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Push-pull molecules with a systematically extended π-conjugated system featuring 4,5-dicyanoimidazole

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ABSTRACT

Eighteen chromophores featuring 4,5-dicyanoimidazole as an acceptor moiety, a systematically enlarged π-conjugated spacer and methoxy and *N*,*N*-dimethylamino groups as donors were synthesised and characterised by X-ray analysis, electrochemistry, UV–Vis and fluorescence spectroscopy whilst NLO properties were calculated. Quantitative relationships between measured properties and structural features of the chromophores were also evaluated.

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1. Introduction

Diverse, push-pull molecules with large delocalized π-electron systems have attracted considerable attention. These materials can be end-capped with electron donors (D) and acceptors (A) arranged in either symmetrical A-π-A, D-π-D or asymmetrical A-π-D chromophore orientations [1–3]. Within recent years, such readily polarisable compounds have been studied owing to their promising optoelectronic properties, especially second- and third-order optical nonlinearities (NLO) [4,5]. Thus, such push-pull chromophores enjoy widespread application in material chemistry as optoelectronic [6] and optical data storage devices [7], organic light-emitting diodes (OLED) [8], organic-inorganic hybrid materials [9], functional polymers [10] and highly functionalised dendrimers [11,12]. A typical organic chromophore consists of strong electron acceptors (e.g. NO_2 or CN groups) and donors (e.g. NR_2 or OR groups) connected by a π-conjugated system. This arrangement ensures efficient intramolecular charge-transfer and enables further fine-tuning of the polarisability of the chromophore [13–16]. Additionally, successful fabrication of such molecules, in particular film deposition, relies on the chromophore possessing good thermal and chemical robustness and being available in reasonable quantities. Hence, various heteroaromates such as pyridine [17] or pyrazine [18] as well as five-membered rings such as triazoles [19], thiophenes [20] or benzothiazoles [21,22] have been widely utilised as robust π-backbones for NLO active compounds. In recent years, 1,3-diazoles – imidazoles [23–31] and benzimidazoles [32–34] have been widely employed as suitable and robust aromatic systems for the construction of promising charge-transfer chromophores. Imidazole-based chromophores usually possess donor/acceptor auxiliaries at C-2 or C-4/C-5 (and vice versa) to form Y-shaped chromophores. The rational design of such organic optoelectronic chromophores involves finding an optimal π-conjugated linkage as well as proper donors and acceptors [35]. In general, charge-transfer chromophores that exhibit large hyperpolarisability, good optical transparency, solubility and thermal stability for fabrication processes are currently in demand (nonlinearity-transparency-solubility-thermal stability trade-off).

Since the first synthesis of 4,5-dicyanoimidazole was reported by Woodward [36,37], this planar heterocyclic compound has been utilised in the construction of the aforementioned push-pull systems

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with applicability in various branches of material science [38–44]. Its widespread use demonstrates that this easily accessible, soluble and robust precursor may act as an efficient acceptor moiety. Recently, the present authors reported the synthesis and properties of several D-π-A chromophores featuring 2,4,5-triphenylimidazole as a basic π-conjugated linkage [45]. Due to the growing interest in stable heterocyclic chromophores as well as our experience in the chemistry of imidazole and charge-transfer chromophores [13–16], this paper concerns the synthesis and properties of imidazole-based chromophores possessing 4,5-dicyanoimidazole as an acceptor moiety, *N*,*N*-dimethylamino and methoxy groups as donors and a systematically extended π-conjugated path (Fig. 1).

2. Experimental

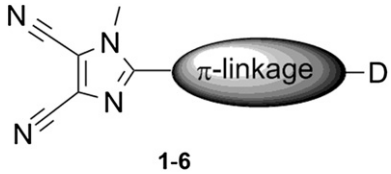
2.1. General

Reagents and solvents were reagent-grade and were purchased from Penta, Aldrich, and Acros and used as received. Boronic acids and esters used in the Suzuki–Miyaura reaction were purchased from Aldrich or synthesised according to literature procedures [46]. 2-Bromo-1-methyl-1*H*-imidazole-4,5-dicarbonitrile (**7**) was synthesised from diaminomaleonitrile according to literature procedures [40,47]. 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 360/400/500 MHz and 90/100/125 MHz, respectively, with a Bruker AMX 360 and Bruker AVANCE 400 or 500 instruments 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; acetone-d_6 – 2.05 and 29.92 ppm). Apparent resonance multiplicities are described as s (singlet), d (doublet) and m (multiplet). Mass spectra were measured on a GC/MS configuration comprised of an Agilent Technologies – 6890 N gas chromatograph equipped with a 5973 Network MS detector (EI 70 eV, mass range 33–550 Da) or on a 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.

2.2. Synthesis

2.2.1. 1-Methyl-1H-imidazole-4,5-dicarbonitrile (**1a**)

The title compound was synthesised from diaminomaleonitrile according to the literature procedure [47] and obtained as white solid. The yield over 2 steps was 85%; mp 87–88 °C (Lit. [47] mp 87–89 °C).



1-6

D = NMe_2, OMe or H

Fig. 1. Molecular structure of the proposed imidazole chromophores.

^{1}H NMR ($CDCl_3$, 360 MHz): δ = 3.89 (s, 3H, CH_3), 7.69 (s, 1H, H_{im}). ^{13}C NMR ($CDCl_3$, 90 MHz): δ = 34.13, 107.92, 111.75, 113.13, 123.09, 141.98. EI-MS (70 eV) *m*/*z* (rel. int.): 132 (M^+, 100), 91 (20), 77 (16), 67 (18). Anal. calcd. for $C_6H_4N_4$: C 54.54, H 3.05, N 42.41; found: C 54.60, H 3.07, N 42.44.

2.2.2. 2-Methoxy-1-methyl-1H-imidazole-4,5-dicarbonitrile (**1b**)

2-Methoxy-1*H*-imidazole-4,5-dicarbonitrile was synthesised according to the literature procedure [48] in 23% yield and further *N*-methylated as described by Rapoport et al. [47]. White solid, yield 90%; mp 61–63 °C (Lit. [48] mp 65–66 °C). ^{1}H NMR ($CDCl_3$, 360 MHz): δ = 3.53 (s, 3H, CH_3), 4.10 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$, 90 MHz): δ = 30.79, 58.61, 108.54, 109.49, 112.12, 118.33, 154.65. EI-MS (70 eV) *m*/*z* (rel. int.): 162 (M^+, 100), 147 (81), 133 (21), 120 (26), 67 (73). Anal. calcd. for $C_7H_6N_4O$: C 51.85, H 3.73, N 34.55; found: C 51.78, H 3.84, N 34.33.

