Proton–Triggered Octopolar NLO Chromophores

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Proton-Triggered Octopolar NLO Chromophores

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C_3-symmetric, octopolar 1,3,5-alkynylbenzenes with terminal pyridyl substituents are presented which show an increase up to 17-fold in the second-order NLO activity upon protonation while maintaining their octopolar character, as confirmed by the depolarization ratios measured.

Introduction

The sustained advance in the design of organic materials for second-order nonlinear optics (NLO) and the ongoing exploitation of new fields of application has kept NLO in the spotlight of scientific interest for more than two decades now.[1] More recently, the intriguing concept of modulating electronic, magnetic, and optical properties on the molecular level by an external stimulus has been extended to the field of nonlinear optics.[2] Driven by the demand for electro-optic devices and biological sensing systems, functional molecules have been designed whose NLO properties respond to electrochemical or chemical inputs such as protons or metal cations.[3] The molecule design follows the same rules as those that apply for conventional linear optical devices. A chromophore unit is equipped with a complexation site or an electrochemically active unit in a way that guarantees efficient electronic communication over the whole conjugated system.[4] Typically, in linear chemosensitive systems of the donor−π−acceptor type, the electron density of the terminal donor or acceptor site is altered upon interaction with a catonic species, resulting in a modulation of the internal charge transfer (CT) character of the dye molecule.[5] Ultimately, this leads to a change in the (nonlinear) optical response. This design principle can be easily applied to nonlinear optical chromophores.[6] In recent examples, the two-photon absorption and fluorescence properties of linear NLO chromophore systems have been modulated upon cation binding[7] or protonation/deprotonation,[8] respectively, at the terminal donor substituent.

Various research groups have approached the preparation of organic electro-optic materials following different strategies to bridge the gap between single molecules and NLO-active bulk materials. Steady advances in poled polymer systems are being reported,[9] among which the design of bulky, dendritic chromophores is occupying a prime position.[10] A different strategy to overcome the antiparallel alignment of dipolar chromophores has been introduced by Zyss et al. with the proposition of octopolar compounds for nonlinear optics. Octopolar molecules are non-centrosymmetric systems with no dipole moment.[11] Because of the absence of a dipole moment, the undesired possibility of an antiparallel alignement of single molecules in the bulk phase is eliminated. A steadily increasing number of octopolar molecules with a great structural variety has given rise to NLO-active polymeric, crystalline, and liquid crystalline

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materials in which the molecular units arrange in a non-centrosymmetric fashion.[12] Despite the growing impact that octopolar systems are having in the field of nonlinear optics, only one report on organic NLO octopoles with switchable second-order nonlinearity has been published so far.[13] Metal−organic alkynyl compounds with C_3 symmetry display switchable third-order nonlinearities.[14] As observed for acetylenic and vinylic pyridinium systems of different geometries,[15] theoretical calculations on octopolar trisacetylene benzenes suggest that the second-order hyperpolarizability β could increase more than an order of magnitude upon introduction of positive charges at the pyridyl end groups, compared with the neutral species.[16]

Results and Discussion

Synthesis. These considerations led us to design the trispyridyl compounds **1**−**3** as second-order NLO chromophores with octopolar symmetry and study their potential as proton-switchable molecular devices (Figure 1). Compound **4** has been reported in the literature previously and is referred to in this study for comparison.[17]

Compounds **1**−**3** are readily synthesized by threefold Sonogashira cross-coupling of the respective triethynylbenzenes with the corresponding bromopyridines (Scheme 1).[18] Compound **2** has recently been reported as a ligand in a coordination polymer without giving experimental details on its synthesis or characterization data other than X-ray structure analysis.[19] The C_3 symmetry of these molecules is reflected by only two ^{13}C NMR signals for the central benzene unit, as well as the reduced number of seven or five signals, respectively, for the three pyridylethynyl systems in each molecule.

