**N,N’-Dibutylbarbituric acid as an acceptor moiety in push–pull chromophores†**

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Twelve novel D–π–A chromophores with the N,N’-dibutylbarbituric acid acceptor, the N,N-dimethylamino donor and a systematically extended π-linker were synthesized. The extent of intramolecular charge-transfer, structure–property relationships and nonlinear optical properties were further investigated by X-ray analysis, electrochemistry, UV/Vis absorption spectra, calculations and EFISH experiments.

**Introduction**

Design, synthesis and application of novel π-conjugated molecules in materials science have been the subject of considerable research interest. In a π-conjugated molecule having an electron-donor (D) and an electron-acceptor (A), the so-called D–π–A or push–pull chromophore, intramolecular charge-transfer (ICT) from the donor to the acceptor occurs. The ICT can easily be illustrated by two limiting resonance forms (aromatic and quinoid/zwitterionic arrangement). The D–A interaction and simultaneous generation of a new low-energy molecular orbital determine the unique properties of push–pull chromophores such as intense colour, dipolar character, electrochemical behaviour, crystallinity, intermolecular interactions (π-stacking) as well as nonlinear optical (NLO) properties. Within the last 30 years or so, it has been realized that prepolariization of an organic molecule in D–π–A arrangement significantly enhances its NLO response. Hence, various π-conjugated backbones and electron donating and withdrawing groups and moieties have been utilized in the construction of NLO-active molecules (NLOphores) to date. Since the first synthesis by Adolf von Baeyer in 1864, barbituric acid (BA) and its derivatives have found widespread application across many branches. The uses of C5-(di)alkylated BAs (barbitals) as hypnotic-sedative, anticonvulsant, antimicrobial, spasmytic, antiinflammatory, antitumoral and fat-reducing agents are apparently the most widely known pharmaceutical applications. Besides this, BA-derived anionic dyes (Oxonols, DiSBACs) may act as fast voltage FRET probes monitoring changes in the cell membrane potential.

However, the pseudoaromatic pyrimidine-2,4,6-trione ring in BA can also be employed as an electron-withdrawing moiety in push–pull chromophores. This class of BA-derived compounds can be represented by mercocyanine dyes, especially by the well-known merocyanine 540. To date, (thio)barbituric acid ((T)BA) and its push–pull derivatives have found an admirable number of applications, especially in materials science. Either N-alkylated or N-unsubstituted (T)BA derivatives showed very strong and distinct solvatochromism and were also widely studied as efficient NLOphores. Hence, C5-(di)alkylated or N-unsubstituted (T)BA derivatives showed important solvent effects, solvent/medium polarity and pH-sensitivity; (ii) to distinguish between the specific and non-specific solvent interactions and (iii) to assess the hydrogen bonding ability. The latter property of hydrogen-bonding was further utilized in supramolecular assemblies of (T)BA derivatives exhibiting photophysical, photoelectrochemical, photorefractive, semiconducting and distinct absorptive properties. Yagai et al. showed several impressive hydrogen-bonded nanorings, nanofibres and rosettes while Bassani et al. demonstrated application of such hierarchical self-assemblies in organic photovoltaic devices.

Push–pull chromophores featuring a (T)BA acceptor unit were also widely studied as efficient NLOphores. Hence, C5 methyldiene substituted (T)BA push–pull derivatives proved to be highly prepolariized and showed high nonlinear optical coefficients β of up to 300 × 10⁻¹⁰ esu. Considering the number of (T)BA push–pull chromophores synthesized to date,
it is somewhat curious that only few efforts were made to systematically study the influence of the structure and length of the π-linker connecting (T)BA acceptor and a given donor.13 Hence, in this work we have focused on push–pull chromophores 1–3 with the π-conjugated system consisting of multiple bonds and 1,4-phenylene moieties end-capped with $N,N'$-dibutylbarbituric acid and the $N,N$-dimethyleneoxy group (Fig. 1). These groups have been chosen as the electron acceptor and donor, while the butyl substituents assure the chromophore sufficient solubility and simultaneously retain the possibility of its crystallization and study by X-ray analysis.

According to the $N,N'$-dibutylbarbituric acid connection to the central π-linker, three series of compounds 1–3 were synthesized. Each series contains four compounds a–d that differ in the length and structures of the π-linker (a – 1,4-phenylene, b – 4,4′-biphenylene, c – (E)-phenylethenylphenyl and d – phenylethenylphenyl). These model push–pull chromophores were further investigated by X-ray analysis, electrochemistry, UV/Vis spectra, calculations and EFISH experiments to evaluate the extent of the ICT and fundamental structure–property relationships.

