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Imidazole as a central π-linkage in Y-shaped push–pull chromophores

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ABSTRACT

Twelve imidazole based Y-shaped push–pull chromophores have been designed, synthesised and fully characterised featuring 4,5-bis(*N*,*N*-dimethylanilino)imidazole as a donor moiety, a systematically enlarged π-linker and nitro and cyano groups as acceptors. The synthesised push–pull systems have been studied by electrochemistry, UV/Vis and IR spectroscopy and nonlinear optical properties have been calculated. Moreover, quantitative relationships between the measured and calculated properties and the structural features have also been evaluated. Electrochemical and spectral properties have mainly been affected by the presence of strongly conjugating acceptors, large π-linkers and the spatial arrangement of the chromophore.

1. Introduction

In the last several years, organic dipolar molecules that are end-capped with electron donors and acceptors have been intensively investigated by organic and material chemists. In contrast to inorganic materials, such organic materials with readily polarisable push–pull systems were recognized as tuneable chromophores for nonlinear optics (NLO) and have found widespread application as two-photon absorbing devices, opto-electronic and optical data storage devices, organic light-emitting diodes (OLED) and organic photovoltaic cells [1–4]. A typical organic D–π–A chromophore consists of strong electron donors (D = NR_2 or OR groups) and acceptors (A = NO_2 or CN groups) connected by a π-conjugated system [5–7]. Optical linear and nonlinear properties of these molecules depend on the polarisability of the electrons localized in π-bonding molecular orbitals [8,9]. The chromophore polarisability depends mainly on its chemical structure, in particular on the length of the π-conjugated spacer and the electronic nature of the donors and acceptors attached. The rational design of a typical chromophore involves finding an optimal π-conjugated linkage in addition to appropriate donors and acceptors [10,11]. Successful application and fabrication of such molecules rely on the chromophore possessing large hyperpolarisability, good thermal and chemical robustness, solubility and being available in reasonable quantities (nonlinearity–transparency–solubility–thermal stability trade-off) [12]. Hence, various heteroaromatics have recently been used for the construction of robust π-backbones in NLO active compounds. Among them, imidazoles [13–17] and benzimidazoles [18–21] have proved to be sufficiently efficient and robust five-membered aromatic systems for such purposes. The imidazole molecule can be substituted with donor and acceptor auxiliaries at C2 and C4/C5 (or vice versa) to form Y-shaped chromophores [22,23].

Recently, we reported the synthesis and properties of several D–π–A chromophores featuring imidazole (**1**–**2**) and 2,4,5-triphenylimidazole (**3**) as simple π-conjugated linkages [24–26]. Both linear and branched chromophores **1**–**2** consist of 4,5-dicyanoimidazole acceptor moieties substituted at C2 with *N*,*N*-dimethylamino donor groups, separated by a systematically extended π-conjugated linker. Chromophores **3**, featuring various acceptors and donors in both orientations, were readily accessible from aldehydes and benzils. In the present work, we have combined both approaches and report the synthesis and properties of imidazole Y-shaped chromophores **4**–**9** bearing *N*,*N*-dimethylanilino (DMA) donors and nitro and cyano acceptor groups. In contrast to their structural analogs **1**–**3**, the newly proposed chromophores **4**–**9** possess donors at C4/C5 and acceptors at C2, separated by an additional π-linker (Fig. 1). We report herein the synthesis, full spectral characterisation and structure–property relationships of chromophores **4**–**9**.

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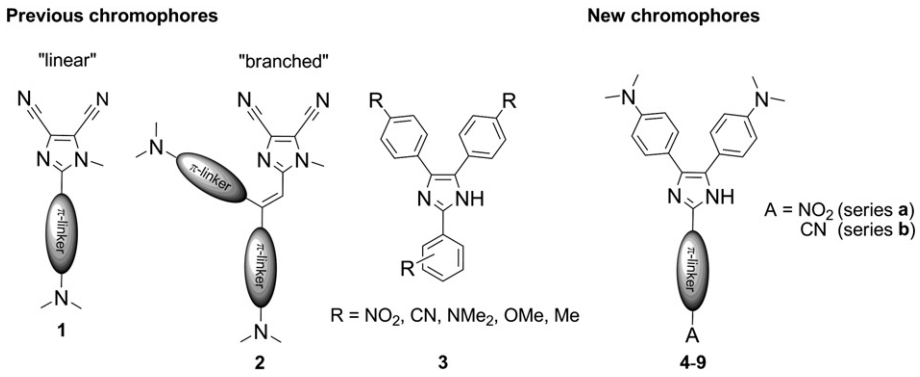


Fig. 1. Molecular structure of the previous and new imidazole chromophores.

2. Experimental

2.1. General

Reagents and solvents were reagent-grade and were purchased from Penta, Aldrich, and Acros and used as received. Starting aldehydes **10a**, **10b** and **11a**, (triphenylphosphoranylidene)acetaldehyde, 4-bromobenzonitrile, 4-bromonitrobenzene, 4-formylphenylboronic acid, vinylboronic acid pinacol ester, 4-ethynylbenzonitrile, 1-ethynyl-4-nitrobenzene and 4-iodobenzaldehyde were commercially available. Aldehydes **11b** (63%), **12a** (41%) and **12b** (64%) were synthesised from **10a** and **10b** according to literature and obtained in the indicated yields [27]. Aldehydes **13a** (85%), **13b** (89%), **14a** (42%), **14b** (40%), **15a** (93%) and **15b** (91%) were synthesised by Suzuki-Miyaura, Heck and Sonogashira cross-coupling reactions [28]. The condensation reactions were carried out in a sealed glass pressure tube (Aldrich). Column chromatography was carried out with silica gel 60 (particle size 0.040–0.063 mm, 230–400 mesh; Merck) and commercially available solvents. Thin-layer chromatography (TLC) was conducted on aluminium sheets coated with silica gel 60 F_{254}, obtained from Merck, with visualisation by UV lamp (254 or 360 nm). Melting points (mp) were measured on a Büchi B-540 melting-point apparatus in open capillaries and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, with a Bruker AVANCE 400 instrument at 25 °C. Chemical shifts are reported in ppm relative to the signal of Me_4Si. The residual solvent signal in the ^{1}H and ^{13}C NMR spectra was used as an internal reference ($CDCl_3$ – 7.25 and 77.23 ppm; DMSO-d_6 – 2.55 and 39.51 ppm). Apparent resonance multiplicities are described as s (singlet), br s (broad singlet), d (doublet) and m (multiplet). Protons of the *N,N*-dimethylanilino group at C4/C5 were marked as DMA. Signals of some carbons in the ^{13}C NMR spectra were not observed as a result of 1*H*-imidazole tautomerism (averaged broad signals – br) [29]. IR spectra were recorded on a Perkin Elmer FT-IR Spectrum BX spectrometer. Mass spectra were measured on a GC/MS configuration comprised of an Agilent Technologies – 6890N gas chromatograph equipped with a 5973 Network MS detector (EI 70 eV, mass range 33–550 Da) or on an LC-MS Micromass Quattro Micro API (Waters) instrument with a direct input (ESI+, CH_3OH, mass range 200–800 Da). Elemental analyses were performed on an EA 1108 Fisons instrument. UV/Vis spectra were recorded on a Hewlett-Packard 8453 spectrophotometer in CH_2Cl_2.

