=C double bond between the benzimidazole and 2-phenyl rings should lead to a significant increase of the second order NLO response of the chromophore. Insertion of the vinylene group was accomplished in a satisfactory manner by using cinnamic acid derivatives (instead of benzoic acid) in building the benzimidazole moiety. The different structures are given in Scheme 3.



Scheme 3

The presence of the C=C double bond has two effects, both pointing toward an enhancement of the hyperpolarizability: a) the 1−6 H···C contact is replaced by a 1−6 H···H contact, allowing for a more planar conformation of the chromophore; b) the conjugation length is increased. MNDO/AM1 computations confirm those expectations: the minimum energy geometry of **BIC2** reported in Table 4 exhibits a more planar arrangement and a significant increase of μβ(0) relative to that of **BI2** (Table 3). The X-ray molecular structure of **ACBIC2**, reported in Figure 2, supports the above arguments.

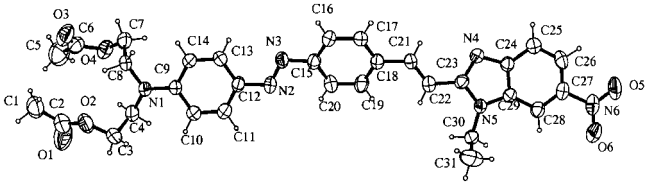


Figure 2. ORTEP drawing of **ACBIC2**; thermal ellipsoids are shown at the 30% probability level

In fact, as compared with **ACBI2**, the chromophore takes up a flatter conformation in the crystals [the maximum atomic distance from the calculated average plane of the conjugated part is 0.367(4) Å for non-H atoms]. The benzimidazole and vinyl groups are close to being coplanar [the dihedral angle is 6.6(4)° between the mean planes] and so are the benzimidazole and the phenyl ring C9 to C14 [dihedral angle of 2.2(2)°], while the dihedral angle between the benzimidazole and phenyl ring C15 to C20 is 22.4(2)° (19° in the MNDO/AM1 computed geometry of **BIC2**). The dihedral angle between the planes of the phenyl rings attached to the azo group [22.0(2)°; 23° in the optimized geometry of **BIC2**] is smaller than in **ACBI2** and it is essentially due to the torsion around the N3−C15 bond. Again, this torsion is expected to be of low energy and without significant influence on β.[12]

In agreement with the theoretical prediction, an increase (+47%) is observed in the experimental value of μβ on going from **BI2** to **BIC2** (see Table 2).