Linear Spectroscopy. Compounds **1**−**3** show narrow, intense absorption maxima around 300 nm with a pronounced vibronic structure, together with a weakly absorptive shoulder situated around 335 nm. In comparison, the protonated forms of **1**−**3** display broad, red-shifted absorption bands with high molar absorptivities (Table 1, Figure 2). In particular, the protonated form of **3** displays a broad, unstructured absorption band indicative of the pronounced charge transfer (CT) behavior of the octopolar **3**$^{3+}$.

The existence of only one clear isosbestic point during the H$^+$ titrations allows for the unequivocal assignment of only two defined species, a neutral and a fully threefold protonated one, while the partially protonated forms supposedly coexist in solution. Assuming a pseudo 1:1 (i.e., 3:3) binding stoichiometry,[20] the pK_a values derived from the titration curves are in
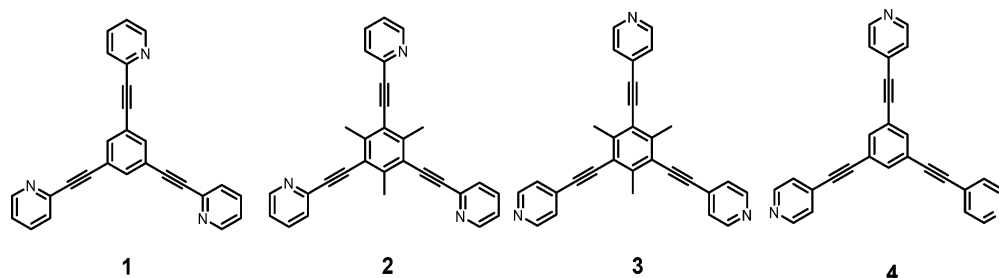
Figure 1. 1,3,5-Tris(pyridylethynyl)benzene derivatives **1**–**4**.

SCHEME 1: Synthesis of Compounds 1–3

1: R = H, Py = 2-pyridyl; 42%
2: R = CH₃, Py = 2-pyridyl; 47%
3: R = CH₃, Py = 4-pyridyl; 26%

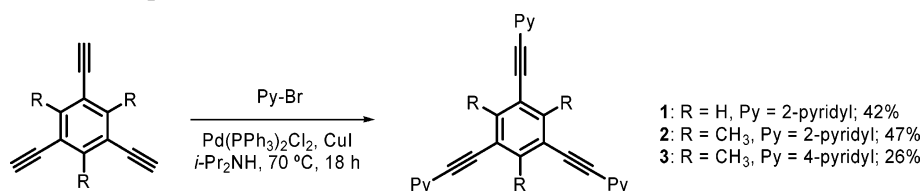**TABLE 1: Spectroscopic Data for 1–3, Their Protonated Forms, and Crystal Violet (CV)**

	λ_{abs}/nm	λ_{em} (λ_{ex})/nm	Φ_{fl}	τ_{fl}/ns[a]	$\beta_{xxx,800}$[b]	β_{xxx0}[c]	ρ[d]
1	308	350 (318)	0.01	1.7 ± 0.2	22 ± 2	8 ± 1	1.2
1³⁺	338	452 (318)	<0.01	n.s.	80 ± 13	19 ± 3	2.4
2	315	362 (325)	0.03	10.7 ± 3.2	29 ± 2	9 ± 1	1.1
2³⁺	340	467 (325)	<0.01	n.s.	178 ± 11	38 ± 2	1.6
3	313	363 (321)	0.04	8.2 ± 1.9	37 ± 3	12 ± 3	1.3
3³⁺	338	483 (321)	0.01	n.s.	623 ± 23	146 ± 5	1.7
CV	583			n.s.	338 ± 60	178 ± 32	1.3

[a] n.s.: no two-photon fluorescence signal detected. [b] Dynamic hyperpolarizability at 800 nm in 10^{-30} esu, HRS data obtained in THF. [c] Static hyperpolarizability in 10^{-30} esu, HRS data obtained in THF–HCl_aq. [d] Accuracy ±0.1.

the typical range for donor-substituted pyridine derivatives.[21] Full protonation is reached in the sub-millimolar range for **2** and **3** and in the millimolar range for **1**, respectively.

