



Branched charge-transfer chromophores featuring a 4,5-dicyanoimidazole unit

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ABSTRACT

Six branched and stable push–pull chromophores featuring 4,5-dicyanoimidazole as an acceptor moiety, an *N,N*-dimethylamino group as a donor and various π -conjugated linkers are reported. Systematic extension of the π -linker revealed that the optical and electrochemical properties of *A*– π –*D* chromophores are mainly affected by the nature of the π -conjugated backbone (length and planarity) as well as by the number of appended donors.

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In the last fifty years, major effort has been devoted to the development of organic π -conjugated compounds, with potential application as efficient materials in organic electronics and optoelectronics.^{1,2} A typical organic chromophore consists of strong electron acceptors (e.g., NO₂ or CN groups), strong electron donors (e.g., NR₂ or OR groups) and a π -conjugated core featuring aromatic rings and double or triple bonds.³ Thus, the π -system end-capped with electron donors (*D*) and acceptors (*A*) allows the arrangement of either symmetrical push–push (*D*– π –*D*) and pull–pull (*A*– π –*A*) chromophores or an asymmetric push–pull chromophore (*A*– π –*D*).⁴ Such aromatic chromophores are easy to synthesize, in particular through cross-coupling reactions, offer facile chemical modification and, moreover, their arrangement ensures efficient charge-transfer and allows further (opto)electronic fine-tuning of the chromophore polarizability.⁵ In general, charge-transfer chromophores that exhibit large hyperpolarizability, good optical transparency, solubility and thermal stability are currently in demand (nonlinear–transparency–solubility–thermal stability trade-off).

Recently, various heteroaromatics have been utilized as spacers in order to design the aforementioned push–pull systems. Incorporation of a heteroaromatic moiety into the chromophore brings higher thermal stability and chemical robustness, while heteroatoms (N, O, S, etc.) may also act as auxiliary donors or acceptors. Electron-rich heterocycles such as thiophene and pyrrole are currently the most studied five-membered heterocyclic compounds used for the construction of charge-transfer chromophores.⁶ However, imidazole also possesses a wide range of interesting properties such as acid–base character, transition metal-binding activity, thermal and chemical robustness, and tautomerism, and has found diverse applications in ionic liquids, ligands, and drugs. Moreover, imidazole

and benzimidazole moieties have been utilized as suitable π -conjugated spacers in charge-transfer chromophores.^{7,8} Since the first report of 4,5-dicyanoimidazole by Woodward⁹ in 1950, 4,5-dicyanoimidazole-derived compounds have mainly been investigated by Rasmussen and co-workers.¹⁰ In the meantime, this molecule has been recognized as an easily accessible acceptor moiety with widespread use in materials chemistry.¹¹ Recently, we reported the synthesis, characterization, and structure–property relationships of ‘linear’ chromophores featuring this moiety (Fig. 1).¹² Figure 1 shows the molecular structures of the previous and newly proposed branched chromophores **1–6** featuring the *N,N*-dimethylamino group as a donor and the 4,5-dicyanoimidazole moiety as an acceptor bridged by various extended π -linkages.

The synthesis of target molecules **1–6** started with condensation of diaminomaleonitrile with trimethyl orthoformate, followed by *N*-methylation using a dimethyl sulfate/NaHCO₃/H₂O alkylating system.¹³ Selective imidazole C-2 lithiation with *n*BuLi followed by formylation with DMF and a quench in phosphate buffer afforded aldehyde **7** in 85% yield. It was essential to maintain the reaction temperature below –100 °C in order to prevent addition of *n*BuLi to the cyano groups and to avoid consecutive polymerization (a yellow solution should persist at all times).^{10d} Finally, Corey–Fuchs

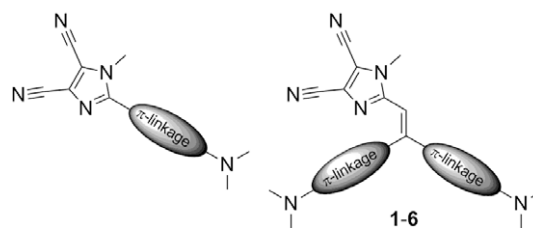


Figure 1. Molecular structure of the previous (left) and new (right) imidazole charge-transfer chromophores.

