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Optical Properties of an Azobenzene Based Octupolar Near-IR Dye

Saumitra Sengupta* and **Subir Kumar Sadhukhan**

Department of Chemistry, Jadavpur University, Kolkata 700 032, India

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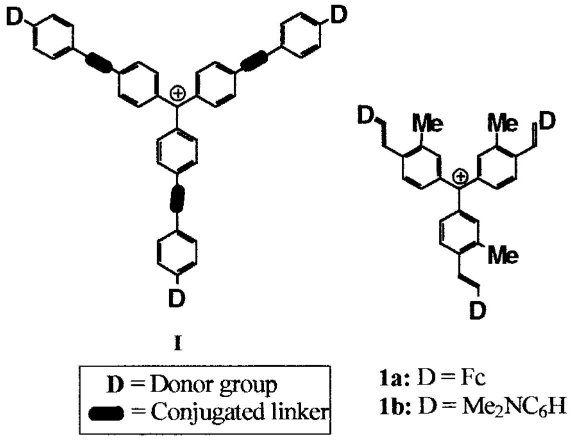
Based on an azobenzene derived octupolar scaffold, a trigonally symmetric near-IR dye **4** (λ_{max} 995 nm) has been prepared from common starting materials. The dye showed a pH dependent as well as a solvent dependent absorption behavior.

Near-infrared (NIR) absorbing dyes ($\lambda_{max} > 700$ nm) are of much current interest because of their potential applications in xerography, infrared photography, as filter elements for optical lasers, etc.[1] Conceptually, a NIR dye can be prepared by end-capping of conjugated organic chromophores with strong donor and acceptor groups which leads to considerable lowering of energy of their charge transfer (CT) transitions. A large majority of NIR dyes that are known today are based on this linear dipolar strategy and are usually comprised of extended conjugated backbones, often in the form of long polyene chains, that are end-capped with heterocyclic units acting as the donor/acceptor substitutents. However, as a consequence, most of these dyes consist of large, complex architectures. For example, in NIR polymethine dyes, a chain of at least eight methine carbons is required to produce absorptions beyond 800 nm.[1c] The structural complexity of these dyes usually calls for multistep synthesis resulting in poor overall yields. Moreover, due to their large molecular weights they are often found to be insoluble in common organic solvents causing difficulties in their purification and applications. In view of these problems, there is a sustained interest in new NIR dyes that are easy to prepare, have improved solubility properties and show strong absorptions at longer wavelengths.

Recently, we described a new structural design **I** (Chart 1) for the synthesis of small molecular weight NIR dyes.[2] The design consists of an extended octupole in which three donor (D) substituted conjugated arms converge on a central carbocation. The major advantages of this design over the linear dipolar strategy are: 1) an octupolar arrangement of chromophores and 2) a strong acceptor center (carbocations are among the strongest acceptor groups known). The octupolar arrangement allows intramolecular electronic interactions to take place between the transition moments of the individual chromophores (excitonic couplings)[3] whereas a strong acceptor center promotes effective mixing of the ground state with the lowest energy excited states. The combined effect gives rise to a low energy transition with increased oscillator strength even when the individual chromophores (dipoles) are relatively small. By using ferrocene or *N*,*N*-dimethylaniline as the donor and styryl groups as the conjugated spacers, we have shown that such an octupolar design leads to NIR dyes **1** with strong absorptions beyond 1000 nm.[2] Based on the same principle, we now describe a new and much easily prepared NIR dye **4** comprised of *N*,*N*-dimethylaniline as the donor and azobenzene as the conjugated spacer. In addition, we also present an interesting pH-dependent study on the absorption behavior of this new dye.



I

1a: D = Fc
1b: D = Me_2NC_6H

Chart 1.

