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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.[1] 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).[2] The D–A interaction and simultaneous generation of a new low-energy molecular orbital determine the unique properties of push–pull chromophores such as intensive 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 prepolarization 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.[3] Since the first synthesis by Adolf von Baeyer in 1864, barbituric acid (BA) and its derivatives have found widespread application across many branches.[4] The uses of C5-(di)alkylated BAs (barbitals) as hypnotic-sedative, anticonvulsant, antimicrobial, spasmolytic, antiinflammatory, antitumoral and fat-reducing agents are apparently the most widely known pharmacological applications.[5] Besides this, BA-derived anionic dyes (Oxonols, DiSBACs) may act as fast voltage FRET probes monitoring changes in the cell membrane potential.[6]

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 merocyanine dyes, especially by the well-known merocyanine 540.[7] 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 investigated as powerful probes (i) to study 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.[8] The latter property of hydrogen-bonding was further utilized in supramolecular assemblies of (T)BA derivatives exhibiting photoelectrochemical, photorefractive, semiconducting and distinct absorption and fluorescent properties.[9] Yagai *et al.* showed several impressive hydrogen-bonded nanorings, nanofibres and rosettes,[10] while Bassani *et al.* demonstrated application of such hierarchical self-assemblies in organic photovoltaic devices.[11]

Push–pull chromophores featuring a (T)BA acceptor unit were also widely studied as efficient NLOphores. Hence, C5 methylidene substituted (T)BA push–pull derivatives proved to be highly prepolarized and showed high nonlinear optical coefficients β of up to 300×10^{-30} esu.[12] Considering the number of (T)BA push–pull chromophores synthesized to date,

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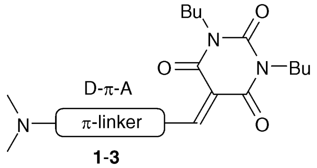
† Electronic supplementary information (ESI) available: Experimental details, characterization of compounds **6–11**, **15–23**, **26–28**, crystallographic data for **1a** and **2a**, full electrochemical data for **1–3**, HOMO–LUMO localizations in **1–3**, ^{1}H and ^{13}C NMR spectra of **1–3**. CCDC 932394 and 932395. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3nj00683b



1-3

Fig. 1 General structure of target push–pull chromophores **1–3**.

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*-dimethylamino 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** – phenylethynylphenyl). 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

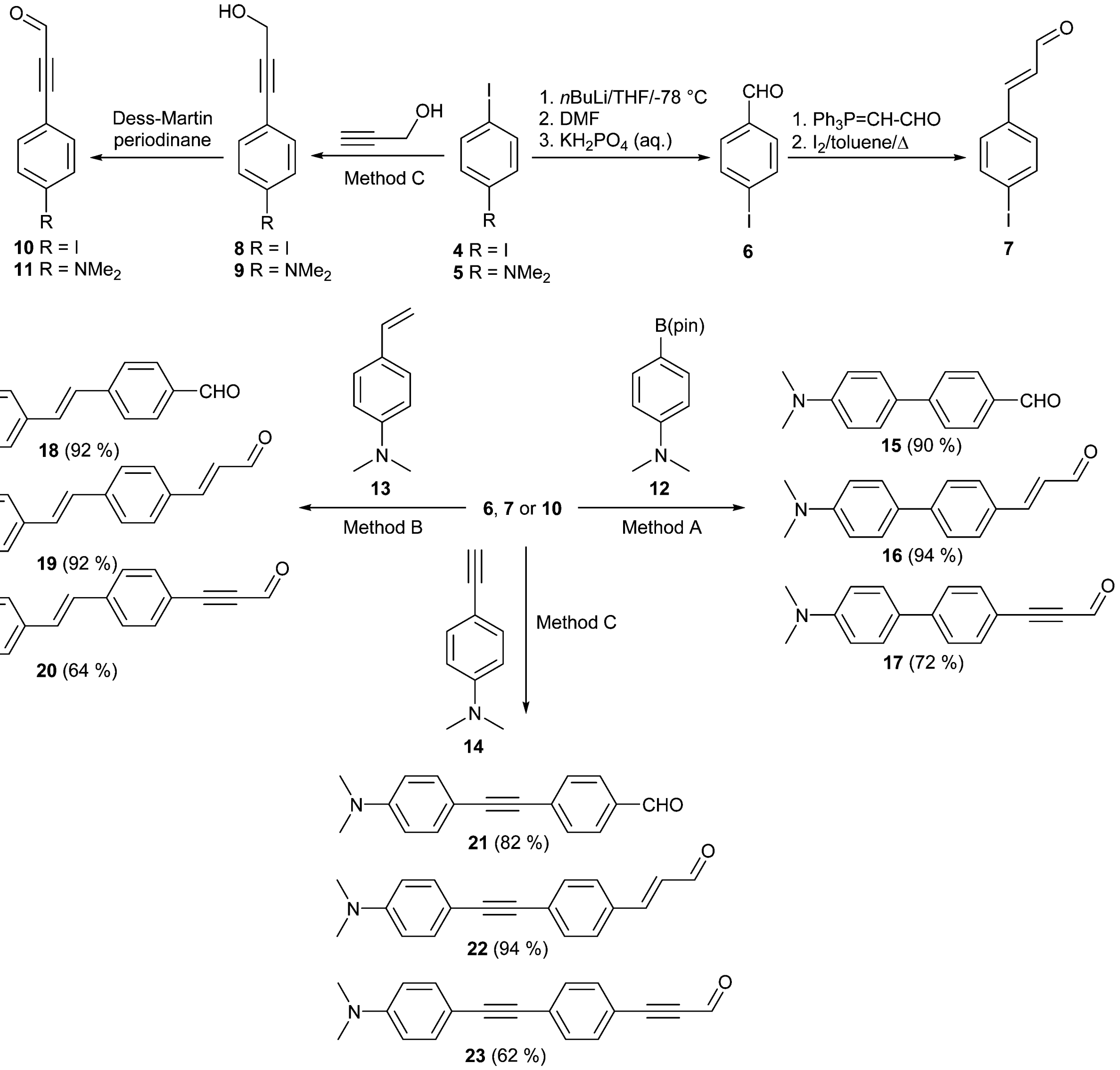
The obvious retrosynthetic strategy leading to target chromophores **1–3** involves the synthesis of *N*,*N*′-dibutylbarbituric acid and its Knoevenagel reaction[14] with extended aldehydes. The barbituric acid was synthesized from *N*,*N*′-dibutylurea, generated from butyl isocyanate and butylamine in 99% yield[15] 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 phenylethynylphenyl 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 Foucaud[20] 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