**Results and discussion**

**Synthesis**

The obvious retrosynthetic strategy leading to target chromophores 1–3 involves the synthesis of $N,N'$-dibutylbarbituric acid and its Knoevenagel reaction14 with extended aldehydes. The barbituric acid was synthesized from $N,N'$-dibutylurea, generated from butyl isocyanate and butylamine in 99% yield15 and its subsequent treatment with malonic acid (91% yield).16 Extended benzaldehydes, cinnamaldehydes and propargyl aldehydes required for the final Knoevenagel condensation were prepared in a modular manner as shown in Scheme 1. 1,4-Diiodobenzene 4 was used as a suitable starting compound. Its formylation afforded 4-iodobenzaldehyde 6 in 44% yield. Transformation into [(E)-4-iodocinnamaldehyde 7 was accomplished via Wittig reaction of 6 with (triphenylphosphoranylidene)acetaldehyde and subsequent isomerization in the overall yield of 59%. Sonogashira cross-coupling on 4 and 4-iodo-$N,N$-dimethylaniline 7 with propargyl alcohol afforded alcohols 8 (51%) and 9 (67%).17 Their oxidation with Dess–Martin periodinane provided extended propargyl aldehydes 10 and 11 in the yields of 94 and 76%, respectively.18 The π-systems of iodo-substituted aldehydes 6, 7 and 10 were further extended by Suzuki–Miyaura (Method A), Heck (Method B) and Sonogashira (Method C) reactions with boronic acid pinacol ester 12, styrene 13 and terminal acetylene 14, respectively. These reactions yielded biphenyl aldehydes 15–17, stilbene aldehydes 18–20 and phenylethenylphenyl aldehydes 21–23 in the indicated yields. For the synthetic details and the characterization of aldehydes 15–23 see the ESI†.

Despite the recent progress made in the catalytic Knoevenagel condensation,19 we have adopted in our strategy very mild and efficient methodology of $Al_{2}O_{3}$-catalyzed reaction developed by Foucaud20 and further applied by Diederich et al. for the construction of the dicyanovinyl acceptor moiety in cyanoethynylethenes (CEEs).21 This methodology proved to be also very useful for the condensation of aldehydes and $N,N'$-dibutylbarbituric acid. Commercially available $4,N,N$-dimethylamino-substituted benzaldehyde 24 and cinnamaldehyde 25 as well as extended aldehydes 11 and 15–23 were converted into target push–pull chromophores 1a–d, 2a–d and 3a–d in the yields of 49–81, 76–91 and 69–82% (Scheme 2). Whereas the products of Knoevenagel reaction 1a, 2a–d and 3a–d could be purified by simple column chromatography, chromophores 1b–d decomposed already during the TLC analysis. It has recently been shown that the exocyclic double bond in BA benzylidene derivatives possesses highly electrophilic character and undergoes facile reaction with various nucleophiles.22 Hence, a retro Knoevenagel reaction with traces of water or acid media most likely takes place during the purification of 1b–d on silica. Therefore, the equilibrium condensation of extended benzaldehydes 15, 18 and 21 was carried out with 2 equivalents of $N,N'$-dibutylbarbituric acid and products 1b–d were purified by repeated precipitation from hot hexane.

Having difficulties with the synthesis of 1b–d, we have attempted an alternative synthetic route as shown in Scheme S1 (see the ESI†). This strategy involves Knoevenagel condensation of iodo-substituted aldehydes 6, 7 and 10 yielding intermediates 26–28 and their subsequent modification via cross-coupling reactions (Methods A–C). However, these procedures led only to isolation of chromophores 2a–b in the yields of 25–70%. The cross-coupling reactions on 26 provided intensively coloured solutions, in which target compounds 1b–d were detected by TLC and HR-MALDI-MS. Nevertheless, isolation of pure chromophores was not possible. On the other hand, cross-coupling reactions on 28 provided directly a mixture of several products of degradation. Most probably, a conjugated nucleophilic addition on the electrophilic triple bond in 28 takes place under the conditions of cross-coupling reactions and caused degradation.21d