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dibromoolefination^{5a,14} of **7** using tetrabromomethane and triphenylphosphine afforded target dibromoolefin **8** in 92% yield (Scheme 1). Slow evaporation of a CH₂Cl₂ solution of **8** at 20 °C afforded crystals suitable for X-ray analysis. The ORTEP plot in Figure 2 confirmed the proposed molecular structure and, in particular, shows a fully planar arrangement of this building block. It is well known that dibromoolefins can be cross-coupled in order to achieve symmetric terminal substitution of the double bond.^{3a,15}

We recently reported a convenient method for preparing π -conjugated linkers as building blocks for modular chemistry.¹⁶ Among others, various *N,N*-dimethylamino substituted acetylenes bearing phenyl, biphenyl, phenylethenylphenyl and phenylethynylphenyl π -conjugated backbones were synthesized. With such coupling partners in hand, we attempted Suzuki–Miyaura and Sonogashira cross-coupling reactions, which afforded the target molecules in good yields (Scheme 1, Table 1). Whereas 4-(*N,N*-dimethylamino)phenylboronic acid is commercially available and the preparation of the first four aforementioned terminal acetylenes has already been published, acetylene **9** (Table 1) bearing four donor groups had to be synthesized. The stepwise synthesis started from Michler's ketone and its transformation into the corresponding triphenylethylene was followed by Sonogashira cross-coupling (see Supplementary data).

Electrochemical investigations of chromophores **1–6** were carried out by cyclic voltammetry (CV) in *N,N*-dimethylformamide containing 0.1 M Bu₄NPF₆. The acquired data are summarized in Table 1. As a general trend, the first oxidation occurs on the *N,N*-dimethylamino donor group, whereas the first reduction involves the π -conjugated backbone bearing the 4,5-dicyanoimidazole moiety.^{10c,12} The reduction potentials (E_{pc}) ranged from –1.96 to –1.16 V. With the same donors and acceptor moiety in chromophores **1–6**, the measured potentials are obviously dependent on the structure of the central π -conjugated linker and the number of appended donors. Throughout the entire series, the reduction potentials were shifted to more positive potentials in the following order: **1**, **2**, **6**, **3**, **4**, and **5**. Chromophores **4** and **5** were easily reduced at the most positive potentials as a consequence of their longest planar arrangement. In contrast to chromophore **4** ($E_{pc} = -1.19$ V), chromophore **6** ($E_{pc} = -1.25$ V) bearing two additional *N,N*-dimethylanilino moieties was reduced at lower potential. However, the two additional *N,N*-dimethylanilino aromatic rings adopt a nonplanar conformation typical of 1,1-diarylethenes^{5a} and, therefore, are engaged in less conjugation. The above statement also holds true for the simplest chromophore **1**, which had the lowest measured reduction potential ($E_{pc} = -1.96$ V). However, in contrast to the others, only chromophore **1** was reduced reversibly. The first oxidation potential (E_{pa}) of chromophores **1–6** ranged from +0.94 to +0.65 V and, similarly to the first reduction, it appeared to be a one-electron process. The first oxidation poten-