2.2. Synthesis

2.2.1. General procedure for the condensation of aldehydes with 4,4′-bis(N,N-dimethylamino)benzil (chromophores **4**–**9**)

A mixture of 4,4′-bis(*N,N*-dimethylamino)benzil (592 mg; 2.0 mmol), aldehyde **10**–**15** (2.0 mmol) and ammonium acetate (1.5 g; 19.5 mmol) was heated in glacial acetic acid (30 mL) in a sealed glass pressure tube at 150 °C for 24 h. The resulting mixture was poured over ice/water, neutralised with ammonia, and the precipitate was separated via filtration. The crude product was purified by column chromatography (SiO_2; CH_2Cl_2/acetone 95:5).

*2.2.1.1. 2-(4-Nitrophenyl)-4,5-bis[4-(N,N-dimethylamino)phenyl]-1H-imidazole (**4a**).* The title compound was synthesised from 4-nitrobenzaldehyde **10a** (302 mg) following the general procedure. Obtained 504 mg (59%) of a red solid; mp 105–106 °C (lit. [26] mp 104–106 °C). NMR, IR and MS spectra were found to be identical to those described in literature [26].

*2.2.1.2. 2-(4-Cyanophenyl)-4,5-bis[4-(N,N-dimethylamino)phenyl]-1H-imidazole (**4b**).* The title compound was synthesised from 4-cyanobenzaldehyde **10b** (262 mg) following the general procedure. Obtained 592 mg (73%) of a yellow solid; mp 123–125 °C (lit. [26] mp 124–126 °C). NMR, IR and MS spectra were found to be identical to those described in literature [26].

*2.2.1.3. (E)-2-(4-Nitrostyryl)-4,5-bis[4-(N,N-dimethylamino)phenyl]-1H-imidazole (**5a**).* The title compound was synthesised from (*E*)-3-(4-nitrophenyl)prop-2-enal **11a** (354 mg) following the general procedure. Obtained 327 mg (36%) of a dark red solid; R_f = 0.20 (SiO_2; CH_2Cl_2/acetone 95:5); mp 163–167 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.96 (br s, 12H, 2 × N(CH_3)$_2$), 6.75 (d, 4H, J = 8.4 Hz, DMA), 7.32 (d, 1H, J = 16.4 Hz, CH=), 7.40 (d, 4H, J = 8.4 Hz, DMA), 7.51 (d, 1H, J = 16.4 Hz, CH=), 7.84 (d, 2H, J = 8.8 Hz, Ph), 8.25 (d, 2H, J = 8.8 Hz, Ph), 12.48 (br s, 1H, NH). ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 40.41, 112.49, 122.39, 124.62, 126.28, 127.43, 128.71 (br), 143.77, 144.27, 146.40, 149.83 (br). ESI-MS: m/z = 454 $(M + 1)^+$, 476 $(M + 23)^+$. IR (neat): ν = 2795, 1611, 1587, 1513 (NO_2), 1477, 1440, 1332 (NO_2), 1198, 1105, 943, 815, 748 cm^{-1}. Anal. calcd. for $C_{27}H_{27}N_5O_2$ (453.54): C 71.50, H 6.00, N 15.44; found: C 71.55, H 6.04, N 15.32.

*2.2.1.4. (E)-2-(4-Cyanostyryl)-4,5-bis[4-(N,N-dimethylamino)phenyl]-1H-imidazole (**5b**).* The title compound was synthesised from (*E*)-3-(4-cyanophenyl)prop-2-enal **11b** (314 mg) following the general procedure. Obtained 269 mg (31%) of a red solid; R_f = 0.18 (SiO_2; CH_2Cl_2/acetone 95:5); mp 142–144 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.96 (br s, 12H, 2 × N(CH_3)$_2$), 6.75 (d, 4H, J = 8.4 Hz, DMA), 7.27 (d, 1H, J = 16.4 Hz, CH=), 7.39 (d, 4H, J = 8.4 Hz, DMA), 7.46 (d, 1H, J = 16.4 Hz, CH=), 7.78 (d, 2H, J = 8.4 Hz, Ph), 7.86 (d, 2H, J = 8.8 Hz, Ph), 12.47 (br s, 1H, NH). ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 40.00, 109.26, 112.02, 119.06, 120.85, 126.52, 126.85, 128.21 (br), 132.69, 141.55, 143.30, 149.33. ESI-MS: m/z = 434 $(M + 1)^+$, 456 $(M + 23)^+$. IR (neat): ν = 2794, 2220 (CN), 1611, 1597, 1519, 1479, 1440, 1349, 1170, 943, 812 cm^{-1}. Anal. calcd. for $C_{28}H_{27}N_5$ (433.55): C 77.57, H 6.28, N 16.15; found: C 77.13, H 6.43, N 16.04.

