Optimization of neutrocyanine chromophores based on five-membered heterocycles for photorefractive applications

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Exceptionally large photorefractive figures-of-merit are observed for neutrocyanine dyes based on dialkylaminothiophenes and −furans linked to quinoid five-membered heterocyclic acceptor groups by a methine bridge.

Chromophores based on 2-dialkylaminothiophenes with strong acceptor units in the 5-position are among the most interesting developments in dye chemistry of the last few years.[1–6] Showing enhanced electron-donating properties compared to *p*-dialkylaminobenzenes and higher thermal and chemical stability than dialkylaminopolyenes, 2-dialkylaminothiophenes became one of the most useful electron donor units for nonlinear optical (NLO) chromophores.[2–5] Furthermore, 5-dimethylamino-5'-nitro-2,2'-bithiophene is among the best indicator dyes for the study of solvent polaritity because of its outstanding positive solvatochromism.[6] Whereas all these dyes bear a chromophoric system which may be considered as ‘polyene-like’ with a large change of dipole moment upon optical excitation, we were recently able to polarize 2-dialkylaminothiophenes by a strong heterocyclic acceptor group up to the *cyanine limit*, which is characterized by equal dipole moments in the ground and the excited states, sharp and very intense absorption bands and vanishing solvatochromism.[7] Based on those highly polarizable dipolar dyes photorefractive (PR) materials[8] of unprecedented performance could be devised.[7,9]

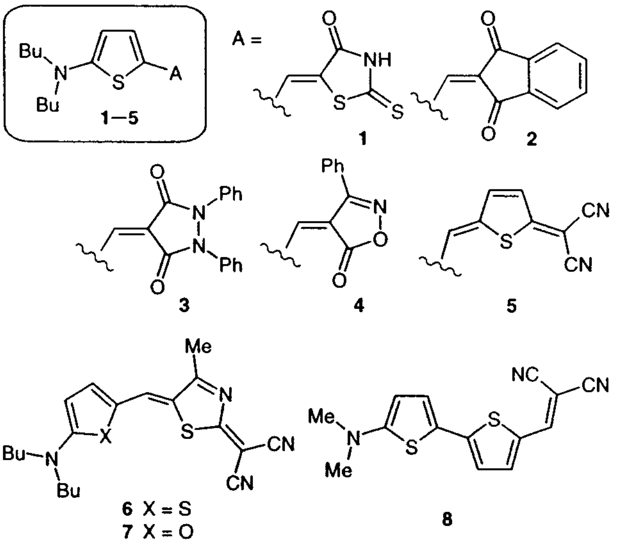
Here we present optical, electrooptical and structural properties of a new series of thiophene-based neutrocyanine dyes. Structure–property relationships will be elucidated which lead to general guidelines for the design of highly efficient PR chromophores.

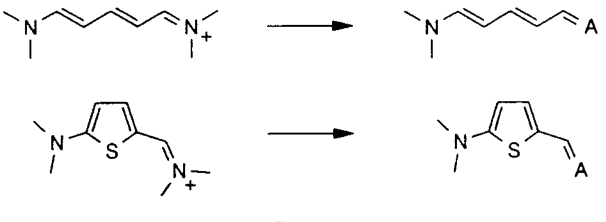
According to Scheme 1, neutrocyanines (top right) are derived from cyanines (top left) by replacement of the iminium unit by non-ionic but very strong acceptor substituents (*e.g.* di- or tri-cyanovinyl). As a result, uncharged but highly dipolar chromophores are obtained. This should also be true if the conjugated chain is part of a heterocyclic system (bottom). However, since the symmetry of the cyanine chromophor is broken and aromaticity comes into play, even the tricyanovinyl acceptor group is not strong enough to polarize 2-dialkylaminothiophene to the cyanine limit.[3b] This goal may be achieved in a quite general way, however, by using heterocyclic acceptor units.

Thiophene dyes **1**−**6** and furan **7** were obtained§ by condensation reactions of the CH-acidic heterocycles with 2-dibutylamino-5-formyl-thiophene and -furan and studied by UV–VIS optical and electrooptical absorption measurements (EOAM).[10] EOAM experiments yield the dipole moment of the electronic ground state μ_g as well as the dipole change upon optical excitation $\Delta\mu = (\mu_a - \mu_g)$, whereas optical spectroscopy provides information on the transition dipole moment μ_{ag} and the absorption maximum λ_{ag}. From these data a PR figure-of-merit F_0 and a resonance parameter c^2 may be calculated according to eqns. (1) and (2).¶

$$F_0 = [54\mu_g\mu_{ag}{}^2\Delta\mu\lambda_{ag}{}^2/(hc_0)^2 + 4\mu_g{}^2\mu_{ag}{}^2\lambda_{ag}/(hc_0kT)]/M \quad (1)$$

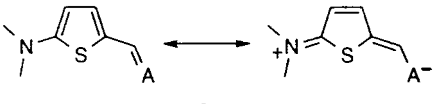
$$c^2 = \tfrac{1}{2}[1-\Delta\mu(4\mu_{ag}{}^2 + \Delta\mu^2)^{-1/2}] \quad (2)$$





Scheme 1

The PR figure-of-merit [eqn. (1)] was derived only recently[11] and established by us and others.[7,9] The two terms in eqn. (1) are commonly referred to as the electrooptical and birefringence contributions. It is found that the latter is usually dominant (>80%).[7,11] Eqn. (2) defines a useful parameter to characterize the charge transfer properties of donor/acceptor-substituted compounds.[11] It is closely related to the BLA-parameter introduced by Marder *et al.*[12a] and the parameter MIX introduced by Barzoukas *et al.*[12b] and can be regarded as a measure of the admixture of the zwitterionic resonance structure (Scheme 2) to the electronic ground state. Thus eqn. (2) allows us to classify donor/acceptor-substituted chain molecules from polyene-type molecules($c^2 \approx 0$) to betaine-type molecules ($c^2 \approx 1$) with the neutrocyanine (‘cyanine limit’) being located in the middle ($c^2 \approx 0.5$).



