Novel linear and V-shaped D-π-A$^+$-π-D chromophores by Sonogashira reaction

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Dedicated to Professor Julio Alvarez-Builla on the occasion of his 65th birthday

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Abstract
Dipolar V-shaped chromophores derived from the pyridinium cation as the acceptor have been synthesized by Sonogashira reaction and their linear and nonlinear optical properties have been studied and compared to those of analogous one-dimensional derivatives.

Keywords: Alkynylazinium, cationic, chromophores, synthesis, NLO properties

Introduction

The growing interest in organic materials for electrooptic device applications has led to the development of NLO chromophores that have large molecular second order nonlinearity (β).[1] Typical second-order NLO chromophores are one-dimensional (1D) π-conjugated systems represented as D-π-A, with donor (D) and acceptor (A) moieties for which hyperpolarizabilities β can be tailored by optimizing the D/A strengths and/or extending the conjugation path.[2] Chromophores of this type usually exhibit a single, intense low-lying longitudinal charge-transfer (CT) excitation and possess optical nonlinearities that are essentially dominated by a single β tensor component. Most attempts to design molecules with large β values have relied on endcapping an optimal π-conjugated bridge with different donors and acceptors.

However, a major problem associated with these 1D dipolar chromophores is the trade-off between optimizing the nonlinearity and transparency, such that the increase in the second-order hyperpolarizability β is usually accompanied by a bathochromic shift of the electronic transition. Thus, in recent years, a new synthetic strategy based on introducing multiple D and/or A substituents has emerged that gives rise to multi-dimensional (MD) organic NLO-chromophores. These systems offer potential advantages over classical 1D dipolar chromophores due to the contribution of the large, off-diagonal component,[3] which provides increased β responses, and the possibility of overcoming the nonlinearity-transparency trade-off.[4] To this end, several kinds of dual (multiple) donor-acceptor substitution chromophores have been developed to circumvent these drawbacks by extending the charge transfer from one to higher dimensions (2D, 3D) ranging from octupolar,[5] star-shaped,[6] Λ-shaped (also called V-shaped),[7] X-shaped,[8] Y-shaped,[9] U-shaped,[10] etc.

On the other hand, the use of charged moieties as acceptor units is restricted to diazonium salts[11] and some heteroaromatic cations such as benzothiazolium[12] and pyridinium salts,[13] which have been studied as cationic and dicationic acceptor 1D chromophores. However, very few charged 2D chromophores have been reported to date[13b,14] (Figure 1).

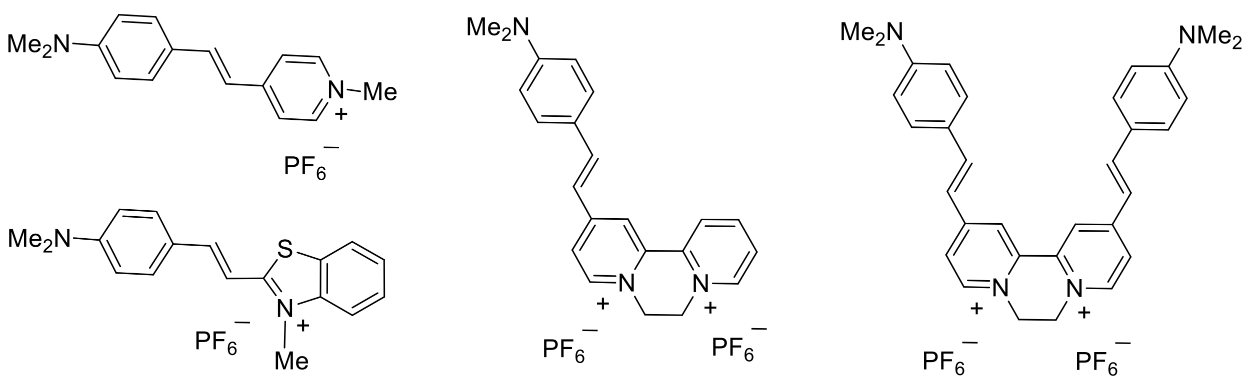


Figure 1. Examples of 1D (D-π-A$^+$) NLO-phores and 2D (D-π-A$^+$-π-D) materials based on heteroaromatic cations as acceptor units.

In this communication, we report our initial results on the synthesis and properties of a number of D-π-A$^+$-π-D noncentrosymmetric molecules based on a charged heterocycle, represented by the pyridinium cation (A$^+$), as potential acceptor units in a variety of NLO-catiophores. The main objective was to relate the nonlinear optical responses to the electronic structures and molecular geometry in order to progress our understanding of these fields. The synthesis of charged chromophores D-π-A$^+$-π-D was achieved by Sonogashira[15]cross-coupling reactions as a basic strategy and this gave rise to 1D and 2D chromophores. The linear and nonlinear optical properties of 2D systems were studied and compared with those of doubly substituted 1D chromophores. The β responses of D-π-A$^+$-π-D systems were determined by Hyper-Rayleigh scattering (HRS)[16] and significant responses were only observed in two-dimensional Λ-shaped molecules in which two charge transfer (CT) axes form an angle[17] between the two donors (Figure 2).