*2.2.1.5. 2-[(1E,3E)-4-(4-Nitrophenyl)buta-1,3-dienyl]-4,5-bis[4-(N,N-dimethylamino)phenyl]-1H-imidazole (**6a**).* The title compound was synthesised from (2*E*,4*E*)-5-(4-nitrophenyl)penta-2,4-dienal **12a** (406 mg) following the general procedure. Obtained 489 mg (51%) of a dark red solid; R_f = 0.19 (SiO_2; CH_2Cl_2/acetone 95:5); mp 157–160 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.96 (br s, 12H, 2 × $N(CH_3)_2$), 6.64–6.86 (m, 5H, DMA + CH═), 6.90 (d, 1H, J = 15.6 Hz, CH═), 7.25–7.50 (m, 6H, DMA + CH═), 7.80 (d, 2H, J = 8.4 Hz, 2H, Ph), 8.24 (d, 2H, J = 8.4 Hz, 2H, Ph), 12.35 (br s, 1H, NH). ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 40.05, 122.66, 127.03, 128.21 (br), 128.66, 128.85, 129.91, 132.85, 134.25, 136.67, 143.62, 143.82, 144.16, 145.83, 149.30. ESI-MS: m/z = 480 (M + 1)$^+$. IR (neat): ν = 2912, 1610, 1578, 1508 (NO_2), 1474, 1330 (NO_2), 1224, 1104, 984, 942, 816, 744 cm^{-1}. Anal. calcd. for $C_{29}H_{29}N_5O_2$ (479.57): C 72.63, H 6.10, N 14.60; found: C 72.62, H 6.19, N 14.46.

*2.2.1.6. 2-[(1E,3E)-4-(4-Cyanophenyl)buta-1,3-dienyl]-4,5-bis[4-(N,N-dimethylamino)phenyl]-1H-imidazole (**6b**).* The title compound was synthesised from (2*E*,4*E*)-5-(4-cyanophenyl)penta-2,4-dienal **12b** (366 mg) following the general procedure. Obtained 291 mg (32%) of a dark red solid; R_f = 0.19 (SiO_2; CH_2Cl_2/acetone 95:5); mp 161–163 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.94 (s, 6H, $N(CH_3)_2$), 2.98 (s, 6H, $N(CH_3)_2$), 6.69–6.81 (m, 6H, DMA + CH═), 7.23–7.43 (m, 6H, DMA + CH═), 7.75–7.85 (m, 4H, Ph), 12.30 (br s, 1H, NH). ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 40.09 (br), 109.05, 112.00 (br), 119.09, 123.56, 126.91, 127.81, 128.56, 130.38, 132.53, 133.12, 135.96, 137.45, 141.95, 143.65, 149.01, 149.56. ESI-MS: m/z = 460 (M + 1)$^+$, 482 (M + 23)$^+$. IR (neat): ν = 2920, 2218 (CN), 1748, 1591, 1508, 1474, 1340, 1162, 1055, 985, 941, 815, 668 cm^{-1}. Anal. calcd. for $C_{30}H_{29}N_5$ (459.58): C 78.40, H 6.36, N 15.24; found: C 78.06, H 6.46, N 15.01.

*2.2.1.7. 2-(4′-Nitrobiphenyl-4-yl)-4,5-bis[4-(N,N-dimethylamino)phenyl]-1H-imidazole (**7a**).* The title compound was synthesised from 4′-nitrobiphenyl-4-carbaldehyde **13a** (454 mg) following the general procedure. Obtained 463 mg (46%) of a dark red solid; R_f = 0.22 (SiO_2; CH_2Cl_2/acetone 95:5); mp 159–162 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.97 (br s, 12H, 2 × $N(CH_3)_2$), 6.77 (br s, 4H, DMA), 7.43 (br s, 4H, DMA), 7.96 (d, 2H, J = 8.4 Hz, Ph), 8.10 (d, 2H, J = 8.4 Hz, Ph), 8.25 (d, 2H, J = 8.4 Hz, Ph), 8.37 (d, 2H, J = 8.4 Hz, Ph), 12.54 (br s, 1H, NH). ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 40.54, 112.55, 124.63, 125.95, 127.98, 128.30 (br), 129.39 (br), 131.69, 136.89, 143.89, 146.48, 147.00. ESI-MS: m/z = 504 (M + 1)$^+$, 526 (M + 23)$^+$. IR (neat): ν = 2920, 1609, 1591, 1505 (NO_2), 1488, 1439, 1336 (NO_2), 1107, 1056, 942, 815, 731 cm^{-1}. Anal. calcd. for $C_{31}H_{29}N_5O_2$(503.59): C 73.93, H 5.80, N 13.91; found: C 73.87, H 5.82, N 13.78.

*2.2.1.8. 2-(4′-Cyanobiphenyl-4-yl)-4,5-bis[4-(N,N-dimethylamino)phenyl]-1H-imidazole (**7b**).* The title compound was synthesised from 4′-cyanobiphenyl-4-carbaldehyde **13b** (414 mg) following the general procedure. Obtained 368 mg (38%) of a yellow solid; R_f = 0.28 (SiO_2; CH_2Cl_2/acetone 95:5); mp 170–173 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.97 (br s, 12H, 2 × $N(CH_3)_2$), 6.77 (br s, 4H, DMA), 7.43 (br s, 4H, DMA), 7.91 (d, 2H, J = 8.0 Hz, Ph), 7.97–8.03 (m, 4H, Ph), 8.23 (d, 2H, J = 8.4 Hz, Ph), 8.37 (d, J = 8.0 Hz, Ph), 12.50 (br s, 1H, NH). ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 40.07, 109.88, 112.05, 118.94, 125.45, 127.27, 128.45 (br), 130.95, 132.86, 136.91, 143.50, 144.02, 149.30. ESI-MS: m/z = 484 (M + 1)$^+$, 506 (M + 23)$^+$. IR (neat): ν = 2794, 2223 (CN), 1736, 1602, 1525, 1494, 1439, 1350, 1225, 1124, 1058, 943, 811, 744 cm^{-1}. Anal. calcd. for $C_{32}H_{29}N_5$ (483.61): C 79.47, H 6.04, N 14.48; found: C 79.43, H 6.30, N 14.18.