Likewise, the structured fluorescence bands of the neutral compounds are broadened and red-shifted more than 100 nm upon protonation, yielding the weakly emissive charged trispyridinium derivatives of **1**–**3** (Table 1, Figure 3). The samples are excited at their isosbestic points as obtained from the UV–vis titrations (λ_{ex}(**1**) = 318 nm; λ_{ex}(**2**) = 325 nm; λ_{ex}(**3**) = 321 nm).

Overall, this linear spectroscopic behavior is characteristic for efficient, degenerate charge transfer from the central benzene core to the electron-deficient pyridyl subunits in the periphery and is in accordance with the properties of similar pyridylacetylene systems.[22]

Nonlinear Optical Spectroscopy. On the basis of the appropriate three-level model for such octopolar chromophores,[23]

the bathochromic shift of the CT absorption band is a first hint that elevated quadratic hyperpolarizabilities can be expected for the charged trispyridyls. For the experimental determination of the second-order nonlinear optical molecular polarizability, or first hyperpolarizability β of octopolar molecules lacking all dipolar properties, only hyper-Rayleigh scattering (HRS) can be used, since there is no orienting interaction with an applied electric field.[24] Additionally, an electric field would cause migration, rather than orientation, for the protonated octopoles because of their ionic nature. Therefore, frequency-resolved femtosecond HRS with fluorescence demodulation has been applied here. For the octopoles measured at 800 nm, we have used the octopolar molecule Crystal Violet with a reference value of 338×10^{-30} esu for its octopolar β_{xxx} value (the z-axis being the unique molecular axis perpendicular to the molecular xy-plane). Because of the identical molecular symmetry for reference and unknowns, there is no need for conversion between dipolar β_{zzz} and octopolar β_{xxx} hyperpolarizability tensor components.

As has been previously observed for similar octopolar structures and as can be expected from the linear (one-photon) fluorescence spectra (Figure 3), multiphoton fluorescence is detected when excited with strong IR pulses.[11c] The additional contribution to the NLO HRS signal at 400 nm has been eliminated by a high-frequency fluorescence demodulation technique based on a femtosecond repetitively pulsed laser operating at 800 nm.[25] This method results in a value for the accurate, fluorescence-free, dynamic hyperpolarizability ($\beta_{xxx,800}$), a relative fluorescence contribution value, and a fluorescence lifetime (τ_{fl}). With the application of the three-level model for octopoles, a value for the dispersion-free static hyperpolariz-
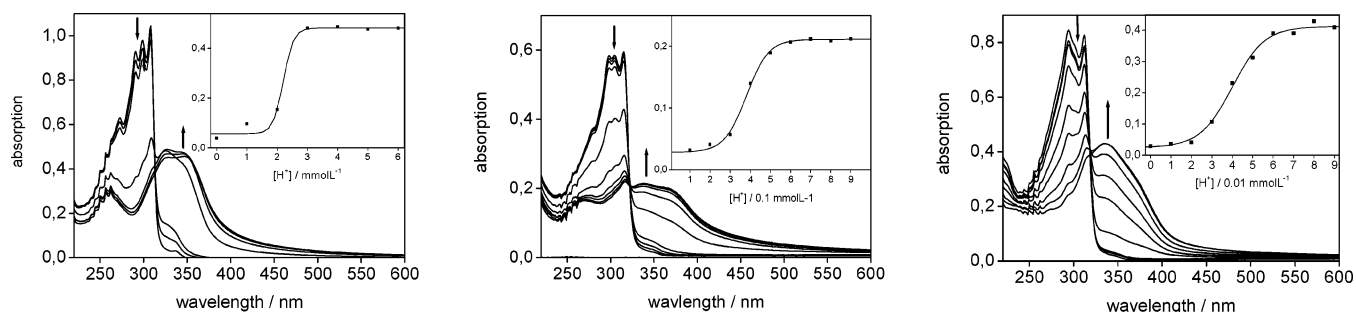