2.2.3. 2-(N,N-Dimethylamino)-1-methyl-1H-imidazole-4,5-dicarbonitrile (**1c**)

A solution of **7** (100 mg; 0.47 mmol), dimethylamine (1 mL; 7.9 mmol; 40% aq. solution) and K_2CO_3 (66 mg; 0.47 mmol) in DMF (5 mL) was heated at 110 °C for 1 h and then cooled to 25 °C, diluted with H_2O (30 mL) and extracted with EtOAc (2 × 30 mL). The combined organic extracts were dried (Na_2SO_4) and the solvent was evaporated to afford pure **1c** as a white solid, yield 75 mg (90%); mp 82–83 °C. ^{1}H NMR ($CDCl_3$, 360 MHz): δ = 2.89 (s, 6H, $N(CH_3)$), 3.62 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 90 MHz): δ = 33.40, 41.82, 109.20, 110.58, 112.42, 120.02, 156.48. EI-MS (70 eV) *m*/*z* (rel. int.): 175 (M^+, 54), 160 (100), 146 (71), 133 (20), 119 (18), 67 (25), 42 (19). Anal. calcd. for $C_8H_9N_5$: C 54.85, H 5.18, N 39.98; found: C 54.78, H 5.23, N 39.97.

2.2.4. General procedure for the synthesis of target chromophores **2**–**6** through Suzuki–Miyaura cross-coupling

$PdCl_2(PPh_3)_2$ (caution: toxic; irritant; incompatible with oxidants, moisture; 33 mg; 0.047 mmol) and Na_2CO_3 (55 mg; 0.52 mmol) were added to a degassed solution of **7** (100 mg; 0.474 mmol) and boronic acid/ester (0.52 mmol) in THF/H_2O (20 mL; 4:1) under an argon atmosphere. The mixture was stirred under Ar at 60 °C for 12 h, diluted with H_2O (30 mL) and extracted with CH_2Cl_2 (2 × 30 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated in vacuo. Subsequent column chromatography afforded pure products **2**–**6**.

2.2.4.1. 1-Methyl-2-phenyl-1H-imidazole-4,5-dicarbonitrile (**2a**).

Obtained 48 mg (49%) of a white solid; R_f = 0.33 (SiO_2; Hexane/EtOAc 2:1); mp 134–136 °C. ^{1}H NMR ($CDCl_3$, 360 MHz): δ = 3.90 (s, 3H, CH_3), 7.52–7.63 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, 90 MHz): δ = 34.84, 99.46, 102.20, 108.58, 111.91, 127.11, 129.25, 129.43, 131.48, 152.8. EI-MS (70 eV) *m*/*z* (rel. int.): 208 (M^+, 65), 207 (100), 103 (12). Anal. calcd. for $C_{12}H_8N_4$: C 69.22, H 3.87, N 26.91; found: C 69.18, H 3.98, N 26.87.

2.2.4.2. 2-(4-Methoxyphenyl)-1-methyl-2-phenyl-1H-imidazole-4,5-dicarbonitrile (**2b**).

Obtained 64 mg (57%) as a white solid; R_f = 0.25 (SiO_2; Hexane/EtOAc 2:1); mp 156–158 °C. ^{1}H NMR ($CDCl_3$, 360 MHz): δ = 3.87 (s, 6H, CH_3 + OCH_3), 7.03 (d, 2H, *J* = 8.8 Hz, Ar), 7.56 (d, 2H, *J* = 8.8 Hz, Ar). ^{13}C NMR ($CDCl_3$, 90 MHz): δ = 34.83, 55.74, 101.81, 108.74, 112.03, 113.96, 114.85, 119.31, 122.36, 130.81, 152.78. EI-MS (70 eV) *m*/*z* (rel. int.): 238 (M^+, 97), 237 (100), 195 (16). Anal. calcd. for $C_{13}H_{10}N_4O$: C 65.54, H 4.23, N 23.52; found: C 65.52, H 4.34, N 23.52.

2.2.4.3. 2-(4-(N,N-Dimethylamino)phenyl)-1-methyl-2-phenyl-1H-imidazole-4,5-dicarbonitrile (**2c**).

Obtained 101 mg (85%) as

a yellowish solid; $R_f = 0.4$ (SiO_2; CH_2Cl_2); mp 263–265 °C. ^{1}H NMR (DMSO-d_6, 360 MHz): $\delta = 3.05$ (s, 6H, $N(CH_3)_2$), 3.89 (s, 3H, CH_3), 6.87 (d, 2H, $J = 8.8$ Hz, Ar), 7.63 (d, 2H, $J = 8.8$ Hz, Ar). ^{13}C NMR (DMSO-d_6, 90 MHz): $\delta = 35.28, 39.02, 109.54, 111.75, 113.04, 113.75, 113.94, 120.30, 130.24, 151.72, 152.88$. EI-MS (70 eV) m/z (rel. int.): 251 (M^+, 100), 250 (98), 234 (12), 145 (13). Anal. calcd. for $C_{14}H_{13}N_5$: C 66.92, H 5.21, N 27.87; found: C 66.92, H 5.24, N 27.87.

*2.2.4.4. (E)-1-Methyl-2-styryl-1H-imidazole-4,5-dicarbonitrile (**3a**) [41].* Obtained 60 mg (54%) as a white solid; $R_f = 0.39$ (SiO_2; Hexane/EtOAc 2:1); mp 252–254 °C. ^{1}H NMR ($CDCl_3$, 360 MHz): $\delta = 3.83$ (s, 3H, CH_3), 6.78 (d, 1H, $J = 15.9$ Hz, CH), 7.31–7.37 (m, 3H, Ar), 7.49–7.53 (m, 2H, Ar), 7.77 (d, 1H, $J = 15.9$ Hz, CH). ^{13}C NMR ($CDCl_3$, 90 MHz): $\delta = 32.77, 108.59, 109.93, 111.90, 127.79, 128.97, 129.25, 130.43, 131.11, 134.82, 141.00, 150.73$. EI-MS (70 eV) m/z (rel. int.): 234 (M^+, 26), 233 (100), 218 (18). Anal. calcd. for $C_{14}H_{10}N_4$: C 71.78, H 4.30, N 23.92; found: C 71.86, H 4.68, N 23.80.

*2.2.4.5. (E)-2-(4-Methoxystyryl)-1-methyl-1H-imidazole-4,5-dicarbonitrile (**3b**).* Obtained 71 mg (57%) as a white solid; $R_f = 0.31$ (SiO_2; Hexane/EtOAc 2:1); mp 217–219 °C. ^{1}H NMR ($CDCl_3$, 360 MHz): $\delta = 3.82$ (s, 3H, CH_3), 3.84 (s, 3H, OCH_3), 6.63 (d, 1H, $J = 15.7$ Hz, CH), 6.91 (d, 2H, $J = 8.7$ Hz, Ar), 7.49 (d, 2H, $J = 8.7$ Hz, Ar), 7.76 (d, 1H, $J = 15.7$ Hz, CH). ^{13}C NMR ($CDCl_3$, 90 MHz): $\delta = 107.52, 108.80, 112.11, 112.69, 114.73, 122.61, 127.56, 129.45, 140.53, 151.17, 161.56$. EI-MS (70 eV) m/z (rel. int.): 264 (M^+, 46), 263 (100), 220 (12). Anal. calcd. for $C_{15}H_{12}N_4O$: C 68.17, H 4.58, N 21.20; found: C 68.15, H 4.67, N 21.09.