**X-ray analysis**

All target compounds 1–3 are thermally stable and intensely coloured solids readily soluble in chlorinated solvents. Target push–pull chromophores 1a and 2a were crystallized by slow diffusion of hexane into their solutions in dichloromethane. Fig. 2 shows the ORTEP plots and confirms the molecular structures assigned to 1a and 2a. Both front and side views are provided. As can be seen, both butyl residues stick oppositely and almost perpendicularly to the π-system mean plane. Average torsion angles between the barbituric acid ring and the adjacent 1,4-phenylene moieties are 4.5° (C2–C3–C6–C7) and 0.4° (C2–C3–C8–C9) for 1a and 2b, respectively. Such a planar...
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The extent of the ICT and molecule polarization can easily be assessed by evaluating quinoid character \( d_r \) and bond length alternation of the \( \pi \)-system used. Average quinoid character of the 1,4-phenylene moieties in 1a and 2a are 0.05 and 0.04, respectively. For benzene, \( d_r = 0 \), while in fully quinoid rings \( d_r \) is equal to 0.08–0.1. Hence, the measured values indicate a considerable \( \pi \)-system polarization and rival those measured for highly polarized CEEs, which exhibited \( d_r \) within the range of 0.03–0.07. Quinoid characters of the propen-1,3-diyl \((C3–C5–C6)\) and pent-1,3-dien-1,5-diyl \((C3–C5–C6–C7–C8)\) \( \pi \)-linker segments in 1a and 2a are 0.04 and 0.06. Fig. S1 and S2 in the ESI† show the crystal packing of 1a and 2a. In the solid state, chromophore 1a doesn’t adopt a D to A molecular arrangement typical for the crystallization of dipolar compounds. This is most likely due to the less extended \( \pi \)-system and significant influence of the butyl residues (interlayer distance of about 3.6 Å). In contrast, the crystal packing of chromophore 2a shows typical D to A intermolecular interactions and \( \pi \)-stacks with the interlayer distance less than 3.4 Å.

**Electrochemistry**

Electrochemical behaviour of chromophores 1–3 was investigated by cyclic voltammetry (CV) and rotating-disc voltammetry (RDV). The measurements were carried out in acetonitrile that contained 0.1 M Bu₄NPF₆ as the electrolyte in a three-electrode cell. A saturated calomel electrode (SCE) separated by a bridge filled with supporting electrolyte and Pt wire were used as the reference and auxiliary electrodes, respectively. The acquired data are summarized in Table 1. Table S1 and Fig. S3–S6 in the ESI† contain full electrochemical data and representative CV curves for compounds 1a, 2b, 2c and 3d. Whereas the first oxidation was likely localized on the \( N,N \)-dimethylamino donor, the first reduction involved the barbituric acid acceptor moiety and the adjacent part of the \( \pi \)-linker. The half-wave potentials \( E_{1/2} \) of the first oxidation and reduction were further recalculated to

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**Scheme 1** Synthetic approach to extended aldehydes 15–23.
afford energies $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$,\textsuperscript{23} that can be compared with the calculated HOMO and LUMO levels.

All target chromophores showed one or more one-electron oxidation processes that are mostly reversible. The first oxidation potential is within the range of +0.99 to +0.58 V. Within the particular series of compounds 1–3, the first oxidation potentials decreased in the following order: a > d > b > c. With the same donor and acceptor moieties and type of the BA connection to the π-linker, this observation reflects the composition and spatial arrangement of the π-linker. Whereas the planar stilbene π-linkers in chromophores c allowed very efficient D–A interaction ($E_{1/2(\text{ox1})} = +0.58$ to +0.59 V), the N,N-dimethylamino donors in chromophores a and b with short 1,4-phenylene π-linkers ($E_{1/2(\text{ox1})} = +0.81$ to +0.99 V) and twisted 4,4\textsuperscript{0}-biphenylene π-linkers ($E_{1/2(\text{ox1})} = +0.76$ to +0.77 V) were engaged in less ICT. In contrast to stilbene π-linkers in c, the planar phenylethynylphenyl π-linkers in chromophores d shifted the first oxidation potential anodically by about 200 mV up to +0.80 V. This clearly shows the difference between the electronegative and insulating acetylenic and polarizable olefinic units.\textsuperscript{2,21d}

A comparison of structural analogues 1b/2b/3b, 1c/2c/3c and 1d/2d/3d revealed almost the same values of the first oxidation potentials +0.76 to +0.77, +0.58 to +0.59 and +0.78 to +0.80 V. This indicates that N,N-dimethylamino donors are in these sets of compounds similarly involved in the ICT. However, compounds 1a/2a/3a with the shortest 1,4-phenylene π-linkers showed the expected trend for the first oxidation potentials (~+0.99/+0.81/+0.94 V). The first oxidation potential decreased upon increasing the overall π-system length and polarizability.

