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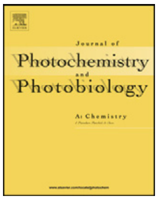

Photophysics and nonlinear absorption of 4,4′-diethynylazobenzene derivatives terminally capped with substituted aromatic rings

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ABSTRACT

The photophysical properties of a series of 4,4′-diethynylazobenzene derivatives terminally capped with substituted aromatic rings (**1a**: R = phenyl; **1b**: R = 4-(diphenylamino)phenyl; **1c**: R = 4-(9*H*-carbazol-9-yl)phenyl; **1d**: R = 9*H*-fluoren-2-yl; **1e**: R = biphenyl-4-yl; **1f**: R = naphthalen-2-yl) were systematically investigated. All compounds exhibit strong $^1\pi,\pi^*$ absorption bands in the UV region; and a broad, structureless charge-transfer band/shoulder in the visible region (except for **1a**), which systematically red-shifts when electron-donating substituents are introduced to the terminal phenyl rings, but blue-shifts when π-conjugation of the terminal aromatic ring increases. All compounds are emissive in solution at room temperature and at 77 K. When excited at the low-energy absorption band, the compounds emit fluorescence between 369 and 419 nm, which can be attributed to $^1\pi,\pi^*/^1$ICT (intramolecular charge transfer) state. Density functional theory (DFT) calculations on **1a**–**1f** in gas phase were also performed to gain insight into the nature of the ground electronic state and the low-lying excited electronic states. **1d**–**1f** exhibit strong triplet transient absorption band(s) in the visible spectral region, which are mainly attributed to the $^3\pi,\pi^*$ state. Reverse saturable absorption (RSA) of these compounds was demonstrated at 532 nm using ns laser pulses. The degree of RSA follows this trend: **1b** > **1c** ≈ **1a** > **1e** > **1f** > **1d**, which is mainly determined by the ratio of the triplet excited-state absorption cross-section to that of the ground-state and the triplet excited-state quantum yield.

1. Introduction

Azobenzene compounds have attracted a great deal of interest in recent years due to their intriguing photophysical properties and versatile applications in photo-responsive materials [1–6], supramolecular structure construction [7–10] and non-linear optics [11,12]. They can undergo reversible *trans*-to-*cis* transformation by illumination with UV/visible light, and the inverse *cis*-to-*trans* reaction can be achieved by irradiation with a different wavelength UV/visible light or by thermal relaxation. This alternation in structure causes a significant change in color, refractive index, dielectric constant, and dipole moment, *etc.*, which makes them attractive in the realms of functional materials [13–17].

Zeitouny and co-workers reported a series of ethynyl-bearing azobenzene compounds with peripheral groups that exhibit substantial *trans*–*cis* isomerization [17], and pyrene-centered molecular arachnoid with four azobenzenyl-ethynyl legs that show photoswitch ability and NIR emitting properties [18]. Tour's group has also developed a class of novel oligo(phenyleneethynylene)azobenzene derivatives as potential candidates for molecular electronic switching devices [19,20]. In addition, they incorporated the azobenzene group in a nanovehicle as photoactive moiety, which exhibits worm-like movement on a surface upon light irradiation [15].

Although the reported work is quite intriguing, the study on the effect of terminally capped chromophores on the photophysics, especially on the nonlinear absorption of phenyleneethynyleneazobenzene compounds is still quite limited. To remedy this deficiency, our group has designed and synthesized a series of 4,4′-diethynylazobenzene derivatives terminally capped with substituted aromatic rings (Chart 1). Compared to the reference compound **1a** with terminal phenyl group, NPh_2 and carbazolyl groups are chosen as electron-donating substituent on the phenyl ring and fluorenyl, biphenylyl and naphthyl groups are chosen as expanded π-electron systems to replace phenyl group in order to study the effect of electron donor and extended π-conjugation on the photophysics and nonlinear absorption of these compounds. Their photophysical properties were systematically investigated with the aim to provide a basis for elucidating

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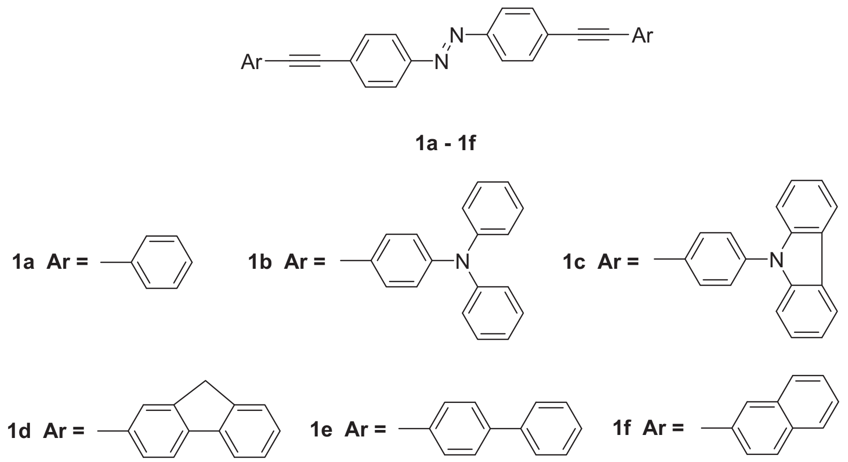