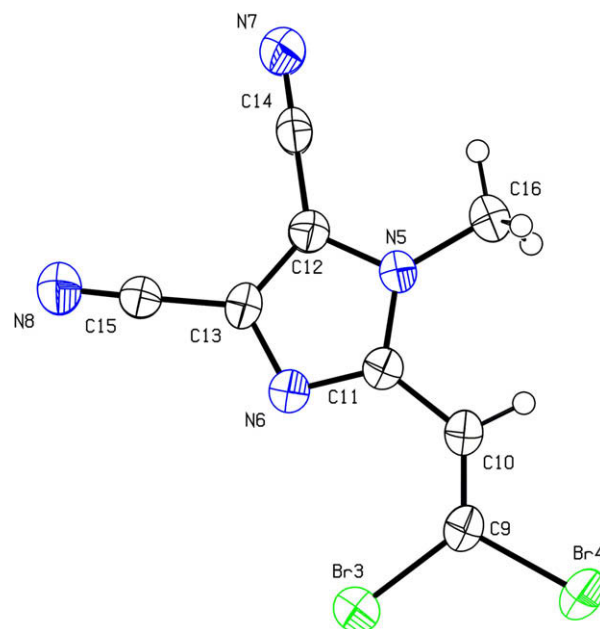
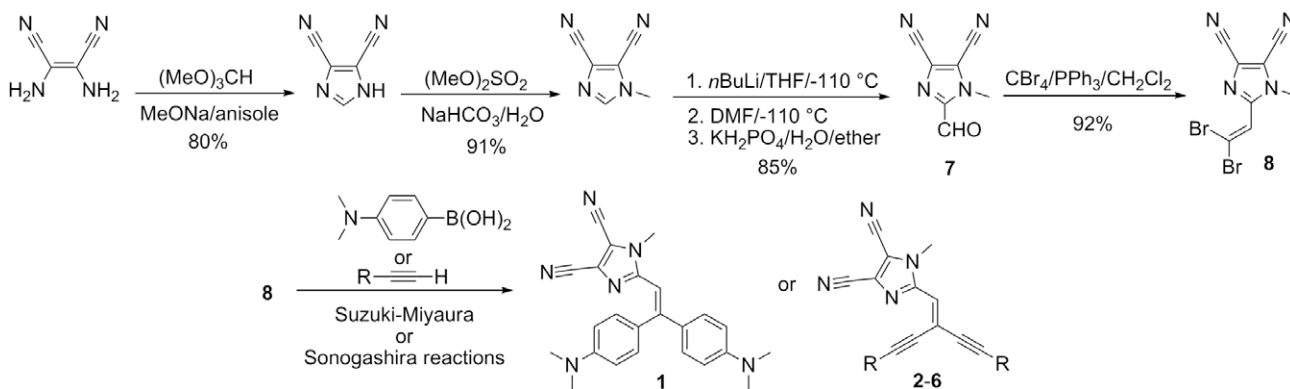


Figure 2. ORTEP view of dibromoolefin **8** with the atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. CCDC 753203. See also Supplementary data.

tials decreased in the following order: **5**, **2**, **3**, **1**, **6**, and **4**. Whereas chromophore **4** ($E_{pa} = +0.65$ V) underwent easy oxidation at the lowest potential, analogous chromophore **5** with a triple bond was reduced at the highest potential ($E_{pa} = +0.94$ V). The electro-negative ethynyl linker in **5** behaves as an electron-withdrawing group¹⁷ which made oxidation of the *N,N*-dimethylamino group more difficult and, on the contrary, reduction of the 4,5-dicyanoimidazole unit was facilitated ($E_{pc} = -1.16$ V for **5** and $E_{pc} = -1.19$ V for **4**, respectively). Hence, the ethynyl linker in **5** acts as an ‘insulator’.

The electronic absorption spectra of chromophores **1–6** measured in CH₂Cl₂ showed intense charge-transfer (CT) absorption bands in the UV–vis region (Fig. 3). The longest-wavelength absorption maxima λ_{max} are summarized in Table 1. As a main feature, the position of the CT-band depends on the length of the π -conjugated backbone between the 4,5-dicyanoimidazole acceptor moiety and the *N,N*-dimethylamino donor groups. The longest-wavelength absorption maxima λ_{max} was shifted bathochromically from 349 (**1**) to 450 nm (**6**). Comparing the λ_{max} of chromophores **1** ($\lambda_{max} = 349$ nm) and **2** ($\lambda_{max} = 429$ nm), the latter showed a considerable bathochromic shift of the CT-band, presumably as a result of its planar arrangement enforced by an additional triple bond linker



Scheme 1. Synthesis of the target imidazole-derived chromophores.