N,N\textsuperscript{0}-Dibutylbarbituric acid can be denoted as the main reduction centre of chromophores 1–3. The observed first reductions were one-electron irreversible processes with $E_{1/2(\text{red1})}$ ranging from –1.26 to –0.79 V. The measured first reduction potentials were again dependent on the structure and length of the π-linker. Within the particular series of compounds 1–3, the values of $E_{1/2(\text{red1})}$ were shifted to more positive values in the following order: d > c ≥ b > a. This observation is in accordance with the previous discussion on their oxidations. Thus, the most positively shifted first reduction potentials −0.79 to −0.83 V were measured for
planar chromophores d with phenylethynylphenyl \( \pi \)-linker. A combination of two electronegative acetylenic units as in 3d caused a shift of \( E_{1/2(\text{red}1)} \) up to \(-0.79 \text{ V} \). Whereas the first reduction potentials of chromophores b and c were almost identical, the most negative first reduction potentials were measured for chromophores a. A comparison across three series 1–3 showed that the first reductions are facilitated upon increasing the length and planarity of the \( \pi \)-linker as well as its connection to the acceptor.

The difference between the first oxidation and reduction potentials \( \Delta E \) (electrochemical gap) assesses the D-A interaction and the extent of the ICT in the best way. The data and energy level diagram in Table 1 and Fig. 3 show a clear trend for decreasing \( \Delta E \) in the order 1 > 2 > 3 and within each series in the order \( a > b > d > c \). Chromophores 1c (\( \Delta E = 1.59 \text{ eV} \)), 2c (\( \Delta E = 1.52 \text{ eV} \)) and 3c (\( \Delta E = 1.45 \text{ eV} \)) showed the lowest electrochemical gaps, mainly due to their raised HOMO level.

<table>
<thead>
<tr>
<th>Comp.</th>
<th>( E_{1/2(\text{ox}1)}^{a} ) [V]</th>
<th>( E_{1/2(\text{red}1)}^{b} ) [V]</th>
<th>( \Delta E^{c} ) [V]</th>
<th>( E_{\text{HOMO}}^{d} ) [eV]</th>
<th>( E_{\text{LUMO}}^{d} ) [eV]</th>
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</thead>
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<td>2.25</td>
<td>-5.42</td>
<td>-3.17</td>
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<td>-3.64</td>
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\( ^{a} E_{1/2(\text{ox}1)} \) and \( E_{1/2(\text{red}1)} \) are the half-wave potentials of the first oxidation and reduction, respectively, as measured by RDE. \( ^{b} \Delta E = E_{1/2(\text{ox}1)} - E_{1/2(\text{red}1)} \) the potentials are given versus SCE. \( ^{c} E_{\text{HOMO}} = E_{1/2(\text{ox}1)}^{\text{a}} + 4.43 \). \( ^{d} E_{\text{LUMO}} = E_{1/2(\text{red}1)}^{\text{d}} + 4.43 \).

**UV/Vis spectra**

All target chromophores 1–3 are coloured compounds. Their electronic absorption spectra were measured in three solvents with different properties - cyclohexane (nonpolar, protic), dichloromethane (nonpolar, aprotic, polarizable) and acetonitrile (dipolar, aprotic, nonpolarizable) at a concentration of \( 2 \times 10^{-5} \text{ M} \). All spectra are shown in Fig. 4 and Fig. S7 and S8 (the ESI†). The optical properties are summarized in Table 2. The measured spectra in all solvents are dominated by intensive longest-wavelength absorption CT-bands with \( \lambda_{\text{max}} \) appearing between 439–495 (cyclohexane), 462–527 (dichloromethane) and 438–516 nm (acetonitrile). The molar absorption coefficients \( \varepsilon \) range from \( 3.5–64.8 \times 10^{3} \text{ mol}^{-1} \text{ cm}^{-1} \) (Table 2). These values are consistent with those measured for previous \( N,N \)-dialkylamino substituted BA derivatives.12

Except for chromophores 1a and 1b, the \( \lambda_{\text{max}} \) values of chromophores 1–3 measured in cyclohexane and dichloromethane are linearly dependent. The slope calculated by orthogonal linear fit is 1.305 (Fig. S9, the ESI†). A similar but less
tight dependence can be derived from the correlation between the \( \lambda_{\text{max}} \) values measured in cyclohexane and acetonitrile (slope = 1.518; Fig. S10, the ESI\(^+\)). These slope values imply that a bathochromic shift of the longest-wavelength absorption maxima is being observed when going from nonpolar aprotic cyclohexane to polarizable dichloromethane or dipolar acetonitrile. This can be explained as a higher solvation stabilization of the excited state than the ground state. This further implies that the excited state is more polarizable and polar (most probably the dominant feature) than the ground state.