*2.2.4.6. (E)-2-(4-(N,N-Dimethylamino)styryl)-1-methyl-1H-imidazole-4,5-dicarbonitrile (**3c**).* Obtained 89 mg (68%) as a yellow solid; $R_f = 0.20$ (SiO_2; Hexane/EtOAc 2:1); mp 290–292 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): $\delta = 3.03$ (s, 6H, $N(CH_3)_2$), 3.90 (s, 3H, CH_3), 6.78 (d, 2H, $J = 8.8$ Hz, Ar), 7.07 (d, 1H, $J = 16.0$ Hz, CH), 7.60–7.68 (m, 3H, CH + Ar). ^{13}C NMR ($CDCl_3$, 90 MHz): $\delta = 32.70, 32.78, 106.19, 109.36, 111.81, 112.48, 112.81, 120.46, 122.55, 129.35, 139.13, 151.26, 151.70$. EI-MS (70 eV) m/z (rel. int.): 277 (M^+, 89), 276 (100), 260 (16), 137 (12). Anal. calcd. for $C_{16}H_{15}N_5$: C 69.29, H 5.45, N 25.25; found: C 69.26, H 5.59, N 25.38.

*2.2.4.7. 2-(Biphenyl-4-yl)-1-methyl-1H-imidazole-4,5-dicarbonitrile (**4a**).* Obtained 78 mg (58%) as a yellowish solid; $R_f = 0.42$ (SiO_2; Hexane/EtOAc 2:1); mp 199–201 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 3.94$ (s, 3H, CH_3), 7.38–7.52 (m, 3H, Ar), 7.62 (d, 2H, $J = 8.0$ Hz, Ar), 7.70 (d, 2H, $J = 8.0$ Hz, Ar), 7.76 (d, 2H, $J = 8.3$ Hz, Ar). ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 34.93, 108.61, 111.92, 114.24, 122.56, 125.81, 127.38, 128.01, 128.57, 129.28, 129.66, 139.65, 144.32, 152.51$. EI-MS (70 eV) m/z (rel. int.): 284 (M^+, 100), 283 (91), 179 (15), 165 (16). Anal. calcd. for $C_{18}H_{12}N_4$: C 76.04, H 4.25, N 19.71; found: C 76.02, H 4.50, N 19.67.

*2.2.4.8. 2-(4′-Methoxybiphenyl-4-yl)-1-methyl-1H-imidazole-4,5-dicarbonitrile (**4b**).* Obtained 85 mg (57%) as a yellowish solid; $R_f = 0.38$ (SiO_2; Hexane/EtOAc 2:1); mp 197–199 °C. ^{1}H NMR ($CDCl_3$, 360 MHz): $\delta = 3.86$ (s, 3H, CH_3), 3.93 (s, 3H, OCH_3), 7.00 (d, 2H, $J = 8.6$ Hz, Ar), 7.56 (d, 2H, $J = 8.6$ Hz, Ar), 7.65–7.73 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, 90 MHz): $\delta = 34.93, 55.62, 108.66, 111.98, 114.19, 114.73, 122.53, 125.13, 127.42, 128.48, 129.64, 132.02, 143.88, 152.64, 160.22$. EI-MS (70 eV) m/z (rel. int.): 314 (M^+, 100), 299 (12), 271 (10). Anal. calcd. for $C_{19}H_{14}N_4O$: C 72.60, H 4.49, N 17.82; found: C 72.56, H 4.58, N 17.95.

*2.2.4.9. 2-(4′-(N,N-dimethylamino)biphenyl-4-yl)-1-methyl-1H-imidazole-4,5-dicarbonitrile (**4c**).* Obtained 127 mg (82%) as a yellow solid; $R_f = 0.38$ (SiO_2; Hexane/EtOAc 2:1); mp 261–263 °C. ^{1}H NMR (DMSO-d_6, 360 MHz): $\delta = 3.02$ (s, 6H, $N(CH_3)_2$), 3.96 (s, 3H, CH_3), 6.88 (d, 2H, $J = 8.6$ Hz, Ar), 7.68 (d, 2H, $J = 8.3$ Hz, Ar), 7.79–7.88 (m, 4H, Ar). ^{13}C NMR (DMSO-d_6, 125 MHz): $\delta = 35.24, 37.40, 109.16, 112.65, 112.72, 114.59, 120.28, 124.32, 125.66, 125.86, 127.45, 129.67, 142.58, 150.46, 152.10$. EI-MS (70 eV) m/z (rel. int.): 327 (M^+, 100), 207 (18), 163 (15). Anal. calcd. for $C_{20}H_{17}N_5$: C 73.37, H 5.23, N 21.39; found: C 73.33, H 5.25, N 21.34.

*2.2.4.10. (E)-1-Methyl-2-(4-styrylphenyl)-1H-imidazole-4,5-dicarbonitrile (**5a**).* Obtained 72 mg (49%) as an off-white solid; $R_f = 0.59$ (SiO_2; Hexane/EtOAc 2:1); mp 183–185 °C. ^{1}H NMR (acetone-d_6, 360 MHz): $\delta = 4.07$ (s, 3H, CH_3), 7.30–7.48 (m, 5H, Ar + CH), 7.65 (d, 2H, $J = 7.5$ Hz, Ar), 7.78–7.83 (m, 4H, Ar + CH). ^{13}C NMR (acetone-d_6, 90 MHz): $\delta = 35.70, 109.63, 113.23, 115.58, 122.13, 127.40, 127.76, 127.78, 128.25, 129.09, 129.71, 130.52, 131.88, 138.01, 140.98, 153.24$. EI-MS (70 eV) m/z (rel. int.): 310 (M^+, 100), 309 (81). Anal. calcd. for $C_{20}H_{14}N_4$: C 77.40, H 4.55, N 18.05; found: C 77.47, H 4.67, N 17.98.

*2.2.4.11. (E)-2-[4-(4-Methoxystyry)lphenyl]-1-methyl-1H-imidazole-4,5-dicarbonitrile (**5b**).* Obtained 78 mg (42%) as a yellow solid; $R_f = 0.42$ (SiO_2; Hexane/EtOAc 2:1); mp 193–195 °C. ^{1}H NMR (acetone-d_6, 360 MHz): $\delta = 3.84$ (s, 3H, OCH_3), 4.06 (s, 3H, CH_3), 6.96 (d, 2H, $J = 8.6$ Hz, Ar), 7.19 (d, 1H, $J = 16.4$ Hz, CH), 7.37 (d, 1H, $J = 16.4$ Hz, CH), 7.59 (d, 2H, $J = 8.6$ Hz, Ar), 7.75–7.80 (m, 4H, Ar). ^{13}C NMR (acetone-d_6, 90 MHz): $\delta = 35.71, 55.74, 109.66, 113.26, 115.71, 115.55, 122.15, 125.95, 126.93, 127.48, 129.13, 130.50, 130.66, 131.58, 114.43, 153.34, 161.01$. EI-MS (70 eV) m/z (rel. int.): 340 (M^+, 100), 281 (20), 207 (21). Anal. calcd. for $C_{21}H_{16}N_4O$: C 74.10, H 4.74, N 16.46; found: C 74.19, H 4.66, N 16.86.