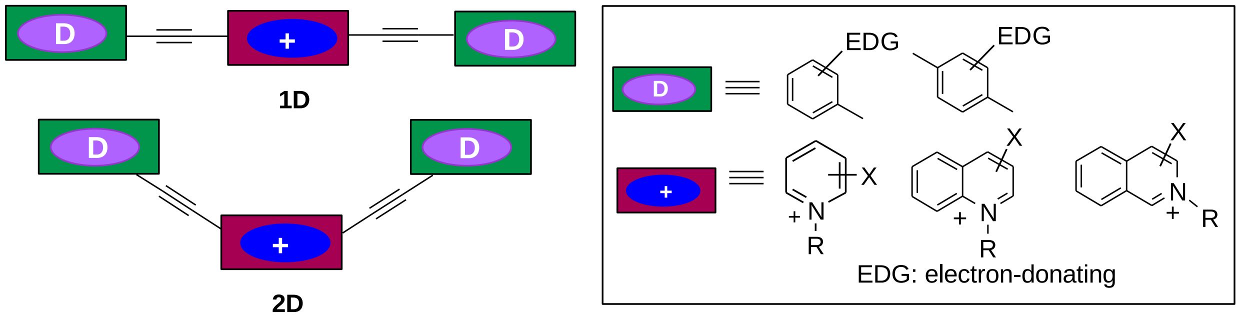
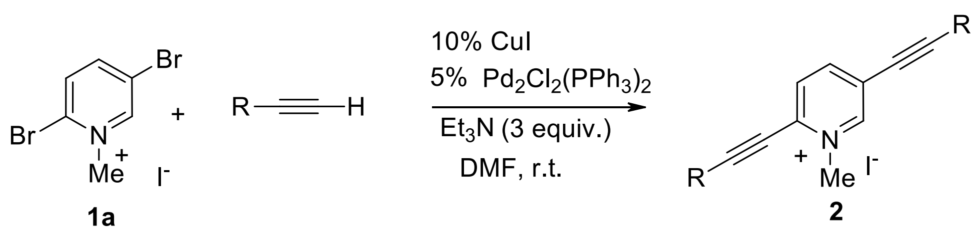


Figure 2. Examples of 1D and 2D molecules incorporating heteroaromatic cations

Results and Discussion

As part of a project focused on the development of the chemistry and applications of heteroaromatic cations,[18] we considered the use of charged moieties as acceptor units in the design of NLO-active cations and the feasibility of using the Sonogashira reaction as a method to synthesize a number of D-π-A$^+$-π-D 1D and 2D charged chromophores.

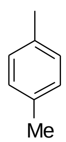
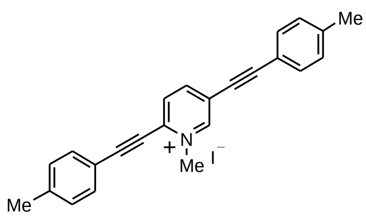
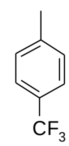
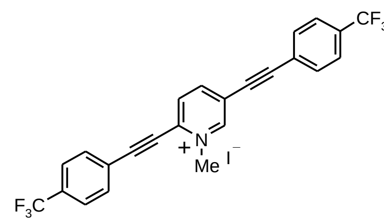
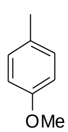
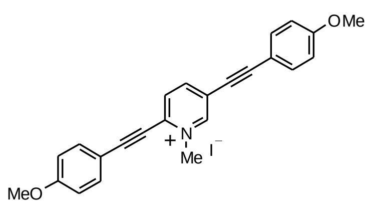
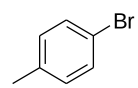
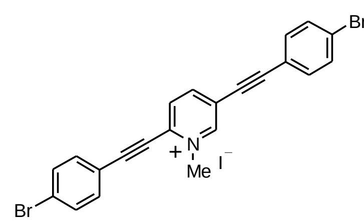
The synthesis of the chromophores, which have the general structure represented in Figure 2 and are denoted as 1D (D-π-A$^+$-π-D), was carried out by reacting 2,5-dibromo-1-methylpyridinium iodide **1a** as the dihalogenated starting material with different alkynes under Sonogashira conditions (Scheme 1). The salt **1a** was initially used to determine the best conditions for the coupling of D-π-A$^+$. Thus, the reaction was carried out with $Pd_2Cl_2(PPh_3)_2$ (5 mol%), CuI (10 mol%) and Et_3N in DMF at room temperature with the only change being the number of equivalents of alkyne (2.4 equiv) and base (3 equiv). Only monocoupling products or



Scheme 1

low yields of the double coupling products were obtained. However, it was found that yields could be improved by prolonging the reaction times and/or carrying out the reaction in highly dilute solution. For instance, a change in the dilution conditions from 0.05 to 0.002 M led to an improvement in the yields of all compounds shown in Table 1, and the yields of cations **2b** and **2f** increased from 51% to 66% and from 53% to 75%, respectively, when the reaction was carried out for 10 h. However, heating the reaction at 60 ºC gave only low yields in the case of **2d** and decomposition products for **2a-c**. Some of these results can be understood by considering the difficulty of the double Sonogashira reaction with some acetylenes, as observed experimentally, because transformation of monocoupled product into the dicoupled compound was only achieved on increasing the reaction time. The differences in yield are probably due to the difficulty of purification process rather than to electronic effects associated with the coupling partners.

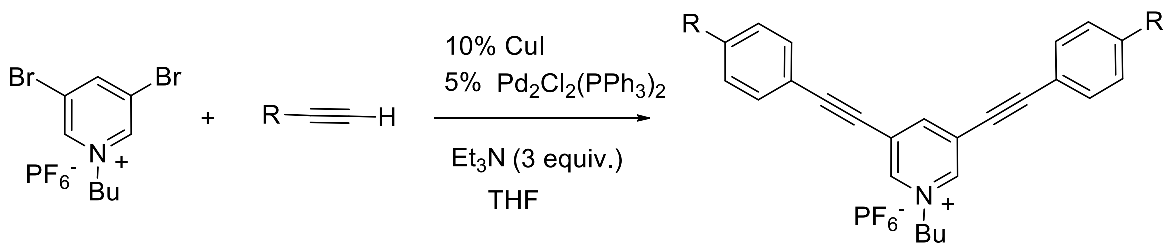
Table 1. Sonogashira reaction on 2,5-dibromo-*N*-methylpyridinium iodide **1a**

Entry	R	Coupling product (Yield %)[a]	Entry	R	Coupling product (Yield %)[a]
1		 **2a** (45%)	3		 **2d** (31%)
2		 **2b** (66%)	4		 **2f**(75%)

[a]Yields refer to isolated yields.