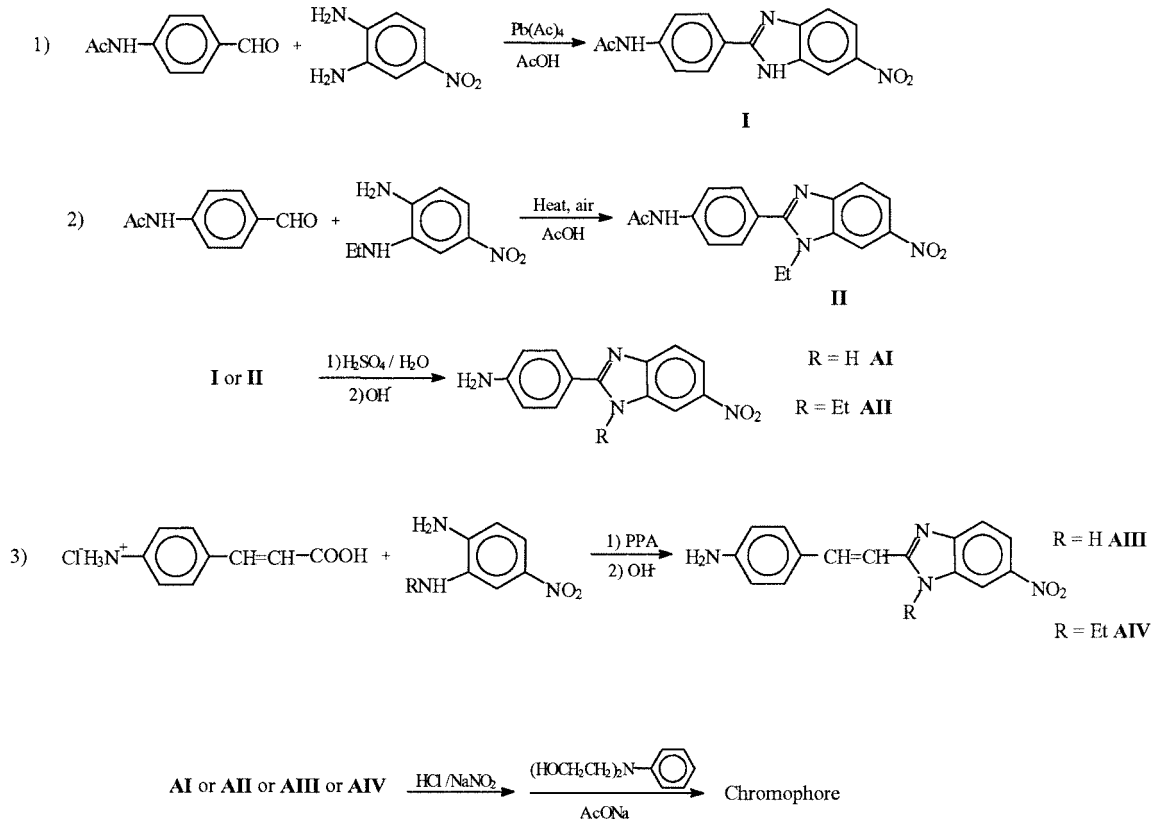
As concerns the alkylation of the 6-nitrobenzimidazole group, the experimental results in Table 2 show that **BIC1** has a slightly higher NLO activity than **BIC2**. Calculations also indicate that the 6-nitro tautomer of **BIC1** is more active than **BIC2** (see Table 3); this effect could be due to the different electronic character of H and ethyl (ethyl is a slight electron donor group). Calculations performed replacing the *N*-ethyl group of **BIC2** by an $N-CF_3$ group (compound **BICF** in Table 3 and 4) show a strong calculated β increase (ca. 28%) and this seems to support the possibility of further improving the second order molecular nonlinearity by selective alkylation of 6-nitrobenzimidazole with strong electron-withdrawing groups.

Experimental Section

Synthesis: Research in the field of second order NLO active compounds is, by necessity, applications oriented. It is therefore worth noting that all the chromophores in this paper have been synthesized (see Scheme 4) from low-cost commercial precursors [4-nitro-1,2-phenylenediamine, technical grade *p*-acetamidobenzaldehyde and *p*-aminocinnamic acid hydrochloride, bis(hydroxyethyl)aniline] in two or three steps, with yields varying from moderate to high; expensive manipulations under inert atmosphere, as well as hyperdrying of reaction solvents, are unnecessary.

The common step for the synthesis of all chromophores is the last one in Scheme 4 — diazotization of a (nitrobenzimidazol-2-yl)-phenylamine and subsequent coupling with commercial bis(2-hydroxyethyl)aniline. Although all the (nitrobenzimidazol-2-yl)-phenylamines could, in principle, be prepared by the same route, the need to increase the final yields of chromophore and to use low-cost commercial starting materials suggested the three different routes shown in Scheme 4.

2-(4-*p*-Acetamidophenyl)-5(6)-nitrobenzimidazole (I): *p*-Acetamidobenzaldehyde (1.066 g, 6.53 mmol) and 2-amino-4-nitroaniline (1 g, 6.53 mmol) were dissolved in 50 mL of glacial acetic acid at 100 °C. After a few minutes the formation of an orange precipitate occurred. At this point lead(IV) tetraacetate (95%, 3.048 g, 6.53 mmol) was added in portions. After some minutes the color of the suspension turned from orange to yellow. The system was



Scheme 4

kept at 100 °C for 1 h and, after cooling to room temperature, the solid was collected by filtration. Yield: 40%. M.p. 344 °C, solid-state phase transition at 183 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 2.078 (s, 3 H), 7.692−7.795 (m, 3 H), 8.071−8.149 (m, 3 H), 8.420 (s, 1 H), 10.247 (s, 1 H), 13.451 (s, 1 H) ppm.