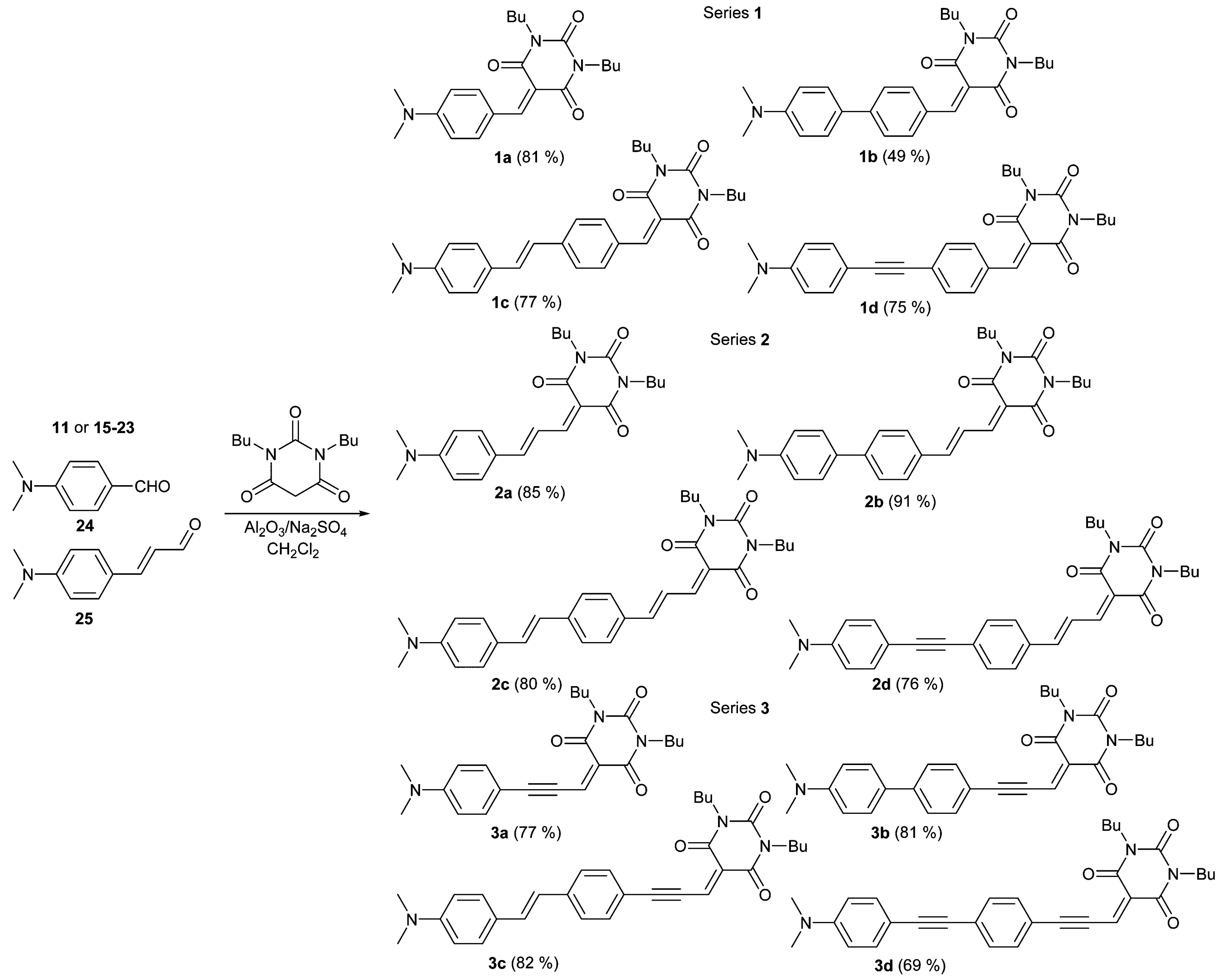


Scheme 1 Synthetic approach to extended aldehydes **15–23**.

arrangement of the π-systems in **1a** and **2a** would allow efficient D–A interaction. The extent of the ICT and molecule polarization can easily be assessed by evaluating quinoid character δr and bond length alternation of the π-system used. Average quinoid character of the 1,4-phenylene moieties in **1a** and **2a** are 0.05 and 0.04, respectively. For benzene, $\delta r = 0$, while in fully quinoid rings δr is equal to 0.08–0.1. Hence, the measured values indicate a considerable π-system polarization and rival those measured for highly polarized CEEs, which exhibited δr within the range of 0.03–0.07.[21] Quinoid characters of the propen-1,3-diyl (C3–C5–C6) and pent-1,3-dien-1,5-diyl (C3–C5–C6–C7–C8) π-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 π-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 π-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 Bu_4NPF_6 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 π-linker. The half-wave potentials $E_{1/2}$ of the first oxidation and reduction were further recalculated to



Scheme 2 Knoevenagel condensation and structures of target chromophores **1–3**.

afford energies E_{HOMO} and E_{LUMO},[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 ($E_{1/2(\mathrm{ox1})}$ = +0.58 to +0.59 V), the *N*,*N*-dimethylamino donors in chromophores **a** and **b** with short 1,4-phenylene ($E_{1/2(\mathrm{ox1})}$ = +0.81 to +0.99 V) and twisted 4,4′-biphenylene π-linkers ($E_{1/2(\mathrm{ox1})}$ = +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.[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*′-Dibutylbarbituric acid can be denoted as the main reduction centre of chromophores **1–3**. The observed first reductions were one-electron irreversible processes with $E_{1/2(\mathrm{red1})}$ 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 $E_{1/2(\mathrm{red1})}$ 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