The synthesis of the V-shaped chromophores denoted as 2D (D-π-A$^+$-π-D) was carried out from 3,5-dibromopyridinium derivative **1b** (Scheme 2). Attempts to overcome problems encountered in the work-up, purification, and reaction time, as well as to improve the yields, led us to use the 3,5-dibromo-1-butylpyridinium material as the PF_6 salt[19]; this salt is soluble in THF and avoids the use of DMF, thus facilitating the work-up. Compound **1b** was reacted with different acetylenes to afford the coupling products **3** as hexafluorophosphates in excellent yields (Table 2).

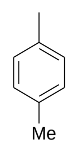
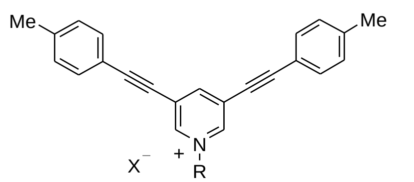
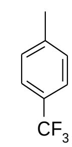
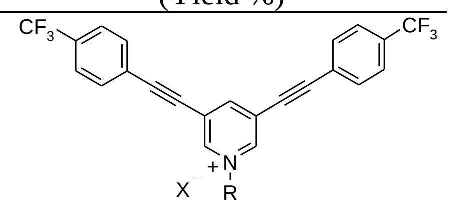
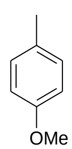
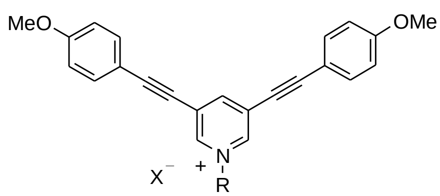
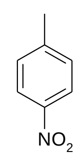
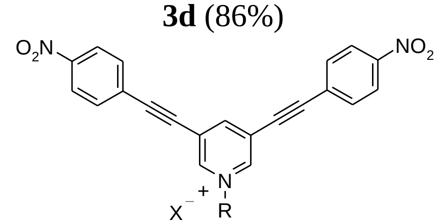
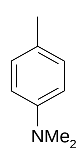
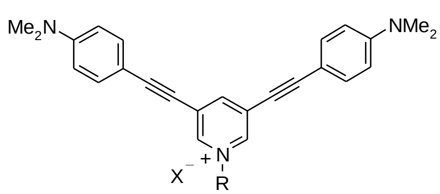
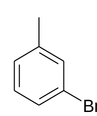
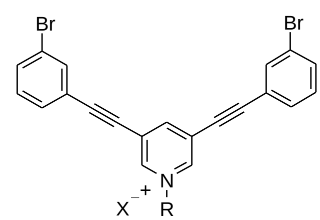
Compounds **3** were also prepared under similar Sonogashira conditions using analogous catalytic systems, the same number of equivalents of the corresponding acetylene derivative and base in THF at room temperature for 1 h. The main differences observed in the reactivity of **1b** were that monocoupling products were not detected –likely due to the more similar reactivity on C3/C5 positions when compared with reactivity on C2/C5 in **1a**- and its reaction with compounds bearing electron-withdrawing substituents, which gave products in good **3d** (86%) or moderate **3e** (41%) yields.



1b **3**

Scheme 2

Table 2. Sonogashira reaction on 3,5-dibromo-*N*-alkylpyridinium hexafluorophosphate

Entry	R	Coupling Product (Yield %)[a]	Entry	R	Coupling Product (Yield %)[a]
1		 **3a** (85%)	4		 **3d** (86%)
2		 **3b** (83%)	5		 **3e** (41%)
3		 3**c** (96%)	6		 **3f** (77%)

[a]Yields refer to isolated yields.

A comparative study of the linear and nonlinear optical properties of the 1 D and 2D (D-π-A$^+$-π-D) chromophores was carried out on systems bearing electron-donating substituents, although chromophores bearing electron-withdrawing substituents were also considered for comparative purposes.

Linear optical properties

The absorption spectra of the compounds depicted in Tables 1 and 2 were recorded in the 220–800 nm range. In general, the absorption spectra shown in Figure 3, for chromophores **2** and **3**, display a characteristic pattern of three absorption bands. The relatively intense peak located at the highest wavelength is ascribed to the π-π* charge transfer absorption band, which is typical for highly conjugated compounds. The maximum of this band is usually quite sensitive to the degree of conjugation and the nature of the electron-donating/withdrawing groups. Most of the D-π-A^+-π-D chromophores (**a**, **b**, **c** and **f**) show a sharp cut off for the low energy π-π* band and they do not exhibit any absorption above this band that could be attributed to a low-lying n-π* transition due to the presence of heteroatoms. However, this sharper cut-off was not observed for **3d**, **3e** or even **2d**, the substituents of which have a certain withdrawing character and whose spectra display π-π* bands that are slightly shifted to the blue. In fact, a distinguishable band was observed at around 400–425 nm for **3e** and a very weak one for **3d**. Nevertheless, these n-π* transitions are characterized by molar absorptivities that are usually at least a factor of 100 lower than those for π-π* transitions.

The 1D chromophores denoted as D-π-A^+-π-D with two substituents located at the C2 and C5 positions in the pyridinium acceptor moiety (Table 1) contribute significantly to the extension of the π conjugation that stabilizes the system. As a consequence, the π-π* band is significantly shifted to the red as compared to the corresponding band for the D-π-A^+ type compounds studied previously,[19] where a single donor group is attached at the C3-position of the pyridinium system. This effect is less marked for the series of compounds **3** (Table 2), whose π-π* absorption bands – except for **3c** – appear at wavelengths close to those of the D-π-A^+ type compounds. The extension of conjugation is more effective in the linear 1D substituted compounds) than in the V-shaped 2D ones **3**. It is noteworthy that the molar absorptivity values for the maxima of the π-π* absorption band are much larger for V-shaped compounds **3** than for compounds **2**.

