

Imidazole as a parent π -conjugated backbone in charge-transfer chromophores

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Review

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Abstract

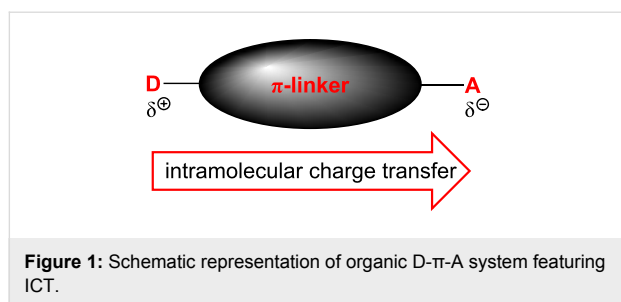
Research activities in the field of imidazole-derived push–pull systems featuring intramolecular charge transfer (ICT) are reviewed. Design, synthetic pathways, linear and nonlinear optical properties, electrochemistry, structure–property relationships, and the prospective application of such D- π -A organic materials are described. This review focuses on Y-shaped imidazoles, bi- and diimidazoles, benzimidazoles, bis(benzimidazoles), imidazole-4,5-dicarbonitriles, and imidazole-derived chromophores chemically bound to a polymer chain.

Introduction

Over the past three decades, great progress has been made in the development and the investigation of new organic push–pull systems. In contrast to inorganic materials, the advent of dipolar (hetero)organic materials with readily polarizable structure was stimulated by their relative ease of synthesis, well-defined structure, chemical and thermal robustness, possibility for further modification, and facile property tuning. Hence, heteroaromatic push–pull chromophores have been targeted and investigated as active components of optoelectronic devices, organic light-emitting diodes (OLED), photovoltaic cells, semiconductors, switches, data-storage devices, etc [1-3]. A typical one-component organic D- π -A chromophore consists of a π -conjugated system end-capped with strong electron donors D

(e.g. NR₂ or OR groups) and strong electron acceptors A (e.g. NO₂ or CN groups). This D- π -A arrangement assures efficient intramolecular charge transfer (ICT) between the donor and acceptor moieties and generates a dipolar push–pull system featuring low-energy and intense CT absorption (Figure 1). The polarizability and the respective optical linear and nonlinear (NLO) properties of these systems depend primarily on their chemical structure, in particular, the electronic behavior of the appended donors and acceptors and the character and length of the π -conjugated linker [4-7].

Recently, it was also recognized that push–pull systems applicable as organic materials should possess high chemical and



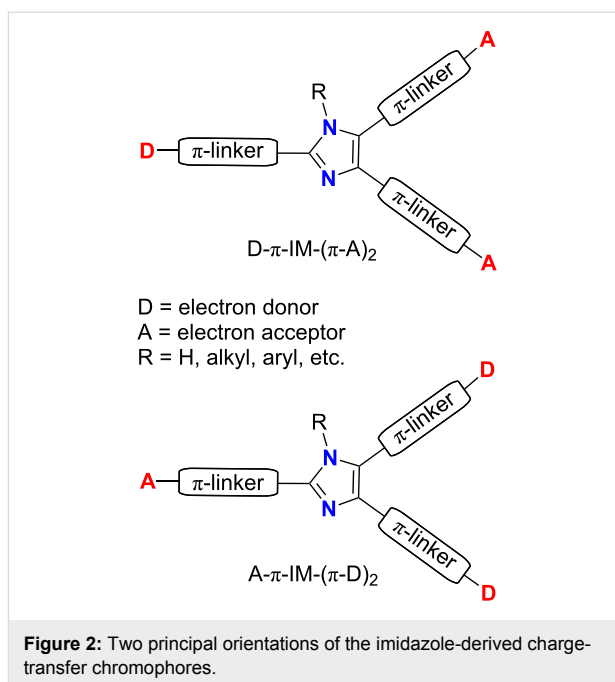
thermal robustness, good solubility in common organic solvents, and should be available in reasonable quantities. Hence, various five- and six-membered heterocycles were utilized as suitable π -conjugated chromophore backbones. Moreover, heteroatoms may act as auxiliary donors or acceptors and improve the overall polarizability of the chromophore. In this respect, five-membered diazoles, in particular imidazole, seem to be suitable parent π -conjugated backbones. Imidazole possesses two nitrogen atoms of different electronic nature, represents a robust and stable heterocycle, and can easily be synthesized and further functionalized at positions C2, C4, and C5 in addition to N1. On the imidazole backbone, two principal orientations of the substituents are possible, and these are most frequently used to generate Y-shaped chromophores as shown in Figure 2. The donor appended through an additional π -linker to the imidazole C2, completed with two peripheral acceptors linked at the imidazole C4/C5 positions, generates the first class of chromophores (D- π -IM-(π -A)₂ systems). The second class (A- π -IM-(π -D)₂ systems) possesses one acceptor and two donors in the reversed orientation. A nonsymmetrical orientation of the donors and acceptors is scarce, most likely due to a more difficult synthesis.

The purpose of this article is to review the recent progress in the design, development, and investigation of imidazole-derived charge-transfer chromophores. Synthetic pathways, linear and nonlinear optical properties, electrochemistry, and the prospective application of such organic materials are described. Metal complexes and metal sensitizers are not covered in this review.

Review

Synthesis of imidazole-derived chromophores

A condensation of α -diketones and aldehydes in the presence of ammonia or ammonium salts (Debus–Radziszewski synthesis) is one of the oldest, most versatile, and most frequently employed methods used for the construction of imidazole (glyoxaline) derivatives [8–10]. This simple synthetic pathway is also widely employed for the construction of variously substituted 2,4,5-triarylimidazole-derived chromophores (lophines), as shown in Scheme 1 [11–15].

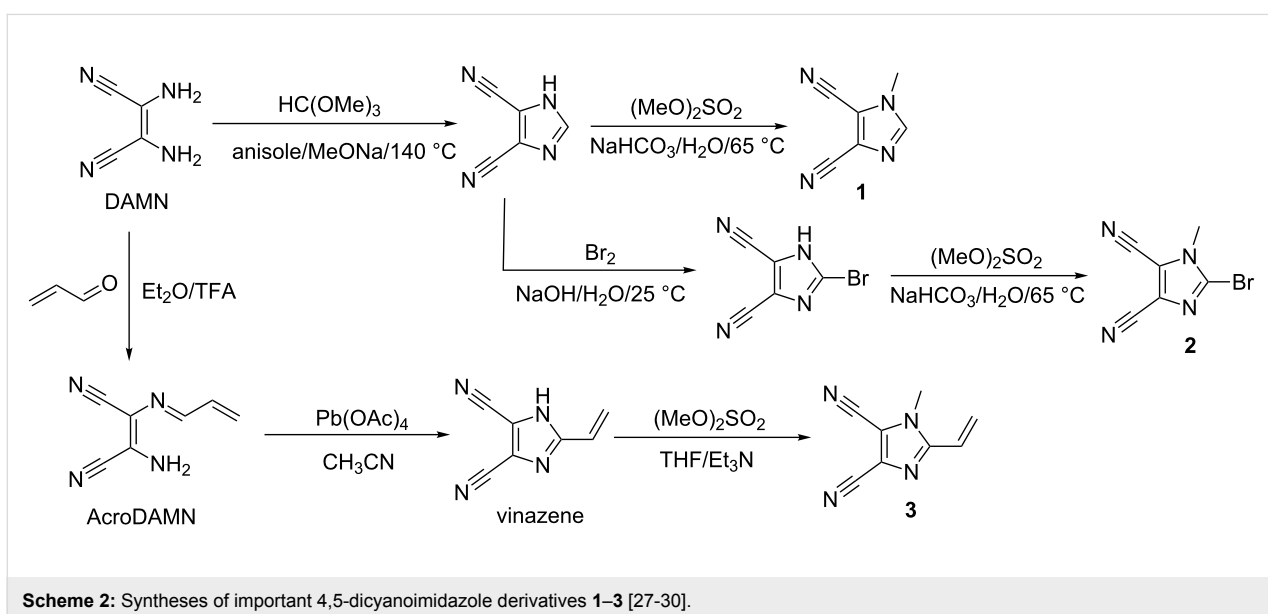
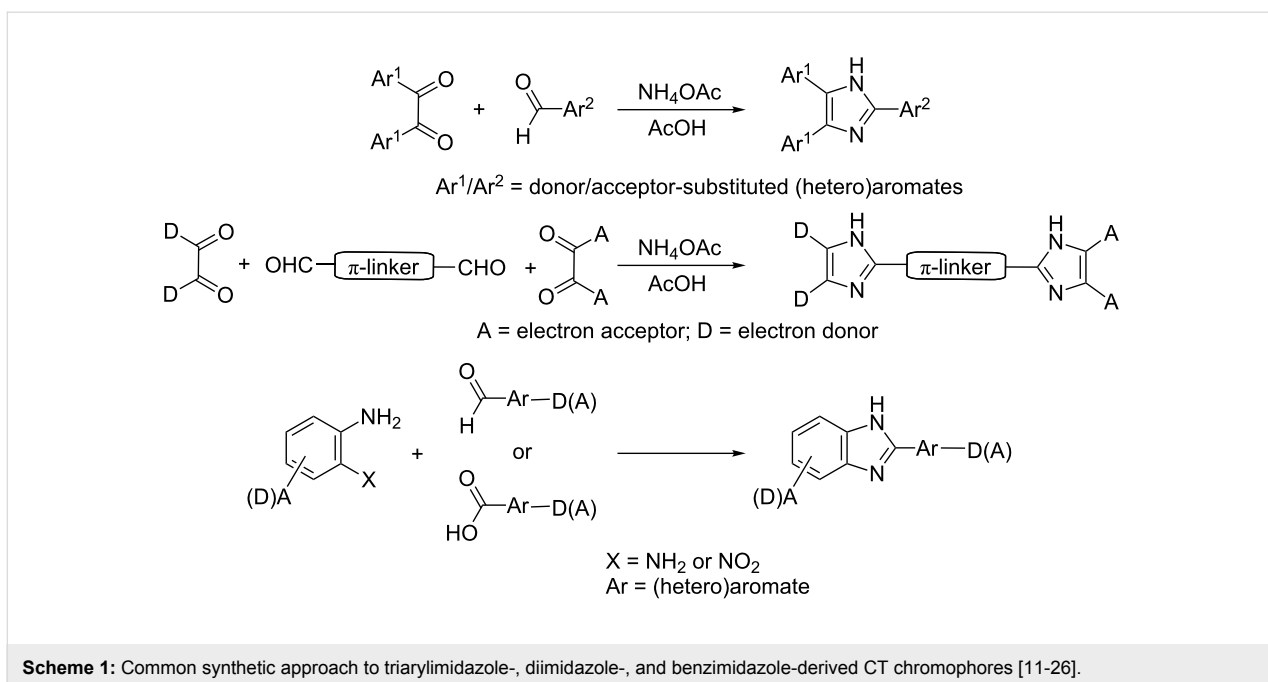


A similar synthetic strategy is used for the construction of diimidazole-type push–pull systems bearing two imidazole rings, which serve as donor and acceptor moieties [16–19]. A sequential construction of the chromophore backbone by modern cross-coupling reactions represents another synthetic approach used for the synthesis of superior diimidazole chromophores [20]. Benzimidazole D- π -A derivatives are a well-investigated class of charge-transfer chromophores. Although many synthetic approaches are known to date [10,21,22], the most popular ones involve the condensation of appropriately substituted arylenediamines or *o*-nitroanilines with an aldehyde or carboxylic acid, as well as Debus–Radziszewski synthesis as shown in Scheme 1 [23–26].

Since the discovery and the first synthesis of 4,5-dicyanoimidazole was reported by Woodward [27], this imidazole derivative became a popular moiety with moderate acceptor power. Starting from diaminomaleonitrile (DAMN), the simple synthesis of 1-methylimidazole-4,5-dicarbonitrile (**1**) is outlined in Scheme 2 along with the preparation of 2-bromo-1-methylimidazole-4,5-dicarbonitrile (**2**) and 1-methyl-2-vinylimidazole-4,5-dicarbonitrile (methylvinazene, **3**) [28–30]. These derivatives were recently utilized as suitable precursors for the construction of various CT chromophores (see below).

Y-shaped imidazole-derived chromophores

Triarylimidazoles (lophines) and derivatives with larger π -linkers represent the simplest D- π -IM-(π -A)₂ and A- π -IM-(π -D)₂ push–pull systems. An initial effort to synthesize and applyazole derivatives as CT chromophores and to study their optical



(non)linearities can be ascribed to Moylan, Miller, and co-workers as early as 1993 [31,32]. Donor–acceptor-substituted imidazoles, oxazoles, and thiazoles were synthesized, and their properties were compared within the individual series of substituents as well as across the three heterocyclic rings (Figure 3, Table 1). These A- π -IM-(π -D)₂ systems possess exceptional thermal stabilities, respectable dipole moments, and significant nonlinearities. It was found that the chromophore nonlinearity depends primarily on the type of substituents A/D and secondarily on the nature of the conjugating heterocyclic ring (Table 1).

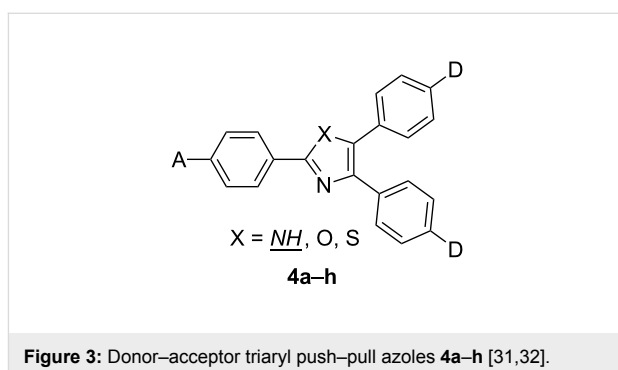


Table 1: Linear (λ_{\max}) and nonlinear (β) optical properties of triarylimidazoles **4a–h** (X = NH) [31].