*2.2.1.9. (E)-2-[4-(4-Nitrostyryl)phenyl]-4,5-bis[4-(N,N-dimethylamino)phenyl]-1H-imidazole (**8a**).* The title compound was synthesised from (*E*)-4-(4-nitrostyryl)benzaldehyde **14a** (507 mg) following the general procedure. Obtained 318 mg (30%) of a red solid; R_f = 0.36 (SiO_2; CH_2Cl_2/acetone 95:5); mp 165–166 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.94 (s, 6H, $N(CH_3)_2$), 3.00 (s, 6H, $N(CH_3)_2$), 6.72 (d, 2H, J = 8.4 Hz, DMA), 6.82 (d, 2H, J = 8.4 Hz, DMA), 7.38 (d, 2H, J = 8.4 Hz, DMA), 7.47 (d, 2H, J = 8.4 Hz, DMA), 7.53 (d, 1H, J = 16.4 Hz, CH═), 7.62 (d, 1H, J = 16.4 Hz, CH═), 7.80 (d, 2H, J = 8.4 Hz, Ph), 7.93 (d, 2H, J = 8.4 Hz, Ph), 8.14 (d, 2H, J = 8.4 Hz, Ph), 8.30 (d, 2H, J = 8.4 Hz, Ph), 12.44 (br s, 1H, NH). ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 40.01, 112.05, 112.08, 118.82, 123.66, 124.10, 125.12, 126.21, 127.25, 127.49, 127.71, 129.06, 130.91, 135.44, 136.89, 143.76, 144.16, 146.12, 148.98, 149.64. ESI-MS: m/z = 530 (M + 1)$^+$, 552 (M + 23)$^+$. IR (neat): ν = 2794, 2924, 1736, 1614, 1590, 1526, 1505 (NO_2), 1440, 1337 (NO_2), 1186, 1108, 964, 945, 846, 816, 750, 696 cm^{-1}. Anal. calcd. for $C_{33}H_{31}N_5O_2$ (529.63): C 74.84, H 5.90, N 13.22; found: C 74.93, H 6.02, N 14.18.

*2.2.1.10. (E)-2-[4-(4-Cyanostyryl)phenyl]-4,5-bis[4-(N,N-dimethylamino)phenyl]-1H-imidazole (**8b**).* The title compound was synthesised from (*E*)-4-(4-cyanostyryl)benzaldehyde **14b** (466 mg) following the general procedure. Obtained 255 mg (25%) of a red solid; R_f = 0.32 (SiO_2; CH_2Cl_2/acetone 95:5); mp 165–168 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.96 (br s, 12H, 2 × $N(CH_3)_2$), 6.78 (br s, 4H, DMA), 7.43 (br s, 4H, DMA), 7.45 (d, 1H, J = 16.4 Hz, CH═), 7.56 (d, 1H, J = 16.4 Hz, CH═), 7.67 (d, 2H, J = 8.4 Hz, Ph), 7.84–7.90 (m, 4H, Ph), 8.13 (d, 2H, J = 8.4 Hz, Ph), 12.44 (br s, 1H, NH). ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 39.99, 109.38, 112.06, 119.09, 121.11, 125.10, 126.66, 127.10, 127.33, 128.36 (br), 131.81, 132.65, 135.56 (br), 141.96, 143.80 (br), 149.32 (br). ESI-MS: ESI-MS: m/z = 510 (M + 1)$^+$, 532 (M + 23)$^+$. IR (neat): ν = 2920, 2219 (CN), 1734, 1558, 1521, 1506, 1457, 1362, 1227, 1205, 1052, 978, 817, 668 cm^{-1}. Anal. calcd. for $C_{34}H_{31}N_5$ (509.64): C 80.13, H 6.13, N 13.74; found: C 80.01, H 6.02, N 13.66.

*2.2.1.11. 2-{4-[(4-Nitrophenyl)ethynyl]phenyl}-4,5-bis[4-(N,N-dimethylamino)phenyl]-1H-imidazole (**9a**).* The title compound was synthesised from 4-[(4-nitrophenyl)ethynyl]benzaldehyde **15a** (502 mg) following the general procedure. Obtained 232 mg (22%) of a red solid; R_f = 0.48 (SiO_2; CH_2Cl_2/acetone 95:5); mp 262–264 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.94 (s, 6H, $N(CH_3)_2$), 3.00 (s, 6H, $N(CH_3)_2$), 6.72 (d, 2H, J = 8.4 Hz, DMA), 6.82 (d, 2H, J = 8.4 Hz, DMA), 7.37 (d, 2H, J = 8.4 Hz, DMA), 7.46 (d, 2H, J = 8.4 Hz, DMA), 7.75 (d, 2H, J = 8.4 Hz, Ph), 7.89 (d, 2H, J = 8.4 Hz, Ph), 8.17 (d, 2H, J = 8.4 Hz, Ph), 8.34 (d, 2H, J = 8.4 Hz, Ph), 12.54 (br s, 1H, NH). ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 40.21, 112.07, 124.02, 124.98, 127.72, 129.07, 129.25, 129.30, 132.12, 132.16, 132.18, 132.54 (low solubility). ESI-MS: m/z = 528 (M + 1)$^+$, 550 (M + 23)$^+$. IR (neat): ν = 2920, 2850, 1738, 1613, 1590, 1505 (NO_2), 1439, 1338 (NO_2), 1226, 1166, 1105, 946, 851, 840, 812, 746, 686 cm^{-1}. Anal. calcd. for $C_{33}H_{29}N_5O_2$ (527.62): C 75.12, H 5.54, N 13.27; found: C 75.29, H 5.61, N 13.12.

*2.2.1.12. 2-{4-[(4-Cyanophenyl)ethynyl]phenyl}-4,5-bis[4-(N,N-dimethylamino)phenyl]-1H-imidazole (**9b**).* The title compound was synthesised from 4-[(4-cyanophenyl)ethynyl]benzaldehyde **15b** (463 mg) following the general procedure. Obtained 254 mg (25%) of a red solid; R_f = 0.42 (SiO_2; CH_2Cl_2/acetone 95:5); mp 162–165 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.94 (s, 6H, $N(CH_3)_2$), 3.00 (s, 6H, $N(CH_3)_2$), 6.72 (d, 2H, J = 8.8 Hz, DMA), 6.81 (d, 2H, J = 8.8 Hz, DMA), 7.37 (d, 2H, J = 8.8 Hz, DMA), 7.46 (d, 2H, J = 8.8 Hz, DMA), 7.71 (d, 2H, J = 8.4 Hz, Ph), 7.80 (d, 2H, J = 8.4 Hz, Ph), 7.96 (d, 2H, J = 8.4 Hz, Ph), 8.17 (d, 2H, J = 8.4 Hz, Ph), 12.52 (br s, 1H, NH). ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 39.98, 88.88, 93.62, 110.84, 112.01, 118.46, 120.02, 123.46 (br), 124.93, 127.25, 127.68 (br), 129.01 (br), 131.33, 132.01, 132.06, 132.63, 143.18, 148.98, 149.67. ESI-MS: m/z = 508 (M + 1)$^+$, 530 (M + 23)$^+$. IR (neat): ν = 2790, 2220 (CN), 1736, 1611, 1597, 1524,

1503, 1438, 1347, 1224, 1162, 1133, 1058, 942, 837, 811, 734 cm^{-1}. Anal. calcd. for $C_{34}H_{29}N_5$ (507.63): C 80.45, H 5.76, N 13.80; found: C 80.36, H 5.87, N 13.99.