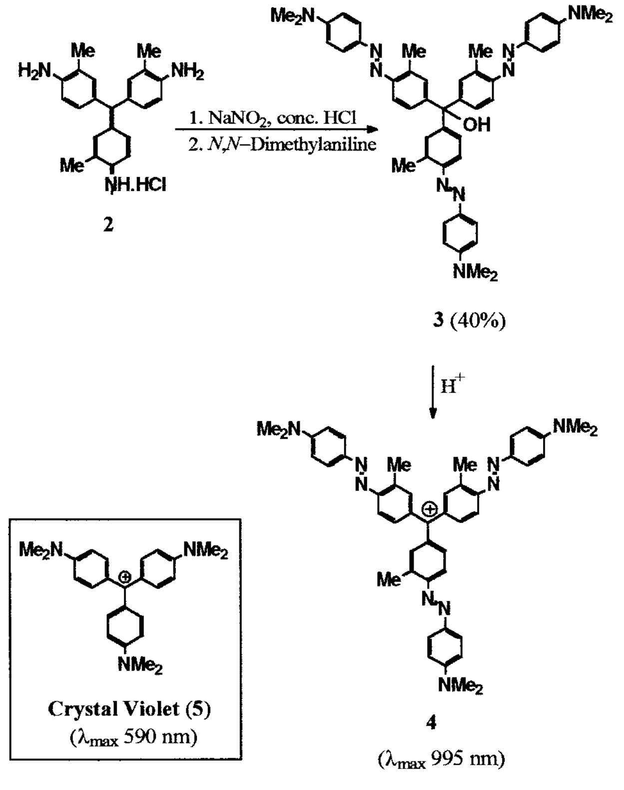
Experimental

General. Melting points are uncorrected. Microanalysis (C, H, N) was performed using a Perkin Elmer 240C elemental analyzer. IR spectra were obtained on a Shimadzu FTIR-8300 instrument with samples prepared as KBr pellets. UV–Vis–NIR spectra were recorded in spectroscopic grade solvents (Merck) on a Shimadzu UV 240 spectrophotometer. NMR spectra were recorded in $CDCl_3$ (Me_4Si standard) on a Bruker Avance 300 (300 MHz) instrument. New Fuchsin (**2**) was purchased from Loba Chemie. Light petroleum refers to the fraction boiling in the 60–80 °C range.

Preparation of Tris(4-dimethylamino-2′-methylazobenzene-4′-yl)methanol (3). A solution of $NaNO_2$ (0.18 g, 2.7 mmol) in water (2 cm^3) was added to a solution of New Fuchsin **2** (0.3 g, 0.83 mmol) in conc. HCl (1 cm^3) at 0 °C. After 30 min, the diazotized solution was added dropwise to a solution of *N*,*N*-dimethylaniline (0.32 g, 2.7 mmol) in a 1 M NaOAc–HOAc buffer (1 M = 1 mol dm^{-3}) (5 cm^3). After 1 h at room temperature, the reaction mixture was diluted with water and the precipitate collected by filtration. The residue was washed with water and purified by preparative thin layer chromatography on silica gel (35% EtOAc in light petroleum) to give **3** as a red solid (0.24 g, 40%); mp 222–225 °C (EtOH); UV-vis λ_{max} (CH_2Cl_2) 423 nm (log ε 4.88); IR ν(KBr) 3413 (br), 1600 (s), 1515 (s), 1442 (w), 1421 (w), 1361 (s), 1147 (s) cm^{-1}; NMR δ_H ($CDCl_3$, 300 MHz) 2.63 (s, 9H, Ar-*Me*), 3.07 (s, 18H, N*Me*$_2$), 6.75 (d, 6H, J = 9.0 Hz, H_3, H_5), 7.18 (d, 3H, J = 8.4 Hz, $H_{5'}$), 7.31 (s, 3H, $H_{3'}$), 7.52 (d, 3H, J = 8.4 Hz, $H_{6'}$), 7.87 (d, 6H, J = 9.0 Hz, H_2, H_6). Anal. Calcd for $C_{46}H_{49}N_9O$: C, 74.29; H, 6.59; N, 16.96%. Found: C, 74.05; H, 6.72; N, 16.78%.

Results and Discussion

Preparation of the Dye Base 3. Our synthesis started with the commercially available New Fuchsin (**2**) which via threefold diazotization (conc. HCl, $NaNO_2$, 0 °C) and subsequent azo-coupling with *N*,*N*-dimethylaniline produced the dye base **3** (40%) after purification by preparative thin layer chromatography on silica gel (Scheme 1). The absorption spectrum of **3** in CH_2Cl_2 showed a strong peak at 423 nm due to the π–π^* transitions of the *p*-dimethylaminoazobenzene chromophores (Fig. 1a). Notably, the molar absorptivity of **3** (ε = 76470 $mol^{-1}\,cm^{-1}$) is less than three times the value of *p*-dimethylaminoazobenzene ($\varepsilon = 30,900$ $mol^{-1}\,cm^{-1}$),[4] indicative of excitonic couplings between the three chromophoric arms of **3**.



Scheme 1.