Comp. X = NH	A	D	λ_{\max}^a [nm]	μ [D]	β^b [10^{-30} esu]
4a^c	NO ₂	OMe	412	6.4	19.9
4b^d	C≡CPhNO ₂	OMe	400	8.1	69.1
4c^d	SO ₂ Ph	OMe	362	8.0	10.1
4d^c	NO ₂	N[c-(CH ₂) ₅]	438	7.2	45.5
4e^c	NO ₂	OCH ₂ (C ₂ H ₅)CHC ₄ H ₉	416	6.3	24.5
4f^c	SO ₂ C ₄ F ₉	OCH ₂ (C ₂ H ₅)CH ₂ CH ₄ H ₉	384	6.5	13.9
4g^d	NO ₂	C≡CPhOMe	344	8.0	53.2
4h^c	NO ₂	N[c-(CH ₂) ₆]	476	8.3	78.7

^aPosition of the longest-wavelength absorption maxima; ^bmolecular first-order hyperpolarizability measured by EFISH experiments at 1064 or 1907 nm; ^cmeasured in CHCl₃; ^dmeasured in 1,4-dioxane.

More recently, Bu and co-workers also contributed significantly to the field of imidazole-derived CT chromophores for NLO. The first class of studied compounds **5a–c** resembles those chromophores reported by Moylan et al.: The parent π -conjugated backbone of *N*-methyllophine end-capped with two donors and one acceptor [33]. Bu's further efforts were focused on (i) the incorporation of an additional, readily polarizable heterocycle, such as thiophene or thiazole; (ii) the improvement of the electron-withdrawing ability of the used acceptor; and (iii) the elongation of the π -conjugated pathway. Thus, the first series of chromophores (**5a–c**) was completed with the thiophene-derived system **6** [14] with a tricyanovinyl acceptor moiety and chromophores **7a–c** [33] featuring a thiophene π -linker and a nitrostyryl acceptor. The molecular structures of compounds **6** and **5c** were also confirmed by X-ray analysis [34]. The last series of investigated compounds

involved donor 4,5-disubstituted imidazoles **8a–d** [35] with acceptors at C2 linked through a thiazole-styryl π -linker (Figure 4). Whereas the series **5a–c** and **7a–c** showed promising optical nonlinearities, high thermal stability, excellent solubility, and good transparency, molecules **8a–d** were investigated as two-photon absorbing chromophores (Table 2). Bu and co-workers also investigated the fluorescence properties of this family of imidazoles [36].

In addition to the work of Moylan and Bu, several other groups, mainly from Asia, reported the synthesis and application of Y-shaped imidazole-derived CT chromophores. Wang and co-workers investigated simple tripodal chromophores **9a–d** with nitro, dialkylamino, and hydroxy groups as acceptor and donors [13]. Whereas the imidazole- and thiazole-based chromophores **10a,b** possess two extended π -linkers with the imino

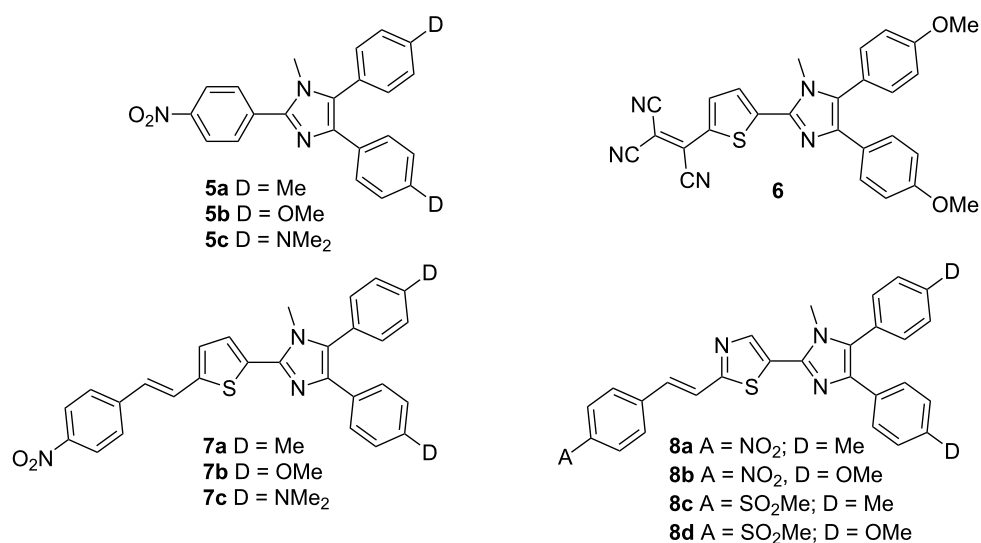
**Figure 4:** Y-shaped CT chromophores with an extended π -conjugated pathway and various donor and acceptor substitution patterns [16,33-35].

Table 2: Selected properties of chromophores **5–8** [33–35].

Comp.	A	D	λ_{\max}^a [nm]	$\mu\beta^b$ [10^{-48} esu]	δ^c [10^{-50} GM]
5a	–	Me	–	145	–
5b	–	OMe	–	130	–
5c	–	NMe ₂	–	360	–
6	–	–	–	–	–
7a	–	Me	432	945	–
7b	–	OMe	436	475	–
7c	–	NMe ₂	463	590	–
8a	NO ₂	Me	422	–	650 (720 nm)
8b	NO ₂	OMe	433	–	1050 (720 nm)
8c	SO ₂ Me	Me	398	–	1400 (740 nm)
8d	SO ₂ Me	OMe	410	–	1700 (760 nm)

^aMeasured in CHCl₃; ^bscalar product of the dipole moment and the molecular first-order hyperpolarizability measured in CHCl₃ by EFISH experiments at 1907 nm; ^cthe 2PA cross section measured in CHCl₃ by Z-scan technique (1 GM = 1×10^{-50} cm⁴·s·photon⁻¹) at the given 2PA wavelengths.

spacers at the imidazole C4/C5 and nitro and dimethylamino groups as acceptor and donor [15], chromophore **11** (VPDPI) represents a polarizable blue-light-emitting material [37]. The newly synthesized chromophores were investigated in terms of their absorption and emission properties, molecular first-order hyperpolarizability β , measured by solvatochromic method at 1907 nm, and thermal stability determined by TGA or DTA (Figure 5, Table 3). Imidazoles **12** (DIYSP, $\delta = 41$ GM,

[38,39]) and **13** (FD3, $\delta = 1556$ GM, [40]) were developed as two-photon absorbing and fluorescent A- π -A' chromophores, which undergo photopolymerization or can be applied as fluorescent sensors for (homo)cysteine. Donor 4,5-disubstituted imidazole derivatives **14** bearing a cyanoacrylic moiety connected to imidazole C2 by thiophene or thiazole π -linkers were recently utilized as dye-sensitized solar cells with an efficiency up to 6.3% [41].

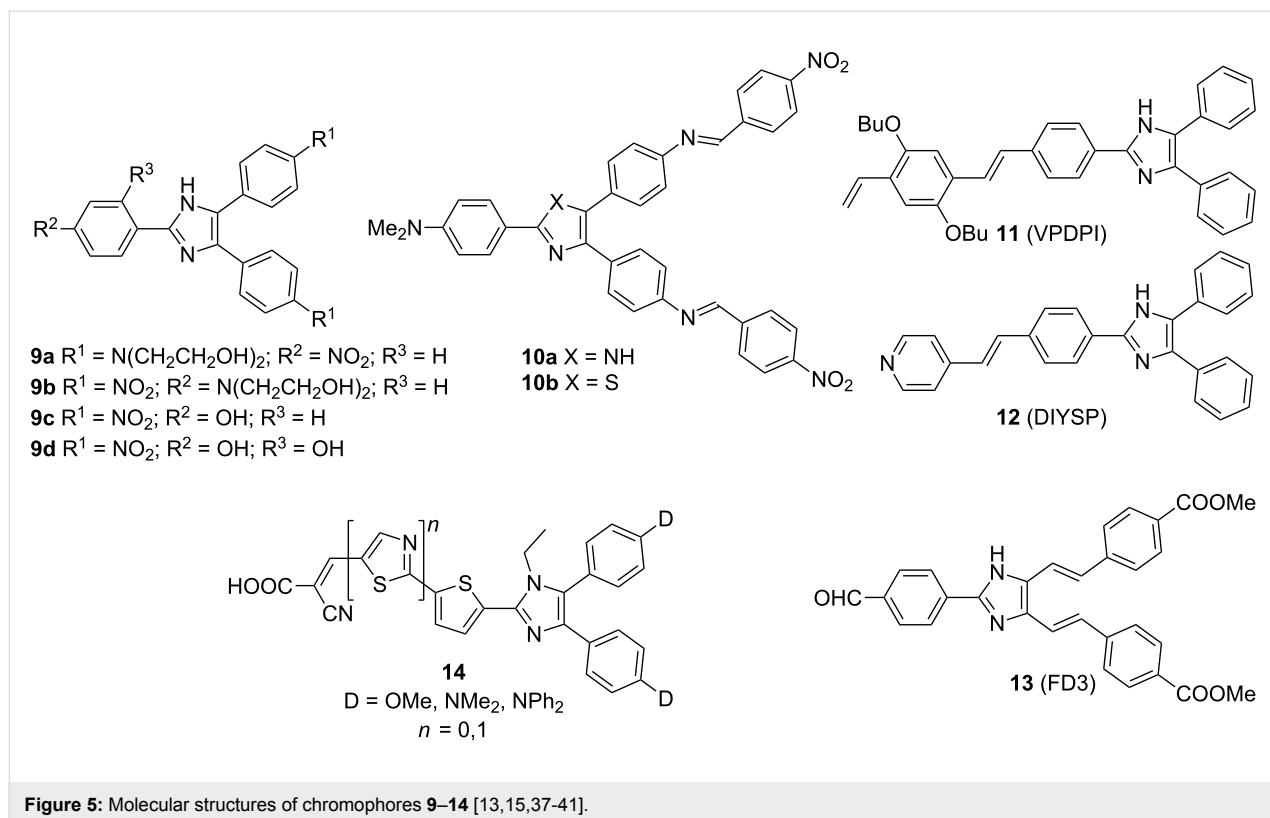
**Figure 5:** Molecular structures of chromophores **9–14** [13,15,37–41].

Table 3: Linear and nonlinear optical properties and thermal stabilities of chromophores **9–11** [13,15,37].

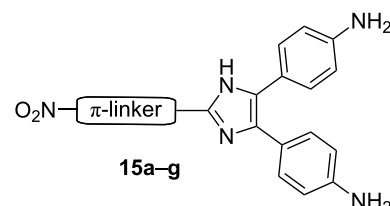
Comp.	$\lambda_{\max, \text{abs}}^a$ [nm]	$\lambda_{\max, \text{em}}^b$ [nm]	β^c [10^{-30} esu]	T_D^d [°C]
9a	403	–	68.42	300
9b	388	–	36.92	282
9c	345	–	89.01	299
9d	380	–	54.65	265
10a	358	–	40.66	227
10b	417	–	17.31	289
11	380	465 ($\Phi = 0.61$)	–	367

^aThe position of the longest-wavelength absorption maxima measured in 1,4-dioxane (**9**), MeOH (**10**), and EtOH (**11**); ^bthe position of the longest-wavelength emission maxima measured in EtOH; ^cmolecular first-order hyperpolarizability measured by solvatochromic method at 1907 nm; ^ddetermined by TGA or DTA.

Several similar classes of imidazole-derived push–pull compounds can be found in the literature. They were mainly investigated in terms of their synthesis and basic (non)linear optical properties [42–46].

Wu et al. utilized 4,5-bis(4-aminophenyl)imidazole as a suitable donor moiety for the construction of the nitro C2-substituted imidazole push–pull systems with extended and varied π -conjugated pathway **15a–g** [16,17,47]. The π -linker comprises 1,4-phenylene (C_6H_4), thiophen-2,5-diyl (C_4H_2S), ethynylene, and azo subunits (Figure 6, Table 4). An evaluation of the NLO data in Table 4 clearly shows that an elongation of the π -linker by polarizable subunits, such as a double bond or a thiophene, increases the measured second-order hyperpolarizability β significantly and also shifts the CT band bathochromically.

In 2009, our group also contributed to Y-shaped imidazole-derived chromophores [11]. We synthesized a library of substituted lophines **16–19** with four types of donor–acceptor orienta-

**Figure 6:** General structure of 4,5-bis(4-aminophenyl)imidazole-derived chromophores **15a–g** with various π -linkers [16,17,47].

tions (Figure 7): D- π -IM-(π -A)₂ (**16**), A- π -IM-(π -D)₂ (**17**), A- π -IM-(π -A)₂ (**18**), and D- π -IM-(π -D)₂ (**19**). 4,5-Bis(4-nitrophenyl)imidazole was utilized as a suitable acceptor moiety and was further modified with a thiophene π -linker as an auxiliary electron donor (**20**). These basic push–pull imidazoles were mainly investigated in terms of their facile synthesis, spectral properties, and thermal stability.

The 4,5-bis[4-(*N,N*-dimethylamino)phenyl]imidazole unit, as in chromophores **17**, was further used for the construction of A- π -IM-(π -D)₂ systems **21–26** with a systematically extended π -conjugated pathway (Figure 8; [12]). These chromophores were synthesized by Debus–Radziszewski synthesis (Scheme 1), as two series of compounds with different acceptors A (NO_2 or CN groups), and were investigated by electrochemistry, UV–vis and IR spectroscopy (CN), and quantum-chemical calculations (Table 5). Considering all the above measured and calculated properties, we can deduce that the following structure–property relationships determine the extent of ICT: (i) The presence of a strongly conjugating acceptor (NO_2 /CN); (ii) the π -system length and structure; and (iii) the overall chromophore planarity. Hence, chromophores **23a,b** with fully planar, central 4-phenylbuta-1,3-dienyl π -linker, end-capped with 4,5-bis[4-(*N,N*-dimethylamino)phenyl]imidazole donor and nitro and cyano acceptors, feature good solubility in

Table 4: Properties of 4,5-bis(4-aminophenyl)imidazole-derived chromophores **15a–g** [16,17,47].

Comp.	π -linker	λ_{\max}^a [nm]	μ [D]	β^b [10^{-30} esu]	T_D [°C]
15a	–(C_6H_4)–	405	7.7	17.19	300
15b	–(C_6H_4)–CH=CH–(C_6H_4)–	401	8.2	34.78	335
15c	–(C_6H_4)–N=N–(C_6H_4)–	461	8.2	41.82	344
15d	–(C_6H_4)–IM–[4,5-di–(C_6H_4)]–	384	10.9	50.91	377
15e	–(C_4H_2S)–	419	8.6	22.52	286
15f	–(C_4H_2S)–CH=CH–(C_6H_4)–	435	9.1	44.56	279
15g	–(C_4H_2S)–CH=CH–(C_4H_2S)–CH=CH–(C_6H_4)–	463	9.1	101.9	268

^aMeasured in THF; ^bcalculated by AM1/FF method (MOPAC).