2.3. Electrochemistry

Electrochemical measurements were carried out in acetonitrile containing 0.1 M Bu_4NPF_6 in a three-electrode cell using dc-polarography, voltammetry on Pt-rotating disk electrode (RDE) and cyclic voltammetry (CV). The working electrode was a mercury drop for reduction experiments and a platinum disc (2 mm in diameter) for oxidation experiments. A saturated calomel electrode (SCE) separated by a bridge filled with acetonitrile/Bu_4NPF_6 and Pt wire was used as the reference and auxiliary electrodes. All potentials are given vs. SCE. Voltammetric measurements were performed using a potentiostat PGSTAT 30 (AUTOLAB, Ecochemie, Utrecht, The Netherlands) operated via GPEs 4.8 software. All polarographic and voltammetric data were fully consistent, and, therefore, only anodic peak potentials ($E_{p,a}$) and cathodic peak potentials ($E_{p,c}$) for oxidation and reduction measured by CV were further considered.

2.4. Quantum and statistical calculations

Initial geometries of the compounds **4**–**9** have been calculated by the PM3 method (ArgusLab, [30]) and subsequently optimised by the PM6 method (MOPAC2009, [31]). The HOMO and LUMO energies and average second-polarisabilities β were further calculated by employing MOPAC2009.

3. Results and discussion

3.1. Synthesis

The retro-synthetic strategy leading to target chromophores **4**–**9** involves facile and one-pot condensation of 4,4′-bis(*N*,*N*-dimethylamino)benzil with extended aldehydes in the presence of ammonium acetate in glacial acetic acid (Scheme 1) similar to that used for the construction of chromophore **3** [26].

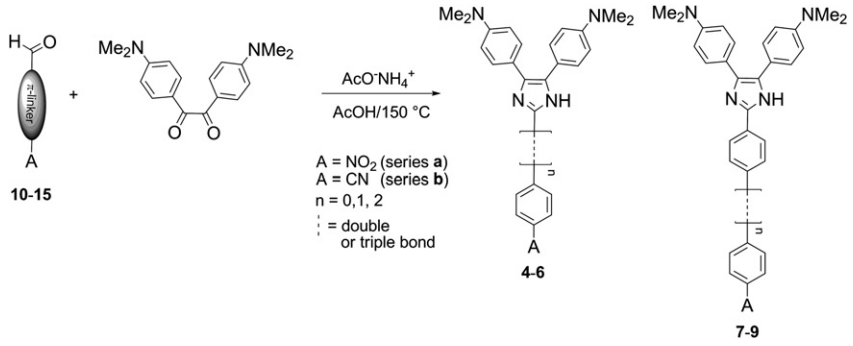
Whereas the starting benzil was commercially available, extended aldehydes **11**–**15** needed to be synthesised (Scheme 2). One-pot treatment of the commercially available 4-nitro and 4-cyanobenzaldehydes **10a** and **10b** with either 1 or 2 equivalents of (triphenylphosphoranylidene)acetaldehyde afforded corresponding cinnamaldehydes **11a** and **11b** or (2*E*,4*E*)-5-(4-nitro (cyano)phenyl)penta-2,4-dienals **12a** and **12b** [27]. We have recently reported a convenient synthesis for preparing donor-substituted π-conjugated linkers as building blocks for modular chemistry [28]. This synthetic approach was further used for the construction of acceptor-substituted aldehydes **13**–**15**. Aldehydes **13a** and **13b** with central biphenyl π-linkers were synthesised by a $PdCl_2(PPh_3)_2$-catalysed Suzuki-Miyaura cross-coupling reaction of 4-nitro- and 4-cyanobromobenzenes with 4-formylphenylboronic acid. Direct Heck cross-coupling of the starting 4-nitro- and 4-cyanobromobenzenes with vinylboronic acid pinacol ester afforded 4-substituted styryldioxaborolanes **16a** and **16b**. These intermediates were further treated with 4-iodobenzaldehyde in a Suzuki-Miyaura reaction to yield the desired aldehydes **14a** and **14b** with the central (*E*)-phenylethenylphenyl π-linker. Sonogashira cross-coupling of 1-ethynyl-4-nitrobenzene or 4-ethynylbenzonitrile with 4-iodobenzaldehyde produced the final aldehydes **15a** and **15b**, with the central phenylethynylphenyl π-linker.

With the systematically extended aldehydes **10**–**15** in hand, the aforementioned condensation of 4,4′-bis(*N*,*N*-dimethylamino) benzil afforded chromophores **4**–**9** as two series, **a** and **b** (Scheme 1, Table 1). Target imidazoles **4**–**9** were isolated in the yields of 22–73%. In some cases, the starting benzil was recovered as a main impurity. All of the newly synthesised compounds were fully characterised by ^1H and ^{13}C NMR, IR, EI(ESI)-MS and elemental analyses.