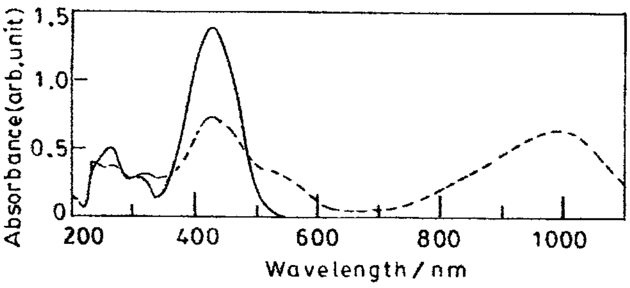


Fig. 1. Absorption spectra of **3** (0.017 mmol dm^{-3} in CH_2Cl_2). TFA concentration: (a) 0 (—), (b) 1.8 mmol dm^{-3} (-----).

Nonaqueous UV–Vis–NIR Studies on the Dye 4. Protonation of **3** with trifluoroacetic acid (TFA)[6] in CH_2Cl_2 then gave rise to the NIR dye **4**, as evident from the appearance of a new absorption band at 995 nm with a high extinction coefficient (log ε = 4.46) (Fig. 1b). The NIR band of **4** is caused by its extended push–pull conjugated system (Me_2N donor–carbocation acceptor) which greatly lowered the energy of its CT transition. The trigonal symmetry in **4** also played a significant role towards this end. Thus, it ensured equal and extensive charge delocalization among all the three chromophoric arms leading to large contributions from the resonance stabilized quinonoid forms to the ground state of **4**. It may be noted that Crystal Violet (**5**), the parent octupolar dye, shows an absorption maximum in the visible region (λ_{max} = 590 nm). Therefore, an extension of conjugation in Crystal Violet while maintaining its trigonal symmetry produced a large bathochromic shift (400 nm) in its absorption maximum. This is in accord with previous observation by us and others that in triphenylmethane dyes, extension of conjugation by a vinylene spacer usually leads to a 100–120 nm bathochromic shift.[2b,7] However, the absorption maximum of **4** is considerably blue shifted compared to that of tris(ferrocenylvinylphenyl)methyl cation **1a** (λ_{max} = 1067 nm)[2a] suggesting that metal to ligand charge transfer transitions (MLCT), especially in acceptor substituted ferrocenes,[8] is a more effective tool in lowering the energy of CT transitions than classical lone pair based delocalizations.

The formation of **4** was found to be highly pH-dependent due to the presence of other protonation sites in the dye (vide infra) which thwarted all our attempts at its isolation. Hence the optical studies were carried out with the in-situ generated dye in solution. However, **4** could be generated in a variety of aprotic solvents ($CHCl_3$, CH_2Cl_2, THF) and once generated, the dye solutions were found to be stable for at least a week at room temperature. Despite this small limitation, **4** represents a readily prepared NIR azo dye, examples of which are few and far between.[1c] The dye solution upon dilution with water or upon neutralization with a base returned the dye base **3** in quantitative yield. Thus, both the dye and its precursor are stable in strongly acidic media.

While protonation of **3** on the 3° hydroxy group led to the NIR dye **4**, the fact that **4** (as well as **3**) has two other protonation sites, the azo β-nitrogens and the terminal NMe_2 groups,[4,5] led us to carry out a pH-dependent study on the absorption behavior of **4**. Thus, further addition of acid to a solution of **4** caused a gradual decrease in intensity of the NIR band with the appearance of a new peak at ~540 nm (Fig 2).). Ultimately, the NIR band vanished and the 540 nm peak became the sole maximum (curve e, Fig 2). We attribute this to the formation of the NMe_2-protonated dye **4H**$^+$ (Scheme 2) which, due to its diminished CT capability, leads to the observed hypsochromic shift. Apparently, further protonation in **4** should have occurred on the azo β-nitrogen to pro-