Chart 1. Structures of 4,4′-diethynylazobenzene derivatives terminally capped with substituted aromatic rings (**1a**–**1f**).

the structure–property correlations and developing new organic nonlinear absorbing materials. Compared to the platinum terdentate/bidentate nonlinear absorbing materials developed by our group [21–24], the azobenzene compounds have the advantage of synthetic convenience and low cost.

The synthesis and structural characterization details of these compounds have been reported previously [25]. In this work, we focus on the photophysical studies and the nonlinear absorption of these compounds for ns laser pulses.

2. Experimental

2.1. Photophysical measurements

A Shimadzu UV-2501 spectrophotometer was used to measure the UV–Vis absorption spectra; and a SPEX fluorolog-3 fluorometer/phosphorometer was utilized to obtain the steady-state emission spectra in different solvents (HPLC grade). The emission quantum yields were determined by the comparative method [26], in which an aqueous solution of quinine bisulfate ($\Phi_{em} = 0.546$, $\lambda_{ex} = 365$ nm) [27] was used as the reference. An Edinburgh LP920 laser flash photolysis spectrometer was used to measure the triplet excited-state lifetimes, the triplet transient difference absorption (TA) spectra, the triplet excited-state quantum yields and the molar extinction coefficients in degassed solutions. The excitation source was the third harmonic output (355 nm) of a Nd:YAG laser (Quantel Brilliant, pulsewidth ~4.1 ns, repetition rate was set at 1 Hz). Each sample was purged with Ar for 30 min prior to measurement. Because the azobenzene molecules can undergo *trans–cis* isomerization under UV/visible light irradiation, special care was taken for each of the photophysical measurement. Each of the sample solution was freshly prepared and kept in dark before the photophysical measurement. Each of the UV–Vis and emission measurement was completed in ~30 s, thus no *trans–cis* isomerization occurred in such a short period of time, and the obtained spectra are all for the *trans* isomers. Even if for the TA spectral measurement that took approximately 30 min, the *trans–cis* isomerization in toluene solution was negligible.

Singlet depletion method [28] was applied to obtain the triplet excited-state molar extinction coefficients (ε_T) at the TA band maximum, in which ε_T was calculated by the following equation [28]:

$$\varepsilon_T = \frac{\varepsilon_S[\Delta OD_T]}{\Delta OD_S}$$

where ε_S is the ground-state molar extinction coefficient at the wavelength of the bleaching band minimum in TA spectrum; ΔOD_S and ΔOD_T are the optical density changes at the minimum of the bleaching band and the maximum of the positive band, respectively. When the ε_T value is obtained, the triplet excited-state quantum yield can be calculated by the relative actinometry [29], in which SiNc in benzene was used as the reference ($\varepsilon_{590} = 70{,}000\ M^{-1}\ cm^{-1}$, $\Phi_T = 0.20$) [30].

2.2. DFT calculations

To understand the nature of the ground state and the low-lying excited states, quantum chemical calculations were performed for compounds **1a**–**1f**. All calculations were conducted at the DFT level of theory, in conjunction with the B3LYP functional [31,32] and the 6-31G* basis set [33–37], as implemented in the Gaussian 09 program package [38]. In this work, geometry optimization and the frontier molecular orbitals were simulated for each of the compound.

2.3. Nonlinear transmission measurement

The nonlinear transmission experiments for compounds **1a**–**1f** at 532 nm were carried out in CH_2Cl_2 solution in a 2-mm cuvette using 4.1 ns laser pulses. The experimental setup and details were described previously [39]. The light source was the second harmonic output ($\lambda = 532$ nm) of a 4.1 ns (fwhm), 10 Hz, Q-switched Quantel Brilliant Nd:YAG laser. An $f = 40$ cm plano-convex lens was used to focus the laser beam to the center of a 2-mm-thick sample cuvette. The linear transmission of the solution was adjusted to 80%. Two Molectron J4-09 pyroelectric probes and an EPM2000 energy/power meter were used to monitor the incident and output energies.

3. Results and discussion

3.1. Electronic absorption

The UV–Vis absorption spectra of **1a**–**1f** in toluene solution at room temperature are shown in Fig. 1, and the band maxima and molar extinction coefficients for each compound are compiled in Table 1. The absorptions of **1a**–**1f** obey Lambert–Beer's law in 1×10^{-6} to 1×10^{-4} mol/L range, suggesting no ground-state aggregation or oligomerization occurs in this concentration range. The intense absorption bands below 400 nm and the broad, weak absorption band between 400 and 500 nm are