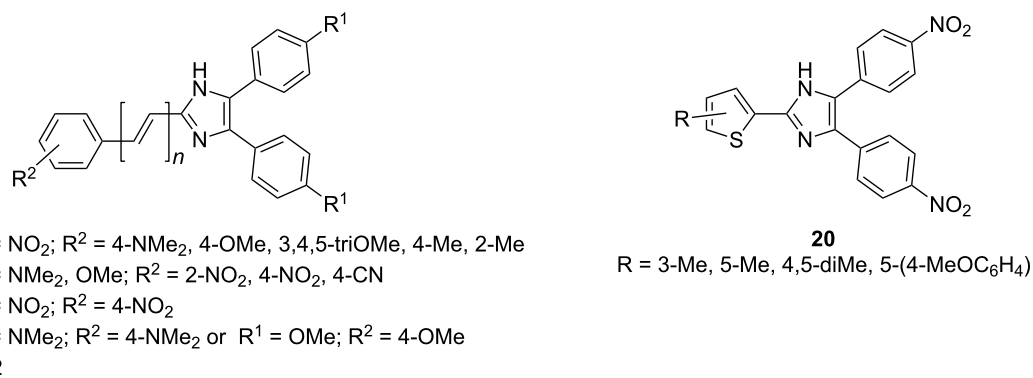


Figure 7: Various orientations of the substituents on the parent lophine π -conjugated backbone (**16–19**) and thiophene-substituted imidazoles **20** [11].

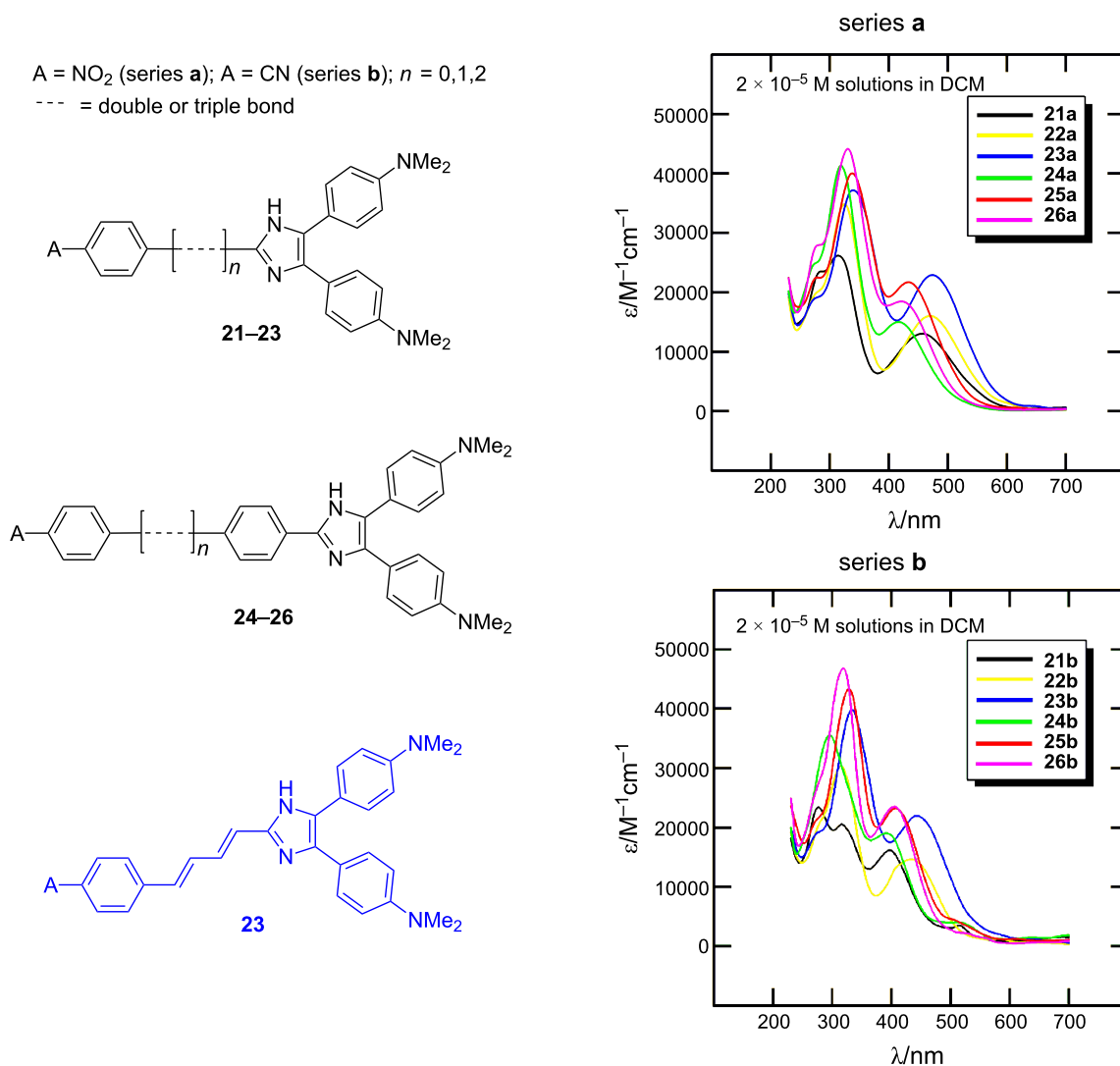


Figure 8: Structure and electronic absorption spectra of chromophores **21–26** [12].

Table 5: Properties of chromophores **21–26** [12].

Comp.	A	<i>n</i>	Bond ^a [.....]	$E_{p,a}-E_{p,c}$ ^b [V]	λ_{max} ^c [nm (eV)]	ν (CN) ^d [cm ⁻¹]	β^e [10 ⁻³⁰ esu]	mp [°C]
21a	NO ₂	0	–	1.62	457 (2.71)	–	57.6	105–106
21b	CN	0	–	2.53	397 (3.12)	2221	36.8	123–125
22a	NO ₂	1	d	1.53	470 (2.64)	–	59.6	163–167
22b	CN	1	d	2.23	434 (2.86)	2220	46.2	142–144
23a	NO ₂	2	d	1.48	474 (2.62)	–	89.8	157–160
23b	CN	2	d	2.06	442 (2.81)	2218	66.9	161–163
24a	NO ₂	0	–	1.57	417 (2.97)	–	48.1	159–162
24b	CN	0	–	2.42	391 (3.17)	2223	39.9	170–173
25a	NO ₂	1	d	1.53	434 (2.86)	–	78.0	165–166
25b	CN	1	d	2.23	407 (3.05)	2219	41.7	165–168
26a	NO ₂	1	t	1.46	420 (2.95)	–	84.6	262–264
26b	CN	1	t	2.26	405 (3.06)	2220	63.1	162–165

^ad/t = double/triple bond; ^b $E_{p,a}$ and $E_{p,c}$ are anodic and cathodic peak potentials measured by CV (potentials given vs. SCE); ^cmeasured in CH₂Cl₂; ^dfrequency of the C≡N stretch (series b); ^ecalculated average second polarizability by AM1/FF (MOPAC).

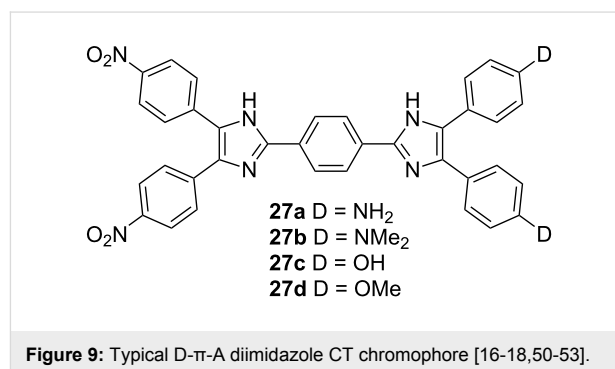
common organic solvents as well as the lowest measured electrochemical gaps $E_{p,a}-E_{p,c}$, the most bathochromically shifted CT bands (λ_{max}), the lowest frequency of CN stretch (**23b**), and the highest calculated average second-order polarizabilities β within the studied series of compounds **21–26**.

The nonlinear optical properties of donor- and acceptor-substituted five-membered heterocycles, such as imidazole, oxazole, and thiazole, were also investigated by DFT calculations [48,49]. These theoretical results confirmed, in general, the experimental data and trends discussed above.

Diimidazole-derived chromophores

The aforementioned charge-transfer chromophores **4–26** consist of a 1,2,4,5-tetrasubstituted imidazole ring, which may act as either a donor or acceptor moiety depending on the orientation of substituents. A π -conjugated backbone end-capped with donor- and acceptor-substituted imidazole rings constitutes a diimidazole-derived push–pull, push–push, and pull–pull charge-transfer chromophore. The most common synthetic approach to diimidazoles, with the rings connected at C2, is shown in Scheme 1. Typical diimidazole chromophores in D- π -A arrangement (Figure 9) were investigated by Wu and Ye et al. [16-18,50-53]. Compounds **27a** ($\lambda_{max} = 384$ nm; $\beta(\text{AM1}) = 50.91 \times 10^{-30}$ esu; $T_D = 377$ °C) and **27c** ($\lambda_{max} = 379$ nm; $\beta(\text{AM1}) = 29.5 \times 10^{-30}$ esu; $\beta(\text{HRS}) = 142 \times 10^{-30}$ esu; $T_D = 360$ °C) with free amino or hydroxy groups were further used as reactive species for the functionalization of various polymers (see below).

Within the last ten years, diimidazole D- π -D systems were extensively studied, in particular for their easy synthesis and

**Figure 9:** Typical D- π -A diimidazole CT chromophore [16-18,50-53].

unique properties [19,54-56]. Their general structure is shown in Figure 10 and selected properties are summarized in Table 6. Compounds **28–31** showed luminescent, photoluminescent, fluorescent or phosphorescent properties with the prospect for application in modern materials chemistry. This year, Liu, Yin, and co-workers [57,58] published a very nice example of photo-switchable diimidazole chromophores **32,33** with a distinct difference in optical properties between the open and closed forms.

N-Unsubstituted diimidazoles can easily be oxidized to the corresponding quinoid structure (2*H*-imidazole derivatives), as shown in Scheme 3 [19,59-61]. In 1999, Ye et al. [61] reported the oxidation of D- π -A diimidazole **27a** to quinoid **34** and a comparison of the linear and nonlinear optical properties. Partially planarized quinoid **34** ($\mu = 19.0$ D; β of 205.7×10^{-30} esu) showed a substantially higher dipole moment and first-order hyperpolarizability than chromophore **27a** (Figure 9; $\mu = 10.9$ D; $\beta = 50.91 \times 10^{-30}$ esu) due to a higher efficiency of D-A conjugation.

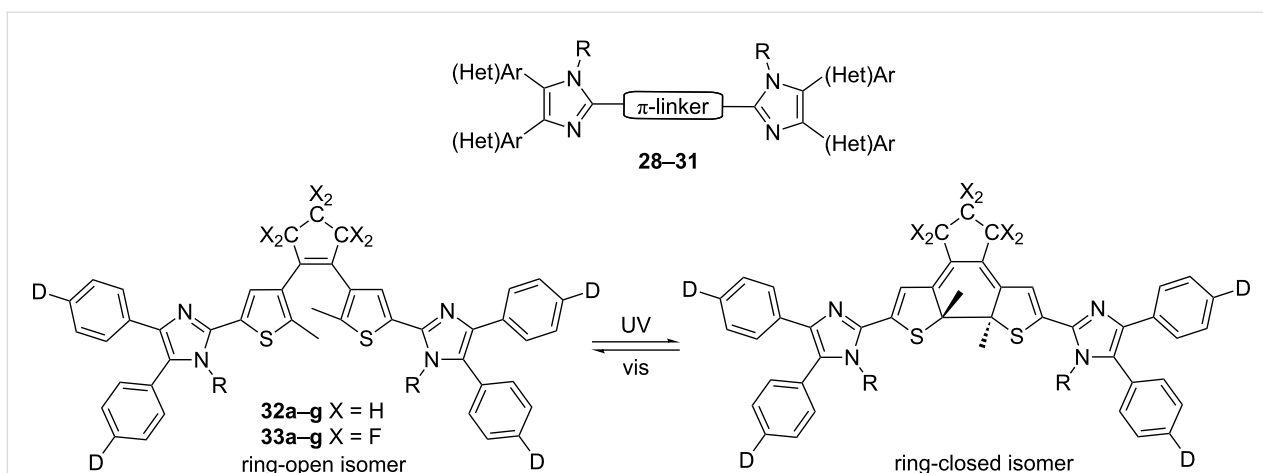


Figure 10: Typical D- π -D diimidazoles **28–31** [19,54–56] and photochromic diimidazoles **32,33** [57,58].

Table 6: Structure and selected properties of diimidazoles **28–33** [19,54–58].