*2.2.4.12. (E)-2-{4-[4-(N,N-Dimethylamino)styryl]phenyl}-1-methyl-1H-imidazole-4,5-dicarbonitrile (**5c**).* Obtained 117 mg (66%) as an orange solid; $R_f = 0.37$ (SiO_2; Hexane/EtOAc 2:1); mp 243–245 °C. ^{1}H NMR (acetone-d_6, 360 MHz): $\delta = 3.00$ (s, 6H, $N(CH_3)_2$), 4.06 (s, 3H, CH_3), 6.76 (d, 2H, $J = 8.7$ Hz, Ar), 7.07 (d, 1H, $J = 16.4$ Hz, CH), 7.32 (d, 1H, $J = 16.4$ Hz, CH), 7.49 (d, 2H, $J = 8.7$ Hz, Ar), 7.71–7.79 (m, 4H, Ar). ^{13}C NMR (acetone-d_6, 90 MHz): $\delta = 35.70, 40.46, 109.70, 113.01, 113.22, 113.23, 123.32, 125.98, 126.30, 127.10, 128.81, 128.95, 130.28, 130.45, 132.36, 142.03, 151.77$. ESI-MS: $m/z = 376$ [$M^+ + Na$]. Anal. calcd. for $C_{22}H_{19}N_5$: C 74.77, H 5.42, N 19.82; found: C 74.79, H 5.54, N 19.99.

*2.2.4.13. 1-Methyl-2-[4-(phenylethynyl)phenyl]-1H-imidazole-4,5-dicarbonitrile (**6a**).* Obtained 61 mg (44%) as a off-white solid; $R_f = 0.42$ (SiO_2; Hexane/EtOAc 2:1); mp 169–171 °C. ^{1}H NMR ($CDCl_3$, 360 MHz): $\delta = 3.93$ (s, 3H, CH_3), 7.35–7.38 (m, 3H, Ar), 7.52–7.56 (m, 2H, Ar), 7.63 (d, 2H, $J = 6.0$ Hz, Ar), 7.68 (d, 2H, $J = 6.0$ Hz, Ar). ^{13}C NMR ($CDCl_3$, 90 MHz): $\delta = 34.98, 88.23, 92.83, 108.51, 111.80, 114.41, 122.65, 122.68, 126.42, 126.83, 128.71, 129.15, 131.09, 131.96, 132.67, 152.03$. EI-MS (70 eV) m/z (rel. int.): 308 (M^+, 100), 307 (65), 203 (16). Anal. calcd. for $C_{20}H_{12}N_4$: C 77.91, H 3.92, N 18.17; found: C 77.96, H 4.03, N 18.08.

*2.2.4.14. 2-[4-(4-Methoxyphenylethynyl)phenyl]-1-methyl-1H-imidazole-4,5-dicarbonitrile (**6b**).* Obtained 88 mg (56%) as a yellow solid; $R_f = 0.47$ (SiO_2; Hexane/EtOAc 2:1); mp 199–201 °C. ^{1}H NMR (acetone-d_6, 360 MHz): $\delta = 3.85$ (s, 3H, OCH_3), 4.08 (s, 3H, CH_3), 7.00 (d, 2H, $J = 8.7$ Hz, Ar), 7.53 (d, 2H, $J = 8.7$ Hz, Ar), 7.71 (d, 2H, $J = 8.2$ Hz, Ar), 7.85 (d, 2H, $J = 8.2$ Hz, Ar), 7.92–7.95 (m, 1H, Ar). ^{13}C NMR (acetone-d_6, 90 MHz): $\delta = 34.54, 55.85, 87.91, 92.92, 109.56, 113.15, 115.27, 115.46, 122.19, 127.01, 128.11, 130.35, 130.84, 132.58, 133.98, 152.80, 161.40$. ESI-MS: $m/z = 361$ [$M^+ + Na$]. Anal. calcd. for $C_{21}H_{14}N_4O$: C 74.54, H 4.17, N 16.56; found: C 74.66, H 4.18, N 16.66.

*2.2.4.15. 2-{4-[4-(N,N-Dimethylamino)phenylethynyl]phenyl-1-methyl-1H-imidazole-4,5-dicarbonitrile (**6c**).* Obtained 127 mg (76%) as a yellow solid; $R_f = 0.35$ (SiO_2; Hexane/EtOAc 2:1); mp 242–244 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 2.99$ (s, 6H, $N(CH_3)_2$), 3.89 (s, 3H, CH_3), 6.64 (d, 2H, $J = 8.8$ Hz, Ar), 7.39 (d, 2H, $J = 8.8$ Hz, Ar), 7.56–7.61 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, 90 MHz): $\delta = 34.97$, 40.36, 86.69, 94.68, 108.58, 109.13, 111.86, 111.98, 114.30, 122.58, 125.40, 127.85, 129.05, 131.11, 131.95, 133.19, 150.72, 152.32. ESI-MS: $m/z = 374$ [$M^+ + Na$]. Anal. calcd. for $C_{22}H_{17}N_5$: C 75.19, H 4.88, N 19.93; found: C 75.29, H 5.07, N 19.81.

2.3. Crystallography

The X-ray data for crystals of **1a, 2a**, **3b** and **4b** were obtained at 150 K using Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo K_α radiation ($\lambda = 0.71073$ Å), a graphite monochromator, and the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN [49]. The absorption was corrected by integration methods [50]. Structures were solved by direct methods (Sir92)[51] and refined by full matrix least-square based on F^2 (SHELXL97)[52]. Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, all hydrogen were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$(pivot atom) or of 1.5 U_{eq} for the methyl moiety with C–H = 0.96 Å, 0.97, 0.98 and 0.93 Å for methyl, methylene, methine and hydrogen atoms in aromatic ring, respectively, and 0.86 Å for N–H bonds.

$R_{int} = \Sigma|F_o^2 - F_{o,mean}^2|/\Sigma F_o^2$, $GOF = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{1/2}$ for all data, $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for observed data, $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{1/2}$ for all data.

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 739987, 739984, 739985 and 739986 for **1c**, **2c**, **3b** and **4b**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44 1223 336033; e mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). For **2c** the Flack parameter has meaningless standard uncertainty [53,54].

2.4. Electrochemistry

Electrochemical measurements were carried out in acetonitrile containing Bu_4NPF_6 in a three-electrode cell by cyclic voltammetry (CV), rotating disc voltammetry (RDV) and DC polarography. The working electrode was a platinum disc (2 mm in diameter) for CV and RDV or dropping mercury electrode (DME). The following conditions were applied for the polarographic measurements: drop time $\tau_D = 1$ s, scan rate $\upsilon = 5$ mV s^{-1}, the reference electrode was a saturated calomel electrode (SCE) separated by a bridge filled with supporting electrolyte and Pt wire, respectively. All potentials are given vs. SCE, the Fc^+/Fc usually used as internal standard, could not be employed due to its interaction with the analyte. Voltammetric measurements were performed using an electrochemical analyser AUTOLAB (model PGSTAT 30; Ecochemie, Utrecht, The Netherlands) operated via GPEs 4.8 software. Polarographic experiments were accomplished with a Polarographic Analyzer PA-3 (Laboratorní přístroje, Prague, Czech Republic) connected to an XY-recorder (ibid.).

2.5. Quantum and statistical calculations

Initial geometries of the compounds **1**–**6** have been calculated by the PM3 method (ArgusLab, [55]) and subsequently optimised by the PM6 method (MOPAC2009, [56]). The HOMO and LUMO energies and average second-polarisabilities β were further calculated by employing MOPAC2009.