The following structure–property relationships were deduced from the spectra measured in acetonitrile (the solvent used for electrochemical measurements). Chromophores 1a (\( \lambda_{\text{max}} = 459 \text{ nm} \)), 2a (\( \lambda_{\text{max}} = 516 \text{ nm} \)) and 3a (\( \lambda_{\text{max}} = 491 \text{ nm} \)) featuring the shortest \( \pi \)-linkers showed remarkably bathochromically shifted CT-bands. However, in comparison with 1b the positions of the longest-wavelength absorption maxima of 2a and 3a shifted bathochromically as a result of their extended \( \pi \)-linkers. A comparison of structurally similar chromophores 1c/1d, 2c/2d and 3c/3d reveals bathochromically shifted CT-bands (\( \Delta \lambda_{\text{max}} = 34–41 \text{ nm} \)) for chromophores in series \( \epsilon \) that feature the olefinic subunit (stilbene). This observation is in agreement with the previous findings made by electrochemistry. Cinnamaldehyde-derived chromophores 2a–d showed the most bathochromically shifted CT-bands (\( \lambda_{\text{max}} = 449–516 \text{ nm} \)) across three series 1–3, which reflects their planar and most polarizable connection of the \( \pi \)-linker to the BA acceptor via a but-1,3-diene spacer.

**Calculations and EFISH experiments**

The calculations were performed with PM3 and PM7 semi-empirical methods implemented in programs ArgusLab\(^24\) and MOPAC2012\(^25\) and visualization in OChem.\(^26\) Energies of HOMO and LUMO, their difference \( \Delta E \), dipole moment \( \mu \) and first hyperpolarizabilities \( \beta \) were calculated (Table 3). Although the PM7 calculated values of \( E_{\text{HOMO}} \) and \( E_{\text{LUMO}} \) are in absolute values different from those measured by CV and RDV, they showed similar trends. Namely, the lowest calculated

<table>
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<th>Comp.</th>
<th>( E_{\text{HOMO}} ) [eV]</th>
<th>( E_{\text{LUMO}} ) [eV]</th>
<th>( \Delta E ) [eV]</th>
<th>( \mu ) [D]</th>
<th>( \beta ) [10(^{28}) esu]</th>
<th>( \mu \beta ) [10(^{48}) esu]</th>
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\(^a\) The data were calculated by PM7 (MOPAC2012). \(^b\) Measured at 1907 nm in CHCl\(_3\), \( \epsilon \) was within the range 10\(^{-3}\) to 10\(^{-2}\) M; \( \mu \beta \pm 10\% \).

![Fig. 4](https://www.njc.rsc.org/content/37/10/4235.full.html)
HOMO–LUMO differences within the series of compounds 1–3 were calculated for chromophores 1c (ΔE = −6.76 eV), 2c (ΔE = −6.40 eV) and 3c (ΔE = −6.50 eV) with a planar stilbene π-linker.

As can be seen from these selected values, a connection of the BA acceptor to the π-system in 2 through a but-1,3-diene spacer allowed the most efficient D–A interaction. Hence, these cinnamaldehyde-derived chromophores generally showed the lowest HOMO–LUMO gap. Localization and gradual separation of the HOMO and the LUMO can be visualized on compounds 2a–d (Fig. 5). For complete listing of the HOMO–LUMO localizations see Fig. S11–S22 in the ESI.[†] As expected, the HOMO is localized on the N,N-dimethylanilino donor moiety, whilst the LUMO is spread over the barbituric acid C5 and adjacent part of the π-linker. This is in agreement with the aforementioned electrochemical conclusions.