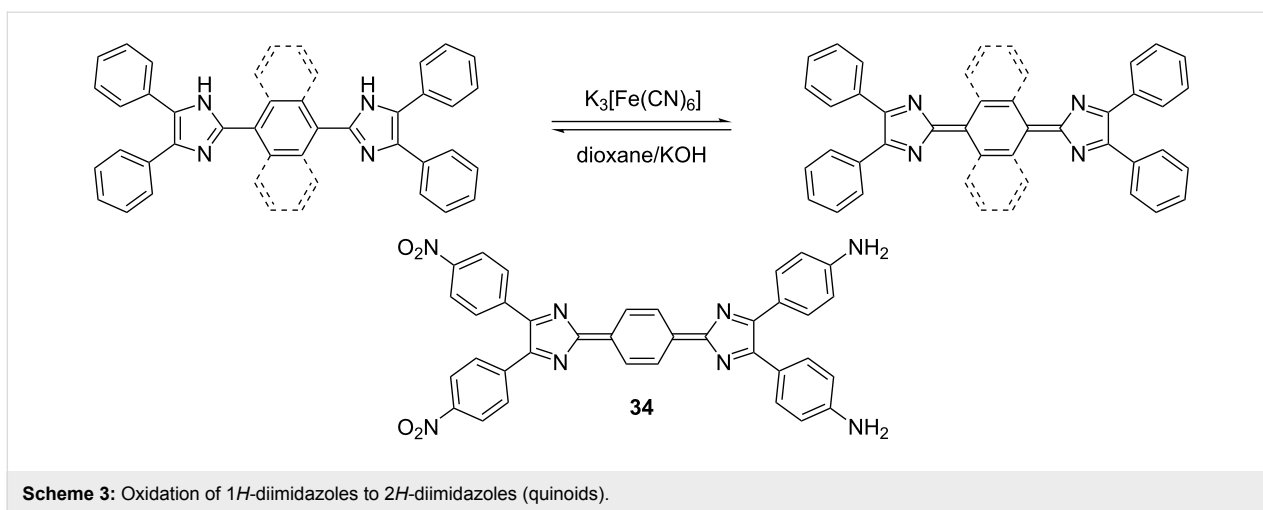
Comp.	π -linker/structure	(Het)Ar/D	R	$\lambda_{\max, \text{abs}}$ [nm]	$\lambda_{\max, \text{em}}$ [nm]	T_D [°C]	Prospective application [reference]
28	9,9,9',9',9''-hexaocylterfluorene	Ph	H	363 ^a	433 ^b	402	luminescence material [54]
29	poly-(1,4-phenylene)	4-C ₈ H ₁₇ Ph	H	378 ^c	478 ^c	220	photoluminescent material [19]
30a	1,4-phenylene	Ph	H	361 ^d	424 ^d	–	
30b	1,4-phenylene	4-MeOPh	H	365 ^d	440 ^d	–	
30c	1,4-phenylene	Ph	Me	337 ^d	417 ^d	–	fluorescent materials – molecular
30d	thiophen-2,5-diyl	Ph	H	385 ^d	458 ^d	–	photonics and sensing [55]
30e	thiophen-2,5-diyl	4-MeOPh	H	393 ^d	470 ^d	–	
30f	thiophen-2,5-diyl	Ph	Me	368 ^d	452 ^d	–	
31a	1,4-phenylene-thiophen-2,5-diyl	thiophene	H	385 ^e	485 ^e	479	fluorescent and phosphorescent
31b	2,2'-bithiophen-5,5'-diyl	thiophene	H	407 ^e	513 ^e	440	materials – light-emitting device [56]
32a	D = H; X = H	–	H	334/550 ^f	400 ^g	–	
32b	D = Me; X = H	–	H	336/552 ^f	403 ^g	–	
32c	D = OMe; X = H	–	H	340/554 ^f	413 ^g	–	
32d	D = NMe ₂ ; X = H	–	H	320/568 ^f	462 ^g	–	photochromic and fluorescent
32e	D = H; X = H	–	Me	296/542 ^f	399 ^g	–	materials – optical switches [57]
32f	D = Me; X = H	–	Me	296/542 ^f	401 ^g	–	
32g	D = OMe; X = H	–	Me	292/544 ^f	412 ^g	–	
33a	D = H; X = F	–	H	332/664 ^f	–	–	
33b	D = Me; X = F	–	H	337/651 ^f	–	–	
33c	D = OMe; X = F	–	H	343/682 ^f	–	–	photochromic materials –
33d	D = H; X = F	–	Me	318/630 ^f	–	–	photoswitches and
33e	D = Me; X = F	–	Me	322/632 ^f	–	–	photoresponsive materials [58]
33g	D = OMe; X = F	–	Me	328/638 ^f	–	–	

^aMeasured in 1,4-dioxane; ^bmeasured in cyclohexane; ^cmeasured in THF; ^dmeasured in MeCN; ^emeasured in EtOH; ^fabsorption maxima of open-ring/closed-ring isomers measured in DMF; ^gemission maxima of open-ring isomer (before UV irradiation) measured in DMF.

Benzimidazole-derived chromophores

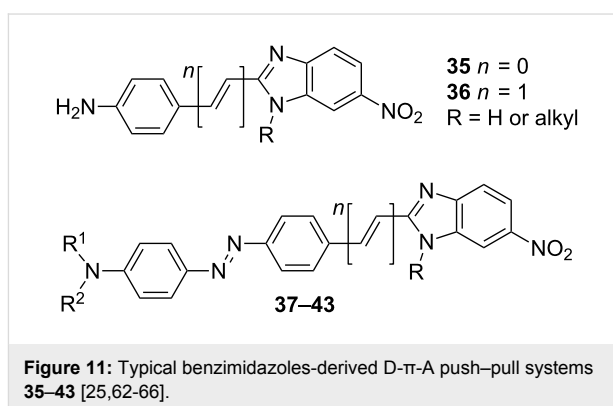
In contrast to imidazoles, benzimidazoles possess fused benzene or higher (hetero)aromates, generally appended at C4/C5. This arrangement enables (i) an extension of the chromophore

π -conjugated system; (ii) a planarization of the molecule; (iii) facile functionalization of the fused aromate by known methods; and (iv) a straightforward synthesis starting from inexpensive and readily available compounds (Scheme 1).



Typical representatives of benzimidazole-derived D- π -A systems are shown in Figure 11. In 2004, Carella, Centore, and co-workers [25] reported the synthesis and further application of nitrobenzimidazole-derived anilines **35** and **36**. These two compounds were further used for the construction of various charge-transfer chromophores **37–43**, in particular by simple diazotation and subsequent azo-coupling of the terminal NH₂ group [62-66]. Chromophores **37–43** found wide application as polymer dopants, cross-linkable organic glasses or inorganic-organic hybrid materials and showed high, stable, and tunable NLO performances, very good thermal stability, and, last but not least, easy synthesis from low-cost commercial precursors (Table 7).

Raposo and co-workers investigated benzimidazole derivatives **44–47** with either a donor- or acceptor-substituted benzene ring, whose π -conjugated pathways comprise thiophene and pyrrole subunits [24]. This series of chromophores was further extended by arylthienylimidazole phenanthrolines **48–52** and oligothiénylimidazole phenanthrolines **53–57** (Figure 12; [23,67]). The

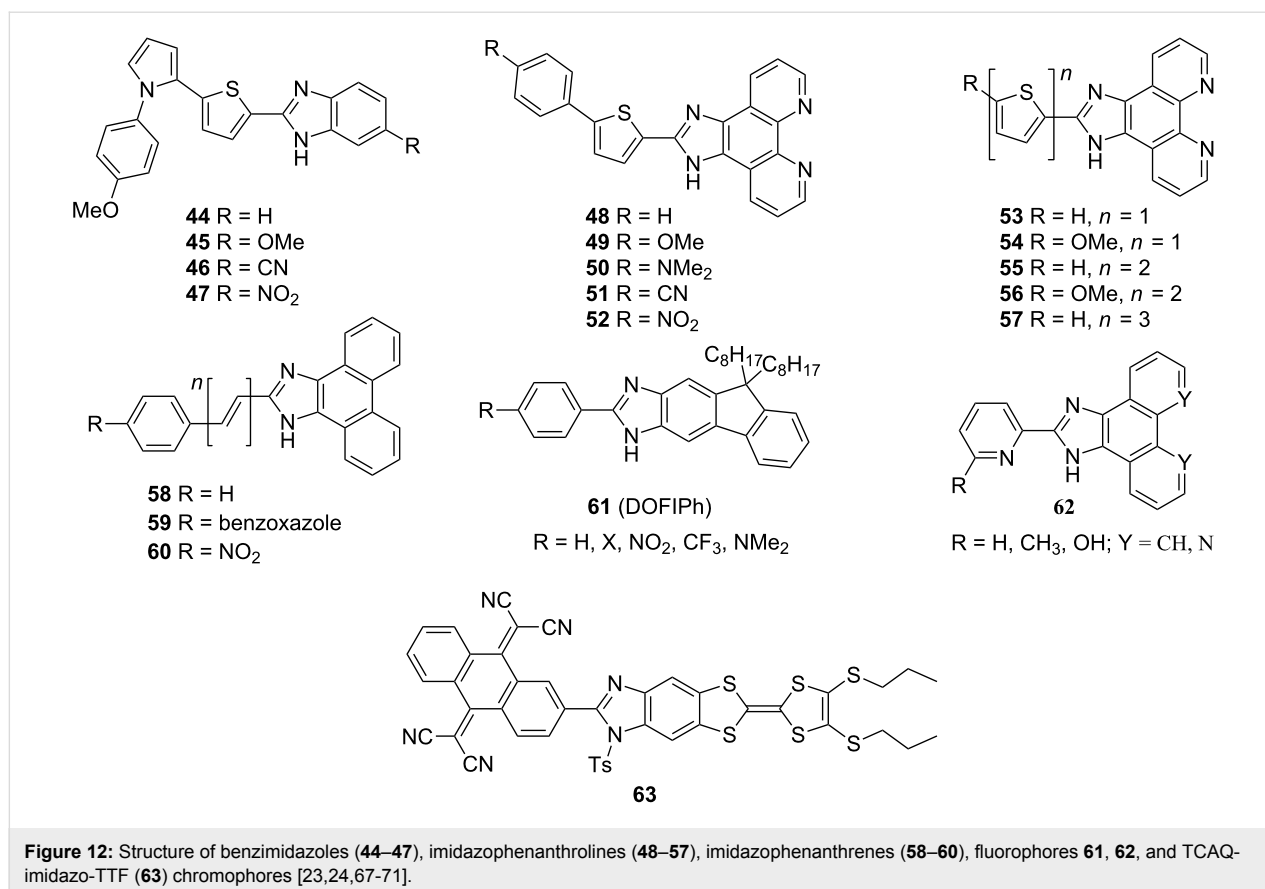


benzo[*d*]imidazole core in compounds **46–57** behaves as an electron acceptor and, when substituted with electron donors at C2, an efficient ICT can be achieved. Consequently, the measured hyperpolarizabilities β increase with the rise in donating ability of the appended donors or extension of the π -conjugated path. Thiophene, used as a part of the π -linker, particularly in chromophores **53–57**, caused β enhancement up

Table 7: Structures and (N)LO properties of benzimidazoles **37–43** [25,62-64].

Comp.	<i>n</i>	R	R ¹	R ²	$\lambda_{\text{max,abs}}^{\text{a}}$ [nm]	$\beta \cdot \mu$	T_{D} [°C]
37	0	H	CH ₂ CH ₂ OH	CH ₂ CH ₂ OH	472	940 ^b	296
38	0	Et	CH ₂ CH ₂ OH	CH ₂ CH ₂ OH	466	950 ^b	295
39	1	H	CH ₂ CH ₂ OH	CH ₂ CH ₂ OH	482	1550 ^b	292
40	1	Et	CH ₂ CH ₂ OH	CH ₂ CH ₂ OH	487	1400 ^b	314
41	0	Et	CH ₂ CH ₂ OMA ^c	CH ₂ CH ₂ OMA ^c	435	660 ^b	300
42	0	H	CH ₂ CH ₂ OH	CH ₂ CH ₃	476	2306 ^d	274
43	1	H	CH ₂ CH ₂ OH	CH ₂ CH ₃	480	3129 ^d	244

^aMeasured in DMF; ^bmeasured in DMF by EFISH technique at 1907 nm (10⁻⁴⁸ esu); ^cMA = methacrylate; ^dmeasured by solvatochromic method at 1907 nm (10⁻³⁰ esu-D).



to 320×10^{-30} esu (Table 8). This clearly demonstrates the beneficial role of the thiophene as a polarizable unit and auxiliary electron donor. A combination of fused phenanthroline-

imidazole acceptor moiety, *N,N*-dimethylamino donor, and arylthienyl π -linker, as in **50**, resulted in a CT chromophore with $\beta = 189 \times 10^{-30}$ esu. It should also be noted that all chromophores showed exceptionally high thermal stability with T_D up to 470 °C.

Table 8: Structure and properties of chromophore **44–57** [23,24,67].

Comp.	<i>n</i>	R	λ_{\max}^a [nm]	β^b [10^{-30} esu]	T_D [°C]
44	–	H	361	60	380
45	–	OMe	364	–	401
46	–	CN	367	114	390
47	–	NO ₂	363	121	365
48	–	H	361	41	470
49	–	OMe	370	145	431
50	–	NMe ₂	391	189	448
51	–	CN	386	91	465
52	–	NO ₂	408	45	450
53	1	H	337	26	441
54	1	OMe	346	110	341
55	2	H	384	46	451
56	2	OMe	393	170	423
57	3	H	412	320	467

^aMeasured in 1,4-dioxane; ^bfirst-order hyperpolarizability measured in 1,4-dioxane by hyper-Rayleigh scattering (HRS) method at 1064 nm.

Recently, Cui et al. investigated simple phenanthro[9,10-*d*]imidazoles **58–60** as two-photon absorbing molecules with blue upconversion fluorescence [68]. These imidazole derivatives proved to be potent two-photon absorbing molecules with TPA cross-section δ up to 20.65 GM at 800 nm. The molecular structure of chromophore **60** was also confirmed by X-ray analysis. Similar derivatives **61** (DOFIPh), based on the fluoreno[2,3-*d*]imidazole core, showed strong and tunable blue emission in the solid state ($\lambda_{\max,em} = 417$ –526 nm in film), which makes these molecules potentially applicable as active layers for OLEDs [69]. Chromophores **62** were investigated as photoluminescence materials with $\lambda_{\max,abs} = 324$ –367 nm and $\lambda_{\max,em} = 393$ –470 nm, respectively [70].