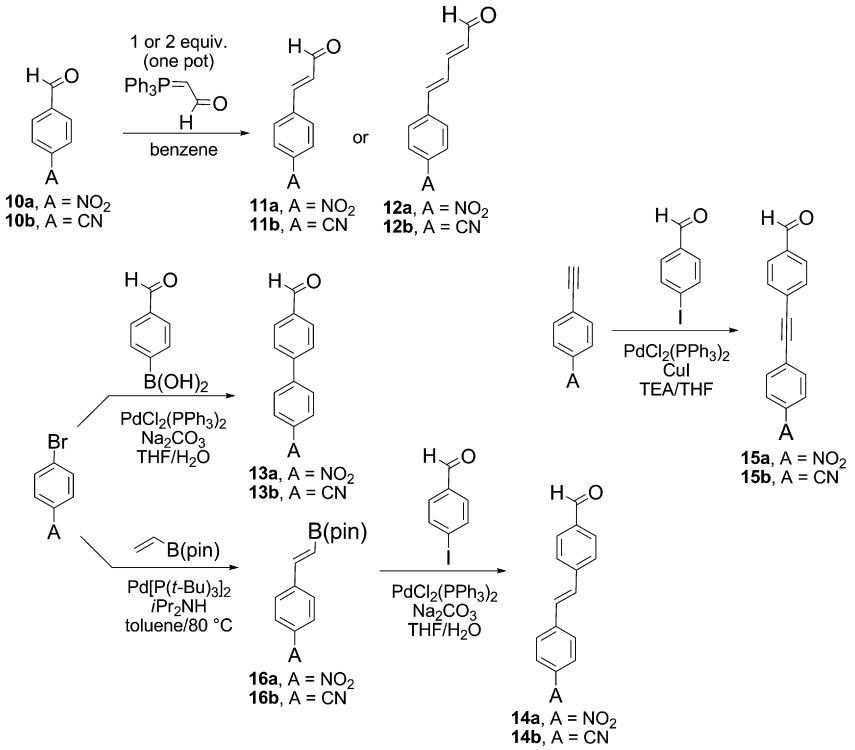
3.2. Electrochemistry

Electrochemical investigations of chromophores **4**–**9** were carried out in acetonitrile by cyclic voltammetry using a platinum stationary disk electrode (scan rates 50–1000 mV/s) and a platinum rotating disk electrode (various frequencies of rotation). The reduction studies were performed by dc-polarography (dropping mercury electrode, DME) and cyclic voltammetry (hanging mercury drop electrode, HMDE). The acquired data is summarized in Table 1 and representative voltammograms of compounds **4a** and **4b** are shown in Fig. 2.

Whereas the electrochemical oxidation processes of chromophores **4**–**9** are most probably localized on the donor *N*,*N*-dimethylanilino moieties, their reductions involve the acceptor NO_2 and CN groups in addition to the π-conjugated system. The first anodic potentials $E_{p,a}$, measured by CV, range from 0.435 to 0.515 V for series **a** (NO_2) and from 0.435 to 0.506 V for series **b** (CN). It is evident that the electronic nature of the appended substituents influences the first oxidation potential only negligibly. Overall, three anodic processes were observed. The first two steps are reversible, diffusion controlled, one-electron oxidations and the third process is an irreversible oxidation accompanied by electrode inhibition (Fig. 2). With the same number of donors and acceptors, the changes in $E_{p,a}$ are clearly caused by the length and spatial arrangement of the used π-linker. The measured anodic peak potential $E_{p,a}$ decreases with the elongation of the π-linker (see chromophores **4**–**5**–**6**) and increasing its planarity – e.g., compare chromophores **4** and **5** or **7** and **8**. Whereas chromophores **4** and **7** possess the 1,4-phenylene moiety connected directly to imidazole



Scheme 1. Synthesis of chromophores **4**–**9**.



Scheme 2. Synthetic approach towards aldehydes **10**–**15** with a systematically extended π-conjugated path.

C2 (a typical torsion angle for 2-phenylimidazoles is about 30° [32]), chromophores **5** and **8** are more planar by an additional CC double bond localized either between the imidazole C2 and the 1,4-phenylene unit (**5**) or between two 1,4-phenylene units in **8**.

The cathodic peak potentials $E_{p,c}$, measured by CV, range from −0.992 to −1.104 V for series **a** and from −1.628 to −2.022 V for series **b**. The first cathodic reductions are mostly irreversible (or quasi-reversible) one-electron processes. The reduction of nitro-substituted chromophores (series **a**) is facilitated as a result of the reduced transfer of electron density from the DMA donors to the nitro acceptor with increasing length and planarity of the π-linker. Among chromophores **4a**–**8a**, chromophore **6a**, featuring a long and planar π-linker, was reduced at the most positive potential $E_{p,c} = -1.044$ V. However, chromophore **9a**, featuring one of the longest but non-planar π-linkers, is reduced even more easily ($E_{p,c} = -0.992$ V). This is caused by the presence of the electronegative CC triple bond, which acts as an insulator [5,25]. Compared to series **a**, the electrochemical reduction of cyano-substituted chromophores in series **b** occurred at more negative potentials, approximately 0.7–0.9 V. However, the general trend in the first reduction potentials for series **b** is analogous to that for series **a**. Thus, elongation and planarisation of the π-conjugated path caused a reduction potential shift with the magnitude of variation decreasing in the following order: **9**, **6**, **5**, **8**, **7**, **4** for series **a** and **6**, **5**, **8**, **9**, **7**, **4** for series **b**. The only difference in the position of the first reduction of chromophore **9a** was discussed above.

A comparison of the measured electrochemical data obtained for chromophore series **1** (Fig. 1, [24]) and series **4**–**9** seems to be reasonable at this point. Both chromophore series differ mainly in the orientation of acceptors and donors appended to the imidazole ring. Whereas the first oxidation potentials of imidazole-separated DMA groups in series **4**–**9** range from 0.435 to 0.515 V, the first reduction potentials showed significant changes from −0.992 to −2.022 V. In contrast to chromophores **4**–**9**, chromophore series **1**

Table 1
Structures, yields, electrochemical data, absorption maxima (λ_{max}), frequency of the C≡N stretch, calculated energies E_{HOMO}, E_{LUMO} and average second-polarisabilities β for chromophores **4**–**9**.

Comp.	A[a]	n[a]	Bond (−)[a]	Yield [%]	$E_{p,a}$[b] [V]	$E_{p,c}$[b] [V]	$E_{p,a} - E_{p,c}$ [V]	λ_{max} [nm (eV)]	ν (CN)[c] [cm^{-1}]	E_{HOMO} [eV]	E_{LUMO} [eV]	$\beta \times 10^{-29}$ [esu]
4a	NO_2	0	×	59	0.515	−1.104	1.62	457 (2.71)	–	−7.87	−1.47	5.76
4b	CN	0	×	73	0.506	−2.022	2.53	397 (3.12)	2221	−7.81	−0.91	3.68
5a	NO_2	1	=	36	0.484	−1.047	1.53	470 (2.64)	–	−7.79	−1.44	5.96
5b	CN	1	=	31	0.458	−1.768	2.23	434 (2.86)	2220	−7.72	−0.93	4.62
6a	NO_2	2	=	51	0.435	−1.044	1.48	474 (2.62)	–	−7.74	−1.59	8.98
6b	CN	2	=	32	0.435	−1.628	2.06	442 (2.81)	2218	−7.68	−1.17	6.69
7a	NO_2	0	×	46	0.469	−1.103	1.57	417 (2.97)	–	−7.75	−1.41	4.81
7b	CN	0	×	38	0.458	−1.964	2.42	391 (3.17)	2223	−7.71	−0.88	3.99
8a	NO_2	1	=	30	0.461	−1.067	1.53	434 (2.86)	–	−7.74	−1.60	7.80
8b	CN	1	=	25	0.454	−1.775	2.23	407 (3.05)	2219	−7.69	−0.95	4.17
9a	NO_2	1	≡	22	0.468	−0.992	1.46	420 (2.95)	–	−7.77	−1.63	8.46
9b	NO_2	1	≡	25	0.466	−1.798	2.26	405 (3.06)	2220	−7.72	−1.21	6.31