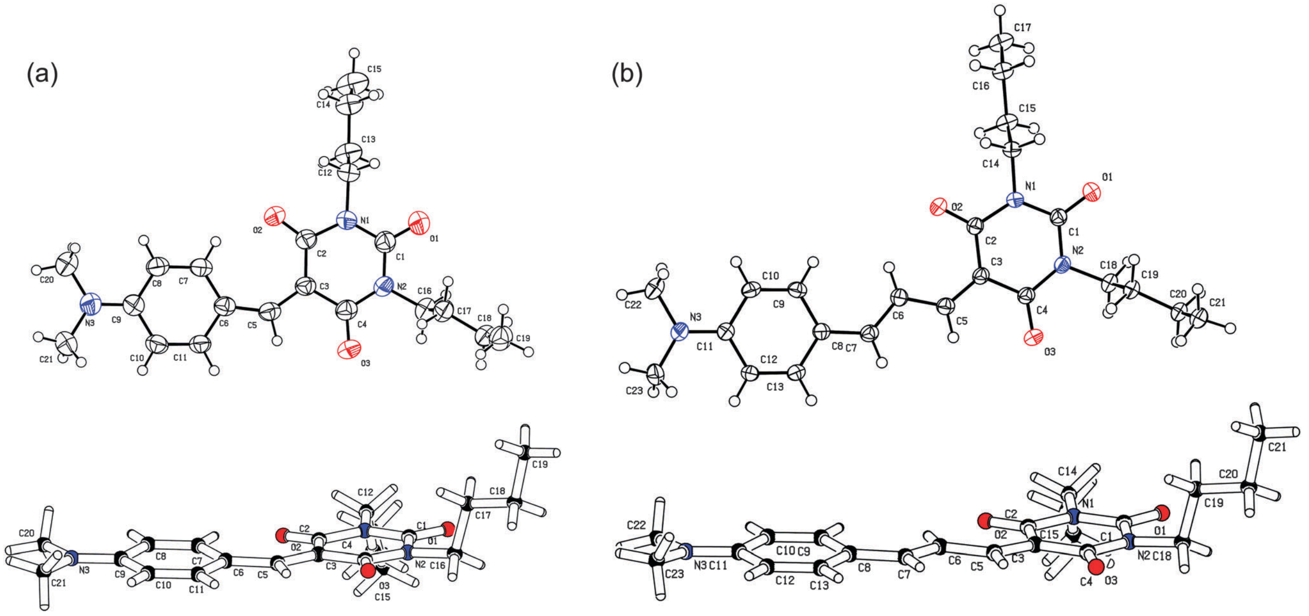


Fig. 2 ORTEP representation of chromophores **1a** (a) and **2a** (b) measured by X-ray analysis at 150 K (50% probability level).

Table 1 Electrochemical data for chromophores **1–3**

Comp.	$E_{1/2(\mathrm{ox1})}$ ^{a} [V]	$E_{1/2(\mathrm{red1})}$ ^{a} [V]	ΔE^b [V]	E_{HOMO} ^{c} [eV]	E_{LUMO} ^{c} [eV]
1a	+0.99	−1.26	2.25	−5.42	−3.17
1b	+0.77	−1.02	1.79	−5.20	−3.41
1c	+0.58	−1.01	1.59	−5.01	−3.42
1d	+0.79	−0.95	1.74	−5.22	−3.48
2a	+0.81	−1.04	1.85	−5.24	−3.39
2b	+0.76	−0.92	1.68	−5.19	−3.51
2c	+0.59	−0.93	1.52	−5.02	−3.50
2d	+0.78	−0.83	1.61	−5.21	−3.60
3a	+0.94	−0.97	1.91	−5.37	−3.46
3b	+0.77	−0.87	1.64	−5.20	−3.56
3c	+0.58	−0.87	1.45	−5.01	−3.56
3d	+0.80	−0.79	1.59	−5.23	−3.64

[a] $E_{1/2(\mathrm{ox1})}$ and $E_{1/2(\mathrm{red1})}$ are the half-wave potentials of the first oxidation and reduction, respectively, as measured by RDV. [b] $\Delta E = E_{1/2(\mathrm{ox1})} - E_{1/2(\mathrm{red1})}$; the potentials are given *versus* SCE. [c] $E^{\mathrm{abs}}_{\mathrm{HOMO/LUMO}} = E_{1/2(\mathrm{ox1/red1})} + 4.43$.

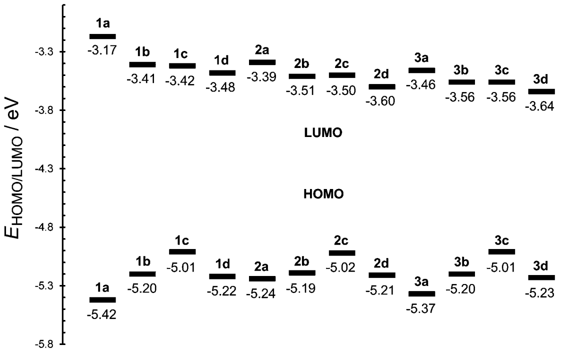


Fig. 3 Energy level diagram of chromophores **1–3**.

planar chromophores **d** with phenylethynylphenyl π-linker. A combination of two electronegative acetylenic units as in **3d** caused a shift of $E_{1/2(\mathrm{red1})}$ up to −0.79 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 π-linker as well as its connection to the acceptor.

The difference between the first oxidation and reduction potentials Δ*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 Δ*E* in the order **1** > **2** ≥ **3** and within each series in the order **a** > **b** > **d** > **c**. Chromophores **1c** (Δ*E* = 1.59 V), **2c** (Δ*E* = 1.52 V) and **3c** (Δ*E* = 1.45 V) showed the lowest electrochemical gaps, mainly due to their raised HOMO level.