The following indicators were chosen as structural characteristics of the studied chromophores: presence of the methoxy (Ind_{MeO}; 0 or 1) or *N*,*N*-dimethylamino donor groups (Ind_{DMA}; 0 or 1), presence of double (Ind_{DB}; 0 or 1) or triple bond (Ind_{TB}; 0 or 1), number of 1,4-phenylene units (n_{Ph}; 0, 1, 2), presence of double bond appended to the imidazole 2-position ($Ind_{Im\text{-}DB}$; 0 or 1) and presence of 1,4-phenylene linker appended to the imidazole 2-position ($Ind_{Im\text{-}Ph}$; 0 or 1). The three of the above structural characteristics that provided the strongest correlations were chosen for the interpretation of the relationships between measured or calculated quantities and structural features. Experimental and computation data was examined by multivariate graphical display methods and subsequently analysed using multiple linear regressions techniques (including *t*-test, F-test, assessing multicollinearity, analysis of residuals). Residuals in all of the presented regressions had Normal distribution. The program OPstat [57] was employed for all statistical calculations.

3. Results and discussion

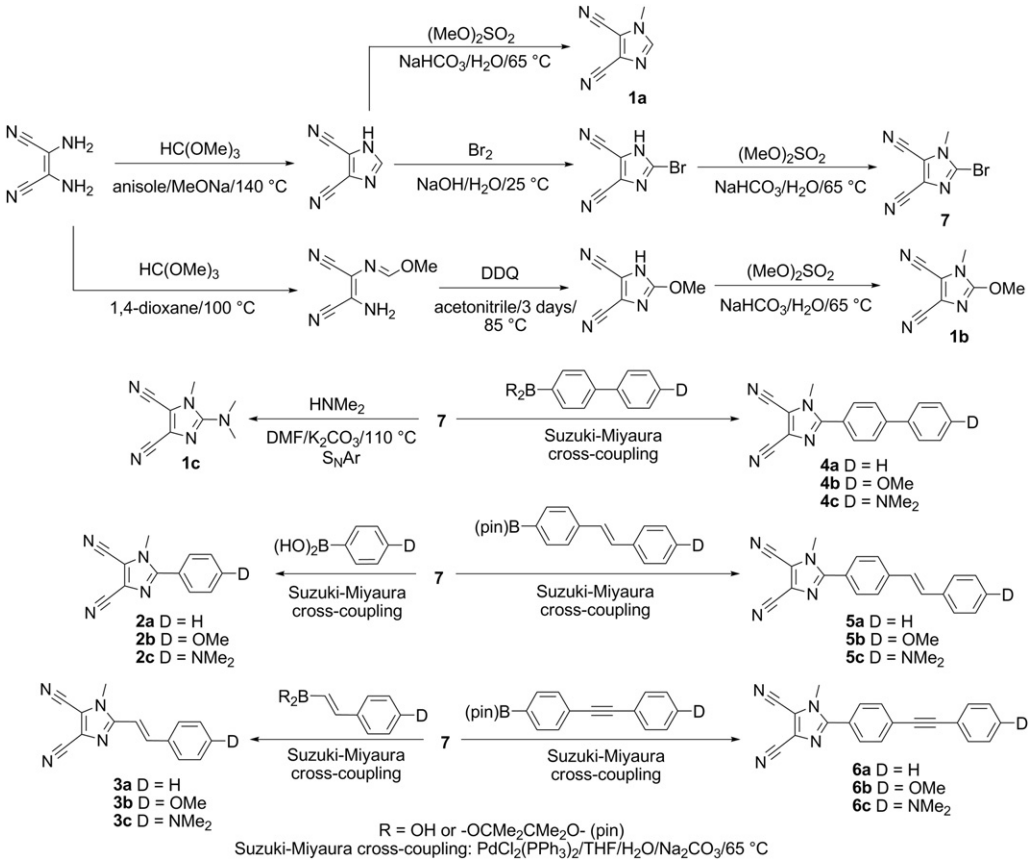
3.1. Synthesis

The 4,5-dicyanoimidazole acceptor moiety was easily prepared by the condensation of diaminomaleonitrile with trimethyl orthoformate in 80% yield. Subsequent bromination and *N*-alkylation [47] smoothly afforded **7** as the starting material for further cross-coupling steps. However, exclusion of the bromination step afforded unsubstituted 1-methyl-1*H*-imidazole-4,5-dicarbonitrile **1a**. The bromoimidazole **7** could be treated with an aqueous solution of dimethylamine to effect aromatic nucleophilic substitution, which afforded the simplest push-pull system **1d** [40]. The methoxy-substituted analogue **1c** had to be prepared from diaminomaleonitrile using stepwise methodology described by Anderson et al. [48] in 21% yield (Scheme 1).

We have recently reported a convenient synthesis for preparing π-conjugated linkers as building blocks for modular chemistry [46]. Either unsubstituted or donor-substituted π-linkers bearing a phenyl, styryl, biphenyl, phenylethenylphenyl or phenylethynylphenyl π-conjugated backbone and pinacol acid/ester functionalities were synthesised in a straightforward manner. With such boronic acids/esters in hand, we were able to carry out $PdCl_2(PPh_3)_2$-catalysed Suzuki–Miyaura cross-coupling reactions on bromoimidazole **7** to yield imidazole-4,5-dicarbonitriles **2**–**6** (Scheme 1, Table 1). Following this procedure, we have prepared 18 imidazole-based push-pull systems with systematically extended π-conjugated backbones. Whereas the reference series **a** is unsubstituted, series **b** and **c** feature methoxy and *N*,*N*-dimethylamino donors (A-π-D chromophore) respectively. The donors were connected either directly to imidazole (**1**) or separated by 1,4-phenylene (**2**), (*E*)-phenylethenyl (**3**), biphenyl (**4**), (*E*)-phenylethenylphenyl (**5**) or phenylethynylphenyl (**6**) π-linkers, respectively. All of the newly synthesised compounds were fully characterised by ^{1}H and ^{13}C NMR as well as EI(ESI)-MS and elemental analysis.

3.2. Crystallography

Slow evaporation of CH_2Cl_2 or EtOAc solutions of chromophores **1c**, **2c**, **3b** and **4b** at 20 °C afforded crystals suitable for X-ray analysis. The ORTEP plots in Fig. 2 confirm the proposed molecular structures. In contrast to the almost coplanar spatial arrangement



Scheme 1. Synthesis of chromophores **1**–**6**.

of the *N*,*N*-dimethylamino group in **2c**, one methyl group of the *N*,*N*-dimethylamino group in **1c** is forced out of the imidazole plane, with a dihedral angle C8N5C1N2 of about 63° as a result of the steric repulsion with the imidazole *N*-methyl group. However, the entire *N*,*N*-dimethylanilino group in **2c** adopts a typical out of imidazole plane deviation with a dihedral angle C8C5C3N1 of about 32 known for 2-phenyl-substituted imidazoles [58]. On other hand, the 4,5-dicyanoimidazole acceptor and the 4-methoxystyryl donor moieties in **3b** are almost coplanar. Chromophore **4b**, which bears a biphenyl central spacer, adopts a typical ‘‘propeller-like” conformation [59]. While the 4,5-dicyanoimidazole and terminal 4-methoxyphenyl ring are almost coplanar, the central 1,4-phenylene unit showed substantial twist with a dihedral angle C8C13C10N1 of about 36°.