Figure 2. Absorption of **1** (left), **2** (middle), and **3** (right); $c = 10^{-5}$ mol L^{-1} in THF–water (1% v/v), upon addition of HCl_aq; the inset shows the titration plots monitored at the absorption maxima for the respective protonated species.
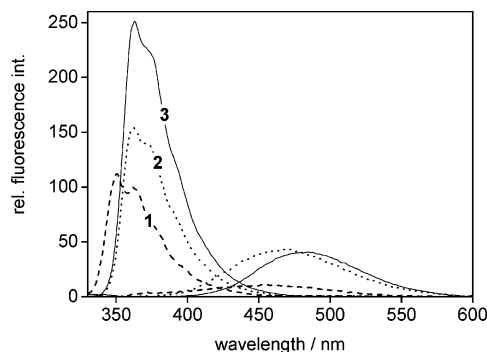
Figure 3. Emission spectra of **1**, **2**, and **3**; $c = 2 \times 10^{-7}$ mol L^{-1} in THF−water (1% v/v); and of the protonated forms, in THF−HCl$_{conc}$ (1% v/v).

ability ($\beta_{xxx,o}$) can be obtained. This value is corrected for the different degree of resonance enhancement, based on the different spectral positions of the charge transfer electronic resonances.

The observed fluorescence quenching and red-shift of the emission upon protonation results in a disappearance of the (multiphoton) fluorescence contribution to the HRS signal at 400 nm. Additionally, the observation of a constant hyperpolarizability value as a function of the modulation frequency guarantees that the high β-values observed for the protonated structures are free from any multiphoton fluorescence contribution.

The hyperpolarizabilities for the neutral species are modest but in good agreement with previous reports on similar donor−acceptor substituted octopolar systems.[11c] The presence of genuine donor substituents (−CH$_3$) on the central benzene core leads to enhanced β-values. This becomes obvious when comparing the values in Table 1 for **1** with **2**, and **3** with the previously reported **4** ($\beta_{xxx} = 31 \times 10^{-30}$ esu).[17]

The generation of charged pyridinium units upon protonation converts the relatively inefficient neutral structures into highly efficient octopoles with degenerate charge transfer from the electron-rich core to the electron-deficient periphery. The proton-triggered NLO response is reflected most significantly by a 17-fold increase of the dynamic hyperpolarizability $\beta_{xxx,800}$ from 37×10^{-30} esu for **3** to 623×10^{-30} esu for the threefold protonated **3**$^{3+}$. This value is among the highest reported so far for organic octopolar systems.[11b,e] Again, in the case of the triply charged compounds, the relative values of the hyperpolarizability reflect the electron donor strength of the core (benzene vs mesitylene) and the degree of conjugation with the periphery (2- vs 4-pyridinium).

This comparison is also valid for the static hyperpolarizability ($\beta_{xxx,o}$) although the increase only amounts to a factor of 12 for compound **3**. This is caused by the larger resonance enhancement of the dynamic hyperpolarizability value for **3**$^{3+}$ with respect to **3** (compare λ_{abs} of 313 nm for **3** with 338 nm for **3**$^{3+}$). So, not only are the nonlinear optical properties triggered by protonation, but this stimulation concomitantly induces a lowering in the transition energy, thereby triggering longer-wavelength absorption. Finally, it is the combination of both linear and nonlinear optical properties triggered by protonation that results in an effective dynamic response at optical wavelengths triggered by such stimulus.

In agreement with the linear optical absorption spectroscopy of the existence of only one isosbestic point, indicative of only two defined species, i.e., the neutral and the threefold protonated one, we observe depolarization ratios (ρ) for both species that conform with an octopolar molecular symmetry. HRS depolar-