As shown in Table 3, a monotonic change towards longer wavelengths (bathochromic effect) is also exerted on the π-π* band due to additional stabilization by donor-to-acceptor intramolecular charge transfer (ICT). This stabilization is greater on increasing the electron-donating character of the substituent. A polarized excited state by ICT is usually more stabilized than the ground state, thus narrowing the transition gap and consequently leading to a bathochromic shift in the absorption band. This phenomenon is especially prevalent in polar solvents.[20] Thus, the maximum of the π-π* absorption band for compound **2b, 3b**, which contains $MeOC_6H_4$– groups, appears almost 40 nm (46 nm) above the band for **2d, 3d**, which contains a deactivating $CF_3C_6H_4$– moiety. Nevertheless, the ICT stabilization effect for the same substituents seems to be quite similar for compounds of both series **3** and **2**. It should be pointed out that there is significant ICT stabilization due the strong activating $Me_2NC_6H_4$– group in **3c** as compared to those containing a strongly withdrawing $F_3CC_6H_4$–substituent **3d**. The location of the maxima for the π-π* absorption bands for the two compounds differs by more than 100 nm.

The fluorescence emission obtained upon excitation at the wavelength (λ_{exc}) of the π–π* band collected in the 350–800 nm range – with the exceptions of **3c** and **3e**, which did not show emission – exhibits features similar to those of the absorption spectra. Thus, monotonic displacements of the emission to longer wavelengths were observed upon increasing the electron-donating strength (CF_3 < Br < Me < MeO). The fluorescence quantum yields (Φ_f) and lifetime averages obtained from the intensity decay profiles, which are superimposed in Figure 3 and included in Table 3, were also evaluated for all of the systems under investigation. In general, with the exceptions of **2a**, **2c** and **3f**, most of the samples exhibit null or very weak fluorescence, with Φ_f values below 0.1. As stated previously, the presence of donor and/or acceptor groups usually leads to efficient charge transfer-like transitions and the fluorescence is

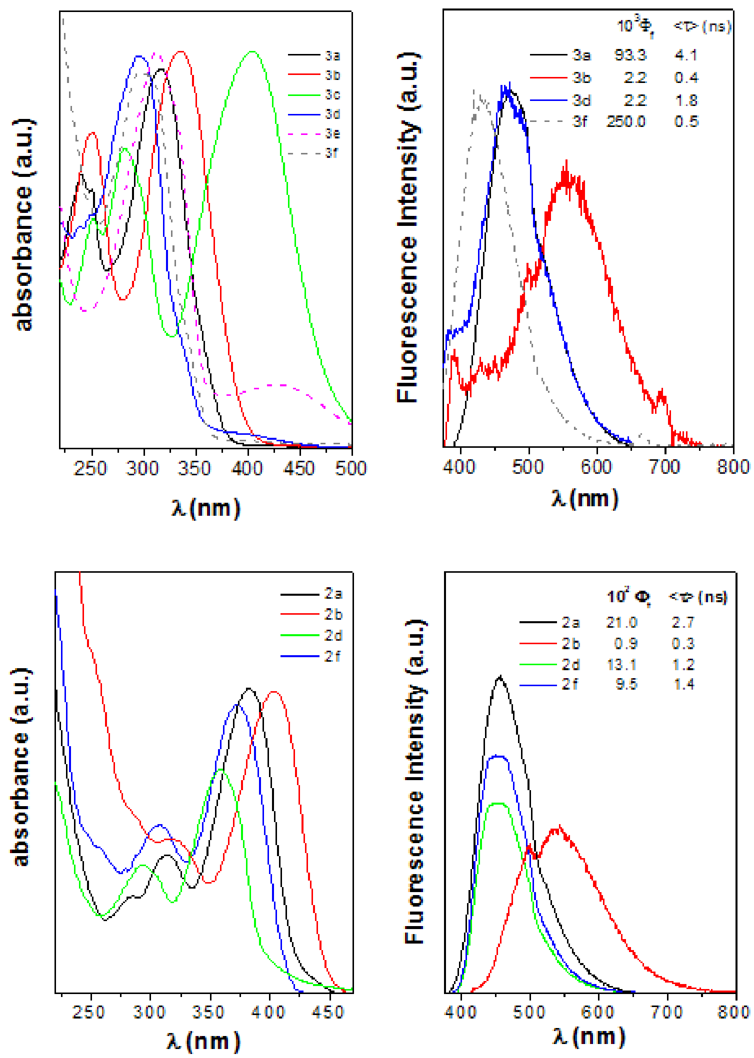


Figure 3. Absorption and fluorescence emission spectra for compounds **2** and **3** in methanol at 25 ºC. Some examples did not exhibit fluorescence. Superimposed are fluorescence quantum yields (Φ_f) and lifetime averages <τ>.

quenched in relatively polar solvents.[21] Fluorescence intensity profiles for all samples were fitted to bi-exponential decays. This indicates that additional processes other than the simple radiative emission from the singlet state were involved and ICT is among them. It is quite difficult to find any correlation between the quantitative values for Φ_f and **<τ>** and the electron-donating strength or location of the substituents on C2,5 (compared with C3,5) for these systems where complex deactivation excited state processes are involved.

Table 3. Wavelength for the maximum of the π-π* charge transfer absorption band (λ_{max}) and emission band (λ_{em}) upon excitation of λ_{exc}, molar absorptivity (ε), fluorescence quantum yields Φ_f, and lifetime averages $<\tau>$ for selected compounds in methanol at 25 ºC.