In 2007, Liu et al. reported a very nice example of D- π -A system **63** based on benzimidazole as a parent π -conjugated backbone fused with TCAQ (tetracyanoanthraquinodimethane) and TTF (tetrathiafulvalene) as acceptor and donor moieties,

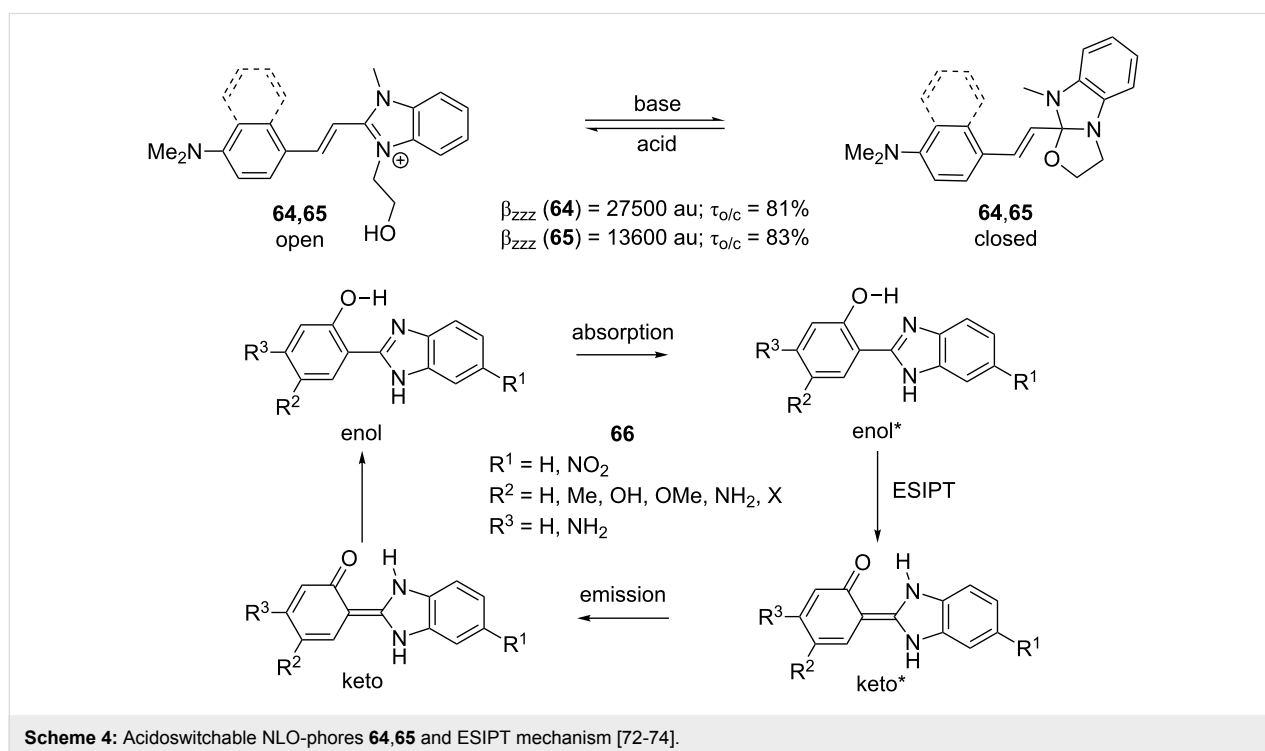
respectively [71]. This molecule was investigated in terms of absorption spectroscopy, X-ray analysis, and electrochemistry and showed remarkable responses as a function of pH. Unfortunately, no NLO properties were investigated.

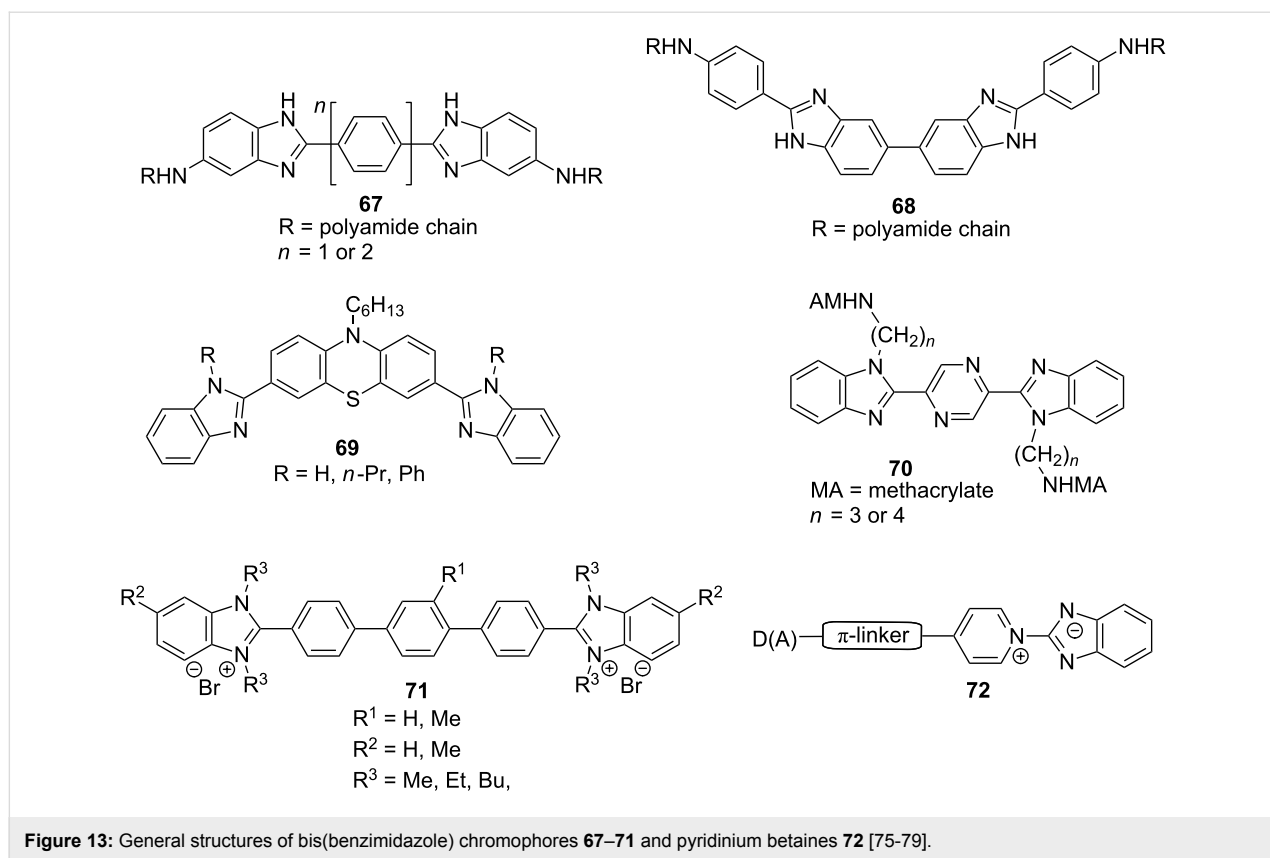
Benzimidazole-derived compounds were recently also used as chromophores with switchable properties. Benzimidazolo[2,3-*b*]oxazolidines **64**, **65** showed acidochromic behavior with remarkable contrast $\tau_{o/c}$ in the NLO responses along the reversible transformation observed by HRS (Scheme 4; [72]). Whereas the open form of **64**, **65** with strong ICT showed λ_{\max} at 402 and 406 nm and longitudinal hyperpolarizabilities β_{zzz} at 27500 and 13600 au, the closed form showed only diminished nonlinearities due to the interruption of efficient D-A conjugation.

Compounds showing excited-state intramolecular proton transfer (ESIPT) represent another example of switchable NLO-phores (Scheme 4). Donor- and acceptor-substituted push-pull systems **66** based on 2-(2-hydroxyphenyl)benzo[*d*]imidazole showed efficient photoinduced blue-green proton-transfer fluorescence [73,74]. Taking the amino/nitro-substituted derivative as an example ($R^1 = \text{NO}_2$; $R^2 = \text{H}$; $R^3 = \text{NH}_2$; LEN [73]), this compound showed absorption and emission maxima at 373 and 448 nm, respectively, and large first-order hyperpolarizability $\beta = 1197 \times 10^{-30}$ esu. The combination of such properties makes this compound a promising material for storing information at the molecular level.

Similar to diimidazole compounds **27–34**, two benzimidazole cores may also be incorporated into the chromophore backbone. The molecular structures of recently investigated bis(benzimidazole)-derived chromophores **67–71** are shown in Figure 13. All these bis(benzimidazole) systems were primarily studied as fluorescent compounds. Polymeric chromophores **67** and **68** showed blue fluorescence with emission maxima at 410–515 nm [75]. A- π -D- π -A molecules **69** featuring a central phenothiazine donor moiety and two peripheral benzimidazole acceptor units were investigated by Ahn et al. [76]. These ambipolar molecules possess energy levels that are well-matched with the Fermi levels of the electrodes to facilitate the electron or hole injection and transfer in OLED devices. 2,5-Bis(benzimidazol-2-yl)pyrazine derivatives **70** (BBIP), with improved solubility through *N,N'*-dialkylation, exhibited high fluorescence intensity even in protic solvents, as well as interesting solvatochromic properties [77]. Terphenyl-bridged bis(benzimidazolium) salts **71**, soluble in water and common organic solvents, emit blue light with $\lambda_{\max,em}$ at 420–441 nm in thin films [78]. This feature makes them potentially applicable as blue-light emitters in OLEDs.

Benzimidazole-based push-pull systems were studied also theoretically. Abe et al. studied pyridinium betaines of general formula **72** consisting of negatively charged benzimidazolate and a positively charged pyridinium ion (Figure 13; [79]). Moreover, the π -conjugated system was systematically enlarged and either donor- or acceptor-substituted in order to generate





D- π -A- π -D and D- π -A- π -A systems. The performed ab initio and INDO/S MO calculations of ground-state dipole moments and first-order hyperpolarizabilities β revealed that the latter chromophore arrangement resulted in significantly enhanced nonlinearities. The benzimidazolate anion as a donor moiety was quantum-chemically studied also by Xu, Su, and co-workers [80]. Structurally highly similar chromophores to **44–47** (Figure 12), reported by Raposo [24], were investigated by means of molecular geometry optimization, absorption/emission spectra, first-order hyperpolarizability calculations, and simulation of NH proton abstraction by using a fluoride anion. Remarkably large differences between the β values of protonated/deprotonated forms showed that benzimidazoles are potent molecules for a new type of NLO molecular switching.

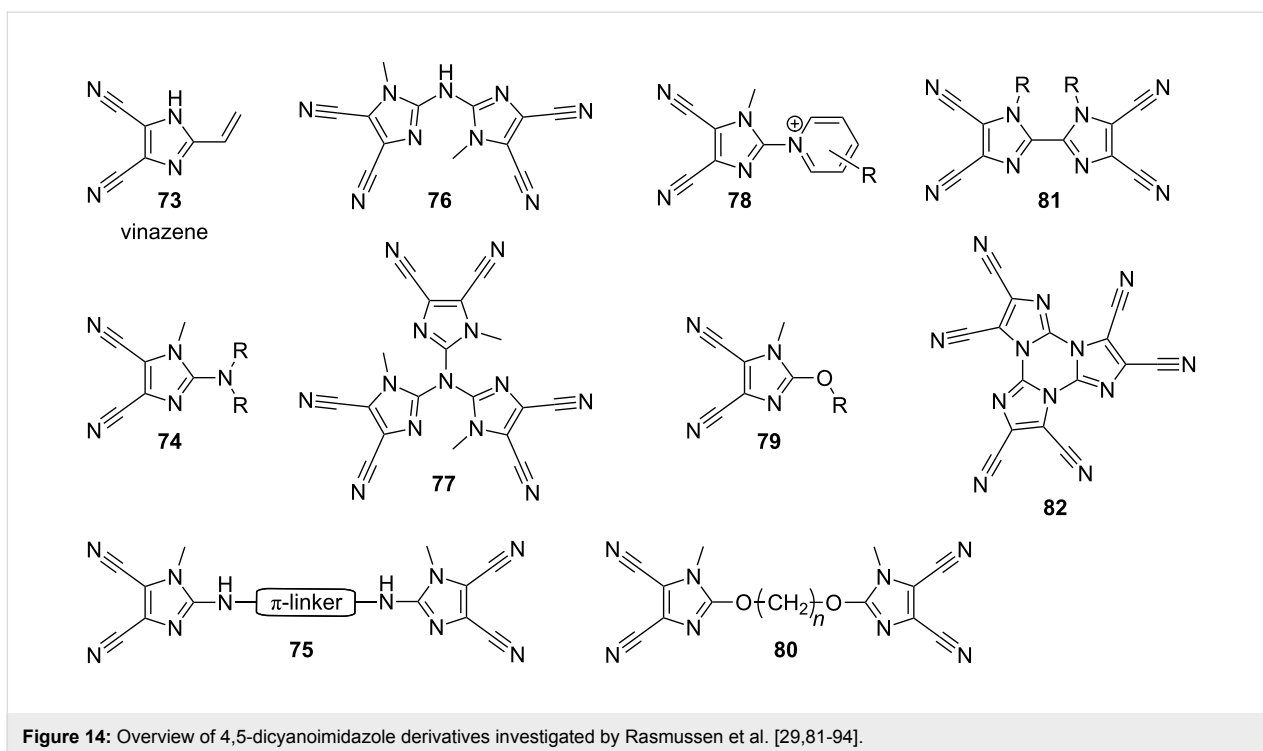
Chromophores featuring a 4,5-dicyanoimidazole acceptor moiety

Since the discovery of 4,5-dicyanoimidazole by Woodward in 1950 (Scheme 2; [27]), this imidazole derivative has become one of the “standard acceptor moieties” used in materials organic chemistry. The primary development and popularization of this molecule can be ascribed to Rasmussen and co-workers as early as the 1980s–1990s. Over a period of 20 years, Rasmussen et al. published an admirable number of articles dealing with the synthesis, combination, functionalization,

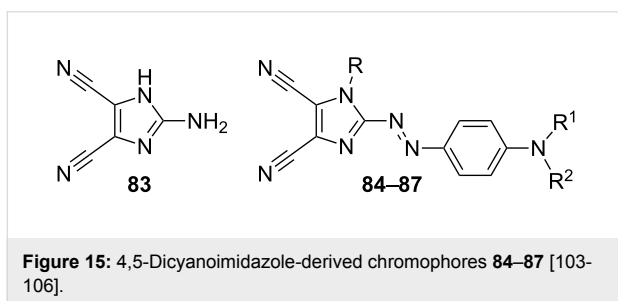
and application of 4,5-dicyanoimidazoles. Figure 14 shows a selection of Rasmussen’s 4,5-dicyanoimidazole derivatives, such as vinazene **73** [29,81], push–pull amines and betaines **74–78** [82-87], alkoxy derivatives **79,80** [88], biimidazoles **81** [89-92], and triimidazoles **82** [93,94], as well as fullerenes [95] and polymers [96-99].

The chemistry of 4,5-dicyanoimidazole was reviewed in 1987 by Donald and Webster [100] and its application in liquid-crystal media and devices was again summarized in a Merck patent in 2004 [101].