Table 1
Yields, m.p., UV–Vis (λ^{A}_{max}) and fluorescent (λ^{F}_{max}) properties as well as calculated energies E_{HOMO}, E_{LUMO} and average second-polarisabilities β for chromophores **1**–**6**.

Comp.	Yield[a] [%]	M.p. [°C]	λ^{A}_{max} [nm (eV)]	λ^{F}_{max} [nm (eV)]	E_{HOMO} [eV]	E_{LUMO} [eV]	β [esu]
1a	85[b]	87–88	244 (5.08)	–	−10.42	−1.23	1.50×10^{-30}
1b	23[b]	61–63	271 (4.58)	–	−9.74	−1.11	3.52×10^{-30}
1c	90[b]	82–83	293 (4.23)	–	−9.50	−0.99	2.71×10^{-30}
2a	49	134–136	264 (4.70)	–	−9.87	−1.18	2.63×10^{-30}
2b	57	156–158	275 (4.51)	–	−9.37	−1.07	8.31×10^{-30}
2c	85	263–265	316 (3.92)	460 (2.70)	−8.67	−0.94	1.46×10^{-29}
3a	54	252–254	313 (3.96)[c]	–	−9.31	−1.33	5.27×10^{-30}
3b	57	217–219	331 (3.75)	–	−8.89	−1.20	1.82×10^{-29}
3c	68	290–292	381 (3.25)	474 (2.62)	−8.35	−1.08	3.27×10^{-29}
4a	58	199–201	286 (4.34)	354 (3.50)	−9.57	−1.19	5.17×10^{-30}
4b	57	197–199	301 (4.12)	396 (3.13)	−9.03	−1.13	1.30×10^{-29}
4c	82	261–263	346 (3.58)	504 (2.46)	−8.38	−1.07	2.19×10^{-29}
5a	49	183–185	325 (3.82)	395 (3.14)	−9.07	−1.29	1.32×10^{-29}
5b	42	193–195	331 (3.75)	432 (2.87)	−8.67	−1.20	3.07×10^{-29}
5c	66	243–245	380 (3.26)	533 (2.33)	−8.19	−1.12	4.91×10^{-29}
6a	44	169–171	308 (4.03)	360 (3.44)	−9.27	−1.31	9.30×10^{-30}
6b	56	199–201	323 (3.84)	408 (3.04)	−8.84	−1.21	2.28×10^{-29}
6c	76	242–244	364 (3.41)	515 (2.41)	−8.31	−1.14	3.71×10^{-29}

[a] Yield of the final cross-coupling step.
[b] See the Experimental section for synthesis details.
[c] Shoulder.

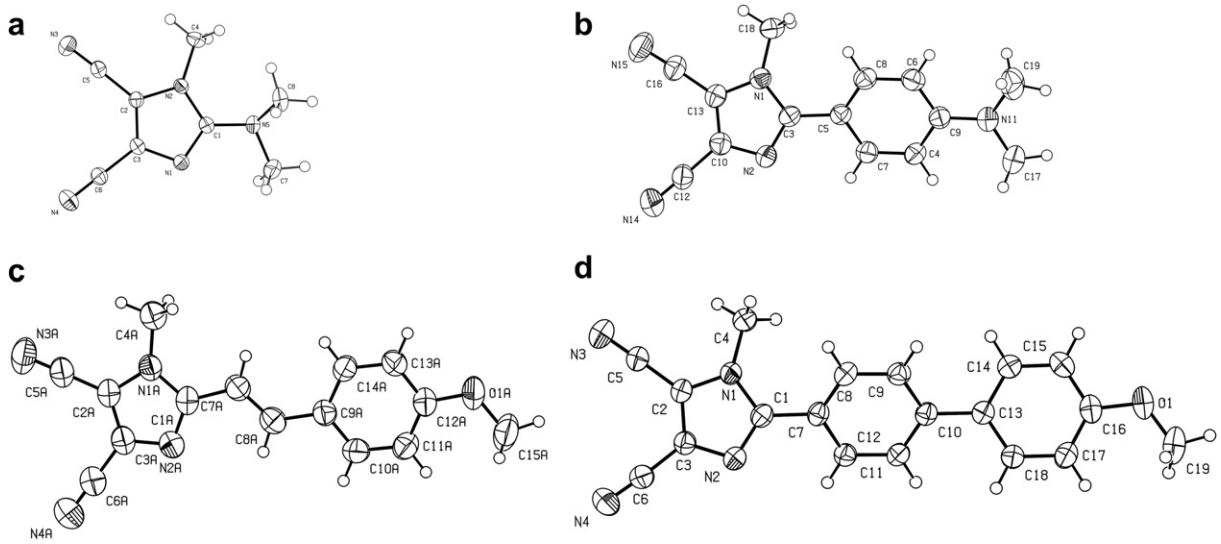


Fig. 2. ORTEP representations of the new chromophores a) **1c**, b) **2c**, c) **3b** and d) **4b** (all measured at 150 K), showing the thermal ellipsoids at 50% probability (arbitrary spheres for H atoms).

3.3. Electrochemistry

Electrochemical investigations of chromophores **1**–**6** were carried out in acetonitrile + 0.1 M Bu_4NPF_6 by CV, RDV and DC polarography. Due to the adsorption phenomena resulting in formation of an insulating film on the electrode either during oxidation or reduction, combination of CV, RDV and DC polarography techniques and polishing the electrodes before each scan needed to be applied to obtain reproducible measurements. The acquired data is summarized in Table 2 (derived from at least two different methods and several times repeated measurements). As a general trend, the first oxidation occurs on the donor groups, whereas the first reduction involves the π-conjugated core bearing the 4,5-dicyanoimidazole moiety. This is consistent with previous studies on analogous donor-substituted chromophores [13,14,38]. All the first reductions of 2-substituted 4,5-dicyanoimidazoles**1**–**6** are reversible, one-electron processes with the reduction potentials range from −1.65 to −1.96 V. The measured potentials are dependent on the structure of the chosen π-conjugated linker, that separates the 4,5-dicyanoimidazole acceptor moiety and the donors. The potentials also seemed to depend on the nature of the appended substituent D. Along the entire series **a**, **b** and **c**, the reduction potentials were shifted to less negative potentials, with $E_{red,1}$ ranging from −1.90 to −1.65 V (series **a**), from −1.75 to −1.91 (series **b**) and from −1.78 to −1.96 V (series **c**, see Table 2) as a result of reduced transfer of electron density from the donor to the 4,5-dicyanoimidazole acceptor moieties with increasing length of the π-conjugated spacer. Thus, elongation of the π-conjugated path caused a reduction potential shift, with of the magnitude of variation decreasing in the following order: **3**, **6**, **5**, **4**, **2**, **1**. It may be the case that this can be explained by the molecular structure and spatial arrangement of the investigated chromophores (see X-ray structures and discussion below). Not surprisingly, CT-chromophores possessing methoxy (series **b**) or *N*,*N*-dimethylamino (series **c**) electron-donating groups showed higher reduction potentials than those observed for series **a**. Dependence of $E_{red,1}$ on the structural characteristics can be described by equation (1).