ization ratios ρ are defined as the ratio between the scattered HRS intensity with polarization parallel to the fundamental vertical laser polarization and the scattered HRS intensity with polarization perpendicular to it. As a comparative value, the depolarization ratio for Crystal Violet is obtained as 1.3 ± 0.1. Ideally, this value should be 1.5, but for realistic nonzero apertures, this value can go down.[26] The inferior depolarization ratio values for the neutral (highly fluorescent) species compared with their charged counterparts can be explained as a consequence of partial rotational relaxation between excitation and emission. However, the range of depolarization values obtained is clearly in agreement with the octopolar symmetry of all species investigated. The large ρ for **1**$^{3+}$ (and to a lesser extent for **3**$^{3+}$) can be understood in terms of relative solvent contribution to the signal. The depolarization values of the neat solvents (THF or THF−HCl$_{aq}$) amount to 2.4 and 2.2, respectively. Because of the increased absorption by the protonated species at the second harmonic wavelength, a lower protonated solute concentration is used to avoid self-absorption of the HRS signal. From the small contribution to the signal in the particular case of **1**$^{3+}$, a strong influence of the default (solute-free) value is retained.[27] The pH at which the HRS measurements are performed ensure a full threefold protonated species with octopolar symmetry rather than the presence of a partially protonated dipolar species.

Conclusions

Protonation of the terminal pyridyl groups of octopolar 1,3,5-trisalkynylbenzenes results in a pronounced red-shift and broadening of their absorption and fluorescence bands, strongly augmenting their CT character. In accordance with the three-level model and as predicted by theoretical calculations,[16] the second-order NLO response of the trisalkynylbenzenes presented can be triggered by protonation, leading to highly efficient octopolar systems which exhibit exceptionally high β-values. Apart from potential applications of these NLO-active compounds in electro-optic materials or in biorelated sensing devices, the nonlinear optical HRS measurements contribute also to the fundamental understanding of the observed processes on the (supra)molecular level.

Experimental Section

General Conditions. All solvents and reagents were used as purchased. Thin-layer chromatography was performed on Alugram Sil G/UV254-coated aluminum sheets (Macherey-Nagel) with UV detection at 254/365 nm. NMR spectra were recorded on Bruker AC-200 (^{1}H) and Bruker AC-300 (^{13}C) spectrometers in deuterated chloroform (deuteration grade >99.80%) with the solvent signal serving as the internal standard. Mass spectra were recorded on a HP1100MSD spectrometer. Spectroscopic measurements were performed using freshly distilled, HPLC-quality solvents, and are solvent-corrected. UV−vis spectra were measured on an HP 8453 (Hewlett-Packard) spectrophotometer. A Perkin-Elmer LS50B luminescence spectrometer was employed for the fluorescence studies, in a four-sided quartz cell at room temperature in a right-angle geometry. Quantum yields were determined using 2-aminopyridine in 0.1 N H$_2$SO$_4$ as the standard.[28]

Materials. *General Procedure for the Synthesis of the 1,3,5-Tris[(pyridyl)ethynyl]benzenes **1**−**3***. Bromopyridine (3.0 mmol) is stirred together with Pd(PPh$_3$)$_2$Cl$_2$ (106 mg, 0.15 mmol) and CuI (28 mg, 0.15 mmol) in degassed diisopropylamine (10 mL) for 30 min at room temperature before the respective trisethynylbenzene derivative (1.0 mmol) is added. The mixture is

heated at 70 °C for 18 h. The solvent is removed, and the remaining solid suspended in water (100 mL) and extracted with dichloromethane (3 × 50 mL). The combined organic layers are dried (MgSO₄) and concentrated in vacuo to give the resulting crude product, which was purified as described below.

*1,3,5-Tris[(2-pyridyl)ethynyl]benzene (**1**).* The crude product is purified by column chromatography (40:1 CH₂Cl₂−MeOH) and subsequent recrystallization from nitromethane. Yield, 42%; mp 193−195 °C. ¹H NMR (δ): 8.64 (bs, 3H), 7.79 (s, 6H), 7.73 (m, 3H), 7.53 (d, J = 8.1 Hz, 3H), 7.25 (m, 3H). ¹³C NMR (δ): 150.0, 142.8, 136.1, 135.2, 127.4, 123.2, 123.1, 89.8, 86.9. EI⁺−HRMS: found, 381.1255; calculated for $C_{27}H_{15}N_3$, 381.1267. R_f = 0.46 (20:1 CH₂Cl₂−MeOH).