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 2×10^{-5} 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 $\lambda_{\max}$ appearing between 439–495 (cyclohexane), 462–527 (dichloromethane) and 438–516 nm (acetonitrile). The molar absorption coefficients ε range from 3.5–64.8 × 10^3 mol^{-1} dm^3 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 $\lambda_{\max}$ 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

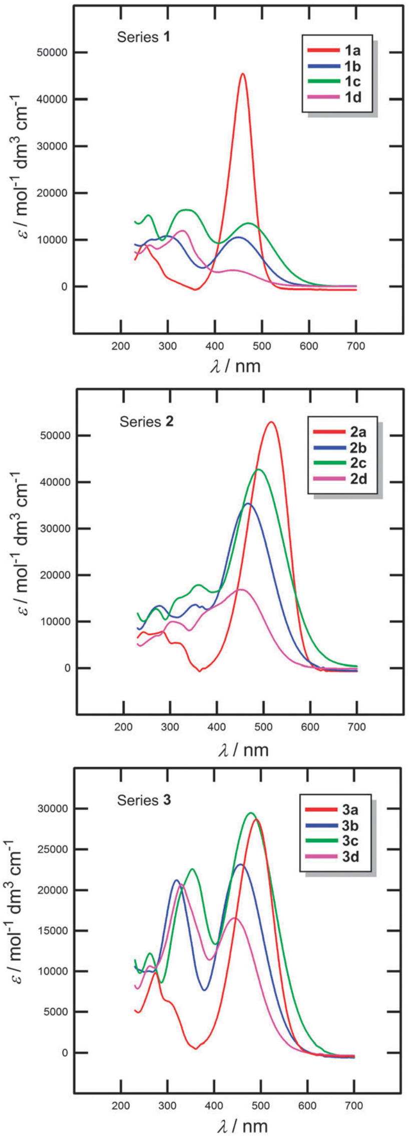


Fig. 4 UV/Vis absorption spectra of chromophores in series **1–3** measured in acetonitrile ($c = 2 \times 10^{-5}$ M).

tight dependence can be derived from the correlation between the λ_{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 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** (λ_{max} = 459 nm), **2a** (λ_{max} = 516 nm) and **3a** (λ_{max} = 491 nm) featuring the shortest π-linkers showed remarkably bathochromically shifted CT-bands. However, in comparison with **1a** the positions of the longest-wavelength absorption maxima of **2a** and **3a** shifted bathochromically as a result of their extended π-linkers. A comparison of structurally similar chromophores **1c**/**1d**, **2c**/**2d** and **3c**/**3d** reveals bathochromically shifted CT-bands ($\Delta\lambda_{max}$ = 34–41 nm) for chromophores in series **c** 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 (λ_{max} = 449–516 nm) across three series **1–3**, which reflects their planar and most polarizable connection of the π-linker to the BA acceptor *via* a but-1,3-diene spacer.

Table 2 Optical properties of chromophores **1–3**

λ_{max} [nm (eV)]/ε(×10^{-3}) [mol^{-1} dm^3 cm^{-1}]			
Comp.	Cyclohexane	Dichloromethane	Acetonitrile
1a	439(2.82)/63.7[a]	462(2.68)/64.8	459(2.70)/45.7
1b	444(2.79)/25.1[a]	467(2.66)/23.7	451(2.75)/10.5
1c	476(2.61)/35.8[a]	493(2.52)/31.0	472(2.63)/13.5
1d	450(2.76)/16.1[a]	460(2.70)/13.9	438(2.83)/3.50
2a	495(2.51)/39.6[b]	527(2.35)/49.4	516(2.40)/53.0
2b	460(2.70)/26.2	481(2.58)/34.4	467(2.66)/35.5
2c	487(2.55)/36.8	508(2.44)/38.3	490(2.53)/42.8
2d	454(2.73)/22.4	470(2.64)/32.4	449(2.76)/16.9
3a	481(2.58)/34.6[c]	503(2.47)/26.6	491(2.53)/28.8
3b	458(2.71)/34.3[a]	476(2.61)/23.4	458(2.71)/23.2
3c	486(2.55)/25.5[a]	501(2.48)/30.9	479(2.59)/29.5
3d	456(2.72)/27.3[a]	467(2.66)/21.7	444(2.79)/16.6

[a] Indistinguishable shoulder. [b] Shoulder at λ = 476 nm (ε = 41.6 × 10^3 mol^{-1} dm^3 cm^{-1}). [c] Shoulder at λ = 454 nm (ε = 26.6 × 10^3 mol^{-1} dm^3 cm^{-1}).

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 OPchem.[26] Energies of HOMO and LUMO, their difference ΔE, dipole moment μ and first hyperpolarizabilities β were calculated (Table 3). Although the PM7 calculated values of E_{HOMO} and E_{LUMO} are in absolute values different from those measured by CV and RDV, they showed similar trends. Namely, the lowest calculated

Table 3 Calculated and measured parameters of chromophores **1–3**

Comp.	E_{HOMO}[a] [eV]	E_{LUMO}[a] [eV]	ΔE[a] [eV]	μ[a] [D]	β[a] [10^{29} esu]	$\mu\beta$ (2ω)[b] [10^{48} esu]
1a	−8.52	−1.23	−7.29	7.47	2.97	270
1b	−8.26	−1.36	−6.90	5.54	3.04	1080
1c	−8.13	−1.37	−6.76	5.92	4.33	1390
1d	−8.14	−1.29	−6.85	5.97	4.09	750
2a	−8.36	−1.49	−6.87	7.93	6.35	1000
2b	−8.25	−1.65	−6.60	6.56	5.99	1040
2c	−8.08	−1.68	−6.40	7.73	10.6	1880
2d	−8.10	−1.64	−6.46	7.66	8.97	1270
3a	−8.55	−1.42	−7.13	7.03	3.22	900
3b	−8.32	−1.56	−6.76	6.68	4.13	940
3c	−8.10	−1.60	−6.50	8.12	8.15	1270
3d	−8.37	−1.61	−6.76	5.94	5.08	870[c]

[a] The data were calculated by PM7 (MOPAC2012). [b] Measured at 1907 nm in CHCl$_3$, c was within the range 10^{-3} to 10^{-2} M; $\mu\beta$ ± 10%. [c] Underestimated due to aggregation.

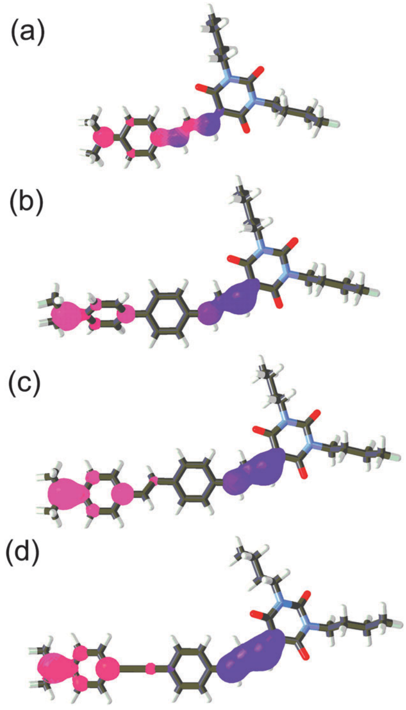


Fig. 5 Optimized geometries and HOMO (red) and LUMO (blue) localizations in chromophores **2a** (a), **2b** (b), **2c** (c) and **2d** (d).