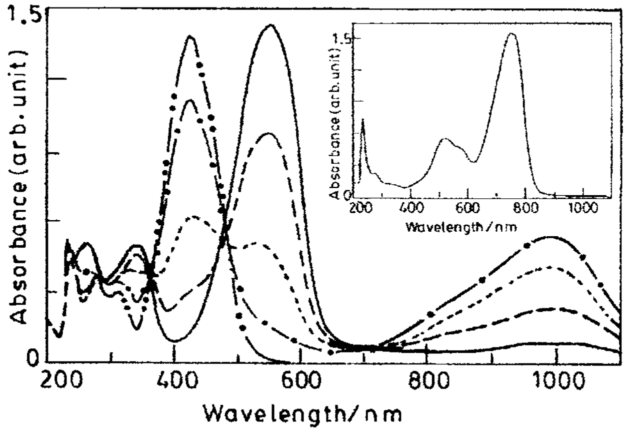
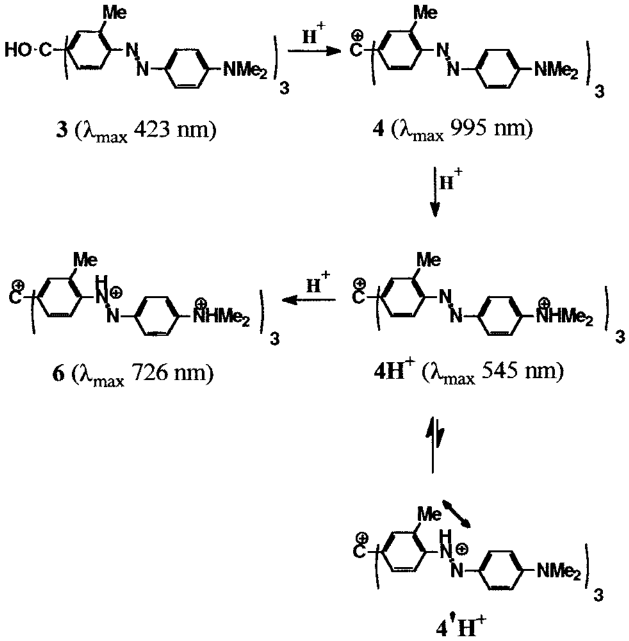


Fig. 2. Absorption spectra of **3** (0.017 mmol dm^{-3} in CH_2Cl_2). TFA concentration: (a) 0 (–••–), (b) 0.7 mmol dm^{-3} (–•–), (c) 3.0 mmol dm^{-3} (- - -), (d) 6.7 mmol dm^{-3} (– – –), (e) 15.0 mmol dm^{-3} (—); 71.9 mmol dm^{-3} (inset).



Scheme 2.

duce the tautomeric species **4′H**$^+$ since the NMe_2 groups of **4** should have had a lower basicity than the azo nitrogens due to extensive delocalization of their lone pair to the carbocationic center.[9] However, in that case, CT from the NMe_2 groups to the central carbocation remains uninhibited and should not have led to the observed hypsochromic shift. Therefore, occurrence of the 540 nm band must be due to protonation of **4** on the NMe_2 groups to produce **4H**$^+$. We believe that **4** is preferentially protonated on the NMe_2 groups because of the base weakening effect on the azo β-nitrogens by the *ortho*-methyl substituents which, via steric interactions, considerably destabilize the azo-protonated conjugate acid **4′H**$^+$. Similar arguments have been made to explain the reduced basicity of 4-dimethylamino-2′-methylazobenzene (pK_a 2.04) *vis-a-vis* 4-dimethylaminoazobenzene (pK_a 2.28)[5b,c] as well as that of *o*-toluidine vis-a-vis aniline. Nevertheless, one can not rule out entirely that some **4′H**$^+$ still remains present in the medium since its absorption maximum would be fairly close to that of **4** and may be indistinguishable from the latter.[10] When the dye solution was made strongly acidic, azo-protonation was indeed observed, albeit in the form of the diprotonated species **6** having a λ_{max} at 726 nm (inset, Fig 2).[5d]

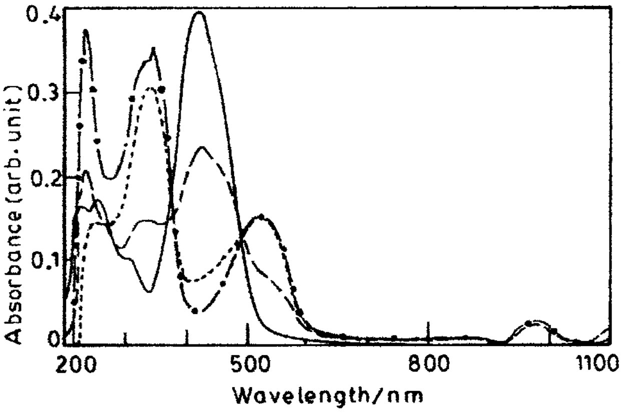
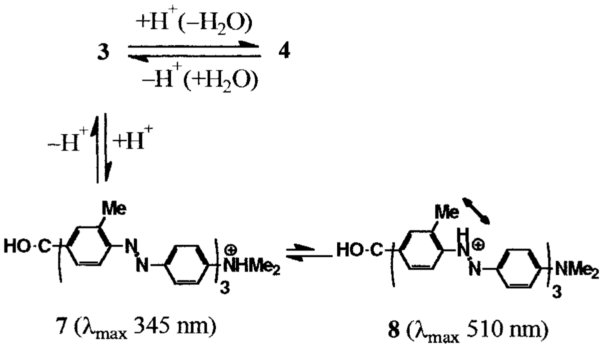