2-(4-Aminophenyl)-5(6)-nitrobenzimidazole (AI): AI aniline was prepared in the same way as AII aniline (see below).Yield 90%. M.p. 259 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 5.778 (broad, 2 H), 6.726 (d, J = 8.3 Hz, 2 H), 7.703 (d, J = 9.28 Hz, 1 H), 7.892 (d, J = 8.3 Hz, 2 H), 8.132 (dd, J_1 = 9.03, J_2 = 1.70 Hz, 1 H), 8.352 (s, 1 H) ppm.

2-Ethylamino-4-nitroaniline: 2-Amino-4-nitroaniline (4 g, 26 mmol) was dissolved in 15 mL of DMF. K_2CO_3 (7.076 g, 52 mmol) and bromoethane (1.9 g, 26 mmol) were then added to the solution and the mixture was stirred at room temperature for 5 days. The inorganic solids were then filtered off and the remaining DMF solution was poured into 100 mL of water. Precipitation of a red solid was observed. The system was stirred in an ice bath for 20 minutes, then the solid was collected by filtration and recrystallized from EtOH/H_2O. Orange needle-like crystals were obtained. Yield: 60%. M.p. 130 °C. ^{1}H NMR ([D$_6$]acetone): δ = 1.309 (t, J = 7.1 Hz, 3 H), 3.243 (q, J = 6.8 Hz, 2 H), 4.298 (s, 1 H), 5.473 (s, 2 H), 6.711 (d, J = 8.8 Hz, 1 H), 7.348 (d, J = 2 Hz, 2 H), 7.553 (dd, J_1 = 8.6, J_2 =2 Hz, 1 H) ppm.

2-(4-Acetamidophenyl)-1-ethyl-6-nitrobenzimidazole (II): A solution of 2-ethylamino-4-nitroaniline (6 g, 33 mmol) and *p*-acetamidobenzaldehyde (5.385 g, 33 mmol) in 30 mL of glacial acetic acid was refluxed for 26 h. The solution was then cooled to room temperature and water was slowly added until the formation of a yellow precipitate was observed. The solid was then collected by filtration. Yield 44%. M.p. 281 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 1.333 (t, J = 7.0 Hz, 3 H), 4.466 (q, J = 7.0 Hz, 2 H), 7.815 (m, 5 H), 8.133 (dd, J_1 = 9, J_2= 2.4 Hz, 1 H), 8.648 (d, J = 2.4 Hz, 1 H), 10.261 (s, 1 H) ppm.

2-(4-Aminophenyl)-1-ethyl-6-nitrobenzimidazole (AII): II (3 g, 9.2 mmol) was added to a solution of 7 mL of 96% H_2SO_4 and 55 mL of water. The resulting suspension was refluxed for 90 minutes. As the temperature increased the solid dissolved to give a dark solution. The solution was then cooled to room temperature and a solution of NaOH (10% by weight) was added dropwise up to pH 5. The formation of a yellow solid was observed which was collected by filtration. Yield 93%. M.p. 211 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 1.368 (t, J = 7.4 Hz, 3 H), 4.450 (q, J = 7.4 Hz, 2 H), 5.797 (s, 2 H), 6.719 (d, J = 8.4 Hz, 2 H), 7.561 (d, J = 8.2 Hz, 2 H), 7.736 (d, J = 8.8 Hz, 1 H), 8.105 (dd, J_1= 9, J_2 = 1.2 Hz, 1 H), 8.555 (d, J = 1.4 Hz, 1 H) ppm.

(*E*)-2-(4-Aminostyryl)-5(6)-nitrobenzimidazole (AIII): 2-Amino-4-nitroaniline (3.00 g, 19 mmol) and *p*-aminocinnamic acid hydro-

chloride (3.339 g, 17 mmol) were mixed with a sufficient quantity of polyphosphoric acid to give a stirrable paste. The temperature was slowly raised to 200 °C. As the temperature increased a dark, viscous solution formed. This solution was stirred at 200 °C for 4 h, then cooled to 100 °C and poured into 400 mL water of in an ice bath. The formation of a solid occurred immediately. The system was basified with aqueous NaOH (50% by weight) to pH 6. The resulting solid was collected by filtration and then treated with boiling ethanol. The insoluble precipitate was removed by filtration and the filtrate was poured into water. The final precipitate was collected by filtration and dried in an oven. Yield: 59%. M.p. 260 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 5.665 (s, 2 H), 6.602 (d, *J* = 8.4 Hz, 2 H), 6.875 (d, *J* = 16 Hz, 1 H), 7.380 (d, *J* = 7.8 Hz, 2 H), 7.627 (d, 2 H), 8.063 (d, *J* = 8.8 Hz, 1 H), 8.335 (s, 1 H), 13.080 (s, 1 H) ppm.