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 $CHCl_3$ solution by the electric-field-induced second-harmonic generation technique (EFISH) which provides information about the scalar product $\mu\beta(2\omega)$ of the vector component of the first hyperpolarisability tensor β and the dipole moment vector.[27] This product is derived according to eqn (1) and considering the third-order term $\gamma_0(-2\omega,\omega,\omega,0)$ as negligible for the push–pull compounds under study. This approximation is usually used for push–pull organic and organometallic molecules.

$$\gamma_{\mathrm{EFISH}} = \mu\beta/5kT + \gamma_0(-2\omega,\omega,\omega,0) \qquad (1)$$

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 $\mu\beta$ 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 $\mu\beta$ values were reached. All the $\mu\beta$ values of compounds **1–3** (Table 3) are positive which indicates more polarized excited than ground states ($\mu_e > \mu_g$). In addition, this implies that the ground and excited states are polarized in the same direction. The $\mu\beta$ values observed are relatively high compared to Disperse Red 1 used as the NLO standard.[28]

A comparison of measured $\mu\beta$ values with the calculated first hyperpolarizabilities β in Table 2 revealed that both quantities correspond to general trends. Namely, the highest $\beta/\mu\beta$ 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 $\lambda_{\max}$. The highest $\mu\beta$ 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* Al_2O_3-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 ($\sim 300 \times 10^{-30}$ esu) known to date and a relatively small π-system of **2c**, its calculated ($\beta = 10.6 \times 10^{-29}$ esu) and measured NLO responses ($\mu\beta = 1880 \times 10^{-48}$ 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–H_2O (20 ml, 4 : 1). Argon was bubbled through the solution for 15 min whereupon [$PdCl_2(PPh_3)_2$] (28 mg, 0.04 mmol) and Na_2CO_3 (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. NH_4Cl (50 ml) and extracted with CH_2Cl_2 (2 × 50 ml). The combined organic extracts were dried (Na_2SO_4), the solvents were evaporated *in vacuo* and the crude product was purified by column chromatography (SiO_2; CH_2Cl_2).

General method for Heck reaction (Method B)

Iodo derivative (1.0 mmol) and styrene **13** (155 mg, 1.05 mmol) were dissolved in toluene (30 ml) and iPr_2NH (0.21 ml, 1.5 mmol) was added. Argon was bubbled through the solution for 15 min whereupon [$Pd(P\text{-}tBu_3)_2$] (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. NH_4Cl (50 ml) and extracted with CH_2Cl_2 (2 × 50 ml). The combined organic extracts were dried (Na_2SO_4), the solvents were evaporated *in vacuo* and the crude product was purified by column chromatography (SiO_2; CH_2Cl_2).

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 Et_3N (5 ml). Argon was bubbled through the solution for 15 min whereupon [$PdCl_2(PPh_3)_2$] (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. NH_4Cl (50 ml) and extracted with CH_2Cl_2 (2 × 50 ml). The combined organic extracts were dried (Na_2SO_4), the solvents were evaporated *in vacuo* and the crude product was purified by column chromatography (SiO_2; CH_2Cl_2).

General method for Knoevenagel reaction

A mixture of *N*,*N*′-dibutylbarbituric acid (240/480 mg, 1.0/2.0 mmol), aldehyde (1.0 mmol), Al_2O_3 (510 mg, 5.0 mmol, activity II–III) and Na_2SO_4 (710 mg, 5.0 mmol) in CH_2Cl_2 (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 (SiO_2; CH_2Cl_2) 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. R_f = 0.67 (SiO_2; CH_2Cl_2). Found: C, 67.47; H, 7.92; N, 11.21. $C_{21}H_{29}N_3O_3$ requires C, 67.90; H, 7.87; N, 11.31%. IR (HATR): ν_{max}/cm^{-1} 2921, 2359, 1712, 1645, 1362, 1090, 1017, 787. ^{1}H NMR (400 MHz; $CDCl_3$): δ_H 0.92–0.96 (6H, m, 2×CH_3), 1.34–1.40 (4H, m, 2×CH_2), 1.60–1.64 (4H, m, 2×CH_2), 3.13 (6H, s, $N(CH_3)_2$), 3.94–3.98 (4H, m, 2×NCH_2), 6.69 (2H, d, *J* = 9.2, CH_{ar}), 8.37 (2H, d, *J* = 9.2, CH_{ar}) and 8.42 (1H, s, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 14.01, 14.04, 20.41, 20.47, 30.43, 30.46, 40.26, 41.69, 42.28, 110.32, 111.20, 121.32, 139.57, 151.53, 154.47, 158.86, 161.56 and 163.96. HR-FT-MALDI-MS (DHB) *m*/*z*: 372.2281 ([M + H]$^+$), $C_{21}H_{30}N_3O_3^+$ requires 372.2282.

Chromophore 1b

Compound **1b** was synthesized from aldehyde **15** (225 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 **1b** was isolated as a red-violet solid (219 mg, 49%). M.p. 166–172 °C. R_f = 0.65 (SiO_2; CH_2Cl_2). Found: C, 71.90; H, 7.38; N, 9.46. $C_{27}H_{33}N_3O_3$ requires C, 72.46; H, 7.43; N, 9.39%. IR (HATR): ν_{max}/cm^{-1} 2922, 2360, 1712, 1654, 1363, 806.^{1}H NMR (400 MHz; $CDCl_3$): δ_H 0.93–0.98 (6H, m, 2×CH_3), 1.40–1.44 (4H, m, 2×CH_2), 1.59–1.68 (4H, m, 2×CH_2), 3.02 (6H, s, $N(CH_3)_2$), 3.94–3.99 (4H, m, 2×NCH_2), 6.78 (2H, d, *J* = 8.8, CH_{ar}), 7.60 (2H, d, *J* = 8.8, CH_{ar}), 7.67 (2H, d, *J* = 8.8, CH_{ar}), 8.22 (2H, d, *J* = 8.4, CH_{ar}) and 8.54 (1H, s, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 13.99, 20.39, 20.43, 30.36, 40.52, 41.97, 42.55, 112.68, 116.20, 125.56, 127.01, 128.19, 130.39, 135.58, 146.32, 150.94, 151.12, 159.02, 160.75 and 162.90. HR-FT-MALDI-MS (DHB) *m*/*z*: 448.2588 ([M + H]$^+$), $C_{27}H_{34}N_3O_3^+$ requires 448.2595.