Table 2
Electrochemical data of chromophores **1**–**6** obtained by DC polarography under conditions: $\tau_D = 1$ s; $\upsilon = 5$ mV s^{-1} and RDV at conditions: 500 rot min^{-1}; $\upsilon = 10$ mV s^{-1} measured in acetonitrile (5×10^{-4} M solutions) containing Bu_4NPF_6 as supporting electrolyte.

Compound	DC polarography $E_{red,1}$ [V][a]	RDV $E_{ox,1}$ [V][a]
1a	−1.90	–
1b	−1.91	2.18
1c	−1.96	1.38
2a	−1.86	2.20
2b	−1.89	1.76
2c	−1.92	0.93
3a	−1.65	1.72
3b	−1.75	1.33
3c	−1.81	0.69
4a	−1.82	1.88
4b	−1.84	1.50
4c	−1.85	0.79
5a	−1.75	1.55
5b	−1.78	1.25
5c	−1.81	0.58
6a	−1.74	1.89
6b	−1.78	1.47
6c	−1.78	0.72

[a] The potentials are given vs. SCE.

$$E_{red,1} = -(1.93 \pm 0.03) - (4.70 \pm 2.03)10^{-2}\mathrm{Ind}_{DMA} + (0.133 \pm 0.026)\mathrm{Ind}_{Im-DB} + (7.22 \pm 0.01)10^{-2}n_{Ph} \quad N = 18,\ s = 3.98 \times 10^{-2},\ R = 0.886,\ F(3,13) = 15.8 \qquad (1)$$

Although the correlation is not as strong as in other cases (see below), it confirms the observations discussed earlier and indicates that the lowered reduction potential is as a result of A-π-D π-system elongation. However, influence of the imidazole-double bond connection (Ind_{Im-DB} characteristic) implies that a planar π-conjugated spacer ensuring good communication of the donor and acceptor moieties is crucial for the stabilisation of the reduced form.

Except **1a,** all chromophores undergo reversible one-electron oxidation processes. The first oxidation potential $E_{ox,1}$ ranges from 2.20 to 0.58 V and is shifted to less positive potentials with increasing length of the π-conjugated path and donating character

of the appended substituent D. The observed trend is similar to that observed for reduction potentials. Dependence of $E_{ox,1}$ on the structural characteristics can be expressed by equation (2).

$$E_{ox,1} = (2.18 \pm 0.11) - (0.894 \pm 0.094)\mathrm{Ind}_{DMA} - (0.325 \pm 0.094)\mathrm{Ind}_{DB} - (0.245 \pm 0.065)\mathrm{n}_{Ph}$$
$$N = 17,\ s = 0.184,\ R = 0.947,\ F(3,13) = 37.6 \quad (2)$$

In contrast to the equation (1), this correlation is significantly stronger. Presence of electron-donating substituents and elongation of the π-conjugated path through a competent π-conjugating linker reduces the oxidation potential. Dependence of $E_{ox,1}$ on the energy of the HOMO (excluding **1c** as outlier) is described by equation (3).

$$E_{ox,1} = -(7.52 \pm 0.46) - (0.995 \pm 0.005)E_{HOMO}$$
$$N = 16,\ s = 0.110,\ r = 0.980,\ F(1,14) = 33.9 \quad (3)$$

This strong correlation unambiguously illustrates the relationship between the energy of the HOMO and the oxidation potential $E_{ox,1}$.

3.4. UV–visible/fluorescent study and structure-hyperpolarisability consideration of chromophores *1*–*6*

Electronic absorption spectra of imidazoles **1**–**6** measured in CH_2Cl_2 showed intense charge-transfer (CT) absorption bands in the UV–visible region (Fig. 3, Table 1). The position of CT-band depends on the electronic nature of the appended donor and length of the conjugated π-backbone. Whereas the chromophores in series **a** exhibited CT-bands with λ_{max} appearing between 244 and 325 nm, the donor-substituted series **b** and **c** showed CT-bands with λ_{max} ranging from 271 to 331 and 293–381 nm, respectively. Compared with the unsubstituted reference series **a**, the longest-wavelength absorption bands of the chromophore series **b** and **c** are significantly bathochromically shifted as a result of the positive mesomeric effect of the donor groups (Fig. 3, Table 1). In general, increasing the strength of the donor or acceptor groups reduces the energy differences between ground and excited states which results in a bathochromically shifted CT-band [31]. This fact could be nicely demonstrated by comparison of the chromophores in series **b** and **c** that contained an identical π-conjugated spacer. The CT-band of chromophores bearing stronger *N*,*N*-dimethylamino group (series **c**) are shifted more bathochromically than those for series **b** with weaker methoxy substituents. On the other hand, the observed bathochromic shift within the individual series **a**–**c** can be rationalised as an effect of the π-conjugated spacer between the appended acceptors and donors. The influence of the spacer on the efficiency of the donor–acceptor conjugation is best evaluated in series **b**–**c**, in which donor–acceptor separation is systematically varied. It has already been demonstrated [13,14], that if strong donor–acceptor conjugation is achieved, the HOMO of the donor is lowered and the LUMO of the acceptor raised. In turn, the convergence of the HOMO and LUMO results in a large optical gap. On the contrary, when the donor and acceptor are insulated by a large π-conjugated spacer, the energy levels of HOMO and LUMO resemble those in the free components, yielding a small optical gap. Therefore, bathochromically shifted CT-bands are being measured. Beginning with the simplest compound in series **c** (**1c**, λ_{max} = 293 nm) the longest-wavelength transition was measured for chromophore **3c** (λ_{max} = 381 nm) with (*E*)-styryl linker. With respect to the performed X-ray analysis (Fig. 2), the phenyl ring connected to C-2 in chromophores with 1,4-phenylene (**2c**, λ_{max} = 316 nm) or biphenyl (**4c**, λ_{max} = 346 nm) spacers is sterically forced out of the mean plane of the 4,5-dicyanoimidazole.