In 2004 and 2005, Carella, Centore, and co-workers utilized 2-amino-4,5-dicyanoimidazole **83** (for X-ray structure analysis, see [102]) in the synthesis of chromophores **84–86** featuring central phenylazo π -linker, 4,5-dicyanoimidazole as acceptor, and *N,N*-dialkylamino donor (Figure 15; [103,104]). The nonlinear optical properties of these three chromophores were investigated by EFISH experiment (Table 9). The molecular structure of chromophore **84** was also confirmed by X-ray analysis. These chromophores, with free terminal OH-functions, were further used as monomers for copolymerization with polyester, polyurethane, and polymethacrylate (see below). Structurally very similar chromophore **87** ($R = \text{H}$; $R^1 = \text{CH}_2\text{CH}_2\text{OH}$; $R^2 = \text{Et}$) was used for incorporation into the sol–gel hybrid



films based on alkoxy silanes [105,106]. This new material is to be applied as an electro-optic modulator.



Our synthetic efforts in the field of 4,5-dicyanoimidazole-derived chromophores began with the initial set of push–pull molecules **88–93** (Figure 16; [30]). Chromophores **88–93** were synthesized by Suzuki–Miyaura cross-coupling reactions [107] on 2-bromoimidazole **2** (Scheme 2) as three series **a**, **b**, and **c**

according to the type of the used donor D (H, OMe, and NMe₂). The π -conjugated path was systematically varied and enlarged in order to study its influence on the chromophore polarizability. The chromophores were primarily investigated by electronic-absorption spectra, electrochemistry, X-ray analysis, and quantum-chemical calculations. The resulting data set was further processed by factor analysis to deduce the structure–property relationships. The most important structural factors affecting the (non)linear optical properties and electrochemical behavior are (i) the presence of a strongly conjugating donor and (ii) the length and (iii) planarity of the π -conjugated system. In this respect, chromophores **90c**, **92c**, and **93c** seem to possess one of the better balances between performance and practicality within the studied series.

The photoinduced absorption, birefringence, and second-harmonic generation of chromophores **88c–93c** (D = NMe₂) embedded within polymethylmethacrylate matrices were

Table 9: Structures, optical (linear and nonlinear), and thermal properties of chromophores **84–86** [103,104].

Comp.	R	R ¹	R ²	λ_{\max}^a [nm]	$\mu\cdot\beta^b$ [10 ⁻⁴⁸ esu]	T _D [°C]
84	H	CH ₂ CH ₂ OH	CH ₂ CH ₂ OH	462	1050	230 ^c
85	H	CH ₃	CH ₂ CH ₂ OMA	459	1000	249
86	Et	CH ₃	CH ₂ CH ₂ OMA	496	800	236

^aMeasured in DMF (**84**) and CHCl₃ (**85**, **86**); ^bmeasured in DMF by the EFISH technique at 1907 nm; ^cmelting point.

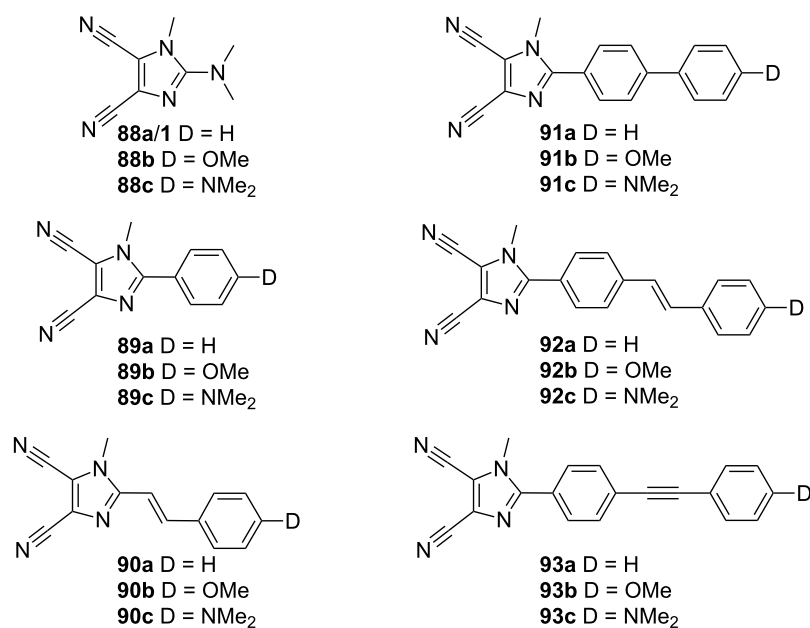


Figure 16: Push–pull chromophores **88–93** with systematically extended π -linker [30].

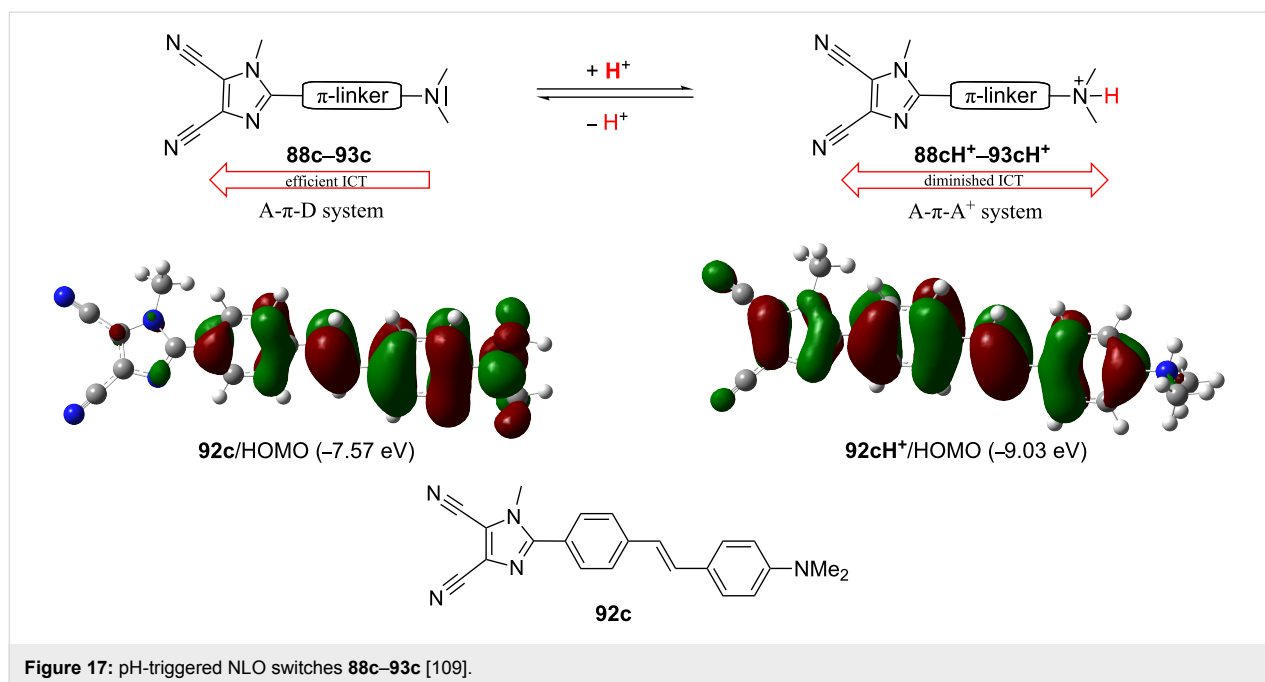
Table 10: Properties of chromophores **88–93** [30,108-110].

Comp.	D	$\Delta(E_{\text{ox},1} - E_{\text{red},1})^{\text{a}}$ [V]	$E_{\text{HOMO}} - E_{\text{LUMO}}$ [eV]	$\lambda_{\text{max,abs}}^{\text{b}}$ [nm (eV)]	$\lambda_{\text{max,em}}^{\text{c}}$ [nm]/ Φ	β^{d} [10^{-30} esu]	$\beta_{\text{av}}^{\text{e}}$ [au]	$\beta_{\text{zzz}}^{\text{f}}$ [au]
88a	H	–	9.19	244 (5.08)	–	1.5	–	–
88b	OMe	4.09	8.63	271 (4.58)	–	3.5	–	–
88c	NMe ₂	3.34	8.51	293 (4.23)	361/0.05	2.7	899	–
89a	H	4.06	8.69	264 (4.70)	320/0.28	2.6	–	–
89b	OMe	3.65	8.30	275 (4.51)	354/0.65	8.3	–	–
89c	NMe ₂	2.85	7.73	316 (3.92)	452/0.37	14.6	5657	9710
90a	H	3.37	7.98	313 (3.96)	–	5.3	–	–
90b	OMe	3.08	7.69	331 (3.75)	–	18.2	–	–
90c	NMe ₂	2.50	7.27	381 (3.25)	470/0.04	32.7	16750	19708
91a	H	3.70	8.38	286 (4.34)	351/0.87	5.2	–	–
91b	OMe	3.34	7.90	301 (4.12)	388/0.98	13.0	–	–
91c	NMe ₂	2.64	7.31	346 (3.58)	485/0.64	21.9	10754	14408
92a	H	3.30	7.78	325 (3.82)	390/0.59	13.2	–	–
92b	OMe	3.03	7.47	331 (3.75)	425/0.15	30.7	–	–
92c	NMe ₂	2.39	7.07	380 (3.26)	528/0.53	49.1	25978	18660
93a	H	3.63	7.96	308 (4.03)	361/0.80	9.3	–	–
93b	OMe	3.25	7.63	323 (3.84)	396/0.83	22.8	–	–
93c	NMe ₂	2.50	7.17	364 (3.41)	515/0.73	37.1	23401	24674

^aMeasured by DC polarography and RDV, potentials are given vs. SCE; ^babsorption maxima measured in CH₂Cl₂; ^cemission maxima/quantum yields measured in EtOAc; ^dPM3/PM6 calculated values (MOPAC); ^emeasured in poly(methyl methacrylate) by SHG experiment at 1064 nm; ^flongitudinal molecular first hyperpolarizabilities measured in CH₂Cl₂ by HRS experiment at 1064 nm.

studied and complimented by quantum-chemical calculations. These doped polymer films showed very efficient and tunable nonlinearities with β_{av} ranging from 899 to 25798 au (Table 10; [108]).

Moreover, the *N,N*-dimethylamino donor in **88c–93c** can easily be protonated. Whereas in the unprotonated form (**88c–93c**), an efficient ICT from the donor to the acceptor exists (*D*- π -*A* system), in the protonated forms (**88cH⁺–93cH⁺**) only dimin-



ished ICT between the π -linker and the peripheral acceptors A and A⁺ takes place (Figure 17; [109]). This results in a high contrast in the nonlinearities between both forms (Table 11) as well as in a raised energy and character of the HOMO (Figure 17). Hence, chromophores **88c–93c** proved to be very efficient pH-triggered NLO switches.

The fluorescent and photophysical properties of chromophores **88–93** were further studied [110,111]. The fluorescence was studied in various solvents and polymer matrices and at various temperatures. Intense fluorescence with quantum yields of 0.05 to 0.98 was observed in nonpolar solvents and polymer matrices within the range of 320 to 528 nm (Table 10).

The first set of 4,5-dicyanoimidazole-derived chromophores **88–93** possessed only one donor at the imidazole C2. Hence, our further synthetic efforts were focused on the synthesis of

branched chromophores **95–100** (Figure 18; [112]). The synthesis of this series of chromophores involved two-fold Suzuki–Miyaura and Sonogashira cross-coupling reactions on dibromoolefin **94** (for X-ray structure see [113]). This compound proved to be a very useful, fully planar precursor for the construction of a chromophore π -conjugated backbone. In

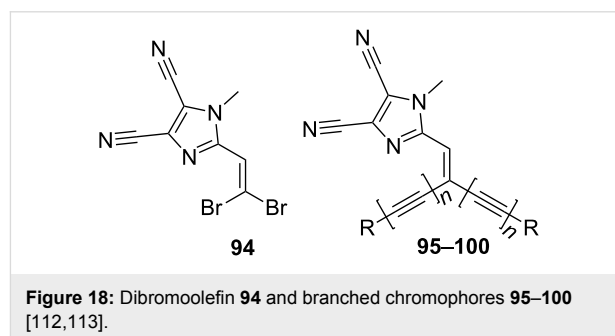


Table 11: HRS first hyperpolarizabilities (β) and depolarization ratios (DR) of **88c–93c** before/after protonation (CH₂Cl₂) [109].

Comp.	Unprotonated		Protonated		Contrast
	$\beta_{\text{HRS}}(-2\omega;\omega;\omega)$ [au]	DR	$\beta_{\text{HRS}}(-2\omega;\omega;\omega)$ [au]	DR	
88c	379	4.87	114	1.78	3.32
89c	1938	5.48	256	1.65	7.57
90c	10485	5.11	541	1.87	19.38
91c	3264	5.40	290	2.28	11.26
92c	8485	5.15	361	1.78	23.50
93c	8236	5.15	639	2.44	12.89

contrast to **88–93**, the presence of two (or four) *N,N*-dimethyl-amino donors and the systematic extension of the π -linkers in **95–100** resulted in a bathochromically shifted CT-band, lowered electrochemically measured and calculated HOMO–LUMO gaps, and enhanced first-order hyperpolarizability up to 70×10^{-30} esu (Table 12).

A combination of donor and acceptor 4,5-disubstituted imidazoles, namely 4,5-bis[4-(*N,N*-dimethylamino)phenyl]imidazole and 4,5-dicyanoimidazole as in **21–26** (Figure 8) and **88–100** (Figure 16 and Figure 18), respectively, resulted in diimidazole-type chromophores **101–111** (Figure 19; [20]). In contrast to a typical synthetic approach to diimidazoles as shown in Scheme 1, we used 4,5-dicyanoimidazole derivatives **1–3** (Scheme 2) and modern direct arylation, Suzuki–Miyaura, Sonogashira, and Heck reactions to construct molecules **101–111**. These chromophores possess two (or three) imidazole parent π -backbones, either as donor or acceptor moieties, and a systematically extended π -linker. Thiophene, in combination with double bonds, was used as a highly polarizable subunit of the π -linker, which resulted in very efficient chromophores with first- and second-order hyperpolarizabilities β and γ up to 526×10^{-30} and 315×10^{-27} esu, respectively (Table 13, chromophore **109**). In general, this series of diimidazole-based compounds featured the most efficient NLO-phores.