Compound	λ_{max}	λ_{exc}	λ_{em}	ε ($M^{-1}cm^{-1}$)	Φ_f (×10^2)	<τ>, ns
2a	380	383	463	5883	21.0	2.7
2b	405	404	540	13144	0.9	0.3
2d	359	350	415	9276	13.1	1.2
2f	372	373	450	579	9.5	1.4
3a	316	320	474	140819	93	4.1
3b	335	350	564	62622	2	1.0
3c	404	---	---	34203	---	---
3d	295	340	468	27118	2	1.8
3e	311	---	---	39437	---	----
3f	297	335	429	36743	250	0.5

Nonlinear optical properties. Hyper-Rayleigh scattering (HRS) studies

Femtosecond hyper-Rayleigh scattering measurements performed at 800 nm on chromophores **3** confirm the potential of these small ionic compounds, which are denoted as linear and V-shaped chromophores (D-π-A$^+$-π-D), for second-order nonlinear optics. In good agreement with the findings from the linear optical (absorption) experiments, the first hyperpolarizability value for the compounds with a pyridinium acceptor is larger when the *N*,*N*-dimethylamino or methoxyphenyl group is present as the aryl donor, *i.e.* **3c** and **3b**, respectively. The double Sonogashira coupling adds a conjugated carbon-carbon triple bonded bridge to the total conjugated system, thereby lowering the transition energy and enhancing the value for the first hyperpolarizability with a significant increase in the nonlinear response. However, in compounds (D-π-A$^+$-π-D) a different type of behaviour is observed. The first hyperpolarizability of linear 1D chromophores (D-π-A$^+$-π-D) with two substituents located at positions C2 and C5 in the pyridinium unit show $\boldsymbol{\beta}_{\mathbf{HRS}}$ values ranging from 3 to 10.10^{-30} esu as these compounds have two contributions that could be cancelled out between the two D-π-A$^+$ units. The results for V-shaped chromophores (D-π-A$^+$-π-D) give high first hyperpolarizability values (Table 3). The replacement of substituents with donors that have a higher electron density contributes to a large molecular optical nonlinearity and chromophore **3c** exhibits an exceptionally high β value and chromophore **3b** gives a value that is nearly double that of the monosubstituted system.[19] The dominant contribution to $\boldsymbol{\beta}$ in **3c** is expected to arise from the off diagonal $\boldsymbol{\beta_{zyy}}$ tensor component. Calculations are in progress to determine the relative magnitudes between the diagonal and the off-diagonal $\boldsymbol{\beta}$ tensor components.

Table 4. Nonlinear optical properties of selected 2D chromophores shown in Table 2[a]

Compound	λ_{max}	β_{HRS}	β_{zzz}	$\beta_{zzz,\,0}$	τ
3a	316	34± 3	82 ± 7	24± 2	4.0 ± 0.7
3b	335	237±9	573±6	81±5	---
3c	405	283±25	684 ± 60	313 ± 27	---
3d	296	48±6	116 ± 15	45 ± 6	2.5 ± 0.6
3e	312	80±8	193 ± 20	63 ± 6	---

[a]Wavelength of absorption maximum λ_{max} (nm), resonance enhanced HRS experimental first hyperpolarizability β_{HRS} (10^{-30} esu), resonance enhanced diagonal component of the molecular first hyperpolarizability β_{zzz} (10^{-30} esu), off-resonance diagonal component of the molecular first hyperpolarizability $\beta_{zzz,0}$ (10^{-30} esu). The values of the fluorescence lifetime, τ (ns), are also included for molecules that showed demodulation.

Conclusions

In addition to D-π-A^+ chromophores, in this study we synthesized linear and V-shaped (D-π-A^+-π-D) catiophores by Sonogashira cross-coupling reactions on dihalogenated pyridinium salts. This procedure afforded good yields of 2D catiophores in 1 hour after a simple work-up procedure. The first hyperpolarizabilities of the series (D-π-A^+-π-D) based on heteroaromatic cations as acceptor units were determined by HRS. The results indicate that a large first hyperpolarizability was obtained in compòunds **3b** and **3c**. The low transition energy and high level of CT are the decisive factors that give a large first hyperpolarizability in **3c**. Theoretical TD-DFT calculations at the B3LYP/6-31G level are in progress in order to gain a better understanding of the NLO properties. The results will be reported in due course to probe the key factors that determine $\boldsymbol{\beta}$ values in 2D structures.

Experimental Section

General. Thin layer chromatography (t.l.c.) was carried out using Merck TLC aluminium sheets (silica gel 60 F_{254}). Flash column chromatography was carried out on Merck silica gel (230–400 mesh). Melting points are uncorrected. All new compounds were fully characterized by standard spectroscopic techniques. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian UNITY-300, Varian-Mercury-VX-300 (300 MHz for ^{1}H and 75 MHz for ^{13}C) or Varian XL-200 NMR spectrometers. Infrared spectra were recorded on a Perkin-Elmer FTIR 1725X or a Perkin-Elmer system 1760 FTIR spectrophotometer as KBr or NaCl pellets and spectral bands are reported in cm^{-1}. Microanalyses were performed on a Heraeus CHN Rapid instrument. The mass spectra (MS) obtained by CI were recorded on a Hewlett-Packard 5988A (70 eV) and by ESI^{+} on an HP 1100MSD (LCQ deca XP Thermo) spectrometer. Dry solvents were obtained from a MBRAUN SPS-800 automatic purification system.