Chromophore 1c

Compound **1c** was synthesized from aldehyde **18** (251 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 **1c** was isolated as a violet solid (364 mg, 77%). M.p. 172–177 °C. R_f = 0.63 (SiO_2; CH_2Cl_2). Found: C, 72.78; H, 7.34; N, 8.75. $C_{29}H_{35}N_3O_3$ requires C, 73.54; H, 7.45; N, 8.87%. IR (HATR): ν_{max}/cm^{-1} 2921, 2360, 1714, 1657, 1363, 789. ^{1}H NMR (400 MHz; $CDCl_3$): δ_H 0.93–0.98 (6H, m, 2×CH_3), 1.34–1.42 (4H, m, 2×CH_2), 1.59–1.68 (4H, m, 2×CH_2), 3.00 (6H, s, $N(CH_3)_2$), 3.94–3.99 (4H, m, 2×NCH_2), 6.70 (2H, d, *J* = 8.8, CH_{ar}), 6.92 (1H, d, *J* = 16.0, CH), 7.22 (1H, d, *J* = 16.0, CH), 7.44 (2H, d, *J* = 8.8, CH_{ar}), 7.53 (2H, d, *J* = 8.4, CH_{ar}), 8.17 (2H, d, *J* = 8.4, CH_{ar}) and 8.49 (1H, s, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 14.01, 20.38, 20.43, 30.35, 40.51, 41.96, 42.54, 112.40, 116.06, 123.10, 124.95, 125.82, 128.82, 131.02, 132.97, 135.57, 144.01, 150.88, 151.11, 158.67, 160.73 and 162.90. HR-FT-MALDI-MS (DHB) *m*/*z*: 474.2752 ([M + H]$^+$), $C_{29}H_{36}N_3O_3^+$ 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. R_f = 0.63 (SiO_2; CH_2Cl_2). Found: C, 74.05; H, 7.12; N, 8.86. $C_{29}H_{33}N_3O_3$ requires C, 73.86;

H, 7.05; N, 8.91%. IR (HATR): ν_{max}/cm^{-1} 2957, 2360, 1712, 1667, 1362, 1221, 1093. ^{1}H NMR (400 MHz; CDCl$_3$): δ_H 0.93–0.98 (6H, m, 2×CH$_3$), 1.37–1.41 (4H, m, 2×CH$_2$), 1.58–1.64 (4H, m, 2×CH$_2$), 3.01 (6H, s, N(CH$_3$)$_2$), 3.93–3.99 (4H, m, 2×NCH$_2$), 6.66 (2H, d, *J* = 8.8, CH$_{ar}$), 7.42 (2H, d, *J* = 8.8, CH$_{ar}$), 7.53 (2H, d, *J* = 8.4, CH$_{ar}$), 8.11 (2H, d, *J* = 8.4, CH$_{ar}$) and 8.49 (1H, s, CH). ^{13}C NMR (100 MHz, CDCl$_3$): δ_C 14.00, 20.38, 20.42, 30.35, 40.37, 42.04, 42.62, 88.19, 96.11, 109.37, 111.95, 117.30, 129.70, 131.01, 131.57, 133.37, 134.34, 150.71, 151.02, 158.19, 160.54 and 162.62. HR-FT-MALDI-MS (DHB) *m*/*z*: 472.2583 ([M + H]$^+$), C$_{29}$H$_{34}$N$_3$O$_3$$^+$ requires 472.2595.

Chromophore 2a

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, 85%). M.p. 169–171 °C. R_f = 0.46 (SiO$_2$; CH$_2$Cl$_2$). Found: C, 69.34; H, 7.85; N, 10.39. C$_{23}$H$_{31}$N$_3$O$_3$ requires C, 69.49; H, 7.86; N, 10.57%. IR (HATR): ν_{max}/cm^{-1} 2923, 2360, 1713, 1648, 1533, 1366, 1223, 1164, 809. ^{1}H NMR (400 MHz; CDCl$_3$): δ_H 0.93–0.97 (6H, m, 2×CH$_3$), 1.33–1.41 (4H, m, 2×CH$_2$), 1.59–1.64 (4H, m, 2×CH$_2$), 3.08 (6H, s, N(CH$_3$)$_2$), 3.91–3.95 (4H, m, 2×NCH$_2$), 6.65 (2H, d, *J* = 8.8, CH$_{ar}$), 7.37 (1H, d, *J* = 14.8, CH), 7.58 (2H, d, *J* = 8.8, CH$_{ar}$), 8.16 (1H, d, *J* = 12.4, CH) and 8.41 (1H, dd, J_1 = 12.4, J_2 = 14.8, CH). ^{13}C NMR (100 MHz, CDCl$_3$): δ_C 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, 162.35 and 162.94. HR-FT-MALDI-MS (DHB) *m*/*z*: 398.2436 ([M + H]$^+$), C$_{23}$H$_{32}$N$_3$O$_3$$^+$ requires 398.2438.

Chromophore 2b

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. R_f = 0.18 (SiO$_2$; CH$_2$Cl$_2$–Hex 1 : 1). Found: C, 73.34; H, 7.57; N, 8.69. C$_{29}$H$_{35}$N$_3$O$_3$ requires C, 73.54; H, 7.45; N, 8.87%. IR (HATR): ν_{max}/cm^{-1} 2924, 2360, 1713, 1653, 1550, 1361, 1222, 809. ^{1}H NMR (400 MHz; CDCl$_3$): δ_H = 0.93–0.98 (6H, m, 2×CH$_3$), 1.35–1.42 (4H, m, 2×CH$_2$), 1.59–1.65 (4H, m, 2×CH$_2$), 3.01 (6H, s, N(CH$_3$)$_2$), 3.92–3.96 (4H, m, 2×NCH$_2$), 6.78 (2H, d, *J* = 7.2, CH$_{ar}$), 7.42 (1H, d, *J* = 15.2, CH), 7.56 (2H, d, *J* = 7.2, CH$_{ar}$), 7.61 (2H, d, *J* = 8.4, CH$_{ar}$), 7.69 (2H, d, *J* = 8.4, CH$_{ar}$), 8.19 (1H, d, *J* = 12.0, CH) and 8.61 (1H, dd, J_1 = 15.2, J_2 = 12.0, CH). ^{13}C NMR (100 MHz, CDCl$_3$): δ_C 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, 127.33, 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]$^+$), C$_{29}$H$_{36}$N$_3$O$_3$$^+$ requires 474.2725.