(*E*)-2-(4-Aminostyryl)-1-ethyl-6-nitrobenzimidazole (AIV): This synthesis was performed similarly to that for **AIII**, the only difference being that the raw product did not need any purification, and so the step with boiling ethanol could be avoided (this greatly improved the yield). Yield: 95%. M.p. 260 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 1.350 (t, *J* = 6.8 Hz, 3 H), 4.527 (q, *J* = 7 Hz, 2 H), 6.597 (d, *J* = 8.4 Hz, 2 H), 7.113 (d, *J* = 15.8 Hz, 1 H), 7.113 (d, *J* = 8.4 Hz, 2 H), 7.648 (d, *J* = 8.8 Hz, 1 H), 7.839 (d, *J* = 15.6 Hz, 1 H), 8.054 (d, *J* = 8.8 Hz, 1 H), 8.503 (s, 1 H) ppm.

2-(4-{[4-Bis(2-hydroxyethyl)amino]phenylazo}phenyl)-5(6)-nitrobenzimidazole (BI1): AI aniline (3 g, 11.8 mmol) was placed in a flask containing 30 mL of H_2O and 3 mL of 37% HCl; the suspension was cooled to 0−5 °C in an ice-water bath. The solution obtained upon dissolving $NaNO_2$ (0.899 g, 13.0 mmol) in about 10 mL of water was then added dropwise to the suspension whilst stirring. Stirring at low temperature was continued for 30 min after the addition of the nitrite solution. A water-ethanol solution containing sodium acetate (3.3 g, 0.04 mol) and bis(2-hydroxyethyl)-aniline (2.136 g, 11.8 mmol) was prepared separately. The suspension containing the diazonium salt was rapidly added to this solution whilst stirring. The mixture became red immediately and after a few seconds a red-brown precipitate of the azo compound formed. This compound was collected by filtration and then recrystallized from DMF/H_2O to give pure **BI1** as a microcrystalline brown-violet product. Yield 71%. ^{1}H NMR ([D$_6$]DMSO): δ = 3.646 (s, 8 H), 4.907 (s, 2 H), 6.925 (d, *J* = 8.79 Hz, 2 H), 7.845 (d, 3 H), 7.875 (d, *J* = 8.24 Hz, 2 H), 8.184 (d, *J* = 7.96 Hz, 1 H), 8.389 (d, *J* = 8.24 Hz, 2 H), 8.593 (s, 1 H), 13.728 (s, 1 H) ppm. $C_{23}H_{22}N_6O_4$: calcd. C 61.88, H 4.97, N 18.82; found C 61.69, H 5.09, N 18.95.

The other three chromophores (**BI2**, **BIC1**, **BIC2**) were synthesized in the same manner from the corresponding aniline.

1-Ethyl-2-(4-{[4-Bis(2-hydroxyethyl)amino]phenylazo}phenyl)-6-nitrobenzimidazole (BI2): M.p. 221 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 1.355 (t, *J* = 7.2 Hz, 3 H), 3.568 (s, 8 H), 4.510 (q, *J* = 6.8 Hz, 2 H), 4.585 (s, 2 H), 6.855 (d, *J* = 8.8 Hz, 2 H), 7.758−7.939 (m, 7 H), 8.142 (d, *J* = 8.8 Hz, 1 H), 8.676 (s, 1 H) ppm. $C_{25}H_{26}N_6O_4$: calcd. C 63.28, H 5.52, N 17.71; found C 63.28, H 5.56, N 17.62.