2,5-Dibromo-1-methylpyridinium iodide (1a). A solution of 2,5-dibromopyridine (4 g, 16.9 mmol) and 1.5 equiv. of iodomethane (1.58 mL, 25.3 mmol) in CH_3CN (40 mL), was heated under reflux for 24 h. After cooling, the reaction mixture was concentrated to dryness, and the residue triturated with Et_2O and filtered to gave **1a** (4.51 g, 70%) as a pale yellow solid. Mp: 253-254 ºC; IR, (KBr) $\nu_{máx}$ (cm^{-1}): 3087, 1590, 1487, 1422, 1361, 1259, 1176, 1119, 829. ^{1}H-RMN (500 MHz, DMSO-d_6) δ (ppm): 9.62 (d, 1H, J = 2.2 Hz), 8.53 (d, 1H, J = 8.7 Hz), 8.39 (dd, 1H, J = 2.2, 8.6 Hz), 4.34 (s, 3H). ^{13}C-RMN (125 MHz, DMSO-d_6) δ (ppm): 148.6, 145.6, 141.9, 140.0, 120.1, 54.3; HRMS (ESI-TOF, MeOH) Calcd. for $C_6H_6{}^{79}Br_2N.I$: $[M]^{+}$: 251.8846. Found: 249.8868 (M^{+}-2, 51.3), 251.8847 (M^{+}, 100), 253.8826 (M^{+}+2, 48.9)

3,5-Dibromo-1-butylpyridinium iodide was obtained by previously reported method (see reference 19)

3,5-Dibromo-1-butylpyridinium hexafluorophosphate (1b). A solution of 3,5-dibromo-1-butylpyridinium iodide in CH_2Cl_2, was treated with a saturated solution of NH_4PF_6, and the resulting phase was extracted with CH_2Cl_2 (3 X15 mL).The organic phase was dried over Na_2SO_4, the solvent was evaporated under reduced pressure, and the product was isolated by column chromatography on silica gel using CH_2Cl_2/MeOH (9.6:0.4) as eluent.

General procedure for the synthesis of D-π-A^{+}- π-D pyridinium salts

A flame-dried flask was charged under argon with 1 equiv. of the appropriate pyridinium salt **1** (0.6834 mmol), 10 mol% CuI (0.0683 mmol, 0.013 g), 5 mol% $PdCl(PPh_3)_2$ (0.0341 mmol, 0.0239 g) in dry THF or DMF (10 mL). The appropriate acetylene (2.4 equiv., 1.6401 mmol) and Et_3N (3 equiv., 2.0502 mmol, 0.2815 mL) were added. The mixture was stirred at room temperature for the time indicated in each case. The resulting solution was filtered through a small pad of Celite and washed with methanol. The solution was concentrated, the solvent was evaporated under reduced pressure, and the solid was purified by column chromatography on silica gel using CH_2Cl_2/MeOH (9.5:0.5) as eluent.

1-Methyl-2,5-bis-(4-tolylethynyl)pyridinium iodide (2a). From **1a** and 1-ethynyl-4-methylbenzene (0.2079 mL) in dry DMF, stirring the reaction mixture for 18 h, gave 0.1380 g (45%) of **2a** as a brown solid. mp 207–209 ºC. IR (KBr): ν_{max} (cm^{-1}) 3448, 2361, 2344, 1528. ^{1}H-NMR (200 MHz, CD_3OD) δ (ppm) 9.28 (s, 1H), 8.60 (d, 1H, J = 8.4 Hz), 8.27 (d, 1H, J = 8.4 Hz), 7.72 (d, 2H, J = 8.1 Hz), 7.56 (d, 2H, J = 8.1 Hz), 7.46–7.30 (m, 4H), 4.54 (s, 3H), 2.48 (s, 3H), 2.44 (s, 3H). ^{13}C-NMR (75 MHz, CD_3OD) δ (ppm) 150.0, 146.5, 144.4, 142.3, 133.7, 133.0, 133.0, 132.3, 130.9, 130.7, 130.6, 128.5, 124.3, 119.1, 117.4, 110.6, 82.8, 80.9, 21.8, 21.6. MS (ES^+) *m*/*z* (relative intensity) 354 (M^+ + MeOH, 100) Anal. Calcd. for $C_{24}H_{20}N.I$: C, 64.15; H, 4.49; N, 3.12. Found. C (64.20), H (4.90), N (3.25).

1-Methyl-2,5-bis-(4-methoxyphenylethynyl)pyridinium iodide (2b). In dry DMF from **1a** and 1-ethynyl-4-methoxybenzene (0.2127 mL), stirring the reaction mixture for 3.5 h, gave 0.2169 g (66%) of **2b** as a yellow solid; mp 202–204 ºC; IR (KBr): ν_{max} (cm^{-1}) 3500, 2978, 2217, 1602, 1530, 1252, 1162; ^{1}H-NMR (200 MHz, DMSO) δ (ppm) 9.40 (s, 1H), 8.46 (d, 1H, *J* = 10.3 Hz), 8.30 (d, 1H, *J* = 8.4 Hz), 7.78 (d, 2H, *J* = 8.8 Hz), 7.59 (d, 2H, *J* = 8.8 Hz), 7.13 (d, 2H, *J* = 9.2 Hz), 7.07 (d, 2H, *J* = 8.8 Hz), 4.38 (s, 3H), 3.85 (s, 3H), 3.82 (s, 3H); ^{13}C-NMR (50 MHz, DMSO) δ (ppm) 161.5, 160.2, 148.3, 144.4, 135.3, 134.2, 133.0, 130.1, 120.6, 114.5, 114.2, 111.5, 110.2, 107.9, 97.5, 81.6, 79.9, 55.1, 54.9, 46.7; MS (ES^+) *m*/*z* (relative intensity) 354 (M^+, 100); Anal. Calcd. for $C_{24}H_{20}NO_2.I$: C, 59.89; H, 4.19; N, 2.91. Found C, 59.84; H, 4.09; N, 2.88.