Table 1
Structure, yields, melting points, optical and electrochemical properties of chromophores 1–6

Chromophore	R	Yield ^a (%)	Mp (°C)	λ_{\max} (nm (eV))	Color	E_{pc}^{b} (V)	E_{pa}^{b} (V)	$E_{\text{pa}} - E_{\text{pc}}$ (V)
1	See Scheme 1	89	218–219	349 (3.55)	Yellow	−1.96	+0.84	2.80
2		96	238–240	429 (2.90)	Orange	−1.45	+0.90	2.35
3		84	206–208	416 (2.98)	Orange–red	−1.23	+0.87	2.10
4		78	222–225	437 (2.84)	Red	−1.19	+0.65	1.84
5		74	126–128	407 (3.05)	Red	−1.16	+0.94	2.10
6		81	183–185	450 (2.76)	Dark red	−1.25	+0.75	2.00

^a Isolated yield of the final cross-coupling step.

^b E_{pc} , E_{pa} —cathodic (anodic) peak potentials measured by CV. All potentials are given versus SCE.

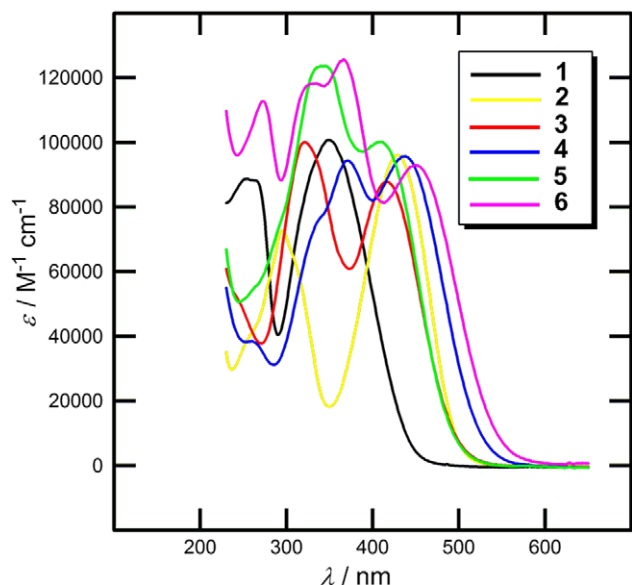


Figure 3. Electronic absorption spectra of chromophores 1–6 measured in CH_2Cl_2 (10^{-5} M solutions).

(see also the discussion above). Planarity—an important aspect of the rational design of organic chromophores—could be further demonstrated by comparison of chromophores **2** ($\lambda_{\max} = 429$ nm) and **3** ($\lambda_{\max} = 416$ nm). The longer, but nonplanar, biphenyl linker caused a smaller bathochromic shift. Considering chromophores **1–5**, having the same number of donors, the most bathochromically shifted CT-band was observed for **4** ($\lambda_{\max} = 437$ nm), bearing a planar (*E*)-phenylethenylphenyl linker. The planar but more electronegative phenylethynylphenyl linker in **5** ($\lambda_{\max} = 407$ nm) shifted the CT-band hypsochromically by 30 nm. Despite the overall nonplanar arrangement of **6** (see above), the four *N,N*-dimethylamino donor groups shifted the CT-band bathochromically to 450 nm.

Considering the planarity, electrochemical behavior (the lowest electrochemical gap $E_{\text{pa}} - E_{\text{pc}}$ of 1.84 V), UV–vis properties (λ_{\max} of 2.84 eV) and high melting point (222–225 °C) of **4**, the (*E*)-phenylethenylphenyl π -conjugated linker seems to possess one of the better balances of performance and practicality within the studied series.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.02.067.

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