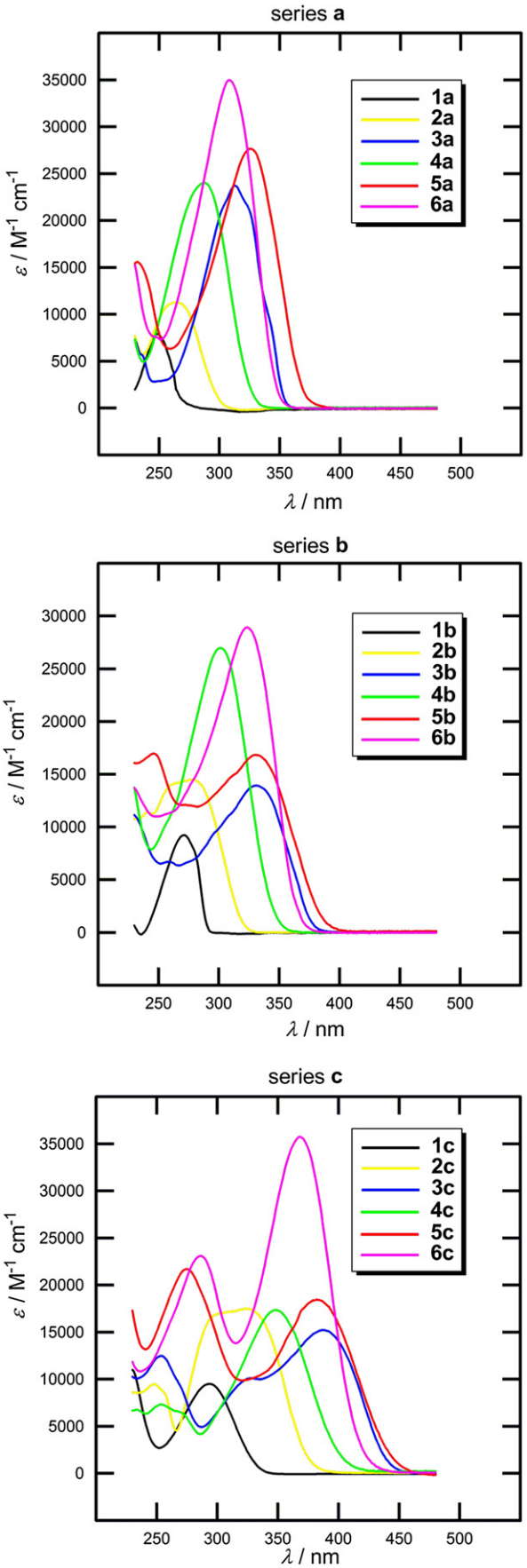


Fig. 3. Electronic absorption spectra of **1**–**6** (10^{-5} M solutions in dichloromethane).

Therefore, the *N*,*N*-dimethylamino donor group is engaged in less conjugation while the bathochromic shift is not as pronounced as for chromophores **3c** featuring styryl spacer. Planarity – an important aspect of rational design of organic chromophores – could be further probed by comparison of chromophore **3c** with chromophore **5c**, which bears an additional 1,4-phenylene unit and, as in **2c** and **4c**, lacks planarity. However, λ_{max} decreased from 381 to 380 nm. On the contrary, the olefinic linker in **5c** proved to be more "transparent" than the more electronegative acetylenic one in **6c** ($\lambda_{max} = 364$ nm). Similar conclusions could be made for the methoxy-substituted chromophores in series **b**. Dependence of $1/\lambda^{A}_{max}$ on the bathochromic shift-inducing factors could be statistically described by equations (4) and (5).

$$\begin{aligned} 1/\lambda^{A}_{max} &= (3.88 \pm 0.08)10^{-3} - (4.78 \pm 0.76)10^{-4}\mathrm{Ind_{DMA}} \\ &\quad - (3.87 \pm 0.77)10^{-4}\mathrm{Ind_{DB}} - (2.67 \pm 0.78)10^{-4}\mathrm{n_{Ph}} \\ &\quad N = 18,\ s = 1.52 \times 10^{-4},\ R = 0.939, \\ &\quad F(3,14) = 35.0 \end{aligned} \tag{4}$$

$$\begin{aligned} 1/\lambda^{A}_{max} &= (3.80 \pm 0.09)10^{-3} - (4.79 \pm 0.85)10^{-4}\mathrm{Ind_{DMA}} \\ &\quad + (5.83 \pm 1.38)10^{-4}\mathrm{Ind_{Im\text{-}Ph}} - (5.97 \pm 0.87)10^{-4}\mathrm{n_{Ph}} \\ &\quad N = 18,\ s = 1.69 \times 10^{-4},\ R = 0.925, \\ &\quad F(3,14) = 27.5 \end{aligned} \tag{5}$$

Those correlations clearly demonstrate that increasing the donating character of the substituent D (indicator $\mathrm{Ind_{DMA}}$), elongation of the π-conjugated path (number of 1,4-phenylene units $\mathrm{n_{Ph}}$) and planarity of the chromophore (indicators $\mathrm{Ind_{DB}}$ vs. $\mathrm{Ind_{Im\text{-}Ph}}$ with opposite sign) caused a bathochromic shift. In addition, $1/\lambda^{A}_{max}$ is highly correlated with the differences between E_{HOMO} and E_{LUMO} according to equation (6).

$$\begin{aligned} 1/\lambda^{A}_{max} &= -(2.05 \pm 0.09)10^{-3} + (6.66 \pm 0.40)10^{-4} \\ &\quad (E_{HOMO} - E_{LUMO}) \quad N = 18,\ s = 9.62 \times 10^{-5}, \\ &\quad r = 0.973,\ F(1,16) = 28.3 \end{aligned} \tag{6}$$

Chromophores with larger π-conjugated systems demonstrated fluorescent behaviour while high fluorescence was observed mainly for the chromophores with biphenyl (**4**), (*E*)-phenylethenylphenyl (**5**) and phenylethynylphenyl (**6**) central spacers. As a general trend, the fluorescence band is being bathochromically shifted with increasing length of the π-conjugated path, which is analogous to that observed in absorption spectra (see above). A full account of the fluorescent properties of the chromophores described in this paper will be presented elsewhere.

In accordance with the above experimental quantities, the calculated average second-polarisabilities β (Table 1) depend on increasing donating character of substituent D (indicator $\mathrm{Ind_{DMA}}$), elongation of the π-conjugated path (number of 1,4-phenylene units $\mathrm{n_{Ph}}$) and planarity of the chromophore (indicators $\mathrm{Ind_{DB}}$), as documented by equation (7).

$$\begin{aligned} \beta &= -(4.00 \pm 0.08)10^{-30} + (1.52 \pm 0.76)10^{-29}\mathrm{Ind_{DMA}} \\ &\quad + (1.08 \pm 0.77)10^{-29}\mathrm{Ind_{DB}} + (8.65 \pm 2.52)10^{-30}\mathrm{n_{Ph}} \\ &\quad N = 18,\ s = 7.87 \times 10^{-30},\ R = 0.854, \\ &\quad F(3,14) = 12.5 \end{aligned} \tag{7}$$

4. Conclusion

Eighteen chromophores **1**–**6** (series **a**, **c** an **d**) featuring 4,5-dicyanoimidazole as an acceptor moiety and *N*,*N*-dimethylamino and methoxy groups as donors with a systematically enlarged π-conjugated spacer have been synthesised mainly by cross-coupling reactions. The prepared push-pull molecules have been further investigated by UV/Vis spectroscopy, electrochemistry, X-ray analysis as well as by quantum-chemical calculations. From the observations made and the performed factor analysis we can deduce the following conclusions: (i) optical properties of polar push-pull chromophores can be easily tailored by the modification of the appended donor or acceptor (compare series **a**, **b** and **c**) and by the extension/shortening of the π-conjugated spacer (compare chromophores **1**–**6**); (ii) electrochemical behaviour of polar push-pull chromophores depends on the length and planarity of the π-conjugated system as well as on the donating character of the appended donor; (iii) the first oxidation potential strongly correlates with the calculated HOMO indicating their close relationship; (iv) likewise, nonlinear optical properties (β) depend on the donating character of the appended donor and on the length and planarity of the π-conjugated system.

Thus, presence of a strongly conjugating donor and the length and planarity of the π-conjugated system are the most important structural factors determining electrochemical, spectral as well as nonlinear optical properties of the studied push-pull A-π-D systems. Considering the planarity, electrochemical behaviour, UV–Vis properties, high melting point, solubility as well as one of the highest calculated average second-polarisabilities β of **3c**, the styryl π-conjugated spacer combined with the strong *N*,*N*-dimethylamino donor group seems to possess one of the better balances of performance and practicality within the studied series.

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