1-Methyl-2,5-bis-(4-trifluoromethylethynyl)pyridinium iodide (2d). In dry DMF from **1a** and 1-ethynyl-4-trifluoromethylbenzene (0.2675 mL), after stirring the reaction mixture for 3 h, 0.1180 g (31%) of **2d** was obtained as a yellow solid; mp 230–232 ºC; IR (KBr): ν_{max} (cm^{-1}) 3111, 2925, 2366, 1618, 1323, 1066, 843; ^{1}H-NMR (300 MHz, CD_3OD) δ (ppm) 9.44 (s, 1H), 8.74 (d, 1H, *J* = 8.4 Hz), 8.42 (d, 1H, *J* = 8.4 Hz), 8.047 (d, 2H, *J* = 8.1 Hz), 7.92–7.8 (m, 6H), 4.601 (s, 3H); ^{13}C-NMR (75 MHz, Acetone-d_6) δ (ppm) 151.4, 150.3, 147.0, 140.6, 133.8, 133.6, 132.3 (q, *J* = 32.99 Hz), 131.7 (q, *J* = 32.3 Hz), 129.8, 129.4, 126.6 (q, *J* = 3.7 Hz), 126.5 (q, *J* = 3.7 Hz), 126.5, 124.6 (q, *J* = 241.28 Hz), 124.5 (q, *J* = 242.29 Hz), 100.7, 96.2, 87.89, 85.54, 48.1; MS (ES^+) *m*/*z* (relative intensity) 430 (M^+, 100); Anal. Calcd. for $C_{24}H_{14}NF_6.I$: C, 51.73; H, 2.53; N, 2.51. Found C, 51.51; H, 2.46; N, 2.27.

2,5-Bis-(4-bromophenylethynyl)-1-methylpyridinium iodide (2f). From **1a** and 1-bromo-4-ethynylbenzene (0.2967 g) in dry DMF, stirring the reaction mixture for 4.5 h, 0.2967 g (75%) of **2f** was obtained as a pale green solid; mp 182–183 ºC; IR (KBr): ν_{max} (cm^{-1}) 3444, 2970, 2761, 2679, 1469, 1034; ^{1}H-NMR (200 MHz, DMSO) δ (ppm) 9.51 (s, 1H), 8.73 (d, 1H, *J* = 8.4 Hz), 8.41 (d, 1H, *J* = 8.4 Hz), 7.80 (d, 2H, *J* = 1.1), 7.74 (d, 2H, *J* = 8.4 Hz), 7.60 (d, 2H, *J* = 8.4 Hz), 7.60 (d, 2H, *J* = 8.4 Hz), 4.41 (s, 3H); ^{13}C-NMR (75 MHz, CD_3OD) δ (ppm) 149.0, 145.0, 134.3, 133.9, 133.2, 131.8, 131.7, 130.7, 125.3, 123.6, 120.6, 118.9, 117.6, 105.3, 95.9, 83.5, 81.0, 47.0; MS (ES^+) *m*/*z* (relative intensity) 450 (M – 2, 48), 452 (M^+, 100), 454 (M + 2, 58); Anal. Calcd. for $C_{22}H_{14}Br_2N.I$: C, 45.63; H, 2.44; N, 2.42. Found C, 45.61; H, 2.45; N, 2.42.

1-Butyl-3,5-bis-(4-tolylethynyl)pyridinium hexafluorophosphate (3a). From **1b** and 1-ethynyl-4-methyl benzene (0.1902 g) in dry THF, stirring the reaction mixture for 1 h, gave 0.2956 g, (85%) of **3a** as a grey solid: mp 257 ºC; IR (KBr): ν_{max} (cm^{-1}) 2218; 1588; ^{1}H-NMR (200 MHz, CD_3OD) δ (ppm)) 9.21 (d, 2H, *J* = 1.4 Hz), 8.7 (s, 1H), 7.56 (d, 4H, *J* = 8.2 Hz), 7.32 (d, 4H, *J* = 8.0 Hz), 4.64 (t, 2H, *J* = 7.6 Hz), 2.43 (s,6H), 2.22 (m, 2H, *J* = 7.6 Hz), 1.53 (m, 2H, *J* = 7.3 Hz), 1.07 (t, 3H, *J* = 7.6 Hz). ^{13}C-NMR (300 MHz, acetone-d_6) δ (ppm) 148.2, 145.6, 141.7, 132.6, 130.2, 125.7, 118.3, 98.7, 81.9, 63.3, 33.5, 21.3, 19.78, 13.4; MS (ESI^+) *m*/*z* (relative intensity) 364 (M^+, 100); Anal. Calcd for $C_{27}H_{26}N.F_6P$: C 63.65; H, 5.14; N, 2.75. Found: C, 63.67; H,5.17; N, 2.76.

1-Butyl-3,5-bis-(4-methoxyphenylethynyl)pyridinium hexafluorophosphate (3b). From **1b** and 1-ethynyl-4-methoxybenzene (0.2164 g) in dry THF, stirring the reaction mixture for 1 h, gave 0.3068 g (83%) of **3b** as a beige solid: mp 249 ºC; IR (KBr): ν_{max} (cm^{-1}) 2212; 1585; ^{1}H-NMR (200 MHz, CD_3OD) δ (ppm) 9.16 (d, 2H, *J* = 1.3 Hz), 8.73 (s, 1H), 7.62 (d, 4H, *J* = 8.8 Hz), 7.04 (d, 4H, *J* = 8.8 Hz), 4.63 (t, 2H, *J* = 7.6 Hz), 3.89 (s, 6H), 2.08 (m, 2H, *J* = 6.0 Hz), 1.5 (m, 2H, *J* = 7.6 Hz); 1.07 (t, 3H, *J* = 7.3 Hz). ^{13}C-NMR (300 MHz, acetone-d_6) δ (ppm) 161.5, 147.1, 144.5, 133.8, 125.3, 114.6, 112.4, 98.4, 80.8, 62.6, 55.0, 32.9, 19.2, 12.8; MS (ESI^+) *m*/*z* (relative intensity) 396 (M^+, 100); Anal. Calcd for $C_{27}H_{26}NO_2.F_6P$: C 59.89; H, 4.84; N, 2.59. Found: C, 59,87; H, 4.86; N, 2.58.