Second-order non-linear optical properties were studied in CHCl₃ solution by the electric-field-induced second-harmonic generation technique (EFISH) which provides information about the scalar product μβ(2ω) of the vector component of the first hyperpolarisability tensor β and the dipole moment vector. This product is derived according to eqn (1) and considering the third-order term γₓ(−2ω,ω,ω,0) as negligible for the push–pull compounds under study. This approximation is usually used for push–pull organic and organometallic molecules.

$$\gamma_{\text{EFISH}} = \mu\beta/5kT + \gamma_0(−2\omega,\omega,\omega,0)$$  

Measurements were performed at 1907 nm, obtained from a Raman-shifted Nd:YAG laser source, which allowed us to work far from the resonance peaks of 1–3. It should be noted that the sign and values of μβ depend on the “direction” of the transition implied in the NLO phenomena and on the direction of the ground-state dipole moment. When β and μ were parallel (antiparallel), positive (negative), maximal μβ values were reached. All the μβ values of compounds 1–3 (Table 3) are positive which indicates more polarized excited than ground states (μ_e > μ_g). In addition, this implies that the ground and excited states are polarized in the same direction. The μβ values observed are relatively high compared to Disperse Red 1 used as the NLO standard.²⁸

A comparison of measured μβ values with the calculated first hyperpolarizabilities β in Table 2 revealed that both quantities correspond to general trends. Namely, the highest β/μβ coefficients were calculated/measured for NLOphores in series 2. Both coefficients increased within the particular series in the order of a > b ≥ d > c. This observed variation in nonlinear optical properties mimics the trends seen in the values of ΔE and λ_max. The highest μβ value (1880 × 10⁻⁴⁸ esu) was measured for NLOphore 2c with the planar and polarizable stilbene π-linker, while NLOphore 1a showed the weakest NLO response (270 × 10⁻⁴⁸ esu). Thus, an insertion of one 1,4-phenylene and two olefinic subunits into the π-linker (2c vs. 1a) enhanced the NLO response seven times.

Conclusions

N,N-Dimethylamino donor-substituted benzaldehydes, cinnamaldehydes and propargyl aldehydes with systematically extended π-systems were prepared and efficiently combined with the N,N'-dibutylbarbituric acid acceptor via Al₂O₃-catalyzed Knoevenagel condensation. Twelve new push–pull chromophores were synthesized and the extent of the ICT was further evaluated by X-ray analysis, electrochemistry, absorption spectra, calculation and EFISH experiments. With the given electron donor and acceptor, the electrochemical, optical and NLO behaviour of charge-transfer chromophores 1–3 can be finely tuned by extension, composition and spatial arrangement of the π-linker used. Push–pull chromophore 2c showed well balanced properties such as electrochemical gap ΔE = 1.52 V, the most bathochromically shifted CT-band appearing at 490 nm (2.53 eV), calculated HOMO–LUMO difference of −6.40 eV, dipole moment μ = 7.73 D and thermal stability (m.p. 228–232 °C). Considering the highest first hyperpolarizability β attained for (T)BA derivatives (~300 × 10⁻³⁰ esu) known to date and a relatively small π-system of 2c, its calculated (β = 10.6 × 10⁻²⁹ esu) and measured NLO responses (μβ = 1880 × 10⁻⁴⁸ esu) are remarkable.

In conclusion, N,N'-dibutylbarbituric acid proved to be a very efficient electron acceptor moiety in push–pull chromophores assuring their large dipolar character and simultaneously maintaining their sufficient solubility in common organic solvents. In view of the current interest in new organic materials for optoelectronics and ease of its synthesis, N,N'-dibutylbarbituric acid can be regarded as an alternative to former BA derivatives.
Experimental

For more synthetic details and instrumentation used see the ESI.† All cross-coupling reactions were carried out in Schlenk flasks dried under vacuum and filled with argon.

General method for Suzuki–Miyaura reaction (Method A)

An iodo derivative (1.0 mmol) and boron ester 12 (259 mg, 1.05 mmol) were dissolved in the mixture of THF–H2O (20 ml, 4:1). Argon was bubbled through the solution for 15 min whereupon [PdCl2(PPh3)2] (28 mg, 0.04 mmol) and Na2SO4 (159 mg, 1.5 mmol) were added and the reaction mixture was stirred at 60 °C for 12 h. The reaction was diluted with aq. NH4Cl (50 ml) and extracted with CH2Cl2 (2 × 50 ml). The combined organic extracts were dried (Na2SO4), the solvents were evaporated in vacuo and the crude product was purified by column chromatography (SiO2; CH2Cl2).

General method for Heck reaction (Method B)

Iodo derivative (1.0 mmol) and styrene 14 (155 mg, 1.05 mmol) were dissolved in toluene (30 ml) and iPr2NH (0.21 ml, 1.5 mmol) was added. Argon was bubbled through the solution for 15 min whereupon [PdCl2(μ-η2-Br2Bu3)] (28 mg, 0.04 mmol) was added and the reaction mixture was stirred at 80 °C for 12 h. The reaction was diluted with aq. NH4Cl (50 ml) and extracted with CH2Cl2 (2 × 50 ml). The combined organic extracts were dried (Na2SO4), the solvents were evaporated in vacuo and the crude product was purified by column chromatography (SiO2; CH2Cl2).