(*E*)-2-(4-{[4-Bis(2-hydroxyethyl)amino]phenylazo}styryl)-5(6)-nitrobenzimidazole (BIC1): ^{1}H NMR ([D$_6$]DMSO): δ = 3.553 (s, 8 H), 4.585 (s, 2 H), 6.820 (d, *J* = 8.2 Hz, 2 H), 7.285 (d, *J* = 16.2 Hz, 1 H), 7.709−7.775 (m, 8 H), 8.063 (d, *J* = 8.8 Hz, 1 H), 8.415 (s, 1 H), 13.267 (s, 1 H) ppm. $C_{25}H_{24}N_6O_4$: calcd. C 63.55, H 5.12, N 17.79; found C 63.26, H 5.18, N 17.57.

(*E*)-1-Ethyl-2-(4-{[4-bis(2-hydroxyethyl)amino]phenylazo}styryl)-6-nitrobenzimidazole (BIC2): M.p. 270 °C (solid state phase transition at 240 °C). ^{1}H NMR ([D$_6$]DMSO): δ = 1.350 (t, *J* = 6.8 Hz, 3 H), 3.565 (s, 8 H), 4.635 (q, *J* = 6.8 Hz, 2 H), 4.840 (s, 2 H), 6.848 (d, *J* = 9.4 Hz, 2 H), 7.619 (d, *J* = 15.6 Hz, 1 H), 7.744−7.829 (m, 5 H), 7.976−8.010 (m, 3 H), 8.012 (dd, J_1 = 8.8, J_2 =2 Hz, 1 H), 8.603 (d, *J* = 2 Hz, 1 H) ppm. $C_{27}H_{28}N_6O_4$: calcd. C 64.79, H 5.64, N 16.79; found C 64.52, H 5.69, N 16.56.

2-[4-[(4-Bis(2-acetyloxyethyl)amino]phenylazo}phenyl)-1-ethyl-6-nitrobenzimidazole (ACBI2) and (*E*)-2-(4-{[4-Bis(2-acetyloxyethyl)amino]phenylazo}styryl)-1-ethyl-6-nitrobenzimidazole (ACBIC2): The synthesis of the diacetate esters of **BI2** and **BIC2** used in the X-ray structure analysis was performed in a similar way to **BI2** and **BIC2** but using bis(2-acetyloxyethyl)aniline instead of bis(2-hydroxyethyl)aniline in the coupling reaction.

ACBI2: M.p. 145 °C (solid state phase transition at 132 °C). ^{1}H NMR ([D$_1$]CDCl$_3$): δ = 1.592 (t, *J* = 7.2 Hz, 3 H), 2.071 (s, 6 H), 3.753 (t, *J* = 5.8 Hz, 4 H), 4.317 (t, *J* = 5.8 Hz, 4 H), 4.460 (q, *J* = 7.2 Hz, 2 H), 6.875 (d, *J* = 8.2 Hz, 2 H), 7.912−8.071 (m, 7 H), 8.298 (d, *J* = 8.8 Hz, 1 H), 8.444 (s, 1 H) ppm.

ACBIC2: M.p. 157 °C. ^{1}H NMR (D$_1$]CDCl$_3$): δ = 1.551 (t, *J* = 7.8 Hz, 3 H), 2.161 (s, 6 H), 3.731 (t, *J* = 6.4 Hz, 4 H), 4.303 (t, *J* = 5.8 Hz, 4 H), 4.424 (q, *J* = 7.4 Hz, 2 H), 6.840 (d, *J* = 8.8 Hz, 2 H), 7.118 (d, *J* = 15.6 Hz, 1 H), 7.722−7.902 (m, 7 H), 8.177 (d, *J* = 8.4 Hz, 1 H), 8.239 (s, 1 H), 8.308 (s, 1 H) ppm.

Physical Measurements: The thermal behavior of the compounds was studied by differential scanning calorimetry (Perkin−Elmer DSC-7, under nitrogen, scanning rate 10 K/min), temperature-controlled polarizing microscopy (Zeiss microscope, Mettler FP5 microfurnace) and TGA-DTA analysis (TA Instruments, air, 10 K/min). ^{1}H NMR spectra were recorded with Varian XL 200 spectrometer.