Fig. 3. Absorption spectra of **3** (0.008 mmol dm^{-3} in aq MeOH). HCl concn: (a) 0 (—), (b) 0.025 mmol dm^{-3} (– –), (c) 0.25 mmol dm^{-3} (- - - -), (d) 0.43 mmol dm^{-3} (–•–•–).

Aqueous UV–Vis–NIR Studies on the Dye 4. The formation of **4** and its pH-dependent behavior was also studied in aqueous methanol. A somewhat different picture emerged in this case (Fig 3). As before, addition of acid (aq HCl) to the free base **3** in MeOH caused a lowering of intensity of the 423 nm peak together with the appearance of a NIR band at 975 nm (curve b, Fig. 3). Evidently, in changing the solvent from CH_2Cl_2 to the more polar MeOH, the NIR band of **4** underwent a hypsochromic shift ($\Delta\lambda = 20$ nm). This blue shift (negative solvatochromism) was as expected since upon excitation, CT transitions in **4** would induce equal and extensive delocalization of the central positive charge among all three chromophoric arms of the dye. However, in contrast to the results in CH_2Cl_2, increasing the acid concentration led to the appearance of two new peaks at 345 and 510 nm which gradually gained in intensity, the 510 nm peak levelling off at a relatively high acid concentration (curves c & d, Fig. 3). Moreover, the NIR band at 975 nm did not disappear and in fact gained slightly in intensity. These features suggested that perhaps different species are involved during protonation studies in aqueous MeOH. We speculate that in an aqueous medium the dye base **3** would remain in equilibrium with the NIR dye **4** (Scheme 3). Similar observations have been made during aqueous pH-dependent studies on Crystal Violet (**5**) where it was shown that even at pH 2, nearly 80% of Crystal Violet remained as the protonated dye base.[11] Also pertinent is the fact that a larger concentration of acid was required to generate **4** in aqueous MeOH than that was required in CH_2Cl_2. Now, since **3** is a stronger base than **4**, further protonation occurs preferentially on **3** and hence with added acid, the NIR band of **4** is not affected. Protonation of **4** (to give **4H**$^+$) is also discouraged by the fact that the central carbocationic charge is



Scheme 3.

less delocalized in **4H**$^+$ and as a result, the latter is more prone to be attacked by water to give the protonated dye base. Such was not the case in CH_2Cl_2 where, in absence of water, the equilibrium between **3** and **4** lied heavily towards the latter at high acid concentrations. Now, in aqueous MeOH, protonation of **3** on the NMe_2 groups give rise to **7** (λ_{max} 345 nm) which, due to its reduced CT capability, induces a blue shift. On the other hand, protonation on the azo β-nitrogens lead to the formation of **8** (λ_{max} 510 nm) which causes a bathochromic shift due to enhanced CT from the NMe_2 groups to the protonated azo β-nitrogens.[5] Since **3** is more likely to be protonated on the NMe_2 group due to the base weakening effect on the azo β-nitrogen by the *ortho*-Me substituent (vide supra), with added acid the concentration of **7** increases at the expense of **8**. Consequently, the 345 nm peak keeps gaining in intensity, whereas the 510 nm peak levels off. At this moment we are not sure whether there is any contribution of **4H**$^+$ to the 510 nm band. But since this band levels off with added acid, the contribution, if any, must be small. Therefore it can be safely assumed that in an aqueous medium **4H**$^+$ is not generated in any detectable amount.

Conclusion

In conclusion, we have described the synthesis and absorption properties of a new NIR dye **4** based on an extended octupolar azobenzene motif. The dye, by virtue of having *p*-dimethylaminoazobenzene chromophores, showed a pH-dependent as well as a solvent-dependent absorption behavior.

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9 4-Dimethylamino-4′-nitroazobenzene is less basic (pK_a 1.81) than 4-dimethylaminoazobenzene (pK_a 2.28). The former is protonated preferentially on the azo β-nitrogen (Ref. 5b, c).

10 The absorption maxima for 4-diethylamino-4′-nitroazobenzene and its azo-protonated species are 495 and 510 nm, respectively (Ref. 5d).

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