General method for Sonogashira reaction (Method C)

Iodo derivative (1.0 mmol) and acetylene 14 (152 mg, 1.05 mmol) were dissolved in THF (20 ml) and Et3N (5 ml). Argon was bubbled through the solution for 15 min whereupon [PdCl2(PPh3)2] (21 mg, 0.03 mmol) and CuI (6 mg, 0.03 mmol) were added and the reaction mixture was stirred at 25 °C for 12 h. The reaction was diluted with aq. NH4Cl (50 ml) and extracted with CH2Cl2 (2 × 50 ml). The combined organic extracts were dried (Na2SO4), the solvents were evaporated in vacuo and the crude product was purified by column chromatography (SiO2; CH2Cl2).

General method for Knoevenagel reaction

A mixture of N,N'-dibutylbarbituric acid (240/480 mg, 1.0/2.0 mmol), aldehyde (1.0 mmol), Al2O3 (510 mg, 5.0 mmol, activity II–III) and Na2SO4 (710 mg, 5.0 mmol) in CH2Cl2 (10 ml) was stirred at 25 °C for 12 h. The suspension was filtered and the solvent was evaporated in vacuo. The crude product was purified by column chromatography (SiO2; CH2Cl2) or by washing with hexane.

Chromophore 1a

Compound 1a was synthesized from commercially available aldehyde 24 (149 mg, 1.0 mmol) and N,N'-dibutylbarbituric acid (240 mg, 1.0 mmol). Compound 1a was isolated as an orange-red solid (300 mg, 81%). M.p. 156–161 °C. Rf = 0.67 (SiO2; CH2Cl2). Found: C, 67.47; H, 7.92; N, 11.21. C22H29N1O5 requires C, 67.90; H, 7.87; N, 11.31. IR (HATR): νmax/cm−1 2921, 2350, 1714, 1652, 1362, 1090, 1017, 787. 1H NMR (400 MHz; CDCl3): δH 0.92–0.96 (6H, m, 2 × CH3), 1.34–1.40 (4H, m, 2 × CH2), 1.60–1.64 (4H, m, 2 × CH2), 3.13 (6H, s, N(CH3)2), 3.94–3.98 (4H, m, 2 × NCH2), 6.69 (2H, d, J = 9.2, CH2), 8.37 (2H, d, J = 9.2, CH2) and 8.42 (1H, s, CH). 13C NMR (100 MHz; CDCl3): δC 141.01, 14.08, 40.23, 40.51, 41.96, 42.54, 112.40, 116.06, 123.10, 124.95, 125.82, 128.82, 131.02, 132.97, 135.57, 137.88, 150.88, 151.11, 158.67, 160.73 and 162.90. HR-FT-MALDI-MS (DHB) m/z: 474.2752 ([M + H]+), C22H28N1O5 requires 474.2751.

Chromophore 1d

Compound 1d was synthesized from aldehyde 21 (249 mg, 1.0 mmol) and N,N'-dibutylbarbituric acid (480 mg, 2.0 mmol). The crude product was purified by repeated washing with hexane. Compound 1d was isolated as a red-violet solid (353 mg, 75%). M.p. 139–143 °C. Rf = 0.63 (SiO2; CH2Cl2). Found: C, 74.05; H, 7.12; N, 8.86. C22H30N1O5 requires C, 73.86;
Compound 2a was synthesized from commercially available aldehyde 25 (175 mg, 1.0 mmol) and N,N'-dibutylbarbituric acid (240 mg, 1.0 mmol). Compound 2a was isolated as a dark violet solid (338 mg, 83%). M.p. 169–171 °C. Rf = 0.46 (SiO₂; CH₂Cl₂). Found: C, 69.34; H, 7.85; N, 10.39. C₂₉H₃₈N₄O₂ requires C, 69.49; H, 7.86; N, 10.57%. IR (HATR): v_max/cm⁻¹ 2929, 2360, 1713, 1648, 1533, 1366, 1223, 1164, 809. ¹H NMR (400 MHz; CDCl₃): δH 0.93–0.97 (6H, m, 2CH₃), 1.33–1.41 (4H, m, 2CH₂), 1.59–1.64 (4H, m, 2CH₂), 3.08 (6H, s, N(CH₃)₂), 3.91–3.95 (4H, m, 2NCH₂), 6.65 (2H, d, J = 8.8, CH₂), 7.37 (1H, dd, J = 14.8, CH), 7.58 (2H, d, J = 8.8, CH₂), 8.16 (1H, d, J = 12.4, CH) and 8.41 (1H, dd, J₁ = 12.4, J₂ = 14.8, CH). ¹³C NMR (100 MHz; CDCl₃): δC 14.01, 14.03, 20.39, 20.49, 30.43, 30.50, 40.33, 41.41, 41.92, 110.53, 112.01, 120.82, 123.66, 132.30, 151.53, 153.14, 157.09, 158.69, 159.29, 163.24 and 169.94. HR-FT-MALDI-MS (DHB) m/z: 398.2436 [M + H⁺], C₂₃H₂₉N₄O⁺ requires 398.2438.