[a] See Scheme 1 for the chromophore structures.
[b] $E_{p,a}$ and $E_{p,c}$ – anodic and cathodic peak potentials measured by CV. All potentials are given vs. SCE.
[c] Frequency of the C≡N stretch (series **b**).

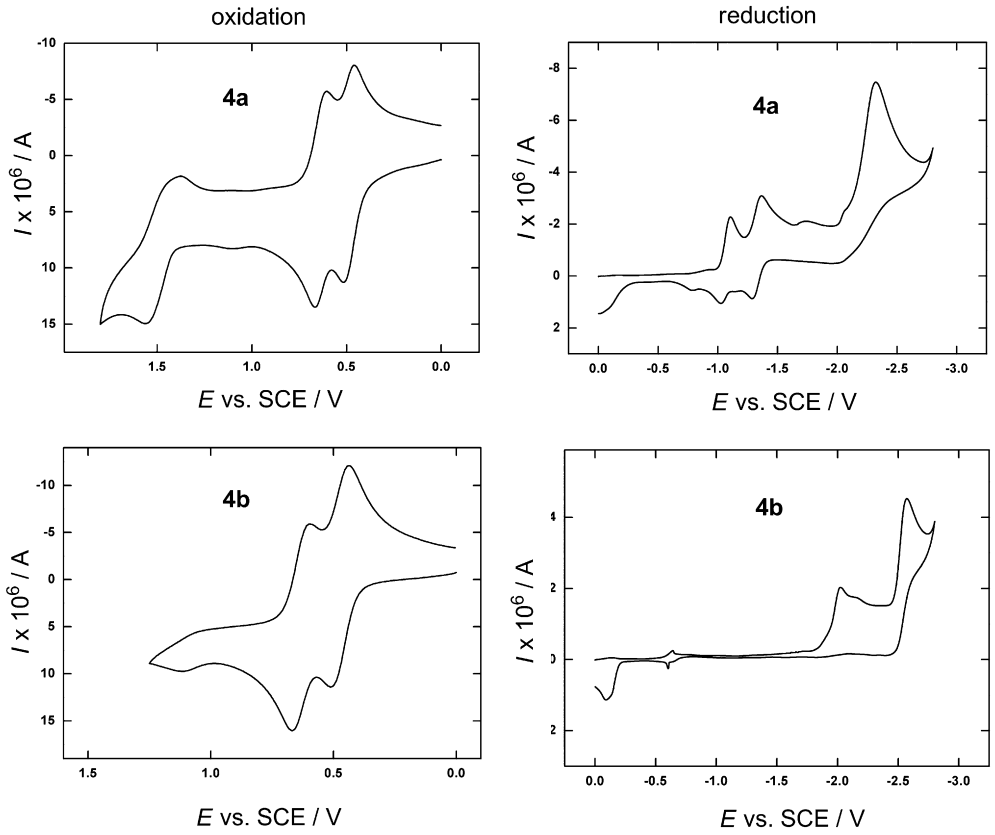


Fig. 2. Representative CV curves of the oxidation and reduction of compounds **4a** and **4b** at Pt (oxidation) or HMDE (reduction) electrodes in acetonitrile.

features cyano groups at imidazole C4/C5 and *N*,*N*-dimethylamino donor groups at imidazole C2, separated by an additional π-linker. The first oxidation potentials of chromophores **1** range from 0.69 to 1.38 V, while the first reduction potentials of imidazole-separated cyano groups differ only slightly (−1.81 to −1.91 V). This implies that either donor- or acceptor-substituted π-linkers in both series are the most electrochemically active parts of the molecule, and that 4,5-bis(*N*,*N*-dimethylanilino)imidazole in **4**–**9** or 4,5-dicyanoimidazole in **1** behave as donor or acceptor moieties, respectively.

*3.3. UV–visible/IR studies and structure-hyperpolarisability consideration of chromophores **4**–**9***

Electronic absorption spectra of imidazoles **4**–**9** measured in CH_2Cl_2 showed intense charge-transfer (CT) absorption bands in the UV–visible region (Fig. 3, Table 1).

As a main feature, the position of the CT-band depends on the electronic nature of the appended acceptors, taking into consideration the length and planarity of the conjugated π-backbone. Whereas the chromophores in series **a** exhibited CT-bands with λ_{max}

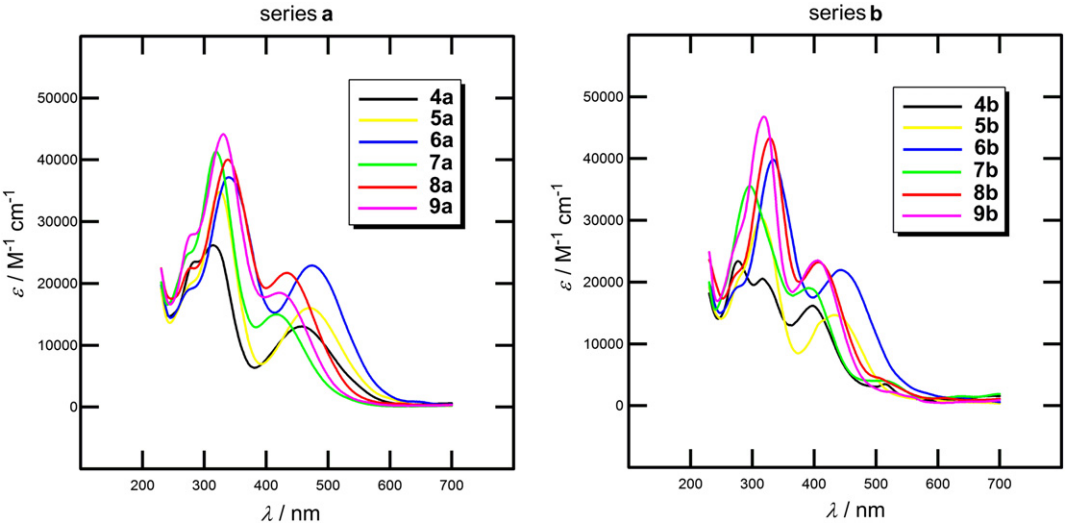


Fig. 3. Electronic absorption spectra of **4**–**9** (2×10^{-5} M solutions in dichloromethane).