Chromophore 2c

Compound **2c** was synthesized from aldehyde **19** (277 mg, 1.0 mmol) and *N*,*N*′-dibutylbarbituric acid (240 mg, 1.0 mmol). Compound **2c** was isolated as a dark violet solid (400 mg, 80%). M.p. 228–232 °C. R_f = 0.73 (SiO$_2$; CH$_2$Cl$_2$). Found: C, 74.42; H, 7.57; N, 8.37. C$_{31}$H$_{37}$N$_3$O$_3$ requires C, 74.52; H, 7.46; N, 8.41%. IR (HATR): ν_{max}/cm^{-1} 2923, 2360, 1715, 1656, 1543, 1396, 1361, 1221, 821. ^{1}H NMR (400 MHz; CDCl$_3$): δ_H 0.93–0.98 (6H, m, 2×CH$_3$), 1.36–1.40 (4H, m, 2×CH$_2$), 1.59–1.65 (4H, m, 2×CH$_2$), 2.99 (6H, s, N(CH$_3$)$_2$), 3.92–3.96 (4H, m, 2×CH$_2$), 6.69 (2H, d, *J* = 8.8, CH$_{ar}$), 6.89 (1H, d, *J* = 16.0, CH), 7.15 (1H, d, *J* = 16.0, CH), 7.37 (1H, d, *J* = 15.2, CH), 7.42 (2H, d, *J* = 8.8, CH$_{ar}$), 7.48 (2H, d, *J* = 8.4 Hz, CH$_{ar}$), 7.62 (2H, d, *J* = 8.4, CH$_{ar}$), 8.18 (1H, d, *J* = 12.0, CH) and 8.55 (1H, dd, J_1 = 15.2, J_2 = 12.0, CH). ^{13}C NMR (100 MHz, CDCl$_3$): δ_C 13.99, 14.02, 20.38, 20.47, 30.37, 30.43, 40.54, 41.63, 42.13, 112.45, 113.93, 123.21, 124.54, 125.15, 126.67, 128.30, 130.03, 131.65, 133.76, 142.14, 150.70, 151.24, 154.45, 157.61, 161.88 and 162.42. HR-FT-MALDI-MS (DHB) *m*/*z*: 500.2893 ([M + H]$^+$), C$_{31}$H$_{38}$N$_3$O$_3$$^+$ requires 500.2908.

Chromophore 2d

Compound **2d** was synthesized from aldehyde **22** (275 mg, 1.0 mmol) and *N*,*N*′-dibutylbarbituric acid (240 mg, 1.0 mmol). Compound **2d** was isolated as a dark violet solid (378 mg, 76%). M.p. 194–199 °C. R_f = 0.85 (SiO$_2$; CH$_2$Cl$_2$). Found: C, 74.28; H, 7.08; N, 8.36. C$_{31}$H$_{35}$N$_3$O$_3$ requires C, 74.82; H, 7.09; N, 8.44%. IR (HATR): ν_{max}/cm^{-1} 2922, 2360, 1713, 1653, 1558, 1397, 1362, 1222, 816. ^{1}H NMR (400 MHz; CDCl$_3$): δ_H 0.93–0.98 (6H, m, 2×CH$_3$), 1.32–1.42 (4H, m, 2×CH$_2$), 1.57–1.65 (4H, m, 2×CH$_2$), 3.00 (6H, s, N(CH$_3$)$_2$), 3.92–3.96 (4H, m, 2×NCH$_2$), 6.65 (2H, d, *J* = 8.8, CH$_{ar}$), 7.37 (1H, d, *J* = 15.6, CH), 7.41 (2H, d, *J* = 8.8, CH$_{ar}$), 7.50 (2H, d, *J* = 8.0, CH$_{ar}$), 7.62 (2H, d, *J* = 8.0, CH$_{ar}$), 8.18 (1H, d, *J* = 12.0, CH) and 8.59 (1H, dd, J_1 = 15.6, J_2 = 12.0, CH). ^{13}C NMR (100 MHz, CDCl$_3$): δ_C 13.99, 14.01, 20.37, 20.46, 30.36, 30.42, 40.37, 41.69, 42.18, 87.96, 95.17, 109.48, 111.96, 114.77, 125.50, 127.80, 129.26, 131.89, 133.20, 134.32, 150.58, 151.17, 153.46, 157.14, 161.77 and 162.30. HR-FT-MALDI-MS (DHB) *m*/*z*: 498.2741 ([M + H]$^+$), C$_{31}$H$_{36}$N$_3$O$_3$$^+$ requires 498.2751.

Chromophore 3a

Compound **3a** was synthesized from aldehyde **11** (173 mg, 1.0 mmol) and *N*,*N*′-dibutylbarbituric acid (240 mg, 1.0 mmol). Compound **3a** was isolated as a dark violet solid (304 mg, 77%). M.p. 144–148 °C. R_f = 0.70 (SiO$_2$; CH$_2$Cl$_2$). Found: C, 69.75; H, 7.41; N, 10.54. C$_{23}$H$_{29}$N$_3$O$_3$ requires C, 69.85; H, 7.39; N, 10.62%. IR (HATR): ν_{max}/cm^{-1} 2923, 2360, 1713, 1362, 1258, 1222, 1090, 1014, 794. ^{1}H NMR (400 MHz; CDCl$_3$): δ_H 0.92–0.97 (6H, m, 2×CH$_3$), 1.33–1.41 (4H, m, 2×CH$_2$), 1.58–1.65 (4H, m, 2×CH$_2$), 3.07 (6H, s, N(CH$_3$)$_2$), 3.91–3.95 (4H, m, 2×NCH$_2$), 6.65 (2H, d, *J* = 8.8, CH$_{ar}$), 7.58 (2H, d, *J* = 8.8, CH$_{ar}$) and 7.81 (1H, s, CH). ^{13}C NMR (100 MHz, CDCl$_3$): δ_C 13.96, 13.98, 20.36, 20.41, 30.34, 40.24, 41.59, 42.12, 94.03, 107.99, 111.77, 121.56, 125.55, 136.29, 137.35, 151.17, 152.53, 159.92 and 161.90. HR-FT-MALDI-MS (DHB) *m*/*z*: 396.2275 ([M + H]$^+$), C$_{23}$H$_{30}$N$_3$O$_3$$^+$ requires 396.2282.