Scheme 2

Table 1 Optical and electrical properties of chromophores **1**–**8** and DANS[a] from UV–VIS and EOAM measurements in dioxane

Compound	λ_{ag}/nm (ε_{max}/l mol^{-1} cm^{-1})	μ_{ag}/D	μ_g/D	$\Delta\mu$/D	c^2	$F_0/10^{-74}$ m^4 C^2 mol V^{-2} kg^{-1}
1	513 (59 100)	8.2	6.7	7.2	0.30	0.32
2	510 (114 600)	9.0	5.7	4.2	0.39	0.24
3	489 (110 900)	9.0	7.0	2.1	0.44	0.26
4	500 (76 800)	8.2	7.9	2.4	0.43	0.35
5	647 (55 400)	9.8	11.2	7.8	0.32	1.44
6	641 (83 250)	9.7	13.6	3.1	0.42	1.84
7	650 (84 920)	9.3	14.6	0.5	0.49	1.98
8[b]	543 (41 000)	8.4	8.7	15.6	0.16	0.60
DANS[a,b]	426 (30 300)	7.7	7.4	21.8	0.09	0.32

[a] 4-Dimethylamino-4'-nitrostilbene. [b] For comparison we used the molar mass of the dibutylamino derivative for the calculation of the F_0 values.

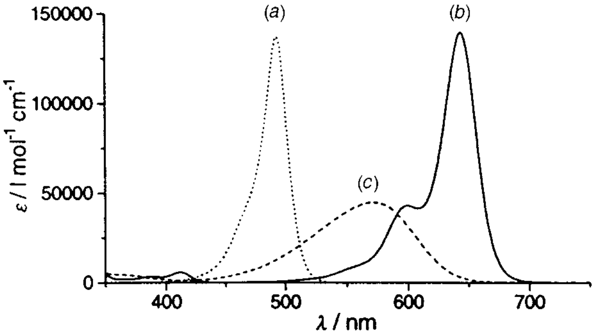


Fig.1 UV–VIS absorption spectra of PR neutrocyanine dyes (*a*) **3** and (*b*) **6** and (*c*) NLO dye **8** in CH_2Cl_2

The optical properties (λ_{ag}, ε_{max}, μ_{ag}) of neutrocyanines **1**–**7** (c^2 = 0.30–0.49) reveal intense transitions with very narrow bandwidths for their main absorption band, which is very favorable for applications in photonics (Table 1, Fig. 1). Thus dyes **1**–**7** may be used at laser frequencies significantly closer to the absorption maximum than for typical NLO chromophores such as **8**,[3] which exhibit very broad absorption bands thus causing absorption problems. Depending on the number of methine groups in the conjugated chain, we observe absorption maxima at *ca.* 500 nm for seven methine groups (**1**–**4**) and *ca.* 650 nm for nine methine groups (**5**–**7**).Whereas the optical properties of **1**–**7** exhibit very similar features, significant differences in the dipolar contributions to F_0 are found. Having about twice the number in their ground-state dipole moments μ_g, compounds **5**–**7** gain a factor of about four [second term in eqn. (1)] to F_0 compared to **1**–**4**. To explain this important point a closer look at the molecular structures and charge distributions in the ground state is helpful.|| Semiempirical calculations indicate a high degree of charge separation for **5**–**7**. The highest electron density is found at the thiazole nitrogen (**6**,**7**) and the dicyanomethylene functionalities (**5**–**7**) of the heterocyclic acceptor at the *opposite* side of the methine bridge. In this way, a fairly extended chromophore is formed. On the other hand, **1**–**4** have their acceptor carbonyl groups *ortho* to the methine bridge. This limits the conjugated path to a rather short distance. Furthermore, the unfavorable orientation of the carbonyl group dipole moment leads to significant cancellation of the total molecular dipole moment.

Finally we note the successful tuning of the c^2 value from 0.32 in **5** to the perfectly equilibrated cyanine point (c^2 = 0.49) in **7**. Concomitantly, both the extinction coefficient and the PR figure-of-merit F_0 could be substantially increased. This improvement is particularly impressive when compared to NLO chromophore **8** which differs from **5** only by the position of the methine bridge. Moreover, the exocyclic dicyanomethylene moiety in **5**–**7** opens the way for an extension of the conjugated chain to long-wavelength neutrocyanine chromophores, which we will address in the future.

In conclusion we have presented a new series of neutrocyanine chromophores based on five-membered heterocycles. Their photorefractive figures-of-merit range from 0.22 up to 1.98, which is the highest value reported. As their use in optical devices depends on transparency at the applied laser frequency, their narrow-band absorption represents another significant advantage over currently available PR chromophores.[7–9] The possibility of building extended π-systems with alternating aromatic and quinoid moieties as suggested by **5**–**7** might be of relevance for the design of IR dyes and low band-gap polymers as well.[13]

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Notes and References

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§ All new compounds had spectral (^{1}H NMR, UV–VIS) and microanalytical properties (C,H,N,S) in agreement with the assigned structures.

¶ M is the molar mass, T is the temperature, c_0 is the speed of light, h is Planck's constant and k isBoltzmann's constant.

|| According to NMR studies all thiophene chromophores exhibit a conformational preference for the structure shown in Scheme 1. This conformation was used as the input geometry for AM1 calculations (structure, charge distribution).

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