appearing between 417 and 474 nm, the cyano-substituted series **b** showed CT-bands with λ_{max} ranging from 397 to 442. The longest-wavelength absorption bands of chromophores bearing NO_2 acceptor groups are shifted more bathochromically than those for chromophores with CN groups, possibly as a result of the strong negative electronic effects of the nitro group. On the other hand, the observed bathochromic shifts within the individual series **a** and **b** can be rationalised as an effect of the π-linker between the appended acceptors and donors. The influence of the spacer on the efficiency of the donor-acceptor conjugation is best evaluated in series **4**–**6** and **7**–**9**, in which donor-acceptor separation is systematically extended. Within the series **4**–**6**, the position of the CT-band is shifted bathochromically with λ_{max} of 457/397 (**4a**/**4b**), 470/434 (**5a**/**5b**) and 474/442 nm (**6a**/**6b**). When comparing chromophores **4** and **5**, the change in λ_{max} can be mainly ascribed to molecule planarisation as a result of the CC double bond insertion between imidazole C2 and the 1,4-phenylene unit. Similar to the measured first reduction potentials (see above), the longest-wavelength transition was measured for chromophores **6a** ($\lambda_{max} = 474$ nm) and **6b** ($\lambda_{max} = 442$ nm), featuring two CC double bonds and one 1,4-phenylene unit in a planar arrangement. In contrast to the simplest chromophores **4a** and **4b**, chromophores **7a** ($\lambda_{max} = 417$ nm) and **7b** ($\lambda_{max} = 391$ nm), bearing a longer twisted biphenyl π-linker [24], showed hypsochromically shifted CT-bands. However, partial planarisation through the insertion of CC double or triple bonds, as in chromophores **8** and **9**, caused a bathochromic shift.

The stretching frequency of the cyano groups, ν (CN), provides another indicator for the efficiency of the intramolecular CT. A moderate trend, similar to the longest-wavelength absorption maxima, can be seen in Table 1, while the lowest energy was measured for planar chromophore **6b** (2218 cm^{-1}). Employing PM3 and PM6 methods, the HOMO and the LUMO energies and average second-polarisabilities β were further calculated (Table 1). The calculated differences of $E_{HOMO} - E_{LUMO}$ have been correlated with the electrochemically measured band gap $E_{p,a} - E_{p,c}$. Fig. 4 shows a good linear correlation between these two quantities ($R = 0.965$). Moreover, the calculated average second-polarisabilities β (Table 1) copies exactly the aforementioned trend that was seen in the measured electrochemical data, λ_{max}, ν (CN) and calculated $E_{HOMO} - E_{LUMO}$. This means that chromophore polarisability depends on the increasing accepting character of substituent A (e.g., β (**6a**) = 8.98 × 10^{-29} esu vs. β (**6b**) = 6.69 × 10^{-29} esu), elongation of the π-conjugated path (e.g., series **4a**, **5a** and **6a** with $\beta = 5.76$, 5.96 and 8.98 × 10^{-29} esu) and planarity of the chromophore (e.g., β (**7a**) = 4.81 × 10^{-29} esu vs. β (**8a**) = 7.80 × 10^{-29} esu).

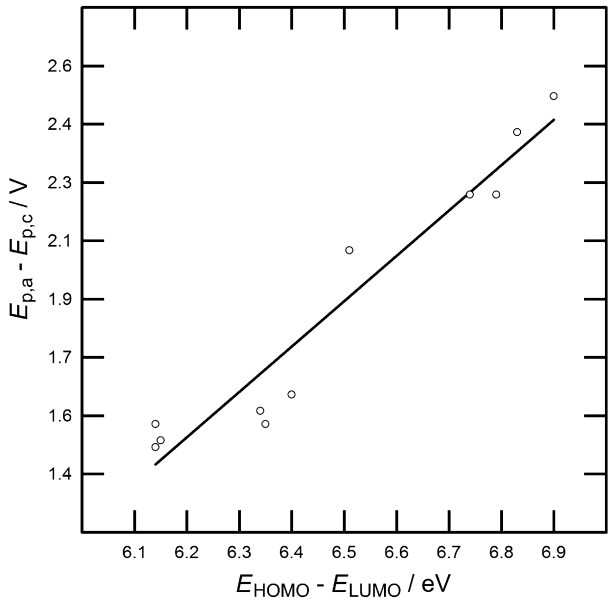


Fig. 4. Linear correlation between the calculated differences $E_{HOMO} - E_{LUMO}$ and electrochemical band gap $E_{p,a} - E_{p,c}$ (excluding **9b** as outlier, $R = 0.965$, $s = 0.115$).

4. Conclusion

Overall, twelve imidazole based Y-shaped chromophores, featuring *N*,*N*-dimethylanilino donors at imidazole C4/C5 and nitro and cyano acceptors at imidazole C2, were synthesised. The acceptor substituents were further separated by an additional systematically enlarged π-linker. The chromophore properties were studied by electrochemistry, UV/Vis and IR spectra, and the experimental results were correlated with calculated properties such as E_{HOMO}, E_{LUMO} and β. Several important structural features affecting intramolecular charge-transfer were revealed. The presence of a strongly conjugating acceptor, the length of the π-conjugated path and overall chromophore planarity proved to be the most important structural factors determining electrochemical and spectral properties of the studied push–pull D–π–A systems. Considering the planarity, electrochemical behaviour, UV–Vis and IR properties, solubility and one of the highest calculated average second-polarisabilities β of chromophores **6a** and **6b**, the 4-phenylbuta-1,3-dienyl π-linker combined with the strong nitro or cyano acceptors seems to possess one of the better balances of performance and practicality within the studied series.

Acknowledgements

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