Organic π -conjugated materials based on 4,5-dicyanoimidazole were recently developed as opto-electronic materials with a practical application. For instance, in 2002 Yang et al. [114] reported a fairly simple organic-electrical bistable device (OBD) based on amine **83** (Figure 15). Yang's OBD consisted of organic material based on **83** with a built-in thin aluminum active layer. The OBD's conductivity in the two electric states was considerably different, and, moreover, the OBD showed remarkable stability without significant device degradation over a million write–erase cycles. Hence, the performance of this device makes OBD attractive for application in rewritable memory cells. In 2007, Sellinger et al. became very interested in the Heck coupling of *N*-alkyl vinazenes with various (hetero)aromatics [115]. This synthetic interest resulted in four new diimidazole compounds **112–115** (Figure 20). This series of basic π -conjugated compounds was significantly extended in 2009 by a library of various π -linkers [116]. As a materials researcher, Sellinger applied these *n*-type conjugated materials as small-molecule electron acceptors. The combination of V-BT (**114**) with polyhexylthiophene donor (P3HT) in an initial organic solar cell showed high external quantum efficiencies exceeding 14%. Sellinger's further efforts were focused on improving optical, photovoltaic, and charge-transport properties as well as efficiencies of V-BT derived solar cells. Thus, he studied new processing techniques for solar cells, the use of

Table 12: Structures and selected properties of branched chromophores [112].

Comp.	R	<i>n</i>	$\Delta(E_{\text{ox},1} - E_{\text{red},1})$ [V]	$E_{\text{HOMO}} - E_{\text{LUMO}}$ [eV]	$\lambda_{\text{max}}^{\text{a}}$ [nm (eV)]	β^{b} [10^{-30} esu]
95		0	2.80	7.48	349 (3.55)	18.3
96		1	2.35	6.85	429 (2.90)	31.2
97		1	2.10	6.68	416 (2.98)	33.1
98		1	1.84	6.48	437 (2.84)	70.2
99		1	2.10	6.61	407 (3.05)	49.0
100		1	2.00	6.64	450 (2.76)	32.6

^aMeasured in CH_2Cl_2 ; ^baverage second-order polarizabilities calculated by PM3/PM6 methods (MOPAC).

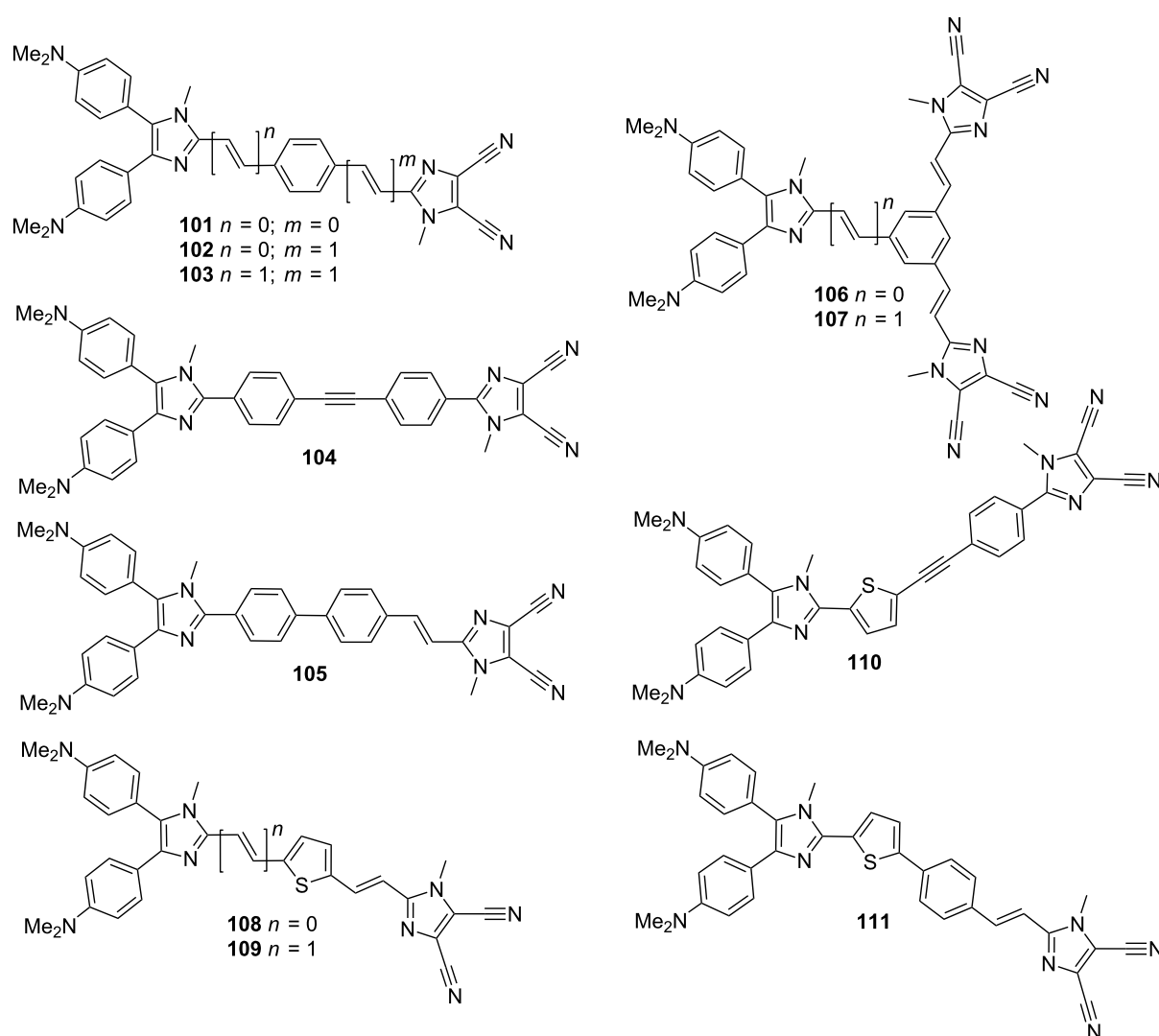
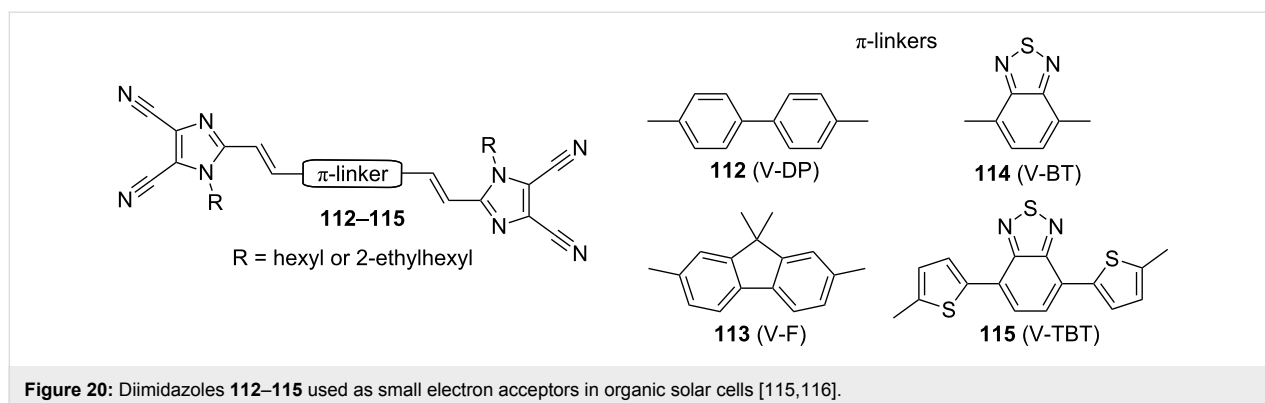


Figure 19: Imidazole as a donor–acceptor unit in CT-chromophores **101–111** [20].

Table 13: Diimidazole chromophores **101–111**; properties [20].

Comp.	$\Delta(E_{\text{ox},1} - E_{\text{red},1})$ [V]	$E_{\text{HOMO}} - E_{\text{LUMO}}$ [eV]	λ_{max}^a [nm (eV)]	β^b [10^{-30} esu]	γ^b [10^{-27} esu]
101	2.39	6.63	366 (3.39)	38.2	3.61
102	2.17	6.48	404 (3.07)	38.2	5.17
103	2.08	6.35	444 (2.79)	66.0	8.99
104	2.31	6.35	373 (3.32)	44.8	6.26
105	2.17	6.38	382 (3.25)	38.4	5.78
106	2.12	6.49	316 (3.92)	25.5	4.51
107	2.10	6.44	394 (3.15)	39.6	5.97
108	2.11	6.65	448 (2.77)	299.0	164.05
109	1.95	6.14	479 (2.59)	526.3	315.15
110	2.27	6.80	413 (3.00)	82.2	45.91
111	2.11	6.47	420 (2.95)	47.9	20.18

^aMeasured in CH_2Cl_2 ; ^baverage second/third-order polarizabilities calculated by PM3/PM6 methods (MOPAC).



various semiconducting donor polymers, nanoimprint lithography, etc. [117-120]. This effort resulted in organic photovoltaic devices with a very high fill factor $FF = 57\%$ and an external quantum efficiency IPCE (incident photons converted to electrons) = 27% . These values rival those measured for popular fullerene acceptors.

Imidazole chromophores incorporated into the polymer

Recently, imidazole-derived CT chromophores found wide application either as polymer dopants (guest–host systems) or in polymers with chemically bonded NLO-phores (side-chain, main-chain, and cross-linked). An incorporation of the chromophore into the polymer backbone brings with it a higher and facile polarizability, higher thermal stability, and NLO responses as well as prospective applicability in modern materials chemistry. The second-order susceptibilities of nonlinear optical polymers are historically referred to as “ d_{ij} ” coefficients ($1/2$ of the respective $\chi_{ij}^{(2)}$ values). The electro-optic coefficient r_{ij} , indicating the degree of the refractive index change caused by a unit increase in the voltage applied across the polymer film, is another important feature of the nonlinear optical polymer waveguides. The relationship between the d and r coefficients can be simplified according to the following equation

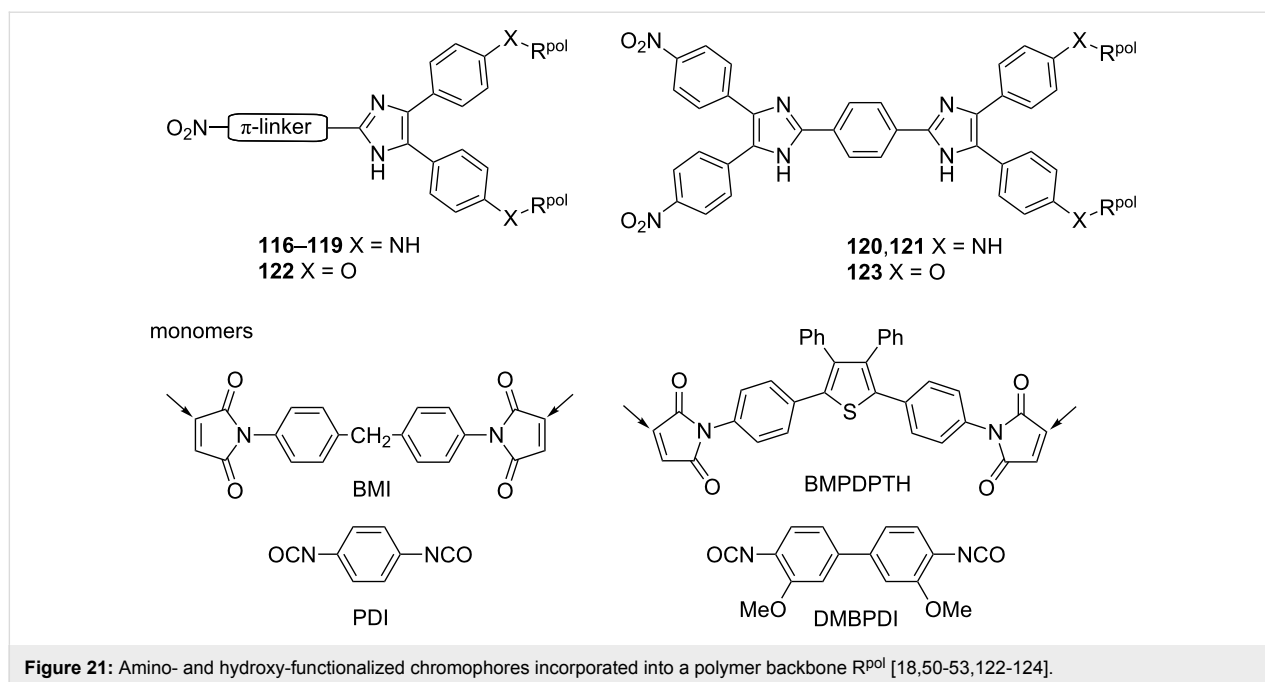
$$r = -4d / n^4, \quad (1)$$

where n is the index of refraction. However, only two components of the d and r coefficients that are parallel and perpendicular to the average dipolar chromophore axis are important and investigated (d_{33} , d_{31} and r_{33} , r_{31}). The physical stability of the nonlinear optical polymers refers to the stability of alignment of the chromophore. The glass transition temperature (T_g) and the decomposition temperature (T_D) are the most widely provided parameters of polymer physical stability. The polar order of the polymer (centrosymmetry removal) is usually achieved by the electric-field, thermal (T_p) and optical poling procedures [121].

Only the polymer systems with covalently attached imidazole CT chromophores will be discussed in the following section.

4,5-Bis(4-aminophenyl)(bi)imidazole (e.g. **15/27a**; Figure 6/ Figure 9) and 4,5-bis(4-hydroxyphenyl)diimidazole (i.e., **27c**; Figure 9) represent simple chromophores with free NH_2 and OH peripheral groups, which can be used to link the chromophore to various polymers (Figure 21). These systems were mainly investigated by Ye et al. (Table 14; [18,50-53,122-124]). The polyimides **116–118** ($X = NH$) were prepared by the copolymerization (Michael addition) of N,N' -bismaleimido-4,4'-diphenylmethane (BMI) with Y-shaped imidazole chromophores **15** featuring a slightly extended π -linker. These polymers were thermally poled to achieve moderate nonlinearity and good thermal stability [122,123]. Similar reaction of 2,5-bis(4-*N*-maleimido)phenyl-3,4-diphenylthiophene (BMPDPTH) with chromophore **15f** afforded system **119** with significantly enhanced nonlinearity ($d_{33} = 32.2$ pm/V) [124] as a result of the π -linker extension through the thiophene and double-bond subunits. Diimidazole **27a** ($X = NH$) was also utilized as a reactive chromophore for copolymerization with BMPDPTH and 1,4-phenylene diisocyanate (PDI) to provide polyimide **120** and polyurea **121** [50-53]. Ye also investigated the similar (bi)imidazole-derived polymers **122** and **123** ($X = OH$) with a polyurethane backbone generated after copolymerization with 3,3'-dimethoxy-4,4'-biphenylene diisocyanate (DMBPDI) [18]. However, the measured nonlinearities and thermal stabilities of these polymers did not exceed that measured for **119** (Table 14).