X-ray Analysis: Single crystals were obtained by slow evaporation from a toluene solution for **ACBI2** and from a chloroform/heptane solution for **ACBIC2**. For **ACBI2** the crystal phase investigated was the one giving the solid-state phase transition at 132 °C; for **ACBIC2** the low melting (134 °C) crystal phase was studied. Data collections were performed on an Enraf Nonius MACH3 automated diffractometer, using graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å). No absorption correction was applied. The structures were solved by direct methods (SIR92 program[13]) and refined by the full-matrix least-squares method (SHELXL program of the SHELX-97 package[14]). In the case of **ACBI2**, one of the two acetyloxyethyl tails is disordered over two sites. These were handled satisfactorily with 0.5 occupation factors and introducing constraints for some bond lengths. The C, N and O atoms of the statistical tails were given isotropic displacement parameters; the remaining C, N and O atoms were refined anisotropically. H atoms were placed in calculated positions and refined by the riding model with U_{iso} equal to U_{eq} of the carrier atom. Some crystal, collection and refinement data are reported in Table 5. All crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC). CCDC-226562 (for **ACBI2**) and -226563 (for **ACBIC2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 5. Crystal collection and refinement data for **ACBI2** and **ACBIC2**

	ACBI2	ACBIC2
Chemical formula	$C_{29}H_{30}N_6O_6$	$C_{31}H_{32}N_6O_6$
Molecular mass	558.59	584.63
T (K)	293	
Crystal system, space group	triclinic, $P\bar{1}$	
a (Å)	9.369(3)	8.739(7)
b (Å)	9.910(3)	12.847(3)
c (Å)	17.085(5)	13.572(4)
α (°)	78.58(3)	84.37(2)
β (°)	83.08(3)	74.31(7)
γ (°)	62.87(3)	89.56(6)
V (Å^3)	1382.9(7)	1460(1)
Z, D_x (Kg/m^3)	2, 1.341	2, 1.330
μ (mm^{-1})	0.096	0.094
θ range	1.22° to 27.97°	1.57° to 27.97°
Data/parameters	6659/364	7031/388
Goodness of fit (GOF) (all data)	1.002	0.916
$R1$ on $F[I>3\sigma(I)]$	0.0756	0.0519
$wR2$ on F^2 (all data)	0.3063	0.2067

$$R1 = \frac{\sum \| F_0 | - | F_c \|}{\sum |F_0|} \; ; \quad wR2 = \left\{ \frac{\sum \left[w\left(F_o^2 - F_c^2\right)^2 \right]}{\sum \left[w\left(F_o^2\right)^2 \right]} \right\}^{1/2}$$

NLO Measurements: The EFISH technique was used for the experimental determination of the μβ nonlinearities of the chromophores (μ is the ground state permanent dipole moment and β the quadratic hyperpolarizability of the molecules). The light source was a Q-switched Nd:YAG laser, whose emission at 1.06 μm was shifted to 1.907 μm by stimulated Raman emission in a high-pressure hydrogen cell. At this wavelength the molecular optical nonlinearities measured are to a large extent free from resonance enhancement. Measurements were calibrated relative to a quartz wedge: the experimental value of $d_{11}^{\text{Quartz}} = 1.2 \cdot 10^{-9}$ esu at 1.06 μm was extrapolated to $1.1 \cdot 10^{-9}$ esu at 1.907 μm. Neglecting the purely electronic contribution compared to the orientational part and allowing Kleinman symmetry for rod-like molecules, the projection, β, of the vector part of the tensor β_{ijk} along the direction of the dipole moment was determined. A detailed description of the experimental apparatus is given elsewhere.[15] Measurements were performed in DMF solution.

Computational Details: Calculations of hyperpolarizabilities were carried out with the MOPAC package,[16] using the MNDO Hamiltonian[11] and the AM1 parametrization.[17] The finite-field approach,[18] employing both an energy and a dipole expansion, was used to calculate the response of the charge density to the zero frequency field. The scalar product $\mu\beta_{vec}$ was calculated from Equation (1) :[19]

$$\mu\beta_{vec} = \frac{3}{5}\sum_i \beta_i \mu_i \text{ with } \beta_i = \sum_j \beta_{ijj} \tag{1}$$

All the structures were fully optimized until the gradient norm dropped below 0.1 kcal/Å. Calculations refer to the gas phase; solvent effects are expected to enhance the nonlinear response and therefore they could be responsible for the significant underestimation of theoretical $\mu\beta_{vec}$'s with respect to the experimental values (see above).

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