Compound 2b was synthesized from aldehyde 16 (251 mg, 1.0 mmol) and N,N'-dibutylbarbituric acid (240 mg, 1.0 mmol). Compound 2b was isolated as a dark violet solid (431 mg, 91%). M.p. 199–204 °C. Rf = 0.18 (SiO₂; CH₂Cl₂–Hex 1: 1). Found: C, 73.34; H, 7.57; N, 8.69. C₂₉H₃₈N₄O₂ requires C, 73.54; H, 7.45; N, 8.87%. IR (HATR): v_max/cm⁻¹ 2924, 2360, 1713, 1653, 1550, 1361, 1222, 809. ¹H NMR (400 MHz; CDCl₃): δH 0.93–0.98 (6H, m, 2CH₃), 1.35–1.42 (4H, m, 2CH₂), 1.59–1.65 (4H, m, 2CH₂), 3.01 (6H, s, N(CH₃)₂), 3.92–3.96 (4H, m, 2NCH₂), 6.78 (2H, d, J = 7.2, CH₂), 7.14 (2H, d, J = 15.2, CH₂), 7.56 (2H, d, J = 7.2, CH₂), 7.61 (2H, d, J = 8.4, CH₂), 7.69 (2H, d, J = 8.4, CH₂), 8.19 (1H, d, J = 12.0, CH) and 8.61 (1H, dd, J₁ = 15.2, J₂ = 8.4, CH). ¹³C NMR (100 MHz; CDCl₃): δC 14.00, 14.02, 20.38, 20.47, 30.37, 30.43, 40.58, 41.63, 42.13, 112.74, 113.98, 124.50, 126.50, 127.73, 127.95, 130.12, 133.12, 144.60, 150.72, 151.25, 154.65, 157.70, 161.87 and 162.43. HR-FT-MALDI-MS (DHB) m/z: 474.2727 [M + H⁺], C₂₉H₂₉N₄O⁺ requires 474.2725.
IR (HATR): $\nu_{\text{max}}$cm$^{-1}$ 2928, 2360, 1717, 1658, 1567, 1598, 1363, 1291, 808. $^1$H NMR (400 MHz; CDCl$_3$): $\delta_H$ 0.93–0.98 (6H, m, 2CH$_3$), 1.32–1.44 (4H, m, 2CH$_2$), 1.58–1.68 (4H, m, 2CH$_2$), 3.51 (6H, S, N(CH$_3$)$_3$), 3.92–3.97 (4H, m, 2NCH$_2$), 6.78 (2H, d, J = 8.8, CH$_2$), 7.55 (2H, d, J = 8.4, CH$_2$), 7.61 (2H, d, J = 8.4, CH$_2$), 7.70 (2H, d, J = 8.8, CH$_2$) and 7.80 (1H, s, CH). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta_C$ 13.39, 14.01, 20.38, 20.43, 29.93, 30.33, 40.57, 41.82, 42.33, 91.41, 112.74, 119.02, 119.51, 124.77, 126.16, 126.24, 128.02, 134.38, 137.63, 144.29, 150.77, 150.92, 159.44 and 161.40. HR-FT-MALDI-MS (DHB) $m/z$: 472.2595 ($[M + H]^+$), C$_{20}$H$_{23}$N$_4$O$_5^+$ requires 472.2595.

Notes and references


10 (a) S. Yagai, Y. Goto, T. Karatsu, A. Kitamura and Y. Kikkawa, Chem.–Eur. J., 2011, 17, 13657; (b) S. Yagai,