*1,3,5-Tris[(2-pyridyl)ethynyl]mesitylene (**2**).* The crude product was purified by column chromatography (10:1 CH₂Cl₂−EtOH) and subsequent recrystallization from *i*PrOH. Yield, 47%; mp 216−218 °C. ¹H NMR (δ): 8.60 (d, J = 4.7 Hz, 3H), 7.64 (t, J = 7.8 Hz, 3H), 7.50 (d, J = 4.8 Hz, 3H), 7.21 (t, J = 6.3 Hz, 3H), 2.77 (s, 9H). ¹³C NMR (δ): 150.0, 143.9, 143.4, 136.0, 127.2, 122.7, 120.5, 96.7, 86.1, 20.4. EI⁺−HRMS: found, 423.1740; calculated for $C_{30}H_{21}N_3$, 423.1735. R_f = 0.59 (20:1 CH₂Cl₂−MeOH).

*1,3,5-Tris[(4-pyridyl)ethynyl]mesitylene (**3**).* The crude product was purified by column chromatography (20:1 CH₂Cl₂−MeOH) and subsequent recrystallization from EtOH. Yield, 26%; mp 242 °C. ¹H NMR (δ): 8.61 (bs, 6H), 7.37 (d, J = 5.5 Hz, 6H), 2.70 (s, 9H). ¹³C NMR (δ): 149.8, 143.7, 131.2, 125.3, 120.7, 95.0, 90.6 20.3. EI⁺−HRMS: found, 423.1731; calculated for $C_{30}H_{21}N_3$, 423.1735. R_f = 0.20 (20:1 CH₂Cl₂−MeOH).

Hyper-Rayleigh Scattering. The fundamental wavelength for the generic femtosecond laser (titanium−sapphire) is 800 nm, resulting in the HRS signal, and potential (multiphoton) fluorescence contribution, at 400 nm. By measuring at successively higher modulation frequencies, the fluorescence contribution is demodulated. The high-frequency limit of the HRS signal is completely free of multiphoton fluorescence and is, hence, a fluorescence-free signal. This is important in the case of the neutral species which exhibit not only linear (one-photon) fluorescence indeed at 400 nm, but also showed the typical frequency-dependent demodulation of the HRS signal at 400 nm. From the observed frequency dependence of the HRS signal, both a hyperpolarizability and a fluorescence liftime can be deduced. For the protonated octopoles, we observed a constant hyperpolarizability value as a function of modulation frequency, precluding any MPF contribution at 400 nm, corroborated by the red-shift away from this wavelength and lower fluorescence quantum yield. Typical estimated uncertainties of the hyperpolarizability values amount to on average <15% (see Table 1).

Because of the nature of the protonation experiment, the neutral octopoles were measured in THF, while the experiments on fully protonated octopoles were performed in THF−HCl$_{aq}$ (1% v/v). The reference molecule was dissolved in methanol. For dipolar molecules, a solvent dependence for the first hyperpolarizability has been observed. Indeed, a β_z value (the vectorial part of the hyperpolarizability tensor, as determined by electric field induced second-harmonic generation) for the dipolar molecule *para*-nitroaniline, has been reported between 16.3 in apolar dioxane and 38.4 in the polar NMP.[29] Hence, the experimentally determined variation in the β_z value amounts to less than a factor of 3. Such a solvent dependence (with the same variation of at most a factor of 3) has also been observed in hyper-Rayleigh scattering[30] and has been rationalized in terms of the dipole reaction field.[31] Therefore, it can be expected, and

it has been experimentally observed that the solvent dependence for the apolar octopoles is negligible indeed (a variation of 20% at most). Therefore, the values for the hyperpolarizability can be directly compared between neutral and protonated species, even if these values have been determined in different solvents.

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(27) Time-delayed fluorescence that is not demodulated at low modulation frequencies lowers the depolarization ratio by polarization scrambling caused by rotational relaxation between excitation (scattering) and emission. Therefore, any value for the depolarization ratio between 1 and 2.5 can be considered indicative of octopolar symmetry, if values lower than 1.3 can be attributed to fluorescence-induced polarization scrambling and if values larger that this, but still smaller than 2, are corroborated with significant dipolar solvent contribution to the HRS signal.

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