Tang et al. showed another approach to producing nonlinear optical polymers. The synthetically easily available hydroxylophine **124** was covalently bonded to the polyphosphazene backbone and subsequently modified by post-azo coupling with variously substituted benzenediazonium salts to afford systems **125–130** (Figure 22; Table 15; [125-127]). These systems possess good optical transparency, high T_g , and large d_{33} (SHG) and photoinduced birefringence values relative to those known

**Table 14:** Nonlinear optical polymers **116–123**; properties [18,50-53,122-124].

Comp.	Chromophore/ π -linker	X	Monomer	d_{33} [pm/V]	T_g [°C]	T_D [°C]
116	15a (65%) / $-(C_6H_4)-$	NH	BMI	–	262	335
117	$-N=N-(C_6H_4)-$	NH	BMI	13.6	250	331
118	$-CH=CH-(C_6H_4)-$	NH	BMI	11.3	258	335
119	15f / $-(C_4H_2S)-CH=CH-(C_6H_4)-$	NH	BMPDPHT	32.2	304	330
120	27a	NH	BMPDPHT	16.4	234	380
121	27a	NH	PDI	24.0	272	290
122	$-(C_6H_4)-$	O	DMBPDI	12.0	202	300
123	27c	O	DMBPDI	15.0	223	335

for polyphosphazenes to date. Last but not least, this simple synthetic pathway opens space for manifold elaboration and functionalization of various prepolymers in order to enhance their nonlinearities.

Table 15: Properties of polyphosphazenes **125–130** [125-127].

Comp.	X	λ_{max} [nm]	d_{33} [pm/V]	T_g [°C]	Δn^a [10 ⁻²]
125	NO ₂	363	–	170	0.45
126	Cl	363	29	158	–
127	F	372	37	157	1.32
128	I	365	23	169	–
129	Me	354	–	165	1.01
130	OMe	375	–	174	1.12

^aPhotoinduced birefringence measured at 633 nm (He–Ne laser).

Recently, Müllen et al. [19] as well as Koszykowska et al. [128] contributed to the field of nonlinear optical polymers (Figure 22). Müllen's imidazole-functionalized poly(*p*-phenylene) **131** proved to be a promising hole-transporting emissive material, which can be oxidized to quinoid (Scheme 3) with an additional low-wavelength absorption at 655 nm (light-absorbing material for solar cells). In 2009, Koszykowska et al. demonstrated facile polymerization of 1-vinylimidazole and subsequent post-azo coupling at imidazole C2 to attach various donor- and acceptor-substituted pendants. Moreover, the poly(*N*-vinyl-2-(phenylazo)imidazoles **132–134** showed interesting switchable photochromic properties.

Typical representatives of benzimidazole CT chromophores **37–43**, intended as reactive monomers for incorporation into the polymer backbone, were investigated by Carella, Centore et al. [62,63] and Cross et al. [65,66] and are shown in Figure 11. The

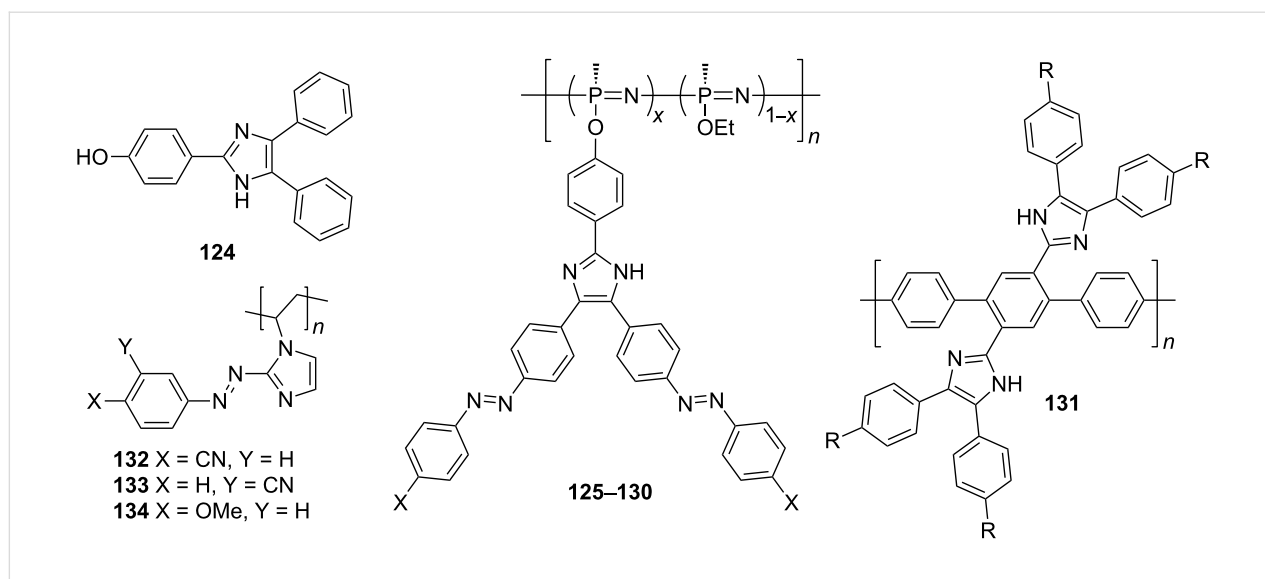


Figure 22: Structure of polyphosphazene polymers bearing NLO-phores [125–127] and some other recent examples of nonlinear optical polymers [19,128].

chromophores **37–43** were attached to polyurethane and polyester by solution copolymerization with tolylene-2,4-diisocyanate (TDI), (2-methoxy)terephthaloyl dichloride [(M)TPC], and isophthaloyl dichloride (IPC) to afford nonlinear optical polymers **135–140**. Polymers **141–143** were synthesized by AIBN-promoted polymerization of the methacrylate terminal functionality. Table 16 summarizes the structures, SHG coefficients d_{33} , and stability parameters T_g and T_D . It is obvious that the three cross-linked nonlinear optical polymers **141–143**, prepared by radical polymerization, possess much higher nonlinearities than the two-component polymers **135–140**. However, the achieved nonlinearities are still lower than those

measured for previous polymeric systems, e.g., **119** and **126–128**.

Chromophores **67** and **68** attached to polyamide and polyester backbones by copolymerization with *m*-phenylenediamide (MPD) and isophthaloyl dichloride (IPC) as well as bis(benzimidazolyl)pyrazines **70** (Figure 13; [75,77]) represent further examples of interesting polymers functionalized with benzimidazole-based CT chromophores. Unfortunately, no NLO properties were investigated. In 2002, Kudryavtsev et al. reported third-harmonic generation in copolymer films (polyamides) featuring a *N*-phenylbenzimidazole motif [129]. These ma-

Table 16: Benzimidazole-derived chromophores embedded into a polymer **135–143** [62,63,65].

Comp.	Chromophore/ Structure ^a	Monomer	d_{33} [pm/V]	T_g [°C]	T_D [°C]
135	38	TDI	1.8	158	275
136	40	TDI	1.2	171	292
137	38	TPC	2.0	149	311
138	38	MTPC	2.2	146	327
139	40	MTPC	0.9	173	292
140	38	IPC	2.3	147	313
141	41		14.0	37	300
142	R = CH ₂ CH(CH ₃)OH R ¹ = CH ₂ CH ₂ OC(O)NHCH ₂ CH ₂ OMA R ² = CH ₂ CH ₃		13.0	128	–
143	R = CH ₂ CH(CH ₃)OH R ¹ = CH ₂ CH ₂ OMA R ² = CH ₂ CH ₃		16.5	151	–

^aSee Figure 11.

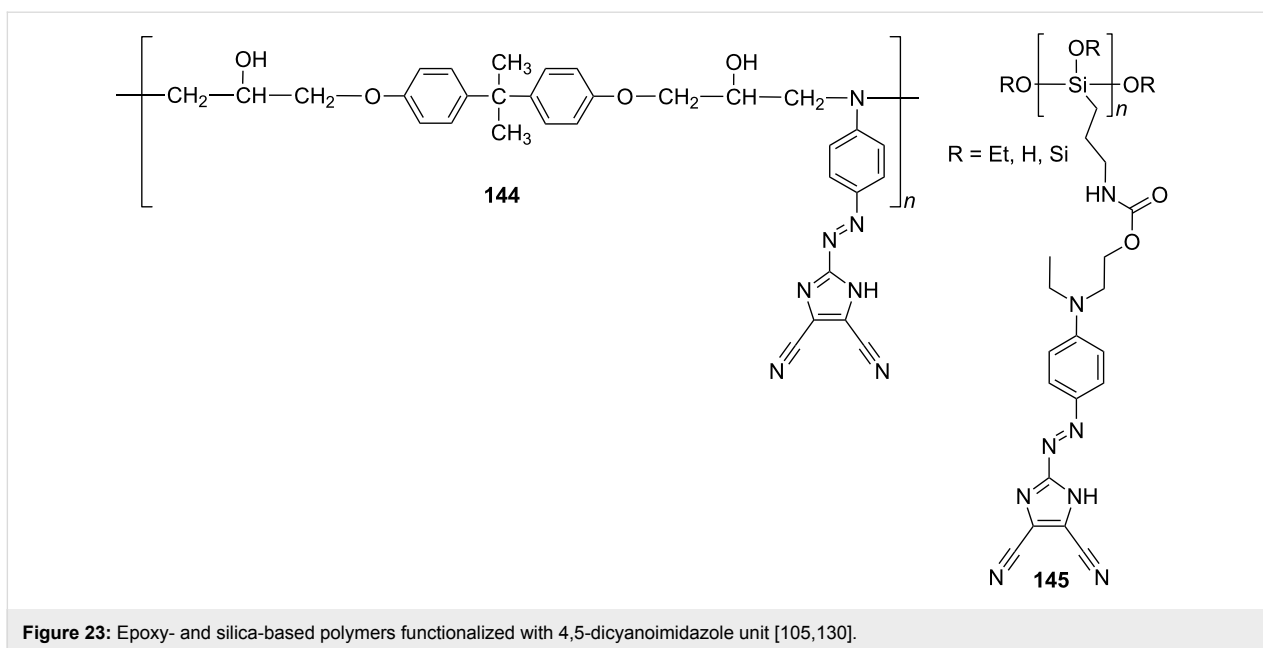


Figure 23: Epoxy- and silica-based polymers functionalized with 4,5-dicyanoimidazole unit [105,130].

materials exhibited their longest absorption maxima λ_{\max} at 490–515 and third-order NLO susceptibility $\chi^{(3)}(3\omega;\omega,\omega,\omega)$ within the range of 1.5 to 2.6×10^{-13} esu (measured by THG at 1064 nm).

Various 4,5-dicyanoimidazole-functionalized polymers were mainly investigated by Rasmussen et al. [29,81,86–88,96–99]. However, these systems were not intended as nonlinear optical polymers. Their properties were primarily studied by electrochemistry, absorption spectroscopy, NMR, FTIR spectroscopy, DSC, and TGA. Nevertheless, in 1998, Tripathy and co-workers reported the synthesis of epoxy-based nonlinear optical polymers **144** functionalized by post-azo coupling (Figure 23; [130]). The parent polymer backbone was synthesized from diglycidyl ether of bisphenol A and aniline and was further functionalized by diazotized amine **83** (Figure 15). This polymeric material possess $\lambda_{\max} = 489$ nm, $T_g = 179$ °C, $T_D = 224$ °C, and a large d_{33} coefficient 24.3 pm/V (1064 nm). Moreover, the NLO properties of this poled polymer exhibited long-term stability at 80 °C. A structurally similar chromophore incorporated into a sol–gel hybrid film, **145**, was investigated by Qian et al. (Figure 20; [105]). This thermally poled film showed $\lambda_{\max} = 487$ nm, $T_D = 272$ °C, exceptionally high $d_{33} = 42.0$ pm/V, but no clear glass-transition behavior between 40–200 °C, because the rigid silica backbone hinders the motion of the molecule at higher temperature.

Conclusion

This review has attempted to show that 1,3-diazole, imidazole, may act as a robust and stable parent π -conjugated backbone for organic chromophores with intramolecular charge transfer. This

synthetically readily accessible five-membered heteroaromatic and its push–pull derivatives are currently of high interest for materials chemists due to their unique and tunable properties. In general, the imidazole-derived chromophores may possess two Y-shaped arrangements: One electron donor at C2 and two electron acceptors at C4/C5 or vice versa. Hence, according to the C4/C5 substitution, the entire imidazole moiety may behave as an electron acceptor or donor. Taking our series of structurally similar chromophores **21–26** and **88–93** as an example, which primarily differ in the orientation of the substituents along the imidazole ring, C4/C5 donor-substituted imidazole derivatives showed higher nonlinearities. This implies that imidazole is more polarizable in the direction C4/C5→C2. However, two imidazole units that are differently C4/C5 substituted and connected at C2 may be employed as acceptor or donor moieties. It was shown that this diimidazole arrangement (e.g., in **101–111**) represents very powerful chromophore with high nonlinearities. Push–pull benzimidazoles feature more-planar π -conjugated systems due to the fused benzene ring. This fact further improves the polarizability of the entire D- π -A chromophore (e.g., compare chromophores **5–8** with **37–40**). The structure and the length of the π -linker connecting both acceptor and donor moieties play a crucial role. It was shown that polarizable subunits, such as olefins and thiophenes, increase the chromophore (hyper)polarizability significantly. Thus, the most important structural factors affecting D–A interaction responsible for the linear and nonlinear optical properties are (i) the strength of the appended donors and acceptors; (ii) the length and electronic nature of the π -conjugated path; and (iii) chromophore overall planarity. These three features mainly dictate the chromophore properties and, therefore, are mainly used to

finely tune the desired (non)linearities. Imidazole-derived chromophores have found also a wide range of practical applications in OLEDs, OPVCs, switches, memories, and polymers. A combination of all of these properties makes imidazole a very promising scaffold for materials chemistry.

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