1-Butyl-3,5-bis-(4-dimethylaminophenylethynyl)pyridinium hexafluorophosphate (3c). From **1b** and 4-ethynyl-4-dimethylaminobenzene (0.2378 g) in dry THF, stirring the reaction mixture for 1 h, gave 0.3719 g, (96%) of **3c** as a black solid: mp 284 ºC; IR (KBr): ν_{max} (cm^{-1}) 2203; 1580; ^{1}H-NMR (200 MHz, CD_3OD) δ (ppm) 9.01 (d, 2H, *J* = 1.3 Hz), 8.56 (s, 1H), 7.48 (d, 4H, *J* = 8.8 Hz), 6.78 (d, 4H, *J* = 9.2 Hz), 4.59 (t, 2H, *J* = 7.9 Hz), 3.06 (s, 12H), 2.1 (m, 2H, *J* = 6.9 Hz), 1.52 (m, 2H, *J* = 7.9 Hz), 1.08 (t, 3H, *J* = 7.3 Hz). ^{13}C-NMR (300 MHz, acetone-d_6) δ (ppm) 151.9, 146.1, 143.5, 133.7, 126.1, 112.0, 106.6, 100.9, 81.0, 62.7, 39.4, 33.2, 19.5, 13.1. MS (ESI^+) *m*/*z* (relative intensity) 423 (M^+, 100); Anal. Calcd for $C_{29}H_{32}N_3.F_6P$: C 61.37; H, 5.68; N, 7.40. Found: C, 61.39; H, 5.66; N, 7.42.

1-Butyl-3,5-bis-(4-trifluoromethylphenylethynyl)pyridinium hexafluorophosphate (3d). From **1b** and 1-ethynyl-4-trifluoromethyl benzene (0.2788 g) in dry THF, stirring the reaction mixture for 1 h, gave 0.3626 g (86%) of **3d** as a brown solid: mp 246 ºC; IR (KBr): ν_{max} (cm^{-1}) 2225; 1580; ^{1}H-NMR (200 MHz, CD_3OD) δ (ppm) 9.36 (d, 2H, *J* = 1.3 Hz), 8.95 (t, 1H, *J* = 1.3), 7.86 (m, 8H, *J* = 5.4 Hz), 4.68 (t, 2H, *J* = 7.9 Hz), 2.1 (m, 2H, *J* = 6.9 Hz), 1.52 (m, 2H, *J* = 7.9 Hz), 1.08 (t, 3H, *J* = 7.3 Hz). ^{13}C-NMR (300 MHz, acetone-d_6) δ (ppm) 148.7, 146.2, 133.5, 132.1 (q, *J* = 33.3 Hz), 125.8, 124.7 (q, *J* = 270.9 Hz), 95.6, 83.6, 62.9, 32.9, 19.2, 12.8; MS (ESI^+) *m*/*z* (relative intensity) 473 (M^+, 100); Anal. Calcd for $C_{27}H_{20}F_6N.F_6P$: C 52.53; H, 3.27; N, 2.27. Found: C, 52.55; H, 3.29; N, 2.28.

1-Butyl-3,5-bis-(4-nitrophenylethynyl)pyridinium hexafluorophosphate (3e). From **1b** and 1-ethynyl-4-nitrobenzene (0.2410 g) in dry THF, stirring the reaction mixture for 1 h, gave 0.1599 g (41%) of **3e** as a brown solid: mp 252 ºC; IR (KBr): ν_{max} (cm^{-1}) 2224; 1519; ^{1}H-NMR (200 MHz, CD_3OD) δ (ppm) 9.5 (d, 2H, *J* = 1.3 Hz), 9.1 (t, 1H, *J* = 1.6 Hz), 8.37 (dd, 4H, *J* = 2.2, 4.8 Hz), 7.94 (dd, 4H, *J* = 2.2, 4.8 Hz), 4.95 (t, 2H, *J* = 7.6 Hz), 2.23 (m, 2H, *J* = 7.6 Hz), 1.53 (m, 2H, *J* = 7.6 Hz), 1.0 (t, 3H, *J* = 7.3 Hz). ^{13}C-NMR (300 MHz, acetone-d_6) δ (ppm) 149.8, 149.3, 147.4, 134.1, 128.0, 125.0, 124.8, 96.0, 86.2, 63.8, 33.7, 20.0, 13.7. MS (ESI^+) *m*/*z* (relative intensity) 426 (M^+, 100); Anal. Calcd for $C_{25}H_{20}N_3O_4.F_6P$: C 52.55; H, 3.53; N, 7.35. Found: C, 52.57; H, 3.52; N, 7.37.

3,5-Bis-(3-bromophenylethynyl)-1-butylpyridinium hexafluorophosphate (3f). From **1b** and 1-bromo-3-ethynyl-benzene (0.2968 g) in dry THF, stirring the reaction mixture for 1 h, gave

0.3267 g, (75%) of **3f** as yellow solid: mp 220–221 ºC; IR (KBr): ν_{max} (cm^{-1}) 2998, 2915, 2218, 1638, 1594, 1477, 1103, 790, 682, 666; ^{1}H-NMR (200 MHz, CD_3OD) δ (ppm) 9.31 (s, 2H), 8.97 (s, 1H), 7.95 (s, 2H), 7.80 (d, 2H, *J* = 8.1 Hz), 7.74 (d, 2H, *J* = 7.7 Hz), 7.52 (t, 2H, *J* = 8.0 Hz), 4.95 (t, 2H, *J* = 7.6 Hz), 2.23 (m, 2H, *J* = 7.6 Hz), 1.53 (m, 2H, *J* = 7.6 Hz), 1.0 (t, 3H, *J* = 7.3 Hz). ^{13}C-NMR (75 MHz, DMSO-d_6) δ (ppm) 146.9, 146.3, 133.3, 132.6, 130.4, 129.9, 121.6, 121.5, 121.1, 94.1, 82.7, 63.8, 33.7, 20.0, 13.7. MS (ESI^+) *m*/*z* (relative intensity) 454 (M^+ + 2, 53), 452 (M^+, 100), 450 (M^+ – 2, 56). Anal. Calcd for $C_{25}H_{20}Br_2NPF_6$: C 46.98; H, 3.15; N, 2.19. Found: C, 46.97; H, 2.96; N, 2.15.

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