Chromophore 3b

Compound **3b** was synthesized from aldehyde **17** (249 mg, 1.0 mmol) and *N*,*N*′-dibutylbarbituric acid (240 mg, 1.0 mmol). Compound **3b** was isolated as a dark violet solid (382 mg, 81%). M.p. 179–184 °C. R_f = 0.77 (SiO$_2$; CH$_2$Cl$_2$). Found: C, 73.66; H, 7.02; N, 8.90. C$_{21}$H$_{33}$N$_3$O$_3$ requires C, 73.86; H, 7.05; N, 8.91%.

IR (HATR): ν_{max}/cm^{-1} 2928, 2360, 1717, 1658, 1567, 1556, 1398, 1363, 1291, 808. ^{1}H NMR (400 MHz; $CDCl_3$): δ_H 0.93–0.98 (6H, m, 2×CH_3), 1.32–1.44 (4H, m, 2×CH_2), 1.58–1.68 (4H, m, 2×CH_2), 3.01 (6H, s, $N(CH_3)_2$), 3.92–3.97 (4H, m, 2×NCH_2), 6.78 (2H, d, J = 8.8, CH_{ar}), 7.55 (2H, d, J = 8.4, CH_{ar}), 7.61 (2H, d, J = 8.4, CH_{ar}), 7.70 (2H, d, J = 8.8, CH_{ar}) and 7.80 (1H, s, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 13.99, 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, 127.24, 128.02, 134.38, 136.73, 144.29, 150.77, 150.92, 159.44 and 161.40. HR-FT-MALDI-MS (DHB) m/z: 472.2589 ($[M + H]^+$), $C_{29}H_{34}N_3O_3^+$ requires 472.2595.

Chromophore 3c

Compound **3c** was synthesized from aldehyde **20** (275 mg, 1.0 mmol) and *N*,*N*′-dibutylbarbituric acid (240 mg, 1.0 mmol). Compound **3c** was isolated as a dark violet solid (408 mg, 82%). M.p. 207–212 °C. R_f = 0.83 (SiO_2; CH_2Cl_2). Found: C, 74.69; H, 7.16; N, 8.36. $C_{31}H_{35}N_3O_3$ requires C, 74.82; H, 7.09; N, 8.44%. IR (HATR): ν_{max}/cm^{-1} 2922, 2360, 1713, 1659, 1565, 1400, 1362, 1222, 825. ^{1}H NMR (400 MHz; $CDCl_3$): δ_H 0.93–0.98 (6H, m, 2×CH_3), 1.34–1.42 (4H, m, 2×CH_2), 1.59–1.66 (4H, m, 2×CH_2), 2.98 (6H, s, $N(CH_3)_2$), 3.90–3.96 (4H, m, 2×NCH_2), 6.68 (2H, d, J = 8.8, CH_{ar}), 6.87 (1H, d, J = 16.0, CH), 7.13 (1H, d, J = 16.0, CH), 7.40 (2H, d, J = 8.8, CH_{ar}), 7.47 (2H, d, J = 8.4, CH_{ar}), 7.62 (2H, d, J = 8.4, CH_{ar}) and 7.78 (1H, s, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 13.92, 13.96, 20.31, 20.37, 30.25, 40.46, 41.74, 42.24, 91.76, 112.37, 119.41, 119.50, 123.03, 124.59, 124.96, 126.21, 128.29, 131.97, 134.24, 136.52, 141.72, 150.66, 150.84, 159.38 and 161.32. HR-FT-MALDI-MS (DHB) m/z: 498.2740 ($[M + H]^+$), $C_{31}H_{36}N_3O_3^+$ requires 498.2751.

Chromophore 3d

Compound **3d** was synthesized from aldehyde **23** (273 mg, 1.0 mmol) and *N*,*N*′-dibutylbarbituric acid (240 mg, 1.0 mmol). Compound **3d** was isolated as a dark violet solid (342 mg, 69%). M.p. 190–195 °C. R_f = 0.71 (SiO_2; CH_2Cl_2). Found: C, 75.10; H, 6.80; N, 8.49. $C_{31}H_{33}N_3O_3$ requires C, 75.13; H, 6.71; N, 8.48%. IR (HATR): ν_{max}/cm^{-1} 2922, 2360, 1715, 1675, 1654, 1567, 1400, 1360, 1094, 789. ^{1}H NMR (400 MHz; $CDCl_3$): δ_H 0.93–0.97 (6H, m, 2×CH_3), 1.32–1.43 (4H, m, 2×CH_2), 1.57–1.67 (4H, m, 2×CH_2), 3.00 (6H, s, $N(CH_3)_2$), 3.92–3.96 (4H, m, 2×NCH_2), 6.65 (2H, d, J = 8.8, CH_{ar}), 7.41 (2H, d, J = 8.8, CH_{ar}), 7.50 (2H, d, J = 8.4, CH_{ar}), 7.63 (2H, d, J = 8.4, CH_{ar}) and 7.78 (1H, s, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 13.95, 13.98, 20.35, 20.40, 29.91, 30.30, 40.35, 41.85, 42.35, 87.71, 91.58, 95.49, 109.36, 111.96, 117.71, 120.45, 125.45, 127.65, 131.50, 133.21, 133.58, 136.26, 150.64, 150.85, 159.34 and 161.26. HR-FT-MALDI-MS (DHB) m/z: 496.2597 ($[M + H]^+$), $C_{31}H_{34}N_3O_3^+$ requires 496.2595.

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